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Analysis of wax hydrocarbons in petroleum source rocks from the Damintun depression, eastern China, using high temperature gas chromatography

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Abstract

A detailed organic geochemical study; utilising petrography, biomarker hydrocarbon analysis and high temperature GC analysis of extractable wax hydrocarbon constituents was performed on four marginally oil window-mature source rocks from the Shahejie Formation (Eocene), Damintun depression in eastern China. The main maceral components in the source rocks were vitrinite, liptinite and exinite, with vitrinite being more abundant (> 50 vol.%) in organic-lean samples whose TOC contents were between 1 and 2 wt.%. Large differences in pristane/phytane ratios suggested that the organic-rich samples were deposited in a less oxic depositional environment than that for the organic-lean rocks. The distribution of extractable wax hydrocarbons, determined by high temperature GC, showed a marked difference between these two sample types. The organic-rich samples contained high molecular weight hydrocarbons (HMWHCs) dominated by macrocrystalline *n*-alkanes (*n*-C₂₃–*n*-C₃₇, typically maximising at *n*-C₂₉), while the organic-lean samples contained lower amounts of extractable wax hydrocarbons but were relatively rich in microcrystalline components (> *n*-C₃₅). In all source rocks (Es3 and Es4), a noticeable odd-over-even predominance (OEP) of *n*-alkane chain lengths (up to *n*-C₆₅) was evident, consistent with a direct biological origin for the long *n*-alkyl chains. They were most probably formed during diagenesis from decarboxylation of predominantly even-carbon-numbered aliphatic acids originating from higher plant or lacustrine algal sources and/or were directly biosynthesised in hydrocarbon form. At least two other homologous series of branched/cyclic HMWHCs were observed, one of which was confirmed as a series of branched alkanes (probably methyl-branched). The carbon number distribution patterns of HMWHCs may be primarily controlled by thermal maturity and biogenic source input as well as being influenced by diagenetic reactions governed by depositional environmental conditions, as shown previously [Carlson, R.M.K., Teerman, S.C., Moldowan, J.M., Jacobson, S.R., Chan, E.I., Dorrrough, K.S., Seetoo, W.C., Mertani, B., 1993. High temperature gas chromatography of high wax oils. In: Indonesian Petroleum Association, 22nd Annual Convention Proceedings. Jakarta, Indonesian, pp. 483–507. Carlson, R.M.K., Jacobsen, S.R., Moldowan, J.M., Chan E.I., 1994. Potential application of high temperature gas chromatography to Middle Eastern petroleum exploration and production. In: Al-Husseini, M.I. (Ed.), *Geo'94*, Vol 1., Selected Middle East Papers from The Middle East Petroleum Geoscience Conference, 1994; Gulf PetroLink. Manama, Bahrain, pp. 258–267]. Our study indicates for the first time that Es3 source rocks as well as Es4 facies contain HMWHCs. The distributions of extractable wax hydrocarbons suggest that both Es4 and Es3 members may potentially serve as important parent source rocks for generating waxy petroleum in this region.

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1. Introduction

An understanding of the origin and composition of high wax crude oil is important since wax deposition in both reservoirs and pipelines is responsible for adversely affecting the production rates of crude petroleum. Hedberg (1968) formalised the concept that high wax oil was derived from terrestrial organic matter and defined oil with an excess of 5 wt.% of C_{22+} paraffin components as a high wax oil. The classical view then was that high wax, low sulfur oils were commonly associated with non-marine strata. Tissot and Welte (1984) further summarised the geological settings for the occurrence of high wax oil as: (i) rift valleys of lower Cretaceous in the area of South Atlantic Ocean; (ii) paralic trough continents where high wax oils are associated with coal beds; (iii) continental lowlands with non-marine sedimentation.

High molecular weight hydrocarbons (HMWHCs) of carbon number ranging from C_{40} to C_{120} and beyond in crude oils have been identified as molecular constituents following the implementation of high temperature gas chromatography, field desorption mass spectrometry and field ionization mass spectrometry (Del Rio and Philp, 1992, 1999; Del Rio et al., 1992; Carlson et al., 1993, 1994; Musser and Kilpatrick, 1998; Thanh et al., 1999; Hsieh et al., 2000; Hsieh and Philp, 2001). Petroleum wax hydrocarbons are not just simply composed of *n*-alkanes. Musser and Kilpatrick (1998) used elemental analysis, FTIR spectroscopy, field desorption mass spectrometry, 1H NMR and ^{13}C NMR spectroscopy to discern two distinct groups of petroleum waxes, which they termed *microcrystalline* and *paraffinic*. The *microcrystalline* waxes were composed of aliphatic hydrocarbon compounds containing a substantial amount of alkyl branching and naphthenic rings in their structures, with molecular weights ranging from 300 amu right up to 2500 amu and with atomic H/C ratios lower than 2.00 (between 1.85 and 1.90). They contained approximately 55% straight chain methylene chains. *Paraffinic* waxes were hydrocarbon chains with few or no branches and containing narrow molecular weight ranges between 350 and 600 amu and atomic H/C ratios of around 2.00. They contained 63–78% straight chain methylene carbon as estimated by FTIR spectroscopy. Hsieh et al. (2000) recently observed at least seven homologous series of organic compounds in petroleum waxes in the C_{35} – C_{40} molecular weight region, using high temperature gas chromatography–mass spectrometry (GC–MS). In addition to *n*-alkanes, other major compound classes included methyl branched alkanes, alkylbenzenes, alkylcyclohexanes and alkylcyclopentanes.

While high wax oil occurrences are often associated with restricted types of basins and stratigraphic sequences, many of which are non-marine in origin, more recent research (Thanh et al., 1999; Hsieh et al., 2000;

Hsieh and Philp, 2001) has shown that HMWHCs are in fact ubiquitous components of crude oil (including marine oils). This implies that macerals other than higher plant exinite and vitrinite, e.g. marine or lacustrine alginite, may be the source of wax hydrocarbons in oils as has been suggested before (Tegelaar et al., 1989). The parent source rock must contain significant concentrations of long-chain and high molecular weight aliphatic structural moieties, either present as free (extractable) compounds or as molecular components covalently-bound within macromolecular organic phases (resins, asphaltenes and kerogen), in order to generate HMWHCs in the oils. Both the initial biological input to sediments and the effect of depositional and diagenetic factors in preserving molecular features of lipids will control the occurrences and concentrations of long-chain aliphatic groups in source rocks, thus critically influencing their capability to generate high wax oil. More work is required then to study the relationship between the nature of the organic facies in source rocks and their wax hydrocarbon composition and wax generation potential.

Previous investigations have generally focused on characterising the HMWHCs in crude oils, while much less attention has been paid to analysing the high molecular weight constituents in petroleum source rock extracts (Mueller and Philp, 1998; Killops et al., 2000; Hsieh and Philp, 2001). This is surprising since it is easier to relate the molecular features of HMWHCs to specific organic facies in the parent organic matter when the actual host source rock is available for visual inspection. In our study, we chose to integrate biogeochemical information gathered from biomarker and petrographic analysis to help gain a better insight into what controls the distribution of waxes in fairly immature source rocks (of marginal oil-window maturity). Lack of suitable analytical techniques, adsorption of these compounds to kerogen and minerals in the host source rock, plus their low solubility in organic solvents such as dichloromethane and methanol are amongst the most likely explanations as to why HMWHCs have not been routinely detected in rock extracts.

In this investigation, a restricted suite of four source rocks from the Damintun depression, eastern China, and a reservoir oil from the region were selected for study to illustrate the distribution and variability of HMWHCs in closely-related source rocks within a particular basin. The Damintun depression is extremely rich in high wax oil accumulations (Tong and Huang, 1991; Huang et al., 1992; Huang and Pearson, 1999). Since there are more than 50 Tertiary depressions in eastern China, all of which share a similar evolution history, it is of particular interest for petroleum explorationists to understand why ultra-high wax oils only occur in Damintun. The objectives of this study were, therefore, to better understand the factors which

control the occurrences of HMWHCs in source rocks and therefore, ultimately, in crude oil.

2. Experimental

2.1. Samples

All source rock samples were taken from sediment cores. Sample descriptions and maceral compositions are listed in Table 1. Dispersed organic matter was visually characterised using transmitted light and reflected UV-fluorescent light microscopy. Total organic carbon (TOC) contents were determined using a LECO analyser. Bitumen extraction was performed sequentially using dichloromethane (DCM)/methanol (93/7 v/v) for 48 h and then toluene for 24 h in a Soxhlet extraction apparatus. Although DCM/methanol is a poor solvent for dissolving wax hydrocarbons, it is used in this context as a polar solvent for opening up the organic pore structure in the sediment by disrupting non-covalent interactions within the host kerogen matrix and allowing efficient release of the bulk of polar bitumen components. The subsequent toluene extraction step recovers any residual free wax components not entrained in the DCM/methanol extracts. Both extracts were combined and then divided into two aliquots. One portion of the extracts was separated into saturated, aromatic and polar fractions for conventional GC and GC–MS analysis (these fractions were not used for high temperature GC analysis) using silica gel thin layer chromatography (TLC; 20 × 20 cm; 0.5 mm thickness; Kieselgel 60G) with petroleum ether as eluant. The other aliquot was prepared for HTGC by wax separation (Section 2.3).

