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Waxy bitumen stranding in southern Australia: a geochemical study of multiple oil families and their likely origins

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1

27   **Abstract**

28

29   Reports of bitumen stranding on the ocean beaches of southern Australia date back to the

30   early days of European settlement. Previous investigations have shown that this 'coastal

31   bitumen' comprises three categories of stranded petroleum: waxy bitumen, asphaltite and oil

32   slicks. All three varieties are physically and chemically distinct from each other, and bear no

33   geochemical resemblance to any indigenous Australian crude oil. This study focuses on the most

34   common variety, waxy bitumen, which accounted for 90% of the strandings on six South

35   Australian beaches repeatedly surveyed during 1991–1992.

36   Geochemical analysis of 96 individual specimens collected from these survey sites and

37   other beaches in South Australia and western Victoria has shown them to be variously weathered

38   high-wax crude oils of paraffinic to aromatic-intermediate bulk composition. Elemental, isotopic

39   and biomarker differences allow their assignment to at least five oil families with inferred source

40   facies that range from deep freshwater lacustrine through paludal and deltaic to euxinic marine,

41   possibly deposited within different sedimentary bains. Family 1, 2 and 3 waxy bitumens all

42   contain biomarkers derived from the freshwater alga *Botryococcus* sp. and tropical angiosperms

43   (notably dipterocarps). Similar biomarker assemblages are unknown in Australian sedimentary

44   basins but are common in Cenozoic crude oils and source rocks throughout western Indonesia.

45   Family 4 waxy bitumens lack these biomarkers but do contain dinosterane and 24-*n*-

46   propylcholestane, indicative of a marine source affinity, while the carbon-isotopic signatures and

47   high pristane/phytane ratios of Family 5 waxy bitumens are consistent with their origin from

48   coal-rich source rocks deposited in fluvial to deltaic sedimentary successions.

49   The majority of these waxy bitumens represent an oceanic influx of non-indigenous,

50   Southeast Asian crude oils carried into the waters of southern Australia by the Leeuwin Current.

51   Although they are likely to originate from natural seepage within the Indonesian Archipelago, it

52   is unknown whether the parent oils emanate from submarine seeps or from inland seepages

53 which are then carried to the sea by rivers. The common practice of tanker cleaning operations in

54 the Java and Banda Seas may augment the supply of natural bitumen to the beaches of Australia.

55

56 **Key words:** waxy bitumen, southern Australia, biomarker alkanes, carbon isotopic signatures,

57 oil families, ocean transport, Indonesian provenance

58

59 **1. Introduction**

60

61   A recent comprehensive review by Edwards et al. (2016) outlined the history and

62 geographic distribution of bitumen stranding on ocean beaches along the southern coastline of

63 Australia. While these 'coastal bitumens' can readily be distinguished from the occasional

64 spillages of crude and refined petroleum from passing maritime traffic (Padley et al., 1993), they

65 are by no means uniform in appearance or composition. Historical records reveal that there are

66 two main types of this 'ocean wanderer' bitumen: hard asphalt-like material ('asphaltum', now

67 known as asphaltite) and softer waxy bitumen (tar balls).

68   Arguably the most distinctive variety, asphaltites are a single family of heavy (4–18 °API

69 gravity) aromatic-asphaltic crudes with very high sulfur contents (3–4%). Their biomarker and

70 isotopic signatures indicate an origin from marine shale deposited during a mid-Cretaceous

71 oceanic anoxic event (Edwards et al., 1998; Totterdell et al., 2008). They are most likely a

72 product of low-intensity seepage from tar mats exposed by the incision of submarine canyons

73 into the continental slope along Australia's southern margin (Hall et al., 2014). While asphaltite

74 appears to have been the main variety referred to in reports from the earlier part of the twentieth

75 century, waxy bitumen is now the most common form of Australian coastal bitumen, accounting

76 for 90% of annual strandings in South Australia and western Victoria during the early 1990s

77 (Padley, 1995; Edwards et al., 2016).

78

79 *1.1 Historical continuity of waxy bitumen stranding*

80

81   Tar balls have been stranding on the beaches of southern Australia for more than 100

82   years, long before the advent of ocean-going tankers and local shipping powered by fuel oil

83   (Sprigg and Woolley, 1963). Moreover, the range of chemical compositions evident in these

84   stranded bitumens has remained relatively constant for at least 65 years (Edwards et al., 2016).

85   They are typically found on sandy west-facing ocean beaches close to the high-water mark.

86   However, there are exceptions to this rule.

87   Among the samples analysed in the present study are several examples of highly

88   weathered 'fossil waxy bitumen'. These were found within a pumice-rich sand layer above a

89   prominent calcrete horizon located close to the base of a coastal sand dune at the top of the

90   present-day beach, as well as on the inland side of this dune in Beachport Conservation Park

91   (Edwards et al., 2016, fig. 4). Fossil waxy bitumen samples were also found in blowouts between

92   and behind barrier dunes within Canunda National Park and as far south as the Admella Dunes

93   (Fig. 1). These Quaternary barrier shoreline deposits, which are preserved along the Coorong

94   Coastal Plain (Bourman et al., 2016) and extend as far south as Portland in Victoria, have been

95   extensively dated using thermoluminescence (Huntley et al., 1993) and amino acid racemisation

96   (Murray-Wallace et al., 2001) techniques. Since the dune is located above present sea level and

97   within the youngest Robe Range (I) coastal sand barrier system, equivalent in age to the

98   Younghusband Peninsula that fronts the Coorong Lagoon, the pumice-rich layer and its

99   contained bitumen may be up to 7 ka in age (Bourman et al., 2016). Geochemically, these fossil

100   bitumen samples appear almost identical to the main family of waxy bitumens now being

101   washed up on southern Australian beaches, thereby negating the possibility of an anthropogenic

102   origin.

103

104   *1.2 Previous geochemical studies*

105

106   The first systematic attempt to characterise the geochemistry of these waxy bitumens was

107   that of McKirdy and Horvath (1976). Using API gravity, US Bureau of Mines (USBM)

108   correlation indices, bulk composition, elemental and isotopic analyses, gas chromatography and

109   trace metal contents, they distinguished two types of waxy bitumen (highly paraffinic to

110   paraffinic, and paraffinic-naphthenic), and inferred that both were derived from early mature

111   lacustrine Cretaceous source rocks suggesting that they may have emanated from seafloor

112   seepage in the western Otway Basin. However, the analytical techniques employed in this initial

113   study did not permit unambiguous determination of their source affinity.

114   In 1983 the South Australian Department of Mines and Energy (SADME) conducted a

115   major survey of stranded bitumen along the South Australian coastline, involving the collection

116   of new samples for more sophisticated analysis, including by gas chromatography-mass

117   spectrometry (GC-MS), in order to promote petroleum exploration within the adjacent offshore

118   Otway and Duntroon basins. Interpretation of the resulting data by McKirdy (1984a, b) led to the

119   recognition of four genetically distinct families (Families 1, 2, 3 and 4, the first three comprising

120   waxy bitumens and the last asphaltite) based on their sulfur content, the carbon isotopic

121   composition of their C_{12+} saturated and aromatic hydrocarbons, and various alkane biomarker

122   ratios, criteria later augmented by other elemental data (viz. C, H and N) and bulk hydrogen and

123   sulfur isotopic signatures (McKirdy, 1985a).

124   Subsequent publications (McKirdy, 1985b; McKirdy et al., 1986, 1988) adopted the

125   aforementioned three-fold classification for the southern Australian waxy bitumens and

126   continued to maintain that they were likely to have originated from lacustrine source beds within

127   the Early Cretaceous rift-fill of the Otway Basin. However, failure to identify their distinctive

128   biomarker assemblage (viz. botryococcane, bicadinanes, oleanane and 4-methylsteranes) in any

129   organic-rich facies of this basin (Padley, 1995) necessitated a wider research area. The fact that

130   this association of biomarkers has so far been found only in Cenozoic lacustrine source rocks

131   and crude oils from Sumatra and Java (Seifert and Moldowan, 1981; Williams et al., 1985;

132   Longley et al., 1990; Schiefelbein and Cameron 1992; Hwang et al., 2002), now suggests that the

133   waxy bitumens represent flotsam which originates from oil seeps in the Indonesian Archipelago

134   and is carried southward into Australian waters by long-distance ocean currents (Currie et al.,

135   1992; McKirdy et al., 1994; Padley, 1995; McGowran et al., 1997; Edwards et al., 2016). That

136   said, there is no agreement on the number of different oil families represented (Table 1), and the

137   locations of their parent seeps are yet to be identified.

138

139   *1.3 Present investigation*

140

141   This paper presents the results of geochemical analyses undertaken by Padley (1995) on a

142   suite of 96 archival and more recently stranded waxy bitumens recovered from ocean beaches

143   between Cape Otway, Victoria and the southern Eyre Peninsula, South Australia (Fig. 1). Most

144   of these samples (n = 53) were collected during 1991 and 1992. When combined with elemental,

145   isotopic, biomarker and bulk compositional information from other sources (McKirdy, 1984a, b,

146   1985a; Tewkesbury, 1989; Watson, 1990), the resulting compilation provided the basis for a

147   revised genetic classification of southern Australian waxy coastal bitumens, and a clearer

148   understanding of their weathering characteristics, source affinity and likely origins. The latter

149   was achieved, first by comparison of our updated classification with those of bitumens found in

150   the Northern Territory (Summons et al., 1993) and Western Australia (Alexander et al., 1994);

151   and then with the various oil families identified in the western Indonesian Archipelago

152   (Robinson, 1987; ten Haven and Schiefelbein, 1995; Schiefelbein and Cameron, 1997; Hwang et

153   al., 2002).

154

155   **2. Materials and methods**

156

157   *2.1 Sample suite*

6

158

159   The bitumen samples examined in this study are listed in Table A1 of the supplementary

160   material, along with their date of collection and, where available, API gravity and sulfur content.

161   The locations of their respective stranding sites are shown in Fig. 1. Each sub-sample taken for

162   analysis came from the interior of the tar ball in order to minimise the effect of weathering on the

163   resulting analytical data. To document these effects in one of the larger specimens (sample 28),

164   three sub-samples were removed from its interior, intermediate and exterior zones and analysed

165   separately.

166

167   *2.2 Sample fractionation*

168

169   A weighed aliquot of pure coastal bitumen was dissolved in a minimum amount of

170   dichloromethane and flooded with petroleum ether (30 ml/g). The solution was then refluxed for

171   2 hours in the presence of activated copper turnings to remove elemental sulfur. The insoluble

172   asphaltenes were separated from the soluble maltenes (asphaltene-free oil) by filtration through

173   pre-extracted filter paper (Whatman Grade 42). The asphaltenes were washed with petroleum

174   ether in Soxhlet apparatus and then recovered by dissolving in dichloromethane. Solvent was

175   removed from the asphaltene and maltene fractions under vacuum in a Büchi rotary evaporator.

176   Each fraction, dissolved in a small volume of solvent, was transferred by Pasteur pipette to a pre-

177   weighed glass vial. Final removal of the solvent was achieved under a stream of nitrogen.

178   Maltenes were separated into hydrocarbons (saturated and aromatic) and polar

179   compounds (resins) by standard liquid chromatography on a column of activated silica over

180   alumina (sample: adsorbent ratio = 1:100). The saturated hydrocarbon fraction was eluted with

181   petroleum ether; mono-, di- and tri-aromatic hydrocarbon fraction with petroleum

182   ether/dichloromethane (91:9); heavy aromatic hydrocarbon fraction with petroleum

183   ether/dichloromethane (40:60); and resins with methanol/dichloromethane (65:35). Thin layer

184   chromatography on Merck Kiesel Gel 60G (0.5 mm thick) was employed whenever the amount

185   of maltenes available was either small (<10 mg) or their content of light aromatic hydrocarbons

186   was relatively high. The sample (~20 mg) was spotted 2 cm from the base of the plate and

187   developed in *n*-hexane. *n*-Hexadecane, naphthalene, anthracene and pyrene were used as

188   reference standards. The separated bands were visualised by spraying with a methanolic solution

189   of Rhodamine 6G and viewing under UV light. Four fractions (saturated hydrocarbons; low-

190   molecular-weight aromatic hydrocarbons; higher molecular-weight aromatic hydrocarbons; and

191   polar compounds) were recovered from the silica gel by desorption using the same solvent

192   mixtures as described for column chromatography. Finally, an aliquot (~10 mg) of the saturated

193   hydrocarbon fraction was treated three times with urea to separate the normal and iso-alkanes

194   (paraffins; adduct) from the cyclic and multibranched alkanes (naphthenes; non-adduct). Further

195   details of this procedure may be found in Padley (1995).

196

197   *2.6 Gas chromatography*

198

199   The saturated hydrocarbon fraction (isolated from each of the bitumen samples attributed

200   to source 1 in Table A1, supplementary material) was dissolved in *n*-hexane and analysed by gas

201   chromatography (GC) in one of two laboratories, employing the following instrumental

202   parameters.

203   In the Department of Geology and Geophysics, University of Adelaide, the instrument

204   was a Varian 3400 gas chromatograph fitted with a DB-1 capillary column (30 m x 0.25 mm i.d.

205   x 0.25 μm film thickness) and a flame ionisation detector (FID). The temperature programme of

206   the oven was 40 °C for 2 min, 40 to 300 °C at 4 °C/min and isothermal at 300 °C for 20 min.

207   Two injection techniques were employed: a Varian split/splitless injector operated in the split

208   mode (ratio 20:1) at a temperature of 300 °C, with hydrogen as the carrier gas at a head pressure

209   of 15 psi; and a SGE on-column injector, with nitrogen as the coolant and hydrogen as the carrier

210   at a linear flow rate of 35 cm/sec.

211   At the Australian Geological Survey Organisation (now Geoscience Australia), Canberra,

212   the instrument was a Hewlett Packard Series II 5890 gas chromatograph fitted with a FID and a

213   HP Ultra-1 capillary column (50 m x 0.2 mm i.d. x 0.33 μm film thickness). The carrier gas was

214   hydrogen at a linear flow rate of 35 cm/sec. The sample was injected on-column at 60 °C and the

215   oven temperature ramped from 60 to 300 °C at 4 °C/min before being held isothermal at 300 °C

216   for 20 min.

217   All quantitative work was carried out in the former laboratory using the on-column

218   injector and 3-methylhenicosane (AC 22; 10 μg/ml) as the internal standard.

219

220   *2.7 High-temperature capillary gas chromatography*

221

222   High-temperature capillary gas chromatography (HTCGC) of the total alkane fraction of

223   six waxy bitumens (samples 28, 50, DB1, 48, 290 and EC1) was undertaken in the then

224   Department of Environmental Sciences at the University of Plymouth, UK. Samples were

225   dissolved in cyclohexane and heated to 55 °C prior to injection into a Carlo Erba HRGC 5300

226   Mega Series gas chromatograph fitted with a SGE HT5 column (12 m x 0.32 mm x 0.1 μm film

227   thickness). The carrier gas was helium at 49 kPa head pressure and kept at a constant flow rate of

228   3 ml/min using the Carlo Erba CP-CF516 module. The sample was injected on-column with air

229   as the coolant and the oven temperature-programmed from 50 to 410 °C at 10 °C/min before

230   being held isothermal at 410 °C for 5 min. It should be noted that no attempt was made to

231   quantify the recoveries of the saturated hydrocarbon fractions through the purification steps

232   undertaken prior to their analysis by HTCGC (see Heath et al., 1995, 1997).

233

234   *2.8 Gas chromatography–mass spectrometry*

9

235

236   Selected total alkane fractions were analysed by gas chromatography–mass spectrometry

237   (GC–MS) in several modes. Routine full scanning (SCAN) and selected-ion monitoring (SIM)

238   were carried out at the Australian Wine Research Institute, Adelaide, using a Varian 3400 gas

239   chromatograph fitted with a DB-1 capillary column (30 m x 0.25 mm x 0.25 μm film thickness)

240   directly connected to the ion source of a TSQ-70 quadrupole mass spectrometer. Samples were

241   dissolved in n-hexane and injected via a split/splitless injector operated in split mode (ratio 20:1)

242   at 300 °C. The carrier gas was hydrogen at a head pressure of 15 psi. The operating conditions of

243   the mass spectrometer were as follows: electron energy 70 eV, emission current 200 μA, source

244   temperature 250 °C, scan dwell time 70 msec, mass range 47–500 amu.

245   The following mass fragmentograms were examined: m/z 123, diterpanes; m/z 177,

246   demethylated triterpanes; m/z 183, acyclic isoprenoid alkanes (including botryococcane);

247   m/z 191, triterpanes (including hopane, moretane, gammacerane and oleanane); m/z 205,

248   methylated triterpanes; m/z 217 and 218, steranes; m/z 231, 4-methyl steranes; and m/z 259,

249   diasteranes. Individual compounds were identified by their mass spectra which were compared

250   to standards and published data, particularly that of Philp (1985).

251   The same instrumentation was used to analyse selected aromatic hydrocarbon fractions,

252   except that they were injected on-column at 60 °C and the carrier gas had a linear flow rate of 35

253   cm/sec. The following mass fragmentograms were examined: m/z 128, naphthalene; m/z 142,

254   methylnaphthalenes; m/z 156, dimethylnaphthalenes; m/z 178, phenanthrene and anthracene; m/z

255   192, methylphenanthrenes; m/z 206, dimethylphenanthrenes.

