



Abstract

Determination of stable carbon ($\delta^{13}\text{C}$) isotope systematics for alkylphenols and light aromatic hydrocarbons (BTEX) in petroleum formation waters and co-produced oils

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Abstract

Solid phase microextraction (SPME) techniques coupled with gas chromatography–isotope ratio mass spectrometry (GC–IRMS) were used to determine the stable carbon ($\delta^{13}\text{C}$) isotopic compositions of aromatic hydrocarbons (BTEX: benzene, toluene, ethylbenzene and xylenes) and phenol in a small suite of co-produced oils and waters from a North Sea oilfield. The $\delta^{13}\text{C}$ patterns and the compound profiles observed are consistent with the theory that the concentrations and distributions of BTEX and alkylphenols in oilfield waters can simply be explained by partition equilibrium between oil and water. The large difference in $\delta^{13}\text{C}$ signatures for phenol compared with benzene and toluene (7–8‰ vs. PDB) in both the oil and water phases strongly suggests that, at least for BTEX and phenols, reversible chemical reactions controlled by master geochemical variables (such as $f\text{O}_2$) do not appear to be important at the temperatures of most oilfields.

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1. Introduction

At temperatures above ca. 100 °C, the generation and destruction of petroleum in sedimentary basins has been generally viewed as an irreversible, kinetically controlled process involving the thermal conversion of organic molecules in source rocks and reservoirs. Over the last decade, however, this conventional view of the petroleum system has been challenged. Diverse experimental (Hoering, 1984; Lewan, 1985; Seewald, 1994; Stalker et al., 1994;

McCollom et al., 1995), theoretical (Helgeson et al., 1993) and empirical (Shock, 1988) evidence has been used to suggest that metastable thermodynamic equilibrium may be attained between petroleum compounds, water, CO_2 and rock minerals in sedimentary basins.

Here, however, we present stable carbon isotopic evidence which supports our previous findings that the concentration and distribution of low molecular weight aromatic hydrocarbons (BTEX: benzene, toluene, ethylbenzene and xylenes) and alkylphenols in oilfield waters are generally not interrelated through redox and hydrolysis reactions. Rather, the concentrations, distributions and stable carbon isotope ($\delta^{13}\text{C}$) signatures of BTEX and alkylphenols are directly inherited from the pattern of compounds generated

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from the parent kerogen. The distribution of BTEX and alkylphenols in oilfield waters simply represents partition equilibrium between oil and water (Dale et al., 1997; Taylor et al., 1997).

2. Samples and methods

Co-produced oil and water samples were collected at well heads from fields in the North Sea and were stored frozen in our laboratories.

Isotopic analysis of BTEX and phenols in aqueous media involved methods based on established solid phase microextraction (SPME) procedures (Buchholz and Pawliszyn, 1994; Dias and Freeman, 1997), used in conjunction with gas chromatography–isotope ratio mass spectrometry (GC–IRMS). All compound-specific $\delta^{13}\text{C}$ analyses were performed on a PDZ Europa GC–IRMS instrument, consisting of a GEO isotope ratio mass spectrometer coupled to a Hewlett Packard 5890 gas chromatograph via an Orchid II combustion interface/prep unit.

3. Results and discussion

Table 1 shows the $\delta^{13}\text{C}$ isotope compositions of BTEX and phenol constituents for three pairs of production waters and co-produced oils obtained from adjacent wells in the same North Sea oilfield. The bulk $\delta^{13}\text{C}$ values for the whole oils are also quoted for comparison. It is obvious that the $\delta^{13}\text{C}$ signature for

simple phenol in both the oil and aqueous phases is consistently and significantly ^{13}C -enriched by 7–8‰ in comparison to all the BTEX components and to the bulk oil itself. The magnitude of this isotopic difference suggests that no significant chemical interconversion of benzene, toluene and alkylphenols has occurred in-reservoir.

Preliminary pyrolysis experiments performed on source rock kerogens have also shown that covalently bound phenol released by thermal fragmentation of the host geopolymer is also typically ^{13}C -enriched in comparison to the $\delta^{13}\text{C}$ of the bulk organic sedimentary carbon. This implies a biological origin of phenol in petroleum systems and sediments predominantly from carbohydrate or protein moieties, e.g. tyrosine, which probably became incorporated into kerogen during early diagenesis as melanoidin-type polymers. So, similar $\delta^{13}\text{C}$ patterns exist in source rocks, oils and formation waters for phenols relative to the bulk organic carbon and this evidence adds further support to our theory that oil–water partitioning of petroleum (itself resulting from kerogen maturation) largely controls the distribution of BTEX and phenols in oilfield waters (Dale et al., 1997; Taylor et al., 1997).

Consistent patterns in isotope compositions can also be observed for BTEX components in each of the three production waters analyzed in this study (Table 1). Ethylbenzene is in each case significantly ^{13}C -depleted in comparison to the other BTEX compounds, with benzene and toluene being the isotopically lightest components. These significant differences in isotopic composition between the different BTEX components

Table 1

Compound-specific $\delta^{13}\text{C}$ signatures (‰ vs. PDB) obtained for selected low molecular weight organic constituents of production waters and co-produced petroleum from a North Sea oilfield

Sample	Whole oil ^a	Benzene	Toluene	Ethylbenzene	<i>m</i> -, <i>p</i> -Xylene	<i>o</i> -Xylene	Phenol
GA13 water		– 29.7 (0.10)	– 29.3 (0.04)	– 26.1 (0.16)	– 27.2 (0.09)	– 27.2 (0.36)	– 21.9 (0.09)
GA13 oil	– 30.1	n.d.	n.d.	n.d.	n.d.	n.d.	– 22.1 (0.32)
GA18 water		– 29.6 (0.02)	– 29.0 (0.11)	– 25.5 (0.38)	– 27.0 (0.18)	– 27.3 (0.43)	– 22.3 (0.15)
GA18 oil	– 30.2	n.d.	n.d.	n.d.	n.d.	n.d.	– 22.5 (0.14)
GA18a water		– 29.3 (0.36)	– 28.8 (0.17)	– 26.0 (0.13)	– 26.6 (0.17)	– 27.2 (0.32)	– 23.1 (0.29)
GA18a oil	– 30.3	n.d.	n.d.	n.d.	n.d.	n.d.	– 22.2 (0.29)

Values in brackets denote analytical precision (as standard deviations) calculated for isotope values obtained from replicate GC–IRMS analyses. $\delta^{13}\text{C}$ values are estimated to be accurate to within $\pm 0.8\%$.

n.d.: not determined.

^a Whole oil values were obtained from conventional offline combustion–IRMS measurements (where standard deviations were typically $< 0.06\%$).

suggest that different biological pools or biochemical precursors (e.g. lipids vs. proteins) contributed to the formation of each compound in different proportions. More work is required, however, to verify whether the isotope patterns detected here mimic a general trend for BTEX in other oils and production waters.

4. Conclusions

The $\delta^{13}\text{C}$ patterns and the compound profiles observed for BTEX and alkylphenols in a suite of North Sea oils and production waters are consistent with the theory that the concentrations and distributions of BTEX and alkylphenols in oilfield waters can simply be explained by partition equilibrium between oil and water. The large differences in $\delta^{13}\text{C}$ signatures for phenol compared with benzene and toluene (7–8‰ vs. PDB) in both the oil and water phases strongly suggests that no significant chemical inter-conversion of benzene, toluene and alkylphenols has occurred in-reservoir through abiotic redox and/or hydrolysis reactions.

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