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Compositions, sources and depositional environments of organic matter from the Middle Jurassic clays of Poland

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Abstract

The comprehensive biomarker characteristics from previously undescribed Middle Jurassic clays of Poland are presented. The molecular composition of the organic matter (OM) derived from clays of Aalenian to Callovian age has not changed significantly through time. High relative concentrations of many biomarkers typical for terrestrial material suggest a distinct dominance of OM derived from land plants. Increasing concentrations of C_{29}-diaster-13(17)-enes towards the northern part of the basin indicate an increase in terrestrial input. This terrestrial material would have originated from the enhanced transport of organic matter from land situated at the northern bank of the basin, i.e., the Fennoscandian Shield. The organic matter was deposited in an oxic to suboxic environment, as indicated by relatively low concentrations of C_{33}–C_{35} homohopanes, moderate to high Pr/Ph ratio values, an absence of compounds characteristic for anoxia and water column stratification, such as isorenieratane, aryl isoprenoids and gammacerane, as well as common benthic fauna and burrows. $\delta^{18}O$ measurements from calcitic rostra of belemnites suggest that the mean value of the Middle Jurassic sea-water temperature of the Polish Basin was 13.1 °C. It is suggested that this mirrored the temperature of the lower water column because belemnites are considered here to be necto-benthic. The organic matter from the Middle Jurassic basin of Poland is immature. This is clearly indicated by a large concentration of biomarkers with the biogenic configurations, such as ββ-hopanes, hop-13(18)-enes, hop-17(21)-enes, diasterenes and sterenes. The identification of preserved, unaltered biomolecules like ferruginol, 6,7-dehydroferruginol and sugiol in *Protopodocarpoxylon* wood samples from these sediments present particularly strong evidence for the presence of immature OM in the Middle Jurassic sediments. Moreover, the occurrence of these polar diterpenoids is important due to the fact that they are definitely the oldest known natural products detected in geological samples.

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1. Introduction

The largest area of Poland where Middle Jurassic deposits occur is a ca. 10–33 km wide belt in the south-central part of the country, the so-called Polish Jura Kraków-Wieluń Upland. The exposed deposits consist mostly of clays, currently used in the production of bricks. Many years ago, massive siderite beds occurring within the clays in several places were mined as Fe ore. The second, a smaller area, where the Middle Jurassic clays are exposed is in the Holy Cross Mountains (Barski, 1999). In the Polish Lowland the Middle Jurassic sediments are covered by younger strata, besides the allochthonous glacially-derived deposits, and thus are only accessible as drill-cores (e.g., Feldman-Olszewska, 1997). To date, investigations of the Middle Jurassic clays have concentrated on stratigraphy and palaeontology (e.g., Matyja and Wierzbowski, 2000; Gedl et al., 2003; Kaim, 2004; Zatoń and Marynowski, 2004, 2006).

The sediments of the epicontinental Middle Jurassic basin contain high concentrations of organic, averaging 5% (Bojesen-Koefoed, 1996; Table 1), and the accessible samples in the numerous active brick-pits not only yield the clays, but also carbonate concretions and numerous wood fragments thus making these deposits important for geochemical investigations. However, such investigations to data have been limited and have included Rock Eval analysis in the context of their petroleum source rock potential (Bojesen-Koefoed, 1996), investigations of organic matter present in some calcitic concretions (Zatoń and Marynowski, 2004), and analysis of clay samples to interpret features of the background depositional environment of sedimentary organic matter (Zatoń and Marynowski, 2006).

Here, for the first time, the complex characteristics of the organic matter (OM) from the Middle Jurassic sedimentary rocks deposited in the epicontinental basin of Poland are reported in terms of their compositions, sources, sedimentary conditions and maturity. Additionally, $\delta^{18}O$ and $\delta^{13}C$ stable isotopic analyses of belemnite rostra were conducted in order to estimate sea-water paleotemperatures.

2. Geological setting

During the Middle Jurassic, the Submediterranean Polish Basin formed the eastern part of the Mid-European Epicontinental Basin (Dadlez, 1989). At that time, the Polish Basin was bounded by the Fennoscandian Shield to the north, the Belorussian High and Ukrainian Shield to the east and the Bohemian Massif to the SW. To the south, the basin was isolated by the pre-Carpathian land (see Ziegler, 1990) (Fig. 1a). It is generally assumed (Dadlez, 1997), that the Fennoscandian Shield and Bohemian Massif had the major influence on the deposition of the clastic material in the basin. During Middle Jurassic time, the epicontinental Polish Basin had a transgressive character, despite two short regressive episodes at the Lower/Upper Bajocian boundary (Niortense Zone) and in the Lower Callovian (Herveyi Zone; Dayczak-Calikowska et al., 1997; Kopik, 1998). The basin was undoubtedly connected with the Tethys, and all transgressive pulses from the Aalenian through Bathonian were related to this ocean (Dayczak-Calikowska et al., 1997). However, their main pathways are still unclear in Poland. Dayczak-Calikowska and Moryc (1988) suggested the East-Carpathian Gate in the SE through the Mid-Polish Trough as the main path (Fig. 1a, arrow). Świdrowska (1994), on the other hand, suggested that at least the Aalenian transgression entered from the west (see also Feldman-Olszewska, 1997).

The samples investigated are derived from 3 main areas of the epicratonic Polish Basin: (1) The Mid-Polish Trough, (2) The Polish Jura and (3) the south-western border of the Holy Cross Mountains (Fig. 1).

The Mid-Polish Trough, located in the Lowland, is the most important palaeotectonic element, which was subjected to slow subsidence during sedimentation in the Middle Jurassic. It was a path for successively developing transgressions reaching the Polish Basin from both the SE (Aalenian-Bathonian) and the Nw (Callovian) (Dayczak-Calikowska and Moryc, 1988; Feldman-Olszewska, 1997). In this area, the complete lithologic-stratigraphical section attains more than 1000 m in thickness (Feldman-Olszewska, 1997). The analysed samples from the Trough consist of dark-grey clays from the Aalenian through Bathonian, and grey clays and marly-clays of Callovian age.

The Polish Jura is a monoclinally extended structure spreading from SE to NW in south-central and central Poland (Fig. 1). The sampled Upper Bajocian through Bathonian sediments in that area are composed mainly of dark-grey clays with many layers of massive siderites, as well as carbonate concretions. This complex in the Polish Jura is known as

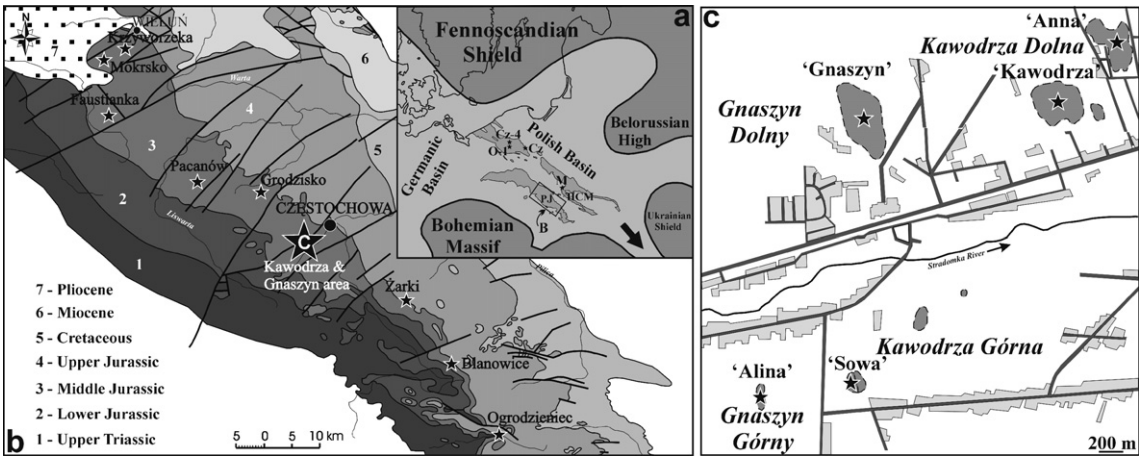

Fig. 1. (a) Jurassic palaeogeography of the Polish part of the Mid-European Epicontinental Basin with Jurassic deposits indicated (adapted from Zatoń and Marynowski, 2006, slightly modified). (b) Geological sketch map of the Polish Jura with sample locations (asterisks). (c) Enlarged Kawodrza and Gnaszyn area, locations of the majority of the active brick-pits (shaded) from where the samples were collected (asterisks). Abbreviations: PJ, Polish Jura; HCM, Holy Cross Mountains; Cz, Czarnowo; Cz-4, Czarne-4; O-1, Okonek-1; M, Marianów.

the Ore-Bearing Częstochowa Clay Formation (see Dayczak-Calikowska et al., 1997; Kopik, 1998; Matyja and Wierzbowski, 2000; Zatoń and Marynowski, 2006). The sediments have a gentle dip angle of <2° in the north-eastern direction (Znosko, 1960). They are often capped by consolidated Callovian deposits, consisting of limestones, sandstones and sandy-limestones (Dayczak-Calikowska et al., 1997).

In the Holy Cross Mountain area, the Middle Jurassic clays are exposed only at two locations: Wola Morawicka and Marianów (Barski, 1999). For the present study, the samples were taken only from clays at Marianów. The section consists of monotonous black clays with rare siderite concretions, >20 m thick (Barski, 1999). The under- and overlying deposits are not well exposed in the field, but according to the data of Barski (1999), the clays are probably underlain by Liassic coarse-grained deposits, and overlain by calcareous gaize of Callovian age. Using dinoflagellates, Barski (1999) dated the clay section at Marianów as the Upper Bathonian (Discus Zone) and/or the Lower Callovian (Herveyi Zone).

3. Materials and methods

3.1. Samples

In total, 48 samples were collected: 34 from the Polish Jura, consisting of clays (13 samples), carbonate concretions and massive siderite layers (8) and wood fragments (13); 3 samples from the Holy Cross Mountains, consisting of two clays and one carbonate concretion; and 10 samples from the Polish Lowland consisting of clays, and additionally one clayey sample from the Carpathian Foredeep area. The details of the sample locales with stratigraphic positions of each are given in Table 1. Most of the samples were collected from active clay-pits located in the Polish Jura and Holy Cross Mountains, with the exception of the drill-core samples taken from the Polish Lowland and Carpathian Foredeep.

3.2. Total organic carbon

The total organic C (TOC) content was determined using an automated LECO CR-12 analyser. Determination of the carbonate percentage was based on the acid method (Durand and Nicaise, 1980).

3.3. Extraction and separation

The clays were Soxhlet-extracted in pre-extracted cellulose thimbles with dichloromethane. Extracts were further separated using preparative pre-washed TLC plates coated with silica gel (Merck, $20 \times 20 \times 0.25$ cm and $10 \times 20 \times 0.25$ cm). Prior to separation, the TLC plates were activated at 120 °C for 1 h. The plates were loaded with the *n*-hexane soluble fraction and developed with *n*-hexane.

Table 1
Bulk geochemical data of the organic matter from clays, carbonate concretions and fossil wood of Middle Jurassic sediments of Poland

Sample/*Lithology*	Age/*Ammonite zone*	Carbonate [%]	TOC [%]	EOM [mg/g TOC]	Aliph [%]	Arom [%]	Polar [%]	$CPI_{(25-31)}$	Pr/Ph	Pr/n-C_{17}	$(nC_{17}+nC_{18}+nC_{19})/(nC_{27}+nC_{28}+nC_{29})$
Kraków-Wieluń Upland											
Anna/*Clay*	U. Bathonian/*Hodsoni*	13.18	1.57	21	24	12	64	2.42	1.34	0.53	1.07
Sowa/*Clay*	U. Bajocian/*Parkinsoni*	16.39	0.77	29	24	22	54	1.81	1.24	0.54	1.30
Grodzisko/*Clay*	U. Bathonian/*Hodsoni*	12.95	1.47	17	14	16	70	1.88	0.50	0.69	0.99
Faustianka/*Clay*	L. Bathonian/*Tenuiplicatus*	5.13	1.94	32	14	20	66	2.35	1.35	0.74	0.61
Pacanów/*Clay*	U. Bajocian	–	–	–	–	–	–	2.16	0.88	0.73	3.48
Mokrsko/*Clay*	U. Bajocian/*Parkinsoni*	12.39	2.16	21	9	11	80	2.67	1.97	1.06	0.69
Kawodrza/*Clay*	M. Bathonian/*Morrisi*	11.46	2.01	52	18	20	62	2.24	1.64	0.81	0.67
Krzyworzeka/*Clay*	U. Bathonian/*Hodsoni-Orbis*	16.49	1.45	22	15	25	60	1.77	2.22	1.67	0.97
Ogrodzieniec #1/*Clay*	U. Bathonian/*Hodsoni*	13.16	1.05	9	33	28	39	2.70	2.18	0.69	0.68
Ogrodzieniec #2/*Clay*	U. Bathonian/*Hodsoni*	15.13	1.17	8	21	11	68	2.59	1.77	0.93	0.54
Żarki/*Clay*	U. Bathonian/*Hodsoni*	11.11	1.54	12	34	15	51	1.59	0.76	0.93	5.01
Blanowice/*Carbonate Clay*	M. Bathonian/*Morrisi*	66.38	0.59	49	16	20	64	1.57	0.75	0.99	2.61
Ogrodzieniec #3/*Carbonate Clay*	U. Bathonian/*Hodsoni*	62.68	0.55	36	20	15	65	1.50	1.30	0.63	1.59
Anna/*Carbonate concr.*	U. Bathonian/*Hodsoni*	80.87	0.55	5	25	16	59	1.65	0.78	0.59	2.11
Grodzisko/*Carbonate concr.*	U. Bathonian/*Hodsoni*	76.18	0.48	–	–	–	–	–	–	–	–
Sowa #A/*Carbonate bed*	U. Bajocian/*Parkinsoni*	75.46	0.37	24	30	15	55	1.50	1.03	0.57	1.72
Sowa #B/*Carbonate bed*	U. Bajocian/*Parkinsoni*	69.34	0.45	13	17	19	64	1.79	1.27	0.60	1.34
Ogrodzieniec/*Carbonate concr.*	U. Bathonian/*Hodsoni*	80.09	0.57	15	20	22	58	1.78	1.33	0.62	5.31
Sowa/*Carbonate concr.*	U. Bajocian/*Parkinsoni*	85.55	0.42	16	15	9	76	1.35	1.08	0.68	1.57
Mokrsko/*Carbonate concr.*	U. Bajocian/*Parkinsoni*	87.10	0.46	15	37	28	37	1.37	0.89	0.62	5.04
Żarki/*Carbonate concr.*	U. Bathonian/*Hodsoni-Orbis*	78.55	0.46	–	–	–	–	–	–	–	–
Sowa/*Wood*	U. Bajocian/*Parkinsoni*	–	–	–	15	19	66	3.41	1.11	0.75	4.33
Kawodrza/*Wood*	M. Bathonian/*Morrisi*	64.03	10.80	–	2	45	53	1.19	0.74	0.71	2.27
Blanowice/*Wood*	M. Bathonian/*Morrisi*	86.36	9.00	–	21	17	62	1.12	1.23	0.99	1.86
Żarki/*Wood*	U. Bathonian/*Hodsoni-Orbis*	37.11	14.31	–	15	10	75	1.07	1.20	0.55	5.50
Mokrsko/*Wood*	U. Bajocian/*Parkinsoni*	–	–	–	23	26	51	1.12	0.71	0.67	3.26
Anna W1/*Wood*	U. Bathonian/*Hodsoni*	–	–	–	9	35	56	2.38	1.34	0.85	0.76
Anna W2/*Wood*	U. Bathonian/*Hodsoni*	–	–	–	9	24	67	1.19	1.41	0.74	3.23
Anna W3/*Wood*	U. Bathonian/*Hodsoni*	77.84	6.90	–	2	20	78	1.10	1.20	0.63	5.31
Anna W6/*Wood*	U. Bathonian/*Hodsoni*	–	–	–	4	19	77	1.26	0.80	0.64	5.20

