Arab J Geosci (2016) 9:391
DOI 10.1007/s12517-016-2397-7

ORIGINAL PAPER

Geochemical correlation of oil and source rocks from selected exploratory wells within Northern Mesopotamian basin, Iraq

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Received: 10 December 2014 / Accepted: 26 February 2016

Abstract Geochemical exploration processes were applied to characterize, analyze, identify, and correlate, 11 crude oils and five source rock samples (core and cuttings), which were recovered from oil exploratory wells within the Mesopotamian basin; this basin is considered as one of the most formative, potential, and promising basin in the Middle East. Remarkable total organic carbon (TOC) identifies good source rocks encountered from Upper and Middle Jurassic deep wells and also extracts from Upper Cretaceous Shiranish formations. Two main families recognized (family A) subsidy to subfamily (a) and subfamily (b), generated by different source rock types, and different ages has been established on the basis of biomarker. This family was generated by marine carbonate–intrashelf subbasin source rocks, occurring in Jurassic–Cretaceous–Neogene reservoir rocks in both Zagros Fold Belt and Mesopotamian basin which are geochemically similar to the extracts from the Middle–Upper Jurassic age (Sargelu and Naokelekan Formations), yielding the majority of petroleum oil and gas fields in Iraq. (Family B) of the Upper Triassic Kurra Chine Formation, shallow marine–lagoonal environment, Upper Cretaceous Shiranish formation. Shale beds of the Middle Jurassic Sargelu formations are the major sources of oil in Iraq; these strata were deposited in euxinic marine environment, and most of rock sample are highly mature, with TOC attaining 16.20 wt% and average hydrogen index (HI) of 499 with relatively low values of oxygen index (OI) and maximum temperature (T_{max}) 446.

Keywords Correlation · Source rocks · Isotopes · Family · Gas chromatography

Introduction

The undertaken study is an aid to resolve so many problems on determining the source of oil in various oil fields of north part of Iraq and may establish adequate, reliable data base for organic geochemical correlation between north and south part of Iraq, preparing and establishing fundamental, basic, and complementary geochemical fashion for the whole Iraqi regions (Fig. 1).

Triassic source rocks are relatively poorly studied in Iraq. Thin shale beds occur in the Upper Triassic Kurra Chine Formation in eastern Syria and have sourced light oils and condensates as well as heavy oils trapped in Triassic carbonate reservoirs depending on the level of maturation reached (Serreya, 1990). Source rocks in the Triassic of Syria are also recognized in the Lower Triassic (Amanus Shale) Abboud et al 2005. The Amanus source layer is 19–50 m thick with an average total organic carbon (TOC) of 3.9 wt% TOC Abboud et al 2005. The calculated maturity for the Upper Triassic source level is shown in Fig. 2.

Triassic source rocks are probably in the oil window in the Sinjar basin in N Iraq and in the Jezira Subzone with higher levels of maturation in the Tayarat and Anah graben (Jassim and Goff 2006). Assessment and correlation with the surrounding countries also contribute in setting up a complementary fashion according to geochemical properties. The initial

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Fig. 1 Studied area within Zagros Fold Belt and locations of oil and gas fields (Pitman et al. 2004)

assessment leads to conclude that there are actually two oil families: (family A) of the Jurassic age and (family B) of the Triassic age. This important and valuable conclusion could really enable us to set up a comprehensive and exploratory survey and give indication to explore more oil reservoir in all parts of Iraq. Estimations may lead also to the discovery of super giant natural gas fields in the western desert of the stable shelf sourced to Paleozoic period.

It is of a great interest to declare that the approaches for setting up comprehensive scenario for more identification and descriptions of the Jurassic rocks in Iraq are currently obvious. Samples were virtually sent to American laboratories for various analyses. The purpose of the current study is to evaluate the geochemical characteristics of the Triassic, Jurassic, and Cretaceous oils in the Mesopotamian basin and to correlate the oils with source rocks in this region.

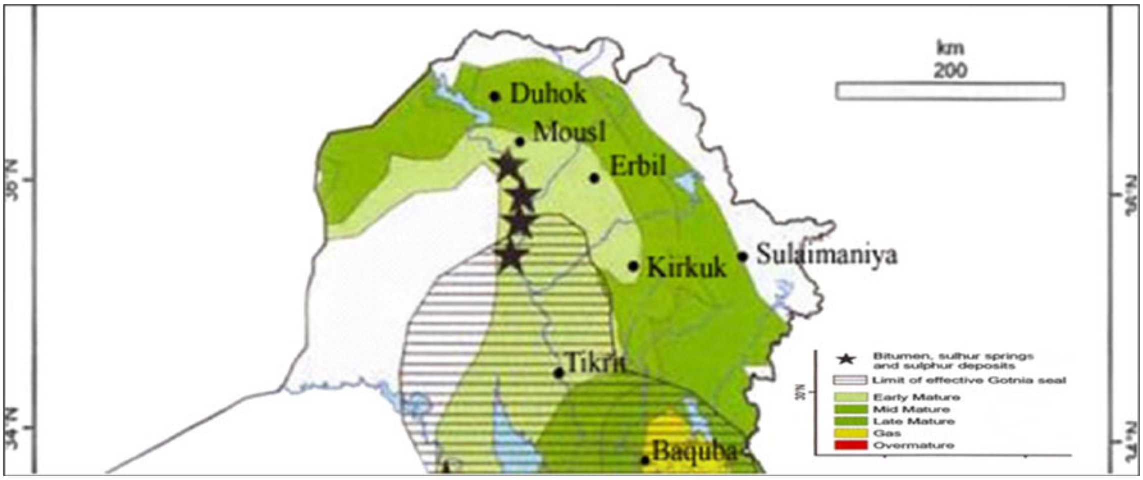

Fig. 2 Mature zones within the study area (Jassim and Goff 2006)

