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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 β (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 S₂ 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 C₁₃
184 to C₃₀. The distribution of *n*-alkanes is relatively similar in all four
185 samples and the most abundant are *n*-C₂₇ and *n*-C₂₉ (Fig. 6). Long chain
186 C₂₃ – C₃₃ *n*-alkanes are characterized by an odd-over-even
187 predominance with a maximum at *n*-C₂₇ (Fig. 6). The carbon preference
188 index (CPI) ranges between 1.65 and 1.93 (Table 1). Series of C₁₄ to C₂₁
189 acyclic isoprenoids dominated by norpristane (C₁₈), pristane (Pr; C₁₉)
190 and phytane (Ph; C₂₀), were also detected (Fig. 6). Pr is the most
191 abundant compound in all the samples except SKT-D, where the *n*-C₂₇
192 alkane is more abundant (Fig. 5). The Pr/Ph ranges from 7.33 to 14.67
193 (Table 1). The Pr/*n*-C₁₇ is more than 1, whereas the Ph/*n*-C₁₈ 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 C₂₇ to C₃₃, with
203 a maximum at C₂₉ or C₃₀ hopanes (Fig. 8).

204 Series of $\beta\alpha$ -moretanes (17 β (H),21 α (H)-moretanes) were also
205 detected ranging from C₂₇ to C₃₂, with a maximum at C₃₀ (Fig. 8). C₂₉
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 C₂₉
214 5 α (H),14 α (H),17 α (H)-20R regular sterane (C₂₉ $\alpha\alpha\alpha$ -sterane; Fig. 9 and
215 10), followed by an important contribution of the $\alpha\beta\beta$ isomer (Fig. 9).
216 Diasteranes are dominated by C₂₉ $\beta\alpha$ -diasteranes. However, series of
217 C₂₇ to C₂₉ $\alpha\beta$ -diasteranes and C₂₇ to C₂₉ $\alpha\beta\beta$ -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 C₁₉ - C₂₀ steroids in comparison with WS
221 samples (Fig. 9).

222

223 4.3.4. Bicyclic alkanes

224 Seventeen bicyclic alkanes ranging from C₁₄ to C₁₆ 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 β (H)-eudesmane; 8 β (H)-drimane;
230 8 β (H)- and 8 α (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 C₁₄ bicyclic alkanes (Fig. 11; e.g.
238 Peaks b and c). 8 β (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 β (H)-eudesmane and 8 β (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 (C₂₀H₃₄) *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 C₁₈ tricyclic
258 hydrocarbon (Fig. 12). This latter compound is particularly abundant in
259 SKT samples, as are C₁₉ and C₂₀ steranes, it could therefore be related
260 to short chain steroids. To our knowledge, the molecular structures for
261 most of the C₁₈ – C₁₉ 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 C₂₀ 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 (Tre¹
362 and Tre²) 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 Tre¹ could be the 1-methyl-1,2,3,4-tetrahydro-
372 8-isopropylphenanthrene (totarane-derived) and Tre² 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 C₂₉ ββ hopane is observed in all samples

387 (Fig. 8; Seifert and Moldowan, 1980). Third, the high thermal maturity
388 markers in sediments 18 α -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*-C₁₇ vs. Ph/*n*-C₁₈ 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 C₂₇, C₂₈ and C₂₉ sterols (Fig. 10).
449 Based on their results, the dominant source of C₂₇ sterols is
450 zooplankton, C₂₈ sterols are generally components of phytoplankton and
451 C₂₉ sterols are mainly derived from terrestrial plants. There are many
452 exceptions on these rules; for instance, C₂₉ 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 C₂₉ steranes (e.g.
456 Fowler et al., 1991; Kashirtsev et al., 2010). Considering this, the
457 dominance of C₂₉ relative to C₂₇ 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 C₁₉ - C₂₀
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 C₁₉ - C₂₀ 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/Sporangioctrobis* (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/Sporangioctrobis*
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 Zygotpteridaceae. 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 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). 4 β (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 fichtelite) 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

745 **References**

746 Achari, R.G., Shaw, G., Holleyhead, R., 1973. Identification of ionene
747 and other carotenoid degradation products from the pyrolysis of
748 sporopollenins derived from some pollen exines, a spore coal and
749 the Green River shale. *Chemical Geology* 12, 229 – 234.

750 Alexander, R., Kagi, R.I., Rowland, S.J., Sheppard, P.N., Chirila, T.V.,
751 1985. The effects of thermal maturity on distribution of
752 dimethylnaphthalenes and trimethylnaphthalenes in some ancient
753 sediments and petroleums. *Geochimica et Cosmochimica Acta* 49,
754 385 – 395.

755 Armstroff, A., Wilkes, H., Schwarzbauer, J., Littke, R, Horsfield, B.,
756 2006. Aromatic hydrocarbon biomarkers in terrestrial organic
757 matter of Devonian to Permian age. *Palaeogeography,*
758 *Palaeoclimatology, Palaeoecology*, 240, 253 – 274.

759 Arouri, K.R., Greenwood, P.F., Walter, M.R., 2000. Biological affinities of
760 Neoproterozoic acritarchs from Australia: microscopic and chemical
761 characterisation *Organic Geochemistry* 31, 75 – 89

762 Asakawa, Y., 2004. Chemosystematics of the Hepaticae. *Phytochemistry*
763 65, 623 – 669.

764 Auras, S., Wilde, V., Scheffler, K., Hoernes, S., Kerp, H., Püttmann, W.,
765 2006. Aromatized arborane/fernane hydrocarbons as biomarkers
766 for Cordaites. *Naturwissenschaften* 93, 616 – 621.

767 Bastow, T., Alexander, R., Sosrowidjojo, I. B., Kagi, R.I., 1998.
768 Pentamethylnaphthalenes and related compounds in sedimentary
769 organic matter. *Organic Geochemistry* 28, 585 – 595.

770 Bastow, T., Singh, R., Van Aarssen, B., Alexander, R., Kagi, R. 2001. 2-
771 methylretene in sedimentary material: a new higher plant
772 biomarker. *Organic Geochemistry* 32: 1211 – 1217.

773 Bechtel, A., Sachsenhofer, R.F., Zdravkov, A., Kostova, I., Gratzner, R.,
774 2005. Influence of floral assemblage, facies and diagenesis on
775 petrography and organic geochemistry of the Eocene Bourgas coal
776 and the Miocene Maritza-East lignite (Bulgaria). *Organic*
777 *Geochemistry* 36, 1498 – 1522.

778 Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to
779 recognition of source beds. *Geochimica et Cosmochimica Acta* 22, 2
780 – 15.

781 Bray, P.S., Anderson, K.B., 2009. Identification of Carboniferous (320
782 Million Years Old) Class Ic Amber. *Science* 326, 132 – 134.

783 Brocks, J.J., Logan, G.A., Buick, R., Summons, R.E., 1999. Archean
784 molecular fossils and the early rise of Eukaryotes. *Science* 285,
785 1033 – 1036.

786 Brocks, J.J., Buick, R., Summons, R.E., Logan, G.A., 2003. A
787 reconstruction of Archean biological diversity based on molecular
788 fossils from the 2.78 to 2.45 billion-year-old Mount Bruce
789 Supergroup, Hamersley Basin, Western Australia. *Geochimica et*
790 *Cosmochimica Acta* 67, 4321 – 4335.

791 Brocks, J.J., Love, G.D., Summons, R.E., Knoll, A.H., Logan, G.A.,
792 Bowden, S.A., 2005. Biomarker evidence for green and purple
793 sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* 437,
794 866 – 870.

795 Chopra, R.N., Kumra, K.P., 1988. *Biology of Bryophytes*. John Wiley &
796 Sons, New York, 350 p.

797 Clarkson, C., Campbell, W.E., Smith, P., 2003. *In vitro* antiplasmodial
798 activity of abietane and totarane diterpenes isolated from
799 *Harpagophytum procumbens* (devil's claw). *Planta Medica* 69, 720 –
800 724.

801 Cox, R.E., Yamamoto, S., Otto, A., Simoneit, B.R.T., 2007. Oxygenated
802 di- and tricyclic diterpenoids of southern hemisphere conifers.
803 *Biochemical Systematics and Ecology* 35, 342 – 362.

804 Day, W.C., Erdman, J.G., 1963. Ionene: a thermal degradation product
805 of β -carotene. *Science* 141, 808.

806 del Río, J. C., Garcia-Molla, J., González-Vila, F. J., Martin, F., 1994.
807 Composition and origin of the aliphatic extractable hydrocarbons in
808 the Puertollano (Spain) oil shale. *Organic Geochemistry*, 21, 897 –
809 909.

810 DiMichele W.A., 1980. Paralycopodites Morey & Morey, from the
811 Carboniferous of Euramerica — A Reassessment of Generic
812 Affinities and Evolution of "Lepidodendron" brevifolium Williamson.
813 *American Journal of Botany* 67, 1466 – 1476.

814 DiMichele, W.A., Phillips, T.L., 1994. Paleobotanical and paleoecological
815 constraints on models of peat formation in the Late Carboniferous
816 of Euramerica. *Palaeogeography, Palaeoclimatology, Palaeoecology*
817 106, 39 – 90.

818 Dimitrova, T.K., Cleal, C.J., Thomas, B.A., 2005. Palynology of late
819 Westphalian-early Stephanian coal-bearing deposits in the eastern
820 South Wales Coalfield. *Geological Magazine* 142, 809 – 821.

821 Disnar, J.R., Harouna, M., 1994. Biological origin of tetra-cyclic
822 diterpanes, *n*-alkanes and other biomarkers found in Lower
823 Carboniferous Gondwana coals (Niger). *Organic Geochemistry* 21,
824 143 – 152.

825 Dzou, L.I.P., Noble, R.A., Senftle, J.T., 1995. Maturation effects on
826 absolute biomarker concentration in a suite of coals and associated
827 vitrinite concentrates. *Organic Geochemistry* 23, 681 – 697.

828 Eble, C.F., 1996. Lower and lower Middle Pennsylvanian coal
829 palynofloras, southwestern Virginia. *International Journal of Coal*
830 *Geology* 31, 67 – 113.

831 Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science*
832 156, 1322 – 1335.

833 Eglinton, T.I., Eglinton, G., 2008. Molecular proxies for
834 paleoclimatology. *Earth and Planetary Science Letters* 275, 1 – 16.

835 Eigenbrode, J.L., Freeman, K.H., Summons, R.E., 2008. Methylhopane
836 biomarker hydrocarbons in Hamersley Province sediments provide

837 evidence for Neoproterozoic aerobiosis. *Earth and Planetary Science*
838 *Letters* 273, 323 – 331.

839 Ellis, L., Singh, R., Alexander, R., Kagi, R., 1996. Formation of isoheptyl
840 alkylaromatic hydrocarbons from aromatization-rearrangement of
841 terpenoids in the sedimentary environment: A new class of
842 biomarker. *Geochimica and Cosmochimica Acta* 60, 4747 – 4763.

843 Espitalié, J., Deroo, G., Marquis, F., 1986. La pyrolyse Rock-Eval et ses
844 applications. *Revue de l'Institut Français du Pétrole* 41, 73 – 89.

845 Fabianska, M. J., Bzowska, G., Matuszewska, A., Racka, A., Skret, U.,
846 2003. Gas chromatography-mass spectrometry in geochemical
847 investigation of organic matter of the Grodziec Beds (Upper
848 Carboniferous), Upper Silesian Coal Basin, Poland. *Geochemistry*
849 63, 63 – 91.

850 Falcon-Lang, H. J., 2000. Fire ecology of the Carboniferous tropical
851 zone. *Palaeogeography, Palaeoclimatology, Palaeoecology* 164, 339 –
852 355.

853 Fleck, S., Michels, R., Izart, A., Elie, M., Landais, P., 2001.
854 Palaeoenvironmental assessment of Westphalian fluvio-lacustrine
855 deposits of Lorraine (France) using a combination of organic
856 geochemistry and sedimentology. *International Journal of Coal*
857 *Geology* 48, 65 – 88.

858 Fleck, S., Michels, R., Ferry, S., Malartre, F., Elion, P., Landais, P.,
859 2002. Organic geochemistry in a sequence stratigraphic framework.

860 The siliciclastic shelf environment of Cretaceous series, SE France.
861 *Organic Geochemistry* 33, 1533 – 1557.

862 Fowler, M.G., Goodarzi, F., Gentzis, T., Brooks, P.W., 1991.
863 Hydrocarbon potential of Middle and Upper Devonian coals from
864 Melville Island, Arctic Canada. *Organic Geochemistry* 17, 681 –
865 694.

866 George, S.C., 1992. Effect of igneous intrusion on the organic
867 geochemistry of a siltstone and an oil shale horizon in the Midland
868 Valley of Scotland. *Organic Geochemistry* 18, 705 – 723.

869 Glasspool, I.J., Hemsley, A.R., Scott, A.C., Golitsyn, A., 2000.
870 Ultrastructure and affinity of Lower Carboniferous megaspores
871 from the Moscow Basin, Russia. *Review of Palaeobotany and*
872 *Palynology* 109, 1 – 31.

873 Hautevelle, Y., Michels, R., Malartre, F., Trouiller, A., 2006. Vascular
874 plant biomarkers as proxies for palaeoflora and palaeoclimatic
875 changes at the Dogger/Malm transition of the Paris Basin (France).
876 *Organic Geochemistry* 37, 610 – 625.

877 Huang, W.-Y., Meinschein, W.G., 1979. Sterols as ecological indicators.
878 *Geochimica et Cosmochimica Acta* 43, 739 – 745.

879 Hunt, J.M., 1995. *Petroleum Geochemistry and Geology*. W.H. Freeman
880 and Co., New York.

881 Iinuma, Y., E. Brüggemann, T. Gnauk, K. Müller, M. O. Andreae, G.
882 Helas, R. Parmar, and H. Herrmann, 2007. Source characterization
883 of biomass burning particles: The combustion of selected European

884 conifers, African hardwood, savanna grass, and German and
885 Indonesian peat, *Journal of Geophysical Research*, 112, D08209.
886 International Committee of Coal Petrology (ICCP), 1975. *International*
887 *Handbook for Coal Petrology*, 2nd ed., CNRS, Paris.

888 Izart, A., Sachsenhofer, R. F., Privalov, V. A., Elie, M., Panova, E. A.,
889 Antsiferov, V. A., Alsaab, D., Rainer, T., Sotirov, A., Zdravkov, A.,
890 Zhykalyak, M. V., 2006. Stratigraphic distribution of macerals and
891 biomarkers in the Donets Basin: Implications for paleoecology,
892 paleoclimatology and eustasy. *International Journal of Coal*
893 *Geology*, 66, 69 – 107.

894 Jiang, C., Alexander, R., Kagi, R.I., Murray, A. P., 1998. Polycyclic
895 aromatic hydrocarbons in ancient sediments and their
896 relationships to palaeoclimate. *Organic Geochemistry* 29, 1721 –
897 1735.

898 Kashirtsev, V.A., Moskvina, V.I., Fomin, A.N., Chalaya, O.N., 2010.
899 Terpanes and steranes in coals of different genetic types in Siberia.
900 *Russian Geology and Geophysics* 51, 404 – 411.

