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Maria-Fernanda Romero-Sarmiento, Armelle Riboulleau, Marco Vecoli, G. Versteegh, Fatima Laggoun-Défarge. Aliphatic and aromatic biomarkers from Carboniferous coal deposits at Dunbar (East Lothian, Scotland): Palaeobotanical and palaeoenvironmental significance. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 2011, 309, pp.309-326. 10.1016/j.palaeo.2011.06.015 . insu-00602822

HAL Id: insu-00602822

<https://insu.hal.science/insu-00602822>

Submitted on 23 Jun 2011

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

Maria-Fernanda Romero-Sarmiento ^{a,1}, Armelle Riboulleau ^{a,*}, Marco Vecoli ^a, Gerard J. M. Versteegh ^b, Fatima Laggoun-Défarge ^c

^a *Université Lille 1 & CNRS FRE 3298, bâtiment SN5, 59655 Villeneuve d'Ascq cedex, France*

^b *MARUM, Universität Bremen, Leobenerstraße, 28359 Bremen, Germany*

^c *Université d'Orléans, CNRS/INSU - Institut des Sciences de la Terre d'Orléans UMR 6113. Campus Géosciences - 1A, rue de la Férollerie, 45071 Orleans cedex 2, France*

* Corresponding author: Tel: +33 3 20 43 41 10; fax: +33 3 20 43 49 10
E-mail address: armelle.riboulleau@univ-lille1.fr

¹ Present address: IFP Energies nouvelles, Direction Géologie-Géochimie-Géophysique, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison cedex

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. Introduction

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

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

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

2. Geological setting and previous studies

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

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

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

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

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

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

3. Analytical methods

3.1. Experimental procedures

The four coal samples (Fig. 2) were studied by Rock-Eval pyrolysis and biomarker analysis. Rock-Eval pyrolysis was performed on 100 mg of ground rock with an Oil Show Analyser device at the University of Paris 6 (France), using the conventional temperature program described in Espitalié et al. (1986). The pyrolysis oven temperature was programmed with 25°/min from 300°C (held 3 min) to 650°C (held 3 min). However, due to the poor estimation of the total organic carbon (TOC) content of coals by Rock-Eval analysis (Espitalié et al, 1986), their TOC content was additionally determined on 100 mg of powdered decarbonated sample using a LECO carbon analyser at the same university (Paris 6, France). The hydrogen index (HI) was calculated using the Rock-Eval S₂ and the LECO TOC values.

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

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

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

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

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

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

3.3. Organic petrography

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

4. Results

4.1. Bulk OM characteristics

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

4.2. Maceral composition and vitrinite reflectance

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

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

4.3. Aliphatic hydrocarbons

4.3.1. Total aliphatic hydrocarbons

The total ion currents (TIC) of the aliphatic fractions of the coal extracts (Fig. 5) are dominated by a series of *n*-alkanes ranging from C₁₃ to C₃₀. The distribution of *n*-alkanes is relatively similar in all four samples and the most abundant are *n*-C₂₇ and *n*-C₂₉ (Fig. 6). Long chain C₂₃ – C₃₃ *n*-alkanes are characterized by an odd-over-even predominance with a maximum at *n*-C₂₇ (Fig. 6). The carbon preference index (CPI) ranges between 1.65 and 1.93 (Table 1). Series of C₁₄ to C₂₁ acyclic isoprenoids dominated by norpristane (C₁₈), pristane (Pr; C₁₉) and phytane (Ph; C₂₀), were also detected (Fig. 6). Pr is the most abundant compound in all the samples except SKT-D, where the *n*-C₂₇ alkane is more abundant (Fig. 5). The Pr/Ph ranges from 7.33 to 14.67 (Table 1). The Pr/*n*-C₁₇ is more than 1, whereas the Ph/*n*-C₁₈ is inferior to 1 (Table 1; Fig. 7). Branched alkanes without odd or even chain length predominance were also recognized in low abundance (Fig. 6). Steranes, hopanes, bicyclic alkanes and several diterpanoids were clearly detected in the aliphatic fractions (Fig. 5).

4.3.2. Hopanoids

Series of αβ-hopanes were detected in all the samples by monitoring the *m/z* 191 ion (Fig. 8). These compounds are dominated by 17α(H),21β(H)-hopanes (22R and 22S epimers) from C₂₇ to C₃₃, with a maximum at C₂₉ or C₃₀ hopanes (Fig. 8).

Series of $\beta\alpha$ -moretanes (17 β (H),21 α (H)-moretanes) were also detected ranging from C₂₇ to C₃₂, with a maximum at C₃₀ (Fig. 8). C₂₉ $\beta\beta$ -hopane was present in all the samples (Fig. 8). Tricyclic terpanes and gammacerane were not observed.

4.3.3. Steroids

Steranes and diasteranes were detected in all the samples using the characteristic fragment at m/z 217 (Fig. 9). Steranes are more abundant than diasteranes and the distribution of these compounds is similar in all the samples (Fig. 9). Steranes are dominated by the C₂₉ 5 α (H),14 α (H),17 α (H)-20R regular sterane (C₂₉ $\alpha\alpha\alpha$ -sterane; Fig. 9 and 10), followed by an important contribution of the $\alpha\beta\beta$ isomer (Fig. 9). Diasteranes are dominated by C₂₉ $\beta\alpha$ -diasteranes. However, series of C₂₇ to C₂₉ $\alpha\beta$ -diasteranes and C₂₇ to C₂₉ $\alpha\beta\beta$ -steranes were also recognized in all the samples (Fig. 9). Additionally, short chain steroids were also detected in low amounts. SKT coals show a marked contribution of short chain C₁₉ - C₂₀ steroids in comparison with WS samples (Fig. 9).

4.3.4. Bicyclic alkanes

Seventeen bicyclic alkanes ranging from C₁₄ to C₁₆ carbon atoms have been identified in the aliphatic extracts of the Scottish coals, using

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

The distribution of bicyclic alkanes is relatively similar in all four coals and the most abundant are C₁₄ bicyclic alkanes (Fig. 11; e.g. Peaks b and c). 8 β (H)-homodrimane (Fig. 11; Peak p) is present in significant proportion in most samples except SKT-D, while the relative abundance of peak h allows differentiate WS coals from SKT samples. The relative abundance of 4 β (H)-eudesmane and 8 β (H)-drimane is similar in all samples (Fig. 11; Peaks i and k; respectively).

4.3.5. Tricyclic and tetracyclic diterpenoids

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

Table 4. The tetracyclic diterpenoids (C₂₀H₃₄) *ent*-beyerane (Peak XII), 16 β (H)-phyllocladane (Peak XIII), *ent*-16 α (H)-kaurane (Peak XV), 16 α (H)-phyllocladane (Peak XVI) and *ent*-16 β (H)-kaurane (Peak XVII) were mainly recognized, by comparison with the published mass spectra of authentic compounds (Noble, 1986; Otto et al., 1997; also in Noble et al., 1985; Philp, 1985; Schulze and Michaelis, 1990).

The peak labelled II has a mass spectrum characterized by a strong fragment at m/z 233 (Fig. 12A). Based on its fragmentation pattern, compound II was tentatively identified as a C₁₈ tricyclic hydrocarbon (Fig. 12). This latter compound is particularly abundant in SKT samples, as are C₁₉ and C₂₀ steranes, it could therefore be related to short chain steroids. To our knowledge, the molecular structures for most of the C₁₈ – C₁₉ diterpenoids identified in this study, have not been previously established (see mass spectra in the appendix).

In most samples, the tetracyclic diterpenoid distribution is dominated by kaurane and phyllocladane. Kaurane isomers, however, are slightly more abundant in SKT samples while phyllocladanes are more predominant in WS coals (Fig. 12). *ent*-Beyarane shows a relatively similar contribution in all samples, and generally is present in low amounts in comparison to the other C₂₀ diterpenoids.

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

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

Dibenzofuran (DBF) and its methyl derivatives (MDBF) were also detected in the aromatic fractions (Fig. 13; Peaks 18, 29, 30 and 31, respectively). The distribution of MDBF is dominated by 2-MDBF (Peak 30) and 4-MDBF (Peak 29). The latter is the most thermodynamically stable isomer (Fig. 13; Radke et al., 2000). Several aromatic compounds with methylated-tetrahydronaphthalene skeletons (Fig. 13; Table 4) were also determined. Accordingly, ionene (1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene) and 1,2,3,4-tetrahydro-6-(1,1-dimethyl)-naphthalene were clearly identified (Fig. 13; Peaks 4 and 17, respectively). Finally, series of C_{17} to C_{19} isohexylalkylnaphthalenes have been also observed (Fig. 19). The contribution of the 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

on their mass spectra and elution times, comparison with the distribution of the established diaromatic tricyclic hydrocarbons simonellite, diaromatic totarane and diaromatic sempervirane (Otto et al., 1997; Otto and Simoneit, 2001; Tuo and Philp, 2005), and the identification of diaromatic totarane and sempervirane in our coals, these compounds were tentatively identified as tetrahydroretene isomers, based on the totarane and sempervirane skeletons, respectively. Compound Tre¹ could be the 1-methyl-1,2,3,4-tetrahydro-8-isopropylphenanthrene (totarane-derived) and Tre² the 1-methyl-1,2,3,4-tetrahydro-6-isopropylphenanthrene (sempervirane-derived; Fig. 20). Their molecular structures are also proposed in Figure 20.

5. Discussion

5.1. Thermal maturity

According to LECO results, the TOC values for these Scottish samples are typical for coals (60.8 and 71.9%; Table 1). Based on such values of TOC, the average T_{max} (426 °C) from Rock-Eval analyses, as well as the vitrinite reflectance (0.45 %), the rank of the studied coals is of subbituminous A, i.e. an immature stage of thermal evolution (Fig. 3). This interpretation is supported by molecular thermal maturity indicators from the aliphatic and aromatic fractions. First, the CPI is high (>1) due to odd predominance (Table 1; Bray and Evans, 1961). Second, the thermally unstable C₂₉ ββ hopane is observed in all samples

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

5.2. Biomarker distributions and palaeoenvironmental conditions

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

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

Other arguments for a purely terrestrial depositional environment are the high Pr/Ph (Table 1) and Pr/*n*-C₁₇ vs. Ph/*n*-C₁₈ ratios (Fig. 7; Hunt, 1995). These ratios characterize the Scottish coals as Type III OM

which is usually derived from terrestrial plants (Peters and Moldowan, 1993) deposited under oxidizing conditions, and in particular, the WS coal level (Fig. 7).

A bacterial contribution to the OM is further evidenced by the occurrence of branched alkanes (Fig. 6; e.g. Shiea et al., 1990), hopanoids (Figs. 5 and 8; Ourisson et al., 1979) and bicyclic alkanes of the drimane and homodrimane series (Fig. 11; Noble, 1986; Noble et al., 1987). Aromatic hydrocarbons often associated to a microbial source include 1,2,3,5,6-pentamethylnaphthalene (1,2,3,5,6-PMN; Fig. 13; Table 5; Bastow et al., 1998) and 1,3,6,7-tetramethylnaphthalene (1,3,6,7-TeMN; Fig. 16; e.g. Jiang et al., 1998).

Steroids have also been used to differentiate depositional settings (Peters et al., 2005). Huang and Meinschein (1979) proposed a useful ternary diagram to identify the source of the OM which can be constructed by the distribution of C₂₇, C₂₈ and C₂₉ sterols (Fig. 10). Based on their results, the dominant source of C₂₇ sterols is zooplankton, C₂₈ sterols are generally components of phytoplankton and C₂₉ sterols are mainly derived from terrestrial plants. There are many exceptions on these rules; for instance, C₂₉ sterols are also found in marine diatoms and dinoflagellates (e.g. Rampen et al., 2010). Nevertheless, the method seemed reliable for other Palaeozoic (Middle Devonian) coals which have a high predominance of C₂₉ steranes (e.g. Fowler et al., 1991; Kashirtsev et al., 2010). Considering this, the dominance of C₂₉ relative to C₂₇ steranes in these coals further

evidences their terrestrial origin (Table 1; Fig. 9). Consistent with the shallow-water environment proposed for Scottish coals (Murchison and Raymond, 1989), the steroids plot in a transitional estuarine-bay environment (Fig. 10). It is interesting to note that short chain C₁₉ - C₂₀ steroids are abundant in SKT coals (Fig. 9). Although these compounds are not commonly described from coals, they have been reported in a Devonian liptobiolith (Kashirtsev et al., 2010). The relative abundance of these C₁₉ - C₂₀ steroids may be characteristic for some primitive coals, suggesting that they could be more specific biomarkers of early plants.

The occurrence of the combustion-derived PAHs pyrene, fluoranthene, benzo[a]anthracene, chrysene and triphenylene (Fig. 13) can be related to the significant presence of the fusinite group, most particularly pyrofusinite, in the organic matter. Charred or fusinized plant debris have been frequently reported in coals from the Midland Valley of Scotland (Murchison and Raymond, 1989; Scott and Jones, 1994; Falcon-Lang, 2000) and combustion-derived PAHs have been observed in coal extracts (Murchison and Raymond, 1989). These compounds and macerals testify that fire events took place contemporarily with coal deposition. Fire events in coals are often related to lightning, but in the case of the Midland Valley of Scotland, volcanic activity also appears as a major cause of wildfires (Murchison and Raymond, 1989; Scott and Jones, 1994; Falcon-Lang, 2000).

5.3. Linking biomarkers, palynology and palaeobotany

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

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

lycopsids, this floral assemblage appears relatively comparable to the anatomically preserved floras of Glenar buck and Pettycur in Scotland (Scott et al., 1984), which are of Viséan age but slightly older than our studied coals. It is notable that although there are some Viséan records of *Cordaite*s (e.g. Wang, 1998), *Cordaite*s remains were not reported from Glenar buck and Pettycur (Scott et al., 1984) nor *Cordaite* spores (e.g. *Florinites*) in the palynofacies from our Scottish coals (Spinner, 1969; Spinner and Clayton, 1973).

