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3   Title: Comparison of tri-, tetra- and pentacyclic caged hydrocarbons in Australian crude

4   oils and condensates

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20 Abstract

21 Thermally stable and biodegradation resistant, the tricyclic and pentacyclic diamondoid

22 caged hydrocarbons are commonly used as source and maturity indicators of oils and

23 potential source-rocks but similar tetracyclic structures appear to have received much

24 less attention. Using two-dimensional gas chromatography – time of flight mass

25 spectrometry (GC×GC-TOFMS), 29 Australian crude oils and condensates were

26 analysed for the presence of caged $C_{12}H_{18}$ tetracyclics such as ethanoadamantane and

27 iceane. The thermodynamically more stable 2,4-ethanoadamantane was identified by

28 comparison with a synthesised authentic standard. Three of its bridgehead methyl-

29 substituted isomers, 6-methylethanoadamantane (6-ME), 1-ME and 2-ME, were

30 tentatively assigned based on mass spectral comparison and relative elution order.

31 Further series of non-bridgehead methyl isomers plus dimethyl isomers were also

32 inferred based on mass spectra and 2D elution positions. The tri-, tetra and pentacyclic

33 caged hydrocarbons and their methyl-substituted homologues were semi-quantified in

34 the Australian oils. The potential of a novel index, the methylethanoadamantane index

35 (MEI), based on the ratio of the more stable bridgehead isomers divided by the sum of

36 all the methyl substituted isomers (MEI = Σ(6-ME + 1-ME + 2-ME)/ΣTotal

37 methylethanoadamantanes), was explored. A significant positive association was found

38 between the MEI and MAI (r^2 = 0.203, $p<0.05$) and a significant negative association

39 was found between MEI and MDI (r^2 = 0.246 p <0.05). Stronger relationships were

40 found for other commonly applied diamondoid ratio indices including Σ Methyl

41 Adamantanes/Σ Methyl Diamantanes (ΣMA/ΣMD) versus ΣMA/ΣME (r^2 = 0.781,

42 $p<0.0001$, n=26). The relatively low volatility of the ethanoadamantanes compared to

43 the adamantanes and their likely greater resistance to microbial attack than the

44 ethyladamantanes may make analysis of these compounds a useful addition to the

45 commonly measured diamondoids.

Highlights

- Caged tetracyclic hydrocarbons found in a range of Australian oils and condensates
- 2,4-ethanoadamantane synthesised and confirmed as present in samples
- Concentrations of ethanoadamantane and homologues generally similar to diamantanes
- Novel ethanoadamantane indices show correlation with some diamondoid indices

1. Introduction

Diamondoids are saturated hydrocarbons with cage-like structures that resemble diamonds. As well as applications in nanotechnology and biomedicine they have been widely applied in organic geochemistry (reviewed by Mansoori et al., 2012). In particular, tricyclic and pentacyclic diamondoid hydrocarbons have been used as maturity and source indicators due to their high thermal stability and resistance to biodegradation (Chen et al., 1996; Dahl et al., 1999; Grice et al., 2000; Mansoori et al., 2012; Marchand, 2003; Moldowan et al., 2015; Stout and Douglas, 2004; Wang et al., 2006), but despite this clear interest in caged hydrocarbons, similar tetracyclic structures do not appear to have been utilised or indeed routinely reported in crude oils.

Pyrolysis experiments have shown that the lower molecular weight diamondoids i.e. the tricyclic adamantane (A; $C_{10}H_{16}$) and the pentacyclic diamantane (D; $C_{14}H_{20}$) are generated early during the formation of oil with destruction later in the cracking process (Fang et al., 2013). The diamantanes have been reported to be generated at greater maturity (1.6–2.7% EasyRo) than the adamantanes (1.0–2.3% EasyRo) (Fang et al., 2013). No similar data concerning the generation of tetracyclic cage structures could be found in the literature but these may have been formed at the same time. The high resistance to biodegradation observed for the tri- and pentacyclic structures is likely to also occur for the caged tetracyclics. The interest in the use of diamondoids as molecular proxies for determining the thermal maturity of oils and source rocks can be attributed to the relative differences in the thermal stability of their methyl substituted isomers (bridgehead substituted have greater stability), and their presence in oils in which other maturity indicators such as hopanes and methylphenanthrenes are absent (e.g. Dahl et al., 1999; Grice et al., 2000; Wei et al., 2007b). For example, Dahl et al. (1999) used variations in the concentrations of 3- + 4-methyldiamantanes within an oil

89   to determine changes in the mass of the oil and to assess the extent of oil cracking.

90   This was based on the assumption that the mass of 3- + 4-methyldiamantanes

91   remained constant during cracking. Various indices have also been applied. For

92   example, Fang et al. (2013) reported that in the generation stage of diamondoids

93   (<2.0% Easy-Ro), the Methyl Adamantane index (MAI) [= 1-MA/(1-MA + 2-MA)], was

94   found to be constant suggesting that it may be source dependent as it appeared to be

95   unaffected by thermal maturation. The authors concluded that MAI together with the

96   dimethyladamantane indices (see below) are useful for determining the source-region

97   affinities of oils at the generation stage. Various other indices have been proposed and

98   used as maturity and oil – source correlation indicators, these include the Methyl

99   Diamantane Index (MDI) [= 4-MD/(1-MD + 3-MD + 4-MD)], the DiMethyl Diamantane

100   Index-1 (DMDI-1) [= 4,9-DMD/(4,9-DMD + 3,4-DMD)], and DMDI-2; = [4,9-DMD/ (4,9-

101   DMD + 4,8-DMD)] (Chen et al., 1996; Zhang et al., 2005). Additional ratios include the

102   Ethyl Adamantane Index (EAI) [= 1-EA/(1-EA + 2-EA)], the DiMethyladamantane Index

103   (DMAI-1) [= 1,3-DMA/(1,2-DMA + 1,3-DMA)] and DMAI-2 [= 1,3-DMA/(1,3-DMA + 1,4-

104   DMA)], and the TriMethyl Adamantane Index (TMAI-1) [= 1,3,5- TMA/(1,3,5-TMA +

105   1,3,4-TMA)], and TMAI-2 [= 1,3,5- TMA/(1,3,5-TMA + 1,3,6-TMA)] (Grice et al., 2000;

106   Schulz et al., 2001; Wei et al., 2007b). Ratios based on methyl-substituted to parent

107   diamondoids e.g. MA/A [(1-MA + 2MA)/A] (Wingert, 1992) and ratios of tri- to

108   pentacyclic structures e.g. A/D (Fang et al., 2013) have also been used. There does

109   not however appear to be any indices based on tetracyclic caged hydrocarbons.

110   There are 5291 possible isomers for the tetracyclic structures of $C_{12}H_{18}$ hydrocarbons

111   with 12 skeletal carbon atoms (Cupas and Hodakows, 1974), of which few are stable.

112   One such is Tetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecane (iceane; Fig. S1) which can be

113   visualised as two chair cyclohexanes connected by three axial bonds (Cupas and

114   Hodakows, 1974). The trivial name iceane was coined by Fieser (cited by Cupas and

115 Hodakows, 1974) due to its structure being the geometrical hydrocarbon analog of

116 crystalline water. Iceane was synthesised in the 1970s (Hamon and Taylor, 1975;

117 Hamon and Taylor, 1976) and its crystal structure determined by X-ray diffraction

118 (Hamon et al., 1977). However, iceane is not the most stable isomer due to the strain

119 energy of *ca* 25 kcal/mole resulting from the three flagpole-flagpole interactions

120 (Farcasiu et al., 1974). The less symmetrical non-diamondoid structure

121 tetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodecane (2,4-ethanoadamantane; Fig. 1, Fig. S1) is reported

122 to be 6-7 kcal/mole more stable than iceane which also possesses unfavourable

123 entropy resulting from its high symmetry (Farcasiu et al., 1974). Of all the possible

124 tetracyclic caged hydrocarbons, the most stable ethanoadamantanes and iceanes are

125 most likely to persist during the cracking process (Osawa et al., 1980).

126 If ethanoadamantanes and/or iceanes are present and widespread in oils and

127 condensates they could assist with source correlation and provide either additional

128 information or help to confirm thermal maturity in conjunction with other indices. For

129 example, the low molecular weight adamantanes are quite volatile and may be lost *via*

130 evaporation at any stage from before the sample is collected to the point at which it is

131 analysed (Li et al., 2012). Hence, where the only diamondoids present are tricyclic

132 adamantanes, having an additional class of compound for reference could be useful as

133 evaporative losses may affect maturity indices. In this preliminary study, we first

134 searched for tetracyclic caged hydrocarbons (molecular ion, M$^+$ 162) and their methyl

135 substituted isomers (M$^+$ 176 and M$^+$ - CH$_3$ *m/z* 161) in a commercial mixture of

136 alkyldiamantanes derived from gas condensate (PolyDiamond Technologies,

137 Pleasanton, CA). This commercial mixture also contained much smaller quantities of

138 adamantanes, triamantanes and tetramantanes, as this was a relatively simple mixture

139 that was free from interferences typically associated with oil analysis. To reduce the

140 complexity further, we applied comprehensive two dimensional gas chromatography

141 with time of flight mass spectrometry (GC×GC-TOFMS) which has previously been

142 used very successfully to analyse diamondoid hydrocarbons in oils (e.g. Li et al., 2012;

143 Silva et al., 2013; Silva et al., 2011; Tran et al., 2010). As neither iceane nor 2,4-

144 ethanoadamantane were readily available commercially, the latter was synthesised

145 using a synthetic protocol previously reported in the literature (Farcasiu et al., 1974;

146 Osawa et al., 1980). Following tentative assignment of peaks present in the

147 alkyldiamantane mixture, their two dimensional (2D) retention times and time of flight

148 mass spectra were used to investigate 29 Australian crude oils and condensates.

149 Compounds were quantified based on concentration response curves of reference

150 standards of adamantane and diamantane.

151

152 **2. Material and Methods**

153 *2.1 Standards*

154 Diamantane (≥99 % purity) and the alkyldiamantane mixture (≥98 % purity, also

155 containing additional diamondoids including adamantanes, triamantanes and

156 tetramantanes) were supplied by PolyDiamond Technologies (Pleasanton, CA).

157 Adamantane (≥99%) was supplied by Sigma-Aldrich (Sydney, Australia). Solvents were

158 Reagent grade supplied by Honeywell International Inc, Muskegon, MI, USA.

159 *2.2 Synthesis of 2,4-ethanoadamantane*

160 Starting materials for the synthesis of 2,4-ethanoadamantane was obtained from

161 Sigma-Aldrich (Sydney, Australia) and used without further purification. Organic

162 solvents used in the reactions were dried prior to performing the reaction. Flash

163 chromatography was conducted using Merck silica gel 60 µm. Reactions were

164 monitored by thin layer chromatography using Merck silica gel 60 µm TLC plates with

165 aluminium backing and containing F254 fluorescent indicator. Compounds were

166 visualized on the TLC plate using potassium permanganate solution containing KMnO$_4$

167 (1.5 g), K$_2$CO$_3$ (10 g), 10% NaOH solution (1.25 mL) diluted to 200 mL with deionised

168 water. NMR spectra were collected using a Bruker Ultraspin 400 MHz spectrometer (^{1}H

169 400 MHz; ^{13}C 100 MHz).

170 The synthesis of 2,4-ethanoadamantane (tetracyclo[6.3.1.0]dodecane) **6** was carried

171 out as described in Fig. 1. The intermolecular Diels-Alder reaction of α-pyrone **1** and

172 *cis,cis*-1,5-cyclooctadiene **2** resulted in the cis-bicyclo[6.4.0]dodeca-4,9,11-triene **3**.

