GEOCHEMICAL CHARACTERIZATION AND PALAEOENVIRONMENTAL IMPLICATIONS OF LIPIDS IN NEOGENE LIGNITES AND LIGNITIC SHALES IN NW POLAND

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Abstract: The lipophilic biomarker distributions in lipids of Neogene lignites and lignitic shales in western Pomerania and the midlands of Poland are presented. Twenty-six lignite samples and seven lignitic shales were obtained from twenty-four boreholes. Their extracts were separated, using thin-layer chromatography, and the saturate and aromatic fractions were analyzed by gas chromatography-mass spectrometry. The molecular compositions of *n*-alkanes, isoprenoids, *n*-alkylcyclohexanes, *n*-alkylbenzenes, tri- and tetracyclic diterpenoids, pentacyclic triterpenoids, as well as polycyclic aromatic hydrocarbons (PAHs) with up to five rings, were determined. The samples displayed *n*-alkane distributions in the range of C_{14}–C_{35} and high odd-over-even carbon number predominances ($CPI_{(25–33)}$ from 2.9 to 7.9). Diterpanes consisted primarily of phyllocladane, abietane, isopimarane, labdane, and kaurane structures, although their abundances varied among the samples. Hopanes exhibited the biological and geochemical characteristics of low-maturity organic matter. Minor oleanane triterpenoids from angiosperms were also found. A few samples displayed evidence of biodegradation on the basis of the advanced isomerization of αβ-hopanes and the presence of short-chained *n*-alkanes, *n*-alkylcyclohexanes, and *n*-alkylbenzenes. A more mature stage of the above biomarkers also may have resulted in part from the oxidation of organic matter. The lignite source materials were derived from conifer and angiosperm flora as well as microbial remnants. The contribution from marine phytoplankton was excluded on the basis of the lack of C_{27} steroids. PAHs were predominantly perylene or phenanthrene, with minor other analogues. Thus, the data support progressive lacustrine/lagoonal sedimentation in the palaeoenvironmental mires.

Key words: Lignites, biomarkers, *n*-alkanes and isoprenoids, diterpenoids, triterpenoids, polycyclic aromatic hydrocarbons.

INTRODUCTION

The extractable organic matter (EOM) of lignites provides useful information on lignite-forming mire environments and the course of molecular transformations during the early stages of diagenesis (e.g., Didyk *et al.*, 1978; Simoneit, 1978; Fu *et al.*, 1990; Püttmann *et al.*, 1991; Dehmer, 1995; Bechtel *et al.*, 2003). At the early post-depositional stage,

these transformations are caused mainly by microbial activity, while during subsequent post-burial stages further alterations are caused by increasing temperature and pressure as well as the catalytic effects of the mineral matrix (Mackenzie and Mckenzie, 1983; Chaffee *et al.*, 1986 and references therein). Biomarkers, found in different types of

sedimentary organic matter (OM), consist of transformed structures inherited from once-living organisms and allow the assessment of the OM source as well as its post-depositional transformation processes (Peters *et al.*, 2005). Extensive research, including both petrographical and geochemical analyses, has been conducted on lignites from numerous global regions, including Poland (Fabiańska, 2007; Fabiańska and Kurkiewicz, 2013; Jaroszewicz *et al.*, 2018; Bechtel *et al.*, 2020).

Distributions of biomarkers are useful in determining the biological sources of the sedimented OM (Moldowan *et al.*, 1985; Simoneit, 1986), reconstructing basin redox conditions (Didyk *et al.*, 1978; Peters and Moldowan, 1993), characterizing salinity levels during OM deposition (Ten Haven *et al.*, 1985, 1988; Volkmann, 1988), as well as assessing coal maturity (Hazai *et al.*, 1988). The biomarker compositions in low-rank coals have been widely investigated (Chaffee and Johns, 1983, 1985; Chaffee *et al.*, 1986; Farnum *et al.,* 1984; Hazai *et al.*, 1988, 1989; Noble *et al.*, 1985; Wang and Simoneit, 1990; Dai *et al.*, 2020) and are readily analyzed, using gas chromatography-mass spectrometry (GC-MS).

The aliphatic hydrocarbons in coal lipids have been studied most extensively. Particularly significant are the *n*-alkanes, since their distribution can be related to the biological origin and rank of the coal (Chaffee *et al.*, 1986). A strong predominance of odd-over-even carbon number of the C_{27}–C_{31} *n*-alkanes is related to a terrestrial, higher-plant origin, particularly angiosperms, where they occur as the main components of epicuticular waxes (Eglinton and Hamilton, 1967). Short-chain *n*-alkanes ($<C_{20}$) are found predominantly in algae and microorganisms (Cranwell, 1977; Volkmann and Maxwell, 1986) and those of intermediate molecular weight (C_{21}–C_{25}) are believed to originate from aquatic macrophytes (Ficken *et al.*, 2000; Nott *et al.*, 2000).

The most frequently reported cyclic (non-aromatic) hydrocarbons in coals are di- and triterpenoids (Jarolím *et al.*, 1965; Streibl and Herout, 1969; Chaffee *et al.*, 1986). Diterpenoid hydrocarbons originate mainly from gymnosperms (conifers) and typically include abietanes, pimaranes, kauranes, phyllocladanes, podocarpanes and labdanes (Noble *et al.*, 1985; Simoneit *et al.*, 1986). Hopanes, in turn, are the most common triterpenoid hydrocarbons, which are derived from bacteria and also certain plants (Ageta and Arai, 1983; Hazai *et al.*, 1988; Shiojima *et al.*, 1990). In lignites, they consist primarily of 17β(H),21β(H)-hopanes and 22*R*-17α(H),21β(H)-homohopane. The minor triterpenoid hydrocarbons, including oleanane, ursane, and lupane structures, are derived from angiosperms (Simoneit, 1986; Otto and Simoneit, 2001).

Steroids, which originate mostly from eukaryotic organisms, occur in lignite lipids in low abundance or are absent. When present, lower-rank coals display a higher relative abundance of C_{29} steranes in comparison to the C_{28} and C_{27} homologues (Norgate *et al.*, 1999), which is consistent with a higher-plant input (Peters and Moldowan, 1993). Aromatic hydrocarbons occur in low concentrations in lignite extracts. Polycyclic aromatic hydrocarbons (PAHs), found in coals and other geological materials, are derived, at least partially, from the aromatization of terpenoids and other

naturally occurring precursors during coalification (Jarolím *et al.*, 1965; Hayatsu *et al.*, 1990; Simoneit, 1998). The PAH concentrations increase with the coal rank up to the peak of the oil window.

In addition to the well-known, large lignite deposits in Poland (Fabiańska, 2007; Fabiańska and Kurkiewicz, 2013), there are frequent lignite occurrences within the sediments of the northwestern Polish Lowlands. Exploration for crude oil and natural gas revealed the redeposition of Neogene and preglacial sedimentary layers with lignite inserts in various areas of the Lowlands and provided the detrital coaly material of the Neogene strata for this study. Geochemical data in this exploration area are scarce and drill-chip samples of immature coals proved valuable for palaeoenvironmental evaluation. Here the authors present the results of a geochemical study of 30 Neogene and 3 Quaternary lignites and lignitic shales in northwestern Poland.

MATERIALS AND METHODS

Geological setting

Exploration activities in the northwestern region of Poland, conducted by the Polish Oil and Gas Exploration Company (PGNiG Capital Group), even though focused on recovering oil and gas from the Rotliegend and Zechstein Main Dolomite deposits, also provided samples of lignite and lignitic shale seams in the Cenozoic formations (Quaternary and Neogene). These formations represent structural units, comprising a continuous sedimentary layer that occurs unconformably on the Permo-Mesozoic complex as a consequence of the Laramide stage movements. A map of the study area, showing the location of the boreholes, is presented in Figure 1; the location names and borehole coordinates are given in Table S1. The study area was subdivided into five regions on geostratigraphic grounds. The distinguishable geological units, i.e., Pomeranian Trough, Pomeranian Swell, Szczecin Trough, Gorzów Block and Fore-Sudetic Monocline (Narkiewicz and Dadlez, 2008) consist of generally horizontally bedded clastic deposits of Oligocene and Neogene sands and gravels, Miocene clayey-silty-sandy series with lignite inserts (lignite formation), and Pliocene variegated clays (Kramarska, 1999; Stankowski, 2000). The Quaternary strata contain post-glacial sediments, commonly consisting of sands, gravels and glacial tills. The total depth of the Cenozoic cover varies from 50 to 300 m. Currently, these deposits represent the fundamental glacial series of the Early Pleistocene (Stankowski, 2001). For this study, 26 lignite and 7 lignitic shale drill-chip samples were collected from 24 boreholes within 33 layers of thickness greater than 1 m.