The relatively similar lycopsid-dominated floras observed in SKT and WS coals (Spinner, 1969; Spinner and Clayton, 1973) are consistent with the relatively similar biomarker content observed in both coals. Some aromatic biomarkers detected in this study can be related to specific plant taxa (Table 7). For instance, the presence of alkyl dibenzofurans (MDBFs) indicates lichen input (Fig. 13; Radke et al., 2000). Although lichen fossils or specific lichen spores have not been reported in Scottish coals (Spinner, 1969; Spinner and Clayton, 1973), it can be safely assumed that Euramerican Coal Measure forests were a good potential habitat for lichens. Among the less specific biomarkers, the detected combustion-derived PAHs cannot be associated to specific kind of plants (Oros and Simoneit 2000a,b; Oros et al. 2006; Iinuma et al., 2007). It is also the case for 1,6-dimethylnaphthalene (1,6-DMN; Fig. 14), 1,2,5-trimethylnaphthalene (1,2,5-TMN; Fig. 15), pimanthrene (1,7-DMP; Fig. 16) and cadalene, which can be produced by aromatization of several different terpenoid

structures and/or which precursors are widespread among terrestrial plants (Table 7). Ionene is a degradation product of β -carotene (Day and Erdman, 1963). It is often observed in coal extracts (e.g. Wang and Simoneit, 1990), but also can be produced from thermal degradation of marine and lacustrine sediments (Day and Erdman, 1963; Achari et al., 1973). 4 β (H)-eudesmane is another non-specific land plant biomarker. This compound has been rarely observed in Palaeozoic coals (del Río et al., 1994; Dzou et al., 1995) and is considered to derive from evolved land plants such as angiosperms and gymnosperms (e.g. conifers; Noble, 1986). However, bicyclic alkanes with an eudesmane skeleton have been also identified in recent bryophytes (Asakawa, 2004). Its oldest reported occurrence in sediments, to our knowledge, is Middle Pennsylvanian (Dzou et al., 1995).

The diterpenoids *ent*-beyerane, abietane, *ent*-kaurane and phyllocladane have been previously described in Carboniferous (e.g. Schulze and Michaelis, 1990; Fleck et al., 2001; among others) and Permian coals (e.g. Noble, 1986; Noble et al., 1985). Abietane precursors occur in all conifer families (Otto and Wilde, 2001; Cox et al., 2007) and this compound has been recently described in the pyrolysate of Late Carboniferous amber (Bray and Anderson, 2009). Kaurane skeletons have been observed in different kinds of plants, and in particular bryophytes (e.g. Noble, 1986; Chopra and Kumra, 1988; Asakawa, 2004). The occurrence of this component in very early terrestrial OM (e.g. Sheng et al., 1992; Disnar and Harouna, 1994; Kashirtsev et al,

2010; Romero Sarmiento et al., 2010) can be therefore related to bryophytes, which represent the earliest land plants. Phyllocladane and *ent-beyerane* have been mostly associated to all conifer families except Pinaceae (e.g. Noble, 1986; Schulze and Michaelis, 1990; among others). However, the oldest recorded occurrences of phyllocladane and *ent-beyerane* are Serpukhovian (Fabianska et al., 2003; Izart et al., 2006) and Middle Devonian (Sheng et al. 1992; Kashirtsev et al., 2010), respectively. The occurrence of these compounds in Carboniferous sediments that predated the evolution of conifers has been related to the Voltziales (e.g. Schulze and Michaelis, 1990) and/or the close relatives *Cordaite*s (e.g. Disnar and Harouna, 1994 and references therein), while in Devonian coals, these compounds were related to pteridophytes (Sheng et al. 1992).

The relative abundance of tricyclic and tetracyclic diterpenoids in coals is affected by the palaeobotanical and palaeoenvironmental conditions and consequently, by the available type of vegetation (e.g. Schulze and Michaelis, 1990; Fleck et al., 2001). In Permian coals, the dominance of tetracyclic diterpenoids, and in particular phyllocladane and kaurane isomers has been related to the pteridosperm *Glossopteris*, while a predominance of tricyclic terpanes (e.g. isopimarane, rimuane, fichtellite) can particularly indicate a Medullosan pteridosperm input (Noble, 1986). A predominance of kaurane has been also observed in 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 *Cordaite*s 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 *Cordaite*s input. This agrees
615 with an absence of *Cordaite*s 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 *Cordaite*s 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. *Cordaite*s 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 *Cordaite*s 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.

6. Conclusions

Numerous land-plant biomarkers have been identified in the aliphatic and aromatic fraction of the extracts of Early Carboniferous

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

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

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

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

Acknowledgements

The authors acknowledge financial support from the “ECLIPSE II
and INSU 2009 – Terrestrialization” grant from the INSU department of
CNRS. Thanks are extended to Dr. Charles Wellman (Department of
Animal and Plant Sciences, University of Sheffield, U.K.) for guidance
and assistance to M.V. during field work; this latter was funded by an
exchange grant from “EGIDE Programme d'Actions Intégrées franco-
britanniques ALLIANCE” of the British Council and the Ministère des
Affaires Étrangères of France, which is also gratefully acknowledged. M-
F. R-S. acknowledges receipt of a scholarship (No. E07D402105VE)
from the Programme Alþan. G. J. M.V. benefited from a position as
invited professor at the Université Lille 1 (France) and a Heisenberg
Stipend by the German Science Foundation (DFG). The authors are
grateful to François Baudin (Université Paris 6) for performing the Rock-
Eval and LECO analyses and to Brigitte Meyer-Berthaud (CNRS-
UMR0931 AMAP) for helpful discussions in palaeobotany. This is a
contribution to the ANR project “Global Perspectives on the
Terrestrialization Process”. The editor Finn Surlyk, Jørgen A. Bojesen-
Koefoed, and an anonymous reviewer are acknowledged for constructive
comments on the manuscript.

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1092

Figure captions

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

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

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

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

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

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

Fig. 7. Plot of Pr/*n*-C₁₇ vs. Ph/*n*-C₁₈ for Scottish coals (diagram from Hunt, 1995).

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

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

Fig. 10. Steroids ternary plot. The contributions of C₂₇, C₂₈ and C₂₉ steranes were calculated using the peak height of $\alpha\alpha\alpha$ (20R) and $\alpha\beta\beta$ (20S) isomers on *m/z* 217 fragmentograms. Paleoenvironmental and source interpretation from Huang and Meinschein (1979).

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

Fig. 12. Partial m/z 109 + 123 + 193 + 233 mass fragmentograms showing the distribution of diterpenoid hydrocarbons (o) in the extracts of Scottish coals. Peak assignments in Table 4. Numbers denote carbon number. (A) Mass spectrum of compound identified as C₁₈ tricyclic hydrocarbon (Peak II).

Fig. 13. Total ion current chromatograms of aromatic fraction from extracts of two selected coal samples. Peak assignments in Table 5

Abbreviations: MN – methylnaphthalene; EN + DMN – ethyl- and dimethylnaphthalene; DBF – dibenzofuran; TMN – trimethylnaphthalene; MDBF – methyldibenzofuran; TeMN – tetramethylnaphthalene; DMDBF – dimethyldibenzofuran; P – phenanthrene; PMN – pentamethylnaphthalene; MP – methylphenanthrene; EP + DMP – ethyl- and dimethylphenanthrene; PAHs – polycyclic aromatic hydrocarbons; X – contaminant (polysiloxanes).

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

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

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

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

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

Fig. 19. Partial m/z 155 + 169 + 183 mass fragmentograms showing a series of C₁₇ to C₁₉ isohexylalkylnaphthalenes in the aromatic fractions of Scottish coals. Peak assignments in Table 5. Abbreviations: iHMN – isohexylalkylnaphthalene, PMN – pentamethylnaphthalene, DMP – dimethylphenanthrene.

Fig. 20. Partial m/z 237 and m/z 223 mass fragmentograms showing the distribution of diaromatic tricyclic hydrocarbons in the aromatic fractions of Scottish coals. Abbreviations: Sim – simonellite, To – diaromatic tricyclic totarane, Semp – diaromatic tricyclic sempervirane, Tre – tetrahydroretene. Peak assignments in Table 5. Mass spectra of the two tentatively identified tetrahydroretene-derived isomers are also showed shown (Tre¹ and Tre²).

Table captions

Table 1

Bulk and molecular geochemical parameters from Scottish coals.

Table 2

Petrographic composition and vitrinite reflectance.

Table 3

Bicyclic alkanes identified.

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**

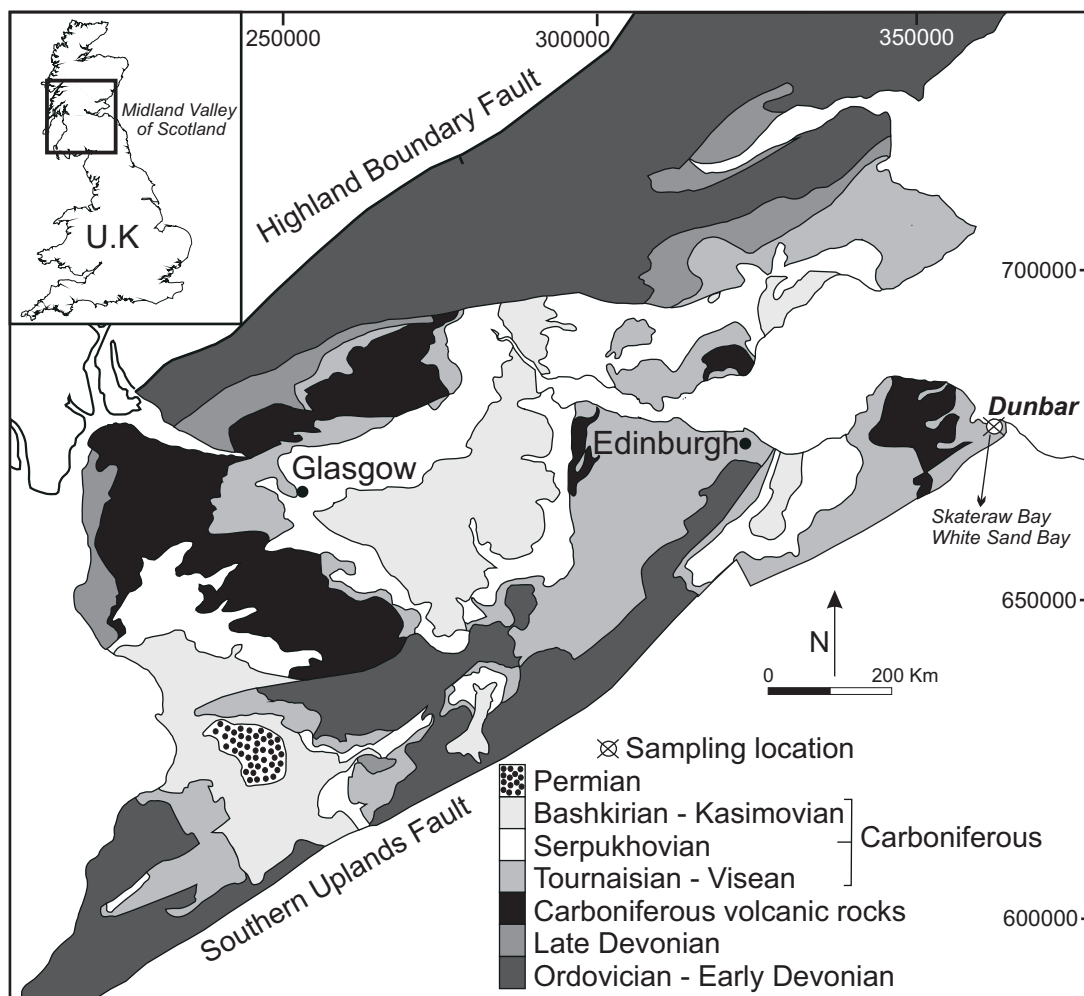
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1223 origin.

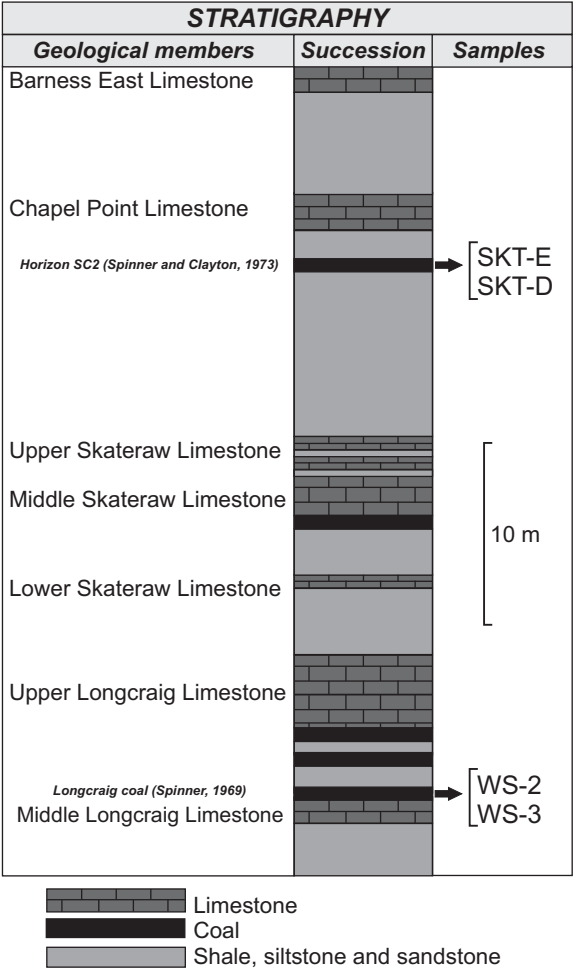
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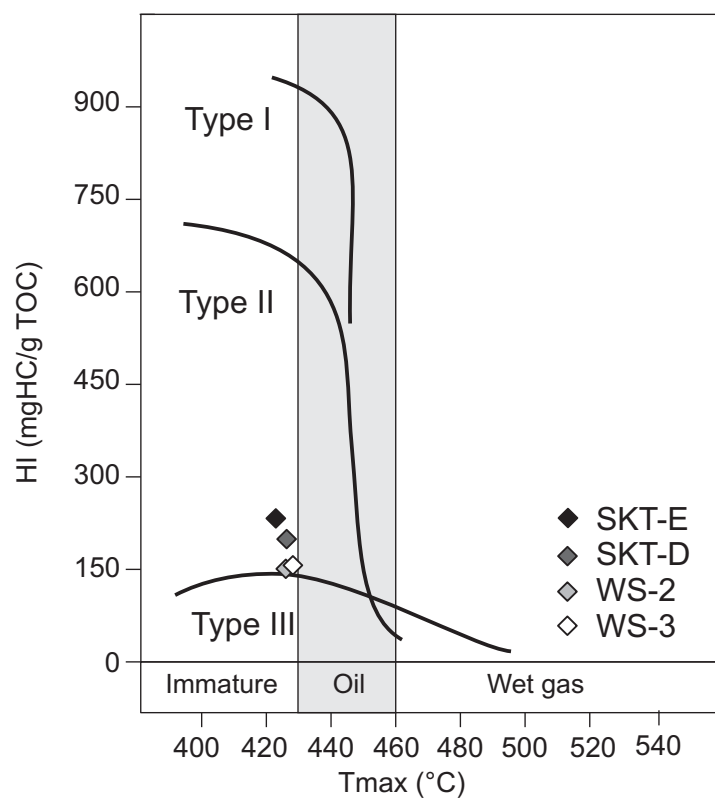
1225 **Appendix**

