

ORGANIC MATTER COMPOSITION AND MATURITY OF THE CALLOVIAN (MIDDLE JURASSIC) SEDIMENTS FROM LITHUANIA

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Abstract: In both the terrigenous Papiłé Formation (Lower Callovian) and shallow- to deeper-marine facies of the Papartiné and Skinija formations (Middle and Upper Callovian, respectively), terrestrial organic matter predominates. This is emphasized by the carbon preference values higher than 1 for all samples and in some cases higher than 2, as well as the occurrence of characteristic higher plants biomarkers like cadalene, dehydroabietane, simonellite and retene. Fragments of charcoal found in the samples of the Papiłé Formation indicate wildfires that took place in the early Callovian of Lithuania. Unlike the Callovian of western Europe, in the Middle Callovian of Lithuania there is no evidence of anoxic conditions occurring in the water column. Measured values of huminite reflectance (R_r) for selected samples are in the range of 0.21% to 0.31%, what is characteristic for immature OM. This indicates that investigated deposits during their whole diagenetic history laid nearly on the surface and the thickness of younger cover does not exceed 500 m. This is supported by biomarkers analysis. In the all Callovian samples less thermally stable $\beta\beta$ -hopanes significantly dominated what suggest immature character of the samples.

Keywords: organic matter, biomarkers, depositional environment, charcoal, maturity

1. Introduction

Recent organic matter (OM) studies of the Callovian deposits of western Europe showed interesting implications, like the presence of anoxia in the water column during sedimentation of the Middle Callovian deposits in the Anglo-Paris Basin (Kenig et al., 2004; Hautevelle et al., 2007). On the other side, investigation of the organic matter enclosed in the Callovian carbonate nodules (Marynowski et al. 2008a), as well as associated fossil wood fragments (Marynowski et al. 2008b) from the classic locality of Łuków in eastern Poland, provided new data about diagenesis, molecular composition and sedimentary conditions of the fossil wood and sedimentary organic matter. The Callovian deposits of Łuków were transported from the north by Pleistocene glaciers. It is assumed that originally the deposits were placed at the bottom of the Baltic Sea (Olempska and Błaszyk, 2001), most probably in the environments of Lithuania. Thus, it was tempting to undertake the detailed investigations of the organic matter coming from the Callovian deposits of Lithuania, using the material coming both from outcrops and drill-holes. It is worth noting that this is the first such complex research of the Callovian sedimentary succession of Eastern

Europe based on the organic geochemical and petrographic analyses.

2. Geological background

The Callovian deposits in Lithuania are chronostratigraphically subdivided into three parts: Lower, Middle and Upper Callovian, that are represented by the Papiłé, Papartiné and Skinija formations, respectively.

The Lower Callovian Papiłé Formation, the stratotype of which is located at the town of Papiłé situated in the N part of Lithuania (Fig. 1), consist of yellow, fine-grained sand with grey clay intercalations. In Papiłé the formation attains 1.5 m of thickness. The sandy and black clay deposits, containing pyrite concretions and charred and non-charred wood fragments, are best seen in the quarry at Karpėnai. The presence of intercalations with foraminifers and thin-shelled molluscs may point to brackish, deltaic to fluvial environment with some intermittent marine incursions.

The Middle Callovian is represented by the Papartiné Formation, the stratotype of which also occurs in the main Papiłé section. In the main

Papilė section, the formation comprises 3.4 m of deposits consisting of conglomerate with ammonites in the lower part and fine-grained grey sands with rich benthic fauna in the upper part of the formation. The deposits overly unconformably the Papilė Formation. The deposits of the formation indicate the major marine transgression during which the shallow sea covered the vast area of the Baltic region, the maximum of which occurred during the Late Callovian when muddy deposits of the Skinija Formation have been deposited.

The Upper Callovian Skinija Formation attains 5.5 m of thickness in the main Papilė section. There, the formation consist of sandstones, limestones and black clays in its uppermost part, showing progressive deepening of the marine basin. The Skinija Formation conformably overlies the Papartinė Formation and unconformably the Papilė Forma-

tion, as well as older strata (see Paškevičius, 1997; Šimkevičius, 1998; Satkūnas and Nicius, 2007; Šimkevičius et al., 2003).

3. Material and Methods

3.1. Samples

The samples come from five outcrops at Papilė (the main Papilė section and the Papilė Jurakalnis outcrop), Šaltiškiai, Menčiai and Karpėnai, and five boreholes: Purmaliai-5, Žvelsenai-8, Jurjonai-10, Šaukliai-12 and Sakūčiai-16 (Fig. 1; Tab. 1).

The formations and lithology of the samples are presented in Table 1.

3.2. TOC

The total organic carbon (TOC) and total sulphur (TS) content was determined using Eltra Elemental Analyser model CS530.

