



Originally published as:

Han, Y., Horsfield, B., Curry, D. J. (2017): Control of facies, maturation and primary migration on biomarkers in the Barnett Shale sequence in the Marathon 1 Mesquite well, Texas. - *Marine and Petroleum Geology*, 85, pp. 106—116.

DOI: <http://doi.org/10.1016/j.marpetgeo.2017.04.018>

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

Yuanjia Han<sup>a, \*</sup>, Brian Horsfield<sup>a</sup>, David J. Curry<sup>b</sup>

<sup>a</sup>German Research Centre for Geosciences (GFZ), Telegrafenberg, Potsdam 14473, Germany

<sup>b</sup>Noble Energy, Inc., 1001 Noble Energy Way, Houston, Texas 77070, United States

\*Corresponding author. Email address: [yuanjia@gfz-potsdam.de](mailto:yuanjia@gfz-potsdam.de)

## 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<sub>27</sub> steranes is uniform in the whole source-rock sequence, while the 20S/(20S+20R) ratio of C<sub>29</sub> steranes shows indistinctly high values in the reservoir unit. The 20S/(20S+20R) ratio of diasteranes and the 22S/(22S+22R) ratio of C<sub>31</sub> 17 $\alpha$ -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.

**Keywords:** Barnett Shale; Biomarkers; Aromatic hydrocarbons; Primary migration

## 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  $5\alpha,14\alpha,17\alpha(\text{H})20\text{S}$  and a relatively large increase in  $5\alpha,14\beta,17\beta(\text{H})20\text{R}$  compared with  $5\alpha,14\alpha,17\alpha(\text{H})20\text{R}$  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,  $17\alpha,21\beta(\text{H})$ -hopanes and  $22\text{S } 17\alpha,21\beta(\text{H})$ -hopanes elute more rapidly than  $17\beta,21\alpha(\text{H})$ -hopanes and  $22\text{R } 17\alpha,21\beta(\text{H})$ -hopanes, rearranged and  $5\alpha,14\beta,17\beta(\text{H})$ -steranes elute faster than  $5\alpha,14\alpha,17\alpha(\text{H})$ -steranes, and  $20\text{S } 5\alpha,14\alpha,17\alpha(\text{H})$ -steranes elute faster than  $20\text{R } 5\alpha,14\alpha,17\alpha(\text{H})$ -steranes. Peters et al. (1990) attempted to mimic the primary migration process using hydrous pyrolysis. While none of their isomerization biomarker ratios showed significant differences between bitumen and the expelled oil – such as  $22\text{S}$  vs  $22\text{R}$   $\text{C}_{32}$   $17\alpha,21\beta(\text{H})$ -homohopanes or  $20\text{S}$  vs  $20\text{R}$  and  $\beta\beta$  vs  $\alpha\alpha$   $\text{C}_{29}$   $5\alpha(\text{H})$ -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%  $R_c$ , 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 2<sup>nd</sup> interval plus the upper part of the 3<sup>rd</sup> 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<sub>17</sub>, *n*-C<sub>18</sub>, 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:  $\delta^{13}\text{C}_{\text{sample}} (\text{‰}) = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}} / ({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}} - 1] \times 1000$ . The resulting isotopic ratios of  $\delta^{13}\text{C}$  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 K $\alpha$  radiation, automatic divergent and anti-scatter slits, and a PIXcel<sup>3D</sup> detector. The diffraction data were

recorded from  $5^{\circ}$  to  $85^{\circ}$   $2\Theta$  with a step width of  $0.013^{\circ}$  and a scan time of 60 s per step.

### 3. Results and discussion

#### *Framework-1: thermal maturity from aromatic compound ratios*

The distributions of alkylated aromatic hydrocarbons and aromatic sulphur compounds are well-developed and established thermal maturity parameters (Alexander et al., 1985; Radke, 1988; Radke et al., 1990; Radke et al., 1984; Radke et al., 1982a; Radke et al., 1986; Radke et al., 1982b), 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, Figure 1A). Methyl- and dimethyl-phenanthrene isomer ratios, in part published previously (MPI1, Han et al., 2015), behave similarly (Table 1, Figure 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., 1986; Radke et al., 1982b) 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; Radke et al., 1986). Accordingly, we calculated the corresponding equivalent vitrinite reflectance (Table 2). The  $R_c$  of 1.00 to 1.10% (Table 2) totally corresponds to that calculated from  $T_{max}$  ( $\sim 1.03\%$   $R_c$ , 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, Figure 1C). However, notably, the MDR4 index implies a considerable maturity deviation for samples of the “false” Barnett (the 1<sup>st</sup> 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  $\delta^{13}\text{C}$  described below (Figure 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  $^{13}\text{C}$  as maturation progresses (Clayton and Bjorøy, 1994), a precise interpretation of source facies based on compound-specific  $\delta^{13}\text{C}$  values is in fact dependent on a fixed maturity level as alluded to above. Likewise, the  $\delta^{13}\text{C}$  values of  $n\text{-C}_{17}$  from the “false” Barnett (the 1<sup>st</sup> interval) show offset from the value (-31‰) established by those of Barnett Shale samples. The same applies to  $n\text{-C}_{18}$  as well (Figure 2A). The carbon isotopic signatures of pristane and phytane show the same, albeit relatively obscure features (Figure 2B). Comparing the  $\delta^{13}\text{C}$  data of Barnett Shale extracts, the  $\delta^{13}\text{C}$  values (2-3 ‰) for  $n\text{-C}_{17}$ ,  $n\text{-C}_{18}$ , pristane and phytane are larger in extracts from sample G009583. As claimed by Chung et al. (1992), in general, the carbon isotopic composition of oils derived from marine carbonates is heavier than that of shales, whilst some exceptions are known for Paleozoic oils (Wenger et al., 1988). In line with this generalization, sample G009583 exhibits high calcite content (64.8%, Table 3).

Thus, we have demonstrated an identical maturity level and a common source facies using non-biomarker molecular parameters in the studied well, with the exception of bitumen extracts



from the “false” Barnett interval. These results are generally in line with our previous interpretations, namely that the Barnett Shale has been shown to possess a rather homogeneous kerogen facies, depositional environment and maturity signature based on bulk geochemical data (Han et al., 2015).

### 3.1. Sterane and diasterane distributions

Sterane homologues (C<sub>27</sub>-C<sub>28</sub>-C<sub>29</sub>) reflect the marine eukaryotic versus terrestrial organic input into sedimentary organic matter (Huang and Meinschein, 1979; Moldowan et al., 1985). Likewise what illustrated in Hill et al. (2007), the ternary diagram of steranes illustrates a similar source facies for Barnett Shale samples, whereas the diasterane diagram (Peters et al., 2005) displays an even tighter distribution in the Marathon 1 Mesquite well (Figure 3). As already pointed out, samples from the “false” Barnett (the 1<sup>st</sup> interval) are anomalous (cf. MDR4 in Figure 1C and  $\delta^{13}\text{C}$  in Figure 2). Correspondently, the triangular plots of C<sub>29</sub> steranes and diasteranes reveal the organic matter of the “false” Barnett to be slightly different (Moldowan et al., 1985; Zumberge, 1987) (Figure 3). Notably, the regular steranes display slightly different trends than the diasteranes. This discrepancy may arise from the relatively low concentration of steranes as exemplified in Figure 4, which may be caused by high maturity (Hill et al., 2007) and may thus result in a lower accuracy of quantification. Due to the excessive background noise observed for C<sub>28</sub> ergostanes (Figure 4), which may bear the problem of coelution (C<sub>28</sub>  $\beta\alpha\alpha$ 20R nearly co-elutes with C<sub>28</sub>  $\alpha\beta\beta$ 20R) (Peters et al., 2005), the C<sub>28</sub> ergostanes are not studied here.

Nevertheless, except for samples from the 1<sup>st</sup> interval, Barnett Shale bitumen extracts from the Marathon 1 Mesquite well exhibit a common source facies. One sample (G009674) from the 4<sup>th</sup> interval also has a slightly different algal input. In addition to organofacies interpretation, steranes are widely used in maturity detection as well.

Steranes with the biological configuration  $5\alpha,14\alpha,17\alpha(H)20R$  systematically decline relative to the geological  $14\beta,17\beta(H)$  and  $20S$  forms. The  $20S/(20S+20R)$  ratio is believed to describe the maturity-driven progress of  $20R$  to  $20S$  isomerization in steranes (Peters et al., 2005). In maturation series, the  $20S/(20S+20R)$  ratio of  $C_{29}$   $5\alpha,14\alpha,17\alpha(H)$  steranes rises from 0 to an equilibrium at about 0.52-0.55 with increasing maturity (Seifert and Moldowan, 1986). With an average value of 0.49 and 0.44 for  $C_{27}$  (Figure 5A) and  $C_{29}$  (Figure 6A)  $5\alpha,14\alpha,17\alpha(H)$  homologues, respectively (Table 4), this ratio exhibits variation in the study well. In these depth profiles, the  $20S/(20S+20R)$   $C_{27}$  cholestane ratio is very stable (Figure 5A), while that of  $C_{29}$  stigmastane seems to exhibit higher values in the reservoir unit (Figure 6A) in which migrated has accumulated (Han et al., 2015).

