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ORIGINAL PAPER

Hydrocarbon potential, thermal maturation of the Jurassic sequences, and the genetic implication for the oil seeps in North Thrust Zone, North Iraq

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Abstract The organic geochemistry is studied for the rocks of three Jurassic formations: Sargelu, Naokelekan, and Chia Gara from the north of Iraq. These rocks comprise bituminous carbonate and shale rocks. The hydrocarbon source rock potential is evaluated by using total organic carbon (TOC) and Rock-Eval Pyrolysis. The prevalence of high values of TOC (2.21–45.12 wt.%) associated with moderate to high values of HI (225–550 mg HC/g TOC), low OI (1–33 CO_2/g TOC), and high S2 values (4.53–181.0) indicate very good to excellent source rock potential for these rocks with mostly type II kerogen and few mixed-type II/III kerogen of oil prone source rocks. This is supported by high values of S2/S3 ratios (>5). Tmax values range from 440 to 447 °C in agreement with the calculated R_o values (0.76–0.90) infer early to peak thermally mature stage. Based on the TOC and pyrolysis data, the rocks of the three formations have indigenous hydrocarbon mature oil prone. The geochemical investigation of biomarker parameters were performed for oil samples from two oil seepages (Banik and Tawke) which are located in the same area using gas chromatography-mass spectrometry and stable carbon isotope measurements. The measured values of Pr/n-C17 for oil samples are low coupled with high values of Ph/n-C18 indicating marine organic matters with type II kerogen accumulated under marine reducing condition. The values and plots of $\delta^{13}C$ (saturate and aromatic) also approve the prevalence of marine reducing condition. The source rocks for the oils of both seepages are interpreted to be carbonate rocks of Mesozoic age by the measured CV values which are <0.47. These oils are characterized by high values of tricyclic terpane C22/C21, low values of C24/C23, C26/C25, and C31R/C30 hopane ratio >0.25. All these data are in consistent with marine carbonate source rocks for these oils. The paleoredox depositional environment for the source rocks is interpreted by the low value of Pr/Ph (0.74 in Banik) and high values of homohopane ratio C35S/C34S (1.21 in Banik and 1.13 in Tawke); the values of C29/C30 (norhopane/hopane >1) as well as the high sulfur content all indicate reducing condition during the deposition of the marine source rocks. The concentrations of C27, C28, and C29 reflect the prevalence of marine algal plankton organic matters. The measured Oleanane index equal zero which indicates age older than Lower Cretaceous for the source rocks. This documented by the calculated values of C28/C29 sterane ratio, and plots on Geomark Research database gives an age of Middle–Upper Jurassic for the source rocks. According to the characteristics of depositional environment of the source rocks, the paleoredox condition, and age estimation, the oils of Banik and Tawke could be derived from the rocks of Sargelu, Naokelekan, and Chia Gara Formations.

Keywords North Thrust Zone · Naokelekan · TOC · Oleanane index · Banik

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Introduction

Oil source rocks are defined as those that have the capability to generate and expel enough hydrocarbons to form an accumulation of oil and/or gas. Organic matter-enriched sedimentary rocks generate hydrocarbon under the effect of pressure and heat with time (Rullkotter 1987). The capacity of the source rock to generate crude oil and natural gas depends on

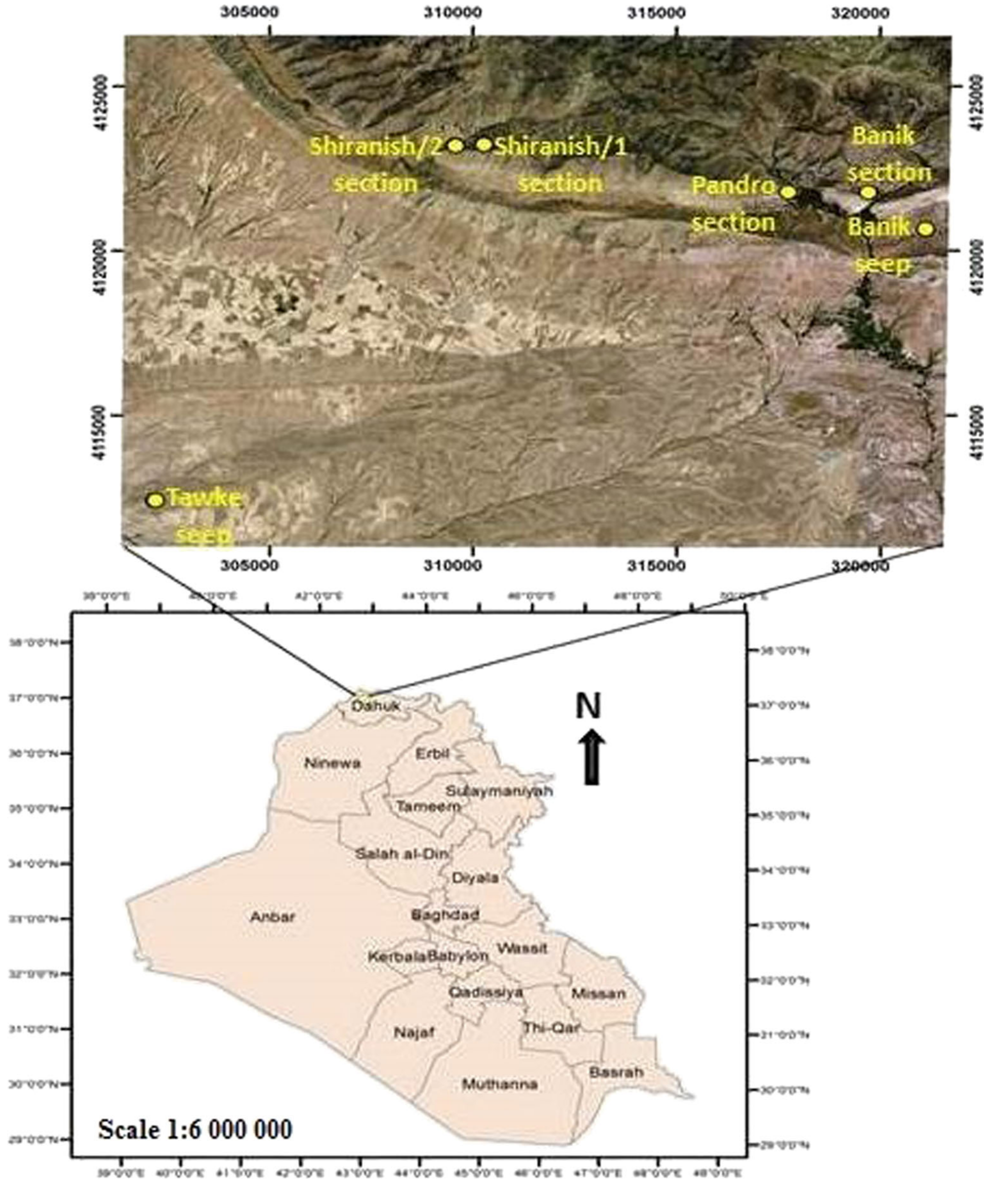


Fig. 1 Location Map of study area spots represent sections and seeps locations

the quantity of total organic carbon (TOC) in the form of kerogen, quality, and thermal maturity of the organic matters (Hunt 1996).

The aim of this study is to determine and offer an appraisal for source rocks petroleum potential and the organic geochemical characteristics for three Jurassic Formations: Sargelu, Naokelekan, and Chia Gara, in north Iraq as well as to study the organic geochemistry of oils from two oil seepages (Banik and Tawke) to verify a correlation between the oils of these seepages and the source rocks.

Regional geology and stratigraphy

Iraq is located between the two major Phanerozoic units of the Middle East that connect the Arabian part of the African platform (Nubio-Arabia) and the Asian part of the Alpine Orogenic Belt. The tectonic configuration and structural patterns of Iraq are the consequence of the tectonic evolution since Pre-Cambrian Orogeny till the latest Alpine Orogeny. According to the geotectonic evolution in the region, Iraq is divided in to three major tectonic zones: (a) the Stable Shelf which is a longitudinal zone trending north–south; (b) the Unstable Shelf that trends NW–SE in northeast Iraq and east–west in north Iraq; and (c) Zagros Suture zone in the extreme northeast part of Iraq (Buday and Jassim 1987; Numan 1997). Buday et al. (1973) designated two different tectonic units for the Unstable Zone which are the Imbricated Zone in northeast Iraq and the North Thrust Zone in north Iraq, with the former corresponding to a trough and the latter to a ridge. From the Late Permian–Middle Cretaceous time,

