



# Phenyldibenzofurans and phenyldibenzothiophenes in marine sedimentary rocks and hydrothermal petroleum

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## Abstract

The phenyl derivatives of dibenzo[*b,d*]furan and dibenzo[*b,d*]thiophene, so far not reported in geological samples, have now been identified in some sedimentary rocks, bitumen and hydrothermal petroleum through a comparison of their retention times and mass spectra with those of authentic standards. All four possible positional isomers were detected for each phenyldibenzo[*b,d*]furan (PhDBF) and phenyldibenzo[*b,d*]thiophene (PhDBT). Their elution sequence is 1-, 4-, 2- and 3-phenyldibenzo[*b,d*]furan and 1-, 4-, 2- and 3-phenyldibenzo[*b,d*]thiophene on apolar stationary phases. In contrast to phenyldibenzofurans, the distributions of the thiophene series is controlled mainly by the organic matter maturity. In the most mature samples 4-, 2- and 3-PhDBTs prevail over 1-PhDBT, while less mature samples contain mainly 4-PhDBT or 1-PhDBT and 2-, 3-PhDBTs occur at comparable concentrations. However, in samples of low maturity, in addition to the phenyldibenzo[*b,d*]thiophene C<sub>18</sub>H<sub>12</sub>S series, other structural isomers of C<sub>18</sub>H<sub>12</sub>S possessing very similar mass spectra were detected. These are likely to be either naphthylbenzo[*b*]thiophenes and/or phenylnaphtho[*b*]thiophenes. PhDBFs and PhDBTs are likely to be intermediate products in the formation of more condensed heterocyclic polycyclic aromatic compounds like triphenyleno[1,12-*bcd*]thiophene and triphenyleno[1,12-*bcd*]furan, and benzobisbenzofurans and benzobisbenzothiophenes, which are commonly detected in geological samples. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Phenylpolyaromatic hydrocarbons and polyphenyls are sometimes the major constituents of the aromatic

fraction of extracts from some marine sedimentary rocks (Marynowski et al., 2001) and coals (Willsch and Radke, 1995) within the maturity range for oil generation. Besides these geological products, compounds containing phenyl groups are formed during combustion and oxidative pyrolysis of coal and coal-derived materials (Bruinsma et al., 1988; Meyer zu Reckendorf, 1997, 2000). Similarly, these are also common products of chemical oxidation and decarboxylation of coals, where the phenyl moiety is considered a structural unit of coal (e.g. Stock and Obeng, 1997). Additionally, phenyl substituted heterocyclic aromatics are present in

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high temperature pyrolysates of coal tars and pitches. The previously unreported occurrence of phenyldibenzo[*b,d*]furans (PhDBF) and phenyldibenzo[*b,d*]thiophenes (PhDBT) has been described recently by Meyer zu Reckendorf (1997, 2000).

It seems striking, however, that phenyl derivatives of dibenzo[*b,d*]furan and dibenzo[*b,d*]thiophene have not been previously reported in sedimentary rocks, despite the fact, that dibenzo[*b,d*]furan and dibenzo[*b,d*]thiophene and their alkyl derivatives are extremely common constituents in a variety of sedimentary rocks. The occurrence of dibenzo[*b,d*]furans was reported, for example, by Püttmann et al. (1990), Abbott et al. (1998), Sephton et al. (1999), Radke et al. (2000), while dibenzo[*b,d*]thiophenes were described, for example, by Radke et al. (1986), Sinninghe Damsté and de Leeuw (1990), Kvenvolden and Simoneit (1990), Rospondek et al. (1994, 1998), Radke and Willsch (1994), Requejo et al. (1996), Chakhmakhev et al. (1997), and Huang and Pearson (1999). The dibenzo[*b,d*]furans can be regarded as potential biomarkers (Radke et al., 2000 and references cited therein) because DBF is the core moiety for many biomolecules encountered in lichen (e.g. Huneck et al., 1993), whereas dibenzo[*b,d*]thiophenes have not been found either in living organisms or in marine particulate matter. Their concentration usually increases with organic matter maturation clearly indicating a diagenetic/catagenetic origin.

Here all positional isomers of the phenyldibenzofurans and phenyldibenzothiophenes were identified in some Tertiary, Mesozoic and Palaeozoic sedimentary rocks, solid bitumens and oceanic-rift-generated hydrothermal petroleum by comparison with authentic standards. To the best of our knowledge this is the first report on their occurrence in geological samples.

## 2. Samples and experimental methods

### 2.1. Samples

The samples analysed were collected from five localities: (1) Middle and Upper Devonian carbonates and shales from the Holy Cross Mountains, Poland (for the detailed description see: Marynowski et al., 2000). (2) Upper Permian (Zechstein) dolomites and shales (Kupferschiefer) from the Fore-Sudetic Monocline, Poland (Rospondek et al., 1994, 1998). The samples were collected from the Polkowice mine at a depth of about 600 m (field H2E, shaft H15), and from the Rudna mine. (3) Cretaceous and Tertiary Flysch samples originate from Podhale Through, the West Carpathians, Southern Poland. (4) Bitumen from Upper Devonian reef limestones from the Wintenberg quarry, the Harz Mountains, Germany (Gischler, 1996).

(5) Hydrothermal petroleum from Guaymas Basin, central part of the Gulf of California, Mexico (e.g. Simoneit and Lonsdale, 1982; Simoneit, 1993). The basic information on the samples is given in Table 1.

### 2.2. Methods

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

GC–MS analysis was carried out with a HP5890 II gas chromatograph equipped with a fused silica capillary columns (30 m or 60 m×0.25 mm i.d.) coated with 95% methyl/5%phenylsilicone phase (HP-5, 0.25- $\mu$ m film thickness) and analysed again on 100% methylsilicone phase (HP-1, 0.25- $\mu$ m film thickness). Helium was the carrier gas used. The GC oven was programmed from 35 to 300 °C at 3 °C min<sup>-1</sup>. The gas chromatograph was coupled with a HP 5971A mass selective detector (MSD). The MS was operated with an ion source temperature of 200 °C, an ionisation energy of 70 eV, and a cycle time of 1 s in the mass range 40–600 daltons. In addition, a sulphur selective FPD detector was used.

### 2.3. Reference compounds

Phenyldibenzofurans (C<sub>18</sub>H<sub>12</sub>O) (all possible isomers 1-, 2-, 3- and 4), phenyldibenzothiophenes (C<sub>18</sub>H<sub>12</sub>S) (all isomers 1-, 2-, 3- and 4) and benzobisbenzo[1,2-*b*;4,5-*b'*]furan (C<sub>18</sub>H<sub>10</sub>O<sub>2</sub>) were purchased from Chiron, Trondheim, Norway. In addition, the authentic standard of triphenyleno[1,12-*bcd*]thiophene (C<sub>18</sub>H<sub>10</sub>S) was purchased from PAH Research Institute, Greifenberg, Germany.

