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# Aromatic hydrocarbon biomarkers in terrestrial organic matter of Devonian to Permian age

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**Abstract**

This paper presents the results of a detailed study on the occurrence and distribution of alkylnaphthalenes and alkylphenanthrenes in 39 coal and sediment samples from the Late Palaeozoic containing predominantly terrestrial organic matter. Most of the samples represent the Euramerian flora realm and originate from locations beyond the Variscan front in Eastern, Northern and Central Europe, i.e. especially England and the Moscow Basin. The samples are of relatively low maturity (0.32 to 1.80% $R_r$) and consist mainly of mixtures of type III and II kerogen. Quantification of the $C_0$- to $C_4$-naphthalenes and the $C_0$- to $C_4$-phenanthrenes showed that these compound classes were highly abundant in all samples. Aromatic hydrocarbon maturity parameters in general are in good agreement with measured vitrinite reflectance values. 1,2,7-Trimethylnaphthalene, an assumed diagenetic product of oleanane type biomarkers was present in all investigated samples. This observation provides evidence that oleanane type lipids were biosynthesised by organisms predating the evolution of angiosperms or that assumed formation pathways for 1,2,7-trimethylnaphthalene are insecure. 1,2,8-Trimethylphenanthrene was significantly enriched in samples from the Permian and the one sample from the Devonian investigated in this study. The precursor(s) of 1,2,8-trimethylphenanthrene therefore may have been produced by organisms which were least abundant in the Carboniferous depositional environments represented by our samples.

*Keywords:* Late Palaeozoic; Terrestrial organic matter; Aromatic biomarkers; Alkylphenanthrenes; Alkylnaphthalenes; Age and source relationship

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## 1. Introduction

Age-specific biomarkers are organic compounds that cannot only be attributed to a certain biological source but that also are specific for a certain geological age. A typical example is oleanane. This compound is suggested to derive from β-amyrin, which is a constituent of angiosperms. The presence of angiosperms, and therefore of β-amyrin appears to be more or less restricted to periods of the Cretaceous and younger. Beside oleanane, few other age-specific biomarkers are known. The occurrence of certain monoaromatic 4-methylsteroids (dinosteroids) in the Palaeozoic and Mesozoic ages correlates with the fossil record of acritarchs and dinoflagellates (Moldowan and Talyzina, 1998). The presence of dinosteroids in fossil organic matter therefore normally is taken as an indication that acritarchs and dinoflagellates had already evolved and

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have been contributors to the organic matter. 24-Norcholestane has been attributed to the presence of diatoms (Holba et al., 1998). Although the biological precursor of 24-norcholestane is unknown, the compound shows a significant increase in samples from the Jurassic and Cretaceous. This strongly correlates with the evolution and distribution of diatoms.

The potential utility of aromatic hydrocarbons as age specific biomarkers has not been addressed to any large extent so far. Aromatic hydrocarbons are particularly abundant in terrestrial organic matter, especially in coals, derived mainly from higher plants (Tissot and Welte, 1984) which evolved during the Palaeozoic. At the beginning of the Palaeozoic, life of fauna and flora was limited to the sea. Terrestrial environments until the end of the Palaeozoic were subject to extreme changes basically due to the evolution of land plants. After early colonization, significant diversification and expansion of land plants is attributed to the Late Palaeozoic. While especially the Carboniferous is characterised by the evolution of new plant groups which in turn influenced the deposition processes of sediments, the Permian is the period at whose end the biggest mass extinction took place and many of the evolved fauna and flora disappeared again. The adaptation of plants to terrestrial environments required several morphological developments which may have been accompanied or preceded by the biochemical evolution of plant constituents.

Many of the potential molecular precursors of aromatic hydrocarbons originating from higher plants show either cyclic or already aromatic structures. Aromatisation, besides defunctionalisation is the main chemical reaction during coalification. Increasing maturity therefore is accompanied by an increase of compounds showing non-functionalised aromatic structures (Teichmüller and Teichmüller, 1968; Hazai et al., 1989). Investigations on brown coals (Chaffee and Johns, 1983; Chaffee and Fookes, 1988; Hazai et al., 1989) showed that pentacyclic monoaromatic ring systems were highly abundant, whereas bi- and tricyclic polyaromatic rings (alkylnaphthalenes and alkylphenanthrenes) were absent. In contrast, bituminous coals, i.e. more mature coals normally are characterised by high proportions of alkylnaphthalenes and alkylphenanthrenes (Hayatsu et al., 1978; Radke et al., 1990).

Alkylnaphthalenes are mainly derived from terrestrial sources (Radke et al., 1994). Cyclic sesquiterpenoids from resinous constituents of conifers are potential precursors of alkylnaphthalenes (Pentegova et al., 1968). 1,2,7-Trimethylnaphthalene is suggested to originate from compounds like β-amyrin that are constituents of angiosperms (Strachan et al., 1988; see also Fig. 1). β-Amyrin and monoaromatic seco-hopanes are among several potential precursors of 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene (Püttmann and Villar, 1987). 1,2,4-Trimethylnaphthalene might originate from α-tocopherol, present in recent marine sediments (Brassell and Eglinton, 1986). 1,2,2,5-Tetramethyltetralin and 1,2,2,5,6-pentamethyltetralin, from microbial sources, might be precursors of 1,2,6-trimethylnaphthalene, 1,2,5,7- and 1,2,3,5-tetramethylnaphthalene (Alexander et al., 1992).

Strachan et al. (1988) suggested that 1,2,5- and 1,2,7-trimethylnaphthalene are degradation products of pentacyclic triterpenoids of the oleanane type, for example β-amyrin (Fig. 1). The degradation of β-amyrin via 8,14-seco-triterpenoids is supposed to additionally yield high proportions of 1,2,5,6-tetramethylnaphthalene (Püttmann and Villar, 1987). 1,2,7-Trimethylnaphthalene has exclusively been attributed to natural precursors produced by angiosperms (Fig. 1). In contrast 1,2,5-trimethyl- and 1,2,5,6-tetramethylnaphthalene may also derive from natural precursors produced by non-angiosperms (Fig. 1). Both 1,2,5-trimethyl- and 1,2,5,6-tetramethylnaphthalene were detected as major constituents in the fluorinite filling of needles from *Abietites linkii*, a gymnosperm (Heppenheimer et al., 1992). 1,2,5-Trimethylnaphthalene (agathalene) may also originate from the dehydrogenation of biological precursors (Fig. 1) like agathic acid, communic acid and manool (Thomas, 1969; Carman and Craig, 1971). The latter compounds are constituents of gymnosperms (Karrer, 1976; Thomas, 1969).

Beside source effects, the distribution of alkylnaphthalenes is strongly influenced by the thermal maturity of organic matter. Increasing maturity for example results in the progressive conversion of 1,2,5-trimethylnaphthalene to the more stable 1,3,6-trimethylnaphthalene and other isomers (Strachan et al., 1988). This results from isomerisation reactions, leading to the predominance of more stable β-isomers with increasing maturity. For example, Radke et al. (1982b) found that samples of enhanced maturity ($>0.9\%$ $R_r$) showed elevated proportions of 2-methylnaphthalene compared to 1-methylnaphthalene (methyl naphthalene ratio MNR) and 2-ethylnaphthalene compared to 1-ethylnaphthalene (ethylnaphthalene ratio ENR). More recently van Aarssen et al. (1999) using results of laboratory experiments established new maturity ratios based on tri- and tetramethylnaphthalenes.

Similar to certain alkylnaphthalenes, certain alkylphenanthrenes can be related to some extent to the biological origin. Diterpenoids with an abietane and pimarane skeleton are likely biological precursors of alkylphenanthrenes (Simoneit et al., 1986). These compounds are constituents of ambers and resins (Thomas, 1969; Simoneit et al., 1986) present in vascular plants. The most prominent alkylphenanthrene, directly attributed to diterpenoids of the abietane type is 1-methyl-7-isopropylphenanthrene (retene). 1,7-Dimethylphenanthrene (pimanthrene) probably originates from diterpenoids of the pimarane type but is also a potential decomposition product of retene (Simoneit et al., 1986). Additionally phenanthrene and alkylphenanthrenes may originate from pentacyclic triterpenoids for example steroids (Streibl and Herout, 1969; Greiner et al., 1976).

Numerous investigations on alkylphenanthrenes addressed their utility as maturity parameters (Radke et al., 1982b). In immature samples 9-methylphenanthrene and 1-methylphenanthrene often are highly abundant, with 9-methylphenanthrene being predominant (Radke et al., 1982a). With increasing maturity 2-methylphenanthrene and 3-methylphenanthrene become more abundant, due to their enhanced thermal stability. Normally 2-methylphenanthrene is present in higher proportions than 3-methylphenanthrene. Based on these observations the Methylphenanthrene Ratio 1 (MPI 1) was established, showing excellent correlation with the vitrinite reflectance for organic

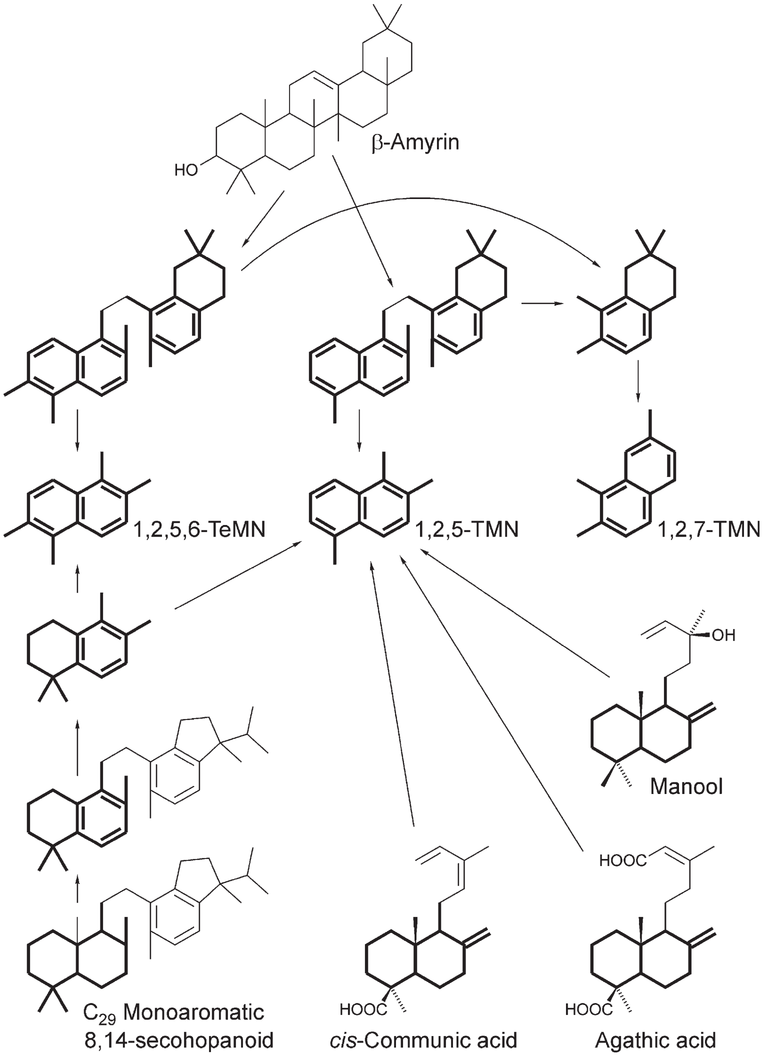

Fig. 1. Possible biological precursors and pathways for the generation of 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN), 1,2,5-trimethylnaphthalene (1,2,5-TMN) and 1,2,7-trimethylnaphthalene (1,2,7-TMN) after Püttmann and Villar (1987) and Strachan et al. (1988).

material of type III kerogen (Radke et al., 1982a). Therefore the vitrinite reflectance of terrestrial organic matter can be approximated by calculation ($R_c = 0.6$ MPI $1 + 0.4$ for $R_o < 1.35\%$; $R_c = -0.6$ MPI $1 + 2.3$ for $R_o > 1.35\%$).

With this background this paper presents a detailed study of aromatic hydrocarbons in 39 coal and sediment samples from the Late Palaeozoic and evaluates their potential as age-related biomarkers. The stratigraphic age of investigated samples extends from the Middle Devonian to the Late Permian. Nine samples were ascribed to the Permian, 23 to the Late Carboniferous, seven to the Early Carboniferous and one to the Devonian period. The investigated samples originate from different locations (Table 1). Although the majority of the samples are coals and coaly shales, some are sediments containing predominantly terrestrial organic matter, and two are fossils of vascular plants. To ensure a relatively low thermal maturity of the samples with respect to their geologic age, locations are limited to areas beyond the Variscan deformation front in Eastern, Northern and Central Europe, i.e. especially England and the Moscow Basin (see Section 2).

Table 1
Description of the investigated samples

| Sample no. | FZJ no. | Period | Epoch | Origin | Location | Depth (m) | Lithology and rank |
|---|---|---|---|---|---|---|---|
| 1 | E 49710 | Permian | Lower Zechstein | South China | Dahe Mine | n.a. | High vol. bit. coal |
| 2 | E 49748 | Permian | Ravnefjeld Formation | East Greenland | Jameson Land | n.a. | Slate |
| 3 | E 49749 | Permian | Ravnefjeld Formation | East Greenland | Gauss Halvø | n.a. | Silt |
| 4 | E 49750 | Permian | Ravnefjeld Formation | East Greenland | Jameson Land | n.a. | Silt–slate |
| 5 | E 49751 | Permian | Ravnefjeld Formation | East Greenland | Kap Stosch | n.a. | Silt, laminated slate |
| 6 | E 48990 | Permian | Guadulupian | Russia | Petchora Basin | n.a. | Medium vol. bit. coal |
| 7 | E 48478 | Permian | Rotliegend | South France | Lodève Basin | n.a. | n.a. |
| 8 | E 48479 | Permian | Rotliegend | South France | Lodève Basin | n.a. | n.a. |
| 9 | E 48996 | Upper Carboniferous | Westphalian D | Germany | Lugau-Oelsnitz | n.a. | High vol. bit. coal |
| 10 | E 48388 | Upper Carboniferous | Westphalian C | North England | Keekle | 32.00 | High vol. bit. coal |
| 11 | E 48389 | Upper Carboniferous | Westphalian C | North England | Keekle | 40.00 | High vol. bit. coal |
| 12 | E 48390 | Upper Carboniferous | Westphalian C | North England | Keekle | 64.00 | High vol. bit. coal |
| 13 | E 48214 | Upper Carboniferous | Westphalian B | North England | Potato Pot | 24.70 | High vol. bit. coal |
| 14 | E 48216 | Upper Carboniferous | Westphalian B | North England | Potato Pot | 29.90 | High vol. bit. coal |
| 15 | E 48430 | Upper Carboniferous | Westphalian B | Germany | Ruhr area | n.a. | *Sigillaria* (fossil) |
| 16 | E 48403 | Upper Carboniferous | Westphalian A | North England | Rowlands Gill | 51.61 | Mud-/siltstone |
| 17 | E 48220 | Upper Carboniferous | Westphalian A | North England | Potato Pot | 77.80 | High vol. bit. coal |
| 18 | E 48392 | Upper Carboniferous | Westphalian A (?) | North England | Distington I | 12.26 | High vol. bit. coal |
| 19 | E 48393 | Upper Carboniferous | Westphalian A (?) | North England | Distington I | 12.66 | High vol. bit. coal |
| 20 | E 48394 | Upper Carboniferous | Westphalian A (?) | North England | Distington I | 12.86 | High vol. bit. coal |
| 21 | E 48395 | Upper Carboniferous | Namurian (?) | North England | Distington I | 35.65 | High vol. bit. coal |
| 22 | E 48396 | Upper Carboniferous | Namurian (?) | North England | Distington I | 56.60 | High vol. bit. coal |
| 23 | E 48397 | Upper Carboniferous | Namurian (?) | North England | Distington I | 72.00 | High vol. bit. coal |
| 24 | E 48398 | Upper Carboniferous | Namurian (?) | North England | Distington I | 110.55 | High vol. bit. coal |
| 25 | E 48400 | Upper Carboniferous | Namurian | North England | Dearham | 44.75 | High vol. bit. coal |
| 26 | E 48401 | Upper Carboniferous | Namurian | North England | Dearham | 55.32 | High vol. bit. coal |
| 27 | E 48405 | Upper Carboniferous | Namurian | North England | Rowlands Gill | 93.80 | High vol. bit. coal |
| 28 | E 48425 | Upper Carboniferous | Namurian C | Germany | Ruhr area | n.a. | *Mesocalamites* cf. *Taitianus* (fossil) |
| 29 | E 48382 | Upper Carboniferous | Unknown | North England | Throckley | 120.73 | Sandstone |
| 30 | E 48383 | Upper Carboniferous | Unknown | North England | Throckley | 170.41 | High vol. bit. coal |
| 31 | E 48384 | Upper Carboniferous | Unknown | North England | Throckley | 258.56 | Mudstone |
| 32 | E 48985 | Lower Carboniferous | Upper Viséan | Russia | Moscow Basin | n.a. | Cannel boghead coal |
| 33 | E 48986 | Lower Carboniferous | Upper Viséan | Russia | Moscow Basin | n.a. | Cannel boghead coal |
| 34 | E 48987 | Lower Carboniferous | Upper Viséan | Russia | Moscow Basin | n.a. | Soft brown coal |
| 35 | E 48988 | Lower Carboniferous | Upper Viséan | Russia | Moscow Basin | n.a. | Soft brown coal |
| 36 | E 48989 | Lower Carboniferous | Upper Viséan | Russia | Moscow Basin | n.a. | Soft brown coal |
| 37 | E 48993 | Lower Carboniferous | Upper Viséan | Germany | Borna–Hainichen | n.a. | High vol. bit. coal |
| 38 | E 48991 | Lower Carboniferous | Upper Viséan | Spitsbergen | Pyramiden | n.a. | High vol. bit. coal |
| 39 | E 48992 | Devonian | Givetium–Frasnium | Spitsbergen | Mimerdalen | n.a. | Cannel coal |

## 2. Geographical and geological setting of the samples

### 2.1. North England

The majority of the investigated samples are of Late Carboniferous age and originate from the Pennine Basin in North England (Table 1). At the beginning of the Carboniferous, Northern Britain was part of the supercontinent Pangea, and continued to drift northwards into tropical latitudes. The area, after Caledonian tectonism and intrusion, was reduced to a peneplain due to erosion and a relatively stable block area was formed. Sedimentation in the Carboniferous was influenced by tectonic, climatic and eustatic forces. In the Dinantian, limestones, shales, sandstones and coals were deposited during repeated cycles of marine transgressions and regressions. In the Namurian to mid-Westphalian the basin experienced influx of terrestrial sediments from the north-west and north-east and a freshwater deltaic environment with lagoons and coal swamps developed. Thin marine bands document periodic marine incursions. During the Westphalian environmental conditions became more continental. The Pennine basin subsided during most of the Westphalian and deposition occurred persistently close to sea level (Guion and Fielding, 1986). The Variscan orogeny resulted in a regional uplift during latest Carboniferous times. For the Pennine Basin these effects are less evident than for continental Europe.

