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Geochemical characterization and origin of the Cretaceous Sa'di, Khasib, Mishrif, and Nahr Umr Crude Oils in Halfaya Oilfield, Southern Mesopotamian Basin, Iraq

Amer Jassim Al-Khafaji^a , Sahar Jassim Yonis^b, Rafid N. Al Ibrahim^c , Shahad Almarsomi^d, and Fadhil Sadooni^e

^aDepartment of Geology, College of Science, University of Babylon, Al Hillah, Iraq; ^bDepartment of Geology, College of Science, University of Baghdad, Baghdad, Iraq; ^cCollege of Science, University of Basra, Basra, Iraq; ^dOil Exploration Company, Baghdad, Iraq; ^eEnvironmental Science Center, Qatar University, Doha, Qatar

ABSTRACT

A suite of crude oil samples from the Cretaceous reservoirs in Halfaya Oilfield, Southern Iraq were analyzed using organic geochemistry analysis to study their geochemical characterization and origin. High sulfur content (3.74 ± 1 wt.%), C_{22}/C_{21} , C_{29}/C_{30} hopane, ratios, and low C_{19}/C_{23} and C_{24}/C_{23} for all oil samples are indicators of marine carbonate environment source. Low pr/pr, Pr/nC_{17} , Ph/nC_{18} , and highest $C_{35}S/C_{34}S$ ratio are consistent with a more reducing carbonate depositional environment. The C_{28}/C_{29} sterane ratio and stable carbon isotope analysis values of crude oils are suggested Upper Jurassic to Middle Cretaceous anoxic marine carbonate source origin.

KEY WORDS

Halfaya Oilfield; Mishrif; Sa'di; Nahr Umr; organic geochemistry; Iraq

Peak assignments for alkane hydrocarbons in the gas chromatograms of saturated fractions in the m/z 191, and 217 mass fragmentograms

Ratio	Biomarker
C_{19}/C_{23}	Tricyclic Terpane C_{19}/C_{23} , peak heights from 191 m/z
C_{22}/C_{21}	Tricyclic Terpane C_{22}/C_{21} , peak heights from 191 m/z
C_{24}/C_{23}	Tricyclic Terpane C_{24}/C_{23} , peak heights from 191 m/z
C_{26}/C_{25}	Tricyclic Terpane C_{26}/C_{25} , peak heights from 191 m/z
Tet/C_{23}	Tetracyclic C_{24} to Tricyclic Terpane C_{23} ratio, peak heights from 191 m/z
C_{28}/H	Bisnorhopane/Hopane
C_{29}/H	Norhopane/Hopane
OL/H	Oleanane/Hopane
$C_{31}R/H$	Homohopane (22R)/Hopane
GA/31R	Gammacerane/Homohopane
$C_{35}S/C_{34}S$	C_{35} Extended Hopane/ C_{34} Extended Hopane (22S)
% C_{27}	Relative % S5B
% C_{28}	Relative % S10B
% C_{29}	Relative % S14B
$C_{27}Ts/Tm$	Trisnorhopane
$C_{29}Ts/Tm$	aka C29D/29H
DM/H	C_{29} demethylated hopane (177 m/z)/Hopane 191 m/z

1. Introduction

The Halfaya Field is one of the giant oilfields in Southeastern Iraq. The field is located at Missan Governorate, 35 kilometers south of the Amara City. The field was discovered by Iraq National Oil Company (INOC) in 1976 but its development was delayed due to the Iraqi-Iranian war since the field is located on the border between the two countries (Figure 1A). The Halfaya Oilfield is a NW-SE trending gentle long-axis anticline 30 km long and around 10 km wide. The field is multi-reservoirs that range in age from Cretaceous to the Miocene. The present estimated reserve of the field is around 4.1 billion barrels of oil. The oil is mostly medium-heavy.

The field is located in the foredeep belt which was formed during the Zagros orogenic movement and has a thick column of sediments that accumulated in the New Tethys Ocean during the Jurassic and Cretaceous periods. These sediments are formed of carbonates, shales and evaporites (Sadooni and Aqrawi 2000) (Figure 1B). There are seven oil-bearing strata in this field. The main reservoirs are Middle Cretaceous carbonates of the Mishrif Formation which are considered as the main producing reservoir in the field as well as the Middle Cretaceous clastics of the Nahr Umr and the Upper Cretaceous carbonates of the Khasib and Sa'di formations.

The Nahr Umr Formation (Late Aptian-Albian) is formed of sandstone and shale and represents alluvial, lower coastal plain, deltaic and shallow marine sediments with some eolian influence in parts of the basin. Aqrawi et al. (2010) described some glauconitic and bituminous sandstone with pyritic shales and plant remains with amber from the Buzurgan Field which is close to the Halfaya Field. The Mishrif Formation (Turonian) is the most important carbonate reservoir in southern Iraq. In Halfaya Field, it consists of open platform to restricted carbonate shelf with some rudist buildups and capped with relatively deeper water carbonates (Aqrawi et al. 2010). The Sa'di Formation (Santonian-Campanian) and Khasib (Coniacian) are the shallowest among the four formations. Sa'di Formation is formed of oligosteginal limestone with chalky and argillaceous limestone containing planktonic foraminifera (Sadooni and Aqrawi 2000). So, the studied samples are derived from two different environmental settings, the Nahr Umr represents a mixed marine-continental system while both Mishrif and Sa'di formations represent marine carbonate system where the Mishrif represents shallow, shelfal carbonates while the Sa'di was deposited under sub-basinal to basinal conditions.