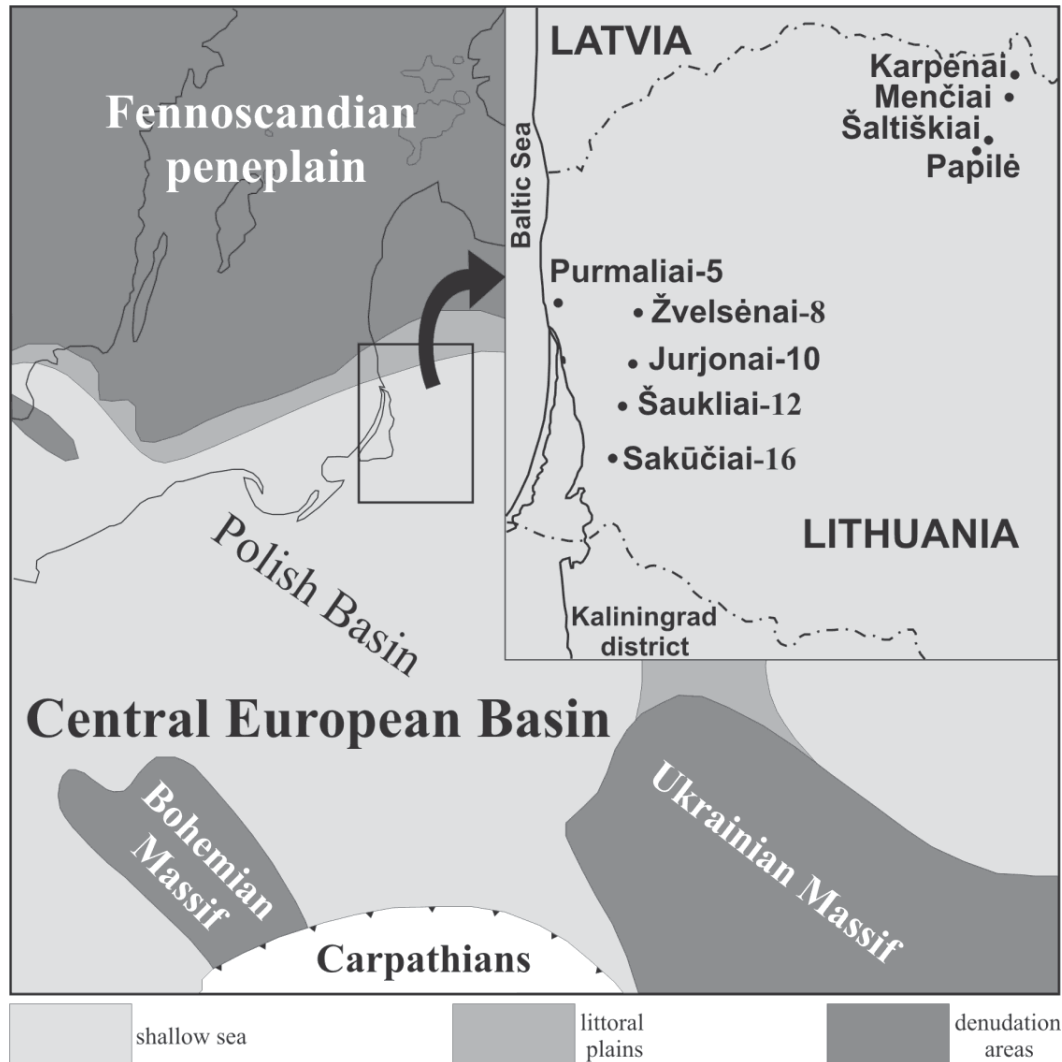


Fig. 1. Study area on the background of palaeogeography during Callovian times (modified after Šimkevičius et al., 2003).

Table 1. Depth and lithology of the samples, bulk geochemical data and percentage yields of fractions and basic molecular parameters based on n-alkanes and isoprenoids distribution. TOC = total organic carbon; TS = total sulphur; Al = aliphatic; Ar = aromatic; Pol = polar. For a formula explanation see Marynowski et al. (2007a).

