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Crude Oil Geochemistry Dependent Biomarker Distributions in the Gulf of Suez, Egypt

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1. Introduction

The Gulf of Suez occupies the northern end of the Red Sea rift (Said, 1962) Figure 1. It is a northwest-southeast fault-forming basin that provided adequate conditions for hydrocarbon generation, maturation and entrapment (Dolson et al., 2000). The Gulf of Suez province has been producing oil since 1908 and is reported to have 1.35 billion barrels of recoverable oil reserves. Intensive exploration has resulted in the discovery of more than 120 oil fields providing more than 50% of the overall daily oil production in Egypt (Egypt Country Analysis Briefs, 2009).

The Precambrian to Holocene lithostratigraphic succession of the Gulf reaches a total thickness of about 6,000 meters (Figure 2), which contributed to the development of different types of structural traps as well as different source, reservoir, and cap rocks (Khalil and Moustafa, 1995). It can be subdivided into three major lithostratigraphic sequences relative to the Miocene rifting of the Afro-Arabian Plate that led to the opening of the Suez rift and deposition of significant syn-rift facies from the Miocene Gharandal and Ras Malaab Groups (Evans, 1990). The pre-rift lithostratigraphic section, starting from the Nubia Sandstone to the Eocene Thebes Formation, rests unconformably on Precambrian basement. Rifting in the Gulf was associated with the upwelling of hot asthenosphere (Hammouda, 1992). Both crustal extension and tectonic subsidence reached their peaks between 19 and 15 Ma (Steckler, 1985; Steckler et al., 1988). Palaeozoic through Tertiary strata and major Precambrian basement blocks are exposed on both sides of the southern province which is characterized by structural and depositional complexity (Winn et al., 2001). The regional dip of strata is towards the SW (Meshref et al., 1988).

Previous geochemical studies throughout the Gulf of Suez have revealed that the oils are derived mainly from marine sources, which may be differentiated into three main groups (Mostafa, 1993 and Barakat et al., 1997). The distribution of these oil families are consistent with the geographic subdivisions of the Gulf of Suez provinces as northern, central and southern (Moustafa, 2002). Crude oil of the northern Gulf of Suez province is characterized by a C_{35}/C_{34} homohopane index <1 and a relatively heavy carbon isotope composition ($\delta^{13}C$ saturate -27‰) suggesting generation from a less reducing marine source rock environment at relatively low levels of thermal maturity. Meanwhile, crude oil of the central province is characterized by low API gravity, a predominance of pristane over phytane, a high C_{35}/C_{34}

homohopane index, and a lighter carbon isotopic composition (δ^{13}C saturate -29‰). oils of the southern province is characterized by a high API gravity, a low sulfur content and intermediate carbon isotopic composition values (δ^{13}C saturate -28 to -29 ‰). These two oil groups are believed to be derived from a marine source and exhibits compositional heterogenity suggesting a complex petroleum system may be present in the Gulf of Suez province.

In the present study saturate and aromatic biomarker distributions as well as stable carbon isotope compositions have been determined for a collection of crude oils of various ages and derived from different source rock types in the Gulf of Suez. These biomarker parameters have been used in an attempt to characterize the types of organofacies, and depositional environments, and to assess the thermal maturity of the source rocks responsible for oil generation.

2. Sampling and analytical techniques

Crude oils of various ages and derived from various source rock types were collected from the giant producing fields in the Gulf of Suez namely: July, Ramadan, Badri, El-Morgan, Sidki, Ras El-Bahar, East Zeit, Hilal, Zeit Bay and Shoab Ali (Fig. 1). These oil samples were collected from syn-rift (Miocene) and pre-rift (Palaeozoic, Lower and Upper Cretaceous) reservoirs (Fig. 2).

The crude oil samples were fractionated using high performance liquid chromatography (HPLC) into saturates, aromatics, and resins following the standard procedures outlined by Peters and Moldowan (1993). Saturate fractions were treated with a molecular sieve (silicate) to remove the *n*-alkanes. The saturate and aromatic fractions were analyzed on a Hewlett Packard 5890 Series-II gas chromatograph equipped with a Quadrex 50m fused silica capillary column. The gas chromatograph was programmed from 40ºC to 340ºC at 10 ºC/min with a 2 min hold at 40º C and a 20 min hold at 340ºC. The saturate and aromatic fractions were also analyzed by gas chromatography-mass spectrometry (GCMS) using a Hewlett Packard 5971A Mass Selective Detector (MSD) to determine terpane (*m/z* 191) and sterane (*m/z* 217) distributions. The aromatic steroid hydrocarbon fractions were analyzed to determine mono- and triaroaromatic (*m/z* 253 and *m/z* 231) steroid hydrocarbon distributions. Aromatic sulphur compounds were monitored to determine dibenzothiophene (*m/z* 184), methyldibenzothiophenes (*m/z* 198), dimethyl-dibenzothiophenes (*m/z* 212), methylnaphthalenes (*m/z* 142, 156 and 170) and phenanthrenes (*m/z* 178, 192 and 206). Stable carbon isotope values (δ^{13}C) were determined for the whole oils, saturate and aromatic hydrocarbon fractions using a Micromass 602 D Mass-Spectrometer. Data are reported as δ^{13}C (‰) relative to the PDB standard. The organic geochemical analyses and stable carbon isotopes for the studied crude oil samples were conducted at the organic geochemical laboratories, Oklahoma State University, USA.

