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The potential of bound biomarker profiles released via catalytic hydropyrolysis to reconstruct basin charging history for oils

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Abstract

Catalytic hydropyrolysis performed in a fixed bed reactor using high hydrogen gas pressures (>10 MPa) has the unique ability to release high yields of biomarker hydrocarbons from macromolecular organic fractions in petroleum source rocks and crude oils whilst minimising alteration to their isomeric distributions. One potential application of such bound biomarker profiles, which is the subject under investigation here, is to act as molecular tracers to aid the reconstruction of secondary migration pathways of oils in basins as well as reservoir filling histories. Our hypothesis is that bound biomarker compounds released from the adsorbed asphaltenes from core petroleum samples along a known migration pathway reveal the maturity and source characteristics of the first oil that came into contact with the carrier substrate. The primary investigation was performed on the Blake Field (Outer Moray Firth, UK North Sea, blocks 13/24 and 13/29), where the solvent-extractable biomarker hydrocarbon distributions exhibit no significant variations throughout the reservoir, offering little information as to reservoir filling events. Bound biomarker characterisation obtained by the hydropyrolysis of the adsorbed asphaltene fractions not only displayed lower overall maturities than the hydrocarbon biomarkers, but significantly exposed a discrete positive trend of maturity emanating from a location in the northwest part of the field which, if the original hypothesis is correct, possibly indicates the location where oil first entered the reservoir. Supplementary information obtained from laboratory experiments where two oils of subtly different composition (in terms of bound biomarker profiles) were consecutively passed through core substrates under anhydrous and hydrous conditions, and eluted with solvents of increasing polarity, revealed that the most strongly adsorbed asphaltenes exhibited bound biomarker distributions indicative of approximately 70 wt% of asphaltenes from the original oil retained on the core substrate, which is compatible with the hypothesis.

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1. Introduction

Novel techniques for probing the organic geochemical properties of petroleum reservoirs have developed significantly over the past 30 years (Larter and Aplin, 1995). Contemporary studies have focussed on providing a better understanding of reservoir filling history, which ultimately may greatly assist in the discoveries of further petroleum accumulations (Pedersen and Throndsen, 2000; Larter, 1992). An excellent overall review of the applications of petroleum geochemistry to the elucidation of secondary migration and reservoir filling history, and indeed to other reservoir management issues, is given by Peters and Fowler (2002).

Historically, the bulk geochemical heterogeneity of petroleum accumulations and reservoir properties have been utilised to decipher filling history and examine such features as compartmentalisation (Leythaeuser and Ruckheim, 1989). Heterogeneity of petroleum fluids in terms of systematic variation in polar compound distributions over lateral distances have also successfully been used to examine secondary migration and thus regional basin filling direction (Larter et al., 1996, 2000).

More recently, however, research has concentrated on the detailed transfer of petroleum fluids into reservoir structures. As the movement of petroleum during secondary migration and the early stages of entrapment occurs within a series of discrete high saturation oil stringers (England et al., 1987), discerning the locations of the entry points into a trap is essential for further discoveries of isolated near field prospects (Larter, 1992). The examination of this phenomenon requires investigation of petroleum fluids on a pore size scale. During the entrapment and filling process, changes in the physicochemical conditions of the reservoir rock cause pore filling cements to precipitate that can potentially occlude or trap any fluids adsorbed to the surface of the mineral grain. The temperature of the relevant diagenetic mineral reactions together with a direct measurement of inclusion formation temperatures, by microthermometry, may be used to indicate the relative timing of inclusion formation, and hence constrain the time when petroleum resided in the trap, which is an important parameter for basin modellers (Karlsen et al., 1993). Subsequent liberation and analysis of the hydrocarbons present in the inclusion can therefore show the character of the palaeo-petroleum composition of the reservoir relative to the currently residing petroleum and provide some indication of the charging history (George et al., 1997, 1998; Bhullar et al., 1999; Swarbrick et al., 2000; Parnell et al., 2001; Pan et al., 2002, 2003).

An alternative approach to the examination of petroleum bearing fluid inclusions has been documented as the study of discrete increments of hydrocarbon fluids trapped or occluded within the layers of adsorbed resins and asphaltenes (Behar and Vandenbrouke, 1988; Wilhelms et al., 1996; Schwark et al., 1997; Leythaeuser et al., 2000). Analytes are obtained by performing sequential solvent extraction (using solvent solutions of increasing polarity) on ground reservoir rock samples with the aim of stripping off adsorbed layers, which represent individual charges of petroleum, and releasing the occluded hydrocarbon fluids (Wilhelms et al., 1996). Hydrocarbon entities adsorbed to asphaltenes of increasing adsorptive strength have also been used to investigate migration related fractionations that might indicate reservoir filling events (Pan et al., 2002, 2003).

However, limitations to the methods previously discussed are inherent due to the quantitatively small amount of information available for analysis. For example, a typical petroleum fluid inclusion study obtains analytes by crushing the mineral matter and liberating the petroleum fluids within an organic solvent medium (Bhullar et al., 1999; Jones and Macleod, 2000). As the target analytes are quantitatively small, great care has to be taken to ensure that the mineral grains are completely free of organic matter; otherwise cross contamination may be a problem.

In this study, we propose that hydropyrolysis should be considered as a valuable supplementary tool for the reconstruction of petroleum reservoir filling history. The technique exploits a highly informative pool of hydrocarbon and biomarker compounds, which are chemically bound or trapped within the macromolecular asphaltene network (Tissot and Welte, 1984; Pelet et al., 1986; Rullkotter and Michaelis, 1990). Previous pyrolysis studies on source rock kerogens and oil asphaltenes have shown that there are striking similarities between generated molecular biomarker profiles and associated reservoired oils (Rubinstein et al., 1979; Behar and Pelet, 1985; Cassani and Eglinton, 1986; Jones et al., 1987; Connan, 1993). Although chemolysis techniques have also been used to investigate biomolecular material bound to asphaltenes and kerogens (Peng et al., 1997; Strausz et al., 1999; Peng et al., 1999a,b), they have rarely been utilised for intensive oil exploration studies due to their extremely time consuming nature. Conventional analytical pyrolysis techniques promote significant isomerisation and thermal cracking of biomarker hydrocarbon skeletons while chemolysis techniques typically generate only low yields of fragmentation products from geomacromolecules. However, hydropyrolysis has been proven to generate representative yields of bound biomarker compounds from macromolecular fractions in source rocks and oils whilst minimising alteration to their isomeric distributions (Love et al., 1995–1997). These unique characteristics dictate that hydropyrolysis can preserve and discern small but significant differences in bound biomarker maturity parameters (Murray et al., 1998).

When applied to asphaltene fractions from oils obtained from different locations in a reservoir/carrier

bed (Snape et al., 2000), it may be possible that biomarker profiles will vary systematically as a function of migration distance. The hypothesis being tested presently is whether bound biomarker compounds released from the adsorbed asphaltenes from core petroleum samples along a known migration pathway reveal the maturity and source characteristics of the oil that first came into contact with the carrier substrate, even in cases where discrete molecular components of oil have already been homogenised. In other words, are the adsorbed asphaltenes representative of the first charge of oil to contact a reservoir core?

This report presents data from an actual petroleum system case study, and together with supplemental information obtained from simple laboratory experiments, indicates that mapping the maturity of biomarkers bound to the adsorbed phase (asphaltenes) can potentially yield valuable information on reservoir filling history.

2. Petroleum geology and geochemistry of North Sea case study

Reservoir core and drill cuttings samples were obtained from the Blake Petroleum Field, Outer Moray Firth, UK North Sea (Blocks 13/24 and 13/29) (Fig. 1). The reservoir is the Lower Cretaceous Captain 'C' Sandstone Unit, which is a massive homogeneous (poorly to moderately sorted sand) linear turbidite channel, elongated in a northwest/southeast direction (Du et al., 2000). Initial reservoir modelling, based on several core plug tests from wells 13/24a-4 and 13/24a-6, which were considered representative of the whole reservoir, revealed a completely homogeneous sand body with no in built heterogeneity. Of course this may not be the entire case with the actual reservoir as there may be small heterogeneities, such as faults and small scale shale plugs that may create local barriers or "baffles" that can reduce sweep or recovery efficiency. Therefore, in an attempt to identify some of these small scale heterogeneities the geochemistry of the reservoir was assessed. Conventional geochemistry identified that oil and associated gases were generated from the Kimmeridge Clay Formation (KCF) (BG Group, unpublished data). Reflectance data indicated that on-structure KCF sediments were immature and that generation had occurred off-structure. Relative migration distances from the source kitchen to Blake Field were estimated at >50 km based on regional geological and basin modelling studies. In order to identify oil migration direction and to provide calibration data to basin modelling studies, benzocarbazole data were obtained (cf. Larter et al., 1996). The benzo[a]carbazole/benzo[c]carbazole ratios were high, which was attributed to the migration of a large oil volume through the structure rather than localised generation, which is in agreement with the reflectance data (BG Group, unpublished data). In addition, relative changes in the benzo[a]carbazole/benzo[c]carbazole ratio indicated that migration had occurred from