256   To detect and confidently identify key biomarker compounds (notably oleanane,

257   bicadinanes and C_{30} desmethyl steranes and 4-methyl steranes) selected total alkane fractions

258   and branched/cyclic (urea non-adduct) were analysed by metastable reaction monitoring (MRM)

259   GC–MS on a magnetic sector double focussing VG 7070E mass spectrometer at the Australian

260   Geological Survey Organisation, Canberra. Details of the instrumentation, operating conditions

261 and parent-to-daughter transitions monitored are reported in McKirdy et al. (1994), although in

262 this study a slightly different temperature program was used (viz. 50 to 180 °C at 8 °C/min, 180

263 to 300 °C at 4 °C/min, and then held isothermal at 300 °C for 20 min). The concentrations of

264 specific biological marker compounds were measured by the addition of a deuterated sterane

265 standard 3-CD_3-5α(H)-cholestane (10 ng/ml).

266

267 *2.9 Stable carbon isotope mass spectrometry*

268

269 Stable carbon isotopic compositions of the total saturated and aromatic hydrocarbon

270 fractions were determined for the purpose of oil-oil correlations, as well as to give an indication

271 of the bitumen's source affinity. Stable carbon isotopic analyses were carried out using a method

272 slightly modified from that of Sofer (1984). Portions (~1.5 mg) of the saturated and aromatic

273 hydrocarbon fractions were oxidised over cuprous oxide (CuO, 150 mg) at 900 °C for 8 hours

274 with silver wire (to remove sulfur and halogens) in evacuated quartz combustion tubes. The

275 resultant carbon dioxide was separated from the co-produced H_2O and other condensable gases

276 (e.g. SO_2) on a vacuum line by cooling with liquid nitrogen-chilled ethanol. The carbon dioxide

277 was retrieved for introduction to the mass spectrometer by condensing the gas into collection

278 tubes using liquid nitrogen. $^{13}C/^{12}C$ ratios were measured on a Micromass 602E isotope mass

279 spectrometer in the Department of Geology and Geophysics, University of Adelaide. The

280 instrument was equipped with a dual inlet system, allowing the sample to be compared directly

281 with a reference gas. The resulting data are presented as $\delta^{13}C$ values relative to the VPDB

282 standard. Reproducibility, as determined from ten duplicate measurements of the TO2 graphite

283 standard, was ±0.06 ‰.

284

285 **3. Results and discussion**

286

287 *3.1 Physical properties and bulk chemical composition*

288

289   The suite of waxy coastal bitumens examined in this study are heavy to light, solid oils

290   with densities varying between 10 and 40 °API (specific gravity = 0.9957–0.8270); pour points

291   (43–82 °C) that reflect their high wax contents; and sulfur contents that range from low to

292   moderate (0.1–2.6%) (Table 1). Collectively, they comprise inspissated residues of crude oils

293   that range in composition from paraffinic, through paraffinic-naphthenic to aromatic

294   intermediate (Fig. 2; based on data in Table A2, supplementary material). Not surprisingly, waxy

295   C_{23+} *n*-alkanes that commonly display an odd-over-even carbon number preference in the C_{25}–C_{31}

296   range are prominent components of their saturated hydrocarbon fractions (Figs. 3). High-

297   temperature gas chromatograms reveal the presence of individual *n*-alkanes up to C_{60+} (Fig. 4),

298   implying that the parent crude oils are exceptionally rich in wax.

299   Most of these bitumens display evidence of pronounced weathering (as discussed in

300   Section 3.3). Accordingly, each bitumen specimen has been assigned an empirical degree of

301   weathering (DOW) value in the range 0–5, based upon the extent of removal of its normal and

302   acyclic isoprenoid alkanes (Tables A2 and A3, supplementary material).

303

304   *3.2 Waxy bitumen families and their source affinities*

305

306   Differences in the sulfur content, carbon isotopic composition and alkane biomarker

307   geochemistry of the waxy bitumens permit their subdivision into five oil families. Based on a

308   larger data set, the new classification (Table 5) expands the three-fold genetic classification

309   originally proposed by McKirdy (1984a, b) and subsequently employed by McKirdy et al. (1986,

310   1988, 1994) to include two additional families, one marine (Family 4) and the other paludal

311   (Family 5). The original classification invoked a similar suite of geochemical criteria, augmented

312   by the hydrogen and sulfur isotopic compositions of the whole bitumen. Comparison of the new

313   classification with those based on sample suites from the Northern Territory (Summons et al.,

314   1993) and Western Australia (Alexander et al., 1994) reveals some overlap but also significant

315   differences (Table 6). Families 1 and 3 are common to all three classification schemes, whereas

316   Families 2, 4 and 5 are not represented in either of these two earlier schemes.

317   The carbon isotopic signatures of the saturated and aromatic hydrocarbon fractions of the

318   waxy bitumens (Table A4, supplementary material) provide the first clue to their likely origin

319   (Fig. 5). They reveal the algal source affinity of the vast majority of the specimens, while at the

320   same time clearly distinguishing them from asphaltite, the other variety of southern Australian

321   coastal bitumen (Volkman et al., 1992; McKirdy et al., 1986, 1994, 2015; Padley, 1995;

322   Edwards et al., 1998, 2016; Hall et al., 2014). The lack of uniformity of the signatures plotted in

323   Fig. 5 highlights the fact that, unlike the asphaltites, the waxy bitumens belong to multiple oil

324   families.

325   Saturated hydrocarbon chromatograms typical of the five families are shown in Fig. 3. Of

326   particular significance is the presence of botryococcane (peak labelled *), a C_{34} irregular acyclic

327   isoprenoid alkane that elutes just before *n*-nonacosane (Peters et al., 2005), in 80% of the waxy

328   bitumens examined. MRM chromatograms illustrating the distributions of triterpanes and

329   steranes in Family 2 and 4 bitumens are shown in Figs. 6 and 7, while those of a Family 1

330   bitumen may be found in McKirdy et al. (1994, fig. 8). The bicadinane and methylbicadinane

331   distributions of Family 1 and 2 bitumens are compared in Fig. 8. A range of source-dependent

332   biomarker signatures derived from the aforementioned chromatograms of 22 representative

333   samples is presented in Table 3 (parameters 1-16). For an explanation of the significance of these

334   parameters the reader is referred to Peters et al. (2005) and references cited therein.

335

336   *3.2.1 Family 1*

337

338   The waxy bitumens of Family 1 are paraffinic to paraffinic-naphthenic crude oils with a

339 relatively homogeneous bulk chemical composition and uniformly low sulfur contents (<0.3%:

340 Tables A1 and A2, supplementary material; Fig. 2). Isotopically they are the heaviest of all the

341 samples analysed in this study (mean $\delta^{13}C_{sat}$ = –25.7‰, mean $\delta^{13}C_{aro}$ = –24.5‰: Table 2; Fig. 5),

342 likely due to the high content of *Botryococcus*-derived alginite in their source rocks (Boreham et

343 al., 1994; see below). This, in turn, is consistent with the mean isotopic composition of

344 botryococcane ($\delta^{13}C$ = –12.4‰), pristane (–25.9‰) and phytane (–26.6‰) in the seven Family 1

345 bitumens reported by Dowling et al. (1995).

346   The biomarker assemblage of the least weathered Family 1 waxy bitumen (sample 28,

347 Fig. 3a) has the following pertinent characteristics (Tables 3 and 4):

348   • a bimodal *n*-alkane distribution with maxima at C_{17} and C_{25}

349   • an intermediate pristane/phytane ratio

350   • a high concentration of botryococcane

351   • an ethylcholestane-dominant 5α(H)-sterane distribution

352   • a diacholestane-dominant diasterane distribution

353   • 4-methyl-24-ethylcholestane in abundance

354   • the absence of dinosterane

355   • a high C_{30} hopane/C_{29} 5α(H)-sterane ratio

356   • the presence of 30-norhopane

357   • an abundance of oleanane, and

358   • relatively high concentrations of bicadinane and methylbicadinane.

359 Its C_{15}–C_{35} *n*-alkane profile (Fig. 3a) is typical of oils derived from a mixture of algal lipids

360 (lower molecular weight *n*-alkanes) and terrestrial plant waxes (higher molecular weight *n*-

361 alkanes), or from the freshwater chlorophyte alga *Botryococcus* sp..

362   With the advent of HTCGC it became possible to resolve and quantify high-molecular-

363 weight (HMW) hydrocarbons in the range *n*-C_{40} to *n*-C_{100} (del Rio and Philp, 1992; Heath et al.,

14

364   1995, 1997). High-temperature chromatograms of the saturated hydrocarbon fractions of five

365   Family 1 waxy bitumens (Fig. 4a–e) reveal marked differences in their C_{35}–C_{70} n-alkane profiles.

366   Making due allowance for the effect of biodegradation on the front ends of the chromatograms

367   (discussed in Section 3.3), the differences are manifest in the relative proportions of two

368   additional modes in their carbon number profiles (with maxima at 41–44 and ~60, respectively).

369   Similar modes have been reported in the wax precipitated in pipes during production of

370   Cenozoic lacustrine oil from the Redwash Field, Uinta Basin, Utah (Carlson et al., 1993). While

371   the origin of this bimodal C_{35+} n-alkane distribution has yet to be established, the aforementioned

372   differences likely point to variations in the mix of lacustrine algae and higher plants contributing

373   resistant biopolymers (algaenans) and long-chain lipids to their respective source rocks (Tegelaar

374   et al., 1989). Another feature reflecting the freshwater lacustrine source affinity of these Family

375   1 bitumens is the marked predominance of normal over branched and monocyclic alkanes in the

376   C_{40}–C_{60} range of their respective saturated hydrocarbon distributions (Fig. 4: Carlson et al.,

377   1993).

378   Botyrococcane is the saturated analogue of a C_{34} isoprenoid alkene synthesized by

379   *Botryocccus braunii* (specifically clonal race B: Metzger et al., 1985). The presence of 4-methyl-

380   24-ethylcholestane and the absence of dinosterane are together diagnostic of the input of

381   freshwater dinoflagellates to their precursor organic matter (Summons et al., 1987). The

382   pristane/phytane ratios of the least weathered Family 1 bitumens (pr/ph = <1–2.6: Table A4,

383   supplementary material) indicate that their precursor organic matter was deposited in an anoxic

384   to sub-oxic lacustrine setting.

385   The sterane distribution of the Family 1 waxy bitumens is unusual in that the regular

386   steranes are dominated by ethylcholestane, whereas diacholestane (*not* ethyldiacholestane) is in

387   most instances the dominant diasterane homologue (parameters 1 and 2, Table 4). This anomaly

388   does not appear to be the result of weathering because the sterane distribution is the same for the

15

389   least and most weathered samples, and ethyldiacholestane is not known to be preferentially

390   removed by biodegradation (Connan, 1984; Peters et al., 2005).

391   The co-dominance of ethylcholestane and diacholestane, therefore, is likely to be the

392   result of the dual input of algal and land-plant detritus to the source kerogen. 4-Methyl-24-

393   ethylcholestane is abundant relative to ethylcholestane (C_{30} 4αMe-ster/C_{29} 5αH-ster = 2:

394   parameter 12: Table 4). The Family 1 waxy bitumens lack both 24-n-propylcholestane (a marine

395   algal marker: Moldowan et al., 1990) and (in most instances) dinosterane, confirming that the

396   predominant algal contribution to their source material was from freshwater species.

397   The high abundance of diasteranes relative to steranes (parameter 5, Table 4) in the

398   Family 1 waxy bitumens reflects the high clay content of their source rock (McKirdy et al.,

399   1983). Further evidence of an argillaceous source lithofacies comes from the dominance of the

400   C_{30} homologue among the C_{27}–C_{35} hopanes and the presence of rearranged hopanes including

401   C_{29}–C_{35} diahopanes and C_{27} and C_{29} 18αH-neohopanes (parameters 7–9, Table 4; ten Haven et al.,

402   1988; Moldowan et al., 1991).

403   In Family 1 waxy bitumens, the hopanes are dominated by αβ-hopane and the

404   hopane/sterane ratio is high (C_{30} hop/C_{29} ster = 1.7–4.5: parameter 6, Table 4) indicating a

405   significant contribution of bacterial lipids to the parent organic matter. Such low sterane

406   abundances relative to hopane are typical of lacustrine-sourced oils (Seifert and Moldowan,

407   1981). Methylhopanes are present in relatively low concentrations.

408   The angiosperm-derived pentacyclic triterpanes oleanane, bicadinane and

409   methylbicadinane are abundant in the Family 1 waxy bitumens (Table 4), indicating that they are

410   derived from source rocks of Upper Cretaceous or younger age (McKirdy et al., 1994 and

411   references therein). Of all the waxy bitumens, those assigned to Family 1 have the highest

412   concentrations of oleanane (ol/hop = 0.04–0.24: parameter 13, Table 4). Methylbicadinane and

413   four isomers of bicadinane were identified in the Family 1 waxy bitumens (Fig. 8). Using the

414   nomenclature of Summons et al. (1993) and Murray et al. (1994a), the C_{30} bicadinane isomers are

16

415 labelled W, T, T1 and R, respectively; and the methylated bicadinane isomers of T and T1, are

416 annotated as MeT and MeT1, respectively. Typically, the relative abundance of bicadinane

417 isomers in Family 1 waxy bitumens is T > T1 > R > W (Table 4).

418   Other biomarkers that provide evidence for the contributions of higher plants to the

419 precursor organic matter of the Family 1 waxy bitumens are diterpanes, notably 16βH-

420 phyllocladane and the C_{18}–C_{20} labdanes (McKirdy et al., 1994). These diterpanes are derived

421 from resin acids produced by both gymnosperms (mainly conifers) and angiosperms (Alexander

422 et al., 1987).

423   Family 1 is an end-member group of high-wax, low-sulfur, paraffinic crude oils derived

424 from an anoxic to suboxic lacustrine facies containing Type I sapropelic kerogen. In this

425 instance, the precursors included freshwater algae (*Botryococcus* sp. and dinoflagellates) and the

426 biodegraded remains of tropical land-plants (specifically angiosperms of the family

427 *Dipterocarpaceae*). High concentrations of the following biomarkers are unique to the Family 1

428 waxy bitumens: botryococcane, 4-methyl,24-ethylcholestane, oleanane and bicadinane.

429 *Botryococcus sp.* is common in non-marine kerogens but its diagnostic biomarker,

430 botryococcane, is geologically rare. The limited occurrence of this saturated hydrocarbon may

431 reflect both the rarity of *Botryococcus braunii* Race B (the only one of several different clonal

432 races known to synthesize botryococcene) and the poor resistance of its biological precursor to

433 bacterial and chemical degradation during deposition under oxic conditions (Derenne et al.,

434 1988).

435

436 *3.2.2 Family 2*

437

438   The Family 2 waxy bitumens, like those of Family 1, also exhibit high concentrations of

439 botryococcane (bot/n-C_{29} = 0.15–0.71: Table 3). However, their sulfur contents (0.6–2% S) are

440 much higher than those of the Family 1 bitumens, and their carbon isotopic compositions are

441 both lighter and far less uniform (Fig. 5). Their bulk chemical composition varies from

442 paraffinic-naphthenic to aromatic-intermediate (Fig. 2) and the proportion of saturated to

443 aromatic hydrocarbons also is highly variable (sat/arom = 2.4–8.6). In the least weathered

444 samples the pristane/phytane ratio is low (pr/ph = 0.7–1.7). This second family of waxy

445 bitumens may be subdivided into Family 2A and Family 2B, the latter distinguished by the

446 presence of a pronounced naphthene hump in their saturated hydrocarbon chromatograms (Fig.

447 3b, c). In the least weathered samples of both sub-families, the n-alkane profile is distinctly

448 bimodal, although the mode centred on n-C$_{17}$ is less dominant in Family 2A. It is largely on the

449 basis of their bot/n-C$_{29}$ values that little weathered samples CB-28 and CB-92 (examples of

450 Family 3 in McKirdy et al., 1994) are herein reassigned to Family 2B (Tables 3 and 4).

451 The biomarker assemblage of this family is similar to that described for Family 1, except

452 that in addition they contain trace quantities of the marine algal biomarkers, 24-n-

453 propylcholestane and dinosterane (Tables 4 and 5). Their apparent mixed source affinity could

454 arise in one of several ways:

455 • Generation of hydrocarbons from Type I/II to Type II/III kerogens with the organic

456 matter being deposited in freshwater lacustrine or deltaic facies which were subjected to

457 episodic marine incursions.

458 • Acquisition of higher plant and/or marine signatures during migration of algal-derived

459 lacustrine oils through deltaic and marine facies.

460 • Reservoirs that have been charged by oils from different source rocks.

461

462 *3.2.3 Family 3*

463

464 The waxy bitumens of Family 3 differ from those of Family 2 in exhibiting a wider

465 spread of bulk compositions (paraffinic to aromatic-intermediate: Fig. 2); lower concentrations

466 of botryococcane (bot/n-C$_{29}$ = 0.04–0.14); and, on average, higher sulfur contents (S = 1.1–2.6

467 %) and somewhat lower pristane/phytane ratios (pr/ph typically <1: Table 3). These latter

468 features indicate that their source rocks were deposited beneath anoxic, saline (sulfate-bearing)

469 bottom waters starved of iron. Their isotopic signatures overlap those of Family 2 waxy

470 bitumens but are much more tightly grouped (Fig. 5). As was the case for Family 2, these

471 bitumens may be assigned to two sub-families, Family 3A and Family 3B, the saturated

472 hydrocarbon chromatograms of the latter displaying a more pronounced naphthene hump than

473 that shown in Fig. 3d.

