Origin and significance of aromatic hydrocarbons in giant iron ore deposits of the late Archean Hamersley Basin, Western Australia

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Abstract

Late Archean to earliest Paleoproterozoic shales associated with two giant iron ore deposits in the Hamersley Province, Western Australia, contain traces of solvent extractable saturated and aromatic hydrocarbons. The host rocks belong to the \( \sim 2.5 \) billion years (Ga) old Mt McRae Shale and Brockman Iron Formation, Hamersley Group, and were collected in mines near Tom Price and Newman (Mt Whaleback). The saturated hydrocarbons in the rock extracts have the composition of highly mature gas condensates. The aromatic fraction predominantly consists of unsubstituted two and three ring hydrocarbons that are demonstrably indigenous and syngenetic based on their unusual pyrolytic composition and the presence of hydrocarbons with similar attributes covalently bound to the kerogen. The bitumen composition is interpreted as recording the interaction of organic matter with hydrothermal fluids or oxidizing solutions overprinted by regional low-grade metamorphism. The organic matter could potentially have recorded flow direction, redox potential and temperature of fluids that formed the iron deposits. Thus, a new organic geochemical approach is suggested for determining hypogene and supergene controls on iron mineralization in the Hamersley Province and related ore deposits.

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1. Introduction

Minimally metamorphosed \( (200–300 \text{ °C}) \) shales of the late Archean Hamersley and Fortescue Groups, Pilbara Craton, Western Australia, contain saturated and aromatic hydrocarbons (Brocks et al., 1999, in press-a). The hydrocarbons, including paleobiologically significant biomarkers, were detected in 2.76–2.48 Ga old shales from a wide range of locations within the Hamersley Province. The composition and syngeneity of the molecules was discussed in detail by Brocks et al. (in press-a) and a paleobiological interpretation of the biomarkers is given by Brocks et al. (in press-b). The present paper concentrates on the unusual composition of aromatic hydrocarbons from shales of the Hamersley Group collected in two giant iron ore deposits, Mt Tom Price and Mt Whaleback. It discusses the composition and distribution of the bitumens, explores possible connections between bitumen alteration and iron precipitation, and proposes a new organic geochemical approach that might help to distinguish between supergene and hypogene regimes of ore formation.
1.1. Supergene and hypogene models of iron ore formation

The host rocks of the bitumens are closely associated with two of the world’s largest iron ore deposits. Mt Tom Price hosts 0.9 billion tons of high-grade hematite ore and Mt Whaleback 1.4 billion tons (Taylor et al., 2001). Most iron ore deposits in the Hamersley Province formed from late Archean to earliest Paleoproterozoic. Martite–goethite banded iron formations (BIF) by oxidation of magnetite to hematite and removal of large volumes of silica and other gangue material. The ore usually conforms to the bedding of the host BIF, and bedding laminae are still partly visible. Ore bodies overprint folds ascribed to early phases of Ophthalmian Orogeny (~2.2 Ga) (Oliver and Dickens, 1999). Ore formation is usually structurally controlled (Harmsworth et al., 1990) and some ore bodies are located at depths >400 m overlain by unmineralized BIF. At deposit margins highly enriched ore grades into iron-poor BIF across centimeter to meter transitions (Barley et al., 1999). The two major ore types are martite-goethite and martite-microplaty hematite ores (martite is hematite after magnetite) (Barley et al., 1999; Harmsworth et al., 1990).

Competing models of ore formation either involve supergene or hypogene controls on iron mineralization, or a combination of both.

1.1.1. Supergene models

According to the CSIRO-AMIRA version of the supergene model (Harmsworth et al., 1990; Morris et al., 1980), the ore body grew from considerable depths towards the surface, replacing BIF gangue minerals with hydrous iron oxides and oxidizing magnetite to martite. The model requires structural conduits, such as faults, that allow the percolation of supergene water from the erosion surface down to great depths. At the erosion surface, supergene fluids dissolved high concentrations of iron from BIF mediated by the reducing capacity of interbedded organic matter. The reduced iron was then transported along faults into underlying strata, where it was oxidized, and replaced dissolved gangue minerals. The gangue material, mostly BIF-silica, was dissolved and removed by cold water. Notably, hot fluids were apparently not involved in silica dissolution. The problematic step in the supergene model, the oxidation of ferrous iron at depth in the absence of oxidizing chemical species, is addressed by proposing an electrochemical redox system. Accordingly, Fe^{2+} was oxidized by electron transfer to BIF magnetite bands that were in conductive contact with the erosion surface. At the surface the ultimate electron acceptor was atmospheric oxygen. The electrochemical cycle was then closed by ionic conduction through groundwater. This process, resulting in the formation of deep martite–goethite ore, evidently took place during exposure of the Hamersley Group about 2.0 Ga ago. The original martite–goethite ore was converted to martite–microplaty hematite ore during low-grade burial metamorphism at about 1.7 Ga. Younger martite–goethite ore frequently found in association with metamorphosed martite-microplaty hematite ores apparently formed in a second mineralization event probably in the Mesozoic-Tertiary.

