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# A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks <sup>☆</sup>

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## ABSTRACT

In this study we compared various maturity dependent aromatic, steroid and triterpenoid hydrocarbon ratios in bitumens that are freely extractable from sedimentary rocks (Bitumen I) with those in second extracts that comprised hydrocarbons closely associated with the kerogen/mineral matrix (Bitumen II). Bitumen II was released through kerogen isolation and demineralisation using HCl and HF/H<sub>3</sub>BO<sub>3</sub>. The samples studied, although of similar age, come from different localities. They represent a range of facies and two kerogen types (II and III), and all were deposited under marine conditions.

The results show that the more stable  $\beta$  isomers of methyl-naphthalene (MN) and methyl-phenanthrene (MP) are relatively more abundant in Bitumen II. The difference between the methyl-naphthalene ratio (MNR) of Bitumens I and II, when plotted against the ratio of clay to total organic carbon (clay/TOC), gives an excellent correlation ( $R^2 = 0.88$ ). The highest clay/TOC ratio corresponds with the biggest difference in MNR for the respective bitumens, consistent with the more stable  $\beta$  isomers being preferentially retained within the clay/kerogen matrix. Since the  $\beta$  MP isomers are higher in Bitumen II than in Bitumen I, it was anticipated that their methyl-phenanthrene index (MPI-1) values, a commonly used measure of thermal maturity, would also be different. For most samples, the measured MPI-1 in Bitumen I is generally higher than that in Bitumen II (except for three samples), thus showing a bias towards a lower thermal maturity for the second extract. The opposite is true of the  $\beta/\alpha$  MP ratio and MNR. This may be attributed to the fact that phenanthrene (P), which is part of the denominator in MPI-1, is more stable than its methylated counterparts.

Steroid and triterpenoid maturity parameters also showed differences between the two extracts, with C<sub>27</sub> diasterane/sterane and Ts/(Ts + Tm) being higher in Bitumen I. Only the former parameter is positively correlated with the clay/TOC ratio, suggesting that clay content probably influences the diagenetic transformation of steroid precursors to diasteranes. The observed differences between the maturity parameters of Bitumen I and Bitumen II may be especially important in sedimentary rocks that contain high percentages of clay minerals.

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## 1. Introduction

Most fossil hydrocarbons exist as isomeric mixtures. Polyaromatic hydrocarbons that have a methyl group at a  $\beta$  position are generally more thermodynamically stable than those with a methyl group at an  $\alpha$  position (Radke, 1987; van Aarssen et al., 1999). Ratios of  $\beta/\alpha$  isomers are therefore maturity dependent, as

has been demonstrated for MNs, dimethylnaphthalenes (DMNs), trimethylnaphthalenes (TMNs) and methylphenanthrenes (MPs) (Radke et al., 1982b; Alexander et al., 1985).

MNs are ubiquitous constituents of sedimentary organic matter (OM) (Tissot and Welte, 1978) and their abundances are highly variable between rock samples due to the effects of source, thermal stress and biodegradation (e.g., van Aarssen et al., 1999). MN has two isomers, 2-MN ( $\beta$  isomer) and 1-MN ( $\alpha$  isomer). The methylnaphthalene ratio (MNR, 2-/1-MN) (Radke et al., 1982b) and the various dimethyl and trimethylnaphthalene ratios (DNR-1 to 5 and TNR-1 and 2; Alexander et al., 1985; Radke et al., 1986) are widely used as maturity parameters. Among the methylphenanthrenes, 2- and 3-MP ( $\beta$  isomers) are more stable than 1- and 9-MP ( $\alpha$  isomers). Therefore, the ratio (2-MP + 3-MP)/(1-MP + 9-MP), previously described as methylphenanthrene index-3 (MPI-3, Radke, 1987) and in this paper referred to as  $\beta/\alpha$  MPs, can likewise be used to estimate thermal maturity.

The original methylphenanthrene index, MPI-1, is defined as  $1.5 \times [(2\text{-MP} + 3\text{-MP})/(1\text{-MP} + 9\text{-MP})]$  (Radke et al., 1982a; Killops and Killops, 2005). In some cases, and especially at higher levels of maturity, MPI-1 appears equivalent or superior to other proxies such as vitrinite reflectance (Radke et al., 1982b; Farrington et al., 1988; Radke, 1988). The formulation of MPI-1 was based on the assumption that 2- and 3-MP originate not only from 1- and 9-MP by rearrangement, but also through methylation reactions of P (Radke et al., 1982a). Radke et al. (1998) reported that the type of OM influences MPI-1 and thus limits its utility as a maturity parameter. As a result, samples of differing maturity can have similar MPI-1 values. For example, in bitumens derived from type II kerogen, the MP distribution does not change with maturity in a regular manner (Radke et al., 1986; Boreham et al., 1988).

Numerous studies have used biomarker distributions in sediments and petroleum to assess thermal maturity (Farrimond et al., 1998) and palaeoenvironmental depositional conditions (van Kaam-Peters et al., 1997; Hetényi et al., 2004). The ratio of  $C_{27}$  18 $\alpha$ (H)-trisorhopane II (Ts) to  $C_{27}$  17 $\alpha$ (H)-trisorhopane (Tm) is one such biomarker parameter that is a function of not only thermal maturity, but also organic facies (Moldowan et al., 1986). During catagenesis Tm is less thermodynamically stable than Ts (Seifert and Moldowan, 1978) and decreases with increasing burial depth. The importance of the host lithofacies and the oxicity of the depositional environment in controlling this ratio is unclear (Peters et al., 2005).

Other processes can also influence the distributions of biomarker hydrocarbons in sediments and sedimentary rocks. For example, some compounds can be preferentially encapsulated in kerogen and/or adsorbed to mineral surfaces. Bergamaschi et al. (1997) determined the effect of grain size and surface area on the concentration and composition of OM preserved in marine sediments and reported differences (especially for carbohydrates) between different textural classes. A number of studies have investigated the encapsulation of biomarkers and proteins within OM (Knicker and Hatcher, 1997; Zang and Hatcher, 2002). Other workers have shown that free radicals in crude oils are shielded against reaction by being caged in the asphaltenes of the oil (Mujica et al., 2000). Likewise hydrocarbons occluded within asphaltenes are protected from secondary alteration (Liao et al., 2006a,b). Lipid biomarker distributions can be influenced by other protective matrices, such as calcite, opal, recalcitrant OM or clay minerals (Hedges and Keil, 1995; Huang et al., 2008; Mead and Goñi, 2008).

