

Organic petrography and biomarker proxies of subbituminous coal from the Dubrava field (Aleksinac Basin, Serbia)

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Органична петрография и биомаркерен анализ на суббитуминозни въглища от Дубравско поле (Алексиначки басейн, Сърбия)

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Резюме. Извършено е цялостно петрографско и биомаркерно изследване за оценка на източниците, палеосредата и зрелостта на органичното вещество (ОВ) в проби от въглища, взети от сондаж BD-4 в Блок Дубрава (Алексиначки басейн, Сърбия). В изследваните проби доминират мацералите от групата на витринита, с променливо съдържание на липтинит и много ниско количество на инертинита. Измерената отражателна способност на витринита, данните от Rock Eval пиролиза и биомаркерния анализ потвърждават суббитуминозния ранг на въглищата. ОВ се намира в късно диагенетичен – ранно катагенетичен стадий на развитие. Съдържанието на общ органичен въглерод и минерално вещество варира в широк диапазон, което показва чести промени в условията на седиментация. Съдържанието на сяра е умерено до много високо. Основните източници на ОВ във въглищата от Алексиначкия басейн са покритосемени растения, папрати и водни макрофити, с подчинен принос на иглолистна растителност. Диагенетните изменения на ОВ се контролират от метанотрофни и хемоавтотрофни бактерии. Отлагането на ОВ е осъществено в ниско разположена блатна среда, показваща намаляваща концентрация на сулфатни йони нагоре в разреза на сондаж BD-4. Отлагането на въглища е прекратено с повишаване на нивото на водата, което води до заливане на благомето и преминаване към езерна среда.

Ключови думи: въглищно органично вещество, мацерали, биомаркери, стабилни изотопи на въглерода, Алексиначки басейн.

Abstract. A comprehensive petrographic and biomarker study has been performed to evaluate sources, paleoenvironment and maturity of organic matter (OM) in coal samples taken from the borehole BD-4 in the Dubrava block (Aleksinac Basin, Serbia). Studied samples are dominated by vitrinite group macerals, with variable content of liptinite and very low amount of inertinite. The measured random vitrinite reflectance, Rock Eval data and biomarker assemblages confirmed subbituminous rank of coal. The OM is at the late diagenetic and early catagenetic stage. Contents of total organic carbon and mineral matter vary in wide range, indicating frequent changes of depositional settings. Content of sulphur is moderate to very high. The main sources of OM in Aleksinac coal were angiosperms, ferns and aquatic macrophytes, with subordinate contribution of conifer paleovegetation. Diagenetic alteration of OM was governed by methanotrophic bacteria and chemoautotrophic bacteria. Deposition of OM occurred in a low-lying mire environment, showing decreasing concentration of sulphate ions upward the borehole BD-4. The coal deposition was terminated by rise of water level, which led to drowning of the mire and transition to lacustrine environment.

Keywords: coal organic matter, macerals, biomarkers, stable carbon isotopes, Aleksinac Basin.

Introduction

For investigation of the origin, depositional environment and maturity of coal organic matter (OM), organic petrography, biomarker analysis in extractable OM and stable carbon isotope measurements on bulk OM and individual biomarkers ($\delta^{13}\text{C}$) are the most common used methods.

Over last 60 years, the Aleksinac Basin has attracted great attention, due to the resources and reserves of oil shale. Total resources of oil shale in the Aleksinac Basin were evaluated at 2,100 Mt, while calculated reserves in the Dubrava block (2.7 km² area in north part of the Aleksinac Basin) amount to 353 Mt (Petrović 2012). While the oil shale was comprehensively studied (e.g. Vitorović et al., 1985; Glumičić et al., 1996; Bechtel et al., 2018; Gajica et al., 2022), a detailed investigation of OM in Aleksinac coal has not yet been performed. Therefore, the current study is aimed to evaluate the sources, depositional environment and maturity of OM in Aleksinac coal. For that purpose organic petrography, elemental analysis, Rock-Eval pyrolysis, biomarker analysis and stable carbon isotopes of bulk OM and individual biomarkers were employed.

Geological setting

The basement of the Aleksinac Basin is represented by the Proterozoic-Palaeozoic crystalline shists. The Lower Miocene fresh-water Aleksinac and Upper Miocene Red clastic series lie transgressively above the basement. The Aleksinac series consists from base to top of alluvial, marginal-lacustrine, and intrabasinal series and is up to 800 m thick (Bechet et al., 2018, and references therein). The alluvial facies of the Aleksinac series consist of red conglomerates and conglomerate sandstone ("red series"), coarse- to fine-grained sandstone in alternation with silty clay and sandy marlstone. The marginal-lacustrine facies, up to 400 m thick is represented by fine-grained sandstones and siltstones with coalified plant fragments and particles of volcanic rocks, as well as two oil shale layers with the Main coal seam in-between. Bituminous marlstone interbedded with oil shale, as well as thin layers of claystone and sandstone are also present. The lower oil shale layer is up to 60 m thick (Petrović, 2012), alternating with thin coal lenses (0.2 to 0.8 m thick) and clayey mica sandstone. The Main coal seam (2 to 6 m thick) is of subbituminous rank with high

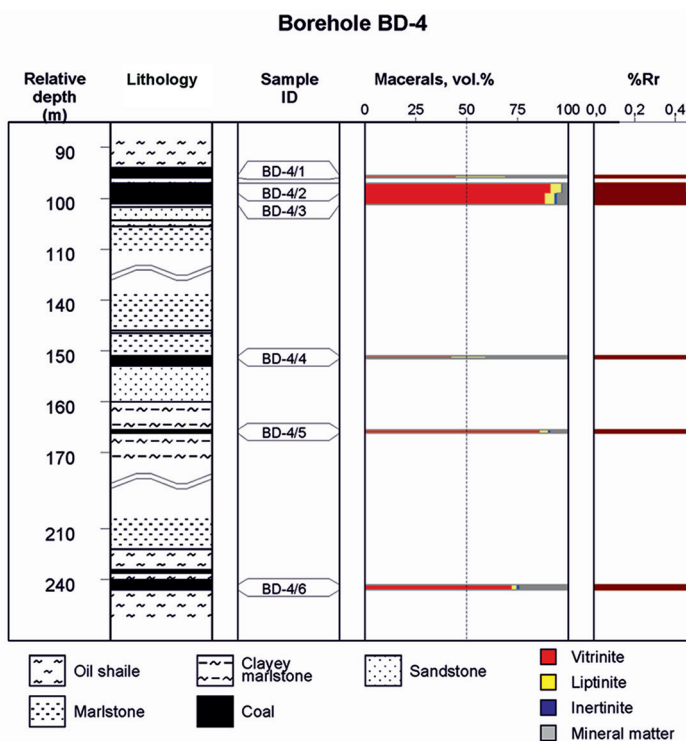


Fig. 1. Lithological profile of the borehole BD-4 with maceral composition and vitrinite reflectance

Фиг. 1. Литолошки профил на сондаж BD-4 с мацерален състав и отражателна способност на витринита

ash yield and high total sulfur content. Coal from the Main seam is of black to dark brown color, with dark scratch, semi-bright to bright and banded. The Upper oil shale layer of the Aleksinac series (up to 80 m thick), as well as the lower layer, belong to the lacustrine lamosite type and contain kerogen type I (dominated by aquatic organisms and bacteria) (Fig. 1).