Geologic setting

In particular, Jurassic geologic conditions and sequences (Fig. 3) of the Arabian subcontinent resulted in deposition of the following ideal sequence of facies in Cretaceous and Neogene rock units and excellent seals, which could ultimately accumulate one of oil primary petroleum system elements (thick oil-prone source rocks), 100–200 m in north Iraq; meanwhile in the southern part, the thickness attained to more than 300 m. In the latest Toarcian time, renewed differential subsidence occurred in the Mesopotamian basin in Iraq and southwest Iran with the onset of deposition of euxinic marine carbonate source rocks. Passive margin condition along the Arabian plate during the Jurassic through the late Cretaceous periods produced a broad stable shelf environment. Flooding of this platform in warm equatorial latitudes allowed for continued deposition of shallow-marine carbonates over the greater Arabian basin (Seifert and Moldowan 1980; AL-Husseini, 1997). In particular, Jurassic geologic condition of the Arabian subcontinent resulted in deposition of the following ideal sequence of primary petroleum system elements thick oil-prone source rocks, extensive reservoir facies, and excellent seals, with secondary elements, widespread Early and Middle Jurassic marine transgression deposited a thick sequence of shallow-marine shelf carbonates and plat from evaporites. Late Jurassic differential subsidence and sea level rise resulted in the formation of broad, intrashelf subbasins, and these intrashelf subbasins were depocenters for the main Jurassic rocks (Upper Jurassic) (Pitman et al. 2004).

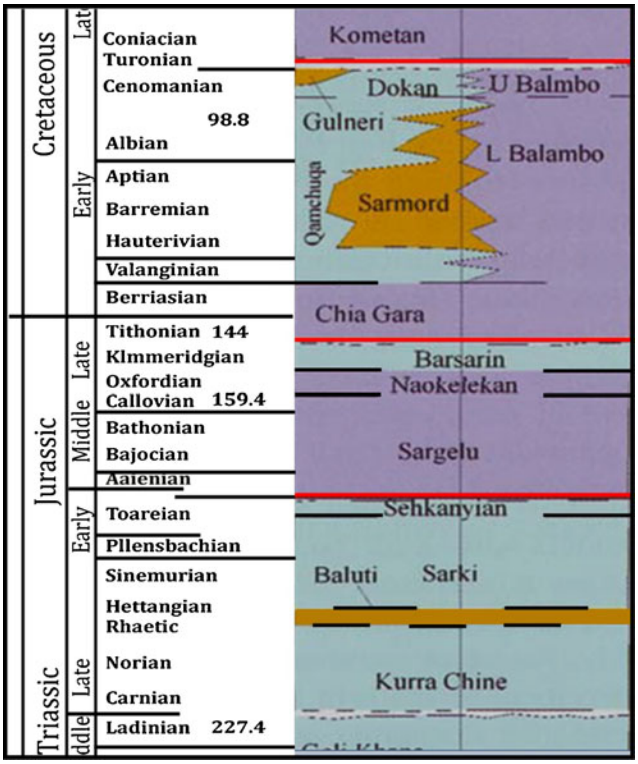

Fig. 3 Stratigraphic section of the studied area and formations (Jassim and Goff 2006)

Samples and methods

A total of 11 oil samples were collected from both Zagros Fold Belt and Mesopotamian basin (Table 1) and five rock samples also recovered from the same place (Table 2). Initially, the rock samples are crushed and extracted with methanol and methylene dichloride. The rock extracts and crude oils were treated to remove asphaltenes by precipitation with *n*-pentane, and the maltenes fractioned by liquid column chromatography (silica gel), using *n*-pentane, methanol, and methylene dichloride into aliphatic hydrocarbons, aromatic hydrocarbons, and NSO components. Silicate column was used for rapid isolation of branched–cyclic alkanes from aliphatic hydrocarbons by elution with *n*-pentane.

Stable carbon isotopic compositions of saturate and aromatic hydrocarbon fractions were determined, and the branched/cyclic fractions were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS).

Pyrolysis data ($S1 + S2$, PI, and $T_{\max}$) were obtained using a pyran level 1-FID system. $S1$ was obtained from the volatilization of liquid hydrocarbons at 300 °C. The thermal cracking of residual organic matter was performed at 300–600 °C with a 25 °C/min temperature gradient and hydrocarbons released as peak $S2$. The production index (PI) is defined as the ratio $S1/(S1 + S2)$. The hydrocarbon index (HI) corresponds to the quantity of pyrolyzable organic compounds from $S2$ relative to the total organic carbon (TOC) in the sample (mg HC/g TOC; (Hunt 1996). The temperature at which the maximum amount of $S2$ hydrocarbons is generated is known as $T_{\max}$. TOC values for the source rocks were determined using a Leco CR-12 carbon determinate.

