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WIDESPREAD UPPER TRIASSIC TO LOWER JURASSIC WILDFIRE RECORDS FROM POLAND: EVIDENCE FROM CHARCOAL AND PYROLYTIC POLYCYCLIC AROMATIC HYDROCARBONS

LESZEK MARYNOWSKI[1]* and BERND R. T. SIMONEIT[2,3]

[1]*Faculty of Earth Sciences, University of Silesia, Będzińska Str. 60, 41-200 Sosnowiec, Poland;* [2]*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA;* [3]*COGER, King Saud University, 11451 Riyadh, Saudi Arabia*

e-mail: leszek.marynowski@us.edu.pl

ABSTRACT

Laboratory tests indicate that 15% O_2, instead of 12%, is required for the propagation of a widespread forest fire, a 3% increase from what was previously assumed. The presence of widespread wildfire records in the Upper Triassic and Lower Jurassic of Central Europe suggests that the lower limit for O_2 during this time was at least 15%. Wildfire records are based on the co-occurrence of charcoal fragments and elevated concentrations of pyrolytic polycyclic aromatic hydrocarbons (PAHs). In all samples charcoal fragments are large to medium-sized and angular, suggesting that they were transported by rivers only short distances after charcoalification. Calculated combustion temperatures vary with stratigraphic position and average 295–377 °C, which is characteristic for ground or near-surface wildfires. The most extensive wildfires occurred in the earliest Jurassic and their intensities successively decreased with time. Average concentrations of the sum of pyrolytic PAHs for the lowermost Jurassic Zagaje Formation reached ~1253 μg/g total organic carbon (TOC), whereas for the Upper Triassic–Lower Jurassic Skłoby Formation they did not exceed ~16 μg/g TOC. Charcoal-bearing sequences were also characterized by the presence of phenyl-PAHs (Ph-PAHs) and oxygen-containing aromatic compounds. The dominance of the more stable Ph-PAH isomers in these immature to low-maturity sedimentary rocks supports their pyrolytic origin. The oxygenated PAHs may also be derived from combustion processes.

INTRODUCTION

Evidence for wildfires is recorded from the Silurian (Glasspool et al., 2004) to the Quaternary (see Scott, 2000, for a review) and is strictly connected with the colonization of the land by vascular plants and with atmospheric oxygen levels (e.g., Chaloner, 1989; Scott, 2000; Berner, 2001, 2006; Scott and Glasspool, 2006). Recognition of wildfires in sedimentary rocks is based on the identification of fossil charcoal (e.g., Scott and Jones, 1991; Scott, 2000; Cressler, 2001), inertinite group macerals, particularly fusain and its constituent macerals (e.g., Scott, 1989; Bustin and Guo, 1999; Scott and Glasspool, 2007), or a predominance of pyrolytic polycyclic aromatic hydrocarbons (PAHs) in the aromatic fraction of rock extracts (Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Kruge et al., 1994; Jiang et al., 1998; Arinobu et al., 1999; Finkelstein et al., 2005; Marynowski and Filipiak, 2007).

The Late Triassic–earliest Jurassic is characterized by relatively poor evidence for paleowildfires (Scott, 2000), probably due to the suggested very low atmospheric oxygen levels of ~10%–13% (Falkowski et al., 2005; Berner, 2006). This, together with reports of only sporadic charcoal (Scott, 2000), suggests a scarcity of wildfires across the T–J boundary. Previous experiments using dry pine dowels (Wildman et al., 2004) implied that combustion of such material required a minimum O_2 level of 12%. More recently, however, Belcher and McElwain (2008), based on burn experiments in a large plant-growth chamber, showed that the lower O_2 limit for combustion in natural environments should be increased from 12% to at least 15%. These authors suggest that oxygen levels during the Mesozoic be revised upward to 15% and imply that the paleoatmospheric O_2 levels for the Mesozoic in Berner (2006) and Falkowski et al. (2005) may need to be reevaluated. Although evidence of wildfires in the Late Triassic–Early Jurassic is sporadic, there are a number of reports worldwide. The first reports on rounded fusain fragments from the Rhaetic–lower Liassic (Hettangian) of East Greenland and South Wales were presented by Harris (1957, 1958). Fossil charcoal has also been found in the Upper Triassic Chinle Formation, Petrified Forest National Park, USA (Jones et al., 2002; Schuneman and Uhle, 2005) and in the Snyder quarry in north-central New Mexico, USA (Chapman et al., 2002; Zeigler et al., 2002). Pieces of charcoal were found in different horizons across the T–J boundary in the Jameson Land Basin, East Greenland (Belcher and McElwain, 2008). Combustion-derived PAHs have been described from Lower Triassic–Middle Jurassic rock samples of the Northern Carnarvon Basin, Western Australia (Jiang et al., 1998). Lower Jurassic (Toarcian) charcoalified leaf mesofossils are known from southwestern Bornholm (Denmark) (McElwain et al., 2005), and charcoal occurrences were mentioned by Ziaja and Wcisło-Luraniec (1999) in Hettangian sedimentary rocks of Odrowąż (commonly known as Sołtyków), in the Holy Cross Mountains, Poland. Inertinite submacerals were found in the Feke-Akkaya and Kozan-Kizilinc Liassic coals from Turkey (Korkmaz and Gülbay, 2007) and in the Sorthat Formation, Bornholm (Petersen et al., 2003).

Here we report the common occurrence of charcoal and pyrolytic PAHs from six Upper Triassic and lowermost Jurassic sites in southern and northern Poland that confirm the presence of wildfires in the Mesozoic of Central Europe and suggest that higher O_2 levels may have been present during this time. Moreover, the paper presents detailed molecular characteristics of the paleowildfire products and changes in their distribution.

GEOLOGICAL BACKGROUND

During the Late Triassic, Central Europe (including southern Poland) was situated within the subtropical convergence zone (Szulc, 2009). As suggested by Kent and Tauxe (2005), the shift to a relatively more moderate climate took place at the end of the Triassic (see also Pieńkowski, 2004). Upper Triassic sedimentary basins are characterized by a predominance of clastic, mainly terrestrial sediments (Szulc, 2009). Dry climatic conditions dominated during the Late Triassic, but several humid intervals have also been recognized during this time in the central European area (Reinhardt and Ricken, 2000; Kuleta and Zbroja, 2006).

The Early Jurassic in Central Europe is a time of mainly continental, but occasionally also marginal-marine and marine sedimentation in a large epeiric basin extending across Poland; the sediments attained a maximum thickness of 1400 m. Sedimentation in that shallow (usually ≤10–20 m), epeiric basin was particularly sensitive to changes in sea

* Corresponding author.

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level (Pieńkowski, 2004). Hettangian rocks in the Holy Cross Mountains are divided into three formations: the Zagaje, Skłoby, and Przysucha Formations (Pieńkowski, 2004); the last is ore bearing. Sediments of all formations consist of quartz and clay minerals (mainly kaolinite and illite), usually with siderite and/or goethite, and are characterized by the absence of carbonates (Brański, 2008). The samples analyzed here are from the Zagaje and Skłoby Formations.

The sedimentary rocks of the Zagaje consist of conglomeratic lithofacies, passing upward into sandstone and conglomerate lithofacies. These sedimentary systems represent alluvial fan and braided-river deposition (Pieńkowski, 2004). Higher up, the section is dominated by sandy-muddy lithofacies of a meandering-anastomosing river system that passes into mudstone-claystone lithofacies with paleosols of lacustrine-backswamp sedimentation (Pieńkowski, 2004). The rocks of the Zagaje Formation belong to the Ia and Ib depositional sequences (Fig. 1) of Pieńkowski (2004, 2008).

The Skłoby Formation in the Holy Cross Mountains comprises various deltaic successions. The deltaic cycles were created by abandonment-reoccupation autocyclic processes (Boyd and Penland, 1984). Two basic types of deltas were distinguished in the Lower Jurassic deposits of Poland: wave-dominated (or mixed wave-fluvial) deltas in the upper Gromadzice outcrop and fluvial-dominated (bird's-foot) deltas in the Podole outcrop (Zatoń et al., 2009). The Skłoby Formation belongs to the Ic, Id, and Ie depositional sequences of Pieńkowski (2004).

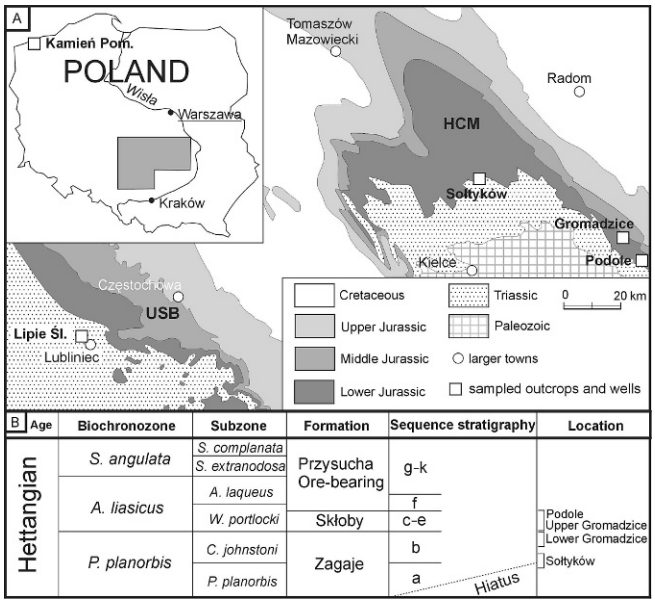

FIGURE 1—Simplified geological map of the Holy Cross Mountains (HCM) and upper Silesian Basin (USB) showing the sampling localities (A) and stratigraphic correlation of the investigated Hettangian outcrops (B). Sequence stratigraphy from Pieńkowski (2004, 2008).

