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Geochemistry of phenanthrenes, dibenzothiophenes and aromatic steroids in the Bazhenov formation's source rock of the south-east of Western Siberia (Tomsk region)

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Abstract. The paper presents the results of studying aromatic compounds (phenanthrenes, dibenzothiophenes, aromatic steroids) in source rock extracts (bitumoids) from the Bazhenov Formation of the Tomsk Region (south-east of Western Siberia, Russia). In addition to holonuclear and monomethyl-substituted structures of the phenanthrene and dibenzothiophene series we also identified their di- and trimethyl-substituted homologues. A comparative analysis of the relative concentrations of the main groups of aromatic compounds calculated by two methods (with and without di- and trimethylphenanthrenes and dibenzothiophenes) showed their identity. The main factor controlling the content and distribution of aromatic compounds has been established as the degree of maturity of organic matter. The most informative molecular maturity indices for the Bazhenov Formation's organic matter whose maturity corresponds to low and medium gradations of catagenesis (PK_3-$MK_1{}^2$) are the ratios of 4-MDBT/1-MDBT, TASI, TAS/MAS, and TMTGP/1,7,8-TMP.

Keywords: organic matter, bitumoids (rock extracts), aromatic compounds, catagenesis, source rocks, Bazhenov formation, Upper Jurassic, Western Siberia

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Introduction

Recently, studying the composition of aromatic fractions of source rock extracts (bitumoids) and crude oils has attracted increasing attention in modern geochemical studies of organic matter (Kashirtsev et al., 2018; Burdel'naya, Bushnev, 2021; Dolzhenko, Fomin, 2022; and others). Phenanthrene tricyclic aromatics, dibenzothiophene sulphur aromatics and aromatic steroids are the most informative aromatic compounds for characterizing dispersed organic matter. They are not 'biomarkers' in the conventional sense. However, they carry the most important information about the conditions under which organic matter was formed and transformed in the geological past (Radke et al., 1986; Cassani et al., 1988; Hughes et al., 1995; Szczerba, Rospondek, 2010; Kolesnikov et al., 1991; Chakhmakhchev, Chakhmakhchev, 1995; Kontorovich et al., 2004; Goncharov et al., 2013; and others).

This article continues a series of papers (Eder et al., 2019; Sotnich, Kostyreva, 2021; Sotnich, Kostyreva, 2024) in which the composition and structure of aromatic and sulfur-aromatic compounds in extracts from the open and closed pore space of the Bazhenov source rocks have been studied using modern analytical techniques. The object of the study is the Bazhenov formation (Tomsk region) from the sections of the wells Pelginskaya-2, Sredneyulzhavskaya-10, Archinskaya-47, Yuzhno-Mayskaya-413, Zapadno-Kvenzerskaya-4 (Figure 1).

Tectonically, the Archinskaya, Yuzhno-Mayskaya and Zapadno-Kvenzerskaya wells are located in the Koltogorsko-Nyurolsky Trough (a negative superorder structure), while the Pelginskaya and Sredneyulzhavskaya wells are located in the Chuziksko-Chizhapskaya mesosaddle and the Severo-Mezhovskaya megamonocline – intermediate tectonic structures on the

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south-eastern side of the Koltogorsko-Nyurolsky Trough (Kontorovich et al., 2001). The Bazhenov Formation in this area accumulated under shallow (100–200 m) marine conditions (Kontorovich et al., 2013) and is predominantly represented by argillaceous and siliceous rocks – siliceous-argillaceous, kerogen-argillaceous-siliceous (close to silicites) and kerogen-siliceous-argillaceous mixtites (Eder et al., 2022). According to the pyrolytic and coal petrographic data, the organic matter is immature/lowly mature (katagenesis grade PK_3-MK_1^1) in the samples from Archinskaya, Yuzhno-Mayskaya, Pelginskaya, Sredneyulzhavskaya wells and mature (grade MK_1^2) in samples of the Zapadno-Kvenzerskaya well (Sotnich, Kostyreva, 2024; Fomin, 2011; Kontorovich et al., 2018).

Materials and methods

The study was conducted according to the methodology of Trofimuk Institute of Petroleum Geology and Geophysics of the Siberian Branch of the Russian Academy of Sciences (Kontorovich et al., 2018), which allows the successive extraction of naphthenes from open (‘free micro-oil’) and closed (autochthonous bitumoids) pore spaces of the source rock (Kontorovich et al., 2018; Sotnich, Kostyreva, 2021; Sotnich et al., 2023). The collection comprised 340 samples of bitumoids, including 67 samples from the Archinskaya well, 65 samples from the Zapadno-Kvenzerskaya well, 53 samples from the Pelginskaya well, 58 samples from the Sredneyulzhavskaya well, and 97 samples from the Yuzhno-Mayskaya well.

The separation of the aromatic (naphthene-aromatic) fraction of bitumoids was carried out by eluent (adsorption-liquid) chromatography.

Chromato-mass-spectrometric studies of the aromatic fraction of bitumoids were carried out on an Agilent Technologies 6890 gas chromatograph with a high-performance mass-selective detector MSD 5973N and computer system (ChemStation) of data registration and processing HPG 1034. Chromatograms for total ion current (TIC), as well as chromatograms for 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 (reten) and m/z 223 (1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene) were obtained. The compounds were identified by retention time and analysis of the obtained mass fragments and mass spectra of the studied components by comparing them with the already available spectra from the library of the National Institute of Standards NIST-05, as well as with published data.

