# Organic geochemistry of the Middle to Upper Jurassic source rocks succession in Balad-1 Well, Balad Oil Field, Central Iraq

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Abstract: Thirty four cuttings samples from the Jurassic rock succession in well Balad-1 in the Balad Oil Field, Central Iraq have been collected. Using various organic geochemical techniques, the organic matter's quantity, quality, maturity, and their source rock's depositional setting were determined. The samples were evaluated to determine the amount of their organic matter content, type of organic matter,  $\delta^{13}$ C carbon isotopes abundance for both saturated and aromatic, and molecular properties. The results of organic geochemistry analysis show that Sargelu, Gotnia, and Chia Gara formations contain fair to decent amounts of organic matter. Naokelekan Formation encompasses fair to excellent organic matter, while Najmah Formation comprises very high to exceptional organic matter. The analyzed samples revealed the existence of kerogen types III and II/III mainly within oil window. Thermal maturity related biomarkers are in a good agreement with Rock-Eval parameters, but did not reach equilibrium phase. Source related biomarkers show that these rock units rich in organic matter were mainly deposited in an anoxic marine depositional setting which consists of carbonate influenced by terrestrial input.

Keywords: Kerogen type, maturity, biomarker, carbon isotope, Balad Oil Field, Iraq

#### INTRODUCTION

Northern and north-eastern parts of Iraq contain substantial prospective Jurassic source rocks. These source rocks are the Aalenian–Bathonian Sargelu, the Callovian– Oxfordian Naokelekan, the Oxfordian–Kimmeridgian Najmah, and Upper Jurassic-Lower Cretaceous Chia Gara Formation (Bellen *et al.*, 1959). They are comprised primarily of carbonates and shales rich in organic-matter that were deposited in marine depositional setting. These source rocks that charged the Cretaceous and Cenozoic petroleum reservoirs discovered in Iraq which are located in the Zagros-Mesopotamian Jurassic and Cretaceous–Tertiary petroleum systems (Ahlbrandt *et al.*, 2000; Abdula, 2017).

Balad Oil Field is considered as one of the main oil fields in Central Iraq. It's located within Salah Al-Din Province alongside the Tigris River and approximately 65 km north of capital city, Baghdad (Figure 1). The area is covered by the Pleistocene and recent sediments represented by alluvial deposits and river terraces. These deposits consist of silt and clay with intercalations of sand and gravel (Abdul-Rahman, 1997).

As Jurassic succession in Iraq includes significant source rocks, this study aims to further evaluate this succession in well Ba-1 in the Balad Oil Field using Rock-Eval pyrolysis technique. In addition, the study investigates the depositional environment and other source rock characterizations utilizing carbon isotope ratios and molecular properties.

# **GEOLOGICAL BACKGROUND**

Iraq is located at the north-eastern edge of the Arabian Plate among three major tectonic units of Phanerozoic age; these are Arabian, Iranian, and Turkish plates (Jassim & Buday, 2006a).

The modern tectonic divisions of Iraq are well represented in Figure 2. Balad Field is situated within the Unfolded Zone. The development of Zagros anticlines in Iraq are related to amalgamation of insensitive twist connecting the basement and delicate distortion directly above a detachment adjacent to the lower boundary of the Palaeozoic sequence. Perhaps in Balad Field, thrust faults regulate the stretched uneven anticlines which are parted by tapered synclines (McQuarrie, 2004).

The study areas' general stratigraphy is summarized in two megasequences of the regional geologic column (Figure 3) which displays the existence of a thick Jurassic and Cretaceous sequence comprised of carbonates, carbonate shales, and evaporites (Bellen *et al.*, 1959; Sharland *et al.*, 2001). The two megasequences are represented by the Middle-Upper Jurassic-Cretaceous succession which consists of carbonate and carbonate shale. This succession includes Sargelu, Najmah, Naokelekan, Gotnia, and Chia Gara formations (Jassim & Buday, 2006b).

# SAMPLES AND ANALYTICAL PROCEDURES

Thirty four cuttings samples from Middle and Upper Jurassic formations in well Ba-1 in the Balad Oil Field,



Figure 1: Map of Iraq shows the well Ba-1, Balad Oil Field, Central Iraq.



Figure 2: Structural elements of Iraq (Buday & Jassim, 1987).

Central Iraq have been collected. The samples were submitted to StratoChem Services, New Maadi Cairo in Egypt.

All the samples were studied for determining the quantity of organic material and Rock-Eval parameters. For further organic geochemical analyses, ten among the



Figure 3: Stratigraphic column in Balad Field, Central Iraq (after JAPEX Company, 2006; Jassim & Buday, 2006b).

collected samples were used for extraction. The extracted organic matter used for studying saturated and aromatic  $\delta^{13}$ C carbon isotopes and existent biomarkers to identify molecular properties using the gas chromatograph and mass spectrometer.

The samples were subjected to 300  $^{\circ}$ C to 850  $^{\circ}$ C (3 minutes and 5 minutes holding time, respectively) in order to warm up at 25  $^{\circ}$ C per minutes for detrmining the total organic carbon (TOC) and Rock-Eval parameters.