(*continued on next page*)

Table 1 (*continued*)

Sample/*Lithology*	Age/*Ammonite zone*	Carbonate [%]	TOC [%]	EOM [mg/g TOC]	Aliph [%]	Arom [%]	Polar [%]	$CPI_{(25-31)}$	Pr/Ph	Pr/n-C_{17}	$(nC_{17}+nC_{18}+nC_{19})/(nC_{27}+nC_{28}+nC_{29})$
Alina/*Wood*	U. Bajocian/*Parkinsoni*	–	–	–	11	22	67	1.34	0.76	0.82	9.00
Grodzisko W1/*Wood*	U. Bathonian/*Hodsoni-Orbis*	26.08	32.50	–	12	21	67	2.13	1.00	0.60	4.84
Grodzisko W2/*Wood*	U. Bathonian/*Hodsoni-Orbis*	–	–	–	5	21	74	1.19	0.99	0.59	3.11
Grodzisko W3/*Wood*	U. Bathonian/*Hodsoni-Orbis*	–	–	–	6	19	75	1.30	1.17	0.67	2.73
Gnaszyn W1/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	28.90	36.17	–	12	28	60	–	1.30	0.77	–
Gnaszyn W2/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	15.62	40.00	–	15	23	62	–	1.23	0.65	–
Gnaszyn W3/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	–	–	–	9	26	65	1.06	1.83	0.71	1.95
Gnaszyn W4/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	–	–	–	4	25	71	4.80	1.78	0.63	0.45
Gnaszyn W5/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	–	–	–	10	16	74	2.12	0.92	0.55	9.57
Holy Cross Mountains											
Marianów #1/*Clay*	Bathonian	16.39	2.63	40	11	13	76	1.75	2.25	0.86	2.36
Marianów #2/*Carbonate Clay*	Bathonian	57.67	0.59	33	42	19	39	1.66	1.53	0.89	2.28
Marianów/*Carbonate concr.*	Bathonian	83.72	0.55	43	29	21	50	1.95	1.40	0.62	4.52
Polish Lowland											
Okonek-1 (316.5 m)/*Clay*	U. Bajocian	13.28	3.95	41	49	13	38	2.33	1.14	0.55	2.82
Brzozówka-1 (669.4 m)/*Marl*	Callovian	67.33	0.46	63	44	25	31	1.24	0.98	0.56	11.69
Czarne-4 (550 m)/*Marly Clay*	Callovian	24.83	0.97	52	35	15	50	1.42	0.95	0.47	2.93
Czarnowo-1 (1496 m)/*Clay*	Bathonian	13.26	3.70	22	37	17	46	1.82	1.67	0.84	2.12
Czarnowo-1 (1599 m)/*Clay*	Bajocian	12.57	4.02	27	14	8	78	1.89	1.56	0.65	2.28
Czarnowo-1 (1655 m)/*Clay*	Aalenian	13.16	5.07	28	36	17	47	1.61	1.19	0.69	4.01
Czarnowo-2 (1438.5 m)/*Clay*	Callovian	6.41	1.38	69	37	14	49	1.47	1.36	0.77	3.95
Czarnowo-2 (1491.7 m)/*Clay*	Bathonian	13.47	4.74	24	31	16	53	1.85	1.63	1.07	1.98
Czarnowo-2 (1500.4 m)/*Clay*	Bajocian	9.19	4.35	26	35	19	46	2.11	1.61	1.29	1.72
Czarnowo-2 (1720.2 m)/*Clay*	Aalenian	9.85	4.63	20	24	36	40	1.79	2.23	0.95	2.65
Carpathian Foredeep											
Łukowa-2 (730.8 m)/*Clay*	Bajocian	18.11	0.95	4	43	18	39	1.07	1.24	0.53	1.08

Bands comprising aliphatic (R_f 0.4–1.0), aromatic (R_f 0.05–0.4) and polar (R_f 0.0–0.05) fractions were collected.

3.4. Derivatization

3.4.1. Methylation

The polar fraction was treated with BF_3/methanol (5 mL; 4 h) and dissolved in dichloromethane.

3.4.2. Silylation

An aliquot of the total extract was converted to trimethylsilyl derivatives by reaction with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine for 3 h at 70 °C.

3.5. Gas chromatography–mass spectrometry (GC-MS)

The GC-MS analyses were performed with an Agilent 6890 Series Gas Chromatograph interfaced to an Agilent 5973Network Mass Selective Detector and Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). A 0.5-μL sample was introduced into the cool on-column injector under electronic pressure control. Helium (6.0 Grade, Linde, Kraków) was used as the carrier gas at a constant flow rate of 2.6 mL/min. The GC separation was on either of two fused-silica capillary columns:

(1) J&W HP5-MS (60 m × 0.32 mm i.d., 0.25 μm film thickness) coated with a chemically bonded phase (95% polydimethylsiloxane, 5% diphenylsiloxane). The GC oven temperature was programmed from 40 °C (isothermal for 1 min) to 120 °C at a rate of 20 °C/min, then to 300 °C at a rate of 3 °C/min. The final temperature was held for 35 min.
(2) J&W DB35-MS (60 m × 0.25 mm i.d., 0.25 μm film thickness) coated with a chemically bonded phase (35% phenyl-methylpolysiloxane). The GC oven temperature was programmed from 50 °C (isothermal for 1 min) to 120 °C at a rate of 20 °C/min, then to 300 °C at a rate of 3 °C/min. The final temperature was held for 45 min.

The GC column outlet was connected directly to the ion source of a mass spectrometer. The GC-MS interface was kept at 280 °C, while the ion source and the quadrupole analyzer were at 230 and 150 °C, respectively. Mass spectra were recorded at *m/z* 45–550 da (0–40 min) and *m/z* 50–700 da (above 40 min). The mass spectrometer was operated in the electron impact mode (ionization energy: 70 eV).

3.6. Quantification and identification

An Agilent Technologies Enhanced ChemStation (G1701CA ver. C.00.00) and the Wiley Registry of Mass Spectral Data (7th ed) software were used for data collection and mass spectra processing. The abundances of the selected compounds were calculated by comparisons of peak areas for internal standards (3-methylheneicosane and 9-phenylindene) with the peak areas of the individual hydrocarbons obtained from the GC-MS ion chromatograms. Identification of individual compounds was aided by comparison with published mass spectra and by interpretation of mass spectrum fragmentation patterns.

3.7. $\delta^{18}O$ and $\delta^{13}C$ stable isotopes

For palaeotemperature determination of seawater, 25 belemnite rostra were collected from the clay sequence of the Polish Jura, mainly from the Częstochowa region. The analysed belemnites represent closely related genera: *Hibolites* and *Belemnopsis*. Unfortunately, more precise identification was not possible because the specimens were incomplete. The belemnites were dark-brown in colour and well-preserved. Examination of several specimens under SEM showed the primary microtexture of radially-arranged calcite prisms which indicates the low diagenetic state of the original calcite. Organic matter occurred in some spots only of longitudinal sections. The chemical analyses of belemnite rostra from these clays showed that they are characterized of low amounts of Mn (6–11 ppm) and Fe (45 ppm) (Piechota, 2001). High amounts of these trace elements (>100 and >250 ppm, respectively) would suggest diagenetic alteration (e.g., Price and Sellwood, 1997; Gröcke et al., 2003; Wierzbowski, 2004).

The materials for analyses were obtained only from within the *rostrum solidum* of the belemnites, the part of the guard which is situated below the conical cavity, i.e., the alveolus (see Niebuhr and Joachimski, 2002). The apical canal was omitted due to its diagenetic infillings (e.g., Podlaha et al., 1998; Niebuhr and Joachimski, 2002; Wierzbowski, 2004). The samples (a few chips from each guard) were then treated with 0.6 M HCl in order to

remove any secondary calcite (see Price and Gröcke, 2002). After drying, the calcite samples from each guard were ground and homogenized in order to avoid seasonal variations in isotopic composition (see Wierzbowski, 2004). About 10 mg of carbonate mineral was reacted with 100% orthophosphoric acid under vacuum at 25 °C (24 h). The gas was cryogenically purified and then introduced to the mass spectrometer (Finnigan-Mat Delta E). Stable isotope ratios of C and O ($\delta^{13}C$ and $\delta^{18}O$) were measured with a precision of 0.05‰. $\delta^{13}C$ and $\delta^{18}O$ values are quoted relative to the Vienna Pee Dee Belemnite (VPDB) international standard.

4. Results and discussion

4.1. Clays

4.1.1. Bulk geochemical data

The clay samples generally contain low amounts of carbonates (5–20%). Only clays with high concentrations of scattered carbonate fossils (called carbonate clays) are significantly enriched in carbonates. Total organic C (TOC) content is in the range of 0.7–5.5% (Table 1). Bojesen-Koefoed (1996) obtained similar TOC values using Rock Eval pyrolysis for 3 Middle Jurassic clay pits (Faustianka, Krzyworzeka and Pacanów). Moreover, based on Rock Eval data, Bojesen-Koefoed (1996) characterized kerogen from the Middle Jurassic clays as type III (according to Espitalié et al., 1985). Fig. 2 shows the relationship between TOC and carbonate contents in the Middle Jurassic clays and concretions from the different regions of Poland. In comparison to other regions, the clays from the Polish Lowland are generally enriched in organic C. Conversely, the carbonate clays and marls are significantly impoverished in TOC (Table 1). They are situated in the same field as carbonate concretions (Fig. 2).

The organic matter (OM) from both the southern and northern parts of Poland is immature. Values of T_{max} obtained from Rock Eval analysis are between 415 and 425 °C (Bojesen-Koefoed, 1996).

4.1.2. n-Alkanes, isoprenoids and fatty acids

The aliphatic fractions of all clay samples are dominated by *n*-alkanes in the range of C_{13}–C_{35}. Two characteristic *C* number maxima (C_{max}) are observed in their distributions (e.g., Fig. 3a). The first C_{max} is between C_{16}–C_{19} and the second, from C_{25}–C_{29}. The relative concentrations of low versus high molecular weight *n*-alkanes differ among the clay samples (Table 1) but in most cases the (n-C_{17} + n-C_{18} + n-C_{19})/(n-C_{27} + n-C_{28} + n-C_{29}) ratios are close to or <1. The C preference index ($CPI_{(25-31)}$) values are significantly >1 for all samples and in the case of 7 clay samples are even >2 (Table 1). The dominance of high molecular weight *n*-alkanes with an odd C number predominance (especially n-C_{25}, n-C_{29}, n-C_{31}) clearly indicates an input of terrestrial organic matter. The distribution of isoprenoids (pristane, Pr and phytane, Ph) in relation to *n*-alkanes is characterized by relatively low values of Pr/n-C_{17} (Table 1), in most cases not exceeding one. Generally, values of the Pr/Ph ratio are diverse (Table 1), but all range within 0.5–3. Large differences between Pr/Ph ratios, even between clay samples from equivalent facies, do not indicate changes in the redox conditions during OM sedimentation (for general details see Didyk et al., 1978; ten Haven et al., 1987). Most likely, the Pr/Ph ratio is controlled mainly by the OM source (e.g., Brown and Kenig, 2004).

The distribution of saturated fatty acids in the clay samples is bimodal with two maxima at n-C_{16} and n-C_{24} or n-C_{26}, with the first maximum clearly dominant (Fig. 4) and suggesting a mixed origin. Both long and short chain saturated fatty acids have a marked even over odd C number predominance. Long chain fatty acids are most probably derived from leaf epicuticular waxes of land plants (Eglinton and Hamilton, 1967; Simoneit, 1978) whereas the origin of short chain fatty acids may be more complex.

