Characterisation of lignite lithotypes from the "Kovin" deposit (Serbia) – Implications from petrographic, biomarker and isotopic analysis

DANICA MITROVIĆ[1], NATAŠA ĐOKOVIĆ[1], DRAGANA ŽIVOTIĆ[2],
ACHIM BECHTEL[3], OLGA CVETKOVIĆ[4] and KSENIJA STOJANOVIĆ[5]*

[1]University of Belgrade, Innovation Center of the Faculty of Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia, [2]University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia, [3]Montanuniversität Leoben, Department of Applied Geosciences and Geophysics, Peter-Tunner-Str. 5, A-8700 Leoben, Austria, [4]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoševa 12, 11000 Belgrade, Serbia and [5]University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia

Abstract: Four lignite lithotypes (matrix coal, xylite-rich coal, mixture of matrix and mineral-rich coal and mixture of matrix and xylite-rich coal), originating from the Kovin deposit, were investigated in detail. The paper was aimed to determine the main maceral, biomarker and isotopic (δ^{13}C) characteristics of investigated lithotypes. Based on these results the sources and depositional environment of organic matter in 4 lithotypes were established. These samples were also used as substrates for investigation of the influence of diagenetic alteration on δ^{13}C signatures of biomarkers, as well as for assessment of the most convenient utilization for each lithotype. The investigated lithotypes differ in accordance with the composition of huminite macerals. Xylite-rich coal notably distinguishes from other lithotypes beacuse of the highest content of conifer resins *vs.* epicuticular waxes. The mixture of matrix and mineral-rich coal is characterised by the greatest contribution of algae and fungi and the most intense methanotrophic activity at the time of deposition. In all coal lithotypes diagenetic aromatisation influenced isotopic composition of individual biomarkers. Xylite-rich coal has the poorest grindability properties. However, this coal lithotype is the most suitable for fluidized bed gasification, whereas the mixture of matrix and mineral-rich coal has the lowest applicability for this process. The calorific value decreases in order: xylite-rich coal > matrix coal > mixture of matrix and xylite-rich coal > mixture of matrix and mineral-rich coal. The increase of organic carbon content and calorific value is controlled by the increase of contribution of wood vegetation *vs.* herbaceous peat-forming plants, as well as by stability of water table during peatification.

Keywords: lignite; lithotype; Kovin deposit; macerals; biomarkers.

INTRODUCTION

The lignite lithotypes can be macroscopically determined based on the differences of the macropetrographic composition, structure, colour and texture of the sample. The lithotype classification system for lignite (soft brown coal) proposed by the International Committee for Coal and Organic Petrology (ICCP)[1] distinguishes: xylite-rich coal, matrix coal, charcoal-rich coal and mineral-rich coal. Xylite-rich coal consists of a layered or lenticular concentration of xylites, representing at least 90 % of the volume. Xylites include all fragments with well-preserved wood structure with a diameter of at least 1 cm. Smaller fragments are classified as humic detritus.[2–4] Matrix coal consists of fine humic particles (detritus), forming a more or less homogeneous macroscopic mass. As a lithotype, it can contain up to 10 % volume of other components. Charcoal-rich coal (or fusain coal) is represented by charred organic matter (OM) and is rarely found in larger amounts in lignite deposits. Mineral-rich coal consists of components of different lithotypes and mineral matter. The inorganic materials are typically represented by quartz, clay, carbonates and sulphides.[5] Mixture of matrix and xylite--rich coal and mixture of xylite-rich and matrix coal belong to the complex lithotypes, built mainly of humic detritus and xylites. The former is dominated by humic detritus, whereas the latter is dominated by xylites, which should account for more than half of the xylites and humic detritus occurring in the specified layer.[3]

Macropetrographic features of lithotypes and their applicability resulted from their composition and the degree of transformation during peat genesis and diagenesis.[3] For establishing of sources of lignite OM and its diagenetic alteration, micropetrographic (maceral) analysis and biomarker composition are the most useful.

Maceral analysis facilitates detection of the complex preserved structures of the parent organic material in the insoluble organic matter (kerogen) such as: plant tissues, represented by huminite group macerals (textinite, ulminite, densinite, atrinite, gelinite and corpohuminite); lipoidal plant components and protozoa residues, represented by liptinite group macerals (sporinite, cutinite, resinite, suberinite, alginite, liptodetrinite, bituminite, chlorophylinite, exudatinite); and the products of their humification and coalification. The maceral analysis is also very useful for the detection of the charred components in lignite OM, represented by inertinite group (inertodetrinite, semifusinite, fusinite, macrinite, micrinite, funginite).[6] However, the compositions and therefore technological properties of individual macerals differ even when the are from the same maceral group, as it was described in numerous investigations.[4,6–11]

Unlike maceral analysis, biomarker analysis is related to extractable OM (bitumen) and enables to identify numerous individual compounds with strong resemblance in structure of their parent organic molecules in living organisms. Also, biomarker assemblages provide important information about depositional

environment of the OM. However, biomarker interpretation may be complicated due to the multiple geneses.[12,13] Compound-specific carbon isotopic measurements represent a powerful tool to overcome this problem, allowing us to establish the relationship between biological precursors and their diagenetic products.[14–18]

The paper was aimed to determine the main maceral, biomarker and isotopic ($\delta^{13}C$) characteristics of four lignite lithotypes (matrix coal, xylite-rich coal, mixture of matrix and mineral-rich coal and mixture of matrix and xylite-rich coal). Lignite originating from the Kovin deposit was used as a substrate. Based on a comprehensive study, the sources of OM and depositional environment of 4 lignite lithotypes have been reconstructed. Alongside, the data from maceral analysis were served for assessment of the most convenient utilization of each lithotype, whereas the results of the isotopic analysis were used for the investigation of the influence of diagenetic alteration on $\delta^{13}C$ signatures of biomarkers.

EXPERIMENTAL

The details related to sampling locations and sample preparation are given in Supplementary material to this paper.

