Origin of perylene in ancient sediments and its geological significance

Chunqing Jiang\textsuperscript{a,}\*, Robert Alexander\textsuperscript{a}, Robert I. Kagi\textsuperscript{a}, Andrew P. Murray\textsuperscript{b}

\textsuperscript{a}Australian Petroleum CRC/Centre for Petroleum and Environmental Organic Geochemistry, School of Applied Chemistry, Curtin University of Technology, GPO Box U 1987, Perth, WA 6001, Australia

\textsuperscript{b}Woodside Australian Energy, 1 Adelaide Tce, Perth, WA 6001, Australia

Abstract

The distributions of polycyclic aromatic hydrocarbons (PAHs) in sediments of three Upper Triassic to Middle Jurassic sedimentary sequences from the Northern Carnarvon Basin, Australia have been investigated. Perylene was found to be a major PAH component in the top Lower to base Middle Jurassic sediments that are immature or at low maturity. Its depth/age profiles are not related to the combustion-derived PAHs that have been believed to be produced during ancient vegetation fires before deposition. This suggests a diagenetic origin for perylene. The concentration of perylene in the sediments is proportional to the amount of terrestrial input, decreasing with distance from the source of land sediments. Its carbon isotope composition is slightly heavier than higher-plant derived PAHs, but still in the range of the terrestrially sourced PAHs including higher-plant PAHs and combustion-derived PAHs as suggested previously. Fungi are proposed to be the major precursor carriers for perylene in sediments based on the facts that (1) perylenequinone structures have been previously suggested to be the natural precursors for perylene; (2) perylenequinone pigments exist in many fungal bodies; (3) fungi have played an important role during geological processes. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: PAHs; Perylene; Fungi; Terrestrial origin; Northern Carnarvon Basin

1. Introduction

Perylene (I) has been found widely in Recent marine sediments (Orr and Grady, 1967; Aizenshstat, 1973; Wakeham et al., 1979; Louda and Baker, 1984; Wilcock and Northcott, 1995), lake sediments (Laflamme and Hites, 1978; Ishiwatari et al., 1980; Wakeham et al., 1980; Gschwend and Hites, 1981; Tan and Heit, 1981; Gschwend et al., 1983; Kawamura et al., 1987; Fernández et al., 1996; Soma et al., 1996), river sediments (Hites et al., 1980) and peats (Gilliland et al., 1960; Aizenshstat, 1973; Venkatesan, 1988). Although it has been reported from fossil crinoids (Blumer, 1960, 1962a,b, 1965; Thomas and Blumer, 1964), oil shales (Aizenshstat, 1973; Garrigues et al., 1988; Golovko et al., 1991; Jacob et al., 1991), bituminous coals (White and Lee, 1980; Garrigues et al., 1988; Lu and Kaplan, 1992) and immature crude oils (Golovko et al., 1991; Lu and Kaplan, 1992), data on its occurrence in ancient sediments are far less than for the Recent ones. Several conclusions about perylene have been drawn mainly based on the studies of its presence in Recent sediments.

Firstly, perylene (I) is a diagenetic product derived from its natural precursors via post-deposition transformation during early diagenesis. Compared with other unsubstituted PAHs, only trace or small amounts of perylene are produced during combustion or by abnormal thermal exposure of organic materials, probably due to its thermodynamic instability (Kawaka and Simoneit, 1990; Jenkins et al., 1996; Simoneit and Fetzer, 1996) or its greater reactivity (Dewar, 1952; Clar, 1972; Zander, 1983). Unlike those combustion-derived unsubstituted PAHs including fluoranthene (II), pyrene (III), benzo[a]anthracene (IV), benzo[fluoranthenes (V), benzo[e]pyrene (VI) and benzo[a]pyrene (VII) which occur in both water-borne particulates and sediments (Kawamura et al., 1987) and whose concentrations
change irregularly with depth in Recent sediments, perylene is detected only in sediments but not water particulates (Kawamura et al., 1987), and its concentration increases rapidly with burial depth (Orr and Grady, 1967; Brown et al., 1972; Aizenshtat, 1973; Ishiwatari et al., 1980; Wakeham et al., 1980; Gschwend et al., 1983; Wilcock and Northcott, 1995; Fernández et al., 1996). This indicates that perylene is not carried and deposited in the sediments, but formed after deposition.