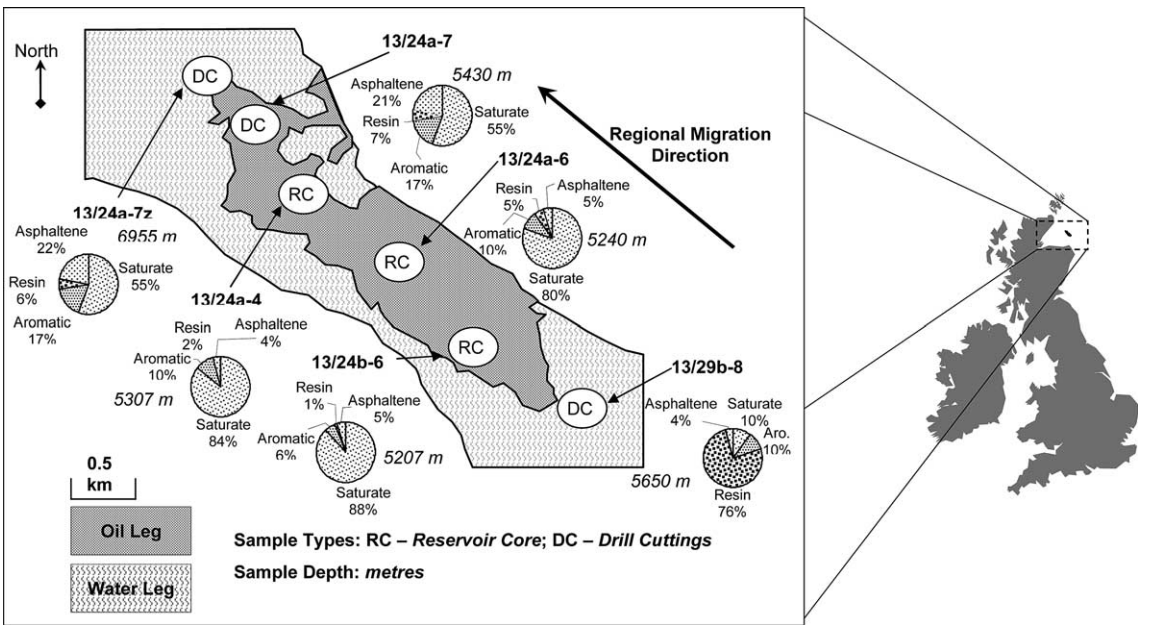

Fig. 1. The location of the Blake Petroleum Field in the Outer Moray Firth. Sample type and spatial distribution within the reservoir and relative to the source area are displayed. Extractable geochemistry of the samples are also shown.

southeast (SE) to northwest (NW), which was consistent with the perceived regional petroleum system. However, it is desirable to obtain additional, supportive data on oil migration directions on a reservoir scale, which could ultimately facilitate the discoveries of further petroleum accumulations.

3. Experimental

3.1. Geological case study

Reservoir core and drill cuttings samples were disintegrated and their individual extractable organic matter content were calculated via reflux with a standard solvent mixture (dichloromethane (CH_2Cl_2):methanol (CH_3OH) (93:7) for 24 h) followed by gentle evaporation to dryness. Asphaltene precipitation began by dissolving the whole extract in a minimum amount of CH_2Cl_2. To this solution, a 40-fold excess of chilled *n*-heptane was added, and mixed for approximately 30 min. The solution was then transferred to centrifuge tubes where the suspension was spun for 5 min at 2500 rpm. The *n*-heptane supernatant, containing the dissolved maltene fraction, was then removed. This process was repeated a minimum of 4 times, or until the *n*-heptane supernatant was pure. The maltene fractions were combined and their weights were calculated by gentle evaporation to dryness.

Asphaltene fractions were prepared for hydropyrolysis by mixing a maximum of 50 mg with silica (1:2 w/w). Each sample was impregnated with an aqueous methanol solution (20% v/v) of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] catalyst to give a nominal loading of 3 wt%. For a detailed description of the hydropyrolysis technique (see Love et al., 1995; Meredith et al., 2004). The temperature program featured resistive heating from ambient temperature (50 °C) to 250 °C at 300 °C min^{-1}, then to 500 °C at 8 °C min^{-1}, whilst maintaining a hydrogen pressure of 15 MPa and a flow rate of 10 $dm^3 min^{-1}$. Products were collected in a dry ice cooled trap containing silica sorbant (Meredith et al., 2004). Maltene fractions and hydropyrolysates were separated into aliphatic and aromatic hydrocarbons, and NSO compounds by open column liquid chromatography, upon which Gas Chromatography (GC) and Gas Chromatography–Mass Spectrometry (GC–MS) were performed.

3.2. Laboratory displacement experiments

The oils chosen for this study, which will be referred to as oil A and oil B and are unrelated to those from the Blake Field, were first characterised by the examination of their free biomarker geochemistry using open column chromatography. The bound molecular distributions were then obtained via precipitation of asphaltenes, followed by hydropyrolysis and open column chromatography. The free and bound aliphatic hydrocarbon fractions were then analysed by GC and GC–MS. To further investigate the subtle differences between the asphaltene bound biomarker distributions of the two oil samples, a series of asphaltene blends were prepared. These mixtures were set up by dissolving the asphaltenes in CH_2Cl_2 to produce known concentrations, then mixing them to the following ratios: 75% oil A and 25% oil B; 50% oil A and 50% oil B; and 25% oil A and 75% oil B. No more than 50 mg of asphaltenes underwent hydropyrolysis at one time. The product tars were then separated and analysed by open column chromatography and GC–MS.

A relatively simple experimental set up was employed to examine asphaltene adsorption and displacement behaviour, one that could be easily repeated under varying experimental conditions. In essence, a glass column was used to contain the oil and sand substrate, where upon consecutive elutions of solvents of increasing polarity would remove asphaltenes of increasing adsorptive strength.

Prior to commencement of any experiments involving oils A and B, it was necessary to investigate the adsorption behaviour and characteristics of the oil that was to simulate the in situ petroleum in the reservoir. Thus, oil A was adsorbed to 10 g of acid washed and pre-extracted sand (surface area 200 $m^2 g^{-1}$) (1:5 w/w) then placed into the column. The oil and sand substrate were then subjected to generous washing with *n*-heptane (approximately 100 ml), with the subsequent eluate undergoing asphaltene precipitation allowing the asphaltene loading on the sand to be calculated. The experiment, identified by the Roman Numeral I (subsequent experiments will also be identified by this method), progressed with the sequential elution of solvent solutions of increasing polarity: from 25%, 50%, 75% and 100% toluene in *n*-heptane, culminating in elution with CH_2Cl_2:CH_3OH solution (93:7 v/v). The asphaltene fractions were then precipitated from each of the sequential solvent eluates and subjected to hydropyrolysis. Hydropyrolysate products were then separated into aliphatic and aromatic hydrocarbons, and NSO compounds by open column chromatography and analysed via GC–MS.

To simulate the penetration of oil B into the reservoir all ready occupied by oil A, three further displacement experiments were performed. The second sequential elution experiment (II) progressed from the initial oil A adsorption stage with the introduction of oil B in such a volume that a similar amount of oil B asphaltenes were present in the experimental system as for oil A. Subsequently, the oil and sand substrate experienced a generous washing in *n*-heptane (approximately 100 ml) from which the adsorbed asphaltene content was calculated.

As with the first experiment, the oil and sand substrate were sequentially eluted with solvent solutions of increasing polarity, and their respective asphaltene fractions were precipitated and subjected to hydropyrolysis, separation and GC–MS analysis. This experimental procedure was repeated a further two times, once using double the quantity of oil B asphaltenes in relation to oil A asphaltenes (III), and secondly, using a sand substrate wetted with water (IV) with equal quantities of asphaltenes in the system. Here, the sand substrate was wetted with distilled water to give a water loading of 20 wt% prior to the adsorption of oil A. From each stage, the asphaltene hydropyrolysis products were separated and their molecular constituents analysed by GC–MS.

3.3. Gas chromatography–mass spectrometry (GC–MS) and gas chromatography (GC)

Analyses of hydrocarbon fractions were carried out on a Carlo Erba/Fisons Instruments 8000 Series (8035) gas chromatograph interfaced to a Fisons Instruments MD 800 mass spectrometer, electron voltage 70 eV with a source temperature of 280 °C. Separation was performed on a DB-1 fused silica column (50 m × 0.32 mm; film thickness 0.25 μm), composed of 100% dimethyl- polysiloxane. The GC oven temperature program began at 50 °C where it remained for 2 min. It then increased to 300 °C at 5 °C min^{-1} where it was held for 28 min. The helium carrier gas flow rate was 1 ml min^{-1} under a pressure of 90 kPa. Single ion monitoring was used to achieve greater sensitivity along with full ion scan for the identification of individual compounds. Molecular maturity parameters and quantification of individual components were facilitated by manipulation of peak area.

