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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 4 $\beta$ (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 **1. Introduction**

2 Biomarkers are molecular compounds which can be extracted  
3 from crude oils, coals and all kinds of sedimentary rocks (Tissot and  
4 Welte, 1984). Biomarkers have numerous biological origins, and their  
5 occurrence can be related to a specific source, giving information of the  
6 type of fauna/flora present in the environment, or to depositional  
7 conditions, such as salinity or temperature (Peters and Moldowan,  
8 1993). For these reasons, biomarkers are regularly used in  
9 palaeoenvironmental studies (e.g. Olcott, 2007; Eglinton and Eglinton,  
10 2008). Recent applications of biomarkers aim at tracing the evolution of  
11 life. In archean rocks, biomarkers give information on the timing and  
12 evolution of early forms of life (e.g. Brocks et al., 1999, 2003, 2005;  
13 Ventura et al., 2007 ; Eigenbrode et al., 2008 ; Waldbauer et al., 2009),  
14 while in more recent rocks and sediments, biomarkers help determining  
15 taxonomic relationships between taxa (e.g. Arouri et al., 2000; Talyzina  
16 et al., 2000). In the last decades, chemotaxonomic applications have  
17 been particularly developed for the study of flora associated with amber  
18 and coal deposits mostly of Mesozoic to recent age (e.g. Simoneit et al.,  
19 1986; Otto et al., 1997, 2002; Bechtel et al., 2005; Stefanova et al.,  
20 2005 among others). Chemotaxonomic studies of Palaeozoic land plant

21 based on extractible biomarkers were developed in the 70's (Niklas,  
22 1976a,b; Niklas and Chaloner, 1976; Niklas and Pratt, 1980) but have  
23 been relatively limited in more recent years (Schultze and Michaelis,  
24 1990; Fleck et al., 2001; Auras et al., 2006), despite the interest of  
25 Palaeozoic plants regarding the evolution of terrestrial life.

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

37

## 38 **2. Geological setting and previous studies**

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

44 and some igneous rocks (Murchison and Raymond, 1989; George, 1992;  
45 Underhill et al., 2008). The Carboniferous rocks in the Midland Valley of  
46 Scotland are only well exposed along coastlines (Murchison and  
47 Raymond, 1989). Coal samples were collected from two outcrop sections  
48 located at Dunbar, East Lothian, on the east coast of southern  
49 Scotland, some 40 km East of Edinburgh (Fig. 1). These sections show a  
50 group of alternating Lower Carboniferous (Viséan) limestones, shales,  
51 sandstones and coals (Fig. 2.; Spinner, 1969; Spinner and Clayton,  
52 1973).

53 SKT coal samples were collected around the bay near Skateraw  
54 Harbour, approximately 6.4 km south-east of Dunbar, whereas WS  
55 coals were taken from rock successions exposed in White Sand Bay  
56 (Fig. 1). Both localities are clearly exposed on a geological map  
57 permanently exhibited just above the shoreline. In stratigraphic order,  
58 the lower seam is located immediately above the Middle Longcraig  
59 Limestone: samples WS-2 and WS-3 (Fig. 2); the upper one (samples  
60 SKT-E and SKT-D) occurs stratigraphically below the Chapel Point  
61 Limestone (Fig. 2). WS samples are equivalent to the Longcraig coal  
62 seam described by Spinner (1969). In contrast, SKT coals are more  
63 comparable to the sample horizon SC2 detailed by Spinner and Clayton  
64 (1973). In order to investigate the possible vertical stratigraphic  
65 variations, two samples were obtained from each coal seam (Fig. 2).  
66 Accordingly, WS coals are separated by approximately 30 cm while SKT  
67 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-

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

95

### 96 **3. Analytical methods**

#### 97 *3.1. Experimental procedures*

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

110         For biomarker analyses, rock fragments were extracted with  
111 dichloromethane (DCM) during 24 h in the refrigerator, in order to  
112 remove possible contamination on the sample surface. After this first  
113 extraction, the rock fragments were crushed to enable extraction of the  
114 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

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

139

### 140 *3.3. Organic petrography*

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

147

## 148 **4. Results**

### 149 *4.1. Bulk OM characteristics*

150 Bulk organic parameters obtained by Rock-Eval and LECO  
151 analyses (Table 1) show that the TOC values for these coal samples  
152 range between 60.8 and 71.9%. HI and  $T_{\max}$  values vary between 144 to  
153 218 mg HC/g TOC and 423 to 428°C, respectively (Fig. 3). The average  
154  $T_{\max}$  is 426 °C. Based on the constructed HI vs.  $T_{\max}$  diagram (Fig. 3;  
155 Espitalié et al., 1986), coal samples plot in the Type II – III kerogen  
156 region.

157

### 158 *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<sub>13</sub>  
184 to C<sub>30</sub>. The distribution of *n*-alkanes is relatively similar in all four  
185 samples and the most abundant are *n*-C<sub>27</sub> and *n*-C<sub>29</sub> (Fig. 6). Long chain  
186 C<sub>23</sub> – C<sub>33</sub> *n*-alkanes are characterized by an odd-over-even  
187 predominance with a maximum at *n*-C<sub>27</sub> (Fig. 6). The carbon preference  
188 index (CPI) ranges between 1.65 and 1.93 (Table 1). Series of C<sub>14</sub> to C<sub>21</sub>  
189 acyclic isoprenoids dominated by norpristane (C<sub>18</sub>), pristane (Pr; C<sub>19</sub>)  
190 and phytane (Ph; C<sub>20</sub>), were also detected (Fig. 6). Pr is the most  
191 abundant compound in all the samples except SKT-D, where the *n*-C<sub>27</sub>  
192 alkane is more abundant (Fig. 5). The Pr/Ph ranges from 7.33 to 14.67  
193 (Table 1). The Pr/*n*-C<sub>17</sub> is more than 1, whereas the Ph/*n*-C<sub>18</sub> 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<sub>27</sub> to C<sub>33</sub>, with  
203 a maximum at C<sub>29</sub> or C<sub>30</sub> hopanes (Fig. 8).

204 Series of  $\beta\alpha$ -moretanes (17 $\beta$ (H),21 $\alpha$ (H)-moretanes) were also  
205 detected ranging from C<sub>27</sub> to C<sub>32</sub>, with a maximum at C<sub>30</sub> (Fig. 8). C<sub>29</sub>  
206  $\beta\beta$ -hopane was present in all the samples (Fig. 8). Tricyclic terpanes  
207 and gammacerane were not observed.

208

#### 209 4.3.3. Steroids

210 Steranes and diasteranes were detected in all the samples using  
211 the characteristic fragment at  $m/z$  217 (Fig. 9). Steranes are more  
212 abundant than diasteranes and the distribution of these compounds is  
213 similar in all the samples (Fig. 9). Steranes are dominated by the C<sub>29</sub>  
214 5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-20R regular sterane (C<sub>29</sub>  $\alpha\alpha\alpha$ -sterane; Fig. 9 and  
215 10), followed by an important contribution of the  $\alpha\beta\beta$  isomer (Fig. 9).  
216 Diasteranes are dominated by C<sub>29</sub>  $\beta\alpha$ -diasteranes. However, series of  
217 C<sub>27</sub> to C<sub>29</sub>  $\alpha\beta$ -diasteranes and C<sub>27</sub> to C<sub>29</sub>  $\alpha\beta\beta$ -steranes were also  
218 recognized in all the samples (Fig. 9). Additionally, short chain steroids  
219 were also detected in low amounts. SKT coals show a marked  
220 contribution of short chain C<sub>19</sub> - C<sub>20</sub> steroids in comparison with WS  
221 samples (Fig. 9).

222

#### 223 4.3.4. Bicyclic alkanes

224 Seventeen bicyclic alkanes ranging from C<sub>14</sub> to C<sub>16</sub> carbon atoms  
225 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, 4 $\beta$ (H)-eudesmane; 8 $\beta$ (H)-drimane;  
230 8 $\beta$ (H)- and 8 $\alpha$ (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<sub>14</sub> bicyclic alkanes (Fig. 11; e.g.  
238 Peaks b and c). 8 $\beta$ (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 4 $\beta$ (H)-eudesmane and 8 $\beta$ (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<sub>20</sub>H<sub>34</sub>) *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<sub>18</sub> tricyclic  
258 hydrocarbon (Fig. 12). This latter compound is particularly abundant in  
259 SKT samples, as are C<sub>19</sub> and C<sub>20</sub> steranes, it could therefore be related  
260 to short chain steroids. To our knowledge, the molecular structures for  
261 most of the C<sub>18</sub> – C<sub>19</sub> 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<sub>20</sub> 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<sup>1</sup>  
362 and Tre<sup>2</sup>) 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<sup>1</sup> could be the 1-methyl-1,2,3,4-tetrahydro-  
372 8-isopropylphenanthrene (totarane-derived) and Tre<sup>2</sup> 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<sub>29</sub> ββ hopane is observed in all samples

387 (Fig. 8; Seifert and Moldowan, 1980). Third, the high thermal maturity  
388 markers in sediments 18 $\alpha$ -22,29,30-trisnorneohopane (Ts) and  $\alpha\beta\beta$ -  
389 steranes (Fig. 9) are absent or very low in abundance (Seifert and  
390 Moldowan, 1978, 1986). This is further attested by the aromatic  
391 hydrocarbon distribution of MN, EN, DMN, TMN, TeMN and MP isomers  
392 again indicating that the coals are immature (Table 6; Radke et al.,  
393 1982, 1986; Alexander et al., 1985; van Aarssen et al., 1999). For  
394 instance, the TeMN compounds show the predominance of 1,2,5,6- and  
395 1,2,3,5-TeMN over the 1,3,6,7-TeMN (Fig. 16; van Aarssen et al., 1999).  
396 The distribution of methyl- and ethyl-naphthalene homologues with 2-  
397 MN and 2-EN dominating is typical for immature samples (Fig. 14;  
398 Table 6; Radke et al, 1982). The alkylphenanthrenes 9-MP and 1-MP are  
399 highly abundant, with 9-MP being predominant (Fig. 17) is another  
400 feature of immature samples (Radke et al., 1982). It is interesting to  
401 note, however, that depending on the maturity index either WS or SKT  
402 samples may be considered to be the more mature. WS samples are  
403 more mature with DNR, TNR1 and TNR2 while SKT samples are more  
404 mature with TMNr, TeMNr, MPI 1 and MPI 2 (Table 6). This feature  
405 probably reflects the control exerted by the source of the organic matter  
406 and depositional environment on these compounds at low maturity  
407 degree.

408

409 *5.2. Biomarker distributions and palaeoenvironmental conditions*

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

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

431 Other arguments for a purely terrestrial depositional environment  
432 are the high Pr/Ph (Table 1) and Pr/*n*-C<sub>17</sub> vs. Ph/*n*-C<sub>18</sub> ratios (Fig. 7;  
433 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<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> sterols (Fig. 10).  
449 Based on their results, the dominant source of C<sub>27</sub> sterols is  
450 zooplankton, C<sub>28</sub> sterols are generally components of phytoplankton and  
451 C<sub>29</sub> sterols are mainly derived from terrestrial plants. There are many  
452 exceptions on these rules; for instance, C<sub>29</sub> 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<sub>29</sub> steranes (e.g.  
456 Fowler et al., 1991; Kashirtsev et al., 2010). Considering this, the  
457 dominance of C<sub>29</sub> relative to C<sub>27</sub> 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<sub>19</sub> - C<sub>20</sub>  
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<sub>19</sub> - C<sub>20</sub> 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*



482 On the basis of the diverse palynomorph assemblages described by  
483 Spinner (1969) and Spinner and Clayton (1973), a relatively detailed  
484 reconstruction of the flora giving rise to the SKT and WS coals can be  
485 provided, though more details are available for SKT coals than for WS  
486 coals. In WS coals, megaspores are dominated by *Zonalesporites* and/or  
487 *Setosisporites*, followed by *Lagenicula* (Spinner, 1969). *Cystosporites* are  
488 also present in minor proportion. In SKT coal, dominant megaspores are  
489 *Lagenicula* and *Setosisporites* followed by ?*Bacutriletes* and  
490 *Zonalesporites* (Spinner and Clayton, 1973). Miospores assemblages are  
491 generally dominated by *Lycospora*, *Calamospora* and *Densosporites*  
492 (Spinner and Clayton, 1973). *Cingulizonates* miospores should also be  
493 abundant in SKT coal. The megaspore *Zonalesporites* as well as the  
494 miospores *Densosporites* and *Cingulizonates* were mostly produced by  
495 *Bodeodendron/Sporangiostrobus* (recently identified as equivalent to  
496 *Omphalophloios*) which was a sub-arborescent lycopsid belonging to the  
497 Isoetales group (Wagner, 1989; Taylor et al., 2009; Opluštil et al., 2010).  
498 *Bacutriletes* miospores were produced by herbaceous and sub-  
499 arborescent lycopsids among which *Bodeodendron/Sporangiostrobus*  
500 (Eble, 1996). *Setosisporites* megaspores mainly derived from  
501 *Bothrodendron* (e.g. Phillips, 1979). *Lagenicula* megaspores and some  
502 *Lycospora* miospores were produced by *Paralycopodites* (also known as  
503 *Anabathra*; DiMichele and Phillips, 1994). Finally, *Cystosporites*  
504 megaspores and some *Lycospora* miospores were produced by  
505 *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 Glenar buck 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 Glenar buck 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  $\beta$ -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). 4 $\beta$ (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 Glenar buck 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.

