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Biomarker composition of higher plant macrofossils from Late Palaeozoic sediments

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Abstract

The main objective of the present study was to clarify if the fernane derivatives 5-methyl-10(4-methylpentyl)-des-*A*-25-norferna-5,7,9-triene (MATH), 25-norferna-5,7,9-triene (MAPH), 24,25-dinorferna-1,3,5,7,9-pentaene (DAPH 1) and iso-25-norferna-1,3,5,7,9-pentaene (DAPH 2) can securely be assigned to one of the three previously proposed source plant groups from some Euramerican Upper Carboniferous coals (uppermost Westphalian and Stephanian). For this purpose remains of conifers, cordaites and pteridosperms were isolated from core and outcrop material from different Euramerican coal basins (e.g. Saar–Nahe Basin, Blanzy–Montceau Basin). Results show that MATH, MAPH, DAPH 1 and DAPH 2 were present in all extracts of cordaite remains. In the sediments surrounding the cordaite macrofossils, the compounds were either not detectable or have been found only in comparatively small amounts obviously due to impregnation originating from imbedded cordaites. Contrarily, the compounds were not detected in the extractable organic matter of conifer macrofossils derived from the Saar–Nahe Basin, from Bletterbach (South Tyrole, Italy), and from Frankenberg (Hessen, Germany). The same is true for remains of horsetails (*Calamites*), giant club mosses (*Lepidodendron* and *Sigillaria*), and ferns (*Pecopteris*) from the Saar–Nahe Basin which have been studied for comparison. The compounds were also lacking in the extractable organic matter of pteridosperms like *Alethopteris*, *Dicroidium*, *Lescuropteris*, *Macroneuropteris* and *Neuropteris*, but were detected in minor amounts in some *Odontopteris* remains from the Blanzy–Montceau Basin (France). However, the sediments surrounding the *Odontopteris* macrofossils yielded even higher concentrations of the compounds. For this reason, the *Odontopteris* macrofossils were most likely impregnated by migrating fernane derivatives from the sediment which were possibly originally originating from cordaite remains. Therefore, cordaites can most probably be considered as one and, possibly, the only biological source of the precursor molecules of the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 in the Upper Carboniferous coal basins.

Keywords: Fernane derivatives; Biomarker analysis; Carbon isotopic ratio; Cordaites; Conifers; Pteridosperms

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1. Introduction

Palynological and palaeobotanical studies on coals from Upper Carboniferous Euramerican coal basins show a major change in the composition of coal-swamp floras throughout the Pennsylvanian, especially at the

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Westphalian–Stephanian (≈Desmoinesian–Missourian) boundary. The lycopod-dominated flora in various Euramerican coal basins changed into a tree fern-dominated flora accompanied by an increasing importance of seed plants such as cordaites, pteridosperms and conifers (Phillips et al., 1974; Phillips and Peppers, 1984; Kerp, 1996a,b; Di Michele et al., 2001).

Biomarker research is one possibility to describe such a floral change on a molecular basis and has preferentially been applied to investigate coals and sediments of Mesozoic and Cenozoic age. A well known example of biomarkers are oleananes, diagenetic products of pentacyclic triterpenoids like amyrines. Oleananes have been used to record the first appearance of angiosperms during the Cretaceous (ten Haven and Rullkötter, 1988; Strachan et al., 1988). The relative abundance of higher-plant-derived biomarkers (e.g. retene, cadalene) as expressed through the higher plant fingerprint (HPF) was previously suggested to reflect palaeovegetational changes during Jurassic times in the Carnarvon Basin, Western Australia (van Aarssen et al., 2000). The HPF is largely determined by the original terrestrial input at the time of deposition while diagenetic and catagenetic processes are relatively unimportant. However, few biomarker studies tracked floral changes in Palaeozoic coals and sediments. For instance, biomarker studies were carried out on Carboniferous coals from the Ruhr Coal Basin (Germany), the Saar–Nahe Basin (Germany), Oklahoma (U.S.A.) and the Ukraine (Schulze and Michaelis, 1990; ten Haven et al., 1992; Stefanova et al., 1995) and on a Carboniferous wood from Scotland (Raymond et al., 1989). Within the scope of these studies phyllocladane and its related tetracyclic diterpenoids were traced back to the Lower Carboniferous and were regarded as biomarkers for gymnosperms (e.g. Noble et al., 1985a,b; Alexander et al., 1987; Raymond et al., 1989). Phyllocladanes were also detected in Upper Carboniferous coals from the Saar–Nahe Basin (Germany) and were attributed to the first appearance of conifers during the Westphalian A (Schulze and Michaelis, 1990). Further combined palynological and organic geochemical analyses of Upper Carboniferous coals from the Saar–Nahe Basin proved the presence of the arborane/fernane derivatives MATH (5-methyl-10(4-methylpentyl)des-A-25-norarbora(ferna)-5,7,9-triene), MAPH (25-norarbora(ferna)-5,7,9-triene), DAPH 1 (24,25-dinorarbora(ferna)-1,3,5,7,9-pentaene) and DAPH 2 (iso-25-norarbora(ferna)-1,3,5,7,9-pentaene) (Fig. 1) in samples beginning with the Upper Westphalian D (Vliex, 1994; Vliex et al., 1994, 1995) which accords well with the floral change at the Westphalian/Stephanian boundary. Isoarborinol and/or fernenes/fernenol were suggested as possible precursor molecules of the arborane/fernane derivatives (Vliex, 1994; Vliex et al., 1994, 1995). Correlation of biomarker data with palynological investigations provided evidence that the arborane/fernane derivatives originate either from cordaites, pteridosperms or conifers; a more detailed identification of their biological source was not yet possible (Vliex, 1994; Vliex et al., 1994, 1995). However, a bacterial origin for arborane/fernane derivatives has been discussed as well (Brassell and Eglinton, 1981; Hauke et al., 1992a,b).

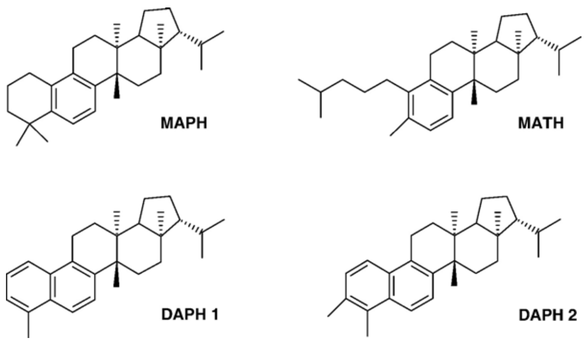


Fig. 1. Molecular structures of the fernane derivatives MAPH, MATH, DAPH 1 and DAPH 2.