The Upper Miocene Red clastic series (up to 250 m thick) consists of conglomerates, conglomeratic sandstones and clayey sandstone, which transgressively cover the Aleksinac series (Fig. 1).

The Aleksinac Basin has a complex tectonical structure and is subdivided into three main blocks (Dubrava, Morava and Logorište), separated by fault zones (Bechtel et al., 2018). The Main coal

seam and both oil shale layers have general strike direction NNW-SSE, with dip angles from 0° to 90° (Čokorilo et al., 2009).

Samples and Methods

Samples were collected from the borehole BD-4 (Dubrava field, Aleksinac Basin), representing different parts of the Main coal seam (BD-4/1 – BD-4/3) and coal layers within (BD-4/4, BD-4/5) and below the lower oil shale sequence (BD-4/6) (Table 1).

Micropetrographic analysis was carried out on polished blocks prepared according to ISO 7404-2 (2009) standard, on the motorized Zeiss Axio Imager II microscope, connected to the Diskus-Fossil

Table 1

Maceral composition and vitrinite reflectance of coal from the Dubrava field (Aleksinac Basin; after Sekulić, 2017)

Таблица 1

Мацерален състав и коефициент на отражение на витринита на въглища от находище Дубрава (басейн Алексинач; по Sekulić, 2017)

Sample	BD-4/1 (95.5–96.0)	BD-4/2 (97.0–99.0)	BD-4/3 (99.0–101.2)	BD-4/4 (151.0–153.0)	BD-4/5 (165.5–166.5)	BD-4/6 (240.0–242.0)
Relative depth (m)						
Maceral composition						
Telinite	0.3	17.9	6.8	0.2	1.8	0.6
Collotelinite	2.5	19.5	33.3	12.9	15.1	37.5
Vitrodetrinite	37.6			20.6		
Collodetrinite	1.9	37.3	27.3	8.8	47.2	32.0
Gelinite	0.7	0.8	0.8	0.1	2.4	1.5
Corpogelinite	1.8	15.8	20.3	0.1	19.7	0.8
Total Vitrinite	44.8	91.3	88.5	42.7	86.2	72.4
Sporinite	1.4	0.6	0.2	0.2	0.2	0.2
Cutinite	1.8	0.6	0.4	0.2		0.5
Resinite		1.0	1.1		0.5	
Suberinite	1.8	1.4	1.9		0.7	0.2
Alginite	4.3					
Liptodetrinite	3.7	1.7	1.3	16.2	2.4	1.4
Bituminite	11.3					
Total Liptinite	24.3	5.3	4.9	16.6	3.8	2.3
Fusinite						0.3
Semifusinite			0.2	0.1	0.4	0.5
Macrinite					0.2	
Funginite		0.6	0.8		0.5	0.6
Inertodetrinite	0.3		0.2	0.1	0.2	
Total Inertinite	0.3	0.6	1.2	0.2	1.3	1.4
Clay	0.3	1.0	0.4	2.6	0.5	0.3
Pyrite	0.4	1.0	4.8	11.5	5.3	18.4
Carbonates	6.8	0.6		1.8	2.9	0.6
Mineral-bituminous groundmass	22.8			19.6		4.1
Minerals other	0.3	0.2	0.2	5.0		0.5
Total mineral matter	30.6	2.8	5.4	40.5	8.7	23.9
Vitrinite reflectance, %R _r	0.44±0.03	0.46±0.03	0.45±0.03	0.46±0.02	0.46±0.02	0.46±0.02

system (ISO 7404-3, 2009) in normal and ultraviolet light. The determination of macerals was performed using the nomenclature for bituminous coals, i.e. for vitrinite (ICCP, 1998), liptinite (Pickel et al., 2017) and inertinite (ICCP, 2001). The vitrinite reflectance measurements were carried out on the Zeiss Axio Imager II microscope coupled to the Diskus-Fossil system for reflectance measurement, following the ISO 7404-5 (2009) standard, with optical standard 0.899% in oil. According to the ISO 11760 (2005) standard, for brown coals with 0.41% Rr to 0.49% Rr the classification scheme of lithotypes, microlithotypes and macerals for bituminous coals must be applied.

Elemental analysis (Vario EL III, CHNS/O Elemental Analyzer, Elementar Analysensysteme GmbH) was performed to determine the contents of total organic carbon (TOC), total nitrogen, total hydrogen and total sulphur. Rock-Eval pyrolysis was performed on a Rock-Eval-6 apparatus following standard procedures described in Espitalié et al. (1985) and Lafargue et al. (1998).

Extractable organic matter (EOM) was isolated from pulverized coal samples using dichloromethane (DCM) in a Dionex ASR 200 accelerated solvent extractor. Asphaltenes were precipitated from EOM using *n*-hexane-DCM mixture (80:1; V:V) and separated by centrifugation. The *n*-hexane-soluble organic compounds (maltenes) were separated into aliphatic, aromatic and polar fractions using medium pressure liquid chromatography (MPLC) with a Köhnen-Willsch instrument (Radke et al., 1980). Aliphatic and aromatic fractions were analyzed using a gas chromatography-mass spectrometry (GC-MS). Details of GC-MS analysis and data processing are given in a previous publication (Životić et al., 2014). Bulk carbon isotope analysis ($\delta^{13}\text{C}$) of TOC was performed following the procedure explained by Bechtel et al. (2018), whereas carbon isotope determination of individual biomarkers in aliphatic and aromatic fractions was carried out using the procedure outlined by Mitrović et al. (2017) and Đoković et al. (2018).

Results and discussion

Maceral composition

Micropetrographic studies (Fig. 2; Table 1) have shown that samples BD-4/2, BD-4/3 and BD-4/5

are characterized by a high content of vitrinite (>85 vol.%), lower content of liptinite (<6 vol.%), a low content of inertinite maceral group (<1.5 vol.%), and low mineral matter (MM) content (<9 vol.%). Lower vitrinite content (<45 vol.%), associated with higher liptinite content (>15 vol.%), low inertinite content (<0.5 vol. %) and high MM content (>30 vol.%) have been detected in two samples (BD-4/1, BD-4/4). The deepest coal sample (BD-4/6) has a high vitrinite content (72.4 vol.%), relatively low liptinite and inertinite content, and extremely high pyrite content (18.4 vol.%; Table 1).