Biomarker and non-biomarker geochemical parameters are best used together to provide the most reliable geologic interpretations to help solve exploration, development, production, and environmental problems, so the ($S1$) values which represent the free hydrocarbons C-1 to about C-23 thermally librated at 300 °C isotherm. As quantity represents the migrated hydrocarbons of immature sediments, oil and gas show.

The $S2$ represents hydrocarbons cracked from kerogen or from C24+ bitumen's hydrocarbons if buried deeper.

$S1 + S2$ is the total genetic potential in mg Hc/g rock.

It is less than 2 for poor source rock, 2–5 for fair, 5–10 for good, and >10 for very good (3).

The $S1$ values ranging from 0.41 to 2.16 mg Hc/g rock is relatively high; this is caused by no losses of extractable hydrocarbons through primary migration (Hunt, 1995).

$S1/(S1 + S2)$ values ranged from 0.03 to 0.12 indicating that substantial generation and expulsion have taken place.

Table 1 Geochemical characteristics of Iraqi oils

Sample no.	Field	Well name	Formation	Age	Depth (m)	Pr/ph	Pr/NC17	Ph/NC18	NC27/n-C17	PI	Sat/Aro	C29/H
Os-1	Kirkuk	Baba 252	Baba	T	704	1.07	0.29	0.33	0.20	0.962	0.95	1.34
Os-2	Kirkuk	Shurau-1	Shurau	T	2278	1.07	0.29	0.33	0.20	0.952	0.96	1.37
Os-3	Kirkuk	Baba-252	U. Qamchuqa	LK	1609	0.89	0.20	0.27	0.18	0.968	0.7	1.49
Os-4	East Baghdad	EB-31	Tannuma	LK	2343.6	0.85	0.26	0.38	0.17	–	0.4	1.39
Os-5	East Baghdad	Eb-5	Khasib	LK	2409	0.85	0.24	0.34	0.14	–	0.5	1.41
Os-6	Jambour	Ja-18	Jeribe	M. Mio.	–	1.12	0.28	0.31	0.10	1.061	1.3	1.38
Kirkuk Basin and East Baghdad												
Os-7	Kirkuk	Ja-15	L. Qam	LK	726	1.11	0.31	0.33	0.19	0.973	1.3	1.54
Os-8	Ain Zala	Ain Zala-16	Shiranish	UK	1117–1198	0.68	2.89	0.44	2.90			0.82
Os-9	Mushorah	Mushorah-1	Sargelu	MJ	1258–1295	0.66	2.11	0.65	3.80			1.24
Os-10	Butmah	Butmah-2	Shiranish	UK	1470–1475	0.81	2.68	0.45				1.08
Os-11	Butmah	Butmah-2	Shiranish	UK	1475	0.78	2.51	0.40	3.00			1.00

Upper most Iraq Mosul

Os oil sample

Gas chromatography (GC)

Saturate, aromatic, and branched/cyclic fractions were analyzed by GC using Hewlett-Packard 5890GC equipped with a 30 × 0.32-mm I.D. DB-1 fused silica capillary column. Rock extracts were fractionated and analyzed in a similar fashion to the oils. Representative gas chromatograms from the oils and rock extracts are shown in Fig. 4. The GC temperature conditions for whole oils were injector temperature, 310 °C, and column temperature, initially 20 °C for 5 min and programmed at 4 to 310 °C where it was held isothermally for 43 min.

Temperature conditions for the saturate, aromatic, and branched/cyclic fractions were injector temperature, 310 °C, and column temperature, 40 to 310 °C for 1.5 min and programmed at 4 to 310 °C where it was held isothermally for 32 min.

High-temperature (HT) gas chromatography

Whole oils were also analyzed by HTGC using a Carlo Erba-GC 8000 with an on-column injector equipped with a SGE HT-5 fused silica capillary column (25 m × 0.32-mm I.D.) The oven temperature was programmed from 40 to 370 °C at 4 °C/min, with flame ionization detector temperature set at 380 °C (total run time of 120 min).

Gas chromatography–mass spectrometry (GC-MS)

GC-MS analyses were investigated, to determine the distribution of steranes and terpanes (Fig. 5). GC-MS analyses were performed to determine the distribution of steranes and terpanes using a Finnigan TSQ-70 interfaced to a Varian 3340 GC and equipped with a 30 × 0.32-mm I.D. fused silica DB-5MS capillary column. The GC conditions were the following: injector temperature, 310 °C; column temperature, 40 °C for 1.5 min; and programmed at 4 °C/min to 310 °C where it was held isothermally for 31 min. The ion source temperature was 200 °C; electron energy and emission current were −70 eV and 200 μA, respectively.

Oil–source rock correlation is based on the concept that certain compositional parameters of migrated oil do not differ significantly from those of bitumen remaining in the source rocks. This similarity through heritage can range from bulk properties, such as stable carbon isotope composition, to individual compound ratios, such as pristane/phytane (Peters et al.