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

650 In summary, most of the aliphatic and aromatic terrestrial  
651 biomarkers observed in the Scottish coals have been related to conifer  
652 families (Table 6). The oldest report of conifer megafossils is in the Late  
653 Carboniferous (Westphalian B/Late Bashkirian; Scott, 1974) and the  
654 oldest occurrence of conifer-related saccate pollens is Early Bashkirian  
655 (Zhou, 1994), so that our coals predate the evolution of conifers. Other  
656 precursor(s) must therefore be proposed to explain the presence of  
657 “conifer biomarkers” in the Viséan Scottish coals. *Cordaites* are closely  
658 related to conifers and have been previously proposed as a source of  
659 supposedly typical conifer biomarkers (e.g. Disnar and Harouna, 1994).  
660 However, no data support the presence of *Cordaites* in the flora that  
661 contributed to our Scottish coals. An alternative origin for these  
662 compounds therefore must be found within the Viséan Scottish flora  
663 which was dominated by arborescent or sub-arborescent lycopsids  
664 (Lepidodendrales and Isoetales) with a contribution from ferns,  
665 sphenopsids and lyginopteridacean pteridosperms. Most of these groups  
666 of plants are extinct (Taylor et al., 2009), so that direct comparison with  
667 present-day plants is not possible. Pteridosperms are the closest  
668 relatives to conifers identified in the Scottish Viséan coals (Taylor et al.,  
669 2009), and therefore could have provided the “conifer biomarkers”.  
670 From the palynological content, pteridosperms were not dominant in  
671 the flora of the studied coals (Spinner, 1969; Spinner and Clayton,



1973); a palynological bias is possible, so that pteridosperm biomass would be underestimated in the palynological content (e.g. Phillips et al., 1985; Dimitrova et al., 2005). Pteridosperms, in particular, produced resin (Taylor et al., 2009) and could be at the origin of the resinous secretions observed in our coal samples (Fig. 4C). Lyginopteridacean pteridosperms probably appeared in the latest Devonian (Taylor et al., 2009) but were preceded in the Middle Devonian by progymnosperms, which could therefore be considered for the origin of the “conifer biomarkers” observed in middle Devonian coals (Sheng et al. 1992; Kashirtsev et al., 2010). Progymnosperms, however, were neither described in Chinese nor in Russian Middle Devonian coals (Volkova, 1994; Yi et al., 2007). An alternative source for the “conifer biomarkers” are the arborescent lycopsids (Lepidodendrales) since palynologically, these plants dominated the Scottish flora (Spinner, 1969; Spinner and Clayton, 1973). Lepidodendrales already existed during the Devonian (Taylor et al., 2009) and a recent palaeobotanical study showed that the Middle Devonian Chinese coals were dominated by Lepidodendrales and Protolepidodendrales (Yi et al., 2007). From these observations, arborescent lycopsids appear as another likely 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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1093

1094 **Figure captions**

1095 **Fig. 1.** Simplified geologic map showing the outcrop sample positions at  
1096 Dunbar (White Sand and Skateraw Bays) in the Midland Valley of  
1097 Scotland (modified from Spinner and Clayton, 1973; Underhill et al.,  
1098 2008).

1099

1100 **Fig. 2.** The outcrop geological succession showing alternating  
1101 Carboniferous limestones, shales, sandstones and coals (modified from  
1102 Spinner and Clayton, 1973).

1103

1104 **Fig. 3.** Plot of HI vs.  $T_{max}$  values for Scottish coals (diagram from  
1105 Espitalié et al., 1986).

1106

1107 **Fig. 4.** Photomicrographs of macerals. A) WS-3, reflected natural light.  
1108 Vitrinite particles : telocollinite (Vt) and desmocollinite (Vd). B) Same  
1109 zone as A, blue light fluorescence emphasizing exinite particles:  
1110 fluorescing spores (S) and cuticles (C). C) SKT-E, blue light  
1111 fluorescence. Exinite particles: fluorescing spores (S) and resinite (R)  
1112 filling conducting canals in a vitrinite particle. D) WS-3, reflected  
1113 natural light. Pyrofusinite (P) and spores (S) in a vitrinite (V)  
1114 groundmass.

1115

1116 **Fig. 5.** Total ion current chromatograms of the aliphatic fraction from  
1117 coal extracts. Numbers above symbols denote to carbon number of *n*-  
1118 alkane

1119

1120 **Fig. 6.** Mass chromatograms *m/z* 57 of aliphatic fractions from coal  
1121 samples, showing the distribution of *n*-alkanes, isoprenoids and  
1122 branched alkanes. Numbers above symbols indicate carbon number.

1123

1124 **Fig. 7.** Plot of Pr/*n*-C<sub>17</sub> vs. Ph/*n*-C<sub>18</sub> for Scottish coals (diagram from  
1125 Hunt, 1995).

1126

1127 **Fig. 8.** Mass chromatograms *m/z* 191 of aliphatic fractions from coal  
1128 samples, showing the distribution of hopanes and moretanes. Numbers  
1129 above symbols indicate carbon number. The molecular structure  
1130 represents the standard hopane skeleton.

1131

1132 **Fig. 9.** Mass chromatograms *m/z* 217 of aliphatic fractions from coal  
1133 samples, showing the distribution of steroids. Numbers above symbols  
1134 indicate carbon number.

1135

1136 **Fig. 10.** Steroids ternary plot. The contributions of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub>  
1137 steranes were calculated using the peak height of  $\alpha\alpha\alpha$  (20R) and  $\alpha\beta\beta$   
1138 (20S) isomers on *m/z* 217 fragmentograms. Paleoenvironmental and  
1139 source interpretation from Huang and Meinschein (1979).

1140

1141 **Fig. 11.** Partial  $m/z$  109 + 123 + 179 + 193 mass fragmentograms  
1142 showing the distribution of bicyclic alkanes (+) in the extracts of  
1143 Scottish coals. Peak assignments in Table 3. Numbers denote carbon  
1144 number.

1145

1146 **Fig. 12.** Partial  $m/z$  109 + 123 + 193 + 233 mass fragmentograms  
1147 showing the distribution of diterpenoid hydrocarbons (o) in the extracts  
1148 of Scottish coals. Peak assignments in Table 4. Numbers denote carbon  
1149 number. (A) Mass spectrum of compound identified as C<sub>18</sub> tricyclic  
1150 hydrocarbon (Peak II).

1151

1152 **Fig. 13.** Total ion current chromatograms of aromatic fraction from  
1153 extracts of two selected coal samples. Peak assignments in Table 5  
1154 Abbreviations: MN – methylnaphthalene; EN + DMN – ethyl- and  
1155 dimethylnaphthalene; DBF – dibenzofuran; TMN –  
1156 trimethylnaphthalene; MDBF – methyldibenzofuran; TeMN –  
1157 tetramethylnaphthalene; DMDBF – dimethyldibenzofuran; P –  
1158 phenanthrene; PMN – pentamethylnaphthalene; MP –  
1159 methylphenanthrene; EP + DMP – ethyl- and dimethylphenanthrene;  
1160 PAHs – polycyclic aromatic hydrocarbons; X – contaminant  
1161 (polysiloxanes).

1162

1163 **Fig. 14.** Partial  $m/z$  142+156 mass fragmentograms showing the  
1164 distribution of methyl-, ethyl- and dimethylnaphthalene isomers in the  
1165 aromatic fractions of Scottish coals. Abbreviations: MN –  
1166 methylnaphthalene; EN – ethylnaphthalene; DMN –  
1167 dimethylnaphthalene. Peak assignments in Table 5.

1168

1169 **Fig. 15.** Partial  $m/z$  170 mass fragmentograms showing the  
1170 distribution of trimethylnaphthalene (TMN) isomers in the aromatic  
1171 fractions of Scottish coals.

1172

1173 **Fig. 16.** Partial  $m/z$  184 mass fragmentograms showing the  
1174 distribution of tetramethylnaphthalene (TeMN) isomers in the aromatic  
1175 fractions of Scottish coals.

1176

1177 **Fig. 17.** Partial  $m/z$  178+192 mass fragmentograms showing the  
1178 distribution of phenanthrene (P), anthracene (A), methylphenanthrene  
1179 (MP) and methylantracene (MA) isomers in the aromatic fractions of  
1180 Scottish coals.

1181

1182 **Fig. 18.** Partial  $m/z$  206 mass fragmentograms showing the  
1183 distribution of ethyl- and dimethylphenanthrene isomers in the  
1184 aromatic fractions of Scottish coals. Abbreviations: EP –  
1185 ethylphenanthrene, DMP – dimethylphenanthrene.

1186

1187 **Fig. 19.** Partial  $m/z$  155 + 169 + 183 mass fragmentograms showing a  
1188 series of C<sub>17</sub> to C<sub>19</sub> isohexylalkylnaphthalenes in the aromatic fractions  
1189 of Scottish coals. Peak assignments in Table 5. Abbreviations: iHMN –  
1190 isohexylalkylnaphthalene, PMN – pentamethylnaphthalene, DMP –  
1191 dimethylphenanthrene.

1192

1193 **Fig. 20.** Partial  $m/z$  237 and  $m/z$  223 mass fragmentograms showing  
1194 the distribution of diaromatic tricyclic hydrocarbons in the aromatic  
1195 fractions of Scottish coals. Abbreviations: Sim – simonellite, To –  
1196 diaromatic tricyclic totarane, Semp – diaromatic tricyclic sempervirane,  
1197 Tre - tetrahydroretene. Peak assignments in Table 5. Mass spectra of  
1198 the two tentatively identified tetrahydroretene-derived isomers are also  
1199 showed shown (Tre<sup>1</sup> and Tre<sup>2</sup>).

1200

## 1201 **Table captions**

### 1202 **Table 1**

1203 Bulk and molecular geochemical parameters from Scottish coals.

1204

### 1205 **Table 2**

1206 Petrographic composition and vitrinite reflectance.

1207

### 1208 **Table 3**

1209 Bicyclic alkanes identified.

1210

1211 **Table 4**

1212 Diterpenoid hydrocarbons identified.

1213

1214 **Table 5**

1215 Aromatic hydrocarbons identified.

1216

1217 **Table 6**

1218 Maturity indicators from aromatic fractions of Carboniferous coal

1219 samples.

1220

1221 **Table 7**

1222 List of target saturated and aromatic land plant biomarkers and their

1223 origin.

1224

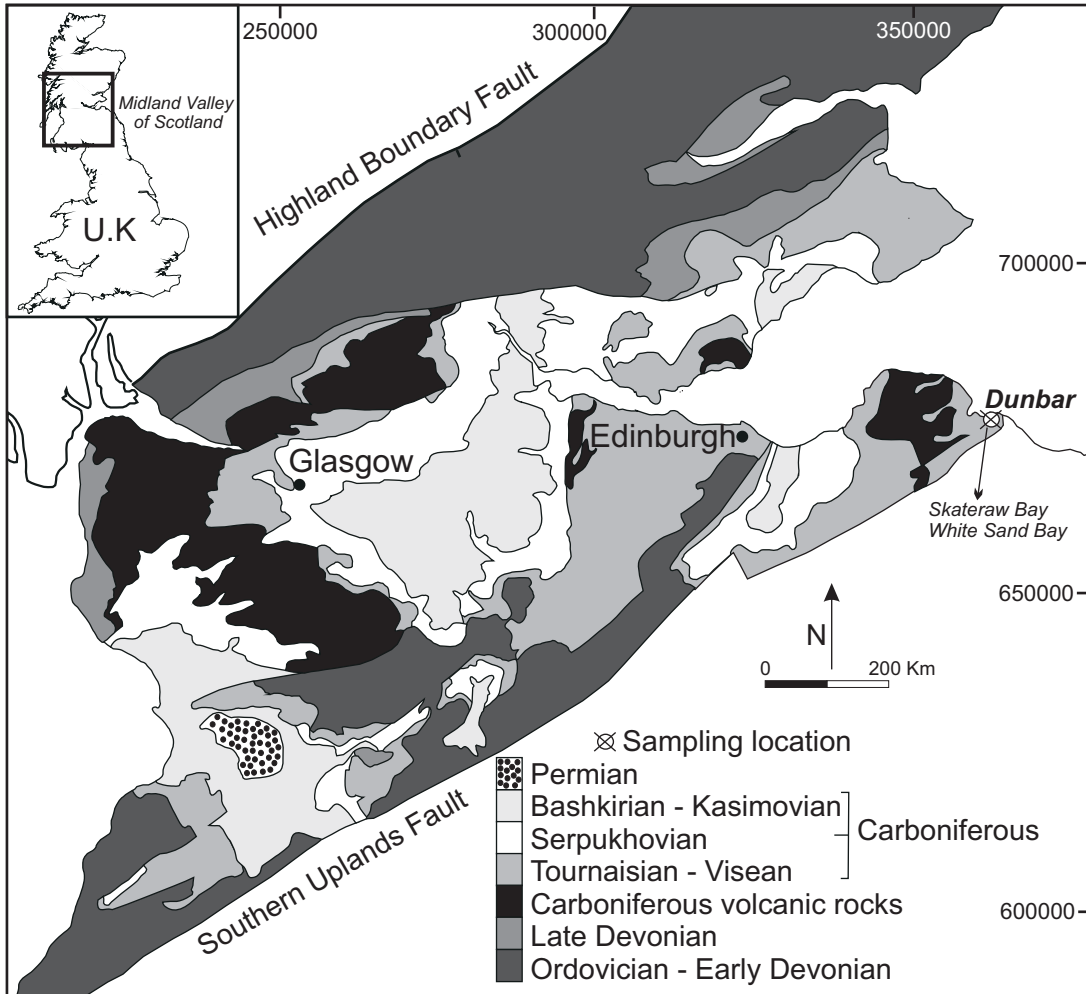
1225 **Appendix**

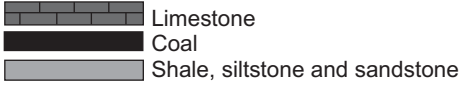
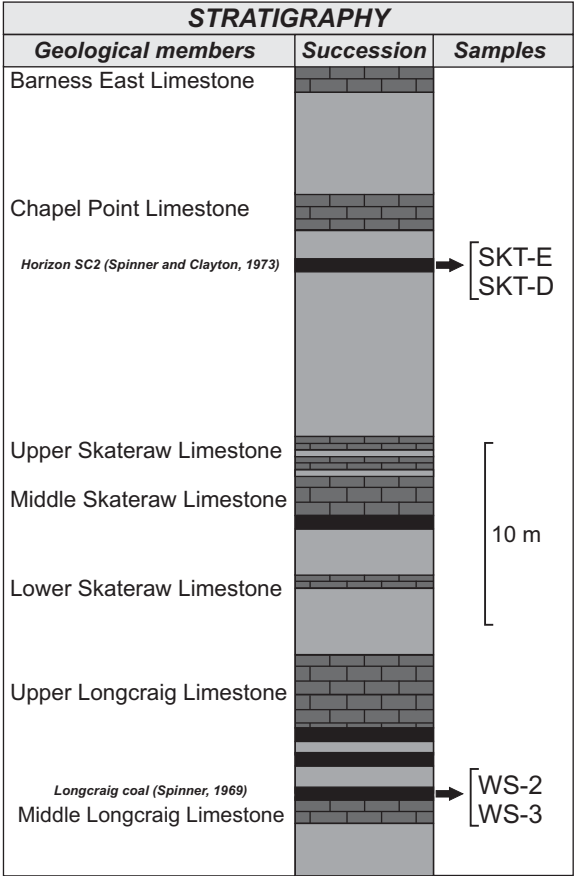
1226 Mass spectra of unknown compounds (Peak assignments in Tables 2

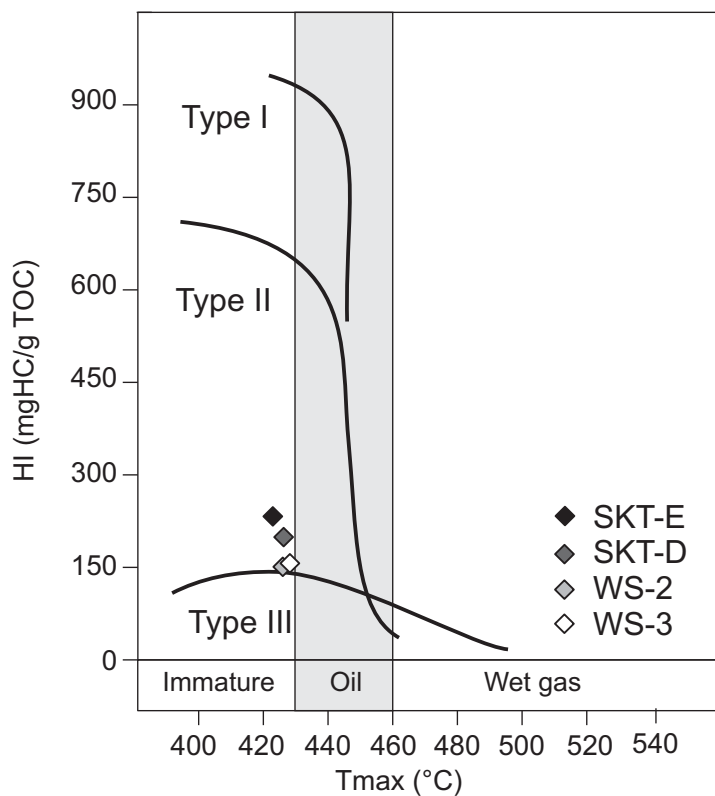
1227 and 3).