3. Results and discussions

Rohrback (1982) concluded that all the crude oils of the Gulf of Suez appear to be of the same genetic family. However, great variations in the biological marker distributions and stable carbon stable isotope compositions of the studied crude oils from this province suggest that this group should be subdivided into two subfamilies consistent vertically with
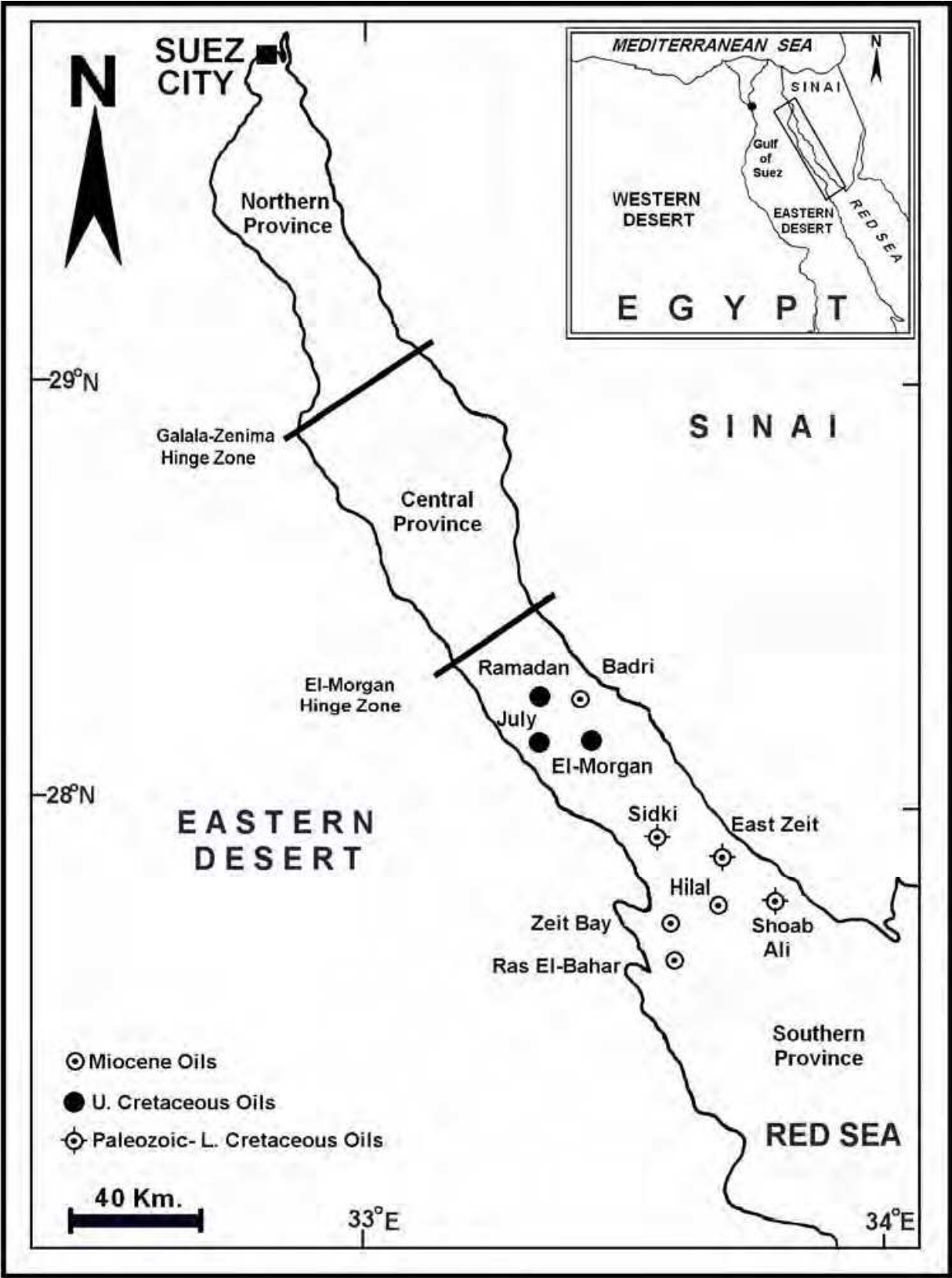
Fig. 1. Map showing the distribution of oil samples from the different fields of the southern Gulf of Suez province.
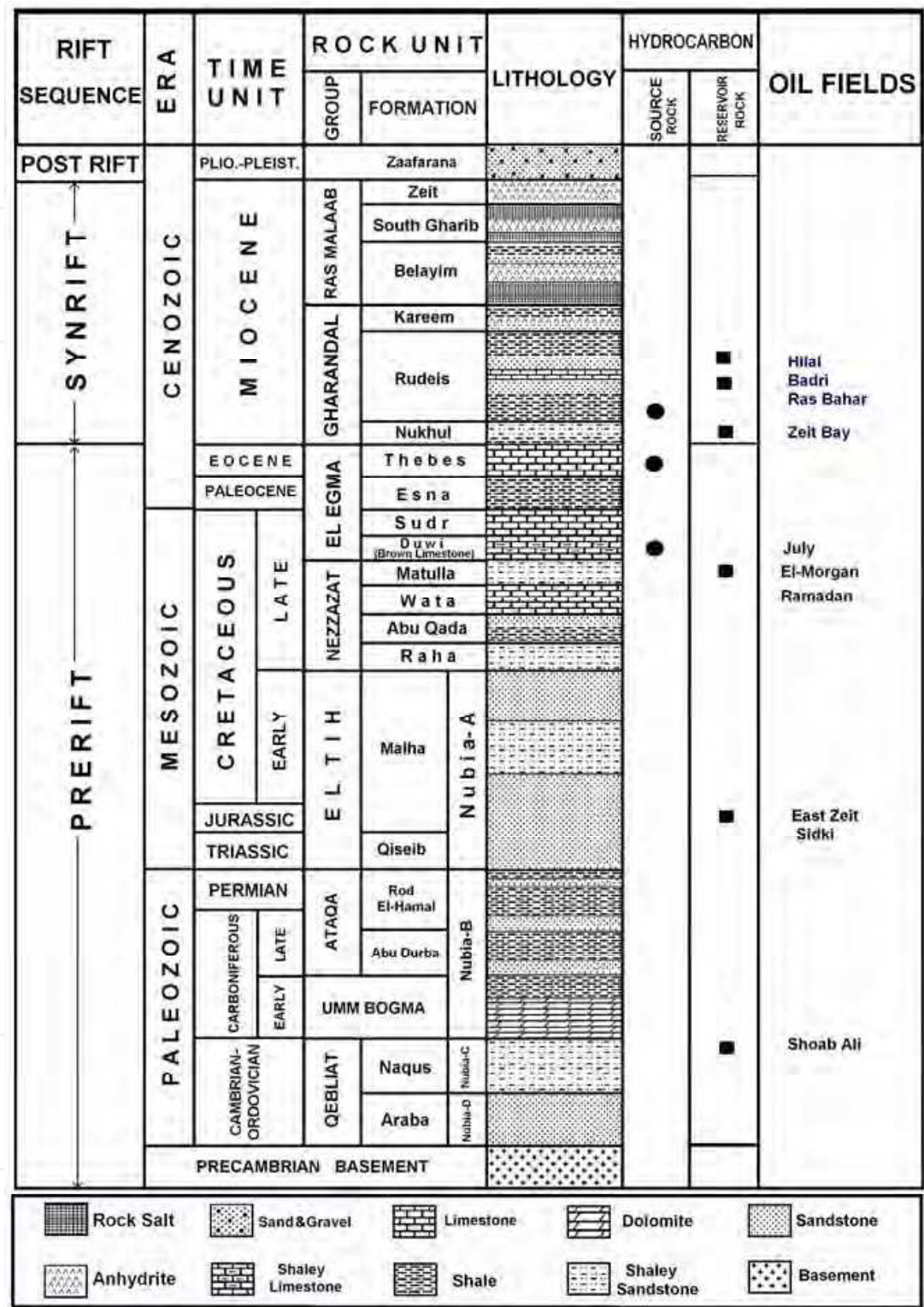
Fig. 2. Generalized lithostratigraphic succession illustrating the rifting sequences and hydrocarbon distributions in the southern Gulf of Suez modified after (Alsharhan, 2003).

the syn-rift and pre-rift tectonic sequences of the Gulf of Suez. Furthermore, the data from the present study suggests two oil families represent two distinct independent petroleum systems for hydrocarbon generation and maturation.

FIELD NAMES / WELL NAMES	HILAL HA-11	BADRI BDR-5	R-BAHAR RB-3	ZEIT BAY ZBC-1	JULY J-26	MORGAN M-208	RAMADAN R-55	E-Z EIT EZA-18	SIDKI GS 382 B-1	SHOAB ALI B-6
OIL TYPES	Type-I	Type-I	Type-I	Type-I	Type-II	Type-II	Type-II	Type-II	Type-II	Type-II
RESERVOIR AGE	Miocene	Miocene	Miocene	Miocene	U.Cretaceous	U.Cretaceous	U.Cretaceous	Paleoz.-L. Cretaceous	Paleoz.-L. Cretaceous	Paleoz.-L. Cretaceouse
BULK PARAMETERS										
AP° gravity	32.2	27.9	34.9	32.2	35.8	34.8	36.8	41.3	37.2	43.2
Sulphur (wt.%)	0.97	0.89	0.98	0.88	1.36	1.32	1.23	1.28	1.33	1.39
GC PARAMETERS										
Pr / Ph	1.37	1.12	1.15	1.13	0.81	0.91	0.93	1.01	0.94	1.03
Pr / n-C17	0.72	0.57	0.52	0.54	0.37	0.37	0.52	0.49	0.33	0.53
Ph / n-C18	0.58	0.58	0.48	0.56	0.46	0.42	0.47	0.48	0.35	0.56
CPI	1.02	1.01	1.01	1	0.99	0.98	0.97	0.99	0.99	1.01
GC- MS (Saturated Hydrocarbons)										
1-Terpanes (m/z 191)										
$Ts/(Ts+Tm)$	0.8	0.56	0.78	0.67	1.01	1.07	1.1	1.03	1.08	1.13
Oleanane Index%	26.42	28.43	23.15	21.4	3.38	4.45	3.09	6.3	5.01	6.03
Gammacerane Index%	9.44	8.62	8.66	7.56	21.7	25.53	23.71	29.19	21.99	25
C_{35}/C_{34} Homohopanes	0.79	0.77	0.81	0.87	1.15	1.04	1.05	1.01	1.25	1.07
2- Steranes (m/z 217)										
C_{27} %	49.5	43.6	47.6	43.8	41.5	44.6	42.6	41.5	44.3	42.6
C_{28} %	25.6	29.8	24.8	28.5	26.7	25.1	23.3	23.4	26.1	27.9
C_{29} %	24.9	26.6	27.6	27.7	31.8	30.3	34.1	35.1	29.6	29.5
$C_{29}\alpha\alpha\alpha\ 20S/(S+R)$	0.32	0.31	0.36	0.34	0.5	0.51	0.49	0.59	0.54	0.59
$C_{29}\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$	0.51	0.48	0.53	0.52	0.59	0.6	0.58	0.67	0.65	0.71
Diasterane Index	0.63	0.61	0.58	0.62	0.71	0.69	0.73	0.75	0.81	0.78
3- Aromatic Steranes										
TAS/(MAS+TAS)	0.46	0.38	0.41	0.45	0.64	0.68	0.62	0.71	0.73	0.76
TAS/MAS% (C_{27}/C_{28})	62.6	54.2	59.6	56.8	67.2	73.1	68.4	75.2	74.4	78.2
TAS/MAS% (all isomers)	66.1	58.6	63.2	64.2	73.8	76.2	72.3	76.5	77.2	83.2
GC-MS (Aromatic Sulfur Compounds)										
4-MDBT/1-MDBT (MDR)	1.87	1.88	1.81	1.85	2.31	2.27	2.34	2.85	2.91	2.87
2,4-DMDBT/1,4-DMDBT	2.13	2.25	2.3	2.46	4.2	4.1	4.56	5.23	5.98	5.45
4,6-DMDBT/1,4-DMDBT	1.98	2.45	2.29	2.84	3.98	4.15	4.38	4.96	5.23	5.58
DBT/P	0.31	0.34	0.37	0.38	0.57	0.62	0.69	0.73	0.94	0.81
Stable Carbon Isotope Composition										
$\delta^{13}C$ Saturate (‰ PDB)	-26.42	-27.26	-27.63	-28.36	-28.76	-28.46	-28.78	-26.31	-28.96	-28.16
$\delta^{13}C$ aromatic (‰ PDB)	-25.2	-26.92	-26.98	-28.04	-27.68	-28.43	-27.57	-26.25	-28.69	-28.06
$\delta^{13}C$ whole oil (‰ PDB)	-25.31	-26.96	-27.31	-27.56	-28.15	-27.78	-28.24	-26.98	-28.5	-27.76
Canonical Variable Parameters	-0.754	-1.407	-1.645	-2.148	-0.339	-2.76	-0.045	-3.365	-2.073	-2.698

Table 1. Bulk, biomarker properties and stable carbon isotope composition of crude oils from the Gulf of Suez.