The maceral analysis of studied coal samples implies changes of the water level in mire during the peat stage. The deepest coal layer (at 241.00 m; sample BD-4/6) was probably formed in the reed marsh zone with the high water level in the strong reducing, probably alkaline environment. The extremely high content of pyrite confirms this statement. The dominance of collodetrinite and liptodetrinite in the sample BD-4/5 indicates the forest swamp zone, under slight alkaline environment or transitional zone between reed marsh and wet forest swamp zone. Higher liptinite content, as well as significant amounts of pyrite and mineral-bituminous groundmass in the sample BD-4/4 indicate deposition of OM in strong reducing and slightly alkaline environment. The high content of telovitrinite with presence of resinite and suberinite in lower and central part of the Main coal seam (samples BD-4/2 and BD-4/3) indicates deposition of terrestrial OM in forest swamp zone. High contents of vitrodetrinite, bituminite, alginite with mineral-bituminous groundmass in the upper part of the Main coal seam (sample BD-4/1) indicate significant changes of water level in the mire. Deposition and peatification of OM occurred in a highly reducing environment with pronounced bacterial activity.

The average vitrinite reflectance ranges from 0.44 ± 0.03 to 0.46 ± 0.02 (Table 1), indicating subbituminous rank of coal. The measured vitrinite reflectance indicates late diagenetic- and early catagenetic stage of OM of Aleksinac coal. The latter is confirmed by the regular presence of higher individual vitrinite reflectance values (>0.50% Rr), observed in all samples.

Bulk organic geochemical parameters and Rock-Eval data

TOC varies in wide range from 24.5% to 64.6% (Table 2) and shows significant negative correlation

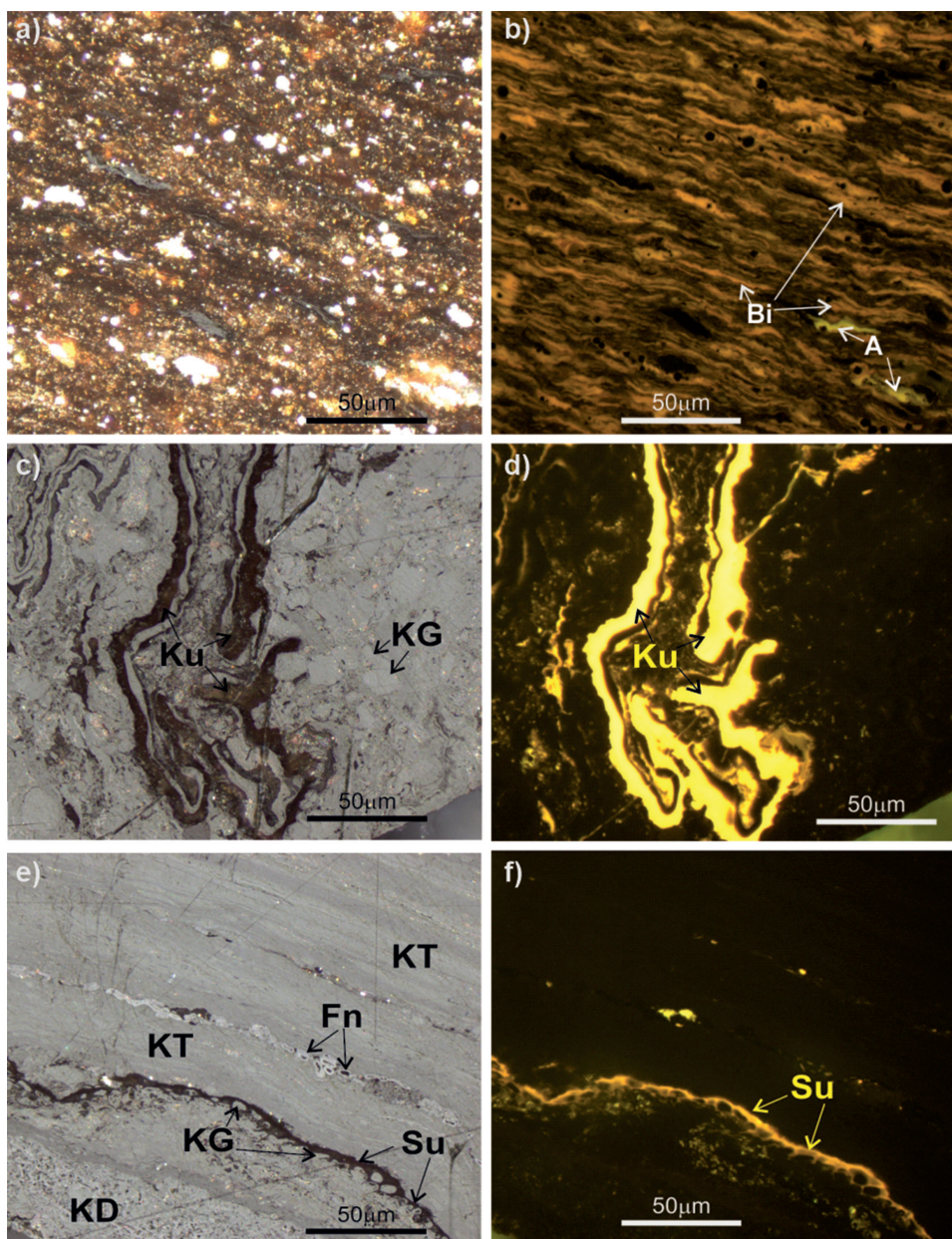


Fig. 2. Photomicrographs of characteristic macerals from the Dubrava field (Aleksinac Basin)

KT – collotelinite, KD – collodetrinite, KG – corpogelinite, Ku – cutinite, A – alginite, Bi – bituminite, Su – suberinite, Fn – funginite. Photomicrographs were taken under reflected white light (a, c, e) and in fluorescence mode (b, d, f).

Фиг. 2. Микрофотографии на характерни мацерали от Блок Дубрава (Алексиначки басейн)

КТ – колотелинит, КД – колодетринит, КГ – корпогелинит, Ку – кутиноит, А – алгинит, Би – битуминит, Су – суберинит, Фн – фунгинит. Микрофотографиите са направени в отразена бяла светлина (а, с, е) и в режим на флуоресценция (b, d, f).