Samples from the Distington and Dearham boreholes in West Cumberland are from the Namurian. The Namurian represents the transition from predominantly marine conditions of the Early Carboniferous to almost exclusively freshwater deltaic environments in the Westphalian (Young and Armstrong, 1989). Namurian sediments of the Hensingham Group consist of mudstones, laminated siltstones and sandstones with thin coal seams (Young and Boland, 1992). Samples from Keekle and Potato Pot represent outliers located in the southern part of the West Cumbrian Coalfield of Westphalian age. The Westphalian strata were deposited on an upper delta plain to lower alluvial plain, extending from present day Northern Europe to North America. Two samples originate from Rowlands Gill, located in the district of Tyne and Wear in Durham, while three were obtained from the Throckley borehole, Northumberland. It has been suggested that these areas in particular in comparison to the rest of the Pennine Basin were slightly elevated during deposition. Therefore marine bands are significantly less abundant and thin in relation to the rest of the Pennine Basin (Jones, 1992). The Throckley borehole has been examined in 1964–1965 aiming to establish a sequence from undoubted Lower Coal Measures down to the Great Limestone (Holliday and Pattison, 1987).

### 2.2. Other samples

Five samples originate from the Moscow Basin and were deposited during the Viséan (Table 1). The Moscow Basin is located on the East European platform, one of the largest Precambrian cratons of the world. The craton is covered by extensive Devonian and Carboniferous sediments which experienced only insignificant intraplate tectonic movements (Alekseev et al., 1996). The Moscow Basin is located in the centre of this craton and extends about 600 km from north to south and more than 1000 km from east to west. Changes in sea level are attributed to tectonic movements of the uplift areas, resulting in regional changes of facies.

Two coals from East Germany originate from the Erzgebirge, Saxony (Table 1). The coal from the Westphalian D originates from Lugau-Oelsnitz and was taken from the Deutschlandschacht at a depth of 2.00 m beneath the ground. The coal from the Viséan originates from a surface seam. During the Carboniferous Saxony was situated in the sub-Variscan foredeep. The Early Carboniferous is characterised by marine dominated depositional environments whereas the Late Carboniferous is predominantly paralic.

Four sediments of the East Greenland Basin (Jameson Land, Kap Stosch and Gauss Halvø) belong to the Ravnefjeld Formation, deposited during the Late Permian, the Capitanian equivalent to the Zechstein 1 (Table 1; Christiansen et al., 1993). Although the depositional environment of the sediments from the Ravnefjeld Formation is primarily marine, the investigated samples contain notable amounts of terrigenous material (personal communication J. A. Bojeson-Koefoed). Therefore the samples are suggested to originate from bioturbated intervals, containing coalified type III kerogen (Piasecki and Stemmerik, 1991).

Two sediment samples originate from the Lodève Basin, South France. The basin is located in the southern part of the French Central Massif. The sediments (Usclas et St. Privat Formation and Formation de Tuilieres-Lorias) were deposited during the Early Permian (Autunian) in a fluvial to lacustrine environment. They discordantly overlie Precambrian and Cambrian slates, gneisses, granites and dolomites.

Two coals originate from Spitsbergen. One of them is a cannel coal which is ascribed to the Upper Givetium or Lower Frasnium (Devonian). It originates from the

Mimerdalen Formation of Dickson Land. The second sample originates from the Mumien Formation, Dickson Land and is a cannel coal. Both coals have been deposited in tropical environments (personal communication W. Peters-Kottig).

The two fossils analysed in this study are a *Mesocalamites* cf. *Taitianus* from the Namurian C and a *Sigillaria* from Westphalian B. Both plants belong to the group of pteridophytes and were predominant in Late Palaeozoic forests. Although pteridophytes inhabited all climatic zones, they diversified strongest and were tallest in tropical regions (Strasburger et al., 1991).

One of the two samples not belonging to the Euramerian flora realm is a coal from the Dahe Mine, Shuicheng Basin, Guizhou Province, in Southwest China. The coal was deposited during the Early Zechstein (personal communication Y. Sun) in a paralic, deltaic depositional system with marine influence on the peat (Zhong and Smyth, 1997).

The second coal not belonging to the Euramerian flora realm comes from the Petchora Basin in Russia which is ascribed to the Siberian region, where from the beginning of the Late Permian a separate flora evolved. This Angara or Kusnezk flora realm in contrast to the Euramerian flora realm was dominated by Cordiates-like plants and pteridosperms, while lycopods where minor contributors (Chaloner and Meyen, 1973).

## 3. Methods

### 3.1. Elemental analysis and Rock-Eval pyrolysis

The samples were crushed to fine powders using a rotating disk mill (0.5 min). Concentrations of total carbon (TC), total organic carbon (TOC) and total sulphur (TS) were determined using a Leco Carbon-Analyser IR-112. For determination of total organic carbon, carbonates were removed from the samples by treatment with hydrochloric acid (25%) at 70 °C prior to measurement. Rock-Eval measurements were carried out using a Rock-Eval II instrument according to the method established by Espitalié et al. (1977). All determinations were carried out in duplicate.

### 3.2. Extraction and liquid chromatography

Amounts of 1–20 g (according to the content of total organic carbon) of homogenised sample were extracted with an azeotropic mixture of chloroform (47 wt.%), acetone (30 wt.%) and methanol (23 wt.%) in two successive 5 min steps, using a modified flow blending method (Radke et al., 1978). After sedimentation of the extraction slurry the supernatant liquid was decanted over a Soxhlet (glass fibre thimbles), concentrated in a Zymark (Hopkinton, MA, USA) Turbovap 500 evaporator and transferred to 10 ml vials. Known amounts of an internal aliphatic standard (α-androstane) and an internal aromatic standard mixture (1-phenylhexane, 1-phenylheptane, 1,8-dimethylnaphthalene, 1-phenylnaphthalene, 2-ethylpyrene and 2-butylpyrene) were added to the powder of the coals prior to extraction. The amounts of added standards depended on the TOC contents of these samples.

For the separation of extracts into compound class fractions the liquid chromatographic method of Willsch et al. (1997) was applied. This method is based on combined polarity/affinity chromatography of the soluble organic matter and produces seven chemically well-defined compound class fractions: (1) aliphatic hydrocarbons, (2) aromatic hydrocarbons, (3) low-polarity nitrogen, sulphur and oxygen (NSO) compounds, (4) medium-polarity NSO compounds, (5) high-polarity NSO compounds, (6) acids and (7) bases. The aliphatic and aromatic hydrocarbon fractions were directly suitable for further analysis.

### 3.3. Gas chromatography (GC)

For quantification of *n*-alkanes, pristane and phytane the total aliphatic fractions were analysed by capillary gas chromatography. A Hewlett Packard 5890 Series II gas chromatograph, equipped with a Gerstel on-column-injector, an electronic pressure control (EPC), a fused silica capillary column (HP Ultra I) of 50 m length, 0.2 mm inner diameter and 0.33 μm film thickness and a standard flame ionization detector (FID) was applied. Hydrogen was used as carrier gas at a flow rate of 1 ml/min (pressure controlled). The oven temperature was programmed from 90 °C (hold time 5 min) to 310 °C at a rate of 4 °C/min. A Multichrom 2-online data system (Fisons) was employed to store and process retention times and peak areas.

### 3.4. Gas chromatography–mass spectrometry (GC–MS)

Aromatic hydrocarbon fractions were analysed by gas chromatography–mass spectrometry (GC–MS) using a Hewlett Packard 5890 B gas chromatograph coupled to a Finnigan MAT 95 SQ mass spectrometer. The gas chromatograph was equipped with a temperature-programmable injection system (KAS 3, Gerstel) and a BPX 5 (0.25 μm film thickness) fused silica capillary column (SGE) of 50 m length and 0.22 mm i.d.

Helium was used as carrier gas utilising electronic pressure control (EPC 1 ml/min). The oven temperature was programmed from 60 to 340 °C (final hold time 8 min) at 3 °C/min. The mass spectrometer was operated in the EI mode at an electron energy of 70 eV and a source temperature of 260 °C. Full scan mass spectra were recorded over the mass range of 50–600 Da at a scan rate of 1 s/decade and an inter scan time of 0.2 s resulting in a scan cycle time of 0.5 s. Identification of individual compounds was based on gas chromatographic and mass spectral data, comparison with literature data and partly on comparison with authentic standards.

## 4. Results

### 4.1. General geochemical characteristics

The TOC content of the investigated samples varies widely ranging from 0.2 to 81.5% (Table 2). Most of the samples including those from North England can be classified as coals because TOC values exceed 50%. TOC values are generally lower (0.2 to 6.2%) for the Permian sediments from East Greenland and South France. TS contents range from 0.1% for a Permian sediment from South France to 9.7% for an Upper Carboniferous coal from North England (Table 2). Carbonate contents normally are low but are distinctly higher in the samples from East Greenland and South France and the Namurian sample from Rowlands Gill (Table 2).

For the majority of the samples vitrinite is the most abundant maceral group (Table 2, Fig. 2), though they are far from being monomaceralic. Indeed, liptinite makes up about 20% of most samples, and inertinite is also present. One coal from Potato Pot is characterised by high proportions of inertinite (57%). Three sediment samples from East Greenland, one sediment sample from South France, the cannel boghead coals from the Moscow basin and the cannel coal from Spitsbergen show high proportions of liptinite. Two samples of the Throckley site, one sample from the Moscow Basin and one sample from Spitsbergen exhibit no preference of a specific maceral group. The *Mesocalamites* cf. *Taitianus* fossil consists of almost pure vitrinite.

The HI vs. $T_{max}$ plot (Fig. 3) indicates that most of the samples consist of a mixture of type II–III kerogen. Exceptions among the North English samples are the Namurian mud-/siltstone from Rowlands Gill, which corresponds to type I kerogen, and the sandstone from Throckley, which may be classified as type III kerogen. The two cannel boghead coals from the Moscow Basin and the cannel coal from Spitsbergen contain a mixture of type I–II kerogen. The two fossils contain mainly type III kerogen. Pristane/phytane ratios indicate variable redox conditions (Table 2). For most of the coals and coaly shales from the Upper Carboniferous, values are above three which shows that the organic matter was deposited under oxic conditions. For the sediment samples from the Permian and the Viséan coals from the Moscow Basin on the other hand, pristane/phytane ratios are clearly lower (0.2–1.7) indicating less oxic to strongly reducing conditions. The kerogen typing is in principal corroborated by the pristane/$n$-$C_{17}$ vs. phytane/$n$-$C_{18}$ plot (Fig. 4).

Maturity assessment is based on vitrinite reflectance, $T_{max}$ values from Rock-Eval pyrolysis and the molecular maturity parameter MPI 1 (Table 2). The vitrinite reflectance of the samples ranges from 0.32 to 1.80% $R_r$ (Table 2). Vitrinite reflectance for the Viséan coals of the Moscow Basin is low and only slightly higher for the German coals from both the Westphalian D and the Viséan (all <0.6% $R_r$; Table 2). Most of the samples including those from North England show a vitrinite reflectance of 0.6 to 1.0% $R_r$ corresponding to the generalised boundaries of the oil window (Table 2). Elevated maturity of 1.0–1.3% $R_r$ is observed for two of the four Upper Permian sediments from East Greenland, the Permian coal from Russia and the two samples from Rowlands Gill. The *Mesocalamites* cf. *Taitianus* fossil shows significantly enhanced maturity (1.80% $R_r$).

In general the maturity assessment based on vitrinite reflectance is corroborated by MPI 1 and – to a lesser extent – $T_{max}$ values from Rock-Eval pyrolysis. Strong deviations of measured vitrinite reflectance and MPI 1 are restricted to the samples predominantly containing type I kerogen, as expected (Fig. 5). For the samples from England $T_{max}$ values (431–438 °C) in relation to vitrinite reflectance are consistently lower than many published data (Tissot et al., 1987; Espitalié and Bordenave, 1992), but they do correspond to values reported by Littke et al. (1990) who suggested lower $T_{max}$ values to be characteristic for coals (Fig. 5).

### 4.2. Distribution of naphthalenes

Representative distributions of alkylnaphthalenes in two significantly differing samples are displayed in Fig. 6, while Table 3 provides the concentrations of the $C_0$- to $C_4$-naphthalenes quantified in this study. The absolute amounts of total alkylnaphthalenes vary widely between 6 and 3228 µg/g TOC (Table 3). Highest proportions were obtained within the maturity range of 0.80–0.88% $R_r$, except for two samples.