### 2.4. Semi-quantitation

Relative abundances of phenyldibenzofurans and phenyldibenzothiophenes were calculated from integration of the appropriate peak areas from *m/z* 244 and *m/z* 260 mass chromatograms. Due to variation in molecule fragmentation patterns within the homologous series of PhDBF and PhDBT, correction factors were calculated by relating the peak area obtained from the FID chromatograms to those from the mass chromatograms of the authentic standards. These factors are as follows: 1—PhDBF = 1.2, 2—PhDBF = 1.0, 3—PhDBF = 0.9, 4—PhDBF = 0.9, 1—PhDBT = 1.2, 2—PhDBT = 0.8, 3—PhDBT = 0.7, 4—PhDBT = 0.7.

Table 1  
Sample descriptions and bulk geochemical data

Locality	Lithology	$R_o$ (%)	TOC (%)	<i>EOM</i> (mg/g TOC)
<i>Holy Cross Mountains, Poland</i>				
Panek (by Bolechowice)	Limestone	0.66	0.14	21
Laskowa Góra	Dolostone	1.20	0.37	11
Radkowice	Greenish shale	0.65	1.13	10
Sitkówa- Kowala	Limestone	0.63	0.25	68
Kowala (Frasnian)	Black shale	0.55	4.00	30
Borhole Janczyce-1 (depth 943.0m)	Dolostone	–	0.03	20
Borhole Janczyce-1 (depth 1239.3m)	Shale	1.15	0.30	30
Góra Łgawa	Marly limestone	0.52	0.73	27
Besówka	Limestone	0.67	0.32	6
Piskrzyn	Dolostone	0.73	n.d.	n.d.
Jaworznia	Limestone	0.63	0.01	20
Skala	Marly limestone	0.84	0.89	14
<i>Fore-Sudetic Monocline, Poland</i>				
Polkowice Mine PW-II/1	Laminated reddish dolostone “Rote Fäule”	0.64	1.00	6
Polkowice Mine PW-III/1	Reddish/black shale “Rote Fäule”	0.6	n.d.	n.d.
Polkowice Mine PW-III/2	Limestone with hematite spots “Rote Fäule” and red gypsum	0.6	n.d.	n.d.
Rudna Mine	Bitumen cementing sandstone	–	–	–
<i>Podhale through, the Carpathians, Southern Poland</i>				
Zakopane	Flysch—Tertiary	0.9	n.d.	n.d.
Poronin PAN-1 (depth 1912 m)	Flysch—Cretaceous	1.5	0.12	n.d.
<i>Harz Mountains, Germany</i>				
Wintenberg	Bitumen	–	–	–
<i>Gulf of California, Mexico</i>				
Guaymas Basin	Hydrothermal oil	–	–	–

n.d., not determined.

### 3. Results and discussion

#### 3.1. Identification of phenyldibenzofurans and phenyldibenzothiophenes

The aromatic fractions of the samples analysed contain, besides the most abundant derivatives of phenanthrene, fluorene, chrysene, terphenyls, dibenzofuran, dibenzothiophene and benzonaphthothiophenes (Fig. 1), an additional abundant series of organic sulphur compounds (OSCs). These additional OSCs, eluting together and directly after the benzonaphthothiophenes, are easily detected on sulphur-sensitive FPD chromatograms. The GC–MS analyses revealed that all these unreported OSCs have very similar mass spectra, which are characterised by the molecular ion as the base peak  $M^+ \bullet 260$  (Fig. 1c). The abundance of biphenyl, terphenyls and other phenyl derivatives of, for example, naphthalene and phenanthrene in these samples suggests that these OSCs can be phenyl derivatives of dibenzo[*b,d*]thiophene  $m/z 184 + 76 = 260$ . Indeed, the four

first eluting compounds have recently been identified, based on authentic standards, in coal tars and pitches and their pyrolysates (Meyer zu Reckendorf, 2000). The compounds encountered here have identical mass spectra and retention times to those of the authentic standards of phenyldibenzo[*b,d*]thiophenes. Fig. 2 shows the mass spectra of the phenyldibenzothiophene reference compounds. All these molecules have little tendency to fragment, so that beside the molecular ion base peak  $M^+ \bullet 260$ ,  $[M-1]^+ \bullet 259$ , and  $[M-2]^+ \bullet 258$ , the other most abundant peaks are from the doubly charged  $M^{2+} \bullet 130$  and  $[M-2]^{2+} \bullet 129$  ions. Only the spectrum of 1-PhDBT (Fig. 2a) differs from the others. The molecular ion peak is accompanied by very intense  $[M-1]^+ \bullet 259$ ,  $[M-2]^+ \bullet 258$  ions indicating hydrogen loss and intra-molecular cyclisation.

The identity of these compounds was confirmed unambiguously by co-injection. Their elution sequence is 1-, 4-, 2- and 3-phenyldibenzo[*b,d*]thiophene on the 95% methyl–5% phenylsilicone stationary phase (HP-5; Figs. 1 and 3). On this stationary phase, 1-PhDBT

