

An experimental investigation of geochromatography during secondary migration of petroleum performed under subsurface conditions with a real rock

Steve Larter,^a Berni Bowler,^{*a} Ed Clarke,^b Colin Wilson,^b Brian Moffatt,^b Barry Bennett,^a Gareth Yardley^c and Dan Carruthers^c

Article

^a*Fossil Fuels and Environmental Geochemistry (Postgraduate Institute) NRG, University of Newcastle, UK. E-mail: b.f.j.bowler@ncl.ac.uk*

^b*BG International, Reading, Berkshire, UK*

^c*Dept of Petroleum Engineering, Heriot-Watt University, Edinburgh, UK*

Received 16th August 2000, Accepted 20th October 2000

Published on the Web 31st October 2000

An understanding of the size of petroleum secondary migration systems is vital for successful exploration for petroleum reserves. Geochemists have suggested that compositional fractionation of petroleum accompanying the migration process (geochromatography) can potentially be used to infer distances petroleum may have travelled and the ratio of oil in the reservoir to that lost in the carrier. To date, this has been attempted by measuring concentrations and distributions of specific steranes, and aromatic oxygen and nitrogen compounds in reservoir oils which have been proposed to respond to migration rather than to source maturity or other effects. We report here an experiment involving oil migration through an initially water wet siltstone under realistic subsurface carrier bed or reservoir conditions (48 MPa, 70 °C) where source facies and maturity effects are eliminated. We show that geochromatography does indeed occur even for initially water saturated rocks and that the migration fractionations observed for alkylcarbazoles, benzocarbazoles and alkylphenols are very similar to those seen in field data sets. In contrast, sterane based migration parameters show no compositional fractionation under these conditions.

Introduction

Petroleum may migrate up to several hundred kilometers from source to reservoir.¹ The physics of fluid flow dictates that this migration takes place in a focussed manner, with only a small fraction of the carrier bed being used.² This makes direct measurement of secondary petroleum migration conduits, by drilling or geophysics, virtually impossible. Consequently, petroleum geochemists have sought to quantify petroleum migration processes by chemical analysis of reservoir oil using the concentrations and distributions of several compound types as migration tracers.

Geochemical migration tracers are components of petroleum systems which partition from petroleum to water/rock, or *vice versa*, during migration. Of all the potential components, it is those that partition from petroleum to the carrier bed medium that constitute the largest group studied to date. Numerous studies have assessed the usefulness of sterane isomers,³ petroleum alkylcarbazoles and benzocarbazoles,⁴⁻⁹ alkylbenzoquinolines¹⁰ and petroleum alkylphenols.^{11,12} Atmosphere derived noble gases which partition from pore water into oil have also been studied¹³ and migration applications of both tracer types reported (Western Canada,¹⁴ Oman,¹⁵ North Sea¹³).

The migration of petroleum from source to reservoir usually results in compositional changes brought about by oil/water/rock partition and distribution processes, collectively termed 'geochromatography'.^{16,17} Large compositional fractionations accompany primary migration as oil leaves the source rock but fractionations occurring during secondary migration are much more subtle⁵⁻⁷ and may be overprinted in reservoir oils with influences attributable to facies and maturity variation in source kitchen areas.^{7-9,14,18,19} By choosing petroleum systems in the North Sea and from the petroleum systems of the Western Canada sedimentary basin where such effects were

minimised, Larter *et al.*⁷ suggested that for benzocarbazoles, migration in clastic carrier beds over distances of more than 100 km resulted in the reduction of absolute concentrations of benzocarbazoles in oils by over an order of magnitude, with

Table 1 Properties of the core and geochemical characteristics of the oil used in the experiment^a

Siltstone, Cadley A mine, Leics.	
Porosity	ca. 12%
Permeability (brine)	0.01–0.02 mD
Total carbon content	0.9%
Total organic carbon content	0.4%
Clay content (estimated XRD)	37%
Oil	
Saturated hydrocarbons	52.4%
Aromatic hydrocarbons	29.4%
Resins (NSO cmpds)	14.5%
Asphaltenes	3.7%
Carbazole	
1-Methylcarbazole	0.9 µg g ⁻¹
Benzo[a]carbazole	1.6 µg g ⁻¹
Benzo[c]carbazole	0.5 µg g ⁻¹
Benzo[e]carbazole	0.2 µg g ⁻¹
Total C ₀ –C ₂ alkylcarbazoles	20.2 µg g ⁻¹
Sum C ₂ alkylcarbazoles	15.4 µg g ⁻¹
Phenol	
<i>o</i> -Cresol	28.3 µg g ⁻¹
<i>m</i> -Cresol	13.7 µg g ⁻¹
<i>p</i> -Cresol	3.3 µg g ⁻¹
2-Ethylphenol	5.9 µg g ⁻¹
4-Ethylphenol	3.5 µg g ⁻¹
2-Isopropylphenol	2.4 µg g ⁻¹
3-Isopropylphenol	0.8 µg g ⁻¹
	1.0 µg g ⁻¹

^aPrefixes C₀, C₁, C₂, C₃ refer to the number of alkyl carbon substituents on the basic phenol or carbazole nucleus.

