1   # δ^{13}C of aromatic compounds in sediments, oils and

2   # atmospheric emissions: a review

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19   **Abstract**

20   This review discusses major applications of stable carbon isotopic

21   measurements of aromatic compounds, along with some specific technical aspects

22   including purification of aromatic fractions for baseline separation. $\delta^{13}C$

23   measurements of organic matter (OM) in sediments and oils are routine in all

24   fields of organic geochemistry, but they are predominantly done on saturated

25   compounds. Aromatic compounds are important contributors to sedimentary

26   organic matter, and provide indication of diagenetic processes, OM source, and

27   thermal maturity. Studies have found evidence for a small ^{13}C-enrichment during

28   diagenetic aromatisation of approximately 1 to 2 ‰, but the formation of polycyclic

29   aromatic hydrocarbons (PAHs) from combustion and hydrothermal processes

30   seems to produce no effect. Likewise, maturation and biodegradation also produce

31   only small isotopic effects. An early application of $\delta^{13}C$ of aromatic compounds was

32   in the classification of oil families by source. Bulk measurements have had some

33   success in differentiating marine and terrigenous oils, but were not accurate in all

34   settings.

35   Compound-specific analyses measure certain aromatics with strong links to

36   source, therefore allowing more accurate source identification. $\delta^{13}C$ measurements

37   of individual aromatic compounds also allow identification of higher plant input

38   in ancient sediments, even after severe diagenetic alteration or combustion to

39   PAHs. Perylene, a PAH with a historically contentious origin, was assigned a

40   source from wood-degrading fungi on the basis of its isotopic composition. Stable

41   carbon isotopic measurements are also important in the analysis of organic matter

42 from Chlorobiaceae, which is an important indicator of photic zone euxinic

43 conditions in ancient sediments. A large range of aromatic products are formed

44 from the carotenoid pigments of Chlorobiaceae, with an enriched carbon isotopic

45 composition characteristic of the reverse tricarboxylic acid photosynthetic

46 pathway employed by this family of organisms. In future, site-specific isotope

47 analysis using techniques such as nuclear magnetic resonance spectrometry and

48 high-resolution isotope ratio mass spectrometry may reveal more information

49 about isotopic effects associated with aromatisation processes and maturation.

50

51 **Highlights**

52 Review of $\delta^{13}C$ of bulk aromatic fractions and individual aromatic hydrocarbons

53 Applications of stable carbon isotopic measurements of aromatic compounds

54 Technical aspects including purification of aromatic fractions

55

56 **Keywords:** compound specific isotope analyses; aromatics; oils; sediments;

57 palaeoenvironment; diagenesis; source; aromatisation

58

59 **1. Introduction and technical aspects**

60   Stable carbon isotopic measurements have historically been of great

61 importance in the analysis of organic matter (OM) in oils and sediments. Early

62 measurements of bulk isotopic composition were applied to petroleum exploration

63 (Sofer, 1984) and palaeoenvironmental studies (Schidlowski, 1988). The

64 development of compound-specific isotope analysis (CSIA) revealed that

65 sedimentary OM contains a wide range of source inputs and isotopic compositions

66 (Freeman et al., 1990; Grice and Brocks, 2011). Compound-specific δ^{13}C

67 measurements are now routinely employed in all aspects of organic geochemistry

68 such as paleo- and modern environmental studies (e.g. Grice et al., 1996b;

69 Diefendorf and Freimuth, 2017), and petroleum exploration (Edwards and

70 Zumberge, 2005; Pedentchouk and Turich, 2018). The majority of studies focus

71 only on saturated compounds, likely due to their generally greater abundance in

72 sediments and oils and their relative ease of sample preparation. Aromatic

73 compounds however are also important constituents of sedimentary OM. They are

74 not biosynthesised in significant quantities by organisms, but are formed from

75 natural precursors by processes including diagenetic alteration, natural

76 combustion processes and anthropogenic emissions (e.g. Wakeham et al., 1980a,

77 b; Venkatesan and Dahl, 1989; Grice et al., 2007). Therefore, the carbon isotopic

78 composition of aromatic compounds has the potential to reveal valuable

79 information about these processes. Despite some analytical challenges, such as

80 generally low abundance in sediments and difficulties achieving baseline

81 separation of peaks, δ^{13}C measurements of aromatic compounds have been

82 employed in oil family classifications and oil-source correlations, source

83 assignment of modern and ancient OM, and palaeoenvironmental studies.

84   In this review, we summarise the range of applications for compound-specific

85 carbon isotope measurements of aromatic compounds in sediments and oils. A

86 review of the carbon isotope geochemistry of polycyclic aromatic hydrocarbons

87   (PAHs) in aquatic environments is included in Abrajano et al. (2014). For detailed

88   discussion of the technical elements of $\delta^{13}C$ measurement, readers are directed to

89   a number of comprehensive reviews, e.g. Sessions (2006), De Groot (2009) and

90   Hoefs (2015), and references therein. Buczyńska et al. (2013) presents a review of

91   analytical methodologies for CSIA of PAHs. Certain aspects related to aromatic

92   compounds in general are discussed below.

93

94   1.1 Separation of aromatic compounds

95   Baseline separation of analyte peaks is a strict requirement of CSIA in order

96   to achieve reliable isotope measurements (Ricci et al., 1994; Sessions, 2006).

97   Separation of oils and source rock extracts into saturated and aromatic fractions

98   by silica gel column chromatography (e.g. Bastow et al., 2007) is standard

99   procedure before gas chromatography – mass spectrometry (GC-MS) and gas

100   chromatography – isotope ratio mass spectrometry (GC-irMS) analysis, but

101   significant co-elution often remains in aromatic fractions (e.g. Budzinski et al.,

102   1995; van Aarssen et al., 1999; Cesar and Grice, 2017). In such cases additional

103   separation steps are required to achieve baseline separation. Techniques to isolate

104   specific sections of the chromatogram include thin-layer chromatography (van

105   Kaam-Peters et al., 1995; Grice et al., 1998a; Grice et al., 2005a), preparative high-

106   performance liquid chromatography (Killops and Readman, 1985) and preparative

107   GC (Summons and Powell, 1987). In addition, alumina column chromatography

108   has been employed to separate aromatic fractions by number of aromatic rings

109   (Summons and Powell, 1987; Jiang et al., 2013).