Gas chromatography was carried out using a Carlo Erba HRGC gas chromatograph with the flame ionisation detector (FID) attached, utilising the same column and conditions as described above.

4. Results and discussion

4.1. Geological case study

The compositions of the reservoired oil samples analysed are presented in Fig. 1. Saturate fractions are >80 wt% extractable organic matter for the reservoir core samples, which is somewhat typical for reservoir sample extracts (Tissot and Welte, 1984). These distributions are markedly higher than the drill cutting samples, especially 29b-8. Samples 24a-7 and 24a-7z show remarkable similarities to each other in terms of hydrocarbon class distribution (Fig. 1). The large resin fraction observed for sample 29b-8 may be attributed to the onset of asphaltene flocculation or deasphalting, which is commonly associated with the occurrence of gas (Tissot and Welte, 1984). Indeed, in this region of the reservoir (southeast, in the water leg) there is thought to be 10 times as much gas compared to the northwest of the reservoir (BG Group, unpublished data).

The asphaltene component of the first four samples of increasing distance from the source area are fairly uniform, with values of ~4 wt% total organic extract, where as the remaining two samples, 24a-7 and 24a-7z, have asphaltene contents exceeding 20 wt% total organic extract.

Gas chromatography, and subsequent GC–MS (Fig. 2) of the aliphatic hydrocarbons revealed the free oil in the reservoir to have experienced minor biodegradation, with only light *n*-alkanes missing (Alexander et al., 1983). Another significant feature of the *n*-alkane mass chromatograms is the relatively high abundance of *n*-C_{16} and *n*-C_{18}, particularly for the drill cuttings samples

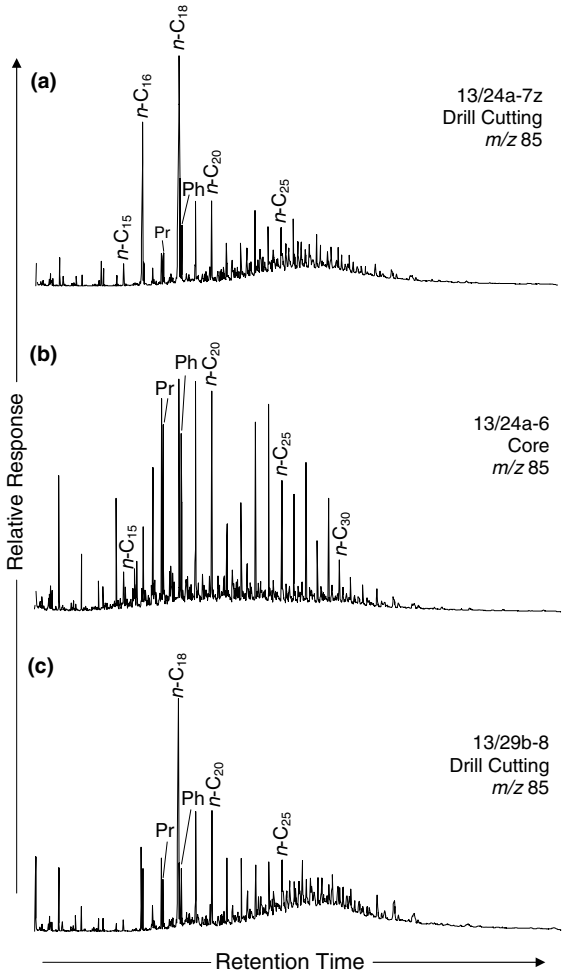

Fig. 2. Partial mass chromatograms showing *n*-alkane distributions from Blake reservoir sample extracts.

(e.g., Fig. 2(a)). These are thought to be artefacts from the drill fluids utilised in this particular field, for example, synthetic α-olefins.

The majority of sterane and hopane aliphatic biomarker maturity parameters generated from these free oil fractions show little variation throughout the reservoir, which is in agreement with earlier studies by BG Group (Table 1). However, considerable variance does exist for the C_{27} (S + R) αββ/(αββ + ααα) maturity parameter. This is thought to be the consequence of slight interference of these αββ isomers by other aliphatic hydrocarbon components that possess similar chromatographic retention times, e.g., diasteranes (Peters and Moldowan, 1993). In summary, the sterane and hopane free oil molecular evidence suggests that the whole reservoir has been completely homogenised, with the selected maturity indices revealing no information as to possible reservoir filling history.

Biomarkers bound to the asphaltene components from each sample extract were liberated via hydropyrolysis. Typical conversions of the asphaltene components were over 80% (±10) by weight product (oil) yield to starting material (Table 2), which indicates that almost all of the macromolecular material can potentially be characterised. Compound class distributions in the HyPy oils also reflect this characterisation with the dominant fraction generally composed of resin material (nitrogen, sulphur and oxygen containing compounds). These results are in agreement with previous approximations of the asphaltene macromolecular make up (e.g., Pelet et al., 1986). Of more interest here are the compositions of the aliphatic hydrocarbon fractions. In terms of commonly calculated molecular maturity parameters, those bound to the asphaltene macromolecular network display lower overall maturities relative to their free oil counterparts. This is a function of the molecule's chemical binding and hence retardation of identical isomerisation reactions that occur in free oils (Murray et al., 1998).

Contrary to the largely uniform aliphatic molecular maturity parameters revealed in the free oils, the parameters calculated from the asphaltene bound molecular components do show significant relative changes (Fig. 3). A notable difference from the free sterane distributions is the lower concentration of diasteranes in the bound profiles, which is a characteristic feature in agreement with previous reports (Murray et al., 1998). This is purely a function of sterane skeletal rearrangement

Table 1
Molecular parameters calculated from the GC–MS analysis of the aliphatic hydrocarbon fractions obtained from conventional solvent extraction of the samples along the Blake Petroleum Field[a]

Sample	C_{27} (S + R) αββ/(αββ + ααα)	C_{27} ααα S/(S + R)	C_{28} (S + R) αββ/(αββ + ααα)	C_{28} ααα S/(S + R)	C_{29} (S + R) αββ/(αββ + ααα)	C_{29} ααα S/(S + R)	Total steranes (μg/g EOM)
Free oil sterane maturity parameters							
13/24a-7z	0.53	0.45	0.70	0.35	0.60	0.51	0.027
13/24a-7	0.57	0.44	0.69	0.67	0.59	0.50	0.026
13/24a-4	0.77	0.46	0.70	0.35	0.59	0.50	0.301
13/24a-6	0.78	0.45	0.68	0.36	0.60	0.51	0.131
13/24b-6	0.67	0.52	0.70	0.35	0.60	0.50	0.536
13/29b-8	0.60	0.46	0.70	0.37	0.60	0.51	0.018

Sample	$T_s/(T_s + T_s)$	C_{29} αβ/(αβ + β α)	C_{30} αβ/(αβ + βα)	C_{31} S/(S + R)	C_{32} S/(S + R)	C_{33} S/(S + R)	C_{34} S/(S + R)	Total Hopanes (μg/g EOM)
Free oil hopane maturity parameters								
13/24a-7z	0.56	0.87	0.90	0.58	0.57	0.64	0.60	0.046
13/24a-7	0.57	0.87	0.89	0.59	0.56	0.63	0.60	0.055
13/24a-4	0.57	0.89	0.90	0.58	0.56	0.62	0.61	0.366
13/24a-6	0.56	0.89	0.89	0.57	0.57	0.64	0.60	0.177
13/24b-6	0.56	0.89	0.89	0.58	0.57	0.64	0.60	0.802
13/29b-8	0.56	0.89	0.88	0.57	0.58	0.63	0.61	0.028

Estimated error is ±5% of the values listed. Unit of measurement is μg/g total extractable organic matter (EOM).

[a] C_{27}–C_{29} (S + R) αββ/(αββ + ααα): [C_{27}–C_{29} 5α(H),14β(H),17β(H)(20S + 20R)]/[C_{27}–C_{29} 5α(H),14β(H),17β(H)(20S + 20R) steranes + C_{27}–C_{29} 5α(H),14α(H),17α(H) (20S + 20R) steranes]; C_{27}–C_{29}ααα S/(S + R): [C_{27}–C_{29} 5α(H),14α(H),17α(H)(20S)]/[C_{27}–C_{29} 5α(H),14α(H),17α(H)(20S) + C_{27}–C_{29} 5α(H),14α(H),17α(H)(20R)]; $T_s/(T_s + T_s)$: 18α,21β(H)-22,29,30-trisnorneohopane/[18α,21β(H)-22,29,30-trisnorneohopane + 17α,21β(H)-22,29,30-trisnorhopane]; C_{29}αβ/(αβ + βα): 17α,21β(H)-30-norhopane/[17α,21β(H)-30-norhopane + 17β,21α(H)-30-normorehopane]; C_{30}αβ/(αβ + βα): 17α,21β(H)-hopane/[17α,21β(H)-hopane + 17β,21α(H)-moretane]; C_{31}–C_{34} S/(S + R): (22S)-17α,21β(H)-homohopanes/[(22S)-17α,21β(H)-homohopanes + (22R)-17α,21β(H)-homohopanes]; μg/g EOM: Total sterane and hopane yields based on molecular ion using 5β(H) cholane internal standard, assuming a relative response factor of 1.

