Significance of non-producible petroleum compounds in reservoirs: Influence on petrophysical / core parameters

by B. Bennett and S.R. Larter

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The petroleum research group at Newcastle has pioneered the application of fluid composition variations to problems in reservoir geology and petroleum geoscience in general (Huang et al., 1996; Karlsen and Larter 1991; Larter and Aplin 1995; Larter et al., 1997; Wilhelms and Larter 1994) with specific interests in reservoir charging, petroleum migration, biodegradation and the engineering / fluid interface. We have developed rapid and inexpensive techniques based on Solid Phase Extraction (Bennett et al., 1996) for the determination of surface active compounds (phenols, carbazoles and fluorenones) in crude oils and core extract petroleum. Typically, geochemical properties measured from the concentrations and distributions of surface active compounds in reservoir cores correlate strongly with petrophysical / core properties suggesting the potential for integrating petroleum engineering and petroleum geochemistry disciplines (Larter et al., 1997; Bennett and Larter 1998). Recent advances suggest chemical logs, equivalent to Amott-Harvey indices based on wettability sensitive petroleum compounds, may allow effective upscaling of limited wettability data to entire cored intervals.

The petroleum research group benefits from academic interaction across multiple disciplines within Fossil Fuels and Environmental Geochemistry, including petroleum geochemistry, archaeology and microbial ecology. Staff includes: 9 lecturers, 17 Research Associates, 6 technicians and 60 postgraduate students. Our laboratory is fully equipped to perform research in organic geochemistry (Gas Chromatography, Gas Chromatography-Mass Spectrometry and High Performance Liquid Chromatography), inorganic geochemistry (Atomic Absorption Spectroscopy, Ion Chromatography, X-Ray Diffraction and Mercury porosimetry) and molecular ecology (molecular biology, biochemistry and immunology).

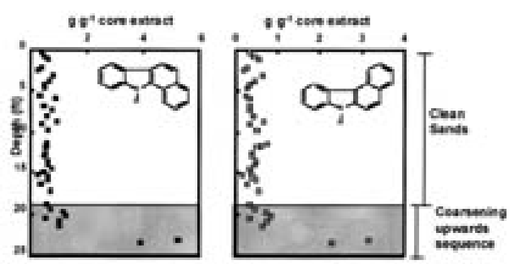
The prediction of fluid flow behaviour in petroleum reservoirs is affected by a number of properties ultimately controlled by rock-fluid interactions. Petroleum contains numerous surface active compounds known to display strong affinity for solid phases (e.g. minerals, organic matter). The surface active compounds are concentrated in the petroleum fraction defined according to bulk composition as resins (containing NSO compounds) and asphaltenes. This resin and asphaltene component of petroleum sometimes displays strong correlations in terms of concentration and composition with reservoir properties such as clay content (Bennett and Larter 1998) and makes a significant contribution to the determination of the wettability state of core samples (Larter et al., 1997). For example, adsorption and / or deposition of organic material originally present in crude oil may affect the wettability of originally water-wet cores (Anderson 1992).

Hitherto, polar compounds represented a notoriously difficult fraction of petroleum to analyse due to the chemical complexity and the low concentrations of some surface active compounds compared to the more prevalent aliphatic and aromatic hydrocarbons. These difficulties are indicated by the lack of literature documenting the integration of detailed petroleum compositional data with conventional wettability measurements. Such studies are usually limited to the correlation of bulk compositional data such as oil total nitrogen content or total sulphur content (Akhlaq et al., 1995) with wettability. Recent advances in polar compound analysis now provide the opportunity to routinely investigate wettability sensitive compounds at the molecular level. We illustrate these advances using some recent results.

Using a rapid method known as Solid Phase Extraction the polar non-hydrocarbon component of petroleum fluids in reservoir rock and produced oils may be isolated. The method described in Bennett et al. (1996) has been modified for analysis of a group of surface active polar non-hydrocarbons, namely aromatic oxygen compounds (alkylphenols and fluorenones) and aromatic nitrogen compounds (carbazoles). These polar non-hydrocarbons have been determined throughout a representative genetic unit from the PEGASUS research programme. The cored section (24ft) was a typical upper shoreface parasequence with a basal coarsening upwards sequence (5ft). The chemical composition of the petroleum fluids in reservoir rocks and produced oils have been characterised (PEGASUS Phase I, project 4) and integrated with petrophysical and core parameter data from other PEGASUS projects. A number of polar non-hydrocarbons showed strong correlations with the core petrophysics data.

