Geologic and Geochemical Features of the Upper Devonian Coals of the North Timan (the Sula River Coal Field)

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Abstract—The composition of the oldest coals of the Timan–northern Urals region has been studied comprehensively, and their hydrocarbon and microcomponent characteristics are given. The relationship between different types of coals and Late Devonian plant communities of the North Timan is revealed. It is also determined that some samples contain microspores, megaspores, and plant remains belonging mainly to the lycopod *Helenia*. The most probable source of jet coals is identified as the wood of the progymnosperm *Callixylon*. The values of vitrinite reflectance and T_{max} and the data on the distribution of polycyclic biomarkers and methylphenanthrenes indicate the low maturation of the coal organic matter. The coal bitumen investigated here is characterized by the dominance of steranes and diaster-13(17)-enes of compositions C_{28} and C_{29}. The following diterpanes are identified: beyerane, 16α(H)-kaurane, 16β(H)-kaurane, and 16α(H)-atisane. At the same time, phyllocladane is absent.

Keywords: coal; coal producers; organic geochemistry; biomarker hydrocarbons; aromatic hydrocarbons; Upper Devonian; North Timan

INTRODUCTION

In the geologic record of the Earth, the oldest coals first occur in Devonian deposits. Not too many thin layers of the first coals are known, and there was not much interest in studying them because of the lack of industrial volumes and low technological qualities. Nevertheless, Devonian coals are widely manifested (Volkova, 1994). The oldest coaly rocks containing plant remains (mainly phytodebris) have been reported and described from the Pragian–Emsian deposits (Lower Devonian, New Brunswick, Canada (Kennedy et al., 2013)). Middle Devonian coals are known from Germany, Kazakhstan, China (Song et al., 2017), Illinois (United States), and other regions. Middle–Late Devonian coals are described on Melville Island in Arctic Canada (Goodarzi and Goodbody, 1990). In Russia, Middle Devonian coals are well known from the Barzas River basin (Snyatkov, 1915; Zalesskii, 1915a, b; Ergol'skaya, 1936). The age of the Barzas coals and the taxonomy of coal-pro-

ducing plants are discussed in detail in (Snigirevskaya, 2010). Middle Devonian coals in Russia are also identified in the Urals, the North Timan, the Voronezh Region, and the Altai–Sayan region.

The Upper Devonian coal-bearing deposits are rather well represented. Aside from Timan, the coaly rocks and coals of this age are known from the central regions of the East European Platform and in numerous borehole cores from the Republic of Tatarstan and the vicinity of Krasnoyarsk. The Upper Devonian coal beds are abundant in Svalbard, Bear Island (Harland et al., 1976), the Canadian Arctic Archipelago (Ellesmere Island and Melville Island), and Franz Josef Land (Goodarzi and Goodbody, 1990; Volkova, 1994; Snigirevskaya, 2010). In the southeast of this archipelago, ashore Graham Bell Island, rounded pebbles of Devonian coals occur. The bedrock deposit of this coal is not exposed, most likely, cropping out below sea level. In the lower reaches of the Yangtze River in China, the Upper Devonian deposits contain lenses and thin layers of coaly rocks (Han, 1989). The single coal fields and accumulations of coalified wood are widely known. Recently, they have been studied in detail in Belgium (Prestianni et

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al., 2010). The plants that produced the earliest coals on the Earth were the dominants of the first forest ecosystems confined to the river valleys and delta and coastal plains of shallow epicontinental seas (Meien, 1989; Snigirevsky et al., 2017).

The Devonian sequence of the North Timan represents one of the oldest coal-bearing deposits in the world. Coaly beds and interlayers are developed here at different levels of the section. The lowermost of them are of the Eifelian–lower Givetian stages. They were first identified in (Chernov, 1938, 1947) in the Kumushka-Belaya River valley and studied in (Pervukhina, 1940). Lignite beds (sapromyxites) with a thickness of up to 0.4 m occur here among clays and quartz sandstones of the Travyanka Formation. Other coal fields are noted for the Kumushka (upper Givetian–lower Frasnian), Grubyi Ruchei (lower Frasnian), Ust'-Bezmoshitsa (upper Frasnian), and Pokayama (Famennian) formations (Kossovoi, 1963, 1966). The three areas of the North Timan (Srednyaya Volonga, Pesha, and Sula) are known for one deposit and more than a dozen fields of Devonian lignite and coal (Cherepanov et al., 2001). The accumulation and burial of plant remains, apparently, took place in relatively low-energy environments of the wide delta plain—various backwaters, oxbow lakes, and coastal lagoons (Beznosov et al., 2018). According to this study, the main producer of the North Timan coals is the lycopod *Helenia*. Some coals are mostly entirely composed of mega- and microspores. In general, the composition of the Devonian coals of the North Timan is quite diverse (Snigirevsky et al., 2017).

This paper presents geochemistry and organic petrography data on the coal organic matter and the coaly shales collected from the Upper Devonian section exposed along the Sula River near the Padun waterfall (North Timan).

METHODS

The content of organic carbon in the rock is determined using an AN-7529 carbon analyzer during the preliminary preparation of an insoluble organic polymer in concentrated hydrochloric acid. Glucose and mild steel are used as the standard. The data based on C_{org} and obtained during the analysis are recalculated for the original rock.

Bitumen is obtained by extracting rocks with chloroform in a Soxhlet device for 40 h. Spongy copper is added to the receiver to remove elemental sulfur. The resulting bitumen is subjected to further fractionation, which is carried out via preliminary precipitation of asphaltenes with *n*-hexane and their subsequent removal. The obtained maltene fraction is separated into apolar (saturate and aromatic) and polar (resins) on a column with aluminum oxide by elution with a 20% solution of dichloromethane in *n*-hexane and a mixture of dichloromethane-ethanol (1/1), respectively. The apolar fraction is separated into a saturated and an aromatic fraction on a silica gel column by elution with *n*-hexane and benzene, respectively. The analysis of the aliphatic fraction

is carried out by gas chromatography (GC) for analyzing normal hydrocarbons and gas chromatography/mass spectrometry (GC-MS) for analyzing polycyclic biomarkers (steranes and hopanes). The composition of the aromatic fraction is investigated by GC-MS.

The hydrocarbon fraction of bitumens is analyzed using a Kristall-2000M gas chromatograph equipped with an SPB-1 (Supelco) capillary column, the length of which is 30 m and inner diameter is 0.32 mm; the thickness of the stationary phase is 0.25 μm. The column oven temperature is set within a range from 110 to 300 °C at a rate of 5 °C/min. The injector and detector temperatures are both 300 °C. Benzene is used as a solvent. The carrier gas is helium.

The GC-MS is performed using Shimadzu QP2010 Ultra. Chromatographic separation is carried out using a DB-5 column (30 m × 0.25 mm); the thickness of the stationary phase is 0.1 μm. Chromatography is carried out at a set temperature of 50 to 300 °C at a rate of 5 °C/min. The temperature in the injector and in the ion source is 300 °C and 250 °C, respectively. The sample is introduced via split injection (1 : 30), and the sample volume is 1 μL. The mass spectrometer is quadrupole with ionization energy of 70 eV.

The analysis of sterane hydrocarbons requires that the aliphatic fraction of rock bitumen is additionally studied by gas chromatography–tandem mass spectrometry (GC-MS/MS). The analysis is carried out using Bruker Scion 436-GC TQ with an HP-1-MS column (30 m; 0.25 mm) with linearly programmed temperature (from 75 to 200 °C at a heating rate of 5 °C/min, from 200 to 315 °C at a heating rate of 5 °C/min, and keeping at 315 °C for 15 min). Data are collected and processed in MS WorkStation. The method is initially tested on Exxon Mobil. The evaporator temperature is 350 °C; the transfer-line temperature is 260 °C; and the ion source temperature is 270 °C. The solvent is *n*-hexane; the volume of the injected sample is 1 μL; and the flow discharge is 10. Transitions 372–217, 386–217, and 400–217 are used to analyze the C_{27}, C_{28}, and C_{29} steranes, respectively.

Kerogen is isolated by successive treatment with concentrated hydrochloric and hydrofluoric acids. The removal of inorganic components is controlled by burning the resulting residue in a muffle furnace for an hour (by determining the ash content). The temperature in the furnace is 1100 °C. The removal of soluble organic components is carried out by extracting kerogen with chloroform. The isolated kerogen is thoroughly dried.

Rock-Eval pyrolysis is carried out in the Laboratory of Geochemistry and Formation Oils at OJSC TomskNIPIneft' by R.S. Kashapov using Rock-Eval 6 Turbo.

The elemental analysis of kerogen is carried out at the Institute of Geology of the Komi Science Center of the Ural Branch of the Russian Academy of Sciences (IG KSC UB RAS (Syktyvkar)) by leading chemical engineer E.A. Tumanova using the EA 1110 (CHNS-O) CE Instruments elemental analyzer.

Organic petrography is studied at the IG KSC UB RAS using MeF-2 and Nikon Eclipse E400Pol microscopes as

well as in the Coal Laboratory of the Department of Geology and Geochemistry of Combustible Fossils at the Faculty of Geology of Lomonosov Moscow State University using QD1302 (CRAIC Technologies) according to (GOST R 55659-2013, 2013; GOST R 55662-2013, 2013; GOST R 55663-2013, 2013). Thin sections and polished sections were investigated in transmitted light, plain white light, and ultraviolet (UV) light, respectively. The vitrinite reflectance (RV, %) is measured according to (GOST R 55659-2013, 2013; ISO 7404-5…, 2009) in oil with a 50X objective and an yttrium–aluminum standard ($RV = 0.905\%$).

RESULTS AND DISCUSSION

Geologic setting and coal content. According to the geological survey (Shlyakhova and Shlyakhov, 1974), a sequence of the Kumushka, Vyuchei, Grubyi Ruchei, and Ras-

sokha formations is exposed along the Sula River valley downstream the Padun (Sula) waterfall (Fig. 1). The latter two formations are considered the lower part of the Upper Devonian delta plain depositions, within which it is very difficult to distinguish local strata of the rank of suites (Beznosov et al., 2018). Owing to the position of the studied coaly bedrocks within the section and the associated vertebrate remains, this interval is correlated with the lower part of the Ust'-Yarega (Sargaevo) Regional Stage of the lower Frasnian Substage of the Upper Devonian (Koren', 2006). Coeval deposits occurring in the south, in the northern part of the Middle Timan (the Tsil'ma River basin), are represented by the Paladino Formation, which formed in a nearshore continental environment. Its sediments, mainly represented by fine-grained sandstones and siltstones, contain only rare coalified plant remains and detritus (Tel'nova and Shumilov, 2021). Further south, in the Pechorskaya Pizhma
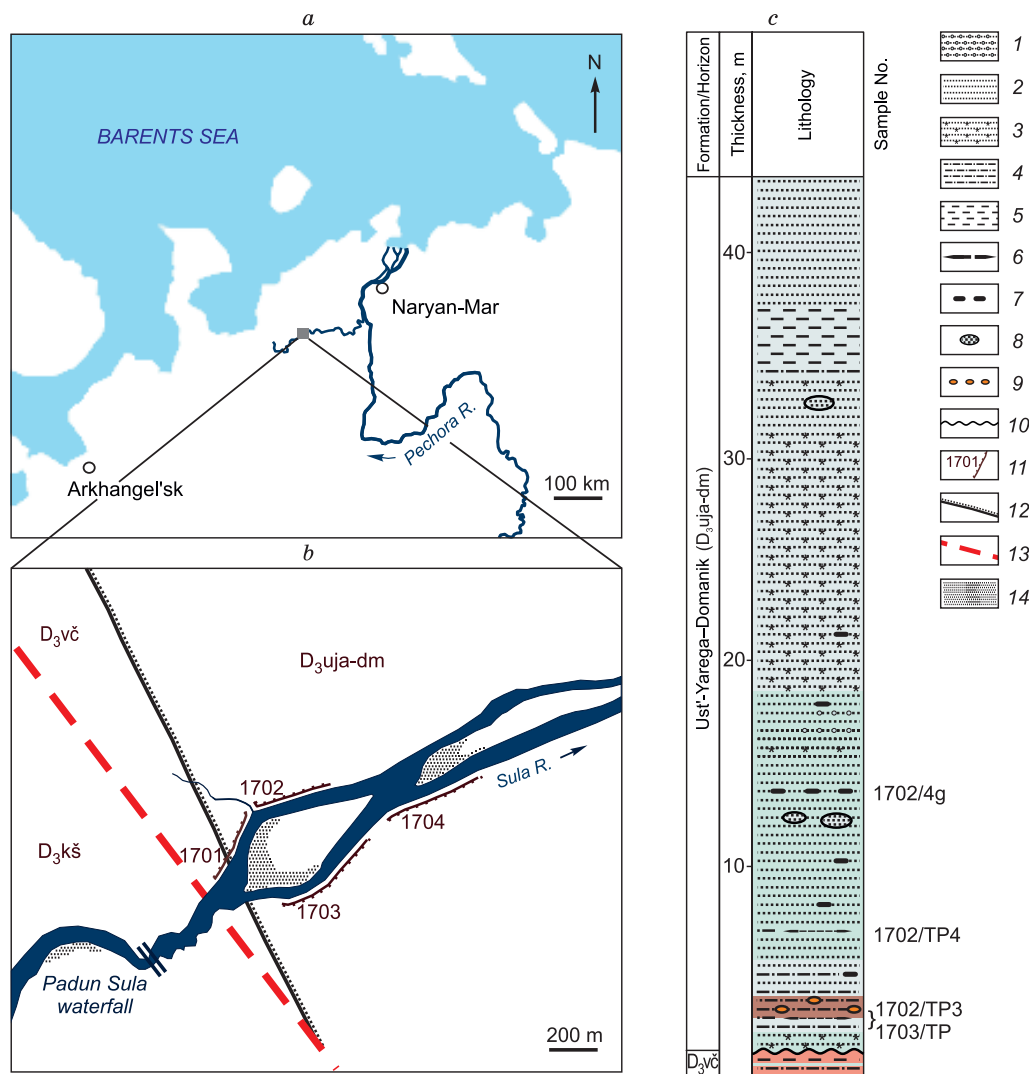

