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6 Stable carbon isotopic compositions of individual aromatic
7 hydrocarbons as source and age indicators in oils from Western
8 Australian basins

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25 **Abstract**

26 The present study aims to establish the factors controlling the stable carbon
27 isotopic compositions of individual aromatic hydrocarbons analysed by compound
28 specific isotope analysis (CSIA) in crude oils from Western Australian petroleum
29 basins of varying age, facies type but of similar thermal maturity. This paper reports
30 $\delta^{13}\text{C}$ values of individual aromatic hydrocarbons, like alkylbenzenes,
31 alkyl-naphthalenes, alkylphenanthrenes and methylated biphenyls. The main aims are to
32 confirm the origin (source) and age of these oils based on CSIA of selected aromatic
33 compounds and to understand why the Sofer plot is ineffective in establishing source
34 of Western Australian petroleum systems. The bulk $\delta^{13}\text{C}$ of saturate and aromatic
35 fractions of crude oils have been previously used to differentiate sources, however,
36 many Australian crude oils do not appear to follow this trend. The oils were classified
37 as marine by the $\delta^{13}\text{C}$ values of individual aromatic compounds, and as terrigenous
38 based on the bulk $\delta^{13}\text{C}$ data. The CSIA data of the aromatic hydrocarbons obtained for
39 the oils provides opposite conclusions regarding the source of the oils compared to
40 bulk data (Sofer plot).

41 The oils where the $\delta^{13}\text{C}$ data of 1,6-DMN and 1,2,5-TMN isomers is most
42 negative are probably derived from marine source, whereas oils containing 1,6-DMN
43 and 1,2,5-TMN with a less negative value are representative of a terrigenous source.
44 The $\delta^{13}\text{C}$ values falling inbetween probably have mixed source(s). Less negative $\delta^{13}\text{C}$
45 values of 1-MP and 1,9-DMP isomers probably reflects the varying inputs of
46 terrigenous organic matter to the source rocks of the oils. Plots of P/DBT and Pr/Ph
47 concentration ratios versus C isotope ratio values of DMP, 1,6-DMN, 1,2,5-TMN, 1-
48 MP and 1,9-MP are constructed to establish the end members of terrigenous and
49 marine sourced oils. The ratio of P/DBT and/or the ratio of Pr/Ph and $\delta^{13}\text{C}$ values of

50 aromatic isomers (such as 1,6-DMN, 1,2,5-TMN, 1-MP and 1,9-MP) when coupled
51 together, provide a novel and convenient way of to infer crude oil source rock origin
52 and sometimes even lithologies.

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58 Key words- Aromatic hydrocarbons, compound specific isotopic analyses (CSIA), age,
59 source, petroleum, Western Australia.

60

61 **1. Introduction**

62 Alkylated aromatic hydrocarbons such as alkylbenzenes (ABs),
63 alkylnaphthalenes (ANs), alkylphenanthrenes (APs) and biphenyls (BPs) are common
64 constituents of petroleum and sedimentary organic matter (OM). Variations in the
65 molecular distributions of aromatic hydrocarbons have received considerable attention
66 in the field of organic geochemistry as indicators of source, thermal history, facies type
67 and paleoenvironments of source rocks offering petroleum potential (Radke et al.,
68 1982; Alexander et al., 1985; van Aarsen et al., 1999; Grice et al., 1998; Grice et al.,
69 2001; Nabbefeld et al., 2010). The distributions of alkylated aromatic hydrocarbons
70 are highly variable amongst oil samples since they are controlled by the effects of
71 source, thermal maturity and secondary alteration processes such as biodegradation
72 (Budzinski et al., 1995; Bastow et al., 1998; van Aarsen et al., 1992, 1999; Trolio et
73 al., 1999; Asif et al., 2009).

74 Aromatic compounds are mainly formed by geosynthetic processes, resulting in a
75 host of isomerised, alkylated and dealkylated components (Alexander et al., 1985;
76 Ioppolo-Armanios et al., 1995; Asif et al., 2010). Previous work has primarily focused
77 on molecular distributions of aromatic hydrocarbons, especially in relation to
78 sedimentary methylation processes accounting for the occurrence of compounds not
79 derived from natural product precursors (Alexander et al., 1985). However, previous
80 researchers have suggested that natural product precursors derived from microbes and
81 land plants may be sources for some aromatic hydrocarbons reported in sediments and
82 crude oils (Püttman and Villar, 1987; Forster et al., 1989; Grice et al., 2009).

83 Some aromatic compounds are thought to form in the subsurface via methyl shift
84 and/or transalkylation reactions and in a study of Australian brown coals 1,2-methyl
85 shift reactions also occur prior to or during aromatization (Radke et al., 1982; Chaffee

86 [and Johns, 1983; Strachan et al., 1988](#)) and based on molecular parameters these
87 reactions have been used to assess thermal history. In general, as thermal maturity
88 increases the more stable geosynthetic isomers are formed. Thus the relative
89 abundance of the isomers derived from natural product precursors decreases with
90 rising thermal maturity (e.g. [Radke et al., 1982; van Aarssen, et al., 1999](#)). Aromatic
91 compounds with alkyl groups in a α position are less stable than those with alkyl
92 groups in a β position. Thus ratios of β -substituted and α -substituted aromatic
93 hydrocarbons have been used to assess the degree of thermal alteration of OM in
94 sediments and crude oils ([Radke et al., 1986; Alexander et al., 1995; van Aarssen et al.,](#)
95 [1999](#)). Recently it has been demonstrated that the more stable β isomers of
96 methylnaphthalene (MN) and methylphenanthrene (MP) are relatively more abundant
97 in a bitumen associated with kerogen referred to as Bitumen II ([Nabbefeld et al.,](#)
98 [2010](#)). The difference between the methylnaphthalene ratio (MNR, ratio between 2-
99 methylnaphthalene and 1-methylnaphthalene; [Radke et al., 1982](#)) of freely extracted
100 bitumen (i.e. Bitumen I) and Bitumen II, when plotted against the ratio of clay to total
101 organic carbon (clay/TOC) shows an excellent correlation. The highest clay/TOC ratio
102 related to the largest difference in MNR for the respective bitumens, is consistent with
103 the more stable β isomers being preferentially retained within the clay/kerogen matrix.

104 The bulk C isotope composition of OM has been used to study secular change in
105 the global carbon cycle (e.g. [Chung et al., 1992; Summons et al., 1995; Andrusevich et](#)
106 [al., 1998](#)), which in the geological record has resulted in changes in the $\delta^{13}\text{C}$ values of
107 inorganic carbon sources (e.g. primary carbonates). Sedimentary OM $\delta^{13}\text{C}$ is driven by
108 water column carbon cycling through organic matter pools, fractionation during
109 photosynthesis, and respiration products contributing to atmospherically-derived
110 dissolved inorganic carbon.(e.g. [Goericke et al., 1994; Hayes, 1993; Popp et al., 1998](#)).

111 Therefore, oil-source correlations based on $\delta^{13}\text{C}$ values of sedimentary OM are often
112 applied to estimate the age (time of deposition) of a potential source rock (e.g. [Chung
113 et al., 1992](#); [Summons et al., 1995](#); [Andrusevich et al., 1998](#)). Bulk isotopic analysis of
114 organic carbon has been used to classify marine and non-marine (terrigenous) crude
115 oils by plotting the bulk $\delta^{13}\text{C}$ values of the saturate fractions against bulk $\delta^{13}\text{C}$ values
116 of aromatic fractions to infer genetic relationships ([Sofer, 1984](#)). [Chung et al. \(1992\)](#)
117 classified over 600 post-Ordovician marine crude oils into four groups, in terms of
118 their depositional environment and age of their source, on the basis of $\delta^{13}\text{C}$ values
119 combined with pristane/phytane (Pr/Ph) ratios and total organic sulfur contents).
120 [Andrusevich et al. \(1998\)](#) reported bulk $\delta^{13}\text{C}$ values of the saturate and aromatic
121 hydrocarbon fractions of over 500 oils. They found that both fractions are enriched in
122 ^{13}C with decreasing geological age including three major isotopic shifts at the
123 Cambrian/Ordovician, Triassic/Jurassic and Paleogene/Neogene boundaries.

124 In Australian petroleum systems, marine and non-marine crude oils do not appear
125 to fit the Sofer plot ([Edwards et al., 2005](#)). For example, oils interpreted to have been
126 generated from a marine source rock are classified as terrigenous sourced on the Sofer
127 plot parameters, while oils interpreted to be generated from a terrigenous source rock
128 are classified as marine.

129 The present study aims to establish factors controlling the stable carbon isotopic
130 compositions ($\delta^{13}\text{C}$) of individual aromatic hydrocarbons (ABs, ANs, APs and BPs) in
131 crude oils from Western Australian petroleum basins of varying age, facies type and
132 thermal maturities. The main aims are to confirm the source and age of these oils based
133 on $\delta^{13}\text{C}$ of selected aromatic compounds and to understand why the Sofer plot is
134 ineffective in establishing source of hydrocarbons in Western Australian petroleum
135 systems.