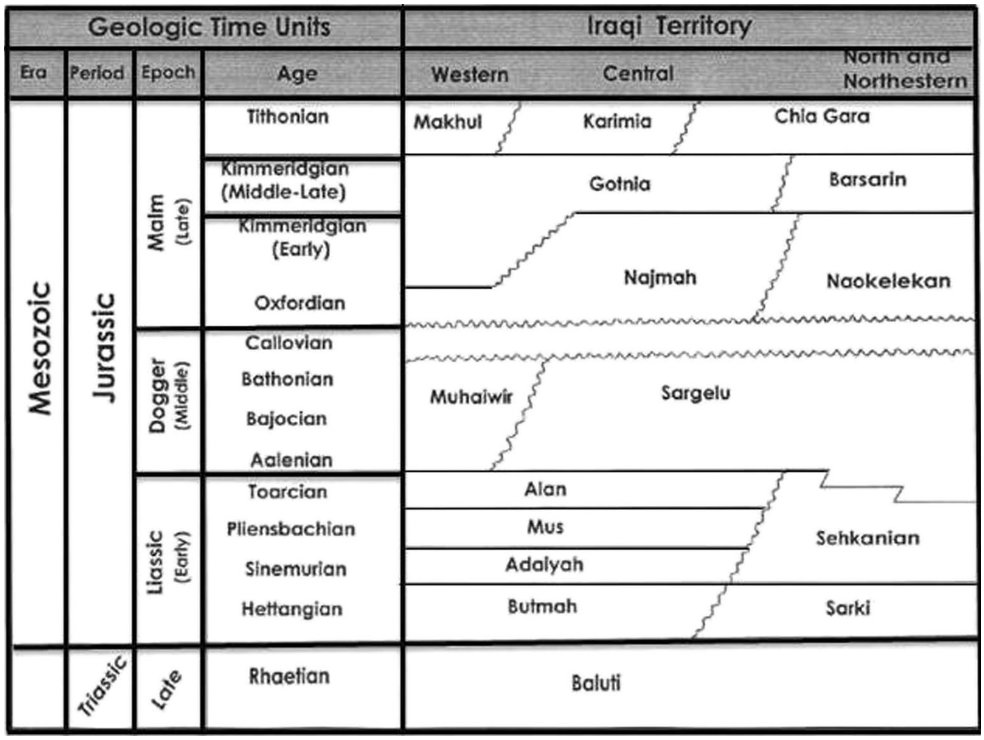


Fig. 2 Geologic column of Jurassic succession in Iraq (modified after Al-Omari and Sadiq 1977)

the northern and eastern Arabian Plate margins were gradually subsiding passive margins along the Neo-Tethys Ocean (Al-Sharhan and Nairn 1997; Sharland et al. 2001, 2004). The Permian subsidence with the origin of the Mesozoic Tethys continued accompanied by sedimentation which was shallow since Triassic as a consequence of the Early Kimmerian movements up to Upper Jurassic where a conspicuous decrease in subsidence occurred evidenced by the facies of Naokelekan and Barsarin. Jassim and Goff (2006) proposed a rifting due to the Middle Triassic–Late Triassic extension occurred around the northern and eastern margins of the Arabian Plate and that this rifting led to the formation of an outer ridge along the northern Thrust Zone accompanied with the deposition of carbonate rocks. The carbonate deposition continued through Jurassic and Early Cretaceous time. The study area and formations are located within this Northern (Tauros Fold-Thrust Belt) which is developed as a result of the collision of the Arabian Plate with the Eurasian Plate and the sedimentary fills of the NeoTethys basin. The northern Thrust is about 15 km wide, with a narrow belt, east–west trending located between Hazil Su Valley in the west and Dirri area in the east along the Turkish frontier. It is characterized by high mountains and overthrusting toward the south. The polyphase sedimentary cycles of carbonate deposition started in Upper Jurassic and ended in Maastrichtian, and then a new carbonate cycle began during the Upper Eocene (Strevanovic and Markovic 2003). The three studied formations (Sargelu, Naokelekan, and Chia Gara) and the tow seepages (Banik and Tawke) are located to the north of Dohuk

Table 1 Results of TOC and Rock-Eval analyses of selected whole rock samples from the three formations

No.	Formation	Sample symbol	TOC Wt. %	S1	S2	S3	Tmax C°
1	Sargelu	BS1/4	9.36	0.41	30.79	1.89	445
2	Sargelu	BS1/12	4.02	0.63	13.60	0.56	443
3	Sargelu	PS1/11	2.21	0.44	5.05	0.54	446
4	Sargelu	PS1/13	17.38	1.50	77.27	0.49	447
5	Sargelu	SS1/6	24.82	1.54	127.02	4.41	442
6	Sargelu	SS1/16	3.99	0.51	17.06	0.39	444
7	Naokelekan	BN1/2	32.66	5.52	147.06	0.42	448
8	Naokelekan	BN1/7	19.73	4.58	97.77	0.23	445
9	Naokelekan	BN1/10	45.12	1.8	123.69	11.69	441
10	Naokelekan	SN1/24	32.32	4.16	177.88	0.53	444
11	Naokelekan	SN1/27	44.39	1.45	175.58	11.52	440
12	Naokelekan	SN1/29	22.38	0.91	99.14	4.15	441
13	Chia Gara	BCH1/2A	33.52	3.92	181.02	0.97	445
14	Chia Gara	BCH1/4A	3.61	1.3	10.18	0.2	447
15	Chia Gara	PCH1/26	8.78	0.64	19.77	2.89	443
16	Chia Gara	PCH1/27	1.69	0.57	4.35	0.35	442
17	Chia Gara	SCH2/1	4	0.96	17.73	0.56	440
18	Chia Gara	SCH2/10	19.23	3.15	85.43	3.19	440

Table 2 Results of calculated parameters of selected whole rock samples from the three formations

No.	Formation	Sample symbol	HI	OI	PI	PP	S2/S3	cal. R_o
1	Sargelu	BS1/4	329	20	0.01	31.2	16.29	0.85
2	Sargelu	BS1/12	338	14	0.04	14.23	24.29	0.81
3	Sargelu	PS1/11	229	24	0.08	5.49	9.35	0.87
4	Sargelu	PS1/13	445	3	0.02	78.77	157.69	0.89
5	Sargelu	SS1/6	512	18	0.01	128.56	20.80	0.80
6	Sargelu	SS1/16	428	10	0.03	17.57	43.74	0.83
7	Naokelekan	BN1/2	450	1	0.04	152.58	350.14	0.90
8	Naokelekan	BN1/7	496	1	0.04	102.35	425.09	0.85
9	Naokelekan	BN1/10	274	26	0.01	125.49	10.58	0.78
10	Naokelekan	SN1/24	550	2	0.02	182.04	335.62	0.83
11	Naokelekan	SN1/27	396	26	0.01	177.03	15.24	0.76
12	Naokelekan	SN1/29	443	19	0.1	100.05	23.89	0.78
13	Chia Gara	BCH1/2A	540	3	0.02	184.94	186.62	0.85
14	Chia Gara	BCH1/4A	282	6	0.11	11.48	50.90	0.89
15	Chia Gara	PCH1/26	225	33	0.03	20.41	6.84	0.81
16	Chia Gara	PCH1/27	257	21	0.12	4.92	12.43	0.80
17	Chia Gara	SCH2/1	443	14	0.05	18.69	31.66	0.76
18	Chia Gara	SCH2/10	444	17	0.04	88.58	26.78	0.76

governorate, in the extreme north of Iraq close to the Iraqi–Turkish border (Fig. 1). The four sections which are mapped and sampled from the three formations are Banik, Pandro, Shiranish-1, and Shiranish-2. These sections contain the stratigraphic succession of Jurassic age/ northern Iraq (Fig. 2), starting from older:

1. Sarki and Sehkanian Formations (Early Jurassic).
2. Sargelu Formation (Middle Jurassic).
3. Naokelekan and Barsarin Formations (Late Jurassic).
4. Chia Gara Formation (Late Jurassic–Early Cretaceous).

Sargelu formation

The lithology of this formation is rather uniform consists of thin bedded, black bituminous limestone, dolomitic limestone, and black papery shale with streaks of thin black chert (Bellen et al. 1959; Buday 1980). The thickness is variable ranging from 20 to 125 m in outcrops and higher in subsurface sections of foothill and Mesopotamian Zone ranging from 250 to 500 m (Ditmar and Iraqi-Soviet 1971). The age of the formation is Upper Liassic at the base grading into Bathonian at the top (Bellen et al. 1959). Jassim and Goff (2006) suggest an age of Bajonian–Bathonian and the basal beds could be Late Toarcian. The depositional environment of Sargelu Formation is basinal euxinic marine (Buday 1980).

Naokelekan formation

This formation is exposed near Naokelekan village within the northern Thrust Zone with thickness ranging from 10 to 30 m comprises a succession of laminated argillaceous bituminous limestone alternating with bituminous shale and thin bedded fossiliferous dolomitic limestone, thin bedded highly bituminous dolomitic limestone with black shale (coal horizon). The depositional environment is euxinic marine with age of Upper Oxfordian–Lower Immeridgian (Bellen et al. 1959) and according to Jassim and Goff (2006), the age extends to Callovian.

