Organic Geochemistry and Thermal Maturity Assessment of Cretaceous Balambo Formation from Selected Sites, Kurdistan, NE Iraq

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Abstract
The Cretaceous Balambo Formation from three sections in Kurdistan Region of Northern Iraq was studied. The selected sections are located in the Zagros Fold-Thrust Belt. Eleven rock samples were analyzed by means of the organic geochemical method, Bitumen extraction method, and gas chromatography/mass spectrometry to determine the bitumen and hydrocarbon content, kerogen types, origin of organic matter, thermal maturity level, and depositional environment. The analyzed samples are considered to have an excellent potential in Baranan-1.G1 and Sazan sections, with poor to fair potential in Baraw section. The Baranan-1.G1 source rocks are of type II kerogen (oil prone), whereas Sazan and Baraw samples are of type II/III (oil/gas prone). Detailed distribution analysis of biomarkers such as normal alkane, isoprenoids, sterane and terpane was performed on saturated hydrocarbons. The mode of normal alkane and isoprenoids distribution in all analyzed samples is similar, with a unimodal distribution that indicates non-biodegraded hydrocarbons, with the same range of alkane compounds between C13-C34 alkanes. The results of n-C17, pristane, n-C18 and phytane, and regular steranes show that the source rocks of Balambo Formation in Baranan-1.G1 are mainly rich with algal marine organic matter deposited under a reducing environment, while Baraw and Sazan sections are composed of mixed marine organic matter that refers to terrestrial land plants input deposited under reducing anoxic/dysoxic environments. Thermal maturation appraisal is deduced from Pristane/n-C17 versus Phytane/n-C18 diagram, Carbon Preference Index (CPI), C29 ββ/ (ββ+αα), C29 20S/ (20S +20R), C32 22S/ (22S+22R), and Ts/ (Ts+Tm). All these parameters indicate that the analyzed samples are mature and have entered the oil window (early to peak oil window). Biomarker ratios of C22/C21, C24/C23 and C26/C25, C31R/C30H show that the Balambo Formation is composed mostly of carbonates with less shale beds.

Keywords: Balambo Formation, Biomarkers, Cretaceous, Iraq, Kurdistan.

الجيوكيميائية العضوية و النضج الحراري تكوين بالامبو الكريتاسي في مواقع مختارة، كوردستان، شمال شرق العراق

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الخلاصة
تمت دراسة تكوين بالامبو الكريتاسي (الطباشيري) في ثلاث مقاطع في أقليم كوردستان شمال شرق العراق. تم تحليل أحد عشر نموذجا صغيريا بالطرق الجيوكيميائية العضوية الجيولوجية و تحليل النضج الحراري بالطرق الكيميائية. تقع المقاطع المدروسة في نطاق الطيارات-الزحف للزاكروس، تم تحليل أحد عشر نموذجا صغيريا بالطرق الجيوكيميائية العضوية. تم استخدام البروميكان و البريستان وปกار و ببتون البترول و الاكريليك و الدهانات لتحديد النسبية النضجية للتكوينات. تم استخراج الدهانات لتحديد النسبية النضجية للتكوينات. تمت دراسة تكوين بالامبو الكريتاسي (الطباشيري) في ثلاث مقاطع في أقليم كوردستان شمال شرق العراق. تم تحليل أحد عشر نموذجا صغيريا بالطرق الجيوكيميائية العضوية. تقع مقاطع الدراسة في نطاق الطيارات-الزحف للزاكروس. تم استخراج الدهانات وتحديد النسبية النضجية للتكوينات. يشير النتائج إلى أن التكوينات تقع في نطاق النضج الزيتي (فترة زيكوس) وتحتاج إلى تنقيح أكثر من التجوية لزيادة النسبية النضجية للتكوينات. يعود هذا النقص إلى التغيرات الجيولوجية في المنطقة والجاذبية الكيميائية للتكوينات. وتظهر النسب النضجية النظرة إلى أن التكوينات كوارية مع تطور النضج والتنوع البيولوجي. يوفر هذا الدراسة أحدث النماذج للتكوينات وتقديرات النسبية النضجية للتكوينات. *Email: razawa.abdulrahman@univsul.edu.iq
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The algal biomarker constraint: Extraction of the biomarkers of the gas chromatographic mass spectrometry and then to determine the duration of the biomarkers and hydrocarbons and the hydrogen index and the thermal interval. It is considered that the shale bearing the sandstone is a good oil-bearing formation in the Baraman-1 and Mazar oil field. An analysis of the other formations and the thermal maturity of the algae in the collection of the algae of the Ratawi, Sulaiy, and Balambo formations (Figure 1). Source rock assessment and petroleum generation potentiality of Cretaceous sediments have been conducted by several researchers [3, 4, 5]. The Balambo Formation is one of the Cretaceous carbonate sequences with narrow geographic distribution and long geologic age (Figure 1). The Balambo Formation was first described in 1947 by Wetzel [6] from Sirwan Valley near the boundary between the Imbricated and High Folded Zones of northeastern Iraq. According to the lithology and age, it is divided into two units of the Lower Balambo (Valanginian- middle Albian), composed of thin bedded ammonite- rich limestone with intercalations of olive- green marls and dark blue shales, and the upper Balambo (Late Albian-Turonian), composed of thin bedded globigerinal, passing downward to radiolarian limestone [6, 7]. It passes westwards and northwards from the type area of the Balambo Formation (Sirwan River, Halabja, etc.) The basal sediments of the formation laterally and gradationally change into neritic sediments of the Sarmord Formation and iron-rich oolitic and arenaceous beds at the base Garagu Formation found in some areas [6]. The middle portion of Balambo Formation (Hauterivian-Albian) laterally passes westwards and northwards, through Sarmord Formation into massive, neritic limestone of Qamchuqa Formation [6, 8, 9] (Figure 1).
The principal source rocks responsible for charging most of Iraqi reservoirs were deposited during Late Jurassic to Early-Middle Cretaceous [11], including Balambo Formation that is considered as good potential source rock [12]. Al-Sharhan and Nairn [11] reported that the hydrocarbon began generating in the lower part of Balambo Formation some 15 Ma ago, and the oil migrated horizontally under the Sarmord seal and was trapped in reservoirs in the Kirkuk, Jambour and Khabaz fields. The formation was also considered as fair to good source rock, with kerogen type II/III of highly oil prone and oil and gas prone [11]. Mahdi [5] determined the depositional conditions of the formation from several oil fields in northern Iraq as distal suboxic to anoxic basin. However, another work [13] considered the Balambo Formation as of little potentiality in northern Iraq. Recently, Sarraj and Mohialdeen [14] studied the formation in three sections in Kurdistan Region and they concluded that the formation is deposited in deep marine-bathyal environment with anoxic to suboxic conditions.

