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Aromatic hydrocarbons from the Middle Jurassic fossil wood of the Polish Jura

Abstract

Aromatic hydrocarbons are present in the fossil wood samples in relatively small amounts. In almost all of the tested samples the dominating aromatic hydrocarbon is perylene and its methyl and dimethyl derivatives. The most important biomarkers present in the aromatic fraction are dehydroabietane, siomonellite and retene, compounds characteristic for conifers. The distribution of discussed compounds is highly variable due to such early diagenetic processes affecting the wood as oxidation and the activity of microorganisms. MPI_1 parameter values (methylphenanthrene index) for the majority of the samples are in the range of 0.1 to 0.5, which results in the highly variable values of Rc (converted value of vitrinite reflectance) ranging from 0.45 to 0.70%. Such values suggest that MPI_1 parameter is not useful as maturity parameter in case of Middle Jurassic ore-bearing clays, even if measured strictly on terrestrial organic matter (OM). As a result of weathering processes (oxidation) the distribution of aromatic hydrocarbons changes. In the oxidized samples the amount of aromatic hydrocarbons, both polycyclic as well as aromatic biomarkers decreases.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are generated in sedimentary rocks by the complex natural processes including aromatization of the steroids, tricyclic diterpenoids or pentacyclic triterpentenoids (e.g. Radke, 1987). They may also formed as a result of bacteria activity (Wakeham et al., 1980) and due to the influence of temperature on OM in the presence of sulfur and/or clay minerals (Eglinon, Murphy, 1969). Tissot et al. (1971) and Radke (1987) found that a small percentage of aromatic hydrocarbons generated from kerogen is formed from natural precursors without significant structural changes. According to the fact that the organisms do not biosynthesize aromatic structures in large quantities, the presence of PAHs in crude oil and sediments should be the result of complex chemical transformation of natural products, characterized by naphthenic or olefinic structure (Hase, Hites, 1976). This transformation runing in the sediment may be caused by microbial activity in the early stages of diagenesis and subsequent transformation during thermal processes, with the additional influence of pressure and mineral matrix as a catalyst (Radke, 1987). Structural relationship between the natural precursors and aromatic hydrocarbons derived from sedimentary organic matter is not always clear. Natural products during diagenetic processes may, in some cases, significantly change the structure of the precursors leading to alkylation (substitution of hydrogen an alkyl radical), dealkylation (cleavage of the hydrocarbon-containing side chain), isomerization or disruption of alicyclic systems (Radke, 1987). Here we are presenting the composition of aromatic hydrocarbons found in the immature fossil wood from the Middle Jurassic ore-bearing sediments, showing source, distribution and diagenetic transformations of PAHs.

Materials

Samples of the Middle Jurassic fossil wood were taken from the ore-bearing clays of the Polish Jura area. Eighteen fossil wood pieces were sampled from the active clay pits which are located in Czestochowa region: Gnaszyn Wienerberger, Sowa, Anna and near to that city between Grodzisko and Wreczyca Wielka (Grodzisko). Middle Jurassic fossil wood from Czestochowa region is characterized by variable preservation and the type and degree of mineralization (Gut – Kałamaga 2000).

Due to the degree of mineralization wood can be divided into:
• non-mineralized wood fragments (xylite type) and gelified wood (jet type),
• wood fragments partly mineralized,
• wood fragments completely mineralized. Due to the degree of oxidation the following wood types can be distinguished:
• not-oxidized wood fragments,
• partly oxidized wood fragments,
• completely oxidized wood fragments.

Methods

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

Extraction and separation
Samples were Soxhlet-extracted with dichloromethane (DCM) for 48 h in cellulose thimbles. Extracts were further separated using silica gel TLC plates (Merck, 20 x 20 x 0.25 cm). Prior to separation, these plates were activated at 120ºC for 1 h. Plates were then loaded with the DCM extracts and developed with n-hexane. Aliphatic, aromatic and polar fractions were eluted and separated with DCM. The aliphatic fractions of samples were further analysed in details 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).
The detailed description of GC-MS method was made by e.g. Marynowski & Zatoń, (2010).