Results

Distribution of the main groups of aromatic compounds

The content of the main groups of aromatic compounds (∑ phenanthrenes, ∑ dibenzothiophenes, ∑ aromatic steroids) was calculated in two ways: 1) according to the method (Kontorovich et al., 2004), the sum of holonuclear phenanthrene, holonuclear dibenzothiophene, their methyl-substituted homologues, monoaromatic steroids

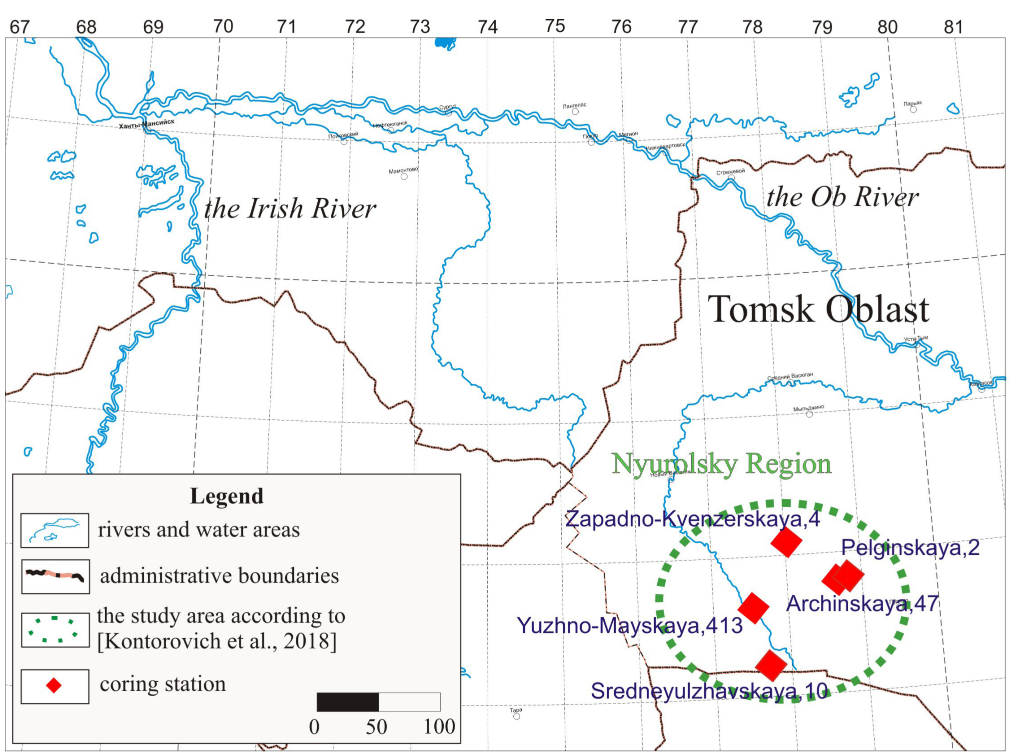

Figure 1. Overview map of the study areas

of C_{27}-C_{30} composition, and triaromatic steroids of C_{20}-C_{21} and C_{26}-C_{28} composition was taken as 100%; 2) the sum of all identified compounds is taken as 100%, including di- and trimethylphenanthrenes, di- and trimethyldibenzothiophenes, as well as the compounds 1-methyl-7-isopropyl-phenanthrene (rethene) and 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene (TMTHP). The levels of aromatic compounds are comparable in both cases, as shown by the analysis of the assessment results (Table 1). The relative content of aromatic groups (phenanthrenes, dibenzothiophenes, aromatic steroids) is presented in the first variant of the calculation, as is more commonly used in geochemical studies. The quantitative assessment of all identified compounds was performed to identify compositional and structural features within each group.

Phenanthrenes and aromatic steroids are the main constituents of the naphthene-aromatic fractions of the bitumoids (Table 1, Figure 2), but their relative content is highly dependent on the maturity of the organic matter. For example, in the immature samples from the Sredneyulzhavskaya-10 well (R^0_{vt} = 0.62% according to A.N. Fomin), aromatic steroids predominate in the composition of aromatic compounds – up to 90%, but their concentrations are reduced in favor of phenanthrenes in the samples from the Pelginskaya-2 and Archinskaya-47 wells (R^0_{vt} up to 0.63%) (Table 1).

The predominance of phenanthrenes is more pronounced (up to 80%) in the samples from the Yuzhno-Mayskaya-413 well (R^0_{vt} = 0.65%). In the most mature organic matter of the Zapadno-Kvenzerskaya-4 well (R^0_{vt} = 0.76–0.78%), phenanthrenes dominate – up to 86% (on average, 79.9%), the content of aromatic steroids does not exceed 5% (on average, 2.8%).

The content of sulfur-aromatic compounds of the dibenzothiophene series in the bitumoids of the Bazhenov Formation of the Tomsk Region varies widely (on average, from 7.5 to 25.7% of ∑ aromatic compounds) and is associated with the environments in which the organic matter accumulated. According to the paleotectonic reconstructions of V.A. Kontorovich et al., “the West Siberian basin underwent regional-scale subsidence relative to its flanking orogenic structures during the whole Mesozoic–Cenozoic history” (Kontorovich et al., 2017), respectively, the Bazhenov Formation in the section of the Archinskaya,

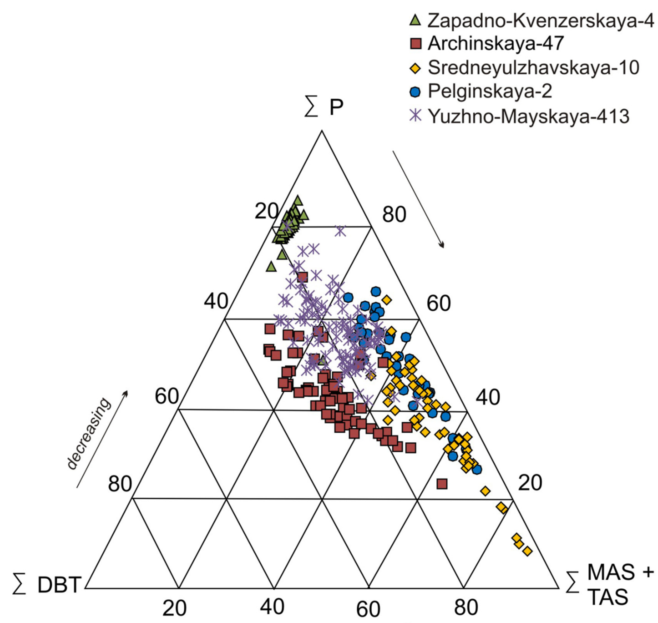

Figure 2. Triangular diagram of main aromatic compound distribution in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region