The main purpose of this paper is to geochemically study the Balambo Formation from three selected sections (two outcrops and one well) in order to determine the type and origin of the organic matter and appraising the thermal maturity of these rocks. For achieving this purpose, an organic geochemical analysis was conducted.

2. Geological setting

The Berriasian-Aptian succession in Iraq is represented by many formations, most of which are occurring on the platform area on both the stable shelf (south and central areas) and unstable shelf (northern areas) [6, 11]. During the Late Tithonian - Cenomanian, the Southern Neo-Tethys was opened. This opening was formed because of the breakup of Gondwana. Deposition of radiolarian chert began in the Tithonian time in southeast Turkey (Karadut Complex) and northeast Iraq (Qulqula Group) [10]. The opening of the Southern Neo-Tethys led to the drifting away of a narrow microcontinent; a new passive margin was formed along the NE margin of the Arabian Plate [13]. During Berriasian - Albain subsidence, carbonate platform margins aggraded and locally prograded into the Balambo-Garau Basin; up to 1500 m of carbonates with significant Berriasian- Hauterivian

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**Figure 1**- Megasequence AP8 showing Balambo Formation equivalents in Iraq and NE Jordan [10]
and Albian siliciclastic intervals were deposited [1, 10].

The studied area is located in the Zagros Fold-Thrust Belt (ZFTB) from Kurdistan region, northeastern Iraq (Figure-2). The ZFTB extends approximately 2000 Km from the Strait of Hormuz southwest Iran to the Kurdistan Region (north Iraq) and southeast Turkey. It is formed from the Zagros Orogeny due to collision between the Arabian and Eurasian plates [15, 16]. The ZFTB is located on the boundary of the Arabian and Eurasian plates, and causes the closure of the Neo-Tethys Ocean. The ZFTB consists of a foreland fold zone and a thrust zone, oriented SE to NW. It consists of suture or thrust along with imbricated, high folded, and low folded zones of Iraq [17, 18]. The ZFTB holds 49% of the global fold-thrust belt hydrocarbons [16]. The Zagros Fold Belt is estimated to contain about 4.5 billion barrels of Iraq’s 153 billion barrels of oil reserves, making Iraq the fourth largest oil reserve in the world [19, 12].

3. Stratigraphy of the studied sections

The detailed description of the Balambo Formation in the three selected sections is as follows (Figures-(2-4):

3.1 Baraw section

The Baraw section is located about 24 km northeast of Sulaimani city with coordinates of 35° 36´ 17´´ N and 45° 41´ 26´´E (Figure-2). The thickness of Balambo Formation in Baraw section is about 234 m. It is composed of alternations of grey to dark colors, medium to thick bedded limestone with organic-rich shale, thin bedded chert, and marlstone at the base (Figure-3 a). The carbonate layers are characterized by the presence of ammonite (Figure-3 b), carbonate concretion, and liesigang ring structures. The underlying formation is Late Jurassic-Early Cretaceous Chia Gara Formation, and the overlying formation is not clear and covered (mostly Kometan Formation) (Figure-1). Based on the field description of Bellen et al. [6], this sequence represents both the lower and upper parts of Balambo Formation.

