Compositional fractionation of petroleum from reservoir to wellhead in the Niobrara shale oil play

Yuanjia Han[a, b, *], Brian Horsfield[b], Nicolaj Mahlstedt[b], Heather LaReau[c], David J. Curry[d]

[a] Key Laboratory of Tectonics and Petroleum Resources, China University of Geosciences, Wuhan 430074, China

[b] German Research Centre for Geosciences (GFZ), Telegrafenberg, Potsdam 14473, Germany

[c] Noble Energy, Inc., 1625 Broadway, Denver, Colorado 80202, United States

[d] Noble Energy, Inc., 1001 Noble Energy Way, Houston, Texas 77070, United States

ABSTRACT

Hydraulic fracturing is routinely used to stimulate unconventional reservoirs. In the Niobrara shale oil play there are several fracking targets, but the actual stimulated rock volume is not well constrained. This means that allocating produced oil to specific reservoirs, in essence oil-reservoir correlation, is not straightforward. The data presented here support that the chalk units are the principal production zones in the Niobrara shale oil play. Several lines of evidence, such as the presence of heavy-end n-alkanes ($> n$-C$_{31}$), consistence in composition of gross fractions, the distribution of C$_{27-28-29}$ diasteranes, as well as the pristane to phytane ratio, all suggest that oils were produced from the A- & B- chalks, particularly from the A-Chalk. During production, a selective partitioning of lighter hydrocarbons into the migrating fluids could nevertheless occur, in particular as regards the n-alkanes domain and their carbon isotopic compositions. Regarding the latter, a depletion of ^{13}C in the produced oil's n-alkanes by more than three per mil relative to all of those core extracts was observed. This finding suggests that compound specific isotope analysis in both oil-reservoir and oil-source rock correlations cannot be taken at face value, i.e. by simple matching of values. Besides that, fractionation appears to result in the enrichment of rather aliphatic nitrogen-containing compounds in crude oils.

Keywords: Shale oil; Oil-reservoir correlation; Carbon isotopes; Biomarker; Niobrara Formation

1. Introduction

The Niobrara Formation is one of the most attractive shale oil resource plays in North America. A rhythmic stratification of chalk-marl beds is characteristic of the Niobrara Formation (Locklair and Sageman, 2008), with the chalks and marls representing the major reservoirs (Jarvie, 2012) and source-rocks (Landon et al., 2001; Sonnenberg, 2011), respectively. In a previous study, a Niobrara core was used to examine the changing composition of petroleum as migrated from the organic-rich marlstones into the juxtaposed chalkstones. A preferential fractionation of saturated hydrocarbons versus aromatic hydrocarbons and polar compounds was reported, while fractionations within compound classes were essentially absent therein (Han, 2016). Neither were commonly used biomarker and non-biomarker ratios fractionated. The same applied to the stable carbon isotopes as well. These observations are consistent with our study on a Barnett Shale core (Han et al., 2017), and thus substantiated the fundamental assumption for oil-source rock correlation, namely that the molecular and isotopic characteristics of hydrocarbons in crude oils closely resemble those in genetically related source rock extracts (Barker, 1979; Peters et al., 2005). However, the question remains as to whether those specific molecular and isotopic attributes are altered during production i.e.

---

[*] Corresponding author. *E-mail address: yuanjia@gfz-potsdam.de*

from reservoir to wellhead. To address this point we have contrasted the compositions of reservoired with produced oil in the Niobrara shale resource play. This exercise has important technical connotations industry-wide: in circumstance where there are several potential fracking targets, the stimulated rock volume is less well known, which leaves the allocation of produced oil to reservoir being a problem. As hydraulic fracturing is routinely used to stimulate unconventional reservoirs, the produced versus reservoired oil correlation is of paramount importance.

2. Samples and methods

The mineralogy and organic geochemistry of 98 core samples from five vertical drilled wells has been reported in previous studies (Han, 2016; Han et al., 2018). A total of 10 wellhead oils (Table 1) from eight wells (Figure 1) drilled horizontally into the Niobrara Formation in Weld County, Colorado, U.S.A. were made available to this study. One oil (G015940) was sampled from a horizontal well (OilWell-0) close to the core well 2, and the remaining nine oils were sampled from a suite of seven wells that were closely distributed within a narrow belt of about 1 mile (Figure 1). This suite of horizontal wells was close to the core well 3, in which reservoir core extracts were available. Two of these seven wells had been re-stimulated (OilWell-8, OilWell-9) and sampled again (G015841, G015842), providing successive insights into oil chemistry.

Produced oil samples were firstly fingerprinted using gas chromatography (GC). Then, they were topped using a rotary evaporation apparatus at 60 °C, and the losses of light hydrocarbons ($<n$-C_{15}) were documented. The topped oils were recovered and fractionated into saturates, aromatics, resins and asphaltenes (SARA) fractions by asphaltene precipitation and medium pressure liquid chromatography fractionation as described by Han et al. (2015). Afterwards, gas chromatography - mass spectrometry (GC-MS), metastable reaction monitoring - gas chromatography - mass spectrometry (MRM-GC-MS), and isotope ratio monitoring - gas chromatography - mass spectrometry (IRM-GC-MS) were carried out on specific oil fractions following the procedures described in published literature (Marquart et al., 1968; Haberer et al., 2006; Kristen et al., 2010). The qualification of steroid compounds was carried out by comparing the peak areas to that of 5α-Androstane, which was added as an internal standard. 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] × 1000. The resulting isotopic ratios of $\delta^{13}C$ are expressed in delta notation following the format given by Coplen (2011). Isotope ratios measured on 5α-Androstane revealed that the determined $\delta^{13}C$ values have an analytical error of less than 1‰.

3. Results and discussion

3.1. Oil-reservoir correlation

In the Niobrara shale oil play, the chalk units are considered the main reservoirs (Sonnenberg and Weimer, 1993; Jarvie, 2012; Welker et al., 2013; Han et al., 2018), but a possible contribution from marl units cannot be excluded. The question nevertheless remains as to which chalk unit is the most productive. The oil-reservoir correlation presented here is based on the hypothesis that certain compositional parameters of produced oil should closely resemble those of the genetically related petroleum remaining in reservoir. A comprehensive comparison was carried out utilising compositional information from bulk (SARA fractions) to molecular levels.

3.1.1. Bulk compositions

Firstly, the chain-length distribution of n-alkanes in pristine produced oils was fingerprinted using gas chromatography (Figure 2A). The n-alkanes distributions for all are closely similar. It should be noted that the light components of the oils amount to 37% to 51% with an average of 45% (Table 1),

but they could not be used in the oil-source correlation because the C_{1-7} light hydrocarbons were generally absent from available cores (Figure 2B, C). This is a fundamental constraint of this study. However, the heavy-end *n*-alkanes ($> n-C_{31}$) are characteristic of oil samples (Figure 2A). The presence of those heavy-end *n*-alkanes in chalkstones (Figure 2B) instead of in shale and marls (Figure 2C) suggest strongly that oils were produced from chalk intervals.

The SARA fractions of the topped oils are proportionally quite similar to one other (Table 1). With the exception of G015840, the investigated oils have on average percentages of 59%, 23%, 12% and 7% for the saturate, aromatic, resin and asphaltene fractions, respectively (Figure 3A). The saturate fraction percentage (59%) is similar to those of chalk extracts (58%, Figure 3B), but clearly higher than those of the shale and marls (47%, Figure 3C). *Vice versa*, the polar fraction in the oils (19%) is significantly lower than those of the shale and marls (32%, Figure 3C), but comparatively close to those of chalk extracts (21%, Figure 3B). Chalk extracts strongly resemble produced oils (Figure 3), suggesting that the chalks are the main reservoir from which the oils were produced. Interestingly, there is no significant fractionation taking place with respect to SARA fractions during production.

3.1.2. Diasteranes

The ratios of $C_{27-28-29}$ regular and rearranged steranes are excellent source-dependent biomarkers (Peters et al., 2005). Due to the relatively low concentrations of steranes (Figure 4), the diasterane homologues are preferentially used here (Table 1). To trace the origin of oils, the $C_{27-28-29}$ diasterane ratios of produced oils were plotted together with corresponding core extracts (Figure 5). An overall increase in the relative abundance of C_{28} diasterane was shown in going from the deep Carlile shale to the shallow Sharon Springs Shale (Figure 5). In this magnified plot, the diasterane distributions of core extracts were further separated into two areas. Samples from the upper Niobrara show an increase in the C_{28} diasterane abundance with ascending depth from the B-Chalk to the Sharon Springs Shale. Meanwhile, core extracts from the B-Marl and deeper intervals had overall lower values. As bitumens may not all be indigenous in the chalks, mixed $C_{27-28-29}$ diasterane signals from sources above and below is a likely scenario. For example, diasteranes in the A-Chalk may mix from the overlying Sharon Springs Shale and the underlying A-marl interval.

For the produced oil samples, G015840 has the lowest C_{28} diasterane abundance and is thus the low C_{28} end-member in the diasterane distributions (Figure 5). This sample was taken from OilWell-0 about 25 miles to the northeast of all the others (Figure 1). There are seven oils (G015843 to G015849) sampled from a suite of horizontal wells that stimulated the Niobrara from bottom to top successively. Accordingly, there is a gradual increase in C_{28} abundance in going from G015843 to G015849. There is a notable overlap between the oils and the upper Niobrara core extracts rather than lower Niobrara extracts, indicating that the upper Niobrara intervals have made a dominant contribution to the produced fluids, even in cases where the lower Niobrara intervals were stimulated.

