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Drmno lignite field (Kostolac Basin, Serbia): origin and palaeoenvironmental implications from petrological and organic geochemical studies

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Abstract: The objective of the study was to determine the origin and to reconstruct the geological evolution of lignites from the Drmno field (Kostolac Basin, Serbia). For this purpose, petrological and organic geochemical analyses were used. Coal from the Drmno field is typical humic coal. Peat-forming vegetation dominated by decay of resistant gymnosperm (coniferous) plants, followed by prokaryotic organisms and angiosperms. The coal forming plants belonged to the gymnosperm families *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae*, *Phyllocladaceae* and *Pinaceae*. Peatification was realised in a neutral to slightly acidic, fresh water environment. Considering that the organic matter of the Drmno lignites was deposited at the same time, in a relatively constant climate, it could be supposed that climate probably had only a small impact on peatification. Therefore, variations in compositions of macerals and biomarkers indicate changes in the water level, due to seasonal drying of the mire, which caused vegetation differences in the palaeoplant communities and changes in the redox conditions (from anoxic to slightly oxic) during peatification. Diagenetic transformations of the organic matter were mainly governed by microbial activity, rather than thermal alteration.

Keywords: lignites; Kostolac Basin; organic matter; macerals; biomarkers; palaeoenvironment.

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INTRODUCTION

Standard methods for the investigation of peat and coal bearing sediments include a complex of petrological, palynological, palaeobotanical and geochemical techniques to acquire information about the sedimentary environment, type of vegetation and its transformation during diagenesis.

The maceral composition is directly dependent on the type of the source material and the environmental settings. Therefore, maceral analysis is widely used to interpret the conditions of peat formation.[1–4] In addition to maceral percentages, two parameters based on the maceral composition, the tissue preservation index (*TPI*) and the gelification index (GI), are of great importance. The *TPI* provides valuable data about peat forming plant communities, water column level, pH and climatic settings.[5–7] The *GI* could be used as an indirect measure for the water column level, as well as for an estimation of the redox conditions of the environment and microbial activity.[4–7]

Elemental analysis, Rock–Eval analysis and other bulk geochemical parameters (*e.g.*, ash content, organic carbon and sulphur contents, and group composition of soluble organic matter) provide basic data for characterizing coals.[8,9]

In the past few decades, molecular organic geochemistry has played an important role in the exploration of coals and fossil fuels generally. It involves the analysis of the soluble organic matter and identification of organic compounds with hydrocarbon skeletons related to biological molecules present in the tissues of living organisms.[10,11] These biomarkers allow for the recognition of the main input of organic matter (OM), an estimation of the palaeoenvironment in which they were deposited and determination of the thermal maturity. For these purposes, numerous biomarkers, *n*-alkanes, isoprenoid aliphatic alkanes, steroids, hopanoids, sesquiterpenoids, diterpenoids, non-hopanoid triterpenoids, were used.

The production of energy in Serbia is based on coal sources (52 %), followed by crude oil (28 %), natural gas (13 %) and hydroenergy (7 %).[12] The largest resources of coals in Serbia represent soft brown coals, *i.e.*, lignites (92 %).[13] The main lignite deposits are located in the Kosovo, Kolubara, Kostolac and Metohija Basins, and in the Kovin deposit.[14] Although the lignite deposits are widespread in Serbia, petrological and geochemical data are either scarce or completely missing.[15,16] The objective of this study was to determine the origin and to reconstruct the geological evolution of lignites from the Drmno field, Kostolac Basin (Serbia), based on comprehensive petrological and organic geochemical analyses.

Geological settings of the Kostolac Basin

The Kostolac Coal Basin, covering an area of 145 km^2, is located about 90 km east of Belgrade. It is divided into three coal fields: the Drmno field in the eastern, the Ćirikovac field in the central and the Smederevsko Podunavlje field

in the western part of the Basin (Fig. 1). The Drmno and Ćirikovac fields are exploited, while the Smederevsko Podunavlje field is still under preliminary exploration.

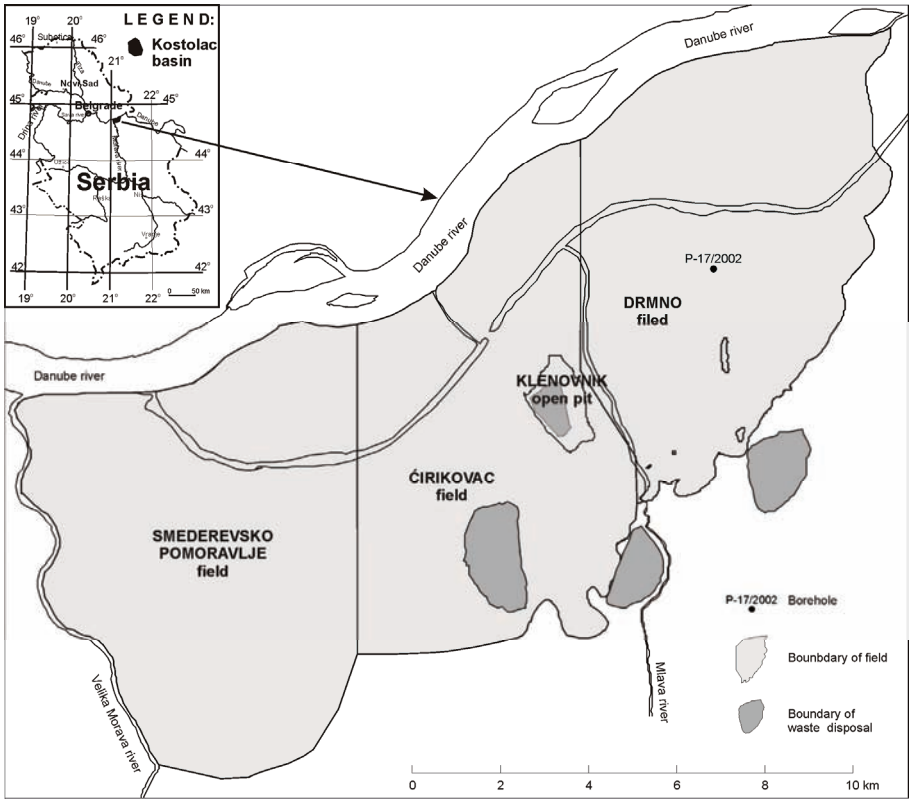

Fig. 1. Location and coal fields of the Kostolac Basin.