Samples	Depth [m]	Formation/Lithology	CaCO ₃ [%]	TOC [%]	TS [%]	Fractions			CPI _{Total}	CPI ₍₂₅₋₃₁₎	Pr/Ph	Pr/n-C ₁₇	Ph/n-C ₁₈	(nC ₁₇ +nC ₁₈ +nC ₁₉)/(nC ₂₇ +nC ₂₈ +nC ₂₉)
						Al [%]	Ar [%]	Pol [%]						
Karpenai/ KARIS2	-	Papilė/clay	0	1.49	0.15	28	9	63	2.27	2.16	1.02	0.64	0.74	0.19
Karpenai/ KARICZ	-	Papilė/black clay	0	20.6	0.06	10	2	88	1.72	1.75	0.93	0.93	0.66	0.42
Karpenai/ KARIHU	-	Papilė/brown clay	0	19.5	0.44	1	4	95	1.52	1.66	0.59	0.80	0.76	0.55
Karpenai/ KARSYD	-	Papilė/syderite	59.9	2.28	0.33	9	6	85	1.61	1.98	1.00	0.55	0.55	0.63
Karpenai/ KARPPCC	-	Papilė/sand	0	9.77	0.23	8	4	89	1.83	1.88	0.63	0.80	1.00	0.40
Karpenai/ KARPPC	-	Papilė/sand	0.01	2.26	0.18	10	7	83	1.75	1.85	0.66	0.85	0.93	0.46
Papile profil/ PAP1	-	Skinija/clay	2.88	1.19	0.11	31	8	62	1.23	1.30	0.95	0.89	0.86	2.01
Papile profil/ PAP2	-	Skinija/clay	2.68	1.63	0.18	26	18	56	1.19	1.22	0.98	0.98	1.19	0.68
Papile profil/ PAP3	-	Skinija/clay	4.85	1.66	0.06	28	20	52	1.43	1.63	0.88	0.89	0.84	0.79
Saltiskiai/ SALTIS	-	Papartine/sandy clay	17.45	1.10	1.24	-	-	-	1.40	1.73	0.76	0.74	0.81	2.15
Saltiskiai/ SALTIS2	-	Papartine/sandy clay	12.31	0.81	1.35	-	-	-	-	-	-	-	-	-
Saltiskiai/ SALPAR	-	Papartine/sandy clay	1.17	5.05	3.43	15	5	80	1.55	1.89	0.66	0.84	0.93	2.41
Menciai	-	Skinija/clay	0.22	2.59	1.21	-	-	-	2.28	2.17	0.80	0.75	0.96	0.90
Jurjonai - 10/ Jur 904	90.4	Skinija/clay	1.88	3.91	1.54	9	6	85	1.99	1.87	1.06	0.72	0.72	6.96
Jurjonai - 10/ Jur 958	95.8	Skinija/clay	2.88	4.10	2.61	37	19	44	2.03	1.35	1.50	0.64	0.64	12.48
Purmaliai - 5/ PU 813	81.3	Skinija/clay	0.10	2.70	0.94	32	13	55	2.29	2.41	0.95	0.64	0.69	3.74
Purmaliai - 5/ PU 853	85.3	Skinija/clay	2.51	2.42	0.75	32	13	55	-	-	-	-	-	-
Purmaliai - 5/ PU 915	91.5	Skinija/clay	4.75	1.25	0.72	29	7	64	2.38	2.27	1.05	0.60	0.69	7.93
Purmaliai - 5/ PU 1018	101.8	Papartine/carbonate	35.58	0.92	1.81	-	-	-	-	-	-	-	-	-
Žvelsnai - 8/ Zv 100	100.8	Skinija/clay	0.30	6.84	1.75	46	7	47	2.42	1.54	1.57	0.65	0.78	13.83
Žvelsnai - 8/ Zv 105	105	Skinija/clay	0.63	3.70	2.07	31	17	52	2.84	2.39	1.19	0.64	0.76	6.84

3.3. Extraction and separation

Cleaned and powdered samples were Soxhlet-extracted with dichloromethane for 48 hours in pre-extracted thimbles. Extracts were further separated using pre-washed TLC plates coated with silica gel (Merck, 20 × 20 × 0.25 cm). Prior to separation, the TLC plates were activated at 120°C for 1h.

3.4. 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). Helium was used as

the carrier gas at a constant flow rate of 2.6 ml/min. The GC separation was on 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. The GC-MS interface was kept at 280 °C, while the ion source and the quadrupole analyzer were at 230 and 150 °C, respectively. For more details see Marynowski et al (2007a).

3.5. Quantification and identification of organic compounds

The method was described in details in Marynowski et al (2007a).

3.6. Charcoal observations

Macroscopically visible charcoal fragments were examined using Philips XL 30 Environmental Scanning Electron Microscope (ESEM) in a back-scattered electron (BSE) mode. Clay samples were also treated with a cold HCl (30%) and cold HF (38%) in order to remove the carbonate and silicate minerals.

3.7. Vitrinite reflectance measurements

Freshly polished rock fragments were used in the reflectance analysis. The analyses were carried out using an AXIOPLAN II microscope adapted for reflected white light in oil immersion and a total magnification of 500X. The standards used were 0.42 % and 0.898 % relative reflectance (R_r).

4. Results and discussion

We provide bulk and molecular analysis of the samples from the Lower (Papilė Formation), Middle (Papartinė Formation) and Upper (Skinija Formation) Callovian sediments of Lithuania in order to show the similarities and differences between organic matter of these three sedimentary environments.

Papilė Formation. Samples from the Papilė Formation do not contain carbonate content. The only one exception is the siderite concretion sample (Tab. 1). The values of the total organic carbon content (TOC) are generally high (>2% wt. of the bulk rock) and very high (>9%) in sands, as well as moderate (>1%) to very high (>19%) in clays. The analysed sample of siderite concretion is characterised by up to 2% of TOC (Tab. 1). All the Papilė Formation samples contain small (0.05 – 0.2%) to moderate (0.2 – 0.5%) amounts of total sulphur (Tab. 1) which is generally characteristic for terrestrial deposits. All samples are characterized by significant prevalence of the polar fraction (>60%, Tab. 1) and approximately similar amounts of aliphatic and aromatic fraction.

n-alkanes are present in all extracts and their distribution ranges from C_{13} to C_{36} carbon atoms in the molecule. In their distribution long-chain *n*-alkanes predominates what is reflected by $(nC_{17}+nC_{18}+nC_{19})/(nC_{27}+nC_{28}+nC_{29})$ ratio values

below 1 (Tab. 1). The carbon preference index (CPI_{Total} and $CPI_{(25-31)}$) values are significantly higher than 1 for all samples and in the case of one sand sample, even higher than 2 (Tab. 1). The distribution of high molecular weight *n*-alkanes with an odd carbon number predominance (especially *n*- C_{25} , *n*- C_{27} , *n*- C_{29} , *n*- C_{31}) clearly indicates an input of terrestrial organic matter. The distribution of two common isoprenoids: pristane (Pr) and phytane (Ph) in relation to *n*-alkanes is characterized by relatively low values of Pr/*n*- C_{17} and Ph/*n*- C_{18} (Tab. 1), in most cases not exceeding 1. Generally, the values of the Pr/Ph ratio are diverse (Tab. 1). This is rather untypical for terrestrial OM, where pristane usually strongly dominates over *n*- C_{17} (Tissot and Welte 1984) and typical values of Pr/Ph ratio are significantly higher than 1 (Powell 1988; ten Haven et al., 1987). However, this large differences between Pr/Ph ratio values are characteristic for immature sediments with significant admixture of terrestrial OM (Marynowski et al., 2007a,b; 2008a), even between samples from equivalent facies.