901 Murchison D. G., Raymond A. C., 1989. Igneous activity and organic
902 maturation in the Midland Valley of Scotland. *International Journal*
903 *of Coal Geology* 14, 47-82.

904 Niklas, K.J., 1976a. The chemotaxonomy of *Parka decipiens* from the
905 lower old red sandstone, Scotland (U.K.). *Review of Palaeobotany*
906 *and Palynology* 21, 205 – 217.

907 Niklas, K.J., 1976b Chemotaxonomy of Prototaxites and evidence for
908 possible terrestrial adaptation. *Review of Palaeobotany and*
909 *Palynology* 22, 1 – 17.

910 Niklas, K.J., Chaloner, W.G., 1976. Chemotaxonomy of some
911 problematic palaeozoic plants. *Review of Palaeobotany and*
912 *Palynology* 22, 81 – 104

913 Niklas, K.J., Pratt, L.M., 1980. Evidence for lignin-like constituents in
914 early silurian (Ilandoverian) plant fossils. *Science* 209, 396 – 397.

915 Noble, R. A., 1986. A geochemical study of bicyclic alkanes and
916 diterpenoid hydrocarbons in crude oils, sediments and coals.
917 Thesis. The University of Western Australia. 398 p.

918 Noble, R. A., Alexander, R., Kagi R.I., Knox, J., 1985. Tetracyclic
919 diterpenoid hydrocarbons in some Australian coals, sediments and
920 crude oils. *Geochimica and Cosmochimica Acta* 49, 2141 – 2147.

921 Noble, R. A., Alexander, R., Kagi R.I., 1987. Configurational
922 isomerization in sedimentary bicyclic alkanes. *Organic*
923 *Geochemistry* 11, 151 – 156.

924 Olcott, A.N., 2007. The utility of lipid biomarkers as paleoenvironmental
925 indicators. *Palaios* 22, 111 – 113.

926 Opluštil, S, Bek, J, Schultka, S, 2009. Re-examination of the genus
927 *Omphalophloios* White, 1898 from the Upper Silesian Coal Basin.
928 *Bulletin of Geosciences* 85, 39 – 52.

929 Oros, D.R., Simoneit, B.R.T., 2001a. Identification and emission factors
930 of molecular tracers in organic aerosols from biomass burning Part

931 1. Temperate climate conifers. *Applied Geochemistry* 16, 1513 –
932 1544.

933 Oros, D.R., Simoneit, B.R.T., 2001b. Identification and emission factors
934 of molecular tracers in organic aerosols from biomass burning Part
935 2. Deciduous trees. *Applied Geochemistry* 16, 1545 – 1565.

936 Oros, D.R., Abas, M.R.b., Omar, N.Y.M.J., Rahman, N.A., Simoneit,
937 B.R.T., 2006. Identification and emission factors of molecular
938 tracers in organic aerosols from biomass burning: Part 3. Grasses.
939 *Applied Geochemistry* 21, 919 – 940.

940 Otto, A., Simoneit, B.R.D., 2001. Chemosystematics and diagenesis of
941 terpenoids in fossil conifer species and sediment from the Eocene
942 Zeitz Formation, Saxony, Germany. *Geochimica et Cosmochimica*
943 *Acta* 65, 3505 – 3527.

944 Otto, A., Wilde, V., 2001. Sesqui-, di- and triterpenoids as
945 chemosystematic markers in extant conifers - A review. *The*
946 *Botanical Review* 67, 141 – 238.

947 Otto, A., Walther, H., Püttmann, W., 1997. Sesqui- and diterpenoid
948 biomarkers preserved in *Taxodium*-rich Oligocene Oxbow Lake
949 Clays, Weissenster basin, Germany. *Organic Geochemistry* 26, 105
950 – 115.

951 Otto, A., Simoneit, B.R.T., Wilde, V., Kunzmann, L., Püttmann, W.,
952 2002. Terpenoid composition of three fossil resins from Cretaceous
953 and Tertiary conifers. *Review of Palaeobotany and Palynology* 120,
954 203 – 215.

- 955 Ourisson, G., Albrecht, P., Rohmer, M., 1979. The hopanoids.
956 Palaeochemistry and biochemistry of a group of natural products.
957 Pure and Applied Chemistry 51, 709 – 729.
- 958 Peters, K.E., Moldowan, J.M., 1993. The Biomarker Guide: Interpreting
959 molecular fossils in petroleum and ancient sediments. Prentice
960 Hall, Englewood Cliffs, New Jersey. 363 p.
- 961 Peters, K.E., Walters, C.W., Moldowan, J.M., 2005. The Biomarker
962 Guide. Cambridge University Press. Cambridge -706 p.
- 963 Philp, R.P., 1985. Fossil Fuel Biomarkers Applications and Spectra.
964 Elsevier, Amsterdam.
- 965 Phillips, T., 1979. Reproduction of heterosporous arborescent lycopods
966 in the Mississippian - Pennsylvanian of Euramerica. Review of
967 Palaeobotany and Palynology 27, 239 – 289.
- 968 Pinto A.C., Zocher D.H.T., Rezende C.M., Gottlieb H.E., 1995. A new
969 diterpene with a totarane skeleton from *Vellozia flavicans*. Natural
970 Product Research 6, 209 – 213.
- 971 Radke, M., Willsch, H., Leythaeuser, D., 1982. Aromatic components of
972 coal: relation of distribution pattern to rank. *Geochimica et*
973 *Cosmochimica Acta* 46, 1831 – 1848.
- 974 Radke, M., Willsch, H., Welte, D.H., 1986. Maturity parameters based
975 on aromatic hydrocarbons: influence of the organic matter type.
976 *Organic Geochemistry* 10, 51 – 63.

- 977 Radke, M., Vriend, S. P., Ramanampisoa, L. R., 2000.
978 Alkyldibenzofurans in terrestrial rocks: Influence of organic facies
979 and maturation. *Geochimica et Cosmochimica Acta* 64, 275 – 286.
- 980 Rampen, S.W, Abbas, B.A., Schouten, S., Sinninghe Damsté, J.S.,
981 2010. A comprehensive study of sterols in marine diatoms
982 (Bacillariophyta): Implications for their use as tracers for diatom
983 productivity. *Limnology and Oceanography* 55, 91 – 105.
- 984 Romero-Sarmiento, M.F., Riboulleau, A., Vecoli, M., Versteegh., G.,
985 2010. Occurrence of retene in upper Silurian – Lower Devonian
986 sediments from North Africa: Origin and implications. *Organic*
987 *Geochemistry* 41, 302 – 306.
- 988 Schulze, T., Michaelis, W., 1990. Structure and origin of terpenoid
989 hydrocarbons in some German coals. *Organic Geochemistry* 16,
990 1051 – 1058.
- 991 Scott, A., 1974. The earliest conifer. *Nature* 251, 707 – 708.
- 992 Scott, A.C., Hemsley, A. R., 1996. Palaeozoic megaspores. Chapter 18G.
993 In: Jansonius, J. & McGregor, D.C. (ed.) *Palynology: principles and*
994 *applications*. American Association of Stratigraphic Palynologists
995 Foundation, Vol. 2, 629 – 639.
- 996 Scott, A.C., Jones, T.P., 1994. The nature and influence of fire in
997 Carboniferous ecosystems. *Palaeogeography, Palaeoclimatology,*
998 *Palaeoecology* 106, 91 – 112.
- 999 Scott, A.C., Galtier, J., Clayton, G., 1984. Distribution of anatomically-
1000 preserved floras in the Lower Carboniferous in Western Europe.

- 1001 Transaction of the Royal Society of Edinburgh: Earth Sciences 75,
1002 311 – 340.
- 1003 Seifert, W.K., Moldowan, J.M., 1978. Applications of steranes, terpanes
1004 and monoaromatics to the maturation, migration and source of
1005 crude oils. *Geochimica et Cosmochimica Acta* 42, 77 – 95.
- 1006 Seifert, W.K., Moldowan, J.M., 1980. The effect of thermal stress on
1007 source rock quality as measured by hopane stereochemistry. In:
1008 Douglas, A.G., Maxwell, J.R. (Eds.), *Advances in Organic*
1009 *Geochemistry*, 1979. Pergamon Press, 229 – 237.
- 1010 Seifert, W.K., Moldowan, J.M., 1986. Use of biological markers in
1011 petroleum exploration. In: Johns, R.B. (Ed.), *Biological Markers in*
1012 *the Sedimentary Record, Methods in Geochemistry and*
1013 *Geophysics*, vol. 24. Elsevier, Amsterdam, pp. 261–290.
- 1014 Sheng, G., Simoneit, B. R. T., Leif, R. N., Chen, X., Fu, J., 1992.
1015 Tetracyclic terpanes enriched in Devonian cuticle humic coals.
1016 *Fuel*, 71, 523 – 532.
- 1017 Shiea, J., Brassell, S.C., Ward, D.M., 1990. Mid-chain branched mono-
1018 and dimethyl alkanes in hot spring cyanobacterial mats: a direct
1019 biogenic source for branched alkanes in ancient sediments?
1020 *Organic Geochemistry* 15, 223 – 231.
- 1021 Simoneit, B. R. T., Grimalt, J. O., Wang, T. G., Cox, R. E., Hatcher, P.
1022 G., Nissenbaum, A., 1986. Cyclic terpenoids of contemporary
1023 resinous plant detritus and of fossil woods, ambers and coals.
1024 *Organic Geochemistry* 10, 877 – 889.

- 1025 Spinner, E., 1969. Megaspore assemblages from Viséan deposits at
1026 Dunbar, East Lothian, Scotland. *Palaeontology* 12, 441 – 458.
- 1027 Spinner, E., Clayton, G., 1973. Viséan spore assemblages from
1028 Skateraw, East Lothian, Scotland. *Pollen et Spores* XV, 139 – 165.
- 1029 Stefanova, M., Markova, K., Marinov, S., Simoneit, B.R.T., 2005.
1030 Molecular indicators for coal-forming vegetation of the Miocene
1031 Chukurovo lignite, Bulgaria. *Fuel* 84, 1830 – 1838.
- 1032 Talyzina, N.M., Moldowan, J.M., Johannisson, A., Fago, F.J., 2000.
1033 Affinities of Early Cambrian acritarchs studied by using
1034 microscopy, fluorescence flow cytometry and biomarkers. *Review of*
1035 *Palaeobotany and Palynology* 108, 37 – 53.
- 1036 Tissot, B., Welte, D.M., 1984. *Petroleum Formation and Occurrence*.
1037 Springer-Verlag, Berlin, 699 p.
- 1038 Taylor, T.N., Taylor, E.L., Krings, M., 2009. *Paleobotany: The Biology*
1039 *and Evolution of Fossil Plants*. Academic Press, 1230 p.
- 1040 Thomas, B. R., 1969. *Organic Geochemistry. Methods and results*,
1041 chapter Kauri resins- modern and fossil. Springer Verlag, Berlin,
1042 599 – 618.
- 1043 Tuo, J., Philp, R. P., 2005. Saturated and aromatic diterpenoids and
1044 triterpenoids in Eocene coals and mudstones from China. *Applied*
1045 *Geochemistry* 20, 367 – 381.
- 1046 Underhill, J. R., Monaghan, A. A., Browne, M. A. E., 2008. Controls on
1047 structural styles, basin development and petroleum prospectivity in

1048 the Midland Valley of Scotland. *Marine and Petroleum Geology* 25,
1049 1000 – 1022.

1050 van Aarssen, B.K.G, Bastow, T.P., Alexander, R., Kagi, R., 1999.
1051 Distributions of methylated naphthalenes in crude oils: indicators
1052 of maturity, biodegradation and mixing. *Organic Geochemistry* 30,
1053 1213 – 1227.

1054 van Aarssen, B.K.G., Alexander, R., Kagi, R.I, 2000. Higher plant
1055 biomarkers reflect palaeovegetation changes during Jurassic times.
1056 *Geochimica et Cosmochimica Acta* 64, 1417 – 1424.

1057 Ventura, G.T., Kenig, F., Reddy, C.M., Schieber, J., Frysinger, G.S.,
1058 Nelson, R.K., Dinel, E., Gaines, R.B., Schaeffer, P., 2007. Molecular
1059 evidence of Late Archean archaea and the presence of a subsurface
1060 hydrothermal biosphere. *Proceedings of the National Academy of*
1061 *Sciences* 104, 14260 – 14265.

1062 Vliex, M., Hagemann, H.W., Püttmann, W., 1994. Aromatized
1063 arborane/fernane hydrocarbons as molecular indicators of floral
1064 changes in Upper Carboniferous/Lower Permian strata of the Saar-
1065 Nahe Basin, southwestern Germany. *Geochimica et Cosmochimica*
1066 *Acta* 58, 4689 – 4702.

1067 Volkova, I.B., 1994. Nature and composition of the Devonian coals of
1068 Russia. *Energy and Fuels* 8, 1489 – 1493

1069 Wagner, R.H., 1989. A late Stephanian forest swamp with
1070 *Sporangiostrobos* fossilized by volcanic ash fall in the Puertollano

- 1071 Basin, central Spain. *International Journal of Coal Geology* 12, 523
1072 – 552.
- 1073 Waldbauer, J.R., Sherman, L.S., Sumner, D.Y., Summons, R.E., 2009.
1074 Late Archean molecular fossils from the Transvaal Supergroup
1075 record the antiquity of microbial diversity and aerobiosis.
1076 *Precambrian Research* 169, 28 – 47.
- 1077 Wang, S. J., 1998. The cordaitan fossil plants from Cathaysian area in
1078 China. *Acta Botanica Sinica* 40, 573 – 579.
- 1079 Wang, T.G., Simoneit, B.R.T., 1990. Organic geochemistry and coal
1080 petrology of Tertiary brown coal in the Zhoujing mine, Baise Basin,
1081 South China. *Fuel* 69, 12 – 20.
- 1082 Wu C.-L., Jong J.-R., 2001. A Cyclic Peroxide of Clerodenoic Acid from
1083 the Taiwanese Liverwort *Schistochila acuminata*. *Journal of Asian*
1084 *Natural Products Research* 3, 241 – 246.
- 1085 Yi, W., Berry, C.M., Shougang, H., Honghe, X., Qiang, F. (2007) The
1086 Xichong flora of Yunnan, China: diversity in late Mid Devonian
1087 plant assemblages. *Geological Journal* 42, 339 – 350.
- 1088 Zhou, Y.X., 1994. Earliest pollen-dominated microfloras from the early
1089 Late Carboniferous of the Tian Shan Mountains, NW China: their
1090 significance for the origin of conifers and palaeophytogeography.
1091 *Review of Palaeobotany and Palynology* 81, 193 – 211.
1092

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*-C₁₇ vs. Ph/*n*-C₁₈ 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 C₂₇, C₂₈ and C₂₉
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 C₁₈ 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 C₁₇ to C₁₉ 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 (Tre¹ and Tre²).

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.

