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Organic matter from the Callovian (Middle Jurassic) deposits of Lithuania: Compositions, sources and depositional environments

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ABSTRACT

This study presents the first organic geochemical and petrographical investigation of the Callovian deposits of the eastern part of the Central European Basin. It is shown that in both the terrigenous Papilé Formation (Lower Callovian) and shallow- to deeper-marine facies of the Papartine and Skinija formations (Middle and Upper Callovian, respectively), terrestrial organic matter predominates. This is reflected by the carbon preference index values higher than 1.2 for all samples and in some cases higher than 2, as well as the occurrence of characteristic higher plant biomarkers like cadalene, dehydroabietane, simonellite and retene. Moreover, in the case of the Papile Formation, sugiol - a natural product terpenoid produced by distinct conifer families, has been detected in clay sediments. The occurrence of such a biomolecule in the Middle Jurassic clays is reported for the first time. Its occurrence is probably connected with the presence of small wood debris in the clay sediments. In samples of the Papile Formation, charcoal fragments co-occurring with unsubstituted polycyclic aromatic hydrocarbons were detected, indicating that wildfires took place during the Early Callovian of Lithuania and/or neighbouring areas. In the Middle and Upper marine Callovian sediments of Lithuania there is no evidence of anoxic conditions occurring in the water column. However, periodic anoxic or strongly dysoxic episodes may have occurred, most probably below the photic zone, during the deepest phase of the Late Callovian transgression, as is evidenced from pyrite framboid diameter distribution and general impoverishment of benthic fauna. Huminite reflectance (R_r) values for the investigated area are in the range of 0.21–0.31%, suggesting the occurrence of immature organic matter. Such values indicate that these investigated deposits were close to the surface during their whole diagenetic history, and the thickness of younger cover did not exceed ca. 500 m. This is also supported by a biomarker analysis in which less thermally stable $\beta\beta$ hopanes and hopenes significantly dominated.

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1. Introduction

Investigation of the organic matter enclosed in Callovian carbonate nodules (Marynowski et al., 2008a), as well as associated fossil wood fragments (Marynowski et al., 2008b) from the famous, fossil-rich locality of Łuków in eastern Poland (e.g., Makowski, 1952; Olempska and Błaszyk, 2001; see also Salamon and Zatoń (2008) for a review) provided new data about diagenesis, sedimentary conditions and molecular composition of the 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 at the bottom of the Baltic Sea (see Olempska and Błaszyk, 2001), most probably in the environs of Lithuania (Graniczny et al., 2007). Thus, it was tempting to undertake detailed investigations of the organic matter from the Callovian deposits of Lithuania, using material from the outcrops and drill-holes. In order to retrieve a full picture of the organic

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matter type and sedimentary conditions, the whole Lower to Upper Callovian sequence at Lithuania, showing a clear facies change from terrigenous to deeper marine, was investigated.

On the other hand, the Callovian deposits are important Jurassic components in the areas of western Europe from palaeoenvironmental and palaeoclimatic points of view. Investigation of the organic matter has shown 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, 2005; Hautevelle et al., 2007), and the isotopic studies of Dromart et al. (2003a,b) even implicated the onset of an ice-age during the Late Callovian–Early Oxfordian even though the Late Callovian is considered to have witnessed a global sea-level rise (e.g., Norris and Hallam, 1995; Wierzbowski et al., 2009).

For this reason, it would be useful to compare the Callovian depositional environments of the eastern European Basin to those of the Anglo-Paris Basin. It is worth noting that this is the first such complex research of the Callovian sedimentary succession of Eastern Europe based on organic geochemical and petrographic analyses.

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2. Geological background

During the Middle and Late Jurassic, Lithuania was part of the Lithuanian–Polish Syneclise which, situated within the East European Platform, was a tectonically quiet area (see Šimkevičius et al., 2003). Palaeogeographically, the studied area constituted a wide bay separating the Fennoscandian plains to the north from the Central European Basin to the south (see Ziegler, 1990; Šimkevičius et al., 2003; Fig. 1 herein). Generally, the Lower to Middle Jurassic deposits of the Lithuanian–Polish Syneclise is incomplete and mainly non-marine, while the Middle to Upper Jurassic sediments are more complete and developed as marine facies. Based upon analyses of clay minerals, Šimkevičius et al. (2003) deduced that the sediment dispersal directions were mainly from the north and sometimes from the SE.

On the basis of the distribution, thickness, facies, and completeness of the rock record, two facies zones have been distinguished within the Lithuanian–Polish Syneclise: South-Western and North-Eastern zones (see Paškevičius, 1997). The South-Western zone, spreading from South-Western Lithuania to North-Eastern Poland, embraces the central part of the Lithuanian–Polish Syneclise. This Jurassic sedimentary record, starting from the Lower Jurassic (Pliensbachian/Toarcian) up to the Upper Jurassic (Tithonian), is the most complete in this zone; however, gaps embracing parts of the Lower, Middle and uppermost Upper Jurassic exist. The North-Eastern Zone spreads across the whole of western Lithuania, but some erosional patches occur in NW Lithuania and SW Latvia. The succession is incomplete, being represented only by the Lower to Middle Callovian and essentially Oxfordian deposits.

The Callovian deposits investigated here were sampled from five outcrops at four sites and five boreholes, all located in the North-Eastern facies zone (Fig. 1). The outcrops are located in the Venta River Valley and its close neighbourhood, and the main point is the Papilė locality where, on the basis of its Jurassic geological values, the Venta Regional Park was established (see Satkūnas and Nicius, 2006, 2007). As the Papilė section (called the main Papilė section thereafter) exposes the Lower to Upper Callovian sequence (Satkūnas and Nicius, 2006, 2007), it is here considered as the best reference point for other localities studied.

The Callovian stage in Lithuania is divided into Lower, Middle and Upper substages. The Lower Callovian is represented by the Papilė Formation, the stratotype of which is located at the town of Papilė (see Paškevičius, 1997; Šimkevičius, 1998). Although in the main Papilė section only 1.5 m of the formation is currently visible (Satkūnas and Nicius, 2006, 2007), its entire thickness is here 13.05 m (see Paškevičius, 1997). The exposed deposits consist of yellow, fine-grained sand with grey clay intercalations (Satkūnas and Nicius, 2006, 2007). The sandy and black clay deposits, containing pyrite concretions and wood fragments, are best seen in the quarry at Karpėnai, and the presence of beds with foraminifera and thin-shelled molluscs (Paškevičius, 1997) may point to a brackish, deltaic to fluvial environment with intermittent marine incursions (see Paškevičius, 1997; Šimkevičius et al., 2003). Recently, Salamon (2008) described crinoids as allegedly coming from the Papilė Formation of the main Papilė section. In fact, however, the material came from the lower part of the Middle Callovian. The Papilė Formation unconformably overlies Lower Triassic, Permian and Devonian rocks (Paškevičius, 1997).

