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Hydrocarbon Generation Potential of Chia Gara Formation in Three Selected Wells, Northern Iraq

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Abstract: In this study collected samples of Chia Gara Formation in Atrush, Shaikhan and Sarsang oilfields are used to geochemical characteristics of organic matter in this formation. This determination was based on Rock-Eval pyrolysis and Biomarker analyses. The Chia Gara Formation can be considered as good to excellent source rock; it's TOC content ranges from 1.14-8.5wt% with an average of 1.85%, 3.91%, and 6.94% in Atush-1, Mangesh-1 and Shaikhan-8 wells respectively. The samples of Chia Gara Formation contain kerogen type II. These properties are considered optimal for oil generation. The low oxygen index (OI) and pristane/phytane (Pr/Ph) ratios (Average 20.73, 0.61 respectively) and high hydrogen index (HI) (average 637.6) indicate that the formation was deposited under anoxic condition. According to regular sterane $(C_{27}\%, C_{28}\%, C_{29}\%)$ and terpanes ratios $(C_{29}/C_{30},$ C₃₁/C₃₀ hopane), the formation was deposited in marine environment.

The average value of the Carbon Preference Index (CPI) is one with T_{max} values of more than 430 $^{\circ}$ C; these indicate peak oil window for the selected samples. Overall, the 20S/(20S+20R), $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ steranes and 22R/(22R+22S)C₃₂homohopane, with Ts/ (Ts+Tm), and moretane/ hopane ratios point to a mature organic matter and to the ability of the formation to generate oil.

Keywords: Chia Gara Formation, Anoxic condition, Biomarker assemblage, Type II kerogen, Mature organic matter, Oil-prone

1 Introduction

Northern Iraq is one of the most suitable locations for deposition of carbonate rocks during Mesozoic Era. As global temperature raised good source rocks in Jurassic and Cretaceous periods are formed, Chia Gara Formation is the most important potential source rocks at these intervals [1]. Chia Gara is the most typical and widespread formation of the Tithonian-Berriasian subcycle [2]. This formation was first introduced by Wetzel in 1950 at its type locality in the Gara anticline, northern Iraq [3]. Lithologically, it consists of thin bedded limestone, argillaceous limestone and fissile black shale. This formation overlies the Barsarin Formation and underlies the Garagu Formation. To determine hydrocarbon potentiality of Chia Gara Formation, three wells which are Atrush-1, Shaikhan-8 and Mangesh-1 in three different blocks in Duhok basin are selected. The studied blocks include of Atrush, Shaikhan and Sarsang as shown in Figure 1 (a, b & c). The thickness of the formation is 196 m (depth from 932 m to 1128 m) in Atrush-1 well, 160 m (depth from 1320 m to 1480 m) in Shaikhan-8 well and 100 m (depth from 2180 m to 2280 m) in Mangesh-1 well. For this study, some organic geochemistry analyses are carried out in groups in order to identify redox conditions, type of organic matter, thermal maturity and hydrocarbon generation potential.

2 Geological Setting

The Zagros Fold Belt is a world-class hydrocarbon province in Iraq, which extends from the Iranian borders in the east to the Turkish borders in the north [1]. The northwestern segment of this belt became a region of interest for hydrocarbon generation and exploration. The studied boreholes are located within the High Folded Zone (Fig. 1a) which is a part of the northwestern segment of the Zagros Fold Belt that covers the deformed portion of the northeastern Arabian platform due to Cenozoic convergence between Eurasia and Arabia. All significant hydrocarbon discoveries in this region occur in compressional structures formed dur-

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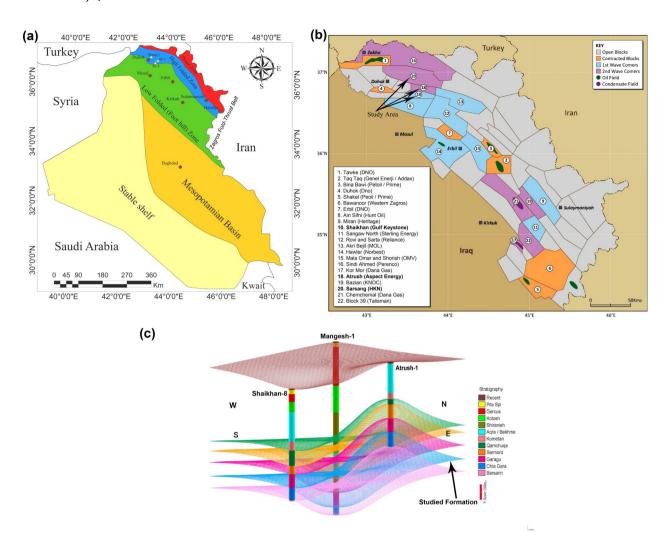


Figure 1: Location map for the northeast Arabian Platform in Iraq, which shows Zagros Thrust-Fold Belt with oil and gas field locations, including studied wells

ing this convergence. The subsidence in the developing Zagros foredeep induced a major phase of source rock evaluation and hydrocarbon expulsion [4]. The main source rock in Zagros Fold Belt during the Late Jurassic to Early Cretaceous period is Chia Gara Formation [5].

Atrush block is located within the Zagros sedimentary basin, 25 km. to the east of the Duhok city. Atrush structure is a fault-related fold that developed along a shallow thrust that is oriented in the east-west direction with the Zagros Orogenic Belt trend. The topography of Atrush block is similar to that of the Shaikhan block, the last one is located 60 km. to the southeast of Duhok city. Shaikhan structure is an anticline at the northwestern terminus of the Zagros Fold Belt and is affected by several faults. It lies in the highly prospective and productive oil province in northern Iraq. Sarsang block is located on the northern limb of the Gara anticline, 50 km to the northeast of Duhok city.

