# Aliphatic and aromatic biomarkers from Carboniferous coal deposits at Dunbar (East Lothian, Scotland): Palaeobotanical and palaeoenvironmental significance.

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**ABSTRACT**

Carboniferous (Viséan) coals from Dunbar, East Lothian, Scotland, contain well-preserved miospore and megaspore assemblages suggesting a lycopod-dominated forest ecosystem with some ferns, sphenopsids and pteridosperms. The low rank of the coals and the well defined microflora permit assessment of the palaeoenvironmental significance of lipid biomarkers during Early Carboniferous times. Rock-Eval, petrographic, and lipid analyses indicate a fully terrestrial depositional environment. Although we also present and discuss a wide diversity of other lipid biomarkers (alkanes, hopanoids, steroids), we focus on the terrestrial-derived biomarkers. Combustion-derived PAHs pyrene, fluoranthene, benzo[a]anthracene, chrysene and triphenylene indicate the occurrence of forest fires in the study areas during Early Carboniferous times. Alkyldibenzofurans derive from lichen-biomass. Retene, cadalene, simonellite, tetrahydroretene and kaurane are poorly specific and can derive from a variety of early Palaeozoic land plants. Abietane, phyllocladane, *ent*-beyerane and 4β(H)-eudesmane, as well as bisnorsimonellite, diaromatic totarane, diaromatic sempervirane and 2-methylretene, however, as yet had only been reported from conifers, which do not appear in the fossil record until the Late Carboniferous. Within the lower Carboniferous forest ecosystem, arborescent lycopsids and pteridosperms are proposed as alternative sources for these compounds.

Keywords: land plant biomarkers; terrestrial terpenoids; combustion derived-PAH; Lower Carboniferous coals; megaspores

## 1. Introduction

Biomarkers are molecular compounds which can be extracted from crude oils, coals and all kinds of sedimentary rocks (Tissot and Welte, 1984). Biomarkers have numerous biological origins, and their occurrence can be related to a specific source, giving information of the type of fauna/flora present in the environment, or to depositional conditions, such as salinity or temperature (Peters and Moldowan, 1993). For these reasons, biomarkers are regularly used in palaeoenvironmental studies (e.g. Olcott, 2007; Eglinton and Eglinton, 2008). Recent applications of biomarkers aim at tracing the evolution of life. In archean rocks, biomarkers give information on the timing and evolution of early forms of life (e.g. Brocks et al., 1999, 2003, 2005; Ventura et al., 2007 ; Eigenbrode et al., 2008 ; Waldbauer et al., 2009), while in more recent rocks and sediments, biomarkers help determining taxonomic relationships between taxa (e.g. Arouri et al., 2000; Talyzina et al., 2000). In the last decades, chemotaxonomic applications have been particularly developed for the study of flora associated with amber and coal deposits mostly of Mesozoic to recent age (e.g. Simoneit et al., 1986; Otto et al., 1997, 2002; Bechtel et al., 2005; Stefanova et al., 2005 among others). Chemotaxonomic studies of Palaeozoic land plant

based on extractible biomarkers were developed in the 70's (Niklas, 1976a,b; Niklas and Chaloner, 1976; Niklas and Pratt, 1980) but have been relatively limited in more recent years (Schultze and Michaelis, 1990; Fleck et al., 2001; Auras et al., 2006), despite the interest of Palaeozoic plants regarding the evolution of terrestrial life.

The aim of this study is to identify and characterise aliphatic and aromatic biomarkers for Lower Carboniferous plants preserved in coals and to relate these biomarkers to specific plant taxa in order to apply chemotaxonomy to Palaeozoic land plants. Biomarker analyses were performed on four Lower Carboniferous (Viséan) coal samples from Dunbar, East Lothian, Scotland. Though megafossils are absent from these coals, their palynological content is rich and comprises abundant miospore and megaspore assemblages (Spinner, 1969; Spinner and Clayton, 1973). This gives us an opportunity to correlate the identified biomarkers with the occurrence of land plant palynomorphs and possibly to terrestrial plant groups or families.

## 2. Geological setting and previous studies

The Midland Valley of Scotland is a rift valley bounded by Highland Boundary and Southern Uplands Faults on the North and the South, respectively (Fig. 1; Murchison and Raymond, 1989; Underhill et al., 2008). This sedimentary basin evolved in response to crustal extension and especially contains Devonian to Carboniferous sediments

and some igneous rocks (Murchison and Raymond, 1989; George, 1992; Underhill et al., 2008). The Carboniferous rocks in the Midland Valley of Scotland are only well exposed along coastlines (Murchison and Raymond, 1989). Coal samples were collected from two outcrop sections located at Dunbar, East Lothian, on the east coast of southern Scotland, some 40 km East of Edinburgh (Fig. 1). These sections show a group of alternating Lower Carboniferous (Viséan) limestones, shales, sandstones and coals (Fig. 2.; Spinner, 1969; Spinner and Clayton, 1973).

SKT coal samples were collected around the bay near Skateraw Harbour, approximately 6.4 km south-east of Dunbar, whereas WS coals were taken from rock successions exposed in White Sand Bay (Fig. 1). Both localities are clearly exposed on a geological map permanently exhibited just above the shoreline. In stratigraphic order, the lower seam is located immediately above the Middle Longcraig Limestone: samples WS-2 and WS-3 (Fig. 2); the upper one (samples SKT-E and SKT-D) occurs stratigraphically below the Chapel Point Limestone (Fig. 2). WS samples are equivalent to the Longcraig coal seam described by Spinner (1969). In contrast, SKT coals are more comparable to the sample horizon SC2 detailed by Spinner and Clayton (1973). In order to investigate the possible vertical stratigraphic variations, two samples were obtained from each coal seam (Fig. 2). Accordingly, WS coals are separated by approximately 30 cm while SKT samples by 15 cm.

68 A fluvio-deltaic environment has been assigned to these
69 Carboniferous coals, which contain mainly land-plant derived organic
70 matter (George, 1992). After deposition, these shallow-water deltaic
71 deposits were mainly influenced by burial history and extensive
72 volcanic, sill and dyke activities (Murchison and Raymond, 1989).

73 The sampled outcrop successions were previously studied
74 palynologically (Spinner, 1969; Spinner and Clayton, 1973). Additional
75 palynological analyses were performed for each of the collected samples
76 for the present study. The WS coal interval is characterized by
77 abundant and well-preserved megaspores such as (Spinner, 1969):
78 *Zonalesporites fusinatus* Spinner 1969, *Lagenicula subpilosa* (Ibrahim)
79 forma *major* Dijkstra ex Chaloner 1954 and *Setosisporites* (Ibrahim)
80 Potonié and Kremp 1954 emend. Spinner 1969. Miospores are less
81 abundant in this lower interval and are dominated by the following
82 taxa: *Lycospora pusilla* (Ibrahim) Somers 1972 with *Calamospora spp.*
83 and *Densosporites* spp. (Spinner and Clayton, 1973). All megaspore
84 specimens recognized in the WS horizon (e.g. *Lagenicula subpilosa*,
85 *Setosisporites* and *Zonalesporites fusinatus*) range through the SKT coal
86 interval but *Zonalesporites* is less abundant (Spinner and Clayton,
87 1973). This upper interval also shows a notable diversity of miospores
88 represented by *Lycospora pusilla*, *Calamospora*, *Densosporites* and
89 *Cingulizonates cf. capistratus* (Hoffmeister, Staplin and Mallow) Staplin
90 and Jansonius *in* Smith and Butterworth, 1967 (Spinner and Clayton,
91 1973). Megafossils are not known from these sediments. A megaspore-

based flora reconstruction suggests that the vegetation consisted of large arborescent lycopsids with long leaves together with some diminutive forms (Spinner, 1969).

## 3. Analytical methods

### *3.1. Experimental procedures*

The four coal samples (Fig. 2) were studied by Rock-Eval pyrolysis and biomarker analysis. Rock-Eval pyrolysis was performed on 100 mg of ground rock with an Oil Show Analyser device at the University of Paris 6 (France), using the conventional temperature program described in Espitalié et al. (1986). The pyrolysis oven temperature was programmed with 25°/min from 300°C (held 3 min) to 650°C (held 3 min). However, due to the poor estimation of the total organic carbon (TOC) content of coals by Rock-Eval analysis (Espitalié et al, 1986), their TOC content was additionally determined on 100 mg of powdered decarbonated sample using a LECO carbon analyser at the same university (Paris 6, France). The hydrogen index (HI) was calculated using the Rock-Eval $S_2$ and the LECO TOC values.

For biomarker analyses, rock fragments were extracted with dichloromethane (DCM) during 24 h in the refrigerator, in order to remove possible contamination on the sample surface. After this first extraction, the rock fragments were crushed to enable extraction of the lipids preserved inside the rock. Approximately 30 g of pulverised

115 samples were extracted with a mixture of methanol (MeOH) and
116 dichloromethane (DCM) (1/2, v/v) for 24 h with extensive stirring. This
117 second extract was dried by means of roto-evaporation and partly re-
118 solubilized in cyclohexane. The cyclohexane-soluble fraction (maltenes)
119 was further separated by column chromatography.

120 The apolar fraction was recovered from the maltenes by elution
121 with cyclohexane on an activated silica column. Subsequent elution
122 with a mixture of cyclohexane - DCM (2/1, v/v) recovered the aromatic
123 fraction after which the polar fraction was recovered by elution with a
124 mixture DCM – MeOH (2/1, v/v).

125

126 *3.2. Gas chromatography – mass spectrometry (GC-MS)*

127 The aliphatic and aromatic fractions were analysed by gas
128 chromatography – mass spectrometry (GC-MS) using a ThermoFinnigan
129 Trace GC 2000 coupled to a ThermoFinnigan DSQ mass spectrometer.
130 The column used was a DB5ht (30 m length, 0.25 mm internal
131 diameter, 0.1 μm film thickness). The oven temperature was
132 programmed as follows 100 °C for 1 minute, 100 °C – 310°C at a rate of
133 4 °C/min followed by an isothermal period of 16.5 min at 310 °C.
134 Helium was used as carrier gas. The mass spectrometer was operated in
135 the EI mode at electron energy of 70 eV. Samples were analysed in full
136 scan (m/z 50 – 700; scan rate 1000 amu/s; scan speed 1.49/s, scan

time 0.67 s). The organic compounds were identified by comparison of their mass spectra and retention times with available published data.

### *3.3. Organic petrography*

Maceral analyses and random vitrinite reflectance measurements (expressed in %) were carried out on embedded grain sections of two coal samples (WS-3 and SKT-E) with a MPVIII Leica microscope using an oil immersion objective (50 X) and following the procedures described in ICCP (1975). Qualitative fluorescence analyses were also performed using a blue light.

## 4. Results

### *4.1. Bulk OM characteristics*

Bulk organic parameters obtained by Rock-Eval and LECO analyses (Table 1) show that the TOC values for these coal samples range between 60.8 and 71.9%. HI and $T_{max}$ values vary between 144 to 218 mg HC/g TOC and 423 to 428°C, respectively (Fig. 3). The average $T_{max}$ is 426 °C. Based on the constructed HI vs. $T_{max}$ diagram (Fig. 3; Espitalié et al., 1986), coal samples plot in the Type II – III kerogen region.

### *4.2. Maceral composition and vitrinite reflectance*

159 The maceral composition of the two samples is very similar (Table
160 2). The two coals are dominated by vitrinite (47-49%), mostly
161 corresponding to telocollinite (Table2; Fig. 4A). Exinite is the second
162 most abundant maceral group (24-26%). It mostly corresponds to
163 microspores and ornamental macrospores (17-20%) with a yellow to
164 yellow-brownish fluorescence, and leaf cuticles with a bright yellow
165 fluorescence (Fig. 4B). Resinous secretions presenting a bright yellow
166 fluorescence also are observed in both samples (Fig. 4C). Although
167 inertinite is the less abundant maceral, it nevertheless represents a
168 substantial fraction of the organic matter (18-20%). This maceral group
169 is dominated by semi-fusinite and fusinite. These macerals correspond
170 to plant material which is partially or totally, respectively, charred or
171 oxidized. Pyrofusinite, distinguished from fusinite by the presence of
172 devolatilisation vacuoles which indicate combustion at high
173 temperature (Fig. 4D), also is present in significant proportion (5%;
174 Table 2).

175 Vitrinite random reflectance values are 0.44% and 0.45% for SKT-
176 E and WS-3, respectively. These values show that the samples are both
177 subbituminous A coals and represent the beginning of the
178 bituminization interval.

179

180 *4.3. Aliphatic hydrocarbons*

181 *4.3.1. Total aliphatic hydrocarbons*

182 The total ion currents (TIC) of the aliphatic fractions of the coal
183 extracts (Fig. 5) are dominated by a series of *n*-alkanes ranging from $C_{13}$
184 to $C_{30}$. The distribution of *n*-alkanes is relatively similar in all four
185 samples and the most abundant are *n*-$C_{27}$ and *n*-$C_{29}$ (Fig. 6). Long chain
186 $C_{23}$ – $C_{33}$ *n*-alkanes are characterized by an odd-over-even
187 predominance with a maximum at *n*-$C_{27}$ (Fig. 6). The carbon preference
188 index (CPI) ranges between 1.65 and 1.93 (Table 1). Series of $C_{14}$ to $C_{21}$
189 acyclic isoprenoids dominated by norpristane ($C_{18}$), pristane (Pr; $C_{19}$)
190 and phytane (Ph; $C_{20}$), were also detected (Fig. 6). Pr is the most
191 abundant compound in all the samples except SKT-D, where the *n*-$C_{27}$
192 alkane is more abundant (Fig. 5). The Pr/Ph ranges from 7.33 to 14.67
193 (Table 1). The Pr/*n*-$C_{17}$ is more than 1, whereas the Ph/*n*-$C_{18}$ is inferior
194 to 1 (Table 1; Fig. 7). Branched alkanes without odd or even chain
195 length predominance were also recognized in low abundance (Fig. 6).
196 Steranes, hopanes, bicyclic alkanes and several diterpanoids were
197 clearly detected in the aliphatic fractions (Fig. 5).

198

199 *4.3.2. Hopanoids*

200 Series of αβ-hopanes were detected in all the samples by
201 monitoring the *m/z* 191 ion (Fig. 8). These compounds are dominated
202 by 17α(H),21β(H)-hopanes (22R and 22S epimers) from $C_{27}$ to $C_{33}$, with
203 a maximum at $C_{29}$ or $C_{30}$ hopanes (Fig. 8).

Series of βα-moretanes (17β(H),21α(H)-moretanes) were also detected ranging from $C_{27}$ to $C_{32}$, with a maximum at $C_{30}$ (Fig. 8). $C_{29}$ ββ-hopane was present in all the samples (Fig. 8). Tricyclic terpanes and gammacerane were not observed.

*4.3.3. Steroids*

Steranes and diasteranes were detected in all the samples using the characteristic fragment at *m/z* 217 (Fig. 9). Steranes are more abundant than diasteranes and the distribution of these compounds is similar in all the samples (Fig. 9). Steranes are dominated by the $C_{29}$ 5α(H),14α(H),17α(H)-20R regular sterane ($C_{29}$ ααα-sterane; Fig. 9 and 10), followed by an important contribution of the αββ isomer (Fig. 9). Diasteranes are dominated by $C_{29}$ βα-diasteranes. However, series of $C_{27}$ to $C_{29}$ αβ-diasteranes and $C_{27}$ to $C_{29}$ αββ-steranes were also recognized in all the samples (Fig. 9). Additionally, short chain steroids were also detected in low amounts. SKT coals show a marked contribution of short chain $C_{19}$ - $C_{20}$ steroids in comparison with WS samples (Fig. 9).

*4.3.4. Bicyclic alkanes*

Seventeen bicyclic alkanes ranging from $C_{14}$ to $C_{16}$ carbon atoms have been identified in the aliphatic extracts of the Scottish coals, using

226 the expanded *m/z* 109 + 123 + 179 + 193 fragmentograms (Fig. 11).
227 Peak assignments for the identified bicyclic alkanes are summarized in
228 Table 3. Based on comparisons with the previously reported mass
229 spectra and the retention times, 4β(H)-eudesmane; 8β(H)-drimane;
230 8β(H)- and 8α(H)-homodrimanes were clearly detected (Fig. 11; Noble,
231 1986; Noble et al., 1987). These compounds are not present as the
232 major constituents of the aliphatic fractions (Fig. 5); however, they have
233 been found in relative significant proportion (Fig. 11). Most of other
234 identified bicyclic alkanes have been previously observed in coal
235 extracts (Noble, 1986; Noble et al., 1987).

236 The distribution of bicyclic alkanes is relatively similar in all four
237 coals and the most abundant are $C_{14}$ bicyclic alkanes (Fig. 11; e.g.
238 Peaks b and c). 8β(H)-homodrimane (Fig. 11; Peak p) is present in
239 significant proportion in most samples except SKT-D, while the relative
240 abundance of peak h allows differentiate WS coals from SKT samples.
241 The relative abundance of 4β(H)-eudesmane and 8β(H)-drimane is
242 similar in all samples (Fig. 11; Peaks i and k; respectively).

243

244 *4.3.5. Tricyclic and tetracyclic diterpenoids*

245 The partial *m/z* 109 + 123 + 193 + 233 fragmentograms from the
246 aliphatic fractions of Lower Carboniferous coals reveal the presence of
247 eighteen tricyclic and tetracyclic diterpenoid hydrocarbons (Fig. 12).
248 Peak assignments for identified aliphatic diterpenoids are shown in

249 Table 4. The tetracyclic diterpenoids ($C_{20}H_{34}$) *ent*-beyerane (Peak XII),
250 16β(H)-phyllocladane (Peak XIII), *ent*-16α(H)-kaurane (Peak XV), 16α(H)-
251 phyllocladane (Peak XVI) and *ent*-16β(H)-kaurane (Peak XVII) were
252 mainly recognized, by comparison with the published mass spectra of
253 authentic compounds (Noble, 1986; Otto et al., 1997; also in Noble et
254 al., 1985; Philp, 1985; Schulze and Michaelis, 1990).