For bitumen extractions, 20 g of crushed cuttings were utilized by Soxhlet apparatus for the duration of 48 hours. A small scale column chromatography with activated silica gel (120 °C, 8 hours) was used to separate the extractable organic matter to its constituent fractions. The extraction of saturated hydrocarbons was done by using n-hexane, the unsatured ring-shaped hydrocarbons by a mixture of dichloromethane and heteroatomic compounds, and non-hydrocarbon by a combination of dichloromethane and methanol (2ml, 1:1) after precipitation of asphaltenes.

The Sofer's (1980) ignition method and a Finnigan Delta E isotope proportion mass spectrometer were used to determine isotopic configuration of stable carbon for the saturated and unsaturated compound portions. Outcomes data were measured comparative to the Pee Dee Beleminite (PDB) standardizing the following Ault & Jensen's (1962) equation:

 $\delta^{13}C \ \% = (R_{sample} / R_{standard}) - 1 \ x \ 1000;$ the R is the proportion of <sup>13</sup>C to <sup>12</sup>C.

In gas chromatography, helium gas was utilized as a transporter. Whole isolated extracts inserted (fragmented type) on a 30 m by 0.32 mm J&W DB-5 column (width of film = 0.2  $\mu$ m) and temperature automated range was between 60 °C and 350 °C at 12 °C per minute utilizing an Agilent 7890A gas chromatograph.

The determination of sterane and terpane biomarker scatterings and magnitudes was achieved by utilizing an



**Figure 4:** Pyrolysis S<sub>2</sub> vs. TOC plot shows quantity and efficiency of organic material within Ba-1 Well in Balad Oil Field, Central Iraq.

Agilent 7890A GC (fragmented insertion) connection to a 5975C mass spectrometer.

# RESULTS AND DISCUSSION Quantity, quality, and thermal maturity of organic carbon

To assess petroleum potential in the Upper to Lower Cretaceous sequence, the study used the Rock-Eval parameters which is listed in Table 1 in combination with total organic carbon (TOC). Based on the analyzed samples Sargelu Formation considered fair to good source rock (0.54 to1.88 wt. % TOC), while Naokelekan Formation has fair to excellent TOC content (0.54 to15.70 wt. %). The Najmah Formation studied samples contains 3.30 to 5.28 wt. % TOC, which describes the sequence as very good to exceptional. Both formations, Gotnia and Chia Gara, contain 0.98 to 1.55 wt. % and 0.73 to 1.90 wt. % TOC, respectively. Accordingly, both formations encompass fair to good amount of organic matter. The plot of S2 versus TOC diagram of Peters & Cassa's (1994) was used to illustrate the petroleum potential of the studied sequences (Figure 4). According to this plot, Sargelu and Gotnia formations have fair petroleum potential, while Naokelekan Formation ranges from fair to excellent. Najmah and Chia Gara formations show good and fair to good source prospective, respectively (Figure 4).

The potentiality of formations for generating petroleum was further evaluated utilizing HI versus OI diagram (Espitalié *et al.*, 1977; Figure 5). Accordingly, the types of kerogen in the studied samples appear to be III and II/III. The HI against  $T_{max}$  diagram (Figure 6) shows similar types of kerogyn for the studied samples. The HI versus  $T_{max}$  plot further shows the organic matter's maturity in the



Figure 5: OI vs. HI scheme for samples from the Balad Oil Field, Central Iraq.

Sample no.	Formation	Depth (m)	TOC wt. %	S <sub>1</sub> mg/g	S <sub>2</sub> mg/g	S <sub>3</sub> mg/g	T <sub>max</sub>	HI	OI	PI	S <sub>1</sub> / TOC
1	Chia Gara	3976	0.80	0.33	1.49	0.79	426	187	99	0.18	41
2	Chia Gara	3980	1.48	0.38	2.25	0.42	439	152	28	0.14	26
3	Chia Gara	3985	1.25	0.54	2.46	2.10	435	197	168	0.12	43
4	Chia Gara	3992	0.73	0.26	0.98	0.92	430	134	126	0.21	36
5	Chia Gara	3999	0.78	0.65	1.55	0.66	432	199	85	0.29	83
6	Chia Gara	4002	1.00	0.42	1.25	0.90	438	125	90	0.20	42
7	Chia Gara	4013	1.48	1.64	3.19	0.44	434	216	30	0.34	111
8	Chia Gara	4025	0.69	0.65	1.24	0.55	431	180	80	0.36	94
9	Chia Gara	4034	0.82	0.58	2.74	0.86	417	335	105	0.17	71
10	Chia Gara	4044	1.00	0.33	1.43	0.90	439	143	90	0.14	33
11	Chia Gara	4053	1.18	0.64	3.20	0.97	428	271	82	0.17	54
12	Chia Gara	4065	1.98	1.17	3.22	0.42	440	163	21	0.32	59
13	Chia Gara	4073	1.53	0.66	3.09	0.72	435	202	47	0.18	43
14	Chia Gara	4081	1.74	0.57	2.44	0.72	439	140	41	0.18	33
15	Chia Gara	4094	2.84	1.60	5.69	0.75	440	200	26	0.22	56
16	Gotnia	4100	0.98	0.95	2.08	0.55	428	213	56	0.31	97
17	Gotnia	4121	1.55	1.33	2.79	0.59	446	180	38	0.32	86
18	Najmah	4141	5.28	1.47	7.88	1.03	446	149	20	0.16	28
19	Najmah	4144	3.30	1.83	5.13	0.55	449	155	17	0.26	55
20	Naokelekan	4146	0.54	0.14	0.72	0.74	437	133	137	0.16	26
21	Naokelekan	4148	0.94	0.38	1.29	0.84	437	138	90	0.23	41
22	Naokelekan	4150	15.70	3.83	28.07	1.07	447	179	7	0.12	24
23	Naokelekan	4152	10.10	2.34	16.18	1.22	448	160	12	0.13	23
24	Naokelekan	4154	3.42	1.01	5.46	0.91	449	160	27	0.16	30
25	Naokelekan	4156	7.89	1.97	12.52	1.00	448	159	13	0.14	25
26	Naokelekan	4158	5.62	2.15	9.87	0.88	449	176	16	0.18	38
27	Naokelekan	4160	2.14	0.65	2.91	0.88	442	136	41	0.18	30
28	Naokelekan	4162	2.74	1.33	4.45	0.86	445	162	31	0.23	49
29	Sargelu	4168	1.88	0.54	2.56	0.86	441	136	46	0.17	29
30	Sargelu	4180	0.63	0.25	1.26	1.03	435	200	163	0.17	40
31	Sargelu	4202	1.08	0.39	1.95	0.74	437	181	69	0.17	36
32	Sargelu	4243	0.80	0.33	1.75	0.77	435	218	96	0.16	41
33	Sargelu	4264	0.54	0.22	1.19	1.85	437	221	343	0.16	41
34	Sargelu	4286	1.31	1.33	3.89	0.57	436	297	44	0.25	102

