Fingerprinting of biomarker characteristics of some Egyptian crude oils in Northern Western Desert as evidence for organic matter input and maturity level assessment

S.M. El-Sabagh a, A.Y. El-Naggar b, M.M. El Nady a, I.A. Badr c, M.A. Ebiad a, E.S. Abdullah a

a Evaluation and Exploration Depts., Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt
b Chemistry Department, Faculty of Science, Taif University, Kingdom, Taif, Saudi Arabia
c Chemistry Dept., Faculty of Science, Ain Shams University, Abasia, Cairo, Egypt

ABSTRACT

This study describes the fingerprinting of crude oils from different Egyptian oil formations using gas chromatography (GC) and gas chromatography mass spectrometry (GC–MS). The samples were obtained from Gindi, Abu El gharadig, south deep Abu El gharadig, Dahab-Merier and Faghur basins from Western Desert. Diagnostic biomarkers parameters applied in this study provide evidences about the source of organic matter, the depositional environment and maturity of the studied oils. The results showed that the crude oils of Faghur basin are believed to be originated from mixed source predominately terrestrial with chief contribution of clastic rocks deposited under anoxic conditions. However, the crude oils from Gindi, Abu El gharadig, South deep Abu El gharadig and Dahab-Merier basins were generated from marine carbonate source rock deposited under anoxic depositional environment.

1. Introduction

The chemical fingerprinting of petroleum is made possible by the multitude of individual hydrocarbon compounds that are present and by the great variability in the relative abundances of these compounds among different crude oils. This variability, which is the basis for chemical fingerprinting, is due to variability in the organisms contributing to the organic matter, the environment in which this organic material was deposited, the thermal maturation history of the sediments, and post-generation modifications [1]. Biomarkers found in crude oils, rocks, and sediments show little or no changes in structures from their parent organic molecules or biogenic precursors (e.g., hopanoids, sterols, and steroids) in living organisms [2].

The North Western consists of a series of small rift basins, most commercial accumulation of petroleum discoveries occur in the basins located in the northern parts of the Desert. The productive studied wells lies in the North Western Desert between latitudes 29° 00’ and 30° 10’ N and longitudes 25° 20’ and 29° 30’ E (Fig. 1).

It is one of the most productive oilfields in the North Western Desert of Egypt and is defined as Late Cretaceous basin. This represents the commercial hydrocarbon bearing formations. Geochemical evaluation of crude oils in the Northern Western Desert oil fields was described in detail by many authors as mentioned in [3–12]. They divided the oil of some oil fields of the North Western Desert into two types. “Type I” waxy oil was originated from non-marine origin. “Type II” non-waxy oil was sourced from carbonates source rocks, as well as, revealed that close genetic relationship in the origin and maturation for the oils and extracts of the Khattaba and Alam El Bueib source rocks. More recently, El Nady and Harb [13] show that the Abu Gharadig oil samples are of marine origin; their source rocks are rich in clay content and were deposited under reducing conditions. Also, these oils have a high maturity level. El Nady and El Naggar [14] showed that the crude oil of some wells in the North Western Desert is originated mainly from marine organic sources deposited in reducing environment.

The main objective of the present study is essentially to describe a comprehensive geochemical study on crude oils from Western Desert using gas chromatography (GC) and gas chromatography mass spectrometry (GC–MS), to characterize the source depositional environments, and to assess the thermal maturity. This target achieved throughout the biomarkers characteristics as n-C15+ alkanes, isoprenoids, triterpanes and steranes.
2. Materials and methods

Nine crude oils (W1 – W9) were collected from different Western Desert basins namely: Gindi basin, South Deep Abu El-Gharadig basin, Abu El-Gharadig basin, Faghur Basin and Dahab-Merier basin (Fig. 1). The following methods were approved:

1. Each Crude oil sample was distilled up to 200 °C at atmospheric pressure. The residual fraction (>200°C) was deasphalted according to IP-143 standard procedure. The deasphalted fraction (maltene) was separated into saturates, naphthens, aromatics and resins by liquid column chromatography. The column used was packed with 1:1 alumina overlying silica gel. Saturates, aromatics and resins fractions were obtained by successive elution with n-pentane, toluene and methanol, respectively.

