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## Preliminary organic geochemical study of lignite from the Smederevsko Pomoravlje field (Kostolac Basin, Serbia) – Reconstruction of geological evolution and potential for rational utilization

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**Abstract:** The study was aimed at determining the origin and geological evolution of lignites from the Smederevsko Pomoravlje field (Kostolac Basin, Serbia). The possibility of a rational utilization of the coal was also considered. For this purpose, numerous organic geochemical analyses were applied to representative lignite samples. The obtained results showed that the coal from the Smederevsko Pomoravlje field is a typical humic coal. The peat-forming vegetation was dominated by gymnosperm plants. The coal-forming plants belonged to the gymnosperm families *Taxodiaceae*, *Cupressaceae*, *Phyllocladaceae* and *Pinaceae*. Other precursors of organic matter (OM) were microbial biomass, ferns and angiosperms. It was established that peatification occurred in a neutral to slightly acidic, fresh water environment under anoxic to suboxic redox conditions. The maturity of the OM is low, in the phase of intense diagenetic processes. The biomarker compositions and values of the corresponding parameters revealed that the Smederevsko Pomoravlje field, the Drmno field (Kostolac Basin) and the “A” field (Kovin deposit) represent a part of a unique lignite basin. The results of this study suggest possible rational utilization of the Smederevsko Pomoravlje lignites in thermal power plants. This is particularly related to samples from coal seam I. A significant amount of gas could be generated from lignites at higher maturities. Eight samples met the basic assumptions for effective gasification.

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## INTRODUCTION

Concerning the significance of the various fossil fuel resources of Serbia, brown coals, particularly lignites, are of great economic importance as they represent the main source for energy production.<sup>1</sup> A significant number of coal bearing basins with huge coal reserves were formed during the Miocene in the territory of Serbia, as a result of favourable peat-forming conditions. The economically most important Upper Miocene coal basins – the Kolubara, Kostolac and Kovin deposits were formed within the Pannonian Basin System in shallow lacustrine, delta plain and fluvial environments.<sup>2</sup> During the early Late Miocene, the Pannonian Basin evolved into the Pannon Lake.<sup>3</sup> The coal deposits have large reserves and resources, and relatively simple exploitation conditions. Annually, the Kolubara Basin produces about 30 Mt of lignite,<sup>4</sup> while the Kostolac Basin produces about 7 Mt.<sup>5</sup> Most of lignite produced (90 %) is used for electricity generation in the thermal power plants (TPP) in Obrenovac and Veliki Crljeni (Kolubara Basin), as well as in Kostolac (Kostolac Basin).

In the past few decades, organic geochemical analysis of coal organic matter has been proved to be a promising tool for an assessment of the possibility of rational utilization of coal,<sup>6–9</sup> as well as for the reconstruction of the vegetation assemblage and palaeoenvironmental conditions in peatlands during the formation of coal-bearing strata.<sup>10–12</sup> For this purpose, proximate and ultimate analyses, Rock–Eval pyrolysis and biomarker analysis were most often used.

In recent years, a new lignite field in the west part of the Kostolac Basin (Serbia), namely Smederevsko Pomoravlje has been investigated. The field is under detailed exploration. In this paper, the organic geochemical features of the Smederevsko Pomoravlje lignite field are presented in detail. Based on comprehensive biomarker analyses, the origin of the organic matter (OM) and the characteristics of the depositional environment of lignites from the Smederevsko Pomoravlje field were reconstructed. The results are compared with lignites from the Drmno field (Kostolac Basin) and the “A” field (Kovin deposit) in order to examine whether the three fields represent a unique productive basin. Moreover, the possibility of rational utilization of coal in order to supply the next generation of Serbian coal-fired power plants or to use lignite as a good raw-material for gasification was also considered.

The lignite samples investigated in this study were of Upper Pontian age (*ca.* 6 Ma) and originated from the boreholes A-339, A2I-414 and A1J-369 of the Smederevsko Pomoravlje field (Fig. S-1 of the Supplementary material to this paper). Samples were collected from the two coal seams, I at a depth interval 23.30 to 67.25 m, and II at a depth interval 56.30 to 85.20 m (Table I). The

thickness of each sample interval was determined as per the changes in the macroscopic lithology of the coal.