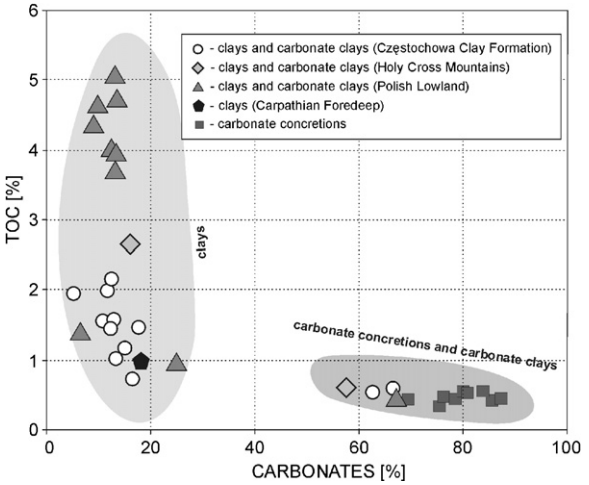

Fig. 2. Correlation diagram of total organic C (TOC) vs. carbonate contents from the Middle Jurassic clays and carbonate concretions.

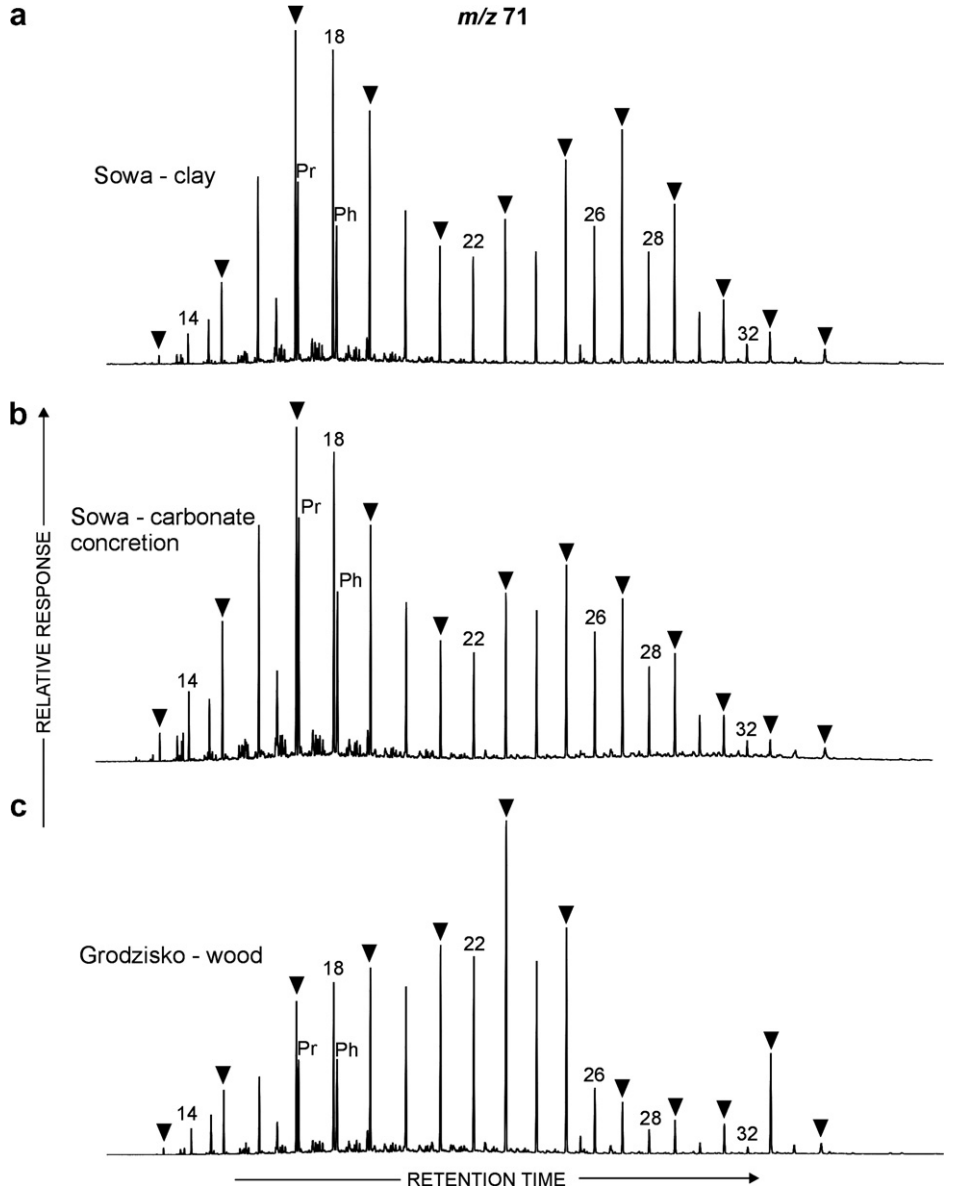

Fig. 3. Mass chromatograms (*m*/*z* 71) showing distribution examples of *n*-alkanes and isoprenoids of: (a) clay from Sowa; (b) carbonate concretion from Sowa and (c) wood from Grodzisko. Odd C number *n*-alkanes are marked by filled triangles. The numbers above peaks indicate C numbers of *n*-alkanes. Pr, pristane; Ph, phytane.

4.1.3. Triterpenoid hydrocarbons

The most abundant hopanes are 17β,21β-hopane or norneohop-13(18)-ene, depending on the samples. In individual samples (from the Holy Cross Mountains and Carpathian Foredeep) 17α,21β-hopane dominate, which is associated with a slightly higher maturity and/or oxidation range (Fig. 5). Also, the ββ/(αβ + βα) hopane ratios (Peters and Moldowan, 1993), shown in Table 2, do not exclusively distinguish the maturity range, but also depend on secondary OM oxidation. For example, samples from separate levels of the same clay pit are characterized by different values of the ββ/(αβ + βα) ratio (see Sowa and Ogrodzieniec in Table 2). A similar interpretation of differences in hopane distribution was presented by Hautevelle et al. (2007). These authors showed that the "mature" distribution of hopanes, present in carbonates was connected with oxidation during diagenesis, while the "immature" distribution present

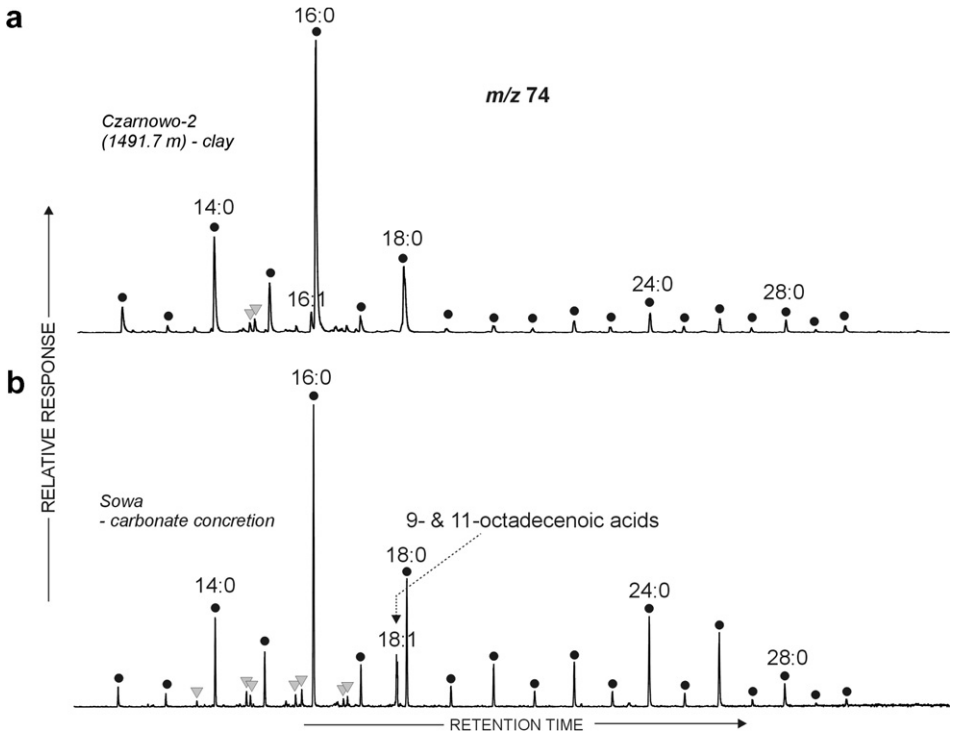

Fig. 4. Mass chromatograms of *m*/*z* 74 showing distribution examples of fatty acids (as methyl esters) of: (a) a clay from the Czarnowo-2 well and (b) a carbonate concretion from Sowa. Key: filled circles, *n*-alkanoic acids; filled triangles, *iso*- and *anteiso*-alkanoic acids.

in clays was connected with physical protection of OM by fine-grained clay minerals.

The distribution of extended C_{31}–C_{35} hopanes is characterized by a strong predominance of the C_{31}(22S+22R) homologues and significant excess of the less stable *R* epimer (Fig. 5). Hopanes with 35 C atoms in the molecule are not detected in any sample and hopanes with 34 C atoms are only present in trace amounts.

Due to the fact that diaster-13(17)-enes may have originated from algal matter and terrestrial plants whereas hopanes and hopenes are connected mainly with bacteria, the ratio of diaster-13(17)-enes/(hopanes + hopenes) was used to characterize the relationship between algal + terrestrial versus bacterial input into OM. This parameter is relatively precise in the Middle Jurassic clays, due to the low OM maturity and consequent low level of sterane and hopane alteration. In most clay samples, the relative concentrations of diaster-13(17)-enes are lower than hopenes + hopanes (D/H parameter – Table 2), but some exceptions (Ogrodzieniec clays) were observed. The ratios for the clays are similar and vary from 0.22 to 1.13 with ~0.4 as a typical value (Table 2). Relatively high concentrations of hopanes and hopenes explain the intensive bacterial activity during and after OM deposition.

In many clay samples (e.g., Fig. 5c, Table 2), fernenes were identified; these natural product biomarkers were first identified in ferns (Ageta and Arai, 1983; Paull et al., 1998). Besides ferns, fern-9(11)-ene was isolated from the extant conifer *Podocarpus saligna* (Silva et al., 1972), while fern-7-ene was found in sediments of a saline Antarctic lake associated with anoxic depositional conditions and associated with unknown bacteria (Volkman et al., 1986). However, the compounds above in the epicontinental Middle Jurassic sediments most likely originated from Caytoniales, a group of Mesozoic pteridosperm plants, since these compounds have been identified in a *Sagenopteris* (Caytoniales) leaflet sample from the Polish Jura (Zatoń et al., 2006). In all samples containing fernenes, a C_{29}-norfern-9(11)-ene is the major compound, but 22,21,30-trisnorfern-9(11)-ene, C_{30}-fern-9(11)-ene, *seco*-bisnorfern-9(11)-ene, as well as C_{29} ferndienes, are also present. The identification of individual fernenes provided, based on mass spectra and authentic standards differ slightly from that proposed by Zatoń et al. (2006). The concentrations of fernenes, in

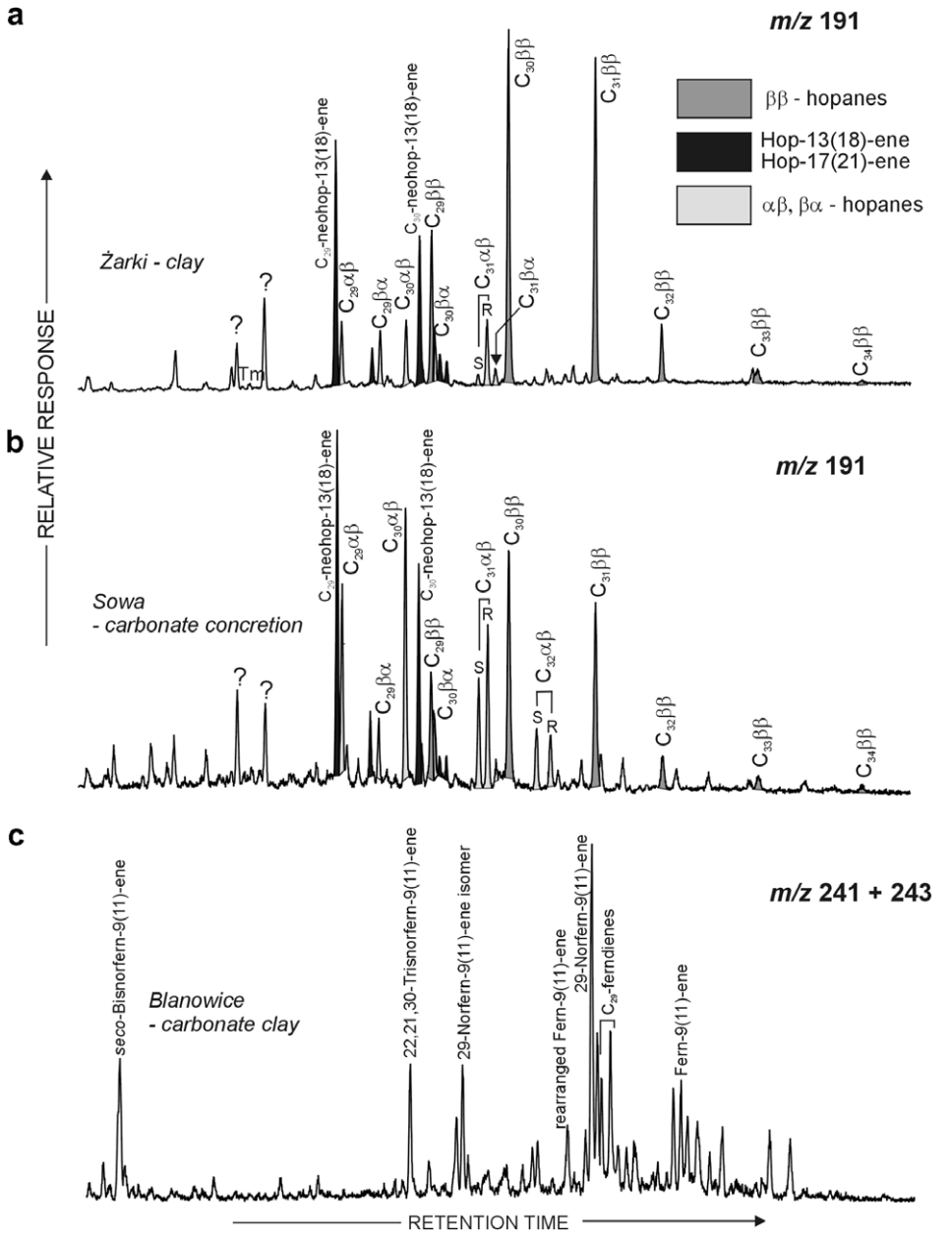

Fig. 5. Partial *m*/*z* 191 mass chromatograms of a clay (a) and siderite (b) bed showing differences in the distributions of hopanes, and (c) partial *m*/*z* 243 mass chromatogram showing a fernene distribution in Blanowice clay.

relation to hopanes, hopenes and diasterenes, the major biomarker groups present in the clays, are relatively small. For example, the concentrations of the most abundant C_{29}-norfern-9(11)-ene ranged from 0.8 to 2 μg/g TOC and C_{30}-fern-9(11)-ene from 0.15 to 0.35 μg/g TOC. However, it is known from previous work (Paull et al., 1998) that fernenes may isomerize to neohop-13(18)-ene, which quantitatively (6.5–22.5 μg/g TOC) is one of the most important compounds in the aliphatic fraction of most clay samples (see Fig. 5).