Two internal standards, deuterated *n*-tetracosane for the aliphatic fraction and 1,1'-binaphthyl for the aromatic fraction were used. Standards diluted in *n*-hexane in concentrations of 10 or 1 mg/cm^3, depending on the weight of the respective fractions, were added to obtain a sample/standard mass ratio of 100:1. Final concentration of the fractions in the vials, prior to gas chromatography-mass spectrometry (GC–MS) analysis, was set to 1 mg/cm^3, by dilution with *n*-hexane. Saturated and aromatic fractions were analysed by GC–MS. A gas chromatograph Agilent 7890A GC (HP5-MS capillary column, 30 m×0.25 mm, 0.25 μm film thickness, Helium carrier gas 1.5 cm^3/min) coupled to a 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, and the final temperature of 310 °C was maintained for an additional 25 min. Individual compounds were identified from the total ion current (*TIC*) by the comparison of mass spectra and retention times with literature data. Absolute concentrations of individual biomarkers were calculated using peak areas (GCMS data analysis software) from the *TIC*s of aliphatic and aromatic fractions in relation to that of internal standards. The concentrations were normalized to the total organic carbon (*TOC*) content. The same quantification method was used in numerous investigations.[19–21]

Carbon isotope determination of individual biomarkers in selected samples, representing all lithotypes was performed using a Trace GC instrument attached to a ThermoFisher Delta-V isotope ratio mass spectrometer *via* a combustion interface (GC Isolink, ThermoFisher). DB--5MS fused silica column (30 m length; i.d. 0.25 mm; 0.25 μm film thickness) was used. The oven temperature gradient was programmed from 70 to 300 °C at 4 °C/min, followed by an isothermal period of 15 min. Helium (flow 1.2 cm^3/min) was used as carrier gas. For calibration, CO_2 was injected at the beginning and end of each analysis. Stable isotope ratios are reported in delta notation ($\delta^{13}C$)[22] relative to the Vienna-Pee Dee Belemnite (V-PDB) standard ($\delta^{13}C = ((^{13}C/^{12}C)\text{sample}/(^{13}C/^{12}C)\text{standard} - 1))$. Delta notation is expressed in parts per thousand (‰). The analytical error was better than 0.2 ‰.

Since *n*-alkanes were not separated from polycyclic biomarkers by molecular sieves, due to the possible superimposition of *n*-alkanes and hopanoids[23] which show notably different $\delta^{13}C$ values, prior to isotopic analysis, abundances and mass spectra of these biomarkers, as well as of all individual compounds, whose $\delta^{13}C$ were determined, were carefully checked. Based on these results, $\delta^{13}C$ was not measured for all individual biomarkers interpreted by isotopic signatures here, in all selected representative lithotypes. Namely, the $\delta^{13}C$ was measured only for those biomarkers present in certain selected sample (please see the Supplementary Material) in adequate amount, which showed at the same time sufficiently pure mass spectra. Moreover the used instrument allows manual integration of the peaks, and therefore even peaks which have close retention times could be separated and measured. Accordance between measured $\delta^{13}C$ values of individual biomarkers and those reported in literature,[16,18,24–28] indicated that selection of samples based on above mentioned characteristics was correct and that manual peak integration was done accurately.

However, despite of the purity of the mass spectra of hopanoids, the interpretation should be taken with certain caution due to the generally low concentration of free hopanoids, since the part of these biomarkers, particularly in immature lignite OM, is still bounded into macro-molecular matrix and occurred as functionalized compounds (*e.g.*, hopanoic acids and alcohols).[29,30]

RESULTS AND DISCUSSION

Maceral composition

Huminite macerals predominate in all lithotypes (Tables S-II and S-III of the Supplementary material). This result indicates the typical humic coals. The content of total liptinites was similar in all lithotypes, whereas the average content of total inertinites was the lowest in the xylite-rich coal (XC) and the highest in the mixture of matrix and mineral-rich coal (MMiC), as given in Table S-II.

The pronounced differences were observed in the composition of the huminite group macerals. Ulminite, followed by textinite or densinite is the dominant huminite maceral in XC (with exception of one sample, 79/04 where textinite prevailed; Tables S-II and S-III). Densinite predominates, whereas ulminite was the second most abundant huminite maceral in three other lithotypes. Since ulminite and particularly densinite have better grindability properties than textinite,[10,31] it can be supposed that XC has poorer susceptibility to grinding. Gelinite and corpohuminite are present in all lithotypes in similar amounts (Table S-II). Due to the substantial fragility, the gelified macerals represent an undesirable component. An important conclusion, which avoids non-rational utilization and consequent cost, is that all studied lithotypes from the Kovin deposit are unsuitable for coal briquetting according to Gelification of coal, ΣG higher than 20 vol. % (Tables S-IV and S-V of the Supplementary material).[10]

The composition of liptinite macerals was similar in all lithotypes, characterising by prevalence of sporinite and liptodetrinite (Tables S-II and S-III). Relatively low content of liptinite in all samples is unfavorable, since net calorific value is proportional to content of this maceral group.[10] On the other hand, the

relatively low content of inertinite macerals in all lignite lithotypes, with the exception of MMiC is considered as favourable because inertinite generally hinders grinding, briquetting and drying of lignite.[10,11] Inertodetrinite prevailed among inertinite macerals in all lithotypes. However, elevated contents of fusinite and semifusinite were observed in MMiC (Tables S-II and S-III).

The results of maceral analysis were applied for an assessment of usefulness for the fluidized bed gasification according to ternary diagram (Fig. S-2 of the Supplementary material) proposed by Bielowicz.[10] This diagram shows that XC is the most suitable for gasification, whereas MMiC demonstrated the lowest applicability.