MATERIALS AND METHODS

Materials

The sample material was collected from five sites, including one abandoned quarry (Podole), one active (Lipie Śląskie) and one inactive (Sołtyków) clay-pit, two natural exposures (lower and upper Gromadzice), and one borehole (Kamień Pomorski IG-1) (Fig. 1).

Lipie Śląskie Clay Pit.— Charcoals occur within carbonate concretions from the unoxidized fluvial-plain–bedded and cross-bedded mudstones and siltstones of the Lipie Śląskie section (Szulc et al., 2006; Marynowski and Wyszomirki, 2008). Sometimes these pedogenic concretions (Szulc et al., 2006) contain well-preserved vertebrate bones including a giant dicynodont, as well as large theropods (Dzik et al., 2008). Palynological and macrofloral evidence indicates a Rhaetian age for this site (Dzik et al., 2008), but the upper Triassic section in Poland is still under study. Four concretions were sampled and one was selected for organic geochemical analysis.

Sołtyków Outcrop.—Thirty-four samples, including sandstones, siltstones, mudstones, and a paleosol were collected and sixteen selected for further analysis. The Sołtyków section belongs to the lower Hettangian Zagaje Formation and is the part of the Ia depositional sequence. This sequence is characterized by continental deposits of a meandering-anastomosing river system (Pieńkowski, 2004). Detailed characteristics of the section lithology are presented by Pieńkowski (2004, 2008).

Lower Gromadzice Exposure.—Six rock samples were collected and four selected for analysis. The samples came from the upper part of the section and lithologically encompass sandstones and mudstones from floodplain and crevasse-splay depositional systems (Pieńkowski, 2004). This section belongs to the lower Hettangian, uppermost Zagaje Formation and is the part of the Ib depositional sequence.

Upper Gromadzice Exposure.—Thirteen samples were collected and included mudstones, siltstones, and sandstones from deltaic and nearshore facies. This section belongs to the middle Hettangian, Skłoby Formation and is part of the Ic and Id depositional sequences. Detailed characteristics of the section lithology are presented by Pieńkowski (2004).

Podole Quarry.—Ten samples were collected and analyzed including prodelta mudstones, mudstones with plant detritus, grey mudstones, sandstones, and heteroliths. The Podole section was assigned by Pieńkowski (2004) to the middle Hettangian Skłoby Formation based on biostratigraphy and sequence stratigraphic correlation, and is the part of the Id and Ie depositional sequences.

Kamień Pomorski IG-1 Borehole.—This borehole is located in the northern part of Poland in the area of the Pomerania Block (Fig. 1). Twenty-two claystone and mudstone core samples were collected and analyzed. These samples are assigned to the Upper Triassic (Norian–Rhaetian) and Lower Jurassic (Hettangian) based on palynological analysis. For a detailed description see Pieńkowski (2004).

Methods

Total Organic Carbon.—The total organic carbon (TOC) content was determined at the University of Silesia using an Eltra Elemental Analyzer model CS530.

Extraction and Separation.— Cleaned and powdered samples were Soxhlet extracted with dichloromethane for 48 hours in pre-extracted thimbles. Extracts were further separated using prewashed thin-layer chromatography (TLC) plates coated with silica gel (Merck, 20 × 20 × 0.25 cm). Prior to separation, the TLC plates were activated at 120 °C for one hour. 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 analyzed in further detail by gas chromatography–mass spectrometry (GC-MS).

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 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. Agilent Technologies J&W HP5-MS (60 m × 0.32 mm, 0.25 µm film thickness) coated with a chemically bonded phase (95% polydimethylsiloxane, 5% diphenylsiloxane). The GC oven temperature

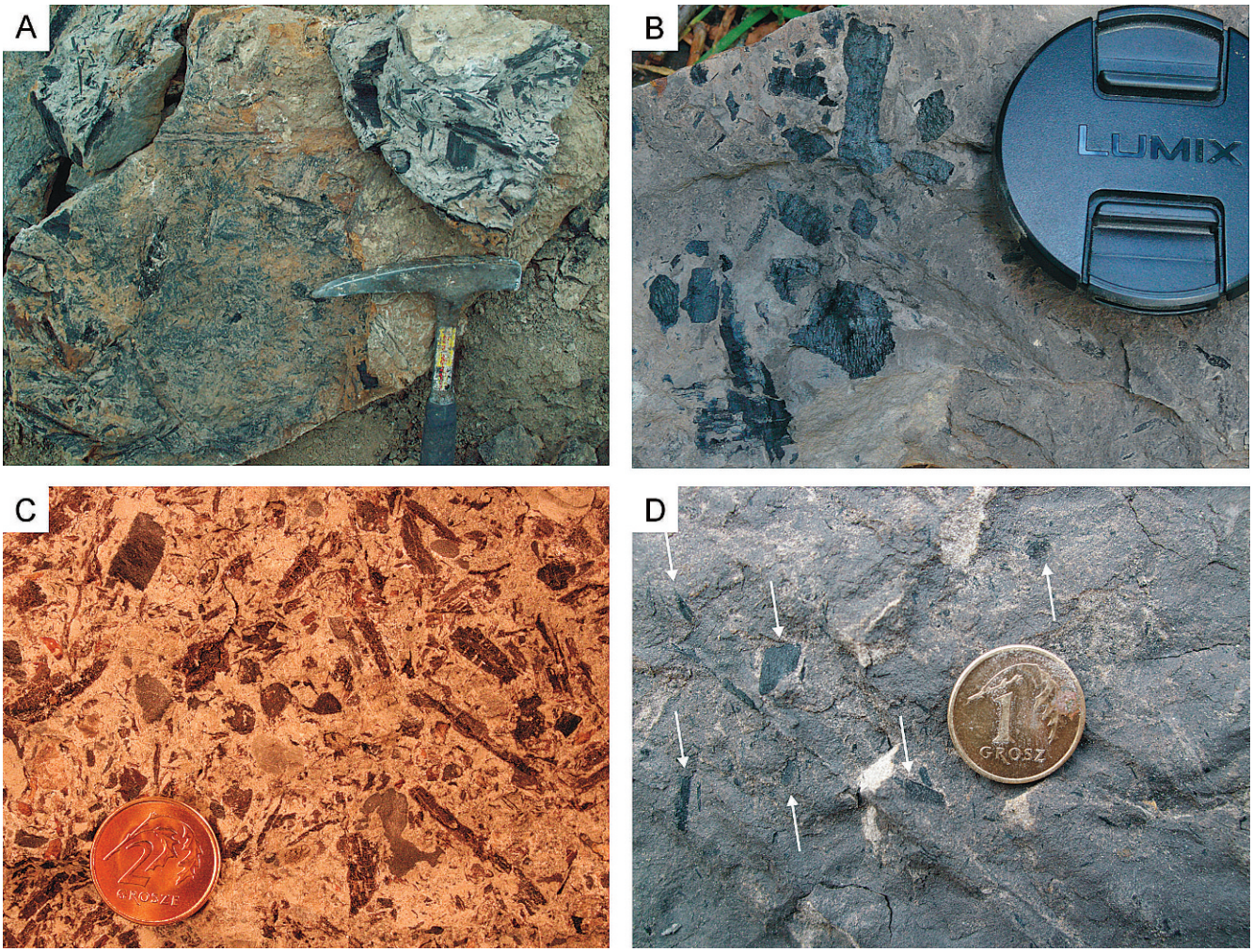

FIGURE 2—Macroscopic charcoal fragments. A–B) Large, angular charcoal fragments, with permineralized wood fragments rare or absent; Sołtyków, sample M9 (A); lower Gromadzice exposure, sample Grom Pc (B), camera lens cover diameter = 6.5 cm. C) Lipie Śląskie, sample Lipie CC; charcoal fragments small and angular; charred wood co-occurs with permineralized wood; coin diameter =1.7 cm. D) Podole, sample PDDM2; charcoal fragments (white arrows) are small and angular; permineralized wood fragments are rare; coin diameter = 1.5 cm.

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 minutes.

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 minutes. It should be noted that this column separates chrysene and triphenylene (see Fig. 8), but not all samples were analyzed using this system.

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 °C and 150 °C, respectively. Mass spectra were recorded at 45–550 daltons (da) (0–40 min) and 50–700 da (>40 min). The mass spectrometer was operated in the electron impact mode (ionization energy: 70 eV).

Quantification and Identification.—An Agilent Technologies Enhanced ChemStation (G1701CA ver.C.00.00) and the Wiley Registry of Mass Spectral Data (7th Edition) 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 (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.

Charcoal Observations.— Charcoal was examined on a Philips XL30 ESEM/TMP environmental scanning electron microscope. Seven samples, taken from the sedimentary rocks and carbonate concretions in form of small chips, were polished, coated with carbon, and then investigated using ESEM. The observations were undertaken in the back-scattered electrons (BSE) mode.

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×. The standards used were 0.42% and 0.898% relative reflectance (R_r).