Results

Aromatic hydrocarbons are present in the tested samples in relatively small amounts, generally not exceeding 40% of all HCs and in most cases ranging between 10 to 25%. Examples of PAHs distribution typical for the most investigated samples are shown in Figures 2, 3, 4. In almost all of the wood samples the dominating aromatic hydrocarbon is perylene and its methyl and dimethyl derivatives (Fig. 3; see also Marynowski et al., 2013). The similar situation was reported from many Miocene brown coals (Fabiańska, 2007). According to our new data, perylene is a product of wood degradation by wood degrading fungi during decay and transportation of the wood (Marynowski et al., 2013; see also Grice et al., 2009; Itoh et al., 2012). In some samples simonellit or retene are the main dominant or the second predominant compounds (Fig. 4). Other quantitatively important unidentified aromatic compounds include the structures with the following molecular ion: $M^+ = 256$ (U1), $M^+ = 394$ (U2), $M^+ = 376$ (U3) (Fig.3) and $M^+ = 364$ (U1), $M^+ = 394$ (U2), $M^+ = 376$ (U3) and $M^+ = 364$ (U4) (Fig.4). Other quantitatively important aromatic compounds are:

• cadalene,
• phenanthrene,
• dehydroabietane,
• simonellite,
• pyrene,
• retene,
• methylpyrenes,
• indeno[1,2,3-*cd*]pyrene,
• benzo[*ghi*]perylene (Figs. 1 – 4).
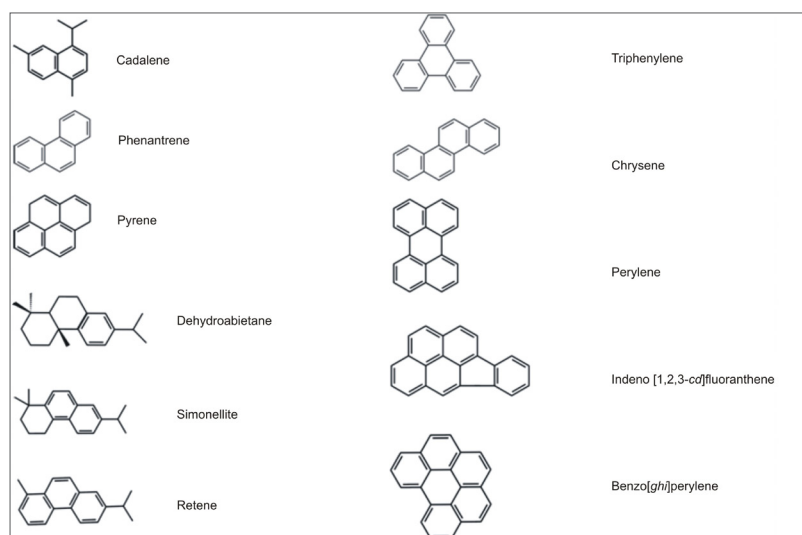
The very important biomarkers present in the aromatic fraction are dehydroabietane, siomonellite and retene. The main precursors of these compounds in the wood samples are most probable ferruginol and sugiol (e.g. Bechtel et al., 2007) - biomolecules characteristic for resinous plant of the genus Cupressaceae, Podocarpaceae and Araucariaceae which are present in polar fraction of the wood (Otto and Wilde, 2001; Otto and Simoneit, 2001; Marynowski et al. 2007b). The distribution of discussed compounds is highly variable (Fig. 2 &. 5, Table 1). Only in one sample (SOW JS7) dehydroabietane dominates accounting for over 60% of the discoursed biomarkers (Fig. 5). In samples SOW JS1 and SOW JS4 dominant compound is retene whereas dehydroabietane accounts for less than 6% (Table 1). Interestingly, wood samples are derived from a very similar stratigraphic intervals, facies and deposits, as well as characterized by the same level of thermal maturity (Marynowski et al. 2007a). Thus, the cause of the distribution diversity of discussed aromatic biomarkers are probably early diagenetic processes affecting the wood, such as oxidation and the activity of microorganisms. In case of samples with low diagenetic changes, cadalene, dehydroabietane and/or siomonellite are dominated (GN JS2, GN JS4, GN JS6, SOW JS2, SOW JS6, SOW JS7 SOW JS10, SOW JS13, GRO JS). Whereas, the samples with high diagenetic changes contain mainly retene (SOW JS1, SOW JS4). On the triangular diagram (Fig. 5), the large differences in the content of these aromatic biomarkers and the lack of any trends suggests influence of early diagenetic process, between which degradation of the wood by microorganisms seems to be the most plausible. Retene and siomonellite could be also derived from the aromatization of α-phyllocladane (Otto and Simoneit, 2001). Phyllocladane was detected only in a few samples of the wood from the Czestochowa region (Marynowski et al. 2008; 2011). There is possible that diversity of dehydroabietane, retene and siomonellite distribution are also associated with different precursors, which were present in each wood species in variable concentrations.