Table 2
Analytical data for Blake Reservoir samples investigated: hydropyrolysate yields and product compositions

Sample/well name	Sample type	HyPy product (wt%)[a]	Saturates (wt%)[b]	Aromatics (wt%)[b]	Resins (wt%)[b]
13/24a-7z	DC	100	12	3	85
13/24a-7	DC	96	22	4	74
13/24a-4	RC	80	21	14	64
13/24a-4 *repeat*	RC	80	25	9	66
13/24a-6	RC	100	20	30	50
13/24b-6	RC	100	14	14	71
13/29b-8	DC	80	50	25	25

A repeat analysis of sample 13/24a-4 is also included.
[a] Hydropyrolysate product oil as weight percent of starting asphaltene fraction ±10, the calculated error of measurement.
[b] Saturate and aromatic hydrocarbons, and resin fractions as percent weight of extractable or hydropyrolysate oil.

being inhibited as they are chemically bound to the macromolecular asphaltene structure. The relatively small concentrations that do exist may be products of sterane rearrangement prior to incorporation into the asphaltene molecular network. The assessment of C_{27} and C_{28} ααα S/(S + R) and (S + R) (αββ + β αα)/((αββ + βαα) + ααα) sterane maturity parameters are therefore less problematic compared to free oil distributions, where co-elution with diasteranes can produce spurious results, as alluded to previously. However, in the case of hydropyrolysis oils, C_{27}–C_{29} sterane αββ isomeric distributions may be slightly enhanced by βαα isomers (Love, *pers. comm.*). Therefore, it is important to note that the assessment of the maturity parameter C_{2n} (S + R) αββ/(αββ + ααα) must include some βαα isomers to give C_{2n} (S + R) (αββ + βαα)/((αββ + βαα) + ααα). Previous examinations of βαα isomers have revealed that they are in relatively small amounts, and therefore will not interfere with the applicability of the isomeric ratio as a useful maturity parameter. The bound profiles also appear to reveal a preferential incorporation of C_{29} isomeric components, notably C_{29} ααα S, therefore generating relatively lower ααα S/(S + R) ratios compared with their C_{27} and C_{28} counterparts (Fig. 3).

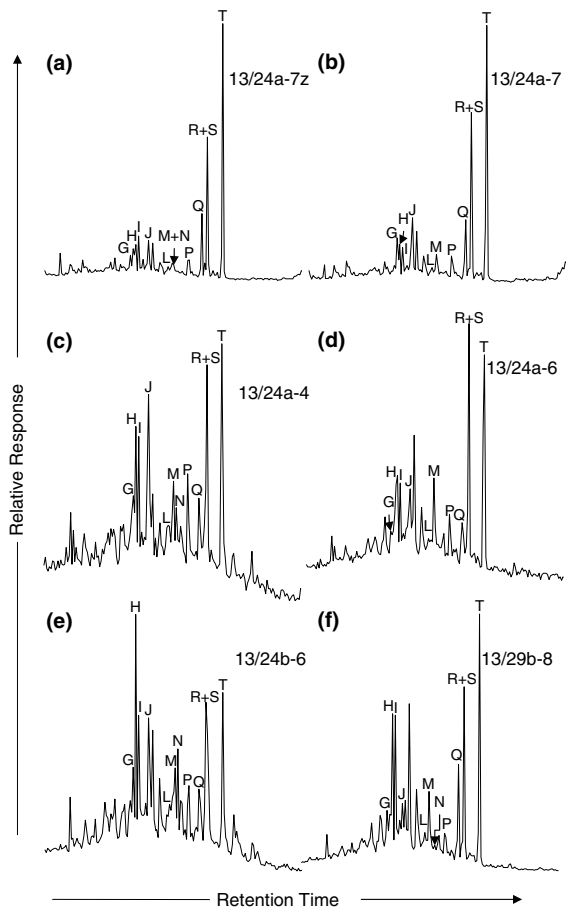

Fig. 3. Asphaltene bound sterane distributions (*m/z* 217) from the Blake Field reservoir samples. Key to labelling system in Table 3.

Where available, it is apparent that asphaltene bound hopane distributions are also different from their free counterparts. However, absolute hopane concentrations are significantly lower than for the sterane biomarkers, and in most cases beyond the analytical capability here. The lack of hopane biomarkers in this instance may also be a consequence of the hopane precursors containing multiple heteroatomic sites available for cross-linking into the asphaltene macromolecular structure, as opposed to one functionalised group available in sterane precursors. Therefore cleavage of only one bond is required to liberate sterane biomarkers, which is relatively easier than the cleavage of several bonds as is the case with the hopanes (Murray et al., 1998; Hoffmann et al., 1992; Mycke and Michaelis, 1986).

Focussing on overall asphaltene bound biomarker maturity patterns within the homogenised free oil reservoir (Fig. 4), one positive trend of maturity exists, which progresses in a SE direction from a source between samples 24a-4 and 24a-7. This is suggested in Fig. 4(a) and (b), where both maturity parameters

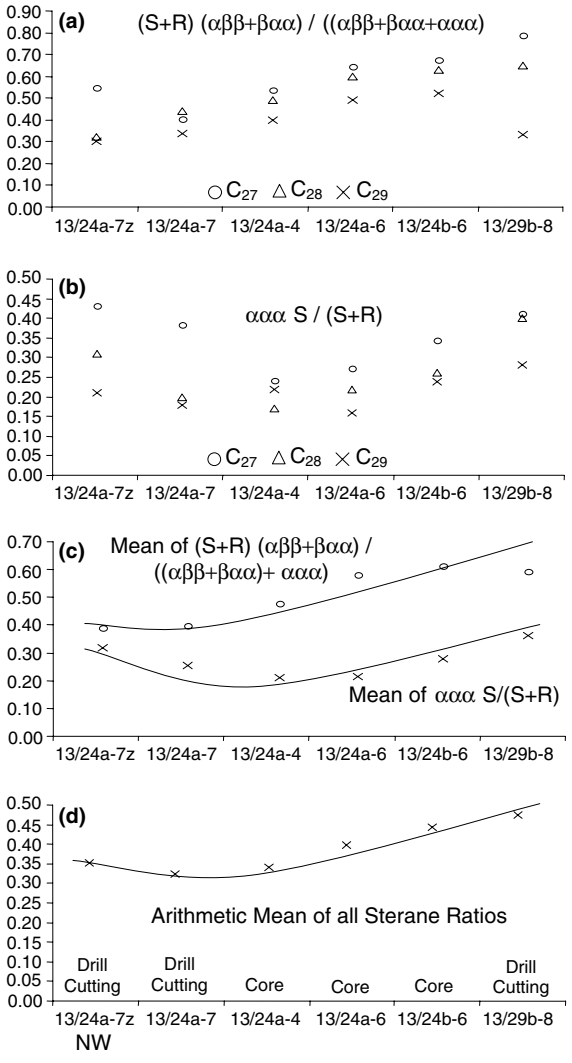

Fig. 4. Variation in sterane biomarker maturity parameters generated by hydropyrolysis of asphaltenes from the Blake Field.

((S + R) (αββ + βαα)/((αββ + βαα) + ααα) and ααα S/(S + R)) exhibit a general correlation to each other between most available sterane homologues. However, spurious data is evident, for example, the ααα S/(S + R) ratio for C_{27} and C_{28} sterane homologues increase from sample 24a-4 to 24a-6 while for sterane C_{29} the ratio decreases. Further, such data are also apparent for samples 24a-7 and 24a-7z. For example, C_{29} ααα S/(S + R) decreases from 24a-4 to 24a-7, whereas the same ratios for C_{27} and C_{28} increase.