C-20 isomerization is reported to occur earlier in diasteranes than in regular steranes (Mackenzie et al., 1980). Change in the  $20S/(20S+20R)$  ratio of  $13\beta,17\alpha(H)$ -diacholestanes equilibrates at about 0.6 in the Paris Basin, which is broadly analogue to our case (Type-II kerogen) (Table 4). That is to say, the stable values that fluctuate around 0.6 (Figure 5B and 6B) fit the expectation that the isomerization of diasteranes has already reached the end-point of equilibrium.

Configuration at the C-14(H) and C-17(H) chiral centres of steroids appears to reach equilibrium slower than C-20 isomerization in sterane and diasteranes (Mackenzie et al., 1980). The  $\beta\beta/(\alpha\alpha+\beta\beta)$  ratio increases from near-zero to equilibrium values of about 0.7 as maturity increases (Peters et al., 2005). It is clear that equilibrium is not reached for  $C_{27}$  and  $C_{29}$   $5\alpha(H)$  sterane homologues (Figure 5C and 6C), which show average values of only 0.48 and 0.57, respectively (Table 4). Data scattering is more pronounced for  $\beta\beta/(\alpha\alpha+\beta\beta)$  steranes than for  $20S/(20S+20R)$  diasteranes (Figure 5B and 6B), in correspondence with their relatively low signal to noise (S/N) ratios compared to diasteranes (Figure 4).

It has been proposed that the rearrangement of methyl groups at the C-5 and C-14 steroid nucleus is clay-catalysed during diagenesis and early catagenesis (Rubinstein and Albrecht, 1975). The diasteranes/steranes ratio increases dramatically after peak oil generation (Peters et al., 1990), up until the regular steranes have totally diminished (Peters et al., 2005). Steranes are still detectable in our samples, albeit in lower concentrations compared to diasteranes (Figure 4). With the exception of only one sample (G009674) with slightly lower diasteranes/steranes values for both the C<sub>27</sub> (Figure 5D) and the C<sub>29</sub> (Figure 6D) steranes, the diasteranes/steranes ratios exhibit no statistical variation.

### 3.2. Migration of steranes

Sterane biomarker fractionation has been reported in both field studies (Seifert and Moldowan, 1978, 1981) and laboratory simulating experiments (Carlson and Chamberlain, 1986; Fan and Philp, 1987; Jiang et al., 1988), with the 20S 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ (H)-steranes eluting through porous media faster than the 20R 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ (H)-steranes; the 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ (H)-steranes elute faster than the 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ (H)-steranes, and the diasteranes elute much more readily than the regular steranes. Notwithstanding, the distributions of steranes and diasteranes do not suggest that fractionations have taken place in the course of intraformational migration of petroleum within the studied Barnett Shale sequence.

The 20S/(20S+20R) ratio of C<sub>27</sub> cholestanes is uniform throughout the investigated shale sequence (Figure 5A), while that of C<sub>29</sub> stigmastanes shows indistinctly higher values in the reservoir unit (the 2<sup>nd</sup> interval plus the upper part of the 3<sup>rd</sup> interval, Figure 6A). For practical

purposes, the C<sub>29</sub> stigmastanes are the most used steranes, as coelutions from other sterane isomers are minor (Seifert and Moldowan, 1979; Seifert and Moldowan, 1986). However, the MRM/GC/MS measurements applied here are reasonably accurate for C<sub>27</sub> cholestanes as well (Peters et al., 2005). For accuracy, the C<sub>27</sub> cholestanes are preferentially drawn on in the following discussion as their signal to noise ratios are higher by comparison (Figure 4). The indistinctly higher values of 20S/(20S+20R) C<sub>29</sub> stigmastanes are interpreted here as a manifestation of intrinsic data scattering (Figure 6A). This interpretation fits the distributions of 20S/(20S+20R) for both C<sub>27</sub> (Figure 5B) and C<sub>29</sub> (Figure 6B) diasteranes, in that there is no noticeable data change as a result of intraformational petroleum migration from the source unit into the reservoir unit. Compared to other steroid ratios, for example  $\beta\beta/(\alpha\alpha+\beta\beta)$  (Figure 5C and 6C) and  $d\beta\alpha/(\alpha\beta\beta+\alpha\alpha\alpha)$  (Figure 5D and 6D), the 20S/(20S+20R) of diasteranes possess the highest signal to noise ratios (Figure 4), and are therefore preferentially drawn on for interpretation.

The discrepancies between what has been reported in field studies (Seifert and Moldowan, 1978, 1981) and this study may be rooted in the fact that the scopes of the investigated processes are different. This study reports on primary migration, while Seifert and Moldowan (1981) focused on the possible geochromatography effects of secondary migration. The primary migration of petroleum within the study source sequence is in the tens of metres in scale, while

that of secondary petroleum migration from source rock to and within reservoirs is likely in the kilometres. Thus, it is also possible that the indistinctly higher values of  $20S/(20S+20R)$  and  $\beta\beta/(\alpha\alpha+\beta\beta)$  at  $C_{29}$  stigmastanes in the reservoir unit (Figure 6A and 6C) constitute the prototype geochromatography effects of short distance migration.

The discrepancies between laboratory simulating experiments (Carlson and Chamberlain, 1986; Fan and Philp, 1987; Jiang et al., 1988) and the current study may arise from the different conditions of temperature and time in which the migrating biomarkers occur. For example, the diasterane  $20S/(20S+20R)$  ratios of our samples (Table 4) have already reached the end-point of equilibrium (0.6). Even if the purported laboratory simulated fractionation effects did indeed once occur in the Barnett Shale when petroleum migrated from the source unit into the reservoir unit, the continuing high ambient thermal stress in the subsurface may have forced the values back to the end-point of equilibrium. Clearly this does not happen in the laboratory. Subsurface petroleum migration is not the same as that seen in the laboratory. As the  $20S/(20S+20R)$  diasterane ratios are not reported to have values significantly higher than 0.6 to the best of our knowledge, we can deduce that the thermal isomerization reactions can predominate over and mask out possible fractionation effects that might have occurred.

If thermal stress can mask out the possible effects of fractionations, the uniform distributions of  $20S/(20S+20R)$  steroid ratios – i.e. the  $C_{27}$  diacholestanes (Figure 5B) and  $C_{29}$  diastigmastanes

(Figure 6B) – should not be employed for interpreting possible biomarker fractionations. As the  $d\beta\alpha/(\alpha\beta\beta+\alpha\alpha\alpha)$  ratios of diasteranes/steranes are certainly not at the end-point of equilibrium (1.0), they are alternatively referenced here (Figure 5D and 6D). In line with previous interpretations, there is an absence of noticeable fractionation features as petroleum migrates from the source unit into the reservoir unit. Only one sample (G009674) shows slightly low diasteranes/steranes values (Figure 5D and 6D), which is probably due to its unique source facies (Figure 3) or lithology compositions (Table 3). Whilst mobility is believed to be higher for rearranged steranes than for steranes (Carlson and Chamberlain, 1986; Fan and Philp, 1987; Jiang et al., 1988; Peters et al., 1990; Seifert and Moldowan, 1978), fractionations of diasteranes/steranes ratios could nevertheless not be observed.

For interpreting the possible fractionation effects on steroid biomarkers, the most suitable data come from the 20S/(20S+20R) ratios of  $13\beta,17\alpha(H)$  diasteranes which are already in equilibrium at the end-point of isomerization reactions. In those cases in which the reaction end-point has not been reached, i.e. the  $C_{27}$  20S/(20S+20R) and  $d\beta\alpha/(\alpha\beta\beta+\alpha\alpha\alpha)$  diasteranes/steranes, steroid biomarkers have nonetheless not undergone significant changes in the course of intraformational migration of petroleum within the Barnett Shale sequence under study here.

### *3.3. Hopane distributions*

Source-input differentiation and thermal-maturity determination using terpanes are also

standard procedures in petroleum system evaluation. Parameters include the distribution of tricyclics/17 $\alpha$ -hopanes, C<sub>31</sub>-C<sub>34</sub> homohopanes, methylhopanes, gammacerane, oleanane and 22S/(22S+22R) homohopanes, moretanes/hopanes, Ts/(Ts+Tm), as reviewed by Peters et al. (2005). Terpanes are either absent or too low to be quantified in the Mesquite well, with the exception of the Ts/(Ts+Tm) ratio of C<sub>27</sub> 22,29,30-trisnorhopanes and the 22S/(22S+22R) ratio of C<sub>31</sub> 17 $\alpha$ -hopanes.