Well (Number of samples)	R^0_{vt}, % (according to A.N. Fomin)	Catagenesis gradation	Calculation way No 1 (according to (Kontorovich et al., 2004))			Calculation way No 2		
			∑P	∑DBT	MAS+TAS	∑P	∑DBT	MAS+TAS
Sredneyulzhavskaya-10 (58 samples)	0.62	PK_3-MK_1^1	(8.7÷63.7)/ 37.7	(2.0÷17.1)/ 7.5	(31.9÷89.3)/ 54.9	(15.7÷60.5)/ 41.6	(0.0 ÷ 15.4)/ 6.9	(34.7 ÷ 82.2)/ 51.6
Pelginskaya-2 (53 samples)	0.63		(26.4÷65.3)/ 49.5	(3.6÷15.6)/ 8.5	(23.8÷70.0)/ 42.0	(20.0÷69.0)/ 50.5	(3.1 ÷ 15.2)/ 8.1	(22.5 ÷ 76.5)/ 41.4
Archinskaya-47 (67 samples)	0.61-0.63		(23.3÷68.6)/ 43.3	(11.7÷35.0)/ 25.7	(10.8÷64.3)/ 31.0	(36.8÷69.0)/ 46.9	(13.8÷34.5)/ 26.2	(5.9 ÷ 45.9)/ 27.0
Yuzhno-Mayskaya-413 (97 samples)	0.65		(41.8÷80.1)/ 57.2	(6.4÷29.2)/ 18.4	(2.7÷49.3)/ 24.4	(43.8÷79.0)/ 58.9	(9.4 ÷ 29.0)/ 18.8	(2.2 ÷ 40.8)/ 22.3
Zapadno-Kvenzerskaya-4 (65 samples)	0.76-0.78	MK_1^2	(50.7÷85.7)/ 79.9	(12.1÷25.0)/ 17.0	(1.6÷5.1)/ 2.8	(51.6÷85.4)/ 80.0	(12.7÷24.3)/ 17.5	(1.4 ÷ 3.2)/ 2.1

Table 1. Content of the main aromatic groups in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region. ∑P – total phenanthrenes, ∑DBT – total dibenzothiophenes, MAS – monoaromatic steroids of C_{27}-C_{30} composition, TAS – triaromatic steroids of C_{20}-C_{21} and C_{26}-C_{28} composition. Value Range: (min ÷ max) / average.

Yuzhno-Mayskaya, and Zapadno-Kvenzerskaya wells accumulated in more submerged (deep-water) conditions compared to the Bazhenov Formation of the Pelginskaya and Sredneyulzhavskaya areas.

The proportions of major groups of aromatic compounds in bitumoids extracted from open and closed pore spaces of Bazhenov Formation rocks were shown to be identical by comparative analysis. Some differences have been observed in the bitumoids from the Sredneyulzhavskaya well, where the ratio of phenanthrenes to aromatic steroids is more even in the bitumoids extracted from the coarse crushed samples (open pore space). Aromatic steroids are predominant among the aromatic compounds in bitumoids extracted from both regular (open pore) and finely crushed (closed pore) samples.

Phenanthrene/dibenzothiophene ratios are often used in the geochemical literature as an indicator of depositional conditions and source rock lithology (Hughes et al., 1995; Kontorovich et al., 2005; and others). For example, the dependence of the dibenzothiophene/phenanthrene ratio (DBT/P) on the isoprene ratio (Pr/Ph) was proposed by (Hughes et al., 1995) to be used for this purpose. Kontorovich A.E. suggested using the ratio (DBT+Σ MDBT) / (P+Σ MP) instead of DBT/P (Kontorovich et al., 2005). For the studied bitumoid collection, both the DBT/P and the (DBT+∑ MDBT) / (P+∑ MP) values are always <1, and the Pr/Ph values vary between 1 and 3, corresponding to the marine and lacustrine clayey rock accumulation zone. Although individual carbonate layers (HCl-insoluble residue <50%) are present in the section, they are not prominent in terms of DBT/P values against the background of other lithotypes.

Distribution of phenanthrene aromatic compounds

The following phenanthrene aromatics were identified: holonuclear phenanthrene (m/z 178), methylphenanthrenes (m/z 192), dimethylphenanthrenes (m/z 206) and trimethylphenanthrenes (m/z 220). Among the trimethylphenanthrenes (Figure 3a), 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene (TMTHP) and 1-methyl, 7-isopropylphenanthrene (rethene) were also identified for fragment ions m/z = 223, M+238 and m/z = 219, M+234.

Analysis of phenanthrene composition and structure in bitumoids from the Bazhenov Formation rocks of the Tomsk region revealed their distribution dependence on the organic matter maturity (Figure 3a, Table 2).

In the immature organic matter from the Sredneyulzhavskaya-10, Pelginskaya-2, Archinskaya-47 and Yuzhno-Mayskaya-413 wells, there is a predominance of holonuclear phenanthrene (25–35%) and methylphenanthrenes (30–40%) over other phenanthrene-related compounds. The content of dimethylphenanthrenes is mainly 15–20%, trimethylphenanthrenes – up to 15% of the total phenanthrenes. We have also identified the following compounds in these samples: 1,7,8-trimethylphenanthrene (partially hydrogenated phenanthrene – an intermediate in the transformation of tricyclic terpanes (Kashirtsev et al., 2018; Burdel'naya, Bushnev, 2021) and retene (1-methyl,7-isopropylphenanthrene). Figure 3b shows the result of quantifying the relative contents of these three compounds.