Pitman, Steinhouer, and Lewan (2004) reported that most of the oils accumulated in the Cretaceous and Tertiary reservoirs of the Mesopotamian Basin were generated in general from Jurassic source rocks. Al-Ameri et al. (2014) studied the petroleum systems and oil geochemistry of the Halfaya Oilfield, and suggested also that these oils which were

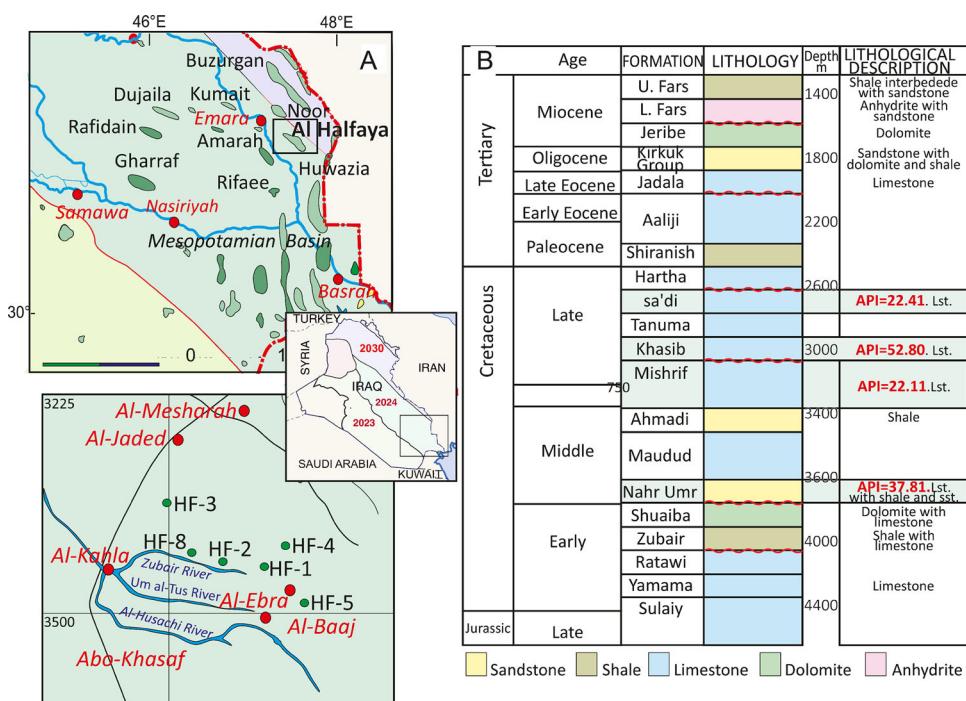


Figure 1. (A) Maps show; the Total Petroleum Systems (TPS) of Iraq, location of Mesopotamian Basin, and locations of oil samples from Halfaya oil wells. (B) Stratigraphic section of the Halfaya oil well-4, shows lithology desecration and approximate ages of formations, and major unconformities.

expelled to the Cretaceous reservoirs were sourced from the Jurassic sediments. Al-Khafaji, Hakimi, and Najaf (2018) and Al-Khafaji (2015) studied the geochemistry of rocks and crude samples of the Mishrif reservoir in many other oilfields in Southern Iraq and concluded that these oils were generated mainly from the Upper Jurassic to Lower Cretaceous source rocks (Abdula 2020; Al-Khafaji et al. 2021)

This study is the first to be concerned with the organic geochemistry of crude oils from the Cretaceous reservoirs in the Halfaya Oilfield. It aims to characterize these oils and to relate their characters to the depositional environments of the related sediments and to understand the genetic of the source rocks responsible for generation and expulsion of oil to the reservoirs.

2. Materials and methods

This study based on results of the organic geochemistry analysis of eleven crude oils taken from Sa'di, Khasib, Mishrif and Nahr Umr reservoirs in Halfaya, in Mesopotamian Basin, south-east Iraq. They were provided by Missan Oil Company in Amara, Southern Iraq. The samples were subjected

Table 1. Bulk property, geochemical composition analysis results and carbon isotope compositions (‰) of the crude oils from Halfaya oilfields in the Southern Mesopotamian Basin, Iraq

SampleID	Oilfield	Well	Formation	Depth (m.)	Age	API	<C15	% S	ppm Ni	ppm V	% Sat	% Aro	% NSO	% Asph	Sat/Aro	¹³ C _S	¹³ C _A	CV	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈
IQ0152	Halfaya	HF-2	Sadi	234.5	Coniacian/ Campanian/	22.41	27.03	4.84	39.00	126.00	22.31	45.68	16.73	15.27	0.49	-27.59	-27.74	-3.43	0.96	0.31	0.42
IQ0441	Halfaya	HF1	Khasib	2470	Turonian/ Coniacian	52.80	88.43	0.63	15	2.00	60.49	29.76	9.76	0.00	2.03	-27.24	-27.44	-3.65	0.85	0.19	0.31
IQ0447	Halfaya	HF6	Mishrif	2500	Cenomanian/	26.10	30.56	3.73	30	135.00	23.21	44.13	15.79	16.87	0.53	-27.40	-27.67	-3.76	0.75	0.20	0.32
IQ0149	Halfaya	HF-2	Mishrif	2857	Cenomanian/	21.23	26.65	4.96	41.00	144.00	22.04	48.57	12.24	17.14	0.45	-27.67	-27.72	-3.18	0.84	0.21	0.32
IQ0442	Halfaya	HF1	Mishrif	2918	Turonian	20.10	32.14	1.48	4	37.00	48.89	32.74	11.28	7.08	1.49	-27.50	-27.40	-2.90	0.73	0.19	0.33
IQ0443	Halfaya	HF9	Mishrif	3025	Cenomanian/	21.30	25.41	2.57	19	59.00	40.90	34.68	14.02	10.40	1.18	-27.81	-27.46	-2.25	0.73	0.19	0.32
IQ0448	Halfaya	HF109	Mishrif	3047	Cenomanian/	21.80	28.06	4.04	41	190.00	21.41	38.25	15.27	25.07	0.56	-27.46	-27.70	-3.67	0.71	0.18	0.33
IQ0153	Halfaya	HF-1	Nahr Umr	3436	Turonian	30.12	34.52	2.74	4.00	20.00	35.50	39.88	12.99	11.63	0.89	-28.12	-27.65	-1.89	0.90	0.26	0.36
IQ0444	Halfaya	HF1	Nahr Umr	3600	Albian	48.30	57.64	2.00	15	45.00	43.34	36.54	13.17	6.95	1.19	-27.88	-27.58	-2.34	0.82	0.18	0.28
IQ0446	Halfaya	HF2	Nahr Umr	3900	Albian	35.00	44.13	3.88	37	163.00	21.35	42.19	13.85	22.62	0.51	-27.46	-27.69	-3.65	0.72	0.18	0.29
IQ0445	Halfaya	HF3	Nahr Umr	3996	Albian	37.80	40.85	3.69	24	108.00	23.40	43.45	13.93	19.22	0.54	-27.51	-27.68	-3.50	0.69	0.17	0.30