1.1.2. Hypogene models

Hypogene models (Barley et al., 1999; Li et al., 1993; Martin et al., 1998; Oliver and Dickens, 1999; Powell et al., 1999) suggest that the giant iron ore deposits were formed by heated fluids ascending from deeper strata. The rising fluids had a deep-seated source (strictly hypogene) or were derived from downward percolating meteoric water driven by orogenic activity (syntectonic-meteoric model). Ascending hydrothermal fluids possibly mixed with descending cool oxygenated meteoric waters and introduced additional iron into the ore body. Chert and other gangue minerals were dissolved under hydrothermal conditions and then substituted by iron minerals. Initial hematite crystallization might have occurred at about 250 °C at high fluid pressures, although fluid temperatures might locally have reached more than 400 °C. Fluid flow was either driven by Ophthalmian orogenesis 2.2–2.4 Ga ago and the eruption of the Cheela Springs Basalt at 2.2 Ga (Powell et al., 1999) or as a response to heat-flux during Wyloo rifting at ~2.0 Ga (Barley et al., 1999).

Taylor et al. (2001) propose a model that involves hypogene as well as supergene fluid flow. This envisages initial hypogene leaching of silica by alkaline basinal brines. These fluids had relatively low-temperatures (150–250 °C) and were reducing. In a second stage, iron minerals were oxidized to martite and microplaty-hematite by deeply circulating, mildly oxidizing, warm (>100 °C) meteoric solutions. In a final process of deep weathering, progressively cooler and more oxidizing supergene fluids leached residual carbonate, calcium, magnesium and phosphorous minerals, and oxidized pyrite to limonite. In contrast to the above models, iron was exclusively enriched by removal of gangue minerals, not by the precipitation of imported iron minerals.

2. Samples and experimental

2.1. Samples and geological setting

The ~2.6–2.45 Ga Hamersley Group is divided into eight formations. These are, from oldest to youngest, the Marr Mamba Iron Formation, Wittenoom Dolomite, Mt Sylvia Formation, Mt McRae Shale, Brockman Iron Formation, Weeli Wolli Formation, Woongarra Volcanics and Boolgeeda Iron Formation.
Iron ore at Mt Tom Price and Mt Whaleback is predominantly located in the Brockman Iron Formation, and the shales analyzed in this study come from the underlying Mt McRae Shale and from the Dales Gorge Member and Whaleback Member of the Brockman Iron Formation. The samples include four shales from the Mt Tom Price mine (Bee1, Rae1, Rae6, and Dal1), one shale from the B26 deposit 24 km west of Mt Tom Price (Rae2), and three shales from Mt Whaleback near Newman (Rae3, Rae5 and Wal2) (Table 1, Fig. 1). Rae3 and Rae6 are unweathered mine-face samples; all other samples were collected from different diamond drill cores.

The Mt McRae Shale has an average thickness of 50 m. The lower 15 m contain massive, highly kerogen-rich black shale interbedded with chert and upwards increasing pyrite content (Harmsworth et al., 1990). The middle 10–15 m of alternating chert and kerogenous shale are highly pyritic, with nodules up to 2 cm in diameter. The unit terminates with two bands up to 20 cm thick of almost massive pyrite overlain by ~10 m of non-pyritic black shale and several meters of BIF and ferruginous chert interbedded with shale. The massive to plane laminated black shales of the Mt McRae Shale are generally very fine grained and have varying contents of kerogen, quartz, muscovite, illite, chlorite, dolomite, pyrite, hematite and magnetite. The Mt McRae Shale grades into the overlying Brockman Iron Formation as BIF contents increase (Harmsworth et al., 1990). The Brockman Iron Formation consists of several hundred meters (620 m at Tom Price and 500 m at Newman) of alternating BIF, chert, shale, dolomite and fine tuff (Harmsworth et al., 1990). Deposition occurred around 2.47 Ga on a clastic-starved open platform or shelf with normal open oceanic circulation. BIF was probably precipitated in a gradually subsiding back-arc continental setting (Blake and Barley, 1992). The Brockman Iron Formation has been subdivided into four members. The lowermost Dales Gorge Member, with an approximate thickness of 150 m, consists of seventeen cycles of oxide facies BIF alternating with shale, chert, carbonate and silicate BIF. The shale layers range from a few centimeters to up to 2 m. The gray or green shales are very fine grained and massive with varying concentrations of kerogen. They predominantly contain stilpnomelane and chlorite and varying amounts of quartz, feldspars, micas and sulfides. The shales probably formed by a combination of chemical precipitation and volcanic ash fall-out, with clear evidence of a terrigenous clastic contribution lacking (Morris and Horwitz, 1983). The overlying ~50 m thick Whaleback Member is comparatively iron-poor and contains alternating bands where shale or BIF and chert is predominant. In comparison to the Dales Gorge Member, Whaleback shales have higher kerogen contents, less stilpnomelane and contain prominent sulfide-rich layers (Morris, 1993). Further sample details and information about regional metamorphism can be found in Brocks et al. (in press-a).

### 2.2. Instrumental analysis

Mineral compositions of rock powder were determined by XRD on a Siemens D501 diffractometer. XRD-data were analyzed using SIROQUANT for Windows 2.0 (CSIRO Australia and Sietronics). Total organic carbon (TOC) and Rock-Eval parameters were determined on a Vinci Rock-Eval 6 instrument according to established procedures (Espitalié et al., 1977).

Bitumen was isolated by Soxhlet extraction of rock powder with dichloromethane, and separated into saturated, aromatic and polar fractions as described by

### Table 1

<table>
<thead>
<tr>
<th>Formation or member</th>
<th>Well</th>
<th>Depth (m)</th>
<th>TOC (%) (^{a})</th>
<th>Sat(^{b}) (ppm)</th>
<th>Aro(^{b}) (ppm)</th>
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<td>Whaleback Mm</td>
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<td>Mine</td>
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<td>86</td>
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</table>

\(^{a}\) Total organic carbon.