The Ts/(Ts+Tm) ratio, sometimes referred to as Ts/Tm, is regarded as the most reliable maturity indicator when there is a proven common source of consistent organic facies (Peters et al., 2005). C<sub>27</sub> 18 $\alpha$ -22,29,30-trisnorhopane-II (Ts) is believed to be more resistant to maturation compared to C<sub>27</sub> 17 $\alpha$ -22,29,30-trisnorhopane (Tm). Therefore, the Ts/Tm ratio increases with maturity (Seifert and Moldowan, 1981) until Tm has been exhausted (Peters et al., 2005). Coelution of Tm and Ts with tricyclic or tetracyclic terpanes on m/z 191 mass chromatograms can result in spurious Ts/(Ts + Tm) values (Peters et al., 2005), but this situation can be remedied by utilizing MRM/GC/MS (Seifert and Moldowan, 1986). In our sample set, the Ts/Tm ratio shows significant variation throughout the whole sequence (Figure 7A).

The epimerization of C-22 asymmetric hopanoid centres during maturation exhibits reaction rates and resultant isomeric mixture ratios (60:40) similar to those displayed by C-20 epimerization in diasteranes (Mackenzie et al., 1980). Thus, the 22S/(22S+22R) profile (Figure 7B) is analogue to that of 20S/(20S+20R) ratios of diasteranes (Figure 5B and 6B). Virtually no systematic change to this ratio can be distinguished, and it appears as though it has reached equilibrium at the end-point of isomerization. The 22S/(22S+22R) ratio for individual C<sub>31</sub>-C<sub>35</sub>

17 $\alpha$ -homohopanes may differ slightly (Peters et al., 2005), whilst the average value of 0.56 (Table 4) fits the calculated ratio (0.55) for 22S/(22S+22R) C<sub>31</sub> 17 $\alpha$ -hopanes (Zumberge, 1987).

#### 3.4. Migration of hopanes

Fractionation of hopane biomarkers has been reported in experimental migration simulations (Fan and Philp, 1987; Jiang et al., 1988; Peters et al., 1990). Preferential migration of tricyclic terpanes versus pentacyclic terpanes has been observed in hydrous pyrolysis experiments (Peters et al., 1990). Besides that, Fan and Philp (1987) and Jiang et al. (1988), simulating migration using an alumina column, showed that 17 $\alpha$ ,21 $\beta$ (H)-hopanes and 22S 17 $\alpha$ ,21 $\beta$ (H)-hopanes elute more rapidly than 17 $\beta$ ,21 $\alpha$ (H)-hopanes and 22R 17 $\alpha$ ,21 $\beta$ (H)-hopanes, and that Ts C<sub>27</sub>-trisorhopane elutes faster than Tm C<sub>27</sub>-trisorhopane.

For the samples reported here, the postmature applicable Ts/(Ts+Tm) ratio exhibits no fractionation-associated effects at all (Figure 7A). Instead, this ratio appears to be sensitive to lithology variations. For example, the purest carbonate sample G009647 (calcite 97.7%, Table 3) obviously has the lowest Ts/(Ts+Tm) ratio (Figure 7A). Corresponding to what Peters et al. (2005) have already clarified, oils derived from carbonates appear to have unusually low Ts/(Ts+Tm) ratios compared with those from shales. Shale is enriched in clay minerals, and hence may enhance the clay-catalyzed reactions (Seifert and Moldowan, 1978). There is a generalised positive correlation ( $R^2 = 0.73$ ) between the content of mixed-layer illite-smectite and



the Ts/(Ts+Tm) ratio values (Figure 8). Therefore, the differences in lithology are responsible for the significant variation in Ts/(Ts+Tm) ratios in the Marathon 1 Mesquite well. The possibility of fractionation in the Ts/(Ts+Tm) ratio, which may be overprinted by in situ clay-catalyzed reactions, is nevertheless not observable here.

It has also been proposed that acidic clays can serve as a catalytic mechanism for the conversion of sterols into diasteranes (Rubinstein and Albrecht, 1975), and hence the low diasteranes/steranes ratios are indicative of clay-poor or carbonate source rocks (Hill et al., 2007; Peters et al., 2005). This hypothesis may explain the low C<sub>27</sub> (Figure 5D) and C<sub>29</sub> (Figure 6D) diasteranes/steranes ratios of sample G009647. It has been reported that the diasterane/sterane ratios do not correlate directly with clay content, but rather depend on the ratio of clay relative to organic matter (clay/TOC) (van Kaam-Peters et al., 1998). However, in our sample set, the C<sub>27</sub> and C<sub>29</sub> diasteranes/steranes ratios show no correlation with illite-smectite content, nor with the TOC-normalized illite-smectite content. Compared with the Ts/(Ts+Tm) ratio, the diasteranes/steranes ratios appear to be less sensitive to changes in lithological compositions.

As also applies to the equilibrated 20S/(20S+20R) diasteranes (Figure 3), the 22S/(22S+22R) ratio of C<sub>31</sub> 17 $\alpha$ -hopanes indicates equilibrium mixtures are obtained as well (Figure 7B). Likewise, the overall distribution of 22S/(22S+22R) C<sub>31</sub> 17 $\alpha$ -hopanes ratio is uniform throughout the whole sequence, for the same reasons as discussed above for the diasteranes.

#### 4. Conclusions

Applying established non-biomarker molecular parameters (naphthalenes, phenanthrenes, dibenzothiophenes) and drawing on compound-specific carbon isotopic ratios has revealed that the Barnett Shale sequence of Marathon 1 Mesquite well has an homogeneous biological source and exhibits identical maturation. Consistencies in source facies and maturity are also confirmed by biomarkers. Most biomarkers are not fractionated as a result of primary petroleum migration within the studied source sequence, as follows:

(1) The  $20S/(20S+20R)$  ratio of  $C_{27}$  steranes is uniform throughout the whole sequence, while the  $20S/(20S+20R)$  ratio of  $C_{29}$  steranes shows indistinctly high values in the reservoir unit.

(2) The  $20S/(20S+20R)$  ratio of diasteranes and the  $22S/(22S+22R)$  ratio of  $C_{31}$   $17\alpha$ -hopanes do not appear to have been fractionated.

(3) Diasteranes/steranes ratios do not exhibit features that suggest an association with fractionation, but rather seem to be affected by lithology.. By comparison, the  $Ts/(Ts+Tm)$  ratio is highly sensitive to changes in mineral composition. Variations in the  $Ts/(Ts+Tm)$  ratio correlate positively ( $R^2 = 0.73$ ) with the mixed-layer illite-smectite content.

For given components, such as the  $20S/(20S+20R)$  diasterane homologues and  $22S/(22S+22R)$   $C_{31}$   $17\alpha$ -hopanes, the isomerization reactions have to reach the end-point of equilibrium under present thermal conditions, regardless of whether they have fractionated or not.

Possible fractionations in diasteranes/steranes and  $T_s/(T_s+T_m)$  ratios, if they did occur, may in fact be overprinted by in situ clay-catalyzed reactions. The behaviour and features of primary petroleum migration in the subsurface are not the same as those observed in the laboratory.

A well-defined sample set is essential for understanding the possible fractionation of biomarkers, which are influenced by various factors like the source-input, maturation, biodegradation etc. With concerns for and interest in shale oils increasing in recent years, we anticipate that more well-defined sample sets shall be drawn on in the future. This study provides a starting point, and the phenomena observed here await future verification.

### **Acknowledgements**

Noble Energy is acknowledged for funding the project *Petroleum Retention in Source Rocks*. Parts of this study were carried out during the course of the “GASH – Gas Shales in Europe” initiative. The authors wish to thank the sponsors of this project, especially Marathon Petroleum Corporation, for providing sample material. The China Scholarship Council (CSC) and the National Natural Science Foundation of China (grant no. 41572109) are also gratefully acknowledged here for funding Yuanjia Han’s research. We extend our gratitude to Cornelia Karger, Anke Kaminsky, Doreen Noack and Andrea Vieth-Hillebrand for their technical support. Special thanks are due to Dr. Kai Mangelsdorf and Dr. Liangliang Wu for their useful discussions and suggestions.