110

111   1.2 Aromatic VOCs

112   Volatile organic compounds (VOCs) are ubiquitous in the atmosphere, and

113   are produced by both natural and anthropogenic processes (Kansal, 2009). Due to

114   the structural simplicity of these compounds, source attribution requires the use

115   of stable isotope measurements. Vitzthum von Eckstaedt developed a method for

116    $\delta^{13}C$ and $\delta^{2}H$ analysis of atmospheric VOCs based on adsorption on TenaxTA resin

117   in sampling tubes, followed by thermal desorption of analyte gasses into the inlet

118   of a GC-irMS system via a cold trap (Vitzthum von Eckstaedt et al., 2011a).

119   Aromatic compounds that were analysed include benzene, toluene, xylenes,

120   ethylbenzene, styrene and naphthalene. Cross plots of $\delta^{13}C$ and $\delta^{2}H$ (Fig. 1) were

121   able to differentiate VOC emissions from a range of sources, including alumina

122   refinery emissions, vehicle exhausts and combustion of C_3 and C_4 plants (Vitzthum

123   von Eckstaedt et al., 2011b; Vitzthum von Eckstaedt et al., 2012).

124

125   1.3 Standard reference materials

126   The analysis of standards with known isotopic composition is vital in any

127   stable isotopic measurement in order to anchor the measured values to the

128   international reference scale (Paul et al., 2007; Brand et al., 2014). Standard

129   reference materials are provided by organisations including the International

130   Atomic Energy Agency (IAEA), National Institute of Standards & Technology

131   (NIST) and United States Geological Survey (USGS), but while these include a

132   number of organic compounds, none are aromatic (Brand et al., 2014;

133   Schimmelmann et al., 2016). A range of organic compounds including aromatics

134   are available from Indiana University (http://pages.iu.edu/~aschimme/hc.html)

135   with accurate $\delta^{13}C$ values measured by offline combustion to CO_2 and calibrated

136   to the VPDB (Vienna Peedee Belemnite) scale using the international standards

137   NBS 19 and LSVEC.

138

2 Effect of aromatisation on $\delta^{13}C$

140   2.1 Diagenetic aromatisation processes

141   The aromatisation of biogenic compounds during diagenesis is an important

142   contributor to the total aromatic compounds in sediments (e.g. Wakeham et al.,

143   1980b; Grice et al., 2007; Grice et al., 2009). Several studies have attempted to

144   determine whether the aromatisation process is accompanied by an isotopic

145   fractionation. In a study of the Eocene Messel Shale, Freeman et al. (1994)

146   measured the $\delta^{13}C$ of diagenetic PAHs as well as their presumed saturated

147   triterpenoid precursors. It was found that aromatic compounds were depleted in

148   ^{13}C by an average of 1.2 ‰ compared to saturated precursors, but the correlation

149   between ^{13}C depletion and number of double bonds was not statistically significant

150   (Fig. 2). Isotopic differences between compound classes were much larger,

151   indicating that $\delta^{13}C$ is controlled primarily by source rather than diagenetic

152   aromatisation processes (Freeman et al., 1994). Small or no differences in $\delta^{13}C$

153   between aromatic and saturated precursors were also observed in diterpenoids,

154   sequiterpenoids and higher plant markers from Tertiary brown coal from south

155   China (Schoell et al., 1994), isorenieratane and triaromatic isorenieratane

156   derivatives in the Lower Jurassic Allgäu Formation (Sinninghe Damsté et al.,

157   1995a), and C_{32}-C_{34} hopanes and benzohopanes from Permian Kupferschiefer

158   sediments (Grice et al., 1996b).

159   In the Ordovician Kukersite shale in Estonia, Liao et al. (2015) found that

160   the δ^{13}C of monoaromatic steranes was within 1 ‰ of diacholestenes, but aromatic

161   hopanes were 2-4 ‰ enriched in ^{13}C compared to saturated hopanes. Early

162   diagenesis of steranes appeared to have produced a varied distribution of

163   rearranged steranes but relatively little aromatisation, with no accompanying

164   change in δ^{13}C. Hopanes however were aromatised more rapidly, likely a result of

165   microbially-mediated processes rather than thermal processes due to the low

166   thermal maturity of the sediment. The enrichment in ^{13}C of benzohopanes was

167   attributed to the contribution of multiple hopanoid precursors and loss of C atoms

168   during aromatisation (Liao et al., 2015).

169

170   2.2 Combustion and hydrothermal PAHs

171   In contrast to diagenetic aromatic compounds, PAHs formed from combustion

172   or hydrothermal processes cannot be linked to direct biological precursors, but

173   their isotopic composition can be compared to that of bulk OM or co-occurring

174   saturated compounds to determine any isotope effects.

175   A study of combustion products from biomass burning found that

176   combustion-derived PAHs (two to four rings) were ^{13}C-enriched by approximately

177   2 to 4 ‰ compared to combustion-derived *n*-alkanes and *n*-alkenes from the same

178   plants, as well as *n*-alkanes extracted from non-combusted plants (O'Malley et al.,

179   1997). PAHs from C_4 plants were enriched in ^{13}C compared to those from C_3 plants

180   by approximately 12 ‰, a similar magnitude to that observed for plant waxes and

181   *n*-alkanes (Collister et al., 1994). This suggests that $\delta^{13}C$ differences in plant

182   biomass are preserved during combustion processes.