1226 Mass spectra of unknown compounds (Peak assignments in Tables 2
1227 and 3).

1228







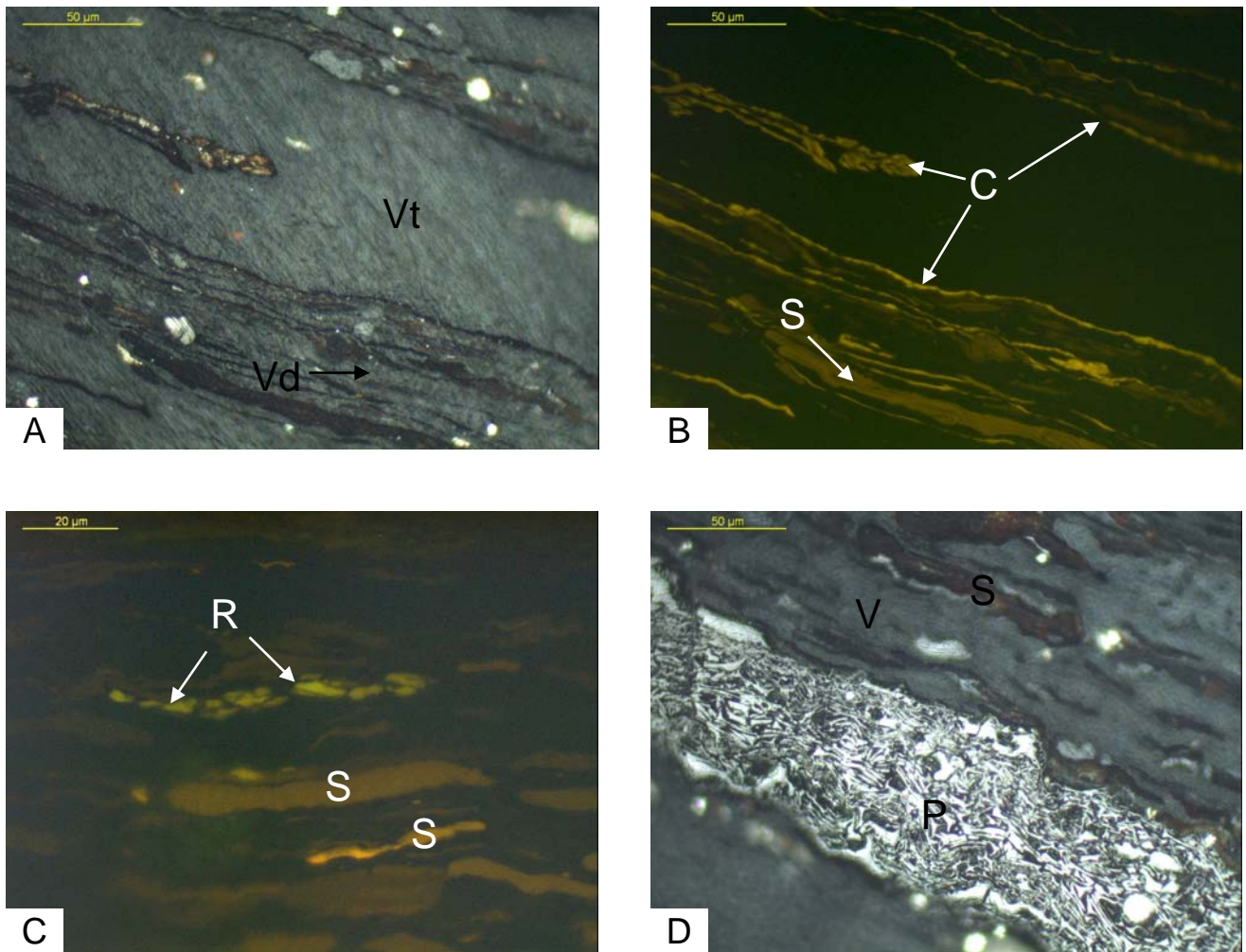
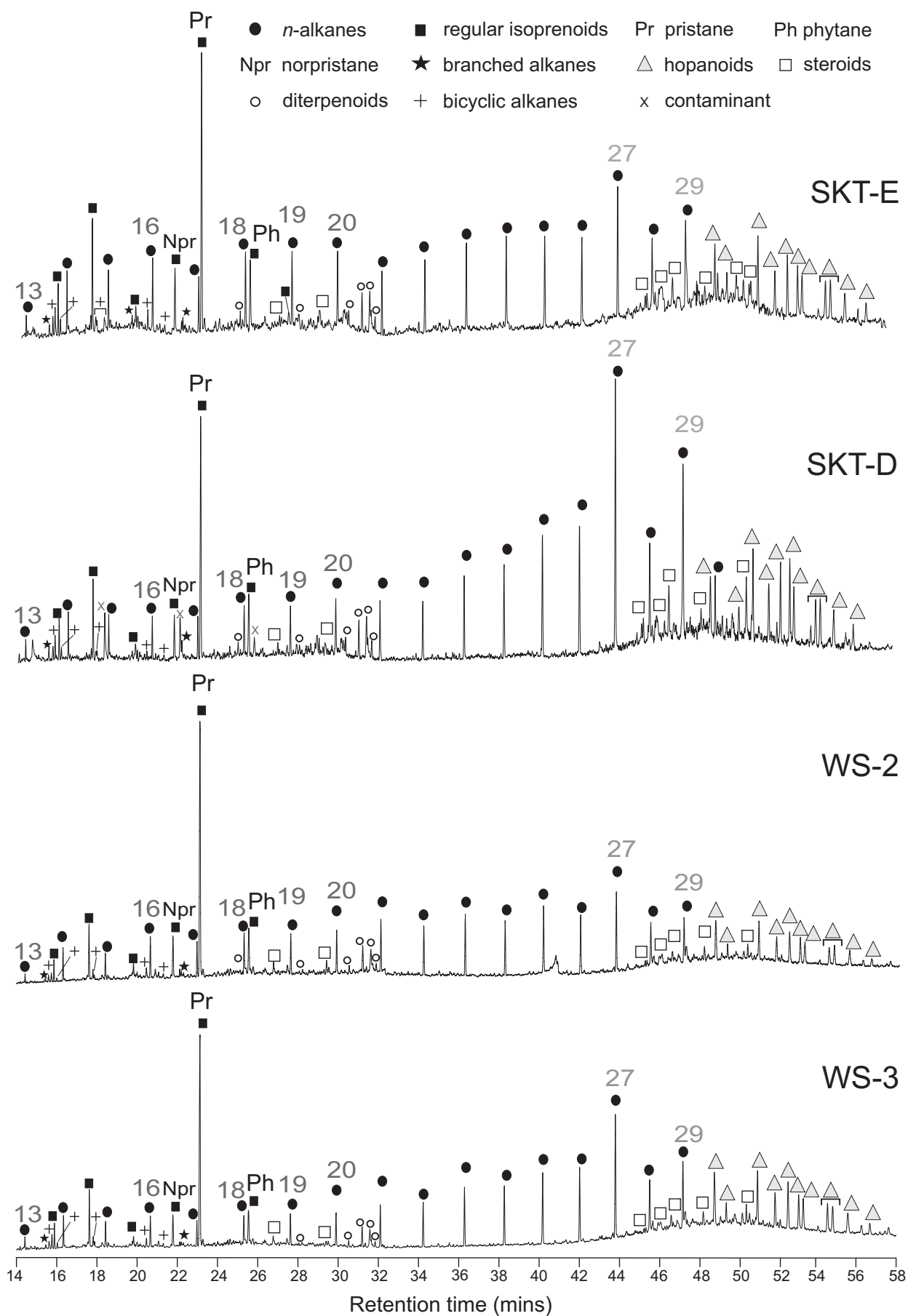
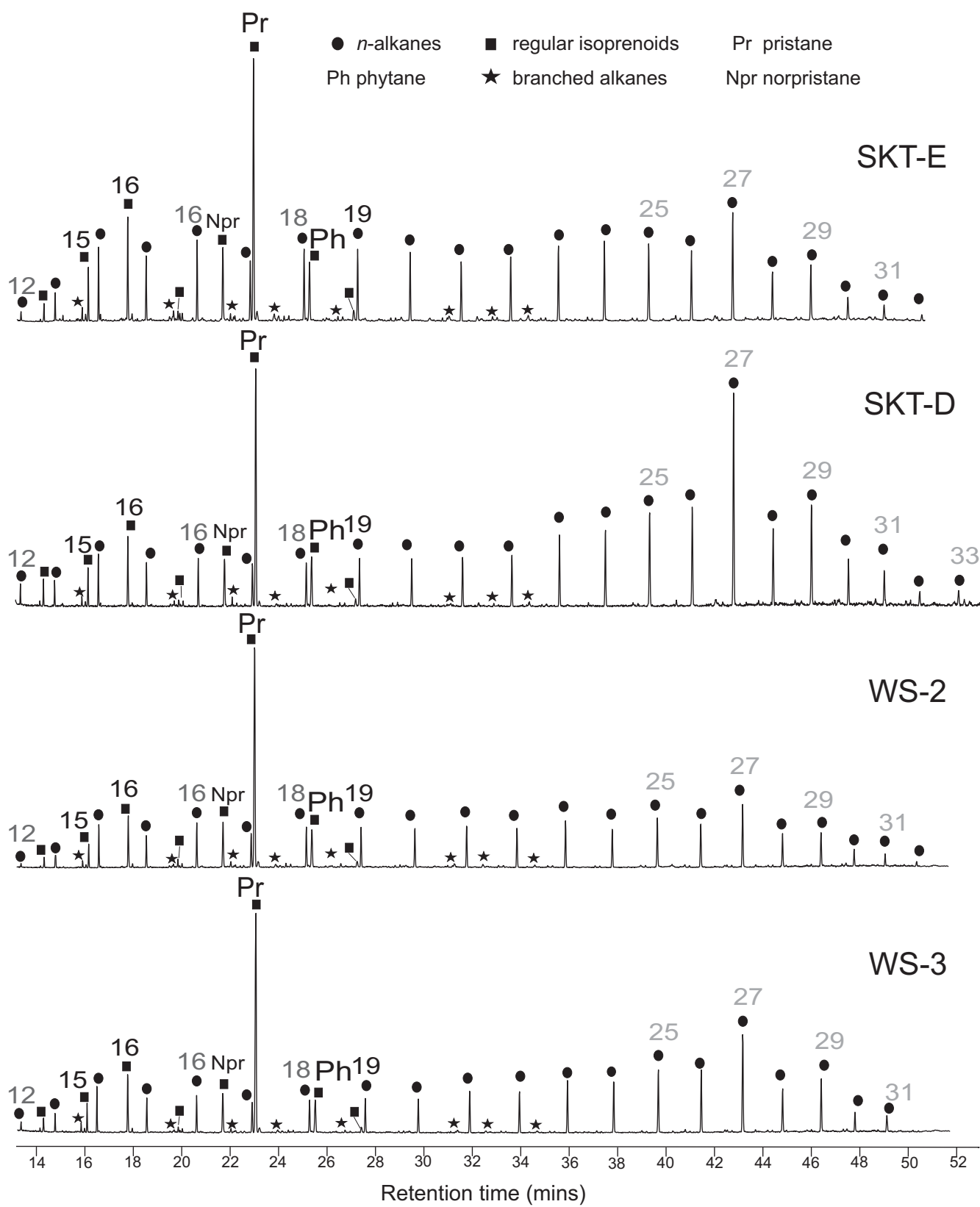
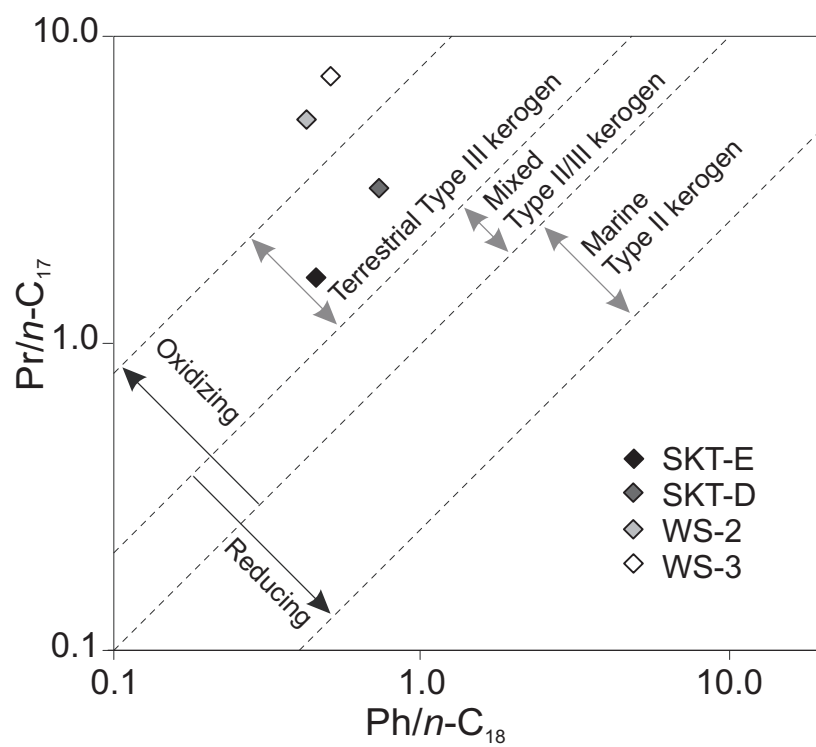
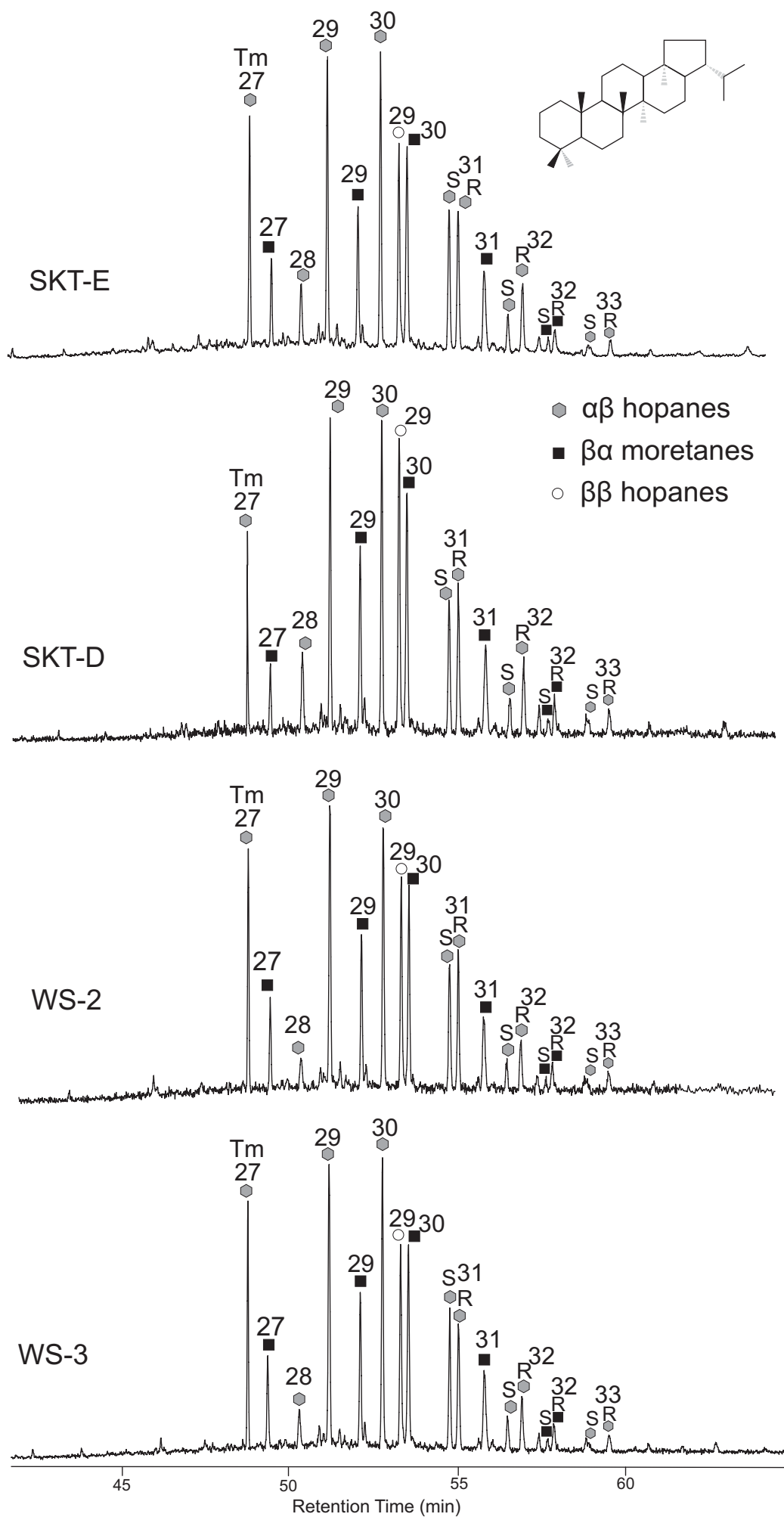