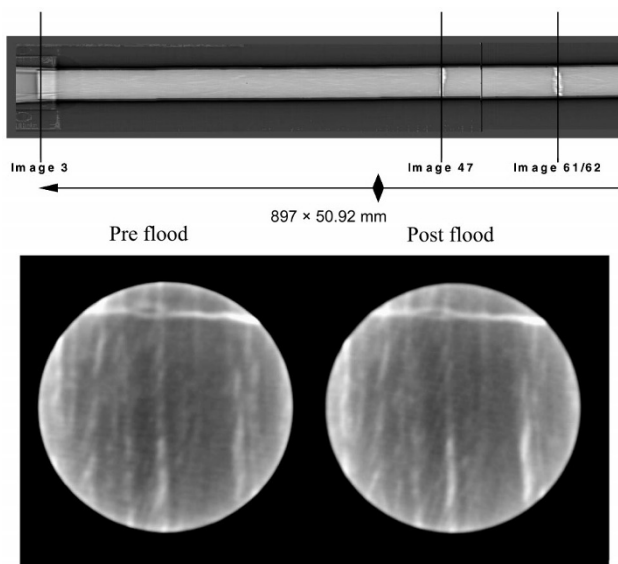


Fig. 1 X-ray tomograms of the whole core prior to flooding with fluid (top), and of the same cross section of the core (bottom), before (left) and after (right) flooding with brine then oil. The bright regions in the CT scans are calcite-filled fractures in the core.

accompanying decreases in the ratio of the benzo[a]carbazole to benzo[c]carbazole isomers, though they did note that in some petroleum systems no fractionations were observed. Li *et al.* similarly suggested,^{5,14} from studies of oils from China and Western Canada, that decreases in absolute alkylcarbazole concentrations in oils and the accompanying increase in the relative proportions of more alkylated carbazoles compared to methylcarbazoles were again related to secondary migration. Li *et al.*⁵ further suggested that changes in the isomer distributions of methyl and dimethyl carbazoles were also migration related. It is difficult to be certain of such effects from field studies, where migration, source facies and maturity effects on oil composition may be combined; consequently, numerous laboratory geochromatography studies have been made.

Demonstrable compositional fractionations during simulated oil migration are numerous,^{17,20,21} but most experiments use unrealistic artificial "carrier beds" or migrating phases other than oil or unrealistic flow sequences. Although useful, these approaches do not simulate continued oil injection into a

consolidated, initially water saturated rock at high temperature and pressure. Here, we discuss a more realistic experiment in which oils of constant initial composition were migrated through a rock under subsurface conditions. The lithology chosen was a siltstone in the microdarcy permeability range typical of portions of carrier systems involved in vertical petroleum migration. There is very little data available for oil flow through such low permeability lithologies even though rocks such as siltstones often form critical parts of carrier systems and seals and may significantly affect basin scale fluid flow. The experiment eliminates source facies and maturity influences on oil composition, allowing detailed investigation of petroleum migration fractionation effects in isolation.

Methods

The main components of the experiment were as follows:

- (i) rock selection and preliminary testing of coreplugs for permeability/sorption properties;
- (ii) computerised tomography (CT) scanning of selected core (before and after core-flooding);
- (iii) core-flooding with synthetic brine to give water saturation;
- (iv) core-flooding with oil;
- (v) chemical analysis of produced fluid samples (brine, oil).

Core selection

The siltstone chosen was from the Cadley Hill A coal mine section of the Westphalian coal measures, East Midlands, UK. An unfractured block was selected and a full length (1000 × 5 cm) core cut and trimmed. Basic data for the core and the initial oil composition are shown in Table 1.

CT scanning

X-ray computerised tomography (CT) scanning of the core with a medical CT scanner before water-flooding and after oil-flooding showed pervasive petroleum flow to have occurred, with no obvious focussing evident (Fig. 1). An iodide enhanced brine was used to improve fluid contrasts. This pervasive flow throughout the core was confirmed subsequently by geochemical analysis of residual core extracts, the results of which will be discussed elsewhere.

Core-flood rig and set-up

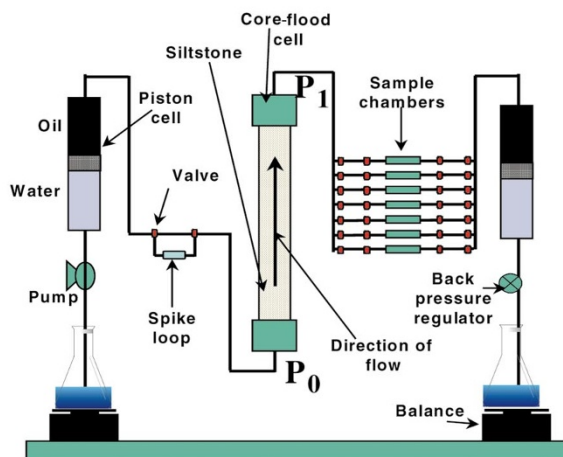


Fig. 2 Diagram of the core-flood experimental set-up, with the actual lab set-up shown right. The core-flood cell was maintained at 7000 psi confining pressure and 70 °C. Pressure differential across $P_0/P_1 = 700$ psi.