136 **2. Sample Material**

137 A set of 19 Mesozoic and Palaeozoic oils from Western Australian petroleum
138 basins was used for the present study, representing fluids derived from a range of
139 source rock types and ages. These oils were chosen according to the depositional
140 setting, dominant lithology of their source rocks, API values of the crude oils (showing
141 a good correlation with biodegradation) and their thermal maturities (the database of
142 Geoscience Australia is used, [Edwards et al., 2005](#)). The oils which were used to show
143 the effects of source on the $\delta^{13}\text{C}$ of aromatic hydrocarbons (Barrow Island, Elang
144 West, Tahbilk, Barnett, N. Scott Reef, Pictor and Meda) have similar thermal
145 maturities in terms of the oil window based on calculated vitrinite reflectance (Vrc
146 ranging between 0.51 and 0.95; Edwards et al., 2005). The remainder of the oils (e.g.
147 Flinders Shoal, Gorgon, and West Kora) were chosen mainly for their age. Mainly, oils
148 with no degradation were selected. Only two oils (West Kora and Flinders Shoal with
149 API values of 23° and 25.3°) (API gravity, The American Petroleum Institute, a
150 hydrometer scale expressed in degrees for the measurement of the specific gravity of
151 petroleum liquids) are characterised as being mildly and heavily biodegraded,
152 respectively ([Edwards et al., 2005](#)). The location of the oil samples are shown in Fig.
153 1. Table 1 lists the crude oils analysed in this study along with the geological age of
154 their inferred source rock, source rock type, reservoir formation and information
155 relating to sample origin including depth, field and sedimentary basin (the database of
156 Geoscience Australia is used, [Edwards et al., 2005](#))

157 In order to understand the relationship between the crude oils within and between
158 basins, the study by [Edwards et al. \(2005\)](#) led to the characterisation of crude oils into
159 33 genetically related families. From a total of 316 samples (n=316), 33 oil/condensate
160 families were identified in the Western Australian Basins—Bonaparte (n=10), Browse

161 (n=2), Canning (n=4), Carnarvon (n=11) and Perth (n=6) (Fig. 1). These samples were
162 previously characterized by bulk geochemical, molecular and bulk stable carbon
163 isotopic analyses. Compound specific isotope analysis (CSIA) of individual aromatic
164 hydrocarbons of these crude oils was first done in this study.

165

166 **3. Analytical Methods**

167 The analytical procedures used are described below. Procedural blanks were
168 carried out in parallel to account for any contamination.

169

170 *3.1. Separation of oils*

171 The crude oil samples (described above) were fractionated using a small scale
172 column liquid chromatography method (Bastow et al., 2007). The sample (10 mg) was
173 applied to the top of a mini column (5 cm x 0.5 cm i.d.) of activated silica gel (150 °C,
174 8 hrs). The saturated hydrocarbon fraction was eluted with *n*-hexane (2 ml); the
175 aromatic hydrocarbon fraction with dichloromethane in *n*-hexane (2 ml, 20%); and the
176 polar fraction with a mixture of dichloromethane and methanol (2 ml, 50%). The
177 saturated and aromatic fractions were analysed without any solvent evaporation by gas
178 chromatography-mass spectrometry (GC-MS). Aromatic hydrocarbon fractions were
179 analysed by gas chromatography-isotope ratio mass spectrometry (GC-irMS)

180

181 *3.2. 5A Molecular sieving*

182 Straight chain hydrocarbons were separated from the branched and cyclic
183 hydrocarbons by treating the saturated fractions with activated (250 °C, 8 hrs) 5A
184 molecular sieves (Murphy, 1969; Dawson et al., 2005; Grice et al., 2008) in
185 cyclohexane. In a typical 5A molecular sieving separation, a portion of the saturated

186 fraction in cyclohexane was added to a 2 ml vial, half of it filled with activated 5A
187 molecular sieves. The vial was capped and placed in a pre-heated aluminum block (85
188 °C, overnight). The resulting solution was then cooled and filtered through a small
189 column of silica plugged with cotton wool (pre-rinsed with cyclohexane) and the
190 sieves were rinsed thoroughly with cyclohexane yielding the branched/cyclic fraction
191 (5A excluded). The branched/cyclic fractions were analysed by GC-MS.

192

193 3.3. GC-MS analysis

194 GC-MS analysis was performed using a HP5973 MSD interfaced to HP6890 gas
195 chromatograph, which was fitted with a DB-1 capillary column (J and W Scientific, 60
196 m, 0.25 mm internal diameter, 0.25µm phase thickness). The GC oven was
197 programmed from 40 °C to 300 °C at a heating rate of 3 °C/min with initial and final
198 hold times of 1 and 30 minutes, respectively. Samples were dissolved in *n*-hexane and
199 injected (split/splitless injector) by a HP6890 auto-sampler using pulsed-splitless
200 mode. Helium was used as the carrier gas at a linear velocity of 28 cm/s with the
201 injector operating at constant flow. The MS was operating with an ionisation energy of
202 70 eV, a source temperature of 180 °C, an electron multiplier voltage of 1800V, and a
203 scanning a mass range of 50 to 550 amu.

204 Aromatic hydrocarbon compounds were identified by comparison of mass
205 spectra and by matching retention times with those of reference compounds reported
206 previously ([Radke, 1987](#); [Budzinski et al., 1992](#); [Grice et al., 2005](#); [Grice et al., 2007](#)).
207 Between 2 and 10 ng µl⁻¹ of each biomarker compound was required for accurate GC-
208 MS analysis. Peak areas of each compound were integrated using the HP ChemStation
209 Data Analysis software.

210

211 *3.4. GC-irMS analysis*

212 CSIA were carried out on a Micromass IsoPrime isotope ratio mass spectrometer
213 connected to a HP 6890 gas chromatograph fitted with the same column to that used
214 for GC-MS analysis. The GC oven, injection conditions and carrier were the same as
215 those described for GC-MS analysis. For the external organic reference compounds,
216 the GC oven was programmed from 50 to 310 °C at a rate of 10 °C/min with initial and
217 final hold times of 1 and 10 minutes, respectively. The aromatic fraction was injected
218 using pulsed splitless mode (30 seconds hold time at 15 psi above the head pressure of
219 the column and 35 seconds purge time). The flow rate used was 1 ml/min. The GC
220 oven was programmed from an initial temperature of 40 °C (1 min) over a temperature
221 ramp of 3 °C/min to 300 °C and held for 30 min. A CO₂ reference gas standard
222 (calibrated to Vienna Peedee Belemnite, VPDB) with a known $\delta^{13}\text{C}$ value was
223 analysed in the irMS and $^{13}\text{C}/^{12}\text{C}$ of each aromatic component is reported in the δ
224 notation (in ‰) relative to the international standard (VPDB). Average values of at
225 least two runs for each compound within each sample were determined and only $\delta^{13}\text{C}$
226 results with a standard deviation of less than 0.4‰ were used. A mix of standard
227 components with known $\delta^{13}\text{C}$ values were analysed daily in order to monitor the
228 instrument's performance, precision and accuracy.

229

230

231 **4. Results and Discussion**

232 *4.1. Experimental remarks*

233 $\delta^{13}\text{C}$ values of selected aromatic hydrocarbons, API gravity, Vrc and ratios of
234 Pr/Ph and P/DBT were determined for 19 Western Australian oils and are given in
235 **Tables 1 and 2.**

236 Almost all samples studied contain high relative abundances of the aromatic
237 compounds identified above. $\delta^{13}\text{C}$ values were obtained for various sub-classes of the
238 aromatic fractions such as DMB, TMB, TeMB, PMB, N, MN, DMN, TMN, BP, MBP,
239 DMBP, P, MP, TMP, and for several isomers of the aromatic fraction such as 1,6-
240 DMN, 1,2,5-TMN, 1-MP and 1,9-DMP (acronyms are defined in Table 2). In order to
241 simplify the results, the $\delta^{13}\text{C}$ values of each isomer series were averaged since they
242 were quite similar (within $\leq \pm 0.4\text{‰}$). However, some specific isomers particularly the
243 ones thought to be mainly influenced by source and depositional environment (Radke
244 et al., 1986; Budzinski et al., 1995) are reported separately. These include 1,2,5-TMN,
245 1,6-DMN and 1,9-DMP (Table 2).

246 $\delta^{13}\text{C}$ values of the individual aromatic compounds in the crude oils range from -
247 32‰ to -22.2‰ (Table 2) and the bulk $\delta^{13}\text{C}$ of the aromatic fractions measured in a
248 previous study for the same set of oils range between -29.9‰ to -25.4‰ (Fig. 2,
249 Edwards et al., 2005). The range of the $\delta^{13}\text{C}$ values for the individual aromatic
250 compounds in this study is much broader than the bulk $\delta^{13}\text{C}$ of the corresponding
251 aromatic fractions (9.8 and 4.5 ‰, respectively). The bulk $\delta^{13}\text{C}$ of saturate and
252 aromatic fractions of crude oils have been previously used to differentiate marine from
253 non-marine sources (Sofer, 1984). However, many Australian crude oils do not appear
254 to follow this trend (Edwards et al., 2005) (Fig. 2). For example, oils derived from
255 marine source rocks are classified as terrigenous based on the Sofer plot. Barnett and
256 Janpan North oils have been correlated to a marine source by Edwards et al. (2005).
257 However, in the Sofer plot (Fig. 2), these oils are classified as terrigenous based on
258 bulk $\delta^{13}\text{C}$ values of the saturate and aromatic fractions. On the other hand, N. Scott
259 Reef oil is classified as a marine source even though it has previously been correlated
260 to a terrigenous source (Fig. 2). The $\delta^{13}\text{C}$ values of the aromatic hydrocarbons obtained

261 for these oils may provide opposing conclusions regarding the source of the oils
262 compared to Sofer plot ($\delta^{13}\text{C}$ saturate versus $\delta^{13}\text{C}$ aromatics).