Sample lithotypes, proximate and ultimate analyses

The analyzed samples, in which the ash content does not exceed 50%[d], represented lignites, while the samples with an ash content above this value represented lignitic shales (Tab. 1). The lignite lithotypes are related to textural appearance. The xylitic lignite contain more than 90% of various fossilised woody fragments, larger than 1 cm. The detritic
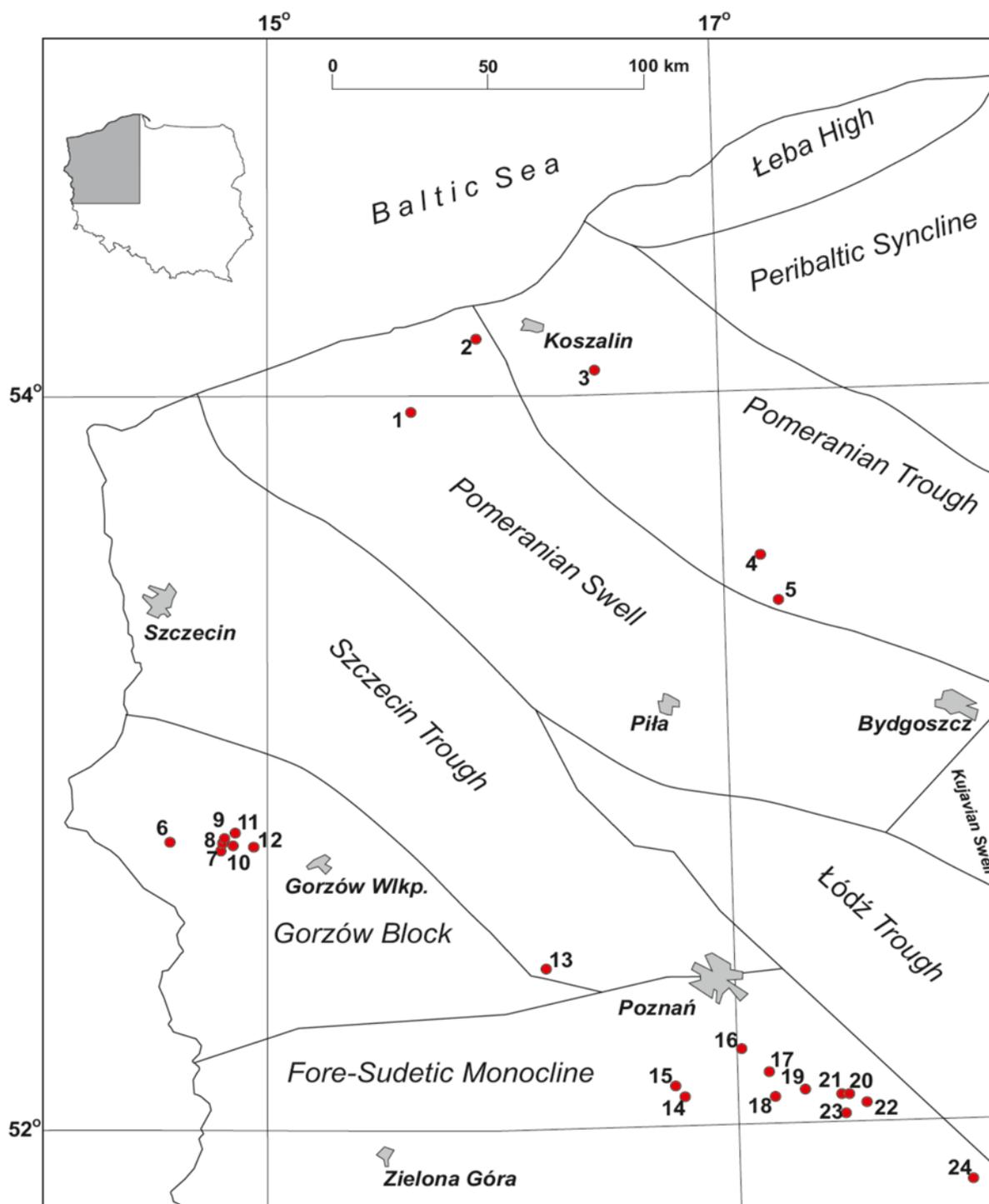
Fig. 1.   Map of borehole locations for the lignite and lignitic shale samples with the geological regional subdivisions of Poland at the sub-Cenozoic palaeosurface (after Narkiewicz and Dadlez, 2008). Borehole location names in accordance with the borehole numbers are given in Table 1.

lignite is composed of smaller sizes of plant detritus (representing not less than 90% of the matrix), distributed irregularly within the detritic matrix. The association of the two earlier mentioned lithotypes within 10–90% of the content represents detro-xylitic or xylo-detritic lignite. In the detro-xylitic lignite, xylites predominate (50–90%), while the opposite is true for xylo-detritic lignite. Each of these

lithotypes may be partly gelified. According to the classification proposed by Kolcon and Sachsenhofer (1999) and Kwiecińska and Wagner (2001), the investigated lignites represented the following lithotypes: detritic (5 samples), xylitic (13 samples), detro-xylitic (5 samples) and xylo-detritic coals (3 samples), whereas the 7 lignitic shales represented the detritic lithotype (Tab. 1). Moisture, ash, and

Table 1

Location name, geological age, lithology, lithotype and proximate analyses of the lignite and lignitic shale samples.

Sample number*	Location name	Strati-graphy	Sample depth** [m]	Lithology	Lithotype	Lithotype description	Moisture M^a [%]	Ash A^d [%]	Volatile matter V^{daf} [%]
1	Słowenkowo	N	145	lignite	xylitic	gelified, black	9.0	12.4	56.4
2	Smolne	Q	25	lignite	xylitic	brittle	11.0	9.4	55.4
3	Grzybnica	N	165	shale	detritic	hard, black	6.3	54.2	65.9
4	Stanisławka	N	245	shale	detritic	soft, black	3.6	82.4	75.5
5	Osowiec	N	90	lignite	xylo-detritic	black	8.2	19.3	66.6
6	Zielin	N	120	lignite	xylitic	brittle	9.5	18.2	61.1
7	Barnówko	N	85	lignite	detro-xylitic	gelified, brown	8.7	32.1	59.4
8	Barnówko	N	100	lignite	detritic	soft	8.2	46.2	58.9
9	Dolsk	Q	55	shale	detritic	black	6.2	62.8	64.9
10	Dolsk	N	70	shale	detritic	gyttia	6.3	63.1	64.8
11a	Gajewo	Q	40	lignite	xylitic	brittle, gelified	8.6	8.6	60.1
11b	Gajewo	N	110	lignite	detritic	brittle, brown	8.1	39.8	62.2
12	Mosina	N	165	lignite	xylitic	brittle, hard	7.2	4.8	65.6
13a	Józefowo	N	110	lignite	xylitic	soft, brown	11.2	13.1	57.3
13b	Józefowo	N	170	shale	detritic	soft, black	7.8	54.3	60.0
13c	Józefowo	N	190	shale	detritic	soft, black	5.5	63.6	61.8
14	Stary Gołębin	N	265	lignite	detro-xylitic	soft, brown	9.2	24.1	64.3
15a	Słonin	N	150	lignite	xylitic	fibrous	9.7	7.2	57.0
15b	Słonin	N	170	lignite	xylo-detritic	black	10.6	19.1	55.9
16a	Radzewo	N	80	lignite	detritic	black	9.0	32.8	65.0
16b	Radzewo	N	120	lignite	xylitic	brittle	8.0	13.9	60.0
16c	Radzewo	N	165	organic rich clay	detritic	gelified	6.1	51.3	62.0
17a	Polesie	N	85	lignite	xylitic	fibrous with detritic inserts	9.1	13.9	60.9
17b	Polesie	N	130	lignite	detritic	brown	8.9	35.4	54.5
18a	Konarzyce	N	80	lignite	detritic	black with fibrous xylite inserts	10.4	10.9	57.3
18b	Konarzyce	N	130	lignite	detro-xylitic	brittle	9.9	27.1	58.4
19	Świączyń	N	80	lignite	xylitic	brittle, gelified	11.2	9.3	58.1
20	Wolica Nowa	N	80	lignite	xylitic	brittle, fibrous	8.5	9.7	61.5
21a	Wolica Kozia	N	110	lignite	xylitic	fibrous	8.0	13.9	65.5
21b	Wolica Kozia	N	115	lignite	xylitic	brittle, fibrous	10.0	13.0	58.6
22	Parzewnia	N	115	lignite	detritic	detritic	9.6	31.1	55.9
23	Mieszków	N	65	lignite	detro-xylitic	brittle	10.6	11.6	58.0
24	Jedlec	N	90	lignite	xylitic	fibrous	8.0	11.7	79.6

* Sample number correlates with the borehole number in Figure 1. The increasing sample depth in a given borehole is designated by the number followed by the letters a, b or c.

** The layer depth from which the drill-chip sample was collected (± 1 m)

N = Neogene; Q = Quaternary.

[a] The data on analytical basis.

[d] The data on dry basis.

[daf] The data on dry ash free basis.

volatile matter contents were determined, following the ISO standards, i.e., ISO 5068:1983; ISO 1171:1997, and ISO 5071-1:1997, respectively (Tab. 1). The elemental analysis of carbon, hydrogen, nitrogen, and sulphur was carried out, using a Leco CHNS multi-element analyzer. C, H and N were reported on a dry, ash-free (daf) basis and total S (mineral + organic) on a dry basis (d); the data are presented in Table 2.

Solvent extraction

Finely powdered lignite and lignitic shale samples (ca. 10 g) in pre-washed thimbles were exhaustively extracted in a Soxhlet apparatus, using an azeotropic mixture of dichloromethane (DCM) and methanol (93:7, v/v). Extracts were filtered through a filter paper to remove insoluble particles. Filtrates were concentrated preliminarily using a rotary

Table 2

Ultimate analysis of the lignite and lignitic shale samples, and yield of the extractable organic matter and its group composition.

Sample number	Location name	Elemental analysis				EOM	EOM fraction		Maltene fraction		
		C^{daf}	H^{daf}	N^{daf}	S_t^{d}		Asphaltenes	Maltenes	Aliphatic	Aromatic	Polar
		[%]				[%^{daf}]	[%]				
1	Słowenkowo	64.39	5.35	0.67	1.74	3.90	35.5	64.5	15.7	36.7	47.6
2	Smolne	68.48	6.06	0.42	1.22	4.12	47.9	52.1	8.7	16.7	74.6
3	Grzybnica	50.60	5.22	0.68	3.66	7.00	32.7	67.3	8.8	76.8	14.4
4	Stanisławka	58.20	5.51	0.74	1.72	2.10	59.4	40.6	63.6	11.6	24.8
5	Osowiec	65.88	6.41	0.84	3.12	9.00	35.1	64.9	10.0	12.7	77.3
6	Zielin	63.11	5.56	0.51	2.38	6.62	54.2	45.8	8.3	29.3	62.4
7	Barnówko	62.78	5.01	0.49	2.47	5.56	34.5	65.5	11.1	14.5	74.4
8	Barnówko	54.30	4.90	0.41	1.40	4.44	44.7	55.3	13.0	12.5	74.5
9	Dolsk	56.59	5.67	0.81	1.71	3.83	45.1	54.9	18.3	11.3	70.4
10	Dolsk	54.46	5.30	0.83	2.12	3.79	37.2	62.8	25.1	8.5	66.4
11a	Gajewo	64.55	5.66	0.38	1.74	2.34	49.2	50.8	12.5	17.0	70.5
11b	Gajewo	64.09	5.80	0.73	1.76	6.55	33.7	66.3	10.0	13.0	77.0
12	Mosina	64.08	5.75	0.13	1.80	2.32	31.4	68.6	11.4	7.0	81.6
13a	Józefowo	64.15	5.51	0.77	0.76	4.91	30.5	69.5	5.4	17.1	77.5
13b	Józefowo	60.40	5.33	0.88	0.75	2.86	50.6	49.4	13.6	11.4	75.0
13c	Józefowo	50.98	5.07	0.59	2.79	8.48	34.4	65.6	25.0	22.2	52.8
14	Stary Gołębin	65.57	5.18	0.58	0.84	5.33	40.4	59.6	7.2	13.8	79.0
15a	Słonin	64.39	5.50	0.70	0.59	5.02	33.9	66.1	5.2	11.4	83.4
15b	Słonin	65.72	5.72	0.56	1.38	4.86	44.3	55.7	5.7	11.5	82.8
16a	Radzewo	61.44	5.52	0.73	1.84	3.17	44.6	55.4	10.6	15.2	74.2
16b	Radzewo	64.01	6.05	0.40	0.92	5.17	26.7	73.3	7.0	28.3	64.7
16c	Radzewo	54.23	5.37	0.55	1.27	4.79	50.2	49.8	11.1	19.7	69.2
17a	Polesie	66.35	6.07	0.50	0.54	7.51	30.8	69.2	5.1	16.6	78.3
17b	Polesie	67.29	5.03	0.47	0.43	4.31	35.0	65.0	9.4	18.2	72.4
18a	Konarzyce	63.70	5.45	0.54	0.77	4.11	43.0	57.0	10.5	9.7	79.8
18b	Konarzyce	65.38	5.27	0.51	1.28	4.28	46.9	53.1	8.7	20.9	70.4
19	Święczyń	65.35	5.76	0.76	0.55	6.50	26.7	73.3	5.0	30.3	64.7
20	Wolica Nowa	63.88	6.05	0.34	0.79	4.13	39.1	60.9	9.4	7.9	82.7
21a	Wolica Kozia	61.36	6.16	0.23	0.64	3.37	44.3	55.7	9.4	10.6	80.0
21b	Wolica Kozia	64.11	5.63	0.55	0.76	3.57	42.4	57.6	6.7	12.7	80.6
22	Parzewnia	64.89	5.31	0.58	0.77	4.60	32.5	67.5	5.2	25.9	68.9
23	Mieszków	65.59	5.79	0.7	0.77	6.38	36.6	63.4	5.6	7.2	87.2
24	Jedlec	56.99	6.22	0.13	0.69	3.31	48.7	51.3	6.2	10.4	83.4