TMTHP, retene and 1,7,8-trimethylphenanthrene proportions were shown in Figure 3b to depend on organic matter accumulation conditions. Comparatively high 1,7,8-trimethylphenanthrene content (40–60%) and low TMTHP concentration (20–40%) are typical for Pelginskaya and Sredneyulzhavskaya bitumoids, while Archinskaya and Yuzhno-Mayskaya samples, on the contrary, are characterized by low 1,7,8-trimethylphenanthrene content (<20%) and high TMTHP content – 40–80%. Rethene concentration in both cases do not normally exceed 40% (the exception is the samples belonging to the upper part of the Yuzhno-Mayskaya borehole section, where lithological features have often been observed to correspond to "oxidative and suboxidative conditions in the bottom waters and the upper part of the sediment" in accordance with (Eder et al., 2022)).

In the composition of the mature organic matter of the Bazhenov Formation from the Zapadno-Kvenzerskaya well, methylphenanthrene and dimethylphenanthrene predominate – they tend to be 35–45% and 30–40%, respectively. The concentration of holonuclear phenanthrene is 10–20% in these samples, the trimethylphenanthrenes content does not usually exceed 20%, whereas the TMTHP and reten compounds are absent.

The distribution of methylphenanthrene isomers (α and β structures) is of interest to petroleum geochemistry due to their ratio being usually used as indicators of the organic matter catagenesis. The content of more thermodynamically stable β isomers is believed to increase with a raise of organic matter maturity level (Radke et al., 1982; Radke, 1988; Cassini et al., 1988; and many others). In the studied bitumoid collection, α-isomers of methylphenanthrenes (9- and 1-MP) predominate over β-isomers (2- and 3-MP) by about 1.5–2 times: the ratio (9+1-MP)/(2+3-MP) averaged 1.4–1.6 in the Sredneyulzhavskaya, Pelginskaya, Archinskaya, Yuzhno-Mayskaya and 1.9 in the Zapadno-Kvenzerskaya samples. Thus 3-MP ≤ 2-MP << 9-MP ≤ 1-MP (2-MP/3-MP averages 0.6–0.7, 9-MФ/1-MФ averages 0.8–0.9), with the exception of the Zapadno-Kvenzerskaya samples, where 9-MP predominates (9-MP/1-MP averages 1.1–1.2).