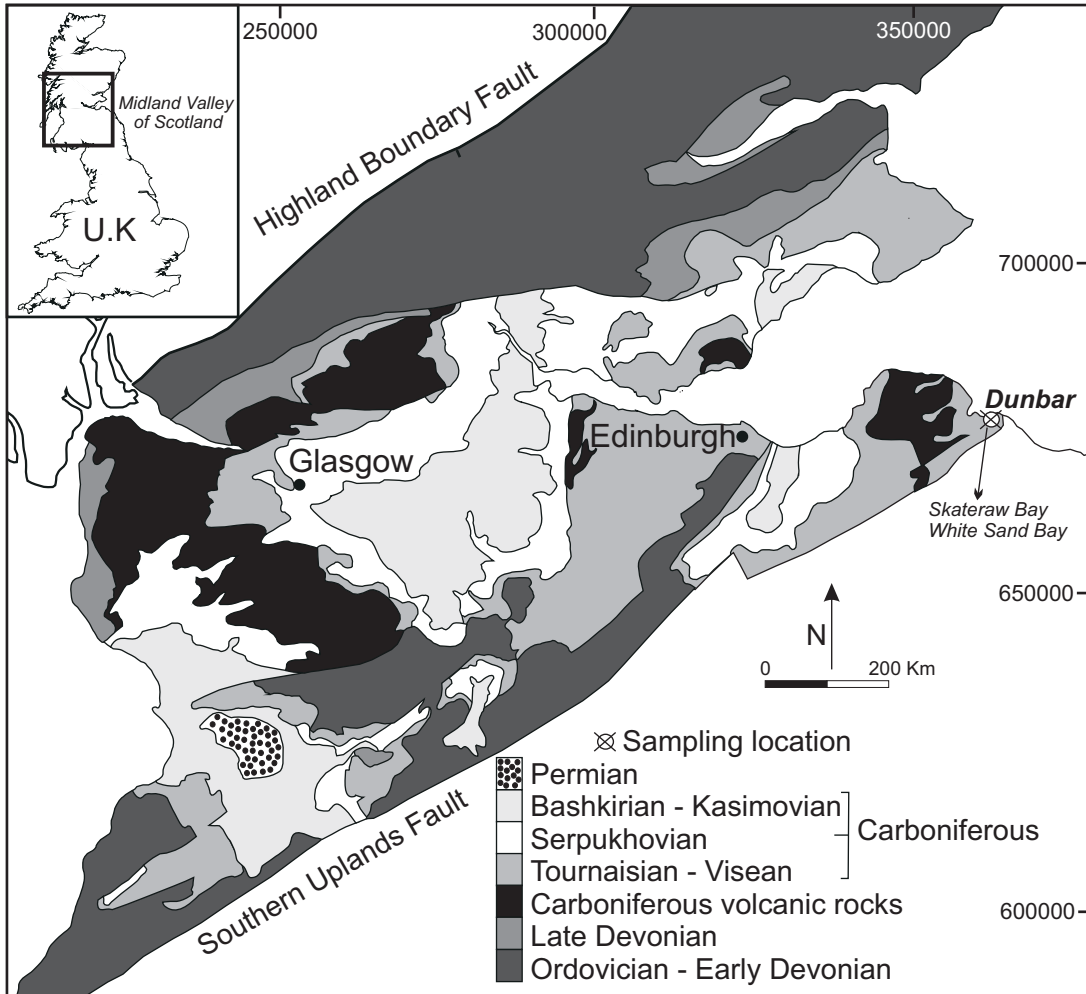
1224

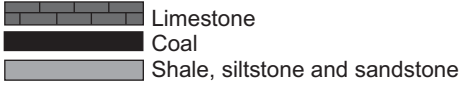
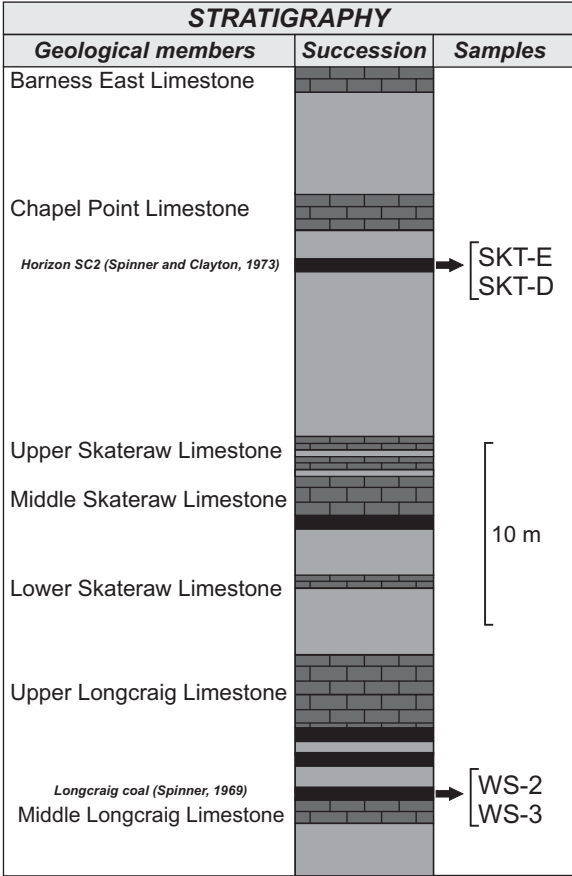
1225 **Appendix**

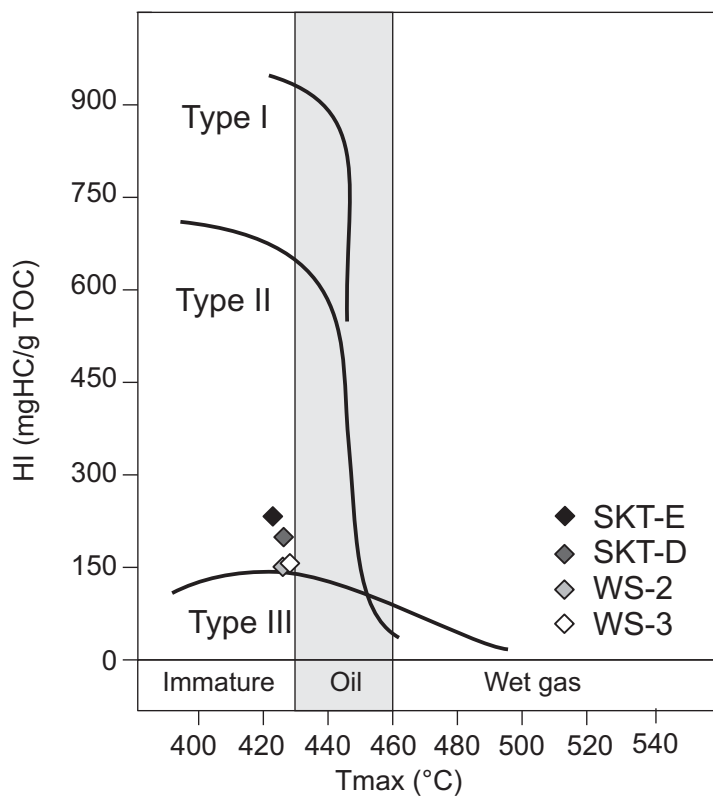
1226 Mass spectra of unknown compounds (Peak assignments in Tables 2

1227 and 3).

