ORIGINAL ARTICLE

DOI: https://doi.org/10.18599/grs.2021.1.4 Russian Original 2021. Vol. 23. Is. 1. Pp. 42–51

Aromatic compounds in bitumoids of the Bazhenov Formation in the North of the Khantey hemiantheclise

I.S. Sotnich, E.A. Kostyreva*

Trofimuk Institute of Petroleum Geology and Geophysics of Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation

Abstract. The main features of the geochemistry of individual aromatic compounds (phenanthrenes, dibenzothiophenes, mono- and triaromatic steroids) in chloroform extracts (bitumoids) from the open (regular form and coarse-crushed (≥0.5 cm) samples) and closed (fine-crushed (0.25 mm) samples) pore space of the Bazhenov Formation have been determined. The differences in the aromatic compounds distribution of organic matter of the Bazhenov Formation in the North of the Khantey hemiantheclise (Surgut region, Khanty-Mansiysk Autonomous District, Western Siberia) are mainly related to its stage of thermal maturity which decreases in the south-west direction within the studying area. The most sensitive to maturity variations at the same catagenesis gradation are the parameters: CPI, Ts/Tm, 1/Ki ((n-C17 + n-C18)/(Pr + Ph)), MDR (4-MDBT/1-MDBT), DBTI ((2+3-MDBT)/DBT) and TASI (TAS I/(TAS I + TAS II)). Based on some indicators (PI, MPI, PP-1, MDR, DBTI etc.), it is possible to notice the decrease and equalization of its values in bitumoids from closed pores compared with those from open ones. It seems to be associated with the removal of the most transformed, light and migratory-capable part of bitumoids during their extraction from the open pore space of rocks.

Keywords: organic matter, bitumoids (chloroform extracts), Bazhenov Formation, aromatic compounds, catagenesis, phenanthrenes, dibenzothiophenes, aromatic steroids

Recommended citation: Sotnich I.S., Kostyreva E.A. (2021). Aromatic compounds in bitumoids of the Bazhenov Formation in the North of the Khantey hemiantheclise. *Georesursy = Georesources*, 23(1), pp. 42–51. DOI: https://doi.org/10.18599/grs.2021.1.4

Introduction

The peculiarities of the composition and structure of petroleum hydrocarbons formed during the evolution of organic matter (OM), especially saturated hydrocarbons – biomarkers, are used as the most informative indicators of the facies-genetic conditions of sedimentation and the degree of transformation of organic matter. The study of aromatic compounds of organic matter can contribute to the confirmation and/or refinement of data obtained as a result of studies of saturated fractions of bitumoids and oils (Alexander et al., 1986; Kolesnikov et al., 1991; Kruge, 2000; Kontorovich et al., 2004; Kashirtsev et al., 2018; Derevesnikova et al., 2019). These aromatic compounds include phenanthrene hydrocarbons, mono- and triaromatic steroids, i.e. polycyclic aromatic hydrocarbons (Radke et al., 1982; Alexander et al., 1986; Cassini et al., 1988; Budzinski et al., 1995; Borrego et al., 1997; and others), as well as sulfur-aromatic compounds (SAC) – benzo- and dibenzothiophenes (Ludwig et al., 1981; Schou, Myhr, 1988; Radke, 1988; Santamaria-Orozco et al., 1998; Chakhmakhchev, Chakhmakhchev, 1995; etc.).

Dibenzothiophenes are known to be good indicators of highly reducing conditions for diagenesis of marine sediments (Kruge, 2000; Chakhmakhchev, Chakhmakhchev, 1995; Kontorovich et al., 2004), since their formation is mainly due to the processes of biochemical sulfurization of lipids at the early stages of diagenesis (Kontorovich et al., 2004). The ratios of dibenzothiophene/phenanthrene and ∑methyldibenzothiophenes/methylphenanthrenes can serve as indicators of paleogeographic and lithofacies settings for the formation of OM and naphthides (Hughes et al., 1995; Chakhmakhchev, Vinogradova, 2003). For reconstructions of sedimentation conditions, the relative distribution of both monoaromatic steroids (C_{27}-C_{30}) and tri-aromatic (C_{20}-C_{21}, C_{26}-C_{28}) (Kolesnikov et al., 1991; Derevesnikova et al., 2019) is used, as well as their ratio TAS/MAS (Kontorovich et al., 2004). In aquagenic OM, according to A.E. Kontorovich with coauthors (Kontorovich et al., 2004), "steroids are converted to a greater extent into TAS, and in terrigenous OM, into MAS...".

*Corresponding author: Inga S. Sotnich
E-mail: SotnichIS@ipgg.sbras.ru

At the same time, the genetic unity of mono- and tri-aromatic steroids makes it possible to use their ratio (TAS/MAS) when assessing the evolution of naphthides: the amount of MAS decreases compared to TAS with increasing maturity (Mackenzie et al., 1982; Gallani and Cassani, 1992; Kruge, 2000). The concentration ratio of high and low molecular weight tri-aromatic steroids (TASI = TAS I/(TAS I + TAS II)) is also used to determine the degree of catagenetic transformation of organic matter (Chakhmakhchev, 1989; Kolesnikov et al., 1991; Kruge, 2000; Kontorovich et al., 2004). Low molecular weight homologues of tri-aromatic steroids TAS I (C_{20}-C_{21}) accumulate during catagenesis either because of their higher relative resistance to thermal transformation compared to high molecular weight TAS II (C_{26}-C_{28}), or because of the separation of the alkyl substituent from the cyclic structure of TAS II under the effect of temperature (Kruge, 2000; Derevesnikova et al., 2019).

During the evolution of naphthides in the structures of phenanthrene and dibenzothiophene, the processes of alkylation and isomerization intensively occur with rearrangement of methyl radicals into a thermodynamically more stable position (Radke et al., 1982; Radke, 1988; Chakhmakhchev, 1989; Chakhmakhchev, Chakhmakhchev, 1995; Budzinski et al., 1995), which allows the use of methylphenatrene and methyldibenzothiophene ratios as indicators of the thermal maturity of OM. Among methylphenanthrene indicators, the most famous and widely used are MPR (Methylphenanthrene ratio), MPI, MPI-1, MPI-2 (Methylphenanthrene Indices), as well as PP-1 and PP- $1_{modified}$ (Phenanthrene parameter) (Table).

In 2004, the phenanthrene index was also proposed (Kontorovich et al., 2004). Among the dibenzothiophene parameters, the most famous are MDR (Methyldibenzothiophene ratio), MDR’, MDR_1, MDR_4, $MDR_{2,3}$ or DBTI (Dibenzothiophene index) (Table).

The informative value of maturity parameters, according to researchers, depends on the genotype of organic matter, for example, phenanthrene maturity parameters show the best informative value for continental OM (type III kerogen) (Radke et al., 1982; Cassini et al., 1988; Farrington et al., 1988; Kruge, 2000). In contrast to phenanthrene indicators, methyldibenzothiophene ratios are equally informative in assessing the maturity of the transformation products of both marine and continental OM (kerogen types II and III) (Chakhmakhchev, Chakhmakhchev, 1995). Among the isomers of methyldibenzothiophene, they are especially sensitive to the OM genotype: 1-MDBT and 4-MDBT (Schou, Myhr, 1988); however, this effect is significant only at shallow depths (in the zones of immature OM distribution).