\(^{b}\) Sat = saturated hydrocarbon fraction of bitumen; Aro = aromatic fraction. 1 ppm = 1 µg hydrocarbons per gram of rock. Quantification was by GC–FID (flame ionization detection) using internal standards (accuracy ±20%).
Fig. 1. Sample locations in the Hamersley Basin. (A) Regional map of the Tom Price and Newman area. The metamorphic zones Z2–Z4 refer to burial metamorphic grades of the Fortescue Group (Smith et al., 1982). Z2 = prehnite–pumpellyite–epidote zone, Z3 = prehnite–pumpellyite–epidote–actinolite zone, Z4 = (prehnite)–epidote–actinolite zone (lower greenschist facies). (B) Detail of the Mt Tom Price mine (geological map of Mt Tom Price courtesy Tony Harding and Rio Tinto Exploration).
Brocks et al. (in press a). Aromatic hydrocarbons were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). GC was performed on a Hewlett Packard HP6890 fitted with a flame ionization detector (FID) and a HP Ultra 1 column (25 m x 0.25 mm i.d., 0.33 μm film thickness) using manual injection in splitless mode and H2 as carrier gas. The oven was programmed at 40 °C (2 min) and heated to 310 °C at 4 °C/min, with a final hold time of 15 min. GC–MS in the full-scan mode and by selected ion recording (SIR) were carried out on a Hewlett Packard 5973 Mass Selective Detector (MSD) equipped with a HP6890 gas chromatograph (Hewlett Packard) and a HP-5 column (50 m x 0.20 mm i.d., 0.11 μm film thickness). Samples were injected in pulsed splitless mode with He as carrier gas. The GC oven was programmed at 40 °C (2 min), heated to 310 °C at 4 °C/min and held at the maximum temperature for 25 min. The MS source was operated in EI-mode at 70 eV.

Total extract yields were determined by GC-FID on the Hewlett Packard 6890 GC system, and individual compounds were quantified using corrected GC–MS (SIR) or full scan signals with d14-para-terphenyl (D14x) and 3-methylenicosa-1,2,4-triene (aC22) as internal standards.

3. Results

3.1. Bulk characteristics and extract yields

The TOC content of the Mt Tom Price samples ranges from 1.3 to 7.8%. The Hamersley Group was regionally metamorphosed to prehnite-pumpellyite facies (Zones II and III in Smith et al., 1982) and, therefore, the hydrogen content of kerogen is low (H/C ≈ 0.1; Hayes et al., 1983). Average reflectance values of kerogens from Mt Tom Price are R0v = 3.5% for the Mt McRae Shale and R0v = 2.5% for shales of the Brockman Iron Formation (Taylor et al., 2001). However, reflectivities in different samples show strong variation and range from less than 2% to more than 5%.

The total yield of bitumen, here defined as the solvent extractable organic matter, also varies markedly between samples. Saturated hydrocarbons range from 0.06 μg/g of rock in Rae6 to 1000 μg/g in Rae2, representing a concentration difference of four orders of magnitude. Aromatic compounds are most abundant in Rae1 (27 μg/g) and lowest in Rae3 (0.03 μg/g). A similar variability was observed in the relative yields of saturated to aromatic hydrocarbons ranging from Sat/Aro = 0.005–110 (Table 1).

3.2. Bitumen composition

Analysis of the bitumens from Mt Tom Price and Mt Whaleback by GC–MS and GC–MS (MRM) (Brocks in press a) revealed the presence of n-alkanes, mid- and end-branched monomethylalkanes, o-cyclohexylalkanes, acyclic isoprenoids, diamondoids, tri- to pentacyclic terpanes, steranes, aromatic steroids and polyaromatic hydrocarbons (PAH). The n-alkane and methylalkane profiles are condensate-like in all samples except Rae6 where diamondoid hydrocarbons are the only non-aromatic constituents. All samples, except Rae3 and Rae6, contain hopane and sterane biomarkers.

While the distribution of saturated hydrocarbons in the Hamersley Group samples is generally similar to bitumens from the underlying 2.7 Ga Fortescue Group (Brocks et al., in press-a), the composition of the aromatic fractions in the two Groups are fundamentally different. Fig. 2 shows GC–MS full scans of the aromatic fraction of a representative sample from the Fortescue Group (TQP3) and the Hamersley Group (Rae5). TQP3 is dominated by alkylated polycyclic aromatic hydrocarbons, especially alkynaphthalenes (C10-Naph) and alkylphenanthrenes (C10-Phen) (Fig. 2A, Table 2), a composition generally similar to most Precambrian and Phanerozoic bitumens and oils (Price and DeWitt, 2001). The predominance of alkylated PAH over parent PAH is also graphically summarized in Fig. 3A.

In contrast to this distribution pattern, almost all extracts from Mt Tom Price and Mt Whaleback contain very high relative abundances of unsubstituted parent compounds, mainly naphthalene (Naph), biphenyl (BP), fluorene (Fl), dibenzofuran (DBF), dibenzothiophene (DBT), phenanthrene (Phen) and phenylpyrene (PhN) (Figs. 2B and 3B-C, E-I). The relative abundance of monomethylated PAH (MPAH) is low and aromatic compounds with two or more substituents occur only in trace amounts or are below the detection limit. The abundance of parent aromatic hydrocarbons relative to the sum of all methylated homologues (PAH/MPAH) for all samples is summarized in Table 2. The ratios naphthalene to methylpyrene (Naph/MN), biphenyl to methylbiphenyls (BP/MBP) and fluorene to methylfluorenes (Fl/MFl) in the Hamersley Group are commonly > 1 and generally higher than in the Fortescue Group. In sample Dal1 from the Brockman Iron Formation (Hamersley Group), these ratios are < 1, probably due to preferential evaporation of parent compounds relative to substituted counterparts (Fig. 3B). The highest PAH/MPAH ratios are observed for dibenzothiophene over methylpyrene (DBT/MBT) and phenanthrene over methylpyrene (Phen/MP) (Table 2). In the Hamersley Group these ratios are generally > 3 and in some cases > 100, while in the Fortescue Group DBT/MBT and Phen/MP are commonly < 0.5. A conspicuous exception to this rule is Hamersley Group sample Rae2 (Fig. 3D). Rae2 was collected from a drill hole 24 km west of Mt Tom Price. It has very low PAH/MPAH ratios and,
therefore, resembles bitumens from the underlying Fortescue Group.

