

# Organic geochemistry of Upper Carboniferous bituminous coals and clastic sediments from the Lublin Coal Basin (Poland)

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## ABSTRACT:

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Bituminous coals and clastic rocks from the Lublin Formation (Pennsylvanian, Westphalian B) were subjected to detailed biomarker and Rock-Eval analyses. The investigation of aliphatic and aromatic fractions and Rock-Eval  $T_{max}$  suggests that the Carboniferous deposits attained relatively low levels of thermal maturity, at the end of the microbial processes/initial phase of the oil window. Somewhat higher values of maturity in the clastic sediments were caused by postdiagenetic biodegradation of organic matter.

The dominance of the odd carbon-numbered  $n$ -alkanes in the range  $n$ -C<sub>25</sub> to  $n$ -C<sub>31</sub>, high concentrations of moretanes and a predominance of C<sub>28</sub> and C<sub>29</sub> steranes are indicative of a terrigenous origin of the organic matter in the study material. This is supported by the presence of eudesmane, bisabolane, dihydro-*ar*-curcumene and cadalene, found mainly in the coal samples. In addition, tri- and tetracyclic diterpanes, e. g. 16β(H)-kaurane, 16β(H)-phylocladane, 16α(H)-kaurane and norisopimarane, were identified, suggesting an admixture of conifer ancestors among the deposited higher plants. Parameters Pr/ $n$ -C<sub>17</sub> and R<sub>dit</sub> in the coal samples show deposition of organic matter from peat swamp environments, with the water levels varying from high (water-logged swamp) to very low (ephemeral swamp). Clastic deposits were accumulated in a flood plain environment with local small ponds/lakes. In pond/lake sediments, apart from the dominant terrigenous organic matter, research also revealed a certain quantity of algal matter, indicated, i. a., by the presence of tricyclic triterpanes C<sub>28</sub> and C<sub>29</sub> and elevated concentrations of steranes.

The Paq parameter can prove to be a useful tool in the identification of organic matter, but the processes of organic matter biodegradation observed in clastic rocks most likely influence the value of the parameter, at the same time lowering the interpretation potential of these compounds.

The value of Pr/Ph varies from 0.93 to 5.24 and from 3.49 to 22.57 in the clastic sediments and coals respectively. The microbial degradation of organic matter in both type of rocks and during early stages of diagenesis is confirmed by a high concentration of hopanes, the presence of drimane homologues, bicyclic alkanes and benzohopanes. Moreover, bacteria could also have been connected with the primary input of organic matter, which is shown by the presence of e.g. C<sub>30</sub> neohop-13(18)-ene.

**Key words:** Lublin Coal Basin; Bituminous coal; Gas chromatography-mass spectrometry; Biomarkers; Terrigenous organic matter.

## INTRODUCTION

The Lublin Coal Basin (LCB) is one of three sites in Poland where bituminous coals occur, the others being the Upper Silesian and Lower Silesian coal basins. It is located in the south-eastern part of the country and covers an area of 4600 km<sup>2</sup> (Text-fig. 1A). The black coal deposits continue to the east, into the Ukraine, where the LCB extends as the L'viv-Volhynian Coal Basin. Black coal from the LCB has been exploited for over 30 years, in the Lubelski Węgiel "Bogdanka" SA Mine. At present, two coal beds, 382 and 385/2, are exploited.

The Carboniferous Lublin Basin deposits have been the topic of numerous geological surveys, the most significant of which are those by Dembowski and Porzycki (1988), Zdanowski and Żakowa (1995), and Narkiewicz (1998). However these studies focussed mainly on lithostratigraphic, petrological and sedimentological issues; only a few on the geochemistry of the organic matter from the LCB area have as yet been written.

The present paper fills a gap in geochemical studies of these sediments. Geochemical studies of bituminous coal and clastic formations enriched by organic coal allow us to reconstruct the environmental conditions in which the sedimentation developed. Additionally geochemical research is essential because of the source rocks' potential. Hydrocarbon fields occur in the Lublin Basin in the Carboniferous strata, i.e. the Stężycza and Świdnik oil fields and the Minkowice gas fields (Helcel-Weil *et al.* 2007).

Kotarba and Clayton (2003) provided isotopic analyses and the analysis of molecular fossils from several

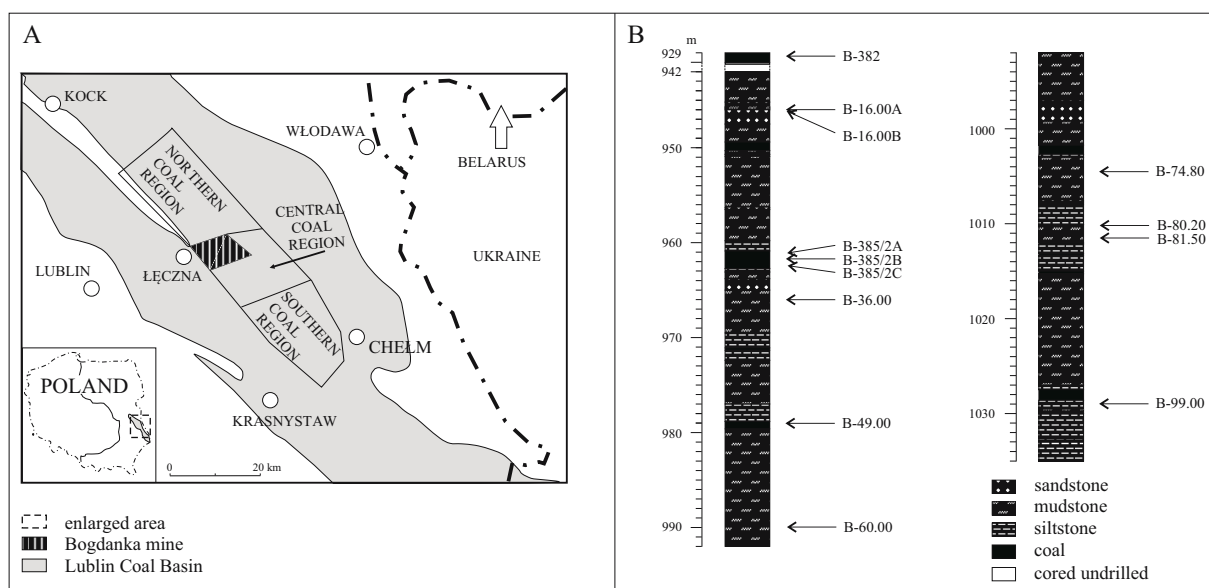
coal samples from the LCB (coal bed no. 382), revealing a prevalent input of higher plant organic matter and a low stage of thermal transformation in the material (Kotarba and Clayton 2003).

Gola *et al.* (2011) dealt with the geochemical analysis of organic matter in bituminous coal from bed no. 385/2, and tonstein found therein. The work also describes, for the first time, the tri- and tetracyclic diterpanes found in the Lublin Carboniferous Basin, as well as aromatic derivatives that suggest the presence of coniferous plants in the formations.

The present paper provides data on biomarker composition and Rock-Eval pyrolysis of sediments of bituminous coal and clastic rocks. The aim was a detailed characterization of the type of deposited organic matter, the reconstruction of palaeoenvironmental conditions and determining the effects of diagenesis on the behaviour of organic matter in the sediment.

## GEOLOGICAL SETTINGS

The LCB constitutes part of the Lublin Carboniferous Basin. In the north-west the Lublin Carboniferous Basin is limited by the Grójec Fault, in the south-west by the Radom-Kraśnik Elevation, and in the south-east it extends into the L'viv-Volhynian Coal Basin (Żelichowski 1972). It is filled with Upper Viséan to Upper Westphalian sediments, including shales, mudstones, sandstones, and numerous black coal beds of variable thickness. Carboniferous sediments lie unconformably on older Palaeozoic and Proterozoic sediments and the crystalline basement of the East European Platform



Text-fig. 1. **A** – The location of Bogdanka Mine (after Bieńko 2004, slightly modified); **B** – schematic profile of studied drill hole BR-9/02

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(Cebulak 1988). They are covered unconformably by Permo-Mesozoic and Cenozoic deposits.

The Bogdanka mine is located in the central part of the LCB in the Central Coal Region (Text-fig. 1A) (Bieńko 2004). Structurally, the mine is located in the axial part of the Radzyń Podlaski – Bogdanka Syncline.

The Lublin Formation is the main productive series within the deposits of the LCB. It is of Pennsylvanian (Westphalian A, B and C) age (Migier 1988; Musiał and Tabor 1988; Soboń-Podgórska 1988; Zdanowski 2007). The exploited coal seams, nos. 382 and 385/2, lie almost horizontally (dip c. 2°), at depth 920 m and 960 m, respectively (Bieńko 2004). A characteristic feature of the Lublin Formation is the dominance of mudstone-claystone deposits over sandstones and the presence of numerous black coal layers and seams, as well as abundant amounts of plant fossils and sideritic concretions (Porzycki 1988). The maximum thickness of the coal seams exceeds 4 m (Zdanowski 2007).

The boundary between Westphalian A and B within the Lublin Formation lies at the base of coal bed no. 391 (Migier 1988).

A bank of S-limestone at the *Dunbarella* level is the highest normal marine sediment in the Carboniferous succession of the Lublin basin. All higher coal seams (nos 391, 389, 385, 384) are characterized already by a continental flora.