255 The peak labelled II has a mass spectrum characterized by a
256 strong fragment at *m/z* 233 (Fig. 12A). Based on its fragmentation
257 pattern, compound II was tentatively identified as a $C_{18}$ tricyclic
258 hydrocarbon (Fig. 12). This latter compound is particularly abundant in
259 SKT samples, as are $C_{19}$ and $C_{20}$ steranes, it could therefore be related
260 to short chain steroids. To our knowledge, the molecular structures for
261 most of the $C_{18}$ – $C_{19}$ diterpenoids identified in this study, have not been
262 previously established (see mass spectra in the appendix).

263 In most samples, the tetracyclic diterpenoid distribution is
264 dominated by kaurane and phyllocladane. Kaurane isomers, however,
265 are slightly more abundant in SKT samples while phyllocladanes are
266 more predominant in WS coals (Fig. 12). *ent*-Beyarane shows a
267 relatively similar contribution in all samples, and generally is present in
268 low amounts in comparison to the other $C_{20}$ diterpenoids.

269 The only tricyclic diterpenoid identified is abietane (Peak XIV; Fig.
270 12). It is present in relatively low abundance in all four samples. Its
271 contribution is however more significant in WS coals (Fig. 12).

317 proportion of 2-MA (Fig. 17). Although 9-MP is the most predominant
318 methylphenanthrene in all the samples, 2-MP and 3-MP are also
319 observed and are relatively present in similar proportions (Fig. 17). The
320 alkylphenanthrene indices (MPR, MPI 1 and MPI 2) are also given in
321 Table 6. Figure 18 displays a partial m/z 206 mass fragmentograms
322 showing the distribution of ethylphenanthrene (EP) and
323 dimethylphenanthrene (DMP) isomers in the aromatic fractions of
324 Scottish coals. Pimanthrene (1,7-DMP) is present in relatively high
325 amounts in all the samples. Actually, it is the most abundant
326 compound in SKT-D sample (Fig. 18).

327 Dibenzofuran (DBF) and its methyl derivatives (MDBF) were also
328 detected in the aromatic fractions (Fig. 13; Peaks 18, 29, 30 and 31,
329 respectively). The distribution of MDBF is dominated by 2-MDBF (Peak
330 30) and 4-MDBF (Peak 29). The latter is the most thermodynamically
331 stable isomer (Fig. 13; Radke et al., 2000). Several aromatic compounds
332 with methylated-tetrahydronaphthalene skeletons (Fig. 13; Table 4)
333 were also determined. Accordingly, ionene (1,2,3,4-tetrahydro-1,1,6-
334 trimethylnaphthalene) and 1,2,3,4-tetrahydro-6-(1,1-dimethyl)-
335 naphthalene were clearly identified (Fig. 13; Peaks 4 and 17,
336 respectively). Finally, series of $C_{17}$ to $C_{19}$ isohexylalkylnaphthalenes
337 have been also observed (Fig. 19). The contribution of the
338 isohexylalkylnaphthalene (iHMN) compounds is relatively similar in all
four samples and the most abundant is $C_{17}$ iHMN except SKT-D, where

341

342 *4.4.3. The land plant- and combustion-derived polycyclic aromatic*
343 *hydrocarbons*

344 Among the polycyclic aromatic hydrocarbons (PAHs), two
345 particular groups have been recognized in these Scottish coals (Fig. 13;
346 Table 5). The first one includes the land-plant-derived PAHs retene (87),
347 cadalene (33), simonellite (74), bisnorsimonellite (57), tetrahydroretene
348 (70), diaromatic totarane (76), diaromatic sempervirane (90) and 2-
349 methylretene (94) whereas the second group comprises the combustion-
350 derived PAHs pyrene (75), fluoranthene (71), benzo[a]anthracene (96),
351 chrysene and triphenylene (97) (Fig. 13; Philp, 1985; Ellis et al., 1996,
352 Otto et al., 1997; Jiang et al., 1998 and references therein; van Aarssen
353 et al., 2000; Otto and Simoneit, 2001; Bastow et al., 2001, Tuo and
354 Philp, 2005).

355 Simonellite (74), diaromatic totarane (76) and diaromatic
356 sempervirane (90) (see also the expanded *m/z* 237 chromatograms; Fig.
357 20) were clearly identified by their mass spectra but the elution pattern
358 slightly differs from one presented in Tuo and Philp (2005). Following
359 the same principles as by Tuo and Philp (2005), another family of
360 diaromatic tricyclic hydrocarbons was detected in the aromatic fractions
361 (Fig. 20). These new, supposedly also diaromatic hydrocarbons ($Tre^1$
362 and $Tre^2$) have very similar mass spectra to tetrahydroretene, exhibiting
363 a base peak at *m/z* 223 and a molecular ion at *m/z* 238 (Fig. 20). Based

364 on their mass spectra and elution times, comparison with the
365 distribution of the established diaromatic tricyclic hydrocarbons
366 simonellite, diaromatic totarane and diaromatic sempervirane (Otto et
367 al., 1997; Otto and Simoneit, 2001; Tuo and Philp, 2005), and the
368 identification of diaromatic totarane and sempervirane in our coals,
369 these compounds were tentatively identified as tetrahydroretene
370 isomers, based on the totarane and sempervirane skeletons,
371 respectively. Compound Tre$^1$ could be the 1-methyl-1,2,3,4-tetrahydro-
372 8-isopropylphenanthrene (totarane-derived) and Tre$^2$ the 1-methyl-
373 1,2,3,4-tetrahydro-6-isopropylphenanthrene (sempervirane-derived; Fig.
374 20). Their molecular structures are also proposed in Figure 20.

375

376 **5. Discussion**

377 *5.1. Thermal maturity*

378 According to LECO results, the TOC values for these Scottish
379 samples are typical for coals (60.8 and 71.9%; Table 1). Based on such
380 values of TOC, the average $T_{max}$ (426 °C) from Rock-Eval analyses, as
381 well as the vitrinite reflectance (0.45 %), the rank of the studied coals is
382 of subbituminous A, i.e. an immature stage of thermal evolution (Fig. 3).
383 This interpretation is supported by molecular thermal maturity
384 indicators from the aliphatic and aromatic fractions. First, the CPI is
385 high (>1) due to odd predominance (Table 1; Bray and Evans, 1961).
386 Second, the thermally unstable $C_{29}$ ββ hopane is observed in all samples

(Fig. 8; Seifert and Moldowan, 1980). Third, the high thermal maturity markers in sediments 18α-22,29,30-trisnorneohopane (Ts) and αββ-steranes (Fig. 9) are absent or very low in abundance (Seifert and Moldowan, 1978, 1986). This is further attested by the aromatic hydrocarbon distribution of MN, EN, DMN, TMN, TeMN and MP isomers again indicating that the coals are immature (Table 6; Radke et al., 1982, 1986; Alexander et al., 1985; van Aarssen et al., 1999). For instance, the TeMN compounds show the predominance of 1,2,5,6- and 1,2,3,5-TeMN over the 1,3,6,7-TeMN (Fig. 16; van Aarssen et al., 1999). The distribution of methyl- and ethyl-naphthalene homologues with 2-MN and 2-EN dominating is typical for immature samples (Fig. 14; Table 6; Radke et al, 1982). The alkylphenanthrenes 9-MP and 1-MP are highly abundant, with 9-MP being predominant (Fig. 17) is another feature of immature samples (Radke et al., 1982). It is interesting to note, however, that depending on the maturity index either WS or SKT samples may be considered to be the more mature. WS samples are more mature with DNR, TNR1 and TNR2 while SKT samples are more mature with TMNr, TeMNr, MPI 1 and MPI 2 (Table 6). This feature probably reflects the control exerted by the source of the organic matter and depositional environment on these compounds at low maturity degree.

*5.2. Biomarker distributions and palaeoenvironmental conditions*

Like most coals, the investigated ones are typically terrestrial. This is evidenced by petrographic examination (Table 2, Fig. 4), palynology (Spinner, 1969; Spinner and Clayton, 1973), and biomarker distributions. In addition to the typical odd numbered long-chain *n*-alkanes (Eglinton and Hamilton, 1967), several aliphatic and aromatic compounds generally used as terrestrial biomarkers have been detected in our Carboniferous coals (Table 7).

The Carboniferous sedimentary rocks in the Midland Valley of Scotland consist of cyclical sequences of coals, oil shales, limestones, shales, mudstones, siltstones and sandstones (Murchison and Raymond, 1989; George, 1992). Coals are usually deposited in swampy terrestrial environments such as deltas and regions with poor drainage. Accordingly, a variety of depositional environments, all relatively shallow-water and predominantly deltaic, has been assigned to these Carboniferous rocks (Murchison and Raymond, 1989). In the case of a deltaic environment (such as in our case) marine intrusions may occur which may be evidenced by means of palynomorphs and lipid biomarkers. Since organic particles of marine origin, i.e. alginite and marine palynomorphs, and marine biomarkers (e.g. cheilantanes) are absent, the (low proportion of) short chain *n*-alkanes in our coals (Fig. 6) must be considered to be of bacterial rather than marine origin.

Other arguments for a purely terrestrial depositional environment are the high Pr/Ph (Table 1) and Pr/*n*-$C_{17}$ vs. Ph/*n*-$C_{18}$ ratios (Fig. 7; Hunt, 1995). These ratios characterize the Scottish coals as Type III OM

434 which is usually derived from terrestrial plants (Peters and Moldowan,
435 1993) deposited under oxidizing conditions, and in particular, the WS
436 coal level (Fig. 7).
437 A bacterial contribution to the OM is further evidenced by the
438 occurrence of branched alkanes (Fig. 6; e.g. Shiea et al., 1990),
439 hopanoids (Figs. 5 and 8; Ourisson et al., 1979) and bicyclic alkanes of
440 the drimane and homodrimane series (Fig. 11; Noble, 1986; Noble et al.,
441 1987). Aromatic hydrocarbons often associated to a microbial source
442 include 1,2,3,5,6-pentamethylnaphthalene (1,2,3,5,6-PMN; Fig. 13;
443 Table 5; Bastow et al., 1998) and 1,3,6,7-tetramethylnaphthalene
444 (1,3,6,7-TeMN; Fig.16; e.g. Jiang et al., 1998).
445 Steroids have also been used to differentiate depositional settings
446 (Peters et al., 2005). Huang and Meinschein (1979) proposed a useful
447 ternary diagram to identify the source of the OM which can be
448 constructed by the distribution of $C_{27}$, $C_{28}$ and $C_{29}$ sterols (Fig. 10).
449 Based on their results, the dominant source of $C_{27}$ sterols is
450 zooplankton, $C_{28}$ sterols are generally components of phytoplankton and
451 $C_{29}$ sterols are mainly derived from terrestrial plants. There are many
452 exceptions on these rules; for instance, $C_{29}$ sterols are also found in
453 marine diatoms and dinoflagellates (e.g. Rampen et al., 2010).
454 Nevertheless, the method seemed reliable for other Palaeozoic (Middle
455 Devonian) coals which have a high predominance of $C_{29}$ steranes (e.g.
456 Fowler et al., 1991; Kashirtsev et al., 2010). Considering this, the
457 dominance of $C_{29}$ relative to $C_{27}$ steranes in these coals further

458 evidences their terrestrial origin (Table 1; Fig. 9). Consistent with the
459 shallow-water environment proposed for Scottish coals (Murchison and
460 Raymond, 1989), the steroids plot in a transitional estuarine-bay
461 environment (Fig. 10). It is interesting to note that short chain $C_{19}$ - $C_{20}$
462 steroids are abundant in SKT coals (Fig. 9). Although these compounds
463 are not commonly described from coals, they have been reported in a
464 Devonian liptobiolith (Kashirtsev et al., 2010). The relative abundance of
465 these $C_{19}$ - $C_{20}$ steroids may be characteristic for some primitive coals,
466 suggesting that they could be more specific biomarkers of early plants.
467 The occurrence of the combustion-derived PAHs pyrene,
468 fluoranthene, benzo[a]anthracene, chrysene and triphenylene (Fig. 13)
469 can be related to the significant presence of the fusinite group, most
470 particularly pyrofusinite, in the organic matter. Charred or fusinized
471 plant debris have been frequently reported in coals from the Midland
472 Valley of Scotland (Murchison and Raymond, 1989; Scott and Jones,
473 1994; Falcon-Lang, 2000) and combustion-derived PAHs have been
474 observed in coal extracts (Murchison and Raymond, 1989). These
475 compounds and macerals testify that fire events took place
476 contemporarily with coal deposition. Fire events in coals are often
477 related to lightning, but in the case of the Midland Valley of Scotland,
478 volcanic activity also appears as a major cause of wildfires (Murchison
479 and Raymond, 1989; Scott and Jones, 1994; Falcon-Lang, 2000).
480
481 *5.3. Linking biomarkers, palynology and palaeobotany*

On the basis of the diverse palynomorph assemblages described by Spinner (1969) and Spinner and Clayton (1973), a relatively detailed reconstruction of the flora giving rise to the SKT and WS coals can be provided, though more details are available for SKT coals than for WS coals. In WS coals, megaspores are dominated by *Zonalesporites* and/or *Setosisporites*, followed by *Lagenicula* (Spinner, 1969). *Cystosporites* are also present in minor proportion. In SKT coal, dominant megaspores are *Lagenicula* and *Setosisporites* followed by ?*Bacutriletes* and *Zonalesporites* (Spinner and Clayton, 1973). Miospores assemblages are generally dominated by *Lycospora*, *Calamospora* and *Densosporites* (Spinner and Clayton, 1973). *Cingulizonates* miospores should also be abundant in SKT coal. The megaspore *Zonalesporites* as well as the miospores *Densosporites* and *Cingulizonates* were mostly produced by *Bodeodendron*/*Sporangiostrobus* (recently identified as equivalent to *Omphalophloios*) which was a sub-arborescent lycopsid belonging to the Isoetales group (Wagner, 1989; Taylor et al., 2009; Opluštil et al., 2010). *Bacutriletes* miospores were produced by herbaceous and sub-arborescent lycopsids among which *Bodeodendron*/*Sporangiostrobus* (Eble, 1996). *Setosisporites* megaspores mainly derived from *Bothrodendron* (e.g. Phillips, 1979). *Lagenicula* megaspores and some *Lycospora* miospores were produced by *Paralycopodites* (also known as *Anabathra*; DiMichele and Phillips, 1994). Finally, *Cystosporites* megaspores and some *Lycospora* miospores were produced by *Lepidodendron* (DiMichele and Phillips, 1994). *Bothrodendron*,

506 *Paralycopodites* and *Lepidodendron* were arborescent lycopsids and
507 belonged to the Lepidodendrales group (Taylor et al., 2009). It must be
508 noted that these different plants are mostly documented from the Late
509 Carboniferous and afterwards, though the corresponding spores
510 appeared earlier, sometimes in the Devonian (Glasspool et al., 2000;
511 Opluštil et al., 2010). The plants from which these spores derived in
512 Viséan coals are not firmly identified, but it is highly probable that they
513 correspond to several groups or families of lycopsids (Glasspool et al.,
514 2000), in particular to Isoetales and Lepidodendrales which already
515 existed during the Viséan (Taylor et al., 2009). Accordingly, though the
516 same lycopsids were present in both coal levels, WS coals vegetation is
517 marked by a higher contribution of Isoetales (*Bodeodendron*-like) while
518 Lepidodendrales, and in particular *Paralycopodites*-like plants, were
519 more abundant in the vegetation of SKT coals. In addition to these
520 dominant plants, the miospore assemblages (Spinner and Clayton,
521 1973) document the presence of a notable contribution of *Calamites*
522 sphenopsids and of small ferns, in particular Botryopteridaceae and
523 Zygopteridaceae. Marattialean tree ferns and the arborescent lycopsid
524 Sigillariaceae are also indicated, as well as Lyginopteridacean
525 pteridosperms documented by the presence of the spore *Schulzospora*
526 (Spinner and Clayton, 1973). Lycopsids were abundant spore producers
527 (DiMichele and Phillips, 1994) and the abundance of spores observed in
528 the organic matter (Table 2; Fig. 4) supports a significant contribution
529 of lycopsids to our Scottish coals. By its diversity and dominance of

530 lycopsids, this floral assemblage appears relatively comparable to the
531 anatomically preserved floras of Glenarbuck and Pettycur in Scotland
532 (Scott et al., 1984), which are of Viséan age but slightly older than our
533 studied coals. It is notable that although there are some Viséan records
534 of *Cordaites* (e.g. Wang, 1998), *Cordaites* remains were not reported
535 from Glenarbuck and Pettycur (Scott et al., 1984) nor Cordaite spores
536 (e.g. *Florinites*) in the palynofacies from our Scottish coals (Spinner,
537 1969; Spinner and Clayton, 1973).
538 The relatively similar lycopsid-dominated floras observed in SKT
539 and WS coals (Spinner, 1969; Spinner and Clayton, 1973) are
540 consistent with the relatively similar biomarker content observed in
541 both coals. Some aromatic biomarkers detected in this study can be
542 related to specific plant taxa (Table 7). For instance, the presence of
543 alkyldibenzofurans (MDBFs) indicates lichen input (Fig. 13; Radke et
544 al., 2000). Although lichen fossils or specific lichen spores have not
545 been reported in Scottish coals (Spinner, 1969; Spinner and Clayton,
546 1973), it can be safely assumed that Euramerican Coal Measure forests
547 were a good potential habitat for lichens. Among the less specific
548 biomarkers, the detected combustion-derived PAHs cannot be
549 associated to specific kind of plants (Oros and Simoneit 2000a,b; Oros
550 et al. 2006; Iinuma et al., 2007). It is also the case for 1,6-
551 dimethylnaphthalene (1,6-DMN; Fig. 14), 1,2,5-trimethylnaphthalene
552 (1,2,5-TMN; Fig. 15), pimanthrene (1,7-DMP; Fig. 16) and cadalene,
553 which can be produced by aromatization of several different terpenoid