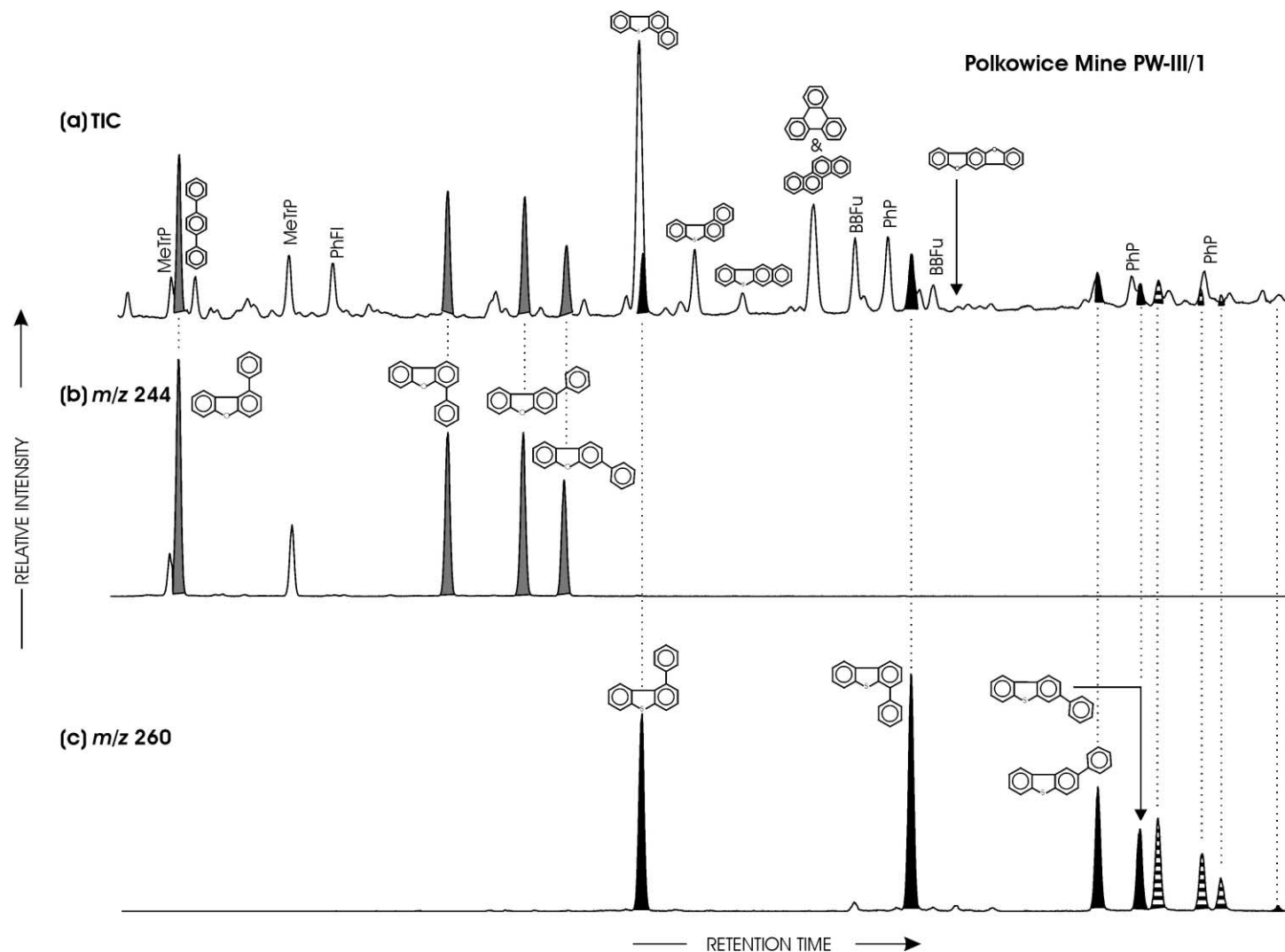


Fig. 1. Partial GC–MS chromatograms for the aromatic compounds in the sample from Polkowice (PWIII/1): (a) TIC chromatogram, (b) mass chromatogram  $m/z$  244,  $C_{18}H_{12}O$ , revealing the distribution of the phenyldibenzo[*b,d*]furan isomers and (c) mass chromatogram  $m/z$  260,  $C_{18}H_{12}S$ , revealing the distribution of the phenyldibenzo[*b,d*]thiophenes; (note the peak intensities are not proportional to the thiophene concentrations due to differences in the fragmentation pattern; MeTrP, methylterphenyls, PhFI, phenylfluorenes, BBFu, benzobisbenzofurans, PhP, phenylphenanthrenes; horizontally hatched peaks denote other isomers of  $C_{18}H_{12}S$ ).

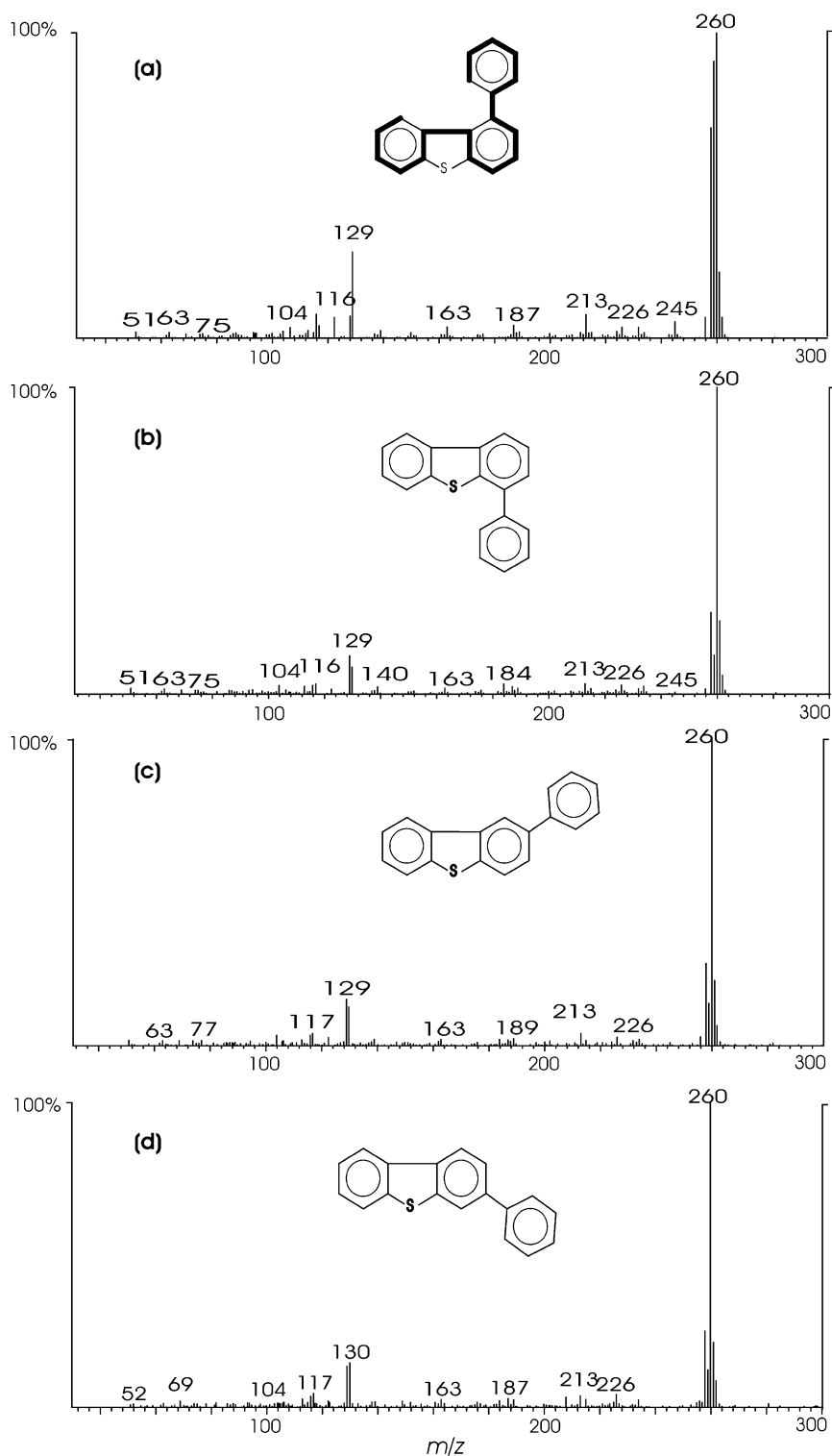


Fig. 2. Mass spectra of phenyldibenzo[*b,d*]thiophenes shown in their elution sequence on an apolar stationary phase: (a) 1-PhDBT having the linear carbon skeleton marked by the bold line, (b) 4-PhDBT, (c) 2-PhDBT, and (d) 3-PhDBT.