Secondly, the natural precursors of perylene could be the structurally related perylenequinones and their derivatives, which are kinds of black pigments widely present in modern plants (Britton, 1983), insects (Cameron et al., 1964), fungi (Thomson, 1971; Hardil et al., 1989; Stierle et al., 1989; Wu et al., 1989; Hashimoto et al., 1994) as well as crinoids (Rideout and Sutherland, 1985; De Riccardis et al., 1991). Perylene and the structurally related oxygen containing compounds have been found together in a Jurassic fossil crinoid from Switzerland (Blumer, 1960, 1962a, b, 1965; Thomas and Blumer, 1964), in marine sediments from the Gulf of California (Louda and Baker, 1984) as well as in soil samples from around Lake Harun, Japan (Ishiwatari et al., 1980). The reduction of these pigments in the laboratory did give rise to related aromatic hydrocarbons.

Thirdly, the presence of perylene in more than trace amounts (e.g. 0.010 ppm) is a palaeo-environmental marker for syn- and post-depositional anoxia. Since quinone compounds are sensitive to oxidation, their preservation in sediments requires a reducing environment (Aizenshtat, 1973). For all of those Recent sediments and that fossil crinoid in which perylene is present, strongly reducing conditions were indicated by either the redox potential of sediments or the presence of reduced inorganic materials in the samples (Blumer, 1965; Orr and Grady, 1967; Aizenshtat, 1973; Wakeham et al., 1979, 1980; Hites et al., 1980; Tan and Heit, 1981; Louda and Baker, 1984; Silliman et al., 1998). In addition, the transportation and sedimentation of perylene precursors should be rapid enough to prevent its degradation before deposition (Orr and Grady, 1967; Aizenshtat, 1973; Louda and Baker, 1984).

However, there is no agreement yet as to whether perylene precursors are of terrestrial or aquatic sources. Although high concentrations of perylene have been detected in diatomaceous sediments (Wakeham et al., 1979; Hites et al., 1980; Venkatesan, 1988), the presence or the uncertainty about the presence of terrestrial organic matter in these sediments makes the proposal of diatoms as a major source of perylene unconvincing. On the other hand, a terrestrial source including plants, fungi and insects has been proposed to be a major, if not the only, source of perylene precursors in sediments (Aizenshtat, 1973; Tan and Heit, 1981; Tan et al., 1996). The latter is also supported by the presence of perylene in sediments from Lake Harun, Japan (Ishiwatari et al., 1980), in terrigenous peats (Gilliland et al., 1960; Aizenshtat, 1973; Venkatesan, 1988, and references therein), in bituminous Kentucky coal (White and Lee, 1980), in Tertiary coals and source rocks from Mahakam Delta, Indonesia (Garrigues et al., 1988), in Late Cretaceous Rocky Mountain coals, USA, in Eocene and Cretaceous Latrobe coals from Gippsland Basin, Australia, as well as in Eocene brown coal from east-central Texas (Lu and Kaplan, 1992). A recent study of the distribution of perylene in two sediment cores from Lake Ontario by Silliman et al. (1998) shows that there are no strong correlations between perylene and land or aquatic sources of organic matter. In this paper, we will report the unusual occurrence of perylene in some Jurassic sediments from the Northern Carnarvon Basin, Australia. Its possible major source and geochemical significance are discussed.

2. Samples and geological setting

Rock samples investigated are from the Upper Triassic to Middle Jurassic sequences of the Delambre-1, Brigadier-1 and Gandara-1 wells located in the Northern Carnarvon Basin, Western Australia (for location see Jiang et al., 1998). The depositional environment in this area during the Late Triassic was fluviodeltaic (Bradshaw et al., 1988; Hocking, 1988; Blevin et al., 1994). Mudstone and sandstone are the major sediments, with occasional occurrence of coals. Early Jurassic times saw deposition in mainly shallow marine environments and mudstone is the major lithology for the three wells. The Middle Jurassic section is a thick set of siltstones/sandstones with occasional occurrence of mudstones and is considered to be deposited under non-marine/fluvialite conditions at Delambre-1. Mainly mudstones were deposited at Brigadier-1 and Gandara-1 in shallow marine depositional environment (Apthorpe, 1994). The Upper Triassic to Middle Jurassic sediments in the study area are believed to have experienced only mild thermal history as shown in Fig. 1.