The basement of the Kostolac Basin is formed of Devonian crystalline rocks overlain by Neogene sediments. The total thickness of the Neogene sediments ranges from 300 to 5000 m in the central part of the depression.[17] The complete Neogene generally dips towards NW at the low angle of 5–15°; the coal seams following the same dip, as well. The Neogene complex consists of several units:[17]

1. Lower Miocene, formed of fluvio-lacustrine and marine metaclastic rocks, siltstone, sandstone, and shales (“redeposited series”), breccia-type material (“transitional zone”), and red to violet sandy marlstone, sandstone, and conglomerate (“red series”);

2. Ottnangian–Karpathian, consisting of fluvial brackish and marine conglomerate, sandstone, siltstone, shale, and marlstone, with local transitions to laminated limestone and tuffaceous sandstone;

3. Badenian, formed of marine sandstone, marlstone, and siltstone;

4. Sarmatian, consisting of clayey and sandy marlstone, marly clay, marly and clayey sandstone, subordinately of gravel and quartz sand, in a shallow brackish–marine environment;

5. Pannonian, made of clastic sediments with two coal seams, the lower up to 6 m in thickness, and the upper of maximum 1 m in thickness;[18]

6. Pontian, consisting of clastic sediments, with economic coal resources. The total thickness of the Pontian sediments is more than 200 m. The Pontian coal-bearing series consists of five coal seams, namely seam III (the oldest and deepest) and the seams II-a, II, I-a, and I. Only coal seams III, II and I have been explored in the Drmno, Ćirikovac and Klenovnik open pits. The average thickness of coal seam III throughout whole basin is 19.38 m, while it is 1.43 m for IIa, 4.14 m for II, 1.53 for Ia and 13.90 m for I coal seam.[19] Average huminite reflectance of coal from the Drmno and Ćirikovac fields (seams II and III) is 0.30 %;[19,20] thus, placing the coal in the soft brown coal (lignite) stage of coalification;

7. Romanian, includes sand, clay, silt, and gravel, disconformably overlying Pannonian or Pontian sediments;

8. Quaternary, formed of fluvial gravel, sand and sandy clay, eolian loess and loess-like clays, all of Pleistocene age.

The lignite samples investigated in this study are of Upper Pontian age (c. 6 Ma) and originated from the borehole P-17/2002 of the Drmno field (Kostolac Basin; Fig. 1). The samples were collected from the two coal seams, II at a depth interval 23.20 to 24.90 m, and III at a depth interval 100.60 to 123.70 m (Table I). The thickness of each sample interval was determined as per the changes in macroscopic lithology of the coal.

TABLE I. The list of investigated samples

Coal seam	Sample	Depth interval, m	Lithology
II	1	23.20–23.40	Mixture of xylitic and matrix coal
	2	23.40–24.40	Mixture of matrix and xylite-rich coal
	3	24.40–24.53	Xylite-rich coal
	4	24.80–24.90	Matrix coal
III	5	100.60–101.00	Mixture of matrix and xylite-rich coal
	6	102.10–102.20	Xylite-rich coal
	7	103.00–104.20	Matrix coal
	8	104.80–104.90	Xylite-rich coal
	9	112.00–112.60	Mixture of matrix and xylite-rich coal
	10	121.40–123.70	Mineral-rich coal

EXPERIMENTAL

For the maceral analyses, the coal samples were crushed to a maximum particle size of 1 mm, mounted in epoxy resin and polished. The maceral analysis was performed on a LEITZ DMLP microscope under monochromatic and UV reflected light on 500 points. The maceral

description used in this article follows the terminology developed by the International Committee for Coal Petrology for low-rank coal.[21]

Elemental analysis was applied to determine the contents of sulphur and organic carbon (C_{org}). The organic carbon content was determined after removal of carbonates with dilute hydrochloric acid (1:3, v/v). The measurements were performed using a Vario EL III, CHNOS elemental analyser, Elementar Analysensysteme GmbH. The measurements of the ash content followed the standard procedure ISO 1171 (1997).[22]

Soluble organic matter (bitumen) was extracted from pulverized lignites (<150 μm) using a Dionex ASE apparatus with a mixture of *iso*-hexane and acetone (1:1, v:v) at a temperature of 80 °C and a pressure of 8 MPa. After extraction, most of the solvent was removed using a vacuum rotary evaporator. The extract yields were weighed. The asphaltenes were precipitated from the bitumen with petroleum-ether and the remainder (maltenes) was separated into three fractions (saturated hydrocarbons, aromatic hydrocarbons and NSO compounds) using column chromatography over silica gel and aluminium oxide. The saturated hydrocarbons fraction was eluted with *iso*-hexane, the aromatic hydrocarbons with dichloromethane and the NSO fractions (polar fraction, which contains nitrogen, sulphur and oxygen compounds) with a mixture of dichloromethane and methanol (1: 1, v:v).

The saturated and aromatic fractions isolated from the bitumen were analyzed by gas chromatography-mass spectrometry (GC–MS). A gas chromatograph Agilent 7890A GC (H5-MS capillary column, 30 m×0.25 mm, He carrier gas 1.5 cm^3 min^{-1}, FID) coupled to an Agilent 5975C mass selective detector (70 eV) was used. The column was heated from 80 to 310 °C at a rate of 2 °C min^{-1}, and the final temperature of 310 °C was maintained for an additional 25 min. The individual peaks were identified by comparison with literature data[10,23-26] and on the basis of the total mass spectra (library: NIST5a). Biomarker parameters were calculated from the GC–MS chromatogram peak areas (software GCMS Data Analysis).

RESULTS AND DISCUSSION

Maceral analysis

Coal from the Drmno field is typical humic coal with huminite concentrations between 50.8 and 89.3 vol. %, liptinite less than 7 vol. % and inertinite between 4.0 and 12.5 vol. %. The most abundant huminite macerals are textinite, ulminite and densinite. Liptodetrinite and sporinite dominated among liptinite macerals, whereas inertodetrinite and fusinite are the most abundant inertinite macerals (Table II).

The tissue preservation index (*TPI*),[27,28] taken as the ratio between structured and unstructured macerals of the huminite and inertinite group, ranges from 0.7 to 4.2 (Table II). The variations of the *TPI* with depth could reflect, at least to some extent, the differences in the type of peat forming plant communities. On the other hand, it was suggested that tissue preservation depends mostly on the relative height of the water level, pH and climatic settings, rather than from the botanical properties of the vegetation.[29] Namely, lowering the water level within the basins during the dry seasons contributes to the establishment of more oxic conditions, resulting in more extensive tissue degradation. Considering that the OM of the Drmno lignites was deposited in the same time, in the relatively

constant climate, it could be supposed that the climate probably had only a small impact on peatification. Therefore, the variations in the maceral composition and the *TPI* could be attributed mainly to changes in the water column level, due to seasonal drying of the mire, which caused vegetation differences in the palaeo-plant communities and changes of redox potential (*Eh*) during peatification.