Fig. 1. Geographic and geologic location of the region under study: *a* – Schematic map of the Northwest of Russia; *b* – geological map of the Padun (Sula) waterfall region; *c* – generalized section of the Frasnian terrigenous deposits exposed on the banks of the river below the Sula waterfall. *1* – conglomerate; *2* – quartz sandstone; *3* – polymictic sandstone; *4* – siltstone; *5* – mudstone; *6* – coal; *7* – coal (jetlike coal) lenses; *8* – bun-shaped sandy concretions; *9* – siderite concretions; *10* – erosion surface; *11* – natural outcrops of Devonian rocks and outcrop numbers; *12* – synchronous stratigraphic boundary; *13* – fault; *14* – modern alluvial deposits.

River basin and in the South Timan, they are represented by the shallow-marine clayey and clay–carbonate deposits of the Ust'-Yarega Formation, which are devoid of coal-bearing signs and contain an abundant fauna of marine invertebrates (Tsyganko, 2006). To the north of the region under study, on the Kanin Peninsula, there was a gap in sedimentation in the Sargaevo time (Beznosov et al., 2019).

In the North Timan, the Ust'-Yarega (Sargaevo) Regional Stage deposits, previously considered in the Grubyi Ruchei Formation, are mainly represented by clastic rocks (Cherepanov et al., 2001; Parmuzin et al., 2015). Their outcrop is poor; one of their most complete sections is composed mainly of sandstones and exposed in the Sula waterfall area (Fig. 1c). They are dominated by greenish gray crossbedded and horizontally bedded sandstones, predominantly quartz in the lower part of the section and polymictic in the upper part. In some places, there are wave-formed ripples, currents, dragging traces, and pebbles of clayey rocks on bedding surfaces. In a few layers, the low-amplitude underwater landslide structures are recognized. They often contain the lens-shaped interlayers of jetlike structureless coals. Nodules of various compositions (pyrite, siderite, and sandy) are identified in the section at several levels. Fossils are represented by rare, often fragmented and abraded fish remains (plates of *Asterolepis radiata* Roh. and *Bothriolepis* cf. *celullosa* Pander and scales of *Glyptolepis* sp. are predominant) as well as coalified plant remains. In addition to sandstones, the section contains rare interlayers of dark gray thin-layered siltstones with plant imprints and gray-brown nodulous mudstones.

The lens-shaped interlayers of coaly rocks lie in the lower part of the section studied. The thickness reaches 0.2 m. These rocks are characterized by a dark color (from grayish brown to almost black), weakly pronounced fracturing, and thin-layered horizontal lamination. In some places, coaly rocks are secondarily ferruginized along the cracks and bed surfaces. There are rare fish remains, among which *Bothriolepis* sp. and Sarcopterygii gen. indet. are determined. Along with laminated coals, the section contains interlayers of coaly siltstones and small lenses of jetlike coal.

It is suggested by the lithologic features of the section that the sediments formed in the shallow coastal-marine conditions near the mouth of a large river, which supplied abundant sandy material to the basin. The absence of remains of marine organisms indirectly indicates that the water salinity was rather low. The hydrodynamic activity caused by the currents is periodically replaced by relatively quiet conditions of sedimentation. The latter can be explained by the development of accumulative landforms (for example, bar bodies), which separated the coastal zone from the rest of the basin. During such periods, a mass of plant residues carried away from the nearby land accumulated in stagnant zones. Deltaic sediments were invaded by sea waters, which formed short-term conditions of coastal-marine sedimentation.

Plant remains in the section under study are mainly represented by poorly preserved fragments of archeopterid trees. On the contrary, the interlayers of coaly rocks contain numerous slender shoots of the herbaceous lycopsid plant *Helenia karakubensis* (Schmalhausen, 1894) Snigirevskaya, 1987, which are rather well preserved. These phytofossils belong to two different ecologic groups. The anthracophilic community of lycopsids represented by *Helenia* inhabited shallow lacustrine–boggy or oxbow-type waters. They were semiaquatic and formed dense thickets. Another type of plant community represents the archeopterid forests growing at a distance from the sea coast. This is indicated by the generally poor preservation of their remains, which is, most likely, due to relatively long transportation. Only wood fragments of archeopterid trees attributed to the genus *Callixylon* are well preserved. In some places, they formed minute accumulations in the coastal zone at the bottom of the sea, producing small lenses of cannel and jetlike coals. Wood fragments that did not fall into the accumulations were not subjected to complete coalification, which is why the tissues were preserved, thereby making it possible to study the anatomic features of the wood (Lyubarova and Snigirevsky, 2020). The wood samples under study contain numerous framboids of pyrite, which usually form at the stage of diagenesis during sedimentation in the places where the organic matter (OM) decomposes owing to bacterial sulfate reduction (Astafieva et al., 2005).

Thus, the coals from the Sula River section belong to two genetic types. The first type is composed of coaly shales and high-ash coals formed under the conditions of shallow lagoons located on the coastal plain. The second one is represented by coalified wood and structureless jetlike coals buried as minute accumulations of plant remains in the sublittoral zone of the sea basin.

Organic petrography

The organic petrography of the OM in high-carbon deposits is used by many specialists to determine the OM type and the maturity of the OM (Kontorovich et al., 1967; Tissot and Welte, 1984; Petrov, 2006; Golitsyn et al., 2012; Petersen et al., 2013; Pickel et al., 2017; Fomin, 2019; Hackley et al., 2020).

The rocks considered in this study are coals and coaly rocks. The OM consists of microcomponents of two main groups: vitrinite and liptinite.

The vitrinite components make up the bulk of the jetlike material, represented by collotelinite (Vt_{ct}) and, more rarely, telinite (Vt_t). The vitrinite substance in shalelike rocks is evenly distributed over the bedding in the form of thin layers (often porous or cracked), veinlets, and lenses (Fig. 2).

The second most common microcomponents belong to sporinite, with the exception of sample 1702/TP4, in which the content of sporinite is slightly higher than that of vitrinite. It is well diagnosed in the study in transmitted, reflec-
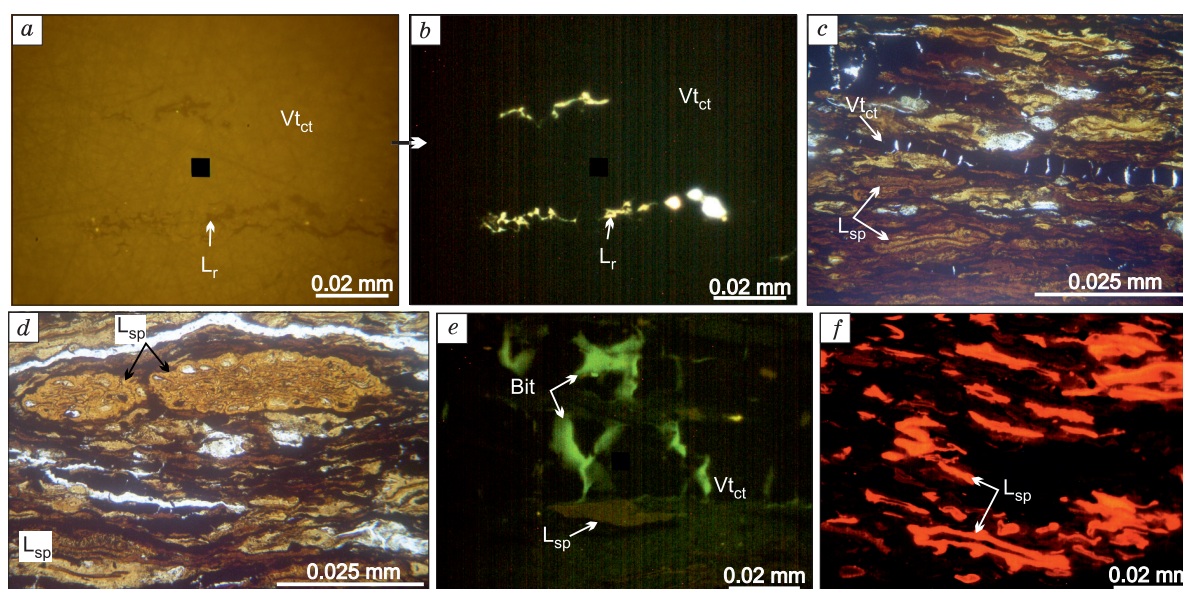
Fig. 2. Microphotographs of OM components in the studied samples: *a* – Reflected light (50X zoom); *b, e, f* – reflected ultraviolet light (50X zoom); *c, d* – transmitted light (50X zoom); Microcomponents: Vt – Vitrinite group (Vt$_{ct}$ – collotelinite); L – liptinite group (L$_{sp}$ – sporinite; L$_r$ – resinite-like substance); Bit – bitumen.

ted, and UV light and is represented by small and large spores and whole sporangia. These components often form whole interlayers (Fig. 2 (L$_{sp}$)).

The rocks also contain rare cutinite (L$_c$), amorphous bituminite (L$_{bit}$), alginite, and a large amount of liptodetrinite fragments (L$_{det}$). The jetlike coal sample (1702/4g) in the pores also contains a resinite-like substance (Fig. 2 (L$_r$)). In catagenetic transformation, bituminous components are formed from liptinite macerals, permeate the entire rock, and are well diagnosed in UV light (Fig. 2 (Bit)). There are single occurrences of fusinite and inertodetrinite (less often up to 5–7%), belonging to the inertinite group.

The reflectance index is measured using the amorphous vitrinite components. In the jetlike coal sample, RV is measured using collotelinite and is equal to 0.47%. In the rest of the samples, the reflectance index is determined using vitrinite interlayers distributed throughout the rock. The measured values of RV are 0.45–0.55%, which corresponds to the catagenetic transformation of the PK$_3$–MK$_1$ OM. The appearance of newly formed liquid bituminous products in the rock (Fig. 2f) indicates the onset of generation and is in good agreement with the MK$_1$ stage.

Elemental analysis data and the isotopic composition of carbon

The elemental analysis confirms the similarity of the OM samples of coal shales 1703/TP, 1702/TP3, and 1702/TP4, which was revealed by organic petrography, and its difference from the jetlike coal sample 1702/4g (Table 1). The latter coal sample, mostly based on vitrinite, is characterized by a lower H/C ratio and an increased O/C ratio. Despite the variability of the elemental analysis data, all the four samples contain type III kerogen.

The variation of the carbon isotope composition δ^{13}C in coals ranges from –25.9 to –24.2‰, which is typical of fossil coals (Galimov, 1975) and indicates that the OM is terrestrial (Kontorovich et al., 1985, 1986). The jetlike coal sample 1702/4g is the most enriched in the heavy isotope ^{13}C (Table 1).

