RESEARCH PAPER

# Biomarker characteristics of organic shale beds of Alam-El Bueib Formation in Tut Oil Field, Shushan Basin, North Western Desert, Egypt: insights from oil/source rock correlation

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## Abstract

Organic shale beds in the Alam El-Bueib (AEB) are thought to provide an excellent source for producing hydrocarbons. Consequently, defining the role of the AEB formation in hydrocarbons generation in the Tut Oil Field is the primary objective of this research. This research presents an analysis of biomarkers in a set of Tut Oil Field AEB extracts and oils to appreciate the basin's hydrocarbons exploration and development. AEB shales have low Pr/Ph ratios (0.5−0.83), low to high values of $C_{22}/C_{21}$ tricyclic terpanes, low values of $C_{19}/C_{23}$ tricyclic terpanes, high values of $C_{31}$ R homohopanes/$C_{30}$ hopanes, and high concentration of regular steranes $C_{27}$ decode that the organic matter was primarily derived from marine algae/bacterial derived organic matter, along with small amounts of land plants formed in a reducing environment. In addition, the maturity-related parameters display values ranging from low to high. The oils recovered from Bahariya and AEB reservoirs have higher Pr/Ph ratios, and high values of tricyclic terpanes ($C_{22}/C_{21}$) decode that the organic matter was primarily derived from marine algae/bacterial-derived organic matter, and an elevated concentration of $C_{29}$ steranes interpret that the organic matter was primarily derived from mixed marine algae/land plant-derived organic matter formed in a suboxic environment. The maturity-related parameters display high maturity values. Based on various biomarker criteria, the hierarchical cluster analysis of crude oils and AEB extract reveals no genetic relationship between the AEB source rock and the studied oils.

Keywords: Alam El-Bueib Fm, Biomarkers, Oil−source correlation, Paleodepositional environment, Tut Oil Field

## 1. Introduction

One of Egypt's most productive petroleum provinces is the Shushan Basin, which is located in the North Western Desert. Hydrocarbon accumulations are thought to have significant potential in the basin.[1,2]

Several scholars have shown interest in the Tut Oil Field, which is one of the largest in the Shushan Basin (Fig. 1).[3] The Jurassic and Cretaceous units contain potential source rocks that are found in the Shushan Basin.[4] The Jurassic Formation (Khatatba) is regarded as a reliable source rock in the Shushan basin. The primary source rock in the Lower Cretaceous successions is the Alam El Bueib (AEB) Formation. The AEB formation acts as a source/reservoir rock in the Tut Oil Field.[5,6] Various authors have evaluated the hydrocarbons potentiality of shale beds in the AEB formation. According to Ramadan et al.,[5] the Tut Oil Field's AEB formation has an organic matter of type III and varies in quality from
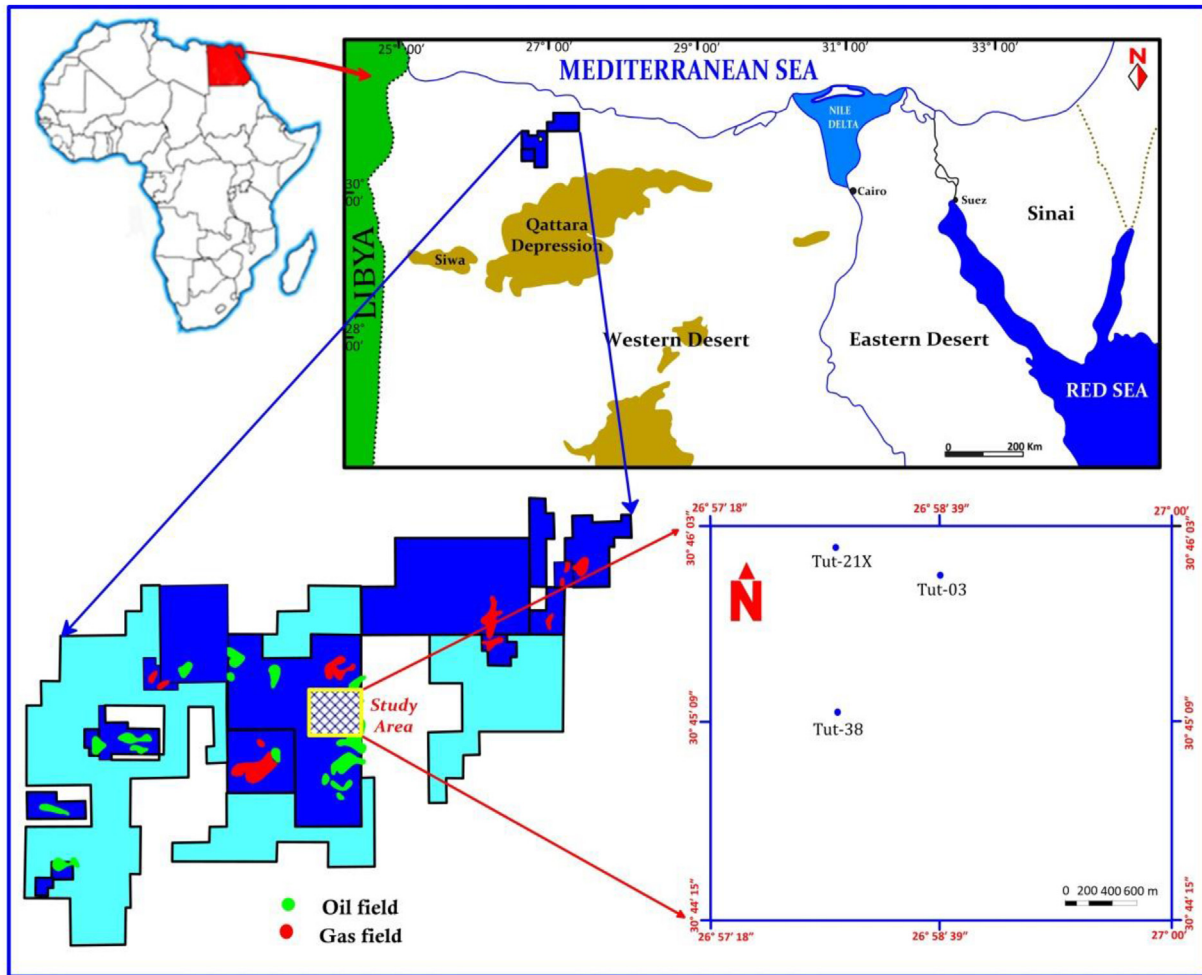
Fig. 1. Location map of the study area in the Shushan Basin, North Western Desert of Egypt, including the studied wells in the Tut Oil Field.

low to very good, and is composed of immature to mature rocks. El Nady and Hakimi[7] showed that the AEB formation in the Tut Oil Field entered only the early-mature stage of oil generation and has not generated hydrocarbons. However, other authors reported that the AEB members reached the oil window in the Cretaceous and Neogene eras. They comprised a mature source rock with good potential for producing oil and gas (II/III).[8]

Based on this discrepancy in evaluating the thermal maturity, the origin of organic matter, and the paleodepositional environment of AEB in the Tut Oil Field, we have investigated in this study the biomarker characteristics of AEB extracts and correlated them with the oil produced from the Tut Oil Field to define the role of AEB formation in the hydrocarbons generation in the studied field. Furthermore, this study considers the consequences of the potential for producing hydrocarbons, which helps to define the migration pathways and

understand the hydrocarbons exploration and development in the basin.

