Bitumen II from the Paleoproterozoic *Here’s Your Chance*

Pb/Zn/Ag deposit: implications for the analysis of depositional environment and thermal maturity of hydrothermally-altered sediments

Alex I. Holman a, Kliti Grice a*, Caroline M. B. Jaraula a, Arndt Schimmelmann b

a Western Australia Organic and Isotope Geochemistry Centre, Department of Chemistry, Curtin University, GPO Box U1987 Perth, WA 6845, Australia

b Department of Geological Sciences, Indiana University, 1001 East 10th Street, Bloomington, IN 47405-1405, USA

* Corresponding author. Tel.: +61(0) 8 9266 2474; fax: +61(0) 8 9266 2300.

E-mail address: K.Grice@curtin.edu.au (Kliti Grice).
Abstract

The formation of sedimentary exhalative (SEDEX) Pb/Zn deposits is linked to ocean euxinia, but recent evidence suggests that ferruginous conditions may have dominated the deep ocean during the Middle Proterozoic, a maximum period for SEDEX distribution. Biomarkers of sulfate-reducing and sulfide-oxidising bacteria are valuable indicators of euxinic conditions in such settings. Organic matter (OM) from SEDEX deposits is often affected by alteration and/or migration, but OM entrapped within the kerogen/mineral matrix (Bitumen II) may be less affected than the freely-extractable OM (Bitumen I). We analysed Bitumen II from the Paleoproterozoic Here’s Your Chance (HYC) Pb/Zn/Ag deposit to find evidence of euxinic conditions in the depositional environment. \(n\)-Alkane distributions in Bitumen II are markedly distinct from previously-reported Bitumen I. Bitumen II contains long-chain \(n\)-alkanes (up to C\textsubscript{36} or C\textsubscript{38}) and a strong even-over-odd distribution in a number of samples, which are 4 to 7‰ depleted in \(^{13}\text{C}\) compared to \(n\)-alkanes in Bitumen I and verified as indigenous by comparison with \(\delta^{13}\text{C}\) of isolated kerogen. These features are interpreted as evidence of sulfate-reducing and sulfide-oxidising bacteria, confirming that HYC was deposited under euxinic conditions. Bitumen II has the potential to reveal information from OM that is degraded and/or overprinted in Bitumen I. Commonly-used methylphenanthrene maturity ratios give conflicting information as to the relative maturity of Bitumens I and II. Bitumen I contains a far higher proportion of methylated
phenanthrenes than Bitumen II. As Bitumen II is sequestered within the
kerogen/mineral matrix it may have restricted access to the ‘methyl pool’ of
organic compounds that can donate methyl groups to aromatic
hydrocarbons. Parameters that include both phenanthrene and
methylphenanthrenes do not appear suitable to compare maturity of
Bitumen I and II; hence there is no clear evidence that Bitumen II is of
lower thermal maturity than Bitumen I.

1. Introduction

Sedimentary exhalative (SEDEX) deposits are stratiform, sediment-hosted Pb/Zn ore bodies dominated by sulfide minerals. The genetic models of these deposits are complex and have been extensively reviewed (e.g. Large et al., 2005); the general aspects are deposition of Pb and Zn from a hydrothermal brine in rifted sedimentary basins. The occurrence of major SEDEX mineralisation from ca 1800 Ma has been linked to the development of widespread oceanic euxinia during the middle Proterozoic (Lyons et al., 2006). Recent evidence however shows that ferruginous conditions may have dominated in the deep ocean during this period, with euxinia being restricted to isolated basins and mid-depth coastal waters (Poulton et al., 2010; Planavsky et al., 2011). Organic biomarkers are a reliable proxy for the presence of euxinic conditions. For example the breakdown products of carotenoid pigments produced by green and purple sulfur bacteria indicate
photic zone euxinia in ancient marine systems (Brocks et al., 2005; Grice et al., 2005).

Organic compounds are also useful as indicators of thermal maturity, providing a valuable indication of fluid temperature for deposits which lack fluid inclusions (e.g. Large et al., 2005). SEDEX and other deposits often contain high abundances of polycyclic aromatic hydrocarbons (PAHs) (Püttmann et al., 1989; Williford et al., 2011), highly condensed aromatic compounds made up of two or more benzene rings. Low-molecular-weight PAHs such as naphthalene and phenanthrene are almost ubiquitous in sediments. They can be formed through diagenetic alteration of natural organic precursors (e.g. Wakeham et al., 1980a; Grice et al., 2007; Grice et al., 2009) or by combustion of biomass (Venkatesan and Dahl, 1989; Nabbefeld et al., 2010a) and fossil fuels (Wakeham et al., 1980b). High-molecular-weight PAHs are found in high abundance in high-temperature (> 300 °C) marine hydrothermal vents (Kawka and Simoneit, 1990), where they are generated by the addition of C₂ or C₂H₄ units to existing aromatic compounds (Stein, 1978). Methylated PAHs are produced by geosynthetic methylation reactions in sediments (Voigtmann et al., 1994). PAHs methylated in β positions are more thermodynamically stable than those in α positions (Szczerba and Rospondek, 2010), and hence the ratios of β to α isomers are frequently used as indicators of thermal maturity. Ratios of methylphenanthrene (MP) isomers include the methylphenanthrene index
(MPI-1) and methylphenanthrene ratio (MPR) (Radke et al., 1982, see Fig 1. for equations).