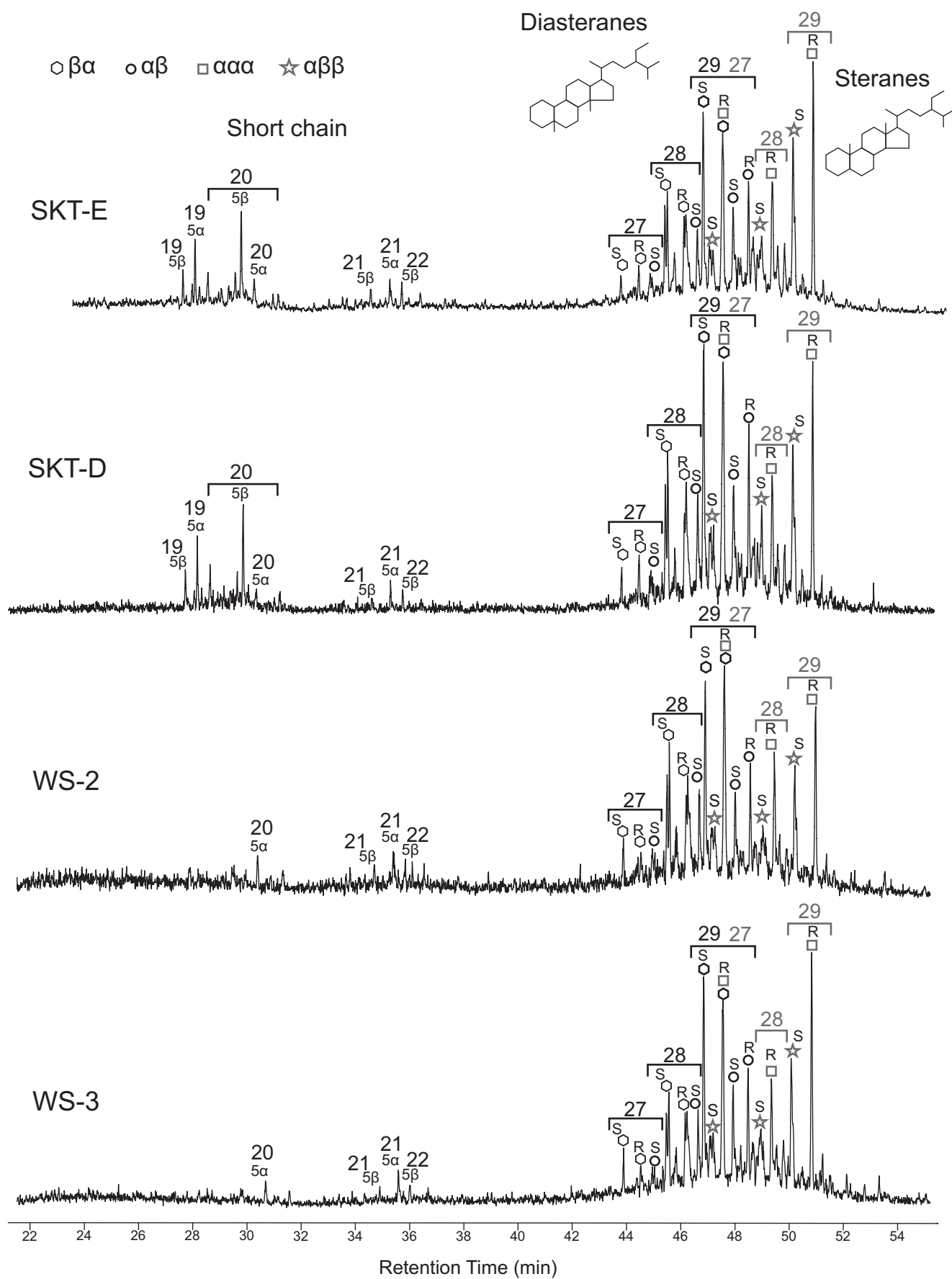
Fig. 4. Photomicrographs of macerals A) WS-3, reflected natural light. Vitrinite particles : telocollinite (Vt) and desmocollinite (Vd). B) Same zone as A, blue light fluorescence emphasizing exinite particles: fluorescing spores (S) and cuticles (C). C) SKT-E, blue light fluorescence. Exinite particles: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

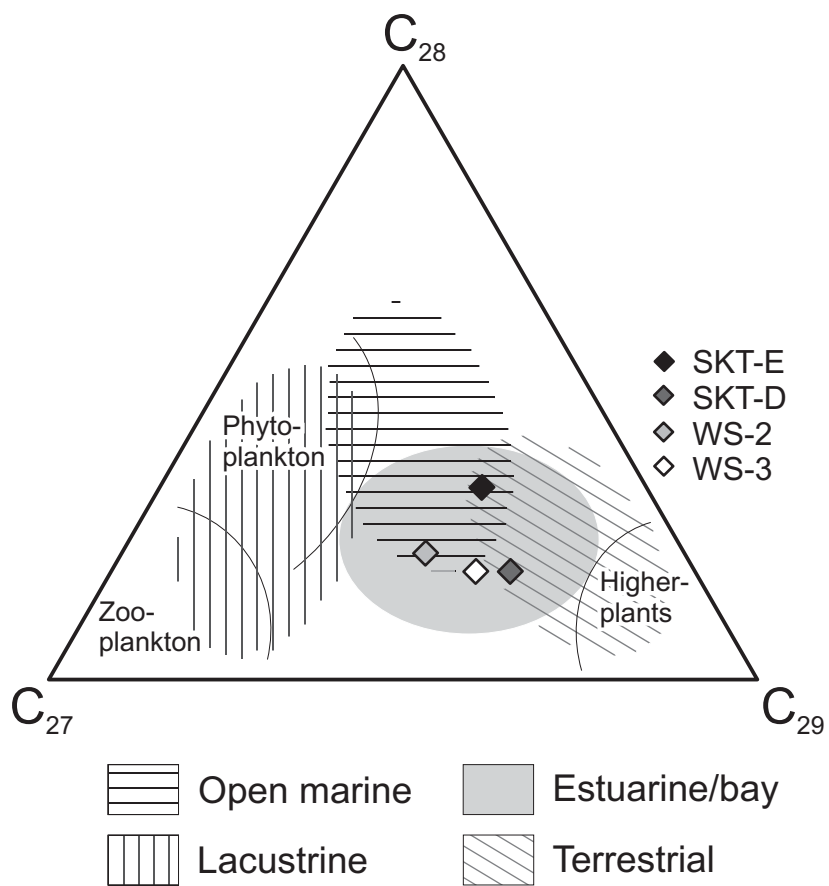


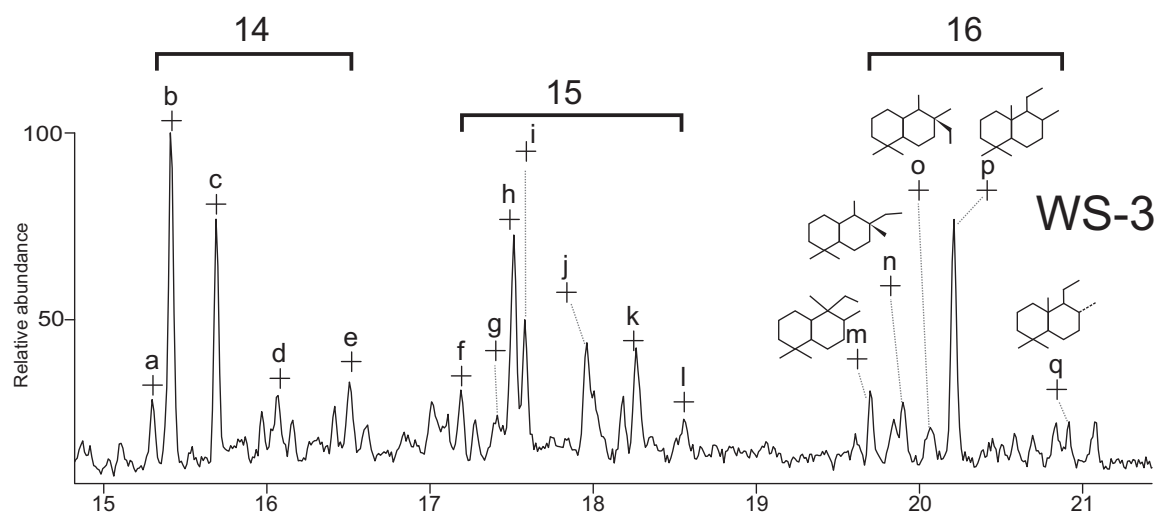
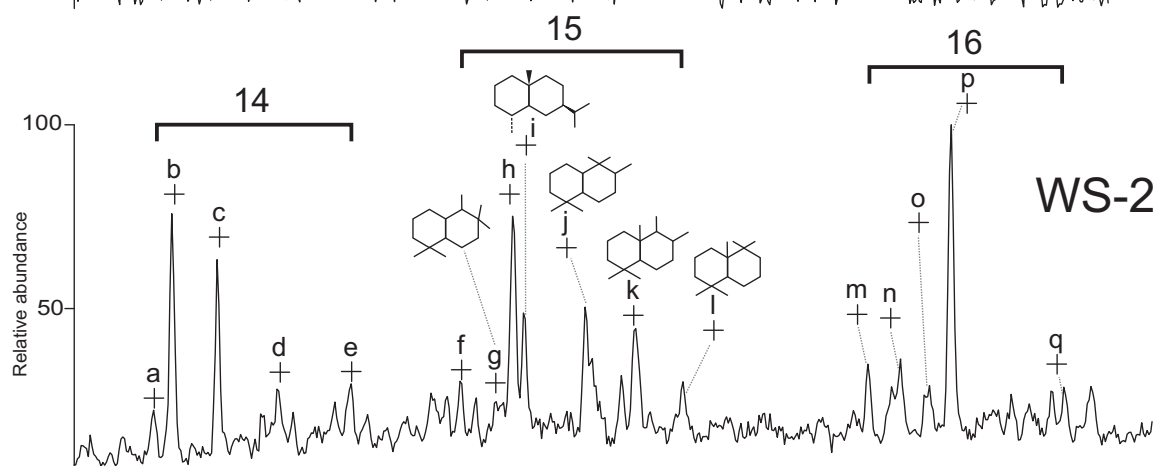
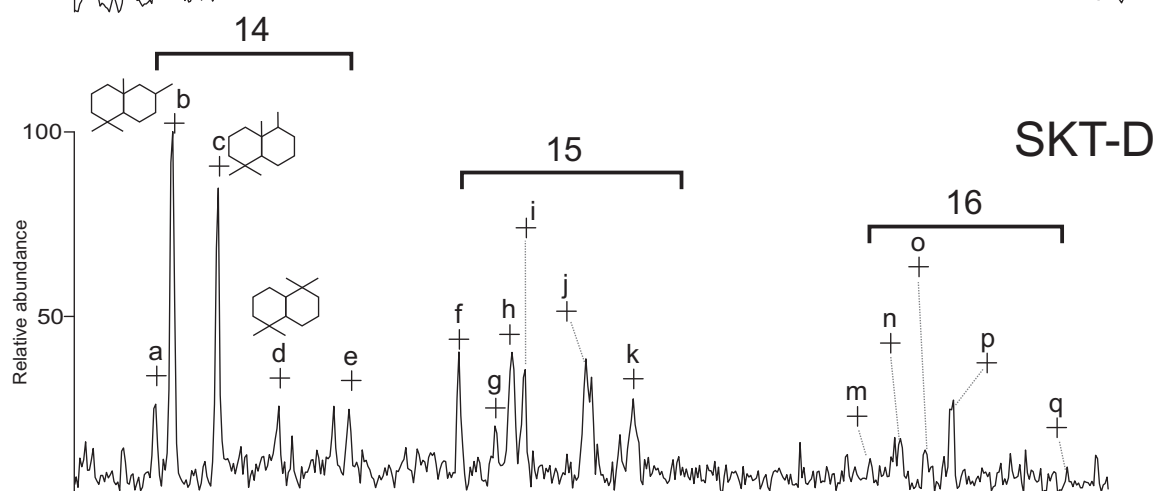
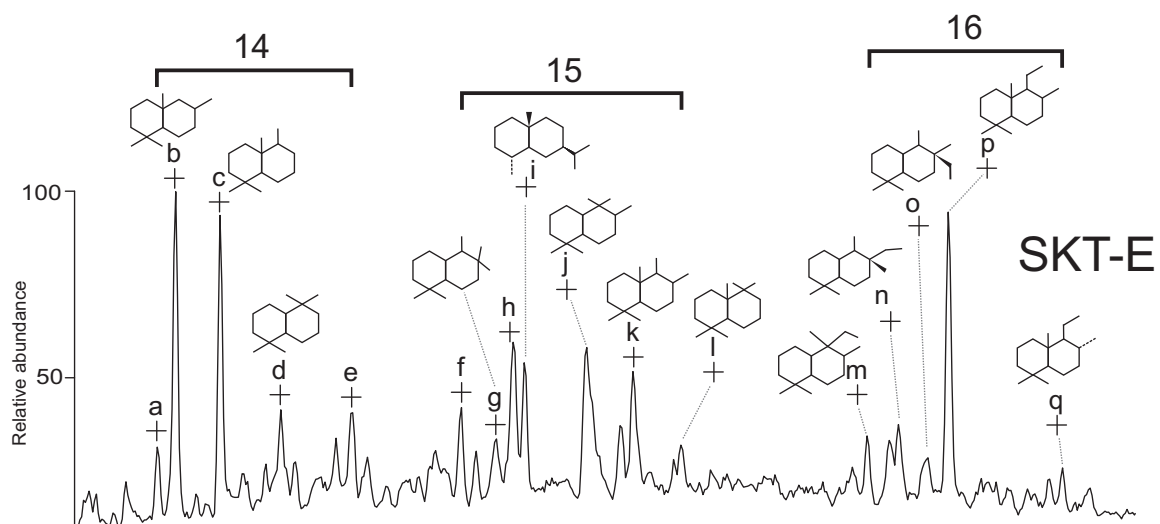