The relationship between ββ-, αβ-hopanes and hopenes is presented in the ternary diagram (Fig. 6). The main factors controlling their distribution are thermal maturity, oxidation and source of organic matter. Significantly higher relative concentrations of the hopenes (C_{29}-neohop-13(18)-ene is always major) in relation to the αβ- and ββ-hopanes

Table 2
Parameters of molecular markers

Sample/*Lithology*	Age/*Ammonite zone*	Diaster-13(17)-enes [%]			ββ/(αβ + βα)-hopanes	Fernenes	D/H	Hopanes and hopenes [%]		
		C_{27}(S+R)	C_{28}(S+R)	C_{29}(S+R)				C_{29}+C_{30}-ene	$C_{29}\alpha\beta + C_{30}\alpha\beta$	$C_{29}\beta\beta + C_{30}\beta\beta$
Kraków-Wieluń Upland										
Anna/*Clay*	U. Bathonian/*Hodsoni*	25	21	54	4.12	+	0.33	52	8	40
Sowa/*Clay*	U. Bajocian/*Parkinsoni*	26	22	52	3.22	+	0.64	53	12	35
Grodzisko/*Clay*	U. Bathonian/*Hodsoni*	22	22	56	3.25	+	0.41	45	14	41
Faustianka/*Clay*	L. Bathonian/*Tenuiplicatus*	20	21	59	2.00	+	0.22	55	15	30
Pacanów/*Clay*	U. Bajocian/*Parkinsoni*	25	19	56	3.61	+	0.47	46	13	41
Mokrsko/*Clay*	U. Bajocian/*Parkinsoni*	23	20	57	2.41	+	0.34	56	10	34
Kawodrza/*Clay*	M. Bathonian/*Morrisi*	24	20	56	4.46	+	0.25	37	12	51
Krzyworzeka/*Clay*	U. Bathonian/*Hodsoni-Orbis*	23	19	58	3.90	+	0.46	46	10	44
Ogrodzieniec #1/*Clay*	U. Bathonian/*Hodsoni*	26	19	55	4.22	+	1.13	57	6	37
Ogrodzieniec #2/*Clay*	U. Bathonian/*Hodsoni*	25	19	56	4.67	+	1.12	58	9	33
Żarki/*Clay*	U. Bathonian/*Hodsoni*	26	18	56	5.20	+	0.36	38	13	49
Blanowice/*Carbonate Clay*	M. Bathonian/*Morrisi*	25	17	58	2.04	+	0.48	41	37	22
Ogrodzieniec #3/*Carbonate Clay*	U. Bathonian/*Hodsoni*	26	17	57	3.46	Traces	0.32	50	9	41
Anna/*Carbonate concr.*	U. Bathonian/*Hodsoni*	–	–	–	2.20	–	0	40	15	45
Sowa #A/*Carbonate bed*	U. Bajocian/*Parkinsoni*	27	22	51	2.19	+	0.77	58	12	30
Sowa #B/*Carbonate bed*	U. Bajocian/*Parkinsoni*	27	21	52	2.61	+	0.55	56	9	35
Ogrodzieniec/*Carbonate concr.*	U. Bathonian/*Hodsoni*	28	19	53	3.65	+	1.34	54	11	35
Sowa/*Carbonate concr.*	U. Bajocian/*Parkinsoni*	19	23	58	0.73	+	0.53	41	34	25
Mokrsko/*Carbonate concr.*	U. Bajocian/*Parkinsoni*	26	22	52	0.91	–	0.70	58	22	20
Sowa/*Wood*	U. Bajocian/*Parkinsoni*	3	24	73	2.91	–	2.50	–	–	–
Kawodrza/*Wood*	M. Bathonian/*Morrisi*	0	17	83	–	–	>20	–	–	–
Blanowice/*Wood*	M. Bathonian/*Morrisi*	0	25	75	–	–	5.25	–	–	–
Żarki/*Wood*	U. Bathonian/*Hodsoni-Orbis*	0	5	95	–	–	>20	–	–	–
Mokrsko/*Wood*	U. Bajocian/*Parkinsoni*	6	19	75	–	–	2.56	–	–	–
Anna W1/*Wood*	U. Bathonian/*Hodsoni*	0	16	84	–	–	3.48	–	–	–
Anna W2/*Wood*	U. Bathonian/*Hodsoni*	0	15	85	–	–	>20	–	–	–
Anna W3/*Wood*	U. Bathonian/*Hodsoni*	0	13	87	–	–	>20	–	–	–
Anna W6/*Wood*	U. Bathonian/*Hodsoni*	0	4	96	–	–	>20	–	–	–
Alina/*Wood*	U. Bajocian/*Parkinsoni*	0	2	98	–	–	7.97	–	–	–
Grodzisko W1/*Wood*	U. Bathonian/*Hodsoni-Orbis*	0	12	88	–	–	4.05	–	–	–
Grodzisko W2/*Wood*	U. Bathonian/*Hodsoni-Orbis*	0	3	97	–	–	>20	–	–	–

Grodzisko W3/*Wood*	U. Bathonian/*Hodsoni-Orbis*	0	4	96	–	–	>20	–	–	–
Gnaszyn W1/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	0	13	87	–	–	>20	–	–	–
Gnaszyn W2/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	0	11	89	–	–	>20	–	–	–
Gnaszyn W3/Wood	M./U. Bathonian/*Morrisi-Hodsoni*	5	12	83	–	–	>20	–	–	–
Gnaszyn W4/Wood	M./U. Bathonian/*Morrisi-Hodsoni*	1	8	91	–	–	>20	–	–	–
Gnaszyn W5/*Wood*	M./U. Bathonian/*Morrisi-Hodsoni*	1	9	90	–	–	>20	–	–	–
Holy Cross Mountains										
Marianów #1/*Clay*	Bathonian	21	20	59	1.36	Traces	0.20	11	37	52
Marianów #2/*Carbonate Clay*	Bathonian	20	18	62	1.29	–	0.31	9	56	35
Marianów/*Carbonate concr.*	Bathonian	22	20	58	0.65	–	0.44	18	37	45
Polish Lowland										
Okonek-1 (316,5 m)/*Clay*	U. Bajocian	16	24	60	2.49	+	0.25	56	6	38
Czarne-4 (550 m)/*Marly Clay*	Callovian	23	19	58	1.47	Traces	0.65	39	27	34
Czarnowo-1 (1496 m)/*Clay*	Bathonian	20	15	65	2.07	–	0.41	25	22	53
Czarnowo-1 (1599 m)/*Clay*	Bajocian	16	14	70	1.96	–	0.24	18	27	55
Czarnowo-1 (1655 m)/*Clay*	Aalenian	13	16	71	1.27	–	0.16	14	36	50
Czarnowo-2 (1438,5 m)/*Clay*	Callovian	19	17	64	2.16	–	0.39	29	23	48
Czarnowo-2 (1491,7 m)/*Clay*	Bathonian	13	15	72	1.79	–	0.57	23	31	46
Czarnowo-2 (1500,4 m)/*Clay*	Bajocian	14	16	70	1.69	Traces	0.54	24	27	49
Czarnowo-2 (1720,2 m)/*Clay*	Aalenian	12	16	72	1.65	–	0.41	14	32	54
Carpathian Foredeep										
Łukowa-2 (730,8 m)/*Clay*	Bajocian	16	14	70	0.87	–	0.85	14	50	36

ββ/(αβ + βα)-hopanes = C_{30}-17β, 21β-hopane/(C_{30}-17α, 21β-hopane+C_{30}-17β, 21α)-hopane ratio. D/H = all diaster-13(17)-enes/(all hopenes + hopanes) ratio.

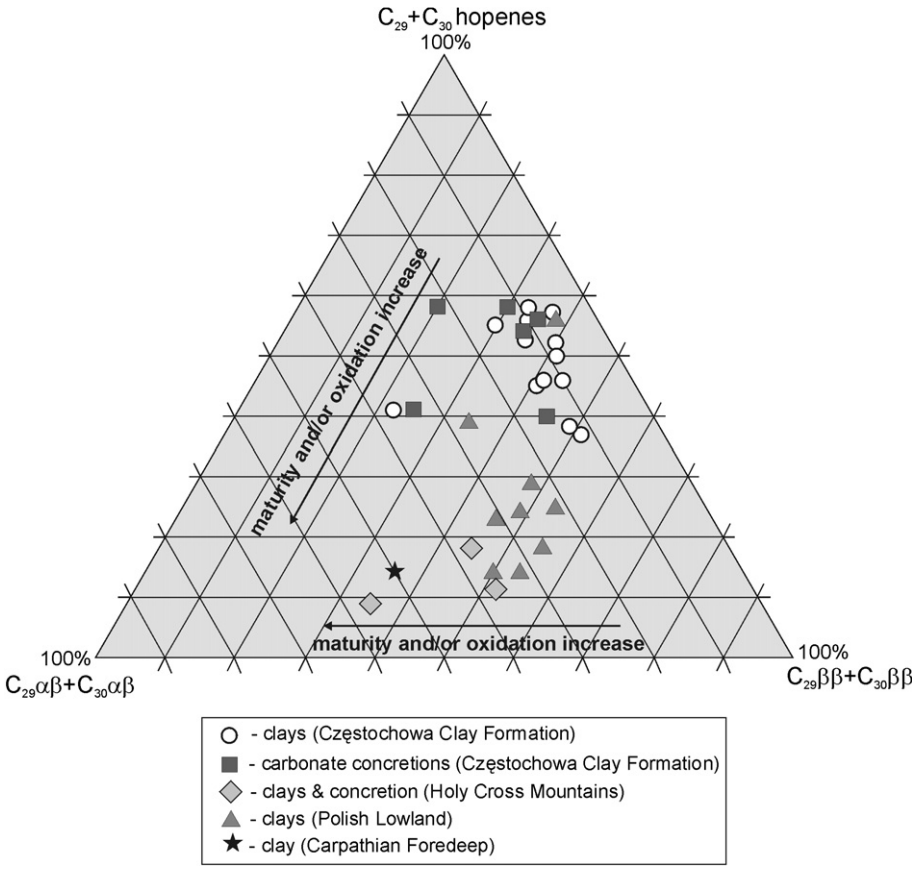

Fig. 6. Ternary diagram showing relationship among ββ-, αβ-hopanes and hopenes for the samples. Additional details in Table 2.

were found in the Częstochowa Clay Formation compared to much lower relative concentrations of hopenes from the Polish Lowland, Carpathian Foredeep and the Holy Cross Mountain samples. At the same time, fernenes are ubiquitous only in the Częstochowa Clay Formation and are absent or present as traces in the other areas. Because neohop-13(18)-ene is the product from an acid-catalysed rearrangement conversion of fernenes (Paull et al., 1998), it is possible that at least some of the hopenes identified in the clays of the Częstochowa Clay Formation are derived from fernenes.

4.1.4. Steroid hydrocarbons

Among the steroids, the diaster-13(17)-enes (20R and 20S epimers) and 4β-methyldiaster-13(17)-enes (20R and 20S epimers) are clearly dominant in all clays (Fig. 7), while Δ^4 and Δ^5 sterenes, steranes and diasteranes are not found, or are found only as traces in some cases. The dominance of diasterenes in the clays is due to early diagenetic acid-catalysed backbone rearrangement processes of steranes (Rubinstein et al., 1975). Relatively small concentrations of diacholestadiene were also found, as Rushdi et al. (2003) identified from a comparable mass spectrum. The abundances of the C_{27}–C_{29} diasterenes (20R and 20S epimers) are presented as a ternary plot in Fig. 8 and discussed below.