The Mt. Isa-McArthur basin system of Northern Australia is host to five supergiant Proterozoic SEDEX deposits; the most significant accumulation of Pb and Zn in the world (Large et al., 2005). The largest of these deposits is the Here’s Your Chance (HYC) deposit, hosted in unmetamorphosed carbonaceous and pyritic shales and siltstones of the Barney Creek Formation (BCF). Organic matter (OM) from HYC has been strongly affected by hydrothermal alteration from the mineralising fluid (see Section 2.1) and diagnostic biomarkers have been degraded and possibly overprinted by non-indigenous OM. Traditional extraction techniques can therefore give limited information on the depositional environment and thermal maturity. Removal of silicate minerals from extracted rock powder by digestion with hydrofluoric acid (HF) liberates a second fraction of extractable OM, which is likely to be protected from migration and alteration (Sherman et al., 2007; Nabbefeld et al., 2010b).

This fraction is referred to as Bitumen II, whereas the first extract is called Bitumen I. The methods used in this study for the extraction of Bitumen II have been previously reported and validated by Holman et al. (2012). In this study we isolate and analyse Bitumen II from a range of HYC samples in an attempt to distinguish between indigenous and migrated OM and reveal evidence that the deposit was formed in a euxinic environment. A previous report has found that PAH maturity ratios in Bitumen II show different
values than those in Bitumen I (Nabbefeld et al., 2010b), so we also evaluate PAH ratios to determine whether Bitumen II has been protected from thermal alteration.

2. Materials and methods

2.1 The Barney Creek Formation and the Here’s Your Chance deposit

The 1640 Ma (Page and Sweet, 1998) carbonaceous, pyritic and tuffaceous shales and siltstones of the Barney Creek Formation (BCF) in the McArthur Basin, Northern Territory, Australia were originally interpreted as a deep marine succession deposited in a reducing environment below the wave base (Bull, 1998). More recently, it has been recognised that these sediments are part of a facies mosaic of time-equivalent shelf, slope and deep-water sediments deposited in a series of tectonically controlled sub-basins (McGoldrick et al., 2010). The BCF has been widely studied as it contains possibly the most well-preserved Proterozoic organic matter (OM) (Summons et al., 1988). BCF black shales generally contain 0.2 to 2 wt.% total organic carbon, and locally greater than 7 wt.% (Powell et al., 1987). Previous studies of low-maturity shales from the Glyde River region of the BCF have found biomarkers of the sulfide-oxidising green and purple sulfur bacteria Chlorobiaceae and Chromatiaceae (Brocks et al., 2005; Brocks and Schaeffer, 2008). These bacteria are known to thrive in marine systems.
where euxinic conditions persist in the photic zone of the water column (e.g. Summons and Powell, 1987; Grice et al., 2005).

The BCF is host to the HYC Pb-Zn-Ag deposit, one of the largest sediment-hosted base metal deposits in the world. The HYC deposit has a total resource of 227 Mt, at 9.25 wt. % Zn, 4.1 wt. % Pb and 41 ppm Ag contained in eight discreet ore lenses (Walker et al., 1977; Large et al., 2005). The deposit is generally considered to have been formed by exhalation of a metal-rich hydrothermal brine into the water column (Croxford, 1968; Ireland et al., 2004a; Large et al., 2005). The OM at HYC has been strongly affected by hydrothermal alteration, but several studies have used OM to investigate the conditions of deposition (Logan et al., 2001; Chen et al., 2003; Williford et al., 2011). HYC n-alkanes are enriched in deuterium by 50 to 60‰ compared to those from the unmineralised BCF, indicating isotopic exchange with a D-enriched evaporitic brine (Williford et al., 2011). Williford et al. also presented carbon isotopic data which suggest that a significant quantity of aromatic hydrocarbons were generated in the underlying Wollogorang Fm and transported to the deposit within the mineralising fluid.

The samples used were collected and analysed by Williford et al. (2011). Five samples of Pb-Zn-Ag sulfide ore were taken from the highly mineralised upper ore body 5 of the deposit (referred to as sample pits 1 to 5), plus one non-mineralised shale sample from the underlying W-Fold Shale member, a sequence of red-green shales and siltstones at the basal 10
to 15 meters of the BCF at and around the area of the mine (Walker et al., 1977).

2.2 Extraction and separation of Bitumen II

The extraction of Bitumen II followed a procedure modified from Robl and Davis (1993) and Nabbefeld et al. (2010b), as detailed by Holman et al. (2012) for the pit 1 sample. The other samples were prepared using the same method. HCl and HF were cleaned prior to use by shaking with dichloromethane (DCM) to remove organic contaminants from the acids. GC-MS analysis (Section 2.4) revealed that saturate and aromatic contaminants were below the limit of detection after cleaning.

Extracted rock powder was digested with HCl (1 M) to remove carbonates then placed into clean 50 mL polyethylene centrifuge tubes (5-6 g of sample per tube). Equal volumes of concentrated HF (48 wt.%) and Milli-Q purified water were added to the tubes and left to digest (1-2 hours) in an ice bath with regular shaking. The supernatant liquid was then decanted and a second volume of acid-water mixture was added. The tubes were left at room temperature (3-4 hours) with occasional shaking to complete the digestion. The solid residue was then washed (3 ×) with Milli-Q water and freeze dried. The samples had decreased in mass by ca. 50%.

After the acid digestion the samples were extracted in a Soxhlet apparatus (72 hours) with 9:1 (v:v) DCM: methanol (MeOH) to extract
Bitumen II, replicating the conditions used by Williford et al. (2011) to isolate Bitumen I. Copper turnings (rinsed with DCM and activated with dilute HCl) were added to the flask to remove elemental sulfur. The extract was evaporated to dryness under a stream of warm N₂, dissolved in a minimum amount of DCM and added to the top of a small column (5.5 cm × 0.5 cm i.d.) of silica gel (activated at 160 °C for 24 hrs). The total extract was separated into saturate, aromatic and polar fractions by elution with n-hexane, 30 vol.% DCM in n-hexane and 1:1 DCM:MeOH respectively. Semi-quantitative analysis of aromatic fractions was done using an internal standard of deuterated p-terphenyl.