Van Kaam-Peters et al. (1998) determined the effect of clay minerals on the diasterane/sterane ratio and found that it is influenced by palaeoenvironmental conditions, maturity and also by the amount of clay relative to the total organic carbon (TOC) content. Earlier research conducted by Rubinstein et al. (1975) and

Peakman and Maxwell (1988) found that  $\Delta^4$ - and  $\Delta^5$ -sterenes can be transformed into  $\Delta^{13(17)}$ -diasterenes via backbone rearrangement, facilitated by clay mineral catalysis (Rubinstein et al., 1975; Sieskind et al., 1979). Pan et al. (2005) investigated the interaction of oil components and clay minerals in reservoir sandstones and established that fractionation of diasteranes and steranes could be unambiguously ascribed to selective adsorption of polar compounds on active clay surfaces. Diasterane/sterane ratios of crude oils are commonly used to distinguish the lithofacies of their respective source rocks (i.e. carbonate versus clastic, Mello et al., 1988). This ratio is usually based on  $[13\beta,17\alpha(\text{H})\ 20\text{S} + 20\text{R}]/\{[5\alpha,14\alpha,17\alpha(\text{H})\ 20\text{S} + 20\text{R}] + [5\alpha,14\beta,17\beta(\text{H})\ 20\text{S} + 20\text{R}]\}$  for the  $C_{27}$ ,  $C_{28}$  and/or  $C_{29}$  steranes (Peters et al., 2005). Like the diasterane/sterane ratio, Ts/(Ts + Tm) is also sensitive to clay interactions. For example, McKirdy et al. (1983, 1984) and Rullkötter et al. (1985) showed that oils from carbonate source rocks appear to have anomalously low Ts/(Ts + Tm) ratios compared to those generated from shale and ascribed the phenomenon to reduced clay mineral catalysis in carbonates.

In this study we compare some of the aforementioned molecular maturity parameters in bitumens recovered via solvent extraction from a suite of powdered whole rock samples of latest Permian and earliest Triassic age with those in second extracts obtained after exhaustive demineralisation. The first bitumen extracted is referred to as “Bitumen I”, and the second extract as “Bitumen II” (Sherman et al., 2007). Although of similar age, the samples are from different localities and represent a range of lithofacies and kerogen types. The parameters measured in Bitumens I and II (viz. MP ratios, MNR, MPI-1, Ts/(Ts + Tm) and  $C_{27}$  diasterane/sterane ratios) were then evaluated with respect to the percentage (wt%) of clay minerals relative to the TOC. Our aims of this study were to demonstrate variations of selected thermal maturity parameters in two different bitumen types and to determine the degree to which these maturity parameters were influenced by the clay/TOC ratios of the host sediments.

## 2. Materials and methods

### 2.1. Samples

This study was a by product of a separate investigation of the D/H ratios of kerogens spanning the P/Tr boundary from well characterised marine sections in Western Australia, East Greenland and Spitsbergen, Norway (Nabbefeld et al., unpublished results).

The Western Australian samples were from a drill core (Hovea-3 petroleum exploration well) located in the Perth Basin (Thomas et al., 2004; Grice et al., 2005). The cored interval was the Hovea Member of the Kockatea Shale. At its base is a distinct organic rich zone of Late Permian age, comprising fossiliferous dark grey mudstone (containing inertinitic OM), sandy siltstone and shelly storm beds. These sediments were deposited at a relatively low palaeolatitude in a shallow marine environment during the earliest stage of a marine transgression. The upper part of the cored interval comprises Lower Triassic mudstone and limestone rich in sapropelic Type II kerogen. The OM here is immature to early mature (vitrinite reflectance  $\leq 0.68\%$ ) (Thomas and Barber, 2004; Dawson et al., 2005).

The East Greenland samples were collected from an outcrop in Jameson Land. The original sediments were deposited at a relatively high northern palaeolatitude and represent a complete, expanded and well documented P–Tr section (Looy et al., 2001; Twitchett et al., 2001; Grice et al., 2005; Fenton et al., 2007). This section comprises Late Permian bioturbated siltstones and Early Triassic laminated siltstones, mudstones and sandstones. The stratigraphic heights referred to in this study were defined by Twitchett et al. (2001).

The lithostratigraphy, biostratigraphy and magnetostratigraphy of the section at Lusitaniadalen in Spitsbergen, also deposited at a relatively high northern palaeolatitude, was described by Mørk et al. (1999). Here the Upper Permian succession consists of massive or cherty fine grained sandstones, while the Lower Triassic comprises fine grained sandstones, siltstones and mudstones. The position of the P–Tr boundary is not precisely defined at this locality, as the zone fossil, which defines the base of the Triassic, *Hindeodus parvus*, has not yet been recovered. All samples up to 16.90 m, where the marine collapse event occurs are Late Permian (Changhsingian) in age, the ones above could be either, Permian or Triassic. In this study we therefore refer to the samples as “Permian” for the sample at 16.39 m and “possibly Triassic” for the samples following the collapse event from 17.12–24.80 m. Correlation with the international timescale was achieved through a combination of ammonoid and conodont biostratigraphic and magnetostratigraphic methods (Mørk et al., 1999; Hounslow et al., 2008). The sample heights used in this study are relative to the base of the measured section (78°17'54.8"N, 016°43'59.3"E).

## 2.2. Extraction methods for Bitumen I

Bitumen I from the Western Australia and East Greenland samples had been previously isolated by Grice et al. (2005) and Fenton et al. (2007). The outcrop samples from Spitsbergen were freshly extracted during this study using the same methodology.

## 2.3. Isolation of Bitumen II

The three sample sets (see Table 1) include composite samples from different heights and depths to ensure that sufficient material was available to isolate Bitumen II. To compare the Bitumen II biomarker ratios to the associated Bitumen I, median ratios were calculated for the composite samples.

The solvent extracted rock samples (residues) with high carbonate content and low TOC (<0.6%) were decarbonated with HCl (6 N) at room temperature (12 h), washed with double distilled water (3×) and dried. The decarbonated residues, together with those of the non-calcareous siliciclastics, were further demineralised using the HF–BF<sub>3</sub> method of Robl and Davis (1993). The sample material was weighed into a 50 ml polyethylene centrifuge container. HF (48%) diluted with an equivalent volume of double distilled water was added to each sample (40 ml g<sup>−1</sup> of sample). After 2 h the containers were sealed and left overnight (approx-

mately 14 h) at room temperature. Because the reaction of boric acid (H<sub>3</sub>BO<sub>3</sub>) with HF is exothermic, the samples were pre-chilled in an ice bath to minimise the loss of BF<sub>3</sub>. Then, H<sub>3</sub>BO<sub>3</sub> was added to the samples to avoid formation of fluorides and again samples were left to react for approximately 14 h at room temperature.

After decanting of the supernatant aqueous phase, the solid residues were washed with warm double distilled water to dissolve and remove excess H<sub>3</sub>BO<sub>3</sub>. Subsequently, most of the water was removed using a Pasteur pipette prior to a heavy liquid separation, which was performed using pre-extracted (with dichloromethane) aqueous zinc bromide solution (ZnBr<sub>2</sub>,  $\rho \approx 2.4 \text{ g ml}^{-1}$ ) for elimination of heavy mineral phases, such as sulfides and titanium oxides that are not acid soluble. The zinc bromide was removed by washing the remaining sample with slightly acidified water. The solid residue was freeze dried and finally extracted using a mixture of dichloromethane and methanol of (9:1) in an ultrasonic bath (1 h) to obtain the Bitumen II.

## 2.4. Fractionation of Bitumens I and II

The Spitsbergen Bitumens I and II for all samples were fractionated using a method similar to that of Fenton et al. (2007), as described by Bastow et al. (2007). In brief, the extracts were applied to the top of a small column, (5.5 cm × 0.5 cm i.d.) of activated silica gel (120 °C, 8 h). The aliphatic hydrocarbon (saturated) fraction was eluted with *n*-pentane (2 ml); followed sequentially by elution of the aromatic fraction with a solution of dichloromethane in *n*-pentane (2 ml, 30 vol% dichloromethane); and finally by elution of the polar fraction with a solution of equal volumes of dichloromethane and methanol (2 ml).