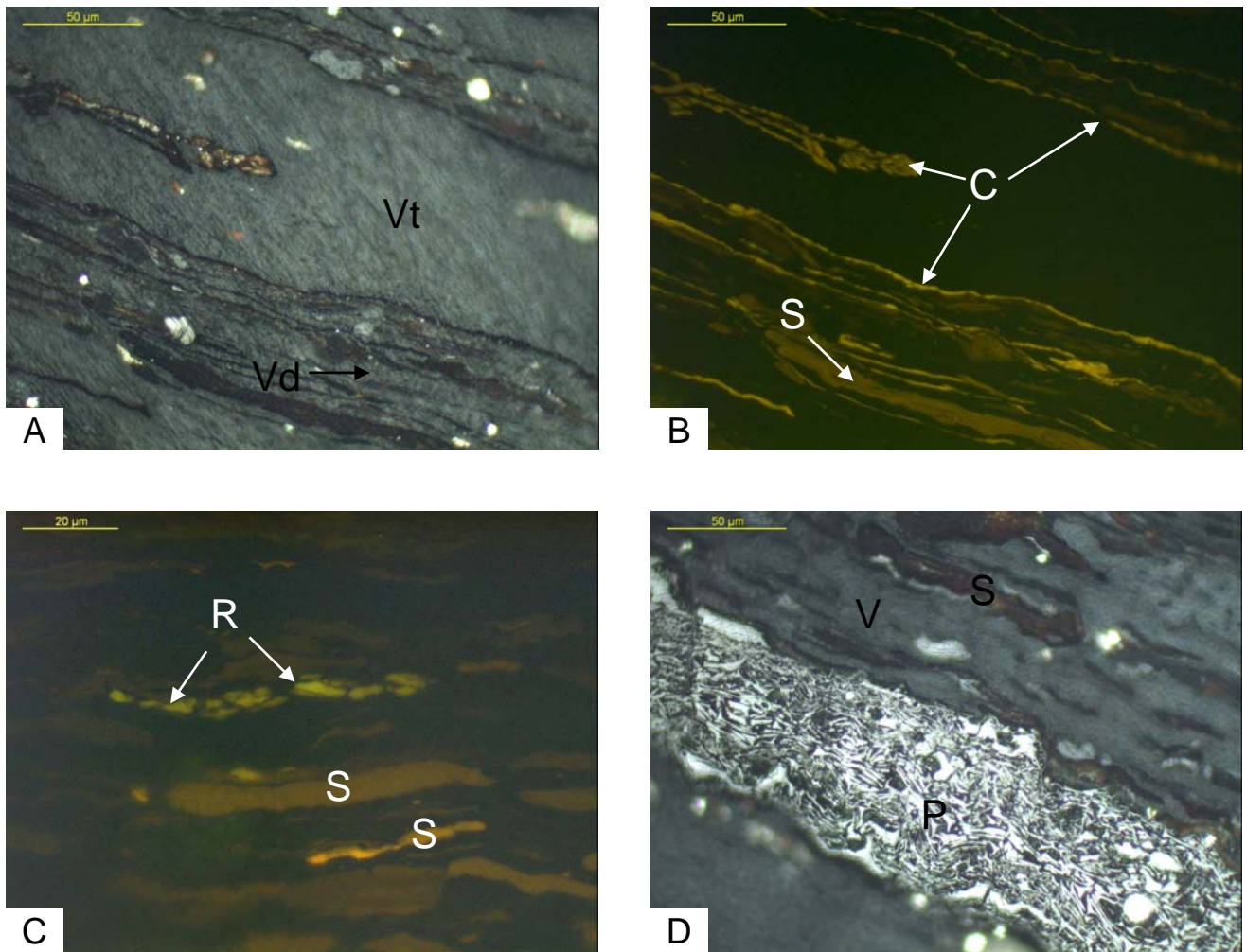
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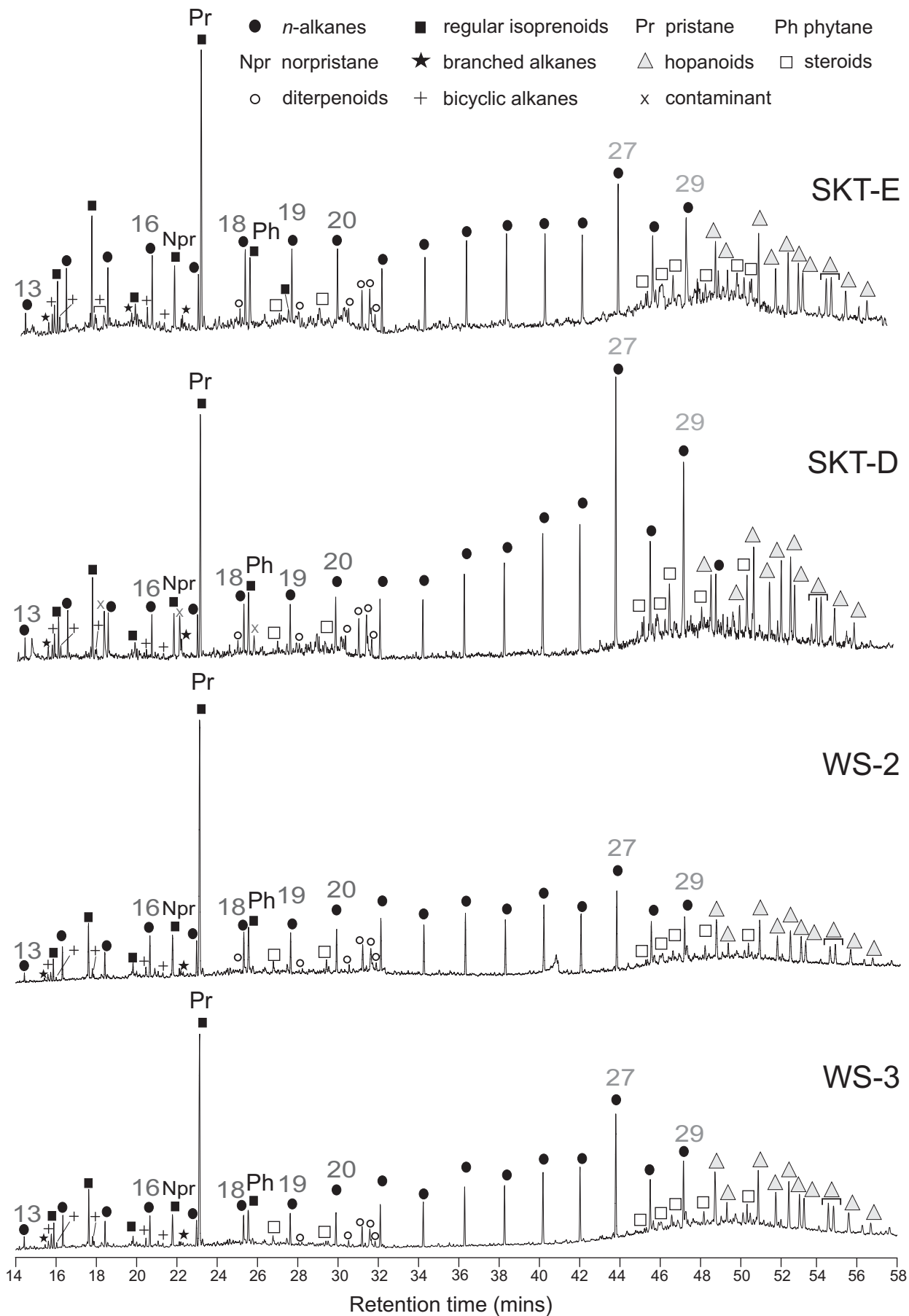