## 2. Stratigraphic setting

As illustrated in Figure 2, the stratigraphic section of the North Western Desert includes the Shushan Basin ranges from the Paleozoic to the Tertiary.[9] According to Sultan and Abd El-Halim and Zein El Din et al.,[10,11] the stratigraphy split into four unconformity-bound cycles. The earliest cycle is composed of the Siliciclastics Formation (Ras Qattara), which is overlain by the Khatatba Formation. The Upper Jurassic sediments formed the Masajid formation and are the highest example of the Jurassic transgression. At the second cycle's base, the Lower Cretaceous AEB and the Masajid formations are separated by a significant unconformity. Marine shale and a series of Neocomian sandstones follow these. This cycle ends with the
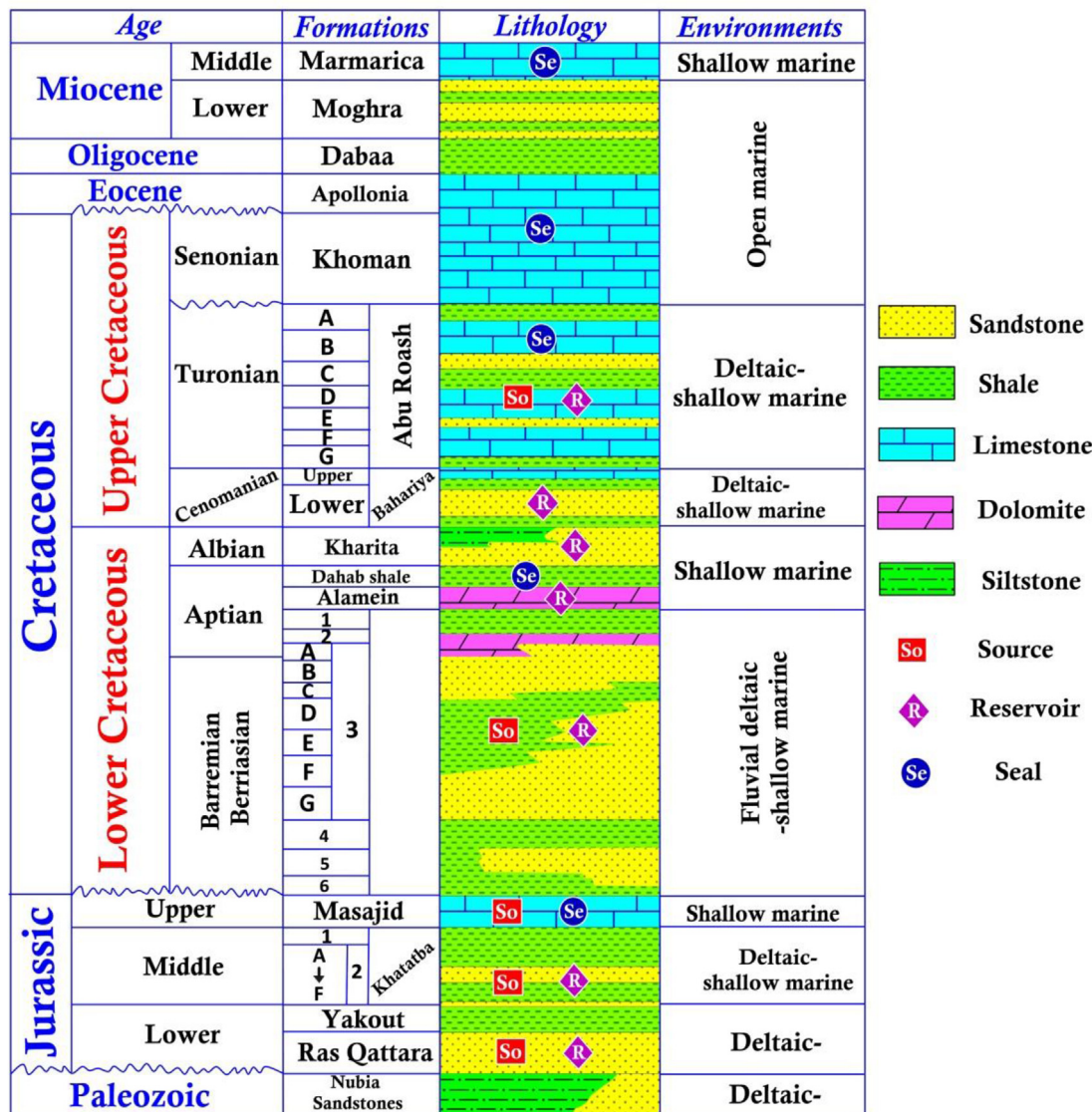
Fig. 2. Generalized stratigraphic column of the North Western Desert including the Shushan Basin.

formation of Dahab Shale. The Bahariya Formation lies on top of the Lower Cenomanian Formation (Kharita). The Abu Roash Member (Upper Cenomanian) deposition indicates a significant depth of depositional conditions. During the Senonian, there was widespread transgression with the sedimentation of the Abu Roash members (F-A). Only in the north Western Desert was the Khoman Chalk Formation, which it unconformably overlies, deposited. The cycle ends with an unconformity over which the Apollonia Formation formed (Eocene).[10]

## 3. Materials and methods

Five ditch and two hydrocarbon samples were collected from three well locations in the Tut Oil Field, namely Tut-21, Tut-3, and Tut-38 (Fig. 1). Cleaning the ditch samples was mostly done to get rid of the drilling mud, then grounded and sieved to be homogenized in size. Approximately 30 g of the pulverized samples were placed in a soxhlet for 72 h to extract the soluble organic matter (bitumen). The extracted material and crude oil samples were deasphalted using n-pentane. The SARA fractions in the samples were separated by gravity column chromatography. The aliphatic fractions (saturates) were then analyzed by gas chromatography (GC). The GC analyses were performed in the sedimentology laboratory of EPRI. The GC analysis was performed using chromatic GC with an oven temperature program raised from 40 to 320 °C at a rate of 10 °C/min.

Afterward, the saturated hydrocarbon fraction in the two selected shale samples and crude oils was determined using GC-MS. This analysis was performed in the StratoChem Services Centre using 6890 GC/5973 MSD using an HP-5MS column type. Base peak responses for steranes at $m/z$ 217 and for terpanes at $m/z$ 191 were used to construct biomarker parameters.