Peak No.	Compound Name
A	C_{19} Tricyclic terpane
B	C_{20} Tricyclic terpane
C	C_{21} Tricyclic terpane
D	C_{22} Tricyclic terpane
E	C_{23} Tricyclic terpane
F	C_{24} Tricyclic terpane
G	C_{25} Tricyclic terpane (22R)
G	C_{25} Tricyclic terpane (22S)
H	C_{24} Tetracyclic terpane
I	C_{26} Tricyclic terpane (22R)
I	C_{26} Tricyclic terpane (22S)
J	C_{28} Tricyclic terpane (22R)
J	C_{28} Tricyclic terpane (22S)
K	C_{29} Tricyclic terpane (22R)
K	C_{29} Tricyclic terpane (22S)
L (Ts)	C_{27} 18α(H)-22, 29, 30- trisnorneohopane
M (Tm)	C_{27} 17α(H)-22, 29, 30- trisnorhopane
N	C_{30} Tricyclic terpane (22R)
N	C_{30} Tricyclic terpane (22S)
P	C_{31} Tricyclic terpane (22R)
P	C_{31} Tricyclic terpane (22S)
Q	C_{29} 18α(H)-norneohopane (29Ts)
R	C_{30} 18α(H)-oleanane
S	C_{30} 17α(H), 21β(H)-hopane
T	C_{30}17β(H), 21α(H)- moretane
U	C_{31} 17α(H), 21β(H)-30 homohopane (22S)
	C_{31} 17α(H), 21β(H)-30 homohopane (22R)
V	C_{30} Gammacerane
W	C_{32} 17 α(H), 21β(H)-30 bishomohopane (22S)
	C_{32} 17 α(H), 21β(H)-30 bishomohopane (22R)
X	C_{33} 17 α(H), 21β(H)-30 trishomohopane (22S)
	C_{33} 17 α(H), 21β(H)-30 trishomohopane (22R)
Y	C_{34} 17 α(H), 21β(H)-30 tetrakishomohopane (22S)
	C_{34} 17 α(H), 21β(H)-30 tetrakishomohopane (22R)
Z	C_{35} 17 α(H), 21β(H)-30 pentakishomohopane (22S)
	C_{35} 17 α(H), 21β(H)-30 pentakishomohopane (22R)

Table 2. Peak identifications in the *m/z* 191 mass fragmentograms.

Peak No.	Compound Name
	13β(H), 17a(H)- diacholestane (20S)
a	13β(H), 17a(H)- diacholestane (20R)
	13a(H), 17β(H)- diacholestane (20S)
b	13a(H), 17β(H)- diacholestane (20R) +
c	24- Methyl-13β(H), 17a(H)- diacholestane (20S)
	24- Methyl-13β(H), 17a(H)- diacholestane (20R)
d	5a(H), 14a(H), 17a(H) – cholestane (20S)
e	5a(H), 14β(H), 17β(H) – cholestane (20R) +
f	24-Ethyl-13β(H), 17a(H)- diacholestane (20S)
g	5a(H), 14β(H), 17β(H) – cholestane (20S) +
	24-Methyl-13β (H), 17a(H)- diacholestane (20R)
h	5a(H), 14a(H), 17a(H) – cholestane (20R)
i	24-Ethyl-13β(H), 17a(H)- diacholestane (20R)
j	24-Ethyl-13 a(H), 17β(H)- diacholestane (20S)
k	5a(H), 14a(H), 17β(H)– 24-methylcholestane (20S)
l	5a(H), 14a(H), 17β(H)– 24-methylcholestane (20R)+
m	24-Ethyl-13 a(H), 17β(H)- diacholestane (20R)
n	5a(H), 14β(H), 17β(H)– 24-methylcholestane (20S)
o	24-Propyl-13a(H), 17β(H)- diacholestane (20S)
p	5a(H), 14a(H), 17a(H)– 24-methylcholestane (20R)
q	5a(H), 14a(H), 17a(H)– 24-ethylcholestane (20S)
r	5a(H), 14β(H), 17β(H)– 24-ethylcholestane (20R)
s	5a(H), 14β(H), 17β(H)– 24-ethylcholestane (20S)
t	5a(H), 14a(H), 17a(H)– 24-ethylcholestane (20R)

Table 3. Peak identifications in the *m/z* 217 mass fragmentograms.

4. Gross geochemical characteristics

The syn-rift oil produced from (Miocene) reservoirs is a naphthenic, non-waxy crude with API gravity ranging from 27.9° to 34.9° and sulfur content between 0.78 to 0.98 wt.% (Table 1). Meanwhile, the second type, which occurs in the pre-rift lithostratigraphic units is paraffinic and waxy with API gravity ranging from 34° to 44° and sulfur content between 1.23 and 1.39 wt.%. The stratigraphic change in gross geochemical characteristics of the crude oils from a naphthenic to a paraffinic type is related probably to the change of source rock types from clastics to carbonate and environment of source rock deposition (Rohrback, 1982). High sulfur oils of the second oil type is indicative of carbonate evaporate source rocks, while the low sulfur concentrations are typical for siliciclastic source rocks (Gransch and Posthuma, 1974). The diversity of the gross geochemical characteristics of the crude oils is consistent vertically with a gradual change in API gravity and maturity variation (Matava et al., 2003).

5. Source-dependent biomarker distributions

Biomarkers are compounds that characterize certain biotic sources and retain their source information after burial in sediments (Meyers, 2003). It is used for oil-oil and oil-source rock correlations to assess the source of organofacies, kerogen types and the degree of thermal maturity (Philp and Gilbert, 1986; Waples and Machihara, 1991; Peters and Moldowan, 1993; Peters and Fowler, 2002). The great variability of saturate and aromatic biomarker indices, listed in Table 1, that enable subdivisions of the studied crude oil into two types referred as type-I and II as illustrated in (Figure 3). The predominance of n-alkanes and acyclic isoprenoids in the C_{11} to C_{35} region of the gas chromatograms is diagnostic of marine organofacies sources (Collister et al., 2004). A predominance of
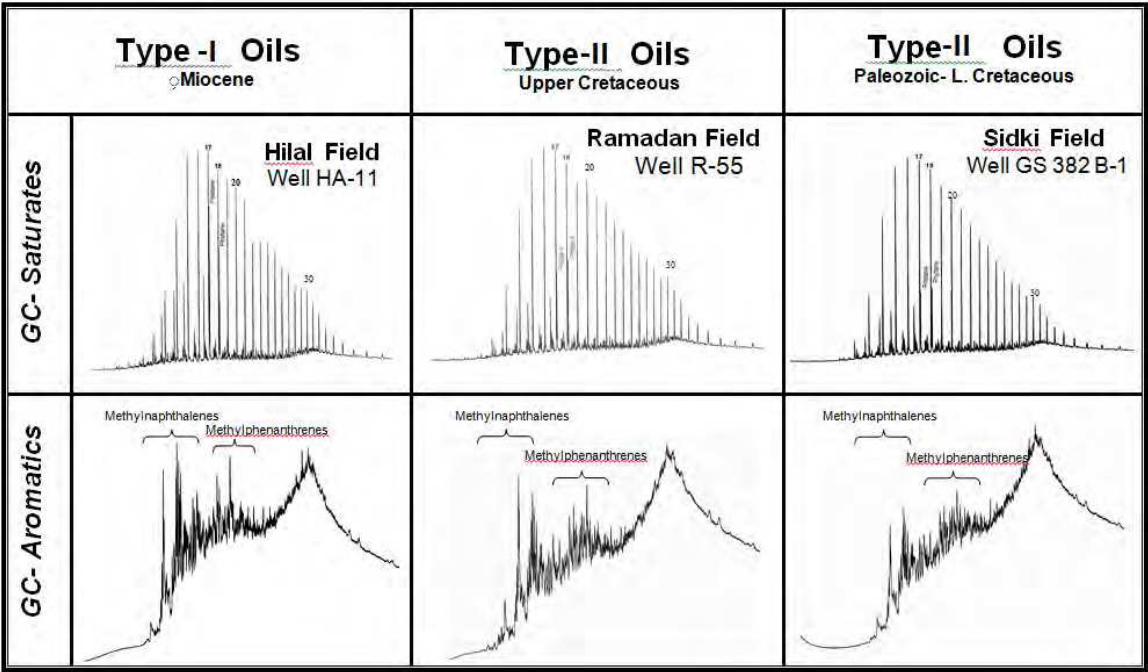