## 2.5. Gas chromatography–mass spectrometry (GC–MS) and metastable reaction monitoring GC–MS (MRM–GC–MS–MS)

The fractions were analysed using GC–MS in full scan mode [aromatic fraction and saturated fraction for the Ts/(Ts + Tm) ratio] and MRM–GC–MS–MS (saturated fraction for the C<sub>27</sub> diasterane/sterane ratio), as described previously (Sherman et al., 2007).

GC–MS analyses were performed on a Hewlett Packard HP 5973 mass selective detector interfaced to a HP 6890 gas chromatograph fitted with a 60 m × 0.25 mm i.d. WCOT fused silica capillary column coated with 0.25 µm thick film (DB-5, J&W Scientific). For these analyses, the GC oven was programmed from 40 to 325 °C at 3 °C min<sup>−1</sup> with initial and final hold times of 1 and

**Table 1**  
Description of the samples used in this study. Samples C1 and C2 are composite samples from various depth intervals indicated; n.d.: not determined, Asterisk (\*): possibly Triassic.  $R_c$  is calculated from  $R_c = 0.6 \times \text{MPI-1} + 0.4$  (for  $R_v < 1.35\%$ ) and  $R_c = 0.6 \times \text{MPI-1} + 2.3$  (for  $R_v > 1.35\%$ ) (Radke and Welte, 1983).

	Combined samples	Depth/height (m)	Age	Organofacies	Kerogen type	$T_{\text{max}}$	Calculated vitrinite reflectance ( $R_c$ , % Radke and Welte 1983)
Spitsbergen		24.8	Triassic*	Vitrinitic/exinitic	II–III	441	0.74
Lusitaniadalen		19.2	Triassic*	Vitrinitic/exinitic	II–III	444	0.68
		18.3	Triassic*	Vitrinitic/exinitic	II–III	440	0.74
		17.12	Triassic*	Vitrinitic/exinitic	II–III	441	0.82
		16.39	Permian	Inertinitic	III	445	0.80
Western Australia		1970.9	Triassic	Sapropelic	II	434	0.75
		1978.15	Triassic	Sapropelic	II	434	0.65
Perth Basin		1979.15	Triassic	Sapropelic	II	435	0.65
Hovea #3		1980.865	Triassic	Sapropelic	II	n.d.	0.61
		1980.875	Triassic	Sapropelic	II	n.d.	0.61
	C1	1980.975–1981.15	Permian	Inertinitic	III	n.d.	n.d.
East Greenland		36.8	Triassic	n.d.	n.d.	n.d.	0.71
	C2	18.15–12.68	Permian	n.d.	n.d.	n.d.	0.64
Jameson Land		12.1–11.08	Permian	n.d.	n.d.	n.d.	0.63
	C1	9.85	Permian	n.d.	n.d.	n.d.	0.58
		8.6	Permian	n.d.	n.d.	n.d.	0.44
		3.8	Permian	n.d.	n.d.	n.d.	0.45

30 min, respectively. Aromatic fractions (in *n*-hexane) were injected in splitless mode using a HP 6890 series autosampler. The carrier gas was ultra-high purity helium with a flow rate of 1 ml min<sup>-1</sup>. The mass spectrometer was operated in full scan mode (*m/z* 50–650). Results were integrated using the HP ChemStation Data Analysis program.

The two thermal maturity parameters based on biomarker alkanes, Ts/(Ts + Tm) (Seifert and Moldowan, 1978) and C<sub>27</sub> diasterane/sterane ratio (Peters et al., 2005), were measured to further explore differences between Bitumens I and II (Table 4). The C<sub>27</sub> hopanoids Ts and Tm were identified using relative retention times in 191 Da ion chromatograms and the full scan mass spectra, whereas rearranged and regular steranes were identified on the basis of relative retention times in the 217 Da ion chromatograms (Peters et al., 2005).

### 2.6. Powder X-ray diffraction (XRD)

Unground samples were separately milled in a McCrone micronizing mill in ethanol for 15 min and dried at 40 °C for 3 h. Each sample was treated with 20% Al<sub>2</sub>O<sub>3</sub> w/w (Baikowski standard C, 1 µm) and thoroughly homogenised for amorphous content determination. Samples were loaded into side packed sample holders to achieve random orientation of the crystallites. X-ray diffraction powder analyses were performed using a SIEMENS D501 (Cu Kα radiation) and a D5005 (Co Kα radiation) Bragg–Brentano diffractometer equipped with a graphite monochromator and a scintillation detector. Samples were analysed over a scan range of 2–70° 2θ, at a step width of 0.02°, and a scan speed of 1° min<sup>-1</sup>. The results were interpreted using the SIEMENS software package Diffracplus Eva (2000) for mineral identification, and the program Siroquant V3 to quantify the mineral and amorphous contents.

### 2.7. TOC and Rock-Eval pyrolysis

These analyses were undertaken using a Rock-Eval 6 instrument. TOC values were generated with the following temperature program: 400 °C for 3 min, 400–750 °C at 25 °C min<sup>-1</sup>, and then held isothermal for 5 min.

## 3. Results and discussion

### 3.1. Organic richness, *T*<sub>max</sub> and kerogen type

The kerogen in the samples from Spitsbergen range from Type II and III in the samples, which are possibly Triassic, to Type III in the Permian samples (Table 1). *T*<sub>max</sub> values determined by Rock-Eval pyrolysis vary from 440–445 °C (Table 1). These are similar to previously reported values (Mørk et al., 1999) suggesting that the entire Spitsbergen sequence lies within the oil window. *T*<sub>max</sub> for the Triassic samples of Western Australia varies between 434 and 435 °C (Table 1), kerogen types vary from type II in the Triassic to type III in the Permian. Data for eastern Greenland could unfortunately not be obtained.

### 3.2. Bitumen II

The procedure by Robl and Davis (1993), outlined in Fig. 1, yielded kerogen from which Bitumen II was extracted. Mead and Goñi (2008) have previously used this method to obtain several different extracts from the same sample. The following sections compare various thermal maturity parameters obtained in Bitumens I and II and correlate these with the clay/TOC ratio.

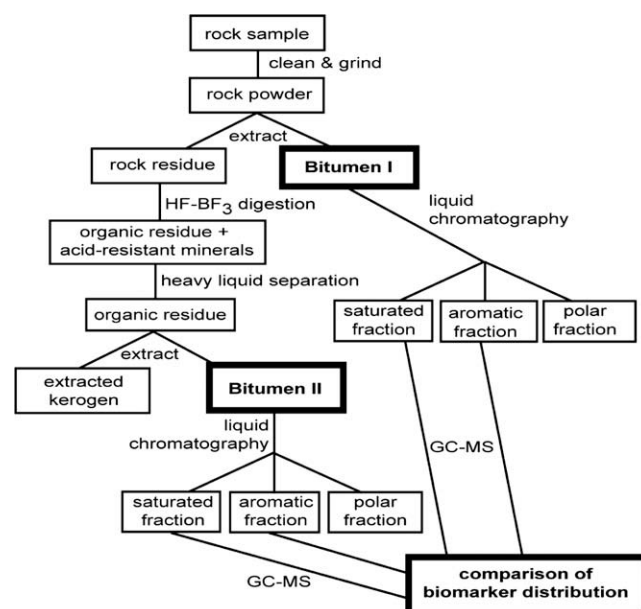


Fig. 1. Flow chart of the experimental procedure used to sequentially isolate Bitumen I and Bitumen II (Robl and Davis, 1993).