183   In a study of hydrothermal petroleum from the Guaymas Basin, the average

184    $\delta^{13}C$ of PAHs was within analytical error of the bulk kerogen, with no observed

185   trend in $\delta^{13}C$ with increasing number of aromatic rings (Schoell et al., 1990;

186   Simoneit and Schoell, 1995). A similar relationship was found in the Escanaba

187   Trough, with hydrothermal PAHs ^{13}C-enriched compared to *n*-alkanes but

188   equivalent in $\delta^{13}C$ to the bulk oil (Simoneit et al., 1997). In contrast, Williford et

189   al. (2011) observed a negative trend in $\delta^{13}C$ with the number of aromatic rings and

190   number of double bonds in hydrothermal PAHs from the Palaeoproterozoic Here's

191   Your Chance (HYC) Pb-Zn-Ag deposit in the Northern Territory of Australia (Fig.

192   3). PAHs in the HYC sediments were found to be 3 ‰ enriched in ^{13}C compared to

193   kerogen, in contrast to the above studies that showed no isotopic difference

194   between hydrothermal PAHs and kerogen. It was hypothesised that HYC PAHs

195   were generated by hydrothermal activity in an underlying formation and

196   transported to HYC by fluid flow, possibly the same fluid which formed the

197   mineral deposit (Williford et al., 2011).

198

199   **3. Isotopic effects of maturation and degradation**

200   Aromatic compounds, especially PAHs, are commonly used as indicators of

201 maturity as the distribution of methylated isomers changes during thermal

202 maturation (e.g. Radke et al., 1982; George and Ahmed, 2002). There is limited

203 information on whether maturation is accompanied by a change in $\delta^{13}C$ of

204 aromatic compounds. Clayton (1991) observed a 2-3 ‰ enrichment in bulk

205 saturate and aromatic ^{13}C with maturation, attributed to the release of ^{13}C-

206 depleted carbon during oil cracking. Individual aromatic compounds similarly

207 tend to a carbon isotopic enrichment during maturation, while source-related

208 isotopic differences between isomers are obscured with increasing maturity

209 (Clayton and Bjorøy, 1994; Fig. 4). Later studies found little or no change in

210 isotopic composition with maturity: phenanthrene and methylphenanthrenes

211 were found not to vary systematically with maturity in coals and coaly shales

212 (Radke et al., 1998), while a study of PAHs along a prograde metamorphic

213 sequence in the Liassic black shale formation in the Swiss Alps (100 to 550 °C)

214 showed no trend in $\delta^{13}C$ with temperature (Schwab et al., 2005).

215   Le Métayer et al. (2014) investigated the carbon isotopic composition of

216 alkylbenzenes, alkylnaphthalenes and alkylphenanthrenes in oils from the North-

217 West Shelf of Australia. The majority of oils exhibited a depletion in ^{13}C with

218 increased degree of methylation, suggesting that methyl groups are ^{13}C-depleted

219 compared to the aromatic ring. This ^{13}C-depletion was found to become

220 incrementally smaller at higher maturity levels. It was proposed that ^{13}C-depleted

221 methyl groups are removed from the 'methyl pool' at higher maturities.

222　　　Biodegradation may affect the isotopic composition of aromatic compounds in

223　sediments and oils, and this has been investigated in a number of studies.

224　O'Malley et al. (1994) found almost no effect of biodegradation on the $\delta^{13}C$

225　environmental PAHs. Subsequent studies measured significant isotopic

226　fractionation during biodegradation of lower molecular weight aromatics such as

227　alkylbenzenes (Meckenstock et al., 1999; Wilkes et al., 2000; Morasch et al., 2002;

228　Steinbach et al., 2004), but no fractionation for PAHs (Mazeas et al., 2002).

229

230　**4. Classification of oils**

231　　　4.1 Bulk isotope measurements

232　　　The first major application for $\delta^{13}C$ measurements of aromatics was in the

233　classification of oil families and oil-source correlations for petroleum exploration.

234　Before the development of CSIA, $\delta^{13}C$ of bulk saturate and aromatic fractions were

235　analysed via offline combustion to CO_2 and directly introduced into the irMS (e.g.

236　Sofer, 1980). Early studies found little difference in the $\delta^{13}C$ of aromatics,

237　saturates and bulk oils (generally less than 1 ‰; Monster, 1972), however

238　numerous authors have used crossplots of saturate and aromatic $\delta^{13}C$ for oil

239　classification (e.g. Koons et al., 1974; Fuex, 1977) and oil-source correlation (Stahl,

240　1978). It was noted that the aromatic fraction tended to have a wide range of $\delta^{13}C$

241　within oil families, and that the saturate fraction may be more useful as a

242　classification tool. In a major study Sofer (1984) compared the $\delta^{13}C$ of bulk

243　saturates and aromatics of 339 oils from the United Kingdom, Africa, the Middle

244　East, Australasia and North and South America (Fig. 5). A grouping was observed

245   which enabled differentiation of 'waxy oils' (predominantly terrigenous origin) and

246   'nonwaxy oils' (predominantly marine origin). A Canonical Variable was proposed

247   and defined as follows: CV = -2.53 $\delta^{13}C_{sat}$ + 2.22 $\delta^{13}C_{aro}$ - 11.65. A CV value greater

248   than 0.47 was interpreted as indicating a terrigenous oil, and one less than 0.47

249   indicating a marine oil.

250   More recently, Andrusevich et al. (1998) measured $\delta^{13}C$ of saturate and

251   aromatic fractions from 514 oils with known source rocks deposited throughout

252   the Phanerozoic. Aromatic fractions were similar in isotopic composition to

253   saturates, with a ^{13}C-enrichment of 1-2 ‰ which was independent of source rock

254   type. This enrichment was also observed by Sun et al. (2005) in oils from the

255   Liaohe Basin, NE China along a natural biodegradation sequence, along with

256   evidence of an approximately 1 ‰ enrichment in ^{13}C in the aromatic fraction from

257   non-biodegraded to severely biodegraded oils. Collister and Wavrek (1996)

258   proposed that bulk saturates were ^{13}C-depleted compared to bulk aromatics,

259   especially in lacustrine oils and bitumens, due to the contribution of ^{13}C-depleted

260   biomass of methanotrophic bacteria.

261   Asif et al. (2011) measured bulk $\delta^{13}C$ of saturates and aromatics of oils from

262   the Potwar Basin, Pakistan, and were able to distinguish three separate oil

263   families. Group A oils, from terrigenous OM deposited under highly oxic/fluvio-

264   deltaic conditions, showed the most negative $\delta^{13}C$ values for both saturate and

265   aromatic fractions. Oils from Group B (clastic-rich source rocks deposited in

266   suboxic environments) and Group C (higher input of algae mixed with terrigenous

267   OM) were equivalent in $\delta^{13}C$ of aromatics, but were differentiated by their saturate

268 δ^{13}C. Bulk OM, extractable OM and pyrolysates of the Duaringa oil shale deposit

269 (Queensland) were found to differentiate between terrigenous and lacustrine

270 facies (Boreham et al., 1994).