2. Saturated fractions were analyzed using Agilent 7890 plus HP gas chromatograph equipped with FID (Flame Ionization Detector) using fused silica capillary column HP–5 of 30 m in length, 0.32 mm in internal diameter and 0.25 μm of film thickness. The elution of the studied liquid was achieved with temperature programming from 80°C to 310°C at a rate of 3°C/min. Helium was used as a carrier gas flowing at a rate of 1 ml/min. The injector and detector temperatures were 320°C and 350°C, respectively.

3. Biomarkers traces in the saturate fractions were analyzed using PerkinElmer Clarus 500 gas chromatograph equipped with mass spectrometry detector using fused silica capillary column HP–5ms of 30 m in length, 0.32 mm in internal diameter and 0.25 μm of film thickness. The elution of the studied fraction was achieved with temperature programming from 80°C to 310°C at a rate of 3°C/min. Helium was used as a carrier gas flowing at a rate of 1.5 ml/min. The injector temperature was 300°C [2].

3. Results and discussions

3.1. Organic matter input

3.1.1. Normal and isoprenoid alkanes

The oil samples (W1-W5) from Gindi, South Deep Abu El gharadig, Abu El gharadig and Dahab- Merier basins (Fig. 2) show unimodal distribution with predominance of low to medium molecular weight hydrocarbons (n-C13–n-C35). A presence of significant amount of waxy alkanes (n-C23+), dominated by odd carbon number was observed giving moderate CPI values ranges from 0.99 to 1.10 (Table 1). These alkanes profiles are consistent with sediment receiving a substantial input of long chain alkanes, either from algae or plant cuticular waxes [15]. On the other hand, the oil samples (W6 – W9) from Faghur basin (Fi. 2) show extended n-alkanes ranging from (n-C13 – n-C35) with bimodal distribution pattern and are characterize by high degree of waxiness ranging from 1.76 to 2.32 and high terrigenous aquatic ratio (TAR) ranging between 0.80 to 1.06 (Table 1) suggesting high contribution of terrigenous organic matter [16].

The pristane and phytane ratio for group I oils (W1-W5) from Gindi, South Deep Abu-Ghardig and Abu-Gharadig, Dahab-Merier basins are in the range of 0.77–1.49 (Table 1) suggested their generation from organic matter input deposited in marine environment under anoxic to relatively suboxic conditions. In contrast, the oil samples from Faghur basin (group II) W6 – W9 possess high Pr/Ph ratios ranging from 2.63 to 3.60 (Table 1) suggesting high contribution of terreginous organic matter deposited under relatively oxic conditions. The lower Pr/C17 and Ph/n-C18 ratios in most of the studied oil samples are probably due to their maturity [17].

3.1.2. Tricyclic and Tetracyclic terpanes

The distribution of tricyclic terpanes in oils and source rocks formed in a variety of depositional environment and showed that the C19 and C20 members are more abundant in terrestrial oils while the C23 member is often the dominant homologue in the crude oils of marine source [18]. C19/C23 and C20/C23TT ratios are useful parameters to differentiate terrestrial versus marine input. The crude oil samples W6 – W9 exhibit these ratios in the range from 3.08 to 20.73 and from 2.18 to 13.08 respectively (Table 1). These high ratios indicate higher contribution of terrestrial organic matter. Also, C24 tetracyclic terpane is present in significant amount in all of the studied oil samples with high relative percentage in Dahab-Merier and Faghur samples (Fig. 3). The C19TT/(C19TT + C23TT) ratio of oil sample from Faghur basin is in the range from 0.76–0.95(Table 1) indicating mixed input predominantly terrestrial organic matter input [2].