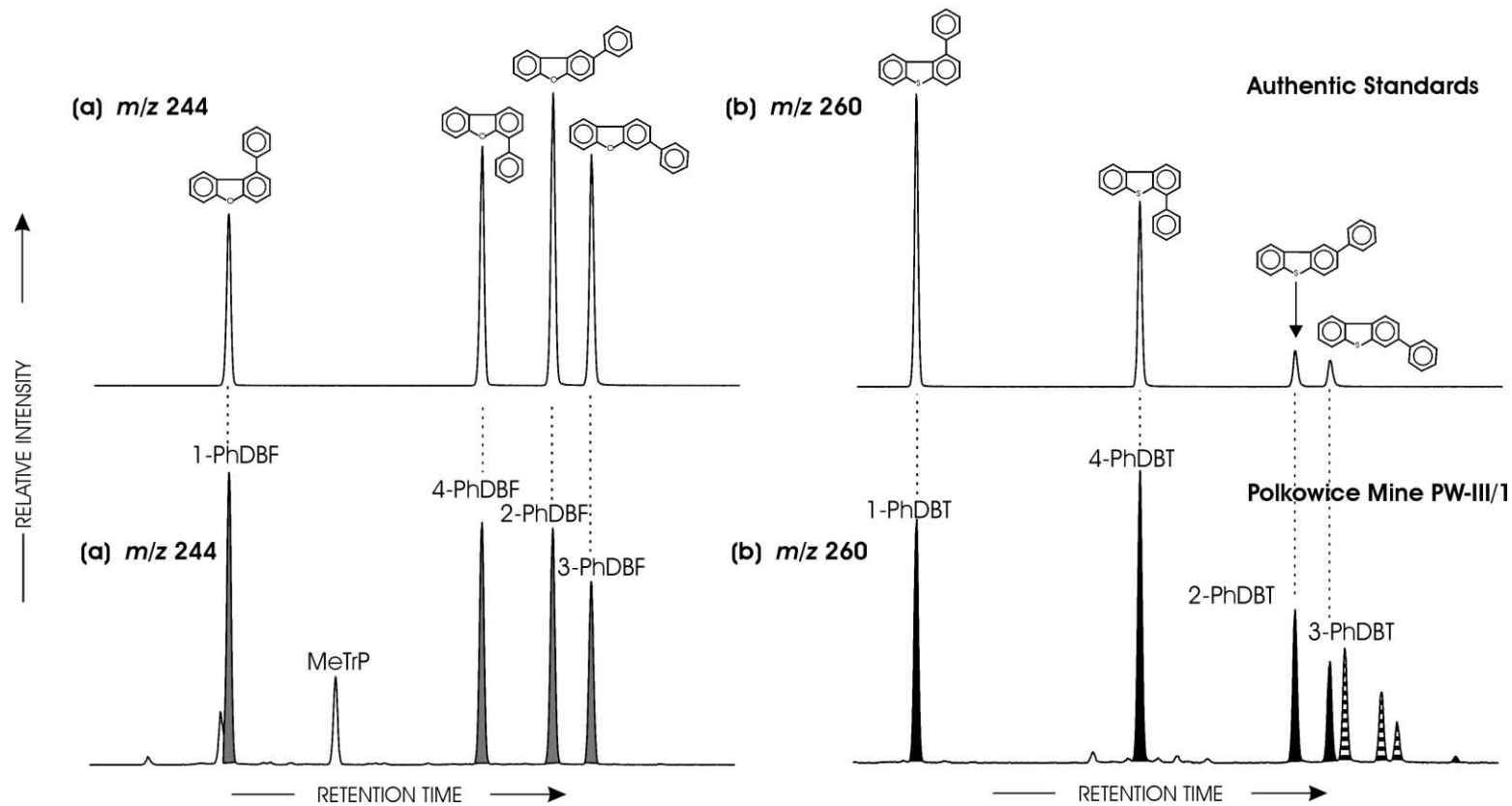


Fig. 3. Identical retention times of authentic standards of the (a) phenyldibenzo[*b,d*]furan and (b) phenyldibenzo[*b,d*]thiophene isomers, and the aromatic fraction of the Polkowice PW-III/1 sample as shown by partial mass chromatograms of (a)  $m/z$  244 and (b)  $m/z$  260; (horizontally hatched peaks. See Fig. 1; MeTrP, methylterphenyls).

Table 2

Relative concentrations of positional isomers of phenyldibenzo[*b,d*]furans, C<sub>18</sub>H<sub>12</sub>O (PhDBF), phenyldibenzo[*b,d*]thiophenes, C<sub>18</sub>H<sub>12</sub>S (PhDBT), and other C<sub>18</sub>H<sub>12</sub>S isomers (calculated from mass chromatograms)

Samples	Relative concentration in %											
	1-PhDBF 359.53 <sup>a</sup>	4-PhDBF 375.94 <sup>a</sup>	2-PhDBF 380.71 <sup>a</sup>	3-PhDBF 383.47 <sup>a</sup>	1-PhDBT 387.94 <sup>a</sup>	4-PhDBT 405.68 <sup>a</sup>	2-PhDBT 418.50 <sup>a</sup>	3-PhDBT 421.07 <sup>a</sup>	<i>m/z</i> 260 422.6 <sup>b</sup>	<i>m/z</i> 260 425.5 <sup>b</sup>	<i>m/z</i> 260 426.8 <sup>b</sup>	<i>m/z</i> 260 431.5 <sup>b</sup>
Panek	10.5	42.5	36.1	10.9	8.0	18.7	8.4	7.4	23.9	18.8	10.4	4.6
Laskowa Góra	9.7	80.0	6.7	3.7	1.1	27.7	38.5	32.8	n.f.	n.f.	n.f.	n.f.
Radkowie	16.2	44.4	26.4	13.0	15.0	23.8	12.0	9.9	23.1	13.8	2.5	n.f.
Sitkówa—Kowala	9.8	28.9	46.0	15.3	6.5	11.7	8.9	9.1	22.7	19.2	11.6	10.3
Kowala (Frasnian)	4.7	30.3	48.1	16.9	9.0	12.4	7.7	6.4	24.4	20.3	10.1	9.8
Janczyce-1 (943.0 m)	Traces	100.0	Traces	Traces	5.5	30.5	38.7	25.2	n.f.	n.f.	n.f.	n.f.
Janczyce-1 (1239.3 m)	Traces	100.0	Traces	Traces	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
Góra Lgawa	8.5	37.0	44.6	9.9	5.4	13.3	4.5	4.9	26.1	22.4	15.4	8.0
Besówka	10.8	44.2	31.6	13.4	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
Piskrzyn	11.7	24.8	44.2	19.3	7.5	24.4	26.6	21.9	7.7	11.9	0.1	n.f.
Jaworznia	11.7	56.6	22.2	9.5	5.9	27.6	15.4	13.2	16.1	15.4	6.3	n.f.
Skała	3.3	37.4	42.6	16.8	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
Polkowice PW-II/1	20.9	27.7	27.1	24.2	9.5	23.6	16.0	15.6	15.9	14.1	4.9	0.4
Polkowice PW-III/1	23.6	27.5	28.3	20.5	10.3	23.9	17.7	13.4	16.6	11.0	6.6	0.5
Polkowice PW-III/2	20.1	29.2	29.1	21.6	11.7	30.8	21.3	17.1	9.3	8.3	1.6	n.f.
Rudna	31.5	22.1	26.7	19.7	23.7	30.1	25.3	20.9	n.f.	n.f.	n.f.	n.f.
Zakopane	16.7	31.5	28.1	23.7	5.8	28.9	18.7	22.1	10.4	10.4	3.7	n.f.
Poronin PAN-1 (1912 m)	Traces	55.8	19.7	24.5	Traces	43.0	34.3	22.8	n.f.	n.f.	n.f.	n.f.
Wintenberg	21.1	48.6	16.2	14.0	12.4	39.5	22.5	25.6	0.1	n.f.	n.f.	n.f.
Guaymas Basin	n.f.	n.f.	n.f.	n.f.	n.f.	26.8	27.7	45.5	n.f.	n.f.	n.f.	n.f.

n.f., Not found.