Table 2
General geochemical characteristics of the investigated samples

| Sample no. | FZJ no. | Vitrinite % | Inertinite % | Liptinite % | Minerals % | $R_r$ % | TC % | TOC % | TS % | Tmax °C | HI mg HC/g TOC | OI mg $CO_2$/g TOC | Pri/Phy | Pri/*n*-$C_{17}$ | Phy/*n*-$C_{18}$ | MNR | ENR | DNR | MPI 1 | DBT/P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | E 49710 | 94.0 | 2.0 | 4.0 | 0.0 | 0.65 | 76.8 | 76.1 | 1.5 | 440 | 312 | 8 | 6.8 | 3.4 | 0.7 | 1.4 | 1.7 | 2.6 | 1.61 | 0.15 |
| 2 | E 49748 | 1.5 | 1.0 | 1.0 | 82.0 | 1.00 | 6.7 | 4.4 | 2.1 | 422 | 273 | 53 | 1.3 | 2.5 | 2.3 | 2.0 | b.d.l. | 9.4 | 0.62 | 0.19 |
| 3 | E 49749 | 0.0 | 0.0 | 2.5 | 97.5 | 0.85 | 2.7 | 0.2 | 1.0 | 481 | 32 | 109 | 1.2 | 1.5 | 1.1 | 1.4 | 1.0 | 2.4 | 0.72 | 0.09 |
| 4 | E 49750 | 0.5 | 0.5 | 9.0 | 86.5 | 1.10 | 5.3 | 1.0 | 1.1 | 424 | 160 | 36 | 1.8 | 0.9 | 0.5 | 1.8 | b.d.l. | 10.7 | 0.75 | 0.09 |
| 5 | E 49751 | 0.5 | 0.5 | 8.0 | 89.5 | 0.84 | 2.5 | 1.4 | 1.0 | 431 | 301 | 14 | 1.7 | 2.5 | 1.5 | 0.9 | 0.7 | 2.5 | 0.57 | 0.09 |
| 6 | E 48990 | 83.5 | 0.0 | 16.5 | 0.0 | 1.08 | 80.0 | 79.4 | 0.5 | 438 | 256 | 7 | 2.9 | 1.1 | 0.4 | 0.3 | 0.4 | 0.6 | 0.82 | 0.05 |
| 7 | E 48478 | n.d. | n.d. | n.d. | n.d. | n.d. | 7.1 | 3.0 | 0.2 | n.d. | n.d. | n.d. | 1.2 | 0.7 | 0.4 | 0.8 | 0.7 | 1.5 | 0.64 | n.d. |
| 8 | E 48479 | 0.5 | 4.0 | 16.0 | 79.5 | 0.59 | 11.5 | 6.2 | 0.1 | n.d. | n.d. | n.d. | 1.7 | 0.5 | 0.3 | 0.9 | 0.9 | 1.4 | 0.46 | n.d. |
| 9 | E 48996 | n.d. | n.d. | n.d. | n.d. | 0.57 | 68.1 | 68.2 | 0.9 | 421 | 271 | 12 | 3.3 | 5.6 | 2.0 | 0.7 | 0.3 | 2.0 | 0.66 | b.d.l. |
| 10 | E 48388 | 60.5 | 13.5 | 21.5 | 4.5 | 0.83 | 71.2 | 69.1 | 2.3 | 435 | 257 | 8 | 3.5 | 3.7 | 0.6 | 1.2 | 1.1 | 4.2 | 0.82 | 0.06 |
| 11 | E 48389 | 67.5 | 5.5 | 23.0 | 4.0 | 0.88 | 78.4 | 76.1 | 1.5 | 437 | 206 | 7 | 4.6 | 2.9 | 0.6 | 1.5 | 1.3 | 5.4 | 0.92 | 0.06 |
| 12 | E 48390 | 73.0 | 10.5 | 15.5 | 1.0 | 0.84 | 78.7 | 78.7 | 0.7 | 435 | 256 | 8 | 5.4 | 2.7 | 0.5 | 1.7 | 1.4 | 5.5 | 0.78 | 0.04 |
| 13 | E 48214 | 25.0 | 57.0 | 11.0 | 7.0 | 0.80 | 75.9 | 74.5 | 1.4 | 432 | 255 | 8 | 5.1 | 2.2 | 0.4 | 1.4 | 1.3 | 4.5 | 0.68 | 0.05 |
| 14 | E 48216 | 76.5 | 10.0 | 11.0 | 2.5 | 0.81 | 75.4 | 71.2 | 1.1 | 431 | 281 | 7 | 5.3 | 4.7 | 0.8 | 1.4 | 1.2 | 4.5 | 0.85 | 0.05 |
| 15 | E 48430 | 76.8 | 2.8 | 0.4 | 20.0 | 0.94 | 66.3 | 61.1 | 1.1 | 443 | 71 | 23 | 6.3 | 2.3 | 0.3 | 1.1 | 1.3 | 2.3 | 0.79 | 0.05 |
| 16 | E 48403 | 18.5 | 2.5 | 0.0 | 79.0 | 1.23 | 63.7 | 62.2 | 7.8 | 456 | 115 | 8 | 3.4 | 1.4 | 0.3 | 0.5 | 0.9 | 4.2 | 1.60 | 0.13 |
| 17 | E 48220 | 73.5 | 10.5 | 14.0 | 1.5 | 0.82 | 77.5 | 77.9 | 0.8 | 393 | 260 | 7 | 5.1 | 2.8 | 0.6 | 0.6 | 1.6 | 4.2 | 0.92 | 0.05 |
| 18 | E 48392 | n.d. | n.d. | n.d. | n.d. | n.d. | 71.2 | 70.2 | 3.7 | 432 | 257 | 8 | n.d. | n.d. | n.d. | 1.2 | 1.5 | 3.4 | 0.48 | 0.03 |
| 19 | E 48393 | 55.0 | 21.5 | 21.0 | 2.5 | 0.76 | 76.7 | 75.1 | 1.0 | 433 | 303 | 7 | 4.4 | 3.0 | 0.7 | 0.6 | 1.0 | 3.0 | 0.51 | 0.04 |
| 20 | E 48394 | 51.0 | 25.5 | 14.5 | 9.0 | 0.81 | 74.5 | 73.0 | 2.4 | 434 | 279 | 8 | 4.9 | 4.4 | 0.9 | 0.3 | 0.9 | 4.1 | 0.49 | 0.03 |
| 21 | E 48395 | 56.0 | 0.0 | 0.0 | 44.0 | 0.78 | 68.5 | 62.8 | 7.6 | 435 | 253 | 8 | 1.3 | 0.2 | 0.1 | 0.5 | 4.4 | 3.8 | 0.57 | 0.04 |
| 22 | E 48396 | 49.0 | 30.0 | 16.5 | 4.5 | 0.68 | 68.7 | 66.8 | 1.8 | 433 | 334 | 6 | 4.4 | 3.3 | 0.8 | 0.1 | 2.9 | 1.4 | 0.54 | 0.03 |
| 23 | E 48397 | 53.5 | 28.5 | 13.5 | 4.5 | 0.97 | 77.7 | 75.9 | 3.4 | 435 | 358 | 6 | 2.9 | 0.7 | 0.2 | b.d.l. | 0.5 | 2.3 | 0.67 | 0.07 |
| 24 | E 48398 | 63.0 | 18.0 | 13.0 | 6.0 | 0.67 | 64.4 | 64.1 | 9.7 | 434 | 280 | 6 | 3.7 | 2.5 | 0.6 | 0.3 | 1.2 | 1.9 | 0.63 | 0.18 |
| 25 | E 48400 | 64.0 | 13.5 | 12.5 | 10.0 | 0.78 | 72.5 | 71.3 | 2.4 | 438 | 289 | 7 | 4.3 | 2.8 | 0.6 | 0.6 | 1.1 | 2.7 | 0.79 | 0.04 |
| 26 | E 48401 | 39.0 | 2.5 | 15.0 | 43.5 | 0.77 | 72.9 | 71.8 | 1.2 | 438 | 240 | 8 | 4.8 | 2.3 | 0.5 | 0.4 | 0.6 | 1.6 | 0.65 | 0.03 |
| 27 | E 48405 | n.d. | n.d. | n.d. | n.d. | 1.26 | 58.3 | 25.2 | 8.8 | 457 | 213 | 5 | 2.3 | 0.5 | 0.2 | 2.3 | 2.2 | 8.9 | 0.99 | 0.04 |
| 28 | E 48425 | 91.2 | 0.0 | 0.0 | 8.8 | 1.80 | 80.7 | 77.9 | 0.9 | 494 | 52 | 5 | 1.1 | 0.8 | 0.9 | b.d.l. | b.d.l. | 6.1 | 2.22 | 0.12 |
| 29 | E 48382 | 19.5 | 8.5 | 29.5 | 42.5 | 0.94 | 12.4 | 12.0 | 4.6 | 436 | 87 | 4 | 5.6 | 3.7 | 0.6 | 1.2 | 1.1 | 2.0 | 0.47 | 0.04 |
| 30 | E 48383 | 61.0 | 2.0 | 26.0 | 11.0 | 0.88 | 70.6 | 66.9 | 2.3 | 436 | 231 | 8 | 5.4 | 5.7 | 1.1 | 0.8 | 1.2 | 2.4 | 0.81 | 0.07 |
| 31 | E 48384 | 16.5 | 23.5 | 23.5 | 20.5 | 0.91 | 26.3 | 29.4 | 0.6 | 437 | 178 | 8 | 2.3 | 0.2 | 0.1 | 1.5 | 1.2 | 2.7 | 0.48 | 0.03 |
| 32 | E 48985 | 0.0 | 2.5 | 61.5 | 36.0 | 0.42 | 66.2 | 66.2 | 4.5 | 437 | 690 | 19 | 0.5 | 0.7 | 1.3 | b.d.l. | 1.1 | 2.3 | 1.35 | 0.11 |
| 33 | E 48986 | 2.0 | 5.0 | 60.5 | 22.5 | 0.39 | 69.8 | 68.4 | 3.9 | 436 | 574 | 18 | 1.0 | 0.4 | 0.4 | 1.3 | 1.5 | 2.6 | 0.25 | 0.04 |
| 34 | E 48987 | 1.5 | 2.5 | 61.5 | 34.5 | 0.32 | 70.6 | 69.7 | 3.7 | 437 | 703 | 18 | 0.8 | 0.2 | 0.2 | 1.3 | 2.0 | 2.8 | 0.31 | 0.02 |
| 35 | E 48988 | 28.0 | 17.5 | 29.5 | 25.0 | 0.41 | 51.4 | 50.8 | 3.5 | 416 | 258 | 37 | 0.6 | 0.8 | 1.0 | b.d.l. | 1.8 | 2.7 | 0.57 | b.d.l. |
| 36 | E 48989 | 66.5 | 10.0 | 14.0 | 9.5 | 0.37 | 55.5 | 54.6 | 2.7 | 412 | 150 | 44 | 0.8 | 0.4 | 0.5 | 1.9 | 2.6 | 4.1 | 0.21 | 0.04 |
| 37 | E 48993 | 65.5 | 19.0 | 13.0 | 2.5 | 0.57 | 61.5 | 58.1 | 0.8 | 430 | 153 | 18 | 3.1 | 1.3 | 0.3 | 0.6 | 1.1 | 0.9 | 0.73 | b.d.l. |
| 38 | E 48991 | 37.0 | 28.0 | 31.0 | 4.0 | 0.88 | 81.7 | 81.5 | 0.5 | 438 | 256 | 7 | 3.4 | 0.6 | 0.2 | 1.1 | 1.3 | 2.5 | 0.71 | 0.03 |
| 39 | E 48992 | 22.0 | 0.0 | 77.0 | 1.0 | 0.76 | 66.5 | 67.2 | 0.4 | 440 | 496 | 5 | 4.8 | 0.8 | 0.2 | 0.9 | 0.9 | 1.3 | 0.50 | 0.03 |

$R_r$, random reflectance; TC, total carbon; TOC, total organic carbon; TS, total sulphur; $T_{max}$, temperature of S2 maximum in Rock-Eval pyrolysis; HI, hydrogen index; OI, oxygen index; Pri/Phy, pristane/phytane ratio; Pri/*n*-$C_{17}$, pristane/*n*-heptadecane ratio; Phy/*n*-$C_{18}$, phytane/*n*-octadecane ratio; MNR, methylnaphthalene ratio (2-methylnaphthalene/1-methylnaphthalene); ENR, ethylnaphthalene ratio (2-ethylnaphthalene/1-ethylnaphthalene); DNR, dimethylnaphthalene ratio ([2,6-+2,7-dimethylnaphthalene]/1,5-dimethylnaphthalene); MPI 1, methylphenanthrene index 1 (1.5[2-+3-methylphenanthrene]/[phenanthrene+1-+9-methylphenanthrene]); DBT/P, dibenzothiophene/phenanthrene ratio.
n.a., not available; n.d., not determined; b.d.l., below detection limit.

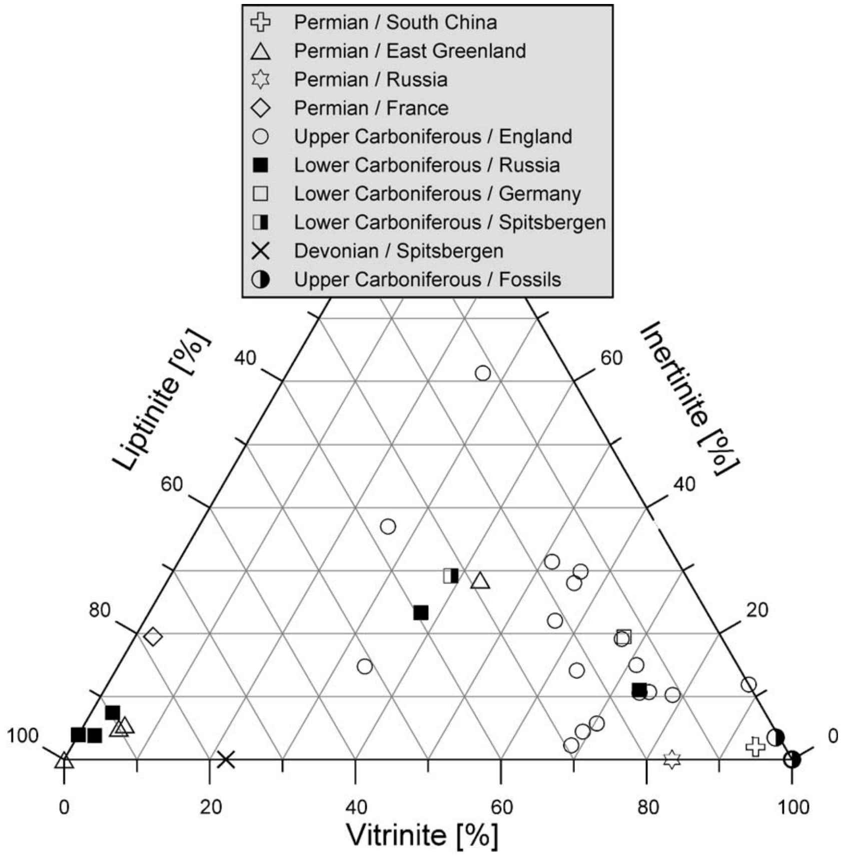

Fig. 2. Maceral group distribution.

Maturity parameters based on the distribution of alkylnaphthalenes show no systematic correlation to the vitrinite reflectance of the samples (Table 2). An increase of the MNR within the maturity range of 0.6–1.5% $R_r$ for example was not observed. A predominance of 2-methylnaphthalene over 1-methylnaphthalene is significant for some of the most immature samples. On the other hand, some of the more mature samples show relatively high proportions of 1-methylnaphthalene. A natural source of 2-methylnaphthalene previously suggested by Borrego et al. (1997) may be the reason for its relatively high abundance in samples of low maturity. However, this does not explain the enhanced proportions of 1-methylnaphthalene in some of the mature samples. The ENR is characterised by the same phenomenon (Table 2). High concentrations of 2-ethylnaphthalene as compared to those of 1-ethylnaphthalene for the immature samples correspond to the high MNR values for these samples (Table 2). The DNR correlates best with the maturity of the samples (Table 2) in particular in the range from 0.70 to 0.88% $R_r$. The Russian coals of low maturity again show relatively enhanced DNR values (Table 2). The Permian sample from Russia in contrast exhibits very low proportions of 2,6- and 2,7-dimethylnaphthalene considering its rather high maturity.

Among the dimethylnaphthalenes, 1,6-dimethylnaphthalene often is highly abundant (Table 3). The relative concentration shows no dependence on either age or maturity of the samples. 1,7- and/or 1,3-dimethylnaphthalene also are major contributors to alkylnaphthalenes for many samples. The two compounds were not quantified separately for most of the samples (Table 3). When quantified separately 1,7-dimethylnaphthalene is more abundant. Enhanced concentrations of the two compounds in comparison to the amounts of summed 2,6- and 2,7-dimethylnaphthalene, even in samples of high maturity, contradict their depleted thermal stability (Budzinski et al., 1993). The low concentrations of 1,5- and 1,2-dimethylnaphthalene in most of the samples on the other hand, can be attributed to their minor thermodynamic stability.

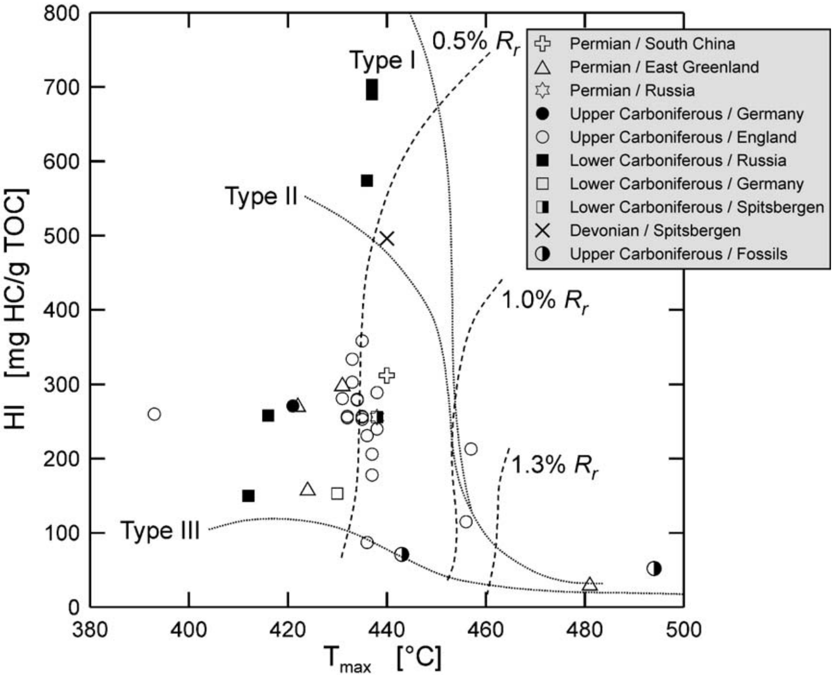

Fig. 3. Cross plot of Hydrogen Index vs. $T_{max}$.

