

Biomarkers Characteristics of Crude Oils from some Oilfields in the Gulf of Suez, Egypt.

M. I. Roushdy, M. M. El Nady, Y. M. Mostafa, N.Sh. El Gendy and *H. R. Ali

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

*hugochem@yahoo.com

Abstract: Seven representative crude oil samples from the Gulf of Suez were chosen for this study. The studied crude oils are Ras Badran, Belayim marine, Belayim Land, Rahmi, West Bakr, Esh El Mellaha and Geisum. The oils were fractionated by medium pressure liquid chromatography into saturated hydrocarbons, aromatic hydrocarbons and polar compounds. The saturated hydrocarbons were determined by gas chromatography and gas chromatography/mass spectrometry (GC/MS). Ratios of certain biomarkers, (Pristane/phytane, isoprenoids/n-alkanes, CPI, Homohopane, Diasteranes, Gammacerane index, C_{29} 20S/20S+20R, C_{29}/C_{30} hopanes and Ts/Tm) referred to as source correlation indices, are sensitive to the geological source of oil. The results of evaluation suggest that two types of oils could be recognized as marine oils. These oils are characterized by high level of maturation and sourced mainly from source rocks rich in marine organic matters with few inputs from terrestrial origin.

[M. I. Roushdy, M. M. El Nady, Y. M. Mostafa, N.Sh. El Gendy and *H. R. Ali. Biomarkers Characteristics of Crude Oils from some Oilfields in the Gulf of Suez, Egypt. Journal of American Science 2010;6(11):911-925]. (ISSN: 1545-1003).

Key words: Egypt, Gulf of Suez, Homohopanes, Diasteranes, Gammacerane index, C_{29} 20S/20S+20R, C_{29}/C_{30} hopanes and Ts/Tm, Crude oils.

1. Introduction:

The biological marker patterns of crude oils are commonly used for oil/oil and oil/source rock correlations and to assess such source rock attributes as lithology, depositional environment, kerogen type and maturity (Waples and Machihara, 1991; Peters and Moldowan, 1993). Exploration applications of biomarkers rest on the pattern of the oil imprinted by the source rock. For example, bulk geochemical evidence and biological markers distributions enable the characterization and distinction of ancient marine and non marine petroleum source rocks (Peters et al., 1986). However, the source-related biomarkers pattern of an oil may have been altered by a number of processes after generation and primary migration (expulsion) from the source rock.

The Gulf of Suez province is highly faulted and corresponds to a continental rift, which started in evolution at the beginning of the Miocene times, consisting of an elongated graben about 300 km long and 30 km wide between the Sinai Peninsula and the Eastern Desert of Egypt (Fig. 1). Various putative source rocks deposited in distinct, well-defined environments exist within the Gulf of Suez basin (Fig. 2).

Source rocks and sandy reservoirs are abundant in both the pre-rift and the post rift sedimentary rocks (Nagaty, 1992 and Shahin and Shehab, 1984). Most accumulations of crude oils in Gulf of Suez are found in different reservoirs and pay zones, ranging in age from Paleozoic to Middle

Miocene (Fig. 2). These accumulations were occurred in structural fault blocks formed at the time of rifting (Chowdhary and Taha, 1987). Since the beginning of this century, the Gulf of Suez has been highly prospective and has drawn the attention of many explorationists.

Previous Work

The geochemical characteristics of crude oils discussed by Abdel Azim (1970) showed, through statistical comparison of specific gravities of the Gulf of Suez crude oils, that the API gravity and paraffinic content increase with the depth. Zein El Din et al. (1981) reported that the oils produced from some fields in the central Gulf of Suez are derived from similar marine source rocks. Roharback (1983) suggested that the oil samples of the major horizon in the Gulf of Suez have the same genetic family, highly similar in their source rocks, as they reflect a marine origin and show no biodegradation. Shaltut et al. (1985) divided the oils of the central Gulf of Suez into two groups based on porphyrins distribution; the first group is characterized by the increase in vanadyl porphyrins distribution with the depth, while the second group shows inverse relation. Mostafa and Khaled (1988) concluded that the reservoir depth of the oils in the Gulf of Suez is not correlated with the oil maturity, based on sulfur percent, specific gravity, NSO compounds, asphaltenes and carbon isotope ratios. Mostafa and Ganze (1990) revealed that the crude oils of the Rudeis oil field are similar in their

