The effect of origin and genetic processes of low molecular weight aromatic hydrocarbons in petroleum on their stable carbon isotopic compositions

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ABSTRACT

Stable carbon isotopic compositions of individual low molecular weight aromatic hydrocarbons, such as alkylbenzenes, alkylnaphthalenes and alkylphenanthrenes, were measured from a set of oils, mostly from the North-West shelf of Australia, of varying age, facies type and thermal maturity. The objective was to assess the influence of thermal maturity and source during generation of these aromatics on their stable carbon isotopic compositions. For most of the oils studied, $\delta^{13}C$ of the aromatic components show a ^{13}C depletion as the degree of methylation increases. For the alkylnaphthalenes, the ^{13}C depletion is most pronounced for low maturity oils compared to high maturity oils. $\delta^{13}C$ of the methyl groups of these alkylnaphthalenes were calculated and the resulting data display significant differences between 'mature' and 'immature' oils, suggesting that isotopically lighter methyl groups are 'released' as thermal maturation proceeds. Therefore, we propose an isotopic fractionation associated with the methyl transfer mechanisms affecting low molecular weight aromatic hydrocarbons during diagenesis.

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1. Introduction

Low molecular weight aromatic hydrocarbons (LMWAHs), which include the C_1–C_5 alkylbenzenes (ABs), C_1–C_3 alkylnaphthalenes (ANs) and C_1–C_2 alkylated biphenyls (ABPs) and higher molecular weight C_1–C_3 alkylphenanthrenes (APs) are ubiquitous constituents of petroleum and sedimentary organic matter (OM). ABs, ANs and APs can be formed by geosynthetic processes, resulting in a host of alkylated, dealkylated and isomerised components (Radke et al., 1982b; Ioppolo-Armanios et al., 1995; Trolio et al., 1999; van Aarssen et al., 1999; Bastow et al., 2000). The main dia-

genetic processes are isomerisation (via methyl shift) and trans-alkylation (via methyl transfer) reactions (Radke et al., 1982b; Alexander et al., 1985; Strachan et al., 1988; van Aarssen et al., 1999; Bastow et al., 2000). These chemical reactions are related to thermal maturity, leading to an increase in the relative abundance of the more thermally stable isomers. According to this concept, many molecular ratios involving LMWAHs have been used to assess the thermal maturity of oils and source rocks (Radke et al., 1982b, 1990a, 1994; Alexander et al., 1995; Budzinski et al., 1995; van Aarssen et al., 1999; Asif et al., 2011). The methylphenanthrene index (MPI 1; see Appendix A), for example, is a commonly used maturity parameter in petroleum exploration (Radke et al., 1982a; Holman et al., 2012; and for a review Holman et al., 2014). Similar isomer ratios have also been proposed for ANs (van Aarssen et al., 1999; see Appendix A).

Biodegradation of petroleum also alters the distribution of aromatic hydrocarbons (AHs) (Volkman et al., 1984; Fisher et al., 1996; Trolio et al., 1999; George et al., 2002; Huang et al., 2004; Asif et al., 2009). The effects of biodegradation on AHs depend on the number of aromatic rings, the degree of alkylation, the relative susceptibilities to microbial alteration for various isomers of a given molecule and the type of bacteria. Demethylation reactions

Abbreviations: ABs, alkylbenzenes; DMBs, dimethylbenzenes; TMBs, trimethylbenzenes; TeMBs, tetramethylbenzenes; N, naphthalene; ANs, alkylnaphthalenes; MNs, methylnaphthalenes; DMNs, dimethylnaphthalenes; TMNs, trimethylnaphthalenes; TeMNs, tetramethylnaphthalenes; PMNs, pentamethylnaphthalenes; P, phenanthrene; APs, alkylphenanthrenes; MPs, methylphenanthrenes; DMPs, dimethylphenanthrenes; TMPs, trimethylphenanthrenes; TeMPs, tetramethylphenanthrenes; ABPs, alkylated biphenyls; MPs, methylbiphenyls; DMBPs, dimethylbiphenyls.

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of substituted compounds have been suggested to occur during the biodegradation processes (Huang et al., 2004).

AHs can be associated with specific microbial and land plant sources, especially in sediments and crude oils of relatively low maturity, where the major isomers may be directly formed from natural products. For example, 1,6-dimethylnaphthalene (1,6-DMN), 1,2,5- and 1,2,7-trimethylnaphthalenes (1,2,5- and 1,2,7-TMNs), 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN) and 1,2,3,5,6-pentamethylnaphthalene (1,2,3,5,6-PMN) can be formed from naturally occurring triterpenoids, hopanoids and/or resinous compounds through a series of aromatisation and cleavage reactions (Puttmann and Villar, 1987; Strachan et al., 1988; Killops, 1991; van Aarssen et al., 1992, 1999; Armstroff et al., 2006). The distributions of methylphenanthrenes (MPs), dimethylphenanthrenes (DMPs) and trimethylphenanthrenes (TMPs) are largely determined by OM type (Radke et al., 1986, 1998; Budzinski et al., 1995).

