



## Chemotaxonomy of fossil woods from the Lower Rhine Embayment, Germany



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### ABSTRACT

In the Lower Rhine Embayment (western Germany), the Neogene lignite bearing sequence is rich in large fossil wood trunks. Woods collected from sand-filled channels of a meandering river system (Pliocene: Reuver series) and from coal seams (Miocene: seams Garzweiler, Frimmersdorf and Morken) were investigated by Curie-point pyrolysis coupled with gas chromatography–mass spectrometry in order to determine their palaeobotanical classification. In comparison with reference data of individual pyrograms of modern woods, it became possible to classify 15 fossil wood trunks chemotaxonomically as follows: eleven samples were identified as *Taxodioxylo* sp. by reference *Sequoia sempervirens*, three samples were identified as *Populoxylo* sp. by reference *Populus nigra* and one sample was identified as *Sciadopityoxylo* sp. by two references of *Sciadopitys verticillata*. Microanatomical crosschecks describe the equivalent samples taxonomically as *Taxodioxylo gypsaceum* (GÖPPERT) KRÄUSEL, *Taxodioxylo germanicum* (GREGUSS) VAN DER BURGH, *Populus nigra* L. and *Sciadopityoxylo wettsteinii* JURASKY, and confirm the chemical classifications. For both fossil and reference woods, our relative quantifications of guaicyl and syringyl moieties are in precise accordance with discriminations of gymnosperms versus angiosperms. This means that not only unknown recent woods can chemotaxonomically accurately be determined by Curie-point pyrolysis gas chromatography–mass spectrometry and their equivalent modern wood reference from our data base, but also the taxonomy of botanically related wood types reaching back to the geological past up to a Miocene age at least.

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### 1. Introduction

With installation of a data base for a fast chemotaxonomic identification of modern woods, the question arises if this data base can also be applied to identify fossil woods. The data base is based on chemical compounds obtained as pyrograms from Curie-point pyrolysis coupled to gas chromatography–mass spectrometry (CPP/GC–MS). Strictly speaking, an evaluation was required to test the potential of recognizing specific wood types (biological family, genus, species) by their specific CPP/GC–MS compound patterns in geological samples. In order to answer this question, a case study from the Miocene/Pliocene lignite bearing sequence of the Lower Rhine Embayment (western Germany) was initiated, because these strata are rich in different types of fossil wood (Slijper, 1932; Kräusel, 1949; van der Burgh, 1973, 1978a,b).

Beside the standard microanatomical approach for identification of fossil woods, chemical determinations of fossil woods by GC–MS analyses of their solvent extracts represent a traditional and successful characterization (Grantham and Douglas, 1980; Laver and Fang, 1986; Obst

et al., 1989; Zavarin and Cool, 1991; Staccioli et al., 1993; Menchi et al., 1997; Otto et al., 1997; Staccioli and Bartolini, 1997; Nagahama et al., 1998; Staccioli et al., 1998a–c, 2002). As further alternative, thermal breaking of large molecules into smaller pyrofragments has extended the use of GC–MS to polymeric materials including natural polymers. Pyrolysis investigations have the advantage of very low sample amounts and short analytical efforts in comparison to conventional solvent extraction followed by liquid chromatography and GC–MS. Reviews of pyrolysis including its application scope and recent trends/developments are given for example by Wampler (1999) and Sobeih et al. (2008). Beside pyrolytic studies of coals (e.g. Nip and de Leeuw, 1992; Dutta et al., 2011, 2012), several investigations of wood, subfractions of wood and degraded wood were carried out (Hatcher et al., 1988; Pouwels and Boon, 1990; Mulder et al., 1991; van der Heiden and Boon, 1994; Müller-Hagedorn et al., 2003; Colombini et al., 2007; Dong et al., 2012; Lucejko et al., 2012). Selected fruit walls were studied, too (van Bergen et al., 1997). The identical experimental approach as in the present study (i.e. based on the same CPP/GC–MS interface) was successfully applied in studies concerning resins (Dutta et al., 2010a,b) and individual palynomorphs (Dutta et al., 2006, 2007, Dutta et al., 2010a,b, Dutta et al., 2013). A further even more detailed

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approach by  $^{13}\text{C}$  labelled tetramethylammonium hydroxide (TMAH) can be used in the thermochemolysis of lignin where lignin phenols can be resolved from tannin-derived phenols (Mason et al., 2009).

The objective of the present study is to review the chances for a chemotaxonomic identification of 3–18 Ma old fossil woods by application of Curie-point pyrolysis coupled with gas chromatography–mass spectrometry without any pretreatment of the wood material, just by comparing the CPP/GC–MS fragmentograms of the fossil wood to modern reference woods.

## 2. Geologic setting and palaeoecology

The Lower-Rhine Basin forms a rift basin (Fuchs et al., 1983; Vinken, 1989) as part of a graben system defined by SE–NW running faults deeply cut into the northwestern headlands of the Rhenish Massif (Schäfer et al., 1996, 2004). North Sea transgressions filled the embayment (Zagwijn and Hager, 1987; Schäfer, 1994) with shallow marine sediments (Boersma, 1991). During Miocene times, peats – the later brown-coal seams – formed in swamps and forests as the phase of transgression had stopped. Figueiral et al. (1999) suggested a position for the approximate coast line during the Miocene (Fig. 1). A fluvial system – the palaeo-Rhine river (Naeth et al., 2004) – developed during the Pliocene, when the North Sea retreated (Boersma et al., 1981). Tidal deltas with strong tidal currents are located between barrier islands (Boersma, 1991). For lithostratigraphic details of the Neogene sedimentary sequence of the Lower Rhine Basin, see Hiß (2007). As already early proposed by Schneider and Thiele (1965), the sedimentary column of the basin fill is still described by consecutive numbers from 1 to 20 including various subunits A–F. Details of the cyclic sedimentation were studied especially by Schäfer et al. (1996).

Palaeobotany and palynology from the Pliocene/Miocene Lower Rhine Embayment were investigated based on investigations of pollen (Von der Brelie and Wolf, 1981; Utescher et al., 2002; Ashraf and Mosbrugger, 1995, 1996; Huhn et al., 1997) and based on analyses of woods, roots, seeds and fruits (van der Burgh, 1964, 1978a,b, 1987; Pinggen, 1990; Belz and Mosbrugger, 1994; Mosbrugger, 1994; Figueiral et al., 2002). For Miocene times, van der Burgh (1973) reports a climatic reconstruction based on palaeobotany with temperatures ranging from 11 to 16 °C and 1000 mm precipitation and later (van der Burgh, 1984) with more uniform climate conditions. Mosbrugger and Utescher (1997) proposed higher temperatures (14–21 °C) based on the coexistence approach of fruits and seeds. Recent studies based on branched glycerol dialkyl glycerol tetraethers (GDGTs) resulted in temperature estimates of 24.4–25.5 °C for coal seam Morken and 23.9–24.1 °C for coal seam Frimmersdorf (Stock et al., 2016).

Based on an overall decline of carbon isotope values within the Garzweiler seam, Lücke et al. (1999) deduced a general cooling trend in the Middle Miocene. Jones et al. (1996) analyzed the lignite matrix of an Upper Miocene profile by stable carbon isotopes. They found a strong correlation with vegetational changes, especially between heavier isotopic compositions and *Sequoiapollenites polyformus*, a species which prefers humid climates.