MPI parameter values (methylphenanthrene index) for the majority of the samples ranged from 0.1 to 0.5. These values calculated to vitrinite reflectance (Rc) are in the range of 0.45% to 0.70% (Table 1). Actual measured

Fig. 1. The most common aromatic hydrocarbons identified in the examined fossil wood samples.

Samples	3-MP [%]	2-MP [%]	9-MP [%]	1-MP [%]	MPI1	Rc [%]	Sim[%] m/z 237	Ret[%] m/z 219	Deh[%] m/z 255
Sowa clay-pit									
SOW JS1	17.1	21.6	29.6	31.8	0.69	0.81	6.6	89.1	4.3
SOW JS2	18.1	17.6	31.5	32.8	0.52	0.71	67.0	17.7	15.4
SOW JS3	18.2	18.2	29.2	34.4	0.43	0.66	16.8	45.3	37.9
SOW JS4	20.5	19.6	31.9	27.9	0.47	0.68	25.7	68.7	5.6
SOW JS6	17.0	19.0	28.8	35.2	0.36	0.62	35.1	37.1	27.8
SOW JS7	17.6	21.2	26.8	34.4	0.33	0.60	30.2	15.7	54.1
SOW JS9	18.4	18.8	29.4	33.4	0.44	0.66	30.6	47.3	22.0
SOW JS10	20.1	19.7	29.1	31.0	0.32	0.59	38.2	36.4	25.4
SOW JS13	18.8	18.2	30.2	32.8	0.40	0.64	40.4	35.0	24.5
Gnaszyn clay-pit									
GN JS2	16.9	15.5	29.6	38.0	0.43	0.66	57.4	21.4	21.2
GN JS4	19.9	17.9	32.6	29.7	0.50	0.70	59.1	24.2	16.7
GN JS6	19.0	21.7	33.1	26.1	0.65	0.79	59.4	25.5	15.1
GNU SR	16.9	18.7	30.0	34.4	0.42	0.65	65.9	27.2	6.9
GNU UT	23.3	31.0	24.5	21.2	0.34	0.61	29.2	42.4	28.4
GN W20	16.8	17.5	31.5	34.1	0.39	0.63	88.5	9.1	2.4
GN W20S	18.0	20.7	29.8	31.4	0.31	0.59	84.9	12.2	2.9
Grodzisko clay-pit									
GRO JS1	15.2	16.8	29.0	39.0	0.44	0.66	33.2	31.2	35.6
Anna clay-pit									
ANNA J1	28.8	33.6	16.7	20.8	0.11	0.47	53.1	33.9	13.0

Table 1. Molecular parameters based on the distribution of aromatic hydrocarbons.