1228







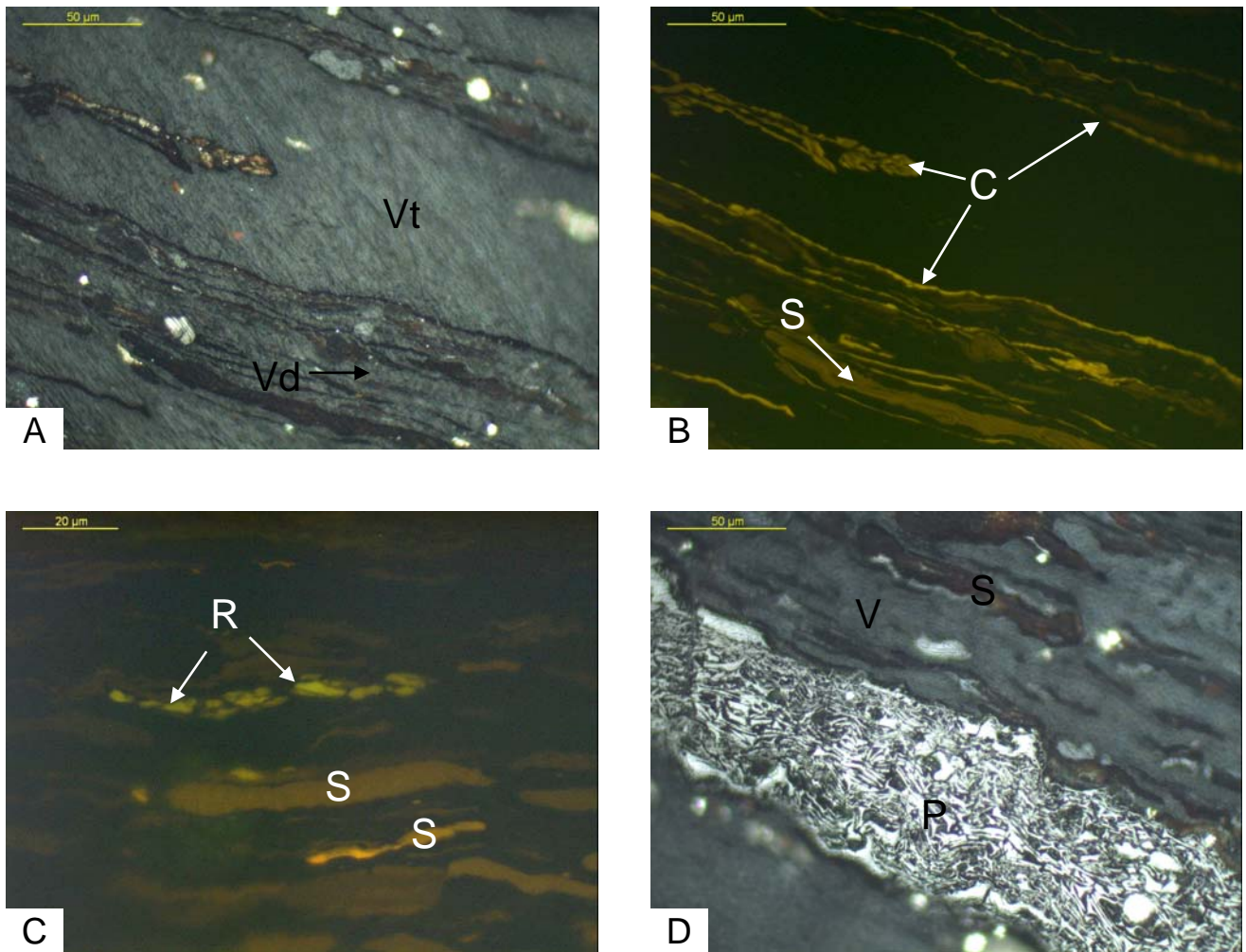
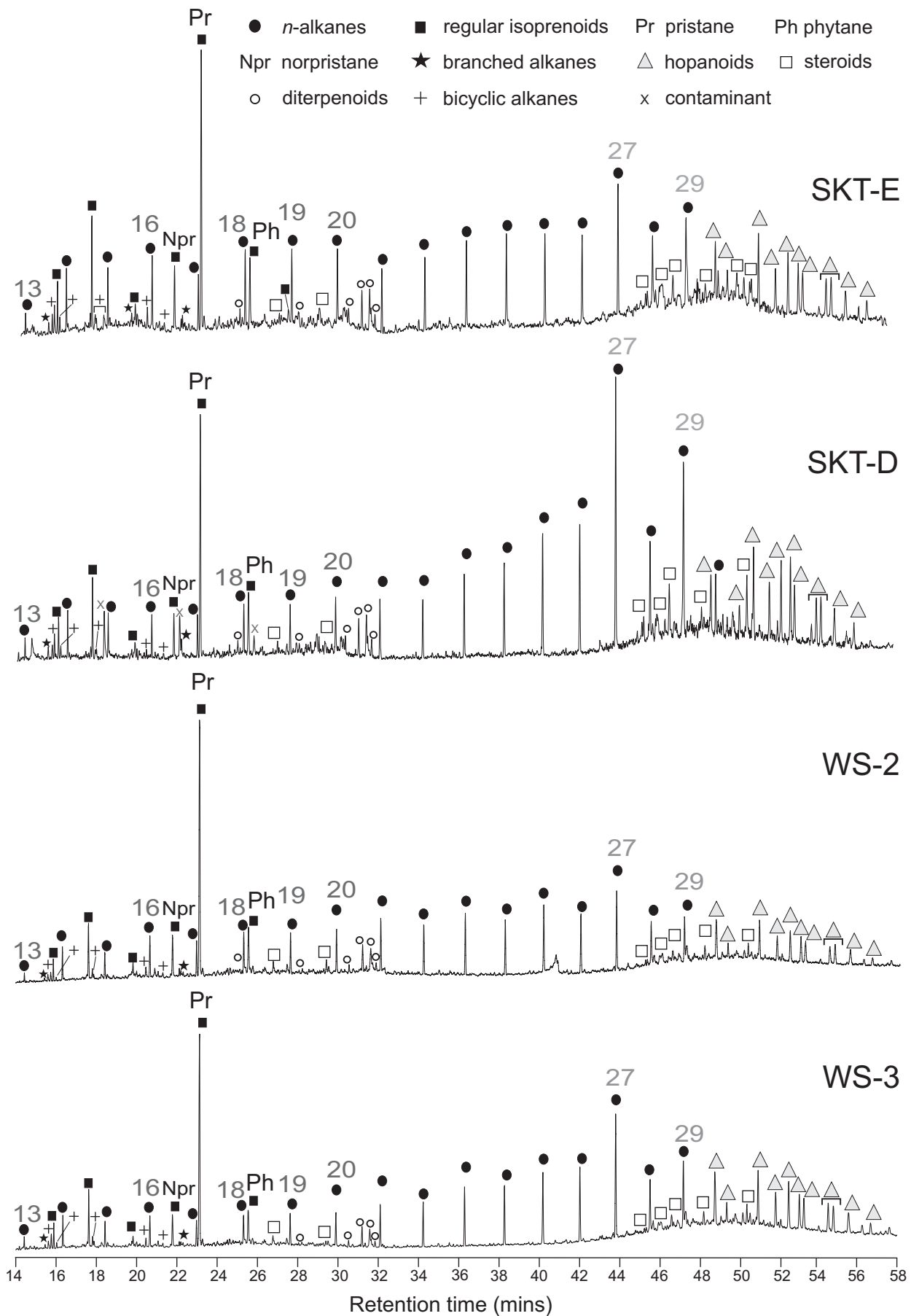
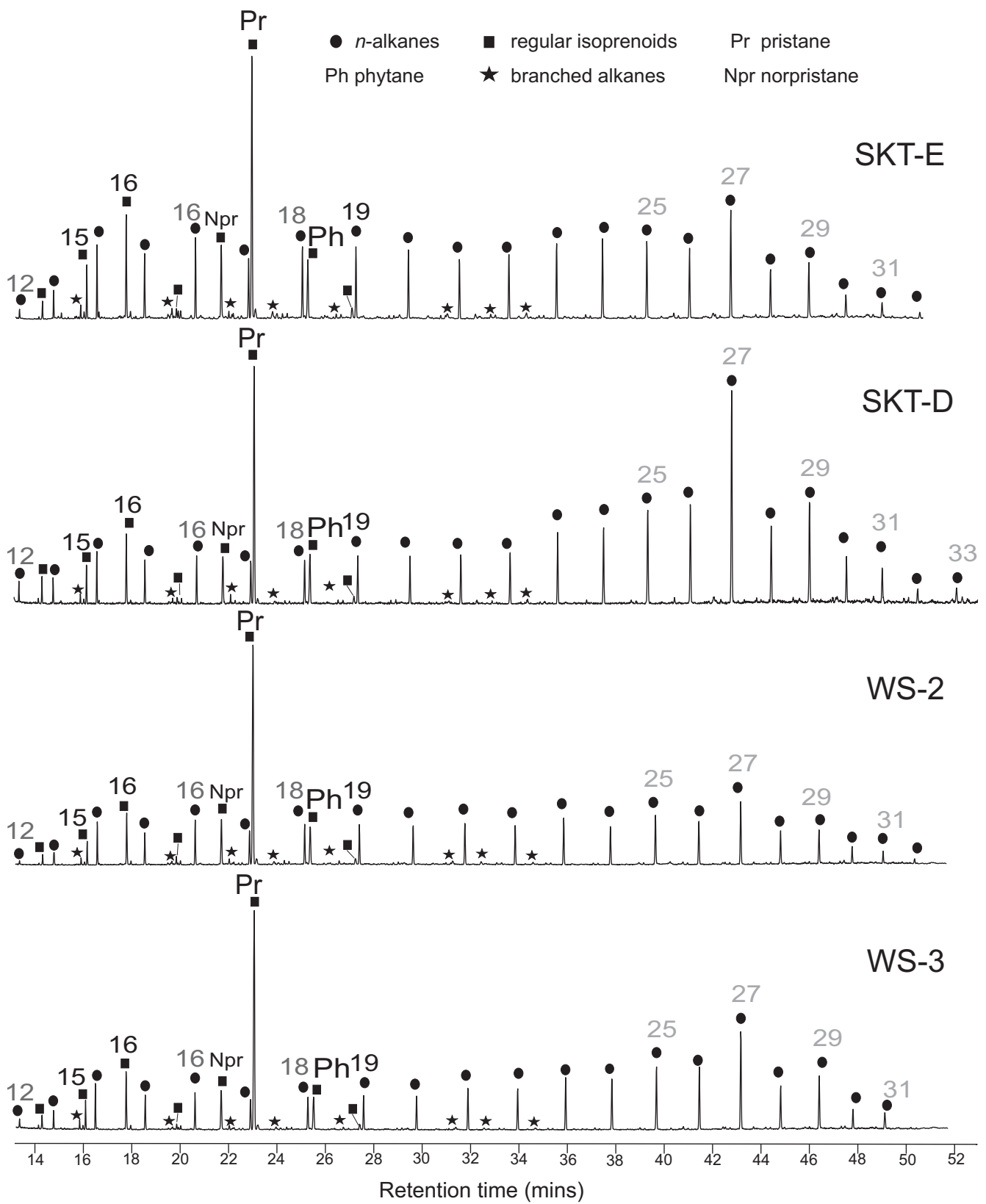
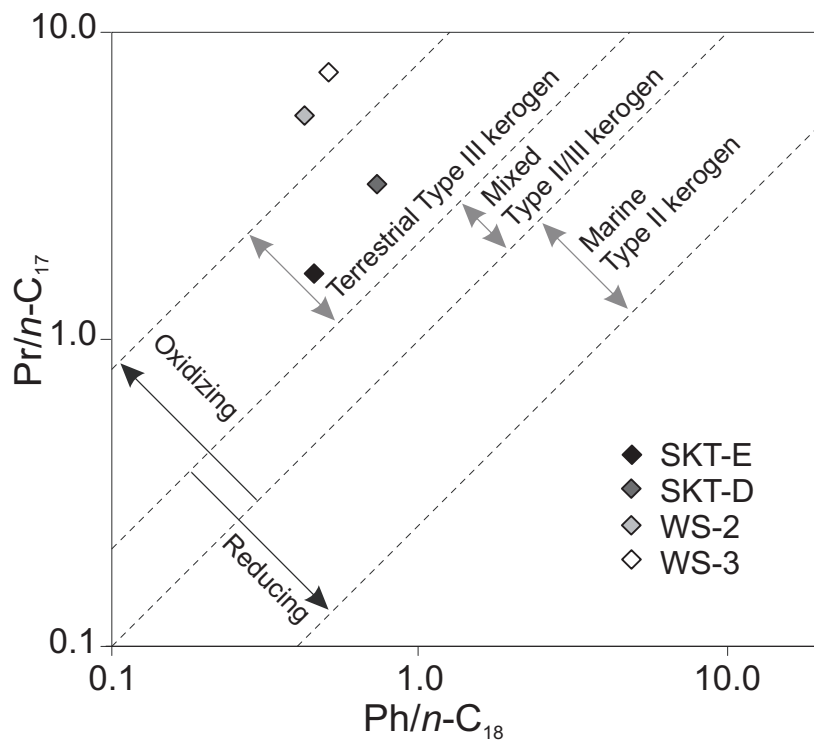
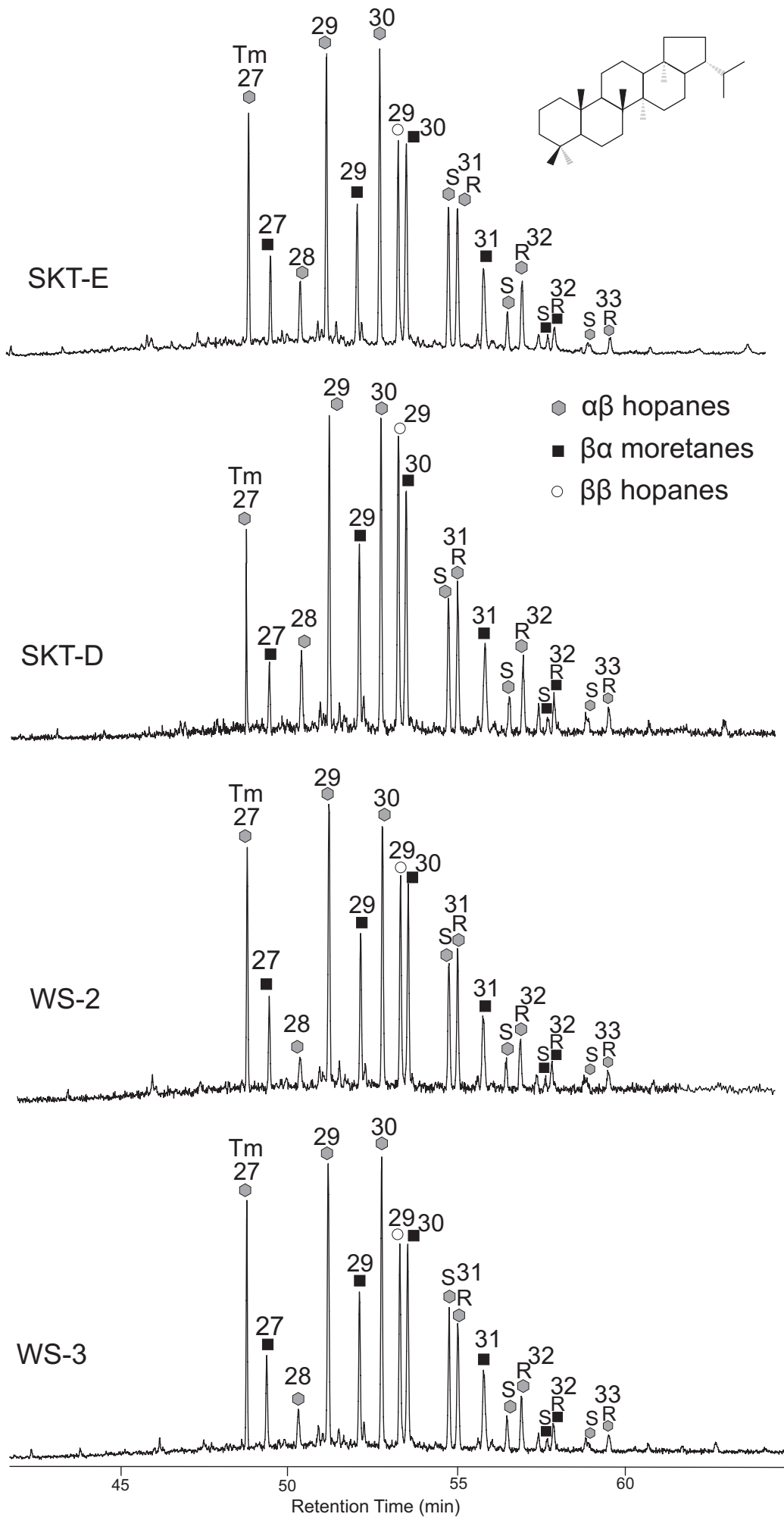


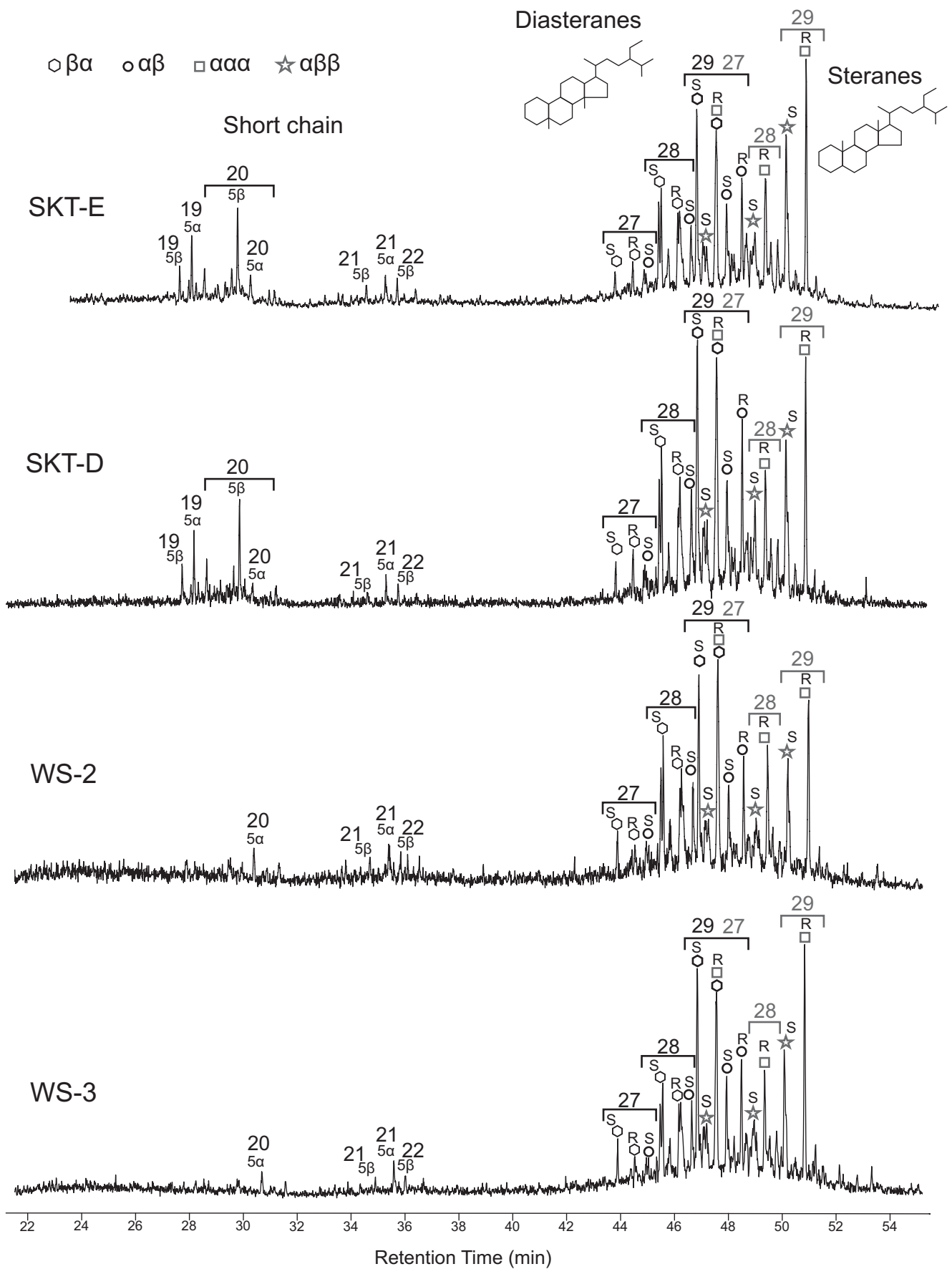
Fig. 4. Photomicrographs of macerals A) WS-3, reflected natural light. Vitrinite particles : telocollinite (Vt) and desmocollinite (Vd). B) Same zone as A, blue light fluorescence emphasizing exinite particles: fluorescing spores (S) and cuticles (C). C) SKT-E, blue light fluorescence. Exinite particles: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