Benzocarbazoles are aromatic nitrogen containing compounds that have been applied to monitor relative migration distances of petroleum accumulations based on the selective removal of benzo[a]carbazole relative to benzo[c]carbazoles (Larter et al., 1996). The behaviour of benzocarbazoles in the core extracts throughout most of the well section is fairly uniform with an increase in concentration and a change in the distribution of isomers in the lower coarsening upwards sequence (Fig. 1).

Figure 1 Plots of concentrations (µg g-1 extract) of benzocarbazole isomers [a] (•) and [c] (°) in core extract petroleum versus depth (ft).



Phenols are a group of hydroxyl aromatic compounds with a wide range of polarities based on the number and position of alkyl substituents relative to the polar hydroxyl group (Fig. 2). They represent potential candidates for investigating the nature of crude oil / brine / rock interactions since partition controls their distribution between three phases in a reservoir. The behaviour of phenols may be considered by plotting relative contents of shielded compounds (methyl groups in proximity to the hydroxyl group) and exposed isomers (no methyl groups neighbouring the hydroxyl group) which are shown in Figure 2. In general, a gradual increase in shielded isomers to the exposed isomers is observed downwards, with much greater change in the basal coarsening upwards sequence.

Figure 2. Ratio of shielded isomers of phenol (e.g. 2,6-dimethylphenol) in core extract petroleum relative to exposed (e.g. 3,5-dimethylphenol) versus depth (ft).

Fluorenones are a group of oxygen containing aromatic compounds which are abundant in core samples, but in contrast they are usually absent in related crude oils produced from the same reservoir. The differences may possibly represent considerable fractionation of reservoir components (phases) between the mobile producable fluid phase (no fluorenones) versus the in-situ petroleum containing a mobile and immobile component (containing fluorenones). Fluorenones show strong relationships with petrophysical / core properties, for example, the correlation of fluorenone concentration and gamma ray log (Fig. 3). The strongest deflection in the gamma ray log occurs in the basal coarsening upwards unit due to increasing contribution from clays downwards, which is also indicated in the fluorenone chemical log.

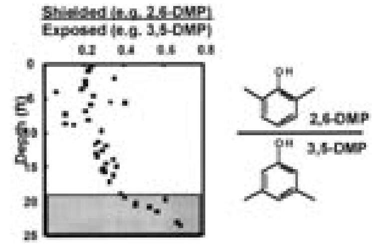
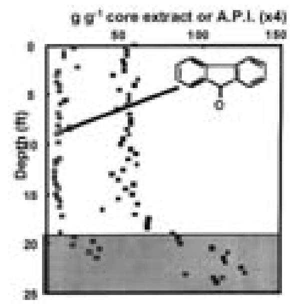


Figure 3 Correlation of depth profiles of petroleum fluorenone (°) concentrations (µg g-1 TSE) versus gamma ray (•) log (A.P.I. x4). Overall, the polar non-hydrocarbons correlated well with clay content, gamma ray logs and deep induction log records from sandstone reservoirs suggesting that these compounds were selectively concentrated in certain reservoir lithologies which also showed more marked oil-wet character.



Despite the excellent correlation of resins and asphaltenes and other compounds with petrophysical properties, the non-hydrocarbon concentrations and distributions seen during our work suggested some of the non-hydrocarbons most associated with reservoir adsorption processes may have an artefactual origin during standard sampling and coring procedures (Bennett and Larter 2000). Wang (1996) showed mixed wettability cores became oil-wet during sample storage after core plugs had become partially dried and the oil had been severely oxidised. Recent work suggests core storage and handling procedures may result in chemical alteration of in-situ oils to produce ketones including possibly the fluorenones. Their sporadic occurrence in crude oils and rock extracts is not yet understood, however, it represents a cause for concern since, in general, old samples appear to contain higher levels of these surface active compounds. However, considering the very important correlations shown between chemical and petrophysical logs, further work is justified into this exciting interface between fluid composition and petrophysics. As chemical logs can be produced rapidly and cheaply and at higher resolution than classical methods such as Amott-Harvey tests, they may have value as detailed logs of key reservoir state properties such as wettability.