The experimental error associated with these measurements was determined by the comparison of C_{27}, C_{28} and C_{29} (S + R) (αββ + βαα)/((αβ β + βαα)+ααα) and C_{27} and C_{29}ααα S/(S + R) obtained from the complete replicate analysis of sample 24a-4, whose hydropyrolysate yield and product composition are outlined in Table 2. The ratio of C_{28} ααα S/(S + R) was omitted due to a spuriously high C_{28} ααα R peak. The error represents the standard deviation about the mean of ratios, and in all cases was calculated to be 0.01, with the exception being C_{28} (S + R) (αββ + βαα)/((αββ + βαα) + ααα), which incorporates a spurious C_{28} ααα R peak, coming out at 0.04. Importantly, such error does not have a significant impact on the observed trend. In an attempt to rationalise the inconsistencies mentioned previously, and also reduce the impact of spurious values such as the C_{27} and C_{29} (S + R) (αββ + βαα)/((αββ + βαα)+ααα) for sample 29b-8, the former showing a value that is above the end point for this particular isomerisation reaction (Peters and Moldowan, 1993), and the C_{29} ααα S/(S + R) ratio for sample 24a-4, the sterane ratios were averaged separately (Fig. 4(c)) and all together (Fig. 4(d)), with the experimental error of approximately 5% also applicable. The values presented here suggest that there is a discrete positive trend in maturity emanating from a source to the northwest of sample 24a-4. This may extend to sample 24a-7, but as there is a relatively poor correlation between the sterane isomerisation ratios for this sample and indeed for 24a-7z, they must be approached with caution i.e. in Fig. 4(c), the arithmetic mean of the (S + R) (αββ + βαα)/((αββ + βαα)+ααα) ratios are lower than sample 24a-4 whereas the average αααS/(S + R) ratios are higher.

It has already been observed that samples 24a-7 and 24a-7z contain considerably higher relative amounts of asphaltenes as compared to the other samples in the series (Fig. 1). The asphaltene bound hopane distributions from these samples were found to contain trace amounts of ββ-hopanes ranging from C_{31} to C_{35}. The origin of this unusual and immature signal could arise from a number of sources. For example, as these samples are drill cuttings, the ββ-hopanes could originate from a heavy oil fraction present as a drill fluid additive, which, in this case, is represented by the increased asphaltene content relative to the other samples. Therefore, these would be precipitated during the experimental procedure together with the indigenous asphaltenes and may provide this very immature bound signal. Alternatively, or additionally, this hopane signal could be an artefact from aerobic microbial attack that the samples may have experienced during storage. It is also important to note that for samples 24a-7 and 24a-7z, C_{29} steranes appear to be slightly enriched relative to their C_{27} and C_{28} sterane homologues compared to the other samples in the set (cf. Fig. 3), and even to the other drill cuttings sample, 29b-8, which incidentally contains no ββ configuration hopanes. This feature could represent an input from an extraneous asphaltic source, and thus account for the lack of correlation between (S + R) (αββ + βαα)/((αββ + βαα) + ααα) and ααα S/(S + R) ratios for

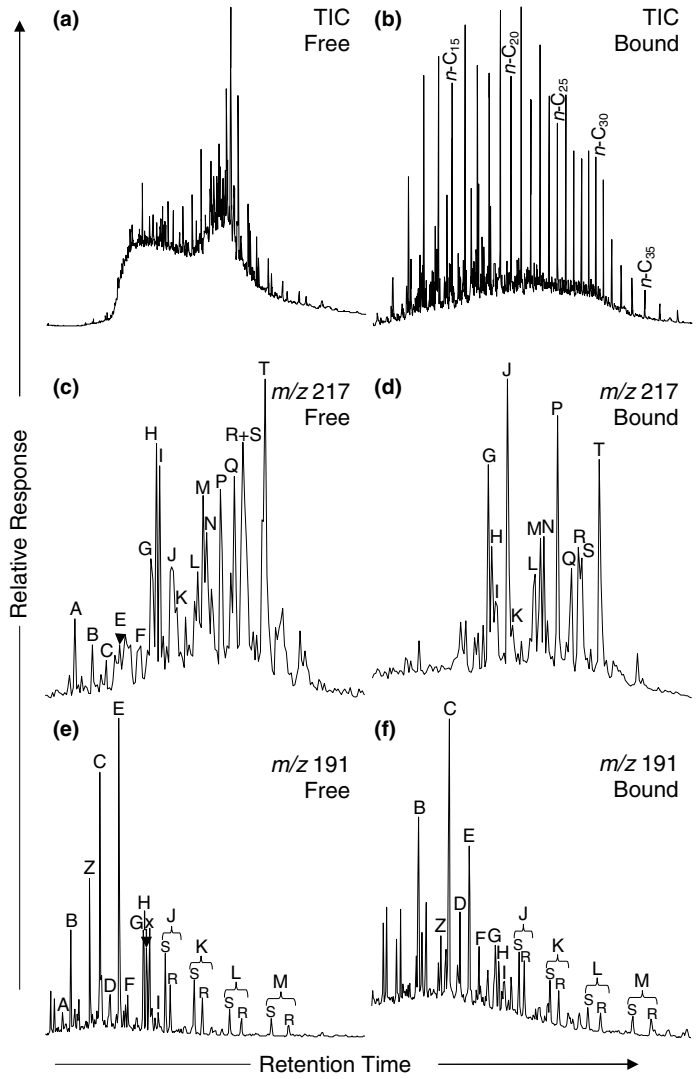

Fig. 5. Free oil and asphaltene bound biomarker distributions for oil A. Key to labelling system in Table 3.

samples 24a-7 and 24a-7z, as shown in Fig. 4. Thus although we believe the sterane signals from samples 29b-8, 24b-6, 24a-6 and 24a-4 to be representative of sample maturity, caution must be observed for the interpretation of samples 24a-7 and 24a-7z, as it appears they have been contaminated by mixing with foreign high molecular mass material present in the drilling fluid, e.g. lignites, which is the most probable explanation in this case. Work in progress therefore involves the isolation of these asphaltic drill fluid additives followed by an examination of their bound biomarker geochemistry.

If the original hypothesis is correct, and the adsorbed asphaltenes on a particular core represent the first charge of oil to contact the rock, the maturity trend revealed by the hydropyrolysis of the adsorbed asphaltenes possibly indicates that at least two thirds of the reservoir may have filled in the direction of northwest to southeast, which is opposite to the regional secondary migration trend. When observed elsewhere, this phenomenon has been recognised as reservoir backfilling. However, the discrete increase in maturity from samples 24a-4 to 24b-6 may not reflect filling direction, but may merely be a consequence of reservoir filling from bottom (sample 24a-4; 5307 m depth) to the top (sample 24b-6; 5207 m depth). If indeed further geochemical evidence can be gathered to confirm the maturity trend from 24a-7 and 24a-7z, then the location of the reservoir fill point can be narrowed down to between sampling localities 24a-4 and 24a-7. Of course, there may be further explanations for the observed maturity trend as the full

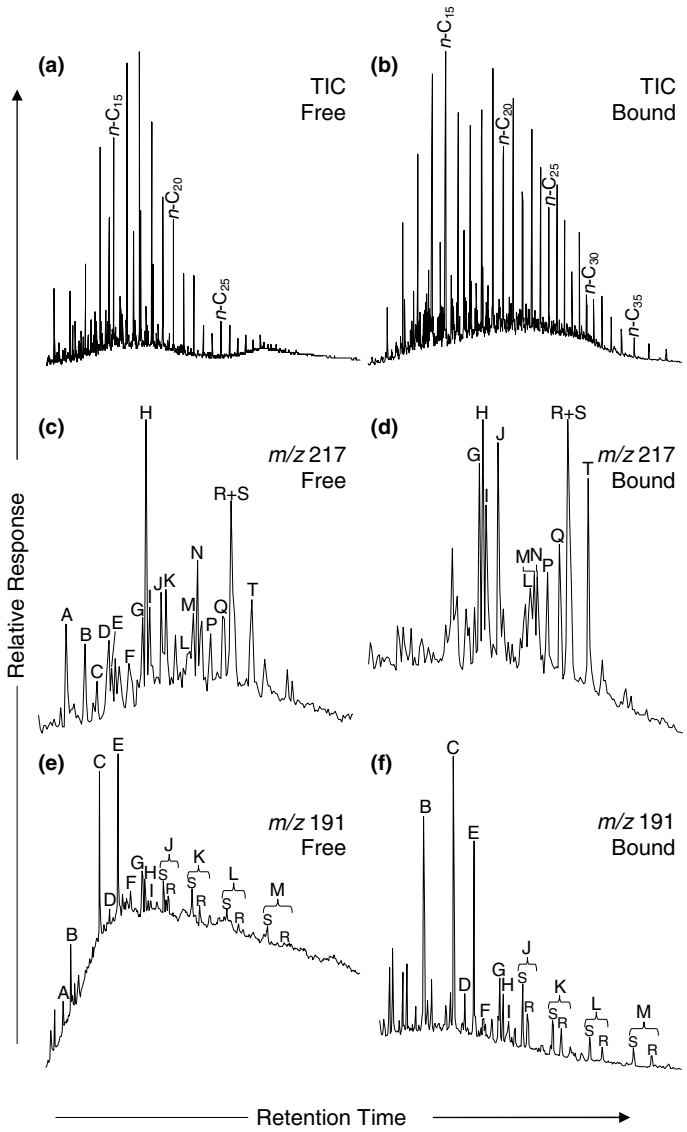

Fig. 6. Free oil and asphaltene bound biomarker distributions for oil B. Key to labelling system in Table 3.

geological picture has yet to be ascertained. Nonetheless, notwithstanding samples 24a7 and 24a-7z, this first examination of reservoir – adsorbed asphaltene – bound biomarkers has indeed produced some indication of reservoir filling history where the use of the conventional biomarker approach is insufficient due to whole reservoir molecular homogenisation.