origin; also they concluded that the Eocene Thebes Formation and the Upper Senonian Brown limestone may act as source for the Abu Rudeis oil. Barakat et al. (1996) divided the oils of the southern part of the Gulf of Suez into three types. Type I is sourced from carbonate source rocks (mainly of marine origin), type II appears to be originated from Tertiary source rocks with contribution from high land plants, and type III is a mixture of type I and type II. Sharaf (1998) recognized two oil groups for the oils from October and Abu Rudeis fields. Group "1" heavy oil, is derived mainly from hypersaline reducing environment and group "2" moderate to light oils, is formed under low salinity environment with minor contribution from terrigenous organic matter. Hammad and Barakat (2000) concluded that the oils from some oil fields in the Gulf of Suez were generated from mixed and algal organic matter deposited in transitional and reducing environments. El Nady (2001) recognized that the crude oils of the Gulf of Suez are sourced mainly from marine organic matters. Barakat et al. (2002) stated that there is a close genetic relation between the oils in the southern part of Gulf of Suez. El Nady and Harb (2005) recognized that the crude oils in the north Gulf of Suez are mature and derived mainly from mixed organic sources (mainly terrestrial with marine input) under transitional environments. El Nady (2006) reported that the crude oils in the south Gulf of Suez are mature, originated mainly from marine sources and show good correlation with the Lower Miocene source rocks in the southern part of Gulf of Suez. El Nady et al., (2007) divided the crude oils in the central part of Gulf of Suez into two groups: The first group includes moderately mature oil from the N. October, Belayim marine, Belayim Land and July fields which are typical of crude oils generated in a strongly reducing (marine). The second group comprises mature oils generated from source rocks deposited in lacustrine palaeoenvironmental conditions and includes oils from Issaran, E. Kareem, El-Khaligie and El Ayun fields. Harb and El Nady (2010) divided crude oils in the Gulf of Suez into 1. Heavy oils characterized by low maturation and originated mainly from terrestrial organic sources. 2. Light oils of high maturity level originated mainly from marine organic sources. Faramawy et al., (2010) classified the crudes in central Gulf of Suez, as aromatic intermediate oils heavy oils of low wax content characterized by high maturity level and derived from mixed organic sources (mainly marine with few inputs from terrestrial origin) belong to the carbonate type, deposited in transitional environments under reducing-oxidizing conditions.

Aim of the Study

The present work attempts to evaluate the geochemical relationships between the oils recovered from some oil fields within the Gulf of Suez to assess and investigate oil characterization, maturation, source depositional environments and oil families. This target was achieved through analytical results of gas chromatography and gas chromatography-mass spectrometry analysis (GC-MS) for "7" crude oil samples collected from seven oilfields namely: Ras Badran, Belayim marine, Belayim Land, Rahmi, West Bakr, Esh El Mellaha and Geisum distributed within the Gulf of Suez (Fig. 1). These samples are representative for the producing horizon zones (Belayim, Rudies and Nuhkul formations.) of Upper-Lower Miocene age (Figure 2) characterized by limestone facies with depths ranging from 2250 to 8286 ft (Table 1). The oil samples were kindly supplied by (EGPC) from Gulf of Suez and Belayim.

2. Experimental

1. The crude oil samples were fractionated by medium pressure liquid chromatography into saturated hydrocarbons, aromatic hydrocarbons and polar compounds. The saturated hydrocarbons were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).
2. Gas chromatographic analysis of the saturated hydrocarbon fractions was achieved by Perkin Elmer Instrument Model 8700, provided with a flame ionization detector (FID). Oven temperature programmed for 100 to 320°C at 3°C/min. and final time 20 min. SPB-1 capillary column of 60 m. in length and 0.53 i.d. Nitrogen was used as carrier gas, the optimum flow rate was 6 ml min.
3. Gas chromatography-mass spectrometry used a 50m x 0.25mm fused silica capillary column of bonded SE 54 installed with a finnigan MAT TSQ-70 combined gas chromatography/quadrupole mass spectrometer. The column oven was programmed from 100 to 310°C at 4°C/min. These analyses were done in the laboratories of the Egyptian Petroleum Research Institute (EPRI).