In contrast to dimethylnaphthalenes, the distribution of trimethylnaphthalenes varies more widely. 1,2,4-Trimethylnaphthalene is usually least abundant (Table 3). 1,2,7-Trimethylnaphthalene is relatively abundant in some of the immature samples from the Viséan. 1,2,5-Trimethylnaphthalene often is a predominant compound. The relative proportion of 1,2,5-trimethylnaphthalene, in contrast to its low thermal stability

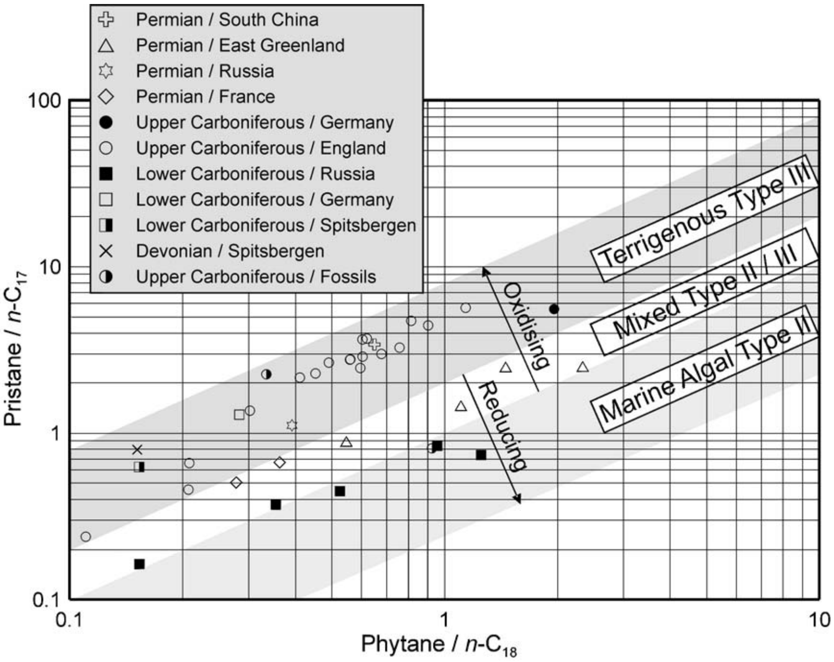

Fig. 4. Cross plot of pristane/$n$-$C_{17}$ vs. phytane/$n$-$C_{18}$.

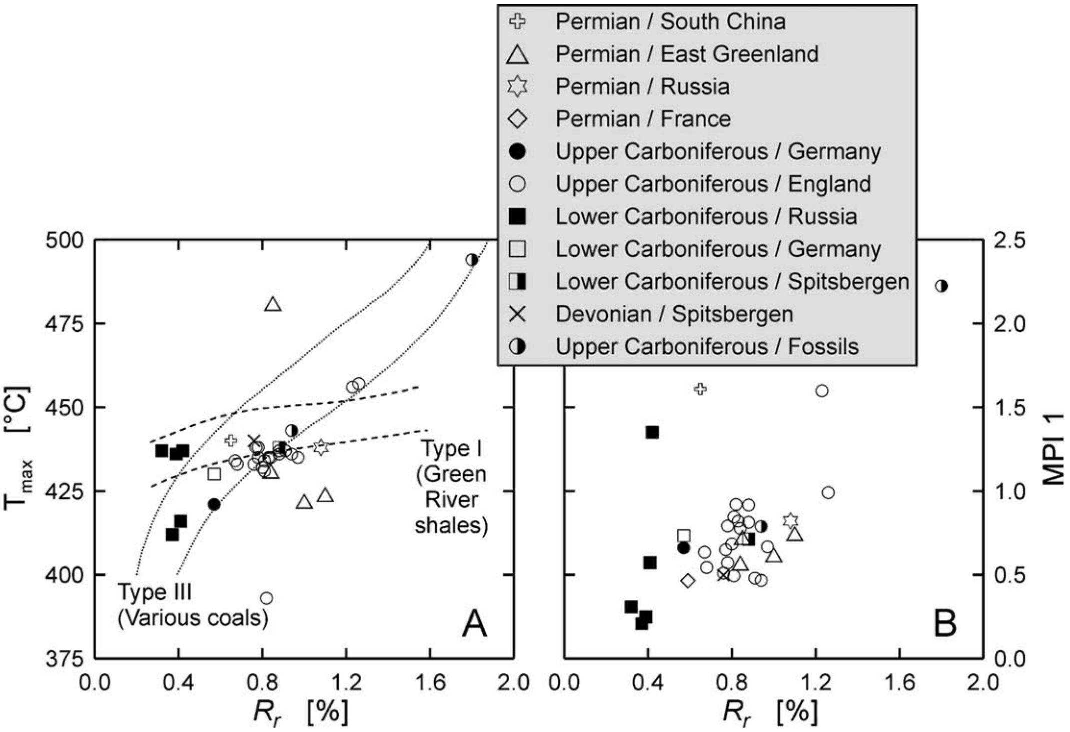

Fig. 5. Cross plot of (A) $T_{max}$ and (B) MPI 1 vs. vitrinite reflectance. Trend lines in Fig. 5a are adopted from Fig. 13 in Tissot et al. (1987).

(Budzinski et al., 1993), is not significantly influenced by the maturity of the samples. Enhanced proportions of 2,3,6- and 1,3,6-trimethylnaphthalene for many samples of rather high vitrinite reflectance correspond to the thermal stability of these isomers.

In many samples 1,2,5,6-, 1,2,3,5-, 1,2,3,6- and 1,3,6,7-tetramethylnaphthalene are highly abundant. Due to the fact that the relative proportions of 1,2,5-trimethylnaphthalene show a strong correlation to the relative amounts of co-eluting 1,2,5,6- and 1,2,3,5-tetramethylnaphthalene, it is assumed that 1,2,5,6-tetramethylnaphthalene is the main contributor to this GC peak. Like 1,2,5-trimethylnaphthalene, 1,2,5,6- plus 1,2,3,5-tetramethylnaphthalene do not show a significant depletion in samples of enhanced maturity. This is in contrast to results reported by Püttmann and Villar (1987), who suggested a recognisable decrease of the two potential biomarkers 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene at elevated thermal maturities. High concentrations of 1,3,6,7-tetramethylnaphthalene correspond to the enhanced thermal stability of this compound (van Duin et al., 1997). It is present in high amounts in most of the samples with a vitrinite reflectance beyond 0.65% $R_r$, but significantly increases for the few samples of maturities above 1.08% $R_r$.

The high proportions of cadalene in most of the immature samples from the Viséan indicate its high abundance in the flora of this region and period. 6-Isopropyl-2-methyl-1-(4-methylpentyl)naphthalene is present in many samples. Except for two samples, it is the only isomer present of the homologous series which Ellis et al. (1996) suggested to originate from resinous diterpenoids. It generally is a minor contributor to the group of alkylnaphthalenes.

### 4.3. Distribution of phenanthrenes

Representative distributions of alkylphenanthrenes in two significantly differing samples are displayed in Fig. 7, while Table 4 provides the concentrations of the $C_0$- to $C_4$-phenanthrenes quantified in this study. The absolute amounts of total alkylphenanthrenes vary widely between 71 and 6160 μg/g TOC (Table 4). They are highly abundant in humic coals, but minor contributors to the samples characterised by low proportions of vitrinite and inertinite.

As pointed out above, MPI-1 in general shows a good correlation to vitrinite reflectance (Fig. 5). However, a more detailed inspection reveals that the calculated vitrinite reflectance is too high for type I kerogen samples of low $R_o$ while they are too low for samples of

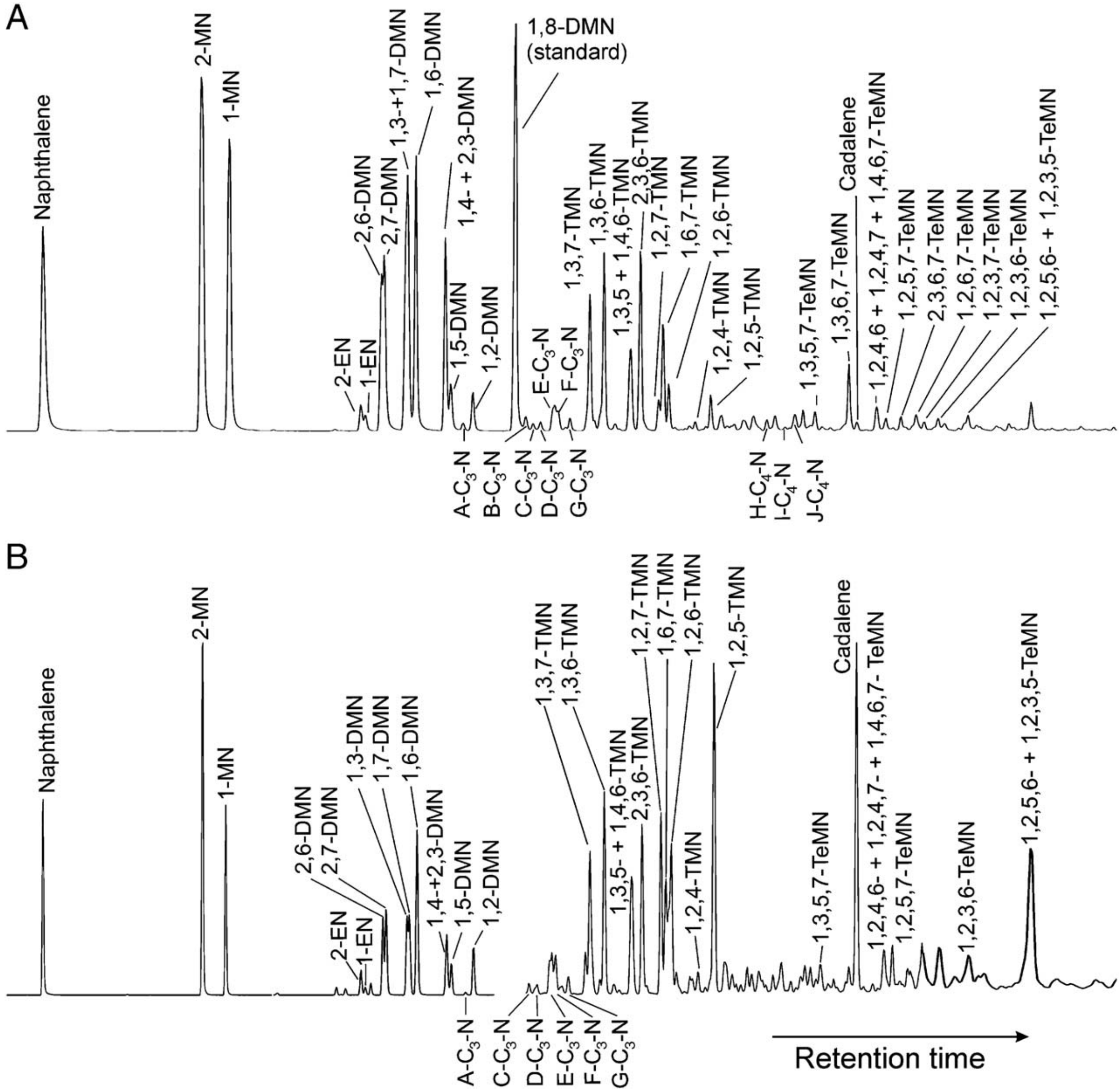

Fig. 6. Extracted ion chromatograms (*m*/*z* 128 + 142 + 156 + 170 + 184 + 198) showing the distribution of alkylnaphthalenes in (A) an Upper Carboniferous (sample 11) and (B) a Lower Carboniferous (sample 36) sample (for the latter sample, the chromatogram has been split due to the high proportions of the internal standard 1,8-dimethylnaphthalene). MN, methylnaphthalene, DMN; dimethylnaphthalene; TMN, trimethylnaphthalene; TeMN, tetramethylnaphthalene.

low TOC content. It is probable that the inorganic matrix influences the thermal behaviour of the organic matter or that the minerals support methyl shift reactions leading to an increase of 9-methylphenanthrene. Most of the samples that show strong deviations are characterised by high proportions of phenanthrene. Normally either 2- or 9-methylphenanthrene are the predominant methylphenanthrenes. With one exception, 2-methylphenanthrene is present in higher amounts than 3-methylphenanthrene.

1,7-Dimethylphenanthrene (pimanthrene) compared to other dimethylphenanthrenes is relatively enriched. The ratio of retene to pimanthrene varies widely in the range of 0.0–5.7. It is significantly high for some immature samples of the Viséan, but also for few samples of the Upper Carboniferous and the *Sigillaria*. A relative increase of pimanthrene at elevated maturities probably results from the destruction of retene. Besides pimanthrene the distribution of $C_2$-phenanthrenes (dimethylphenanthrenes and ethylphenanthrenes) does not vary significantly. Variations seem to be mainly influenced by the maturity of the samples, e.g. the dimethylphenanthrene ratio DPR (Radke et al., 1986) shows a good correlation to $R_o$ for most of the samples. A relative enrichment of 1,9- and 4,9-dimethylphenanthrene for samples that show enhanced proportions of 9-methylphenanthrene indicates a relationship between these compounds. 3,6-Dimethylphenanthrene is present in relatively high concentrations in some samples that show no high thermal maturity. High proportions of this compound have been attributed to samples of enhanced maturities (Budzinski et al., 1995) while a potential biological precursor is unknown.

$C_3$-Phenanthrenes and $C_4$-phenanthrenes are normally present in lower amounts than their lower homologues. This does not account for retene. Additionally the relative amounts of 1,2,8-trimethylphenanthrene vary widely. The 3-methylphenanthrene/retene ratio proposed as a maturity indicator by Wilhelms et al. (1998) shows no correlation to vitrinite reflectance.

## 5. Discussion

A generally accepted age-specific biomarker is 18α-oleanane the assumed diagenetic product of the angiosperm biomarker α-amyrin. Although oleananes have been found in samples that predate the Cretaceous, concentrations have been reported to increase significantly when angiosperms evolved (Moldowan et al., 1994). The presence of oleananes in samples that predate the evolution of angiosperms has been attributed to a possible separate lineage leading to the angiosperms or to a related plant type that possessed the availability to synthesise oleanane precursors (Moldowan et al., 1994). Remarkably, Tori et al. (1995) isolated an 18*a*-oleanane type triterpene ester from the liverwort *Frullania* sp. from South America, although compounds of the oleanane type normally are not found in liverworts.

In this study compounds of the oleanane type could not be detected in any of the analysed samples which appears to correspond well to the fact that angiosperms had not yet evolved in the Late Palaeozoic. In contrast, 1,2,7-trimethylnaphthalene, also attributed to precursors of the oleanane type (Püttmann and Villar, 1987; Strachan et al., 1988; Forster et al., 1989), was generally present. In the study of Strachan et al. (1988), high amounts of 1,2,7-trimethylnaphthalene compared to 1,3,7-trimethylnaphthalene distinguished samples from the Cretaceous and younger from those where oleanane and its precursors were generally absent. This led to the suggestion that 1,2,7-trimethylnaphthalene originates from the diagenetic transformation of triterpenoids of the oleanane type and hence may be regarded as an age specific biomarker related to the organic matter from angiosperms. An overview of the proposed formation pathways of 1,2,7-trimethylnaphthalene is provided in Fig. 1. The plot proposed by Strachan et al. (1988) for the samples investigated in this study reveals that 1,2,5- and 1,2,7-trimethylnaphthalene are present in relatively high proportions in many samples (Fig. 8). This does not hold true for the Upper Carboniferous samples from England and the Permian samples from South France which are characterised by relatively high concentrations of 1,2,5-trimethylnaphthalene only, or low proportions of both compounds, respectively. Both plots, the one of Strachan et al. (1988) and the one of this study (Fig. 8) are characterised by a similar pattern of samples.

These observations clearly indicate that the significance of 1,2,7-trimethylnaphthalene as a potential age specific biomarker related to angiosperms is questionable. Either the significance of the 1,2,7-trimethylnaphtahlene/1,3,7-trimethylnaphthalene ratio is questionable, or 1,2,7-trimethylnaphthalene may originate from another natural source, yet unknown. The above mentioned identification of an 18α-oleanane-type triterpene ester in a liverwort (Tori et al., 1995) documents that the capability to biosynthesise such triterpenoids might have evolved long before the advent of the angiosperms. It cannot be excluded that this capability was common to a wider range of organisms contributing to the organic matter deposited during the Late Palaeozoic which might be one explanation for the widespread occurrence of 1,2,7-trimethylnaphthalene in coals and sediments of this age reported in the present study.