Table 2. Various biomarker parameters ratios of the crude oil samples from Halfaya Oilfield, Southern Mesopotamian Basin, South Iraq

SampleID	Oilfield	Formation	Depth (m.)	Age	C_{19}/C_{23}	C_{22}/C_{21}	C_{24}/C_{23}	C_{26}/C_{25}	C_{29}/H	OL/H	$C_{31}R/H$	GA/	$C_{35}S/$	$C_{38}/$	$C_{27}Ts/$	$C_{29}Ts/$	TAS3 (CR)	$Ts/(Ts + Tm)$		
IQ0152	Halfaya	HF-2	Sadi	234.50	Campanian/ Coniacian/	0.14	1.08	0.25	0.77	1.80	0.01	0.35	0.23	1.06	0.69	0.20	0.08	0.34	0.836	
IQ0441	Halfaya	HF1	Khasib	2470	Turonian/ Coniacian	0.08	1.13	0.26	0.69	1.77	0	0.27	0.21	0.98	0.5	0.69	0.18	0.07	0.36	0.152
IQ0149	Halfaya	HF-2	Mishrif	2857.00	Cenomanian/ Turonian	0.15	1.07	0.25	0.75	1.75	0.01	0.34	0.24	1.06	0.66	0.58	0.20	0.08	0.32	0.163
IQ0442	Halfaya	HF1	Mishrif	2918	Cenomanian/ Turonian	0.1	1.11	0.25	0.74	1.82	0	0.31	0.24	1.02	0.45	0.59	0.18	0.07	0.31	0.150
IQ0443	Halfaya	HF9	Mishrif	3025	Cenomanian/ Turonian	0.1	1.12	0.25	0.72	1.69	0	0.3	0.23	1.03	0.46	0.62	0.17	0.07	0.30	0.144
IQ0447	Halfaya	HF6	Mishrif	2500	Cenomanian/ Turonian	0.10	1.09	0.26	0.69	1.70	0.00	0.32	0.23	1.07	0.47	0.62	0.18	0.07	0.31	0.151
IQ0448	Halfaya	HF109	Mishrif	3047	Cenomanian/ Turonian	0.10	1.07	0.25	0.75	1.73	0.00	0.32	0.24	1.04	0.46	0.60	0.17	0.07	0.30	0.146
IQ0153	Halfaya	HF-1	Nahr Umr	3436.50	Albian	0.24	0.92	0.30	0.78	1.46	0.00	0.36	0.13	1.07	0.74	0.64	0.25	0.09	0.30	0.197
IQ0444	Halfaya	HF1	Nahr Umr	3600	Albian	0.22	0.94	0.28	0.69	1.65	0.00	0.35	0.15	1.01	0.54	0.61	0.25	0.08	0.33	0.200
IQ0445	Halfaya	HF3	Nahr Umr	3996	Albian	0.22	0.88	0.30	0.77	1.47	0.00	0.33	0.13	0.99	0.62	0.61	0.24	0.08	0.29	0.193
IQ0446	Halfaya	HF2	Nahr Umr	3900	Albian	0.19	0.92	0.30	0.74	1.48	0.00	0.34	0.14	1.02	0.57	0.59	0.24	0.08	0.30	0.192

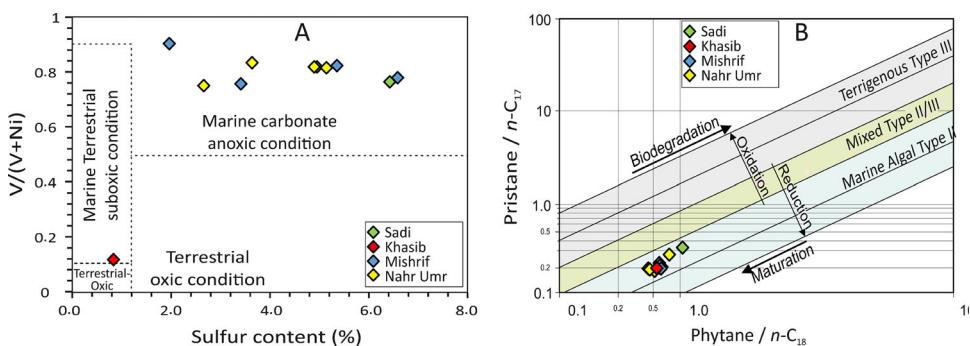


Figure 2. (A) Cross plot of $V/(V + Ni)$ versus sulfur concentrations indicate marine carbonate, anoxic condition. (B) Plot of $pr/n\text{-C}_{17}$ vs. $ph/n\text{-C}_{18}$ from whole-oil chromatograms for oils analyzed indicate non-biodegradation oils, and anoxic condition, marine organic matter type II in the source rock depositional environment (Peters et al., 1999) in Peters, Walters, and Moldowan (2005).

to techniques including gas chromatography (GC) and gas chromatography—mass spectrometry (GC/Ms), and stable carbon isotope analysis at GeoMark Research, Texas, USA (Tables 1 and 2).

3. Results and discussions

3.1. Crude oils bulk properties

The bulk chemical parameters of the Khasib and Nahr Umr reservoir crude oils are slightly different from those of the Mishrif and Sa'di oils. As the API gravities can be used as a crude indicator of thermal maturity as suggested by (Hunt 1996), the Khasib and Nahr Umr oils have higher API gravity up to (52.8 and 48.3) respectively, lowest sulfur content (0.63 and 2), and ppm Ni metals (15 and 15) respectively, than the Mishrif and Sa'di formations oils. High sulfur content values suggest that these oils were derived from type II-S kerogen. The Ni and V metals are usually associated with heavy polar NSO fractions of crude oils (Table 1) (Hunt 1996). The wide range of the Ni and V trace elements values and high ratios of $V/(V + Ni)$ of Mishrif and Sa'di oils, associated with high sulfur content, suggest anoxic environment conditions (Tissot and Welte 1984) (Figure 2A). These differences in the characters of the crude oils may be due to differences in their maturity. According to (Tissot and Welte 1984) the fractionations of the analyzed oils include hydrocarbons and non-hydrocarbons, were classified as non-biodegraded and are an aromatic intermediate oil