<sup>a</sup> Retention time indices (95% methyl/5% phenylsilicone stationary phase) after Meyer zu Reckendorf (2000) calculated according to Vassilaros et al. (1982).

<sup>b</sup> Mean retention time indices based on this study.

(*I*<sub>Ri</sub> 387.9) practically co-elutes with benzo[*b*]naphtho[2,1-*d*]thiophene (*I*<sub>Ri</sub> 388.1; Meyer zu Reckendorf, 2000), which is usually the most abundant benzonaphthothiophene isomer in most geological samples (Fig. 1a). On the other hand, on the 100% methylsilicone stationary phase (HP-1) 1-PhDBT elutes very slightly after benzo[*b*]naphtho[2,1-*d*]thiophene.

Furthermore, in less mature samples the PhDBT series described is accompanied by an additional series of other unidentified C<sub>18</sub>H<sub>12</sub>S (*m/z* 260) isomers, represented by at least four C<sub>18</sub>H<sub>12</sub>S compounds. (Fig. 1c and Table 2). These are most likely to be either phenylnaphtho[*b*]thiophenes or/and naphthylbenzo[*b*]thiophenes. The mass spectra of some of these compounds have been published. The mass spectrum of 3-phenylnaphtho[2,1-*b*]thiophene was described (Porter, 1985) and some others were published in the Wiley/NBS database (McLafferty and Stauffer, 1989). The mass spectra of phenylnaphtho[*b*]thiophenes are extremely similar to those of naphthylbenzo[*b*]thiophenes, and in turn, these both are similar to the mass spectra of phenyldibenzo[*b,d*]thiophenes, thus enabling firm identification of this additional series.

In this set of samples the second analogous compound series consist of the phenyldibenzofurans (Fig. 1b). Their elution sequence of 1-, 4-, 2- and 3- is the same as that for PhDBT (Meyer zu Reckendorf,

2000). All four isomers can be clearly identified (Fig. 3a) based on co-injection with authentic standards. Mass spectra for the furans are analogous to those of the thiophenes with the exception of 1-PhDBF. In contrast to 1-PhDBT, the mass spectrum of 1-PhDBF is similar to those of the other PhDBF isomers with a slight increase in (*M*-2)<sup>+</sup> ion intensity. A detailed description of these and the phenyldibenzothiophene mass spectra is given by Meyer zu Reckendorf (2000).

### 3.2. Controls on distribution of PhDBFs and PhDBTs

Less mature samples contain either 4-PhDBT or 1-PhDBT as the dominant isomer, while 2-, 3-PhDBTs occur at comparably low concentrations (Fig. 4). In turn, more mature samples contain 4-, 2- and 3-PhDBTs, which prevail over 1-PhDBT. The 1-PhDBT isomer is minor or practically absent at maturities ranging from 0.9 to 1.5% *R*<sub>o</sub> as well as in the hydrothermal petroleum, thus suggesting that increased maturity either removes 1-PhDBT or allows for its' isomerisation. This decrease is similar to the widely-described reductions in the 1-methyldibenzothiophene concentration, and generally of 1-alkyl isomers, with increasing maturity (Radke et al., 1986; van Aarssen et al., 2001). This suggests a maturity control on the PhDBT distribution.

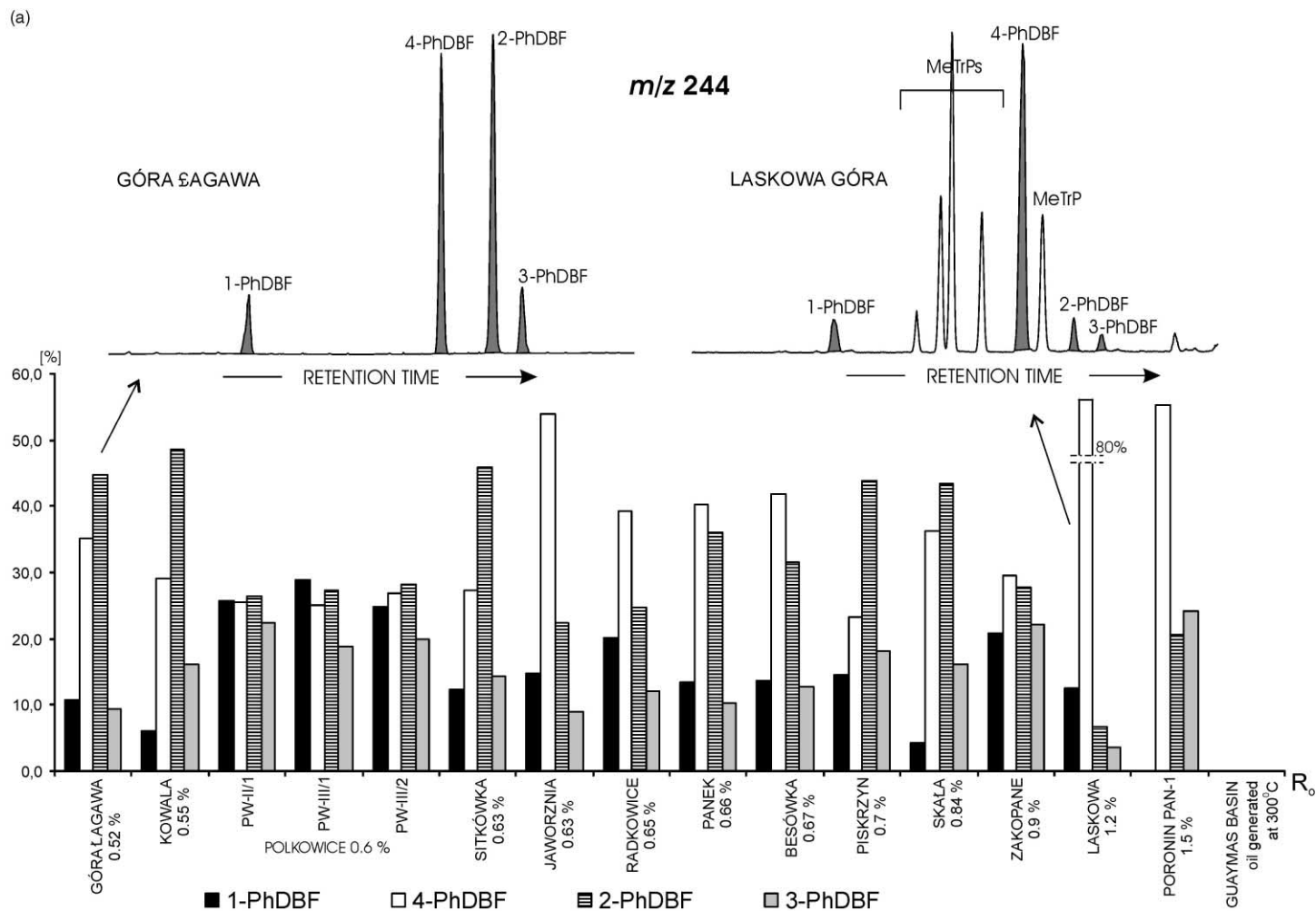


Fig. 4. Relative abundance of (a) phenyldibenzo[*b,d*]furans *m/z* 244, and (b) phenyldibenzo[*b,d*]thiophenes (corrected for differences in the fragmentation pattern of PhDBFs and PhDBTs) plotted against the mean maturity with examples of mass chromatograms given for the lowest range of the oil window,  $R_o = 0.52\%$  (Góra Łgawa), and the upper range of the oil window  $R_o = 1.22\%$  (Laskowa Góra); horizontally hatched peaks denote other isomers of the *m/z* 260 series ( $C_{18}H_{12}S$ ), MeTrP, methylterphenyls.