![Fig. 1. Location map showing the studied crude oil in the North Western Desert, Egypt.](image-url)
However, all other samples exhibit this ratio in lower ranging from 0.04–0.48 suggesting marine organic matter input except W5 from Dahab basin which reveal mixed organic matter. In addition, the \(\frac{C_{24}TeT}{(C_{24}TeT + C_{23}TT)}\) ratio for the oil samples ranges from 0.55–0.79 for Faghur basin (Table 1). The high TeT along with relatively high Pr/Ph ratio and high \(\frac{C_{19}TT}{(C_{19}TT + C_{23}TT)}\) ratios indicate terrestrial organic matter input for the source rock generating the oils. Very low values were observed for Gindi (0.15), Abu El gharadig basins (0.06–0.28) and South Deep Abu El gharadig suggesting marine organic matter input. The intermediate value of W5 refers to its mixed origin.

3.1.3. \(C_{35}/C_{34}\) homohopane

The extended hopanes are dominated by \(C_{31}\) homohopane and decreasing towards \(C_{35}\) homohopane (Fig. 3). The \(C_{35}/C_{34}\) ratio is commonly used as an indicator of depositional environment of

![Fig. 2. Gas Chromatograms of the saturate fractions of Western Desert crude samples.](image)
source rocks generating oils. Higher C35/C34 hopane ratio is associated with anoxic conditions, while the lower values indicate suboxic to oxic depositional environment. The studied oil samples from Gindi, South Deep Abu El gharadig, Abu El gharadig and Dahab-Merier basins (W1 – W5) have higher C35/C34 ratios ranging from 0.84 to 0.98 (Table 1) suggesting their marine anoxic depositional environment. However, oil samples from Faghur basin (W6 – W9) have lower ratios (0.26–0.51, Table 1) indicating that oils were derived from source rocks deposited under relatively oxic conditions [2].

The relatively higher concentration of C35 homohopane indicates highly reducing depositional environment and exponential decrease in homohopanes concentration can be linked with oxic environment of deposition. Low values of this ratio result from oxidation process which reduces the side chain length and indicates oxic environment of deposition [17]. A C35 homohopane index (HHI) is shown in (Table 1) indicates that Faghur basin samples are terrestrial oils deposited under oxic depositional environment while others are marine deposited under anoxic depositional environment. On the other hand, the majority of the analyzed samples (W1 – W5) have relatively high concentrations of C29 hopanes with C29/C30 hopane ratios ranging from 0.49 to 0.85 (Table 1). This refers to a marine environment with organic rich carbonate and evaporates, while the oil samples of Faghur basin (W6 – W9) have low C29/C30 hopane ratio in the range of 0.41–0.60 (Table 1), those having oxic depositional conditions. This is supported by disterane/sterane ratio. Low disterane/sterane ratios designate anoxic clay-poor source rock e.g. carbonate, whereas high values reveal oxic and clay rich environment of organic rich matter [2].

The abundance of C3017s-diahopane (C30D) relative to C2918a (H)-30-norneohopane (C29Ts) is sensitive to redox conditions. The oxygen concentration can be detected by applying C30D/C29Ts ratio. The higher values (>1) of C30D/C29Ts ratio indicate high oxygen concentration [2]. Faghur basin samples show high C30D/C29Ts ratio in the range of 1.22–2.05 (Table 1) suggesting more oxygen depositional environment for the source rocks generating such oils. On the other hand, Gindi, South Deep Abu El gharadig, Abu El gharadig and Dahab-Merier basins crude oil samples have C30D/C29Ts ratio <1 indicating comparatively lower oxygen concentrations.

3.1.4. Oleanane/Hopane

Oleanane in trace proportion occurs widely in Cretaceous marine sediments and abounds in Tertiary sediments. Oleanane may be derived from betulins and other pentacyclic triterpenes found in angiosperms [2]. In this study, oleanane is present only in Abu El gharadig and South Deep A Abu El gharadig basins (Fig. 3, see peak identification in Table 2) suggesting their generation from Cretaceous or early Tertiary source rocks.