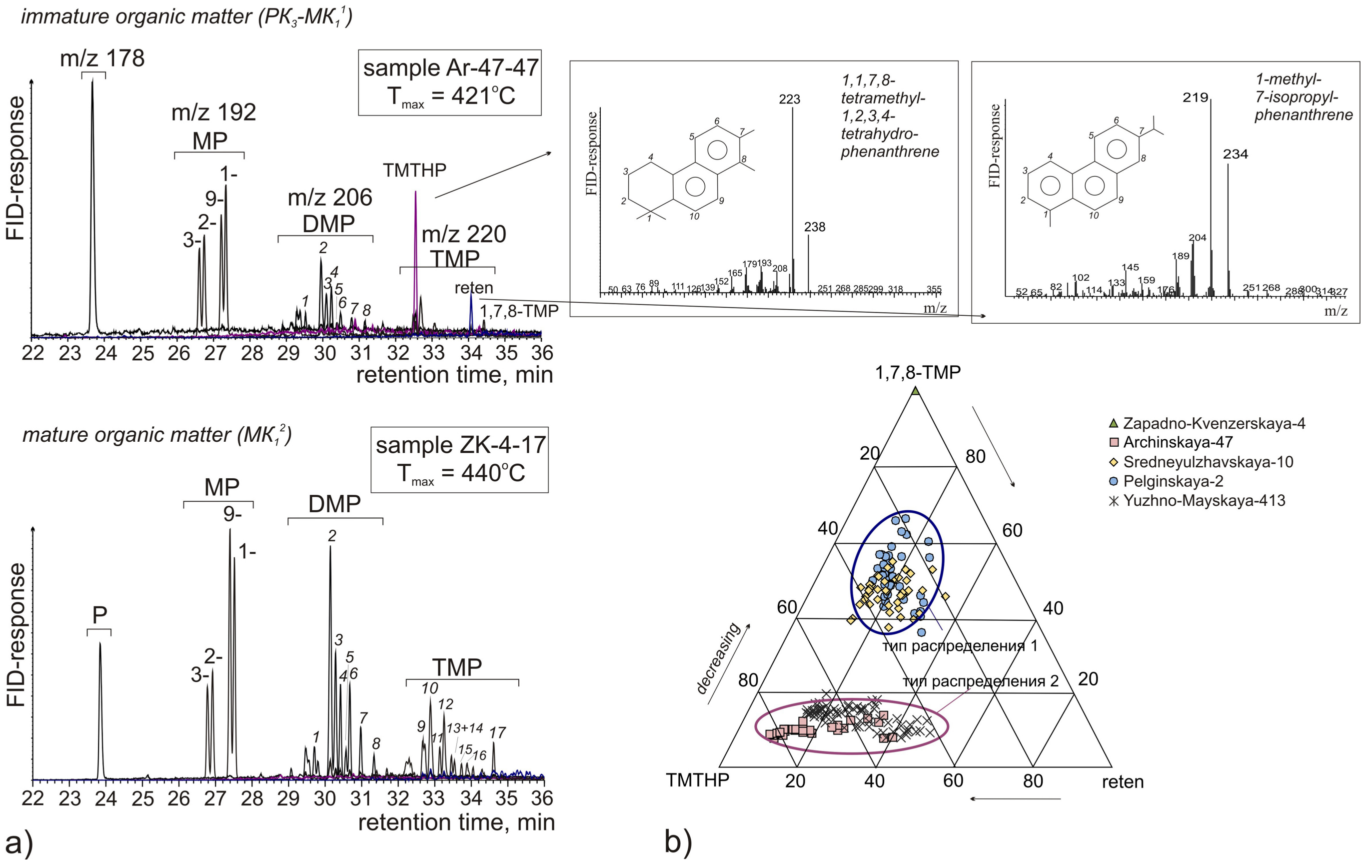

Figure 3. Typical mass fragmentograms of phenanthrenes (a) and triangular diagram of 1,7,8-trimethylphenanthrene, 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene and retene (b) in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region. P – holonuclear phenanthrene (m/z 178), MP – methyl- (m/z 192), DMP – dimethyl- (m/z 206), TMP – trimethylphenanthrenes (m/z 220); TMTHP – 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene; rethene – 1-methyl, 7-isopropylphenanthrene. Peaks: 1 – 2,6-+2,7-DMP, 2 – 1,3-+3,9-+2,10-DMP, 3 – 1,6-+2,5-+2,9-DMP, 4 – 1,7-DMP, 5 – 2,3-DMP, 6 – 1,9-+4,9-+4,10-DMP, 7 – 1,8-DMP, 8 – 1,2-DMP, 9 –1,3,6-+1,3,10- +2,6,10-TMP, 10 – 1,3,7-+2,7,9-+2,6,9-TMP, 11 – 1,3,9-+2,3,6-TMP, 12 – 1,6,9-+1,7,9-+2,3,7-TMP, 13–14 – 1,3,8-+2,3,10-TMP, 15–16 – 1,7,7-TMP, 17 – 1,7,8-TMP (or 1,2,8-TMP).

Well	Content, in % of ∑ phenanthrenes					
	P	∑ MP	∑ DMP	∑ TMP	TMTHP	Rethene
Sredneyulzhavskaya-10	28.6	35.5	18.2	12.4	3.3	2.0
Pelginskaya-2	29.3	36.1	18.1	12.2	2.6	1.7
Archinskaya-47	29.5	34.4	16.5	6.9	10.1	2.7
Yuzhno-Mayskaya-413	27.5	35.8	18.2	8.0	7.0	3.5
Zapadno-Kvenzerskaya-4	15.7	38.3	33.0	13.1	0	0

Table 2. Average content of phenanthrene compounds in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region. P – holonuclear phenanthrene, ∑ MP – the total methylphenanthrenes, ∑ DMP – the total dimethylphenanthrenes, ∑ TMP – the total trimethylphenanthrenes (without TMTHP and rethene), TMTHP – 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene, Rethene – 1-methyl, 7-isopropylphenanthrene. The table has been partially published in the work (Sotnich, Kostyreva, 2024).

The values of molecular indicators widely used to determine the organic matter maturity, based on the distribution of methylphenanthrenes, are shown in Table 3. Some indicators were found to be uninformative for the bitumoid collection of the Bazhenov Formation, as previously noted in works (Goncharov et al., 2004; 2013).

Distribution of dibenzothiophene aromatic compounds

The following sulfur-containing aromatic compounds of the dibenzothiophene series were identified: holonuclear dibenzothiophene (m/z 184), its methyl- (m/z 198), dimethyl- (m/z 212) and trimethyl- (m/z 226) substituted homologues (Figure 4).

Based on the analysis of the distribution of sulphur-aromatic compounds of the dibenzothiophene series in the bitumoids, methyl-substituted structures were found to dominate among the dibenzothiophenes – up to 40–50% of Σ DBT (35–45% in the Zapadno-Kvenzerskaya samples). The dimethyldibenzothiophenes content varies between 30 and 45% (usually 35–40%) in the Zapadno-Kvenzerskaya samples, 20–30% in the rest. Trimethylbenzothiophenes content in all bitumoids tends not to exceed 15–20%. The concentration of holonuclear dibenzothiophene is very variable, ranging from 5–15% in the Zapadno-Kvenzerskaya samples to 25–30% in the Yuzhno-Mayskaya and Archinskaya samples.

Among the methyldibenzothiophenes, 1-MDBT concentration does not exceed 20% in Zapadno-Kvenzerskaya bitumoids and varies from 40–55% in others (Table 4). The concentration of 4-MDBT increases in proportion to the decrease of 1-MDBT, while the content of 2+3-MDBT remains at the level of 20% of Σ MDBT.

The methyldibenzothiophene ratio (MDR) and the dibenzothiophene index (DBTI) are well established as indicators of organic matter maturity (Goncharov et al., 2005; Kontorovich et al., 2004; Radke, 1988;