RESULTS AND DISCUSSION

Macroscopic and Microscopic Charcoal Characteristics

Lipie Śląskie.— Charcoal fragments are found within carbonate concretions present in the greenish unoxidized mudstones and siltstones (Marynowski and Wyszomirski, 2008). The fragments are small and co-occur with permineralized wood (Fig. 2C). The fragments are angular and range in size from ~1 mm to 1–2 cm. Sometimes charcoal fragments are robust due to calcite and barite mineralization at the

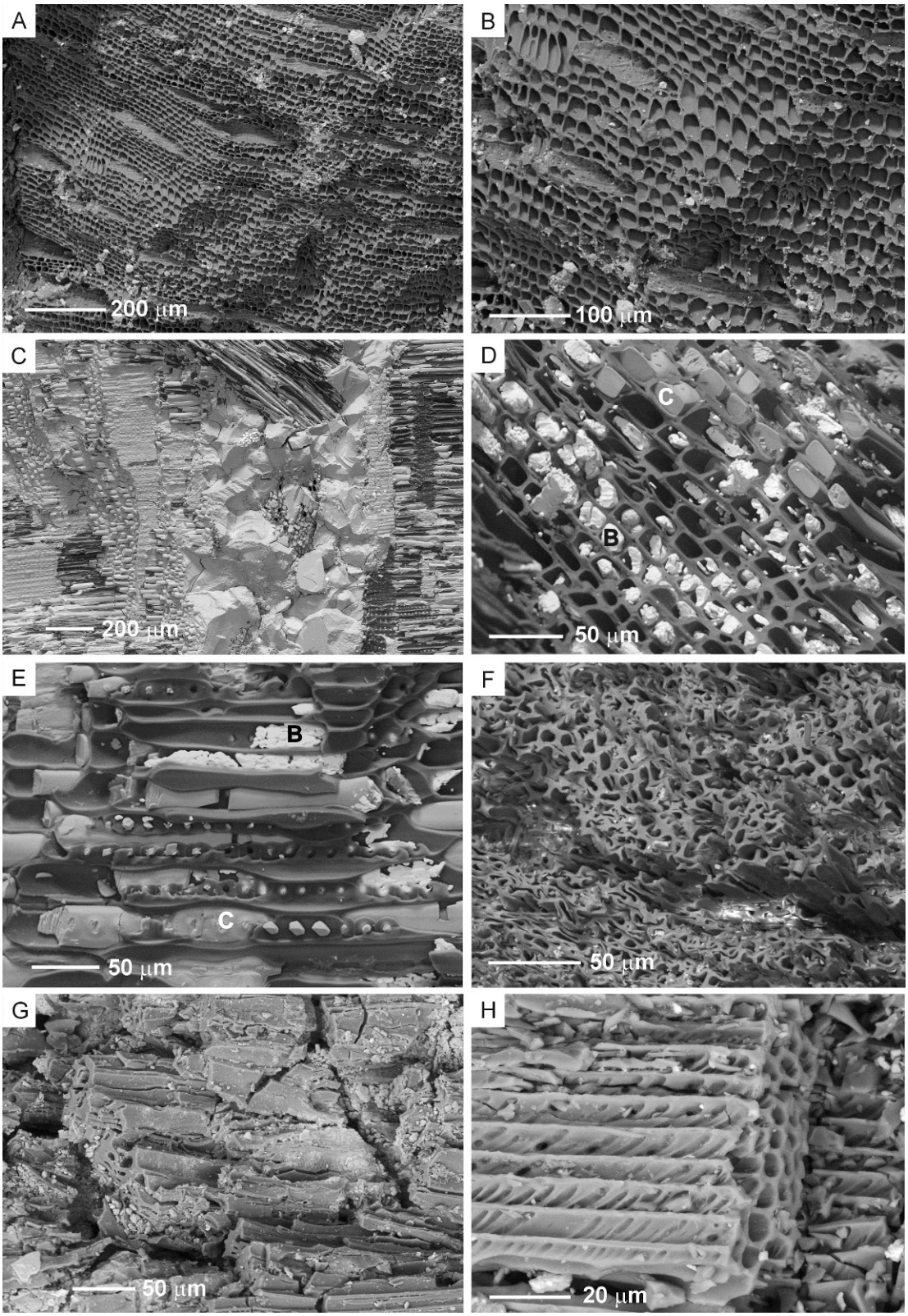

FIGURE 3—Scanning electron micrographs of fossil charcoal. A–B) Tangential sections of well-preserved charcoal from the Sołtyków exposure. C) Specimen almost completely replaced by calcite with overall cellular structure preserved; Lipie Śląskie exposure. D) Tangential section of fragment with calcite (C) and barite (B) mineralization; Lipie Śląskie exposure. E) Radial section of partially mineralized charcoal; Lipie Śląskie exposure; C = calcite, B = barite. F) Fragments crushed and disintegrated by compaction; lower Gromadzice exposure, sample Grom Pc. G) Small crushed fragment; upper Gromadzice exposure, sample GroZ2A. H) Relatively well preserved specimen; upper Gromadzice exposure, sample GroZ3; such fragments are rare in this section.

TABLE 1—Vitrinite and fusinite reflectance values (calculated from data in Jones and Lim, 2000); calculated combustion temperatures (°C) = 184 + 118•*X*, where *X* is the fusinite reflectance value; Avg = Average, SD = Standard Deviation, Min = Minimum, Max = Maximum, n = number of measurements. Calculated from data presented in Jones and Lim (2000).

Location	Vitrinite reflectance (%)					Fusinite reflectance (%)					Combustion temp. (°C)*		
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n	Avg	Min	Max
Sołtyków M9	0.59	0.07	0.47	0.75	50	1.63	0.71	0.79	3.46	100	377	277	592
Lower Gromadzice Ex. Grom Pc	0.47	0.11	0.24	0.65	80	0.94	0.36	0.62	2.35	55	295	257	462
Lower Gromadzice Ex. Grom Cl	0.54	0.09	0.24	0.66	50	1.17	0.41	0.64	2.73	130	322	259	507
Lipie Śląskie CC	0.22	0.05	0.14	0.40	80	0.96	0.73	0.47	2.84	50	297	240	519

* Calculated combustion temperature (°C) = 184 + 118•*X*, where *X* is the fusinite reflectance value.

TABLE 2—Concentrations of rarely identified polycyclic aromatic compounds (PACs) from selected charcoal-bearing samples (listed in their elution order on a 60-m DB-5MS capillary column). MS = mass spectrum interpretation; n.f. = not found.

m/z	Identified compounds	Occurrence and concentrations in the selected samples[1]				Identification
		GroZ4	PDDM2	M17	KP5	
Phenyl derivatives of PAC						
204	1-phenylnaphthalene	0.01	0.07	0.24	0.46	Marynowski et al., 2001
230	*o*-terphenyl	n.f.	0.01	n.f.	0.08	Marynowski et al., 2001
204	2-phenylnaphthalene	0.03	0.73	0.90	1.07	Marynowski et al., 2001
230	*m*-terphenyl	0.01	0.05	0.03	0.04	Marynowski et al., 2001
244	1-phenyldibenzo[*b,d*]furan	0.01	0.04	n.f.	n.f.	Marynowski et al., 2002
230	*p*-terphenyl	0.01	0.02	0.08	0.01	Marynowski et al., 2001
244	4-phenyldibenzo[*b,d*]furan	0.03	0.24	n.f.	n.f.	Marynowski et al., 2002
244	2-phenyldibenzo[*b,d*]furan	0.02	0.12	n.f.	n.f.	Marynowski et al., 2002
244	3-phenyldibenzo[*b,d*]furan	0.05	0.13	n.f.	n.f.	Marynowski et al., 2002
254	1,2′-binaphthyl	0.05	0.05	0.06	n.f.	Rospondek et al., 2009
254	9-phenylphenanthrene	0.02	0.07	0.16	0.02	Rospondek et al., 2009
254	1-phenylphenanthrene	0.01	0.05	0.03	0.01	Rospondek et al., 2009
254	3-phenylphenanthrene	0.17	0.14	0.44	0.06	Rospondek et al., 2009
254	2,2′-binaphthyl	0.22	0.08	0.17	0.05	Rospondek et al., 2009
254	2-phenylphenanthrene	0.11	0.09	0.25	0.05	Rospondek et al., 2009
Oxygen-containing aromatic compounds						
168	dibenzofuran	n.f.	0.03	2.97	3.79	Radke et al., 2000
182	benzophenone	n.f.	0.05	n.f.	n.f.	MS
180	9H-fluoren-9-one	n.f.	0.38	0.45	n.f.	MS
182	4-methyldibenzofuran	n.f.	0.01	1.55	2.41	Radke et al., 2000
182	2- + 3-methyldibenzofuran	n.f.	0.01	2.67	3.29	Radke et al., 2000
182	1-methyldibenzofuran	n.f.	0.01	1.12	1.22	Radke et al., 2000
196	dimethyldibenzofurans[2]	n.f.	0.58	10.4	15.6	MS
210	trimethyldibenzofurans[2]	n.f.	0.50	7.90	8.03	MS
194	anthrone and/or phenanthrone isomers (at least 4 isomers)	0.01	0.10	0.33	n.f.	MS
196	xanthone	n.f.	n.f.	0.88	n.f.	MS
208	9,10-anthracenedione	0.01	0.06	0.07	n.f.	MS
204	cyklopenta[*def*]phenanthrenone	n.f.	0.37	n.f.	n.f.	MS
218	benzo[*b*]naphtho[2,1-*d*]furan	0.13	1.64	2.22	0.47	MS
218	benzo[*b*]naphtho[1,2-*d*]furan	0.11	0.97	1.82	0.21	MS
218	benzo[*b*]naphtho[2,3-*d*]furan	0.20	0.80	1.33	0.15	MS
218	benzo[*k*]xanthene	0.02	n.f.	0.71	0.06	MS
232	methyl derivatives of m/z 218[2]	0.20	0.75	12.2	0.64	MS
230	11*H*-benzo[*a*]fluoren-11-one	n.f.	1.78	2.15	n.f.	Wilkes et al., 1998
230	7*H*-benzo[*c*]fluoren-7-one	n.f.	0.23	0.35	n.f.	Wilkes et al., 1998
230	11*H*-benzo[*b*]fluoren-11-one	n.f.	0.24	1.85	n.f.	Wilkes et al., 1998
258	benzobisbenzofurans (4 isomers)[2]	1.15	2.00	2.40	n.f.	MS
230	benzanthrone	n.f.	0.03	n.f.	n.f.	Spitzer and Takeuchi, 1995
258	benz[*a*]anthracene-7,12-dione	n.f.	0.11	n.f.	n.f.	MS
242	naphtho[2,1,8,7-*klmn*]xanthene	0.57	0.67	n.f.	0.81	MS
268	dinaphthofurans and benzophenanthrofurans (c.a. 7 isomers)[2]	8.64	3.05	6.89	5.03	MS
280	dibenzanthrones and/or benzochrysenones[2]	n.f.	0.57	n.f.	n.f.	MS