Diagrams based on maceral indices[32,33] gelification Index (*GI*) *vs*. tissue preservation index (*TPI*) and groundwater Index (*GWI*) *vs*. vegetation Index (*VI*) (Table S-IV) are shown in Fig. S-3 of the Supplementary material. XC was formed in dry to wet forest swamp (slightly domed ombrotrophic to mesotrophic conditions), whereas the matrix coal (MC) and MMiC originated from a topogenous fresh water peat mire with open water areas (limnic conditions). The mixture of matrix and xylite-rich coal (MXC) plotted in between matrix and xylite-rich coal, however closer to the former, indicating bush moor. The values of *VI* suggest that the contribution of arboreal vegetation relative to the impact of herbaceous peat-forming plants decreases in the following order: XC > MC > MXC > MMiC (Tables S-IV and S-V). Consistently the values of *TPI* showed the same trend of OM preservation. Based on *GI* and *GWI*, the fluctuations of water level were most pronounced during peatification of MMiC and MXC. Therefore, the lower average *TPI* for these two coal lithoptypes (Table S-IV) is probably associated with an unstable water table which may have caused increased tissue degradation because of possible aeration and oxidation of OM.[34]

Bulk organic geochemical parameters

Total organic carbon (*TOC*) was the highest in XC and lowest in MMiC (Table S-IV). The gross and net calorific value (dry basis) of the samples ranges from 15.7 to 28.3 MJ kg^{-1} and from 14.3 MJ to 27.2 MJ kg^{-1}, respectively (Tables S-IV and S-V), which is in range for the rational utilization of lignite in thermal power plants (TPP) recommended by American Lignite Council.[35] Moreover, all lithotypes have higher net calorific values than recommended for ex-Yugoslavia (8.89 MJ kg^{-1}).[36] The significant positive correlation between calorific value and *TOC* (Table S-V) is observed (correlation coefficient, $r = 0.94$), as expected, and the average calorific values of coal lithoptypes decrease in the same order as the average values of *TOC* (Table S-IV). The good accordance between maceral indices, *TOC* and calorific value (Table S-IV) indicates that the increase of *TOC* content and consequently the calorific value is controlled by the increase of the impact of wood vegetation *vs*. herbaceous peat-forming plants, as well as

by the stability of water table. As expected, contents of ash and mineral matter showed the trend opposite from *TOC* and the calorific value (Tables S-II and S--IV). Sulphur content has an uniform range for all coal lithotypes. Generally low to moderate content of sulphur (0.21–4.40 %; Tables S-IV and S-V) implies the deposition of OM in fresh water environment. The content of bitumen, representing the extractable OM is lower in XC than in other lithotypes probably due to the greater impact of arboreal vegetation. Bulk composition of bitumen is uniform for all lithotypes and characterised by sharp prevalence of asphaltenes + *NSO*-compounds over saturated- and aromatic hydrocarbons, as expected for the immature terrestrial organic material (Tables S-IV and S-V).

Molecular composition of the organic matter

General characteristics. Diterpenoids are the most abundant hydrocarbons in all lithotypes, prevailing over *n*-alkanes, hopanoids, non-hopanoid triterpenoids and steroids (Figs. S-4 and S-5; Tables I and S-VI of the Supplementary material). However, the proportion of total diterpenoids (related to sum of total quantified compounds) was the highest in XC. MC, MMiC and MXC have high content of *n*-alkanes. XC notably differs from the other lithotypes according to the highest diterpenoids/*n*-alkanes ratio (Table I), which indicates the contribution of conifer resins *vs.* epicuticular waxes. The content of total hopanoids is more uniform than the content of *n*-alkanes, showing slightly elevated values in MC and MXC, consistent with elevated *GI* values (Tables I and S-IV). Non-hopanoid triterpenoids are present in the low amount, being the lowest in XC, consistent with formation in the forest swamp (Fig. S-3). The ratio of diterpenoids to the sum of di- and triterpenoids, *Di*/(*Di+Tri*) exhibits high and uniform ratios for all lithotypes (Tables I and S-VI), indicating prevalence of gymnosperms (conifers) over angiosperms. Predominance of gymnosperms over angiosperms derived OM in matrix lithotypes possibly implies significant input of needle leaves,[37] consistent with high content of *n*-alkanes (Table I).

Diterpenoids and triterpenoids with non-hopanoid skeleton. Among the individual diterpenoids no specific differences were observed, *e.g.*, pimarane and particularly 16α(H)-phyllocladane are dominant by far in the saturated fraction, whereas simonellite and dehydroabietane are the major diterpenoid constituents of aromatic fraction of all investigated lithotypes (Figs. S-4 and S-5 of the Supplementary material). High amount of 16α(H)-phyllocladane indicates that the lignite forming plants belonged to the conifer families *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae* and *Phyllocladaceae*. The abundant pimarane suggests *Pinaceae*, *Taxodiaceae* and *Cupressaceae*.[12,38,39]

The average δ^{13}C values of beyerane, pimarane and 16α(H)-phyllocladane for lignite lithotypes differ up to 1 ‰ (Tables II and S-VII of the Supplementary material) suggesting similar conifer sources. In all lithotypes average δ^{13}C values

TABLE I. Contents of biomarkers, μg (g TOC)$^{-1}$ and values of biomarker ratios of lignite lithotypes; values of parameters for individual samples are given in Table S-VI of the Supplementary material; Di – diterpenoids; Tri – non-hopanoid triterpenoids

Parameter	Matrix coal (MC)				Xylite-rich coal (XC)				Mixture of matrix and mineral-rich coal (MMiC)				Mixture of matrix and xylite-rich coal (MXC)			
	Mean	Max.	Min.	SD	Mean	Max.	Min.	SD	Mean	Max.	Min.	SD	Mean	Max.	Min.	SD
Di[a]	1363.4	3463.6	343.1	1215.4	1015.6	1986.9	286.7	711.7	994.1	1973.1	235.9	499.6	1345	2934	390	839.6
Tri[b]	112.5	206.6	59.4	62.0	75.2	131.9	49.6	29.3	127.3	277.5	15.6	76.3	149.4	318.2	30.4	94.5
n-Alkanes	489.0	708.2	149.2	210.8	192.4	300.0	62.4	85.5	431.0	1076.7	104.9	288.0	535.6	1483	248	435.3
Hopaoids	229.9	417.5	139.6	93.4	190.6	499.9	93.6	145.9	189.2	355.9	53.7	104.9	225.8	322.9	117.3	84.3
Steroids	23.7	45.5	9.2	12.2	24.0	54.8	10.5	15.7	18.5	33.4	3.5	9.8	20.6	35.1	8.8	8.3
Proportion of Di	0.5	0.8	0.3	0.2	0.6	0.9	0.4	0.2	0.6	0.8	0.5	0.1	0.6	0.8	0.3	0.2
Di/n-alkanes	3.2	7.7	0.6	2.8	8.4	31.8	1.1	10.8	3.4	11.0	1.2	3.5	3.8	10.7	0.7	3.5
$Di/(Di+Tri)$	0.9	1.0	0.7	0.1	0.9	1.0	0.8	0.1	0.9	1.0	0.8	0.1	0.9	1.0	0.7	0.1
Aromatic Di	162.7	383.9	56.5	116.9	185.9	481.6	35.7	176.7	204.2	384.7	98.0	111.5	192.1	408.9	135.8	97.1
Perylene	8.5	16.6	2.4	5.6	6.4	18.2	1.9	5.6	14.3	25.0	0.6	8.9	13.0	23.2	3.6	7.4