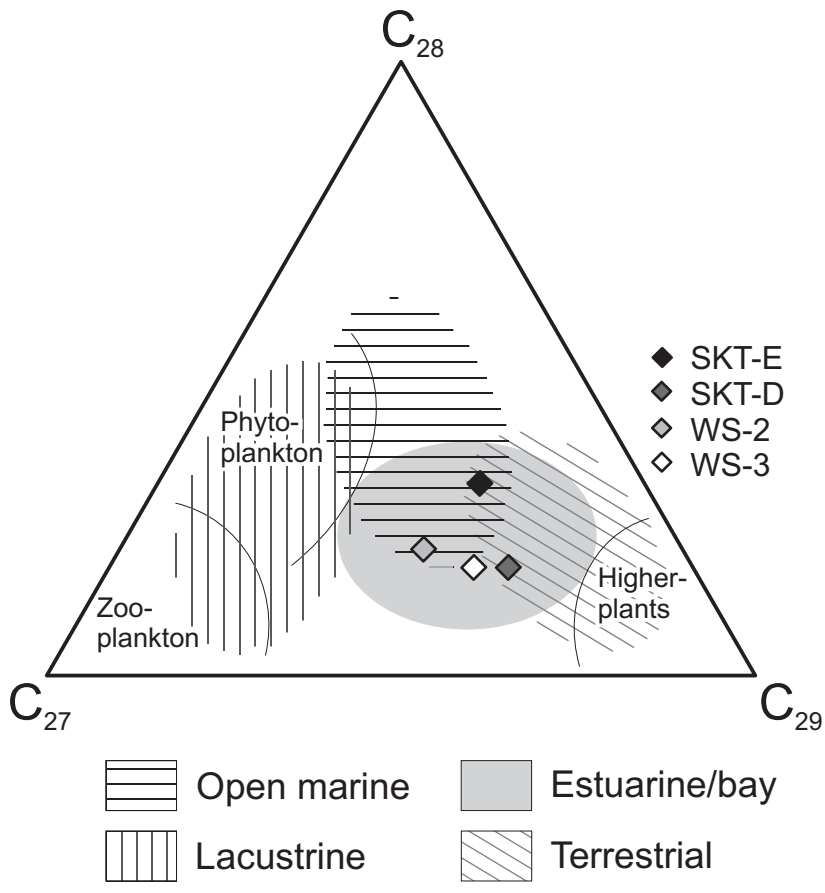


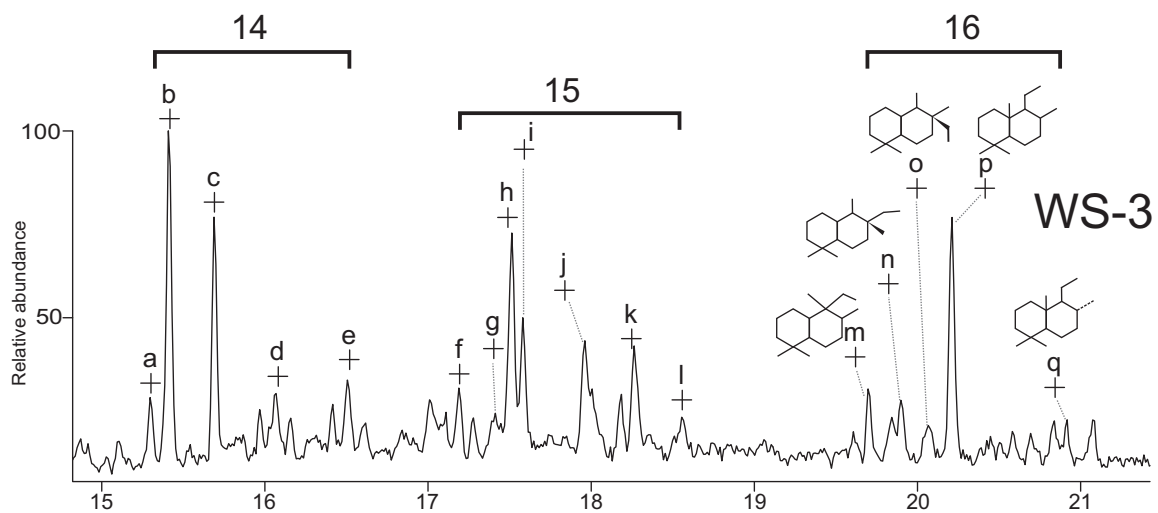
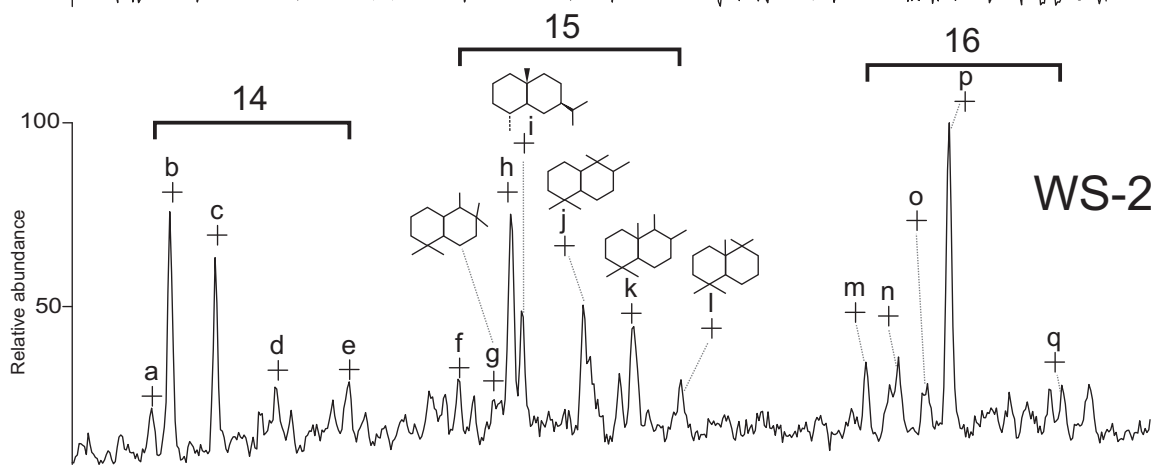
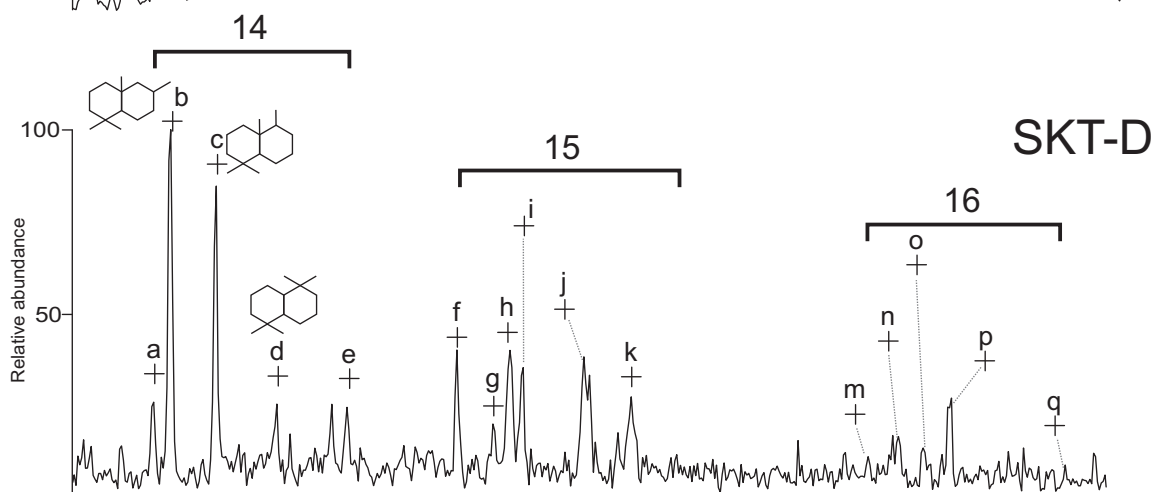
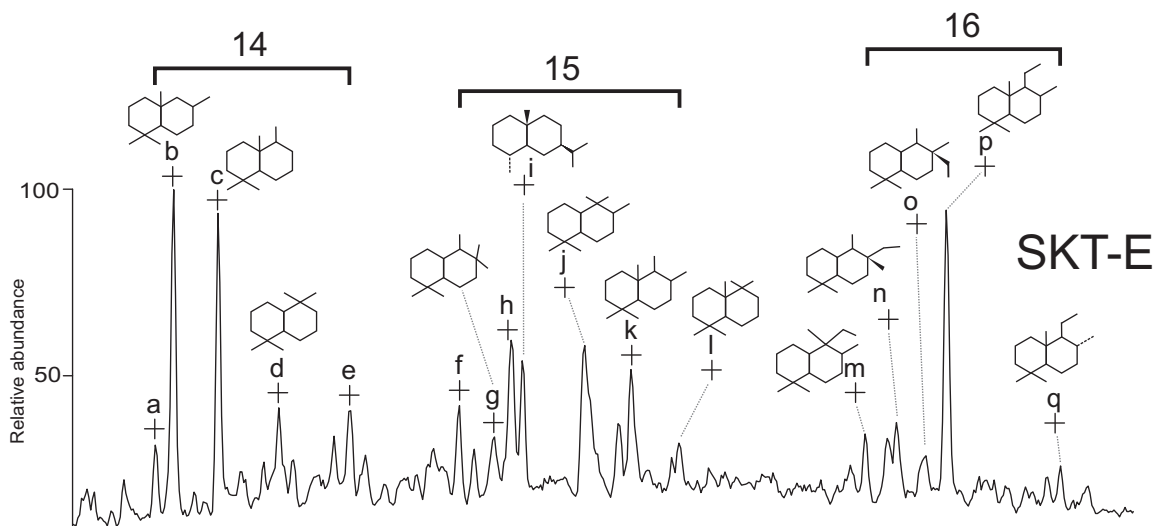




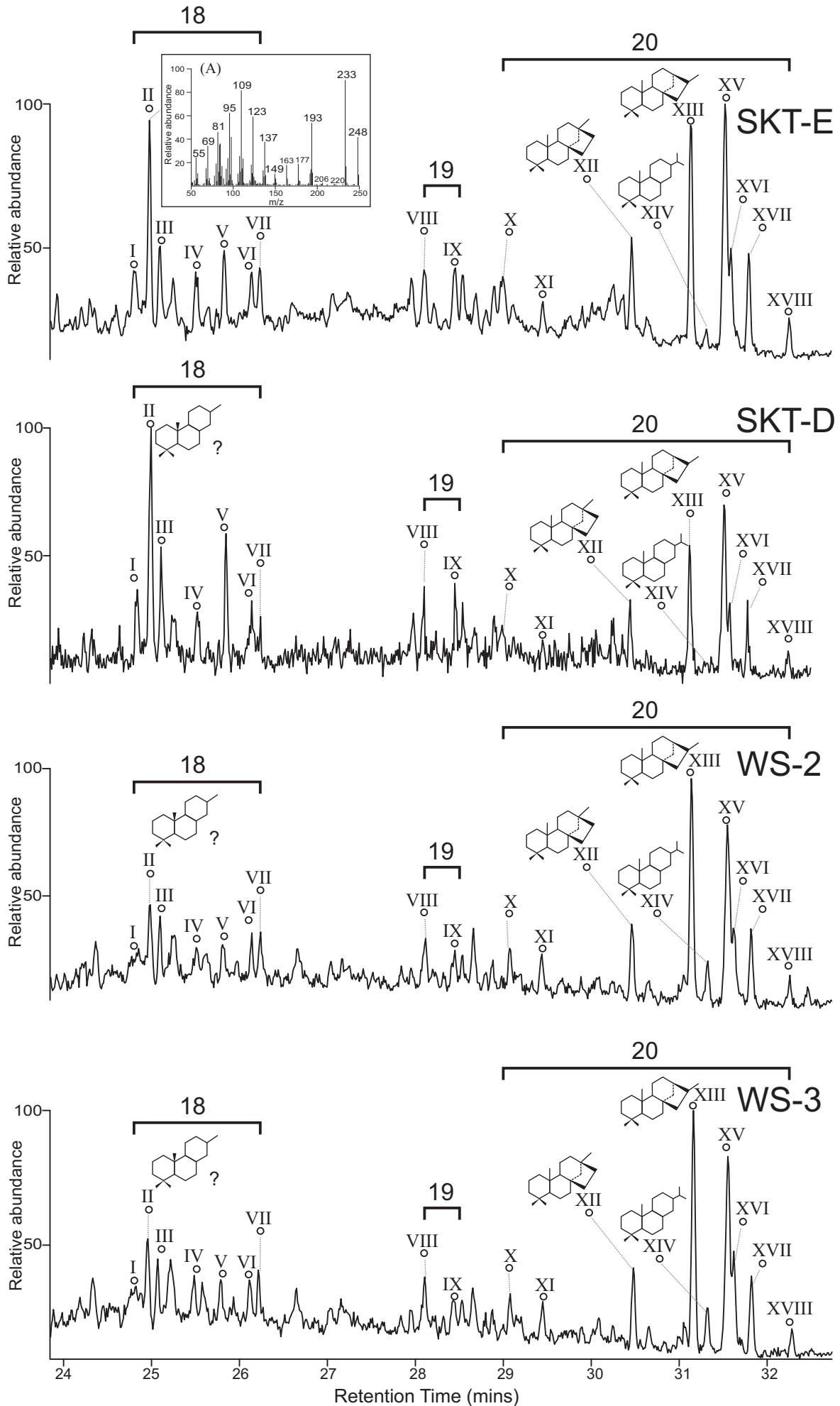




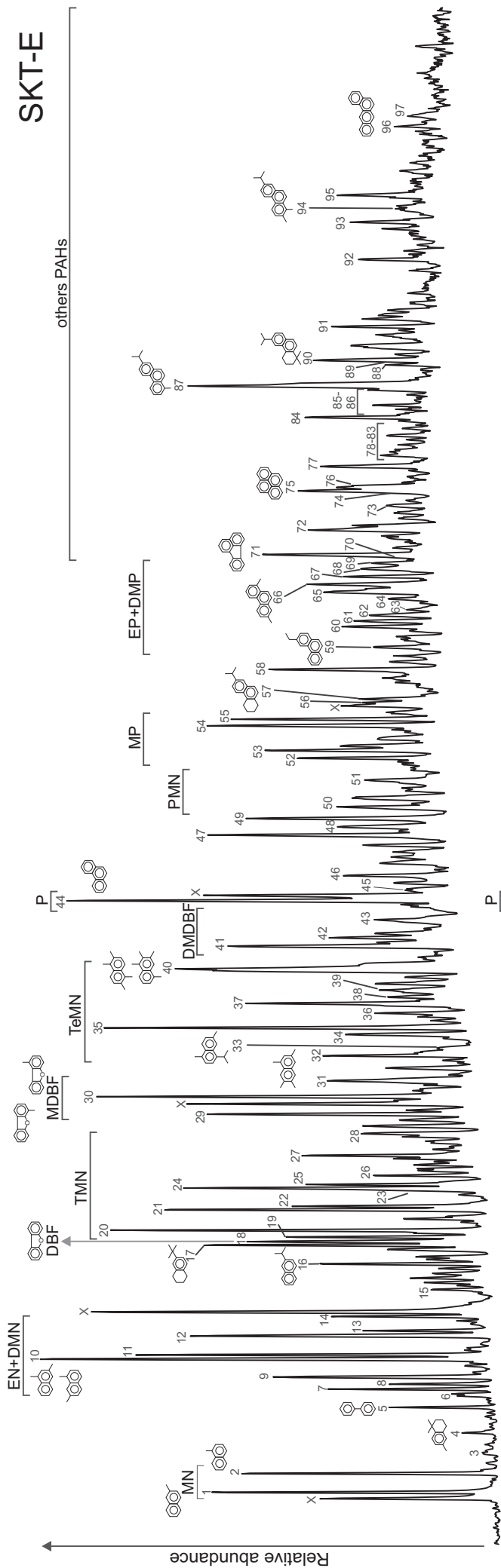




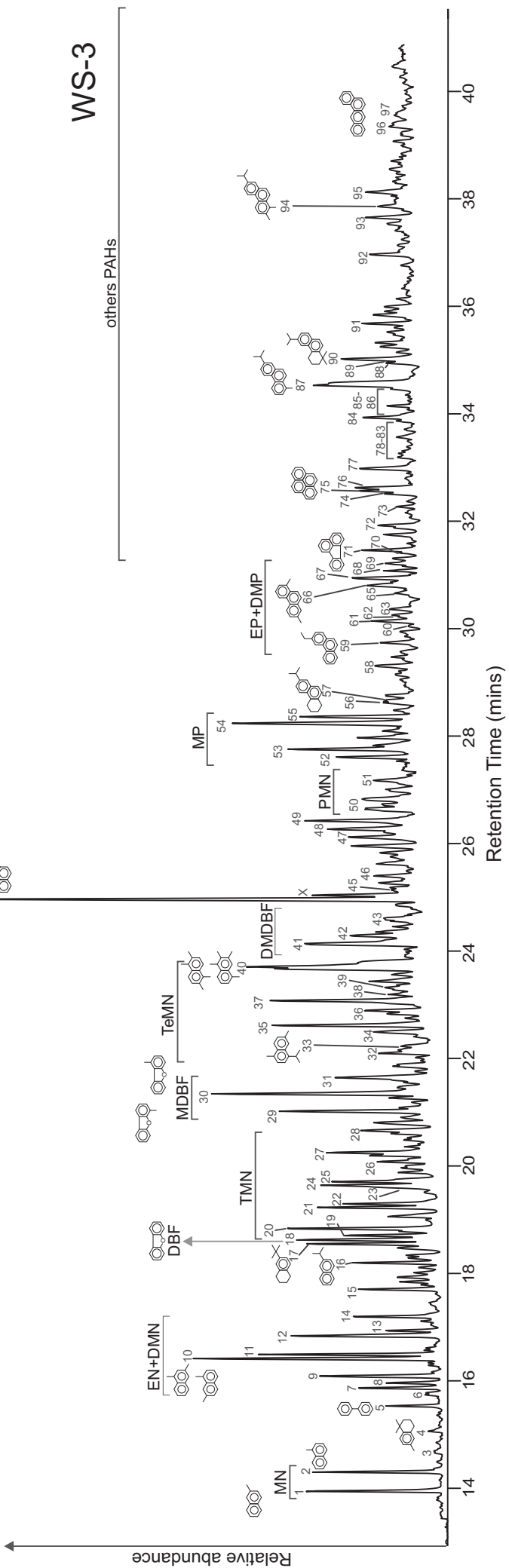
Retention Time (mins)