3.2 Sazan Section

The Sazan section is located about 72 km southeast of Sulaimaniya city with coordinates of 35° 7´ 14´´ N and 46° 1´ 38´´ E (Figure-2). The thickness of Balambo Formation is sixty-three meters, situated in a highly folded and faulted area in northern Iraq. The study sections were carefully selected to avoid repeating due to intensive folding in the region. The section is characterized by light grey limestone beds containing organic rich bands with shale layers in the middle and upper parts (Figure-4 a). The carbonate layers are characterized by the presence of ammonite impressions (Figure-4 b), lamination, carbonate concretion, and liesigang ring structures. Chia Gara Formation is underlying the Balambo Formation in this section. However, the overlying unit is unclear and not recognized. Balambo Formation of Sazan section represents both parts of the sequence [6].

3.3 Baranan-1.G1 (Bn-1) section

This subsurface section was taken from a recently drilled well by TOTAL Company, which reaches to Lower Balambo Formation. The well is about 30 km southeast of Sulaimaniya with coordinates of 35° 17´ 54.6´´ N and 45° 32´ 08.4´´ E (Figure-2). Both parts of Balambo Formation are recognized and determined. The Upper Balambo Formation is of 3831 to 4172 m depth, with thickness of about 341 m, being composed of limestone, marlstone, and argillaceous limestone. The lower Balambo Formation starts from depth 4290 to 4355 m., which is composed of marlstone and limestone with traces of chert (Figure-5). The Gamma Ray log (GR) shows a high GR peak at depth 3832m from the upper part of Upper Balambo Formation which could be a thin layer of shale, and also at the depth interval 4313.5-4314.5m from lower Balambo Formation. The high GR could be a thin layer of shale, while the remaining layers are homogenous throughout the section (Figure-5).
Figure 2: Location of the studied Baraw, Bn-1 and Sazan sections, Kurdistan Region, NE Iraq.
Figure 3- Field photographs of Balambo Formation in Baraw section: a- The lithology of the Balambo Formation, b- Ammonite impression.
Figure 4 - Field photographs of Balambo Formation in Sazan section: a- The Balambo Formation lithology, b- Ammonite macrofossil.
4. Samples and experimental methods

Ninety-nine rock samples of Balambo Formation were taken from three sections. The Bn-1 samples were provided from the store of the Ministry of Natural Resources in Erbil Governorate. Eleven rock samples were subjected to organic geochemical techniques; bitumen extraction, gas chromatography (GC), and gas chromatography-mass spectrometry (GC/MS). The GC/MS analysis was carried out at the organic geochemistry laboratory in the Geology Department at the University of Malaya, Malaysia.

Approximately 30g of powdered sample was Soxhlet extracted for 72 hours using an azeotropic mixture of dichloromethane and methanol (93:7) [20]. The asphaltene precipitation was achieved using the ASTM procedure (ASTM D2007-80). The accurate volume of the extracted
bitumen was measured into a test tube. About 20 times that volume of n-heptane was added to the test tube, making the ratio of n-heptane to extracted bitumen about 95:5. The test tubes were slotted in a tabletop centrifuge and the motor was spun for about 20 minutes. The maltene (liquid at the top of the tube after centrifugation, containing aliphatic, aromatic and NSO) was collected. These steps were repeated until the supernatant became colorless. The maltene was separated into saturated hydrocarbon, aromatic hydrocarbon, and NSO compound fractions by liquid column chromatography. A chromatographic column (30x0.72 cm) was packed with silica gel of 60–120 mesh that was activated for 2 hours at 120 °C and capped with alumina. The column was then developed with solvents of increasing polarity, i.e. light petroleum (100 ml), dichloromethane (.100 ml) and methanol (50 ml). The eluates were collected in separate 250 ml round-bottom flasks. The solvent was later reduced using a Buchi apparatus and the weights of the eluates were recorded.

The GC and GC/MS were used to analyze the aliphatic hydrocarbons that predominantly consist of saturated hydrocarbons. The gas chromatography analysis was performed using HP-5MS column with a temperature programmed at 40 to 300 °C with a rate of 4 °C/min, which was then held for 30 min at 300 °C. The aliphatic fractions were subsequently analyzed using an Agilent 5975B inert MSD mass spectrometer with a gas chromatograph attached directly to the ion source (70 eV ionization voltage, 100 mA filament emission current, 230 °C interface temperature) . Selected peaks (e.g. n-alkanes, hopanes, tricyclic terpanes, and steranes) were identified based on their retention times and comparison with identifications reported by previous researchers [20, 21, 22]. The selected ion monitoring capabilities of the data acquisition system permitted specific ions to be monitored, such as n-alkanes (m/z 85), triterpanes (m/z 191), and steranes (m/z 217) of saturated hydrocarbon ratios, as presented by previous works [21, 22]. Terpane and sterase distributions were quantified by measuring peak heights in the m/z 191 and m/z 217 chromatograms, respectively.