263 Both relative abundances and $\delta^{13}\text{C}$ values of individual aromatic compounds in
264 crude oils are probably controlled by their source, relative thermal maturity and age of
265 their source rock. In addition, it is known that secondary alterations such as
266 biodegradation, in-reservoir mixing and water washing can alter the composition of
267 aromatic hydrocarbons in crude oils (e.g. Volkman et al., 1984, Trolio et al., 1999).
268 The following sub-sections describe these effects on $\delta^{13}\text{C}$ for the various aromatic
269 compounds.

270 It is noted that there is generally depletion in the ^{13}C of individual aromatic
271 compounds both with increasing methylation and increasing number of aromatic rings
272 (e.g. Figs. 3 and 4). This trend is evident for all the oils analysed in this study. With
273 decreasing methylation, ^{13}C of ABs and APs within their sub-groups show a more
274 obvious depletion compared to ANs (e.g. Figs. 3 and 4). In an unpublished study (Le
275 Metayer personal communication), $\delta^{13}\text{C}$ values of ANs are shown to be strongly
276 related to thermal maturity, contrary to the $\delta^{13}\text{C}$ of ABs and APs. The oil samples
277 chosen in this study were of similar maturity in terms of the oil window
278 (a temperature dependant interval in the subsurface where oil is generated and expelled
279 from the source rocks) and therefore maturity probably has a negligible effect on the
280 $\delta^{13}\text{C}$ differences of ANs (Table 1).

281

282 4.2. $\delta^{13}\text{C}$ of aromatic isomers indicative of source

283 $\delta^{13}\text{C}$ measurements were carried on 1,6-DMN, 1,2,5-TMN, 1-MP, and 1,9-DMP
284 for eight oils (in Section 2) from different basins around WA, generated from various

285 source rock ages and types (Table 2, Fig. 5). The source effects on $\delta^{13}\text{C}$ of the
286 individual aromatic isomers are discussed in this section.

287 $\delta^{13}\text{C}$ values of 1,6-DMN from each oil are given in Table 2. The largest $\delta^{13}\text{C}$
288 difference for 1,6-DMN (4.6‰) is observed between Pictor (Canning Basin) and Elang
289 West (Bonaparte Basin). The 1,6-DMN is an isomer which is thought to be derived
290 largely from OM of higher plants (Alexander et al., 1992); an aromatization product of
291 several natural product precursors (Püttmann and Villar, 1987; Alexander et al., 1992).
292 It is assumed that the $\delta^{13}\text{C}$ difference between 1,6-DMN in the oils is indicative of
293 terrigenous and marine derived end members (Fig. 5). The oils where the $\delta^{13}\text{C}$ values
294 of 1,6-DMN isomer is most negative are probably derived from marine source,
295 whereas oils containing 1,6-DMN with a less negative value are representative of a
296 terrigenous source. The $\delta^{13}\text{C}$ values falling inbetween probably have mixed source(s).

297 Generally the higher $\delta^{13}\text{C}$ values of organic matter suggest a higher
298 contribution of terrestrial plant material to the marine biomass, due to the pre-Miocene
299 having ^{13}C -enriched terrestrial organic matter relative to marine organic matter (e.g.,
300 Lewan, 1986; Popp et al., 1989). Based on $\delta^{13}\text{C}$ data for the 1,6DMN appears to have a
301 marine signal but it is unclear what the natural precursor would be.

302
303 In Fig. 5, the arrow represents an increase in terrigenous/deltaic source for the
304 oils. When we compare these results with the Sofer plot (Fig. 2), the oils previously
305 classified as terrigenous in origin i.e. Janpam North (Canning Basin) are interpreted to
306 have a marine source based on $\delta^{13}\text{C}$ of 1,6-DMN. Similarly, the Barnett oil is classified
307 as terrigenous based on bulk $\delta^{13}\text{C}$ values (Sofer plot), however based on $\delta^{13}\text{C}$ of 1,6-
308 DMN this oil may be classified as having a mixed source. $\delta^{13}\text{C}$ of the 1,6-DMN falls
309 inbetween marine and terrigenous oils (Fig.5).

310 Conifer resins and their catagenetic products in oils and sediments are
311 isotopically heavy compared with angiosperm resins and compounds derived from
312 them (Murray et al., 1998). This distinction has existed since at least the Late
313 Mesozoic and is probably a result of fundamental differences in the gas exchange
314 behaviour of conifers and angiosperms and their relative efficiencies of carbon
315 assimilation. The heavier δ values of terrigenous derived oils in WA basins are most
316 probably for the same reason. Modern plant resins are isotopically depleted compared
317 to their fossil counterparts. The reasons for this are not yet clear but may include
318 secular change in the isotopic composition and partial pressure of atmospheric CO₂.
319 Resin derived compounds in oils and sediments, especially those associated with
320 conifers, are isotopically heavier than other hydrocarbons (Murray et al., 1998).

321 $\delta^{13}\text{C}$ values of 1,2,5-TMN for each oil are given in Table 2. The largest
322 difference for $\delta^{13}\text{C}$ values of 1,2,5-TMN (4.9‰) is observed between Tahbilk
323 (Bonaparte Basin) and Pictor (Canning Basin) oils. The oils from the Canning Basin
324 where 1,2,5-TMN is most negative are probably derived from marine sources, whereas
325 oils containing 1,2,5-TMN with a more positive $\delta^{13}\text{C}$ value are representative of a
326 terrigenous source. Since the oils are of similar thermal maturity in terms of oil
327 window, it is reasonable to assume that $\delta^{13}\text{C}$ of this isomer is largely determined by
328 source. Similarly, Le Metayer (unpublished data) has suggested that all the TMN
329 isomers, 1,2,5-TMN is most influenced by source. 1,2,5-TMN is suggested to be
330 bacterial in origin, resulting from the degradation of D-ring monoaromatic 8,14-
331 secohopanoids representing a dominant marine source (Püttmann and Villar, 1987). In
332 Fig. 5, based on $\delta^{13}\text{C}$ values of 1,2,5-TMN it can be interpreted that Pictor with the
333 most depleted $\delta^{13}\text{C}$ value is a marine sourced oil whereas Tahbilk with the most
334 enriched $\delta^{13}\text{C}$ value is the a terrigenous sourced oil. In addition to Pictor, Meda and

335 Janpam North have depleted $\delta^{13}\text{C}$ values of 1,2,5-TMN representing a marine source
336 for Canning Basin oils rather than biological or thermal maturity factors. The oils
337 (Barnett, Elang West, Barrow Island, N.Scott Reef) plot in between Canning Basin oils
338 and Tahbilk oil have varying terrigenous input in their source based on the $\delta^{13}\text{C}$ values
339 of 1,2,5-TMN.

340 [Budzinski et al. \(1995\)](#) have investigated the source effect on the MP, DMP and
341 TMP distributions for various crude oils and source rocks. From these studies, it has
342 been established that the MPs are mostly influenced by source. 1-MP is generally
343 dominant in terrigenously sourced oils ([Heppenheimer et al., 1992](#)); 9-MP is generally
344 dominant in marine sourced oils ([Isaksen, 1991](#)). The 2-MP and 3-MP isomers are
345 usually dominant compounds in highly mature lacustrine and/or marine sourced oils
346 ([Radke et al., 1986](#)).

347 The stable carbon isotopic compositions of P and MPs reported previously in
348 coaly shales and coals at marginal to full thermal maturity are consistent with organic
349 matter type rather than maturity ([Radke et al., 1998](#)). Authors reported that maturity
350 differences in Lower Jurassic Posidonia shale samples had little effect on $\delta^{13}\text{C}$ of P and
351 MPs. Similar results were also reported by [Clayton and Bjorøy \(1994\)](#) for a number of
352 North Sea crude oils. [Radke et al. \(1998\)](#) reported that sediments containing marine
353 derived organic matter had P and MPs up to 7‰ more depleted in ^{13}C compared with
354 those containing terrigenous derived organic matter.

355 In [Fig. 5](#), $\delta^{13}\text{C}$ values of 1-MP and 1,9-DMP in Canning Basin oils range from -
356 29.3‰ to -28.5‰ and -30.3‰ to -30.0‰ to, respectively. For oils from the other basins
357 (Bonaparte, Carnarvon, Browse), the $\delta^{13}\text{C}$ of 1-MP and 1,9-DMP ranges from -27.5‰
358 to -24.1‰ and -28.0‰ to -25.1‰, respectively. $\delta^{13}\text{C}$ values of 1-MP and 1,9-DMP are

359 less negative probably reflecting the varying inputs of terrigenous organic matter to the
360 source-rocks of these oils (N.Scott Reef, Elang West, Tahbilk, Barnett, Barrow Island).

361

362 *4.2.1. Relationship of aromatic ratios and $\delta^{13}C$ of aromatic isomers indicative of*
363 *source*

364 [Hughes et al. \(1995\)](#) proposed to identify the depositional environment of a
365 source rock and associated lithologies by using the plot of DBT/P versus the Pr/Ph.
366 They measured these ratios for 75 crude oils from 41 known source rocks ranging in
367 age from Ordovician to Neogene and classified them into the following groups; marine
368 carbonate, lacustrine sulfate poor, marine/lacustrine shale/fluvial deltaic carbonaceous
369 shale and coal. Similarly, [Edwards et al. \(2005\)](#) used Pr/Ph and P/DBT ratios to
370 classify marine and terrigenous oils.