**Table 1:** Source rock property parameters of cuttings from Jurassic formations within well Ba-1, Balad Oil Field, Central Iraq.

TOC= total organic carbon;  $S_1$ = total free hydrocarbons (from  $S_1$  peaks);  $S_2$ = amount of remaining hydrocarbon or amount of hydrocarbon gained by heating during pyrolysis (from  $S_2$  peaks);  $S_3$ = amount of carbon dioxide (CO<sub>2</sub>) released through heating organic matter (from  $S_3$  peaks);  $T_{max}$ = highest temperature for generating a maximum amount of hydrocarbon during pyrolysis; HI= hydrogen index; OI= oxygen index; PI= production index.

studied formations. According to this plot and Table 1, the organic material in the studied samples are predominantly mature and within oil window.

# Depositional setting of organic carbon

Stable carbon isotope configuration of the extracted bitumen from source rock samples is one of the main tools

for determining the depositional environment (Alexander *et al.*, 1981). Stable carbon isotopic arrangements of both saturated and unsaturated hydrocarbon portions of source rock extracts were defined for ten cuttings samples (Table 2). The  $\delta^{13}C_{sat.}$  and  $\delta^{13}C_{aro.}$  for source rock extracts are between –25.8 and –27.7 ‰ and –26.0 and–27.7 ‰, respectively. The cross-plot of  $\delta^{13}C_{sat.}$  versus  $\delta^{13}C_{aro.}$  portions (Figure 7)

was used to determine the source of the studied sequences. The analyzed cuttings samples of the Sargelu, Naokelekan, Najmah, Gotnia, and Chia Gara formations from the Balad Oil Field fall below the boundary line of Sofer's (1984) cross plot signifying a marine derived source.

Sofer (1984) and Peters *et al.* (2005) used canonical variable (CV) to differentiate between terrigenous and marine source for bitumen extractions and crude oils, values of CV >0.47 indicate waxy terrigenous environment and values <0.47 indicate mainly non-waxy marine environment. The relation between CV and isotope configuration of the saturated and unsaturated, paraffin and aromatic, hydrocarbons is:



**Figure 6:** HI vs.  $T_{max}$  plot for organic material within well Ba-1 in Balad Oil Field, Central Iraq.



The oils' CV values sorts between -4.23 and -2.14 (Table 2) indicating that the bitumen extract samples are non-waxy and were originated from marine source rock.

The proportion of pristane/phytane is utilized to recognize the specific deviations in the comparative quantities between land-derived and marine hydrocarbons in sediment or rock extracts (Bourbonniere & Meyers, 1996). It is a sign of the palaeodepositional setting with little precision due to the interventions by thermal maturity and source contributions (Didyk *et al.*, 1978; Philp, 1985). The dissemination of the n-alkanes and isoprenoids in all extracted source samples is similar, indicating the nonbiodegraded hydrocarbons and almost no obvious odd-toeven prevalence was detected, n-alkane display front-end-



Figure 7: Carbon isotope configurations of saturated vs. unsaturated portions for extracted samples from Balad Oil Field, Central Iraq.