Having the highest C_{28} diasterane abundance in the produced oil samples, G015848 and G015849 are implied to show significant contributions from the Sharon Springs Shale (Figure 5), though the *n*-alkane distribution (Figure 2) and the SARA composition (Figure 3) of oils are not consistent with an origin from the Sharon Springs Shale. As biomarkers occur in petroleum only in trace amounts, it is dangerous to base hypotheses on these components alone (Curiale, 2008). In comparison with G015848 and G015849, the re-stimulated oil fluids (G015841 and G015842) from the same two wells indicate a main contribution from the A-Chalk. Overall, all analysed oils are showing $C_{27-28-29}$ diasterane distributions centred on the A-Chalk, signifying it to be the main production reservoir.

The biomarker ratios are routinely applied for oil-source rock correlations (Peters et al., 2005). More recently, the biomarker concentrations were proposed to determine the possible oil contributing sources (Peters et al., 2008; Zhan et al., 2016; Zhan et al., 2017). In this study, the $C_{27-28-29}$ diasterane concentrations in produced oils are nevertheless not matching those of core extracts (Figure 6). Neither

were the concentrations normalized to the saturate fractions matching (Figure 7). The concentration of diasteranes in oils is higher than in core extracts (Figure 6), which suggests the oils have higher maturity than the core extracts, whereas the sterane maturity ratio [Dia/(Dia+Reg)] suggests the opposite. The values of C_{29} [Dia/(Dia+Reg)] ratio in oils (0.47-0.52, Table 2) point to a lower maturity compared to core extracts (0.60-0.75) (Han, 2016). In comparison to diasterane ratios (Figure 5), the concentrations of $C_{27-28-29}$ diasteranes are anyhow influenced by other factors such as the fractionation (Seifert and Moldowan, 1981).

3.1.3. Pristane and phytane

The pristane to phytane ratio (Pr/Ph) is routinely used to assess the origin of petroleum with respect to kerogen type and depositional environment (Brooks et al., 1969; Powell and McKirdy, 1973; Didyk et al., 1978; Powell et al., 1988; Peters et al., 1999; Hill et al., 2007). Building on the discussions above, the Pr/Ph ratio is plotted versus the percentage of C_{29} in total C_{27-29} diasteranes (Figure 8).

For produced oils, a positive correlation ($R^2 = 0.77$) was found between the Pr/Ph ratio and the C_{29}/C_{27-29} diasterane ratio (Figure 8), with G015840 having the highest values (Table 1). Since the Pr/Ph and C_{29}/C_{27-29} diasterane ratios are believed to not be influenced by maturity in the oil-window (Tissot and Welte, 1984; Peters et al., 2005), some variability in source facies is indicated. Considering the oil G015840 was sampled 25 miles away from the others, a varying depositional environment and kerogen type is to be expected.

For core extracts, there is no trend detectable between the Pr/Ph and C_{29}/C_{27-29} diasterane ratios (Figure 8). There is an overlap between oils and core extracts from the A- & B- chalks. With the exception of oil G015840, the other oils have ratios of Pr/Ph and C_{29}/C_{27-29} between 1.4-1.6 and 22%-25%, respectively. This stripe-like range, covering particularly the distributions of core extracts from the A-Chalk (Figure 8), strongly suggests a close genetic relationship.

Compared with the ternary diagram of C_{27-29} diasteranes (Figure 5), the cross-plot of the Pr/Ph and C_{29}/C_{27-29} diasterane ratios (Figure 8) clearly excludes the Sharon Springs Shale and the A-Marl interval as possible contributors to the produced oils. This in turn supports our previous interpretations based on bulk petroleum compositions, e.g. oils are recovered mainly from chalk intervals.

In summary, the close resemblances between chalk extracts and produced oils suggest that the chalks are the main reservoirs. According to commonly used biomarker ratios, such as the ratios of Pr/Ph and C_{27-29} diasteranes, the A-Chalk interval is believed the most productive irrespective of the landing zone.

3.2. Isotopic fractionation of petroleum during production

Carbon isotopes are routinely used in studies of oil-oil and oil-source rock correlations. According to Peters et al. (2005), crude oil is depleted in ^{13}C by less than 1.5‰ compared with genetically related source rock extracts, and $\delta^{13}C$ differences greater than 2-3‰ is a general rule for distinguishing oils with different origins. While isotope analysis of bulk fractions is a well-tried correlation tool (Stahl, 1977; Schoell, 1984; Sofer, 1984), the application of compound specific isotopes is less widely tested. To our best knowledge, there is no good match in the $\delta^{13}C$ values of n-alkanes from oils and source rock extracts. In most cases (Odden et al., 1998; Abdullah and Connan, 2002; Odden et al., 2002; Murillo et al., 2016), two end member source rocks, i.e., one source rock is isotopically lighter and another is isotopically heavier than the produced oils, are given to make a satisfactory story. In the cases where there is only isotopically heavier source rock presented, an undrilled source rock was proposed (Li et al., 2010; Yu et al., 2012). We here evaluate the applicability of compound specific isotopes by building on the foregoing biomarker discussion, and introducing the possible influence of phase separation.

A fractionation of lighter carbon isotopes into the hydrocarbons of the vapour phase has been reported to occur during phase separation (Carpentier et al., 1996; Curiale and Bromley, 1996). Carbon isotope analyses on our samples show the δ^{13}C values of pristane and phytane range from -36 to -37 ‰ in most oil samples (Figure 9), except two re-stimulated oils which are about 3‰ heavier (Table 3), and those of core extracts are about 5‰ heavier. Analytical error can be excluded as the cause since it is less than 1‰.

As concluded previously, oils were produced mainly from the A- & B- chalks. Accordingly, the Pr/Ph ratio for most oils indicates source facies consistent with that of A- & B- chalks (Figure 9A). However, there is no good match in their δ^{13}C values (Figure 9B, C). Since hydrocarbons can become isotopically enriched in ^{13}C as maturation progresses (Sofer, 1984; Clayton and Bjorøy, 1994; Whiticar, 1996), it is then important to consider oil-bitumen pairs of equal maturity (Peters et al., 2005).

The calculated vitrinite reflectance of core extracts considered here is on average 0.9% R_c, covering a range of 0.8% to 1.0%, as signaled using several parameters (Han, 2016). As far as the oils are concerned, their equivalent vitrinite reflectance calculated from dibenzothiophenes (0.74% R_c) (Radke et al., 1986) and phenanthrenes (0.82% R_c) (Radke et al., 1982) is lower (Table 2). The same applies to the triaromatic steroids ratio [TA(I)/TA(I+II)] (0.56 vs 0.70) and the rearranged to regular C_{29} steranes ratio [Dia/(Dia+Reg)] (0.49 vs 0.67). Since oils were produced from wells about 2 miles away from the core well 3 (Figure 1), a slight maturity difference like this is acceptable. However, there is no maturity difference between the initial and re-stimulated fluids (Table 2), whilst the δ^{13}C values of pristane and phytane in the two re-stimulated oils (G015841 and G015842) are anyhow different from those of other oils (Figure 9B, C). The variation in δ^{13}C due to the possible effect of maturity is not evident. Notwithstanding, maturity differences are believed to account for up to 2-3‰ isotopic variations of oils from an identical source (Clayton, 1991; Peters et al., 2005).

Given the relatively lighter δ^{13}C values of oils are derived from phase separation, the more extreme the exsolution is, the lighter is the carbon isotopic composition of vapour phase. Gas exsolution in subsurface was thought to take place when the reduction in temperature and pressure is sufficient (Thompson, 1987; Larter and Mills, 1991), especially in pressure (Price et al., 1983). In that regard, the pressure drop after re-fracturing is likely to be less extreme due to the initial loss of fluids, result in a weaker partitioning effect. This appears reasonable when the n-alkane distribution is taken into consideration (Figure 10). Compared to the initial fractured fluids (G015848 and G015849), the re-stimulated oils (G015841 and G015842) exhibit a lower proportion of gasoline range hydrocarbons. A lower extent of partitioning is therefore suggested for the re-stimulation.

The carbon isotopes of n-alkanes display a fractionation similar to that of isoprenoids as discussed above (Figure 11). For core extracts, the δ^{13}C value of n-alkanes ranges between -28‰ to -33‰, without any detectable variation between intervals. For the oils, the ^{13}C/^{12}C compositions of n-alkanes are in general lighter than -35‰, with the exception of the two re-stimulated fluids whose δ^{13}C values are closer to those of the core extracts. Yet large variations (>2-3‰) are observed here between produced oils and associated core extracts. The tentative interpretation of this is that the lighter carbon isotopes have been fractionated into the produced fluids during production.

As oil G015840 was sampled 25 miles away from all the others (Figure 1), a varying source facies was illustrated (Figure 5, 8). Given the differences exist in source facies and perhaps in maturity as well, the pristane and phytane δ^{13}C values of G015840 are still similar to those of the re-stimulated oils (Table 3). The same applies to the δ^{13}C values of n-alkanes. Therefore, the observed carbon isotopic difference between oils and core extracts is likely caused principally by fractionation during production. Considering the artificial fracturing is routinely used to stimulate Niobrara reservoirs, the phase separation that is likely to occur during hydraulic fracturing may be the underlying mechanism.