Rock-Eval pyrolysis data

The values of T_{max} for samples 1703/TP, 1702/TP3, and 1702/TP4 are practically the same (Table 1). The maximum yield of hydrocarbons is already achieved when the samples are heated to a temperature of 425–427 °C, which is a sign of the low stage of the OM transformation, and it allows the rocks to be attributed to the lignite stage in the case of coaly matter. The enrichment of the OM of the rock in hydrogen can be estimated from the hydrogen index (HI). It is maximum in the case of sample 1702/TP4. Here, the OM forms up to 318 mg HC/g C$_{org}$ rock. The OM of all the studied samples is weakly oxidized, as evidenced by a moderately elevated oxygen index (OI) (Table 1). The OM of samples 1702/TP3 and 1702/TP4 can be determined as type III kerogen capable of producing some gaseous hydrocarbons under favorable conditions. When it comes to sample 1702/4g, its HI is significantly lower than that of others, even though the OI is the same, and the T_{max} of sample 1702/4g is slightly higher than that of more hydrogen-enriched samples.

Distribution of *n*- and isoalkanes

The samples under study somewhat differ in the distribution of acyclic hydrocarbons (Fig. 3). Bitumens 1702/TP3 and 1702/TP4 are characterized by the predominance of

Table 1. Geochemical characteristics of the Upper Devonian coals of the North Timan

Parameter	1702/4g	1702/TP3	1702/TP4	1703/TP
	Jetlike coal	Coal shale		
C_{org}, %	63.1	20.3	26.9	39.4
RV, %	0.47	0.52	0.55	0.45
$\delta^{13}C$, ‰	−24.2	−25.1	−25.9	−25.3
Bituminological data				
CBA, %	0.21	0.22	0.28	0.29
β_{CB}, %	0.33	1.38	1.04	0.74
Rock-Eval data				
TOC, %	71.3	20.0	18.5	41.1
T_{max}, ºC	427	425	425	422
S2, mg HC/g rock	36.2	32.1	59.0	161.3
HI, mg HC/g C_{org}	51	161	318	393
OI, mg HC/g C_{org}	25	25	26	18
Elemental composition				
C, %	69.2	68.7	70.5	70.6
H	3.8	5.6	6.1	5.4
N	0.75	0.97	1.13	1.11
O	21.1	16.8	17.1	18.7
O/C	0.23	0.19	0.18	0.20
H/C	0.67	0.99	1.05	0.93
***n*- and isoalkanes**				
P_{aq}	1.00	0.71	0.77	0.51
P_{wax}	0.18	0.49	0.49	0.61
Pr/Ph	3.42	7.09	7.43	8.65
Polycyclic biomarkers				
Ratio of the sums of all steranes, according to the GC-MS/MS data				
C_{27}	7	5	10	–
C_{28}	27	36	44	–
C_{29}	58	49	40	–
Ratio of the ααα 20R steranes, according to the GC-MS/MS data				
C_{27}	7	6	13	–
C_{28}	32	40	47	–
C_{29}	61	55	41	–
Ratio of the ααα 20R steranes, according to the GC-MS data and ion 217				
C_{27}	7	9	16	8
C_{28}	33	41	50	61
C_{29}	60	49	34	31
Triterpane hydrocarbons				
βα, % C_{30} moretane	26	40	38	39
22S/(22S + R) C_{31}	0.44	0.24	0.27	0.24
αβ:βα:ββ C_{30}	66:23:11	46:31:23	46:29:25	43:28:29
Aromatic hydrocarbons				
MPI-1	0.36	0.12	0.27	0.11
MPI-2	0.55	0.15	0.40	0.14
MNR	0.40	0.45	0.46	0.39
DMR	0.47	0.63	0.71	0.50
R^o, %	0.58	0.44	0.53	0.44

N o t e. P_{aq} = (C23 + C25)/(C23 + C25 + C29 + C31); P_{wax} = (C27 + C29 + C31)/(C23 + C25 + C27 + C29 + C31); MPI-1 = 1.5 × (2-MP + 3-MP)/(P + 1-MP + 9-MP); MPI-2 = 3 × 2-MP/(P + 1-MP + 9-MP); MNR = 2-MN/1-MN; DMR = (2,6-DMN + 2,7-DMN)/1,5-DMN; R^o = 0.6 × MPI-1 + 0.37 (Radke et al., 1982).
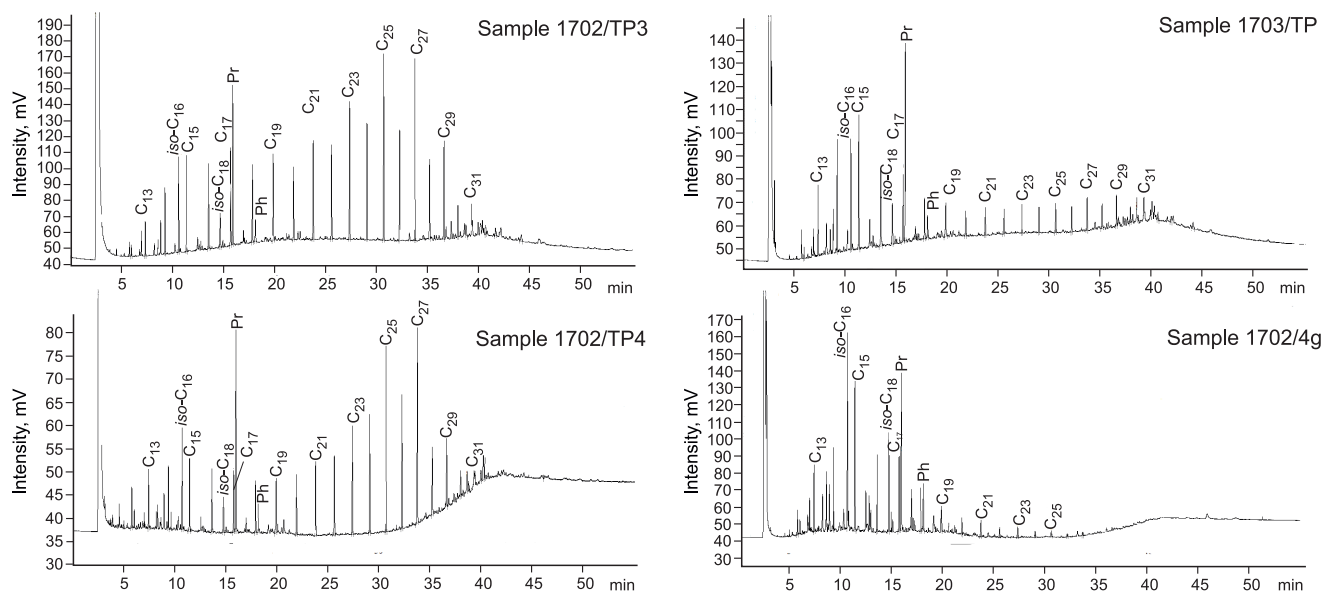
Fig. 3. Distribution of *n*- and isoalkanes in the bitumens of the samples studied. Pr – Pristane; Ph – phytane; C_{num} – *n*-alkanes.

high-molecular-weight *n*-alkanes. For 1702/TP3, these are C_{23}, C_{25}, C_{27}, and C_{29}; for 1702/TP4, these are predominantly C_{25} and C_{27}. It is assumed that individual odd *n*-alkanes reflect the contribution of different groups of producers to the composition of the initial OM. If the C_{27}, C_{29}, and C_{31} hydrocarbons are typical of terrestrial vegetation residues (Zheng et al., 2007), then the C_{23} and C_{25} *n*-alkanes are considered markers of aquatic vegetation, namely, algae and submerged macrophytes (Ficken et al., 2000). In this work, *Callixylon* and *Helenia* represent the higher terrestrial vegetation and the aquatic vegetation, respectively.

For samples 1702/TP3 and 1702/TP4, the values and ratios of P_{aq} and P_{wax} are close. At the same time, P_{aq} is slightly superior to P_{wax}, which can be considered a sign of a significant contribution of aquatic vegetation to the composition of the fossil OM. For sample 1703/TP, the distribution of acyclic hydrocarbons is somewhat different. This sample is noted for lower concentrations of high-molecular *n*-alkanes compared to the C_{14}–C_{18} hydrocarbons. The values of P_{aq} and P_{wax} in the bitumen are different: P_{wax} is noticeably higher, and P_{aq} is lower. In this bitumen, the relative content of the odd C_{15}–C_{19} hydrocarbons is slightly higher (Table 1). The origin of the latter is associated with the penetration of phytoplankton remains into the sediment (Hunt, 1995).

The distribution of *n*-alkanes in samples 1702/4g differs sharply from that in the first three samples and is characterized by a "narrow" monomodal distribution with a maximum in the *n*-C_{15} range. A similar distribution was earlier observed in jetlike coal from Devonian deposits in the outcrop of the middle reaches of the Tsil'ma River on the Middle Timan (Shumilov, 2015). Presumably, the remains of archeopterid trees served as the initial material for gagatization. The increased content of short-chain *n*-alkanes may indicate a microbial source and the formation of coal or-

ganic mass, represented by transformed lignocellulosic fragments, which do not contain waxes (Ghosh et al., 2022). This agrees well with the Rock-Eval pyrolysis data. An increased content of such structures leads to a decrease in the hydrogen index.

The most important and widely used geochemical indicator based on data on the distribution of acyclic hydrocarbons is the pristane/phytane ratio (Pr/Ph). This value ranges from 7.1 to 8.6 in samples 1703/TP, 1702/TP3, and 1702/TP4 and equals 3.4 in sample 1702/4g (Table 1). If the values of Pr/Ph are above 3, it indicates sedimentation in oxidizing conditions with the influx of a large amount of terrigenous materials (Peters et al., 2005). At the same time, in the case of coals, the Pr/Ph ratio typically changes depending on the maturation of the OM (Radke et al., 1980; Diessel, 1992). The maximum values of Pr/Ph are characteristic of coals with the reflectance index *RV* ranging from 0.50% to 1.12%.

Composition of polycyclic biomarkers

The distribution of sterane hydrocarbons in bitumens of Devonian coaly deposits from the section of the Sula River is studied by GC-MS and GC-MS/MS. The construction of mass chromatograms based on fragmentary ion 217 does not provide complete information on the composition of steranes. In the studied fractions, the ααα 20R C_{27}–C_{29} steranes are identified (Table 1). More reliable results are obtained by tandem mass spectrometry. The construction of mass chromatograms on the basis of transitions 372–217, 386–217, and 400–217 makes it possible to properly study the molecular weight distribution of isomers and diastereomers of the C_{27}–C_{29} steranes (Table 1).

The distribution of the C_{27}–C_{29} sterane hydrocarbons is used as a marker for the composition of bioproducers
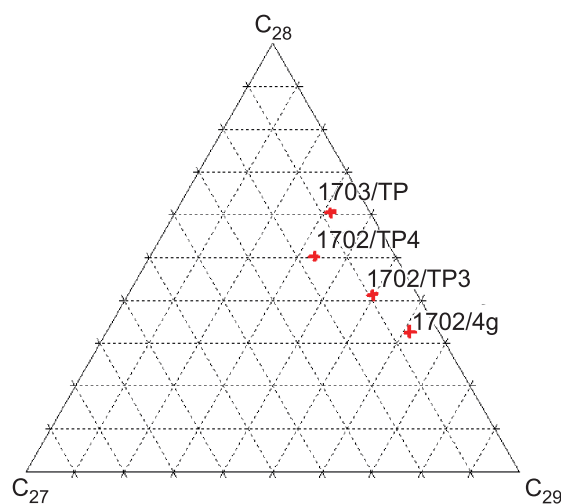
Fig. 4. Triangular distribution chart for the αββ C_{27}–C_{29} steranes.

(Huang and Meinschein, 1979; Petrov, 1987; Peters et al., 2005). It is known that the OM produced by marine phytoplankton mainly produces the C_{27} steranes, while the humic OM produces the C_{29} steranes. For example, the previously studied coals from the Permian deposits of the Pechora Basin contain bitumens strongly dominated by the C_{29} steranes (Boushnev et al., 2016). The difference between the currently studied coal-bearing rocks of the Late Devonian of Timan and the Pechora coals is the high concentration of the C_{28} sterane (Table 1, Fig. 4). A number of ancient marine sediments that do not contain higher vegetation remains are also characterized by elevated concentrations of ethylcholestane (C_{29}), which are also typical of a number of ancient source rocks and their corresponding oils (Kashirtsev et al., 1999; Kontorovich et al., 1999). For example, they are found in the Precambrian oils of the Siberian and Arabian platforms (Kashirtsev et al., 2015).