Oils eluting from core

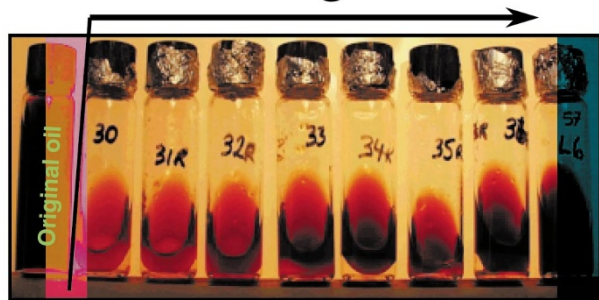


Fig. 3 Geochromatography in action! The colour of the eluted oil changes during the experiment; the earliest eluting oils (vials 30–36) are light orange, subsequent samples rapidly becoming darker through the experiment, the final eluted oil (vial 57) being of similar colour to the original oil.

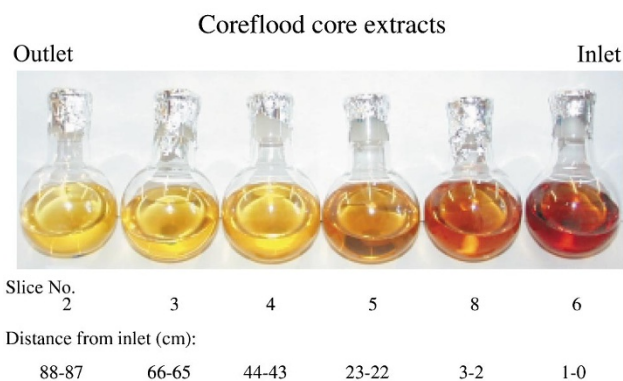


Fig. 4 Dichloromethane–methanol (2 : 1) extracts of 1 cm thick slices along the core show that most coloured material removed from the injected oil has been retained near the inlet.

Core-flood

The experimental set-up is shown diagrammatically in Fig. 2. The Viton jacketted core was installed vertically with flow from base to top, parallel to bedding. The oil-flood commenced after initial saturation of the siltstone core with a synthetic N. Sea formation water was achieved.

A typical 41° API gravity, non-biodegraded North Sea black oil was filtered (0.45 µm mesh sieve) and homogenised prior to sub-sampling. A 400 ml volume of oil was taken for the main charge. Five additional sub-samples were taken and mixed with different aliphatic hydrocarbon standards (at 10 mg g⁻¹ oil) to form five distinct spiked oils of essentially the same composition as the main oil but which could be differentiated by gas chromatography to track oil movement through the core. For practical reasons no hydrocarbon solution gas was present, although the oils were saturated with nitrogen prior to injection; this is thought unlikely to affect the results observed.

After stabilisation of the core under water-saturated conditions, oil was flowed at typical subsurface conditions *i.e.*, 70 °C, 48.3 MPa (7000 psi) confining pressure controlled by a pressure differential of *ca.* 4.8 MPa (700 psi) along the core. The target flow rate for the oil, determined by time constraints and core-plug screening work, was set and maintained at 2.4 ml per day (0.01 ml h⁻¹).

The spiked oils were injected periodically and “produced fluid” flowing through the outlet valve was collected in 1.6 ml pressurised sample chambers, minimising cross-contamination during sampling. Injected oil volumes are used for reference in this paper as they could be determined more reliably than eluted oil volumes. The spiked oil data will be discussed elsewhere.

Chemical analysis of eluted oils

The produced fluid samples were comprised largely of oil and a small amount (<20%) of water, both at “oil breakthrough” and during the remaining time of the experiment. Periodically the sample loops were depressurised and the contents decanted into glass vials where the two phases readily separated. Samples of the oil were analysed for bulk composition using Iatroscan,²² and for alkylcarbazoles, benzocarbazoles and alkylphenols using solid-phase extraction (SPE) and GC-MS methods.^{7,23,24} Briefly, a hydrocarbon fraction and non-hydrocarbon fraction were obtained using C18 modified non-encapped silica SPE cartridges and elution with hexane to give the hydrocarbon fraction and with dichloromethane (DCM) to give the phenol and carbazole fractions. The hydrocarbon fraction was further fractionated into saturated hydrocarbons and aromatic hydrocarbons by silver ion SPE, as described by Bennett and Larter.²⁵ A subsample of the SPE DCM fraction was derivatised using BSTFA after addition of internal standards, and phenol and the C₁–C₃ alkylphenols were analysed by GCMS in selected ion monitoring (SIM) mode.²³ Carbazole and benzocarbazole analyses were performed by direct GCMS-SIM analysis of the SPE DCM fraction.⁷

Results and discussion

Oil was flowed for 89 days; oil breakthrough occurred after 58 d, when 121 ml of oil (57% of core pore volume) had been injected into the core. Prior to oil breakthrough, the samples of produced fluid collected in the sample loops consisted of the brine used to achieve initial water-saturation. These were analysed for dissolved BTEX compounds (benzene, toluene, ethylbenzenes and xylenes) by purge and trap-GC but none were found at the >10 ppb level. At oil breakthrough, water production dropped to approximately 20% of produced fluid volume before steadily reducing to less than 10% by the end of the experiment. Oil saturation was 57% of the pore volume at breakthrough increasing to approximately 65% at the end of the experiment, after 205 ml of oil had been injected (97% pore volume).