evaporator and residual solvent was removed by evaporation at room temperature to constant mass. Extract yields of the samples are reported on a dry, ash-free basis (EOM^{daf}, Tab. 2).

Maltene fractionation

Asphaltenes were removed from the extracts by precipitation with an excess of *n*-hexane. The *n*-hexane soluble fraction (maltenes) was further separated, using pre-washed silica gel thin-layer chromatography (TLC) plates (Merck Kieselgel 60H, 20 × 20 × 0.025 cm). Prior to the separation, the TLC plates were activated at 150°C for 3 h. The TLC plates were loaded with ca. 50 mg of the *n*-hexane soluble fraction and developed with an *n*-hexane-DCM mixture (9:1, v/v). Specific bands were visualized under UV light and consisted of saturate (lack of fluorescence, R_f 0.4–1.0), aromatic (blue-violet fluorescence, R_f 0.05–0.4) and polar (R_f 0.0–0.05) fractions. These fractions were subsequently collected and recovered by DCM dissolution from the silica gel. The contents of the saturated, aromatic, and polar fractions in the maltenes are presented in Table 2.

Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) analyses of saturated and aromatic fractions were carried out using an HP5890 II gas chromatograph, interfaced with an HP 5971A mass spectrometer detector. The GC was equipped with a fused silica capillary column (30 m × 0.25 mm i.d.), coated with diphenylpolysiloxane (HP-5, 0.25 µm film thickness), and helium was used as a carrier gas at a rate of 1 cm^3 × min^{-1}. The GC oven was programmed from 25 to 290°C at a rate of 3°C × min^{-1} and a 30-min hold at the final temperature. The MS was operated in the electron impact mode with an ionization energy of 70 eV and an ion source temperature of 200°C. Samples were analyzed, using the full scan mode (mass range 40–600 Da with a cycle time of 1 s). Homologous compound series were identified, using diagnostic fragment ions in the total ion current (TIC) chromatograms. Compound identification was based on the comparison of GC retention times with known retention times of reference standards, and literature mass spectra as well as the interpretation of MS fragmentation patterns. The key *m/z* ions, used for the compound identification, are indicated in discussions of the data and in the figure descriptions.

RESULTS AND DISCUSSION

Bulk properties

The bulk properties of the lignites and lignitic shales (lithotypes, ultimate analysis, elemental composition) are presented in Tables 1 and 2. Both ash and total sulphur (TS) contents varied considerably. High ash, above 30%^{d}, as well as elevated TS contents, were found for humodetritous lignites and lignitic shales, while xylitic lignites had lower ash, typically below 10%^{d} w/w, and lower TS. The elevated mineral content in some samples was indicative of mire deposition in a swampy environment with favourable conditions

for such accumulations. The carbon content was within the range of 51–68%^{daf} and the hydrogen content varied from 4.9 to 6.4%^{daf}, indicating the low maturity of the lignites. The atomic H/C and O/C ratios were in the range of 0.9–1.3 and 0.3–0.6, respectively, and when plotted on the correlation diagram (Tab. 2, O^{daf} by difference to 100%: Fig. 2), the data are within a narrow immature zone of Type III kerogen (Van Krevelen, 1993).

The EOM yields were in the range of 2.1–9.0%^{daf}, and the saturated and aromatic hydrocarbons comprised less than 20% of the total extract mass. Resin (polar, non-hydrocarbon) and asphaltene fractions were predominant, representing more than 80% of the EOM for most samples. Such high amounts of asphaltenes and polar components in EOM are typical of low-maturity OM.
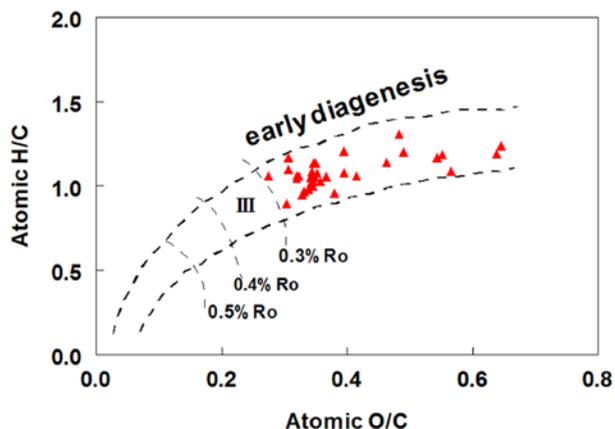
Fig. 2. Correlation diagram of the atomic O/C versus H/C ratios of the lignite and lignitic shale samples.

Molecular compositions of lipids

The GC-MS analyses of the saturated and aromatic fractions provided the compositions and distributions of the homologous series of *n*-alkanes, *n*-alkylcyclohexanes, *n*-alkylbenzenes, saturated and unsaturated as well as partly aromatized di- and triterpenoid biomarkers, and also polycyclic aromatic hydrocarbons (PAHs). Unresolved complex mixtures (UCM) of branched and cyclic compounds were observed in the TIC traces of the saturated fractions of some lignites.

n-Alkanes

The typical distribution of *n*-alkanes in most of the lignite samples was an unimodal profile in the range of C_{15}–C_{37} with a strong predominance of odd-over-even carbon number homologues (e.g., Fig. 3A for sample 22). The most common carbon number maximum (C_{max}) is at 29 or 31. A C_{max} at 29 has been attributed to the input of epicuticular wax from angiosperms, while C_{max} at 31 indicated either wax from grass or semi-tropical plants (Eglinton and Hamilton, 1967; Simoneit, 1978; Cranwell, 1982; Bechtel *et al.*, 2003, 2005). High carbon preference index $CPI_{(25–33)}$ values in the range of 2.9–7.9 (Tab. 3) indicate low maturity of the OM (Wang and Simoneit, 1990), which is consistent with the rank of the lignites. Such *n*-alkane distributions in immature sediments
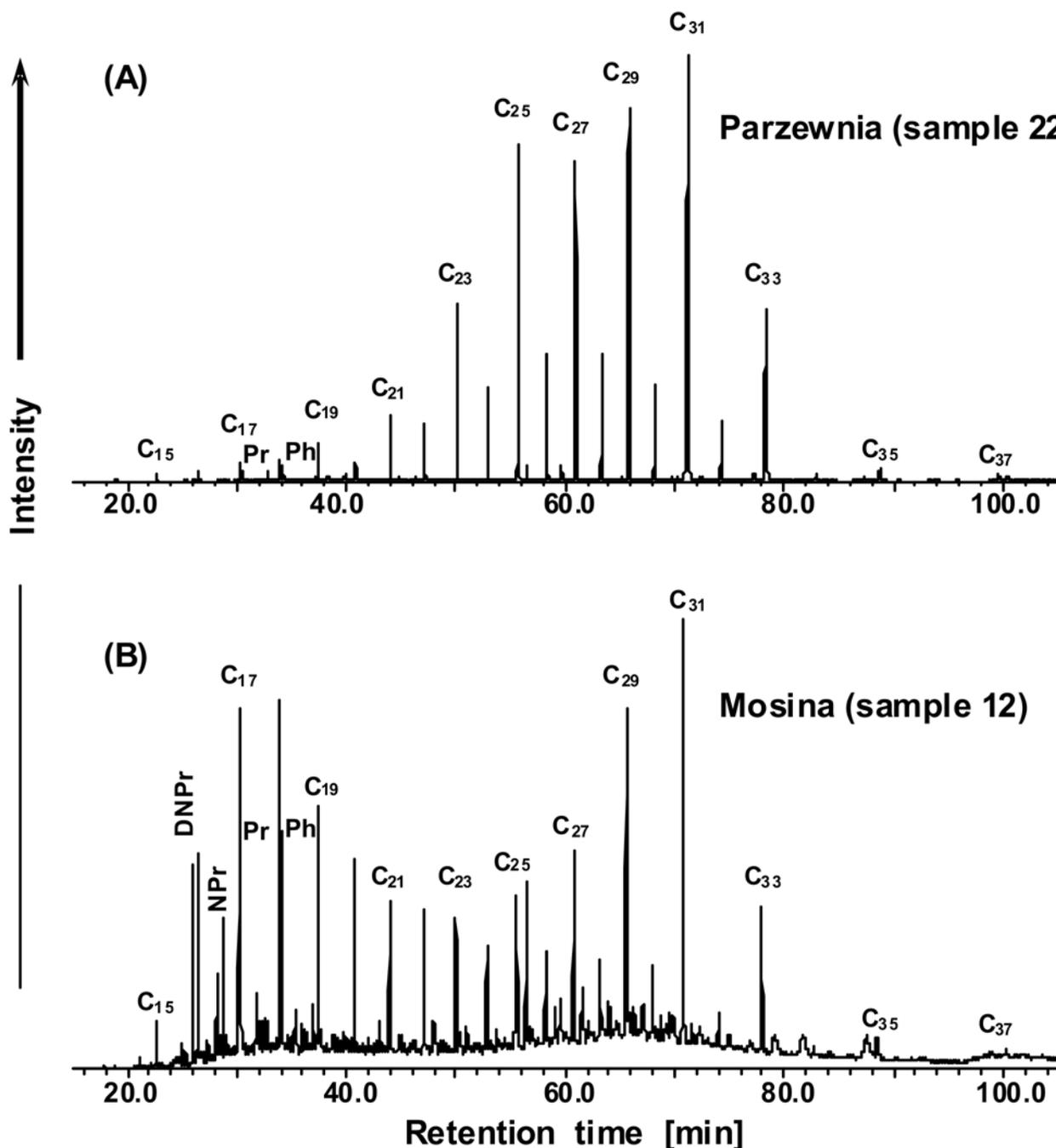
Fig. 3.   Homologue distributions of *n*-alkanes and isoprenoids (*m/z* 71) in extracts from (**A**) sample 22, and (**B**) sample 12.

reflect the direct input of intermediate chain length (C_{20}–C_{25}) from *Sphagnum* or aquatic macrophytes (Cranwell *et al.*, 1987; Ficken *et al.*, 2000; Nott *et al.*, 2000), and mainly longer-chain homologues (C_{27}–C_{33}) from higher plants (Eglinton and Hamilton, 1967; Simoneit, 1978).