The n -alkanes and acyclic isoprenoids are less resistant to biodegradation than steranes and terpanes (Peters, Walters, and Moldowan 2005). All studied samples were found to be non-biodegraded as indicated by the high abundance of low-weight molecular n -alkanes, low value of pristane/ $n\text{-C}_{17}$, phytane/ $n\text{-C}_{18}$ ratios, shows that all samples are non-biodegraded,

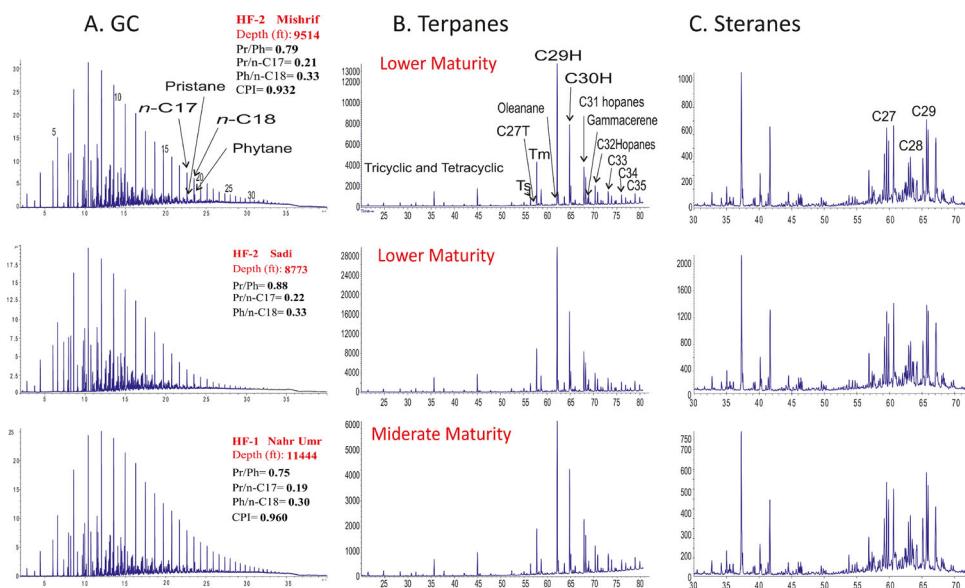


Figure 3. Representative chromatograms of; (A) *n*-alkanes, (B) tricyclic terpanes and pentacyclic terpanes, (C) steranes for the oil analyzed samples from Halfaya Oilfield.

anoxic marine algae kerogen type II-s source, and confirmed by the shape of the gas chromatogram of the samples (Figure 3A).

3.2. Source rocks depositional environment and source rock lithology

Biomarker analyses (terpane, Figure 3B, and steranes Figure 3C), and stable carbon isotope ratios are usually used to describe lithology, type of organic matter, geologic age, redox conditions characteristics of the source rock (Peters, Walters, and Moldowan 2005). The oil samples show high sulfur content (3.74 ± 1 wt.%) with the exception of the Khasib sample of (0.6 wt%), $\text{Ph}/n\text{C}_{18}$ (0.37 ± 0.05), $\text{C}_{22}/\text{C}_{21}$ (1.02 ± 0.05) (Figure 4A), $\text{C}_{29}/\text{C}_{30}$ hopane (1.67 ± 0.13) ratio (Figure 4B) and low $\text{C}_{19}/\text{C}_{23}$ (0.18 ± 0.4), $\text{C}_{24}/\text{C}_{23}$ (0.27 ± 0.03), and $\text{C}_{26}/\text{C}_{25}$ tricyclic terpane (0.77 ± 0.03) ratios (Figure 4C). These values are indicative of marine carbonate deposition. Likewise, the high $\text{C}_{31}\text{R}/\text{H}$ ratio (0.35 ± 0.01) is also consistent with carbonate deposition. High $\text{C}_{29}/\text{C}_{30}$ hopane (>0.6) combined with high $\text{C}_{35}\text{S}/\text{C}_{34}\text{S}$ hopanes (>0.8) for all samples support the notion of marine carbonate source rocks (Figure 4D; Peters, Walters, and Moldowan 2005). The dibenzothiophene/phenanthrene (DBT/P) ratio (>1) is typical of carbonate lithology. Accordingly, we note that the DBT/P ratio is (2.96 ± 0.9) for the Mishrif and Sa'di oils, which confirms that the source rocks are carbonates, while the Nahr Umr and Khasib oils have a value (1.62 and 1.53), respectively, which indicates carbonate intermediate with shale source rocks.

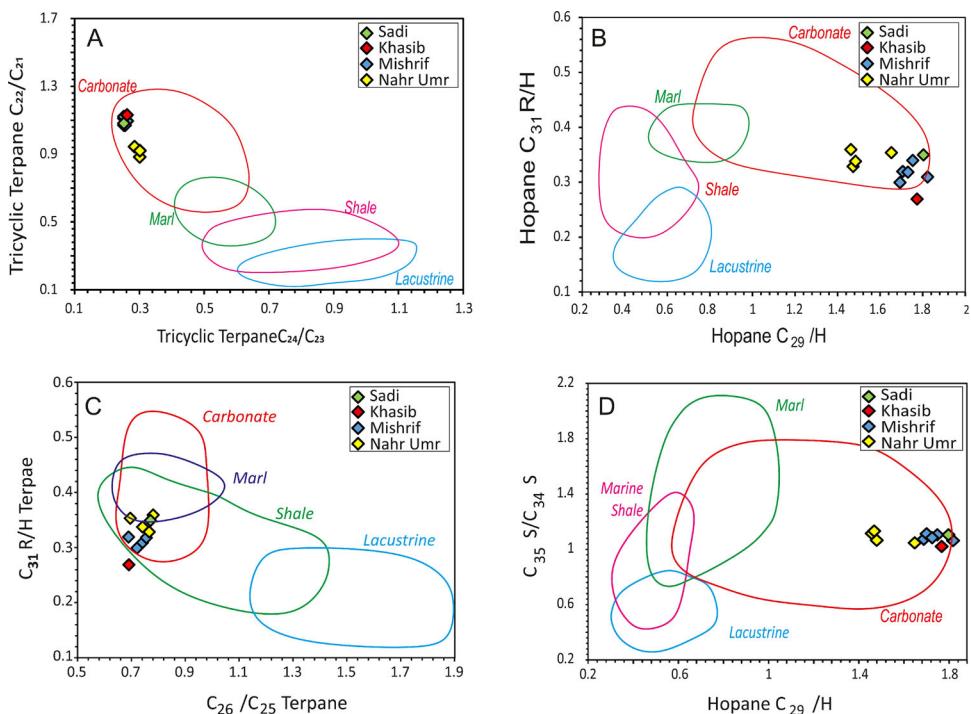


Figure 4. Various biomarker parameters ratios for the Halfaya oilfield indicate carbonate source rock lithology (Peters, Walters, and Moldowan 2005).