[1] Concentrations in μ*g*/*g TOC*

[2] Calculated as sum of all isomers

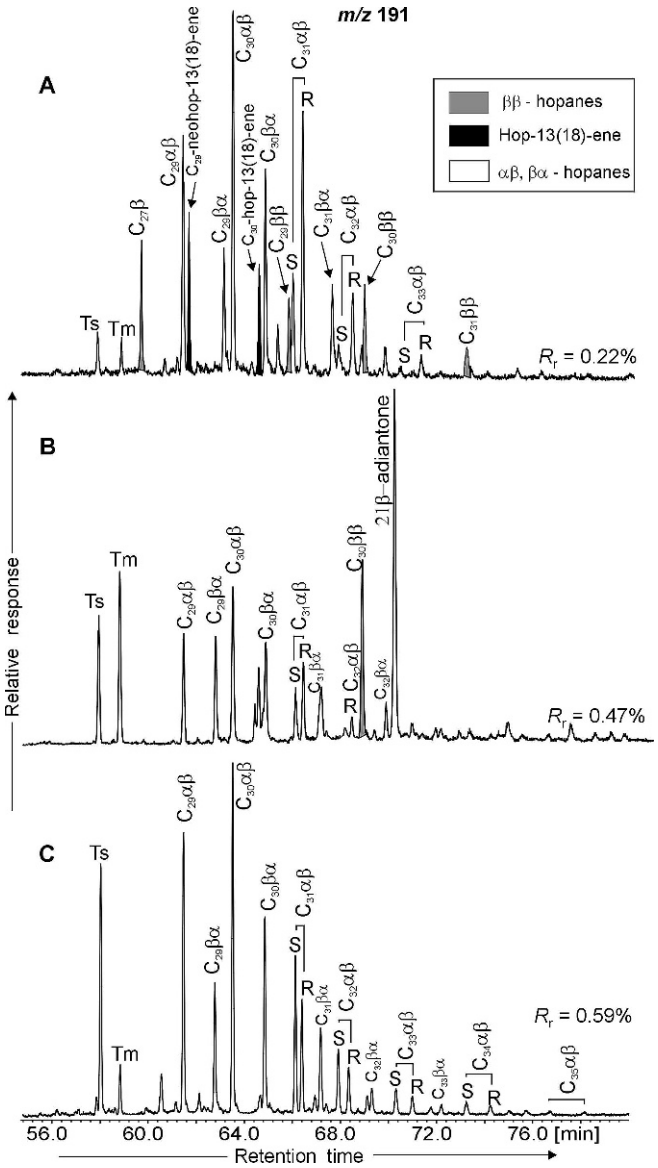

FIGURE 4—Partial *m/z* 191 mass chromatograms for extracts of sample numbers Lipie CC (A), Gromadzice GroZ4 (B), Sołtyków M25 (C), showing the different distributions of pentacyclic triterpenoids.

early stages of diagenesis (Fig. 3C–E). In some fragments open cellular spaces are completely filled with calcite (Fig. 3C), but the overall anatomical structure is still preserved. Similar charcoal fragments from the Upper Triassic green-colored sediments of the Chinle Formation in Petrified Forest National Park were described by Jones et al. (2002).

Sołtyków.— Charcoal is present throughout the section, in sandstones, siltstones, and mudstones. Charcoal fragments from sandstones usually are large, angular, and range from ~1 mm to ≤5 cm in size (Fig. 2A); they are well preserved, with discernible anatomical preservation in many fragments (Fig. 3A–B). Charcoalified fragments from the other lithological types are smaller and less numerous.

Lower Gromadzice Exposure.—Fossil charcoal is most frequent in the lower part of the crevasse splays and upper part of floodplain depositional subsystems (Pieńkowski, 2004). Similar to the Sołtyków locality, charcoals in the sandstones are large, angular, and range from ~1 mm to ≤5 cm (Fig. 2B). They are generally poorly preserved, crushed, and partially coalified, but their anatomy is still identifiable (Fig. 3F).

Upper Gromadzice Exposure.— Charcoal fragments are found only in the lower part of the section (samples GroZ2A to GroZ4). They are small, from ~1 mm to 1–2 cm, angular, and occur singly in the rock matrix. Fragments are usually crushed (Fig. 3G) and rarely somewhat well preserved (Fig. 3H).

Podole Quarry.— Charcoal fragments are found in all samples, but the section is most enriched in the upper part (PDDM1, PDDM2). As is the case for the upper Gromadzice exposure, the charcoal fragments are small, from ~1 mm to 1 cm, angular, and are placed singly in the rock matrix (Fig. 2D). The fragments are usually flattened, but their plant anatomy is still identifiable.

Kamień Pomorski IG-1 Borehole.—Due to the small pieces of core samples, reliable macroscopic observations were not possible with this material. SEM observations of the 5PIE sample show the presence of many poorly preserved and crushed, angular charcoal fragments.

Reflectance of Vitrinite and Fusinite

Vitrinite reflectance values are rather homogeneous for all samples analyzed and exhibit a relatively narrow range. The average R_r values differ between samples and range from 0.47% to 0.59% (Table 1) for the Lower Jurassic samples from the Holy Cross Mountains and up to 0.22% (Table 1) for the Upper Triassic Lipie Śląskie site from the upper Silesian Basin. Fusinite fragments show a wide range of values, but averages are significantly higher than those of vitrinite (Table 1). Calculated temperatures of charcoal formation, based on the formula presented by Jones and Lim (2000), range from ~240 to 520 °C for the Gromadzice and Lipie samples and from 275 to 595 °C for the Sołtyków sample.

Organic Geochemistry

Bulk Data.—The samples contain different amounts of total organic carbon (TOC; see Supplementary Data[1]), depending on facies differences (Pieńkowski, 2004) and, in the case of sandstones deposited in crevasse splay and lacustrine delta facies, on the charcoal amount and secondary processes. The distributions of *n*-alkanes are typical for terrestrial organic matter (OM) with a predominance of high molecular-weight *n*-alkanes with an odd carbon number preponderance (especially n-C_{25}, n-C_{29}, n-C_{31}) (e.g., Eglinton and Hamilton, 1967). The distributions of hopanes are also characteristic for terrestrial OM deposited in rather oxic conditions with low relative concentrations of C_{33}–C_{35} αβ-homohopanes (Peters et al., 2005). Some of the samples have triterpenoids ranging only from C_{27} to C_{31} (Fig. 4B) with distribution patterns analogous to those of smoke particles from biomass burning or immature coals (Oros and Simoneit, 2000; Abas et al., 2004). This provides possible supporting evidence for biomarker tracers from burning processes preserved in these sediments. Furthermore, the presence of 21β-adiantone (17β(H),21α(H)-29-norhopan-22-one, Fig. 4B) may also indicate such an origin. The hopanes reflect the differences in OM maturity of the particular samples. For example, the Lipie CC sample, with its low maturity (R_r = 0.22%, Table 1), contains hopanes and hopenes with a biological configuration, e.g., ββ-hopanes and hop-13(18)-enes (Fig. 4A). These thermally less-stable compounds are not found in the more mature samples from Gromadzice and Sołtyków (Fig. 4C).

Polycyclic Aromatic Hydrocarbons (PAHs).—Unsubstituted PAHs are used extensively as wildfire indicators in environmental and sedimentary rock samples due to their pyrolytic origin (Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Kruge et al., 1994; Jiang et al., 1998; Arinobu et al., 1999; Finkelstein et al., 2005; Marynowski and Filipiak, 2007). Some PAHs may also originate from algal OM (Grice et al., 2007); hydrothermal petroleum (Kawka and Simoneit 1990;