Samples 2, 4, 6, 8, 12, 18b, 21a, and 24 contained *n*-alkanes with an additional Gaussian distribution of lower molecular weight homologues ($<C_{22}$) and C_{max} at 17 or 18 (e.g., Fig. 3B for sample 12). Short-chain n-alkanes indicate phytoplankton and benthic algae, or microbial activity (Simoneit *et al.*, 1979; Cranwell, 1982). The content of short-chain *n*-alkanes was low for the other samples, as assessed by the ratios of $\sum(C_{16}$–$C_{22})/\sum(C_{23}$–$C_{30})$, using the

m/z 71 mass fragmentograms (Tab. 3). Samples 4, 12, and 24 exhibited remarkably elevated concentrations of these homologues, with no odd-over-even carbon number predominance (Fig. 3B). The occurrence of shorter chain *n*-alkanes was attributed to microbial activity, as no indications of algal input were observed. A bacterial source of C_{12}–C_{19} *n*-alkanes with neither odd nor even carbon number predominance was previously reported (Simoneit and Didyk, 1978; Simoneit *et al.*, 1979). The presence of a minor UCM in the samples supports the biodegradation of organic detritus, as was noted for samples 4, 12 (Tab. 3B), and 24. Microbial activity can also lower the $CPI_{(25–33)}$ of *n*-alkanes (Allen *et al.*, 1971) and in fact, the lowest

Table 3

Selected geochemical parameters of aliphatic biomarkers.

Sample number	C_{max}	$CPI_{(25-33)}$ $(C_{25} - C_{33})$	$\frac{\sum(C_{16} - C_{22})}{\sum(C_{23} - C_{30})}$	Pr/Ph	Integration ratios		Triterpane ratios		
					$\sum$diterpanes/ C_{max}	$\sum$diterpanes/ $\sum$hopanes	C_{27} $17\alpha/(17\alpha + 17\beta)$	C_{31} $\beta\beta/(\alpha\beta + \beta\beta)$[a]	$C_{31}\alpha\beta$ $S/(R + S)$[b]
1	29	5.8	0.08	2.0	0.18	0.06	0.05	0.08	0.02
2	31	4.6	0.83	0.4	3.58	0.76	0.05	0.10	0.03
3	29	3.5	0.06	0.9	0.11	0.09	0.09	0.20	0.06
4	29	2.9	2.38	0.8	0.00	0.00	0.16	0.73	0.20
5	29	3.9	0.06	1.0	0.15	0.11	0.09	0.08	0.04
6	31	6.2	0.74	0.9	1.08	1.34	0.05	0.09	0.03
7	31	7.9	0.20	0.6	0.08	0.15	0.05	0.09	0.05
8	31	4.2	0.33	0.7	3.04	1.75	0.13	0.12	0.05
9	29	4.8	0.29	0.7	0.19	0.12	0.06	0.14	0.07
10	29	4.5	0.21	0.5	0.07	0.06	0.07	0.15	0.04
11a	29	5.4	0.23	–	0.21	0.06	0.09	0.11	0.04
11b	29	4.3	0.13	0.7	0.10	0.23	0.05	0.15	0.08
12	31	3.7	0.82	0.7	0.54	1.26	0.39	0.05	0.11
13a	29	5.3	0.08	0.8	1.55	1.22	0.05	0.07	0.02
13b	29	5.8	0.12	0.9	0.29	0.50	0.09	0.16	0.01
13c	29	4.4	–	–	0.11	0.15	0.07	0.16	0.05
14	29	4.4	0.11	0.5	0.43	0.50	0.05	0.11	0.03
15a	29	6.3	0.08	0.6	0.25	0.33	0.05	0.10	0.03
15b	29	5.0	0.18	0.5	0.57	0.31	0.05	0.11	0.04
16a	29	6.6	0.09	1.0	0.08	0.56	0.09	0.19	0.12
16b	29	3.5	0.13	0.6	1.06	0.65	0.06	0.09	0.03
16c	29	3.8	0.09	0.5	0.12	0.11	0.07	0.14	0.05
17a	29	5.3	0.20	0.7	0.35	0.64	0.06	0.11	0.04
17b	31	5.5	0.15	0.7	0.17	0.16	0.09	0.10	0.05
18a	31	6.0	0.26	0.4	1.05	0.81	0.06	0.07	0.02
18b	29	4.3	0.34	0.7	1.71	1.42	0.06	0.14	0.06
19	29	5.4	0.07	0.7	0.09	0.12	0.05	0.08	0.03
20	29	4.8	0.21	0.7	7.93	3.23	0.07	0.07	0.03
21a	29	4.3	0.62	0.5	0.87	0.35	0.06	0.08	0.04
21b	29	5.9	0.13	0.4	1.36	1.12	0.07	0.10	0.02
22	31	5.9	0.10	0.7	0.04	0.07	0.06	0.09	0.06
23	29	5.4	0.12	0.7	0.14	0.12	0.05	0.08	0.03
24	31	2.9	2.50	0.5	1.17	0.68	0.12	0.10	0.03

[a] $C_{31}\beta\beta/(\alpha\beta+\beta\beta)$ = 17β(H),21β(H)-22R homohopane/(17α(H),21β(H)-22R homohopane+17β(H),21β(H)-22R homohopane); $m/z – 191$, thermal maturity parameter (modified from Seifert and Moldowan, 1980).

[b] $C_{31}\alpha\beta$ S/(S+R) = 17α(H),21β(H)-22S homohopane/(17αH),21β(H)-22S homohopane +17α(H),21β(H)-22R) homohopane; $m/z – 191$, thermal maturity parameter (Seifert and Moldowan, 1980).

values were observed for the same samples 4, 12 and 24, which also had low EOM yields (Tab. 2). Obvious indications of biodegradation of the above-mentioned lignite samples do not exclude partial molecular modification of lipids towards the generation of stable biomarkers by the oxidative alteration of organic matter that may have occurred during breaks in peat bog sedimentation (Elie *et al.*, 2000).

Such bimodal *n*-alkane distributions may indicate mixed sources of the OM, i.e., input from both terrigenous, higher-plant waxes as well as algal or bacterial material, where longer-chain *n*-alkanes tend to predominate in detritic lignites, while shorter-chain *n*-alkanes are common in xylites (Fabiańska and Kurkiewicz, 2013). However, the $\sum(C_{16}–C_{22})/\sum(C_{23}–C_{30})$ ratios for these lignites did not confirm this pattern, as both low and high values were observed

for detritic and xylitic lignites (Tab. 3). This discrepancy may be related to variable sources of OM.

Isoprenoids

The samples contained pristane (Pr) and phytane (Ph) (Fig. 3) and the Pr/Ph ratios varied from 0.4 to 2.0 (Tab. 3). Pr and Ph originate predominantly from the phytyl side chain of chlorophyll *a* in phototrophic organisms and bacteriochlorophyll *a* and *b* in purple sulphur bacteria (Brooks and Smith, 1969; Didyk *et al.*, 1978). The hydrolytic release of the chlorophyll isoprenoid side chain may further lead to the formation of Ph or Pr, depending on the depositional and post-depositional redox conditions. Under oxygen-depleted, reducing conditions, the hydrolytic process leads to the formation of dihydrophytol, which is ultimately dehydrated and reduced to Ph. Oxic conditions, in turn, promote the conversion of phytol to Pr by oxidation of phytol to phytenic acid, decarboxylation and final reduction to Pr (Peters *et al.*, 2005; see Supplementary Fig. S1). On the basis of the formation pathways, Didyk *et al.* (1978) proposed the Pr/Ph ratio as an indicator of redox conditions of the palaeoenvironment. It was postulated that ratios <1.0 reflect anaerobic conditions (lower E_h environments), while values >1.0 indicate oxic conditions (higher E_h, suboxic-oxic environments) during OM deposition. Only sample 1 had Pr/Ph >1, with all others exhibiting values <1 indicating semi-oxic depositional conditions (Tab. 3). However, it should be noted that Pr/Ph could be impacted to some extent by evaporative losses during the analytical procedure, since Pr is slightly more volatile than Ph. Also, there are some limitations to the use of this ratio as a redox indicator. The value of the ratio can be affected by kerogen maturity (Tissot and Welte, 1984) and these isoprenoids also can be derived from tocopherols or chromans (Goossens *et al.*, 1984) as well as from phytanyl ether lipids of archea (Ten Haven *et al.*, 1987).

n-Alkylcyclohexanes and n-alkylbenzenes

n-Alkylcyclohexanes (*m/z* 82) and *n*-alkylbenzenes (*m/z* 92) were observed in the extracts of most lignites and both compound series displayed similar unimodal Gaussian distributions of C_{15}–C_{27} and C_{max} of 17 or 18. In most samples, their relative concentrations in comparison to *n*-alkanes were low and paralleled the concentrations of lower molecular weight *n*-alkanes. Indeed, the highest concentrations of *n*-alkylcyclohexanes and *n*-alkylbenzenes were for samples 4, 12, and 24, where the lower molecular weight *n*-alkanes also were elevated (see Fig. 3B). Similar distribution patterns of lower molecular weight *n*-alkanes, *n*-alkylcyclohexanes, and *n*-alkylbenzenes indicate a diagenetic relationship among these compounds.

n-Alkylcyclohexanes and *n*-alkylbenzenes are generated during the catagenetic maturation of bitumen and oil. It is postulated that the thermal alteration of poly-unsaturated *n*-alkanoic acids can yield *n*-alkylcyclohexanes, which subsequently are converted to *n*-alkylbenzenes (Rubinstein and Strausz, 1979; Dong *et al.*, 1993). In general, double bonds present in alkyl chains (e.g., lycopene, squalene, polyunsaturated *n*-alkanoic acids) may act as reaction centres, at which ring closure can occur, leading ultimately to the formation of an aromatic moiety (Gorchs *et al.*, 2003).