However, it should be noted that for none of the samples investigated in this study, 1,2,7-trimethylnaphthalene showed an extraordinary low or high proportion but normally strongly correlated to most of the other trimethylnaphthalenes. Some of the Cretaceous samples examined by Strachan et al. (1988) also showed no significantly enhanced proportions of 1,2,7-trimethylnaphthalene in comparison to other isomers. This indicates that concentrations of 1,2,7-trimethylnaphthalene may be significantly more influenced by maturation than has been suggested by Strachan et al. (1988). We therefore suggest that the relative abundance of 1,2,7-trimethylnaphthalene does not only depend on the origin from specific biological precursors but also on isomerisation reactions related to thermal stress (van Aarssen et al., 1999).

Table 3
Concentrations of $C_0$ to $C_4$ alkylnaphthalenes in the investigated samples (as the percentage of all reported naphthalenes)

| Sample no. | FZJ no. | Sum (µg/g TOC) | N | 2-MN | 1-MN | 2-EN | 1-EN | 2,6-DMN | 2,7-DMN | 1,3-+1,7-DMN | 1,3-DMN | 1,7-DMN | 1,6-DMN | 1,4-+2,3-DMN | 1,5-DMN | 1,2-DMN | 1,3,7-TMN | 1,3,6-TMN | 1,3,5-+1,4,6-TMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | E 49710 | 1046 | 0.4 | 5.3 | 3.8 | 1.8 | 1.0 | 1.9 | 1.7 | n.d. | 2.2 | 3.2 | 5.8 | 4.3 | 1.4 | 2.4 | 2.2 | 3.0 | 3.4 |
| 2 | E 49748 | n.d. | 23.8 | 21.4 | 10.7 | b.d.l. | b.d.l. | 0.9 | 0.9 | n.d. | 0.9 | 1.5 | 3.7 | 1.8 | 0.2 | b.d.l. | 0.9 | 1.7 | 2.5 |
| 3 | E 49749 | n.d. | 11.3 | 17.3 | 12.1 | 1.5 | 1.5 | 1.8 | 2.1 | n.d. | 2.0 | 3.2 | 4.9 | 3.5 | 1.6 | 2.2 | b.d.l. | 0.5 | 0.1 |
| 4 | E 49750 | n.d. | 28.0 | 20.3 | 11.3 | 0.7 | b.d.l. | 0.4 | 0.4 | n.d. | b.d.l. | b.d.l. | 1.9 | 0.7 | 0.1 | 0.3 | b.d.l. | 0.1 | 0.2 |
| 5 | E 49751 | n.d. | 0.7 | 6.8 | 7.2 | 1.1 | 1.7 | 3.0 | 3.9 | n.d. | 4.1 | 6.6 | 9.4 | 5.4 | 2.7 | 3.4 | 0.9 | 2.6 | 4.4 |
| 6 | E 48990 | 42 | n.d. | 0.2 | 0.9 | 0.1 | 0.2 | 0.4 | 0.6 | n.d. | 2.4 | 4.7 | 3.3 | 3.0 | 1.8 | 1.4 | 7.4 | 8.0 | 9.6 |
| 7 | E 48478 | n.d. | 0.1 | 1.5 | 1.9 | 0.4 | 0.5 | 1.1 | 2.1 | n.d. | 3.6 | b.d.l. | 4.6 | 2.7 | 2.1 | 1.0 | 3.0 | 5.5 | 4.1 |
| 8 | E 48479 | n.d. | 0.2 | 3.1 | 3.5 | 0.3 | 0.4 | 1.3 | 1.5 | n.d. | 3.8 | b.d.l. | 7.1 | 1.6 | 2.0 | 1.4 | 3.3 | 6.8 | 5.0 |
| 9 | E 48996 | 194 | 0.1 | 0.3 | 0.4 | 0.2 | 0.8 | 0.5 | 0.1 | n.d. | 0.3 | 0.8 | 0.6 | 3.1 | 0.3 | 0.9 | 2.7 | 1.8 | 6.6 |
| 10 | E 48388 | 2408 | 1.9 | 17.4 | 14.1 | 0.9 | 0.8 | 2.8 | 3.4 | 8.5 | n.d. | n.d. | 6.0 | 4.8 | 1.5 | 1.5 | 4.0 | 4.4 | 3.4 |
| 11 | E 48389 | 1261 | 4.5 | 22.6 | 15.4 | 0.8 | 0.6 | 2.7 | 4.0 | 8.1 | n.d. | n.d. | 5.5 | 4.2 | 1.2 | 1.2 | 3.4 | 4.1 | 2.5 |
| 12 | E 48390 | 1594 | 4.8 | 27.6 | 16.5 | 1.0 | 0.7 | 2.9 | 3.7 | 7.7 | n.d. | n.d. | 5.0 | 3.8 | 1.2 | 1.2 | 3.0 | 3.2 | 2.2 |
| 13 | E 48214 | 1825 | 1.7 | 19.8 | 14.1 | 1.0 | 0.8 | 3.0 | 3.6 | 8.5 | n.d. | n.d. | 6.1 | 4.6 | 1.5 | 1.5 | 3.7 | 4.3 | 2.9 |
| 14 | E 48216 | 2175 | 2.5 | 19.9 | 14.5 | 0.7 | 0.6 | 3.1 | 2.9 | 8.0 | n.d. | n.d. | 5.4 | 4.2 | 1.3 | 1.4 | 4.0 | 4.4 | 3.3 |
| 15 | E 48430 | n.d. | 0.3 | 9.9 | 9.0 | 1.4 | 1.1 | 3.3 | 2.8 | n.d. | 5.3 | 5.5 | 7.6 | 8.2 | 2.6 | 3.2 | 2.1 | 1.5 | 3.6 |
| 16 | E 48403 | 98 | 0.1 | 0.3 | 0.7 | 0.2 | 0.3 | 1.8 | 2.0 | 3.3 | n.d. | n.d. | 1.1 | 3.6 | 0.9 | 1.2 | 11.2 | 13.0 | 9.2 |
| 17 | E 48220 | 609 | b.d.l. | 1.3 | 2.2 | 0.5 | 0.3 | 2.9 | 2.2 | 5.3 | n.d. | n.d. | 3.2 | 5.0 | 1.2 | 1.1 | 6.7 | 7.1 | 5.7 |
| 18 | E 48392 | 383 | 0.6 | 7.9 | 6.8 | 1.7 | 1.1 | 4.1 | 4.0 | 7.9 | n.d. | n.d. | 5.4 | 8.0 | 2.4 | 2.1 | 4.2 | 3.8 | 3.5 |
| 19 | E 48393 | 350 | 0.1 | 3.2 | 5.4 | 1.2 | 1.2 | 3.2 | 3.3 | 7.6 | n.d. | n.d. | 5.7 | 8.2 | 2.1 | 1.9 | 4.9 | 4.7 | 4.3 |
| 20 | E 48394 | 417 | 0.1 | 0.6 | 2.2 | 0.7 | 0.8 | 3.1 | 3.5 | 3.9 | n.d. | n.d. | 2.2 | 9.3 | 1.6 | 1.0 | 5.4 | 4.8 | 5.2 |
| 21 | E 48395 | 231 | 0.2 | 2.4 | 4.8 | 2.6 | 0.6 | 3.5 | 3.8 | 6.5 | n.d. | n.d. | 4.1 | 6.5 | 2.0 | 2.1 | 5.9 | 5.5 | 3.8 |
| 22 | E 48396 | 282 | 0.1 | 0.2 | 3.0 | 2.0 | 0.7 | 2.0 | 1.3 | 5.1 | n.d. | n.d. | 1.7 | 7.0 | 2.4 | 2.6 | 5.6 | 4.1 | 5.4 |
| 23 | E 48397 | 124 | b.d.l. | 0.1 | b.d.l. | 0.1 | 0.2 | 0.7 | 0.5 | 0.9 | n.d. | n.d. | 0.5 | 1.9 | 0.5 | 0.6 | 3.8 | 3.0 | 5.1 |
| 24 | E 48398 | 117 | 0.1 | 1.2 | 3.8 | 1.3 | 1.0 | 1.9 | 1.7 | 5.2 | n.d. | n.d. | 2.8 | 5.1 | 1.8 | 1.7 | 5.4 | 4.0 | 4.9 |
| 25 | E 48400 | 415 | 0.2 | 4.9 | 8.4 | 1.0 | 0.9 | 2.2 | 2.6 | 8.3 | n.d. | n.d. | 5.3 | 5.2 | 1.8 | 1.8 | 5.4 | 5.9 | 4.8 |
| 26 | E 48401 | 379 | b.d.l. | 0.5 | 1.4 | 0.3 | 0.5 | 0.9 | 1.6 | 5.1 | n.d. | n.d. | 3.8 | 3.3 | 1.5 | 1.5 | 5.8 | 6.3 | 5.9 |
| 27 | E 48405 | 378 | 1.8 | 27.4 | 12.1 | 1.3 | 0.6 | 4.3 | 7.6 | 9.7 | n.d. | n.d. | 6.2 | 3.4 | 1.3 | 0.6 | 3.5 | 4.0 | 1.8 |
| 28 | E 48425 | n.d. | b.d.l. | b.d.l. | 2.5 | b.d.l. | 0.0 | 2.4 | 6.0 | n.d. | 2.4 | 3.9 | 6.5 | 4.1 | 1.4 | 0.9 | 6.5 | 10.7 | 3.7 |
| 29 | E 48382 | 419 | 1.6 | 22.2 | 18.8 | 1.8 | 1.7 | 1.5 | 2.2 | 7.6 | n.d. | n.d. | 5.3 | 5.9 | 1.8 | 2.8 | 2.0 | 1.9 | 1.6 |
| 30 | E 48383 | 1372 | 0.6 | 9.7 | 12.4 | 0.9 | 0.8 | 2.3 | 2.4 | 7.4 | n.d. | n.d. | 6.1 | 4.5 | 1.9 | 2.4 | 2.9 | 3.5 | 3.0 |
| 31 | E 48384 | 141 | 3.8 | 24.6 | 16.8 | 1.1 | 0.9 | 1.7 | 2.9 | 6.7 | n.d. | n.d. | 5.7 | 3.5 | 1.7 | 2.0 | 1.9 | 2.4 | 1.7 |
| 32 | E 48985 | n.d. | b.d.l. | b.d.l. | b.d.l. | 0.4 | 0.4 | 1.3 | 1.5 | 3.5 | n.d. | n.d. | 3.5 | 2.2 | 1.2 | 1.4 | 4.2 | 5.9 | 4.6 |
| 33 | E 48986 | 21 | 0.5 | 5.0 | 3.8 | 0.4 | 0.3 | 1.3 | 1.9 | n.d. | 1.6 | 2.1 | 4.5 | 1.7 | 1.2 | 1.8 | 2.8 | 3.8 | 3.3 |
| 34 | E 48987 | 6 | 0.7 | 4.7 | 3.7 | 0.7 | 0.4 | 1.6 | 2.8 | n.d. | 1.8 | 3.2 | 5.8 | 2.6 | 1.6 | 2.3 | 4.2 | 5.1 | 4.0 |
| 35 | E 48988 | 144 | b.d.l. | b.d.l. | b.d.l. | 0.3 | 0.2 | 0.9 | 2.5 | n.d. | 1.7 | 3.0 | 7.9 | 2.4 | 1.3 | 0.8 | 4.5 | 4.7 | 7.1 |
| 36 | E 48989 | 150 | 4.4 | 24.1 | 12.4 | 1.1 | 0.4 | 2.3 | 2.9 | n.d. | 2.6 | 2.9 | 5.1 | 2.4 | 1.3 | 2.2 | 1.9 | 2.3 | 2.1 |
| 37 | E 48993 | 189 | b.d.l. | 1.5 | 2.4 | 0.9 | 0.8 | 0.7 | 0.8 | n.d. | 1.5 | 3.1 | 2.3 | 4.5 | 1.7 | 2.1 | 1.8 | 2.5 | 4.7 |
| 38 | E 48991 | 3228 | b.d.l. | 4.6 | 4.3 | 0.8 | 0.6 | 2.3 | 2.5 | n.d. | 2.7 | 3.7 | 5.4 | 4.4 | 1.9 | 2.7 | 3.4 | 4.6 | 4.9 |
| 39 | E 48992 | 1237 | b.d.l. | 10.0 | 10.7 | 1.0 | 1.1 | 1.3 | 1.6 | n.d. | 1.8 | 3.8 | 6.2 | 3.2 | 2.2 | 3.2 | 1.1 | 1.7 | 2.9 |

N, naphthalene; MN, methylnaphthalene; EN, ethylnaphthalene; DMN; dimethylnaphthalene; TMN, trimethylnaphthalene; TeMN, tetramethylnaphthalene; (A–G)–$C_3$–N, sum of unknown $C_3$ naphthalenes; (H–J)–$C_4$–N, sum of unknown $C_4$ naphthalenes.
n.d., not determined; b.d.l., below detection limit.

