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Perylene as an indicator of conifer fossil wood degradation by wood-degrading fungi

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ABSTRACT

The occurrence of perylene in Middle Jurassic fossil wood and Miocene xylites from Poland is described, along with its correlation with unsubstituted polycyclic aromatic hydrocarbons (PAHs) as well as cellulose content. Both Middle Jurassic and Miocene wood remnants were of relatively low maturity [ca. 0.2–0.3% vitrinite reflectance (R_r)], had excellent preservation of biomarkers and biomolecules and, in the case of the Middle Jurassic fossil wood samples, generally good preservation of anatomical structures due to early diagenetic mineralisation. The results from 42 Middle Jurassic and 8 Miocene (most taxonomically defined) fossil wood fragments demonstrated a negative correlation between the concentration of perylene and those of generally typical conifer biomarkers (e.g. cadalene, dehydroabietane, simonellite and retene). In addition, good correlation (R^2 0.81) was observed between the ratio of perylene to the above conifer biomarkers and the ratio of PAHs (phenanthrene and fluoranthene and pyrene) to the conifer biomarkers. This implies that the high concentration of perylene in fossil wood indicate its extensive degradation during decay, transport and early diagenesis. We defined a *conifer wood degradation index* as:

$$\mathrm{CWDI} = \mathrm{perylene}/(\mathrm{perylene} + \mathrm{cadalene} + \mathrm{retene} + \mathrm{simonellite} + \mathrm{dehydroabietane}),$$

and observed a wide range of values (0.001 for less degraded wood to 0.95 for highly degraded samples). Anatomical wood preservation was associated with CWDI values. In most of the samples characterised by poorly preserved anatomy, high CWDI values were observed, while anatomically well-preserved samples generally had lower CWDI values. We determined similar $\delta^{13}C$ values for perylene from the fossil wood samples (−26.4% to −27.8%), whereas the values for the conifer biomarkers were slightly higher and varied from −25.6% to −26.6%. In contrast, pyrene was depleted in ^{13}C (−27.5% to −28.2%). The carbon isotope values of perylene are consistent with an origin from wood-degrading fungi.

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1. Introduction

Perylene is especially common in immature/low maturity organic matter (OM), largely of terrestrial origin (e.g. Aizenshtat, 1973; Golovko et al., 1999; Jiang et al., 2000). It has been found in diverse recent environments, such as marine (e.g. Orr and Grady, 1967; Wakeham et al., 1979) and terrestrial sediments (Hodgson et al., 1968; Itoh and Hanari, 2010), including peats (Malawska et al., 2002, 2006), as well as ancient deposits, including brown coal and hard coal, crude oil and sedimentary rocks (e.g. Louda and Baker, 1984; Bechtel et al., 2007; Jiang and Liu, 2008; Grice et al., 2009; Suzuki et al., 2010; Fan et al., 2011; Marynowski et al., 2011a) and at the extinction interval of the Permian/Triassic boundary of Meishan, China (e.g. Nabbefeld et al., 2010).

Louda and Baker (1984) first related its occurrence to fungal activity, suggesting it was a transformation product of perylene quinone pigments. Later, Jiang et al. (2000) concluded that it was a diagenetic product of perylene quinones and associated derivatives produced by higher plants, fungi and insects, among which fungi seemed to be the most probable source. At the same time, Silliman et al. (1998, 2001) suggested that it was most likely formed due to specific microbial activity during the earliest stages of diagenesis. A recent investigation of its occurrence in Holocene sediments rich in fungal spores, along with isotopic relationships, implicated wood degrading fungi as the main source (Grice et al., 2009). In addition, Suzuki et al. (2010) showed that it was enriched in ^{13}C compared with higher plant markers and proposed that its

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origin was connected with fungi. Itoh and Hanari (2010) obtained diverse ^{13}C isotopic values for it and connected its origin to gymnosperms. However, in very recent work by Itoh et al. (2012), 4,9-dihydroxyperylene-3,10-quinone (DHPQ) was proposed to be the parent compound on the basis of laboratory stepwise transformation of DHPQ. These authors also reported that the major source of DHPQ in Lake Biwa sediments was *Cenococcum geophilum* Fr., an ectomycorrhizal fungus (Ascomycota) associated with some forest tree species. Accordingly, terrestrial OM could be degraded by fungi under aquatic conditions after deposition (Fan et al., 2011; Itoh et al., 2012).

White rot fungi and brown rot fungi are known as the main wood degrading groups of basidiomycetes, preferentially utilising cellulose and hemicellulose (Enoki et al., 1997; Xu and Goodell, 2001), but are also able to decompose lignin, especially in co-cultured groups (Chi et al., 2007). Moreover, brown rot fungi can develop a unique wood-degrading system that can split both cellulose and lignin into metabolisable fragments (Enoki et al., 1997).

Aromatic conifer biomarkers, such as cadalene, dehydroabietane, simonellite and retene, are common constituents of immature fossil wood samples of different ages and taxonomy (e.g. Otto and Simoneit, 2001; Otto et al., 2002; Marynowski et al., 2007a,b; Zdravkov et al., 2011; Sawada et al., 2013; Fabiańska and Kurkiewicz, 2013). They originate from terpenoids as cadinols, abietic acid, hinokione, ferruginol and sugiol, as well as isopimaranes, pimaranes and labdanes, via early diagenetisis, and their concentration decreases with maturity and secondary processes such as weathering (Otto and Wilde, 2001; Otto and Simoneit, 2001; Stefanova et al., 2002; Bechtel et al., 2007; Marynowski et al., 2011a).