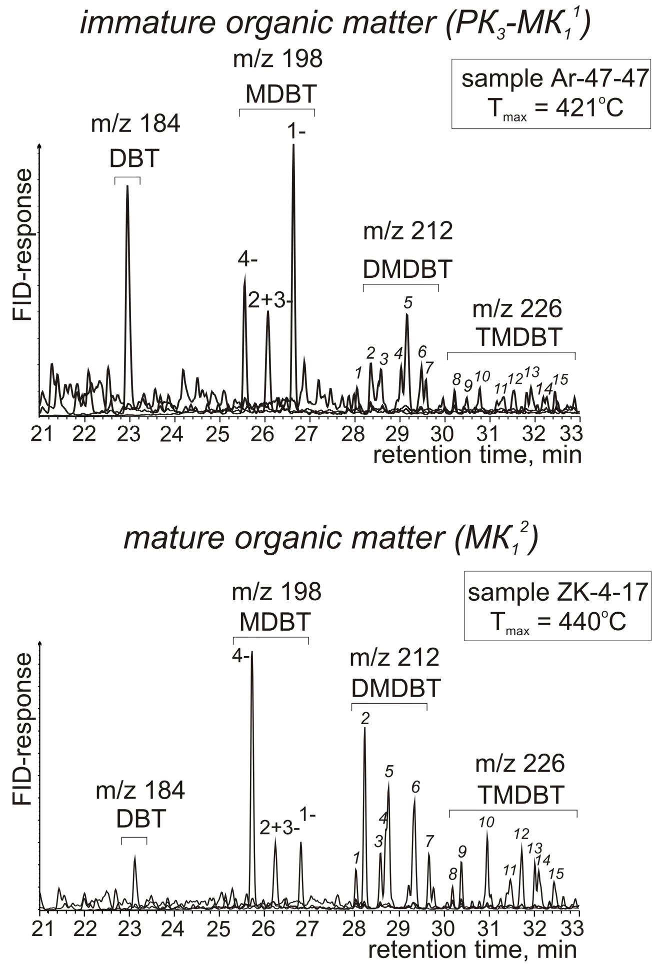

Figure 4. Typical mass fragmentograms of dibenzothiophenes in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region. DBT – holonuclear dibenzothiophene (m/z 184), MDBT – methyldibenzothiophenes (m/z 198), DMDBT – dimethyldibenzothiophenes (m/z 212), TMDBT – trimethyldibenzothiophenes (m/z 226). Peaks: 1 – 4,6-DMDBT, 2 – 2,4-DMDBT, 3 – 2,6-+3,6-DMDBT, 4 – 3,7-DMDBT, 5 – 1,4-+1,6-+1,8-DMDBT, 6 – 1,2-+1,3-DMDBT, 7 – 1,7-+1,9-+3,4-DMDBT; peaks 8–15 – 2,4,6-, 2,4,8-, 2,4,7-, 1,4,6-, 1,4,8-, 3,4,6-, 2,6,7-, 1,4,7-, 1,3,7-, 3,4,7-, 1,2,4- and 2,3,7-TMDBT (Li et al., 2014).

Well	MPI	MPI-1	MPI-2	PP-1	(2+3-MP)/(9+1-MP)
Sredneyulzhavskaya-10	0.5	0.5	0.3	0.8	0.6
Pelginskaya-2	0.5	0.5	0.3	0.8	0.6
Archinskaya-47	0.5	0.5	0.3	0.8	0.7
Yuzhno-Mayskaya-413	0.5	0.6	0.3	0.8	0.7
Zapadno-Kvenzerskaya-4	0.6	0.5	0.3	0.9	0.5

Table 3. Average values of phenanthrene molecular indicators of the organic matter maturity in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region

Well	Average concentration, in % of ∑ MDBT			MDR	DBTI
	4-MDBT	2+3-MDBT	1-MDBT		
Sredneyulzhavskaya-10	32.9	18.3	48.8	0.7	0.4
Pelginskaya-2	36.9	18.8	44.3	0.8	0.4
Archinskaya-47	26.5	22.4	51.1	0.5	0.4
Yuzhno-Mayskaya-413	33.0	20.5	46.5	0.7	0.4
Zapadno-Kvenzerskaya-4	70.3	17.0	12.8	5.7	0.8

Table 4. Methyldibenzothiophenes distribution in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region. Author's note: Molecular maturity indicators – Methyldibenzothiophene ratio MDR = 4-MDBT/1-MDBT according to (Radke, 1988; Goncharov et al., 2005); Dibenzothiophene Index DBTI = 2+3-MDBT/DBT according to (Schou, Myhr, 1988; Kontorovich et al., 2004).

Schou, Myhr, 1988). In the case of the studied bitumoids collection, the molecular indicators have close values for samples from the Sredneyulzhavskaya, Pelginskaya, Archinskaya, and Yuzhno-Mayskaya wells and differ greatly in samples from the Zapadno-Kvenzerskaya well, confirming the difference in organic matter maturity of these two sample groups.

Distribution of aromatic steroids

Monoaromatic steroids C_{27}-C_{30} (m/z 253) and triaromatic steroids C_{20}-C_{21} and C_{26}-C_{28} (m/z 231) were identified in the composition of the Bazhenov Formation bitumoids (Figure 5).

In the Sredneyulzhavskaya and Pelginskaya samples, triaromatic steroids (up to 50% of ∑ arom.comp.) dominate over monoaromatic ones (up to 20% of ∑ arom.comp.), mainly due to the high molecular weight TAS C_{26}-C_{28} (Figure 5). TAS/MAS ratio varies from 2 to 5, with an average of 3. The values of the triaromatic steroid index (TASI = TAS I / (TAS I + TAS II)) do not exceed 0,15.

The MAS content in the bitumoids from the Archinskaya well is up to 30% of the aromatics, almost double that of TAS (not more than 15%). The TAS/MAS values vary from 0.2 to 0.7, with an average of 0.4. The TASI tends to be less than 0.2.