TABLE II. Maceral composition (vol. %) and petrographic indices of the Drmno field coals

Maceral	Sample									
	1	2	3	4	5	6	7	8	9	10
Textinite	17.1	19.7	48.3	16.1	17.3	14.3	15.7	15.8	11.4	3.7
Ulminite	10.6	5.4	15.8	11.8	15.5	26.7	13.1	32.8	38.9	15.3
(Total telohuminite)	27.7	25.1	64.1	27.9	32.8	41.0	28.8	48.6	50.3	19.0
Attrinite	3.0	13.6	3.9	14.5	7.9	6.6	3.5	2.4	0.6	2.7
Densinite	30.0	25.8	9.4	31.0	31.5	32.3	39.1	19.7	17.1	22.6
(Total detrohuminite)	33.0	39.4	13.3	45.5	39.4	38.9	42.6	22.1	17.7	25.3
Gelinite	4.0	2.3	3.1	3.0	3.2	3.0	0.5	4.0	7.2	5.5
Corpohuminite	1.5	1.8	2.0	5.0	5.4	6.4	0.9	6.3	4.7	1.0
(Total gelohuminite)	5.5	4.1	5.1	8.0	8.6	9.4	1.4	10.3	11.9	6.5
Total huminite	66.2	68.5	82.6	81.4	80.8	89.3	72.8	81.0	79.9	50.8
Sporinite	1.4	1.5	1.3	2.0	1.4	0.6	0.7	0.5	1.1	0.8
Cutinite	0.1	0.2	0.0	0.4	0.2	0.0	0.2	0.0	0.1	0.3
Resinite	0.1	0.0	0.2	0.4	0.2	0.4	0.2	0.5	0.2	0.4
Suberinite	0.1	0.2	0.0	0.9	0.2	0.2	0.2	0.4	0.9	0.0
Alginite	0.4	0.5	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.3
Liptodetrinite	1.2	2.1	1.1	2.7	1.9	1.2	1.2	1.1	0.2	1.3
Other – liptinite	1.0	1.2	0.7	0.4	0.2	0.4	0.7	0.5	0.0	0.0
Total liptinite	4.3	5.7	3.3	6.8	4.3	2.8	3.4	3.0	2.5	3.1
Fusinite	1.5	2.3	2.7	0.6	0.5	0.4	1.1	1.1	4.0	1.8
Semifusinite	0.3	1.0	0.4	0.4	0.4	0.0	1.2	0.4	3.8	1.2
Macrinite	0.0	0.2	0.2	0.0	0.2	0.0	0.2	0.5	0.2	0.8
Funginite	1.2	0.3	0.2	1.7	0.9	0.8	0.5	0.7	0.4	0.5
Inertodetrinite	1.0	3.9	2.4	1.4	3.0	0.7	9.2	1.3	4.1	6.1
Total inertinite	4.0	7.7	5.9	4.1	5.0	1.9	12.2	4.0	12.5	10.4
Total coal	74.5	82.0	91.7	92.3	90.1	94.0	88.4	88.0	94.9	64.3
Clay	21.8	11.1	1.4	5.3	8.3	3.5	6.1	9.7	4.3	31.6
Pyrite	2.3	2.2	1.8	0.9	0.5	1.9	3.2	1.8	0.8	1.9
Carbonates	0.7	0.8	0.9	0.4	0.4	0.0	1.6	0.0	0.0	0.9
Other minerals	0.7	3.9	4.2	1.1	0.7	0.6	0.7	0.5	0.0	1.3
Total mineral	25.5	18.0	8.3	7.7	9.9	6.0	11.6	12.0	5.1	35.7
TPI[a]	0.8	0.7	4.2	0.7	0.9	1.1	0.7	2.1	2.5	0.7
GI[b]	1.9	0.9	0.5	1.5	1.8	3.0	1.7	2.8	2.8	2.6

[a]*TPI* = (textinite+ulminite+corpohuminite+fusinite+semifusinite)/(gelinite+macrinite+detrohuminite);[27,28] [b]*GI* = = (ulminite+densinite+gelinite+corpohuminite)/(textinite+attrinite+inertinite)[27,28]

The gelification index (*GI*),[27,28] expressed as the ratio of gelified (ulminite, densinite, gelinite and corpohuminite) to non-gelified (textinite and attrinite) macerals, is used as an indirect measure for the height of the water level, because

gelification of the tissues requires the continuous presence of water. Lignites from the Drmno field have a *GI* value ranging between 0.5 and 3.0 (Table II). The variation of this ratio with depth also indicates changes in the height of the water level and consequently changes of the *Eh* conditions during peatification. Based on the generally higher *TPI* and *GI* values in coal seam III than in coal seam II, it could be assumed that the water column level during peatification was lower in coal seam II.

The content of mineral matter shows a comparatively wide range 5.1–35.7 % (Table II). An increase in the mineral content is often related to more intensive degradation of organic matter and/or contribution of clastic material. The domination of clays and very low carbonate content in the mineral matter (Table II) suggest a neutral to slightly acidic environment. As expected, a significant positive correlation (correlation coefficient, $r = 0.98$) is observed between the mineral matter content (Table II) and the ash content (Table III).

TABLE III. Values of group organic geochemical parameters

Coal seam	Sample	Ash, %, db[a]	C_{org}[b] %, db	S %, db	Bitumen ppm	Asp[c] %	Saturated HC[d], %	Aromatic HC, %	NSO %
II	1	35.62	38.41	0.85	15333	59.22	2.56	2.67	35.54
	2	18.44	49.13	3.42	12292	42.03	5.71	3.60	48.67
	3	8.72	58.09	1.80	98666	64.54	2.33	3.79	29.33
	4	9.82	55.12	1.58	11628	51.23	2.63	3.58	42.56
III	5	10.52	54.58	0.63	10631	41.41	3.90	4.51	50.18
	6	4.53	N.D.[e]	N.D.	79400	70.93	13.22	2.17	13.69
	7	13.17	51.32	1.03	6645	42.20	3.25	4.20	50.35
	8	17.26	51.04	1.32	40000	63.63	6.50	3.71	26.15
	9	9.66	56.67	0.90	18272	45.87	6.90	3.40	43.83
	10	47.04	30.72	1.23	14950	42.40	2.23	5.50	49.87

[a]Dry basis; [b]organic carbon content; [c]asphaltenes; [d]hydrocarbons; [e]not determined

Group organic geochemical parameters

The contents of organic carbon (C_{org}) are within the limits typical for lignite[7,30] and vary between 30.72 and 58.09 % (Table III). The significant negative correlation between C_{org} and the mineral matter content ($r = 0.98$) indicates that the differences in the C_{org} contents of the lignites are mainly controlled by the varying amounts of mineral matter. The content of sulphur does not exceed 2 %, with exception of sample 2 (Table III). This result implies the relatively low sulphate content of the waters within the peat (peatification in fresh water environment).[3,31]

The yield of the soluble organic matter (bitumen) varies over a wide range 6645–98666 ppm, in concordance with the variation in C_{org}. The soluble organic matter is mainly represented by asphaltenes (41.41–70.93 %) and polar, NSO compounds (13.69–50.35 %). The relative contents of saturated and aromatic

hydrocarbons are low, which is in accordance with the low maturity of the organic matter (Table III).