173 The intermediate **3** cyclizes *via* an intramolecular Diels-Alder reaction to yield

174 tetracyclo[6.4.0.0.0]dodec-10-ene **4** in 60% yield. The subsequent hydrogenation of

175 compound **4** yielded tetracyclo[6.4.0.0.0]dodecane **5** in excellent yield. 2,4-

176 ethanoadamantane **6** was then conveniently prepared by the Lewis acid catalysed

177 isomerization of compound **5**. The identity of compound **6** was confirmed by NMR

178 spectroscopy and mass spectral comparison (Fig. 1, Fig. S4). Further details of the

179 synthesis method are supplied in Supplementary Information.

180 *2.3 Samples*

181 Crude oils and condensates were supplied by Geoscience Australia or were available

182 from a previous study (Grice et al., 2000). Basic information concerning the properties

183 of the samples are presented in Table 1 and Fig. S2. Further information is available

184 from previous studies (Alexander et al., 1983; Edwards and Zumberge, 2005; Grice et

185 al., 2000; Palu et al., 2017; Spaak, 2017; Spaak et al., 2016; Volkman et al., 1983). To

186 minimise evaporative losses, the samples were analysed as *n*-hexane-soluble fractions

187 of whole crude oils and condensates. To check for possible interferences from aromatic

188 compounds, the Carnarvon oils were also fractionated by silica gel chromatography to

189 produce a 'Saturated' (*n*-hexane elution) and 'Aromatic' (7:3 *n*-hexane:dichloromethane

190 elution) fraction. Additional oils from older sources and outside of the Australian region

191 were also checked for the presence/absence of the of $C_{12}H_{18}$ tetracyclic hydrocarbons

192 but were not quantified.

193 *2.4 GC×GC-TOFMS analysis*

194 The *n*-hexane-soluble fractions of whole oils and condensates plus saturated and

195 aromatic fractions were analysed using a Leco Pegasus IV system equipped with dual

196 stage cryogenic modulator (Leco, Saint Joseph, MI, USA). For all samples the primary

197 column was a 60 m × 0.25 mm × 0.25 µm Rxi 5Sil MS (Restek, Bellefonte, PA, USA).

198 For the Carnarvon and Gippsland oils the primary column was coupled to a secondary

199 1.4 m × 0.25 mm × 0.25 µm DB-17ms (Agilent) column (Set-1). For the remaining oils

200 and condensates, the secondary column was a 1.3 m × 0.18 mm × 0.18 µm RXi-17MS

201 (Restek) (Set-2). Adamantane, diamantane, and the alkyldiamantane mixture plus a

202 subset of the Browse oils and condensates were analysed on both column sets to

203 ensure consistent results. The carrier gas was ultrahigh purity helium with constant flow

204 of 2 mL min^{-1} for Set-1 and 1 mL min^{-1} for Set-2. The inlet temperature was 310 °C with

205 1 µL injection. For Set-1 the conditions were: 40 °C (1 min isothermal), then 3 °C min^{-1}

206 to 320 °C, (isothermal 30 min) and a modulation period of 3 s, with secondary oven

207 offset of 1 °C and modulator offset 15 °C. For Set-2, the conditions were: 50 °C (1 min

208 isothermal), then 2.5 °C min^{-1} to 200 °C then 20 °C min^{-1} to 320 °C, (isothermal 10

209 min) with a modulation period of 4 s, with secondary oven offset 5 °C and modulator

210 offset 15 °C. The mass spectrometer electron ionisation was 70 *eV;* the ion source

211 temperature was 250 °C and the transfer line 320 °C. The scan speed was 100 Hz with

212 a range of 45–580 Daltons (Da). ChromaTOF (LECO) software package was used for

213 instrument control and data analysis. Minimum acceptable signal to noise ratio was

214 30:1. Coefficient of variation for triplicate analyses of lowest concentrations of

215 standards (0.25 µg mL^{-1}) was <3%. Mass spectra were compared with National

216 Institute of Standards & Technology (NIST, Gaithersburg, MD, USA) libraries plus in-

217 house TOFMS libraries.

218 2.4 Semi-quantification of tri-, tetra- and pentacyclic caged hydrocarbons

219 Adamantanes and diamantanes were quantified using external calibration curves of

220 adamantane and diamantane. Linear concentration response curves (r^2 > 0.99) were

221 generated from seven concentrations ranging from 0.25 µg mL^{-1} to 50 µg mL^{-1}. Peak

222 areas were calculated from the respective base peaks. The external calibration curves

223 were determined daily and selected standard concentrations were analysed after every

224 fourth sample to account for any variation throughout the sample sequence. As

225 ethanoadamantane was not available in pure crystalline form for quantification, the

226 peaks assigned as tetracyclic caged structures were semi-quantified based on the

227 linear concentration response curves of adamantane and diamantane standards which

228 gave very similar concentrations.

229 *2.5 Molecular properties computation*

230 Molecular properties and energies were computed using Spartan '16 version 2.0.7

231 (Wavefunction Inc, Irvine, CA). Strain energies were calculated using the program

232 settings 'Molecular mechanics'; total energies and thermodynamic properties were

233 calculated using 'Equilibrium Geometry' at ground state with 'Density Functional'

234 ωB97X-D and 6-31G*.

235

236 **3. Results and Discussion**

237 *3.1 Chromatography and peak assignment of alkyldiamantane mixture*

238 The orthogonal nature of GC×GC results in ordered chromatograms in which

239 relationships between molecules in terms of carbon number and polarity are easily

240   visualised. Analysis of the alkyldiamantane mixture revealed a clear linear relationship

241   between the carbon number of diamondoids and their 2D elution positions (Fig. 2). A

242   peak eluting midway between adamantane and diamantane, and between nC_{13} and

243   nC_{14} (Kovats Index for DB5 column (on GC×GC) = 1363.0), was found to have a

244   basepeak and M^+ of m/z 162 consistent with a C_{12} tetracyclic hydrocarbon (Fig. S3

245   peak i and Fig. S4A). The mass spectrum of this peak was very similar to that of iceane

246   (NIST library, Fig. S4B). However, the mass spectrum of the thermodynamically more

247   stable ethanoadamantane, isolated from Hodonin oil (Czechoslovakia) reported over

248   50 years ago (Hála et al., 1966), was also similar although the relative intensity of the

249   fragment ions were generally lower (Fig. S4C). As authentic standards of iceane and

250   ethanoadamantane were not available, we synthesised the latter (as this was the most

251   likely candidate due to its thermodynamic stability) in order to ascertain which C_{12}

252   tetracyclic hydrocarbon was present. The synthesised 2,4-ethanoadamantane eluted at

253   the same apolar and polar retention times as the tentatively assigned $C_{12}H_{18}$ tetracyclic

254   hydrocarbon and possessed an identical mass spectrum and we were therefore able to

255   unambiguously assign the m/z 162 peak as 2,4-ethanoadamantane (Fig. 1 and 3). As

256   only one peak with molecular ion m/z 162 was present, iceane was concluded not to be

257   present.

258   Eluting just before in the second dimension, i.e. less polar, the ethanoadamantane

259   peak were three peaks with basepeak m/z 161 and molecular ion m/z 176 ($C_{13}H_{20}$),

260   consistent with methyl substituted C_{12} tetracyclic hydrocarbons (Fig. S5 corresponding

261   to peaks ii – iv in Fig. S3). Due to the symmetry of iceane, only two methyl substituted

262   isomers are possible with one substituted on the thermally more stable bridgehead

263   carbon (Fig. S1, Table S1). No library mass spectra for methyliceanes were available

264   for comparison. With less symmetry than iceane, ethanoadamantane can have multiple

265   methyl substitutions including four possible bridgehead substituted structures (Fig. S1),

266   although it was previously reported that 8-methylethanoadamantane could not be

267   synthesised *via* bromination of 2,4-ethanoadamantane (Osawa et al., 1980).

268   Comparison of the mass spectra for 1-, 6- and 2-methylethanoadamantanes reported

269   by Osawa et al. (1980) with the three peaks in the alkyldiamantane mixture (Fig. S6

270   and S7), revealed reasonable matches for 1- and 6-methylethanoadamantane for the

271   first two eluting peaks (ii and iii) respectively although the mass spectra of these two

272   peaks are very similar. Based on the elution order and relative intensities of the base

273   peaks *m/z* 161 to *m/z* 176 reported by Osawa et al. (1980), the first eluting peak (ii)

274   should be 1-methylethanoadamantane and second (iii) 6-methylethanoadamantane

275   (Fig. S3 and S5A). However, the methylethanoadamantanes were previously analysed

276   (Osawa et al., 1980) using a different column configuration (highly polar

277   Nitroterephthalic acid modified polyethylene glycol capillary (FFAP) column compared

278   to the non-polar Phenyl Arylene polymer (virtually equivalent to a (5%-Phenyl)-

279   methylpolysiloxane) DB5 in the current study) and different types of mass

280   spectrometers were used. Hence, the peak assignment must be considered tentative.

281   For methyl-substituted adamantanes and diamantanes, the most stable isomer elutes

282   first on non-polar capillary columns but this is not necessarily the case for

283   methylethanoadamantanes. The second eluting peak (peak iii Fig. S3 and S5B) was

284   the most abundant as might be expected for the most stable isomer present in

285   relatively mature oils and condensates. The reported mass spectrum for 2-

286   methylethanoadamantane (Osawa et al., 1980) showed a molecular ion of *m/z* 176 that

287   was more abundant than that of *m/z* 161; the reverse was true for the third eluting peak

288   (iv) in the alkyldiamantane mixture (Fig. S6 and S5). In the alkyldiamantane mixture we

289   therefore assign the peak (i) with M^+ 162 as 2,4-ethanoadamantane and tentatively

290   assign the first two eluting peaks with M^+ 176, as 1- and 6-methylethanoadamantane

291   respectively. The third in the series and least abundant peak in the alkyldiamantane

292   mixture could either be the fourth bridgehead substituted isomer 8-

293   methylethanoadamantane or possibly a less stable non-bridgehead substituted isomer.

294   The 2D elution region for the tentatively assigned ethanoadamantane peaks is also that

295   of alkylbenzenes. However, there was no evidence to suggest that any aromatic

296   hydrocarbons or heterocyclic compounds were present in the alkyldiamantane mixture.

297   The third $C_{13}H_{20}$ peak in the alkyldiamantane mixture (peak iv Fig. S3 and S5C) could

298   therefore not be assigned. Additional peaks with elution positions and mass spectra

299   consistent with dimethylethanoadamantanes were also present in low abundance.

300   *3.2 Peak assignment of Australian oils and condensates*

301   Having recorded the 2D elution times of 2,4-ethanoadamantane plus the tentatively

302   assigned peaks corresponding to the methyl-substituted homologues and obtained

303   GC×GC-TOFMS mass spectra, a range of Australian crude oils and condensates were

304   assessed. Peaks matching the elution times and mass spectra were present for 2,4-

305   ethanoadamantane and the tentatively assigned 1- and 6-methylethanoadamantanes

306   in most of the oils analysed. Interestingly, many oils also contained an additional peak

307   eluting at the same time (within the modulation period) as the unassigned peak in the

308   alkyldiamantane mixture but with mass spectra more closely matching that reported by

309   Osawa et al. (1980) for 2-methylethanoadamantane (Fig. S6). The main difference

310   being more intense *m/z* 79 and 91 ions in the TOF mass spectrum of the peak within

311   the oils compared to the reported quadrupole mass spectrum (Fig. S6) as also

312   observed for the parent compound (Fig. 1). As the oils and condensates had been

313   analysed as *n*-hexane-soluble fractions of whole oils to minimise losses for

314   quantification purposes, there was however a possibility of interferences from

315   alkylbenzenes. The oils were therefore subject to silica gel chromatography to

316   fractionate them into saturate and aromatic fractions. All of the peaks attributed to

317   caged tetracyclic hydrocarbons were present only in the saturated fraction.