Another noteworthy characteristic of the aromatic hydrocarbon distribution of all samples is the low relative abundance of PAH with four aromatic rings or more. The abundance of pyrene (Pyr) is one to three orders of magnitude lower than that of phenanthrene while aromatic five-ring systems were usually below the detection limit. Dibenzofuran and dibenzothiophene and their methylated homologs are the only NSO-compounds detected in the Archean samples. 1- and 2-phenyl-naphthalene (1-PhN and 2-PhN), eluting between phenanthrene and pyrene and identified in \( m/z = 204 \) mass-chromatograms, occur in unusually high relative concentrations (Fig. 2B). In Mt Whaleback samples, the sum of the abundance of 1-PhN and 2-PhN is 30% of the abundance of phenanthrene, and in Mt Tom Price samples it is 3–15%. The 1-PhN/2-PhN ratio is markedly different for Mt Whaleback (1-PhN/2-PhN = 6–9) and Mt Tom Price (1-PhN/2-PhN = 0.1–0.3) (Table 2). It has been observed that the 1-PhN/2-PhN ratio decreases with increasing thermal maturity, probably as the results of clay catalyzed isomerization of the thermodynamically less stable 1-PhN isomer to 2-PhN (Marynowski et al., 2001). However, in the Hamersley bitumens, thermal equilibration between the two isomers is probably not a constraint. The thermal history at both Tom Price and Mt Whaleback was similarly extreme, and the lithology of the source rocks is similar.

Fig. 2. GC–MS full scans of the aromatic fractions of (A) shale TQP3 from the \(~2.78~\text{Ga}\) Mt Roe Formation, Fortescue Group (Tassie Queen Mine near Marble Bar, Pilbara) and (B) sample Rae5 from the \(~2.5~\text{Ga}\) Mt McRae Shale, Hamersley Group (Mt Whaleback Mine). The chromatogram in (A) is magnified 140 times relative to (B) with respect to absolute extract yields. Naph = naphthalene; BP = biphenyl; Fl = fluorene; Phen = phenanthrene; DBF = dibenzofuran, DBT = dibenzothiophene; PhN = phenylnaphthalene; \( C_x \) refers to the total carbon number of substituents. X is an unidentified signal with \( m/z = 179(100\%), 178(41), 194(36), 180(15), 89(14), 176(11), 177(7), 165(7), 152(7), 76(7) \).
3.3. Bitumen thermal maturity

The thermal maturity of bitumens extracted from shales of the Hamersley Group were discussed in detail by Brocks in press a). In short, condensate-like \( n \)-alkane profiles, very high triaromatic and monoaromatic sterol parameters and very high methyladamantane and methyldiamantane indices indicate maturities in the wet-gas zone. The upper limit of thermal maturity is bracketed by the preservation of traces of steranes and hopanes. The very high relative abundance of parent over alkylated aromatic hydrocarbons is also consistent with maturity in the wet-gas zone and might indicate bitumen alteration during pulses of pyrolytic heat (George, 1992).

3.4. Sample integrity

Aliphatic hydrocarbons and biomarkers are characterized as ‘probably syngenetic’ with their host rock mainly based on signatures consistent with high thermal maturity, typical Precambrian characteristics and the prevalence of very similar bitumens over a wide geographic range in the Hamersley Basin (Brock et al., in press-a). adamantanes, diamantanes and aromatic compounds are interpreted as ‘certainly syngenetic’ based on their unusual composition and the results of pyrolysis experiments on kerogens (Brocks et al., 2003).

3.5. Biodegradation, water washing and aerial oxidation

Post Archean biodegradation, water washing or weathering might have affected the original composition of the bitumens and could so have contributed to the unusual distribution observed now. However, the abundance of \( n \)-alkanes relative to branched and cyclic hydrocarbons is high in almost all samples, indicating that the bitumens are unaffected by biodegradation. Moreover, microbial degradation, as well as water washing, reduce the abundance of parent PAH relative to alkylated PAH (Rowland et al., 1986), contrary to the trend observed. Aerial oxidation of aromatic hydrocarbons could potentially have increased the PAH/MPAH ratios (Smith et al., 2001) but most analyzed shales contain unweathered pyrite indicating that exposure to oxygen was low.