554 structures and/or which precursors are widespread among terrestrial
555 plants (Table 7). Ionene is a degradation product of β-carotene (Day and
556 Erdman, 1963). It is often observed in coal extracts (e.g. Wang and
557 Simoneit, 1990), but also can be produced from thermal degradation of
558 marine and lacustrine sediments (Day and Erdman, 1963; Achari et al.,
559 1973). 4β(H)-eudesmane is another non-specific land plant biomarker.
560 This compound has been rarely observed in Palaeozoic coals (del Río et
561 al., 1994; Dzou et al., 1995) and is considered to derive from evolved
562 land plants such as angiosperms and gymnosperms (e.g. conifers;
563 Noble, 1986). However, bicyclic alkanes with an eudesmane skeleton
564 have been also identified in recent bryophytes (Asakawa, 2004). Its
565 oldest reported occurrence in sediments, to our knowledge, is Middle
566 Pennsylvanian (Dzou et al., 1995).
567 The diterpenoids *ent*-beyerane, abietane, *ent*-kaurane and
568 phyllocladane have been previously described in Carboniferous (e.g.
569 Schulze and Michaelis, 1990; Fleck et al., 2001; among others) and
570 Permian coals (e.g. Noble, 1986; Noble et al., 1985). Abietane precursors
571 occur in all conifer families (Otto and Wilde, 2001; Cox et al., 2007) and
572 this compound has been recently described in the pyrolysate of Late
573 Carboniferous amber (Bray and Anderson, 2009). Kaurane skeletons
574 have been observed in different kinds of plants, and in particular
575 bryophytes (e.g. Noble, 1986; Chopra and Kumra, 1988; Asakawa,
576 2004). The occurrence of this component in very early terrestrial OM
577 (e.g. Sheng et al., 1992; Disnar and Harouna, 1994; Kashirtsev et al,

578 2010; Romero Sarmiento et al., 2010) can be therefore related to
579 bryophytes, which represent the earliest land plants. Phyllocladane and
580 *ent*-beyerane have been mostly associated to all conifer families except
581 Pinaceae (e.g. Noble, 1986; Schulze and Michaelis, 1990; among
582 others). However, the oldest recorded occurrences of phyllocladane and
583 *ent*-beyerane are Serpukhovian (Fabianska et al., 2003; Izart et al.,
584 2006) and Middle Devonian (Sheng et al. 1992; Kashirtsev et al., 2010),
585 respectively. The occurrence of these compounds in Carboniferous
586 sediments that predated the evolution of conifers has been related to
587 the Voltziales (e.g. Schulze and Michaelis, 1990) and/or the close
588 relatives *Cordaites* (e.g. Disnar and Harouna, 1994 and references
589 therein), while in Devonian coals, these compounds were related to
590 pteridophytes (Sheng et al. 1992).
591 The relative abundance of tricyclic and tetracyclic diterpenoids in
592 coals is affected by the palaeobotanical and palaeoenvironmental
593 conditions and consequently, by the available type of vegetation (e.g.
594 Schulze and Michaelis, 1990; Fleck et al., 2001). In Permian coals, the
595 dominance of tetracyclic diterpenoids, and in particular phyllocladane
596 and kaurane isomers has been related to the pteridosperm *Glossopteris*,
597 while a predominance of tricyclic terpanes (e.g. isopimarane, rimuane,
598 fichtellite) can particularly indicate a Medullosan pteridosperm input
599 (Noble, 1986). A predominance of kaurane has been also observed in
600 Late Carboniferous rocks (Fabianska et al., 2003) whereas

601 phyllocladane isomers are more predominant in Lower Carboniferous
602 rocks (Viséan; Disnar and Harouna, 1994).
603 Following the observations of Noble (1986), the abundance of
604 tetracyclic phyllocladanes and kauranes compared to the tricyclic
605 abietane in our coals (Fig. 12) would point to a contribution of non-
606 Medullosan pteridosperms. This is consistent with the spore content of
607 these coals (Spinner and Clayton, 1973), and the described megaflora of
608 Glenarbuck and Pettycur (Scott et al., 1984). In addition, the
609 abundance of *ent*-beyerane compared to *ent*-kaurane has been linked to
610 a considerable contribution of *Cordaites* in late Carboniferous coals
611 from France and Germany (e.g. Schulze and Michaelis, 1990; Vliex et
612 al., 1994; Fleck et al., 2001; Auras et al., 2006). According to these
613 previous studies, the low abundance of *ent*-beyerane in the Scottish
614 coals can therefore indicate the absence of *Cordaites* input. This agrees
615 with an absence of *Cordaites* contribution in the palynological record
616 (Spinner, 1969; Spinner and Clayton, 1973; Scott et al., 1984), and the
617 absence of the arborane/fernane derivatives MATH, MAPH DAPH1 and
618 DAPH2 which have been recently suggested to be of *Cordaites* origin
619 (Auras et al., 2006).
620 Similarly, abietane, retene, tetrahydroretene, bisnorsimonellite and
621 simonellite (Figs. 13 and 20) have been widely accepted as conifer
622 biomarkers (van Aarssen et al., 2000; Hautevelle et al., 2006). Actually,
623 abietic acid, the major constituent of conifer resin, has been often
624 considered as the biological precursor for retene and its related

625 aromatic compounds (van Aarssen et al., 2000; Hautevelle et al., 2006).
626 However, most of these compounds, except abietane and
627 bisnorsimonellite, have been recently identified in upper Silurian to
628 lower Devonian sediments and are supposedly associated with early
629 Palaeozoic bryophytes (Romero-Sarmiento et al., 2010). Following Ellis
630 et al. (1996), the higher abundance of alkylphenanthrene compounds
631 compared to isohexylalkylnaphthalenes in the Scottish coals (Fig 13
632 and 19) could indicate a resin acid source. The presence of resinite
633 macerals in both analysed samples (Fig. 4), though in low abundance,
634 gives support to this interpretation. The hypothesis that abietic acid
635 synthesis had already evolved in early land plants, prior to the
636 emergence of true conifers (Romero Sarmiento et al., 2010) gains
637 therefore support with this observation. Similarly, Bray and Anderson
638 (2009) concluded that biosynthetic mechanisms specific to angiosperms
639 had already appeared in the Late Carboniferous, far before the
640 emergence of true angiosperms. 2-Methylretene is commonly associated
641 with retene; it is only known from Permian and younger sediments and
642 considered a conifer biomarker (Bastow et al., 2001). The diaromatic
643 tricyclic totarane and sempervirane also typically co-occur with retene
644 and related hydrocarbons. These biomarkers typically derive from a
645 restricted number of conifer families: mostly Podocarpaceae and
646 Cupressaceae (Otto and Wilde, 2001; Cox et al., 2007), though the
647 totarane skeleton has been also observed in some angiosperms (e.g.

Pinto et al, 1995; Clarkson et al., 2003) and a bryophyte (e.g. Wu and Jong, 2001).

In summary, most of the aliphatic and aromatic terrestrial biomarkers observed in the Scottish coals have been related to conifer families (Table 6). The oldest report of conifer megafossils is in the Late Carboniferous (Westphalian B/Late Bashkirian; Scott, 1974) and the oldest occurrence of conifer-related saccate pollens is Early Bashkirian (Zhou, 1994), so that our coals predate the evolution of conifers. Other precursor(s) must therefore be proposed to explain the presence of "conifer biomarkers" in the Viséan Scottish coals. *Cordaite*s are closely related to conifers and have been previously proposed as a source of supposedly typical conifer biomarkers (e.g. Disnar and Harouna, 1994). However, no data support the presence of *Cordaites* in the flora that contributed to our Scottish coals. An alternative origin for these compounds therefore must be found within the Viséan Scottish flora which was dominated by arborescent or sub-arborescent lycopsids (Lepidodendrales and Isoetales) with a contribution from ferns, sphenopsids and lyginopteridacean pteridosperms. Most of these groups of plants are extinct (Taylor et al., 2009), so that direct comparison with present-day plants is not possible. Pteridosperms are the closest relatives to conifers identified in the Scottish Viséan coals (Taylor et al., 2009), and therefore could have provided the "conifer biomarkers". From the palynological content, pteridosperms were not dominant in the flora of the studied coals (Spinner, 1969; Spinner and Clayton,

672 1973); a palynological bias is possible, so that pteridosperm biomass
673 would be underestimated in the palynological content (e.g. Phillips et
674 al., 1985; Dimitrova et al., 2005). Pteridosperms, in particular,
675 produced resin (Taylor et al., 2009) and could be at the origin of the
676 resinous secretions observed in our coal samples (Fig. 4C).
677 Lyginopteridacean pteridosperms probably appeared in the latest
678 Devonian (Taylor et al., 2009) but were preceded in the Middle Devonian
679 by progymnosperms, which could therefore be considered for the origin
680 of the "conifer biomarkers" observed in middle Devonian coals (Sheng et
681 al. 1992; Kashirtsev et al., 2010). Progymnosperms, however, were
682 neither described in Chinese nor in Russian Middle Devonian coals
683 (Volkova, 1994; Yi et al., 2007). An alternative source for the "conifer
684 biomarkers" are the arborescent lycopsids (Lepidodendrales) since
685 palynologically, these plants dominated the Scottish flora (Spinner,
686 1969; Spinner and Clayton, 1973). Lepidodendrales already existed
687 during the Devonian (Taylor et al., 2009) and a recent palaeobotanical
688 study showed that the Middle Devonian Chinese coals were dominated
689 by Lepidodendrales and Protolepidodendrales (Yi et al., 2007). From
690 these observations, arborescent lycopsids appear as another likely
691 source for the so-called typical conifer biomarkers.
692
693 **6. Conclusions**
694 Numerous land-plant biomarkers have been identified in the
695 aliphatic and aromatic fraction of the extracts of Early Carboniferous

696 coals from Scotland. Among these compounds, several have been
697 classically considered to be conifer-derived. However, micro and
698 macrofossil evidence for conifers does not go further back than the
699 Upper Carboniferous while palynological and palaeobotanical data
700 indicate that these coals mainly derive from arborescent lycopsid
701 (Lepidodendrales)-dominated forest. This discrepancy between the lipid
702 and other fossil records leads to the following hypotheses:

703 1. Conifers had evolved already in the Early Carboniferous and this
704 has now been evidenced with lipids.
705 2. The metabolic pathways giving rise to the observed biomarkers
706 had evolved already in the Early Carboniferous in plants which
707 are related to the conifers.
708 3. The identified biomarkers are derived from terrestrial plants
709 which are not closely related to the conifers. This implies the
710 evolution of a separate, possibly extinct, or as yet unidentified
711 metabolic pathway for these and associated products.

712 An argument for hypothesis 3 is that retene, simonellite and
713 tetrahydroretene – which are generally related to conifers – could also
714 derive from the degradation of kaurane-type compounds synthesised by
715 the early bryophytes. The Lower Carboniferous Scottish coals can be
716 related to a flora dominated by arborescent lycopsids in conjunction
717 with some ferns, sphenopsids and pteridosperms. Among these plants
718 which are presently extinct, pteridosperms, which are relatively closely
719 related to conifers, and arborescent lycopsids, which are not related to

720 conifers, appear as the best possible sources for the “typical conifer”
721 biomarkers. Therefore hypotheses 2 and 3 seem the most likely at
722 present.
723
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744

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1092

**Figure captions**

**Fig. 1.** Simplified geologic map showing the outcrop sample positions at Dunbar (White Sand and Skateraw Bays) in the Midland Valley of Scotland (modified from Spinner and Clayton, 1973; Underhill et al., 2008).

**Fig. 2.** The outcrop geological succession showing alternating Carboniferous limestones, shales, sandstones and coals (modified from Spinner and Clayton, 1973).

**Fig. 3.** Plot of HI vs. $T_{max}$ values for Scottish coals (diagram from Espitalié et al., 1986).

**Fig. 4.** Photomicrographs of macerals. A) WS-3, reflected natural light. Vitrinite particles : telocollinite (Vt) and desmocollinite (Vd). B) Same zone as A, blue light fluorescence emphasizing exinite particles: fluorescing spores (S) and cuticles (C). C) SKT-E, blue light fluorescence. Exinite particles: fluorescing spores (S) and resinite (R) filling conducting canals in a vitrinite particle. D) WS-3, reflected natural light. Pyrofusinite (P) and spores (S) in a vitrinite (V) groundmass.

**Fig. 5.** Total ion current chromatograms of the aliphatic fraction from coal extracts. Numbers above symbols denote to carbon number of *n*-alkane

**Fig. 6.** Mass chromatograms *m/z* 57 of aliphatic fractions from coal samples, showing the distribution of *n*-alkanes, isoprenoids and branched alkanes. Numbers above symbols indicate carbon number.

**Fig. 7.** Plot of Pr/*n*-$C_{17}$ vs. Ph/*n*-$C_{18}$ for Scottish coals (diagram from Hunt, 1995).

**Fig. 8.** Mass chromatograms *m/z* 191 of aliphatic fractions from coal samples, showing the distribution of hopanes and moretanes. Numbers above symbols indicate carbon number. The molecular structure represents the standard hopane skeleton.

**Fig. 9.** Mass chromatograms *m/z* 217 of aliphatic fractions from coal samples, showing the distribution of steroids. Numbers above symbols indicate carbon number.

**Fig. 10.** Steroids ternary plot. The contributions of $C_{27}$, $C_{28}$ and $C_{29}$ steranes were calculated using the peak height of ααα (20R) and αββ (20S) isomers on *m/z* 217 fragmentograms. Paleoenvironmental and source interpretation from Huang and Meinschein (1979).

**Fig. 11.** Partial *m/z* 109 + 123 + 179 + 193 mass fragmentograms showing the distribution of bicyclic alkanes (+) in the extracts of Scottish coals. Peak assignments in Table 3. Numbers denote carbon number.

**Fig. 12.** Partial *m/z* 109 + 123 + 193 + 233 mass fragmentograms showing the distribution of diterpenoid hydrocarbons (o) in the extracts of Scottish coals. Peak assignments in Table 4. Numbers denote carbon number. (A) Mass spectrum of compound identified as $C_{18}$ tricyclic hydrocarbon (Peak II).

**Fig. 13.** Total ion current chromatograms of aromatic fraction from extracts of two selected coal samples. Peak assignments in Table 5 Abbreviations: MN – methylnaphthalene; EN + DMN – ethyl- and dimethylnaphthalene; DBF – dibenzofuran; TMN – trimethylnaphthalene; MDBF – methyldibenzofuran; TeMN – tetramethylnaphthalene; DMDBF – dimethyldibenzofuran; P – phenanthrene; PMN – pentamethylnaphthalene; MP – methylphenanthrene; EP + DMP – ethyl– and dimethylphenanthrene; PAHs – polycyclic aromatic hydrocarbons; X – contaminant (polysiloxanes).

**Fig. 14.** Partial *m/z* 142+156 mass fragmentograms showing the distribution of methyl-; ethyl- and dimethylnaphthalene isomers in the aromatic fractions of Scottish coals. Abbreviations: MN – methylnaphthalene; EN – ethylnaphthalene; DMN – dimethylnaphthalene. Peak assignments in Table 5.

**Fig. 15.** Partial *m/z* 170 mass fragmentograms showing the distribution of trimethylnaphthalene (TMN) isomers in the aromatic fractions of Scottish coals.

**Fig. 16.** Partial *m/z* 184 mass fragmentograms showing the distribution of tretramethylnaphthalene (TeMN) isomers in the aromatic fractions of Scottish coals.

**Fig. 17.** Partial *m/z* 178+192 mass fragmentograms showing the distribution of phenanthrene (P), anthracene (A), methylphenanthrene (MP) and methylanthracene (MA) isomers in the aromatic fractions of Scottish coals.

**Fig. 18.** Partial *m/z* 206 mass fragmentograms showing the distribution of ethyl- and dimethylphenanthrene isomers in the aromatic fractions of Scottish coals. Abbreviations: EP – ethylphenanthrene, DMP – dimethylphenanthrene.

**Fig. 19.** Partial *m/z* 155 + 169 + 183 mass fragmentograms showing a series of $C_{17}$ to $C_{19}$ isohexylalkylnaphthalenes in the aromatic fractions of Scottish coals. Peak assignments in Table 5. Abbreviations: iHMN – isohexylalkylnaphthalene, PMN – pentamethylnaphthalene, DMP – dimethylphenanthrene.

**Fig. 20.** Partial m/z 237 and m/z 223 mass fragmentograms showing the distribution of diaromatic tricyclic hydrocarbons in the aromatic fractions of Scottish coals. Abbreviations: Sim – simonellite, To – diaromatic tricyclic totarane, Semp – diaromatic tricyclic sempervirane, Tre - tetrahydroretene. Peak assignments in Table 5. Mass spectra of the two tentatively identified tetrahydroretene-derived isomers are also showed shown ($Tre^1$ and $Tre^2$).

**Table captions**

**Table 1**

Bulk and molecular geochemical parameters from Scottish coals.

**Table 2**

Petrographic composition and vitrinite reflectance.

**Table 3**

Bicyclic alkanes identified.

**Table 4**

Diterpenoid hydrocarbons identified.

**Table 5**

Aromatic hydrocarbons identified.