(correlation coefficient, $r = -0.94$) with MM content (Table 1). Total sulphur content (S) is moderate to high, reaching 13.10% in the sample BD-4/6 (Table 2). The Hydrogen Index (HI), derived from the Rock Eval pyrolysis, indicates a high hydrocarbon potential of the sample BD-4/1 (HI = 498 mg HC/g TOC) that may be caused by the presence of

interbedded oil shale intervals. HI notably decreases downward through the Main seam and particularly in the samples below Main seam. Rock-Eval maximal temperature (T_{max}) and production index (PI) reveal immaturity of OM (Table 2). The $\delta^{13}C$ values of TOC are very similar in all samples (-25.5 to -26.1%), being somewhat lower in the sample

Table 2
Bulk organic geochemical parameters and results of Rock-Eval pyrolysis

Таблица 2
Общ геохимичен състав и резултати от Rock-Eval пиролиза

Sample	BD-4/1	BD-4/2	BD-4/3	BD-4/4	BD-4/5	BD-4/6
TOC (wt. %)	25.77	64.64	54.15	24.49	59.05	47.67
H (wt. %)	2.38	4.58	3.78	2.36	3.94	3.41
N (wt. %)	1.01	3.00	2.40	1.19	2.81	1.50
S (wt. %)	1.45	3.05	4.30	6.62	7.53	13.10
$\delta^{13}\text{C}$ (TOC)	-25.6	-26.1	-25.7	-26.6	-25.8	-25.5
EOM (mg/g TOC)	16.3	7.9	8.6	7.6	5.7	9.6
Aliphatic fraction (wt. %)	5.1	4.2	7.4	17.3	7.9	10.6
Aromatic fraction (wt. %)	6.7	7.4	12.8	9.6	13.8	9.9
Polar (NSO) fraction (wt. %)	44.7	43.3	53.4	46.6	59.5	52.3
Asphaltenes (wt. %)	43.4	45.1	26.4	26.5	18.9	27.2
S1 (mg HC/g sample)	1.4	1.3	1.1	0.5	0.9	0.7
S2 (mg HC/g sample)	128.3	103.7	73.4	10.4	34.0	26.7
T_{max} (°C)	431	412	412	423	416	411
HI (mg HC/g TOC)	498	160	136	43	58	56
PI	0.01	0.01	0.01	0.04	0.03	0.02

TOC – Total organic carbon, EOM – Extractable organic matter, S1 – Free hydrocarbons (mg HC/g sample), S2 – Pyrolysate hydrocarbons (mg HC/g sample), HC – Hydrocarbons, T_{max} – Temperature corresponding to S2 peak maximum (°C), HI – Hydrogen Index = (S2 x 100)/TOC (mg HC/g TOC), PI – Production Index = S1/(S1+S2).

TOC – Общ органичен въглерод, EOM – Екстрахируемо органично вещество, S1 – Свободни въглеводороди (mg HC/g проба), S2 – Пиролизат на въглеводороди (mg HC/g проба), HC – Въглеводороди, T_{max} – Температура, съответстваща на S2 пиков максимум (°C), HI – Водороден индекс = (S2 x 100)/TOC (mg HC/g TOC), PI – Индекс на продуктивност = S1/(S1+S2).

BD-4/4 (-26.6‰), which may be indicative for pronounced early diagenetic microbial activity. Content of EOM is similar in studied samples (5.7–9.6 mg/g TOC), with exception of the sample BD-4/1, which has two times higher amount of EOM. EOM is dominated by polar compounds; however elevated amount of aliphatic fraction in the sample BD-4/4 is obvious (Table 2).

Biomarker composition

Aliphatic fractions of studied coal samples consist of *n*-alkanes, hopanoids, steroids, diterpenoids, non-hopanoid triterpenoids, fernenes, isoprenoids and sesquiterpenoids (detected in very low amounts). *n*-Alkanes (the most abundant in samples BD-4/3 – BD-4/6) and hopanoids (the most abundant in samples BD-4/1 and BD-4/2) prevail in aliphatic fraction of all samples (Fig. 3; Table 3). Constituents of aromatic fractions are non-hopanoid triterpenoids which predominate in all samples, diterpenoids, lanosta(eupha)hexaene derivatives, aromatized hopanoids, fernenes and sesquiterpenoids (Fig. 4;

Table 3). Polycyclic aromatic hydrocarbons (phenanthrene, fluoranthene, pyrene and its methylated counterparts) are detected in minor concentrations (Fig. 4), consistent with low amount of inertinite group macerals (Table 1). Biomarker distributions (Figs. 3, 4) and values of corresponding maturity ratios (Table 3) reveal low maturity of OM, corresponding to the late diagenetic stage.

Sources of organic matter

Generally low content of diterpenoids (with exception of the sample BD-4/1) is indicative to low contribution of conifer vegetation. Diterpenoid type constituents of the aliphatic fraction are norpimarane, pimarane, 16 α (H)- and 16 β (H)-phylocladane, which prevailed in all samples. The aromatic diterpenoids consist of norabieta-6,8,11,13-tetraene, norabieta-8,11,13-triene, dehydroabietane, simonellite, retene, sempervirane, totarane, hibaene and tetrahydroretene, with retene predominating in all of the samples (Fig. 4). The detected diterpenoid assemblages are indicative for contribution of Pinacea

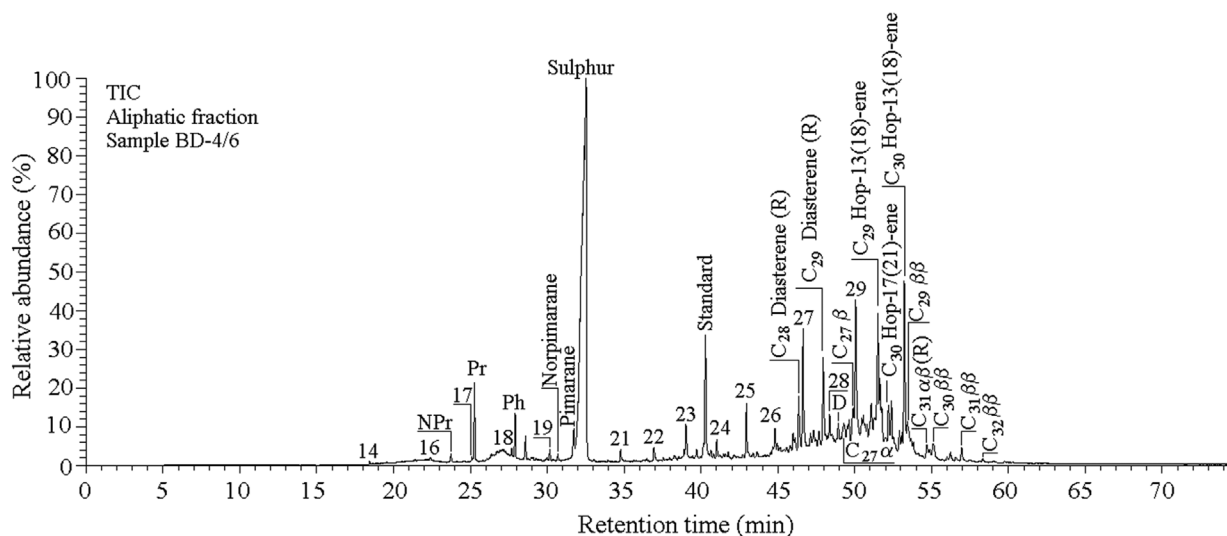


Fig. 3. Total ion chromatogram (TIC) of aliphatic fraction, typical for investigated samples (sample BD-4/6) *n*-Alkanes are labelled according to their carbon number; NPr – Norpristane; Pr – Pristane; Ph – Phytane; $\beta\beta$, $\beta\alpha$ and $\alpha\beta$ designate configurations at C-17 and C-21 in hopanes; D – Dammarane; Standard – Deuterated *n*-tetracosane.