Among the aromatic compounds of the phenanthrene series, attention is drawn to 1,2,8-trimethylphenanthrene and 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene (TMTHF), which have a related structure (Killops, 1991; Borrego et al., 1997; Kashirtsev et al., 2018; Burdelnaya et al., 2018). In the series of trimethyl-substituted phenanthrene derivatives, the predominant form is always 1,2,8-trimethylphenanthrene, which is found in all types of OM (Killops, 1991; Budzinski et al., 1995; Borrego et al., 1997). Since TMTHF is a genetic “precursor” of 1,2,8-trimethylphenanthrene (Kashirtsev et al., 2018; Burdelnaya et al., 2018), their ratio can also be used as an additional indicator of maturity.

The aim of this work is to study the peculiarities of the distribution of aromatic compounds in bitumoids extracted from the open and closed pore space of the rocks of the Bazhenov Formation.

Materials and methods

Organic matter of the Bazhenov Formation in the central regions of Western Siberia, which is in the main phase of oil formation (MK12), was selected as the object of study (Fomin, 2011). The collection of core material was taken from sections of the Bazhenov Formation of the Druzhnaya, Novoortyagunskaya, Povkhovskaya and Yuzhno-Yagunskaya areas (north of the Khantey hemianteclise, Surgut District, Khanty-Mansiysk Autonomous Okrug) confined to the following elements: 1) Surgut arch, 3) South Nadym homocline and 4) the junction zone of hemiantheclise and homocline (Fig. 1).

The Bazhenov Formation in the study area is represented by thin-layered and fine-crystalline rocks composed of clayey, chemogenic siliceous and carbonate materials (mixtites, silicites, carbonates and their “kerogen” varieties) (Kontorovich et al., 2016; Eder et al., 2016). General geochemical characteristics of organic matter, the results of the study of open pore bitumoids according to the developed at the Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences (IPGG SB RAS), methodology and features of organic matter in carbonate rocks of the Bazhenov Formation were previously published (Kostyreva, Sotnich, 2017; Kontorovich et al., 2018; Eder et al., 2019). The research technique used in this work was developed for sedimentary rocks enriched in organic matter, which include the Bazhenov Formation (Kontorovich et al., 2018). The technique allows in a single cycle of studies to determine the porosity and oil saturation of the rocks of the Bazhenov Formation and to study the geochemistry (distribution, composition and genesis) of bitumoids filling open and closed pores, as well as rocks sorbed on a matrix (Kontorovich et al., 2018a, b). In this work, the main attention is paid to the study of the aromatic fraction of bitumoids (437 samples), extracted from both open and closed pore spaces of rocks, by the method of chromatography-mass spectrometry.

Chromato-mass spectrometric (CMS) studies were carried out on a system including an Agilent Technologies 6890 gas chromatograph, which has an interface with a high-performance mass-selective detector MSD 5973N and a computer system (ChemStation) for recording and processing information HPG 1034. The chromatograph is equipped with an HP-5 quartz capillary column length 30 m, diameter 0.25 mm. Helium was used as a carrier gas with a flow rate of 1 ml/min. The evaporator temperature was 290 °C. Sample injection was performed without flow division. Temperature programming began from 100 °C (isotherm 4 min) followed by a rise to 290 °C at a rate of 4 °C/min and a final isotherm for 30 min. The ionizing voltage of the source is 70 eV, the temperature is 230 °C.

Indicator	Formula / Usage		Source
OM genotype :			
TAS/MAS	The predominance in aquagenous OM - TAS, in terrigenous - MAS		Kontorovich et al., 2004
Relative distribution TAS (C_{26}-C_{28})	Prevalence of C_{27} in aquagenic organic matter		Kolesnikov et al., 1991; Derevesnikova et al., 2019
DBT/P, ∑ MDBT/∑ MP	Increased concentrations of DBT and MDBT indicate the reducing conditions for diagenesis of marine sediments		Hughes, Holba, Dzou, 1995; Chakhmakhchev, Vinogradova, 2003; Kontorovich et al., 2004
Distribution of MDBT	Prevalence of 4-MDBT in aquagenic OM		Schou, Myhr, 1988; Parfenova, 2017
The degree of transformation of OM :			
Methylphenanthrene ratio, MPR	2MP/1MP	Increasing with an increase in the degree of transformation of OM	Radke et al., 1982; Radke, 1988; Farrington et al., 1988; Chakhmakhchev et al., 1995
Methylphenanthrene Index, MPI	1.5*(2MP+3MP)/(0.69*P+1MP +9MP)		Radke et al., 1982; Radke, 1988; Farrington et al., 1988; Chakhmakhchev, 1989
MPI-1	(1.89*(2MP+3MP))/(P+ 1.26*(1MP+9MP))		Cassani et al., 1988
MPI-2	(2MP+3MP)/(P+1MP+9MP))		Kolesnikov et al., 1991
Phenanthrene parameter, PP-1	1MP/(2MP+3MP)		Alexander et al., 1986
$PP\text{-}1_{modified}$	(1MP+9MP)/(2MP+3MP)		Cassani et al., 1988; Gallango, Cassani, 1992; Chakhmakhchev et al., 1995
Phenanthrene index, PI	2MP/P		Kontorovich et al., 2004
Methyldibenzothiophene ratio, MDR	4-MDBT/1- MDBT		Radke, 1988; Chakhmakhchev & Chakhmakhchev 1995; Goncharov et al., 2005
MDR’	4-MDBT /(1-MDBT + 4-MDBT)		Santamaria-Orozco et al., 1998; Kruge, 2000
MDR_1, MDR_4	MDR_1= 1-MDBT/DBT MDR_4 = 4-MDBT/DBT		Schou, Myhr, 1988; Santamaria-Orozco et al., 1998
$MDR_{2,3}$ or DBTI (dibenzothiophene index)	(2+3MDBT)/DBT		Schou, Myhr, 1988; Santamaria-Orozco et al., 1998; Kontorovich et al., 2004
Triaromatic sterane index, TAS I	TAS I/(TAS I+TAS II)		Chakhmakhchev, 1989; Kolesnikov et al., 1991; Kruge, 2000; Kontorovich et al., 2004

Table. The main indicators of aromatic compounds for determining the genotype of OM and the degree of its transformation