Formation	Depth	Depth SAT		NSO	ASPH	S 13C	\$ 13C	CV	D <sub>w</sub> /Dh	Dru/m C	Dh/m C	CDI
Formation	(m)	wt. %	wt. %	wt. %	wt. %	o "C <sub>sat</sub> .	0 <sup></sup> C <sub>aro</sub> .	CV	Pr/Pn	Pr/n-C <sub>17</sub>	Pn/n-C <sub>18</sub>	CPI
Chia Gara	4013	42.62	21.02	20.45	15.91	-27.7	-27.7	-3.06	0.56	0.12	0.17	0.98
Chia Gara	4073	47.06	17.65	26.47	8.82	-27.6	-27.7	-3.32	0.71	0.12	0.16	1.01
Chia Gara	4094	37.51	16.07	35.71	10.71	-27.3	-27.6	-3.85	0.15	0.13	0.14	1.04
Gotnia	4100	35.36	14.14	23.23	27.27	-27.1	-26.6	-2.14	0.69	0.13	0.18	0.93
Najmah	4141	29.42	11.76	21.57	37.25	-26.1	-26.4	-4.23	1.17	0.11	0.12	0.94
Najmah	4146	17.17	21.21	31.99	29.63	-25.8	-26.0	-4.10	0.96	0.14	0.18	0.90
Naokelekan	4152	18.74	21.88	35.84	23.44	-26.1	-26.1	-3,56	1.00	0.13	0.16	0.83
Naokelekan	4156	17.70	20.00	35.38	26.92	-26.1	-26.3	-4.00	0.90	0.13	0.17	0.87
Sargelu	4168	9.25	10.98	20.23	59.54	-27.5	-27.2	-2.46	0.66	0.24	0.28	0.93
Sargelu	4202	24.16	17.45	29.53	28.86	-26.1	-26.4	-4.23	1.14	0.14	0.16	0.90

Table 2: Gas chromatography data of extracted cuttings within well Ba-1, Balad Oil Field, Central Iraq.

SAT= Relative % saturated hydrocarbons; ARO= Relative % aromatics hydrocarbons; NSO= Relative % nitrogen, sulfur and oxygen; ASPH= Relative % asphaltines hydrocarbons;  $\delta^{13}C_{sat}$  = stable carbon isotopic composition of the saturated hydrocarbon fraction;  $\delta^{13}C_{aro}$  = stable carbon isotopic composition of the aromatic hydrocarbon fraction; canonical variable (CV)=-2.53  $\delta^{13}C_{sat}$  +2.22  $\delta^{13}C_{aro}$  - 11.65; Pr/Ph=pristane/phytane ratio; Pr/n-C<sub>17</sub>=Pristane/n-C<sub>17</sub> ratio; Ph/n-C<sub>18</sub> = Phytane/n-C<sub>18</sub> ratio; carbon preference index (CPI)=  $\frac{1}{2}[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})].$  biased scatterings with the extreme short chain hydrocarbon series (Figure 8), typical of hydrocarbons generated from algae and preserved in anoxic marine environment (Brassell *et al.*, 1978).

Materials deposited under similar condition produce petroleum with similar Pr/Ph proportion (Alexander *et al.*, 1981). Powel & McKirdy (1973) mentioned that the ratio reflects the oxicity of the depositional environment. Didyk *et al.* (1978) demonstrated that when the ratio of Pr/Ph <1 anoxic marine source-rock depositions is expected while Pr/ Ph >1 indicates oxic terrigenous deposition. The relation of Pr/Ph and the canonical variable (Sofer, 1984; Figure 9) readily distinguish that all the extract source samples are from carbonate and carbonate– shale deposits in anoxic marine environment. Both Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub> are maturity's measurement indicators, nonetheless are also exaggerated by biodegradation and further source progressions. Because of the special generation of n-alkanes, these proportions decline with progressing maturity (Horsfield & Rulkötter, 1994). The isoprenoid/n-alkane proportions are frequently utilized for estimating precisely the maturity phases of nonbiodegraded oils (Alexander *et al.*, 1981). Pr/n-C<sub>17</sub> ratio for the same kind of organic material are considered sensitive to thermal maturity (Connan & Cassou, 1980). In early maturity stages, the high Ph/n-C<sub>18</sub> was reported in oil and extract and the value reaches below unity during maturation (Brooks *et al.*, 1969; Albrecht *et al.*, 1976).

The Pr/Ph values range from 0.15 to 1.17 (Table 2). The lower amount of pristane than phytane is linked to reducing settings during deposition of source rock and/or to



Figure 8: Gas chromatograms for rock extracts from the Balad Oil Field, Central Iraq.

contributions by marine organic carbon (Welte & Waples, 1973). The arrangement of  $Pr/n-C_{17}$  versus  $Ph/n-C_{18}$  proportions (Figure 10) is aided to determine the type and the depositional environment of organic material. The Pr/n-C<sub>17</sub> versus Ph/n-C<sub>18</sub> plot (Figure 10) designates the marine source organic carbon accumulation deposited under reducing conditions.

The virtual richness of odd to even carbon numbered n-alkanes are widely aided to determine a rating of the oil and source extraction's thermal maturity; however, this is also exaggerated by the nature of organic matter contribution including the carbon preference index (CPI) (Bray & Evans, 1961), which is odd-even dominance expression in the n-alkane spectrum (Héroux et al., 1979). The values of CPI of the extract samples are between 0.83 and 1.04 (Table 2),



Figure 9: Pristane (Pr)/phytane (Ph) vs. the canonical variable (CV) for bitumen extract samples from Balad Oil Field, Central Iraq (modified from Sofer, 1984).

which are equal to or close to unity (CPI ~1), indicating higher thermal maturity.