371 P/DBT and Pr/Ph ratios of the WA crude oils and $\delta^{13}C$ of source related aromatic
372 isomers are given in [Table 2](#). The relationship between $\delta^{13}C$ values of 1,6-DMN and
373 P/DBT, and Pr/Ph ratios of the oils is shown in [Fig.6](#). The plot reveals that oils
374 generated by source rocks of similar depositional environment and lithologies tend to
375 group together. Thus, oils from marine anoxic environments, predominantly marine
376 carbonaceous source rocks have low P/DBT and Pr/Ph ratios and the most negative
377 $\delta^{13}C$ values for 1,6-DMN. In contrast, oils either from terrigenous siliciclastic or with a
378 terrigenous source input have high P/DBT and Pr/Ph ratios, and also high $\delta^{13}C$ values
379 for 1,6-DMN ([Fig. 6](#)).

380 Janpam North, Pictor and Meda oils have a low P/DBT ratio and $\delta^{13}C$ of 1,6-
381 DMN is most depleted. These oils are from a marine source ([Fig. 6a](#)). Janpam North
382 oil with a low Pr/Ph ratio relative to other marine oils of Canning Basin (Pictor and
383 Meda) represents a more calcareous source rather than a shaley source rock ([Fig. 6b](#)).

384 Crocetane, an irregular tail-to-tail C₂₀ isoprenoid, was found to be present in the
385 Canning Basin oils (Maslen et al., 2009). Crocetane coelutes with phytane. However
386 the percentage of crocetane is low (~4 %) in abundance and therefore has a negligible
387 influence on Pr/Ph ratios for the Canning Basin oils.

388 The $\delta^{13}\text{C}$ values of aromatic isomers (1,6-DMN and 1,2,5-TMN) of Barnett oil
389 suggest a mixed source, however when these data are plotted with the P/DBT and
390 Pr/Ph ratios (Figs. 6b, 7b and 8b) it points to a marine source similar to the Canning
391 Basin oils. The Barnett oil shows a distinction from the other mixed source oils with its
392 Pr/Ph ratio plotting in between the Canning Basin oils and the other WA oils (Figs. 6b,
393 7b and 8b). Elang West, N. Scott Reef, Barrow Island and Tahbilk oils show highly
394 variable P/DBT and Pr/Ph ratios reflecting varying degrees of terrigenous inputs to
395 their source rocks. When $\delta^{13}\text{C}$ of 1,6-DMN (Fig. 6b), 1,2,5-TMN (Fig. 7b) and DMP
396 (Fig. 8b) are plotted versus Pr/Ph ratios, these oils plot together with higher Pr/Ph
397 ratios and less negative $\delta^{13}\text{C}$ values of selected aromatic isomers(1,6-DMN, 1,2,5-
398 TMN) relative to Canning Basin oils and to Barnett oil.

399 $\delta^{13}\text{C}$ of 1,2,5-TMN (Fig. 7a) and $\delta^{13}\text{C}$ of DMP (Fig. 8a) are plotted versus
400 P/DBT ratios help to discriminate any source effects in WA oils. As discussed above,
401 the Canning Basin oils (Janpam North, Pictor and Meda) group together with their low
402 P/DBT ratios and more negative $\delta^{13}\text{C}$ values reflecting a marine source. However,
403 compared to other diagrams where it shows more marine effect (Figs. 6b, 7b and 8b),
404 Barnett oil plots closer to the other WA oils from Bonaparte, Carnarvon and Browse
405 Basins reflecting a higher terrigenous input (Figs. 6a, 7a and 8a). Elang West, N. Scott
406 Reef, Barrow Island and Tahbilk oils make a group with high P/DBT ratios and less
407 negative $\delta^{13}\text{C}$ values representing varying contributions of terrigenous organic matter
408 to their source.

409 As discussed above (Section 4.2), by studying the relative ratios of APs from oils
410 of different sources, [Budzinski et al. \(1995\)](#) proposed that several specific MP, DMP
411 and TMP isomers can be characteristic either of marine carbonate or terrigenous
412 siliciclastic depositional environments. Using the isotopic approach, [Radke et al.](#)
413 [\(1998\)](#) proposed that $\delta^{13}\text{C}$ of P and MPs reflect organic matter type rather than thermal
414 maturity. Amongst all the alkylated Ps, the MPs have been shown to be the most
415 indicative of source(s). Plots of P/DBT versus $\delta^{13}\text{C}$ values of 1-MP and 1,9-MP ([Fig.](#)
416 [9a and b, respectively](#)) help to discriminate between the end members of terrigenous
417 and marine sourced oils. The oils of the Canning Basin (Pictor, Meda and Janpam
418 North) are classified as marine having low P/DBT ratios and the most negative $\delta^{13}\text{C}$
419 values for 1-MP and 1,9-MP isomers ([Figs. 9a and 9b](#)). The other 5 oils (N. Scott Reef,
420 Barrow Island, Elang West, Tahbilk and Barnett) are more terrigenous derived having
421 higher P/DBT ratios and more positive $\delta^{13}\text{C}$ values for 1-MP and 1,9-MP. From most
422 terrigenously sourced (all with less negative $\delta^{13}\text{C}$ values relative to Canning Basin
423 oils) to least terrigenously sourced the oils can be put in an order as follows; N.Scott
424 Reef, Barrow Island, Elang West, Tahbilk, Barnett oils ([Figs. 9a and 9b](#)).

425 As a general conclusion, for the oils we have analysed ($\delta^{13}\text{C}$ of individual
426 aromatic hydrocarbons) that are identified on the Sofer plot, Pictor and Meda
427 (Canning) appear to follow the same trend (marine sourced). On the other hand,
428 Canning Basin oil (Janpam North) gives a marine signature based on $\delta^{13}\text{C}$ of
429 individual aromatic hydrocarbons in contrast to its terrigenous signature based on bulk
430 $\delta^{13}\text{C}$ data from the Sofer plot. From $\delta^{13}\text{C}$ data of aromatic isomers (1,6-DMN; 1,2,5-
431 TMN; 1MP and 1,9-DMP) Tahbilk and Barnett oils provide different conclusions to
432 those drawn from the Sofer plot showing mixed inputs with some and terrigenous

433 contribution. To clarify this, $\delta^{13}\text{C}$ values coupled with P/DBT and Pr/Ph ratios show
434 that the Tahbilk and Barnett oils are consistent with mixed oils.

435 When we compare bulk ^{13}C values of aromatic hydrocarbons of the same oils
436 (Fig.2, Sofer Plot) opposite conclusions can be drawn. $\delta^{13}\text{C}$ values of individual
437 aromatic compounds provide an insight to classify WA oils based on their source.

438

439 *4.3 $\delta^{13}\text{C}$ of aromatic sub-classes (age and basin for oils)*

440 Previously attempts have been made to correlate oils to their geological age and
441 origin (e.g. Sofer, 1984; Andrusevich et al., 1998). Most of the previous studies have
442 used molecular characteristics and bulk $\delta^{13}\text{C}$ of saturates and aromatics. Previous
443 applications of bulk $\delta^{13}\text{C}$ for constraining the geologic ages of crude oils and their
444 respective petroleum basins have only been met with limited success. This is a
445 consequence of the large range of bulk $\delta^{13}\text{C}$ values for crude oils from any specific age
446 interval. In general, oils tend to become enriched in ^{13}C with decreasing geological age
447 (Andrusevich et al., 1998). Such changes are thought to be independent of the source
448 rocks from which the oils are derived.

449 $\delta^{13}\text{C}$ distributions of individual aromatic sub-classes (ABs, ANs, BPs and APs)
450 of two Mesozoic and three Paleozoic oils from WA petroleum basins are illustrated in
451 Figs. 3 and 4. We have tried to observe if there is any trend in $\delta^{13}\text{C}$ values of
452 individual aromatic hydrocarbons with respect to age and basin of the oils. Overall,
453 Cretaceous Elang West oil from the Bonaparte Basin (Fig. 3a) ($\delta^{13}\text{C}$ of individual
454 aromatics ranges between -28.3 to -23.6‰) has less negative ^{13}C values than Flinders
455 Shoal a Jurassic aged oil from the Carnarvon/Barrow Basin (Fig. 3b) ($\delta^{13}\text{C}$ ranges
456 between -28.7 to -25.0‰). These data is consistent with the previous study of
457 Andrusevich et al. (1998) showing that oils become enriched in ^{13}C both saturate and

458 aromatic hydrocarbons with decreasing source age. The change in ^{13}C of these two oils
459 are believed to be directly age and source related because their thermal maturities are
460 similar (Table 1, $V_{rc} = 0.63$ and 0.68 for Elang West and Flinders Shoal, respectively).
461 Flinders Shoal is a mixture of heavily biodegraded and non-degraded oil (Grice et al.,
462 2000). It is likely that the aromatic hydrocarbons in Flinders Shoal mainly derive from
463 the non-degraded oil; however, biodegradation may still have an effect on the $\delta^{13}\text{C}$ of
464 individual aromatic hydrocarbons.

465 Carboniferous West Kora oil from the Canning Basin (Fig. 4a) has individual
466 aromatic hydrocarbons with $\delta^{13}\text{C}$ values ranging between -32.0 to -27.5‰ (Table 2).
467 Devonian Meda oil from the Canning Basin has $\delta^{13}\text{C}$ values ranging from -31.8 to $-$
468 27.0‰ (Fig. 4b and Table 2). Ordovician Pictor oil from the Canning Basin has $\delta^{13}\text{C}$
469 values ranging from -31.0 to -26.9‰ (Table 2). Contrary to Mesozoic oils shown in
470 Fig. 3, Paleozoic oils do not follow the trend of enrichment in ^{13}C with decreasing
471 source age. The Ordovician oil Pictor has the most enriched ^{13}C values of individual
472 aromatic hydrocarbons on average relative to Carboniferous West Kora and Devonian
473 Meda oils though it was the oldest oil analysed (Fig. 4c). The change in $\delta^{13}\text{C}$ values of
474 Ordovician oil might be more affected by thermal maturity rather than age since the
475 Ordovician oil is the most mature oil of the Paleozoic oils in the present study ($V_{rc} =$
476 0.95 , Table 1). However, in general Mesozoic oils in WA basins have more enriched
477 values in their ^{13}C of aromatic sub-classes relative to older Paleozoic oils.