3.3. Molecular fractionation of petroleum during production

3.3.1. Saturate hydrocarbons

One of the most significant molecular alterations of petroleum during production is probably the selective partitioning of lighter hydrocarbons into the mobile phase (Thompson, 1987; Larter and Mills, 1991), i.e., fractionation. As shown in figure 2, all analysed oils exhibit a bimodal distribution of n-alkanes with maxima at n-C_5 and n-C_{13}. While some gas loss has occurred, since C_{1-3} gas hydrocarbons are depleted, the produced oils are nevertheless enriched in gasoline range hydrocarbons. Compared with the overall absence of gasoline range n-alkanes ($<C_7$) from core samples, a selective partitioning of light hydrocarbons into the produced oils is recognisable (Figure 12). Notably, the second maxima of pristine oils at n-C_{13} (Figure 2A) is lighter than the maxima of n-alkanes vaporised from the chalks (n-C_{15}, Figure 2B), which suggests that oils were mainly produced from the chalks but slightly fractionated. As far as the core samples are concerned, it is possible that the absence of gasoline range hydrocarbons is due to evaporative loss during sample storage and handling (Larter, 1988; Sandvik et al., 1992).

3.3.2. Aromatic hydrocarbons

In line with n-alkanes, a selective partitioning of lighter aromatic hydrocarbons into the produced oils is probably the case (Figure 13A). In comparison to the dominant alkylnaphthalenes in chalks, the lighter alkylbenzenes are significantly enriched in pristine oils (74-80%, Table 4). This is probably a reflection of different methods of data obtaining (Tvap-GC vs GC), and the possibility of gas loss during core sample storage and handling. Interestingly, and in contrast to the case of the chalks, the mono-, di-, and tri- aromatic hydrocarbons in the marls are rather similar to those of produced oils (Figure 13A). The same applies to the C_{1-}, C_{2-} and C_{3-} alkylbenzenes, which are totally absent in chalks (Figure 13B). As the previous oil-reservoir correlation was based on C_{15+} fractions, a possible contribution of light hydrocarbons from shale and marl intervals to the produced oils cannot be excluded. Notably, the C_{1}-, C_{2}- and C_{3}- alkylphenanthrenes are remarkably unaltered (Figure 13B), which substantiates the previous use of phenanthrenes in maturity assessment.

3.3.3. Polar compounds

Ternary plots reflecting the variations of nitrogen-, oxygen-, and sulfur- containing compounds among oils and core extracts are given in figure 14A. The relative abundance of nitrogen-containing compounds (46-84%), i.e., the sum of carbazoles and benzocarbazoles, predominate over the oxygen- and sulfur- containing compounds in the produced oils (Table 5). In comparison, it is the oxygen-containing compound class (fluorenones and benzofluorenones) that is dominating core extracts (Figure 14A). This likely suggests the preferential adsorption of oxygen-containing compounds in core samples. Oxidation might also occur during storage (Bennett and Larter, 2000) or in-situ by rock-fluid interactions (Surdam et al., 1989).

The distributions of C_{1-3} alkylated homologs from carbazoles, benzofluorenones, and dibenzothiophenes are presented in figure 14B. Within the sulfur-containing compounds, the C_{1}-, C_{2}- and C_{3}- alkylated dibenzothiophenes are remarkably unaltered. This observation substantiates the previous use of dibenzothiophenes in assessing the maturity. Within the nitrogen-containing compounds, a relative enrichment of higher to lower (C_3 vs. C_1) alkylated carbazole homologues was shown in crude oils, which may attributed to migration-associated fractionation effects (Yamamoto et al., 1991; Yamamoto, 1992; Li et al., 1995; Bennett et al., 2002).

4. Conclusions

Hydraulic fracturing is routinely used to stimulate unconventional reservoirs. In the Niobrara shale oil play there are several fracking targets, but the actual stimulated rock volume is not well constrained. The A & B- chalks have here been deduced to be the main production zones because:

(1). The SARA fraction of core extracts from the chalk intervals closely resemble those of produced oils.

(2). The heavy-end *n*-alkanes are characteristic of the A- & B- chalks. The presence of *n*-C_{31+} alkanes in pristine oils suggests strongly that oils were produced from the A- & B- chalks.

(3). Certain hydrocarbons might have been sourced from organic-rich layers, such as the $C_{27-28-29}$ diasteranes suggest a commingling of oils from the Sharon Springs Shale and the A-Marl interval.

(4). The resemblances in the Pr/Ph and C_{29}/C_{27-29} diasterane ratios indicate that the A-Chalk interval is the most productive.

Importantly, all of the above correlations are based on C_{15+} components; an absence of gasoline range hydrocarbons ($<C_7$) is a fundamental constraint of this study.

As oil is flowing from the reservoir to wellhead, a selective partitioning between the mobile oil and residual bitumen is considered to have occurred. Oils are consequently enriched in lighter hydrocarbons in molecular level, and depleted in ^{13}C by more than three parts per thousand relative to core extracts in isotopic level. Besides that, fractionation of polar compounds was shown to result in the enrichment of rather aliphatic nitrogen-containing compounds in produced oils.

Acknowledgments

References

Abdullah, F.H., Connan, J., 2002. Geochemical study of some Cretaceous rocks from Kuwait: comparison with oils from Cretaceous and Jurassic reservoirs. Organic Geochemistry 33, 125-148.

Barker, C., 1979. Organic Geochemistry in Petroleum Exploration.

Bennett, B., Chen, M., Brincat, D., Gelin, F.J.P., Larter, S.R., 2002. Fractionation of benzocarbazoles between source rocks and petroleums. Organic Geochemistry 33, 545-559.

Bennett, B., Larter, S.R., 2000. The isolation, occurrence and origin of fluorenones in crude oils and rock extracts. Organic Geochemistry 31, 117-125.

Brooks, J.D., Gould, K., Smith, J.W., 1969. Isoprenoid hydrocarbons in coal and petroleum. Nature 222, 257-259.

Carpentier, B., Ungerer, P., Kowalewski, I., Magnier, C., Courcy, J.P., Huc, A.Y., 1996. Molecular and isotopic fractionation of light hydrocarbons between oil and gas phases. Organic Geochemistry 24, 1115-1139.

Clayton, C.J., 1991. Effect of maturity on carbon isotope ratios of oils and condensates. Organic Geochemistry 17, 887-899.

Clayton, C.J., Bjorøy, M., 1994. Effect of maturity on 13C/12C ratios of individual compounds in North Sea oils. Organic Geochemistry 21, 737-750.

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.

Curiale, J.A., 2008. Oil–source rock correlations – Limitations and recommendations. Organic Geochemistry 39, 1150-1161.

Curiale, J.A., Bromley, B.W., 1996. Migration induced compositional changes in oils and condensates of a single field. Organic Geochemistry 24, 1097-1113.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 272, 216-222.

Haberer, R.M., Mangelsdorf, K., Wilkes, H., Horsfield, B., 2006. Occurrence and palaeoenvironmental significance of aromatic hydrocarbon biomarkers in Oligocene sediments from the Mallik 5L-38 Gas Hydrate Production Research Well (Canada). Organic Geochemistry 37, 519-538.

Han, Y., 2016. Oil retention and migration in the Barnett, Posidonia, and Niobrara shales. Technische Universität Berlin, Berlin, Germany, p. 180.

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, 106-116.

Han, Y., Horsfield, B., Mahlstedt, N., Wirth, R., Curry, D., LaReau, H., 2018. Factors controlling source and reservoir characteristics in the Niobrara shale-oil system, Denver Basin. AAPG Bulletin (Accept Pending Revisions).

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.

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.

Jarvie, D.M., 2012. Shale resource systems for oil and gas: Part 2 —Shale-oil resource systems, in: Breye, J.A. (Ed.), Shale reservoirs—Giant resources for the 21st century: AAPG Memoir 97, pp. 89-119.

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.

Landon, S.M., Longman, M.W., Luneau, B.A., 2001. Hydrocarbon source rock potential of the Upper Cretaceous Niobrara Formation, Western Interior Seaway of the Rocky Mountain Region. The Mountain Geologist 38, 1-18.

Larter, S., 1988. Some pragmatic perspectives in source rock geochemistry. Marine and Petroleum Geology 5, 194-204.

Larter, S., Mills, N., 1991. Phase-controlled molecular fractionations in migrating petroleum charges. Geological Society, London, Special Publications 59, 137-147.

Li, M., Larter, S.R., Stoddart, D., Bjorøy, M., 1995. Fractionation of pyrrolic nitrogen compounds in petroleum during migration: derivation of migration-related geochemical parameters. Geological Society, London, Special Publications 86, 103-123.

Li, S., Pang, X., Jin, Z., Yang, H., Xiao, Z., Gu, Q., Zhang, B., 2010. Petroleum source in the Tazhong Uplift, Tarim Basin: New insights from geochemical and fluid inclusion data. Organic Geochemistry 41, 531-553.