2.2. Standard biomarker analysis

Conventional gas chromatographic (GC) analysis of the saturate fractions from TLC separation was performed on a Carlo Erba Fractovap 4160 instrument utilising on-column injection and flame ionisation detection (FID). A 30 m DB-1 capillary column (0.32 mm i.d. and

0.25 µm film thickness) was temperature programmed from 80 °C (2 min hold) to 275 °C (30 min hold) at 4 °C min⁻¹ and hydrogen was used as the carrier gas.

GC–MS analysis of the saturate fractions from TLC separation was carried out in the multiple ion detection (MID) mode on a HP 5890 gas chromatograph interfaced to a HP 5970 mass spectrometer. An ionisation energy of 70 eV was used. Samples were introduced by on-column injection on to a 30 m HP-1MS capillary column (0.25 mm i.d. and 0.25 µm film thickness) which was temperature programmed from 80 °C (2 min hold) to 290 °C at 4 °C min⁻¹ (30.5 min hold). Helium was used as the carrier gas.

Selected free (extractable) biomarker molecular parameters are listed in Table 2. Pristane/phytane (Pr/Ph) ratios were measured by GC–FID peak areas. For molecular maturity parameters, C₂₉ ααα sterane 20S/(20S+20R) ratios were quantified from *m/z* 217 ion chromatograms while C₃₂ αβ hopane 22S/(22S+22R) ratios were measured from *m/z* 191 ion chromatograms. Peak identification was based on relative retention times and reference to previously published studies. The molecular parameters were calculated from peak areas and relative response factors of unity were assumed for all compounds investigated.

2.3. High temperature gas chromatographic analysis of wax hydrocarbons

HMWHCs were analysed using high temperature GC–FID. The wax preparation procedure was similar to that previously described by Thanh et al. (1999) except that toluene was used as a substitute solvent for *p*-xylene. Aliquots of total rock extract or oil (ca. 0.2–0.4 g) were dissolved in hot toluene at ca. 80 °C on a hot plate and then adsorbed on alumina (pre-activated for 3 h at 500 °C). The vials that contained the extracts were subsequently washed with about 3 ml of hot toluene to completely dissolve any residual wax crystals and these washings were also added to the alumina. The alumina mixture was then itself extracted by toluene for 6 h using a Gerhardt Soxtherm extraction apparatus. The toluene solution containing the waxes of interest was

Table 1
Sample description, mean vitrinite reflectance and maceral composition of the petroleum source rocks

Sample no.	Well	Formation	Depth (m)	TOC (%)	Ro (%)	Extract yield (wt.%) ^a	Heavy wax (%) ^b	Liptinite (%)	Exinite (%)	Vitrinite (%)	Inertinite (%)
GD32	Sh154	Es3	3103.2	1.67	0.65	0.4	2.1	23	12	58	7
GD39	An64	Es4	2212.5	1.6	0.57	0.5	7.1	7	32	52	9
GD68	An112	Es4	2458.2	4.71	0.55	1	11	28	27	37	8
GD69	An109	Es3	2269.3	8.66	0.44	2.5	22.4	43	16	38	3

^a Weight percent of total rock (as received).

^b Weight percent of extract which is waxy and insoluble in cold *n*-hexane (see Section 2.3).

recovered while macromolecular components (asphaltenes and some resins) were retained by adsorption on the alumina. Following extraction, the toluene washings were dried under nitrogen, dissolved in 30 ml distilled acetone and placed in a freezer ($-21\text{ }^{\circ}\text{C}$, 12 h). The sample was centrifuged at high speed (2000 rpm for 10 min) and the precipitate obtained represents the whole wax fraction (Burger et al., 1981). For the further separation, an aliquot of whole wax was then dissolved in 30 ml n-hexane and the sample chilled at $-21\text{ }^{\circ}\text{C}$ in order to precipitate out the microcrystalline wax. Whole waxes and microcrystalline waxes were subjected to analysis by high temperature gas chromatography (HTGC).

HTGC analysis of wax concentrates was performed on a Carlo Erba 5300 gas chromatograph, equipped with a J&W Scientific DB-5HT capillary column (0.1 μm film thickness, 30 m \times 0.25 mm i.d.), using capillary cold on-column injection. The oven temperature programme was set from $60\text{ }^{\circ}\text{C}$ (2 min) to $390\text{ }^{\circ}\text{C}$ (35 min) at $4\text{ }^{\circ}\text{C min}^{-1}$ and hydrogen was used as the carrier gas. The sample was dissolved in hot toluene (ca. $80\text{ }^{\circ}\text{C}$) prior to injection (note, it is the thermal stability of the DB-5HT stationary phase (which has an upper operating temperature limit of $400\text{ }^{\circ}\text{C}$) which limits the analytical window to observation only up to ca. C_{65} compounds, rather than the procedure for extraction or wax preparation).

2.4. GC–chemical ionisation (CI)–MS

For one sample (GD69), GC–CI–MS was carried out on a Hewlett-Packard 5890 II GC interfaced with a Hewlett-Packard 5972 quadrupole mass selective detector to elucidate basic structural information and help ascribe which homologous series of HMW alkane compounds were present. Methane was used as the reagent gas at a

pressure of 7.7×10^{-5} Torr. The sample (1 μm) was dissolved in hot toluene and manually injected (using an injection temperature of $390\text{ }^{\circ}\text{C}$) and the split opened after 1 min. The MS was operated in full scan mode (monitoring in the mass range: 500–800 amu). The source temperature was $250\text{ }^{\circ}\text{C}$ and the interface temperature was set to $390\text{ }^{\circ}\text{C}$. Separation was again performed on the J&W Scientific DB-5HT capillary column (0.1 μm film thickness, 30 m \times 0.25 mm i.d.). The GC oven was temperature programmed from $50\text{ }^{\circ}\text{C}$ (5 min hold time) to $200\text{ }^{\circ}\text{C}$ (1 min) at $15\text{ }^{\circ}\text{C min}^{-1}$, then to $250\text{ }^{\circ}\text{C}$ (1 min) at $10\text{ }^{\circ}\text{C min}^{-1}$, and finally to $390\text{ }^{\circ}\text{C}$ (20 min) at $5\text{ }^{\circ}\text{C min}^{-1}$. Helium was used as the carrier gas.

3. Geological setting

The Damintun depression is known for the unusually high wax content of the oils it produces, with about two thirds of its production containing wax contents above 30 wt.% (known as ultra-high wax oils) and some even containing up to 70 wt.% (Huang et al., 1992; Ge and Chen, 1993). The Damintun depression is one of a number of fault-bounded Tertiary depressions in the Bohai Bay basin located in eastern China (Fig. 1). The detailed petroleum geology of this region has been described by Ge and Chen (1993) and summarised by Huang and Pearson (1999).

The basement of the depression is mainly composed of Archaeozoic granite-gneiss and magmatic granites, Middle-Upper Proterozoic carbonate rocks, plus some Mesozoic formations in the northern parts of the depression. When fracturing became well developed, the basement rocks then served as high quality reservoirs (Tong and Huang, 1991). The depression commenced its lacustrine sedimentation in the Early Tertiary. The Palaeocene sequence can be divided into two formations: Shahejie and Dongyin. The Shahejie Formation is widely distributed in the Bohai Bay basin. It has a thickness of 2000–4000 m and lies unconformably over the underlying formation. It contains the most important source rocks and reservoirs in the entire basin and is the only formation considered here. Based on its lithology and fossil assemblages, it can be further divided into four members (Es4, Es3, Es2, and Es1, moving upwards).

Fig. 2 shows the reconstructed stratigraphy for the Damintun depression. The Es4 member consists of interbedded sandstones and grey-brown mudstones and intercalated oil shales, which form the first source rock interval. It is about 600–700 m thick. The Es3 member developed when rifting prevailed. The lower part of Es3 consists of sandstones and conglomerates and intercalated thin grey mudstones. It is 500–600 m thick. The middle part of Es3 consists of grey mudstones and interbedded sandstones and is about 600–700 m thick. Both intervals can serve as potential

Table 2

Biomarker molecular parameters calculated for the source rocks and a related oil

Sample no.	Pr/Ph ^a	CPI1 ^b	CPI2 ^c	CPI3 ^d	22S/(S+R) ^e	20S/(S+R) ^f
GD32	8.84	1.43	1.24	0.66	0.54	0.38
GD39	5.23	1.41	1.33	0.74	0.51	0.24
GD68	2.34	1.78	1.38	0.54	0.43	0.19
GD69	2.24	1.75	1.40	0.57	0.46	0.14
An12	2.21	1.02	0.98	1.03	0.51	0.46

^a Pristane/phytane from GC-FID peak areas.