4.1.5. Polycyclic aromatic compounds

Perylene is usually the dominant compound among the polycyclic aromatic hydrocarbons (PAHs) in these samples (Fig. 9). Methyl (*m*/*z* 266) and dimethyl (*m*/*z* 280) derivatives of perylene are also present in relatively high concentrations, representing diagenetic methylation products (see Alexander et al., 1995). Although the occurrence of perylene may be genetically connected with both marine and terrestrial OM (Jiang et al., 2000; Silliman et al., 2000), this PAH is characteristic for terrestrial material in the clays because it has a high concentration in the fossil wood (see Section 4.3,

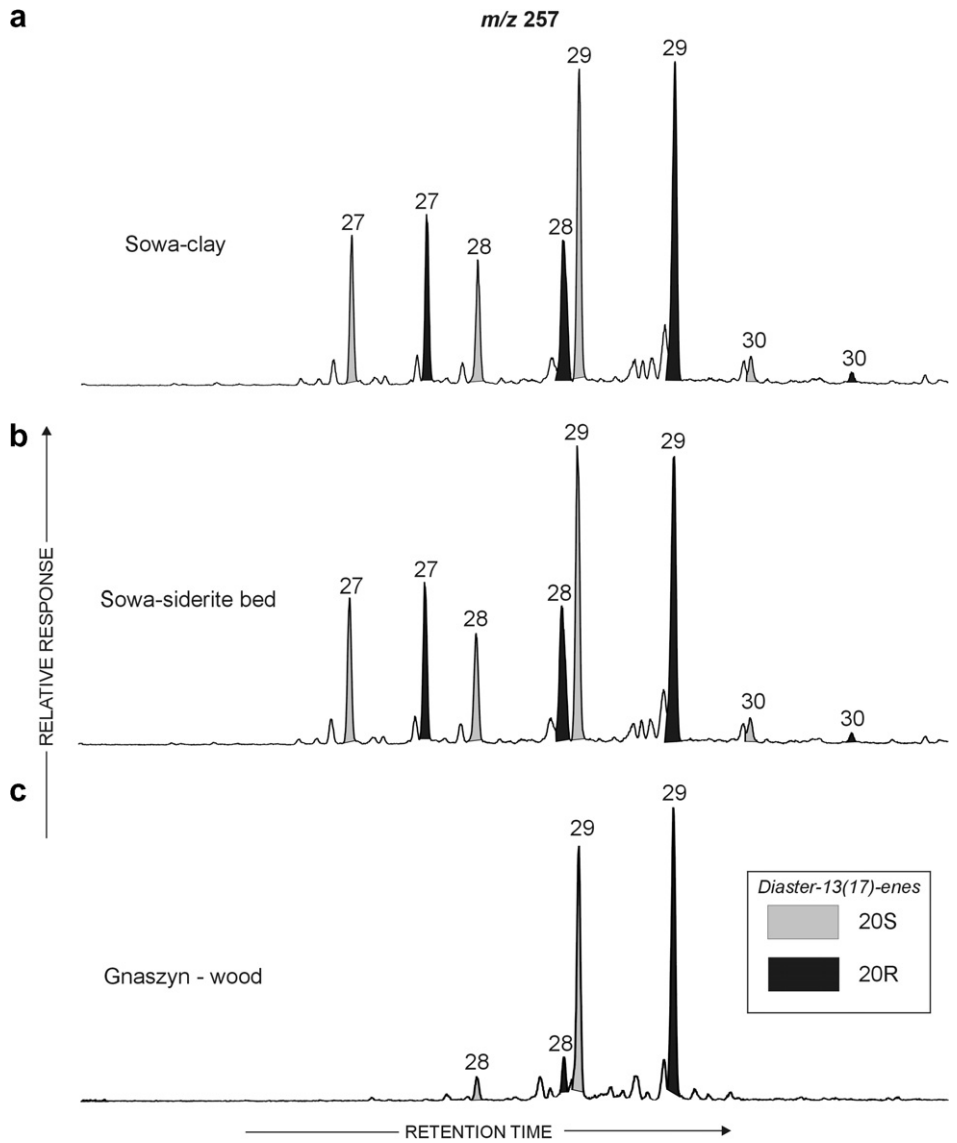

Fig. 7. Partial *m*/*z* 257 mass chromatograms showing differences in the distributions of the diaster-13(17)-enes for a clay, siderite bed and wood.

Table 3). Other quantitatively important aromatic biomarkers are cadalene, simonellite and retene, and the sesqui- and diterpenoids such as calamenene, cadina-1(10),6,8-triene and dehydroabietane are less common, found only in some clay samples. Dehydroabietane, simonellite and retene are interpreted as diagenetic products of abietane type diterpenoids such as abietic acid (Otto and Simoneit, 2001). Other possible pathways for the formation of aromatic abietanes are the degradation and aromatisation of pimarene and phyllocladane precursors (Alexander et al., 1987), but such diterpenoids were not found in the aliphatic fraction. Tetracyclic diterpanes (including phyllocladane) are not present in the clays probably due to their complete early diagenetic alteration under acidic conditions, catalysed by clays and/or by microbial activity (see Bechtel et al., 2001). Cadalene, calamenene and 5,6,7,8-tetrahydrocadalene are derived from cadalene-type sesquiterpenoids, such as cadinenes and cadinols (Simoneit et al., 1986). Both groups of compounds are characteristic of conifers (Otto and Wilde, 2001), but they also occur widely in the plant kingdom and are thus non-specific (Karrer et al., 1977).

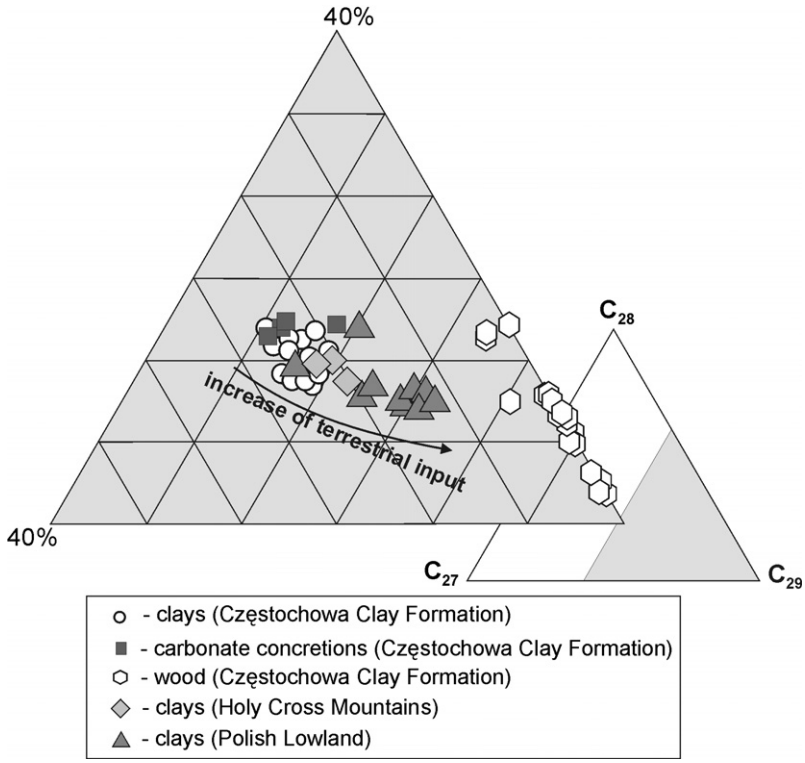

Fig. 8. Ternary diagram showing the relative abundance of C_{27}-, C_{28}- and C_{29}-diaster-13(17)-enes [20S+20R] in the saturate fraction of clay, wood and carbonate concretion samples from the Middle Jurassic (note that all wood samples contain almost exclusively only C_{29}-diaster-13(17)-enes).

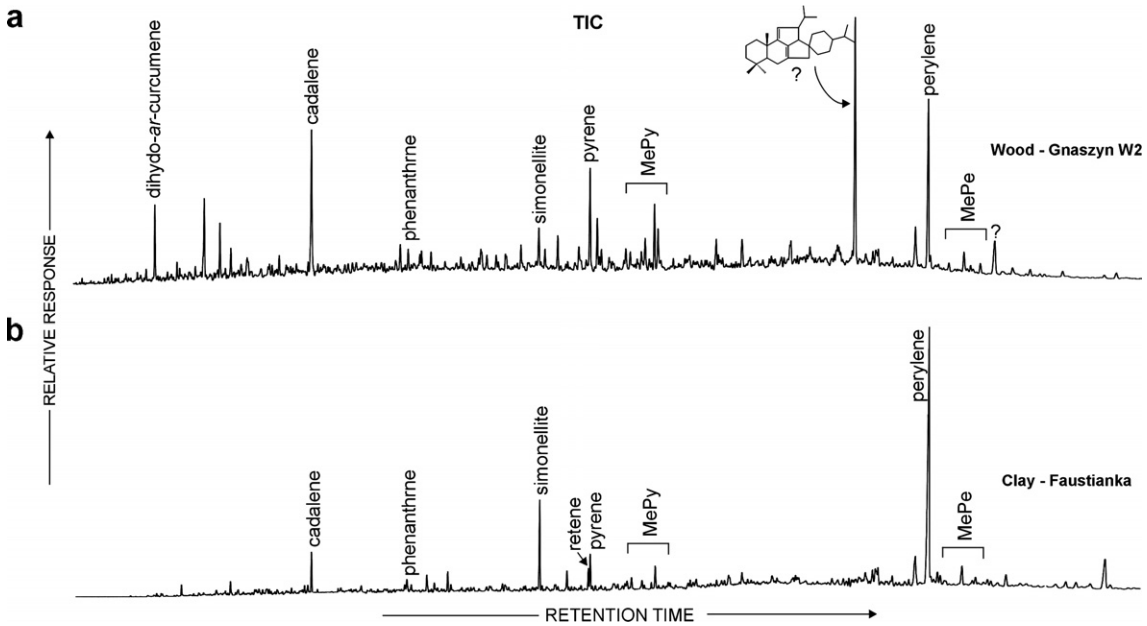

Fig. 9. Representative total ion current chromatograms (TIC) of aromatic fractions from: (a) a *Protopodocarpoxylon* wood sample and (b) a clay sample. MePy, methyl pyrenes; MePe, methyl perylenes.

Table 3
Aromatic hydrocarbons and their methyl derivatives identified in clay, concretion and wood samples from the Middle Jurassic deposits of Poland

Compound	Occurrence and relative abundance in the selected samples[a]						Identification
	Kawod-rza/*Clay*	Faustian-ka/*Clay*	Sowa *Concr.*	Sowa B *Carb. bed*	GNW2	GNW3	
Sesquiterpenoids							
Calamenene	–	–	–	0.4	1.2	0.9	Simoneit and Mazurek (1982)
Cadina-1(10),6,8-triene	0.3	–	0.6	1.3	6.8	2.2	Simoneit and Mazurek (1982)
Cadalene	1.3	7.6	12.4	24.5	61.9	47.5	Standard
1,7-Dimethyl-4-isopropylnaphthalene	–	–	–	–	1.0	1.6	Elias et al. (1997)
Dihydro-*ar*-curcumene	–	–	–	0.5	19.5	0.8	Ellis et al. (1995)
Isodihydro-*ar*-curcumene	–	–	–	0.1	–	–	Bastow et al. (1997)
Diterpenoids							
Abietanes							
Dehydroabietane	–	–	2.4	5.4	20.8	31.1	Standard
16,17-Bisnordehydroabietane	–	–	–	–	19.7	2.6	MS
18,19-Bisnorsimonellite	–	–	–	–	4.2	1.2	MS
Simonellite	2.8	20.2	10.3	12.7	48.2	*100*	Standard
Retene	4.9	4.4	2.5	3.2	30.5	40.9	Philp (1985)
1,2,3,4-Tetrahydroretene	–	–	–	–	7.2	2.8	Philp (1985)
2-Methylretene	1.1	0.9	–	–	5.5	3.6	Bastow et al. (2001)
Polycyclic aromatic hydrocarbons (PAHs)							
Naphthalene	0.2	–	–	–	0.5	–	Standard
2-Methylnaphthalene	0.8	0.1	1.2	–	0.5	–	Standard
1-Methylnaphthalene	0.3	0.1	1.2	–	0.9	–	Standard
ΣDMe-naphthalenes	3.6	3.9	12.4	3.8	1.1	0.9	MS
ΣTMe-naphthalenes	4.0	5.1	18.9	9.2	4.3	3.6	MS
ΣTeMe-naphthalenes	4.9	2.1	10.8	11.5	5.1	2.5	MS
Biphenyl	0.8	0.4	1.0	0.4	0.3	–	Standard
ΣMe-biphenyls	1.6	0.8	4.6	1.6	5.1	0.9	MS
Fluorene	2.6	0.5	4.8	2.6	1.7	0.5	Standard
Phenanthrene	10.0	4.6	14.1	15.1	7.3	1.2	Standard
Anthracene	0.1	–	–	–	0.6	0.05	Standard
3-Methylphenanthrenes	2.4	1.0	1.5	2.1	1.7	0.3	Radke et al. (1986)
2-Methylphenanthrene	3.3	0.9	2.6	3.4	1.8	0.3	Radke et al. (1986)
9-+4-Methylphenanthrene	3.4	1.8	2.9	6.1	2.9	0.4	Radke et al. (1986)
1-Methylphenanthrene	3.6	1.4	3.6	6.8	3.1	0.4	Radke et al. (1986)
1-Phenylnaphthalene	1.5	0.7	0.9	0.5	0.6	0.2	Standard
2-Phenylnaphthalene	3.3	1.2	1.9	1.3	6.5	1.2	Standard
ΣDMe-Phenanthrenes	1.5	2.6	4.6	12.1	2.7	1.4	MS
Fluoranthene	7.1	4.8	3.4	6.9	14.1	1.5	Standard

(*continued on next page*)

Table 3 (*continued*)

Compound	Occurrence and relative abundance in the selected samples[a]						Identification
	Kawod-rza/*Clay*	Faustian-ka/*Clay*	Sowa *Concr.*	Sowa B *Carb. bed*	GNW2	GNW3	
Pyrene	17.4	7.8	8.7	15.2	36.3	7.6	Standard
Benzo[*ghi*]fluoranthene	5.1	1.6	1.9	3.6	11.7	0.6	MS
ΣMe-pyrenes + Me-fluoranthenes	26.7	10.0	10.9	15.7	56.8	14.2	MS
Benz[a]anthracene	2.6	2.3	1.1	3.5	12.8	0.3	Standard
Chrysene/triphenylene	3.3	3.9	1.3	5.6	6.2	0.2	Standard
Benzo[*b*]fluoranthene	3.4	2.2	2.6	4.4	6.1	0.7	Wise et al. (2004)
Benzo[*k*]fluoranthene	3.8	2.2	1.8	2.4	10.4	0.6	Wise et al. (2004)
Benzo[*j*]fluoranthene	2.5	1.4	3.8	4.7	5.5	0.7	Wise et al. (2004)
Benzo[*e*]pyrene	4.5	2.1	3.3	6.4	8.3	0.6	Standard
Benzo[*a*]pyrene	4.8	2.1	2.6	4.9	20.6	0.8	Standard
Perylene	*100*	*100*	*100*	*100*	*100*	31.0	Standard
ΣMe-perylenes	24.5	12.6	19.3	31.0	16.1	8.1	MS
Indeno[1,2,3-cd]pyrene	10.7	3.6	7.2	4.4	3.5	0.9	Wise et al. (2004)
Benzo[*ghi*]perylene	23.0	7.9	17.0	12.1	4.3	0.8	Wise et al. (2004)

MS, Mass spectrum interpretation; GNW, Gnaszyn wood; Me, methyl; DMe, dimethyl; TMe, trimethyl; TeMe, tetramethyl.
[a] Abundance relative to major peak.