| 2,3,6-TMN | 1,2,7-TMN | 1,6,7-TMN | 1,2,6-TMN | 1,2,4-TMN | 1,2,5-TMN | (A–G)–$C_3$–N | 1,3,5,7-TeMN | 1,3,6,7-TeMN | 1,2,4,6-+ 1,2,4,7-+ 1,4,6,7-TeMN | 1,2,5,7-TeMN | 2,3,6,7-TeMN | 1,2,6,7-TeMN | 1,2,3,7-TeMN | 1,2,3,6-TeMN | 1,2,5,6-+ 1,2,3,5-TeMN | (H–J)–$C_4$–N | Cadalene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3.1 | 1.4 | 3.5 | 3.4 | 1.3 | 15.6 | 6.7 | 0.2 | 0.5 | 2.2 | 1.9 | 0.4 | 1.3 | 0.6 | 1.8 | 9.5 | 1.1 | 1.8 |
| 1.9 | 1.1 | 1.6 | 2.0 | 0.8 | 5.3 | 1.1 | 0.3 | b.d.l. | 1.8 | 1.4 | b.d.l. | 1.0 | 0.4 | 2.4 | 4.4 | 1.3 | 2.2 |
| b.d.l. | b.d.l. | 0.4 | 0.8 | b.d.l. | 3.9 | 1.8 | 0.3 | b.d.l. | 2.6 | 1.6 | b.d.l. | 2.0 | 0.5 | 5.3 | 15.1 | b.d.l. | 0.0 |
| 0.3 | b.d.l. | 0.2 | 0.4 | b.d.l. | 2.3 | b.d.l. | 0.6 | b.d.l. | 2.7 | 2.0 | 0.5 | 2.3 | 0.8 | 7.2 | 16.3 | b.d.l. | 0.0 |
| 3.4 | 1.7 | 3.1 | 2.8 | 0.9 | 5.2 | 5.0 | 0.3 | 1.8 | 1.6 | 1.5 | 0.5 | 1.1 | 0.4 | 1.8 | 3.5 | 0.7 | 1.0 |
| 5.1 | 3.7 | 6.2 | 2.9 | 1.6 | 8.0 | 4.1 | 1.4 | 4.8 | 4.4 | 3.0 | 1.1 | 2.2 | 1.3 | 2.3 | 3.2 | b.d.l. | 0.6 |
| 4.3 | 1.0 | 3.4 | 4.0 | 0.7 | 6.5 | 4.2 | 1.4 | 3.8 | 4.0 | 4.3 | 1.5 | 3.2 | 2.2 | 6.3 | 12.7 | 2.0 | 0.4 |
| 3.1 | 1.2 | 2.7 | 5.0 | 0.8 | 8.5 | 2.4 | 3.1 | 3.3 | 4.3 | 4.0 | 1.1 | 2.7 | 1.9 | 4.2 | 8.6 | 2.0 | 0.0 |
| 2.1 | 1.5 | 12.2 | 1.0 | 1.5 | 3.1 | 9.0 | 4.0 | 5.6 | 7.0 | 2.6 | 1.7 | 2.9 | 1.5 | 2.7 | 11.6 | 6.7 | 3.5 |
| 4.3 | 0.7 | 3.0 | 1.9 | 0.4 | 1.8 | 3.7 | 0.8 | 1.9 | 1.1 | 0.6 | 0.5 | 0.8 | 0.3 | 0.7 | 1.0 | 1.1 | 0.2 |
| 3.9 | 0.6 | 2.4 | 1.2 | 0.3 | 0.9 | 3.1 | 0.7 | 1.5 | 0.7 | 0.4 | 0.5 | 0.5 | 0.2 | 0.5 | 0.6 | 1.1 | 0.2 |
| 3.1 | 0.5 | 1.8 | 1.0 | 0.3 | 0.8 | 2.9 | 0.5 | 1.1 | 0.6 | 0.3 | 0.3 | 0.4 | 0.2 | 0.3 | 0.5 | 0.6 | 0.1 |
| 4.1 | 0.8 | 2.7 | 1.7 | 0.4 | 1.5 | 3.2 | 0.9 | 1.6 | 0.9 | 0.5 | 0.5 | 0.6 | 0.3 | 0.7 | 0.9 | 1.3 | 0.2 |
| 4.1 | 0.7 | 2.7 | 1.6 | 0.5 | 1.4 | 3.2 | 0.8 | 1.9 | 1.2 | 0.6 | 0.6 | 0.7 | 0.3 | 0.8 | 0.9 | 1.3 | 0.2 |
| 5.8 | 2.2 | 6.3 | 2.7 | 0.3 | 8.7 | 6.4 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.0 |
| 9.5 | 1.2 | 6.5 | 3.0 | 0.6 | 2.8 | 9.9 | 2.2 | 4.5 | 2.0 | 0.8 | 1.5 | 0.9 | 0.5 | 1.1 | 1.0 | 3.0 | 0.3 |
| 9.1 | 1.6 | 5.9 | 2.5 | 0.9 | 2.9 | 7.1 | 2.3 | 4.9 | 3.0 | 1.5 | 1.6 | 1.9 | 0.9 | 2.2 | 2.7 | 3.5 | 0.5 |
| 5.3 | 1.7 | 4.5 | 2.3 | 0.5 | 3.0 | 7.3 | 1.4 | 2.1 | 1.2 | 0.8 | 0.4 | 1.0 | 0.4 | 0.9 | 1.3 | 1.7 | 0.2 |
| 6.0 | 1.4 | 5.2 | 2.6 | 0.7 | 3.7 | 7.6 | 1.7 | 2.7 | 1.8 | 1.0 | 0.7 | 1.2 | 0.6 | 1.3 | 2.2 | 2.2 | 0.5 |
| 7.6 | 2.0 | 6.8 | 2.5 | 0.7 | 5.1 | 8.5 | 2.3 | 3.9 | 2.5 | 1.6 | 1.0 | 1.7 | 0.8 | 1.7 | 3.1 | 3.2 | 0.6 |
| 6.6 | 1.1 | 4.6 | 3.5 | 0.6 | 2.9 | 11.3 | 1.6 | 2.3 | 1.2 | 0.9 | 0.8 | 1.2 | 0.5 | 1.4 | 2.0 | 2.7 | 0.5 |
| 5.7 | 1.9 | 6.3 | 3.7 | 1.1 | 5.5 | 10.2 | 2.2 | 2.9 | 2.2 | 1.6 | 0.9 | 1.9 | 0.8 | 1.9 | 3.7 | 3.9 | 0.3 |
| 6.5 | 2.4 | 6.4 | 5.1 | 0.9 | 10.8 | 7.3 | 1.2 | 4.9 | 4.4 | 4.0 | 1.2 | 3.9 | 1.5 | 3.3 | 12.4 | 5.5 | 0.3 |
| 5.1 | 1.7 | 5.0 | 2.9 | 1.1 | 4.2 | 10.7 | 2.6 | 3.5 | 2.6 | 2.0 | 1.3 | 2.5 | 1.1 | 2.3 | 4.2 | 4.7 | 0.6 |
| 5.6 | 1.1 | 4.5 | 2.5 | 0.7 | 3.1 | 6.5 | 1.7 | 3.1 | 1.9 | 1.1 | 0.9 | 1.5 | 0.6 | 1.3 | 2.4 | 2.2 | 0.4 |
| 6.7 | 1.5 | 5.4 | 4.2 | 1.1 | 4.4 | 6.1 | 2.7 | 5.3 | 3.6 | 2.3 | 1.8 | 3.0 | 1.2 | 2.9 | 5.1 | 3.8 | 0.6 |
| 3.6 | 0.3 | 1.5 | 0.6 | 0.2 | 0.3 | 4.8 | 0.4 | 0.7 | 0.3 | 0.1 | 0.3 | 0.2 | 0.1 | 0.2 | 0.1 | 0.6 | 0.1 |
| 14.2 | b.d.l. | 4.9 | b.d.l. | b.d.l. | 19.7 | 6.0 | b.d.l. | 4.1 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.0 |
| 2.0 | 0.7 | 2.4 | 1.5 | 0.5 | 2.4 | 5.2 | 0.8 | 0.8 | 0.5 | 0.4 | 0.2 | 0.7 | 0.2 | 0.6 | 1.4 | 0.8 | 0.1 |
| 3.3 | 1.2 | 3.0 | 3.6 | 0.7 | 9.3 | 4.1 | 1.0 | 1.4 | 1.3 | 1.1 | 0.4 | 1.2 | 0.4 | 1.3 | 4.4 | 1.2 | 0.2 |
| 1.8 | 0.6 | 1.9 | 2.2 | 0.4 | 3.6 | 3.9 | 0.5 | 0.7 | 0.7 | 0.8 | 0.2 | 0.7 | 0.2 | 0.7 | 2.9 | 0.6 | 0.1 |
| 5.1 | 4.0 | 3.8 | 4.0 | 1.0 | 11.1 | 5.0 | 2.2 | 4.6 | 4.0 | 2.7 | 1.0 | 2.6 | 2.4 | 3.9 | 7.4 | b.d.l. | 5.0 |
| 2.6 | 7.1 | 2.0 | 3.1 | 0.4 | 9.8 | 2.6 | 1.1 | 0.9 | 2.2 | 2.1 | 0.9 | 1.8 | 1.6 | 1.9 | 7.1 | b.d.l. | 17.0 |
| 4.2 | 4.0 | 3.5 | 4.2 | 0.7 | 13.3 | 4.0 | b.d.l. | b.d.l. | b.d.l. | 2.3 | b.d.l. | b.d.l. | b.d.l. | 2.5 | 7.2 | 0.9 | 8.2 |
| 3.7 | 2.5 | 11.4 | 2.2 | b.d.l. | 27.1 | b.d.l. | 2.6 | 6.1 | 6.9 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.0 |
| 2.0 | 4.4 | 1.5 | 1.9 | 0.3 | 4.5 | 2.3 | 0.5 | b.d.l. | 0.7 | 0.6 | 0.3 | 0.6 | 0.4 | 0.6 | 2.2 | b.d.l. | 6.4 |
| 2.3 | 2.3 | 4.1 | 2.7 | 2.5 | 5.4 | 5.4 | 2.1 | 3.3 | 3.8 | 2.8 | 0.7 | 2.3 | 1.4 | 2.6 | 17.3 | 3.1 | 4.5 |
| 5.1 | 1.9 | 4.3 | 4.7 | 1.1 | 6.6 | 5.2 | 1.2 | 3.1 | 2.8 | 2.4 | 1.0 | 2.5 | 1.0 | 2.5 | 5.2 | 0.3 | 0.5 |
| 1.4 | 1.8 | 2.0 | 3.4 | 0.8 | 19.2 | 3.3 | 0.4 | 1.0 | 1.1 | 2.3 | 1.1 | 0.3 | 0.3 | 0.9 | 8.4 | 0.5 | 0.0 |

Table 4

Concentrations of $C_0$ to $C_4$ alkylphenanthrenes in the investigated samples (as the percentage of all reported phenanthrenes)

| Sample no. | FZJ no. | Sum (µg/g TOC) | P | 3-MP | 2-MP | 9-MP | 1-MP | 3-EP | 2-EP | 3,6-DMP | 9-EP | 2,6-DMP | 2,7-DMP | 1,3-+2,10-+3,9-+3,10-DMP | 1,6-+2,9-DMP | 1,7-DMP | 2,3-DMP | 1,9-+4,6-DMP | 1,8-DMP | 1,2,8-TMP | Retene | (A–T)–$C_3$–P | (U–AE)–$C_4$–P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | E 49710 | 1118 | 12.6 | 4.9 | 5.1 | 7.4 | 6.3 | 0.4 | 0.7 | 0.5 | 0.4 | 0.8 | 0.6 | 5.4 | 1.4 | 8.5 | 4.0 | b.d.l. | 2.6 | 3.9 | 2.9 | 22.1 | 9.6 |
| 2 | E 49748 | n.d. | 15.5 | 6.5 | 7.4 | 9.4 | 8.5 | 1.4 | 2.0 | 2.3 | 1.9 | 1.2 | 0.9 | 6.2 | 1.7 | 3.9 | 1.6 | 2.5 | 2.1 | 3.5 | 2.6 | 16.7 | 2.0 |
| 3 | E 49749 | n.d. | 7.2 | 4.2 | 5.8 | 7.0 | 6.5 | 0.8 | 0.9 | 1.4 | b.d.l. | 1.1 | 1.0 | 7.0 | 1.5 | 5.1 | 1.7 | 2.3 | 1.9 | 18.8 | 1.8 | 20.0 | 3.9 |
| 4 | E 49750 | n.d. | 6.6 | 4.0 | 5.7 | 6.9 | 6.2 | 0.8 | 1.1 | 1.3 | b.d.l. | 1.1 | 1.1 | 6.9 | 1.4 | 5.3 | 1.8 | 2.2 | 1.9 | 18.7 | 1.9 | 19.7 | 5.5 |
| 5 | E 49751 | n.d. | 18.4 | 7.2 | 7.5 | 10.8 | 9.3 | 0.5 | 1.0 | 0.7 | 0.6 | 1.2 | 0.9 | 7.9 | 2.0 | 3.8 | 1.3 | b.d.l. | 1.8 | 8.3 | 0.8 | 13.2 | 2.6 |
| 6 | E 48990 | 282.8 | 4.8 | 4.4 | 6.1 | 5.6 | 8.8 | 0.4 | 0.4 | 1.6 | 1.0 | 1.4 | 1.2 | 6.1 | 2.1 | 7.1 | 1.2 | 2.5 | 1.5 | 0.6 | 11.9 | 29.9 | 1.4 |
| 7 | E 48478 | n.d. | 9.2 | 3.4 | 4.5 | 5.5 | 3.9 | 0.3 | 0.4 | 1.2 | 0.3 | 1.1 | 0.9 | 6.0 | 3.1 | 4.4 | 1.1 | 1.4 | 1.2 | 15.3 | 0.9 | 27.0 | 8.9 |
| 8 | E 48479 | n.d. | 12.4 | 3.2 | 4.0 | 6.5 | 4.3 | 0.3 | 0.6 | 1.1 | 0.4 | 1.0 | 0.8 | 7.8 | 3.7 | 4.0 | 1.0 | 2.0 | 1.3 | 8.4 | 0.5 | 29.2 | 7.6 |
| 9 | E 48996 | 268.8 | 15.0 | 7.0 | 7.7 | 10.7 | 7.6 | 2.8 | 1.4 | 2.6 | 0.8 | 0.8 | 0.9 | 7.4 | 2.9 | 1.6 | 2.5 | 3.1 | b.d.l. | b.d.l. | 2.3 | 22.6 | 0.7 |
| 10 | E 48388 | 1360.5 | 12.8 | 7.1 | 8.6 | 8.6 | 7.2 | 0.8 | 0.5 | 2.0 | 0.7 | 1.7 | 1.1 | 8.2 | 4.1 | 2.7 | 2.5 | 2.0 | 1.4 | 1.2 | 1.2 | 20.8 | 4.7 |
| 11 | E 48389 | 790 | 12.9 | 7.8 | 9.3 | 8.9 | 6.2 | 0.7 | 0.4 | 2.0 | 0.5 | 1.8 | 1.2 | 8.5 | 4.0 | 2.6 | 2.7 | 1.6 | 1.1 | 1.0 | 0.7 | 20.8 | 5.2 |
| 12 | E 48390 | 691.1 | 18.5 | 7.7 | 9.9 | 8.9 | 6.5 | 0.8 | 0.5 | 2.1 | 0.5 | 1.6 | 1.2 | 8.5 | 4.7 | 1.9 | 2.5 | 1.7 | 1.1 | 0.7 | 0.7 | 17.0 | 3.0 |
| 13 | E 48214 | 935.8 | 20.9 | 7.6 | 9.3 | 9.1 | 7.0 | 0.8 | 0.5 | 1.9 | 0.7 | 1.5 | 1.0 | 7.4 | 3.9 | 2.2 | 2.2 | 1.8 | 1.2 | 0.8 | 1.0 | 16.0 | 3.4 |
| 14 | E 48216 | 1331.5 | 11.6 | 6.7 | 8.0 | 8.4 | 6.0 | 0.7 | 0.5 | 1.9 | 0.5 | 1.7 | 1.1 | 9.4 | 4.4 | 2.4 | 2.7 | 2.0 | 1.2 | 1.2 | 1.0 | 23.0 | 5.6 |
| 15 | E 48430 | n.d. | 10.9 | 5.7 | 7.6 | 7.0 | 7.4 | 0.8 | 5.2 | 0.5 | 0.6 | 0.7 | 1.4 | 1.3 | 1.8 | 4.5 | 2.1 | 2.4 | 1.7 | 3.7 | 15.9 | 17.9 | 0.8 |
| 16 | E 48403 | 732.9 | 7.4 | 13.5 | 11.7 | 10.1 | 6.2 | 0.7 | 0.2 | 2.5 | 0.1 | 3.4 | 3.0 | 11.8 | 5.3 | 3.9 | 2.3 | 1.9 | 0.5 | 0.2 | b.d.l. | 15.3 | b.d.l. |
| 17 | E 48220 | 1129.3 | 9.0 | 7.7 | 7.8 | 9.9 | 6.4 | 0.9 | 0.6 | 2.2 | 0.6 | 1.7 | 1.2 | 10.0 | 4.7 | 2.1 | 2.6 | 2.2 | 1.3 | 1.3 | 1.1 | 22.0 | 4.7 |
| 18 | E 48392 | 378.1 | 27.9 | 7.0 | 8.3 | 12.0 | 8.0 | 0.9 | 0.6 | 1.7 | 0.9 | 1.0 | 0.7 | 5.7 | 3.3 | 1.7 | 1.6 | 1.8 | 1.1 | 0.7 | 2.0 | 11.4 | 1.7 |
| 19 | E 48393 | 393.7 | 21.6 | 6.2 | 7.3 | 11.2 | 7.0 | 0.9 | 0.6 | 1.7 | 0.7 | 1.1 | 0.8 | 6.2 | 3.6 | 2.2 | 1.6 | 1.7 | 1.1 | 0.8 | 4.6 | 16.2 | 2.8 |
| 20 | E 48394 | 658 | 21.6 | 6.2 | 7.0 | 11.6 | 7.0 | 0.9 | 0.6 | 1.9 | 0.7 | 1.0 | 0.8 | 6.5 | 3.3 | 1.9 | 1.7 | 2.2 | 1.0 | 0.9 | 4.1 | 16.2 | 2.9 |
| 21 | E 48395 | 351.7 | 26.8 | 8.5 | 9.5 | 12.9 | 7.4 | 1.0 | 0.7 | 2.2 | 0.9 | 1.1 | 0.7 | 6.6 | 3.3 | 1.3 | 1.6 | 1.8 | 0.9 | 0.5 | 0.7 | 10.1 | 1.3 |
| 22 | E 48396 | 406.7 | 22.5 | 7.4 | 8.2 | 12.2 | 8.5 | 1.1 | 0.7 | 2.2 | 1.0 | 1.0 | 0.8 | 6.5 | 3.3 | 1.9 | 1.8 | 2.0 | 1.2 | 1.0 | 0.6 | 13.8 | 2.3 |
| 23 | E 48397 | 351.2 | 14.7 | 8.6 | 7.1 | 11.6 | 8.9 | 1.3 | 1.3 | 2.2 | 1.5 | 1.1 | 0.7 | 7.9 | 3.8 | 2.4 | 1.7 | 2.8 | 1.4 | 2.1 | 0.8 | 15.5 | 2.6 |
| 24 | E 48398 | 294.5 | 20.5 | 8.5 | 8.3 | 11.9 | 7.2 | 1.3 | 0.8 | 2.8 | 1.0 | 1.3 | 0.7 | 7.5 | 3.8 | 1.7 | 1.4 | 2.3 | 1.2 | 0.9 | 0.6 | 14.0 | 2.1 |
| 25 | E 48400 | 551.7 | 12.3 | 7.5 | 8.5 | 10.6 | 7.3 | 1.1 | 0.6 | 2.4 | 0.7 | 1.4 | 1.0 | 9.1 | 4.7 | 2.1 | 2.2 | 2.1 | 1.4 | 1.2 | 1.4 | 19.2 | 3.1 |
| 26 | E 48401 | 1341.3 | 13.8 | 6.5 | 7.6 | 11.5 | 7.2 | 1.0 | 0.7 | 2.3 | 1.0 | 1.5 | 0.9 | 8.5 | 4.2 | 2.0 | 2.0 | 2.5 | 1.2 | 1.1 | 2.1 | 19.0 | 3.4 |
| 27 | E 48405 | 864.7 | 30.7 | 13.1 | 16.4 | 8.2 | 5.8 | 0.6 | 0.1 | 2.0 | b.d.l. | 2.3 | 1.8 | 6.2 | 3.0 | 1.6 | 1.7 | 0.7 | 0.3 | b.d.l. | b.d.l. | 5.5 | b.d.l. |
| 28 | E 48425 | n.d. | 24.2 | 18.5 | 26.8 | 3.3 | 3.0 | 0.6 | 3.0 | 0.2 | 0.8 | 2.1 | 5.9 | 4.3 | 0.8 | 1.1 | 1.6 | b.d.l. | b.d.l. | 0.1 | 0.1 | 3.5 | b.d.l. |
| 29 | E 48382 | 617.9 | 32.8 | 7.4 | 10.1 | 15.2 | 8.3 | 0.8 | 0.7 | 1.7 | 0.6 | 0.7 | 0.5 | 4.5 | 2.0 | 1.1 | 1.3 | 1.5 | 0.9 | 0.6 | 0.6 | 7.7 | 1.1 |
| 30 | E 48383 | 1058.9 | 13.1 | 8.3 | 10.5 | 12.1 | 9.6 | 0.8 | 0.4 | 2.0 | 0.7 | 1.4 | 1.0 | 7.3 | 3.9 | 2.5 | 2.0 | 2.2 | 1.2 | 2.1 | 0.9 | 15.5 | 2.7 |
| 31 | E 48384 | 145.8 | 27.1 | 7.0 | 8.3 | 12.9 | 7.8 | 0.6 | 0.6 | 1.4 | 0.7 | 0.9 | 0.6 | 6.4 | 3.1 | 2.3 | 1.2 | 2.4 | 1.0 | 2.0 | 0.3 | 11.7 | 1.6 |
| 32 | E 48985 | n.d. | 25.5 | 13.6 | 18.3 | 5.4 | 4.6 | 0.8 | 0.4 | 0.8 | 2.0 | 3.6 | 2.5 | 4.8 | 3.1 | 2.0 | 1.0 | 0.9 | b.d.l. | 1.3 | 1.4 | 7.3 | 0.6 |
| 33 | E 48986 | 71.1 | 64.1 | 5.5 | 6.8 | 4.2 | 5.5 | 0.3 | 0.1 | 0.3 | 0.3 | 0.6 | 0.4 | 2.0 | 1.3 | 1.8 | 0.4 | 0.4 | 0.3 | 0.4 | 3.0 | 2.4 | b.d.l. |
| 34 | E 48987 | 73.3 | 52.4 | 5.3 | 7.4 | 3.7 | 5.9 | 0.3 | 0.1 | 0.5 | 0.5 | 0.8 | 0.7 | 2.6 | 1.8 | 2.6 | 0.5 | 0.5 | b.d.l. | 0.5 | 9.8 | 4.0 | b.d.l. |
| 35 | E 48988 | 930.3 | 9.8 | 4.2 | 5.0 | 9.0 | 5.6 | 0.9 | 0.1 | 1.0 | 1.0 | 1.2 | 1.2 | 9.6 | 10.5 | 4.0 | 2.1 | 4.0 | b.d.l. | b.d.l. | 1.4 | 27.3 | 2.3 |
| 36 | E 48989 | 151.8 | 69.2 | 4.9 | 5.8 | 3.4 | 4.2 | 0.3 | 0.1 | 0.4 | 0.4 | 0.5 | 0.3 | 1.6 | 1.1 | 1.3 | 0.3 | 0.5 | 0.3 | 0.3 | 2.8 | 2.2 | 0.2 |
| 37 | E 48993 | 233.2 | 9.4 | 4.7 | 4.6 | 4.9 | 4.7 | 1.2 | 0.8 | 1.5 | 0.8 | 0.4 | 0.3 | 5.1 | 5.4 | 2.1 | 1.7 | 1.2 | 1.9 | 2.6 | 30.6 | 14.9 | 1.1 |
| 38 | E 48991 | 6160.2 | 14.5 | 7.1 | 8.1 | 9.0 | 8.4 | 0.9 | 0.9 | 0.7 | 0.7 | 1.4 | 1.1 | 7.8 | 2.5 | 3.2 | 2.3 | 2.5 | 2.1 | 1.9 | 1.2 | 21.1 | 2.6 |
| 39 | E 48992 | 1053.7 | 21.6 | 7.4 | 8.0 | 13.6 | 11.1 | 0.9 | 1.1 | 1.1 | 1.2 | 0.6 | 0.4 | 5.9 | 3.1 | 3.2 | 1.4 | 2.5 | 2.0 | 4.5 | 1.4 | 8.2 | 0.8 |