318   Alkylbenzenes containing the same fragment ions as the tetracyclic hydrocarbons i.e.

13

319 *m/z* 91, 105, 119, 133 were present in the aromatic fraction of some of the oils close to,

320 but not at exactly the same elution times as, the assigned peaks. We therefore

321 tentatively assigned this additional peak with molecular ion *m/z* 176 as

322 2-methylethanoadamantane and rejected the possibility of major interferences from

323 alkylbenzenes. To check that the assigned peaks were not just an Australian oils

324 phenomena or restricted to a limited range of reservoir age, some additional oils,

325 including non-Australian and older reservoirs, were analysed and all were found to

326 contain at least one of the tentatively identified compounds thus suggesting that they

327 are common and therefore may have universal application (data not shown).

328

329 *3.3 Semi-quantification of Australian oils and condensates*

330 The assigned peaks were semi-quantified based on external calibration curves of

331 adamantane and diamantane standards. These produced the same or very similar

332 calculated concentrations and therefore an average was taken where a small

333 difference occurred. For all of the oils analysed, the concentrations of the tentatively

334 identified ethanoadamantane were less than that of adamantane but typically similar to

335 that of the diamantane (Table S2 and Fig. S7). For two oils, Caswell-1 and Caswell-2,

336 both ethanoadamantane and diamantane were absent (Table S2). Both of these oils

337 are non-biodegraded but cluster with other Cretaceous oils of the Browse basin (Family

338 IV, Table 1, Fig. S2). The highest concentrations of ethanoadamantane (up to 859

339 ppm) were recorded in the same family (IV) but were biodegraded (Tables 1 and S2,

340 Fig. S2). For the light Rough Range oil, originating from Australia's first bore in 1953 in

341 the Carnarvon basin, 2,4-ethanoadamantane was present at low abundance (7 ppm)

342 but diamantane was not observed (Table S2). Of the methyl substituted isomers, the

343 second eluting peak, tentatively assigned as 6-methylethanoadamantane, was

344 consistently the most abundant despite the crude oils and condensates possessing a

14

345 range of maturities and levels of biodegradation (Tables 1 and S2). Generally, the

346 concentrations of the tentatively identified methylethanoadamantanes relative to the

347 parent structure showed a similar pattern to that of the diamondoids (Table S2, Fig.

348 S7). This is explored further in section 3.5.

349 The high resistance to biodegradation observed for the tri- and pentacyclic

350 diamondoids, appears to also apply for the tetracyclics. Although concentrations vary

351 considerably (Table S2) for the two most biodegraded oils, Mardie (Peter and

352 Moldowan (P&M; scale 8 (Peters et al., 2007)) and Lakes Entrance (P&M scale 7)

353 (Grice et al., 2000; Volkman et al., 1983), this is likely source-related as the former is

354 from the Carnarvon basin and the latter from Gippsland basin (Tables 1 and S2). Both

355 of these oils contained lower concentrations of diamondoids in general compared to the

356 biodegraded Cretaceous oils of the Browse basin and less than the light Jurassic

357 Montara oil from the Bonaparte basin (Table S2 and Fig. S7).

358

359 *3.4 Fate of ethanoadamantanes and diamondoids*

360 Despite the recalcitrant nature of the diamondoids, biodegradation does appear to

361 occur as evidenced by the presence of their corresponding carboxylic acids discovered

362 in oil sands process-affected waters (OSPW) derived from the oil extraction industry in

363 Alberta Canada (Rowland et al., 2011a; Rowland et al., 2011b). Similarly there is

364 evidence for biodegradation of the alkylsubstituted homologues of ethanoadamantane

365 to their corresponding carboxylic acids (Wilde and Rowland, 2018). By converting the

366 acids extracted from OSPW to hydrocarbons, Wilde and Rowland (2018) not only

367 confirmed the presence of numerous tri- and pentacyclic diamondoid acids, they also

368 tentatively assigned several peaks as "alkyl 2,4-cyclopentano-adamantanes" i.e.

369 alkylated ethanoadamantanes and by inference their corresponding carboxylic acids.

370 Mass spectra obtained by GC×GC-TOFMS assigned by Wilde and Rowland (2018) as

371 methyl, dimethyl and trimethyl substituted ethanoadamantane closely matched mass

372 spectra observed in the oils reported herein. Peaks with mass spectra consistent with

373 higher degrees of alkylation were most prominent in biodegraded Cretaceous oils from

374 the Browse basin e.g. Cornea-1 (Fig.3 and Fig. S8). A study of the relative abundance

375 of the ethanoadamantane acids compared to the diamondoid acids might prove

376 informative e.g. when interpreting diamondoid indices.

377

3.5 Comparison of ethanoadamantane and diamondoid indices

379 The diamondoid indices MAI and MDI have been widely applied (e.g. Chen et al., 1996;

380 Fang et al., 2013; Grice et al., 2000; Li et al., 2000; Li et al., 2012; Schulz et al., 2001;

381 Wang et al., 2006; Wei et al., 2007a; Wei et al., 2007b) but some limitations seem to

382 apply. For example, MDI was found not to be a useful maturity parameter for over-

383 mature carbonate-rich source rocks (>2.0% Ro) (Li et al., 2000). The MAI may be

384 compromised due to evaporative processes affecting the lower molecular weight

385 compounds (Li et al., 2012). Having additional indices to help corroborate the MAI or

386 MDI may therefore be useful or may highlight unusual samples. However, the

387 diamondoid indices are based on the relative concentrations of bridgehead to total

388 methyl isomers whereas our study has only tentatively assigned bridgehead isomers.

389 Many of the samples also possessed additional peaks eluting later in the apolar

390 primary dimension with base peak or prominent fragment ions *m/z* 161 and M$^+$ 176

391 (Fig. 3 and Fig. S8). These tended to be more prominent in biodegraded oils such as

392 Lakes Entrance and Cornea-1. These are likely to be non-bridgehead

393 methylethanoadamantanes but further research would be required to unambiguously

394 confirm this. As diamondoid indices tend to be applied in the absence of other maturity

395 or source indicators, the limited presence of these additional peaks in non-biodegraded

396   oils may not be problem. Within our sample set, 24 of the oils and condensates

397   possessed at least some of these additional methylethanoadamantanes, so we

398   hypothesised that a relationship might exist related to their thermal stability. We

399   therefore explored the potential of a novel index, the methylethanoadamantane index

400   (MEI) based on the same thermal stability rationale as MAI and MDI. For the MEI, this

401   is the ratio of the combined peak areas of the three stable bridgehead isomers i.e. 6-

402   methylethanoadamantane (6-ME) + 1-ME + 2-ME divided by the sum of peak areas for

403   all methyl substituted isomers present (ΣTotal ME; Equation 1).

404   Equation 1: MEI = Σ(6-ME + 1-ME + 2-ME)/ΣTotal ME

405   Combining data from 24 crude oils and condensates regardless of basin, reservoir or

406   biodegradation status (including only peaks with acceptable mass spectra and elution

407   times) allowed linear regression to be performed on a reasonable sized dataset to test

408   for association between the MEI and the equivalent diamondoid indices (Table 2). A

409   significant positive association was found between the MEI and MAI (r^2 = 0.203,

410   p<0.05) and a significant negative association was found between MEI and MDI (r^2 =

411   0.246 p <0.05). This suggests that the MEI could be used as a substitute for MAI if

412   water washing or evaporative losses were suspected.

413   Fang et al. (2013) reported that the ratios A/D and MA/MD increase with increasing

414   thermal maturity in the range 1.0–2.0% EasyRo, suggesting that these diamondoid

415   concentration ratios can be used to assess the thermal maturity of oils at this maturity

416   stage. Using the combined dataset of Australian oils with acceptable criteria (Table 2),

417   it was found that there was a significant association between A/D and the ratio

418   Ethanoadamantane/Diamantane (E/D) with r^2 of 0.204 (p < 0.05, n = 26) and a stronger

419   association between A/D and A/E with r^2 of 0.460 (p < 0.0005, n = 26). Even stronger

420   associations were found for the methyl isomer versions of these ratios: the linear

421   regression of ΣMA/ΣMD and ΣME/ΣMD had r^2 of 0.287 (p < 0.005, n = 26) and

17

422 ΣMA/ΣME had r^2 = 0.781 (p < 0.0001, n = 26; Fig. 4). For all of the plots, there were

423 some noticeable deviations from the regression line of fit, e.g. for the regression of all

424 oils for ΣMA/ΣMD versus ΣMA/ΣME, Tuna-4 showed considerable deviation from the

425 linear regression line whereas the biodegraded Lakes Entrance oil, from the same

426 basin, plotted very close to the line (Fig. 4). As these deviations may be related to

427 either the reservoir age, basin or their biodegradation level, the relationships between

428 ratios were explored further based on previously established grouping of the oils and

429 condensates (Alexander et al., 1983; Edwards et al., 2016; Edwards and Zumberge,

430 2005; Grice et al., 2000; Palu et al., 2017; Volkman et al., 1983).

431 From assessing the data based on hierarchical cluster analysis reported for families of

432 oils and condensates shown in Fig. S2 (Edwards et al., 2016; Palu et al., 2017), it was

433 found that only family IV did not show a significant relationship (r^2 = 0.472, p = 0.2, n =

434 5) between ΣMA/ΣMD and ΣMA/ΣME (Table 2). The regression excluded the light

435 non-biodegraded oils from the Caswell field as only the five biodegraded oils from this

436 Cretaceous family (Table 1) contained ethanoadamantanes and diamantanes

437 suggesting that biodegradation may influence the relationship. However, the Carnarvon

438 oils, containing the heavily biodegraded Mardie crude oil, light oils e.g. Barrow and

439 mixtures (Table 1), showed a strong positive linear relationship for this ratio (r^2 = 0.881,

440 p <0.01, n = 6) despite the range in biodegradation status suggesting that this is not a

441 major factor. Clearly there are many aspects that may affect biomarker and other

442 indicator ratios so more research is required to tease out possible influences on the

443 concentrations and ratios reported in this preliminary study.

444 *3.6 Potential uses and future work*

445 The relatively low volatility of the ethanoadamantanes compared to the adamantanes

446 may provide a useful check on indices based on the latter. Although the ethyl

447 substituted adamantanes, which have a similar molecular weight (164 Da as

448 ethanoadamantane (162 Da), are less volatile than the methyladamantanes they are

449 more likely to be affected by biodegradation due to the exposed ethyl group and hence,

450 the use of the Ethyl Adamantane Index (EAI) as an alternative to the MAI maturity

451 indicator is problematic. For example, the oils of the Carnarvon basin were found to

452 have reasonably similar MAI, consistent with a previous study (Grice et al., 2000), as

453 expected for maturity indicators unaffected by biodegradation but calculation of EAI

454 revealed a high degree of variation between light, heavy biodegraded and mixed oils

455 e.g. Barrow 19%, Mardie 74% and Windalia 39% (Table 2). Also, in situations where

456 diamantanes are absent, the ethanoadamantanes could be used as a substitute given

457 their close association with diamantane and methyldiamantane concentrations (Table

458 2, S2, Fig. 4). Ideally, future studies could unambiguously confirm the identity of the

459 less stable non-bridgehead methylethanoadamantanes which will improve the MEI

460 which could then be applied to a larger selection of oils with a greater range of

461 maturities.