It is not possible to identify from the mass spectra obtained from GC/MS analyses whether the diagenetic products MATH, MAPH, DAPH 1 and DAPH 2 in the sediment extracts have either an arborane or a fernane skeleton. A possibility to distinguish between these stereoisomeric compounds represents the measurement of the optical rotation $[\alpha]_D$ of the isolated molecules (Hauke et al., 1995). Hauke et al. (1995) isolated several aromatized compounds with an arborane/fernane skeleton (e.g. des-*A*-arbora-5,7,9-triene, MAPH and DAPH 1) from the Eocene Messel oil shale, Jurassic to Permian lacustrine sediments and from a Stephanian coal from the Saar–Nahe Basin. The optical rotation values of MAPH from a Carboniferous coal from the Saar–Nahe Basin were in accordance with a fernane-type structure ($[\alpha]_D=-12$; compared to $[\alpha]_D=-23$ for synthetically derived MAPH). In contrast, MAPH ($[\alpha]_D=+16$), des-*A*-arbora-5,7,9-triene ($[\alpha]_D$-values between +25 and +37) and DAPH 1 ($[\alpha]_D=+31$) isolated from younger sediments (Permian to Eocene) provided optical rotation values related to an arborane-type structure with isoarborinol as the presumed precursor molecule (Hauke et al., 1995). By analogy in Upper Carboniferous samples, the compounds MATH, MAPH, DAPH 1 and DAPH 2 can therefore be assigned to have a

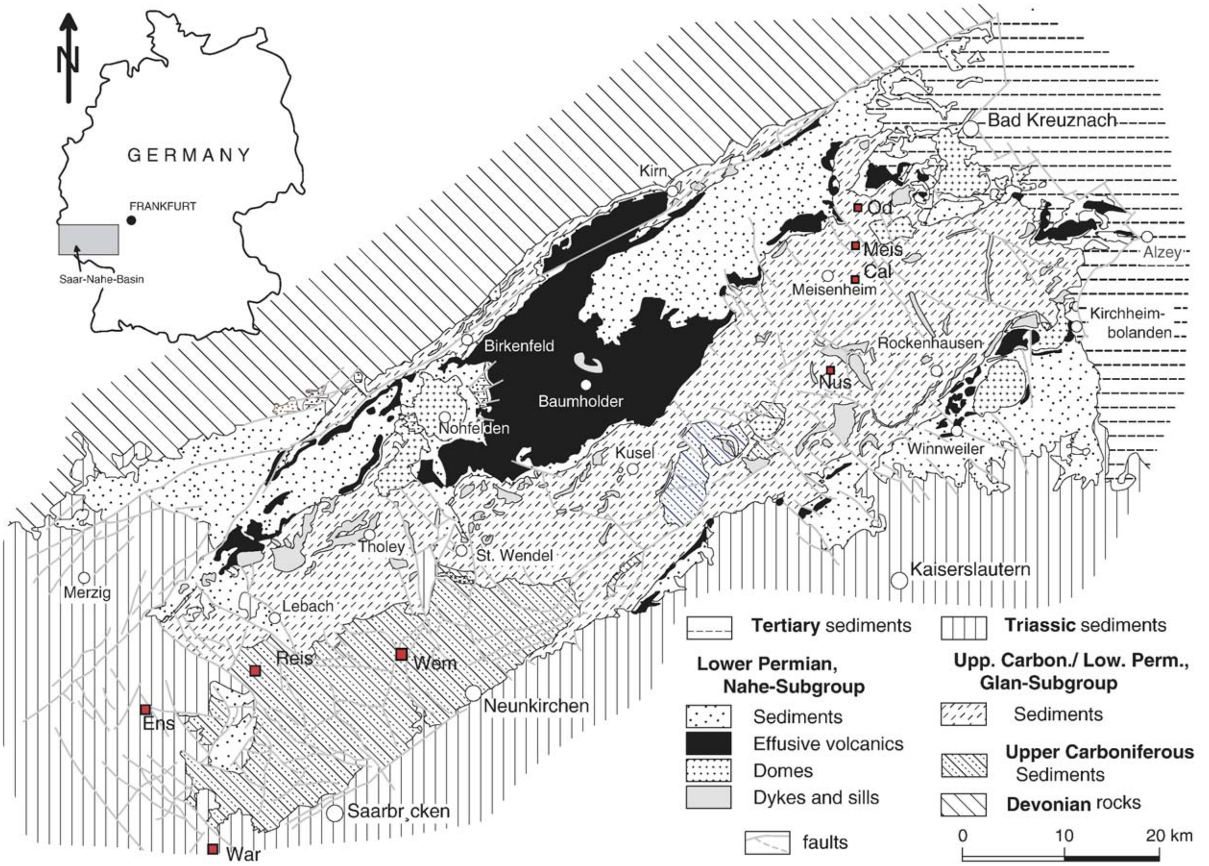


Fig. 2. Geological map of the Saar–Nahe Basin. Wem ≡ bore hole Wemmetsweiler-Nord; Od ≡ bore hole Odernheim; Cal ≡ bore hole Callbach; Ens ≡ mine Ensdorf; War ≡ mine Warndt; Reis ≡ mine Reisbach (modified, from: Lorenz and Haneke, 2004).

fernane-type structure and are referred to as fernane derivatives (Fig. 1).

The aim of the present study was to determine whether the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 in the Upper Carboniferous coals can be assigned either to cordaites, conifers or pteridosperms. Therefore, solvent extracts of various cordaite-, conifer- and pteridosperm macrofossils from different locations (Saar–Nahe Basin, Germany: cores Wemmetsweiler-Nord, Odernheim and Callbach, mines Reisbach, Warndt and Ensdorf; outcrops of Blanzy and Lally, France) were analysed by gas chromatography-mass spectrometry (GC/MS). The plant fossils suitable for analysis had to be of low maturity ($Rr < 0.9\%$) because the fernane derivatives are sensitive to heat and can therefore not be identified in material of higher maturity (Vliex, 1994). Additionally, the compounds MATH, MAPH, DAPH 1 and DAPH 2 were quantified in bulk material from the core Wemmetsweiler-Nord (Saar–Nahe Basin), to refine the previously available data (Vliex et al., 1994) on the variation of the amount of fernane derivatives in sediments of Westphalian/Stephanian age. The $\delta^{13}C$ values of extant C_3-plants cover a rather wide range between $-23‰$ and $-34‰$ (Schoell, 1984; Faure, 1986). In order to investigate if the different fossil plant groups vary over a similar range the $\delta^{13}C$ values of selected plant fossils were determined in addition to the biomarker analyses.