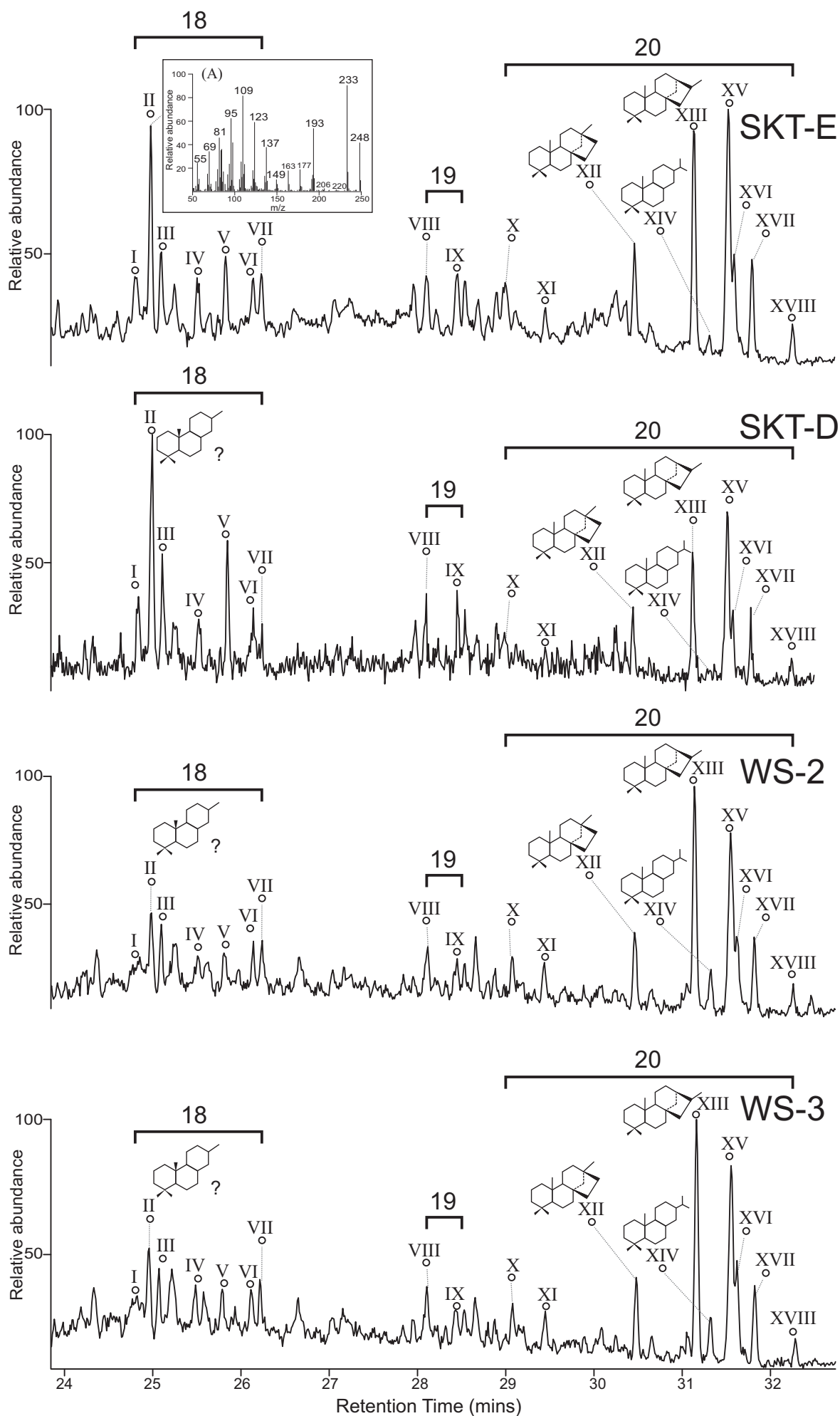




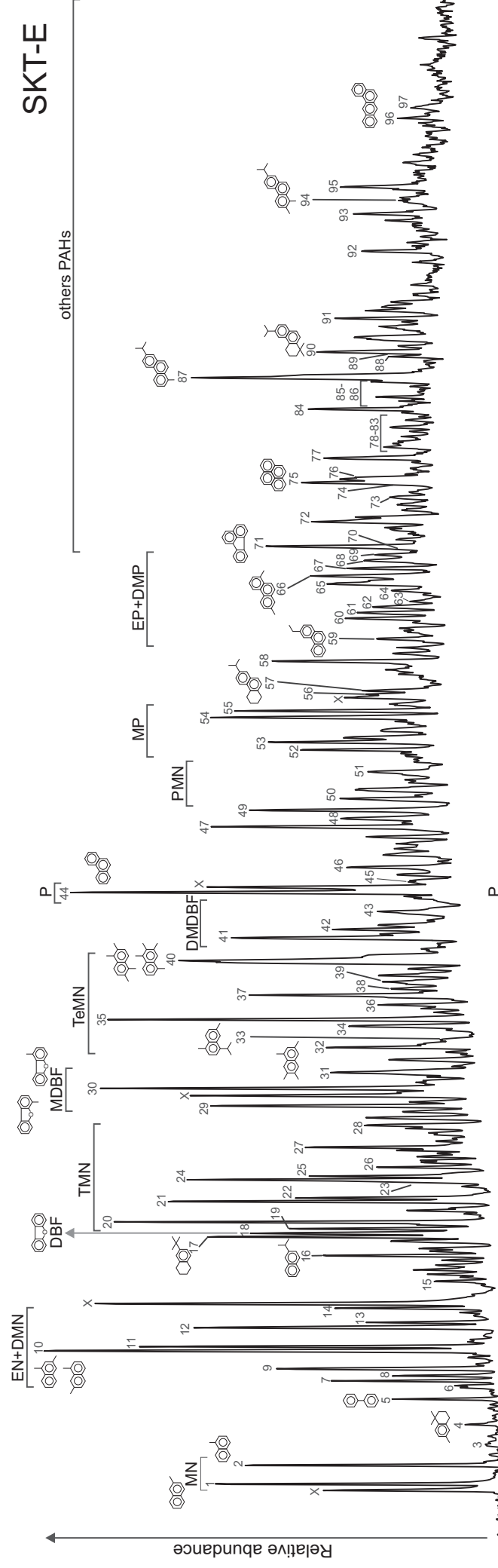




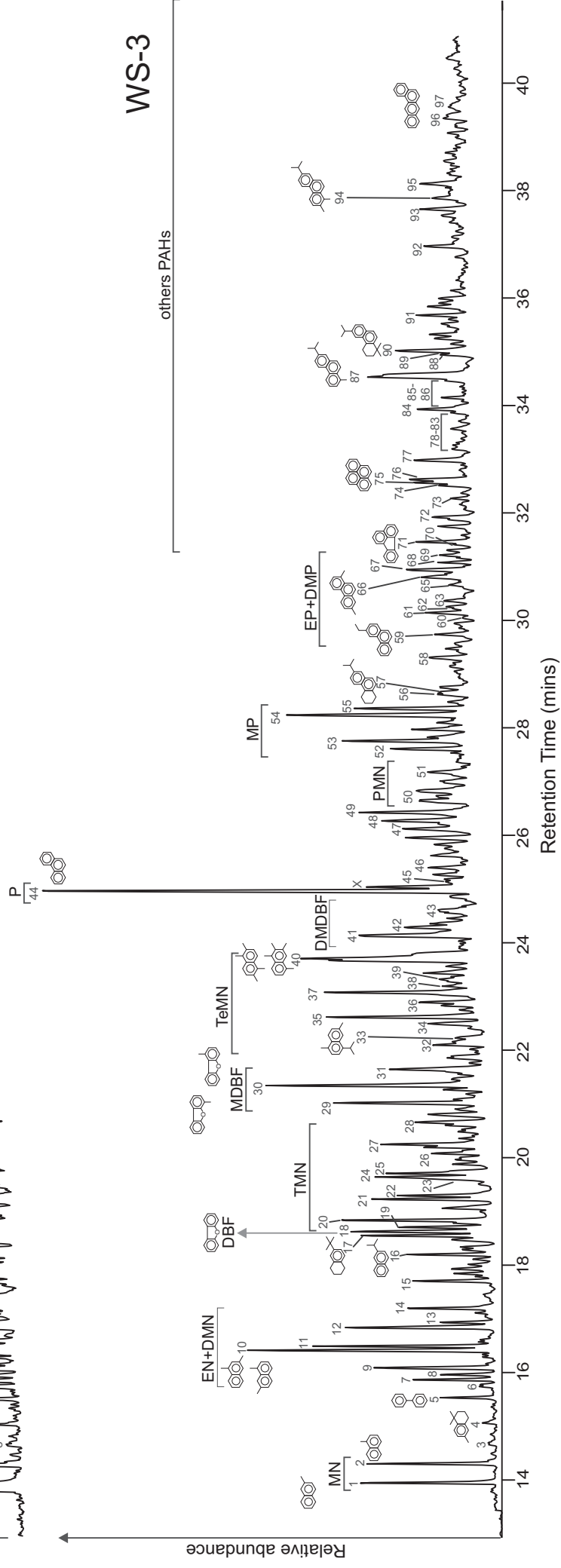
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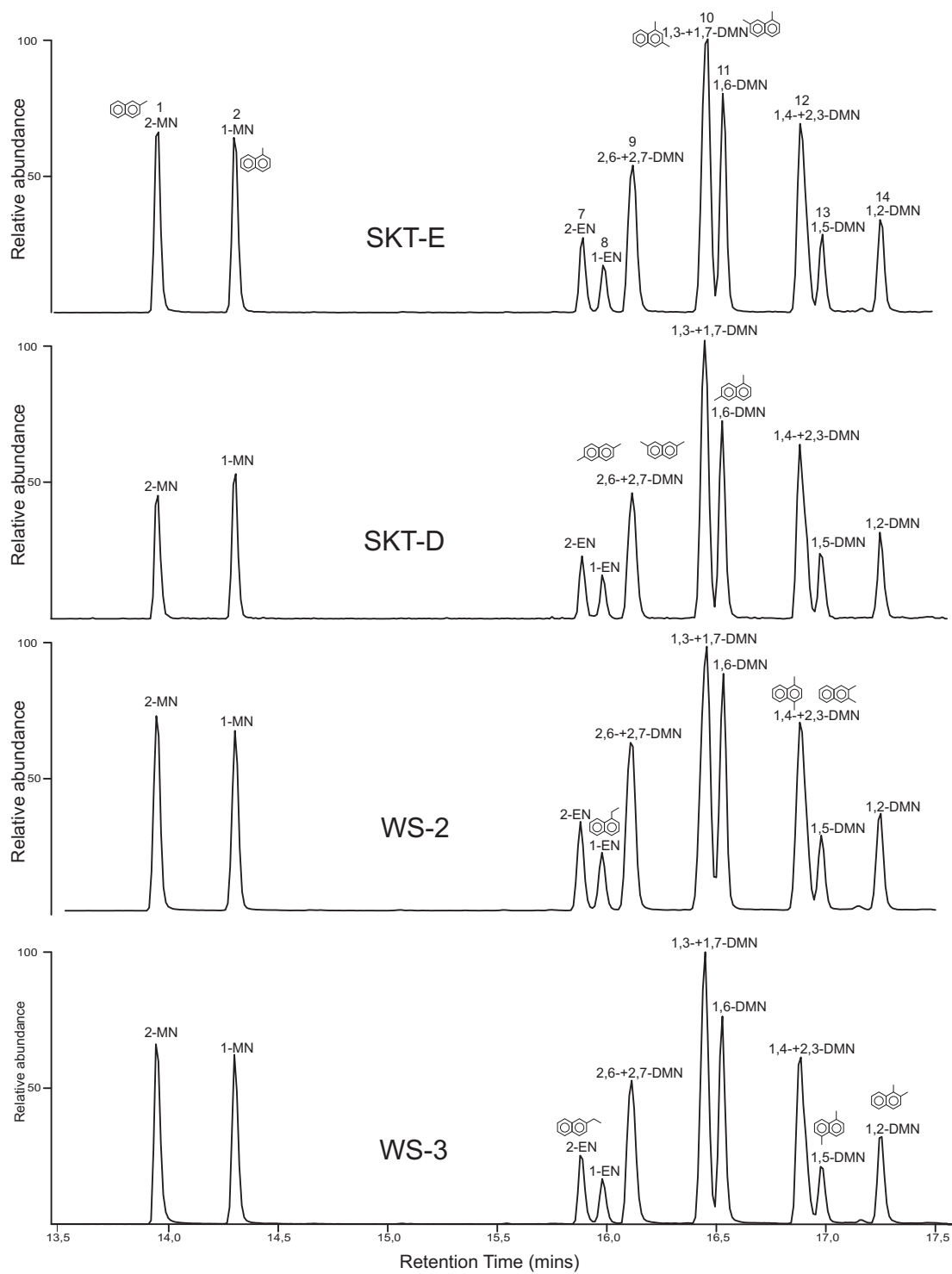