Chia Gara formation

The type locality is at Chia Gara anticline, south of Amadia town in High Folded Zone, northern part of Iraq. The thickness in the type locality is 230 m but

Table 3 The minimum, maximum, and average values and their interpretations of TOC and Rock-Eval analyses (S1, S2, and Tmax) in the three formations

Formation	Value limit.	TOC Wt.%		S1 mg HC/g rock		S2 mg HC/g rock		Tmax Co	
		Value	Property	Value	Property	Value	Property	Value	Maturity/HC product
Sargelu	Min.	2.21	V. g	0.41	P	5.05	G	442	M/OW
	Max.	24.82	Ex	1.54	G	127.0	Ex	447	M/OW
	Av.	10.29	Ex	0.83	F	45.13	Ex	444.5	M/OW
Naokelekan	Min.	19.73	Ex	0.91	F	97.77	Ex	440	M/OW
	Max.	45.12	Ex	5.52	Ex	177.8	Ex	448	M/OW
	Av.	32.76	Ex	3.07	V. g	136.8	Ex	443.2	M/OW
Chia Gara	Min.	1.69	G	0.57	F	4.53	F	440	M/OW
	Max.	33.52	Ex	3.92	V. g	181.0	Ex	447	M/OW
	Av.	11.80	Ex	1.75	G	53.08	Ex	442.8	M/OW

P poor, *F* fair, *G* good, *V. g* very good, Ex excellent, *M* mature, *OW* oil window

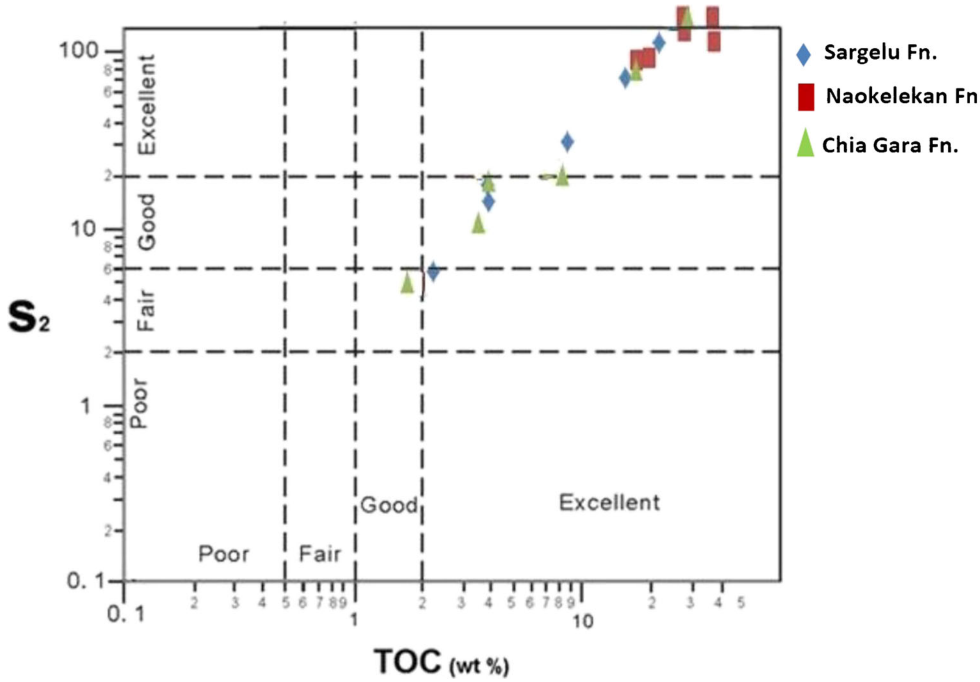


Fig. 3 Potential of source rocks in the three formations depending on S2 versus total organic carbon (TOC) (Hunt 1996)

varies in other localities ranging from 30 to 300 m (Buday 1980). The lithology is uniform consists of thin bedded limestone and calcareous shale. The age of the formation is proposed to be Middle Tithonian–Berriasian (Bellen et al. 1959). Dunnington (1958) described the Tithonian–Barriasian sediments as basinal euxinic radiolarian shale and limestone. Al-Qayim and Saadallah (1992) studied the formation from Bekhma Gorge and Rawanduz areas in north Iraq and concluded that the formation has deep marine characters.

Material and method

The research method comprises two types: the field work and laboratory analysis. Eighteen bulk rock

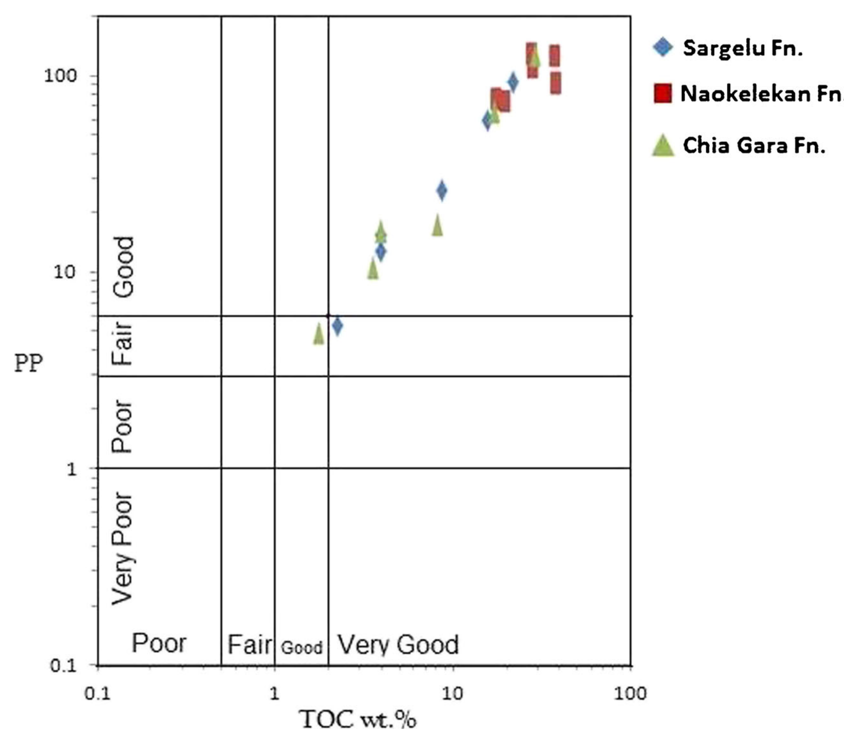


Fig. 4 Potential of source rocks in the three formations depending on petroleum potential (PP) versus total organic carbon (TOC) (modified from Ghori 2002)

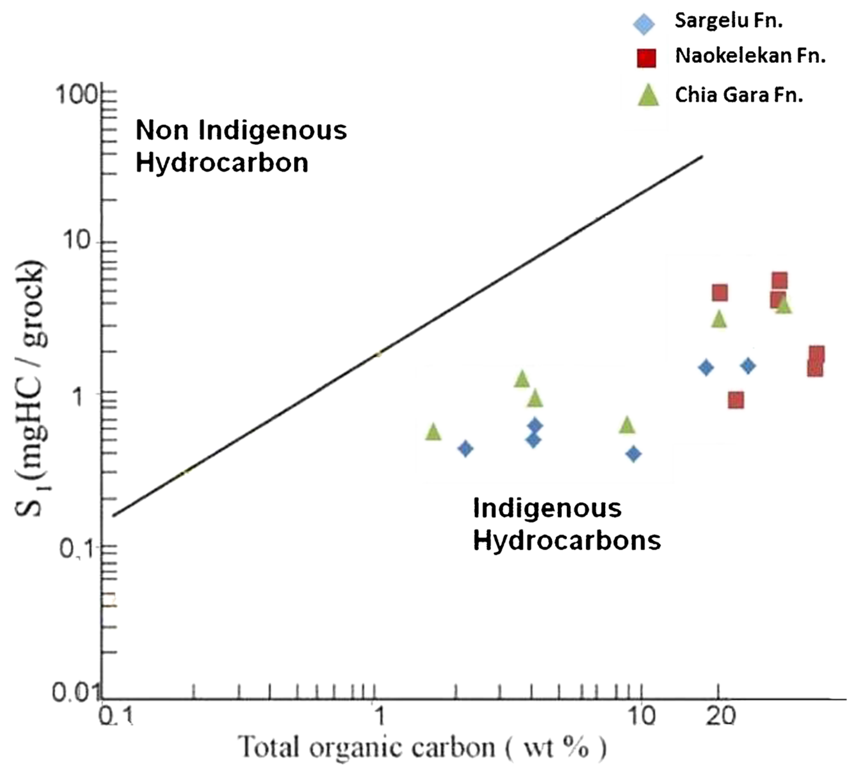


Fig. 5 Migration or contaminant hydrocarbons in the three formations depending on S1 versus total organic carbon (TOC) (Hunt 1996)

samples are chosen from the three formations for total organic carbon (TOC) and Rock-Eval Pyrolysis analysis. The organic geochemical analyses are carried out in the Laboratory of Oil Research Center, Ankara/Turkey, for bulk samples using Rock-Eval 6 instrument. For analysis, 100 gm of each pulverized rock samples was used. The samples were heated at a rate of 25 °C/min in a helium stream from 300 to 600 °C. Heating through this range of temperature is to produce three parameters: S1 and S2 as oil pulses and S3 as a gas pulse, and also to measure the maximum temperature reached (Tmax) at the peak of S2. From these measured parameters, HI, OI, PP, and other parameters are calculated to provide the required information. Details of the analytical methods are based on Espitalie´ et al. (1977); Tissot and Welte (1984), and peters (1986). The analysis of the spot seepage samples were done in the Laboratory of Geomark Research (USA) using gas chromatography-mass spectrometry (GC-MS) technique. This technique is the most widely used for detection and identification of the biomarkers to evaluate the paleoredox depositional environment, type of the source rocks and origin. GC-MS is a combination of gas chromatography and mass spectrometry consisting of a magnet tube-mass analyser followed by ion detection with electron multiplier to detect the different biomarker parameters. To achieve more reliable results, this is supported by stable carbon isotope measurement.

Quality of the source rocks (richness)

The type and amount of organic matters are the main factors in the assessment of the quality of the source rocks and hydrocarbon generation potential. Therefore, the measurement of total organic carbon (TOC) and thermal cracking of the organic matters by pyrolysis (S1 and S2) are essential in the evaluation of source rocks and the nature of hydrocarbon products (oil and gas). Results of the analysis of TOC and parameters of Rock-Eval pyrolysis (S1, S2, S3), Tmax, and the calculated data of hydrogen index (HI), oxygen index (OI), petroleum potential (PP), production index (PI), and vitrinite reflectance (R_o) of selected samples from the three formations (Sargelu, Naokelekan and Chia Gara) are listed in Tables 1 and 2. Table 3 lists the minimum, maximum, and average values of TOC and Rock-Eval data and their interpretation. For the study formations, the obtained data of TOC and Rock-Eval pyrolysis show good to excellent organic matter richness and generation potential (Figs. 3 and 4). The TOC ranges from 1.69 to 45.12 wt.% with an average of 10.29, 32.76, and 11.81 wt.% for Sargelu, Naokelekan, and Chia Gara samples, respectively. The average S2 value (Table 3) is 45.13 for Sargelu, 136.8 for Naokelekan, and 53.08 for Chia Gara samples.