4.2. Laboratory experiments

Wilhelms et al. (1996) and Schwark et al. (1997) describe a conceptualised model to illustrate the progressive filling of reservoir rock pore space networks; i.e. the "onion skin" model. This dictates that petroleum migration into fresh reservoir pore space is followed by adsorption of polar/asphaltene material onto water wet mineral grains. Subsequent adsorption onto this initial layer may trap or occlude small increments of the migrating petroleum, which when analysed may provide information on reservoir charging events. However, as the focus of attention in this study is on the potential of adsorbed asphaltene layers to provide information as to reservoir filling history, it is necessary to investigate whether the asphaltenes of increasing adsorptive strength/polarity have a systematic effect on bound biomarker distributions, and to examine which of the

Table 3
Labelling system for hopane (*m/z* 191) and sterane (*m/z* 217) partial mass chromatograms

Peak	Compound name (hopanes, *m/z* 191)	Formula	Peak	Compound name (steranes, *m/z* 217)	Formula
A	18α,21β(H)-22,29,30-Trisnorneohopane	$C_{27}H_{46}$	A	(20S)-13β,17α(H)-Diacholestane	$C_{27}H_{48}$
B	17α,21β(H)-22,29,30-Trisnorhopane	$C_{27}H_{46}$	B	(20R)-13β,17α(H)-Diacholestane	$C_{27}H_{48}$
Z	17α,18α,21β(H)-28,30-Bisnorhopane	$C_{28}H_{48}$	C	(20S)-13α,17β(H)-Diacholestane	$C_{27}H_{48}$
C	17α,21β(H)-30-Norhopane	$C_{29}H_{50}$	D	(20S)-13β,17α(H)-24-Methyldiacholestane	$C_{28}H_{50}$
D	17β,21α(H)-30-Normorehopane	$C_{29}H_{50}$	E	(20S)-13α,17β(H)-24-Methyldiacholestane	$C_{28}H_{50}$
E	17α,21β(H)-Hopane	$C_{30}H_{52}$	F	(20R)-13β,17α(H)-24-Methyldiacholestane	$C_{28}H_{50}$
F	17β,21α(H)-Moretane	$C_{30}H_{52}$	G	(20S)-5α,14α,17α(H)-Cholestane	$C_{27}H_{48}$
G	(22S)-17α,21β(H)-Homohopane	$C_{31}H_{54}$	H	(20R)-5α,14β,17β(H)-Cholestane	$C_{27}H_{48}$
H	(22R)-17α,21β(H)-Homohopane	$C_{31}H_{54}$	I	(20S)-5α,14β,17β(H)-Cholestane	$C_{27}H_{48}$
x	Gammacerane	$C_{30}H_{52}$	J	(20R)-5α,14α,17α(H)-Cholestane	$C_{27}H_{48}$
I	17β,21α(H)-Homomoretane	$C_{31}H_{54}$	K	(20S)-13β,17α(H)-24-Ethyldiacholestane	$C_{29}H_{52}$
J	(22S)-17α,21β(H)-Dihomohopane	$C_{32}H_{56}$	L	(20S)-5α,14α,17α(H)-24-Methylcholestane	$C_{28}H_{50}$
	(22R)-17α,21β (H)-dihomohopane	$C_{32}H_{56}$	M	(20R)-5α,14β,17β(H)-24-Methylcholestane	$C_{28}H_{50}$
K	(22S)-17α,21β(H)-Trihomohopane	$C_{33}H_{58}$	N	(20S)-5α,14β,17β(H)-24-Methylcholestane	$C_{28}H_{50}$
	(22R)-17α,21β(H)-Trihomohopane	$C_{33}H_{58}$	P	(20R)-5α,14α,17α(H)-24-Methylcholestane	$C_{28}H_{50}$
L	(22S)-17α,21β(H)-Tetrahomohopane	$C_{34}H_{60}$	Q	(20S)-5α,14α,17α(H)-24-Ethylcholestane	$C_{29}H_{52}$
	(22R)-17α,21β(H)-Tetrahomohopane	$C_{34}H_{60}$	R	(20R)-5α,14β,17β(H)-24-Ethylcholestane	$C_{29}H_{52}$
M	(22S)-17α,21β(H)-Pentahomohopane	$C_{35}H_{62}$	S	(20S)-5α,14β,17β(H)-24-Ethylcholestane	$C_{29}H_{52}$
	(22R)-17α,21β(H)-Pentahomohopane	$C_{35}H_{62}$	T	(20R)-5α,14α,17α(H)-24-Ethylcholestane	$C_{29}H_{52}$

asphaltenes are most susceptible to displacement by further petroleum charges.

The oil samples selected for this purpose were on the basis of distinct free oil biomarker distributions, with the premise that these differences could be reflected in bound profiles. Typical biomarker characterisation of the samples, referred to as oil A and oil B, in both free and bound phases are displayed in Figs. 5 and 6, respectively. The asphaltene component of oil A is ~12 wt% and oil B is ~5 wt% of total oil separated.

In terms of free *n*-alkane distributions, it appears that oil A (Fig. 5(a)) has experienced moderate biodegradation (level 5) (Alexander et al., 1983), with the *n*-alkane distributions removed and the isoprenoid concentrations greatly reduced, whereas oil B (Fig. 6(a)) appears relatively less affected by such processes. Further differences are apparent with regard to commonly observed sterane and hopane biomarker distributions (Figs. 5 and 6(c) and (e)), with oil B exhibiting a greater overall maturity than oil A. Also of particular value is the occurrence of gammacerane in oil A, which is not apparent in significant quantities in oil B. The *n*-alkane distributions generated from oil A asphaltenes (Fig. 5(b)) indicate how powerful the application of hydropyrolysis can be when used on biodegraded heavy oil fractions. A pristine *n*-alkane distribution is revealed, with chain lengths exceeding *n*-C_{35}, which incidentally exceeds those displayed for free oil B.

Unfortunately, bound gammacerane from oil A is present in much lower amounts relative to regular hopanes in comparison with free hydrocarbons. Indeed, there appears to be very little significantly useful disparities between oil A and oil B bound hopane distributions (see Figs. 5(f) and 6(f)), but within the steranes there remains large differences, particularly for the C_{29} homologues. For example, the C_{29} (S + R) αββ/(αββ + ααα) maturity parameter for asphaltene bound oil A is 0.41 compared to 0.54 in oil B.

Although key differences to the bound biomarker distributions monitored in this study are mainly restricted to the C_{28} and C_{29} steranes, this may actually reflect the situation in a real geological setting where only subtle differences in maturity are available as indicators of different source rock facies input (see Table 3).

As the major discriminating parameters for oil A and oil B asphaltene bound biomarker distributions have been identified, it is important to obtain some indication as to the relative contribution from each heavy oil fraction to the overall sterane pool. Crucially, it appears that absolute concentrations of C_{27} – C_{29} steranes between the asphaltene fractions from oil A and oil B are within the same order of magnitude (oil A and oil B asphaltenes yielding 0.12 and 0.035 $\mu g\, g^{-1}_{asphaltene}$, respectively). The overall biomarker contributions from each oil asphaltene were further examined by the analysis of a series of mixtures (Table 4). Certain molecular tracking indices show remarkable agreement with the predicted values, such as C_{28} (S + R) αββ/(αββ + ααα), whereas other parameters displayed a greater variability or hardly any difference at all (e.g. C_{29} (S + R) αββ/(αββ + ααα)). In an attempt to compensate for these inconsistencies, the arithmetic mean of all the sterane molecular tracking parameters were calculated and compared to the predicted values. Here, the actual values are exactly as

Table 4
Oil A and oil B asphaltene component mixtures generated from hydropyrolysis

Sample	C_{27} sterane (S + R) αββ/(αβ β + ααα)	C_{27} sterane ααα S/(S + R)	C_{28} sterane (S + R) αββ/(αββ + ααα)[a]	C_{28} sterane ααα S/(S + R)	C_{29} sterane (S + R) αββ/(αββ + ααα)	C_{29} sterane ααα S/(S + R)	Arithmetic mean
Oil A asphaltene	0.32	0.36	0.41	0.36	0.41	0.33	0.37
75% A 25% B measured	0.41	0.39	0.43	0.31	0.49	0.37	0.40
75% A 25% B *predicted*	0.37	0.37	0.44	0.40	0.44	0.36	0.40
50% A 50% B measured	0.51	0.41	0.48	0.26	0.49	0.41	0.43
50% A 50% B *predicted*	0.41	0.39	0.48	0.43	0.48	0.38	0.43
25% A 75% B measured	0.46	0.47	0.52	0.30	0.47	0.43	0.44
25% A 75% B *predicted*	0.46	0.40	0.51	0.47	0.51	0.41	0.46
Oil B asphaltene	0.50	0.41	0.54	0.50	0.54	0.43	0.49

[a] For a definition of molecular parameters refer to Table 3.

predicted for the 75% A–25% B and 50% A–50% B mixtures, and fall slightly below the 25% A–75% B value (Table 4). This may be attributed to the slightly less overall sterane contribution coming from oil B as mentioned earlier. Nevertheless, all the actual values are within experimental error (±5%), indicating that this interpretative process has potential to be used to track the relative inputs from oil A and oil B during the forthcoming experiments.

