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Research paper

Control of facies, maturation and primary migration on biomarkers in the Barnett Shale sequence in the Marathon 1 Mesquite well, Texas

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ABSTRACT

A great deal is known about the genetic relationships between biomarkers and their biogenic precursors in organic rich rocks. The same is true of the way in which biomarker compound ratios change during maturation. On the other hand, very little is known about whether a crude oil can fully retain its inherent compositional ancestry during expulsion from a source rock. Thanks to shales being characterized in great detail for their unconventional resource potential, new information is gradually coming to light. Here we report on observations in biomarker geochemistry of a thermally mature core of the Barnett Shale, in which organofacies and maturity are essentially the same, but where intraformational sources and reservoirs have already been reported.

Our results indicate that most biomarkers are not fractionated as the primary migration of petroleum within source rocks takes place. The 20S/(20S + 20R) ratio of C_{27} steranes is uniform in the whole source-rock sequence, while the 20S/(20S + 20R) ratio of C_{29} steranes shows indistinctly high values in the reservoir unit. The 20S/(20S + 20R) ratio of diasteranes and the 22S/(22S + 22R) ratio of C_{31} 17α-hopanes do not appear to have been fractionated, which may be a result of the thermal isomerization reactions predominating over and masking out the possible fractionation effects. Diasteranes/steranes ratios do not exhibit features that suggest an association with fractionation, but rather are broadly correlated with lithology. However, compared to the diasteranes/steranes ratios, the Ts/(Ts + Tm) ratio is much more sensitive to changes in mineral compositions. Variations in the Ts/(Ts + Tm) ratio show a positive correlation ($R^2 = 0.73$) with mixed-layer illite-smectite content. Fractionation in the Ts/(Ts + Tm) ratio, if it has so occurred, may be subsequently overprinted by in-situ clay-catalyzed reactions.

1. Introduction

Biomarkers are complex molecular fossils derived from once living organisms that have been preserved in sediments (Peters et al., 2005; Tissot and Welte, 1984). The general application of biomarkers for inferring paleoflora, paleoenvironments and the origin of life on Earth, as well as for providing a zonation for diagenetic change, is well established practice. The concept of oil-oil and especially oil-source correlation assumes that the distribution of biomarkers in non-biodegraded petroleum fluids is inherited from precursor biota and thermal maturity, and has remained unchanged during the migration processes. While migrational fractionation was postulated forty years ago by Seifert and Moldowan (1978), the small size of their dataset precluded unambiguous interpretation. In a later study, a slight increase in 5α,14α,17α(H)20S and a relatively large increase in 5α,14β,17β(H) 20R compared with 5α,14α,17α(H)20R steranes was attributed to migrational changes (Seifert and Moldowan, 1981). Variations in the relative abundance of mono-/tri-aromatic steroids have also been ascribed to the migration effect (Hoffmann et al., 1984). Fan and Philp (1987) and Jiang et al. (1988) crudely simulated migration using an alumina column, and observed greatly exaggerated fractionation effects, i.e. the elution of tricyclic terpanes prior to pentacyclic terpanes, 17α,21β(H)-hopanes and 22S 17α,21β(H)-hopanes elute more rapidly than 17β,21α(H)-hopanes and 22R 17α,21β(H)-hopanes, rearranged and 5α,14β,17β(H)-steranes elute faster than 5α,14α,17α(H)-steranes, and 20S 5α,14α,17α(H)-steranes elute faster than 20R 5α,14α,17α(H)-steranes. Peters et al. (1990) attempted to mimic the primary migration process using hydrous pyrolysis. While none of their isomerization biomarker ratios

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showed significant differences between bitumen and the expelled oil – such as 22S vs 22R C_{32} 17α,21β(H)-homohopanes or 20S vs 20R and ββ vs αα C_{29} 5α(H)-steranes – they observed a preferential migration of mono- over tri- aromatic steroids, tricyclic terpanes over hopanes, and diasteranes over steranes. The question remains as to whether petroleum fractionation in the subsurface is fundamentally the same as seen in such laboratory chromatographic systems (Krooss et al., 1991).

The lack of direct observations of petroleum in the act of moving in the subsurface from one place to another constitutes a major obstacle to our understanding of migration, especially primary migration (Leythaeuser et al., 1984). As most biomarkers are source- and maturity- sensitive, an unambiguous observation of biomarker alterations during or resulting from migration can only be possible for a given set of samples with identical maturity and a similar source.

In spite of many constraints, a recently published paper on the Barnett Shale (Han et al., 2015) may provide a sound basis for conclusive interpretation. In the Marathon 1 Mesquite well, the Mississippian Barnett Shale was shown to possess a rather homogeneous kerogen facies (Type-II marine), depositional environment and maturity signature (1.0% Rc, calculated vitrinite reflectance). The 175-ft thick Barnett Shale sequence has been subdivided top down into five intervals, in which the second interval is abundant in porous sponge spicules and behaves like a reservoir-unit, while the third interval consists mainly of organic-rich mudstones and constitutes the best source-rock. The fluorescing oil, occurring both in the chamber of sponge spicules and sorbed on organic particles, is enriched in saturated hydrocarbons, whereas the dispersed oil from the underlying argillaceous source interval is enriched in resins and asphaltenes. Mass-balance calculations have shown evidence of accumulations of non-indigenous hydrocarbons in the reservoir unit (the 2nd interval plus the upper part of the 3rd interval). This observation, in conjunction with the abovementioned geological circumstances, led us to conclude that short-distance migration of petroleum into the reservoir unit fractionates the oil into a higher quality liquid by preferential retention in the order polar compounds > aromatic hydrocarbons > saturated hydrocarbons within the underlying organic-rich interval. At that time, we hypothesized that it is the intraformational migrated hydrocarbons that accumulated in the reservoir unit, though we presented no biomarker data. Here, we have re-examined the consistency in source facies and thermal maturity using various non-biomarker and biomarker parameters. The aim of this study is, therefore, to use our well-characterized samples as a reliable test set to obtain an understanding of the possible effects of migration on biomarker parameters and other well-known thermal maturity ratios.