The high concentrations of ergostane are usually associated with the presence of remains of lacustrine vegetation in the fossil OM (Huang and Meinschein, 1979; Zhang et al., 2020). It is noteworthy that the distribution of regular steranes with high concentrations of the C_{28} sterane was previously identified in cannel coals containing a large number of spores of higher plants and coals from Melville Island (Middle and Upper Devonian, Arctic Canada (Fowler et al., 1991)). Here, the portion of the C_{28} sterane becomes higher with an increase in the portion of sporinite in coals (Fowler et al., 1991). The elevated concentrations of ergostane are characteristic of the upper Carboniferous bituminous coals of the Polish Lublin Basin (Gola et al., 2013).

Another feature of the distribution of sterane hydrocarbons in the deposits under study is the presence of high concentrations of rearranged compounds (Fig. 5). For the C_{27}–C_{29} steranes in samples 1702/TP3 and 1702/TP4, the concentrations of 13β and 17α (20R and 20S) compounds exceed the concentrations of the αββ regular steranes and

are only slightly lower than that of the ααα 20R (biologic) sterane. In sample 1702/4g, which is somewhat more thermally transformed, the diasterane peaks are superior to those of regular steranes.

The fraction of aliphatic hydrocarbons in the studied bitumens also contains high concentrations of diaster-13(17)-enes (Fig. 5).

The unsaturated hydrocarbons of the sterane series are intermediate compounds between natural sterols and steranes of the fossil OM. The diaster-13(17)-enes in the aliphatic fraction are identified using data from (Peakman and Maxwell, 1988) on the elution order of diastereomers of diasterenes and data from (Peakman et al., 1988) on the mass spectral features of these compounds. Like regular steranes, diaster-13(17)-enes are predominantly represented by the C_{28} and C_{29} hydrocarbons, and the concentration of diacholest-13(17)-enes is negligible. The quantitative determination of the ratio of the C_{27}–C_{29} diaster-13(17)-enes is difficult because of coelution.

Terpane distribution

There are noticeably large concentrations of tetracyclic diterpanes in sample 1702/TP3 (Fig. 6). The analysis of the published data (Noble et al., 1985a; Sheng et al., 1992; Peters et al., 2005; Song et al., 2017) makes it possible to identify beyerane, 16α(H)-kaurane, 16β(H)-kaurane, and 16α(H)-atisane. This is supported by the comparative analysis of the mass spectra of kauranes and phyllocladanes (Sheng et al., 1992), the elution order, and the relative retention times (Noble et al., 1985a). No identifiable amount of phyllocladanes could be determined in the samples of Timan coals from the Sula River.

It is revealed that the Middle Devonian Chinese coals of the Hefeng basin (Song et al., 2017) and the Luquan basin (Sheng et al., 1992) contain only hydrocarbons of the kaurane and beyerane series. Previously (Schulze and Michaelis, 1990; Romero-Sarmiento et al., 2011), phyllocladane was identified in samples of hard coals from Germany and Scotland, respectively, and is widely distributed in younger coals (Noble et al., 1985b). Thus, the tetracyclic diterpanes identified in this study are noteworthy for two reasons: Their individual composition of isomers is similar to that of the Middle Devonian coals, and the absence of phyllocladane makes them fundamentally different from younger Carboniferous coals identified in numerous samples of different sections. A number of diterpane hydrocarbons have been previously identified in the Devonian barzassite from the Kuznetsk Basin (Kashirtsev et al., 2010).

The distribution of hydrocarbons of the hopane series ($m/z = 191$) in the aliphatic fractions of the bitumens under study does not fundamentally differ from that in other previously researched objects that are at low stages of OM transformation, such as the Inta deposit coals (Boushnev et al.,
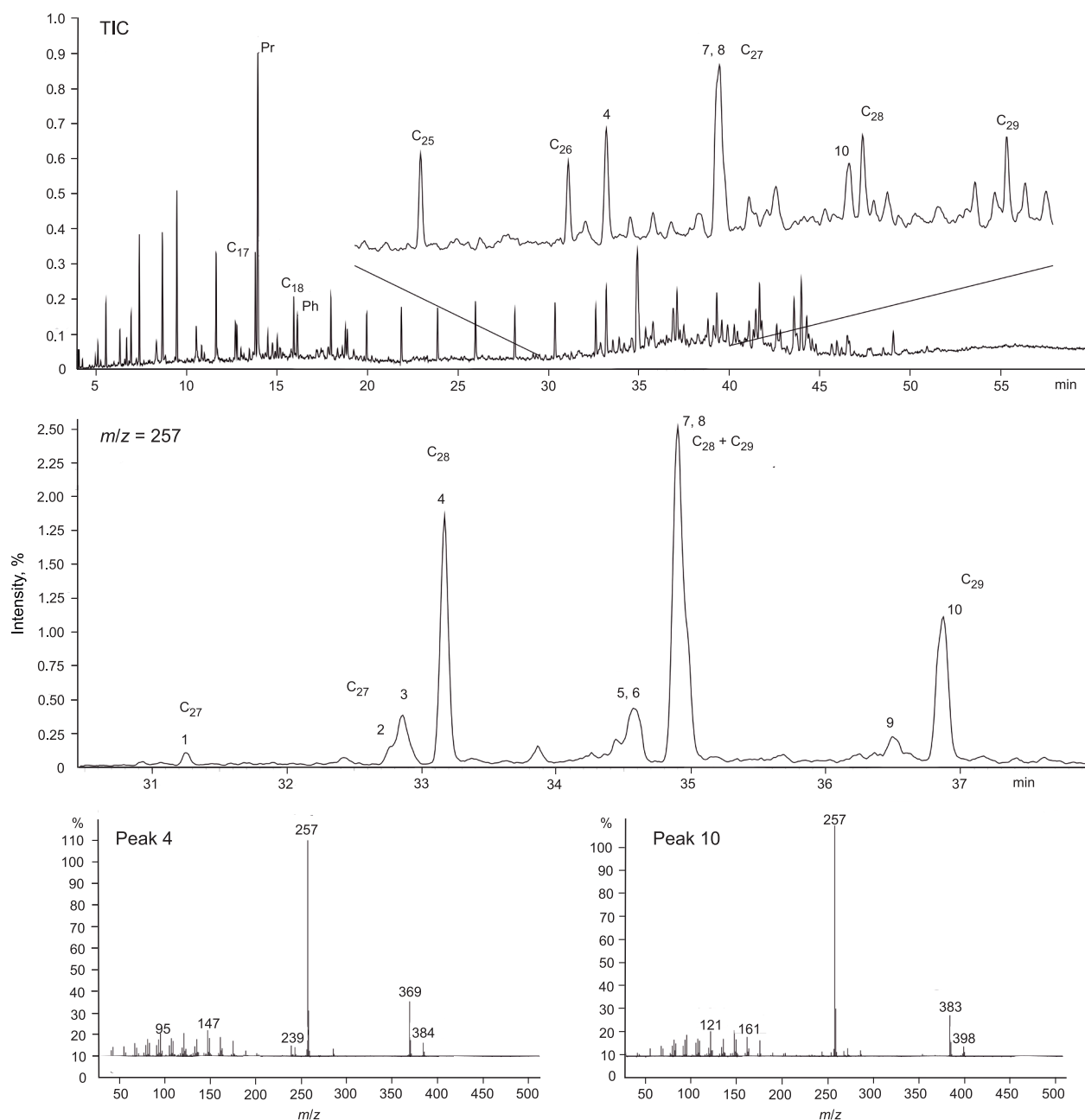
Fig. 5. Mass fragmentograms of the aliphatic bitumen fraction based on TIC and the characteristic ion of diaster-13(17)-enes with *m/z* = 257, respectively. Peak numbers: 1 – 20S-10α-24-diacholest-13(17)-ene; 2 – 20R-10α-24-diacholest-13(17)-ene; 3 – 20S-10β-24-methyldiacholest-13(17)-ene; 4 – 20S-10α-24-methyldiacholest-13(17)-ene; 5 – 20R-10β-24-methyldiacholest-13(17)-ene; 6 – 20S-10β-24-ethyldiacholest-13(17)-ene; 7 – 20R-10α-24-methyldiacholest-13(17)-ene; 8 – 20S-10α-24-ethyldiacholest-13(17)-ene; 9 – 20R-10β-24-ethyldiacholest-13(17)-ene; 10 – 20R-10α-24-ethyldiacholest-13(17)-ene.

2016). The ββ, βα, and αβ hopanes are present here (Fig. 7). The ββ hopanes are known as biologic hopanes, and their presence is characteristic of immature OM. For example, they are abundant in the bitumens of the Jurassic oil shale (Bushnev and Lyyurov, 2002). Also, the bitumens of Devonian coaly rocks contain high concentrations of moretane, and the value of the ratio 22S/(S + R) is far from the equilibrium value (Table 1). In addition to saturated hydrocarbons,