478

479 **5. Conclusions**

480 Molecular approaches were complimented with compound specific isotope
481 (CSIA) approach for individual aromatic compounds in Western Australia crude oils to
482 differentiate source and age. $\delta^{13}\text{C}$ values were obtained for various sub-classes of the

483 aromatic fractions such as DMB, TMB, TeMB, PMB, N, MN, DMN, TMN, BP, MBP,
484 DMBP, P, MP, TMP, and for several isomers of the aromatic fraction such as 1,6-
485 DMN, 1,2,5-TMN, 1-MP and 1,9-DMP.

486 The bulk $\delta^{13}\text{C}$ of saturate and aromatic fractions of crude oils have been
487 previously used to differentiate sources, however, many Australian crude oils do not
488 appear to follow this trend. Oils from marine basins based on their $\delta^{13}\text{C}$ values of
489 individual aromatic compounds are classified as terrigenous based on their bulk $\delta^{13}\text{C}$
490 values. The CSIA data of the aromatic hydrocarbons obtained for the oils provides
491 opposite conclusions regarding the source of the oils compared to bulk data (Sofer
492 plot).

493 The oils where the $\delta^{13}\text{C}$ of 1,6-DMN and 1,2,5-TMN isomers is most negative
494 are probably derived from marine source, whereas oils containing 1,6-DMN and 1,2,5-
495 TMN with a less negative value are representative of a terrigenous source. The $\delta^{13}\text{C}$
496 values falling in between probably have mixed source(s). Less negative $\delta^{13}\text{C}$ values of
497 1-MP and 1,9-DMP isomers probably reflects the varying inputs of terrigenous organic
498 matter to the source rocks of the oils.

499 Plots of P/DBT and Pr/Ph versus $\delta^{13}\text{C}$ of DMP; 1,6-DMN; 1,2,5-TMN; 1-MP
500 and 1,9-MP are constructed to establish the end members of terrigenous and marine
501 sourced oils.

502 The ratio of P/DBT and/or the ratio of Pr/Ph and $\delta^{13}\text{C}$ of aromatic isomers (such
503 as 1,6DMN; 1,2,5-TMN; 1-MP and 1,9-MP) when coupled together, provide a novel
504 and convenient way of to infer crude oil source rock origin and sometimes even
505 lithologies.

506

507

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730

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734

735 Fig. 3. Trends of $\delta^{13}\text{C}$ of individual aromatic compounds in crude oils of Mesozoic age in
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737 alkylphenanthrenes, other abbreviations given in Table 2).

738

739 Fig. 4. Trends of $\delta^{13}\text{C}$ of individual aromatic compounds in crude oils of Paleozoic age in
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741 alkylphenanthrenes, other abbreviations given in Table 2).

742

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746 and 9.

747

748 Fig. 6. Plots of $\delta^{13}\text{C}$ of 1,6-DMN (DMN: dimethylnaphthalene) versus (a) P/DBT (P:
749 phenanthrene, DBT: dibenzothiophene and (b) Pr/Ph (Pr: Pristane, Ph: Phytane) ratios in
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751 source). Same legend is used in Figs. 6, 7, 8 and 9.

752

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754 phenanthrene, DBT: dibenzothiophene and (b) Pr/Ph (Pr: Pristane, Ph: Phytane) ratios in
755 WA crude oils as an indication of source. (Arrow shows the increasing input of terrigenous
756 source). Same legend is used in Figs. 6, 7, 8 and 9.

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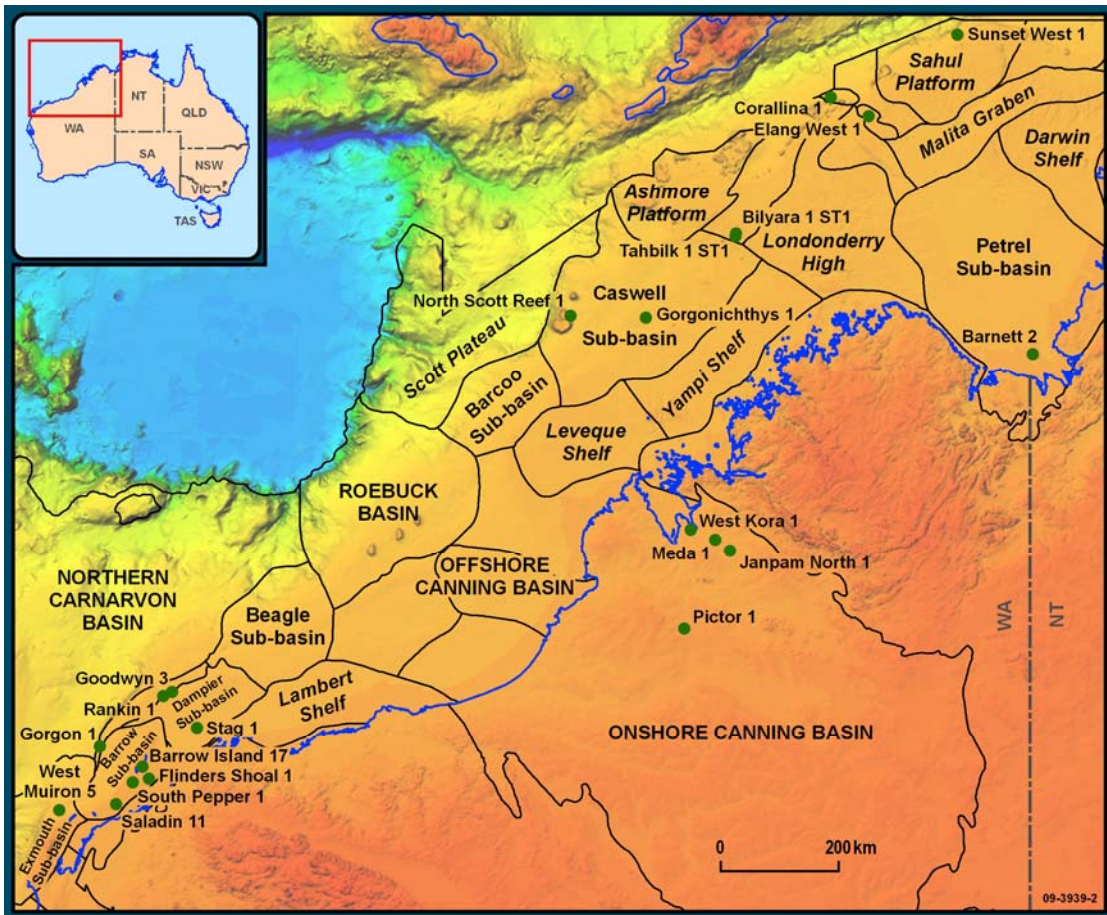
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759 phenanthrene, DBT: dibenzothiophene and (b) Pr/Ph (Pr: Pristane, Ph: Phytane) ratios in
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761 source). Same legend is used in Figs. 6, 7, 8 and 9.

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763

764 Fig. 9. Plots of P/DBT versus (a) $\delta^{13}\text{C}$ of 1-MP (b) $\delta^{13}\text{C}$ of 1,9-MP in WA crude oils as an
765 indication of source. (Arrow shows the increasing input of terrigenous source). Same
766 legend is used in Figs. 6, 7, 8 and 9.

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782 Fig.1.