2.3 Isolation of kerogen

Following the extraction of Bitumen II a fraction of each sample was taken for the isolation of kerogen, following the procedure of Nabbefeld et al. (2010b). A small amount of sample was placed into glass centrifuge tubes (<1 g per tube) and shaken with 2-3 mL of saturated aqueous zinc bromide solution (ρ ≈ 2.4 g mL⁻¹). After centrifugation (2000 RPM, 5 min) the acid-insoluble minerals settled to the bottom of the vial while the isolated kerogen remained floating on or suspended in the ZnBr solution. The liquid was then decanted and diluted with Milli-Q water to allow the kerogen to settle. The kerogen was washed with Milli-Q water (×3) and freeze-dried.
30-50 mg of kerogen was isolated for each sample from 3-5 g of acid-digested rock powder.

2.4 Gas chromatography mass spectrometry (GC-MS)

Saturate and aromatic fractions were analysed by GC-MS using a Hewlett Packard (HP) 6890 gas chromatograph coupled to a HP 5973 mass selective detector, following the procedure of Holman et al. (2012). Fractions were dissolved in n-hexane and injected into a split-splitless injector in pulsed splitless mode. A DB5-MS column (Agilent Technologies, 60 m length, 0.25 mm i.d., 0.25 μm film thickness) was used with He as the carrier gas. The GC oven temperature was increased from 40 °C to 310 °C at 3 °C min⁻¹ then held isothermally for 30 min. Data were acquired in full scan mode (m/z 50–550).

2.5 Stable carbon isotope analysis

Compound-specific stable carbon isotope ratios (δ¹³C) of the saturate fractions were measured using a HP 6890 gas chromatograph coupled to a Micromass IsoPrime isotope ratio monitoring mass spectrometer (irm-MS). The GC oven was held at 50 °C for 1 min, increased to 310 °C at 3 °C min⁻¹ then held isothermally for 20 min. The GC column was the same as that described in Section 2.4. δ¹³C values are reported relative to CO₂ reference
gas calibrated to the Vienna Pee Dee Belemnite (VPDB) scale. Samples were analysed 2 to 5 times each, and standard deviations for measured compounds ranged from 0.2 to 0.5‰. The instrument was calibrated daily with a mixture of compounds of known $\delta^{13}C$ to monitor the precision and accuracy of analysis. The aromatic fractions were of insufficient quantities to perform compound-specific isotope analysis.

Bulk stable carbon isotope ratios of isolated kerogens were measured using a Delta V Plus mass spectrometer connected to a Thermo Flush 1112 elemental analyser via a Conflo IV (Thermo-Finnigan/Germany).

3. Results

3.1 Bitumen II saturated hydrocarbons

Total ion chromatograms (TICs) of Bitumen II saturated hydrocarbon fractions from sample pits 1 and 3, which together exemplify the most important features of all the samples, are displayed in Fig. 2. Samples from pits 1, 5 and the W-Fold Shale show a significant predominance of $n$-alkanes with even carbon numbers, while this pattern is less pronounced in ore from pits 2, 3 and 4. Long-chain $n$-alkanes up to $n$-C$_{36}$ are present in all samples, with $n$-C$_{37}$ and $n$-C$_{38}$ present only in pits 1 and 5. These distributions are characterised by Average Chain Length (ACL) and Carbon Preference Index (CPI), which are presented in Table 1. The ACL in Bitumen II ranges from
25.4 to 26.9, which is greater than the Bitumen I ACL of roughly 18
(Williford et al., 2011).

CPI measures the ratio of $n$-alkanes with odd carbon numbers over
those with even carbon numbers, and is calculated here using the formula of
Marzi et al. (1993). The Bitumen I $n$-alkanes reported by Williford et al.
(2011) show no predominance of odd or even carbon numbers and hence the
CPI will approximately equal one. The CPI of Bitumen II from pits 1, 5 and
the W-Fold Shale samples range from 0.59 to 0.83, showing a strong
prevalence of even-numbered $n$-alkanes that is seen in Fig. 2a. The
remaining samples have CPI values much closer to one and show no obvious
carbon number preference (Fig. 2b).

3.2 Stable carbon isotope analysis

Compound-specific stable carbon isotope ratios for Bitumen II $n$-
alkanes and isolated kerogen are listed in Table 1. Values are reported in
the ranges $C_{16}$ and $C_{18}$, and $C_{24}$ to $C_{32}$, as these were the compounds that
were of sufficient abundance to measure $\delta^{13}C$. The $\delta^{13}C$ values of Bitumen II
$n$-alkanes (-34.4 to -31.6‰) are 4 to 7‰ lower than those in Bitumen I
(Williford et al., 2011). Within Bitumen II the long chain $n$-alkanes ($C_{24}$ to
$C_{32}$) are generally 1 to 3‰ lighter than to $C_{16}$ and $C_{18}$, although the two
values are within error for pit 1 and there was insufficient abundance of $n$-
$C_{16}$ and $n$-$C_{18}$ from pit 2 to measure their isotopic composition. Bulk kerogen
Δ13C ranges from -37 to -34.2‰, which is 1 to 4‰ lower than Bitumen II long-chain alkanes. No consistent trend in Δ13C is observed between samples for either n-alkanes or kerogen (Fig. 3).