Molecular composition of the organic matter

General characteristics. The main constituents of the saturated fraction of the coals are diterpenoids, followed by *n*-alkanes and hopanoids. Steroids and non-aromatic, non-hopanoid triterpenoids were identified in relatively low amounts (Fig. 2). The main components in the aromatic fractions of the Drmno coals are diterpenoids. Other constituents of the aromatic fractions are non-hopanoid triterpenoids, sesquiterpenoids, aromatized hopanoids, long-chain acyclic alkan-2-ones, monoaromatic steroids and perylene (Fig. 3).

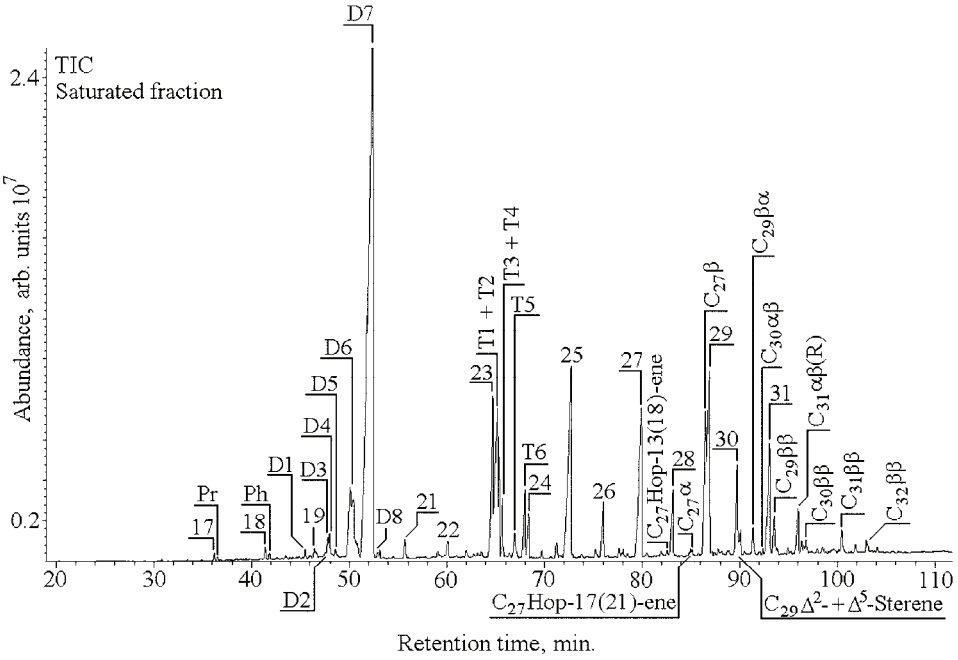

Fig. 2. *TIC* (total ion current) of a saturated fraction typical for the investigated samples. Peak assignments: *n*-alkanes are labelled according to their carbon number; Pr – pristane; Ph – phytane; D1 – isopimaradiene; D2 – norabietane; D3 – norpimarane; D4 – beyerane; D5 – isophyllocladene; D6 – pimarane; D7 – 16α(*H*)-phyllocladane; D8 – 16α(*H*)-kaurane; T1 – des-A-olean-13(18)-ene; T2 – des-A-olean-12-ene; T3 – des-A-olean-18-ene; T4 – des-A-urs-13(18)-ene; T5 – des-A-urs-12-ene; T6 – des-A-lupane; $\beta\beta$, $\beta\alpha$ and $\alpha\beta$ designate configurations at C_{17} and C_{21} in hopanes, *R* designates configuration at C_{22} in hopanes.

The domination of diterpenoids in both the saturated and aromatic fractions shows that the main sources of organic matter were gymnosperms (conifers). The presence of hopanoid biomarkers indicates the contribution of prokaryotic orga-

nisms, such as bacteria and fungi, whereas the identification of non-hopanoid triterpenoids implies a contribution of angiosperms to the lignite organic matter (Figs. 2 and 3).