Фиг. 3. Обща йонна хроматограма (TIC) на алифатна фракция, характерна за изследваните проби (проба BD-4/6) *n*-алканите са описани според техния въглероден номер; NPr – Норпристан; Пр – Пристан; Ph – Фитан; $\beta\beta$, $\beta\alpha$ и $\alpha\beta$ означават конфигурации при C-17 и C-21 в хопани; D – Дамаран; Стандарт – деутериран *n*-тетракозан.

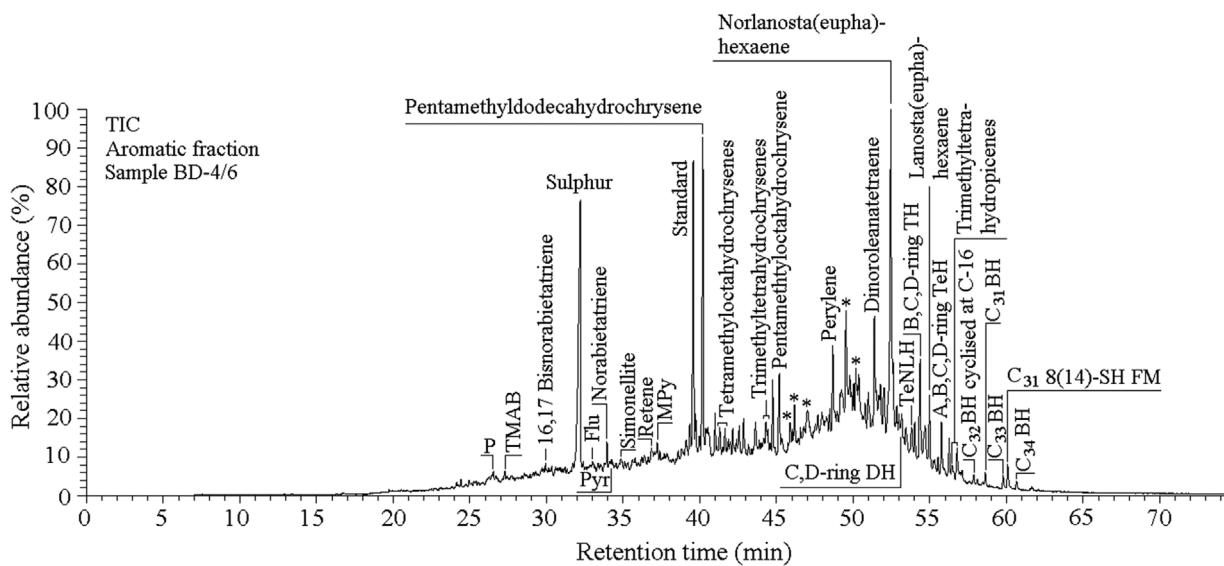


Fig. 4. Total ion chromatogram (TIC) of aromatic fraction, typical for investigated samples (sample BD-4/6) P – Phenanthrene; TMAB – Trimethylalkylbenzene; Flu – Fluoranthene; Py – Pyrene; Mpy – Methylpyrene; * – Monoaromatic compounds with fernene skeleton; TeNLH – tetranor-lupa-1,3,5(10),6,8,11,13-heptaene; DH – Diaromatic hopane; TH – Triaromatic hopane; TeH – Tetraaromatic hopane; BH – Benzohopane; 8(14)-SH FM – C₃₁ Aromatic 8(14)-secohopanoid with fluorene moiety; Standard – 1,1' Binaphthyl.

Фиг. 4. Обща йонна хроматограма (TIC) на ароматна фракция, характерна за изследваните проби (проба BD-4/6) P – фенантрен; TMAB – триметилалкилбензен; Flu – флуорантен; Py – пирен; Mpy – Метилпирен; * – Моноароматни съединения с ферненов скелет; TeNLH – тетранор-лупа-1,3,5(10),6,8,11,13-хептаен; DH – диароматен хопан; TH – Триароматен хопан; TeH – тетраароматен хопан; BH – Бензохопан; 8(14)-SH FM – C₃₁ Ароматен 8(14)-секохопаноид с флуоренова част; Стандарт – 1,1' бинафтил.

Table 3
Concentrations of identified biomarker classes ($\mu\text{g/g TOC}$) and values of biomarker parameters

Таблица 3
Концентрации на идентифицирани класове биомаркери ($\mu\text{g/g TOC}$) и стойности на параметрите на биомаркера

Sample	Sesquiterpenoids	Diterpenoids	Non-hopanoid triterpenoids	<i>n</i> -Alkanes	Hopanoids	Steroids	Femene derivatives	Lanosta(eupha)-hexaene derivatives	Isoprenoids
BD-4/1	1.17	46.57	88.41	37.42	134.43	21.07	81.47	23.48	2.14
BD-4/2	0.27	4.20	39.12	28.95	36.69	10.68	10.95	11.76	3.59
BD-4/3	1.55	16.28	93.92	58.76	31.72	15.05	58.93	32.08	6.66
BD-4/4	1.54	18.05	39.72	226.09	84.62	17.18	6.61	4.82	38.49
BD-4/5	0.16	4.23	54.06	50.13	21.95	11.70	19.63	14.13	4.59
BD-4/6	0.47	7.12	50.24	54.49	45.74	16.90	12.92	22.57	8.72

Sample	Di/(Di + Tri)	CPI	C ₁₅ -C ₂₀ (%)	C ₂₁ -C ₂₅ (%)	C ₂₆ -C ₃₃ (%)	<i>n</i> -Alkane maximum	P _{aq}	Pr/Ph	C ₃₀ $\beta\beta$ /($\beta\beta$ + $\alpha\beta$) hopanes
BD-4/1	0.34	1.68	20.30	21.14	58.56	C ₂₇	0.37	1.16	0.72
BD-4/2	0.10	3.70	8.96	18.27	72.77	C ₂₉ , C ₃₁	0.23	1.45	0.71
BD-4/3	0.15	2.72	6.83	21.35	71.82	C ₃₁	0.26	2.44	0.67
BD-4/4	0.31	3.34	7.02	30.57	62.41	C ₂₇	0.58	0.96	0.61
BD-4/5	0.07	3.00	5.24	14.17	80.58	C ₃₁	0.15	3.11	0.73
BD-4/6	0.12	4.66	6.46	23.19	70.34	C ₂₇ , C ₂₉	0.30	1.75	0.48