3. Experimental

Full details of experimental procedures have been given elsewhere (Jiang et al., 1998). Finely ground shaly rock samples were extracted ultrasonically for 2 h with dichloromethane. Silica gel column chromatography separation of extracts was performed to obtain the aliphatic, aromatic and polar fractions. GC/MS analyses of aromatic fractions of sedimentary extracts were carried out on a Hewlett-Packard 5890 Series II GC coupled to a Hewlett-Packard 5971 series Mass Selective Detector (MSD) operating in total ion acquisition mode. Automatic cool-on-column injection was employed into a 50m×0.25mm×0.25μm J&W BP-5 capillary column.
Helium was used as carrier gas. The GC temperature program was 60°C(1 min) → 300°C(30 min).

Compounds were identified by comparison of mass spectra and by matching retention times with those of reference compounds available in this laboratory or published previously. PAH recovery estimate and quantification were achieved by using both internal standards (deuterated PAHs) and a normalization standard (m-terphenyl). Recoveries for the five internal standards were 70–90% for naphthalene-d8, 84–96% for acenaphthene-d10, 85–95% for phenanthrene-d10, 85–98% for chrysene-d12 and 70–90% for perylene-d12.

4. Results and discussion

4.1. The occurrence of perylene in the studied sediments

Fifty-eight aromatic fractions of sediment extracts from the three Upper Triassic to Middle Jurassic sequences were subjected to detailed GC/MS analysis. Shown in Fig. 2 are selected partial total ion chromatograms (TICs), demonstrating the GC behaviours of the various aromatic hydrocarbons. In all of these ancient sediments, methyl-napthalenes are the most abundant PAHs based on the TICs of the aromatic fractions. For ≥ three-ring PAHs, the unsubstituted PAHs are always more abundant than their alkyl derivatives (Jiang, 1998). A combustion source as the result of ancient vegetation fires has been attributed to most of the unsubstituted PAHs including fluoranthene (II), pyrene (III), benzo[a]anthracene (IV), benzo[e]pyrenes (V), benzopyrenes (VI and VII) and indeno[123-cd]pyrene (VIII), and probably phenanthrene (IX) as well as chrysene (X) in the sediments (Jiang, 1998; Jiang et al., 1998). Shown in Fig. 3 are the summed mass chromatograms of m/z (178 + 202 + 228 + 252 + 276) for selected sediment samples of this study, demonstrating the relative distribution of ≥ three-ring unsubstituted PAHs. Perylene (I) is one of the most prominent individual
Fig. 2. Typical total ion chromatograms of aromatic fractions for sediments from the Delambre-1 well (1: naphthalene-d₈; 2: naphthalene; 3: 2-methylnaphthalene; 4: 1-methylnaphthalene; 5: acenaphthene-d₁₀; 6: cadalene; 7: phenanthrene-d₁₀; 8: phenanthrene; 9: fluoranthene; 10: pyrene; 11: m-terphenyl; 12: retene; 13: benzo[a]anthracene; 14: chrysene-d₁₂; 15: chrysene; 16: benzo[a]fluoranthene; 17: benzo[e]pyrene; 18: benzo[a]pyrene; 19: perylene-d₁₂; 20: perylene; 21: indeno[123-cd]pyrene; 22: benzo[g,h,i]perylene. Deuterated compounds were used as internal standards in the concentrations of 0.40 ppm of dry sediments; m-terphenyl was used as a normalization standard in the concentration of 0.42 ppm of sediments).
PAHs in the aromatic fractions of some sediments (Figs. 2 and 3); the relative importance of perylene varies with the age of sample. It is much more abundant than those combustion-derived PAHs in the sediments from the top Lower Jurassic to base Middle Jurassic interval such as sediment samples 3052.5 m and 3547.5 m in the Delambre-1, 2975.5 m in the Brigadier-1 and 3092 m in the Gandara-1 (Fig. 3). Perylene is present in very low concentrations relative to other unsubstituted PAHs in the Upper Triassic sediments. Quantification results for selected sediment samples from the Delambre-1 well also indicate that perylene is most abundant in the sediments from the middle section of the Lower to Middle Jurassic (0.161–0.669 ppm for 3817.5–3052.5 m of Delambre-1) and least abundant in the Upper Triassic sediments (0.008–0.102 ppm) (Table 1 in Jiang et al., 1998). It is clear that perylene is much more abundant in the sediments of this study than in the Upper Jurassic Swiss fossil crinoid sample (0.002 ppm of dry sediments: Thomas and Blumer, 1964). The occurrence of perylene in these ancient sediments is at a similar level to some Recent sediments (Orr and Grady, 1967; Wakeham et al., 1979, 1980; Tan and Heit, 1981; Soma et al., 1996).