## 3. Experimental

### 3.1. Sampling methodology

Neogene wood samples from the open pit mine Garzweiler of the Rhenish lignite district near Bedburg, Germany (see white asterisk, Fig. 1), were collected from the Reuver subformation (approx. 3 Ma) and

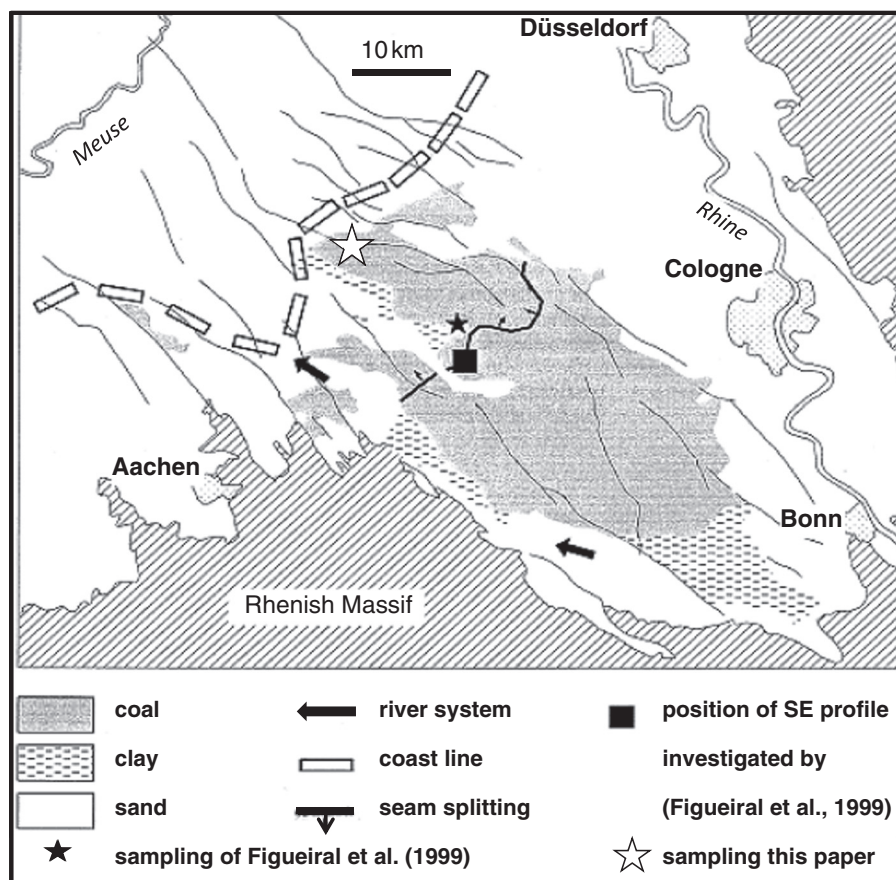


Fig. 1. Location of the Lower Rhine Embayment, approximate coast line during Miocene time, selected lithofacial and structural details, and sampling position within the basin (after Figueiral et al., 1999).

from coal seams Garzweiler (approx. 11 Ma), Frimmersdorf (approx. 13 Ma) and Morken (approx. 18 Ma). From the Reuver series (units 10, 11B and 11D according to Schneider and Thiele, 1965), we took three slices from different wood trunks out of the channel sand of a meandering river (Fig. 2). From the coal seams (units 6A, 6C, and 6E according to Schneider and Thiele, 1965) we took up to 5 individual samples directly from the freshly scraped seams. Basic information of all samples investigated is summarized in Table 1. To avoid extensive wood rupture, firstly all samples were slowly dried at room temperature. After separation of representative subsamples for microanatomy, samples for chemical analyses were freeze-dried, ground and submitted to elemental and CPP/GC–MS analyses. Samples were not extracted prior to analyses.

### 3.2. Microanatomy

The material was cut with a razorblade in three different planes. The thin sections were studied with a light microscope. They were compared with descriptions and plates from recent and fossil wood in the literature (Greguss, 1955; Greguss, 1972; van der Burgh, 1973; Dolezych, 2005).

### 3.3. Elemental analyses

Total organic carbon contents were determined by a LECO instrument. Basic differences of organic matter were obtained by using a “Turbo” Rock-Eval-6® pyrolyser manufactured by Vinci Technologies. The full description of the method is given by Lafargue et al. (1998). Briefly, samples are first pyrolysed from 100 °C to 650 °C at a rate of 25 °C/min under an inert N<sub>2</sub> atmosphere and the residual carbon is subsequently burnt in an oxidation oven at 400 °C. The amount of released hydrocarbons (HC) is detected with a flame ionisation detector (FID), while online infrared detectors continuously measure the released CO and CO<sub>2</sub>.

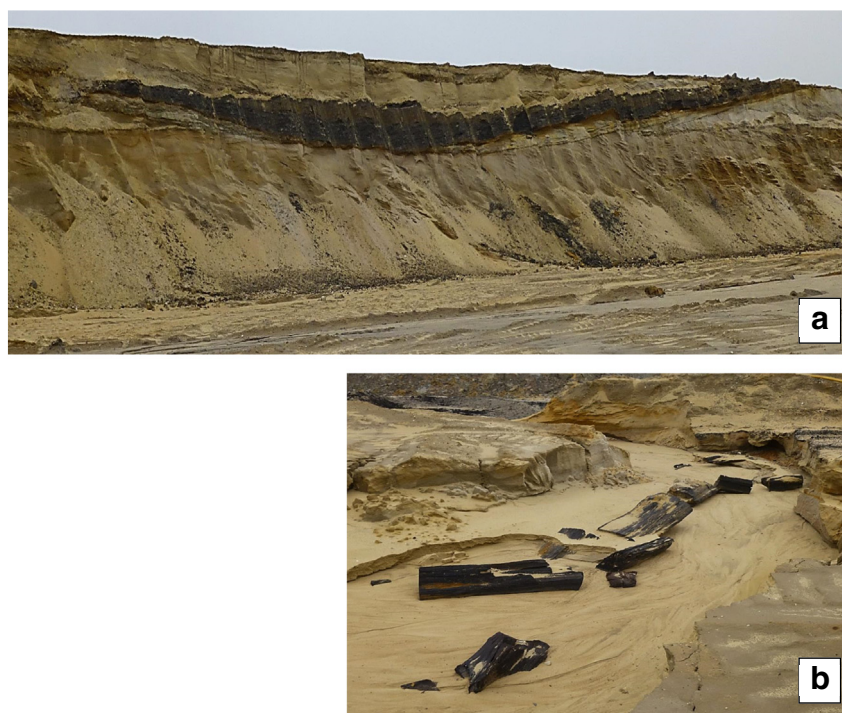
**Table 1**

Sample identification number (#), geological information (subformation or coal seam, series or epoch, and unit according to Schneider and Thiele, 1965), approximate numerical age (Ma), and results of elemental analyses (TOC: %; HI: mg HC/g of TOC; OI: mgCO<sub>2</sub>/g of TOC; T<sub>MAX</sub>: °C).

Sample ID #	Subformation or coal seam	Series or epoch	Unit	Num. age	TOC	HI	OI	T <sub>MAX</sub>
R1	Reuver Series	Pliocene	10–11D	3.0	54	190	35	343
R2	Reuver Series	Pliocene	10–11D	3.0	46	143	55	335
R3	Reuver Series	Pliocene	10–11D	3.0	52	221	38	339
G1	Seam Garzweiler	Miocene	6E	11.5	53	383	37	351
G2	Seam Garzweiler	Miocene	6E	11.5	51	405	42	346
G3	Seam Garzweiler	Miocene	6E	11.5	58	285	45	344
F1	Seam Frimmersdorf	Miocene	6C	13.0	55	325	48	345
F2	Seam Frimmersdorf	Miocene	6C	13.0	66	301	38	345
F3	Seam Frimmersdorf	Miocene	6C	13.0	60	223	48	348
F4	Seam Frimmersdorf	Miocene	6C	13.0	62	369	30	350
F5	Seam Frimmersdorf	Miocene	6C	13.0	55	331	52	341
M1	Seam Morken	Miocene	6A	18.0	57	274	51	338
M3	Seam Morken	Miocene	6A	18.0	61	253	42	343
M4	Seam Morken	Miocene	6A	18.0	68	192	49	338
M5	Seam Morken	Miocene	6A	18.0	56	281	44	338

### 3.4. Curie-point pyrolysis GC–MS

The pyrolysis temperature represents the most fundamental criterion for Curie-point pyrolysis in order to discriminate successfully polymeric materials like wood (consisting basically of a composition of the three principle molecular structures of lignin, cellulose and resin): on one side, the temperature should not be too low to avoid too big and complex pyrofragments; on the other side, the temperature should not be too high to avoid too small and too simple pyrofragments which may not be characteristic for specification of the sample. Our



**Fig. 2.** Example for the depositional environment of several sandy subunits of the Reuver series a) cut through a channel deposit b) small channel sands with individual wood trunks (origin of samples R1–3).