3.3 Bitumen II aromatic hydrocarbons

Quantification of selected PAHs in Bitumen II (reported in ng of compound per g of TOC) is presented in Table 2 along with selected ratios of aromatic compounds. Data from pit 1 have been previously reported (Holman et al., 2012). Several methylphenanthrene ratios are also included from Bitumen I, calculated from data reported by Williford et al. (2011). The amounts of aromatic compounds measured in Bitumen II are commonly 5 to 15% that of Bitumen I. As in Bitumen I there is no clear trend in PAH concentrations from pits 1 to 5.

The methylphenanthrene ratios MPI-1 and MPR are plotted for Bitumens I and II in Fig. 4. Both parameters are designed to be a measure of maturity (Radke et al., 1982), however the relationships between the parameters in Bitumens I and II are distinct. MPI-1 for Bitumen I is consistently significantly higher than in Bitumen II (Fig. 4a), whereas the MPR is generally higher in Bitumen II than Bitumen I (Fig. 4b). These differences may be explained by the increased ratio of phenanthrene to methylphenanthrenes (P/MPs) in Bitumen I (Table 2), indicating that
Bitumen I contains a greater proportion of methylated isomers (see Section 4.2 for discussion).

4. Discussion

4.1 Sources of saturated compounds

The Bitumen II \( n \)-alkanes reported in this study differ from those previously found in Bitumen I in three main aspects: a marked predominance of even carbon numbers in three out of six samples (Fig. 2), the presence of long-chain alkanes up to \( C_{38} \), and reduced \( \delta^{13}C \) values of -34 to -31‰ (Fig. 3). These features have not previously been observed together in samples from HYC. Alkane distributions previously reported from HYC Bitumen I have been limited to \( C_{32} \) or \( C_{33} \), with \( \delta^{13}C \) between -30 and -27‰ (Logan et al., 2001; Williford et al., 2011). Logan et al. (2001) observed \( n \)-alkanes with a strong even-over-odd distribution in highly mineralised samples from ore body 2, however there is evidence that these samples were contaminated with hydrocarbons from plastic sample bags (Grosjean and Logan, 2007) and thus results from this study should be treated with caution.

The significant differences between the \( n \)-alkanes in Bitumens I and II may be due to a different source of OM, a difference in the response to hydrothermal alteration, or a combination of both. \( n \)-Alkanes from Proterozoic sediments are typically enriched 2 to 3‰ in \( ^{13}C \) compared to the
source kerogen (Logan et al., 1995). Carbon isotopic data (Table 1) shows that $n$-alkanes in HYC Bitumen II bear this exact relationship with the isolated kerogens from HYC. These data strongly suggest that Bitumen II $n$-alkanes are indigenous to HYC, in accordance with the contention that Bitumen II is less likely to be overprinted by migrated OM (Sherman et al., 2007). It was proposed by Williford et al. (2011) that aromatic hydrocarbons in Bitumen I were transported to HYC from the underlying Wollogorang Fm. The similar $\delta^{13}C$ of aromatics and $n$-alkanes in Bitumen I (Williford et al., 2011) suggest that saturated compounds may also have been transported. The migration of non-indigenous $n$-alkanes would obscure the even-over-odd distribution, resulting in the more typical Proterozoic distribution of Bitumen I.

A strong even-over-odd preference of $n$-alkanes is uncommon in the geological record, but has been observed in a variety of marine sediments (e.g. Dembicki Jr et al., 1976; Simoneit, 1994). George et al. (1994) studied solid bitumens from the ca 1400 Ma Roper Group in the McArthur Basin. Several of these samples displayed a slight even-over-odd $n$-alkane predominance. These alkanes were also depleted in $^{13}C$ compared to those which did not show an even-over-odd distribution. It was concluded that solid bitumens in the Roper Group incorporate multiple sources of organic input, including one which is isotopically light and contains a high proportion of even-numbered alkanes (George et al., 1994). Possible origins of this input were not discussed in detail, but a number of studies have
connected similar \(n\)-alkane distributions with the presence of sulfate-
reducing and sulfide-oxidising bacteria. For instance, a strong
predominance of isotopically light even-numbered \(n\)-alkanes in microbial
mat facies of the Neoproterozoic Centralian Super-basin was ascribed to the
activity of purple or colourless sulfur bacteria (Logan et al., 1999). A recent
report of a 380 Ma fossil invertebrate preserved within a carbonate
concretion in the Canning Basin, Western Australia also showed \(n\)-alkanes
with a pronounced even-over-odd distribution in the desulfurised fossil
extract, along with \(^{13}\)C-depleted long-chain \(n\)-alkanes in the fossil nucleus
and carbonate matrix (Melendez et al., 2013). Biomarker and isotopic
evidence revealed the strong activity of sulfate reducing bacteria and green
sulfur bacteria (Chlorobi) in conditions of photic zone euxinia at the time the
fossil was preserved.

Analyses of lipids from microbial cultures have shown that the
phototrophic sulfur bacterium Chlorobi produces \(n\)-alkanes with a marked
even-over-odd distribution over the range \(C_{15}\) to \(C_{28}\), while the sulfate-
reducing bacterium \textit{Desulfovibrio Hildenborough} produces a similar but less
pronounced distribution over the range \(C_{19}\) to \(C_{31}\) (Han and Calvin, 1969).
Sulfate reducing bacteria are known to generate long-chain lipids: \textit{D. desulfuricans} produces \(n\)-alkanes predominantly in the range \(C_{25}-C_{35}\)
(Ladygina et al., 2006), while long chain fatty acids up to \(C_{34}\) were found in
\textit{Desulfotomaculum} (Řezanka et al., 1990). Both sulfate-reducing bacteria
and phototrophic sulfur bacteria produce lipids that are significantly
depleted in $^{13}$C compared to the biomass. Lipids from sulfate reducing bacteria were found to be depleted 4 to 17‰ (Londry et al., 2004) and lipids from purple sulfur bacteria were depleted by up to 20‰ (Madigan et al., 1989).