The first oil samples produced from the core were a clear orange colour, contrasting markedly with the black colour of the initial oil (Fig. 3). Subsequently produced oil samples became progressively darker as the experiment continued. The removal of colour in the first-eluted oil samples is a dramatic demonstration of (geo)chromatography in its original sense. Analysis of the core extracts showed that most of the pigmented compounds are removed near the core inlet (Fig. 4); these coloured polar species will be discussed elsewhere. Changes in the bulk composition of the produced oil were small, the resin content, for example, reducing from *ca.* 15% in the original oil to *ca.* 10% in the first-eluted oil. This was accompanied by a similarly small increase in saturated hydrocarbons content. By the end of the experiment, the bulk composition and colour of the produced oil samples were similar to those of the original oil.

Fractionation of migration tracers

Comparison of the sterane based “Biomarker migration index” of Siefert and Moldovan³ (ratio of C₂₉ sterane 5α,14β,17β (S + R)/[5α,14β,17β (S + R) + 5α,14α,17α (S + R)] isomers) and a typical biomarker maturity related ratio (the ratio of the 20S/(20S + 20R) isomers for the regular C₂₉ steranes) in the original and migrated oils showed no statistically detectable variation even with the first produced orange oils. A similar absence of variation accompanied most hydrocarbon biomarker ratios used for facies and maturity assessment.

In contrast, non-hydrocarbons containing nitrogen and oxygen showed substantial changes in concentration and

composition as the experiment proceeded. Fig. 5 shows the normalised concentrations of representative prospective migration tracers in the sequentially eluted oils. Nitrogen compounds (carbazoles and benzocarbazoles) show reduced concentrations in the early eluted oils, with no benzocarbazoles being detectable in the first samples of oil produced from the core. Thereafter, concentrations rise to values near 80% of the initial oil by the end of the experiment. The larger scatter in the benzocarbazole data reflects analytical error associated with the low concentrations in the oils (peak height data were used in this case for quantitation to minimise interference from closely eluting compounds in the GCMS analysis). This elution profile is typical of other aromatic heterocyclic compounds, such as 9-fluorenone,²⁶ which show similar elution characteristics to carbazole. In contrast, alkylphenols, represented here by *p*-cresol, are severely depleted in all the oils collected, and the total C₀–C₃ alkylphenols concentrations in the eluted oils reach only 10% of initial oil concentrations by the end of the experiment.

Distributions of different isomeric and homologous carbazoles and phenols also show systematic trends in the migrated (eluted) oils. Fig. 6 shows relative abundances of higher to lower alkylcarbazole homologues in the migrated oils. The first oil samples from the core are characterised by enrichment in higher alkyl homologues (*cf.* C₂ carbazoles; sum of dimethyl- and ethylcarbazoles) relative to lower homologues. As more oil is flowed, the homologue ratios decrease towards the initial value for the oil. Except in the very first eluted oils, no significant fractionations of isomeric methyl or dimethylcarbazoles were observed.

Benzocarbazoles are very strongly sorbed by the siltstone and isomeric fractionations are also seen, with the first oils to contain both benzocarbazole [*a*] and benzocarbazole [*c*] having a reduced [*a*]/[*c*] ratio compared to that of the initial oil, as shown in Fig. 7.

In contrast to the alkylcarbazoles, where concentrations attained 80% of that in the initial oil by the end of the experiment, alkylphenol concentrations reached only 10% of that in the original oil, indicating much more extensive removal of phenols by the core. Fractionations between alkylphenol homologues and isomers were marked, the early eluting oils being enriched in phenol relative to higher homologues, possibly due to the higher water content of the earlier-eluted fluids. Substantial isomeric ratio variations were also seen in the alkylphenols between *ortho*-isomers (where the OH group on the phenol molecule is shielded by an adjacent alkyl substituent) and *meta*- and *para*-isomers (where there is no alkyl substituent in the *ortho* position, the OH group thus being

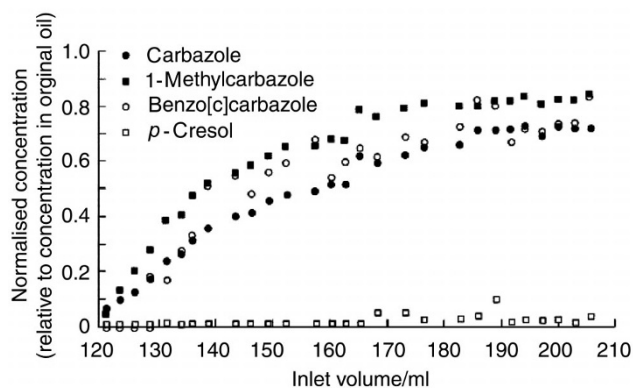


Fig. 5 Variation in concentrations of selected representative non-hydrocarbons in oil samples collected at the core outlet during the core flood experiment. Concentration data has been normalised to values obtained for the original (input) oil (see Table 1). Note that phenols (as exemplified here by *p*-cresol) show much stronger depletion than carbazoles. The first oil was eluted from the core after *ca.* 120 ml of oil had been injected.