## References

- Alexander, R., Kagi, R.I., Rowland, S.J., Sheppard, P.N., Chirila, T.V., 1985. The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalenes in some Ancient sediments and petroleums. *Geochimica et Cosmochimica Acta* 49, 385-395, doi:10.1016/0016-7037(85)90031-6.
- Carlson, R.M.K., Chamberlain, D.E., 1986. Steroid biomarker-clay mineral adsorption free energies: Implications to petroleum migration indices. *Organic Geochemistry* 10, 163-180, doi:10.1016/0146-6380(86)90020-3.
- Chung, H.M., Rooney, M.A., Toon, M.B., Claypool, G.E., 1992. Carbon isotope composition of marine crude oils. *AAPG Bulletin* 76, 1000-1007.
- Clayton, C.J., BJORØY, M., 1994. Compound-Specific Isotope Analysis in Biogeochemistry and Petroleum Research Effect of maturity on  $^{13}C/^{12}C$  ratios of individual compounds in North Sea oils. *Organic Geochemistry* 21, 737-750, doi:10.1016/0146-6380(94)90016-7.
- Coplen, T.B., 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Communications in Mass Spectrometry* 25, 2538-2560, doi:10.1002/rcm.5129.
- Fan, Z., Philp, R.P., 1987. Laboratory biomarker fractionations and implications for migration studies. *Organic Geochemistry* 11, 169-175, doi:10.1016/0146-6380(87)90020-9.
- Han, Y., Mahlstedt, N., Horsfield, B., 2015. The Barnett Shale: compositional fractionation associated with intraformational petroleum migration, retention and expulsion. *AAPG Bulletin* 99, 2173-2202, doi:10.1306/06231514113.
- Hill, R.J., Jarvie, D.M., Zumberge, J., Henry, M., Pollastro, R.M., 2007. Oil and gas geochemistry and petroleum systems of the Fort Worth Basin. *AAPG Bulletin* 91, 445-473, doi:10.1306/11030606014.
- Hoffmann, C.F., Mackenzie, A.S., Lewis, C.A., Maxwell, J.R., Oudin, J.L., Durand, B., Vandenbroucke, M., 1984. A biological marker study of coals, shales and oils from the Mahakam Delta, Kalimantan, Indonesia. *Chemical Geology* 42, 1-23, doi:10.1016/0009-2541(84)90002-0.
- Huang, W.-Y., Meinschein, W.G., 1979. Sterols as ecological indicators. *Geochimica et Cosmochimica Acta* 43, 739-745, doi:10.1016/0016-7037(79)90257-6.
- Jiang, Z., Philp, R.P., Lewis, C.A., 1988. Fractionation of biological markers in crude oils during migration and the effects on correlation and maturation parameters. *Organic Geochemistry* 13, 561-571, doi:10.1016/0146-6380(88)90076-9.
- Kristen, I., Wilkes, H., Vieth, A., Zink, K.G., Plessen, B., Thorpe, J., Partridge, T.C., Oberhänsli, H., 2010. Biomarker and stable carbon isotope analyses of sedimentary organic matter from

- Lake Tswaing: evidence for deglacial wetness and early Holocene drought from South Africa. *J Paleolimnol* 44, 143-160, doi:10.1007/s10933-009-9393-9.
- Krooss, B.M., Brothers, L., Engel, M.H., 1991. Geochromatography in petroleum migration: a review. Geological Society, London, Special Publications 59, 149-163.
- Leythaeuser, D., Mackenzie, A., Schaefer, R.G., Bjoroy, M., 1984. A novel approach for recognition and quantification of hydrocarbon migration effects in shale-sandstone sequences. *AAPG Bulletin* 68, 196-219.
- Leythaeuser, D., Radke, M., Willsch, H., 1988. Geochemical effects of primary migration of petroleum in Kimmeridge source rocks from Brae field area, North Sea. II: Molecular composition of alkylated naphthalenes, phenanthrenes, benzo- and dibenzothiophenes. *Geochimica et Cosmochimica Acta* 52, 2879-2891, doi:10.1016/0016-7037(88)90155-X.
- Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M., Durand, B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France—I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochimica et Cosmochimica Acta* 44, 1709-1721, doi:10.1016/0016-7037(80)90222-7.
- Marquart, J.R., Dellow, G.B., Freitas, E.R., 1968. Determination of noraml paraffins in petroleum heavy distillates by urea adduction and gas chromatography. *Analytical Chemistry* 40, 1633-1637, doi:10.1021/ac60267a002.
- Moldowan, M.J., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *AAPG Bulletin* 69, 1255-1268.
- Peters, K.E., Fraser, T.H., Amris, W., Rustanto, B., Hermanto, E., 1999. Geochemistry of crude oils from eastern Indonesia. *AAPG Bulletin* 83, 1927-1942.
- Peters, K.E., Moldowan, M.J., Sundararaman, P., 1990. Effects of hydrous pyrolysis on biomarker thermal maturity parameters: Monterey Phosphatic and Siliceous members. *Organic Geochemistry* 15, 249-265, doi:10.1016/0146-6380(90)90003-I.
- Peters, K.E., Walters, C.C., Moldowan, M.J., 2005. *The biomarker guide*. Cambridge University Press.
- Radke, M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology* 5, 224-236, doi:10.1016/0264-8172(88)90003-7.
- Radke, M., Garrigues, P., Willsch, H., 1990. Methylated dicyclic and tricyclic aromatic hydrocarbons in crude oils from the Handil field, Indonesia. *Organic Geochemistry* 15, 17-34, doi:10.1016/0146-6380(90)90182-Y.
- Radke, M., Leythaeuser, D., Teichmüller, M., 1984. Relationship between rank and composition of aromatic hydrocarbons for coals of different origins. *Organic Geochemistry* 6, 423-430, doi:10.1016/0146-6380(84)90065-2.

- Radke, M., Welte, D.H., Willsch, H., 1982a. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* 46, 1-10, doi:10.1016/0016-7037(82)90285-X.
- Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. *Organic Geochemistry* 10, 51-63, doi:10.1016/0146-6380(86)90008-2.
- Radke, M., Willsch, H., Leythaeuser, D., Teichmüller, M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* 46, 1831-1848, doi:10.1016/0016-7037(82)90122-3.
- Rubinstein, I., Albrecht, P., 1975. The occurrence of nuclear methylated steranes in a shale. *Journal of the Chemical Society, Chemical Communications*, 957-958, doi:10.1039/C39750000957.
- Seifert, W.K., Moldowan, M.J., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochimica et Cosmochimica Acta* 42, 77-95, doi:10.1016/0016-7037(78)90219-3.
- Seifert, W.K., Moldowan, M.J., 1979. The effect of biodegradation on steranes and terpanes in crude oils. *Geochimica et Cosmochimica Acta* 43, 111-126, doi:10.1016/0016-7037(79)90051-6.
- Seifert, W.K., Moldowan, M.J., 1981. Paleoreconstruction by biological markers. *Geochimica et Cosmochimica Acta* 45, 783-794, doi:10.1016/0016-7037(81)90108-3.
- Seifert, W.K., Moldowan, M.J., 1986. Use of biological markers in petroleum exploration. Johns, R. B. [Hrsg.], *Biological markers in the sedimentary record, (Methods in Geochemistry and Geophysics ; 24)* 24, 261-290.
- Sofer, Z., 1984. Stable carbon isotope compositions of crude oils; application to source depositional environments and petroleum alteration. *AAPG Bulletin* 68, 31-49.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum formation and occurrence*. Springer, Verlag, Berlin, Heidelberg, New York, Tokyo.
- van Kaam-Peters, H.M.E., Köster, J., van der Gaast, S.J., Dekker, M., de Leeuw, J.W., Sinninghe Damsté, J.S., 1998. The effect of clay minerals on diasterane/sterane ratios. *Geochimica et Cosmochimica Acta* 62, 2923-2929, doi:10.1016/S0016-7037(98)00191-4.
- Wenger, L.M., Baker, D.R., Chung, H.M., McCulloh, T.H., 1988. Environmental control of carbon isotope variations in Pennsylvania black-shale sequences, Midcontinent, U.S.A. *Organic Geochemistry* 13, 765-771, doi:10.1016/0146-6380(88)90099-X.
- Zumberge, J.E., 1987. Terpenoid biomarker distributions in low maturity crude oils. *Organic Geochemistry* 11, 479-496, doi:10.1016/0146-6380(87)90004-0.