[1] www.paleo.ku.edu/palaios

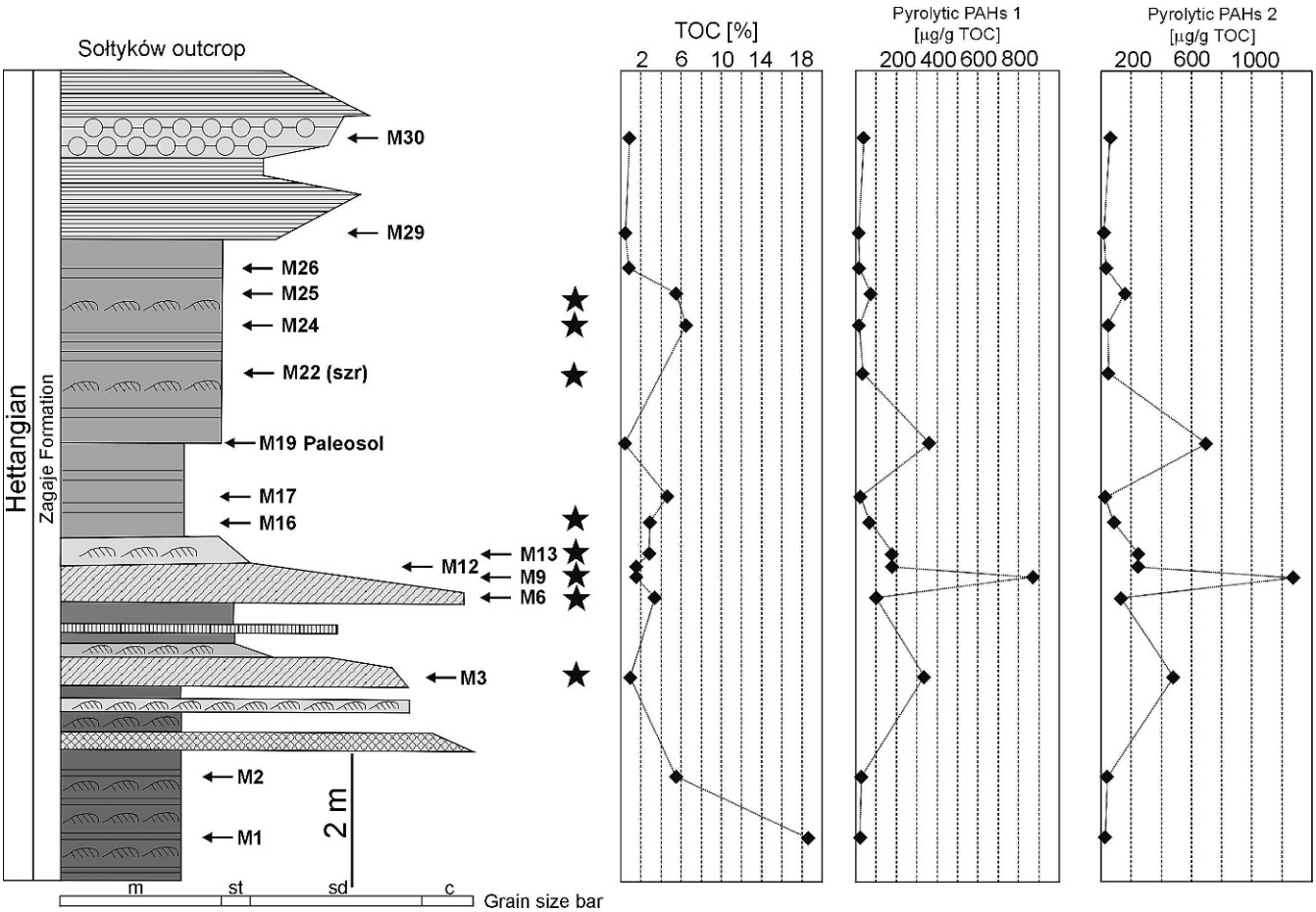

FIGURE 5—Composite plot of the Sołtyków section showing bulk TOC and PAH data. For detailed lithological explanation, see Pieńkowski (2004). Stars = beds with macroscopic charcoal fragments, c = conglomerate, sd = sandstone, st = siltstone, m = mudstone.

Simoneit and Fetzer 1996); extraterrestrial OM (Basile et al., 1984; Naraoka et al., 2000; Sephton et al., 2005a); pyrolytic processes connected with intrusion contact (George, 1992); higher plants, fungi, and insects (Jiang et al., 2000); and from hydrothermal OM oxidation (Marynowski et al., 2002, 2008; Rospondek et al., 2007). In terrestrial sediments with co-occurring charcoal fragments, however, high concentrations of unsubstituted PAHs are undoubtedly connected with wildfires. In addition to the concentrations of individual, most-typical pyrolytic PAHs (presented as µg/g TOC; see Supplementary Data[1]), we summed the amounts of some characteristic aromatic hydrocarbons with the most appropriate formulas to construct composite pyrolytic PAH curves. The first (PAHs1) is based on data from this study and the second (PAHs2) is adopted from Finkelstein et al. (2005) (see Supplementary Data[1]).

The highest concentrations of PAHs were noted in the lowermost Hettangian Sołtyków section. The most enriched samples have PAHs1 concentrations of >300 µg/g TOC and PAHs2 of >500 µg/g TOC (see Supplementary Data[1], Fig. 5), but PAHs are important constituents of the OM and co-occur with charcoal in all sections. The distribution of PAHs in the Sołtyków section differs among samples; the major identified compounds in most samples are: phenanthrene, 2-phenylnaphthalene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, triphenylene, benzofluoranthenes, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, and coronene with more or less intense methyl derivatives of the respective compounds (see Supplementary Data[1], Fig. 6B). Quantitatively, the most important compounds in this section are phenanthrene (1.88–449.15 µg/g TOC), benzo[*ghi*]perylene (0.32–517.48 µg/g TOC), pyrene (0.64–342.54 µg/g TOC), and benzo[*e*]pyrene (0.27–285.14 µg/g TOC) (see Supplementary Data[1]). Some samples, however, almost exclusively contain high molecular-weight PAHs, with benzo[*e*]pyrene, benzo[*ghi*]perylene, and coronene predominant (Fig. 6A). This is characteristic for the single paleosol sample from the Sołtyków section (M19) and is probably connected with dissolution, oxidation, and migration of low molecular-weight PAHs by meteoric waters (Kawka and Simoneit, 1990). Such processes can lead to the concentration of less-soluble, high molecular-weight PAHs in paleosol samples. This is a good example of early diagenetic differentiation of PAHs and shows that the distribution of wildfire-derived PAHs in sediments does not depend solely on combustion temperature (e.g., Arinobu et al., 1999).

It is potentially possible that elevated PAH concentrations in the lowermost Hettangian Sołtyków samples may be derived from activity in the central Atlantic Ocean Large Igneous Province (Coffin and Eldholm, 1992)—for example, via magmatic intrusions into organic-rich rocks and thermogenesis (van de Schootbrugge et al., 2009). However, the co-occurrence of charcoal and PAHs, differences in PAH concentrations through the section, and aromatic compound distributions with higher plant biomarkers (cadalene and retene) typical of biomass burning (Ramdahl, 1983; Simoneit, 2002), excluded such a possibility.

In the lower Gromadzice exposure, the general distribution of PAHs is similar to the Sołtyków section, but concentrations are generally lower (see Supplementary Data[1]). Only one sample (Grom Pc) is characterized by elevated PAH1 and PAH2 values (see Supplementary Data[1]) comparable to samples from the upper part of the Sołtyków section (M22–M30, Fig. 5).

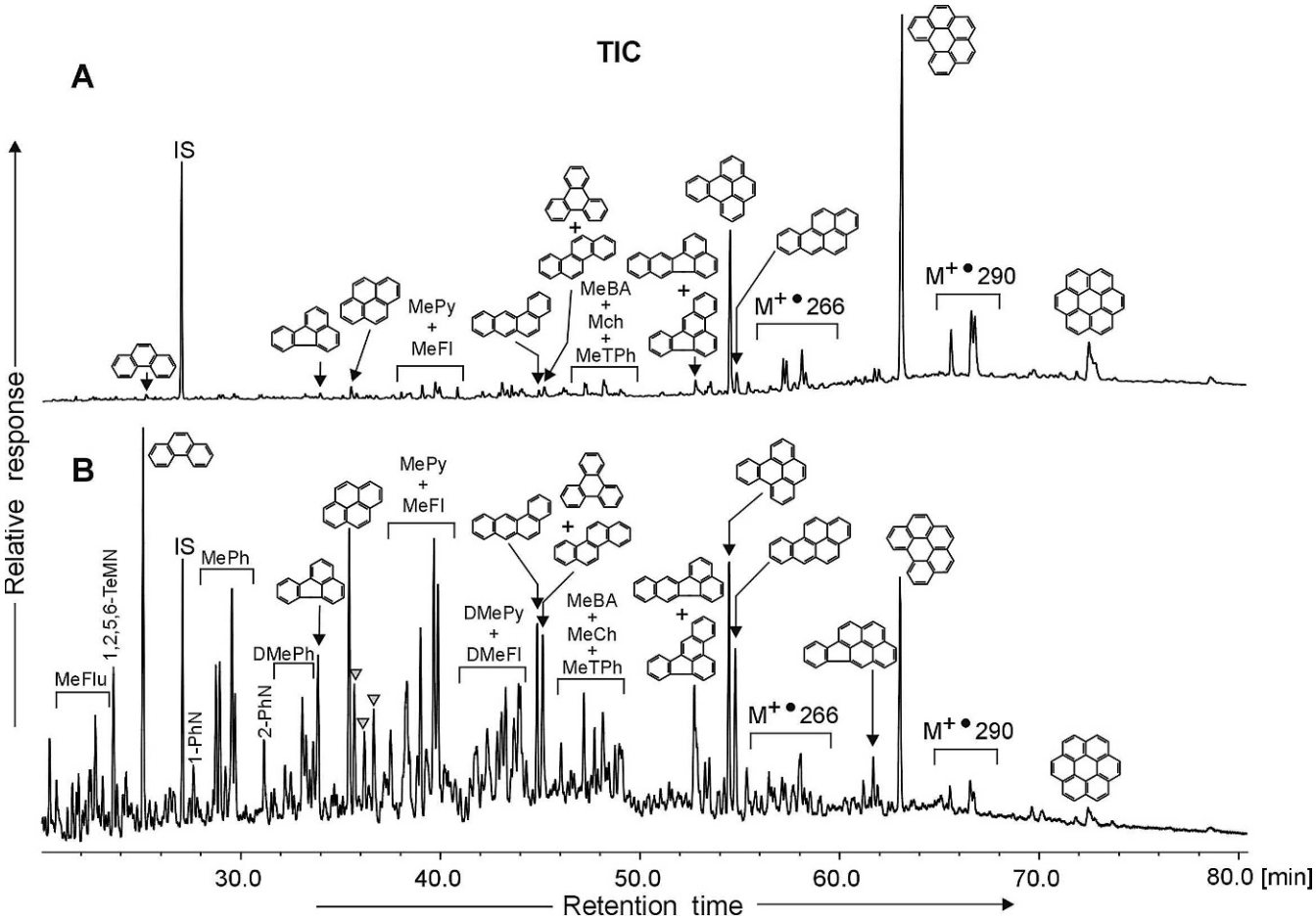

FIGURE 6—Total ion current (TIC) traces of aromatic fractions for Sołtyków samples, M19 paleosol (A) and M6 (B), showing high concentrations of unsubstituted PAHs; a DB-5MS column was used. Triangles = benzo[*b*]naphthofuran isomers (i.e., MeFlu = methylfluorenes, TeMN = tetramethylnaphthalene, PhN = phenylnaphthalene, MePh = methylphenanthrenes, DMePh = dimethylphenanthrenes, MePy = methylpyrenes, MeFl = methylfluoranthenes, DMePy = dimethylpyrenes, DMeFl = dimethylfluoranthenes, MeBA = methylbenz[*a*]anthracenes, MeCh = methylchrysenes, MeTPh = methyltriphenylenes); IS = internal standard.