Structurally, this block is more complex than the Atrush and Shaikhan blocks. The Sarsang block is characterized by several faults that have horst and graben structures.

3 Material and method

Thirty cutting samples from Chia Gara Formation were selected and analyzed by Rock-Eval pyrolysis-6 in both Kurdistan Institution for Strategic Studies and Scientific Research/Sulaimaniya Governorate and Scientific Research Center-Soran University/ Erbil Governorate.

The samples were powdered and subjected to Rock-Eval pyrolysis to determine their TOC, volatile hydrocarbon (S1), remaining hydrocarbon generation potential (S2), and T_{max} value. This technique uses temperature

programmed heating of a small amount of rock sample (50 mg) in an inert atmosphere (nitrogen). The samples were heated from 300 °C for 3min to 650 °C at a rate of 25 °C/min; the instrument is equipped with two ovens for pyrolysis and combustion processes respectively. The hydrocarbons generated during a Rock-Eval analysis are monitored by a Flame Ionization Detector (FID) whereas the non-hydrocarbons compounds like $\rm CO_2$ and $\rm CO$ released during pyrolysis and oxidation stages are monitored by an infra-red detector.

Nine rock samples out of total thirty samples were analyzed by gas chromatography mass spectrometer (GC/MS) instrument. The analyses were performed at Organic Geochemistry Laboratory in Department of Geology and Petroleum Geology at University of Aberdeen/Scotland-UK.

Organic matter extraction (soxhlet extraction)

30 g of the crushed samples were weighed and extracted for forty eight hours (48 hrs.) with 93:7 dichloromethane/methanol (DCM/MeOH) via soxhlet-extraction. Then, the extracts were fractionated into saturated, aromatic and polar compounds using silica column chromatography. Saturated fractions were dissolved in certain amount of hexane and finally detected and analyzed by GC-MS apparatus. GC-MS analysis of the saturate fraction was performed using an Agilent 6890N GC. Relative abundances of n-alkanes (m/z 85), triterpanes (m/z 191) and steranes (m/z 217) were calculated by measuring peak heights.

Column Gas Chromatography (CC)

The extracted organic matter from soxhlet was fractionated by Column chromatography (CC). A short pipette stopped with a little clean cotton bud was loaded with clean silica gel (1/2 to 1/3 of column length). The silica gel about 60-120 mesh laboratory reagent was activated at 120 °C in oven for 24 hrs prior to use.The saturated fraction was eluted with 3 mL of n-hexane, the aromatic fraction with 3 mL mixture of n-hexane and DCM (3:1) v/v and polar fraction with 3 mL mixture of DCM and methanol (2:1) v/v. The eluted fractions were evaporated under a stream of dry nitrogen gas to remove the solvent. After removing the solvent the glass vials of each fraction were reweighed determine masses.

Gas chromatography-mass spectrometry (GC-MS) procedure

Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent Technologies 6890N Network GC system fitted with a 30.0 \times 250.0 μm i.d; film thickness 0.25 μm fused silica DB-5 column coupled to an AT 5975 quadrupole mass selector detector for identification (electron input energy 70 eV, source temperature 250 $^{\circ}$ C) with helium as carrier gas, normal initial flow: 1.3mL min-1. The saturated hydrocarbon fractions were analysed using an oven program at 60 $^{\circ}$ C (2.0 min) to 120 $^{\circ}$ C at 20 $^{\circ}$ C/min to 290 $^{\circ}$ C at 4 $^{\circ}$ C/min and held at 290 $^{\circ}$ C for 23 min. Data acquisition was controlled by CHEMSTATION software in ion selection monitoring (SIM) for saturated.

4 Results

4.1 Total Organic Carbon (TOC) and Rock-Eval Pyrolysis

The TOC and Rock-Eval analyses were conducted on thirty samples of Chia Gara Formation in Duhok basin. TOC values increase gradationally from 1.14-3.73 wt% in Atrush-1 well to 3.97-4.39 wt% in Mangesh-1 well and 4.85-8.5 wt% in Shaikhan-8 well (Table 1). Hydrogen index (HI) values in the three studied boreholes are too high ranging between 468-713 mg HC/g TOC. In contrast, values of oxygen index (OI) are too low (8-51 mg CO2/g TOC). The average T_{max} value of Chia Gara Formation is 434.7 °C. The average potential product value (GP) decreases from 49.81 mg HC/g TOC in Shaikhan-8 well to 27.92 and 11.0 mg HC/g TOC in Mangesh-1 and Atrush-1 wells respectively with the average production index (PI) value is 0.06. Production index values indicate the oil generative potential, but at low level to early mature stages.

4.2 Molecular composition and biomarker assemblages

4.2.1 Isoprenoids / n-alkanes (m/z 85) distribution

According to GC/MS analysis results, n-alkanes range from C_{14} to C_{35} in the analyzed samples. The distribution of n-alkanes of studied samples contains a much higher concentration of short molecular weight components than the long molecular weight n-alkanes (Fig. 2). The long-chain homologues are known to be derived from higher plant waxes [6]. Carbon preference index (CPI) is obtained by di-