^b $[\text{C}_{25} + \text{C}_{33} + 2 \times (\text{C}_{27} + \text{C}_{29} + \text{C}_{31})] / 2 \times (\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32})$ for C_{25-33} n-alkanes.

^c $[\text{C}_{47} + \text{C}_{55} + 2 \times (\text{C}_{49} + \text{C}_{51} + \text{C}_{53})] / 2 \times (\text{C}_{48} + \text{C}_{50} + \text{C}_{52} + \text{C}_{54})$ for C_{47-55} n-alkanes.

^d $[\text{C}_{51} + \text{C}_{59} + 2 \times (\text{C}_{53} + \text{C}_{55} + \text{C}_{57})] / 2 \times (\text{C}_{52} + \text{C}_{54} + \text{C}_{56} + \text{C}_{58})$ for C_{51-59} main family of branched alkanes.

^e C_{31} 17 α ,21 β (H)-homohopane.

^f C_{29} 5 α ,14 α ,17 α (H)-24-ethylcholestane.

source rocks. The upper part is generally characterised by a coarse-grained siliciclastic facies consisting of siltstone and sandstone which serves as an important reservoir. It is about 1000 m thick.

By the end of Es3 deposition, uplift prevented the formation of Es2 deposits in this region and the existing Es3 member became eroded in the northern part of the depression. The Es1 interval is composed of grey-green mudstones and intercalated sandstones. This member is about 400 m thick, has a low organic carbon content and is thermally immature. The shale in this member may act as the regional seal. The Eocene Dongying Formation (Ed) and the Neocene Guantao Formation (Ng) and Minhuazhen Formation (Nm) provide overburden rocks for the petroleum system (Fig. 2).

The Damintun depression represents, therefore, an early developed depression in the Bohai Bay Basin which had a high subsidence rate during the Eocene, and slow burial rates during the Oligocene and Neogene. The effective parent source rock of petroleum is present in Eocene strata which have undergone a relatively low thermal evolution.

4. Results and discussion

Organic facies can change significantly, both laterally and vertically, in sediments from the Damintun depression

due to the small surface area and volume of the overlying water body which prevailed during deposition. The organic matter content and maceral composition of source rocks from this region reflect this kind of variability. Four samples from a large sample set were selected (Table 1). Two were chosen from each important stratigraphic member (Es3 and Es4), of which one was organic-rich with a TOC content above 4 wt.% and the other was organic-lean with TOC content between 1 and 2 wt.%. Vitrinite reflectance data indicate that these samples are of marginal to early maturity with respect to the oil-generation window, with mean vitrinite reflectance (R_o) values ranging between 0.44 and 0.65%.

4.1. Maceral composition

As a result of fairly recent work it has become clear that the *n*-alkane constituents of oil may be generated from the thermal cracking during catagenesis of selectively preserved, highly aliphatic, resistant biomacromolecules present in the parent source rocks (e.g. Philp and Calvin, 1976; Hatcher et al., 1983; Tegelaar et al., 1989), as well as from free lipid constituents. Such refractory polymers are present in algal cell walls (algaenan), in high plant leaf cuticles and the tegmen layer of seed coats (cutan and other unnamed compounds) and in the bark of woody plants (e.g. Largeau et al., 1984; Nip et al., 1986; Goth et al., 1988; de Leeuw

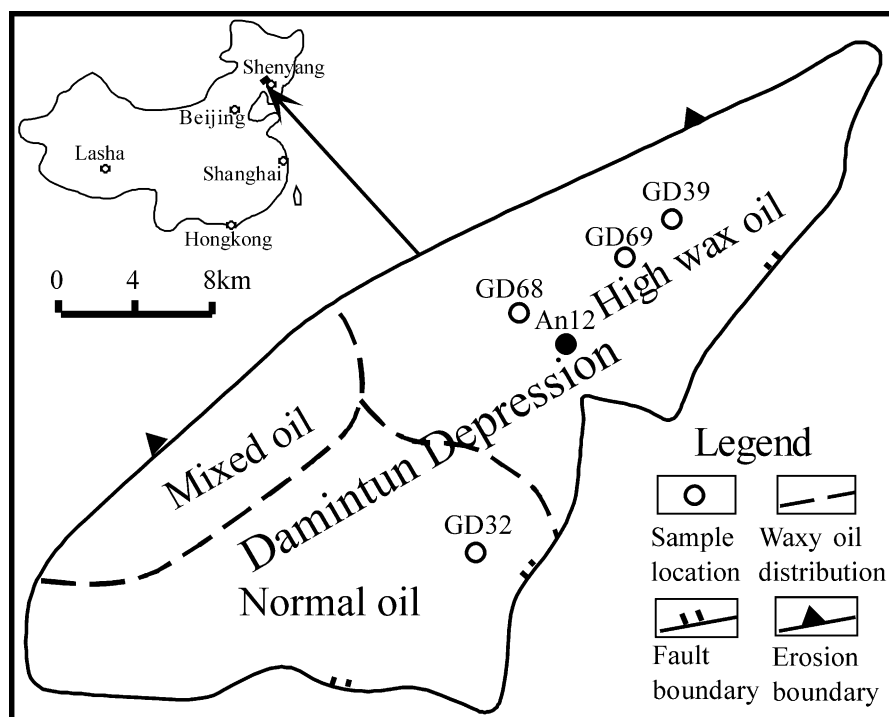


Fig. 1. Map of the Damintun depression, showing the location of sampled wells and the geographical distribution of different oil types according to wax content.

et al., 1991; Tegelaar et al., 1991; Collinson et al., 1994; Gelin et al., 1997, 1999). Many reviews have discussed in detail the geochemical and organic petrological issues related to the nature of, and recognition of, oil-prone source rocks in terrestrial sequences by reference to the molecular composition of non-marine oils and their precursors (Collinson et al., 1994; Curry et al., 1994; Powell and Boreham, 1994). The maceral composition provides a means of constraining the nature of the organic input to source rocks.

Maceral compositions of source rock organic matter were determined from prepared whole rock thin sections. The macerals were classified here into four main groups: liptinite (alginite and amorphous matrix), exinite (sporinite, cutinite, resinite, and liptodetrinite), vitrinite and inertinite. The inertinite and vitrinite macerals are derived predominantly from the structural parts of terrestrial higher plants. Sporinite, cutinite, resinite and suberinite are the primary macerals of the exinite group and are derived from spores, cutin, resin and suberin, respectively. The various forms of alginite (from algae) and amorphous matrices (again, predominantly algal-derived) are distinguished here from the exinite macerals and together these comprise an

individual *liptinite* group. This scheme is slightly different from traditional coal petrographic classification (e.g. Powell and Boreham, 1994, and references therein) and reflects the importance of aliphatic carbon-rich liptinite and exinite macerals in determining the overall oil-generation potential of source rocks.

The maceral compositions show some variation with organic carbon content, especially in the amount of vitrinite content (Table 1). The content of vitrinite in organic-rich samples is lower than 40 vol.%, while in organic-lean samples it is higher than 50 vol.%. Inertinite contents are below 10% in all four samples. Liptinite is generally higher in the organic-rich samples than the organic-lean ones, although a difference of only 5 vol.% of liptinite is apparent between samples GD32 and GD68. Exinite contents show no clear difference between the two sample sets. In a previous study of 43 rock samples from the Damintun depression (Huang et al., 2001), the average maceral composition of liptinite, exinite, vitrinite and inertinite groups in the Es3 mudstones was found to be 22, 33, 38 and 7%, respectively and for the Es4 mudstone were 24, 27, 43 and 6%, respectively. There was no significant difference between these two members, whereas oil shale (organic-rich sediment, here with TOC > 5 wt.%), found in both Es3 and Es4 member facies, contained high amount of liptinite components of up to 66 vol.% (Huang et al., 2001). It would seem then, in general, that the aliphatic-rich maceral content is better preserved in the organic-rich samples and this aspect is more clearly seen within a large data set. It has been recently proposed that oil shales, in particular, have made a significant contribution to high wax oil generation in the Damintun depression (Huang et al., 2003).