#### EXPERIMENTAL

Elemental analysis was applied to determine the contents of sulphur, nitrogen and organic carbon ( $C_{org}$ ). The organic carbon content was determined after removal of carbonates with diluted hydrochloric acid (1:3, V/V). The measurements were performed using a Vario EL III, CHNS/O Elemental Analyser, Elementar Analysensysteme GmbH. The ash content measurements followed the standard procedure ISO 1171 (1997).<sup>13</sup> Analytical moisture determination followed the SRPS B.H8.390/1987 standard (1987).<sup>14</sup> The calorific value measurements were performed on IKA-Calorimeter adiabatic C400, following the standard procedure SRPS B.H8.318/1972 (1972).<sup>15</sup>

TABLE I. A list of the investigated samples

Borehole	Coal seam	Sample	Depth interval, m	Lithology
A-339	I	1	23.30–26.00	Xylite-rich coal
	I	2	26.00–28.00	Mixture of matrix and mineral-rich coal
	I	3	34.30–37.00	Xylite-rich coal
	I	4	40.50–42.70	Mixture of matrix and mineral-rich coal
	I	5	43.20–46.90	Xylite-rich coal
	II	6	56.30–58.20	Matrix coal
A2I-414	I	7	27.40–30.40	Xylite-rich coal
	I	8	30.40–33.30	Mixture of xylite-rich and matrix coal
	I	9	34.90–38.00	Xylite-rich coal
	I	10	41.00–44.00	Mixture of mineral-rich and matrix coal
	I	11	44.00–46.20	Mineral-rich coal
	I	12	65.45–67.25	Mixture of xylite-rich and matrix coal
A1J-369	II	13	67.95–69.50	Mixture of matrix and mineral-rich coal
	I	14	43.85–48.35	Xylite-rich coal
	I	15	48.35–50.70	Mineral-rich coal
	I	16	51.80–54.80	Mixture of xylite-rich and matrix coal
	I	17	54.80–56.35	Xylite-rich coal
	I	18	57.10–60.00	Mineral-rich coal
	I	19	60.00–63.05	Mixture of matrix and mineral-rich coal
	II	20	80.25–83.20	Mixture of matrix and mineral-rich coal
	II	21	83.20–85.20	Mineral-rich coal

Rock-Eval pyrolysis was performed using a TOC/Rock-Eval-6 apparatus.<sup>16</sup> The sample aliquot was 12–14 mg. The IFP 160000 standard ( $\approx 60$  mg) was used for calibration.

Bitumens were extracted (42 h) using a Soxhlet apparatus with an azeotropic mixture of dichloromethane and methanol. The asphaltenes were precipitated with *n*-heptane and the remainder (maltenes) was separated into three fractions using column chromatography over silica gel. The saturated hydrocarbons fraction was eluted with *n*-hexane, the aromatic hydrocarbons with a mixture of *n*-hexane and dichloromethane (3:1, V/V) and the NSO fractions (polar fraction, which contains nitrogen, sulphur, and oxygen compounds) with a mixture of chloroform and methanol (1: 1, V/V).

The saturated fractions isolated from the bitumen were analyzed by gas chromatography-mass spectrometry (GC-MS). A gas chromatograph Agilent 7890A GC (HP5-MS capillary column, 30 m×0.25 mm, He carrier gas 1.5 cm<sup>3</sup> min<sup>-1</sup>) coupled to an Agilent 5975C mass selective detector (70 eV) was used. The column was heated from 80 °C to 310 °C at a rate of 2 °C min<sup>-1</sup>, and the final temperature of 310 °C was maintained for an additional 25 min. The individual peaks were identified by comparison with the literature data<sup>17-20</sup> and based on the mass spectra (library: NIST5a). Quantification of the compounds for calculating the biomarker parameters was performed by integration of peak areas (software GCMS Data Analysis) in the appropriate mass chromatograms (*m/z* 71 for *n*-alkanes, *m/z* 215 for sterenes and *m/z* 191 for hopanoids), with the exception of the diterpenoids and non-hopanoid triterpenoids that were integrated from the total ion currents (TICs) of the saturated fraction.

