Fractionation of pyrrolic nitrogen-containing compounds during primary migration of petroleum within the Barnett Shale sequence of Marathon 1 Mesquite Well, Texas

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ABSTRACT: The primary migration of petroleum has been recently described in detail for a thermally mature core of the Barnett Shale with almost nonvariant organofacies and maturity. Here, we use samples from the same well to provide new insights into the fractionation of pyrrolic nitrogen compounds during primary migration. Using gas chromatography-mass spectrometry (GC-MS), a decrease in concentration of carbazoles and benzocarbazoles was observed which correlated with migration distance. However, a preferential removal of individual isomers like benzocarbazole [a] relative to benzocarbazole [c] could not be detected. Enlarging the analytical window, we studied the effect of primary migration on high molecular weight nitrogen-containing compounds using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) combined with electrospray ionization (ESI) in the negative ion mode. Compounds with one or two nitrogen atoms are most abundant. Amongst the N_1

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compounds, those with 12, 15, 18, 20 and 23 double bond equivalents (DBEs) were dominating classes representing carbazole-type compounds (amongst others) with one to three *ortho*-annelated benzene rings (12, 15 and 18) and four to five *ortho-* and *peri*-annelated benzene rings (20, 23). In comparison, the N_2 compound class mainly consists of compounds with 12, 15, 17, 20 and 23 DBEs representing (amongst other compounds) biindoles with zero to one *ortho*-annelated benzene ring (12, 15) and carbazolocarbazoles with zero to two *ortho*-annelated benzene rings (17, 20 and 23). A relative enrichment of biindole-type compounds in comparison to carbazolocarbazoles in migrated petroleum was shown. This might indicate that aromatic compounds with separated ring systems like biindoles are less strong retained in the source rock than fully annelated polycyclic aromatic compounds like carbazolocarbazoles. Within DBE classes of N_1 and N_2 compounds, very similar carbon number (CN) distributions were illustrated, i.e., a predominance of C_{0-5} alkylated homologs maximizing at C_2 or C_3 substitutes. Regardless of fractionation, the overall similar distributions in DBE and CN suggest that pyrrolic nitrogen-containing compounds have restricted precursors and common mechanisms of formation. Nonfluorescent chlorophyll catabolites (NCCs), the final breakdown products of chlorophyll, were tentatively suggested as possible precursors.

1. INTRODUCTION

Molecular distributions of low molecular weight nitrogen-containing compounds in crude oils and source-rock bitumens have been widely used to study petroleum migration processes.[1-8] The relative enrichment of nitrogen-shielded compared to nitrogen-exposed isomers and of higher alkylated compared to lower alkylated homologues in migrated crude oils was attributed to fractionation during migration.[1-3,5] The more rod-shaped benzocarbazole[a] was hence

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preferential removed from oils by selective sorption on solid organic/mineral phases than the sub-spherical benzocarbazole[c],[4] which could be also shown by laboratory experiments.[9] Accordingly, the benzocarbazole [a]/([a] + [c]) ratio was widely applied as a measure for secondary oil migration.[4,7,8,10] Both carbazoles and benzocarbazoles were shown to undergo a general decrease in concentration with increasing migration distance.

It is generally believed that the major quantitative fractionation of pyrrolic nitrogen compounds occurs during primary migration and expulsion, while secondary migration over large distance leads to significant changes in pyrrolic nitrogen compound distributions.[3-5,11,12] However, all previous studies used crude oils to assess primary migration which does not allow assessing fractionation processes occurring during migration within the source rock from those occurring during migration through the carrier bed. In this paper, we provide insights into the primary migration behaviours of nitrogen-containing compounds within the first meters of the source rock and expulsion into the reservoir rock detected solely on bitumen extracts. The distributions of low molecular weight nitrogen compounds were quantitatively studied using gas chromatography coupled with mass spectrometry (GC-MS), while Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) was used to characterize the relative distribution of pyrrolic nitrogen compounds in the medium to high molecular weight range.

Due to analytical limitation of GC-MS (*m/z* 50-330), high molecular-weight nitrogen containing compounds cannot be readily studied. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) broadens the analytical window up to more than 800 Daltons.[13] With the help of a constant high magnetic field strength (e.g. 12 Tesla), the resolving power in a required mass spectrum can easily excess one million. It is now possible to identify the elemental composition ($C_cH_hN_nO_oS_s$) of thousands of organic compounds in crude oils.[14] Using

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electrospray ionisation in the negative ion mode, pyrrolic nitrogen-containing compounds can be ionized. Previous studies on a maturity sequence of the Posidonia Shale using FT-ICR-MS showed that condensation and aromatization reactions of pyrrolic nitrogen compounds plays a major role during petroleum maturation., i.e., the DBEs (double bond equivalents) increased gradually from about 10 to more than 30.[15] Aromatization was found to occur at the expense of aliphatic carbon resulting in an enrichment of polyaromatic heterocompounds in source rocks.[16] The compositional differences between retained and expelled fluids were thought partly but not exclusively due to expulsion fractionation.[16] Nevertheless, high molecular-weight nitrogen compounds have not been used yet to describe migration fractionation.

The present paper focuses on unravelling the differences in nitrogen compounds between retained and primarily migrated fluids from the Barnett Shale sequence of Marathon 1 Mesquite Well, Hamilton County, Texas.[17] Results from GC-MS are compared and extended to those from FT-ICR-MS. Possible structures and precursors of pyrrolic nitrogen-containing compounds have been proposed and discussed.

2. SAMPLES AND METHODS

2.1. Samples and Geological Settings

Fifteen core samples (Table 1) were obtained from the Mississippian Type-II marine Barnett Shale of Marathon 1 Mesquite Well, which has been subdivided top down into five discrete intervals. The primary migration of petroleum in this core has been documented.[17] Compositional fractionation of the SARA fractions (saturates, aromatics, resins and asphaltenes) was shown to occur during petroleum migrating from the organic-rich source-rock (the lower part of 3rd interval) into the siliceous reservoirs (the 2nd interval), while selected compound ratios were not affected by fractionation, such as the C_{27-29} diasterane ratios, methyl naphthalene ratio

(MNR), and methyl phenanthrene index (MPI1) (Table 1). The upper part of the 3rd interval embedded between reservoir and source-rock units is an organic-rich transition zone that is characterized by migrated oil.[17] Bitumens extracted from the transition zone account for 9-10% of total organic carbon (TOC), which is in between those of reservoirs (19-22% TOC) and source-rocks (5-6% TOC). Other features like lithology and SARA compositions also indicate a "mixed" character of source/reservoir for the upper part of 3rd interval (Table 1). Nevertheless, a rather homogeneous kerogen facies (C_{27-29} diasteranes) and maturity signature (1.0% R_o, vitrinite reflectance) was proven in this core (Table 1).[18]

2.2. Extraction and fractionation

The bitumen samples investigated here were extracted using the ternary azeotropic solvent mixture (acetone: chloroform: methanol, v/v = 38: 32: 30). After asphaltene precipitation, a SARA fractionation was done using medium pressure liquid chromatography (MPLC) as described in Han, Mahlstedt and Horsfield.[17] Prior to MPLC fractionation, androstanone was added as internal standard.

2.3. GC-MS Analysis

GC-MS measurements of the resin fraction were performed using a Hewlett Packard 5890B gas chromatograph (GC) coupled with a Finnigan MAT 95SQ mass spectrometry (MS). The GC was equipped with a programmable temperature vaporizer (PTV) injector (KAS 3, Gerstel GmbH) and a BPX5 fused silica capillary column of 50 m length, 0.22 mm inner diameter and 0.25 um film thickness. The PTV temperature was increased from 50°C to 300°C at 10°C/sec (held for 10 min). Helium was used as the carrier gas at a constant flow of 1 mL/min. The initial GC oven temperature of 50°C was held for 1 min and then increased to 310°C at 3°C/min (held for 30 min). The MS was operated in the electron impact (EI) mode with an electron energy of

70 eV and 230°C source temperature. Full scan mass spectra were recorded over a mass range *m/z* 50-330 at a scan rate of 1.5 scans/sec. Carbazoles and benzocarbazoles were identified using the following mass traces: *m/z* 167 (carbazole), 181 (methylcarbazoles), 195 (C_2 alkylcarbazoles), 209 (C_3 alkylcarbazoles), 223 (C_4 alkylcarbazoles), 217 (benzocarbazoles), 231 (methylbenzocarbazoles), 245 (C_2 alkylbenzocarbazoles), 259 (C_3 alkylbenzocarbazoles) and 273 (C_4 alkylbenzocarbazoles). The assignment of carbazole, C_{1-2} alkylcarbazoles, benzocarbazole and C_1 alkylbenzocarbazoles was done according to the Norwegian Standard Oil (NSO-1).[19] Quantification was done using 5(alpha)-Androstan-17-one as internal standard. Higher alkylated carbazoles and benzocarbazoles were not identified individually due to co-elution problems. Nevertheless, the summed concentrations of C_3 and C_4 alkylcarbazoles and C_2, C_3 and C_4 alkylbenzocarbazoles were determined following the baseline integration procedure described by Clegg, et al. [20].