The calculated values of HI for the three formations are high ranging from 225 to 550 mg HC/g TOC with average values 380 mg HC/g TOC in Sargelu, 434 mg HC/g TOC in Naokelekan, and 365 mg HC/g TOC in Chia Gara samples.

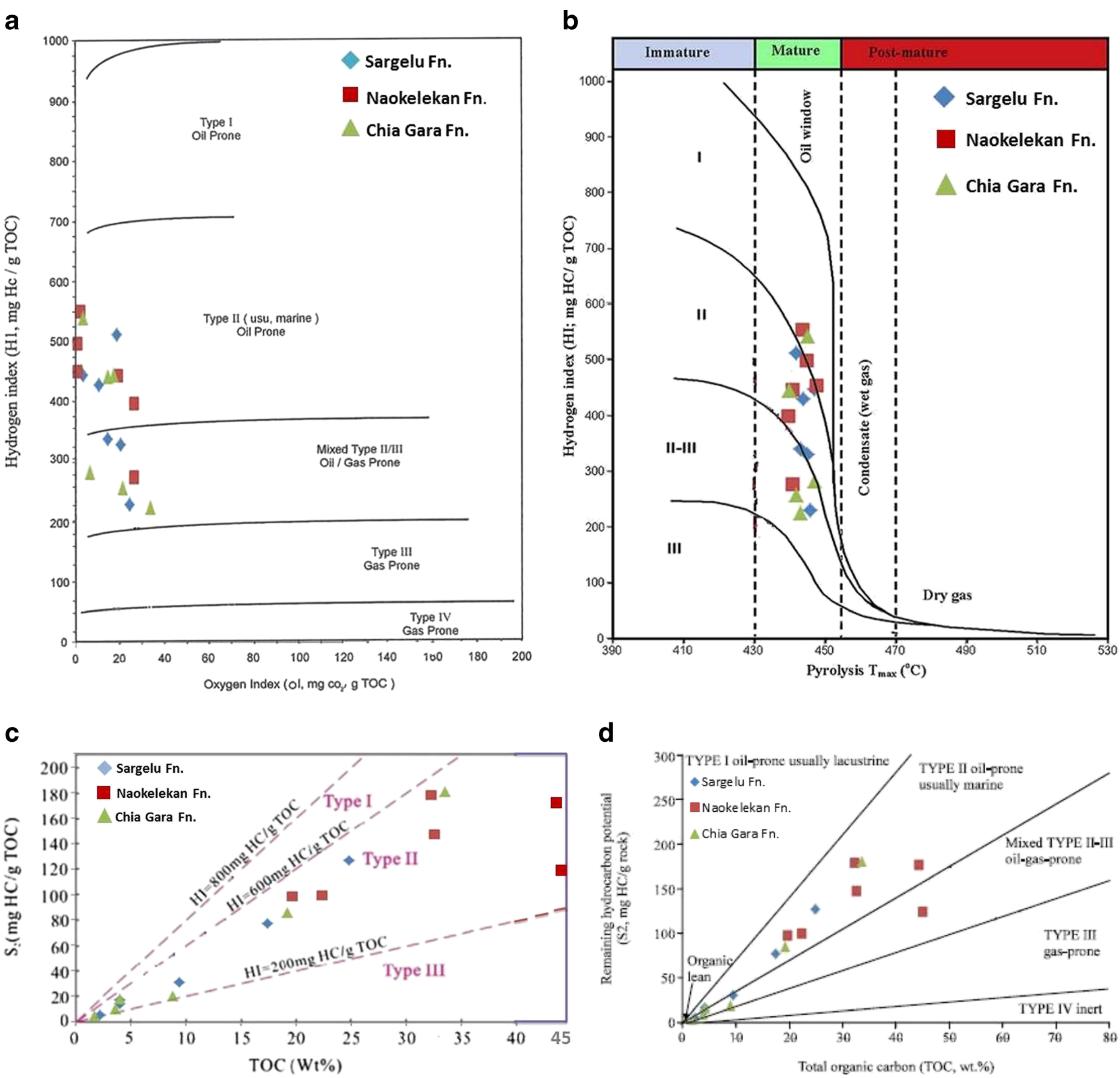


Fig. 6 **a** Types of kerogen in the three formations depending on Van Krevelen plots (hydrogen index (HI) versus oxygen index (OI)). **b** Types of kerogen, product zone, and maturity in the three formations depending on the hydrogen index (HI) and Tmax (Mukhopadhyay et al. 1995). **c** plot of TOC versus S2 indicating the types of kerogen (modified from Dahl et al. 2004). **d** plot of TOC versus S2 indicating types of kerogen for three formations (after Langford and Blanc-Valleron 1990)

The moderate to high HI values in conjugation with high S2 and high TOC content infer good to excellent source rocks potential for these rocks. Among the three formations, the rocks of Naokelekan Formation have the highest average values of TOC, S2, and HI (Tables 1, 2, and 3), indicating high content of hydrogen-rich organic matters and hence, have the higher capacity to generate and yield more amount of oil (Ojo et al. 2009), compared with the rocks of the two other formations.

The calculated S2/S3 ratio values are more than 5 (>5) in the three formations, indicating that their hydrocarbon type (potential) is mainly oil-prone (peters 1986; peters et al. 2005).

For the evaluation of the migrated hydrocarbons, the relationship between S1 and TOC gives a clear indication of indigenous and non-indigenous hydrocarbons. High S1 values coupled with high TOC content are characteristic of indigenous hydrocarbon (Hunt 1996; Peters and Cassa 1994; Rabbani and Kamali 2005). The cross-plots of S1 versus

TOC% of the study rocks of the three formations show the presence of indigenous hydrocarbons in these rocks (Fig. 5).

Kerogen type and hydrocarbon quality

Hydrocarbon type depends on the kerogen type and thermal history. The determination of the kerogen type is entirely depends on HI (Hunt 1996). As previously mentioned, the HI values are high ranging from 225 to 550 mg HC/g TOC. This corresponds with kerogen type II with contribution of the mixed type II/III and hydrocarbon product of oil prone and oil/gas prone (Table 3). From the cross-plot of HI versus OI, HI versus Tmax, and S2 versus TOC (Fig. 6a, b, c, and d), it appears that type II kerogen is the dominant with few mixed-type II/III kerogen. The moderate to high HI values within mature stage approve the prevalence of oil prone and oil/gas prone hydrocarbon potential of study rocks. Furthermore, the calculated vitrinite reflectance (R_o) values can also be useful indicator for thermal maturity and whether the source rocks are oil- or gas-prone. According to Hunt (1996), the higher values of R_o (>1.5 %) indicate dry gas; the lower values ($0.6 < R_o < 0.8$) refer to oil prone whereas the intermediate values are characteristics of oil prone with the tendency toward lower gas generation. For the study of rocks of the three formations, R_o values (0.76–0.9) (Table 2) and cross-plots of HI versus R_o (Fig. 7) indicate oil window and type II and mixed-type II/ III kerogen.