The second important group of compounds from the aliphatic fraction of the Papilė Formation samples are hopanes. The distribution of hopanes in all samples is generally similar. The most abundant are C_{29} , C_{30} or C_{31} , 17 β ,21 β -hopane, depending on the samples (Fig. 2). Extended C_{31} to C_{35} hopanes characterized by a strong predominance of the $C_{31}(22S+22R)$ homologues and significant excess of the less stable *R* epimer (Fig. 2). Hopanes with 34 and 35 carbon atoms in the molecule are not detected in any sample and hopanes with 33 carbon atoms are only present in trace amounts. The $C_{30}\beta\beta/C_{30}\alpha\beta$ and $S/(S+R)$ hopane ratios (Peters et al. 2005), shown in Tab. 2, are high and very low respectively, which is characteristic of the low maturity range. Some differences noted in the case of KARPPCC sample may depend on secondary OM oxidation (e.g. Marynowski et al. 2007a; Marynowski and Wyszomirski 2008).

Interestingly, in comparison to the Upper Bajocian and Bathonian Ore-Bearing Częstochowa Clay Formation samples (Marynowski et al., 2007a), neohop-13(18)-enes are in relatively low concentrations in all Callovian Formations (Fig. 2). As it is known from previous work (Paull et al. 1998), these compounds are products from an acid-catalysed rearrangement conversion of fernenes. The lack of fernenes in the Callovian sediments investigated here and the simultaneously low

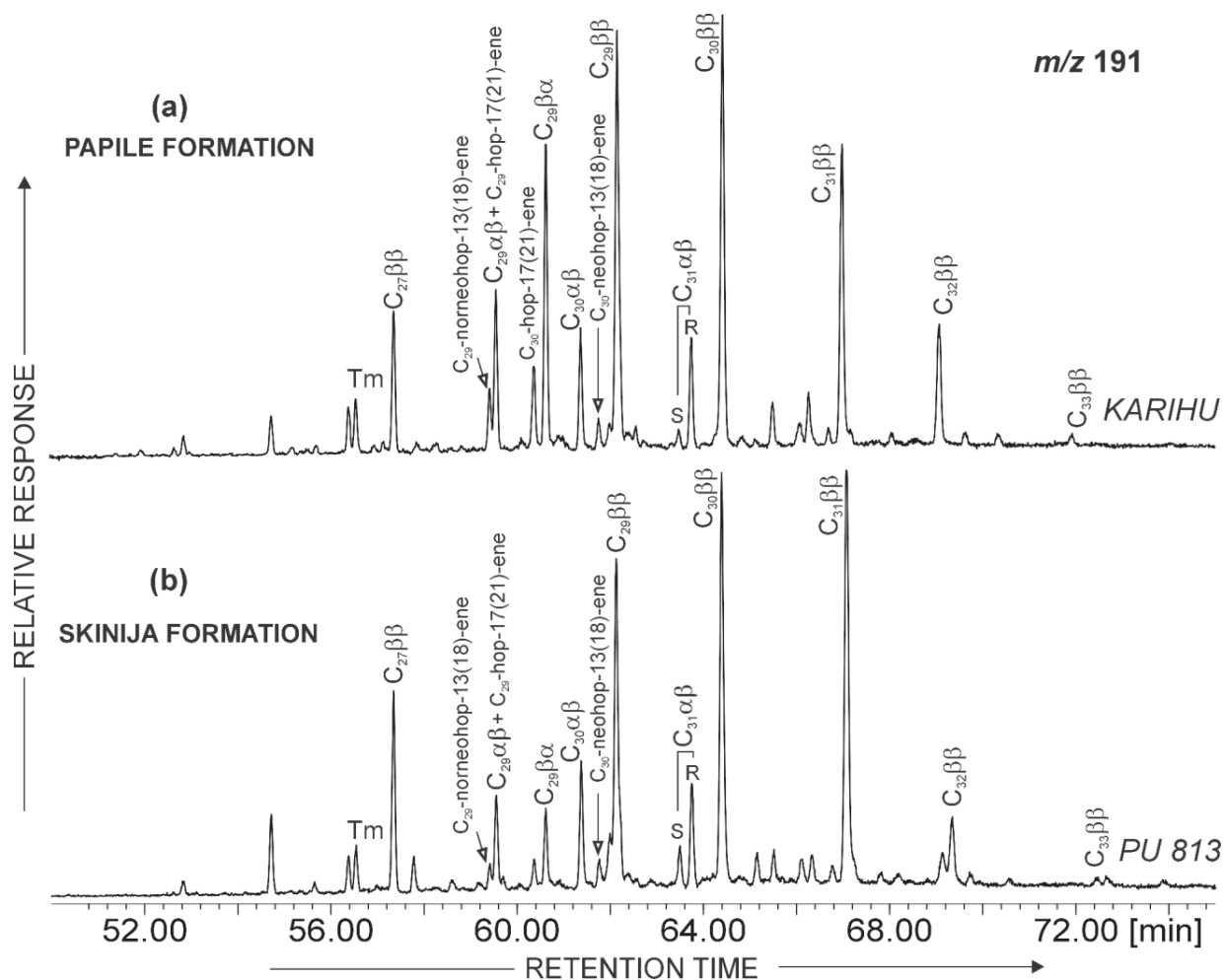


Fig. 2. Partial m/z 191 mass chromatogram showing distribution of hopanes and hopenes from the Papile (a) and Skinija Fm. (b)