474   The Family 3 waxy bitumens can be further distinguished from those of Families 1 and 2

475 by the dominance of cholestane and diacholestane in their C_{27}–C_{30} $5\alpha(H)$-sterane and diasterane

476 distributions, the presence of 24-*n*-propylcholestane and dinosterane, and the fact that bicadinane

477 and oleanane are present in only trace quantities (Tables 4 and 5). The Family 3 parent oils were

478 generated from a mixture of algal lipids and higher plant waxes, with the former providing the

479 greater input to their source kerogen. The change in overall geochemical character from Family

480 1 to 3 reflects a progressive decrease in the amount of terrestrial influence and a corresponding

481 increase in marine algal source affinity. An accompanying decline in the triterpane ratio Ts/Tm,

482 from values ≥3 in Family 1 to ≈1 in Family 3 (Table 4), is consistent with a change in source

483 lithofacies from anoxic shale for Family 1 to predominantly carbonate for Family 3 (Peters et al.,

484 2005).

485

486 *3.2.4 Family 4*

487

488   Family 4 comprises seven miscellaneous samples of waxy, paraffinic to paraffinic-

489 naphthenic bitumen (Fig. 2) which have bimodal *n*-alkane profiles, with maxima at C_{18} and either

490 C_{31} or C_{34}, but notably lack botryococcane. For such a little-weathered bitumen (DOW = 0.5), the

491 saturated hydrocarbon distribution of sample EC 1 (Figs. 3d and 4f) is highly unusual in that it is

492 dominated *n*-alkanes in the range C_{30}–C_{50}. It bears a striking resemblance to that of wax

493   precipitated from a marine-sourced crude oil during production (Philp, 1994, fig. 2).

494   MRM data were acquired for four of these samples (Table 4). The presence of trace

495   quantities of 24-n-propylcholestane and dinosterane, but no oleanane or bicadinanes (Fig. 7)

496   provides evidence for their marine source affinity. In the absence of appropriate MRM data

497   showing its lack of bicadinanes, sample CB-31-1 was originally assigned to Family 2 (McKirdy

498   et al., 1994). The relatively low abundance of diasteranes in sample EC 1 (C_{29} dia/ster = 0.18),

499   together with the obvious presence of 30-norhopanes (C_{29}/C_{30} hopane = 1.8) and its bulk C-

500   isotopic composition (CV <0.47; Fig. 5), implies that its parent oil was derived from a marine

501   carbonate source rock containing predominantly algal organic matter. Higher diasterane

502   abundances in the other three samples are more typical of an argillaceous source rock. This

503   implied difference in source facies in turn is consistent with the fact that sample EC 1 is

504   appreciably more depleted in ^{13}C than the other Family 4 bitumens and hence plots as an outlier

505   in Fig. 5. It is therefore apparent that the Family 4 waxy bitumens originated from several

506   different source rocks of varying marine lithofacies. The highly weathered state of more than

507   half the samples assigned to this family (Table A3, supplementary material) precluded their

508   definitive assignment to sub-families.

509   The waxy bitumens of Family 4 differ from those of Family 1, 2 and 3 in lacking

510   botryococcane, oleanane and bicadinanes (Table 5). While not necessarily precluding an origin

511   in Southeast Asia, the absence of these biomarkers raises the possibility that the Family 4 waxy

512   bitumens could be products of a petroleum system located within the offshore Otway Basin

513   and/or Bight Basin, although the Bremer Basin and offshore Perth Basin could also be

514   possibilities given the west to east current direction that transports the waxy bitumens in

515   southern Australian waters (Edwards et al, 2016). Further afield, the basins on Australia's North

516   West Shelf are also worthy of consideration since they lie in the path of the Leeuwin Current.

517   The highly weathered state of more than half the samples (Table A3, supplementary material)

518   prevented their definitive assignment to sub-families.

519

520   *3.2.5 Family 5*

521

522   Family 5 comprises five samples of soft bitumen colonised by goose barnacles (Edwards

523   et al., 2016, fig. 5g). These waxy bitumens have a paraffinic bulk composition (Fig. 2) and are

524   sulfur-poor (S = 0.2 %: Table A1, supplementary material). Their *n*-alkane distribution is

525   unimodal (maximum at C_{27}) with the lower molecular weight homologues (C_{15}–C_{21}) largely

526   intact (Fig. 3). Pristane is much more abundant than phytane (pr/ph >4). The other key

527   characteristics which distinguish the Family 5 waxy bitumens from Families 1 to 4 are that they

528   do not contain botyrococcane (Fig. 3f), they are isotopically more depleted in ^{13}C, and their CV

529   values are >0.47 (Table 5), highlighting their land-plant source affinity (Fig. 5). Together these

530   features indicate their likely derivation from coal-rich fluvial to deltaic sediments. MRM

531   analysis of their saturated hydrocarbon fractions is required to further constrain the age and

532   location of their source lithofacies.

533

534   *3.3 Weathering characteristics*

535   The weathering of an oil at or near the sea surface involves a combination of evaporation,

536   photo-oxidation, water washing and biodegradation and causes a marked change in its chemical

537   composition (National Research Council, 2003). The most significant effects are evaporative

538   loss of the light ends (C_1–C_{12}), dissolution of monoaromatic hydrocarbons (e.g. benzene, toluene)

539   and the selective removal of the C_{12}–C_{23} *n*-alkanes by bacteria, followed at a slower rate by the

540   low-molecular-weight isoprenoid alkanes. Overall, there is an increase in the proportion of non-

541   hydrocarbons (resins and asphaltenes), mainly at the expense of the saturated hydrocarbons as

542   illustrated by sub-sampling of Family 1 bitumen 28 (Table A2, supplementary material).

543   The aromatic hydrocarbon fractions of eleven samples (representative of all but Family

544   4) were analysed by SIM GC-MS to augment the limited aromatic maturity data already

545 available on southern Australian waxy bitumens (McKirdy et al., 1994). However, inspection of

546 their respective mass chromatograms revealed that in more than half the samples phenanthrene

547 and the methylphenanthrenes, along with naphthalene and the methylnaphthalenes, had largely

548 been removed by weathering. A combination of water washing and biodegradation (Palmer,

549 1993; Peters et al., 2005) is likely to have been responsible for their removal.

550   The Family 1 waxy bitumens include some of the most highly weathered samples (i.e. *n*-

551 alkanes below C_{23} and light isoprenoid alkanes totally removed). These paraffinic to paraffinic-

552 naphthenic bitumens typically contain high concentrations of saturated hydrocarbons (Table A3,

553 supplementary material) which would not normally be expected to remain in extremely

554 weathered oil samples. A selection of these bitumens with DOW values in the range 0–5 exhibit

555 a progressive depletion of the C_{14}–C_{32} *n*-alkanes (Fig. 4a–e) which is typical of oils that have

556 been degraded by aerobic bacteria (Bailey et al., 1973). The pristane/phytane ratio systematically

557 decreases with increased weathering as pristane is more volatile than phytane. A marked increase

558 in the pristane/*n*-heptadecane and the phytane/*n*-octadecane ratios is observed as biodegradation

559 proceeds (Table 3). The botryococcane/*n*-nonacosane ratio in both Family 1 and Family 2

560 bitumens likewise increases with increasing biodegradation.

561   In some of the Family 1 waxy bitumens analysed by MRM (viz. A923.152A, 48 Dune

562 and 68), the sterane distributions have been impacted by weathering (DOW = 2–4: Table A2,

563 supplementary material), displaying a preferential loss of the biological isomer (20R). Two of

564 these samples have also lost their bicadinanes and methylbicadinanes (Table 4). That said, there

565 are other similarly weathered samples in which these biomarkers are intact, although this may

566 also reflect variations in the input of dipterocarp resins to the source rocks.

567   The extensive biodegradation displayed by the most severely weathered waxy bitumens

568 is most likely to have occurred during their exposure to the marine environment. However,

569 another possibility is that their parent oils may have been degraded in the reservoir. For example,

570 similar highly biodegraded oils are produced from the Duri Field in Sumatra (Seifert and

571 Moldowan, 1981). From the biomarker information obtained for these waxy bitumen samples it

572 is not possible to differentiate between *in situ* reservoir alteration and biodegradation in the

573 marine environment.

574   The fact that the waxy bitumens form tar balls means that they can survive in the ocean

575 for long (albeit unquantified) periods of time. Their resistance to weathering is not unique as

576 there are many documented cases of large pieces of bitumen surviving in the sea for more than a

577 year (Blumer et al., 1973; Butler et al., 1976; Lee, 1980; Warnock et al., 2015).

578

579 *3.4 Evidence for a Southeast Asian origin*

580

581   The unusual assemblage of the age-specific biomarkers botryococcane, oleanane and

582 bicadinanes found in the Family 1, 2 and 3 waxy bitumens (Table 5), suggests that their parent

583 oils originated from one or more Cenozoic basins somewhere in the Indonesian Archipelago

584 (Fig. 9).

585   Botryococcane has previously been identified only in Cenozoic lacustrine oils and source

586 rocks from Central Sumatra (notably the Minas, Duri and South Bekasap fields: Seifert and

587 Moldowan, 1981) and the Eocene Maoming Oil Shale, Maonan Basin, China (Brassell et al.,

588 1986, 1988). High concentrations of 4-methyl-24-ethylcholestane are also diagnostic of

589 lacustrine environments. This sterane is abundant in the Messel Shale (Rubinstein and Albrecht,

590 1975) and many non-marine Chinese oils (Shi et al., 1982; Wolff et al., 1986a, b; Philp and Fan,

591 1987; Fan and Baisheng, 1988). However, the association of high concentrations of

592 botryococcane and 4-methylsteranes has been rarely documented, a notable exception being the

593 aforementioned Maoming Oil Shale. Oleanane first appeared during the Late Cretaceous (late

594 Campanian) but high concentrations of this pentacyclic triterpane have only been observed in

595 Cenozoic sediments and oils, corresponding to the time when angiosperms became the dominant

596 flora. Bicadinane has been identified in Cenozoic oils throughout Indonesia, southern China,

23

597 Papua New Guinea, the Philippines and New Zealand (van Aarssen et al., 1990; Murray et al.,

598 1993, 1994a, b). However, high concentrations of bicadinane appear to be confined to Cenozoic

599 sediments and associated oils from Southeast Asia.

600   Bicadinanes are derived principally from tropical angiosperms of the family

601 *Dipterocarpaceae*, trees that first appeared in the Oligocene and now dominate the lowland rain

602 forests of Southeast Asia, but do not grow in Australia (Paijmans, 1976; Ashton, 1982; Ghazoul,

603 2016). Fossil evidence suggests that they originated in Africa, and subsequently migrated via

604 India to Asia. However, no dipterocarp micro- or megafossils have been identified in Cenozoic

605 sedimentary successions within Australia (Hill, 1994). The trace levels of bicadinanes (±

606 oleanane) found in a Jurassic crude oil and source rock from the Eromanga Basin (Armanios et

607 al., 1995), Jurassic oils and condensates from the Perth Basin (Summons et al., 1995) and Late

608 Cretaceous-sourced oils in the Gippsland Basin (George et al., 1998; Volk et al., 2011) are

609 attributable to a more general angiosperm flora (van Aarssen et al., 1994; Murray et al., 1994b).

610 Therefore, it seems reasonable to conclude that these Family 1–3 waxy bitumens do not originate

611 from Australian sedimentary basins.

612   High concentrations of bicadinane are in fact typical of Cenozoic oils and source rocks

613 from Indonesia (Cox et al., 1986; Teerman et al., 1987; van Aarssen et al., 1992; Sosrowidjojo et

614 al., 1994) and Papua New Guinea (Murray et al., 1993; Waples and Wulff, 1996). They reflect

615 the predominance of dipterocarps in the Cenozoic flora of this region. Given that the biomarker

616 signatures of the complete range of waxy bitumens indicate their derivation from lacustrine

617 through marginal marine to paludal (coal-bearing) organic facies (Table 5), it is informative to

618 note similar signatures and source affinities in oils from Indonesia (Table 7).

619   Waxy oils of lacustrine source affinity are confined to basins located in western

620 Indonesia (Fig. 9). Arguably the best documented are those in the onshore Central and South

621 Sumatra basins and the offshore Sunda and East Java basins (Pramono et al., 1990; Schiefelbein

622 and Cameron, 1997; Hwang et al., 2002). Their respective source rocks, viz. the Brown Shale

623   Formation, Pematang Group (Williams et al., 1985) and the Banuwati Shale (Robinson, 1987),

624   are of Eocene to Oligocene age. The former unit generated the oil reserves of the giant Minas (4

625   billion barrels) and Duri (3 billion barrels). Lacustrine oils likewise occur further north in the

626   offshore East Natuna, West Natuna and Anambas basins (Noble et al., 2009).

627   Seifert and Moldowan (1981) were the first to report that lacustrine oils produced from

628   the Central Sumatra Basin have divergent geochemical signatures. The biomarker assemblage of

629   the heavily biodegraded Duri-1 crude oil matches that of the Minas-1 oil, both containing

630   abundant botryococcane. In other oils, such as the South Bekasap-1 crude, the concentration of

631   botryococcane is much lower; and in the Pematang-1 oil this freshwater algal marker is entirely

632   absent, a more saline lagoonal setting for its source rock being indicated by the presence of

633   gammacerane (Table 7). With access to larger datasets, subsequent workers have divided the

634   Indonesian lacustrine oil family into subgroups: Type A, B and C (ten Haven and Schiefelbein,

635   1995) and Groups I–V (Hwang et al., 2002). Across Sumatra this compositional heterogeneity

636   has been attributed to differences in water chemistry in different sub-basins (Katz and Mertani,

637   1989) or, alternatively, variation of the Brown Shale source rock facies within a single deep

638   lakeee system (Schiefelbein and Cameron, 1997).

639   The biomarker assemblages of the southern Australian waxy bitumens (particularly

640   Families 1–3) show many similarities to some of the lacustrine West Indonesian oils (Table 7),

641   but an exact match is not evident. For example, the deep lacustrine Minas-1 oil from the Central

642   Sumatra Basin is a high wax, low sulfur, paraffinic crude oil that closely resembles the Family 1

643   bitumens. As previously reported (Seifert and Moldowan, 1981; Currie et al., 1992; Summons et

644   al., 1993; McKirdy et al. 1994; Peters et al., 2005), its biomarker signatures include unusually

645   high concentrations of botryococcane, C_{30} 4-methylsteranes, bicadinane and methylbicadinane; a

646   ethylcholestane-dominant sterane distribution; the presence of oleanane; and an absence of C_{30}

647   24-n-propylcholestane and dinosterane, all features of the Family 1 bitumens (Table 5).

648   Moreover, its C-isotopic signatures ($\delta^{13}C_{sat} = -26.2‰$, $\delta^{13}C_{aro} = -24.7‰$, CV = -0.17: Peters et

649   al., 2005) also plot close to those of the Family 1 bitumens (Fig. 5). However, its bicadinane

650   distribution differs significantly from that of a typical Family 1 bitumen (Fig. 10), as does its

651   HMW C_{40}–C_{60} alkane distribution and those of several other fresh/brackish water lacustrine oils

652   from Central Sumatra (Carlson et al., 1993), preventing their exact correlation.

653   Other Indonesian waxy crude oils originated from coal-rich fluvial deltaic sediments of

654   Oligocene-Miocene age and are assigned to the terrigenous family (Table 7). Source rocks in this

655   category include the coals of the Sihapas Group, Central Sumatra Basin and the coals and shales

656   of the Talang Akar Formation in the South Sumatra Basin, the Sunda Basin and the Ardjuna

657   Sub-basin (Robinson, 1987; Pramono et al., 1990; Noble et al., 1991). The Australian waxy

658   bitumens of Family 5 (Table 5) are insufficiently characterised to ascertain the degree to which

659   they resemble the terrigenous oils of western Indonesia, but warrant further research.

660   With the exception of several examples from the North Sumatra and East Natuna basins,

661   most Indonesian crude oils of marine origin are located in the eastern half of the archipelago (ten

662   Haven and Schiefelbein, 1995; Noble et al., 2009). Here their source rocks may be of either

663   Cenozoic or Mesozoic age and include both carbonate and shale lithofacies, whereas in western

664   Indonesia oil-prone marine source rocks are both less common and all of Cenozoic age (Price et

665   al., 1987; Robinson, 1987; Peters et al., 1999). It is in Eastern Indonesia that most of the known

666   offshore oil seeps occur (Fig. 9). Those located in Seram and the Timor Sea are of marine source

667   affinity and thought to have originated in Mesozoic carbonate and shale lithofacies (Price et al.,

668   1987; Noble et al., 2009). In this respect, they appear similar to the Family 4 waxy bitumens

669   which notably lack oleanane and bicadinanes (Table 5).

670   An alternative origin for the marine waxy bitumens of Family 4 is from the Australian

671   North West Shelf and Perth basins where marine oils are known (Edwards and Zumberge, 2005

672   and references therein). In contrast to Southeast Asia, the passive margin of Australia has few

673   documented seepage sites. Where detected, seepage appears to be predominantly gas rather than

674   oil (Logan et al., 2010). However, in the Browse Basin on the Yampi Shelf (in the vicinity of the

675   Cornea field) natural oil and gas seeps have been sampled (Rollet et al., 2006; Burns et al.,

676   2010), and a microseep of oil was also found at one site in the southern Bonaparte Basin

677   (Stalvies et al., 2017; Fig. 9). These seeps were correlated with crude oils (Cornea and Gwydion)

678   from the Yampi Shelf and determined to be sourced by the Early Cretaceous Echuca Shoals

679   Formation (Logan et al., 2008; Stalvies et al., 2017). However, the C-isotopic compositions of

680   these oils and source rocks are lighter than those displayed by the Family 4 waxy bitumens (Fig.