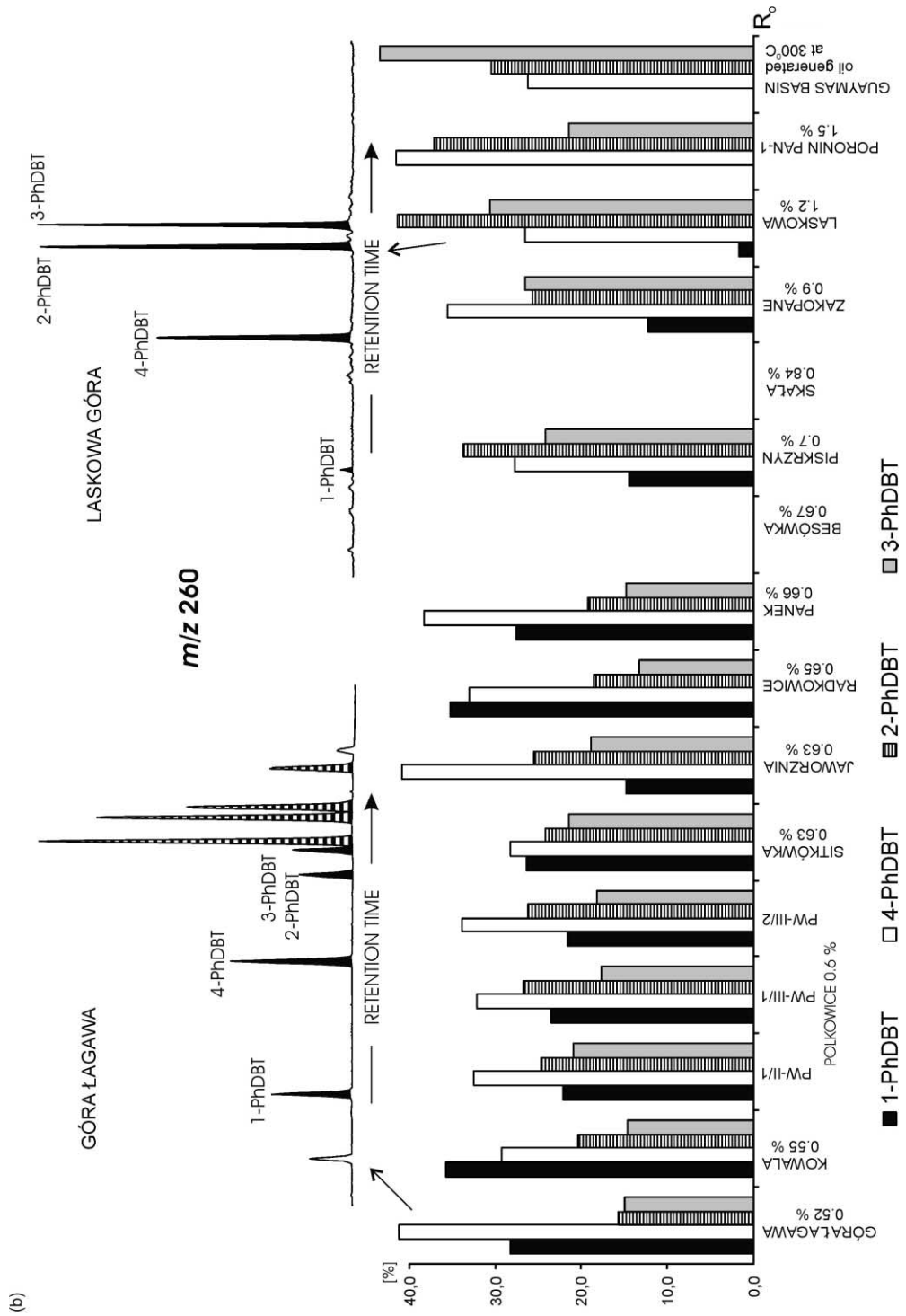


Fig. 4. (continued)

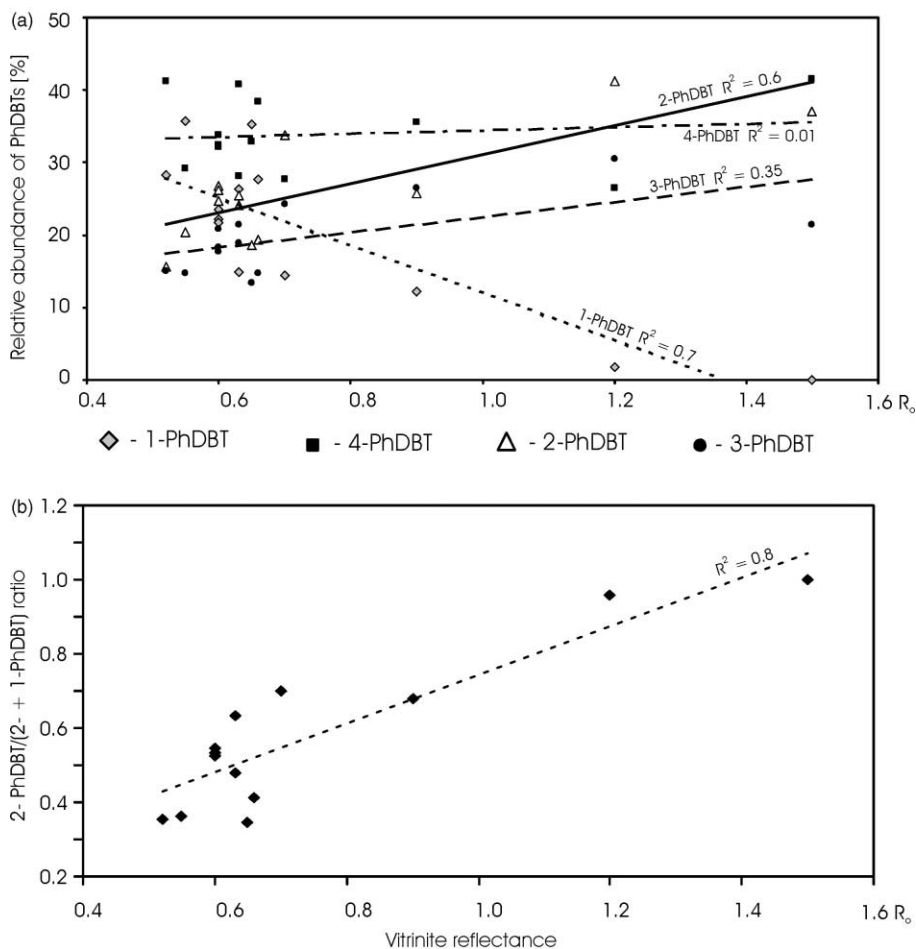


Fig. 5. Correlation of (a) relative abundance of PhDBTs and (b) preliminary PhDBT maturity parameter  $2\text{-PhDBT}/(2\text{-} + 1\text{-PhDBT})$  versus vitrinite reflectance. Abundances of PhDBTs are shown after correcting the differences resulting from the PhDBT fragmentation patterns.