Characteristic constituents of OM from clay sediments are dihydro-*ar*-curcumene (identification based on mass spectrum published by Ellis et al. (1995), see also Czechowski et al., 1996) and at relatively low concentration isodihydro-*ar*-curcumene (identification based on mass spectrum and retention time published by Bastow et al. (1997)). The former compound is a product from natural sesquiterpenoids, such as bisabolene or curcumene (Ellis et al., 1995) and the latter is derived from dihydro-*ar*-curcumene via sedimentary rearrangement processes (Bastow et al., 1997).

In addition, other common aromatic constituents of the clay sedimentary organic OM include the PAHs: naphthalene, phenanthrene, fluoranthene, pyrene and their alkyl derivatives (Fig. 10a and b, Table 3) as well as the more condensed PAHs: benzo[*ghi*]fluoranthene, benz[*a*]anthracene, chrysene + triphenylene, indeno(1,2,3-*cd*)pyrene and benzo[*ghi*]perylene. Moreover, dibenzothiophene with the methyl-, dimethyl- and trimethyl-derivatives, biphenyl, dibenzofuran, benzonaphthothiophenes and benzonaphthofurans were also detected, usually at much lower concentrations (Table 3). Benzohopanes and monoaromatic steroid hydrocarbons were found only in trace amounts in the clay samples.

4.2. Carbonate concretions

XRD analysis has shown that all carbonate concretions, except those with a dominant carbonate phase, also contain smaller amounts of clay minerals (~2–10%) (illite and kaolinite), quartz (~3–20%), pyrite (~ < 1–8%) and trace amounts of feldspars. With the exception of the two samples from Blanowice, where the carbonate consists of calcite with only minimal amounts of Mg^{2+} and Ca^{2+} structurally substituted in the lattice, the carbonates of the other samples generally consist of minerals from the $FeCO_3$ to $MnCO_3$ and $CaCO_3$ to $MgCO_3$ series.

The Middle Jurassic concretions are uniform in their structure and therefore concentric growth zones are not obvious, except for some calcitic concretions where a thin outer rim enriched in quartz is clearly visible (Zatoń and Marynowski, 2004). Some concretions also possess distinct limonitized outer rims, but this is due to weathering processes.

The concretions contain much lower amounts of TOC than clays (Table 1, Fig. 2) due to dilution of the organic C by early diagenetic carbonates as well

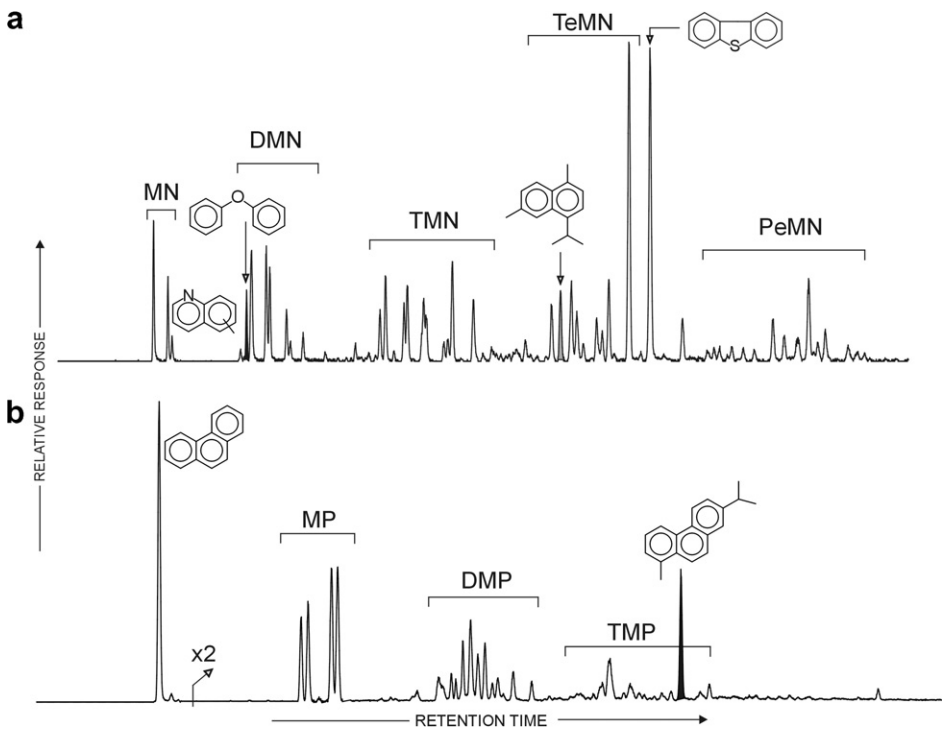

Fig. 10. (a) Distributions of alkylnaphthalenes (*m/z* 142 + 156 + 170 + 184 + 198) and (b) alkylphenanthrenes (*m/z* 178 + 192 + 206 + 220 + 234) from the Kawodrza clay sample. MN, methylnaphthalenes; DMN, dimethylnaphthalenes; TMN, trimethylnaphthalenes; TeMN, tetramethylnaphthalenes; PeMN, pentamethylnaphthalenes; MP, methylphenanthrenes; DMP, dimethylphenanthrenes; TMP, trimethylphenanthrenes.

as bacterial OM degradation. The compositions of OM trapped in carbonate concretions are similar to those of the parent clays (Table 3, Fig. 3 a vs. b and Fig. 7 a vs. b), which is also observed for nodule growth in sediments affected by hydrothermal activity (Boni et al., 1994). However, some exceptions were observed in the fatty acid distributions. Straight chain saturated fatty acids in the carbonate concretions show bimodal distributions, and strong even C number predominances, similar to those in the clays (Fig. 4). Low molecular weight (LMW) *n*-alkanoic acids clearly dominate over the high molecular weight (HMW) *n*-alkanoic acids with an obvious dominance of palmitic acid ($C_{16:0}$). The distributions of the HMW acids are characteristic of terrestrial OM with a low maturity (Simoneit, 1978; Tissot and Welte, 1984). However, unsaturated fatty acids are present in high relative concentrations in the concretions, and much lower in the clays. They are represented by the $C_{18:1}$ fatty acids, occurring as isomeric mixtures of 9-octadecenoic and 11-octadecenoic acids (Fig. 4), and very low concentrations of other LMW unsaturated fatty acids (for comparison see Wolff et al., 1992; Kiriakoulakis et al., 2000). 10-Methylhexadecanoic acid, which is derived from sulphate reducing bacteria and would support the formation of concretions in the sulphate reduction zone (Kiriakoulakis et al., 2000), was not found. However, the occurrence of the $C_{18:1}$ fatty acids may be connected with sedimentary bacteria, which actively degrade OM and provide CO_2 for the formation of carbonates (see Boni et al., 1994). Such processes may take place during methanogenesis and Fe/Mn reduction (see Wolff et al., 1992).

In many carbonate concretions, the soluble OM is characterized by higher relative concentrations of thermally more stable biomarkers (e.g., αβ-hopanes, steranes) and lower $CPI_{(25-31)}$ values than in the parent clays (Tables 1 and 2, Fig. 5). That cannot be correlated with maturity differences, because the concretions and clays were generally collected from the same localities and essentially the same stratigraphic levels. The most plausible explanations for such a situation are processes of secondary oxidation and/or early microbial diage-

netic degradation of OM trapped in the carbonate concretions. This may be due to the fact that during the formation of the concretions or siderite beds, there was more intensive contact between organic matter and water, even water-bearing horizons from which the carbonates precipitated, thus driving more extensive oxidation of the OM.

It is known that oxidation processes cause similar molecular changes within sedimentary OM compared to thermal maturation (Elie et al., 2000), especially due to the catalytic effects of clay minerals during oxidation (Faure and Landais, 2000). Moreover, mineralization processes, including calcitization, sideritization and pyritization, taking place in clay sediments are strictly related to bacterial activity during the early stages of diagenesis, and for that reason with early diagenetic bacterial OM degradation.

4.3. Fossil wood

Wood fragments occur frequently in siderite nodules or host sediments, where several conifer taxa have been described (Philippe et al., 2006). The samples Gnaszyn: W1, W2, and Anna W6 are clearly assigned as the genus *Protopodocarpoxylon* Eckhold (Philippe et al., 2002). However, samples Sowa, Blanowice and Mokrsko are assigned as araucarian type (genus *Agathoxylon*) (Philippe, pers. comm., 2004, 2005). The remaining wood samples are poorly preserved or were not analyzed.

4.3.1. n-Alkanes, isoprenoids and fatty acids

In most of the wood samples the distribution of *n*-alkanes is bimodal, with a considerable dominance of the LMW over HMW *n*-alkanes [see $(n\text{-}C_{17} + n\text{-}C_{18} + n\text{-}C_{19})/(n\text{-}C_{27} + n\text{-}C_{28} + n\text{-}C_{29})$ parameter in Table 1], but some exceptions were noted (Anna W1). The HMW *n*-alkanes have an odd over even C number predominance, but in many cases this dominance is not as clear as in the clays and concretions (see $CPI_{(25-31)}$ values in Table 1). Moreover, in the case of the wood samples, only the $n\text{-}C_{23}$, $n\text{-}C_{25}$ or $n\text{-}C_{27}$ alkanes are dominant. One exception is the Grodzisko W1 wood sample where the HMW $n\text{-}C_{33}$ alkane is significant (Fig. 3c). This is due to the fact that the HMW *n*-alkanes with odd C chains are characteristic for epicuticular waxes of extant leaves and are not dominant in wood.

Pr/Ph ratios are near one and never exceed 2 in these wood samples. This is atypical because values of Pr/Ph ratio for terrestrial OM usually exceed 3 (Peters and Moldowan, 1993). Such low values may indicate that the OM from the wood fragments originated not only from wood samples, but also from other sources, namely from bacterial lipids. Some wood samples contain squalane.

The distributions of fatty acids are generally similar to those of the clays and carbonate concretions, but the HMW *n*-alkanoic acids are present in higher relative concentrations. Moreover, the $C_{18:1}$ fatty acids were not detected, although 5,9,13-trimethyltetradecanoic acid, 2,6,10,14-tetramethylpentadecanoic (pristanic) acid and 3,7,11,15-tetramethylhexadecanoic (phytanic) acid were identified.

4.3.2. Steroid hydrocarbons

Similar to the clays, the diaster-13(17)-enes and 4β-methyldiaster-13(17)-enes are certainly the dominant steroid hydrocarbons in the wood samples. However, the wood is characterized by different diaster-13(17)-ene distributions (Fig. 7), showing a C_{29} (S+R) diasterenes dominance, the presence of C_{28} (S+R) diasterene isomers and complete absence of C_{27} (S+R) diasterenes. The occurrence of minor amounts of the diacholest-13(17)-enes in two wood samples (Table 2) is probably associated with contamination from clays. Some wood samples also contain significant amounts of 1,9-dimethyldiacholest-13(17)-enes (S+R) and 1,1,9-trimethyldiacholest-13(17)-enes (S+R) (Table 4) as well as small concentrations of regular C_{29} ααα steranes and traces of sterenes besides the diaster-13(17)-enes.

4.3.3. Aromatic biomarkers and PAHs

The aromatic biomarkers and PAHs of *Protopodocarpoxylon* and *Agathoxylon* wood fragments have a dominance of perylene, cadalene and/or simonellite. Other significant compounds are: dihydro-*ar*-curcumene, isodihydro-*ar*-curcumene, calamenene, cadina-1(10),6,8-triene, dehydroabietane, retene and 2-methylretene (Fig. 9, Tables 3 and 4), similar to OM from some clays and carbonate concretions. Moreover, the woods include sesqui- and diterpenoids that were neither detected in concretions nor clays, such as 1,7-dimethyl-4-isopropylnaphthalene, 16,17-bisnordehydroabietane, 18,19-bisnorsimonellite and 1,2,3,4-tetrahydroretene.