### 3.3. Methylphenanthrene distributions in Bitumens I and II

P and the MPs were identified using the *m/z* 178 and 192 ions, respectively. Their identifications were made using relative retention times and mass spectral data from Radke et al. (1982a). Typical 192 Da ion chromatograms for the MPs of Bitumens I and II isolated from a selected Triassic sample (e.g. Western Australia, Hovea-3, 1979.15 m) are shown in Fig. 2. The more stable MPs with a β configuration (2-MP and 3-MP) occur in a slightly higher relative abundance in the aromatic fraction of Bitumen II than that of Bitumen I (Fig. 2a and b, Table 2).

### 3.4. β/α MP ratios in Bitumens I and II

A plot of the more stable β isomers (3-MP + 2-MP) over the less stable α isomers (9-MP + 1-MP) for Bitumens I and II for all the

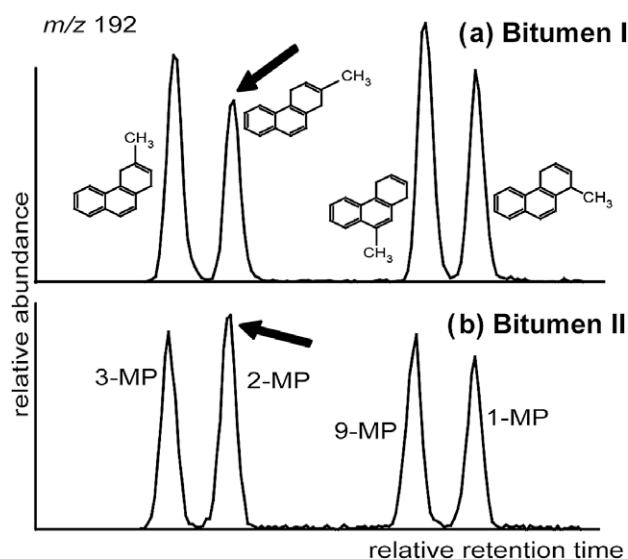


Fig. 2. GC-MS data showing 192 Da ion chromatograms for Bitumen I and II from the Hovea-3 drill core at 1979.15 m depth. Arrows identify the enhanced abundance of 2-MP in Bitumen II.



**Table 2**

Thermal maturity ratios and indices of the samples: MPI-1 from Bitumen I, MPI-1 from Bitumen II, and  $(\text{MPI-1}_{\text{Bitumen I}} - \text{MPI-1}_{\text{Bitumen II}})$ ,  $[\text{Ts}/(\text{Ts} + \text{Tm})]_{\text{Bitumen I}}$ ,  $[\text{Ts}/(\text{Ts} + \text{Tm})]_{\text{Bitumen II}}$ ,  $[\text{Ts}/(\text{Ts} + \text{Tm})]_{\text{Bitumen I} - \text{Bitumen II}}$ ,  $(\text{C}_{27} \text{ diasterane/sterane})_{\text{Bitumen I}}$ ,  $(\text{C}_{27} \text{ diasterane/sterane})_{\text{Bitumen II}}$ ,  $(\text{C}_{27} \text{ diasterane/sterane})_{\text{Bitumen I} - \text{Bitumen II}}$ ; n.d.: not determined.

	Depth/ height (m)	MPI-1 Bitumen I	MPI-1 Bitumen II	MPI-1 Bitumen I – MPI-1 Bitumen II	Ts/(Ts + Tm) Bitumen I	Ts/(Ts + Tm) Bitumen II	Ts/(Ts + Tm) Bitumen I – Ts/ (Ts + Tm) Bitumen II	C <sub>27</sub> diasteranes/ steranes Bitumen I	C <sub>27</sub> diasteranes/ steranes Bitumen II	C <sub>27</sub> diasteranes/ steranes Bitumen I – C <sub>27</sub> diasteranes/ steranes Bitumen II
Spitsbergen	24.8	0.56	0.45	0.12	0.91	0.60	0.30	n.d.	n.d.	n.d.
Lusitaniadalen	19.2	0.46	0.31	0.15	0.88	0.53	0.34	3.38	2.16	1.22
	18.3	0.57	0.30	0.26	0.87	0.48	0.39	n.d.	n.d.	n.d.
	17.12	0.69	0.22	0.48	0.90	0.55	0.35	n.d.	n.d.	n.d.
	16.39	0.67	0.27	0.40	0.84	0.52	0.32	1.53	0.87	0.66
Western Australia	1970.9	0.59	0.45	0.14	0.57	0.55	0.02	0.47	0.74	–0.27
	1978.15	0.41	0.36	0.05	0.60	0.52	0.08	n.d.	n.d.	n.d.
Perth Basin	1979.15	0.41	0.40	0.01	0.64	0.60	0.04	0.94	0.55	0.39
Hovea-3	1980.865	0.36	0.41	–0.06	0.58	0.38	0.20	n.d.	n.d.	n.d.
	1980.875	0.36	0.35	0.00	0.61	0.42	0.19	n.d.	n.d.	n.d.
	1980.975–1981.15	n.d.	0.48	n.d.	0.34	0.19	0.15	n.d.	n.d.	n.d.
East Greenland	36.8	0.52	0.45	0.07	0.62	0.44	0.18	n.d.	n.d.	n.d.
	18.15–12.68	0.40	0.35	0.05	0.42	0.34	0.08	n.d.	n.d.	n.d.
Jameson Land	12.1–11.08	0.38	0.35	0.03	0.36	0.46	–0.10	n.d.	n.d.	n.d.
	9.85	0.30	0.17	0.13	0.17	0.19	–0.02	n.d.	n.d.	n.d.
	8.6	0.07	0.16	–0.09	0.33	0.34	–0.01	n.d.	n.d.	n.d.
	3.8	0.09	0.19	–0.10	n.d.	0.22	n.d.	n.d.	n.d.	n.d.

sample sets (Fig. 3) reveals a general pattern of higher  $\beta/\alpha$  MP ratios in Bitumen II than in Bitumen I (Table 4), with the exception of two samples from the Western Australian section (1980.865 m and 1980.875 m), one sample from Spitsbergen (16.39 m) and one sample from East Greenland (9.85 m). These discrepancies might be facies related and associated with higher relative abundances of 1-MP in Bitumen II. A previous study showed that 1-MP can be more abundant than 9-MP in humic coals (Radke et al., 1998). As part of the present study, the ratio 1-MP/9-MP was calculated for all samples. However, our results do not show an exceptionally high relative abundance of 1-MP in the samples containing more plant material, i.e. the Permian samples of the Western Australia sample set (Thomas et al., 2004) (see Table 1).

For the Western Australia sample set,  $\beta/\alpha$  MP values range from 0.73 to 1.26 for Bitumen II and from 0.90 to 0.21 for Bitumen I. In the Spitsbergen samples the values range from 0.62 to 0.72 for Bitumen I and from 0.65 to 1.18 for Bitumen II. Finally, for the East Greenland samples, the ranges are from 0.50 to 1.02 for Bitumen I and 0.57–1.30 for Bitumen II. Thus, there is a tendency for the relative amounts of  $\beta$  substituted MPs to be higher in Bitumen II, indicating that the  $\beta$  isomers are preferentially encapsulated in the mineral and/or kerogen matrix.