Coal beds of the Lublin Formation were formed under conditions of gradual replenishment and freshening of the sedimentary basin, accompanied by a gradual increase of formation potential. Coal seams could have formed in all three varieties of telematic facies (Kmieciak and Knafel 1988).

The bituminous coal under exploitation is mainly gas-flame coal type 32 (Bieńko 2004). Flame coal type 31, gas coal type 33 and gas-coke coal type 34 are also present (Stachowicz 2005). The mean ash content amounts to 8.37–13.12%, total sulfur to 1.11–1.40%, and calorific to 25 972–26 427 kJ/kg (Stachowicz 2005).

## MATERIALS AND METHODS

A geotechnical borehole (BR-9/02) was drilled in the Bogdanka mine, from the base of coal bed no. 382. The borehole was 105 m long, of which the uppermost, initial 12 m, were uncored (Text-fig. 1B). As a result, 93 m of the core were obtained, documenting the lithological variability of the upper Westphalian B, in the vicinity of the principal coal beds of the LCB. The succession is dominated by mudstones (67.63%) and claystones (19.25%), and the percentage of sandstones

and coals is equal (6.56%). Nine coal beds with thickness varying from 0.10 to 1.70 m, including bed no. 385/2 located 30.95–32.65 m below the surface, were drilled through.

Subsequent to macroscopic and microscopic observations (unpublished data), samples were selected for biomarker study and Rock-Eval pyrolysis. Nine rocks from borehole BR-9/02 were composed of grey mudstone, grey fine-grained sandstone and coal (Text-fig. 1B). Additionally, coal samples from beds no's. 382 (B-382) and 385/2 (B-385/2A, B-385/2B, B-385/2C) were taken from the mine workings.

Total organic carbon analysis (TOC) and Rock Eval pyrolysis were performed on Rock-Eval 6 and Leco apparatus in seven samples (Table 1).

For thirteen samples biomarker analysis was performed. The samples were powdered and Soxhlet-extracted by dichlorometan:methanol (97:3) in pre-extracted thimbles for about 72 hours. The extract was separated into aliphatic, aromatic and polar fractions with the use of thin layer chromatography (TLC) (glass plate 10x20, 20x20, with Kieselgel 60 F<sub>254</sub>, Merck Co.). As an eluent, *n*-hexane was used. Fractions were separated under UV light. The aliphatic and aromatic fractions were subjected to gas chromatography analysis coupled with mass spectrometry (GC-MS) analysis on the Clarus 500 (Perkin Elmer) apparatus. The apparatus was equipped with a silica capillary column Elite-5MS (30x0.25mm i.d., 0.25µm film thickness). The transfer line temperature was 300°C, whilst the ion source temperature was 200°C.

For the saturated hydrocarbon fractions, a GC oven temperature program was initially set to 40°C, maintained for 1 minute, and the heating rate to 120°C was set at 20°C/min, whilst to 300°C at 3°C/min; the temperature of 300°C was held for 30 minutes (total analysis time: 95 minutes). For the aromatic fractions, the GC oven temperature program was initially set to 40°C, maintained for 2 minutes, the temperature increased 10°C/min to 120°C, and 4°C/min to 300°C; the temperature of 300°C was maintained for 35 minutes (total of 90 minutes). Helium was used as a carrier gas. The mass spectrometer was operating in the EI (electron impact) mode, at an electron energy of 70 eV and scanned mass interval ranging from 40 to 600 Da (1s total scan time).

Analysis of particular organic compounds was based on a comparison of the mass spectra obtained with published data and spectra retention times (e.g. Seifert and Moldowan 1978; Noble *et al.* 1985; Philp 1985, 1994; Peters *et al.* 2005). In addition, the Ultra Scientific PM-525 (PAH mixture) inner standard was used while studying the aromatic fractions.

parameter	sample	B-382	B-16.00A	B-16.00B	B-385/2A	B-385/2B	B-385/2C	B-36.00	B-48.80	B-60.70	B-74.80	B-80.20	B-81.50	B-99.00
Depth [m]		929	945.8	946	961.5	961.6	961.7	966	976.8	990.7	1004.8	1010.2	1011.5	1029
Lithology		coal	sandstone	coal	coal	coal	coal	mudstone	mudstone	mudstone	mudstone	mudstone	mudstone	mudstone
TOC [wt %]		61.63	1.77	54.39	n.a.	61.63	n.a.	0.73	n.a.	n.a.	n.a.	0.69	0.59	n.a.
T <sub>max</sub> [°C]		427	434	430	n.a.	425	n.a.	436	n.a.	n.a.	n.a.	434	435	n.a.
S1 [mg HC g <sup>-1</sup> rock]		0.4	0.04	0.51	n.a.	0.47	n.a.	0.03	n.a.	n.a.	n.a.	0.05	0.02	n.a.
S2 [mg HC g <sup>-1</sup> rock]		157.71	1.72	99.71	n.a.	139.23	n.a.	0.39	n.a.	n.a.	n.a.	0.68	0.84	n.a.
HI [mg HC g <sup>-1</sup> TOC]		298	97	183	n.a.	226	n.a.	53	n.a.	n.a.	n.a.	99	142	n.a.
OI [mg CO <sub>2</sub> g <sup>-1</sup> TOC]		6	16	4	n.a.	4	n.a.	26	n.a.	n.a.	n.a.	13	15	n.a.
EOM [%]		6.43	0.01	3.75	4.77	1.32	2.22	0.008	0.027	0.047	0.07	0.027	0.022	0.068
Fraction		26	11	22	10	15	13	26	16	14	14	17	22	11
Aliphatic [%]		32	24	10	44	22	18	19	14	8	9	17	14	12
Aromatic [%]		42	65	68	46	63	69	56	70	78	77	66	64	77
Polar [%]		1.38	1.14	1.47	1.61	1.45	1.53	1.2	1.43	1.53	1.55	1.22	1.21	1.52
CPI		3.49	3.11	3.69	8.05	17.73	22.57	0.93	2.23	3.41	5.24	1.59	2.08	4.56
Pr/Ph		2.22	1.35	2.09	6.61	6.42	15.29	0.71	1.68	2.46	3.62	1.21	1.43	5.26
Pr/n-C <sub>17</sub>		1.31	0.6	0.59	1.09	0.44	1.08	0.62	0.73	0.69	0.71	0.74	0.67	1.11
Ph/n-C <sub>18</sub>		2.77	0.31	2.7	2.01	1.4	2.07	1.55	1.02	0.69	0.88	2.3	1.24	0.47
DW		0.48	0.65	0.54	0.5	0.45	0.4	0.62	0.66	0.7	0.51	0.51	0.72	0.69
Faq		7	17	12	9	16	8	27	29	22	10	19	18	19
sterans		38	35	34	42	37	40	30	25	27	28	25	22	13
C <sub>27</sub> :C <sub>28</sub> :C <sub>29</sub>		56	48	54	49	46	52	43	40	51	63	56	60	68
steranes/17α(H)hopanes		0.08	0.75	0.14	0.14	0.05	0.06	0.21	0.12	0.11	0.09	0.13	0.06	0.09
(C+R) <sub>N</sub>		17.82	0	11.36	5.29	5.95	10.6	0	1.57	2.6	1.71	0.52	3.5	3.93
Pe <sub>N</sub>		0.24	2.9	0.43	0.12	0.33	0.62	0	0.32	0.07	0.31	2.6	0.59	0.47
R <sub>dit</sub>		1.06	1.16	1.27	1.09	0.83	0.9	0	0.87	1.41	1.08	1.09	1.03	0.73
20S [%]		34	39	32	35	38	36	44	36	43	34	41	43	48
αβ [%]		23	44	33	28	20	19	43	37	39	19	38	39	48
Rcs [%]		0.56	0.6	0.59	0.56	0.71	0.61	0.57	0.55	0.54	0.56	0.67	0.65	0.6

Table 1. **EOM** – extractable organic matter; **CPI** (Carbon Preference Index) =  $[(n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} - n-C_{33}) / (n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32} + n-C_{34})] + ((n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} - n-C_{33}) / (n-C_{24} + n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32})) / 2$  (Bray and Evans, 1961); **Pr/Ph** = pristane/phytane; **Pr/n-C<sub>17</sub>** = pristane/*n*-heptadecane (Scheffler, 2004); **Ph/n-C<sub>18</sub>** = phytane/*n*-octadecane (Scheffler, 2004); **DW** – (degree of waxiness) =  $(\sum n-C_{21} - n-C_{31}) / (\sum n-C_{15} - n-C_{20})$ ; **Paq** =  $(n-C_{23} + n-C_{25}) / (n-C_{23} + n-C_{25} + n-C_{29} + n-C_{31})$  (Ficken *et al.*, 2000); **Steranes C<sub>27</sub>:C<sub>28</sub>:C<sub>29</sub>** = relative abundances of C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub> regular steranes 5α,14α,17α(H) 20R; **steranes/17α(H)hopanes** = C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub> regular steranes 20S+R (*m/z* 217)/17α(H)hopanes (*m/z* 191) (Peters *et al.*, 2005); **(C+R)<sub>N</sub>** = cadalane + retene/1,3,6,7-tetramethylnaphthalene; **Pe<sub>N</sub>** = perylene/1,3,6,7-tetramethylnaphthalene; **R<sub>dit</sub>** = 19-norisopimarane + iso-pimarane + 16α(H)-kaurane)/(*ent*-beyerane + 16β(H)-phytylocladane + 16α(H)-phytylocladane); **20S** = 20S/(S+R) - 5α,14α,17α(H)-stigmastane 20S/(5α,14α,17α(H)-stigmastane 20S + 5α,14α,17α(H)-stigmastane 20R) (Justwan *et al.*, 2006); **αβ** = (5α,14β,17β(H)-stigmastane 20R and 20S/5α,14β,17β(H)-stigmastane 20R and 20S + 5α,14α,17α(H)-stigmastane 20R and 20S) (Justwan *et al.*, 2006); **Rcs** (calculated vitrinite reflectance) = 0.51 + 0.073(MDR); MDR (methylidibenzothiophene ratio) = (4-MDBT)/(1-MDBT) (Radke and Willisch 1994). See text for detail.