Explanation of the Table 1:
Sim – simonellite
Ret – retene
Deh – dehydroabietane
MP – methylophenanthrenes
$MPI1 = 1.5(MP+3MP)/ (P+MP+9MP)$
$Rc [\%] = 0.4+0.6(MPI_1)$

values of vitrinite reflectance for four samples from Gnaszyn and Anna (Marynowski et al. 2007b) are in the range of 0.25% to 0.30% for the samples non-oxidized and 0.45% to 0.50% for the partially oxidized samples (see also Marynowski et al., 2011). Differences between measurements and calculated values of vitrinite reflectance are connected with the restrictions on the use of MPI1. This parameter describing thermal maturity in the range of 0.5% to greater than 2% while the analyzed fossil wood samples are below that maturity range. Thus, the use of MPI1 parameter for the thermal maturity characterization of the Middle Jurassic sediments is not recommended. Summing, both MPI1 as well as ratios of simonellite and dehydroabietane to retene do not work as thermal maturity parameters in case of the fossil wood from the Czestochowa region. Therefore, the most useful indicator remains vitrinite reflectance measurements. As a result of weathering processes (oxidation) the distribution of aromatic hydrocarbons

changes. On the Figures 6 & 7 a comparison of the distribution pattern and the selected aromatic hydrocarbons such as perylene, benzo[a]pyrene, benzo[e]pyrene (Fig. 6) as well as dehydroabietane, simonellite and retene (Fig. 7) is shown. For example, the ratio of standard compound to perylene, calculated from the peak area, for an unoxidized sample GNU SR is 0.54, and the same value for the oxidized sample GNU UT is 3.93.

This clearly indicates the degradation of aromatic hydrocarbons, both polycyclic (Fig. 6) as well as aromatic biomarkers (Fig. 7). Degradation of these last biomarkers in the oxidized sample is almost complete. Simultaneously, the oxidized sample has higher relative concentration of the compounds from the methylphenanthrene group (Marynowski et al., 2011). What is surprising, the oxidation processes usually lead to the degradation of methyl derivatives of aromatic hydrocarbons (Bechtel et al., 2001) what is not confirmed in case of fossil wood samples.