271

272 4.2 Compound-specific isotope measurements

273 δ^{13}C measurements of bulk aromatic (and saturate) fractions have

274 contributed to numerous oil-source correlations, but this approach is not

275 applicable to all cases. While bulk δ^{13}C gives an overall picture of an oil, CSIA is

276 required to measure the multiple sources of OM that can contribute to an oil (e.g.

277 Grice and Brocks, 2011). In a large study of West Australian oils, Edwards and

278 Zumberge (2005) found that although the Sofer (1984) plot is effective in

279 distinguishing oil families from WA basins, it is often incorrect in assigning a

280 terrigenous or marine origin for these oils. For example Papuan oils from the Juha,

281 Piri and Mananda wells are marine with minor land-plant input based on

282 biomarker data but plot in the terrigenous region of the Sofer plot, while oils from

283 the Laminaria High region of the Bonaparte Basin have a mixed terrigenous and

284 marine source but plot well within the marine region. Maslen et al. (2011)

285 attempted to find reasons for these inaccuracies using CSIA of alkylated

286 naphthalenes and phenanthrenes. Individual aromatic compounds were found to

287 exhibit a much greater range of δ^{13}C values than the bulk aromatics. The δ^{13}C of

288 1,6-dimethylnaphthalene (1,6-DMN), 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1-

289 methylphenanthrene (1-MP) and 1,9-dimethylphenanthrene (1,9-DMP) correlate

290 well with source, becoming more negative with greater marine input. When

291 plotted against phenanthrene / dibenzothiophene (P/DBT) or pristane / phytane

292 (Pr/Ph), these compounds were able to distinguish marine, terrigenous and mixed

293 oils (Fig. 6). These isomers were chosen as they are thought to be strongly

294 influenced by source and depositional environment, e.g. 1,2,5-TMN derived from

295 D-ring monoaromatic 8,14-secohopanoids (Grice et al., 2001). In a further study of

296 oils focussed mainly on the North-West Shelf of Australia, 1,6-DMN, 1,2,5-TMN

297 and 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN) showed large variations in

298 $\delta^{13}C$ independent of maturity, which were attributed to source variations (Le

299 Métayer et al., 2014).

300   Cesar and Grice (2017) investigated source rocks from the Northern

301 Carnarvon Basin of Western Australia. The $\delta^{13}C$ of 1,2,5-TMN and 1,3,6,7-TeMN

302 were found to be more sensitive to facies changes than other, combustion-derived

303 isomers of TMN and TeMN. The plot of $\delta^{13}C_{1,3,6,7\text{-TeMN}}$ against the abundance of

304 combustion PAHs benzo[e]pyrene and coronene was found to differentiate marine-

305 influenced and terrigenous OM. The value of $\delta^{13}C_{\text{combustion PAH}}$ - $\delta^{13}C_{1,3,6,7\text{-TeMN}}$ was

306 proposed as a source indicator, with negative values from delta-plain / front-deltaic

307 or coaly fluvial deltaic facies, and positive values from transitional estuarine /

308 lagoonal environments. The same also applies to $\delta^{13}C_{\text{combustion PAH}}$ - $\delta^{13}C_{\text{phenanthrene}}$

309 (Fig. 7). Phenanthrene is formed both from combustion processes (Laflamme and

310 Hites, 1978) and diagenesis of natural products (Wakeham et al., 1980b), hence

311 $\delta^{13}C$ of phenanthrene can help to distinguish between terrigenous and marine

312 source inputs.

313

5. Source differentiation

5.1 Plant markers

Aromatic compounds may be generated from higher plant OM through diagenetic aromatisation of natural products (Wakeham et al., 1980b) or by combustion of plant biomass (O'Malley et al., 1997). Carbon isotope measurements can provide valuable information on the source of these aromatics, contributing to palaeoenvironmental and palaeoecological investigations. In a study of organic-rich torbanites from the Late Carboniferous to the Late Permian, Grice et al. (2001) found aromatics including alkylnaphthalenes, alkylphenanthrenes, higher-MW PAHs and C_{31-34} benzohopanes (Fig. 8). Benzohopanes had similar $\delta^{13}C$ values to that of saturated hopanes from the same sample, indicating a common cyanobacterial source. The $\delta^{13}C$ of retene and methylphenanthrenes (-23 to -24 ‰) were consistent with a land plant origin from a phyllocladane precursor, while the slight ^{13}C-depletion of 1,7-DMP (-24 to -25.5 ‰) may indicate its formation from a pimarane-type precursor. Alkylnaphthalenes had similar to $\delta^{13}C$ values to drimanes and hopanes, suggesting a common source from cyanobacterial hopanoids (Grice et al., 2001). In fluvial / deltaic Triassic-Jurassic sediments from Western Australia, the $\delta^{13}Cs$ of retene (-26.9 to -24.9 ‰) is consistent with a source from class I conifer resins, indicating an increase in the abundance of conifers during the Early-Middle Jurassic (Grice et al., 2005a).

Abundant aromatic biomarkers were detected in a Palaeocene–Eocene sediment core from the central Arctic Ocean, including dehydroabietane and simonellite derived from gymnosperm and a tetra-aromatic ß-amyrin derivative

337   from angiosperms (Schouten et al., 2007). All compounds exhibited a negative

338   carbon isotope excursion during the Palaeocene–Eocene thermal maximum

339   (PETM), but the angiosperm marker showed a much greater depletion in ^{13}C (6

340   ‰) than the gymnosperm markers (3 ‰). It was suggested that this isotopic

341   variation in the different vegetation types was a result of varied physiological

342   responses to the extreme climate conditions of the PETM.