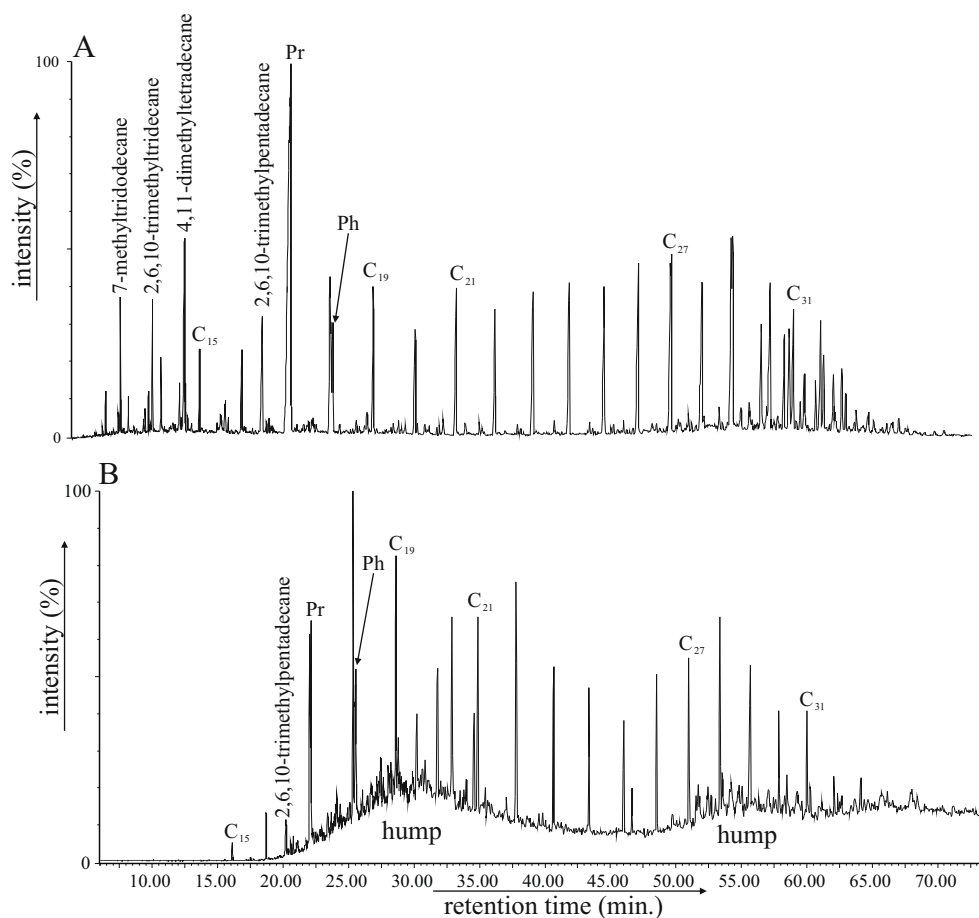
## RESULTS

The bituminous coal samples contained high contents of extractable organic matter (EOM), from 1.32% (B-385/2B) to 6.43% (B-382) (Table 1). In contrast, the content of bitumens in the clastic rocks is low, from 0.008% (sample B-36.00) to 0.070% (sample B-74.80). The bitumens have a high content of the polar fraction, up to 78%. The percentage of the aliphatic fraction varies from 10 to 26% in sample, and of the aromatic fraction from 8 to 44% (Table 1). Organic compounds found in the aliphatic and aromatic fractions constituted the subject of detailed analytical research.

A significant presence of HUMP (unresolved complex mixture) was observed in samples derived solely from clastic rocks, confirming biodegradation (Text-fig. 2B; Peters *et al.* 2005). This finding was also confirmed by the partial removal of the short-chain *n*-alkanes and isoprenoids in the samples. The level of biodegradation is presumably average (Peters *et al.* 2005). None of the norhopane group compounds was detected and the distribution of hopanes and steranes seems to be intact.

## Molecular markers in the aliphatic fraction

A monomodal distribution of *n*-alkanes was observed in the coal samples, with odd-over-even predominance in the range *n*-C<sub>15</sub> to *n*-C<sub>33</sub> (Text-fig. 3A). A dominance of long-chain compounds was observed, with maximum intensities at *n*-C<sub>27</sub> and *n*-C<sub>29</sub> (CPI from 1.38 to 1.61, after Bray and Evans 1961). The distribution of *n*-alkanes in most samples of the clastic sediments is monomodal, with maximum levels in the short-chain homologues (Text-fig. 3B). Only in samples B-80.20 and 81.50 was the distribution bimodal. In the first sample, a dominance of long-chain compounds (maximum in *n*-C<sub>25</sub> and *n*-C<sub>27</sub>) over the short-chain compounds (maximum in *n*-C<sub>18</sub>) was observed, and in the second sample the middle-chain compounds (maximum by *n*-C<sub>22</sub>) dominated over short-chain compounds (maximum in *n*-C<sub>18</sub>). A distinct presence of odd-over-even dominance in the long-chain homologues was observed in all of the samples discussed above (CPI from 1.14 to 1.55).

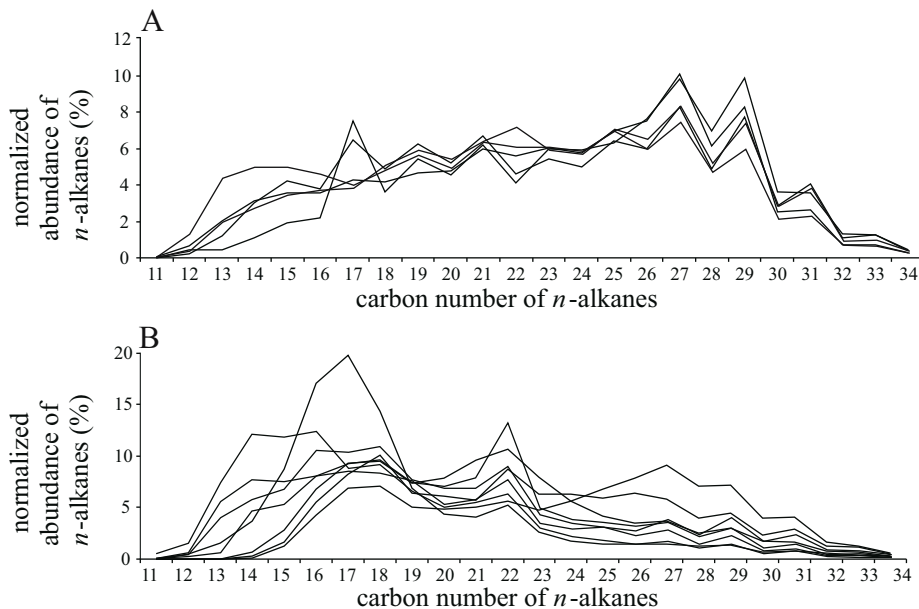


Text-fig. 2. TIC (total ion chromatogram) of aliphatic fractions in samples: **A** – B-382 (coal); **B** – B-16.00A (sandstone). Annotation: **Pr** – pristane; **Ph** – phytane; **C<sub>5</sub>** – *n*-alkane