3.6. Postmetamorphic methylation of phenanthrene

In bitumen and oil that is at thermal equilibrium 3-methylphenanthrene (3-MP) and 2-MP have sig-

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<table>
<thead>
<tr>
<th>Table 2</th>
<th>Ratios of aromatic hydrocarbons and dibenzothiophenes a</th>
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<tbody>
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<td>Naph/MN</td>
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<td>Bec1</td>
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<td>WRL-1</td>
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</tbody>
</table>

a Concentrations were determined using corrected GC-MS signal areas of the molecular ion in the SIR or full scan mode. Compound abbreviations are as follows: Naph = naphthalene; MN = methyl[naphthalenes; BP = biphenyl; MBP = methyl[biphenyls; Fl = fluorene; MFl = methylfluorenes; DBT = dibenzothiophene; MDBT = methyl[dibenzothiophenes; Phen = phenanthrene; MP = methylphenanthrenes; DMP = dimethylphenanthrenes; PhN = phenylnaphthalenes. PAH/MPAH ratios (Naph/MN; BP/MBP etc) were calculated using the absolute concentrations of the parent compound divided by the sum of the absolute concentration of all methylated isomers. b The listed values are the average of seven samples from the Fortescue Group (Hardy to Jeerinah Formation) from drill core WRL-1 (Brocks et al., in press-a).
significantly higher concentrations than the less stable isomers 9-MP and 1-MP, and the ratio 9-MP/1-MP is close to unity (Fig. 4A). However, despite high thermal maturities, all bitumens from Mt Tom Price have anomalously high relative concentrations of 9-MP, leading to 9-MP/1-MP ratios significantly > 1 (Fig. 4B; Table 2). A probable explanation for this phenomenon is the kinetically controlled methylation of phenanthrene at the 9-position, as described by Alexander et al. (1995). At low temperatures phenanthrene might react with methyl donors to yield predominantly 9-MP. Therefore, bitumens that contain high relative con-
centrations of parent phenanthrene, as the samples from Mt Tom Price, likely also contain elevated concentrations of 9-MP. As the methylation of phenanthrene occurs at low temperatures (Alexander et al., 1995), the generation of 9-MP in the metamorphosed Archean samples must have occurred in the post-peak metamorphic cooling period.

3.7. Correlation between bitumen composition and oxidation state of iron minerals

To explore a possible correlation between the oxidation state of iron minerals in the host rocks and the degree of dehydrogenation of bitumen, approximate contents of iron oxides and sulfides were determined by X-ray diffraction (XRD) and compared with the ratio of saturated to aromatic hydrocarbons (Sat/Aro) (Table 3). No correlation between the net oxidation state of iron minerals and Sat/Aro was observed. However, possible redox-relationships might be indicated by (1) the high pyrite content and high Sat/Aro ratio in Rae3 (low degree of mineral oxidation and bitumen dehydrogenation) and (2) the high hematite content and low Sat/Aro ratio in Rae6 (high degree of mineral oxidation and bitumen dehydrogenation). A greater number of samples and more accurate measurements of the redox state of minerals are required to determine whether a trend exists.

4. Discussion

The bitumens from the iron ore mines at Mt Tom Price and Mt Whaleback are unusual. They are characterized by high relative concentrations of parent aromatic hydrocarbons, high relative concentrations of dibenzofuran, dibenzothiophene and phenylnaphthalenes, very low relative concentrations of hydrocarbons with four or more aromatic rings, large variations in the relative concentration of saturated over aromatic hydrocarbons, large variations in absolute bitumen yield, condensate-like n-alkane profiles and the presence of sterane and hopane biomarkers. Four processes that could have been responsible for bitumen alteration in the iron mines are outlined below.

The Hamersley Group in the Tom Price and Newman areas was regionally metamorphosed to prehnite–pumpellyite facies at temperatures between 200 and 300 °C (Brock et al., in press-a). Thus, metagenesis induced by burial might have caused the aromatization and dealkylation.

Sediments and iron ore in the Tom Price area are intruded by northwest-trending dolerite dikes that have been interpreted as feeders to the 2.2 Ga Cheela Springs Basalt (Powell et al., 1999). Emplacement of magma into the black shales would have caused short periods of pyrolytic temperatures in the aureole of the intrusion (Clayton and Bostick, 1985) potentially contributing to the varied pyrolytic bitumen signatures (Simoneit et al., 1981).

Bitumen alteration in Mt Tom Price might have been hydrothermal. Fluid inclusions trapped in vein quartz contain brines trapped at 140 to 230 °C and locally up to 350 °C (Taylor et al., 2001). The activity of a paleo-hydrothermal system is also supported by the presence of hydrothermal breccias, the removal of huge amounts of silica from BIF, the deep subsurface position of some ores (Barley et al., 1999), regional disturbances of isotopic and elemental ratios (Powell et al., 1999), and extensive hydrothermal alteration of mafic dikes (Taylor et al., 2001). The hydrothermal fluid flow was either driven by the Ophthalmian orogenesis 2.2–2.4 Ga ago and the eruption of the Cheela Springs Basalt at 2.2 Ga (Powell et al., 1999), or was a response to heat-flux during Wyloo rifting at about 2.0 Ga (Barley et al., 1999).

The composition of the Hamersley bitumens could also be the result of non-thermal dehydrogenation of

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**Fig. 4. GC-MS partial mass-chromatograms m/z = 192 of the isomer distribution of methylphenanthrenes (MP).** (A) Equilibrium distribution of MP isomers after laboratory treatment at 520 °C under a hydrogen atmosphere (sample Bee1, Mt McRae Shale, Mt Tom Price). (B) Distribution of MP isomers in bitumen from sample Rae6, Mt McRae Shale, Mt Tom Price. The elevated concentration of 9-MP in Rae6 is probably the result of kinetically controlled alkylation of phenanthrene by a methyl donor (Ar–Me) (see text).