the aliphatic bitumen fraction contains unsaturated hydrocarbons of hopane structure. As in the bitumen of the Inta coal, the C_{29} and C_{30} neohop-13(18)-enes are identified here (Fig. 7). It is evidenced by the maturity indicators (calculated from the composition of hopane hydrocarbons) and the sterane and Rock-Eval pyrolysis data that the transformation of OM from sample 1702/4g is somewhat higher than that of OM from samples 1703/TP, 1702/TP3, and 1702/TP4.
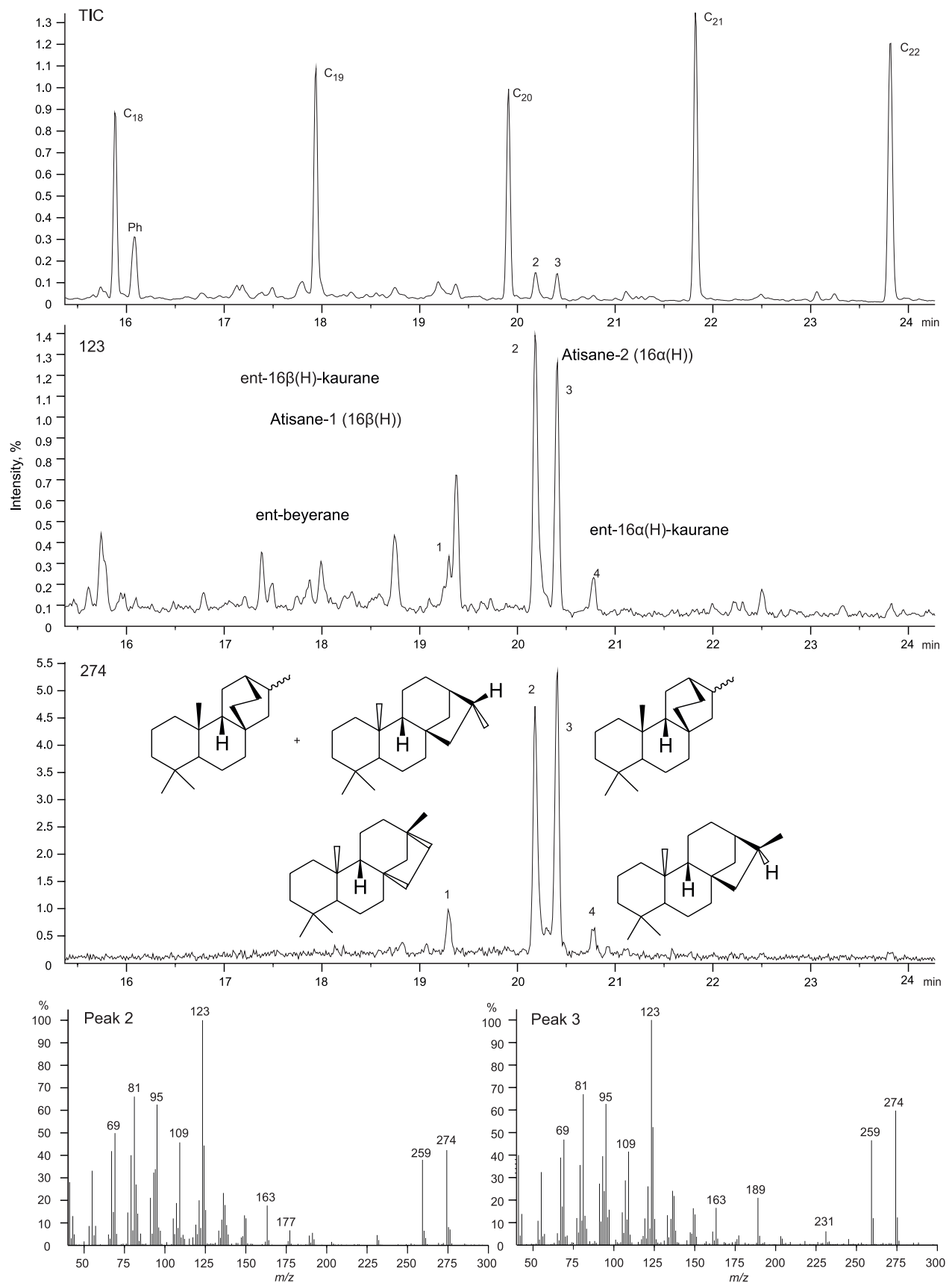
Fig. 6. Mass fragmentograms based on TIC and the characteristic ions with *m/z* = 123 and *m/z* = 274 ions, typical of diterpane hydrocarbons.
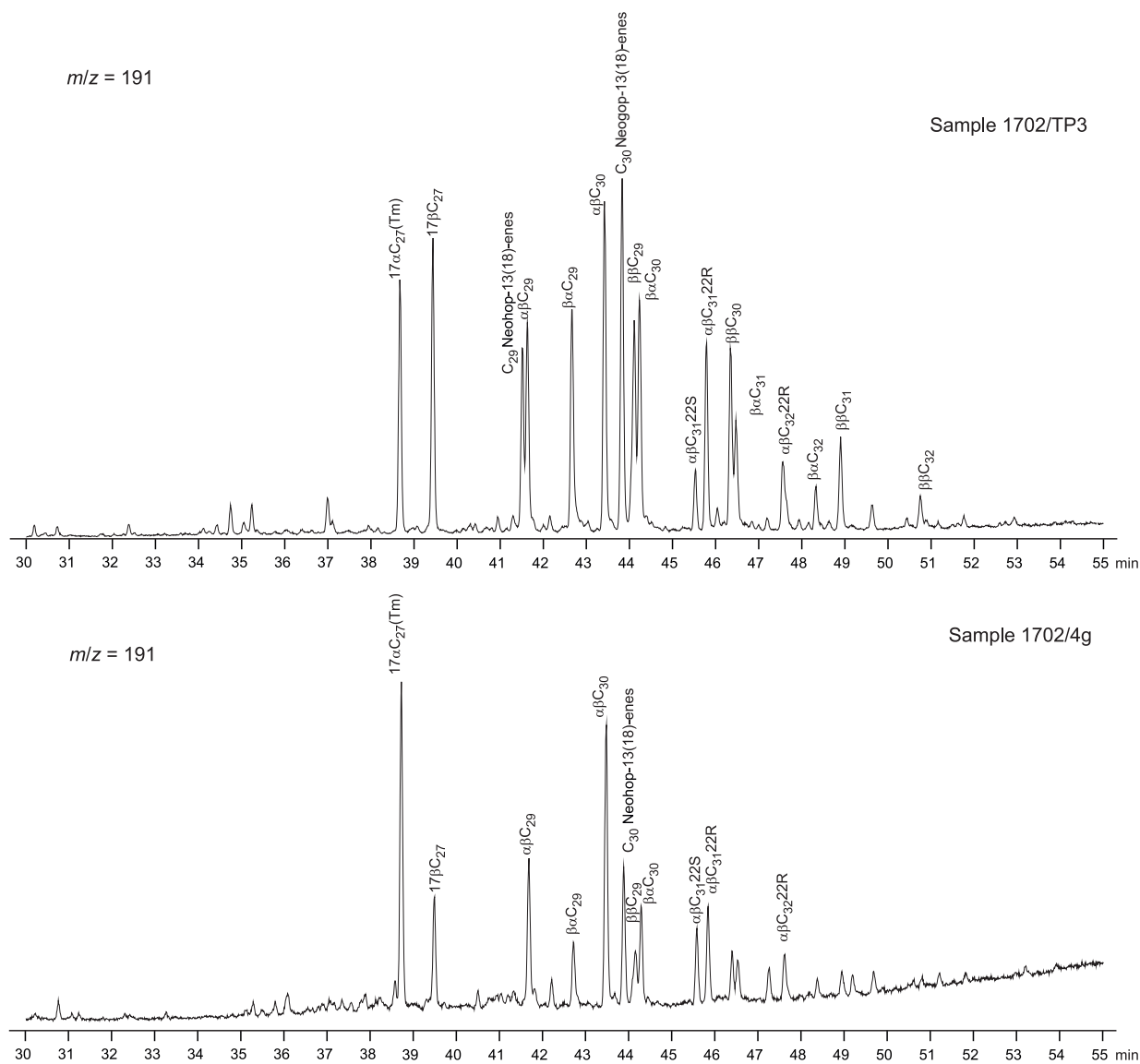
Fig. 7. Distribution of tricyclic terpanes and hydrocarbons of the hopane series over the ion with *m/z* = 191.

Aromatic hydrocarbons of bitumens

The aromatic fraction is a significant part of all the bitumens under study. It accounts for 27 to 38% of the original chloroform bitumen. As a rule, aromatization is the predominant chemical process in OM coalification (Teichmüller and Teichmüller, 1968). At the same time, the molecular composition of the OM of coals is determined by the dominance of macerals. Thus, the high content of aromatic structures in coals is associated with an increased content of vitrinite components (Ghosh et al., 2022).

Studies on the composition of polyaromatic hydrocarbons of dispersed OM of different genetic types on the example of bitumens from the marine deposits of the Upper Jurassic strata of West Siberia and the Middle Jurassic deposits of the Siberian Platform show a direct relationship with its nature. For example, the terrestrial OM is enriched in anthracene hy-

drocarbons and polyaromatics relative to marine OM, which is adequately explained by the specific precursor structures of these compounds (Kontorovich et al., 1973).

The main set of aromatic compounds is the same for all the samples and is represented by methyl-/polymethylnaphthalenes, phenanthrene, its methyl derivatives (pyrene and 1-methylpyrene), dimethyl-substituted pyrene derivatives (fluoranthene and methyldibenzofurans), chrysene, its methyl derivatives, and benzo[a]anthracene (Fig. 8).

Compounds are identified on the basis of their mass spectra and retention times (Romero-Sarmiento et al., 2011; Fabiańska et al., 2013). There are some variations in the content of aromatic components among the samples; the maximum concentrations are observed for phenanthrene and 1-methylpyrene, while the content of other hydrocarbons is lower. The most significant differences are typical of sample 1702/4g, in which the content of pyrene, methyl- and di-
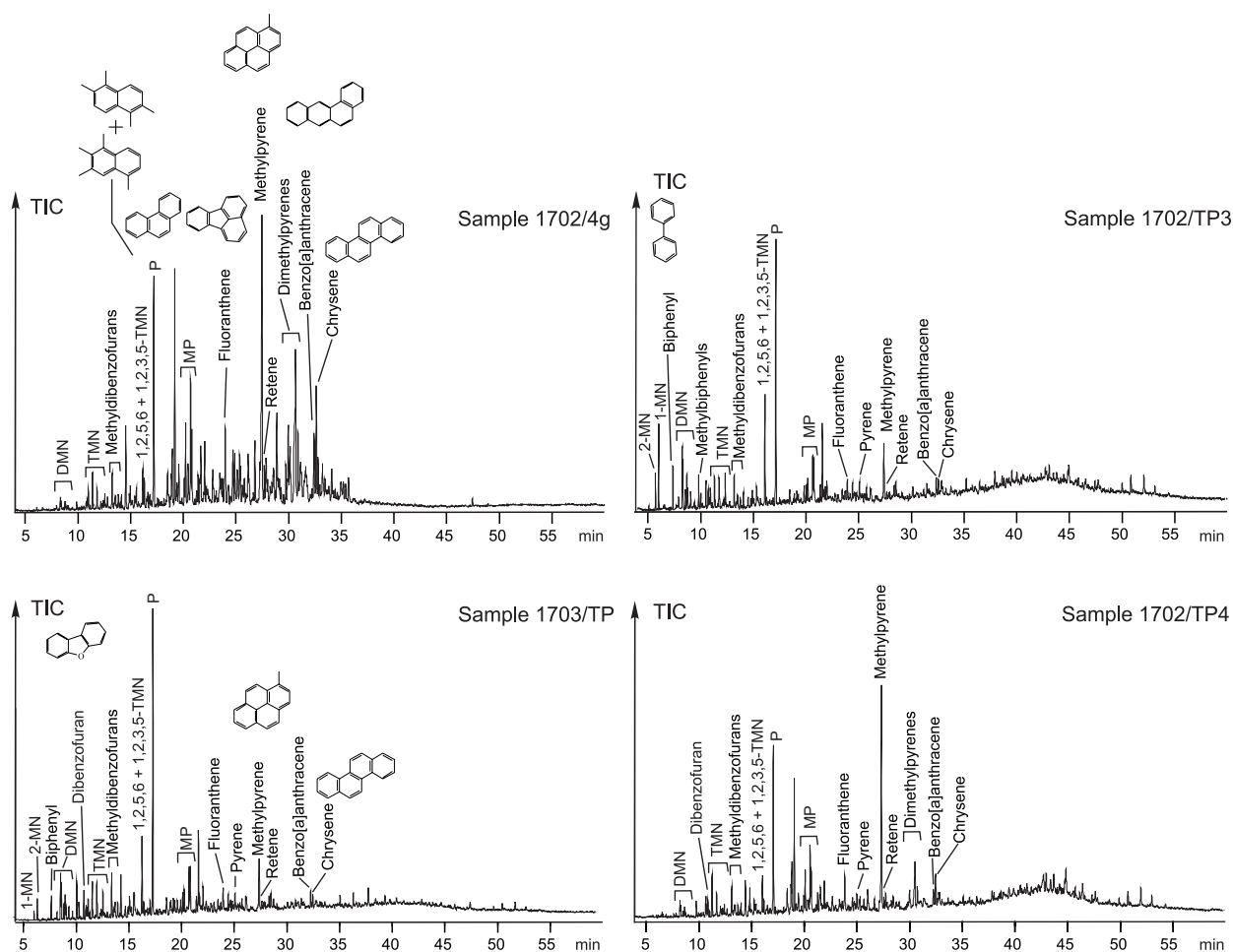
Fig. 8. Total ion current based mass chromatograms of the aromatic fraction of bitumens of the coaly rocks studied.

methylpyrenes, fluoranthene, chrysene, and benzo[a]anthracene is significantly higher than that in other samples. Samples 1703/TP, 1702/TP3, and 1702/TP4 are characterized by the predominance of bi- and tricyclic aromatic compounds, whereas sample 1702/4g contains mostly polyaromatic (tri- and tetracyclic) hydrocarbons. The results obtained for the composition of aromatic components are in good agreement with the organic petrography data, in which vitrinite makes up the bulk of the jetlike coal material (sample 1702/4g).