## 4. Results

### 4.1. Bulk composition and physical properties

The AEB oil sample contains a low sulfur content (0.05%) and a high API degree (42.7 °C). Bahariya oil has a slightly higher sulfur content (0.12%) and a lower API degree (38%) (Table 1) reflecting very light and light oils, respectively. For the examined oil samples, the plot of the sulfur content against API gravity demonstrates a tendency of decreasing sulfur content with increasing API gravity, which is partially explained by the increasing thermal maturity (Fig. 3a).

The examined oil samples (AEB and Bahariya) have a high saturated content, with values of 64.1 and 65.2% indicating paraffinic oils, respectively. Meanwhile, AEB extracts demonstrate notable differences among the extracted samples. The extracted samples have saturate, aromatic, and asphaltene/resin contents ranging from 4.59 to 46.2%, 9.3–49.61%, and from 40 to 52.47%, respectively, indicating paraffinic and paraffinic-naphthenic oils (Table 1; Fig. 3b).

### 4.2. Acyclic hydrocarbons (n-alkanes and isoprenoids)

Chromatograms of the selected oil and extracted samples are shown in Figure 4. All samples display a high abundance of medium-chain n-alkanes between n-$C_{15}$ and n-$C_{23}$. Subordinate amounts of the long-chain n-alkanes (n-$C_{25}$-n$C_{35}$) are observed in all samples.

From this distribution of n-alkanes, the almost AEB rock samples result in a low carbon preference index (<1) as shown in Table 1. Meanwhile, the oil samples display slightly higher values ($\approx$1).

Moreover, AEB extract samples have a range of 0.50–0.83 for Pr/Ph ratios, while the examined oil samples show higher values (>1; 1.58–1.68).

The isoprenoids Pr and Ph exhibit low dominance compared with n-alkanes. This appears in the low ratios of Pr/n-$C_{17}$ and Ph/n-$C_{18}$. AEB extract ratios are in the range of 0.28–0.47 and 0.16–0.43, respectively. AEB and Bahariya oil ratios are 0.43, 0.32 and 0.37, 0.28, respectively (Table 1).

### 4.3. Biomarkers

Figure 5 and Table 2 show the concentrations of steranes and terpanes in two selected extract and hydrocarbon samples. Compared with tricyclic terpanes, pentacyclic terpanes, or hopanes have shown up in higher amounts. $C_{30}$ hopanes and $C_{29}$ nor-hopanes dominate the hopanes. There are also notable concentrations of other hopane compounds, such as moretane, Ts, and Tm (Fig. 5; Table 2).

AEB extracts show distinct distributions of regular steranes ($\alpha\alpha$R) in steranes chromatograms. They exhibit dominance of $C_{27}$ regular steranes, while the oil samples exhibit dominance of $C_{29}$ steranes (Fig. 5, Table 2). Table 2 displays the various terpane and sterane ratios that have been computed.

Table 1. Physical, bulk compositions, and gas chromatography parameters of Alam El-Bueib extracts and crude oils from the Tut Oil Field.

| Sample type | Formation | Physical properties | | Bulk chemical composition | | | GC parameters | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | API | S% | Sat. % | Arom. % | Asphaltene + resin % | Pristane/phytane (Pr/Ph) | Pristane (Pr)/n-$C_{17}$ | Phytane (Ph)/n-$C_{18}$ | Carbon preference index |
| | | | | 46.2 | 9.3 | 44.5 | 0.64 | 0.39 | 0.43 | 1.09 |
| | | | | 4.59 | 49.61 | 45.8 | 0.5 | 0.33 | 0.16 | 0.49 |
| Extract | AEB | nd | nd | 27.76 | 32.24 | 40 | 0.67 | 0.47 | 0.36 | 0.8 |
| | | | | 19.02 | 32.17 | 48.81 | 0.63 | 0.34 | 0.26 | 0.63 |
| | | | | 18.32 | 29.21 | 52.47 | 0.83 | 0.28 | 0.17 | 0.44 |
| Oil | AEB | 42.7 | 0.05 | 64.1 | 28.5 | 7.4 | 1.68 | 0.43 | 0.32 | 1.05 |
| | Bahariya | 38 | 0.12 | 65.2 | 26.4 | 8.4 | 1.58 | 0.37 | 0.28 | 1.01 |

Carbon preference index (CPI) = $1/2\{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})\}$.
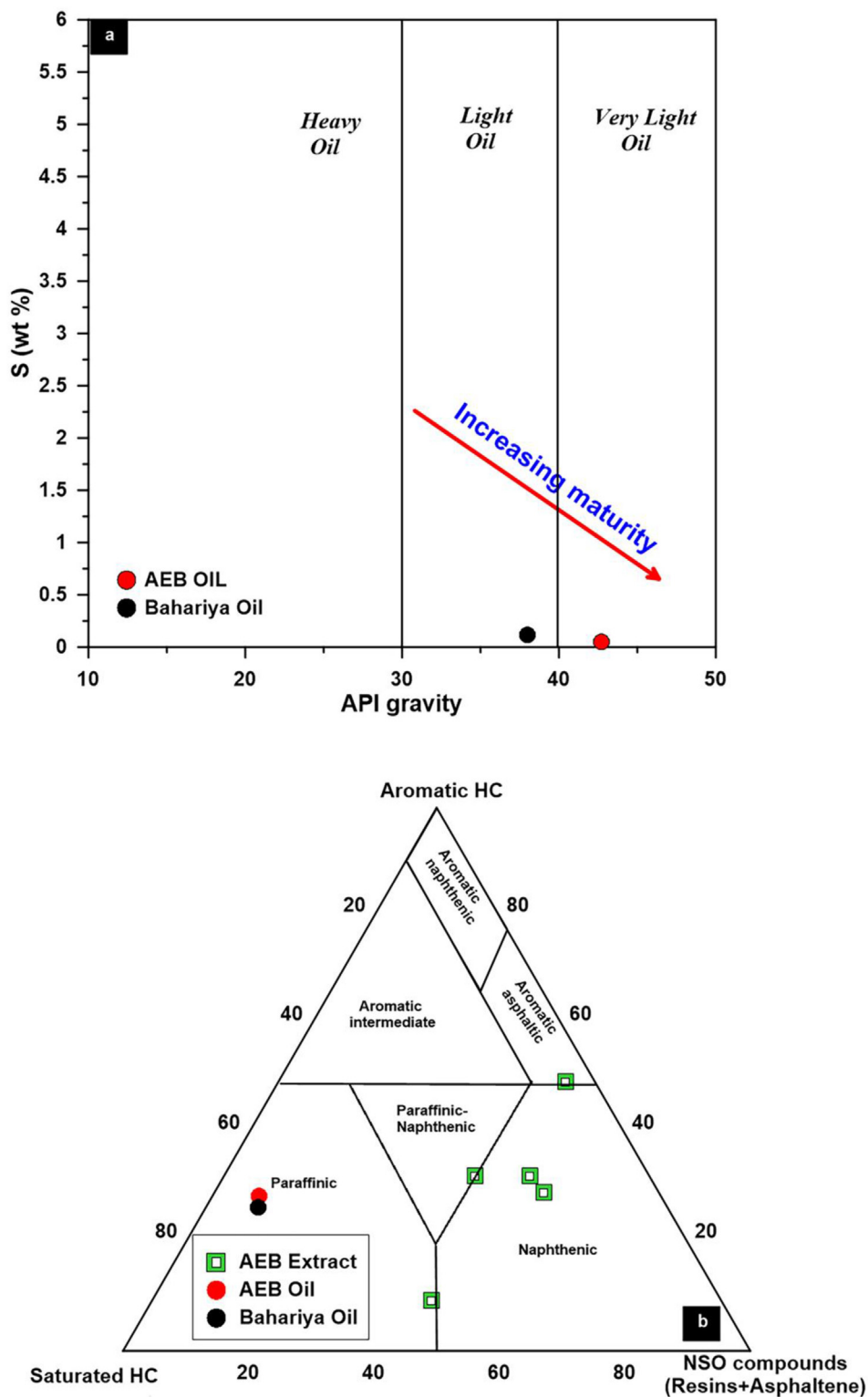
AEB, Alam El-Bueib; GC, gas chromatography.