P, phenanthrene; MP, methylphenanthrene; EP, ethylphenanthrene; DMP, dimethylphenanthrene; TMP, trimethylphenanthrene; (A–T)–$C_3$–P, sum of unknown $C_3$ phenanthrenes; (U–AE)–$C_4$–N, sum of unknown $C_4$ phenanthrenes.

n.d., not determined; b.d.l., below detection limit.

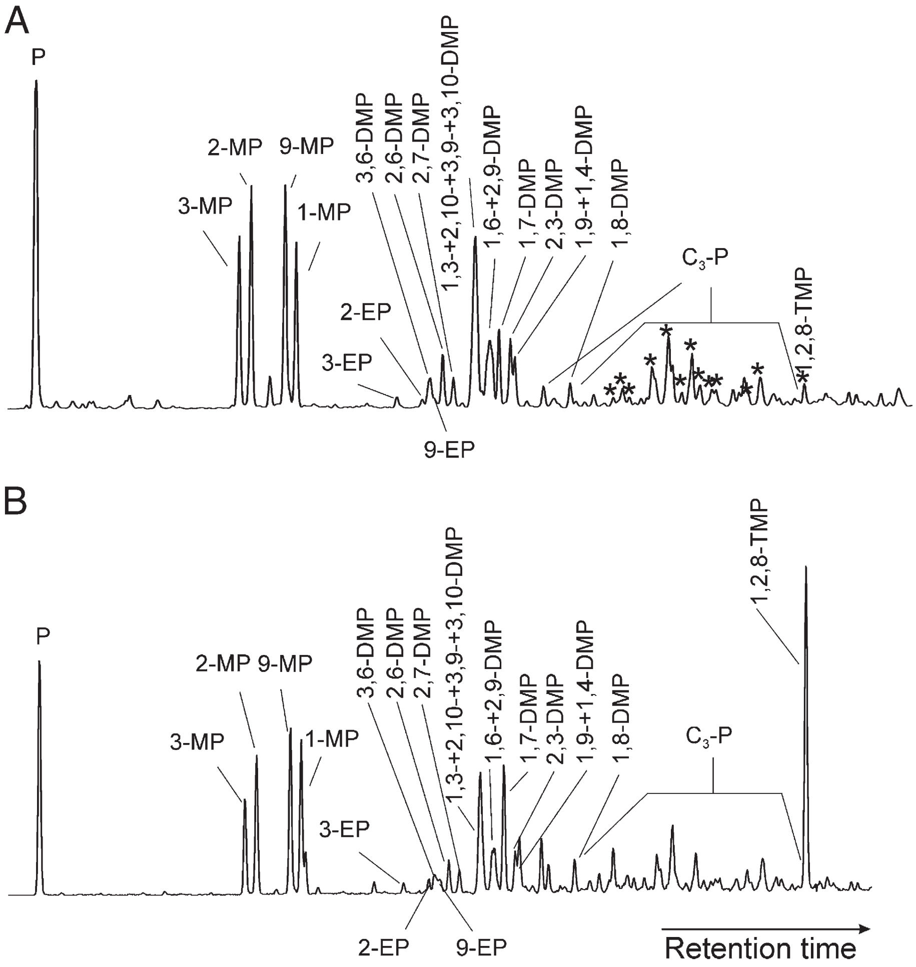

Fig. 7. Extracted ion chromatograms (*m*/*z* 178 + 192 + 206 + 220 + 234) showing the distribution of alkylphenanthrenes in (A) an Upper Carboniferous (sample 14) and (B) a Permian (sample 3) sample. Asterisks mark $C_3$ phenanthrenes used in Fig. 9. P, phenanthrene; MP, methylphenanthrene; DMP, dimethylphenanthrene; TMP, trimethylphenanthrene.

Although alkylphenanthrenes have been attributed to terrestrial plants in general, their significance as more specific biomarkers is to date rather limited. As proposed by Budzinski et al. (1995), 1,2,8-trimethylphenanthrene might be an exception. The compound was highly abundant in samples from the Early Cretaceous and younger (Budzinski et al., 1995). The authors suggested that it may derive from the degradation of certain ubiquitous triterpenoids or hopanoids. Additionally high proportions of 1,2,8-trimethylphenanthrene according to Budzinski et al. (1995) indicate a low maturity of organic matter. More recently, Kruge (2000) tentatively identified 1,2,8-trimethylphenanthrene in shales and coals of Devonian and Late Carboniferous age.

In the present study, 1,2,8-trimethylphenanthrene has been positively identified by co-elution with an authentic standard. Its relative concentration, in comparison to the amounts of summed $C_3$-phenanthrenes, is significantly elevated for the majority of the Permian samples (Fig. 9). In agreement with Budzinski et al. (1995) a dependence of its relative amounts on the thermal maturity cannot be excluded. Samples of enhanced maturities are characterised by a relative depletion of 1,2,8-trimethylphenanthrene in comparison to other isomers. 1,2,8-Trimethylphenanthrene is relatively enriched in most of the low maturity samples of the Lower Carboniferous.

Besides this possible dependence on thermal maturity, the high proportions of 1,2,8-trimethylphenanthrene for most of the Permian samples may indicate an age specific trend. Considering the low maturities of the Lower Carboniferous samples the high proportions of 1,2,8-trimethylphenanthrene for the significantly more

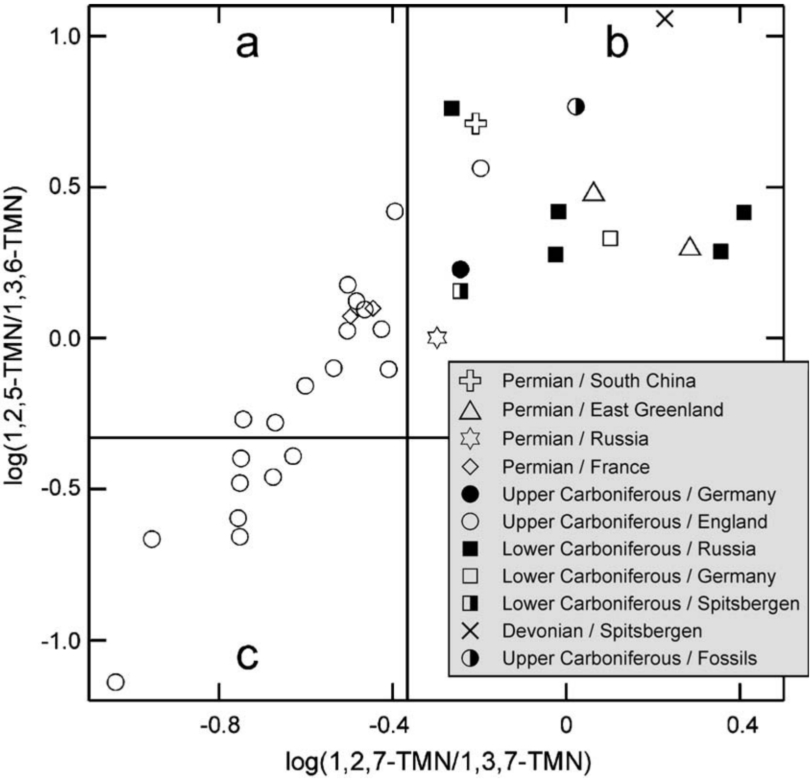

Fig. 8. Cross plot of the logarithm of the 1,2,7-trimethylnaphthalene/1,3,7-trimethylnaphthalene ratio vs. the logarithm of the 1,2,5-trimethylnaphthalene/1,3,6-trimethylnaphthalene ratio and benchmark values for the ratios according to Strachan et al. (1988).

mature Permian samples are indeed rather significant. High amounts apparently present in a Devonian sample investigated by Kruge (2000) on the other hand agree well with the high proportions of 1,2,8-trimethylphenanthrene in the Devonian sample analysed in the present study. This indicates that the potential organism(s) that produced the precursors of 1,2,8-trimethylphenanthrene may have existed in the Devonian while being less dominant in the Carboniferous.

Facies variations may also play a role with respect to the varying proportions of 1,2,8-trimethylphenanthrene. Relative amounts of 1,2,8-trimethylphenanthrene are higher in the two samples from East Greenland with the higher proportion of liptinite in comparison to other maceral groups. Besides their low thermal maturity most of the Lower Carboniferous samples are also characterised by enhanced proportions of liptinite. The two samples from South France are supposed to contain high amounts of marine derived material. This might indicate that 1,2,8-trimethylphenanthrene does not originate from a terrestrial source. The formation of 1,2,8-trimethylphenanthrene from lanosterol via dehydrogenation (King and de Mayo, 1964) shows that steroids are among the potential precursors. It appears likely that other steroids bearing methyl groups at carbon atoms 4, 13 and 14 of the steroid skeleton such as cyclolaudenol (McCaffrey et al., 1989) do also form 1,2,8-trimethylphenanthrene. Sediments, in which compounds of the lanostane type have been identified were deposited in marine or hypersaline environments (Ping'an et al., 1998; Chen and Summons, 2001). Recently, isotopically light lanostane derivatives likely originating from methanotrophs have been reported from a Miocene methane-seep limestone (Peckmann et al., 2004). In agreement with these considerations, our observations would suggest that type III kerogen might be excluded as a major source of 1,2,8-trimethylphenanthrene. However, it must be noted that the *Sigillaria* which consists of almost pure type III kerogen has the highest relative amounts of 1,2,8-trimethylphenanthrene among all studied samples from the Upper Carboniferous. This sample also has a relatively elevated thermal maturity which furthermore would be in contradiction to high relative amounts of 1,2,8-trimethylphenanthrene (see above). It may be concluded that 1,2,8-trimethylphenanthrene shows some promise as an age-related

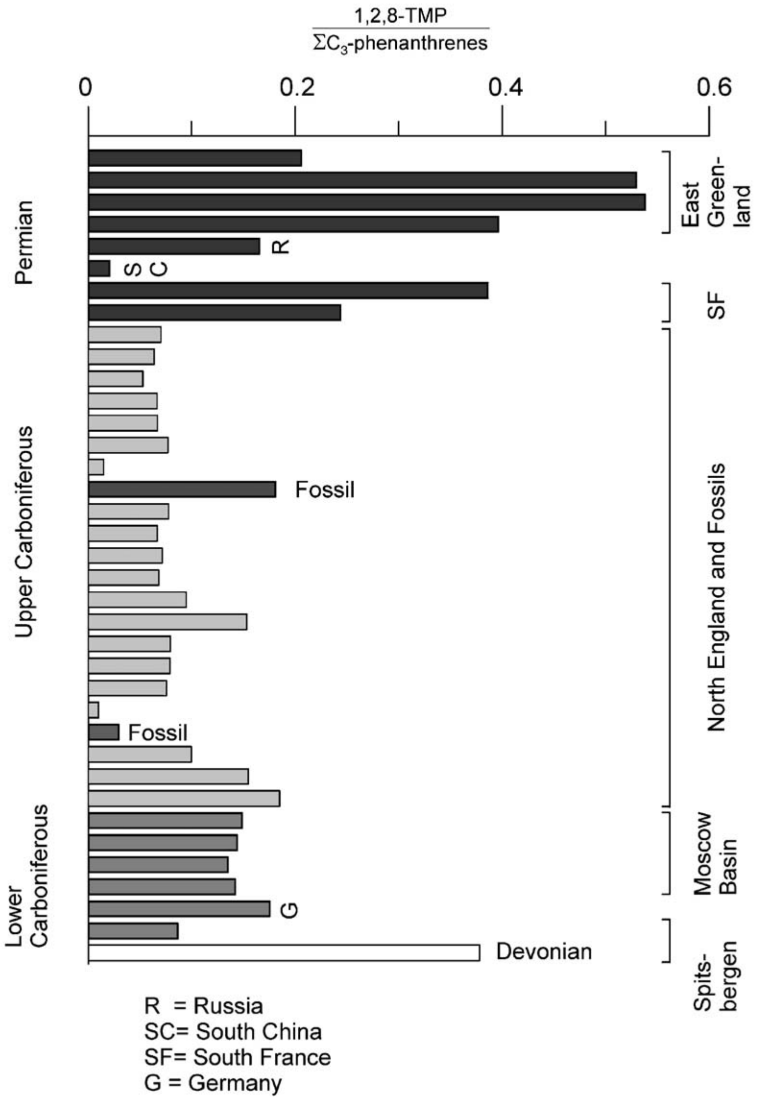

Fig. 9. Bar diagram showing the relative abundance of 1,2,8-trimethylphenanthrene (1,2,8-TMP) among the $C_3$-phenanthrenes marked by asterisks in Fig. 7.

biomarker in the Late Palaeozoic but further studies are required to elucidate the origin of this compound.