Shown in Fig. 4 are the m/z 252 mass chromatograms of the samples typical of relevant depth intervals for the three sedimentary sequences. The abundance of perylene relative to benzyopyrenes varies with depth/time, and this does not seem to be maturity dependent. In sediments from the depth intervals 2632.5–3907.5 m for Delambre-1, 2875.5–3375.5 m for Brigadier-1 and 2950–3412 m for Gandara-1 which all range in age from Toarcian (Lower Jurassic) afterward, perylene is more abundant than both benzo[e]pyrene and benzo[a]pyrene. Perylene is present at lower concentrations than benzo[pyrenes in sediments from deeper sections (Upper Triassic and base Lower Jurassic), and exists only in traces in some of these sediments. In the 2557.5 m sample from Delambre-1 which is the shallowest sediment available in this study, perylene is also less abundant than benzo[a]pyrene. This means the relative distribution of benzyopyrenes and perylene (m/z 252 in Fig. 4) is mainly related to the source of organic materials in the sediments rather than maturity.

Aromatic GC/MS analysis for Upper Jurassic source rocks from the Northern Carnarvon Basin also showed lower concentration of perylene (I) than both benzo[e]-pyrene (VI) and benzo[a]pyrene (VII). This has been shown in the m/z 252 mass chromatograms for two representative sequences (Fig. 5). It can therefore be concluded, based on the distribution pattern of m/z 252 mass chromatograms, that perylene predominates over benzo[a]pyrenes in the top Lower Jurassic to base Middle Jurassic sediments (i.e. equivalent horizons of 2632.5–3907.5 m of Delambre-1, 2875.5–3375.5 m of Brigadier-1 and 2950–3412 m of Gandara-1), and is less abundant than benzo[a]pyrenes in the sediments from the Upper Triassic, base Lower Jurassic, top Middle Jurassic, and Upper Jurassic sections in the Northern Carnarvon Basin. It seems that, as indicated by the results of many studies on PAHs in Recent sediments (Venkatesan, 1988, and references therein), the abundant occurrence of perylene in ancient sediments is also not a ubiquitous phenomenon. The source of organic input into the sediments and the post-depositional processes must have played an important role.

4.2. Perylene being a diagenetic product

Combustion processes do not seem to be the major contributor to the occurrence of abundant perylene in the sediments, especially the middle section of Lower to Middle Jurassic sediments of this study. The depth profiles of benzo[e]pyrene, typical of the distributions of the combustion-derived PAHs in the studied sediments (Jiang, 1998; Jiang et al., 1998), are shown together with those of perylene in Fig. 6. As in Recent sediments of various geological settings (Wakeham et al., 1980; Tan and Heit, 1981; Wilcock and Northcott, 1995; Fernández et al., 1996; Tan et al., 1996), the occurrence of perylene in the Upper Triassic to Middle Jurassic sequences of the Northern Carnarvon Basin also does not follow that of the combustion-derived PAHs. Therefore, the combustion process is not expected to be responsible for such high abundance of perylene as in the Lower to Middle Jurassic sediments from the Northern Carnarvon Basin where perylene is more abundant than combustion-derived PAHs. Even for the Upper Triassic and base Lower Jurassic sections where only background levels of perylene exists, combustion is not a major source since its distribution in these sections does not follow combustion-derived PAHs either vertically or laterally. It is reasonable to conclude that the major source of perylene in the sediments of this study is not combustion related but formed during post-depositional processes.