The low pristane/phytane ratio of (0.9 ± 0.05) , $\text{Pr}/n\text{C}_{17}$ (0.15 ± 0.01) , $\text{Ph}/n\text{C}_{18}$ (0.37 ± 0.05) (Figure 2B) and the high $\text{C}_{35}\text{S}/\text{C}_{34}\text{S}$ (1.06 ± 0.01) ratio, and $\text{GA}/\text{C}_{31}\text{R}$ ratios (Figure 5A), higher sulfur content (2.74 to 4.96) (Figure 5B), and higher C_{29}/H ratio (1.67 ± 0.21) , are consistent with anoxic marine carbonate source rocks. These show that Nahr Umr oils are slightly more oxic condition than other oils. The $\text{CPI} \sim 1$, are also consistent with a more reducing carbonate depositional environment, and the predominance of marine input. High concentrations of BNH is typical of a source rocks that was deposited under anoxic conditions. High BNH/H ratios for all the analyzed samples are consistent with an anoxic carbonate source, dominated by pelagic organic matter with little plant input (Peters, Walters, and Moldowan 2005).

The oil samples in general, show low $\text{C}_{19}/\text{C}_{23}$ and Ol/H ratios which indicate relatively low higher plant input and angiosperm. The $\text{C}_{19}/\text{C}_{23}$ via Ol/H ratios, on the (Figure 6A, B), showed that Nahr Umr oils are slightly different from other oils, with average of (0.22 versus 0.11) and (0.001 versus 0.004), respectively. This difference indicates a slight variation in higher plant input during the source rock deposition or may be due to their maturation. The canonical variable (CV) from stable carbon isotope measurements of crude oils is considered as the best parameter to distinguish between marine and lacustrine crude oil in combination with other

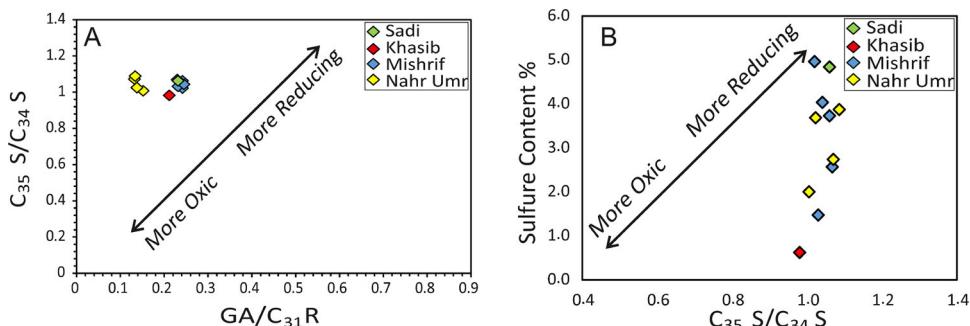


Figure 5. (A) C_{35}/C_{34} homohopanes versus Gammacerane index indicates anoxic source rock depositional conditions. (B) Wt% sulfur content versus C_{35} homohopane index indicates anoxic depositional environment for source rock of the Halfaya oilfield.

parameters, such as $C_{31}R/C_{30}$ hopane, and C_{26}/C_{25} tricyclic terpanes. The canonical variable values of Nahr Umr oil via other oils are different average (-3.26‰ versus -2.85‰). This suggests a more marine character of the depositional environment (Sofer 1984). The isotopes ($\delta^{13}\text{C}_{\text{sat.}}$, $\delta^{13}\text{C}_{\text{aro.}}$) are also considered as source rock parameters, and are not significantly affected by biodegradation, migration, and thermal maturation (Peters, Walters, and Moldowan 2005). The $\delta^{13}\text{C}_{\text{sat.}}$ ($27.79 \pm 0.30\text{‰}$), $\delta^{13}\text{C}_{\text{aro.}}$ and ($-27.70 \pm 0.05\text{‰}$) values, of the oil samples from Halfaya Oilfield are consistent with a marine carbonate depositional environment and Upper Jurassic source rocks (Figure 7A; Al-Khafaji, Sadooni, et al. 2019).

3.3. Age-related geochemical parameters

Three biomarkers and carbon isotope parameters were used to identify the age of source rocks for the studied oil samples. Oleanane is a biomarker from the Cretaceous or younger age terrigenous sediment with higher plants. All the studied samples lacked oleanane (OL/H ratio from 0 to 0.01) which is considered as indication of Jurassic marine source rock. The C_{28}/C_{29} sterane ratio for all oils are greater than 0.7. This is consistent with an Upper Jurassic source rock (Peters, Walters, and Moldowan 2005). The variation in the abundance ^{13}C isotopes in the organic materials of source rocks is related mainly to the changes in the depositional environment of the source rocks and the degree of thermal maturation. The stable carbon isotope ratios for all these oil samples are in the range of -27.59 to -28.12 , which are a characteristic of most upper Jurassic to Lower Cretaceous source rocks (Sofer 1984; Al-Khafaji, Al Najm, et al. 2019). The C_{28}/C_{29} sterane ratio (Figure 7B; Peters, Walters, and Moldowan 2005) is the first, and stable carbon isotope values are the second (Figure 7C; Sofer 1984). Figure 7A corresponds with Figures 7B and C which suggested that the Khasib oil sample origin was from the Upper Jurassic to Lower