Table 1: Pyrolysis results of Chia Gara Formation in the studied wells

Wells	Depth (m)	TOC (Wt %)	S ₁ (mg/g)	S ₂ (mg/g)	S ₃ (mg/g)	Tmax (°C)	HI (S ₂ /TOC*100)	ō	(S ₃ /TOC*100) GP (S ₁ +S ₂)	PI _{\$1/} (\$ ₁ +\$ ₂)	
AT-1	945	1.26	0.39	7.09	0.34	431	563	27	7.48	0.05	
	955	1.14	0.10	6.58	0.58	433	577	51	6.68	0.01	
	975	1.24	0.10	5.89	0.39	434	468	31	5.99	0.02	
	985	1.63	0.49	10.02	0.34	434	615	21	10.51	0.05	
	1000	2.51	0.81	14.52	0.37	436	578	15	15.33	0.05	
	1015	1.50	0.76	9.37	0.38	435	625	25	10.13	0.08	
	1035	1.50	0.84	10.01	0.36	433	667	24	10.85	0.08	
	1060	2.11	0.83	11.61	0.40	436	550	19	12.44	0.07	
	1100	3.73	1.32	18.29	0.45	437	544	12	19.61	0.07	
Sh-8	1333	6.81	2.76	44.92	1.00	434	660	15	47.68	0.06	
	1345	6.94	2.66	46.92	0.92	435	676	13	49.58	0.05	
	1360	7.04	2.65	49.40	1.07	436	702	15	52.05	0.05	
	1372	6.24	2.19	43.71	1.11	436	700	18	45.90	0.05	
	1384	7.47	2.53	52.58	0.83	437	704	11	55.11	0.05	
	1396	7.37	2.68	52.40	0.87	436	711	12	55.08	0.05	
	1408	8.50	2.91	60.00	0.84	436	706	10	62.91	0.05	
	1420	7.11	2.55	43.33	2.15	431	609	30	45.88	0.06	
	1432	4.89	2.44	29.22	1.16	431	598	24	31.66	0.08	
	1444	4.85	2.12	34.29	0.57	437	707	12	36.41	0.06	
	1456	8.23	2.48	56.21	0.69	435	683	8	58.69	0.04	
	1468	8.28	2.40	56.58	0.75	437	683	9	58.98	0.04	
	1480	6.54	2.15	45.46	0.56	437	695	9	47.61	0.05	
Mang-1	2186	3.97	4.00	18.44	1.75	436	464	44	22.45	0.18	
	2198	3.91	2.38	19.44	1.95	439	497	50	21.82	0.11	
	2213	3.84	2.23	27.27	0.64	434	710	17	29.50	0.08	
	2225	4.00	2.63	28.28	0.81	433	707	20	30.91	0.09	
	2240	3.95	2.23	26.28	0.89	433	665	23	28.51	0.08	
	2255	3.79	2.21	27.01	0.73	432	713	19	29.22	0.08	
	2270	4.39	2.48	30.00	0.72	435	683	16	32.48	0.08	
	2280	3.94	2.24	26.30	0.88	432	668	22	28.54	0.08	

TOC: Total Organic Carbon, wt.%; S_1 : Volatile hydrocarbon (HC) content, mg HC/g rock; S_2 : Remaining HC generative potential, mg HC/g rock; S_3 : Carbon dioxide content, mg CO₂ / g rock, **Tmax**: Maximum Temperature. **HI**: Hydrogen Index = S_2 /TOC*100 mgHC/g TOC; **OI**: Oxygen Index= S_3 /TOC*100, mgCO₂/g TOC; **GP**: Genetic Potential= (S_1+S_2); **PI**: Production Index= [$S_1/(S_1+S_2)$]

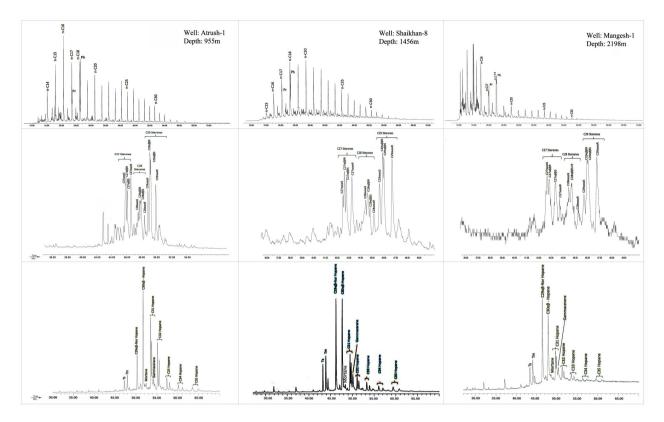


Figure 2: Molecular compositions, Isoprenoids/n-alkanes (m/z 85) and Biomarker assemblages, Steranes (m/z 217) and Terpanes (m/z 191) distribution of Chia Gara Formation in the studied wells

viding the sum of the odd carbon-numbered alkanes (C_{25} - C_{33}) by the sum of the even carbon numbered alkanes (C_{24} - C_{34}) [7], and the observed values are in between 0.98-1.09, except in one sample, which is 0.89 and this is low as compared to the other samples. The isoprenoid hydrocarbons pristane (Pr) and phytane (Ph) are present in all analyzed samples. Generally Chia Gara Formation has low Pr/Ph ratios ranging from 0.39 to 0.96. Pr/n- C_{17} and Ph/n- C_{18} ratios range from 0.48 to 1.13 and 0.76 to 1.59 respectively (Table 2). These values are used to determine the type of organic matter and deposition conditions for the studied samples.

4.2.2 Steranes (m/z 217) distribution

Steranes are a class of tetracyclic, saturated biomarkers constructed from six isoprene subunits (nearly C_{30}) [8]. They originate from sterols, which are important membrane and hormone components in eukaryotic organisms. The most commonly used steranes are in the range of C_{26} - C_{30} and are detected using mass/charge 217 mass chromatograms [8]. The regular steranes (C_{27} , C_{28} and C_{29}) are found in all samples. The samples have high per-

centage value of C₂₉ and C₂₇, especially in Atrush-1 and Shaikhan-8 wells and their abundances are ordered as C₂₉ >C₂₇>C₂₈(Fig. 2). The dominance of C₂₉ and C₂₇ homologs indicates an open marine organic matter input [9–11].The values of 20S/(20S+20R) C₂₉ and $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$) C₂₉ vary from 0.32 to 0.48 and 0.55-0.61 with an average value of 0.40 and 0.58 respectively; these two parameters are used to determine maturation level of Chia Gara Formation.