The relative concentrations of 1- and 2-PhDBT correlate best with the mean vitrinite reflectance (Fig. 5a) in the set of the samples investigated varying in maturity from  $R_o$  0.55% to 1.5% (Table 1). These isomer concentrations were used to calculate a maturity parameter  $2\text{-PhDBT}/(2\text{-} + 1\text{-PhDBT})$ , for which correlation with the mean vitrinite reflectance is the best and reaches  $r^2 = 0.8$  (Fig. 5b). At lower levels of maturity alkyldibenzothiophene distributions are known to be considerably affected by depositional and diagenesis environments, and lithology, while beyond  $R_o$  1.35% they are controlled essentially by maturity (for references see: Radke et al., 2000). Thus, the tentatively proposed maturity parameter based on PhDBT concentrations is expected to be strongly influenced by other factors as in the case of alkyldibenzothiophenes.

In samples of lower maturity (e.g. Góra Łgawa) the additional series of the  $m/z$  260 compounds prevails

over all PhDBTs (Table 2 and Fig. 4b). With increasing maturity (e.g. Laskowa Góra Fig. 4b) they disappear indicating their lower thermal stability relative to PhDBTs. This is also confirmed by their absence in hydrothermal petroleum (Fig. 6), and in oxidative pyrolysis products from ring furnace five gases (Meyer zu Reckendorf, 1997, 2000).

In contrast to the maturation trends observed for the PhDBT distribution, the behaviour of PhDBFs is equivocal. The less mature samples ( $\sim R_o$  0.5–0.8%) contain either 2- or 4-PhDBF as the dominant isomer (Table 2 and Fig. 4a). For example, 4-PhDBF dominates in the samples from Jaworzna, Radkowiec, Panek and Beśówka, while 2-PhDBF prevails in Góra Łgawa, Kowala, Piskrzyn and Sitkówka (Fig. 4a). In turn, in Polkowice ( $\sim R_o$  0.6%) both 4- or 2-PhDBF are observed in almost equal concentrations. The samples of higher maturity ( $\sim R_o$  0.9–1.5%) contain predominantly

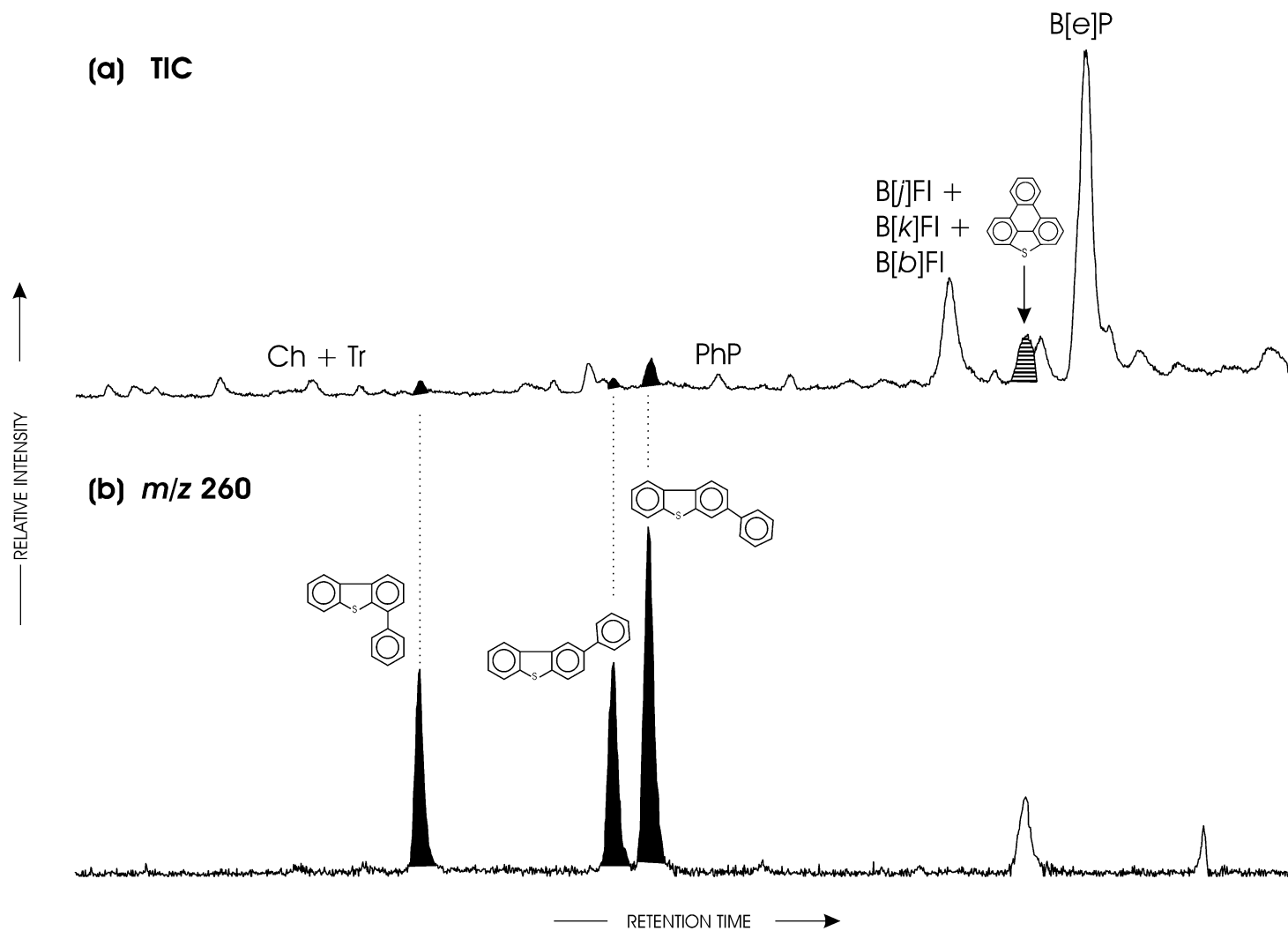


Fig. 6. Partial GC-MS chromatograms for the aromatic compounds in a hydrothermal petroleum from Guaymas Basin: (a) TIC trace showing the presence of triphenyleno[1,12-*bcd*]thiophene (Ch, chrysene; Tr, triphenylene; PhP, phenylphenanthrenes; BFl, benzo[*f*]fluoranthenes B[e]P, benzo[*e*]pyrene) and (b) mass chromatogram  $m/z$  260.

4-PhDBF. These random fluctuations in distribution of the isomers are somewhat like those observed for alkyl-dibenzofurans, for which maturity dependent trends are observed beyond  $R_o$  1.0% (Radke et al., 2000). Unfortunately, such a maturation range is not well enough represented in the set of the samples investigated (Table 1).