concentrations of neohop-13(18)-enes (Fig. 2) confirm co-occurrence of these two group of compounds in the Middle Jurassic sediments (see Marynowski et al. 2007a). Sterenes, steranes and diasteranes are absent or present in the samples as traces only.

Extracts from Papilè Formation samples contain higher plant biomarkers including cadalene, dehydroabietane, simonellite and retene (Fig. 3). What is also interesting, clay samples contain low relative concentrations of sugiol, a natural product terpenoid produced by distinct conifer families (*Cupressaceae* s. l., *Podocarpaceae* and *Araucariaceae*). Such old biomolecules were recently described from the fossil woods coming both from the Bathonian Czestochowa Ore-Bearing Clay Formation and Callovian clay-pit at Łapiguz near Łuków, Poland (Marynowski et al. 2007b; 2008b).

Small, but macroscopically visible charcoal fragments were found in the Karpénai outcrop, solely

in the sand units. These fragments are rounded, and range from ~1 mm to ~3 cm in size. Black clay from Karpénai (sample KARICZ) also contain charcoal, but its fragments are very small (< 0.5 mm) and visible only using ESEM, after removing of the mineral phases.

The charcoal fragments from sands (Fig. 4a) are very well-preserved, with exceptional three-dimensional cellular preservation in many fragments (Fig. 4b). On the contrary, charcoals from black clay samples are small-sized, crushed, with angular and sometimes ragged margins. It may be connected with compaction which in clays much stronger influenced on charcoals.

Huminite reflectance values are homogenous for all samples from the Karpénai quarry ranging from 0.21% to 0.35%. This variation is interpreted as caused by differences in lithology and TOC content. The lowest values were measured for organic-rich fossil wood (only analysed microscopically)