**Table 2**

List of compounds used for chemotaxonomic differentiation (a) and relative quantification for individual wood types identified (b).

a) Compounds with Kovats Index, CAS registry Number, compound name, and compound source according to the three monolignols (guaiacyl, syringyl, and coumaryl moieties = G, S and C), etheric oil, and diagenetic neo-formation or unknown origin (the following Kovats indices as marked in figures 3–5 are not yet identified, but applied for wood differentiations: 1498, 1501, 1562, 1603, 1620, 1648, 1717, 1761, 1785, 1814, 1823, 1837, 1878, 2344, 2360, 2419, 2545, 2553; for Kovats indices 1778, 1786, 1817 and 1996, mass spectra are given).

b) Composition of chemotaxonomic identified fossil gymnosperm (g, G) and angiosperm (a, A) woods. R and r indicate compounds present only in the respective reference wood (small or capital letter indicates contents below or above 3.5%, respectively, based on a relative quantification of 42 compounds).

Kovats index	CAS Registry Number	Compound name	a)			Other origin than monolignols, etheric oils or resins: diagenetic neo-formation or pyrolysis product	b)					
			Guaiacyl m.	Syringyl m.	Coumaryl m.		Etheric oil and resin	<i>Taxodioxylon</i> sp.	<i>Sciadopityoxylon</i> sp.	<i>Populoxylon</i> sp.		
878	98–01–1	Furfural				x						
987	108–95–2	Phenol					x					
1075	108–39–4	m-Cresol										x
1075	106–44–5	p-Cresol										x
1104	90–05–1	Guaiacol	x									
1193	120–80–9	1,2-Benzenediol										x
1198	123–31–9	1,4-Benzenediol										x
1206	93–51–6	4-Methylguaiacol	x									
1219	2628–17–3	4-Vinylphenol					x					x
1266	488–17–5	3-Methylcatechol										x
1270	4179–19–5	3,5-Dimethoxytoluene										x
1274	934–00–9	1,2-Benzenediol										x
1291	2785–89–9	4-Ethylguaiacol	x									
1294	452–86–8	4-Methylcatechol										x
1327	7786–61–0	4-Vinylguaiacol	x									
1364	91–10–1	Syringol		x								
1370	97–53–0	Eugenol	x									
1372	703–23–1	1-(2-Hydroxy-6-methoxyphenyl)ethanone					x					
1379	2785–87–7	4-Propylguaiacol	x									
1416	121–33–5	Vanillin	x									
1421	5912–86–7	(Z)-Isoeugenol	x									
1438	469–61–4	α-Cedrene					x					
1448	546–28–1	β-Cedrene						x				
1461	6638–05–	4-Methyl-syringol		x								
1465	5932–68–3	(E)-Isoeugenol	x				x					
1481	5703–24–2	Homovanillin	x									
1503	498–02–2	Acetovanillone	x									
1539	38790–14–6	4-Ethylsyringol		x								
1547	2503–46–0	Guaiacylacetone	x									
1579	28343–22–8	4-Vinylsyringol		x								
1596	69056–21–9	(Z)-Coniferylalcohol	x									
1600	1835–14–9	Propiovanillone	x									
1614	6627–88–9	Allylsyringol		x								
1636	77–53–2	Cedrol						x				
1665	306–08–1	Homovanillic acid	x									
1679	134–96–3	Syringaldehyde		x								
1722	no CAS	Homosyringaldehyde		x								
1753	2478–38–8	Acetosyringone		x								
1758	458–36–6	Coniferylaldehyde	x									
1778		175, 119, 190, 191										
1786		173, 133, 188										
1817		173										
1996		276, 121, 107, 136, 149										
2002	4206–58–0	Trans-3,5-dimethoxy-4-Hydroxycinnamaldehyde		x								
2363	67884–30–4	Gigantol	x									

optimization results in pyrolyzing at 590 °C about 500 µg of sample material for 9.9 s using a Pilodist Curie point pyrolyser coupled directly to a ThermoFisher Scientific Trace Ultra gas chromatograph (GC) and a ThermoFisher Scientific ITQ 900 mass spectrometer (MS). All analyses were made in duplicate. The GC is operated in the splitless mode, equipped with a Phenomenex ZB 5 HT fused silica capillary column

[60 m × 0.25 mm × 0.25 µm df] with helium as carrier gas. The temperature program starts at 80 °C heating to 340 °C with 5 °C min<sup>-1</sup>, hold for 10 min. The MS is operated in electron impact mode with ionization energy of 70 eV and source temperature of 260 °C. Full scan mass spectra are recorded over a mass range of 41–600 Da. Data system for control-ling, identification and quantification was XCALIBUR (ThermoFisher

Scientific). Compound identifications (CAS numbers) were made comparing the obtained mass spectra to several spectra libraries (Wiley registry 8E, 2006; NIST 08, Wiley FFMSC 2, 2011; Philp, 1985).

All Neogene wood samples are compared to reference wood samples (provided by the Johann Heinrich von Thünen-Institut, Hamburg University, Germany, and the Geological Survey North Rhine-Westphalia, Krefeld). For the comparison of this sample set, in total 41 identified chemical compounds (assigned according to their CAS numbers, see Table 2a) and 21 unidentified compounds (assigned according to their mass spectra) were used. Shifts in retention time were corrected by means of standards. Duplicates varied in 5–10% of relative intensity.

## 4. Results

### 4.1. Maturity, quantity and quality of organic matter

According to the range of 335–360 °C for the  $T_{max}$  data of the fossil samples from Rock-Eval analyses (Table 1), and a range of 320–350 °C for the reference samples of modern wood from our data base, any maturity discrimination between individual samples is impossible. Variations of total organic carbon (TOC) between 46 and 70% and between 190 and 405 mg hydrocarbons per gram of sample for the hydrogen index (Table 1) point to a considerable variation for amount and quality of organic matter. Oxygen index values exhibit a relatively narrow range of 27–55 mg CO<sub>2</sub> per gram of sample.

### 4.2. Chemotaxonomic wood identification versus microanatomic crosscheck

GC–MS analysis allows to compare the presence/absence of specific compounds and changes in their intensities. For a straight forward identification of a specific wood type (genus, possibly species, too, in specific cases) from the same environment and of the same age, a nearly 100% compound correspondence between two modern wood samples is necessary, whereas for fossil wood relative intensities will vary in most cases, primarily due to the fact that specific depositional environments and specific diagenetic/catagenetic burial histories will cause a different way and timing of chemical alteration and fossilization. For comparisons between modern and fossil woods, the increasing destruction of organic matter has to be considered which finally leads to both the complete degradation of cellulose and lignin. Accordingly, general reductions of individual compounds up to their complete disappearance and subsequently the formation of new components have to be taken into account.

An overlook of all compounds by which the three different fossil wood types could be differentiated, is provided by Table 2b. Individual details of the chemotaxonomic characterization are described below.