681   5), ruling out the Browse Basin as their potential source. Likewise, the Early Triassic-sourced

682   marine oils from the Perth Basin have significantly lighter isotopic compositions than the Family

683   4 waxy bitumens and contain a distinctive C_{33} n-alkylcyclohexane (Summons et al., 1995;

684   Thomas and Barber, 2004) not found in the bitumens, thereby precluding their correlation. The

685   majority of Jurassic marine oils in the Northern Carnarvon and Bonaparte basins are non-waxy

686   crudes sourced by organic-rich marine shales within the Dingo Claystone and Vulcan Formation

687   (Edwards and Zumberge, 2005). However, since these basins also host some waxy Jurassic oils

688   that are isotopically similar to the Family 4 waxy bitumens, further work is required to evaluate

689   their possible common origin.

690   In summary, the southern Australian coastal waxy bitumens cannot yet be

691   precisely correlated with any Southeast Asian oils. Nevertheless, the Family 1–3 waxy bitumens

692   (comprising ~80% of the samples examined in this study) display sufficient similarities with oils

693   from Indonesia to be most likely derived from this region. An Australian origin for the Family 4

694   and 5 waxy bitumens remains a possibility, notwithstanding the fact that they do not match any

695   of the oils so far discovered in the Otway Basin, nor any of the minor oil shows (e.g. Greenly-1,

696   Duntroon Sub-basin; Jerboa-1, Eyre Sub-basin) encountered during drilling in the Bight Basin

697   (Ruble et al., 1991; Padley, 1995; Edwards et al., 1999). A potential origin for the Family 5

698   bitumens in the Gippsland Basin was considered but dismissed because, although Latrobe

699   Group-sourced oils have similar pristane/phytane ratios (pr/ph = 3–11), they are significantly

700   more enriched in ^{13}C ($\delta^{13}C_{sat}$ = –25.2 to –28.0‰; $\delta^{13}C_{arom}$ = –24.6 to –26.9‰: Summons et al.,

701 2002). Further studies of potential source rocks and generated hydrocarbons within the basins

702 along Australia's southern margin and North West Shelf are required for definitive oil-source and

703 oil-oil correlations.

704

705 *3.5 Possible modes of origin*

706

707   Accepting that the majority of the waxy coastal bitumens are the remains of weathered

708 Southeast Asian crude oils, their occurrence in southern Australia has several possible

709 explanations: jettisoned oil cargoes, tanker washings, leakage from oil pipelines, or natural ocean

710 flotsam emanating from oil seeps.

711   Australia began importing crude oil during the mid-1950s and continues to import large

712 quantities from Southeast Asia. The composition of many of these imported crudes is

713 documented in a national oil-on-the-sea database (NOSID: Sandison and Edwards, 2001). Oil

714 slicks from tanker washings and petroleum accidentally spilled from local shipping

715 intermittently strand along the Victorian and South Australian coastline (Padley et al., 1993).

716 The physical and chemical properties of these freshly spilled oils readily distinguish them from

717 weathered waxy bitumen (Edwards et al., 2016). The latter is therefore thought not to be a by-

718 product of local maritime activity in southern Australian waters. However, the Straits of Malacca

719 and the Sunda Strait are major shipping routes where tanker cleaning operations are undertaken

720 prior to reloading at Singapore (Fig. 9). Regular oil spills in the western Java Sea since 2004

721 have been linked to both the high density of maritime traffic and leakage from submarine

722 pipelines carrying oil from offshore production platforms (Putri et al., 2016).

723   Active onshore oil seeps are common throughout the Indonesian Archipelago (Fig. 9) and

724 Papua-New Guinea (Livsey et al., 1992; Waples and Wulff, 1996), but few overlie known oil

725 fields and none of the giant fields are associated with seeps (Macgregor, 1993, 1995). In the case

726 of the giant Minas Field, the low ratio of gas to oil has reduced the capacity for vertical

727   migration, making it difficult for the oil to escape to the surface (Thompson et al., 1991). Unless

728   adjacent to major rivers, the inland locations of these surface seeps make them less likely sources

729   for the Australian waxy bitumens.

730   Submarine seeps such as those recently identified by multibeam echo sounder

731   bathymetry and backscatter imaging in combination with deep-sea piston coring (Fig. 9: Noble et

732   al., 2009; Orange et al., 2009) are potential sources for the Australian coastal waxy bitumens. As

733   previously mentioned, the seeps located offshore from the islands of Timor and Seram are

734   potential points of origin for the marine Family 4 waxy bitumens. It is also worth noting that the

735   asphalt deposit on Buton (Fig. 9) originates from a marine crude oil (Satyana et al., 2013). While

736   no seeps have yet been identified in the offshore Sunda Basin (Macgregor, 1995), this Cenozoic

737   lacustrine depocentre is the site of major lacustrine oil production and remains a possible source

738   for the Family 1 bitumens. Likewise, the co-occurrence of Cenozoic lacustrine and marine oils in

739   the offshore East Natuna Basin (Noble et al., 2009) makes it a potential source for the mixed

740   lacustrine/marine bitumens of Families 2 and 3 (Table 5). Natural seafloor seepage of crude oil

741   into the ocean throughout the Indonesian Archipelago is now well established and would readily

742   give rise to the seaborne waxy bitumens (tar balls) that ultimately strand in southern Australia.

743   However, the fact that such seeps are generally episodic and ephemeral (Kvenvolden and

744   Cooper, 2003) adds to the difficulty of linking a given bitumen stranding to its parent seep.

745   The possibility that Southeast Asian oils could be transported as flotsam into Australian

746   waters via the Leeuwin Current (McGowran et al., 1997) was invoked by Currie et al. (1992) as

747   an explanation for the geochemical similarity of the Western Australian coastal bitumens and

748   certain Indonesian crude oils. For details of the complex system of ocean currents that flow

749   through the Indonesian Archipelago (Fig. 9) the reader is referred to Gordon (2005), Gordon et

750   al. (2012) and Susanto et al. (2016), while the manner in which they feed into the headwaters of

751   the Leeuwin Current and ultimately into the coastal current and South Australian Current that

752   traverse Australia's southern continental margin (Middleton and Bye, 2007) is summarised in

753 Edwards et al. (2016). A new study, aimed at more closely linking the stranding pattern of

754 coastal bitumen in South Australia to offshore oceanographic conditions during the last three

755 years (2014–2016), is well advanced (Corrick et al., 2016).

756

757 **4. Conclusions**

758

759   Geochemical analysis of 96 waxy bitumens recovered from the coastline of southern

760 Australia has shown them to be inspissated high-wax crude oils of paraffinic to aromatic-

761 intermediate bulk composition. Subtle elemental, isotopic and biomarker differences evident in

762 these bitumens allow their assignment to at least five different oil families. Their inferred source

763 facies range from deep freshwater lacustrine through paludal to estuarine and deltaic marine,

764 possibly deposited within different sedimentary basins.

765   The Family 1, 2 and 3 waxy bitumens all contain biomarkers derived from the freshwater

766 alga *Botryococcus* sp. and tropical angiosperms (notably dipterocarps). Similar biomarker

767 assemblages are unknown in Australian crude oils and source rocks but are common in the

768 Cenozoic basins of Indonesia. The Family 4 bitumens lack these biomarkers but do contain

769 dinosterane and 24-*n*-propylcholestane, indicative of a marine source affinity, while the C-

770 isotopic signatures and high pristane/phytane ratios of Family 5 waxy bitumens are consistent

771 with an origin from coal-rich source rocks. Hence, it is believed that the majority of the waxy

772 bitumens represent an oceanic influx of non-indigenous, Indonesian crude oil into the waters of

773 southern Australia. Further studies on the Family 4 and 5 waxy bitumens are required, since their

774 origin from seepage in offshore Australian basins has not been ruled out.

775   The body of geochemical and oceanographic evidence assembled herein points to the

776 origin of the Family 1–3 waxy bitumens from long-term natural seepage within the Indonesian

777 Archipelago. However, it is unknown whether their parent oils emanate from submarine seeps

778 or, less likely, from inland seepages which are then carried to the sea by rivers. The common

779 practice of tanker cleaning operations in the Java and Banda Seas may augment the supply of

780 coastal bitumen to the beaches of Australia. Further work is required to determine whether such

781 an anthropogenic input makes a significant contribution to the natural background level of

782 seaborne oil within the region.

783

784 **Acknowledgements**

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References

807

808 van Aarssen, B. G. K., Cox, H. C., Hoogendoorn, P., de Leeuw, J. W., 1990. A cadinene

809   biopolymer in fossil and extant dammar resins as a source for cadinanes and bicadinanes in

810   crude oils from southeast Asia. Geochimica et Cosmochimica Acta 54, 3021–3031.

811 van Aarssen, B.G.K., Hessels, J.K.C., Abbink, O.A., de Leeuw, J.W., 1992. The occurrence of

812   polycyclic sesqui-, tri-, and oligoterpenoids derived from a resinous polymeric cadinene in

813   crude oils from southeast Asia. Geochimica et Cosmochimica Acta 56, 1231–1246.

814 van Aarssen, B.G.K., de Leeuw, J.W., Collinson, M., Boon, J., Goth, K., 1994. Occurrence of

815   polycadinene in fossil and recent resins. Geochimica et Cosmochimica Acta 58, 223–229.

816 Alam, M., Pearson, M.J., 1990. Bicadinanes in oils from the Surma Basin, Bangladesh. Organic

817   Geochemistry 15, 461–464.

818 Alexander, R., Noble, R.A., Kagi, R.I., 1987. Fossil resin biomarkers and their application in oil

819   to source-rock correlation, Gippsland Basin, Australia. Australian Petroleum Exploration

820   Association Journal 27(1), 63–71.

821 Alexander, R., Currie, T.J., Kagi, R.I., 1994. The origin of coastal bitumens from Western

822   Australia. Australian Petroleum Exploration Association Journal 34(1), 787–798.

823 Armanios, C., Alexander, R., Sosrowidjojo, I.B., Kagi, R.I., 1995. Identification of bicadinanes

824   in Jurassic organic matter from the Eromanga Basin, Australia. Organic Geochemistry

825   23, 837–843.

826 Ashton, P.S., 1982. *Dipterocarpaceae*. Flora Malesiana 9(2), 237–552.

827 Bailey, N.J.L., Krouse, H.R., Evans, C.R., Rogers, M.A., 1973. Alteration of crude oil by waters

828   and bacteria – evidence from geochemical and isotopic studies. American Association of

829   Petroleum Geologists Bulletin 57, 1276–1290.

830   Blumer, M., Ehrhardt, M., Jones, J.H., 1973. The environmental fate of stranded crude oil. Deep-

831   Sea Research 20, 239–259.

832   Boreham, C.J., Summons, R.E., Roksandic, Z., Dowling, L.M., Hutton, A.C., 1994. Chemical,

833   molecular and isotopic differentiation of organic facies in the Tertiary lacustrine Duaringa

834   Oil Shale deposit, Queensland, Australia. Organic Geochemistry 21, 685–712.

835   Bourman, R.P., Murray-Wallace, C.V., Harvey, N., 2016. Coastal Landscapes of South

836   Australia. University of Adelaide Press, Adelaide, pp. 145–176. DOI:

837   http://dx.doi.org/10.20851/coast-sa

838   Brassell, S.C., Eglinton, G., Fu, J., 1986. Biological marker compounds as indicators of the

839   depositional history of the Maoming Oil Shale. In: Leythaeuser, D., Rullkötter, J. (Eds.),

840   Advances in Organic Geochemistry 1985, Pergamon, Oxford, pp. 927–941.

841   Brassell, S.C., Sheng, G., Fu, J., Eglinton, G., 1988. Biological markers in lacustrine Chinese oil

842   shales. In: Kelts, K., Talbot, M., Fleet, A.J. (Eds.), Lacustrine Petroleum Source Rocks.

843   Geological Society Special Publication No. 40, Blackwell, Oxford, pp. 229–308.

844   Burns, K.A., Brinkman, D.L., Brunskill, G.J., Logan, G.A., Volk, H., Wasmund, K., Zagorskis,

845   I., 2010. Fluxes and fate of petroleum hydrocarbons in the Timor Sea ecosystem. Marine

846   Chemistry 118, 140–155.

847   Butler, J.N., Morris, B.F., Sleeter, T.D., 1976. The fate of petroleum in the open ocean. In:

848   Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. American

849   Institute of Biological Sciences, Washington D. C., pp. 287–297.

850   Carlson, R.M.K., Teerman, S.C., Moldowan, J.M., Jacobson, S.R., Chan, E.I., Dorrough,

851   K.S., Seetoo, W.C., Mertani, B., 1993. High temperature gas chromatography of high-wax

852   oils. In: Proceedings of the Indonesian Petroleum Association, pp. 483–507.

853   Connan, J., 1984. Biodegradation in reservoirs. In Brooks, J. and Welte, D.H. (Eds.), Advances

854   in Petroleum Geochemistry, Vol. 1. Academic Press, London, pp. 299–335.

855   Corrick, A.J. Hall, P.A., McKirdy, D.M., Gong, S., Trefry, C., Dyt, C., Angelini, Z., Ross, A.S.,

856   Kempton, R., Armand, S., White, C., 2016. A revised oil family classification scheme and

857   geochemical weathering proxies for South Australian coastal bitumen strandings. 19th

858   Australian Organic Geochemistry Conference, Conference Handbook and Abstracts, pp.

859   24–25.

860   Cox, H.C., de Leeuw, J.W., Schenck, P.A., van Koningsveld, H., Jansen, J.C., van de Graaf, B.,

861   van Geerestein, V.J., Kanters, J.A., Kruk, C., Jans, A.W.H., 1986. Bicadinane, a C_{30}

862   pentacyclic isoprenoid hydrocarbon found in crude oil. Nature, 319, 316–318.

863   Currie, T.J., Alexander, R., Kagi, R.I., 1992. Coastal bitumens from Western Australia – long

864   distance transport by ocean currents. Organic Geochemistry 18, 595–601.

865   Derenne, S., Largeau, C., Casadevall, E., Connan, J., 1988. Mechanism of formation and

866   chemical structure of coorongite – II. Structure and origin of the labile fraction. Fate of

867   botryococcenes during early diagenesis. Organic Geochemistry 13, 965–971.

868   Dowling, L.M., Boreham, C.J., Hope, J.M., Murray, A.P., Summons, R.E., 1995. Carbon

869   isotopic composition of hyrdocarbons in ocean-transported bitumens from the coastline of

870   australia. Organic Geochemistry 23, 729–737.

871   Edwards, D.S., Zumberge, J.E., 2005. The oils of western Australia II. Regional petroleum

872   geochemistry and correlation of crude oils and condensates from western Australia and

873   Papua New Guinea. Geoscience Australia and GeoMark Research Ltd, Canberra and

874   Houston, unpublished. http://www.ga.gov.au/metadata

875   gateway/metadata/record/gcat_37512

876   Edwards, D.S., McKirdy, D.M., Summons, R.E., 1998. Enigmatic asphaltites from the southern

877   Australian margin: molecular and isotopic composition. PESA Journal 26, 106–129.

878   Edwards, D.S., Struckmeyer, H.I.M., Bradshaw, M.T., Skinner, J.E., 1999. Geochemical

879   characteristics of Australia's southern margin petroleum systems. Australian Petroleum

880   Production and Exploration Association Journal 39(1), 297–321.

881   Edwards, D.S., Vinall, D.R., Corrick, A.J., McKirdy, D.M., 2016. Natural bitumen stranding on

882   the ocean beaches of southern Australia: a historical and geospatial review. Transactions of

883   the Royal Society of South Australia 140(2), 152–185.

884   Fan Pu, Baisheng, Z., 1988. Biomarker characteristics of nonmarine oils in China. Organic

885   Geochemistry 13, 627–632.

886   George, S.C., Eadington, P.J., Lisk, M., Quezada, R.A., 1998. Geochemical comparison of oil

887   trapped in fluid inclusions and reservoired oil in Blackback oilfield, Gippsland Basin,

888   Australia. PESA Journal No. 26, 64–81.

889   Ghazoul, J., 2016. Dipterocarp Biology, Ecology and Conservation. Oxford University Press,

890   Oxford, 320 p.

891   Gordon, A.L., 2005. Oceanography of the Indonesian seas and their throughflow. Oceanography

892   13, 14–27.

893   Gordon, A.L., Huber, B.A., Metzger, E.J., Susanto, R.D., Hurlburt, H.E, Adi, T.R., 2012. South

894   China Sea throughflow impact on the Indonesian throughflow. Geophysical Research

895   Letters 33(11), http://dx.doi.org/10.1029/2012GL052021.

896   Grantham, P.J., Posthuma, J., Baak, A.,1983. Triterpanes in a number of Far Eastern crude oils.

897   In: Bjorøy, M. et al. (Eds.), Advances in Organic Geochemistry 1981, Wiley, Chichester,

898   pp. 675-683.

899   Hall, P.A., McKirdy, D.M., Grice, K., Edwards, D.S., 2014. Australasian asphaltite strandings:

900   their origin reviewed in light of the effects of weathering and biodegradation on their

901   biomarker and isotopic profiles. Marine and Petroleum Geology 57, 572–593.

902   ten Haven, H.L., Schiefelbein, C., 1995. The petroleum systems of Indonesia. In: Proceedings of

903   the Indonesian Petroleum Association 24th Annual Convention, pp. 443–459.