Fig. 3. Gas chromatograms of saturate and aromatic hydrocarbon fractions for representative crude oil types I and II.
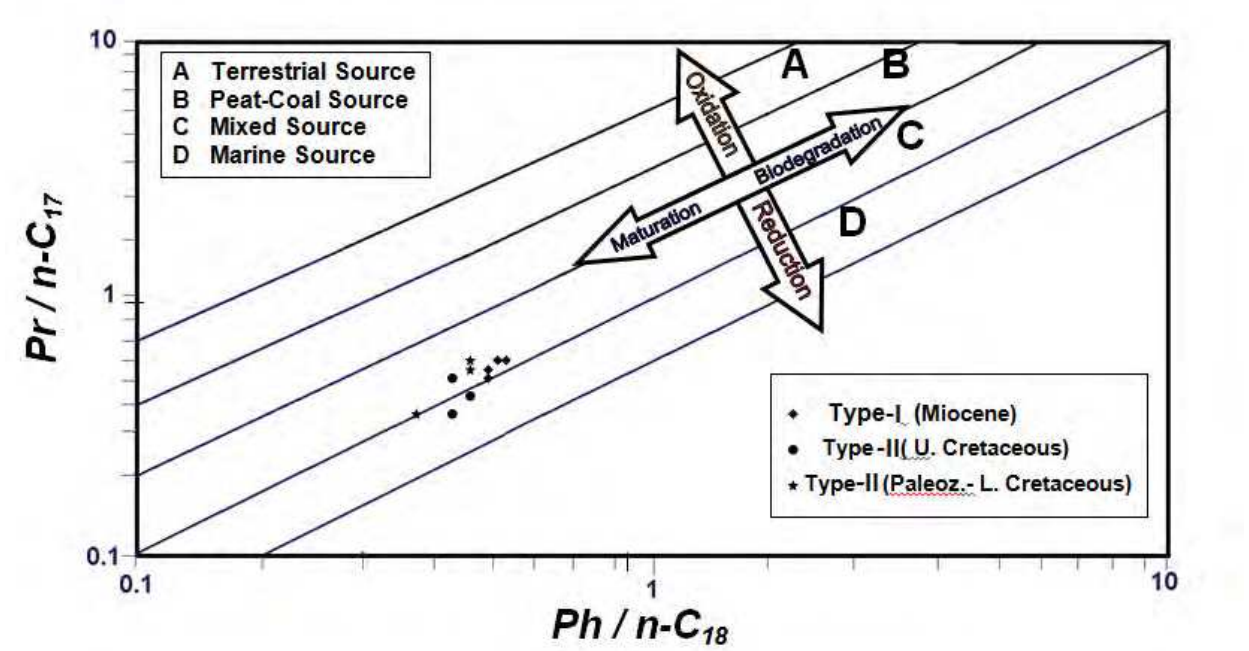
Fig. 4. Relationship between isoprenoids and *n*-alkanes showing source and depositional environments (Shanmugam, 1985) of the oil samples from the Gulf of Suez. All samples are located within the mixed to marine reducing depositional environments.

Peak No.	Compound Name
A	C_{20} Triaromatic Sterane
B	C_{21} Triaromatic Sterane
C	C_{26} Triaromatic Sterane (20*S*)
D	C_{26} Triaromatic Sterane (20*R*)+
	C_{27} Triaromatic Sterane (20*S*)
E	C_{28} Triaromatic Sterane (20*S*)
F	C_{27} Triaromatic Sterane (20*R*)
G	C_{28} Triaromatic Sterane (20*R*)

Table 4. Peak identifications in the *m/z* 231 mass fragmentograms.

pristane over phytane (Pr/Ph ratio >1) and the high odd-even carbon preference index (CPI>1) for the type-I oil is typical of crude oils generated from source facies containing terrigenous, wax-rich components (Peters et al., 2000). Type-II oil has lower Pr/Ph ratios (<1) and a slight even-carbon preference index (CPI<1) indicating algal/bacterial organic detritus in the kerogen (Collister et al., 2004), typical for a marine source rock deposited under less reducing conditions (Lijmbach, 1975). The nature of the source rock depositional environments can be further supported from the plotting of the isoprenoid ratios Pr/*n*-C_{17} versus Ph/*n*-C_{18} (Shanmugam,1985). It can be seen from Fig. 4 that both of the oil types plotted in the border region of marine-mixed organic matter with the source rocks being deposited under less reducing conditions and receiving significant clastic input (Bakr and Wilkes, 2002).

Peak No.	Compound Name
a	5 β- C_{27} Monoaromatic Sterane (20*S*)
b	dia- C_{27} Monoaromatic Sterane (20*S*)
c	5 β- C_{27} Monoaromatic Sterane (20*R*)+
	dia- C_{27} Monoaromatic Sterane (20*R*)
d	5 α- C_{27} Monoaromatic Sterane (20*S*)
e	5 β- C_{28} Monoaromatic Sterane (20*S*)+
	dia- C_{28} Monoaromatic Sterane (20*S*)
f	5 α- C_{27} Monoaromatic Sterane (20*R*)
g	5 α- C_{28} Monoaromatic Sterane (20*S*)
h	5 β- C_{28} Monoaromatic Sterane (20*R*)+
	dia- C_{28} Monoaromatic Sterane (20*R*)
i	5 β- C_{29} Monoaromatic Sterane (20*S*)+
	dia- C_{29} Monoaromatic Sterane (20*S*)
j	5 α- C_{29} Monoaromatic Sterane (20*S*)
k	5 α- C_{28} Monoaromatic Sterane (20*R*)
l	5 β- C_{29} Monoaromatic Sterane (20*R*)+
	dia- C_{29} Monoaromatic Sterane (20*R*)
m	5 α- C_{29} Monoaromatic Sterane (20*R*)

Table 5. Peak identifications in the m/z 253 mass fragmentograms.

Terpane biomarker distributions derived from the *m/z* 191 mass chromatograms are shown in (Figure 5) and peak identifications are given in (Table 2). The ratio of Ts/(Ts+Tm) is considered as a facies and depositional environmental parameter of the relevant source rocks (Bakr and Wilkes, 2002). It is also considered a maturation parameter due to the greater thermal stability of Ts (18α(H)-22,29,30-trisnorneohopane) than its counterpart Tm (17α (H)-22,29,30-trisnorhopane) (Seifert and Moldowan, 1978; Cornford et al., 1988; Isaksen, 2004). Ts/(Ts+Tm) ratio for the crude oil is generally consistent with the carbon preference index CPI, indicating an anoxic marine depositional environment (Mello et al., 1988). The C_{35}/C_{34} homohopane ratio was found to be less than unity for type-I oil, suggesting a reducing marine environment. The Ts/(Ts+Tm) ratio is greater than unity for type-II oil suggesting a higher contribution of bacterial biomass to the sediments possibly reflecting a highly saline reducing environment (ten Haven et al., 1988; Mello et al., 1988).

Depositional environment biomarker parameters based on the terpanes (*m/z* 191), such as the oleanane index [oleanane/(oleanane+hopane)] and gammacerane index [gammacerane/(gammacerane+hopane)], illustrate that type-I oil is highly enriched in oleanane compared to the type-II oil. The oleanane ratio are 28.4% in some samples clearly demonstrating an enrichment of angiosperm higher land plant input to the source kerogen of Tertiary age (Ekweozor et al., 1979; Moldowan et al., 1994). Meanwhile, the low oleanane index in the type-II oil, ranging from 3.4 to 6.3%, suggesting generation from an Upper Cretaceous source rock or older (Moldowan et al., 1994). Higher values of the gammacerane index for type-II oil (21.7 to 25.5%) compared to type-I oil (7.6 to 9.4%) indicates a highly saline depositional environment associated with an evaporitic-carbonate deposition and low terrigenous input (Rohrback, 1982; Mello et al., 1988; Peters and Moldowan, 1994).

Sterane distributions for the two oil types (m/z 217) are shown in (Figures 5) and compound identifications are given in (Table 3). The predominance of C_{27} steranes (Table 1) and the presence of C_{30} *n*-propyl steranes (Figure 5) further support the idea of generation from bacterial-algal marine source rocks (Moldowan et al., 1985; Peters and Moldowan, 1991). Type-II oil is highly enriched in αββ sterane isomers relative to the type-I oil, which suggests that the type-II oil is probably generated from an evaporitic-carbonate source rock.