462 At present, despite increasing popularity, the availability of GC×GC-TOFMS is still

463 limited compared to GC-MS. However, analysis of the current samples by GC-MS in

464 full-scan mode produced unresolved complex mixtures in many of the oils. To test if

465 2,4-ethanoadamantane and the tentatively assigned methyl-substituted isomers could

466 be detected using GC-MS selected ion monitoring (SIM), the alkyldiamantane mixture

467 plus both a saturates only and a combined saturates and aromatics fraction of the

468 biodegraded Lakes Entrance crude oil were analysed using a SIM method (Fig. S9).

469 Although both the parent and methyl isomers could be detected in all the analyses,

470 care would need to be taken if aromatics were present due to the similarities of

471 alkylbenzene mass spectra and the elution time window. Due to their alkyl chain,

472 alkylbenzenes can elute with the saturated fraction during commonly used fractionation

473 procedures so it is recommended that protocols are checked to ensure that pure

474 saturates fractions are obtained in order to reduce the risk of misidentification of peaks.

475 Analyses of source rocks was outside the scope of this study. Further research could

476 be focused on the relative concentrations of ethanoadamantanes in rocks of varying

477 maturity and possibly pyrolysis experiments (*sensu* Fang et al., 2013) to ascertain

478 when these compounds are generated.

479

4. Conclusions

481 This study has for the first time identified and semi-quantified the $C_{12}H_{18}$ caged

482 hydrocarbon 2,4-ethanoadamantane and tentatively assigned three of its

483 methyl-substituted isomers in a range of Australian crude oils and condensates. Peaks

484 consistent with additional methyl and dimethyl substituted homologues were also

485 observed. Like the diamondoids, these tetracyclic structures appear to be highly

486 resistant but not immune to biodegradation. Concentrations of these compounds were

487 generally similar to that of the pentacyclic diamondoids (diamantanes) producing

488 significant linear relationships between A/D and A/E, and also the equivalent methyl

489 isomer ratios. A novel ratio, MEI, based on the relative thermal stabilities of the

490 methylethanoadamantanes showed statistically significant relationships ($p < 0.05$) with

491 diamondoid maturity indices. The relatively lower volatility of ethanoadamantanes

492 compared to adamantanes in conjunction with their resistance to microbial attack make

493 these tetracyclic structures suitable for studies where evaporative losses and

494 biodegradation are an issue. Measurement of ethanoadamantane and its alkylated

495 homologues in conjuncture with the commonly applied diamondoids may therefore

496 prove useful for oil-source correlations and maturity studies but further investigation of

497 a wider range of samples is necessary.

Supporting information

Additional synthesis method details and NMR spectra; molecular properties of tri-, tetra- and pentacyclic caged hydrocarbons; concentrations of ethanoadamantanes and diamondoids in crude oils and condensates; comparative chemical structures of iceane and 2,4-ethanoadamantane with carbon position numbers; dendrogram comparing Basin fluid families; GC×GC-TOFMS chromatograms of elution region of tetracyclic caged hydrocarbon peaks referred to in text with associated mass spectra; a clustered barchart giving an overview of concentrations; and a GC-MS SIM chromatogram of the ethanoadamantanes and diamantanes.

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Table and Figure Legends

Tables

Table 1: Locations and ages of Australian crude oils and condensates sampled

Table 2 Comparison of indices derived from 2,4-ethanoadamantanes and diamondoids

Figures

Fig. 1: Synthesis of 2,4-ethanoadamantane and mass spectra produced by (A) GC-MS (quadrupole mass spectrometer) and (B) GC×GC-TOFMS (time of flight mass spectrometer).

Fig. 2: Two dimensional gas chromatography elution positions of tetracyclic caged hydrocarbons (red squares) relative to diamondoids and *n*-alkanes. MA = methyladamantane, EA = ethyladamantane, MD = methyldiamantane, *n*Cx = alkane carbon number.

Fig. 3: Peaks with mass spectra consistent with methyl (C1), dimethyl (C2) and trimethyl (C3) ethanoadamantanes present in the Cretaceous Cornea-1 oil. Some peaks were also present in other oils and condensates, and in the alkyldiamantane mixture.

Fig. 4: Linear regression of the ratio of the sum of methyladamantanes (ΣMA)/sum of methylethanoadamantanes (ΣME) versus ΣMA/sum of methyldiamantanes (ΣMD). Closed black circles highlight biodegraded oils. Names of oils referred to in text are highlighted for reference.

646   Table 1 Locations and ages of Australian crude oils and condensates sampled

Well	Family*	Sample	Basin	Reservoir Age	Biodeg
Caswell-1	IV	Light oil	Browse	Cret.	N
Caswell-2	IV	Light oil	Browse	Cret.	N
Gwydion-1	IV	Oil	Browse	Cret.	Y
Cornea-1	IV	Oil	Browse	Cret.	Y
Focus-1	IV	Oil	Browse	Cret.	Y
Sparkle-1	IV	Oil	Browse	Cret.	Y
Cornea South	IV	Oil	Browse	Cret.	Y
Titanichthys-1	III	Condensate	Browse	L. Jura. – E. Cret.	N
Ichthys-1A	III	Condensate	Browse	L. Jura. – E. Cret.	N
Dinichthys-1	III	Condensate	Browse	L. Jura. – E. Cret.	N
Dinichthys North-1	III	Condensate	Browse	Jura.	N
Concerto-1	III	Condensate	Browse	Jura.	
Kronos-1	III	Condensate	Browse	Jura.	N
Prelude-1A	III	Condensate	Browse	L. Jura. – E. Cret.	N
Mimia-1	III	Condensate	Browse	L. Jura. – E. Cret.	N
Scott Reef-1	II	Condensate	Browse	Jura.	N

North Scott Reef-1	II	Condensate	Browse	Jura.	N
Calliance-1	II	Condensate	Browse	Jura.	N
Brecknock-2	II	Condensate	Browse	Jura.	N
Gorgonichthys-1	II	Condensate	Browse	Jura.	N
Montara	I	Light oil	Bonaparte	Jura.	N
Mardie		Oil	Carnarvon	Cret.	Severe (8)
Windalia		Oil	Carnarvon	Cret.	Mix
Barrow		Oil	Carnarvon	Cret.	N (0)
Rough Range		Oil	Carnarvon	Cret.	N (0)
Rankin-1		Oil	Carnarvon	Triassic	Mixed
Eaglehawk		Oil	Carnarvon	Triassic	Mixed
Tuna-4		Oil	Gippsland	Tertiary	Mod (3)
Lakes Entrance		Oil	Gippsland	Tertiary	Severe (7)

647   *Family grouping by Geoscience Australia cluster analysis (Fig. S2). Cret. = Cretaceous; Jura = Jurassic; L. = Late; E. Early; Biodeg =

648   biodegraded; Peters and Moldowan biodegradation scale, if previously reported (cited in text), given in parentheses, if not then typical

649   indicators of biodegradation e.g. absence of *n*-alkanes, presence of unresolved complex mixture (UCM) indicated by Y = Yes or N = No

650

Table 2 Comparison of indices derived from 2,4-ethanoadamantanes and diamondoids

Oil well	MEI*	MAI	EAI	MDI	A/D	A/E	E/D	ΣMA/ΣMD	ΣMA/ΣME*	ΣME*/ΣMD
Caswell-1	n/a	0.53	n/a	0.32	n/a	n/a	n/a	7.1	n/a	n/a
Caswell-2	n/a	0.56	n/a	0.31	n/a	n/a	n/a	5.7	n/a	n/a
Gwydion-1	0.73	0.69	0.47	0.40	5.19	5.01	1.03	7.2	4.6	1.6
Cornea-1	0.67	0.72	0.56	0.36	2.88	5.58	0.52	5.0	4.9	1.0
Focus-1	0.72	0.81	0.47	0.38	4.34	5.70	0.76	11.0	9.2	1.2
Sparkle-1	0.61	0.69	0.43	0.41	5.00	4.42	1.13	9.0	5.7	1.6
Cornea South	0.70	0.64	0.46	0.39	6.47	5.25	1.23	9.2	5.2	1.8
Titanichthys-1	0.76	0.63	0.33	0.38	5.81	3.94	1.47	10.5	6.8	1.6
Ichthys-1A	0.72	0.63	0.34	0.33	5.79	4.33	1.34	8.4	7.9	1.1
Dinichthys-1	0.77	0.63	0.34	0.31	5.23	3.90	1.34	9.0	6.6	1.4
Dinichthys N-1	0.73	0.75	0.47	0.37	8.06	6.25	1.29	12.4	7.3	1.7
Concerto-1	0.80	0.68	0.39	0.39	7.77	6.74	1.15	12.0	7.4	1.6
Kronos-1	0.67	0.69	0.47	0.48	5.78	6.75	0.86	9.4	6.7	1.4
Prelude-1A	0.75	0.67	0.33	0.33	7.01	4.88	1.44	10.9	6.7	1.6
Mimia-1	0.75	0.67	0.21	0.33	10.59	8.53	1.24	18.4	10.5	1.8
Scott Reef-1	n/a	0.71	0.42	0.41	5.70	5.68	1.00	10.0	7.4	1.4

N. Scott Reef-1	0.73	0.71	0.42	0.38	6.44	5.66	1.14	13.1	8.3	1.6
Calliance-1	0.80	0.70	0.42	0.40	6.83	4.62	1.48	11.3	7.8	1.4
Brecknock-2	0.83	0.72	0.43	0.41	6.36	5.62	1.13	12.3	8.5	1.4
Gorgonichthys-1	0.77	0.74	0.45	0.38	8.33	7.57	1.10	15.7	9.3	1.7
Montara	0.71	0.67	0.05	0.40	2.59	3.13	0.83	3.9	5.9	0.6
Mardie	0.58	0.63	0.74	0.48	0.30	0.32	0.93	0.7	0.7	1.1
Windalia	0.57	0.64	0.39	0.48	2.36	8.93	0.26	10.0	5.1	2.0
Barrow	0.74	0.70	0.19	0.47	5.37	3.84	1.40	18.2	13.8	1.3
Eaglehawk	0.64	0.66	0.46	0.52	n/a	1.23	n/a	8.5	6.3	1.4
Rankin	0.55	0.58	0.34	0.38	0.84	0.86	0.98	1.8	1.8	1.0
Roughrange	n/a	0.69	0.24	n/a	3.43	2.58	1.33	2.0	4.6	0.4
Lakes entrance	0.61	0.63	0.35	0.48	3.91	2.16	1.81	4.8	5.1	0.9
Tuna4	n/a	0.64	0.31	0.67	2.07	2.64	0.78	9.3	4.0	2.3

MEI = Methyl Ethanoadamantane Index: Σ(6-ME + 1-ME + 2-ME)/ΣTotal methylethanoadamantanes (ME)

MAI = Methyl Adamantane Index: 1-MA/(1-MA + 2-MA)

EAI = Ethyl Adamantane Index: 1-EA/(1-EA + 2-EA)

MDI = Methyl Diamantane Index: 4-MD/(1-MD + 3-MD + 4-MD)

A/D = Adamantane/Diamantane

A/E = Adamantane/Ethanoadamantane

E/D = Ethanoadamantane/Diamantane

ΣMA/ΣMD = (1-MA + 2-MA)/(1-MD + 3-MD + 4-MD)

ΣMA/ΣME = (1-MA + 2-MA)/(6-ME + 1-ME + 2-ME)

ΣME/ΣMD = (6-ME + 1-ME + 2-ME)/1-MD + 3-MD + 4-MD)

n/a = not applicable e.g. due to undetected peaks

*Note that methylethanoadamantane assignment tentative

Fig. 1: Synthesis of 2,4-ethanoadamantane and mass spectra produced by (A) GC-MS (quadrupole mass spectrometer) and (B) GC×GC-TOFMS (time of flight mass spectrometer).