343   Although PAHs from biomass burning do not retain structural information

344   about their natural precursors, their carbon isotopic composition can allow source

345   differentiation. O'Malley et al. (1994) measured δ^{13}C of two- to five-ringed PAHs

346   from various primary emission sources, as well as environmental PAHs from

347   Canadian estuarine sediments. Carbon isotopic differences were observed between

348   different primary sources, such as vehicle emissions (overall range -25.4 to -22.6

349   ‰) and home fireplaces (-26.4 to -24.0 ‰). The δ^{13}C of the measured environmental

350   PAHs indicated a mixture of input sources, with a dominant wood burning source

351   and contributions from petroleum products (O'Malley et al., 1994). It has also been

352   shown that PAHs from biomass burning retain the characteristic difference in δ^{13}C

353   between C_3 and C_4 plants, potentially allowing vegetation type to be determined

354   from ancient fire events (O'Malley et al., 1997). Lichtfouse et al. (1997) analysed

355   PAHs in modern soils from two maize fields in northern France, and found

356   predominantly combustion-derived compounds from a combination of fossil fuel

357   and vegetation fires.

358   PAHs are abundant in sediment cores spanning the Permian-Triassic

359   extinction event, from Western Australia, South China, East Greenland and

360   Western Canada (Grice et al., 2007; Nabbefeld et al., 2010a). In the Perth Basin

361   core, an abrupt change in $\delta^{13}C$ between the Permian (-24.7 to -29.9 ‰) and the

362   Triassic (-30.0 to -33.3 ‰) was interpreted as a shift from a primarily terrigenous

363   combustion origin in the Permian to a mainly algal origin in the Triassic (Grice et

364   al., 2007).

365

366   5.2 Origin of perylene

367   Perylene is a five-ringed PAH found extensively in recent sediments

368   (Laflamme and Hites, 1978; Wakeham et al., 1980b), oils (Grice et al., 2009) and

369   organic-rich shales (Jiang et al., 2000), though its origin has historically been

370   contentious. Unlike other five-ringed PAHs such as benzo[e]pyrene, perylene is

371   not produced by combustion processes (Venkatesan, 1988), and a reported increase

372   in abundance with depth suggests an in situ source for this compound (Silliman

373   et al., 2000; Grice et al., 2009). In a recent sediment core from Saanich Inlet,

374   British Columbia, perylene was consistently ^{13}C-depleted compared to bulk TOC

375   (Silliman et al., 2000), indicating a source distinct from the marine algae and soil

376   humic material that make up the majority of OM in the sediment.

377   Perylene is structurally similar to perylenequinone pigments found in fungi

378   (Stierle et al., 1989; De Riccardis et al., 1991), hence a fungal source for perylene

379   in sediments has been investigated by a number of researchers. In Holocene

380   sediments from the Quinpu trench, China, perylene was found only in the deepest,

381   most oxic zone, along with abundant fungal spores (Grice et al., 2009). The $\delta^{13}C$

382   of perylene (-26.5 to -27.5 ‰) was more positive than that of n-alkanes (-29.8 to -

383   36.0 ‰), and consistent with an origin from lignin-degrading saprophytic fungi

384   (Hobbie et al., 1999). Together with a decrease in the guaiacol / phenol ratio used

385   as a proxy for lignin concentration, this was interpreted as evidence that perylene

386   is derived from pigments of wood-degrading fungi (Grice et al., 2009). Suzuki et al.

387   (2010) found that perylene in the Late Cretaceous to Palaeogene MITI Sanriku-

388   oki borehole, north-eastern Japan, was ^{13}C-enriched compared to gymnosperm

389   and angiosperm markers, again consistent with a fungal source (Fig. 9).

390

391   5.3 Other sources of OM

392   Carbon isotopic measurements have contributed to source assignments of

393   aromatics in varied depositional settings, including novel biomarkers. In the

394   Permian Kupferschiefer, ^{13}C-enriched benzhopanes from phytoplankton indicate

395   high algal productivity in an environment of limited $^{12}CO_2$ (Grice et al., 1996b).

396   Similarly, tricyclic aromatics with high δ^{13}C were found in a tasmanite oil shale

397   from Tasmania, likely sourced from ^{13}C-enriched algae (Revill et al., 1994;

398   Boreham and Wilkins, 1995). Isotopic measurements of free and sulfur-bound

399   hopanoid derivatives in the Upper Cretaceous Jurf ed Darawish Oil Shale (Jordan)

400   contributed to a proposed diagenetic scheme for their formation from

401   bacteriohopanepolyols (Sinninghe Damsté et al., 1995b), revealing complex

402   diagenetic pathways which likely proceed from a number of different

403   bacteriohopanepolyol precursors. Schaeffer et al. (1995) identified two novel

404   monoaromatic triterpenoids in Eocene Messel shale (Germany), and on the basis

405   of structure and $\delta^{13}C$ attributed them to a source from protozoa or purple

406   phototrophic bacteria, and from a bacterial hopanoid.

407

6. Aryl isoprenoids and carotenoids

409   Chlorobiaceae (green sulfur bacteria) are photolithotrophs which use

410   dissolved hydrogen sulfide as the electron donor during photosynthesis, hence

411   exist only in conditions of photic zone euxinia (PZE) in the water column

412   (Overmann, 2006). Biomarkers of these bacteria are important indicators of PZE

413   in ancient sediments (e.g. Summons and Powell, 1986; Grice et al., 2005b).

414   Chlorobiaceae fix CO_2 using the reverse tricarboxylic acid (TCA) cycle (Evans et

415   al., 1966), hence their biomass is enriched in ^{13}C compared to organisms using the

416   C_3, C_4 and CAM pathways (Quandt et al., 1977; Sirevåg et al., 1977).

417   In their work on Canadian oils from the Silurian (Michigan Basin) and

418   Devonian (Alberta Basin), Summons and Powell (1986, 1987) found high

419   abundances of 1-alkyl-2,3,6-trimethylbenzenes with 13 to 31 total carbon atoms

420   (C_{13} to C_{31} aryl isoprenoids). The structure of these compounds is consistent with

421   the diagenetic breakdown of the carotenoid pigments chlorobactene and

422   isorenieratene, produced by Chlorobiaceae (Overmann, 2006). These aryl

423   isoprenoids were enriched in ^{13}C by 7-8 ‰ compared to the bulk saturate fraction,