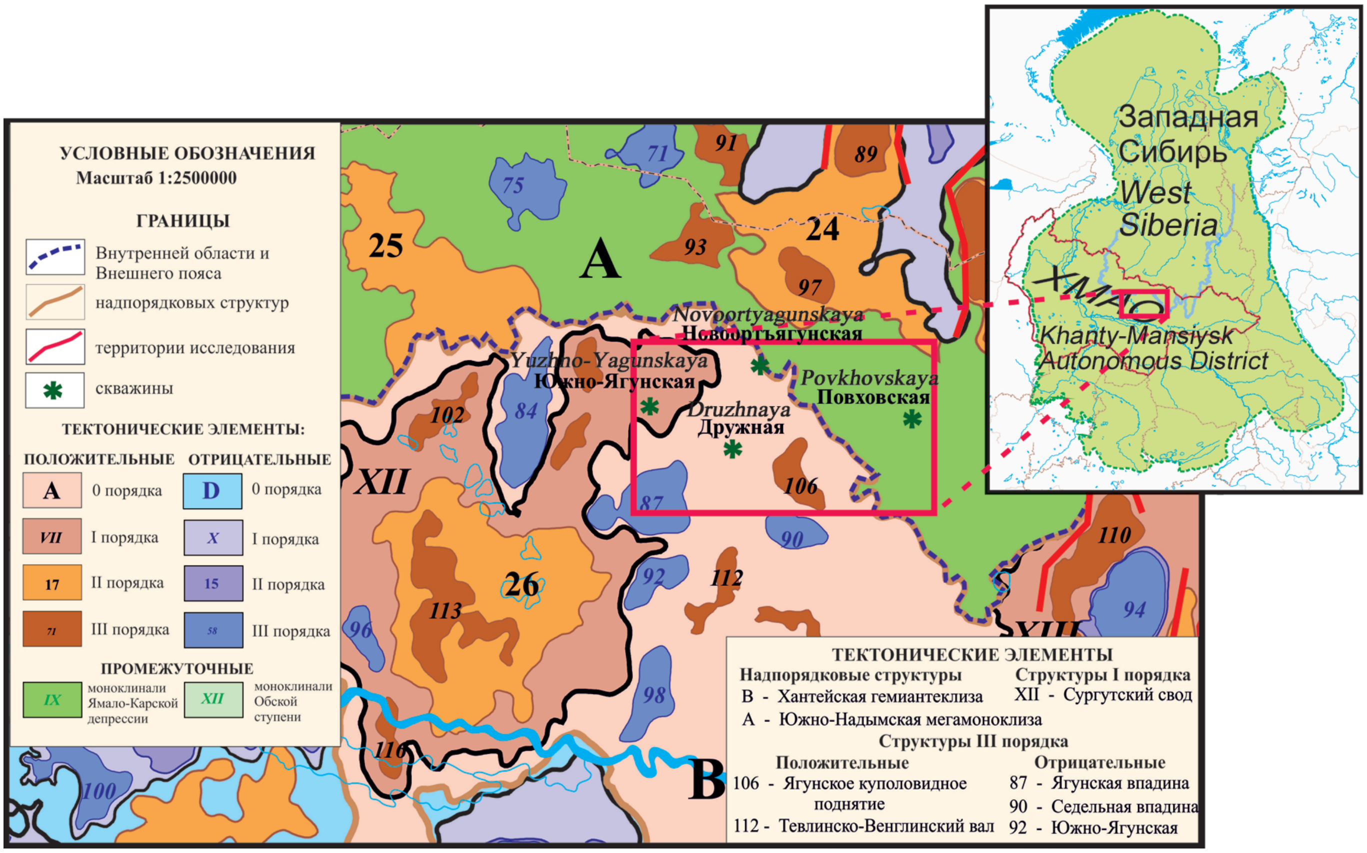

Fig. 1. Fragment of tectonic map of the Jurassic structural stage of the West Siberian oil and gas province (Tectonic basis – Kontorovich et al., 2001). The map was previously published in (Eder et al., 2019).

Mass chromatograms of hydrocarbons (HC) were obtained by total ionic current (TIC), fragment and molecular weight ions m/z 178, 192, 206, 220 (phenanthrenes), m/z 184, 198, 212, 226 (dibenzothiophenes), m/z 253, 231 (mono- and triaromatic steroids), as well as m/z 219 (for retene) and m/z 223 (for 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene). Typical chromatography – mass fragmentograms of aromatic compounds of chloroform bitumoids of the Bazhenov Formation of all lithological varieties, including carbonate ones (published earlier in (Eder et al., 2019)) are shown in Fig. 2. Identification of compounds was carried out by retention time by comparing the obtained mass fragmentograms with already available, as well as with published data, including the library of the National Institute of Standards and Technology, NIST.

Research results

Facial-genetic type of organic matter

The composition and distribution of aromatic compounds of bitumens (phenanthrenes, dibenzothiophenes, and aromatic steroids) well reflect the genetic type of OM (Kolesnikov et al., 1991; Hughes et al., 1995; Chakhmakhchev, Chakhmakhchev, 1995; Kruge, 2000; Kontorovich et al., 2004).

In the composition of phenanthrenes, which make up 40–60% of the total of all aromatic compounds, holonuclear phenanthrene, methylphenanthrenes, dimethylphenanthrenes, and trimethylphenanthrenes were identified (Fig. 2). Methyl- and dimethylphenanthrenes predominate among them in the Povkhovskaya and Novoortyagunskaya areas, while naked phenanthrene varies in a wide range – from almost complete absence to concentrations at the level of methylphenanthrenes. The concentrations of methylphenanthrenes increase in the series 3-MP <2-MP <1-MP <9-MP, while the content of 9-MP is about 30-50% of the total methylphenanthrenes, 1-MP is 25-30%, and the content of 2- and 3-MP do not exceed 20%. In the Druzhnaya and Yuzhno-Yagunskaya areas, the highest concentrations of holonuclear phenanthrene and methylphenanthrene are present, with holonuclear phenanthrene dominating in most of the samples. A similar distribution of the phenanthrene series was noted in the Upper Jurassic-Lower Cretaceous oils of the Koltogorskiy trough (Belitskaya et al., 2008).

Among the trimethyl-substituted phenanthrene derivatives (TMP), high concentrations of 1,7,8- (or 1,2,8-) trimethylphenanthrene are observed in all areas. The high content of 1,7,8-TMF in the Bazhenov Formation can be explained by its origin from bacteria through the degradation of hopanoids (Killops, 1991). In the Yuzhno-Yagunskaya area, 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene (TMTHF) was also identified in the studied bitumoids – up to 3.5% of the sum of all compounds of the phenanthrene series. Increased concentrations of TMTHF, according to

V.A. Kashirtsev et al. (Kashirtsev et al., 2018), along with high concentrations of 1,7,8-trimethylphenanthrene among trimethylphenanthrenes, indicate the plankton-algal-bacterial composition of the initial OM. In the composition of hydrocarbons of the phenanthrene series in the bitumens of the Yuzhno-Yagunskaya and Novoortyagunskaya areas, the compound 1-methyl, 7-isopropyl-phenanthrene (retene) was also identified – up to 2.5% of the sum of all compounds of the phenanthrene series. The presence of TMTHF and retene was previously noted in the oils of the Cretaceous and Jurassic deposits of Western Siberia (Belitskaya et al., 2008).

In the composition of the studied aromatic compounds, an increased (up to 45% and higher) content of sulfur-aromatic compounds of the dibenzothiophene series (holonuclear dibenzothiophene (C12H8S), its methyl-, dimethyl-, and trimethyl-substituted homologues) is recorded (Fig. 2). According to A.E. Kontorovich and