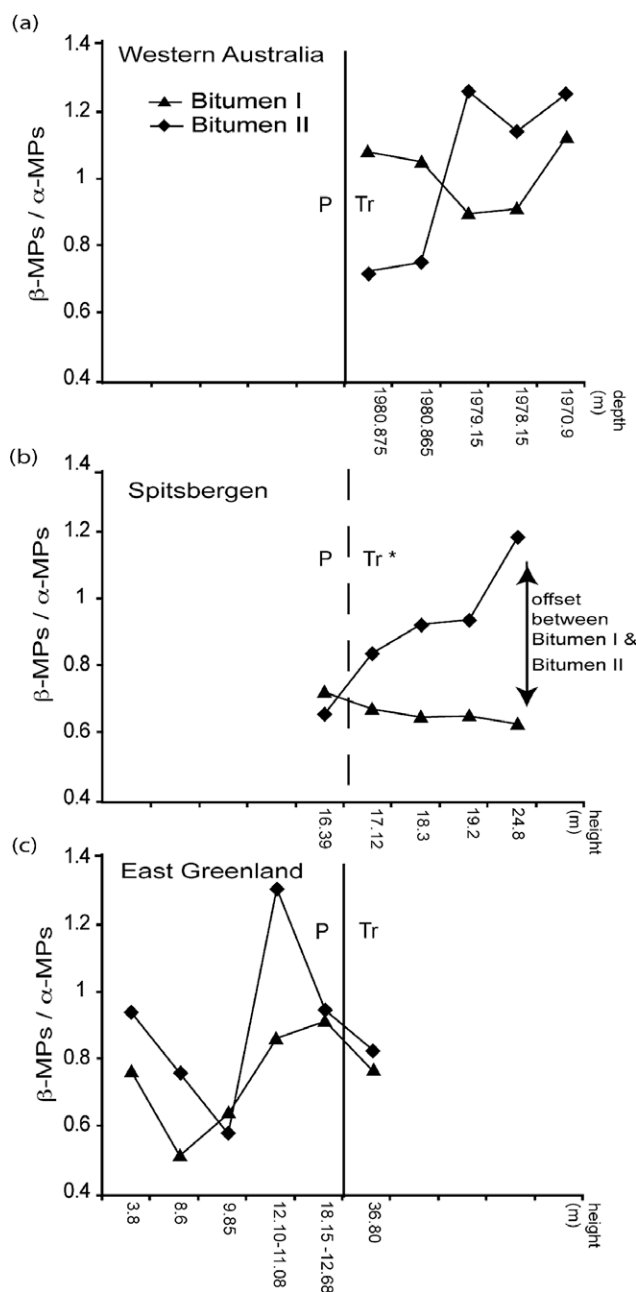
Protective matrices for sedimentary hydrocarbons include calcite, opal, recalcitrant organics and clay minerals (Mead and Goñi, 2008). Now it is widely accepted that labile compounds can be protected from microbial decay via their adsorption to clay minerals (Hedges and Keil, 1995). Van Kaam-Peters et al. (1998) determined the effect of clay minerals on the diasterane/sterane ratio and found no direct correlation with clay content. However, there was a correlation with the amount of clay relative to the amount of OM (clay/TOC). Thus, the relationship between the clay/TOC ratio and the differences between the  $\beta/\alpha$  MP ratios of the two bitumens  $[(\beta\text{-MP}/\alpha\text{-MP})_{\text{Bitumen I}} - (\beta\text{-MP}/\alpha\text{-MP})_{\text{Bitumen II}}]$  were investigated (Fig. 4a). For the Spitsbergen samples there is a good correlation ( $R^2 = 0.69$ ) between clay/TOC and the  $(\beta\text{-MPs}/\alpha\text{-MPs})_{\text{Bitumen I} - \text{Bitumen II}}$  (Table 4). The samples with a relatively high clay/TOC ratio show a larger difference between the  $\beta/\alpha$  MP ratios, which is consistent with the more stable  $\beta$  isomers being more abundant in the clay/kerogen matrix. However, an opposite trend is observed for clay/TOC versus

$(\beta\text{-MPs}/\alpha\text{-MPs})_{\text{Bitumen I} - \text{Bitumen II}}$  for the Western Australia sample set, despite an excellent correlation ( $R^2 = 0.95$ ). It seems that samples with very low clay/TOC values exhibit a different trend when compared to those with higher values. Samples from Greenland with very high clay/TOC ratios show no correlation ( $R^2 = 0.09$ ) with  $(\beta\text{-MPs}/\alpha\text{-MPs})_{\text{Bitumen I} - \text{Bitumen II}}$  (Table 4). The different trends are more likely to be related to kerogen type, (viz. inertinitic in the Permian samples and sapropelic or vitrinitic/liptinitic in the Triassic ones: Table 1).

### 3.5. MNR in Bitumens I and II

Only two samples of each set contained naphthalene (N) and methylnaphthalenes (MNs) in high relative abundance. The lack of MNs in the other samples is probably due to evaporative loss of these compounds during sample preparation. The samples containing MNs from Western Australia and Spitsbergen are of Triassic age, whereas the East Greenland samples are of Permian age. The  $\beta/\alpha$ -MN ratio (MNR, Radke et al., 1982a) ranges from 0.89 to 0.94 for Bitumen I and from 0.99 to 1.10 for Bitumen II in the Western Australia samples. The Spitsbergen samples have MNR values of 0.78–0.79 for Bitumen I and 1.20–1.28 for Bitumen II whereas the corresponding values for the East Greenland samples are 0.99–1.02 and 1.80–1.88 (Fig. 5, Table 3). In all cases, but most markedly in the two Permian samples from Greenland, the  $\beta$  isomer is clearly more abundant in Bitumen II (Table 4). These data are consistent with the  $\beta/\alpha$  MP ratios discussed above, at least for most of the samples (Table 3). Again the thermally more stable  $\beta$  isomers are preferentially retained within the mineral and/or kerogen matrix. These differences between the three sections could be associated with the type of kerogen and/or the mineral content.