Locklair, R.E., Sageman, B.B., 2008. Cyclostratigraphy of the Upper Cretaceous Niobrara Formation, Western Interior, U.S.A.: A Coniacian–Santonian orbital timescale. Earth and Planetary Science Letters 269, 540-553.

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.

Murillo, W.A., Vieth-Hillebrand, A., Horsfield, B., Wilkes, H., 2016. Petroleum source, maturity, alteration and mixing in the southwestern Barents Sea: New insights from geochemical and isotope data. Marine and Petroleum Geology 70, 119-143.

Odden, W., Barth, T., Talbot, M.R., 2002. Compound-specific carbon isotope analysis of natural and artificially generated hydrocarbons in source rocks and petroleum fluids from offshore Mid-Norway. Organic Geochemistry 33, 47-65.

Odden, W., Patience, R.L., Van Graas, G.W., 1998. Application of light hydrocarbons (C4–C13) to oil/source rock correlations. Organic Geochemistry 28, 823-847.

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., Scott Ramos, L., Zumberge, J.E., Valin, Z.C., Bird, K.J., 2008. De-convoluting mixed crude oil in Prudhoe Bay Field, North Slope, Alaska. Organic Geochemistry 39, 623-645.

Peters, K.E., Walters, C.C., Moldowan, M.J., 2005. The biomarker guide. Cambridge University Press.

Powell, T.G., McKirdy, D.M., 1973. Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. Nature Physical Science 243, 37-39.

Powell, T.G., Ten Haven, H.L., Rullkotter, J., De Leeuw, J.W., Damste, J.S.S., 1988. Pristane/phytane ratio as environmental indicator. Nature 333, 604-604.

Price, L.C., Wenger, L.M., Ging, T., Blount, C.W., 1983. Solubility of crude oil in methane as a function of pressure and temperature. Organic Geochemistry 4, 201-221.

Radke, M., Welte, D.H., Willsch, H., 1982. 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.

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.

Sandvik, E.I., Young, W.A., Curry, D.J., 1992. Expulsion from hydrocarbon sources: the role of organic absorption. Organic Geochemistry 19, 77-87.

Schoell, M., 1984. Stable isotopes in petroleum research, in: Brooks, J., Welte, D.H. (Eds.), Advances in Petroleum Geochemistry. Academic Press, New York, pp. 215-245.

Seifert, W.K., Moldowan, M.J., 1981. Paleoreconstruction by biological markers. Geochimica et Cosmochimica Acta 45, 783-794.

Sofer, Z., 1984. Stable carbon isotope compositions of crude oils; application to source depositional environments and petroleum alteration. AAPG Bulletin 68, 31-49.

Sonnenberg, S.A., 2011. The Niobrara petroleum system, a major tight resource play in the Rocky Mountain Region. Search and Discovery Article # 10355, http://www.searchanddiscovery.com/documents/2011/10355sonnenberg/ndx_sonnenberg.pdf.

Sonnenberg, S.A., Weimer, R.J., 1993. Oil Production from Niobrara Formation, Silo Field, Wyoming: Fracturing Associated with a Possible Wrench Fault System(?). The Mountain Geologist 30, 39-54.

Stahl, W.J., 1977. Carbon and nitrogen isotopes in hydrocarbon research and exploration. Chemical Geology 20, 121-149.

Surdam, R.C., Crossey, L.J., Hagen, E.S., Heasler, H.P., 1989. Organic-Inorganic Interactions and Sandstone Diagenesis. AAPG Bulletin 73, 1-23.

Thompson, K.F.M., 1987. Fractionated aromatic petroleums and the generation of gas-condensates. Organic Geochemistry 11, 573-590.

Tissot, B.P., Welte, D.H., 1984. Petroleum formation and occurrence. Springer, Verlag, Berlin, Heidelberg, New York, Tokyo.

Welker, C., Stright, L., Anderson, T., 2013. Geologic Controls on Oil Production from the Niobrara Formation, Silo Field, Laramie County, Wyoming. Unconventional Resources Technology Conference, Denver, Colorado, USA, 146-153.

Whiticar, M.J., 1996. Stable isotope geochemistry of coals, humic kerogens and related natural gases. International Journal of Coal Geology 32, 191-215.

Yamamoto, M., 1992. Fractionation of azaarenes during oil migration. Organic Geochemistry 19, 389-402.

Yamamoto, M., Taguchi, K., Sasaki, K., 1991. Organic Geochemistry of Hydrocarbon Basins Basic nitrogen compounds in bitumen and crude oils. Chemical Geology 93, 193-206.

Yu, S., Pan, C., Wang, J., Jin, X., Jiang, L., Liu, D., Lü, X., Qin, J., Qian, Y., Ding, Y., Chen, H., 2012. Correlation of crude oils and oil components from reservoirs and source rocks using carbon isotopic compositions of individual n-alkanes in the Tazhong and Tabei Uplift of the Tarim Basin, China. Organic Geochemistry 52, 67-80.

Zhan, Z., Zou, Y., Pan, C., Sun, J., Lin, X., Peng, P., 2017. Origin, charging, and mixing of crude oils in the Tahe oilfield, Tarim Basin, China. Organic Geochemistry 108, 18-29.