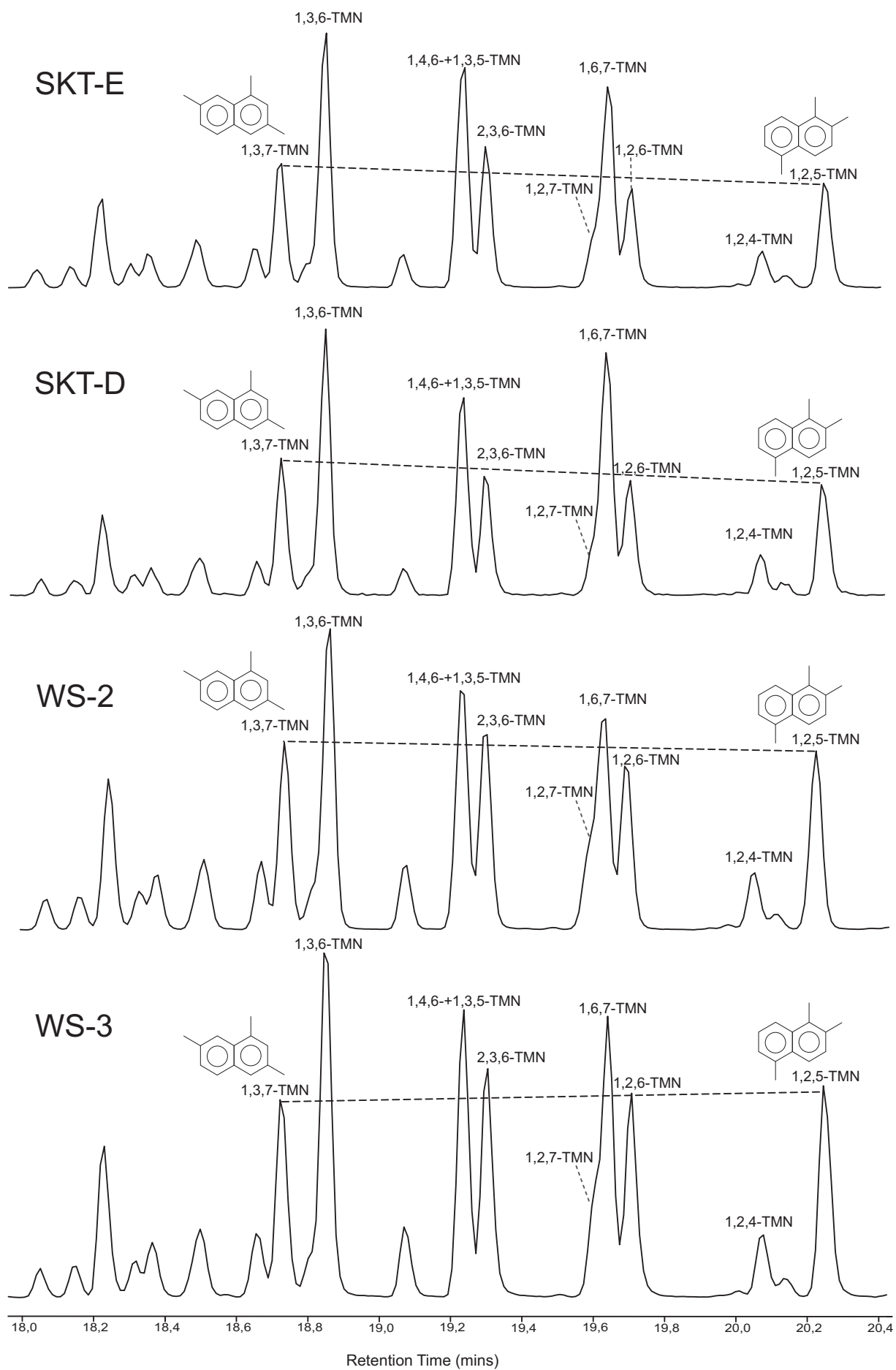
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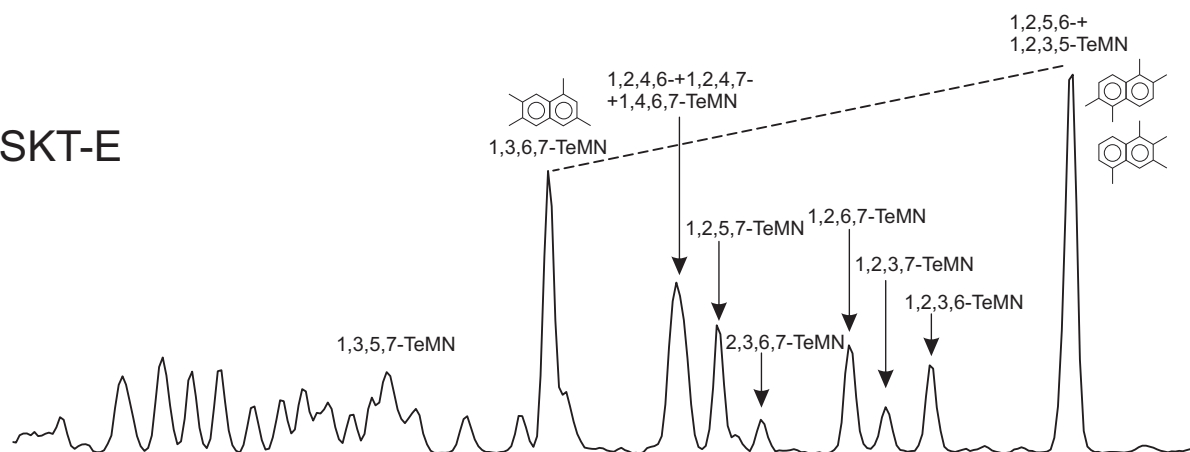
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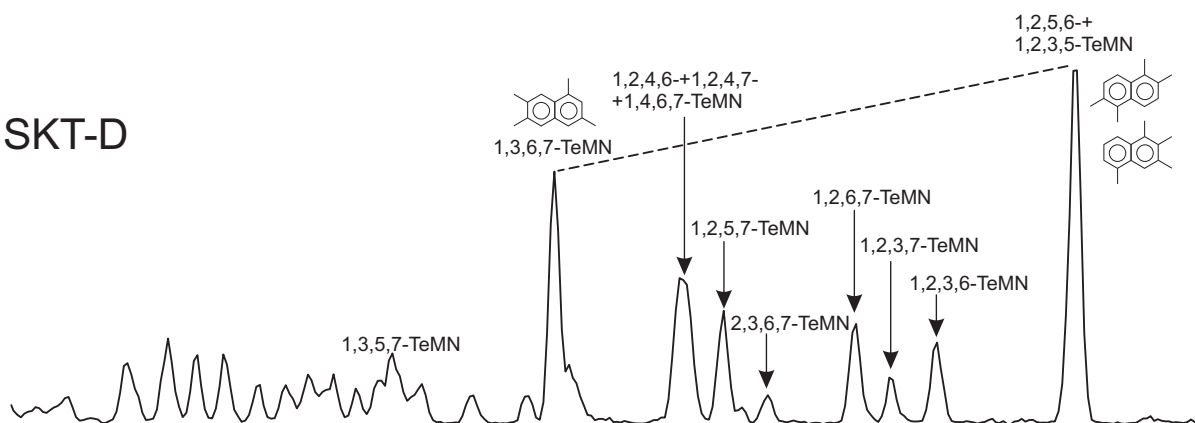




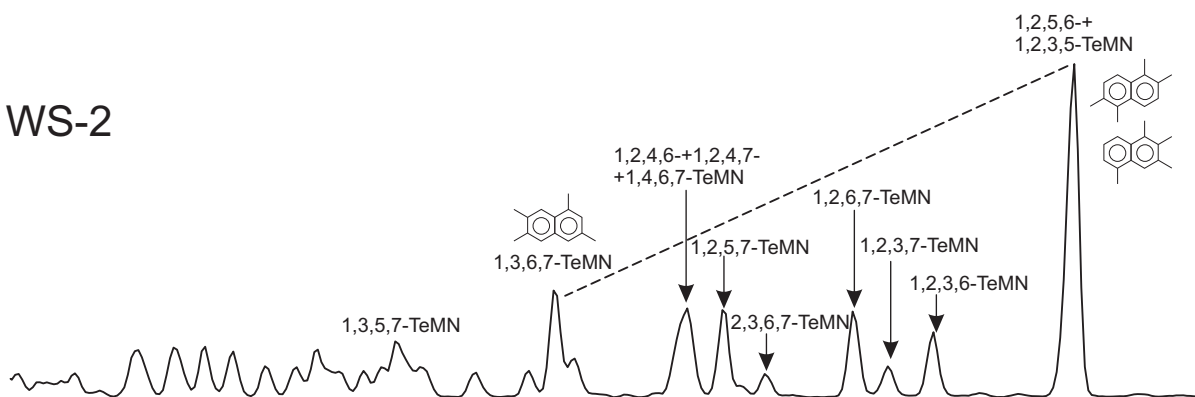
SKT-E



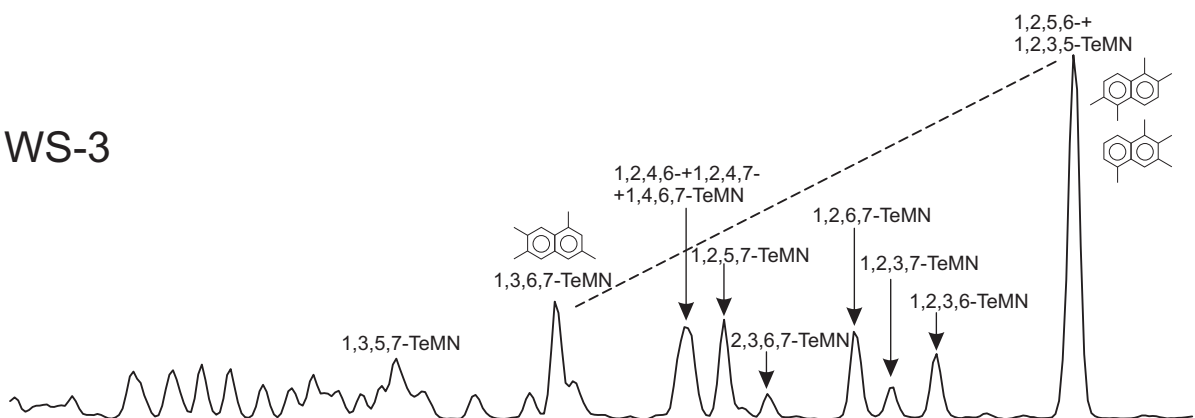
SKT-D



WS-2



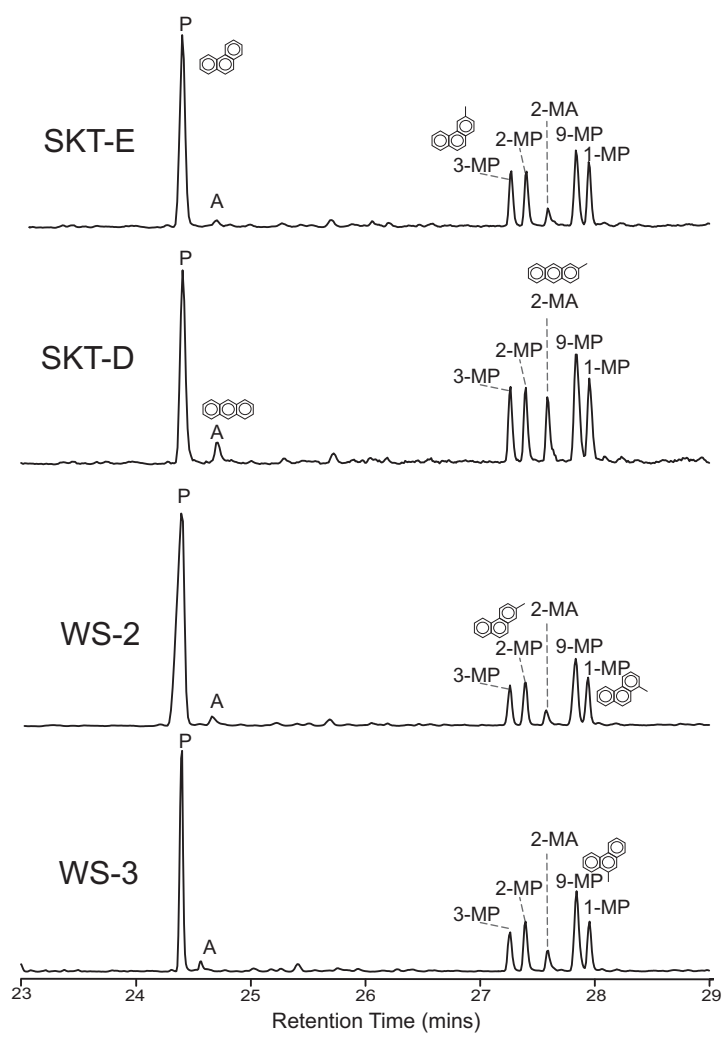
WS-3



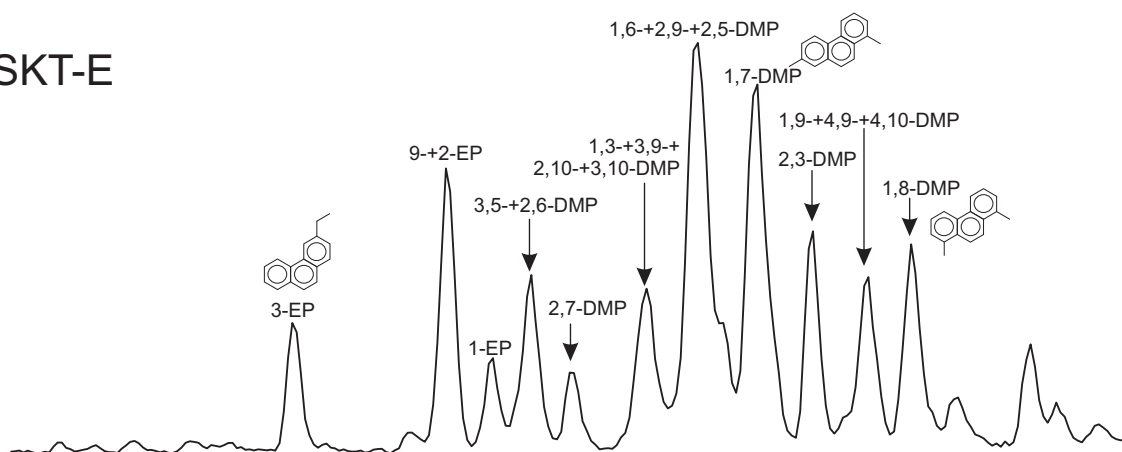
21,0

Retention Time (mins)