3. Results and Discussion

Normal -alkanes Characteristics

The distribution of n-alkanes in crude oils can be used to indicate the organic matter source (Duan and Ma, 2001). Figure 3 shows the fingerprints of gas chromatography for the saturated hydrocarbons of the

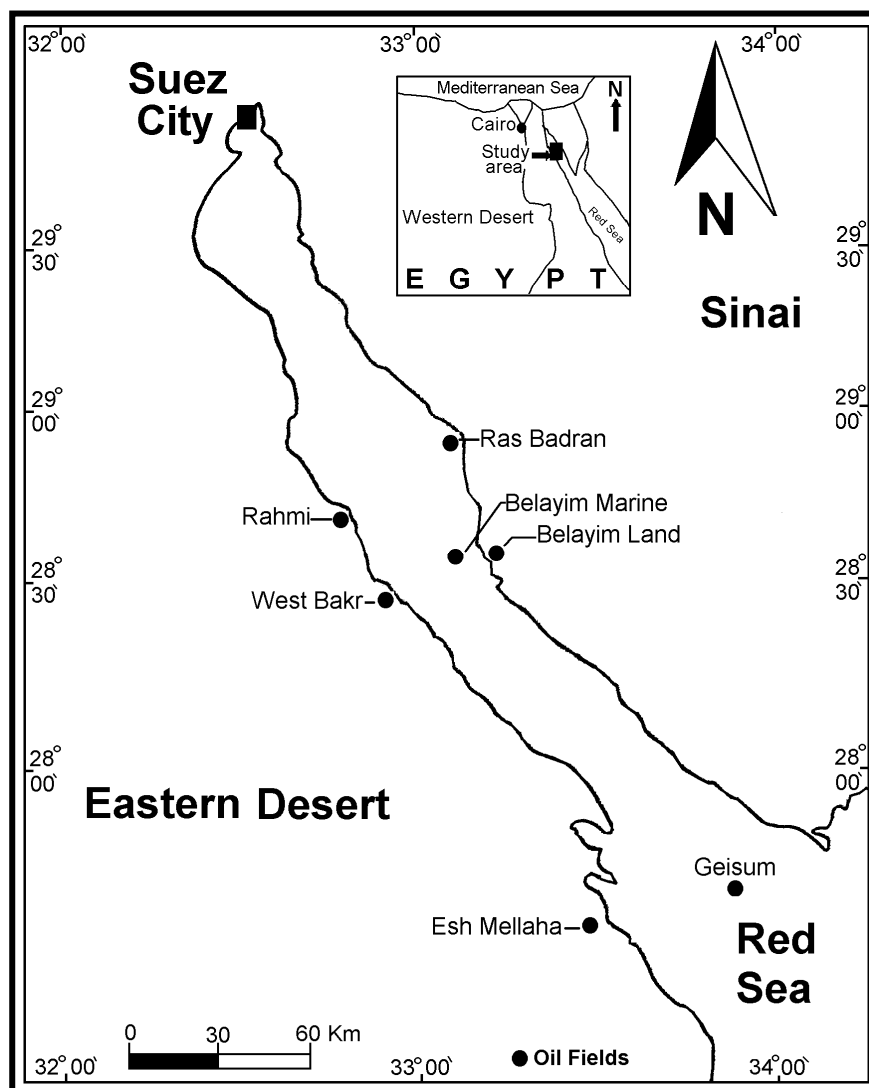


Fig.1. Location map of the studied oilfields in the Gulf of Suez, Egypt.