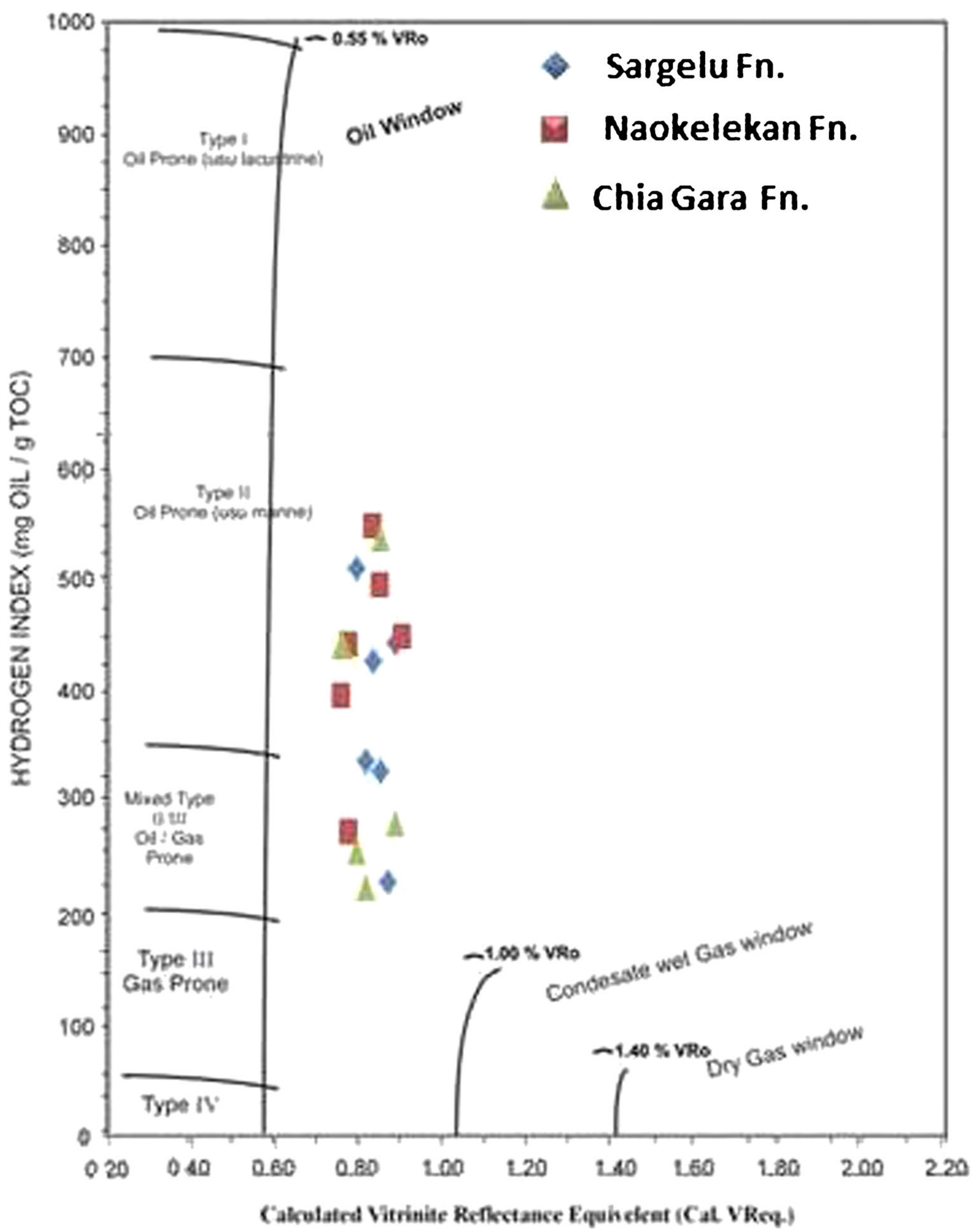


Fig. 7 Types of kerogen in the three formations depending on the hydrogen index (HI) and calculated R_o (Ghori 2002)

Thermal maturity of the source rocks

The terms mature and immature are commonly refer to the organic matter in the source rocks and also to the current state of kerogen in rocks. Throughout this study, assessment of the organic matter thermal maturity is defined in terms of a combination of the most commonly used and widely quoted parameters such as Tmax, R_o, and PI as maturity indicators. The measured Tmax values in the study rocks of the three formations vary from 440 to 448 °C, with the calculated R_o values (Tables 2 and 3) in agreement with thermally mature organic matters of the source rocks, within the range of early to peak mature stage, although the PI values are low (mostly <0.1). This is coupled with the cross-plots of HI versus Tmax (Fig. 6b) confirming that the rocks of the three formations are at mature stage and within catagenesis zone (R_o>0.5).

Organic geochemistry of oil seepages

Different biomarker parameters are utilized for fingerprinting the hydrocarbon generation providing clues to the identity of source rocks, the thermal history (maturity), the environmental conditions, and the degree of biodegradation if present. For the detection and identification of the biomarker parameters, GC-MS method is used. Table 4 lists the measured values of different biomarkers for the oil samples of Banik and Tawke seepages.

Pristane (Pr)/phytane (Ph) ratio is the most widely used biomarker parameter to define the paleoredox conditions and organic matter source (Tissot and Welte 1984; Chandra et al. 1994; Large and Gize 1996). Oil with Pr/Ph values of this a cyclic isoprenoid ratio (<1) indicate an organic-rich anoxic or highly reducing depositional environment of carbonate source rocks; Pr/Ph ratio values >1 indicate oxic conditions of sedimentation. The values of Pr/Ph ratio in oil samples of

Table 4 Values of different biomarkers which have been used to identify the types of the source rocks and organic matters, paleoredox, paleoenvironment, thermal maturity, and age for the investigated oil samples from Banik and Tawke seepages

Biomarker	Banik oil seepage	Tawke oil seepage	Interpretation
Pr/Ph	0.74	-	Marine, carbonate rocks, anoxic environment.
Pr/n-C17	0.68	-	Mostly type II kerogen, reducing condition,
Ph/n-C18	1.16	-	mature, moderate biodegradation.
δ C15+Saturate	-27.95	-27.30	Mainly of marine with slightly mixed origin
δ C15+Aromatic	-27.87	-27.00	oils.
Canonical Variable (CV)	-2.81	-2.52	Predominantly marine organic source.
C22/C21	0.93	0.84	Marine carbonate source rocks.
C24/C23	0.40	0.37	
C26/C25	0.75	0.85	Marin depositional environment.
C31R/H	0.34	0.34	
C35S/C34S	1.21	1.13	Marine carbonate source rocks, anoxic envir.
C29/H	1.33	1.75	, thermal maturity.
%C27 sterane	31.3	28.4	Marine carbonate source rocks, marine
%C28 sterane	23.6	25.8	organic matter (planktonic) with contribution
%C29 sterane	45.1	45.8	of land plant (terrestrial contribution).
C28/C29	0.52	0.56	Middle and Upper Jurassic source rocks
OL/H	0.00	0.00	Earlier than Cretaceous age
δ ^{13}C‰	-27.91	-27.15	Jurassic-Paleocene age
C29 20S/R	0.72	0.76	Thermal maturity.
Tet/C23	1.91	2.66	Thermal maturity.
Sulfur (S%)	5.44	3.21	Marine carbonate source rocks.
C27/C29	0.69	0.62	Predominance of marine organic matters with land plant contributions.

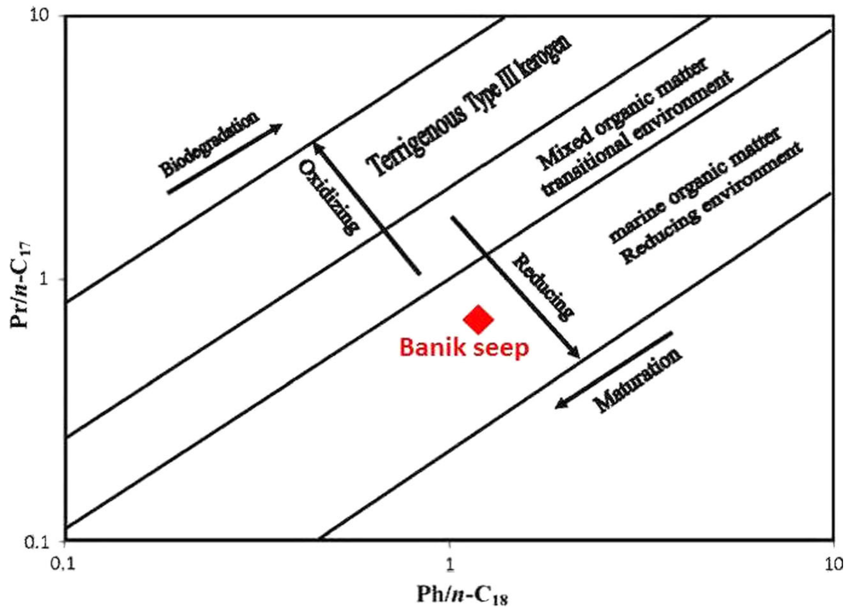


Fig. 8 (Pr/n-C17) versus (Ph/n-C18), showing depositional conditions of Banik seepage (modified after Shanmugam 1985)

Banik is 0.74 (Table 4) indicating their derivation from marine carbonate rocks that were deposited under anoxic conditions.

The relationship between normal alkanes (Pr/n-C17) and (Ph/n-18) is useful to distinguish the condition of depositional environment and the type of organic matter of the crude oil (Lijambach 1975). Low Pr/n-17 (<1) coupled with high Ph/n-18 (>1) of Banik oil sample (Table 4) demonstrate marine organic matter (mostly type II kerogen) accumulated under reducing conditions in the basin of deposition (Fig. 8) (Didyk et al. 1978; Powell 1988; Hughes et al. 1995; Peters et al. 2005).

The stable carbon isotope composition of the saturate and aromatic hydrocarbons in Banik oil sample is (−27.30) and (−27.00) (Table 4). This approves oils of marine origin with significant contribution of algal organic matters (Roger 1980; Sofer 1984; Meyers 2003; Younes and Philp 2005). On Sofer plot of δ^{13}C values of the aromatic and saturate hydrocarbon, the oil samples of both seepages, (Fig. 9) show the marine origin.