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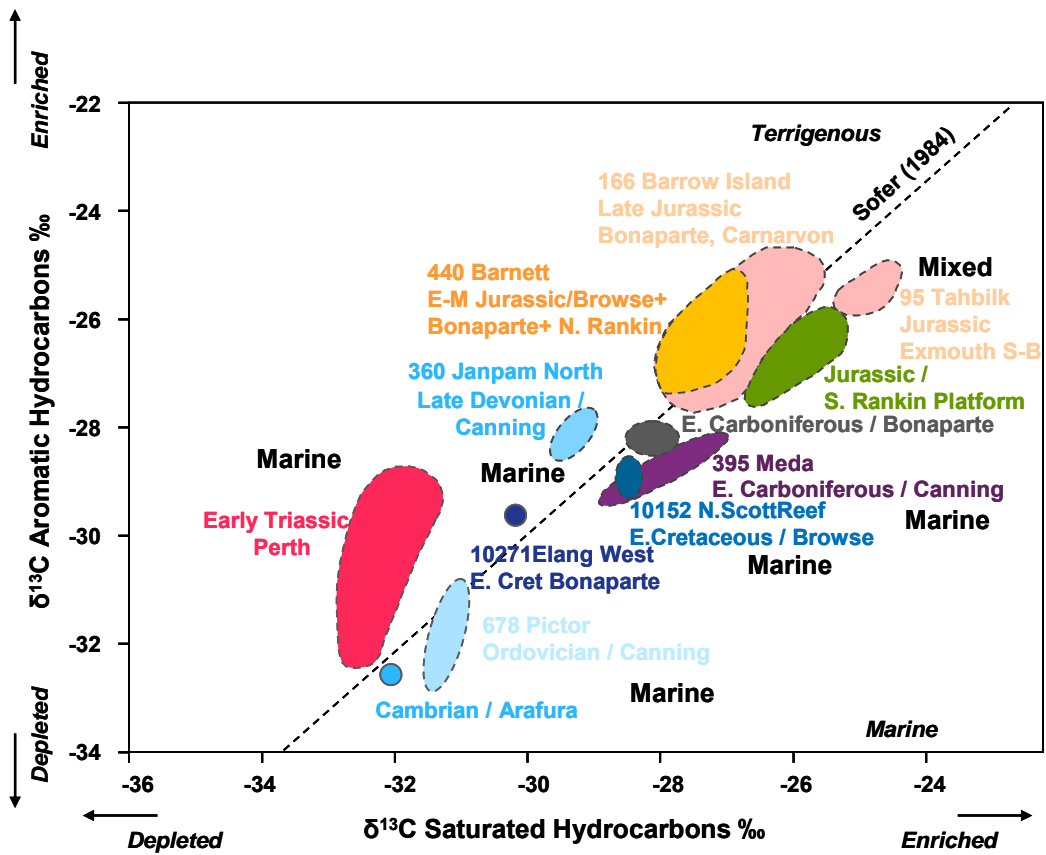
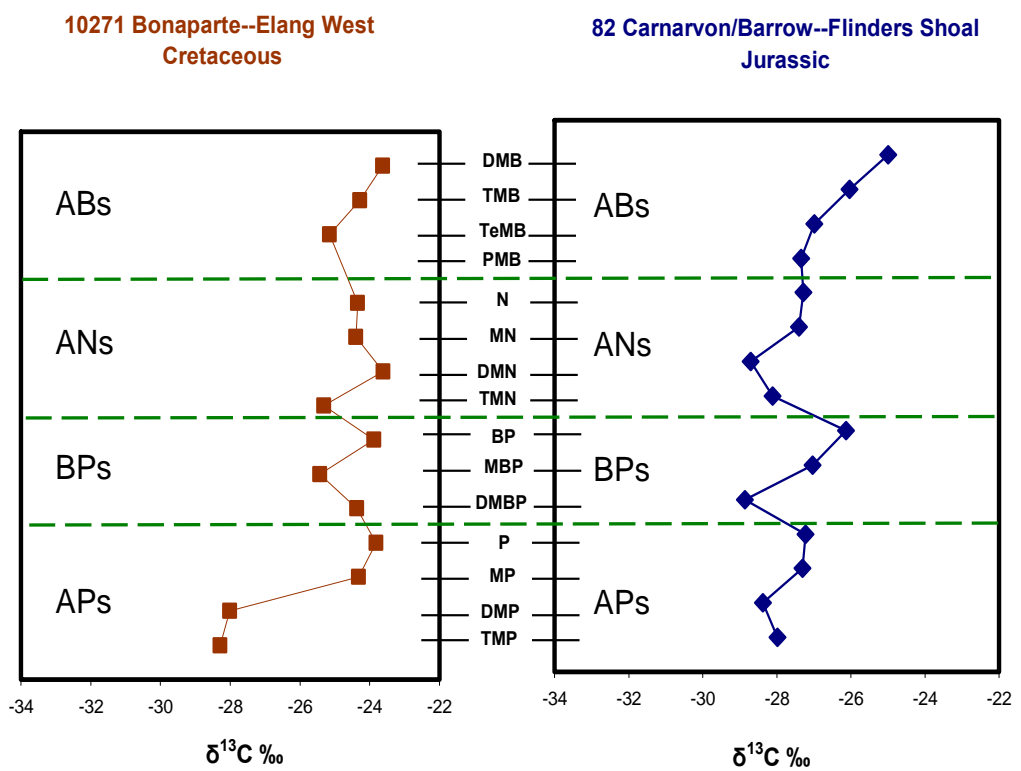


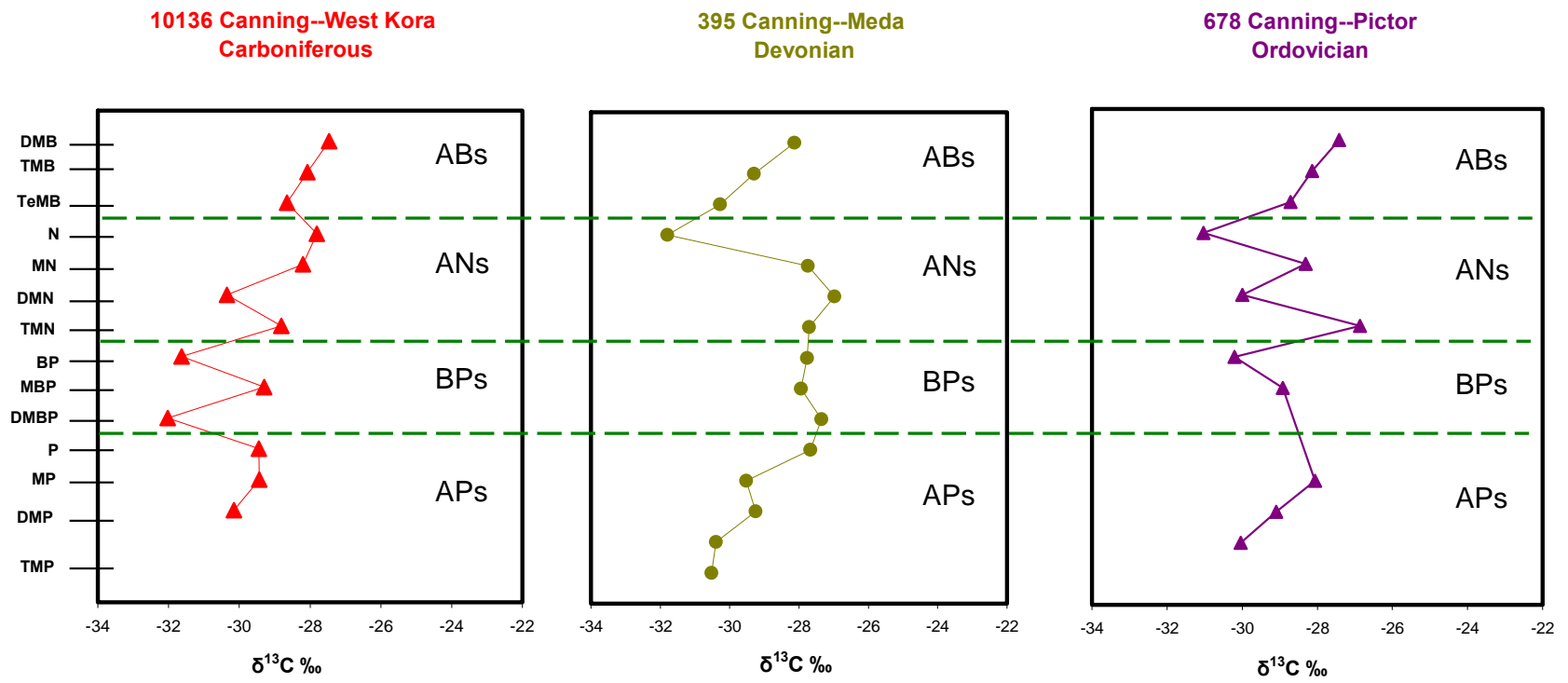
Fig. 2.

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Fig. 3.



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825 Fig. 4.

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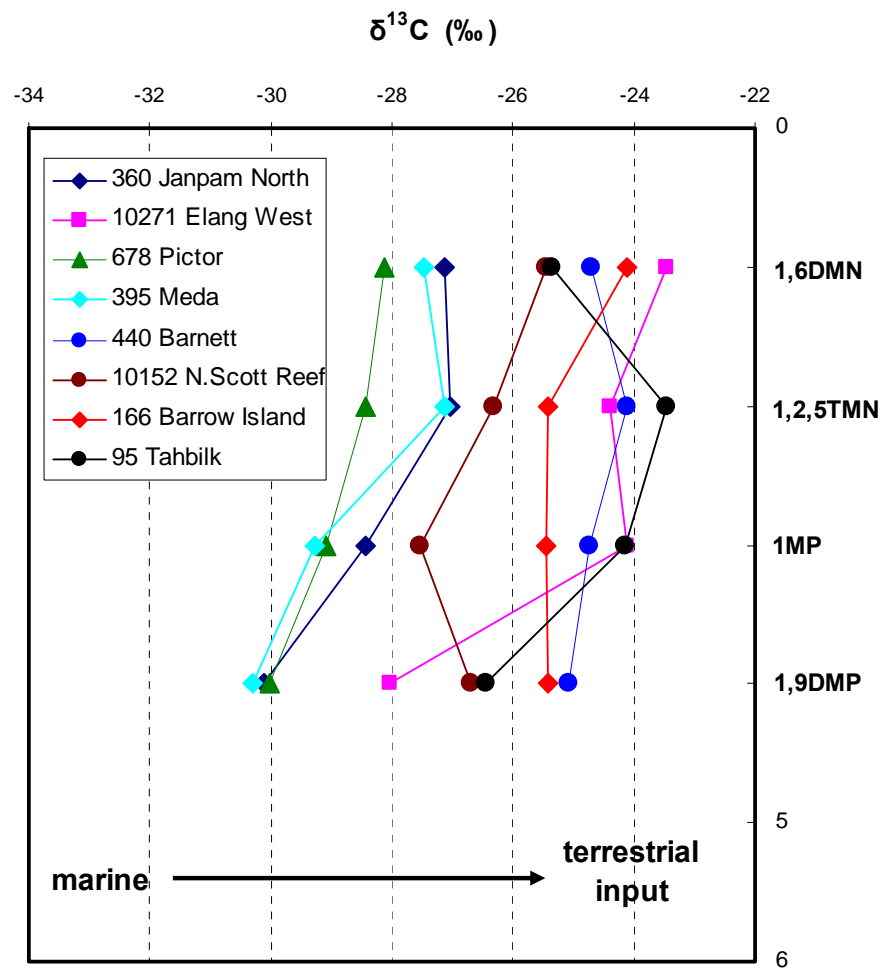


Fig. 5.