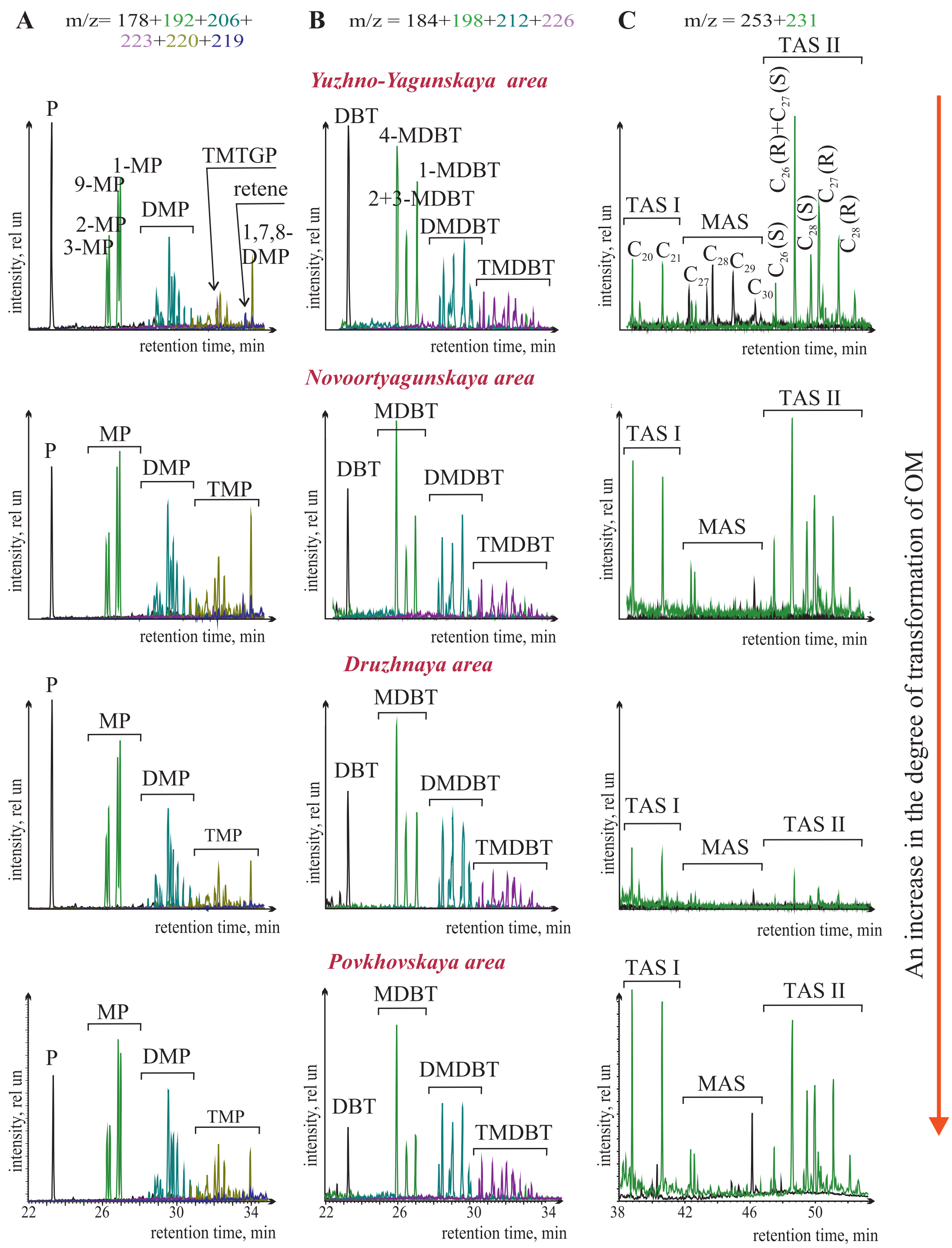

Fig. 2. Typical chromatography-mass fragmentograms of aromatic compounds in chloroform bitumoids of the Bazhenov Formation (according (Eder et al., 2019) with updates): A – tricyclic aromatic hydrocarbons of the phenanthrene series: P – phenanthrene, MP – methylphenanthrenes, DMP – dimethylphenanthrenes, TMP – trimethylphenanthrenes, THP – tetrahydrophenanthrene; B – seroaromatic compounds of the dibenzothiophene series: DBT – dibenzothiophene, MDBT – methyldibenzothiophenes, DMDBT – dimethyldibenzothiophenes, TMDBT – trimethyldibenzothiophenes; C – aromatic steroids: MAS – monoaromatic steroids of the composition C_{27}-C_{30}; TAS I – C_{20}-C_{21} triaromatic steroids, TAS II – C_{26}-C_{28} triaromatic steroids.

E.A. Belitskaya et al., Such an increased content of SAC in the OM and oils of the Bazhenov horizon may be evidence of hydrogen sulfide contamination of the bottom waters of the West Siberian sea basin in the Volgian time (Kontorovich et al., 2004; Belitskaya et al., 2008, etc.).

Methyldibenzothiophenes, which prevail over other homologues in the studied bitumens of the Bazhenov Formation, are represented by 1-, 2-, 3-, and 4-methyl-substituted isomers; their content in bitumoids increases in the series 2 + 3-MDBT <1-MDBT <4-MDBT (in proportions, on average, 20:30:50), which is also typical for aquagenic OM (Schou, Myhr, 1988; Parfenova, 2017).

The distribution of monoaromatic steroids in the bitumoids of the Bazhenov Formation changes irregularly. Their concentrations vary widely, from rather significant to almost complete absence (Fig. 2). The TAS/MAS ratio in the studied collection of bitumoids always exceeds 2.

Among the triaromatic steroids, both high molecular weight (TAS II) with the composition C_{26}-C_{28} and low molecular weight (TAS I) with the composition C_{20}-C_{21} were identified. Elevated concentrations of TAS I are noted at the Druzhnaya (40–60% of the total TAS) and Povkhovskaya (30–50%) areas; at the Yuzhno-Yagunskaya and Novoortyagunskaya, TAS II prevails (more than 70% of the total TAS). Among the high molecular weight triaromatic steroids C_{26}-C_{28}, C_{26} is present in the highest concentrations in all bitumoids, which is consistent with the concept of the mechanism of the formation of the aromatic steroid C_{26} from the preceding sterane C_{27} (Kolesnikov et al., 1991; Derevesnikova et al., 2019). Triaromatic steroids C_{27} and C_{28} are in approximately equal concentrations.

Thus, the distribution of aromatic compounds (high concentrations of dibenzothiophenes, increased values of the TAS/MAS ratio, increased concentrations of triaromatic steroids C_{26}) confirm the aquagenic nature of the OM of the Bazhenov Formation, which is consistent with the results of studying the individual composition of the saturated fraction of bitumen n-alkanes of composition C_{16}-C_{19}, Pr/Ph ratio ≤ 1, sterane index C_{29}/C_{27} = 0.6-0.8, tricyclane index Itc = 0.2-0.6, homogopane ratios C_{35}/C_{34} = 0.7-1.0).

Catagenetic transformation (maturity) of organic matter

As indicators of the maturity of organic matter based on the distribution of aromatic compounds, the following parameters are considered, as indicated above (table): phenatrene index (PI), methylphenanthrene indices (MPI, MPI-I, MPI-2, PP-1 and PP -$1_{modified}$), dibenzothiophene index (DBTI), methyldibenzothiophene ratio (MDR), triaromatic sterane index (TASI).

The phenanthrene index (PI) in bitumens of the Bazhenov Formation in all areas varies mainly from 0.3 to 0.5, however, increased values (0.6–1.0) are noted in the samples of the Povkhovskaya and Novoortyagunskaya areas of open-pore bitumens (Fig. 3).

Methylphenanthrene indices (MPI, MPI-1 and MPI-2) in bitumoids vary mainly within the range of 0.4–0.6. In bitumen of open pores, the values of these parameters are higher than in closed ones (Fig. 3). The bitumoids of the Povkhovskaya and Novoortyagunskaya areas are characterized by increased values of these parameters (up to 1.0), which indicates their greater transformation in comparison with the bitumoids of the Druzhnaya and Yuzhno-Yagunskaya areas.