2.4. FT-ICR-MS Analysis

For FT-ICR-MS measurement, a 12 Tesla FT-ICR mass spectrometer equipped with an Apollo II electrospray source from Bruker Daltonik GmbH (Bremen, Germany) were used. Poetz, Horsfield and Wilkes provided the details of sample preparation, measurement condition, mass calibration and data analysis.[15] In brief, whole bitumens were diluted in methanol and toluene mixtures (v/v = 1:1) to give a concentration of 100 µg/mL, to which a concentrated aqueous NH_3 solution was added (10µL/mL sample solution) in order to facilitate the deprotonation of nitrogen compounds. Sample solutions were then fused via the Apollo II electrospray source in the negative mode at 150µL/h with a syringe pump. The capillary column voltage was set to 3000 V and an additional CID (collision-induced dissociation) voltage of 70 V was applied in the source to avoid cluster and adduct formation. Ions were accumulated in the collision cell for 0.05

s and transferred to the ICR cell within 1 ms. For each mass spectrum, a number of 200 scans have been co-added over the range of m/z 147 to 750 Da. The FT-ICR mass spectrometer was firstly calibrated using an external calibration mixture containing fatty acids and modified polyethylene glycols, and then internally recalibrated using known homologous series. Elemental formulas were assigned to peaks with S/N (signal to noise) ratio greater than 9, allowing 0−100 C, 0−200 H, 0−4 O, 0−4 N, and 0−4 S atoms. Data evaluation was done with the help of the software packages Data Analysis 4.0 SP5 (Bruker Daltonik GmbH, Germany).

In the negative electrospray ionization (ESI) mode, only negative single charged compounds were formed, m/z and mass are thus used synonymously in this study. In subsequent analysis, different nitrogen-containing compounds were classified according to the double bond equivalent (DBE). For a given compound, $C_cH_hN_nO_oS_s$, its DBE can be calculated according to the formula: DBE = c - 0.5h + 0.5n + 1. The DBE is a measure for the degree of unsaturation in a molecule and expresses the numbers of its double bonds and rings.[15]

3 RESULTS AND DISCUSSION

3.1. Quantitative Fractionation of Carbazoles and Benzocarbazoles

We showed in a previous study that hydrocarbons primarily migrated within the Barnett Shale of the Mesquite Well from the source unit (the lower part of 3rd interval plus the upper part of 4th interval) into the reservoir (the 2nd interval).[17] Here, we determine the amounts and relative distributions of small pyrrolic nitrogen compounds in source rock and reservoir rock intervals following this migration pathway. Besides migration fractionation, factors like organic facies, depositional environment and thermal stress have been shown to influence the relative distributions of carbazole and benzocarbazole derived compounds.[5,20-26] An independent study of migrational fractionation of pyrrolic nitrogen compounds has to unravel the impact of source and

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maturity.[6,11,24,25] The Barnett Shale of Marathon 1 Mesquite Well has a considerable homogeneous source facies (Type-II marine) and a constant maturity level (1.0% R_o, vitrinite reflectance) (Table 1) excluding any source or maturation effect on carbazole or benzocarbazole distributions.

Typical extracted-ion chromatograms of the small pyrrolic nitrogen compounds are shown in Figure 1. In general, benzocarbazoles and alkylated benzocarbazoles were more abundant in the samples than carbazole and its alkylated isomers. A decrease in concentration relative to the total resin fraction (µg/g resins) as well as to the total bitumen (µg/g bitumen) was observed with increasing distance from the source unit for all pyrrolic nitrogen compounds (Figure 2) indicating their preferential removal from the oil during primary migration. This appears consistent with the previous observations based on crude oils[4,6,9,10] and crude oils and bitumen extracts[3,5].

Fractionation between different carbazole or benzocarbazole isomers was observed during secondary oil migration. For example, the ratios of alkylcarbazoles/alkylbenzocarbazoles, 1-/4-methylcarbazole (MC), 1,8-/3,5-dimethylcarbazole (DMC) were reported to be higher in migrated oils than in source rock extracts.[3] In the investigated well, there is no noticeable enrichment of neither carbazole (Figure 3a) nor 1-methylcarbazole (Figure 3b) nor 1,8-dimethylcarbazole (Figure 3b) in relative to specific compounds. As the most commonly used oil migration parameters, a decrease in concentration of benzocarbazoles and of the ratio of benzocarbazole isomers [a]/([a] + [c]) with increasing migration distance was described.[4,9-11] However, in the Marathon 1 Mesquite Well, none of these ratios was found to be higher in the reservoir than in the source rock intervals (Figure 3d-e). Instead, the ratios remained constant

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displaying identical relative distributions of small pyrrolic nitrogen compounds which are not changed during primary migration.

Notably, the primary oil migration distance within the studied core is in the tens of metres, while that of secondary migration from the source rock to reservoirs is from hundreds of meters to kilometres. Therefore, we agree that with respect to individual pyrrolic nitrogen compounds, the extent of fractionation may depend on migration distance.

3.2. Fractionation of Medium to High Molecular Weight Pyrrolic Nitrogen Compounds

Nitrogen compounds in petroleum are classified as basic pyridinic type (such as pyridine, quinolone, benzoquinoline and etc.) and neutral pyrrolic type (like pyrrole, indole, carbazole, benzocarbazole and etc.).[27] In the negative-ion ESI mode, only the pyrrolic nitrogen-containing compounds can be ionized. Therefore, the N_1 and N_2 compounds that are most abundant in investigated samples are those compounds containing at least one pyrrolic nitrogen ring. In this case, the combination of unsaturation degree (DBE) and the carbon number distribution enables us to link elemental compositions to molecular information. For a given level of unsaturation (DBE class), the compound with the smallest carbon number (C_{min}) describes the smallest molecule that is thermodynamically stable. These stable molecules are thus highly aromatic non-alkylated compounds with a pyrrolic ring. In the following, we refer to these compounds as the "core structure" of a DBE class. We derived a general chemical formula $C_{core}H_{core}NR$ for all compounds in the same DBE class, where R describes the number of methylene units $[CH_2]_r$ (r = 0, 1, 2, 3 …) situated in alkyl side chains that do not alter DBE.

3.2.1. N_1 compounds

Pyrrolic N_1 compounds are frequently detected by ESI(-) FT-ICR-MS in crude oils,[28-32] bitumens,[15,33,34] and petroleum pyrolysates.[16,35-37] Looking at N_1 DBE class 9, the smallest

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chemical structure can be built up with 12 carbon atoms: pyrrole and two additional *ortho*-annelated benzene rings. Polycyclic ring structures, in which any two adjacent rings have two and only two commonly used (carbon) atoms, are called *ortho*-fused[15]. Considering the presence of carbazole has been shown in various studies by GC-MS while no other benzo-annelated indole has been detected yet, the resulting molecule is likely carbazole amongst the other *ortho*-annelated benzoindoles. To build up a molecule with 9 DBE that has pyrrolic nitrogen but another structure of the carbon skeleton at least 16 carbon atoms are needed. That means in DBE class 9 molecular compositions with 12 to 15 carbon atoms represent strictly carbazoles (amongst other benzoindoles) alkylated with zero to three CH_2 methylene units. For compounds with a carbon number higher than 15, the contribution of molecules with not fully aromatized carbon skeletons may increase. Accordingly, the lowest chemically possible carbon number of a pyrrolic compound with 12 DBE is 16 representing compounds with a pyrrolic ring and three *ortho*-annelated benzene rings like benzocarbazoles or other naphthalene annelated indoles.

We determined the carbon number distribution of benzocarbazoles using GC-MS (Figure 4a) to show that the distribution of C_{0-4} alkylated benzocarbazoles is comparable to those of the C_{16-21} 12 DBE N_1 compounds detected by FT-ICR-MS (Figure 4b). Both GC-MS and ESI(-) FT-ICR-MS measurements illustrate a similar carbon number distribution in which the C_2 substituted benzocarbazoles/C_{18} 12 DBE N_1 compounds show highest intensities among C_{0-4} benzocarbazoles/C_{16-21} 12 DBE N_1 compounds (Figure 4). We interpret this similarity as an indication that the major part of 12 DBE N_1 compounds detected by ESI(-) FT-ICR-MS are benzocarbazole homologs.

The N_1 compounds show maxima at 12, 15, 18, 20 and 23 DBE (Figure 5) are therefore representing carbazole-type compounds with a different number and type of fused benzene rings

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(Figure 6). In specific, 12 DBE class consists mainly of benzocarbazole type compounds with a chemical formula $C_{16}H_{11}NR$ (Figure 6a), DBE class 15 contains dibenzocarbazole or naphtocarbazole type compounds ($C_{20}H_{13}NR$) (Figure 6b), and 18 DBE class represents benzonaphthocarbazoles type compounds ($C_{24}H_{15}NR$) (Figure 6c). 12, 15 and 18 DBE N_1 compounds are built up by *ortho*-fusion of benzene rings with a carbazole unit ($C_{12}H_9N$). Notably, the 9 DBE carbazoles are extremely depleted relative to the 12, 15 and 18 DBE classes (Figure 5). The transformation of carbazoles to higher DBE classes via cyclization and aromatisation reactions was observed at oil-mature Posidonia Shale (0.88% R_o),[15,16] and this also is very likely the case in studied Barnett Shale samples (1.0% R_o). For the 12, 15 and 18 DBE N_1 classes, a similar carbon number distribution is observed with a dominance of C_{0-5} alkylated core structures. A general order in relative abundance was observed as follows: $C_2 > C_3 > C_1 > C_4 > C_5 \geq C_0$ (Figure 6).

The *ortho-* and *peri*-fused benzopyrenoindole (Figure 7a) and naphthopyrenoindole (Figure 7b) are proposed as possible core structures for 20 and 23 DBE N_1 classes, respectively. N_1 compounds in DBE classes 20 and 23 can be described using the general formulas $C_{26}H_{15}NR$ and $C_{30}H_{17}NR$ (Figure 7). The carbon number distributions of 20 and 23 DBE classes are primary consisting of C_{0-5} substituted homologues, in which either the C_2 or C_3 alkylated compound dominates the distribution.