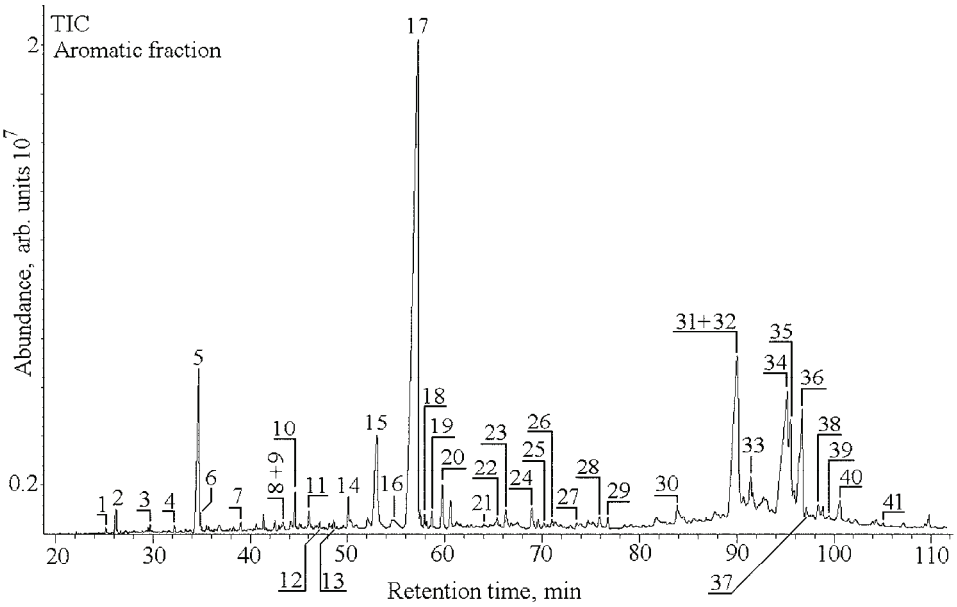

Fig. 3. *TIC* (total ion current) of an aromatic fraction typical for the investigated samples. Peak assignments: **1** – cuparene; **2** – calamenene; **3** – cadina-1(10),6,8-triene; **4** – 5,6,7,8-tetrahydrocadalene; **5** – cadalene; **6** – isocadalene; **7** – phenanthrene; **8** – 19-norabieta-8,11,13-triene; **9** – 6,10,14-trimethylpentadecan-2-one; **10** – 18-norabieta-6,8,11,13-tetraene; **11** – 16,17-bisnordehydroabietane; **12** – hibane; **13** – 16,17-bisnorsimonellite; **14** – 18-norabieta-8,11,13-triene; **15** – dehydroabietane; **16** – 1,2,3,4-tetrahydroretene; **17** – simonellite; **18** – totarane; **19** – sempervirane; **20** – retene; **21** – ferruginol; **22** – pentamethylocatahydrochrysene; **23** – 2-methylretene; **24** – 3,4,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene; **25** – 3,3,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene; **26** – pentamethyldecahydrochrysene; **27** – triaromatic des-A-lupane; **28** – 3,4,7-trimethyl-1,2,3,4-tetrahydrochrysene; **29** – 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene; **30** – perylene; **31** – 24,25-dinoroleana-1,3,5(10)-12-tetraene; **32** – D-ring monoaromatic hopane; **33** –24,25-dinorlupa-1,3,5(10)-triene; **34** – 1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene; **35** – 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene; **36** – 24,25-dinoroleanapentaene; **37** – 4-methyl-24-ethyl-19-norcholesta-1,3,5(10)-triene; **38** – 7-methyl-3'-ethyl-1,2-cyclopentanochrysene; **39** – C_{31} *n*-alkan-2-one; **40** – 1,2,9-trimethyl-1,2,3,4-tetrahydropicene; **41** – C_{33} *n*-alkan-2-one.

n-Alkanes and isoprenoids. n-Alkanes are relatively abundant in the total ion current (*TIC*) of the saturated fraction (Fig. 2). Based on the *m*/*z* 71 mass chromatogram of the saturated fraction (Fig. 4a), *n*-alkanes were identified in the range C_{17} to C_{35}. The *n*-alkane patterns of the coal samples are dominated by long-

chain homologues (C_{27}–C_{31}) with a maximum at *n*-C_{29} and a marked odd over even predominance, indicating a significant contribution of epicuticular waxes.[11] The values of the *CPI* (carbon preference index) and *OEP* 2 (odd–even predominance) range between 3.21–5.61 and 3.24–6.30, respectively (Table IV), which are in accordance with the low rank of the lignites.

TABLE IV. Values of parameters calculated from distributions and abundances of *n*-alkanes, isoprenoids and terpenoids

Coal seam	Sample	CPI[a]	OEP 1[b]	OEP 2[c]	Pr/Ph[d]	Di/(Di+Tri)[e]
II	1	3.23	0.89	3.58	0.27	0.66
	2	5.24	1.65	4.57	0.38	0.84
	3	4.37	0.94	3.36	1.20	0.99
	4	5.08	0.92	5.13	1.26	0.95
III	5	4.36	1.65	4.39	0.41	0.97
	6	N.D.[f]	N.D.	N.D.	N.D.	0.99
	7	4.97	1.40	6.30	0.08	0.96
	8	3.21	1.25	3.75	N.D.	0.99
	9	3.92	1.89	3.24	N.D.	0.88
	10	5.61	5.50	4.52	0.62	0.62

[a]Carbon preference index determined for the full distribution of *n*-alkanes C_{23}–C_{33} (mass chromatogram *m/z* 71), $CPI = 1/2[\Sigma odd(n\text{-}C_{23}–n\text{-}C_{33})/\Sigma even(n\text{-}C_{22}–n\text{-}C_{32}) + \Sigma odd(n\text{-}C_{23}–n\text{-}C_{33})/\Sigma even(n\text{-}C_{24}–n\text{-}C_{34})]$; [b]$OEP\ 1 = 1/4[(n\text{-}C_{21}+6\ n\text{-}C_{23}+n\text{-}C_{25})/(n\text{-}C_{22}+n\text{-}C_{24})]$; [c]$OEP\ 2 = 1/4[(n\text{-}C_{25}+6\ n\text{-}C_{27}+n\text{-}C_{29})/(n\text{-}C_{26}+n\text{-}C_{28})]$; [d]Pr/Ph = = pristane/phytane; [e]Di/(Di+Tri) = Σaromatic diterpenoids/(Σaromatic diterpenoids + Σaromatic triterpenoids), calculated from the *TIC* of aromatic fraction, Σaromatic diterpenoids = (18-norabieta-6,8,11,13-tetraene + 19-norabieta-8,11,13-triene + 18-norabieta-8,11,13-triene + 2-methyl-1-(4'-methylpentyl)-6-isopropylnaphthalene + dehydroabietane + simonellite + retene + sempervirane + totarane + hibaene + ferruginol + 6,7-dehydroferruginol + 2-methylretene + 12-hydroxysimonellite + 16,17-bisnordehydroabietane + 16,17-bisnorsimonellite + 1,2,3,4-tetrahydroretene), Σaromatic triterpenoids = (24,25-dinoroleana-1,3,5(10),12-tetraene + 24,25-dinoroleana-1,3,5(10),12,14-pentaene + 24,25-dinorursa-1,3,5(10),12-tetraene + 24,25-dinorlupa-1,3,5(10)-triene + pentamethylocatahydrochrysene + pentamethyldecahydrochrysene + 3,4,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene + 3,3,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene + 3,4,7-trimethyl-1,2,3,4-tetrahydrochrysene + 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene + 1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene + 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene + 1,2,9-trimethyl-1,2,3,4-tetrahydropicene + triaromatic des-A-lupane); [f]not determined due the absence of *n*-alkanes and isoprenoids

The mid-chain *n*-alkanes (*n*-C_{21}–C_{25}), originating from vascular plants, microalgae, cyanobacteria, sphagnum and aquatic macrophytes,[32–34] are present in a lower amount in comparison with the long-chain homologues. The slight predominance of odd over even carbon-numbered *n*-alkanes in the mid-range *n*-alkanes (parameter *OEP* 1; Table IV) in the samples from coal seam III suggests a microbial origin. Moreover, the relatively high abundance of C_{23} and C_{25} *n*-alkane homologues implies an input of aquatic macrophytes to the organic matter.

Short chain *n*-alkanes (<*n*-C_{20}) are found mostly in algae and microorganisms.[11] In the studied lignites, short chain *n*-alkanes are absent or present in low quantities (Fig. 4a), which is consistent with the results of the maceral analysis (low liptinite content; Table II).