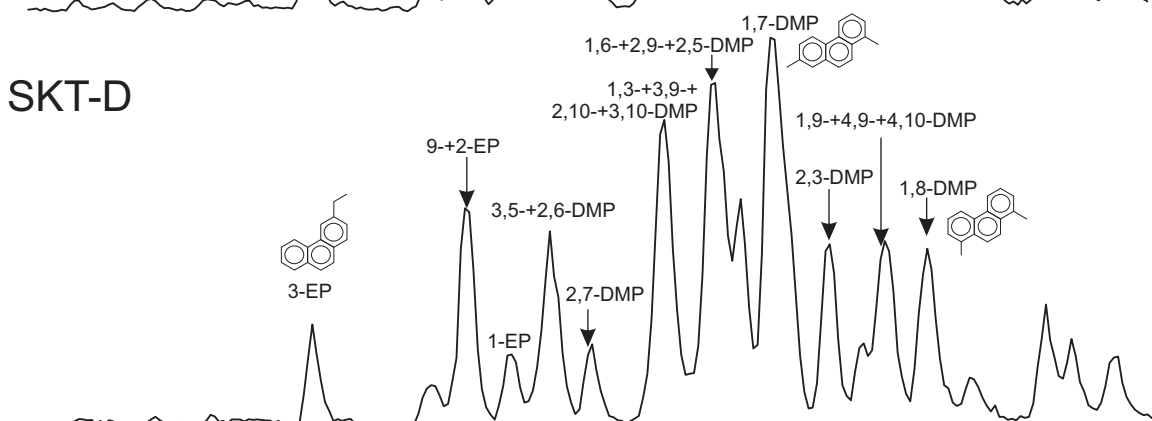
24,0



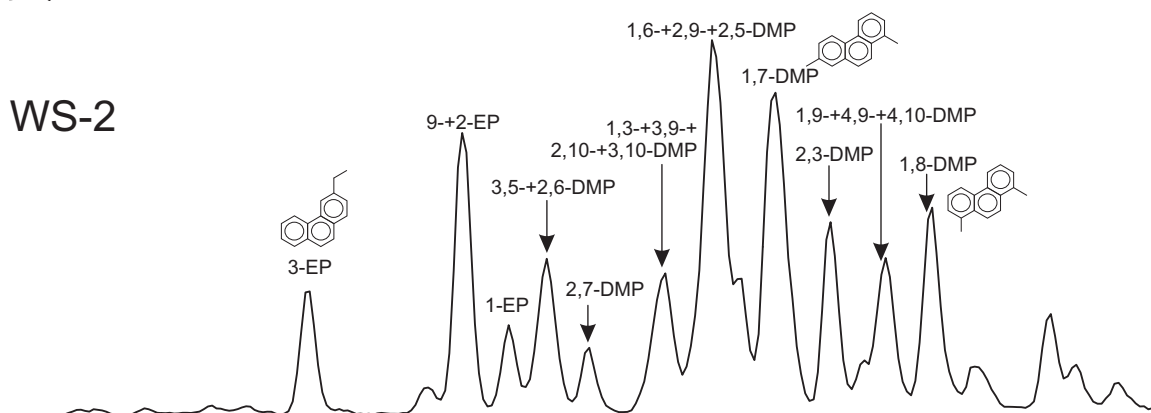
SKT-E



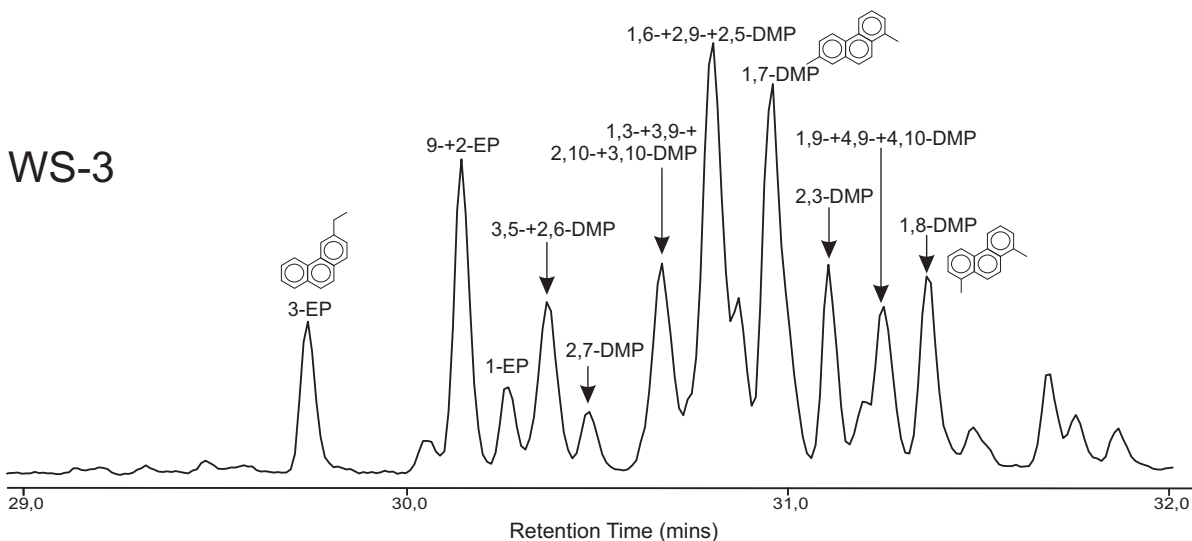
SKT-D

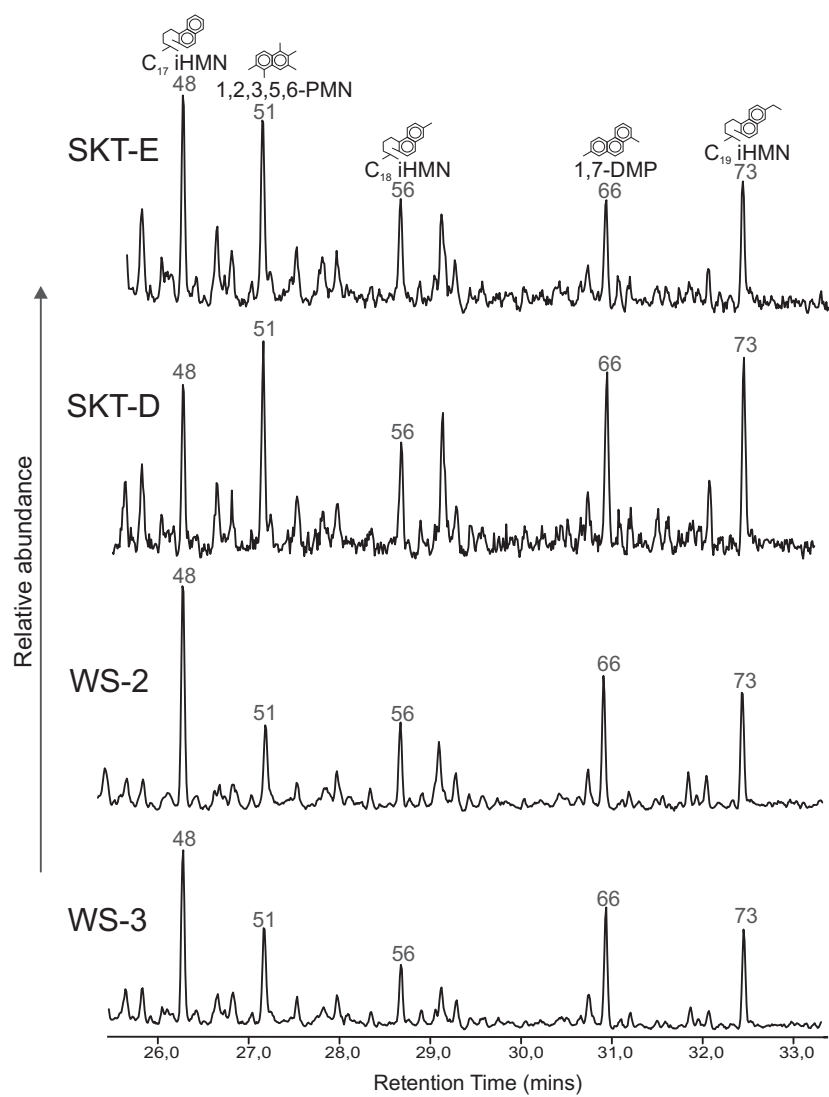


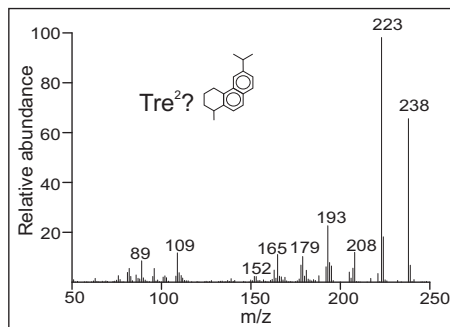
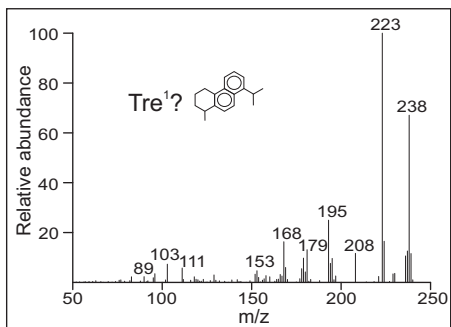
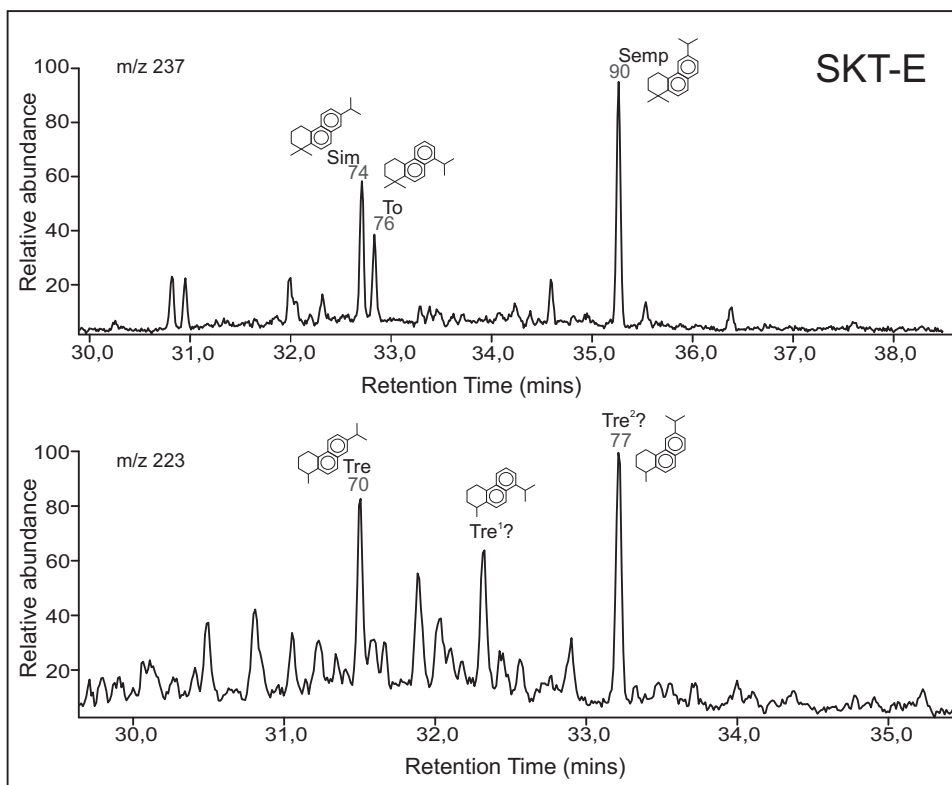
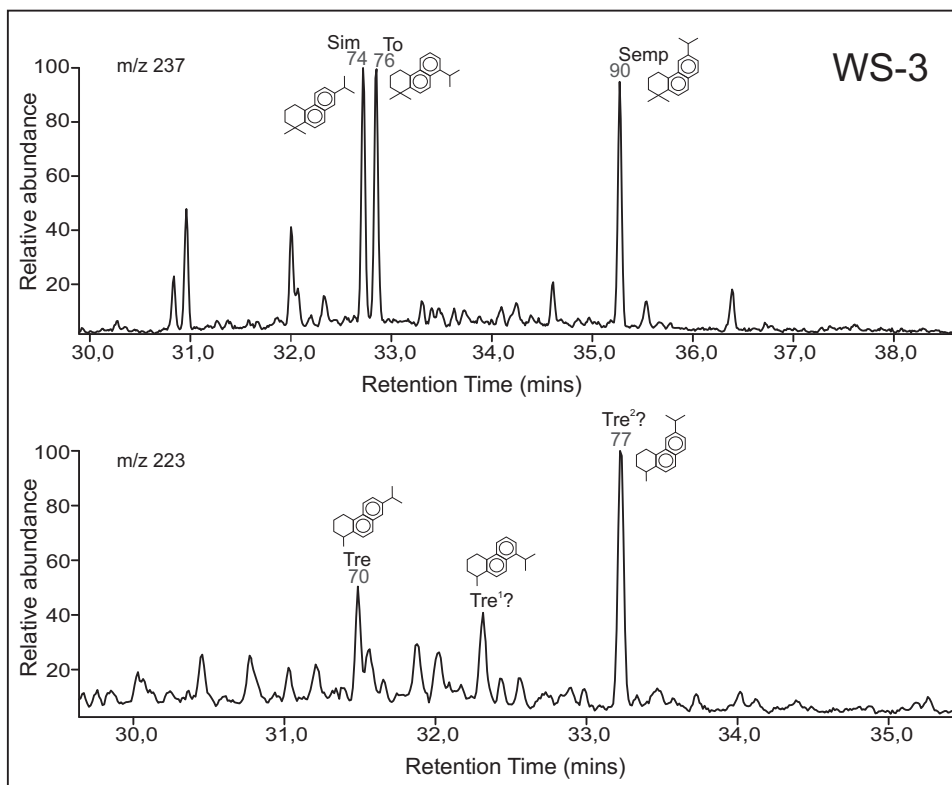
WS-2