**Table 6**

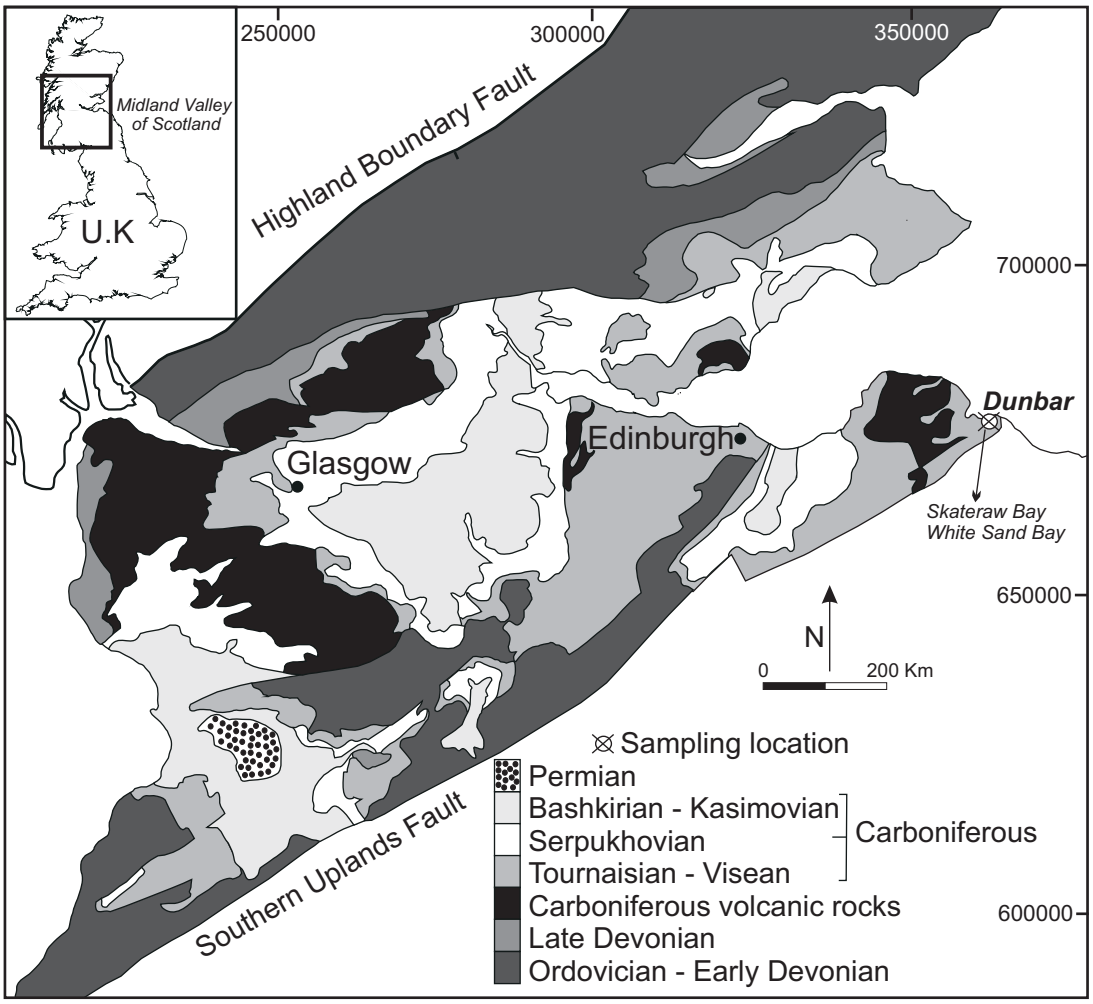
Maturity indicators from aromatic fractions of Carboniferous coal samples.

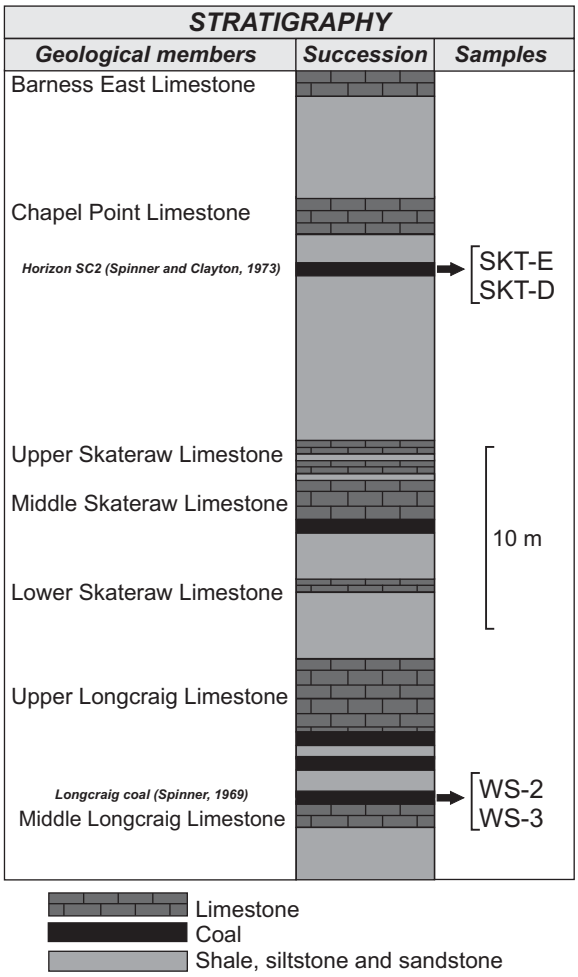
**Table 7**

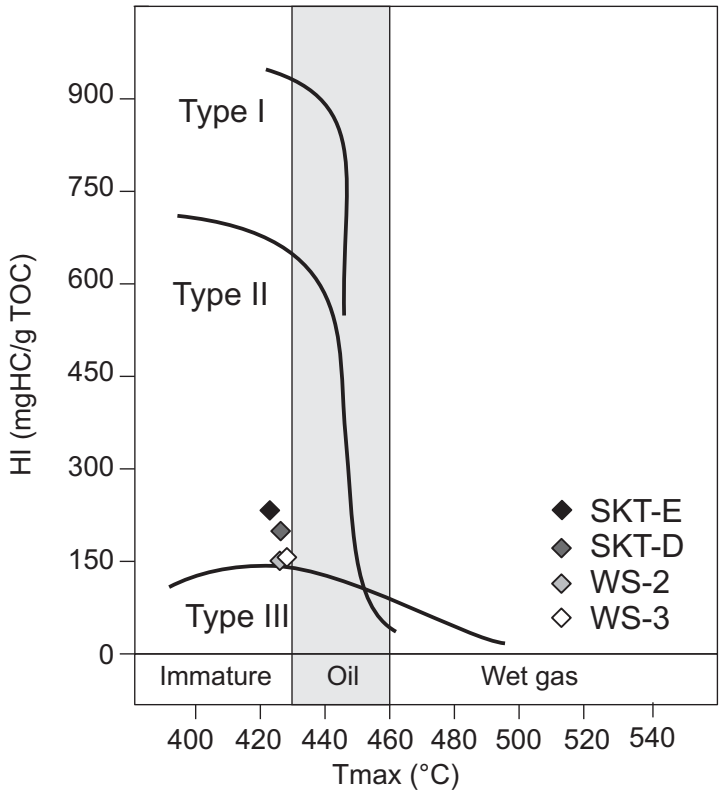
List of target saturated and aromatic land plant biomarkers and their origin.

**Appendix**

Mass spectra of unknown compounds (Peak assignments in Tables 2 and 3).


250000
300000
350000
700000
650000
600000
Midland Valley of Scotland
U.K
Highland Boundary Fault
Southern Uplands Fault
Glasgow
Edinburgh
Dunbar
Skateraw Bay
White Sand Bay
N
0
200 Km
Sampling location
Permian
Bashkirian - Kasimovian
Serpukhovian
Tournaisian - Visean
Carboniferous
Carboniferous volcanic rocks
Late Devonian
Ordovician - Early Devonian


STRATIGRAPHY
Geological members
Succession
Samples
Barness East Limestone
Chapel Point Limestone
Horizon SC2 (Spinner and Clayton, 1973)
SKT-E
SKT-D
Upper Skateraw Limestone
Middle Skateraw Limestone
Lower Skateraw Limestone
10 m
Upper Longcraig Limestone
Longcraig coal (Spinner, 1969)
Middle Longcraig Limestone
WS-2
WS-3
Limestone
Coal
Shale, siltstone and sandstone


900
750
600
450
300
150
0
HI (mgHC/g TOC)
Type I
Type II
Type III
SKT-E
SKT-D
WS-2
WS-3
Immature
Oil
Wet gas
400
420
440
460
480
500
520
540
Tmax (°C)

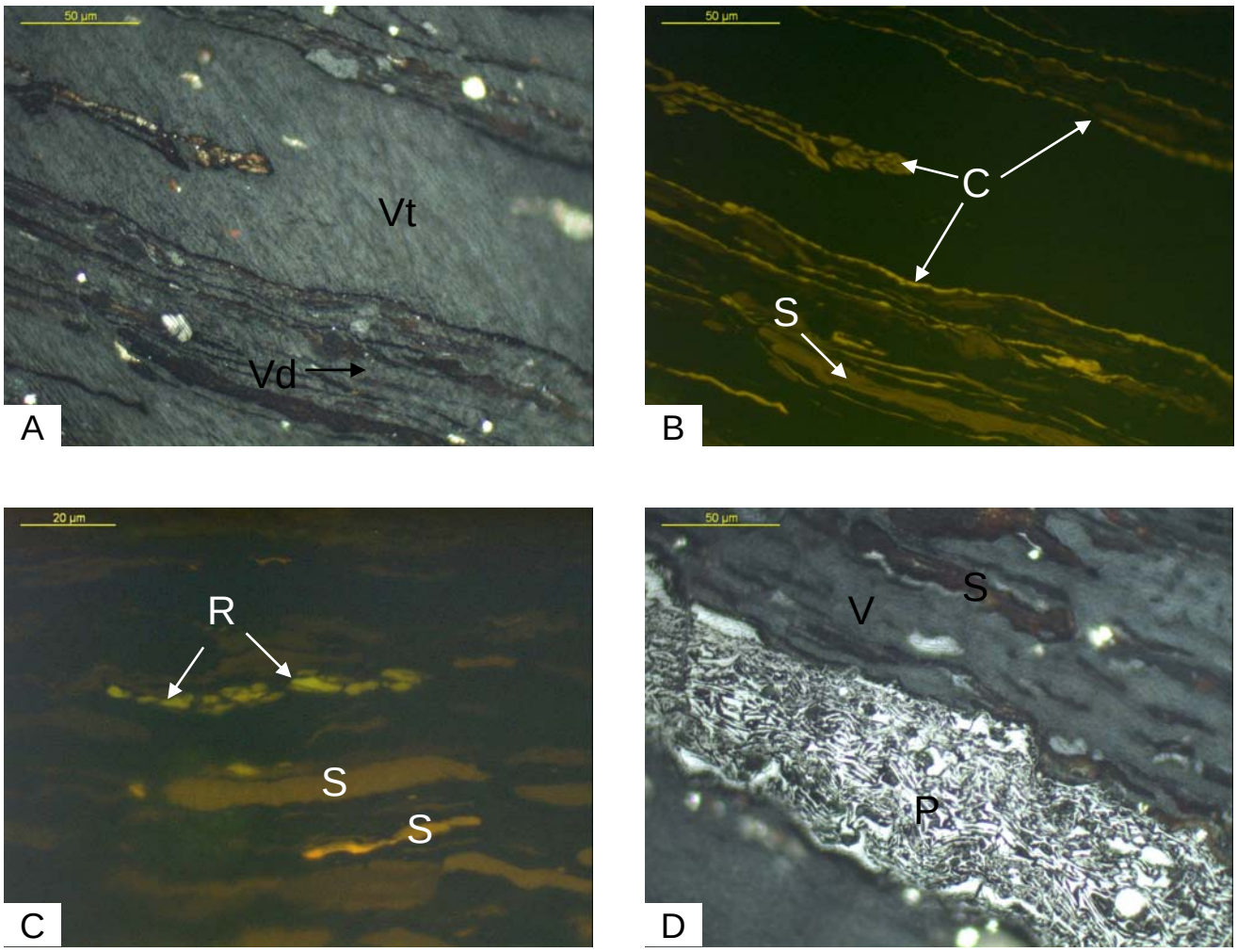
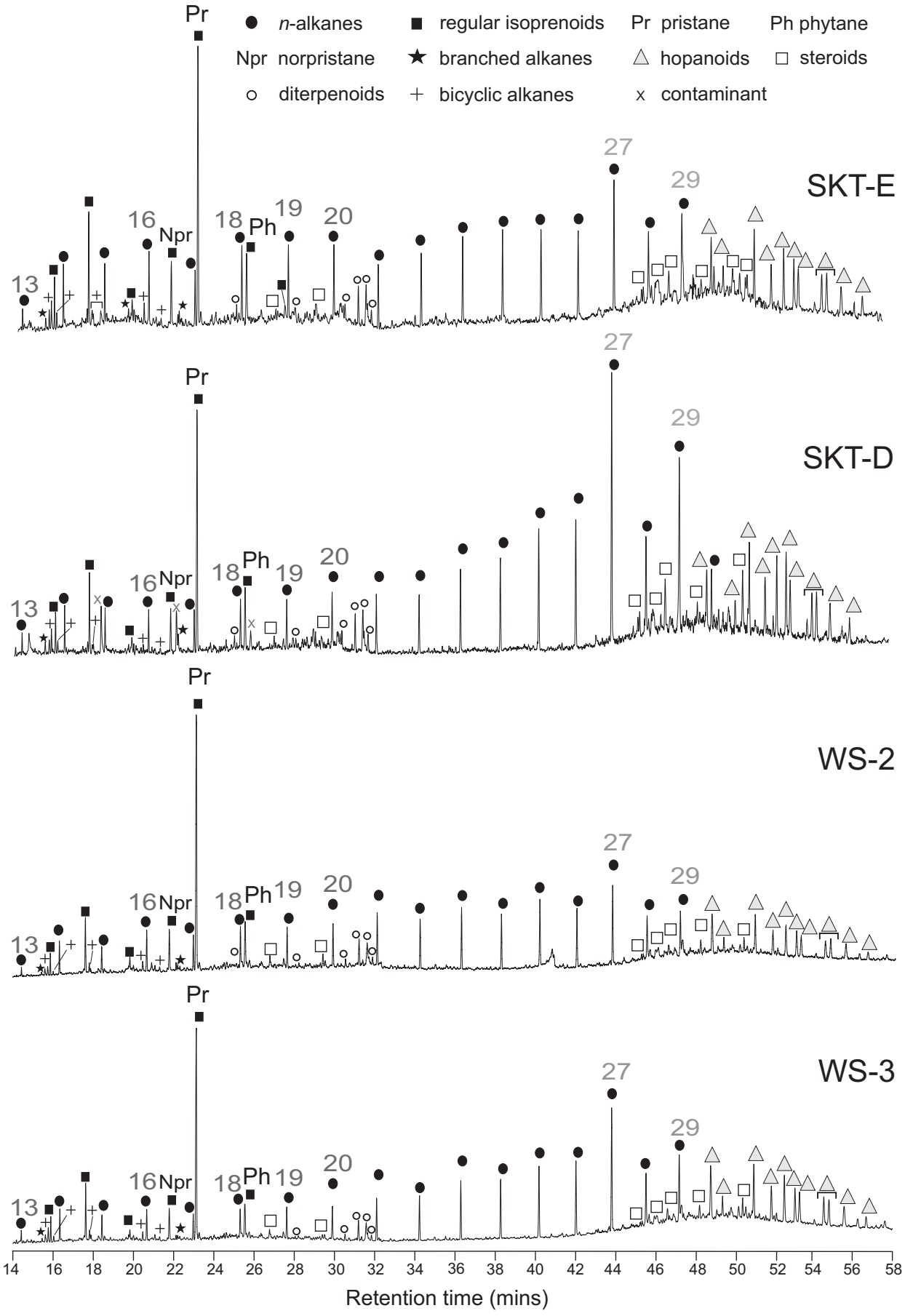
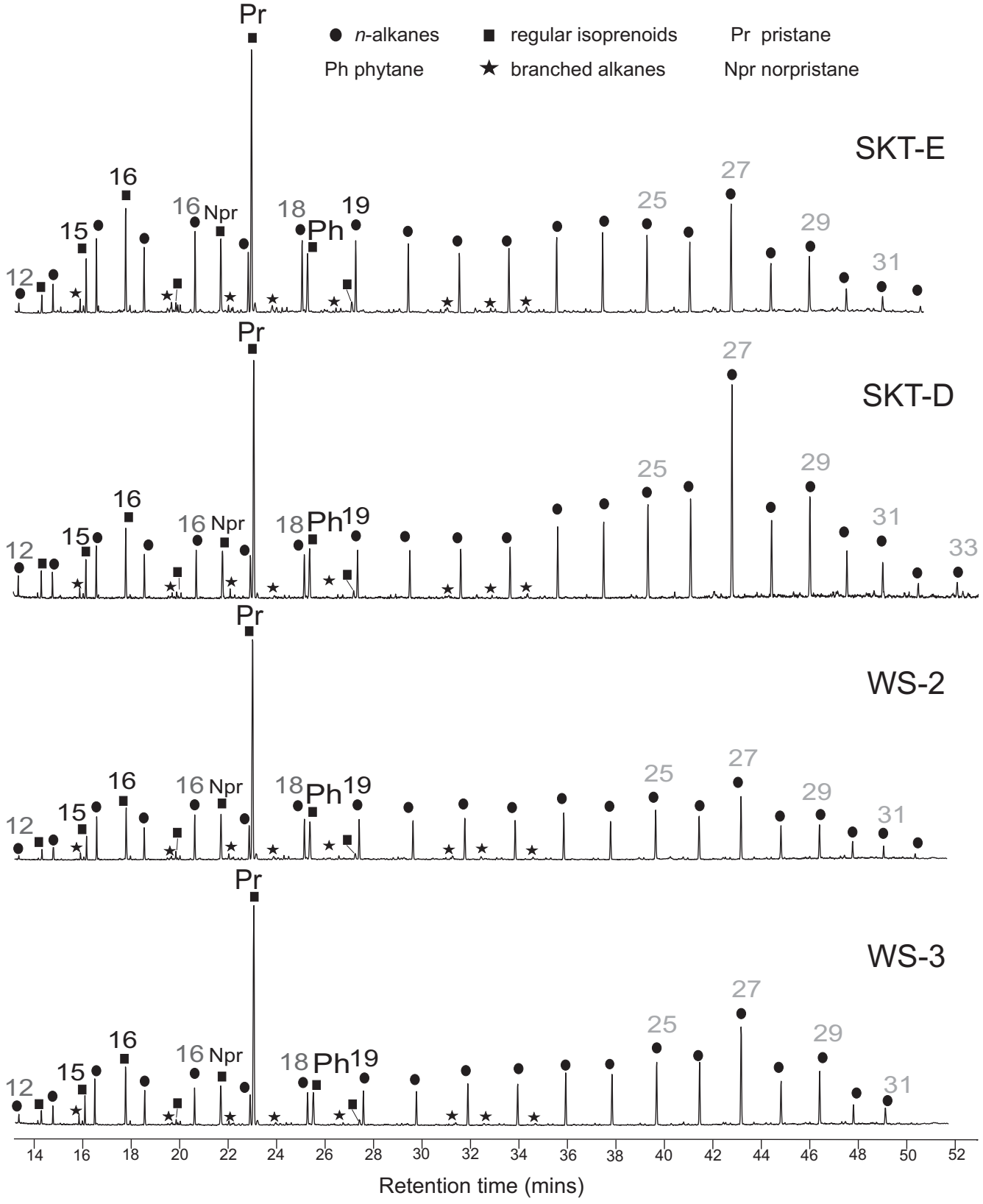
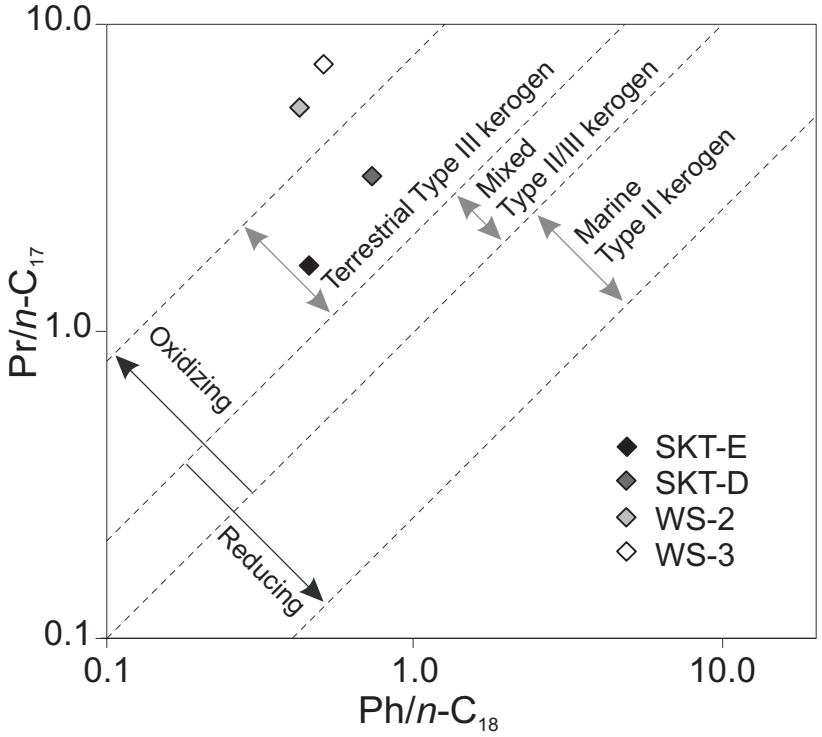
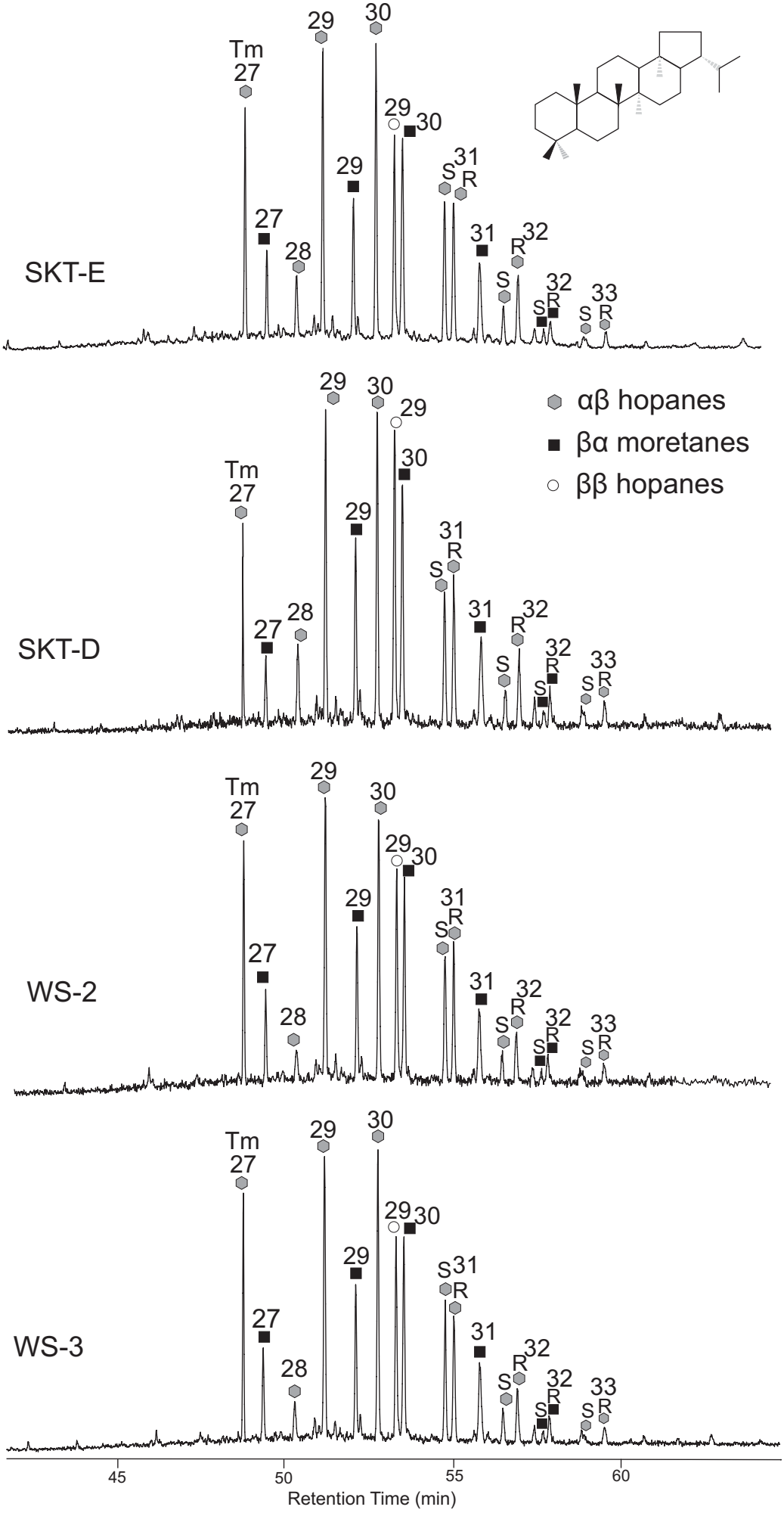