Prior to the oil A and oil B asphaltene displacement experiment, the bound molecular profiles from asphaltene layers of increasing polarity were inspected so that any discernable fractionation of biomarker parameters could be assessed. This is extremely important as any significant difference between biomarker parameters from asphaltenes of different polarity could seriously undermine the results for a multi-oil asphaltene displacement system. The analytical mass balance for single oil A sequential elution is outlined in Table 5, (experiment I). Importantly the solvent gradient employed yields significant quantities of asphaltene fractions that equate to asphaltenes of increasing polarity. The quantities of the asphaltene fractions generated from sample solutions of 50% toluene in *n*-heptane and above are about double those of the maltene fractions. This is a significant factor as previous studies that have employed sequential solvent extraction (e.g. Wilhelms et al., 1996; Schwark et al., 1997) utilise maltene fractions that become increasingly small quantitatively, whereas in this study the asphaltene fractions are continuously of substantial quantities to enable hydropyrolysis to provide consistently representative aliphatic hydrocarbon distributions.

The sterane parameters generated from each asphaltene fraction are listed in Table 6. Here, the sterane molecular tracking indices generated from the asphaltenes from each solvent elute are listed. Also quoted are the arithmetic mean of each parameter (last row), which should equate to the value obtained from the hydropyrolysis of the whole asphaltene fraction from oil A (first row). These values show remarkable agreement with those obtained from hydropyrolysis of asphaltenes from whole oil A, which is borne out by the fact that arithmetic mean of all the averaged sterane parameters from each eluate are almost identical to that of whole oil A. In context of the overall differences between oil A and oil B asphaltene bound sterane distributions, the ratios from the increasingly polar asphaltene fractions generated from the solvent gradient display relatively insignificant variations. Essentially, this single oil asphaltene sequential elution experiment indicates that there is very little fractionation of biomarker distributions between asphaltenes of different polarity. Therefore, the degree of displacement encountered by oil A asphaltenes by the introduction of oil B should be accurately examined.

Table 5
Analytical mass balance for sequential solvent elution experiments: I involving only oil A asphaltenes; II involving equal amounts of oil A and oil B asphaltenes

	I		II										I	II
Starting oil A (mg)	1500			1714					Starting oil B (mg)				0	3721
Starting asphaltenes A (mg)	195			222.8					Starting asphaltenes B (mg)				0	223.3
Solvent solution	0%[a]		25%		50%		75%		100%		CH_2Cl_2: CH_3OH[b]		Total recovery	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Maltene fraction (wt% total oil)	77.27	85.3	6.27	2.2	1.13	0.2	0.27	0.1	0.2	0.02	0.47	0.02	85.6 wt%[c]	87.9 wt%[c]
Asphaltenes in eluant (mg)	10	189	16	10	31	24	26	17	10	7	14	36	107 mg	283 mg
Asphaltenes in eluant (wt% total asphaltene)	5	42.5	8	2	16	5	13	4	5	2	7	8	55 wt% (±10)[d]	63 wt% (±10)[d]
Asphaltene fraction (wt% Total Oil)	0.67	3.5	1.07	0.2	2.07	0.4	1.73	0.3	0.67	0.1	0.93	0.7	7.14 wt%[c]	5.2 wt%[c]
											Overall Loss		7.25 wt% (±10)[c]	6.96 wt% (±10)[c]
Asphaltene substrate loading (wt%)	1.85	2.6	1.69	2.9	1.38	2.9	1.12	2.8	1.02	3.0	0.85	2.7		
Composition of asphaltene hydropyrolysis oils														
Aliphatic hydrocarbons (mg/g total oil)	0.67	2.69	2.00	0.24	3.33	0.44	1.33	0.37	0.67	0.11	0.67	0.44	8.67	4.29
Aliphatic hydrocarbons (wt% total asphaltene)	0.5	2.1	1.5	0.3	2.6	0.5	1.1	0.4	0.5	0.1	0.5	0.5	6.7	3.9

[a] % toluene in *n*-heptane.
[b] A 93:7 v/v mixture of CH_2Cl_2 and CH_3OH.
[c] wt% Total Oil.
[d] wt% total asphaltene.

Table 6
Selected sterane (*m/z* 217) maturity parameters monitored for Oil A Sequential Elution and hydropyrolysis of asphaltenes

Sample	C_{27} sterane (S + R) αββ/(αββ + ααα)	C_{27} sterane ααα S/(S + R)	C_{28} sterane (S + R) αββ/(αββ + ααα)	C_{28} sterane ααα S/(S + R)	C_{29} sterane (S + R) αββ/(αββ + ααα)	C_{29} steran ααα S/(S + R)	Arithmetic mean
Oil A	0.32	0.36	0.41	0.36	0.41	0.33	0.37
0% toluene	0.36	0.42	0.43	0.42	0.42	0.32	0.40
25% toluene	0.29	0.35	0.37	0.42	0.41	0.26	0.35
50% toluene	0.30	0.35	0.39	0.40	0.40	0.32	0.36
75% toluene	0.28	0.31	0.39	0.34	0.43	0.32	0.35
100% toluene	0.15	0.29	0.43	0.45	0.43	0.29	0.34
CH_2Cl_2:CH_3OH	0.30	0.37	0.43	0.42	0.41	0.31	0.37
Arithmetic Mean	0.28	0.35	0.41	0.41	0.42	0.31	0.36

Analytical data for the oil A and oil B sequential elution experiment are also displayed in Table 5 (experiment II). Once again there is a dramatic fall off in the quantities of maltene material accompanied by a continual increase in asphaltenes with solvent solutions of increasing polarity.

According to the hypothesis, the introduction of oil B asphaltenes into the experimental system will not displace the previous adsorbed asphaltenes from oil A. Therefore, it was expected that the solvent solutions that liberate the relatively more tightly bound asphaltene fractions should exhibit sterane molecular parameters more characteristic of oil A than oil B asphaltenes, as oil A was the first oil to contact the pore system. The selected sterane parameters from the most strongly adsorbed asphaltene fraction (liberated by CH_2Cl_2:CH_3OH elution) are listed in Table 8 together with the overall values for oil A and oil B asphaltenes for comparison. Here the arithmetic mean of all the sterane parameters equate to 0.40, which indicates that approximately 75% of the asphaltenes liberated by CH_2Cl_2:CH_3OH originate from oil A.

Further experiments were conducted using double the quantity of oil B asphaltenes as opposed to oil A (experiment III), and using similar quantities of oil A and oil B asphaltenes but with a water wet sand substrate (experiment IV). The mass balance for these experiments is displayed in Table 7. When double the quantity of oil B asphaltenes as opposed to oil A enters the system, there appears to be a large displacement of both asphaltenes from the substrate sand. Approximately 70 wt% of the total asphaltenes are removed with elution of the first solvent. Although there are less asphaltenes in the experimental system and therefore less asphaltenes on which to perform hydropyrolysis, reliable biomarker fingerprints were still generated, often from as little as 2 mg. The use of a water wet sand substrate appears to slightly decrease the efficiency of the adsorptive processes of the asphaltenes. Relative to experiment II, the total amount of asphaltenes recovered from the first elution with *n*-heptane is approximately 10 wt% higher. Overall, at each elution step, more asphaltenes are liberated compared to experiment II, which culminates in negligible experimental loss. The values from the sterane parameters generated by the hydropyrolysis of the most strongly adsorbed asphaltenes in experiments III and IV are again listed in Table 8. The arithmetic mean of the sterane parameters from experiment III (double the quantity of oil B asphaltenes in system as opposed to oil A) is slightly higher relative to experiment II, where there are similar quantities of asphaltene in the system. Nonetheless, the most strongly adsorbed asphaltenes still retain an approximate sterane signature from oil A of 70%. The presence of water in the asphaltene elution system appears not to have greatly altered the results using dry (anhydrous) sand (experiment II). Indeed the arithmetic mean of the sterane parameters is identical to that of the dry sand experiment.

Overall assessment of the selected sterane parameters monitored indicates that approximately 70 wt% of oil A asphaltenes remain adsorbed to the column substrate, even when the system is saturated to excess with oil B. This connection is clearly displayed in Fig. 7, which shows the close visual relationship of the most strongly adsorbed asphaltene fractions from each experiment (Fig. 7(c)–(f)) to that of the sterane distributions generated from oil A asphaltenes (Fig. 7(a)), which is quite different from that of oil B (Fig. 7(b)).