The Middle Callovian is represented by the Papartine Formation, the stratotype of which also occurs in the main Papile section (see Paškevičius, 1997; Šimkevičius, 1998). 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 (Satkūnas and Nicius, 2006, 2007, pers. observ.). To the SW the deposits of this formation may attain 20 m in thickness (Paškevičius, 1997). The deposits unconformably overly the Papile Formation. The age of the formation was established on the basis of ammonoid fauna (see Paškevičius, 1997; Šimkevičius, 1998; Satkūnas and Nicius, 2006, 2007). The deposits of the formation indicate a major marine transgression during which a 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 were deposited (Šimkevičius et al., 2003).

The Upper Callovian Skinija Formation is 5.5 m thick in the main Papilė section, but in its parastratotype (Lesnoye-50 borehole) it is ca. 54 m thick (see Šimkevičius, 1998). In the main Papilė section it consist of sandstones, limestones and black clays in its uppermost part (see Satkūnas and Nicius, 2006, 2007, pers. observ.) showing progressive deepening of the marine basin (Paškevičius, 1997; Šimkevičius et al., 2003). The Skinija Formation conformably overlies the Papartinė Formation and is unconformable on the Papilė Formation, as well as older strata (see Paškevičius, 1997). The formation was dated as Upper Callovian on the basis of ammonites as well as foraminifera (see Paškevičius, 1997; Šimkevičius et al., 2003; Satkūnas and Nicius, 2006, 2007).

3. Material and methods

3.1. Material and its provenance

In total 29 samples were used in the present investigation. 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, Žvelsėnai-8, Jurjonai-10, Šaukliai-12 and Sakūčiai-16 (Fig. 1).



Fig. 1. Palaeogeographical map of the Callovian of Northern Europe and position of the studied area (modified after Šimkevičius et al., 2003).

The samples from the main Papilė section, Papilė Jurakalnis and Menčiai come from the Upper Callovian Skinija Formation and consist of black clays. The samples from Šaltiškiai represent Middle Callovian sandy clays of the Papartinė Formation. From Karpėnai the samples were derived from sand and brown and black clays, as well as from siderite, and all represent the Lower Callovian Papilė Formation.

The samples taken from the boreholes consist of carbonaceous sandstones of the Middle Callovian Papartinė Formation (Purmaliai-5 borehole) and clays of the Upper Callovian Skinija Formation (Purmaliai-5, Jurjonai-10 and Žvelsėnai-8 boreholes). All core samples from the Upper Callovian Skinija Formation are represented by black to grey clays and sandy clays. One organic-poor carbonate sandstone sample from the Purmaliai-5 borehole represents the Middle Callovian (Papartinė Formation) (Table 1).

For the purpose of biomarker analysis, 24 samples were investigated (Table 2).

3.2. Instrumental geochemical analysis

3.2.1. TOC

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

3.2.2. Extraction and separation

Cleaned and powdered samples were Soxhlet-extracted with dichloromethane for 48 h in pre-extracted thimbles. Extracts were further separated using pre-washed TLC plates coated with silica gel (Merck, $20 \times 20 \times 0.25$ cm). Prior to separation, the TLC plates were activated at 120 °C for 1 h. Plates were then loaded with the *n*-hexane soluble fraction and developed with *n*-hexane. Aliphatic hydrocarbon (R_f 0.4–1.0), aromatic hydrocarbon (R_f 0.05–0.4) and polar compound (R_f 0.0–0.05) fractions were eluted and separated with dichloromethane. The aliphatic and aromatic fractions of all samples were analysed in further detail by gas chromatography–mass spectrometry (GC–MS).

3.2.3. GC-MS

The GC–MS analyses were performed with an Agilent 6890 Series Gas Chromatograph interfaced to an Agilent 5973 Network Mass Selective Detector and Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). A 0.5 μ L 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% poly-dimethylsiloxane, 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 ($60 \text{ m} \times 0.25 \text{ mm}$ i.d., $0.25 \mu \text{m}$ film thickness) coated with a chemically bonded phase (35% phenyl-meth-ylpolysiloxane). 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 analyser were at 230 and 150 °C, respectively. Mass spectra were recorded at m/z 45–550 (0–40 min) and m/z 50–700 (above 40 min). The mass spectrometer was operated in the electron impact mode (ionization energy: 70 eV).

3.2.4. Quantification and identification

An Agilent Technologies Enhanced ChemStation (G1701CA ver.C.00.00) and the Wiley Registry of Mass Spectral Data (8th ed.) software were used for data collection and mass spectra

Table 1

Depth and lithology of the samples, bulk geochemical data and percentage yields of fractions. TOC = total organic carbon; TS = total sulfur; Al = aliphatic; Ar = aromatic; Pol = polar.