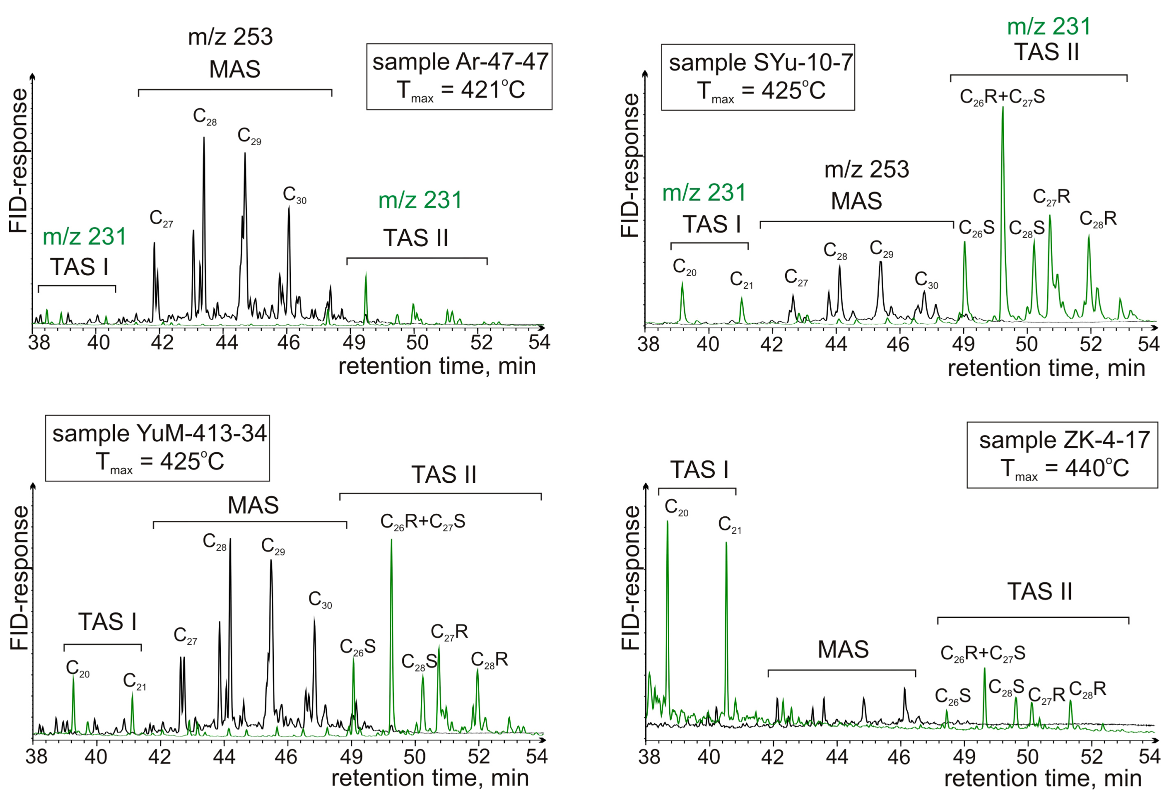

Figure 5. Typical mass fragmentograms of aromatic steroids in the composition of source rock extracts (bitumoids) from the Bazhenov formation, Tomsk region. MAS – monoaromatic steroids C_{27}-C_{30}; TAS I – triaromatic steroids C_{20}-C_{21}, TAS II – triaromatic steroids C_{26}-C_{28}.

In the samples from the Yuzhno-Mayskaya well, the ratio TAS/MAS varies irregularly along the section: MAS predominates in some bitumoids (about 2/3 of the collection), TAS in others. The TAS/MAS values are between 0.5 and 2.6, with an average of 0.8. MAS concentrations drop to TAS I levels in some samples (mainly in the lower part of the section) and to background levels in isolated cases. The TASI values vary from 0.1 to 0.25.

In the Zapadno-Kvenzerskaya samples the content of aromatic steroids is very low – less than 5%, while the MAS concentrations are mostly ≤ 0.5%. The ratio of TAC to MAS is always greater than 4 (up to 20). Among the triaromatic steroids in these bitumoids, the low molecular weight ones (TAS I) predominate: the TASI values vary from 0.6 to 0.7.

Discussion

The distribution of phenanthrenes, dibenzothiophenes, aromatic steroids in the composition of source rock extracts (bitumoids) from the Bazhenov formation of the Tomsk region has been found to depend on both the accumulation conditions and the maturity of the organic matter.

The DBT/F and Pr/Ph ratios confirm Bazhenov Formation organic matter accumulation under marine conditions at depths of 100–200 m (Kontorovich et al., 2013). However, the lower content of dibenzothiophenes and a different distribution pattern in the three-component system TMTGF-1,7,8-TMF-retene suggest shallower marine conditions for the Pelginskaya and Sredneyulzhavskaya areas compared to the other three. The remaining calculated molecular indicators show no differences in the facies-genetic depositional environment of the organic matter and are mostly dependent on the maturity level. With growing thermal maturation of the organic matter from the end of protocatagenesis (gradation PK_3) to the middle of mesocatagenesis (gradation MK_1^2), the following directional changes in the distribution of aromatic compounds were observed:

• In the naphtheno-aromatic fraction of the bitumoids, the relative content of phenanthrenes and dibenzothiophenes is increasing due to a significant decrease in the proportion of aromatic steroids. In the immature organic matter the aromatic concentrations decrease in the order MAS+TAS > P > DBT or P > MAS+TAS > DBT, in the mature organic matter P > DBT > MAS+TAS.

• In the composition of phenanthrenes and dibenzothiophenes, the relative content of mono-, di- and trimethyl-substituted structures increases, while the holonuclear compounds decrease. The most pronounced growth is observed in the concentrations of dimethyl-substituted homologues: while in immature organic matter their concentrations are at the level of holonuclear compounds, in mature organic matter they are more than twice as high;

• The concentrations of the α-isomers of methylphenanthrene (9- and 1-MP), which are considered to be less thermodynamically stable than the β-isomers (2- and 3-MP), increase; this discrepancy can be explained by the fact that the rearrangement of methyl substituents from the α- to the β-position begins to play a leading role only after the catagenesis gradation of MK_2 (Radke, 1988; Cassini et al., 1988; Szczerba, Rospondek, 2010). It also explains the uninformativeness of some molecular indices based on methylphenanthrene distribution (e.g. MPI, MPI-1, MPI-2), since the studied collection of Bazhenov Formation samples contains aquagenic organic matter at a lower catagenesis level (MK_1^1-MK_1^2). It should be noted that a predominance of 9- and 1-MPs over 2- and 3-MPs has also previously been observed in samples from other source rocks with marine organic matter at the early and middle stages of the 'oil window' (Kashirtsev et al., 2018; Kontorovich et al., 2005; Duda et al., 2020).

• The compound 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene (TMTHP) has been identified in immature organic matter from the Bazhenov Formation of the Tomsk region. It is considered to be a hydrogenated precursor of 1,7,8-trimethylphenanthrene and is absent in mature organic matter. Previously, TMTHP has also been identified in the Bazhenov Formation of the North Surgut region in central Western Siberia (Sotnich, Kostyreva, 2021, 2024), but at much lower concentrations due to the higher maturity of the organic matter. Comparative analysis of TMTGP distribution in Tomsk and North Surgut bitumoids suggests that the TMTGP disappearance begins at the end of the gradation MK_1^1 (at T_{max} about 435 °C). N.S. Burdel'naya and D.A. Bushnev had also identified TMTHP in organic matter from domanik deposits of the Timan-Pechora petroleum province and came to a similar conclusion, proposing the use of the TMTHF/1,7,8-TMF ratio as an indicator of organic matter maturity (Burdel'naya, Bushnev, 2021). They also noted: "As the variation of this ratio occurs in a rather narrow thermal ripening interval of OM, it will be useful to study the OM composition at low and middle catagenesis gradations..." (Burdel'naya, Bushnev, 2021).