Cross plots of the Pr/Ph ratio for the two oil types against various depositional environment biomarker indices show an obvious separation of the two oil types, and a direct relationship of the Pr/Ph ratio with the oleanane index and an inverse relationship with gammacerane and the C_{35}/C_{34} homohopane ratio. An inverse relationship also exists between the oleanane and gammacerane indices for the two oil types (Figure 6). The separation of the two oil types is interpreted to indicate the presence of two independently sourced oils that consistent vertically with the pre-rift and syn-rift tectonic sequences of the Gulf of Suez.
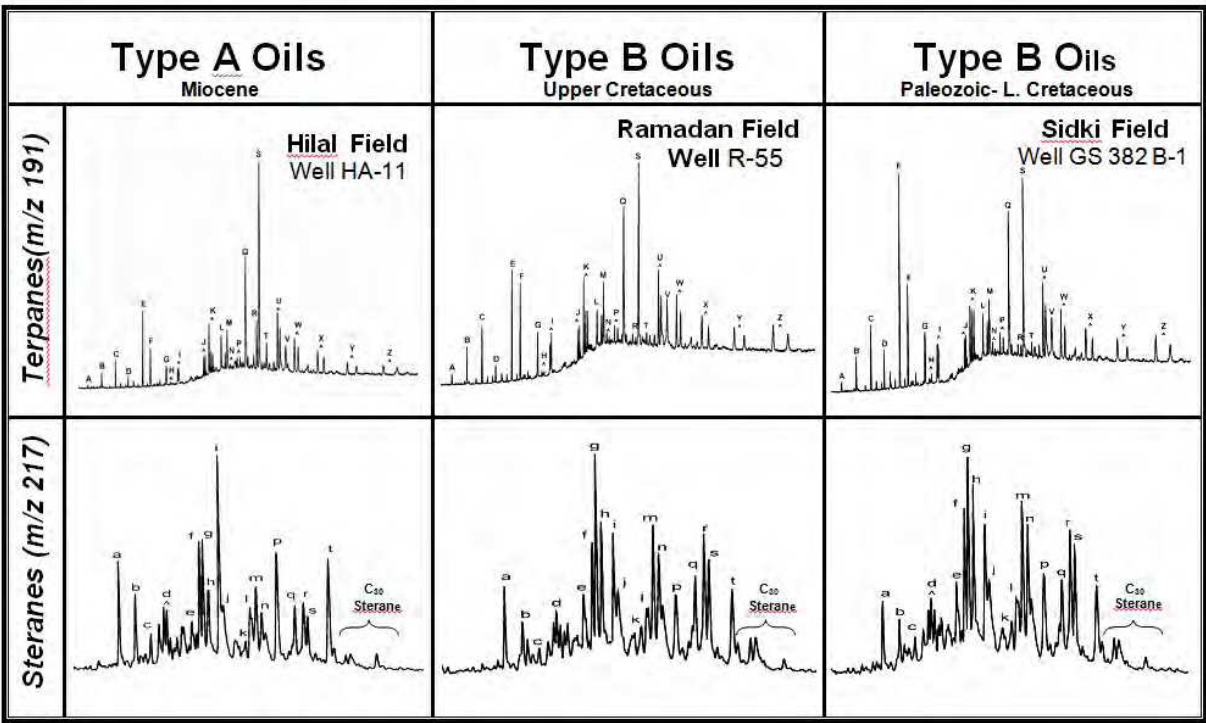
Fig. 5. Triterpane (m/z 191) and sterane (m/z 217) distribution patterns of the saturate hydrocarbon fractions from the two oil types in the Gulf of Suez. Labeled peaks are identified in Tables 2 and 3.
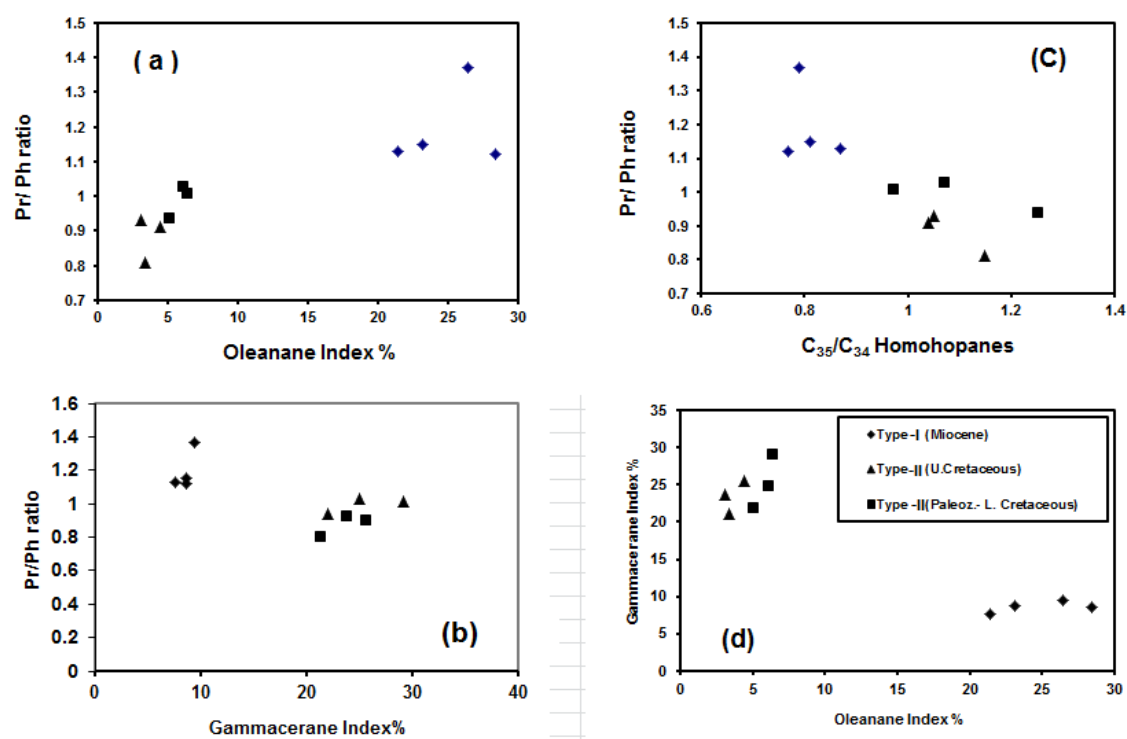
Fig. 6. A cross plot relation of source parameter Pr/Ph ratio for the studied crude oils that enable from differentiation of crude oils into two groups and show a direct relationship between Pr/Ph ratio with oleanane index and reverse relation with gammacerane and C_{35}/C_{34} homohopanes. A reverse relationship is shown on the basis of oleanane versus gammacerane indices.
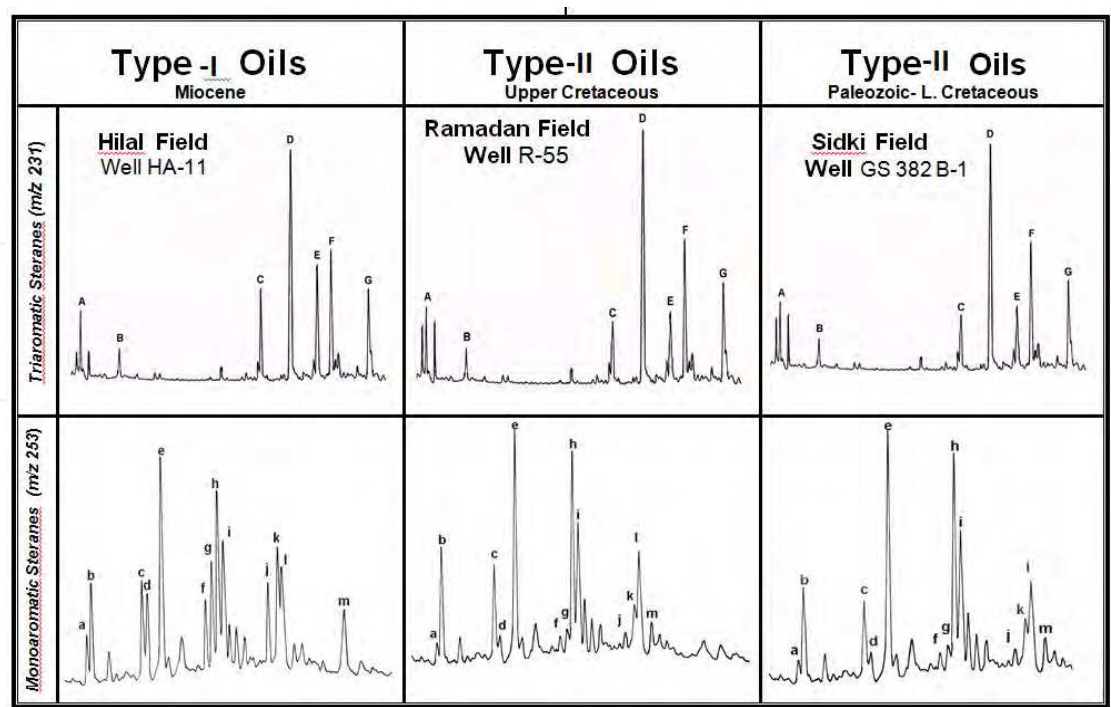