904   ten Haven, H.L., de Leeuw, J.W., Sinninghe Damsté, J.S., Schenck, P.A., Palmer, S.E.,

905   Zumberge, J.E., 1988. Application of biological markers in the recognition of

906   palaeohypersaline environments. In: Fleet, A.J., Kelts, K, Talbot, M.R. (Eds.), Lacustrine

907   Petroleum Source Rocks. Geological Society of London Special Publication 40, Blackwell,

908   Oxford, pp. 123-130.

909 Heath, D., Moffatt, B., Lowry, R., Rowland, S., 1995. Quantification of the C_{30+} fraction of

910   North Sea gas condensates by high temperature capillary gas chromatography. Analytical

911   Proceedings 32, 485–487.

912 Heath, D.J., Lewis, C.A., Rowland, S.J., 1997. The use of high temperature gas chromatography

913   to study the biodegradation of high molecular weight hydrocarbons. Organic Geochemistry

914   26, 459–473.

915 Hill, R.S. (ed.), 1994. History of the Australian Vegetation: Cretaceous to Recent. Cambridge

916   University Press, Cambridge, 433 p.

917 Holba, A.G., Tegelaar, E., Ellis, L., Singletary, M.S., Albrecht, P., 2000. Tetracyclic

918   polyprenoids: Indicators of freshwater (lacustrine) algal input. Geology 28, 251–254.

919 Huntley, D.J., Hutton, J.T., Prescott, J.R., 1993. The stranded beach-dune sequence of south-east

920   South Australia: a test of thermoluminescence dating, 0-800 ka. Quaternary Science

921   Reviews 12, 1–20.

922 Hwang, R.J., Heidrick, T., Mertani, B., Qivayanti, M.L., 2002. Correlation and migration studies

923   of North Central Sumatra oils. Organic Geochemistry 33, 1361–1379.

924 Katz, B.Z., Mertani, B., 1989. Central Sumatra – a geochemical paradox. In: Proceedings of the

925   Indonesian Petroleum Association 18th Annual Convention, pp. 403–425.

926 Kvenvolden, K.A., Cooper, C.K., 2003. Natural seepage of crude oil into the marine

927   environment. Geo-Marine Letters 23, 140–146.

928 Lee, R.F., 1980. Processes affecting the fate of oil in the sea. In: Geyer, R.A. (Ed.), Marine

929   Environmental Pollution. 1. Hydrocarbons. Elsevier Science, Amsterdam, pp. 337–351.

930 Livsey, A.R., Duxbury, N., Richards, F., 1992. The geochemistry of Tertiary and Pre-Tertiary

931   source rocks and associated oils in Eastern Indonesia. In: Proceedings of the Indonesian

932   Petroleum Association 21st Annual Convention, pp. 499–520.

933   Logan, G.A., Jones, A.T., Ryan, G., Wettle, M., Thankappan, M., Grosjean, E., Rollet, N.,

934   Kennard, J.M., 2008. Review of Australian offshore natural hydrocarbon seepage studies.

935   Geoscience Australia Record, 2008/17.

936   Logan, G.A., Jones, A.T., Kennard, J.M., Ryan, G.J., Rollet, N., 2010. Australian offshore

937   natural hydrocarbon seepage studies, a review and re-evaluation. Marine and Petroleum

938   Geology 27, 26–45.

939   Longley, I.M., Barraclough, R., Bridden, M.A., Brown, S., 1990. Pematang lacustrine petroleum

940   source rocks from the Malacca Strait PSC, Central Sumatra, Indonesia. In: Proceedings of

941   the 19th Annual Convention of the Indonesian Petroleum Association, pp. 279–297.

942   Macgregor, D.S., 1993. Relationships between seepage, tectonics and subsurface petroleum

943   reserves. Marine and Petroleum Geology 10, 606–619.

944   Macgregor, D. S., 1995. The exploration significance of surface oil seepage: an Indonesian

945   perspective: In: Proceedings of the Indonesian Petroleum Association 24th Annual

946   Convention, pp. 97–109.

947   McGowran, B., Li, Q., Cann, J., Padley, D., McKirdy, D.M., Shafik, S., 1997. Biogeographic

948   impact of the Leeuwin Current in southern Australia since the late middle Eocene.

949   Palaeogeography, Palaeoclimatology, Palaeoecology 136, 19–40.

950   McKirdy, D.M., 1984a. Coastal bitumens and potential source rocks in the western Otway Basin,

951   South Australia and Victoria. AMDEL Report F 5840/84 for Australian Aquitaine

952   Petroleum Pty Ltd. and Ultramar Australia Inc., South Australian Department of Mines and

953   Energy Open File Envelope No. 5876, pp. 3–365.

954   McKirdy, D.M., 1984b. Coastal bitumens and potential source rocks, Duntroon Basin, South

955   Australia. AMDEL Report F 5769/84 for Getty Oil Development Company Ltd., South

956   Australian Department of Mines and Energy Open File Envelope No. 5876, pp. 366–402.

957   McKirdy, D.M., 1985a. Otway Basin coastal bitumens: elemental and stable isotopic

958   compositions, and biological marker geochemistry. AMDEL Report F 6176/85 for South

959 Australian Department of Mines and Energy (unpubl.). S. Aust. Dept. of Mines and Energy

960 Open File Envelope No. 5876, pp. 403-440.

961 McKirdy, D.M., 1985b. Coorongite, coastal bitumen, and their origins from the alga

962 *Botryococcus* in the western Otway Basin. In Otway 85 – Earth Resources of the Otway

963 Basin. Geological Society of Australia, Adelaide, pp. 34–49.

964 McKirdy, D.M., Horvath, Z., 1976. Geochemistry and significance of coastal bitumen from

965 southern and northern Australia. Australian Petroleum Exploration Association Journal

966 16(1), 123–136.

967 McKirdy, D.M., Aldridge, A.K., Ypma, P.J.M., 1983. A geochemical comparison of some crude

968 oils from Pre-Ordovician carbonate rocks. In: Bjorøy, M., Albrecht, P., Cornford, C., et al.

969 (Eds.), Advances in Organic Geochemistry 1981. John Wiley, Chichester, pp. 99–107.

970 McKirdy, D.M., Cox, R.E., Volkman, J.K., Howell, V.J., 1986. Botryococcane in a new class of

971 Australian non-marine crude oils. Nature 320, 57–59.

972 McKirdy, D.M., Cox, R.E., Morton, J.G.G., 1988. Biological marker, isotopic and geological

973 studies of lacustrine crude oils in the western Otway Basin, South Australia. In: Fleet, A.J.,

974 Kelts, K., Talbot, M.R. (Eds.), Lacustrine Petroleum Source Rocks. Geological Society of

975 London Special Publication 40, Blackwell, Oxford, p. 327

976 McKirdy, D.M., Summons, R.E., Padley, D., Serafini, K.M., Boreham, C.J., Struckmeyer,

977 H.I.M., 1994. Molecular fossils in coastal bitumens from southern Australia: signatures of

978 precursor biota and source rock environments. Organic Geochemistry 21, 265–286.

979 McKirdy, D.M., Corrick, A.J., Ross, A.S., Gong, S., Trefry, C., Dyt, C., Z. Angelini, Z., Jobin,

980 O., Hall, P.A., Edwards, D.S., 2015. Understanding the geographical distribution of

981 historical and modern asphaltite strandings along the South Australian coastline. AAPG

982 International Conference and Exhibition, Melbourne, Abstract.

983 Metzger, P., Casadevall, E., Pouet, M. J., Pouet, Y., 1985. Structures of some botryococcenes:

984   branched hydrocarbons from the B-race of the green alga *Botryococcus braunii*.

985   Phytochemistry 24, 2995–3002.

986 Middleton, J.F., Bye, J.A.T., 2007. A review of the shelf-slope circulation along Australia's

987   southern shelves: Cape Leeuwin to Portland. Progress in Oceanography, 75, 1–41.

988 Moldowan, J.M., Fago, F.J., Lee, C.Y., Jacobson, S.R., Watt, D.S., Slougui, N.E., Jeganathan,

989   A., Young, D.C., 1990. Sedimentary 24-*n*-propylcholestanes, molecular fossils diagnostic

990   of marine algae. Science 247, 309–312.

991 Moldowan, J.M., Fago, F.J., Carlson, R.M.K., Young, D.C., van Dutne, G., Clardy, J., Schoell,

992   M., Pillinger, C.T., Watt, D.S., 1991. Rearranged hopanes in sediments and petroleum.

993   Geochimica et Cosmochimica Acta 55, 3333–3353.

994 Murray, A.P., Summons, R.E., Bradshaw, J., Pawih, B., 1993. Cainozoic oil in Papua New

995   Guinea–evidence from geochemical analysis of two newly discovered seeps. In: Carman,

996   G.J., Carman, Z. (Eds.), Petroleum Exploration and Development in Papua New Guinea

997   Proceedings of the 2nd Papua New Guinea Petroleum Convention, Port Moresby, pp. 489–

998   498.

999 Murray, A., Padley, D., McKirdy, D.M., Summons, R.E., Booth, W.E., 1994a. Oceanic transport

1000   of fossil dammar resin: the chemistry of coastal resinites from South Australia.

1001   Geochimica et Cosmochimica Acta 58, 3049–3059.

1002 Murray, A.P., Summons, R.E., Boreham, C.J., Dowling, L.M., 1994b. Biomarker and *n*-alkane

1003   isotope profiles for Tertiary oils: relationship to source rock depositional setting. In:

1004   Telnæs, N., van Graas, G., Øygard, K. (Eds.), Advances in Organic Geochemistry 1993,

1005   Elsevier Science, Amsterdam, pp. 521–542.

1006 Murray-Wallace, C.V., Brooke, B.P., Cann, J.H., Belperio, A.P., Bourman, R.P., 2001. Whole-

1007   rock aminostratigraphy of the Coorong Coastal Plain, South Australia: towards a 1 million

1008   year record of sea-level highstands. Journal of the Geological Society, London 158, 111–

1009   124.

1010 National Research Council (NRC), 2003. Oil in the Sea: Inputs, Fates, and Effects. National

1011   Academies Press, Washington, D.C., 280 p.

1012 Noble, R.A., Wu, C.H., Atkinson, C.D., 1991. Petroleum generation and migration from Talang

1013   Akar coal and shales offshore N.W. Java, Indonesia. Organic Geochemistry 17, 363–374.

1014 Noble, R., Orange, D., Decker, J., Teas, P., Baillie, P., 2009. Oil and gas seeps in deep marine

1015   sea floor cores as indicators of active petroleum systems in Indonesia. In: Proceedings of

1016   the Indonesian Petroleum Association 33rd Annual Convention, pp. 385–394.

1017 Orange, D.L., Teas, P.A., Decker, J., Baillie, P., Johnstone, T., 2009. Using SeaSeep surveys to

1018   identify and sample natural hydrocarbon seeps in offshore frontier basins. In: Proceedings

1019   of the Indonesian Petroleum Association 33rd Annual Convention, 21 p.

1020 Padley, D., 1995. Petroleum geochemistry of the Otway Basin and the significance of coastal

1021   bitumen strandings on adjacent southern Australian beaches. Ph.D. thesis, University of

1022   Adelaide. http://hdl.handle.net/2440/48539

1023 Padley, D., McKirdy, D.M., Murray, A., Summons, R.E., 1993. Oil strandings on the beaches of

1024   southern Australia: origins from natural seepage and shipping. In: Oygard, K. (Ed.),

1025   *Organic Geochemistry*. Poster sessions from the 16th International Meeting on Organic

1026   Geochemistry, Stavanger. Falch Hurtigtrykk, Oslo, pp. 660–663.

1027 Paijmans, K. (Ed.), 1976. *New Guinea vegetation*. Australian National University Press,

1028   Canberra, 212 p.

1029 Palmer, S.E., 1993. Effect of biodegradation and water washing on crude oil composition. In:

1030   Engel, M.H., Macko, S.A. (Eds.), Organic Geochemistry. Plenum Press, New York, pp.

1031   511–533.

1032 Peters, K.E., Fraser, T.H., Amris, W., Rustanto, B., Hermanto, E., 1999. Geochemistry of crude

1033   oils from eastern Indonesia. American Association of Petroleum Geologists Bulletin 83,

1034   1927–1942.

1035 Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide, 2nd Edition. Volume

1036   2: Biomarkers and Isotopes in Petroleum Systems and Earth History. Cambridge

1037   University Press, pp. 475–1155.

1038 Philp, R.P., 1985. Fossil Fuel Biomarkers, Applications and Spectra. Methods in Geochemistry

1039   and Geophysics, 23. Elsevier, New York.

1040 Philp, R.P., 1994. Geochemical characteristics of oils from predominantly from terrigenous

1041   source materials. In: Scott, A.C., Fleet, A.J. (Eds.), Coal and Coal-bearing Strata as Oil-

1042   prone Source Rocks? Geological Society Special Publication 77, 71–91.

1043 Philp, R.P., Fan, Zhoa-an, 1987. A geochemical investigation of oils and source rocks from

1044   Qianjiang depression of Jianghan Basin, a terrigenous saline basin, China. Organic

1045   Geochemistry 11, 549–562.

1046 Pramono, H., Wu, C.C.H., Noble, R.A., 1990. A new oil kitchen and petroleum bearing sub-

1047   basin in the offshore northwest Java Basin. In: Proceedings of the Indonesian Petroleum

1048   Association 19th Annual Convention, pp. 254–277.

1049 Price, P.L., O'Sullivan, T., Alexander, R., 1987. The nature and occurrence of oil in Seram,

1050   Indonesia. In: Proceedings of the Indonesian Petroleum Association 16th Annual

1051   Convention, pp., 141–173.

1052 Putri, M.R., Setiawan, A., Pohlmann, T., Mayer, B., Gade, M., 2016. The assessment of oil

1053   pollution in Seribu Islands based on remote sensing and numerical models. Proceedings of

1054   the Living Planet Symposium 2016, Prague, Czech Republic, 9–13 May 2016 (ESA SP-

1055   740, August 2016).

1056 del Rio, J.C., Philp, R.P., 1992. High-molecular-weight hydrocarbons: a new frontier in organic

1057   geochemistry. Trends in Analytical Chemistry 11, 187–193.

1058 Robertson, 2017. Robertson Tellus Sedimentary Basins of the World Map,

1059   http://www.datapages.com/gis-map-publishing-program/gis-open-files/global-

1060   framework/robertson-tellus-sedimentary-basins-of-the-world-map

1061 Robinson, K.M., 1987. An overview of source rocks and oils in Indonesia. In: Proceedings of the

1062   Indonesian Petroleum Association 16th Annual Convention, pp. 97–122.

1063 Rollet, N., Logan, G.A., Kennard, J.M., O'Brien, P.E., Jones, A.T., Sexton, M., 2006.

1064   Characterisation and correlation of active hydrocarbon seepage using geophysical data

1065   sets: an example from the tropical, carbonate Yampi Shelf, Northwest Australia. Marine

1066   and Petroleum Geology 23, 145–164.

1067 Rubinstein, I., Albrecht, P., 1975. The occurrence of nuclear methylated steranes in shale.

1068   Journal of the Chemical Society, Chemical Communications, 957–958.

1069 Ruble, T.E., Logan, G.A., Blevin, J.E., Struckmeyer, H.I.M., Liu, K., Ahmed, M., Eadington,

1070   P.J., Quezada, R.A., 2001. Geochemistry and charge history of a palaeo-oil column:

1071   Jerboa-1, Eyre Sub-basin, Great Australian Bight. In: Hill, K.C., Bernecker, T. (Eds.),

1072   Eastern Australasian Basins Symposium: a refocused energy perspective for the future.

1073   Petroleum Exploration Society of Australia, Special Publication, pp. 521–529.

1074 Sandison, C., Edwards, D., 2001. National Oil-on-the-Sea Identification Database (NOSID)

1075   Users' Guide. Australian Geological Survey Organisation, Australian Government

1076   Analytical Laboratories and Australian Maritime Safety Authority, 39 p.

1077 Satyana, A.H., Irawan, C., Kurniawan, W., 2013. Revisit geology and geochemistry of Buton

1078   asphalt deposits, SE Sulawesi: implications for petroleum exploration of Buton area. In:

1079   Proceedings of the Indonesian Petroleum Association 37th Annual Convention &

1080   Exhibition. IPA13-G-170.

1081 Scheifelbein, C., Cameron, N., 1997. Sumatra/Java oil families. In: Fraser, A.J., Matthews, S.J.,

1082   Murphy, R.W. (Eds.), Petroleum Geology of Southeast Asia. Geological Society Special

1083   Publication 126, Blackwell, Oxford, pp. 143-146.

1084 Seifert, W.K., Moldowan, J.M., 1981. Palaeoreconstruction by biological markers. Geochimica

1085 et Cosmochimica Acta 45, 783–794.

1086 Shi, J.-Y., Mackenzie, A. S., Alexander, R., Eglinton, G., Gower, A.P., Wolff, G A., Maxwell,

1087 J.R., 1982. A biological marker investigation of petroleums and shales from the Shengli

1088 oilfield, the People's Republic of China. Chemical Geology 35, 1–31.

1089 Sofer, Z., 1984. Stable isotope compositions of crude oils: application to source depositional

1090 environments and petroleum alteration. Bulletin of the American Association of Petroleum

1091 Geologists 68, 31–49.

1092 Sosrowidjojo, I.B., Alexander, R., Kagi, R.I., 1994. The biomarker composition of some crude

1093 oils from Sumatra. Organic Geochemistry 21, 303–312.