#### 4.2.1. Identification of *Taxodioxylo* sp.

Eleven samples from the total sample suite could chemically be identified as the fossil wood genus *Taxodioxylo* by comparison to the reference of modern redwood which is botanically classified as subfamily Sequoideae, genus *Sequoia*, species *sempervirens* (D. Don) Endl. Already at a first glance, the high congruence of the four total ion chromatograms (TIC) of our modern reference wood (Fig. 3a) with three selected examples from the three coal seams (Fig. 3b–d) can be recognized. In the lower-molecular range (at retention time of 7–27 min, Kovats indices range of 878–1879), the same compounds are found with very similar relative intensities as in the reference sample. Individual major compounds with contents of more than 3.5% are guaiacol, 4-methyl-/4-ethyl-/4-vinylguaiacols, guaiacylacetone, vanillin, (E)-isoeugenol and homovanillinic acid. Compounds with minor contents are furfural, phenol and 4-vinylphenol, m- and p-cresol, 3-methylcatechol, 1,2-benzendiol, syringol, eugenol, 1-(2-hydroxy-6-methoxyphenyl)ethanone, 4-propyl-guaiacol, (Z)-isoeugenol, 4-methylsyringol, acetovanillone, (Z)-coniferylalcohol, propiovanillone,

syringaldehyde and coniferylaldehyde. Furthermore, at the higher-molecular range (at retention time of 39–45 min), beside gigantol, four identical and relatively prominent compounds (Kovats indices 2344, 2419, 2545 and 2553) can be identified in all samples (Fig. 3a–d). Equivalent peaks for some not yet identified compounds (at retention times of 28–35 min) which are present only in the fossil wood samples from seams Garzweiler (Fig. 3b) and Frimmersdorf (Fig. 3c), could not be found in our modern reference sample. These compounds must have either an origin based on an additional organic matter source, a specific depositional environment or another diagenetic pathway. Furthermore, 3-methylcatechol is only present in the fossil woods (Fig. 3b–d), but not in the modern reference.

In order to demonstrate the high congruence of modern and fossil wood samples, a detailed comparison based on presence/absence and relative intensity of individual biomarkers in both the modern wood reference from the data base and 11 fossil wood samples from different coal seams is presented in Table 3. Relative standard deviations (RSD) calculated for the major compounds are in the range of 15–33%, and for the minor compounds in the range of 20–154%.

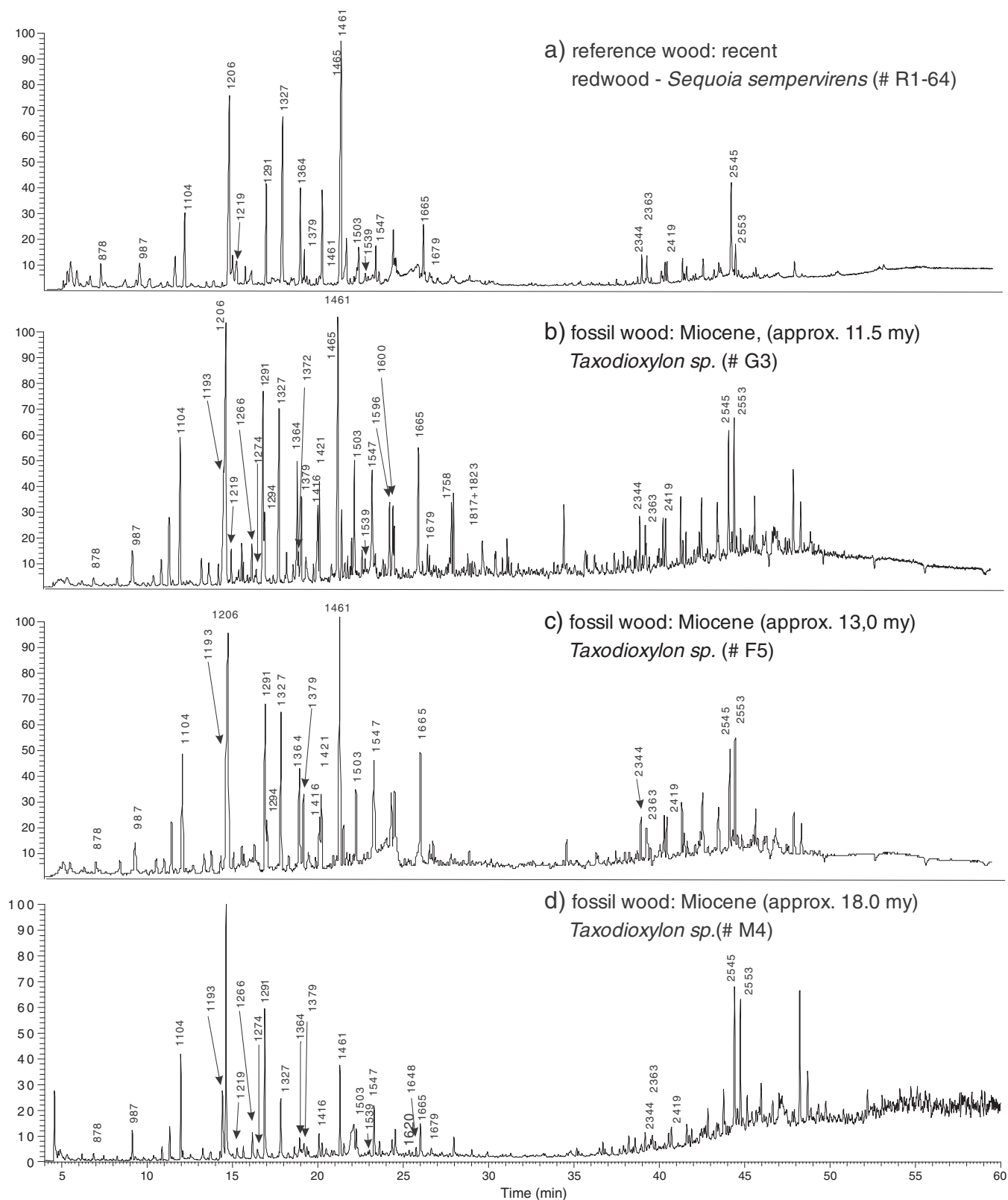
Three wood samples (Ga3, Mo4, Mo5) were crosschecked by micro-anatomical analyses. All have the same overall structure: wood without resin ducts but wood parenchyma present, especially in the latewood. The horizontal walls in the wood parenchyma tend to be thin and only granular (Mo4, Mo5) or somewhat thicker with clear knots and pits in between (Ga3). The rays are up to 20 cells high and show thin unpitted horizontal and tangential walls or somewhat thicker pitted walls. The pits to the tracheids are taxodioid in shape or too much destroyed to be clear, but all are about 8 µm in diameter. The pits in the walls of the early wood are 20 µm in diameter and occur two next to one another, accompanied by rims of Sanio.

This wood is assignable to two related wood species: *Taxodioxylo gypsaceum* (GÖPPERT) KRÄUSEL with thin walled parenchyma and ray parenchyma and *T. germanicum* (GREGUSS) VAN DER BURGH with somewhat thicker walls in parenchyma and ray parenchyma. These species are very often occurring together and can be interpreted as two extremes in the variability of the wood structure of the same botanical species, which is *Sequoia abietina* (BRGT.) KNOBL., the fossil counterpart of recent *Sequoia sempervirens* (LAMB.) ENDL.

#### 4.2.2. Identification of *Populoxylon* sp.

All samples from the Reuver subseries exhibit a compound composition with the two overall predominating components of hardwood 4-methylsyringol (9.6–13.7%) and 4-vinylsyringol (7.6–10.6%). Other syringyl compounds with contents between 1.0 and 7.2% are syringol, 4-ethylsyringol, allylsyringol, syringaldehyde and acetosyringol. Compounds with guaiacol moieties (>2%) are guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, vanillin, (E)-isoeugenol, homovanillin and guaiacylacetone. Furthermore, the range between 24 and 35 min retention time (Kovats indices between 1579 and 2002) reveals a series of compounds which are detected in the fossil woods from the Reuver subformation only (Fig. 4a, b). In comparison to the modern reference data, the TICs from the Reuver series identify these three samples as black poplar, botanically as subfamily Saliaceae, genus *Populus*, species *nigra* (L.).