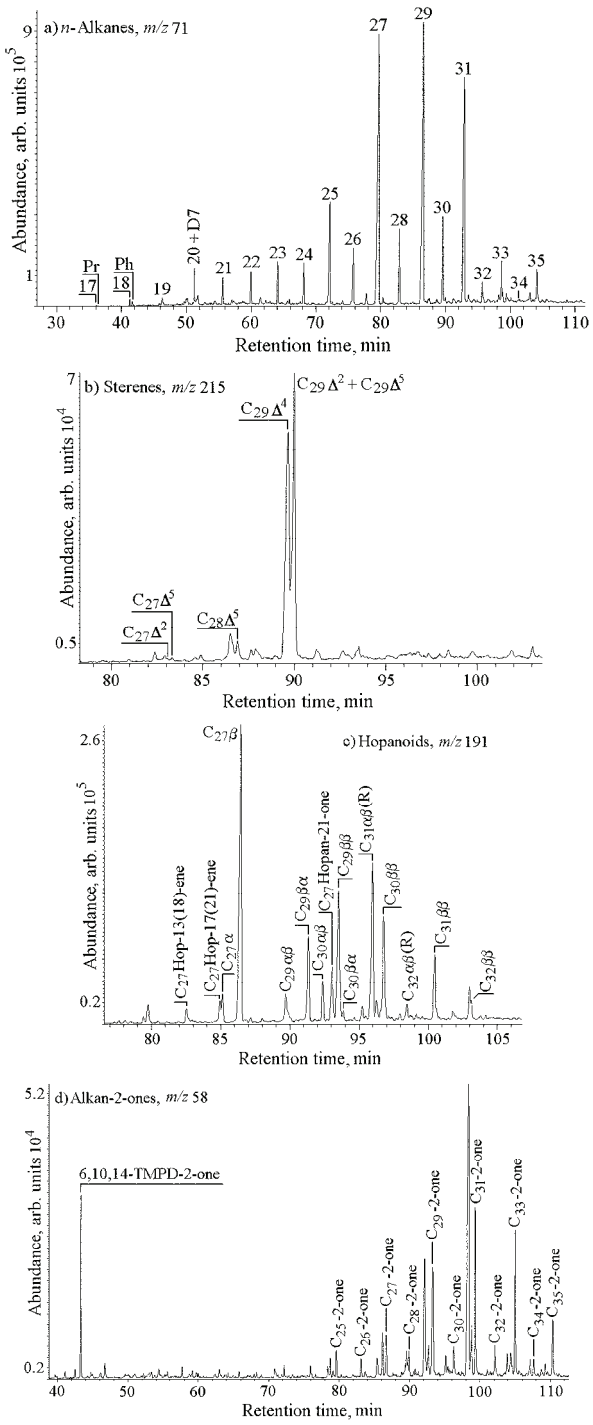

Fig. 4. GC–MS Mass chromatograms of *n*-alkanes, *m/z* 71 (a), sterenes, *m/z* 215 (b), hopanoids, *m/z* 191 (c) and alkan-2-ones, *m/z* 58; d) typical for the investigated samples 6,10,14-TMPD-2-one – 6,10,14-trimethylpentadecan-2-one; for other peak assignments, see the legend to Fig. 2.

The isoprenoids pristane (Pr) and phytane (Ph) are present in Drmno lignites in low amounts or are not identified (Fig. 2; Table IV). Low concentrations of pristane and phytane are often reported in immature organic matter.[35–37] This is probably related to the fact that isoprenoid precursors incorporate into the macromolecular kerogen matrix either by esterification[38] or natural sulphurization[39] during early diagenesis and the release of saturated isoprenoids occurs after the thermal maturity of the organic matter increases.[37] The Pr/Ph ratio is widely used as indicator for the *Eh* settings of the depositional environment. However, this parameter is known to be also affected by maturation.[11] For this sample set, the influence of maturity on the pristane/phytane ratios can be ruled out. Therefore, the Pr/Ph ratio varying between 0.08 and 1.26 (Table IV) may be considered as an indicator of changing of Eh settings from anoxic to slightly oxic during peat deposition in the Drmno seam.[40] This result is consistent with the variations in the *TPI* and *GI* parameters.

Sesquiterpenoids, diterpenoids and triterpenoids with a non-hopanoid skeleton. In all samples, aromatic sesquiterpenoids were observed in low quantities (Fig. 3). Cadalene predominates over isocadalene, calamenene and 5,6,7,8-tetrahydrocadalene. Other sesquiterpenoid constituents of the lignite extracts are cuparene and cadina-1(10),6,8-triene, whereas dihydro-ar-curcumene, 1-methyl-7--isopropyltetrahydronaphthalene and 1-methyl-7-isopropylnaphthalene (eudalene) were identified only in two samples. Sesquiterpenoids are used as markers for higher land plants. However, sesquiterpenoid biomarkers are often not useful for an unambiguous determination of the precursor plant community,[25,41,42] with exception of cuparene, the presence of which clearly indicates a contribution of *Cupressaceae*, a family of gymnosperms, to the precursor OM.[43,44]

Diterpenoids are the main constituents of both the saturated and aromatic fraction, indicating a significant contribution of gymnosperms to the precursor OM. Pimarane and particularly 16α(*H*)-phyllocladane are dominant by far in the saturated fractions. Other diterpenoid-type constituents of the saturated fraction are norpimarane, norabietane, beyerane, 16α(*H*)-kaurane, isopimaradiene, isophyllocladene and abietane (Fig. 2). The high amount of 16α(*H*)-phyllocladane indicates that the coal forming plants belonged to the conifer families *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae* and *Phyllocladaceae*, while the high abundance of pimarane suggests *Pinaceae, Taxodiaceae* and *Cupressaceae*.[41,43,45,46]

The aromatic diterpenoids consist of norabieta-6,8,11,13-tetraenes, norabieta-8,11,13-trienes, 2-methyl-1-(4'-methylpentyl)-6-isopropylnaphthalene, 16,17--bisnordehydroabietane, dehydroabietane, simonellite, retene, sempervirane, totarane, hibaene, ferruginol, 6,7-dehydroferruginol, 12-hydroxysimonellite, 16,17--bisnorsimonellite and 2-methylretene. Simonellite is the predominant aromatic

diterpenoid, with the exception of two samples in which the most prominent are dehydroabietane and retene, respectively (Fig. 3).

Almost of all the aromatic diterpenoids are non-specific conifer markers, because they are the diagenetic products of a great variety of abietane-type precursors that are common constituents of all conifers except *Phyllocladaceae*.[41,46,47] In contrast, the presence of cuparene, ferruginol, totarane and hibaene in the aromatic fraction of the Drmno lignite extracts clearly indicates the contribution of *Cupressaceae*, *Taxodiaceae*, *Podocarpaceae* and *Araucariaceae* to the precursor biomass,[43] which is consistent with the observation derived from the analysis of the saturated diterpenoids.