Table 2 Geochemical characteristics of source rocks

Sample no.	Well name	Depth (m)	Toc	*S*1	*S*2	*S*3	T_{max}	Oil % Ro	HI	OI	PI
Sr-1	Bm-15	2030	2.07	0.42	3.91	0.27	446	0.87	97	45	0.10
Sr-2	Bm-15	2036	1.70	0.41	3.15	0.19	445	0.85	185	11	0.12
Sr-3	Mk-2	2256	16.20	2.16	80.89	0.84	441	0.78	499	5	0.03
Sr-4	Jk-1	2057	1.84	0.92	9.07	0.52	434	0.65	493	28	0.09
Sr-5	Ain Zala-16	2121	1.34	0.20	1.00	0.10	443	0.81		29	0.17

Sr source rock

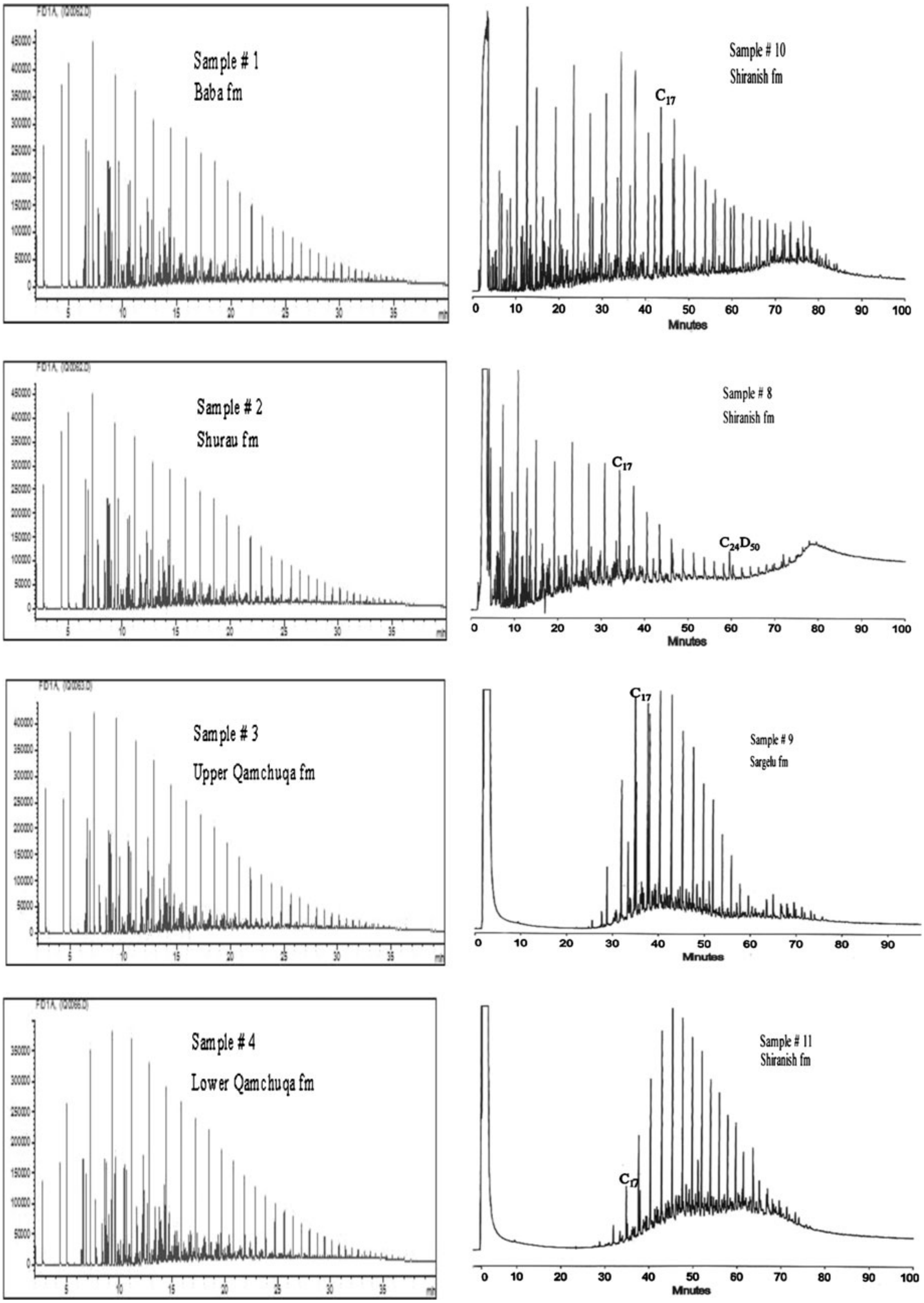

Fig 4 Gas chromatograms for representative oils recovered from the Middle–Upper Jurassic age and Upper Triassic. *First row*: *sample # 1* Baba fm, *sample # 10* Shiranish fm. *Second row*: *sample # 2* Shauran fm, sample # 8, Shiranish fm. *Third row*: *sample # 3* Upper Qamchuqa, *sample # 9* Sargelu fm. *Fourth row*: *sample # 4* Lower Qamchuqa, *sample # 11* Shiranish fm