Terpanes (m/z191 mass chromatogram) are typically generated from bacteriohopanetetrol that are formed in whole organisms and signify the major subordinate metabolites (Ajikumar et al., 2008). These products comprise numerous homologous sequence compounds represented by acyclic, bicyclic, tricyclic, tetracyclic, and pentacyclic which have been utilized to compare between oil and produced source rock. Figure 11 shows the gas chromatogram-mass fragmentograms and the peak identification. The most important biomarker ratios of triterpanes for the analyzed cuttings are recorded in Table 3. The widely occurrence of the tricyclic terpanes in oils and extracts has been noticed



Figure 10: Pristane/n-C<sub>17</sub> vs. phytane/n-C<sub>18</sub> of extract cuttings within well Ba-1 in Balad Oil Field, Central Iraq.

Formation	Depth	Tri/	ααS	ββR	Dia/	C <sub>28</sub> +C <sub>29</sub>	0/ C	0/ C	0/ C	C /C	Ster	DBT	
Formation	-					20 2)	<b>%</b> (	% (	1 % (				6

Table 3: Summary of biomarker characteristics of samples from the Balad Oil Field, Central Iraq.

Formation	Depth (m)	Tri/ Ster	ααS C <sub>29</sub>	$\begin{array}{c} \beta\beta R\\ C_{_{29}}\end{array}$	Dia/ ster	C <sub>28</sub> +C <sub>29</sub> /Ts	% C <sub>27</sub>	% C <sub>28</sub>	% C <sub>29</sub>	C <sub>28</sub> /C <sub>29</sub>	Ster /H	DBT /P	% Rc	T/T + M	${\rm T}^{}_{28}_{/~{\rm T}^{}_{28}}{\rm +T}^{}_{29}$
Chia Gara	4013	0.93	0.41	0.56	0.12	0.35	56.60	15.20	28.20	0.53	0.33	2.97	0.80	0.71	0.71
Chia Gara	4073	2.56	0.46	0.46	0.29	0.22	55.00	12.90	32.00	0.40	0.12	0.46	0.95	0.94	1.00
Chia Gara	4094	0.86	0.47	0.50	0.96	0.19	44.00	18.00	38.00	0.47	0.27	0.26	0.75	0.97	1.00
Gotnia	4100	2.05	0.41	0.48	0.36	0.21	59.50	9.70	30.80	0.31	0.17	3.18	0.89	0.73	0.71
Najmah	4141	1.89	0.44	0.56	0.22	0.27	66.40	11.30	22.30	0.50	0.23	1.77	0.79	0.70	0.48
Najmah	4146	1.13	0.41	0.52	0.20	0.36	53.20	15.70	31.10	0.50	0.18	1.96	0.80	1.00	1.00
Naokelekan	4152	1.27	0.42	0.52	0.44	0.32	40.60	19.40	40.00	0.48	0.17	1.97	0.80	1.00	1.00
Naokelekan	4156	1.41	0.40	0.50	0.33	0.25	41.30	18.30	40.40	0.45	0.15	1.65	0.80	1.00	1.00
Sargelu	4168	1.43	0.42	0.57	0.08	0.47	55.90	16.00	28.10	0.56	0.14	2.25	0.85	0.59	0.58
Sargelu	4202	1.42	0.41	0.50	0.50	0.23	41.10	18.70	40.20	0.46	0.18	1.41	0.81	1.00	1.00

 $\begin{aligned} &\text{Tri/Ster} = \text{tricyclic terpanes/steranes;} \ \alpha \alpha S \ C_{29} = 20S/(20S+20R) \ \text{sterane ratio;} \ \beta \beta R \ C_{29} = \alpha \beta \beta / (\alpha \beta \beta + \alpha \alpha) \ \text{sterane ratio;} \ \text{dia/ster} = 13\beta(\text{H}), 17\alpha(\text{H}) \ 20S \ C_{27} \ \text{diasterane/5}\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H}) \ 20R \ C_{27} \ \text{regular sterane ratio;} \ C_{28} + C_{29}/\text{Ts} = C_{28} \ \text{and} \ C_{29} \ \text{tricyclic terpanes/18}\alpha(\text{H}) - 22, 29, 30 \ \text{trisonrenohopane;} \ &\text{C}_{27} \ (\text{m/z} \ 217) = 100 \times C_{27} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{28} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{28} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R + C_{28}R + C_{29}R); \ &\text{C}_{29} \ (\text{m/z} \ 217) = 100 \times C_{29} R/(C_{27}R +$ ster/H = steranes/hopanes; DBT/P = dibenzothiophene (DBT)/phenanthrene (P); methylphenanthrene index (MPI-1) = 1.5(2-MP + 3-MP)/(P + 3-MP)/(P+ 1-MP + 9-MP) (Radke & Welte, 1983); calculated vitrinite reflectance (%Rc) = 0.6×MPI-1 + 0.4 (Radke *et al.*, 1984); T/T+M = triaromatic steranes/triaromatic steranes+monoaromatic steranes;  $T_{28}/T_{28}+T_{29} = C_{28}$  triaromatic/ $C_{28}$  triaromatic+ $C_{29}$  triaromatic steroids.