While the molecular distributions of these LMWAHs and their relationship with maturity, biodegradation and source have been widely studied, their stable carbon isotopic compositions ($\delta^{13}C$) have not been extensively investigated. Compound specific isotope analysis (CSIA) has been shown to provide useful information about source(s) of individual hydrocarbons (e.g., Freeman et al., 1990; Grice et al., 1998, 2001, 2005, 2007, 2009; Fenton et al., 2007; Maslen et al., 2011). The thermal maturity has long been known to have an effect on the $\delta^{13}C$ of hydrocarbons (Bigeleisen, 1949). We propose to extend the aforementioned molecular studies by measuring the variations in $\delta^{13}C$ of individual LMWAHs (ABs, ANs, APs) present in crude oils from the NW shelf of Australia of varying age, facies type and thermal maturity, in an attempt to obtain additional insights into geochemical processes that determine the distribution of AHs in petroleum. Relationships between the $\delta^{13}C$ of LMWAHs, thermal maturity and source are mainly discussed. Calculations to determine the specific $\delta^{13}C$ of the methyl groups of these LMWAHs are also provided in the present work.

2. Materials and methods

2.1. Samples

A set of 16 crude oils and condensates of varying age, facies type and maturity was used for the present study. Most of these oils come from the NW shelf of Australia (Carnarvon Basin, see Table 1). This sample set includes oils generated from varying source rock types, of various thermal maturities and different levels of biodegradation. These oils were chosen from a set of 139 crude oils analysed by van Aarssen et al. (1999). The latter study investigated the isomeric distributions of selected ANs and provided the basis for the present study. Trimethylnaphthalene ratio (TMNr), tetramethylnaphthalene ratio (TeMNr) and pentamethylnaphthalene ratio (PMNr), defined by van Aarssen et al. (1999) are described in Appendix A and are mostly determined by thermal maturity (see Section 3.1 for more information). These ratios are given in Table 1 and provide compositional information.

2.2. Fractionation

In a typical separation, approximately 50–100 mg of crude oil was fractionated by silica gel liquid chromatography [column length used was 20 cm (silica) × 0.9 cm (i.d.)]. Silica for liquid chromatography was activated (overnight at 120 °C) and washed with *n*-pentane prior to use. The saturated hydrocarbons were eluted with *n*-pentane (35 ml) and were analysed using gas chromatography–mass spectroscopy (GC–MS) and gas chromatography isotope-ratio mass spectroscopy (GC–irMS). AH fractions were

eluted with a mixture of *n*-pentane:dichloromethane (7:3 v:v, 40 ml) and were analysed by GC–MS. GC–irMS analyses of AHs were performed after some additional separation steps (see below) because the GC baseline separation for the whole aromatic fractions was too poor to provide accurate $\delta^{13}C$ measurements for some of the target compounds.

A further fractionation step was required for the AH fractions using activated silica and the same column dimensions described above. The first aromatic sub-fraction was eluted with a solvent mixture of *n*-pentane:dichloromethane (19:1 v:v, 15 ml, corresponding to the solvent front). A second sub-fraction was eluted with a further 40 ml of the same solvent mixture, *n*-pentane:dichloromethane (19:1 v:v). A third sub-fraction was eluted with a mixture of *n*-pentane:dichloromethane (7:3 v:v, 40 ml). These three aromatic sub-fractions were analysed by GC–MS and GC–irMS and were found to correspond to mono-, di- and tri-aromatic hydrocarbon classes. The latter procedure was selected because it ensured GC baseline separation of the individual AHs and, thus, more reliable isotopic data (c.f. Section 2.4). The target components were well separated with naphthalene the only exception, which was present in both the first and the second aromatic sub-fractions for several samples. The two $\delta^{13}C$ values measured for naphthalene in both fractions were identical (within instrument precision) suggesting that isotopic fractionation did not occur during this separation procedure. However, $\delta^{13}C$ values of coeluting compounds were systematically excluded and, for these few specific cases, we attempted to obtain $\delta^{13}C$ values from the whole aromatic fractions.

2.3. GC–MS

GC–MS analyses were carried out with a HP 6890 GC coupled to a HP 5973 mass selective detector (MSD) operating in electron ionisation mode (70 eV). Chromatographic separation was achieved using an WCOT fused silica capillary column (60 m × 0.25 mm i.d.) with a 0.25 µm 5% phenyl–methyl–silicon stationary phase (DB-5), using helium as the carrier gas at a linear velocity of 1 ml/min. Samples were dissolved in *n*-hexane and 1 µl of solution was injected using a HP 6890 auto-sampler. The GC oven temperature programme was 40–325 °C (3 °C/min), followed by an isothermal period at 325 °C for 45 min.

The MS identification of target aromatic compounds was made by comparison of relative retention times and mass spectra with those reported in the literature (Laflamme and Hites, 1978; Forster et al., 1989; Radke et al., 1990b; Hartgers et al., 1992; Ellis et al., 1996; van Aarssen et al., 1999; Kruge, 2000; Grice et al., 2001, 2005; Nabbefeld et al., 2010a, 2010b; Maslen et al., 2011).

2.4. GC–irMS

GC–irMS was carried out on a Micromass IsoPrime isotope ratio mass spectrometer coupled to a HP 6890 GC. Chromatographic separation was achieved using the same conditions described above for GC–MS analyses. The only difference was the initial temperature of the GC oven, adjusted to 50 °C instead of 40 °C for GC–MS analyses (above).

The $^{13}C/^{12}C$ ratios were calculated from the abundances of the masses 44, 45 and 46 ion currents of the CO_2 peaks produced by combustion (copper oxide reaction furnace at 850 °C) of the hydrocarbons separated by GC. $^{13}C/^{12}C$ of each component are reported in the δ notation (in per mil) relative to a CO_2 reference gas calibrated to Vienna Peedee Belemnite (VPDB). A mixture of standard components with known $\delta^{13}C$ values was analysed prior to sample analyses in order to ensure the instrument accuracy. Each sample was injected at least two times consecutively and the *m/z* 45/44