2. Geological settings and sample material

2.1. Coals and sediments from the Saar–Nahe Basin

The Permo-Carboniferous Saar–Nahe Basin is part of the much larger Lorraine–Saar–Nahe–Hessen Basin (Falke, 1971) and is situated within the former Variscan mountain range in the southwest of Germany (Fig. 2). The sequence of Upper Carboniferous and Lower Permian (Upper Rotliegendes) age outcrops over an area of about 100 × 40 km. However, the total extent of the basin including areas below a Mesozoic cover is about 300 × 100 km. The Upper

Carboniferous sediments of the basin are 4100 m thick. Peats (=coals) were mainly deposited during the humid period of the Westphalian, beginning with the Westphalian A. During the drier periods of the Stephanian and the Lower Rotliegendes, number and thickness of the peat layers decreased (Falke, 1971; Schäfer, 1989). Within the Saar–Nahe Basin, the Holzer Konglomerat is generally regarded to represent the boundary between Westphalian D and Stephanian A (Guthörl, 1954; Kneuper, 1966, 1976; Schäfer, 1980, 1986, 1989). But, the conglomerate has an erosional base obviously representing a major gap in the sedimentary record. It has a thickness ranging from 30 m in the Saar–Nahe Basin to more than 50 m in the adjacent Lorraine Basin (Rücklin, 1955).

The 1400 m thick core of Wemmetsweiler-Nord (Fig. 2) is located in the north of the Saarbrücker Hauptsattel (Main Saarbrücken Anticline). It covers the Westphalian beginning with the Lower Heiligenwald–Schichten (Westphalian D) and the Stephanian up to the Heusweiler–Schichten (Stephanian B; Schäfer, 1986, 1989). For the present study, 33 samples of this core characterised by visually high organic carbon contents were selected. The samples cover the Stephanian A and B between a depth of 269 and 826 m and the Westphalian C between a depth of 926 and 1362 m. The samples had to be of limited maturity ($Rr < 0.9\%$) because the fernane derivatives are sensitive to heat and disappear at higher maturity (Vliex, 1994).

2.2. Plant fossils from various Euramerican coal basins

Most of the individual plant fossils for the present study were derived from the Saar–Nahe Basin (Germany) and the Blanzy–Montceau Basin in France. As the Saar–Nahe Basin is concerned, the plant fossils were taken from the cores of Wemmetsweiler-Nord (various remains of cordaites, pteridosperms, horsetails, club mosses and ferns), Odernheim (five specimens of conifer remains), Callbach (one cordaite specimen), the mines Ensdorf (two cordaite specimens), Warndt (one specimen of *Odontopteris reichiana* Gutbier) and Reisbach (various remains of cordaites and pteridosperms) (Fig. 2). Three specimens of cordaites and four of pteridosperms come from the intramontaneous Blanzy–Montceau Basin which is located in the northeastern part of the French Massif Central. The Carboniferous sequence of this basin covers a range from the Stephanian B to the Stephanian D (Doubinger et al., 1995). In addition, a cordaite from Lally (France), conifer remains from Bletterbach (South Tyrole, Italy) and Frankenberg (Germany), as well as a *Dicroidium* specimen (pteridosperm) from Jordan were analysed, all of Permian age.

3. Analytical methods

3.1. Extraction

The bulk samples were finely ground and then Soxhlet-extracted for 24 h with dichloromethane. The coaly material of the plant fossils was carefully separated from the surrounding sediment and then extracted twice by ultrasonic agitation with organic solvent (dichloromethane:methanol 5:1; v:v). Aliquots of the total extracts were converted to trimethylsilyl derivatives by reaction with *N*,*O*-(bis)-trimethysilyl-trifluoroacetamide (BSTFA) and pyridine for 2 h at 60 °C.

3.2. Gas chromatography-mass spectrometry (GC/MS)

GC/MS analyses of the derivatized total extracts were performed on a Thermo Quest GC 8000 series coupled to a Thermo Quest MD 800 mass spectrometer. Separation of the compounds was achieved using a fused silica capillary column coated with ID-BPX5 ($30\ \mathrm{m} \times 0.25\ \mathrm{mm}$ i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 80–300 °C at a rate of $4\ °\mathrm{C\ min}^{-1}$ followed by an isothermal period of 20 min at 300 °C. Helium was used as carrier gas. The samples were injected in the splitless mode with the injector temperature at 280 °C. The mass spectrometer was operated in the electron impact mode (EI) at 70 eV ionization energy and scanned from 50 to 600 Da. Data were acquired and processed with the MassLab™ v1.3 software. Individual compounds were identified by comparison of their mass spectra with published data (identification of the fernane derivatives: Vliex, 1994); squalane was used as internal standard. Quantification of the fernane derivatives was performed on the basis of their characteristic ion traces (MAPH: m/z 377; MATH: m/z 393; DAPH 1: m/z 374; DAPH 2: m/z 388).

3.3. Carbon isotopic ratios

The carbon isotope measurements were performed with an ANCA-SL (**a**utomated **n**itrogen **c**arbon **a**nalysis for **s**olids and **l**iquids) coupling a preparation system employing the Dumas principle with a stable isotope mass spectrometer. After removing carbonate with HCl aliquots of the sample material were loaded into tin capsules and dropped into a furnace at 1000 °C while in an atmosphere of oxygen. After complete combustion carbon dioxide (CO_2) and nitrogen (N_2) were separated and detected in a gas chromatograph followed by a stable isotope mass spectrometer. The system was calibrated using certified flour as standard (δ^{13}C= −25.34‰; %C=40.37%; δ^{15}N=3.01‰; %N=1.67%). The results are reported relative to the PDB standard.

4. Results and discussion

4.1. Organic geochemistry of coal and sediment samples from the drilling core Wemmetsweiler-Nord (Saar–Nahe Basin)

By GC/MS analyses of derivatized extracts from all samples of the core Wemmetsweiler-Nord abundant compounds were identified that were previously detected in other Carboniferous coals of lower maturity as well (Stefanova et al., 1995), e.g. a series of *n*-alkanes (n-C_{11} to n-C_{36}), aromatic hydrocarbons, hopanoids and terpenoids. Most of the biomarkers like the bicyclic sesquiterpanes (Philp et al., 1981; Raymond et al., 1989; Püttmann and Kalkreuth, 1989) or the naphthalenes, phenanthrenes, biphenyls, dibenzofuranes and fluorenes (Radke et al., 1982a,b; Chaffee and Johns, 1984; Püttmann and Kalkreuth, 1989) indicate that the Carboniferous organic matter originated predominantly from higher terrestrial plants. This applies also to the tetracyclic diterpenoids, compounds used as biomarkers for modern (e.g. Podocarpaceae and Araucariaceae) and Palaeozoic conifers (Noble et al., 1985a; Schulze and Michaelis, 1990; Stewart and Rothwell, 1993; Otto and Wilde, 2001). Moreover, hopanoids and benzohopanoids as identified in the samples can be assigned to microbial influence (Albrecht and Ourisson, 1971; Ourisson et al., 1979; Hussler et al., 1984). Rather unspecific biomarkers like naphthalenes and phenanthrenes (Radke et al., 1982a,b) are prominent constituents of the extracts. An even more detailed analysis concerning these biomarker groups within coals and sediments from the Saar–Nahe Basin can be found elsewhere (Vliex, 1994; Vliex et al., 1994; Auras, 2004). However, all the biomarker groups are not suitable to track the floral change at the Westphalian/Stephanian boundary because they can be found throughout the whole sequence. In contrast, the fernane derivatives MAPH, MATH, DAPH 1 and DAPH 2 show significant differences between samples from the Westphalian and the Stephanian strata. Comparing the chromatograms displayed in Fig. 3 it becomes apparent