424   consistent with formation via the reverse TCA cycle. Oil-source correlations show

425   that these oils were sourced from restricted, hypersaline basins with strongly

426   reducing bottom waters, ideal conditions for the establishment of PZE (Powell et

427   al., 1984). Aryl isoprenoids were therefore proposed as biomarkers for

428 Chlorobiaceae and PZE conditions (Summons and Powell, 1986, 1987). [13]C-

429 enriched aryl isoprenoids and intact isorenieratane have subsequently been found

430 in a variety of ancient sediments, including the Upper Devonian Duvernay

431 Formation (Hartgers et al., 1994a, b), the Late Devonian Canning Basin (Tulipani

432 et al., 2015), the Permian Kupferschiefer (Grice et al., 1996b, 1997) and

433 Palaeocene-Eocene lacustrine source rocks from the Jianghan Basin, China (Grice

434 et al., 1998b) and used as evidence for PZE conditions. ^{13}C-enriched isorenieratane

435 has also been reported in more recent settings, such as Holocene Black Sea

436 sediments (Sinninghe Damsté et al., 1993).

437   In addition to aryl isoprenoids, a large variety of aromatic compounds in

438 sediments and oils have been interpreted as diagenetic products of Chlorobiaceae

439 lipids on the basis of their enrichment in [13]C. Hartgers et al. (1994a, b) found a

440 distribution of tetramethylbenzenes, aryl isoprenoids and intact isorenieratane in

441 source rocks and oils from the Upper Devonian Duvernay Formation (Western

442 Canada). These compounds were ^{13}C-enriched compared to isoprenoids, *n*-alkanes

443 and total oil, indicating a source from Chlorobiaceae. Pyrolysis of kerogens from

444 Duvernay Formation source rocks released tetramethylbenzenes that were

445 enriched in ^{13}C by an average of 12 ‰ compared to alkanes / alkenes and bulk

446 kerogen. This shows that diaromatic carotenoids from Chlorobiaceae become

447 macromolecularly bound in kerogen during diagenesis, but retain their structure

448 and isotopic composition (Hartgers et al., 1994b).

449   The characteristic ^{13}C-enrichment of Chlorobiaceae has been observed in a

450 wide range of isorenieratane derivatives from Ordovician to Miocene sediments

451 (Sinninghe Damsté et al., 1995a; Koopmans et al., 1996a; van Kaam-Peters et al.,

452 1997). Free and S-bound lipids from the Permian Kupferschiefer contained a wide

453 range of mono-, di- and triaromatic isoprenoid compounds that were enriched in

454 ^{13}C, as well as ^{13}C-enriched isorenieratane (Grice et al., 1996b, 1997). Maleimides,

455 breakdown products from the porphyrin rings of bacteriochlorophylls, were also

456 found in Kupferschiefer sediments. The methyl n-propyl and methyl isobutyl

457 maleimides, which are believed on the basis of structure to come from

458 bacteriochlorophylls c, d and e produced by Chlorobiaceae, were significantly ^{13}C-

459 enriched compared to other maleimides such as methyl ethyl maleimide with a

460 likely phytoplanktonic origin (Grice et al., 1996a). High abundances of C_{18} and C_{19}

461 alkyl biphenyls have been observed in sediments from the Permian Kupferschiefer

462 (Grice et al., 1996b) and in a Permian / Triassic section from Spitsbergen

463 (Nabbefeld et al., 2010b). These compounds vary similarly with depth to the aryl

464 isoprenoids, and are enriched in ^{13}C by 10 to 16 ‰ compared to phytoplankton-

465 derived compounds, hence are interpreted as diagenetic products of isorenieratene

466 and / or chlorobactene.

467　Koopmans et al. (1996b) demonstrated the necessity of δ^{13}C measurements

468 before using any aromatic compound as evidence for the presence of Chlorobiaceae.

469 In a North Sea oil, 2,3,6-substituted aryl isoprenoids were found along with

470 isorenieratane and ß-isorenieratane. Isorenieratane was strongly ^{13}C enriched

471 compared to saturate compounds as expected for Chlorobiaceae, but ß-

472 isorenieratane showed no carbon isotopic enrichment. Aryl isoprenoids had a

473 mixed δ^{13}C signal, in between that of isorenieratane and ß-isorenieratane.

474 Laboratory experiments confirmed that ß-isorenieratane can be produced by

475   aromatisation of ß-carotane, and can further degrade to produce aryl isoprenoids

476   with a non-enriched ^{13}C signal (Koopmans et al., 1996b). Therefore aryl

477   isoprenoids do not necessarily indicate the presence of Chlorobiaceae, and δ^{13}C

478   measurements are required to confirm. The same appears to be true of other

479   potential carotenoid breakdown products. Pyrolysis-δ^{13}C of lacustrine Lower

480   Cretaceous source rocks from West African rift basins was used to distinguish

481   alkylbenzenes generated from ß-carotene (produced by lacustrine algae) and those

482   from isorenieratene and chlorobactene (Pedentchouk et al., 2004; Fig. 10).

483

484   **7. Future work – site-specific isotope analysis**

485   In the above discussion we have demonstrated the contribution of δ^{13}C

486   measurements of aromatics to diverse subjects in the fields of petroleum and

487   palaeoenvironment. CSIA has revealed the complex mixture of sources that

488   contribute to OM in sediments and oils, but further questions remain as to the

489   mechanisms by which aromatic compounds are formed, as well as the behaviour

490   of aromatics during maturation. A developing field that may help to answer these

491   questions is site-specific isotope analysis, which allows the δ^{13}C measurement of

492   specific atoms within the molecule. Such measurements could reveal more on the

493   processes of aromatisation during diagenesis, and provide explanations for

494   isotopic effects such as the ^{13}C-depletion with methylation observed by Le Métayer

495   et al. (2014).

496   The site-specific isotopic composition of light hydrocarbons such as ethane

497   and propane has been successfully measured using high-resolution gas source

498   mass spectrometry (Eiler et al., 2013; Piasecki et al., 2016). This technique is

499   suitable only for pure gasses, but may potentially be applied to volatile aromatic

500   compounds. Likewise site-specific isotope measurement by tunable infrared laser

501   direct absorption spectroscopy (TILDAS), as demonstrated by Ono et al. (2014), is

502   currently applicable only to simple gasses such as methane (e.g. Wang et al., 2018).