decrease in the following order: beyerane > pimarane > 16α(H)-phyllocladane (Fig. S-6a of the Supplementary material). Considering that the isotopic differences evident at *TOC* level are extend to the individual hydrocarbons that are produced from the resins,[16] slightly lower average δ^{13}C values of beyerane in XC and MMiC can be attributed to the greater impact of *Cupressaceae*. Somewhat lower average δ^{13}C values of pimarane in these two lignite lithotypes can be related to greater impact of both, *Cupressaceae* and *Pinaceae* (Fig. S-6a; Table II), since it was shown that these two families have more negative $\delta^{13}C$ values than *Araucariaceae* and *Taxodiaceae*.[40]

TABLE II. The δ^{13}C values of individual diterpenoids and non-hopanoid triterpenoids of lignite lithotypes; values of parameters for individual samples are given in Table S-VII of the Supplementary material; A – 24,25-dinorlupa-1,3,5(10)-triene; B – 2,2,4a,9-tetramethyl--1,2,3,4,4a,5,6,14b-octahydropicene

Lithotype	Value	Beyer-ane	Pima-rane	16α(H)--Phyllo-cladane	Dehyd-roabi-etane	Simon-ellite	Retene	A	B
Matrix coal	Mean	–25.8	–26.1	–26.8	–26.72	–27.1	–28.2	–28.4	–29.2
(MC)	Max.	–25.1	–25.7	–25.9	–25.53	–25.9	–27.6	–27.6	–28.5
	Min.	–27.0	–27.0	–27.4	–27.20	–28.1	–29.3	–29.2	–30.3
	SD	0.7	0.5	0.5	0.63	0.8	0.8	0.7	0.8
Xylite-rich	Mean	–26.2	–26.7	–26.8	–26.83	–27.3	–28.8	–28.9	–29.6
coal (XC)	Max.	–25.3	–25.9	–26.3	–26.35	–26.6	–27.5	–28.1	–28.7
	Min.	–27.3	–27.5	–27.8	–27.54	–28.2	–30.8	–30.3	–30.0
	SD	0.7	0.6	0.6	0.44	0.7	1.4	0.7	0.6
Mixture of	Mean	–26.1	–26.6	–27.1	–26.18	–26.6	–28.4	–28.7	–29.2
matrix and	Max.	–25.6	–25.6	–26.7	–25.16	–25.2	–28.3	–27.9	–27.9
mineral-rich	Min.	–26.9	–27.4	–27.3	–27.21	–28.4	–28.5	–29.3	–30.5
coal (MMiC)	*SD*	0.7	0.9	0.3	0.86	1.2	0.2	0.7	1.3
Mixture of	Mean	–25.9	–26.0	–26.6	–26.58	–27.0	–28.6	–28.9	–29.5
matrix and	Max.	–25.7	–25.4	–26.2	–25.81	–26.2	–28.3	–27.4	–27.8
xylite-rich	Min.	–26.0	–26.5	–26.9	–27.05	–27.5	–28.9	–29.7	–30.7
coal (MXC)	*SD*	0.1	0.5	0.4	0.51	0.6	0.5	1.1	1.5

Dehydroabietane, simonellite and retene belong to aromatic abietane type diterpenoids which differs from pimarane (pimarane skeleton) and particularly from tetracyclic diterpenoids, beyerane and 16α(H)-phyllocladane. Abietanes are the most widespread class of diterpenoids, being identified in all conifer families with exception of *Phyllocladaceae*.[12] The average δ^{13}C values of dehydroabietane, simonellite and retene are similar to average δ^{13}C values of saturated diterpenoids, confirming the common conifer origin. The average δ^{13}C values show the decreasing trend with the increasing of aromatisation (Fig. S-6a; Tables II and S-VII of the Supplementary material).

This result is in agreement with the earlier investigations, that showed that the aromatised molecules are generally depleted in ^{13}C by about 1–2 ‰ relative to their presumed precursors.[27,41] Very close average $\delta^{13}C$ values of dehydro-abietane and simonellite indicate the direct precursor-product connection (Fig. S-6a; Table II). The average $\delta^{13}C$ values of retene differ more (Fig. S-6a; Table II), which probably results from the possibility of different formation pathways of retene from dehydroabietane,[39,42–44] confirming that the diagenetic aromatisation influences $\delta^{13}C$.

Average $\delta^{13}C$ values of dehydroabietane in MC, XC and MXC are depleted in ^{13}C in comparison to those of saturated diterpenoids, whereas MMiC showed opposite trend (Fig. S-6a; Table II). On one hand, this result can be attributed to the wider range of abietane producing conifers.[12] On the other hand, considering that in immature OM, the aromatisation of biomarkers is mediated by microorganisms, but also favoured by the catalytic influence of clay minerals, the elevated $\delta^{13}C$ values of dehydroabietane in MMiC can result from different bacterial communities and/or clay catalytic processes. This latter assumption is in agreement with the highest content of aromatic diterpenoids in MMiC (Tables I and S-VI).