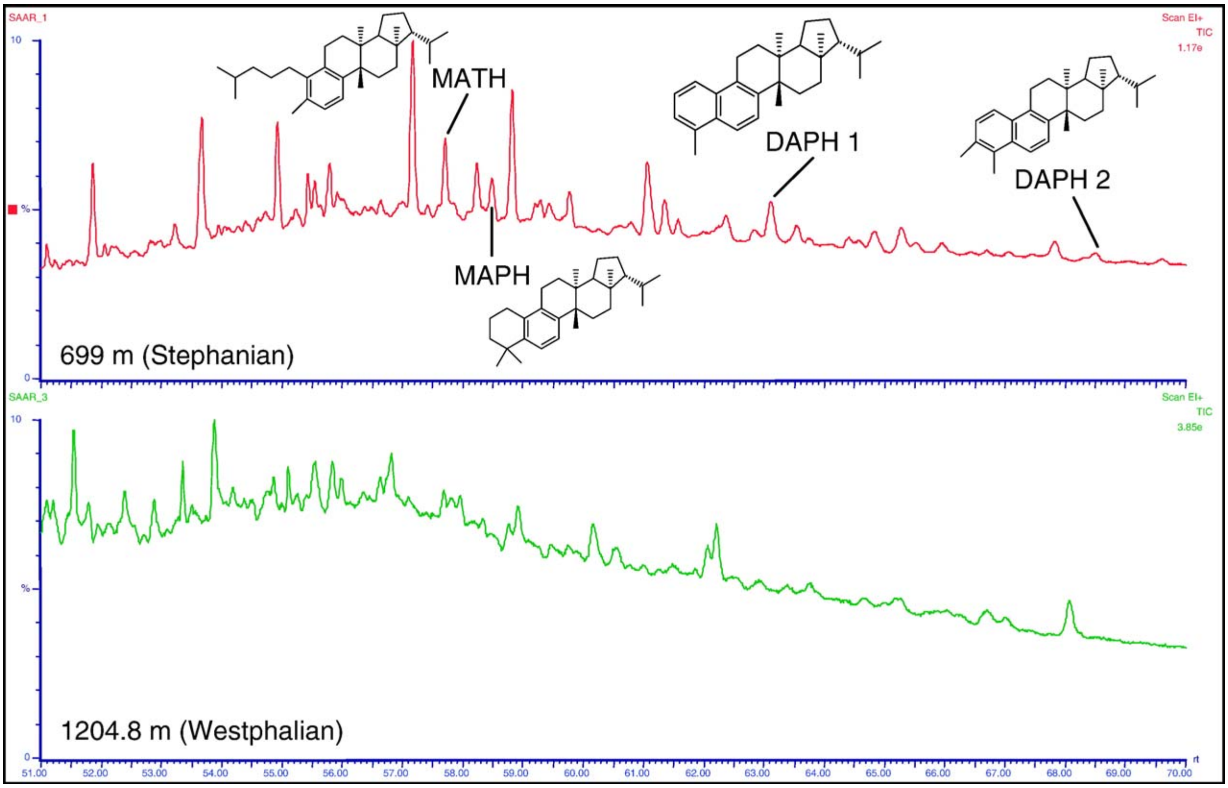


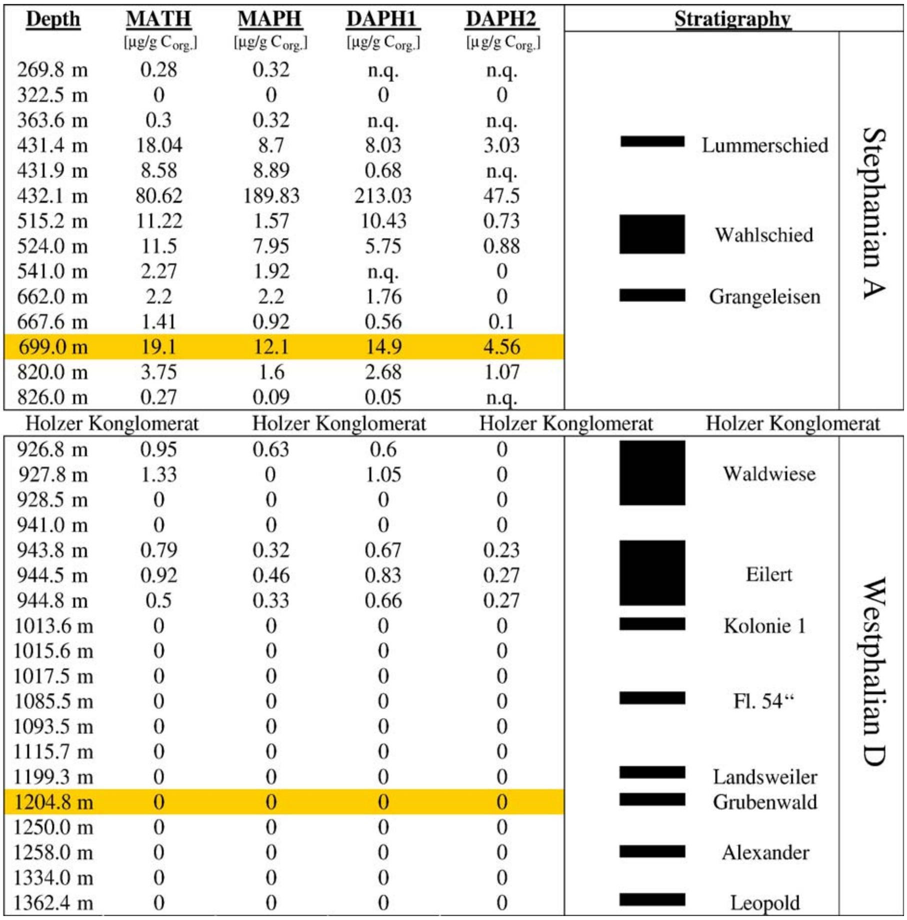
Fig. 3. Comparision of the total ion chromatograms (retention time: 51–70 min) of extracts derived from a Westphalian (1204.8 m) and a Stephanian (699 m) sample from the drilling core Wemmetsweiler-Nord.

that the fernane derivatives can be identified in the Stephanian strata, e.g. at a depth of 699 m, whereas they are missing in the Westphalian strata, e.g. at a depth of 1204.8 m, except for the uppermost Westphalian D (see below).