1094 Sprigg, R.C., Woolley, J.B., 1963. Coastal bitumen in southern Australia, with special reference

1095 to observations at Geltwood Beach, south-east South Australia. Transactions of the Royal

1096 Society of South Australia 86, 67–103.

1097 Stalvies, C., Talukder, A., Ross, A., Grosjean, E., Carr, A., Williams, A., Gresham, M., Binning,

1098 M., Jablonski, D., 2017. Establishing hydrocarbon seepage to the Ashmore Platform,

1099 Bonaparte Basin, Australia: a natural seeps study. Marine and Petroleum Geology 8, 56–

1100 68.

1101 Subroto, E.A., Alexander, R., Pranyoto, U., Kagi, R.I., 1992. The use of 30-Norhopanes series,

1102 a novel carbonate biomarker, in source rock to crude oil correlation in the North Sumatra

1103 Basin, Indonesia. In: Proceedings of the Indonesian Petroleum Association, 21st Annual

1104 Convention, pp. 145-163.

1105 Summons, R.E., Volkman, J.K., Boreham, C.J., 1987. Dinosterane and other steroidal

1106 hydrocarbons of dinoflagellate origin in sediments and petroleum. Geochimica et

1107 Cosmochimica Acta 51, 3075–3082.

1108　Summons, R.E., Bradshaw, J., Brooks, D.M., Goody, A.K., Andrew P. Murray, A.P., Foster,

1109　　　C.B., 1993. Hydrocarbon composition and origins of coastal bitumens from the Northern

1110　　　Territory, Australia. PESA Journal No. 21, 31–42.

1111　Summons, R.E., Boreham, C.J., Foster, C.B., Murray, A.P., Gorter, J.D., 1995.

1112　　　Chemostratigraphy and the composition of oils in the Perth Basin, Western Australia.

1113　　　APEA Journal 35(1), 613–632.

1114　Summons, R.E., Zumberge, J.E., Boreham, C.J., Bradshaw, M.T., Brown, S.W., Edwards, D.S.,

1115　　　Hope, J.M., Johns, N., 2002. The Oils of Eastern Australia. Petroleum Geochemistry and

1116　　　Correlation. Geoscience Australia, Canberra and GeoMark Research, Houston.

1117　　　https://ecat.ga.gov.au/geonetwork/srv/eng/search#!a05f7892-ff6d-7506-e044-

1118　　　00144fdd4fa6

1119　Susanto, R.D., Wei, Z., Adi, T.R., Zheng, Q., Fang, G., Fan, B., Supangat, A., Agustiadi, T., Li,

1120　　　S., Trenggono, M., Setiawan, A., 2016. Oceanography surrounding Krakatau Volcano in

1121　　　the Sunda Strait, Indonesia. Oceanography 29(2), 264–272.

1122　Sutton, P.A., Rowland, S.J., 2012. High temperature gas chromatography–time-of-flight-mass

1123　　　spectrometry (HTGC–ToF-MS) for high-boiling compounds. Journal of Chromatography

1124　　　A 1243, 69–80.

1125　Sutton, P.A., Wilde, M.J., Martin, S.J., Cvacka, J., Rowland, S.J., 2013. Studies of long chain

1126　　　lipids in insects by high temperature gas chromatography and high temperature gas

1127　　　chromatography–mass spectrometry. Journal of Chromatography A 1297, 236–240.

1128　Teerman, S.C., Hwang, R.J., Williams, H.H., 1987. Liquid hydrocarbon potential of Sumatran

1129　　　resinite. In: Proceedings of the Indonesian Petroleum Association 16th Annual

1130　　　Convention, pp. 231–240.

1131　Tegelaar, E.W., Matthezing, R.M., Jansen, J.B.H., Horsfield, B., de Leeuw, J.W., 1989. Possible

1132　　　origin of *n*-alkanes in high-wax crude oils. Nature 342, 529–531.

1133   Tewksbury, P.S., 1989. Organic geochemistry of oil seeps in the Otway Basin. B.Sc. Honours

1134   thesis, University of Adelaide (unpublished).

1135   Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence. Springer-Verlag, Berlin.

1136   Thomas, B.M., Barber, C.J., 2004. A re-evaluation of the hydrocarbon habitat of the northern

1137   Perth Basin. The APPEA Journal, 44(1), 13-57.

1138   Thompson, M., Reminton, C., Purnomo, J., MacGregor, D., 1991. Detection of liquid

1139   hydrocarbon seepage in Indonesian offshore frontier basins using airborne laser

1140   fluorosensor (ALF). The results of a Pertamina/BP Joint study. In: Proceedings of the

1141   Indonesian Petroleum Association 20th Annual Convention, pp. 663–689.

1142   Totterdell, J.M, Struckmeyer, H.I.M., Boreham, C.J., Mitchell, C.H., Monteil, E., & Bradshaw,

1143   B.E., 2008. Mid–Late Cretaceous organic-rich rocks from the eastern Bight Basin:

1144   implications for prospectivity. In: Blevin, J.E., Bradshaw, B.E., Uruski, C. (Eds.), Eastern

1145   Australasian Basins Symposium III, Petroleum Exploration Society of Australia, Special

1146   Publication, pp. 137–158.

1147   Volk, H., Ahmed, M., Gong, S., Boreham, C., Tingate, P., Edwards, D., 2011. Land plant

1148   markers in Gippsland Basin oils, Australia. 25th International Meeting on Organic

1149   Geochemistry, Interlaken, Abstracts, p. 414.

1150   Volkman, J.K., O'Leary, T., Summons, R.E., Bendall, M.R., 1992. Biomarker composition of

1151   some asphaltic coastal bitumens from Tasmania, Australia. Organic Geochemistry 18,

1152   669–682.

1153   Waples, D.W., Wulff, K.J., 1996. Genetic classification and exploration significance of oils and

1154   seeps of the Papuan Basin. In: Buchanan, P.G. (Ed.), Petroleum Exploration, Development

1155   and Production in Papua New Guinea. Proceedings of the 3rd Papua New Guinea

1156   Petroleum Convention, Port Moresby, pp. 417–430.

1157   Warnock, A.M., Hagen, S.C., Passeri, D.L., 2015. Marine tar residues: a review. Water, Air &

1158   Soil Pollution 226: 68. DOI 10.1007/s11270-015-2298-5

1159 Watson, B., 1990. Coastal bitumen study. AMDEL Report 009/130 for South Australian

1160   Department of Mines and Energy (unpubl.).

1161 Williams, H.H., Kelley, P.A., Janks, J.S., Christensen, R.M., 1985. The Paleogene Rift Basin

1162   source rocks of Central Sumatra. In: Proceedings of the Indonesian Petroleum Association

1163   14th Annual Convention, pp. 57–90.

1164 Wolff, G.A., Lamb, N.A., Maxwell, J.R., 1986a. The origin and fate of 4-methyl steroid

1165   hydrocarbons. I. Diagenesis of 4-methyl steranes. Geochimica et Cosmochimica Acta 50,

1166   335–342.

1167 Wolff, G.A., Lamb, N.A., Maxwell, J.R., 1986b. The origin and fate of 4-methyl steroid

1168   hydrocarbons. II. Dehydration of stanols and occurrence of C_{30} 4-methyl steranes. Organic

1169   Geochemistry 10, 965–976.

1170

Table 1.   Previous geochemical studies of Australian waxy coastal bitumen

Location	No. of samples	No. of oil families	Data source
South Australia & Northern Territory	11	2	1
South Australia & Western Victoria	27	3	2
South Australia & Western Victoria	96	5	3
Northern Territory	22	2	4
Western Australia	70	8	5

1. McKirdy & Horvath (1976)
2. McKirdy et al. (1984a, b, 1985b, 1986, 1994)
3. Padley (1995)
4. Summons et al. (1993)
5. Alexander et al. (1994)

Table 2.   Summary of waxy bitumen bulk properties*

Specific gravity °API	Pour point** °C	Sulfur content wt %	Oil type***
10 – 40 mean = 22 n = 42	43 – 82 mean = 61 n = 33	0.1 – 2.6 mean = 1.3 n = 45	P (n = 16) P-N (n = 36) Ar-I (n = 21)

* Based on information compiled in Appendix Table A1 (see supplementary data)
** Measured using standard method IP 15/67
*** P = paraffinic, P-N = paraffinic-naphthenic, Ar-I = aromatic-intermediate (after Tissot and Welte, 1984)

47

Table 3.   Source-dependent biomarker parameters of selected waxy bitumens

Sample ID	Steranes						Triterpanes		
	27 : 28 : 29 ster	27 : 28 : 29 dia	27/29 ster	30/29 ster	29 dia/ster	30/29 hop/ster	27 Ts/Tm	29/30 hop	30 dia/hop
Family 1									
28	37:26:37	51:21:28	1.0	0	0.70	2.8	3.7	0.61	0.17
4066	21:25:54	nd	0.38	0	0.70	3.5	3.6	0.84	0.19
Gelt (318)	22:20:58	45:22:33	0.38	0	0.44	3.1	2.1	0.82	0.17
Devil's (317)	29:22:49	35:31:33	0.57	0	0.20	1.7	0.77	1.0	0.09
CB-38 (378)	32:19:49	11:37:52	0.65	0	0.46	4.2	2.7	0.68	0.10
59	nd	nd	0.68	0	0.41	4.5	3.1	0.51	0.09
A923.152A	x	x	x	x	x	x	3.2	1.0	0
48 Dune	x	x	x	x	x	x	3.0	0.88	0.21
148 Dune	28:21:51	39:26:34	0.56	0	0.65	2.1	3.1	0.90	0.21
68	x	x	x	x	x	x	2.7	0.49	0.18
290	30:18:52	45:21:34	0.59	0	0.46	2.9	3.5	0.78	0.11
Family 2									
CB-37	35:11:54	nd	0.64	0.22	0.60	6.7	2.3	0.52	0.11
CB-92 (606)	30:20:50	45:25:30	0.61	0.22	0.22	1.4	1.1	1.3	0
CB-28 (605)	37:26:37	42:28:30	0.98	0.23	0.32	1.1	1.4	1.2	0.03
Family 3									
CH 8	41:22:37	37:32:31	1.1	0	0.26	0.61	1.3	1.5	0
CB-35	43:25:32	47:24:29	1.3	0	0.32	1.3	1.0	1.2	nd
CB-8	43:19:38	37:23:40	1.1	0.05	0.25	0.93	1.1	1.7	0.04
Family 4									
CB31-1 (379)	33:14:53	47:22:31	0.62	nd	0.60	0.78	3.3	1.2	nd
CB31-2 (608)	37:20:43	49:16:35	0.87	0.05	0.96	0.97	3.4	1.0	nd
EC 1	nd	nd	0.83	nd	0.18	nd	0.63	1.8	0
ST 15	nd	nd	nd	nd	0.35	1.8	1.9	2.1	0
Parameter	1	2	3	4	5	6	7	8	9

Ratios calculated from peak areas in MRM mass chromatograms as follows:

1. $C_{27} : C_{28} : C_{29}$ 5α,14α,17α (H) (20*R*) steranes
2. $C_{27} : C_{28} : C_{29}$ 13β,17α (H) (20*R*) diasteranes
3. C_{27} 5α,14α,17α (H) cholestane (20*R*) / C_{29} 5α,14α,17α (H) ethylcholestane (20*R*)
4. C_{30} 5α,14α,17α (H) *n*-propylcholestane (20*R*) / C_{29} 5α,14α,17α (H) ethylcholestane (20*R*)
5. C_{29} 13β,17α (H) diasteranes (20*S* + 20*R*) / C_{29} 5α,14α,17α (H) steranes (20*S* + 20*R*)
6. C_{30} 17α,21β (H) hopane / C_{29} 5α,14α,17α (H) steranes (20*S* + 20*R*)
7. C_{27} 18α (H)-22,29,30-trisnorneohopane / C_{27} 17α (H)-22,29,30-trisnorhopane
8. C_{29} 17α,21β (H) hopane / C_{30} 17α,21β (H) hopane
9. C_{30} 17α (H) diahopane / C_{30} 17α,21β (H) hopane

Table 4 continued.

Sample ID	C$_{30}$ Steranes			Triterpanes			
	24-*n*-propyl	dino	4α-Me/ 29 ster	ol/ hop	bicad T/ hop	ol/ ∑bicad	Major bicadinanes
				Family 1			
28	A	A	nd	0.09	0.66	0.09	T, MeT, R, T1, W
4066	A	A	nd	0.04	nd	nd	T, MeT, T1, R, W
Gelt (318)	A	A	nd	0.08	0.37	nd	T, T1, R, W*
Devil's (317)	A	A	nd	0.24	1.5	nd	T, MeT, T1, R, W
314	A	A	nd	nd	2.9	nd	T, T1, MeT, W
CB-38 (378)	A	A	2.1	0.08	0.48	0.09	T, MeT, T1, R, W
59	A	P?	nd	0.05	nd	nd	x
A923.152A	A	A	nd	nd	2.1	0.31	T, MeT, T1, R, W
48 Dune	A	A	nd	0.06	nd	nd	x
148 Dune	A	A	nd	0.04	1.2	0.03	T, T1, R, W*
68	A	A	nd	0.09	nd	nd	T, MeT, T1, R, W
290	A	P?	nd	0.07	0.46	0.10	T, MeT, T1, R, W
				Family 2			
CB-37 (604)	P	P	5.5	0.06	0.22	0.24	T, T1, MeT, R, W
CB-92 (606)	P	P	0.88	0.05	nd	nd	T1, MeT, T, R, W
CB-28 (605)	P	P	0.61	0.05	0.07	0.61	T, MeT, T1, R, W
				Family 3			
CH8	nd	nd	nd	x	0.14	x	T, MeT, T1, R, W
CB-35	A	A	0.83	nd	0.08	nd	T1, T, MeT, R, W
V2-6	P	P	nd	x	x	x	x
CB-8	P	P	0.28	0.02	nd	nd	T1, T, R, W*
				Family 4			
CB-31-1 (379)	P	P	0.18	0	0	0	A
CB-31-2 (608)	P	P	nd	0	0	0	A
EC 1	nd	nd	nd	0	0	0	A
ST 15	nd	nd	nd	0	0	0	A
Parameter	10	11	12	13	14	15	16

10. 24-*n*-propylcholestane
11. dinosterane (4,23,24-trimethylcholestane)
12. 4α-methyl-24-ethylcholestane (20*R*) + 4α-methyl-23,24-dimethylcholestane (20*R*) / 24-ethylcholestane (20*R*)
13. oleanane / C$_{30}$ 17α,21β (H) hopane
14. bicadinane T / C$_{30}$ 17α,21β (H) hopane
15. oleanane / bicadinanes T + T1 + R (see Fig. 8)
16. Bicadinanes listed in order of decreasing abundance. Isomers labelled as in Grantham et al. (1983), Alam and Pearson (1990), Summons et al. (1993) and McKirdy et al. (1994). * Methylbicadinane M$^+$ 426 → *m/z* 383 not recorded.

A = absent
P = present
nd = not determined because peak not integrated or appropriate MRM chromatogram not acquired
x = not determined because compound(s) removed by severe weathering

Table 4. **Diagnostic characteristics and source affinity of waxy bitumen families**

Family	S wt %	Pr/Ph	BI*	Bot/n-C_{29}	Steranes	24-n-Propyl	Dino
1 n = 35	<0.3	0.2–2.6	530–870	0.16–0.86	29 > 27 > 28	A	A
2 n = 17	0.6–2	0.7–1.7	nd	0.15–0.71	29 ≥ 27 > 28	P	P
3 n = 33	1.1–2.6	0.5–1.1	104–173	0.04–0.14	27 > 29 > 28	P or A	P or A
4 n = 7	0.9	0.5–1.4	0	0	29 ≥ 27 > 28	P	P
5 n = 5	0.2	4–11	nd	nd	nd	nd	nd

Family	Hop/Ster	Oleanane	Bicadinanes	CV**	Source affinity
1	1.7–4.5	P	P	<0.47	Lacustrine shale Anoxic–suboxic Cenozoic
2	1.1–6.7	P	P	<0.47	Lacustrine shale > marine carbonate Anoxic–suboxic Cenozoic
3	0.6–1.3	P	P	<0.47	Marine carbonate > lacustrine shale Anoxic/euxinic Cenozoic
4	0.8–1.8	A	A	<0.47	Marine carbonate or calcareous shale Anoxic–suboxic Mesozoic
5	nd	nd	nd	>0.47	Non-marine (?) coal Oxic

Pr/Ph = pristane/phytane   Bot = C_{34} botryococcane

* Botryococcane Index = C_{34} botryococcane x 100 / $\sum C_{37}$–C_{40} head-to-head isoprenoid alkanes (Seifert and Moldowan, 1981)

** CV = $-2.53\delta^{13}C_{sat} + 2.22\delta^{13}C_{aro} - 11.65$ (Sofer, 1984)

See Table 3 for key to other parameters

Table 5.   Comparison of oil family classifications for Australian waxy coastal bitumens