Fig. 2. Mass chromatogram showing dehydroabietane, simonellite and retene distribution of the Middle Jurassic fossil wood samples from the clay-pits Sowa and Gnaszyn.
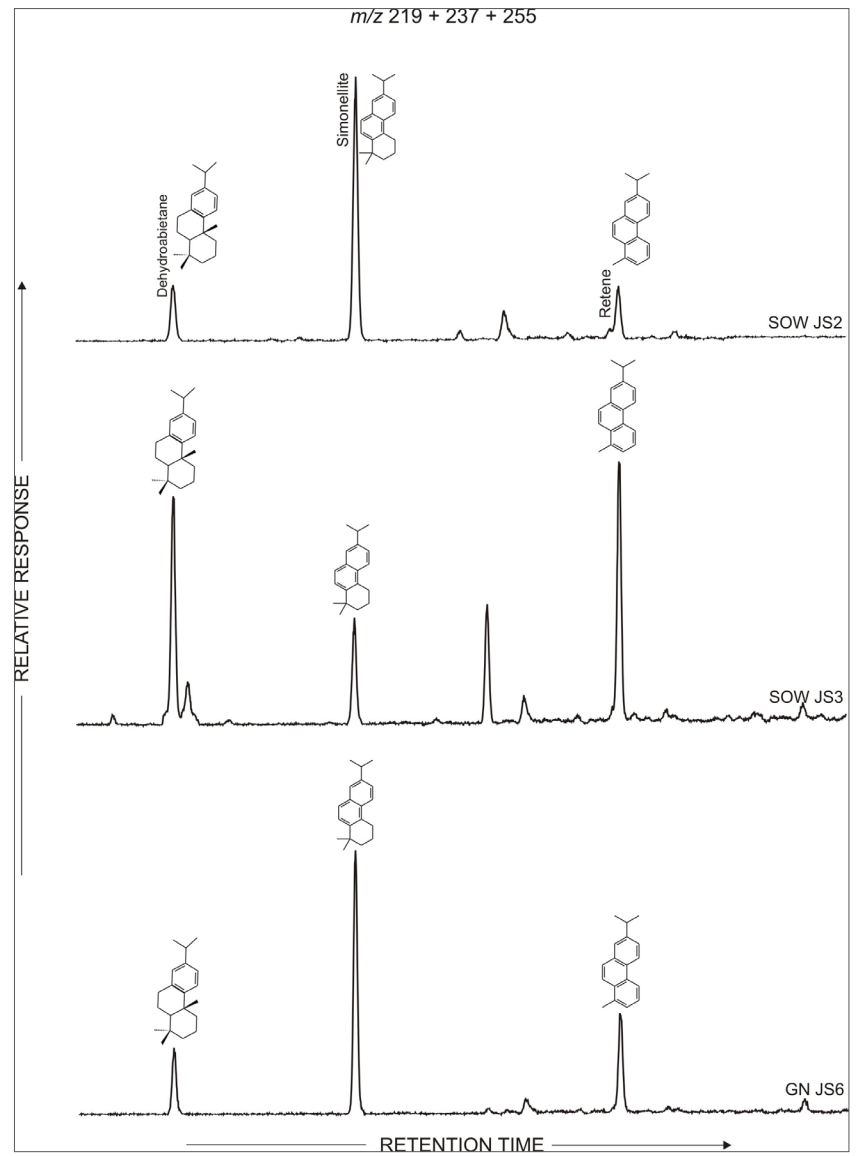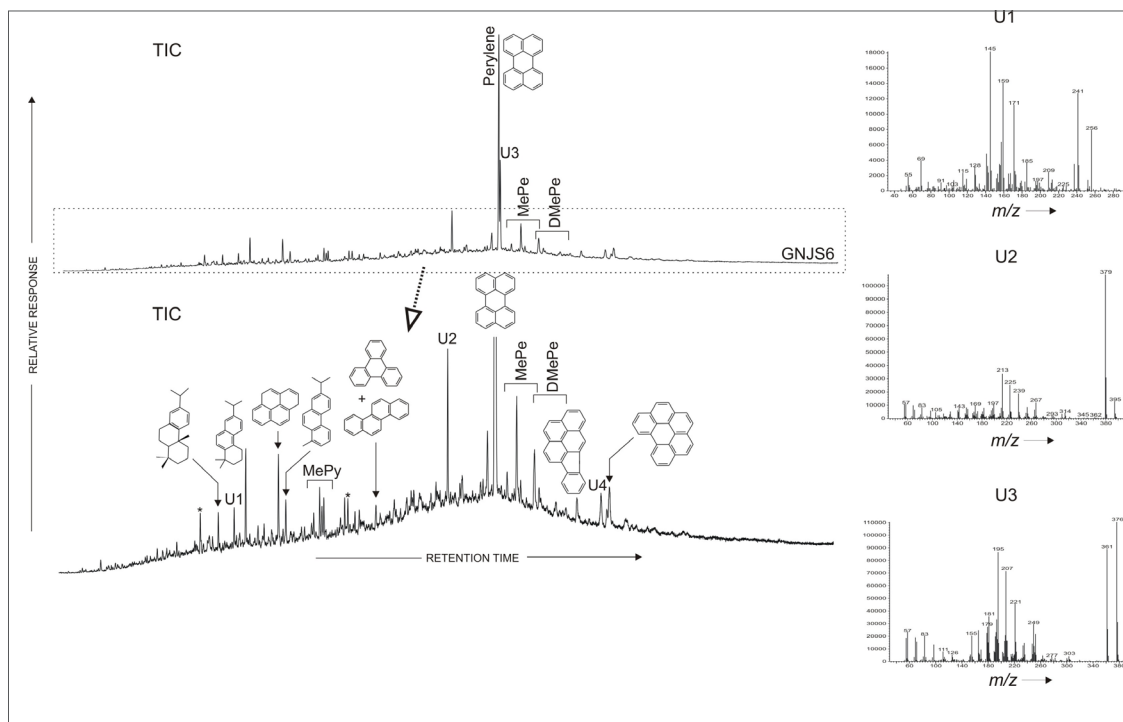