In most of the samples from core Wemmetsweiler-Nord (Fig. 4), MATH is present with the highest concentration of the four compounds. The relatively strong variations of the concentrations of fernane derivatives in the Stephanian samples are noticeable: MATH for instance has the lowest concentration in the sample derived from a depth of 826 m (0.27 µg/g $C_{org.}$) while the highest concentration of the compound is 80.62 µg/g $C_{org.}$ in the sample derived from a depth of 432.1 m.

The fernane derivatives were identified (with one exception, a sample derived from a depth of 322.5 m) in all samples from the Stephanian of the core Wemmetsweiler-Nord (Fig. 4). Contrarily, the compounds were not detectable in most of the samples from the Westphalian strata. Only in two samples from the Upper Westphalian D (coal seams Waldwiese and Eilert), the compounds were detected in relatively low concentrations. In previous investigations (Vliex, 1994) MATH was already identified in a sample from coal seam Waldwiese. The detection of fernane derivatives in coal seam Eilert even at a higher depth in the core now confirms the appearance of the compounds already below the Holzer Konglomerat within the Westphalian D. This observation is of importance since the Holzer Konglomerat obviously represents a gap in the sedimentary record of more than 3 million years (Burger et al., 1997).

Some reasons must be discussed for the disappearance of the fernane derivatives with increasing depth. One important factor is the maturity (coalification) of the sample material. MATH, MAPH, DAPH 1 and DAPH 2 were detected in samples with a maturity index (coalification rank) up to 0.97% Rr (Vliex, 1994). The lack of the compounds in samples of higher rank could



Depth	MATH [µg/g $C_{org.}$]	MAPH [µg/g $C_{org.}$]	DAPH1 [µg/g $C_{org.}$]	DAPH2 [µg/g $C_{org.}$]
269.8 m	0.28	0.32	n.q.	n.q.
322.5 m	0	0	0	0
363.6 m	0.3	0.32	n.q.	n.q.
431.4 m	18.04	8.7	8.03	3.03
431.9 m	8.58	8.89	0.68	n.q.
432.1 m	80.62	189.83	213.03	47.5
515.2 m	11.22	1.57	10.43	0.73
524.0 m	11.5	7.95	5.75	0.88
541.0 m	2.27	1.92	n.q.	0
662.0 m	2.2	2.2	1.76	0
667.6 m	1.41	0.92	0.56	0.1
699.0 m	19.1	12.1	14.9	4.56
820.0 m	3.75	1.6	2.68	1.07
826.0 m	0.27	0.09	0.05	n.q.
Holzer Konglomerat		Holzer Konglomerat	Holzer Konglomerat	
926.8 m	0.95	0.63	0.6	0
927.8 m	1.33	0	1.05	0
928.5 m	0	0	0	0
941.0 m	0	0	0	0
943.8 m	0.79	0.32	0.67	0.23
944.5 m	0.92	0.46	0.83	0.27
944.8 m	0.5	0.33	0.66	0.27
1013.6 m	0	0	0	0
1015.6 m	0	0	0	0
1017.5 m	0	0	0	0
1085.5 m	0	0	0	0
1093.5 m	0	0	0	0
1115.7 m	0	0	0	0
1199.3 m	0	0	0	0
1204.8 m	0	0	0	0
1250.0 m	0	0	0	0
1258.0 m	0	0	0	0
1334.0 m	0	0	0	0
1362.4 m	0	0	0	0

Fig. 4. Concentration [µg/g $C_{org.}$] of the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 in extracts of samples from the drilling core Wemmetsweiler-Nord (n.q. ≡ not quantifiable).

be due to their decomposition or further transformation due to effects of increased temperature. The samples of the present study are characterized by a calculated vitrinite reflectance R_c ranging between 0.42% and 0.88% based on the distribution of methylphenanthrenes according to Radke and Welte (1981). Consequently, the lack of the fernane derivatives in the Westphalian below seam Eilert cannot be the result of overmaturation of the samples at greater depth. As far as the generation of the fernane derivatives is concerned, the depositional environment could have been another important factor (Vliex, 1994; Vliex et al., 1994). Acidic conditions are characteristic of freshwater swamps ("coal swamps") that were common in the Saar–Nahe Basin during the Upper Carboniferous (pH 3–4; Bustin et al., 1989). The pristane/phytane ratios (this work: 1.28–7.05; Vliex, 1994: 1.3–9.9) additionally suggest a continuously oxidizing depositional environment (Didyk et al., 1978). Therefore, the absence of the fernane derivatives in the Westphalian samples below seam Eilert can not be explained with changes in the depositional environment. Since neither the sample maturity nor the depositional environment explains the lack of the fernane derivatives in the Westphalian samples, it is probable that the precursor compounds were missing in the originally deposited plant material. Consequently, another factor for the presence of the fernane derivatives in the geological record could be the existence and availability of source plants.

4.2. Organic geochemistry of fossil plant remains from various Euramerican coal basins

Fernanes were previously identified in extant subtropical and tropical plants. For example, fern-9(11)-en-3β-ol and the corresponding ether were identified in the grass *Imperata cylindrica* (Nishimoto et al., 1968) whereas fern-9(11)-ene, fern-7,9(11)-diene and fern-7-ene were identified in the fern *Davallia mariesii* (Shiojima and Ageta, 1990). Moreover fern-9(11)-ene was also reported from the conifer *Podocarpus saligna* (Silva et al., 1972). In order to clarify if the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 can be assigned to a specific plant group, plant fossils from different Euramerican coal basins were analysed by GC/MS. All samples are characterised by a calculated vitrinite reflectance R_c ranging between 0.52% and 0.86% based on the distribution of methylphenanthrenes according to Radke and Welte (1981). Since the fernane derivatives were detected in coal samples with a vitrinite reflectance of up to 0.97% Rr (Vliex, 1994) their lack in several samples of the present study can not be due to their exceeding maturity. Moreover, the samples are characterised by continuously oxidizing depositional conditions as suggested by their pristan/phytane ratios (1.2–8.7). Most of the compounds detected in the coal and sediment samples obtained from the core Wemmetsweiler-Nord were also identified in the extractable organic matter of the plant fossils. As expected, biomarkers indicative of higher terrestrial land plants (e.g. bicyclic sesquiterpanes, biphenyls or dibenzofuranes) and also hopanoids indicative of microbial activity were detected.

In accordance to earlier speculations based on palynological data (Vliex, 1994), the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 were lacking in the extractable organic matter of macrofossils from horsetails (*Calamites*), ferns (*Pecopteris*) and giant club mosses (*Lepidodendron*, *Sigillaria*). Thus, these plant groups can be precluded as biological source of the precursor molecules of the fernane derivatives.