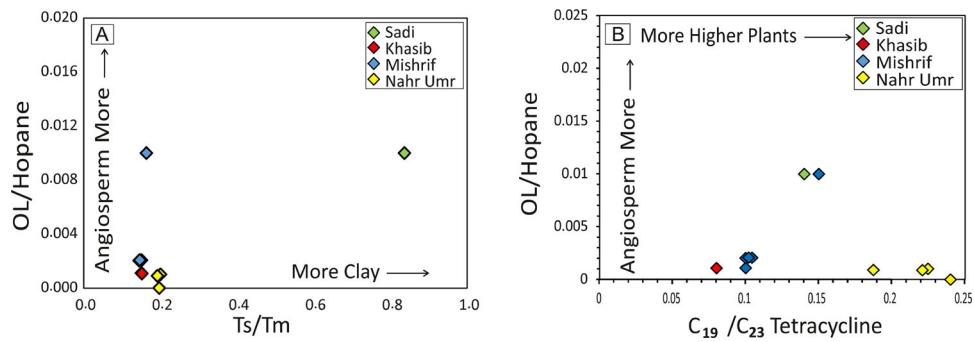


Figure 6. (A) C_{19}/C_{23} tricyclic terpanes versus Ts/Tm suggest that the Sa'di and Nahr Umr oil source elevated more clay. (B). Higher C_{19}/C_{23} tricyclic terpanes versus oleanane/hopane suggest that the Nahr Umr oil sample elevated higher-plant input (Peters, Walters, and Moldowan 2005).

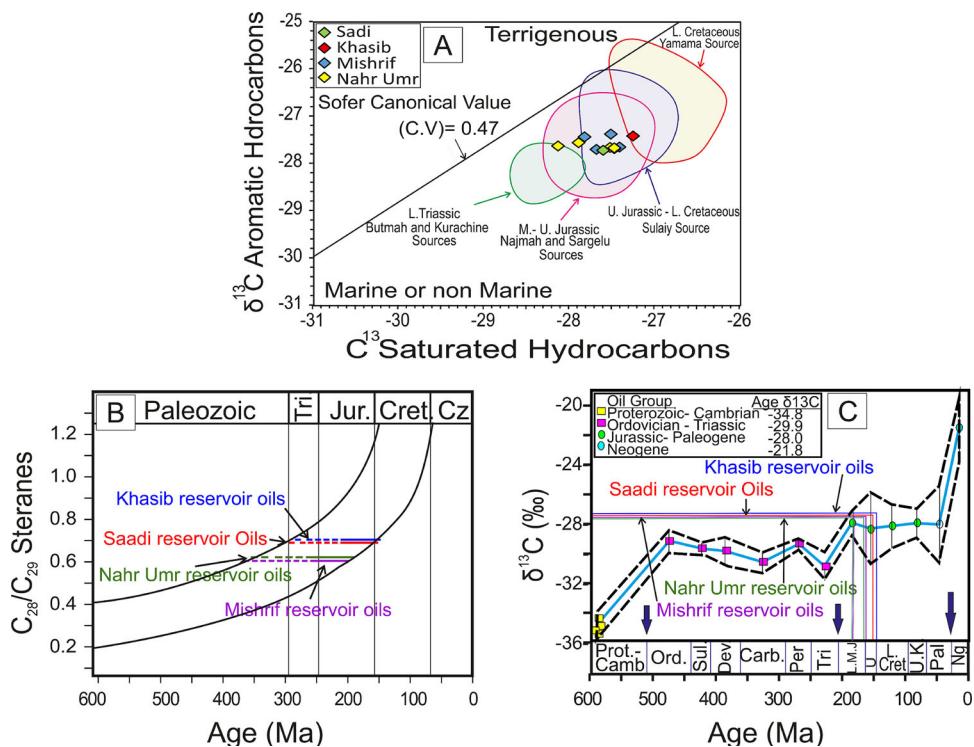


Figure 7. (A) Stable carbon—isotope ratios of saturate and aromatic hydrocarbons indicate marine organic matter. (Sofer 1984). Fields for L. Cretaceous, U. Jurassic and L. Triassic oils are plotted after (Al-Khafaji, Al Najm, et al. 2019b). (B) Average C_{28}/C_{29} sterane ratio (Peters et al., 2008). (C) The average of the stable carbon isotopic ratios (Sofer 1984), shows, the origin of the oil samples source.

Cretaceous Sulaiy and mixed with oils from the Lower Cretaceous Yamama source. Other oil samples originated from the Middle to Upper Jurassic Sargelu source, and these were mixed with oils from the Upper Jurassic to Lower Cretaceous Sulaiy source.

3.4. Thermal maturity

Hopane, sterane and triaromatic steroids ratios are commonly used tools to assess the thermal maturity of oils such as C_{29} sterane $20S/(20S + 20R)$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ stereoisomer, $C_{27}Ts/Tm$, $C_{29}Ts/Tm$, and triaromatic steroids (Peters, Walters, and Moldowan 2005). The maturity level indicators for Nahr Umr and Khasib oils versus Mishrif and Sa'di oils are different. These include $C_{27}Ts/Tm$ (0.23 versus 0.18), $C_{29}Ts/Tm$ (0.08 versus 0.07), C_{29} sterane $20S/(20S + 20R)$ (0.59 versus 0.53) and triaromatic steroids 3 (TAS3) (0.32 versus 0.31). The C_{29} sterane $20S/(20S + 20R)$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ stereoisomer are considered as a sensitive biomarker at high thermal maturity. The C_{29} $20S/R$ ratios of Mishrif and Sa'di oils ranging between 0.45 to 0.69 indicate lower maturity source rocks, while Nahr Umr and Khasib oils have ratios up to 0.75, indicates moderate maturity (Figure 8A). The $Ts/(Ts + Tm)$ ratio is considered as a maturity indicator but affected by lithology and oxygen content of the depositional environment. Because Mishrif and Sa'di oils show similar maturity, variations in the Ts/Tm (0.84 and 0.16 respectively) may indicate differences in the catalytic clay content. Since the triaromatic steroid cracking TAS3(CR) is less dependent on the source organofacies than $Ts/(Ts + Tm)$, thus it is considered as a more universal indicator of maturity (Zumberge, Russell, and Reid 2005). The sulfur-rich Mishrif and Sa'di oils have low TAS3(CR) ratios (0.31 ± 0.1) suggesting a lower thermal maturity.