It has long been established that naphthalene with Friedel-Crafts reagents such as aluminium trichloride yields in the first instance binaphthalene, which undergoes further loss of hydrogen to give perylene (Campbell and Andrew, 1979). Data analysis showed that neither a positive nor a negative relationship exists between the distributions of naphthalene and perylene. Furthermore, there was no binaphthalene (m/z 254) detected in the sediments. Therefore, they do not appear to share a genetic relationship. This excludes the sedimentary coupling of naphthalene as a source of any significance for perylene in these ancient sediments.

It can be seen that the top Lower Jurassic to base Middle Jurassic sediments containing abundant perylene (Figs. 3 and 4) are immature or at low maturity as indicated by their $T_{\text{max}}$ (°C) data from Rock-Eval analysis and vitrinite reflectance values [Ro(%)] (Fig. 1). Listed in Table 1 are the sediment samples from other
Fig. 3. Summed mass chromatograms $m/z \ (178 + 202 + 228 + 252 + 276)$ showing the distribution of unsubstituted PAHs for selected samples from the three wells (P: phenanthrene; An: anthracene; Fla: fluoranthene; Pyr: pyrene; BaAn: benzo[a]anthracene; Chry: chrysene and triphenylene; Bflas: benzo[ghi]perylene; BePy: benzo[e]pyrene; BaPy: benzo[a]pyrene; Pery: perylene; InPy: indeno[123-cd]pyrene; Bpery: benzo[ghi]perylene).
wells of the Northern Carnarvon Basin, and from other Basins that exhibit higher abundances of perylene than benzopyrenes. They are also at low maturity stage. This means the sedimentary formation of perylene occurs during diagenesis. Studies on the PAH distributions in Recent sediments also support this viewpoint (Orr and Grady, 1967; Brown et al., 1972; Aizenshtat, 1973; Laflamme and Hites, 1978; Ishwatari et al., 1980; Wakeham et al., 1980; Gschwend et al., 1983; Louda and Baker, 1984; Wilcock and Northcott, 1995; Fernández et al., 1996).

4.3. Major precursor carriers of perylene related to terrestrial input

It is evident that the major source of perylene in the Upper Triassic to Middle Jurassic sediments from the Northern Carnarvon Basin is terrestrially dependent. Shown in Fig. 6 are the depth profiles of perylene (I), benzo[ap]yrene (VI) and cadalene (XII) relative to the microbe-derived 1,3,6,7-tetramethylphenanthrene (1367-TeMN; XIII, van Aarssen et al., 1996; Jiang et al., 1998) for the three sedimentary sequences from the Northern Carnarvon Basin. Combustion marker benzo[ap]yrene and higher-plant derived cadalene are indicators for terrestrial input to the sediments (Jiang et al., 1998). Although the depth profile of perylene does not follow those of benzo[ap]yrene and cadalene, the maximum relative concentration of perylene, like the terrestrial markers, decreases from Delambre-1 well to Brigadier-1 and Gandara-1 wells. Geological study showed that the depositional environment during the late Early Jurassic to Middle Jurassic was shallow-marine to fluvial-deltaic at Delambre-1 and was shallow-marine at Brigadier-1 and Gandara-1 (Apthorpe, 1994). This means the concentration of perylene in the sediments is proportional to the amount of terrestrial materials, suggesting that the major origin of perylene is related to the input of terrigenous materials.

There are two possible sources for perylene which may be related to the input of terrigenous materials in the aquatic environments. One is the terrestrial organic materials themselves. These may include land plants and other associated terrestrial organisms such as fungi and insects. The other source is from aquatic organisms whose growth is dependent upon the terrestrial materials deposited in an aquatic environment. Among the aquatic organisms, diatoms have been implied by some authors (Wakeham et al., 1979; Hites et al., 1980; Venkatesan, 1988) to be a possible source for perylene in Recent diatomaceous sediments. However, diatoms do not seem to be a major potential source of perylene in our samples which are of Late Triassic to Middle Jurassic age. Firstly, Cretaceous diatoms are the oldest diatoms known at present (Streltnikova, 1974; Tissot and Welte, 1984), and no fossil diatoms have been reported in the Triassic and Jurassic sedimentary sequences of this study. Secondly, structures of perylene have not been reported in diatoms up to this time. Thirdly,