Figure 11: Chromatograms of m/z 191 and m/z 217 GC-MS for selected extract cuttings within well Ba-1 in Balad Oil Field, Central Iraq.

(Aquino Neto *et al.*, 1983), and because of the high stability of it against the biodegradation, its component are utilized for correlating petroleum with extracts, for describing source rock properties, and evaluating the stages of thermal alteration (Seifert & Moldowan, 1981; Zumberge, 1987; Peters *et al.*, 1990). The various values of  $C_{19}/C_{26}$  terpane ratios are illustrated in Table 4. The  $C_{24}/C_{23}$  versus  $C_{22}/C_{21}$  tricyclic terpanes plot (Figure 12) displays that the selected

Formation	Depth	C /C	C /C	C /C	C <sub>26</sub> /C <sub>25</sub>	C <sub>24</sub> TT/	NorH/	G/	C /C	Ts/	Ts/	C <sub>29</sub> Ts/	M/	C D/II
	(m)	$C_{19}/C_{23}$	$C_{22}/C_{21}$	$C_{24}/C_{23}$		C <sub>26</sub> T	C <sub>30</sub> H	C_{_{30}}H	$C_{35}/C_{34}$	Tm	(Ts+Tm)	C_29H	C <sub>30</sub> H	C <sub>31</sub> K/H
Chia Gara	4013	0.19	0.86	0.33	0.82	5.10	1.53	0.09	0.75	1.97	0.66	0.37	0.09	0.30
Chia Gara	4073	0.22	0.66	0.36	0.80	3.83	1.36	0.12	1.14	5.68	0.85	0.72	0.14	0.49
Chia Gara	4094	0.38	0.59	0.50	0.93	2.43	0.79	0.14	1.12	5.99	0.86	1.03	0.16	0.48
Gotnia	4100	0.47	0.61	0.49	0.78	6.70	1.30	0.24	0.45	3.79	0.79	0.44	0.10	0.18
Najmah	4141	0.83	0.50	0.49	0.87	9.06	2.18	0.13	0.94	1,34	0.57	0.23	0.08	0.19
Najmah	4146	0.87	0.48	0.53	0.66	11.02	1.76	0.17	0.98	0.77	0.43	0.15	0.10	0.26
Naokelekan	4152	0.77	0.50	0.50	0.70	9.12	1.74	0.18	0.98	0.90	0.47	0.17	0.10	0.25
Naokelekan	4156	0.75	0.56	0.51	0.72	9.01	1.71	0.19	0.98	1.29	0.56	0.19	0.10	0.24
Sargelu	4168	0.12	1.16	0.33	0.64	8.36	1.91	0.10	0.59	0.47	0.32	0.08	0.06	0.21
Sargelu	4202	0.81	0.49	0.51	0.77	8.44	1.76	0.20	0.85	1.43	0.59	0.20	0.10	0.25

Table 4: GC-MS data of cuttings from Jurassic formations within well Ba-1, Balad Oil Field, Central Iraq.

 $C_{19}/C_{23} = C_{19}/C_{23} \text{ tricyclic terpanes}; C_{22}/C_{21} = C_{22}/C_{21} \text{ tricyclic terpanes}; C_{24}/C_{23} = C_{24}/C_{23} \text{ tricyclic terpanes}; C_{26}/C_{25} = C_{26}/C_{25} \text{ tricyclic terpanes}; C_{24}TT/C_{26}T = C_{24} \text{ teracyclic terpanes}/C_{26} \text{ tricyclic terpanes}; Norhop/C_{30}H = C_{29} \text{ norhopane}/C_{30} \text{ hopane}; G/C_{30}H = \text{gammacerane}/C_{30} \text{ hopane}; C_{35}/C_{34} = C_{35}S+R/C_{34}S+R$  homohopanes; Ts/Tm = 18 $\alpha$ (H)-22, 29, 30 trisnorneohopane/17 $\alpha$ (H)-22, 29, 30 trisnorhopane; C\_{29}Ts/C\_{29}H = C\_{29}Ts/C\_{29} \text{ norhopane}; M/C\_{30}H = 17\beta(H), 21 $\alpha$ (H) moretane/17 $\alpha$ (H), 21 $\beta$ (H) hopane; C\_{31}R/H = C\_{31} 22R homohopane/C\_{30} \text{ hopane}.

samples are abundant marine carbonate rocks. The rich  $C_{24}$  tetracyclic terpanes appear to be an indicator in oils and extracts from evaporitic and carbonate deposits (Connan *et al.*, 1986). Oils derived from terrigenous sources also contain extraordinary concentration of  $C_{24}$  tetracyclic terpane (Philp & Gilbert, 1986).

 $C_{24}$ TT/ $C_{26}$  tetracyclic terpane ratios (Table 4) range from 2.43 to 11.02, this can be a result of carbonate and evaporitic depositional environment as well as terrestrial source material content (Zumberge *et al.*, 2005). The  $C_{29}$ 17 $\alpha$ -norhopane rivals as an indicator of lithology and depositional environment when norhopane/hopane ratio is > 1.0 for numerous anoxic carbonate or marl source rocks deposited under anoxic condition and related oils, while generally it is < 1.0 for other samples (Connan *et al.*, 1986).