## RESULTS AND DISCUSSION

### *Group organic geochemical parameters*

The organic carbon contents ( $C_{\text{org}}$ ) are within the limits typical for lignite<sup>21-23</sup> and vary between 29.7 and 55.3 % (Table S-I of the Supplementary material to this paper). The gross and net calorific value (dry basis) of the lignite samples ranges from 9.0 to 25.3 MJ kg<sup>-1</sup> and from 8.5 to 24.5 MJ kg<sup>-1</sup>, respectively, which is in range for rational utilization of lignite in thermal power plants (TPPs) recommended by the American Lignite Council.<sup>23</sup> Moreover, all samples (with exception of sample 20) have higher net calorific values than recommended for SFR Yugoslavia (8.89 MJ kg<sup>-1</sup>).<sup>24</sup> A significant positive correlation between the calorific value and  $C_{\text{org}}$  was observed (correlation coefficient,  $r = 0.92$ ), as expected. Therefore, organic carbon contents and calorific values represent the first criteria that indicate possible rational utilization of Smederevsko Pomoravlje lignites in TPPs. This is particularly related to samples from coal seam I at a depth down to 50 m, which generally have higher  $C_{\text{org}}$  and calorific value (Table S-I). The significant negative correlation between  $C_{\text{org}}$  and ash content ( $r = -0.97$ ) indicates that the differences in the  $C_{\text{org}}$  contents of the lignites are mainly controlled by the varying amounts of mineral matter.

One of the basic assumptions ensuring efficiency of fluidized bed gasification is the optimal maximum ash content recalculated to a dry basis at 20 %.<sup>25</sup> Data from Table S-I show that 8 samples, particularly those from the upper part of coal seam I meet this basic criteria. Concerning the utilization of this deposit for power production, it is evident that the high proportion of ash, attaining more

than 40 % in some samples (Table S-I), should be taken into consideration in order to optimize the burnout behaviour.

The content of sulphur (dry basis) does not exceed 1.5 %, with the exception of samples 13 and 16 (Table S-I). This result implies a relatively low content of sulphate in the waters within the peat (peatification in a fresh water environment).<sup>26,27</sup> On the other hand, the content of sulphur is an important quality parameter of lignite, due to its corrosive influence on the furnace and is the main cause of “acid rains” after combustion. The sulphur content of Smederevsko Pomoravlje lignites is in range as for other Serbian lignites (Drmno field, Kostolac Basin, “A” field, Kovin deposit, “D” field, Kolubara Basin, Table S-I),<sup>28,21,22</sup> Achlada and Mavropigi Basins in Greece<sup>6</sup> and even lower than in lignites from Bulgarian deposits (Staniantsi and Beli Breg),<sup>11</sup> which have been extensively utilized for electric energy production. This indicates that the content of this element is not a limiting factor for usage of Smederevsko Pomoravlje lignites in TPPs.

The values of the *C/N* mole ratio exceed 60 in all the studied samples (Table S-I), which is typical for terrestrial flora.<sup>29,30</sup> This result indicates that Smederevsko Pomoravlje lignites are typical humic coals. This observation is important, because recent investigations showed that coal should contain at least 80 % huminite (mineral-matter free basis) to be useful for fluidized bed gasification.<sup>25</sup> However, the possibility of gasification of Smederevsko Pomoravlje lignites should be further investigated in more detail by petrographic analysis. On the other hand, recent investigations showed that extremely high values of *C/N* mole ratio (>100), which indicate terrestrial plants with a domination of lignin tissue,<sup>31</sup> may hinder the grindability properties of lignite, also important parameter for coal utilization. According to data from Table S-I, only two samples (3 and 15) have unfavourable *C/N* ratios.