Samples/abbreviation	Depth (m)	Formation/lithology	CaCO ₃ (%)	TOC (%)	TS (%)	Fractions		
						Al (%)	Ar (%)	Pol (%)
Outcrops								
Karpenai/KARIS2	-	Papilė/clay	0	1.49	0.15	28	9	63
Karpenai/KARICZ	-	Papilė/black clay	0	20.6	0.06	10	2	88
Karpenai/KARIHU	-	Papilė/brown clay	0	19.5	0.44	1	4	95
Karpenai/KARSYD	-	Papilė/siderite	59.9	2.28	0.33	9	6	85
Karpenai/KARPPCC	-	Papilė/sand	0	9.77	0.23	8	4	89
Karpenai/KARPPC	-	Papilė/sand	0.01	2.26	0.18	10	7	83
Papilė Jurakalnis/PAPJUR	-	Skinija/clay	2.75	1.60	4.23	35	13	52
Papilė/PAP1	-	Skinija/clay	2.88	1.19	0.11	31	8	62
Papilė/PAP2	-	Skinija/clay	2.68	1.63	0.18	26	18	56
Papilė/PAP3	-	Skinija/clay	4.85	1.66	0.06	28	20	52
Saltiskiai/SALTIS	-	Papartinė/sandy clay	17.45	1.10	1.24	-	-	-
Saltiskiai/SALTIS2	-	Papartinė/sandy clay	12.31	0.81	1.35	-	-	-
Saltiskiai/SALPAR	-	Papartinė/sandy clay	1.17	5.05	3.43	15	5	80
Menciai/MENC	-	Skinija/clay	0.22	2.59	1.21	-	-	-
Boreholes								
Jurjonai-10/JUR 828	82.8	Skinija/clay	12.75	2.94	1.61	-	-	-
Jurjonai-10/JUR 877	87.7	Skinija/clay	1.38	2.10	2.16	-	-	-
Jurjonai-10/JUR 904	90.4	Skinija/clay	1.88	3.91	1.54	9	6	85
Jurjonai-10/JUR 958	95.8	Skinija/clay	2.88	4.10	2.61	37	19	44
Purmaliai-5/PU 813	81.3	Skinija/clay	0.10	2.70	0.94	32	13	55
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
Purmaliai-5/PU 932	93.2	Skinija/clay	4.88	1.18	0.72	38	16	47
Purmaliai-5/PU 1018	101.8	Papartine/carbonate sandstone	35.58	0.92	1.81	-	-	-
Žvelsnai-8/ZV 100	100.8	Skinija/clay	0.30	6.84	1.75	46	7	47
Žvelsnai-8/ZV 105	105	Skinija/clay	0.63	3.70	2.07	31	17	52
Žvelsnai-8/ZV 114	114.4	Skinija/clay	2.13	1.78	0.85	26	9	65
Žvelsnai-8/ZV 118	117.6	Skinija/clay	1.63	1.30	0.64	34	18	48

Table 2

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Basic molecular parameters based on *n*-alkanes and isoprenoids distribution.

Samples/abbreviation	Depth (m)	CPI _{Total}	CPI(25-31)	Pr/Ph	$Pr/n-C_{17}$	Ph/n-C ₁₈	$(n-C_{17} + n-C_{18} + n-C_{19})/(n-C_{27} + n-C_{28} + n-C_{29})$
Papilė Formation							
Karpenai/KARIS2	-	2.27	2.16	1.02	0.64	0.74	0.19
Karpenai/KARICZ	-	1.72	1.75	0.93	0.93	0.66	0.42
Karpenai/KARIHU	-	1.52	1.66	0.59	0.80	0.76	0.55
Karpenai/KARSYD	-	1.61	1.98	1.00	0.55	0.55	0.63
Karpenai/KARPPCC	-	1.83	1.88	0.63	0.80	1.00	0.40
Karpenai/KARPPC	-	1.75	1.85	0.66	0.85	0.93	0.46
Papartine Formation							
Saltiskiai/SALTIS	-	1.40	1.73	0.76	0.74	0.81	2.15
Saltiskiai/SALPAR	-	1.55	1.89	0.66	0.84	0.93	2.41
Skinija Formation							
Papilė Jurakalnis/PAPJUR	-	1.29	1.38	0.94	0.89	0.88	1.49
Papilė/PAP1	-	1.23	1.30	0.95	0.89	0.86	2.01
Papilė/PAP2	-	1.19	1.22	0.98	0.98	1.19	0.68
Papilė/PAP3	-	1.43	1.63	0.88	0.89	0.84	0.79
Menciai/MENC	-	2.28	2.17	0.80	0.75	0.96	0.90
Jurjonai-10	82.8	1.65	1.20	0.70	0.60	0.71	9.71
Jurjonai-10	87.7	1.60	1.11	0.71	0.62	0.68	2.98
Jurjonai-10	90.4	1.99	1.87	1.06	0.72	0.72	6.96
Jurjonai-10	95.8	2.03	1.35	1.50	0.64	0.64	12.48
Purmaliai-5	81.3	2.29	2.41	0.95	0.64	0.69	3.74
Purmaliai-5	91.5	2.38	2.27	1.05	0.60	0.69	7.93
Purmaliai-5	93.2	2.29	1.99	1.15	0.62	0.73	5.07
Žvelsnai-8	100.8	2.42	1.54	1.57	0.65	0.78	13.83
Žvelsnai-8	105	2.84	2.39	1.19	0.64	0.76	6.84
Žvelsnai-8	114.4	2.80	2.27	1.23	0.63	0.78	7.15
Žvelsnai-8	117.6	2.18	2.11	1.04	0.58	0.78	7.84

 $CPI_{(Total)} - carbon preference index 0.5[\sum (C_{25}-C_{33})_{odd} + [\sum (C_{23}-C_{31})_{odd}]/\sum (C_{24}-C_{32})_{even}.$ $CPI_{(25-31)} - carbon preference index: (C_{25} + C_{27} + C_{29}) + (C_{27} + C_{29} + C_{31})/2(C_{26} + C_{28} + C_{30}).$

Pr, Pristane; Ph, Phytane.

processing. The abundances of the selected compounds were calculated by comparisons of peak areas for internal standards (9-phenylanthracene and 9-phenylindene) with the peak areas of the individual hydrocarbons obtained from the GC-MS ion chromatograms. Peak identification was carried out by comparison of retention times with standards and by interpretation of mass spectrum fragmentation patterns.

3.3. Petrographic analysis

3.3.1. Pyrite framboid diameter analysis

Pyrite framboids were used to decipher the redox conditions during deposition of the investigated sediments. As a promising tool for interpretation of the redox conditions, pyrite framboids were first applied by Wilkin et al. (1996) to modern sediments. They found that framboids of particular diameters correspond to specific environments in which they form: from the water column under euxinic conditions to surficial sediments below dysoxic, anoxic or oxic water columns. After the work of Wignall and Newton (1998), who first applied them to ancient deposits, many other papers utilising pyrite framboids in palaeoenvironmental studies based on various sedimentary rocks of different ages have appeared (e.g., Wignall and Twitchett, 2002; Wignall et al., 2005; Racki et al., 2004; Bond and Wignall, 2005; Shen et al., 2007; Raiswell et al., 2008; Zatoń et al., 2009). As a thorough and excellent discussion of pyrite framboids as palaeoenvironmental indicators has already been presented by Wignall and Newton (1998), it will not be repeated here. It must be stressed here, however, that, as was earlier stated by Wilkin et al. (1997), the framboid pyrite diameter study may be especially useful when used in combination with organic biomarker analyses, as was done for this work.

For the present investigation, 16 samples were prepared for the pyrite framboid analysis, but three were completely barren of framboids. The majority of samples were taken from the boreholes (11 samples) and two samples from the Papilé Jurakalnis and Šaltiškiai outcrops. The majority of the samples represent the Upper

Callovian Skinija Formation, and only two samples come from the Lower and Middle Callovian Papilė and Papartinė formations, respectively.