Summary

A number of polar non-hydrocarbons present in petroleum from core samples and production fluids from a North Sea reservoir show correlations with petrophysical signals and may allow re-scaling of few classical measurements in mixed state cores. These findings were realised only through detailed integration with all PEGASUS results demonstrating the benefits of the multidisciplinary approach provided by the PEGASUS programme.

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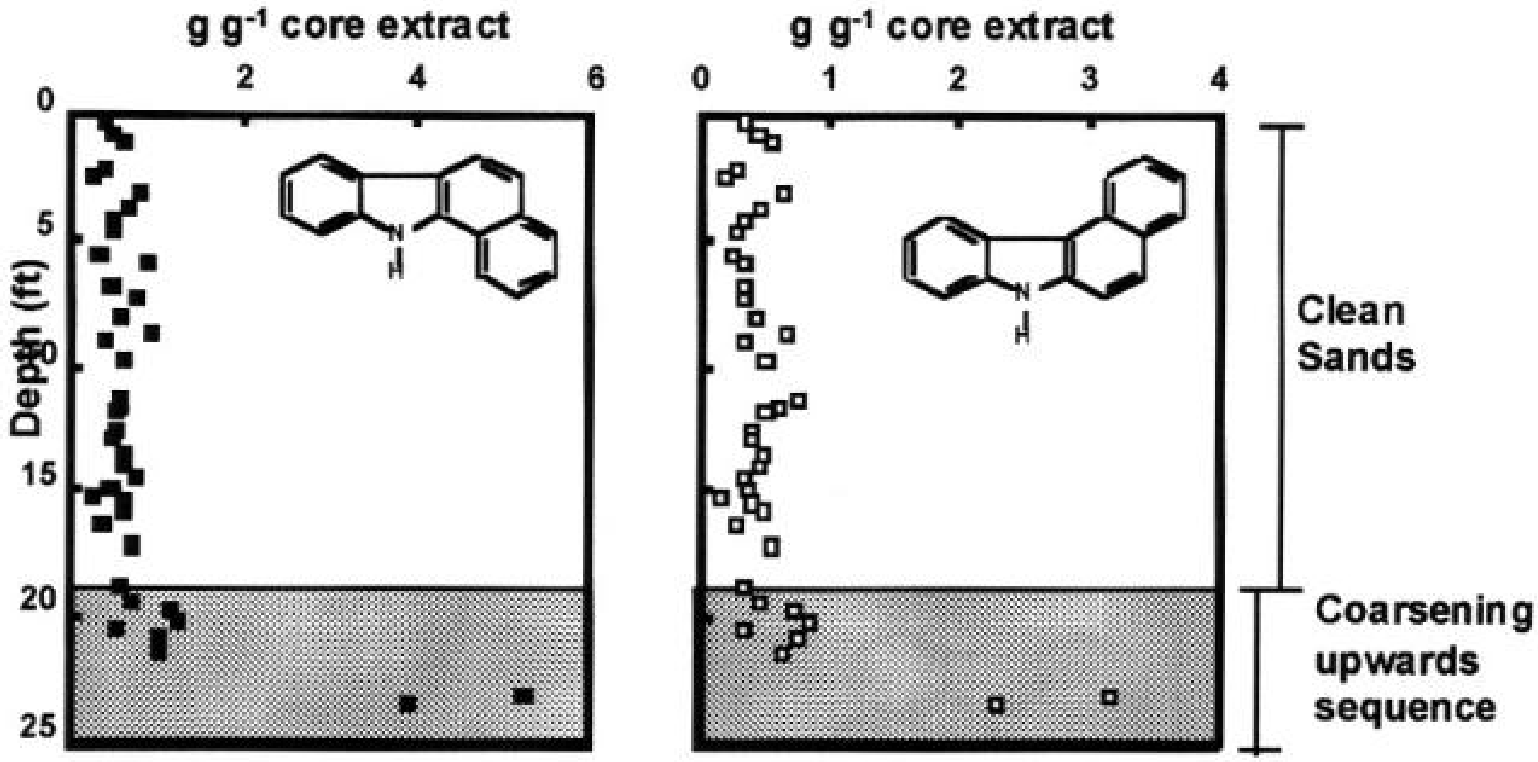