Fig. 7. Triaromatic (*m/z* 231) and monoaromatic (*m/z* 253) distribution patterns for two oil types from the Gulf of Suez. Labeled peaks are identified in Tables 4 and 5.
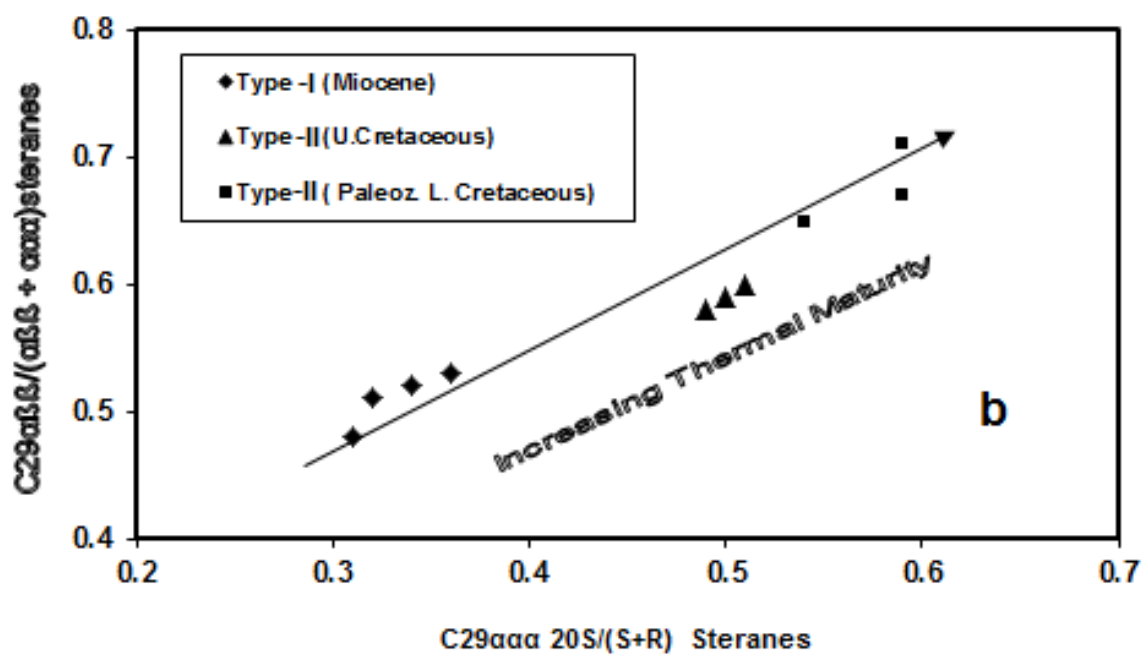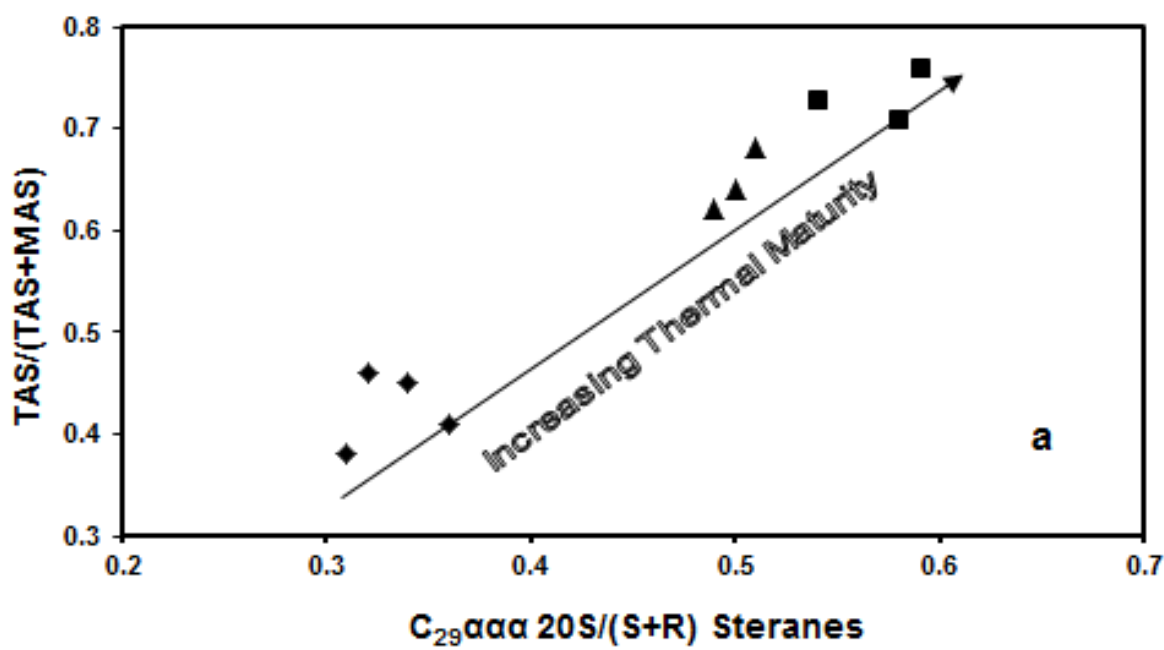
Fig. 8. Regular relationship between sterane maturity biomarkers C_{29} $\alpha\alpha\alpha$ 20S/(S+R) sterane with [(TAS/(TAS+MAS))] and $C_{29}\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$.

Peak No.	Compound Name
	Naphthalenes
A	2-Methylnaphthalene
B	1-Methylnaphthalene
C	2-Ethylnaphthalene
D	1-Ethylnaphthalene
E	2,6+2,7-Dimethylnaphthalene
F	1,3+1,7-Dimethylnaphthalene
G	1,6-Dimethylnaphthalene
H	1,4+2,3-Dimethylnaphthalene
I	1,5-Dimethylnaphthalene
J	1,2-Dimethylnaphthalene
K	1,3,7-Trimethylnaphthalene
L	1,3,6-Trimethylnaphthalene
M	1,3,5+1,4,6-Trimethylnaphthalene
N	2,3,6-Trimethylnaphthalene
O	1,2,4-Trimethylnaphthalene
P	1,2,5-Trimethylnaphthalene
	Phenanthrenes
a	Phenanthrene (P)
b	3-Methylphenanthrene
c	2-Methylphenanthrene
d	9-Methylphenanthrene
e	1-Methylphenanthrene
f	2,6+3,5-Dimethylphenanthrene
g	2,7-Dimethylphenanthrene
h	1,3+2,10+3,10+3,9-Dimethylphenanthrene
i	1,6-Dimethylphenanthrene
j	1,7-Dimethylphenanthrene
k	2,3-Dimethylphenanthrene
l	1,9-Dimethylphenanthrene
	Dibenzothiophenes
1	Dibenzothiophene
2	4-Methyldibenzothiophene
3	3,2-Methyldibenzothiophene
4	1-Methyldibenzothiophene
5	4-Ethyldibenzothiophene
6	4,6-Dimethyldibenzothiophene
7	2,4-Dimethyldibenzothiophene
8	1,4-Dimethyldibenzothiophene

Table 6. Peak identifications of the aromatic sulfur compound mass fragmentograms.

6. Maturation-dependent biomarker distributions

The Gulf of Suez province is characterized by local areas of higher heat flow due to the presence of hot spots in the southernmost Gulf and northern Red Sea (Alsharhan, 2003). Biomarker maturity parameters, including the sterane isomerization , C_{29} $\alpha\alpha\alpha20S/(S+R)$, and ratios based on the mono-and triaromatic steroidal hydrocarbon distributions (*m/z* 253 and 231) are shown in (Figure 7) with compound identifications in (Tables 4 and 5). These parameters also clearly distinguish the two different oil types on the basis of their different maturity levels consistent with the pre-rift and syn-rift tectonic sequences of the Gulf of Suez. Increasing source rock maturation from diagenesis to catagenesis is accompanied by an increase in the degree of aromaticity that converts monoaromatic steroids (MAS) to triaromatic steroids (TAS) lead to an increase thermal maturity through diagenetic/catagenetic processes results in the conversion of monoaromatic steroid to triaromatics (Seifert and Moldowan, 1978).

The triaromatic/monoaromatic maturity parameters (TAS/MAS) for all isomers and C_{27}/C_{28} ratios found to be 60% for type-I oil. For type-II B oil these ratios reaches more than 75%. Both of these ratios indicate a predominance of triaromatic relative to monoaromatic steroids for type-II oil compared to type-I oil which in turn reflect the higher maturity level for the type-II oil. Thus, it is proposed that type-II oil was generated from high mature source rock compared to type-I oil which are considered to be derived from a marginally mature source rock in the Gulf of Suez.

A plot showing the relationship between the sterane isomerization ratios $C_{29}\alpha\alpha\alpha$ $20S/(S+R)$ and $C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ and TAS/(MAS+TAS), that according to Seifert and Moldowan (1981), are genetically related to the effect of thermal maturity processes are shown in (Figure 8). It shows that there is a direct relationship between $C_{29}\alpha\alpha\alpha$ $20S/(S+R)$ and both TAS/(MAS+TAS) and $C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ increasing with burial depth of the source rocks (Matava et al., 2003). Type-II oil has a maximum value of 0.71 for the sterane isomerization ratio and 0.59 for the $C_{29}\alpha\alpha\alpha$ $20S/(S+R)$ ratio, while these ratios for type-I oil is 0.53 and 0.36 respectively. The API gravity is directly proportional to the maturity biomarker parameters as $C_{29}\alpha\alpha\alpha$ $20S/(S+R)$, $C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$, TAS/(MAS+TAS) and C_{35}/C_{34} homohopanes as shown in (Figure 9). These relationships also support the high thermal maturity level of the type-II oil compared to the type-I oil in the Gulf of Suez province.