<table>
<thead>
<tr>
<th>Well</th>
<th>Depth (m)</th>
<th>Age</th>
<th>Locality</th>
<th>Lithology</th>
<th>Maturity levela</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>2412</td>
<td></td>
<td>Carnarvon, Australia</td>
<td>Sand-/silt-stone</td>
<td>0.19</td>
</tr>
<tr>
<td>DA-1</td>
<td>920</td>
<td>Lower Cretaceous</td>
<td>Carnarvon, Australia</td>
<td>Sandstone</td>
<td>0.07</td>
</tr>
<tr>
<td>DO-1</td>
<td>1898</td>
<td>Middle Jurassic</td>
<td>Carnarvon, Australia</td>
<td>Sandstone</td>
<td>0.21</td>
</tr>
<tr>
<td>DO-1</td>
<td>2702</td>
<td>Upper Triassic</td>
<td>Carnarvon, Australia</td>
<td>Siltstone</td>
<td>0.23</td>
</tr>
<tr>
<td>O-1</td>
<td>1195</td>
<td>Lower Cretaceous</td>
<td>Carnarvon, Australia</td>
<td>Siltstone</td>
<td>0.36</td>
</tr>
<tr>
<td>P-1</td>
<td>3325</td>
<td></td>
<td>Carnarvon, Australia</td>
<td></td>
<td>0.31</td>
</tr>
<tr>
<td>SA-1</td>
<td>1405</td>
<td>Lower Cretaceous</td>
<td>Carnarvon, Australia</td>
<td>Siltstone</td>
<td>0.12</td>
</tr>
<tr>
<td>SO-1</td>
<td>1542</td>
<td>Cretaceous</td>
<td>Carnarvon, Australia</td>
<td>Sand-/silt-stone</td>
<td>0.15</td>
</tr>
<tr>
<td>WA-1</td>
<td>590</td>
<td>Cretaceous</td>
<td>Carnarvon, Australia</td>
<td>Reservoir</td>
<td>0.43</td>
</tr>
<tr>
<td>Mayneside-1</td>
<td>2970</td>
<td>Cretaceous</td>
<td>Eromanga, Australia</td>
<td>Shale</td>
<td>Low maturity</td>
</tr>
<tr>
<td>Mayneside-1</td>
<td>3000</td>
<td>Cretaceous</td>
<td>Eromanga, Australia</td>
<td>Shale</td>
<td></td>
</tr>
<tr>
<td>Mayneside-1</td>
<td>3050</td>
<td>Cretaceous</td>
<td>Eromanga, Australia</td>
<td>Shale</td>
<td></td>
</tr>
<tr>
<td>Volador-1</td>
<td>3033</td>
<td>Upper Cretaceous</td>
<td>Gippsland, Australia</td>
<td>Sandstone</td>
<td>0.15</td>
</tr>
<tr>
<td>Volador-1</td>
<td>3315</td>
<td>Upper Cretaceous</td>
<td>Gippsland, Australia</td>
<td>Sandstone</td>
<td>0.23</td>
</tr>
<tr>
<td>Volador-1</td>
<td>3405</td>
<td>Upper Cretaceous</td>
<td>Gippsland, Australia</td>
<td>Siltstone</td>
<td>CPE: 2.27</td>
</tr>
<tr>
<td>Volador-1</td>
<td>3498</td>
<td>Upper Cretaceous</td>
<td>Gippsland, Australia</td>
<td>Siltstone</td>
<td>0.21</td>
</tr>
<tr>
<td>Volador-1</td>
<td>3573</td>
<td>Upper Cretaceous</td>
<td>Gippsland, Australia</td>
<td>CPE: 2.31</td>
<td></td>
</tr>
<tr>
<td>Volador-1</td>
<td>3675</td>
<td>Upper Cretaceous</td>
<td>Gippsland, Australia</td>
<td>Ro: 0.70%</td>
<td></td>
</tr>
<tr>
<td>Julia Creek</td>
<td>1114</td>
<td>Cretaceous</td>
<td>Queensland, Australia</td>
<td>Oil shale</td>
<td>0.28</td>
</tr>
<tr>
<td>GNK-67</td>
<td>1351</td>
<td>Middle Miocene</td>
<td>S. Sumatra, Indonesia</td>
<td>Shale</td>
<td>0.17</td>
</tr>
<tr>
<td>GNK-67</td>
<td>1514</td>
<td>Lower Miocene</td>
<td>S. Sumatra, Indonesia</td>
<td>Shale</td>
<td>0.14</td>
</tr>
<tr>
<td>Maniguin-2</td>
<td>2268</td>
<td>Miocene</td>
<td>SE Luzon, Philippines</td>
<td>Coal</td>
<td>Ro: 0.66%</td>
</tr>
</tbody>
</table>