Fig. 3. (a) API gravity versus sulfur content for studied oils and (b) bulk composition ternary plot for oils and extracted samples.
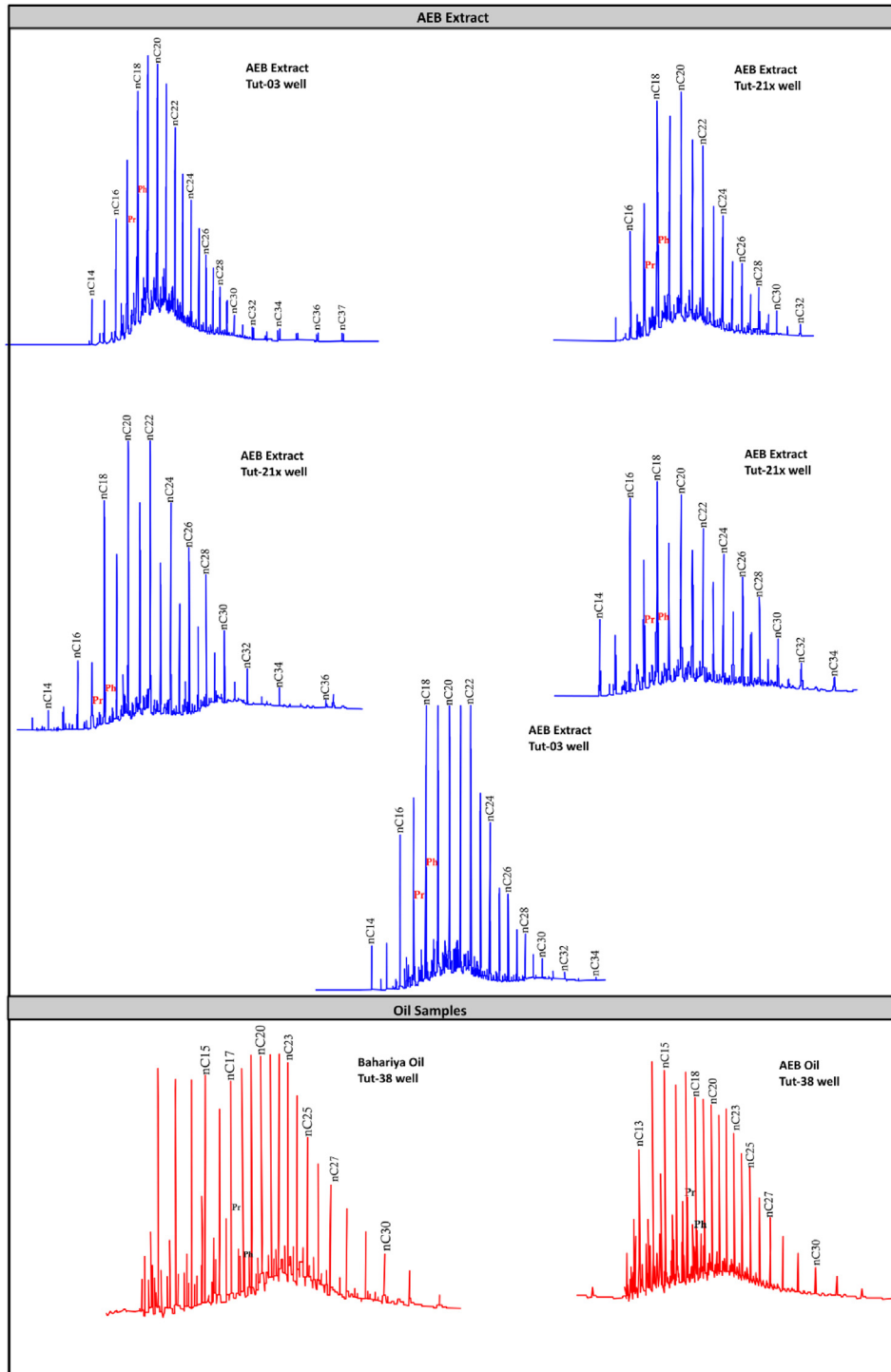
Fig. 4. N-alkanes and isoprenoid concentrations in the saturated fractions of the examined extract and oil samples (GC fingerprint). GC, gas chromatography.
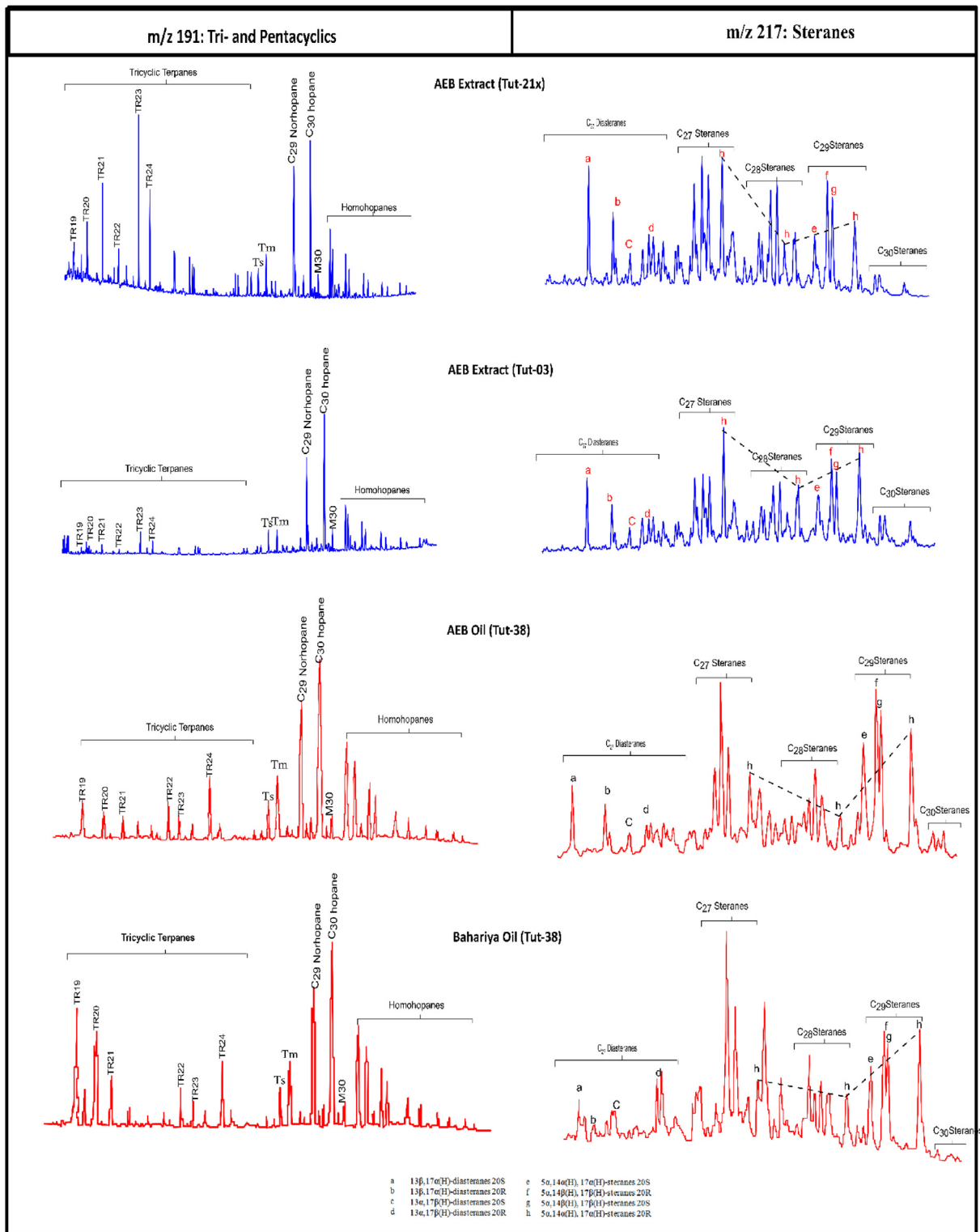
Fig. 5. Terpane and sterane biomarkers in m/z 191 and 217 mass fragmentograms of the aliphatic hydrocarbon fraction in the examined samples.