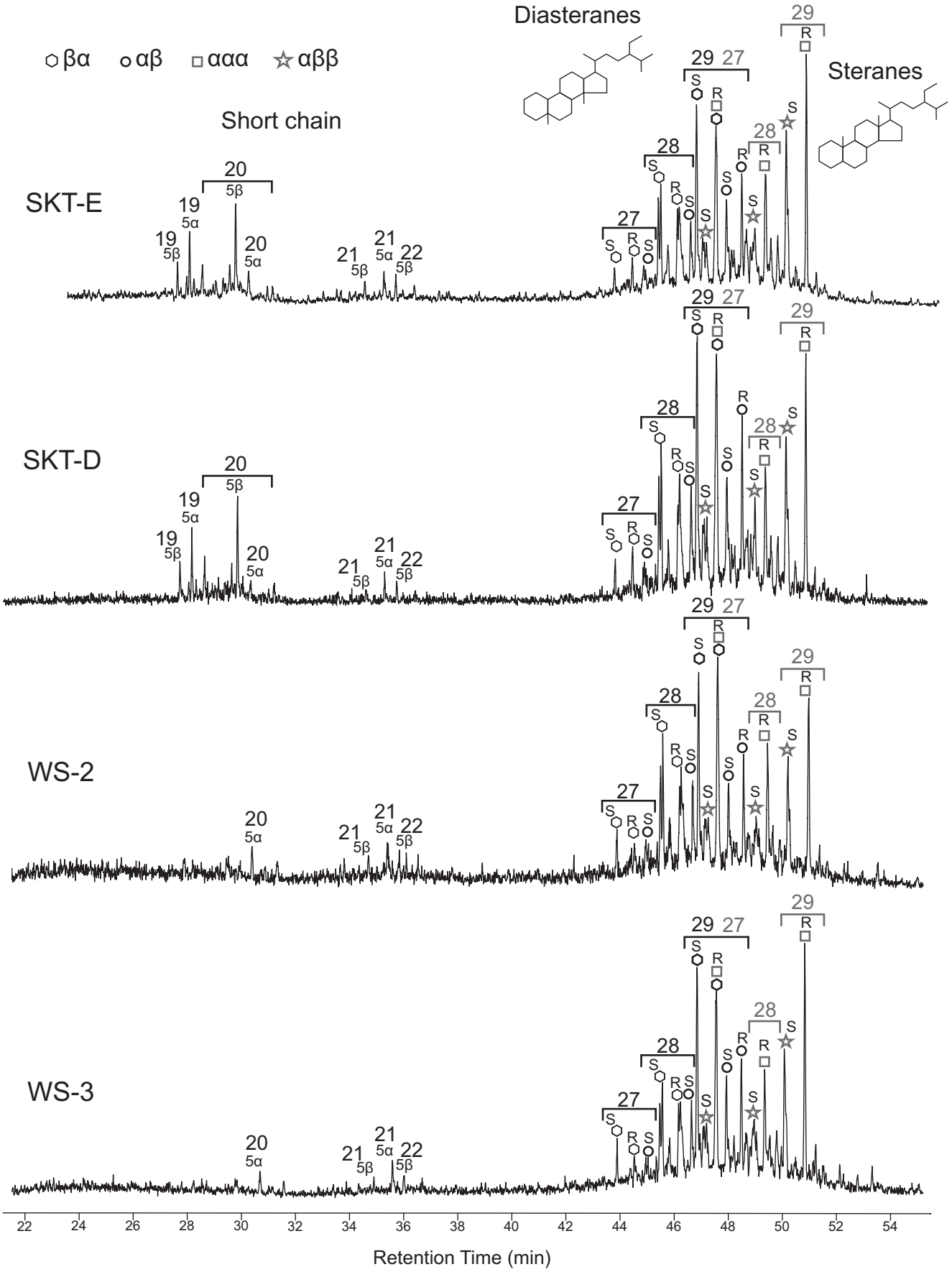

**Fig. 4.** Photomicrographs of macerals A) WS-3, reflected natural light. Vitrinite particles : telocollinite (Vt) and desmocollinite (Vd). B) Same zone as A, blue light fluorescence emphasizing exinite particles: fluorescing spores (S) and cuticles (C). C) SKT-E, blue light fluorescence. Exinite particles: fluorescing spores (S) and resinite (R) filling conducting canals in a vitrinite particle. D) WS-3, reflected natural light. Pyrofusinite (P) and spores (S) in a vitrinite (V) groundmass.

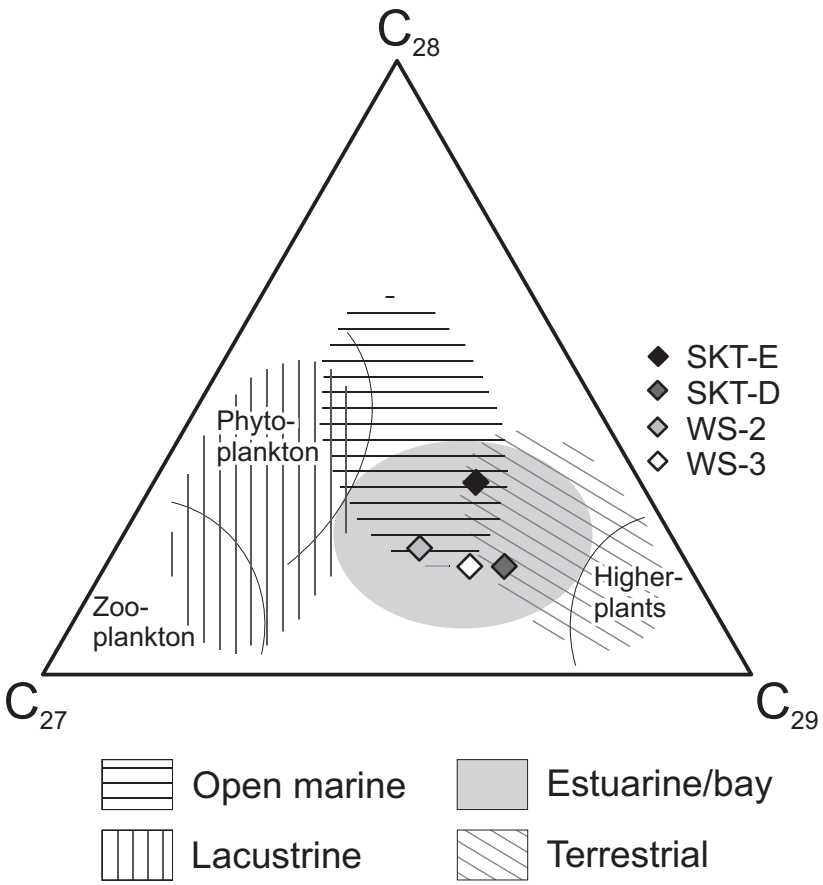

Pr
n-alkanes
regular isoprenoids
Pr pristane
Ph phytane
Npr norpristane
branched alkanes
hopanoids
steroids
diterpenoids
bicyclic alkanes
x contaminant
SKT-E
SKT-D
WS-2
WS-3
13
16
Npr
18
Ph
19
20
27
29
14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58
Retention time (mins)

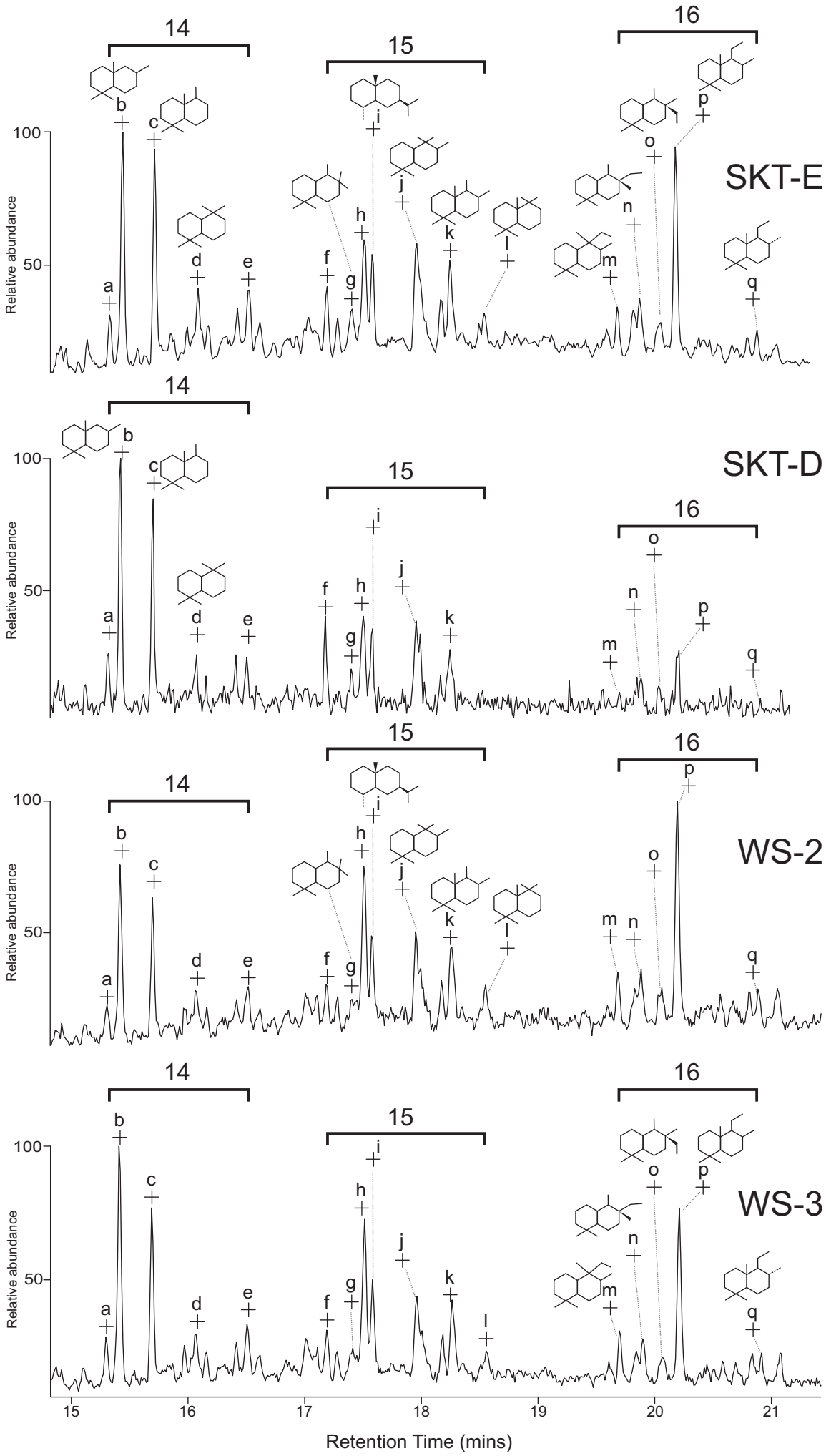

Pr
n-alkanes
regular isoprenoids
Pr pristane
Ph phytane
branched alkanes
Npr norpristane
SKT-E
SKT-D
WS-2
WS-3
12
15
16
16 Npr
18
Ph
19
25
27
29
31
33
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
Retention time (mins)