Zhan, Z., Zou, Y., Shi, J., Sun, J., Peng, P., 2016. Unmixing of mixed oil using chemometrics. Organic Geochemistry 92, 1-15.
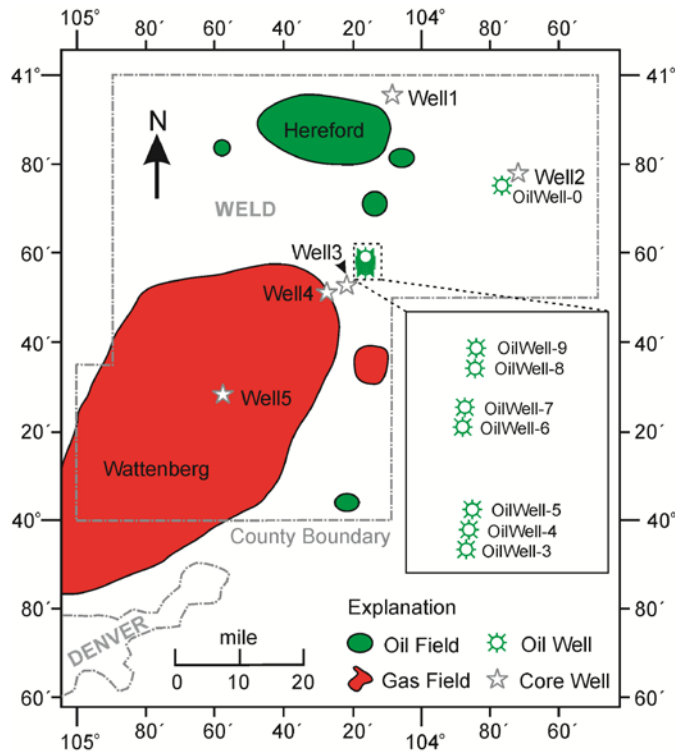
Figure 1. Maps showing fields and sampled wells. Detailed information concerning the name and the precise location of wells are not presented due to confidential reasons.
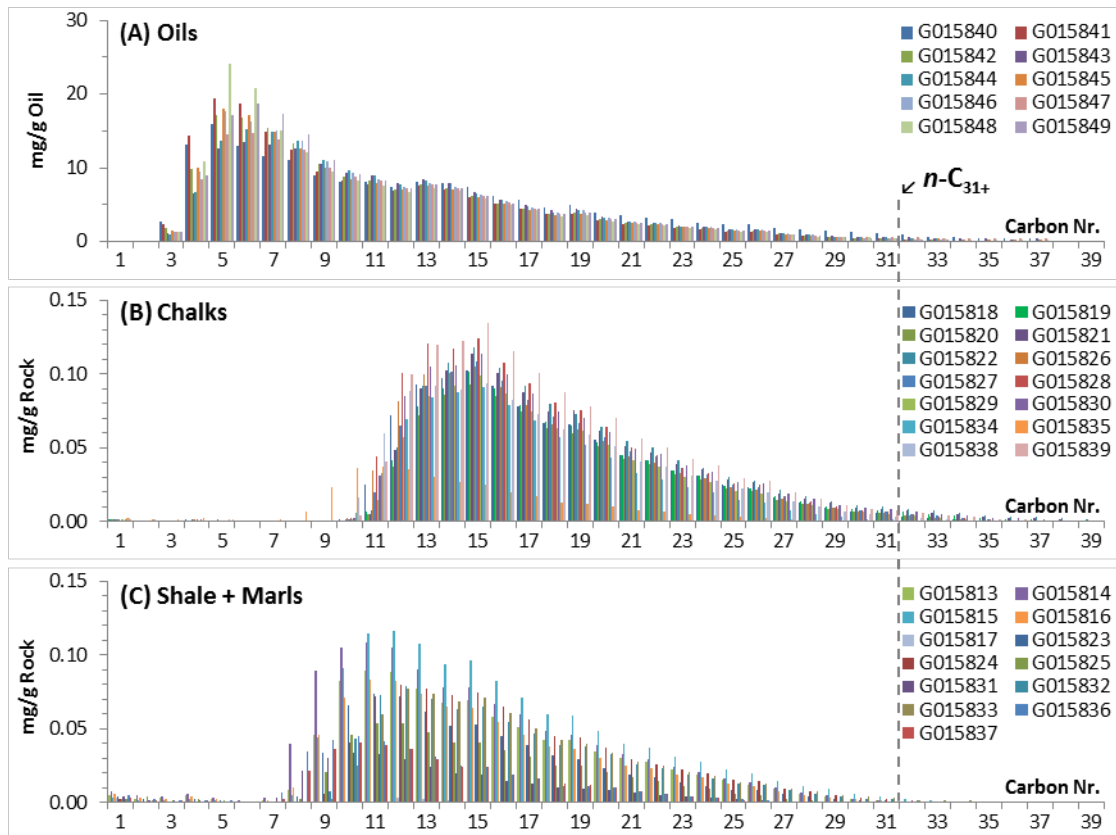
Figure 2. GC detected *n*-alkane distribution in (A) pristine oils, (B) chalk intervals, (C) shale and marl intervals. Numbers on the x-axis indicate the chain length of *n*-alkanes.
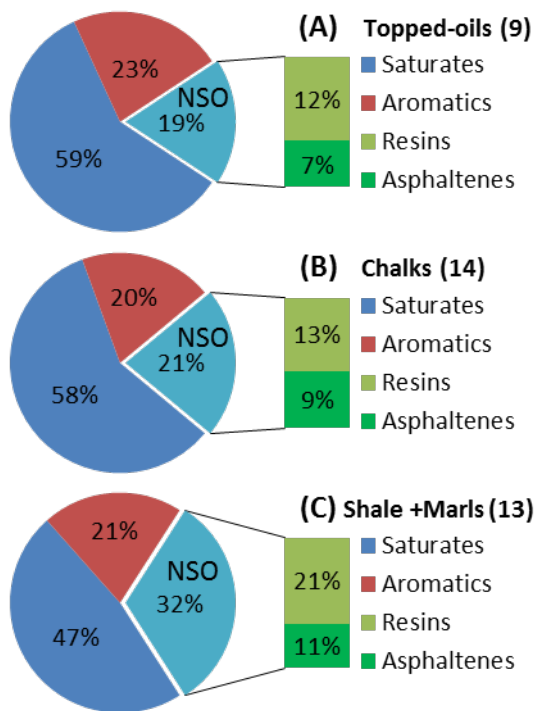
Figure 3. Average SARA fractions (saturates, aromatics, resins and asphaltenes) of (A) topped oils, (B) chalk extracts, (C) shale and marl extracts. The number of analyzed samples was noted in parentheses. Sample G015840 is excluded from plotting due to the loss of its aromatic fraction during experiment. Note: NOS containing polar compounds = resins + asphaltenes.
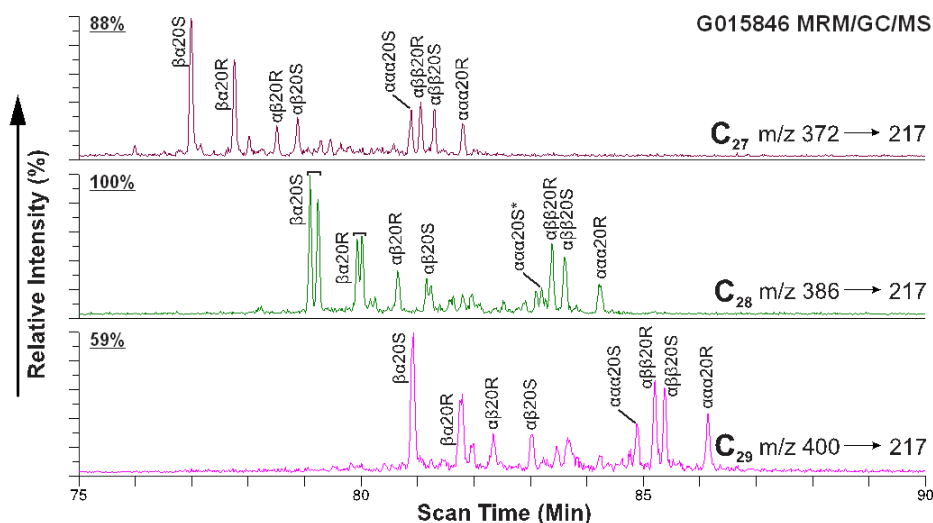
Figure 4. MRM-GC-MS results of sterane and diasterane homologs ($M^+ \rightarrow 217$) detected on the saturate fractions as exemplified by sample G015846. βα20S(R) refers to diasteranes with the 13β,17α(H)20S(R) stereochemistry, αβ20R(S) are the 13α,17β(H)20R(S) diasterane epimers, ααα20S(R) refers to steranes with the 5α,14α,17α(H)20S(R) stereochemistry, αββ20R(S) are the 5α,14β,17β(H)20R(S) sterane epimers. The peak of tentatively identified C_{28} ααα20S sterane is asterisk marked.
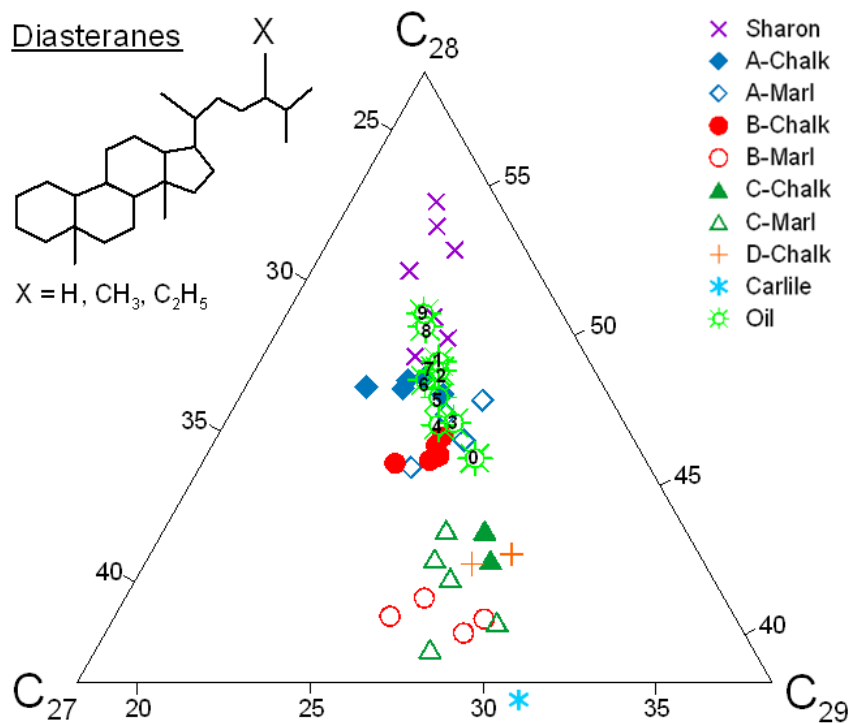
Figure 5. Partly magnified ternary diagram showing the distributions of $C_{27\text{-}28\text{-}29}$ diasteranes detected by MRM-GC-MS. Oils were plotted together with bitumen extracts from the core wells 3+4.The last sample number is indicated within its symbol for oils. The Carlile Shale sample is shown schematically as beneath the axis.
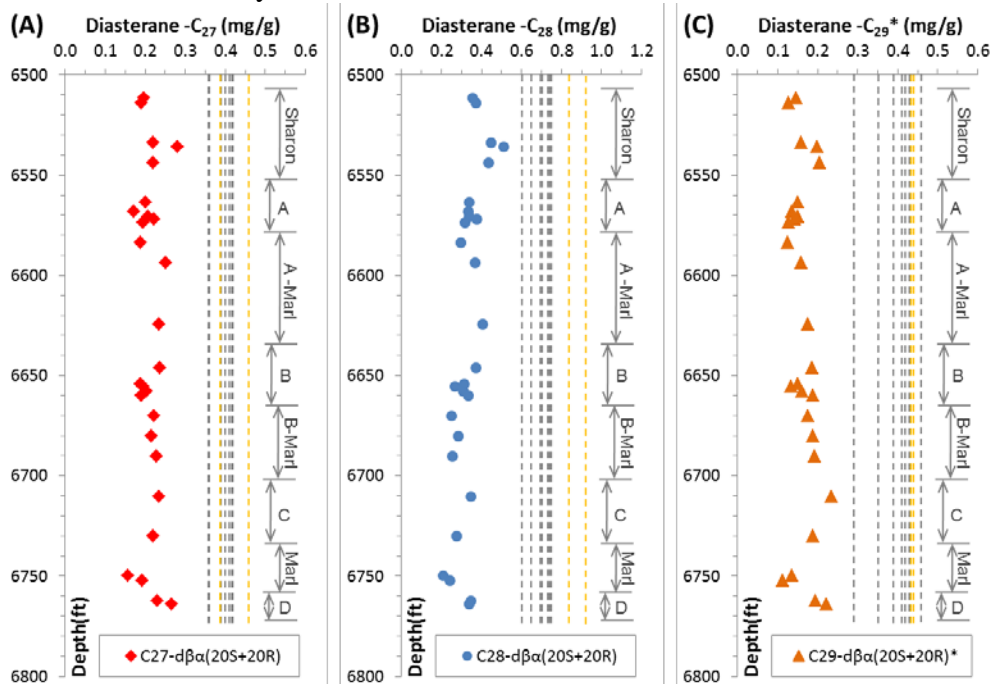
Figure 6. Variations in concentration of $C_{27\text{-}28\text{-}29}$ diasteranes (mg/g extracts) detected by GC-MS. Note: dash lines are used to show the concentrations of oil samples (mg/g topped-oil), in which the re-stimulated oils G015841 and G015842 are highlighted in yellow. Sample G015840 is not shown. $13\beta,17\alpha(H)20S$ C_{29} diasterane may coelute with $5\alpha,14\beta,17\beta(H)20R$ C_{27} sterane.
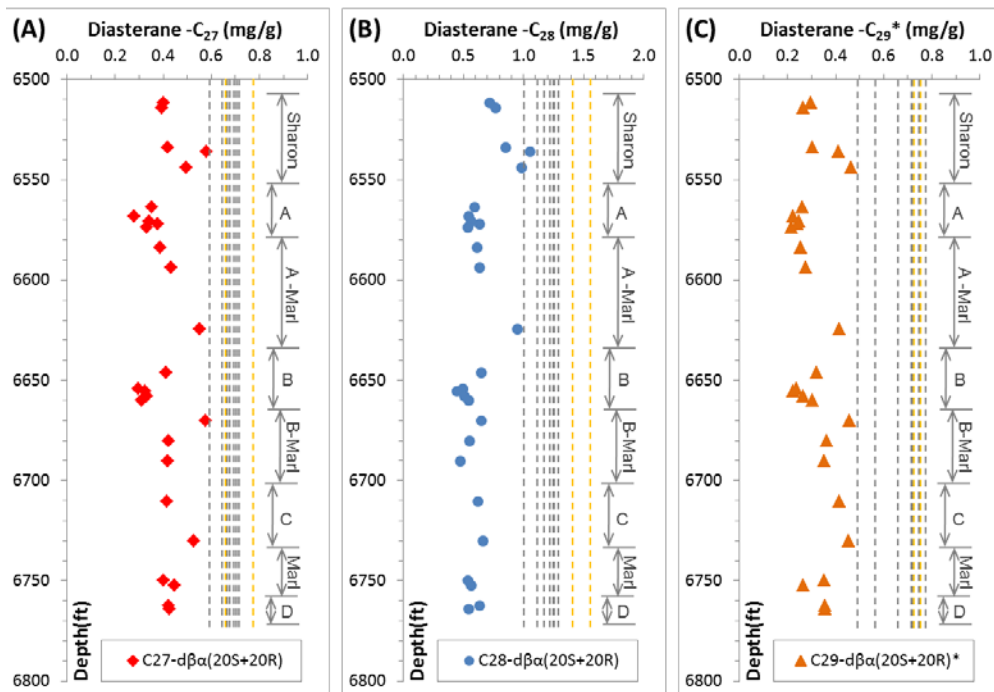