Fig. 2: Two dimensional gas chromatography elution positions of tetracyclic caged hydrocarbons (red squares) relative to diamondoids and *n*-alkanes. MA = methyladamantane, EA = ethyladamantane, MD = methyldiamantane, *n*Cx = alkane carbon number.

Fig. 3: Peaks with mass spectra consistent with methyl (C1), dimethyl (C2) and trimethyl (C3) ethanoadamantanes present in the Cretaceous Cornea-1 oil. Some peaks were also present in other oils and condensates, and in the alkyldiamantane mixture.

Fig. 4: Linear regression of the ratio of the sum of methyladamantanes (ΣMA)/sum of methylethanoadamantanes (ΣME) versus ΣMA/sum of methyldiamantanes (ΣMD). Closed black circles highlight biodegraded oils. Names of oils referred to in text are highlighted for reference.

Supplementary Information

Title: Comparison of tri-, tetra- and pentacyclic caged hydrocarbons in Australian crude oils
and condensates

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Synthesis of 2,4-ethanoadamantane

Experimental

1. Tetracyclo[6.4.0.0.0]dodec-10-ene (**4**)
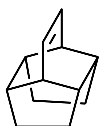

A mixture of *cis,cis*-1,5-cyclooctadiene (0.5 mL) and α-pyrone (0.1 mL, 1.0 mmol) was heated under reflux for 24 h. The reaction mixture was then diluted with DCM (20 ml) and absorbed on to silica gel. The material was then purified by flash column chromatography to yield tetracyclo[6.4.0.0.0]dodec-10-ene **4** (0.1 g, 60%) as a white powder. ^{1}H NMR (CDCl$_3$, 400 MHz): 6.20 (dd, 2H, J = 3.5 Hz, J = 4.8 Hz), 2.22-2.15 (m, 2H), 1.76-1.67 (m, 4H), 1.50-1.40 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): 131.1, 42.7, 40.2, 25.8; [GC-MS]: 160 m/z

2. Tetracyclo[6.4.0.0.0]dodecane **(5)**
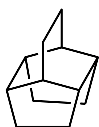
A solution of compound **4** (80 mg, 0.5 mmol) and catalytic amount of platinum oxide (approx. 10 mg) in anhydrous DCM (10 mL) was stirred under a hydrogen atmosphere for 24 h. The reaction mixture was filtered over a pad of celite and concentrated under reduced pressure to obtain tetracyclo[6.4.0.0.0]dodecane **5** (65 mg, 80%) as a yellowish powder. The crude material was used without further purification. ^{1}H NMR (CDCl$_3$, 400 MHz): 2.02-1.92 (m, 3H), 1.68-1.59 (m, 9H), 1.27-1.56 (m, 6H); [GC-MS]: 162 m/z.

3. 2,4-ethanoadamantane **(6)**
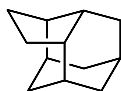
A solution of tetracyclo[6.4.0.0.0]dodecane **5** in anhydrous DCM (5 mL) was added dropwise to a stirred cooled (0 ˚C) suspension of pulverized aluminium chloride (1.5 g) in anhydrous DCM (10 mL) under an inert atmosphere. The reaction mixture was then brought up to r.t. and stirred for 1 h. The

reaction mixture was then cooled to 0 ˚C and water was added dropwise to decompose the $AlCl_3$. The organic layer was then extracted, dried ($MgSO_4$) and concentrated under reduced pressure to yield 2,4-ethanoadamantane **6** (49 mg, 75%). The isolated material did not require purification. ^{13}C NMR (CDCl₃, 100 MHz): 42.0, 39.6, 37.1, 33.3, 32.1, 29.6, 26.7; [GC-MS]: 162 m/z.

Table S1 Molecular properties and calculated energies of tri-, tetra- and pentacyclic caged hydrocarbons computed using Spartan '16 version 2.0.7 (Wavefunction Inc, Irvine, CA). Strain energies were calculated using the program settings 'Molecular mechanics'; total energies and thermodynamic properties were calculated using 'Equilibrium Geometry' at ground state with 'Density Functional' ωB97X-D and 6-31G*.

Molecule	Formula	Mol Wt. (amu)	Energy (total) (au)	Energy (strain) (kJ/mol)	ZPE kJ/mol	H^O (au)	Cv (J/mol.K)	S^O (J/mol.K)	G^O (au)
Adamantane (A)	$C_{10}H_{16}$	136.238	-390.627	74.35	649.20	-390.372	133.60	340.10	-390.411
1-MA	$C_{11}H_{18}$	150.265	-429.935	108.94	722.14	-429.651	159.09	365.31	-429.692
2-MA	$C_{11}H_{18}$	150.265	-429.931	100.44	725.04	-429.646	155.61	363.68	-429.687
Iceane (I)	$C_{12}H_{18}$	162.276	-468.012	202.71	748.16	-467.719	153.46	346.26	-467.758
1-MI	$C_{13}H_{20}$	176.303	-507.320	240.21	823.08	-506.997	176.96	374.30	-507.040
2-MI	$C_{13}H_{20}$	176.303	-507.310	252.99	823.14	-506.987	176.66	382.12	-507.030
Ethanoadamantane (E)	$C_{12}H_{18}$	162.276	-468.023	162.12	746.44	-467.730	155.33	358.65	-467.770
6-ME	$C_{13}H_{20}$	176.303	-507.328	211.22	820.22	-507.005	180.37	382.18	-507.049
1-ME	$C_{13}H_{20}$	176.303	-507.330	199.61	819.05	-507.008	181.27	384.21	-507.052
2-ME	$C_{13}H_{20}$	176.303	-507.329	203.03	820.02	-507.007	180.56	382.71	-507.050
Diamantane (D)	$C_{14}H_{20}$	188.314	-545.445	156.03	842.67	-545.115	176.92	374.12	-545.157
4-MD	$C_{15}H_{20}$	202.341	-584.750	203.07	917.01	-548.390	201.35	396.80	-584.435
1-MD	$C_{15}H_{20}$	202.341	-584.750	203.03	916.99	-584.390	201.50	397.14	-584.435
3-MD	$C_{15}H_{20}$	202.341	-584.748	182.30	917.78	-584.390	200.08	399.17	-584.434

M = methyl

amu = atomic mass units

au = atomic units (1 atomic unit = 2625 kJ/mol)

ZPE = Zero point energy

H^O = enthalpy

Cv = Heat capacity at constant volume

S^O = Entropy (note that calculations are problematic in part due to the harmonic approximation.)

G^O = Gibbs free energy

Table S2 Concentrations (µg/g oil) of tri-, tetra- and pentacyclic caged hydrocarbons in a range of Australian crude oils and condensates

Oil well	A	1-MA	2-MA	E	1-ME*	6-ME*	2-ME*	D	4-MD	1-MD	3-MD
Caswell-1	144	500	443	0	0	0	0	0	42	55	36
Caswell-2	118	487	378	0	0	0	0	0	48	60	44
Gwydion-1	3914	10485	4766	781	864	1817	634	754	847	670	589
Cornea-1	4792	11745	4575	859	977	1804	560	1666	1179	1208	863
Focus-1	2645	14327	3446	464	535	1076	312	609	608	578	432
Sparkle-1	1629	5996	2646	369	365	909	243	326	393	315	250
Cornea South	1526	4100	2324	291	311	718	198	236	271	233	195
Titanichthys-1	286	959	563	73	47	118	60	49	55	42	48
Ichthys-1A	203	571	342	47	0	75	41	35	36	35	38
Dinichthys-1	259	839	489	66	52	102	47	49	46	50	51
Dinichthys N-1	1020	3361	1110	163	138	367	108	127	132	115	114
Concerto-1	615	1785	843	91	92	187	75	79	86	68	65
Kronos-1	1387	3610	1593	206	194	430	156	240	264	152	137
Prelude-1A	309	886	508	63	54	100	54	44	42	45	41
Mimia-1	996	3171	1542	117	110	260	79	94	84	89	83
Scott Reef-1	827	2687	1099	146	129	270	110	145	153	112	112
N. Scott Reef-1	825	2996	1228	146	129	270	110	128	122	103	98
Calliance-1	496	1851	777	107	82	174	80	73	93	72	68
Brecknock-2	585	2109	833	104	93	185	68	92	98	73	68
Gorgonichthys-1	907	3726	1281	120	138	298	101	109	121	99	98
Montara	755	2714	1345	241	192	398	93	291	422	380	249
Mardie	25	132	77	78	87	153	69	84	137	90	58
Windalia	166	779	446	19	63	137	41	70	58	38	26
Barrow	252	1037	441	66	37	48	22	47	38	26	17

Eaglehawk	383	2092	1074	148	128	288	90	112	192	87	92
Rankin	54	255	188	63	58	145	41	64	94	83	68
Roughrange	9	48	22	7	5	10	0	0	5	4	26
Lakes entrance	303	1536	891	115	113	271	89	147	244	156	109
Tuna4	119	476	258	55	57	102	26	30	22	24	33

Adamantane (A), 2,4-ethanoadamantane (E), Diamantane (D) and their methyl-substituted isomers (M).