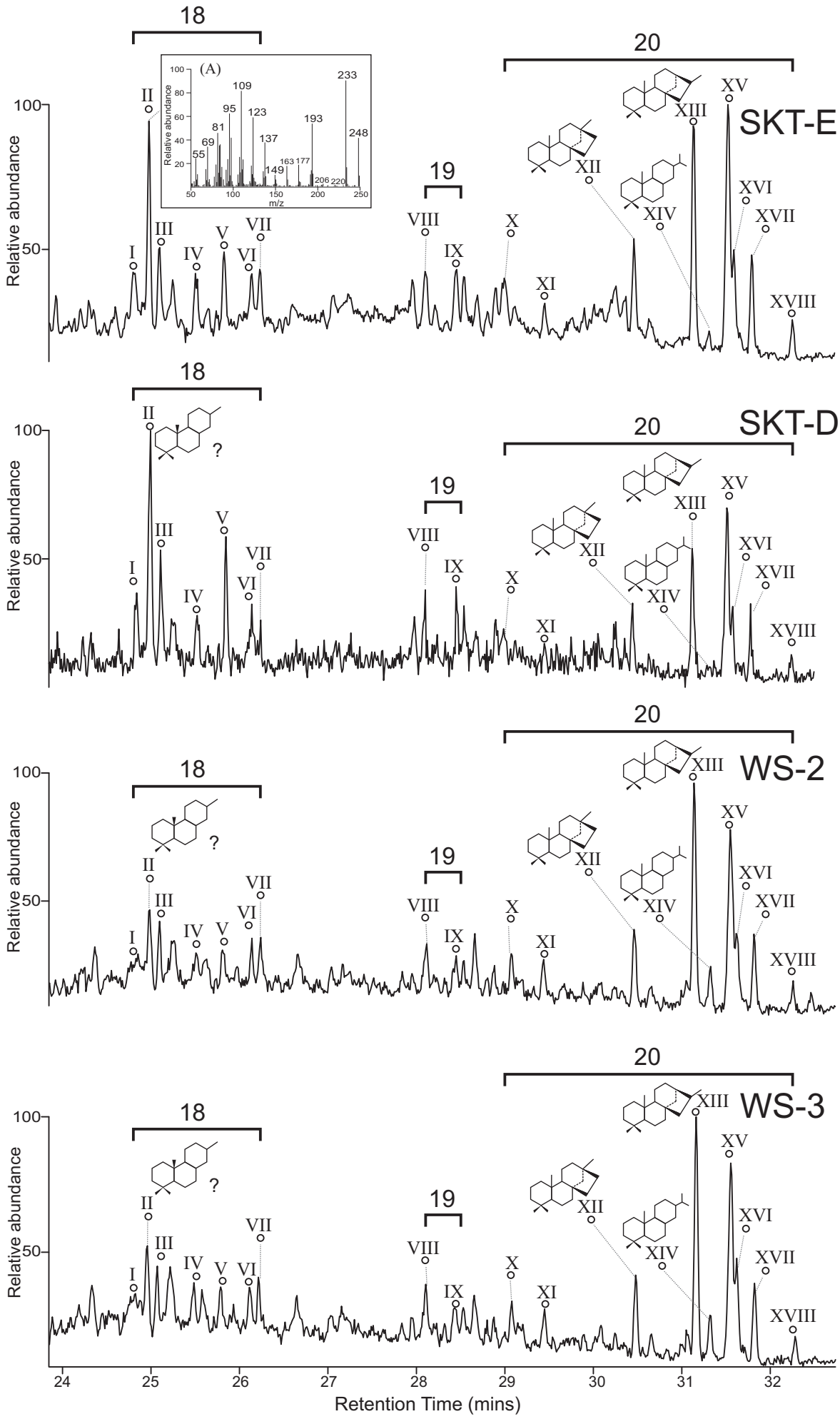

10.0
1.0
0.1
0.1
1.0
10.0
Pr/n-C17
Ph/n-C18
Terrestrial Type III kerogen
Mixed
Type II/III kerogen
Marine
Type II kerogen
Oxidizing
Reducing
SKT-E
SKT-D
WS-2
WS-3

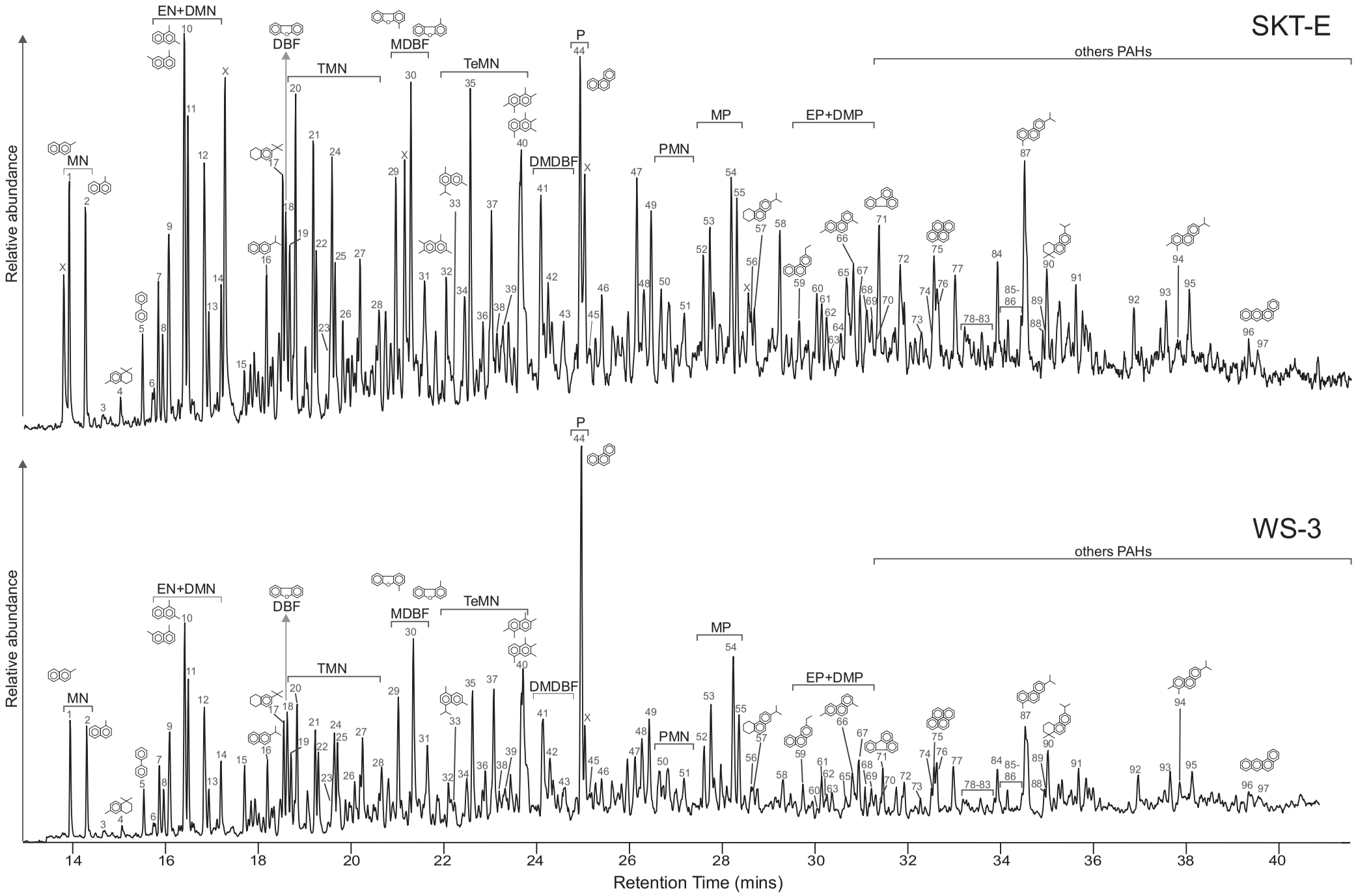

SKT-E
SKT-D
WS-2
WS-3
αβ hopanes
βα moretanes
ββ hopanes
Tm
27
28
29
30
31
32
33
S
R
45
50
55
60
Retention Time (min)

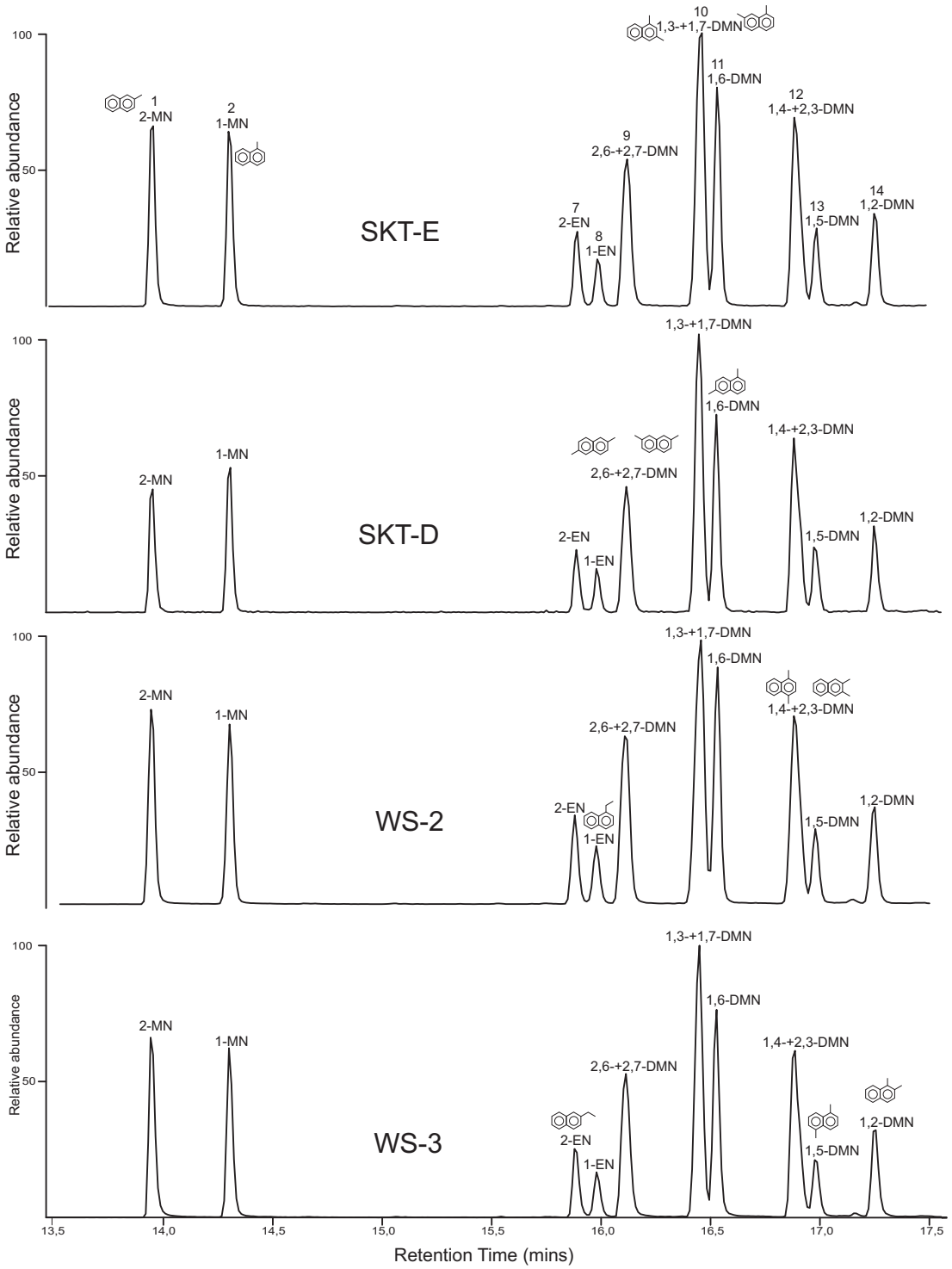

βα
αβ
ααα
αββ
Short chain
Diasteranes
Steranes
SKT-E
SKT-D
WS-2
WS-3
20 5β
19 5α
19 5β
20 5α
21 5β
21 5α
22 5β
27
28
29
R
S
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
Retention Time (min)

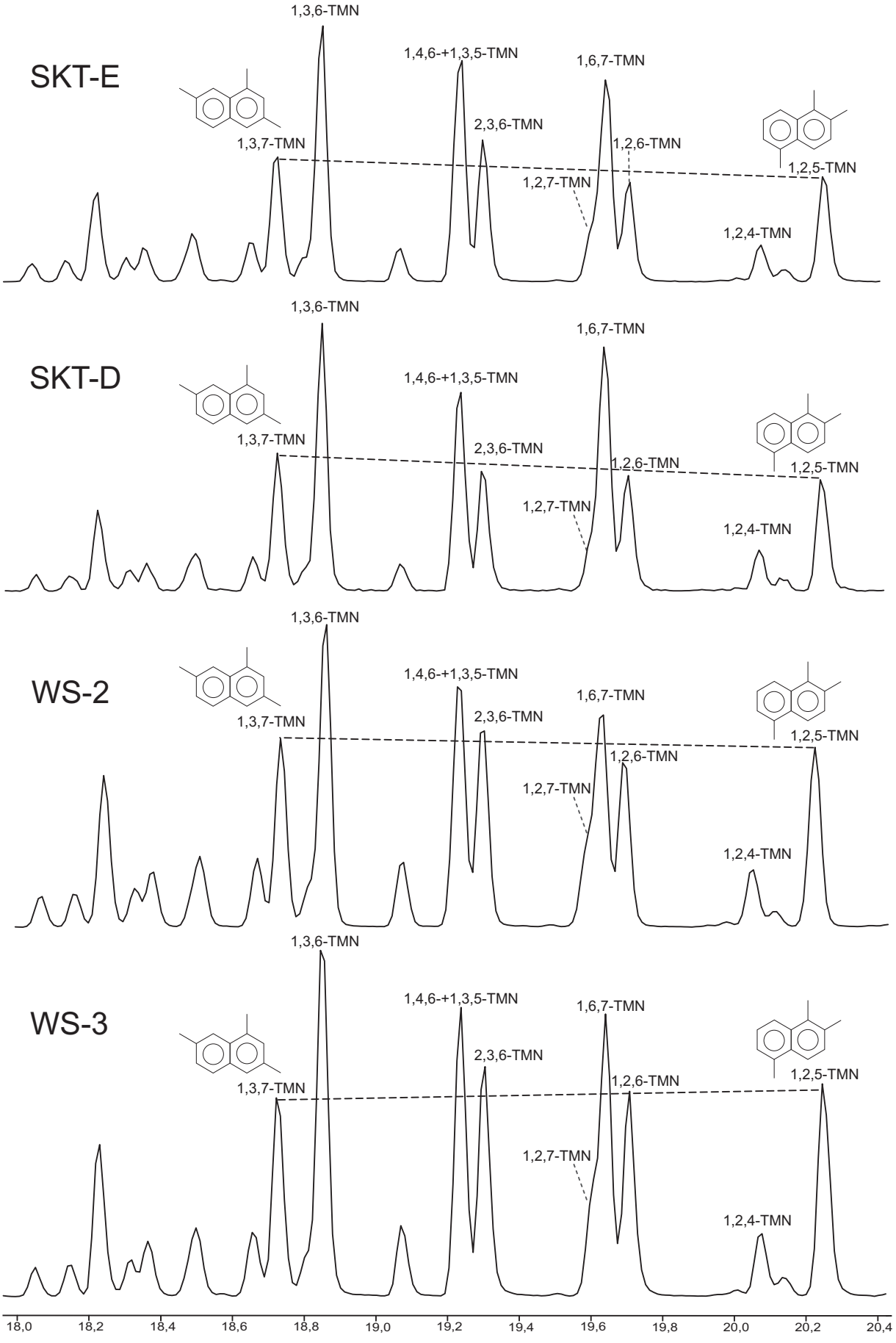

C28
C27
C29
Phyto-
plankton
Zoo-
plankton
Higher-
plants
SKT-E
SKT-D
WS-2
WS-3
Open marine
Estuarine/bay
Lacustrine
Terrestrial

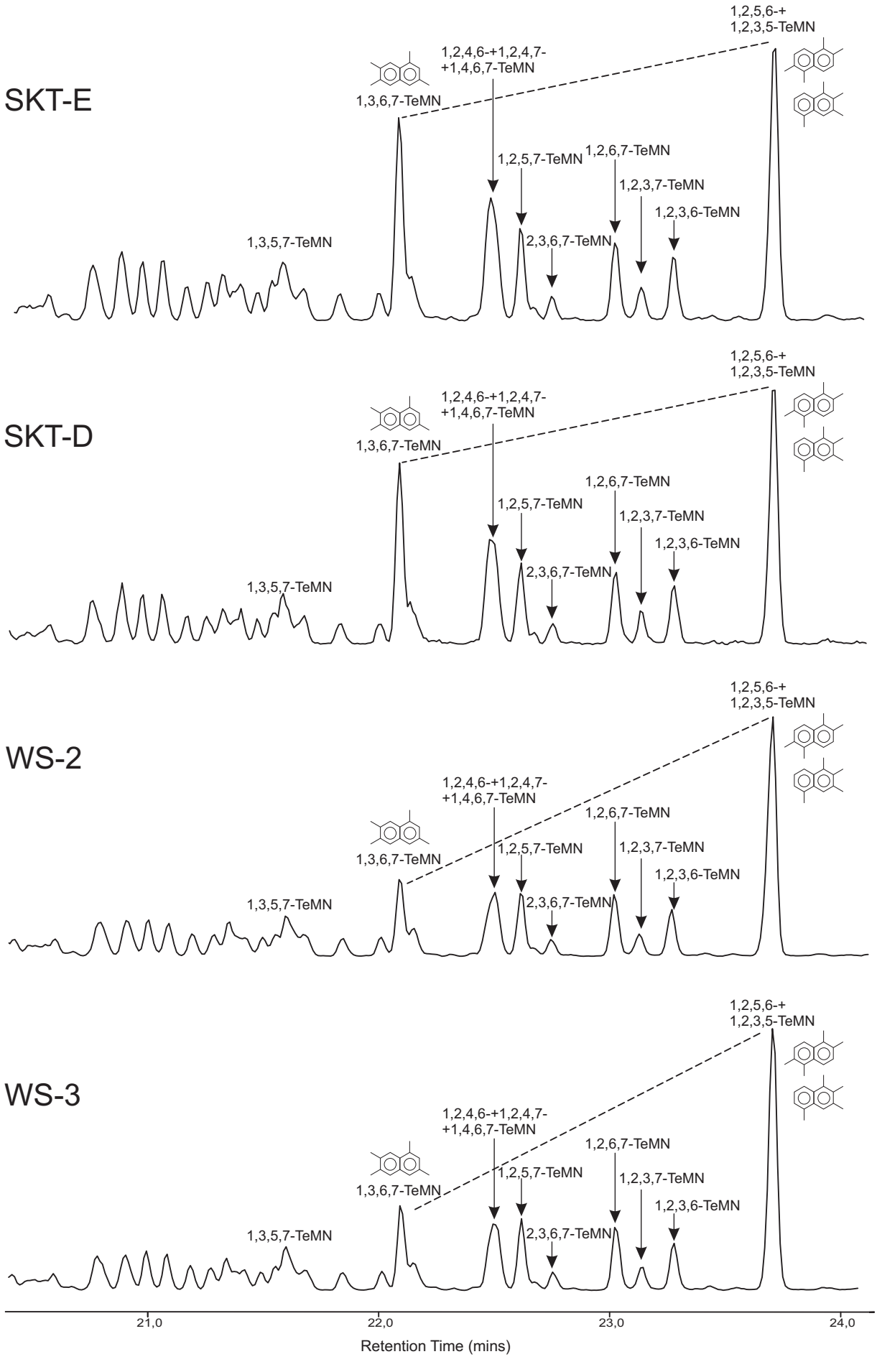

14
15
16
SKT-E
SKT-D
WS-2
WS-3
Relative abundance
100
50
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
15
16
17
18
19
20
21
Retention Time (mins)