RIFTING	ERA	TIME UNIT	GROUP	FORMATION <i>Member</i>	LITHOLOGY	TYPE SECTION	THICKNESS (m)				
SYN - RIFT SEDIMENTS	CENOZOIC	POST MIOCENE		ZAAFARANA WARDAN							
		MIOCENE	Ras Maalab		ZEIT		Jabal Zeit-2	940			
				BELAYIM		SOUTH GHARIB		⊗ South Gharib-2	700		
						Hammam Faraun		▬	Belayim 112-12 Well	302	
						Feiran		⊗			
					Sidri		▬				
					Baba		⊗				
			GHARANDAL		KAREEM <small>Shagar Rahmi</small>		▬	Gharib N-2 Abu Zenima-1	461		
				RUDEIS		⊗	Rudeis-2	780			
					NUKHUL <small>Shoab Ali Ghara</small>		▬	Zeit Bay-1	427		
		OLIGOCENE			RED BEDS						
		EOCENE	El Egma		THEBES		▬	Luxor	423		
		PALEOCENE			ESNA		▬	Esna	60		
					SUDR		▬	Wadi Sudr	137		
						DUWI		▬	Jabal Duwi	38	
		PRE - RIFT SEDIMENTS	MESOZOIC	LATE CRETACEOUS	Nezzazat		MATULLA		⊗	Wadi Matulla	170
							WATA			Wadi Wata	64
							ABU QADA		⊗	Wadi Gharandal	25
	RAHA						⊗	Raha Scarp	120		
EARLY CRETACEOUS	El Tih				MALHA			Wadi Malha	149		
JURASSIC					QISEIB			Wadi Qiseib	44		
TRIASSIC	Ataqa				ROD EL HAMAL		▬	Wadi Rod El Hamal	274		
LATE CARBONIFEROUS					ABU DURBA		▬	Jabal Durba	122		
				EARLY CARBONIFEROUS		UMM BOGMA			Jabal Nukhul	45	
PALEOZOIC	CAMBRIAN-ORDOVICIAN			Qibliat		NAQUS			Jabal Naqus	410	
			ARABA				Jabal Qubliat	133			
			PRECAMBRIAN BASEMENT								

Fig. 2: Stratigraphic column of the Gulf of Suez (Alsharhan and Salah, 1997). Oil reservoirs are indicated by green circles (●), source rocks as flags (▬) and seals (⊗)