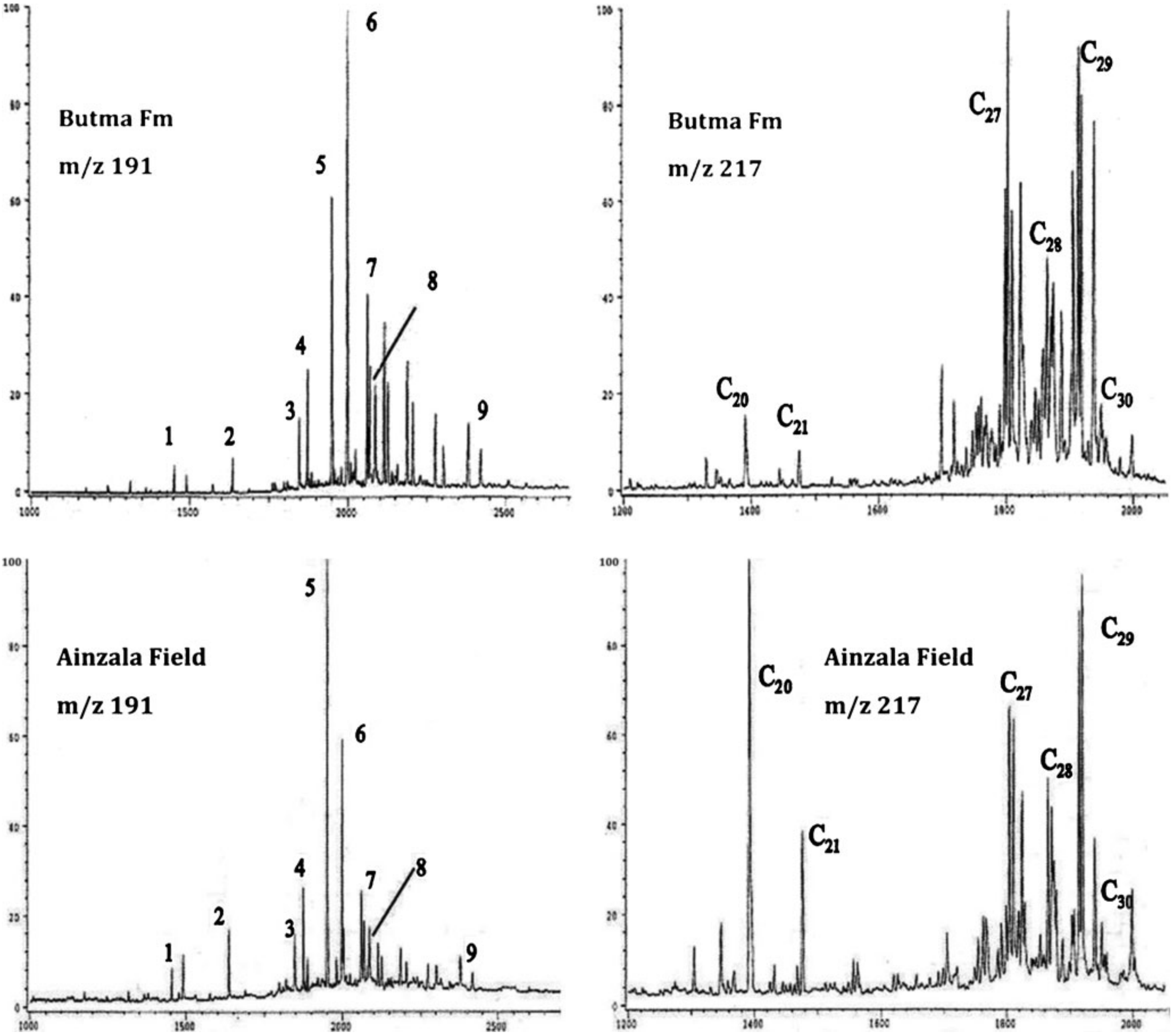

Fig. 5 Terpane (M/Z 191) and sterane (M/Z 217) chromatograms for representative oils

2005). Detailed oil–source rock correlation provides important information on the origin and possible paths of migration of oils that can lead to additional exploration plays.

Geochemical correlation accordingly depends mainly on GC-MS of biomarkers (Siefert et al. 1978; Magoon and Claypool 1981; Mackenzie 1984).

Biomarker correlations of crude oils with each other, and with their source rocks, improve understanding of reservoir relationships, petroleum migration pathways, and possible new exploration plays (Peters et al. 2005) (Figs. 5 and 6).

Results and discussion

Correlations between samples generally become more reliable (Fig. 7)when more parameters are compared. The multiparameter approach and independent measurements of biomarkers like carbon isotope data and other genetic parameters support obvious correlation. The undertaken study is a type of advanced achievements among the kind of the studies performed previously, as the application of this type of comparisons and correlations for the problems arising when the migrated oil is exposed to so many variations while an upward migration changes the main characteristics of the oil, this may lead to misleading in the determination for acute results and serious consequences.

Carbon isotope data

The stable carbon isotopic composition of organic matter is an important tool with which to differentiate algal and land plant source materials and marine source from