The distinctive even-over-odd distribution of $n$-alkanes in Bitumen II was likely generated by phototrophic sulfur bacteria, while the $^{13}$C-depleted long-chain $n$-alkanes in Bitumen II indicate sulfate-reducing bacteria. Their presence in Bitumen II, closely associated with the kerogen/mineral matrix, implies that these bacteria were present at the time of ore deposition. This evidence is consistent with deposition under euxinic conditions, as required for the formation and preservation of large-scale sulfide deposits (Lyons et al., 2006). The extent of euxinia into the photic zone is evidenced by the presence of phototrophic sulfur bacteria. The results fit the generally-held model in which a metal-rich hydrothermal brine was vented into the basin, reacting with bacterially-produced sulfide to form fine-grained base metal sulfides (Ireland et al., 2004b; Large et al., 2005). Recent findings of widespread ferruginous conditions in the McArthur Basin (Planavsky et al., 2011) suggest that euxinia was restricted to localised settings, such as the HYC sub-basin (McGoldrick et al., 2010) and the Glyde River region studied by Brocks et al. (2005). A increased supply of sulfate to a basin would promote euxinia over ferruginous conditions (Poulton et al., 2010). Sulfate carried by the oxidised hydrothermal fluid (Cooke et al., 2000) may have contributed to the development of euxinic conditions during the deposition
of HYC. It is notable that the evidence of euxinia is seen only in Bitumen II; the distinctive features from sulfate-reducing and sulfide-oxidising bacteria have been removed from Bitumen I by the actions of hydrothermal alteration and migration of non-indigenous OM.

4.2 Aromatic hydrocarbons in Bitumens I and II

The aromatic fractions of both Bitumens I and II are dominated by PAHs. The distribution of PAHs (Fig. 2c) follows the most thermodynamically favourable pathway for the creation of condensed aromatic molecules (Stein, 1978) and is typical of those found in hydrothermal systems (e.g. Kawka and Simoneit, 1990). The high abundance of PAHs indicates that Bitumen II, like Bitumen I, has experienced significant hydrothermal alteration. The quantity of PAHs in Bitumen II (Table 2) is much lower than found in Bitumen I (Williford et al., 2011). This could indicate that Bitumen II has been partially shielded from alteration, although it also likely reflects the small amounts of OM available within the kerogen/mineral matrix.

A variety of parameters have been developed to evaluate thermal maturity based on the ratios of various methylated isomers of PAHs. Ratios based on methylphenanthrene (MP) isomers have been found in a study of the McArthur Basin to be sensitive to changes in maturity throughout the oil window (George and Ahmed, 2002). Two common MP ratios, MPI-1 and
MPR are shown in Fig. 3 for both Bitumens I and II. The value of MPI-1 in Bitumen I exceeds that of Bitumen II in every sample. If MPI-1 is taken to be a true indicator of maturity this would indicate that Bitumen I is of higher maturity than Bitumen II, suggesting that Bitumen II has been protected from thermal alteration. A different relationship however is observed for MPR. The values for Bitumens I and II are similar, and in some samples Bitumen II exceeds Bitumen I. Both parameters are expected to be indicative of maturity (Radke et al., 1982) but it is apparent that other factors are affecting the behaviour of these two ratios. Williford et al. (2011) proposed that PAHs in Bitumen I were generated at high temperatures (>250 °C) in the underlying Wollogorang Fm, whereas Bitumen II is likely indigenous to HYC and has experienced temperatures of less than 200 °C (Cooke et al., 2000; Large et al., 2005). The different thermal histories are consistent with the increased MPI-1 values in Bitumen I but cannot explain why MPR is often greater in Bitumen II. Notably this is not the first study that has reported such behaviour. In a study of marine sediments from multiple locations spanning the Permian/Triassic boundary by Nabbefeld et al. (2010b) the same relationships were found. MPI-1 is consistently greater in Bitumen I but the β/α MP ratio, which is similar to MPR but includes all four isomers rather than only 2- and 1-MP, is frequently greater in Bitumen II. The samples analysed by Nabbefeld et al. are of greatly different age and thermal history to those from this study, hence it appears that the
relationships between MPI-1 and MPR are not unique to HYC but rather are a result of fundamental differences between Bitumens I and II.

The major difference between MPI-1 and the MPR or β/α MP ratio is that the unmethylated phenanthrene is included in the denominator of MPI-1 but does not appear in the other ratios. Fig. 5 shows that Bitumen II contains far higher proportions of phenanthrene than Bitumen I.

Phenanthrene is more abundant than the MPs in Bitumen II for all samples except the W-Fold Shale, but in Bitumen I it is less abundant than most or all of the MP isomers. The inclusion of phenanthrene in the denominator of MPI-1 causes this ratio to give much lower values for Bitumen II. Higher proportions of phenanthrene in Bitumen II were reported by Nabbefeld et al. (2010b), who also observed that Bitumen II contained a greater proportion of β methylated isomers compared to Bitumen I. The relationship between β and α isomers is less consistent in HYC, and the proportion of β to α isomers appears similar in Bitumens I and II.