Present study	Previous studies		Key biomarker characteristics	Source affinity
South Australia & western Victoria	Northern Territory	Western Australia		
Family 1	Family 1	Group 1	Botryococcane $C_{29} > C_{27} > C_{28}$ sterane C_{30} 4α-methylsterane Bicadinanes	Lacustrine shale Cenozoic
Family 2	NR	NR	As for Family 1, plus 24-*n*-propylcholestane & dinosterane	Lacustrine shale & marine carbonate Cenozoic
NR	NR	Groups 2 & 3	Bicadinanes abundant Oleanane /C_{30} hopane >0.1	Deltaic Cenozoic
Family 3	Family 2	Group 4	C_{29}/C_{30} hopane >1 C_{29} diasterane/sterane <0.4 Bicadinanes & oleanane contents very low	Marine carbonate Cenozoic
NR	NR	Groups 5, 6 & 7	As for Group 4, but with significant oleanane & variable bicadinane contents	Marine carbonate Cenozoic
NR	NR	Group 8	$C_{27} > C_{29} > C_{28}$ sterane Bicadinanes & oleanane absent	Marine siliciclastic Mesozoic
Family 4	NR	NR	$C_{29} > C_{27} > C_{28}$ sterane C_{29}/C_{30} hopane >1 Bicadinanes & oleanane absent	Marine carbonate & calcareous shale Mesozoic
Family 5	NR	NR	Pr/Ph $\geq$4 CV >0.47	Non-marine paludal (coal)
Reference:	Summons et al. (1993)	Alexander et al. (1994)		

NR = not represented

Table 6.   **Biomarker characteristics of West Indonesian oil families**

Family	Key biomarker signatures	Basins	Source lithofacies & age	Data sources
Fresh/deep lacustrine	Botryococcane C_{30} Tetracyclic polyprenoid (TPP)* C_{30} 4-methylsteranes C_{26}/C_{25} tricyclic terpane >>1 Ts/Tm >1 Oleanane Bicadinanes Hopanes > Steranes Pristane/phytane = 1.5–3 24-n-Propylcholestane absent	Central Sumatra South Sumatra Sunda	Shale Cenozoic	1, 2, 3, 4, 7
Brackish lacustrine	As above, but with minor or no botryococcane & higher abundances of terrigenous triterpanes (oleanane, bicadinanes) Gammacerane present	Central Sumatra South Sumatra Ombilin East Java	Shale Cenozoic	1, 2, 3, 4, 7
Terrigenous (fluvio-deltaic)	C_{29} sterane dominant Bicadinanes Oleanane C_{26}/C_{25} tricyclic terpane <1 Pristane/phytane >3	North Sumatra Central Sumatra South Sumatra West Natuna Northwest Java	Coal, carbonaceous shale Cenozoic	2, 3, 4, 5
Marine	C_{27} sterane dominant 24-n-Propylcholestane present C_{29}/C_{30} hopane >1 Pristane/phytane = 1–2.5	North Sumatra East Natuna	Carbonate Cenozoic	2, 3, 4, 6

* Reported as unknown 'lacustrine classifier' by ten Haven & Schiefelbein (1995); subsequently identified by Holba et al. (2000)

Key to data sources:
1. Seifert & Moldowan (1981)
2. Robinson (1987)
3. ten Haven & Schiefelbein (1995)
4. Schiefelbein & Cameron (1997)
5. van Aarssen et al. (1992)
6. Subroto et al. (1992)
7. Hwang et al. (2002)

Figure captions

Figure 1. Map showing the location of waxy bitumen stranding sites in South Australia and western Victoria.

Figure 2. Bulk composition of coastal waxy bitumens according to classification of Tissot and Welte (1984).

Figure 3. Gas chromatograms of the saturated hydrocarbon fractions in representative waxy coastal bitumens. Key: Pr = pristane; Ph = phytane; * = C_{34} botryococcane; IS = internal standard, 3-methylheneicosane; numbers refer to chain length of *n*-alkanes.

Figure 4. High temperature gas chromatograms of the saturated hydrocarbon fractions in representative waxy bitumens: Family 1 (a-e), showing effects of increasing weathering; Family 4 (f). Key as for Fig. 3.

Figure 5. Carbon isotopic compositions of C_{12+} saturated and aromatic hydrocarbon fractions in coastal waxy bitumens and asphaltites from southern Australia. The oblique line corresponds to a CV value of 0.47, where CV = $-2.53\delta^{13}C_{sat} + 2.22\delta^{13}C_{aro} - 11.65$, which according to Sofer (1984; reinterpreted by McKirdy et al., 1986) separates oils of land-plant origin from those of algal origin.

Figure 6. MRM chromatograms showing the distribution of A) triterpanes ($M^{.+} \to 191$) and B) steranes ($M^{.+} \to 217$ and 231) in a Family 2 waxy bitumen (sample CB-28).

Figure 7. MRM chromatograms showing the distribution of A) triterpanes ($M^{.+} \to 191$) and B) steranes ($M^{.+} \to 217$ and 231) in a Family 4 waxy bitumen (sample CB-31-2).

Figure 8. MRM chromatograms showing the contrasting bicadinane and methylbicadinane signatures of representative Family 1 and Family 2 waxy bitumens.

Figure 9. Map of selected sedimentary basins within the Indonesian Archipelago showing the location of oil seeps (after Livsey et al., 1992; Macgregor, 1995; Noble et al., 2009) and pathways of the Indonesian and South China Sea throughflows (after Gordon, 2005; Gordon et al., 2012; Susanto et al., 2016). Sedimentary basin outlines are from Robertson (2017).

Figure 10. Partial MRM 412 → 369 chromatograms illustrating the C_{30} bicadinane

distributionsin a Family 1 waxy bitumen and crude oils from Indonesia and Papua New Guinea.

SUPPLEMENTARY MATERIAL

Table A1. **Waxy bitumen inventory (locations listed from west to east), bulk properties and classification**

Sample ID	Location	Date sample collected	Specific gravity °API	Pour point °C	Sulfur content wt %	Data source
		Family 1				
376	Anxious Bay, Eyre Pen., SA	10.10.1992	nd	nd	nd	1
CB-71	Sheringa Beach, Eyre Pen., SA	6.9.1983	nd	nd	0.2	4,8
Coles Point	Coles Point, Eyre Pen., SA	10.12.1990	nd	nd	nd	1
CB-67	Avoid Bay, Eyre Pen., SA	6.9.1983	nd	nd	0.1	4,8
A923.152A	Thistle Island, offshore Eyre Pen., SA	19.4.1984	nd	nd	nd	1
CB-51	Gym Beach, Yorke Pen., SA	6.9.1983	nd	73	0.2	4,8
296	Ravine des Casoars, K.I., SA	20.9.1991	nd	nd	nd	1
79	West Bay, K.I., SA	15.10.1990	nd	nd	nd	1
CB-84	Sandy River Beach, K.I., SA	14.12.1983	35	68	0.2	4,8
290	Hanson Bay, K.I., SA	19.9.1991	27	nd	0.1	1
VB 3	Vivonne Bay, K.I., SA	14.9.1989	nd	nd	nd	1
287	Bales Bay, K.I., SA	19.9.1991	nd	nd	nd	1
Pen 8	Pennington Bay, K.I., SA	15.9.1989	nd	nd	nd	1
CB-77	Pennington Bay, K.I., SA	12.12.1983	38	68	0.1	4,8
68	Pennington Bay, K.I., SA	14.10.1990	32	nd	0.1	1
67	Wilson River, K.I., SA	14.10.1990	22	nd	nd	1
192	False Cape, K.I., SA	22.2.1991	nd	nd	nd	1
248	Windmill Bay, K.I., SA	30.5.1991	nd	nd	nd	1
A923.158	Encounter Bay, Port Elliot, SA	26.5.1990	nd	nd	nd	1
59	The Granites, Long Beach, SA	1.10.1990	nd	nd	0.2	1
CB-38 (378)	5 km N of The Granites, Long Beach, Kingston, SA	30.8.1983	25	68	0.3	1,3,5,8
43	Beachport C.P., SA	30.9.1990	nd	nd	nd	1
48 Dune	Beachport C.P., SA	30.9.1990	11	nd	nd	1
50	Beachport C.P., SA	30.9.1990	36	nd	0.2	1
148 Dune	Beachport C.P., SA	28.11.1990	nd	nd	nd	1
358	Beachport C.P., SA	26.9.1990	nd	nd	nd	1
Gelt (318)	Geltwood Beach, Canunda N.P., SA	1960	nd	nd	nd	1
4066	Geltwood Beach, Canunda N.P., SA	1961	nd	nd	0.1	1
Devil's (317)	Devils Gap, Canunda N.P., SA	1961	nd	nd	<0.3	1
17	Canunda N.P., SA	28.9.1990	nd	nd	nd	1
28	Canunda N.P., SA	29.9.1990	40	nd	0.3	1
DB 1	Descartes Bay, Vic	17.4.1990	17	nd	nd	1
314	Descartes Bay, Vic	24.9.1991	nd	nd	nd	1
314HW	Descartes Bay, Vic	24.9.1991	nd	nd	nd	1
CB-1	Bridgewater Bay, Vic	26.8.1983	27	71	0.3	3,5,8
		Family 2A				
A923.157	Corny Point, Yorke Pen., SA	3.199	nd	nd	nd	1,7
CB-36	Wright Bay, SA	30.8.1983	nd	nd	1	6
CB-37	The Granites, Long Beach, SA	30.8.1983	nd	nd	0.6	1,6,8
CB-34	Eve's Cove, Cape Lannes, SA	29.8.1983	nd	nd	0.8	6

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CB-30	Beachport C.P., SA	29.8.1983	nd	nd	1.9	6
CB-16	Canunda N.P., SA	28.8.1983	nd	nd	1.5	6
CB-21	Canunda N.P., SA	28.8.1983	nd	nd	1.8	6
CB-11	Douglas Point, SA	27.8.1983	nd	nd	1.7	3,6
CB-93	Cape Bridgewater, Vic	11.1991	nd	nd	1.3	6
	Family 2B					
CB-52	Daly Head, Yorke Pen., SA	6.9.1983	nd	74	1.4	4
CB-39	The Granites, Long Beach, SA	30.8.1983	nd	nd	1.3	6
CB-28 (605)	Beachport C.P., SA	29.8.1983	17	72	1.3	1,3,6,8
CB-29	Beachport C.P., SA	29.8.1983	nd	nd	1.3	6
CB-92 (606)	Geltwood Beach, Canunda N.P., SA	8.1961	nd	nd	2	1,3,6,8
CB-23	Canunda N.P., SA	28.8.1983	23	61	1.2	3,6
CB-25	Canunda N.P., SA	28.8.1983	nd	nd	0.8	6
CB-14	Admella Dunes, SA	27.8.1983	20	57	1.3	3,6
	Family 3A					
CB-73	Petrel Cove, Fleurieu Pen., SA	12.12.1983	nd	nd	2.6	4,8
Pen 6	Pennington Bay, K.I., SA	15.9.1989	nd	nd	nd	1
Bitumen B	Unspecified, K.I., SA	3.1990	nd	nd	nd	1,7
CB-35 (607)	Guichen Bay, Robe, SA	30.8.1983	17	59	2.3	1,3,6,8
A923.99	Canunda N.P., SA	8.1983	nd	nd	nd	1
CB-17	Canunda N.P., SA	28.8.1983	nd	nd	1.1	6
12	Canunda N.P., SA	27.9.1990	17	nd	nd	1
200	Canunda N.P., SA	26.2.1991	nd	nd	nd	1
33	Beachport C.P., SA	30.9.1990	13	nd	nd	1
349	Canunda N.P., SA	26.9.1990	nd	nd	nd	1
CB-12	Douglas Point, SA	27.8.1983	16	57	2	3,6,8
3	Nene Valley C.P., SA	27.9.1990	nd	nd	nd	1
91	Picaninnie Ponds, SA	25.11.1990	nd	nd	nd	1
CB-9	Cape Northumberland, SA	26.8.1983	21	59	1.9	3,6
CB-10	Cape Northumberland, SA	26.8.1983	24	57	1.8	3,5,8
GB 22	Port Campbell N.P., SA	16.4.1990	nd	nd	nd	1
93	Nelson, Discovery Bay, Vic	25.11.1990	nd	nd	1.3	1,6
CB-7	Nobles Rocks, Discovery Bay, Vic	26.8.1983	17	58	1.9	3,6,8
CB-2	Bridgewater Bay, Vic	26.8.1983	nd	nd	nd	6
A923.198	Lake Yambuk, Vic	5.1.1991	nd	nd	nd	1
CH 1	Childers Cove, Vic	14.9.1990	nd	nd	nd	1
CH 3	Childers Cove, Vic	14.4.1990	nd	nd	nd	1
CH 8	Childers Cove, Vic	14.4.1990	20	nd	nd	1
V2-6	Castle Cove, Vic	16.4.1991	nd	nd	nd	1
ST 16	Station Beach, Cape Otway, Vic	14.4.1990	nd	nd	nd	1
CB-376	Lion Headland, Vic	13.10.1985	13	57	2.1	5,8
	Family 3B					
CB-20	Canunda N.P., SA	28.8.1983	21	59	2	3,6
CB-18	Geltwood Beach, Canunda N.P., SA	28.8.1983	20	58	2.6	3,8
CB-15	Admella Dunes, SA	27.8.1983	19	55	1.8	3,6
CB-13	Nene Valley C.P., SA	27.8.1983	18	59	1.4	3,5,8
CB-8 (380)	Nelson, Vic	26.8.1983	16	58	2.4	3,5,8

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CB-5	Swan Lake, Discovery Bay, Vic	26.8.1983	19	57	1.7	3,6
CB-3	Descartes Bay, Vic	26.8.1983	26	51	2.1	3,5,8
CB-4	Descartes Bay, Vic	26.8.1983	15	53	1.6	3,5,8
	Family 4					
EC 1	Eve's Cove, Cape Lannes, SA	1979	10	nd	nd	1
CB-31-1 (379)	Beachport C.P., SA	29.8.1983	21	66	0.9	1,3,8
CB-31-2 (608)	Beachport C.P., SA	29.8.1983	nd	nd	nd	1,6
257	Beachport C.P., SA	26.9.1991	34	nd	nd	1
323	Nene Valley C.P., SA	25.9.1991	nd	nd	nd	1
312	Bridgewater Bay, Vic	24.9.1991	nd	nd	nd	1
ST 15	Station Beach, Cape Otway, Vic	14.4.1990	nd	nd	nd	1
	Family 5					
295	Ravine des Casoars, K.I., SA	20.9.1991	nd	nd	0.2	1
375	D'Estrees Bay, K.I., SA	16.2.1992	nd	nd	nd	1
363	Little Dip C.P., SA	26.9.1991	nd	nd	nd	1
357	Beachport C.P., SA	26.9.1991	nd	nd	0.2	1
313	Descartes Bay, Vic	24.9.1991	nd	nd	nd	1
	Unassigned					
MH6	Sleaford Bay, Eyre Pen., SA	16.8.1961	21	66	<0.3	2
CB-64	Sleaford Bay, Eyre Pen., SA	17.9. 1983	nd	62	0.4	4
CB-48	Sturt Bay, Yorke Pen., SA	6.9.1983	nd	nd	1.3	4
CB-89	Ravine des Casoars, K.I., SA	15.12.1983	nd	67	1.2	4
CB-82	West Bay, K.I., SA	14.12.1983	nd	67	0.5	4
CB-87	Rocky River, K.I., SA	14.12.1983	nd	78	0.2	4
MH1	Geltwood Beach, Canunda N.P., SA	6.1961	28	43	<0.3	2
MH2	Geltwood Beach, Canunda N.P., SA	8.1961	20	nd	<0.3	2
MH4	Devils Gap, Canunda N.P., SA	16.8.1961	19	nd	<0.3	2
MH5	Cape Northumberland, SA	23.8.1963	28	58	<0.3	2
MH3	Discovery Bay, Vic	8.10.1961	27	82	<0.3	2
MH7	Bridgewater Bay, Vic	9.10.1961	28	71	<0.3	2

C.P. = Conservation Park
N.P. = National Park
K.I. = Kangaroo Island
Pen. = Peninsula
nd = not determined

Key to data sources:
1. This study   2. McKirdy and Horvath (1976)   3. McKirdy (1984a)   4. McKirdy (1984b)
5. McKirdy (1985)   6. Tewksbury (1989)   7. Watson (1990)   8. McKirdy et al. (1994)