Table 1. Maturity parameters based on aromatic hydrocarbons and sulfur compounds

| Sample  | Interval         | Depth<br>(ft) | Naphthalenes |      |      |      | Phenanthrenes |      |      |      | Dibenzothiophenes |        |      |
|---------|------------------|---------------|--------------|------|------|------|---------------|------|------|------|-------------------|--------|------|
|         |                  |               | MNR          | DNR  | TNR1 | TNR2 | MPR           | DPR  | MPI1 | MPI2 | MDR1              | MDR2,3 | MDR4 |
| G009583 | 1st              | 3684.80       | 0.78         | 3.91 | 1.11 | 0.92 | 1.24          | 0.26 | 1.03 | 1.17 | 0.22              | 1.11   | 3.57 |
| G009584 | 1st              | 3686.65       | 1.00         | 5.03 | 1.06 | 0.87 | 1.24          | 0.26 | 1.04 | 1.17 | 0.37              | 1.30   | 5.05 |
| G012611 | 2nd              | 3710.26       | 1.30         | 5.00 | 0.97 | 0.82 | 1.26          | 0.26 | 1.25 | 1.41 | 0.36              | 1.31   | 5.88 |
| G009600 | 2nd              | 3710.30       | 1.20         | 4.87 | 0.95 | 0.81 | 1.29          | 0.25 | 1.03 | 1.18 | 0.29              | 1.08   | 5.46 |
| G009601 | 2nd              | 3712.40       | 1.18         | 5.09 | 0.97 | 0.83 | 1.21          | 0.25 | 1.02 | 1.14 | 0.38              | 1.29   | 5.66 |
| G009602 | 2nd              | 3715.00       | 0.80         | 5.54 | 1.03 | 0.84 | 1.46          | 0.22 | 1.09 | 1.24 | 0.55              | 1.35   | 6.40 |
| G012612 | 2nd              | 3720.59       | 0.97         | 4.15 | 0.93 | 0.82 | 1.24          | 0.24 | 1.01 | 1.13 | 0.27              | 1.17   | 6.31 |
| G012613 | 2nd              | 3722.69       | 0.84         | 3.79 | 0.95 | 0.82 | 1.24          | 0.24 | 1.01 | 1.14 | 0.33              | 1.26   | 6.25 |
| G012616 | 2nd              | 3731.66       | 1.29         | 5.00 | 0.99 | 0.82 | 1.23          | 0.25 | 0.97 | 1.09 | 0.35              | 1.31   | 6.18 |
| G009616 | 3rd <sup>U</sup> | 3742.60       | 1.10         | 4.61 | 1.02 | 0.83 | 1.25          | 0.25 | 0.98 | 1.14 | 0.35              | 1.09   | 6.30 |
| G012617 | 3rd <sup>U</sup> | 3745.49       | 0.95         | 4.21 | 1.00 | 0.83 | 1.24          | 0.25 | 0.97 | 1.11 | 0.39              | 1.33   | 5.99 |
| G009619 | 3rd <sup>L</sup> | 3746.70       | 0.90         | 4.30 | 1.12 | 0.89 | 1.25          | 0.24 | 1.01 | 1.16 | 0.39              | 1.44   | 6.94 |
| G012618 | 3rd <sup>L</sup> | 3746.80       | 1.41         | 5.46 | 1.12 | 0.87 | 1.28          | 0.25 | 1.00 | 1.15 | 0.33              | 1.24   | 6.23 |
| G009621 | 3rd <sup>L</sup> | 3749.20       | 1.30         | 5.10 | 1.05 | 0.87 | 1.27          | 0.26 | 0.98 | 1.12 | 0.34              | 1.21   | 6.35 |
| G012622 | 4th <sup>U</sup> | 3767.13       | 1.20         | 4.51 | 1.01 | 0.83 | 1.28          | 0.26 | 1.04 | 1.19 | 0.29              | 1.25   | 5.89 |
| G009647 | 4th <sup>L</sup> | 3797.50       | n.d.         | 3.57 | 1.30 | 0.84 | 1.25          | 0.22 | 0.93 | 1.02 | 0.42              | 1.55   | 5.42 |
| G009650 | 5th              | 3802.70       | 1.08         | 4.38 | 1.00 | 0.85 | 1.19          | 0.25 | 1.05 | 1.16 | 0.39              | 1.28   | 5.58 |

Methyl Naphthalene Ratio (MNR) = [2-MN]/[1-MN], Dimethyl Naphthalene Ratio (DNR) = [2,6-DMN+2,7-DMN]/[1,5-DMN], Trimethyl Naphthalene Ratio 1 (TNR1) = [2,3,6-TMN]/[1,3,5-MN+1,4,6-TMN], Trimethyl Naphthalene Ratio 2 (TNR2) = [1,3,7-TMN+2,3,6-TMN]/[1,3,5-TMN+1,3,6-TMN+1,4,6-TMN], Methyl Phenanthrene Ratio (MPR) = [2-MP]/[1-MP], Dimethyl Phenanthrene Ratio (DPR) = [2,6-DMP+2,7-DMP+3,5-DMP]/[1,3-DMP+1,6-DMP+2,5-DMP+2,9-DMP+2,10-DMP+3,9-DMP+3,10-DMP], Methyl Phenanthrene Index 1 (MPI1) = 1.5\*[2-MP+3-MP]/[P+1-MP+9-MP], Methyl Phenanthrene Index 2 (MPI2) = 3\*[2-MP]/[P+1-MP+9-MP], Methyl Dibenzothiophene Ratio 1 (MDR1) = [1-MDBT]/[DBT], Methyl Dibenzothiophene Ratio 2,3 (MDR2,3) = [2-MDBT+3-MDBT]/[DBT], Methyl Dibenzothiophene Ratio 4 (MDR4) = [4-MDBT]/[DBT], n.d. = not determined.

Table 2. Averaged maturity parameters based on aromatic hydrocarbons and sulfur compounds

| Ratios | References             | Calibrated Equation                      | Valid Range<br>Ro (%) | Mass Spectra<br>m/z | Mean Value<br>- | Calculated<br>Rc (%) |
|--------|------------------------|--|-----------------------|---------------------|-----------------|----------------------|
| MNR    | Radke et al., 1984     | $Rc = 0.17 \times MNR + 0.82$            | 0.7 - 1.5             | 142                 | 1.08            | 1.00                 |
| DNR    | Radke et al., 1984     | $Rc = 0.046 \times DNR + 0.89$           | 0.7 - 1.5             | 156                 | 4.62            | 1.10                 |
| TNR1   | Alexander et al., 1985 |  |                       | 170                 | 1.03            |                      |
| TNR2   | Radke et al., 1986     |  |                       | 170                 | 0.85            |                      |
| MPR    | Radke et al., 1984     | $Rc = 0.99 \times \log_{10}(MPR) + 0.94$ | 0.4 - 1.7             | 192                 | 1.26            | 1.04                 |
| DPR    | Radke et al., 1986     |  |                       | 206                 | 0.25            |                      |
| MPI1*  | Radke et al., 1986     | $Rc = 0.60 \times MPI1 + 0.40$           | 0.4 - 1.35            | 178 & 192           | 1.03*           | 1.02*                |
| MPI2   | Radke et al., 1986     |  |                       | 178 & 192           | 1.16            |                      |
| MDR1   | Radke et al., 1982     |  |                       | 198 & 184           | 0.35            |                      |
| MDR2,3 | Radke et al., 1982     |  |                       | 198 & 184           | 1.27            |                      |
| MDR4   | Radke et al., 1982     |  |                       | 198 & 184           | 5.85            |                      |

\*MPI1 calculated vitrinite reflectance was published in a previous study (Han et al., 2015).



Table 3. Bulk mineralogical compositions by the X-ray powder diffraction (XRD).

| Sample  | Interval         | XRD (%)  |         |         |          |          |          |            |      |        |        |        |
|---------|------------------|----------|---------|---------|----------|----------|----------|------------|------|--------|--------|--------|
|         |                  | Ankerite | Apatite | Calcite | Chlorite | Dolomite | Feldspar | Illite_mix | Mica | Pyrite | Quartz | Rutile |
| G009583 | 1st              | 0.0      | 0.0     | 64.8    | 0.0      | 5.5      | 2.2      | 1.2        | 0.0  | 0.3    | 26.0   | 0.0    |
| G009584 | 1st              | 0.0      | 0.0     | 27.5    | 0.0      | 2.2      | 3.3      | 3.8        | 0.0  | 0.8    | 62.4   | 0.0    |
| G012611 | 2nd              | 4.3      | 3.0     | 14.7    | 0.0      | 0.0      | 15.3     | 19.9       | 0.0  | 2.3    | 40.4   | 0.0    |
| G009600 | 2nd              | 6.3      | 6.7     | 10.5    | 0.0      | 0.0      | 13.8     | 17.3       | 0.0  | 2.7    | 42.8   | 0.0    |
| G009601 | 2nd              | 1.1      | 1.3     | 2.3     | 0.0      | 0.0      | 13.8     | 23.0       | 0.0  | 3.4    | 55.1   | 0.0    |
| G009602 | 2nd              | 0.0      | 0.0     | 91.8    | 0.0      | 2.6      | 0.0      | 0.0        | 0.0  | 0.2    | 5.4    | 0.0    |
| G012612 | 2nd              | 3.6      | 4.8     | 22.6    | 0.0      | 1.9      | 14.8     | 7.8        | 10.1 | 1.9    | 32.5   | 0.0    |
| G012613 | 2nd              | 0.0      | 1.9     | 3.8     | 0.0      | 3.0      | 17.5     | 20.4       | 0.0  | 2.6    | 50.8   | 0.0    |
| G012616 | 2nd              | 3.8      | 4.4     | 10.9    | 0.0      | 1.1      | 14.4     | 10.3       | 12.7 | 2.3    | 40.1   | 0.0    |
| G009616 | 3rd <sup>U</sup> | 0.0      | 0.0     | 0.0     | 4.0      | 0.9      | 14.7     | 24.4       | 25.4 | 2.9    | 26.9   | 0.9    |
| G012617 | 3rd <sup>U</sup> | 0.0      | 19.3    | 0.0     | 3.6      | 3.4      | 7.9      | 14.6       | 16.3 | 1.8    | 32.6   | 0.5    |
| G009619 | 3rd <sup>L</sup> | 0.0      | 10.7    | 0.0     | 3.2      | 1.6      | 9.1      | 21.9       | 24.8 | 3.9    | 24.1   | 0.8    |
| G012618 | 3rd <sup>L</sup> | 0.0      | 1.1     | 0.0     | 3.7      | 0.7      | 10.3     | 26.3       | 26.1 | 6.1    | 24.8   | 1.0    |
| G009621 | 3rd <sup>L</sup> | 0.0      | 4.5     | 0.0     | 3.8      | 1.4      | 9.5      | 25.2       | 24.8 | 3.6    | 26.3   | 0.8    |
| G012622 | 4th <sup>U</sup> | 0.0      | 6.4     | 0.0     | 0.0      | 2.8      | 10.4     | 13.7       | 35.7 | 4.8    | 26.2   | 0.0    |
| G009647 | 4th <sup>L</sup> | 0.0      | 0.0     | 97.7    | 0.0      | 0.0      | 0.2      | 0.0        | 0.0  | 0.1    | 2.0    | 0.0    |