The increased proportion of phenanthrene in Bitumen II from multiple locations and maturities implies that the cause of the increase is unrelated to location or thermal history. Nabbefeld et al. (2010b) suggest that phenanthrene is preferentially preserved in Bitumen II as it is more stable than the MPs, just as the more stable β-isomers are preserved over the α-isomers. Comparisons of thermodynamic properties of both phenanthrene and MPs, either experimental or theoretical, are rare, and the relative stabilities are strongly dependent on redox conditions (Püttmann et al.,
Regardless of their relative stabilities it is not clear why phenanthrene should be preferentially retained in Bitumen II over the MPs. Evidence for the retention of the more stable β-MPs is limited in HYC, but is seen to a greater extent in the results of Nabbefeld et al. (2010b). Previous studies have explained the retention of β-isomers in coals not by thermodynamic stability but by a ‘molecular sieve’ effect whereby larger molecules are trapped by pores in the coal structure (Vahrman and Watts, 1972). This effect does not explain the retention of the less bulky unmethylated molecule. In a study of the chromatographic behaviour of organic compounds moving through a column of montmorillonite clay, Brothers et al. (1991) found that 2-MP appears to be more strongly adsorbed to the clay than P. This is the opposite effect to that seen in Bitumen II. Studies of the relative adsorption behaviour of phenanthrene and MP are limited, but the available evidence does not seem to support the preferential retention of phenanthrene within the kerogen/mineral matrix. An alternative explanation for the high proportion of phenanthrene in Bitumen II is that the MP isomers are prevented from forming within the kerogen/mineral matrix. MPs in sediments are generated by geosynthetic reactions in which methyl groups are added to unmethylated phenanthrene (Voigtmann et al., 1994). Methylation of phenanthrene has been achieved in the laboratory under moderate temperature conditions in the presence of a clay catalyst, but requires the addition of a methyl donor such as methane (Voigtmann et al., 1994) or existing methylated aromatic compounds.
(Alexander et al., 1995). A hydrous pyrolysis study found that phenanthrene alone does not undergo methylation even with prolonged heating, but significant methylation occurs with the addition of formic acid (McCollom et al., 1999). From these results it can be inferred that MPs will only form when other organic compounds are present that are able to donate methyl groups. This was recognised by van Aarssen et al. (1999) who proposed the concept of a ‘methyl pool’ that can be accessed by all aromatic compounds in the sediment. Compounds that are preserved within the kerogen/mineral matrix as part of Bitumen II may have restricted access to the methyl pool and thus display reduced levels of methylation. It has been demonstrated that phenanthrene that is intercalated in clay minerals is significantly less available to biodegrading microorganisms (Theng et al., 2001), and it is feasible that it would experience reduced access to the methyl pool as well. This mechanism can explain the increased proportion of phenanthrene in Bitumen II from both this study and Nabbefeld et al. (2010b).

Oxidation state can also affect the proportions of phenanthrene and MPs. A study of the Kupferschiefer deposit (southwest Poland) found increased proportions of phenanthrene in zones of higher oxidation state (Püttmann et al., 1989). PAHs in Bitumen I are believed to have been transported by a fluid that was likely oxidised (Cooke et al., 2000), hence the low proportions of phenanthrene in Bitumen I suggest that redox is not a significant control at HYC.
MPI-1 is commonly used to indicate thermal maturity, but results from this study have shown that the parameter can be heavily influenced by factors that affect the methylation of P. Prior reports have noted that MPI-1 is also strongly influenced by demethylation reactions that occur at high temperatures (Garrigues et al., 1990). The inclusion of phenanthrene in the denominator of MPI-1 means that this ratio is not simply an indicator of maturity, but also reflects the source of OM and the degree of methylation. As such MPI-1 is not a suitable parameter to compare the maturity of Bitumens I and II. Ratios such as MPR, which are based only on MP isomers, are perhaps better suited as indicators of maturity alone. As MPR from Bitumens I and II is generally similar it appears that the two extracts are of approximately equal maturity, and there is no conclusive evidence from MP ratios in this study that Bitumen II is significantly protected from thermal alteration. These results do not support a high-temperature origin for Bitumen I PAHs, as proposed by Chen et al. (2003), although the isotopic evidence for migration of hydrocarbons is strong (Section 4.1).

5. Conclusions

Organic matter at HYC has experienced significant hydrothermal alteration, but Bitumen II may be protected from alteration and migration. Bitumen II prepared from HYC samples reveals highly distinct distributions of saturated and aromatic compounds. Bitumen II $n$-alkanes show a
predominance of even carbon numbers, a preservation of long-chained \( n \)-alkanes up to \( C_{38} \) and a marked depletion in \( ^{13}C \). These features are indicative of strong contribution from sulfate-reducing and sulfide-oxidising bacteria. Comparison with \( \delta^{13}C \) of isolated kerogen confirms that \( n \)-alkanes in Bitumen II are indigenous to HYC, indicating that the deposit formed under euxinic conditions. This evidence supports the generally-held model whereby lead and zinc reacted in the water column with sulfide produced by bacterial sulfate reduction. Bitumen II appears useful in the study of environments that have experienced significant alteration and/or migration, where diagnostic features in Bitumen I have been destroyed or overprinted.

Bitumens I and II both contain high abundances of PAHs. The common maturity parameters MPI-1 and MPR display inconsistent results, with MPI-1 greater in Bitumen I but MPR often greater in Bitumen II. This behaviour is due to the far higher proportion of phenanthrene in Bitumen II compared to Bitumen I. We believe that this is a fundamental property of Bitumen II resulting from restricted access to the ‘methyl pool’ that contributes to methylation reactions. As MPI-1 is so heavily affected by access to the methyl pool it is not a suitable parameter for comparing the thermal maturity of Bitumens I and II.