*carbon numbers of methyl isomers of ethanoadamantane tentatively assigned.
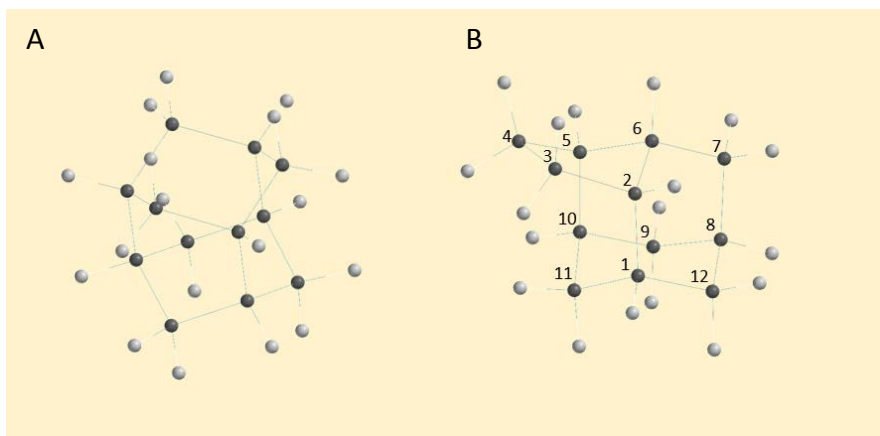
Fig. S1. Chemical structures of iceane (A) and 2,4-ethanoadamantane showing bridgehead positions at 1, 2, 6 and 8 (B).
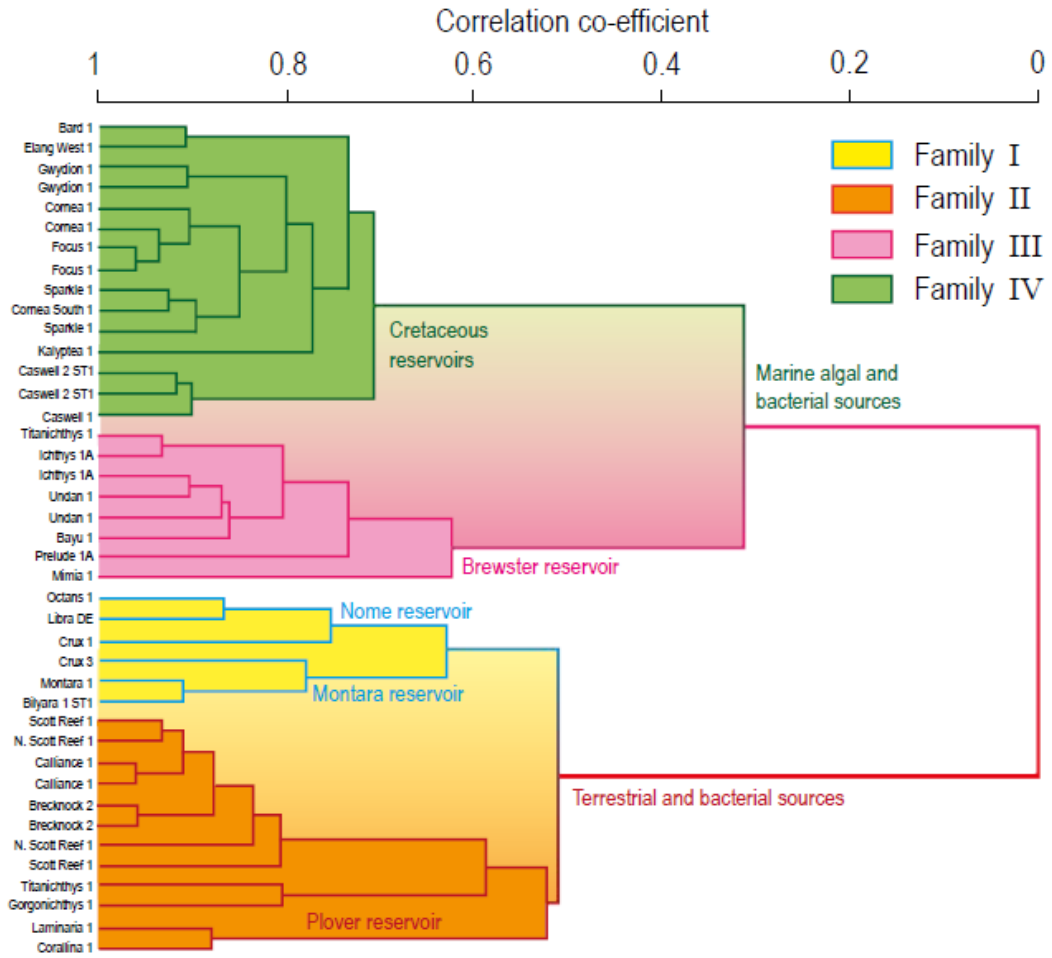
Fig. S2: Dendrogram comparing Browse Basin fluid families with those of selected samples from the Bonaparte Basin based mainly on ^{13}C of saturates and aromatics, tri- and tetracyclic terpanes and sterane biomarkers (after Edwards et al., 2016).
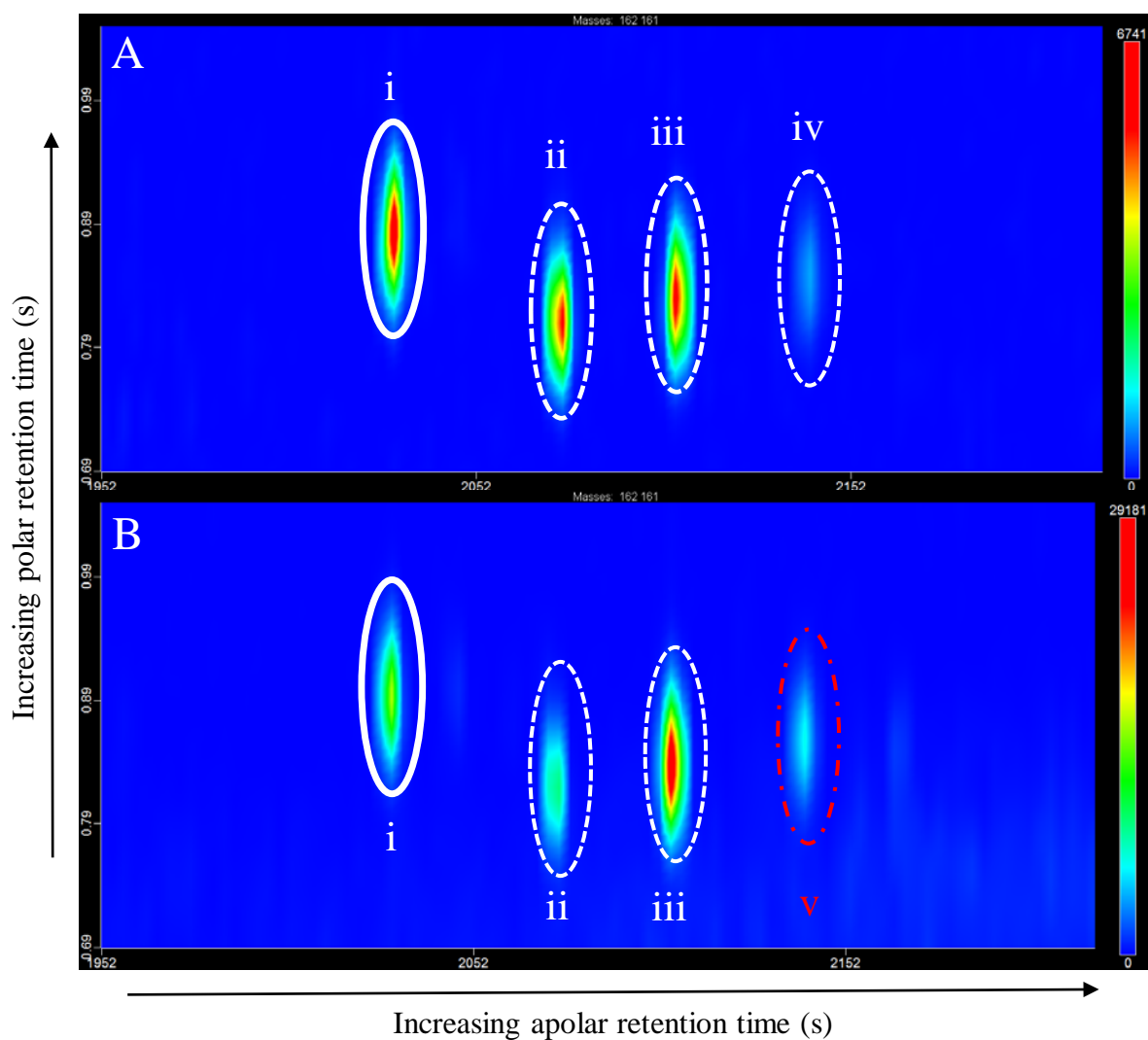
Fig. S3. GC×GC-TOFMS chromatograms of elution region of tetracyclic caged hydrocarbons in alkyldiamantane mixture (A) and biodegraded Mardie crude oil (B). Peak i is the parent structure $C_{12}H_{18}$ with molecular ion m/z 162 (Figure S4A) and peaks ii – v correspond to methyl substituted structure with molecular ion m/z 176. Peaks i – iii in (A) and (B) have identical mass spectra but iv and v are clearly different (Figure S5).
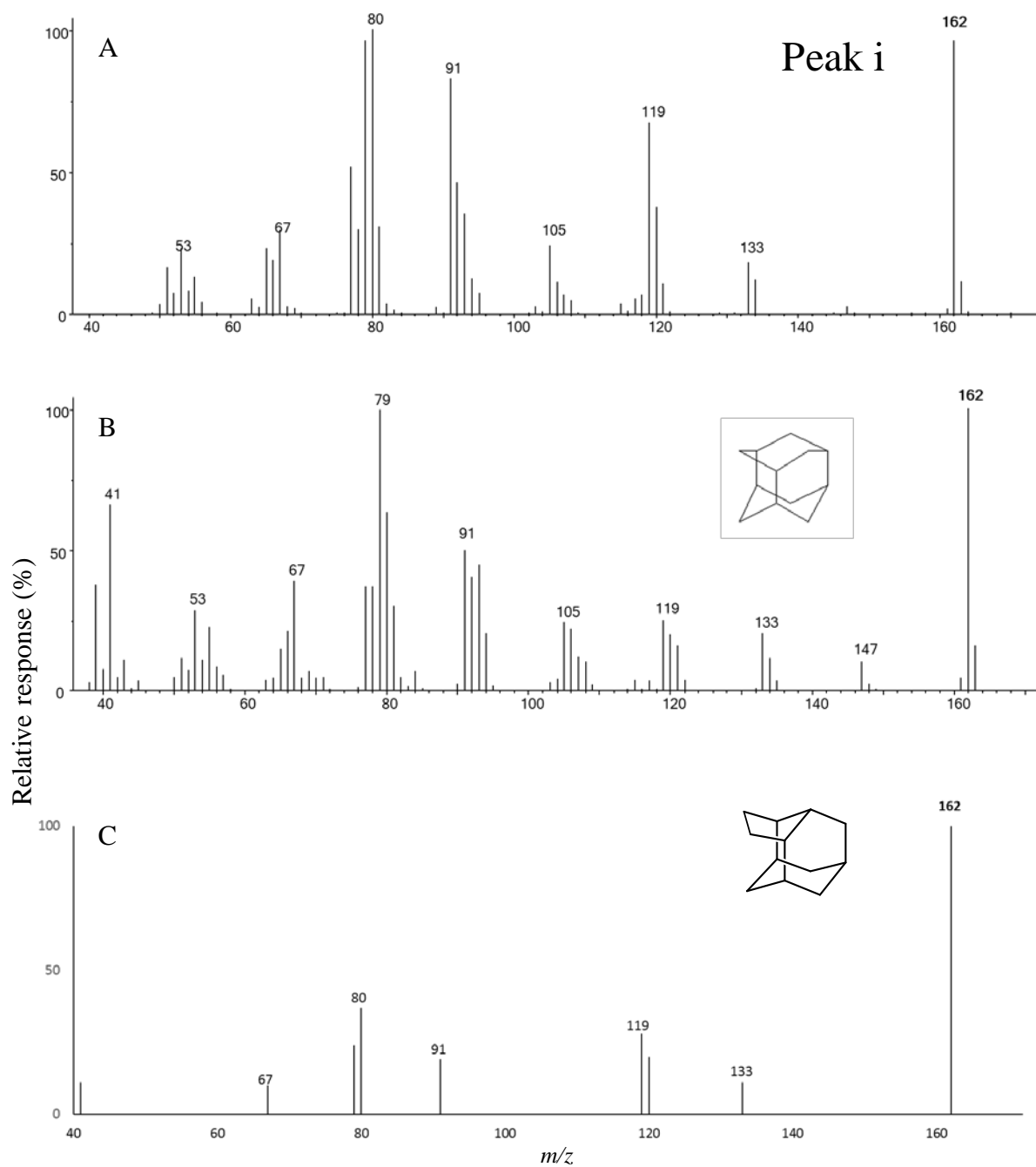