Di/(Di+Tri) = Σ Diterpenoids/(Σ Diterpenoids + Σ Non-hopanoid triterpenoids),

CPI – Carbon Preference Index determined for full range of *n*-alkanes, $\text{CPI} = 1/2 \times [\Sigma\text{odd}(n\text{-C}_{15} - n\text{-C}_{33})/\Sigma\text{even}(n\text{-C}_{14} - n\text{-C}_{32}) + \Sigma\text{odd}(n\text{-C}_{15} - n\text{-C}_{33})/\Sigma\text{even}(n\text{-C}_{16} - n\text{-C}_{34})]$,

C₁₅-C₂₀ (%) = $(\Sigma n\text{-C}_{15} - n\text{-C}_{20}) \times 100/\Sigma$ of total *n*-alkanes (*n*-C₁₅ – *n*-C₃₃),

C₂₁-C₂₅ (%) = $(\Sigma n\text{-C}_{21} - n\text{-C}_{25}) \times 100/\Sigma$ of total *n*-alkanes (*n*-C₁₅ – *n*-C₃₃),

C₂₆-C₃₃ (%) = $(\Sigma n\text{-C}_{26} - n\text{-C}_{33}) \times 100/\Sigma$ of total *n*-alkanes (*n*-C₁₅ – *n*-C₃₃),

P_{aq} = $(n\text{-C}_{23} + n\text{-C}_{25})/(n\text{-C}_{23} + n\text{-C}_{25} + n\text{-C}_{29} + n\text{-C}_{31})$ (Ficken et al., 2000),

Pr/Ph = Pristane/Phytane (Didyk et al., 1978),

$\beta\beta$ and $\alpha\beta$ designate configurations at C₁₇ and C₂₁ in hopanes.

Di/(Di+Tri) = Σ дигтерпеноиди/(Σ дигтерпеноиди + Σ нехопаноидни тритерпеноиди),

CPI – въглероден предпочитателен индекс, определен за пълен набор от *n*-алкани, $\text{CPI} = 1/2 \times [\Sigma\text{нечетни}(n\text{-C}_{15} - n\text{-C}_{33})/\Sigma\text{четни}(n\text{-C}_{14} - n\text{-C}_{32}) + \Sigma\text{нечетни}(n\text{-C}_{15} - n\text{-C}_{33})/\Sigma\text{четни}(n\text{-C}_{16} - n\text{-C}_{34})]$,

C₁₅-C₂₀ (%) = $(\Sigma n\text{-C}_{15} - n\text{-C}_{20}) \times 100/\Sigma$ от общото количество *n*-алкани (*n*-C₁₅ – *n*-C₃₃),

C₂₁-C₂₅ (%) = $(\Sigma n\text{-C}_{21} - n\text{-C}_{25}) \times 100/\Sigma$ от общите *n*-алкани (*n*-C₁₅ – *n*-C₃₃),

C₂₆-C₃₃ (%) = $(\Sigma n\text{-C}_{26} - n\text{-C}_{33}) \times 100/\Sigma$ от общите *n*-алкани (*n*-C₁₅ – *n*-C₃₃),

P_{aq} = $(n\text{-C}_{23} + n\text{-C}_{25})/(n\text{-C}_{23} + n\text{-C}_{25} + n\text{-C}_{29} + n\text{-C}_{31})$ (Ficken et al., 2000),

Pr/Ph = Пристан/Фитан (Didyk et al., 1978),

$\beta\beta$ и $\alpha\beta$ означават конфигурации при C₁₇ и C₂₁ в хопаните.

and Cupressaceae species (Otto and Wilde, 2001). The $\delta^{13}\text{C}$ values of diterpenoids (Di) range from -26.3 to -25.1 ‰ and are very similar or slightly higher than the $\delta^{13}\text{C}$ values of bulk OM (Tables 2, 4). The obtained results are consistent with data reported in literature (Bechtel et al., 2012; Mitrović et al., 2017; Đoković et al., 2018). Furthermore, almost identical $\delta^{13}\text{C}$ values of individual diterpenoids in all samples denote the same conifer precursors of Aleksinac coal (Table 4).

Non-hopanoid triterpenoids (Tri) predominate in hydrocarbon fractions of all samples (Table 3). The

ratio of diterpenoids to the sum of diterpenoids and non-hopanoid triterpenoids, Di/(Di+Tri) is significantly lower than 1 in all samples, indicating prevalence of angiosperms over conifers in the precursor OM (Bechtel et al., 2008; Table 3). This is consistent with results of petrographic analysis which implied deposition of OM in reed marsh zone with a high water level or transitional zone between reed marsh and wet forest swamp. Slightly elevated Di/(Di+Tri) ratios of samples BD-4/1 and BD-4/4 can be partly attributed to enhanced degradation of angiosperm remnants, which are more prone to micro-

Table 4
Carbon isotopic composition ($\delta^{13}C$, ‰) of individual biomarkers

Таблица 4
Изотопен състав на въглерода ($\delta^{13}C$, ‰) на отделни биомаркери

n -Alkanes													
$\delta^{13}C$	C_{19}	C_{20}	C_{21}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	
Sample													
BD-4/1	/	-31.5	/	-27.6	/	-26.9	-32.0	-30.5	/	-31.1	-30.7	-27.6	
BD-4/3	-28.7	-29.8	-27.1	-28.3	/	-28.4	-30.7	-30.9	-31.3	-30.0	/	-28.3	
BD-4/4	-33.8	-32.7	-34.8	-38.6	-34.1	-34.3	-36.2	-37.6	-36.9	-33.4	-32.7	-38.6	
BD-4/6	-30.9	-30.7	-29.4	-27.8	-29.8	-29.3	-31.2	-30.9	-29.9	-30.6	-30.8	-27.8	
$\delta^{13}C$	Fermene derivatives												
Sample	Norpimarane	Pimarane	16 α (H)- phylloladane	Dehydroabietane	Simonellite	Retene	C_{29} Fermene	C_{26} MF	C_{27} MF	C_{28} MF	C_{29} MF		
BD-4/1	-25.6	-26.2	-25.6	-25.5	-25.5	/	-30.7	-30.7	-30.4	-30.4	-30.4		
BD-4/3	-25.1	-26.5	-25.6	-25.8	/	-25.8	-30.4	/	/	/	-30.1		
BD-4/4	-24.7	-25.4	-25.6	/	/	/	/	/	/	/	/		
BD-4/6	/	-26.3	-25.4	/	/	/	-30.2	/	/	/	/		
$\delta^{13}C$	Hopanoids												
Sample	C_{30} Hop- 17(21)-ene	C_{30} $\alpha\beta$ Hopane	Hop-13(18)-ene	C_{29} $\beta\beta$ Hopane	C_{31} $\alpha\beta$ (22R) Hopane	C_{30} $\beta\beta$ Hopane	C_{33} BH	Norlanost	Lanost	Lanost	Methyl- lanost		
BD-4/1	-56.9	-44.5	-49.4	-55.9	-38.7	-43.4	-44.1	-28.6	-28.7	-28.7	-29.0		
BD-4/3	-44.5	-41.5	/	/	/	/	-40.4	-27.9	/	/	-28.3		
BD-4/4	-51.6	-50.6	/	/	-50.2	-49.7	/	/	/	/	/		
BD-4/6	-39.0	-41.0	/	-53.7	-40.9	-39.4	/	-27.7	-28.0	-28.0	/		
$\delta^{13}C$	Isoprenoids												
Sample	Tri 1	Tri 2	Tri 3	Tri 4	C_{29} Diaster	Pristane	Phytane						
BD-4/1	-27.3	-27.7	-27.1	/	-29.0	-29.3	-29.9						
BD-4/3	-27.7	-27.4	/	-27.3	-28.2	-29.7	-30.8						
BD-4/4	/	/	/	/	/	-31.5	/						
BD-4/6	-26.6	-27.1	/	-26.8	-28.0	-29.0	-31.9						