Taking into account all aforementioned data, it could be assumed that lignite from coal seam I of borehole A-339 shows the best quality.

The yield of the soluble organic matter (bitumen) varies in a wide range 12754–36409 ppm. The soluble organic matter is mainly represented by asphaltenes (40.1–53.2 %) and polar, NSO compounds (36.7–47.1 %). The relative contents of saturated and aromatic hydrocarbons are low, which is as expected for immature terrestrial organic material (Table S-I).

#### *Rock–Eval pyrolysis*

Rock Eval analysis revealed a high amount of free ( $S_1$ ) and pyrolysable hydrocarbons ( $S_2$ ), consistent with the high content of biogenic and diagenetic compounds. The  $S_3$  peak, which is proportional to the content of oxygen in kero-gen, is also relatively high in accordance with immature terrestrial OM rich in lignin and cellulose (Table S-II of the Supplementary material). As expected, a

significant positive correlation was observed between the content of organic carbon and values of  $S_1$ ,  $S_2$  and  $S_3$  (correlation coefficients  $> 0.80$ ).

The production index ( $PI$ ) and maximal temperature ( $T_{max}$ ) imply low OM maturity (phase of intense diagenesis, Table S-II).<sup>32</sup>

The values of the  $S_2/S_3$  ratio and the hydrogen index ( $HI$ ), in the ranges 2.08–3.39 and 157–200, respectively, indicate sufficient gas potential of lignite at higher maturity.<sup>32</sup> The modified van Krevelen hydrogen index vs. oxygen index diagram (Fig. 2) indicates kerogen type III, with a certain contribution of kerogen type II/III, confirming the respectable gas potential. Moreover, the contribution of kerogen type II/III suggests some liquid hydrocarbon potential. The presence of kerogen type II/III is consistent with the presence of short chain *n*-alkanes (see Section *n-Alkanes and isoprenoids* later on) and  $C_{27}$ – $C_{28}$  sterene homologues (Section *Steroids and hopanoids* later on).

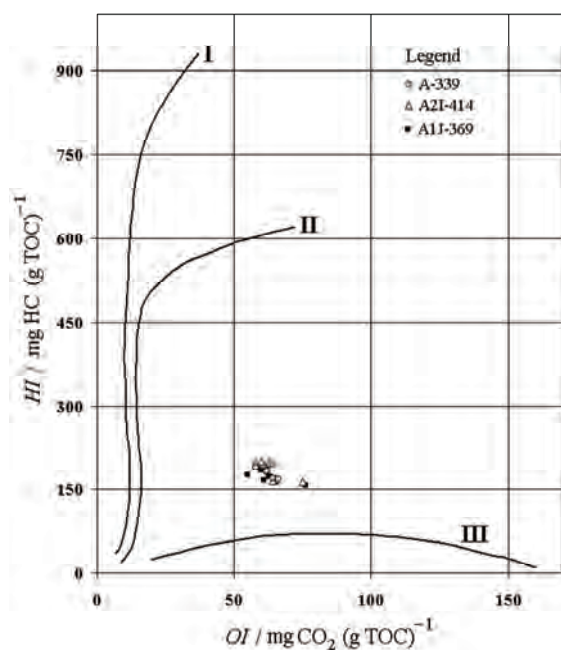


Fig. 2. Modified van Krevelen diagram – hydrogen index ( $HI$ ) vs. oxygen index ( $OI$ ).

#### *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-hopanoid triterpenoids were identified in low amounts (Fig. S-2 of the Supplementary material).

Domination of diterpenoids shows that the main sources of organic matter were gymnosperms (conifers), which confirms that the investigate lignites are

typical humic coals. The presence of hopanoid biomarkers indicates a contribution of prokaryotic organisms, such as bacteria and fungi, whereas the identification of non-hopanoid triterpenoids implies a contribution of angiosperms to the lignite OM (Fig. S-2).