Figure 7. Variations in concentration of $C_{27\text{-}28\text{-}29}$ diasteranes (mg/g saturates) detected by GC-MS. Note: dash lines are used to show the concentrations of oil samples (mg/g saturates), in which the re-stimulated oils G015841 and G015842 are highlighted in yellow. Sample G015840 is not shown. $13\beta,17\alpha(H)20S$ C_{29} diasterane may coelute with $5\alpha,14\beta,17\beta(H)20R$ C_{27} sterane.
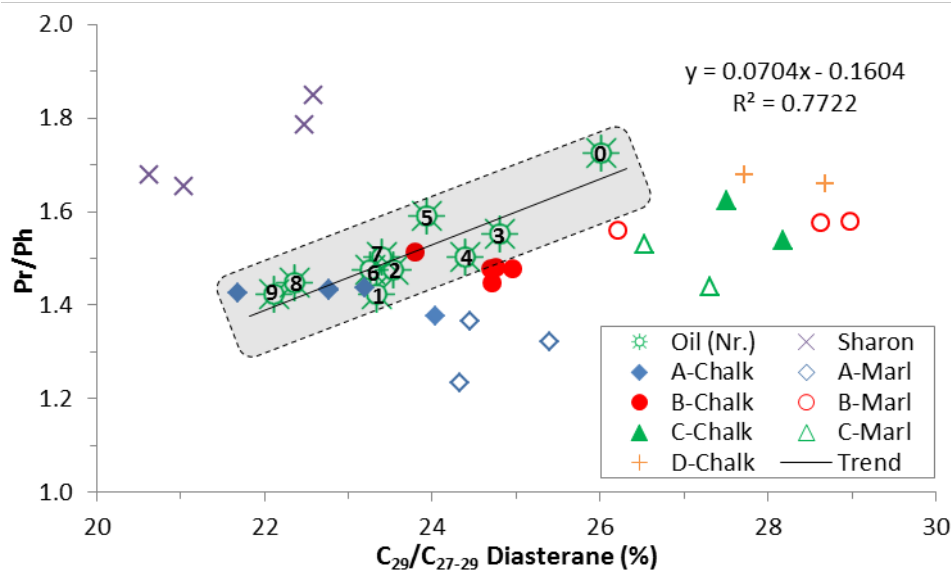
Figure 8. A cross-plot of the pristane/phytane (Pr/Ph) ratio versus the C_{29}/C_{27-29} diasterane ratio. The last digit of sample number is shown with symbol for oils.
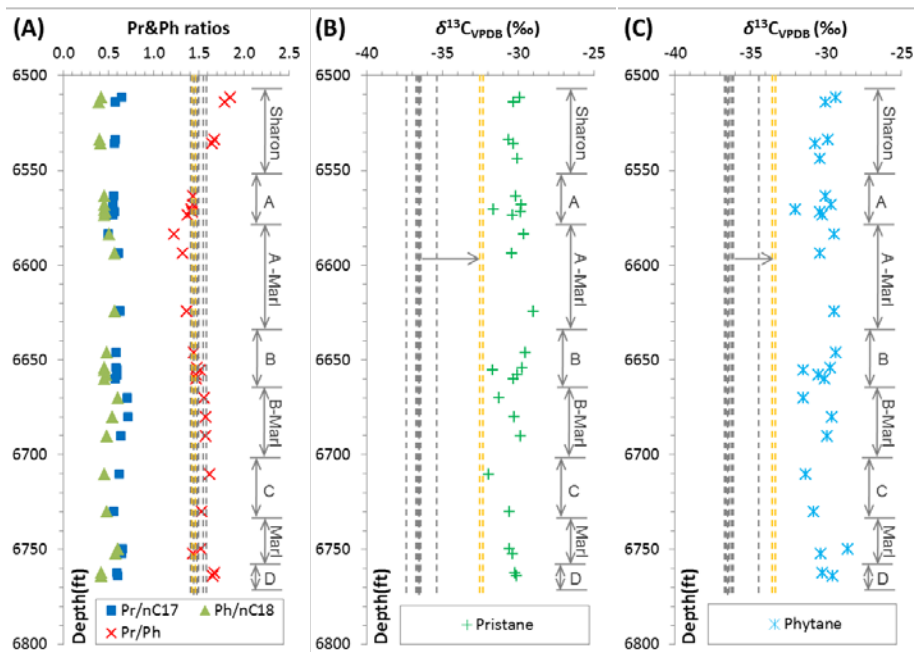
Figure 9. Variations of (A) pristane and phytane ratios detected by GC, (B-C) stable carbon isotope values of pristane and phytane detected by IRM-GC-MS, respectively. Note: the dash lines are used to represent oil samples, in which the re-stimulated oils G015841 and G015842 are highlighted in yellow. Sample G015840 is not shown.
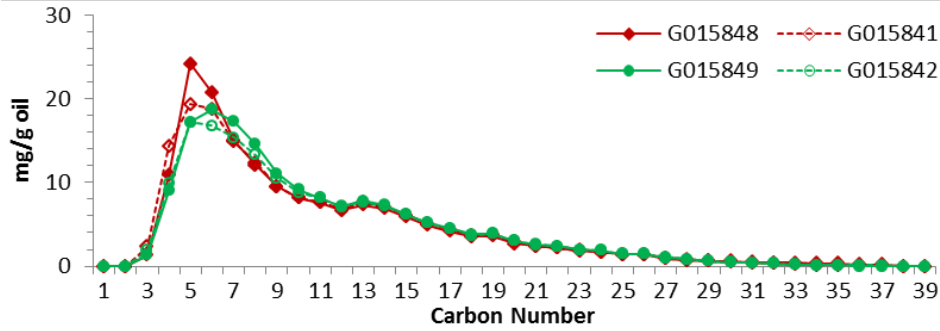
Figure 10. Comparison of *n*-alkane distributions in produced oils from two stimulations. G015841 and G015842 are re-stimulated oil fluids in reference to G015848 and G015849, respectively.
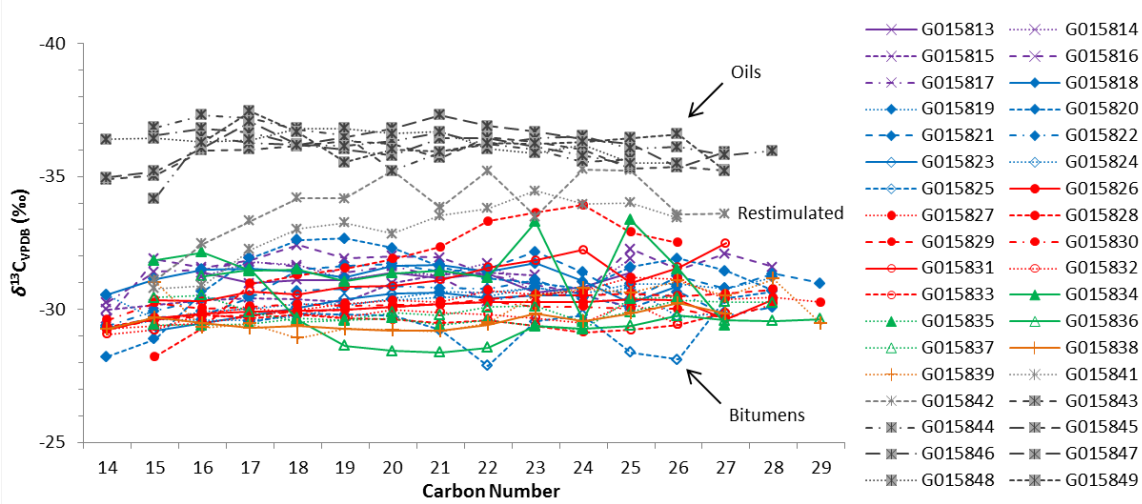
Figure 11. Comparison of carbon isotope ratios of *n*-alkanes from oils and core extracts. Sample G015840 is not shown. G015841 and G015842 are re-stimulated oil fluids.
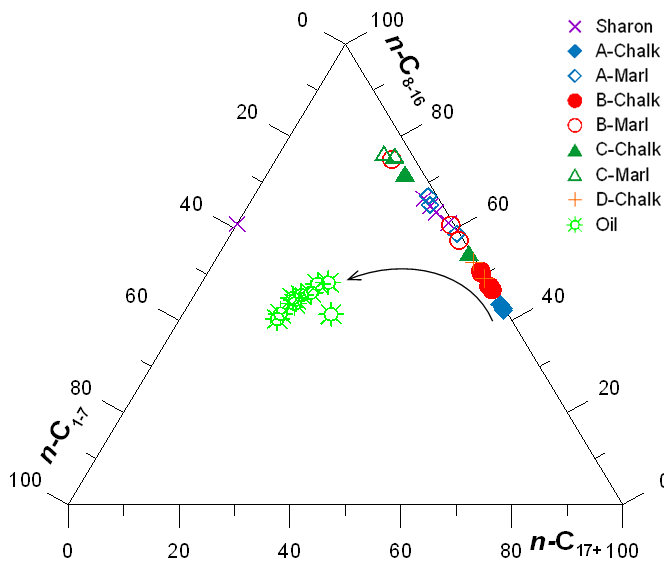
Figure 12. Gas chromatography *n*-alkane distribution in pristine oils and cores. Ternary diagram using the sum of *n*-C_{1-7} versus *n*-C_{8-16} versus *n*-C_{17+} alkanes.
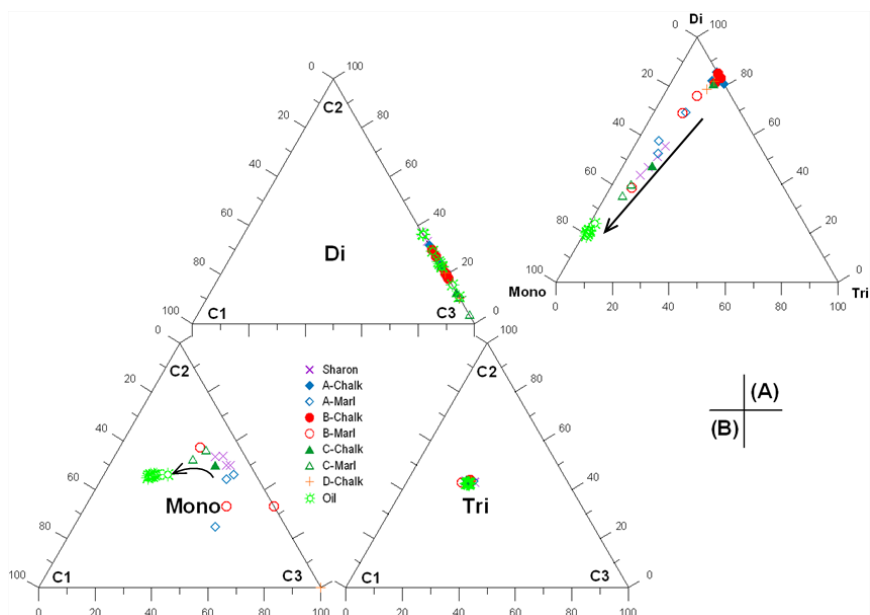
Figure 13. Aromatic hydrocarbon composition of C_1-, C_2- and C_3- alkylated (mono-aromatic) benzenes, (di-aromatic) naphthalenes, and (tri-aromatic) phenanthrenes detected by GC-MS. The black arrow indicates the compositional difference between cores and oils.
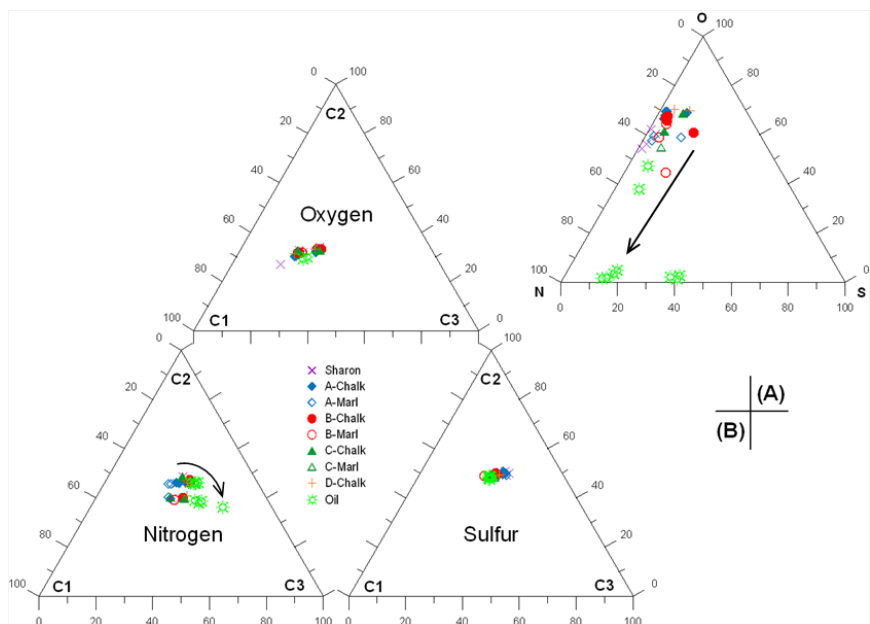
Figure 14. Polar compound composition of nitrogen (C_{0-4} alkylated carbazoles and C_{0-4} alkylated benzocarbazoles), oxygen (C_{0-2} alkylated fluorenones and C_{0-3} alkylated benzofluorenones), and sulfur (C_{0-3} alkylated dibenzothiophenes) containing compounds detected by GC-MS. C_{1-3} alkylated homologs from carbazoles, benzofluorenones, and dibenzothiophenes are presented as examples of specific polar compounds. The black arrow indicates the compositional difference between cores and oils.