According to microscopy, this wood exhibits bore traces of foreign material, which gave at first sight the impression of wide multicellular rays. By investigating them, they turned out to be foreign structures, but were so much destroyed that no identification could be made. The wood itself has uniseriate rays up to 20 cells high with border cells longer than high. The pitting to the vessels is coarse, in much cases horizontally elongated. The vessels have simple perforations, are wide and partly filled with thylls. Based on the shape of the border cells in the rays this material is identified as *Populus*. *Populus nigra* is known as having thylls regularly, so the identification is *Populus nigra* L.



**Fig. 3.** Total ion chromatograms of a) the modern reference for the redwood *Sequoia sempervirens* from our data base in comparison to three representative samples from coal seams b) Garzweiler (G3), c) Frimmersdorf (F4), and d) Morken (M4). Compounds are assigned by Kovats indices (for respective CAS Registry Number and compound name, see Table 2).

#### 4.2.3. Identification of *Sciadopityoxylon* sp.

One sample from coal seam Frimmersdorf (F4, Fig. 5a) could chemotaxonomically neither be related to *Taxodioxylyon* nor to *Populus*.

As major compounds (with contents > 4.0%), we identified guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, 4-propylguaiacol, vanillin, (E)-isoeugenol, acetovanillone, guaiacylacetone, cedrol and

**Table 3**

Relative amounts of chemical constituents for *Taxodioxyton* wood samples from coal seams Garzweiler, Frimmersdorf and Morken based on a quantification of 37 compounds, in comparison to mean values (M), absolute (SD) and relative standard deviation (RSD), and the composition of the respective modern redwood reference (RR) *Sequoia sempervirens* (contents > 3.5% are marked in bold; compounds identified by Kovats indices; for CAS Registry Numbers and compound names, see Table 2).

Kovats index	Fossil wood seam Garzweiler			Fossil wood seam Frimmersdorf				Fossil wood seam Morken				Statistics			
	G1	G2	G3	F1	F2	F3	F5	M1	M3	M4	M5	M	SD	RSD	RR
878	0.58	1.14	0.69	1.62	1.13	0.35	1.20	1.14	0.48	1.04	2.93	1.12	0.71	63	2.39
987	0.48	0.09	1.74	2.67	1.42	2.11	1.59	1.45	2.29	1.64	0.73	1.47	0.78	53	2.00
1075	1.45	0.29	3.56	5.20	2.93	4.33	2.94	3.56	5.12	2.93	0.83	3.01	1.62	54	2.61
<b>1104</b>	<b>5.83</b>	<b>5.27</b>	<b>6.80</b>	<b>6.87</b>	<b>6.56</b>	<b>7.32</b>	<b>6.46</b>	<b>7.12</b>	<b>8.02</b>	<b>9.43</b>	<b>6.06</b>	<b>6.88</b>	<b>1.13</b>	<b>16</b>	<b>4.96</b>
1193	2.83	1.87	3.25	4.08	3.12	5.75	2.50	6.32	4.85	5.21	1.47	3.75	1.61	43	1.29
1198	2.87	1.86	3.20	4.04	3.44	5.96	2.46	6.15	4.99	0.00	0.15	3.19	2.06	64	1.08
<b>1206</b>	<b>15.52</b>	<b>15.31</b>	<b>16.66</b>	<b>18.00</b>	<b>17.72</b>	<b>16.00</b>	<b>17.41</b>	<b>15.85</b>	<b>19.11</b>	<b>23.59</b>	<b>19.06</b>	<b>17.66</b>	<b>2.38</b>	<b>13</b>	<b>16.14</b>
1219	0.50	1.17	2.33	1.21	1.50	1.70	1.74	1.70	1.23	0.74	1.52	1.40	0.50	36	5.84
1266	1.30	0.36	1.44	2.83	1.04	3.45	0.88	1.55	3.95	2.60	0.00	1.76	1.27	72	0.24
1274	0.04	0.00	0.05	0.07	0.07	0.07	0.07	0.06	0.12	0.05	0.01	0.06	0.03	58	0.00
<b>1291</b>	<b>7.95</b>	<b>7.92</b>	<b>9.21</b>	<b>9.69</b>	<b>10.35</b>	<b>9.02</b>	<b>9.88</b>	<b>6.57</b>	<b>12.58</b>	<b>9.23</b>	<b>7.04</b>	<b>9.04</b>	<b>1.67</b>	<b>19</b>	<b>6.58</b>
1294	2.66	1.33	2.95	4.84	2.92	5.61	2.12	5.45	5.16	2.52	0.12	3.24	1.80	55	0.26
<b>1327</b>	<b>8.07</b>	<b>10.03</b>	<b>7.13</b>	<b>5.44</b>	<b>6.70</b>	<b>6.68</b>	<b>7.00</b>	<b>5.78</b>	<b>3.78</b>	<b>4.81</b>	<b>10.00</b>	<b>6.86</b>	<b>1.96</b>	<b>29</b>	<b>12.40</b>
1364	0.04	0.01	0.08	0.01	0.04	0.17	0.02	0.05	0.03	0.12	0.10	0.06	0.05	83	0.02
1370	2.15	2.19	1.43	1.89	1.58	1.06	1.62	0.59	0.96	0.58	1.30	1.40	0.56	40	1.97
1372	0.65	0.21	0.68	0.78	0.79	0.78	0.84	0.32	1.44	0.58	0.21	0.66	0.35	52	0.33
1379	2.49	2.70	2.64	3.51	3.42	2.36	3.59	1.07	3.66	1.33	1.71	2.59	0.92	35	3.50
<b>1416</b>	<b>6.06</b>	<b>4.60</b>	<b>4.16</b>	<b>3.23</b>	<b>3.20</b>	<b>2.72</b>	<b>3.35</b>	<b>3.81</b>	<b>2.70</b>	<b>2.44</b>	<b>3.96</b>	<b>3.66</b>	<b>1.04</b>	<b>28</b>	<b>1.70</b>
1421	1.76	1.84	1.42	1.65	1.36	1.09	1.49	0.55	0.91	0.64	0.28	1.18	0.53	45	1.71
1461	0.00	0.00	0.06	0.02	0.05	0.20	0.04	0.00	0.21	0.49	0.19	0.12	0.15	31	0.91
<b>1465</b>	<b>9.32</b>	<b>12.17</b>	<b>6.64</b>	<b>7.15</b>	<b>7.35</b>	<b>4.95</b>	<b>7.90</b>	<b>3.98</b>	<b>3.79</b>	<b>3.93</b>	<b>9.46</b>	<b>6.97</b>	<b>2.69</b>	<b>39</b>	<b>12.66</b>
1481	2.90	3.28	2.30	1.31	1.70	0.85	1.96	1.98	0.83	1.15	3.54	1.98	0.94	48	3.23
1503	4.95	3.80	3.92	2.89	3.37	2.82	3.61	3.20	2.30	2.71	3.55	3.37	0.72	21	2.78
1539	0.17	0.16	0.19	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.06	0.08	43	0.00
<b>1547</b>	<b>4.18</b>	<b>5.29</b>	<b>5.36</b>	<b>5.08</b>	<b>6.37</b>	<b>6.80</b>	<b>6.95</b>	<b>4.77</b>	<b>2.39</b>	<b>5.51</b>	<b>10.09</b>	<b>5.71</b>	<b>1.93</b>	<b>34</b>	<b>2.65</b>
1579	0.00	0.00	0.14	0.00	0.00	0.17	0.00	0.00	0.05	0.09	0.00	0.04	0.06	54	0.00
1596	2.57	3.22	1.93	1.18	1.81	0.45	1.92	1.66	1.00	5.70	9.64	2.83	2.66	94	1.58
1600	2.54	2.18	2.66	2.02	2.81	2.56	2.69	1.84	1.14	2.57	4.01	2.46	0.71	29	1.33
<b>1665</b>	<b>5.99</b>	<b>8.04</b>	<b>4.27</b>	<b>1.89</b>	<b>4.27</b>	<b>2.52</b>	<b>4.33</b>	<b>6.40</b>	<b>1.50</b>	<b>2.27</b>	<b>0.00</b>	<b>3.77</b>	<b>2.40</b>	<b>64</b>	<b>2.97</b>
1758	2.18	2.05	1.04	0.13	0.44	0.65	0.16	0.50	0.09	0.75	0.00	0.73	0.76	04	0.00
2363	1.18	1.21	1.45	0.02	1.07	0.67	1.44	1.00	0.03	1.17	0.00	0.84	0.57	68	1.45