In contrast to hopanes, moretaenes seem to be abundant in organic material of terrestrial origin [19]. The lower abundance of moretane relative to hopane may reflect a weak terrigenous input. The ratio of 17α(H),21α(H) Moretane to the corresponding 17α(H),21β(H) Hopane (Bio归纳) of oil samples (W1 – W5) ranges from 0.05 to 0.14 (Table 1). These relatively low values reflect an open sea with minimal contribution from terrestrial material. However, samples (W6 – W9) from Faghur basin have high Moretane/Hopane ratio (0.55–0.74, Table 1). This reflects higher contribution of terrestrial input.

3.1.5. Gammacerane/C35 hopane

High gammacerane index (Gammacerane/C35 αβ hopane) is interpreted to indicate highly reducing hypersaline condition during deposition. However, relatively high gammacerane abundance is also generally regarded as an indicator of stratified water column [20]. The gammacerane index varies from 0.10 to 0.15 in oil samples (W1 – W5, Table 1) from Gindi, South Deep Abu El gharadig, South Deep Abu El gharadig, Abu El gharadig and Dahab-Merier basins.
Abu El gharadig and Dahab-Merier basins which combined with relatively low Pr/Ph ratio. Since the gammacerane index and Pr/Ph ratios are low, the environment of source rock deposition cannot be definitely interpreted as hypersaline, but their presence certainly points to water–column stratification [21]. While Faghur basin samples have very low gammacerane index and high Pr/Ph ratio probably indicate that these oils were deposited under oxic conditions.

3.1.6. Distribution of C_{27}-C_{28}-C_{29} steranes
The prevalence of C_{27} steranes is related with the marine phytoplankton contribution while predominance of C_{28} steranes and C_{29} steranes indicate a strong influence of lacustrine algae and terrestrial input respectively [2]. All samples exhibit high abundance of C_{29} regular steranes compared to C_{27} and C_{28} (Fig. 4, see peak identification in Table 2). Faghur basin samples show the highest abundance of this compound indicating higher contribution of...
terrestrial land plant organic matter to the source rocks originating these oils. However, origin of oil samples from other basins were indicated to be from mixed terrestrial and marine organic facies.

3.1.7. C29 Diasteranes/C29 steranes

Diasteranes/steranes ratio differentiates carbonate versus clastic source rocks. Low ratios of diasteranes/steranes are linked with anoxic, lean in clay contents and carbonate rich source rocks, while high ratios are, in general, found in oils produced from clastic sediments. Low ratios of diasteranes/steranes are linked with anoxic, lean in clay contents and carbonate rich source rocks, while high ratios are, in general, found in oils produced from clastic sediments where clay minerals perform catalytic activity in the formation of diasteranes [2]. The samples from Gindi, Abu-Gharadig, South Deep Abu El qharadig and Dahab-Mireir basins show that this ratio is close to the 0.48 to 0.59 indicating that these oils are maturing maturation. The crude oil samples analyzed in this study show this ratio in the range of 0.48 to 0.59 indicating that these oils are thermally mature and reach equilibrium stage.

Another hopane based maturity parameter is the ratio of 17α (H), 21β(H)-hopane to 17β (H), 21β(H)-moretane for C29 and C30 compounds, reaching equilibrium stage at somewhat higher thermal maturities [2]. The crude oil samples show C29 αβ/βα and C30 αβ/βα ratios in the range of 0.85 to 0.95 and 0.87 to 0.96 respectively (Table 1) which are characteristic of oils generated from source rocks containing mature organic matter.

3.2. Maturity assessment

3.2.1. Homohopane Isomerization [C29 22S/(22S + 22R)]

The extent of isomerization at C-22 position in homohopanes has widely been used to assess thermal maturation of petroleum samples [22]. The biologically produced precursors for hopanes (22R) are gradually converted to a mixture of 22R and 22S diasteroeeomers. Typically C32 homohopanes are used for calculations of the 22S/(22S + 22R) ratio. The ratio 22S/(22S + 22R) for homohopanes increases with maturity. The equilibrium stage is the closing stage of the reaction in the oil generation zone [23]. The ratio rises from 0 to about 0.6 (Equilibrium = 0.54 – 0.56) during maturation. The crude oil samples analyzed in this study show this ratio in the range of 0.48 to 0.59 indicating that these oils are thermally mature and reach equilibrium stage.