However, low-maturity lignites were not exposed to sufficient thermal stress after deposition and therefore the low concentrations of *n*-alkylcyclohexanes and *n*-alkylbenzenes in these samples are more likely to be the products of microbial alteration of *n*-alkenoic acids under semi-oxic conditions during the early stages of diagenesis.

Diterpenoids

The distribution of non-functionalized diterpenoids was assessed, using the *m/z* 123 fragmentograms. The diterpenoids in the lignites included a relatively wide range of structures with varying abundances of individual compounds, as illustrated by the examples (Fig. 4).

Diterpenoids were not found in the lignitic shale with the highest mineral content (sample 4 with 82.4%[d] ash). The relative abundances of individual diterpanes, based on the integration from *m/z* 123 fragmentograms and assuming the same response factors, are summarized in Table 4. Their identification was based on standards, published MS data, as well as known GC retention times (Thomas, 1969; Simoneit, 1977; Hagemann and Hollerbach, 1979; Philp *et al.*, 1981; Noble *et al.*, 1985; Tuo *et al.*, 2003). The structures of these diterpanes are presented in the Supplemental Material (Supplementary Fig. S2).

16α(H)-Phyllocladane (XIX) (Tab. 4; Fig. 4) was the predominant diterpane in most samples and has often been reported as the most common diterpane in lignites (Noble *et al.*, 1985; Alexander *et al.*, 1987). It was proposed as an indicator of the Cupressaceae, Podocarpaceae and Araucariaceae families, but excluding Pinaceae, where it does not occur (Otto *et al.*, 1997; Otto and Wilde, 2001). Samples 8 and 20 are unique with a relatively low abundance of 16α(H)-phyllocladane (Tab. 4). The lack or low concentrations of the thermodynamically more stable 16β(H)-phyllocladane (XVI) in comparison its less stable epimer in the lignites is in accord with their low maturity.

Isopimarane (XV) and 18-norisopimarane (X) were the second most common compounds of the diterpenoid class, with the first one present at elevated concentrations (>50 units) in samples 1, 2, 3, 6, 11b, 15b, 17b, 18a, 21b, 22 and 24. High abundances of pimaranes (indicators of conifer families such as Pinaceae and Cupressaceae), as well as isopimaranes (common in all conifer families except Cephalotaxaceae; Otto and Wilde, 2001), are consistent with earlier reports postulating these compounds as conifer markers (Noble *et al.*, 1986; Blunt *et al.*, 1988; Philp, 1994). Sample 6 exhibited a high relative concentration of isophyllocladene (XIII, Fig. 4B), in addition to the typically high abundance of 16α(H)-phyllocladane.

12β(H)-Sempervirane (II), 14β(H)-totarane (VIII), abietane (XVII), *ent*-beyerane (XXI), and cassane (XXII) (Tab. 4) were predominant in fibrous xylites (Fig. 4C, D for samples 17a and 20), while sample 8 (detritic lignite), apart from the first two diterpanes, contained mainly fichtelite (XIV) with a low abundance of 16α(H)-phyllocladane (Fig. 4E). Semperviranes and totaranes, with abietanes in part, were derived from their phenolic diterpenoid precursors by hydrogenation (Simoneit *et al.*, 2019, 2021). Abietane (XVII) was found in 29 samples and its relative concentration averaged 25 units as the third most common diterpane
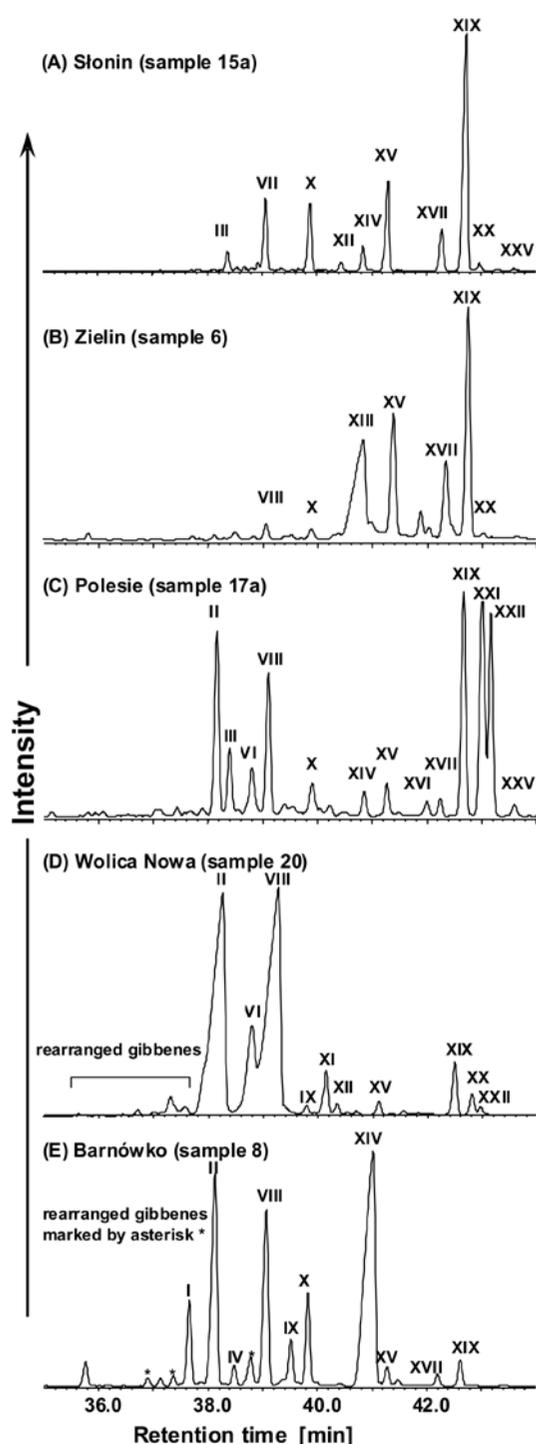
Fig. 4. Mass fragmentograms (*m/z* 123) of diterpanes in selected lignites. Peak numbers refer to compounds in Table 4 and the structures in Supplementary Figure S2.

(Tab. 4). The occurrence of semperviranes, totaranes and abietanes was accompanied by ferruginol (XXV), sugiol (XXVII), 6,7-dehydroferruginol (XXIV), 5,6-dehydrosugiol (XXVI), and 12-hydroxysimonellite (XXVIII), are all characteristic of Cupressaceae and Podocarpaceae conifer families (Simoneit, 1977; Otto and Simoneit, 2001, 2002; Stefanova *et al.*, 2002; Simoneit *et al.*, 2019, 2021). Fichtelite may be formed from abietic acid *via* reductive processes, i.e., decarboxylation and hydrogenation (Swan, 1968).

Partially or fully aromatized abietane counterparts, i.e., simonellite (XXIX) and retene (XXX), were found in low concentrations in only 7 lignites, indicating their low maturity. The majority of the samples displayed low abundances of fichtelite and 14β(H)-totarane, apart from 18-norisopimarane and abietane, as mentioned earlier. The remaining diterpanes were minor, occurring only in some samples (Tab. 4). The mass spectra of these diterpanes and a *seco*-derivative are presented in Supplementary Figure S3.

Such a diverse diterpane distribution in the samples from numerous locations and depths indicated their origin from various gymnosperms and reflected variations in the peat-forming palaeovegetation (Simoneit *et al.*, 1986; Dev, 1989; Otto *et al.*, 1997). Diterpanes, such as phyllocladanes, kauranes and beyeranes, the precursors of which are not widespread in extant conifer resins, likely indicate that their biological precursors originate from species of the Podocarpaceae, Araucariaceae, and Cupressaceae families (Alexander *et al.*, 1987; Dev, 1989; Otto *et al.*, 1997, 2002; Bechtel *et al.*, 2002; Tuo and Philp, 2005). However, such diterpenoid precursors also have been found in angiosperms, pteridophytes, and bryophytes (Noble *et al.*, 1985; Sheng *et al.*, 1992). Abietane is important for palaeochemotaxonomy, as abietic acid and its derivatives are major compounds of ancient and modern Pinaceae resins (Otto and Simoneit, 2001, 2002; Otto and Wilde, 2001; Hautevelle *et al.*, 2006). Semperviranes, totaranes and some of the abietanes are not known in nature. Their possible origin from hydrogenation of their aromatic precursors (i.e., sempervirol, totarol and ferruginol in part) in these lignites may be from species in the Cupressoideae subfamily of the Cupressaceae (Simoneit *et al.*, 2021).

The input of resinous and non-resinous source materials varies quantitatively in lignite lithotypes and can be characterized by the abundance of certain biomarkers (Fabiańska and Kurkiewicz, 2013). Generally, detritic material sourced from non-resinous plants is enriched in higher molecular weight *n*-alkanes and depleted in diterpanes. Detritic remnants from resinous plants contain relatively lower concentrations of aliphatic compounds and are enriched in diterpenoids. Additionally, all organic detritus undergoes extensive reworking by bacteria at the early post-depositional stage, leading to an elevated hopanoid content. Xylitic material, independent of its source (angiosperms or gymnosperms), is characterized by a relatively lower content of *n*-alkanes, while the content of terpenoids, which are resistant to biodegradation, is source-dependent. Considering the variations and complexity in source materials, forming lignites and their post-depositional alteration, it seems possible to assess the type of source material, using selected biomarker ratios. The authors demonstrate this attempt with ratios of the relative abundance of the gymnosperm-derived diterpanes to the most abundant higher molecular weight *n*-alkanes (C_{29} or C_{31}, Tab. 3). The Σditerpanes/C_{max} ratios, based on the summed data of the diterpanes (from *m/z* 123) and the C_{max} (from *m/z* 71), respectively, vary from 0.0 to 7.9 (Tab. 3). The decreasing order of this ratio clearly showed that xylitic and xylo-detritic lignites fall within a value above 0.3 (Fig. 5). Sample 8, with its ratio of 3.04, is the exception, falling within the set of xylitic lignites, although

Table 4

The relative abundance of diterpenoids in the lignite and lignitic shale samples.