The non-hopanoid triterpenoids are present in relatively low amounts in the saturated fraction of the Drmno lignites and consist of olean-12-ene, olean-13,18--ene, des-A-oleanenes, des-A-ursenes and des-A-lupane. A marked domination of des-A-ring degraded compounds is observed, and only in two samples were non-degraded oleanenes identified (Fig. 2).

Although the non-hopanoid triterpenoids represent a minor component of the saturated fraction, these compounds are slightly more abundant in the aromatic fraction of the coal extracts (Fig. 3). This result shows that angiosperms also contributed to the organic matter. The higher abundance of aromatized in comparison to non-aromatized angiosperm triterpenoids indicates significant aromatization of the triterpenoids during diagenesis. The same result that aliphatic angiosperm-derived triterpenoids are more easily altered to aromatic derivatives, in comparison with gymnosperm-derived diterpenoids, resulting in the selective loss of such aliphatic compounds, was also reported by Kalkreuth *et al*. (1998)[48] and Nakamura *et al*. (2010).[49]

All samples contain des-A-ring degraded aromatic triterepenoids, represented by tetramethyloctahydrochrysenes and trimethyltetrahydrochrysenes. In four samples (1, 2, 9 and 10), which have generally higher amounts of triterpenoids (see next paragraph and Table IV), in addition to the des-A-ring degraded aromatic triterepenoids, pentacyclic aromatic triterpenoids (ring-A-monoaromatic triterpenoids, tetramethyloctahydropicenes and trimethyl-tetrahydropicenes) were also identified. Degradation of the A-ring of triterpenoids followed by intensive aromatization suggests microbial activity, which is consistent with relatively abundant hopanoids (Figs. 2 and 3).

In order to estimate the contribution of gymnosperm and angiosperm vegetation in the ancient peat bogs, the ratio of diterpenoid and angiosperm-derived triterpenoid aromatic biomarkers (Di/(Di+Tri) was used, Table IV). The values of this parameter show the dominant role of gymnosperms for peat formation in the Drmno field. The lower values of Di/(Di+Tri) ratio in upper part of upper seam (samples 1 and 2) and lower part of lower seam (samples 9 and 10), indicate the higher contribution of angiosperms to precursor biomass (Table IV). This result

implies changes in palaeoenvironment in the mire during coal formation, consistent with conclusions derived from the TPI, the GI and the Pr/Ph ratio.

Steroids and hopanoids. The analysis of the aliphatic fraction revealed low contents of steroids (Fig. 2). Steroid biomarkers (based on the *m/z* 215 mass chromatogram of the saturated fraction; Fig. 4b) consist predominantly of C_{29} Δ^4-, Δ^2- and Δ^5-sterenes. C_{28}-sterenes (Δ^4-, Δ^2- and Δ^5) were identified in low amounts, whereas the corresponding C_{27} homologues are present in several samples. The marked predominance of C_{29} sterenes (Fig. 4b; Table V) clearly indicates peat formation from terrigenous plants.

TABLE V. Values of parameters calculated from the distributions and abundances of steroids and hopanoids

Coal seam	Sample	% C_{27}[a]	% C_{28}[b]	% C_{29}[c]	Ster Hop[d]	$C_{30}\beta\beta$ ($\beta\beta$+$\alpha\beta$)[e]
II	1	2.30	6.44	91.25	0.07	0.80
	2	2.43	5.28	92.29	0.08	0.72
	3	0.00	0.00	100.00	0.17	0.53
	4	4.55	3.00	92.45	0.11	0.90
	5	1.45	5.93	92.62	0.24	0.70
III	6	N.D.[f]	N.D.	N.D.	N.D.	N.D.
	7	1.07	3.59	95.34	0.25	0.87
	8	0.00	15.94	84.06	0.22	0.84
	9	0.26	6.00	93.74	0.18	0.77
	10	0.00	3.04	96.96	0.09	0.78

[a]%C_{27} = 100C_{27}(Δ^2 + Δ^4 + Δ^5)-sterenes/Σ(C_{27}–C_{29})(Δ^2 + Δ^4 + Δ^5)-sterenes; [b]%C_{28} = 100C_{28}(Δ^2 + Δ^4 + Δ^5)-sterenes/Σ(C_{27}–C_{29})(Δ^2 + Δ^4 + Δ^5)-sterenes; [c]%C_{29} = 100C_{29}(Δ^2 + Δ^4 + Δ^5)-sterenes/Σ(C_{27}–C_{29})(Δ^2 + Δ^4 + Δ^5)-sterenes; [d]Ster/Hop = [Σ(C_{27}–C_{29})(Δ^2 + Δ^4 + Δ^5)-sterenes]/[Σ(C_{29}–C_{32})17α(*H*)21β(*H*)-hopanes + Σ(C_{29}–C_{30})17β(*H*)21α(*H*)-hopanes + Σ(C_{29}–C_{31})17β(*H*)21β(*H*)-hopanes + C_{27}17α(*H*)-hopane + C_{27}17β(*H*)-hopane + Σ(C_{29}–C_{30})-hop-17(21)-enes + C_{27}-hop-17(21)-ene +C_{27}-hop-13(18)-ene]; [e]$C_{30}\beta\beta$/($\beta\beta$+$\alpha\beta$) = C_{30}17β(*H*)21β(*H*)-hopane/(C_{30}17β(*H*)21β(*H*)-hopane + C_{30}17α(*H*)21β(*H*)-hopane). The sterenes were quantified from the *m/z* 215 mass chromatogram, and the hopenes and hopanes from the *m/z* 191 mass chromatogram; [f]not determined due the absence of sterenes and hopanes

Hopanoids are more abundant than steroid biomarkers in the Drmno lignite extracts (Ster/Hop ratio < 0.25; Table V). This result indicates a bacteria-influenced facies and argues for the role of microorganisms in the degradation of plant tissue.

Based on the *m/z* 191 mass chromatogram of the saturated fraction, the hopane composition in all samples is characterized by the presence of 17α(*H*)21β(*H*), 17β(*H*)21α(*H*) and 17β(*H*)21β(*H*) compounds with 27 and 29–31 carbon atoms, with exception of C_{31}17β(*H*)21α(*H*) moretane. Other hopanoid-type constituents of the saturated fraction are C_{27} hop-13(18)-ene, C_{27} hop-17(21)-ene and C_{27}hopan-21-one. Several samples contain $C_{32}\alpha\beta$(*R*)-hopane and C_{30} hop-17(21)-ene (Fig. 4c).