4.2.3 Terpanes (m/z 191) distribution

The detectable hopanes ranged from C_{27} to C_{35} in all of the hopane bearing samples. The $C_{29}17\alpha$, 21β (H)-30-norhopane and $C_{30}17\alpha$, 21β (H)-hopane were the most abundant. The biomarkers parameters such as high C_{29}/C_{30} 17α (H) hopane ratio can be considered as the evidence of carbonate-rich source rocks [12]. In this study the relative C_{30} nor-hopane abundance is typically more than C_{30} hopane (Fig. 2). The values of C_{35}/C_{34} and C_{29}/C_{30} hopane are more than 0.8 and 0.6 respectively. Most oils from marine carbonate source rocks show high C_{35}/C_{34} hopane (>0.8) combined with high C_{29}/C_{30} hopane (>0.6) (Table 2) [8]. The analyzed samples contain detectable

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Table 2: Gas Chromatography/ mass spectrometer results of Chia Gara Formation in the studied wells

Isoprenoid /n-alkane						Sterane					Hopane						
Wells	Depths (m)	Pr/Ph	Pr/n-C ₁₇	Ph/ <i>n</i> -C ₁₈	ā	C ₂₇ %	C ₂₈ %	C ₂₉ %	20S/(20S+20R) C ₂₉	ββ/(ββ+αα) С29	C3122R/ C30 Hopane	C_{29 norhopane $/C_{30}$ Hopane	Ts / (Ts+Tm)	Mortane index C ₂₉	15	22S/(22R + 22S) C ₃₂	
	955	0.45	0.48	1.04	0.89	43	19	38	0.48	0.61	0.49	0.65	0.39	0.07	0.09	0.61	
	985	0.73	0.67	0.76	0.99	37	18	45	0.42	0.59	0.43	1.15	0.36	0.08	0.12	0.59	
7	1060	0.77	0.95	1.59	1.00	35	17	48	0.39	0.60	0.47	1.05	0.37	0.07	0.12	0.58	
AT-1	1100	0.42	0.64	1.35	0.98	43	17	40	0.45	0.60	0.47	0.60	0.41	0.08	0.11	0.59	
	1345	0.47	0.75	1.30	1.01	35	17	48	0.40	0.55	0.36	1.06	0.33	0.06	0.11	0.60	
Sh-8	1408	0.39	0.82	0.92	1.03	37	15	48	0.41	0.57	0.38	1.06	0.34	0.06	0.12	0.59	
S	1456	0.63	0.69	0.79	1.02	33	17	50	0.41	0.55	0.31	1.00	0.40	0.05	0.16	0.60	
Mang-1	2198	0.70	1.13	1.12	1.08	26	18	56	0.32	0.56	0.38	1.24	0.42	0.12	0.18	0.59	
Маі	2255	0.96	0.61	0.94	1.09	27	19	54	0.37	0.55	0.43	1.25	0.43	0.11	0.19	0.58	

Pr: Pristane

Ph: Phytane

CPI: Carbon preference index= $\frac{1}{2}(C_{25}:C_{33}/C_{24}:C_{32}) + (C_{25}:C_{33}/C_{26}:C_{34})$

GI: Gammacerane index = (Gammacerane/Gammacerane+ C_{30} $\alpha\beta$)

Moretane Index=C₃₀ moretane/C₃₀ hopane

Ts: $18\alpha(H)$, $21\beta(H)$ -22, 29, 30-trisnorneohopane, Ts, (C_{27})

Tm:17 α (H),21 β (H)-22,29,30-trisnorhopane, Tm, (C₂₇)

 C_{32} 17 α (H),21 β (H)-30,31-bishomohopane (22S)

 C_{32} 17 α (H),21 β (H)-30,31-bishomohopane (22R)

 C_{29} 5 α (H),14 α (H),17 α (H) sterane (20S)

 C_{29} 5 α (H),14 β (H),17 β (H) sterane (20R)

 C_{29} 5 α (H),14 β (H),17 β (H) sterane (20S)

 C_{29} 5 α (H),14 α (H),17 α (H) sterane (20R)

amounts of C_{31} hopanes. The gammacerane index is calculated using the peaks of gammacerance and C_{30} $\alpha\beta$ hopane identified on m/z 191. This parameter is very specific for the hypersaline environment [13]. The values of gammacerane index ranges from 0.09 to 0.19 (low value). The ratio of 17β ,21 α (H)-moretanes to their corresponding 17α ,21 β (H)-hopanes decreases with increasing maturity from 0.8 in immature bitumens to <0.15 in mature source rocks and oils to a minimum of 0.05 [14, 15]. Biomarker maturity ratio 22S/(22S +22R) describing the conversion of the biological 22R to the geological 22S configuration of homohopane molecules was calculated. Typically, this ratio is calculated for the C_{32} 17 α -homohopanes, which varies from 0.58 to 0.61 (Table 2). The Ts/ (Ts+Tm) ratio (sometimes reported as Ts/Tm) is extensively applied in petroleum geochem-

istry as maturity parameter [16]. It is calculated for all samples in Chia Gara Formation which ranging between 0.33-0.43.