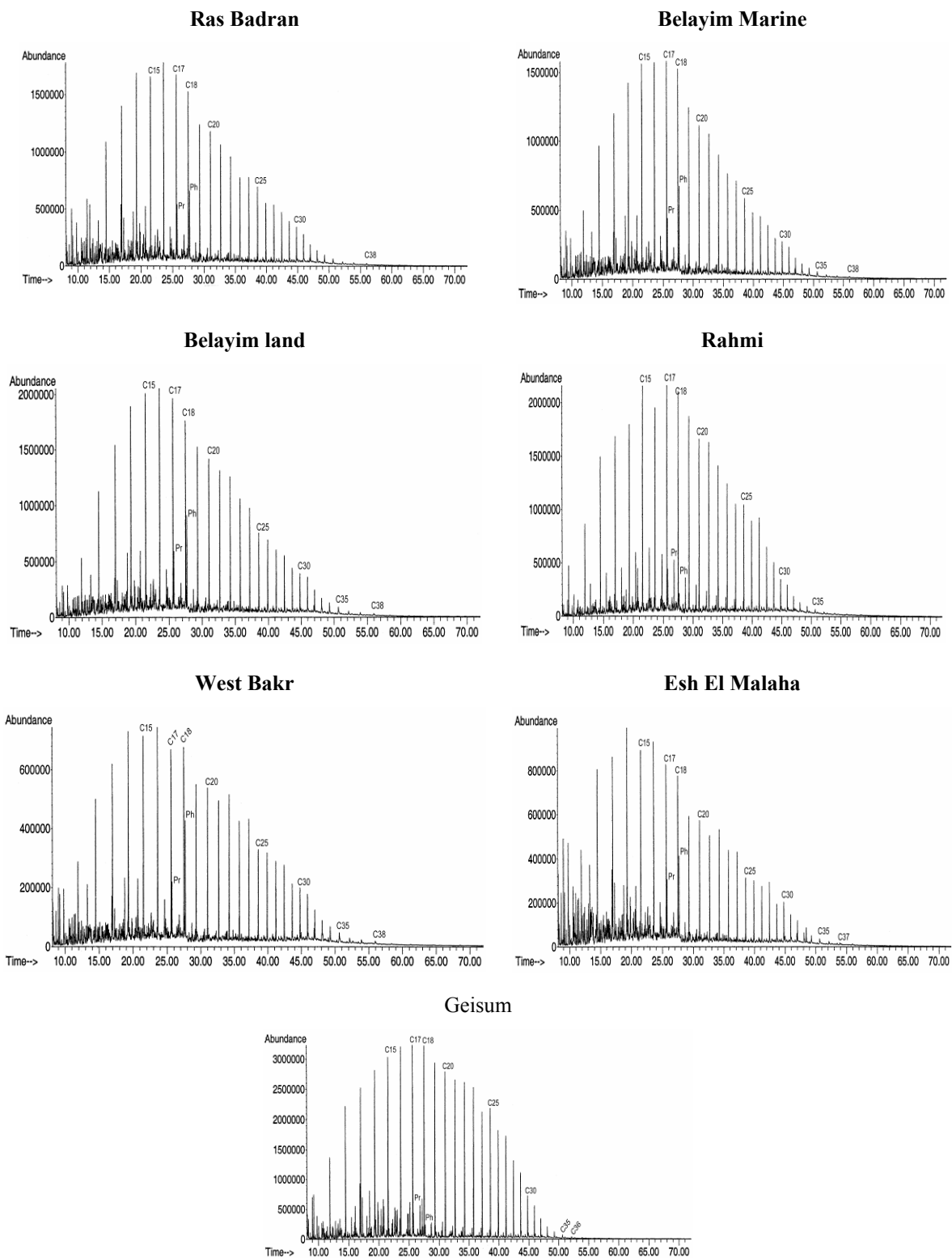


Fig. 3. Gas chromatograms of saturated hydrocarbons of the studied oil samples in the Gulf of Suez, Egypt

studied crude oil samples. These fingerprints show that the studied oils appear to be mature, based on the abundance of n-alkanes in the range n-C₁₅ to n-C₂₀, slightly even carbon preference and moderately to low concentration of heavy normal alkanes. The increase in the n-C₁₅ to n-C₂₀, suggests marine organic matters with contribution to the biomass from algae and plankton (Peters and Moldowan, 1993). The striking molecular feature of oils is that all are characterized by uniformity in n-alkanes distribution patterns, suggesting that they are related and have undergone similar histories, with no signs of water washing or biodegradation (Ficken et al. 2000 and Duan and Ma, 2001). The carbon preference index (CPI) of the studied oils ranging from 1.00 to 1.1 (Table 1) generally shows no even or odd carbon preference, indicate mature samples (Tissot and Welte, 1984).

Degree of Waxiness

The standard method of categorizing the amount of land-derived organic material in an oil is to determine its degree of waxiness. This method assumes that terrigenous material contributes a high molecular-weight normal paraffin components to the oil (Kök et al., 1997). Thus, recent studies about oil classification by source input have relied heavily on waxiness as an environmental source input parameter (Connan and Cassou, 1980). The degree of waxiness in this study is expressed by the $\Sigma C_{21}-C_{31}/\Sigma C_{15}-C_{20}$, ratios (Table 1).

The studied oils are characterized by high abundance of of n-C₁₅to n-C₂₀ n-alkanes in the saturate fractions reflecting low waxy (Moldowan et al., 1994). The degree of waxiness ($\Sigma C_{21}-C_{31}/\Sigma C_{15}-C_{20}$ ratios)ranging from 0.68 to 0.94 (Table 1) confirms low waxy nature and suggests marine organic sources (Peters and Moldowan, 1993).mainly of higher plants, deposited under reducing condition.