In Figure 7, all N_1 compounds with a DBE higher than 20 have a slightly higher relative abundance in the reservoir samples (red-filled rectangle) than in source rocks (green-filled triangle) while those with a DBE smaller than 18 have a slightly lower relative abundance. The intensity (%) was normalized here to the total ion abundance of N_1 compounds. Therefore, these results might hint to a) an enrichment of N_1 compounds with DBE >20 or b) a depletion of N_1

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compounds with DBE <18 during primary migration. GC-MS results showing a decrease in concentration of carbazoles and benzocarbazoles during primary migration strongly support a depletion of N_1 compounds with low DBE leading to a relative enrichment of higher DBE pyrrolic nitrogen compounds in migrated oils. We conclude from this that fractionation of pyrrolic N_1 compounds occurs to a small extent during primary migration with respect to molecular size while chemical structure (e.g. type of aromatic ring annelation or grade of alkylation) appears to have no influence.

3.2.2. N_2 compounds

N_2 compounds are also frequently examined by ESI(-) FT-ICR-MS, while they appears more abundant in bitumens and pyrolysates[15,16,36,37] than in crude oils[28-32]. It is more difficult to get structural information for N_2 compounds since only one nitrogen atom has to be in a pyrrolic form while the second can be either pyrrolic or pyridinic. In the studied Barnett Shale bitumens, the relative abundance of N_2 compounds is comparable to those of the N_1 compounds. The DBE class distribution of N_2 compounds shows maxima at 12, 15, 17, 20 and 23 DBE (Figure 8).

For the 12 and 15 DBE classes, the general chemical formulas of the core structures according to their minimum carbon numbers are $C_{16}H_{12}N_2R$ and $C_{20}H_{14}N_2R$. To our knowledge, biindoles (Figure 9a) and benzobiindoles (Figure 9b) are the only compound types with a completely aromatized carbon skeleton and pyrrolic nitrogen suiting to this formula. Notably, there is often more than one isomer of core structures according to different configuration of benzene and pyrrole rings (see Figure 9b benzobiindole-1 and -2). If one nitrogen atom would be pyridinic or in the same five-membered ring as the other nitrogen, the carbon number of a nonalkylated but fully aromatized core structure would be odd since the nitrogen replaces a carbon atom. Besides, 12 is the minimum DBE value for the N_2 compounds (Figure 8), which strongly supports

biindole as the basic structure unit. However, there are more than one possible positional isomers of biindoles as illustrated in Figure 9a. The connection of the two indole subunits can between the five-membered rings, between the benzene rings, between one five-membered and one benzene ring and on every possible position.

Biindoles have not been identified in petroleum samples yet. Their increased polarity (two pyrrolic nitrogen atoms) impedes their geochemical analysis by conventional GC-MS methods. It is very likely that biindole type compounds are enriched in the asphaltene fraction after sample preparation which is commonly not investigated on a molecular level.[30] In comparison, indoles were not only identified in pyrolysates generated from biomass (i.e., algae, bacteria and archaea) but also the major sediments pyrolysis products with a predominance of $C_2 > C_1 > C_0$ substituted homologues.[38] The C_3 substituted indoles were not studied therein by GC-MS,[38] probably due to the lack of standard compounds. The C_{0-2} indoles were not detected herein by FT-ICR-MS due to their low molecular mass (<147 Da). In spite of that, the partial mass chromatograms of summed ions representing C_{0-3} indoles ($m/z = 117, 131, 145, 159$) are comparable to the total ion current (TIC) traces (Figure 10). The mass spectra of five selected peaks are correspondingly dominated by major ions of indoles (Figure 11). Thus, we highly assume that biindoles are common compounds in petroleum source rocks.

For the 17, 20 and 23 DBE N_2 classes, carbazolocarbazole, benzocarbazolocarbazole and dibenzocarbazolocarbazole compounds were assigned with respect to their general formulas $C_{22}H_{14}N_2R$, $C_{26}H_{16}N_2R$ and $C_{30}H_{18}N_2R$, respectively (Figure 12). It is probably necessary to mention that the carbazolocarbazole-type structures are not the only possible forms for 17, 20 and 23 DBE N_2 classes since the relative order or position of ring annelation could be different. The carbon number distributions of 17, 20 and 23 DBE N_2 classes are consisting of mainly C_{0-5}

substituted homologues, in which either C_2 or C_3 substituted compound predominates over the others (Figure 12).

A relative enrichment of 12 and 15 DBE N_2 compounds in the reservoir samples is observed (Figure 8) indicating an increased expulsion of N_2 compounds with 12 and 15 DBE compared to those with 17, 20 and 23 DBE from the source rock into the reservoir. The carbon number distributions of 12 and 15 DBE N_2 classes are nevertheless unaltered (Figure 9). For example, the predominance of C_3 substituted 12 DBE N_2 compound in source rock bitumens is unchanged in reservoir extracts (Figure 9a). The same applies to the predominance of C_2 substituted N_2 compounds in the 15 DBE N_2 class (Figure 9b). In contrast to the biindole-type compounds (N_2 DBE 12, 15), the 17, 20 and 23 DBE N_2 classes seems not to be altered by fractionation (Figure 8). The carbon number distributions of 17, 20 and 23 DBE N_2 classes are consisting of mainly C_{0-5} substituted homologues, in which either C_2 or C_3 substituted compound predominates over the others (Figure 12). These features remain constant during primary migration.

3.3. Origin of Nitrogen Compounds

The nature of nitrogen compounds has long been of interest from the standpoint of its possible relation to the origin of petroleum.[27] Recently, nitrogen-containing compounds have received renewed attention because of their predominance in the mass spectrum of ESI(-) FT-ICR-MS.[15,16,29,31,32,37,39,40] As shown in this study, the similar DBE and carbon number distributions of nitrogen compounds (Figures 4-12) suggest their restricted precursors and common mechanisms of formation.

Chlorophyll, the light-absorbing green pigment for plants, photosynthetic bacteria, and blue-green algae, is a prerequisite for photosynthesis that accomplishes the mass production of organic matter on earth.[41] The nitrogen-containing tetrapyrrolic nucleus of chlorophyll is

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believed to be the main precursor of petroleum porphyrins.[42-46] Besides the preservation as petroleum porphyrins, chlorophyll in the high plants was recently recognized and reviewed to involve a largely common and regulated pathway of breakdown,[47,48] which finally formed a group of colourless tetrapyrroles known as nonfluorescent chlorophyll catabolites (NCCs).[49] It is estimated that more than 10^9 tons of chlorophyll are annually biosynthesized and breakdown on the earth.[50] Therefore, considerable amount of NCCs will be incorporated into sediments, followed by a subsequent transformation from biological organic matter into geological organic matter, i.e., kerogen. In this process, a progressive elimination of labile functional groups (especially the oxygen-containing groups such as amide, carbonyl, carboxyl, hydroxyl, ester) and of the linkages between nuclei (including carbon chains) would occur.[41] With increasing temperature and pressure, aromatization will then increases in the catagenesis stage.[41]

Based on above observations (i.e., deoxygenation, cracking and then aromatization), we propose here a schematic evolution of NCCs in Figure 13, which includes all pyrrolic nitrogen core structures we found with (-) ESI FT-ICR-MS as final diagenesis and or catagenesis products.

SUMMARY AND CONCLUSION

The dataset from the Barnett Shale of Marathon 1 Mesquite Well provides valuable insights into the migrational behaviours of pyrrolic nitrogen compounds. A preferential removal of low molecular weight carbazoles and benzocarbazoles from migrated oils was revealed by GC-MS. However, no isomeric fractionation was detected for many examined isomer ratios, such as the benzocarbazole [a]/([a] + [c]) ratio.

Using FT-ICR-MS for medium to high molecular weight pyrrolic nitrogen compounds, we showed that a preferential removal of N_1 compounds of carbazole type with lower DBE

(DBE<18) during primary migration was observed by GC-MS and FT-ICR-MS, which seems controlled primarily by molecular size. In comparison, the N_2 compounds showed a preferential enrichment of 12 and 15 DBE N_2 classes representing biindole compounds compared to carbazolocarbazoles (17, 20, 23 DBE) during primary migration which can be associated with molecule structure. Within N_1 and N_2 compound classes the overall DBE range of 10-30 remains unchanged. The carbon number distributions of each DBE class are quite similar, i.e., a predominance of either C_2 or C_3 alkylated compounds amongst C_{0-5} homologues. These observations suggest that those pyrrolic nitrogen-containing compounds have restricted precursors and common mechanisms of formation. Nonfluorescent chlorophyll catabolites (NCCs), the final breakdown products of chlorophyll, were tentatively suggested as a possible precursor of pyrrolic nitrogen compounds. Possible reaction pathways were given to exemplify the formation of the different *ortho-* and *peri-*annelated as well as carbon-bond-linked aromatic core structures of pyrrolic N_1 and N_2 compounds from the NCC nuclei via thermally-induced cracking, deoxygenation and aromatization.

We think that our findings are of great relevance to the general understanding of fractionation processes in petroleum systems. Fluid physical properties of petroleum are defined by chemical composition. Therefore, a fundamental knowledge of retained and migration petroleum fluid chemical composition is indispensable. What is more, a potential precursor was given for pyrrolic nitrogen-containing compounds which commonly present in petroleum fluids.