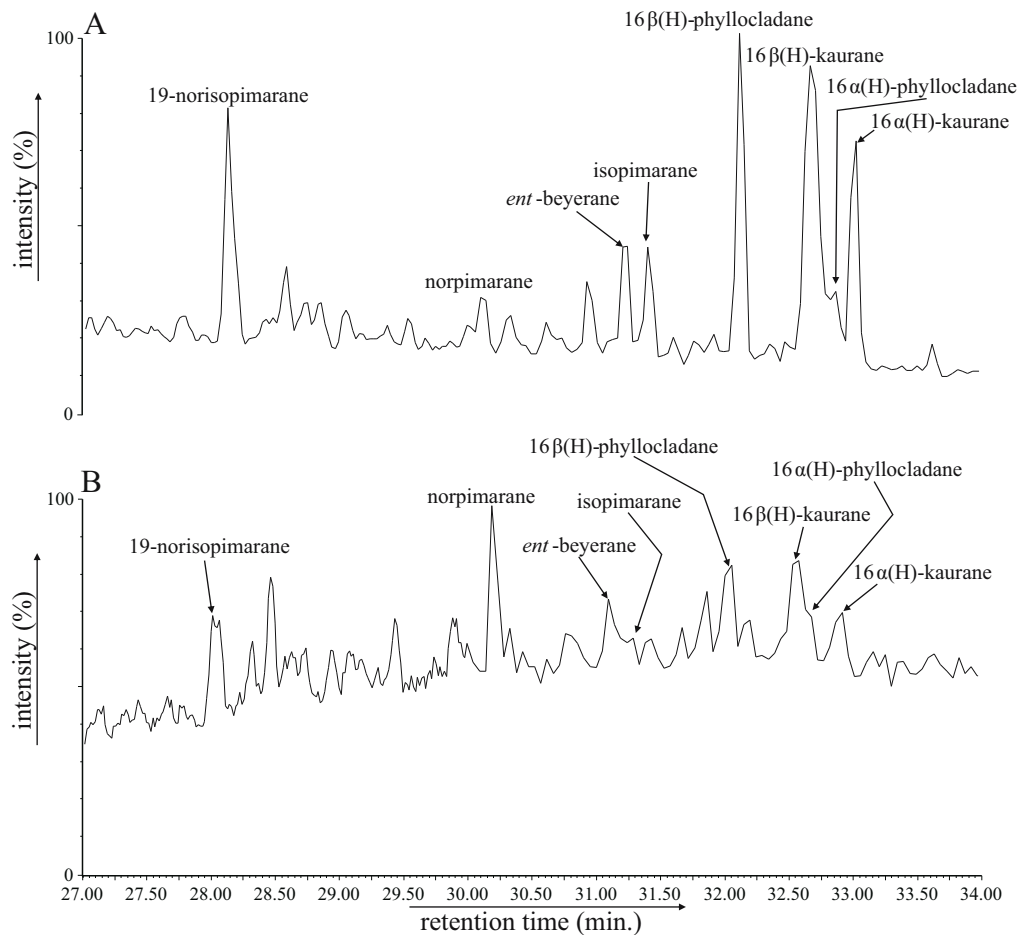


In all coal samples and three clastic sediment samples (B-60.70, B-74.80 and B-99.00) the Pr/*n*-C<sub>17</sub> ratio

was greater than 2.0 (Table 1). The amount of phytane in samples B-382, B-385/2A, B-385/2C and B-99.00



Text-fig. 3. Normalized *n*-alkanes distribution (*m/z* 71) in samples: **A** – coals; **B** – clastic sediments



Text-fig. 4. Tri- and tetracyclic triterpanes, *m/z* 123 ion fragmentograms in samples: **A** – B-382 (coal); **B** – B-81.50 (mudstone)

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was higher than that of *n*-octadecane. Lower acyclic isoprenoids also occurred, but in lesser amounts: 2,6,10-trimethyl-pentadecane, 4,11-trimethyl-tetradecane and 7-methylododecane (Text-fig. 2A). In the remaining clastic sediment samples the Pr/*n*-C<sub>17</sub> ratio was lower (slightly above 1.0), whilst the content of phytane was approximately 50% lower than *n*-C<sub>18</sub>. The lower acyclic isoprenoids occurred mainly in trace amounts (Text-fig. 2B).

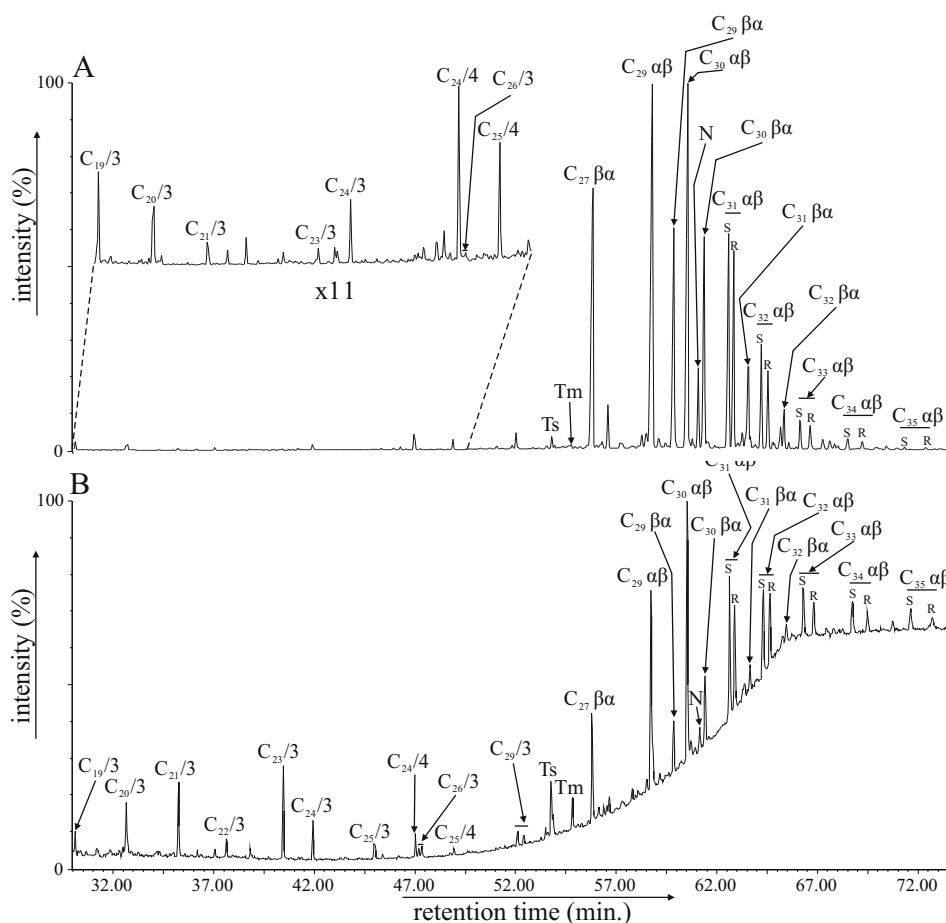
The presence of bicyclic sesquiterpanes, tri- and tetracyclic diterpanes was confirmed. Among sesquiterpanes a predominance of C<sub>16</sub> sesquiterpane – 8-β(H)-homodrimane in respect to lower homologues was observed. The presence of C<sub>15</sub> sesquiterpane – 4-β(H)-eudesmane was observed in coal samples and a single clastic rock.

Tri- and tetracyclic diterpanes were found for the first time in the LCB, in coal extracts from the 385/2 seam (Gola *et al.* 2011). In the study coal samples and in B-99.00, 16β(H)-kaurane, 16β(H)-phyllocladane, 16α(H)-kaurane and 19-norisopimarane were domi-

nant, whilst 16α(H)-phyllocladane, *ent*-bayerane, norpimarane and isopimarane were present in insignificant amounts (Text-fig. 4A).

A different compound distribution was observed in the clastic rocks, in which the above compounds were present in only trace quantities. Among them norpimarane, and at times – 19-norisopimarane, were dominant (Text-fig. 4B). The low contents of diterpanes in clastic sediments are probably linked with the low contents of their precursors at the time of organic matter deposition or resulted from dilution by other compounds (Fleck *et al.* 2001).

The content of pentacyclic triterpanes is many times higher than that of tri- and tetracyclic compounds (Text-fig. 5A, 5B). Among hopanes, 17α(H),21β(H)-hopane C<sub>30</sub> typically dominates over 17α(H),21β(H)-norhopane, and 17α(H)-22,29,30-trisnorhopane (Tm) over 18α(H)-22,29,30-trisnorneohopane (Ts). In the case of triterpanes C<sub>27</sub> the Tm concentration is even several dozen times higher in the coal sediments.



Text-fig. 5. Tri-, tetra- and pentacyclic triterpanes, *m/z* 191 ion fragmentograms in samples: **A** – B-382 (coal); **B** – B-36.00 (mudstone). Annotation: C<sub>19</sub>/3 - tricyclic triterpanes C<sub>19</sub> etc., C<sub>24</sub>/4 – tetracyclic triterpanes C<sub>24</sub> etc., Ts – C<sub>27</sub> 18α(H),22,29,30-trisnorneohopane, Tm – C<sub>27</sub> 17α(H),22,29,30-trisnorhopane, C<sub>30</sub>αβ – C<sub>30</sub>17α(H),21β(H)-hopane, etc., C<sub>27</sub>βα - C<sub>27</sub>17β(H),21α(H)-moretane, etc., N – C<sub>30</sub> neohop-13(18)-ene

