Petroleum Geochemical Responses to Reservoir Rock Properties

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Summary

The polar non-hydrocarbon composition of petroleum was investigated in core samples from petroleum reservoirs and a core flood experiment. A group of aromatic oxygen (C_0-C_3-phenols and alkylfluorenones) and aromatic nitrogen (alkylcarbazoles) compounds present in petroleum appear to respond to variations in fluid-rock properties in petroleum reservoirs indicated by the strong correlations shown between gamma ray and geochemical logs. In the core flood experiment, increasing C_0-C_3-phenol concentrations correlates with increasing hydrophobicity of core surfaces indicated by Environmental Scanning Electron Microscopy (ESEM). The results confirm that polar non hydrocarbons possess unique surface active properties which may be exploited for development as proxies for fluid-rock properties in petroleum reservoirs.

Introduction

Reservoir geochemistry involves the study of compositional variations of petroleum reservoir fluids (waters, oils and gases) at a variety of spatial and temporal scales, and reveals information about petroleum basin development, the details of reservoir filling and leaking, and petroleum mixing and alteration (Larter et al., 1997). By their very nature, polar non-hydrocarbons are sensitive to fluid-rock interactions, and if properly exploited they may be utilised as proxies for describing reservoir properties that are sensitive to fluid-rock interactions.

Petroleum contains numerous surface active compounds that are sensitive to interactions with minerals and organic matter. The prediction of fluid flow behaviour in petroleum reservoirs is influenced by the physical and chemical processes active in interacting crude oil / brine / rock systems. It is usually not possible to assess these complex systems directly so proxies for molecular scale behaviour are needed. The distribution of rock sensitive compounds such as benzocarbazoles (Larter et al., 1996) and alkylfluorenones (Bennett and Larter, 1998) often reveal compositional heterogeneity on a sub-meter scale in reservoir core studies, implying this group of compounds may be developed to probe the nature of the fluid-rock environment throughout sampled reservoir intervals. Recent advances in separation methods targeting the NSO compounds in petroleum now provide the geochemist with the means to develop statistically significant correlations of polar non hydrocarbon concentration data with reservoir properties (Bennett et al.,

2007). Here we describe the behaviour of polar non hydrocarbon compounds of petroleum in relation to the changes in rock petrophysics and reservoir wettability.

Method

A core-flood experiment was undertaken on a Carboniferous aged siltstone core (89.7 cm long and 5.09 cm diameter) obtained from the West Midlands (U.K.). Details of the core-flood experiment are described in Bennett et al. (2004). On completion of the experiment, 1 cm thick (5 cm diameter) sections were cut from the core and quartered into approximately 15 gram portions.

A suite of reservoir core (41) samples were made available from a North Sea oilfield. The sample derive from a typical upper shoreface para-sequence with a basal coarsening upwards sandstone unit (5ft) with the following rock properties: porosity 17.4 – 20.6%; permeability 5 - 69 milliDarcies (mD). The coarsening upwards unit is overlain by a clean sandstone unit (19ft) with porosities of 11.7 – 21.1% and permeabilities of 428 - 1240 mD.

All core samples (ca. 15g) were extracted with an azeotropic mixture of dichloromethane (CH_2Cl_2): methanol (93: 7 v/v) for 8 hours in a Soxtherm apparatus. The alkylcarbazoles and alkylfluorenones were isolated from core extracts by using the method described in Bennett et al. (2002). For the analysis of C_0-C_3-phenols, a modification of the method described in Bennett et al. (2007) was employed.

Results and Discussion

The behaviour of petroleum components following simulated petroleum migration through a continuous siltstone core revealed dramatic changes in the composition and distributions of polar non-hydrocarbons compared to the original crude oil. Bennett et al. (2004) showed that C_0-C_3-phenols in produced oils only amounted to 5% recovery compared to the C_0-C_3-phenols in the original oil, while fluoren-9-one, carbazole and benzocarbazoles were ultimately recovered up to 90% of the original quantities. The core extract petroleum was also investigated to monitor compositional changes along the core which showed that C_0-C_3-phenol concentrations decreased from inlet to outlet suggesting these species are sensitive to crude oil / brine / rock interactions (Fig. 1).