Hopane is less constant compared to norhopane at advanced levels of thermal alteration. Therefore, in an assemblage of associated oils, 30-norhopane/hopane ratio can rise through thermal alteration (Peters et al., 2005). The norhopane/hopane proportion for the extracts from nine samples exceeds one; this can be attributed to the anoxic carbonate source in addition to the thermal alteration of the studied cuttings (Table 4). Gammacerane is frequently professed in fresh water deposits due to occurrence of water column stratification (Brocks & Summons, 2003). Gammacerane amount rises in marine and lacustrine saline depositional setting (Peters & Moldowan, 1993). The values of gammacerane index in the studied samples are between 0.09 and 0.24 (Table 4) which are relatively moderate representing reducing normal marine conditions. The disseminations of the  $C_{31}$ - $C_{35}$  extended hopanes (homohopanes) aids to assess source-rock redox settings throughout the preservation and can give a glance of the inherent associations among oils and extract samples (Ourisson et al., 1979, 1984; Rohmer, 1987). The proportion of  $C_{31}$ – $C_{35}$  17 $\alpha$  22S and 22R homohopanes are used in petroleum as a pointer of



**Figure 12:** Relationships between  $C_{24}/C_{23}$  and  $C_{22}/C_{21}$  tricyclic terpanes for assessing source origin in the studied formations in Balad Oil Field, Central Iraq.

the redox prospective (Eh) at the time of source deposition and exaggerated by thermal alteration (Peters & Moldowan, 1991). Extraordinary  $C_{35}$  homohopanes ratios are frequently linked to carbonates or evaporitic sediments (Fu *et al.*, 1986; Mello *et al.*, 1988). The  $C_{35}$  homohopanes in the source-rock extracts are derived from marine carbonates or evaporates preserved in anoxic environments (Riediger *et al.*, 1990). The homohopane index ratios for the bitumen extracts from Ba-1 Well source rock formations range from 0.45 to 1.14 (Table 4) indicate abundant anoxic marine carbonates and evaporitic environments.

 $C_{31}/C_{30}$  hopanes are applied to differentiate marine from lacustrine source-rock depositional setting also called  $C_{31}$  22R/  $C_{30}$  hopane ( $C_{31}$ R/H). The  $C_{31}/C_{30}$  hopane proportions ranging between 0.18 and 0.49 (Table 4) indicates that the deposition was mainly under anoxic marine condition (Peters *et al.*, 2005). Moreover, the  $C_{31}/C_{30}$  hopane versus Pr/Ph (Figure 13) displays that all the source rock cuttings are originated from transitional marine to lacustrine anoxic environment.

The proportion of Ts/Ts+Tm increases when maturity rises (Seifert & Moldowan, 1978), and it is more reliable in samples with identical organic matter (Peters & Moldowan, 1993). It is a valuable indicator particularly throughout the oil window before reaching the unity in high maturity level (Murray & Boreham, 1992). The proportion is also liable to facies inconsistency (Seifert & Moldowan, 1978; Moldowan et al., 1986). The oils and extracts originated from carbonate have low ratios in comparison to those generated from shale (McKirdy et al., 1983). The Ts/Ts+Tm proportion in the analyzed samples (Table 4) are under the unity, and ranges between 0.32 and 0.86. The ratio shows a trend of increase with depth in Chia Gara Formation, and similar trends can be observed in Naokelekan and Sargelu formations. This escalation in the Ts/Ts+Tm values can be accredited to the increase in thermal maturity.

Steranes gas chromatograms-mass fragmentograms are displayed in Figure 11 for selected samples from the studied formations and the commonly used biomarker ratios of steranes are shown in Table 3.

The comparative richness of  $C_{27}$ ,  $C_{28}$  and  $C_{29}$  steranes are sensitive types of organic material. The main sources of C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub> steranes are marine phytoplankton, lacustrine algae, and contribution of sophisticated plants, respectively (Waples & Machihara, 1991; Volkman, 2003; Bachir et al., 2006). High  $C_{29}/C_{27}$  steranes ratio greater than one testifies in sediments with rich land derived organic matter (Czochanska et al., 1988), and rocks containing marine algae show the reverse. The C27, C28, and C29 sterols' distribution of the extract samples of Jurassic formations from the well Ba-1, Balad Oil Field (Figure 14) shows that the formations are deposited in a mixed to marine predominantly depositional setting. The  $C_{22}/C_{22}$  ratio (Table 3) ranging between 0.33 and 0.98 concludes similar results. The ratio is close to the unity for the samples analyzed from Naokelekan Formation; this could be a result of more

terrestrial materials input in this formation in comparison with other studied sequences.

The diasteranes/regular steranes ratio increases with maturity (Seifert & Moldowan, 1978). Additionally, the ratio can describe the source of hydrocarbon either from carbonate or clastic origin (Brincat & Abbott, 2001). The diasterane/sterane ratios for the extracts reaches up to 0.96 (Table 3) demonstrating their origination from source rocks that contain diverse clay with rich anoxic clay-poor carbonate (McKirdy *et al.*, 1983). The effect of the maturity also can be observed within a formation, in Chia Gara Formation, for example, the ratio increase from 0.12 to 0.96. Additionally, the relation of the diasterane/sterane ratios versus Ts/Tm (Figure 15) shows that the analyzed samples are abundant in marine carbonate with poor clay content.