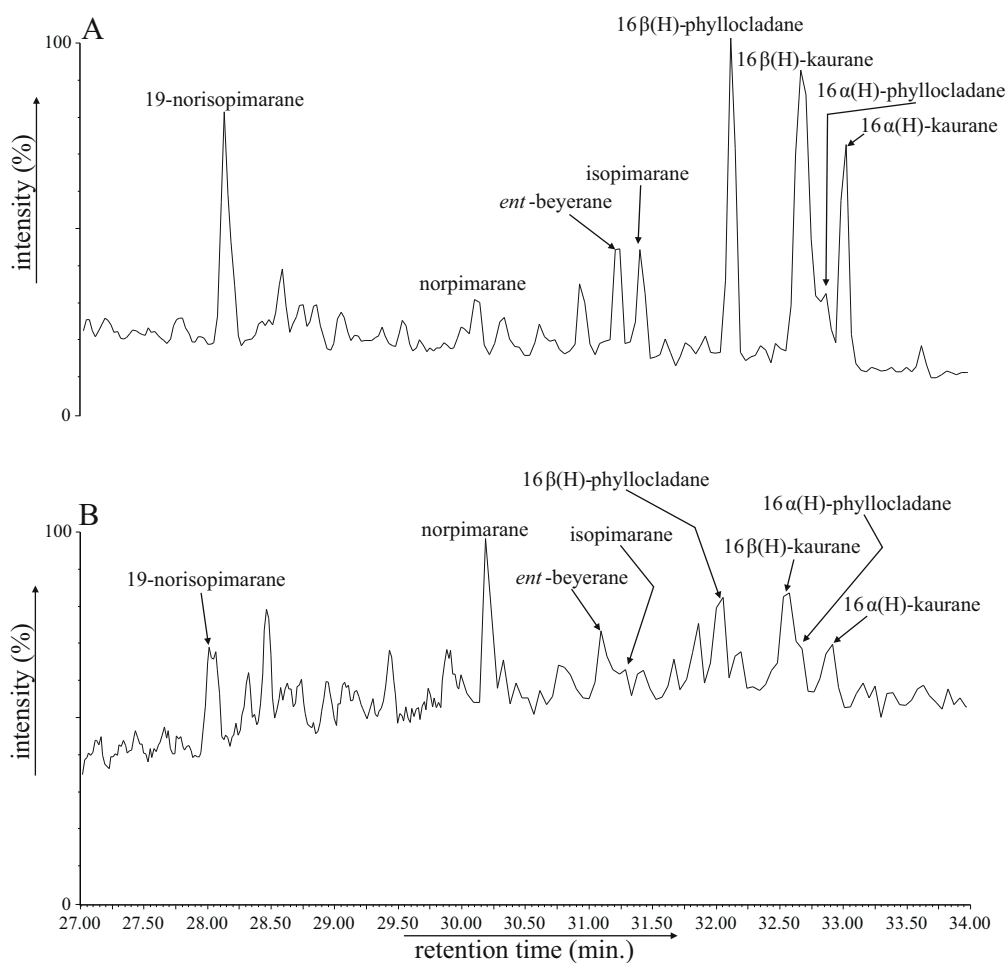
The samples are characterized by a gradual decrease in the homohopane content, with a low concentration of homohopanes  $C_{34}$  and  $C_{35}$  (22S and 22R) in the clastic rocks (Text-fig. 5B) and trace amounts in the coal samples (Text-fig. 5A). A very high content of homohopanes  $C_{31}$  in the coal samples is also notable, almost twice that in the neighbouring homohopanes  $C_{32}$ . In the clastic sediments variation between the contents of these compounds exists, but is even lower.

Gammacerane was not identified in the analysis. This compound was found by Kotarba and Clayton (2003) in samples from bed no. 382, collected at the mine. The presence of gammacerane, a biomarker, has been taken to suggest hypersaline conditions (Haven *et al.* 1989) or stratification of the water column during organic matter deposition (Sinninghe Damstè *et al.* 1995). According to Kotarba and Clayton (2003) the presence of gammacerane in coal does not imply hypersaline conditions. They suggested that its presence can be connected to other, unknown sources, or to the provenance of the parent organisms

from different, salinity-independent depositional environments.

A lack of gammacerane in the research material can be explained by the coelution of these compounds with other hopanes, which makes identification impossible. An alternative explanation is the input of local organic matter and/or environmental conditions atypical of the whole swamp/peat accumulation area. The issue requires more detailed studies, i.e. with the use of GC-MSMS on a higher number of samples from particular coal-bearing beds.

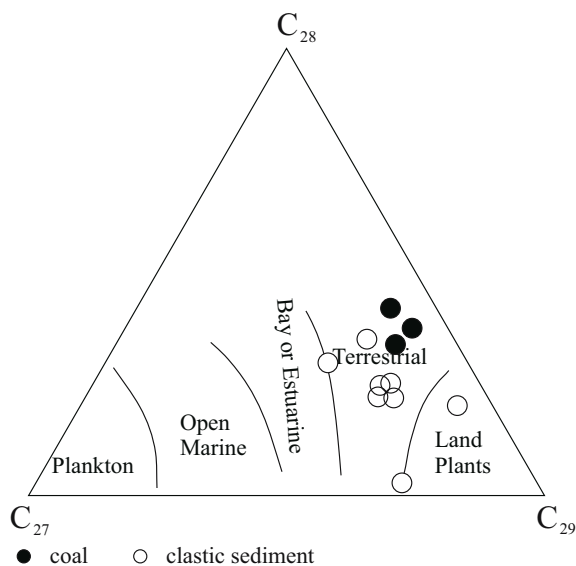
The  $C_{27}:C_{28}:C_{29}$   $\alpha\alpha\alpha$  20R sterane distribution is dominated by the  $C_{29}$  compound (Table 1, Text-fig. 6A, 6B and Text-fig. 7). The concentration of sterane  $C_{29}$  in the coal samples varies from 49% (B-385/2) to 56% (B-382); however in the clastic rocks it ranges from 43% (B-36.00) to 60% (B-81.50) (Table 1). The coal samples are also have a high content of sterane  $C_{28}$ , reaching up to 38%, several times higher than the  $C_{27}$  compound. In the clastic rocks, the abundance of  $C_{28}$  sterane is only slightly higher than  $C_{27}$ .



Text-fig. 6. Steranes,  $m/z$  217 ion fragmentograms in samples: **A** – B-382 (coal), **B** – B-80.20 (mudstone). Annotation: D- $C_{27}20S$  – diasterane  $C_{27}$  20S, etc.;  $C_{27}\alpha\alpha\alpha 20R$  – sterane  $C_{27}$   $\alpha\alpha\alpha$  20R, etc.



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Text-fig. 7. Ternary diagram of the relative abundance of regular steranes  $C_{27}:C_{28}:C_{29}$  (after Huang and Meinschein 1976)

## Molecular markers in the aromatic fraction

The coal samples no. B-382 and B-385/2A, B-385/2B, B-385/2C differ from the remaining samples in containing a unique distribution of aromatic compounds (Text-fig. 12). Here, the dominating compounds are retene, dihydro-*ar*-curcumene, 1,2,3,4-tetrahydro-5,6,7,8-tetramethylnaphthalene, cadalene, isocadalene (3-isopropyl-1,6-dimethylnaphthalene), pyrene, 1,2,5,6-

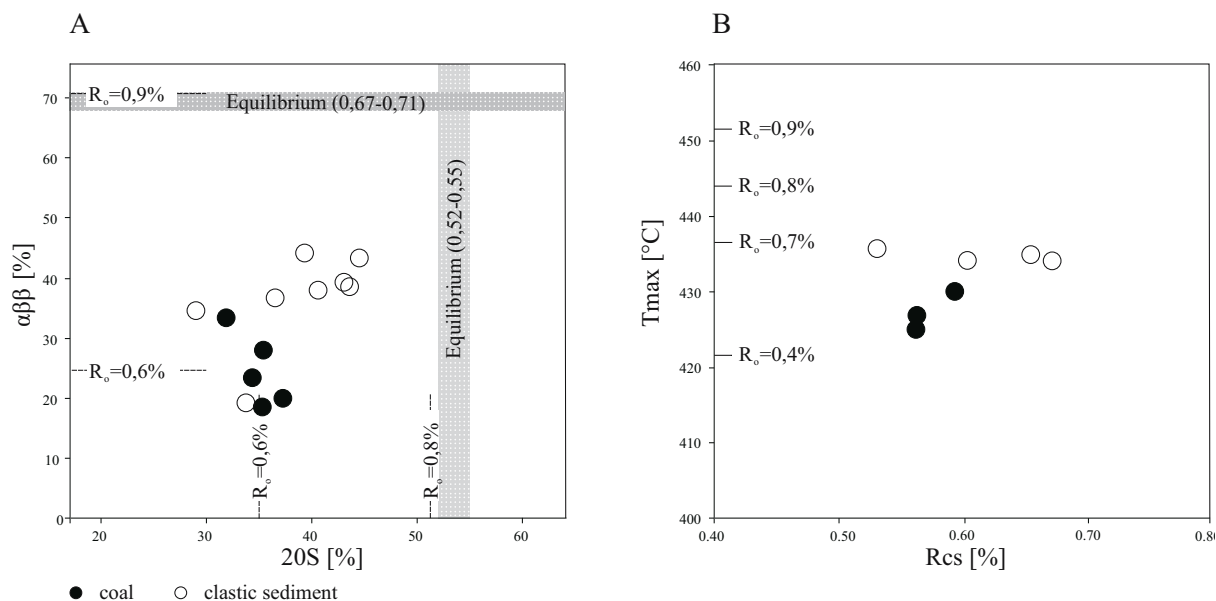
+ 1,2,3,5- tetramethylnaphthalene. Phenanthrene, dibenzothiophene and their alkyl derivatives occur in low and very low concentrations. Among the alkyl derivatives of naphthalenes, tetramethylnaphthalenes occur most commonly, and among triaromatic steroids the long-chain compounds are the most frequent. In addition, low contents of isohexylnaphthalenes (after Ellis *et al.* 1996) were confirmed. Among them 2-methyl-1-(4-methylpentyl)naphthalene, 2,6-dimethyl-1-(4-methylpentyl)naphthalene and 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene dominate. Moreover, the coal samples also contain benzohopanes from  $C_{32}$  to  $C_{34}$ .

The clastic rock samples and one coal sample, B-16.00B, are devoid of isohexylnaphthalenes and benzohopanes. The dominant compounds are phenanthrene, dibenzofuranes and their methyl derivatives. Retene and cadalene occur in low and very low concentrations. Among the alkyl derivatives of naphthalene, di- and trimethylnaphthalene compounds prevail.

## DISCUSSION

## Maturity of organic matter

Rock-Eval  $T_{max}$  values vary from 425 to 430°C in the coal samples and from 434 to 436°C in the clastic sediment samples (Table 1). Such values are typical of sediments at the end of the microbial stage/early mature window (Hunt 1996).