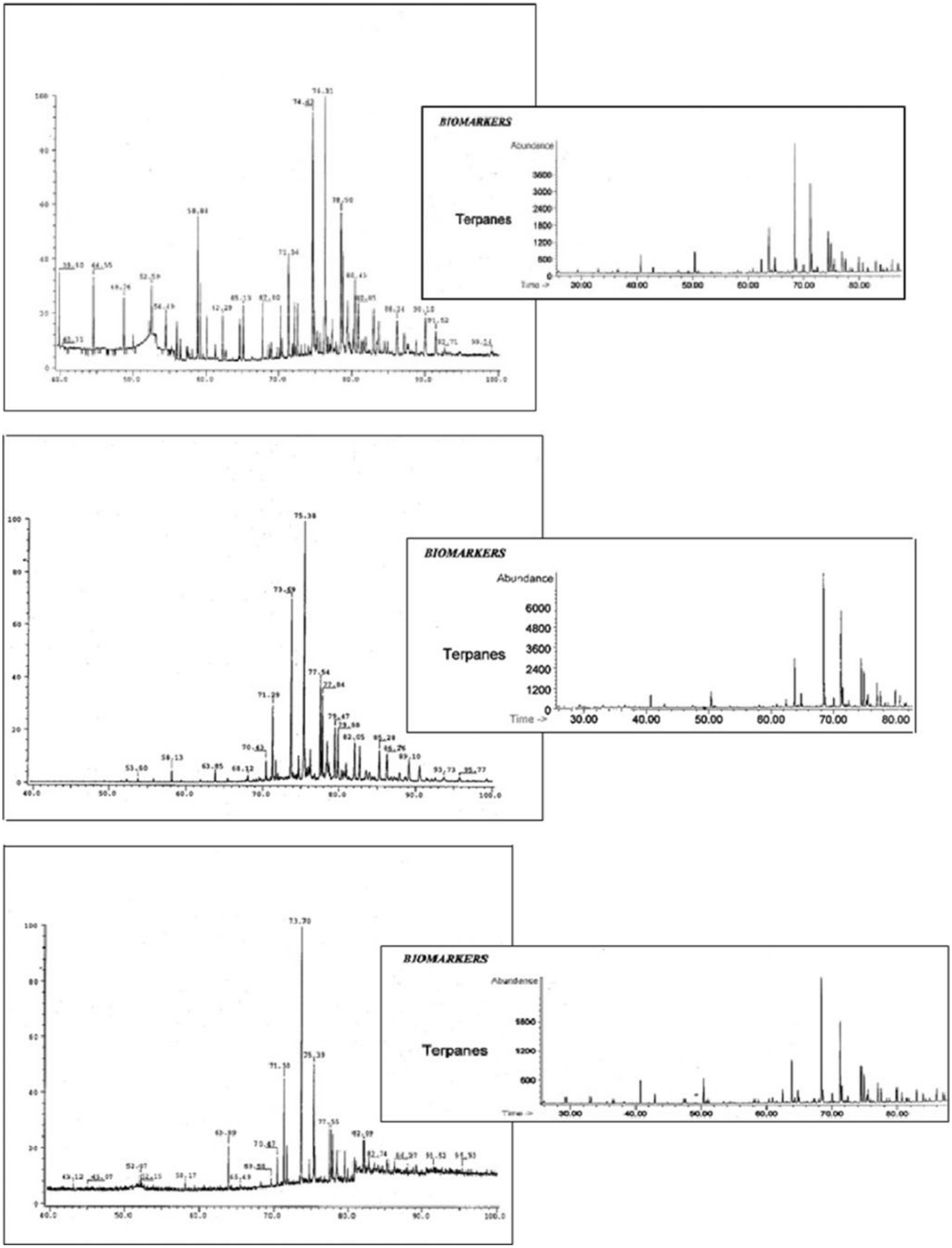

Fig 6 Comparison between oil extracted and crude oil of the Jurassic period

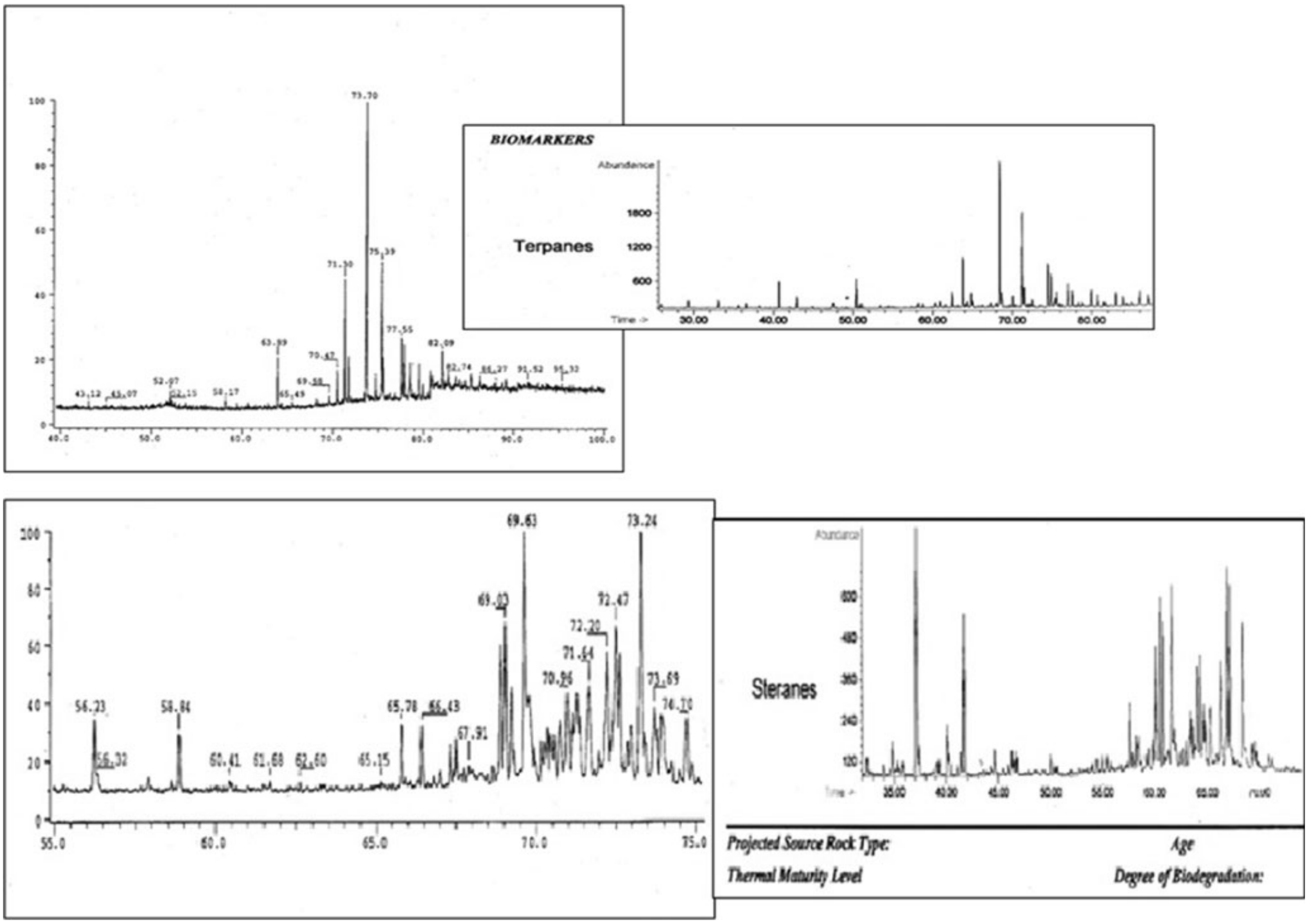

Fig. 6 (continued)

continental depositional environments. Sofer (1984) concluded that the stable carbon isotope values of crude oils are dependent mainly on the depositional environment of the source rock and the degree of thermal maturity at which the oil was expelled. The carbon isotopic signature of bitumen is relatively heavy for predominantly higher plant-sourced oil. Carbon isotope ratio of whole oils by themselves are generally not used for correlation because of the narrow range in δ^{13}C values for all oils of about 15 ‰ (−18 to −33 ‰).

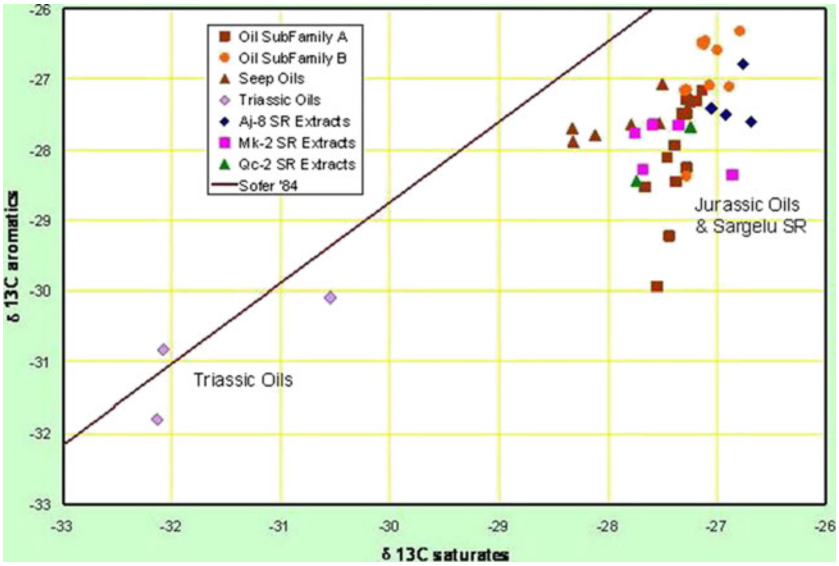

Fig. 7 Stable carbon isotopes of rock samples recovered from the Jurassic age showing obviously the Jurassic and Triassic oils (Al Ahmed 2006)

In fact, most oils are concentrated between −25 and −31 ‰, which causes considerable overlap. Consequently, oil–oil correlation are usually made using cross plots of carbon and hydrogen isotopes or by comparing oil fractions. Burwood et al. (1990) found that the crude oils of Lower Congo Coastal Basin of Angola overlapped in $\delta^{13}C$ values. They separated them into two different genetic groups, however, by using a cross plot of $\delta^{13}C$ versus $\delta^{2}H$ (Hunt 1996). The oils were nicely separated into two groups by plotting $\delta^{13}C$ of the aromatic versus saturated hydrocarbons. Sofer (1984) compared the $\delta^{13}C$ of the C15 + aromatic and saturate fractions of 339 oils and concluded that such plots could be used to distinguish oil families and to infer a marine (non-waxy) versus a terrestrial (waxy) source (Magoon and Claypool 1981).

The isotopic relationship developed by Sofer (1984) is as follows:

For marine source: $\delta^{13}C_{ARO} = 1.10\ \delta^{13}C_{SAT} + 3.75$ (non-waxy oils)

For terrestrial source: $\delta^{13}C_{ARO} = 1.12\ \delta^{13}C_{SAT} + 5.45$ waxy oils

Terrestrial waxy oils are considered to originate from land-derived OM deposited in a lacustrine paralic or deltaic environment, whereas non-waxy oils are from OM deposited in open marine environments with minor contribution of terrestrial OM.