MF – Monoaromatic fermene, BH – Benzohopane, Norlanost – Norlanosta(eupha)hexaene, Lanost – Lanosta(eupha)hexaene, Methyl-lanost – Methylated lanosta(eupha)hexaene, Tri 1 – Pentamethyl-dodecahydrochrysenе, Tri 2 – Trimethyl-1,2,3,4-tetrahydrochrysenе, Tri 3 – 24,25 Dinoroleana/ursa-1,3,5(10),12-tetraene, Tri 4 – tetramethyl-1,2,3,4,4a,1,1,1,1,1,1,1,2a-octahydrochrysenе, C_{29} Diaster – C_{29} Diaster-13(17)-ene (20R), $\beta\beta$ and $\alpha\beta$ designate configurations at C_{17} and C_{21} in hopanes, / – Not measured.

MF – Monoaromatic fermene, BH – Бензохопан, Norlanost – Норланоста(еуфа)хексаен, Lanost – Ланоста(еуфа)хексаен, Methyl-lanost – Метилиран ланоста(еуфа)хексаен, Tri 1 – Пентаметилдодехидрохризен, Tri 2 – Триметил-1,2,3,4-тетрахидрохризен, Tri 3 – 24,25 Диноролена/урса-1,3,5(10),12-тетраен, Tri 4 – тетраметил-1,2,3,4,4а,1,1,1,1,1,1,1,2а-октаидрохризен, C_{29} Diaster – C_{29} Диастер-13(17)-ен (20R), $\beta\beta$ и $\alpha\beta$ обозначават конфигурации при C_{17} и C_{21} в хопаните, / – Не е измерено.

bial alteration than gymnosperm tissues, since these samples have notably higher content of hopanoids (Table 3). Non-hopanoid triterpenoids with oleanane and ursane skeleton predominate over lupane derivatives. Non-hopanoid triterpenoids are non-specific angiosperm markers; however subordinate amounts of lupane derivatives can be indicative for minor impact of Betulaceae family to the precursor OM (Regnery et al., 2013). Pentacyclic non-hopanoid triterpenoids prevail over des-A-degraded counterparts in both aliphatic and aromatic fractions. Urs-12-ene and norurs-12-ene are the most abundant in the aliphatic fraction, whereas dinoroleana-/ursatetraene and pentamethyldodecahydrochrysene dominate in aromatic fraction. Considering the relatively high amount of hopanoids in all samples, which indicates enhanced microbial activity, this result may be indicative for deposition of OM in reducing to transitional environment. The $\delta^{13}\text{C}$ values of angiosperm derived aromatic non-hopanoid triterpenoids are 2‰ depleted in ^{13}C compared to aromatic diterpenoids (Table 4), consistent with report of Bechtel et al. (2008). Almost identical $\delta^{13}\text{C}$ values of individual non-hopanoid triterpenoids in BD-4/1 and BD-4/3 denote the same angiosperm precursors, whereas slightly higher values (up to 1‰) are observed in the sample BD-4/6.

Hopanoids are important constituents of hydrocarbon fractions of studied coal. The hopane composition in aliphatic fractions is characterized by the presence of $\text{C}_{27}\text{-C}_{31}$ $17\alpha(\text{H})21\beta(\text{H})$, $\text{C}_{29}\text{-C}_{30}$ $17\beta(\text{H})21\alpha(\text{H})$ and $\text{C}_{27}\text{-C}_{33}$ $17\beta(\text{H})21\beta(\text{H})$ compounds, as well as unsaturated C_{27} hop-13(18)-ene, C_{29} hop-13(18)-ene, C_{30} neohop-13(18)-ene and C_{30} hop-17(21)-ene. In all samples C_{29} hop-13(18)-ene and C_{30} neohop-13(18)-ene are the most abundant, followed by C_{30} hop-17(21)-ene (Fig. 3). Tri and tetra- orphan aromatic hopanoids bearing an ethyl group at C-21 (being the most abundant), as well as C_{31} benzohopane cyclised at C-16 and series of $\text{C}_{32}\text{-C}_{35}$ benzohopanes cyclised at C-20 are identified in the aromatic fraction (Fig. 4). Due to the high content of sulphur in Aleksinac coal (Table 2), sulphate-reducing bacteria as a possible source of C_{30} hop-17(21)-ene (Wolff et al., 1992) can be expected. Elevated contents of C_{30} hop-17(21)-ene and C_{30} neohop-13(18)-ene coincide with relatively high amounts of fernene derivatives (Table 3). The $\delta^{13}\text{C}$ values of hopanoids in Aleksinac coal range from -56.9 to -38.7 ‰ (Table 4). This is in agreement with results reported by Simoneit et al. (1995),

Duan et al. (2004) and Mitrović et al. (2017). The $\delta^{13}\text{C}$ values of hopanoids (from -34 to -45 ‰) are indicative of chemoautotrophic bacteria which are amphiaerobic carbon fixers (Freeman et al., 1990; Collister et al., 1992), living at the oxycline. The $\delta^{13}\text{C}$ values of hopanoids less than -38.4 ‰ have been related to methanotrophic bacteria (Duan et al., 2004). Therefore, the obtained results (Table 4) indicated that the main sources of hopanoids in studied samples were methanotrophic bacteria and chemoautotrophic bacteria. More ^{13}C depleted values of hopanoids in BD-4/1 and BD-4/4 denote more active methane cycle at the time of deposition of these samples.