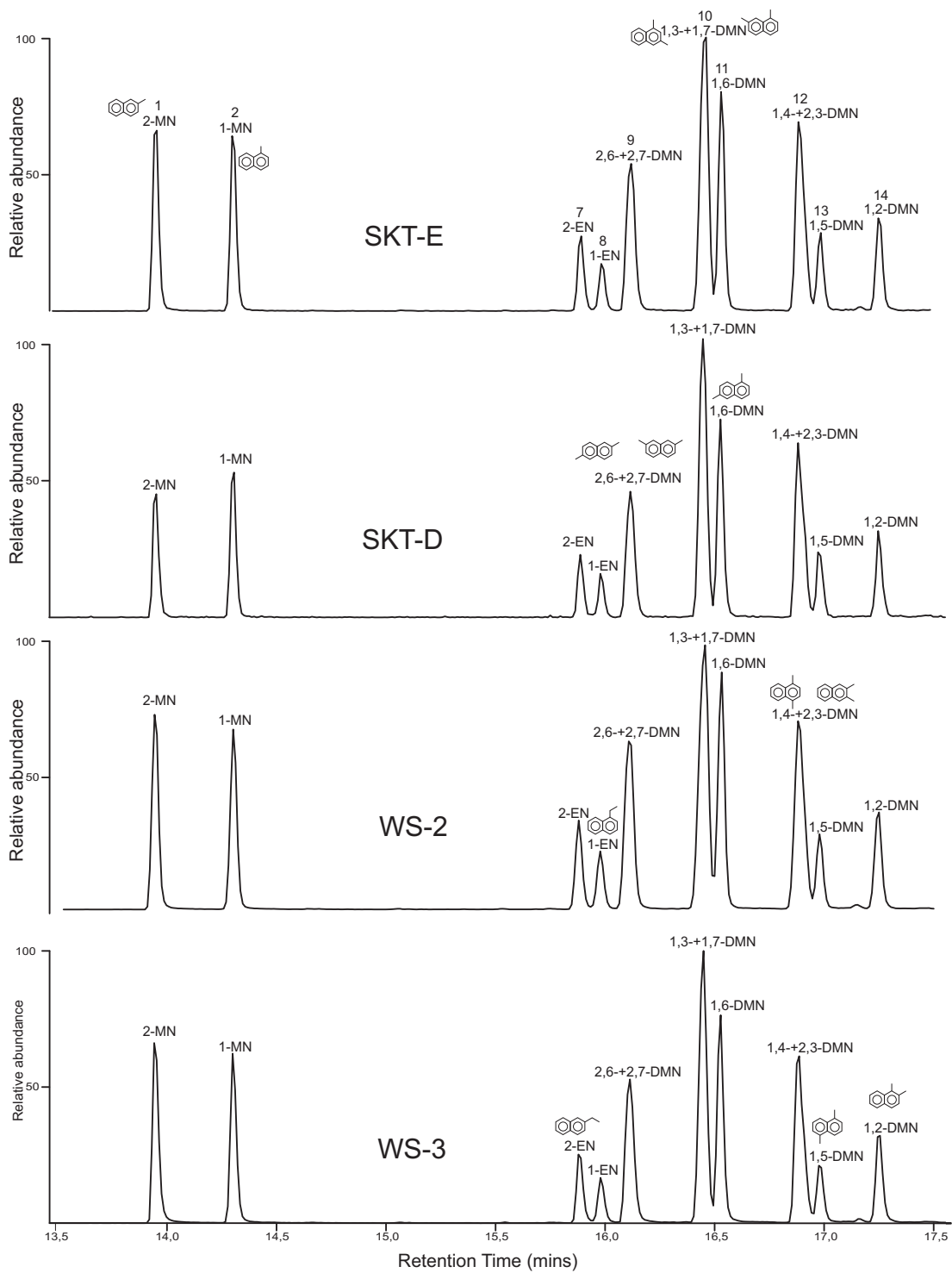


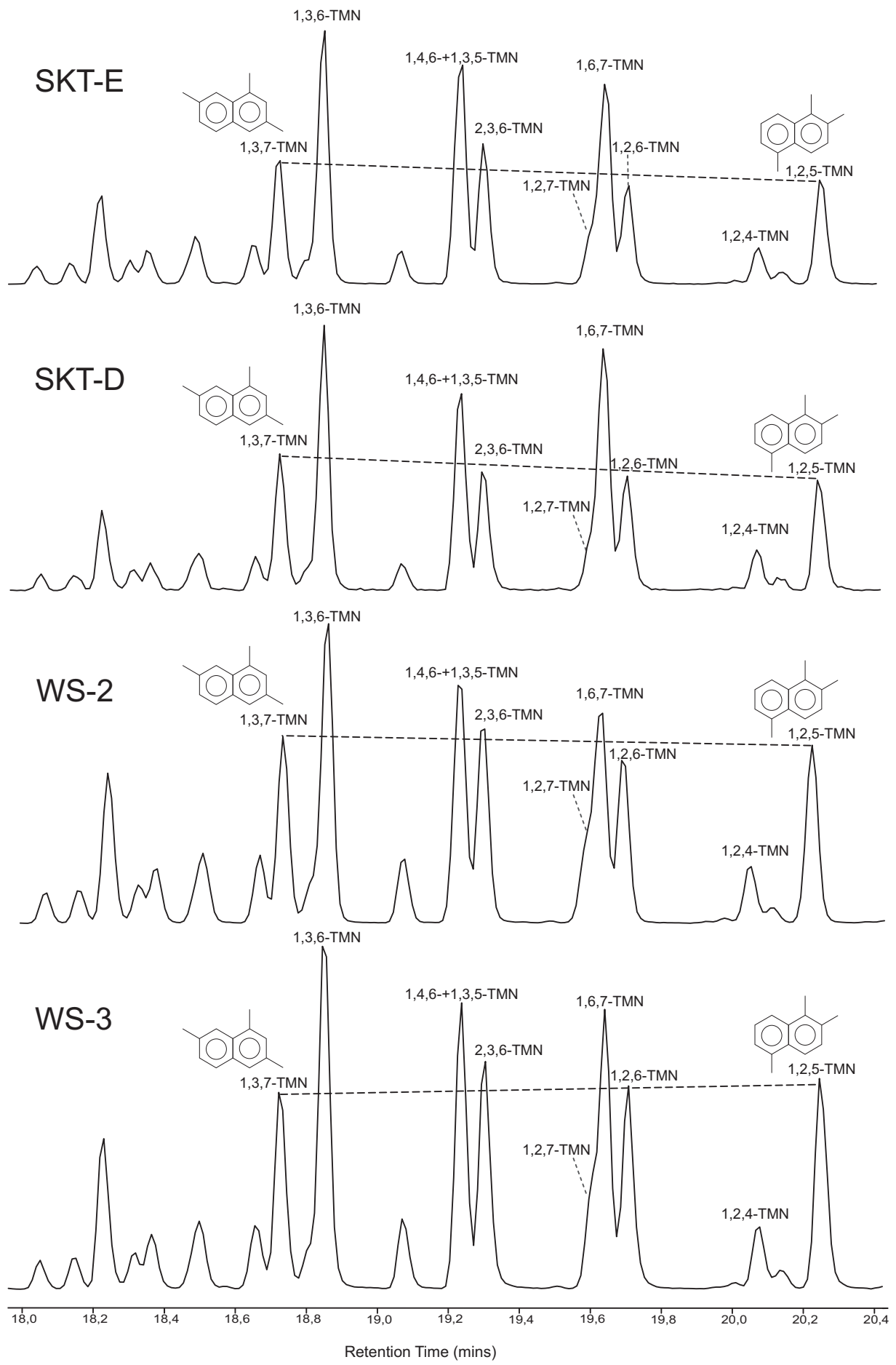
SKT-E



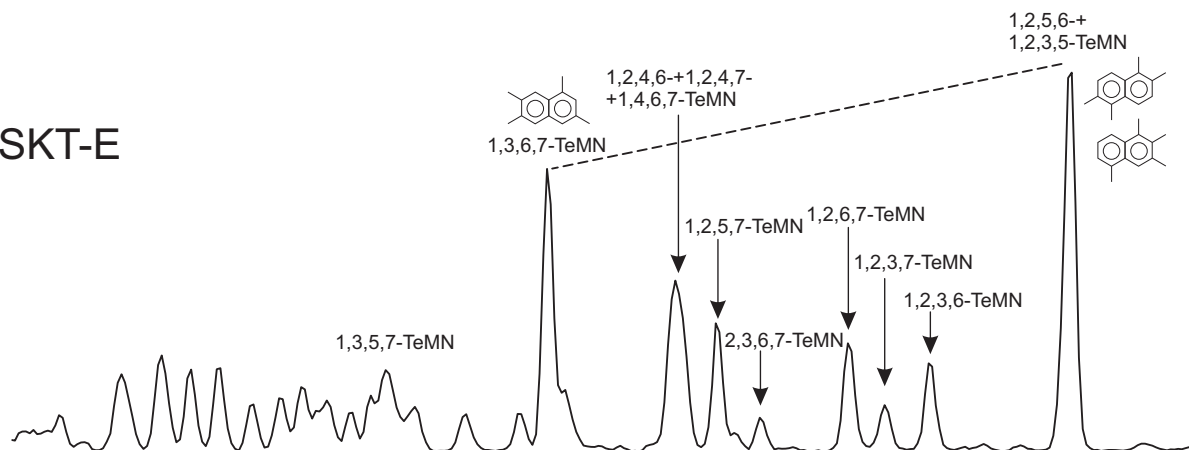
WS-3



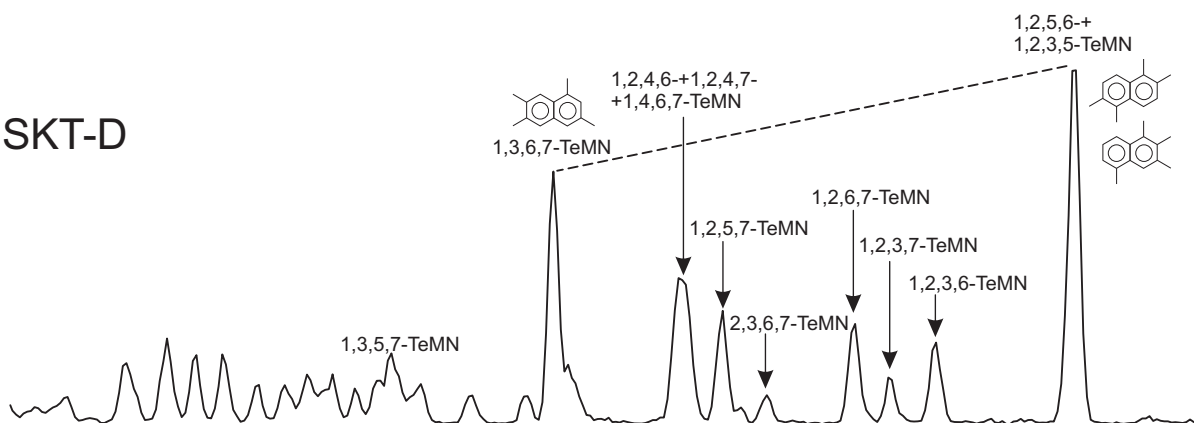




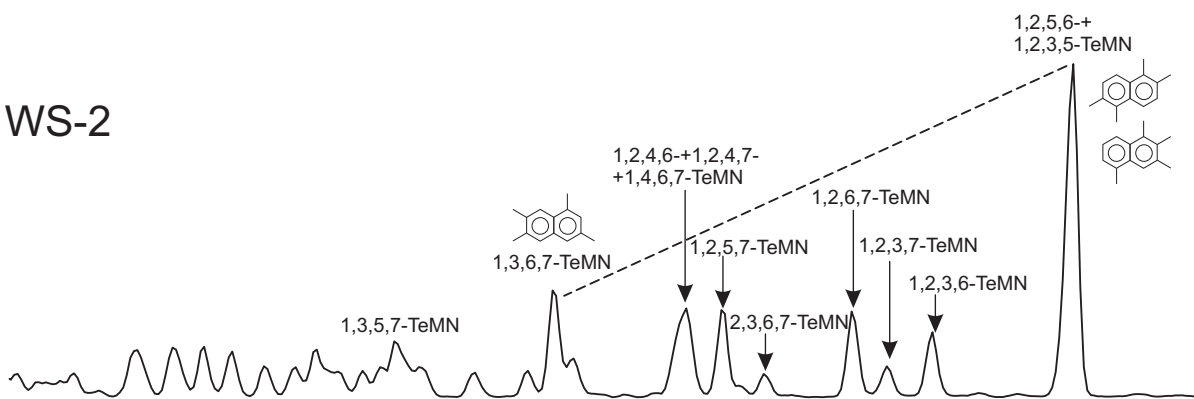
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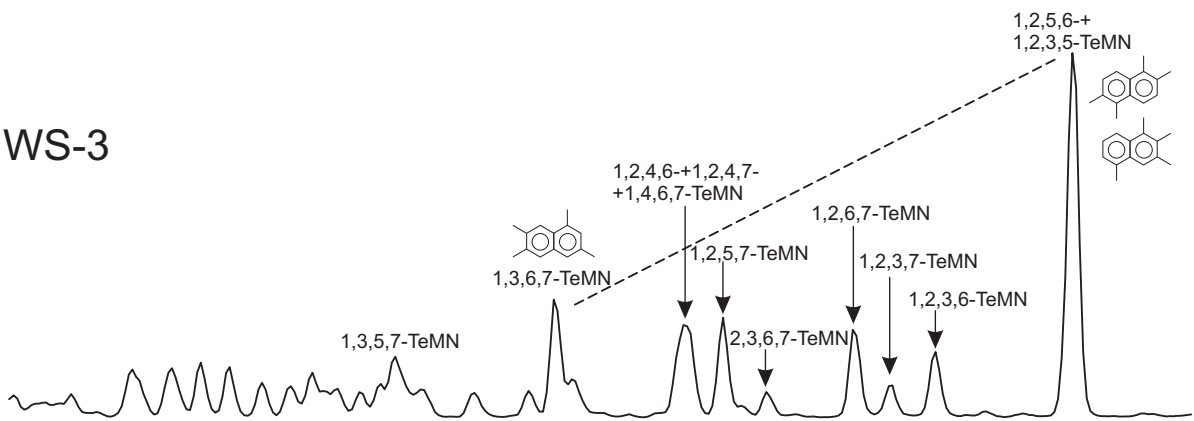
SKT-D