5 Discussions

5.1 Quantity of organic matter

The quantity of organic matter is usually expressed as Total Organic Carbon [13]. The Total Organic Carbon (TOC, wt%) of a sedimentary rock is defined as the weight percentage of organic carbon in the rock [17]. Typical oilprone, marine source rocks contain 2-5 wt% of TOC. Chia Gara Formation in Duhok basin is organically rich showing

TOC values ranging between 1.14-3.73 and 3.79-4.39 wt% in Atrush-1 and Mangesh-1 wells respectively. The high TOC content is mainly due to good preservation of organic matter in marine environment under reducing conditions. Similar TOC values within Chia Gara Formation have been recorded in Shorish-1 well in the Erbil Governorate [18], but strata in the range of 5-20 % are known to occur in high yield petroleum system [19] which is the case in Shaikhan-8 well that shows values of TOC between 4.85-8.5 wt% (Fig. 3). Same high TOC content with values of more than 5% has been recorded in Hr-1, Bj-1 and Tk-3 wells in the Kirkuk and Tkrit Governorates in northern Iraq [20]. In Atrush-1 well, the values of S1, S2, and TOC are low compressive in contrast to the other sections, the lithological compositions were directly affected the organic matter richness of the formation, in Shaikhan-8 well it consists of alternation between very thin black shale and argillaceous limestone, whereas in Mangesh-1 well the formation is mainly composed of argillaceous limestone and little limestone, while in Atrush-1 well the lower part is argillaceous limestone and limestone increases towards the upper part of the formation (Fig. 3). In addition, the configuration of the basin can affect the distribution of the organic matter throughout the basin. It is thought that towards the center of the basin, the percentage of the TOC is possibly increases. This configuration of the basin may show that the organic productivity in the area around the Atrush-1 is low in comparison to the other two localities (The Atrush area might be away from the center of the basin in comparison to Shaikhan and Sarsang areas).

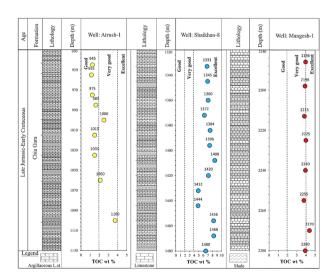


Figure 3: Total Organic Carbon (TOC wt%) of Chia Gara Formation in the studied wells

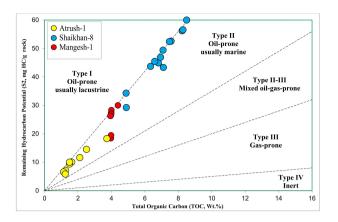


Figure 4: TOC vs. S2 showing type II kerogen of Chia Gara Formation in the studied wells

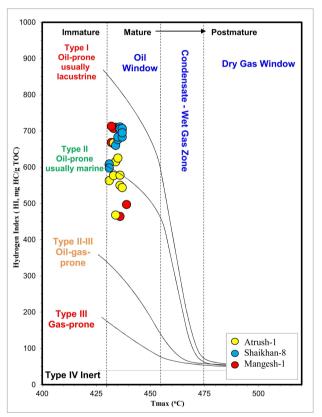


Figure 5: T_{max} vs. HI showing type II kerogen and early mature-peak oil window of Chia Gara Formation in the studied wells

5.2 Quality of organic matter

The type of organic matters controls the type of the kerogen formed later, which in turn controls the type of hydrocarbon generated subsequently. This means some kerogens are only oil prone (type I), some are only gas prone (type III), and others are oil, gas-prone (type II) [21]. To determine the organic matter type of Chia Gara Forma-

tion S2 vs. TOC [22] and HI vs. T_{max} kerogen classification diagrams were manipulated [23]. In both diagrams, samples of Chia Gara Formation are plotted in type II kerogen field (Figs. 4 and 5). Type II kerogen is from algae, spores, pollen and steam cuticles of land plants. On the other hand, the Pr/n-C17 vs. Ph/n-C18 diagram shows that the samples derived from Chia Gara Formation are marine algal which represented by type II kerogen (Fig. 6). Regionally most of the recent literatures claimed this type of kerogen (type II) for Chia Gara Formation in different parts of Iraq, in Shorish-1 well Erbil province [18]; in Kirkuk-109 (K109) well Kirkuk province [24, 25], in outcrop at Banik area in Duhok province [26]. This type of kerogen can be type II-S kerogen [27], because the most of the Jurassic source rocks in Iraq are commonly comprised of carbonates rather than pure shaly sediments. As published in literature sulfur content in type II kerogen is generally higher than in type I or type III kerogens and may be particularly high in sulfur-rich rocks. Type II-S kerogens are derived from marine carbonate environments. The reason for this is that clay-poor carbonate source rocks contain insufficient iron to utilize the available sulfide, much of which becomes incorporated into the kerogen network. The C_{29}/C_{30} hopane ratios of the studied samples are relatively more than one in most of the analyzed samples (except two samples in well Atrush-1) which can confirm that the kerogen type II-S (from a carbonate source rock).

5.3 Depositional environment

The most widely used biomarker parameter for the assessment of redox (reducing and oxidizing) conditions during sediment accumulation is pristane/phytane ratio [28]. According to [8] Pr/Ph ratios substantially below unity can be taken as an indicator of petroleum origin and/or highly reducing depositional environments. Certain depositional environments and lithologies are associated with specific values of the Pr/Ph ratio [29]. Values less than 1 have been associated with marine carbonates, between 1 and 3 with marine shales, and larger than 3 with non-marine shales and coals [30]. In the current study the values of the Pr/Ph ratio are less than one (Table 2). This indicates that Chia Gara Formation was deposited under reducing environment and lithologically is associated with marine carbonate rocks [30]. The marine source of organic matter deposited under reducing conditions is also supported by the position of the samples in the plot of pristane/n- C_{17} versus phytane/n-C₁₈ (Fig. 6). Although the low oxygen index (OI) values show that the formation was deposited under reducing conditions. Similar conclusions concerning the

depositional environment of this formation have been recently reported by [20] in Hr-1, Bj-1 and Tk-3 wells northern Iraq. Regardless of thermal maturity, the values of carbon preference index (CPI) in all analyzed samples are around one and some of the values are less than this figure, this indicates marine and anoxic conditions. Samples of Chia Gara Formation are plotted in the open marine area on the $C_{27}\%$, $C_{28}\%$, and $C_{29}\%$ regular steranes ternary diagram especially in Atrush-1 and Shaikhan-8 wells with few slides of the samples in the Mangesh well (Fig. 7) [9]. Gammacerane index varies between 0.09-0.19, no hypersaline condition of deposition for the initial organic matter within the analyzed samples has been detected, it could be assessed that the formation is deposited in anoxic basin (Fig. 8) [31].