Because living organisms do not biosynthesize aromatic hydrocarbons in appreciable quantities, their ubiquitous occurrence in petroleum is thought to be due to multifaceted alterations of naturally derived naphthenic and olefinic (Hase & Hites, 1976). Distinguishing certain marine oil from fresh water setting oil can be inferred by using Pr/Ph ratio versus DBT/Phenantheren ratio (Tables 2 and 3) (Hughes et al., 1995). The Pr/Ph ratio versus DBT/Phenantheren ratio diagram (Figure 16) shows that the extract samples' source from Jurassic formations from the studied area descends from marine carbonate mixed environment (Figure 16). Sulfur-encompassing compounds can also be useful for differentiating fresh water from marine sediments since sea water contains more sulfates besides the existence of sulfate reducing bacteria (Killops & Killops, 2005).

Highly specific immature to mature range sterane isomerization is measured via m/z 217 or rather by GC-MS examination of  $C_{29}$  steranes (Peters *et al.*, 2005). Cis/ trans isomers in the  $C_{29}$  5 $\alpha$ , 14 $\alpha$ , 17 $\alpha$  (H) - steranes at C-20 controls 20S/ (20S + 20R) increase from zero to nearly



**Figure 13:**  $C_{31}/C_{30}$  hopane versus Pr/Ph for extracted source samples from Balad Oil Field, Central Iraq (Peters *et al.*, 2005).



**Figure 14:** Ternary diagram of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  regular steranes for the extracts from the Balad Oil Field, Central Iraq.



Figure 15: Relation of the diasterane/sterane ratios versus Ts/Tm for the extracted source samples from Balad Oil Field, Central Iraq.

0.50 (0.52-0.55 = stability) through cumulative thermal maturity (Seifert & Moldowan, 1986). Cis/trans isomer proportions built on the  $C_{27}$  and  $C_{28}$  steranes frequently display intervention via co-eluting peaks. Nevertheless, GC-MS extents permit practically decent precision for  $C_{27}$ ,  $C_{28}$ , and  $C_{20} 20S/(20S+20R)$ , entirely of which have comparable prospective as maturity constraints when restrained by this process. The 5 $\beta$ , 14 $\alpha$ , 17 $\alpha$  (H) 20R stereoisomer co-elutes with various other espiers were used in this ratio (Seifert & Moldowan, 1986). All the extracts of analyzed samples have not extended to equilibrium phase for the sterane cis/ trans isomers (Figure 17), and this is in a good agreement with the outcomes shown in Figure 6. The cis/trans isomers in the  $C_{_{31}}$ – $C_{_{35}}$  17 $\alpha$ -hopanes at C-22 arises prior to numerous biomarkers e.g. cis/trans isomers in the consistent steranes at C-20 and the equilibrium for  $C_{32}$  hopanes arises at approximately 0.5 % Ro (Peters et al., 2005).

#### CONCLUSIONS

Thirty four cuttings samples that belong to the Jurassic succession were studied from Ba-1 Well in Balad Oil Field, Central Iraq. The study performed using organic geochemistry techniques, and the following results are concluded:

- All studied sequences considered source rocks according to the amount of the TOC wt. %.
- The organic matter belongs to kerogen types III and II/III, with mainly reasonable generation prospective.
- The organic matter in the studied sequences, based on the Rock-Eval specific parameters, are mature and within oil generation window.
- The analyzed samples show the range of  $\delta^{13}C_{sat.}$  and  $\delta^{13}C_{aro}$  from -25.8 to -27.7 ‰ and -26.0 to -27.7 ‰ respectively, which indicates marine derived source materials. Similarly, canonical variable values also suggest marine source.
- Fingerprints of n-alkanes from source rock extracted materials show non-biodegraded hydrocarbons originated from marine source organic matter deposited



Figure 16: Cross plot between Pr/Ph and DBT/Phenanthrene ratios for the selected extracted cuttings within well Ba-1 in Balad Oil Field, Central Iraq.



**Figure 17:** Relationship between  $C_{29} \alpha \alpha \alpha 20S/(S+R)$  and  $C_{29} \alpha \beta \beta / (\alpha \beta \beta + \alpha \alpha \alpha)$  for samples from the Balad Oil Field, Central Iraq.

under anoxic conditions.

- The tricyclic terpane indicates that the analyzed samples are abundant marine carbonate rocks.
- High C<sub>24</sub> tetracyclic terpane in the samples can be a result of the carbonate source; also it might be attributed to terrigenous input.
- The high norhopane/hopane ratio in the samples is a result of anoxic carbonate source as well as the thermal maturity.
- High C<sub>27</sub> steranes in comparison to C<sub>28</sub> and C<sub>29</sub> in the samples indicates abundant marine depositional environment.
- Maturity indicator biomarkers prove that the existed organic matters in the studies sequences reached maturity stage, but the indicators did not reach the equilibrium phase.

ORGANIC GEOCHEMISTRY OF THE MIDDLE TO UPPER JURASSIC SOURCE ROCKS SUCCESSION IN BALAD-1 WELL

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