WS-2



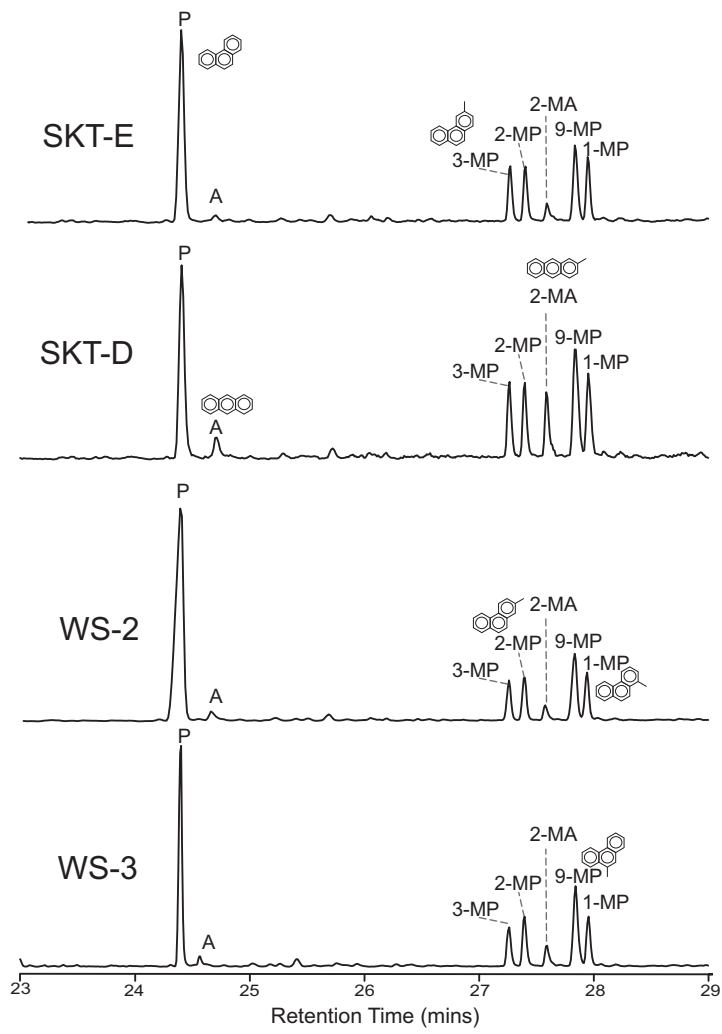
WS-3



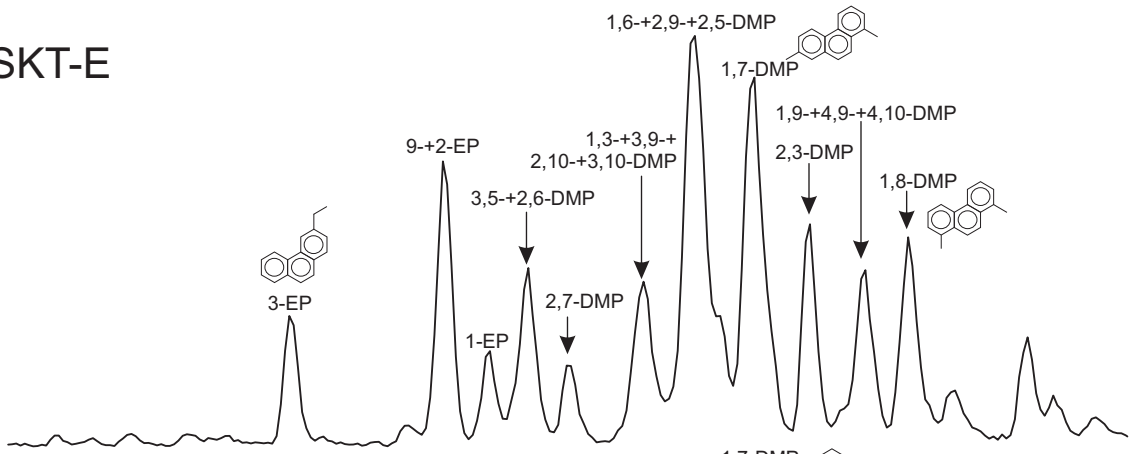
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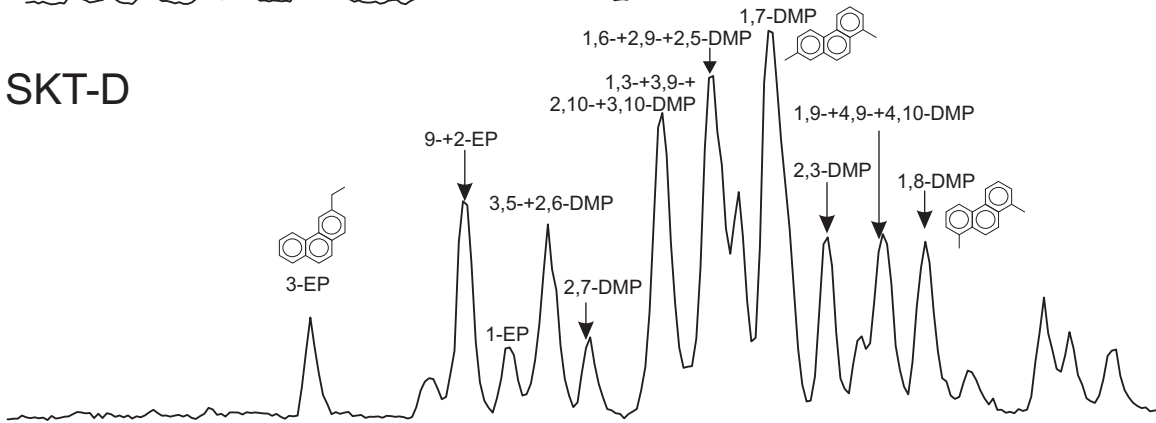
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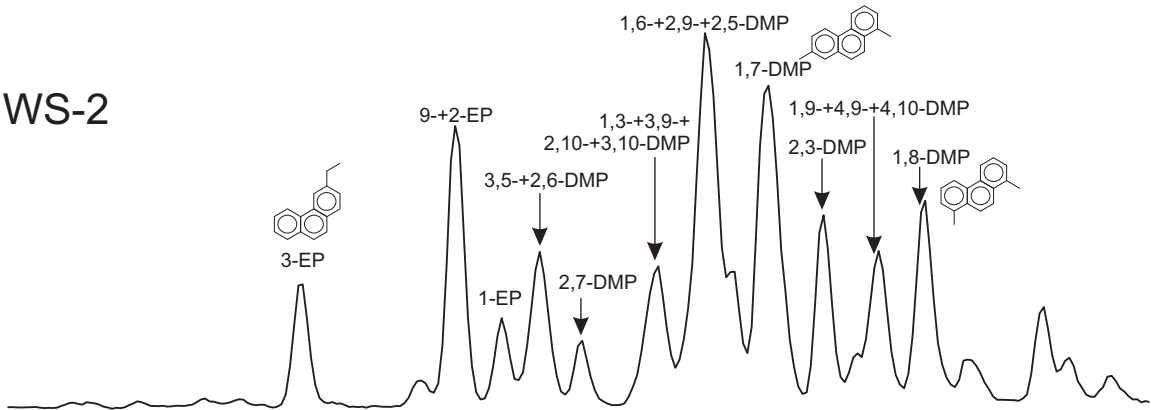
SKT-E



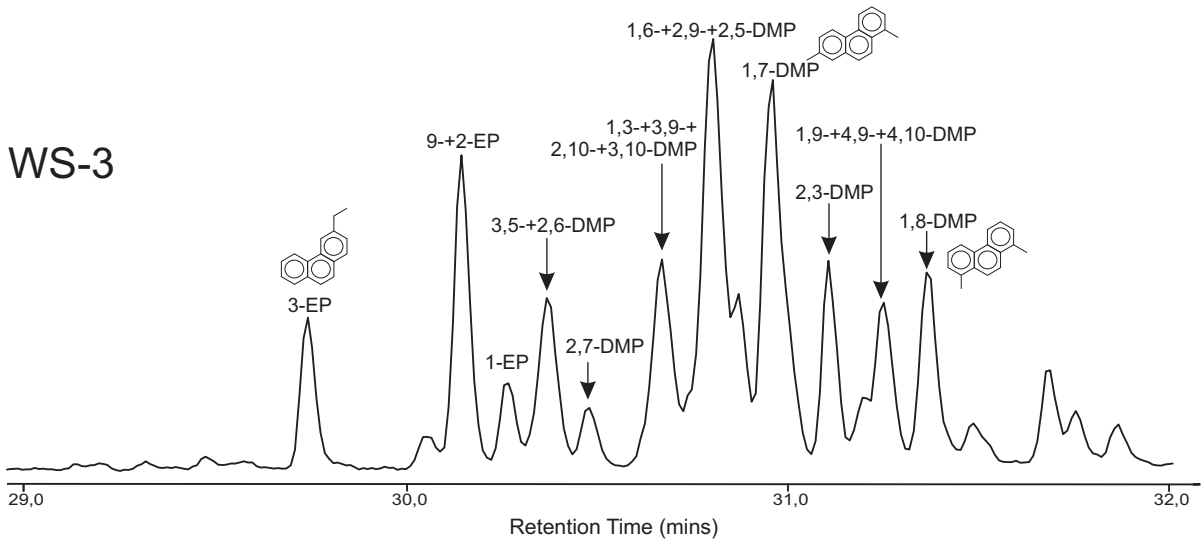
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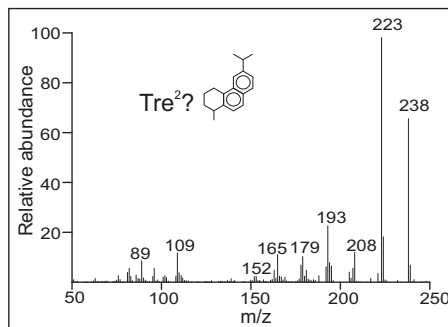
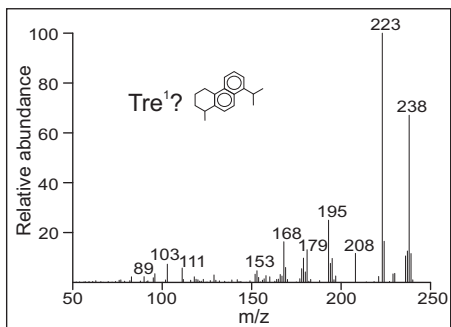
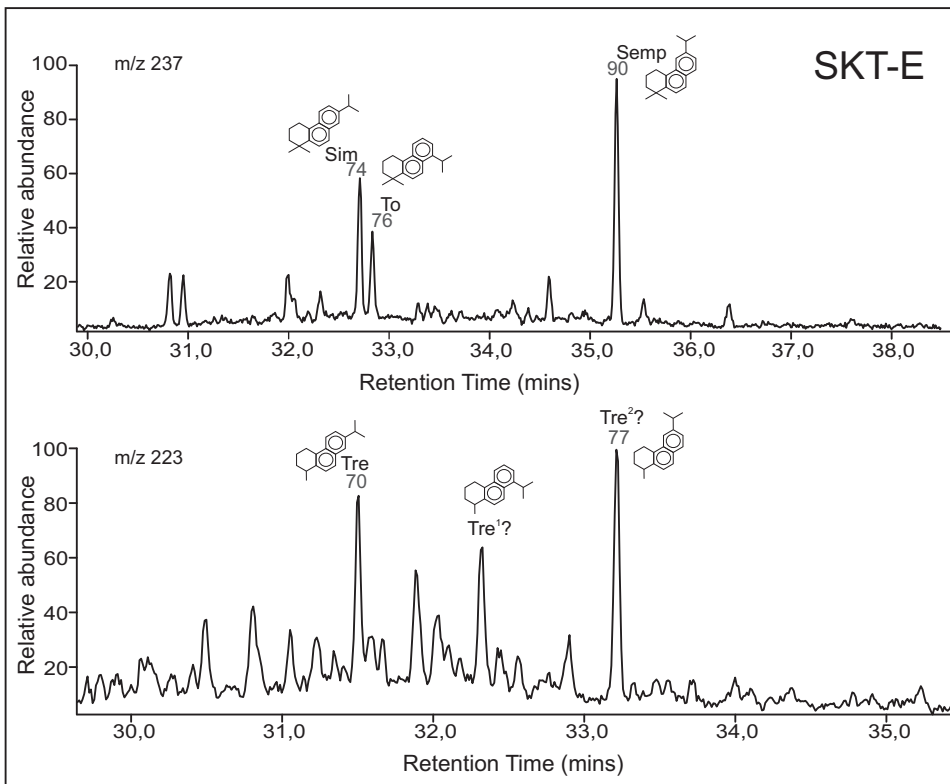
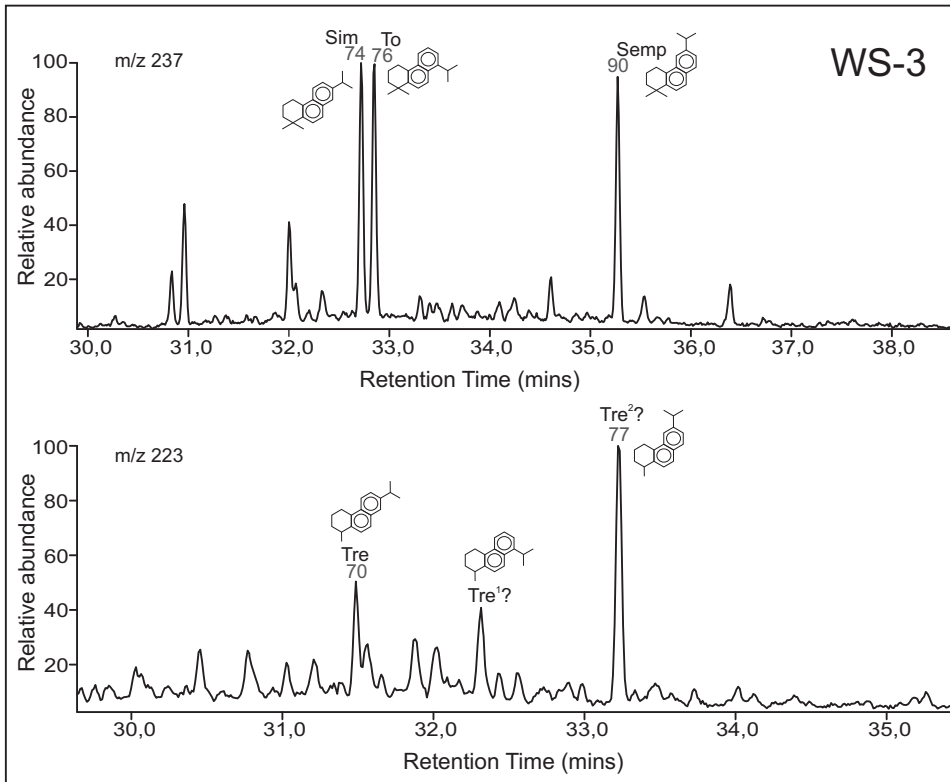