5. Results
5.1 Organic matter richness

The amount of extractable organic matter (EOM) together with the relative proportions of saturated, aromatic fractions, and nitrogen, sulphur, and oxygen (NSO) compounds were calculated and tabulated (Table-1). The extract yields expressed as part per million (ppm) are cross plotted against TOC (wt. %) in Figure-6. Based on the classification by Peters and Cassa [23], the samples from Baraw possess a poor to fair value for the bitumen/EOM and hydrocarbon (HC) content. The samples from Bn-1 and Sazan sections generally possess excellent HC content with a value of >4,000 ppm (Table-1, Figure-6).

The EOM values of the Baraw samples are 226 and 745 ppm, that can be considered as poor to fair source rocks, while the EOM yield values of Bn-1 section ranged from 10,690 to 16,918 ppm, and that of Sazan sample was 20,221 ppm. This indicates that the latter two sections are organic-rich sediments and excellent source rocks (Figure-6). The percentages of the maltene and asphaltene fractions are shown in Table-1. Maltene represents major fractions of the analyzed samples. The maltene fractions compose a proportion of 50.5%-66.1%, whereas asphaltene fractions range from 33.9% to 49.5%. However, the two Baraw samples show the absence of maltene and asphaltenes. The normal procedure was not applied for these two samples because they possessed a low amount of EOM (0.0032 and 0.0108). The most important fraction to be analyzed is the saturated organic matter. Thus, the EOM was first precipitated to obtain asphaltene and maltene, then 80% of EOM was separated (directly with no asphaltenes precipitation analysis) to ensure sufficient saturation. For the remaining (20%) of the EOM, the normal procedure was used, but there was a very low amount of about 0.000001 or lower.

The saturated and NSO components represent major fractions of the analyzed samples. The saturated fractions and NSO compounds are ranging from 32.3% to 40.2% and 30.0% to 46.1%, respectively. The aromatic fractions range from 18.3% to 33.4%. (Table-1, Figure-7).
**Figure 6** - Relationship between Total Organic Carbon (TOC wt. %) content versus Extracted Bitumen (ppm) of Balambo Formation in the three sections, Kurdistan, Iraq.

**Figure 7** - Ternary diagram of saturated, aromatic hydrocarbons and NSO components for the studied samples of Balambo Formation.
Table 1- Extractable organic matter (EOM) yield and asphaltene precipitation data of Balambo Formation in Baraw, Bn-1 and Sazan sections, NE Iraq

| Section | Sample number | EOM | Asphaltene | Maltene | EOM | SAT % | ARO % | NSO % | Asphaltene | Maltene | TOC wt. % |
|---------|---------------|-----|------------|---------|-----|-------|-------|-------|------------|---------|-----------|
| Baraw   | 14            | 0.0032 | 0          | 0       | 226 | 141   | 33.3  | 26.7  | 40         | 0       | 1.97      |
| Baraw   | 28            | 0.0108 | 0          | 0       | 745 | 359   | 40.2  | 20.7  | 39.1       | 0       | 2.09      |
| Bn-1    | 1             | 0.2373 | 0.0814     | 0.1519  | 16918 | 5254 | 39.8  | 19.8  | 40.3       | 34.9    | 65.1      |
| Bn-1    | 5             | 0.2005 | 0.0983     | 0.1002  | 16344 | 4932 | 32.3  | 21.6  | 46.1       | 49.5    | 50.5      |
| Bn-1    | 7             | 0.1664 | 0.0595     | 0.1039  | 10690 | 4259 | 32.6  | 25.3  | 42.1       | 36.4    | 63.6      |
| Bn-1    | 11            | 0.202  | 0.0911     | 0.11    | 13142 | 4502 | 36.3  | 27.3  | 36.3       | 45.3    | 54.7      |
| Bn-1    | 15            | 0.1705 | 0.057      | 0.1112  | 12162 | 5115 | 30    | 33.4  | 36.6       | 33.9    | 66.1      |
| Bn-1    | 21            | 0.2074 | 0.0771     | 0.1293  | 13554 | 4202 | 38.3  | 24.7  | 37         | 37.4    | 62.6      |
| Bn-1    | 25            | 0.2191 | 0.08       | 0.12    | 13146 | 4596 | 36.1  | 22.7  | 41.2       | 40      | 60        |
| Bn-1    | 29            | 0.2    | 0.0873     | 0.11    | 11001 | 4505 | 36.3  | 18.3  | 45.4       | 44.2    | 55.8      |
| Sazan   | 14            | 0.3033 | 0.1092     | 0.1911  | 20221 | 6620 | 39.6  | 30.3  | 30         | 36.4    | 63.6      |

EOM: Extractable organic matter (EOM) yield and Asphaltene precipitation, TOC wt.%: Total organic carbon, ARO: Aromatic hydrocarbons, NSO: Nitrogen, Sulfur, Oxygen components, HCs: Hydrocarbon fractions (Saturated + Aromatic), ppm: part per million.

5.2. Molecular composition
The biomarkers distribution may provide information about organic matter facies and depositional environment, origin, kerogen type and maturation [24]. In this study, detailed biomarkers distribution within the Balambo Formation, such as normal alkane, isoprenoids, steranes and terpanes were performed on saturated hydrocarbons (Table-2, Appendix) and their traces, recorded on m/z 85, m/z 191 and m/z 217 mass fragmentograms, respectively (Figures- 8-10).