Detailed analysis of the lower Gromadzice exposure (Fig. 7) shows elevated concentrations of PAHs in the lower part of the section (i.e., samples GroZ3 and GroZ4). The high PAH concentrations co-occur with microscopic charcoal fragments that were found only in this part of the section. PAH levels in these charcoal-bearing samples are generally much lower than in the Sołtyków samples (see Supplementary Data[1]). The remaining sections have only trace amounts of PAHs, even those enriched in TOC (Fig. 7; see Supplementary Data[1]). The PAH distribution is also different from that characteristic of the Sołtyków samples. Quantitatively, the most important compounds are benzofluoranthenes (4.34–9.03 μg/g TOC), benzo[*e*]pyrene (2.42–3.56 μg/g TOC), and benzo[*ghi*]perylene (0.70–2.15 μg/g TOC) (see Supplementary Data[1]). In comparison to the Sołtyków paleosol sample, however, those from Gromadzice contain many three- and four-ring PAHs (Fig. 8A–8B; Fig. 6A) and oxygen-containing aromatic compounds (see below).

Five samples from the Podole profile, collected from the levels with macroscopic charcoal, also contain elevated concentrations of unsubstituted PAHs (see Supplementary Data[1]). Their ranges and distributions are similar to those in the upper Gromadzice, with a predominance of benzofluoranthenes (2.51–6.26 μg/g TOC), benzo[*e*]-pyrene (0.59–1.85 μg/g TOC) and benzo[*ghi*]perylene (0.45–1.68 μg/g TOC), and an exceptionally high concentration of four-ring chrysene and triphenylene (see Supplementary Data[1]).

The only sample analyzed from the Lipie Śląskie pit contains relatively low concentrations of PAHs, within the range of those samples from the upper Sołtyków, Gromadzice, and Podole sections (see Supplementary Data[1]). The most abundant are low molecular-weight PAHs: phenanthrene (8.18 μg/g TOC), fluoranthene (4.1 μg/g TOC), and pyrene (5.68 μg/g TOC). High molecular-weight PAHs do not exceed 2 μg/g TOC, with the highest concentrations noted for benzo[*ghi*]perylene (1.97 μg/g TOC) and coronene (1.85 μg/g TOC, see Supplementary Data[1]).

The Kamień Pomorski IG 1 well profile includes both Upper Triassic and Lower Jurassic rocks. Almost all samples have elevated concentrations of PAHs; however, the Rhaetian sample KP5 and samples from the T–J boundary (KP9.2–KP10.2, see Supplementary Data[1], Fig. 9), as well as two Hettangian samples (KP11–KP12, see Supplementary Data[1]; shaded areas in Fig. 9), obviously differ from the others. The PAH concentrations in these samples are significant and range from ~17 to 32 μg/g TOC for PAHs1 and from ~24 to 111 μg/g TOC for PAHs2. In both Upper Triassic and Lower Jurassic samples, the low and high molecular-weight PAHs are present in similar concentrations (see Supplementary Data[1]), with phenanthrene, fluoranthene, pyrene, and benzo[*ghi*]perylene most abundant.

It is difficult to unambiguously determine a background PAH level for samples in which PAHs are not derived from wildfires, due to the secondary processes affecting PAH distributions and concentrations. Based on the occurrences of charcoal and the PAH concentrations and distributions in this set of samples, the approximate value characteristic for the non-charred OM PAHs1 parameter is <3 μg/g TOC and for the PAHs2 parameter, <4 μg/g TOC (see Supplementary Data[1]).

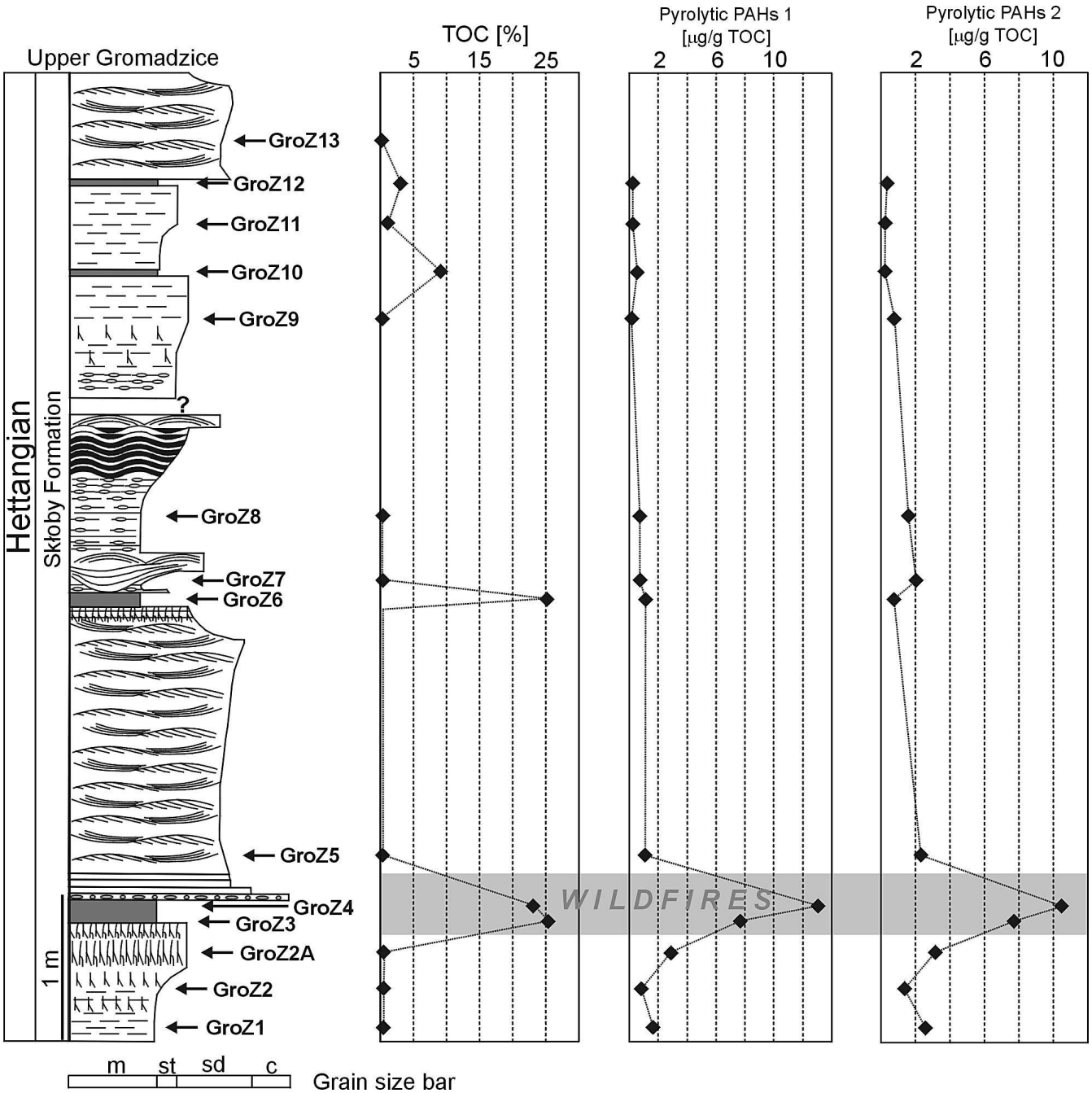

FIGURE 7—Composite plot of the upper Gromadzice section showing bulk TOC and PAH data; for detailed lithological explanation, see Pieńkowski (2004); c = conglomerate, sd = sandstone, st = siltstone, m = mudstone.

Other Polycyclic Aromatic Compounds (PACs).—Phenyl (Ph) and naphthyl derivatives of polycyclic aromatic compounds are present in charcoal-bearing sedimentary rocks (Fig. 10); these PAC derivatives comprise 1- and 2-phenylnaphthalene; *o*-, *m*-, and *p*-terphenyls (Marynowski et al., 2001); phenylphenanthrenes and binaphthyls (Rospondek et al., 2009); and phenyldibenzofurans (Marynowski et al., 2002). Their concentrations are usually about twenty times lower than unsubstituted PAHs, but they are characteristic for all samples with elevated PAH concentrations and are absent in the others. Although Ph derivatives of PAHs in rocks typically originate from phenyl radical phenylation of the corresponding unsubstituted aromatic moieties during kerogen oxidation (Marynowski et al., 2002; Rospondek et al., 2007, 2009), they are also detectable in ambient air particles (e.g., Tong and Karasek, 1984; Aceves and Grimalt, 1992; Marynowski et al., 2004; Ré-Poppi and Santiago-Silva, 2005; Wang et al., 2007), suggesting their alternative, pyrolytic origin. In our samples the thermodynamically more-stable *β*-, *m*-, and *p*- isomers dominate over the less-stable α- and *o*- isomers, which suggests a pyrogenic, high-temperature origin of the PACs (Marynowski et al., 2001; 2002; Rospondek et al., 2007, 2008, 2009) in immature to low-maturity sedimentary rocks (Table 1; Fig. 4). Some less stable isomers, such as *o*-terphenyl, 4-phenylphenanthrene, or 1,1′-binaphthyl, sometimes occur as traces in these samples.