The samples as small chips were embedded in epoxy resin, polished, and then the framboid diameters were measured using a Philips XL 30 Environmental Scanning Electron Microscope (ESEM) in a back-scattered electron (BSE) mode. The diameters were measured using the ESEM internal measuring device. Where possible, at least 100 framboids were measured per sample; however, for six samples it was impossible due to the general low number of framboids. For each sample, such statistical parameters (see Wignall and Newton, 1998) as minimum and maximum values, mean value and standard deviation were calculated.

3.3.2. Charcoal observations

Macroscopically visible charcoal fragments were examined using ESEM (see above). Two clay samples were treated with a cold HCl (30%) and cold HF (38%) in order to remove the carbonate and silicate minerals. The residue was then washed with demineralised water until a neutral pH was reached, dried and separated on laboratory sieves. The obtained residues were attached to small metal stubs using carbon tape and examined using the ESEM.

3.3.3. Vitrinite and fusinite 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 $500 \times$. The standards used were 0.42%, 0.898% and 1.42% relative reflectance (R_r).

4. Results

Bulk and molecular analysis of the samples from the Lower (Papilė Formation), Middle (Papartinė Formation) and Upper (Skinija Formation) Callovian sediments of Lithuania are given here in order to show the similarities and differences between these *m/z* 71

MMAS

nC.

21

19

19

17

b

nC.

three sedimentary environments. General information concerning lithology, carbonate contents, TOC, TS and percentage of the individual organic fractions of extracts is presented in Table 1.

4.1. Papilė Formation (Lower Callovian)

4.1.1. TOC and molecular biomarkers

The values of the 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 one analysed sample of siderite is characterized by up to 2% of TOC (Table 1). These flat siderite concretions are the only samples containing carbonates in the Papilė Formation (Table 1). The Papilė Formation samples contain small (0.05-0.2%) to moderate (0.2-0.5%) amounts of total S (Table 1) which is generally characteristic for terrestrial sediments. Taking into account fractional composition of the extracts, all samples are characterized by significant prevalence of the polar fraction (>60\%, Table 1).

n-Alkanes are abundant in all extracts and their distribution ranges in C-chain length from C₁₃ to C₃₆. In their distribution long-chain *n*-alkanes predominates what is reflected by values below 1 of the $(n-C_{17} + n-C_{18} + n-C_{19})/(n-C_{27} + n-C_{28} + n-C_{29})$ ratio (Ta-

а

С

Relative Response

m/z 71

15

ble 2; Fig. 2d). The C 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 (Table 2). The dominance of high molecular weight *n*-alkanes with an odd C number preponderance (especially n-C₂₅, n-C₂₇, n-C₂₉, n-C₃₁ see Fig. 2d) 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-C₁₇ and Ph/n-C₁₈ (Table 2), in most cases not exceeding 1. Generally, the values of the Pr/Ph ratio are diverse (Table 2). These large differences between Pr/Ph ratios are typical for immature sediments with large admixtures of terrestrial OM (Marynowski et al., 2007a, 2008a; Zatoń and Marynowski, 2006), even between samples from equivalent facies. In such a case, the Pr/Ph ratio does not indicate changes in the redox conditions during OM sedimentation (see Didyk et al., 1978; ten Haven et al., 1987).

The most abundant hopanes are C_{29} , C_{30} or C_{31} , 17β , 21β -hopane, depending on the samples (Fig. 3). 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. 3). Hopanes with 34 and 35 C atoms in the molecule are not detected in any sample and hopanes with 33 C

SKINIJA FORMATION

PAPARTINE FORMATION

JUR 904

SAL PAR

33



Fig. 2. Reconstructed mass chromatogram (m/z 71) of saturated hydrocarbon fraction of the: (a) Skinija Formation; (b) enlarged fragment of the JUR 904 sample with C₁₈, 2-to 7-monomethyl alkanes (MMAs), (c) Papartinė Formation and (d) Papilė Formation. Pr – pristane, Ph – phytane, nPr – norpristane.

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 Table 3, are high and very small, respectively, which distinguishes the low maturity range. Some differences noted in the case of the KARPPCC sample may depend on secondary OM oxidation (e.g., Elie et al., 2000; Marynowski et al., 2007a; Marynowski and Wyszomirski, 2008).

Interestingly, in comparison to the Upper Bajocian and Bathonian Ore-Bearing Częstochowa Clay Formation samples (see Figs. 5 and 6 in Marynowski et al., 2007a), neohop-13(18)-enes have very low relative concentrations in all the Callovian formations (Fig. 4). As is known from previous work (Paull et al., 1998), these compounds are products of an acid-catalysed rearrangement conversion of fernenes. The lack of fernenes in the Callovian sediments and low concentrations of neohop-13(18)-enes (Fig. 4) confirm their co-occurrence in the Middle Jurassic sediments (see Marynowski et al., 2007a).

Sterenes, steranes, diasteranes and diasterenes are absent or present in the samples as traces only.

Samples from the Papilé Formation contain higher plant biomarkers including cadalene, dehydroabietane, simonellite and retene (Figs. 5 and 6). What is especially interesting, clay samples contain sugiol (Fig. 6), a natural product terpenoid produced by distinct conifer families (Cupressaceae s. l., Podocarpaceae and Araucariaceae). Such old biomolecules were recently described from fossil wood coming both from the Bathonian Częstochowa Ore-Bearing Clay Formation and the Callovian clay-pit at Łapiguz near Łuków, Poland (Marynowski et al., 2007b, 2008b). Identification of sugiol in the Lower Callovian clays is the oldest find of such biomolecules occurring directly within the sediments. However, this compound is not present in sand samples due to their higher oxidation range.

4.1.2. Charcoal detection

4.1.2.1. Macro- and microscopic observations. Macroscopically visible charcoal fragments were found in the Karpėnai outcrop, solely in the sand units. These fragments are rounded, and range from \sim 1 mm to \sim 3 cm in size. Black clay from Karpėnai (sample KARICZ) also contains charcoal, but its fragments are very small (<0.5 mm) and visible only using ESEM, after removing the mineral phases.

The charcoal fragments from the sands are very well-preserved, with exceptional three-dimensional cellular preservation in many fragments (Fig. 7c and d). In contrast, charcoals from the black clay samples are small, crushed, with angular and sometimes ragged margins (Fig. 7e) and rarely well-preserved (Fig. 7f).