Sample number — Abundance (relative%)

	Diterpane	KI[a]	1	2	3	5	6	7	8	9	10	11a	11b	12	13a	13b	13c	14	15a	15b	16a	16b	16c	17a	17b	18a	18b	19	20	21a	21b	22	23	24
(I)	19-norpimarane	1905						22.4	16.1																									
(II)	12β(H)-sempervirane	1919					51.5																	79.9					94.9	6.0	6.0			
(III)	13-methyl-9,10-seco-podocarpane	1926																	7.1	5.9		1.1			8.6	100	3.7							
(IV)	19-noriso-pimarane	1930							3.8																12.1	35.9	4.3			6.1				
(V)	8α(H)-labdane	1932		16.0																					16.5									
(VI)	12α(H)-sempervirane	1938																						28.4					14.2					
(VII)	18-norpimarane	1946	2.3		2.1	8.4							18.3			2.3			25.1	6.3		1.0										20.5		
(VIII)	14β(H)-totarane	1947		5.0	2.1	8.6	6.8	23.6	38.4	19.3	8.3				9.0			9.0				1.1		62.3	18.3	13.4	6.4	18.8		7.4	5.4	12.4	23.0	
(IX)	13α(H)-fichtelite	1961													4.5														1.60					
(X)	18-noriso-pimarane	1970	10.7	21.7	30.4	16.8	5.7	78.6	16.2	11.0	11.3	13.8	29.3		12.9	10.3	8.4	8.1	24.1	13.2	10.2	1.3	7.7	18.6	19.2	32.1	22.0	20.4		7.8	4.9	44.0	17.4	74.0
(XI)	14α(H)-totarane	1982																											8.2				4.8	
(XII)	pimarane	1987	4.1	9.9						6.2	2.0		9.2		2.0			2.5	3	1.8			25.4						1.8					
(XIII)	isophyllocladene	1997					98.8								3.0																			
(XIV)	fichtelite	1999	7.3	7.3	20.4	30.8	3.1	35.1	100	10.8	11.4	3.1	18.7		17.6	4.8	9.6	3.6	8.7	6.6		1.2	38.9	11.4	40.1	18.8	7.4	37.7	2.4	6.2	2.2	74.3	24.8	
(XV)	isopimarane	2012	100	77.9	61.6	20.5	58.1	48.6	3.1	19.2	14.0	18.0	54.1	20.5	44.4	33.9	27.4	28.3	33.4	94.8	7.8	38.7		13.5	81.7	98.8	17.4	63.4		9.1	94.0	94.6	38.2	95
(XVI)	16β(H)-phyllocladane	2034	2.7			1.7									2.6					2.1				7.3		2.0								
(XVII)	abietane	2042	21.7	29.7	19.7	4.8	36.4	46.0	2.6	13.3	8.9	2.9	26.3	5.3	19.3	44.1	20.6	55.1	15.6	19.7		14.6	3.9	7.8	22.0	28.0	1.6	12.0		4.0	4.4	31.4	7.3	
(XVIII)	13β(H)-kaur-16-ene	2054		6.0																12.4					10.8		3.6							
(XIX)	16α(H)-phyllocladane	2056	78.9	100	100	100	100	100	4.8	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	94.1	100	100	8.8	100	100	100	100	100
(XX)	dehydroabietane	2067	1.3	1.3		1.0	3.1			4.0		2.5							2.0	2.4		1.0	2.1						3.6					
(XXI)	ent-beyerane	2065	1.2	1.2										2.1	2.7							1.0	3.2	99.6										
(XXII)	cassane	2070	1.0	1.0											2.3								1.9	82.6					1.5					
(XXIII)	ent-16α(H)-kaurane	2085	8.1	2.2		2.5				5.0	1.0	3.5	6.5	1.0	2.1				1.0	2.6		1.5	1.8	6.3						1.7			3.7	

[a] KI – Kovats index versus *n*-alkanes on HP-5 column phase (Kovats, 1958).

it is specified macroscopically as detritic. As shown earlier, its detritus contains significant amounts of resinous matter, mainly fichtelite, 12β(H)-sempervirane and 14β(H)-totarane. All other detritic, as well as gelified xylitic (samples 1, 11a, 19) and gelified detro-xylitic (sample 7) lignites exhibited a ratio < 0.3, which reflects their low diterpane content, relative to the higher molecular weight *n*-alkanes (Fig. 5), and further supports a significant input from angiosperms.

Triterpenoids

Hopanoids. Triterpenoids with a hopane skeleton represented a significant proportion of the saturated hydrocarbon fraction in the samples. Variations in their distributions are illustrated for selected samples by means of the *m/z* 191 mass fragmentograms (Fig. 6) and represented two major series of 17β(H),21β(H)- and 17α(H),21β(H)-hopanes in the range of C_{27}–C_{32} without the C_{28} homologue. The C_{29}, $C_{30,}$ and C_{31} ββ-homologues were predominant, with comparable relative concentrations in some samples (Fig. 6A). The 22*R*-17α(H),21β(H)-homohopane predominated in the other samples (Fig. 6B, C). These hopanes are interpreted as originating from the bacteriohopanetetrol, present in bacterial cell membranes (Ourisson *et al.*, 1979; Rohmer and Bisseret, 1994), as well as from mosses and ferns (Bottari *et al.*, 1972). Here αβ-homohopane-22R was predominant, while

the relative abundances of the 22S epimer and other homologues were significantly lower (Fig. 6A, B). Specifically, the predominance of αβ-homohopane-22R in peat and low-rank coals is a product of oxidation and subsequent decarboxylation of the bacteriohopanetetrol side chain, with some catalytic isomerization at position C-17 under acidic conditions in mires (Van Dorsselaer *et al.*, 1974; Quirk *et al.*, 1984; Dehmer, 1995). The presence of ββ-hopanes with the stereochemical configuration, inherited from living organisms, indicates bacterial reworking of primary OM under oxic-dysoxic conditions and low thermal stress during burial. Other hopanes, such as 17β(H)-22,29,30-trisnorhopane, minor 22,29,30-trisnorhop-17(21)-ene, and 17β(H),21α(H)-normoretane, also were significant in all samples.