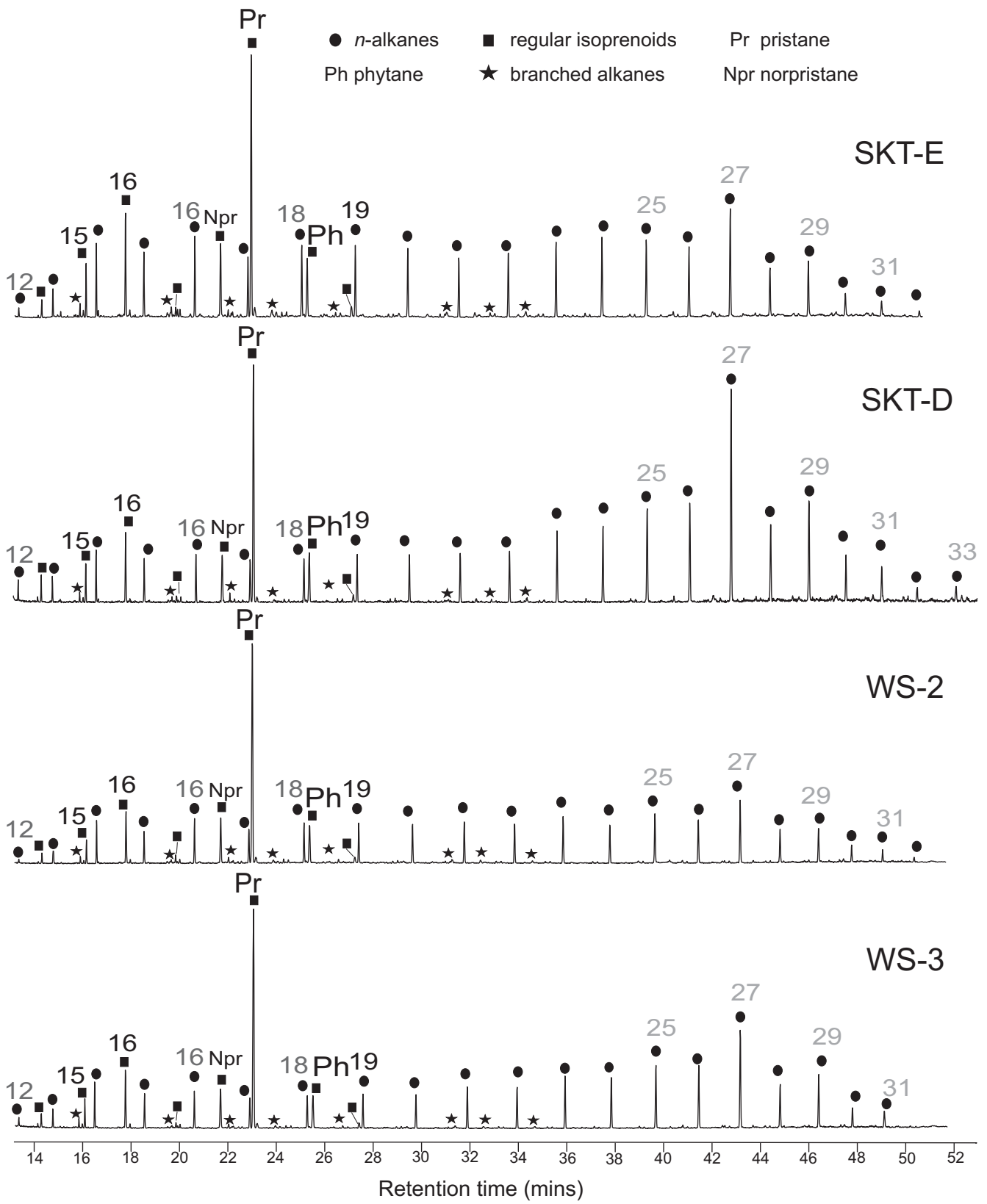


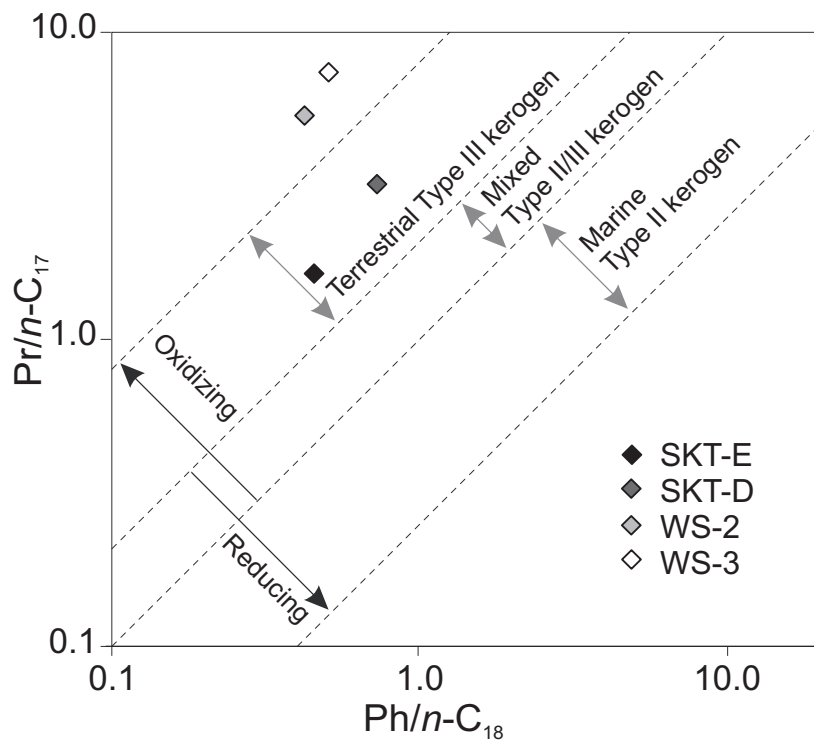


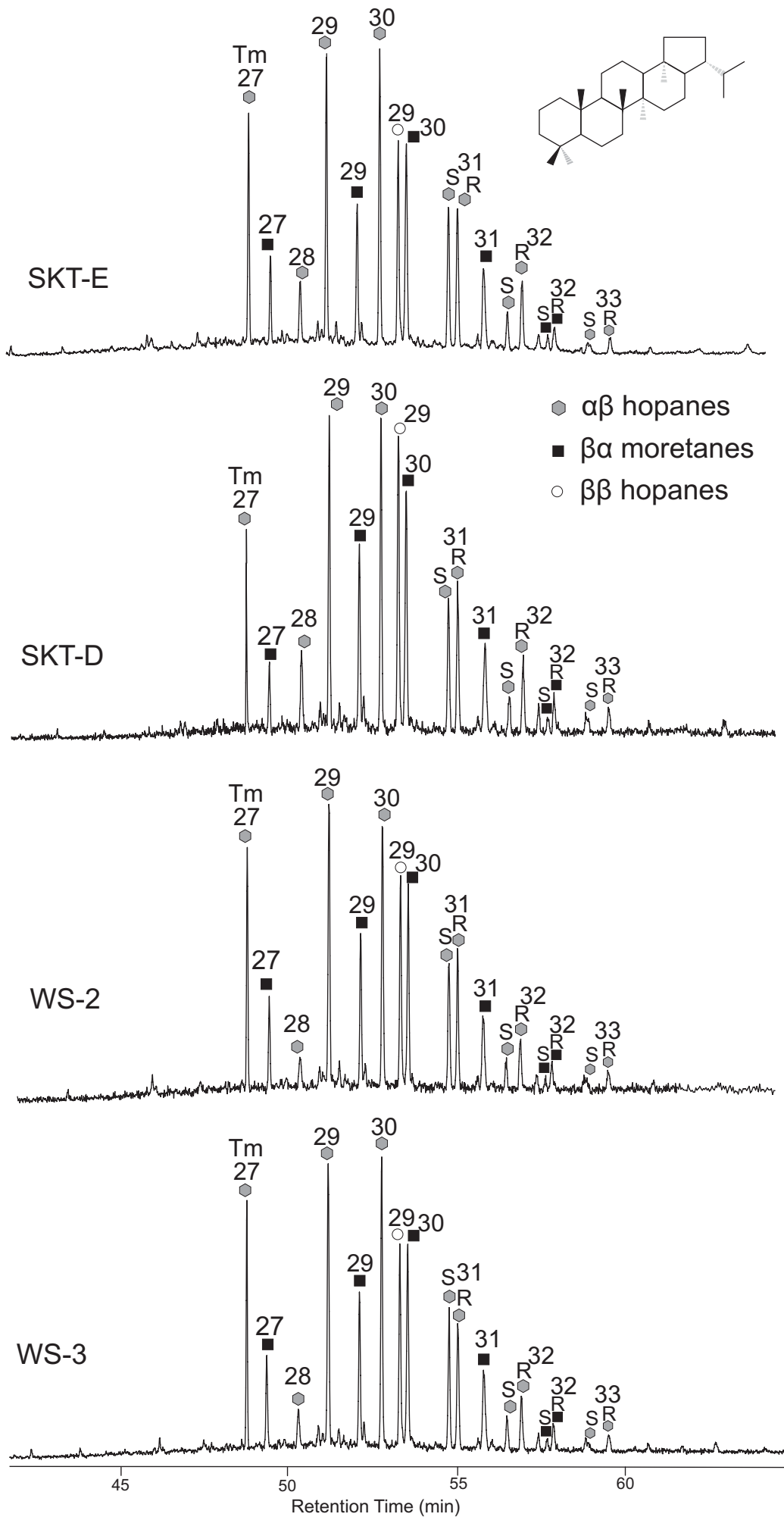


**Fig. 4.** Photomicrographs of macerals A) WS-3, reflected natural light. Vitrinite particles : telocollinite (Vt) and desmocollinite (Vd). B) Same zone as A, blue light fluorescence emphasizing exinite particles: fluorescing spores (S) and cuticles (C). C) SKT-E, blue light fluorescence. Exinite particles: 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.

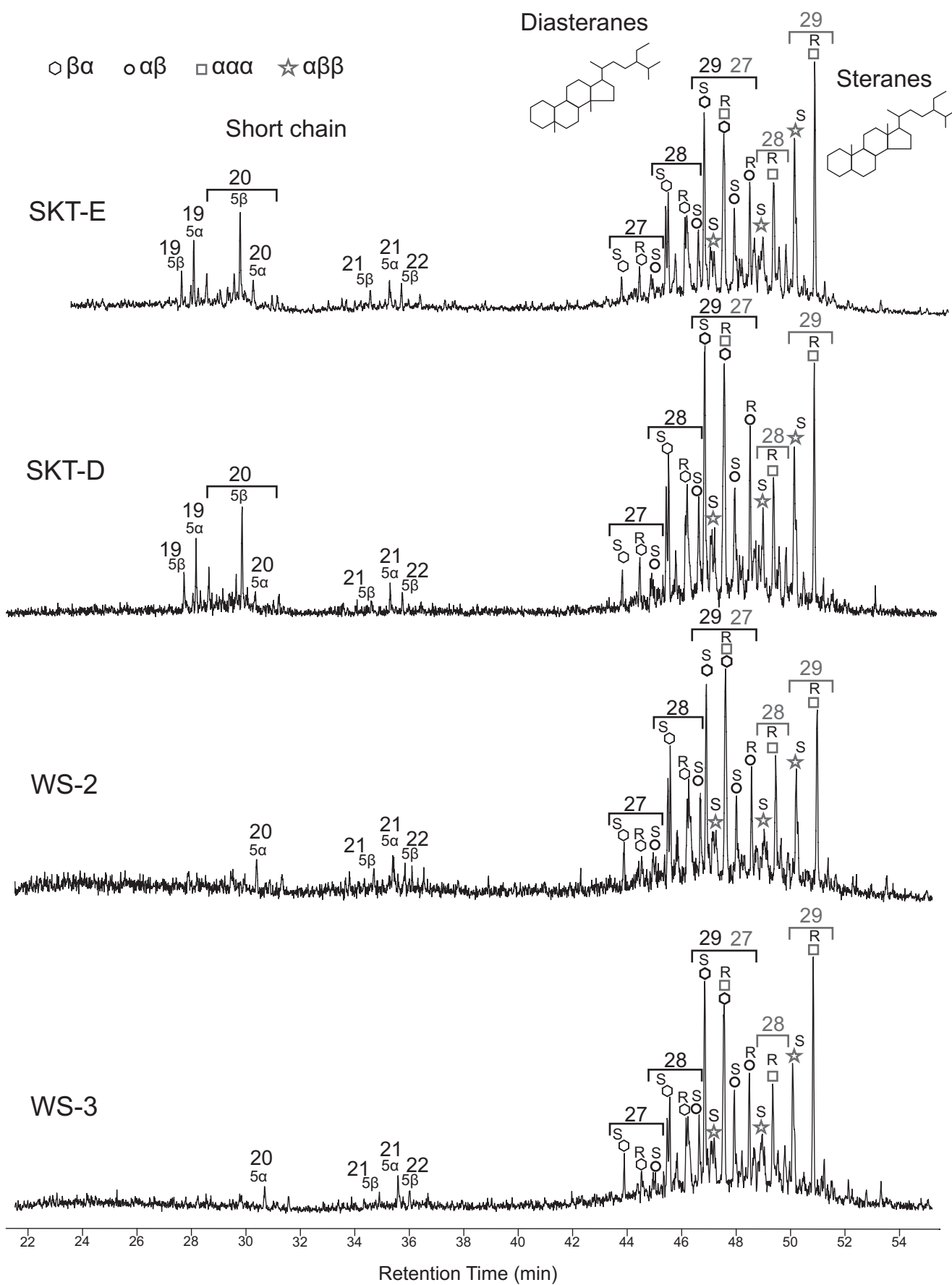


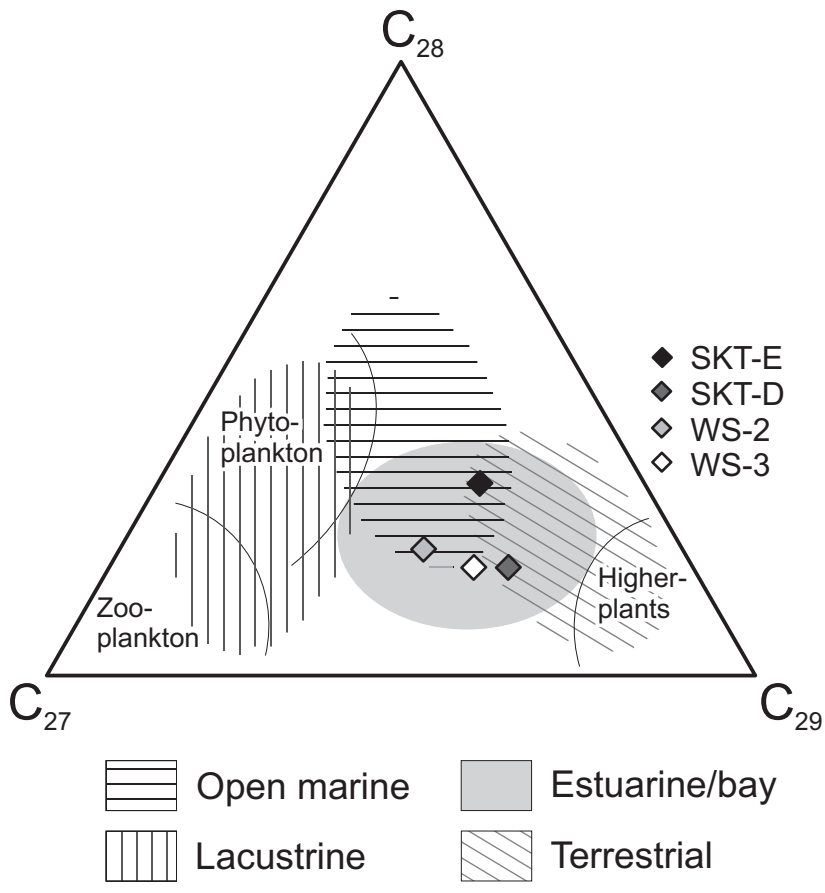


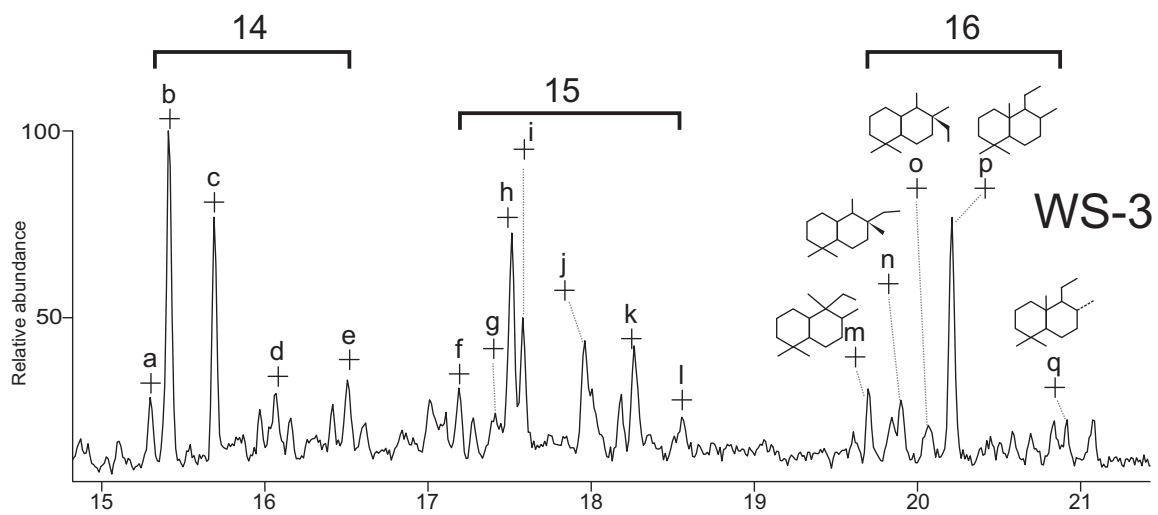
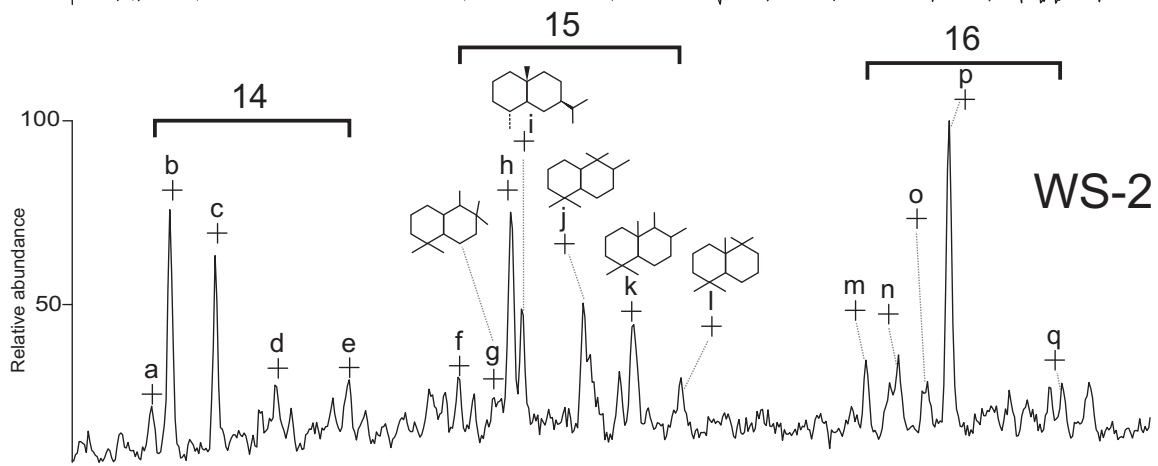
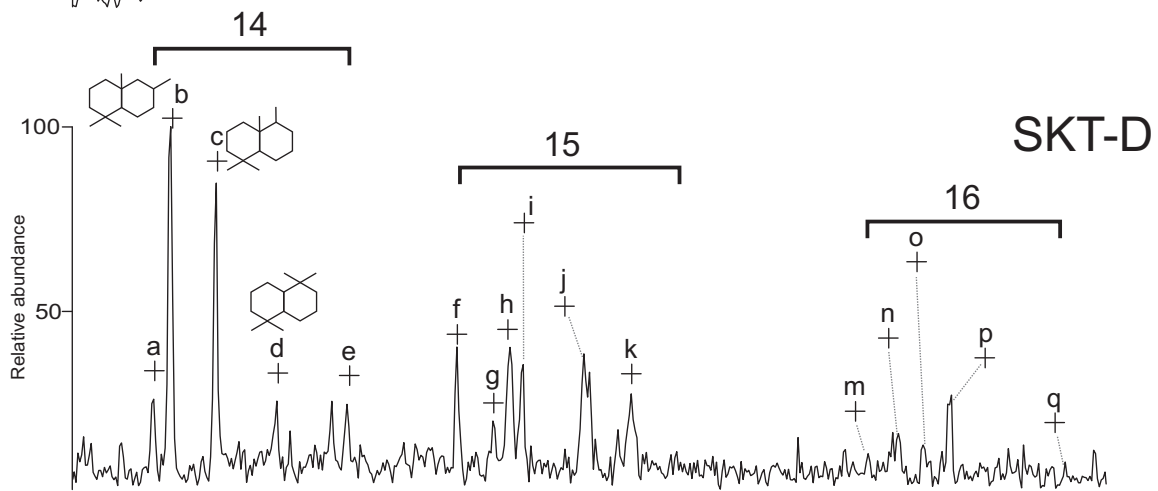
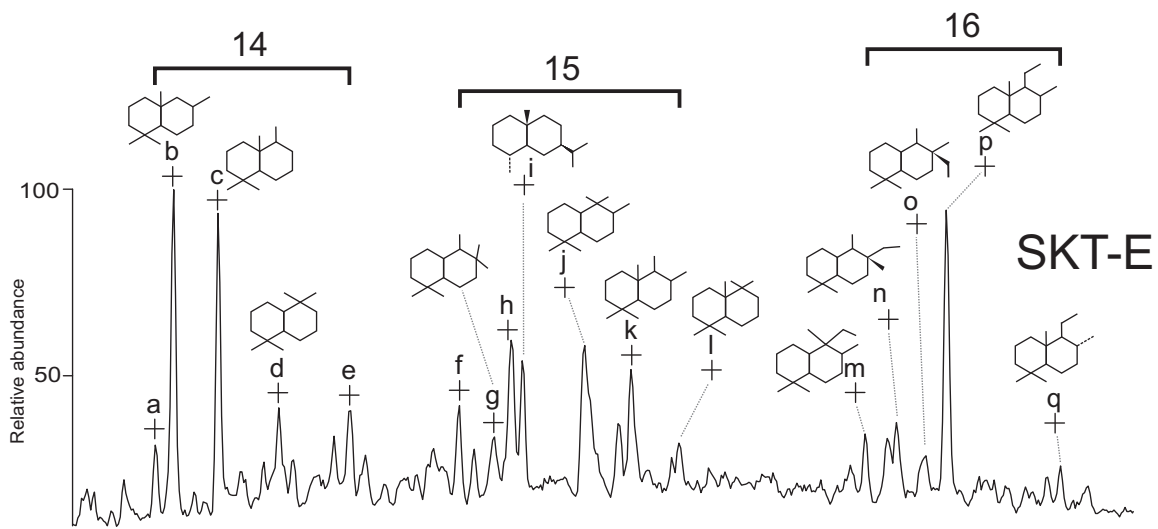