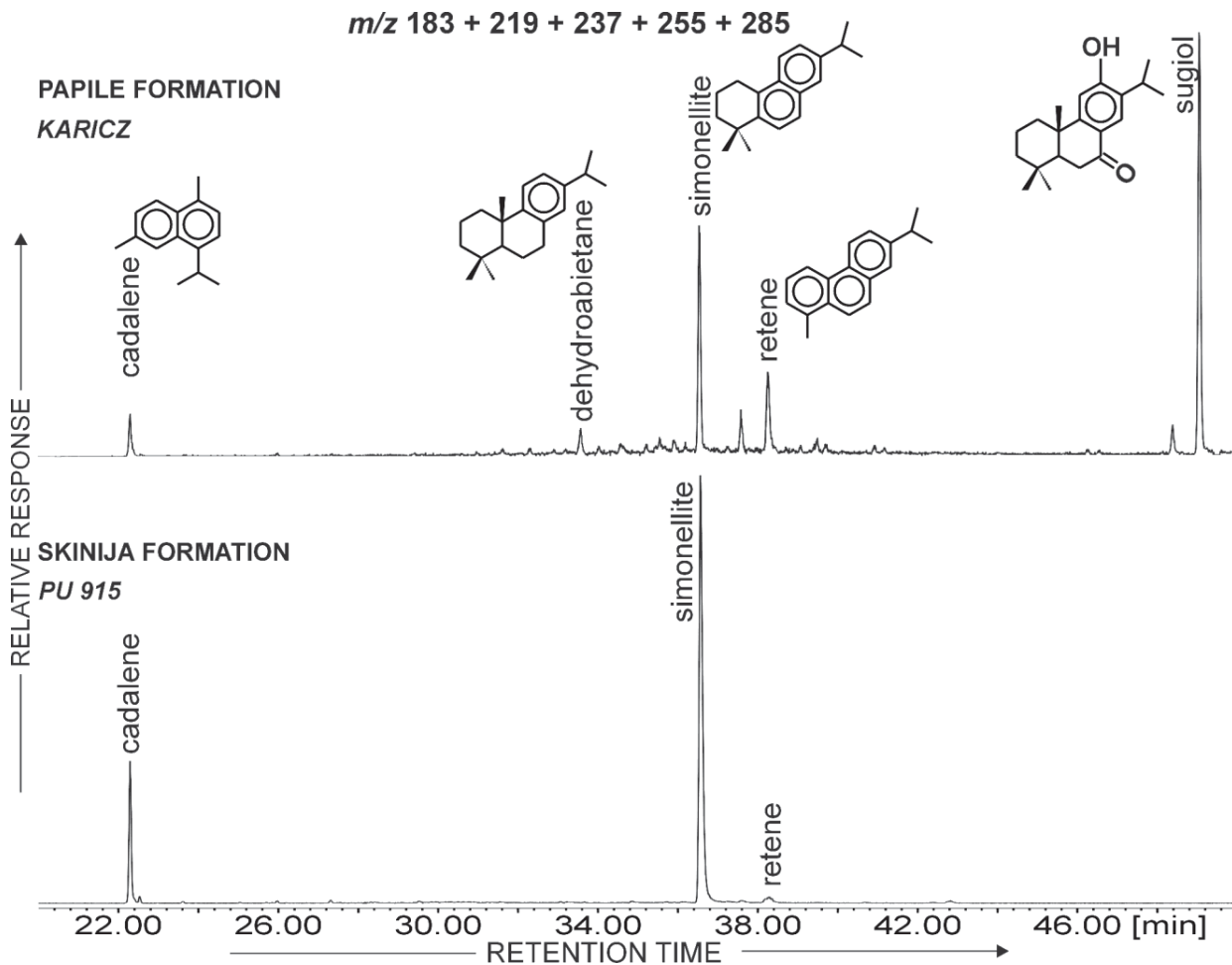


Fig. 3. Summed mass chromatogram for m/z 183+219+237+255+285 showing the distribution of aromatic biomarkers from the Papilè and Skinija Formation.

and black shale samples (KARICZ). The values measured for brown shale (KARIHU) are slightly higher. Nevertheless, all measured huminite reflectance values are very low and are characteristic for brown coal maturity range (e.g. Hunt 1995).

Papartinè and Skinija Formations. The values of the total organic carbon content (TOC) for both Formations are generally high (>2% wt. of the bulk rock) to moderate (0.5 to 2%) (Tab. 1). However, some Papartinè Formation horizons, e.g., sandstones and sands from the Papilè section are OM-poor and due to this they were not analysed here.

The total sulphur content is variable for Papartinè and Skinija Formation which most probably depend on pyrite content and oxidation range (Tab. 1). Generally, sulphur content is much higher than in the Papilè Formation and in some cases may exceed 2-3% (Tab. 1). Similarly to the Papilè Formation, important dominance of the polar fraction is observed in most of the samples (44-85%, Tab. 1).

Distribution of *n*-alkanes differs from that of the Papilè Formation. Short-chain *n*-alkanes predominate in most of the samples, excluding those slightly biodegraded/affected by water washing (Papilè section and Menčiai), what is revealed by values above 1 of the $(nC_{17}+nC_{18}+nC_{19})/(nC_{27}+nC_{28}+nC_{29})$ ratio (Tab. 1). What is important, only outcrop samples are characterized by partial degradation of the short-chain *n*-alkanes, what support the conclusion about biodegradation/water washing affection of these samples.

Despite of the higher concentrations of short-chain *n*-alkanes, between long-chain *n*-alkanes, that with an odd carbon number predominates (especially *n*-C₂₅, *n*-C₂₇, *n*-C₂₉ and *n*-C₃₁) indicating higher plants input. This is emphasized by the carbon preference index (CPI_{Total} and CPI₍₂₅₋₃₁₎) values which are higher than 1 for all samples and in some cases higher than 2 (Tab. 1). The values of Pr/*n*-C₁₇, Ph/*n*-C₁₈ and Pr/Ph (Tab. 1), similar to the case of

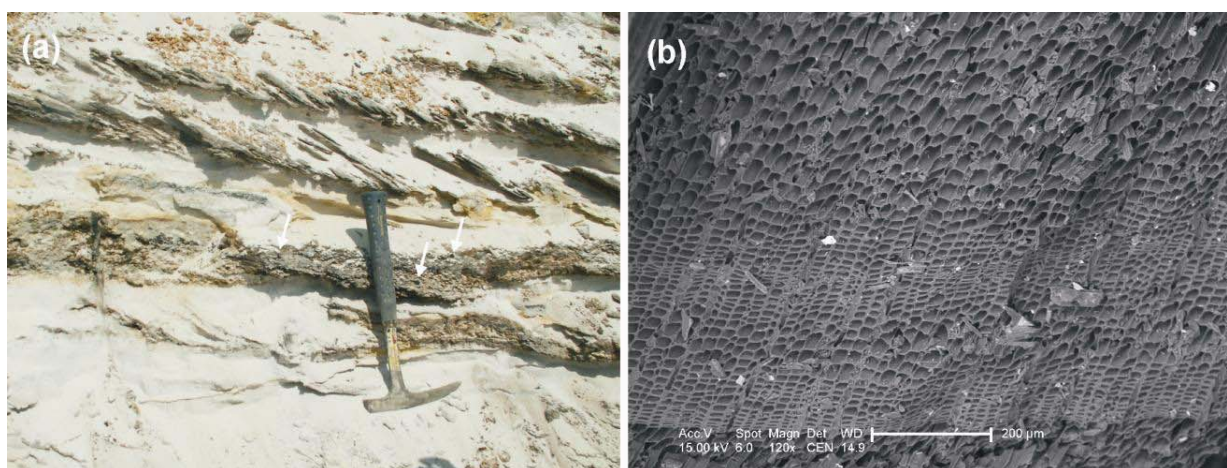


Fig. 4. Fluvial sandstones of the Karpėnai exposure. Arrows shows small charcoal fragments (a) and scanning electron micrograph of tangential section of well preserved charcoal from the Karpėnai exposure (b).

the Papilė Formation are diverse and not indicating (see above).