The *n*-alkane patterns of Aleksinac coal dominate by long chain odd homologues with maxima at C_{27} , C_{29} or C_{31} (Fig. 3; Table 3), indicating a significant contribution of epicuticular waxes. The CPI (Carbon Preference Index) values of full range *n*-alkanes vary from 1.68 to 4.66 (Table 3). Considering uniform maturity of studied samples, the lowest CPI value (1.68) and notably higher abundance of short-chain ($\text{C}_{15}\text{-C}_{20}$) homologues in the sample BD-4/1 (Table 3) indicate elevated contribution of aquatic OM, consistent with higher amount of lipinite and presence of alginite (Table 1). Samples BD4/1 and BD-4/4 are characterized by higher content of mid-chain ($\text{C}_{21}\text{-C}_{25}$) *n*-alkanes, associated with higher P_{aq} values (0.37–0.58; Table 3; Ficken et al., 2000) which are indicative for aquatic macrophytes. Based on the P_{aq} ratio (0.15–0.26; Table 3) and $\delta^{13}\text{C}$ values of C_{23} and C_{25} *n*-alkanes which are apparently higher than those of odd $\text{C}_{27}\text{-C}_{31}$ homologues (Table 4), contribution of aquatic macrophytes can be also proposed in all other samples. The prevalence of C_{31} *n*-alkane in samples BD-4/3 and BD-4/5 may be indicative for herbaceous plants and shrubs. The $\delta^{13}\text{C}$ values of C_{27} to C_{31} odd *n*-alkanes in BD-4/1, BD-4/3 and BD-4/6 range from -30.0 to -31.1 ‰, indicating a carbon source from lipids of C_3 higher plants (O’Leary, 1981). Notably lower $\delta^{13}\text{C}$ values of *n*-alkanes in the sample BD-4/4 (-32.7 to -38.6 ‰) are indicative for prominent microbial activity (Table 4).

Typical characteristic of Aleksinac coal is relatively high amounts of fernenes and lanosta(eupha) hexaene derivatives (Table 3). Fernenes could originate from bacteria, but also from ferns. However, significantly more positive $\delta^{13}\text{C}$ values of fernenes (-30.7 to -30.1 ‰, consistent with data from Hauke et al., 1992 and Simoneit et al., 1995)

compared to hopanoids, unambiguously confirm contribution of ferns to the precursor OM (Table 4). The $\delta^{13}\text{C}$ values of lanosta(eupha)hexaene derivatives in range from -27.7 to -29.0 ‰ (Table 4) and significant positive correlation between contents of lanosta(eupha)hexaenes and non-hopanoid tripterpenoids ($r = 0.85$; Table 3) imply angiosperm origin of these biomarkers.

Depositional environment of organic matter

Diagenetic alteration of OM by chemoautotrophic and methanotrophic bacteria indicates reducing to slightly oxic depositional settings, which is consistent with the pristane/phytane ratio (Pr/Ph) ranging from 0.96 to 3.11 (Table 3).

The deepest sample BD-4/6 is characterized by moderate content of TOC and MM, very high content of sulphur and pyrite, associated with low amounts of clay and carbonate (Tables 1, 2). These results imply deposition of terrestrial, mostly angiosperm-derived OM under moderate-high water column, rich in sulphate and iron. Sulphates were reduced to elemental sulphur (present in EOM; Figs. 3, 4) and sulfide by sulphate-reducing bacteria. The latter reacted with iron ions and formed pyrite. Low amount of clays and distribution of hopanoids argue against frequent flooding followed by deposition of siliciclastic material and infiltration of oxygen-rich waters.

Significant differences between samples BD-4/5 and BD4/4 confirm frequent changes in depositional environment, observed also during investigation of lower oil shale sequence of the Aleksinac Basin (Bechtel et al., 2018). The sample BD-4/5 has somewhat higher content of TOC and carbonates, and lower amount of MM, sulphur and pyrite than sample BD-4/6 (Tables 1, 2). Biomarker assemblages are generally similar (Table 3). These results indicate deposition of terrestrial, mostly angiosperm-derived OM under moderate-high water column with lower content of sulphates compared to BD-4/6, but of higher pH, consistent with higher content of carbonates. Sample BD-4/4 has low TOC content, high MM with abundant pyrite, suggesting sulphate-enriched water column. The Pr/Ph ratio less than 1 and the presence of β -carotane which was detected in this sample only, argue for deposition of OM in reducing conditions. Very high content of hopanoids, derived from methanotrophic

bacteria, associated with notably depleted $\delta^{13}\text{C}$ values of *n*-alkanes (Tables 3, 4) may be explained by “CO₂ recycling” of degradation products. In reducing environments accumulation of dissolved CO₂ in the water column, originating from degradation of OM (e.g., sulphate reduction, methane oxidation) occurs. Subsequent incorporation of this ^{13}C depleted CO₂ into the biomass by photosynthetic organisms results in isotopically depleted $\delta^{13}\text{C}$ values of the OM (Lewan, 1986; Frimmel et al, 2004). Low amount of TOC, despite reducing conditions may be attributed to strong microbial activity (methanotrophs, sulphate-reducing bacteria), producing CO₂ and sulfide. The latter formed pyrite, which indirectly reduced concentration of OM in sediment. On the other hand, limited activity of photosynthetic organisms under such restricted conditions led to reduced bioproductivity.

Samples from the Main coal seam (BD-4/3 – BD-4/1) are characterized by lower amounts of sulphur and pyrite, revealing upward decrease of concentration of sulphate ions in the water body. Samples BD-4/3 and BD-4/2 are typical humic coals showing moderate to high TOC and low MM content (Tables 1, 2). Predominantly angiosperm-derived OM was deposited under stable moderate to high water column. On the other hand, the sample BD-4/1 exhibits characteristics of coaly shale with low TOC, high MM and bituminite content, and certain contribution of algal precursor biomass (Tables 1, 2), denoting subaquatic deposition and representing transition from coaly facies to upper oil shale sequence.

Conclusions

Petrographic analysis showed that the vitrinite is dominant or prevailed maceral group in all samples. The content of the liptinite is relatively low in two samples, while the content of inertinite is extremely low in all studied coals. Three of six samples have high content of MM. The measured random vitrinite reflectance, Rock Eval parameters, T_{max} and PI, as well as biomarker patterns confirmed sub-bituminous rank of coal from the Dubrava field (Aleksinac Basin). OM is immature, at the late diagenetic- and early catagenetic stage.

The main sources of OM in Aleksinac coal were angiosperm paleovegetation (including herbaceous plants, shrubs and aquatic macrophytes), ferns,

methanotrophic bacteria and chemoautotrophic bacteria. Certain contribution of conifers, represented by Pinacea and Cupressacea species is also confirmed. The presence of algal OM is detected in sample BD-4/1. Both, the Main coal seam and coal layers within and below lower oil shale sequence represent a low-lying mire environment. Frequent changes in depositional environment, enriched in sulphates, are observed during deposition of coal layers within/below lower oil shale sequence. Upward decrease of salinity in the water body through the Main coal seam is detected. The lower and central part of the Main coal seam is represented by humic coal showing moderate to high TOC and low MM content. The upper part of the Main coal seam consists of coaly shale, indicating a rising water table and transition to the upper oil shale sequence.

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