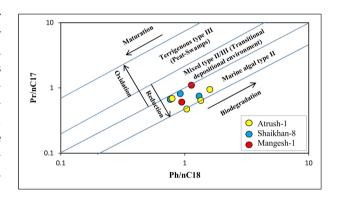


Figure 6: Phytane/n- C_{18} vs. pristane/n- C_{17} showing variation of organic matter type, thermal maturity and depositional environment of Chia Gara Formation in the studied wells

5.4 Thermal maturation

Maturity history of Chia Gara Formation is modeled by [32] in Hr-1 and Aj-12 wells, northern Iraq; the results indicate that the formation is thermally mature within the peak oil window. The thermal maturation level of Chia Gara Formation in the current study is deduced from the T_{max} values. T_{max} is the temperature at which the maximum amounts of S2 hydrocarbons will generate during rock-Eval pyrolysis. T_{max} depends on the type of kerogen that presents in the source rock. Values between 430-450 °C indicate "oil window" condition (mature organic matter) [33]. In the studied oilfields, Chia Gara Formation is thermally mature source rock and ranges from early-mature to peak oil-generation window (T_{max} values ranges between 431-439 °C) (Table 1, Fig. 5). In addition, Chia Gara Formation samples with T_{max} values up to 430 °C have been detected

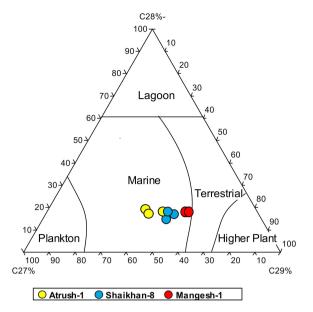


Figure 7: Ternary diagram of C_{29} %, C_{28} %, C_{27} % regular steranes showing marine depositional environment of Chia Gara Formation in the studied wells

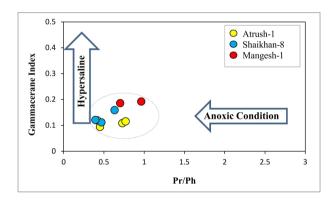


Figure 8: Pristane/phytane (Pr/Ph) vs. Gammacerane Index (GI) showing anoxic condition of Chia Gara Formation in the studied wells

in outcrops in the northern Iraq [26, 34]. Also biomarker maturity parameters are used to determine the maturity level of the formation. The values of CPI in nine rock samples is close to one express mature sample [35]. Although, the concentration of the even carbon number is higher than odd carbon number, indicates that the organic matter in the samples of the formation is mature [36]. Isoprenoids/n-alkanes (Pr/n- C_{17} and Ph/n- C_{18}) ratios provide valuable information on biodegradation, maturation and diagenetic conditions [8]. According to the values of the isoprenoid/n-alkane, samples of the formation have not been affected by biodegradation process, and thermally they are mature (Fig. 6). This study determined the maturial

rity by following the 20S/(20R +20S) C_{29} and $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ sterane values [37, 38]. According to these relationships, samples of Chia Gara Formation are located within the early mature to peak oil window (Fig. 9). The obtained data of the C_{29} Moretane index $(17\beta 21\alpha \text{ norhopane}/17\alpha 21\beta)$ norhopane) are in the range (0.05-0.12) (Table 2) indicating mature source rocks [12]. Increasing Ts relative to the Ts/ (Ts + Tm) hopane ratios together with the decrease in the C₂₉ Moretane index are shown in Figure 10. Equilibrium values for 20S/(20S+20R) C₂₉ sterane ratios are in the range of 0.32-0.48, whereas equilibrium values for $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ sterane and 22S/(22S+ 22R) C₃₂ homohopane ratios are 0.55-0.61 and 0.58-0.61 [12, 31]. These values indicate that the analyzed samples have at least reached the early stage of thermal maturity and peak oil window (Fig. 11).

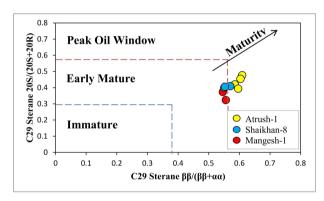


Figure 9: Cross plot of 20S/(20S+20R) vs. $\beta\beta$ S/ ($\beta\beta$ S+ $\alpha\alpha$ R) C₂₉ steranes showing early mature- peak oil window of Chia Gara Formation in the studied wells

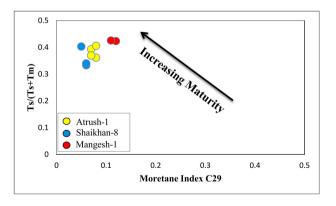


Figure 10: Cross plot of Ts/(Ts+Tm) vs. Moretane Index C₂₉ showing maturity of Chia Gara Formation in the studied wells

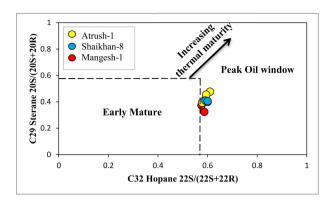


Figure 11: Cross plot of (20S/20S+20R) C₂₉ Sterane vs. 22S/(22S+22R) C₃₂ Hopane showing maturity and potentiality of Chai Gara Formation in the studied wells

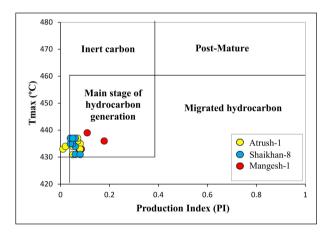


Figure 12: Plot of pyrolysis T_{max} vs. production index (PI), showing the maturation and nature of the hydrocarbon products of Chia Gara source rock in the studied wells