homovanillinic acid beside four yet unknown compounds (Kovats indices = 1778, 1786, 1817 and 1996). At retention times of 39–50 min, in total eleven, mostly unknown compounds (2344, 2363 = gigantol, 2419, 2545, 2553 and four additional ones) are present. Our best correlation points to the modern wood of *Sciadopitys verticillata* SIEB. ET ZUCC. Nevertheless, the differentiation between *Sciadopitys* and *Taxodioxyton* is based only on higher contents of syringol, 4-propylguaiacol, (Z)-isoeugenol, acetovanillone and a series of four yet unknown components (Kovats indices 1778, 1786, 1817, 1996). Because of only one fossil wood sample of this kind (Fig. 5a), we present it in comparison to two modern references (Fig. 5b, c). However, there are three remarkable differences between fossil and modern wood: in contrast to the fossil sample, both references exhibit high contents of cedrol, a sesquiterpene alcohol, and  $\alpha$ - and  $\beta$ -cedrene, two isomers of sesquiterpene.

Microscopy reveals that already the slides of this specimen were although brown somewhat paler than those of the other specimens. The late wood was rather good preserved, the early wood very bad. The wood is characterized by the absence of wood parenchyma, and the presence in the rays of fenestriform pits. The rays themselves are up to 7 narrow cells high. This combined with the absence of resin ducts is only known from *Sciadopitys*. So the identification is *Sciadopityoxylon wettsteinii* JURASKY. The pale colour of the wood is in the field sometimes a help for field-identifications, however, some species of *Picea* have the same pale colour, so a microscopical analysis is always necessary.

## 5. Discussion

### 5.1. Maturity, organic carbon and hydrocarbon content

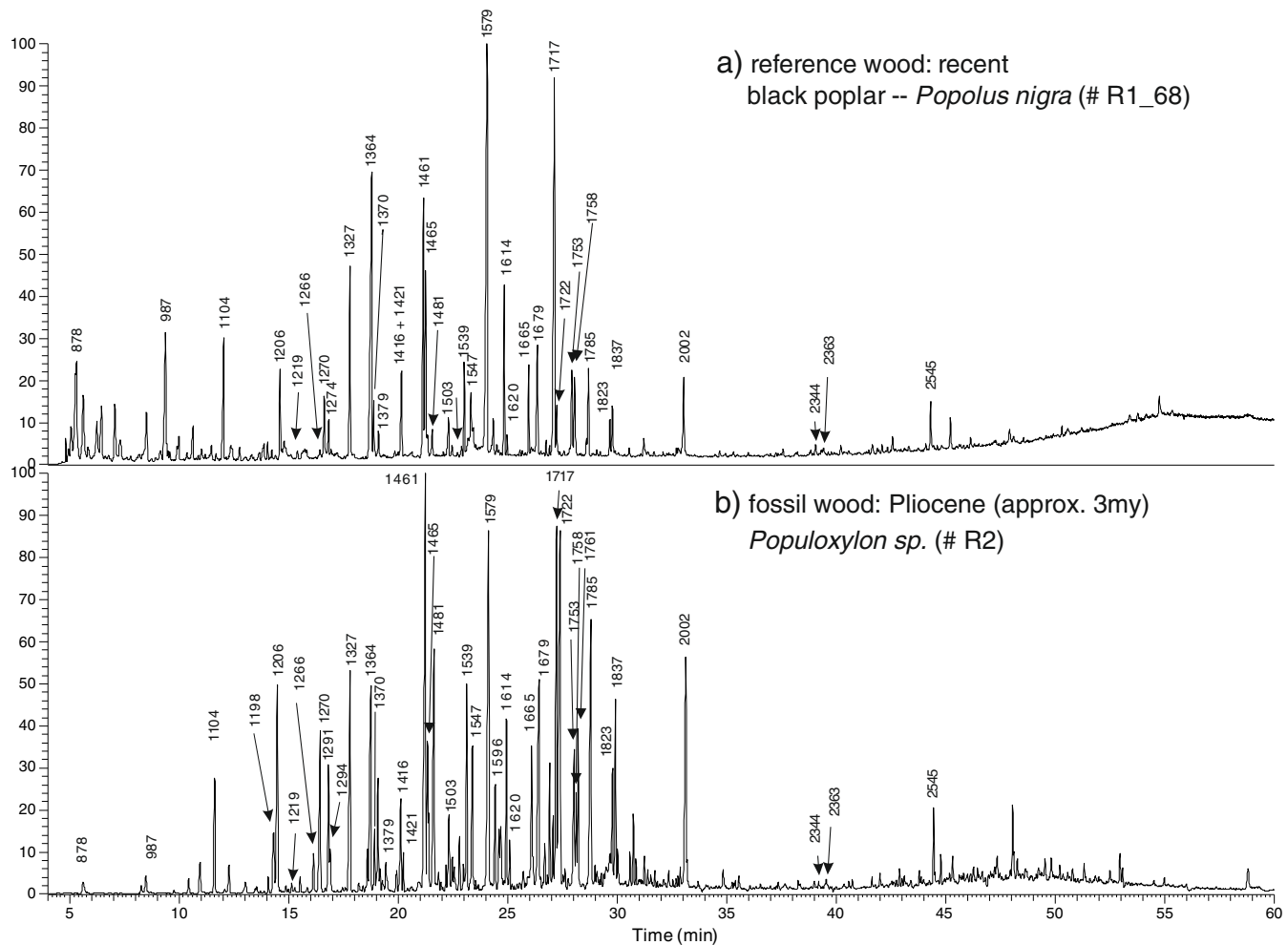
A mean  $T_{max}$  value of 343 °C for all 15 fossil samples confirms the lignite stage of the investigated sample series. The broad range of 335–

351 °C has to be interpreted as the result of varying depositional environments and slightly different early diagenetic pathways (Naeth et al., 2004). Similarly, although TOC mean values for fossil gymnosperm wood is about 2–4% higher than for fossil angiosperm wood (Frielingsdorf, 1993), TOC data do not allow any kind of wood discrimination as the total variation of 46–68% is lower than that generally found for individual tree rings of the same tree (Frielingsdorf, 1992). In contrast to TOC contents, hydrocarbon yields correlate well with the chemotaxonomic findings by pyrolysis GC-MS: nearly all *Taxodioxyton* woods and the *Sciadopityoxylon* wood exhibit relatively high hydrocarbon contents and mirror the generally higher resin content of conifers in contrast to the hardwood of *Populoxylon* with very low values.

### 5.2. Diagenesis, etheric oil and resin

The compound 3-methylcatechol was detected in Miocene *Taxodioxyton* sp. and *Sciadopityoxylon* sp. samples only, not in Pliocene *Populodioxylon* sp. We interpret this as an effect of specific conditions at the local depositional environment as well as of diagenesis that during coalification the methoxyl groups from lignin structures are lost first via demethylation and later the resulting alkylated catechols are converted to alkylated phenols (Stout et al., 1988; Hatcher et al., 1989a,b; Hatcher and Clifford, 1997). Vane and Abbott (1999) showed in the laboratory that lignin phenols were also demethylated to form alkylcatechols.