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Table 1: Bulk Geochemical Characteristics of Barnett Shale Samples from the Marathon 1 Mesquite Well[a]

Sample	Interval	Depth (ft)	XRD (%) Calcite	XRD (%) Quartz	XRD (%) Clays	TOC (wt.%)	Bitumen (%TOC)	SARA (%) Sat.	SARA (%) Aro.	SARA (%) Res.	SARA (%) Asp.	Diasteranes (%) C_{27}	Diasteranes (%) C_{28}	Diasteranes (%) C_{29}	R_o (%) MNR	R_o (%) MPI1
G009584	1st	3686.65	28	62	4	1.12	11	41	11	37	11	40	27	33	0.99	1.02
G012611	2nd	3710.26	15	40	20	3.34	20	62	14	21	2	41	24	34	1.04	1.15
G009600	2nd	3710.30	11	43	17	3.04	21	63	13	20	4	41	27	32	1.02	1.02
G009602	2nd	3715.00	92	5	0	0.78	15	38	8	47	7	37	25	38	0.96	1.05
G012612	2nd	3720.59	23	33	18	3.11	22	63	16	17	4	42	24	34	0.98	1.01
G012613	2nd	3722.69	4	51	20	3.25	19	61	16	20	4	41	24	35	0.96	1.01
G012616	3rd[U]	3731.66	11	40	23	6.38	9	51	17	26	5	38	29	33	1.04	0.98
G009616	3rd[U]	3742.60	0	27	50	5.60	10	49	15	29	7	41	26	32	1.01	0.99
G012617	3rd[L]	3745.49	0	33	31	6.67	6	47	21	25	7	41	25	34	0.98	0.98
G009619	3rd[L]	3746.70	0	24	47	8.35	5	29	20	42	9	40	26	34	0.97	1.01
G012618	3rd[L]	3746.80	0	25	52	8.69	5	43	20	32	5	41	25	34	1.06	1.00
G009621	3rd[L]	3749.20	0	26	50	7.53	5	42	16	35	7	37	25	38	1.04	0.99
G012622	4th[U]	3767.13	0	26	49	5.01	8	46	19	29	6	39	25	36	1.02	1.02
G009647	4th[L]	3797.50	98	2	0	0.65	45	30	5	23	43	36	26	38	n.a.	0.96
G009650	5th	3802.70	8	70	11	4.30	17	55	17	25	3	n.a.	n.a.	n.a.	1.00	1.03

[a]Data are taken from Han et al.[17] and Han et al.[18]. The content of clays is the sum of illite-smectite mixed layers and mica minerals determined by X-ray diffraction (XRD). The content of total organic carbon (TOC) was determined by Leco method. Bitumen was extracted using the ternary azeotropic solvent system (acetone: chloroform: methanol, v/v = 38: 32: 30), and subjected to SARA (saturates, aromatics, resins and asphaltenes) fractionation. Diasteranes include 13β,17α(H) (20S + 20R) isomers determined by metastable reaction monitoring/gas chromatography/mass spectrometry (MRM/GC/MS) ($M^+ \rightarrow 217$) in the *n*-alkane removed saturate fractions. Methyl naphthalene ratio (MNR) = [2-MN]/[1-MN] and methyl phenanthrene index 1 (MPI1) = 1.5×[2-MP+3-MP]/[P+1-

MP+9-MP] were determined by gas chromatography/mass spectrometry (GC/MS) ($M^+\rightarrow142/178/192$) in the aromatic fractions. Vitrinite reflectance ($\%R_o$) was calculated according to equations R_o (%) = 0.17×MNR + 0.82 and R_o (%) = 0.60×MPI1 + 0.40, respectively (see details in Han et al.[18] and references therein).