The differences between marine and terrigenous oils can be evaluated by using a statistical parameters, canonical variable (CV). CV>0.47 indicates predominantly terrigenous organic matter source for oil, and CV<0.47 is characteristic of marine organic matter source (Sofer 1984; Chung et al. 1992). For Banik and Tawke oil samples, the calculated values are (−2.81) and (−2.52), respectively, (Table 4) which indicate marine organic matter source. The ratio of the isoprenoid alkanes Pr/Ph shows correlation with the stable carbon isotopic composition or in other words with CV. The plot of CV data versus Pr/Ph ratio value for Banik oils shows their derivation from marine carbonate source rocks (Fig. 10a and b). Also

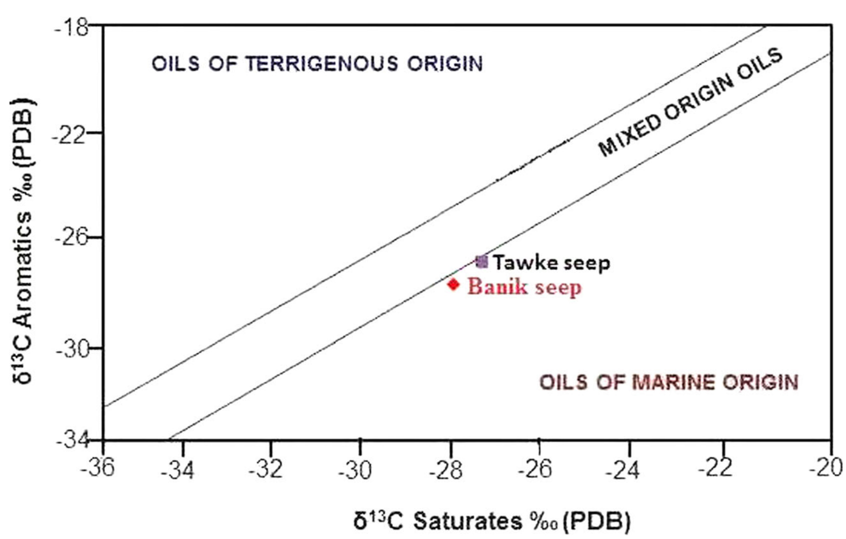


Fig. 9 Stable carbon isotope composition of aromatics versus saturates hydrocarbons for seepage oils from Banik and Tawke localities; δ^{13}C values are in ppt relative to PDB (after Sofer 1984)

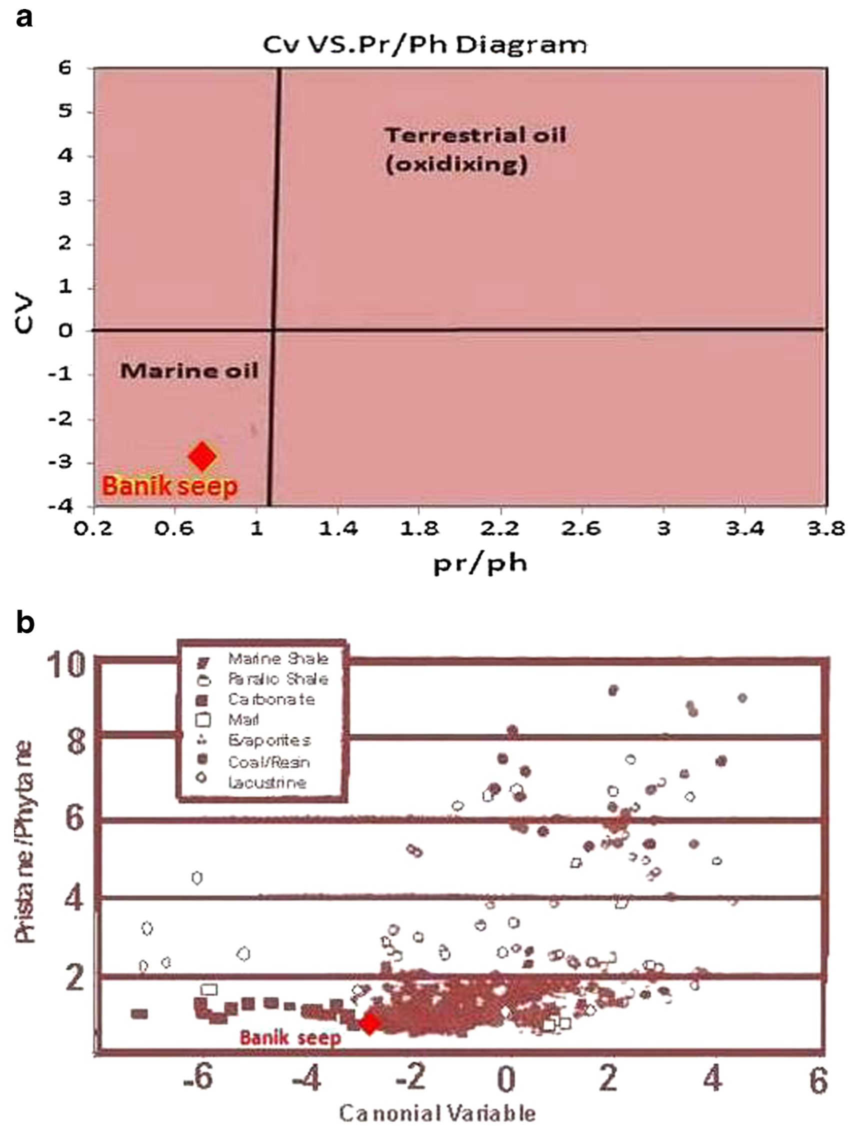


Fig. 10 **a** Canonical variable (CV) versus Pr/Ph (Chung et al. 1992). **b** Canonical variable (CV) versus Pr/Ph to distinguish oils from different source rocks (Sofer 1984)

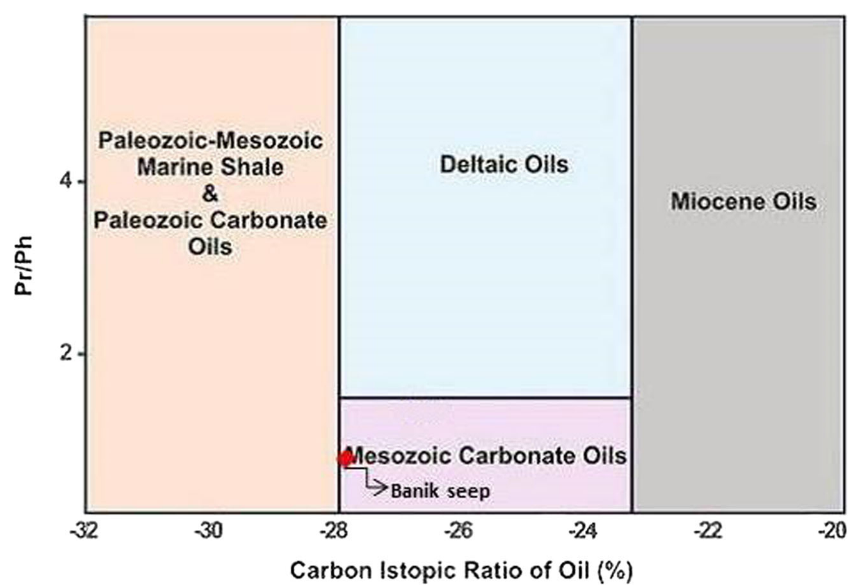
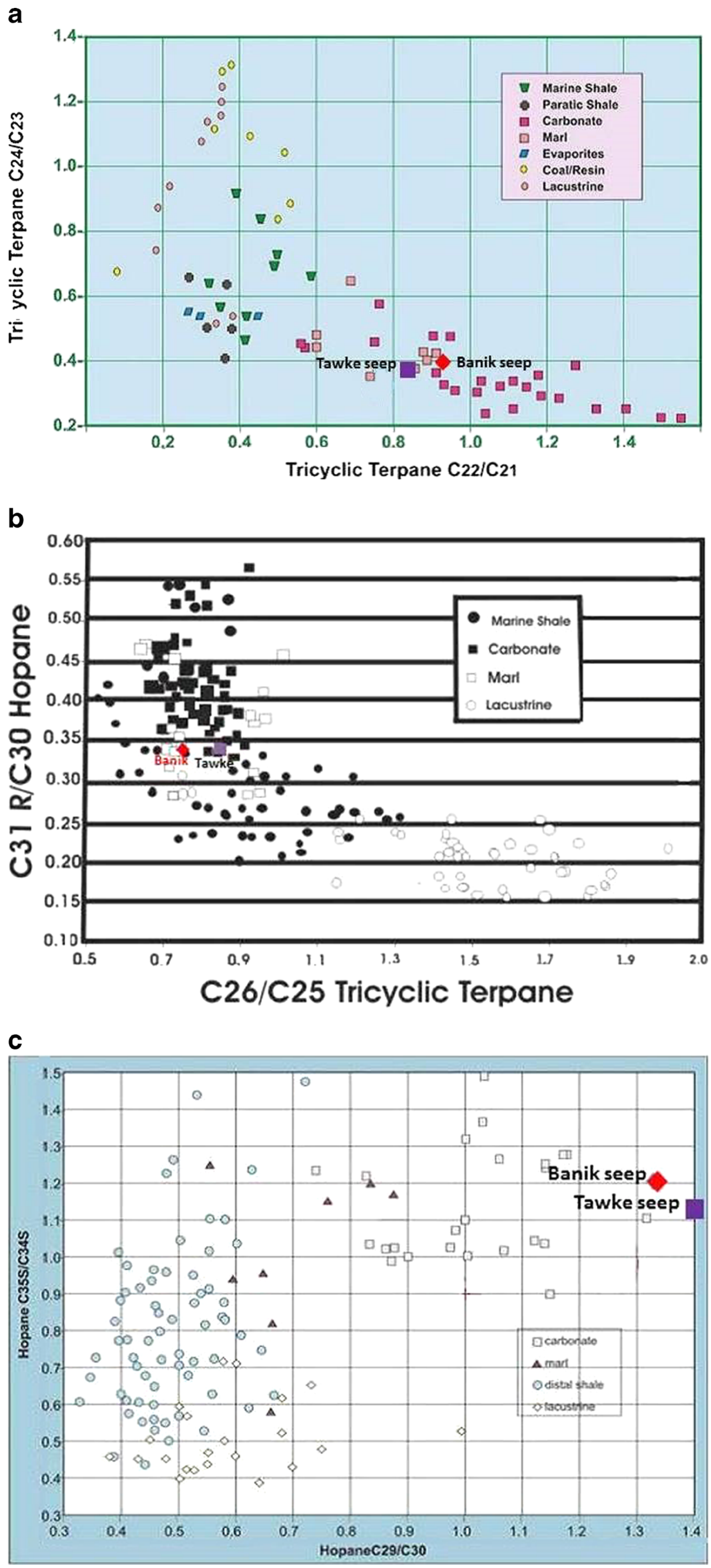