• Among the methyldibenzothiophenes, 1-MDBT dominates in the immature organic matter, while in the mature organic matter it is the more thermodynamically stable 4-MDBT that prevails. The content of 2+3-MDBT in the collection of bitumoids studied is always lower in relation to the others, but its ratio to the holonuclear dibenzothiophene (DBTI) increases with the growth of the OM catagenesis. Both ratios (4-MDBT/1-MDBT and DBTI) are informative indicators of OM maturity in the Bazhenov Formation, as noted by previous researchers (Kontorovich et al., 2004; Goncharov et al., 2004, 2005; and orhers), but differ in their sensitivity to OM transformation. For example, the 4-MDBT/1-MDBT ratio shows a much wider range of values between mature and immature OM. Contrary to pyrolytic and petrographic parameters, molecular indices are more accurate because "...the isomerization transition from 1-MDBT to 4-MDBT is independent of the sample origin and reflects only the equilibrium state determined by time and temperature..." (Goncharov et al., 2004).

• The elevated monoaromatic steroid (MAS) content observed in immature organic matter decreases rapidly with thermal maturation, and by MK_1^2 catagenesis, MAS concentrations reach background levels; in some cases, MAS are unidentified. Previously (Kontorovich et al., 2004), it was noted that for marine OM of the Bazhenov Formation, "besides phenanthrenes, triaromatic steroids usually play a significant role" and "...the TAS/MAS ratio usually varies between 2.0 and 5.0". In addition, a number of "anomalous" samples from the Bazhenov Formation were found to contain organic matter with high concentrations of phenanthrene, low concentrations of aromatic steroids, and a predominance of MAS versus TAS, which is similar in nature to the distribution of aromatic compounds in the continental organic matter of the Tyumen Formation, suggesting that the OM from individual layers of the Bazhenov Formation contains the remains of higher terrestrial vegetation. The analysis of the distribution of aromatic steroids in source rock extracts from the Bazhenov Formation of the Tomsk region allows to determine the significant change of the relative content of TAS/MAS in the marine OM of the Bazhenov Formation without the introduction of terrigenous OM.

• Among the triaromatic steroids, the predominance of the high-molecular-weight TAC II with a composition of C_{26}-C_{28} is observed in the immature OM, whereas in the mature OM it is TAS I with a composition of C_{20}-C_{21}. In (Kontorovich et al., 2004), such a regularity was also found, and on the basis of it, the "triaromatic sterane maturity index" TASI = TAS I / (TAS I + TAS II) was proposed. It shows a rather strong correlation with the reflectivity of vitrinite. It has been argued (Kontorovich et al., 2005; Parfenova, 2015) that the ratio of low- and high-molecular steroids depends on the redox conditions of accumulation and the organic matter content in rocks, so "the use of TASI for the assessment of OM thermal maturity should be of greater caution". Based on analysis of TASI values, as well as TASI's dependence on organic matter (C_{org}) and Pr/Ph contents, it was found that TASI can be used as an indicator of OM maturity for this collection of Bazhenov Formation bitumoids in Tomsk region.

Conclusion

The main factor controlling the distribution of aromatic compounds (phenanthrenes, dibenzothiophenes, aromatic steroids) in organic matter of the Bazhenov Formation from Tomsk region, as revealed by compositional and structural analysis, is the degree of organic matter maturity (OM). Directional changes are observed both in the proportions of the main aromatic groups (increasing phenanthrene content, decreasing aromatic steroid content) and within these groups (decreasing concentrations of holonuclear and increasing concentrations of di- and trimethyl substituted structures, rearrangement of methyl substituents, etc.) as the organic matter matures from the PK_3 to MK_1^2 gradation. The study has shown that not all molecular indicators (MPI, MPI-1, MPI-2, PP-1, PP-1_{mod}, DBTI, TASI, etc.) widely used in geochemical research practice for the assessment of organic matter maturity are equally informative for marine organic matter of the Bazhenov Formation at low and middle stages of catagenesis. The most "sensitive" to the degree of OM maturity are the 4-MDBT/1-MDBT, TASI, TAS/MAS and TMTGF/1,7,8-TMF ratios.

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IN RUSSIAN

Геохимия фенантренов, дибензотиофенов и ароматических стероидов в битумоидах баженовской свиты юго-востока Западной Сибири (Томская область)

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В работе представлены результаты изучения ароматических соединений (фенантренов, дибензотиофенов, ароматических стероидов) в битумоидах баженовской свиты Томской области (юго-восток Западной Сибири). Среди соединений фенантренового и дибензотиофенового рядов, помимо голоядерных и монометилзамещенных структур, идентифицированы их ди- и триметилзамещенные гомологи. Сравнительный анализ относительных концентраций основных групп ароматических соединений, рассчитанных двумя способами (с учетом и без учета ди- и триметилфенантренов и дибензотиофенов), показал их идентичность. Установлено, что основным фактором, контролирующим содержание и распределение ароматических соединений, является степень зрелости органического вещества. Наиболее информативные молекулярные показатели зрелости для органического вещества баженовской свиты низких и средних градаций катагенеза ($ПК_3$-$МК_1{}^2$) – отношения 4-МДБТ/1-МДБТ, ТАСИ, ТАС/МАС, а также ТМТГФ/1,7,8-ТМФ.

Ключевые слова: органическое вещество, битумоиды, ароматические соединения, катагенез, нефтематеринские породы, баженовская свита, верхняя юра, Западная Сибирь

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