* Unless otherwise stated in the table, values are for the maturity parameter C29 ∑22 steranes 20S/(20S + 20R).
diatoms do not seem to be a potential precursor source for perylene even in Recent sediments. Crinoids, another type of aquatic organism containing perylene related structures can also be excluded as the major precursor carriers for perylene. This is because (1) no fossil crinoid remains have been reported from the Upper Triassic and Jurassic sediments from the Northern Carnarvon Basin; (2) the concentration of perylene in the Upper Jurassic Swiss fossil is much lower than in the Jurassic sediments of this study; and (3) the structure of compound XX isolated from modern crinoids by Rideout and Sutherland (1985) and De Riccardis et al. (1991) is far more complex than perylene, and perylene is expected to be only a minor product of their reduction reactions. On the other hand, fungi communities colonizing the aquatic environment as parasites, symbionts and saprobes (Kohlmeyer and Kohlmeyer, 1979; Hyde, 1996) are a possible contributor of perylene in the Lower to Middle Jurassic sediments of this study.

4.4. The major precursors for perylene being terrigenous

The precursors of perylene are most likely the structurally related perylenequinones and associated derivatives, and higher plants, fungi and insects are the most likely carriers of these precursors. Considering that fungi are predominantly terrestrial, with less than 2% of the species being aquatic (Ingold and Hudson, 1993), and that the diversification of insects in the marine environment is very limited (Gullan and Cranston, 1994), it can be said reasonably that these three kinds of organisms, live or dead, are generally of terrestrial affinity. Therefore, a high abundance of perylene in these ancient sediments is suggested to be an indicator for terrestrial input. Data from GC–ir–MS analysis of aromatic fractions of samples from the 3367.5–3727.5 m interval of Delambre-1 well performed at the Australian Geological Survey Organization seem to support this. The stable carbon isotope composition of perylene (−23.63 to −23.96‰) is in the same range as aromatic land plant biomarkers (−24.88 to −26.64‰ for cadalene; −24.46 to −25.90‰ for retene and −24.63 to −25.22‰ for simonellite) and combustion-derived PAHs (−23.19 to −24.19‰ for benzo[a]pyrene and benzo[e]pyrene).

The suggestion that perylene in the Upper Triassic to Middle Jurassic sediments of the Northern Carnarvon Basin, especially in the top Lower to base Middle...
Jurassic sediments where it is very abundant, is mainly of terrigenous origin seems reasonable if one considers the following facts:

1. **Perylene concentration in the sediments:** Quantification results (Jiang et al., 1998) show that the sample from 3457.5m of the Delambre-1 well contains perylene in highest abundance (0.669 ppm). The total organic carbon (TOC) of this sample is 1.85%, which means the content of total organic matter in the sediments should be in the range of 2.18 to 2.74% if 1.18 or 1.48 are taken as the conversion factors for computation of total organic matter from TOC (Tissot and Welte, 1984). Therefore, perylene is about 0.0024 to 0.0031% (or 24 to 31 ppm) of the total sedimentary organic material in the Delambre-1 3457.5 m sample.

2. **Perylenequinone pigment concentration in fungi and insects:** The contents of binaphtyl and binaphthyl (XV) in fungus Daldinia concentrica were reported to be 0.394 and 0.016% of its dry body (Hashimoto et al., 1994). Perylenequinone pigments (XIX) from insect species Aphididae were isolated in the yields of 0.3 to 1% of the live insect weight (Cameron and Todd, 1967).