2. Experimental

Seventeen bitumen extracts from the comprehensively studied Barnett Shale in the Marathon 1 Mesquite well were extracted and fractionated into compound classes, as described by Han et al. (2015). Metastable reaction monitoring/gas chromatography/mass spectrometry (MRM/GC/MS) was conducted in addition, because many biomarkers were in too low a concentration as to be detected by GC/MS. The saturate fraction was subjected to urea adduction following the procedure of Marquart et al. (1968) in order to concentrate the branched-cyclic biomarkers. The corresponding separated alkanes (i.e. n-C_{17}, n-C_{18}, pristane and phytane) were further analysed using isotope ratio monitoring/gas chromatography/mass spectrometry (IRM/GC/MS) on a system described by Kristen et al. (2010). All stable carbon isotope values were measured in triplicate against Vienna PeeDee Belemnite (VPDB) as follows: $\delta^{13}C_{sample}$ (‰) = $[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1] \times 1000$. The resulting isotopic ratios of $\delta^{13}C$ are expressed in delta notation following the format given by Coplen (2011). X-ray powder diffraction (XRD) measurement was carried out using a PANalytical Empyrean powder diffractometer with Cu Kα radiation, automatic divergent and anti-scatter slits, and a PIXcel^{3D} detector. The diffraction data were recorded from 5° to 85° 2Θ with a step width of 0.013° and a scan time of 60 s per step.

3. Results and discussion

3.1. Framework-1: thermal maturity from aromatic compound ratios

The distributions of alkylated aromatic hydrocarbons and aromatic sulfur compounds are well-developed and established thermal maturity parameters (Alexander et al., 1985; Radke, 1988; Radke et al., 1982a, 1982b, 1984, 1986, 1990), which were believed not to be affected by geochromatographic fractionations (Leythaeuser et al., 1988; Radke et al., 1990). In line with this, methyl-, dimethyl- and trimethyl-naphthalene isomer ratios (MNR, DNR, TNR1 and TNR2, respectively) exhibit a uniform thermal maturity level in the Marathon 1 Mesquite well (Table 1, Fig. 1A). Methyl- and dimethyl-phenanthrene isomer ratios, in part published previously (MPI1, Han et al., 2015), behave similarly (Table 1, Fig. 1B). The thermal rearrangement and methylation reactions are thought to result in a pronounced increase in specific ratios, such as the MNR (Radke, 1988; Radke et al., 1982b, 1986) and MPI1 (Alexander et al., 1985; Radke, 1988; Radke et al., 1982a). Based on this hypothesis, alkylated aromatic hydrocarbon derived maturation ratios – for example MNR, DNR, MPR and MPI1 – were calibrated against the measured vitrinite reflectance (Radke et al., 1984, 1986). Accordingly, we calculated the corresponding equivalent vitrinite reflectance (Table 2). The Rc of 1.00–1.10% (Table 2) totally corresponds to that calculated from T_{max} (~1.03% Rc, Han et al., 2015). A possible impact of organic matter type on the distribution of naphthalene and phenanthrene isomers (Radke, 1988; Radke et al., 1986) was not evident in this study.

Comparing with alkylated aromatic hydrocarbons, the alkylated dibenzothiophene (DBT) derived maturity ratios rely on the same chemical basis, i.e. a shift in predominance from thermally relatively unstable isomers towards more stable isomers with increasing maturation (Radke, 1988). In the Marathon 1 Mesquite well, some DBT-derived maturation ratios illustrate identical thermal maturity, for instance MDR1 and MDR2,3 (Table 1, Fig. 1C). However, notably, the MDR4 index implies a considerable maturity deviation for samples of the "false" Barnett (the 1st interval). In accordance with the original statement of Radke et al. (1986), the noticeably low MDR4 was indicative of the variations in source facies, a point which is also supported by the excursion in $\delta^{13}C$ described below (Fig. 2).

3.2. Framework-2: source facies from compound-specific stable carbon isotope ratios

Stable carbon isotope ratio is a widely used tool in source facies correlation (Chung et al., 1992; Peters et al., 1999; Sofer, 1984). However, since hydrocarbons can become isotopically enriched in ^{13}C as maturation progresses (Clayton and Bjorøy, 1994), a precise interpretation of source facies based on compound-specific $\delta^{13}C$ values is in fact dependent on a fixed maturity level as alluded to above. Likewise, the $\delta^{13}C$ values of n-C_{17} from the "false" Barnett (the 1st interval) show offset from the value (−31‰) established by those of Barnett Shale samples. The same applies to n-C_{18} as well (Fig. 2A). The carbon isotopic signatures of pristane and phytane show the same, albeit relatively obscure features (Fig. 2B).