### 3.3. Origin of PhDBFs and PhDBTs in geological samples

Most of the samples investigated contain both phenyldibenzo[*b,d*]furans and phenyldibenzo[*b,d*]thiophenes, although there are exceptions (Table 2, Fig. 4a and b). It is clear that a prerequisite for PhDBT formation is the presence of sulphidic sulphur in the rocks, which is the case for most marine sediments. An early incorporation of inorganic sulphur species into unsaturated chain hydrocarbon moieties (Sinninghe Damsté and de Leeuw, 1990) or carbohydrates (Sinninghe Damsté et al., 1998) might finally lead to 1-PhDBT formation, since it is the only PhDBT isomers that possess a linear carbon skeleton (Fig. 2a). A hypothesis for the formation of phenyl-polyaromatic hydrocarbons and polyphenyls, which starts from carbohydrates, was proposed by Marynowski et al. (2001) for the samples originating from the Holy Cross Mountains. Early formation of 1-PhDBF and 1-PhDBT, compared to other isomers, is evident from the fact that their relative concentrations are higher in less mature samples (Fig. 4a and b). On the other hand, phenyl free radical substitution of DBF would also lead to the 1-PhDBF isomer (Southwick et al., 1961) making the products of both these processes indistinguishable.

Among the samples investigated phenyl derivatives seem to be important constituents in rocks with low or moderate organic carbon content. This suggests the importance of diagenetic/catagenetic oxidation in their formation. Intriguingly, PhDBT and PhDBF are entirely absent in organic carbon-rich samples (ranging from ca. 10 to 23% TOC) from the same outcrops, which contain high concentrations of isorenieratane derivatives (Marynowski et al., 2000). Simultaneously, these samples do not contain dibenzothiophene, dibenzofuran and their alkyl derivatives as possible precursors for PhDBFs and PhDBTs. An important role of organic matter oxidation in their formation is deduced from the fact that these compounds, especially PhDBTs, are the most abundant ones in rocks affected by hydrothermal oxidation resulting in the formation of Rote Fäule in the Kupferschiefer. Rote Fäule are hematite-rich zones, where hematite was formed at the expense of primary pyrite during late stages of the rock diagenesis (catagenesis in terms applied to organic matter; Oszcypalski, 1989). In the Rote Fäule zones the PhDBTs are among the most abundant sulphur com-

pounds (Fig. 1), only secondary to dibenzo[*b,d*]thiophene and benzonaphthothiophenes (Fig. 1a; Rospondek et al., 1998). The Rote Fäule zones are also enriched in other phenyl and naphthyl derivatives of benzo[*b*]thiophene, dibenzo[*b,d*]thiophene and the benzonaphthothiophenes. The most abundant phenylated compounds are phenylbenzo[*b*]thiophene (first reported by Püttmann et al., 1990; Rospondek, 1998), diphenylbenzo[*b*]thiophene and diphenyldibenzo[*b,d*]thiophenes (Rospondek, 1998). Interestingly, phenyldibenzothiophenes are present in hydrothermal petroleum (Table 2 and Fig. 6) generated at the sea floor spreading centre of the Guaymas Basin, Gulf of California. This petroleum was formed at an estimated temperature of  $> 300$  °C (Kawka and Simoneit, 1990; Simoneit, 1993). It contains, in addition to the most abundant dibenzothiophene, the benzonaphthothiophenes and high molecular weight aromatic thiophenes, 4-, 2- and 3-PhDBTs. In this sample 1-PhDBT was absent (Fig. 6), evidently as a result of its loss by intramolecular cyclisation. The hydrogen loss from 1-PhDBT observed in the gas phase in the mass spectrometer (Fig. 2a) obviously operates in the geosphere under thermal stress, which results in the formation of triphenyleno[1,12-*bcd*]thiophene  $M^+ \bullet 258$ . Triphenyleno[1,12-*bcd*]thiophene is present in a number of the samples investigated as revealed by co-elution with the authentic standard. Another  $M^+ \bullet 258$  compound eluting before triphenyleno[1,12-*bcd*]thiophene is present in some samples (e.g. Polkowice). This can be tentatively assigned as benzo[*b*]thiopheno[2,3,4,5-*def*]phenanthrene based on its mass spectrum. However, the presence of triphenyleno[1,12-*bcd*]furan can not be easily confirmed due to the presence of many compounds with  $m/z$  242 having similar mass spectra. Reactions analogous to the 1-PhDBT cyclisation were described for *o*-methylbiphenyl and *o*-terphenyl by Kagi et al. (1990) and by Marynowski et al. (2001), respectively. Such cyclisation was induced by clay mineral catalysis (Marynowski et al., 2001). Moreover, intramolecular introduction of an additional heteroatom can lead to the formation of benzobisbenzofurans or benzobisbenzothiophenes (Meyer zu Reckendorf, 2000). This can all proceed via suitable phenolic *p*-polyphenyl intermediates (resorcinol-type) as proposed by Pring (1973a). The benzobisbenzofurans and benzobisbenzothiophenes have been described from Kupferschiefer (Rospondek, 1998; Bechtel et al., 2001) and from the Holy Cross Mountains (Marynowski et al., 2001), although the detailed assignment of individual isomers is still needed. In many of these samples at least four benzobisbenzofuran and benzobisbenzothiophene isomers are present. The identity of only benzobisbenzo[1,2-*b*;4,5-*b'*]furan (Fig. 1a), eluting as the third isomer, can be firmly established based on co-elution with the authentic standard. The mass spectra of all

isomers are similar to each other (Pring, 1973b), and therefore useless for their closer identification.

#### 4. Conclusions

All four possible positional isomers of phenyldibenzofuran and phenyldibenzothiophene were unambiguously identified in sedimentary rocks ranging in maturity from below to within the oil window as well as in solid bitumen and hydrothermal petroleum. Their elution sequence on apolar stationary phases is 1-, 4-, 2- and 3-phenyldibenzo[*b,d*]furan, and likewise 1-, 4-, 2- and 3-phenyldibenzo[*b,d*]thiophene. The distribution of phenyldibenzothiophenes is controlled primarily by the organic matter maturity. In the most mature samples 4-, 2- and 3-PhDBT prevail over 1-PhDBT, while less mature samples contain mainly 4-PhDBT or 1-PhDBT but 2-, 3-PhDBTs occur at comparable concentrations. However, in samples of lower maturity only, exclusive of the phenyldibenzo[*b,d*]thiophene series, other structural isomers with the same molecular weight and empirical formula ( $C_{18}H_{12}S$ ) were detected. These are likely to be either phenylnaphtho[*b*]thiophenes and/or naphthylbenzo[*b*]thiophenes. In samples of lower maturity this additional series prevails over all PhDBT. With increasing maturation they disappear indicating their lower thermal stability relative to PhDBTs. This is confirmed by their absence in hydrothermal petroleum and in high temperature pyrolysis products of coals. In contrast to the maturation trends observed for the PhDBT distribution, the controls on PhDBTs distribution are unclear.

PhDBTs and PhDBTs are likely to be the intermediate products in the formation of more condensed heterocyclic polycyclic aromatic compounds like triphenyleno[1,12-*bcd*]thiophene and triphenyleno[1,12-*bcd*]furan, benzobisbenzofurans and benzobisbenzothiophenes, which are commonly detected in geological samples.

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