**Table 3**

<table>
<thead>
<tr>
<th>Pyrite (%)</th>
<th>Magnetite (%)</th>
<th>Hematite (%)</th>
<th>Sat/Aro (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dal1</td>
<td>&lt;1</td>
<td>–</td>
<td>8.5</td>
</tr>
<tr>
<td>Rae1</td>
<td>&lt;1</td>
<td>&lt;1%</td>
<td>16</td>
</tr>
<tr>
<td>Rae2</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Rae6</td>
<td>7</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>Bee1</td>
<td>3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Wal2</td>
<td>–</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Rae3</td>
<td>34</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rae5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

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a Absolute error ~2%. 
b ‘-’ = Not detectable.
hydrocarbons by oxidizing fluids, similar to the ‘ascending brine theory’ of copper mineralization in the Permian Kupferschiefer in Europe (Püttmann et al., 1990).

The possible contributions of these four processes to organic matter alteration are considered in more detail in the following sections.

4.1. Burial metamorphism

The bitumen composition in the mines was necessarily affected by regional metamorphism in the Hamersley Basin. The generally very high thermal maturity of all samples is therefore at least partially a result of burial. However burial metamorphism alone is not sufficient to explain all of the observed hydrocarbon patterns:

1. The uniform temperature regime associated with burial is inconsistent with the large variations in bitumen composition. For example, the relative abundances of saturated and aromatic hydrocarbons fluctuate between Sat/Aro = 0.005 and 110 in samples from Mt Tom Price and between 5 and 70 from Mt Whaleback. Absolute concentrations of aromatic hydrocarbons in Mt Whaleback sample Rae5 are more than 500 times higher than in Rae3. Rae2 has low relative concentrations of unsubstituted aromatic hydrocarbons (PAH/MPAH < 0.5) while all other shales from the Tom Price area have very high, but varying, relative concentrations of parent PAH (PAH/MPAH > > 1) (Table 1).

2. The thermal stress exerted by burial metamorphism generally lasts several million years. If heat-flow prevailed over such extended periods of time, then a temperature regime hot enough to cause massive dealkylation of aromatic hydrocarbons would almost certainly also have led to the quantitative loss of sterane and hopane biomarkers. However, the preservation of these complex structures suggests that PAH-dealkylation was a rapid and localized event (compare George, 1992; Gieskes et al., 1988; Püttmann et al., 1990).

Thus, bitumens from the Hamersley Group near Tom Price and Newman were thermally altered by burial metamorphism, but the large variations in composition and extract yields, and the co-occurrence of parent PAH with C30+ biomarkers suggest that localized and short-term events must have caused additional alteration or bitumen redistribution.

4.2. Contact metamorphism

Dikes and sills intruding kerogenous sediments exert a short pulse of pyrolytic heat (Clayton and Bostick, 1985) leading to localized changes in organic matter distribution (Murchison and Raymond, 1989; Simoneit et al., 1981). For example, George (1992) studied the composition of bitumen from a siltstone close to a 3.5 m thick quartz–dolerite dike. At 2.5 m distance from the intrusion the composition of aromatic hydrocarbons was virtually unaffected by the heat source, and alkylated aromatic hydrocarbons, PAH with more than three aromatic rings and waxy alkanes were all abundant. At 18 cm distance from the dike the composition was very different. Parent aromatic hydrocarbons relative to alkylated homologues were very high and the abundance of PAH with more than three aromatic rings diminished. Moreover, aliphatic hydrocarbons close to the dike had the typical composition of gas-condensates. However, hopane and sterane biomarkers were preserved.

Thus, the composition of saturated and aromatic hydrocarbons at 18 cm distance from the dike was remarkably similar to many bitumens from the Hamersley Group.

In this study three samples (Dal1, Rae1 and Bee1) were collected from cores that were drilled in the vicinity of dolerite dikes (Fig. 1B), although exact distances of the samples from the intrusions are not known. However, it is exceedingly unlikely that all Hamersley Group samples were close enough to a dike to generate the pyrolytic hydrocarbon signatures. The extent of thermal aureoles around intrusions rarely exceeds 30–200% of dike or sill thickness (Bishop and Abbott, 1995; George, 1992). While the temperature in samples in direct contact with small intrusions is in the range of 500–700 °C for a short period (days to months) and can be as high at 1200 °C, the maximum temperatures at 100% distance of intrusion thickness are commonly only around 250 °C (Bishop and Abbott, 1995; Meyers and Simoneit, 1999). Therefore, pyrolytic alteration of bitumen is only discernible in proximity to the heat source. While it is possible that intrusions were very close to some of the Mt Tom Price and Mt Whaleback samples, it is highly unlikely that all samples were so affected. In particular, the pyrolytic composition of mine-face sample Rae6 from Mt Tom Price would require very close contact to a volcanic intrusion. However, intrusions were not visible in the vicinity of the outcrop. Thus, although contact metamorphism might have contributed to the pyrolytic composition of some samples, it fails to explain the prevalence of the pyrolytic signal over a range of samples.

4.3. Hydrothermal activity

According to hypogene models of iron ore mineralization, Mt Tom Price and Mt Whaleback were ancient hydrothermal systems. Therefore, comparison of the Hamersley bitumens with petroleum that is generated today in active hydrothermal systems might give information about processes that occurred at Mt
Tom Price. For instance, in the Guaymas spreading center, hydrothermal fluids with temperatures of 60 °C to more than 400 °C rise through several hundred meters of sediments deposited in a rift basin (Simoneit, 1993). Organic matter in contact with these hot fluids generates hydrothermal petroleum in a rapid, pyrolytic process (Simoneit, 1985). In the hottest areas, unsubstituted PAH and dibenzothiophene are formed in high relative abundances and the n-alkane distribution resembles gas condensates (Gieskes et al., 1988). The generated petroleum has a high solubility in the near-critical to supercritical fluids, and the products are therefore rapidly removed from the heat source by hydrothermal fluid advection (Simoneit, 1985).