Table 1 Geochemical parameters derived from GC and GC-MS analyses of studied oilfields in the central Gulf of Suez, Egypt

	Oilfields						
	Ras Badran	Belayim marine	Belayim Land	Rahmi	West Bakr	Esh El Mellaha	Geisum
Depth(ft)	2250	8286	7786	2600	2268	3254	2897
Reservoirs	L. Rudies	Belayim	Belayim	Up. Rudies	L. Rudies	Rudies	Nuhkul
Age	L. Miocene	U. Miocene	U. Miocene	L. Miocene	L. Miocene	Miocene	L.Miocene
Lithology	Sandstone	Limestone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone
Pristane/phytane	00.32	00.26	00.14	00.30	00.31	00.36	00.20
Pristane/n-C17	00.32	00.26	00.14	00.30	00.31	00.36	00.20
Phytane/n-C18	00.42	00.43	00.17	00.51	00.63	00.54	00.19
CPI	1.003	1.054	0.997	1.009	1.012	0.992	1.046
$\Sigma C_{21}-C_{31}/\Sigma C_{15}-C_{20}$	00.75	00.68	00.79	00.83	00.83	00.81	00.94
C27 Steranes (%)	32.24	24.04	25.83	17.14	44.76	30.00	13.18
C28 Steranes (%)	27.03	35.24	27.97	29.27	30.01	30.00	38.45
C29 Steranes (%)	40.74	40.72	46.37	53.58	25.23	40.00	48.37
Homohopane index ^a	00.56	00.74	00.98	00.79	00.58	00.21	00.94
Diasteranes index ^b	00.11	00.11	00.11	00.11	00.10	00.08	00.11
Gammacerane index ^c	00.44	00.47	00.45	00.44	00.49	00.43	00.46
C ₂₉ 20S/20S+20R ^d	00.11	00.12	00.09	00.10	00.10	00.08	00.09
C ₂₉ /C ₃₀ hopane ^e	00.04	00.04	00.05	00.05	00.07	00.05	00.04
Steranes/hopanes ^f	01.25	01.28	01.30	01.28	02.00	00.57	00.82
Ts/Tm ^g	00.54	00.53	00.60	00.58	00.62	00.60	00.65

CPI: $\Sigma \text{odd}/\Sigma \text{even}$ carbon numbers,

a; Homohopane index: $(C_{35} \text{ homohopane S} + R)/(C_{31} + C_{32} + C_{33} + C_{34} + C_{35} \text{ homohopanes S} + R)$.

b: Diasteranes index: $(C_{27} \text{ diasteranes S} + R)/[(C_{27} \text{ diasteranes} + R) + C_{29} \text{ steranes S} + R]$.

c: Gammacerane index: $\text{gammacerane}/(\text{gammacerane} + C_{30} \text{ hopane})$.

d: C₂₉ 20S/20S+20R,

e: C₂₉/C₃₀ hopane,

f: Steranes/17 α (H)-hopanes ratio

g: Ts/Tm: Trisnorneohopanes/Trisnorhopanes ratios.

Isoprenoids

Pristane/Phytane

The pristane/phytane (Pr/Ph) ratio is one of the most commonly used geochemical parameters and

has been used as an indicator of depositional environment with low specificity due to the interferences by thermal maturity and source inputs (Didyk et al., 1978, Peters et al., 2005). ten Haven et

al. (1987) stressed that high Pr/Ph (>3.0) indicates terrigenous input under oxic conditions and low Pr/Ph (<0.8) indicates anoxic/hypersaline or carbonate environments. According to Lijmbach (1975) low values (Pr/Ph <2) indicate aquatic depositional environments including marine, fresh and brackish water (reducing conditions), intermediate values (2–4) indicate fluviomarine and coastal swamp environments, whereas high values (up to 10) are related to peat swamp depositional environments (oxidizing conditions).