The methylphenanthrene ratio (PP-1) varies from 0.8 to 1.0 in all areas. The values of this parameter in bitumen of closed pores compared with open ones increases in the Druzhnaya area, decreases in Povkhovskaya and Novoortyagunskaya (Fig. 3). Unlike PP-1, the values of the modified parameter PP-$1_{modified}$ remain constant. In the southern Yagunskaya and friendly bitumoids, the range of PP-$1_{modified}$ values is, as a rule, 1.5–2.0, and in the Novoortyagunskaya and Povkhovskaya bitumoids, it is 2.0–4.0.

The values of the methyldibenzothiophene ratio (MDR) in closed-pore bitumens are differentiated by area, increasing in the series: Yuzhno-Yagunskaya (1.1 ÷ 1.5, with an average of 1.3) → Novoortyagunskaya (1.5 ÷ 2.3, with an average of 1.8) → Druzhnaya (1.7 ÷ 2.3, with an average of 2.0) → Povkhovskaya (2.1 ÷ 2.9, with an average of 2.5) (Fig. 3). For bitumen of open pores, the tendency remains, but less contrasting.

The increased values (up to 4.0) of the dibenzothiophene index (DBTI) confirm that the most transformed is the organic matter of the Bazhenov Formation of the Povkhovskaya and Novoortyagunskaya areas, while in the bitumens of closed pores this parameter decreases to 1.0 (Fig. 3). For the southern Yagunskaya and Druzhnaya bitumoids, this indicator does not change for open and closed pores – 0.3–0.6 (Fig. 3).

The distribution of the higher and lower homologues of triaromatic steroids in the bitumens of the Bazhenov Formation indicates a greater transformation of the organic matter of the Druzhnaya and Povkhovskaya areas in comparison with the Yuzhno-Yagunskaya and Novoortyagunskaya.

The TASI values in all bitumoids of the Povkhovskaya and Druzhnaya areas vary mainly from 0.3 to 0.6, in Novoortyagunskaya and Yuzhno-Yagunskaya – from 0.1 to 0.3 (Fig. 3).

To clarify the degree of catagenetic transformation of OM, the indices calculated by saturated HC biomarkers, such as CPI, Ts/Tm, sterane ratios αα20S/αα20R C_{29} and (ββ20S + 20R)/αα20R C_{29}, as well as the ratio $1/K_i$ = (n-C_{17} + n-C_{18})/(Pr + Ph) (Chakhmakhchev et al., 1995;

2021. V. 23. Is. 1. Pp. 42–51

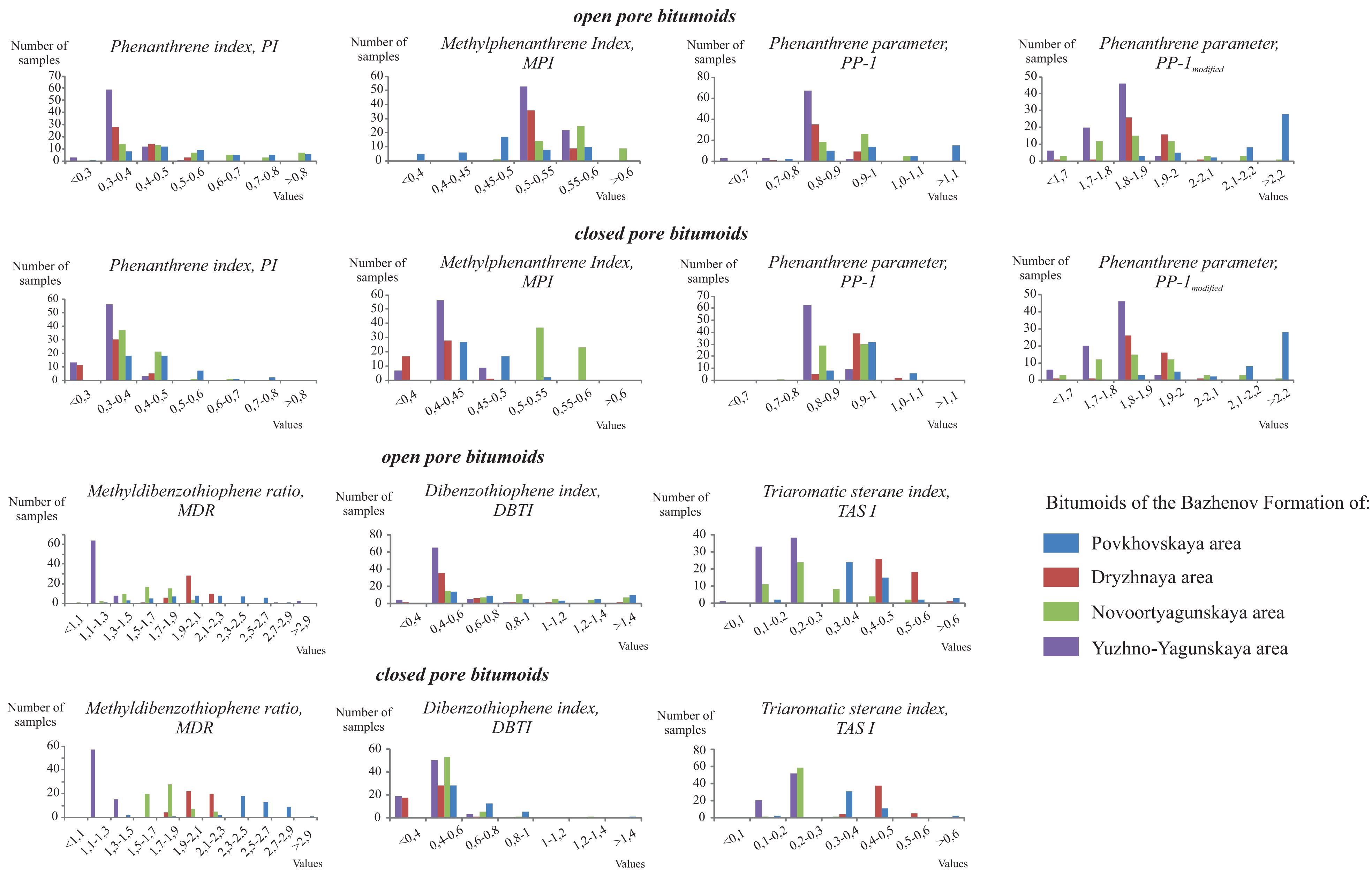

Fig. 3. Values of indicators of the catagenetic transformation of organic matter of the Bazhenov Formation, calculated from the concentrations of aromatic compounds in chloroform bitumoids of open and closed pores.

Petrov, 1984; Kontorovich et al., 2004; Peters et al., 2005; Goncharov et al., 2004, 2013, etc.).

The CPI index values in bitumoids of the Bazhenov Formation, both open and closed pores, vary from 0.8 to 1.2, and 85% of the entire study sample falls within the range of 0.9–1.0.

The values of the $1/K_i$ parameter vary from 1 to 3.5, reaching the highest values in bitumen in the open pores of the Povkhovskaya and Druzhnaya areas (> 2.5).

In closed-pore bitumens, the $1/K_i$ values of these samples decrease to 2–2.5. The values of the indicator for the samples of the Novoortyagunskaya and Yuzhno-Yagunskaya areas vary mainly within the range of 1–1.5 in closed-pore bitumen and 1–2 in open-pore bitumen.