Table 1. Geochemical parameters of oil samples for oil-reservoir correlation

Oil Sample	Well Name	Loss (wt.%)	Oil Residual (%)				Diasteranes (%)			Pr/n-C$_{17}$	Ph/n-C$_{18}$	Pr/Ph
			Sat.	Aro.	Res.	Asp.	C$_{27}$	C$_{28}$	C$_{29}$			
G015840	OilWell-0	42	53	n.a.	15	6	28	46	26	0.55	0.38	1.72
G015841	OilWell-8	51	55	23	14	8	28	49	23	0.61	0.51	1.42
G015842	OilWell-9	46	59	23	12	6	28	49	24	0.62	0.51	1.47
G015843	OilWell-3	37	61	21	12	6	28	47	25	0.62	0.48	1.55
G015844	OilWell-4	44	59	24	12	6	29	47	24	0.63	0.50	1.50
G015845	OilWell-5	44	61	21	12	6	28	48	24	0.63	0.47	1.59
G015846	OilWell-6	45	58	22	12	8	28	48	23	0.60	0.48	1.47
G015847	OilWell-7	44	59	22	12	7	28	49	23	0.61	0.49	1.50
G015848	OilWell-8	48	59	23	11	6	27	50	22	0.62	0.51	1.44
G015849	OilWell-9	46	59	23	11	6	27	51	22	0.60	0.50	1.42
Average		45	59	23	12	7	28	49	23	0.62	0.49	1.49

Note: Loss (wt.%) = the weight loss of oil after artificial evaporation at 60 °C; Sat. = Saturates, Aro. = Aromatics, Res. = Resins, Asp. = asphaltenes. n.a. = not available. 13β,17α(H) (20S + 20R) C$_{27-29}$ diasteranes were detected by MRM-GC-MS on the saturate fraction of topped oils. The aromatic fraction of oil sample G015840 was lost during experiment, and thus is excluded from averaging.