4.2. Depositional environment molecular markers

The ratio of the isoprenoids, pristane and phytane, has long been associated with the nature of the redox conditions prevailing in the depositional environments (Didyk et al., 1978), although other factors can play an important role in determining their relative abundances (ten Haven et al., 1987). In the light of this, we adopt a conservative approach and define that, where the pristane/phytane (Pr/Ph) ratio is greater than 4.0, then the original depositional environment was probably oxidising (Mello and Maxwell, 1990; Philp, 1994). In the source rocks analysed here (Table 2), high Pr/Ph ratios (>5.0) are characteristic of organic-lean samples and are probably more a reflection of depositional environment than source organic material or maturity differences between samples. The original environment in which the higher plant matter was deposited would probably have been sub-oxic, such as peat swamps or deltaic environments. The Pr/Ph ratio falls below 2.5 in the two organic-rich samples, indicating less oxic

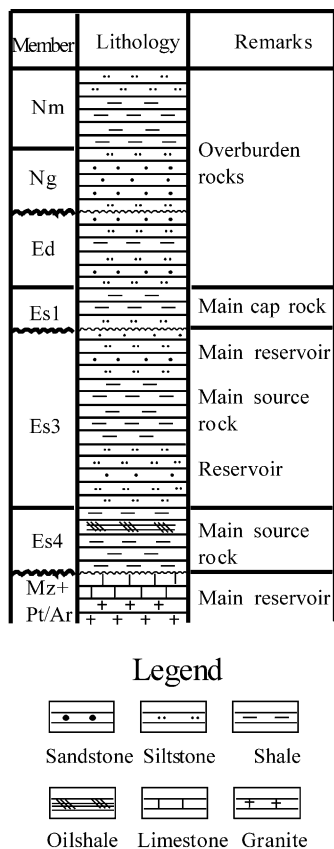


Fig. 2. Stratigraphic profile for the Damintun depression.

depositional conditions, most likely associated with a semi-deep lacustrine body of water.

Sterane and hopane biomarker distributions are shown in Fig. 3. Sterane mass chromatograms (m/z 217) are characterised by a predominance of C_{29} compounds relative to C_{28} and C_{27} compounds and this is often associated with a significant input of terrestrial higher plant matter (Mackenzie, 1984; Moldowan et al., 1985), although algal sources of C_{29} steranes are also possible (Volkman, 1986). Triterpane distributions (m/z 191) are

dominated by the normal hopane series, while compounds such as $18\alpha(H)$ -oleanane, gammacerane, rearranged hopanes (C_{30} diahopane and C_{29} Ts) are present in very low concentrations or cannot be observed (Fig. 3). The low relative abundance of extended homohopanes ($>C_{31}$) and small amounts of gammacerane, a marker of water column stratification (Sinninghe Damsté et al., 1995), are together indicative of a freshwater depositional environment for these sediments (Mello and Maxwell, 1990; Volkman, 1988).

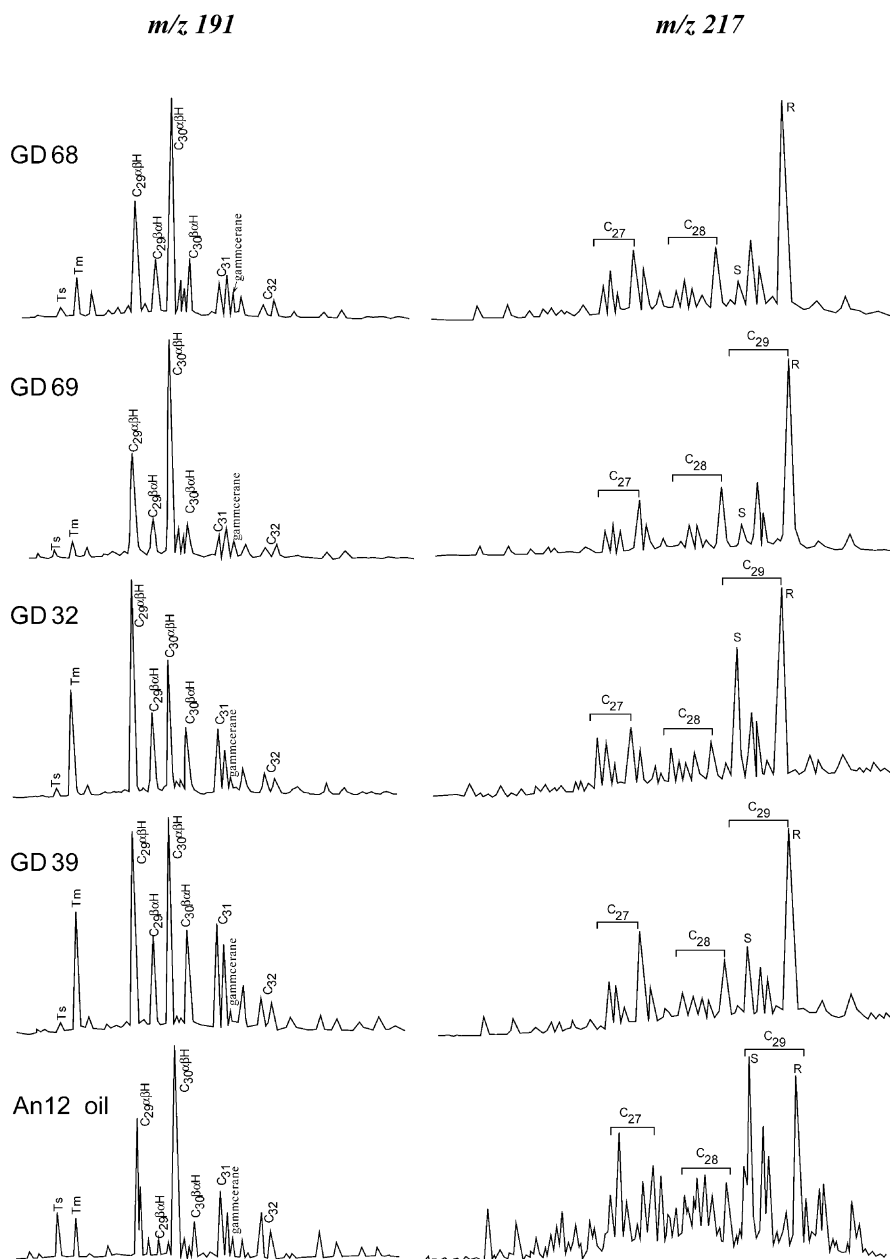


Fig. 3. Distribution of triterpane (from m/z 191 ion chromatograms) and sterane (from m/z 217 ion chromatograms) biomarkers for the four source rocks and one oil.

4.3. High temperature GC (HTGC) alkane profiles

The *n*-alkane distributions of many waxy oils often appear to maximise in the range C₂₀–C₄₀ (Tissot and Welte, 1984). Figure 4 shows the distribution of total extractable aliphatic compounds present in the four source rock samples as determined by standard GC–FID analysis using a conventional capillary column (with an upper operating temperature limit of 320 °C as dictated by the thermal stability of the stationary phase). This compound distribution is somewhat misleading because of the analytical limitations imposed by the GC conditions and it can be observed that no HMWHC (> C₄₀) compounds can be discerned in any of these traces. With the implementation of newly-available HTGC capillary columns the possibility now, however, exists to extend our analytical window to the analysis of high wax oils where the carbon numbers of individual compounds extend to ca. C₆₀ and higher,

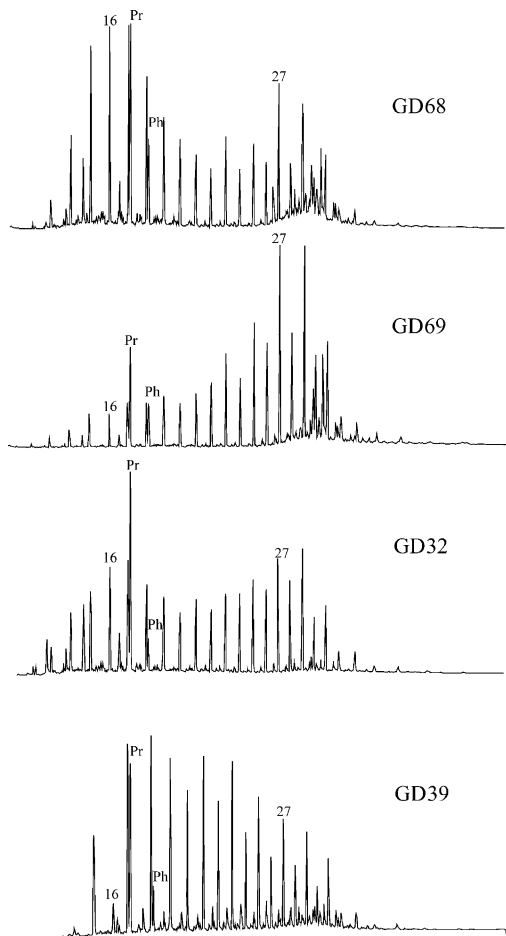


Fig. 4. Conventional gas chromatograms (using a DB-1 stationary phase) of the extractable saturate fractions of the source rocks.

depending on column specification (Del Rio and Philp, 1992, 1999; Del Rio et al., 1992; Carlson et al., 1993, 1994; Thanh et al., 1999; Hsieh et al., 2000; Hsieh and Philp, 2001). In this study, a HTGC column was chosen (see Experimental) which allows excellent resolution of compounds in mixtures up to a ca. C₇₀ boiling pt. range. Other columns are commercially available which can extend the analytical window to include even higher molecular weight compounds although a concomitant loss of chromatographic resolution is inevitable.