Fig. 11 Pr–Ph versus carbon isotope composition (whole oil carbon isotope) of the Banik seepage for determination of source rocks age (Hunt 1996)

Fig. 12 **a** Tricyclic terpane (C22/C21 vs. C24/C23) diagram for Banik and Tawke oil seepages to determine source rock lithology (Zumberge et al. 2005; Peters et al. 2005). **b** Cross-plot between C26/C25 and C31R/H indicate depositional environments of oil source rocks (Peters et al. 2005). **c** Cross-plot between C29/H and C35S/C34S indicate source rock depositional environments for Banik and Tawke oil seepages (Zumberge et al. 2005; Peters et al. 2005)



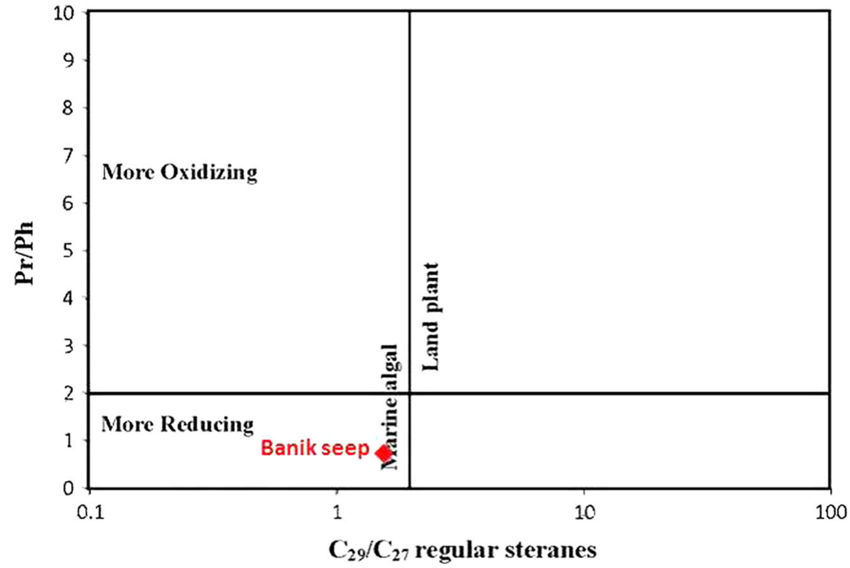


Fig. 13 C29/C27 steranes versus pristane/phytane diagram, showing the depositional environment conditions of the Banik oil seepage, which are derived mainly from marine algal organic matter under reducing conditions (Hakimi et al. 2011; Hakimi and Abdullah 2013)

shown in Fig. 10b are the data of the average values for oil samples of different types of source rocks from Geomark database.

Pr/Ph ratio versus whole oil carbon isotopic composition can be used to support the genetic relationship among oils and to infer the depositional environment (Hunt 1996). The plot of the isoprenoid alkanes (Pr/Ph) versus whole oil carbon isotope ratio of Banik oils (Fig. 11) indicates that they are derived from Mesozoic carbonate of marine origin.

High values of tricyclic terpane (C22/C21) ratio for oil samples of Banik and Tawke (0.93 and 0.84 respectively) coupled with low values of tricyclic terpane (C24/C23) ratio (0.4 and 0.37 respectively) (Table 4) (Fig. 12a) reflect marine carbonate source rocks for these oils. The values of tricyclic terpane (C26/C25) ratio (>1) are characteristic of marine depositional environment (Hanson et al. 2000; Gulbay and Korkmaz 2008). For the oil samples of both seepages, the values of C26/C25 ratio are 1.33 for Banik and 1.17 for Tawke which confirm their generation from marine source rocks. According to Peters et al. (2005), the values of C31R/C30 hopane ratio in marine derivative oils are >0.25, and the value of this ratio for oil samples of both seepages is 0.34, which also support marine source rocks for oils (Table 4); the cross-plot of C26/C25 versus C31R/C30 hopanes (Fig. 12b) of oil samples of Banik and Tawke show their source rocks of carbonate affinity. Furthermore, the homohopane index C35S/C34S ratio is applied as indicator for redox condition of marine sediments and sedimentary rocks. High values

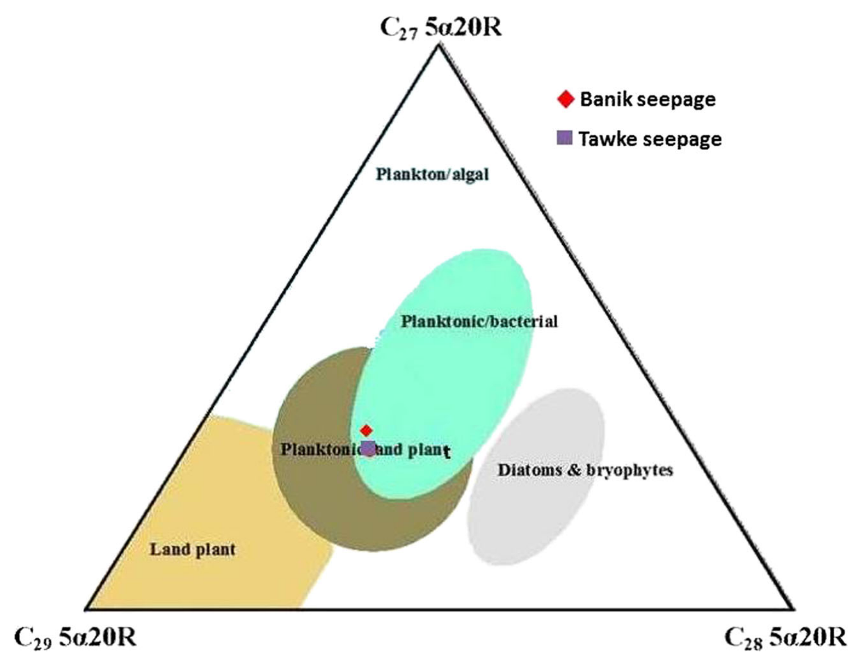


Fig. 14 Carbon number abundance plot of regular steranes C27–C28–C29 ternary plot, showing that the two oil seepages are derived from mixed marine/terrigenous organic matter (modified after Huang and Meinschein 1979)

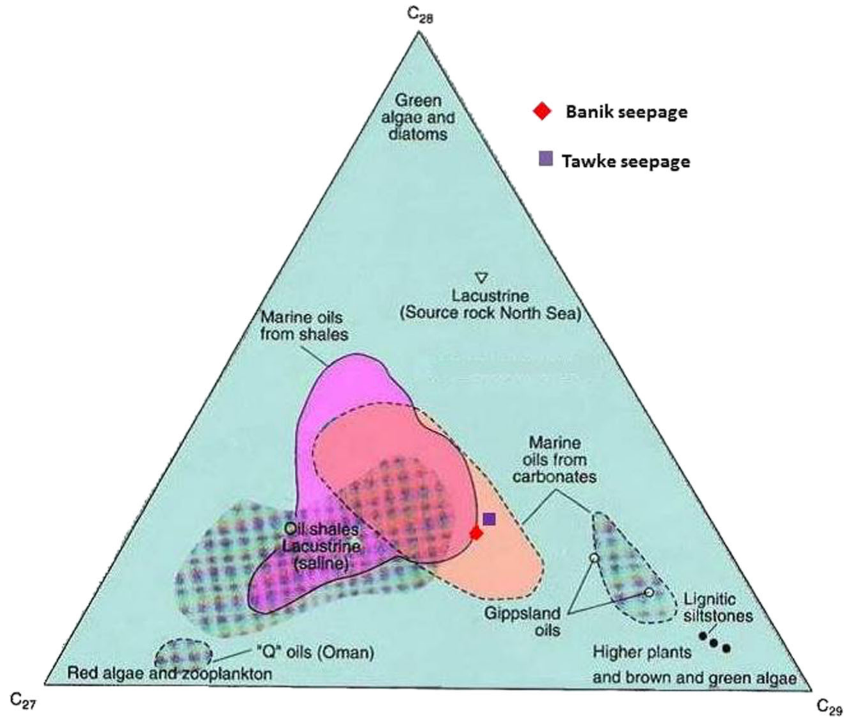


Fig. 15 Ternary plot of C27, C28, and C29 steranes (fields after Peters et al. 2005), showing that the two oil seepages from the Banik and Tawke localities are created mainly from marine carbonate source rocks

(>0.8) in oils indicate association with marine reducing conditions (Connan et al. 1986; Mello et al. 1988a, 1988b; Peters et al. 2005). Also, C29/C30 (norhopane/hopane) ratios >1 reflect anoxic marine carbonate source rocks (Clark and Philp 1989; Peters and Moldowan 1991; Peters et al. 2005). For oil samples of Banik and Tawke, the value of (C35S/C34S) (1.21 and 1.13) and (C29/H) (1.33 and 1.75) (Table 4) and their relationship (Fig. 12c) indicate marine carbonate source of anoxic conditions.

The abundance of reduced sulfur species, specifically phytane (Ph) and homohopane (C35) which are preserved under reducing environmental conditions (H_2S available) tend to distinguish carbonate or evaporate source rocks from clastic source (Moldowan et al. 1985; Peters and Moldowan 1993; Hughes et al. 1995). In Banik and Tawke oil samples, the sulfur content is high (5.44 % for Banik and 3.21 % for Tawke) which infer reducing condition of the source rocks.