Another hopane based maturity parameter is the ratio of 17α (H), 21β(H)-hopane to 17β (H), 21β(H)-moretane for C29 and C30 compounds, reaching equilibrium stage at somewhat higher thermal maturities [2]. The crude oil samples show C29 αβ/βα and C30 αβ/βα ratios in the range of 0.85 to 0.95 and 0.87 to 0.96 respectively (Table 1) which are characteristic of oils generated from source rocks containing mature organic matter.

3.2.2. Sterane Isomerization

The relative abundance of 20S/(20S + 20R) is widely used as maturity parameter. Isomerization at C-20 in the C29 5x (H), 14x (H), 17x (H)-steranes causes 20S/20S + 20R ratio to rise from 0 to about 0.50. After that equilibrium is reached (equilibrium = 0.52 – 0.55) an additional maturation does not change the ratio [2]. Gindi and Dahab Mierir Basins samples show that this ratio is close to the equilibrium value (0.49 and 0.50). On other hand, all other samples show this ratio in the range (0.53–0.55, Table 1) indicating that organic matter derived from these sediments is at mature stage.

---

Table 2

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Name</th>
<th>Peak No.</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C24 Tricyclic Terpane</td>
<td>A</td>
<td>C21 sterane</td>
</tr>
<tr>
<td>2</td>
<td>C24 Tricyclic Terpane</td>
<td>B</td>
<td>C22 sterane</td>
</tr>
<tr>
<td>3</td>
<td>C24 Tricyclic Terpane</td>
<td>C</td>
<td>C27 13(H) 17x(H) Diacholestane (20S)</td>
</tr>
<tr>
<td>4</td>
<td>C24 Tricyclic Terpane</td>
<td>D</td>
<td>C27 13(H) 17x(H) Diacholestane (20R)</td>
</tr>
<tr>
<td>5</td>
<td>C24 Tricyclic Terpane</td>
<td>E</td>
<td>C27 13(H) 17x(H) Diacholestane (20R)</td>
</tr>
<tr>
<td>6</td>
<td>C24 Tricyclic Terpane</td>
<td>F</td>
<td>C28 8xDiacholestane (20S)</td>
</tr>
<tr>
<td>7</td>
<td>C24 Tricyclic Terpane (R + S)</td>
<td>G</td>
<td>C28 8xDiacholestane (20R)</td>
</tr>
<tr>
<td>8</td>
<td>C24 Tetracyclic Terpane</td>
<td>H</td>
<td>C27 5x(H) 14x(H) 17x(H) cholestane (20S)</td>
</tr>
<tr>
<td>9</td>
<td>C24 Tricyclic Terpane (22R)</td>
<td>I</td>
<td>C27 13(H) 17x(H) Diacholestane (20R)</td>
</tr>
<tr>
<td>10</td>
<td>C24 Tricyclic Terpane (22S)</td>
<td>J</td>
<td>C27 5x(H) 14x(H) 17x(H) cholestane (20R)</td>
</tr>
<tr>
<td>11</td>
<td>C24 Tricyclic Terpane (22R)</td>
<td>K</td>
<td>C27 5x(H) 14x(H) 17x(H) cholestane (20R)</td>
</tr>
<tr>
<td>12</td>
<td>C24 Tricyclic Terpane (22S)</td>
<td>L</td>
<td>C29 24ethyl, 13(H) 17x(H) Diacholestane (20R)</td>
</tr>
<tr>
<td>13</td>
<td>C24 Tricyclic Terpane (22R)</td>
<td>M</td>
<td>C28 8x(H) 14x(H) 17x(H) ergostane (20S)</td>
</tr>
<tr>
<td>14</td>
<td>C24 Tricyclic Terpane (22S)</td>
<td>N</td>
<td>C28 5x(H) 14x(H) 17x(H) cholestane (20R)</td>
</tr>
<tr>
<td>15</td>
<td>C29 18β(H)-22, 29, 30-trisnorhopane (Ts)</td>
<td>O</td>
<td>C28 5x(H) 14x(H) 17x(H) cholestane (20S)</td>
</tr>
<tr>
<td>16</td>
<td>C29 17x(H)-22, 29, 30-trisnorhopane (Tm)</td>
<td>P</td>
<td>C28 5x(H) 14x(H) 17x(H) cholestane (20R)</td>
</tr>
<tr>
<td>17</td>
<td>C29 Tricyclic Terpane (22R)</td>
<td>Q</td>
<td>C29 5x(H) 14x(H) 17x(H) stigmastane (20S)</td>
</tr>
<tr>
<td>18</td>
<td>C29 Tricyclic Terpane (22S)</td>
<td>R</td>
<td>C29 5x(H) 14x(H) 17x(H) stigmastane (20R)</td>
</tr>
<tr>
<td>19</td>
<td>C29 Tricyclic Terpane (22R)</td>
<td>S</td>
<td>C29 5x(H) 14x(H) 17x(H) stigmastane (20S)</td>
</tr>
<tr>
<td>20</td>
<td>C29 Tricyclic Terpane (22S)</td>
<td>T</td>
<td>C29 5x(H) 14x(H) 17x(H) stigmastane (20R)</td>
</tr>
</tbody>
</table>