This composition of sesqui- and diterpenoids is typical for a conifer source (Otto and Wilde, 2001). The occurrence of such high concentrations of perylene in wood samples suggests a terrestrial origin of this compound in the Middle Jurassic clays from Poland. The common PAHs of sedimentary

Table 4
Biomarkers identifed in the Jurassic *Protopodocarpoxylon* Eckhold wood from south-central Poland (after Marynowski et al., 2007, improved)

Compound	Occurrence and relative abundance in the samples[a]					Source[b]	Identification
	ANNA W6	GNW2	GNW3	GNW4	GNW5		
Aliphatic lipids							
n-Octacosan-10-ol	–	–	–	1.3	11.3	Pl	MS
n-Nonacosan-10-ol[c]	100	–	–	–	–	Pl	Franich et al. (1979)
n-Nonacosanediols (4 isomers)[c]	27.8	–	–	–	–	Pl	Franich et al. (1979)
n-Tetradecanoic acid	–	–	40.8	–	–	P1	MS
n-Hexadecanoic acid	–	52.0	23.2	12.4	9.5	Pl	Standard
n-Octadecanoic acid	–	23.8	16.4	12.1	6.6	Pl	MS
n-Docosanoic acid	1.0	9.2	14.0	26.7	2.6	Pl	MS
n-Tricosanoic acid	0.9	–	12.1	4.8	0.6	Pl	MS
n-Tetracosanoic acid	13.7	8.4	–	*100*	2.1	Pl	MS
n-Pentacosanoic acid	0.7	–	–	5.4	0.5	Pl	MS
n-Hexacosanoic acid	5.4	–	–	80	0.7	Pl	MS
Sesquiterpenoids							
Calamenene	0.6	1.2	0.9	–	–	C	Simoneit and Mazurek (1982)
Cadina-1(10),6,8-triene	1.9	6.8	2.2	0.5	0.4	C	Simoneit and Mazurek (1982)
Cadalene	7.9	61.9	47.5	4.9	10.1	C	Standard
1,7-Dimethyl-4-isopropylnaphthalene	2.1	1.0	1.6	0.4	0.6	C	Elias et al. (1997)
Dihydro-*ar*-curcumene	3.9	19.5	0.8	0.3	0.7	C	Ellis et al. (1995)
Diterpenoids							
Abietanes							
Dehydroabietane	0.8	20.8	31.1	0.9	1.1	C	Standard
16,17-Bisnordehydroabietane	–	19.7	2.6	–	0.2		MS
18,19-Bisnorsimonellite	–	4.2	1.2	1.2	0.2	C	MS
Simonellite	0.8	48.2	*100*	25.2	5.0	C	Standard
Retene	0.9	30.5	40.9	8.3	1.5	C	Philp (1985)
1,2,3,4-Tetrahydroretene	–	7.2	2.8	1.5	0.3	C	Philp (1985)
2-Methylretene	–	5.5	3.6	1.6	0.4	C	Bastow et al. (2001)
Dehydroabietic acid	0.6	–	–	0.7	0.9	C	Standard
6,7-Dehydroferruginol	4.3	–	–	–	–	PCA	Enzell and Ryhage (1967)
Ferruginol[c]	5.8	3.5	3.7	5.4	0.7	PCA	Standard
Sugiol[c]	1.4	29.7	88.4	20	6.4	PCA	Standard
7-Acetoxy-6,7-dehydroroyleanone[c]	3.6	–	–	–	–	PCA	Otto et al. (2002)
11,14-Dioxopisiferic acid[c]	7.4	–	–	–	–	PCA	Otto et al. (2002)

(*continued on next page*)

Table 4 (*continued*)

Compound	Occurrence and relative abundance in the samples[a]					Source[b]	Identification
	ANNA W6	GNW2	GNW3	GNW4	GNW5		
Labdanes							
Labdanoic acid	1.5	–	–	–	–	C	Otto and Simoneit (2001)
Communic acid[c]	3.7	–	–	0.6	–	C	Standard
Lambertianic acid[c]	10.4	–	–	1.1	–	C	Standard
Totaranes							
2-Ketototarol[c]	5.8	–	–	3.8	0.6	PCA	MS
Triterpenoids							
24,25-Dinorlupatriene	10.1	–	–	–	–	Pl	Wolff et al. (1989)
Homohopane	4.2	–	6.4	1.3	1.5	B	Philp (1985)
C_{30} hop-17(21)-ene	1.2	–	–	0.8	–	B, Pl	MS
Steroids							
Campesterol	–	–	–	1.2	7.2	Pl	MS
Cholesterol	–	–	15.3	9.5	11.9	Pl, F	Standard
Stigmastene	6.8	–	–	–	–	Pl	Philp (1985)
Stigmastanone	3.3	–	–	–	–	Pl	Wiley MS library
Sitosterol[c]	7.3	12.0	17.6	6.2	*100*	Pl	Standard
Stigmastanol	1.3	–	–	–	–	Pl	Standard
Stigmasta-3,5-dien-7-one	–	–	–	–	6.4	Pl	Rubinstein et al. (1975)
C_{29} 20S-diaster-13(17)-enes	2.4	5.4	4.4	3.4	1.3	Pl	Rubinstein et al. (1975)
C_{29} 20R-diaster-13(17)-enes	1.6	5.3	4.1	3.9	1.6	Pl	MS
20S-1,9-Dimethyldiacholest-13(17)-ene	–	10.2	9.2	–	–	Pl	MS
20R-1,9-Dimethyldiacholest-13(17)-ene	–	10.0	9.5	–	–	Pl	MS
20S-1,1,9-Trimethyldiacholest-13(17)-ene	–	2.1	1.1	–	–	Pl	MS
20R-1,1,9-Trimethyldiacholest-13(17)-ene	–	1.9	1.3	–	–	Pl	MS
Polycyclic aromatic hydrocarbons (PAHs)[d]							
Perylene	5.1	*100*	31.0	27.3	14.2	–	Standard

MS, Mass spectrum interpretation; GNW, Gnaszyn wood.

[a] Abundance relative to major peak.

[b] C = conifers, PCA = podocarpaceae, cupressaceae + araucariaceae, Pl = plants, B = bacteria, F = fauna.

[c] Unaltered natural products (biomolecules).

[d] Only perylene is present as major peak. For other PAHs see Table 3.

OM such as: naphthalene, alkylnaphthalenes, phenanthrene, alkylphenanthrenes, fluoranthene, pyrene and their alkyl-derivatives, benzo[*ghi*]fluoranthene,benz[*a*]anthracene, chrysene + triphenylene, indeno(1,2,3-*cd*)pyrene and benzo[*ghi*]perylene are also present (Table 3). Pyrene and methylpyrenes are usually the most abundant (Fig. 9).

4.3.4. Polar biomarkers

The major polar compounds present in the wood samples are aliphatic lipids, diterpenoids, triterpenoids and steroids (Table 3, Fig. 11). The aliphatic lipids are composed of long-chain (C_{24}–C_{29}) *n*-alkanols and *n*-alkanoic acids which are typical constituents of higher plant waxes (Simoneit, 1978; Baker, 1982; Barthlott et al., 1998). Other major constituents of the wood extracts are diterpenoids of the abietane, labdane, and totarane classes which are known as common constituents of conifer resins (e.g., Otto and Wilde, 2001). Due to the excellent preservation of the organic molecules in the wood, the constituents of the solvent extract can be used as chemosystematic markers, especially as the composition of diterpenoids correlates with patterns observed in extant conifers (Hegnauer, 1962, 1986; Otto and Wilde, 2001). The labdane derivatives and non-phenolic abietanes such as dehydroabietane or dehydroabietic acid occur in most conifer families and are therefore non-specific conifer markers (Otto and Wilde, 2001). In contrast, phenolic abietanes like ferruginol and its derivatives (6,7-dehydroferruginol, sugiol, 11,14-dioxopisiferic acid) are produced only by distinct conifer families (Cupressaceae s. l., Podocarpaceae and Araucariaceae) and can be used as their characteristic biomarkers (Hegnauer, 1962, 1986; Otto and Wilde, 2001). The chemosystematic characteristics of the fossil wood analyzed here are in accordance with the botanical assignment to the Podocarpaceae based on morphological and anatomical characteristics (Marynowski et al., 2007). The presence of the same cadalane type sesquiterpenoids and phenolic abietane type diterpenoids in all wood samples reflects their origin from the same conifer family (Podocarpaceae). Comparable compositions of polar biomarkers have until now only been reported from much younger geological samples, namely fossil plants, resins and coals of Tertiary or Cretaceous age (e.g., Grimalt et al., 1988; Alonso et al., 2000; Otto and Simoneit, 2001; Otto et al., 2002, 2003, 2005; Stefanova et al., 2002).

4.4. $\delta^{18}O$ and $\delta^{13}C$ values

The belemnites in the study area are typically scattered throughout the whole clay sequence, but appear to be completely absent in some levels. During the current investigations, the authors tried to

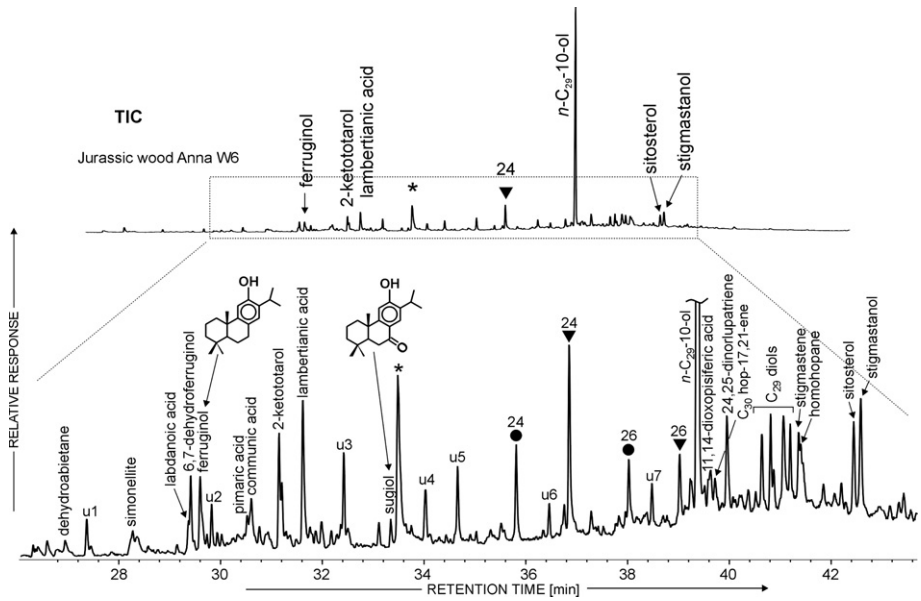

Fig. 11. GC-MS TIC chromatogram of the total solvent extract of a Jurassic *Protopodocarpoxylon* wood sample. ✻ = contamination, ● = *n*-alkanols, ▼ = *n*-alkanoic acids, u1–u7 = unknown compounds. Numbers indicate the number of carbons in the aliphatic lipid series.

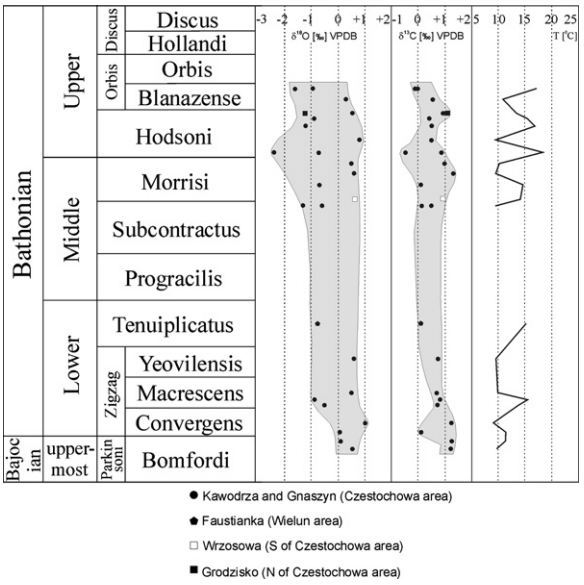

Fig. 12. $\delta^{18}O$ and $\delta^{13}C$ values obtained from belemnite rostra, and the calculated palaeotemperatures during the Late Bajocian-Bathonian in the Polish Basin.

sample the levels belonging to every ammonite (sub)-zone represented in the Polish Jura. Some of them (especially the Progracilis Zone) need further faunal confirmation, because they lack the index ammonite fossils. As dinoflagellate dating has shown (Poulsen, 1998; Barski et al., 2004), the uppermost Bathonian (Discus Zone) is considered to occur in the northern and southern part of the Polish Jura, but as yet has not been confirmed by ammonite fauna.

The $\delta^{18}O$ values of belemnite rostra from the Polish Jura range from −2.4 to +1.03‰ VPDB (Fig. 12). The values are rather uniform, except one value from the lower part of the Hodsoni Zone (−2.4‰). The $\delta^{13}C$ values range from −0.49 to +1.3‰ VPDB, with some positive values near the Bajocian/Bathonian (B/B) boundary and in the upper part of the Middle Bathonian (Fig. 12). Generally, the $\delta^{18}O$ and $\delta^{13}C$ values are comparable to the values obtained from the Upper and Middle Jurassic belemnites of Poland by Wierzbowski (2002, 2004), as well as Wierzbowski and Joachimski (2006).

5. Implications

5.1. Source and sedimentary environment of OM deposition

The diaster-13(17)-enes, identified as one of the major compound groups in most samples, provide supporting data concerning the source and transport of OM. The abundances of individual C_{27}–C_{29} diasterenes differ significantly among samples (Fig. 8). Wood samples contain essentially no diacholest-13(17)-ene (Figs. 7 and 8). In contrast, the distributions of diaster-13(17)-enes in the clays are dependent on sample location in the basin (Fig. 1a); clays from the Polish Lowland contain relatively higher amounts of C_{29}-diaster-13(17)-enes than clays from the Częstochowa Clay Formation, whereas the amounts detected in samples from the Holy Cross Mountains are intermediate (Fig. 8). There are many known exceptions from the generally accepted view that C_{29} sterols are derived solely from higher plants (Peters and Moldowan, 1993). However, taking into account the high concentrations of C_{29}-diaster-13(17)-enes in all wood fragments (Figs. 7 and 8) and uniform distribution of diasterenes in the entire region investigated, it is concluded that C_{29}-diaster-13(17)-enes are mainly of a terrestrial origin in this case (cf. Brassell et al., 1985). If the increase in concentration of the C_{29}-diaster-13(17)-enes indicates an increase of terrestrial input, this terrestrial OM would have originated from an enhanced transport of sediment from the land situated at the northern bank of the basin, that is the Fennoscandian Shield (see Fig. 1a). During the Jurassic, the Fennoscandian Shield was the large land mass which most likely could have provided a greater quantity of terrestrial OM than the southern Bohemian Massif.

The occurrence of high amounts of other biomarkers typical for terrestrial OM in clays, suggests a distinct dominance of OM derived from land plant material. The most abundant of such biomarkers are: cadalene, simonellite and retene, all typical for conifers. Some clays and carbonate concretions contain: calamenene, cadina-1(10),6,8-triene, dihydro-*ar*-curcumene and dehydroabietane, also characteristic for conifers. All the biomarkers mentioned above, as well as other sesqui- and diterpenoids (Tables 3 and 4), were identified from wood fragments that are plentiful in the Middle Jurassic clays between Kraków and Wieluń. The PAH compositions are also similar for clays, concretions and wood fragments; however, a somewhat greater contribution of methyl-derivatives of PAHs (e.g. alkylnaphthalenes and alkylphenanthrenes) is observed in the concretions and clays (Table 3).