*n-Alkanes and isoprenoids.* Considering the low OM maturity, *n*-alkanes were abundant in the total ion current (*TIC*) of the saturated fraction of the lignites (Fig. S-2). Based on the *m/z* 71 mass chromatogram of the saturated fraction (Fig. S-3a of the Supplementary material), *n*-alkanes were identified in the range C<sub>15</sub>–C<sub>35</sub>, or C<sub>16</sub>–C<sub>35</sub> (Table S-III). The *n*-alkane patterns were dominated by long-chain homologues (C<sub>27</sub>–C<sub>31</sub>), maximizing at *n*-C<sub>29</sub> (Fig. S-3a; Table S-III) and an expressed odd over even predominance, indicating a significant contribution of epicuticular waxes. The values of carbon preference index (*CPI*)<sup>33</sup> for the full range of *n*-alkanes C<sub>16</sub>–C<sub>34</sub> and an odd–even predominance<sup>34</sup> (*OEP*) 2 value higher than 3, *i.e.*, 2, respectively (Table S-III) are in accordance with the low rank of the lignites. Mid-chain *n*-alkanes (*n*-C<sub>21</sub>–*n*-C<sub>25</sub>), originating from vascular plants, microalgae, cyanobacteria, sphagnum and submerged aquatic macrophytes,<sup>35–38</sup> are present in lower amount in comparison with the long-chain odd homologues (Fig. S-3a). The predominance of odd over even carbon-number *n*-alkanes in the mid-range *n*-alkanes (parameter *OEP* 1; Table S-III), suggests a microbial input, consistent with presence of hopanoids (Fig. S-3c). Moreover, the dominance of C<sub>23</sub> and C<sub>25</sub> *n*-alkane homologues in mid chain range (Fig. S-3a) implies an input of submerged aquatic macrophytes. Variations of *OEP* 1 ratio (Table S-III) suggest variations in bacterial input/communities and the contribution of submerged aquatic macrophytes to the precursor OM. These variations most probably could be attributed to changes in the depositional environment (water column level), due to the pronounced seasonality during the Upper Miocene (hot and humid summers and dry and relatively cold winters).<sup>39,40</sup>

In all the investigated samples, short chain *n*-alkanes ( $\leq$  C<sub>20</sub>) were present in low quantities (Fig. S-3a), consistent with typical humic OM. The main precursors of the short chain *n*-alkanes are algae, and photosynthetic and non-photosynthetic bacteria.<sup>41,42</sup> The low values of the sterane to hopane ratio (see Section *Steroids and hopanoids* later on and Table S-V) indicate a greater contribution of prokaryotic organisms than eukaryotic algae to the OM. Therefore, it could be assumed that the short chain *n*-alkanes mainly originated from bacteria. The significant variations of the *CPI* values for the short chain *n*-alkanes (*CPI*<sub>16–20</sub>; Table S-III) confirmed changes in bacterial communities during diagenesis, consistent with above discussed *OEP* 1 ratio.

Isoprenoids pristane (Pr) and phytane (Ph) were present in low amounts in the lignite extracts (Figs. S-2 and S-3a). Low concentrations of pristane and phytane were often reported in immature organic matter.<sup>43–45</sup> The Pr/Ph ratio is

widely used as an indicator for the redox (*Eh*) conditions of the depositional environment.<sup>46</sup> However, this parameter is also known to be affected by maturation<sup>41</sup> and by differences in the precursors for acyclic isoprenoids, *i.e.*, bacterial origin,<sup>47,48</sup> and the formation of pristane from tocopherols or chromanes.<sup>49</sup> For this lignite sample set, an influence of maturity on the pristane/phytane ratio could be ruled out. In addition, the low maturity of the lignite probably argues against the formation of pristane from tocopherols.<sup>49</sup> Therefore, the Pr/Ph ratio, varying between 0.66–1.65 (Table S-III), may be considered as an indicator of the changing of the *Eh* settings from anoxic to slightly oxic during peat deposition. This change was also related to a change in the water level, *i.e.*, pronounced seasonality. Namely, an increase in *Eh* of the environment is often associated with a decrease in water level and in some cases drainage of peat bogs.