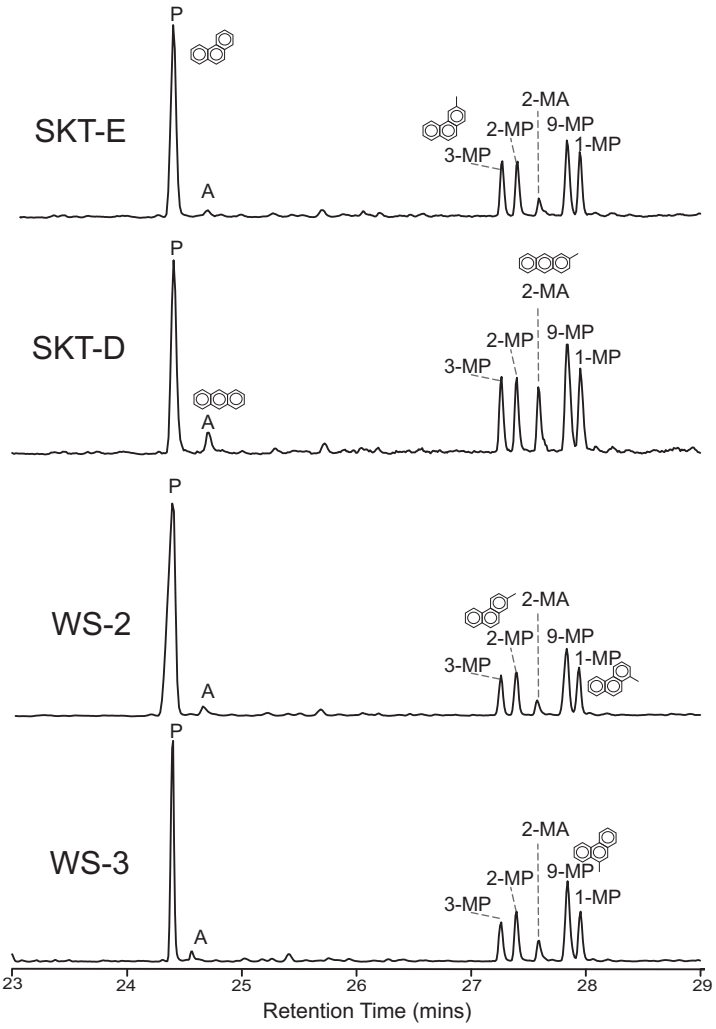

SKT-E
SKT-D
WS-2
WS-3
18
19
20
(A)
Relative abundance
m/z
Retention Time (mins)
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII
?

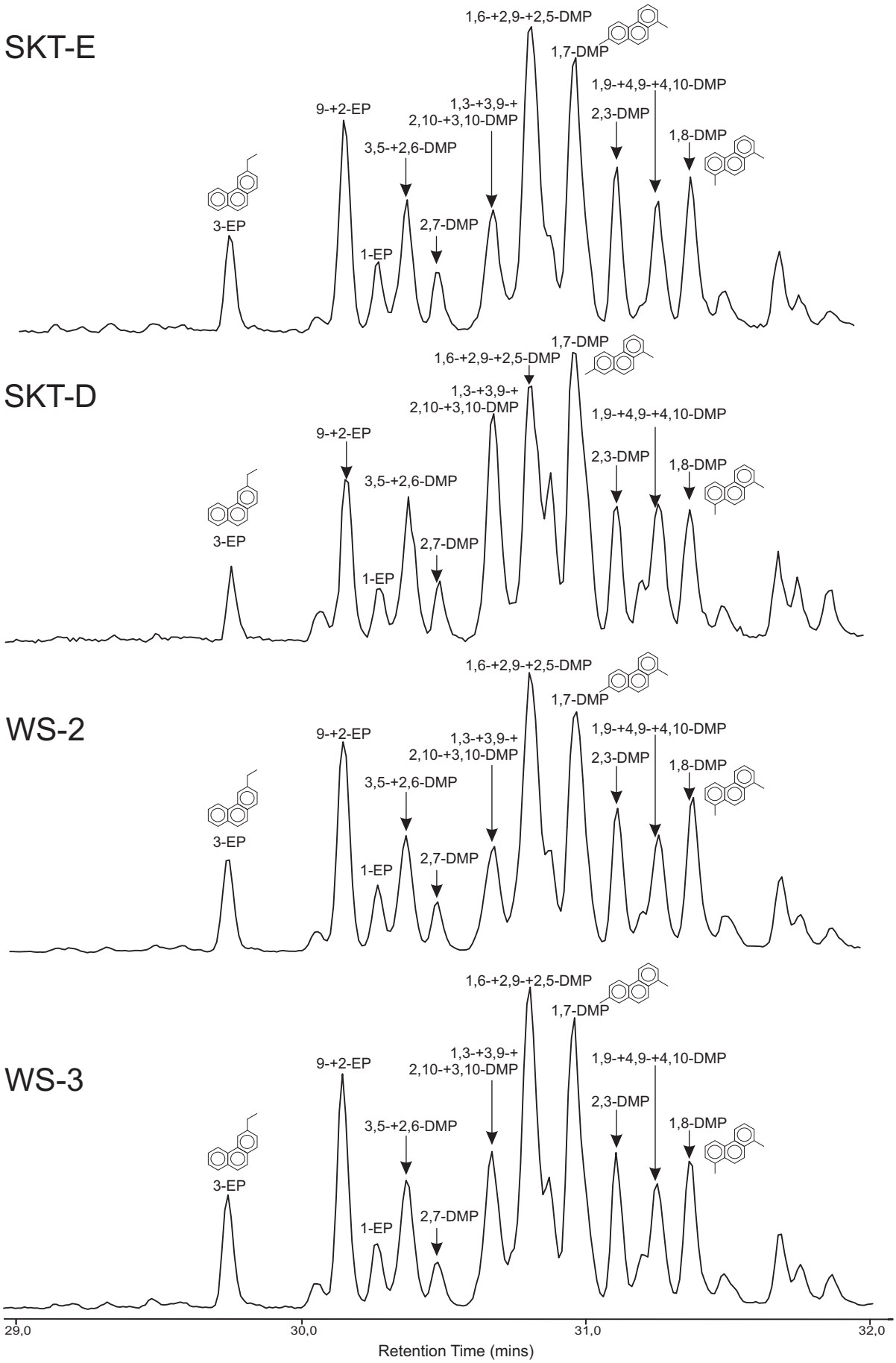

SKT-E
WS-3
Relative abundance
Retention Time (mins)
MN
EN+DMN
DBF
MDBF
TMN
TeMN
DMDBF
P
PMN
MP
EP+DMP
others PAHs
78-83
85-86
14
16
18
20
22
24
26
28
30
32
34
36
38
40

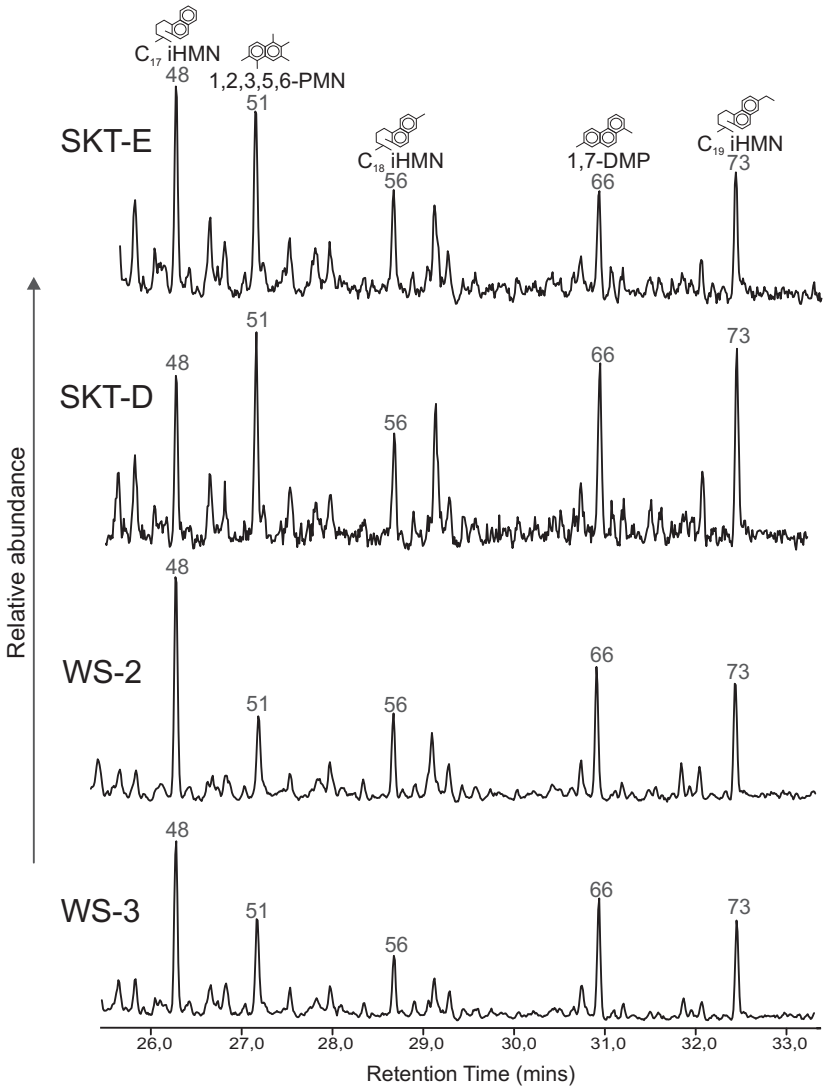

SKT-E
SKT-D
WS-2
WS-3
Relative abundance
100
50
1
2-MN
2
1-MN
7
2-EN
8
1-EN
9
2,6-+2,7-DMN
10
1,3-+1,7-DMN
11
1,6-DMN
12
1,4-+2,3-DMN
13
1,5-DMN
14
1,2-DMN
13,5
14,0
14,5
15,0
15,5
16,0
16,5
17,0
17,5
Retention Time (mins)

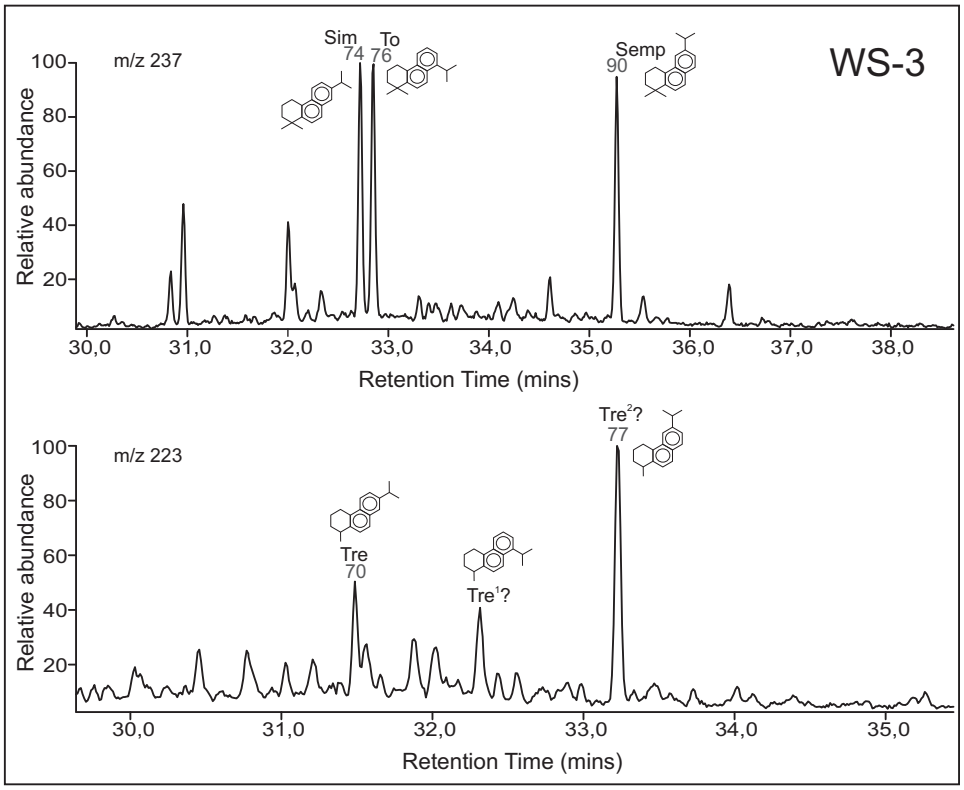

SKT-E
1,3,6-TMN
1,4,6-+1,3,5-TMN
1,6,7-TMN
2,3,6-TMN
1,3,7-TMN
1,2,6-TMN
1,2,5-TMN
1,2,7-TMN
1,2,4-TMN
SKT-D
1,3,6-TMN
1,6,7-TMN
1,4,6-+1,3,5-TMN
1,3,7-TMN
2,3,6-TMN
1,2,6-TMN
1,2,5-TMN
1,2,7-TMN
1,2,4-TMN
WS-2
1,3,6-TMN
1,4,6-+1,3,5-TMN
1,6,7-TMN
1,3,7-TMN
2,3,6-TMN
1,2,5-TMN
1,2,6-TMN
1,2,7-TMN
1,2,4-TMN
WS-3
1,3,6-TMN
1,4,6-+1,3,5-TMN
1,6,7-TMN
2,3,6-TMN
1,3,7-TMN
1,2,6-TMN
1,2,5-TMN
1,2,7-TMN
1,2,4-TMN
18,0
18,2
18,4
18,6
18,8
19,0
19,2
19,4
19,6
19,8
20,0
20,2
20,4
Retention Time (mins)

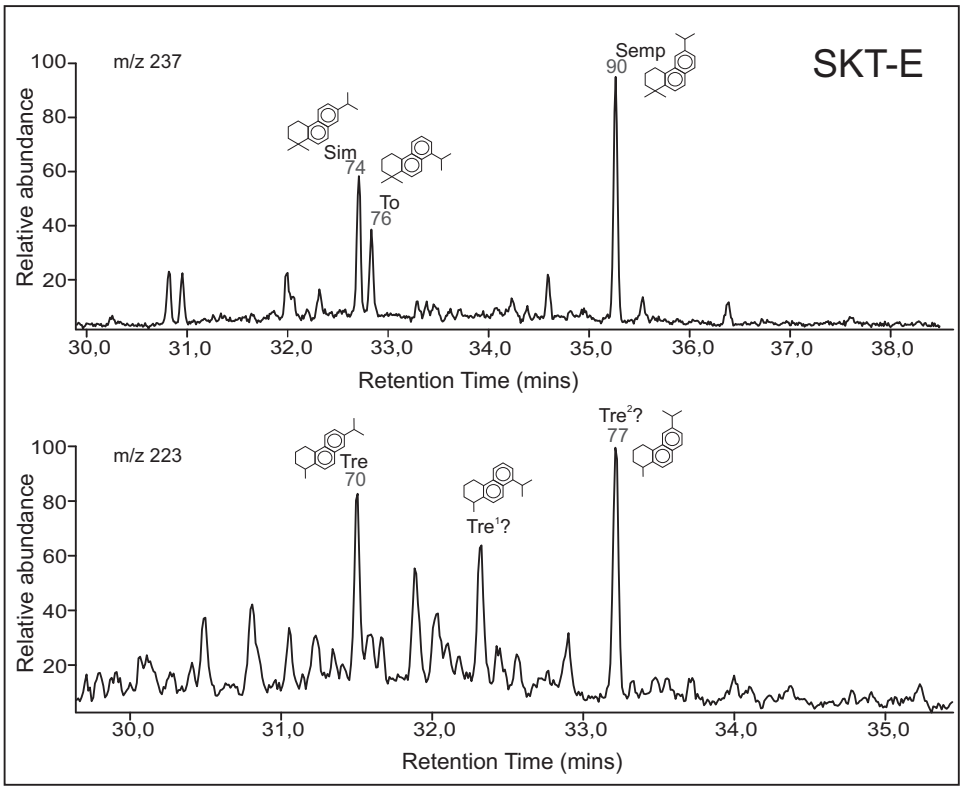

SKT-E
1,3,5,7-TeMN
1,3,6,7-TeMN
1,2,4,6-+1,2,4,7-
+1,4,6,7-TeMN
1,2,5,7-TeMN
2,3,6,7-TeMN
1,2,6,7-TeMN
1,2,3,7-TeMN
1,2,3,6-TeMN
1,2,5,6-+
1,2,3,5-TeMN
SKT-D
1,3,5,7-TeMN
1,3,6,7-TeMN
1,2,4,6-+1,2,4,7-
+1,4,6,7-TeMN
1,2,5,7-TeMN
2,3,6,7-TeMN
1,2,6,7-TeMN
1,2,3,7-TeMN
1,2,3,6-TeMN
1,2,5,6-+
1,2,3,5-TeMN
WS-2
1,3,5,7-TeMN
1,3,6,7-TeMN
1,2,4,6-+1,2,4,7-
+1,4,6,7-TeMN
1,2,5,7-TeMN
2,3,6,7-TeMN
1,2,6,7-TeMN
1,2,3,7-TeMN
1,2,3,6-TeMN
1,2,5,6-+
1,2,3,5-TeMN
WS-3
1,3,5,7-TeMN
1,3,6,7-TeMN
1,2,4,6-+1,2,4,7-
+1,4,6,7-TeMN
1,2,5,7-TeMN
2,3,6,7-TeMN
1,2,6,7-TeMN
1,2,3,7-TeMN
1,2,3,6-TeMN
1,2,5,6-+
1,2,3,5-TeMN
21,0
22,0
23,0
24,0
Retention Time (mins)