Therefore, the analysis of the most strongly adsorbed asphaltene fractions should yield molecular information representative of the oil that first penetrated the pore space network of a reservoir rock. Although further research is required to investigate the adsorption behaviour of asphaltenes in greater detail, for example, in a system that is more representative of actual reservoir conditions i.e. pressures, temperatures, brines etc., the preliminary study out-

Table 7
Analytical mass balance for sequential solvent elution experiments: III involving double the quantity of oil B asphaltenes as opposed to oil A; IV involving similar amounts of asphaltenes but on a water wet sand substrate with an initial water loading of 20 wt%

	II		IV										III	IV
Starting oil A (mg)	1545		1583				Starting oil B (mg)						6696.7	3434
Starting asphaltenes A (mg)	200.9		205.8				Starting asphaltenes B (mg)						401.8	206.0
Solvent solution	0%[a]		25%		50%		75%		100%		Cl_2CH_2: CH_3OH[b]		Total recovery	
	III	IV	III	IV	III	IV	III	IV	III	IV	III	IV	III	IV
Maltene fraction (wt% total oil)	82.5	94.6	0.12	1.6	0.06	0.2	0.01	0.04	0.01	0.01	0.01	0.02	82.7 wt%[c]	96.5 wt%[c]
Asphaltenes in eluant (mg)	427	213.8	2	7.4	10	30	2	31.5	3	6.2	6.6	9.8	450.6 mg	298.7 mg
Asphaltenes in eluant (wt% Total Asphaltene)	70.9	51.9	0.3	1.8	1.7	7.3	0.3	7.6	0.5	1.5	1.1	2.4	75 wt% (±10)[d]	72.5 wt% (±10)[d]
Asphaltene fraction (wt% total oil)	5.18	4.3	0.02	0.1	0.12	0.6	0.02	0.6	0.04	0.1	0.08	0.1	5.46 wt%[c]	5.9 wt%[c]
											Overall Loss		11.84 wt% (±10)[c]	0 wt% (±10)[c]
Asphaltene substrate loading (wt%)	1.9	2.1	1.8	2.1	1.8	1.8	1.8	1.5	1.8	1.4	1.8	1.3		
Composition of asphaltene hydropyrolysis oils														
Aliphatic hydrocarbons (mg/g total oil)	0.50	0.80	0.02	0.20	0.16	0.76	0.08	0.62	0.04	0.20	0.12	0.24	0.92	2.81
Aliphatic hydrocarbons (wt% total asphaltene)	0.93	0.92	0.03	0.54	0.22	0.92	0.12	0.75	0.05	0.24	0.17	0.29	1.52	3.38

[a] % toluene in *n*-heptane.
[b] A 93:7 v/v mixture of CH_2Cl_2 and CH_3OH.
[c] wt% Total oil.
[d] wt% Total asphaltene.

Table 8
Oil A and oil B sequential elution

Sample	C_{27} sterane (S + R) αββ/(αββ + ααα)	C_{27} sterane ααα S/(S + R)	C_{28} sterane (S + R) αββ/(αββ + ααα)	C_{28} sterane ααα S/(S + R)	C_{29} sterane (S + R) αββ/(αββ + ααα)	C_{29} sterane ααα S/(S + R)	Arithmetic mean
Oil A	0.32	0.36	0.41	0.36	0.41	0.33	0.37
I	0.30	0.37	0.43	0.42	0.41	0.31	0.37
II	0.36	0.37	0.43	0.43	0.46	0.34	0.40
III	0.43	0.40	0.47	0.34	0.48	0.36	0.41
IV	0.39	0.37	0.43	0.36	0.48	0.37	0.40
Oil B	0.50	0.41	0.54	0.50	0.54	0.43	0.49

Values shown are generated from the most strongly adsorbed asphaltenes obtained from the CH_2Cl_2:CH_3OH eluate. Roman numerals represent individual experiments as in Tables 5 and 7.

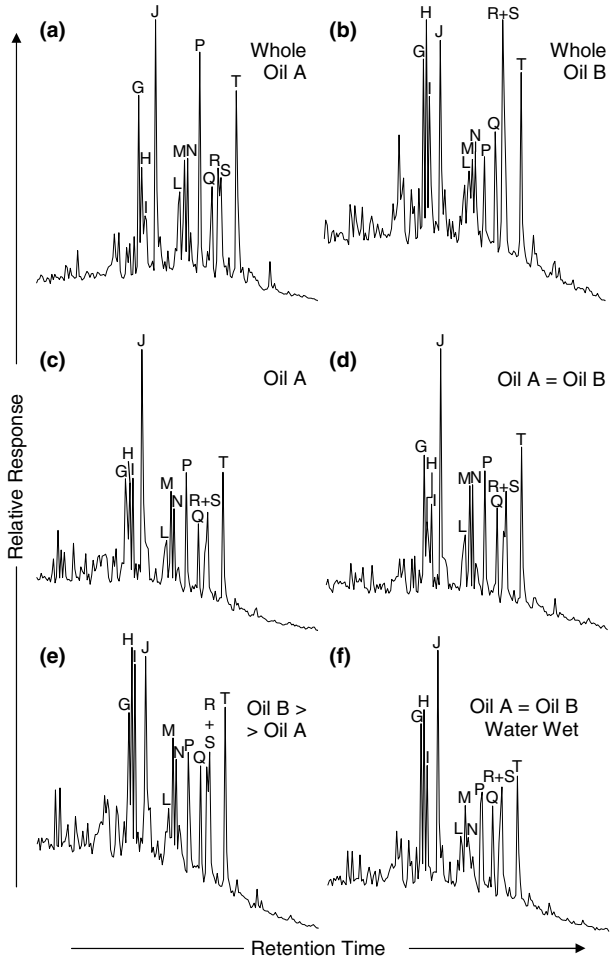

Fig. 7. Asphaltene bound sterane distributions (*m/z* 217) bound to the most strongly adsorbed asphaltenes from each experiment: (a) Whole oil A asphaltenes; (b) Whole oil B asphaltenes; (c) single oil sequential elution; (d) Oil B asphaltene quantity is equal to oil A; (e) Oil B asphaltenes are double the quantity relative to oil A asphaltenes; (f) Using wet sand substrate, oil B asphaltene quantity is equal to oil A. The key to labelling system in Table 3.

lined in this report suggests that the application of sequential extraction and the subsequent hydropyrolysis of the most strongly adsorbed heavy oil fractions can potentially provide detailed insight into secondary migration pathways and reservoir filling.

5. Conclusions

The Blake Field (Outer Moray Firth, UK North Sea, Blocks 13/24 and 13/29) contains petroleum fluids that are completely homogenised in terms of conventionally acquired mobile oil biomarker distributions. Such reservoir conditions were ideal to examine a novel approach to the investigation of reservoir filling history. The analytical system utilised catalytic hydropyrolysis to liberate biomarker distributions bound to asphaltenes adsorbed to core sample substrates, with the premise that these profiles would reveal systematic relative maturity differences as a function of migration distance. Indeed, if the original hypothesis is correct, one possible explanation for the discrete changes to asphaltene bound sterane distributions could be that oil may have first entered the reservoir strata at a point towards the northwest of well 13/24a-4 and proceeded to fill towards the southeast, which is opposite to the direction of regional secondary migration. These results indicate that the analysis of such asphaltene bound biomarker distributions may have the potential to reveal detailed information concerning secondary migration pathways and reservoir filling history.

The credibility of these findings were confirmed by simple laboratory experiments designed to examine asphaltene adsorption and displacement characteristics. Two oil samples were employed whose asphaltene bound sterane profiles were sufficiently different to permit their differentiation. The applicability of these sterane distributions were successfully tested by analysis of a series of oil A and oil B asphaltene component mixtures.

Importantly, sequential elution of oil A core substrate adsorbed asphaltenes revealed no significant fractionation of sterane biomarker compound distributions with increasing asphaltene adsorptive strength / polarity. Further sequential elution experiments involving the introduction of oil B in similar quantities to oil A on anhydrous sand, in double quantities of oil A, and again using similar quantities of oil B but on a water wet sand substrate showed that overall, approximately 70 wt% of oil A asphaltenes remained adsorbed to the sand substrate. Therefore, although such rudimentary experiments have been performed without simulating sub-surface reservoir conditions, these findings suggest that the asphaltenes adsorbed on a particular core rock are representative of the first charge of oil to contact the rock. This is an significant finding, as in actual geological situations where two or more source rock facies maybe available to feed a reservoir, sequential extraction of core samples culminating with hydropyrolysis of the most tightly adsorbed asphaltenes has the potential to reveal accurate molecular information as to the oil that first entered the porous network of the reservoir rock, and thus provide detailed information as to the secondary migration pathways of oils in basins and reservoir filling events.

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