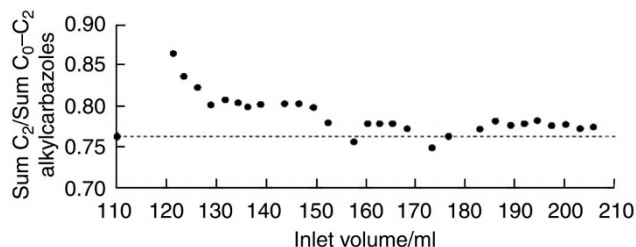


Fig. 6 Variation in the abundance ratio of higher alkylated carbazole homologues (C₂ alkylcarbazoles) relative to total (C₀–C₂) alkylcarbazoles in outlet oil during the coreflood [C₂/(C₀ + C₁ + C₂) ratio]. The value for the original oil is shown at inlet volume = 110 ml and by the dotted horizontal line. The first eluted oil at 120 ml shows significant relative enrichment in C₂ alkylcarbazoles.

exposed). The ratios of *ortho*-substituted to *meta*- and *para*-substituted isomers for the C₃ and C₂ alkylphenols in eluted oils seem to increase to a maximum and then gradually decrease with further oil flow to values close to those seen in natural oils. The C₁ phenols, however, show only a rise in this ratio to high values unlike those seen in natural crude oils. These variations suggest involvement of non-equilibrium competitive sorption–desorption processes in controlling the relative abundance of phenol isomers in the migrated oils and these will be discussed elsewhere.

Geological implications

The experiment clearly shows that even with short rapid transits through initially water saturated rocks, hydrophobic components such as carbazoles and benzocarbazoles can be effectively removed from migrating petroleum by partition–sorption processes. It is clear that at least in the case of the alkylphenols the core and oil are far from equilibrium at the end of the experiment, with isomer ratios in migrated/eluted oils very different from those in normal crude oils. Even for the (more hydrophobic) nitrogen compounds, equilibrium was only just being approached, with carbazole and benzocarbazole concentrations and isomer distributions reaching only *ca.* 20% of values in the initial oil by the end of the experiment. While these differences in equilibration time are significant on a lab timescale they are unlikely to be evident in field data sets.

The dramatic removal of alkylphenols from migrated oils in the experiment confirms field observations^{11,12,27} that phenol concentrations in migrated oils are rapidly attenuated over migration distances of only a few tens of kilometers through sandstones. Petroleum phenols can sorb to both minerals and solid organic matter in sediments,¹¹ and rapid wettability changes have been reported in initially water wet sandstones,

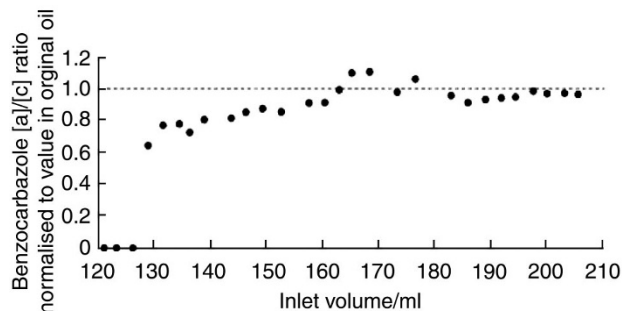


Fig. 7 Variation in benzocarbazole [*a*]/[*c*] isomer ratios in outlet oil samples, determined from peak heights in *m/z* 217 mass chromatograms of the SPE DCM fraction. The values are normalised to the value in the original oil. The benzocarbazoles were completely depleted in the first three oil samples collected, and subsequent samples to *ca.* 160 ml showed statistically significant depletion of benzo[*a*]carbazole relative to benzo[*c*]carbazole compared to later eluted oils. The horizontal dotted line is the reference (injected) oil value at 1.0.

brought about by synthetic oils containing small surfactant molecules such as phenols.²⁸ The rapid sorption of hydrophilic compounds such as the phenols might be expected, as they would readily partition from oil to water and then to solid phases.¹¹ It seems however that even with free water phases initially present in the rock, large hydrophobic molecules such as benzocarbazoles, with estimated oil–water partition coefficients (P) in the range of 10^4 – 10^5 ,²⁹ are also very quickly removed. While oil wet kerogen in the core may be responsible for some of this sorption, prior sorption of surfactant moieties such as alkylphenols, with very low subsurface oil–water partition coefficients ($P \ll 50$)³⁰ may also aid in the rapid sorption of carbazoles to organic and mineral surfaces. Molecular dynamics studies suggest that, indeed, prior sorption of alkylphenols to silica and calcite mineral surfaces effectively aids in subsequent sorption of hydrophobic moieties (van Duin and Larter—in preparation). The rapid oil wetting of pore surfaces in such fine grained rocks has major implications for cap rock sealing mechanisms and this will be discussed elsewhere. Similar synergistic processes may well aid in the removal of hydrophobic pollutants from water to mineral surfaces within aquifers.

The reduction in oil alkylcarbazole and benzocarbazole concentrations during the experiment, the enhancement in the $C_2/(C_0 + C_1 + C_2)$ alkylcarbazole ratio and the reduction in the benzocarbazole $[a]/[c]$ ratio is similar to the compositional changes seen in migrated oil field data sets^{5,7,14,15} and suggests that these compounds do respond to secondary petroleum migration. The fractionations observed are similar to those seen in normal phase chromatographic separations in the laboratory,³¹ and it is likely that both mineral and organic matter sorption processes contribute to the effects seen.