Table 2. Sterane and terpane parameters of Alam El-Bueib extracts and crude oils from the Tut Oil Field.

| Sample types | Fm | Source input parameters | | | | | | | | | | | Maturity indicators | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Extract | AEB | 0.11 | 1 | 0.67 | 1.03 | 0.64 | 0.16 | 0.27 | 1.02 | 41 | 28 | 31 | 6.88 | 0.37 | 0.45 | 0.57 |
| | AEB | 0.24 | 0.44 | 0.62 | 0.63 | 0.9 | 0.18 | 0.35 | 0.83 | 39 | 27 | 34 | 3.57 | 0.38 | 0.55 | 0.6 |
| Oil | AEB | 1 | 1.7 | 2.4 | 0.6 | 0.74 | 0.11 | 0.41 | 0.83 | 31 | 14 | 56 | nd | 0.43 | 0.57 | 0.57 |
| | Bahariya | 2.7 | 0.83 | 1.83 | 0.62 | 0.73 | 0.16 | 0.42 | 0.66 | 25 | 22 | 53 | nd | 0.46 | 0.53 | 0.57 |

1: $C_{19}/C_{23}$ tricyclic terpanes; 2: $C_{22}/C_{21}$ tricyclic terpanes; 3: $C_{24}/C_{23}$ tricyclic terpanes; 4: Ts/Tm trisnorhopanes; 5: norhopane/hopane; 6: moretane/hopane; 7: $C_{31}R$ homohopane/$C_{30}$ hopane; 8: H35/H34 homohopanes; 9: %$C_{27}$ αααR(217) steranes; 10: %$C_{28}$ αααR (217) steranes; 11: %$C_{29}$ αααR (217) steranes; 12: $C_{30}$ S + R sterane index; 13: 20 S/(S + R) ($C_{29}$) (217); 14: ββ/(ββ+αα) ($C_{29}$) (217); 15: H32 S/(R + S) homohopanes.
AEB, Alam El-Bueib.

## 5. Discussion

### 5.1. Organic matter input and sedimentation environment

The analyzed extracts and oil samples display the fingerprint of marine origin (algae and cyanobacteria). This is inferred from the GC shape, where the samples include all of the low to medium molecular weight (n-$C_{15}$-n-$C_{25}$) n-alkanes (Fig. 4). Moreover, the occurrence of high molecular weight n-alkanes indicates a significant input of terrigenous organic matter (land plants).

The contribution of the different organic matter types and their depositional redox conditions may also be deduced using pristane (Pr) and phytane (Ph) and their ratios (Pr/n-$C_{17}$ and Ph/n-$C_{18}$).

Low ratios of phytane/n-$C_{18}$ and pristane/n-$C_{17}$, along with isoprenoid quantities relative to n-alkanes, imply that AEB bitumen and oil samples likely originated in a transitional environment (suboxic conditions) (Fig. 6a).

The pristane/phytane ratios (Pr/Ph) were less than 1 in bitumen from AEB formation. These values are associated with anoxic environments. Oil samples have Pr/Ph ratios of more than 1, which is typical of a suboxic environment.[12] The relation between Pr/Ph ratios and carbon preference index values further revealed that the source rocks of oil samples contain heterogeneous organic matter and suboxic depositional environments (more oxidizing than the AEB extract) (Fig. 6b).

This result is further interpreted by the distribution of different steranes and terpanes (Fig. 5).

The majority of the organic matter input in AEB rock samples is generally marine, as shown by the abundance of tricyclic terpanes, the high $C_{27}/C_{29}$ sterane ratio, and the existence of $C_{30}$ steranes[13,14] (Fig. 5).

Many terpane and sterane biomarkers have been used to identify the characteristics of organic matter, including the facies, organic matter precursors, and depositional settings.[13,15,16]

Tricyclic terpane ratios that are specific can reveal important details on the organic matter input, water salinity, and depositional environment.