The qualitative composition of methyl-substituted naphthalenes is the same for all the samples (Fig. 9). In samples 1702/TP3 to 1702/4g, the content of methyl- and dimethyl-naphthalenes decreases, and the relative content of tri- and tetramethylnaphthalenes increases. It is assumed that the methyl derivatives of naphthalene are the degradation products of natural terpenoids, carotenoids, and cyclic sesquiter-penoids identified in significant concentrations in the initial biomass of higher plants (Simoneit, 1985; Püttman and Villar, 1987; Armstroff et al., 2006). These compounds are widely distributed in extracts of coals, sediments, recent deposits, and oils of different ages (Tissot and Welte, 1984). Among the methyl-substituted naphthalenes in samples

1702/TP3 and 1703/TP, there is a sharp peak typical of coeluting 1,2,5,6- and 1,2,3,5-tetramethylnaphthalenes (peak 24). It is assumed that 1,2,5,6-TeMN is of relict character (Püttmann and Villar, 1987) and its formation together with 1,2,5-TMN is associated with the transformation of oleanane-type pentacyclic triterpenoids during diagenesis, which is characteristic of angiosperms. As the occurrence of angiosperms has been recorded since the Cretaceous Age, it is rather unreasonable to associate the origin of these naphthalene derivatives found in the composition of OM of Devonian coaly deposits with oleanane structures. Bacteria are considered to be a possible source of these compounds. Such naphthalenes are formed upon the destruction of the D-ring of monoaromatic 8,14-secohopanes under acidic conditions (Püttmann and Villar, 1987; Bastow et al., 2000). The detection of 1,1,5,6-tetramethyl-1,2,3,4-tetrahydro-naphthalene in the composition of the samples studied, which is an intermediate product of the conversion of seco-hopanoids into 1,2,5-TMN and 1,2,5,6-TeMN, formed owing to aromatization and disintegration of the C-ring (Killops, 1991), may somewhat confirm the bacterial nature of 1,2,5,6-TeMN (Fig. 10a).
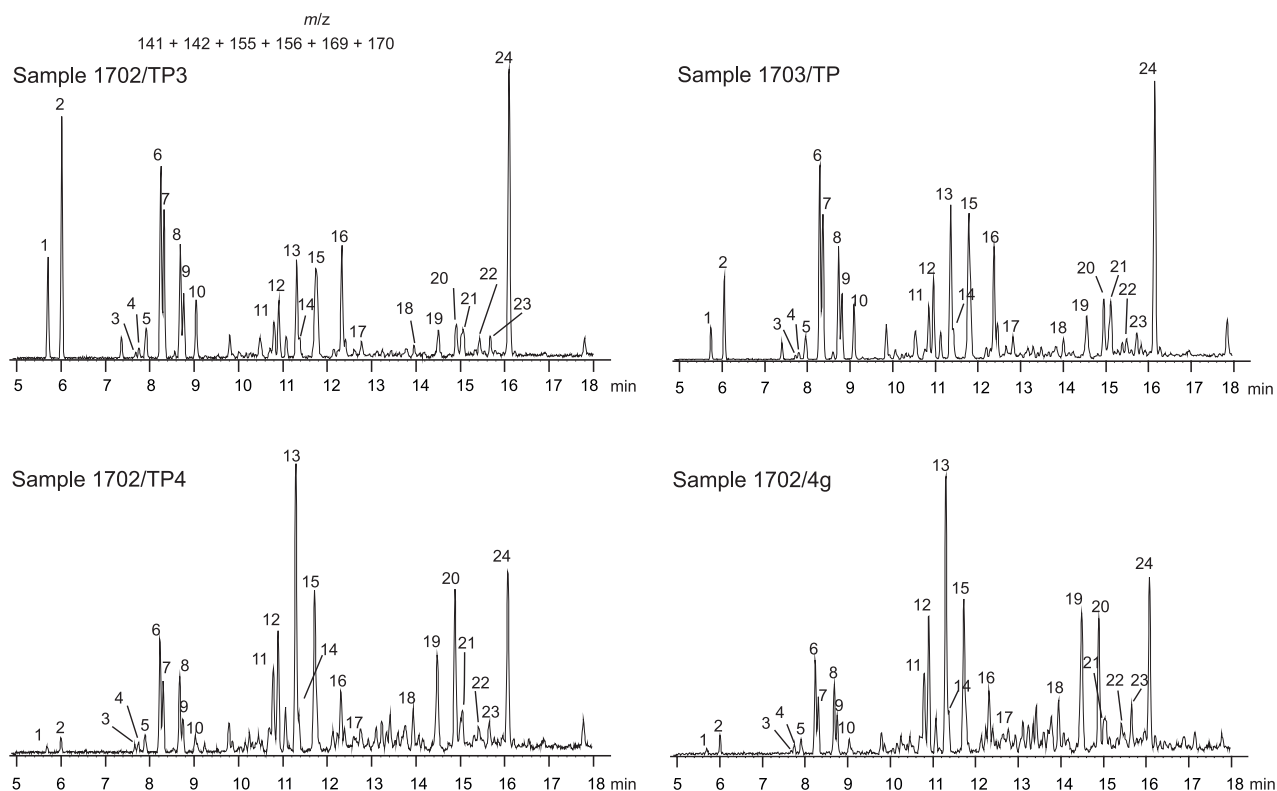
Fig. 9. Mass chromatogram of methyl-substituted naphthalenes plotted from the sum of ions with $m/z = 141 + 142 + 155 + 156 + 169 + 170$. Peak numbers: 1 – 2-methylnaphthalene; 2 – 1-methylnaphthalene; 3 – 2-ethylnaphthalene; 4 – 1-ethylnaphthalene; 5 – 2,6- + 2,7-dimethylnaphthalenes (DMN); 6 – 1,3- + 1,7-DMN; 7 – 1,6-DMN; 8 – 1,4- + 2,3-DMN; 9 – 1,5-DMN; 10 – 1,2-DMN; 11 – 1,3,7-trimethylnaphthalene (TMN); 12 – 1,3,6-TMN; 13 – 1,4,6- + 1,3,5-TMN; 14 – 2,3,6-TMN; 15 – 1,2,7- + 1,6,7- + 1,2,6-TMN; 16 – 1,2,5-TMN; 17 – 1,2,3-TMN; 18 – 1,3,5,7-tetramethylnaphthalene (TeMN); 19 – 1,3,6,7-TeMN; 20 – 1,2,4,7-TeMN; 21 – 1,2,5,7-TeMN; 22 – 1,2,6,7-TeMN; 23 – 1,2,3,6-TeMN; 24 – 1,2,5,6- + 1,2,3,5-TeMN.

Phenanthrenes are represented mainly by holonuclear (unsubstituted) phenanthrene and methyl-substituted derivatives, while the content of di- and trimethyl-substituted derivatives is negligible. The high content of phenanthrene observed for all the samples is often characteristic of the OM formed by terrestrial vegetation. This value is rather high in many coal areas: For example, in the coals of the upper Carboniferous of the Ruhr coal basin (Germany), it is more than 70% of the total content of aromatic components (Radke et al., 2000). This high value can be explained by the presence of different steroid precursors (Ellis et al., 1994). In the presented samples, phenanthrene is dominant among its methyl-substituted derivatives. The coefficients calculated using the methylnaphthalene (MNR) and dimethylnaphthalene (DMN) indices indicate that the OM of coals is uniformly transformed during thermal evolution and fully correspond to the measured values of *RV* (Table 1), while the methylphenanthrene (MPI-1 and MPI-2) indices show slightly higher maturity of sample 1702/4g (Table 1). According to (Radke et al., 1982), the calculated values of *RV* (R^o, %), determined by the equation $R^o = 0.60 \cdot \text{MPI-1} + 0.37$, are 0.44–0.58% (Table 1) and are in good agreement with the measured vitrinite reflectance. In general, the coef-

ficients are low and characterize the OM of coals as immature.

Retene is identified in the composition of the aromatic fraction of the deposits studied, and the peak related to retene is most intense in sample 1702/4g (Fig. 8). Retene (1-methyl-7-isopropylphenanthrene) is identified on the basis of the mass spectral data (Fig. 10*b*) and the comparison of the retention index (368) with data from the literature (368.67 (Lee et al., 1979)).

Retene itself is a conversion product of abietic acid, which is present in the resins of coniferous plants and often occurs in higher concentrations in the OM of coals formed in the post-Devonian period (van Aarssen et al., 2000). For example, the extracts of Permian hard coals from the Pechora coal basin contain large concentrations of retene (Bushnev et al., 2017). The less transformed brown coals from the same basin also contain its hydrogenated analogs—dehydroabietane, dehydroabietine (or 18-norabieta-8,11,13-triene), and simonellite (Burdel'naya et al., 2021). Nevertheless, retene was also revealed in extracts from lower Paleozoic and Precambrian rocks (Wen et al., 2000; Kashirtsev et al., 2018). It was shown in (Wen et al., 2000) that the pyrolysis of pure strains of green algae *Chlorella*
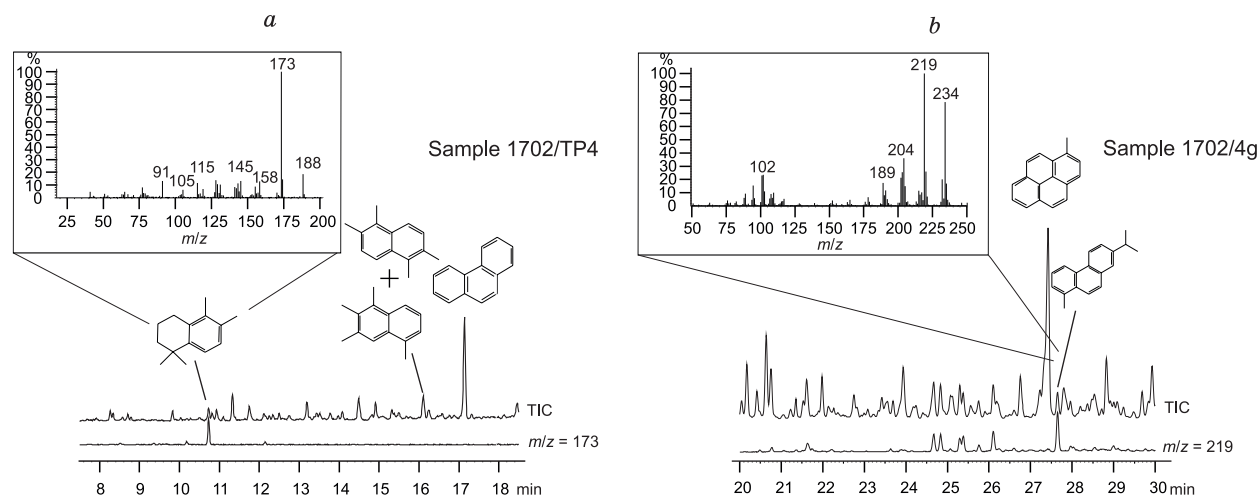
Fig. 10. Identification of 1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene (mass chromatogram based on ion 173 and the mass spectrum of the compound) (*a*) and retene (mass chromatogram based on ion 219 and mass spectrum corresponding to retene) (*b*).

protothecoides and cyanobacteria *Synechocystis* sp. forms a whole complex of compounds associated with the dehydroabietane structure: dehydroabietine, simonellite, 1,2,3,4-tetrahydroretene, and retene. This proves that phytoplankton can also be a source of retene in modern and ancient sediments. Retene is also present in the upper Silurian–Lower Devonian deposits of the Ghadamis Basin (Tunisia, North Africa), the possible source of which was bryophytes (Romero-Sarmiento et al., 2010). This led to the conclusion that the synthesis of abietic acid proceeded before the occurrence of gymnosperms or that compounds with a kaurane skeleton, actively synthesized by early Paleozoic bryophytes, were possible precursors of retene (Romero-Sarmiento et al., 2010).

As for the coals under study, the question remains open in this case. It should be noted that, according to the organic petrography data, a resinite-like substance is recorded in jetlike coal pores. Thus, it is the bitumen from sample 1702/4g (jetlike coal) that contains higher concentrations of retene.

Pyrene and chrysene identified in the OM of coals are considered products of pyrolytic decomposition of OM or "combustion" products, most often being part of coal tar (Blumer, 1976; Jiang et al., 1998). However, these compounds also occur in immature coals and modern sediments, and the natural source of pyrene and chrysene remains unknown. Pyrene and its methyl-substituted derivatives are abundant in oils and rock extracts of different origins (Kruge, 2000; Fang et al., 2015).

CONCLUSIONS

The individual composition of biomarker hydrocarbons from Devonian coals and coaly mudstones of the North Timan has been characterized in detail for the first time. Coal-bearing deposits formed in shallow coastal-marine conditions with terrigenous sedimentation and variable hyd-

rodynamic parameters of the environment. The initial organic matter of coaly rocks was represented mainly by spores of herbaceous lycopsids that occupied the coastal zone and the forest-forming archeopterid plants that grew at a distance from the coastline. In terms of the composition of coaly microcomponents, the organic matter of the three samples under study was represented mainly by vitrinite and liptinite. The fourth sample (jetlike coal) was mainly composed of vitrinite with a resinite-like substance. According to the vitrinite reflectance (RV = 0.45–0.55%), the level of maturity of the organic matter corresponded to PK_3–MK_1.

According to the results of the analysis of sterane and hopane hydrocarbons, the organic matter of the coaly rocks under study can be characterized as immature, as evidenced by the maturity coefficients ($\alpha\beta\beta/\alpha\alpha\alpha$ + $\alpha\beta\beta$, 20S/20S + R, 22S/22S + R, and $\beta\alpha/\alpha\beta$ + $\beta\alpha$) and the presence of $\beta\beta$ hopanes, hop-17(21)-enes, and diasterenes. The distribution of steroid structures (both saturated $\alpha\alpha\alpha/\alpha\beta\beta$ structures and rearranged unsaturated ones) has a pronounced dominance of C_{28} and C_{29} components. The high concentrations of methylcholestenes are characteristic of many ancient coals and lacustrine sapropels. The distribution of normal alkanes indicates that the remains of terrestrial and aquatic vegetation made a significant contribution to the composition of the organic matter of the 1703/TP–1702/TP3–1702/TP4 rocks, which, in particular, is confirmed by the values of the coefficients P_{aq} and P_{wax}.