Table 2. Maturity parameters of topped oils

Oil Sample	Well Name	Vr-DBT (R_c%)	Vr-P (R_c%)	TA(I)/ TA(I+II)	Dia/ (Dia+Reg)
G015840	OilWell-0	n.a.	n.a.	n.a.	0.48
G015841	OilWell-8	0.75	0.81	0.55	0.49
G015842	OilWell-9	0.74	0.82	0.57	0.49
G015843	OilWell-3	0.75	0.84	0.60	0.52
G015844	OilWell-4	0.75	0.83	0.58	0.49
G015845	OilWell-5	0.75	0.83	0.57	0.49
G015846	OilWell-6	0.74	0.81	0.56	0.48
G015847	OilWell-7	0.74	0.82	0.55	0.48
G015848	OilWell-8	0.73	0.80	0.53	0.49
G015849	OilWell-9	0.74	0.80	0.54	0.47
Average		0.74	0.82	0.56	0.49

Note: Vr-DBT refers to the dibenzothiophene (DBT) calculated vitrinite reflectance [R_c (%) = 0.14 × 4,6DMDBT/1,4DMDBT + 0.57], Vr-P refers to the phenanthrene (P) calculated vitrinite reflectance [R_c (%) = 0.9 × (2MP + 3MP)/(P + 1MP + 9MP) + 0.4], and [TA(I)/(TA(I+II)] refers to the triaromatic (TA) steroids ratio that detected by GC-MS on the aromatic fractions. The aromatic fraction of oil sample G015840 was lost during experiment, and this sample is excluded from averaging. n.a. = not available. The rearranged to regular C_{29} steranes ratio [Dia/(Dia+Reg)] was detected by MRM-GC-MS on the saturate fraction of topped oils.

Table 3. Carbon isotope ratios (in ‰ with respect to VPDB, $\delta^{13}C_{VPDB}$) of individual hydrocarbons

Sample	Well	Pr	Ph	$n\text{-}C_{14}$	$n\text{-}C_{15}$	$n\text{-}C_{16}$	$n\text{-}C_{17}$	$n\text{-}C_{18}$	$n\text{-}C_{19}$	$n\text{-}C_{20}$
G015840	OilWell-0	-31.76	-33.31		-32.69	-33.05	-33.74	-34.03	-34.29	-34.39
G015841	OilWell-8	-32.59	-33.38		-30.79	-30.89	-32.26	-33.03	-33.26	-32.85
G015842	OilWell-9	-32.34	-33.32		-31.11	-32.47	-33.33	-34.19	-34.18	-35.22
G015843	OilWell-3	-36.49	-36.20	-34.89	-35.03	-35.98	-36.02	-36.15	-36.35	-36.24
G015844	OilWell-4	-35.47	-34.35		-36.84	-37.31	-37.21	-36.75	-36.56	-35.22
G015845	OilWell-5	-37.09	-36.37	-34.96	-35.19	-36.07	-37.06	-36.20	-36.49	-36.81
G015846	OilWell-6	-36.68	-36.78		-36.54	-36.80	-36.65	-36.19	-36.01	-35.79
G015847	OilWell-7	-36.40	-36.14		-34.18	-36.51	-36.26	-36.18	-36.14	-36.34
G015848	OilWell-8	-36.42	-36.69	-36.39	-36.43	-36.29	-36.37	-36.81	-36.80	-36.61
G015849	OilWell-9	-36.54	-35.26			-36.29	-37.46	-36.66	-35.54	-36.02
Average		-35.56	-35.39	-35.41	-34.51	-35.40	-35.85	-35.80	-35.70	-35.68

Table 3. Continue

Sample	Well	$n\text{-}C_{21}$	$n\text{-}C_{22}$	$n\text{-}C_{23}$	$n\text{-}C_{24}$	$n\text{-}C_{25}$	$n\text{-}C_{26}$	$n\text{-}C_{27}$	$n\text{-}C_{28}$	$5\alpha\text{-A.}$
G015840	OilWell-0	-34.56	-33.24	-34.31	-33.69	-34.41	-33.20	-32.47	-30.78	-29.49
G015841	OilWell-8	-33.52	-33.79	-34.46	-33.95	-34.02	-33.43			-29.58
G015842	OilWell-9	-33.83	-35.21	-33.50	-35.27	-35.23	-33.57	-33.59		-29.20
G015843	OilWell-3	-35.69	-36.47	-36.29	-36.01	-35.31	-35.35	-35.23		-29.27
G015844	OilWell-4	-35.89	-36.22	-36.01	-35.55	-35.66				-29.16
G015845	OilWell-5	-37.30	-36.89	-36.68	-36.41	-36.23	-35.34	-35.93		-29.55
G015846	OilWell-6	-36.43	-36.45	-36.10	-35.79	-35.43				-29.23
G015847	OilWell-7	-36.65	-36.18	-36.43	-36.52	-36.06	-36.10	-35.81	-35.97	-29.35
G015848	OilWell-8	-36.68	-36.04	-35.87	-36.18	-35.50	-35.50			-29.66
G015849	OilWell-9	-35.93	-36.25	-36.24	-36.30	-36.45	-36.59	-35.19		-29.42
Average		-35.77	-35.94	-35.73	-35.78	-35.54	-35.13	-35.15	-35.97	-29.38

Note: Pr = pristane, Ph = phytane, 5α-A. = 5α-Androstane. Sample G015840 is excluded from averaging.

Table 4. Aromatic hydrocarbons composition of oil samples

Oil Sample	Well Name	Aromatics (%)			Mono-aromatics (%)			Di-aromatics (%)			Tri-aromatics (%)		
		Mono	Di	Tri	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
G015840	OilWell-0	74	24	2	31	46	23	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
G015841	OilWell-8	78	21	1	39	45	16	0	11	89	35	43	22
G015842	OilWell-9	79	20	1	37	46	17	0	16	84	35	43	22
G015843	OilWell-3	77	21	1	35	46	19	0	25	75	35	43	22
G015844	OilWell-4	78	21	2	36	46	18	0	25	75	35	43	22
G015845	OilWell-5	79	20	1	37	45	18	0	23	77	36	43	22
G015846	OilWell-6	79	20	1	37	46	17	0	36	64	35	42	23
G015847	OilWell-7	78	21	1	36	46	18	0	23	77	35	43	23
G015848	OilWell-8	79	20	1	37	46	17	0	30	70	36	42	21
G015849	OilWell-9	80	19	1	38	46	16	0	37	63	36	43	21
Average		78	20	1	37	46	17	0	25	75	35	43	22

Note: GC detected composition of n-C_{5+}/aromatics, mono-, di-, and tri- aromatic hydrocarbons, and C_1-, C_2- and C_3- alkylated mono-aromatics (alkyl-benzenes) on pristine oils; GC-MS detected composition of C_1-, C_2- and C_3- alkylated di-aromatics (naphthalenes) and tri-aromatics (phenanthrenes) on the aromatic fraction of topped oils. The aromatic fraction of sample G015840 was lost during experiment, and this sample is excluded from averaging. n.a. = not available.

Table 5. Polar heterocompounds composition of oil samples

Oil Sample	Well Name	NOS (%)			Carbazoles (%)			Benzofluorenones (%)			Dibenzothiophenes (%)		
		Ni.	Oxy.	Sul.	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
G015840	OilWell-0	n.a.	n.a.	n.a.	17	36	46	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.
G015841	OilWell-8	83	2	15	22	46	32	n.d.	n.d.	n.d.	27	47	26
G015842	OilWell-9	60	2	38	25	38	37	n.d.	n.d.	n.d.	26	48	25
G015843	OilWell-3	46	47	7	21	46	33	45	30	25	27	48	25
G015844	OilWell-4	57	3	40	23	39	38	n.d.	n.d.	n.d.	26	48	25
G015845	OilWell-5	53	38	9	22	46	32	47	29	24	27	48	26
G015846	OilWell-6	79	4	17	22	46	32	n.d.	n.d.	n.d.	27	48	25
G015847	OilWell-7	78	5	17	23	46	31	n.d.	n.d.	n.d.	26	49	26
G015848	OilWell-8	84	2	14	23	46	30	n.d.	n.d.	n.d.	26	49	25
G015849	OilWell-9	58	2	40	26	39	35	n.d.	n.d.	n.d.	26	49	25
Average		66	12	22	23	44	33	n.d.	n.d.	n.d.	26	48	25

Note: MPLC detected composition of aromatics/resins; GC-MS detected composition of nitrogen (C_{0-4} alkylated carbazoles and C_{0-4} alkylated benzocarbazoles), oxygen (C_{0-2} alkylated fluorenones and C_{0-3} alkylated benzofluorenones), and sulfur (C_{0-3} alkylated dibenzothiophenes) containing compounds, C_1-, C_2- and C_3- alkylated carbazoles, C_1-, C_2- and C_3- alkylated benzofluorenones, and C_1-, C_2- and C_3- alkylated dibenzothiophenes on topped oils. The aromatic fraction of oil sample G015840 was lost during experiment, and this sample is excluded from averaging. n.a. = not available, n.d. = not detected, Aro. = Aromatics, Res. = Resins, Ni. = nitrogen, Oxy. = oxygen, Sul. = sulfur.