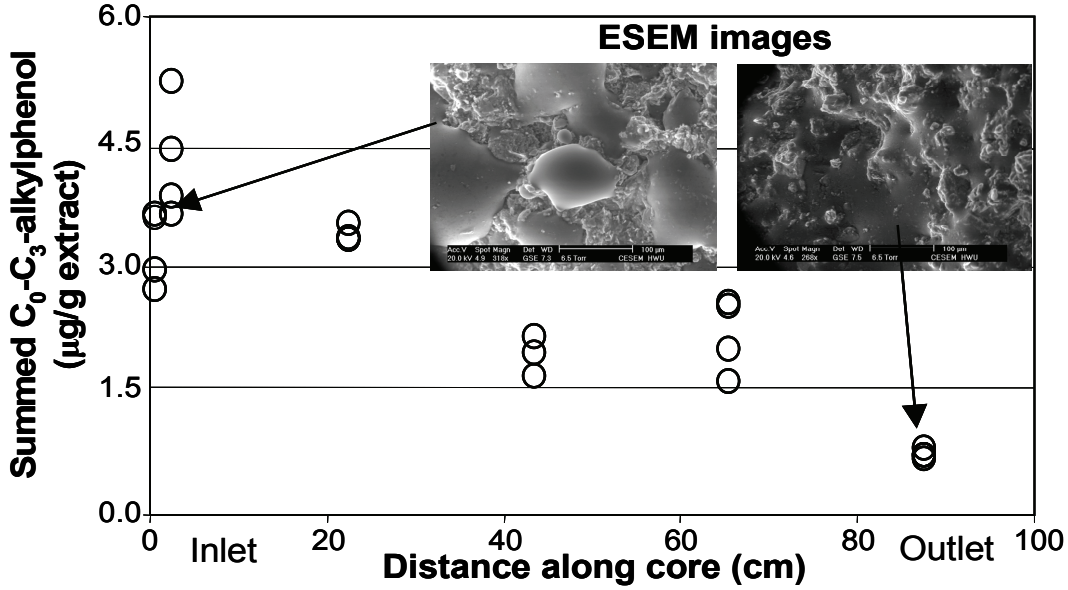

Figure 1: Plot showing the change in concentrations (µg /g extract) of total summed C_0-C_3-phenols in core extract petroleum recovered from core samples as a function of distance (cm) along the core and ESEM images depicting changes in relative hydrophilic / hydrophobic behavior of water during condensation upon core chips (modified from Bennett et al., 2004).

Also shown in Figure 1, are the photomicrographs displaying the morphology of water droplets following interactions with core chip surfaces during condensation cycles under ESEM conditions. Interestingly, at the inlet of the core, where C_0-C_3-phenol concentrations are the highest, hydrophobic behaviour is exhibited by the morphology of water appearing as discrete globules with high contact angles (Fig. 1). A sample from the outlet shows water spreading across the surface in a continuous sheet indicating hydrophilic behaviour (Fig. 1) which coincides with the lowest C_0-C_3-phenol concentrations. Thus the ESEM descriptions of the interaction of water upon core surfaces appear to be consistent with the compositional changes encountered in the core extract petroleum which shows the removal of low molecular weight hydrophilic components including C_0-C_3-phenols.

The behaviour of polar non hydrocarbons was investigated in core samples obtained from a North Sea petroleum reservoir. Figure 2a shows a plot of the fluoren-9-one concentrations in core extract petroleum, along with the wireline gamma ray log for a 24ft reservoir interval. The strongest deflections in both the gamma ray log and fluoren-9-one chemical log are observed in the basal coarsening upwards unit. The response in the gamma ray log is due to the increasing clay content towards the base of the core, thus it appears that fluoren-9-one concentration may also be sensitive to clay content. Strong correlations between other geochemical parameters and the gamma ray log, particularly in the basal coarsening upwards unit, are also recorded, for example the behaviour of C_2-phenol isomers (Fig. 2b). A dramatic change in the ratio of shielded (methyl groups adjacent to the hydroxyl functionality) and exposed (methyl groups located away from the hydroxyl functionality) isomers in the C_2-phenols also corresponds to the basal coarsening upwards sequence.