4.1.2.2. Huminite and fusinite reflectance. Huminite reflectance values are homogenous for all the analysed samples and reveal a relatively narrow range. Measured samples come from one outcrop (Karpėnai) but the results obtained differ slightly from each other. Huminite reflectance values (R_r) are in the range of 0.21–0.35% (Table 4). These discrepancies are interpreted as caused by differences in lithology and TOC content. The lowest values were measured for organic-rich fossil wood and black to brown shale (KARICZ and KARIHU) samples, while the sandstone (KARPPCC) sample is characterized by the highest huminite reflectance values are very low and are characteristic of the brown coal maturity range (e.g., Hunt, 1995).



Fig. 3. Partial m/z 191 mass chromatograms showing distribution of hopanes and hopenes from the (a) Papartinė (KARIS2) and (b) Skinija (JUR 904) formations.

Table 3

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

Samples	Depth (m)	LMWn-a/(n-a + hop)	HMWn-a/(n-a + hop)	$C_{30}\beta\beta/C_{30}\alpha\beta$	22S/(22S + 22R)	Ph/(Ph + Sim)	Ph/(Ph + Ret)	Ph/(Ph + Cad)
Papile 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								
Papilė Iurakalnis PAPILIR	_	0.60	0.47	3 09	017	0.92	0.66	1.00
Papilė PAP1	_	0.48	0.61	2.07	037	1.00	0.57	0.98
Papilė PAP2	_	0.40	0.49	2.85	0.19	0.84	0.53	0.96
Papilė PAP3	_	0.45	0.28	4.50	0.20	0.95	1.00	0.95
Menciai MENC	-	0.76	0.28	5.90	0.22	1.00	0.97	0.94
Jurjonai-10	82.8	0.80	0.56	7.18	0.21	1.00	0.97	1.00
Jurjonai-10	87.7	0.56	0.19	5.08	0.26	0.87	0.96	0.93
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
Purmaliai-5	93.2	0.90	0.42	1.23	0.44	1.00	0.99	0.93
Žvelsnai-8	100.8	0.81	0.45	1.29	0.47	1.00	0.99	0.90
Žvelsnai-8	105	0.88	0.57	4.25	0.27	0.97	0.99	0.91
Žvelsnai-8	114.4	0.85	0.52	5.18	0.16	0.75	0.98	0.87
Žvelsnai-8	117.6	0.60	0.47	2.94	0.29	0.92	0.66	0.98

 $LMWn-a/(n-a + hop) - low molecular weight n-alkanes to hopanes ratio: (n-C_{17} + n-C_{18} + n-C_{19})/(n-C_{17} + n-C_{18} + n-C_{19} + C_{29}\beta\beta-norhopane + C_{30}\beta\beta-hopane + C_{31}\beta\beta-hopane).$

HMWn-a/(n-a + hop) – high molecular weight n-alkanes to hopanes ratio: $(n-C_{25} + n-C_{27} + n-C_{29})/(n-C_{25} + n-C_{27} + n-C_{29} + C_{29}\beta\beta$ -norhopane + $C_{30}\beta\beta$ -hopane + $C_{31}\beta\beta$ -homohopane).

 $C_{30}\beta\beta/C_{30}\alpha\beta - C_{30}$ -17 β , 21 β -hopane/C₃₀-17 α , 21 β -hopane ratio.

22S/(22S + 22R) – C_{31} -17 α , 21 β -homohopane homologues 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.



Fig. 4. Ternary diagram showing relationship between $\beta\beta$ -, $\alpha\beta$ -hopanes and hopenes (sum of neohop-13(18)-enes and hop-17(21)-enes) for the Callovian samples from Lithuania.

In contrast to huminite, fusinite fragments show a wide range of values. The average fusinite reflectance values are significantly higher than those of huminite (Table 4) and range from 0.80% to 0.99% $R_{\rm r}$. Calculated temperatures of charcoal formation, based

on the Scott (in press) plot ranged from 320 to 470 °C for the KAR-PPCC sample, 320–420 °C for the KARICZ sample and 310–335 °C for the KARIHU sample (Table 4).

4.1.2.3. Polycyclic aromatic compounds (PACs). An alternative and complementary method to determine the occurrence of wildfires in the geological record is detection of high concentrations of unsubstituted polycyclic aromatic hydrocarbons (PAHs) (Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Jiang et al., 1998; Arinobu et al., 1999; Finkelstein et al., 2005; Scott et al., in press). In some cases, where charcoals are very small, rounded and poorly preserved, detection of PAHs is an excellent method to support the wildfire evidence (Marynowski and Filipiak, 2007; Marynowski et al., in press). Despite some exceptions (e.g., Simoneit and Fetzer, 1996; Grice et al., 2007; Rospondek et al., 2009; see also Marynowski and Simoneit, 2009), wildfires are the main source of unsubstituted PAHs in the geological records.

The charcoal-bearing sediments examined here contain elevated concentrations of polycyclic aromatic compounds compared to the other samples, characterized by a distribution with significant predomination of unsubstituted polycyclic aromatic compounds over their alkyl derivatives (Fig. 5). The sum of concentrations of the pyrolytic polycyclic aromatic hydrocarbons, including fluoranthene, pyrene, benzofluoranthenes, benzo[*e*]pyrene, benzo[*ghi*]perylene and coronene (adopted from Finkelstein et al., 2005) ranged from 4.66 to 6.57 µg/g TOC for charcoal-bearing clay and samples, respectively, while for the rest of the samples, the obtained values are below 0.5 µg/g TOC. Concentrations of PAHs are significantly lower than those from the Hettangian Sołtyków samples

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Fig. 5. TIC trace (a) of the aromatic fraction of the KARICZ sample (Lower Callovian, Karpėnai locality), showing the predominance of high molecular-weight PAH and relatively high amounts of O-containing aromatic compounds and (b) partial mass chromatogram for *m*/*z* 252 of the 5-ring PAH showing non-combustion perylene (Grice et al., 2009) and other combustion aromatics. B[*b*]NF – benzo[*b*]naphthofuran isomer, BBF – benzobisbenzofuran isomers, DNF – dinaphthofuran isomers, IS – internal standard, a DB-35MS column was used.