5.2.1. n-alkanes and isoprenoids
The saturated gas chromatograms of the analyzed Balambo extracts reveal a full suite of saturated hydrocarbons between C\textsubscript{13}-C\textsubscript{34} n-alkanes and isoprenoids pristane (Pr) and Phytane (Ph) (Figure-8). The n-alkane patterns are dominated by short (n-C\textsubscript{15} – n-C\textsubscript{20}) to middle (n-C\textsubscript{21} – n-C\textsubscript{25}) chain n-alkanes with the presence of certain waxy alkanes (+n-C\textsubscript{23}), which caused moderate Carbon Preference Index (CPI) values (CPI < 1.16).

The abundant source of pristane (C\textsubscript{19}) and phytane (C\textsubscript{20}) is the phytal side chains of chlorophyll in photomorphic organisms and bacteriochlorophyll in purple sulphur bacteria [21, 25]. The modes of n-alkane and isoprenoids distributions in all the analyzed samples are similar. The results showed a unimodal distribution, non-biodegraded hydrocarbons, and marine source organic matter enriched with algal and/or bacterial organisms, with the same range of alkane compounds; between C\textsubscript{13} - C\textsubscript{34} n-alkanes (Figure-8).

The CPI is a mathematical expression of the odd over even predominance between n- C\textsubscript{24} and n- C\textsubscript{34} [21, 26]. A CPI value higher than 1 indicates thermally mature source rocks, with CPI equal to or lower than 1 may arise from a predominance of marine input and/or thermal maturation, while high CPI indicates low maturity [27]. The CPI values of the analyzed samples range from 0.93-1.16. The majority of the samples have CPI higher than 1. except Sazan sample, sample no.14 of Baraw, and no.25 of Bn-1, which show values lower than or around 1 (Table- 2).

The most important acyclic isoprenoids in hydrocarbons are Pristane (Pr) and Phytane (Ph) [25],

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both reflecting the paleoenvironmental conditions of source rocks and are considered as indicators for the redox conditions during sedimentation and diagenesis [28, 29]. The Pr/Ph ratio was calculated based on m/z 85 mass fragmentograms of saturated hydrocarbon fractions. The Pr/Ph ratio increases with increasing thermal maturity. The analyzed samples of Bn-1 and Sazan sections show higher Ph content than that of Pr, causing a low Pr/Ph ratio of 0.37 to 0.60, whereas the Sazan sample has a Pr/Ph ratio of 0.91. The two Baraw samples show higher Pr content than that of Ph, causing a Pr/Ph ratio of 1.10 (Table -2). According to Peters and Moldowan [30], the terrestrial plants have a high Pr/Ph ratio of >3 which indicate oxidizing conditions, while low values of Pr/Ph (<1) indicate anoxic conditions and values between 1 and 3 indicate intermediate (Suboxic) conditions. From this point of view, the Balambo Formation in Bn-1 and Sazan sections show anoxic conditions, while Baraw samples indicate suboxic condition.

The ratio of Pr/ n-C17 is useful for differentiating organic matter of swamp environment (higher than1.0) from those formed under marine environment (lower than 0.5). However, this ratio is affected by maturity, as well as biodegradation [31]. The ratio of Pr/n-C17 in all Bn-1 samples range from 0.17 to 0.32 (i. e. < 0.5) indicating a marine environment, while that of Baraw and Sazan samples range from 0.51 to 0.57, indicating dysoxic condition (Figure-11). The Ph/ n-C18 ratio is higher than that of Pr/ n-C17 in all samples of Bn-1 and Sazan sections, but not in the two Baraw samples (Table- 2). A cross plot of Pr / n-C17 and Ph/n-C18 that was proposed by Shanmugam [32] provides good information about organic matter type, organic facies, biodegradation, and maturation level. All the analyzed samples are mature and no obvious biodegradation occurred (Figure-11).

The Terrigenous/ Aquatic Ratio (TAR) was determined for the Balambo Formation samples using the equation (C27+C29+C31)/ (C18+C17+C19). The results ranged from 0.15 to 1.07 (Table -2).

5.2.2. Terpane biomarkers

Many terpanes in petroleum originate from bacterial prokaryotic membrane lipids [24]. These bacterial terpanes include a series of several homologues including acyclic, bicyclic, tricyclic, tetracyclic and pentacyclic compounds [21]. The tricyclic terpanes extends from C19 to at least C54 because of their isoprenoid side chains [33]. Tetracyclic terpane from C24 to C27 appeared to be more resistant to biodegradation than the hopanes, which are pentacyclic terpanes that extend from C27 to C35, originating from precursors bacterial membranes [21].