Source facies and maturity effects sometimes exert a major role in controlling the nitrogen compound composition of source rock petroleum.^{6–9,19} We suggested previously⁷ that for some clastic oil source rocks, primary migration fractionations effectively removed any source related maturity influence on benzocarbazole composition from the secondary migrated oil, but in a study of the carbonate sourced Sonde de Campeche petroleum system of Mexico, where prolific vertical petroleum migration dominates, there is further evidence that maturity effects do sometimes dominate the carbazole and benzocarbazole compositions in the reservoir oils.^{8,9} In this case, the benzocarbazole $[a]/[c]$ ratios and concentrations in the oils increase in the vitrinite reflectance defined maturity range up to 0.9% Ro (Ro , vitrinite reflectance; source temperatures *ca.* 140 °C). Terken and Frewin¹⁵ confirm that maturity effects on benzocarbazole distributions are sometimes present in oil datasets from around the world but in many cases they are not.

Our experience is that for shale-sourced petroleum systems with oils generated in the maturity range up to 0.9% Ro , the concentration of benzocarbazoles in the migrated petroleum is typically an order of magnitude lower, or less, than that in the mature source petroleum.^{27,32,33} Thus, while mature Kimmeridge Clay Formation source rocks typically have benzocarbazole concentrations of 15–60 ppm in their source petroleum, North Sea oils derived from this source rock typically have only a few ppm of benzocarbazoles present.³³ In contrast, Horsfield and coworkers^{8,9} report that for the Sonde de Campeche carbonate-sourced petroleum system, both reservoir oil and source rock petroleum have very similar concentrations of these compounds in this same maturity range. This suggests greater primary migration fractionations in clastic source rock systems compared to carbonate source rocks which may variably affect inherited source-related nitrogen compound signals in the expelled oils.

For a series of petroleum reservoirs along a migration pathway where maturity gradients are present from field to field, it is often the case that the fields nearest the source kitchen contain the most mature petroleum and those more distal

contain less mature petroleum. In this common scenario, the effects of any transmitted source maturity effect and secondary migration fractionation of benzocarbazole concentrations and distributions, as demonstrated here, would appear to have the potential to operate in concert, with further migrated oils tending to be less mature and more migration fractionated, and *vice versa*. Both effects would result in greater reductions in concentrations and benzocarbazole $[a]/[c]$ ratios in the further migrated and least mature oils. This may explain the very low values of isomer ratios and concentrations seen in some migrated oils. While our core flood experiment confirms that these compounds do have the potential to work as migration indicators, a thorough maturity/source facies assessment of fluids in a possible migration suite is, as always, necessary.^{5,8,14,15}

Simple chromatographic theory¹⁷ indicates that for equilibrium sorption of a tracer to a rock, the tracer concentration in a reservoir is not a simple function of distance migrated but depends critically on sorption properties of the carrier system and on the relationship between the volume of carrier rock accessed by the oil and the volume of oil migrated through it to reservoirs. Our theoretical studies³⁴ suggest that the concentration of tracer in a migrated oil in local equilibrium with its carrier rock correlates inversely and linearly with the ratio of carrier bed pore volume transgressed to oil volume transmitted through it (*i.e.*, volume carrier/volume oil transmitted).

This simple result can be thought of in terms of high and low throughput carrier systems. The petroleum in a low throughput carrier system comprised of small reservoirs charged *via* a comparatively long migration pathway (*i.e.*, volume carrier/volume reservoir oil is large) will be characterised by large reductions in tracer concentration during migration. Such examples would be the highly fractionated petroleum in the 2nd White Speckled Shale (source)—Cardium/Viking Formation (carrier/reservoir) petroleum systems of the Western Canada foreland sedimentary basin,⁷ the Bakken oils in the Canadian portion of the Williston basin with source kitchens in the USA,³⁵ and the Dhahaban sourced oils of Oman which have also travelled well over 200 km from their source basin.¹⁵ In contrast, in prolific basins (*i.e.*, with high throughput carriers), large volumes of oil will be charged through the same carrier volume, ultimately saturating the carrier to equilibrium saturation with the feed oil, with little net tracer removal seen in the final reservoir oil. An example would be the Kimmeridge Clay Formation (source)—Hugin Formation/Paleocene/Eocene sand (carrier/reservoir) petroleum systems of the Tertiary reservoirs in the Viking Graben, North Sea,³⁶ where many reservoir volumes of oil have been charged through a single focussed pathway. The Sonde de Campeche system⁹ is probably a somewhat similar setting.

Even when maturity, facies and in-reservoir alteration complications can be resolved, in many prolific petroleum systems, where large volumes of petroleum pass through the same carrier system, it is likely that little or no net tracer fractionation may be observed. Large fractionations are most likely to be observed in basins with relatively small fields at the end of long migration routes, as seen in foreland basins¹ or where carriers involve highly sorptive siltstones or mudstones. Thus, large reductions in benzocarbazole ratios and concentrations are seen in reservoir oils in the foreland basin settings of Western Canada and Oman,^{7,14,15} and for vertically migrated oils in the Gulf of Mexico and in the Kekeya Field of the Tarim Basin³⁷ which must have migrated through kilometers of mudstones.³⁶

Conclusions

A core-flood experiment in which oil is flowed through water saturated siltstone under subsurface conditions of temperature

and pressure confirms that geochromatographic fractionation of petroleum does occur during migration through water wetted rocks. While hydrocarbon fractions showed little fractionation, the more polar non-hydrocarbon fraction showed substantial compositional change. The systematic removal of carbazoles, benzocarbazoles and phenols during migration under subsurface conditions is similar to that inferred previously from field data. As expected from physicochemical properties, phenols were removed much more actively than carbazoles.