Fig. S4. Time-of-flight mass spectum for unknown peak (Figure S3 peak i) in alkyldiamantane mixture consistent with $C_{12}H_{18}$ tetracyclic hydrocarbon (A), unspecified mass spectrum in NIST library for iceane (B) and unspecified mass spectrum of 2,4-ethanoadamantane reproduced from Hála et al. (1966) (C).
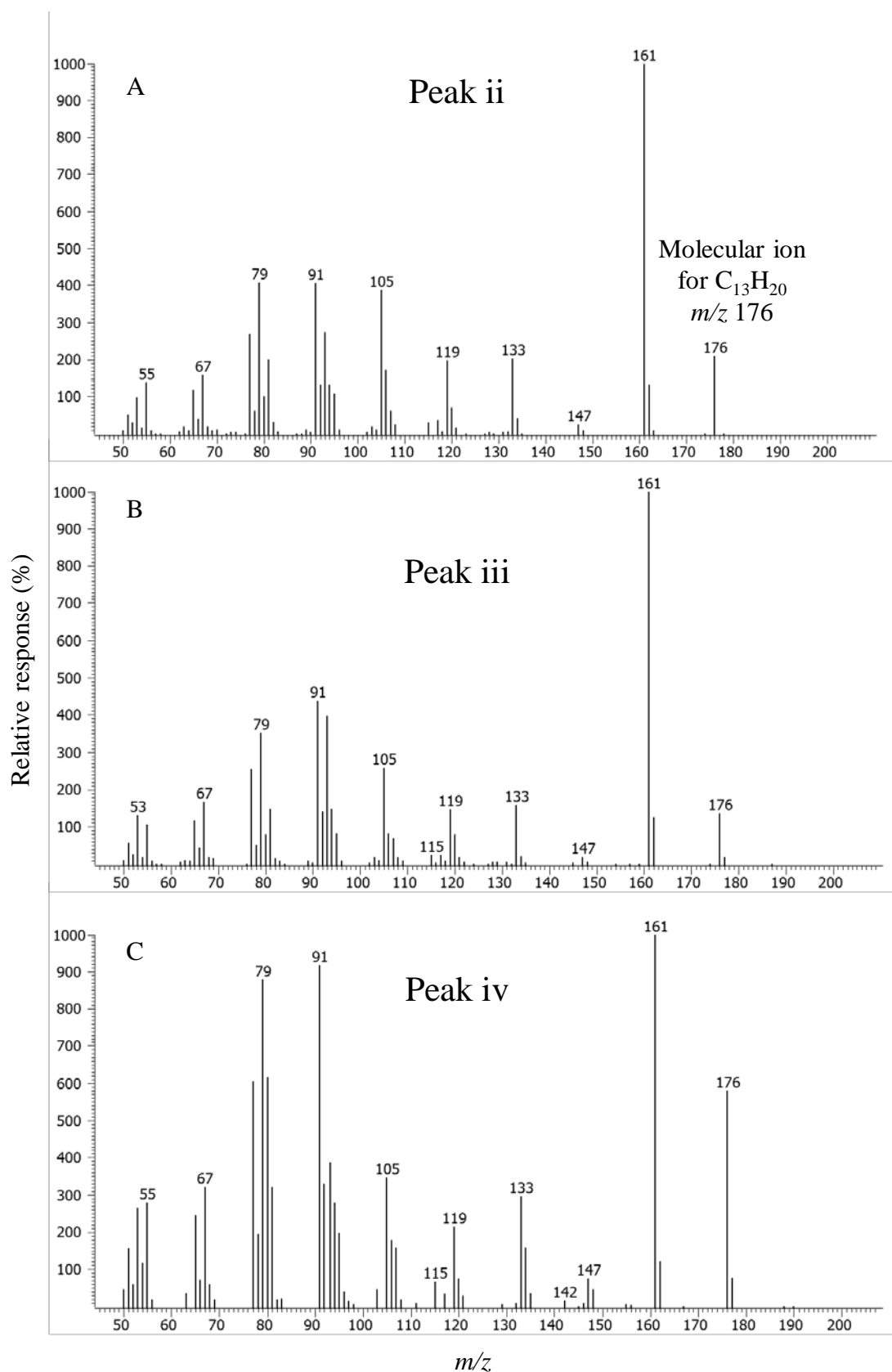
Fig. S5. Time-of-flight mass spectra for peaks (corresponding to ii – iv in Fig. S3) consistent with methyl-substituted isomers of $C_{12}H_{18}$ caged tetracyclic hydrocarbons in alkyldiamantane mixture.
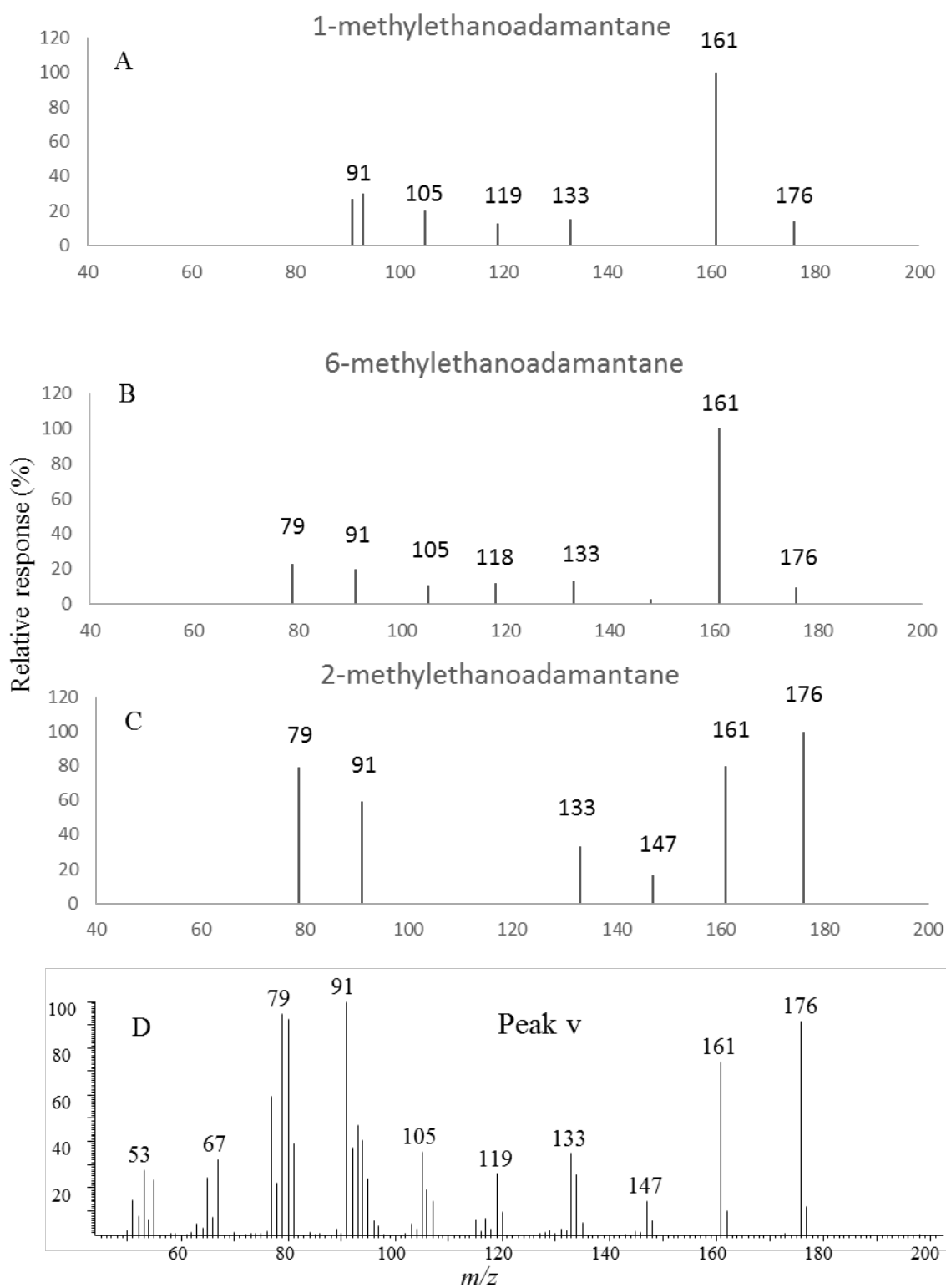
Fig. S6. Mass spectra reproduced from Osawa et al (1980) for 1-methylethanoadamantane (A), 6-methylethanoadamantane (B) and 2-methylethanoadamantane (C), and time-of-flight mass spectrum of peak v observed in many oils eluting at the same 2D times as peak iv in alkyldiamantane mixture (see Fig. S3 and S5).
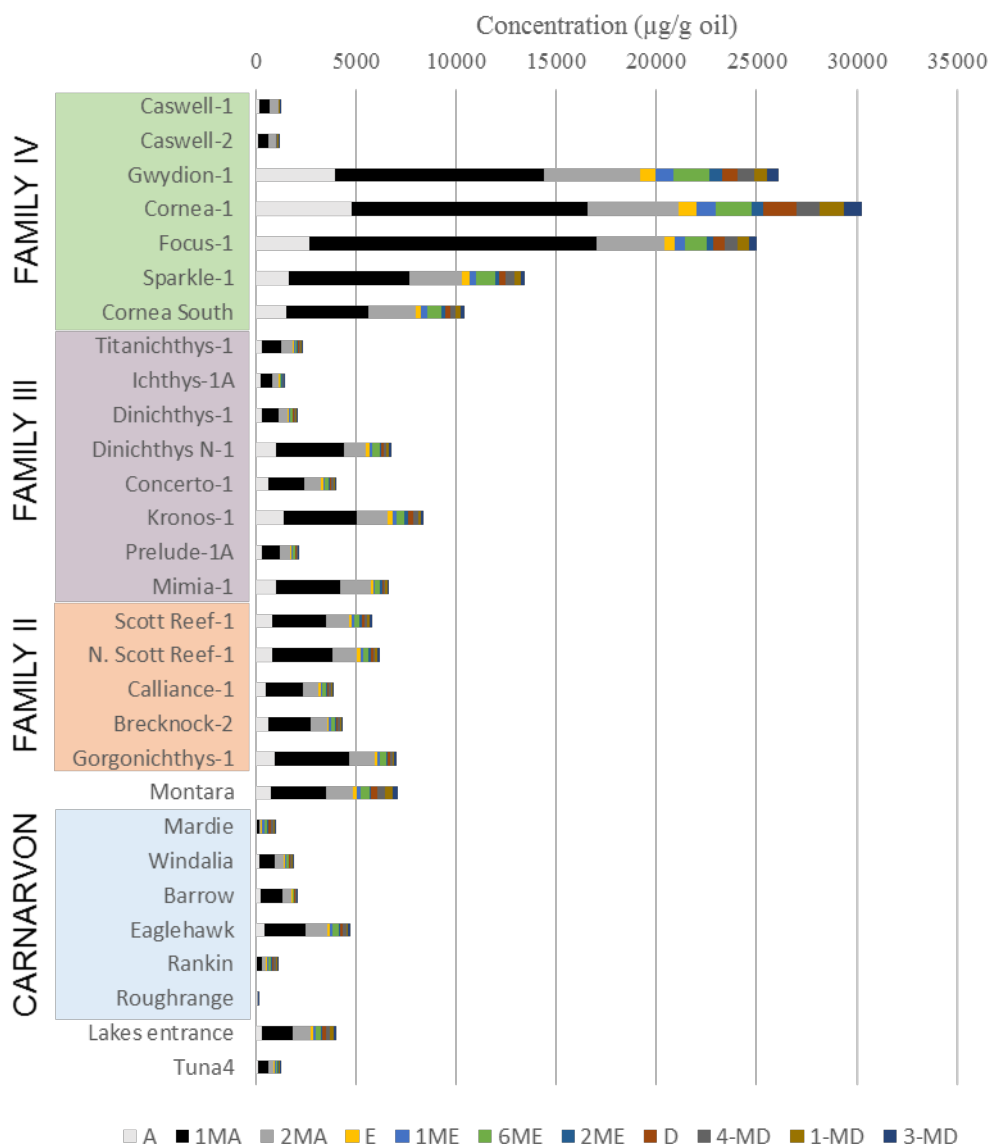
Fig. S7. Relative concentrations of adamantane (A), ethanoadamantane (E) and diamantane (D) plus their methyl substituted isomers numbered by carbon substitution position e.g. 4-MD = 4-methyldiamantane. Families