Diasterane/sterane ratios are highly dependent on both the nature of the source rock and level of thermal maturity. This ratio is commonly used to distinguish carbonate from clay rich source rocks and can be used to differentiate immature from the highly mature oils (Seifert and Moldowan, 1978). Type-I oil is slightly depleted in diasteranes relative to type-II oil, probably reflecting differences in their level of thermal maturity and also differing clastic input to their source rocks (Kennicutt et al., 1992). Aromatic sulfur compounds such as dibenzothiophene (DBT), methyldibenzothiophenes (MDBT) and dimethyldibenzo-thiophenes (DMDBT) can be used as maturity indicators of source rock and petroleum (Chakhmakhchev et al., 1997; Radke et al., 1997). Figure (10) displays representative partially expanded mass chromatograms of the aromatic sulfur hydrocarbons representing naphthalenes, phenanthrenes and dibenzothiophenes with compound identifications given in (Table 6). Previous studies (e.g. Radke et al., 1997) have demonstrated that the relative distributions of methylated aromatic compounds are thermodynamically controlled and, with increasing maturity, a decrease is observed in the amount of the less stable *α-*

substituted isomer (1-MDBT) compared with the amount of the more stable ß-substituted isomer (4-MDBT). A number of ratios are applicable for thermal maturity assessments on the basis of aromatic sulphur compounds. Logarithmic scale cross-plots of 4-MDBT/1-MDBT (MDR) parameter versus the three maturity parameters (4,6-/1,4-DMDBT; 2,4-/1,4-DMDBT; and DBT/Phenanthrene ratios) is presented in (Figure 11). An increase of MDR is accompanied by an increase of the 4,6-/1,4-DMDBT, 2,4-/1,4-DMDBT and DBT/Phenanthrene ratios, reflects the differences in aromatic sulfur compound maturity from the marginally mature type-I oil (syn-rift Miocene Rudeis Shale) to fully mature type-II oils (pre-rift Upper Cretaceous Brown Limestone and Middle Eocene Thebes Formation) in the Gulf of Suez.
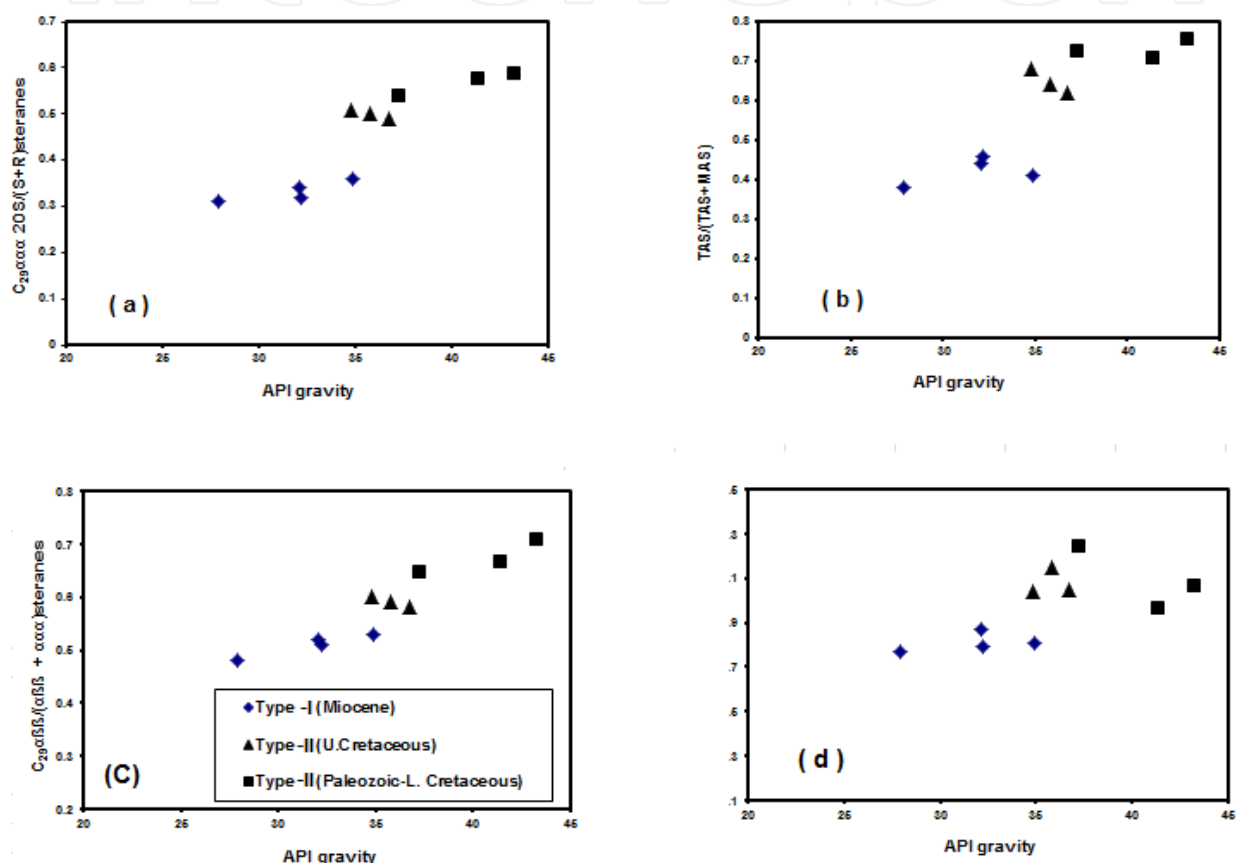
Fig. 9. Illustrates the direct relationship between gross geochemical attribute API gravity of crude oils and the sterane and triterpane maturity biomarkers C_{29} $\alpha\alpha\alpha$ 20S/(S+R), [(TAS/(MAS+TAS)], $C_{29}\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ and C_{35}/C_{34} homohopanes.

6.1 Stable carbon isotopic compositions

The stable carbon isotopic composition of organic matter is an important tool in differentiating algal from land plant source materials and marine from continental depositional environments (Meyers, 2003). Rohrback (1982) and Zein El-Din and Shaltout (1987) found that the crude oils of the Gulf of Suez were relatively light with δ^{13} C values for the saturate fractions between -27‰ to -29‰. They concluded that the stable carbon isotope values of crude oils are dependent mainly on the depositional environment of the source rock and the degree of thermal maturity at which the oil was expelled.

Sofer (1984) distinguished oils derived from marine and non-marine sources from different parts of the world, including Egypt on the basis of the δ^{13}C composition of the saturate and aromatic hydrocarbon fractions.

Using the canonical variable relationship CV= $-2.53\delta^{13}C_{sat.}+ 2.22\delta^{13}C_{arom.}– 11.65$, postulated by Sofer (1984), the Gulf of Suez province oil yield canonical variable values between -3.365 and -0.045. These values are generally lower than 0.47 indicating typical marine (non-waxy) oils. Stable carbon isotope data of the saturate and aromatic hydrocarbons and whole oils are shown in (Table 1) and plotted in (Figure 11). The stable carbon isotope composition of the saturate fraction ranges between -28.96 and -26.42‰, while the aromatic fraction has a range of -28.69 to –25.2‰. The results show an almost complete separation of the type-I and II oils. The results of the stable carbon isotope values are consistent with the results obtained by Rohrback (1982) and Alsharhan (2003), who concluded that all the Gulf of Suez crude oils were derived from marine source rocks. Type-I oil is generally exhibit heavier isotopic values than type-II oil, which is consistent with source rock variations. Miocene oil from the Zeit Bay well has a stable carbon isotope composition, which is more consistent with Type-II oil. Paleozoic-Lowe Cretaceous oil from the well East Zeit A-18 has a stable carbon isotope composition which is more like type-I oil.
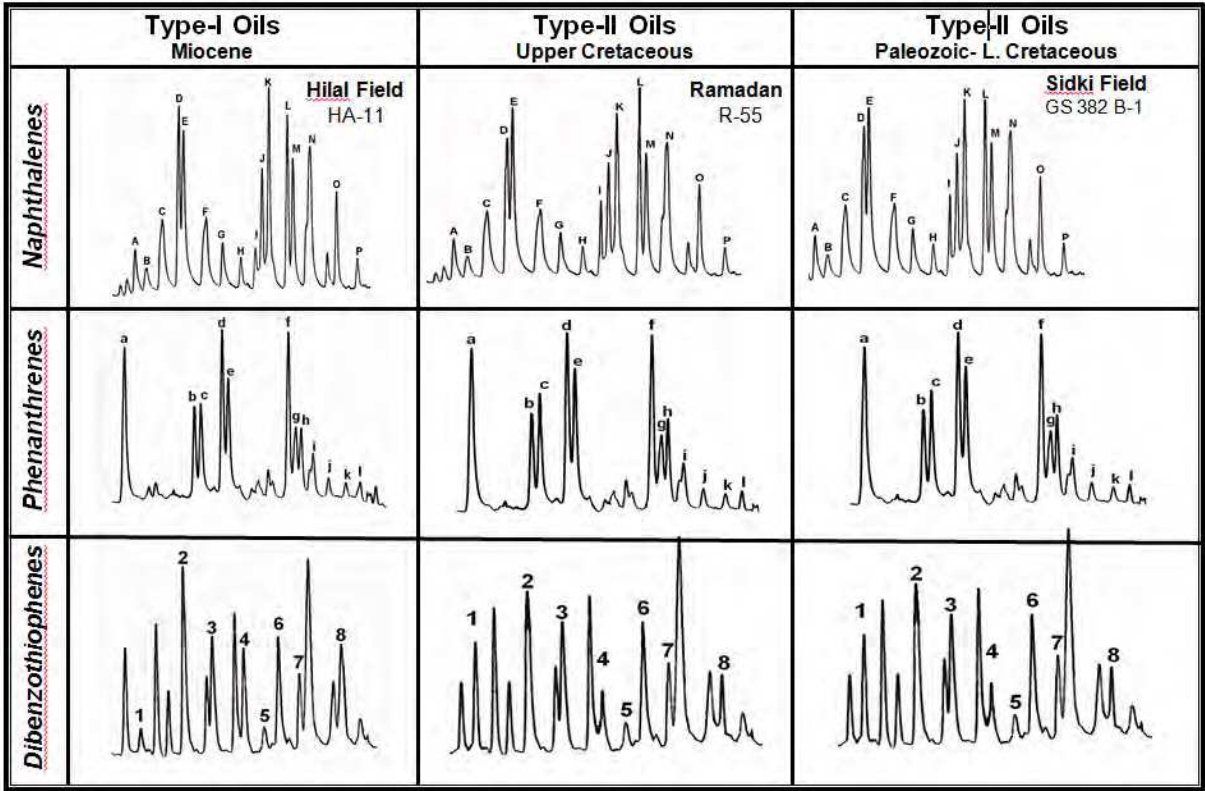