Please cite this article in press as: S.M. El-Sabagh et al., Fingerprinting of biomarker characteristics of some Egyptian crude oils in Northern Western Desert as evidence for organic matter input and maturity level assessment, Egypt. J. Petrol. (2017), http://dx.doi.org/10.1016/j.ejpe.2017.05.004
Another maturity parameter derived from C$_{29}$ regular sterane is the proportion of 5α(H), 14β(H), 17β(H) to 5α(H), 14β(H), 17β(H) + 5α(H), 14α(H), 17α(H) ratios expressed as $\alpha\beta/\alpha\alpha\alpha$ sterane. With increasing in maturity, the biologically produced $\alpha\alpha\alpha$ form converts gradually into a mixture of $\alpha\beta\beta$ and $\alpha\alpha\alpha$. This ratio appears to be independent of source organic matter input and is rather slower to reach equilibrium compared to 20S/(20S + 20R) ratio, thus making it effective at higher levels of thermal maturity [2]. The samples (W1–W9) show this ratio in the range of 0.56, 0.65 (Table 1) suggesting the sediments under study are just
reaching maturity. The $\frac{\alpha\beta}{(\alpha\beta + \alpha\alpha\alpha)}$ sterane ratio responds differently to different source rock lithologies. The higher values of this ratio have been noted for the hypersaline rocks compared with adjacent shales. In addition to this, lower values of this ratio reflect non-migrated hydrocarbons.

4. Conclusions

1. The oil samples from Gindi, South deep Abu El ghradig, Abu El gharadig and Dahab-Merier basins, show unimodal distribution with predominance of low to medium molecular weight hydrocarbons suggesting high contribution of terrigenous organic matter. The oil samples from Gindi, South deep Abu- Gharadig, Abu-Gharadig and Dahab- Merier basins have higher $C_{33}/C_{34}$ ratios suggesting their marine anoxic depositional environment. However, oil samples from Faghur basin have lower ratios indicating that oils were derived from source rocks deposited under relatively oxic conditions.

2. All samples from Western Desert, exhibit high abundance of $C_{29}$ regular steranes compared to $C_{27}$ and $C_{28}$, Faghur basin samples show the highest abundance of this compound indicating higher contribution of terrestrial land plant organic matter to the source rocks originating these oils. However, origin of oil samples from other basins were indicated to be from mixed terrestrial and marine organic facies and are thermally mature and reach equilibrium stage.

References