The non-hopanoid triterpenoids are present in low amounts in all lithotypes (Tables I and S-VI). In the saturated fraction they consist exclusively of des-A--degraded compounds (Fig. S-4 of the Supplementary material). In the aromatic fraction both, pentacyclic, *i.e.*, non-degraded and des-A-degraded compounds were identified (Fig. S-5 of the Supplementary material). Among the non-hopanoid triterpenoids, des-A-lupane was the most abundant in the saturated fraction, whereas 24,25-dinorlupa-1,3,5(10)-triene prevailed in the aromatic fraction of all samples (Figs. S-4 and S-5). The predominance of lupane derivatives indicates that *Betulaceae* was one of the main angiosperm sources.[45,46]

Due to the low concentration of the aromatic non-hopanoid triterpenoids, $\delta^{13}C$ was measured at very limited number of the samples. Average $\delta^{13}C$ of angiosperm derived aromatic non-hopanoid triterpenoids are 2–3 ‰ depleted in ^{13}C compared to the aromatic diterpenoids (gymnosperm origin) (Fig. S-6a and b; Table II), consistent with report of Bechtel *et al.*,[14] Tuo *et al.*[18] and Schoell *et al.*[27] Comparison of $\delta^{13}C$ values of 24,25-dinorlupa-1,3,5(10)-triene and its aromatised counterpart 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene indicated slight depletion in ^{13}C during aromatisation. The obtained result is consistent with observation for aromatisation of diterpenoids (Fig. S-6 a,b; Table II).

Gymnosperms are more resistant to degradation than angiosperms. However, the positive correlation between *TPI* (Table S-V) and the content of diterpenoids (Table S-VI) is observed only for MMiC ($r = 0.67$), indicating that in conditions of topogenous fresh water peat mire with open water areas, the contribution of gymnosperms (most probably from the surroundings) is the dominant factor controlling OM preservation. For all other lithotypes, the absence of correlation

between *TPI* and content of diterpenoids suggest that *TPI* was predominantly controlled by relative height of the ground water table (humidity) rather than by input of decay-resistant conifers. Although between *TPI* and content of non-hopanoid triterpenoids negative correlation could be expected, this is not observed here for any of lithotypes (Tables S-V and S-VI). The obtained result can be attributed to low concentration of this biomarker class (Tables I and S-VI) and already discussed impact of *Betulaceae*, which is characterised by relatively high tree density, being therefore resistant to degradation.

n-Alkanes. The *n*-alkane patterns of all lithotypes were dominated by long-chain odd homologues (C_{27}–C_{31}) maximizing at *n*-C_{27} or *n*-C_{29} (Fig. S-4) and showed expressed odd over even predominance (carbon preference index, *CPI*; Tables S-VIII and S-IX of the Supplementary material), consistent with peat formation from terrigenous plants.

All lithotypes are characterised by prevalence of long-chain (C_{26} to C_{35}) *n*-alkanes. However, the proportion of short- (C_{15} to C_{20}) and medium- (C_{21} to C_{25}) chain homologues was higher in MMiC indicating slightly higher contribution of *n*-alkanes derived from bacteria and algae (Table S-VIII of the Supplementary material).

The $\delta^{13}C$ values of C_{25} to C_{33} odd *n*-alkanes range from –27.2 to –32.0 ‰ (Fig. S-6c; Tables S-X and S-XI of the Supplementary material), indicating a source, corresponding to the lipid carbon pool of C_3 higher plants.[47] Marked differences between $\delta^{13}C$ values of C_{27}–C_{33} *n*-alkanes and C_{25} *n*-alkane were not observed (Fig. S-6c; Table S-X), indicating that later mainly originated from higher plants. However, in all lithotypes C_{25} *n*-alkane is slightly more enriched in ^{13}C than odd *n*-alkane homologues (C_{27}–C_{33}). This result can be attributed to the slight impact of the emergent aquatic macrophytes. For all homologues (with exception of *n*-C_{31}), xylite-rich coal showed the most positive values (Fig. S-6c; Table S-X). This result is consistent with the highest relative content of woody vegetation from diterpenoids. Depletion in ^{13}C of C_{29} and C_{33} odd *n*-alkanes in other lithotytpes in comparison to XC imply greater influence of herbaceous plants,[48] consistent with lower *TPI* and *VI* ratios (Table S-IV). Elevated average $\delta^{13}C$ values of C_{29} and C_{31} *n*-alkanes for MMiC (Fig. S-6c; Table S-X), having the lowest *TPI* and *VI* (Table S-IV), can be attributed to the greater impact of fungi, since it was showed that fungi are relatively less depleted in the ^{13}C isotope, and that fungal spores generally contain C_{14}-C_{37} *n*-alkanes, often maximizing at C_{27}, C_{29} and C_{31}.[49,50] This assumption is supported by the highest content of perylene in MMiC (Table I).

Hopanoids and steroids. The hopane composition in the saturated fraction is characterised by the presence of 17α(H)21β(H), 17β(H)21α(H) and 17β(H)21β(H) compounds with 27 and 29-32 carbon atoms. Other hopanoid type constituents are unsaturated hopenes: C_{27} neohop-13(18)-ene, C_{27} hop-17(21)-

-ene, C_{28} neohop-13(18)-ene, C_{30} hop-17(21)-ene and C_{30} neohop-13(18)-ene. The aromatic hopanoids with one to four aromatic rings consist of series of orphan aromatic hopanoids bearing an ethyl group at C-21 (Figs. S-5 and S-7 of the Supplementary material). Among the aromatic hopanoids, D-ring monoaromatic hopane prevailed in all samples, being even the most abundant compound in the aromatic fraction of several samples (Fig. S-5).

The $\delta^{13}C$ values of individual hopanoids C_{30} hop-17(21)-ene, $C_{27}17\beta(H)$-hopane and $C_{29}17\beta(H)21\beta(H)$-hopane (in range –36.8 to –51.4; Fig. S-6d; Tables S-X and S-XI) indicate the contribution of chemoautotrophic- and methanotrophic-bacteria.[15,41,51] For mentioned hopanoids a decrease of average $\delta^{13}C$ values is observed in order: XC > MXC > MC > MMiC (Fig. S-6d; Table S-X), suggesting the decreasing methanotrophic activity (active methane cycle at the time of deposition) from forest swamp to topogenous fresh water peat mire.

Although measured at limited number of samples, due to the low concentration, the $\delta^{13}C$ values of $C_{31}17\alpha(H)21\beta(H)22(R)$-hopane are relatively uniform and notably distinct from $\delta^{13}C$ values of the other hopanoids, ranging from –24.2 to –27.5 ‰ (Tables S-X and S-XI). The observed $\delta^{13}C$ range indicates heterotrophic bacteria that consumed higher-plant-derived OM.[16,26]

The average concentrations of individual hopanoids (Table S-VIII) imply the predominance of C_{30} hop-17(21)-ene in all lignite lithotypes. However, in MC, MMiC and MXC the second most abundant hopanid was $C_{27}17\beta(H)$-hopane, whereas XC is characterised by elevated content of $C_{31}17\alpha(H)21\beta(H)22(R)$-hopane. Since isotopic composition (Table S-X) suggested that the later mostly originated from heterotrophic bacteria, it can be concluded that this type of bacteria had greater impact on the peatification of xylite-rich coal.