HTGC profiles of whole waxes are shown in Fig. 5 and enlarged HMWHC distributions are shown in Fig. 6. For the entire carbon number range, the two most organic-rich samples (GD68 and GD69) show a similar hydrocarbon distribution pattern. A strong odd/even predominance (OEP) can be observed in the elution region of C₂₅–C₃₃, with a maximum at C₂₇/C₂₉. CPI1 values in the C₂₅–C₃₃ range [CPI1 = (C₂₅ + C₃₃ + 2 × (C₂₇ + C₂₉ + C₃₁)) / (2 × (C₂₆ + C₂₈ + C₃₀ + C₃₂))] are 1.78 and 1.75 (Table 2) as measured from GC–FID profiles. The distinct odd/even predominance for *n*-alkanes extends to the highest molecular mass range (Fig. 6), up to *n*-C₆₅ and beyond. CPI2 values in the C₄₇–C₅₅ range [CPI2 = (C₄₇ + C₅₅ + 2 × (C₄₉ + C₅₁ + C₅₃)) / (2 × (C₄₈ + C₅₀ + C₅₂ + C₅₄))] are 1.38 and 1.40. The OEP is not quite as marked for the highest carbon numbered compounds as compared with the medium molecular weight range. Hydrocarbons of medium carbon chain length (C₂₂–C₃₇, termed *macrocrystalline waxes*) dominate the chromatogram for all the samples investigated. HMWHCs are relatively low in abundance for the two most organic-rich samples.

Verification that the main homologous series of compounds comprised *n*-alkanes was achieved by (i) co-injection of selected wax samples with up to three authentic long chain *n*-alkane standards (*n*-C₄₀, *n*-C₅₀ and *n*-C₆₀) followed by subsequent GC–FID analyses to confirm that these exactly co-eluted with three members of the main homologous series (see Fig. 6) and by (ii) confirmation of the molecular weights of the principal individual components by GC–MS analysis performed in the chemical ionisation (CI) mode using methane as the reagent gas. Under these CI–GC–MS conditions, the parent ions of *n*-alkanes were principally detected as [M–H]⁺ i.e. 1 atomic mass unit less than the actual molecular weight (Fig. 7), and from this it was apparent that the structure of the main homologous series is consistent with an empirical formula of C_{*n*}H_{2*n*+2}. The combination of factors (i) and (ii) together, points to a series of *n*-alkanes.

The two organic-lean samples show a different hydrocarbon distribution pattern in the C₂₂–C₃₆ region compared with the organic-rich ones (Fig. 5). These HTGC profiles demonstrate that the wax composition of the low TOC samples comprises a broader envelope of medium molecular weight C_{25–35} *n*-alkanes and an

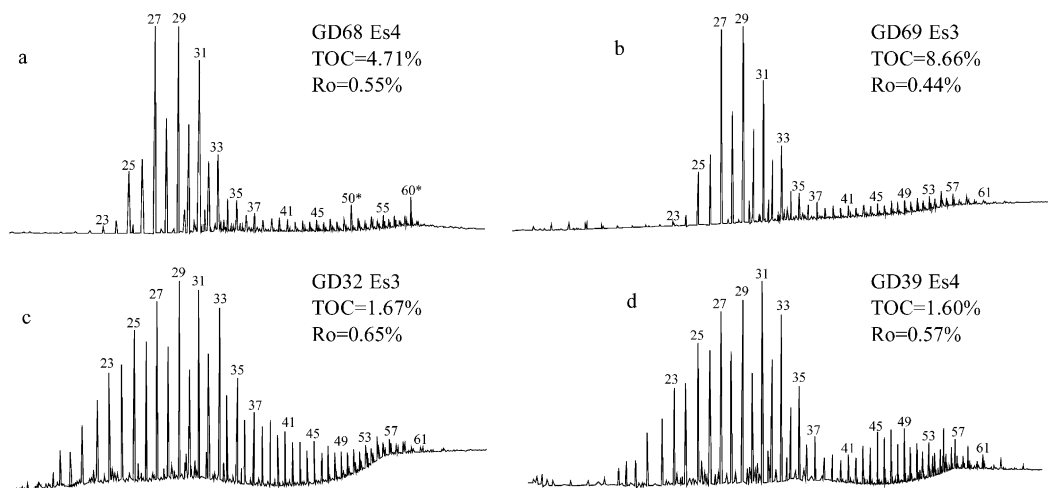


Fig. 5. High temperature chromatograms showing the distributions of total wax hydrocarbons, prepared by precipitation in chilled acetone (*co-injected n -C₅₀ and n -C₆₀ alkane standards).

enhanced concentration of HMWHCs (C₃₆–C₆₅) than for the higher TOC samples. A bimodal distribution of n -alkanes ranging up to C₆₇ with maximum at C₂₉/C₃₁ and a sub-maximum around C₄₅/C₄₉ can actually be observed for sample GD39. The OEP in the region of C₂₅–C₃₃ is not as strong as that found in the more organic-rich samples. CPI1 values in the C₂₅–C₃₃ carbon number range are 1.43 and 1.41 while CPI2 values in the C₄₇–C₅₅ range are 1.24 and 1.33. It should be remembered though that the two organic-lean samples are slightly more thermally mature as indicated by biomarker isomerization ratios [C₃₁ hopane 22S/(22S+22R) and C₂₉ sterane 20S/(20S+20R), Table 2] and vitrinite reflectance (Fig. 5). Hence, they would be expected to possess a less pronounced OEP of n -alkane components as a result of experiencing a higher degree of thermal cracking.

Odd-over-even carbon number preferences (OEP) in the n -C₂₃– n -C₃₈ alkane range are typically diagnostic of continental higher plant wax inputs, such as vascular plant cuticles, to sedimentary organic matter (Eglinton and Hamilton, 1967), although significant contributions from algal sources cannot be discounted (Love et al., 1998; Allard et al., 2002). Since the source rocks under investigation here are mainly composed of higher plant macerals (exinite, vitrinite and inertinite), it seems reasonable to assume that macrocrystalline wax distributions (<C₄₀) detected in these samples originated, at least partly, from a higher plant origin. The fact that an OEP extends all the way up to the highest molecular weights (n -C₆₅) detectable here also offers compelling evidence that these extremely long alkyl chains have also been directly biosynthesised, largely by continental higher plants. An OEP has been observed and reported previously for extractable microcrystalline n -alkanes in coals from the Taranaki Basin, New Zealand (Killops et

al., 2000), although the OEP was only really pronounced in the C₅₁–C₅₇ range. The authors proposed that these extremely long-chain n -alkanes must have been derived at early maturity from molecular components of a higher plant lipinite (here defined as exinite) source, particularly cutan/cutin. This theory is consistent with our views regarding the biogenicity of the long-chain n -alkane components in this source rock suite from the Damintum depression, although algal contributions are possible. More rigorous quantitation of the wax content in source rocks and determination of the stable carbon isotopic composition ($\delta^{13}\text{C}$) of wax components, with respect to the bulk maceral composition of the source rocks, is needed to help elucidate the relative contribution of terrestrial high plants and algae in the parent biomass as a source of wax hydrocarbons; this will be the subject of future studies. To our knowledge, only one compound-specific, stable carbon isotope study of individual petroleum wax hydrocarbon components (up to C₇₄) has been published (Carlson et al., 1997) and this showed, albeit for a small suite of oils, that stable carbon isotopic signatures for HMWHCs are generally similar to those determined for lower n -alkanes (C₂₀–C₄₀) within the same petroleum sample.

Laboratory studies using closed-system vacuum pyrolysis (300 °C for 168 h) have suggested that clay-catalysed oligomerisation reactions of free fatty acids during late diagenesis/early catagenesis provide a feasible alternative mechanism to explain the formation of high molecular weight hydrocarbons (Del Rio and Philp, 1992). Furthermore, odd-numbered n -alkane products can be preferentially formed (versus even-carbon numbered n -alkanes) from the coupling (dimerisation) of biologically-derived even-carbon-numbered fatty acids. It should be noted, however, that such clay-catalysed reactions also tend to produce significant

amounts of rearranged branched and cyclic compounds as by-products [which elute as clusters of unresolved complex mixtures (UCMs)] and so this mechanism is unlikely to account for the continuous and smooth envelope of *n*-alkane components (always exhibiting a

distinct OEP) and low amounts of branched and cyclic compounds that are observed in our HTGC traces.