Distribution of hopanes is similar to that from the Papilė Formation with C_{29} , C_{30} or C_{31} , $17\beta,21\beta$ -hopane domination, depending on the samples (Fig. 2). Also distribution of extended C_{31} to C_{35} hopanes is characterized by a predominance of the $C_{31}(22S+22R)$ homologues while that with 34 and 35 carbon atoms in the molecule are not detected in any of the samples. Moreover, significant excess of the less stable R epimer is observed what is emphasized by $22S/(22S+22R)$ ratio values (Tab. 2; Fig. 2). The $C_{30}\beta\beta/C_{30}\alpha\beta$ hopane ratio shown in Table 2 is high, what confirm the low maturity of the samples from the Papartinė and Skinija formations. Also in the case of the Middle and Upper Callovian samples, sterenes, steranes and diasteranes are absent or present in samples as traces what may suggest intensive bacterial reworking of sedimentary OM.

The aromatic higher plant biomarkers like: cadalene, dehydroabietane, simonellite and retene were identified in both the Papartinė and Skinija formations, but natural product terpenoids like sugiol were not found. The ratios of phenanthrene to simonellite, retene and cadalene are calculated and showed in table 2.

4.1. Organic matter maturity and oxidation effects

All the analysed samples are characterized by a prevalence of the polar fraction (Tab. 1), what is generally characteristic for immature organic matter (Tissot and Welte 1984). For comparison, similar polar fraction predominance is characteristic for the immature Callovian-Oxfordian sedimentary se-

ries of the Paris Basin, reported recently by Hautevelle et al. (2007). Measured values of huminite reflectance (R_f) are in the range of 0.21% to 0.35%, which is characteristic for immature OM (Tissot and Welte 1984). In our opinion, the huminite reflectance values c. 0.2% measured on the wood fragments, most probably correspond to the real stage of thermal maturity, what in turn correspond to very low mature brown coals of the xylite-type. If it does, the deposits investigated during their whole diagenetic history laid nearly to the surface (thickness of the younger sequences do not exceed 200-300 m). This is supported by a very low calculated thickness of the post-Callovian deposits, that do not exceed 500 m even in SW part of Lithuania, where thickness of younger strata was greatest (Marek and Grigelis, 1998).

The major factors controlling the distribution of hopanes are thermal maturity, oxidation and source of organic matter. In all Callovian samples less thermally stable $\beta\beta$ -hopanes significantly dominated which suggest immature character of the samples (Peters et al., 2005). Some of the samples, especially sandstones and sands are slightly oxidised but changes of the extract composition are not very important. General conclusion is that all these Callovian sequences have never been buried by more than 500 meters of younger sediments.

4.2. Depositional environment and palaeogeographic implications

In the Lower to Upper Callovian samples investigated in this study, there is no evidence of anoxic (euxinic) conditions prevailing in the water column. Careful examination of the samples has not revealed isorenieratane, aryl isoprenoids or other

isorenieratane derivatives, biomarkers of photic zone anoxia in the Callovian Lithuanian formations. Moreover, no other compounds like gammacerane or high concentrations of C₃₃, C₃₄ or C₃₅ homohopanes, characteristic for stratification of water column or bottom waters anoxia (Sinninghe Damsté et al. 1995; Peters et al. 2005), have been found.

thors' pers. observ.; see also: Paškevičius 1997; Satkūnas and Nicius 2007), a fact that exclude the possibility of predominance of anoxic conditions in the environment during this period.

In both the terrigenous Papilė Formation and shallow- to deeper-marine facies of the Papartinė and Skinija formations, terrestrial organic matter with

Table 2. Molecular parameters based on *n*-alkanes, hopanes and aromatic biomarkers distribution.

Samples	Depth [m]	LMWn-a/(n-a+hop)	HMWn-a/(n-a+hop)	C ₃₀ ββ/C ₃₀ αβ	22S/(22S+22R)	Ph/(Ph+Sim)	Ph/(Ph+Ret)	Ph/(Ph+Cad)
Papilė Formation								
Karpenai KARIS2	-	0.17	0.57	3.94	0.14	0.92	0.85	0.89
Karpenai KARICZ	-	0.56	0.32	2.56	0.28	0.80	0.90	0.73
Karpenai KARIHU	-	0.16	0.27	4.08	0.16	1.00	0.97	0.92
Karpenai KARSYD	-	0.14	0.34	5.42	0.17	0.69	0.80	0.68
Karpenai KARPPCC	-	0.70	0.80	1.28	0.41	0.91	0.96	0.73
Karpenai KARPPC	-	0.36	0.49	3.88	0.16	0.92	0.85	0.89
Papartine Formation								
Saltiskiai SALTIS	-	0.70	0.50	2.60	0.24	0.59	0.91	0.93
Saltiskiai SALPAR	-	0.63	0.42	1.89	0.39	0.31	0.96	0.98
Skinija Formation								
Papile profil PAP1	-	0.48	0.61	2.07	0.37	1.00	0.57	0.98
Papile profil PAP2	-	0.40	0.49	2.85	0.19	0.84	0.53	0.96
Papile profil PAP3	-	0.45	0.28	4.50	0.20	0.95	1.00	0.95
Menciai	-	0.76	0.28	5.90	0.22	1.00	0.97	0.94
Jurjonai - 10	90.4	0.61	0.18	7.07	0.16	0.92	0.93	0.97
Jurjonai - 10	95.8	0.67	0.43	2.18	0.38	0.97	0.97	0.87
Purmaliai - 5	81.3	0.89	0.60	4.09	0.27	0.97	0.97	0.86
Purmaliai - 5	91.5	0.83	0.57	3.14	0.29	0.70	0.98	0.89
Žvelsenai - 8	100.8	0.81	0.45	1.29	0.47	1.00	0.99	0.90
Žvelsenai - 8	105	0.88	0.57	4.25	0.27	0.97	0.99	0.91