The occurrence of fungi in geological settings has been a ubiquitous phenomenon (Moore, 1969; Tissot and Welte, 1984; Truswell, 1996; Walker, 1996). For example, possible ancestors of higher fungi Ascomycetes, to which the perylenequinone and binaphthyl containing Daldinia concentrica and Elsinoe belong (Lousberg et al., 1969; Bougher and Syme, 1998), have been reported from a silicified peat deposit of Triassic age from the Antartica (White and Taylor, 1988). Taking into account the contents of perylenequinone pigments in fungi, it is reasonable to suggest that fungi may...
Fig. 6. Lateral change of the concentrations of perylene, benzo[e]pyrene and cadalene relative to 1,3,6,7-tetramethylnaphthalene for Delambre-1 to Brigadier-1 and Gandara-1 wells.
have been the major precursor carriers for perylene in these ancient sediments, and also for perylene in Recent sediments. The application of fungal spores and their fruiting bodies in biostratigraphy and palaeoclimatic interpretations is not yet well known (Kalgutkar, 1997). Their importance in geological studies has been recognized probably only in the past two decades, as spores of fungi were not discussed in the *Handbook of Palynology* published in 1969 (Erdtman, 1969). Therefore, it is not surprising that there has been no report on the presence of fungal remains in the sediment samples from the three wells in this study, which were drilled during 1979–1981. However, it has been suggested that deltaic sediments provide substrates for the activity of saprophytic fungi (Traverse, 1988).

The proposal that fungi may be the major precursor carriers for perylene in sediments can be supported by the geochemical study of a Miocene coal sample from the Maniguin Island, Philippines. Perylene was found to be a prominent unsubstituted PAH in the aromatic fractions from this coal sample (Fig. 7). The *m/z* 252 mass chromatogram showing the relative distribution of five-ring PAHs (Fig. 7) is very similar to some of the sediments from the Jurassic section of the Northern Carnarvon Basin (Figs. 3 and 4), with perylene being much more abundant than benzopyrenes. Palynological examination revealed that fungal remains are the second most abundant palynomorphs after large cuticular fragments of unknown plant affinity, and are more abundant than fern spores and angiosperm pollen (Murray et al., 1997).

5. Conclusions

Unusually high abundance of perylene has been detected in some Lower Jurassic to Middle Jurassic sediments from the Northern Carnarvon Basin. It is believed that perylene is mainly of terrigenous source based on the facts that its lateral distribution in the study area is consistent with terrestrial markers and that its isotope composition is in the same range as terrestrial markers. Its natural precursors are possibly the perylenequinone pigments which have been found in higher plants, fungi and insects. Fungi are likely the major precursor carriers for perylene in sediments considering their content of perylenequinone pigments and their geological significance. The abundant occurrence of perylene in sediments may be an indicator of the contribution of fungi to the formation of sedimentary organic matter in terms of both their alteration to other organisms and the accumulation of their bodies in the sediments.

Acknowledgements

CJ acknowledges the financial supports of his PhD study by Curtin University of Technology and Australian Petroleum Cooperative Research Centre. We thank Mr. G. Chidlow for assistance with GC–MS analysis. Drs. Z. Aizenshtat and P. Garrigues are thanked for their constructive reviews of the manuscript.
Appendix. Molecular structures cited in the text

I. Perylene
II. Fluoranthene
III. Pyrene
IV. Benzo[a]anthracene
V. Benzo[j]fluoranthene
VI. Benzo[e]pyrene
VII. Benzo[a]pyrene
VIII. Indeno[cd-123]pyrene
IX. Phenanthrene
X. Chrysene
XI. Benzo[ghi]perylene
XII. Cadalene
XIII. 1,3,6,7-Tetramethylnaphthalene
XIV. Perylenequinone
XV. Binaphthyl
XVI. Cercosporin
XVII. Shiraiachrome
XVIII. Stemphyperylenol
XIX. Erythrosphin
XX. Gymnochrome
References


Jenkins, B.M., Jones, A.D., Turn, S.C., Williams, R.B., 1996. Emission factors for polycyclic aromatic hydrocarbons from
biomass burning. Environmental Science and Technology 30, 2462–2469.
novel fungal perylenequinone pigments from *Shiraia Bam-
busicola*. Journal of Natural Products 52, 948–951.
Zander, M., 1983. Physical and chemical properties of poly-
cyclic aromatic hydrocarbons. In: Bjoresth, A. (Ed.), Hand-
book of Polycyclic Aromatic Hydrocarbons. Marcel Dekker,