Conifers were suggested to represent one of the possible sources for the fernane derivatives (Vliex, 1994) but conifers did not contribute in significant quantities to Upper Carboniferous floras with the extinct Voltziales as only representatives (Stockey, 1981; Stewart and Rothwell, 1993). However, in the extracts of eight conifer fossils the fernane derivatives could not be identified by GC/MS analyses of the biomarker composition (Fig. 5). Thus, conifers can most probably also be precluded as the biological source of the precursors of the fernane derivatives since the lack of the compounds can neither be ascribed to increased coalification nor to the depositional environment of the samples.

Another possible origin for the fernane derivatives which was suggested according to earlier palynological studies (Vliex et al., 1994) are the cordaites, a group of gymnosperms that are thought to have become extinct at the end of the Permian (Stewart and Rothwell, 1993). The cordaites first appeared subordinate in the middle of the Carboniferous before they became more important, especially around the Westphalian/Stephanian boundary (Stewart and Rothwell, 1993). During the Upper Carboniferous, they represented an important constituent of the flora. As seed plants, the cordaites were independent of humid habitats and could therefore better withstand a drying up of the climate as suggested for the uppermost Carboniferous than other plant groups (e.g. the giant club mosses). Cordaites are sometimes regarded as ancestral to conifers because of fertile structures similar to those of early conifers (Stewart and Rothwell, 1993; Di Michele and Phillips, 1994; Di Michele, 2000). Beginning with the Upper Permian the

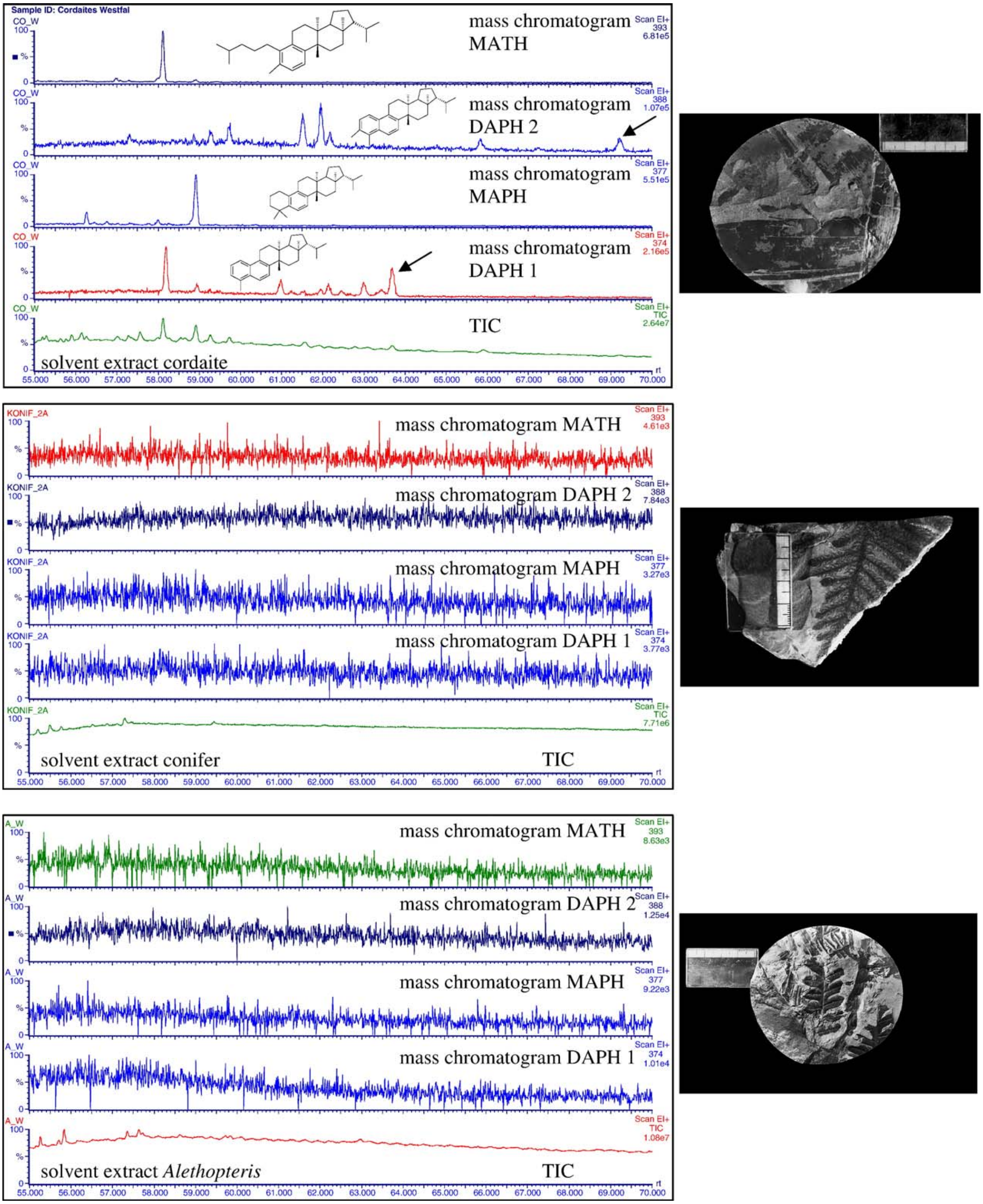


Fig. 5. Photographs of fossil cordaite (bore hole Wemmetsweiler-Nord), conifer (bore hole Odernheim) and *Alethopteris* remains (bore hole Wemmetsweiler-Nord) and the corresponding chromatograms (retention time: 55–70 min; MAPH: *m*/*z* 377; MATH: *m*/*z* 393; DAPH 1: *m*/*z* 374; DAPH 2: *m*/*z* 388) obtained from GC/MS analyses of the derived extracts.

Table 1
Concentration [μg/g $C_{org.}$] of the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 in extracts of selected cordaite and pteridosperm fossils (n.d. ≡ not detectable; n.q. ≡ not quantifiable)

Sample	MATH [μg/g $C_{org.}$]	MAPH [μg/g $C_{org.}$]	DAPH 1 [μg/g $C_{org.}$]	DAPH 2 [μg/g $C_{org.}$]
Wemmetsweiler-Nord cordaite	32.02	25.16	9.15	3.43
Surrounding sediment	n.d.	n.d.	n.d.	n.d.
Ensdorf cordaite	2.56	1.11	1.11	n.d.
Surrounding sediment	n.d.	n.d.	n.d.	n.d.
Blanzy cordaite 1	3.08	0.86	n.d.	n.d.
Surrounding sediment	0.55	0.16	n.d.	n.d.
Cordaite 2	1.11	0.49	n.d.	n.d.
Surrounding sediment	0.31	0.13	n.d.	n.d.
Cordaite 3	6.22	1.61	0.29	n.q.
Surrounding sediment	1.01	0.35	n.d.	n.d.
Grube Warndt *Odontopteris reichiana*	n.d.	n.d.	n.d.	n.d.
Surrounding sediment	n.d.	n.d.	n.d.	n.d.
Blanzy *Odontopteris brardii*	0.28	0.16	n.d.	n.d.
Surrounding sediment	1.7	1.34	n.d.	n.d.
Odontopteris brardii	4.35	0.97	n.q.	0.73
Surrounding sediment	2.76	0.92	n.q.	0.92
Odontopteris subcrenulata	0.57	0.3	0.12	n.q.
Surrounding sediment	0.48	0.16	0.16	n.q.

cordaites declined and then finally disappeared at the end of the Permian (Stewart and Rothwell, 1993).