During migration of the hydrothermal solution upward through the sediment pile, organic constituents start to condense according to ambient temperature and pressure conditions. PAH and sulfur condense in hot areas, higher alkanes precipitate in intermediate temperature regions (20–80 °C) and more volatile components collect in cold areas (Simoneit, 1985). Thus, the complex temperature regime in hydrothermal systems and the transport of petroleum in supercritical fluids result in a redistribution of aromatic and saturated constituents. The mixing of pyrolytic hydrocarbons with less mature petroleum at different locations results in considerable variations in hydrocarbon composition. Hydrothermal transport and fractionation of PAH may even lead to the precipitation of pure PAH minerals (Blumer, 1975).

The bitumen compositions and distributions at Mt Tom Price and Mt Whaleback are consistent with the observations in the Guaymas system. Typical hydrothermal signatures in the Archean bitumens include the inhomogeneous distribution of aromatic and saturated hydrocarbons within the mines, the co-occurrence of pyrolytic hydrocarbons and thermally less stable biomarkers, the unusually high concentrations of parent PAH and dibenzothiophene and the condensate-like composition of the saturated hydrocarbon fraction (compare Fig. 22d in Gieskes et al., 1988). The only marked difference to recent hydrothermal petroluem is the very low relative abundance of PAH with more than three aromatic rings. However, the distribution of high molecular weight PAH apparently strongly depends on the position of the sample in the fluid flow path. Hence, hydrothermal activity in the Tom Price and Newman areas, together with burial metamorphism and possibly contact metamorphism, is probably sufficient to explain all compositional characteristics. However, a second model that is also consistent with all observations is discussed in the next section.

4.4. Cool oxidizing brines

The Permian Kupferschiefer horizon in southwest Poland contains an assemblage of saturated and aromatic hydrocarbons (Püttmann et al., 1988) that is strikingly similar to the bitumens found in Mt Tom Price and Mt Whaleback (Fig. 5). The upper part of the 1 m thick marl section in the Kupferschiefer contains bitumen rich in saturated hydrocarbons, comparatively low in PAH and with relatively low ratios of parent over alkylated PAH (e.g. Phen/MP=2) (Fig. 5A). Down section the saturated hydrocarbons gradually disappear while the absolute and relative concentrations of parent PAH increase (Fig. 5B–D). In the bottom sample the ratio Phen/MP is >10 and the dominant compounds are naphthalene, biphenyl, dibenzofuran, dibenzothiophene and phenanthrene (Fig. 5D). In the Kupferschiefer, this bitumen distribution is always associated with copper mineralization and Rote Fäule, a hematite stained irregular oxidation front arising from underlying strata (Püttmann et al., 1988).

According to Püttmann’s ‘ascending brine theory’, oxidizing solutions transported large amounts of base metals from underlying red beds into the Kupferschiefer where organic matter supplied the reducing capacity to precipitate copper sulfides. Oxidized species in the solutions dehydrogenated the kerogen, generated unsubstituted PAH and destroyed saturated hydrocarbons (Püttmann et al., 1990, 1991). This alteration process apparently occurred at temperatures of less than 150 °C (Sun and Püttmann, 1996). The unsubstituted PAH in the Kupferschiefer are therefore not the products of thermal degradation, as in hydrothermal systems, but of chemical dehydrogenation.

A mechanism for a similar process was suggested by Gize (1999) in which metal sulfides are oxidized to elemental sulfur by oxygen-charged brines, and saturated hydrocarbons are dehydrogenated and aromatized by reacting with the elemental sulfur. Sulfur is also incorporated into dehydrogenation products to form aromatic sulfur-heterocycles, such as dibenzo thiophene. Dibenzothiophene is also abundant in the Hamersley Group. Gize (1999) further argued that the state of organic matter in iron–copper deposits is controlled by the thermodynamic system iron–sulfur–organic matter. According to this hypothesis, aliphatic hydrocarbons exist in geological systems where pyrite is the stable iron phase but are oxidized to PAH in the hematite stability field, which, in the case of the Kupferschiefer, is the Rote Fäule zone.

There are strong similarities between bitumens in the Permian Kupferschiefer and in the Archean iron deposits. The Kupferschiefer is a kerogenous marly shale associated with copper mineralization and modified by oxidizing solutions, whereas the Mt McRae Shale is a highly kerogenous shale associated with oxidative iron mineralization. Both yield extracts with extremely variable Sat/Aro ratios, from almost purely aromatic to highly saturate-dominated (Fig. 5). In the Mt McRae Shale and in the Kupferschiefer, higher alkanes are significantly depleted and the bitumen has a condensate-like profile. In both, polycyclic biomarkers in the ~C_{30}
range are preserved despite almost complete loss of \( n \)-alkanes \( > n-C_{26} \) (Püttmann et al., 1989). Ratios of parent over alkylated PAH are extremely high in both, and the dominant aromatic compounds are naphthalene, biphenyl, dibenzothiophene and phenanthrene, while higher molecular weight aromatic hydrocarbons such as pyrene are far less abundant or absent. Concentrations of phenylnapthalenes, less common compounds in most bitumens, are high in both the Mt McRae Shale and Kupferschiefer (Püttmann and Gössel, 1990). Differences between the Kupferschiefer and Hamersley shales are minor. Dibenzofuran and other oxygen-containing compounds are abundant in the former (Püttmann et al., 1989) but less significant in the Archean shales. Thus, the activity of oxidizing brines is consistent with the composition of individual bitumens in Mt Tom Price and Mt Whaleback and also accounts for differences between samples from the same location and formation.