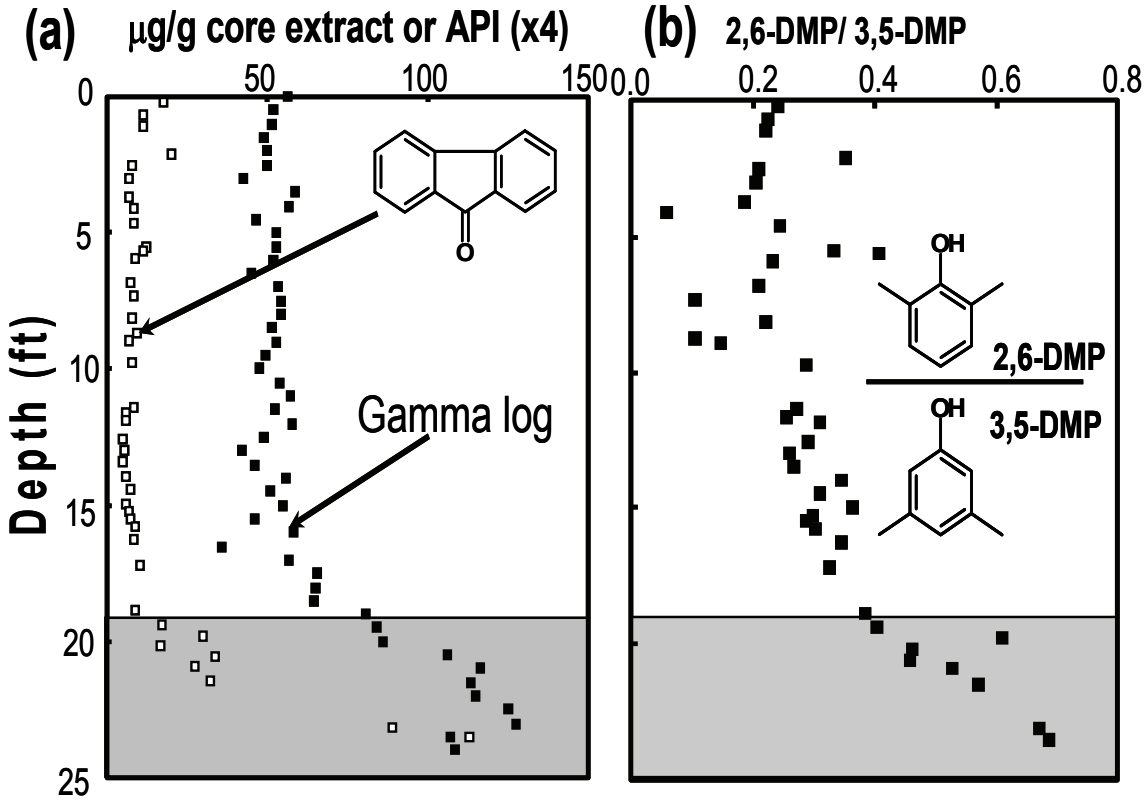

Figure 2: (a) Comparison of gamma ray log (API x 4) and fluorenone concentrations (µg / g extract) and (b) the behaviour of 2,6-dimethylphenol / 3,5-dimethylphenol versus depth in a North Sea reservoir.

In summary, a combination of geochemical and petrophysical measurements of petroleum sandstone reservoirs showed that geochemical logs based on alkylfluorenones and C_0-C_3-phenols correlated well with clay content measured by gamma ray logs suggesting that these non-hydrocarbons were selectively concentrated in certain reservoir lithologies. While these correlations exist it is not always possible to tell if the compositional changes occurred in the subsurface or after sampling and storage. Nonetheless compositional change does seem to reflect mineralogy and rock environment.

Conclusions

Polar non-hydrocarbon compounds are sensitive to reservoir rock properties Wettability changes described by ESEM appeared to correspond to changes in hydrophilic non-hydrocarbon compounds such as the C_0-C_3-phenols, though multifunctional compounds with one or more N, S or O atom are likely to be important facilitators of wettability alteration.

Correlations exist between molecular markers, such as fluoren-9-one and total and gamma ray. Molecular parameters based on the polar non-hydrocarbon composition of petroleum could be used to differentiate between different units, such as clean sand units and adjacent coarsening upward muddy sand sequences, showing that reservoir geochemical parameters provide an independent response to those properties defined by petrophysical methods.

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