Fig. 3. Distribution example of aromatic fraction of GNJS6 sample with structures of identified compounds. With the letter "U" stated unknown aromatic compounds and their mass spectra. MePy - methylopyrenes and methylophluorantenes. MePe - methyloperylenes. DMePe - dimethyloperylenes.
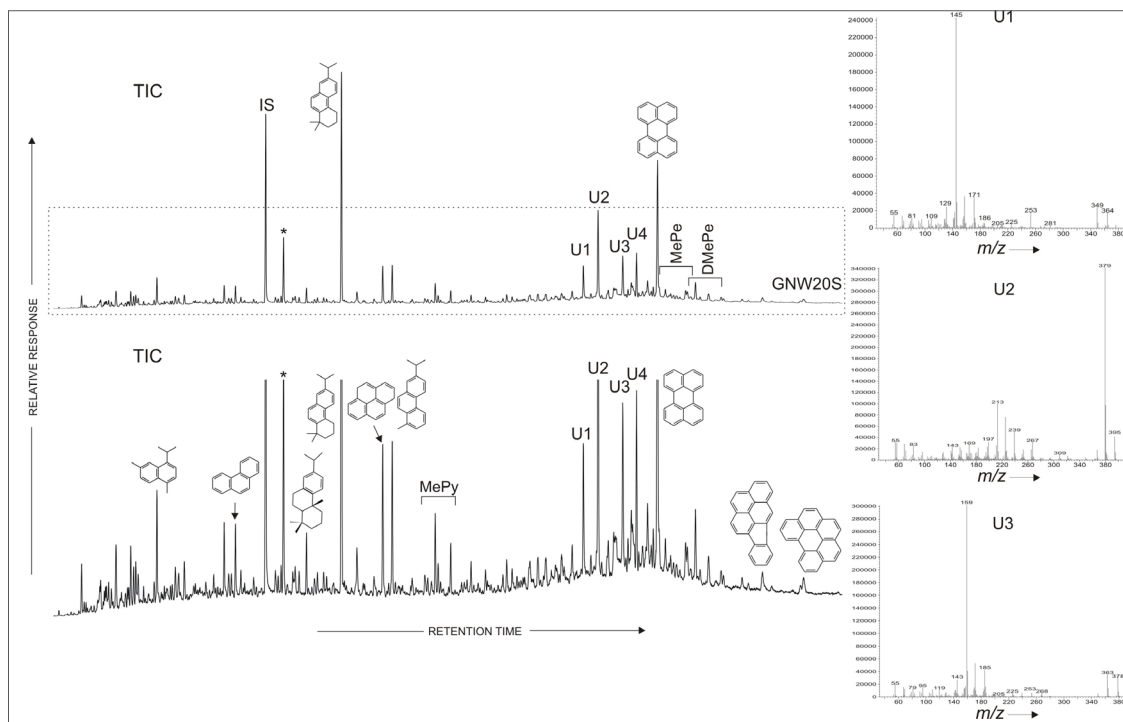