Fig. 6. Summed mass chromatogram for *m*/*z* 183 + 219 + 237 + 255 + 285 showing the distribution of aromatic biomarkers from the: (a) Papile, (b) Papartine and (c) Skinija formations. DB-35MS column was used.

from Poland and similar to the Podole and Lower Gromadzice locations (Marynowski and Simoneit, 2009). This may be connected with partial organic matter oxidation and dissolution processes which in consequence led to a decrease of PAH concentrations. This



Fig. 7. Scanning electron photomicrographs of: (a) relatively large framboids from the Papartinė Formation (sample SALPAR); (b) euhedral pyrite crystals most probably grown after framboid pyrite disintegration, Papartinė Formation (sample SALPAR); (c) and (d) tangential section of well preserved charcoal from the Karpėnai exposure (sample KARPPCC); (e) small and crushed charcoal fragments from the residue of Karpėnai clay (sample KARICZ); and (f) relatively well-preserved charcoal fragment from the clays of the Karpėnai exposure (sample KARICZ).

Table 4	4
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Vitrinite	and	fusinite	reflectance	value
vittille	anu	Iusinite	renectance	value

Location	Vitrinite	/itrinite (Huminite) reflectance (%)				Fusinite	Fusinite reflectance (%)				Combustion temp. $(^{\circ}C)^{*}$		
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n	Avg	Min	Max
Karpenai KARPPCC	0.35	0.05	0.23	0.50	120	0.99	0.37	0.62	2.43	80	360	320	470
Karpenai KARICZ	0.25	0.06	0.16	0.50	115	0.86	0.20	0.60	1.59	95	350	320	420
Karpenai KARIHU	0.31	0.10	0.14	0.54	100	0.80	0.18	0.54	1.28	90	350	310	400
Karpenai WOOD	0.21	0.03	0.15	0.36	100	-	-	-	-	-	-	-	-

Avg, average; SD, standard deviation; Min, minimum; Max, maximum; *n*, number of measurements.

* Calculated combustion temperature from data presented in Scott (in press).

is supported by PAC distribution (Fig. 5). The high molecularweight compounds like benzo[*ghi*]perylene, benzofluoranthenes, benzo[*e*]pyrene or indeno[1,2,3-*cd*]pyrene are significantly dominant (Fig. 5), through what interpreted as oxidation, dissolution and migration of more soluble lower molecular-weight PACs by meteoric waters or waters originated from melting glacier (Kawka and Simoneit, 1990; Marynowski and Simoneit, 2009). Due to the occurrence of such secondary processes, the analysed samples do not contain phenyl-derivatives of PAHs, which have been identified in the Lower Jurassic charcoal-bearing units from Poland (Marynowski and Simoneit, 2009). Besides the PAHs, the charcoal-bearing samples are characterized by the occurrence of O-containing aromatic compounds. The most common are benzo[*b*]naphthofurans, dinaphthofurans, and benzobisbenzofurans (Fig. 5). These compounds were also detected in the Lower Jurassic samples from Poland. However, these samples additionally contain lower molecular-weight O compounds like: dibenzofuran and its methyl-, dimethyl- and trimethyl derivatives (Marynowski and Simoneit, 2009). The above-mentioned, low molecular-weight O compounds were not detected in the Lower Callovian sediments. This also may suggest the presence of secondary processes which affected organic matter composition.

4.2. Papartine and Skinija formations (Middle and Upper Callovian)

 Table 5

 Framboid pyrite diameter data (μ m). n – number of famboids measured, max –

The TOC for both formations are generally high (>2% wt. of the bulk rock) to moderate (0.5–2%) (Table 1). However, some Papartine Formation horizons, e.g., sandstones and sands from the Papile section, are OM-poor and due to this they were not analysed here.

The total S content is variable for the Papartine and Skinija Formation which most probably depends on pyrite content and oxidation range (Table 1). General S content is higher than in the Papile Formation and in some cases may exceed 2–3% (Table 1). Similar to the Papile Formation, important dominance of the polar fraction is observed in most of the samples (44–85%, Table 1).

Distribution of *n*-alkanes differs from that of the Papilė Formation. Short-chain *n*-alkanes predominate in most of the samples, excluding those slightly biodegraded/affected by water washing (Papilė section and Menčiai), which is revealed by values above 1 of the $(n-C_{17} + n-C_{18} + n-C_{19})/(n-C_{27} + n-C_{28} + n-C_{29})$ ratio (Table 2; Fig. 2a and c). Despite higher relative concentrations of short-chain *n*-alkanes over long-chain *n*-alkanes, those with an odd C number significantly predominate (especially $n-C_{25}$, $n-C_{27}$, $n-C_{29}$ and $n-C_{31}$ see Fig. 2d) indicating higher plant inputs. This is emphasized by the C preference index (CPI_{Total} and CPI₍₂₅₋₃₁₎) values which are higher than 1 for all samples and in some cases higher than 2 (Table 2). The values of Pr/ $n-C_{17}$, Ph/ $n-C_{18}$ and Pr/Ph (Table 2), similar as in the case of the Papilė Formation, are diverse and not indicative.

As distinct from the Papilė Formation, the samples from the Papartinė and Skinija formations contain monomethyl alkanes (MMAs), ranging from $C_{15}-C_{21}$ (Fig. 2c) and with distribution similar to that presented by Bauersachs et al. (2009). MMAs series contain from 2-, to 7-MMAs with generally similar relative concentrations (Fig. 2b and c). The mid-chain branched monomethyl alkanes have been reported as compounds characteristic of modern and ancient cyanobacteria (e.g., Summons, 1987; Kenig et al., 1995; Köster et al., 1999; Bauersachs et al., 2009). Similarly to the Papartinė Formation, in all the Skinija Formation samples monomethyl alkanes (MMAs) were detected, with distribution almost the same in all samples (Fig 2a and c).

The distribution of hopanes is similar to that from the Papilė Formation with C_{29} , C_{30} or C_{31} , 17β , 21β -hopane domination, depending on the samples (Figs. 3 and 4). Also distribution of extended C_{31} - C_{35} hopanes is characterized by a predominance of the $C_{31}(22S + 22R)$ homologues while those with 34 and 35 C atoms in the molecule are not detected in any of the samples. Moreover, significant excess of the less stable *R* epimer is observed and is emphasized by the 22S/(22S + 22R) ratio values (Table 3; Fig. 3). The $C_{30}\beta\beta/C_{30}\alpha\beta$ hopane ratio shown in Table 3 is high, what confirms the low maturity of the samples from the Papartine 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 which may suggest intensive bacterial reworking of sedimentary OM.

The aromatic higher plant biomarkers like cadalene, simonellite and retene were identified in both the Papartine and Skinija formations (Fig. 6), but natural product terpenoids like sugiol were not found. The ratios of phenanthrene to simonellite, retene and cadalene are calculated and shown in Table 3.