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Fig. 6.

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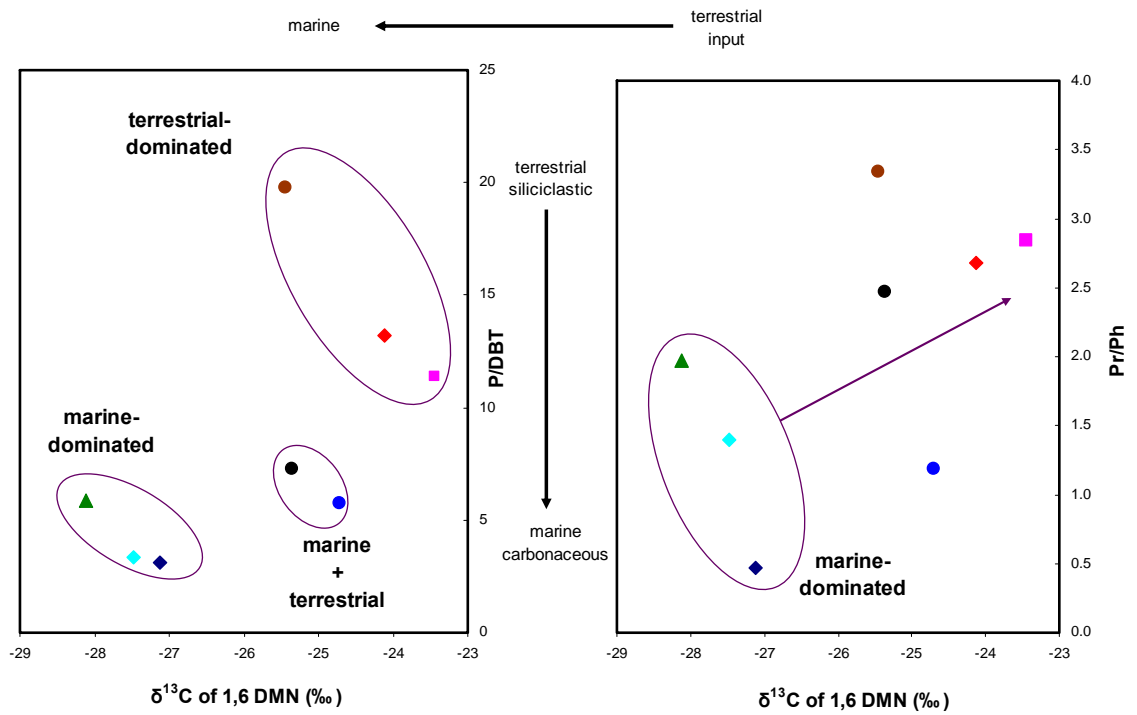
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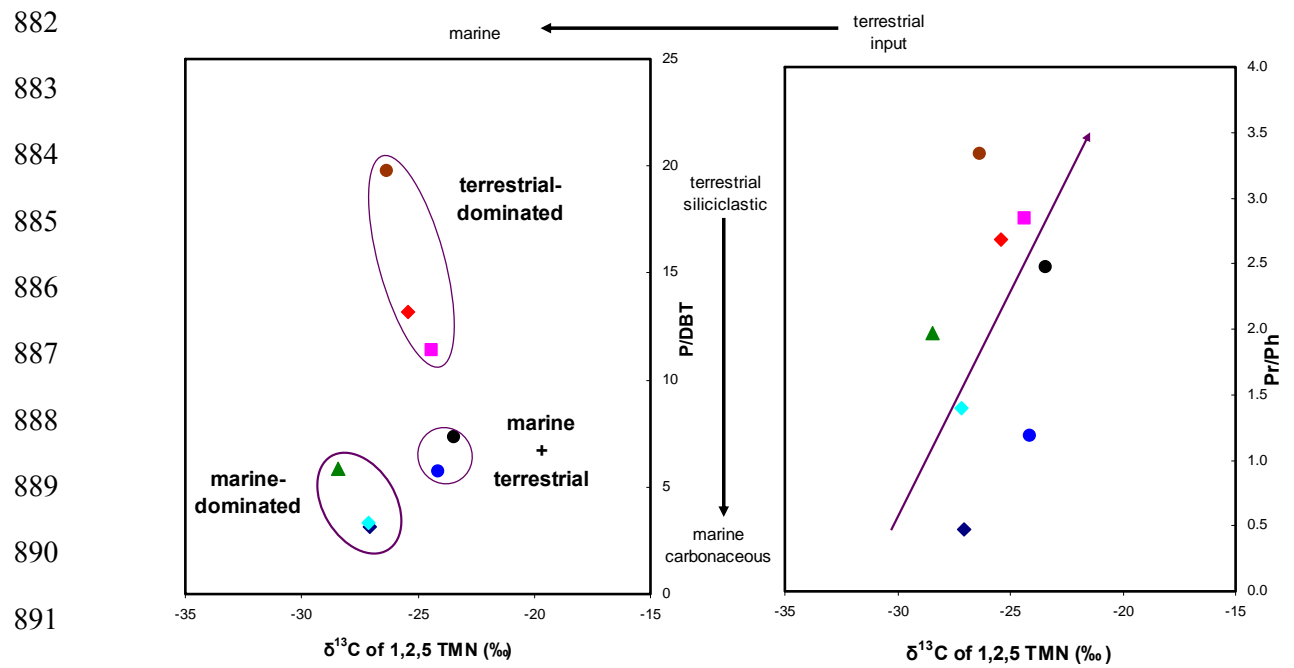
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893 Fig. 7.

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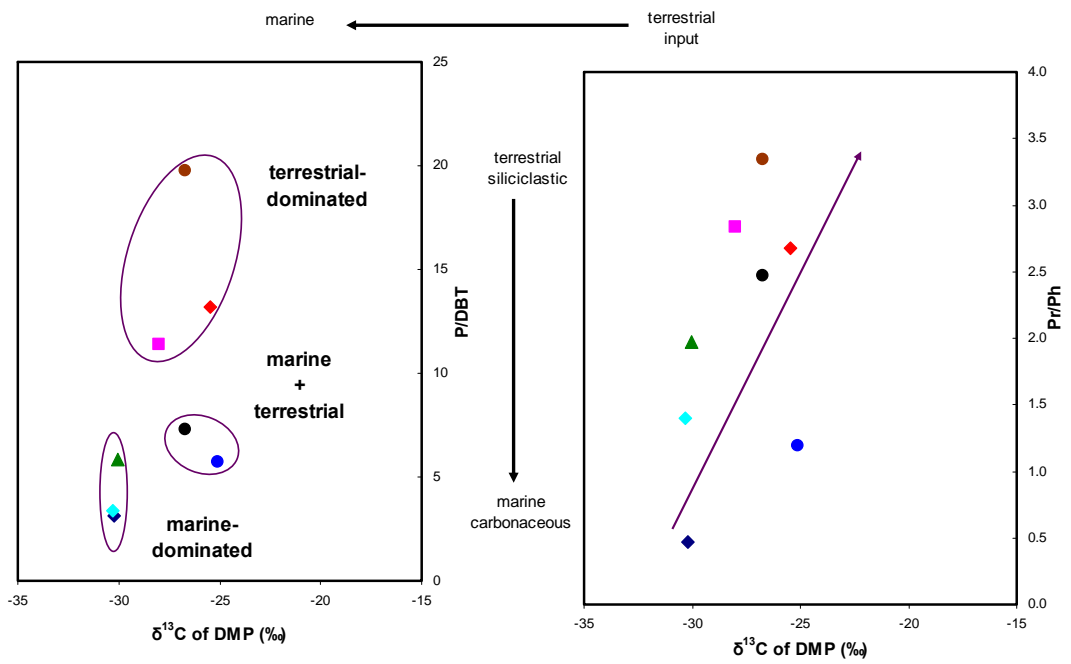
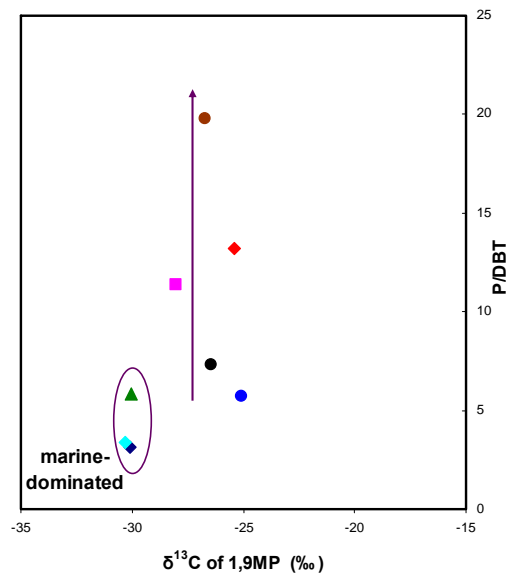
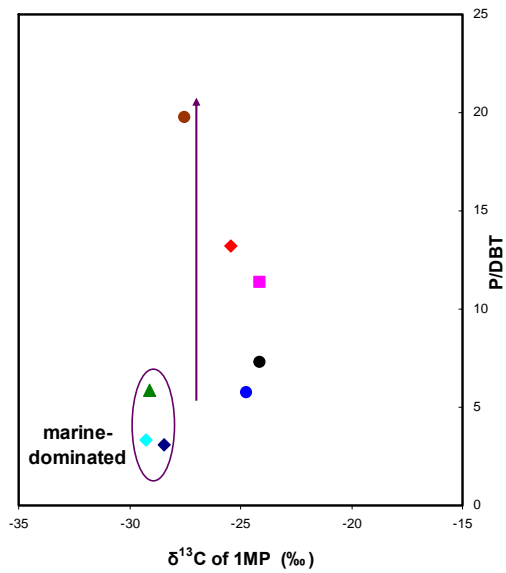


Fig. 8.