The typical feature of all lithotypes is prominent C_{28} 28,30-bisnorneohop13-(18)-ene (C_{28} neohop-13(18)-ene, Table S-VIII). Considering lignites, to the best of our knowledge C_{28} neohop-13(18)-ene was only reported in the sediments and fossil conifer extracts from the Upper Eocene Zeitz formation in the Schleenhain open pit near Borna (Saxony, Germany)[42] and in samples from the Miocene Tokiguchi Porcelain Clay Formation at the Onada mine, central Japan (although in that case without the defined position of double bond).[52] The $\delta^{13}C$ values of C_{28} neohop-13(18)-ene range from –33.6 to –36.6 ‰ and differ from $\delta^{13}C$ values of other hopanoids (Fig. S-6d; Tables S-X and S-XI). The obtained values can imply that C_{28} neohop-13(18)-ene is sourced from a certain type of chemoautotrophic bacteria.[15,41,51] The activity of chemoautotrophic bacteria during diagenesis has already been assumed based on the $\delta^{13}C$ values of $C_{27}17\beta(H)$- and $C_{29}17\beta(H)21\beta(H)$ hopanes. C_{28} neohop-13(18)-ene showed the same $\delta^{13}C$ trend in studied lignite lithotypes, as it was observed for other hopanes, with a single difference, that average $\delta^{13}C$ values for XC and MXC were almost equal (Fig. S-6d; Table S-X).

In some earlier investigations,[17,53] it was supposed that C_{28} neohop-13(18)--ene could be a logical direct precursor of series of orphan aromatic hopanoids (containing an ethyl group at C-21) by the progressive aromatisation (Fig. S-7). In order to check this assumption $\delta^{13}C$ values of C_{28} neohop-13(18)-ene and orphan aromatic hopanoids (D-ring monoaromatic hopane and ABCD-ring tetra-aromatic hopane; Fig. S-7) were measured, for the first time in the same series of samples, to the best of our knowledge. D-ring monoaromatic hopane has similar average $\delta^{13}C$ values as C_{28} neohop-13(18)-ene, particularly for XC and MXC (Fig. S-6d; Table S-X) confirming that C_{28} neohop-13(18)-ene can be an important precursor of orphan aromatic hopanoids. However the greater range of $\delta^{13}C$ values of D-ring monoaromatic hopane than of C_{28} neohop-13(18)-ene (Fig. S--6d; Tables S-X and S-XI) is in accordance with the well known fact that the degradation of a side chain and aromatisation of other hopanoids may also result in the formation of aromatic hopanes. It is interesting that the ABCD-ring tetra-aromatic hopane has higher average $\delta^{13}C$ value in comparison to D-ring mono-aromatic hopane for all lithotypes (Fig. S-6d; Table S-X) which is consistent with the observation that some type of aromatics can be enriched in ^{13}C relative to their precursors.[27] Recently, Liao *et al.*[54] also established that aromatisation of hopanoids is followed by ^{13}C isotopic enrichment.

The contents of total steroids were low and relatively uniform (Tables I and S-VI) which could be explained by the fact that in the investigated samples steroids mostly originate from higher plants, which contain very low amount of these biomarkers. Therefore the determination of isotopic composition was impossible. The steroid biomarkers in all lithotypes are represented by C_{27}–C_{29} (Δ^4-, Δ^2- and Δ^5-) sterenes and A-ring monoaromatic sterane. Distribution of sterenes in all lithotypes was notably dominated by C_{29} homologues (Tables S-VIII and S-IX), consistent with peat formation from terrigenous plants. However, average proportion of C_{27} sterenes was the highest in MMiC (Table S-VIII) indicating the higher contribution of algae. This result is in accordance with the higher proportion of short-chain *n*-alkanes in MMiC (Table S-VIII). In addition, this coal lithotype also contains slightly higher average proportion of C_{28} sterenes (Table S-VIII), indicating greater contribution from fungi, that has already been assumed, based on average $\delta^{13}C$ values of C_{29} and C_{31} *n*-alkanes (Fig. S-6c; Table S-X), as well as by the highest content of perylene (Table I).

CONCLUSION

The coal lithotypes differ according to the composition of huminite macerals. Ulminite, followed by textinite or densinite is the dominant huminite maceral in XC, whereas densinite followed by ulminite prevailed in three other lithotypes, indicating that XC has poorer susceptibility to grinding. On the other hand, XC is the most suitable for fluidized bed gasification, whereas MMiC has the

lowest applicability. All studied lithotypes from the Kovin deposit are unsuitable for coal briquetting, but meet requirements for the rational utilization in thermal power plants.

XC was formed in forest swamp, whereas MC and MMiC originated from a topogenous fresh water peat mire with open water areas. MXC was formed in the bush moor. Main sources of OM in all lithotypes were gymnosperms (conifers). The predominance of gymnosperms over angiosperms derived OM in the lithotypes comprising matrix coal implies significant input of needle leaves, consistent with high content of *n*-alkanes. Lignite forming plants belonged to the gymnosperm families *Taxodiaceae*, *Cupressaceae*, *Araucariaceae*, *Phyllocladaceae* and *Pinaceae*. MC and MXC are characterised by the slightly greater impact of *Taxodiaceae* and *Araucariaceae*, whereas two other lithotypes had greater impact of *Cupressaceae* and *Pinacea.* In all studied lithotypes *Betulaceae* was the main angiosperm source. XC notably differs from the other lithotypes because of the highest contribution of conifer resins *vs.* epicuticular waxes. MMiC is characterised by the greatest contribution of algae and fungi. *TOC* content and consequently calorific value decreased in the following order: XC > MC > MXC > MMiC, indicating that the increase of the impact of wood vegetation (mostly conifers) *vs*. herbaceous peat-forming plants and more stable water table during peatification in the forest swamp, in comparison to topogenous water peat mire, positively influences these parameters.