Text-fig. 8. Maturity parameters: A – sterane 20S vs.  $\alpha/\beta$  (after Justwan *et al.* 2006, slightly modified); B – Rcs vs.  $T_{max}$

The parameters of the thermal transformation of organic matter based on the concentration of steranes  $C_{29} - 20S$  and  $\alpha\beta\beta$  (Text-fig. 8A) – show that the sediments were transformed to a stage corresponding to over 0.6% vitrinite reflectance (Peters *et al.* 2005; Farrimond *et al.* 1998). Both parameters are slightly lower for the coals than for the clastic rocks. Differences in the value of these parameters are probably linked with the biodegradation of organic matter in mineral-rich environments, as opposed to peat environments, confirmed in the samples of clastic sediments (Jasper *et al.* 2009). The distributions of methyl dibenzothiophenes were used to calculate the vitrinite reflectance  $R_{cs}$  (Radke and Willsch 1994; Chakhmakhchev and Suzuki 1995; Chakhmakhchev *et al.* 1997). The value of  $R_{cs}$  for the coals ranged from 0.56 to 0.59%, and in the surrounding rocks from 0.54 to 0.67% (Table 1; Text-fig. 8B). These results are similar to those obtained for the LCB by Kotarba and Clayton (2003) and Gola *et al.* (2011), suggesting the low maturity of the organic matter. The lower maturity of coals than of clastic rocks may be explained either by (1) their biodegradation or (2) by a significant enrichment in organic matter, which causes limited contact with clay minerals, responsible for acceleration of the catalytic reactions.

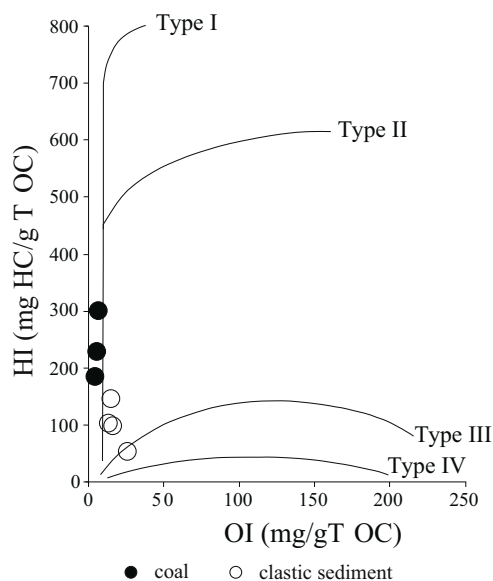
### Type of organic matter

In the clastic samples, the results of Rock-Eval pyrolysis averaged  $S_2 > 2$  mgHC/g rock, implying a poor hydrocarbon potential (Table 1). Low values of the Hydrogen Index (HI), 142 mg HC/g TOC, are characteristic of gas-prone, Type III organic matter (Text-fig. 9). However, the coal samples have a very good hydrocarbon potential, with  $S_2$  values ranging from 99.71 to 157.71 mg HC/g rock (Table 1). An HI ranging from 183 to 298 mg HC/g TOC indicates that the formations can produce not only liquid, but also gaseous hydrocarbon (Text-fig. 9; Hunt 1996; Kotarba *et al.* 2002; Jasper *et al.* 2009).

The geochemical studies of Kotarba and Clayton (2003) and of Gola *et al.* (2011) indicate that the dominant compound in bituminous coal from the LCB is organic material composed of higher plant matter. This dominance is confirmed by the present study.

The geochemical data allow us to perform a particularisation test on the organic matter from the sediment and to compare the results with the type of depositional environment (e.g. Peters *et al.* 2005).

The odd carbon-numbered compounds in the entire range of *n*-alkanes present in the coal samples can be due to one or many biological precursors. It has mainly been observed in lacustrine shales (e.g. del Rio *et al.*



Text-fig. 9. Classification of samples on a pseudo-van Krevelen diagram based on pyrolysis data

1994; Krabbe 1996). Gelpi *et al.* (1970) showed that some non-marine algal species, e.g., *Botryococcus braunii*, can be a source of *n*-alkanes with characteristic odd-over-even predominance, in the short- as well as middle- and long-chain ranges. Furthermore, in modern bog vegetation, Nott *et al.* (2000) identified plants, e.g., *Calluna vulgaris* and *Vaccinium oxycoccus*, with a distribution of *n*-alkanes ranging from *n*-C<sub>19</sub> to *n*-C<sub>35</sub>, with a clearly marked predominance of odd carbon-numbered compounds. Odd-over-even predominance in the range of low-molecular *n*-alkanes, particularly with a high concentration of *n*-C<sub>17</sub>, can point to both algae (e.g. Gelpi *et al.* 1970; Blumer *et al.* 1971) and bacteria (Oró *et al.* 1967). Ficken *et al.* (2000) observed a high concentration of *n*-C<sub>23</sub> and *n*-C<sub>25</sub> in submerged and floating macrophytes in aquatic plants from lakes on Mt. Kenya. Nott *et al.* (2000) and Pancost *et al.* (2002) drew attention to the *Sphangum* species, whose leaf wax is characterized by a high concentration of odd carbon-numbered compounds, from *n*-C<sub>21</sub> to *n*-C<sub>25</sub>, with prevailing *n*-C<sub>23</sub>, and in addition a clearly marked but usually lower-grade superiority of odd carbon-numbered compounds of high molecular weight.

Odd-over-even predominance in the range of high molecular weight alkanes in all samples is a characteristic feature of organic matter derived from terrigenous plants (Tissot and Welte 1984). These compounds arise due to the diagenetic transformation of carboxylic acids and alcohols, present in leaves and cuticular waxes (Tissot and Welte 1984). Additionally, the predominance of short-chain *n*-alkanes in the clastic sediments

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suggests the presence of algae and/or bacterial biomass. An absence, when compared to the coal samples, of odd-over-even predominance in the short- and middle-chain compounds is most likely related to a change in the input of organic matter type or with higher biodegradation levels (Allen *et al.* 1971; Peters *et al.* 2005).

Based on the concentration of short, middle- and long-chain *n*-alkanes, the degree of waxiness (DW) was calculated as  $(\Sigma n-C_{21}-n-C_{31})/(\Sigma n-C_{15}-n-C_{20})$ . High values of this parameter in coal samples and in B-36.00 and in B-74.80 indicate a predominance of the epicuticular waxes of vascular plants (Text-fig. 10A). In other samples the strong predominance of short *n*-alkanes suggests that these sediments were derived from low waxy organic matter, probably of algal and/or bacterial origin.

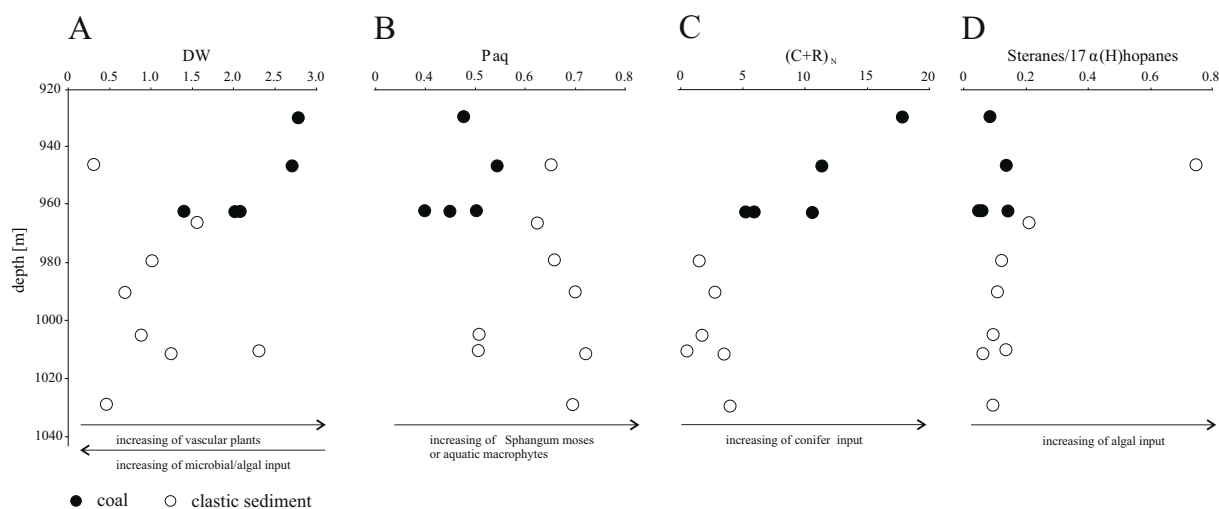
Ficken *et al.* (2000) suggested that the *Paq* parameter ( $n-C_{23}+n-C_{25}/n-C_{23}+n-C_{25}+n-C_{29}+n-C_{31}$ ) determines submerged/floating macrophyte input versus emergent and terrestrial plant input to lake sediments. Values of  $Paq < 0.1$  are characteristic of terrestrial plants,  $Paq = 0.1 - 0.4$  for emerged macrophytes and  $Paq = 0.4 - 1.0$  for submerged/floating macrophytes (Ficken *et al.* 2000). Nichols *et al.* (2006) pointed out that the same parameter can be applied to determining the relative abundance of peat-forming plants – higher values for *Sphangium* species input and lower for non-*Sphangium* species. In clastic rocks the *Paq* parameter is high and ranges from 0.51 to 0.72 (Table 1; Text-fig. 10B). Consequently it suggests either a partial contribution from submerged/floating macrophytes or a high contribution of *Sphangium* mosses in the input of primary organic matter. Moreover, the *Paq* parameter value in coals is low, ranging from 0.40 to 0.54, indicating higher con-

tributions from vascular plants. Due to the low levels of thermal maturity of the tested sediments, the *Paq* parameter could prove to be a useful tool in organic matter identification. It is also worth remembering that aside from the type of organic matter, postdiagenetic processes also influence the concentration of *n*-alkanes. The biodegradation of organic matter observed in clastic rocks will also most likely influence the value of the *Paq* parameter, at the same time decreasing the interpretation potential of these compounds.