5.5 Hydrocarbon generation potential

The most important factor controlling the generation of oil and gas is the hydrogen content of the organic matter (OM), Genetic potential represents the amount of petroleum (oil and gas) that kerogen able to generate [39]. If the value of genetic potential is more than six, it can be considered as a good source rocks for evaluation but if the value is less than two, it is a poor source rock and cannot be evaluated [40]. Generation potential of the studied samples derived from Chia Gara Formation is more than six (Table 1) and this is an indicator of very good to excellent generation potential; in addition to, samples with TOC content greater than 1% with hydrogen index more than 300 mg HC/g TOC and containing a significant amount of type II kerogen can generate oil [41], these properties are present in all analyzed samples, indicates that the formation is suitable for commercial hydrocarbon generation. Moreover, rock-Eval

 T_{max} and the production index (PI) values indicate that most of the analysed samples are within the main stage of hydrocarbon generation (Fig. 12).

6 Conclusions

The hydrocarbon genetic potential of Chia Gara Formation seemed to be dependent on TOC wt% and maturity in the tested sections, accordingly, all sections have good-excellent potential to generate oil due to high enough maturity level reached and excellent marine organic matter content.

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References

- Jassim S.Z., Goff J.C., Geology of Iraq. Brno, Czech Republic: Dolin, Prague and Moravian Museum, 2006
- [2] Buday T., The Regional Geology of Iraq, volume 1, Stratigraphy and pale geography, Dar Al-Kutub publishing house, university of Mosul, Iraq, 1980
- [3] Bellen R.C., Dunnington H.V., Wetzel R., Morton D., Lexique Stratigraphic International. Asie, Fasc. 10a, Iraq, Paris, 1959
- [4] Joseph M.E., Grenville L., Luke F., George Y., Geologic Evolution of the Iraqi Zagros, and its Influence on the Distribution of Hydrocarbons in the Kurdistan Region. AAPG Bull., 2015, 99, 231-272. DOI: 10.1306/06271413205
- [5] Hakimi M.H., Najaf A.A., Origin of crude oils from oil-fields in the Zagros Fold Belt Basin, Southern Iraq, and related to organic matter input and paleoenvironmental conditions. Marine Petl. Geol., 2016, 78, 547-561. DOI: 10.1016/j.marpetgeo.2016.10.012
- [6] Eglinton G., Hamilton, R.J., Leaf epicuticular waxes, 1967, 156, 1322-1335. DOI: 10.1126/science.156.3780.1322
- [7] Taylor G.H., TeichmUller M., Davis A., Diessel C.F.K., Littke R., Rober P., Organic petrology. Handbook, Berlin; Stuttgart: Gebrudre Borntraeger, 1998
- [8] Peters K.E., Walters C.C., Moldowan J.M., The Biomarker Guide, 2nd Edi., Volume I, Biomarkers and Isotopes in Petroleum Systems and Human History, United Kingdom at the Cambridge University Press, 2005
- [9] Huang W.Y., Meinschein W.G., Sterols as ecological indicators. Geochimica et Cosmochimica Acta, 1979, 43, 739 –745.

- [10] Czochanska Z., Gilbert T.D., Philp R.P., Sheppard C.M., Weston R.J., Wood T.A., Woolhouse A.D., Geochemical application of sterane and triterpane biomarkers to a description of oils from the taranaki basin in New Zealand. Org. Geochem., 1988, 12, 123-135. DOI.org/10.1016/0146-6380 (88)90249-5
- [11] Abrams M.A., Apanel A.M., Timoshenko O.M., Kosenkova N.N., Oil families and their potential sources in the northeasthern timan pechora basin, Russia. AAPG Bull., 1999, 83, 553-577. DOI: 10.1306/00AA9BF6-1730-11D7-8645000102C1865D
- [12] Waples D.W., Machihara T., Biomarkers for Geologists-a Pratical Guide to the Application of Steranes and Triterpanes in Petroleum Geology. AAPG, 1991, Methods in Exploration Series, No: 9
- [13] Hunt J.M., Petroleum geochemistry and geology. 2^{nd} Edition, Cambridge, USA, 1996
- [14] Mackenzie A.S., Patience R.L., Maxwell J.R., Vandenbroucke M., Durand B., Molecular parameters of maturation in the toarcian shales, paris Basin-1. Changes in the configurations of cyclic isoprenoid alkanes and triterpanes. Geochim. Cosmochim. Acta, 1980, 44, 1709-1721. DOI.org/10.1016/0016-7037(80)90222-7
- [15] Seifert W.K., Moldowan J.M., The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. Phy and Chem of the Earth, 1980, 12, 229-237. DOI.org/10.1016/0079-1946(79)90107-1
- [16] Farrimond P., Bevan J.C., Bishop A.N, Hopanoid hydrocarbon maturation by an igneous intrusion. Org. Geochem., 1996, 25, 149-164. DOI.org/10.1016/S0146-6380 (96)00128-3
- [17] Peters K.E., Guidelines for evaluating petroleum source rock using programmed pyrolysis. AAPG Bull., 1986, 70, 318-329. DOI: 10.1306/94885688-1704-11D7-8645000102C1865D
- [18] Sachsenhofer R.F., Bechtel A., Gratzer R., Rainer T.M., Source-rock maturity, hydrocarbon potential and oil-source-rock correlation in well shorish-1, Erbil province, north of Iraq. J. of Petrl Geol., 2015, 38, 357-382. DOI.org/10.1111/jpg.12617
- [19] Walters C.C., The origin of petroleum. In: Hsu C.S, Robinson P.R (Ed), Practical Advances in Petroleum Processing. Springer, 2006, 79-101
- [20] Mohialdeen I.M.J., Hakimi M.H., Al-Beyati F.M., Geochemical and petrographic characterization of Late Jurassic-Early Cretaceous Chia Gara Formation in Northern Iraq: palaeoenvironment and oil-generation potential. Marine Petrl Geol., 2013, 43, 166-177. DOI.org/10.1016/j.marpetgeo.2013.02.010
- [21] Peters K.E., Cassa M.R., Applied Source Rock Geochemistry. In: Magoon L.B., and Bow W.G (Ed). The petroleum system- from source to trap, chapter 5. AAPG Memoir, 1994, 93-120
- [22] Langford F.F., Blanc-Valleron M.M., Interpreting rock-eval pyrolysis data using graphs of pyrozilable hydrocarbons vs. Total organic carbon. AAPG Bull., 1990, 74, 799-804.
- [23] Mukhopadhyay P.K., Wade J.A., Kruge M.A., Organic facies and maturation of Jurassic/Cretaceous rocks, and possible oilsource rock correlation based on pyrolysis of asphaltenes, scotian basin, Canada. Org. Geochem., 1995, 22, 85-104. DOI.org/10.1016/0146-6380(95)90010-1
- [24] Mohialdeen I.M.J., Hakimi M.H., Geochemical characterisation of Tithonian-Berriasian Chia Gara. Organic-rich rocks in northern Iraq with an emphasis on organic matter enrichment and the relationship to the bioproductivity and anoxia conditions. Asian Earth Sci., 2016, 116, 181-197. DOI.org/10.1016/j.jseaes.2015.11.004