The values of the ratio of steranes (ββ20S + 20R)/αα20R C_{29} in bitumoids vary from 3.0 to 5.5, with no differentiation across the territory. The αα20S/αα20R ratios of C_{29} steranes in the samples from the Povkhovskaya area vary mainly from 0.6 to 1.0, in the samples from the Druzhnaya and Yuzhno-Yagunskaya areas – from 0.8 to 1.2, in the samples from the Novoortyagunskaya area – from 1.0 to 1.6. In bitumoids of closed pores, in comparison with bitumoids of open pore space, there is a tendency to underestimate the values of these parameters.

The trisnorhopane ratio Ts/Tm fairly well delineates the collection of bitumoids in the study area, while the bitumoids of the open and closed pore spaces of the rocks are characterized by similar values. The spread of Ts/Tm values is determined by the intervals: at Povkhovskaya area (76% of samples) – 1.25–1.5, Druzhnaya area (82%) – 1.0–1.25, Novoortyagunskaya area (67%) – 0.75 –1, in the South Yagunskaya area (92%) – 0.5–0.75. The average values of this parameter in the samples of the Povkhovskaya, Druzhnaya, Novoortyagunskaya and Yuzhno-Yagunskaya areas are 1.3; 1.0; 0.8 and 0.6, respectively.

Thus, the analysis of molecular parameters showed a decrease in the degree of maturity of the organic matter of the Bazhenov Formation within the Khantey hemianteclise in the southwestern direction – from the Povkhovskaya area to the Yuzhno-Yagunskaya (Fig. 1, 4). According to the results of coal-petrographic (vitrinite reflectance $R_{vt}° = 0.67–0.78$) and pyrolytic ($T_{max} = 436–449$ °C) core studies (according to A.N. Fomin and V.N. Melenevskiy data) – OM is in the main phase of oil formation, as far as gradation of catagenesis is MK_1^2 (Fomin, 2011; Kontorovich et al., 2018; Lopatin, Emets, 1987; Gramberg et al., 2001).

Since the processes of the catagenetic transformation of OM to the same extent affect the bitumoids from the open and closed pore space of rocks, the differences in the values of the maturity of OM are explained by the influence of migration processes, which, first of all, affect the bitumoids of open pores (Beletskaya, Borovaya, 1977). According to G.N. Gordadze. and Rusinova G.V., the true degree of OM maturity during geological time can be "shaded" due to the constant replenishment of thermodynamically less stable newly formed hydrocarbons, and, all other things being equal, the degree of OM maturity correlates with the group composition of oils (and bitumoids) (Gordadze, Rusinova, 2003). According to the results of bituminological analysis, the group composition of the studied closed-pore bitumoids is characterized by a lower content of hydrocarbons, a higher content of asphaltenes in comparison with open-pore bitumoids.

The HC content in open pore bitumoids reaches 80% per bitumen, and the concentration of asphaltenes is about 10%. In closed-pore bitumens, the HC content varies from 40 to 60% per bitumoid, and content of asphaltenes increases to 20%. The lightest group composition is observed in bitumoids of open pores of Novoortyagunskaya and Povkhovskaya areas, where there are 2 times more saturated hydrocarbons than aromatic ones. In the bitumoids of the Druzhnaya and Yuzhno-Yagunskaya areas, the concentration of aromatic hydrocarbons increases (the ratio of saturated hydrocarbons/aromatic hydrocarbons on average is ~ 1). In bitumen of closed pores, the ratio of saturated hydrocarbons/aromatic hydrocarbons on average decreases compared to open ones (1.29; 0.98; 0.81; 0.67,

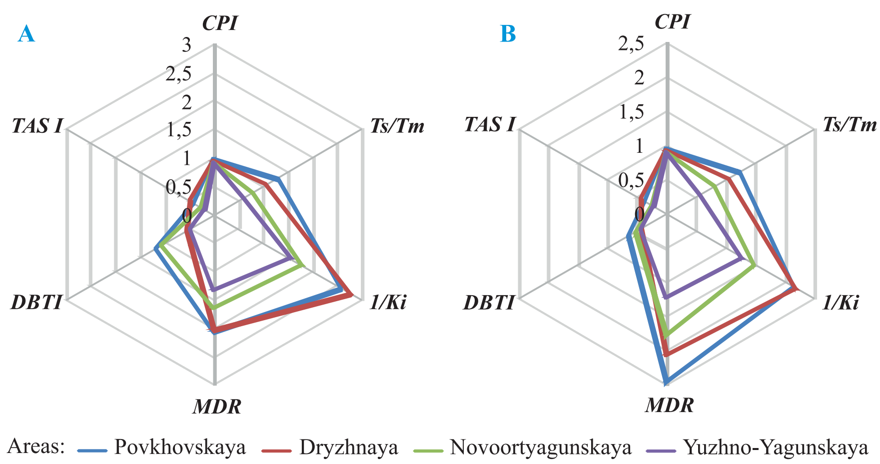

Fig. 4. Transformation of OM of the Bazhenov Formation in bitumoids from the open (A) and closed (B) pore space of rocks

respectively, for the Povkhovskaya, Novoortyagunskaya, Druzhnaya and Yuzhno-Yagunskaya areas).

Discussion and conclusions

The nature of the distribution of aromatic compounds in the bitumens of the Bazhenov Formation on the territory of the Khantey hemianteclise is well comparable with the distribution of individual compounds of the saturated fraction of bitumen, which makes it possible to use them to determine the conditions for the formation and further transformation of organic matter during catagenesis.

Analysis of molecular parameters characterizing the facies-genetic type of the initial organic matter, such as the distribution of normal alkanes, Pr/Ph ratio, sterane index, tricyclane index, homogopane index, as well as an increased content of dibenzothiophenes, distribution of methyldibenzothiophenes, prevalence of triaromatic steroids over monoaromatic steroids, predominance of C_{26} among triaromatic steroids, confirms the drastic reduction situation in sediments during diagenesis and the aquagenic nature of the OM of the Bazhenov Formation, as well as the genetic unity of bitumoids extracted from the open and closed pore space of rocks.

Differences in the distribution of OM aromatic compounds in the study area are mainly associated with the degree of its catagenetic transformation (maturity). Despite the rather close territorial location of the studied areas, the transformation of OM in the north of the Khantey hemianteclise (Surgut area of the Khanty-Mansiysk Autonomous District) decreases in the southwestern direction: from the Povkhovskaya area, confined to the South Nadym homocline, to the Novoortyagunskaya (the junction zone of the South Nadym homocline) and Druzhnaya (actually Khantey hemianteclise) areas, and then to the South Yagunskaya area (Surgut arch).

According to the informativeness of use, the indicators characterizing the degree of maturity of the OM can be divided into informative and less informative. The first include CPI, Ts/Tm, $1/K_i = (n\text{-}C_{17} + n\text{-}C_{18})/(Pr + Ph)$, MDR = 4-MDBT/1-MDBT, DBTI = (2 + 3-MDBT)/DBT and TASI = TAS I/(TAS I + TAS II) (Fig. 4), to the latter – the ratios of steranes αα20S/αα20R C_{29} and (ββ20S + 20R)/αα20R C_{29}, phenanthrene indices MPI, MPI-1, MPI-2, PP-1 (except maybe $PP\text{-}1_{modified}$). The most informative and contrasting geochemical indicators of the catagenetic transformation of OM are the ratios of alkanes ($1/K_i$), trisnorgopanes (Ts/Tm), and dibenzothiophenes (MDR and DBTI). Earlier, researchers (Kontorovich et al., 2004; Goncharov et al., 2004; 2013) have already noted the effectiveness of these parameters for the OM of the Bazhenov Formation.