Another widespread group of PACs that are found in most of the samples are oxygen-containing aromatic compounds. The most common are furans, including dibenzofuran, methyldibenzofurans, dimethyldibenzofurans, trimethyldibenzofurans, benzo[*b*]naphthofurans (Fig. 11; Table 2), dinaphthofurans, and benzobisbenzofurans

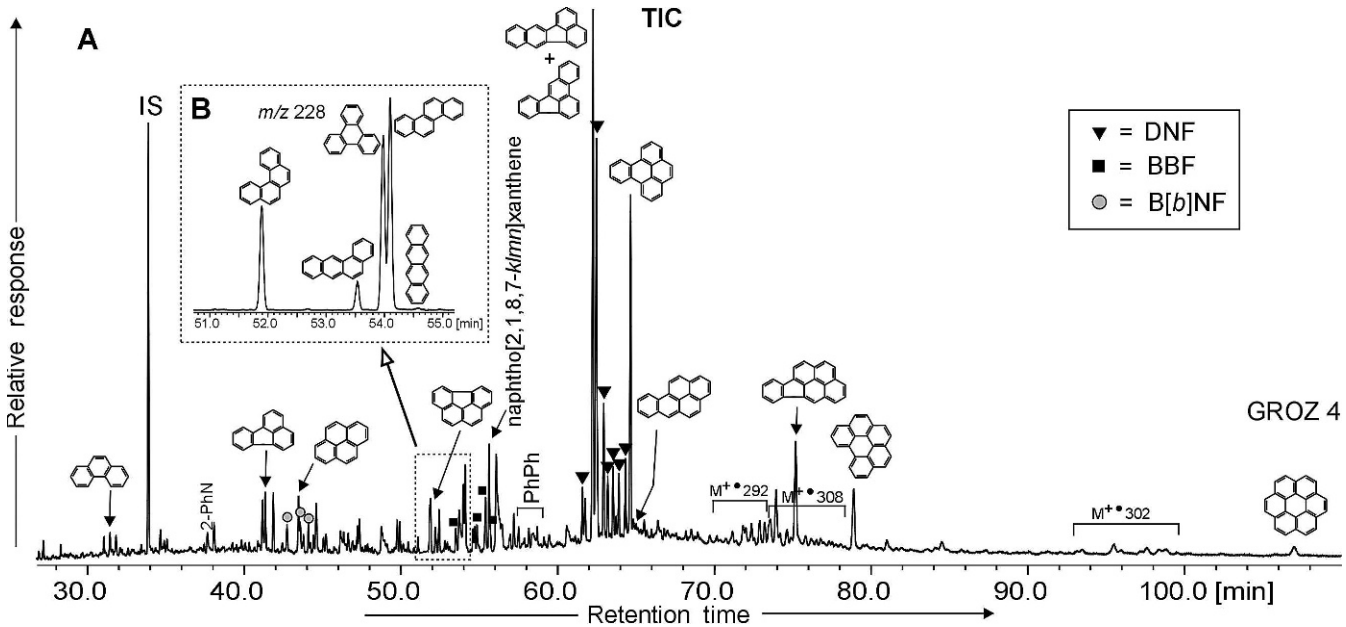

FIGURE 8—TIC trace (A) of the aromatic fraction of sample GroZ4, showing the predominance of high molecular-weight PAHs and high amounts of oxygen-containing aromatic compounds, and (B) partial mass chromatogram for *m/z* 228 of the four-ring PAHs with a distribution typical for combustion processes; a DB-35MS column was used; B[*b*]NF = benzo[*b*]naphthofuran isomers, BBF = benzobisbenzofuran isomers, DNF = dinaphthofuran isomers, PhN = phenylnaphthalene, PhPh = phenylphenanthrene isomers, IS = internal standard.

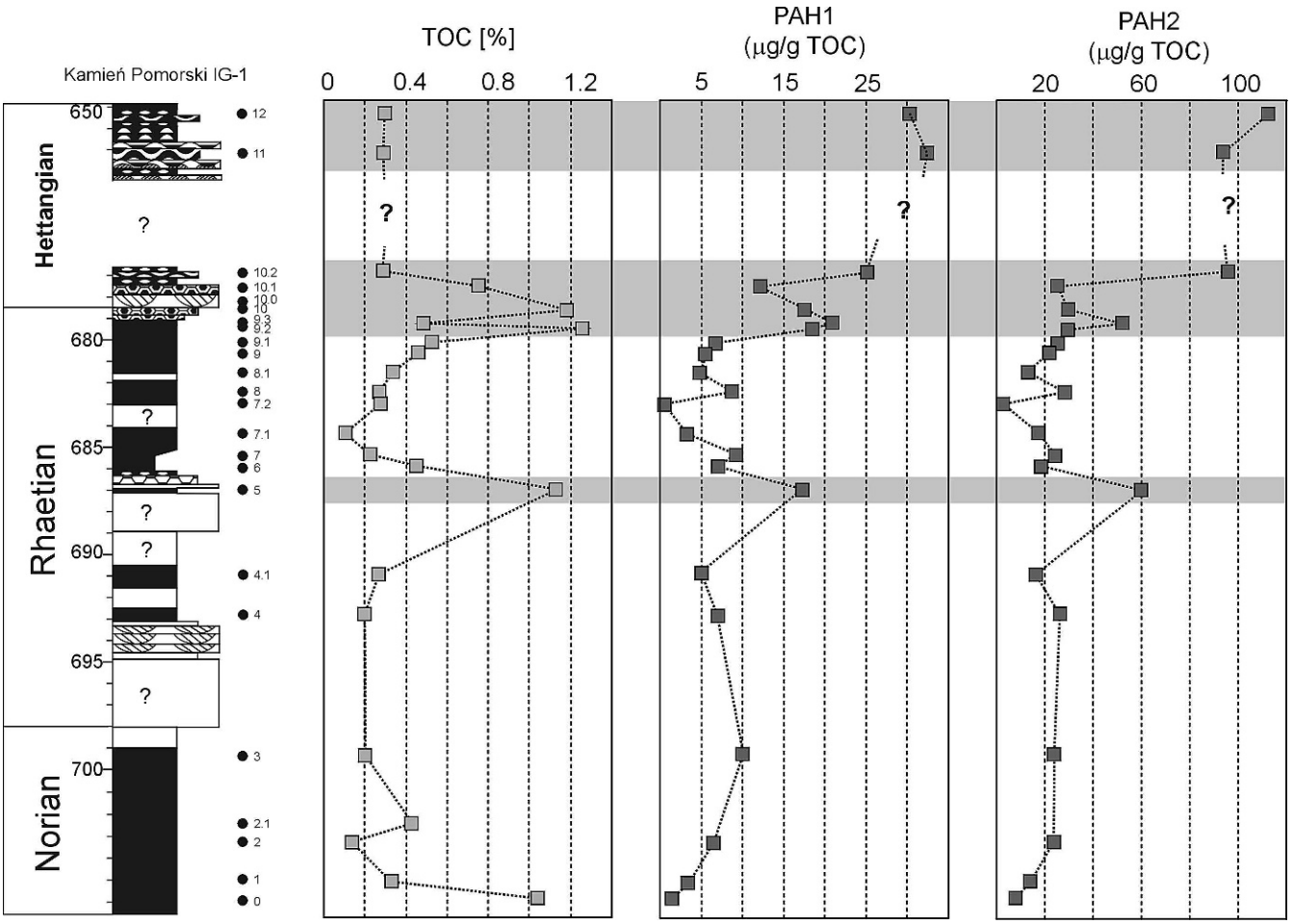

FIGURE 9—Composite plot of the Kamień Pomorski IG1 section showing the bulk TOC and PAH data; for detailed lithological explanation, see Pieńkowski (2004).

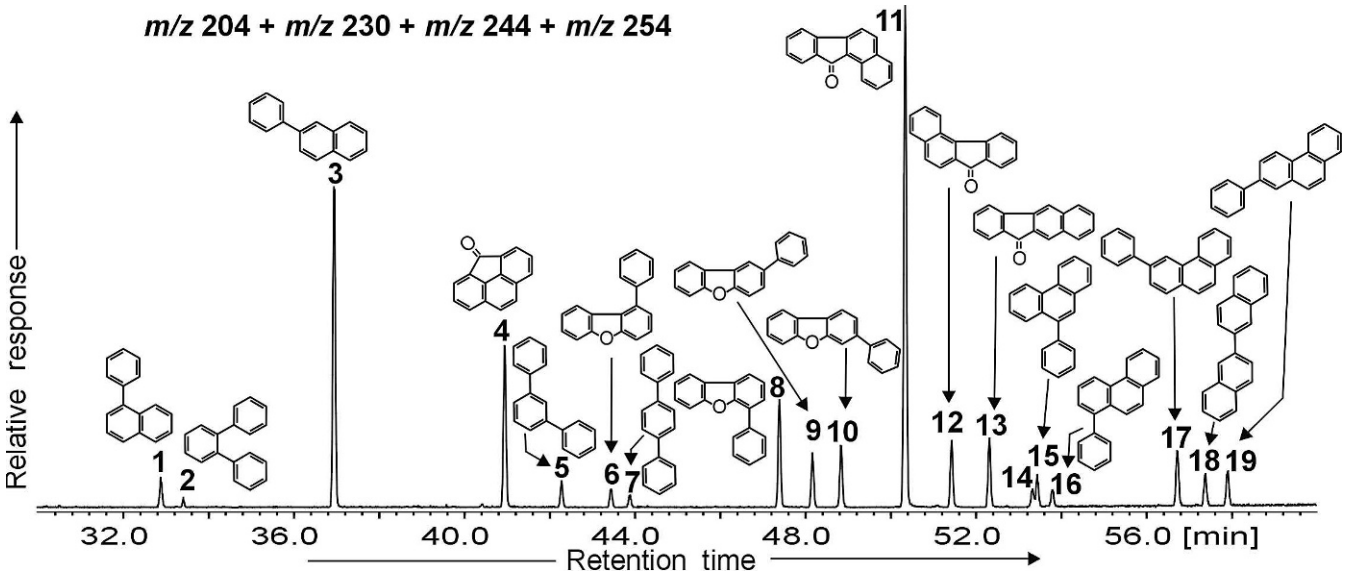

FIGURE 10—Summed mass chromatogram for *m*/*z* 204 + 230 + 244 + 254, showing the distribution of phenyl derivatives of PACs and oxygenated PACs from Podole sample PDDM2; a DB-35MS column was used. 1 = 1-phenylnaphthalene, 2 = *o*-terphenyl, 3 = 2-phenylnaphthalene, 4 = cyclopenta[*def*]phenanthrone, 5 = *m*-terphenyl, 6 = 1-phenyldibenzo[*b,d*]furan, 7 = *p*-terphenyl, 8 = 4-phenyldibenzo[*b,d*]furan, 9 = 2-phenyldibenzo[*b,d*]furan, 10 = 3-phenyldibenzo[*b,d*]furan, 11 = *11*H-benzo[*a*]fluoren-11-one, 12 = *7*H-benzo[*c*]fluoren-7-one, 13 = *11*H-benzo[*b*]fluoren-11-one, 14 = 1,2′-binaphthyl, 15 = 9-phenylphenanthrene, 16 = 1-phenylphenanthrene, 17 = 3-phenylphenanthrene, 18 = 2,2′-binaphthyl, 19 = 2-phenylphenanthrene.