To ascertain the lithology of the source rock, tricyclic terpane ratios ($C_{19}/C_{23}$, $C_{22}/C_{21}$, $C_{24}/C_{23}$, and the $C_{31}R$ homopane/$C_{30}$ hopane ratios) were used.
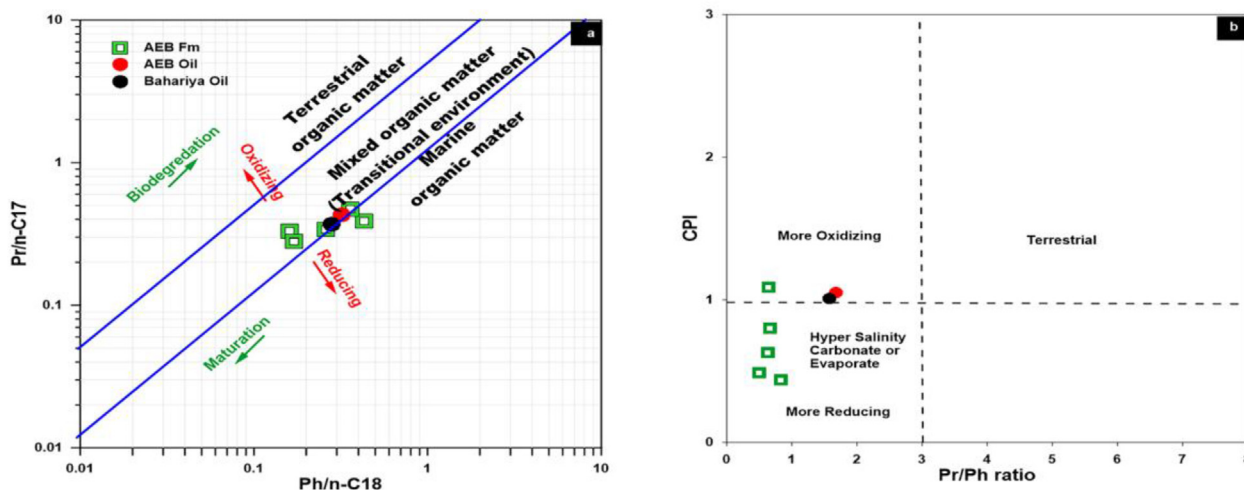


Fig. 6. (a) Pr/n-$C_{17}$ versus Ph/n-$C_{18}$ cross plot and (b) Pr/Ph versus the CPI from which depositional environments were detected for the studied samples. CPI, carbon preference index.

Low values of $C_{19}/C_{23}$ and $C_{24}/C_{23}$ (<0.6), high values of $C_{22}/C_{21}$ (>0.5), low Ts/Tm (<1), and $C_{31}$ R homohopane/$C_{30}$ hopane ratios more than 0.25 are the characteristics of oils from carbonate source rocks according to Peters et al.[14] So, the values obtained for these ratios suggest that AEB organic matter originated from either lacustrine shale or mixed marine carbonate-shale source rock, and AEB and Bahariya oils originated from mixed marine shale and carbonate source rock (Table 2).

This interpretation is further supported by the correlation between the $C_{31}R$ homohopane/$C_{30}$ hopane and Pr/Ph ratios, and the Ts/Tm and $C_{29}$ norhopane/$C_{30}$ hopane ratios (Fig. 7).

However, the high $C_{19}/C_{23}$ and $C_{24}/C_{23}$ tricyclic terpane ratios, which were recorded in the studied oil samples can be interpreted as an indicator of the high clastic and terrestrial input to the studied oils[17–19] (Table 2).

The detection of moretane in low amounts in the studied oils and extracts reflects their origin from a marine source rock, which received a small influx of terrestrial organic matter (Table 2).

To evaluate paleo-redox conditions, the homohopane index ($C_{35}H/C_{34}H$) was also computed. Crude oils and AEB formation exhibit moderate homohopane index values, indicating anoxic–suboxic conditions during the source rock deposition[20] (Table 2).

The preponderance of $C_{27}$ $\alpha\alpha\alpha$ (20 R)-cholestane is the most noticeable characteristic in the sterane (m/z 217) chromatograms of AEB rock samples. Conversely, the oil samples display a high abundance of $C_{29}$ $\alpha\alpha\alpha$ (20 R)-stigmastane (Table 2; Fig. 5). The

ternary diagram sterane distribution supports the inference of primarily planktonic and bacterial origin, with a small input of organic matter derived from plants in AEB rocks and planktonic/land plant origin of oil samples (Fig. 8).

$C_{30}$ steranes were demonstrated to be a reliable biological marker for paleo-marine biotic input.[21–23] The existence of marine organic matter from specific marine algae is confirmed by the presence of $C_{30}$ steranes in AEB rock samples (Figs 5 and 8).

### 5.2. Biomarkers maturation

Among the most trustworthy biomarkers for determining the maturity of crude oil or source rock extracts are the sterane and homohopane isomerization as well as the Moretane index.[16,24,25]

$C_{32}$ homohopane isomerization ratios range from 0.53 to 0.58, which is when they approach the peak oil window. High values (0.57–0.6 and 0.57) for AEB bitumen and oil samples, respectively, indicate that they are sourced from mature source rock (Table 2).

This level of maturity is also inferred from the 20S/(20S + 20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ $C_{29}$ sterane ratios. The oil generation stage has been reached if these ratios are more than 0.30 and 0.40, respectively.[16,24,26,27]

In this study, AEB extracts have 20S/(20S + 20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ $C_{29}$ sterane ratios ranging from 0.37 to 0.38 and from 0.45 to 0.55, respectively, indicating that the range of AEB formation maturity is early to highly mature.