Tetracyclic diterpanes, abundant in sample 1702/TP3, are represented by beyerane, atisane, and kaurane. Phyllocladane structures are not identified anywhere, which is consistent with the pre-Carboniferous age of the rocks studied. The presence of tetracyclic ditherapanes in only one sample may point to the limited distribution of plants producing these hydrocarbon structures and their precursors, the organic matter of which did not contribute to all the coal localities of the North Timan.

The distribution of aromatic components of the coaly rocks under study does not have any specific genetic features of bioproduction except for retene, which is a derivative of abietic acid. Retene itself is a typical biomarker of coniferous vegetation in the post-Devonian period (Romero-Sarmiento et al., 2011). At the same time, there are many assumptions about the existence of other sources of this compound, namely, bryophytes and/or phytoplankton, obtained on the basis of small concentrations in Silurian and Devonian deposits in the OM. As it is well known that conifers occurred in the early Carboniferous, one can assume that the development of abietic acid biosynthesis processes began much earlier (or long before) their occurrence. This is confirmed by the discovery of a resinite-like substance in the composition of sample 1702/4g. More significant differences in the composition of aromatic components are recorded between sample 1702/4g and the group of samples 1703/TP, 1702/TP3, and 1702/TP4. Here, in the first case, the content of polyaromatic components (pyrene, methyl- and dimethylpyrenes, fluoranthene, chrysene, and benzo[a]anthracene) is significantly higher than in the other samples. This corresponds to the organic petrography data, according to which vitrinite makes up the main part of jet-like coal.

The composition of aromatic hydrocarbons also confirms the low maturity of the OM of the studied coals: low MPI and NR values correspond to the lignite stage. Also, the low maturity of the organic matter in many samples may be indicated by the elevated concentrations of 1,2,5,6-TeMN, which is of relict origin. The concentration of this hydrocarbon is maximum in sample 1702/TP3, lower in samples 1703/TP and 1702/TP4, and its peak is less pronounced in sample 1702/4g. The presence of 1,2,5,6-TeMN in the bitumen in combination with the presence of 1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene in the sample indicates that this hydrocarbon may be of bacterial origin.

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REFERENCES

Armstroff, A., Wilkes, H., Schwarzbauer, J., Littke, R., Horsfield, B., 2006. Aromatic hydrocarbon biomarkers in terrestrial organic matter of Devonian to Permian age. Palaeogeogr. Palaeoclimatol. Palaeoecol. 240, 253–274, doi: 10.1016/j.palaeo.2006.03.052.

Astafieva, M.M., Rozanov, A.Yu., Hoover, R., 2005. Framboids: Their structure and origin. Paleontol. J. 39 (5), 457–464.

Bastow, T.P., Alexander, R., Fisher, S.J., Singh, R.K., van Aarssen, B.G.K., Kagi, R.I., 2000. Geosynthesis of organic compounds. Part V – methylation of alkylnaphthalenes. Org. Geochem. 31, 523–534, doi: 10.1016/S0146-6380(00)00038-3.

Beznosov, P.A., Snigirevsky, S.M., Naugolnykh, S.V., Lukševičs, E.V., 2018. The Upper Devonian delta plain deposits of North Timan. Vestnik IG KNTs UrO RAN, No. 1, 25–44.

Beznosov, P.A., Snigirevsky, S.M., Sivkova, A.P., Pavlova, M.A., Zarkhidze, D.V., 2019. Sedimentary sequences of Devonian deposits of the eastern part of the Kanin Peninsula, in: Geology and Mineral Resources of the European North-East of Russia. Proc. 17th Geol. Congr. Komi Republic [in Russian]. Syktyvkar, Vol. 2, pp. 135–137.

Blumer, M., 1976. Polycyclic aromatic compounds in nature. Sci. Am. 234, 35–45.

Boushnev, D.A., Valyaeva, O.V., Kotik, I.S., Burdelnaya, N.S., Burtsev, I.N., 2016. Composition of biomarkers of bitumen from coals and enclosing deposits in north-eastern Pechora coal basin. Vestnik IG KNTs UrO RAN, No. 6, 3–10.

Burdel'naya, N.S., Bushnev, D.A., Kotik, O.S., Ondar, S.A., Beznosov, P.A., 2021. Aromatic biomarkers of extracts from a number of immature coals in Russia, in: Collection of Scientific Papers Based on the Materials of the International Scientific and Practical Conference "New Ideas in the Geology of Oil and Gas. New Reality 2021" [in Russian]. MGU, Moscow, pp. 45–48.

Bushnev, D.A., Lyyurov, S.V., 2002. Organic geochemistry of Jurassic sedimentary deposits in the Sysola shale-bearing region, Komi Republic. Geochem. Int. 40 (2), 189–195.

Bushnev, D.A., Burdelnaya, N.S., Kuzmin, D.V., Ryabinkin, S.V., Mokeev, M.V., 2017. Coal of Vorkuta region, composition of hydrocarbons of biomarkers, possibility of obtaining an ashless concentrate. Vestnik IG KNTs UrO RAN, No. 9, 3–11.

Cherepanov, A.A., Eryukhina, N.A., Zatul'skaya, T.Yu., 2001. State Geological Map of the Russian Federation, Scale 1 : 200,000. Timan Ser., Sheets Q-39-VII and -VIII (Kovriga Marsh) [in Russian]. St. Petersburg.

Chernov, A.A., 1938. Mineral resources of the northern part of the North Timan. Sovetskii Sever, No. 4, 40–51.

Chernov, A.A., 1947. Geological Study of the North Timan [in Russian]. Izd. MOIP, Moscow, Issue 6 (10).

Diessel, C.F.K., 1992. Coal-Bearing Depositional Systems. Springer, Berlin, Heidelberg.

Ellis, L., Alexander, R., Kagi, R.I., 1994. Separation of petroleum hydrocarbons using dealuminated mordenite molecular sieve–II. Alkylnaphthalenes and alkylphenanthrenes. Org. Geochem. 21 (8–9), 849–855, doi: 10.1016/0146-6380(94)90044-2.

Ergol'skaya, Z.V., 1936. Petrographic study of Barzas coals, in: Transactions of TsNIGRI, Vol. 70, pp. 5–54.

Fabiańska, M.J., Ćmiel, S.R., Misz-Kennan, M., 2013. Biomarkers and aromatic hydrocarbons in bituminous coals of Upper Silesian Coal Basin: Example from 405 coal seam of the Zaleskie Beds (Poland). Int. J. Coal Geol. 107, 96–111, doi: 10.1016/j.coal.2012.08.003.

Fang, R., Li, M., Wang, T.-G., Zhang, L., Shi, S., 2015. Identification and distribution of pyrene, methylpyrenes and their isomers in rock extracts and crude oils. Org. Geochem. 83–84, 65–76, doi: 10.1016/j.orggeochem.2015.03.003.

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic

macrophytes. Org. Geochem. 31, 745–749, doi: 10.1016/S0146-6380(00)00081-4.

Fomin, A.N., 2019. Fundamentals of Geology and Petrology of Solid Fossil Fuels [in Russian]. NSU Publishing and Printing Center, Novosibirsk.

Fowler, M.G., Goodarzi, F., Gentzis, T., Brooks, P.W., 1991. Hydrocarbon potential of Middle and Upper Devonian coals from Melville Island, Arctic Canada. Org. Geochem. 17 (6), 681–694, doi: 10.1016/0146-6380(91)90012-9.

Galimov, E.M., 1975. Carbon Isotopes in Oil-Gas Geology. NASA, Washington, D.C.

Ghosh, S., Dutta, S., Bhattacharyya, S., Konar, R., Priya, T., 2022. Paradigms of biomarker and PAH distributions in lower Gondwana bituminous coal lithotypes. Int. J. Coal Geol. 260, 104067, doi: 10.1016/j.coal.2022.104067.

Gola, M.R., Karger, M., Gazda, L., Grafka, O., 2013. Organic geochemistry of Upper Carboniferous bituminous coals and clastic sediments from the Lublin Coal Basin (Poland). Acta Geol. Pol. 63, 425–442, doi: 10.2478/agp-2013-0018.

Golitsyn, M.V., Golitsyn, A.M., Pronina, N.V., Makarova, E.Yu., Bogomolov, A.Kh., 2012. Geology and Geochemistry of Fossil Fuels, Part 2: Solid Fossil Fuels [in Russian]. KDU, Moscow.

Goodarzi, F., Goodbody, Q., 1990. Nature and depositional environment of Devonian coals from western Melville Island, Arctic Canada. Int. J. Coal Geol. 14, 175–196, doi: 10.1016/0166-5162(90)90002-G.

GOST R 55663-2013 (ISO 7404-2:2009), 2013. Methods for Petrographic Analysis of Coals. Part 2. Methods for Preparing Coal Samples [in Russian].

GOST R 55662-2013 (ISO 7404-3:2009), 2013. Methods for Petrographic Analysis of Coals. Part 3. Method for Determining the Maceral Composition [in Russian].

GOST R 55659-2013 (ISO 7404-5:2009), 2013. Methods for Petrographic Analysis of Coals. Part 5. Method for Determining Vitrinite Reflectance Using a Microscope [in Russian].

Hackley, P.C., Araujo, C.V., Borrego, A.G., Bouzinos, A., Cardott, B.J., Carvajal-Ortiz, H., Rocio López Cely, M., Chabalala, V., Crosdale, P.J., Demchuk, T.D., Eble, C.F., Flores, D., Furmann, A., Gentzis, T., Gonçalves, P.A., Guvad, C., Hámor-Vidó, M., Jelonek, I., Zapata, J.E.J., et al., 2020. Testing reproducibility of vitrinite and solid bitumen reflectance measurements in North American unconventional source-rock reservoir petroleum systems. Mar. Pet. Geol. 114, 1–17, doi: 10.1016/j.marpetgeo.2019.104172.

Han, D.X., 1989. The features of Devonian coal-bearing deposits in South China, The People's Republic of China. Int. J. Coal Geol. 12, 209–223.

Harland, W.B., Pickton, C.A.G., Wright, N.J.R., Croxton, C.A., Smith, D.G., Cutbill, J.L., Henderson, W.G., 1976. Some coal-bearing strata in Svalbard. Norsk-Polarinstitutt, Skr. 164.

Huang, W.-Y., Meinschein, W.G., 1979. Sterols as ecological indicators. Geochim. Cosmochim. Acta 43, 739–745.

Hunt, J.M., 1995. Petroleum Geochemistry and Geology. W.H. Freeman, New York.

ISO 7404-5:2009, 2009. Methods for the Petrographic Analysis of Coals – Part 5: Methods of Determining Microscopically the Reflectance of Vitrinite. International Organization for Standardization, Geneva, Switzerland.

Jiang, C., Alexander, R., Kagi, R.I., Murray, A.P., 1998. Polycyclic aromatic hydrocarbons in ancient sediments and their relationships to palaeoclimate. Org. Geochem. 29 (5–7), 1721–1735, doi: 10.1016/S0146-6380(98)00083-7.

Kashirtsev, V.A., Kontorovich, A.E., Filp, R.P., Chalaya, O.N., Zueva, I.N., Memetova, N.P., 1999. Biomarkers in the oils of the eastern regions of the Siberian Platform as indicators of depositional environments of oil-generating rocks. Russ. Geol. Geophys. 40 (11), 1672–1683.

Kashirtsev, V.A., Moskvin, V.I., Fomin, A.N., Chalaya, O.N., 2010. Terpanes and steranes in coals of different genetic types in Si-

beria. Russ. Geol. Geophys. 51 (4), 404–411, doi: 10.1016/j.rgg.2010.03.007.

Kashirtsev, V.A., Kontorovich, A.E., Kim, N.S., Chalaya, O.N., Zueva, I.N., 2015. Steranes in Neoproterozoic oils from the Nepa-Botuoba anteclise in the Siberian platform and the South Oman salt basin in the Arabian platform. Pet. Chem. 55, 186–194, doi: 10.1134/S0965544115020139.

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 the oils of the Siberian Platform. Russ. Geol. Geophys. 59 (10), 1380–1388, doi: 10.1016/j.rgg.2018.09.013.