- [25] El Beialy S.Y., Al-Tarif A.M., Mahdi A.Q., El Diasty W.S.h., Integrated organic geochemistry with palynofacies analysis of the Chia Gara Formation in the Kirkuk and Hamrin oilfields, North Iraq. Kirkuk Uni J., 2016, 11, 315-330
- [26] Edilbi A.N., Stratigraphy and Petroleum Potential of Chia Gara Formation (Tithonian- Berriasian) in Selected Sections in North Iraq, Msc. Thesis. Salahaddin University., 2010
- [27] Greenwood P.F., Mohammed L., Grice K., McCulloch M., Schwark L., The application of compound-specific sulfur isotopes to the oil-source rock correlation of Kurdistan petroleum. Org Geochem., 2018, 117, 22-30. DOI.org/10.1016/j.orggeochem.2017.11.016
- [28] Shanmugam G., Significance of coniferous rain forests and related oil, Gippsland Basin, Australia. AAPG Bull., 1985, 69, 1241-1254. DOI: 10.1306/AD462BC3-16F7-11D7-8645000102C1865D
- [29] Hughes W.B., Holba A.G., Dzou L.I.P., The ratio of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum in source rocks. Geochim Cosmochim Acta, 1995, 59, 3581-3598. DOI.org/10.1016/0016-7037(95)00225-0
- [30] Koopmans M.P., Rijpstra W.I.C., Klapwijk M.M., Leeuw J.W., de Lewan M.D., A thermal and chemical degradation approach to decipher pristane and phytane precursors in sedimentary organic matter. Organ. Geochem., 1999, 30, 1089-1104. DOI.org/10.1016/S0146-6380 (99)00088-1
- [31] Peters K.E., Moldowan J.M., The Biomarker Guide, Interpreting molecular fossils in petroleum and ancient sediments, Prentice Hall, 1993.
- [32] Hakimi M.H., Mohialdeen I.M.J., Al-Ahmed A.A., El-Nady M.M., Thermal modeling and hydrocarbon generation of the Late Jurassic-Early Cretaceous Chia Gara Formation in Iraqi, northern Zagros Fold Belt, Egypt. J. Petrol., 2017, 1-13. DOI.org/10.1016/j.ejpe.2017.10.007
- [33] Espitalie J., Marquis F., Barsony I., Geochemical logging. In Voorhees K.J (Ed), Analytical pyrolysis: techniques and application. London: Butterworths, 1984, 276-304. DOI.org/10.1016/B978-0-408-01417-5.50013-5
- [34] Odisho K.Y., Othman R.S., Preliminary geochemical evaluation of hydrocarbon source rocks in northern part of Iraq. Iraq Geol J., 1992, 25, 136-153
- [35] Maioli O.L., Rodrigues K.C., Knoppers B.A., Azevedo D.A., Distribution and sources of aliphatic and polycyclic aromatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems, Contin. Shelf Res., 2011, 31, 1116-1127. DOI.org/10.1016/j.csr.2011.04.004
- [36] Powell T.G., McKirdy D.M., Relationship between ratio of pristane to phytane, crude oil composition and geological environment. Nature, 1973, 243, 37-39. DOI:10.1038/physci243037a0
- [37] Waples D.W., Machihara T., Application of sterane and terpanes biomarkers in petroleum exploration. Bull. of Canadian Petrol. Geol., 1990, 38, 357-380
- [38] Bacon C.N., Calver C.R., Boreham C.J., Lenman D.E., Morrison K.C., Revill A.T., Volkman J.K., The Petroleum Potential of Onshore Tasmania. Geol Surv Bull., 2000, 71, 1-93
- [39] Tissot B.P., Welte D.H., Petroleum Formation and occurrence: A new approach to oil and gas exploration. 2nd Edi: Springer- Verlage, Berlin, 1984
- [40] Tissot B. P., Welte D.H., Petroleum formation and occurrence: a new approach to oil and gas exploration. Springer-Verlag, Berlin, 1978

[41] Bordenave M.L., Espitalié L., Leplat P., Oudin J.L., Vandenbroucke M., Screening techniques for source rock evaluation. In: Bordenave ML (Ed.), Applied Petroleum Geochemistry. Editions Technip, Paris, 1993, 217-278