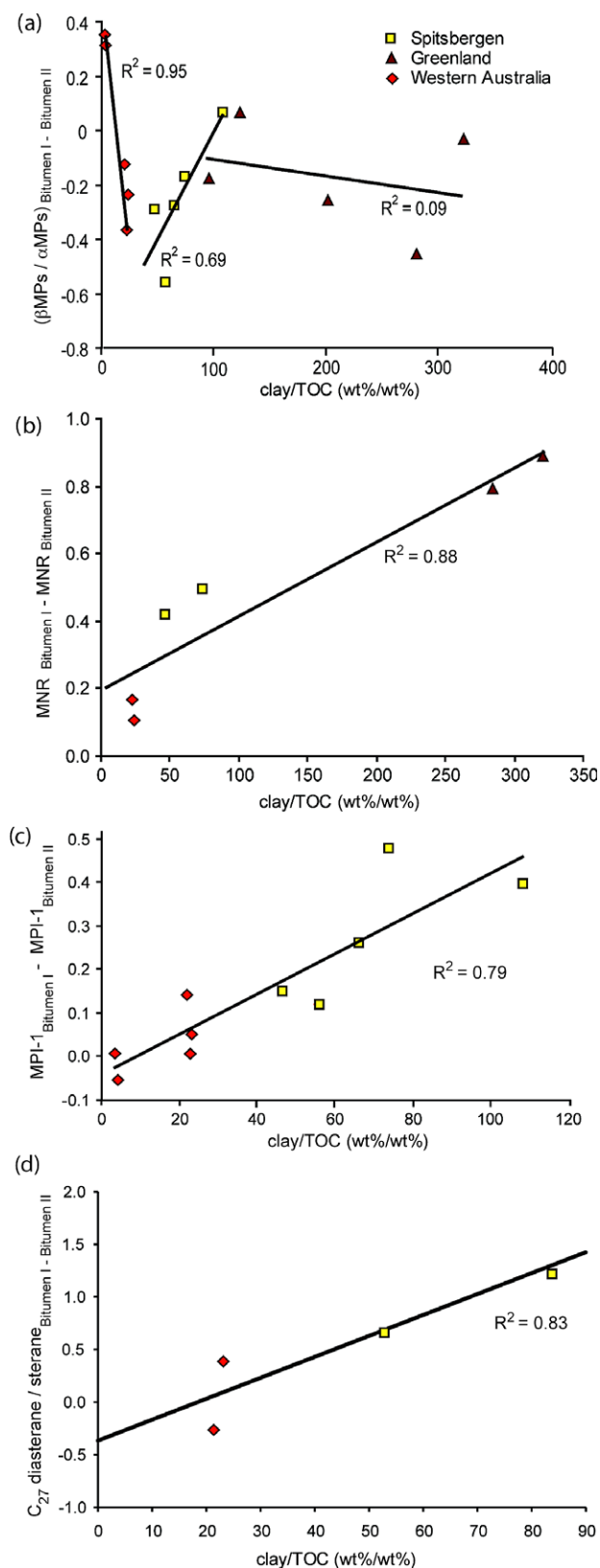
The difference in MNR between Bitumens I and II displays an excellent correlation ( $R^2 = 0.88$ ) with clay/TOC. Interestingly, samples with the highest clay/TOC ratio show the largest difference in MNR between the bitumens. It is apparent from these data that the clay/TOC ratio rather than the kerogen type is the main control on the observed MNR differences.



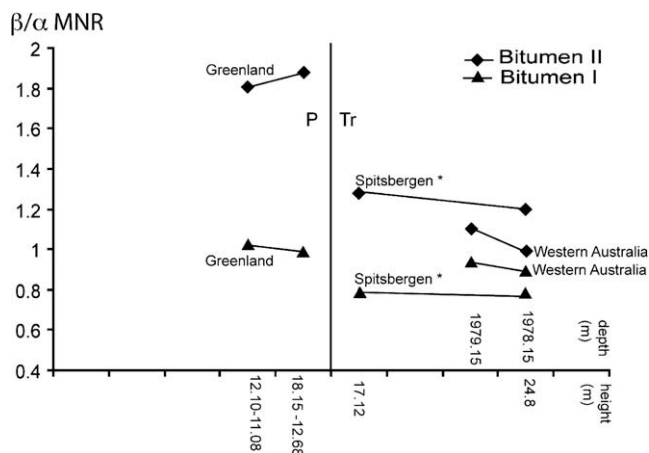
**Fig. 3.** Methylphenanthrene ratio ( $\beta$ -MPs/ $\alpha$ -MPs) versus depth for samples from, (a) Hovea-3, Western Australia, (b) Lusitaniadalen, Spitsbergen and (c) Jameson Land, East Greenland. Bitumen I is represented by a triangular symbol, whereas Bitumen II is depicted by a rhombus. Asterisk (\*): possibly Triassic.

### 3.6. MPI-1 in Bitumens I and II

Since the more stable  $\beta$  isomers of MP are more abundant than the  $\alpha$  isomers in Bitumen II, it was anticipated that the two bitumens would have different MPI-1 values. Fig. 6 illustrates that this is indeed true (see also Table 2). Moreover, except for three samples, MPI-1 is higher in Bitumen I (Table 4). Thus, MPI-1 shows a bias toward lower interpreted thermal maturity in Bitumen II. It should be noted that the three sample sets display considerable variation [calculated vitrinite reflectance,  $R_c$  (Radke and Welte, 1983), Table 1]. For the Western Australia samples, MPI-1 generally increases with decreasing depth and age (from 0.59 to 0.36 in Bitumen I, and from 0.48 to 0.35 in Bitumen II; Fig. 6a). A converse relationship is apparent for the MPI-1 values of the two bitumens



**Fig. 4.** (a) Differences between  $\beta$ / $\alpha$  MP ratio in Bitumens I and II [ $(\beta\text{-MPs}/\alpha\text{-MPs})_{\text{Bitumen I}} - \text{Bitumen II}$ ] versus the ratio of wt% clay relative to wt% TOC. (b) Differences between MNR in Bitumens I and II ( $\text{MNR}_{\text{Bitumen I}} - \text{MNR}_{\text{Bitumen II}}$ ) against the ratio of wt% clay relative to wt% TOC. (c) Differences between MPI-1 ratios in Bitumens I and II [ $\text{MPI-1}_{\text{Bitumen I}} - \text{MPI-1}_{\text{Bitumen II}}$ ] versus the ratio of wt% clay relative to wt% TOC. (d) Differences in  $C_{27}$  diasterane/sterane ratios between Bitumen I and II ( $C_{27} \text{ diasterane/sterane}_{\text{Bitumen I}} - \text{Bitumen II}$ ) versus the ratio of wt% clay relative to wt% TOC.



**Fig. 5.** Methylanththalene ratio (MNR) versus depth for samples from Hovea-3, Western Australia, Lusitaniadalen, Spitsbergen and Jameson Land, East Greenland. Asterisk (\*): possibly Triassic.

in the Spitsbergen sample set (from 0.67 to 0.46 in Bitumen I, and from 0.22 to 0.45 in Bitumen II; Fig. 6b). The East Greenland sample set shows MPI-1 values increasing markedly up section over a very narrow stratigraphic interval (from 0.07 to 0.52 in Bitumen I and from 0.16 to 0.45 in Bitumen II; Fig. 6c).

The general MPI-1 offset between the two bitumens in all samples implies that there were either different OM sources, and/or different impacts on the OM with burial. As described above, the OM in the Permian samples is mainly inertinitic, while

sapropelic OM of algal origin predominates in the Triassic. Given the differences in MPI-1 between Bitumens I and II, varying source inputs cannot account for these discrepancies, and so it is likely that they are related to variations in the mineral matrix of the host rocks.

The Spitsbergen samples display the greatest differences in MPI-1 between the two bitumens. Here, the MPI-1 values for Bitumen II record apparently lower relative thermal maturities than those measured for Bitumen I (Fig. 6b). The Western Australian samples also show significant offsets between the MPI-1 profiles of the two bitumens consistent with a lower thermal maturity for Bitumen II (Fig. 6a). In most East Greenland samples the MPI-1 of Bitumen I suggests a significantly higher relative thermal maturity. The exceptions are two samples, which show the lowest relative thermal maturity of all the samples analysed. Here the offsets between the MPI-1 vary from −0.09 to +0.13 (Fig. 6c, Table 2), comparable to the offsets observed for the Western Australia sample set.