A distinctive hopane distribution was found for sample 12 (Fig. 6C). The ββ-hopanes were low, compared to the αβ-hopanes, which extended to C_{35} and C_{31}-22R predominant. The C_{32}–C_{35} homologues had 22S/(22S + 22R) epimerization ratios >0.50, implying a different maturity level (Seifert and Moldowan, 1980; Peters and Moldowan, 1991). Low maturity is characterized here by minor ββ-hopanes and predominant αβ-homohopane-22R, while high maturity, corresponding to the onset of the oil window, is indicated by the extended C_{32}–C_{35} αβ-hopanes with the epimerization ratio close to equilibrium (0.55). No other geochemical
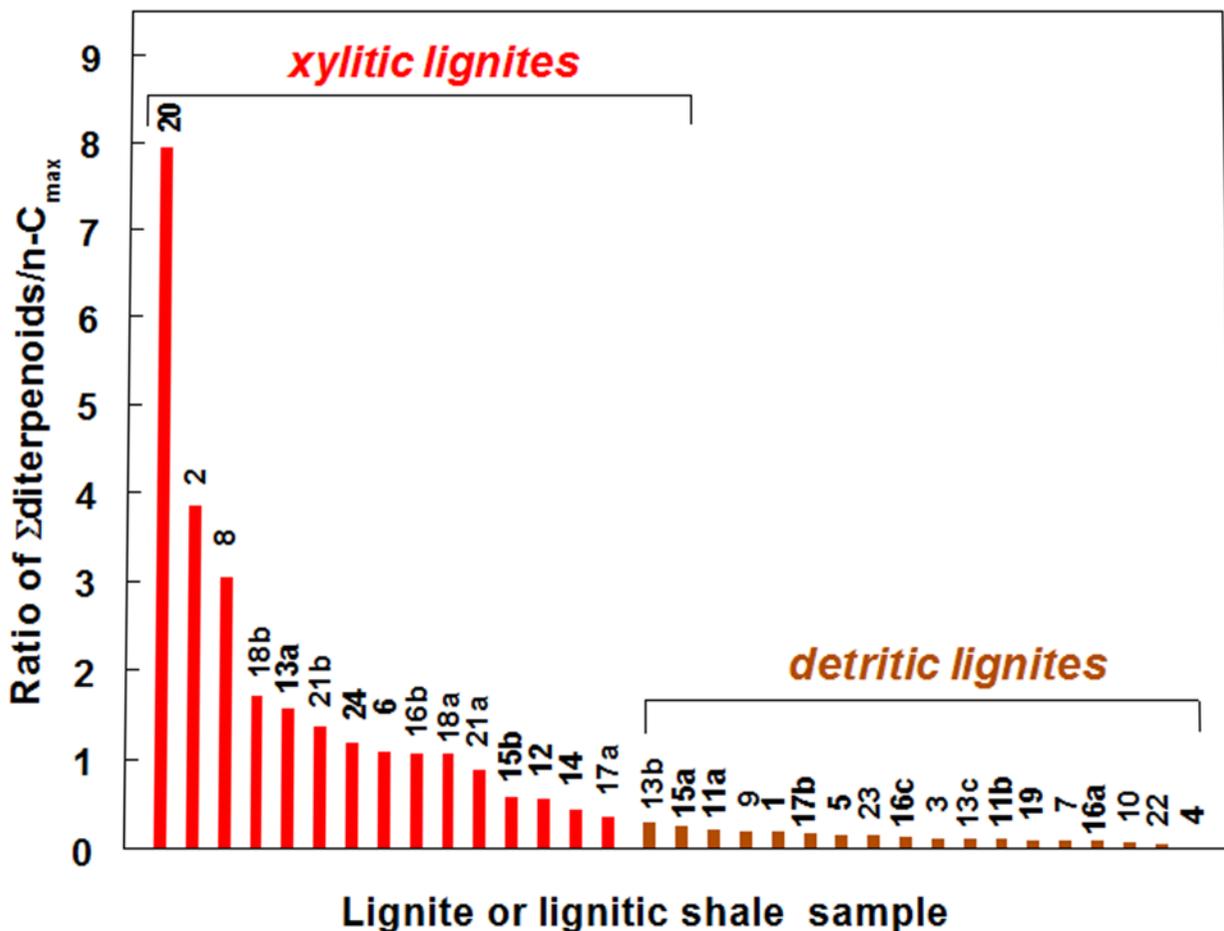
Fig. 5. The ratio of the sum of diterpenoids (integrated area *m/z* 123) to C_{max} (integrated area *m/z* 71). The sample number corresponds with the number in Tables 1–4.
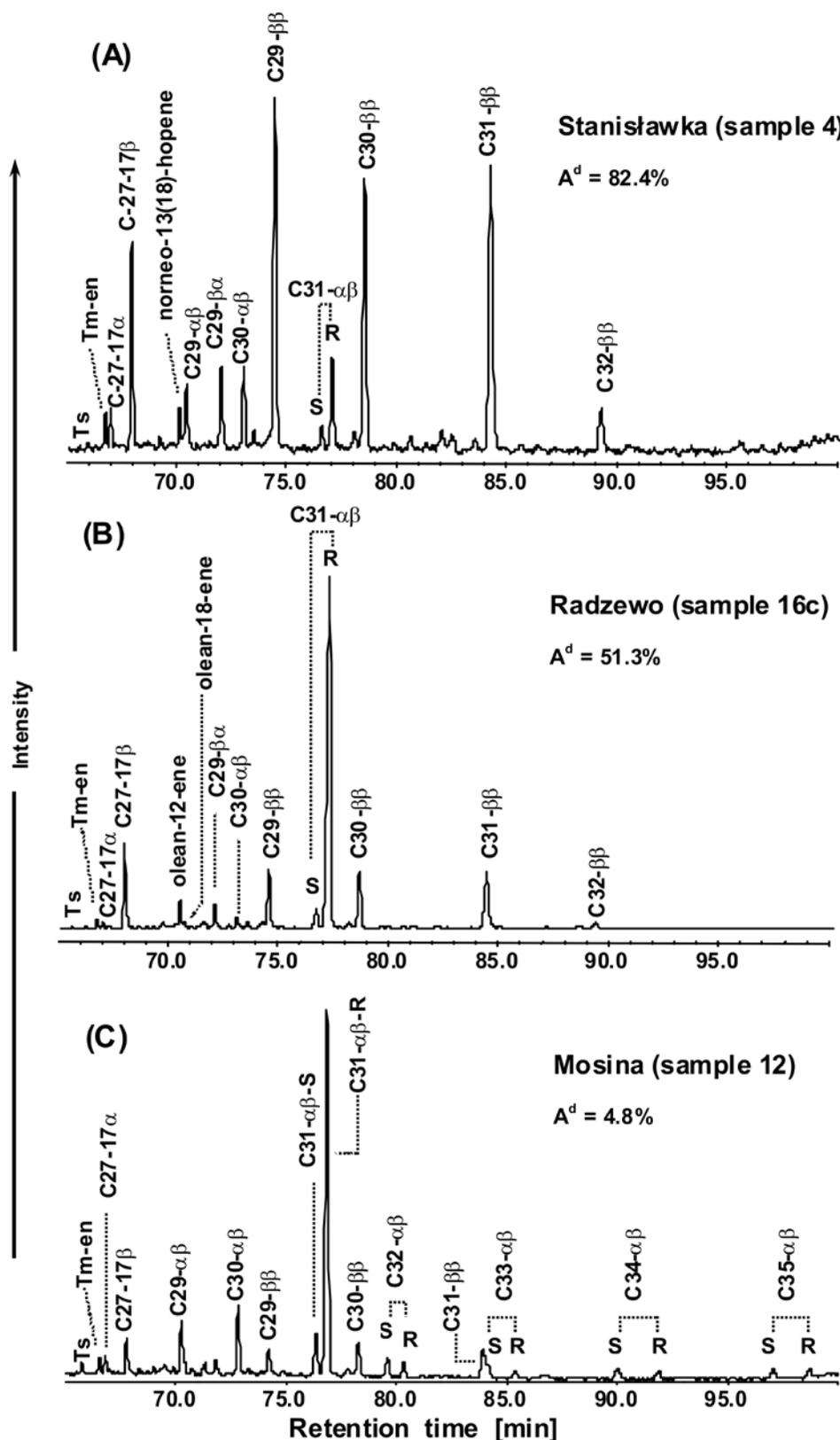
Fig. 6. The molecular composition of hopanes (m/z 191). **A.** Sample 4. **B**. Sample 16c. **C. S**ample 12. Ts – 18α(H),21β(H)-22,29,30-trisnorneohopane; Tm-en – 22,29,30-trisnorhop-17(21)-ene; C27-17α – 17α(H),21β(H)-22,29,30-trisnorhopane (Tm); C27-17β – 17β(H)-22,29,30-trisnorhopane; C29-αβ – 17α(H),21β(H)-norhopane; C29-βα – 17β(H),21α(H)-normoretane; C30-αβ – 17α(H),21β(H)-hopane; C29-ββ – 17β(H),21β(H)-norhopane; C31-αβ-S – 17α(H),21β(H)-homohopane (22S); C31-αβ-R – 17α(H),21β(H)-homohopane (22R); C30-ββ – 17β(H),21β(H)-hopane; C32-αβ-S/R – 17α(H),21β(H)-bishomohopane (22S/22R); C31-ββ – 17β(H),21β(H)-homohopane (22R); C33-αβ-S/R – 17α(H),21β(H)-trishomohopane (22S/22R); C32-ββ – 17β(H),21β(H)-bishomohopane (22R); C34-αβ-S/R – 17α(H),21β(H)-tetrakishomohopane (22S/22R); C35-αβ-S/R – 17α(H),21β(H)-pentakishomohopane (22S/22R).

parameters provide evidence for a high maturity of sample 12. Oil contamination, which could interfere with the hopane identification, was excluded as no saturated steranes or any other oil-derived biomarkers were detected in this sample. Unusual hopane distributions were previously reported in other lignites (Van Dorsselaer *et al.*, 1977; Del Rio *et al.*, 1992). The distinctive pattern, indicating the high maturity of this sample, may be caused by a specific stereochemical isomerization of the biological precursors, occurring during the decomposition of a lignin-related polyphenolic matrix in highly acidic conditions.

The distributions of ββ- and αβ-hopanes varied in the samples with ββ/(αβ + ββ) ratios for the C_{31} homologue in the range of 0.05–0.20, except sample 4, for which this value was 0.73 (Tab. 3). The values are in agreement with the data, reported previously for other lignites (Gross *et al.*, 2015). It should be noted, that the proportion of ββ-epimers in the hopane compositions increases with the ash content, as illustrated for samples 4, 16c, and 12 with contents of 82.4, 51.3 and 4.8%[d], respectively (Fig. 6), while the corresponding ββ/(αβ + ββ) ratios for the C_{31} homohopane were 0.73, 0.14 and 0.05, respectively (Tab. 3). The relationship between the C_{31} hopane ββ/(αβ + ββ) ratio and ash content in these samples mostly shows a good correlation (Fig. 7). This supports the earlier observation of more extensive oxidative transformations of primary OM in less mineralized deposits, leading to the formation of mainly αβ-homohopane-22R (Dehmer, 1995). In contrast, as oxygen availability becomes limited for microorganisms, existing in highly mineralized organic sediments, the ββ-hopanes undergo slower epimerization in such environments. This can be seen in the progressive change of hopane distributions for the samples, displaying gradual decreased ash contents (Fig. 6). However, the data point scatter in the correlation (Fig. 7) indicates that some caution should be taken, when assessing the redox conditions of primary OM reworking. Recently, Inglis *et al.* (2018) demonstrated a positive correlation

between C_{31} hopane isomerisation and environment pH and indicated the usefulness of geohopanoid ββ/(αβ + ββ) indices to assess pH within modern and ancient mire-forming environments.

Other triterpenoids. Varying abundances of other pentacyclic triterpenoids were identified in the saturated fractions of the samples. Olean-12-ene was often predominant, but not observed in samples 4, 13a, 20, and 24, and olean-13(18)-ene and urs-12-ene, often reported in other lignites (Ten Haven and Rullkötter, 1989; Logan and Eglinton, 1994; Rullkötter *et al.*, 1994), were low and only in some samples. These triterpenes are alteration products of bioterpenoids, such as β- and α-amyrin, derived from angiosperms (Dev, 1989; Ten Haven *et al.*, 1992), and also isomerize under acidic conditions to olean-13(18)-ene and urs-13(18)-ene, respectively. The des-A tetracyclic triterpenoids were found at various low levels in samples 1, 2, 3, 5, 7, 9, 10, 11b, 13a, 16a, 16b, 16c, 18a, 18b, 21b, and included des-A-olean-13(18)-ene, des-A-olean-12-ene, des-A-urs-13(18)-ene, des-A-urs-12-ene and des-A-lupane (He *et al.*, 2018), with des-A-lupane being frequently predominant. The origin of des-A-lupane is probably from lupeol or lupanol, and it exhibits greater resistance to diagenetic alteration in comparison to other saturated des-A-triterpenoids (Jacob *et al.*, 2007; Bree *et al.*, 2016).