The biological precursors of the long *n*-alkanes (up to *n*-C₆₅) were likely to have existed initially in the form of free or macromolecularly-bound *n*-carboxylic acid

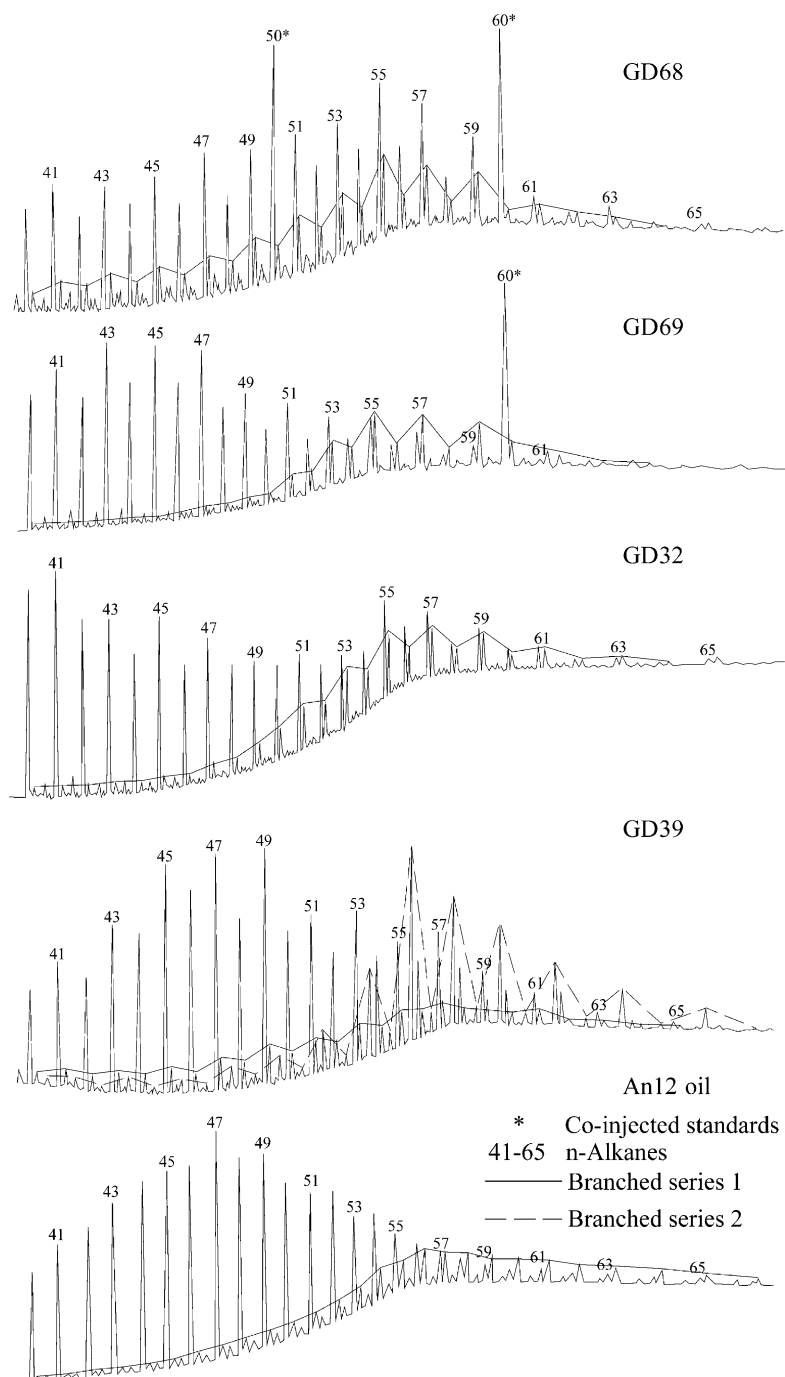


Fig. 6. Partial high temperature gas chromatograms showing the distribution of HMW hydrocarbons in the heavy wax (*n*-hexane-insoluble) fractions prepared from the four source rock bitumens and from a waxy oil from the Damintum region (An12). Numbers refer to the carbon chain lengths of *n*-alkane components.

compounds (containing one additional carbon atom, consisting of a terminal carboxyl group, more than the corresponding alkanes) which were decarboxylated during diagenesis to form a series of *n*-alkanes with a distinct OEP, and/or directly biosynthesised in the *n*-hydrocarbon form. By choosing sufficiently immature

source rocks (which have not yet reached the principal zone of oil-generation) and a high temperature capillary GC column which allowed excellent chromatographic resolution of alkanes, an extended OEP of *n*-alkanes has been observed here across the entire carbon number range from *n*-C₂₂ up to *n*-C₆₅ for the first time. At higher

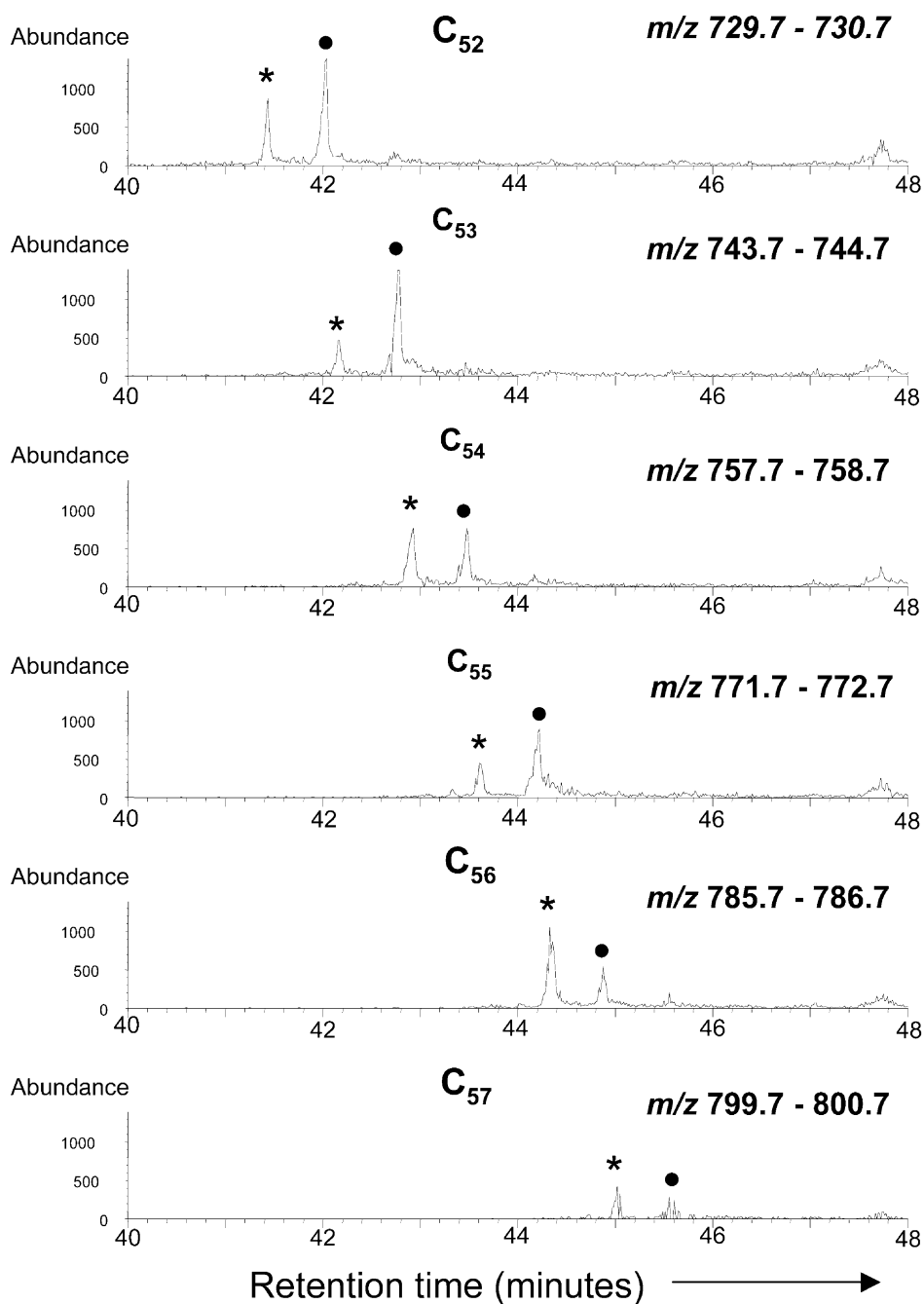


Fig. 7. Identification of two different series of alkane compounds, with the general formula C_nH_{2n+2} , using GC–CI–MS (with CH_4 as the reagent gas). Note, the mass chromatograms shown correspond to $(M-1)^+$, where M is the molecular mass of the compounds (* denotes an unknown branched alkane series while ● indicates *n*-alkanes).

maturity, this OEP for free waxy *n*-alkanes would be expected to be masked by the catagenetic release of non-specific *n*-hydrocarbon moieties bound within macromolecular organic phases (resins, asphaltenes and kerogen) of the source rock and also by the effects of thermal cracking on free hydrocarbons (Killops et al., 2000).