Values of aforementioned *n*-alkane parameters and Pr/Ph ratio are in range for those parameters observed for lignite extracts from the Drmno field (Kostolac Basin) and “A” field (Kovin deposit) (Table S-III), suggesting very similar origin and palaeoenvironment of the precursor OM.<sup>21,28</sup>

*Diterpenoids and triterpenoids with a non-hopanoid skeleton.* Diterpenoids were the main constituents of lignite extracts, indicating a significant contribution of gymnosperms to the precursor OM. Pimarane and particularly 16 $\alpha$ (*H*)-phylocladane were dominant by far in the saturated fractions (Fig. S-2). A high amount of 16 $\alpha$ (*H*)-phylocladane indicates that the coal-forming plants belonged to the conifer families *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae* and *Phyllocladaceae*, while a high abundance of pimarane suggests *Pinaceae*, *Taxodiaceae* and *Cupressaceae*.<sup>50–53</sup> Other diterpenoid type constituents of the saturated fraction were  $\alpha$ -labdane,  $\beta$ -labdane, isopimaradienes, norisopimarane, pimaradiene, atisene, norpimarane, beyerane, isophyllocladene, isopimarane, fichtelite, 16 $\beta$ (*H*)-phylocladane and 16 $\alpha$ (*H*)-kaurane (Fig. S-2). In all samples, tetracyclic terpenoids predominated over tricyclic terpenoids (with exception of sample 18), whereas bicyclic diterpenoids were present in low amounts (Table S-IV of the Supplementary material).

The pimarane/16 $\alpha$ (*H*)-phylocladane ratio and the ratio of tricyclic to tetracyclic diterpenoids are higher in the upper part of coal seam I in all three boreholes (Table S-IV), which may imply a greater contribution of *Pinacea* to the precursor OM. These samples also contained higher amount of  $C_{org}$  (Table S-I). The mentioned results indicate peatification of lignite from the upper part of coal seam I under a higher water level, which contributed to better preservation of OM and growth of *Pinacea*.

The non-hopanoid triterpenoids were present in low amount in the saturated fraction of Smederevsko Pomoravlje lignites and consisted exclusively of des-A-degraded triterpenoids: des-A-olean-enes, des-A-urs-enes, des-A-oleanadiene,



des-A-oleanane and des-A-lupane (Fig. S-2). The presence of des-A-degraded triterpenoids implies microbial activity, consistent with relatively abundant hopanoids (Figs. S-2 and S-3c). The small amount of non-hopanoid triterpenoids indicates a small contribution of angiosperms to the precursor OM. This result is also important for lignite utilization, because recent studies\* showed that elevated amounts of angiosperm organic matter may lower the grindability properties of lignite.

Very similar distributions of diterpenoids and non-hopanoid triterpenoids were observed during investigations of lignites from the Drmno field (Kostolac Basin) and the "A" field (Kovin deposit),<sup>21,28</sup> Table S-IV, indicating that these two fields along with the Smederevsko Pomoravlje field represent parts of a unique basin.

*Steroids and hopanoids.* Steroid biomarkers of Smederevsko Pomoravlje lignites (based on the  $m/z$  215 mass chromatogram of the saturated fraction; Fig. S-3b) consisted predominantly of C<sub>29</sub>  $\Delta^4$ -,  $\Delta^2$ - and  $\Delta^5$ -sterenes. The C<sub>27</sub>- and C<sub>28</sub>-homologues were identified in notably lower amounts (Table S-V). The marked predominance of C<sub>29</sub> sterenes (Fig. S-3b; Table S-V) clearly indicates peat formation from terrigenous plants.

Hopanoids were more abundant than steroid biomarkers in the coal extracts ( $\Sigma$ steroids/ $\Sigma$ hopanoids ratio < 0.26; Table S-V). These results indicate a bacteria-influenced facies and argue for the role of microorganisms in the degradation of the plant tissue.