In contrast to the extracts of the plant groups mentioned so far, the GC/MS analysis of the extractable organic matter of a fossil cordaite leaf from the Saar–Nahe Basin (core Wemmetsweiler-Nord, Westphalian D) revealed the presence of the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 in high proportions (Fig. 5). The fernane derivatives MATH (m/z 393) and MAPH (m/z 377) represent the two main components of the sector displayed in Fig. 5 whereas the two other fernane derivatives DAPH 1 (m/z 374) and DAPH 2 (m/z 388) were identified only in lower amounts. Analyses of fossil cordaite leaves from other locations in the Saar–Nahe Basin and from the Blanzy–Monteceau Basin as well as from Lally (both in France) showed similar results. The fernane derivatives were identified in all these samples in varying concentrations. Thus, their occurrence in the extractable organic matter of cordaites is not erratic, but can be observed in different Euramerican coal basins. Furthermore, the fernane derivatives were also found in the extractable organic matter of a Lower Permian cordaite from Lally (France) proving that not only cordaites from the Upper Carboniferous produced the precursor molecules of the compounds.

The occurrence of the fernane derivatives is largely limited to the extractable organic matter of cordaites. Analyses of the sediments surrounding the cordaite macrofossils have shown that the compounds identified in the extracts of the fossils were either not detectable in the extractable organic matter of the surrounding sediments (Saar–Nahe Basin; Table 1) or only present in comparatively small amounts (Blanzy–Montceau Basin; Table 1). MATH, for example, was found in a cordaite from Ensdorf (Saar–Nahe Basin) with 2.56 μg/g $C_{org.}$ while missing in the corresponding sediment sample. Small amounts of the fernane derivatives in sediment samples from Blanzy, e.g. 1.01 μg/g $C_{org.}$ of MATH compared to 6.22 μg/g $C_{org.}$ in the corresponding cordaite extract, are probably the result of the impregnation of the sediment by bitumen originating from imbedded cordaites because the maturity of the samples (R_c between 0.52% and 0.68%) permits a migration of mobile organic compounds (Allan and Larter, 1981). As a consequence, the cordaites must be considered as one source of the presumed precursor molecules (fernenes/fernenol) of the fernane derivatives. It is striking that the concentrations of the fernane derivatives in some of the cordaite fossils (Table 1) are lower than the concentrations of the fernane derivatives in the bulk samples from the core Wemmetsweiler-Nord (Fig. 4). Unfortunately, only fossil cordaite leaves were available in the sediments for the analyses of isolated plant fossils, while the coals derived from the core Wemmetsweiler-Nord are composed amongst others of the entire cordaite plants. Wood and bark of trees can be expected to contain higher terpenoid proportions than the leaves (Hrutfiord et al., 1974; Latta et al., 2000). This might explain why the fernane derivatives are lower concentrated in some of the cordaite fossils.

A third possible origin for the fernane derivatives which was postulated according to earlier palynological studies are the pteridosperms, an extinct group of gymnosperms widespread in the Upper Carboniferous lowlands. Pteridosperms formed the bulk of the underwood in the coal swamps, but were also found at drier places like sandy river banks (Stewart and Rothwell, 1993; Di Michele and Phillips, 1994; Kerp, 1996a,b; Di Michele, 2000).

GC/MS analyses of the biomarker content of pteridosperm remains from six different genera revealed the following results: fernane derivatives were not identified in the extracts of *Alethopteris* (Fig. 5), *Dicroidium*, *Lescuropteris*, *Macroneuropteris* and *Neuropteris* as well as in the extract of a pteridosperm crotch. Consequently, these pteridosperm genera can be precluded as biological origin of the precursor molecules of the fernane derivatives.

On the other hand, MATH and MAPH were detected in some fossil *Odontopteris* remains (*Odontopteris brardii* and *Odontopteris subcrenulata*) which were derived from the Blanzy–Montceau Basin as well as in the corresponding sediment samples (Table 1). In this regard it is striking that the sediment adjacent to the plant fossils contains similar or even higher amounts of the fernane derivatives compared to the corresponding *Odontopteris* extracts. This is different compared to the conditions as observed for sediment samples taken adjacent to the cordaite remains. Thus, the occurrence of the fernane derivatives in the sediment samples surrounding the *Odontopteris* fossils can most probably not be ascribed to an impregnation of the sediment originating from the *Odontopteris* remains. In fact, it is much more probable that the occurrence of the compounds in the *Odontopteris* extracts is vice versa caused by an impregnation of the plant remains originating from the surrounding sediment. Regrettably, the origin of the fernane derivatives in these sediments is still unclear. However, because of the fact that the *Odontopteris* remains have been found in sediments with high amounts of cordaite remains, an origin from cordaites is possible. Furthermore, the fernane derivatives were detectable neither in the extractable organic matter of *O. reichiana* Gutbier derived from the mine Warndt (Saar–Nahe Basin) nor in the extractable organic matter of *Lescuropteris genuina* remains derived from Blanzy (*L. genuina* is a pteridosperm species often compared to *Odontopteris*; Krings and Kerp, 1997). These results can also be used as an argument against considering *Odontopteris* as source of the fernane derivatives.

The results of the GC/MS analyses of the extractable organic matter of fossil plant remains from the studied Upper Carboniferous (Westphalian D/Stephanian A) samples can be summarized as follows:

1. Plants other than gymnosperms can be precluded as the biological source of the fernane derivatives.
2. Conifers can also be precluded as the biological source of the fernane derivatives.
3. The cordaites can be considered as one and, possibly, the only biological source of the precursor molecules (fernenes/fernenol) of the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2.
4. It cannot completely be precluded that pteridosperms, and especially species of *Odontopteris* produced the precursor molecules of the fernane derivatives as well.

4.3. Carbon isotopic composition of the fossil plant remains

Analyses of the carbon isotopic ratios of the fossil plant remains used for the present study show that their δ^{13}C values are comparable to the δ^{13}C values of extant C_3-plants (δ^{13}C between −23‰ and −34‰; Schoell, 1984; Faure, 1986). This is not surprising as plants with an alternative C_4- or CAM-photosynthetic pathway are first known beginning with the Cretaceous (Jones, 1994). Though there seem to be at first glance no major differences between the δ^{13}C values of the plant fossils, slight variations between individual plant groups can be recognised when considering their mean δ^{13}C values (Fig. 6).