4.3. Pyrite framboid diameter study

The range of pyrite framboid diameters varies greatly in particular samples studied (see Table 5); they range from as tiny as less than 3 μ m, up to 27 μ m in diameter. However, these very large (>20 μ m) framboids occur sporadically and as single individuals only. The mean values of framboid diameters in particular samples is quite uniform, generally ranging from 6.4 to 8.7 μ m, with overall

naximum value, min – minimum value, mean – mean value, SD – standard deviation.										
Locality (sample number)	Formation	n	Max	Min	Mean	SD				
Šaltiškiai (SALPAR)	Papartinė	102	27.3	4.39	9.78	4.2				
Purmaliai (Pu 93,2)	Skinija	133	26.2	3.68	8.74	2.4				
Žvelsnai (Zv 114,4)	Skinija	50	20.08	4.64	8.06	2.82				
Purmaliai (Pu 81,3)	Skinija	11	9.77	4.82	6.77	1.36				
Purmaliai (Pu 91,5)	Skinija	50	20.2	4.23	8.52	3.69				
Jurjonai (JUR 87,7)	Skinija	100	11.7	2.82	6.41	1.96				
Žvelsnai (Zv 100,8)	Skinija	100	13.9	2.54	6.91	2.25				
Jurjonai (JUR 82,8)	Skinija	100	15.6	4.39	8.16	2.4				
Jurjonai (JUR 90,4)	Skinija	50	15.5	2.23	6.96	2.21				
Jurjonai (JUR 95,8)	Skinija	101	24.3	2.59	7.0	3.48				
Žvelsnai (Zv 118,4)	Skinija	70	14.5	2.73	7.61	2.32				
Žvelsnai (Zv 105)	Skinija	102	14.4	4.35	7.96	2.08				

very low values of standard deviations (see Table 5). The dominant values of pyrite framboid diameters in particular samples are similar as well, often ranging from 6 to 9 μ m. However, in four black clay samples derived from the Upper Callovian Skinija Formation (Jur 87.7, Jur 95.8, Zv 100.8 and Sa 105.6) the dominants are lower, ranging from 4 μ m to at most 6 μ m.

5. Discussion

5.1. Maturity and organic matter preservation

All analysed samples are characterized by more or less prevalence of the polar fraction (Table 1), which is generally characteristic for immature organic matter (Tissot and Welte, 1984). For comparison, similar polar fraction predominance is characteristic for the immature Callovo-Oxfordian sedimentary series of the Paris Basin, recently reported by Hautevelle et al. (2007). Measured values of huminite reflectance (R_r) differ between the samples and are in the range of 0.21-0.35% (Table 4), but all these values are low and characteristic of immature OM (Tissot and Welte, 1984). In the authors' opinion, the huminite reflectance values (c. 0.2%, see Table 3) measured on the wood fragments most probably correspond to the real stage of thermal maturity, which in turn correspond to very low mature brown coals of the xylite-type. If it does, the deposits investigated were close to the surface during their whole diagenetic history (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 the SW part of Lithuania, where the thickness of younger strata is maximal (Marek and Grigelis, 1998).

The relationship between $\beta\beta$ -, $\alpha\beta$ -hopanes and hopenes is presented in a ternary diagram (Fig. 4). The major factors controlling their distribution are thermal maturity, oxidation and source of organic matter. In all Callovian samples less thermally stable $\beta\beta$ -hopanes significantly dominated which suggest an 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. The general conclusion is that all these Callovian sequences were never buried by more than 500 m of sediment.

5.2. Depositional environments and palaeogeographic implications

In all the Lower to Upper Callovian samples investigated, 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 in the Lithuanian Callovian formations. Moreover, no other compounds like gammacerane or high concentrations of C₃₃, C₃₄ or C₃₅

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homohopanes, characteristic for stratification of the water column or bottom water anoxia (Sinninghe Damsté et al., 1995; Peters et al., 2005), have been found.

Taking into account the framboid pyrite diameters greater than 5 μ m, it may be concluded that depositional conditions were oxic to suboxic. It must be noted here, however, that for the Papilė and Papartinė formations, the framboid measurements were possible only for single samples, as the majority of the material analysed lacked framboids.

Recently, Kenig et al. (2004) and Hautevelle et al. (2007) described the evidence for 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 Lithuania this was a time-period when the sedimentary conditions changed from terrigenous (deposits of the Papilė Formation) to shallow marine due to a transgression (Šimkevičius et al., 2003). The deposits representing the Middle Callovian (Papartine Formation) consist mainly of organic-poor sands and sandstones with a rich faunal content (e.g., ammonites, belemnites, bivalves, gastropods, various echinoderms, serpulids, brachiopods among others; authors' pers. observ.; see also Paškevičius, 1997; Satkūnas and Nicius, 2006, 2007; Salamon, 2008). This type of sedimentation excludes the presence of anoxic conditions in the water column. The pyrite framboid size distribution, characterized by a domination of framboids greater than 6 µm in diameter (Fig. 8a), is also indicative of aerated bottom waters (e.g., Wignall and Newton, 1998). Additionally, anoxia has not been detected during the deepening phase when the clay deposits of the Upper Callovian Skinija Formation were deposited, but the small framboid pyrite diameters measured in some samples (Jur 87.7, Zv 100.8 and Sa 105.6) may point to anoxic or strongly dysoxic conditions (Table 5, Fig. 8b). Here, the pyrite framboids are dominated by a small-sized population, and are completely devoid of large-sized (>20 µm) framboids (Fig. 8b). It is highly probable that during the deepest phase of the transgression in the Late Callovian, when the black clays were deposited, the basin witnessed anoxia below the photic zone. This would explain, and does not contradict, the lack of biomarker evidence in the form of isorenieratane, which needs the photic zone to be formed (e.g., Koopmans et al., 1996). Periodic O₂-deficient conditions at the sea-floor may also be supported by the general scarcity of fauna occurring in the black clays. Despite nectonic animals, such as ammonites and belemnites, the benthos is mainly represented by bivalves Astarte (see Paškevičius, 1997; Satkūnas and Nicius, 2006, 2007), that sometimes may be quite common (Paškevičius, 1997). This may indicate the periodic nature of O_2 -deficient conditions followed by episodes of oxygenation events. Interestingly, Salamon (2008) did not notice any isocrinid crinoids in the deepsea black clays of the Skinija Formation even though the isocrinids are known to occur in deeper parts of the marine basins. The onset of anoxic or strongly dysoxic conditions on the sea-bottom environment may be strongly linked with the maximum transgression during the Late Callovian, which resulted in the deposition of black clays. Recently, Wierzbowski et al. (2009), based on the isotopic record from Poland, found a prominent positive excursion of δC^{13} in the uppermost Callovian. This may be linked with the enhanced organic C storage during the transgressive event, which is consistent with an overall major global sea-level rise during the Late Callovian (Norris and Hallam, 1995).