Fig. 10. Representative partial expanded gas chromatograms-mass spectrometry of the aromatic fractions to the naphthalenes (*m/z* 142, 156 and 170), phenanthrenes (*m/z* 178, 192 and 206) dibenzothiophenes, methyldibenzothiophenes, and dimethyldibenzothiophenes (*m/z* 184, 198 and 212) with peak identifications in   Table 6.
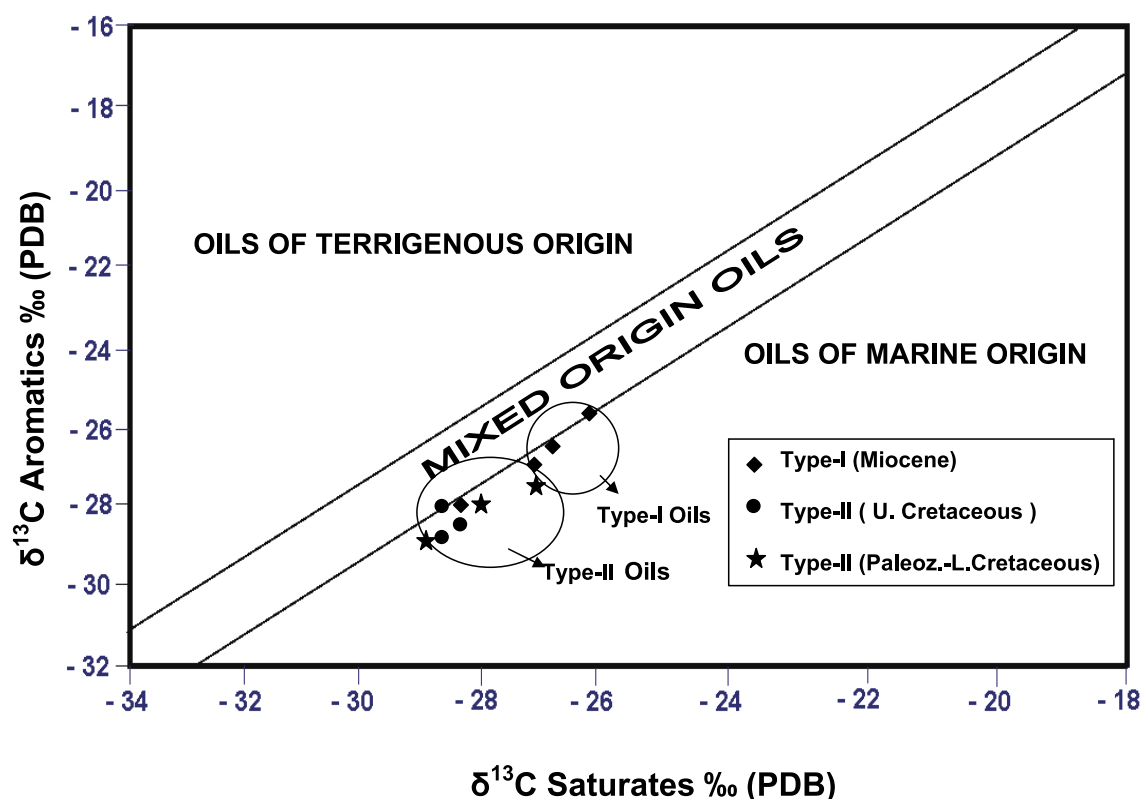
Fig. 11. Relationship between the carbon stable isotopic composition of the saturate and aromatic fractions for crude oils from the southern Gulf of Suez province (Sofer,1984).

7. Inferred oil to source rock correlation

Comprehensive studies published on the source rock potential in the Gulf of Suez were by Shahin and Shehab, 1984; Chowdhary and Taha, 1987; Alsharhan and Salah,1995; Barakat et al., 1997; Lindquist, 1998; Weaver, 2000; Younes, 2001; Younes, 2003 a and b; Alsharhan, 2003; and El-Ghamri and Mostafa, 2004. They found that the Black Shale of the Nubia-B, Upper Cretaceous Brown Limestone, Middle Eocene Thebes Formation and the Lower Miocene Rudeis Shale all appear to have good source rock potential in the Gulf of Suez.

As mentioned above, detailed biomarker distributions in conjunction with stable carbon isotopic composition distinguished the studied crude oils into two types referred to as type-I and II consistent vertically with the pre-rift and syn-rift tectonic rift sequences of the Gulf of Suez province. High oleanane, low gammacerane and marginally mature type-I oil possess organic geochemical characteristics with close similarities to the Tertiary Lower Miocene Rudeis Shale source rock. This formation reached the oil generation window at vitrinite reflectance measurements Ro% between 0.60 and 0.85 at 3-4 Ma and began to generate oils at a depth of 3000 meters in the deeper basin of the Gulf of Suez. Meanwhile, type-II oil, characterized by low oleanane, high gammacerane indices and high level of thermal maturity are fully mature with more advanced level of aromatization and complete sterane isomerisation ratios. Type-II oil has been generated at a depth of approximately 5000 meters in a deeper kitchen within the pre-rift source rocks

(Upper Cretaceous Brown limestone and Middle Eocene Thebes Formation) that entered the oil generation window at vitrinite reflectance measurements Ro% between 0.85-1.35 at 8-10 Ma (Younes, 2003a).

8. Conclusions

Two independent petroleum systems for oil generation, maturation and entrapment consistent vertically with the pre-rift and syn-rift tectonic sequences of the Gulf of Suez province were revealed from biomarker distributions in conjunction with stable carbon isotopic compositions of crude oils. Biomarker variations in crude oils of various ages and source rock types dividing the Gulf of Suez crude oils into two oil types referred as type-I and II that were generated from two types of source rocks of different levels of thermal maturation. Type-I oil is characterized by a predominance of oleanane and low gammacerane indices suggesting an angiosperm higher land plants input of terrigenous organofacies source rock within the marginally mature syn-rift Lower Miocene Rudeis Shale. By contrast, type-II oil is distinguished by a relatively high gammacerane content and low oleanane indices, and may be generated from fully mature marine carbonate source rocks within the Upper Cretaceous Brown Limestone to Middle Eocene Thebes Formation. The higher sterane isomerization as well as aromatic sulfur compound further support the higher thermal maturation level for the type II oils rather than type I.

9. Acknowledgements

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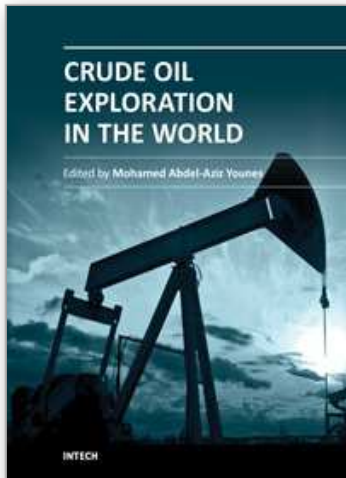
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