503   ^{13}C nuclear magnetic resonance (NMR) spectrometry has the potential to provide

504   site-specific isotopic information of more complex molecules. This technique has

505   been applied to compounds such as *n*-alkanes (Gilbert et al., 2013) and isolated

506   plant metabolites (Gilbert et al., 2012), as well as aromatic pharmaceuticals

507   (Silvestre et al., 2009) and flavour compounds (Remaud & Akoka, 2017). The above

508   techniques have been demonstrated for pure compounds, but their application to

509   the complex mixtures of aromatic compounds in sediment extracts and petroleum

510   is likely to be challenging. Offline separation may be employed to simplify

511   aromatic fractions before analysis, but aromatic fractions often contain many

512   structurally-similar compounds (such as methylated naphthalenes) which are

513   very difficult to separate by offline methods. Site-specific isotope techniques that

514   can be coupled to on-line GC are therefore desirable. NMR also suffers from low

515   sensitivity compared to irMS (Gilbert et al., 2013), limiting its applicability to

516   geochemical samples.

517   Early attempts at position-specific isotope analysis involved offline

518   fragmentation of analyte molecules for irMS analysis, from which the distribution

519   of isotopes within the original molecule was reconstructed (e.g. Monson & Hayes,

520   1982). Hattori et al. (2011) employed a GC-pyrolysis-GC-irMS system, in which

521   compounds are separated by the first GC column before passing through an online

522 pyrolysis reactor. Pyrolysis products are then separated by the second GC column

523 and analysed by the irMS. This system has been used for analysis of light

524 hydrocarbons, including those produced by serpentinite-hosted hot springs

525 (Gilbert et al., 2016; Suda et al., 2017). Difficulties may still be encountered,

526 however, in the analysis of more complex mixtures which will not be so cleanly

527 separated by the first GC column. Perhaps the most promising development for

528 site-specific isotope analysis of aromatic fractions is the recent demonstration by

529 Eiler et al. (2017) of site-specific Orbitrap mass spectrometry. The Orbitrap mass

530 analyser allows for the isolation and high-resolution analysis of fragment ions

531 produced by the ion source, from which the isotopic distribution of the analyte

532 molecule can be determined. The coupling of Orbitrap mass spectrometry with GC

533 separation has great potential for the site-specific analysis of complex aromatic

534 fractions from geochemical samples. This technique is still in the early stages of

535 development, but one of the initial applications was isomers of ethyl toluene from

536 a West Australian condensate (Eiler et al., 2017). Site-specific isotope analysis

537 represents the frontier of isotopic measurements, and with further development

538 will provide a wealth of new information for researchers with an interest in

539 aromatic compounds.

540

546

547 **Figure captions**

548 *Figure 1:* $\delta^{13}C$ and δ^2H of benzene, toluene and naphthalene from atmospheric

549 emissions sources, showing groupings of car exhaust emissions, industrial

550 alumina refinery emissions, and combustion of C_3 and C_4 plants. Data from

551 Vizthum von Eckstaedt et al. (2011b; 2012).

552 *Figure 2*: Carbon isotopic composition of PAHs formed by diagenesis of plant and

553 bacterial biomarkers. No clear trend in $\delta^{13}C$ with number of double bonds is

554 observed, and isotopic differences appear to be primarily source-controlled.

555 Redrawn from Freeman et al. (1994).

556 *Figure 3*: Carbon isotopic composition of hydrothermal PAHs from the Here's

557 Your Chance Pb-Zn-Ag deposit, showing a trend of depletion in ^{13}C with

558 increased number of aromatic rings and double bonds. TMN:

559 trimethylnaphthalene, TeMN: tetramethylnaphthalene, P: phenanthrene, MP:

560 methylphenanthrene, DMP: dimethylphenanthrene, Py: pyrene, TriPh:

561 triphenylene, BePy: benzo[e]pyrene. Redrawn from Williford et al. (2011).

562 *Figure 4*: Carbon isotopic composition of aromatic compounds from a series of

563 North Sea oils of differing maturities. There is a general trend of ^{13}C-enrichment

564 from Buchan (least mature) to Bruce (most mature). MN: methylnaphthalene,

565 DMN: dimethylnaphthalene, MP: methylphenanthrene. Redrawn from Clayton

566 and Bjorøy (1994).

567

568   *Figure 5*: Bulk carbon isotopic composition of C_{15+} saturate and aromatic

569   fractions of waxy (terrigenous) and non-waxy (marine) oils. Red line indicates the

570   optimal separation between the two groups. Redrawn from Sofer (1984).

571   *Figure 6*: $\delta^{13}C$ of 1,6-dimethylnaphthalene (DMN) of oils from West Australian

572   basins, plotted against the ratios of phenanthrene / dibenzothiophene (P/DBT)

573   and pristane / phytane (Pr/Ph). Marine, terrigenous and mixed source oils, as

574   assigned by Edwards and Zumberge (2005) based on biomarker data, are

575   separated on these plots. Redrawn from Maslen et al. (2011).

576   *Figure 7*: Difference in $\delta^{13}C$ of benzo[e]pyrene (BePy) and phenanthrene (P) in

577   Northern Carnarvon Basin source rocks, plotted against the ratio of BePy/P.

578   BePy is a combustion-sourced PAH, while P may be formed by combustion or by

579   diagenesis of natural products (Laflamme and Hites, 1978; Wakeham et al.,

580   1980b). The difference in $\delta^{13}C$ of these two PAHs indicates a facies change from

581   deltaic or fluvial-deltaic facies in the Triassic to transitional estuarine or

582   lagoonal facies in the Jurassic. Redrawn from Cesar and Grice (2017).