The C-ring from C20-C24 tri and the tetracyclic compounds can be detected at m/z191 mass chromatograms. Most of the analyzed samples have C23 of larger peak than the others except samples 28 of Baraw section and 29 of Bn-1 section (Figure- 9). The relatively low C29/C30 (Table -2) is consistent with clay-rich rocks (e.g. shale). C29/C30 ratio of higher than 1 is commonly associated with carbonate source rocks, but this is not always the case [34]. The enhanced C29-norhopane input may also be associated with land plant input [35]. In this study, the C29/C30 ratio ranges from 0.81 to 1.13, this indicates a mixed carbonate and clay rock (shale).

The homohopane series (C31-C34) of this study is decreasing toward C34. The absence or minor C34 and C35 (Gammaacerane) indicates samples of normal salinity [36]. The Oleanane compound is not detected in the analyzed samples (Figure-9).

5.2.3 Sterane biomarkers

The occurrence of C27-C29 regular steranes indicates the contribution of eukaryotic organisms [37]. The sterane and diasterane biomarkers of the analyzed Balambo samples, as detected in the m/z 217 fragmentograms, are calculated. Nearly all the analyzed samples are similar (C27>C29 >C28), except sample no. 25 of the Bn-1 section which has the order of C29>C27>C28 (Table- 2). The ratio of C27/C29 is also determined, where the results show a range of 1.02-1.55; only the sample no. 25 of Bn-1 section has a lowest value (0.80).
Figure 8- Mass chromatograms ($m/z$ 85) of saturated hydrocarbon fractions showing the $n$- alkanes and isoprenoids distribution.
Figure 9. Mass chromatograms ($m/z$ 191) of saturated hydrocarbon fractions showing the distribution of hopanes (detailed compound abbreviations are shown in the appendix).
6. Discussion

6.1. Origin of organic matter and paleodepositional environment

The $n$-alkane distributions and their envelopes are unimodal, with short-chain compounds in the range of $n$-$C_{14}$ to $n$-$C_{22}$ being predominant (Figure-8). However, some differences are noticed for samples of Baraw, which are richer in light hydrocarbons as compared to the other sections. This type of distribution usually indicates marine plankton [24]. Heavy $n$-alkanes in the range of $C_{30}$ to $C_{40}$ are very low, which is pointing to the contribution of higher plant waxes [38]. The amount of $C_{26}$ to $C_{32}$ $n$-alkanes in Bn-1 section is higher than that in the other sections, indicating some input of higher plants to the organic matters of Balambo Formation (Figure- 8). The same conclusions are obtained with the TAR ratio, in which the Baraw and Sazan samples have low value (0.15-0.25), indicating dominance of aquatic organic matter. While the Bn-1 samples have moderate to high (0.45-1.07) ratio, which indicates moderate terrigenous organic matter input (Table-2). Additionally, the ternary diagrams of $C_{27}$, $C_{28}$, and $C_{29}$ steranes in the Baraw and Sazan samples show planktonic-bacterial origin, while
those of the Bn-1 samples are of both planktonic bacterial and planktonic-land plants origins (Figure-12).

Values lower than 0.85 for C27/C29 sterane ratios are believed to be indicative of terrestrial organic matter, whilst values between 0.85 and 1.43 indicate mixed organic material, and values higher than 1.43 suggest an input of predominantly marine organic matter [29, 39, 40]. The results of the C27/C29 ratio of the analyzed samples show that sample no. 25 of Bn-1 section has a value of 0.8, which indicates terrestrial organic matter, while the Bn-1 samples and sample no. 28 of Baraw section have a range from 1.02 to 1.36, indicating mixed algal and land plants origin with deposition under anoxic condition. Sample no. 14 of Baraw section and Sazan sample have values of 1.50 and 1.55 (> 1.43), respectively, indicating an input of marine organic matter (Figure-13). The same conclusion is obtained from the ratios of C31-22R-hopane/C30-hopane, which is used to distinguish between different depositional environments, with a value higher than 0.25 indicating a marine environment [21]. The analyzed samples have a range between 0.23 and 0.41 (Table-2), with most of them having values of > 0.25, indicating a marine environment. Exceptions include samples number 5, 11, and 25 of the Bn-1 section that show values lower than 0.25, which is possibly caused by some terrestrial input.

The cross plot of Pr/n-C17 versus Ph/n-C18 indicates that the Baraw and Sazan samples are located at the border between algal marine and mixed OM transitional environment. They have kerogen type II/III and algal marine organic matter of type II kerogen, while all Bn-1 samples are of algal marine organic matter of type II kerogen field (Figure-11). It has been suggested that marine phytoplankton is characterized by the dominance of C27 steranes, whereas the preponderance of C29 compounds indicates strong terrestrial contributions [39].

The absence of Gammacerane is an indicator of normal marine water depositional environment of Balambo Formation. The absence of Oleanane indicates that the sediments were deposited far from the input of the angiosperm higher plant, since their deposition occurred prior to the evolution of angiosperms [41, 42]. The m/z 191 chromatograms of Balambo Formation show no Oleanane compounds (Figure-9), because Oleanane has been reported in Upper Cretaceous and Tertiary source rocks [42]. In addition, some of the samples show a terrestrial input, where Oleanane was also not detected.