While little fractionation of sterane based migration parameters in migrated oils was observed, there was a systematic increase in the proportion of C₂ alkylcarbazoles compared to lower homologues, and a reduction in the benzocarbazole [a]/[c] ratio. The variations in homologue and isomer ratios were accompanied by reductions in absolute concentrations of these nitrogen compounds. These observations support field data reported earlier and suggest that while maturity effects may have a local influence on nitrogen compound distributions in reservoir oils, these species do track secondary migration processes *via* both concentration and isomer ratio variation.

Alkylphenols are very strongly absorbed by the siltstone and the phenol distributions in the migrated oils do not resemble those we see in nature. Non-equilibrium sorption-desorption processes within the timescale of the experiment are indicated, with rapid removal of phenols possibly resulting in the subsequent enhanced removal of more hydrophobic components such as alkylcarbazoles.

Acknowledgements

The research was supported by the EU FP4 SMACCERS project. Andy Aplin, Yunlai Yang, Maowen Li (GSC-Calgary), Kim Noke, Trevor Whitfield, Rob Hunter and Paul Donohoe are thanked for comments and technical assistance.

References

- 1 S. Creaney and J. Allan, in *Classic Petroleum Provinces*, ed. J. Brooks, Geological Society of London Special Publication 50, London, 1990, p. 189.
- 2 W. A. England, A. S. Mackenzie, D. M. Mann and T. M. Quigley, The movement and entrapment of petroleum fluids in the subsurface, *J. Geol. Soc. London*, 1987, **144**, 327.
- 3 W. K. Seifert and J. M. Moldowan, Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils, *Geochim. Cosmochim. Acta*, 1978, **42**, 77.
- 4 M. Li, S. R. Larter, D. Stoddart and M. Bjorøy, Liquid chromatographic separation schemes for pyrrolic and pyridinic nitrogen aromatic heterocycle fractions from crude oils suitable for rapid characterisation of geochemical samples, *Anal. Chem.*, 1992, **64**, 1337.
- 5 M. Li, S. R. Larter, D. Stoddart and M. Bjorøy, in *The Geochemistry of Reservoirs*, ed. W. A. England and J. Cubitt, Geological Society Special Publication, London, 1995, p. 103.
- 6 M. Li, H. Yao, L. D. Stasiuk, M. G. Fowler and S. R. Larter, Effect of maturity and petroleum expulsion on pyrrolic nitrogen compound yields and distributions in Duvernay Formation petroleum source rocks in central Alberta, *Org. Geochem.*, 1997, **26**, 731.
- 7 S. R. Larter, B. F. J. Bowler, M. Li, M. Chen, D. Brincat, B. Bennett, K. Noke, P. Donohoe, D. Simmons, M. Kohonen, J. Allan, N. Telnaes and I. Horstad, Molecular indicators of secondary oil migration distances, *Nature*, 1996, **383**, 593.
- 8 H. Clegg, H. Wilkes, T. Oldenburg, D. Santamaria Orozco and B. Horsfield, Influence of maturity on carbazole and benzocarbazole distributions in crude oils and source rocks from the Sonda de Campeche, Gulf of Mexico, *Org. Geochem.*, 1998, **29**, 183.
- 9 B. Horsfield, H. Clegg, H. Wilkes and D. Santamaria Orozco, Effect of maturity on carbazole distributions in petroleum systems: new insights from the Sonda de Campeche, Mexico, and Hils syncline, *Naturwissenschaften*, 1998, **85**, 288.