Acknowledgements
All authors acknowledge the CSIRO Flagship Collaboration Fund Cluster for Organic Geochemistry of Mineral Systems led by Curtin University. A.H. thanks Curtin University for an Australian Postgraduate Award and CSIRO for a top-up scholarship. The Institute for Geoscience Research (TIGeR) and the John de Laeter Centre for Isotope Research provided additional funding. The authors thank Geoff Chidlow and Peter Sauer for GC-MS technical support, Stephen Clayton for GC-irMS technical support, and Grzegorz Skrzypek for bulk kerogen $\delta^{13}$C measurements. Peter McGoldrick, an anonymous reviewer and Associate Editor Thomas Wagner provided helpful reviews, and Chris Yeats, Jochen Brocks and Katy Evans gave comments on earlier versions of the manuscript.

References


Ireland T., Large R. R., McGoldrick P. and Blake M. (2004b) Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore


Davis, A. T. Fisher and J. F. Slack). Ocean Drilling Program, College
Station, Texas. pp. 447-465.

Stein S. E. (1978) On the high temperature chemical equilibria of polycyclic

source rocks and crude oils: biological markers for the green sulphur

and geochemistry of the Middle Proterozoic McArthur Basin, Northern

Szczerba M. and Rospondek M. J. (2010) Controls on distributions of
methylphenanthrenes in sedimentary rock extracts: critical evaluation
**41**, 1297-1311.

Theng B. K. G., Aislabie J. and Fraser R. (2001) Bioavailability of
phenanthrene intercalated into an alkylammonium–montmorillonite

Vahrman M. and Watts R. H. (1972) The smaller molecules obtainable from
carbon and their significance: Part 6. Hydrocarbons from coal heated in


Captions of tables and figures

Table 1

Average chain length (ACL) and carbon preference index (CPI) for Bitumen II n-alkanes, plus stable carbon isotope ratios ($\delta^{13}C$) of n-alkanes and isolated kerogen. $\delta^{13}C$ is given as the average of repeated analyses, with one standard deviation shown in parentheses and the number of analyses in superscript. CPI was calculated using the generalised formula of Marzi et al. (1993), with $n = 7$ and $m = 17$. WFS – W-Fold Shale unit.

Table 2

Quantification of selected PAHs present in Bitumen II aromatic fractions, plus calculated PAH ratios for Bitumens I and II. Bitumen I ratios were calculated from data presented by Williford et al. (2011).

Figure 1

Structures of PAHs discussed in the text. Positions of methylation are indicated for phenanthrene. Equations of the methylphenanthrene index (MPI-1) and methylphenanthrene ratio (MPR) are taken from (Radke et al., 1982).
Figure 2
Total ion chromatograms of (A) pit 1 Bitumen II saturate fraction, (B) pit 3 Bitumen II saturate fraction and (C) pit 1 Bitumen II aromatic fraction. $n$-Alkanes in (A) and (B) are marked with open circles and even carbon numbers are labelled. Labels in (C) are a: phenanthrene, b: methylphenanthrenes, c: pyrene, d: chrysene + triphenylene, e: benzo[e]pyrene, f: benzo[ghi]perylene and g: coronene.

Figure 3
$\delta^{13}$C of $n$-alkanes from Bitumens I (carbon number range C$_{18}$ to C$_{21}$), Bitumen II (ranges C$_{16}$ + C$_{18}$ and C$_{24}$ to C$_{32}$) and bulk $\delta^{13}$C of isolated kerogen from HYC sample pits. Bitumen I data was taken from Williford et al. (2011). Error bars are one standard deviation.

Figure 4
Selected PAH ratios calculated for Bitumens I and II. (A) methylphenanthrene index (MPI-1) and (B) methylphenanthrene ratio (MPR). Equations of MPI-1 and MPR are shown in Fig. 1. Bitumen I data was taken from Williford et al. (2011).
Figure 5

Relative proportion of phenanthrene (P) and methylphenanthrenes (MP) for (A) Bitumen I and (B) Bitumen II. Bitumen I data was taken from Williford et al. (2011).
<table>
<thead>
<tr>
<th>Distance from pit 1 (m)</th>
<th>Pit 1</th>
<th>Pit 2</th>
<th>Pit 3</th>
<th>Pit 4</th>
<th>Pit 5</th>
<th>WFS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>104</td>
<td>372</td>
<td>553</td>
<td>710</td>
<td>-</td>
</tr>
</tbody>
</table>

*Molecular parameters*

<table>
<thead>
<tr>
<th>ACL</th>
<th>Pit 1</th>
<th>Pit 2</th>
<th>Pit 3</th>
<th>Pit 4</th>
<th>Pit 5</th>
<th>WFS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>26.3</td>
<td>26.9</td>
<td>26.7</td>
<td>25.6</td>
<td>25.4</td>
<td>25.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CPI</th>
<th>Pit 1</th>
<th>Pit 2</th>
<th>Pit 3</th>
<th>Pit 4</th>
<th>Pit 5</th>
<th>WFS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.67</td>
<td>0.91</td>
<td>0.98</td>
<td>0.94</td>
<td>0.83</td>
<td>0.59</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\delta^{13}C$ (%)</th>
<th>Pit 1</th>
<th>Pit 2</th>
<th>Pit 3</th>
<th>Pit 4</th>
<th>Pit 5</th>
<th>WFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{16} + C_{18}$</td>
<td>-32.2 (0.3)</td>
<td>-32.5 (0.2)</td>
<td>-32.1 (0.4)</td>
<td>-32.4 (0.3)</td>
<td>-31.6 (0.5)</td>
<td></td>
</tr>
<tr>
<td>$C_{24} - C_{32}$</td>
<td>-32.3 (0.3)</td>
<td>-31.7 (0.2)</td>
<td>-34.2 (0.2)</td>
<td>-34 (0.3)</td>
<td>-33.4 (0.5)</td>
<td>-34.4 (0.5)</td>
</tr>
<tr>
<td>Kerogen</td>
<td>-35.5 (0.1)</td>
<td>-36.3 (0.1)</td>
<td>-35.6 (0.1)</td>
<td>-37.0 (0.1)</td>
<td>-34.2 (0.1)</td>
<td>-35.5 (0.1)</td>
</tr>
</tbody>
</table>
# Table 2