The studied oils have higher values than AEB rock samples suggesting highly mature crude oils.
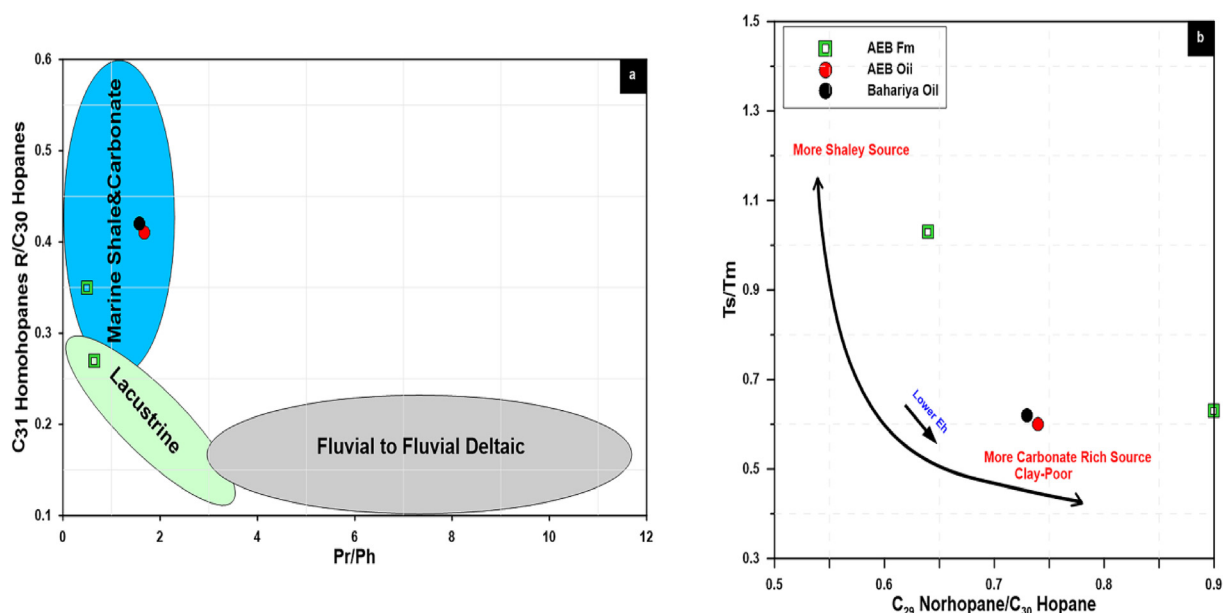


Fig. 7. Relationships between (a) Pr/Ph ratio and $C_{31}R$ homohopane/$C_{30}$ hopane and (b) $C_{29}$ norhopane/$C_{30}$hopane and Ts/Tm.
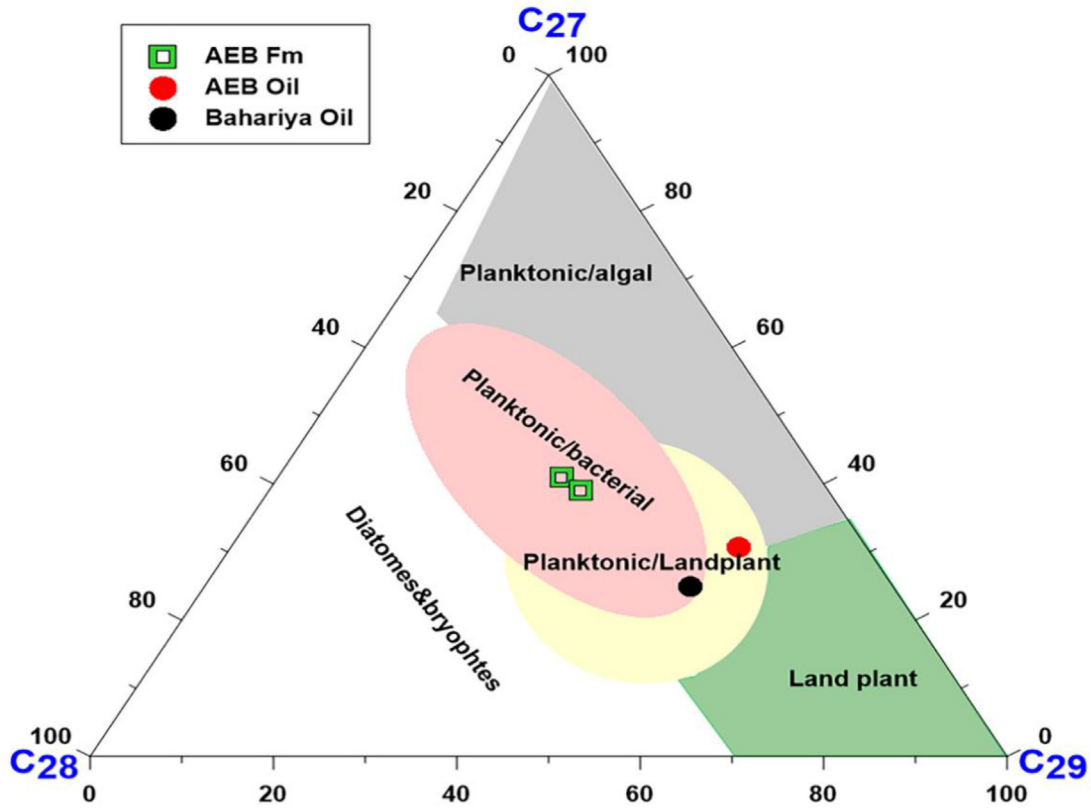
Fig. 8. Ternary plot of the relative amounts of $C_{27}$, $C_{28}$, and $C_{29}$ steranes from which the source input and depositional environment can be detected for the studied samples.
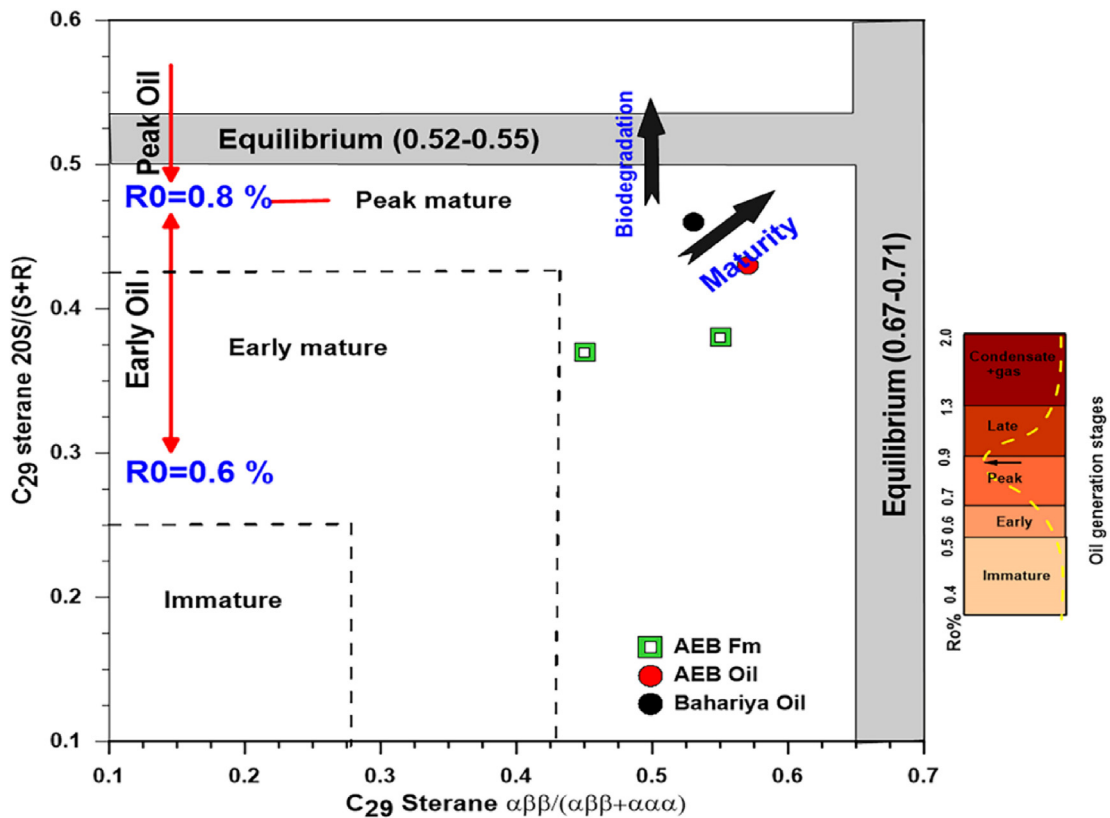