The C29 norhopane /C30 hopane ratio is used to distinguish the carbonate (>1.0) and clastic lithology (clay rich, shale source rock <1.0). In this study, this ratio ranges from 0.81 to 1.13 (Table-2), indicating the mixed carbonate and shale facies of the Balambo Formation. Similar conclusion is obtained from the ratio of C22/C21 versus C24/C23 tricyclic terpane (Figure-14). These results are concordant with the lithology of Balambo Formation, which is mostly composed of limestone and less shale layers.

Figure 11- Cross plot of Pristane/n-C17 versus Phytane/n-C18 (32) showing that the Baraw and section samples are located in the marine and transitional environment, while Bn-1 samples are located in the marine environment.
**Figure 12**- Ternary diagram of regular steranes (C$_{27}$-C$_{29}$) indicating the relationship between sterane compositions in relation to organic matter input.

**Figure 13**- Cross plot of C27/C29 steranes and Pristane/Phytane ratio for the study samples from Balambo Formation, Northeastern Iraq.

**Figure 14**- Plot of C$_{22}$/C$_{21}$ Tricyclic terpane and C$_{24}$/C$_{23}$ tricyclic terpane, with location of samples [21].
**Table 2** - Bulk organic geochemical biomarker parameters and ratios of n- alkanes, isoprenoides hopanes, tricyclic, tetracyclic terpanes and steranes of the analyzed samples form Baraw, Bn-1 and Sazan sections, Northeast Iraq, Kurdistan Region

| Section  | Sample No. | Pr/Ph | PhC17 | PhC18 | CPI | TAR | C25 | C29H27(22S+2R) | C29H(C29H30H) | Ts/Tm | T5(Ts/Tm) | HC31RC30H | C30M/C30H | C26Tri/C25Tri | C29Tri/C24Tri | C29Tri/C24Ter | C29Tri/29S(29S+20R) | C29Tri/29S(29S+20R) | C29ββ/20S(29S+20R) | C27 | C28 | C29 |
|----------|------------|-------|-------|-------|-----|-----|-----|----------------|----------------|-------|------------|------------|------------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|-----|-----|-----|
| Baraw    | 1          | 1     | 0.5   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.6           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 2          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 3          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 4          | 1     | 0.5   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.6           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 5          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
| Bn-1     | 1          | 1     | 0.5   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.6           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 2          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 3          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 4          | 1     | 0.5   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.6           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 5          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
| Sazan    | 1          | 1     | 0.5   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.6           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 2          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |
|          | 3          | 1     | 0.0   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0            | 0.0            | 0.0   | 0.0        | 0.0         | 0.0         | 0.0           | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0 | 0.0 | 0.0 |

Pr: Pristane; Ph: Phytane; CPI – Carbon preference index = \( (2 \cdot \text{C}_{21} + \text{C}_{27} + \text{C}_{29} + \text{C}_{29}) / (\text{C}_{21} + \text{C}_{27} + \text{C}_{29}) \)

Ts: \( \text{C}_{27} \) 18α (H)-22, 29, 30-trisnorneohopane; Tm: \( \text{C}_{27} \) 17α (H)-22, 29, 30-trisnorneohopane; HCR31/C30H: \( \text{C}_{31} \) regular homohopane/C30 hopane; \( \text{C}_{29} \)H/C30H: \( \text{C}_{29} \) norhopane/C30 hopane; \( \text{C}_{30} \)M/C30H: \( \text{C}_{30} \) moretane/C30 hopane; TAR: Terrigenous Aqueous Ratio (Terrigenous/ aquatic) ratio= \( \text{C}_{27} + \text{C}_{29} + \text{C}_{31} / (\text{C}_{17} + \text{C}_{19} + \text{C}_{19}) \)

6.2. Thermal Maturity Assessment

Several parameters were used in this study to evaluate the level of organic matter maturity. These include CPI, Ts/Tm, C32 hopane 22S/ (22S+22R), C29 ββ/ (ββ+αα), and C29- sterane 20S/ (20S+20R) ratios.

The CPI values of the seven samples of Bn-1 and one sample of Baraw indicate maturation, while the other samples show a predominance of marine input and/or thermal maturation. The ratios of \( \text{C}_{29} \) 20S/ (20S+20R) and \( \text{C}_{29} \) ββ/ (ββ+αα) steranes increase with increasing maturity [4, 44]. The relationship between \( \text{C}_{29} \) ββ/ (ββ+αα) and \( \text{C}_{29} \) 20S/ (20S+20R) steranes of the studied samples indicate a peak mature zone (Table 2; Figure-15).

\( \text{C}_{29} \) 22S/22S+22R homohopane ratio increases from zero to about 0.6 at equilibrium during maturation [45]. Values in the range of 0.50 to 0.54 have barely entered oil generation, whereas ratios from 0.57 up to 0.62 indicate an oil window zone [21]. All the analyzed samples have a range from 0.57 to 0.66, which suggests that they have entered oil generation and that the oil window has been reached (Figure-16).