The aromatic fractions of the samples contained small concentrations of β-amyrin, α-amyrin, olean-12-en-3-one, and abundant friedelan-3-one, reflecting carry over from the polar fraction during separation. Such triterpenoids with functionality at the C-3 position (alcohols, ketones) are susceptible to microbial or photochemical alteration, leading to des-A-triterpenoids (Corbet *et al.*, 1980; Simoneit *et al.*, 2009). The monoaromatic triterpenoid hydrocarbons consisted of 24,25-bisnoroleana-1,3,5(10),12-tetraene (major in some samples), 24,25-bisnorursa-1,3,5(10),12-tetraene (minor), 24,25-bisdinoroleana-1,3,5(10)-triene (most often dominant) and 24,25-bisnorlupa-1,3,5(10)-triene. Additional aromatized intermediate compounds were observed in some samples and included 2,2,4a,9-tetramethyl-1,1a,2,3,4,4a,5,6-octahydropicene, 1,2,9-trimethyl-1,2,3,4-tetrahydropicene and 2,2,9-trimethyl-1,2,3,4-tetrahydropicene. These aromatized triterpenoids are the diagenetic products of progressive aromatization and demethylation of their natural product precursors, occurring under microbial mediation (Chaffee and Johns, 1983; Lohmann *et al.*, 1990; Simoneit, 1998). These triterpenoids have been reported in lignites and organic sediments from different locations by many researchers (Jarolím *et al.*, 1965; Czochanska *et al.*, 1988; Stout, 1992; Bechtel *et al.*, 2002, 2004, 2020; Simoneit *et al.*, 2003; Otto *et al.*, 2005; Stefanova *et al.*, 2005; Fabiańska and Kurkiewicz, 2013; Jaroszewicz *et al.*, 2018, and numerous reports cited therein). The presence of non-hopanoid triterpenoids in these samples, especially the functionalized and aromatized oleanane or ursane–type structures, indicate low maturity and input from angiosperms to the mire-forming OM.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) were minor components of the aromatic fractions and included phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene,
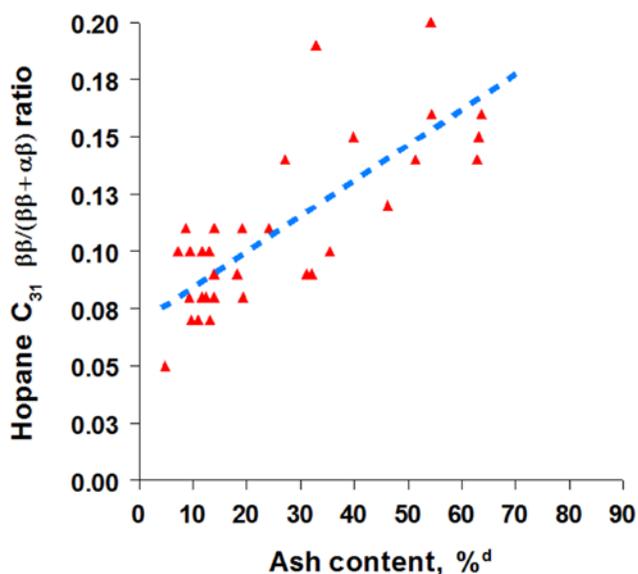
Fig. 7. Correlation of the C_{31} ββ/(αβ + ββ) hopane ratio and ash content of the samples.
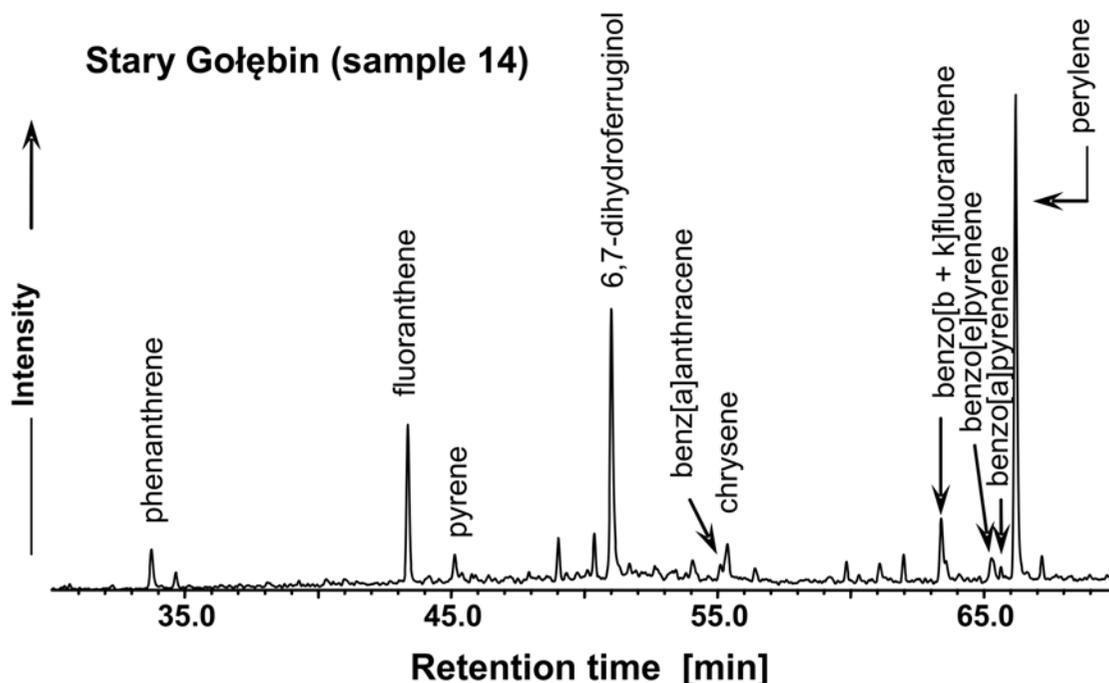
Fig. 8. Polycyclic aromatic hydrocarbons in sample 14 (summation of *m/z* 178 + 202 + 228 + 252).

benzofluoranthenes, benzopyrenes, and perylene (Fig. 8). Their relative abundances are presented in Supplementary Table S2. Perylene was predominant in most lignites, except for samples 6, 15a, 18b, 19 and 24, which had high abundances of phenanthrene. The dominance of perylene in these samples is intriguing. Perylene has been proposed as being derived from specific precursor components, such as perylenequinone (4,9-dihydroxyperylene-3,10-quinone) or 4,4',5,5'-tetrahydroxy-1,1'-binaphthyl, produced by fungi and insects in terrestrial environments (Sato, 1976; Jiang *et al.*, 2000; Itoh and Hanari, 2010). Defunctionalization and transformation of these compounds under anaerobic sedimentological conditions can lead to the formation of perylene (Jiang *et al.*, 2000). Thus, the presence of perylene supports fungal activity in the mire environment (Marynowski *et al.*, 2013).

Fluoranthene and benzo[b+k]fluoranthenes were also significant, while benzo[e]- and benzo[a]pyrene, benz[a]anthracene and chrysene occurred only in some lignites at low concentrations. These trace PAHs, coupled with phenanthrene, may indicate a trace input from palaeofires or more mature OM (especially sample 15a,b). PAHs are considered products from bacterial degradation of biological precursors (Wakeham *et al.*, 1980) as well as from thermal processes, at least partly, during wildfires. However, fusinite, which also forms during wildfires, was not observed macroscopically in these lignites. The abundance of methylphenanthrenes was generally low, allowing the calculation of the methylphenanthrene index (MPI-1, Radke *et al.*, 1986) for only some samples (Tab. S2). The low abundance or lack of lower molecular weight PAHs in highly mineralized samples may be related to their removal by water-washing at the early deposition stage. The MPI-1 values confirmed the lignite immaturities.

OVERVIEW

Ash and total sulphur contents of the lignites were related to lithotype. Humodetritus lignites exhibited generally higher ash and total sulphur contents in comparison to xylitic lignites. In some samples, the elevated mineral content indicated mire deposition in a swampy environment. The OM of the lignites and lignitic shales was classified as Type III, on the basis of the van Krevelen correlation. Relatively low carbon contents, as well as atomic H/C and O/C ratios, were characteristic of immature OM, which also was reflected in the predominance of asphaltene and polar components in the extracts.

The distributions of the homologous lipids and biomarkers allowed a more detailed evaluation of their source, maturity levels, and palaeoenvironmental conditions in the mires, not discernable by bulk analysis. The *n*-alkanes with strong odd-over-even carbon number predominances (CPI$_{(25–33)}$ 2.9–7.9) were indicative of input of epicuticular waxes from higher plants, and reflected the low maturity of the lignites. Additionally, the C$_{max}$ at 29 or 31 potentially could be used to differentiate between input from temperate or semi-tropical sources. Some samples displayed bimodal *n*-alkane distributions, which indicated microbial activity without any observed algal input. This biodegradation was evident in a few samples based on the presence of an UCM, with low CPI$_{(25–33)}$ values of the *n*-alkanes and low EOM yields. The prevalence of longer-chain *n*-alkanes in detritic lignites, with a shorter-chain *n*-alkane predominance in xylites, was not observed for these samples.

16α(H)-Phyllocladane was the most common diterpane in the majority of the samples, which is typical of many lignites. The low concentrations of the thermodynamically more stable 16β(H)-phyllocladane in comparison to its

epimer were further support for the immaturity of the samples. Even though tetracyclic diterpanes are widely used as conifer indicators, characteristic of the Podocarpaceae, Araucariaceae and Cupressaceae families, they can also be found in other angiosperms. Isopimarane and 18-nor-isopimarane were the second and abietane the third most abundant diterpanes, supporting a conifer input in those samples.

The high abundances of 12β(H)-sempervirane and 14β(H)-totarane in three samples are uncommon in lignites. Their phenolic diterpenoid precursors are dominant in some members of the extant Cupressoideae family and were preserved in fibrous xylite in a swampy anaerobic environment.

The ratios of the relative concentrations of the diterpanes to the most abundant, higher molecular weight *n*-alkanes (C_{29} or C_{31}) were used as a measure of the angiosperm *vs.* gymnosperm contribution to the source of the OM. The Σditerpanes/C_{max} ratios for these samples displayed values for xylitic and xylo-detritic lignites of >0.3, while detritic, gelified xylitic and gelified detro-xylitic samples were less than 0.3. This ratio proved useful in distinguishing between resinous and non-resinous source materials.

The hopanoids, as indicators of bacterial activity, were abundant, including primarily the 17β(H),21β(H)- and 17α(H),21β(H)-hopanes in the range of C_{27}–C_{32} with no C_{28} homologue, and αβ-homohopane-22R predominant in most samples. The ratio of ββ/(ββ + αβ) homohopane-22R was used to assess redox conditions in the mire. It increased with the ash content of the lignites.

The other triterpenoids in most samples were dominated by hydrocarbon products from β- and α-amyrin, i.e., oleanene and ursene–type structures. These compounds are indicative of an angiosperm input to the mire-forming environment and the low maturity of the lignites. The des-A tetracyclic derivatives with dominant des-A lupane were present at low concentrations and represent microbially mediated derivatives of biological precursors in the depositional environment.

PAHs were present in low concentrations with a predominance of perylene and a few samples with high phenanthrene. Other trace PAHs were fluoranthene, pyrene, benz[a]anthracene, chrysene, benzofluoranthenes, and benzopyrenes. Low levels or the absence of methylphenanthrenes limited the application of the methylphenanthrene index (MPI-1). Some of the values ranged from 0.16–0.46, confirming the low maturity of those samples.

CONCLUSIONS

These geochemical data demonstrated a wide lateral and vertical variability of the floral communities forming the OM in the mires of the Neogene and Quaternary lignites and lignitic shales in NW Poland. Their OM is immature and represents Type III kerogen. The high odd-over-even carbon number predominances of the long-chain *n*-alkanes indicated input from epicuticular waxes of terrestrial higher plants. Diterpanes of variable compositions represented influx from conifers and probably also angiosperms but were not species-specific. Partially aromatized and des-A-triterpenoid

hydrocarbons, derived from natural product precursors, were also encountered, indicating an angiosperm input. The assessment of the contributions from gymnosperms and angiosperms to the palaeovegetation was proposed on the basis of the ratio of diterpanes as conifer markers to C_{max}, assuming that angiosperm flora contributed significantly more to the *n*-alkane contents. This ratio allowed the distinction of samples as xylitic or detritic lignites. Regional differences in the E_h and pH values in the sedimentary environments were reflected in variations in the Pr/Ph ratios and hopane configurations. Their values are associated with the water level in the mire and oxygen availability and thus influenced microbial activity in reworking the sedimentary OM. For some lignites, enhanced biodegradation was manifested in the presence of a UCM in saturated fraction chromatograms. The predominance of perylene among the PAHs indicated additional alteration of OM by fungi in the mires.

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