Generally, the sedimentary conditions during which the Skinija Formation was deposited were very similar to those when the Upper Bajocian and Bathonian Częstochowa Ore-Bearing Clay Formation formed, and in the both cases the sedimentation took place in the epicontinental basins (e.g., Marynowski et al., 2007a; Zatoń et al., 2009). Similar results were also obtained for the Callovian sediments of the Łuków locality, eastern Poland (Marynowski et al., 2008b). However, in both the ore-bearing clays and Łuków sediments, there is no evidence of even periodic anoxia based on both organic biomarker and pyrite framboid analyses.

In both the terrigenous Papile Formation and the shallow- to deeper-marine facies of the Papartine and Skinija formations, terrestrial organic matter with odd-over-even predominance of the long-chain n-alkanes (Fig. 2), and terrestrial biomarkers like cadalene, simonellite or retene (Figs. 5 and 6; Table 3) 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. Plots shown on Fig. 9, which are based on the short-chain n-alkanes to hopanes ratio vs. long-chain n-alkanes to hopanes ratio, low molecular weight to high molecular weight *n*-alkanes and phenanthrene to (phenanthrene + cadalene) ratio, show some differences between composition of extracts of the Callovian marine vs. terrestrial conditions. Nevertheless, these differences are not very substantial due to an important input of terrestrial OM in both cases. 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 mainly terrestrial OM character has been recently affirmed for the Callovian of the Staffin Bay and Staffin Shale formations (Isle of Skye, Scotland) based on Rock Eval



Fig. 8. Framboid pyrite size distributions in the Middle Callovian Papartinė Formation (Šaltiškiai, SALPAR sample) (a) and Upper Callovian Skinija Formation (Žvelsėnai-8 borehole, sample Zv 100.8) (b).

analysis (Nunn et al., 2009) and using biomarkers (Foster et al., 2003). Also Hautevelle et al. (2007) implies that OM from the Callovian deposits of the Paris Basin is a mixture of autochthonous marine biomass and allochthonous OM initially synthesized by terrestrial plants. All this evidence indicates that climatic conditions on the land areas surrounding the Middle Jurassic Anglo-Paris and Central European Basins were favourable for intensive terrestrial vegetation during the Callovian. The general scenario of depositional environment changes during the Callovian in the Lithuania area is presented on Fig. 10.

5.3. Lower Callovian wildfires

To the best of the authors' knowledge, reports on charcoals from the Callovian sedimentary rocks with their detailed microscopic documentation and description have not been published. However, some reports have mentioned an inertinite content in the Callovian coals (see e.g., Petersen and Rosenberg, 1998 and the summary in Diessel, in press), which is treated as wildfire evidence (e.g., Scott



Fig. 9. Plots of low molecular weight *n*-alkanes to hopanes ratio vs. high molecular weight *n*-alkanes to hopanes ratio (a) low molecular weight to high molecular weight *n*-alkanes ratio (b) and phenanthrene to (phenanthrene + cadalene) ratio (c) showing differences between molecular composition of extracts from the Callovian formations of Lithuania. See Table 3 for abbreviations explanation.



Fig. 10. The general scenario of depositional environment changes during the Callovian of the Lithuania area.

and Glasspool, 2007). Moreover, strong predomination of the unsubstituted PAHs over their methylated counterparts, interpreted as originating from palaeovegetation fires, but without charcoal detection was reported by Hautevelle (2005) and Hautevelle et al. (2007) from the Callovo-Oxfordian claystones from the Paris Basin. Here, definite documentation of the Lower Callovian wildfires based on charcoal identification and polycyclic aromatic compounds detection are presented (Figs. 5 and 7).

Although fusinite reflectance values differ between samples (Table 4), all charcoal fragments (=semifusinites *sensu* Scott and Glasspool, 2007) are formed at relatively low temperatures. These temperatures did not exceed 470 °C, which is characteristic of ground and/or surface fires (Scott, 2000, in press; Scott and Glasspool, 2006). Similar low-temperature wildfires were described recently by Marynowski and Simoneit (2009) from the Upper Triassic and Lower Jurassic of Poland. In the case of the Lower Jurassic wildfires from Poland, however, they sporadically reached the crown as well.

The most recent revised GEOCARBSULF model assumed that O_2 values for the Middle Jurassic were not lower than 15% (Berner, 2009) which, according to Belcher and McElwain (2008), indicate that combustion could have occurred at that time. However, relatively low O_2 values may implicate rather scarce and low-temperature wildfires (Table 4).

6. Conclusions

Both in the terrigenous Lower Callovian Papile Formation and shallow- to deeper-marine facies of the Papartine and Skinija formations, respectively, a significant part of the compounds found in the extracts are of terrestrial origin. In the case of the Papilė Formation, apart from typical land-derived biomarkers such as cadalene, dehydroabietane, simonellite and retene, natural product terpenoids like sugiol, produced by distinct conifer families, have been detected in clay sediments. The occurrence of such biomolecule in the Middle Jurassic clays is reported for the first time and most probably is connected with the presence of small wood debris in the investigated clays. Moreover, clays and sands of the Papilė Formation are characterized by the presence of charcoal fragments and elevated concentrations of polycyclic aromatic compounds. This is evidence of wildfires taking place in the territory of Lithuania during the Early Callovian, and the complex data from the results of petrographic and geochemical investigations in relation

to the Callovian deposits have been used (to the best of the authors' knowledge) for the first time. Based on the fusinite reflectance data there is evidence that the Callovian wood was burnt in a moderate temperature ($350-360 \ ^{\circ}C$) ground fire and this temperature did not exceed 470 $^{\circ}C$.

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 whole Callovian section of Lithuania there is no evidence of anoxic (euxinic) conditions occurring in the water column. However, periodic anoxic episodes below the photic zone during the deepest phase of transgression in the Late Callovian may have occurred, as is shown by pyrite framboid diameter distribution and general impoverishment of benthic fauna.

Measured values of huminite reflectance are in the range of 0.21–0.35% 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 ~300–500 m.

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