583   *Figure 8*: $\delta^{13}C$ of aromatic compounds from Late Carboniferous to Late Permian

584   torbanites. The isotopic composition of retene and alkylphenanthrenes is

585   consistent with a land plant origin, while ^{13}C-depleted alkylnaphthalenes and

586   benzohopanes indicate a bacterial source. DMN: dimethylnaphthalenes, TMN:

587   trimethylnaphthalenes, TeMN: tetramethylnaphthalenes, Alk-N: long-chain *n*-

588   alkylnaphthalenes, MP: methylphenanthrenes, DMP: dimethylphenanthrenes,

589   TMP: trimethylphenanthrenes, Ret: retene, BH: benzohopanes. Data from Grice

590   et al. (2001).

591   *Figure 9*: δ^{13}C of perylene, retene (gymnosperm marker) and several angiosperm

592   markers from the Late Cretaceous to Palaeogene MITI Sanriku-oki borehole,

593   north-eastern Japan. The carbon isotopic enrichment of perylene compared to

594   plant markers supports a proposed origin from wood-degrading fungi. Data from

595   Suzuki et al. (2010).

596   *Figure 10*: Carbon isotopic composition of 1,2,4-trimethylbenzene and 1,2,3,4-

597   tetramethylbenzene from pyrolysis of Lower Cretaceous source rocks from West

598   African basins. Chlorobiaceae-sourced and mixed-source aromatics from Well A,

599   Kwanza Basin, are distinguished from algal-sourced aromatics from the ONEZ-1

600   well, Gabon. Redrawn from Pedentchouk et al. (2004).

601

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Table 1

Compounds	Setting	$\delta^{13}C$ (‰ VPDB)	Reference
Petroleum			
Bulk aromatics	Waxy oils	-31.2 to -21.8	Sofer, 1984
Bulk aromatics	Non-waxy oils	-31.0 to -16.8	Sofer, 1984
Bulk aromatics	Phanerozoic oils	-28.59 to -26.30	Andrusevich et al., 1998
Alkylated PAHs	West Australian crude oils	-30.3 to -23.5	Maslen et al., 2011
Alkylated PAHs	West Australian crude oils	-33.3 to -21.3	Le Métayer et al., 2014
PAHs	Carnarvon Basin source rocks	-31.2 to -23.1	Cesar and Grice, 2017
Higher plant sources			
Aromatised gymnosperm and angiosperm markers	Torbanites	-25.5 to -23.0	Grice et al., 2001
Aromatised gymnosperm and angiosperm markers	Central Arctic Ocean PETM sediments	-33 to -25	Schouten et al., 2007
Aromatised gymnosperm and angiosperm markers	Eocene Messel Shale	-33.2 to -23.3	Freeman et al., 1994
Aromatised gymnosperm and angiosperm markers	Tertiary brown coal	-29	Schoell et al., 1994
Combustion PAHs	C3 plants	-28.8 to -28.0	O'Malley et al., 1997
Combustion PAHs	C4 plants	-17.1 to -15.8	O'Malley et al., 1997
Combustion PAHs	Perth Basin Permian sediments	-24.7 to -29.9	Grice et al., 2007
Retene	Fluvial / deltaic Triassic-Jurassic sediments	-26.9 to -24.9	Grice et al., 2005a
Cyanobacterial / algal sources			
Benzohopanes	Torbanites	-30.6 to -27.9	Grice et al., 2001
Diagenetic PAHs	Perth Basin Jurassic sediments	-30.0 to -33.3	Grice et al., 2007

Benzohopanes	Permian Kupferschiefer	-30 to -29.6	Grice et al., 1996b
Tricyclic aromatics	Tasmanite oil shale, Tasmania	-9 to -6	Revill et al., 1994
Fungal sources			
Perylene	Saanich Inlet, British Columbia	-27.7 to -23.6	Silliman et al., 2000
Perylene	Quinpu trench, China	-26.5 to -27.5	Grice et al., 2009
Perylene	Late Cretaceous to Paleogene terrestrial sediments	-24.5 to -21.1	Suzuki et al., 2010
Chlorobiaceae			
Isorenieratane	Upper Devonian Duvernay Formation	-13.2 to -5.7	Hartgers et al., 1994b
Isorenieratane	Permian Kupferschiefer	-16.4 to -13.4	Grice et al., 1996b, 1997
Isorenieratane	Jianghan Basin, China	-17.3 to -16.1	Grice et al., 1998b
Isorenieratane	Holocene Black Sea	-17.4 to -14.8	Sinninghe Damsté et al., 1993
Isorenieratane	West African Lower Cretaceous source rocks	-14.5	Pedentchouk et al., 2004
Aryl isoprenoids	Silurian and Devonian Canadian oils	-24.74 to -21.61	Summons and Powell, 1986
Aryl isoprenoids	Upper Devonian Duvernay Formation	-17.7 to -5.9	Hartgers et al., 1994b
Aryl isoprenoids	Late Devonian Canning Basin	-21 to -17	Tulipani et al., 2015
Aryl isoprenoids	Permian Kupferschiefer	-20.4 to -15.6	Grice et al., 1996b, 1997
Isorenieratane derivatives	Ordovician to Miocene sediments	-19.0 to -16.3	Sinninghe Damsté et al., 1995a
Tetramethylbenzenes	Upper Devonian Duvernay Formation	-19.4 to -17.5	Hartgers et al., 1994b
Alkylbenzenes	West African Lower Cretaceous source rocks	-22.8 to -19.3	Pedentchouk et al., 2004

C$_{19}$ alkyl biphenyl	Permian / Triassic Spitsbergen sediments	-17 to -9	Nabbefeld et al., 2010b
methyl n-propyl and methyl *iso*butyl maleimides	Permian Kupferschiefer	-18.1 to -16.7	Grice et al., 1996a

Table 1: Summary of $\delta^{13}C$ values of aromatic compounds from studies discussed in the text.

Figure axes: y-axis: $\delta^{13}C$ (‰), ranging from -20 to -50. x-axis: number of double bonds, with values 3, 5, 7, 9.

Legend:
- oleanane series (blue circle)
- ursane series (red square)
- des-A-lupane series (black triangle)
- deS-A-arborane series (green diamond)
- des-A-gammacerane series (purple square)
- PAH hopanoid series (grey circle)

$\delta^{13}C$ aro = 1.14 $\delta^{13}C$ sat + 5.46

- Waxy oils
- Nonwaxy oils