Sofer (1984) carried out a stepwise discriminate analysis excluding biodegraded oils to determine the best straight line separating the two groups. It is

$\delta^{13}C_{ARO} = 1.14\ \delta^{13}C_{SAT} = 5.46$ (Hunt 1996)

So the bulk isotopic compositions of the saturate and aromatic fractions of crude oils have long been used for correlation purposes (Fuex 1977). The results in this study (Table 3) show approximate values between C15 + saturates and C15 + aromatics providing good support. Isotope profiles should be compared between oils that are at about the same maturity level based on biomarkers or other maturity indicators. This is necessary because thermal maturation causes the interpretation of isotope profiles requiring an understanding of not only thermal maturation but also other factors, such as biodegradation and water washing.

Isotopic analysis of sedimentary organic matter

Rock samples that had been powdered in a ball mill for liberation of residual gas were used for elemental analyses and stable isotope ratio determinations. Before analyses, rock powders were treated with 2 N hydrochloric acid at room temperature to decompose carbonates, followed by thorough washing with deionized water and freeze drying. The TOC and total nitrogen contents and isotopic compositions of TOC and total nitrogen in terms of customary $\delta^{13}C$ and $\delta^{15}N$ values in parts per thousand (‰) were determined in continuous flow with an elemental analyzer attached to a Thermo Finnigan Delta Plus XP isotope ratio mass spectrometer (EA-IRMS, Indiana University). Normalizations of isotopic scales were accomplished with international measurement standards NBS 19, L-SVEC, IAEA-N-1, and IAEA-N-2 (Table 3).

Oil–source rock correlation

Although, there are difficulties exposed in this type of correlation compared with oil–oil correlation because many problems are involved in both sampling and interpreting the data. Removing oil from a source rock by conventional extraction results in the loss of hydrocarbons up to the C12–C15 range (Hunt 1996).

Evaporation reservoir oil samples are necessary in the time of comparing the extracts to constant weight at a certain temperature, such as 45 °C (113 F) in order to remove the same range of volatile hydrocarbons. The C2–C15 range can be compared separately using low-temperature heating of the mature source rock and GC-MS analyses of the product and the reservoir oil (Hunt 1996).

The following comparison between the extracted rock-oil fingerprints shows slight variations so the differences in the procedure of extraction might be due to the composition of bitumen which is variable in yielding and may be the main reason that makes this type of correlation difficult (Price and Clayton 1992; Hunt 1996). In addition, a few source rock samples cannot adequately represent oil generated from a thick source interval of varying composition; meanwhile, the

Table 3 Stable carbon isotope composition, units are per mil (‰) PDB

Sample no.	Well name	Field	C15 + saturates	C15 + aromatics
1	Baba-252	Kirkuk	−27.05	−26.74
2	Shurau-1	Kirkuk	−27.00	−26.75
3	Baba-252	Kirkuk	−27.28	−27.38
4	EB-31	East Baghdad	−27.56	−27.87
5	EB-5	East Baghdad	−27.60	−27.83
6	Ja-18	Jambour	−27.30	−27.16
7	Ja-15	Jambour	−27.22	−26.96

analyzed three samples are cuttings and only Makhul-2 is a core sample, and this may also complicate the scene (Hunt 1996). Oil–source rock correlation is based accordingly on the concept that certain compositional parameters of migrated oil do not differ significantly from those of bitumen remaining in the source rock (Peters et al. 2005). There is considerable evidence that indicates that the oil fractionates during the process of leaving the source rock and migrating to the reservoir rock, and the source rocks do not yield oils of the same composition throughout their generation history (Hunt 1996).

The majority of different age source rock samples characterized in the undertaken study with certain chemical and biomarker parameters of oil samples indicate migrating hydrocarbon, with the variety of source rocks that generates hydrocarbon in both middle and northern part of Iraq.

Determination of families A and B

Family A of the Jurassic period with two subfamilies a and b within the studied area according to the data recovered from both rock and oil samples is characterized via geochemical technique assigned by a correlation showing similarity between the extracted oils from core and cutting rocks and the oils itself, which is recovered according to the scenario planned for this reason.

This type of study pointed successful exploration program and enabled to identify the role of the source rocks, Sargelu and Naokelekan formations, and Middle and Upper Jurassic period, respectively (Al-Ahmed and Asker 2006) that gives and refers to wide potentiality in generating oil and gas according to the results of TOC and the relative HC yielded (hydrogen index, oxygen index). The existence of additional rock package belonging to the Triassic period may be considered as family B, extending locally to nearby Mosul and Zakho regions of the uppermost Iraq, frontiers of Syria and Turkey. Planning for more drilling oil exploratory wells within the sequences of the studied area which leads to better identification and understanding that enhanced upstream sector; so the future researches will determine a new horizon of paying zones, but the evidences is not yet available to accomplish the whole scope in almost all parts of the region generally and in Iraq defiantly; thus, the doubts is still intensively focused on the most promising western desert (virgin area) in accumulating thermogenic gases (dry gas).

Acknowledgments I would like to express my sincere appreciation for the cooperation and assistance given to me by the GeoMark Research Inc., Houston, Texas in performing the oil analysis for the undertaken study and the Oklahoma University for helping me in performing rock evaluation pyrolysis and GC-MS for extracting oil in its laboratory in Oklahoma University.

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