Table 4. Biomarker ratios determined by metastable reaction monitoring/gas chromatography/mass spectrometry (MRM/GC/MS) ( $M+ \rightarrow 217/191$  for sterane and hopane respectively) in the aliphatic fractions of *n*-alkane removed (by urea adduction).

| Sample                     | Interval         | 20S/(20S+20R) $\alpha\alpha\alpha$ |                 | 20S/(20S+20R) $d\beta\alpha$ |                 | $\beta\beta/(\alpha\alpha+\beta\beta)$ 20R |                 | $d\beta\alpha/(\alpha\beta\beta+\alpha\alpha\alpha)$ |                 | Hopanes             |                      |
|----------------------------|------------------|------------------------------------|-----------------|------------------------------|-----------------|--|-----------------|--|-----------------|---------------------|----------------------|
|                            |                  | C <sub>27</sub>                    | C <sub>29</sub> | C <sub>27</sub>              | C <sub>29</sub> | C <sub>27</sub>                            | C <sub>29</sub> | C <sub>27</sub>                                      | C <sub>29</sub> | Ts%-C <sub>27</sub> | 22S%-C <sub>31</sub> |
| G009583                    | 1st              | 0.43                               | 0.39            | 0.59                         | 0.57            | 0.37                                       | 0.51            | 0.59   | 0.53            | 0.59                | 0.59                 |
| G009584                    | 1st              | 0.53                               | 0.42            | 0.55                         | 0.59            | 0.36                                       | 0.57            | 0.62   | 0.57            | 0.50                | 0.54                 |
| G012611                    | 2nd              | 0.51                               | 0.43            | 0.56                         | 0.58            | 0.48                                       | 0.60            | 0.68   | 0.63            | 0.76                | 0.57                 |
| G009600                    | 2nd              | 0.55                               | 0.52            | 0.54                         | 0.56            | 0.50                                       | 0.67            | 0.68   | 0.64            | 0.78                | 0.48                 |
| G009601                    | 2nd              | 0.55                               | 0.55            | 0.53                         | 0.60            | 0.48                                       | 0.68            | 0.61   | 0.60            | 0.69                | 0.63                 |
| G009602                    | 2nd              | 0.53                               | 0.39            | 0.62                         | 0.59            | 0.49                                       | 0.48            | 0.56   | 0.52            | 0.52                | 0.60                 |
| G012612                    | 2nd              | 0.48                               | 0.43            | 0.54                         | 0.59            | 0.53                                       | 0.54            | 0.66   | 0.62            | 0.60                | 0.53                 |
| G012613                    | 2nd              | 0.49                               | 0.51            | 0.58                         | 0.56            | 0.51                                       | 0.61            | 0.69   | 0.67            | 0.76                | 0.65                 |
| G012616                    | 2nd              | 0.49                               | 0.44            | 0.57                         | 0.62            | 0.52                                       | 0.57            | 0.62   | 0.59            | 0.67                | 0.56                 |
| G009616                    | 3rd <sup>U</sup> | 0.50                               | 0.53            | 0.59                         | 0.56            | 0.51                                       | 0.64            | 0.66   | 0.61            | 0.65                | 0.51                 |
| G012617                    | 3rd <sup>U</sup> | 0.49                               | 0.39            | 0.55                         | 0.56            | 0.56                                       | 0.50            | 0.62   | 0.62            | 0.65                | 0.48                 |
| G009619                    | 3rd <sup>L</sup> | 0.46                               | 0.45            | 0.55                         | 0.56            | 0.46                                       | 0.58            | 0.65   | 0.59            | 0.82                | 0.59                 |
| G012618                    | 3rd <sup>L</sup> | 0.49                               | 0.44            | 0.57                         | 0.56            | 0.54                                       | 0.60            | 0.68   | 0.69            | 0.80                | 0.58                 |
| G009621                    | 3rd <sup>L</sup> | 0.49                               | 0.48            | 0.61                         | 0.56            | 0.51                                       | 0.59            | 0.61   | 0.63            | 0.74                | 0.56                 |
| G012622                    | 4th <sup>U</sup> | 0.46                               | 0.36            | 0.57                         | 0.57            | 0.47                                       | 0.52            | 0.69   | 0.67            | 0.65                | 0.58                 |
| G009647                    | 4th <sup>L</sup> | 0.46                               | 0.34            | 0.58                         | 0.59            | 0.38                                       | 0.49            | 0.58   | 0.51            | 0.48                | 0.54                 |
| Average $X_A$              |                  | 0.49                               | 0.44            | 0.57                         | 0.58            | 0.48                                       | 0.57            | 0.64   | 0.61            | 0.67                | 0.56                 |
| $\delta = \sum(X - X_A)^2$ |                  | 0.02                               | 0.06            | 0.01                         | 0.01            | 0.05                                       | 0.06            | 0.03   | 0.04            | 0.18                | 0.03                 |

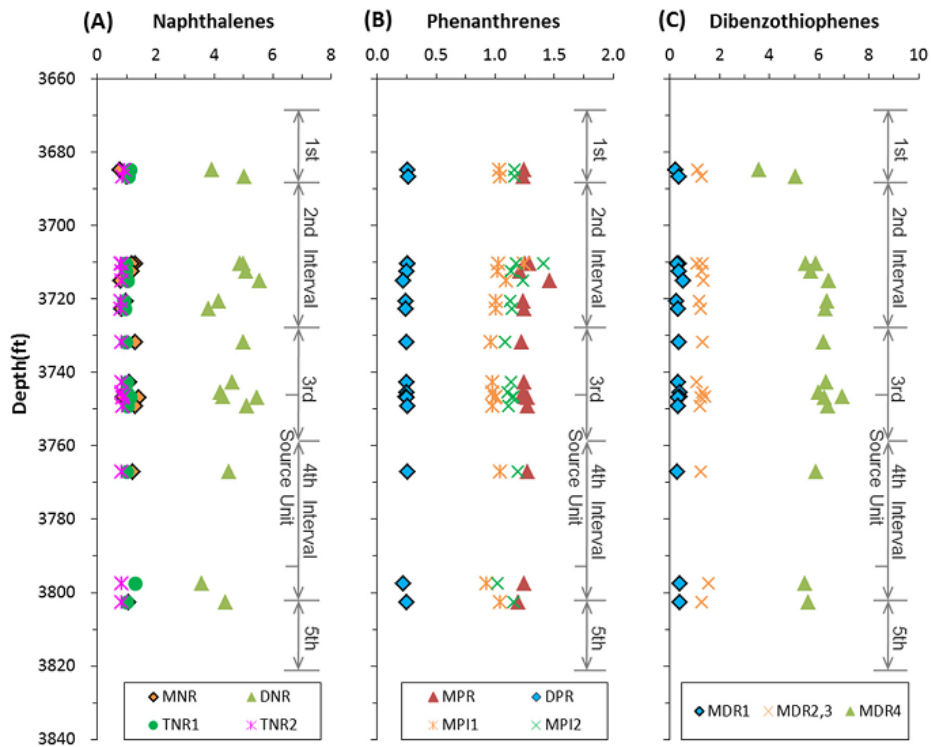


Fig. 1. Variation of maturity parameters derived from alkyl homologues of naphthalene (N), phenanthrene (P) and dibenzothiophene (DBT) by gas chromatography/mass spectrometry (GC/MS). (A) Alkylated naphthalenes maturity ratios, (B) Alkylated phenanthrenes maturity ratios, (C) Alkylated dibenzothiophenes maturity ratios. Source unit include the lower part of 3rd interval plus the upper part of 4th interval, where organic matter is richest (see details in Han et al., 2015).