The studied oil samples are characterized by pristane/phytane ratios (0.14 to 0.36) and waxiness values (0.68 to 0.94, Table 1), confirming that these oils have been originated from marine organic source deposited under suboxic conditions. Figure 4 exhibiting the relationship between Pr/Ph and waxiness confirms this conclusion. Furthermore, the cross plot of Pr/Ph versus CPI (Figure 5) shows that, the oils fall in the field of more reducing zone of thermal maturation level.

Isoprenoides/n-alkanes ratios

In crude oil studies, the ratios of isoprenoids to n-alkanes are widely used since they provide informations on maturation and biodegradation as well as source (Ficken et al., 2002). Consequently, a plot of Pr/n-C₁₇ versus Ph/n-C₁₈ in Figure 6 as originally proposed by Lijmbach (1975). The isoprenoids/n-alkanes ratios (pr/n-C₁₇ and ph/n-C₁₈, shown in Table 1), suggest marine organic matters source (mainly algae) deposited under reducing environment. It also indicates a genetic close relation between the studied oils.

Steranes (m/z 217) Distribution

The distribution of steranes is best studied on GC/MS by monitoring the ion m/z=217 which is a characteristic fragment in the sterane series. The resulting mass chromatograms for the representative samples are shown in Fig. (7) and the labeled peaks are summarized in Table (2). The compounds were identified in their key fragmentograms based on the relative retention times and by comparison of their mass spectra with the published data. It is agreed that the relative amounts of C₂₇-C₂₉ steranes can be used to give indication of source differences (Lijmbach, 1975)

The studied crude oils of Ras Badran, Belayim, West Bakr and Esh Elmalaha are characterized by predominance of C₂₈, C₂₉ and C₃₀ steranes (20S and 20R, Fig. 7, see peak identifications in Table 2)

which indicate an origin of the oils derived mainly from mixed terrestrial and marine organic sources, While oil samples from Rahmi and Geisum (Fig. 7) show slightly low abundance of C₂₈ and C₂₉, and relatively higher concentrations of C₂₇steranes (20S and 20R, see peak identifications in Table 2) which indicate more input of marine organic source. The steranes diagram (Fig. 8) confirms these assumptions.

The amount of C₂₇ diasteranes, diasteranes index and concentration of (20S) and (20R) isomers influences the maturity level of crude oils. Peters and Moldowan (1993); Petersen et al., (2000) and Andrew et al. (2001) recognized that the maturity level of oils increases with the increase of these parameters (i.e. high concentration of C₂₇ diasteranes, >0.1 diasteranes index, and >0.5 C₂₉ 20S/20S+20R). Thus, it is obvious that the studied oils have slightly high concentration of C₂₇ diasteranes (20S and 20R) peaks A, B and C with diasteranes index range from 0.10 to 0.11 and C₂₉ 20S/20S+20R from 0.1 to 0.12 (Table 1). These data reveal that the studied oils are characterized by high maturity level.