Figure 1. Isomeric distribution of (a-e) C_0-C_4 carbazoles (m/z = 167, 181, 195, 209, 223) and (f-j) C_0-C_4 benzocarbazoles (m/z = 217, 231, 245, 259, 273) in the resins fraction of a bitumen extracted by the ternary solvent mixtures (acetone: chloroform: methanol, v/v = 38: 32: 30). The number above specific peak refers to the methylation site.
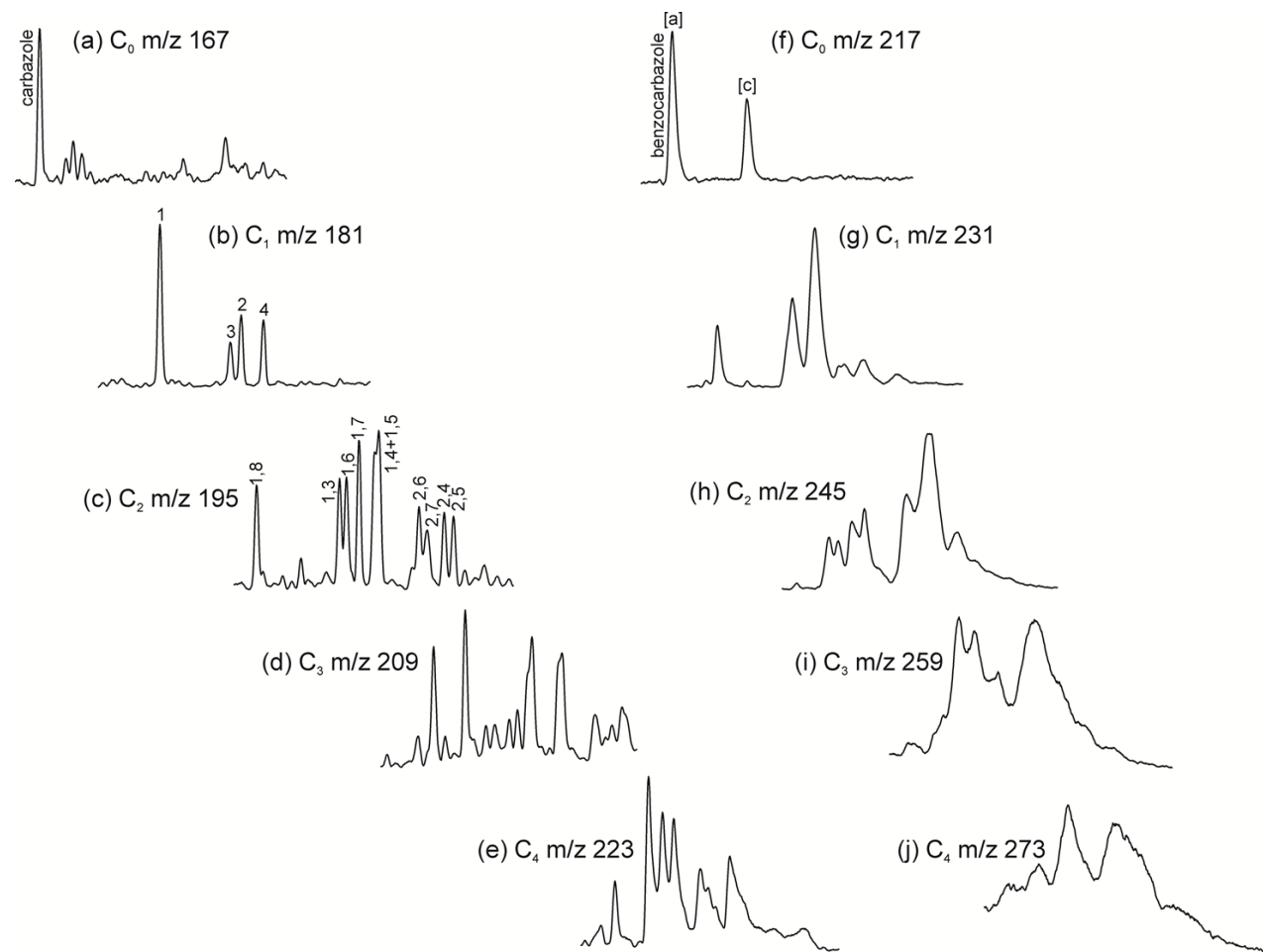
Figure 2. Variation in concentrations of (a) carbazole, (b) methylcarbazoles, (c) dimethylcarbazoles, (d) benzocarbazoles, and (e) alkylbenzocarbazoles determined in resins (ug/g) from the Barnett Shale extracts of Marathon 1 Mesquite Well. The concentration in relative to bitumen (µg/g bitumen) can be readily converted by multiplying the specific percentage of resins in SARA fractions.
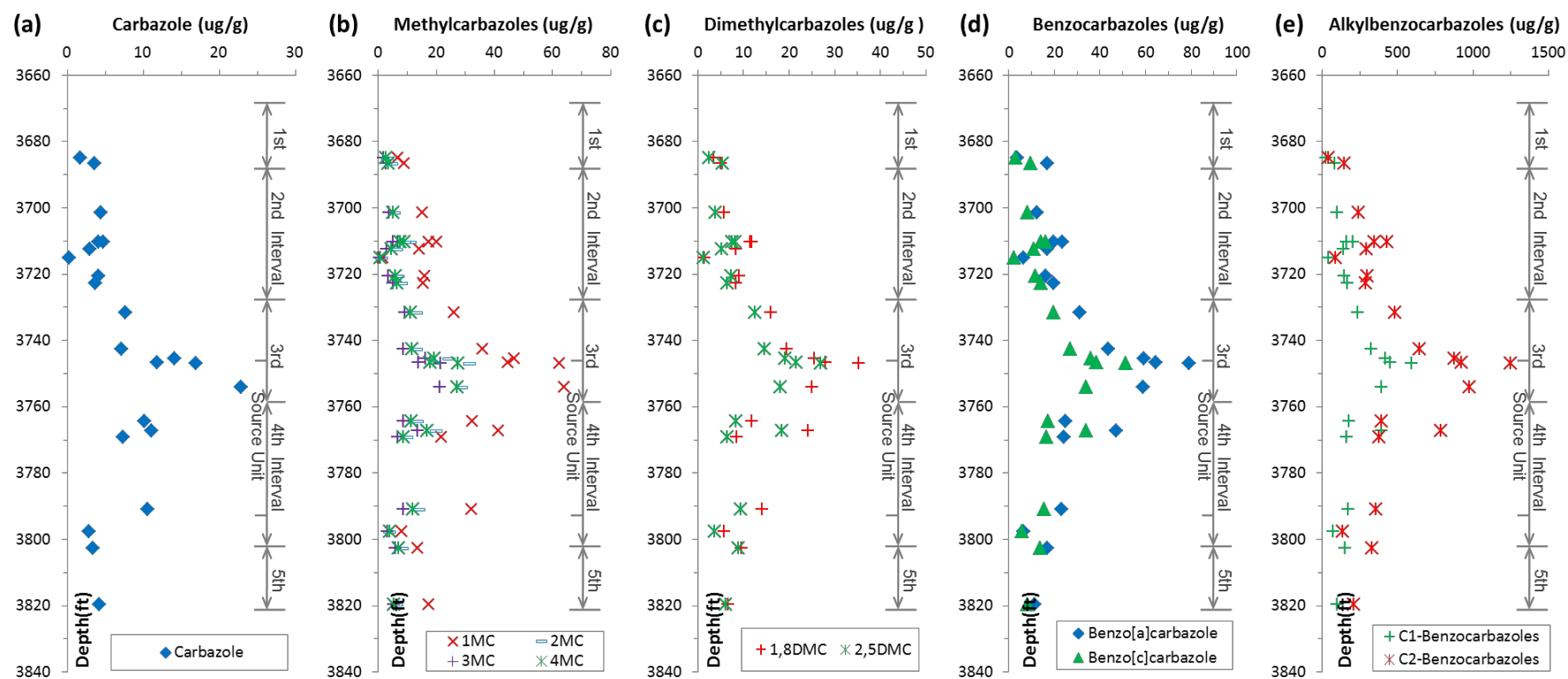
Figure 3. Variation in ratios of (a) C_{1-2} carbazoles/benzocarbazoles, (b) methylcarbazoles, (c) dimethylcarbazoles, (d) benzocarbazoles, and (e) alkylbenzocarbazoles in resins from the Barnett Shale extracts of Marathon 1 Mesquite Well.
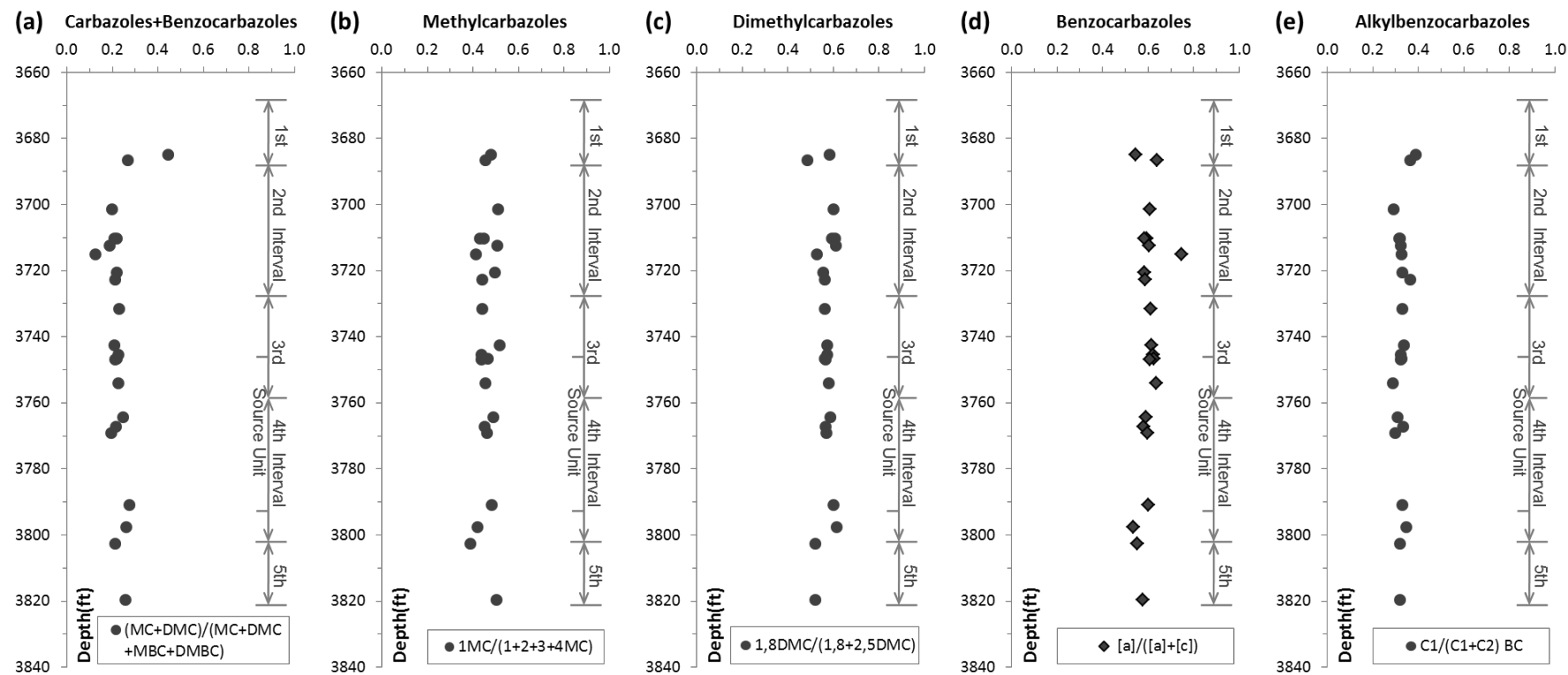
Figure 4. Carbon number distribution of (a) benzocarbazoles detected by GC-MS, and (b) 12 DBE class of N_1 compounds detected by ESI(-) FT-ICR-MS. The normalized intensity (%) is in relative to C_2 substituted species. A possible structure of 12 DBE benzocarbazoles ($C_{16}H_{11}NR$) is exemplified, in which R is an alkyl chain or chains $[CH_2]_r$ (r = 0, 1, 2, 3 …) that substituted on the exemplified core structure which has more than one isomers.