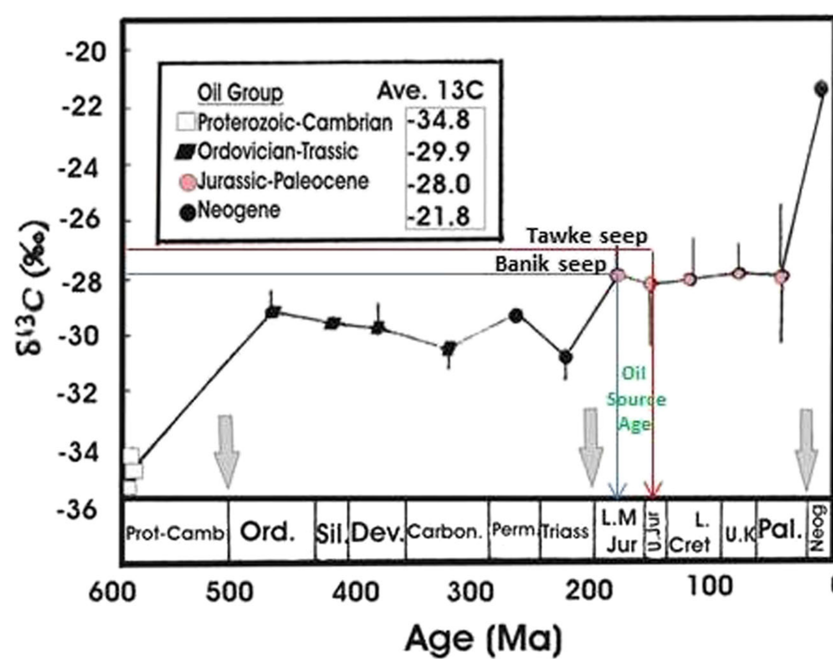


Fig. 16 Carbon isotopes source age assignment that confirm the Middle and Upper Jurassic age for Banik and Tawke oil seepages

The concentration of the sterane components, C27, C28, C29, in oils is useful in defining the type of organic matters in the source rocks (marine phytoplankton, lacustrine algae, or land plant organic matter input) (Huang and Meinschein 1979; Waples and Machihara 1991; Rinna et al. 1996; Gurgey 1999; Bacon et al. 2000; Bachir et al. 2006). The relationship between C29/C27 sterane ratio and the acyclic isoprenoids (Pr/Ph) ratio are also useful in the predication of the organic matter input (Hakimi et al. 2011; Hakimi and Abdullah 2013). The plot of Pr/Ph ratio versus C29/C27 ratio for Banik oil (Fig. 13) reveals the predominance of marine organic matters (algal) in the source rocks under reducing conditions. The value of C27/C29 ratio of Tawke oil is 0.62 which is very close to that of Banik oil (0.69) (Table 4), which can give an estimation of same result. On ternary diagram of the regular sterane (C27, C28, C29) (Fig. 14), the oil samples of both seepages fall within marine planktonic/bacterial field with contribution of land plant inflows. Furthermore, based on the relative abundance of these compounds, the ternary diagram (Fig. 15) shows the marine carbonate source rocks for oils of both seepages.

Various biomarker parameters are used to identify the degree of thermal maturity of the organic matter in oil seepages. Among these are C29 20S/R ratio (20S/20+20R), the norhopane/hopane (C29/H) ratio, and the tetracyclic (Tet)/C23 (C24 tetracyclic terpane ratio), which increase with increasing of maturity (from equilibrium stage at 0.52–0.55) (Seifert and Moldowan 1981; Gallegos and Moldowan 1992). In Banik and Tawke oil samples, the values of C29 20S/R ratio are high (0.72 and 0.76 respectively) (Table 4) indicating thermally mature organic matters. The value norhopane/hopane (C29/H) ratio is (>1) for both corroborating thermally mature state due to the more stability of norhopane relative to hopane at high levels of maturity (Peters et al. 2005). The values of Tet/C23 ratio also increase with increasing maturity of oil (Peters et al. 2005). For Banik and Tawke oil samples, the values of these ratios are high (1.91 in Banik and 2.66 in Tawke oils) (Table 4) which is another indicator for mature condition of the organic matters within the studied oil samples of both seepages.

The Oleanane index (OL/H or OL/C30 hopane) is considered an important index for the estimation the age of the source rocks (Alberdi and Lopez 2000). Oleanane is a biomarker from angiosperm common in source rocks of Cretaceous or younger crude oils. The values of OL/H >0.2 (>20 %) indicate ages younger than Lower Cretaceous, whilst values <0.2 (<20 %) are for Lower Cretaceous (Peters and Moldowan 1993; Murray et al. 1994). In Banik and Tawke oil samples, the Oleanane index is zero (Table 4), indicating age earlier than Lower Cretaceous. This is enhanced by the measured values of the stable carbon isotope and plots (Table 4 and Fig. 16) which indicate Jurassic age as the source rocks from which these oils are derived.

The calculated values of C28/C29 sterane ratio are 0.52 for Banik oil and 0.56 for Tawke oil samples (Table 4). By comparing these values with the average values of C28/C29 sterane for oils from marine carbonates and marls of the global petroleum system proposed by Grantham and Wakefield (1988) and plotting the data of Banik and Tawke oils on Geomark Research Oil database (Fig. 17), the age of the source rocks are found to be Middle–Upper Jurassic.

According to the obtained results and interpretations, it is obvious that there is a similarity in paleoredox condition, maturity, type of organic matters, and type of source rocks

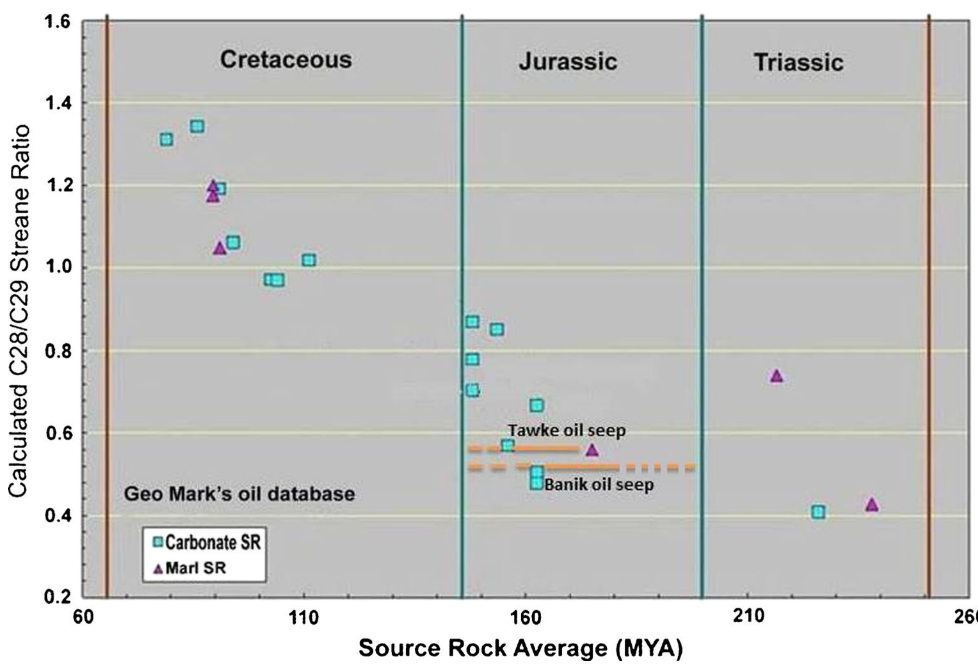


Fig. 17 C28/C29 sterane ratio of Banik and Tawke oil seepages suggesting oil affinity with Middle and Upper Jurassic rocks (from GeoMark Research OILS™ database)

between Banik and Tawke oil seepages. Furthermore, the age of their source rocks is estimated to be Middle–Upper Jurassic. All these lead to the conclusion that the source rocks for these seepages are equivalent to Sargelu, Naokelekan, and could be Chia Gara with the emphasis on the rocks of Naokelekan as the more probable source for these oil seepages.

Conclusion

– In the current study, the hydrocarbon potential and maturity of the organic matters for the rocks of three Jurassic formations: Sargelu, Naokelekan, and Chia Gara were studied by organic geochemistry including TOC and Rock-Eval pyrolysis. These formations consist of bituminous carbonate and shale rocks. The rocks of the three formations are characterized by high TOC content up to 45.12 wt.%, high HI up to 550 mg HC/g TOC, low OI up to 33 mg CO_2/g TOC, and high S2 reaching 181.0 mg HC/g rock indicating very good to excellent source rock potential. Among these, the rocks of Naokelekan have the highest values. The Tmax data (440–447 °C) together with R_o values (0.76–0.90) show early-peak mature stage of organic matters mainly of type II kerogen with contribution of type II/III kerogen oil-prone source rock potential.
– The analysis of biomarker parameters of oil samples from two seepages (Banik and Tawke) show low Pr/Ph ratio, high homohopane index, and the concentrations of C27 and C29 steranes indicating reducing marine environment with type II kerogen and prevalence of marine planktonic. The stable carbon isotope of both saturate and aromatic fractions demonstrates that the oils of both seepages are originated from a common marine carbonate source rocks. The calculated C28/C29 sterane ratios and plots on Geomark Research database give an age of Middle–Upper Jurassic for the source rocks. Accordingly, we conclude that these oil seepages are derived from a common source rocks which could be related to the rocks of Sargelu, Naokelekan, and Chia Gara.

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