Triterpanes (m/z 191) Distribution

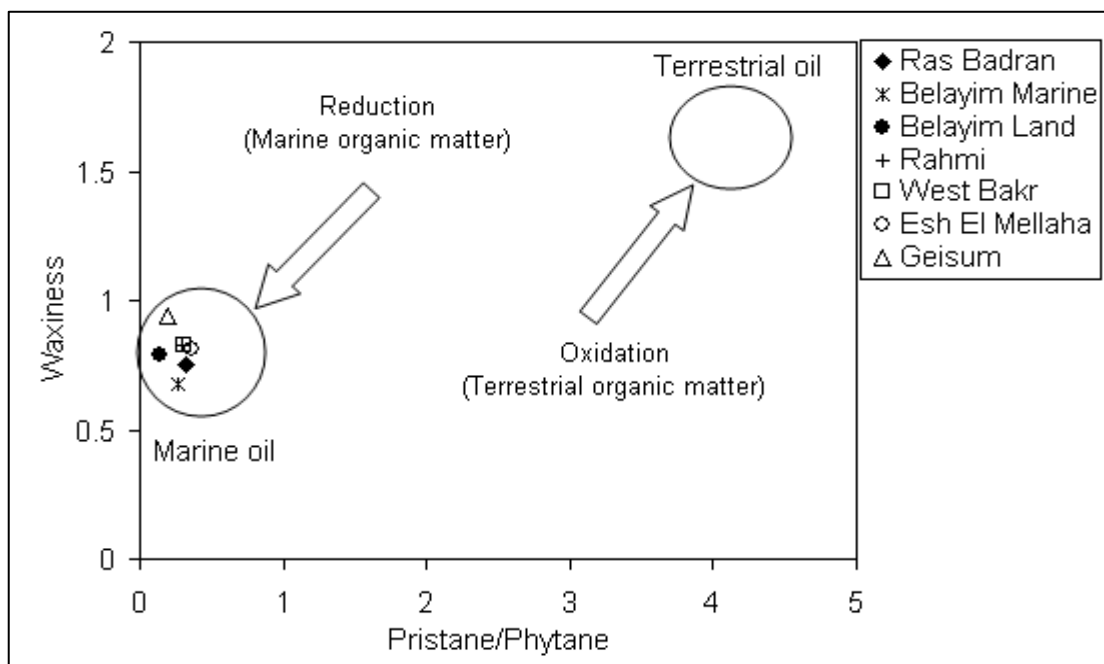
Together with steranes, triterpanes belong to the most important petroleum hydrocarbons that retain the characteristic structure of the original biological compounds. Tricyclic, tetracyclics, hopanes, and other compounds contribute to the terpane fingerprint mass chromatogram (m/z=191) are commonly used to relate oils and source rocks (Hunt, 1996). Mass fragmentogram at m/z=191 was used to detect the presence of triterpanes in the saturate hydrocarbon fraction of the studied oils (Fig. 9). The assignment of the peaks labeled in fig. (9) are listed in Table (2). The most distinct features are Tricyclic Terpanes, Ts/Tm and C₂₉/C₃₀ hopane ratios

Tricyclic Terpanes

The concentration of tricyclic terpanes in crude oils is more sensitive to the specific paleoenvironments (Waples and Machihara, 1992 and Andrew et al., 2001). In addition it has been used as a qualitative indicator of maturity (Van Grass, 1990). In high mature oils, the tricyclic terpanes is dominated more than in low mature oils (Hunt, 1996). Aquino et al. (1983) indicated that tricyclic terpanes are normally associated with marine source. Our study reveals that the concentration of C₂₂ tricyclic terpanes peak B in the studied oil samples (Fig. 9, see peak identifications in Table 2) is higher which may support the idea that the oils are more

Table 2. Identification of peaks in triterpanes (m/z 191) and steranes (m/z 217) mass fragmentograms.

Triterpanes (m/z 191)		Steranes (m/z 217)	
Peaks	Compounds Name	Peaks	Compounds Name
A	C ₂₁ Tricyclic terpane	A	C ₂₇ $\alpha\beta$ diasterane (20S)
B	C ₂₂ Tricyclic terpane	B	C ₂₈ $\beta\alpha$ diasterane (20S)
C	C ₂₃ Tricyclic terpane	C	C ₂₈ $\beta\alpha$ diasterane (20R)
D	C ₂₄ Tricyclic terpane	D	C ₂₇ $\alpha\alpha\alpha$ sterane (20S)
E	C ₂₅ Tricyclic terpane (22R)	E	C ₂₇ $\alpha\beta\beta$ sterane (20S)
F	C ₂₄ Tricyclic terpane	F	C ₂₇ $\alpha\alpha\alpha$ sterane (20R)
G	C ₂₈ Tricyclic terpane (22R)	G	C ₂₉ $\beta\alpha$ diasterane (20R)
H	C ₂₈ Tricyclic terpane (22S)	H	C ₂₉ $\beta\alpha$ diasterane (20S)
I	C ₂₈ Tricyclic terpane (22S)	I	C ₂₈ $\alpha\alpha\alpha$ sterane (20S)
J	C ₂₇ 18 α H-Trisnorneohopane (Ts)	J	C ₂₈ $\alpha\beta\beta$ sterane (20R)
K	C ₂₇ 17 α H-Trisnorhopane (Tm)	K	C ