Petroleum potentiality of the Balambo Formation in Bekhme and Razan sections, Kurdistan region, northeastern Iraq

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ABSTRACT

Balambo Formation (Early Cretaceous) had been studied in Razan and Bekhme sections, Erbil Governorate, Kurdistan Region-Iraq, to determine the hydrocarbon generation potentiality for the studied rocks. The samples were analyzed for TOC, Rock Eval pyrolysis and GC-MS technique. The Balambo Formation’s TOC wt. % content is relatively high, ranging between 0.95 to 7.59 wt.% (average 2.91 wt.%). The Formation has the potentiality to generate gas and oil owing to its suboxic-anoxic depositional environment, marine origin organisms, suitable maturity level, and the type of kerogen is predominantly types III and subordinate amount of mixed type II-III according to the Rock-Eval pyrolysis data and isoprenoid/n-alkane. The C₂₇%, C₂₈% and C₂₉% regular steranes distribution suggested the studied formation is deposited in marine environment. The samples were proven to be mature based on the ratios of the Tmax, steranes 20S/(20S+20R)C₂₉ to ββS/(ββS+ααR)C₂₉ steranes and C₃₂₂₂S/(22S+22R) hopane. Although the Ts/(Ts+Tm) ratio data point to an early mature stage, vitrinite reflectance predictions ranged from 0.55 to 0.75%, once more pointing to a mature stage.

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1. Introduction

According to Jassim and Buday [1], one of the Cretaceous formations with an important thickness and extensive distribution in northern Iraq is the Balambo Formation. The formation is a carbonatesiliciclastic unit composed of grayish-gray-black marly limestones and thin, dolomitic limestones that alternate with gray-black shales that are thin and medium-bedded. Wetzel initially characterized the Balambo Formation in 1947 from the Sirwan Valley, which is located close to the line between the High Folded Zones and Imbricated Zone in northern Iraq [2]. Al-Dulaimi and Mahdi [3] claimed that the formation deposited in Late Albian-Early Turonian based on richness and variety of Radiolarians, which were investigated from well Jambur-18. The Ratawi, Sulaiy, and Balambo formations are among sequences that might create excellent source rocks, but the bulk of the Cretaceous rock units found in Iraq's petroleum system are reservoirs, including the Qamchuqa, Dokan, Kometan, and Shiranish formations [4]. Some studies have evaluated the potential of source rocks and the capacity of Cretaceous sediments to produce petroleum, one research was carried out by Sarraj and Mohialdeen [5] which studied Balambo Formation in Sulaimani Governorate. According to the findings, the formation has type II kerogen (oil prone), and type II/III (oil/gas prone) kerogen and based on the GC-MS parameters the samples are mature, although Al-Habba and Abdullah [6] in their study entitled, a geochemical study of hydrocarbon source rocks in northwestern Iraq, indicated that the Balambo Formation can be considered excellent source rock. One of the Cretaceous carbonate rocks selected for this study is Balambo Formation which covers an extensive region and has a long geologic age. The main goals in this investigation are determining petroleum potentiality of Cretaceous rock (Balambo Formation) in both Bekhme and Razan in High Folded and Imbricates Zones, respectively in northern Iraq using geochemical analyses such as rock Eval-pyrolysis and gas chromatography-mass spectrometer.

2. Geological Setting

Two surface sections (outcrops) of the Balambo Formation in two different tectonic zones (Imbricated and High Folded zones) were chosen for the purpose of the current study (Fig. 1). The distance between the two selected sections is approximately 50 km. The first section is known as Razan which is located within Erbil Governorate in northeastern Iraq. It was chosen near Razan Village in the Imbricated Zone and nearly 12 km west of Choman City, at Latitude 44˚ 47′ E and Longitude 36˚ 35’ N. Fig. 2. The second section is Bekhme section in Gelly-Bekhme beside the main road to Bekhme dam tunnel and located about 92 km north east of the Erbil City at Latitude 44˚ 16’ E and Longitude 36˚ 41’ N (Fig. 2).

![Bekhme section](image1)

![Razan Section](image2)

*Fig. 1: Outcrops of the Balambo Formation in Razan and Bekhme sections.*

The formation is widely exposed in the cores and limbs of several anticlines in Imbricate and High Folded zones and consists of thin to medium bedded limestone with interbedded of dark grey marl and shale [2]. In both the studied sections, the Balambo Formation underlies by the Chia Gara Formation and...
overlies by the Qamchuqa Formation [7, 6]. The Balambo Formation was divided into two units, the lower unit represents the Valanginian- Albian and the Upper unit which represents the Cenomanian-Turonian [7, 6]. Upper part of the Balambo Formation is equivalent to Sarvak Formation in Iran to the east of the Zagros Mountain [8]. Structurally, the studied sections of the Balambo Formation are situated in the Imbricated and High Folded zones (Fig. 2). The Balambo Formation from Razan section exists in the Imbricated Zone of northeastern part of Iraq and exposed at the northeastern limb of Spibaliates Anticline, it is asymmetrical anticline with a fold axis of NW-SE trend. The anticline is double plunging, and the length is around 26 km, the NE limb has a steep dip angle while the SW limb in some places has dip angle of 50° approximately. This anticline exposes the Jurassic rocks in the core such as Sarki and Sehkanian formations. While Cretaceous rocks cropped out on the limbs of the anticline, Balambo and Qamchuqa formations [9]. On the other hand, Bekhme section is exposing at the northeastern limb of Berat Anticline in the High Folded Zone, it is asymmetrical and double plunging anticline has a fold axis of NW-SE direction and changed to E-W trend toward the western part [10]. Berat Anticline located between two synclines, in northeast Hanara-Darbanuk Syncline and in southwest Sharafona Syncline [11]. Jurassic rocks (Chia Gara Formation) form the core of the anticline, and Cretaceous to Upper Miocene rocks are from the limbs of the anticline.

Fig. 2: Location map of the studied sections with tectonic subdivisions of northern Iraq

3. Materials and Methods

To determine the organic geochemistry of the selected formation. The darkest layers were prioritized of each analyzed outcrop, where grey, dark grey, semi-black, and black fine-grained rocks were found. The initial field expedition gathered 18 samples from the Balambo Formation in the Bekhme region. 20 samples were gathered during the second campaign in the Razan area. As a result, 38 samples were obtained for this study. The Rock-Eval analysis were done in Scientific Research Center, at Soran University-Erbil Governorate.

Rock–Eval pyrolysis offers a useful way to determine the amount and type of organic material present in sediments, as well as its maturity level [12]. The samples were ground down from each section, then tested approximately 100 mg of them with a Rock–Eval/TOC device, following protocols by Espitalié et al. [13]. The amount of the sample’s free hydrocarbons (gas and oil) is released at 300 °C which is shown by parameter S1., while peak S2 gives us an understanding of hydrocarbon emitted during temperature programmed pyrolysis (300-600°C), TOC is calculated by oxidizing pyrolysis residues in another oven at 600°C. With the measured values, other parameters can be derived such as OI (S3/TOC) and HI (S2/TOC) both are the normalized S3 and S2 values articulated as mg HC/g TOC respectively, which allows us to make an estimation about the kind of organic material and CO2 presence. On the other hand, the GC/MS have been tested in the Cairo, Egypt. Using helium (He) as the carrier gas and a typical initial flow of 1.3 mL/s, the GC-MS analysis was performed using an Agilent Technologies 6890N Network GC/MS system equipped with a 30.0 m 250.0 m i.d film thickness 0.25 m fused silica DB-5 column connected to an AT 5975 quadrupole mass selector detector (electron energy 70 eV, source 250 °C). In order to measure saturated hydrocarbons, the temperature program for the GC called for holding at 60 °C for two minutes, increasing at 20 °C/min to 120 °C, rising at 4 °C/min to 290 °C, and holding for 23 minutes. Chemstation Software used to coordinate data gathering for ion selection monitoring for saturation.

4. Results

4.1 TOC and Rock-Eval pyrolysis:

The total organic carbon (TOC) wt.% content and pyrolysis data were utilized to determine the source generation potentiality, kerogen type, and thermal maturation of the organic matter in the Early Cretaceous Balambo Formation. The results show that the sediments have an average TOC of roughly 2.91 wt.%. The organic carbon content of the Balambo Formation extends from 0.95 wt.% to 7.59 wt.%, the TOC values of the Bekhme and Razan sections vary from 2.54 wt.% to 7.59 wt.%, with an average of 4.38 wt.%, and from 0.95 wt.% to 2.91 wt.%, with an average of 1.45 wt.%, correspondingly (Table 1). S2 concentrations vary from 0.21 to 8.12 mg HC/g sample, this range shows that the source rock potential is quite varied. At the Razan section, the average free hydrocarbon S1 is 0.06 mg HC/g rock, and it rises significantly to 0.11 mg HC/g rock at the Bekhme section. HI readings are range from 14 to 212 mg HC/g TOC, with an average of around 84 mg HC/g TOC indicating the generation of gas. OI ranges from 15 to 122 mg CO2/g TOC, with a mean
of 54 mg HC/g TOC. The organic matter in the samples may be classed as type II-III kerogen based on the HI vs. OI diagram. The Razan sediments' Rock-Eval S2 values are less than 2 mg HC/g sample. This suggests that this unit has little generation potential; nonetheless, the other section include ideal source rocks for oil and gas development. Maximum temperature at S2 peak (T_max), a measure of thermal maturity, with a typical range of values between 439 and 448 °C. The average T_max temperature is 443 °C.

4.2 Molecular Geochemistry:
The samples under evaluation contain n-alkanes with a C_{16} to C_{35} range, per the findings of the GC analysis. Less than C_{16} are not apparent, perhaps as a result of natural degradation or the loss of more volatile chemicals during sample preparation. Low molecular weight components are substantially more concentrated than long molecular weight n-alkanes in the studied samples (Fig. 3a). Higher plant waxes are known to offer the long-chain n-alkane homologues, despite the fact that aquatic species are thought to give the short carbon preference index (CPI) often fall between 0.39 to 0.96. (Table 2). The sequence of their relative abundance was C_{27}>C_{29}>C_{28} (Fig. 2b). The presence of C_{27} homologues implies the existence of biological molecules from the deep sea [16]. The Balambo Formation's maturity level is defined by the values of 20S/(20S+20R) and ββ/(ββ+αα)C_{29}, which have average values of 0.51 and range from 0.47 to 0.54 and 0.49-0.52, respectively. Hopanes ranged from C_{27} to C_{35} on the m/z 191 fragmentogram, with C_{29} 17,21(H)-30-norhopane and C_{30} 17,21(H)-hopane being the two most common. One indicator of a carbonate-rich source rock is the significant C_{29}/C_{30} 17 (H) hopane ratio [17]. In this study, C_{30} norhopane was shown to be more prevalent than C_{30} hopane (Fig. 2c). The hopane ratios for C_{35}/C_{34} and C_{29}/C_{30} were both larger than 0.8 and 0.6 (Table 2). The majority of oils produced from marine carbonate source rocks have significant levels of C_{35}/C_{34} hopanes (>0.8) and C_{29}/C_{30} hopanes (>0.6) [15]. The range of the gammacerane index is 0.12 to 0.19 (small value) this feature only exists in a hypersaline environment [18]. In immature bitumens, the ratio of 17,21(H)-moretanetes to 17,21(H)-hopanes is 0.8; in mature source rocks and oils, it is 0.15; and at the lowest point, it is 0.05 [19], [20]. This ratio ranged from 0.07 to 0.11 for all of the samples in the Balambo Formation that were examined. The homohopane molecules were converted from their 22R to 22S form using the biomarker maturity ratio 22S/(22S + 22R). Usually, the C_{17} homohopanes are used to compute this ratio, which ranges from 0.53 to 0.62 (Table 2). The ratio Ts/(Ts+Tm) ranges from 0.40 to 0.45.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Sections</th>
<th>Rock-Eval Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S1 mg/g</td>
</tr>
<tr>
<td>Balambo</td>
<td>Bebkame</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>Balambo</td>
<td>Razan</td>
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# Table 2: Biomarker results for the Balambo Formation in both sections

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<tr>
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<th>Pr / nC</th>
<th>Ph / nC</th>
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<th>C28%</th>
<th>C29%</th>
<th>20S / (20S + 20R) C29</th>
<th>ββS / (ββS + ααR) C29</th>
<th>Ts / (Ts + Tm)</th>
<th>Mortane index C29</th>
<th>GI = (G. / G.+ C30αβ)</th>
<th>22S / (22R + 22S) C32</th>
<th>C29 / C30 Hop</th>
<th>C34H / C35H Hop</th>
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<td>0.60</td>
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Fig. 3a: n-alkanes distribution (m/z 85) of the Balambo Formation in the studied sections

Fig. 3b: Steranes distribution (m/z 217) of the Balambo Formation’s organic matter in the studied sections.
5. Discussion
5.1 Quality and Quantity of the Organic Matter

When assessing sediments as a source for petroleum, it’s necessary to consider how the rock samples are rich in organic carbon (TOC wt.%). Based on the TOC wt.% and Rock-Eval pyrolysis data, Tissot and Welte [21], Peters and Cassa [22] and Peters [23] proposed a scale for evaluating the potentiality of source rocks, which TOC is greater than one. According to the results in Table 1, the Balambo Formation’s total organic carbon content range from 0.95 to 7.59 wt.%, with just one sample having value less than that, suggesting fair to good source rock in Razan section whereas, very good to excellent total organic content in Bekhme section. The TOC wt.% against S2 plot supports this result (Fig. 4). Using a graphical comparison of S2 and TOC, the kerogen type of several data source rocks from the Razan and Bekhme sections was identified in this work [24]. It was found that the mixed kerogen type II/III with III characteristics are present in the Balambo Formation, the Bekhme portion has a more diverse kerogen type that varies from kerogen type II-III to kerogen type III, but the Razan section is governed by kerogen type III (Fig. 4). The most frequent method of degrading organic material is oxidation. HI are often low because oxidation remove hydrogen and add oxygen to the kerogen [25]. Because of this, the Razan component is more oxidized when compare with Bekhme section. Figure 5 shows the relationship between Pr/n-C_{17} versus Ph/n-C_{18}, which shows the type of kerogens within the two selected sections. According to this relationship, the Balambo Formation is containing type II-III and type III of kerogens, indicating oil-gas generation prone if the other conditions are present. Biomarker results claimed the same outcomes extracted from pyrolysis analysis when using isoprenoid parameters. The same finding was asserted by Sarraj and Mohialdeen [26]. By analyzing the data from the geochemical pyrolysis of the rock, it is possible to determine the generation potentiality of the source rock. Pyrolysis Yield (PY) in source rock is determined by the addition of S1 and S2. According to [18], the genetic potential (GP) of the analyzed samples is divided into three categories: fair (2-5), good (5-10), and very good (>10) mg HC/g rock. The potential for producing hydrocarbons from the Balambo Formation is acceptable. The potential for HC formation of all samples from the Razan and Bekhme fits in the good to very good zone of the diagram in Figure (6) according to the cross plot of the samples at the GP versus TOC diagram by [27].

On the other hand, the Balambo Formation includes gas of oil resources for nearly all of the samples in both the Razan and Bekhme sections.

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Fig. 3c: Hopanes distribution (m/z 191) of the Balambo Formation’s organic matter in the studied sections

Fig. 4: The relationship between TOC wt.% and S2 of the studied samples from Early Cretaceous rocks in selected sections, showing quantity and quality of organic matter
The potential for oil and gas can be determined by classifying source rock depending on the type of kerogen present. Regarding to [28], the kerogen types present in these rocks are explained by the known amounts of HI from a source rock. A source rock can possibly produce gas if it has hydrogen concentrations of less than 150 mg/g (often kerogen type III), a combination of oil and gas if it has hydrogen concentrations between 150 and 300 mg/g, and more oil if it has higher hydrogen concentrations (kerogen type II and III).

5.2 Biomarker-related depositional environment and source material

Biomarkers were employed to differentiate between source materials and to identify depositional settings. Predicting source rock quality within a basin requires determining the depositional environment of a source rock, especially the degree of oxygenation which substantially effects organic matter preservation [15]. Abdullah and Balaky [29] studied X-ray diffraction (XRD) of Balambo Formation, the study claimed that is phyllosilicate present, which has a lot of calcite, common quartz, and a modest amount of fluorapatite with little dolomite, the major clay mineral in the formation is illite, which denotes to hot, arid climate during most of the Cretaceous Period. In order to evaluate the redox conditions during sediment deposition, the pristane/phytane ratio can be utilized. Particular depositional settings and lithologies are linked with particular values of the Pr/Ph ratio [30; 31]. This ratio indicates the presence of marine carbonate rocks if it is less than 1.0, as shown in the Balambo Formation in both sections [32]. The environment where source rock deposition took place may be reflected in the tendency for odd or even carbon numbered paraffins [33]. Odd carbon values in the C_{25} to C_{35} range are more abundant than even carbon numbers in larger plant origin profiles [34]. As opposed to high CPI levels or a preference for an odd-numbered n-alkane, which indicate origin from terrestrial plant material, CPI values near 1.0 may indicate a predominance of marine input. The carbon preference index which is computed by dividing the sum of the odd carbon-numbered alkanes (C_{25}-C_{33}) by the sum of the even carbon-numbered (C_{24}-C_{34}) alkanes values in the examined samples are less than or around one, indicating suboxic-anoxic depositional settings. On a ternary diagram with the regular steranes C_{27}%, C_{28}%, and C_{29}%, the environment of the Balambo Formation started from open marine; the same conclusion has been claimed by [35] (Fig. 7).

5.3 Thermal Maturation

T_{max}, PI, R_o, T_s/(T_s+T_m) and some markers that can be used to determine the amount of maturity that happened on the OM in the parent rock. Immature OM is taken into account when calculating thermal maturity as a function of burial depth in the basin, which is influenced by the kind of OM and age of source rocks in the case of PI 0.1, T_{max} 430 °C, and R_o 0.62. PI > 0.4, T_{max} > 450-460 °C, and R_o 0.9 define the top of the oil window, while T_{max} > 470 °C, PI > 1, and R_o > 1.35 characterize postmature OM [21;22;36], and the condense gas (late mature OM) is...
placed between the oil and dry gas windows. According to Mackenzie et al. [20], the Ro values of the oil window vary depending on the kerogen present. The researchers discovered that the oil window’s Ro values for type I, type II, and type III are respectively begun at 0.64%, peaked at 1.1%, and eliminated at 1.4% Ro. The HI vs. T\text{max} plot, developed by Espitalié et al. [13], was utilized to generate kerogen classification diagrams based on pyrolysis data, which are used to identify the kerogen type and maturity. (Fig. 8). The results demonstrate that samples from the Balambo Formation are plotted in the mature zone with predominant type II-III and type III kerogen. On the other hand, the ratios of isoprenoids to n-alkanes (Pr/n-C17 and Ph/n-C18) offer important insights on diagenetic circumstances, maturation, and biodegradation [15]. The samples examined are thermally mature, according to these ratios. Since the samples’ values for the carbon preference index were close to 1.0, and even carbon predominated over odd carbon, it is obvious that the samples had matured [37; 34]. To demonstrate the association of thermal maturity characteristics based on apparent isomerization of asymmetric centers at C_{29} steranes for extract samples, a cross-plot of the $\beta\beta S/(\beta\beta S+\alpha\alpha R)$ and 20S/(20S+20R) ratios is employed. This figure is particularly useful for expressing the thermal maturity of both oils and source rocks, as stated by Seifert and Moldowan [38]. All samples in the Balambo Formation, are in the mature (Fig. 9a). Petroleum geochemistry frequently uses the Ts/(Ts+Tm) ratio and 22R/(22R+22S) hopane versus 20S/(20S+20R) sterane as a maturity criterion [39]. While equilibrium values for 22S/(22S+ 22R) C_{32} homohopane ratios vary from 0.53 to 0.62, those for 20S/(20S+ 20R) C_{29} sterane ratios are in the range of 0.47 to 0.54. These results show that the examined materials have at least attained the thermal maturity stage (Fig. 9b). Finally, the vitrinite reflectance values were calculated using the correlation chart between maturation parameters in steranes and hopanes (Fig. 10). The results are nearly the same to the results verified by rock-eval pyrolysis which revealed that the analyzed samples of the Balambo Formation are mature and have all entered the stage of early hydrocarbon generation because the value of the vitrinite reflectance ranges from 0.55 to 0.75%. (Fig. 10 and Table 2).
investigated samples from the Bekhme section included a very good amount of total organic matter (TOC range from 2.54 to 7.59). Although the Rock-Eval pyrolysis results indicate the examined formation has good genetic potential (average 2.91 mg/g) the possibility for oil-gas production is just a chance for hydrocarbon generation since the organic matter has matured due to the Tmax value in average 443 °C and the finding of CPI is less than one. Additionally, the Rock-Eval pyrolysis show that the most common kerogen types are II-III and III, this result is supported by GC/MS parameter while the Ph/nC18 is greater than Pr/nC17 and low Pr/Ph ratio. In addition to, regarding to sterane and hopane parameters ($\beta\beta$S/($\beta\beta$S + $\alpha$R)), 20S/(20S + 20R), Ts/(Ts+Tm), 22R/(22R+22S) the rock samples of the Balambo Formation in two selected sections are mature and contain type III kerogen with mixed type II-III kerogen.

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