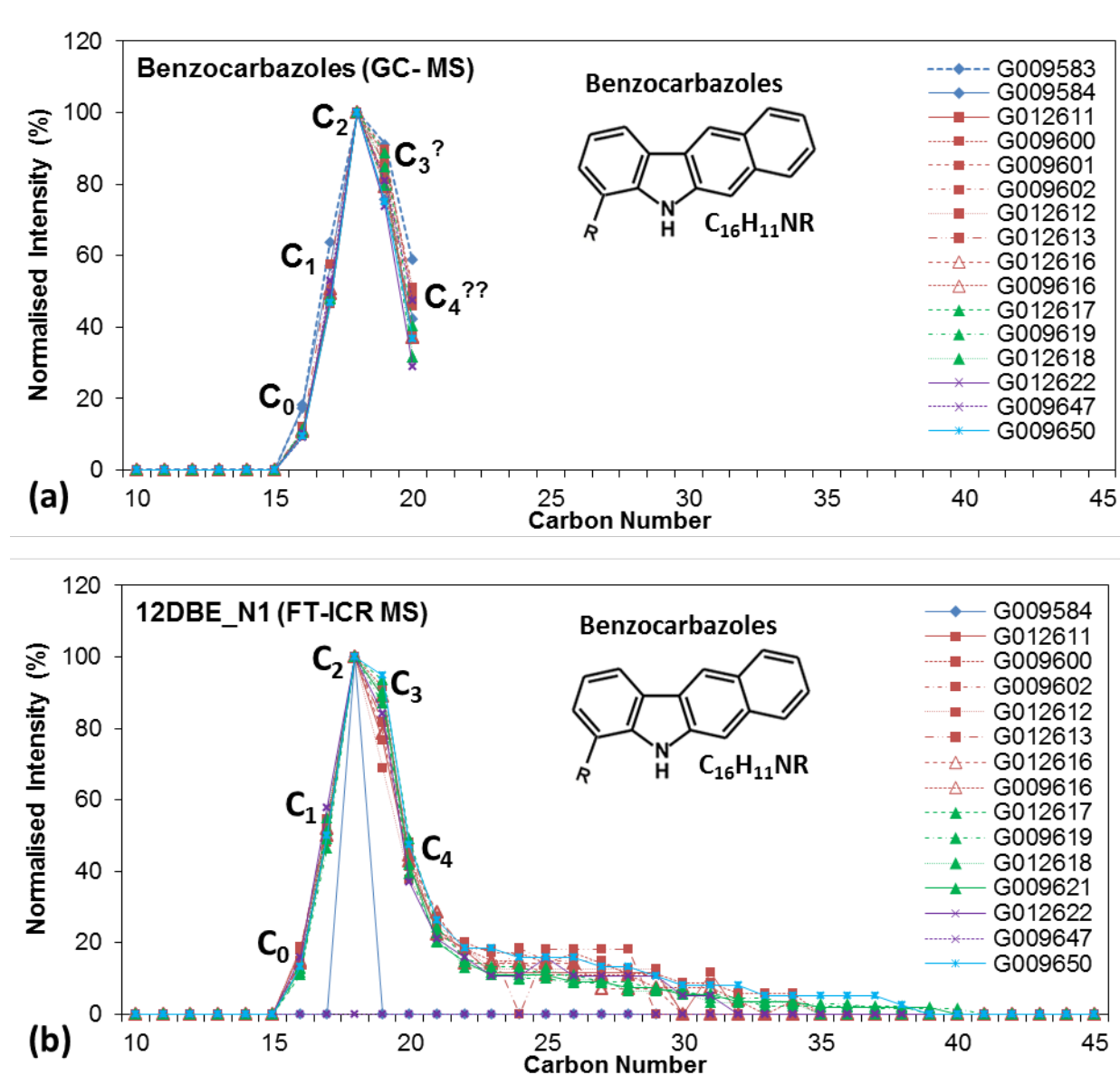
Figure 5. DBE distribution of N_1 compounds detected by ESI(-) FT-ICR-MS. The intensity of each DBE class was expressed in percentage of the total ion abundance of N_1 compounds. A difference of 3 in the DBE value indicates structures that differ by one *ortho*-fused benzene ring. The primary DBE classes are numerically marked up, in which the 20 and 23 DBE classes (*ortho-* and *peri*-fused) are selectively underlined. The reservoir and source-rock samples are marked with red-filled rectangles and green-filled triangles, respectively.
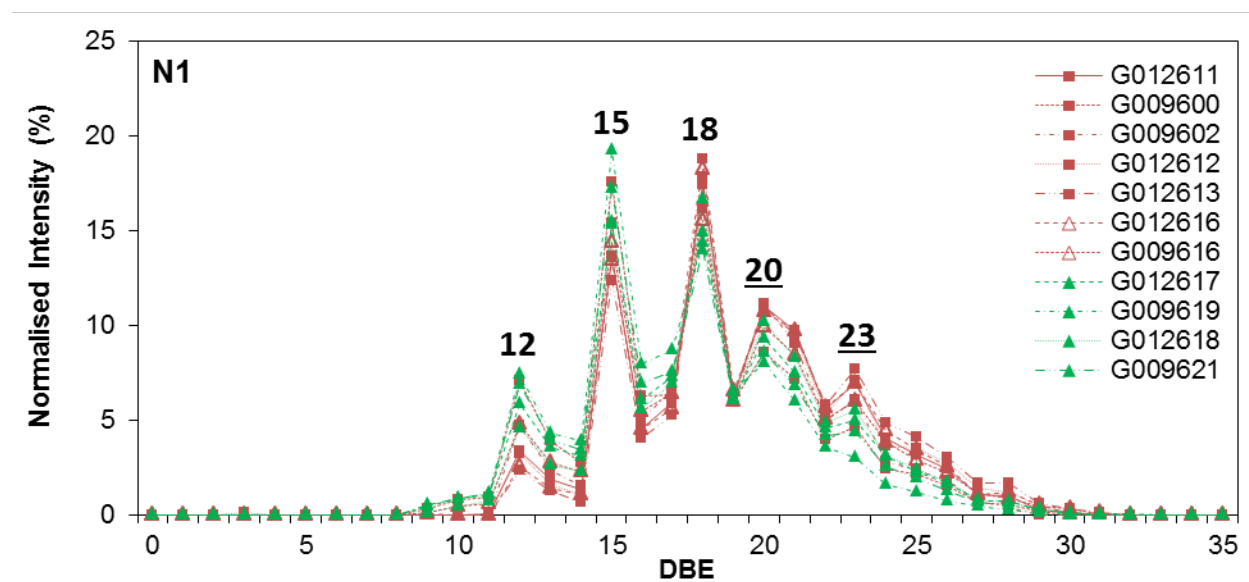
Figure 6. Carbon number distribution of (a) 12 DBE class, (b) 15 DBE class, and (c) 18 DBE class of N_1 compounds detected by ESI(-) FT-ICR-MS. The normalized intensity (%) was expressed in relative to the total ion abundance of N_1 compounds. R is an alkyl chain or chains $[CH_2]_r$ (r = 0, 1, 2, 3 …) that substituted on the exemplified core structure which normally has more than one isomers.
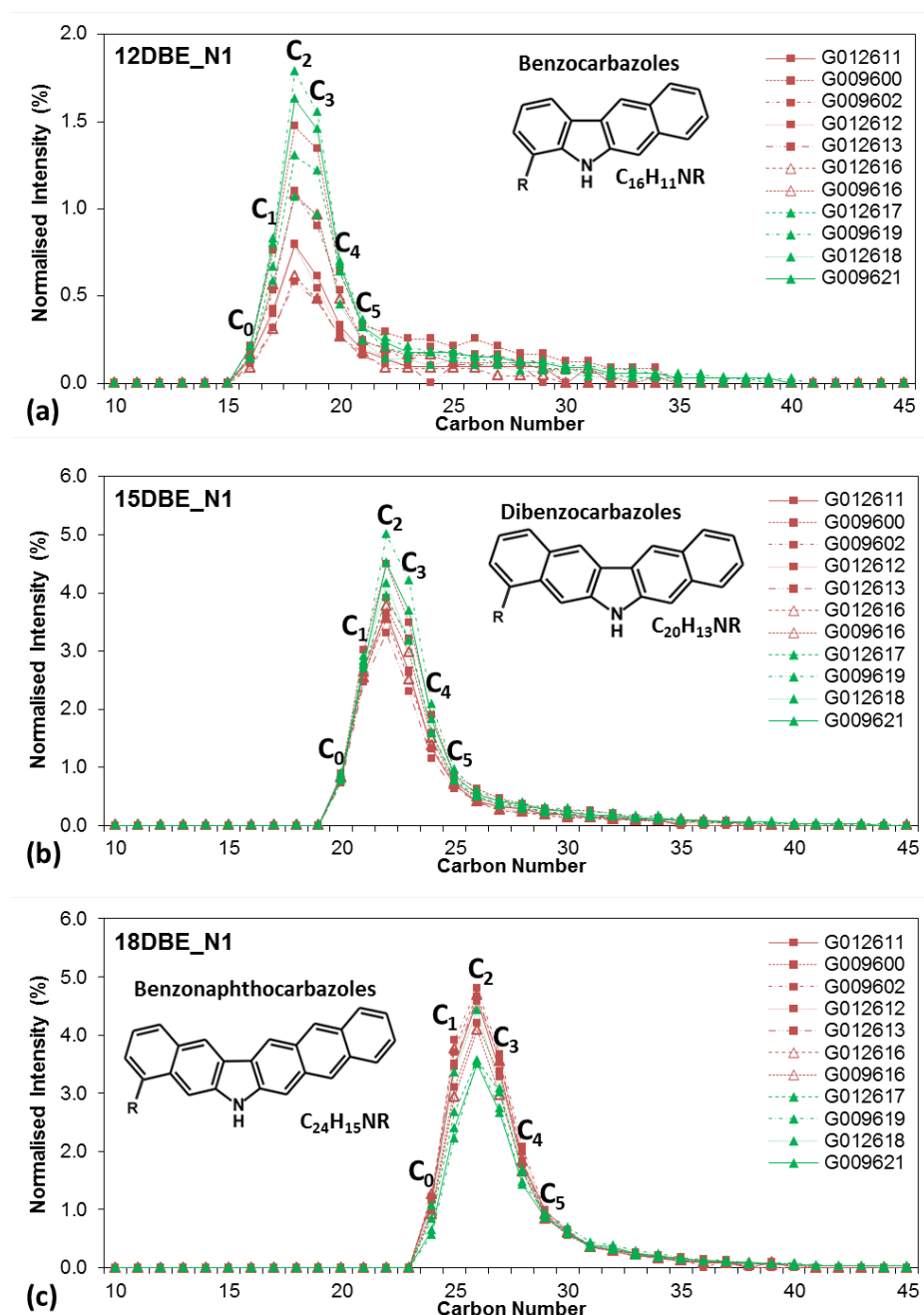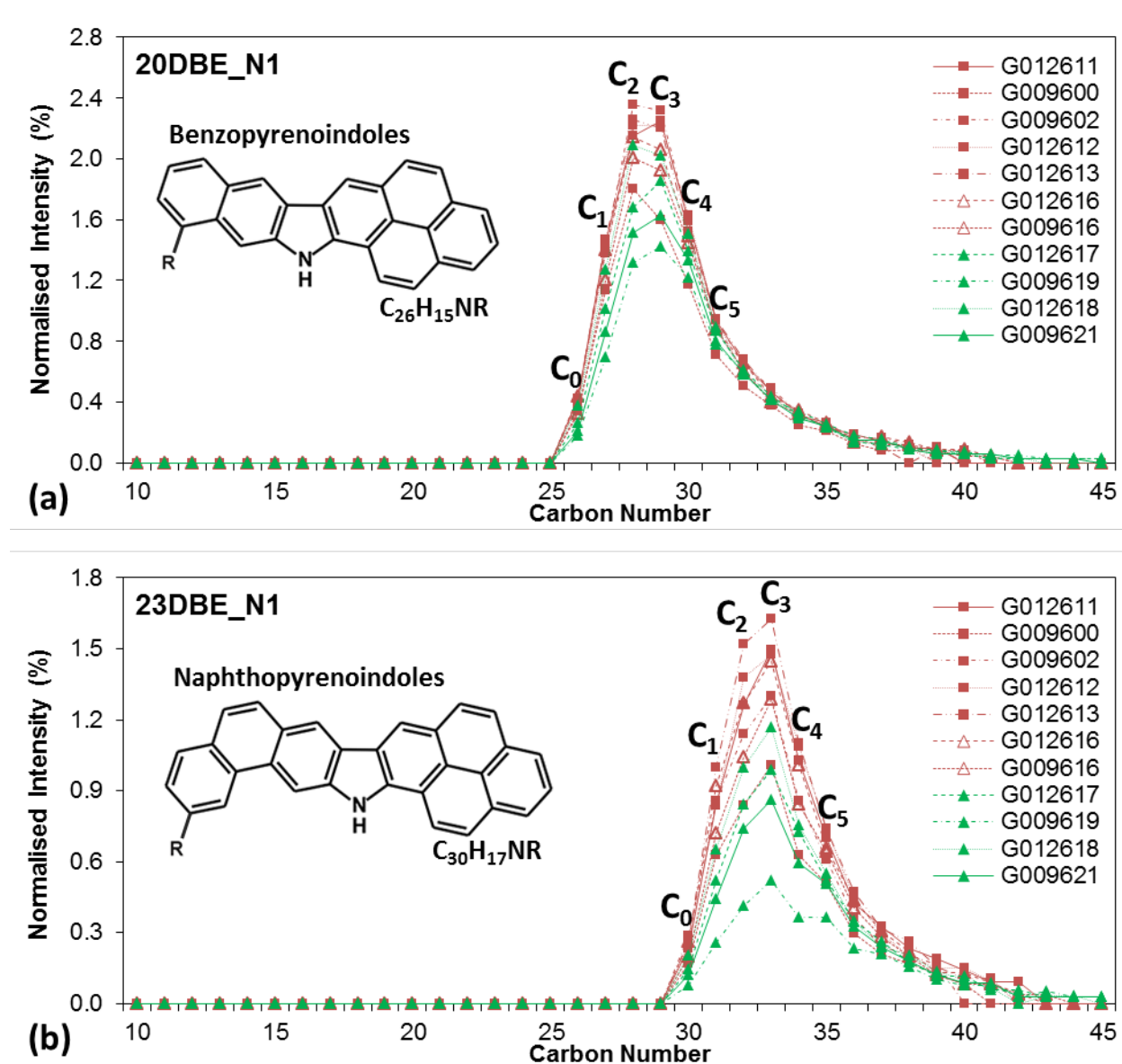
Figure 7. Carbon number distribution of (a) 20 DBE class and (b) 23 DBE class of N_1 compounds detected by ESI(-) FT-ICR-MS. The normalized intensity (%) was expressed in relative to the total ion abundance of N_1 compounds. R is an alkyl chain or chains $[CH_2]_r$ (r = 0, 1, 2, 3 …) that substituted on the exemplified core structure which normally has more than one isomers.