The ratio of \( \text{C}_{30} \)M /\( \text{C}_{30} \)H decreases with increasing maturity from 0.15 immature bitumens to a minimum of 0.05 mature source rock and oils [46]. The analyzed samples show that this ratio ranges from 0.07 to 0.22, indicating their early mature to mature character (Table-2).
The ratio of $\frac{Ts}{(Ts+Tm)}$ or $\frac{Ts}{Tm}$ is another indicator of the rock maturity [30, 47]. It increases with maturity but may also be influenced by source lithology. Carbonate rocks appear to have a low $\frac{Ts}{(Ts+Tm)}$ ratio as compared to shale [21, 47]. In this study, this ratio ranges between 0.36 and 0.57 (Table-2), which is an indication that the analyzed samples are mostly composed of mixed carbonate and shale facies, and are thermally mature source rock.

**Figure 15**- Cross plot of $C_{29}$ sterane $\beta\beta/ (\beta\beta+\alpha\alpha)$ and $C_{29}$ sterane $20S/ (20S+20R)$ [21].

**Figure 16**- $C_{32}$ hopane $22S/ (22S+22R)$ ratio and $C_{29}$ sterane $\beta\beta/ (\beta\beta+\alpha\alpha)$ ratio indicating early-peak oil window of the studied samples.

7. **Conclusions**

The evaluation of rock samples from Balambo Formation in three sections (Baraw, Bn-1, and Sazan) was geochemically accomplished through analyzing them by GC/MS to determine their kerogen types, hydrocarbon potentiality, depositional setting, and maturity of the source rock. The following key points can be drawn:

1- According to the EOM or bitumen content, both Bn-1 and Sazan samples are considered as organic rich sediments, while the Baraw samples are poor to fair source rocks. Based on TOC wt. % data, both Bn-1 and Sazan samples are considered as excellent source rocks.
The Bn-1 samples are of kerogen type II (oil prone), whereas Sazan and Baraw samples are of type II/III (oil/gas prone).

By plotting regular steranes in the ternary of C27, C28, and C29, the origin of the organic matter within rocks of Balambo Formation in Bn-1 section is of both planktonic/bacterial and planktonic/land plants, whereas both Baraw and Sazan organic matters have the origin of planktonic-bacterial.

Facies-indicating parameters, such as C25/C21, C22/C23, C23R/C20 H, C26/C25, and C29H/C30 H show that the Balambo Formation is composed mostly of carbonate, with minor shale beds, which is consistent with the lithology of the formation.

Thermal maturity related biomarkers, such as C29 sterane αα, ββ, 20S, C32 hopane 22S, Ts/ (Ts+Tm), and C30M/C30 H show that all the investigated samples are mature and have entered the oil window (early-peak).

Depending on Pr/n-C17 and Ph/n-C18, the depositional environment of the Balambo Formation in Bn-1 was found to be a marine and reduced environment, while in the Baraw and Sazan sections are of mixed marine and transitional environments.

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Appendix
Peak assignment for hydrocarbons in the gas chromatograms of saturated fractions in the m/z 191 (I) and 217 (II) mass fragmentograms.

(I) Peak no.     Compound abbreviation
C20             C20 Tricyclic (Cheilanthane)     Tri C20
C21             C21 Tricyclic (Cheilanthane)     Tri C21
C22             C22 Tricyclic (Cheilanthane)     Tri C22
C23             C23 Tricyclic (Cheilanthane)     Tri C23
C24             C24 Tetracyclic                      Tet C24
C24             C24 Tricyclic (Cheilanthane)     Tri C24
C25             C25 Tricyclic (Cheilanthane)     Tri C25
C26             C26 Tricyclic (Cheilanthane)     Tri C26
C27             C27 Tricyclic (Cheilanthane)     Tri C27
C28             C28 Tricyclic (Cheilanthane)     Tri C28
C29             C29 Tricyclic (Cheilanthane)     Tri C29
Ts              18α (H), 22, 29, 30-trisnorhopane    Ts
Tm              17α (H), 22, 29, 30-trisnorhopane    Tm
C29             17α, 21β (H)-nor-hopane            C29 hop
C30 H           17α, 21β (H) - hopane              Hopane
C30 M           17α, 21β (H)- Mortane           C30 Mortane
C31 S           17α, 21β (H) - homohopane (22S)    C31 (22S)
C31 R           17α, 21β (H) - homohopane (22R)    C31 (22R)
C32 S           17α, 21β (H) - homohopane (22S)    C32 (22S)
C32 R           17α, 21β (H) - homohopane (22R)    C32 (22R)
C33 S           17α, 21β (H) - homohopane (22S)    C33 (22S)
C33 R           17α, 21β (H) - homohopane (22R)    C33 (22R)
C34 S           17α, 21β (H) - homohopane (22S)    C34 (22S)
C34 R           17α, 21β (H) - homohopane (22R)    C34 (22R)

(II) Peak no.

a  13β, 17α (H)- diasteranes 20S          Diasteranes
b  13β, 17α (H)- diasteranes 20R          Diasteranes
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