Fig. 4. Distribution example of aromatic fraction of the GNW20S sample with structures of identified compounds. With the letter "U" stated unknown aromatic compounds and their mass spectra. MePy - methylpyrenes and methylfluoranthenes. MePe - methylperylenes. DMePe – dimethylperylenes, IS – standard.

Fig. 5. Ternary diagram showing the relative percentage content of aromatic biomarkers: dehydroabietane, simonellite and retene in the examined samples of fossil wood.
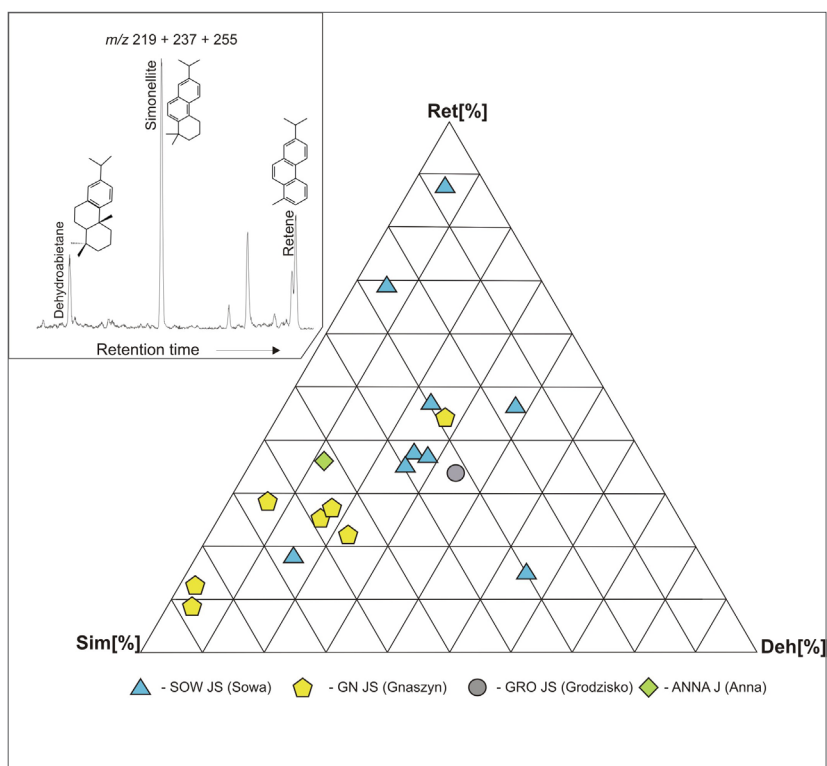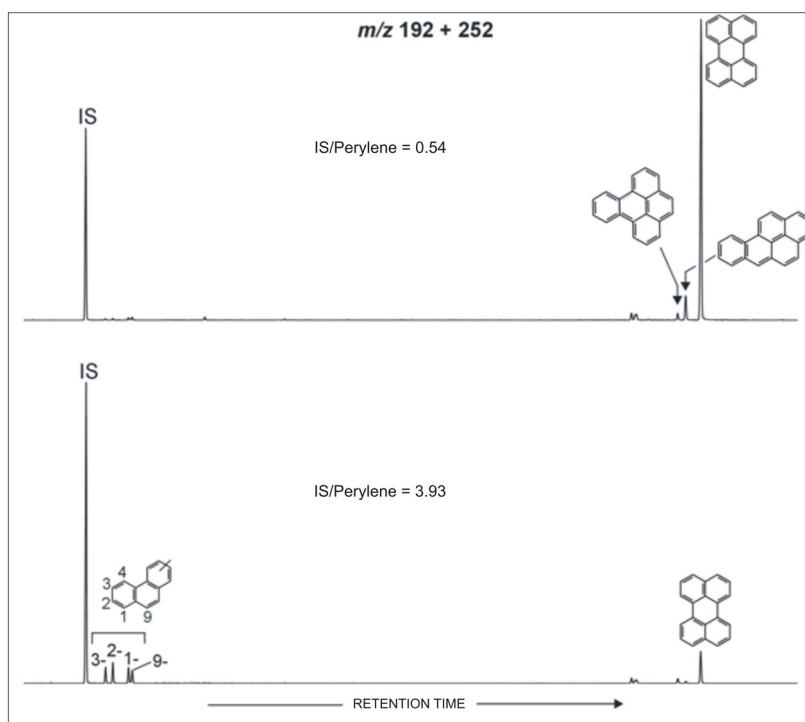

Fig. 6. The mass chromatogram showing the relative concentrations of internal standard (IS), perylene and other PAHs (m/z 252) in samples GNU SR (upper chromatogram), and GNU UT (lower chromatogram).