Figure 8. DBE distribution of N₂ compounds detected by ESI(-) FT-ICR-MS. The intensity of each DBE class was expressed in percentage of the total ion abundance of N₂ compounds. The principle DBE classes are numerically marked up, in which the 12 and 15 DBE classes (biindoles) are selectively underlined. The reservoir and source-rock samples are marked with red-filled rectangles and green-filled triangles, respectively.
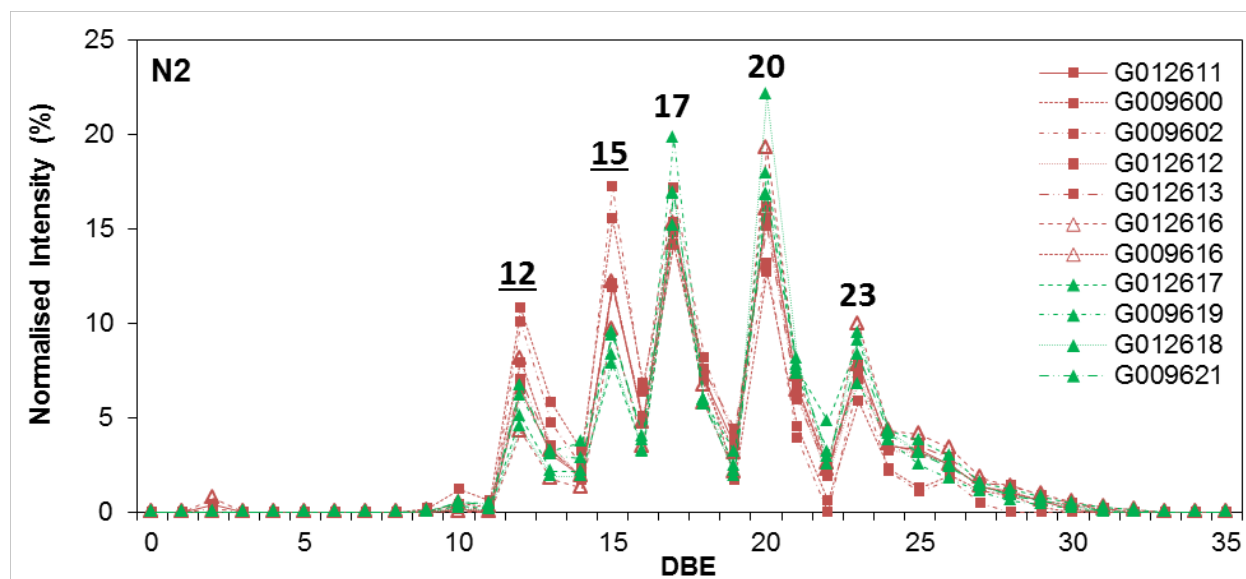
Figure 9. Carbon number distribution of (a) 12DBE class and (b) 15 DBE class of N_2 compounds detected by ESI(-) FT-ICR-MS. The normalized intensity (%) was expressed in relative to the total ion abundance of N_2 compounds. R is an alkyl chain or chains $[CH_2]_r$ (r = 0, 1, 2, 3 …) that substituted on the exemplified core structure which normally has more than one isomers (two structural isomers were suggested for benzobiindoles).
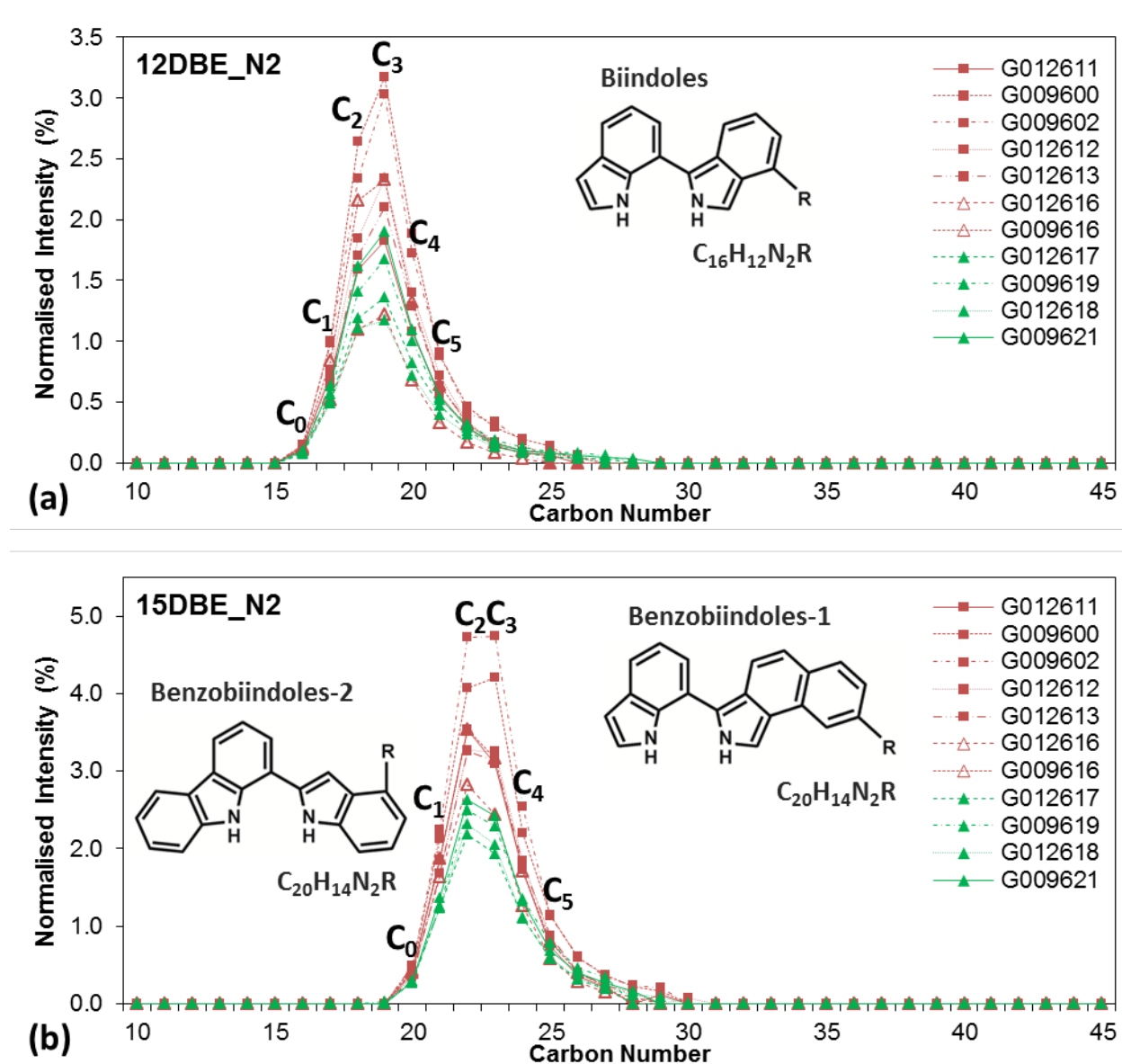
Figure 10. GC-MS traces of total ion current (TIC) for indoles (a), and partial mass chromatograms of summed ions (m/z = 117, 131, 145, 159) representing C_{0-3} indoles (b).
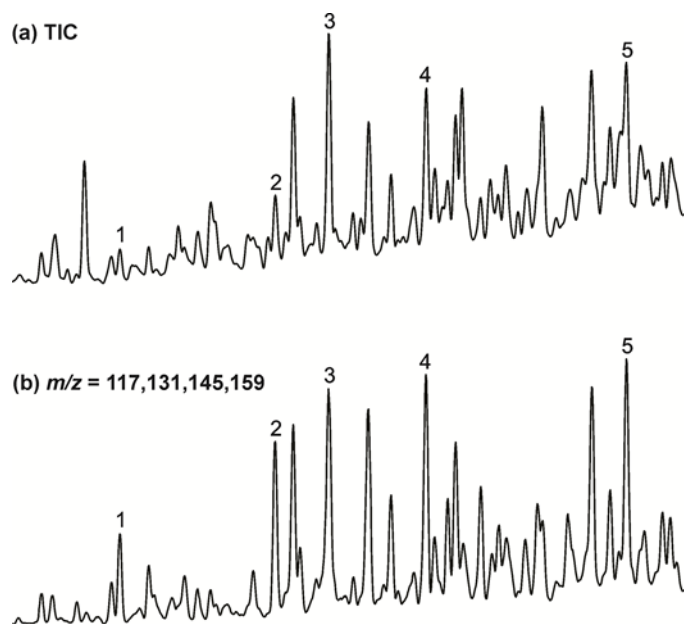
Figure 11. Mass spectra of (a) peak 1, (b) peak 2, (c) peak 3, (d) peak 4, and (e) peak 5 in Figure10.
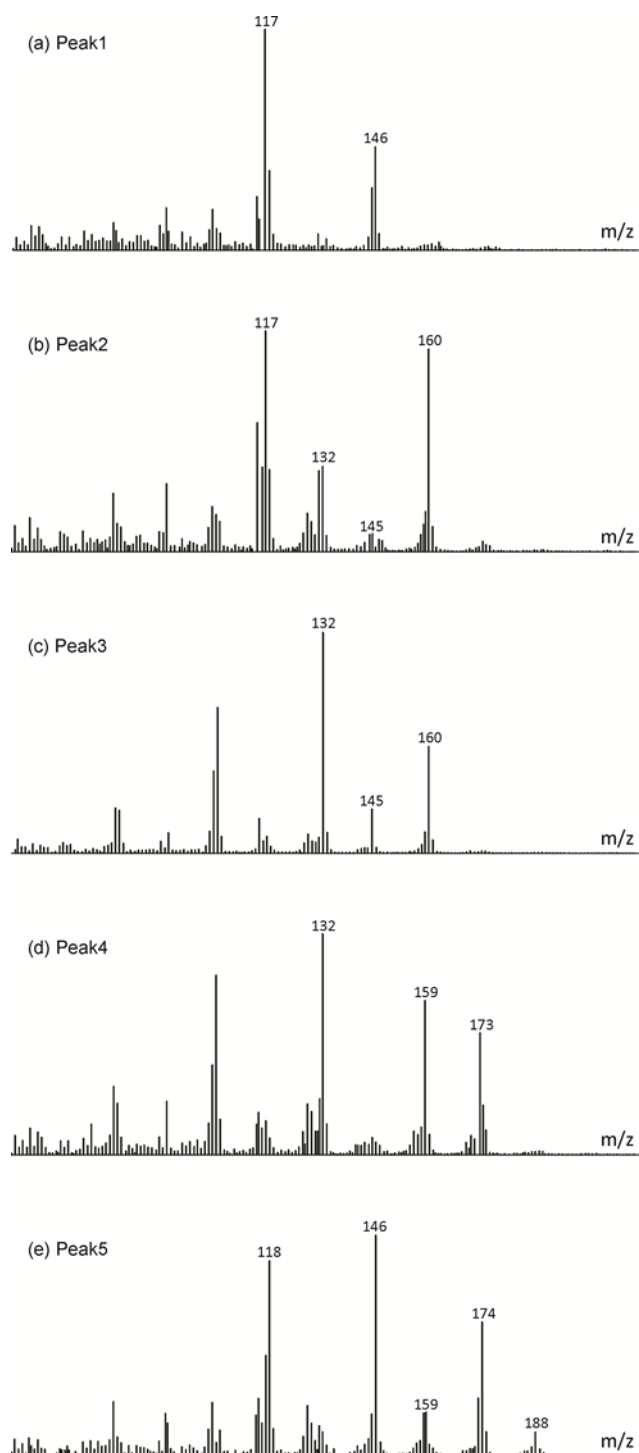
Figure 12. Carbon number distribution of (a) 17DBE class, (b) 20 DBE class, and (c) 23 DBE class of N_2 compounds detected by ESI(-) FT-ICR-MS. The normalized intensity (%) was expressed in relative to the total ion abundance of N_2 compounds. R is an alkyl chain or chains $[CH_2]_r$ (r = 0, 1, 2, 3 …) that substituted on the exemplified core structure which normally has more than one isomers.
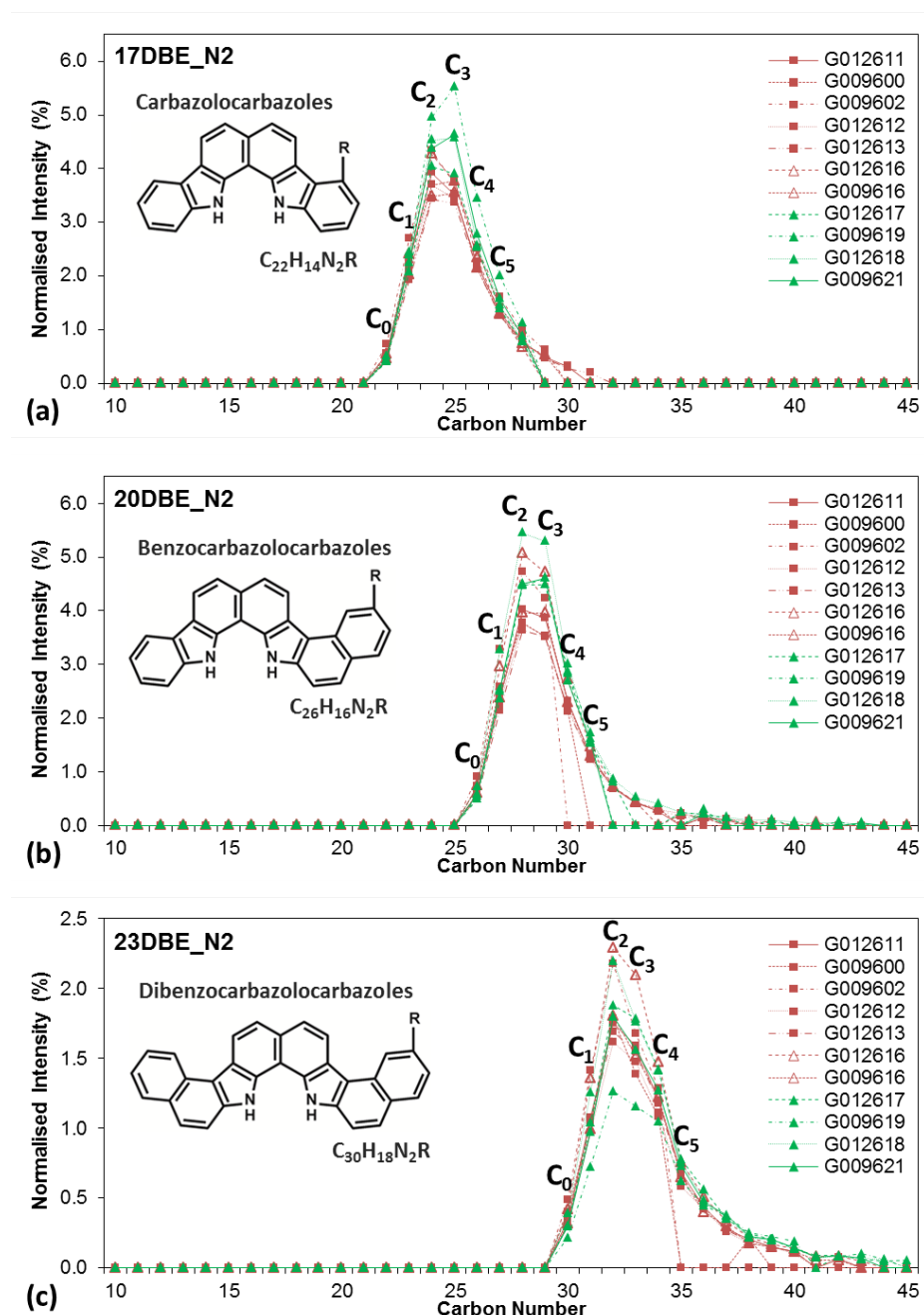
Figure 13. Possible reaction pathways of the NCC (nonfluorescent chlorophyll catabolite), in which R represents a generalized alkyl chain that substituted on the core structure.