The presence of high values of sterane  $C_{29}$  indicates a predominance of the input of higher plants (after Huang and Meinschein 1976; Moldowan *et al.* 1985) in both coal and clastic deposits. In addition, the high concentration of sterane  $C_{28}$ , especially in the coal samples (between 34% and 42%, Table 1), points to the decomposition of wood fungi and/or input of lacustrine algae in peats/swamps with a high water table (Huang and Meinschein 1976; Izart *et al.* 2006).

Additionally, in the coal samples, the presence of higher plant indicators such as 4 $\beta$ (H)-eudesmane (Alexander *et al.* 1983), monocyclic bisabolane and its aromatic equivalent, dihydro-*ar*-curcumene (Ellis *et al.* 1995), is especially worth mentioning. The last compound mentioned is regarded as an unspecific indicator of higher plant input, due to its presence in sediments of Devonian to Tertiary age, both in gymnosperms and angiosperms (Ellis *et al.* 1995).

The following flora dominated during the Westphalian B in the Carboniferous Lublin Basin (Migier 1988): Pteridosperame, Cordaitopsida and Lycopodiophyta. It is thus remarkable to find tri- and tetracyclic diterpanes in coal as well as in clastic rock samples. The presence of these compounds has already been observed



Text-fig. 10. Biomarker ratios for characterization of type of organic matter input. A – DW (degree of waxiness parameter); B – *Paq*; C –  $(C+R)_N$ ; D – steranes/17 $\alpha$ (H)hopanes

in Carboniferous sediments and coals excavated in Poland (Fabińska *et al.* 2003; Gola *et al.* 2011). It is believed that the biological precursor of diterpanes with skeletons of pimaranes, abietanes and phyllocladanes, are conifer families, including Araucariaceae, Podocarpaceae, Cupressaceae and Taxodiaceae (Simoneit 1977; Noble *et al.* 1985; van Aarssen *et al.* 1992; Philp 1994; Otto *et al.* 1997; Otto and Simoneit 2001). In addition, diterpanes such like pimaranes and kaurane, can be derived from Pteridophytes (i.e. Filicales) and Bryophytes (mosses) (Philp 1994).

The most probable source of tri- and tetracyclic diterpanes and their aromatic derivatives in the Carboniferous strata are conifers, Voltziales or Cordaitales (e.g. Schultze and Michaelis 1990; Philp 1994; Fabińska *et al.* 2003; Rothwell *et al.* 2005). The presence of compounds such as retene, cadalene or isohexylnaphthalenes can also suggest a genesis from the ancestors of conifers. Ellis *et al.* (1996) suggest that a potential source of isohexylnaphthalenes are the terpenoids abundant in plant resins, with podocarpane, pimarane, abietane and phyllocladane-type carbon skeletons. The precursors of cadalane are cadinenes and cadinols, occurring mainly in plant resins but also occur in bryophytes and fungi (Alexander *et al.* 1994; Elias *et al.* 1997). Retene is derived from abietic acid, particular to conifer resins (Otto and Simoneit 2001).

The concentration of retene and cadalene has been normalised to 1,3,6,7-tetramethylnaphthalene (1,3,6,7-TeMN), a microbe-derived compound occurring in sediments of all ages (Jiang *et al.* 1998). Particularly high concentrations of these compounds in coals and in the B-99.00 sample (stigmarian soil) with low water-levels (data below) allow us to conclude that a biological forerunner of these compounds had been growing in the place of organic matter deposition, but it is not an allochthonous material (Text-fig. 10C).

The input of higher plants was accompanied by an input of fungi. The presence of the latter, besides high concentrations of steranes  $C_{28}$ , is indicated by the presence of perylene. It is believed that the source of the compound is perylenequinone, found in fungal bodies (Jiang *et al.* 2000). Particularly high contents of perylene were discovered in samples B-16.00A and B-80.20. Unfortunately it does not correspond with the concentration of sterane  $C_{28}$ , suggesting either varied fungi species as the source of these compounds or some other biological forerunner. The issue is dealt with by Jiang *et al.* (2000) and Bakhtiari *et al.* (2009).

In all analyzed samples, high concentrations of 17 $\beta$ (H), 21 $\alpha$ (H)-moretanes were also observed among pentacyclic compounds, with dominant  $C_{27}$ ,  $C_{29}$  and  $C_{30}$  compounds (Text-fig. 5A, 5B). It is believed that

17 $\beta$ (H),21 $\alpha$ (H)-moretanes are a product of diagenesis typical of immature sediments 17 $\beta$ (H),21 $\beta$ (H)-hopanes (Ourisson *et al.* 1979; Quirk *et al.* 1984). In the course of thermal changes in sediments, the transformation of a more thermodynamically stable configuration of 17 $\alpha$ (H),21 $\beta$ (H)-hopanes takes place. The high amount of moretanes cannot be due to the presence of microbial matter, but is directly linked with non-microbial organisms, such as ferns (Mostafa and Younes 2001).

The regular steranes/17 $\alpha$ (H)hopanes ratio reflects the input of eukaryotic organisms versus prokaryotic (Peters *et al.* 2005). The low values of the parameter observed in the majority of our samples are typical of terrestrial and/or bacterially reworked organic matter. The values are elevated in only two samples (B-16.00A and B-36.00), suggesting a contribution from algal matter (Text-fig. 10D). Moreover, extensive tricyclic terpanes, mainly  $C_{28}$  and  $C_{29}$  compounds, which can also be ascribed to algae (Simoneit *et al.* 1990; 1993; Azavedo *et al.* 1992; Holba *et al.* 2003), have been found in these samples.

As might be expected, in the tested sediments, apart from the dominant terrestrial organic matter and locally occurring algal matter, microbial matter was also detected. It seems that the elevated concentrations of short-chain *n*-alkanes in the elastic rocks are above all else connected with the presence of the microbial matter.

The presence of microbial matter is confirmed by the occurrence of drimane homologues (Alexander *et al.* 1983; Philp 1985), benzohopanes (Hussler *et al.* 1984), and very high concentrations of 17 $\alpha$ (H)hopanes (Peters *et al.* 2005). The presence of these compounds indicates a very intensive microbial transformation of organic matter during deposition and early diagenesis and/or high ratios of microbial matter in primary organic material supplied to the sedimentary basin (Alexander *et al.* 1983; Philp 1985; Peters *et al.* 2005; Jiang *et al.* 2001).

Additionally, the high concentration of homohopane  $C_{31}$  can be connected with the character of the deposition of organic matter. Quirk *et al.* (1984) observed a high concentration of homohopane  $C_{31}$   $\alpha\beta$  (22R) in peat deposits. This compound is connected with the bacterial decay of higher plant matter and is formed at the very earliest stages of diagenesis (Quirk *et al.* 1984).

$C_{30}$  neohop-13(18)-ene was detected in moderate amounts in the coal samples and in low amounts in the clastic rock samples (Text-fig. 7). This compound was probably derived from methylotrophic bacteria (Mostafa and Younes 2001 and references therein). Methylotrophic bacteria inhabit the surface of plant organisms (Hornschuh *et al.* 2006).

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**Depositional environment**

The Westphalian B in the LCB was deposited in an environment of lakes, marginal lakes, swamps and river beds. In these rocks it is possible to find the sediment sequences characteristic of meandering rivers: gritstone and medium-grained sandstone formed in river beds, siltstone and mudstone formed in environments outside river beds, on the floodplain, mudstone and claystone - in marginal lakes and lakes in general and levels of stigmariamian soils and coals deposited in swamps of the flood plain (Porzycki 1988; Waksmundzka 1998, 2010, 2012).

The clastic rocks selected for geochemical research, mostly mudstone and siltstone, often contain plant chaff. The rocks were deposited outside the river bed, in a floodplain, where conditions favourable for the development of peatbogs occurred periodically. Furthermore the organic matter deposition was *in situ* which suggests the presence of fossil soils with *Stigmaria* (B-99.00) (Gradziński *et al.* 2005)

A value of  $Pr/n-C_{17} > 2.0$ , determined in coal samples and the B-60.70, B-74.80 and B-99.00 rock samples, can be ascribed to deposition of organic matter in peat-swamp environments (Text-fig. 11; Volkman and Maxwell 1986; Peters *et al.* 2005). In the remaining samples low amounts of pristane in relation to  $n-C_{17}$  suggest deposition in open-water environments (Volkman and Maxwell 1986; Fleck *et al.* 2001).