Table A2.   Bulk composition, oil type and degree of weathering of waxy bitumens

Sample ID	Par %	Naph %	Arom %	Res %	Asph %	Oil type	Degree of weathering*
			Family 1				
28 interior	52.8	28.0	11.1	4.2	3.9	P	0
28 intermediate	— 68.7 —		15.2	7.2	8.9	nd	0
28 exterior	— 64.6 —		17.2	9.1	9.1	nd	0
4066	56.7	23.3	10.0	4.8	5.4	P	0
192	39.3	29.5	7.8	4.7	18.8	P-N	0
Gelt (318)	— 72.6 —		9.2	— 18.2 —		nd	0
Devils (317)	— 20.7 —		24.4	— 54.9 —		nd	0.5
314	39.3	28.2	14.3	9.2	9.0	P-N	1
314HW	— 61.1 —		10.5	13.8	14.6	nd	1
CB-77	35.2	21.9	3.0	34.7	5.2	P-N	1
Coles Point	36.2	26.5	8.8	5.8	22.6	P-N	1
CB-84	29.5	28.4	0.5	36.2	5.4	P-N	1
VB3	— 61.4 —		8.6	7.4	22.6	nd	1
CB-67	25.1	21.3	6.0	42.7	4.9	Ar-I	1
CB-1	38.0	15.2	8.3	34.8	3.7	P-N	2
CB-71	30.8	26.3	4.1	34.8	4.0	P-N	2
CB-38 (378)	45.6	17.7	8.6	23.9	4.2	P	2
17	— 68.0 —		6.8	2.5	22.7	nd	2
CB-51	22.3	24.3	2.3	43.6	7.5	Ar-I	2
50	41.3	21.8	10.5	5.1	21.3	P	2
59	32.8	28.4	14.7	8.6	15.5	P-N	2
79	48.3	22.3	12.0	4.9	12.6	P	2
376	— 59.0 —		9.6	5.9	25.5	nd	2
A923.152A	53.9	18.1	10.1	8.6	9.4	P	3
DB 1	44.4	20.5	15.8	5.5	13.8	P	3
Pen 8	33.7	20.6	16.4	8.1	21.2	P-N	3
48 Dune	25.9	21.9	4.8	2.1	45.3	Ar-I	3
287	27.6	26.3	21.7	8.8	15.6	P-N	4
296	— 51.2 —		21.1	10.0	17.8	nd	4
358	30.3	30.3	18.6	7.9	13.1	P-N	4
148 Dune	— 65.8 —		28.5	11.6	1.2	nd	4
67	— 50.7 —		18.4	12.1	18.9	nd	4
A923.158	— 59.3 —		20.0	9.0	11.8	nd	4
248	34.8	20.4	16.2	11.1	17.6	P-N	4
68	28.2	27.9	21.4	8.0	14.6	P-N	4
43	— 50.6 —		14.9	5.0	29.5	nd	4
290	— 47.0 —		22.5	11.0	19.5	nd	5
			Family 2A				
CB-93	26.3	21.4	20.3	21.7	10.2	Ar-I	0.5
CB-30	14.2	32.8	12.6	29.5	10.9	Ar-I	0.5
CB-37	22.1	36.1	6.8	26.3	8.7	P-N	1+
CB-16	20.6	27.6	10.7	24.4	16.7	Ar-I	2
CB-36	36.6	14.2	9.0	35.5	4.7	P-N	4
CB-34	13.5	34.6	9.0	33.7	9.2	Ar-I	4
A923.157	23.5	20.5	8.0	43.5	4.6	Ar-I	5
CB-11	18.9	23.6	18.2	26.3	13.1	Ar-I	5
CB-21	19.7	21.1	9.1	33.2	16.9	Ar-I	5
			Family 2B				
CB-92 (606)	27.9	21.7	12.2	25.1	13.1	Ar-I	0.5
CB-28 (605)	25.9	7.7	11.1	29.7	25.7	Ar-I	0.5

CB-23	14.8	36.0	14.2	22.2	5.7	P-N	2
CB-14	19.6	42.9	15.9	18.1	3.5	P-N	2
CB-29	29.4	38.6	8.0	16.7	7.3	P-N	2
CB-25	26.7	31.9	9.7	24.1	7.6	P-N	2
CB-39	14.5	31.3	10.0	31.1	13.1	Ar-I	2
CB-52	24.0	20.2	6.0	40.2	9.6	Ar-I	2+
Family 3A							
CB-10	52.0	14.0	12.9	18.2	2.9	P	0
A923.99	— 64.2 —		17.2	10.2	8.4	nd	0.5
CB-17	32.7	30.1	14.2	16.5	6.5	P-N	0.5
12	46.2	20.4	17.5	7.6	8.2	P	0.5
CH 8	42.2	26.8	19.6	5.1	6.3	P	0.5
CB-376	22.0	44.3	18.3	8.1	7.3	N	0.5
CH 1	30.3	30.3	22.7	9.8	6.9	P-N	0.5
Bitumen B	17.6	22.5	6.5	29.7	23.7	Ar-I	0.5
A923.198	30.0	26.8	18.5	18.5	6.3	P-N	0.5
200	— 49.9 —		22.1	22.0	12.6	nd	0.5
93	30.0	31.5	21.5	21.4	14.6	nd	0.5
33	34.6	29.0	14.6	15.5	6.2	P-N	0.5
3	37.4	22.8	17.9	13.2	8.7	P-N	0.5
CB-35 (607)	— 53.9 —		14.8	25.8	5.5	nd	2
CB-12	19.6	42.9	15.9	18.1	3.5	P-N	2
CB-7	13.2	29.4	14.4	36.1	6.9	Ar-I	2
CB-9	20.2	32.7	15.6	24.5	7.0	P-N	2
CH-3	17.8	15.4	40.2	16.5	10.1	Ar-I	2
Pen 6	28.0	37.5	18.4	11.7	4.8	P-N	2
349	— 52.5 —		24.6	9.8	13.0	nd	2
CB-2	16.0	27.8	21.6	23.7	10.9	Ar-I	2
V2-6	38.0	24.1	18.5	12.4	7.0	P-N	2
GB 22	29.3	27.4	22.2	14.6	6.6	P-N	2
ST 16	— 52.1 —		20.3	20.3	7.4	nd	4
91	25.8	28.8	23.3	13.8	8.3	P-N	5
Family 3B							
CB-4	42.5	12.4	13.8	24.2	7.1	P	0.5
CB-18	44.8	16.3	10.0	23.0	5.9	P	0.5
CB-8 (380)	28.9	23.1	14.5	28.0	5.5	P-N	0.5
CB-20	34.6	26.0	9.5	24.2	5.7	P-N	2
CB-5	24.7	33.9	17.0	19.0	5.4	P-N	2
CB-3	23.8	20.8	14.4	33.9	7.1	Ar-I	2
CB-15	17.1	28.9	15.7	34.6	4.1	Ar-I	2
CB-13	28.9	4.2	13.3	47.4	6.2	Ar-I	2
Family 4							
CB-31-1 (379)	62.7	11.1	7.2	14.9	4.1	P	0
CB-31-2 (608)	36.4	23.1	7.7	29.2	3.6	P-N	0
Eves Cove	36.8	14.3	12.9	12.8	23.1	P-N	0.5
312	34.8	19.6	11.8	11.7	22.1	P-N	3
323	37.4	30.7	12.5	7.0	12.5	P-N	3
257	45.0	18.1	11.5	7.0	18.4	P	3
ST15	— 24.5 —		6.5	4.2	64.9	nd	4
Family 5							
357	— 72.7 —		16.0	7.4	3.9	nd	0.5
313	— 68.8 —		17.3	11.1	2.8	nd	0.5
375	45.2	26.1	18.5	5.6	4.8	P	0.5
363	— 74.7 —		12.9	9.6	2.8	nd	0.5
295	57.4	17.2	16.7	4.9	3.6	P	0.5

* The degree of weathering has been determined from the GC-FID trace of the saturated hydrocarbon fraction. Numerical values are defined in Table A.2.

Par = paraffins (*n-* + *iso*-alkanes)
Naph = naphthenes (multibranched + cycloalkanes)
Arom = aromatic hydrocarbons
Res = resins
Asph = asphaltenes

P = paraffinic
P-N = paraffinic-naphthenic
Ar-I = aromatic-intermediate

nd = not determined

Table A3.   Extent to which weathering has altered the composition of a waxy bitumen based on the appearance of its saturated hydrocarbon chromatogram

Degree of weathering	Compounds removed	Comments
Unaffected		
0	Evaporative loss of n-alkanes up to C_{12}	No evidence of biodegradation Light ends lost during sample preparation
Slight		
0.5	Depletion of n-alkanes up to C_{15}	
1	Removal of n-alkanes up to C_{15}	Pristane $< n\text{-}C_{17}$ Phytane $< n\text{-}C_{18}$
2	Depletion of n-alkanes up to C_{21}	Pristane $> n\text{-}C_{17}$ Phytane $> n\text{-}C_{18}$
3	Removal of n-alkanes up to C_{21}, pristane & phytane	Appearance of UCM
Moderate		
4	Removal of n-alkanes up to C_{23}	
5	Removal of n-alkanes up to C_{26}	

Table A4.   Alkane parameters and bulk isotopic composition of waxy bitumen families

Sample ID*	n-Alkane profile range	maxima	Pr/Ph	Pr/n-C$_{17}$	Ph/n-C$_{18}$	Bot/n-C$_{29}$	BI	$\delta^{13}C_{sat}$ ‰	$\delta^{13}C_{aro}$ ‰
				Family 1					
28 interior	10 – 40	17, 25	2.4	0.38	0.16	0.24	nd	−25.9	−24.8
28 intermediate	10 – 39	15, 27	2.9	0.35	0.13	0.26	nd	nd	nd
28 exterior	10 – 39	15, 27	2.9	0.35	0.13	0.29	nd	nd	nd
4066	12 – 44	17, 27	2.2	0.29	0.14	0.28	nd	−25.9	−24.5
192	12 – 40	20, 29	2.6	0.38	0.13	0.31	nd	nd	nd
Gelt (318)	8 – 40	17, 28	2.3	0.33	0.15	0.23	nd	nd	nd
Devils (317)	8 – 40	19	1.3	0.24	0.13	0.18	nd	nd	nd
314	15 – 40	27	1.9	0.50	0.21	0.28	nd	nd	nd
CB-77	16 – 37	23	0.56	0.90	0.18	0.28	530	−25.6	nd
Coles Point	16 – 42	27	1.4	0.81	0.40	0.39	nd	nd	nd
CB-84	15 – 38	27	1.2	1.8	0.75	0.30	530	−25.4	nd
VB3	16 – 42	27	1.6	1.3	0.57	0.33	nd	nd	nd
CB-67	15 – 39	29	0.71	0.40	0.22	0.67	870	−25.4	−24.6
CB-1	14 – 40	27	2.2	2.6	1.0	0.27	740	−25.1	−24.3
CB-71	15 – 40	27	0.22	0.93	2.4	0.35	600	−25.5	−24.5
CB-38 (378)	16 – 40	27	2.0	7.3	3.8	0.45	560	−25.2	−24.2
17	18 – 43	27	1.8	x	x	0.41	nd	nd	nd
CB-51	17 – 39	29	0.74	3.9	5.9	0.50	580	−25.1	−24.4
50	17 – 44	29	1.4	4.1	x	0.31	nd	−25.6	−24.7
59	22 – 44	27	1.1	x	x	0.36	nd	−25.5	−24.8
79	16 – 42	27	0.70	x	1.4	0.16	nd	nd	nd
376	18 – 42	27	x	x	x	0.40	nd	nd	nd
A923.152A	19 – 44	28	x	x	x	0.14	nd	nd	nd
DB1	21 – 50	35	x	x	x	0.56	nd	−26.4	−25.5
Pen 8	22 – 44	29	x	x	x	0.79	nd	nd	nd
48 Dune	22 – 44	29	x	x	x	0.36	nd	−26.0	−24.6
287	23 – 44	29	x	x	x	0.62	nd	nd	nd
296	22 – 44	20	x	x	x	0.70	nd	nd	nd
358	23 – 42	29	x	x	x	0.24	nd	nd	nd
148 Dune	24 – 44	29	x	x	x	0.65	nd	nd	nd
67	23 – 44	29	x	x	x	0.18	nd	−25.9	-24.8
A923.158	24 – 44	29	x	x	x	0.57	nd	nd	nd
248	25 – 44	29	x	x	x	0.86	nd	−25.5	−24.4
68	25 – 44	31	x	x	x	0.24	nd	−26.2	−24.5
43	25 – 43	29	x	x	x	0.65	nd	nd	nd
290	25 – 44	31	x	x	x	0.68	nd	−26.0	−24.7
				Family 2A					
CB-93	9 – 40	17, 29	1.1	0.47	0.49	0.25	nd	−26.9	−26.4
CB-30	11 – 40	16, 29	1.2	0.58	0.52	0.50	nd	−26.1	−26.2
CB-37	9 – 40	29	1.7	0.99	0.78	0.63	nd	−26.0	−25.2
CB-16	9 – 40	11, 28	1.0	0.97	2.0	0.53	nd	−26.0	−25.4
CB-36	23 – 40	29	x	x	x	0.48	nd	−26.0	−25.1
CB-34	24 – 40	29	x	x	x	0.56	nd	−25.9	−24.3
A923.157	24 – 36	28	x	x	x	0.19	nd	nd	nd
CB-11	25 – 40	32	x	x	x	0.15	nd	−27.2	−26.5
CB-21	24 – 40	29	x	x	x	0.71	nd	−26.0	−25.0
				Family 2B					
CB-92 (606)	13 – 39	29	0.70	0.71	0.73	0.19	nd	−26.9	−27.6
CB-28 (605)	14 – 40	17, 27	1.2	0.93	0.82	0.24	nd	−27.2	−27.1
CB-23	14 – 40	20, 30	1.0	0.84	1.1	nd	nd	−27.2	−26.8

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CB-14	15 – 40	29	0.98	2.8	2.8	0.38	nd	−26.0	−24.9
CB-29	17 – 40	29	0.70	2.4	0.97	0.50	nd	−26.0	−25.3
CB-25	15 – 40	27	0.90	1.3	1.1	0.42	nd	−25.6	−24.9
CB-39	9 – 40	29	0.88	1.4	2.0	0.42	nd	−25.9	−26.2
CB-52	14 – 41	27	0.95	6.2	2.7	0.28	460	−25.7	−25.5
				Family 3A					
CB-10	12 – 40	18, 30	1.0	0.57	0.54	0.08	113	−26.4	−26.0
A923.99	13 – 42	18, 30	1.1	0.32	0.30	0.05	nd	nd	nd
CB-73	14 – 40	18, 29	1.5	0.30	0.19	0.22	1200	−26.6	−25.7
CB-17	12 – 40	19, 29	0.97	0.46	0.52	0.09	nd	−26.9	−26.4
12	13 – 44	32	0.95	0.56	0.58	0.06	nd	−26.5	−26.5
CH 8	13 – 44	34	0.77	0.41	0.41	0.07	nd	−26.7	−26.4
CB-376	13 – 44	19, 31	0.81	0.90	0.79	0.05	129	−26.7	−26.4
CH1	13 – 44	32	1.0	0.78	0.82	0.09	nd	nd	nd
Bitumen B	15 – 36	29	0.56	0.25	0.71	0.12	nd	nd	nd
A923.198	14 – 44	32	0.98	0.96	1.0	0.06	nd	nd	nd
200	14 – 42	30	0.82	0.87	1.0	0.06	nd	nd	nd
93	13 – 42	31	0.88	0.94	1.0	0.06	nd	nd	nd
33	14 – 42	32	0.96	1.4	1.2	0.05	nd	nd	nd
3	16– 43	32	0.85	0.87	0.83	0.04	nd	nd	nd.
CB-35 (607)	14 – 41	18, 31	0.99	1.6	1.6	0.07	nd	−27.1	−25.4
CB-12	14 – 40	31	0.96	2.4	2.2	0.06	nd	−26.9	−26.6
CB-7	13 – 40	30	0.77	4.9	5.7	0.08	nd	−27.9	−26.5
CB-9	16 – 40	31	0.88	5.5	4.6	0.07	nd	−27.0	−25.2
CH-3	14 – 42	32	0.93	1.6	2.8	0.06	nd	nd	nd
Pen 6	17 – 42	31	0.82	2.9	4.0	0.09	nd	nd	nd
349	16 – 40	30	0.61	3.2	4.1	0.11	nd	nd	nd
CB-2	23 – 40	32	0.73	x	x	0.14	nd	−27.2	−26.5
V2-6	18 – 44	33	0.55	1.0	x	0.11	nd	−26.9	−26.3
GB 22	22 – 44	32	x	x	x	0.06	nd	nd	nd
ST 16	24 – 44	32	0.49	x	3.8	0.09	nd	−26.7	−26.3
91	24 – 44	32	x	x	x	0.06	nd	nd	nd
				Family 3B					
CB-4	14 – 40	18, 31	1.1	0.79	0.67	0.04	137	−26.4	−26.0
CB-18	13 – 40	18, 30	1.0	0.99	0.95	0.06	104	−26.6	−26.1
CB-8 (380)	14 – 40	18, 31	0.90	0.93	0.93	0.05	137	−26.1	−26.0
CB-20	14 – 40	19, 30	0.88	1.1	1.2	0.07	nd	nd	nd
CB-5	14 – 40	18, 30	0.88	1.3	1.2	0.06	nd	−26.8	−26.3
CB-3	14 – 40	19, 31	1.0	1.6	1.6	0.06	173	−26.5	−25.9
CB-15	14 – 40	18, 31	0.88	2.5	2.4	0.10	nd	nd	nd
CB-13	17 – 40	31	0.86	7.2	7.7	0.06	119	−26.2	−25.9
				Family 4					
CB-31-1 (379)	14 – 40	19, 31	0.49	0.13	0.19	[0.02]	[10]	−26.1	−25.3
CB-31-2 (608)	14 – 40	19, 31	0.90	0.13	0.19	0	0	nd	nd
EC 1	13 – 44	18, 34	0.77	0.77	0.41	0	0	−27.4	−26.3
312	20 – 40	34	1.4	x	x	0	0	nd	nd
323	22 – 40	27	x	x	x	0	0	−25.7	−25.0
257	22 – 44	35	x	x	x	0	0	−26.3	−25.6
ST 15	25 – 50	39	x	x	x	0	0	−26.2	−26.0
				Family 5					
357	11 – 40	17, 27	4.0	0.62	0.15	nd	nd	−28.5	−26.9
313	11 – 40	15, 27	5.1	0.53	0.12	nd	nd	−28.4	−26.8
375	10 – 40	15, 27	11.1	0.51	0.07	nd	nd	nd	nd
363	11 – 40	16, 27	4.0	0.48	0.14	nd	nd	nd	nd
295	11 – 40	15, 27	4.4	0.59	0.14	nd	nd	−28.5	−26.9

*Samples in each family are listed in order of increasing degree of weathering

x = compounds removed by weathering
na = not applicable
nd = not determined
[ ] = unreliable
Pr = pristane
Ph = phytane
Bot = C_{34} botryococcane
BI = botryococcane index (Seifert and Moldowan, 1981)