4.5. A proposal for a new approach to distinguish hypogene and supergene processes of iron ore formation

To develop new exploration targets for ore bodies, it is crucial to understand the mechanisms of ore genesis,
in particular the structural controls that govern origin and properties of circulating fluids. Although it was not yet possible in this preliminary study to pin down attributes of ore forming fluids in the Hamersley Basin, the collected information is sufficient to devise a new strategy to recognize hypogene and supergene controls.

During both modes of fluid flow, hypogene and supergene, organic matter could have played an active part in the ore forming process. BIF in Mt Tom Price and Mt Whaleback is interbedded and underlain by organic-rich shales that probably generated large volumes of hydrocarbons. Generally, organic matter is known to affect the solubility of inorganic species by complexation and by modification of the solvation properties of water. Organic matter also serves as a redox partner in mobilization and precipitation of metal ions and sulfur species (Landais and Gize, 1997). In some ore deposits, studies of bitumen have helped to constrain the redox state and composition of circulating fluids, the temperature during ore formation and the possible role of biological activity and meteoric weathering (Gize, 1999; Landais and Gize, 1997; Simoneit, 1993).

In shales of Mt Tom Price and Mt Whaleback, the composition and distribution of bitumen reflect the activity of hydrothermal and/or oxidizing solutions overprinted by regional metamorphism and locally by contact metamorphism. Thus, even if organic matter only played a passive role during ore formation, it may have recorded the conditions of the ore enrichment process. By analyzing the bitumen distribution in the giant iron ore deposits of the Hamersley Province, it might be possible to reconstruct fluid flow pathways, and to constrain fluid redox potential and local temperature conditions. Supergene and hypogene mechanisms of ore formation require different regimes of fluid flow. Therefore, the respective models will predict different bitumen compositions in shales at different locations within the ore bodies.

The CSIRO-AMIRA supergene model requires the percolation of oxygenated meteoric water into weathering BIF. Near the surface, Fe(III) minerals are thought to be reduced and mobilized by oxidation of organic matter and transported as ferrous iron in aqueous solutions to greater depths. Near-surface shales, which should have recorded signs of Fe(III)-organic matter interaction, were most likely either removed by erosion or, if preserved, affected by post-metamorphic meteoric weathering causing total kerogen and bitumen destruction. The descending brines, loaded with Fe(II), should be reducing and cold. The interaction of these brines with organic matter between the erosion horizon and deep-seated ore should have left indigenous bitumen unaltered. In the growing ore body, Fe(II) is thought to be oxidized in an electrochemical process by an anode at depth. Direct anodic oxidation of hydrocarbons in shales seems unlikely, but it is conceivable that anodically oxidized inorganic species diffused into shale interbedded with ore and created a bitumen oxidation pattern congruent with Fig. 5A–D. Along the diffusion pathway, Sat/Aro ratios should increase and PAH/MPAH ratios decrease. The dehydrogenation state of bitumen should also correlate with the oxidation state of iron minerals in the host shale. It is further predicted that under a supergene regime shales underlying the ore body and distal to mineralization or distal to locations of electrochemical oxidation should be unaffected by organic matter dehydrogenation and therefore contain unoxidized, aliphatic-rich bitumen similar to Rae2 (Fig. 5E) in combination with a reduced iron phase (e.g. pyrite).

Hypogene models suggest that hydrothermal fluids ascended from deeper strata. The point of entry of the hot fluids into the deposit will be characterized by low quantities of highly pyrolyzed bitumen, similar to Rae6 (Fig. 5H). With increasing distance from the thermal maximum, along the trajectories of fluid flow, aromaticity and PAH/MPAH ratios will decrease and absolute bitumen concentrations and the relative abundance of polycyclic biomarkers increase. Shales distal to hydrothermal pathways should contain unaltered bitumen similar to Rae2 (Fig. 5E).

To distinguish between hypogene and supergene influences of ore formation and to determine major paths of fluid flow, future research should concentrate on systematic changes in bitumen composition at faults and veins, and at centers of iron oxidation and silica dissolution. Freshly exposed sample material should be collected distal to the ore body, from shales underlining and overlying zones of mineralization and from rocks interbedded with ore. Correlation between the dominant iron phase (pyrite, hematite, magnetite, goethite etc.) and the oxidation state of bitumen and kerogen might then reveal a thermodynamic link between iron minerals and organic matter.

5. Conclusions

2.5 Ga old Archean shales from two giant iron ore deposits, Mt Tom Price and Mt Whaleback in the Hamersley Province, Western Australia, contain traces of saturated and aromatic hydrocarbons. The host shales were regionally metamorphosed to prehnite-pumpellyite facies and are kerogen-rich. The compositions of the aromatic fractions are unusual. Parent PAH are abundant while alkylated homologues occur only in traces. The main constituents are naphthalene, biphenyl, dibenzothiophene and phenanthrene while higher molecular weight PAH are scarce. Large variations in the composition of bitumen between different samples within iron ore deposits, the condensate-like nature of
the saturated hydrocarbon fractions and the high ratios of parent over alkylated aromatic hydrocarbons are consistent with the effects of hydrothermal fluids or oxidizing brines overprinted by regional low-grade metamorphism and igneous intrusions. The composition and distribution of organic matter might have recorded information about redox conditions and temperature in the ore body. Thus, a systematic study of shales collected in giant iron ore mines in the Hamersley Province could help to determine supergene and hypogene controls on ore formation, an approach that might be generally applicable to mineral deposits in sedimentary and low-grade metasedimentary rocks.

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