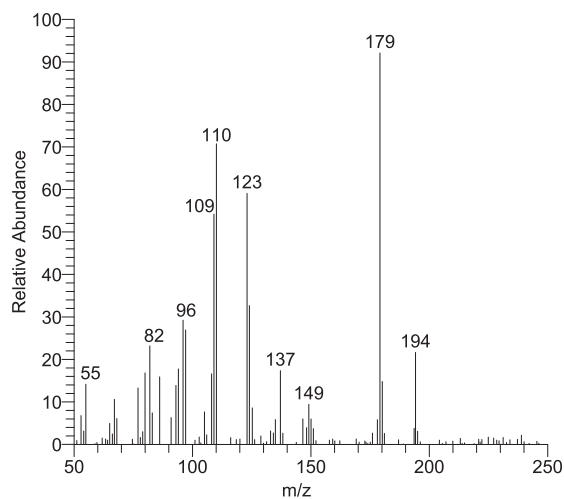


WS-3

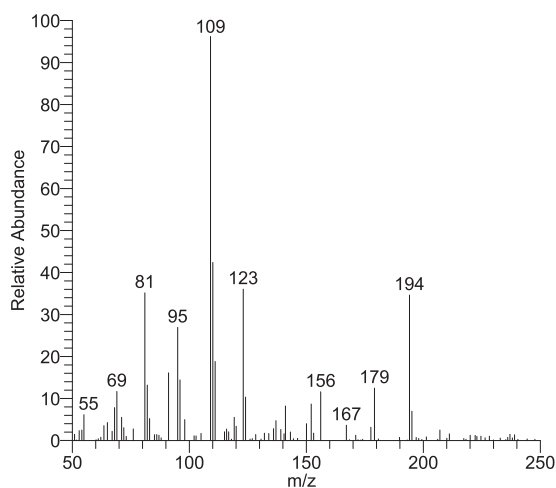




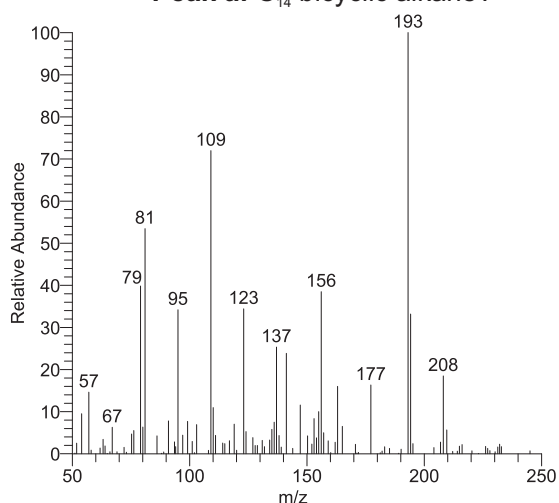




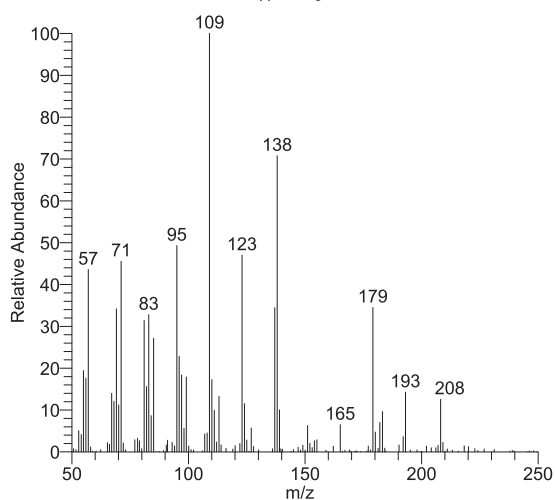
Peak a: C₁₄ bicyclic alkane?



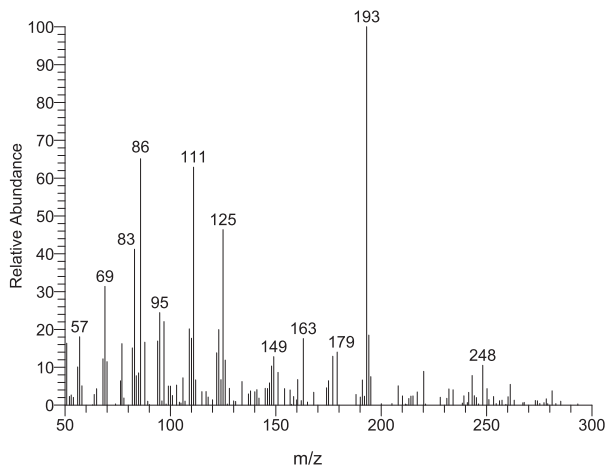
Peak e: C₁₄ bicyclic alkane?



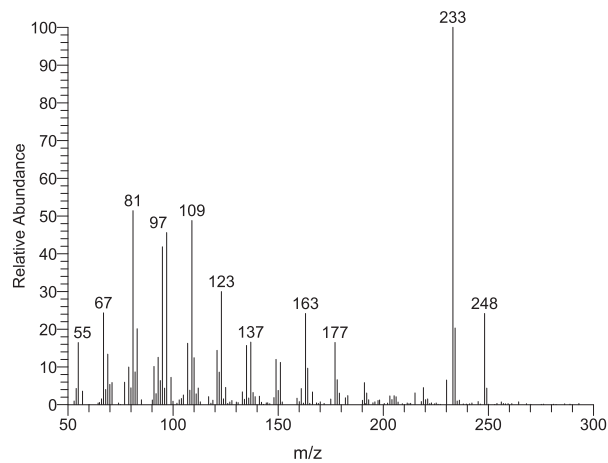
Peak f: C₁₅ bicyclic alkane?



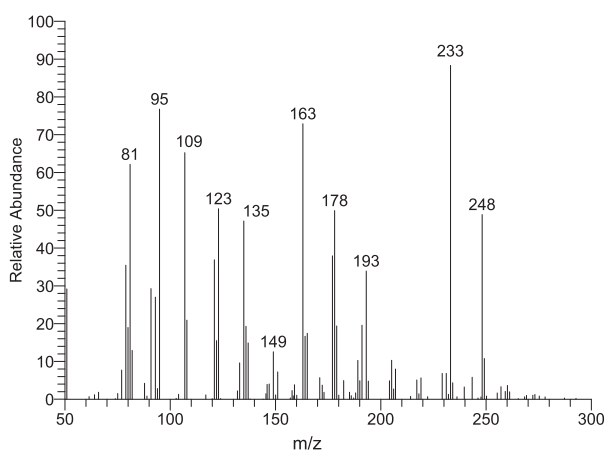
Peak h: C₁₅ bicyclic alkane?



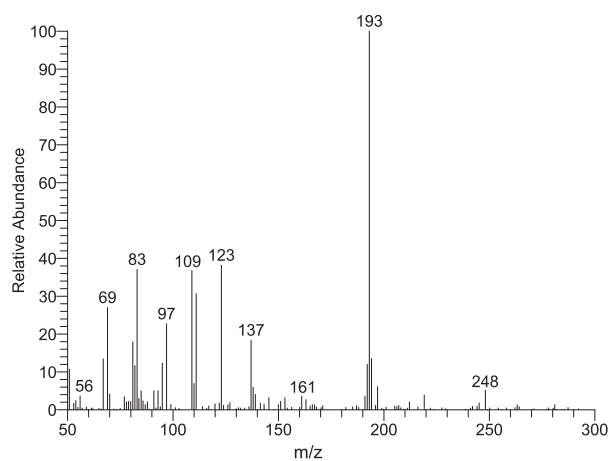
Peak I: C₁₈ tricyclic hydrocarbon?



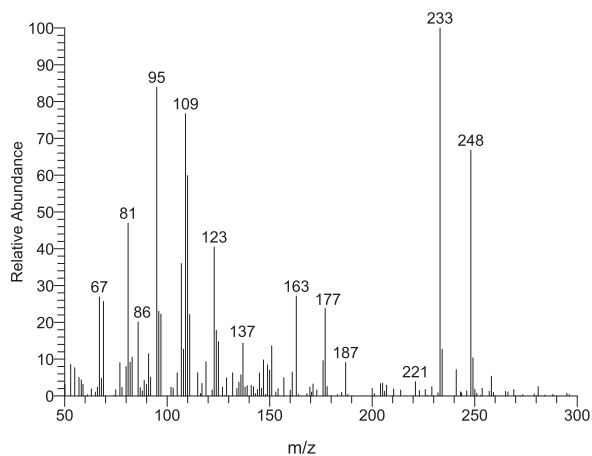
Peak III: C₁₈ tricyclic hydrocarbon?



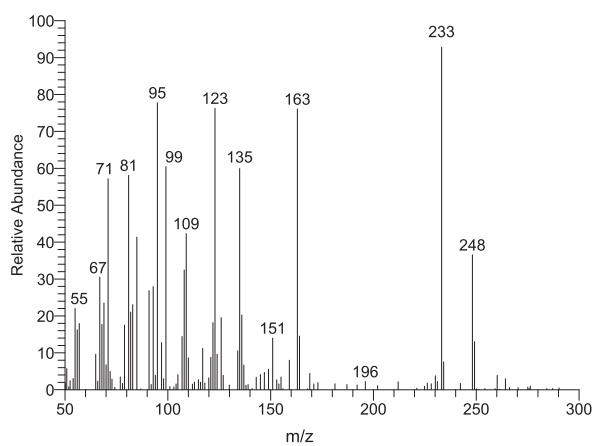
Peak IV: C₁₈ tricyclic hydrocarbon?



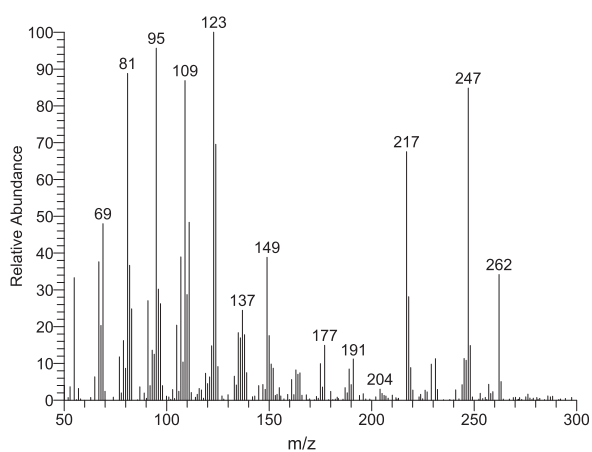
Peak V: C₁₈ tricyclic hydrocarbon?



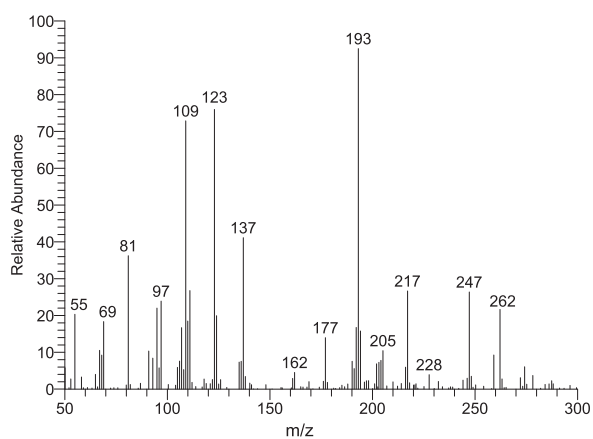
Peak VI: C₁₈ tricyclic hydrocarbon?



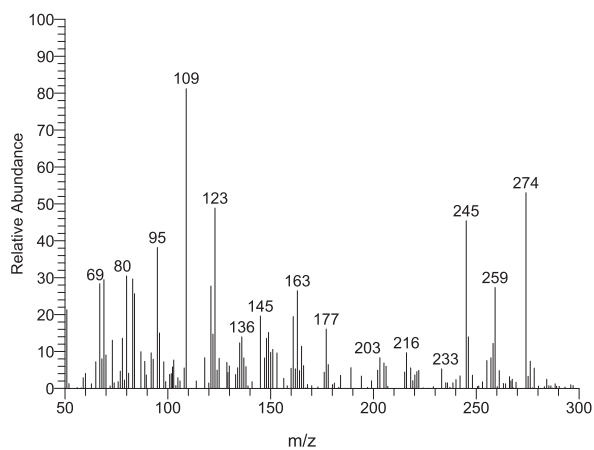
Peak VII: C₁₈ tricyclic hydrocarbon?



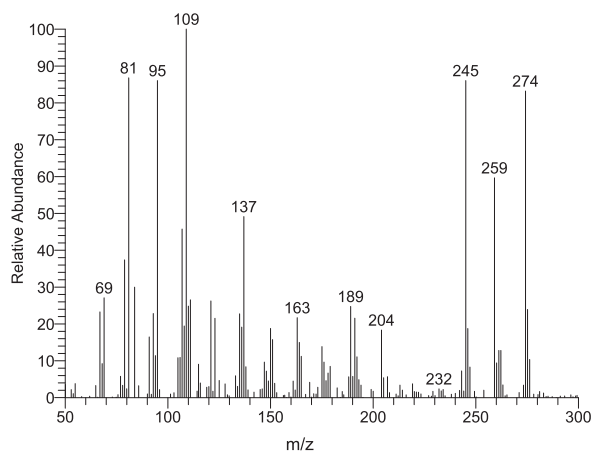
Peak VIII: C₁₉ tricyclic hydrocarbon?



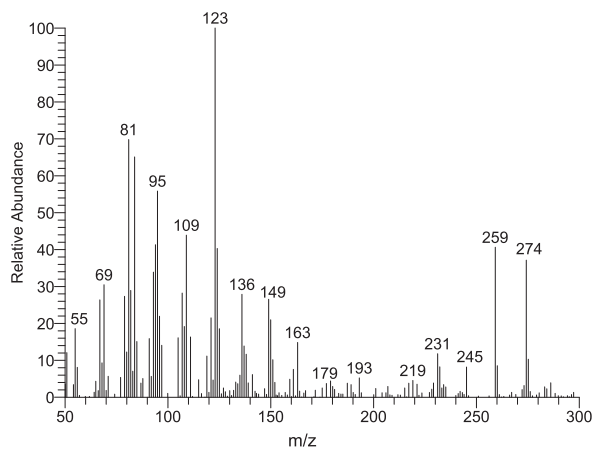
Peak IX: C₁₉ tricyclic hydrocarbon?



Peak X: C₂₀ tetracyclic diterpenoid?



Peak XI: C₂₀ tetracyclic diterpenoid?



Peak XVIII: C₂₀ tetracyclic diterpenoid?