Based on the  $m/z$  191 mass chromatogram of the saturated fraction, the hopane composition was characterized by the presence of  $17\alpha(H)21\beta(H)$ ,  $17\beta(H)21\alpha(H)$  and  $17\beta(H)21\beta(H)$  compounds with 27 and 29–32 carbon atoms (Fig. S-3c). Other hopanoid-type constituents of the saturated fraction were C<sub>27</sub> hop-13(18)-ene, C<sub>27</sub> hop-17(21)-ene and C<sub>30</sub> hop-17(21)-ene. Moreover, several samples contained hopanoid ketones, C<sub>27</sub> hop-21-one and C<sub>30</sub> hop-17(21)-en-20-one (Fig. S-3c). C<sub>27</sub> Hop-21-one was also observed in lignite extracts from the Drmno field, Serbia,<sup>28</sup> and it was reported in microbial mats and the black sandstone from the Be'eri deposit, Israel.<sup>54</sup> C<sub>30</sub> hop-17(21)-en-20-one could have been formed by oxidation of the highly sensitive allylic position of hop-17(21)-ene present in the herein studied samples (Fig. S-3c) and resulting either from elimination of an alcohol group on hydroxyhopanoids followed by migration of the double-bond (favoured in acidic conditions),<sup>55</sup> or by bacterial dehydrogenation of saturated hopane skeletons.<sup>56</sup> Therefore, the presence of C<sub>30</sub> hop-17(21)-en-20-one could indicate slightly acidic suboxic conditions in the mire, which is consistent with the relatively low sulphur content.

In the majority of the samples, the hopane distribution was dominated by C<sub>27</sub>  $17\beta(H)$ -hopane; however, in several samples, the most abundant hopanoid

\* A. Bechtel, personal communication, 2013.

biomarker was  $C_{31} 17\alpha(H)21\beta(H)22(R)$ -hopane (Table S-V). The prominent  $C_{27}17\beta(H)$ -hopane in distribution of total hopanoids, followed by sharp domination of lower homologues,  $C_{27}17\beta(H)$  and  $C_{29}17\beta(H)21\beta(H)$  in the distribution of  $C_{27}$ – $C_{31}$   $\beta\beta$ -hopanes in all samples (Fig. S-3c; Table S-V) could signify that the precursor hopanoid lipids partly originated from methanotrophic bacteria (*e.g.*, *Methylococcus capsulatus* or *Methylomonas methanica*).<sup>57</sup> On the other hand, prominent  $C_{31}\alpha\beta(R)$ -hopane was often reported in low rank coals.<sup>45,52,53</sup> Killops *et al.*<sup>58</sup> suggested that the decarboxylation of 31,32-bishomohopanoic acid, which is generally abundant in peats and soils,<sup>59,60</sup> could result in the formation of  $C_{31}17\alpha(H)21\beta(H)$ -hopane in immature coals. The presence of 22(*R*)-bishomohopanoic acid in the “geological”  $17\alpha(H)21\beta(H)$  configuration in living microbial mats,<sup>61</sup> supports the assumption that the  $C_{31}$   $\alpha\beta$ -hopane could be derived directly from microorganisms by decarboxylation. According to van Dorselaer *et al.*,<sup>62</sup> a high amount of  $C_{31}\alpha\beta(R)$ -hopane implies complex reactions in acidic environments under oxic conditions. The observed distributions of hopanes in the Smederevsko Pomoravlje lignites indicate changes in the microbial population, which is consistent with changes in palaeoenvironment, from anoxic to suboxic.

The ratio of  $17\beta(H)21\beta(H)$  to  $(17\beta(H)21\beta(H) + 17\alpha(H)21\beta(H))$   $C_{30}$ -hopanes is within the limits established for lignite (0.5–0.7; Table S-V),<sup>63</sup> in accordance with low thermal maturity of the OM.

Based on the  $m/z$  191 mass chromatogram, compounds with the fernene skeleton, fern-9(11)-ene and fern-8-ene, were also identified (Fig. S-3c). Ferrenes mainly originate from ferns, which are often typical members of herbaceous precursor vegetation.<sup>39,64</sup> It was shown that ferns could also be the source of hopanes with fewer than 30 carbon atoms. Therefore, it could be speculate that the predominance of  $C_{27}$  and  $C_{29}$  hopanoids with the  $\beta\beta$ -configuration in the studied lignites could be attributed, at least to some extent, to sources other than bacteria, probably ferns.