(A1-C1) Formation of *ortho*-fused (DBE = 12, 15, 18) N_1 compounds from the NCC nuclei via thermally-induced cracking, deoxygenation and aromatization. (D1-E1) Formation of *ortho*- and *peri*-fused (DBE = 20, 23) N_1 compounds via *peri*-fused aromatization. In general, there is more than one isomer (aromatization pathway) for the exemplified core structure.

(A2-B2) Formation of biindole (12 DBE) and benzobiindole (15 DBE) compounds from the NCC nuclei via thermally-induced cracking, deoxygenation and aromatization. (C2-E2) Formation of *ortho*-fused (DBE = 17, 20, 23) N_2 compounds via *ortho*-fused aromatization. In general, there is more than one isomer (aromatization pathway) for the exemplified core structure.

DBE12
$C_{16}H_{11}NR$

(B1)

DBE15
$C_{20}H_{13}NR$

(C1)

DBE18
$C_{24}H_{15}NR$

(A1) cracking, -O
aromatization

NCC

H

(D1)
peri-fused

DBE20

(E1)

DBE23

$C_{26}H_{15}NR$

$C_{30}H_{17}NR$

(A2) cracking, -O
aromatization

DBE12

(B2)

DBE15

$C_{16}H_{12}N_2R$

$C_{20}H_{14}N_2R$

(C2)
ortho-fused

DBE17

(D2)

DBE20

(E2)

DBE23

$C_{22}H_{14}N_2R$

$C_{26}H_{16}N_2R$

$C_{30}H_{18}N_2R$