It is apparent that CPI values calculated for *n*-alkanes in our samples become lower with increasing carbon number, which differs from the observation of Killops et al. (2000) for the Tara-1 well coals. Differences in CPI values in our samples may perhaps signify variation in the relative inputs of different biological sources, e.g. algal and higher plant sources, across the total *n*-alkane profile or it may just reflect a greater degree of diagenetic alteration and cracking of the longest *n*-alkyl chains. The lack of a significant OEP for C₄₀–C₆₀ *n*-alkane components is evident for a waxy oil (An12) produced from the Damintun depression (Fig. 6), whose HMWHC distribution more closely resembles a more mature equivalent of that observed for the GD69 source rock (Es3 facies). Although the Es4 facies has traditionally been viewed by explorationists as being the principal parent source rock facies for high wax oils found in the Damintun depression (Huang et al., 1992; Ge and Chen, 1993), our study indicates that the Es3 source rock facies also contains significant amounts of HMWHCs and so must also be viewed as a potentially important source of the waxy petroleum deposits found in this region.

The C₄₀₊ alkane distributions in the source rock extracts and oil are dominated by *n*-alkanes, but two other compound series are visible in the higher molecular weight range (Fig. 6). More quantitatively-significant and ubiquitous is one series of aliphatic compounds, which elutes immediately after each of the *n*-alkane homologues in all of the chromatograms. GC–CI–MS analysis reveals that this compound series possesses the general empirical formula of C_{*n*}H_{2*n*+2}, consistent here with a branched alkane structure (since they cannot have a linear chain structure). It is tempting to suggest that this family corresponds to methyl-branched alkanes, although the exact nature and positioning of the alkyl branching could not be confirmed. Hsieh and Philp (2001) suggested that a similar series of compounds found in crude oils, which eluted immediately after the *n*-alkanes, comprised alkylcyclopentanes. The empirical formula evaluated from our GC–CI–MS analyses confirms that the compounds cannot be alkylcyclopentanes in our samples. One other unidentified family of branched or cyclic aliphatic compound series can also be discerned for sample GD39 (Fig. 7) although, unfortunately, no GC–CI–MS analysis was performed on this sample.

Previous work (Carlson et al., 1993, 1994; Thanh et al., 1999; Hsieh et al., 2000; Hsieh and Philp, 2001) has shown that the distribution of branched/cyclic

HMWHC compounds in an oil can be extremely useful for providing information regarding the depositional environment of the parent source rock. Carlson et al. (1993, 1994) distinguished lacustrine-sourced oil from marine-sourced oil by variations in the relative distributions of these compound types. In marine oils, this series of compounds has a distinct odd/even predominance pattern, whereas oils from saline lacustrine environments demonstrate a high even/odd predominance pattern, and freshwater lacustrine oils are characterized by a low even/odd to no clear carbon predominance pattern. Thanh et al. (1999) extended this work to distinguish more subtle differences in organic facies, principally in salinity, based on the carbon number preference indices of different series of HMWHCs.

A discernible even-over-odd carbon number predominance (EOP) is observed in our source rock samples for the dominant and ubiquitous branched alkane compound series. The CPI3 values calculated for these branched alkane GC distribution profiles [CPI3 = (C₅₁ + C₅₉ + 2 × (C₅₃ + C₅₅ + C₅₇)) / (2 × (C₅₂ + C₅₄ + C₅₆ + C₅₈))], calculated in carbon-number ranges of C₅₁–C₅₉, are 0.54 and 0.57 for the two organic-rich samples, while for organic-lean ones are 0.66 and 0.74 (Table 2). The oils used generally exhibit low concentrations of branched/cyclic hydrocarbons in comparison with straight chain compounds and there is very weak even over odd carbon number predominance (EOP) for this series of compounds (Fig. 7). It appears to us that both the nature of the biogenic input and the degree of thermal maturity will play just as an important role as the depositional environment conditions (of oxicity and aridity) prevailing in controlling the carbon number distributions of HMWHCs.

Further investigation is required to ascertain whether these, as yet unidentified, branched alkane skeletons are directly biosynthesised by living organisms, and so might comprise a new class of high molecular weight biomarker, or whether they arise from microbially-mediated alkylation (particularly methylation) of higher plant wax components. The fact that the different homologues exhibit different carbon number patterns, which do not parallel the *n*-alkane distribution pattern, hints that these branched alkane skeletons are most probably directly biosynthesised by different types of organisms.

5. Conclusions

High molecular weight hydrocarbon (HMWHC) components of petroleum source rocks from the Damintun depression in eastern China were analysed using high temperature gas chromatography. In all four source rocks investigated (from both Es3 and Es4 facies), a noticeable odd-over-even predominance (OEP)

in *n*-alkane carbon chain lengths (from *n*-C₂₃ right up to *n*-C₆₅) was evident, consistent with a direct biological origin for these long *n*-alkyl chains. The precursor compounds may have been even-carbon-numbered carboxylic acids (each containing one additional carbon atom more than the corresponding *n*-alkane) which were decarboxylated during diagenesis and/or the *n*-alkanes may have been directly biosynthesised in *n*-hydrocarbon form. The macrocrystalline *n*-alkane envelope (from *n*-C₂₃ to *n*-C₃₇) was more evident relative to the recalcitrant microcrystalline *n*-alkane components (*n*-C₃₇–*n*-C₆₅) in the higher TOC sediments. The maceral composition of all four source rocks was made up largely of vitrinite plus higher plant exinite maceral groups. It is likely then that the *n*-alkane series observed here is simply an extension (up to higher carbon numbers) of the commonly observed OEP of *n*-alkanes, ranging from *n*-C₂₂ to *n*-C₃₅ compounds when using conventional gas chromatographic columns. Although this hydrocarbon number pattern is often associated with an input from continental plant waxes, possible contributions from algal sources cannot be completely ruled out, since alginite was found in all samples.

Besides the waxy *n*-alkane series, at least two different families of cyclic/branched hydrocarbons were also detected in the high molecular weight region of the gas chromatograms (C₄₀–C₆₅). GC–CI–MS analyses revealed that one compound series corresponded to a family of branched alkanes, possibly methyl-substituted alkanes. A discernible even-over-odd predominance (EOP) was observed for this homologous series, in contrast to the OEP observed for *n*-alkanes, although the different homologies exhibit different carbon number distribution patterns. The exact chemical structure and biological origin of these two families of branched alkanes are as yet unclear.

Organic petrography and molecular biomarker analyses together indicated that the organic-lean sediments were likely to have been deposited in more oxic depositional environments than the higher TOC sediments, when water depths were lower than normal and terrestrial plants made a dominant contribution to the total preserved organic matter. Although the Es4 facies has traditionally been viewed by explorationists as being the principal parent source rock facies for high wax oils found in the Damintum depression, our study indicates that the Es3 facies also contains long-chain *n*-hydrocarbons and must also be viewed as a potentially important source of waxy petroleum in this region.

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References

- Allard, B., Rager, M.-N., Templier, J., 2002. Occurrence of high molecular weight lipids (C₈₀₊) in the trilaminar outer cell walls of some freshwater microalgae. A reappraisal of algalen structure. *Organic Geochemistry* 33, 789–801.
- Burger, E.D., Perkins, T.K., Striegler, J.H., 1981. Studies of wax deposition in the Trans Alaska Pipeline. *Journal of Petroleum Technology* 33, 1075–1086.
- Carlson, R.M.K., Teerman, S.C., Moldowan, J.M., Jacobson, S.R., Chan, E.I., Dorrough, K.S., Seetoo, W.C., Mertani, B., 1993. High temperature gas chromatography of high wax oils. In: Indonesian Petroleum Association, 22nd Annual Convention Proceedings, Jakarta, Indonesia, pp. 483–507.
- Carlson, R.M.K., Jacobsen, S.R., Moldowan, J.M., Chan, E.I., 1994. Potential application of high temperature gas chromatography to Middle Eastern petroleum exploration and production. In: Al-Husseini, M.I. (Ed.), *Geo'94*, Vol 1. Selected Middle East Papers from The Middle East Petroleum Geoscience Conference. Gulf PetroLink, Manama, Bahrain, 1994, pp. 258–267.
- Carlson, R.M.K., Dias, R.F., Schoell, M., 1997. Origins of high molecular weight alkanes >C₄₀ in waxes from natural crude oils and bitumens based on carbon isotopic evidence. In: 18th International Meeting on Organic Geochemistry, 22–26 September, Maastricht, The Netherlands, pp. 399–400 (abstract).
- Collinson, M.E., van Bergen, P.F., Scott, A.C., De Leeuw, J.W., 1994. The oil-generating potential of plants from coal and coal-bearing strata through time: a review with new evidence from Carboniferous plants. In: Scott, A.C., Fleet, A.J. (Eds.), *Coal and Coal-bearing Strata as Oil-prone Source Rocks? Special Publication No. 77*. Geological Society, London, pp. 31–70.
- Curry, D.J., Emmett, J.K., Hunt, J.W., 1994. Geochemistry of aliphatic-rich coals in the Cooper Basin, Australia, and Taranaki Basin, New Zealand: implications for the occurrence of potentially oil-generative coals. In: Scott, A.C., Fleet, A.J. (Eds.), *Coal and Coal-bearing Strata as Oil-prone Source Rocks? Special Publication No. 77*. Geological Society, London, pp. 149–182.
- Del Rio, J.C., Philp, R.P., 1992. Oligomerization of fatty acids as a possible source for high molecular weight hydrocarbons and sulphur-containing compounds in sediments. *Organic Geochemistry* 18, 869–880.