In addition, the values of some indicators (PI, MPI, PP-1, MDR, DBTI, 1/ K_i, (ββ20S + 20R)/αα20R C_{29}, αα20S/αα20R C_{29}) differ in bitumoids extracted from open and closed pore spaces of rocks. A clear tendency towards a decrease and leveling of the values of these parameters in closed-pore bitumoids compared to open-pore bitumen was noted. Previously, such an effect was noted when comparing the “bonded” and “freely soluble” bitumen of the Bazhenov Formation of the Salym field (Snimshchikova et al., 1989). Apparently, such a regularity is associated with the removal of the most transformed, lightweight and migration-capable part of the bitumen from the rock during the extraction of bitumoids from open pores.

Acknowledgments

This work was supported by the Basic Scientific Research Projects No. 0331-2019-0022 «Organic geochemistry and the history of geological development of the dominant oil and gas systems of the Upper Proterozoic and Phanerozoic of Siberia» and No. 0266-2019-0006 «Development of resource assessment methodologies, exploration and calculation of reserves of hard-to-recover oil in carbonate-argillaceous-siliceous, carbonate and saline sand reservoirs».

The authors are grateful to the reviewer for the high quality, professional and detailed analysis of the article, as well as for valuable and helpful comments and remarks.

References

Alexander R., Strachan M.G., Kagi R. I., Van Bronswuk W. (1986). Heating rate effects on aromatic maturity indicators. *Org. Geochem.*, 10, pp. 997–1003. https://doi.org/10.1016/S0146-6380(86)80038-9

Beletskaya S.N., Borovaya G.M. (1977). Distribution patterns of mobile components of dispersed organic matter in the pore system of rocks. *Proc. VIII Int. Congress on Organic Geochemistry*, I, pp. 90–96. (In Russ.)

Belitskaya E.A., Serebrennikova O.V., Kadycharov P.B. (2008). Crude oils from the Koltogor rift and adjacent areas (West Siberia): Specifics of the composition of aromatic compounds. *Petroleum Chemistry*, 48(4), pp. 260–268. https://doi.org/10.1134/S0965544108040038

Borrego A.G., Blanco C.G., Püttmann W. (1997). Geochemical significance of the aromatic hydrocarbon distribution in the bitumens of the Puertollano oil shales, Spain. *Organic Geochemistry*, 26(3/4), pp. 219–228. https://doi.org/10.1016/S0146-6380(96)00158-1

Budzinski H., Garrigues PH., Connan J., Devillers J., Domine D., Radke M., Oudin J.L. (1995). Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. *Geochimica et Cosmochimica Acta*, 59(10), pp. 2043–2056. https://doi.org/10.1016/0016-7037(95)00125-5

Burdelnaya N.S., Bushnev D.A., Derevesnikova A.A. (2018). 1,2,8–trimethylphenanthrene in bitumen and Domanik oils of the Timan–Pechora oil and gas province. *Proc. Int. Conf.: Advanced materials with a hierarchical structure for new technologies and reliable structures” and “Chemistry of oil and gas”*. Tomsk: TSU, p. 671. DOI: 10.17223/9785946217408/420 (In Russ.)

Cassini F., Gallango O., Talukdar S., Vallejos C., Ehrmann U. (1988). Methylphenanthrene maturity index of marine source rock extracts and crude oils from the Maracaibo Basin. *Organic Geochemistry*, 1–3, pp. 73–89. https://doi.org/10.1016/0146-6380(88)90027-7

Chakhmakhchev V.A. (1989). Hydrocarbons – geochemical indicators of the oil and gas content of the subsoil. *Geokhimiya*, 8, pp. 1108–1119. (In Russ.)

Chakhmakhchev A.V., Chakhmakhchev V.A. (1995). Aromatic sulfur compounds as indicators of the thermal maturity of hydrocarbon systems. *Geokhimiya*, 11, pp. 1656–1669. (In Russ.)

Chakhmakhchev A.V., Vinogradova T.L., Agafonova Z.G., Gordadze T.I., Chakhmakhchev V.A. (1995). Benzothiophenes are highly informative indicators of the hydrocarbon systems catagenesis. *Geologiya nefti i gaza = Russian Oil and Gas Geology*, 7, pp. 32–37. (In Russ.)

Chakhmakhchev V.A., Vinogradova T.L. (2003). Geochemical indicators of facies and genetic types of parent organic matter. *Geochemistry International*, 5, pp. 497–502.

Derevesnikova A.A., Bushnev D.A., Burdelnaya N.S. (2019). Aromatic biomarkers of sterane and hopane series in upper devonian oils and bitumoids of domanik deposits of the Timan-Pechora basin. *Vestnik of the Institute of Geology of the Komi Science Centre UB RAS*, 5, pp. 3–12. DOI: 10.19110/2221-1381-2019-5-3-12 (In Russ.)

Eder V.G., Zamiraylova A.G., Zhigul'skiy I.A. (2016). Lithology of the Bazhenov Formation in the Khanteyskaya Hemianteclise and Mezhovsky Megamys of the West Siberian Oil and Gas Basin. *Geologiya nefti i gaza = Russian Oil and Gas Geology*, 6, pp. 87–96. (In Russ.)

Eder V.G., Kostyreva E.A., Yurchenko A.Yu., Balushkina N.S., Sotnich I.S., Kozlova E.V., Zamiraylova A.G., Savchenko N.I. (2019). New data on lithology, organic geochemistry and accumulation conditions of the Bazhenov Formation in Western Siberia. *Georesursy = Georesources*, 21(2), pp. 129–142. https:// doi.org/10.18599/grs.2019.2.129–142 (In Russ.)

Farrington J.W., Davis A.C., Tarafa M.E., McCarrrey M.A., Whelan J.K., Hunt J.M. (1988). Bitumen molecular maturity parameters in the Ikpikpuk well, Alaskan North Slope. *Organic Geochemistry*, 13(1–3), pp. 303–310. https://doi.org/10.1016/0146-6380(88)90049-6

Fomin A.N. (2011). Catagenesis of organic matter and petroleum potential of Mesozoic and Paleozoic deposits of the West Siberian megabasin. Novosibirsk: IPGG SB RAS, 331 p. (In Russ.)

Gallango O., Cassani F. (1992). Biological marker maturity parameters of marine crude oils and rock extracts from the Maracaibo Basin, Venezuela. *Organic Geochemistry*, 18(2), pp. 215–224. https://doi.org/10.1016/0146-6380(92)90133-I

Goncharov I.V., Samoylenko V.V., Oblasov N.V., Nosova S.V. (2004). Molecular parameters of organic matter catagenesis in rocks of the Bazhenov Formation, Tomsk Region. *Geologiya nefti i gaza = Russian Oil and Gas Geology*, 5, pp. 53–60. (In Russ.)

Goncharov I.V., Samoylenko V.V., Nosova S.V., Oblasov N.V. (2005). Method for determining mature oil source rocks. Patent 2261438 RF (In Russ.)