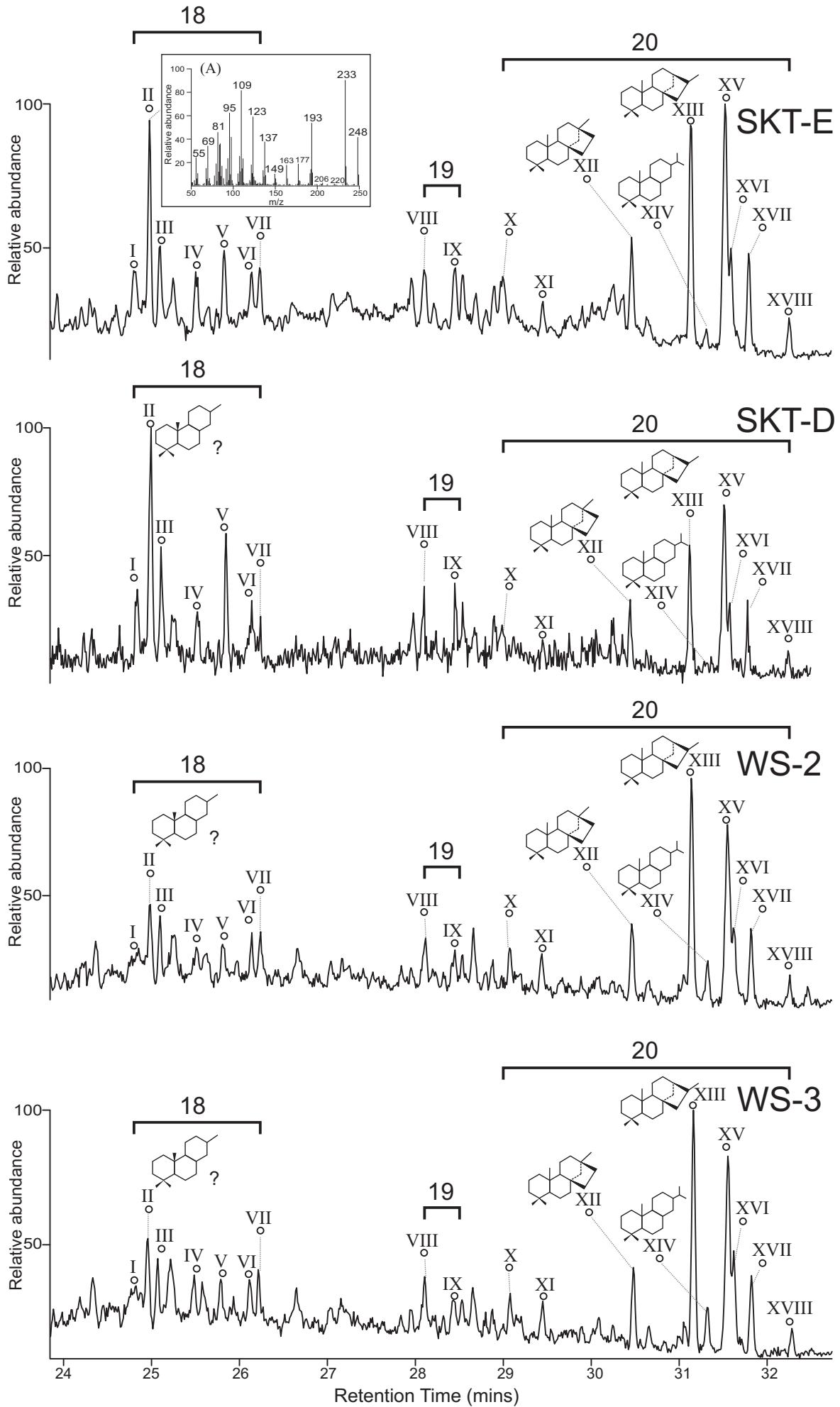




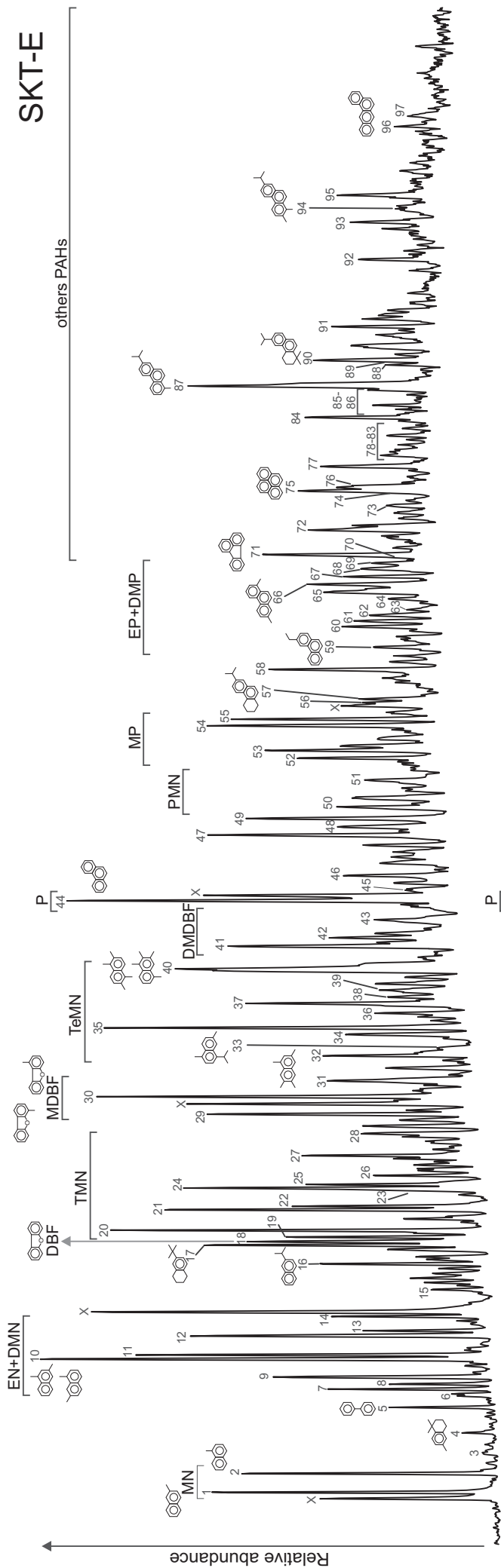




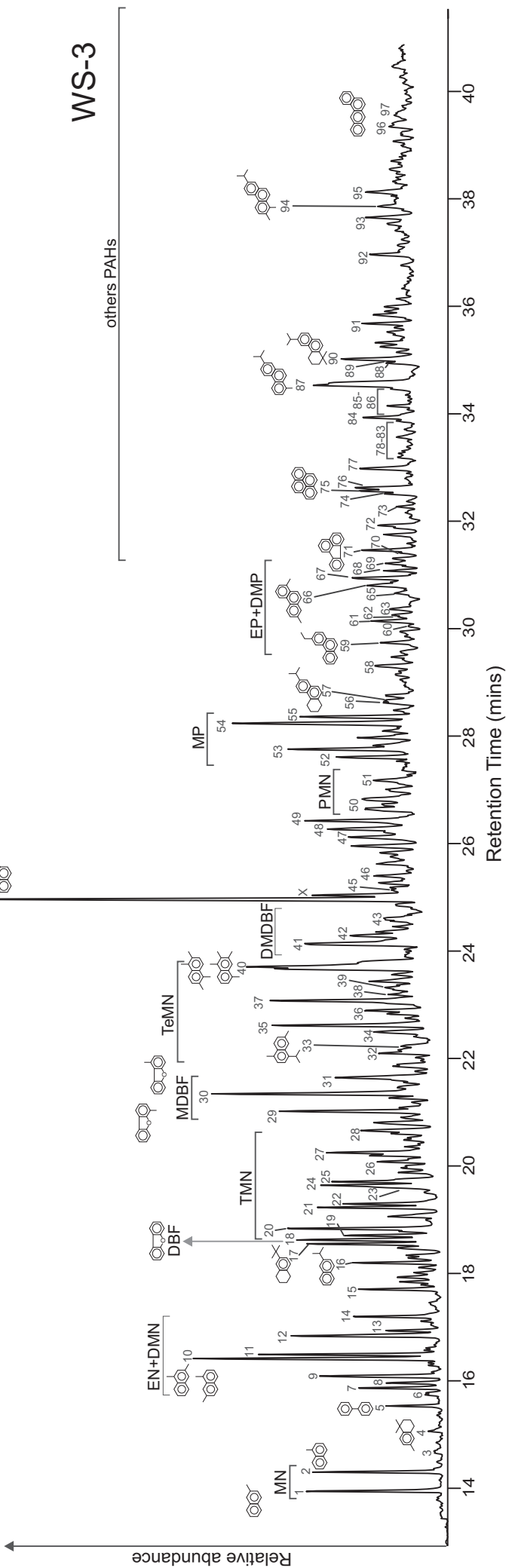
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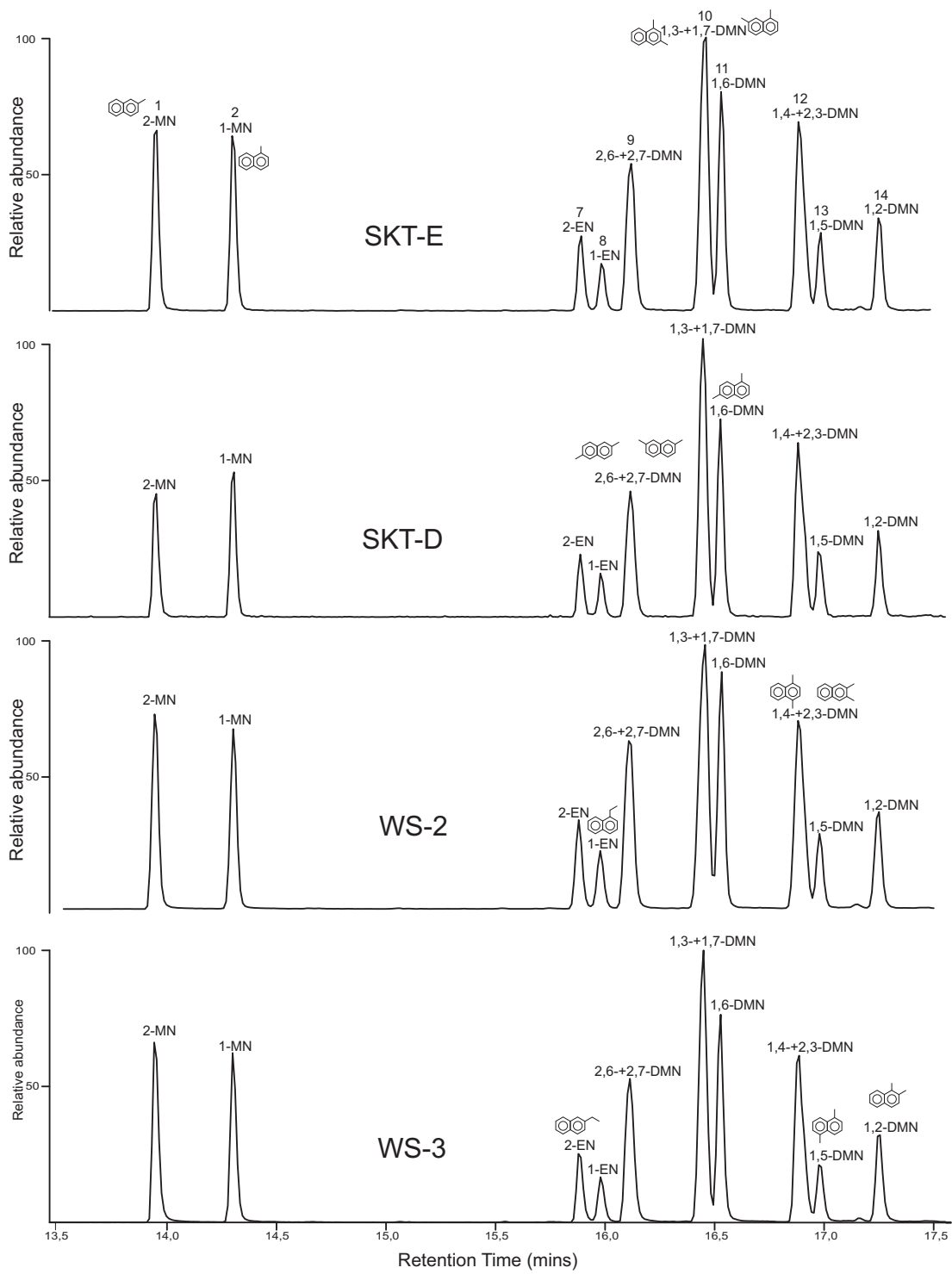