- Del Rio, J.C., Philp, R.P., Allen, J., 1992. Nature and geochemistry of high molecular weight hydrocarbons (above C₄₀) in oils and solid bitumens. *Organic Geochemistry* 18, 541–553.
- Del Rio, J.C., Philp, R.P., 1999. Field ionization mass spectrometric study of high molecular weight hydrocarbons in a crude oil and a solid bitumen. *Organic Geochemistry* 30, 279–286.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* 272, 216–222.
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1335.
- Ge, T., Chen, Y., 1993. Liaohe Oilfield. *Petroleum Geology of China*, 3. Petroleum Industry Press, Beijing (in Chinese).
- Gelin, F., Boogers, I., Noordeloos, A.A.M., Sinninghe Damsté, J.S., Riegman, R., de Leeuw, J.W., 1997. Resistant biomacromolecules in marine microalgae of the classes Eustigmatophyceae and Chlorophyceae; geochemical implications. *Organic Geochemistry* 26, 659–675.
- Gelin, F., Volkman, J.K., Largeau, C., Derenne, S., Sinninghe Damsté, J.S., de Leeuw, J.W., 1999. Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae. *Organic Geochemistry* 30, 147–159.
- Goth, K., de Leeuw, J.W., Püttman, W., Tegelaar, E.W., 1988. Origin of Messel oil shale kerogen. *Nature* 336, 759–761.
- Hatcher, P.G., Spiker, E.C., Szverenyi, M., Maciel, G.E., 1983. Selective preservation: the origin of petroleum forming aquatic kerogen. *Nature* 305, 498–501.
- Hedberg, H.D., 1968. Significance of high wax oils with respect to genesis of petroleum. *AAPG Bulletin* 52, 736–750.
- Hsieh, M., Philp, R.P., del Rio, J.C., 2000. Characterization of high molecular weight biomarkers in crude oils. *Organic Geochemistry* 31, 1581–1588.
- Hsieh, M., Philp, R.P., 2001. Ubiquitous occurrence of high molecular weight hydrocarbons in crude oils. *Organic Geochemistry* 31, 1581–1588.
- Huang, H., Pearson, M.J., 1999. Source rock palaeoenvironments and controls on the distribution of dibenzothiophenes in lacustrine crude oils, Bohai Bay basin, eastern China. *Organic Geochemistry* 30, 1455–1470.
- Huang, H., Li, H., Ma, K., He, H., 2001. Formation condition of high wax oils in Damintun sag. *Zhiyou Yu Tianranqi Dizhi* (Oil and Gas Geology) 22, 64–67, 71 (in Chinese with English abstract).
- Huang, H., Zhen, Y., Zhang, Z., Li, J. Lacustrine biomass—a significant precursor of high wax oil. *Chinese Science Bulletin* (in press).
- Huang, Y., Geng, A., Fu, J., Sheng, G., Zhao, B., Cheng, Y., Li, M., 1992. The investigation of characteristics of biomarker assemblages and their precursors in Damintun ultra-high wax oils and related source rocks. *Organic Geochemistry* 19, 29–39.
- Killops, S.D., Carlson, R.M.K., Peters, K.E., 2000. High temperature GC evidence for the early formation of C₄₀₊ n-alkanes in coals. *Organic Geochemistry* 31, 589–597.
- Largeau, C., Casadevall, E., Kadouri, A., Metzger, P., 1984. Formation of immature Torbanite and of the resistant biopolymer (PRB A) isolated from the extant alga *Botryococcus braunii*: mechanism of formation and structure of Torbanite. *Organic Geochemistry* 10, 1023–1032.
- de Leeuw, J.W., van Bergen, P.F., van Aarsen, B.G.K., Gattelier, J.P., Sinninghe Damsté, J.S., Collinson, M.E., 1991. Resistant biomacromolecules as major contributors to kerogen. *Philosophical Transactions of the Royal Society of London B* 333, 329–337.
- Love, G.D., Snape, C.E., Fallick, A.E., 1998. Differences in the mode of incorporation and biogenicity of the principal aliphatic constituents of a Type I oil shale. *Organic Geochemistry* 28, 797–811.
- Mackenzie, A.S., 1984. Application of biological markers in petroleum geochemistry. In: Brooks, J., Welte, D. (Eds.), *Advance in Petroleum Geochemistry*, Vol. 1. Academic, London, pp. 115–214.
- Mello, M. R., Maxwell, J.R., 1990. Organic geochemical and biological marker characterization of source rocks and oils from lacustrine environments in the Brazilian Continental Margin. In: Katz, B. J. (Ed.), *Lacustrine Basin Exploration*. AAPG Memoir 50, pp. 77–97.
- Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *AAPG Bulletin* 69, 1255–1268.
- Mueller, E., Philp, R.P., 1998. Extraction of high molecular weight hydrocarbons from source rocks: an example from the Green River Formation, Uinta Basin, Utah. *Organic Geochemistry* 28, 625–631.
- Musser, B., Kilpatrick, P.K., 1998. Molecular characterization of wax isolated from a variety of crude oils. *Energy and Fuels* 12, 715–725.
- Nip, M., Tegelaar, E.W., de Leeuw, J.W., Schenck, P.A., Holloway, P.J., 1986. Analysis of modern and fossil plant cuticles by Curie point Py-GC and Curie Point Py-GC-MS: recognition of a new, highly aliphatic and resistant biopolymer. *Organic Geochemistry* 10, 769–778.
- Philp, P.R., Calvin, M., 1976. Possible origin for insoluble organic (kerogen) debris in sediments from insoluble cell wall materials of algae and bacteria. *Nature* 262, 134–136.
- Philp, P.R., 1994. Geochemical characteristics of oils derived predominantly from terrigenous source materials. In: Scott, A.C., Fleet, A.J. (Eds.), *Coal and Coal-bearing Strata as Oil-prone Source Rocks? Special Publication No. 77*. Geological Society, London, pp. 71–91.
- Powell, T.G., Boreham, C.J., 1994. Terrestrially source oils: where do they exist and what are our limits of knowledge? In: Scott, A.C., Fleet, A.J. (Eds.), *Coal and Coal-bearing Strata as Oil-prone Source Rocks? Special Publication No. 77*. Geological Society, London, pp. 11–29.
- Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. *Geochimica et Cosmochimica Acta* 59, 1895–1900.
- Tegelaar, E.W., Matthezing, R.M., Jansen, J.B.H., Horsfield, B., de Leeuw, J.W., 1989. Possible origin of n-alkanes in high wax crude oils. *Nature* 342, 529–531.
- Tegelaar, E.W., Kerp, H., Visscher, H., Schenk, P.A., de Leeuw, J.W., 1991. Bias of the paleobotanical record as a consequence of variations in the chemical composition of higher vascular plant cuticles. *Palaeobiology* 17, 133–144.
- ten Haven, H.C., de Leeuw, J.W., Rullkotter, J., Sinninghe Damsté, J.S., 1987. Restricted utility of the pristane/phytane ratio as paleoenvironmental indicator. *Nature* 330, 641–643.

- Thanh, N.X., Hsieh, M., Philp, R.P., 1999. Waxes and asphaltenes in crude oils. *Organic Geochemistry* 30, 119–132.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*, second ed.. Springer-Verlag.
- Tong, X., Huang, Z., 1991. Buried-hill discoveries of the Damintun depression in North China. *AAPG Bulletin* 75, 780–794.
- Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry* 9, 83–100.
- Volkman, J.K., 1988. Biological marker compounds as indicators of the depositional environments of petroleum source rocks. In: Fleet, A.J., Kelts, K., Talbot, M.R. (Eds.), *Lacustrine Petroleum Source Rocks*. Geological Society Special Publication 40. Blackwell, Oxford, pp. 103–122.