(Fig. 8; Table 2). Dibenzofurans and similar oxygen-containing aromatic compounds have been proposed to be derived from terrestrial OM (Watson et al., 2005; Sephton et al., 1999, 2005b; Wang and Visscher, 2007), but it is difficult to determine if these compounds formed during thermal decomposition of OM or from unburned terrestrial material. Benzo[*b*]naphthofurans, dinaphthofurans, and benzobisbenzofurans are usually present in these samples, while lower molecular-weight compounds, such as dibenzofuran and its methyl derivatives, are sometimes absent (Table 2), most probably due to water washing processes.

Other oxygenated polycyclic aromatic hydrocarbons (Oxy-PAHs) identified in some samples are represented by fluoren-9-one; benzophenone, anthracene-9,10-dione; cyclopenta[*def*]phenanthrone; three isomers of benzofluorenones (Fig. 10, peaks 11–13); and benz[*a*]anthracene-7,12-dione (Table 2). Some of these compounds were reported from sedimentary organic matter (Wilkes et al., 1998), but they are typical products of incomplete OM combustion and are common in air particulate matter (Allen et al., 1997; Marynowski et al., 2004; del Rosario Sienra, 2006).

Based on mass spectra we tentatively identified naphtho[2,1,8,7-*klmn*]xanthene ($M^{+\bullet}$ = 242) and a group of compounds with molecular ion $M^{+\bullet}$ = 292 (Fig. 8), suggesting one ortho-ring addition ($M^{+\bullet}$ = 242 + 50) to the naphtho[2,1,8,7-*klmn*]xanthene moiety. It appears that the same process is responsible for the formation of compounds with $M^{+\bullet}$ = 308 (Fig. 8). These are benzobisbenzofurans ($M^{+\bullet}$ = 258) with addition of one ortho ring. For more details on the formation mechanism see Sullivan et al. (1989) and Simoneit and Fetzer (1996). Naphtho[2,1,8,7-*klmn*]xanthene is found in samples GroZ3 and GroZ4 from the upper Gromadzice exposure (Fig. 8) and in some samples from the Podole and Kamień Pomorski sections. It is a minor

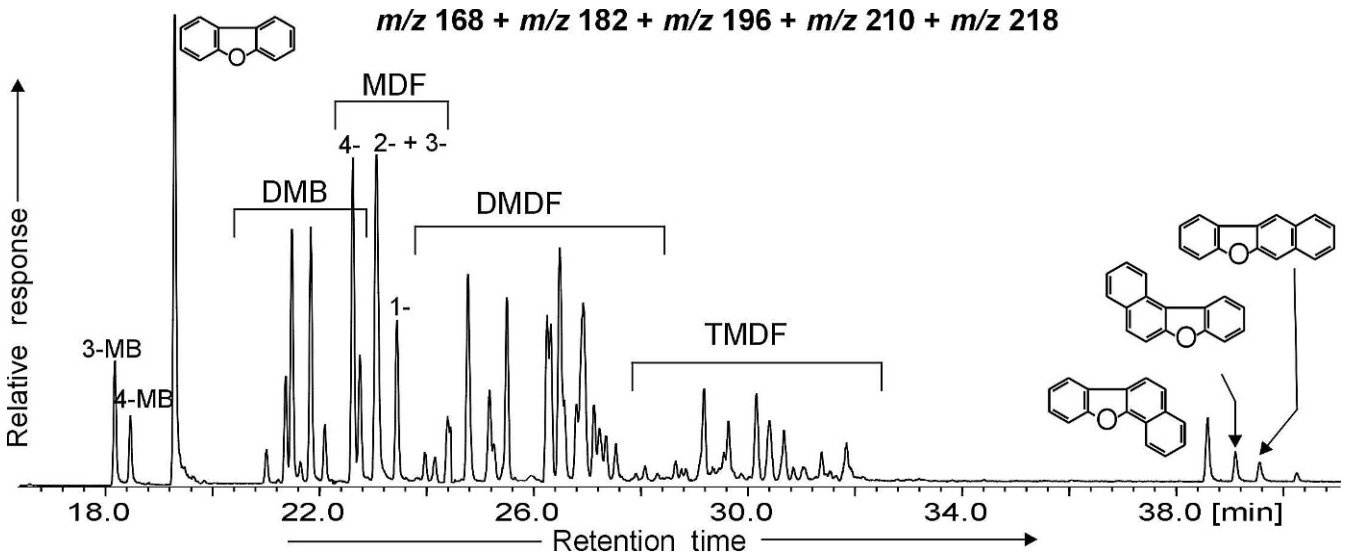

FIGURE 11—Summed mass chromatogram for *m*/*z* 168 + 182 + 196 + 210 + 218, showing the distribution of dibenzofuran and its methyl derivatives, as well as benzo[*b*]naphthofurans in sample KP5; a DB-5MS column was used. MB = methylbiphenyl, DMB = dimethylbiphenyl, MDF = methyldibenzofurans, DMDF = dimethyldibenzofurans, TMDF = trimethyldibenzofurans.

constituent of the aromatic fraction (Fig. 8) with concentrations varying from 0.24 to 0.81 μg/g TOC. Concentrations of each individual $M^{+}\bullet$ 292 isomer are even lower (Fig. 8). The absence of the corresponding aromatic thiophenes (e.g., dibenzothiophene, naphthobenzothiophenes), common in crude oils and anoxic sediments, coupled with the enhanced concentrations of the aromatic furans, further supports the pyrogenic origin of the aromatic furans.

Implications of Results

Transport and Taphonomy of Charcoals.—It is well known that charcoal fragments >200 μm are usually transported via hydraulic flow and not by wind (e.g., Collinson et al., 2007). A recent report, however, showed that intensive crown fires cause long-distance transport of macroscopic (≤1.3 cm) charcoal fragments (Tinner et al., 2006). For all sites described here, the charcoal fragments are significantly >200 μm. They are characterized by sharp, angular shapes that may suggest transport over rather short distances after charcoalification. Moreover, all macroscopic charcoal fragments occur in typically fluvial, meandering river depositional systems (Figs. 2, 5; Pieńkowski, 2004), indicating that the charcoals were incorporated into the sediments after a relatively short transport.

In the instance of the Sołtyków or lower Gromadzice charcoal-bearing sandstones, the plant fossils commonly consist exclusively of charcoal fragments. Therefore, it is possible that degradation processes, such as biodegradation and oxidation, occurred during the early stages of diagenesis and removed the less-resistant higher-plant remains, but were insufficient to degrade the more resistant charcoal (Jones et al., 2002). At other sites (Lipie Śląskie, upper Gromadzice, Kamień Pomorski) and in facies with less-extensive oxidation—for example, alluvial plain or muddy nearshore facies—charcoal occurs together with plant fossils.

Types of Wildfires.—The charred wood fragments from our samples are semifusinites and formed at relatively low temperatures, based on the definition of Scott and Glasspool (2007). On the basis of inertinite reflectance measurements, these temperatures are calculated to have been 295–377 °C (Table 1). This suggests that the charcoal formed in lower-temperature, ground or surface fires (Jones and Lim, 2000; Scott, 2000), which only sporadically reached the crown (highest values in the Sołtyków exposure). It is interesting that the highest temperatures noted for the Sołtyków exposure correlate with the highest PAH concentrations (see Supplementary Data[1], Table 2). This may suggest that the most intensive wildfires took place in the earliest Jurassic (Sołtyków) and that their intensity decreased with time (lower Gromadzice–upper Gromadzice–Podole see also Kamień Pomorski section).

During the Late Triassic, the only definite evidence of wildfire—one sample in the Kamień Pomorski and one in the Lipie Śląskie section—suggests that wildfires burned at lower temperatures (Table 1) and were rather sporadic (Fig. 9; see Supplementary Data[1]). Other, previously analyzed Upper Triassic sections from Poland did not reveal evidence for wildfires (Marynowski and Wyszomirski, 2008), probably due to oxidation and decay of the organic matter. However, unoxidized Upper Triassic green shales from other Polish sites (e.g., Zawiercie and Poręba) do contain charcoal fragments (Marynowski, unpublished data, 2009).

CONCLUSIONS

The presence of charcoal fragments and high concentrations of pyrolytic PAHs in two Upper Triassic and five Lower Jurassic sedimentary sections provides evidence for wildfires in the region of Poland during these time periods. The highest fire temperatures coupled with the highest PAH concentrations were found in the lowermost Jurassic and both factors successively decrease with time. The wildfires occurred on the ground or near the surface and charred wood fragments were subsequently incorporated into sediments by river transport over short distances.

Aside from the high concentrations of PAHs, the charcoal-bearing samples also contain many rarely identified compounds, including phenyl-polycyclic aromatic compounds (Ph-PACs) and oxygen-containing PACs. The prevalence of the more stable Ph-PAC isomers in the immature to low-maturity sedimentary rocks supports their pyrolytic and not diagenetic origin. The oxygenated PACs may also be derived from combustion processes, but an origin from unburned terrestrial material could not be ruled out.

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