LMWn-a/(n-a+hop) – low molecular weight *n*-alkanes to hopanes ratio: (*n*-C₁₇ + *n*-C₁₈ + *n*-C₁₉)/ (*n*-C₁₇ + *n*-C₁₈ + *n*-C₁₉ + C₂₉ββ-norhopane + C₃₀ββ-hopane + C₃₁ββ-homohopane), **HMWn-a/(n-a+hop)** - high molecular weight *n*-alkanes to hopanes ratio: (*n*-C₂₅ + *n*-C₂₇ + *n*-C₂₉)/ (*n*-C₂₅ + *n*-C₂₇ + *n*-C₂₉ + C₂₉ββ-norhopane + C₃₀ββ-hopane + C₃₁ββ-homohopane), **C₃₀ββ/C₃₀αβ** – C₃₀-17β, 21β-hopane / C₃₀-17α, 21β-hopane ratio, **22S/(22S+22R)** - C₃₁-17α, 21β-homohopane homologs ratio, **Ph/(Ph+Sim)** – phenanthrene to (phenanthrene + simonellite) ratio, **Ph/(Ph+Ret)** – phenanthrene to (phenanthrene + retene) ratio, **Ph/(Ph+Cad)** – phenanthrene to (phenanthrene + cadalene) ratio.

Recently, Kenig et al. (2004) and Hautevelle et al. (2007) described the evidences of water column anoxia in the Middle Callovian of England (Peterborough Member of the Oxford Clay Formation) and France, respectively. Hautevelle et al. (2007) mentioned that such anoxic conditions occurred during a relatively brief event at the beginning of the Middle Callovian. In the Lithuanian territory, this was a time-period when the sedimentary conditions changed from terrigenous (deposits of the Papilė Formation) to shallow marine due to a sea transgression (Šimkevičius et al. 2003). The deposits representing the Middle Callovian (Papartinė Formation) consist mainly of organic-poor sands and sandstones with a rich faunal content (e.g., ammonites, belemnites, bivalves, gastropods, various echinoderms, serpulids and brachiopods; au-

odd-over-even predominance of the long-chain *n*-alkanes, and terrestrial biomarkers like cadalene, simonellite or retene (Fig. 3; Tab. 2) occur. However, in the marine Papartinė and Skinija formations, the short-chain *n*-alkanes dominated over long-chain ones which may indicate a marine input. The intensive transport of terrestrial OM into the Middle Jurassic epicontinental seas is not only characteristic for the Central European Basin (Marynowski et al., 2007a; 2008a and this study). The terrestrial character of OM has been recently confirmed for the Callovian Staffin Bay and Staffin Shale Formations (Belemnite Sands, Dunas Shale and Dunas Clay Members), based on the Rock Eval analysis (Nunn et al., 2009). Also Hautevelle et al., (2007) state that OM from the Callovian deposits of the Paris Basin are a mixture of autochthon-

ous marine biomass and allochthonous OM initially synthesized by terrestrial plants.

To the best of our knowledge, reports on charcoals from the Callovian sedimentary rocks with their detail microscopic documentation and description have not been published, so far. However, some reports mentioned an inertinite content in the Callovian coals (see e.g. Petersen and Rosenberg 1998 and summary in Diessel 2009), which is treated by some authors as wildfire evidences (e.g. Scott and Glasspool, 2007).

The most recent revised GEOCARBSULF model assumed that O₂ values for the Middle Jurassic were not lower than 15 percent (Berner 2009) which, according to Belcher and McElwain (2008), indicate that combustion could have occurred at that time. However, relatively low O₂ values may indicate rather scarce and low temperature wildfires (Marynowski and Zatoń in preparation).

5. Conclusions

Both in the terrigenous Lower Callovian Papilė Formation and shallow- to deeper-marine facies of the Papartinė and Skinija formations respectively, a significant compound of extracts are of terrestrial origin. In the case of the Papilė Formation, apart of typical land-derived biomarkers as cadalene, dehydroabietane, simonellite and retene, natural product terpenoid - sugiol have been detected in clay sediments. The occurrence of such biomolecules in the Middle Jurassic clays is reported for the first time and most possibly is connected with a presence of small wood debris in the investigated clays. Moreover, clays and sands of the Papilė Formation are characterised by the presence of charcoal fragments what indicate evidences of wildfires taking place in the territory of Lithuania during the early Callovian times.

Unlike the Callovian of western Europe, including the Peterborough Member of the Oxford Clay Formation (UK) and eastern part of the Paris Basin, in the Middle Callovian section of Lithuania there is no evidence of anoxic (euxinic) conditions occurring in the water column.

Measured values of huminite reflectance are in the range of 0.21% to 0.31% which together with domination of hopanes with biological $\beta\beta$ configuration indicate that OM from all the Callovian samples of Lithuania is immature and the thickness of younger strata never exceeded ~500 meters.

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