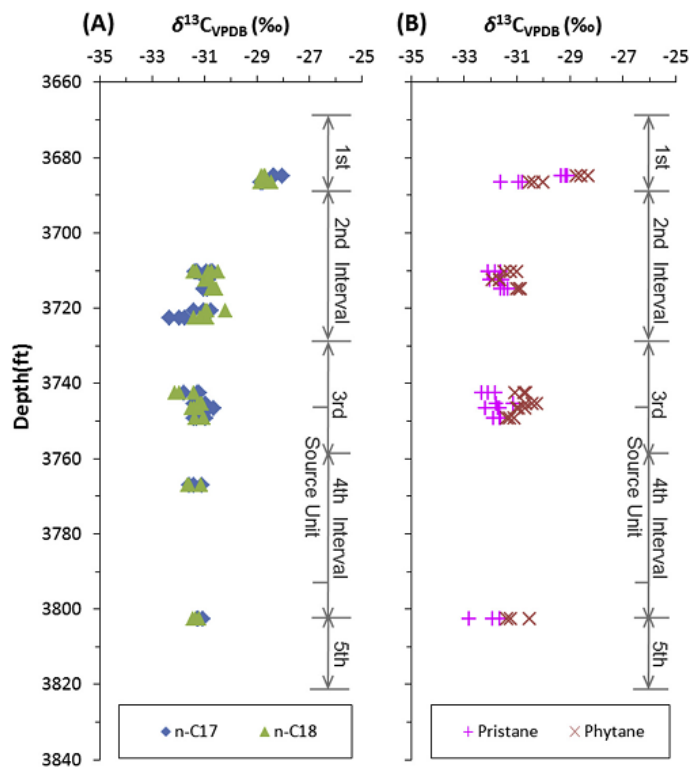
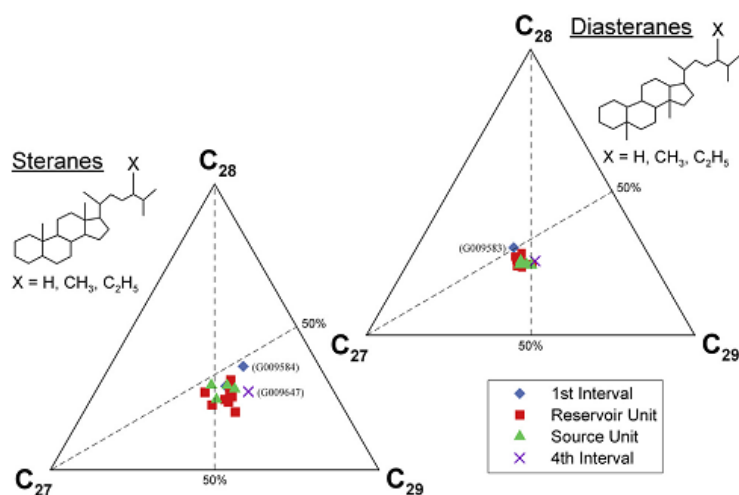
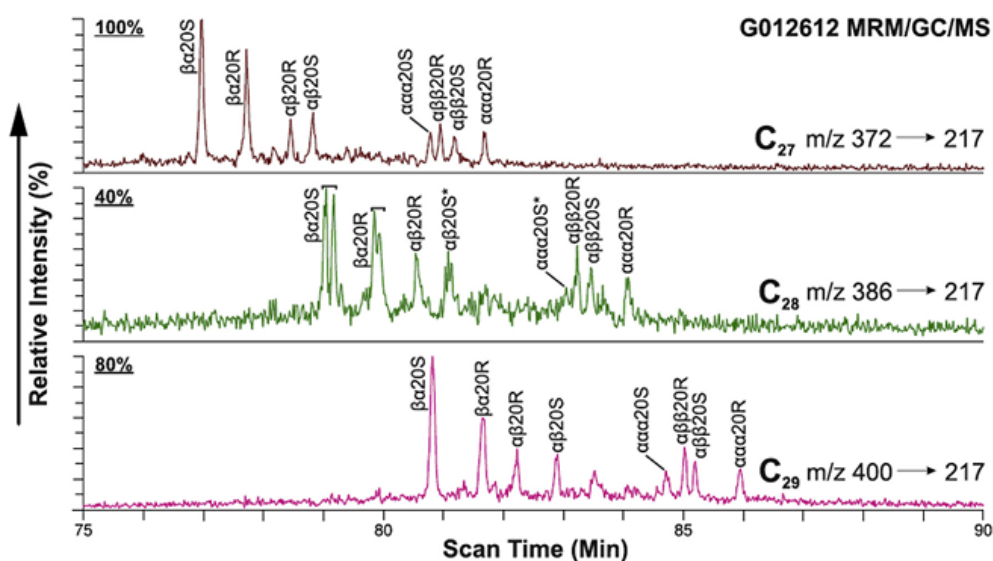


Fig. 2. Variation of stable carbon isotope ratios (VPDB standard) for (A) n-C<sub>17</sub> and n-C<sub>18</sub>, (B) pristane and phytane from bitumen extracts in the Marathon 1 Mesquite well. All samples were measured in triplicate as plotted.



**Fig. 3.** Ternary diagrams of steranes and diasteranes showing the relative abundances of C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub> homologues. The regular steranes include 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ (H) (20S + 20R) isomers, and the rearranged diasteranes include 13 $\beta$ ,17 $\alpha$ (H) (20S + 20R) isomers. Both sterane and diasterane compounds are determined by metastable reaction monitoring/gas chromatography/mass spectrometry (MRM/GC/MS) ( $M^+ \rightarrow 217$ ) in the *n*-alkane removed aliphatic fractions of bitumen extracts. Reservoir unit consist of the 2nd interval plus the upper part of 3rd interval, where hydrocarbons migrated and accumulated therein (see details in Han et al., 2015). Sample number is given in parentheses.



**Fig. 4.** Metastable reaction monitoring/gas chromatography/mass spectrometry (MRM/GC/MS) analysis of steranes ( $M^+ \rightarrow 217$ ) in exemplified aliphatic fraction of *n*-alkane removed (by urea adduction).  $\beta\alpha 20S$ (R) refers to diasteranes with the 13 $\beta$ ,17 $\alpha$ (H)20S(R) stereochemistry,  $\alpha\beta 20R$ (S) are the 13 $\alpha$ ,17 $\beta$ (H)20R(S) diasterane epimers,  $\alpha\alpha\alpha 20S$ (R) refers to steranes with the 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ (H)20S(R) stereochemistry,  $\alpha\beta\beta 20R$ (S) are the 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ (H)20R(S) sterane epimers. Concentrations of diasteranes are obviously higher than steranes. Intensity of m/z 386 → 217 mass spectra is relatively low, peaks of tentatively identified C<sub>28</sub> steranes are therefore asterisk marked.

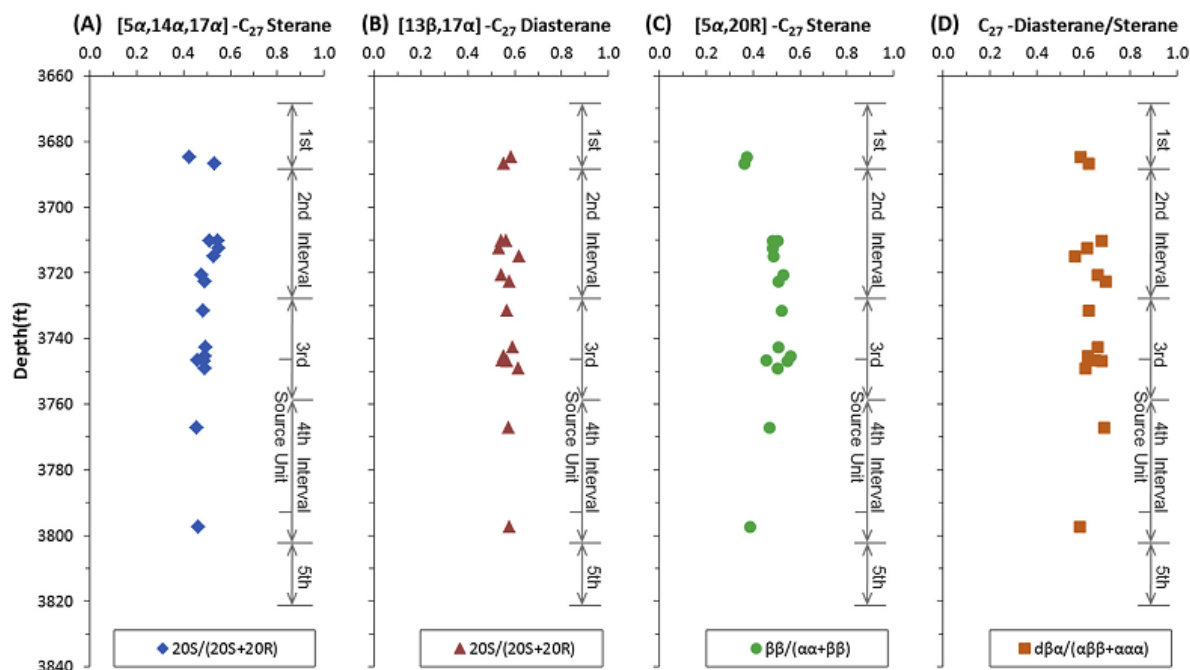


Fig. 5. Variation of  $C_{27}$  steroid maturity ratios in (A)  $20S/(20S + 20R)$  of  $5\alpha,14\alpha,17\alpha(H)$   $C_{27}$  cholestanes, (B)  $20S/(20S + 20R)$  of  $13\beta,17\alpha(H)$   $C_{27}$  diacholestanes, (C)  $\beta\beta/(\alpha\alpha + \beta\beta)$  of  $5\alpha(H)$   $20R$   $C_{27}$  cholestanes, and (D)  $d\beta\alpha/(\alpha\beta\beta + \alpha\alpha\alpha)$  of  $(20S + 20R)$   $C_{27}$  diacholestanes and cholestanes.