II, III and IV refer to Browse basin groupings in dendogram Fig. S2. The Carnarvon basin oils are related but of varying biodegradation levels. Montara is a light oil from the Bonaparte basin and Tuna4 and Lakes Entrance are from Gippsland (Table 1).
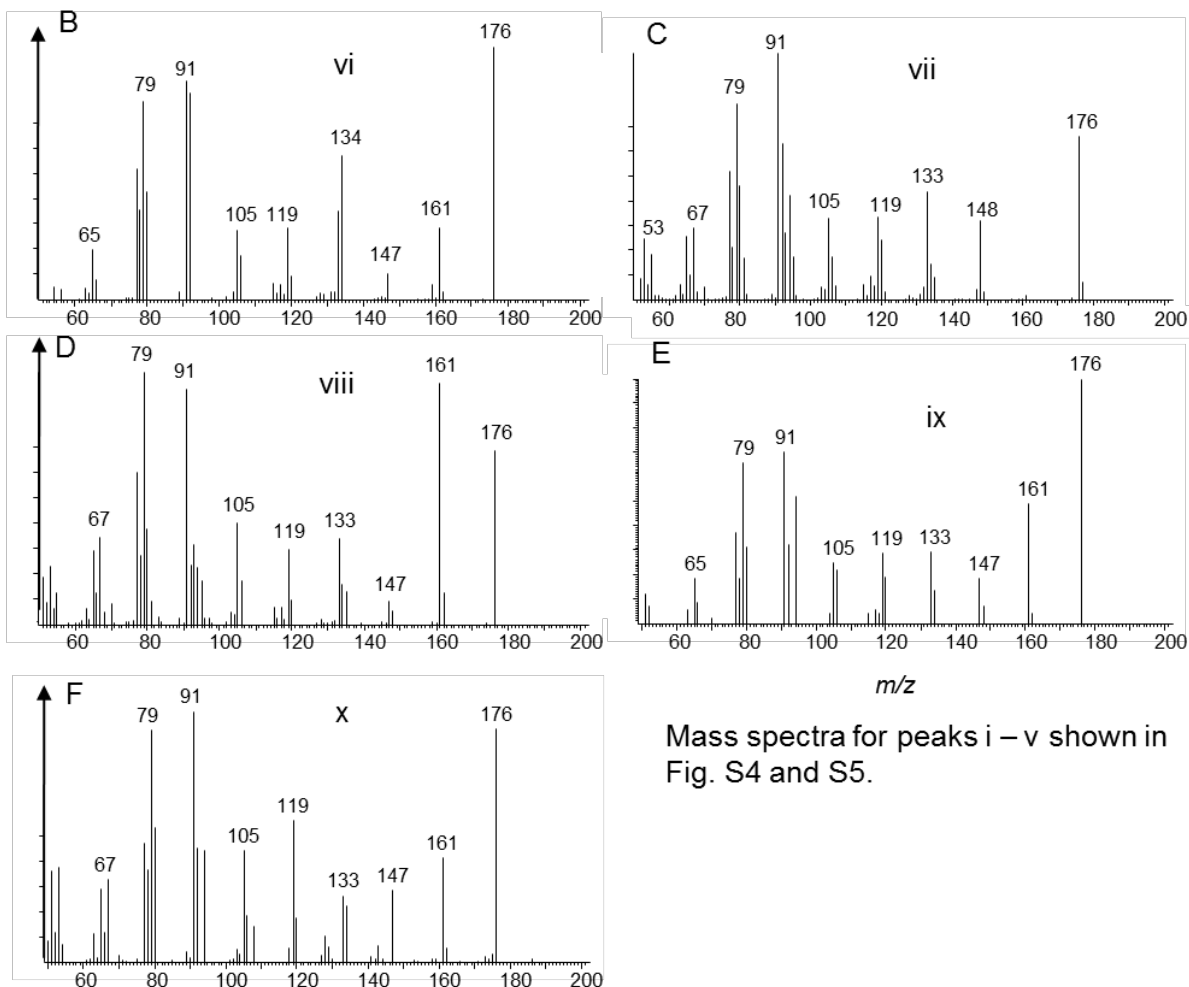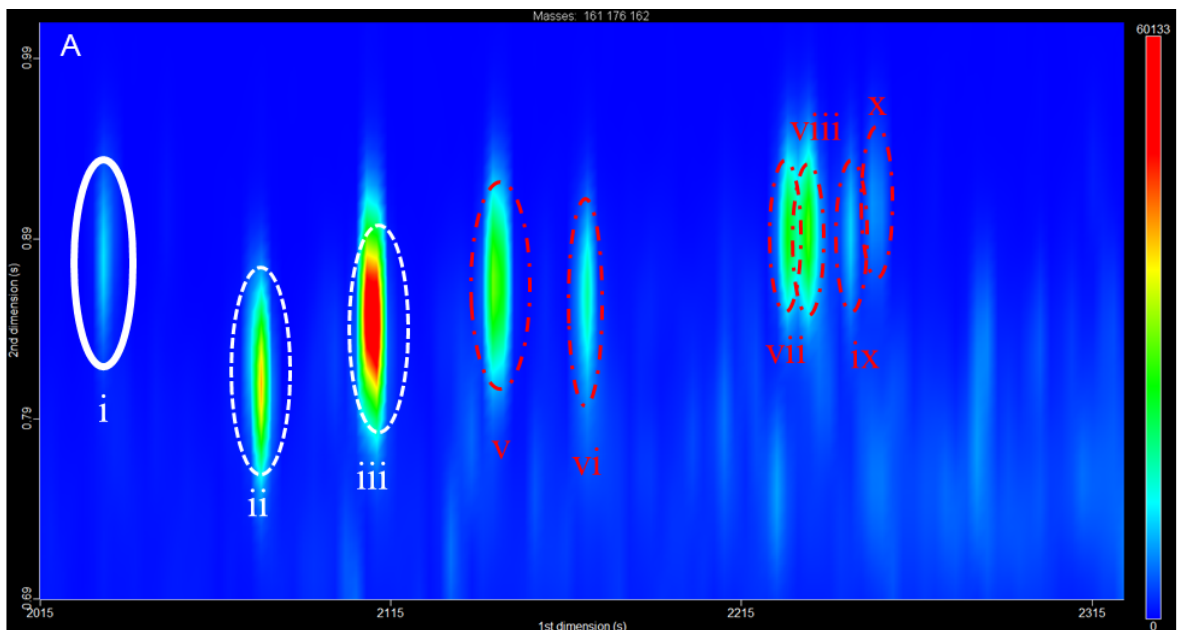
Fig. S8 GCxGC-TOFMS extracted ion chromatogram (*m/z* 161, 162, 176) of Lakes Entrance oil (A) showing elution positions of 2,4-ethanoadamantane (i) and possible methyl isomers ii – x with mass spectra corresponding to peaks vi – x (B – F) observed more prominently in biodegraded oils and condensates.
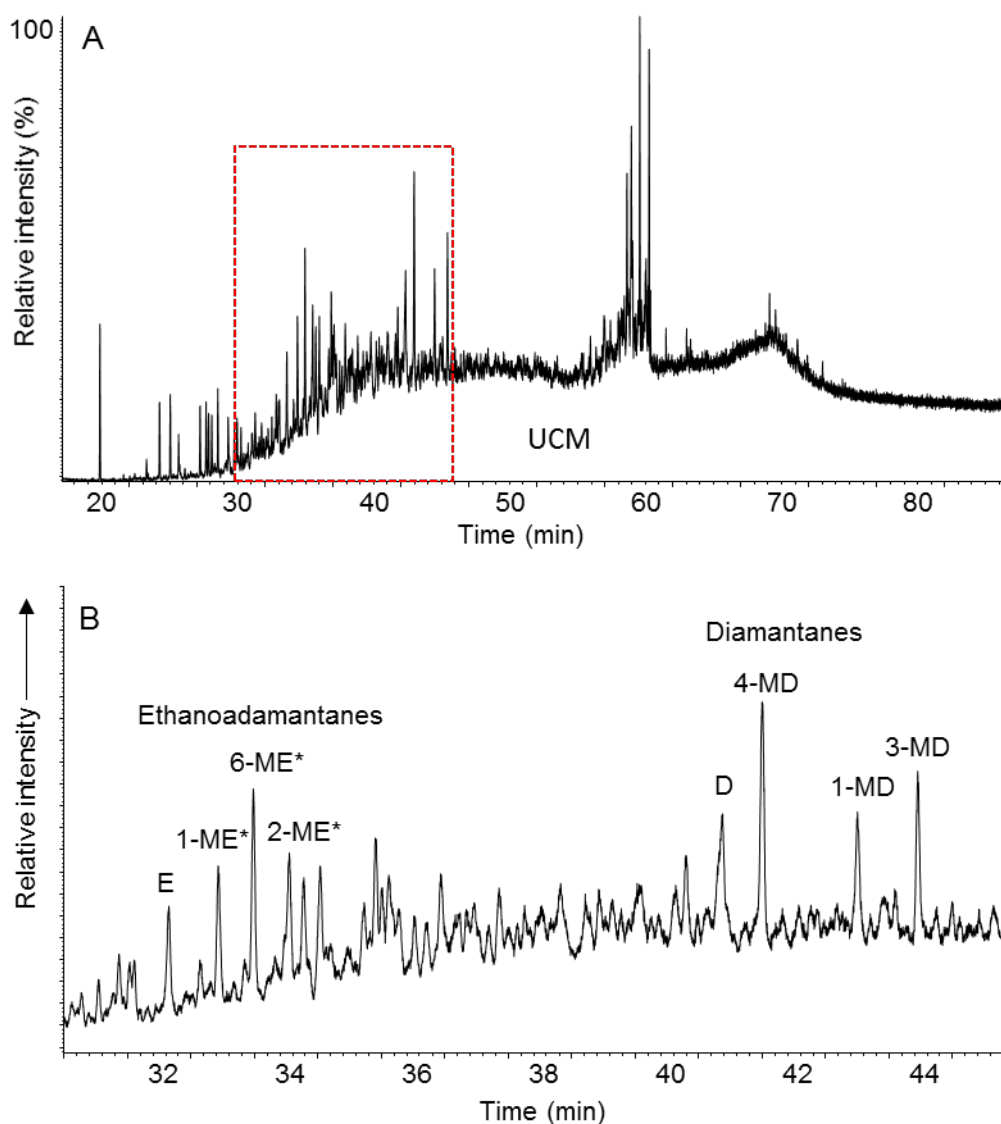
Fig. S9. GC-MS Selected Ion Monitoring chromatogram (A) with zoomed in region highlighted by red box (B) showing peaks ethanoadamantane (E) and tentatively assigned methyl isomers (ME) substituted at the 1-, 6- and 2- bridgehead positions. Also shown are diamantane (D) its methyl isomers 4-MD, 1-MD and 3-MD.

Ions monitored were *m/z* 162, 161 and 176 for ethanoadamantanes, *m/z* 188, 187 and 202 for diamantanes.