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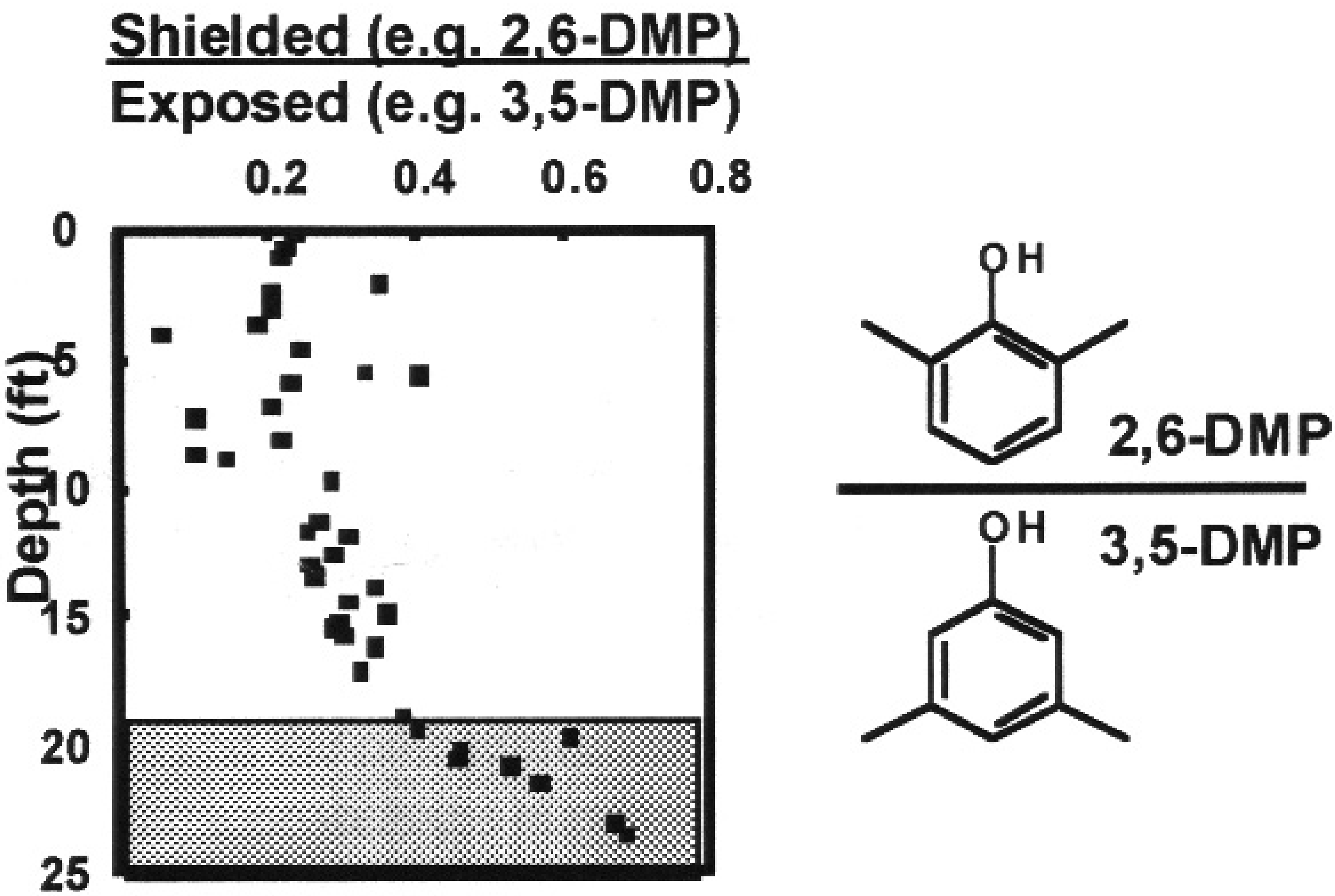