Fig. 9. Relationship between $C_{29}$ steranes $20 S/(S + R)$ and $C_{29}$ steranes $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ to identify the maturity level of the studied samples.
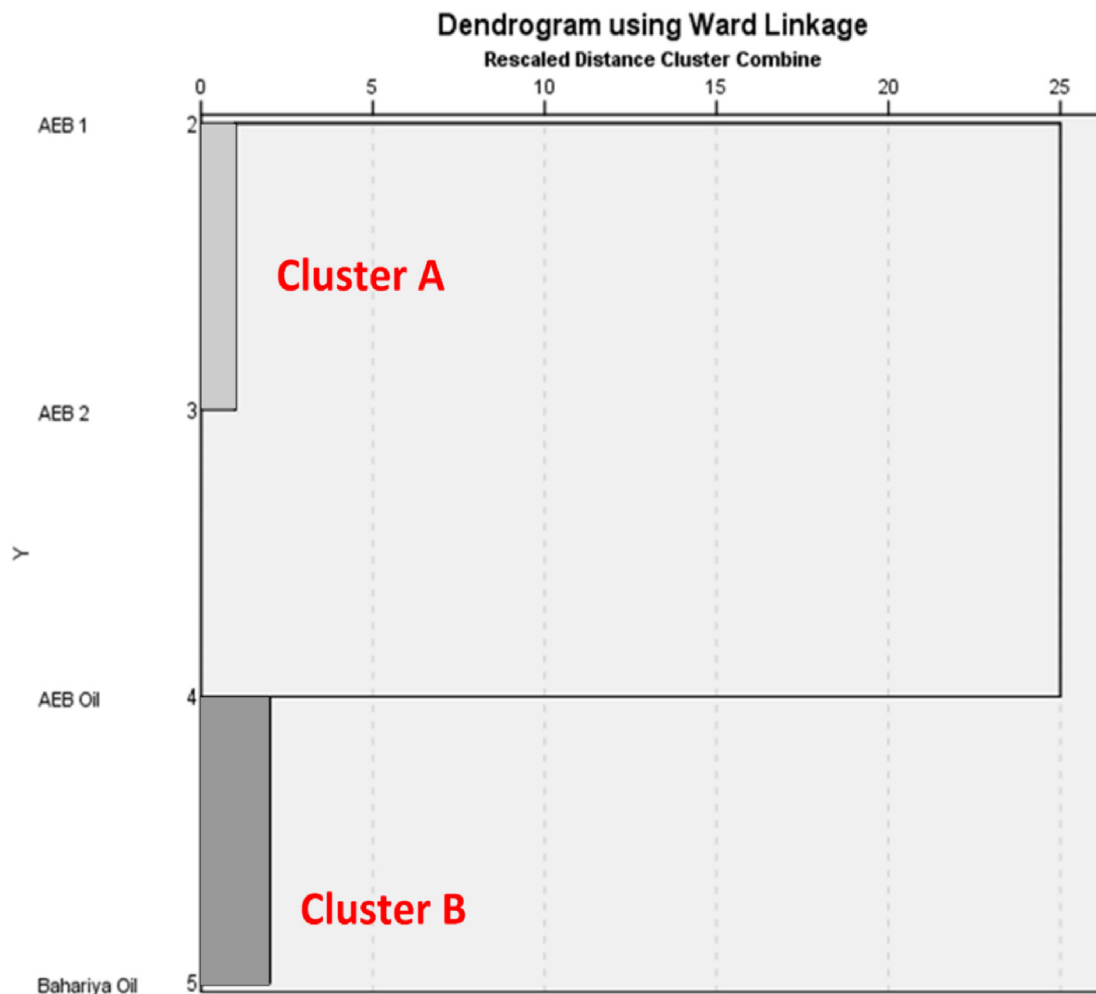
Fig. 10. Hierarchical cluster analysis (HCA) dendrogram identified the genetic correlation between oils and AEB formation in the Tut Oil Field using Ward's method.

Combining the relationship between two ratios, as seen in Figure 9, further confirms this interpretation.

Maturity was also assessed using the moretane/hopane ratio. According to Seifert and Moldowan[16] and McKenzie et al.,[24] the ratio's values decrease going from ~0.8 in immature rocks to less than 0.15 in mature source rocks, and ultimately nearing a minimum of 0.05. The moretane/hopane ratios for AEB formation and Bahariya oils are 0.16—0.18 and 0.16, respectively (Table 2), indicating a high maturity stage (Table 2).

### 5.3. Oil/oil and oil—source correlation

In this study, many parameters have been used for oil—source correlation depending mostly on the preburial environments of the living organisms, the depositional environments of the organic matter, and the diagenetic processes in the source rocks.

Based on certain source-related and maturity biomarker criteria, hierarchical cluster analysis (HCA) is a potent technique for classifying oils of varying origin and correlating them to the specific source rock.[28] In this study, 15 biomarker parameters are selected to perform the HCA (Fig. 10). HCA classified the studied samples into two groups: group A is related to AEB organic matter, which originated from algae and bacterial with a little influx of land plants and formed in early mature to mature stage, and group B includes AEB and Bahariya oils, which originated mainly from high mature planktonic/land plant organic matter (Fig. 8).

Finally, we can assume that Tut oils is not sourced from AEB source rocks but may be sourced from deeper source rocks.[29]

### 5.4. Conclusion

The aforementioned discussions of geochemical characterization of the extract and oil—source rock correlations reveal the following:

(1) The biomarker characteristics of AEB formation reveal that the AEB organic matter is originated in a reducing environment.

(2) A mixture of algae/bacteria and land plants (II/III), varying in maturity from early mature to high mature, are the primary precursors of AEB organic matter.

(3) Bahariya and AEB oils in Tut Oil Field were expelled from deeper source rocks than AEB formation.

(4) The gross composition and biomarker analyses of source rock extracts and oils support the indigenous mixed source.

(5) AEB organic matter originated from lacustrine shale/carbonated and mixed marine shales and carbonate source rock.

(6) AEB organic matter is formed in marine and lacustrine environment.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper..

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