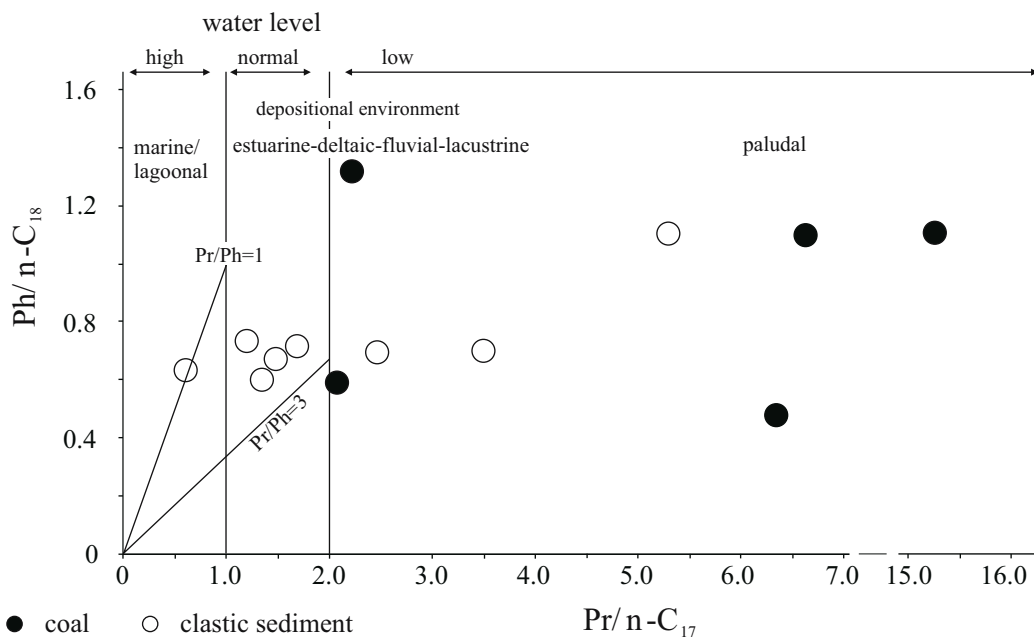
A low concentration of steranes  $C_{27}$  in coal samples suggests swamp water levels, the presence of development hindering plankton and/or algal matter. Similar conclusions can be drawn from the analysis of param-

eter  $R_{dit}$  based on diterpanes. Its value in samples B-385/2A and B-382 equals approximately 1 and in samples B-385/2B and B-385/2C  $R_{dit}$  is above 1 (Table 1). Consequently in the two first samples its value suggests mid-level water tables and in the remaining two low-level water tables (Fleck *et al.* 2001; Piedad-Sánchez *et al.* 2004). Differences in diterpanes concentrations in coal samples from the B-385/2 bed suggest ephemeral peat swamp occurring at least locally.

The B-16.00B coal sample contained the highest values of the  $R_{dit}=1.27$  parameter (Table 1) and values of the  $Pr/n-C_{17}$  parameter relatively low for coal, suggesting the highest of the tested coal levels of water in the deposition pool and probably water-logged swamps.

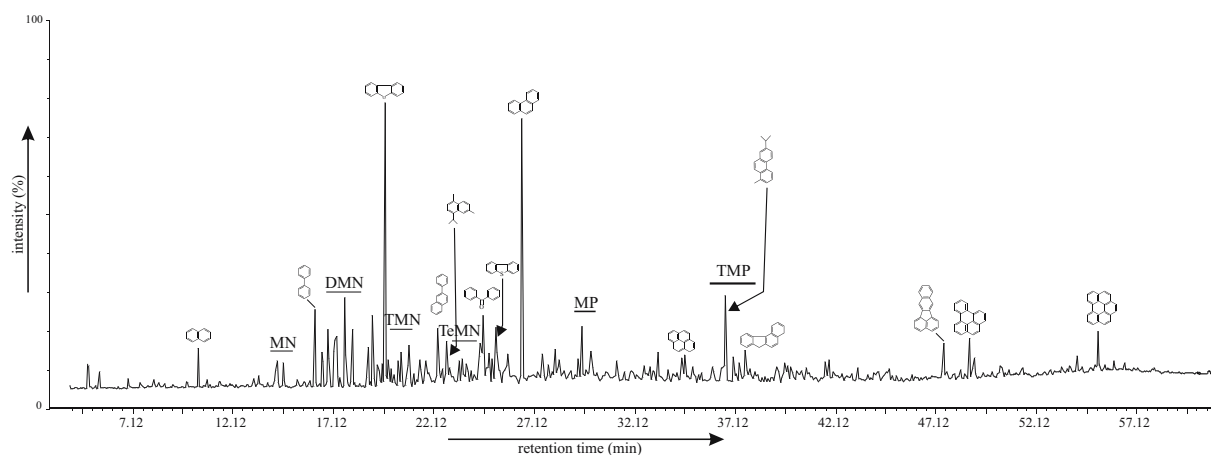
For clastic sediment the  $R_{dit}$  value ranged from 0.73 to 1.41 (Table 1), indicating flood plain water table levels, varying from very low (B-99.00 – stigmariamian soil) to high (B-60.70). Samples B-16.00 and B-36.00, which displayed a high concentration of steranes, especially the compound  $C_{27}$  and the presence of extended tricyclic triterpanes, allowed us to infer the periodic existence of small ponds.

The value of the  $Pr/Ph$  (pristane/phytane) parameter for most of the analyzed samples varied from 0.93 to 3.11 (for clastic rocks) and from 3.49 to 22.57 (for coals, Table 1). Such a distribution suggests the deposition of organic matter under variable dysoxic and oxic conditions in the case of clastic rock samples, and highly oxic for the coal samples (Didyk *et al.* 1978; ten Haven *et al.* 1987; Rontani and Volkman 2003). The  $Pr/Ph$  parameter should, however, be used with caution because it is known that chlorophyll is not the only source of



Text-fig. 11. The  $Pr/n-C_{17}$  vs.  $Ph/n-C_{18}$  diagram (after Scheffler 2004, slightly modified)





Text-fig. 12. TIC (total ion chromatogram) of aromatic fractions in samples: B-99 (mudstone) Annotation: MN – methylonaphthalens, DMN – dimethylnaphthalens, TMN – trimethylnaphthalens, TeMN – tetramethylnaphthalens, MP – methylphenantrens, TMP – trimethylphenantrens

these isoprenoids, especially when the value of this ratio exceeds 3.00. This value indicates that a pristine precursor could be tocopherols (Peters *et al.* 2005). Therefore, the Pr/Ph ratios in the samples do not indicate changes in the redox conditions during sedimentation, but rather a terrigenous plant input under suboxic conditions (Brown and Kenig 2004; Marynowski and Filipiak 2007; Peters *et al.* 2005).

Samples of both coal and clastic rocks clearly indicate the presence of tetracyclic triterpanes  $C_{24}$  and  $C_{25}$  (Text-fig. 5A), with the  $C_{24}$  compound dominating over tricyclic  $C_{26}$ . The presence of tetracyclic compounds in sediment was ascribed to terrigenous matter (Philp 1985; Grice *et al.* 2001). Philp (1994) suggested that the occurrence of these compounds can reflect depositional conditions rather than the primary source of organic matter. In deltaic and swamp environments, the oxic conditions will favor an increase of bacterial activity and the production of hopanoid precursors. Subsequently, the bacterial activity led to a degradation of hopanes and the production of tetracyclic triterpanes (Philp 1994). Due to the degradation of tricyclic diterpenoids derived from conifer resin, i.e. abietane and pimarane, bicyclic alkanes were produced (Miranda *et al.* 1999). These compounds are present in the coal samples only. The presence of such compounds can point to bacterial degradation of plant material *in situ*, before the burial of organic matter (Fleck *et al.* 2001).

## CONCLUSIONS

- The calculated parameters of the degree of thermal transformation of organic matter suggest that the sediments were altered at a low-grade, at the margin of the early microbial transformation stage and the initial

oil-window stage. This is consistent with results of Kotarba and Clayton (2003) and of Gola *et al.* (2011), for the LCB sediments. Differences in the value of the maturity parameters, e. g., on the concentration of the  $C_{29}$  steranes or  $T_{max}$ , are probably connected with biodegradation of organic matter, confirmed in the clastic sediments.

- Organic matter in the Lublin Formation is dominated by terrigenous organic material: higher plants and fungi. This is indicated by the predominance of odd-over-even carbon-numbered *n*-alkanes in the range of long-chain compounds, the presence of eudesmane, bisabolane and dihydro-*ar*-curcumene, and high contents of  $C_{28}$  and  $C_{29}$  steranes. The presence of phyllocladanes, kauranes, cadalane and retene suggests, in addition, the role of conifer precursors as the organic matter source. A high concentration of moretanes indicates the presence of ferns.
- The values of parameters Pr/*n*- $C_{17}$  and  $R_{dit}$  suggest that water tables varied during deposition of the formation. In the case of peat swamp coals the initial water levels ranged from very high level water-logged swamps to very low level ephemeral swamps.
- The elevated concentrations of steranes/17 $\alpha$ (H)hopanes observed in some cases and extensive tricyclic terpanes suggest the presence of algal matter in the input of primitive organic matter. The conditions favourable for the development of this group could, most probably, have developed on flood plains.
- The large amount of pentacyclic triterpanes in relation to steranes indicates the presence of drimane homologues, and the presence of the benzohopanes suggest



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that the terrigenous organic matter underwent an intensive bacterial transformation. This process most likely took place during transport to the sedimentary basin and during early diagenesis. The microbial matter was one component of the primary organic matter input delivered to the sedimentary basin.

- Our results should be regarded as preliminary. A more detailed geochemical investigation is necessary to perform an analysis of coal macerals and a pyrolytic Rock-Eval analysis.

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