Diagenetic alteration of all lignite lithotypes was governed by chemoautotrophic-, methanotrophic- and heterotrophic-bacteria. Methanotrophic activity decreases in the following order: XC > MXC > MC > MMiC. On the other hand, heterotrophic bacteria had the greatest influence on peatification of XC. These results show that activity of methanotrophs is greater in topogenous water peat mire, whereas heterotrophic bacteria more affect OM in forest swamp.

In all coal lithotypes the diagenetic aromatisation influenced isotopic composition of individual biomarkers. The aromatisation of diterpenoids and non-hopanoid triterpenoids may result in a depletion of ^{13}C, whereas aromatisation of hopanoids is followed by ^{13}C enrichment. Direct precursor-product relationship between C_{28} neohop-13(18)-ene and the series of orphan aromatic hopanoids was confirmed for the first time in all studied lithotypes.

SUPPLEMENTARY MATERIAL

Experimental data and theoretical models are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

И З В О Д

КАРАКТЕРИЗАЦИЈА ЛИТОТИПОВА ЛИГНИТА ИЗ ЛЕЖИШТА „КОВИН" (СРБИЈА) НА ОСНОВУ ПЕТРОГРАФСКЕ, БИОМАРКЕРСКЕ И ИЗОТОПСКЕ АНАЛИЗЕ

ДАНИЦА МИТРОВИЋ[1], НАТАША ЂОКОВИЋ[1], ДРАГАНА ЖИВОТИЋ[2], АСHIM BECHTEL[3], ОЛГА ЦВЕТКОВИЋ[4]
и КСЕНИЈА СТОЈАНОВИЋ[5]

[1]Универзитет у Београду, Иновациони центар Хемијског факултета, Студентски трг 12–16, 11000 Београд, [2]Универзитет у Београду, Рударско-геолошки факултет, Ђушина 7, 11000 Београд, [3]Montanuniversität Leoben, Department of Applied Geosciences and Geophysics, Peter-Tunner-Str. 5, A-8700 Leoben, Austria, [4]Универзитет у Београду, Центар за хемију, ИХТМ, Његошева 12, 11000 Београд и [5]Универзитет у Београду, Хемијски факултет, Студентски трг 12-16, 11000 Београд

Четири литотипа лигнита (барски, ксилитни, мешавина барског и ксилитног и мешавина барског и земљастог угља) из лежишта Ковин су детаљно проучавани. Циљ рада био је да се одреде главна мацерална, биомаркерска и изотопска својства испитиваних литотипова. На основу тих резултата утврђени су порекло и средина таложења органске супстанце за ова 4 литотипа. Ови узорци су такође послужили као супстрати за испитивање утицаја дијагенетских промена на δ^{13}C вредности биомаркера, као и за процену најпогодније примене за сваки од литотипова. Литотипови се разликују према саставу мацерала хуминитске групе. Ксилитни угаљ се разликује од осталих литотипова по највећој заступљености смола голосеменица у односу на епикутикуларне воскове. Највећи допринос гљива и алги запажен је у органској супстанци мешавине барског и земљастог угља. Формирање овог литотипа било је праћено најинтензивнијом метано-трофном активношћу. Код свих испитиваних литотипова дијагентска ароматизација утиче на изотопски састав индивидуалних биомаркера. Ксилитни угаљ има најлошију мељивост. С друге стране, ксилитни угаљ је најпогоднији за гасификацију у флуидизо-ваном слоју, док је мешавина барског и земљастог угља показала најлошију примен-љивост за овој процес. Топлота сагоревања опада у следећем низу: ксилитни > барски > мешавина барског и ксилитног > мешавина барског и земљастог угља. Пораст садржаја органског угљеника и топлоте сагоревања је резултат пораста удела дрвенасте вегетације у односу на зељасте биљке у тресету, као и стабилности нивоа воденог стуба током про-цеса хумификације.

(Примљено 22. новембра 2016, ревидирано 17. фебруара, прихваћено 27. фебруара 2017)

REFERENCES

1. G. H. Taylor, M. Teichmüller, A. Davis, C. F. K. Diessel, R. Littke, P. Robert, *Organic Petrology*, Gebrüder Borntraeger, Berlin, 1998
2. I. Kolcon, R. F. Sachsenhofer, *Int. J. Coal Geol.* **41** (1999) 275
3. B. Kwiecińska, M. Wagner, *Classification of Qualitative Features of Brown Coal from the Polish Deposits According to Petrographical, Chemical and Technological Criteria*, Wydawnictwo Centrum PPGSMiE PAN, Kraków, 1997
4. B. Kwiecińska, M. Wagner, *A Petrographic Atlas of Brown Coals (Lignites) from the Polish Deposits*, Wydawnictwo JAK Andrzej Choczewski, Kraków, 2001
5. L. J. Thomas, *Coal Geology*, John Wiley & Sons, Ltd, Chichester, 2002
6. E. Stach, M. Mackowsky, M. Teichmüller, G.H. Taylor, D. Chandra, R. Teichmüller, *Stach's Textbook of Coal Petrology*, Gebrüder Borntraeger, Berlin, 1982
7. D. C. Cronauer, J. T. Joseph, A. Davis, J. C. Quick, P. T. Luckie, *Fuel* **71** (1992) 65
8. A. B. Stankiewicz, M. A. Kruge, M. Mastalerz, *Org. Geochem.* **24** (1996) 531