Etheric oils and resins in woods are composed of more or less wood specific compounds as their syntheses are genetically programmed (Bohlmann et al., 1998). Within this study, it was surprising that both references of the Japanese umbrella tree *Sciadopitys verticillata* exhibit relatively high contents of  $\alpha$ - and  $\beta$ -cedrene as well as cedrol (beside other potential resin contributors like (E)-isoeugenol, phenol, 4-



**Fig. 4.** Total ion chromatograms of a) the modern reference for the black poplar *Populus nigra* from our data base in comparison to b) a fossil wood sample from the Reuver subformation (R2). Compounds are assigned by Kovats indices (for respective CAS Registry Number and compound name, see Table 2).

vinylphenol and furfural and possibly also the compounds with Kovats indices 1778, 1786, 1817, and 1996). It is remarkable, that especially the resin and etheric oil components of *Sciadopitys verticillata* are preserved at least 70, but probably more than 100 years inside of the wood without any specific preservation conditions (Richter, pers. com., concerning the sampling age of the respective reference samples). In contrast, the fossil equivalent does not contain any of these three major components. Accordingly, our interpretation favors a diagenetic loss of these components. Nevertheless, it cannot be ruled out that, without consideration of a diagenetic loss, at least the etheric oil/resin components of the fossil wood were different. This would mean, our results cannot support the interpretation of Wolfe et al. (2009) that “conifers of the family *Sciadopityaceae*, closely allied to the sole extant representative, *Sciadopitys verticillata*, were involved in the genesis of Baltic amber.” Accordingly, other sources like *Araucaraceae* (e.g. Mills et al., 1984) or *Pinaceae* (e.g. Schubert, 1961) are more likely.

### 5.3. Fossil wood identification

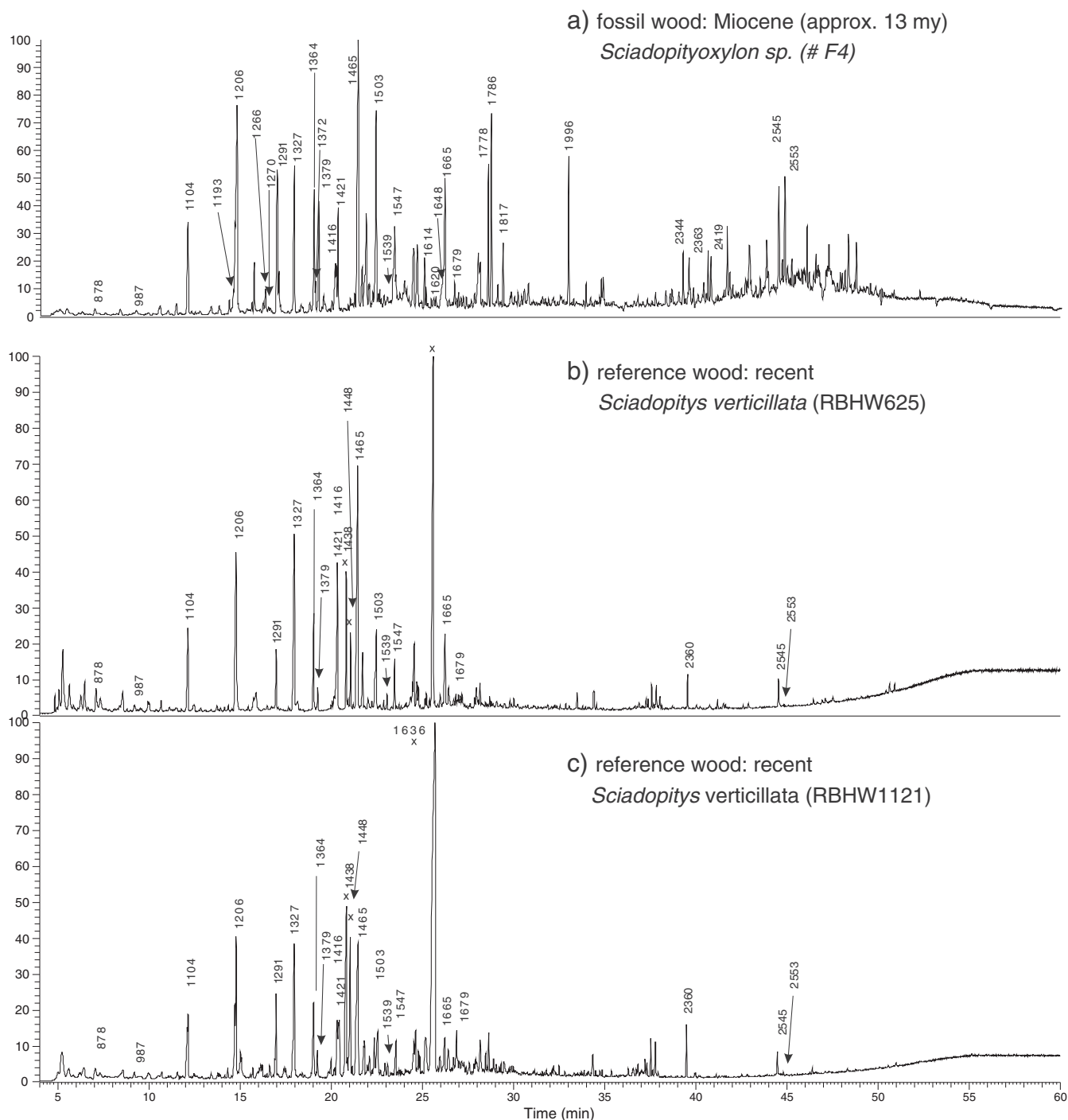
#### 5.3.1. Chemotaxonomic results versus fossil woods of the same genera

Our specific chemical wood identifications versus references from our data base can be verified not only by the above described microanatomical analyses, but also by previous findings of fossil woods of these genera in the Rhenish lignite area. *Taxodioxylon* sp. are described as *Taxodioxylon gypsaceum* from coal seams (van der Burgh, 1973), as

*Taxodioxylon germanicum* from the Reuver series (van der Burgh, 1978a,b), and as *Taxodioxylon sequoianum* – in fact a more recent synonym of *Taxodioxylon gypsaceum* (Kräusel, 1949) – from the Oberflözgruppe and the Hauptkies series (Frielingsdorf, 1992). Already very early, the close botanical relationship between *Taxodioxylon* sp. and *Sequoia* sp. became evident (van der Burgh, 1978a, 1978b). Von der Brélie and Wolf (1981) found the related pollen flora *Sequoiapollenites polyformosus* in core samples from drilling activities near Bergheim. *Taxodioxylon* is known from Lower Cretaceous to Cenozoic sediments of all over the Northern hemisphere and much more species have been found up to today (see Yang and Zheng, 2003, and references therein).

The large trunks from the channel sands (Fig. 2) identified as *Populoxylon* sp. can be verified as well by previous palaeobotanical descriptions. The microanatomically found bore traces were probably caused by piddocks, which definitively identify this trunk as driftwood. Laurant and Marty (1923; in Slijper, 1932) found probably the first two *Populoxylon* species. A summarizing compilation of seed/fruit-, wood-, and leaf-floras identifies *Populus* sp. as one of the contributors to the canopy of Miocene and Pliocene vegetation (van der Burgh, 1994; including all earlier findings by Reid and Reid, 1915; Laurant and Marty, 1923; Slijper, 1932; Kramer, 1974; van der Burgh, 1978a,b, 1984, 1987; Verkuil, 1984; Zagwijn, 1987; van Lidde de Jeude and van der Burgh, 1989; Belz, 1992). Up to today, about 500 very old trees of black poplar (*Populus nigra* spp. *nigra*) can still be found not only in





**Fig. 5.** Total ion chromatograms of a) a fossil wood sample from coal seam Frimmersdorf (F4) in comparison to b and c) two modern references (RBHW 625 and 1121) for the Japanese umbrella pine (*Sciadopitys verticillata*). Compounds are assigned by Kovats indices (for respective CAS Registry Number and compound name, see Table 2).

the Lower Rhine Basin at various sites in total North-Rhine Westphalia, but also in many other parts of Europe as companion along bigger rivers (Schmitt et al., 2006).