Kennedy, K.L., Gibling, M.R., Eble, C.F., Gastaldo, R.A., Gensel, P.G., Werner-Zwanziger, U., Wilson, R.A., 2013. Lower Devonian coaly shales of northern New Brunswick, Canada: Plant accumulations in the early stages of terrestrial colonization. J. Sediment. Res. 83, 1202–1215, doi: 10.2110/jsr.2013.86.

Killops, S.D., 1991. Novel aromatic hydrocarbons of probable bacterial origin in a Jurassic lacustrine sequence. Org. Geochem. 17, 25–36, 10.1016/0146-6380(91)90037-K.

Kontorovich, A.E., Parparova, G.M., Trushkov, P.A., 1967. Metamorphism of organic matter and some issues of oil and gas potential (on the example of the Mesozoic deposits of the West Siberian plain). Geologiya i Geofizika, No. 2, 16–29.

Kontorovich, A.E., Babina, N.M., Danilova, V.P., Zueva, T.V., Mel'nikova, V.M., 1973. Polynuclear aromatic hydrocarbons of diffuse organic matter. Geologiya i Geofizika, No. 14, 84–91.

Kontorovich, A.E., Bogorodskaya, L.I., Golyshev, S.I., 1985. Principles of fractionation of carbon isotope in sedikachites. Sov. Geol. Geophys. 26 (9), 31–39.

Kontorovich, A.E., Verkhovskaya, N.A., Timoshina, I.D., Fomichev, A.S., 1986. Carbon isotopic composition of dispersed organic matter and bitumens and some disputed problems of the theory of oil formation. Sov. Geol. Geophys. 27 (5), 1–10.

Kontorovich, A.E., Bakhturov, S.F., Basharin, A.K., Belyaev, S.Yu., Burshtein, L.M., Kontorovich, A.A., Krinin, V.A., Larichev, A.I., Li Goudu, Melenevskii, V.N., Timoshina, I.D., Fradkin, G.S., Khomenko, A.V., 1999. Heterochronous centers of naphthide formation and accumulation in the North Asian craton. Russ. Geol. Geophys. 40 (11), 1647–1665.

Koren', T.N., 2006. Zonal Stratigraphy of the Phanerozoic of Russia [in Russian]. Izd. VSEGEI, St. Petersburg.

Kossovoi, L.S., 1963. Devonian System: North Timan, in: Geology of the Soviet Union, Vol. 2, Part 1 [in Russian]. Moscow, pp. 290–300.

Kossovoi, L.S., 1966. Geologic Structure of the North Timan (Stratigraphy, Magmatism, Tectonics, and Lithologic Characteristics of Paleozoic Sedimentary Rocks), Vol. 1: Stratigraphy [in Russian]. Leningrad.

Kruge, M.A., 2000. Determination of thermal maturity and organic matter type by principal components analysis of the distributions of polycyclic aromatic compounds. Int. J. Coal Geol. 43, 27–51, 10.1016/S0166-5162(99)00053-1.

Lee, M.L., Vassilaros, D.L., White, C.M., Novotny, M., 1979. Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. Anal. Chem. 51, 768–774, doi: 10.1021/ac50042a043.

Lyubarova, A., Snigirevsky, S.M., 2020. New investigations of Upper Devonian wood from the north of the European part of Russia. Acta Palaeobot. 60, 143–155, doi: 10.35535/acpa-2020-0006.

Meien, S.V., 1989. Introduction into the Theory of Stratigraphy [in Russian]. Nauka, Moscow.

Noble, R., Knox, J., Alexander, R., Kagi, R., 1985a. Identification of tetracyclic diterpene hydrocarbons in Australian crude oils and sediments. J. Chem. Soc. D, 32–33, doi: 10.1039/C39850000032.

Noble, R., Alexander, R., Kagi, R., Knox, J., 1985b. Tetracyclic diterpenoid hydrocarbons in some Australian coals, sediments and

crude oils. Geochim. Cosmochim. Acta 49, 2141–2147, doi: 10.1016/0016-7037(85)90072-9.

Parmuzin, N.M., Mazurkevich, K.N., Semenova, L.R., Kossovaya, O.L., et al., 2015. State Geological Map of the Russian Federation, Scale 1 : 1,000,000 (3rd Generation). Mezenskaya Ser. Sheet Q-39 – Naryan-Mar [in Russian]. Kartograficheskaya Fabrika VSEGEI, St. Petersburg.

Peakman, T.M., Maxwell, J.R., 1988. Acid-catalysed rearrangements of steroid alkenes. Part 1. Rearrangement of 5α-cholest-7-ene. J. Chem. Soc., Perkin Trans. 1, 5, 1065–1070, doi: 10.1039/P19880001065.

Peakman, T.M., Ellis, K., Maxwell, J.R., 1988. Acid-catalysed rearrangements of steroid alkenes. Part 2. A re-investigation of the backbone rearrangement of cholest-5-ene. J. Chem. Soc., Perkin Trans. 1, 5, 1071–1075, doi: 10.1039/P19880001071.

Pervukhina, A.E., 1940. Devonian coals of the North Timan. Sov. Geol., No. 8, 73–76.

Peters, K.E., Walters, C.W., Moldowan, J.M., 2005. The Biomarker Guide. Cambridge University Press, Cambridge, doi: 10.1017/CBO9780511524868.

Petersen, H.I., Schovsbo, N.H., Nielsen, A.T., 2013. Reflectance measurements of zooclasts and solid bitumen in Lower Paleozoic shales, southern Scandinavia: Correlation to vitrinite reflectance. Int. J. Coal Geol. 114, 1–18, doi: 10.1016/j.coal.2013.03.013.

Petrov, A.A. (Ed.), 1987. Petroleum Hydrocarbons. Springer, Berlin, Heidelberg.

Petrov, O.V., 2006. Petrological Atlas of Fossil Organic Matter in Russia [in Russian]. VSEGEI, St. Petersburg.

Pickel, W., Kus, J., Flores, D., Kalaitzidis, S., Christanis, K., Cardott, B.J., Misz-Kennan, M., Rodrigues, S., Hentschel, A., Hamor-Vido, M., Crosdale, P., Wagner, N., ICCP, 2017. Classification of liptinite – ICCP System 1994. Int. J. Coal Geol. 169, 40–61, doi: 10.1016/j.coal.2016.11.004.

Prestianni, C., Decombeix, A.-L., Thorez, J., Fokan, D., Gerrienne, P., 2010. Famennian charcoal of Belgium. Palaeogeogr. Palaeoclimatol. Palaeoecol. 291, 60–71, doi: 10.1016/j.palaeo.2009.10.008.

Püttmann, W., Villar, H., 1987. Occurrence and geochemical significance of 1,2,5,6-tetramethylnaphthalene. Geochim. Cosmochim. Acta 51, 3023–3029, doi: 10.1016/0016-7037(87)90375-9.

Radke, M., Schaefer, R.G., Leythaeuser, D., 1980. Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. Geochim. Cosmochim. Acta 44, 1787–1800, doi: 10.1016/0016-7037(80)90228-8.

Radke, M., Welte, D.H., Willsch, H., 1982. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. Geochim. Cosmochim. Acta 46, 1–11, doi: 10.1016/0016-7037(82)90285-X.

Radke, M., Vriend, S.P., Ramanampisoa, L.R., 2000. Alkyldibenzofurans in terrestrial rocks: Influence of organic facies and maturation. Geochim. Cosmochim. Acta 64, 275–286, doi: 10.1016/S0016-7037(99)00287-2.

Romero-Sarmiento, M.-F., Riboulleau, A., Vecoli, M., Versteegh, G.J.M., 2010. Occurrence of retene in upper Silurian–lower Devonian sediments from North Africa: Origin and implications. Org. Geochem. 41, 302–306, doi: 10.1016/j.orggeochem.2009.10.003.

Romero-Sarmiento, M.-F., Riboulleau, A., Vecoli, M., Laggoun-Défarge, F., Versteegh, G.J.M., 2011. Aliphatic and aromatic biomarkers from Carboniferous coal deposits at Dunbar (East Lothian, Scotland): Palaeobotanical and palaeoenvironmental significance. Palaeogeogr. Palaeoclimatol. Palaeoecol. 309, 309–326, doi: 10.1016/j.palaeo.2011.06.015.

Schulze, T., Michaelis, W., 1990. Structure and origin of terpenoid hydrocarbons in some German coals. Org. Geochem. 16, 1051–1058, doi: 10.1016/0146-6380(90)90142-M.

Sheng, G.Y., Simoneit, B.R.T., Leif, R.N., Chen, X.J., Fu, J.M., 1992. Tetracyclic terpanes enriched in Devonian cuticle humic coals. Fuel 71, 523–532, doi: 10.1016/0016-2361(92)90149-I.

Shlyakhova, Kh.T., Shlyakhov, V.I., 1974. Geological Map of the Soviet Union, Scale 1 : 200,000 [in Russian]. Timanskaya Ser., Sheet Q-39-VIII. Moscow.

Shumilov, I.Kh., 2015. Unusual Devonian coal: A new type of jet. Russ. Geol. Geophys. 56 (10), 1461–1474, doi: 10.1016/j.rgg.2015.09.008.

Simoneit, B.R.T., 1985. Cyclic terpenoids in the geosphere, in: Johns, R.B. (Ed.), Methods in Geochemistry and Geophysics. Elsevier, Vol. 25, pp. 43–99.

Snigirevskaya, N.S., 2010. Status of lycopsids and some problems of Devonian coal formation. Botanicheskii Zhurnal 95 (6), 758–776.

Snigirevsky, S.M., Kocheva, L.S., Beznosov, P.A., Pavlova, M.A., 2017. The North Timan as one of the oldest coal-bearing regions of the Earth, in: Natural Geologic Heritage of the European North of Russia. Proc. All-Russ. Sci. Conf. [in Russian]. Syktyvkar, pp. 77–80.

Snyatkov, A., 1915. Tomite as a new kind of fossil fuel. Geologicheskii Vestnik 1 (4), 248–249.

Song, D., Simoneit, B.R.T., He, D., 2017. Abundant tetracyclic terpenoids in a Middle Devonian foliated cuticular liptobiolite coal from northwestern China. Org. Geochem. 107, 9–20, doi: 10.1016/j.orggeochem.2017.02.010.

Teichmüller, M., Teichmüller, R., 1968. Cainozoic and Mesozoic coal deposits of Germany, in: Murchison, D.G., Westoll, T.S. (Eds.), Coal and Coal-Bearing Strata. Oliver and Boyd, Edinburgh, pp. 347–377.

Tel'nova, O.P., Shumilov, I.Kh., 2021. A new straton in the Late Devonian sedimentation in the Tsil'ma river basin of the Middle Timan. Lithosphere (Russia) 21 (5), 625–642.

Tissot, B.T., Welte, D.H., 1984. Petroleum Formation and Occurrences. Springer, Berlin.

Tsyganko, V.S., 2006. Devonian of the Timan ridge: Main structural features and resource potential, in: Problems of Geology and Mineralogy [in Russian]. Syktyvkar, pp. 363–384.

van Aarssen, B.G.K., Alexander, R., Kagi, R.I., 2000. Higher plant biomarkers reflect palaeovegetation changes during Jurassic times. Geochim. Cosmochim. Acta 64, 1417–1424, doi: 10.1016/S0016-7037(99)00432-9.

Volkova, I.B., 1994. Nature and composition of the Devonian coals of Russia. Energy Fuels 8, 1489–1493, doi: 10.1021/ef00048a039.

Wen, Z., Ruiyong, W., Radke, M., Qingyu, W., Guoying, S., Zhili, L., 2000. Retene in pyrolysates of algal and bacterial organic matter. Org. Geochem. 31, 757–762, doi: 10.1016/S0146-6380(00)00064-4.

Zalesskii, M.D., 1915a. Natural History of One Coal (Trans. Geol. Committee, a New Ser., Issue139) [in Russian]. St. Petersburg.

Zalesskii, M.D., 1915b. New type of coal. Geologicheskii Vestnik 1 (4), 234–238.

Zhang, Y., Sun, Y., Chen, J., 2020. Stable carbon isotope evidence for the origin of C_{28} steranes in lacustrine source rocks from the Qikou Sag, Bohai Bay Basin, Eastern China. Org. Geochem. 145, 104028, doi: 10.1016/j.orggeochem.2020.104028.

Zheng, Y., Zhou, W., Meyers, P., Xie, S., 2007. Lipid biomarkers in the Zoigê-Hongyuan peat deposit: Indicators of Holocene climate changes in West China. Org. Geochem. 38, 1927–1940, doi: 10.1016/j.orggeochem.2007.06.012.