The C_{27} Ts is a thermally sensitive terpane biomarker due to its high resistance to biodegradation. The average of the C_{27} Ts/Tm ratios of Mishrif and Sa'di oils is 0.18, while Nahr Umr and Khasib is 0.23. This confirms that the Nahr Umr and Khasib reservoir oils may be derived from source rocks whose maturity is higher than the source rocks from which the Mishrif and Sa'di reservoir oils were derived (Figure 8B). Higher API gravities and low sulfur contents are generally associated with thermal maturity and non-biodegraded oils (Tissot and Welte 1984). The API gravity for Mishrif and Sa'di oils varying from 20.1° to 26.1° API, with 1.48%–4.96% sulfur content, while Nahr Umr and Khasib oils the API varying from 30.12° to 52.8° with 0.6%–3.88% sulfur. The differences in sulfur content and API gravity for the oil samples (Figure 8C) can be explained by differences in their thermal maturity. Therefore, the Khasib oil considered as higher maturity, Nahr Umr oil was moderate maturity, while the Mishrif and Sa'di oils were of lower maturity.

The maturation order of the samples of Halfaya Oilfield shows an unusual inverse relationship dependence on depth (Table 1). Reservoir formations schematic diagram of Halfaya Oilfield is shown in Figure 1B. The deepest crudes (Nahr Umr) and the top oils (Khasib) are the higher maturity, rather than Sa'di and Mishrif oils, Figure 6C. The explanation of this

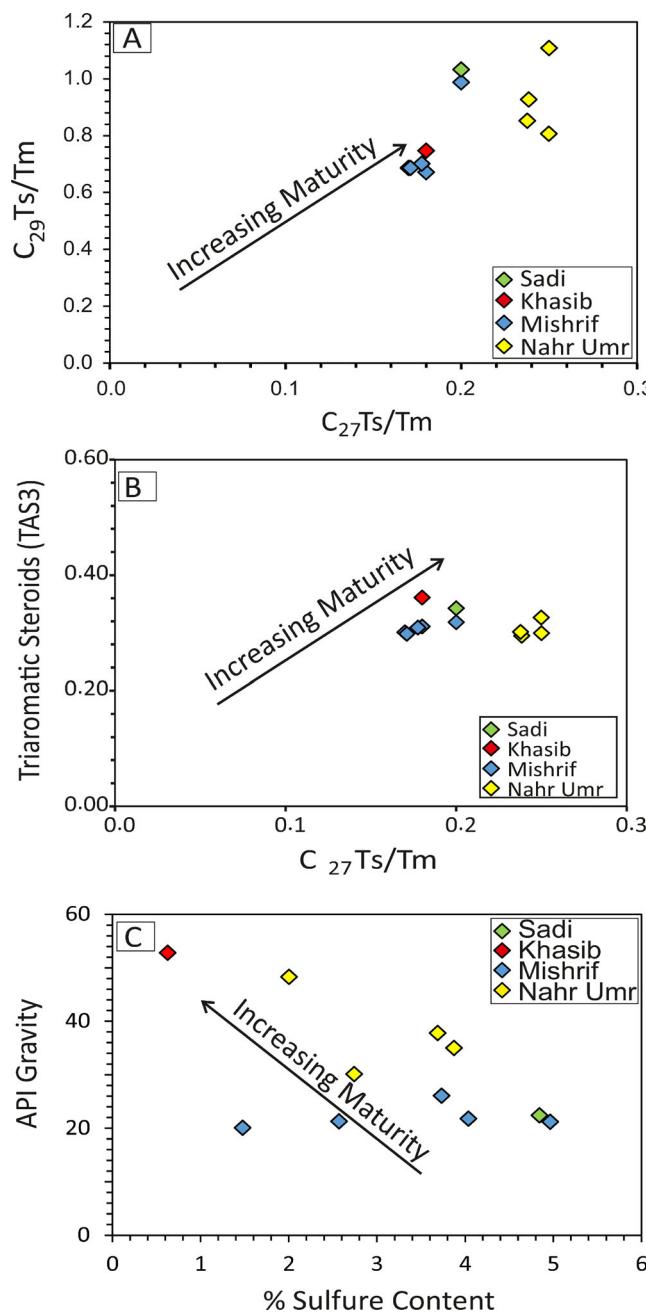


Figure 8. Mishrif and Sa'di oils have similar, low thermal maturity, while Nahr Umr and Khasib oils are moderate maturity based on a plot of $C_{29}Ts/Tm$ versus $C_{27}Ts/Tm$ maturity parameters (A), heavy-end biomarker maturity (B), and average API Gravity versus weight % sulfur content (C).

phenomenon is the Mishrif and Sa'di oils, which may be generated first from less source maturity then having migrated upwards. The Nahr Umr and Khasib oils either formed later from the same source when it became

higher maturity or generated from different source rocks (mixed oils) (Al-Khafaji, Sadooni, et al. 2019; Al-Khafaji, Al Najm, et al. 2019; Al-Khafaji et al. 2021) believes that the Yamama and Zubair source formations have contributed to the generation of oil and its expulsion to Cretaceous reservoirs.

4. Conclusions

The abundance of the *n*-alkanes and acyclic isoprenoids in all samples suggests non-biodegraded oils. Higher sulfur content, Ph/nC₁₈, C₂₂/C₂₁, and C₂₉/C₃₀ hopane ratios associated with lower C₁₉/C₂₃, C₂₄/C₂₃, and C₂₆/C₂₅ tricyclic terpane ratios, indicated that all oils were generated from marine carbonate deposition source. The low pristane/phytane ratio and the high C₃₅S/C₃₄S, GA/C₃₁R ratios for oils are consistent with anoxic depositional condition. The C₂₉ sterane 20S/(20S + 20R) and $\beta\beta/(\beta\beta + \alpha\alpha)$ stereoisomer, Ts/Tm, C₂₇Ts/Tm, C₂₉Ts/Tm, and TAS3(CR), ratios indicated that maturity level of Nahr Umr and Khasib oils were higher than Mishrif and Sa'di oils, maybe due to difference in their source related genetic. The slight variations in C₁₉/C₂₃ and Ol/H ratios, canonical variable (CV) values combination with C₃₁R/C₃₀ hopane, and C₂₆/C₂₅ tricyclic terpanes ratios maybe due to difference in the source rocks which were generated and expelled oils to reservoirs.