For the first time, *Sciadopityoxylon* sp. was described from the Rhenish lignite area by Jurasky (1928). He found it in the open cast mine “Zukunft” near Düren. Furthermore, this coniferous wood is known from other areas close by seam II of mine “Zukunft-West” and the Rotton of mine “Fortuna-Garsdorf” (van der Burgh, 1973, 1978a). Frielingsdorf (1992) found this wood type within the “Neurather Sand” in between seam Garzweiler II/III and seam Frimmersdorf b, but specifically within the same sample unit like ours, which means within

seam Frimmersdorf. The respective pollen grains are known, too (Von der Brélie and Wolf, 1981). Wood-anatomical evidence of occurrence of the genus *Sciadopitys* is also known from the Middle Miocene Second Seam horizon of the Lusatian brown coal field in the Lower Lusatia region, Brandenburg, Germany, by the presence of conifer remains of *Sciadopityoxylon wettsteinii* Jurasky (Dolezych and Schneider, 2007).

### 5.3.2. Differentiations by guaiacyl, syringyl, and hydroxyphenyl moieties

According to the conclusions of several authors (e.g. Zhou et al., 2011), the three lignin precursors p-hydroxycinnamyl (= coumaryl-)

**Table 4**  
Characterization of all fossil and reference wood samples analyzed for this study by their relative content of guaiacyl ( $\sum G$ ) and syringyl ( $\sum S$ ) building blocks as well as by the respective ratio of  $\sum G/(\sum G + \sum S)$ .

Sample identification by - age (modern/fossil) - rock unit or botanical name - sample number	Approx. numerical age (Ma)	$\sum$ compounds with guaiacyl moieties (G) (%)	$\sum$ compounds with syringyl moieties (S) (%)	Ratio $\sum G/(\sum G + \sum S)$
Fossil wood Reuver R1	3.0	30.56	62.71	0.328
Fossil wood Reuver R2	3.0	36.67	57.43	0.390
Fossil wood Reuver R3	3.0	31.50	60.82	0.341
Modern reference wood <i>Populus nigra</i> R1–68	0.0	27.69	55.34	0.333
Fossil wood Garzweiler G1	11.5	85.64	0.21	0.998
Fossil wood Garzweiler G2	11.5	91.10	0.17	0.998
Fossil wood Garzweiler G3	11.5	79.00	0.47	0.994
Fossil wood Frimmersdorf F1	13.0	71.95	0.04	1.000
Fossil wood Frimmersdorf F2	13.0	80.09	0.09	0.999
Fossil wood Frimmersdorf F3	13.0	68.54	0.84	0.988
Fossil wood Frimmersdorf F5	13.0	81.75	0.06	0.999
Fossil wood Morken M1	18.0	66.66	0.05	0.999
Fossil wood Morken M3	18.0	64.80	0.29	0.996
Fossil wood Morken M4	18.0	77.79	0.71	0.991
Fossil wood Morken M5	18.0	89.70	0.29	0.997
Modern reference wood <i>Sequoia sempervirens</i> R1–64	0.0	77.63	0.94	0.988
Fossil wood Frimmersdorf F4	13.0	83.25	0.84	0.990
Modern reference wood <i>Sciadopitys verticillata</i> 625	0.0	66.59	0.60	0.991
Modern reference wood <i>Sciadopitys verticillata</i> 1121	0.0	81.84	1.26	0.985

alcohol, coniferyl alcohol, and sinapyl alcohol result in the formation of three main building blocks of *p*-hydroxyphenyl/coumaryl (C), guaiacyl (G), and syringyl (S). Based on these criteria, a principal classification of biological materials was also proposed for woods by Suzuki et al. (1997). In general, gymnosperms contain about 95% guaiacyl and 1% syringyl moieties, whereas angiosperms contain about 40–60% syringyl moieties (Stihole, 2000). Based on the added relative amounts of 17 components with guaiacyl and 9 components with syringyl building blocks (see Table 2), the pyrograms of CPP/GC–MS analyses confirm these values (Table 4): for the angiosperm *Populoxylon* samples, we calculated 57–63% syringyl type components (modern reference *Populus nigra* = 55%), whereas for the gymnosperm samples of *Taxodioxylo*n only contents of 0.04–0.84% (modern reference *Sequoia sempervirens* = 0.94%) and also for *Sciadopityoxylon* only 0.84% (modern references *Sciadopitys verticillata* 0.60% and 1.26%) were determined. This results in a ratio of guaiacyl to (guaiacyl + syringyl) moieties from 0.33 to 0.39 for angiosperm wood and 0.99–1.00 for gymnosperm woods (Table 4). The perfect consensus with the ranges provided by Stihole (2000), see above), confirms not only our correct qualitative but especially also our quantitative approach for the three different monolignols. Accordingly, we can recommend applying this ratio - as it is generally done in botanical sciences for various plant differentiations - also based on CPP/GC–MS, especially for a rapid chemical screening of fossil wood types with unknown botanical classification. Moreover, this ratio can also be applied for characterization of the local source, i.e. site and provenance of one specific wood (plant) type (Rodrigues et al., 1999). According to the overall chemical difference of gymnosperm and angiosperm wood, it can be supposed that this might also partly explain the 2.8‰ difference of  $^{13}\text{C}$  isotope discriminations in different lignite samples (Lücke et al., 1999).

## 6. Conclusion

Neogene wood samples are usually assigned to modern tree genera based on wood anatomical analyses. Our study demonstrates that CPP/GC–MS is an additional and very sensitive tool to decipher taxonomic

relations between fossil wood genera and their modern relatives: 15 fossil wood samples from the Neogene of the Lower Rhine Embayment could successfully be identified as *Taxodioxylo*n sp., *Populoxylon* sp. and *Sciadopityoxylon* sp. by comparison to their modern wood analogues. Microanatomical crosschecks could confirm the chemical classification. The angiosperm *Populoxylon* samples contain about 57–63% syringyl type components in contrast to the gymnosperm samples with only 0.04–0.84% for *Taxodioxylo*n and 0.84% for *Sciadopityoxylon*. The differentiation between *Sciadopityoxylon* and *Taxodioxylo*n is based on higher contents of syringol, 4-propylguaiacol, (Z)-isoeugenol, acetovanillone and a series of four yet unknown components (Kovats indices 1778, 1786, 1817, 1996).

At the moment, chemotaxonomy by CPP/GC–MS is able to identify the genus of the wood. Only in exceptional cases, chemotaxonomy is able to identify the individual species like microanatomy may do that. Furthermore, the chemotaxonomic classification is clearly limited by the number of references already included in the data base. However, chemotaxonomic classifications by CPP/GC–MS can overcome the problem of limited amounts of sample material, whenever there is no chance for a microanatomical section. Furthermore, it is objective, reproducible and in the course of time, when the data base has become more complete, then the chemotaxonomic approach will be able to supplement the (palaeo-) botanist's experience.

Based on the analyzed sample set in combination with modern analogues from our data base, we see an excellent chance for a distinct and fast identification of fossil wood types, at least in low temperature-time windows, but possibly in geologic older case studies, too.

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organizing the tour with a rich pool of geologic information. We are indebted to two anonymous reviewers for their constructive comments which have improved the manuscript.

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