Goncharov I.V., Samoylenko V.V., Oblasov N.V., Fadeeva S.V. (2013). Organic matter catagenesis of the Bazhenov Formation rocks in the southeast of Western Siberia (Tomsk region). *Neftyanoe khozyaystvo = Oil industry*, 10, pp. 32–37. (In Russ.)

Gordadze G.N., Rusinova G.V. (2003). The reliability of assessing the degree of organic matter maturity by hydrocarbon-biomarkers. *Proc. V Int. Conf.: Chemistry of oil and gas*. Tomsk: NIIC SB RAS, pp. 127–129. (In Russ.)

Gramberg I.S., Evdokimova N.K., Suprunenko O.I. (2001). Catagenetic zoning and petroleum potential of the sedimentary cover of the Barents sea shelf. *Geologiya i geofizika = Russian Geology and Geophysics*, 42(11–12), pp. 1808–1820. (In Russ.)

Hughes W.B., Holba A.G., Dzou L.I.P. (1995). The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochimica et Cosmochimica Acta*, 59(17), pp. 3581–3598. https://doi.org/10.1016/0016-7037(95)00225-O

Kashirtsev V.A., Parfenova T.M., Golovko A.K., Nikitenko B.L., Zueva I.N., Chalaya O.N. (2018). Phenanthrene biomarkers in the organic matter of Precambrian and Phanerozoic deposits and in oils of the Siberian platform. *Russian Geology and Geophysics*, 59(10), pp. 1380–1388. https://doi.org/10.1016/j.rgg.2018.09.013

Killops S.D. (1991). Novel aromatic hydrocarbons of probable bacterial origin in a Jurassic lacustrine sequence. *Organic Geochemistry*, 17(1), pp. 25–36. https://doi.org/10.1016/0146-6380(91)90037-K

Kolesnikov A.Yu., Naydenov O.V., Matveeva I.A. (1991). Relict polycyclic aromatic hydrocarbons as indicators of the conditions for the genesis of oils. *Petroleum Chemistry*, 31(6), pp. 723–736. (In Russ.)

Kontorovich, V.A., Belyaev S.Yu., Kontorovich A.E., Krasavchikov V.O., Kontorovich A.A., Suprunenko O.I. (2001). Tectonic structure and development history of the West Siberian geosyneclise in the Mesozoic and Cenozoic. *Geologiya i geofizika = Russian Geology and Geophysics*, 42(11–12), pp. 1832–1845. (In Russ.)

Kontorovich A.E., Melenevskiy V.N., Ivanova E.N., Fomin A.N. (2004). Phenanthrenes, aromatic steranes and dibenzothiophenes in Jurassic deposits of the West Siberian oil and gas basin and their importance for organic geochemistry. *Geologiya i geofizika = Russian Geology and Geophysics*, 45(7), pp. 873–883. (In Russ.)

Kontorovich A.E., Yan P.A., Zamiraylova A.G., Kostyreva E.A., Eder V.G. (2016). Classification of rocks of the Bazhenov Formation. *Russian Geology and Geophysics*, 57(11), pp. 1606-1612. https://doi.org/10.1016/j.rgg.2016.10.006

Kontorovich A.E., Kostyreva E.A., Rodyakin S.V., Sotnich I.S., Yan P.A. (2018a). Geochemistry of Bazhenov Formation bitumoids. *Geologiya nefti i gaza = Russian Oil and Gas Geology*, 2, pp.79–88. (In Russ.)

Kontorovich A.E., Rodyakin S.V., Burshteyn L.M., Kostyreva E.A., Ryzhkova S.V., Yan P.A. (2018b). Porosity and oil saturation of pore space in the Bazhenov Formation rocks. *Geologiya nefti i gaza = Russian Oil and Gas Geology*, 5, pp. 61–73. (In Russ.)

Kostyreva E.A., Sotnich I.S. (2017). Geochemistry of organic matter of the Bazhenov Formation in the north of the Khantey anteclise. *Russian Geology and Geophysics*, 58(3–4), pp. 434–442. https://doi.org/10.1016/j.rgg.2016.09.019 (In Russ.)

Kruge M.A. (2000). Determination of thermal maturity and organic matter type by principal components analysis of the distributions of polycyclic aromatic compounds. *International Journal of Coal Geology*, 43, pp. 27–51. https://doi.org/10.1016/S0166-5162(99)00053-1

Lopatin N.V., Emets T.P. (1987). Pyrolysis in petroleum geochemistry. Moscow: Science, 144 p. (In Russ.)

Ludwig B., Hussler G., Wehrung P., Albrecht P. (1981). C_{26}-C_{29} triaromatic steroid derivatives in sediments and petroleums. *Tetrahedron Lett.*, 22, pp. 3313–3316. https://doi.org/10.1016/S0040-4039(01)81893-1

Mackenzie A.S., Brassell S.C., Eglinton G., Maxwell J.R. (1982). Chemical fossil: the geological fate of steroids. *Science*, 217, pp. 491–504. DOI: 10.1126/science.217.4559.491

Parfenova T.M. (2017). Geochemistry of Sulfur and Sulfur Compounds of the Cambrian Kuonamka Complex (Eastern Siberian Platform). *Georesursy = Georesources*, 19(1), pp. 45–51. http://doi.org/10.18599/grs.19.1.8

Petrov Al.A. (1984). Petroleum hydrocarbons. Moscow: Science, 264 p. (In Russ.)

Peters K.E., Walters C.C., Moldowan J.M. (2005) The biomarker guide. V.2. New York: Cambridge University Press, 1155 p.

Radke M. (1988). Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology*, 5, pp. 224–236. https://doi.org/10.1016/0264-8172(88)90003-7

Radke M., Willsch H., Leuthaeuser D., Teichmuller M. (1982). Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta*, 46, pp. 1831–1848. https://doi.org/10.1016/0016-7037(82)90122-3

Santamaria-Orozco D., Horsfield B., Di Primio R., Welte D.H. (1998). Influence of maturity on distributions of benzo- and dibenzothiophenes in Tithonian source rocks and crude oils, Sonda de Campeche, Mexico. *Organic Geochemistry*, 28(7–8), pp. 423–439. https://doi.org/10.1016/S0146-6380(98)00009-6

Schou L., Myhr M.B. (1988). Sulfur aromatic compounds as maturity parameters. *Organic Geochemistry*, 13, pp. 61–66. https://doi.org/10.1016/0146-6380(88)90025-3

Snimshchikova E.V., Trofimova I.A., Rudneva N.M., Severinova L.P. (1989). Readily soluble and bound bitumen of the Bazhenov Formation. Geochemical problems of assessing oil and gas content. Moscow: IGIRGI, pp. 122–127. (In Russ.)

About the Authors

Inga S. Sotnich – Researcher, Laboratory of the Problems of Geology, Exploration and Development of hard-to-recover oil fields; Researcher of the Laboratory of Petroleum Geochemistry, Trofimuk Institute of Petroleum Geology and Geophysics of Siberian Branch of the Russian Academy of Sciences

3, Ak. Koptyug ave., Novosibirsk, 630090, Russian Federation

Elena A. Kostyreva – Cand. Sci. (Geology and Mineralogy), Senior Researcher of the Laboratory of Petroleum Geochemistry, Trofimuk Institute of Petroleum Geology and Geophysics of Siberian Branch of the Russian Academy of Sciences

3, Ak. Koptyug ave., Novosibirsk, 630090, Russian Federation

Manuscript received 7 May 2020;
Accepted 15 October 2020; Published 30 March 2021