The main source rocks that generated the oils in the South Mesopotamian Basin are the Middle Jurassic Sargelu and Upper Jurassic Najmah formations (Pitman, Steinhouer, and Lewan 2004; Al-Ameri et al. 2014; Al-Ameri, Al-Marsoumi, and Al-Musawi 2015; Abeed, Alkhafaji, and Littke 2011; Al-Khafaji et al. 2021). In addition, some recent studies (e.g., Al-Khafaji, Sadooni, et al. 2019; Al-Khafaji, Al Najm, et al. 2019), confirmed that the Yamama and Zubair source rocks also contributed to the expulsion of oil to the Cretaceous reservoirs.

The analyses of oil of this study suggested that the Khasib oil source rocks' origin appears to be formed at the latest age than the rest of the oil samples, which were maybe mixed oils, originated from many source rocks.

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ORCID

Amer Jassim Al-Khafaji  <http://orcid.org/0000-0001-8489-394X>

Rafid N. Al Ibrahim  <http://orcid.org/0000-0002-7410-0149>

Fadhil Sadooni  <http://orcid.org/0000-0001-5027-0648>

References

Abeed, Q., A. Alkhafaji, and R. Littke. 2011. Source rock potential of the upper Jurassic–Lower Cretaceous succession in the southern Mesopotamian basin, southern Iraq. *Journal of Petroleum Geology* 34 (2):117–34. doi:[10.1111/j.1747-5457.2011.00497.x](https://doi.org/10.1111/j.1747-5457.2011.00497.x).

Abdula, R. A. 2020. Crude oil classification based on age and provenance from the Southern Iraq: A review. *Bulletin of the Geological Society of Malaysia* 70 (1):87–102. doi:[10.7186/bgsm70202007](https://doi.org/10.7186/bgsm70202007).

Al-Ameri, T., S. W. Al-Marsoumi, and F. A. Al-Musawi. 2015. Crude oil characterization, molecular affinity, and migration pathways of Halfaya oil field in Mesan Governorate, South Iraq. *Arabian Journal of Geosciences* 8 (9):7041–58. doi:[10.1007/s12517-014-1733-z](https://doi.org/10.1007/s12517-014-1733-z).

Al-Ameri, T. K., A. A. Najaf, A. S. Al-Khafaji, J. Zumberge, and J. Pitman. 2014. Hydrocarbon potential of the Sargelu formation, North Iraq. *Arabian Journal of Geosciences* 7 (3):987–1000. doi:[10.1007/s12517-013-0875-8](https://doi.org/10.1007/s12517-013-0875-8).

Al-Khafaji, A. J. 2015. The Mishrif, Yamama, and Nahr Umr reservoirs petroleum system analysis, Nasiriyah oilfield, Southern Iraq. *Arabian Journal of Geosciences* 8 (2):781–98. doi:[10.1007/s12517-014-1277-2](https://doi.org/10.1007/s12517-014-1277-2).

Al-Khafaji, A. J., F. M. Al Najm, R. N. Al Ibrahim, and F. N. Sadooni. 2019. Geochemical investigation of Yamama crude oils and their inferred source rocks in the Mesopotamian Basin, Southern Iraq. *Petroleum Science and Technology* 37 (18):2025–33. doi:[10.1080/10916466.2019.1578801](https://doi.org/10.1080/10916466.2019.1578801).

Al-Khafaji, A. J., F. N. Sadooni, and M. H. Hindi. 2019. Contribution of the Zubair source rocks to the generation and expulsion of oil to the reservoirs of the Mesopotamian Basin, Southern Iraq. *Petroleum Science and Technology* 37 (8):940–9. doi:[10.1080/10916466.2019.1575869](https://doi.org/10.1080/10916466.2019.1575869).

Al-Khafaji, A. J., M. H. Hakimi, and A. A. Najaf. 2018. Organic geochemistry characterisation of crude oils from Mishrif reservoir rocks in the southern Mesopotamian Basin, South Iraq: Implication for source input and paleoenvironmental conditions. *Egyptian Journal of Petroleum* 27 (1):117–30. doi:[10.1016/j.ejpe.2017.02.001](https://doi.org/10.1016/j.ejpe.2017.02.001).

Al-Khafaji, A. J., M. H. Hakimi, I. M. J. Mohialdeen, R. M. Idan, W. E. Afify, and A. A. Lashin. 2021. Geochemical characteristics of crude oils and basin modelling of the probable source rocks in the Southern Mesopotamian Basin, South Iraq. *Journal of Petroleum Science and Engineering* 196:107641. doi:[10.1016/j.petrol.2020.107641](https://doi.org/10.1016/j.petrol.2020.107641).

Aqrabi, A., J. Goff, A. Horbury, and F. Sadooni. 2010. *The petroleum geology of Iraq*, 424. Beaconsfield, UK: Scientific Press Ltd.

Hunt, J. M. 1996. *Petroleum geochemistry and geology*, 743. New York, NY: W.H. Freeman and Company.

Peters, C. C., Walters, and J. M. Moldowan. 2005. *The biomarker guide: Biomarkers and isotopes in petroleum exploration and earth history*, 2nd ed., vol. 2. Cambridge, UK: Cambridge University Press.

Pitman, J. K., D. Steinhouer, and M. D. Lewan. 2004. Petroleum generation and migration in the Mesopotamian Basin and Zagros Fold Belt of Iraq: Results from a basin modelling study. *GeoArabia* 9:41–72.

Sadooni, F. N., and A. A. M. Aqrabi. 2000. Cretaceous sequence stratigraphy and petroleum potential of the Mesopotamian Basin, Iraq. Special Publication Society for Sedimentary Geology, vol. 69, 315–34.

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., and D. H. Welte. 1984. *Petroleum formation and occurrence*. 2nd ed., 699. Berlin, Heidelberg: Springer Verlag.

Zumberge, J. E., J. A. Russell, and S. A. Reid. 2005. Charging to Elk Hills reservoirs as 1495 determined by oil geochemistry. *AAPG Bulletin* 89 (10):1347–71. doi:10.1306/05100504003.