## CONCLUSIONS

Smederevsko Pomoravlje lignites are typical humic coals. The main sources of the organic matter were gymnosperms (conifers). Other precursors of OM were microbial biomass, ferns and angiosperms. Based on the composition of diterpenoids, it was established that the coal-forming plants belonged to the gymnosperm families *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae*, *Phyllocladaceae* and *Pinaceae*.

Peatification was realized in a neutral to slightly acidic, fresh water environment. Pronounced seasonality caused changes in the water table, which resulted in changes in the redox potential (*Eh*) during peatification, as well as microbial and to lesser extent, vegetation differentiations in the palaeo-communities.

The obtained results indicated low OM maturity (phase of intense diagenetic processes).

Based on the very similar distributions of molecular “fingerprints” and the values of biomarker ratios in Smederevsko Pomoravlje lignites and lignites from the Drmno field (Kostolac Basin) and the “A” field (Kovin deposit), it was established that these three fields represent part of a unique productive basin.

Concerning potential rational utilization of Smederevsko Pomoravlje lignites, the following conclusions were drawn. The group organic geochemical data and net calorific value signified possible usage of the lignites in thermal power plants. This was particularly related to samples from coal seam I (depth down to 50 m). The investigated lignites demonstrated sufficient gas potential and some liquid hydrocarbons potential at higher maturities. Eight samples meet the basic conditions to ensure efficiency of fluidized bed gasification of the lignite.

#### SUPPLEMENTARY MATERIAL

Geological settings, group organic geochemical parameters, results of the Rock Eval pyrolysis, abundance data for of *n*-alkanes, isoprenoids, diterpenoids, non-hopanoid triterpenoids, steroids and hopanoids, as well as figures showing total ionic currents and GC-MS diagrams are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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#### ИЗВОД

#### ПРЕЛИМИНАРНА ОРГАНСКО-ГЕОХЕМИЈСКА СТУДИЈА ЛИГНИТНОГ ПОЉА СМЕДЕРЕВСКО ПОМОРАВЉЕ (БАСЕН КОСТОЛАЦ) – РЕКОНСТРУКЦИЈА ГЕОЛОШКЕ ЕВОЛУЦИЈЕ И МОГУЋНОСТ РАЦИОНАЛНЕ УПОТРЕБЕ УГЉА

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Циљ рада је био да се утврди порекло и геолошка еволуција лигнита из поља Смедеревско Поморавље, басен Костолац. Разматрана је и могућност рационалне употребе угља. Бројне органско-геохемијске анализе су изведене на репрезентативним узорцима лигнита. Добијени резултати показују да су лигнити поља Смедеревско Поморавље типични хумусни угљеви. Гимносперме (голосеменице) су биле главни извор органске супстанце лигнита. Материјал потиче од следећих фамилија гимносперми: *Taxodiaceae*, *Cupressaceae*, *Phyllocladaceae* и *Pinaceae*. Остали извори органске супстанце лигнита били су

микробна биомаса, папрати и ангиосперме (скривеносеменице). Утврђено је да се хумификација органске супстанце одвијала у слатководној, неутралној до слабо киселој средини, при аноксичним до благо оксичним условима. Органска супстанца је незрела и налази се на стадијуму дијагенезе. Састав биомаркера и вредности одговарајућих параметара указују на то да поља Смедеревско Поморавље, Дрмно (басен Костолац) и „А“ (лежиште Ковин) представљају део јединственог басена. Резултати овог истраживања упућују на могућу рационалну употребу лигнита Смедеревско Поморавље у термоелектранама. То се посебно односи на узорке из првог угљеног слоја. Органска супстанца лигнита може генерисати значајне количине гаса на вишем ступњу зрелости. Осам узорака задовољава основне критеријуме за ефикасну гасификацију.

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