The presence of retene and enhanced proportions of 1,2,5-trimethylnaphthalene throughout the sample set point to an enhanced contribution of gymnosperm derived organic matter. The strong correlation of 1,7-dimethylphenanthrene and 1,2,5-trimethylnaphthalene for immature samples indicates that agathic acid is a potential precursor (Thomas, 1969; Carman and Craig, 1971). Another potential biomarker among the aromatic hydrocarbons is 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene which was detected in minor amounts in many of the investigated samples. 6-Isopropyl-2-methyl-1-(4-methylpentyl)naphthalene is supposed to be an aromatic degradation product of phyllocladane (Ellis et al., 1996). Compounds of the phyllocladane, *ent*-beyerane and kaurane type are normally attributed to gymnosperms. Nevertheless, Disnar and Harouna (1994) found these compounds in organic matter predating the evolution of gymnosperms and therefore suggested that they have been constituents of the ancestors of gymnosperms. However, compounds of the phyllocladane type are not present in Pinaceae. This indeed would indicate that the evolution of conifers of the Pinaceae type and other conifers separated early. This has been suggested by many authors (Hart, 1987; Bowe et al., 2000; Chaw et al., 2000; Schmidt and Schneider-Poetsch, 2002) and the observations made here would indicate that this separation at least occurred in the Early Carboniferous.

## 6. Conclusions

Alkylnaphthalenes and -phenanthrenes are abundant constituents of all investigated samples from the Late Palaeozoic, this being typical for terrestrial organic matter of the investigated maturity range. Our results do not indicate specific peculiarities of naphthalene and phenanthrene distributions in comparison to terrestrial organic matter from other geological periods. We therefore conclude that the potential of aromatic hydrocarbons as age related biomarkers is limited. The results on the other hand reveal that potential precursors of certain aromatic hydrocarbons regarded as biomarkers were biosynthesised throughout the Late Palaeozoic. This indicates that either the evolution of these biomarkers has preceded the evolution of the organisms known to produce them or that assumed diagenetic pathways leading to the formation of certain aromatic hydrocarbons are at least incomplete. Based on the presented data the significance of 1,2,7-trimethylnaphthalene as a marker of angiosperms is at best questionable. In contrast, 1,2,8-trimethylphenanthrene appears to be highly abundant in the Permian and the Devonian but significantly less abundant in the Carboniferous indicating that it shows some promise as an age-related biomarker in the Late Palaeozoic.

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## Appendix A

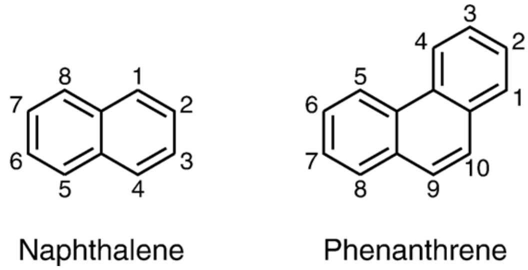

Fig. A1. Structures of naphthalene and phenanthrene illustrating the numbering conventions.

## References

Alekseev, A.S., Kononova, L.I., Nikishin, A.M., 1996. The Devonian and Carboniferous of the Moscow Syneclise (Russian Platform): stratigraphy and sea-level changes. Tectonophysics 268, 149–168.

Alexander, R., Bastow, T.P., Kagi, R.I., Singh, R.K., 1992. Identification of 1,2,2,5-tetramethyltetralin and 1,2,2,3,4-pentamethyltetralin as racemates in petroleum. Journal of the Chemical Society, Chemical Communications 1906, 1712–1714.

Borrego, A.G., Blanco, C.G., Püttmann, W., 1997. Geochemical significance of the aromatic hydrocarbon distribution in the bitumens of the Puertollano oil shales, Spain. Organic Geochemistry 26, 219–228.

Bowe, L.M., Coat, G., dePamphilis, C.W., 2000. Phylogeny of seed plants based on all three genomic compartments: extant gymnosperms are monophyletic and Gnetales' closest relatives are conifers. Proceedings of the National Academy of Sciences of the United States of America 97, 4092–4097.

Brassell, S.C., Eglinton, G., 1986. Molecular geochemical indicators in sediments. In: Sohn, M. (Ed.), Marine Organic Geochemistry. American Chemical Society, Washington, D.C., pp. 10–32.

Budzinski, H., Garrigues, P., Radke, M., Connan, J., Rayez, J.C., Rayez, M.T., 1993. Use of molecular modelling as a tool to evaluate thermodynamic stability of alkylated polycyclic aromatic hydrocarbons. Energy and Fuels 7, 505–511.

Budzinski, H., Garrigues, P., Connan, J., Devillers, J., Domine, D., Radke, M., Oudins, J.L., 1995. Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. Geochimica et Cosmochimica Acta 59, 2043–2056.

Carman, R.M., Craig, W., 1971. Diterpenoids XXVII. The selenium dehydrogenation of manool. Australian Journal of Chemistry 24, 361–370.

Chaffee, A.L., Fookes, C.J.R., 1988. Polycyclic aromatic hydrocarbons in Australian coals: III. Structural elucidation by proton nuclear magnetic resonance spectroscopy. Organic Geochemistry 12, 261–271.

Chaffee, A.L., Johns, R.B., 1983. Polycyclic aromatic hydrocarbons in Australian coals: I. Angularly fused pentacyclic tri- and tetraaromatic components of Victorian brown coal. Geochimica et Cosmochimica Acta 47, 2141–2155.

Chaloner, W.G., Meyen, S.V., 1973. Carboniferous and Permian floras of the northern continents. In: Hallam, A. (Ed.), Atlas of Palaeobiogeography. Elsevier, Amsterdam, pp. 169–186.

Chaw, S.-M., Parkinson, C.L., Cheng, Y., Vincent, T.M., Palmer, J.D., 2000. Seed plant phylogeny inferred from all three plant genomes: monophyly of extant gymnosperms and origin of Gnetales from conifers. Proceedings of the National Academy of Sciences of the United States of America 97, 4086–4091.

Chen, J., Summons, R.E., 2001. Complex patterns of steroidal biomarkers in Tertiary lacustrine sediments of the Biyang Basin, China. Organic Geochemistry 32, 115–126.

Christiansen, F.G., Piasecki, S., Stemmerik, L., Telnæs, N., 1993. Depositional environment and organic geochemistry of the Upper Permian Ravnefjeld Formation source rock in East Greenland. The American Association of Petroleum Geologists Bulletin 77, 1519–1537.

Disnar, J.R., Harouna, M., 1994. Biological origin of tetracyclic diterpanes, n-alkanes and other biomarkers found in Lower Carboniferous Gondwana coals (Niger). Organic Geochemistry 21, 143–152.

Ellis, L., Singh, R.K., Alexander, R., Kagi, R.I., 1996. Formation of isohexyl alkylaromatic hydrocarbons from aromatization–rearrangement of terpenoids in the sedimentary environment: a new class of biomarker. Geochimica et Cosmochimica Acta 60, 4747–4763.

Espitalié, J., Bordenave, M.L., 1992. Tools for source-rock routine analysis. In: Bordenave, M.L. (Ed.), Applied Petroleum Geochemistry. Éditions Technip, Paris, pp. 237–261.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mètres, de leur potentiel pétrolier et de leur degré d'évolution. Revue de l'Institut Français du Pétrole 32, 23–43.

Forster, P.G., Alexander, R., Kagi, R.I., 1989. Identification and analysis of tetramethylnaphthalenes in petroleum. Journal of Chromatography, A 483, 384–389.

Greiner, A., Spyckerelle, C., Albrecht, P., 1976. Aromatic hydrocarbons from geologic sources I. New naturally occurring phenanthrene and chrysene derivatives. Tetrahedron 32, 257–260.

Guion, P.D., Fielding, C.R., 1986. Westphalian A and B sedimentation in the Pennine Basin. Meeting. University of Keele, United Kingdom, pp. 35–37.

Hart, J., 1987. A cladistic analysis of conifers: preliminary result. Journal of the Arnold Arboretum 68, 269–307.

Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P., Studier, M.H., 1978. Trapped organic compounds and aromatic units in coals. Fuel 57, 541–548.

Hazai, I., Alexander, G., Szekely, T., 1989. Study of aromatic biomarkers in brown coal extracts. Fuel 68, 49–54.

Heppenheimer, H., Steffens, K., Püttman, W., Kalkreuth, W., 1992. Comparison of resinite-related aromatic biomarker distributions in Cretaceous–Tertiary coals from Canada and Germany. Organic Geochemistry 18, 273–287.

Holba, A.G., Tegelaar, E.W., Huizinga, B.J., Moldowan, J.M., Singletary, M.S., McCaffrey, M.A., Dzou, L.I.P., 1998. 24-Norcholestanes as age-sensitive molecular fossils. Geology 26, 783–786.

Holliday, D.W., Pattison, J., 1987. Carboniferous geology of Corbridge and Prudhoe. Technical Report WA/90/13. British Geological Survey.

Jones, N.S., 1992. Sedimentology of Westphalian coal-bearing strata and applications to opencast coal mining, west Cumbrian Coalfield, U.K. Ph.D. thesis. Oxford Brookes University.

Karrer, W., 1976. Konstitution und Vorkommen der organischen Pflanzenstoffe (exklusive Alkaloide). Birkhäuser Verlag, Basel.

King, J.F., de Mayo, P., 1964. Terpenoid rearrangements. In: de Mayo, P. (Ed.), Molecular Rearrangements Part 2. Interscience Publishers, New York, pp. 771–840.

Kruge, M.A., 2000. Determination of thermal maturity and organic matter type by principal components analysis of the distributions of polycyclic aromatic compounds. International Journal of Coal Geology 43, 27–51.

Littke, R., Leythaeuser, D., Radke, M., Schaefer, R.G., 1990. Petroleum generation and migration in coal seams of the Carboniferous Ruhr Basin, northwest Germany. Organic Geochemistry 16, 247–258.

McCaffrey, M.A., Farrington, J.W., Repeta, D.J., 1989. Geochemical implications of the lipid composition of *Thioploca* spp. from the Peru upwelling region — 15°. Organic Geochemistry 14, 61–68.

Moldowan, J.M., Talyzina, N.M., 1998. Biogeochemical evidence for dinoflagellate ancestors in the early Cambrian. Science 281, 1168–1170.

Moldowan, J.M., Dahl, J., Huizinga, B.J., Fago, F.J., Hickey, L.J., Peakman, T.M., Taylor, D.W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. Science 265, 768–771.

Peckmann, J., Thiel, V., Reitner, J., Taviani, M., Aharon, P., Michaelis, W., 2004. A microbial mat of a large sulfur bacterium preserved in a Miocene methane-seep limestone. Geomicrobiology Journal 21, 247–255.

Pentegova, V.A., Dubovenko, Z.V., Vol'skii, L.N., Vasilyuk, S.M., Chirkova, M.A., Schmidt, E.N., 1968. Sesquiterpenoid hydrocarbons from the oleoresins of some Siberian conifer species. Siberian Chemistry 211–214.

Piasecki, S., Stemmerik, L., 1991. Late Permian anoxia in central East Greenland. In: Tyson, R.V., Pearson, T.H. (Eds.), Modern and Ancient Continental Shelf Anoxia. Geological Society, London, pp. 275–290.

Ping'an, P., Morales-Izquierdo, A., Jiamo, F., Guiying, S., Ji'gang, J., Hogg, A., Strausz, O.P., 1998. Lanostane sulphides in an immature crude oil. Organic Geochemistry 28, 125–134.

Püttmann, W., Villar, H., 1987. Occurrence and geochemical significance of 1,2,5,6-tetramethylnaphthalene. Geochimica et Cosmochimica Acta 51, 3023–3029.

Radke, M., Sittardt, H.G., Welte, D.H., 1978. Removal of soluble organic matter from rock samples with a flow-through extraction cell. Analytical Chemistry 50, 663–665.

Radke, M., Welte, D.H., Willsch, H., 1982a. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. Geochimica et Cosmochimica Acta 46, 1–10.

Radke, M., Willsch, H., Leythaeuser, D., Teichmüller, M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. Geochimica et Cosmochimica Acta 46, 1831–1848.

Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. Organic Geochemistry 10, 51–63.

Radke, M., Garrigues, P., Willsch, H., 1990. Methylated dicyclic and tricyclic aromatic hydrocarbons in crude oils from the Handil field, Indonesia. Organic Geochemistry 15, 17–34.

Radke, M., Rullkötter, J., Vriend, S.P., 1994. Distribution of naphthalenes in crude oils from the Java Sea: source and maturation effects. Geochimica et Cosmochimica Acta 58, 3675–3689.

Schmidt, M., Schneider-Poetsch, H.A.W., 2002. The evolution of gymnosperms redrawn by phytochrome genes: the Gnetatae appear at the base of the gymnosperms. Journal of Molecular Evolution 54, 715–724.

Simoneit, B.R.T., Grimalt, J.O., Wang, T.G., Cox, R.E., Hatcher, P.G., Nissenbaum, A., 1986. Cyclic terpenoids of contemporary resinous plant detritus and of fossil woods, ambers and coals. Organic Geochemistry 10, 877–889.

Strachan, M.G., Alexander, R., Kagi, R.I., 1988. Trimethylnaphthalenes in crude oils and sediments: effects of source and maturity. Geochimica et Cosmochimica Acta 52, 1255–1264.

Strasburger, E., Noll, F., Schenck, H., Schimper, A.F.W., 1991. Lehrbuch der Botanik für Hochschulen. Gustav Fischer Verlag, Stuttgart.

Streibl, M., Herout, V., 1969. Terpenoids — especially oxygenated mono-, sesqui-, di-, and triterpenes. In: Eglinton, G., Murphy, M.T.J. (Eds.), Organic Geochemistry. Springer Verlag, Berlin, pp. 401–424.

Teichmüller, M., Teichmüller, R., 1968. Cainozoic and Mesozoic coal deposits of Germany. In: Murchison, D.G., Westoll, T.S. (Eds.), Coal and Coal-Bearing Strata. Oliver and Boyd, Edinburgh, pp. 347–377.

Thomas, B.R., 1969. Kauri resins — modern and fossil, organic geochemistry. Methods and Results. Springer Verlag, Berlin, pp. 599–618.

Tissot, B.P., Pellet, R., Ungerer, P., 1987. Thermal history of sedimentary basins, maturation indices, and kinetics of oil and gas generation. AAPG Bulletin 71, 1445–1466.

Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence. Springer Verlag, Heidelberg.

Tori, M., Aoki, M., Nakashima, K., Asakawa, Y., 1995. Terpenoids from the liverworts *Symphyogyna brasiliensis* and unidentified *Frullania* species. Phytochemistry 39, 99–103.

van Aarssen, B.G.K., Bastow, T.P., Alexander, R., Kagi, R.I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Organic Geochemistry 30, 1213–1227.

van Duin, A.C.T., Baas, J.M.A., van de Graaf, B., de Leeuw, J.W., Bastow, T.P., Alexander, R., 1997. Comparison of calculated equilibrium mixtures of alkylnaphthalenes and alkylphenanthrenes with experimental and sedimentary data; the importance of entropy calculations. Organic Geochemistry 26, 275–280.

Wilhelms, A., Telnæs, N., Steen, A., Augustson, J., 1998. A quantitative study of aromatic hydrocarbons in a natural maturity shale sequence — the 3-methylphenanthrene/retene ratio, a pragmatic maturity parameter. Organic Geochemistry 29, 97–105.

Willsch, H., Clegg, H., Horsfield, B., Radke, M., Wilkes, H., 1997. Liquid chromatographic separation of sediment, rock and coal extracts and crude oil into compound classes. Analytical Chemistry 69, 4203–4209.

Young, B., Armstrong, M., 1989. The applied geological mapping of the Dearham and Gilcrux area, Cumbria. Technical Report WA/92/70. British Geological Survey.

Young, B., Boland, M.P., 1992. Geology and land-use planning: Great Broughton–Lamplugh area, Cumbria. Technical Report WA/92/54. British Geological Survey.

Zhong, N.N., Smyth, M., 1997. Striking liptinitic bark remains peculiar to some Late Permian Chinese coals. International Journal of Coal Geology 33, 333–349.