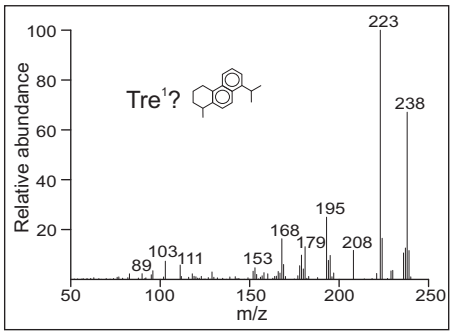

SKT-E
SKT-D
WS-2
WS-3
P
A
2-MA
2-MP
9-MP
1-MP
3-MP
23
24
25
26
27
28
29
Retention Time (mins)

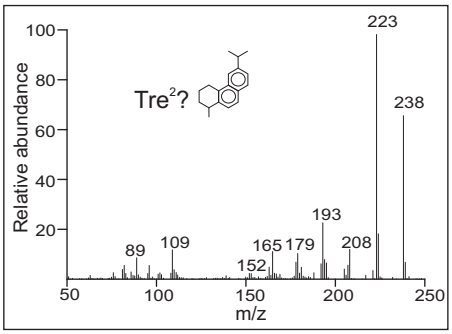

SKT-E
1,6-+2,9-+2,5-DMP
1,7-DMP
1,9-+4,9-+4,10-DMP
2,3-DMP
1,8-DMP
9-+2-EP
1,3-+3,9-+
2,10-+3,10-DMP
3,5-+2,6-DMP
3-EP
2,7-DMP
1-EP
SKT-D
1,7-DMP
1,6-+2,9-+2,5-DMP
1,3-+3,9-+
2,10-+3,10-DMP
1,9-+4,9-+4,10-DMP
9-+2-EP
2,3-DMP
1,8-DMP
3,5-+2,6-DMP
3-EP
2,7-DMP
1-EP
WS-2
1,6-+2,9-+2,5-DMP
1,7-DMP
9-+2-EP
1,3-+3,9-+
2,10-+3,10-DMP
1,9-+4,9-+4,10-DMP
2,3-DMP
1,8-DMP
3,5-+2,6-DMP
3-EP
1-EP
2,7-DMP
WS-3
1,6-+2,9-+2,5-DMP
1,7-DMP
9-+2-EP
1,3-+3,9-+
2,10-+3,10-DMP
1,9-+4,9-+4,10-DMP
2,3-DMP
3,5-+2,6-DMP
1,8-DMP
3-EP
1-EP
2,7-DMP
29,0
30,0
31,0
32,0
Retention Time (mins)

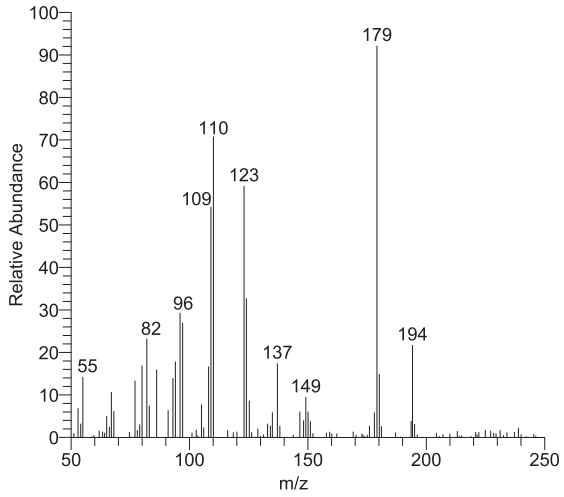

C17 iHMN
48
1,2,3,5,6-PMN
51
C18 iHMN
56
1,7-DMP
66
C19 iHMN
73
SKT-E
SKT-D
WS-2
WS-3
Relative abundance
26,0
27,0
28,0
29,0
30,0
31,0
32,0
33,0
Retention Time (mins)


WS-3
m/z 237
Sim
74
To
76
Semp
90
Relative abundance
Retention Time (mins)
m/z 223
Tre
70
Tre¹?
Tre²?
77

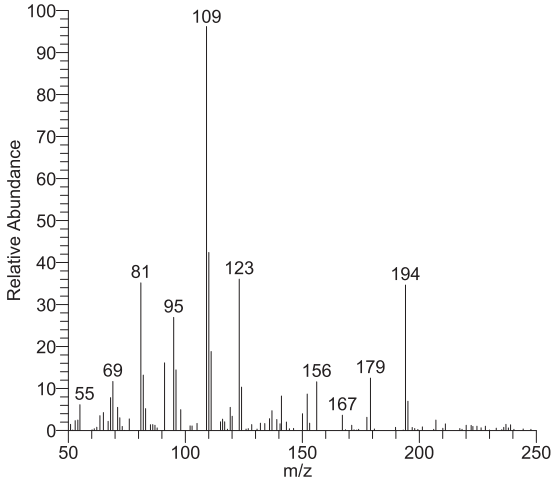

SKT-E
m/z 237
Semp
90
Sim
74
To
76
Relative abundance
Retention Time (mins)
m/z 223
Tre
70
Tre¹?
Tre²?
77


Tre¹?
223
238
195
168
179
208
103
111
89
153
Relative abundance
m/z

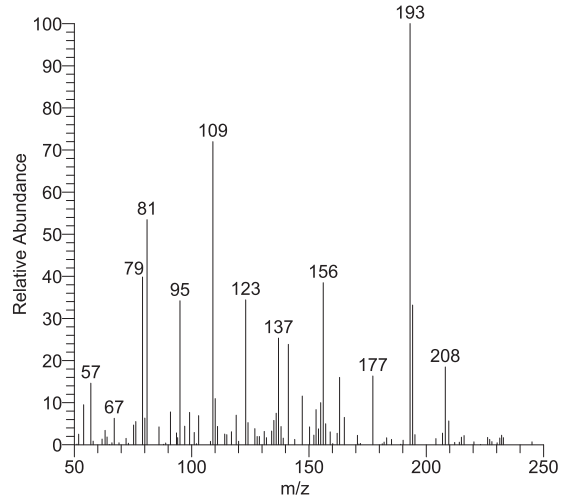

Tre²?
223
238
193
165
179
208
89
109
152
Relative abundance
m/z



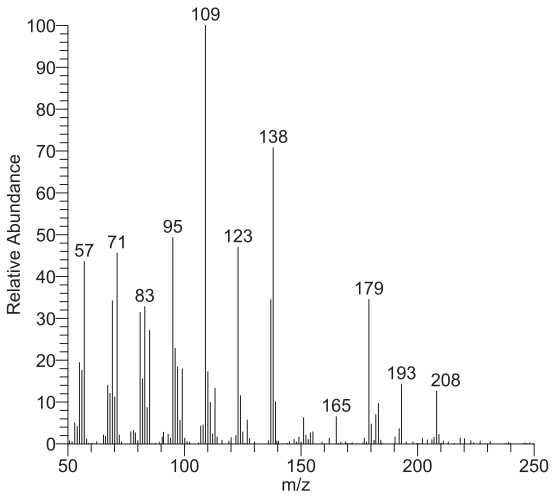

**Peak a:** $C_{14}$ bicyclic alkane?



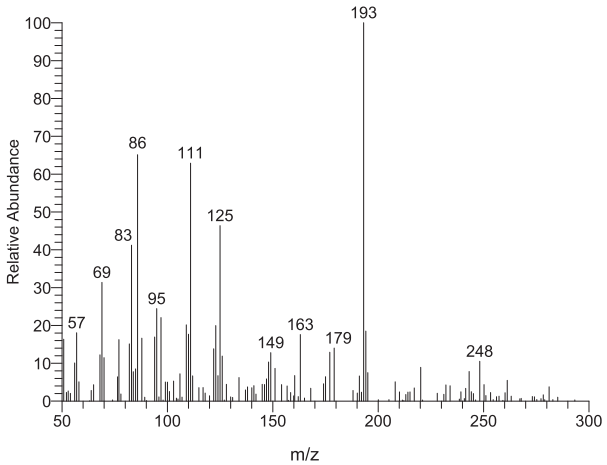

**Peak e:** $C_{14}$ bicyclic alkane?



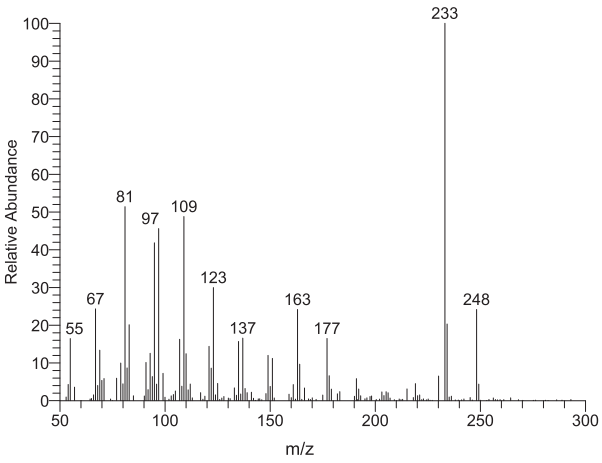

**Peak f:** $C_{15}$ bicyclic alkane?



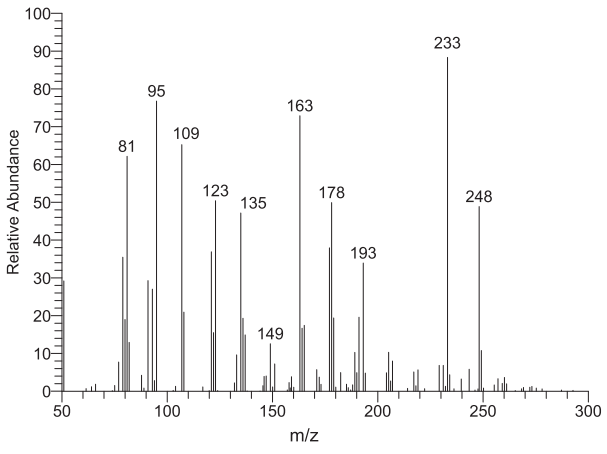

**Peak h:** $C_{15}$ bicyclic alkane?



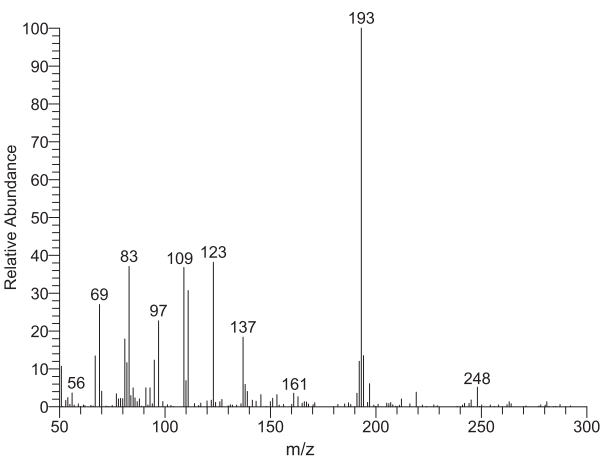

**Peak I:** $C_{18}$ tricyclic hydrocarbon?



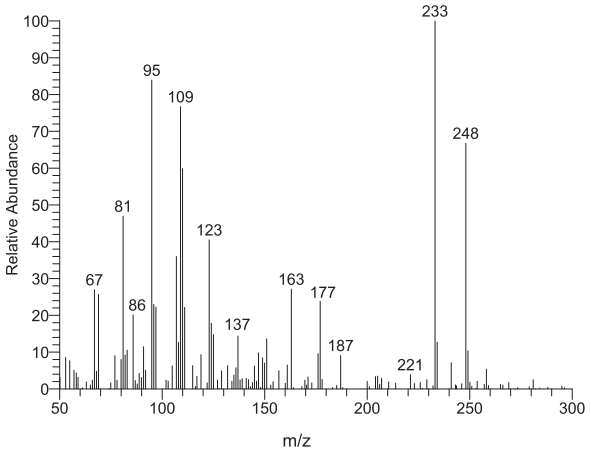

**Peak III:** $C_{18}$ tricyclic hydrocarbon?



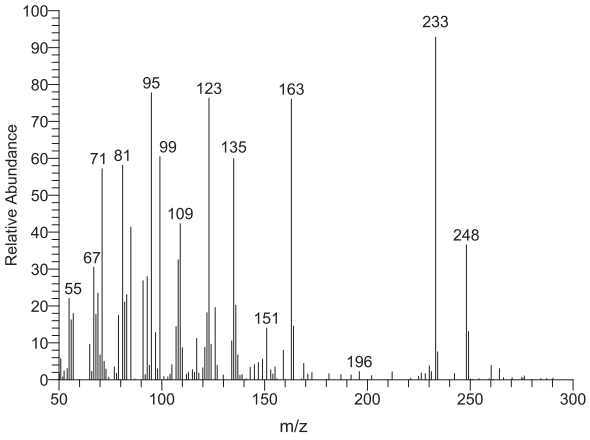

**Peak IV:** $C_{18}$ tricyclic hydrocarbon?



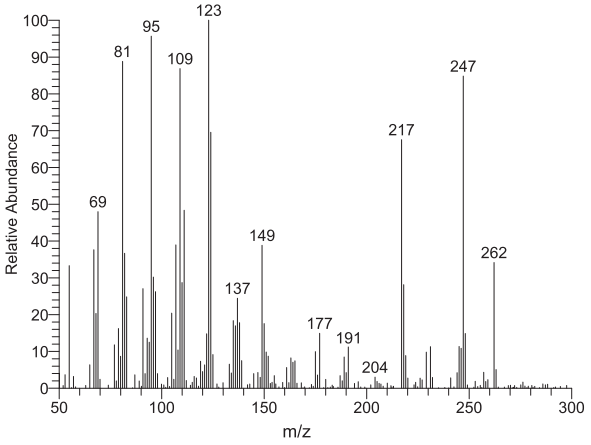

**Peak V:** $C_{18}$ tricyclic hydrocarbon?



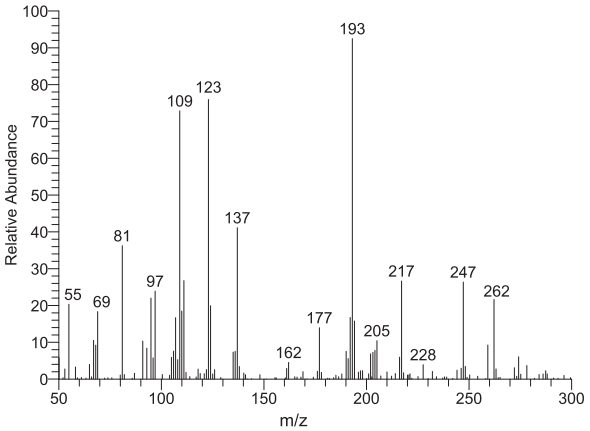

**Peak VI:** $C_{18}$ tricyclic hydrocarbon?



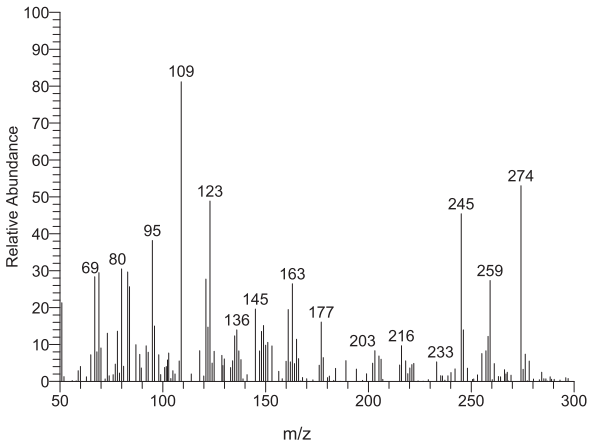

**Peak VII:** $C_{18}$ tricyclic hydrocarbon?



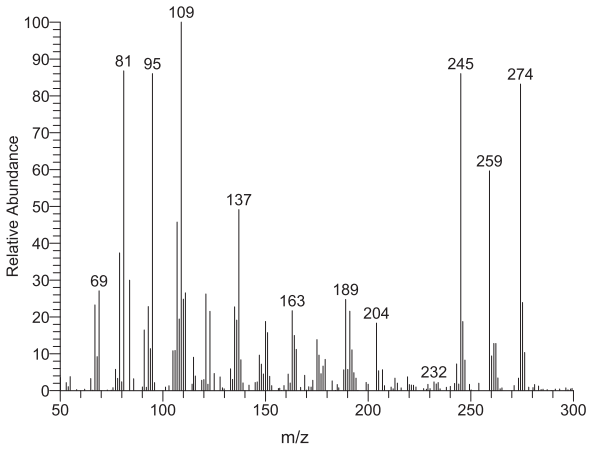

**Peak VIII:** $C_{19}$ tricyclic hydrocarbon?



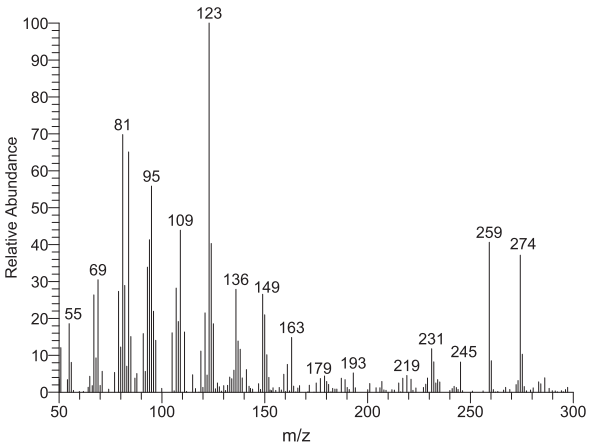

**Peak IX:** $C_{19}$ tricyclic hydrocarbon?




**Peak X:** $C_{20}$ tretracyclic diterpenoid?




**Peak XI:** $C_{20}$ tetracyclic diterpenoid?




**Peak XVIII:** $C_{20}$ tetracyclic diterpenoid?