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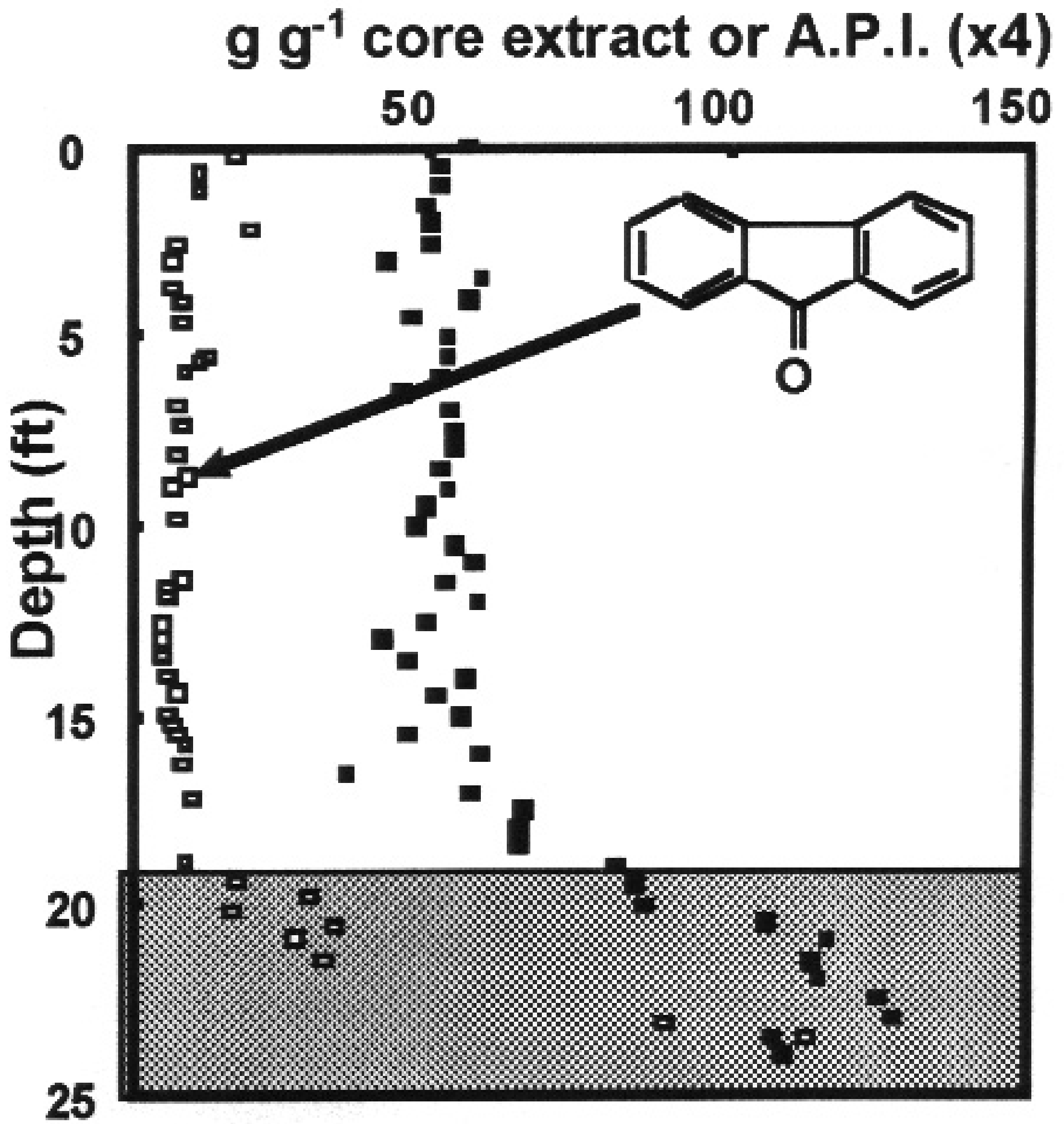

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