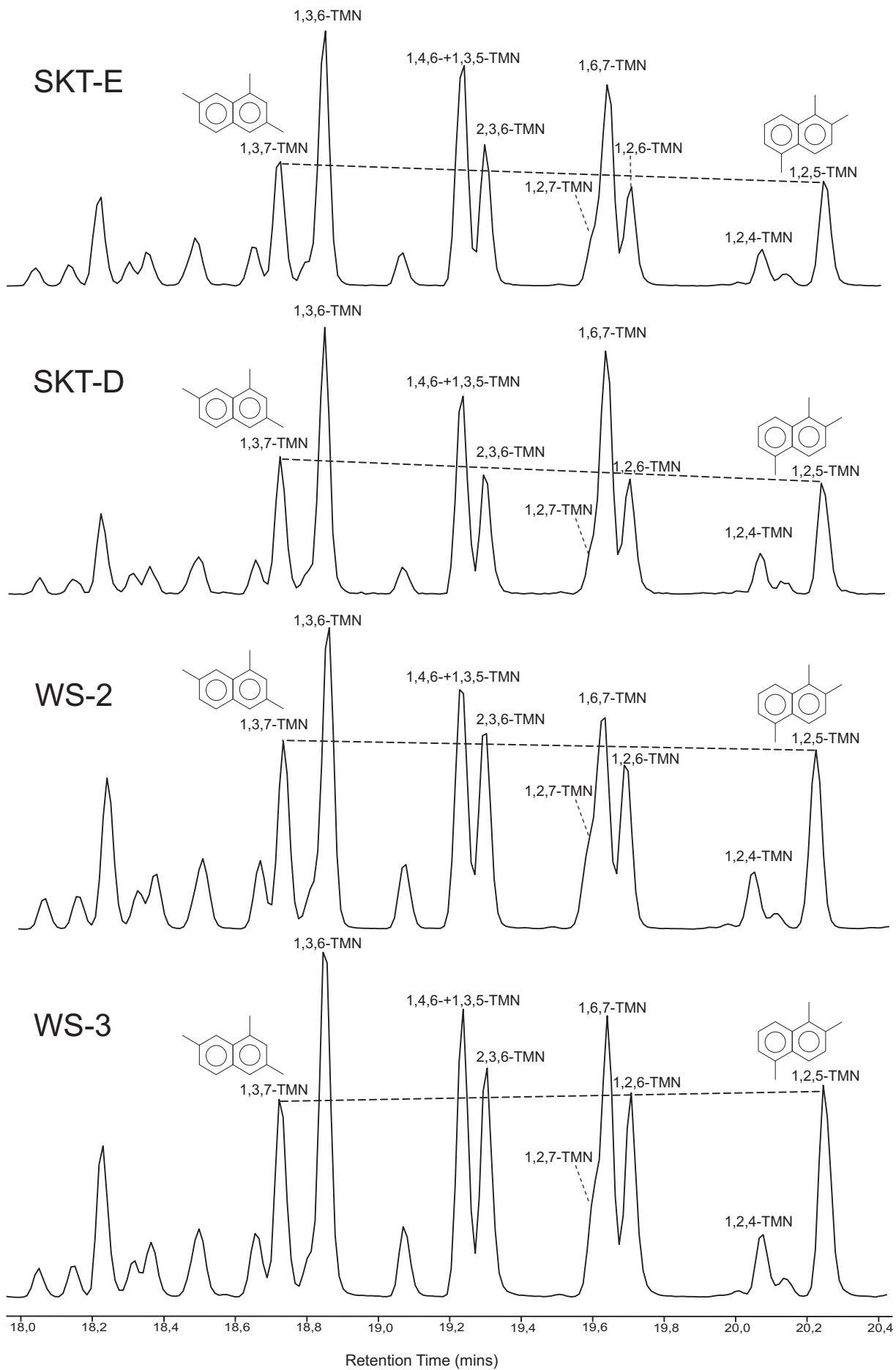
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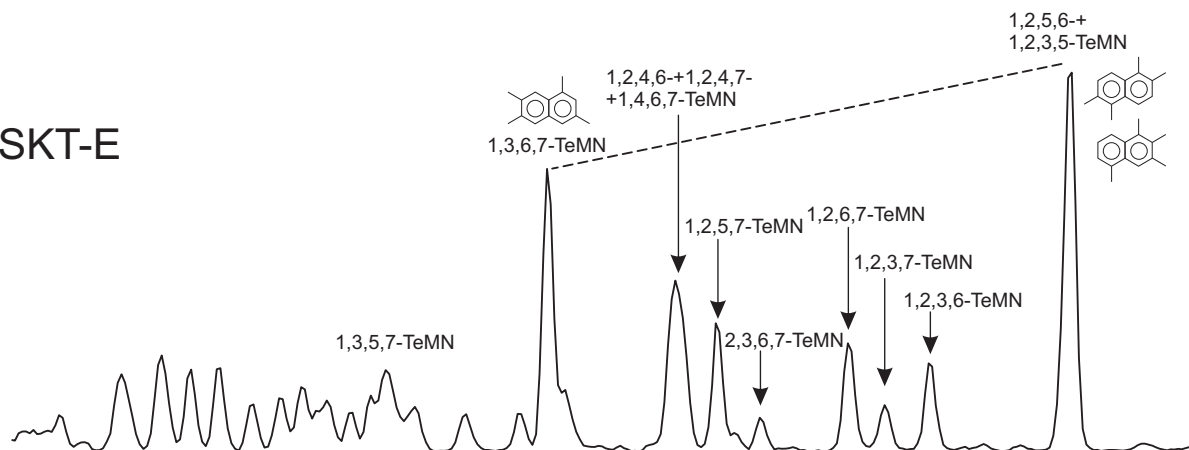
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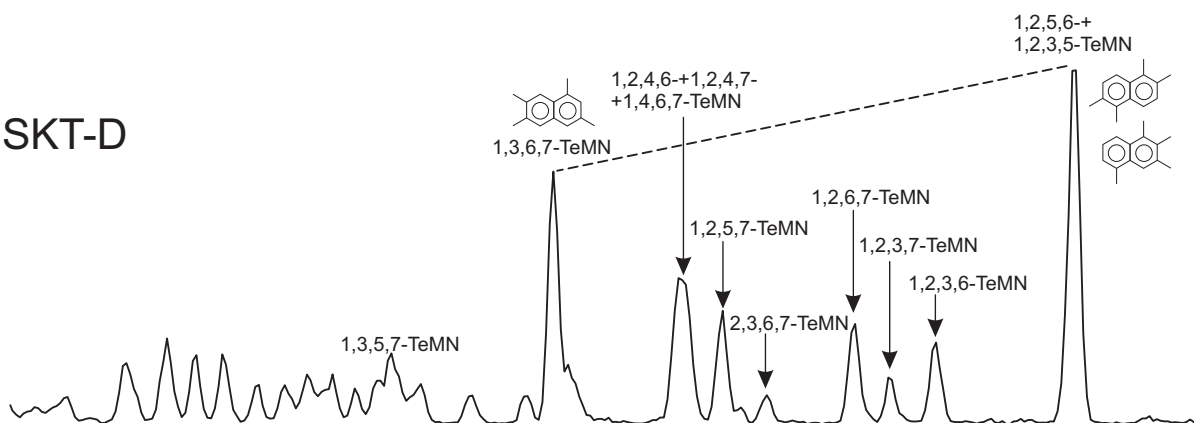




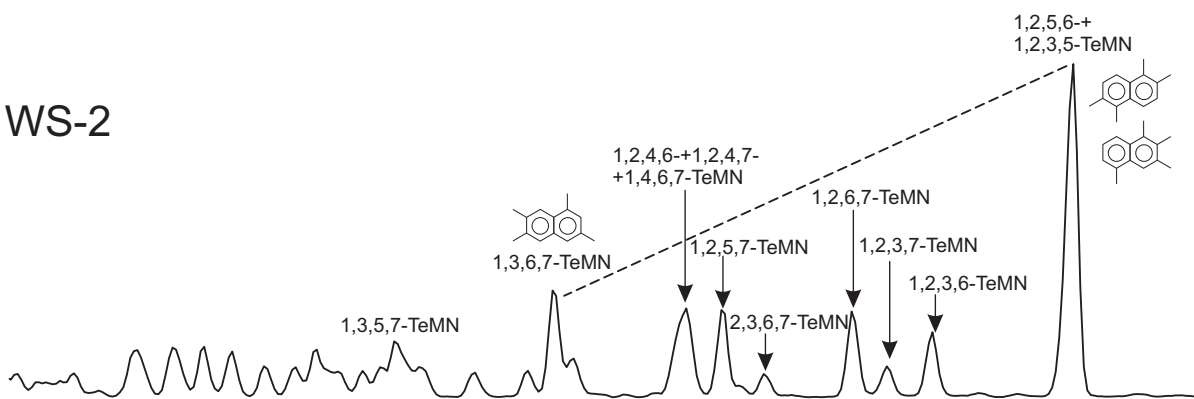
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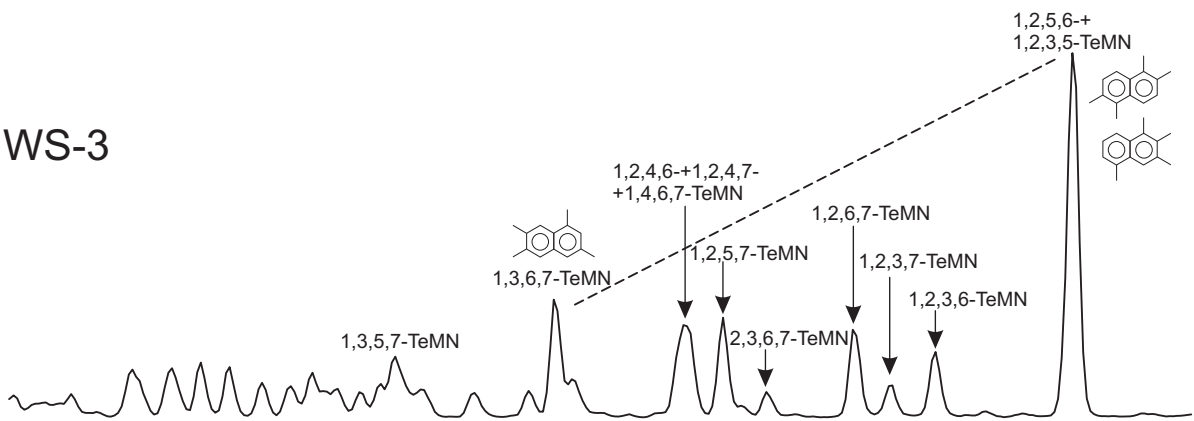
SKT-D