Unlike the  $\beta/\alpha$  MP and MNR ratios for the two bitumens, MPI-I is generally higher in Bitumen I (Table 4). This may be a reflection of the stability of P compared to each of its methylated counterparts. P is also the most abundant of the phenanthrenes in all aromatic fractions of the samples. The presence of P in the MPI-1 parameter is the likely explanation for the differences observed between the MPI-1 and the  $\beta/\alpha$  MP ratio. Our data are consistent with the findings of Radke (1987), in that MPI-I relates to the change in relative abundance of the  $\beta$  to the  $\alpha$  isomers (i.e. MP ratio) and also allows for the change in relative abundance of P thereby compensating for facies dependent variations in the degree of its methylation.

**Table 3**

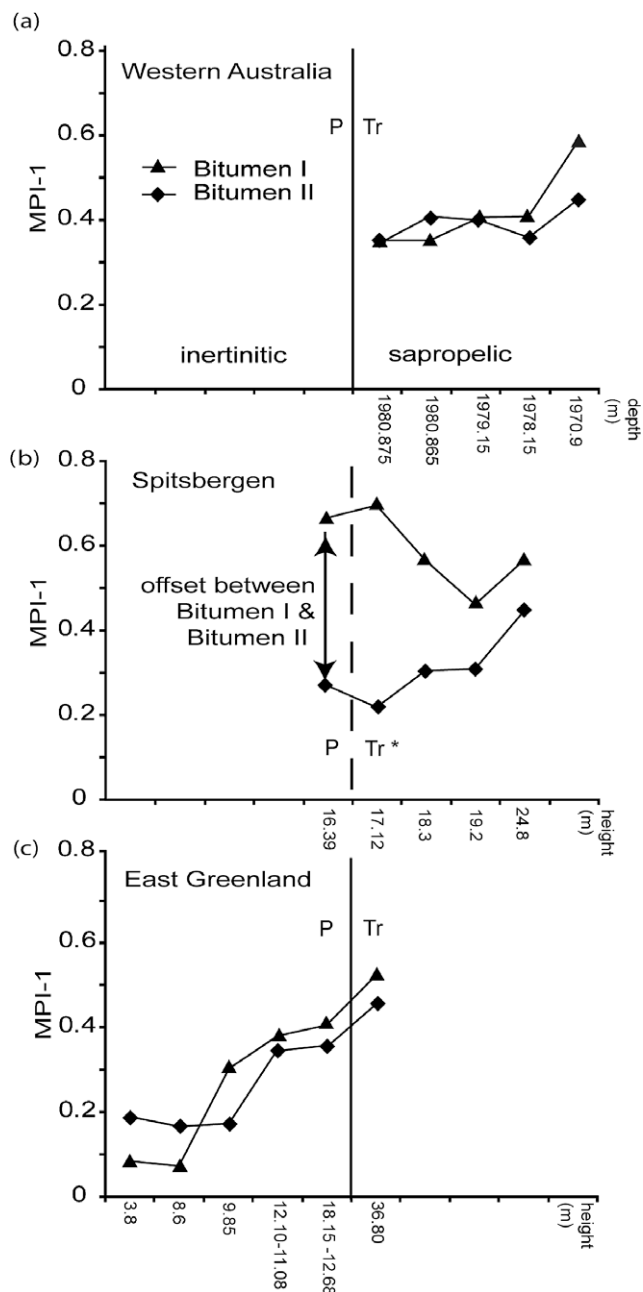
Composition and biomarker ratios: clay in wt%, TOC in wt%, clay/TOC ratio,  $\beta/\alpha$  MPs of Bitumen I,  $\beta/\alpha$  MPs of Bitumen II,  $\beta/\alpha$  MPs Bitumen I – Bitumen II,  $\beta/\alpha$  MNs of Bitumen I,  $\beta/\alpha$  MNs of Bitumen II,  $\beta/\alpha$  MNs Bitumen I – Bitumen II; n.d.: not determined.

	Depth/ height (m)	Clay (%)	TOC (%)	Clay/ TOC	$\beta/\alpha$ MPs Bitumen I	$\beta/\alpha$ MPs Bitumen II	$\beta/\alpha$ MPs Bitumen I – $\beta/\alpha$ MPs Bitumen II	$\beta/\alpha$ MN Bitumen I	$\beta/\alpha$ MN Bitumen II	$\beta/\alpha$ MN Bitumen I – $\beta/\alpha$ MN Bitumen II
Spitsbergen	24.8	55.4	0.99	56.0	0.62	1.18	−0.56	1.20	0.78	0.42
Lusitaniadalen	19.2	63.7	1.37	46.5	0.65	0.94	−0.29	n.d.	n.d.	n.d.
	18.3	59.0	0.90	65.6	0.64	0.92	−0.28	n.d.	n.d.	n.d.
	17.12	56.0	0.76	73.7	0.67	0.84	−0.17	1.28	0.79	0.50
	16.39	51.9	0.48	108.1	0.72	0.65	0.07	n.d.	n.d.	n.d.
Western	1970.9	53.4	2.50	21.4	1.12	1.25	−0.13	n.d.	n.d.	n.d.
Australia	1978.15	61.4	2.66	23.1	0.91	1.14	−0.23	0.99	0.89	0.10
Perth Basin	1979.15	65.0	2.83	23.0	0.90	1.26	−0.36	1.10	0.94	0.17
Hovea-3	1980.865	32.6	7.65	4.3	1.05	0.75	0.30	n.d.	n.d.	n.d.
	1980.875	23.7	6.89	3.4	1.08	0.73	0.35	n.d.	n.d.	n.d.
	1980.975– 1981.15	42.1	2.31	18.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
East	36.8	17.6	n.d.	n.d.	0.8	0.82	−0.06	n.d.	n.d.	n.d.
Greenland	18.15–12.68	26.7	0.08	320.8	0.9	0.94	−0.03	1.88	0.99	0.89
Jameson	12.1–11.08	55.5	0.20	282.4	0.9	1.30	−0.45	1.80	1.02	0.79
Land	9.85	19.8	0.16	123.8	0.6	0.57	0.06	n.d.	n.d.	n.d.
	8.6	64.0	0.32	200.0	0.5	0.75	−0.25	n.d.	n.d.	n.d.
	3.8	51.7	0.55	94.0	0.8	0.93	n.d.	n.d.	n.d.	n.d.

**Table 4**

Summary of maturity parameters, relative abundances in Bitumen I and II and correlation of the maturity parameters with clay/TOC.