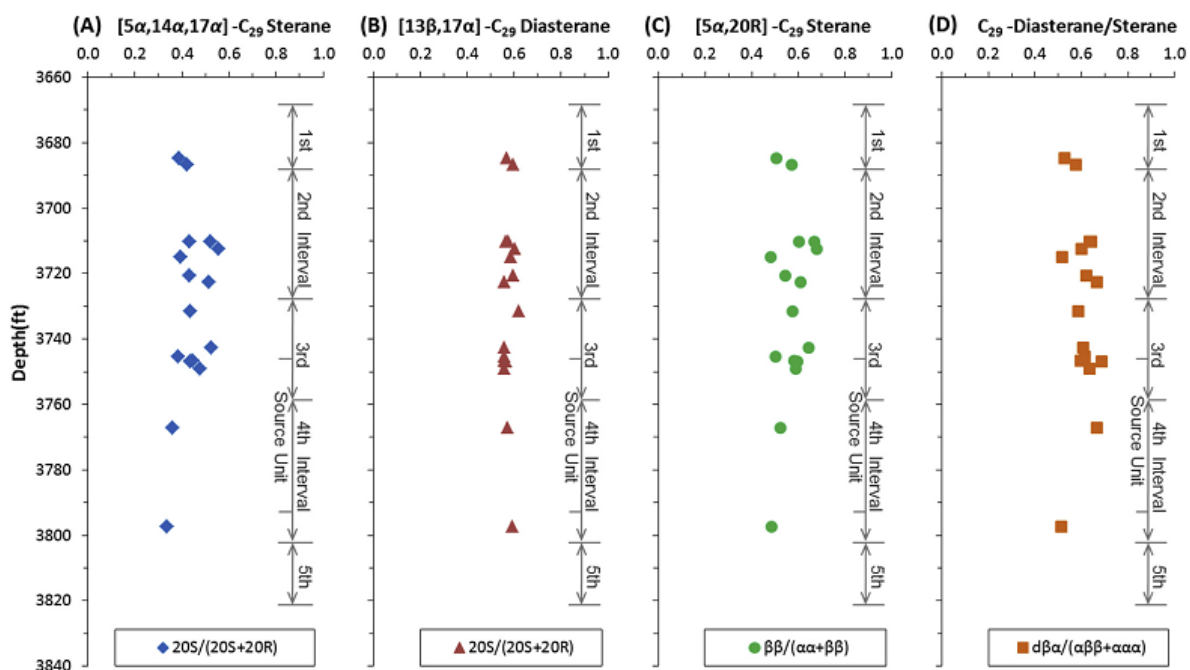


Fig. 6. Variation of  $C_{29}$  steroid maturity ratios in (A)  $20S/(20S + 20R)$  of  $5\alpha,14\alpha,17\alpha(H)$   $C_{29}$  stigmastanes, (B)  $20S/(20S + 20R)$  of  $13\beta,17\alpha(H)$   $C_{29}$  diastigmastanes, (C)  $\beta\beta/(\alpha\alpha + \beta\beta)$  of  $5\alpha(H)20R$   $C_{29}$  stigmastanes, and (D)  $d\beta\alpha/(\alpha\beta\beta + \alpha\alpha\alpha)$  of  $(20S + 20R)$   $C_{29}$  diastigmastanes and stigmastanes.

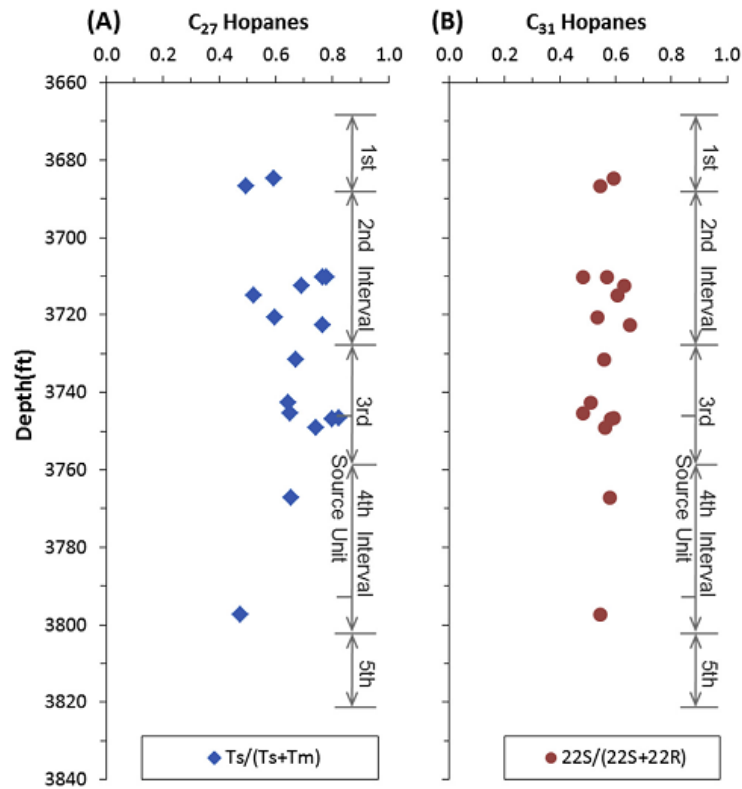


Fig. 7. Variation of maturity parameters in (A)  $Ts/(Ts + Tm)$  ratio of  $C_{27}$  22,29,30-trisnorhopanes, and (B)  $22S/(22S + 22R)$  ratio of  $C_{31}$  17 $\alpha$ -hopanes, determined by metastable reaction monitoring/gas chromatography/mass spectrometry (MRM/GC/MS) ( $M+ \rightarrow 191$ ) in the aliphatic fractions of n-alkane removed (by urea adduction).

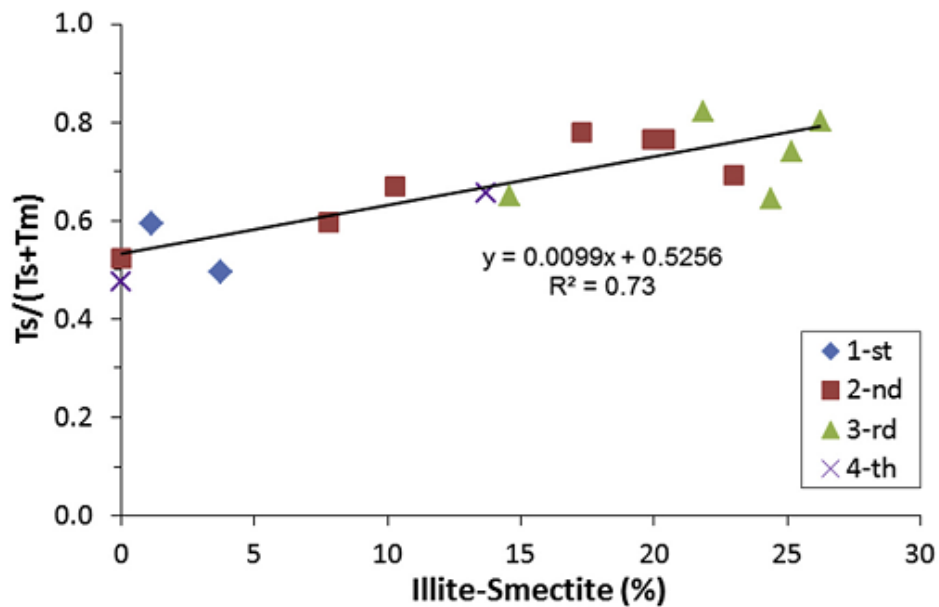


Fig. 8. The content of mixed-layer illite-smectite versus the ratio  $Ts/(Ts + Tm)$  of  $C_{27}$  22,29,30-trisnorhopanes.