The δ^{13}C values of the cordaite remains range between −21.45‰ and −24.65‰, with a mean of −22.79‰. The mean value is in good accordance to other values reported in the literature (e.g. Beerling et al., 2002: *Cordaites borassifolius*, $\delta^{13}\text{C} = -23.8$‰). It is important to mention that some cordaite fossils derived from the same location have varying δ^{13}C values. For example, δ^{13}C values of different cordaite fossils from the mine Reisbach range between −21.82‰ and −22.67‰. It could be speculated that these fossils represent different species which can not be distinguished on the base of characters apparent from the fossil fragments. According to Faure (1986), individual plants of the same species growing in the same habitat should have almost equal δ^{13}C values.

The mean δ^{13}C value for the pteridosperms is −23.62‰. Almost similar δ^{13}C values of −23.65‰ and −23.38‰ were measured comparing the δ^{13}C value of an *Alethopteris* from the core Wemmetsweiler-Nord with the value of another *Alethopteris* from the mine Reisbach. This accords with the suggestion that plants of the same species grown in the same habitat are characterized by almost identical carbon isotopic ratios (Faure, 1986). The conifer remains provided a mean δ^{13}C value of −23.38‰, which is between the mean δ^{13}C values of cordaites and pteridosperms. It is striking

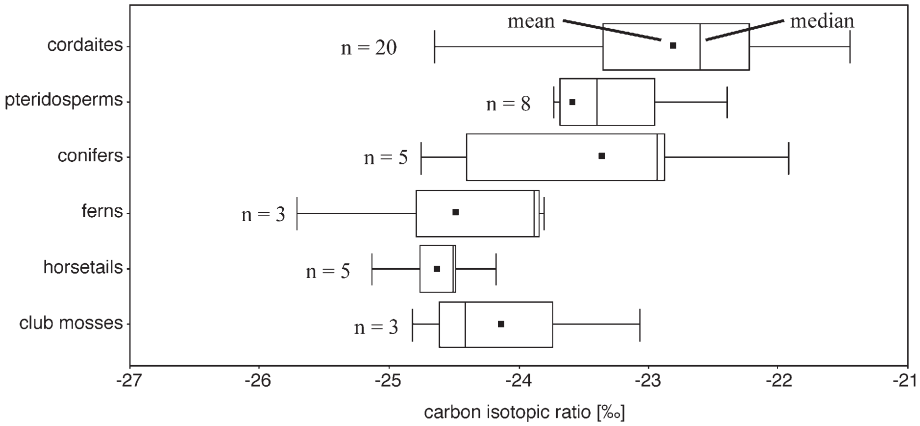


Fig. 6. Mean and median carbon isotopic ratios of different fossil plant groups (box: range between 25% and 75% percentile).

that fossil leafy shoots of conifers (δ^{13}C between −24.75‰ and −24.40‰) derived from the core at Odernheim showed a lower carbon isotopic ratio compared to a fossil conifer wood compression (δ^{13}C: −22.88‰) from the same core.

Fossil ferns (in our study only *Pecopteris* from the Saar–Nahe Basin) yielded a mean δ^{13}C value of −24.47‰ (cp. Beerling et al., 2002: *Pecopteris plumosa-dentata*: $\delta^{13}\mathrm{C}=-24.2$‰) and horsetails (*Calamites*) showed a mean δ^{13}C value of −24.59‰ (Fig. 6). The giant club mosses provided a mean δ^{13}C value of −24.14‰ (cp. Beerling et al., 2002: *Lepidostrobus variabilis*: $\delta^{13}\mathrm{C}=-24.3$‰). Considering the giant club mosses, specimens of *Sigillaria* and *Lepidodendron*, both from the Westphalian of the core Wemmetsweiler-Nord, yielded δ^{13}C values of −24.82‰ and −23.07‰, respectively. This again supports the suggestion that different genera of one plant group growing in the same habitat can show varying carbon isotopic ratios (Faure, 1986).

Finally it has to be mentioned that the comparison of the carbon istopic ratios of individual fossil plant remains from the core Wemmetsweiler-Nord with the carbon isotopic ratios of their corresponding adjacent sediment samples showed only insignificant variations. Even the maximum variations were only +0.69‰ (*Neuropteris* ↔ corresponding sediment sample) and −1.14‰ (Calamites ↔ corresponding sediment sample), respectively.

5. Conclusions

The present study has shown that the floral change at the Westphalian/Stephanian boundary is reflected by a molecular signal as well. With respect to most organic compounds, the composition of the solvent extracts of Upper Carboniferous coals and shales from the core Wemmetsweiler-Nord (Saar–Nahe Basin) is similar regardless of an origin from Westphalian or Stephanian strata. However, GC/MS analyses indicate for the higher boiling point range of the chromatograms a significant difference between Westphalian and Stephanian samples. The fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 were identified in the Stephanian samples while lacking in most Westphalian samples, except for those from the coal seams Waldwiese and Eilert of the uppermost Westphalian D. These fernane derivatives are thus suitable for tracking the floral change at the Westphalian/Stephanian boundary on a molecular basis.

The δ^{13}C values of the plant remains suggest that Upper Carboniferous and Permian plants were characterized by a C_3-photosynthetic pathway similar to that of extant C_3-plants. The δ^{13}C values of fossil plant remains support moreover that different species of one plant group grown in the same habitat can show varying carbon isotopic ratios. Considering the mean δ^{13}C values also slight variations between the individual plant groups were detected.

The analysis of the biomarker content of extracts derived from individual plant fossils of low maturity is a particularly suitable tool to assign individual biomarkers to distinct plants respectively plant groups. The fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 can be assigned to cordaites while conifers, ferns (*Pecopteris*), horsetails (*Calamites*) and giant club mosses (*Lepidodendron*, *Sigillaria*) can be largely precluded as source of the presumed precursor molecules (fernenes/fernenol) of the fernane derivatives. As the pteridosperms are concerned, there is a slight uncertainty regarding the *Odontopteris* from the Blanzy–Montceau Basin (France) which also contained the fernane derivatives. However, quantitative data indicate that their occurrence in these samples is probably caused by an impregnation of the plant remains by compounds originating from the surrounding sediments. As a consequence, the cordaites can be considered as one and, possibly, the only biological source of the precursor molecules of the fernane derivatives MATH, MAPH, DAPH 1 and DAPH 2 as detected in the studied section from the Upper Carboniferous.

The study documents the potential of quantitative biomarker analyses of macrofossils as a suitable tool for the investigation of major floral changes in earth history. The fernane derivatives can now be used to distinguish small pieces of cordaite wood from wood of other biological origin. Tracking the respective biomarkers over the Permian/Triassic boundary may show a signal reflecting the extinction of cordaites (Stewart and Rothwell, 1993). On the other hand, systematic connections to surviving plant groups may be revealed.

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