Besides the dominance of conifer biomarkers, the sedimentary OM in samples from the southern part of the Polish Mid-European Epicontinental Basin contains fernenes, biomarkers characteristic for ferns. A possible source of fernenes are plants

belonging to Caytoniales, the most common of pteridosperms in the Jurassic (Paull et al., 1998; Zatoń et al., 2006). Although an origin of fernenes from conifers cannot be excluded, because they have been reported from a single species of the Podocarpaceae (Silva et al., 1972), the authors have not found these compounds in any wood sample analysed here.

As mentioned above, the Fennoscandian Shield could have provided more terrestrial OM than the Bohemian Massif, located in the SW (Fig. 1). However, the occurrence of fernenes only in the southern part of the basin (in the Polish Jura, Fig. 8) suggests, that pteridosperm detritus was derived mainly from the nearer Bohemian Massif. Generally, a predominance of terrestrial OM in Middle Jurassic marine sediments may be a result of intensive transport of plant material from land and/or a greater resistance of terrestrial vs. marine OM to bacterial reworking and oxidation processes (Prahl et al., 1997), which influenced the organic matter during transport to post-sedimentation.

Kenig et al. (2004) showed that a large part of the Callovian Oxford Clay Formation (south-central England) was deposited during intermittent euxinia. Hautevelle et al. (2006) also reported euxinia in the Proto-Atlantic, South-Central England and Paris basin at the beginning of the early Callovian. Organic geochemical investigations of the Middle Jurassic epicontinental basin of Poland have not provided any indication that the OM was deposited under conditions of water column anoxia. In fact, in the individual regions, the composition of the Middle Jurassic OM does not appear to have changed significantly through time. The relatively low concentrations of C_{33}–C_{35} homohopanes (Fig. 5), moderate to high Pr/Ph values (Table 1), no compounds characteristic for anoxia and water column stratification (e.g., isorenieratane, aryl isoprenoids or gammacerane) and common benthic fauna and burrows all indicate rather oxic depositional conditions of the OM. During sedimentation, suboxic conditions could have occurred at the sea-bottom due to decay of OM. The decay processes occurred on a greater scale below the sediment-water interface, within the sediment leading to reducing conditions. It is well-known (e.g., Coleman et al., 1993; Sellés-Martínez, 1996) that the origin of carbonate concretions, including those with fossils, is associated with anaerobic decay by sulphate-reducing bacteria during early diagenesis. The concretions studied here contain more $CaCO_3$ than pyrite. Precipitation of $CaCO_3$ predominates in open conditions when diffusion prevails, such as in normal marine systems (Sagemann et al., 1999). Moreover, burrowing organisms may stimulate the anaerobic decay of organic matter. Then the rate of sulphate reduction may be even up to 3 times higher than in sediments without bioturbation (Orr et al., 2003).

5.2. Palaeotemperature estimation of the Middle Jurassic sea-water based on $\delta^{18}O$

Low-Mg calcitic belemnite rostra have been, and still are, widely used to reconstruct the O isotopic composition of past oceans and in palaeotemperature calculations (e.g., Price and Sellwood, 1994, 1997; Podlaha et al., 1998; Niebuhr and Joachimski, 2002; McArthur et al., 2004; Rosales et al., 2004; Wierzbowski, 2004; Fürsich et al., 2005). However, it is unclear whether the observed variations, for a given time interval, of the isotopic ratios detected in belemnite calcite reflect primary differences in the palaeoenvironment or an important fractionation effect (Wefer and Berger, 1991; Niebuhr and Joachimski, 2002). Belemnites are extinct cephalopods, thus the problem of a 'significant effect' on the isotopic values is still not resolved. The O isotope compositions of aragonite shells of modern cephalopods, such as *Sepia* and *Nautilus*, appear to be in isotopic equilibrium with the ambient seawater (Taylor and Ward, 1983; Wefer and Berger, 1991; Landman et al., 1994; Bettencourt and Guerra, 1999). Recently, Dettman et al. (1999) showed that the $\delta^{18}O$ of unionid bivalve shells are also controlled by the temperature and ^{18}O content of the water in which they live. Nonetheless, it is considered (e.g., Price and Sellwood, 1997; Podlaha et al., 1998; Fürsich et al., 2005) that a metabolic fractionation effect has not occurred in belemnites, and these animals most likely precipitated the calcite of their rostra in isotopic equilibrium with the ambient sea-water.

For palaeotemperature calculations, the equation proposed by Anderson and Arthur (1983) was adopted, with a background δ_{water} value for non-glacial seawater of $-1‰$ (ice-free), as has been applied in many prior papers concerning palaeotemperatures of the Jurassic seas (e.g., Price and Sellwood, 1997; Podlaha et al., 1998; Niebuhr and Joachimski, 2002; Rosales et al., 2004; Wierzbowski, 2004; Fürsich et al., 2005). During Bajocian-Bathonian times, the Polish Basin was surrounded by land-masses from which river influx might have resulted in slightly lower sea-water salinity (e.g., Epstein and Mayeda, 1953; Price and Gröcke, 2002). Thus, the

$\delta^{18}O_{water}$ value of −1‰ seems reasonable for palaeotemperature calculations (Rosales et al., 2004). However, if decreased salinity truly occurred, it must have been slight, because of the presence of many stenohaline taxa, such as ammonites, echinoderms or rhynchonellid brachiopods in the basin (e.g., Zatoń and Marynowski, 2004).

The calculated palaeotemperature values are shown in Fig. 12 and the $\delta^{18}O$ values obtained from different guards from the same horizon are presented as an average. The calculated palaeotemperature values range from 8 to 17 °C throughout the section. Only one belemnite gave 22 °C, while another from the same horizon was 15 °C, and the mean value of all samples was 13 °C (Zatoń, 2007). As Rosales et al. (2004) pointed out, in addition to regional variations in the isotopic composition of sea-water, the crucial information in such palaeotemperature interpretations is the habit of the marine organisms. The problem is that belemnites are extinct, so their palaeoecology is still a matter of debate. Some researchers have considered that belemnites had a nectonic mode of life (Seilacher, 1968; Doyle and Macdonald, 1993; Niebuhr and Joachimski, 2002; Rosales et al., 2004; Fürsich et al., 2005), lived in the middle and upper part of the water column (Wilby et al., 2004; Rosales et al., 2004), or had a necto-benthonic mode of life (Anderson et al., 1994; Wierzbowski, 2004).

Taking into account that belemnites may have migrated through the thermocline during their whole life cycle (Rosales et al., 2004), and that their rostra were precipitated all year round, the derived palaeotemperatures will thus reflect an annual average of sea-water temperature throughout the life of the animal (Price and Sellwood, 1997). The best method for closer evaluation of belemnite habitat based on stable isotopes is by also checking the values of co-occurring organisms. Wierzbowski (2002) analysed both belemnites and brachiopods from the Oxfordian of the Polish Jura and obtained similar $\delta^{18}O$ values for both groups. On this basis, he concluded a necto-benthonic mode of life for belemnites, as observed for the present-day *Sepia*. However, Fürsich et al. (2005) analysed both the belemnites and brachiopods from the Middle Jurassic of Kachchh, India and found that belemnites (interpreted as nectonic) gave lower temperatures than benthonic brachiopods. They interpreted this phenomenon as migration of belemnites into the Kachchh Basin from their original cooler environment, the Malagassy Gulf.

Apart from possible seasonal migration through the water column, the belemnites from the uppermost Bajocian-Bathonian may have been necto-bethonic rather than permanently nectonic, living in the upper part of the water column. Support for this assumption can be found in the isotopic data obtained from co-existing ammonites (Zatoń, 2007). The calculated palaeotemperatures of the ammonite shells gave much higher values than for belemnites, ranging from 15 to 22 °C (mean value 19 °C). That may reflect the palaeotemperatures of the upper part of the water column. Thus, the palaeotemperature values obtained from belemnite guards clearly mirror the deeper, thus colder, parts of the basin. Similar, higher values of palaeotemperatures for ammonites and lower for belemnites, were obtained for the Callovian of England by Anderson et al. (1994), as well as recently by Wierzbowski and Joachimski (2006) for the Upper Bajocian-Bathonian of the Polish Jura. Thus, the present results are comparable to those obtained by Wierzbowski and Joachimski (2006), and therefore it is reasonable to state, that the water masses in the epicontinental Polish Basin during the Late Bajocian-Bathonian were thermally stratified.

As mentioned above, the widely scattered values may be due to periodic migration of different individuals through the water column, e.g., caused by search for food or breeding (Doyle and Macdonald, 1993). It is worth noting that Longinelli et al. (2003) using phosphate from the Middle Bathonian (Morrisi Zone) of the Polish Jura, obtained a similar palaeotemperature of around 15 °C.

The large differences in palaeotemperatures obtained for belemnite rostra from the same horizon (15 vs. 22 °C in the Upper Bathonian, lower Hodsoni Zone, and 9–17 °C in the upper Hodsoni Zone) may be due to regional variations in the isotopic composition of sea-water, as mentioned above. Furthermore, small differences in salinity of different areas may be a factor (9 °C was obtained for a belemnite from Gnaszyn, and 17 °C for a specimen from Grodzisko, located several km NW of the Gnaszyn area), or alternatively differences in depth of habitat of *Hibolites* and *Belemnopsis* could contribute (McArthur et al., 2004).

5.3. $\delta^{13}C$ composition

As mentioned above, the $\delta^{13}C$ values of carbonates are low and comparable with those presented by Wierzbowski (2002, 2004) for the Upper Jurassic

of Poland. They are also similar to those reported by Price and Gröcke (2002) for the Falkland Plateau and, as Wierzbowski (2004) concluded, most likely characterize the C isotope composition of the global ocean being similar to that of the Submediterranean Province of Europe. Such uniform $\delta^{13}C$ values, ranging from +1 to −0.5‰, for all belemnites studied may demonstrate similar palaeoenvironmental conditions (Wierzbowski, 2004). Some more positive $\delta^{13}C$ values, especially around the B/B boundary, may indicate an increased burial rate of organic C. It is interesting that at the B/B boundary, Gruszczyński (1998) detected a negative shift in the $\delta^{13}C$ values reaching −4‰ for ammonite shells. Some belemnite samples from the Australo-New Zealand Province showed more positive $\delta^{13}C$ values, around 0‰, but negative $\delta^{18}O$ values, reaching −5‰ (Gruszczyński, 1998). Generally, based on different organisms, at the B/B boundary there is a distinct positive correlation of $\delta^{13}C$ and $\delta^{18}O$, which may indicate global geochemical perturbations (Gruszczyński, 1998). However, here the $\delta^{13}C$ values are positive which may reflect greater TOC accumulation. However, more detailed study, based on larger samples and different groups of organisms, is needed to further clarify the B/B problem in the Middle Jurassic epicontinental basin of Poland.

5.4. Thermal maturity

The OM from the Middle Jurassic basin of Poland is immature. This is indicated by the biomarkers with biological configurations, such as ββ-hopanes, hop-13(18)-enes and hop-17(21)-enes, diaster-13(17)-enes and sterenes. Dehydroabietane and simonellite are additional characteristics for immature OM. Particularly strong evidence for immature OM is the presence of unaltered diterpenoids, such as ferruginol, 6,7-dehydroferruginol and sugiol in *Protopodocarpoxylon* wood samples. Insignificant changes in the thermal maturity of OM in Middle Jurassic deposits are connected with its sedimentary, as well as diagenetic oxidation.

Higher OM maturity in the Middle Jurassic occurs only in the Mid-Polish Trough (Fig. 1a) because of the greatest subsidence of that area and the greatest thickness of younger deposits. Vitrinite reflectance (Ro) values for the Middle Jurassic sediments from there vary between 0.5% and 0.55% for the Krośniewice well, 0.7–0.75% for the Budziszowice well and 0.8–1% for the Zgierz IG-1 well (Poprawa and Grotek, 2004), but samples from that region were not analysed in this study. As discussed here (Tables 1 and 2) and by Bojesen-Koefoed (1996), the remaining sediments of the Middle Jurassic in Poland are characterised by immature OM.

Relatively immature OM was also reported from the Middle Jurassic of south-eastern Poland by Kotarba et al. (2003). However, based on those and the present results (cf., Łukowa-2 well 730.8 m sample, Tables 1 and 2), the maturation of OM from S-E Poland is slightly more advanced than the OM from the Polish Jura and the Holy Cross Mountains.

6. Conclusions

The compositions of the solvent extractable OM from the Middle Jurassic clays of Poland, deposited in the eastern part of the Mid-European Epicontinental Basin, have not changed significantly over time in the various regions. It is characterized by a dominance of terrestrial material. A large amount of terrestrial OM was eroded from the Fennoscandian Shield; however, the potential pteridosperm biomarkers were derived mainly from plants growing close to the Polish Basin, i.e., the Bohemian Massif.

The depositional conditions during OM sedimentation were oxic to suboxic, as indicated by relatively low concentrations of C_{33}–C_{35} homohopanes, moderate to high Pr/Ph values, no compounds characteristic of anoxia and water column stratification, and common fossils of benthic fauna and burrows. The $\delta^{18}O$ data for calcitic rostra of belemnites showed a mean palaeotemperature of 13.1 °C for the Middle Jurassic sea-water of the Polish Basin. That may reflect a rather deeper part of the water column.

The OM from the Middle Jurassic basin is thermally immature. This is based on the presence of biomarkers with biological configurations, such as ββ-hopanes, hop-13(18)-enes, hop-17(21)-enes, diaster-13(17)-enes and sterenes. Wood fragments identified as *Protopodocarpoxylon* contain unaltered, diterpenoids such as ferruginol, 6,7-dehydroferruginol and sugiol, which is particularly strong evidence for immature OM. Moreover, the occurrence of those polar diterpenoids is of relevance, because they are the oldest known biomolecules from conifers detected in geological samples.

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