Maturity parameter	Significance Bitumen I	Significance Bitumen II	Observation	Correlation with clay/TOC
Ts/(Ts + tm)	High	Low	Less stable compound Tm higher in Bitumen II	No
Distance/sterane	High	Low	Less stable compound steranes higher in Bitumen II	Yes
$\beta/\alpha$ MPs	Low	High	More stable compound $\beta$ higher in Bitumen II	Yes, except for East Greenland
MNR	Low	High	More stable compound $\beta$ higher in Bitumen II	Yes
MPI-1	High	Low	More stable compound $\beta$ higher in Bitumen II, (phenanthrene influence)	Yes, except for East Greenland



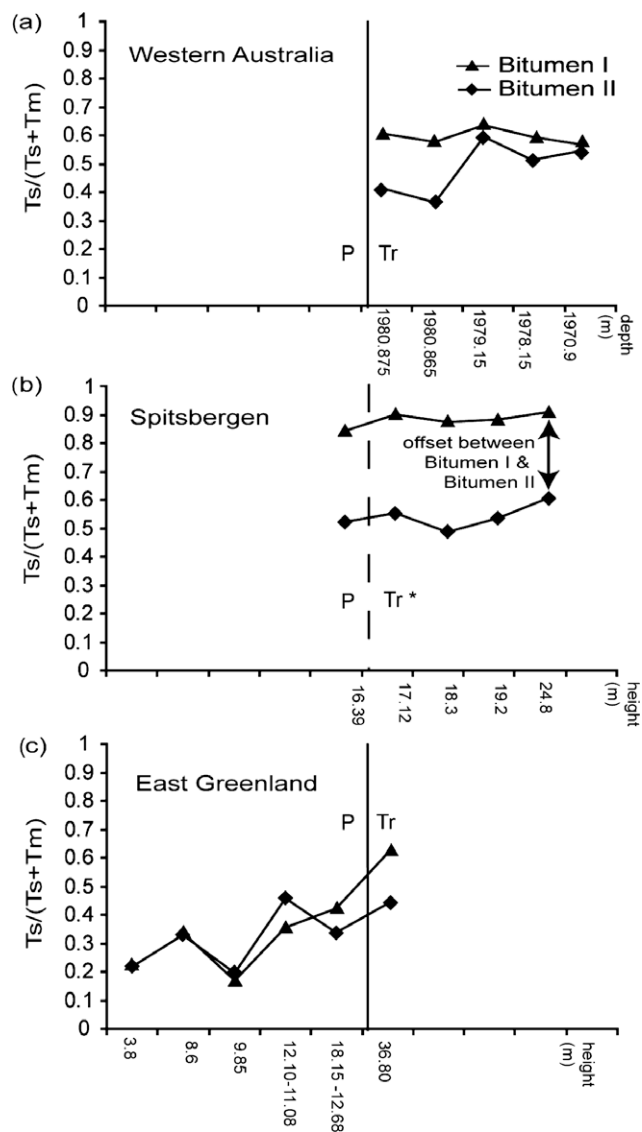
**Fig. 6.** Methylphenanthrene Indices 1 (MPI-1s) against stratigraphic height/depth of the samples from (a) Hovea-3, Western Australia, (b) Lusitaniadalen, Spitsbergen and (c) Jameson Land, East Greenland. Asterisk (\*): possibly Triassic.

For the Spitsbergen and the Western Australian samples there is a good correlation between clay/TOC ratio and the MPI-1 offset of the two bitumens ( $R^2 = 0.79$ ; Table 4). This suggests that the relative clay content may have influenced MPI-1 (Fig. 4c). The slightly higher relative abundance of 2-MP in Bitumen II compared to Bitumen I (Fig. 2a and b) indicates that it is the  $\beta$  isomer most affected by variations in the clay/TOC ratio. Ellis et al. (1994) reported that mordenite (clay) sieves were useful to separate 9-MP from 3-MP, 2-MP and 1-MP. Due to their structure, the latter three isomers are preferentially retained in the sieve. In this study, we see no evidence of a similar effect operating in nature. Since the other isomers are also observed in Bitumen II, it appears that the clay matrix may be protecting a larger portion of the OM and especially the more stable  $\beta$  isomers.

### 3.7. Differences between biomarker ratios of Bitumen I and II

For the samples from Western Australia and Spitsbergen, the hopanoid ratio  $Ts/(Ts + Tm)$  is consistently higher in Bitumen I than in Bitumen II, the offset ranging from 0.02 to 0.20 and 0.30 to 0.39, respectively (Fig. 7a and b, Table 3). Through the East Greenland section the offset is somewhat smaller ( $\leq 0.18$ ), and for three samples  $Ts/(Ts + Tm)$  is actually higher in Bitumen I than in Bitumen II (Fig. 7c). No significant correlation is observed when we compare the  $Ts/(Ts + Tm)$  offsets between the bitumens to the clay/TOC ratio (Table 4).

The measured  $C_{27}$  diasterane/sterane ratios for the bitumen samples from Spitsbergen and Western Australia fall within the range 0.55–3.38 (Table 2). The ratio is generally higher in Bitumen I except for one sample from Western Australia (Fig. 8). As demonstrated for the  $Ts/(Ts + Tm)$  ratio, the Spitsbergen samples differ in having a high offset (0.60–1.22) between Bitumen I and Bitumen II (Fig. 8). In the Spitsbergen samples the  $C_{27}$  diasterane/sterane ratios for Bitumen I range from 1.53 to 3.38 and from 0.87 to 2.16



**Fig. 7.**  $Ts/(Ts + Tm)$  versus stratigraphic height/depth of samples from (a) Hovea-3, Western Australia, (b) Lusitaniadalen, Spitsbergen and (c) Jameson Land, East Greenland. Asterisk (\*): possibly Triassic.



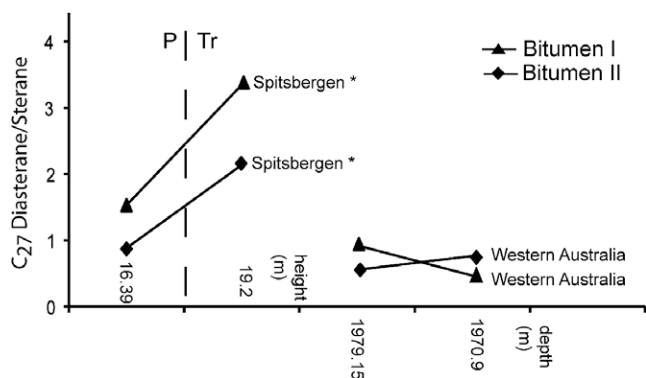


Fig. 8.  $C_{27}$  diasteranes/steranes versus stratigraphic height/depth for samples from Hovea-3, Western Australia and Lusitaniadalen, Spitsbergen. Asterisk (\*): possibly Triassic.

for Bitumen II. Much smaller offsets of  $-0.27$  and  $+0.39$  characterises the bitumens from Western Australia.

In the case of this sterane maturity parameter, plotting the differences between the two bitumens [ $C_{27}$  diasterane/sterane  $_{\text{Bitumen I}} - \text{Bitumen II}$ ] against clay/TOC reveals an excellent correlation ( $R^2 = 0.87$ ) for all sample sets (similar to that seen for  $\beta/\alpha$  MP, MNR and MPI-1 data: Fig. 4d, Table 4).

#### 4. Conclusions

In sedimentary rocks hydrocarbons are known to be encapsulated within diagenetic mineral phases such as calcite and quartz (Dutkiewicz et al., 2004) and within the kerogen itself. Removal of the carbonate and silicate minerals has the potential to liberate those otherwise mobile components that were protected by minerals, as well as improving the exposure of kerogen to the extracting solvent. The low temperature demineralisation method of Robl and Davis (1993) is relatively mild and can be used to investigate biomarkers that are not extractable from crushed whole rock.

The application of this technique to three suites of Permo-Triassic sedimentary rocks, and detailed analysis of selected PAH and biomarker alkanes in their respective Bitumen I and II fractions, has revealed a clear relationship between well established molecular proxies of thermal maturity and the clay/TOC ratio of the host rock. A detailed assessment of the specific types of clay minerals capable of influencing the distribution of hydrocarbons in OM would be desirable. The information on thermal maturity data preserved within Bitumen II might be useful in petroleum exploration studies, as migrated bitumen may overprint the original thermal maturity signal of Bitumen I.

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