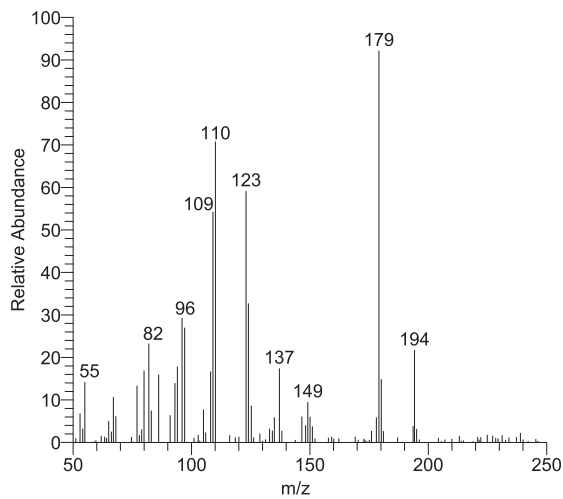
WS-2



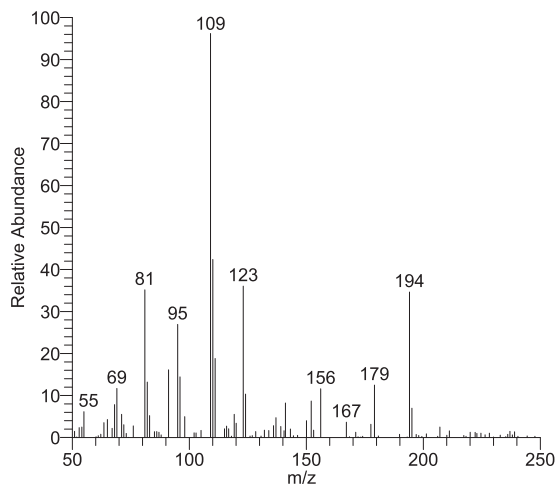
WS-3



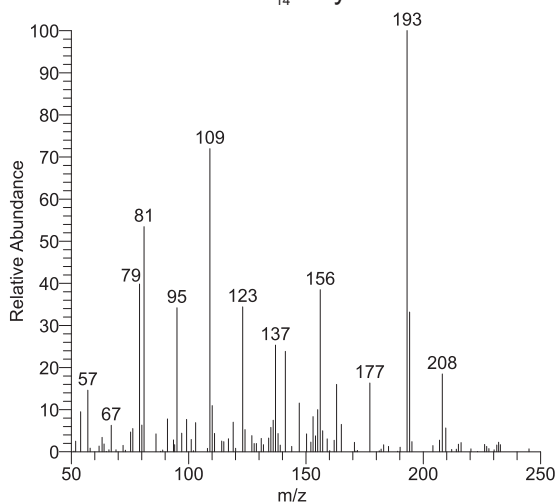




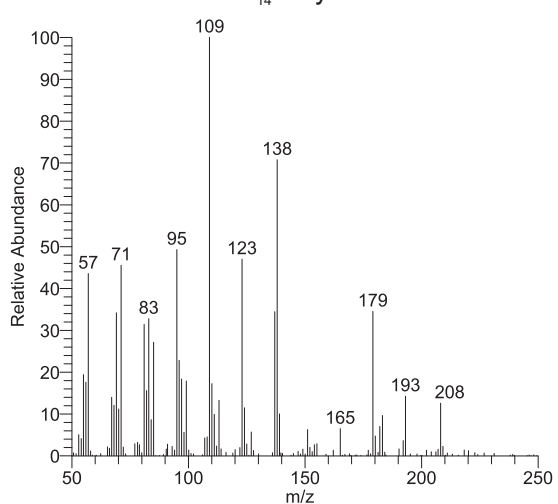
Peak a: C₁₄ bicyclic alkane?



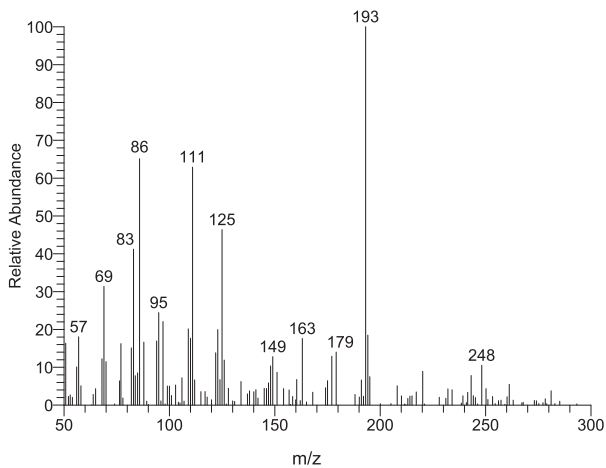
Peak e: C₁₄ bicyclic alkane?



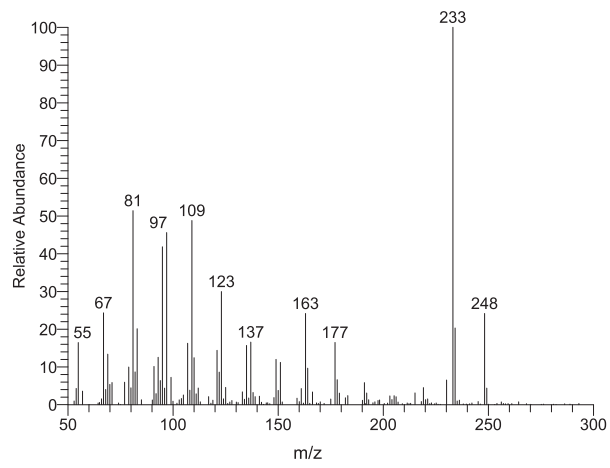
Peak f: C₁₅ bicyclic alkane?



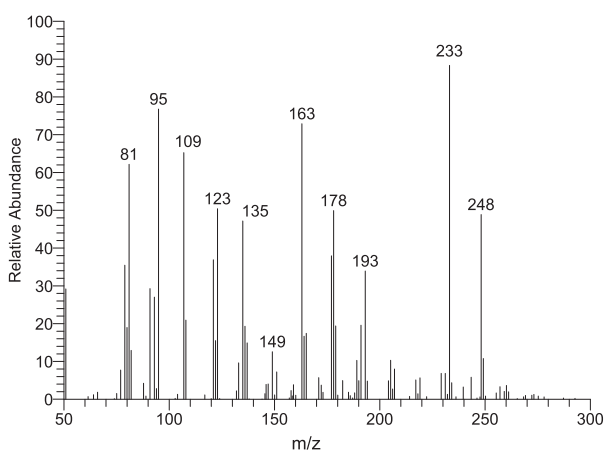
Peak h: C₁₅ bicyclic alkane?



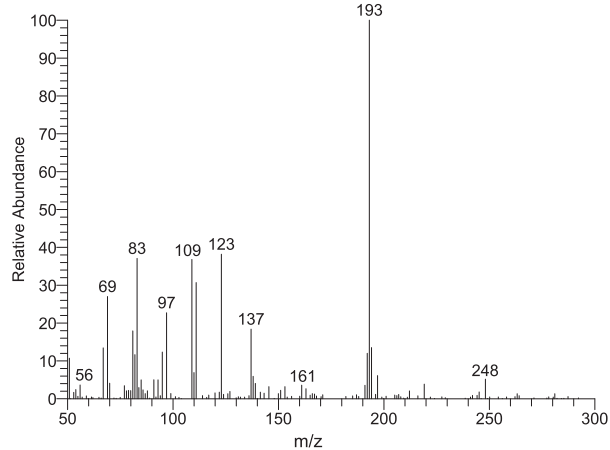
Peak I: C₁₈ tricyclic hydrocarbon?



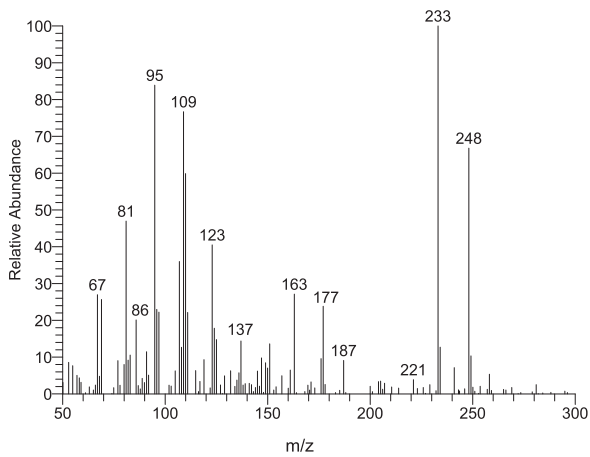
Peak III: C₁₈ tricyclic hydrocarbon?



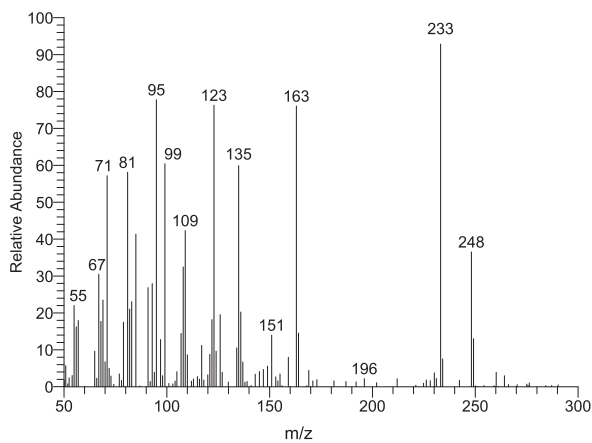
Peak IV: C₁₈ tricyclic hydrocarbon?



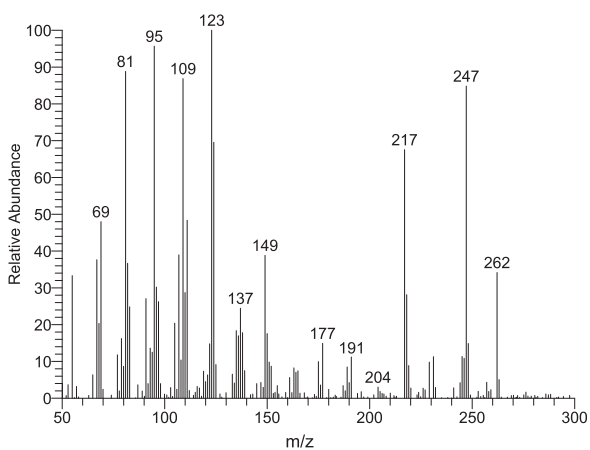
Peak V: C₁₈ tricyclic hydrocarbon?



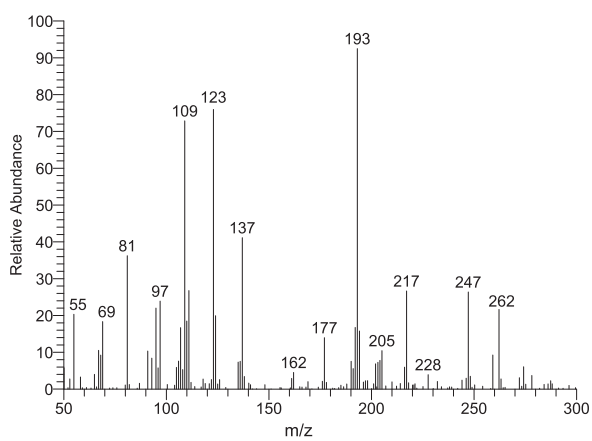
Peak VI: C₁₈ tricyclic hydrocarbon?



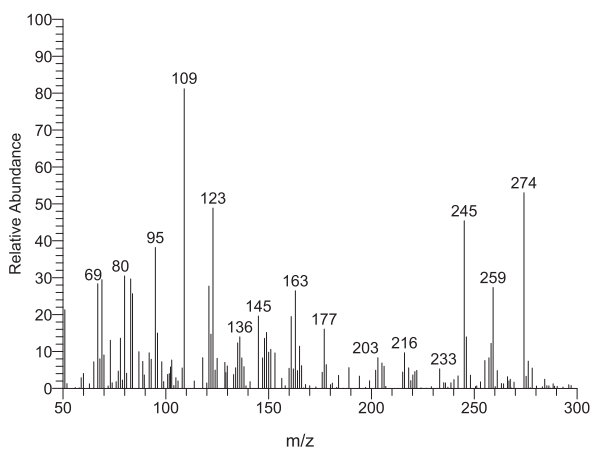
Peak VII: C₁₈ tricyclic hydrocarbon?



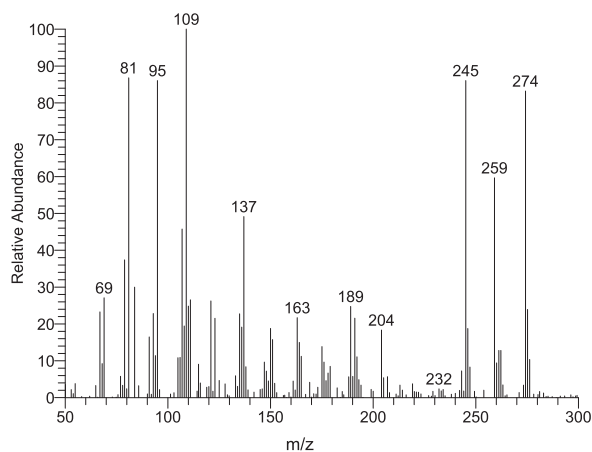
Peak VIII: C₁₉ tricyclic hydrocarbon?



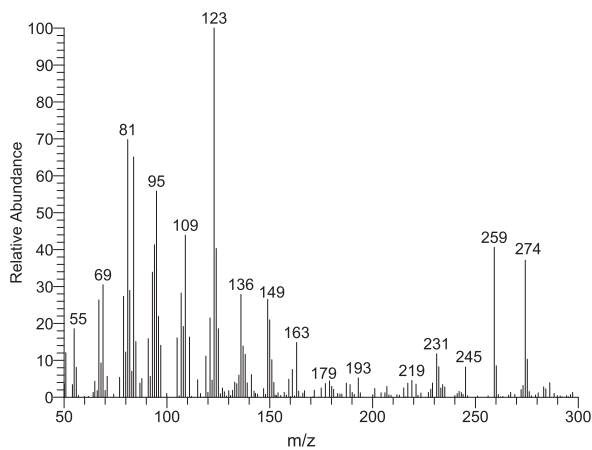
Peak IX: C₁₉ tricyclic hydrocarbon?



Peak X: C₂₀ tetracyclic diterpenoid?



Peak XI: C₂₀ tetracyclic diterpenoid?



Peak XVIII: C₂₀ tetracyclic diterpenoid?