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933 Fig. 9.

934 Table 1. Location, reservoir and age data of crude oils from Western Australia Basins. API, Vrc (calculated vitrinite reflectance) data are taken from
 935 Edwards et al. (2005). Mild and heavy biodegradation approximately corresponds to the levels 2-4, 5-7, respectively (Volkman et al., 1984; Peters and
 936 Moldowan, 1993; Grice et al., 2000). The term polyhistory used for reservoirs that have experienced several phases of recharge.
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Sample ID	Basin	Field	Depth (m)	Reservoir Formation	Reservoir Age	Source Age	API	Vrc	Biodegradation	Source Type
<i>Western Australian</i>										
82	Carnarvon/Barrow	Flinders Shoal	786.1-799.2	Birdrong	E. Cretaceous	Jurassic	25.30	0.63	heavy	Distal Marine Shale/Paralic-Deltaic Marine Shale
881	Carnarvon/Barrow	South Pepper	2214-2217	Barrow Gp	E. Cretaceous	Jurassic	43.80	0.76	polyhistory	Paralic-Deltaic Marine Shale
166	Carnarvon/Barrow	Barrow Island	2282.9-2312.2	Muderong	E. Cretaceous	Jurassic	36.70	0.78	polyhistory	Paralic-Deltaic Marine Shale
233	Carnarvon/N. Rankin	Rankin	2954	Mungaroo	L. Triassic	Triassic-Jurassic	33.60	1.05	polyhistory	Distal Marine Shale/Paralic-Deltaic Marine Shale
128	Carnarvon/N. Rankin	Goodwyn	2879-2891	Mungaroo	L. Triassic	Triassic-Jurassic	52.50	0.80	polyhistory	Paralic-Deltaic Marine Shale
154	Carnarvon/S. Rankin	Gorgon	3973-4002	Mungaroo	L. Triassic	Triassic-Jurassic	45.10	0.79	non-degraded	Distal Marine Shale/Paralic-Deltaic Marine Shale
10057	Carnarvon/Barrow	Saladin	1647-2436	Mardie	E. Cretaceous	Jurassic	53.40	0.69	polyhistory	Distal Marine Shale/Paralic-Deltaic Marine Shale
10271	Bonaparte/Flamingo High	Elang West	3007-30016	Jamieson - Flamingo	E.-L. Cretaceous	E. Cretaceous	39.00	0.68	non-degraded	Distal Marine Shale
95	Bonaparte/Vulcan	Tahbilk	2690.2	n/a	L. Jurassic	Jurassic	34.70	0.51	non-degraded	Paralic-Deltaic Marine Shale
36	Bonaparte/Vulcan	Bilyara	2708	Montara	L. Jurassic	E.-M. Jurassic	33.90	0.73	non-degraded	Paralic-Deltaic Marine Shale
440	Bonaparte/Petrel	Barnett	1491-1497	U.Kuriyippi	L. Carboniferous-E. Permian	E. Carboniferous	36.90	0.86	polyhistory	Distal Marine Shale
10300	Bonaparte/Laminaria High	Corallina	3186-3196	Laminaria	M.-L. Jurassic	Jurassic	58.20	0.62	non-degraded	Paralic-Deltaic Marine Shale
354	Bonaparte/Sahul Platform	Sunset West	2189-2207	Plover	M. Jurassic	E.-M. Jurassic	61.80	0.53	non-degraded	n/a
10152	Browse/Scott Reef	N. Scott Reef	4223-4283	unnamed	E. Jurassic	E.-M. Jurassic	47.90	0.89	non-degraded	Paralic-Deltaic Marine Shale
98	Browse/Yampi Shelf	Gorgonichthys	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
678	Canning	Pictor	929-956	Nita	Ordovician	Ordovician	43.80	0.95	non-degraded	Distal Marine Shale
360	Canning	Janpam North	1644-1661	Nullara	L. Devonian	Devonian	23.00	0.82	mild	Calcerous Marine Shale
10136	Canning	West Kora	1735-1751	Anderson	E. Carboniferous	E. Carboniferous	46.90	0.67	polyhistory	Distal Marine Shale
395	Canning	Meda	1557-1564	Laurel	L. Carboniferous	E. Carboniferous	39.00	0.72	non-degraded	Distal Marine Shale

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939 n/a; no data
 940 E.; Early, L.; Late, M.; Middle

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947 Table 2. Results of $\delta^{13}\text{C}$ of individual aromatic hydrocarbons from crude oils analysed in this study (DMB, dimethylbenzene; TMB, trimethylbenzene;
 948 TeMB, tetramethylbenzene; PMB, pentamethylbenzene; N, naphthalene; MN, methylnaphthalene; DMN, dimethylnaphthalene; TMN,
 949 trimethylnaphthalene; Bp, biphenyl; MBp, methylbiphenyl; DMBp, dimethylbiphenyl; P, phenanthrene; MP, methylphenanthrene; DMP,
 950 dimethylphenanthrene; TMP, trimethylphenanthrene; Pr, Pristane; Ph, Phytane; DBT, dibenzothiophene).

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Sample ID	DMB	TMB	TeMB	PMB	N	MN	DMN	1,6 DMN	TMN	1,2,5 TMN	BP	MBP	DMBP	P	MP	IMP	DMP	1,9 DMP	TMP	Pr/Ph	P/DBT
$\delta^{13}\text{C}(\text{‰})$																					
<i>Western Australian</i>																					
82	-25.0	-26.0	-27.0	-27.3	-27.3	-27.4	-28.1		-27.0		-28.7	-26.1	-26.1	-27.2	-27.3		-28.4		-28.0		
881		-27.0	-27.8	-28.5																	
166	-25.6	-25.9	-27.6		-26.1	-24.1	-25.3	-24.1	-26.5	-25.4		-27.0	-26.0	-26.3	-25.7	-25.5	-25.5	-25.4	-28.8	2.68	13.18
233	-26.4	-26.3	-26.6	-25.5	-27.8	-27.7	-26.0		-27.8		-25.0	-24.7	-26.7	-27.0	-27.7		-28.2		-29.5		
128	-25.3	-26.2	-26.8	-27.0	-23.6	-24.0	-25.3		-27.9		-25.2	-25.1		-25.5	-24.7		-25.4		-27.6		
154	-25.3	-26.4	-26.3		-23.4	-24.3	-25.3		-28.8		-25.2	-24.9		-24.1	-24.3						
10057	-25.1	-26.1	-27.0	-27.2	-25.3	-27.4	-28.3		-28.1		-26.1	-26.8	-28.9	-28.2	-27.8		-28.3				
10271	-23.6	-24.3	-25.2		-24.3	-24.4	-25.3	-23.5	-25.4	-24.4	-23.6	-23.9	-24.4	-23.8	-24.3	-24.1	-28.0	-28.0	-28.3	2.84	11.38
95	-25.7	-26.3	-27.3	-26.7	-24.2	-22.2	-23.9	-25.4		-23.5	-25.3	-26.2	-26.4	-24.1	-24.8	-24.1	-26.7	-26.5	-27.0	2.47	7.30
36	-25.7	-27.1	-26.7		-23.1	-24.3	-24.8		-25.8		-25.2	-25.7	-26.0	-25.6	-27.3		-28.1		-29.9		
440	-25.9	-26.5	-27.3	-28.3	-24.0	-24.6	-25.2	-24.7	-26.6	-24.1	-25.8	-26.5	-26.5	-25.0	-24.8	-24.7	-25.1	-25.1	-27.0	1.19	5.74
10300	-28.4	-26.7	-28.1	-26.2	-26.7	-27.3	-25.6				-25.5	-26.5		-26.6	-26.7						
354	-25.7	-27.5	-27.7	-26.2	-25.9	-23.7	-26.5		-25.5		-26.0		-25.5	-27.2	-28.5						
10152	-24.7	-25.1	-25.3		-26.3	-27.0	-28.0	-25.5	-27.4	-26.3	-23.1	-23.6	-25.4	-25.5	-27.8	-27.5	-26.7	-26.7	-26.7	3.34	19.78
98	-23.4	-26.0	-28.8	-26.3	-26.1	-27.8	-27.1		-28.1		-27.8	-25.6	-27.0	-28.0	-27.8		-27.0		-27.5		
678	-27.4	-28.1	-28.7	-31.0	-28.3	-30.0	-30.2	-28.1	-30.2	-28.4	-26.9	-28.9		-28.1	-29.1	-29.1	-30.0	-30.0		1.97	5.84
360	-28.5	-29.7	-31.3	-30.8	-26.8	-26.6	-27.5	-27.1	-27.7	-27.0	-27.3	-27.4	-27.1	-29.5	-29.0	-28.5	-30.2	-30.1	-30.2	0.47	3.11
10136	-27.5	-28.1	-28.7	-27.8	-28.2	-30.3	-31.6		-32.0		-28.8	-29.3	-29.5	-29.4	-30.2						
395	-28.1	-29.3	-30.3	-31.8	-27.7	-27.0	-27.8	-27.5	-27.4	-27.1	-27.7	-27.9	-27.7	-29.5	-29.3	-29.3	-30.4	-30.3	-30.5	1.4	3.35

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