Here we link perylene, a product of wood-degrading fungi, to conifer biomarkers in fossil wood material of different ages. On one hand, this could confirm a fungal origin of perylene in ancient sediments and on the other hand the activity of wood-degrading fungi can explain the formation of unsubstituted polycyclic aromatic hydrocarbons (PAHs) in unburned fossil wood fragments.

2. Material and methods

2.1. Samples

In total, 32 taxonomically defined and 10 undefined Middle Jurassic fossil wood samples, and 8 Miocene xylite samples were analysed. Details of sample location and stratigraphic position are given in Table 1. Most of the Middle Jurassic samples were collected from active or closed clay pits in the Polish Jura, Polish Lowland and Lithuania, while the Miocene fossil wood samples were taken from the Lubstów Graben (Polish Lowland) and from the Tarnów Gumniska locality of southern Poland (Klusek, 2013).

The taxonomy was studied with an array of techniques: (i) geologic thin sections (polished face of the sample glued onto glass and ground to the desired thickness), (ii) razor blade thin sections (sample boiled in water and glycerol for 4–5 h and hand cut with a disposable razor blade), (iii) pyroxylin casts (Parlodion® dissolved in isoamyl acetate applied to a radial fracture of the sample, allowed to dry for 24 h and then peeled back) and (iv) scanning electron microscopy (samples mounted on Al stubs, coated with Au/Pd, and observed with a Jeol 35-CF microscope under 10 kV acceleration voltage). Taxonomic determination followed the procedures of Philippe and Bamford (2008).

All the samples were characterised by low maturity [ca. 0.2–0.45% vitrinite reflectance (R_r)], excellent preservation of biomarkers and biomolecules and, for the Middle Jurassic samples, generally good preservation of the anatomical structure as a result of early diagenetic mineralisation by calcite and/or siderite (Bojesen-Koefoed, 1996; Philippe et al., 2006; Bechtel et al., 2007; Marynowski et al., 2007a,b, 2008a,b). It is also important to note that only unweathered wood fragments were selected, on the basis of macro- and microscopic observation (occurrence or lack of goethite; Marynowski et al., 2011a; Smolarek, 2012). Further, detailed geologic information is reported by Bechtel et al. (2007), Klusek, (2013), Matyja and Wierzbowski (2000) and Marynowski et al. (2007a).

2.2. Total organic carbon (TOC) content

The abundance of total carbon (TC) and total inorganic carbon (TIC) were determined with an Eltra CS-500 IR analyzer with a TIC module. Total organic carbon (TOC) was calculated as the difference between TC and TIC. Both TC content and TIC content were measured using an infrared cell detector for the CO_2 evolved by combustion under an O_2 atmosphere for TC, and was obtained from reaction with 50% H_3PO_4 and, in case of siderite, mineralisation with 50% HCl for TIC. Analytical precision and accuracy were better than ± 2% for TC and ± 3% for TIC.

2.3. Extraction and separation

The crushed samples were Soxhlet-extracted in pre-extracted cellulose thimbles with CH_2Cl_2. Extracts were separated using preparative pre-washed TLC plates coated with silica gel (Merck, 20 × 20 × 0.25 cm and 10 × 20 × 0.25 cm). Prior to separation, the plates were activated at 120 °C for 1 h. They were loaded with the *n*-hexane soluble fraction and developed with *n*-hexane. Bands comprising aliphatic (R_f 0.4–1.0), aromatic (R_f 0.05–0.4) and polar (R_f 0.0–0.05) fractions were collected.

2.4. Gas chromatography – mass spectrometry (GC–MS)

GC–MS was performed with an Agilent 6890 Series gas chromatograph interfaced to an Agilent 5973 Network mass selective detector (MSD) and Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). A 0.5 µl aliquot was introduced into the cool on-column injector under electronic pressure control. He (6.0 Grade, Linde, Kraków) was used as carrier gas at a constant flow 2.6 ml/min. Separation was on either of two fused silica columns:

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

(ii) J&W DB35-MS (60 m × 0.25 mm i.d., 0.25 µm film thickness) coated with a chemically bonded phase (35% phenyl, 65% methylsiloxane). The GC oven temperature was programmed from 50 °C (1 min) to 120 °C at 20 °C/min, then to 300 °C (held 45 min) at 3 °C/min. The GC column outlet was connected directly to the ion source of the MSD. The GC–MS interface was at 280 °C, while the ion source and the quadrupole analyzer were at 230 and 150 °C, respectively. Spectra were recorded from *m*/*z* 45–550 (0–40 min) and *m*/*z* 50–700 (> 40 min). The mass spectrometer was operated in the electron impact mode (ionisation energy 70 eV).

2.5. Quantification and identification

An Agilent Technologies MSD ChemStation E.02.01.1177 and the Wiley Registry of Mass Spectral Data (9th edition) software were used for data collection and spectra processing. Abundance

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