WS-2



WS-3

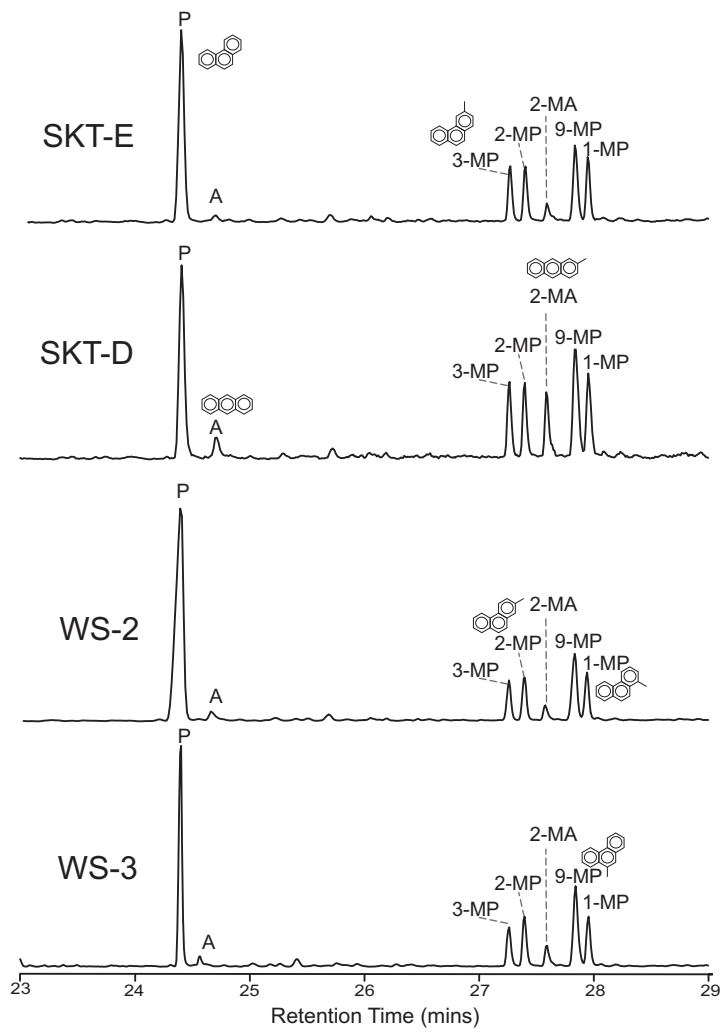


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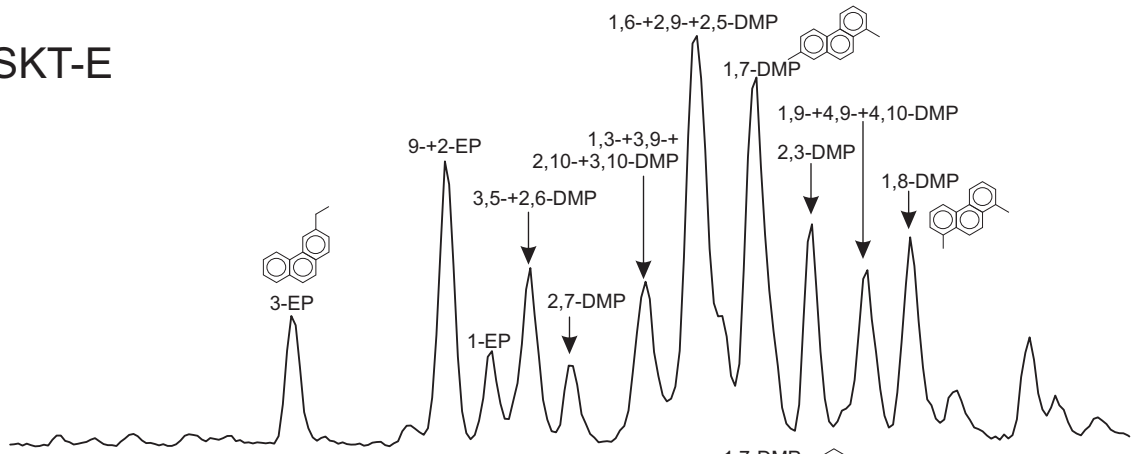
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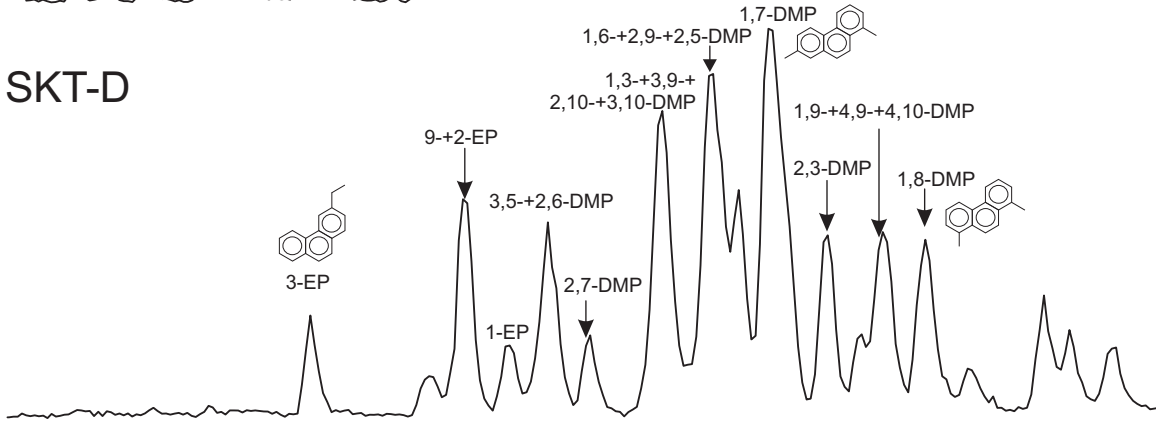




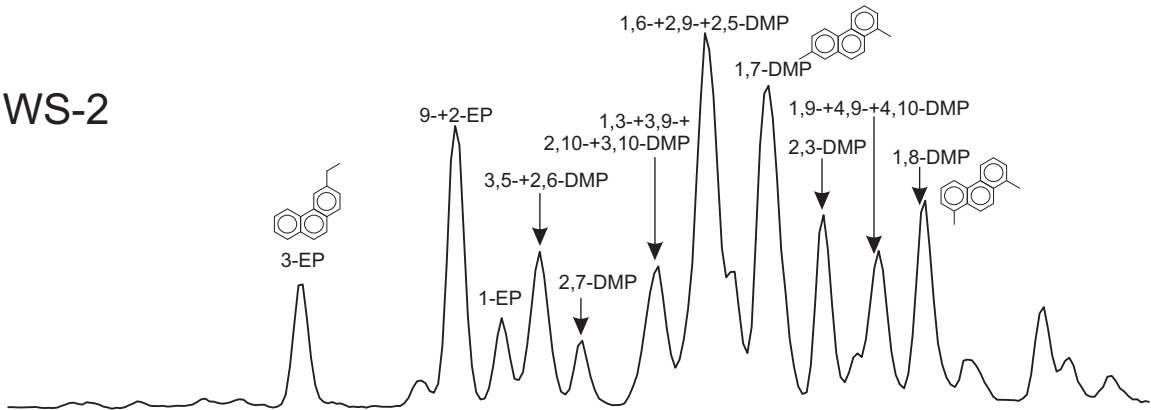
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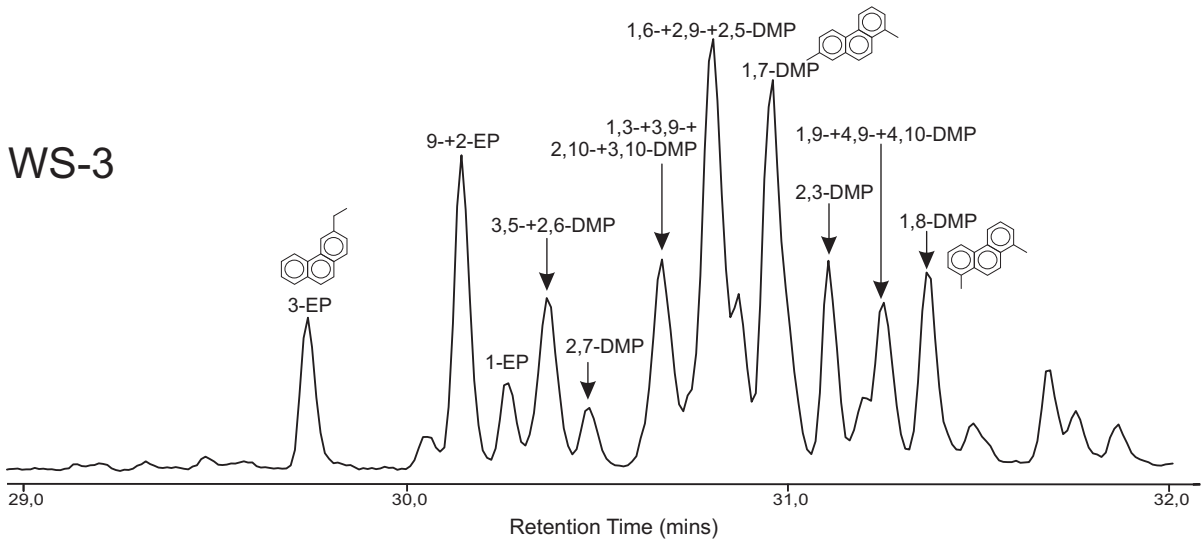
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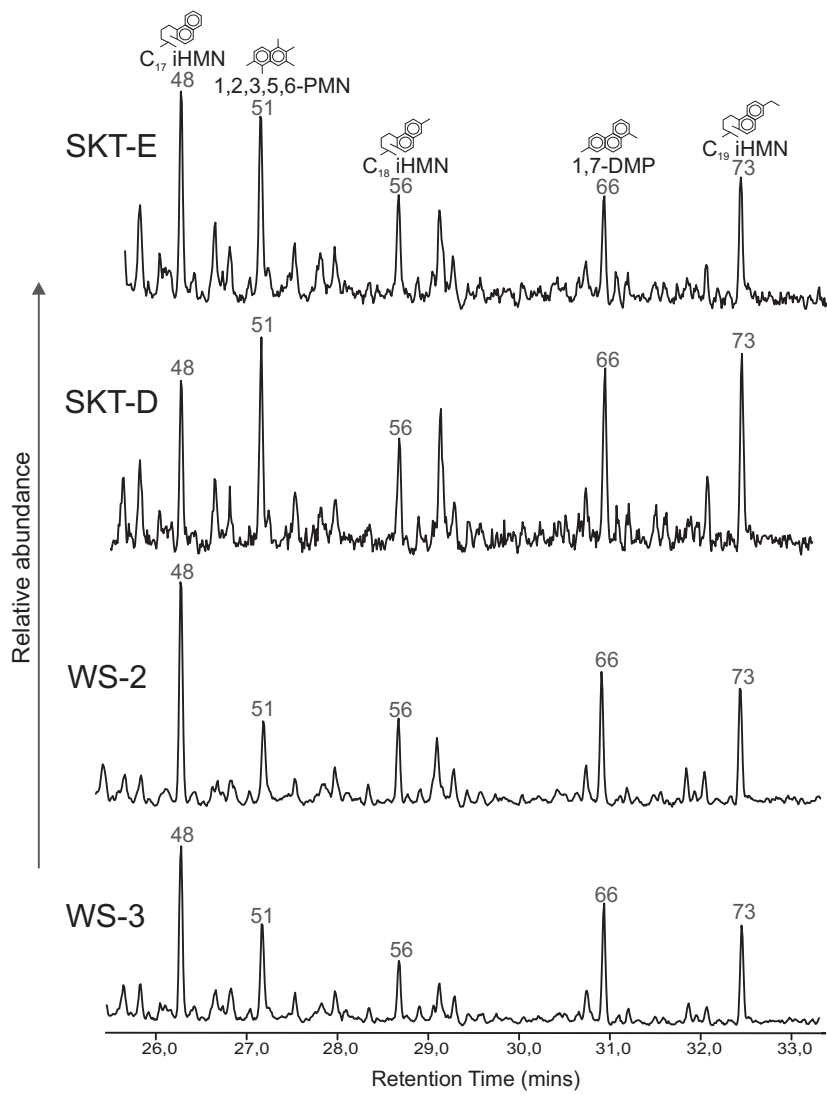


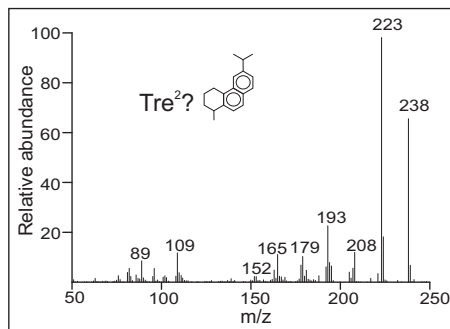
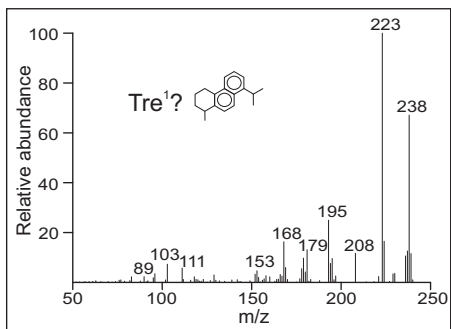
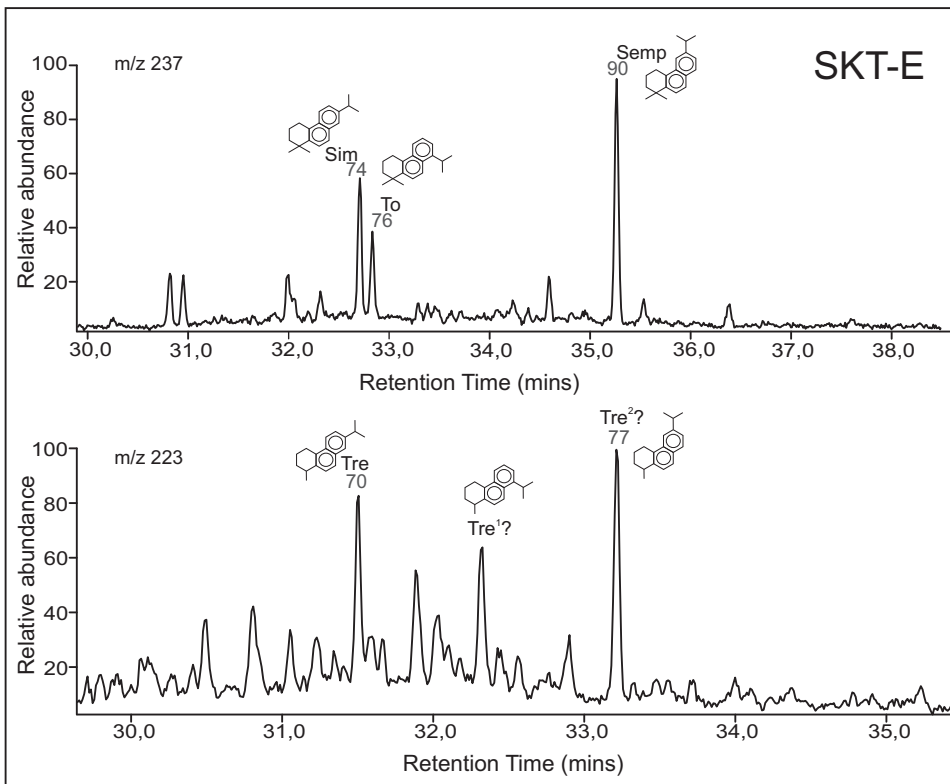
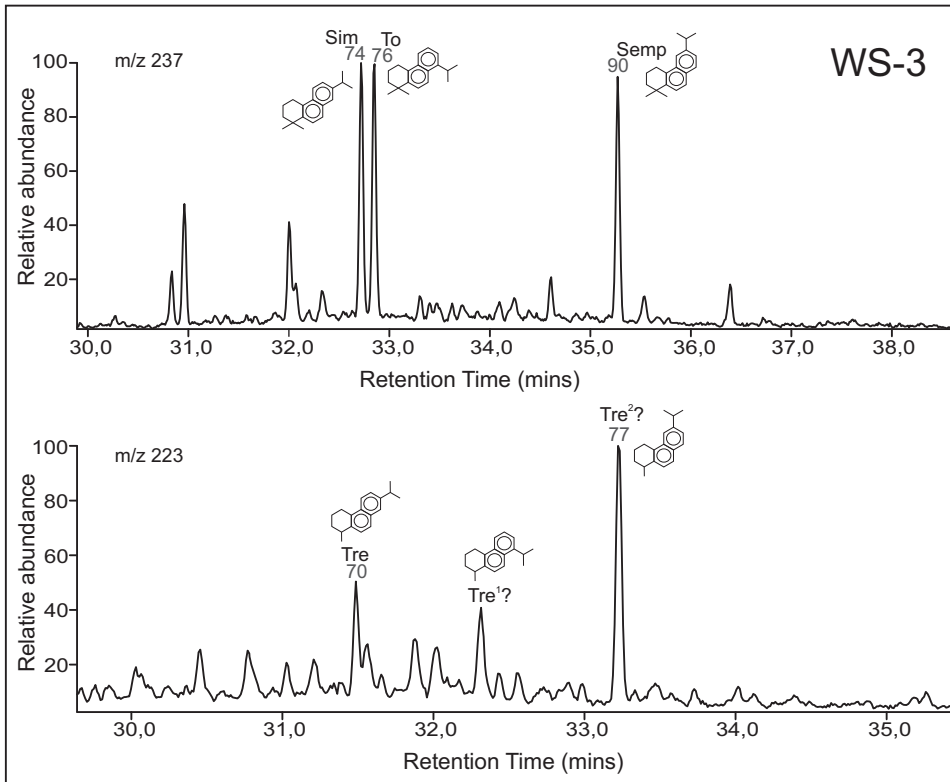
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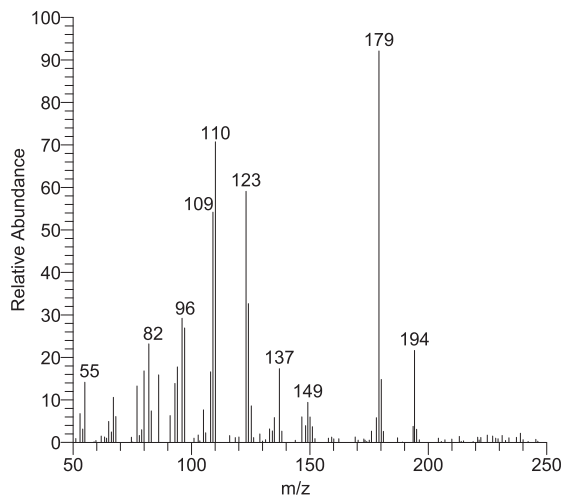