- 10 M. Yamamoto, Fractionation of azaarenes during oil migration, *Org. Geochem.*, 1992, **19**, 389.
- 11 P. Taylor, S. Larter, M. Jones, J. Dale and I. Horstad, The effect of oil-water-rock partitioning on the occurrence of alkylphenols in petroleum systems, *Geochim. Cosmochim. Acta*, 1997, **61**, 1899.
- 12 R. Galimberti, C. Ghiselli and M. A. Chiaromonte, Acidic polar compounds in petroleum: a new analytical methodology and applications as molecular migration indexes, in *Extended abstracts of the 19th Intl. Meeting on Organic Geochemistry, 6-10 Sept. 1999, Istanbul, Turkey*, TUBITAK Marmara Research Center, Gebze-Kocaeli, 1999, p. 147.
- 13 C. J. Ballentine, R. K. O'Nions and M. L. Coleman, A Magnus Opus: Helium, neon and argon isotopes in a North Sea oilfield, *Geochim. Cosmochim. Acta*, 1996, **60**, 831.
- 14 M. Li, H. X. Yao, M. G. Fowler and L. D. Stasiuk, Geochemical constraints on models for secondary petroleum migration along the upper Devonian Rimbey-Meadowbrook reef trend in central Alberta, Canada, *Org. Geochem.*, 1998, **29**(1-3), 163.
- 15 J. M. J. Terken and N. L. Frewin, The Dhahaban petroleum system of Oman, *Bulletin A. A. P. G.*, 2000, **84** ((4)), 523.
- 16 B. Nagy, Review of the chromatographic plate theory with reference to fluid flow in rocks and sediments, *Geochim. Cosmochim. Acta*, 1960, **19**, 289.
- 17 B. M. Krooss, L. Brothers and M. H. Engel, in *Petroleum Migration*, ed. W. A. England and A. J. Fleet, Geological Society Special Publication, 1991, p. 149.
- 18 H. Clegg, B. Horsfield, L. Stasiuk, M. Fowler and M. Vliex, Geochemical characterisation of organic matter in Keg River Formation (Elk point group, Middle Devonian), La Crete Basin, Western Canada, *Org. Geochem.*, 1997, **26**, 627.
- 19 H. Clegg, H. Wilkes and B. Horsfield, Carbazole distributions in carbonate and clastic source rocks, *Geochim. Cosmochim. Acta*, 1997, **61**, 5335.
- 20 T. Greibrokk, E. Lundanes, H. R. Norli, K. Dyrstad and S. D. Olsen, Experimental simulation of oil migration—distribution effects on organic compound groups and on metal/metal ratios, *Chem. Geol.*, 1994, **116**, 281.
- 21 J. V. Bonilla and M. H. Engel, Chemical and isotopic redistribution of hydrocarbons during migration. Laboratory simulation experiments, *Org. Geochem.*, 1986, **10**, 181.
- 22 D. A. Karlsen and S. R. Larter, Analysis of petroleum fractions by TLC-FID: applications to petroleum reservoir description, *Org. Geochem.*, 1991, **17**, 603.
- 23 B. Bennett, B. F. J. Bowler and S. R. Larter, Determination of C₀-C₃ alkylphenols in crude oils and waters, *Anal. Chem.*, **68**, (20), 3697.
- 24 B. F. J. Bowler, S. R. Larter, H. Clegg, H. Wilkes, B. Horsfield and M. Li, Dimethylcarbazoles in crude oils: comment on "Liquid Chromatographic Separation Schemes for Pyrrole and Pyridine Nitrogen Aromatic Heterocyclic Fractions from Crude Oils Suitable for Rapid Characterization of Geochemical Samples", *Anal. Chem.*, 1997, **69**, 3128.
- 25 B. Bennett and S. R. Larter, Quantitative Separation of Aliphatic and Aromatic Hydrocarbons Using Silver Ion-silica Solid Phase Extraction, *Anal. Chem.*, 2000, **72**, 1039.
- 26 B. Bennett and S. R. Larter, The isolation, occurrence and origin of fluorenones in crude oils and rock extracts, *Org. Geochem.*, 2000, **31**, 117.
- 27 M. Chen, S. R. Larter, S. Petch, B. Bowler and A. C. Aplin, in *Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History*, ed. J. O. Grimalt and C. Dorronsoro, A.I.G.O.A., Danostia-San Sebastian, Spain, 1995, p. 288.
- 28 Y. Huang, P. S. Ringrose and K. S. Sorbie, *The effects of heterogeneity and wettability on oil recovery from laminated sedimentary structures*, Society of Petroleum Engineers, Texas, 1995, p. 30781.
- 29 A. C. T. Van Duin and S. R. Larter, Application of molecular dynamics calculations in the prediction of dynamical molecular properties, *Org. Geochem.*, 1998, **29**, 1043.
- 30 B. Bennett and S. R. Larter, Partition behaviour of alkylphenols in crude oil-brine systems under subsurface conditions, *Geochim. Cosmochim. Acta*, 1997, **61**, 4393.
- 31 M. Li, S. R. Larter and Y. B. Frolov, Adsorptive interactions between nitrogen compounds and organic and/or mineral phases in subsurface rocks, *J. High Resolut. Chromatogr.*, 1994, **17**, 230.
- 32 M. Chen, PhD Thesis, University of Newcastle, 1995.
- 33 B. Bennett, M. Chen and S. R. Larter, Benzocarbazoles: fractionations in clastic and carbonate systems, Abstract 19, *219th ACS National Meeting*, American Chemical Society, San Francisco, March 2000.

- 34 Y. Yang, S. R. Larter, A. C. Aplin and D. Carruthers, *Theoretical study of natural tracers to determine migration routes and distances: models and applications*, *Abstracts AAPG Annual Meeting*, American Association of Petroleum Geologists, San Antonio, 1999, A156.
- 35 M. Li, K. G. Osadetz, M. G. Fowler, L. R. Snowdon, L. D. Stasiuk, H. Yao, R. J. Hwang, P. Jenden, B. Grant and E. Idiz, Case studies on secondary oil migration in the Williston Basin, in *Proceedings of the 8th International Williston Basin Symposium*, ed. J. Christopher, C. F. Gilboay and D. F. Paterson, Geol. Survey Special Publication 13, 1998, Saskatchewan, pp. 247–253.
- 36 S. R. Larter, A. C. Aplin, B. Bennett, B. Bowler, K. Noke, E. Harrison, N. Telnaes, A. Wilhelms, T. Eglinton and J. Whelan, *An assessment of vertical migration mechanisms in mudstone rich basins using organic geochemistry*, *Extended abstracts 18th Intl. Meeting on Organic Geochemistry 1997*, 1998, p. 13.
- 37 M. Li, R. Lin, P. Wang, Y. Liao, L. R. Snowdon and P. Li, Organic geochemistry of oils and condensates from the Kekeya Field, Tarim basin, *Org. Geochem.*, 1999, **30**, 15.