The presence of unsaturated hopenes and the domination of *ββ*-isomers in range C_{27}, C_{29}–C_{30} over *αβ*-hopanes confirm an immature stage of the organic matter. The ratio of 17*β*(*H*)21*β*(*H*) to (17*β*(*H*)21*β*(*H*) + 17*α*(*H*)21*β*(*H*)) C_{30}-hopanes (Table V) is within the limits established for lignite, 0.5–0.7,[50] or even higher, consistent with deposition of the OM in an anoxic to slightly oxic environment.[51]

The C_{27}17*β*(*H*)-hopane and the C_{29}17*β*(*H*)21*β*(*H*)-hopane dominate the distribution of C_{27}–C_{31} *ββ*-homologues (Fig. 4c). The predominance of the short-chain homologues can be interpreted as being indicative of rather oxidizing palaeoconditions, but may also indicate that the precursor hopanoid lipids were functionalized at position 29, such as aminobacteriohopanepentol that is abundant in methanotrophic bacteria (*e.g.*, *Methylococcus capsulatus* or *Methylomonas methanica*).[52] This particular hopanoid functionalized at position 29 cannot, however, be taken as the exclusive precursor of C_{29} hopanes, considering the high sensitivity of the side chains from biologic hopanoids.[53]

The identification of the D-ring monoaromatic hopanes, 7-methyl-3'-ethyl--1,2-cyclopentanochrysene and 4-methyl-24-ethyl-19-norcholesta-1,3,5(10)-triene[10] in the aromatic fraction of all the investigated samples (Fig. 3) suggests partial aromatization of the hopanoids and steroids during diagenesis, in accordance with the aromatization of the diterpenoids and particularly the triterpenoids.

Alkan-2-ones. Based on the *m/z* 58 mass chromatogram of the aromatic fraction (Fig. 4d), *n*-alkan-2-ones were identified in the range C_{25} to C_{35}, with the even C_{26}–C_{30} homologues being absent in several samples. Similar to the distribution of the *n*-alkane, the *n*-alkan-2-ones patterns of the coal samples are dominated by odd long-chain homologues C_{29}–C_{33}. Although the distributions of the *n*-alkanes and the *n*-alkanones are generally similar, two main differences could be seen. First, even C_{26}–C_{30} homologues of *n*-alkan-2-ones are absent in several samples, although *n*-alkanes with the same number of carbons were identified. Secondly, in almost all of the samples, *n*-alkanes have maximum at C_{29}, followed by C_{27}, whereas the most abundant *n*-alkan-2-one is C_{31} followed by C_{33}. The obtained results indicate that *n*-alkan-2-ones probably have few sources: a) the direct contribution of ketones from higher plant waxes, which consist of C_{23}–C_{33} homologues with a significant odd C number predominance and C_{max} at C_{29} or C_{31}; b) microbially mediated *β*-oxidation of the corresponding *n*-alkanes in the sediments or prior to incorporation into the sediments; c) oxidative decarboxylation of *n*-fatty acids and oxidized alcohols as well as elongation of a suitable fatty acid precursor and subsequent decarboxylation, which would yield longer-chain alkanones with a pronounced odd C predominance and C_{27}, C_{29} and C_{31} as major constituents.[26]

In addition to *n*-alkan-2-ones, 6,10,14-trimethylpentadecan-2-one (6,10,14--TMPD-2-one), an isoprenoidal ketone, was also found in half of the studied samples (Fig. 4d). Since pristane was identified in low amounts, it could be supposed that the main pathways of TMPD-2-one formation are bacterial degradation[38] and photosensitized oxidation[54] of free phytol and/or photodegradation of chlorophyll-*a*.[55]

The presence of alkan-2-ones in the lignite extracts confirms microbial activity, assumed also basis on the distribution of hopanoids and angiosperm derived triterpenoids.

CONCLUSIONS

The origin and geological evolution of organic matter of upper Miocene lignites from the Drmno field, Kostolac Basin (Serbia) were evaluated using coal petrology and the composition of biomarkers.

Coal from the Drmno field is typical humic coal. The composition of the biomarkers shows that the peat-forming vegetation dominated by decay resistant gymnosperm plants, followed by prokaryotic organisms and angiosperms. Based on the composition of the saturated and aromatic diterpenoids, it was established that the coal forming plants belonged to the gymnosperm families *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae*, *Phyllocladaceae* and *Pinaceae*.

Peatification was performed in a limnic, neutral to slightly acidic environment. The variations in the maceral and biomarker ratios showed that the lignite seams were formed under variable *Eh* conditions (anoxic to slightly oxic), probably as a result of seasonal drying of the mire. The water column level was lower in coal seam II than in coal seam III during peatification. Changes in the water level also caused vegetation differences in the palaeoplant communities.

Group organic geochemical parameters and biomarker compositions indicate low OM maturity (phase of intensive diagenetic processes). The abundance of hopanoid biomarkers, intensive degradation of the A-ring of triterpenoids followed by aromatization and the presence of alkan-2-ones indicate that the diagenetic changes in the organic matter were mainly governed by bacterial activity, rather than thermal degradation.

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ИЗВОД

ЛИГНИТИ ЛЕЖИШТА ДРМНО (БАСЕН КОСТОЛАЦ): ПОРЕКЛО И ПАЛЕОУСЛОВИ СТВАРАЊА НА ОСНОВУ ПЕТРОГРАФСКИХ И ОРГАНСКО-ГЕОХЕМИЈСКИХ ИСТРАЖИВАЊА

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Циљ рада био је да се утврди порекло и геолошка еволуција лигнита лежишта Дрмно басена Костолац. Примењене су петрографске и органско геохемијске методе. Лигнити лежишта Дрмно су типични хумусни угљеви. Главни извор органске супстанце биле су гимносперме (голосеменице), а затим прокариотски организми и ангиосперме (скривеносеменице). Утврђено је да прекурсорски органски материјал потиче од следећих фамилија гимносперми: *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae*, *Phyllocladaceae* и *Pinaceae*. Таложење и хумификација органске супстанце лигнита одвијали су се у слатководној, неутралној до слабо киселој средини. Узимајући у обзир да се стварање лигнита у лежишту Дрмно одигравало у исто време, претпостављено је да климатски фактор није могао значајније утицати на састав органске супстанце. Разлике у саставу мацерала и биомаркера у испитиваним лигнитима последица су колебања нивоа воденог стуба у средини таложења услед сезонских промена у количини падавина. Ово колебање воденог стуба узроковало је промене како у саставу палеовегетације, тако и у редокс потенцијалу средине таложења (од аноксичне до благо оксичне). Дијагентске промене органске супстанце одвијале су се уз интензивну микробну активност, док је термичка деградација била готово безначајна.

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