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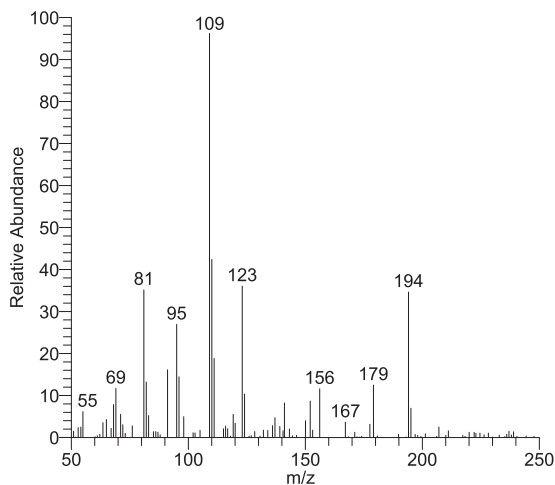




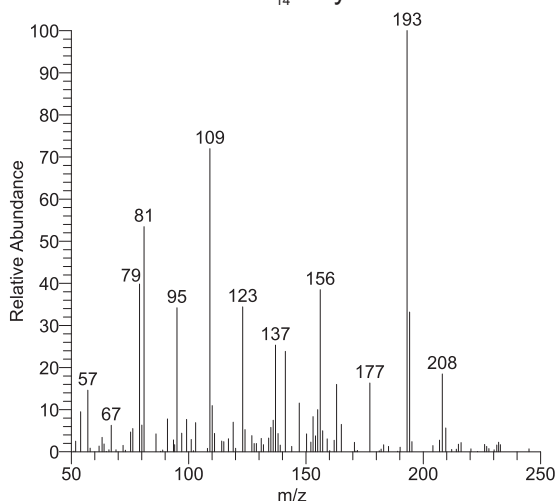




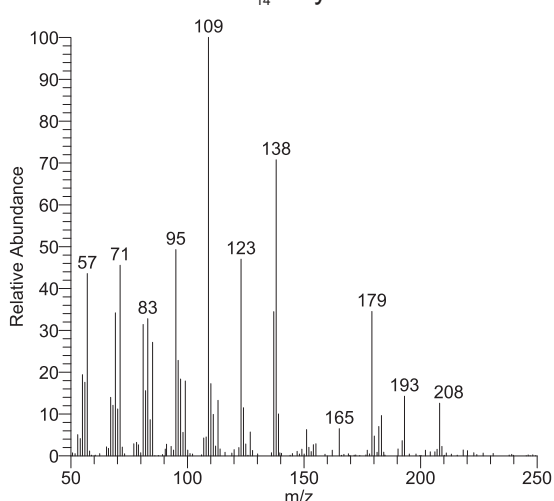
Peak a: C<sub>14</sub> bicyclic alkane?



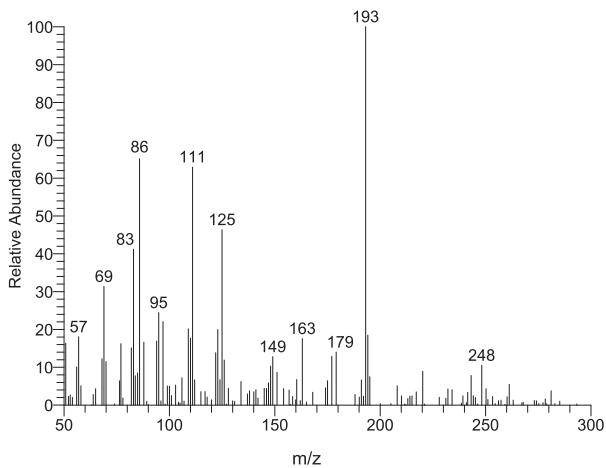
Peak e: C<sub>14</sub> bicyclic alkane?



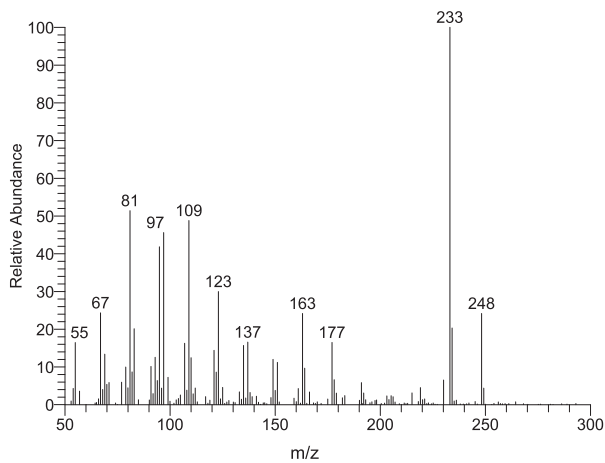
Peak f: C<sub>15</sub> bicyclic alkane?



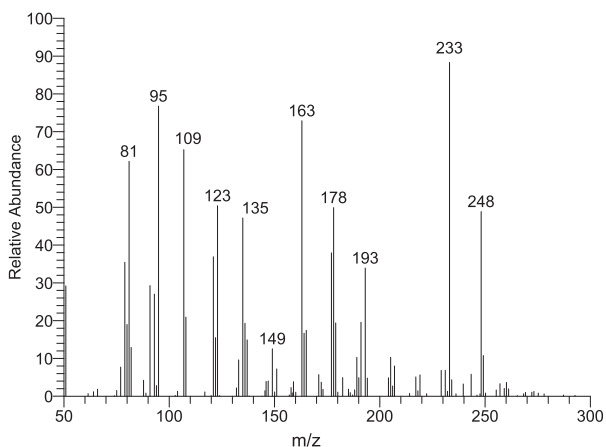
Peak h: C<sub>15</sub> bicyclic alkane?



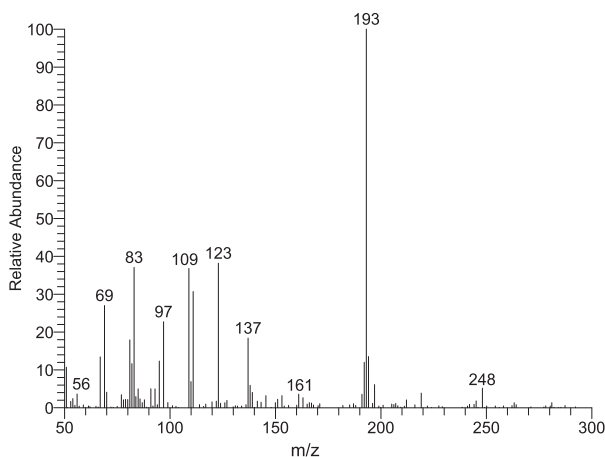
Peak I: C<sub>18</sub> tricyclic hydrocarbon?



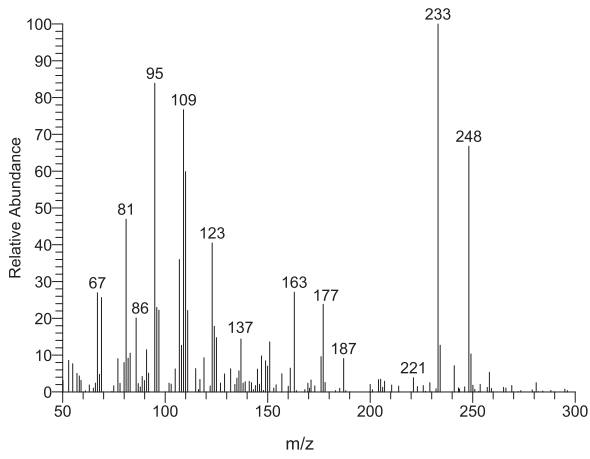
Peak III: C<sub>18</sub> tricyclic hydrocarbon?



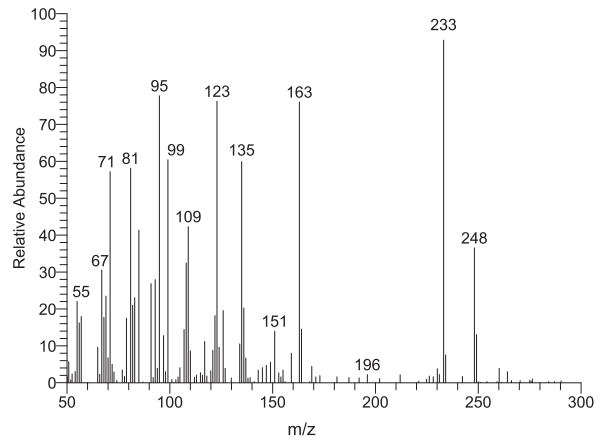
Peak IV: C<sub>18</sub> tricyclic hydrocarbon?



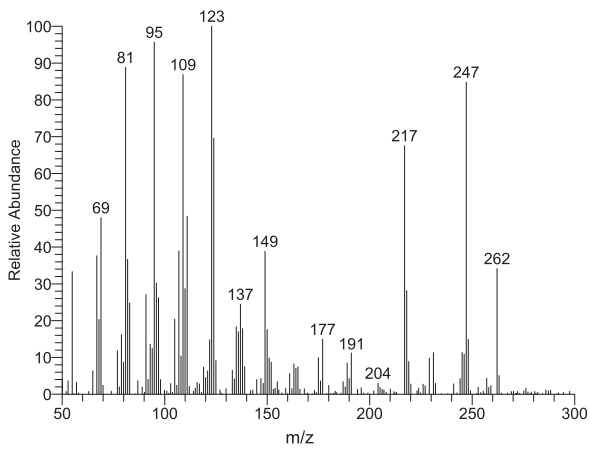
Peak V: C<sub>18</sub> tricyclic hydrocarbon?



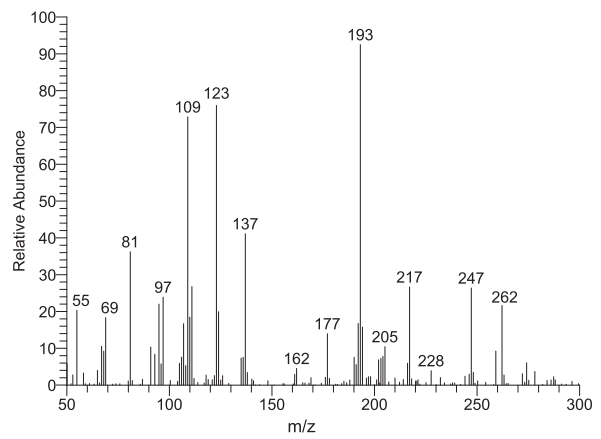
**Peak VI: C<sub>18</sub> tricyclic hydrocarbon?**



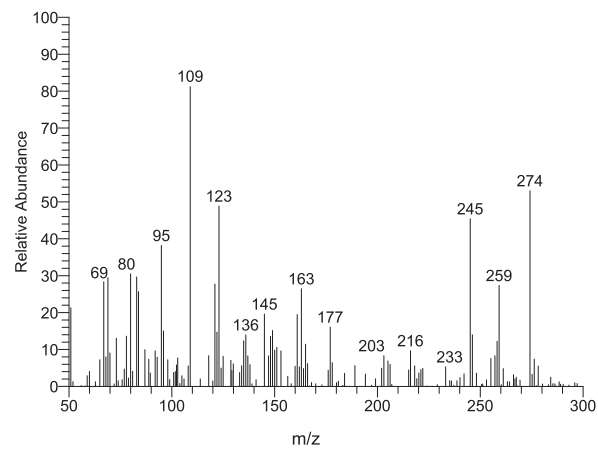
**Peak VII: C<sub>18</sub> tricyclic hydrocarbon?**



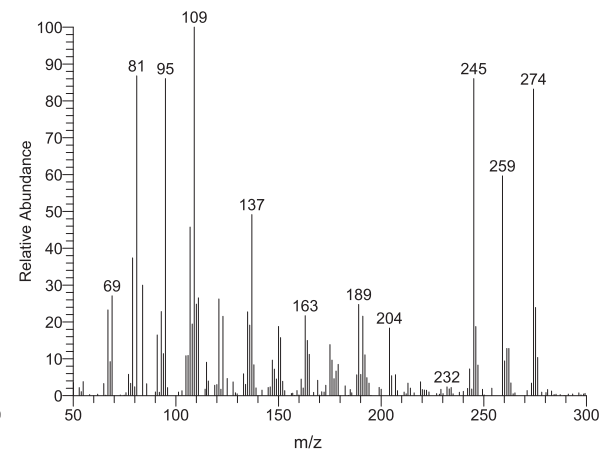
**Peak VIII: C<sub>19</sub> tricyclic hydrocarbon?**



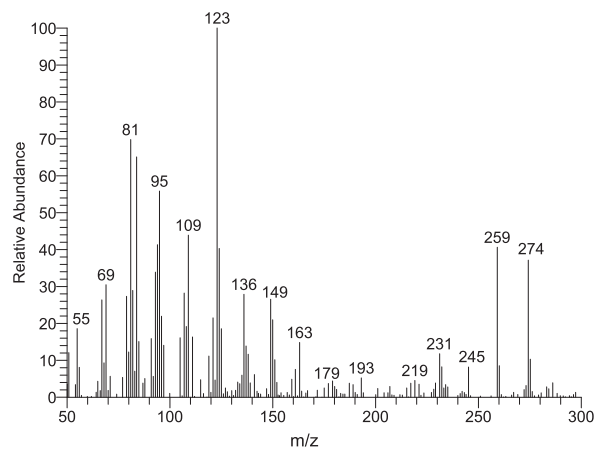
**Peak IX: C<sub>19</sub> tricyclic hydrocarbon?**



**Peak X: C<sub>20</sub> tetracyclic diterpenoid?**



**Peak XI: C<sub>20</sub> tetracyclic diterpenoid?**



**Peak XVIII: C<sub>20</sub> tetracyclic diterpenoid?**