9. I. Sykorovà, W. Pickel, K. Christanis, M. Wolf, G.H. Taylor, D. Flores, *Int. J. Coal Geol.* **62** (2005) 85
10. B. Bielowicz, *Int. J. Coal Geol.* **116**–**117** (2013) 236
11. B. Bielowicz, *Fuel* **96** (2012) 497
12. A. Otto, V. Wilde, *Bot. Rev.* **67** (2001) 141
13. K. E. Peters, C. C. Walters, J. M. Moldowan, *The Biomarker Guide, Volume 2: Biomarkers and Isotopes in Petroleum Exploration and Earth History,* Cambridge University Press, Cambridge, 2005
14. A. Bechtel, R. Gratzer, R. F. Sachsenhofer, J. Gusterhuber, A. Lücke, W. Püttmann, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **262** (2008) 166
15. Y. Duan, B. Wu, G. Zheng, H. Zhang, C. Zheng, *Chin. Sci. Bull.* **49** (2004) 369
16. A. P. Murray, D. Edwards, J.M. Hope, C. J. Boreham, W. E. Booth, R. A. Alexander, R. E. Summons,. *Org. Geochem.* **29** (1998) 1199
17. J. S. Sinninghe Damsté, S. Schouten, J. K. Volkman, *Geochim. Cosmochim. Acta* **133** (2014) 402
18. J. Tuo, X. Wang, J. Chen, B. R. T. Simoneit, *Org. Geochem.* **34** (2003) 1615
19. A. Bechtel M. Hamór-Vidó, R. F. Sachsenhofer, D. Reischenbacher, R. Gratzer, W. Püttmann, *Int. J. Coal Geol.* **72** (2007) 33
20. A. Zdravkov, A. Bechtel, R.F. Sachsenhofer, J. Kortenski, R. Gratzer, *Org. Geochem.* **42** (2011) 237
21. Y. Song, A. Bechtel, R. F. Sachsenhofer, D. Gross, Z. Liu, Q. Meng, *Org. Geochem.* **104** (2017) 19
22. T. B. Coplen, *Rapid Commun. Mass Spectrom.* **25** (2011) 2538
23. J. Schwarzbauer, R. Littke, R. Meier, H. Strauss, *Int. J. Coal Geol.* **107** (2013) 127
24. Y. Huang, M. J. Lockheart, J. W. Collister, G. Eglinton, *Org. Geochem.* **23** (1995) 785
25. B. R. T. Simoneit, M. Schoell, M. Stefanova, G. Stojanova, I. E. Nosyrev, M. Goranova, *Fuel* **174** (1995) 1194
26. R. D. Pancost, D. S. Steart, L. Handley, M. E. Collinson, J. J. Hooker, A. C. Scott, N. V. Grassineau, I. J. Glasspool, *Nature* **449** (2007) 332
27. M. Schoell, B. R. T. Simoneit, T.-G. Wang, *Org. Geochem.* **21** (1994) 713
28. H. P. Nytoft, J. A. Bojesen-Koefoed, F. G. Christiansen, *Org. Geochem.* **31** (2000) 25
29. J. S. Sinninghe Damsté, A. C. T. van Duin, D. Hollander, M. E. L. Kohnen, J. W. de Leeuw, *Geochim. Cosmochim. Acta* **59** (1995) 5141
30. P. Farrimond, G. D. Love, A. N. Bishop, H. E. Innes, D. F. Watson, C. E. Snape, *Geochim. Cosmochim. Acta* **67** (2003) 1383
31. D. Životić, A. Bechtel, R. Sachsenhofer, R. Gratzer, D. Radić, M. Obradović, K. Stojanović, *Int. J. Coal Geol.* **131** (2014) 344
32. J. H. Calder, M. R. Gibling, P. K. Mukhopadhyay, *Bull. Soc. Géol. Fr.* **162** (1991) 283
33. C. F. K. Diessel, in *Proceedings of the 20th Newcastle Symposium on "Advances in the Study of the Sydney Basin"*, 1986, Newcastle, Australia, *Proceedings - Publication 246*, Department of Geology, University of Newcastle, 1986, p. 19
34. J. Dehmer, *Int. J. Coal Geol.* **28** (1995) 111
35. http://energy.about.com/od/Coal/a/Lignite.htm (last accessed November 21, 2016)
36. P. Lj. Stefanović, Z. J. Marković, V. V. Bakić, D. B. Cvetinović, V. D. Spasojević, N. V. Živković, *Therm. Sci.* **16** (2012) 805
37. M. J. Fabiańska, S. Kurkiewicz, *Int. J. Coal Geol.* **107** (2013) 24
38. A. Otto, H. Walther, W. Püttmann, *Org. Geochem.* **26** (1997) 105
39. M. Stefanova, K. Markova, S. Marinov, B. R. T. Simoneit, *Bull. Geosci.* **80** (2005) 93

40. B. N. Smith, S. Epstein, *Plant Physiol.* **47** (1971) 380
41. K. H. Freeman, J. M. Hayes, J. M. Trendel, P. Albrecht, *Nature* 343 (1990) 254
42. A. Otto, B. R. T. Simoneit, *Geochim. Cosmochim. Acta* **65** (2001) 3505
43. A., Otto, B. R. T. Simoneit, *Org. Geochem.* **33** (2002) 1241
44. M. R. Haberer, K. Mangelsdorf, H. Wilkes, B. Horsfield, *Org. Geochem.* **37** (2006) 519
45. E. W. H. Hayek, U. Jordis, W. Moche, F. Sauter, *Phytochem.* **28** (1989) 2229
46. J. Regnery, W. Püttmann, A. Koutsodendris, A. Mulch, J. Pross, *Org. Geochem*. **61** (2013) 73
47. M. H. O'Leary, *Phytochem.* **20** (1981) 553
48. C. J. Nott, S. Xie, L. A. Avsejs, D. Maddy, F. M. Chambers, R. P. Evershed, *Org. Geochem.* **31** (2000) 231
49. J. D. Weete, in *Chemistry and Biochemistry of Natural Waxes*, P.E. Kolattukudy, Ed., Elsevier, Amsterdam, 1976, p. 349
50. Y. Huang, R. Bol, D. D. Harkness, P. Ineson, G. Eglinton, *Org. Geochem.* **24** (1996) 273
51. J. W. Collister, R. E. Summons, E. Lichtfouse, J. M. Hayes, *Org. Geochem.* **19** (1992) 265
52. K. Sawada, H. Nakamura, T. Arai, M. Tsukagoshi, *Int. J. Coal Geol.* **107** (2013) 78-89
53. D. Mitrović, N. Đoković, D. Životić, A. Bechtel, A, Šajnović, K. Stojanović, *Int. J. Coal Geol.* **168** (2016) 80
54. J. Liao, H. Lu, G. Sheng, P. Peng, C. S. Hsu, *Energy Fuels* **29** (2015) 3573.