<table>
<thead>
<tr>
<th>Compounds (ppb/TOC)</th>
<th>Pit 1</th>
<th>Pit 2</th>
<th>Pit 3</th>
<th>Pit 4</th>
<th>Pit 5</th>
<th>WFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>615</td>
<td>327</td>
<td>379</td>
<td>1156</td>
<td>334</td>
<td>231</td>
</tr>
<tr>
<td>3-Methylphenanthrene</td>
<td>424</td>
<td>190</td>
<td>263</td>
<td>754</td>
<td>232</td>
<td>249</td>
</tr>
<tr>
<td>2-Methylphenanthrene</td>
<td>479</td>
<td>283</td>
<td>339</td>
<td>948</td>
<td>274</td>
<td>250</td>
</tr>
<tr>
<td>9-Methylphenanthrene</td>
<td>358</td>
<td>181</td>
<td>247</td>
<td>616</td>
<td>243</td>
<td>277</td>
</tr>
<tr>
<td>1-Methylphenanthrene</td>
<td>358</td>
<td>174</td>
<td>260</td>
<td>689</td>
<td>263</td>
<td>315</td>
</tr>
<tr>
<td>Pyrene</td>
<td>391</td>
<td>192</td>
<td>156</td>
<td>558</td>
<td>160</td>
<td>202</td>
</tr>
<tr>
<td>Chrysene</td>
<td>327</td>
<td>125</td>
<td>356</td>
<td>481</td>
<td>273</td>
<td>477</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>772</td>
<td>180</td>
<td>830</td>
<td>490</td>
<td>658</td>
<td>1025</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>358</td>
<td>111</td>
<td>266</td>
<td>185</td>
<td>254</td>
<td>317</td>
</tr>
<tr>
<td>Coronene</td>
<td>101</td>
<td>-</td>
<td>57</td>
<td>-</td>
<td>42</td>
<td>27</td>
</tr>
</tbody>
</table>

*Bitumen I PAH ratios*

<table>
<thead>
<tr>
<th>MPI-1</th>
<th>1.02</th>
<th>1.04</th>
<th>1.02</th>
<th>1.04</th>
<th>0.90</th>
<th>0.91</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPR</td>
<td>1.34</td>
<td>1.62</td>
<td>1.31</td>
<td>1.38</td>
<td>1.04</td>
<td>0.79</td>
</tr>
<tr>
<td>MP/P</td>
<td>2.63</td>
<td>2.53</td>
<td>2.93</td>
<td>2.60</td>
<td>3.03</td>
<td>4.72</td>
</tr>
<tr>
<td>BePyr/Pyr</td>
<td>1.97</td>
<td>0.94</td>
<td>5.33</td>
<td>0.88</td>
<td>4.11</td>
<td>5.08</td>
</tr>
<tr>
<td>BePyr/Chry</td>
<td>2.36</td>
<td>1.44</td>
<td>2.33</td>
<td>1.02</td>
<td>2.41</td>
<td>2.15</td>
</tr>
<tr>
<td>Chry/Phen</td>
<td>0.53</td>
<td>0.38</td>
<td>0.94</td>
<td>0.42</td>
<td>0.82</td>
<td>2.06</td>
</tr>
<tr>
<td>BePery/Phen</td>
<td>0.58</td>
<td>0.34</td>
<td>0.70</td>
<td>0.16</td>
<td>0.76</td>
<td>1.37</td>
</tr>
<tr>
<td>BePery/Pyr</td>
<td>0.92</td>
<td>0.58</td>
<td>1.71</td>
<td>0.33</td>
<td>1.59</td>
<td>1.57</td>
</tr>
<tr>
<td>BePery/Chry</td>
<td>1.09</td>
<td>0.89</td>
<td>0.75</td>
<td>0.38</td>
<td>0.93</td>
<td>0.66</td>
</tr>
<tr>
<td>BePery/BePyr</td>
<td>0.46</td>
<td>0.61</td>
<td>0.32</td>
<td>0.38</td>
<td>0.39</td>
<td>0.31</td>
</tr>
</tbody>
</table>

*Bitumen I PAH ratios*

<table>
<thead>
<tr>
<th>MPI-1</th>
<th>1.38</th>
<th>1.41</th>
<th>1.26</th>
<th>1.49</th>
<th>1.34</th>
<th>1.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPR</td>
<td>1.37</td>
<td>1.32</td>
<td>1.21</td>
<td>1.35</td>
<td>1.12</td>
<td>1.26</td>
</tr>
<tr>
<td>MP/P</td>
<td>5.00</td>
<td>6.26</td>
<td>5.31</td>
<td>7.05</td>
<td>9.32</td>
<td>4.67</td>
</tr>
</tbody>
</table>
naphthalene

phenanthrene (P)

pyrene

chrysene

triphenylene

benzo[e]pyrene

benzo[ghi]perylene

coronene

\[
\text{MPI}-1 = 1.5 \, \frac{2 \text{-MP} + 3 \text{-MP}}{P + 1 \text{-MP} + 9 \text{-MP}} \quad \text{MPR} = \frac{2 \text{-MP}}{1 \text{-MP}}
\]