Conclusions

- Aromatic hydrocarbons are present in the fossil wood samples in relatively small amounts. In almost all of the samples the dominating aromatic hydrocarbon is perylene and its methyl- and dimethyl- derivatives. In some samples simonellite is the dominant or the second predominant compound.

- Both perylene and simonellite are genetically related to the fossil wood. The first one is connected with degradation of wood by fungi, while the second one is the geochemical transformation product of such primary compounds as: dehydroabietane, ferruginol, sugiol and/or á-phyllocladane.

- The distribution of dehydroabietane, simonellite and retene is highly variable. The cause of such diversity is probably due to early diagenetic processes affecting the wood, such as oxidation and the activity of microorganisms.

- MPI_1 (methylphenanthrene index) parameter values for the majority of the samples are in the range of 0.1 to 0.5, which results in the Rc values ranged from 0.45 to 0.70%.

- Differences between measured vitrinite reflectance and calculated values of the parameter MPI1 results from the fact that the methylophenanthrene index is a parameter describing thermal maturity in the range from about 0.5% to greater than 2%.

- The use of MPI_1 parameter for the thermal maturity characterization of Middle Jurassic wood is not recommended. Both MPI_1 as well as simonellite and dehydroabietane to retene ratio do not work as thermal maturity parameters in the Middle Jurassic clays of the Czestochowa region. The most useful indicator remains vitrinite reflectance measurements.

- As a result of weathering processes (oxidation) the distribution of aromatic hydrocarbons changes. In the oxidized samples the amount of aromatic hydrocarbons, both PAHs as well as aromatic biomarkers decreases.

Fig. 7. The mass chromatogram showing the relative concentrations of internal standard (IS) as well as dehydroabietane, simonellite and retene in samples GNU SR (upper chromatogram), and GNU UT (lower chromatogram).
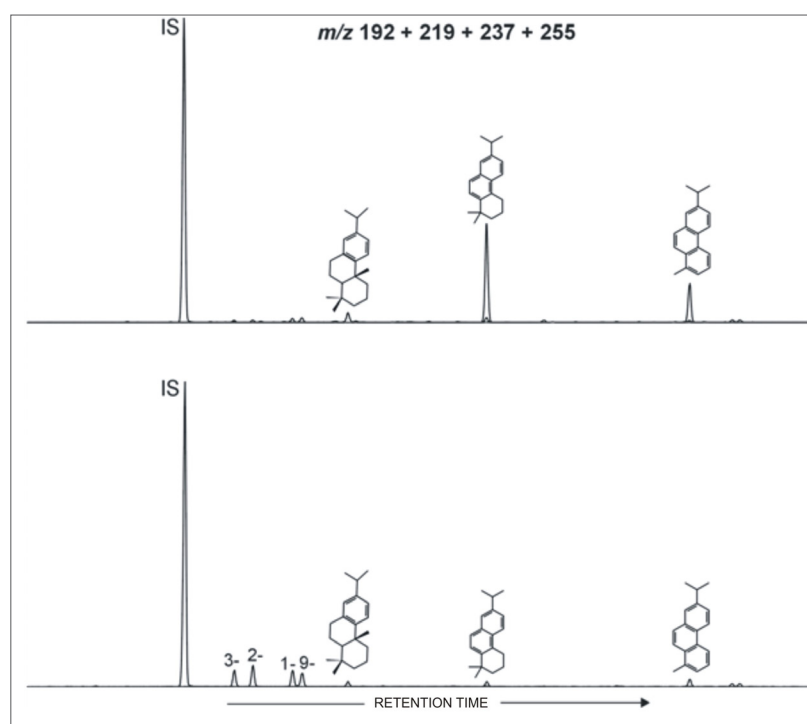
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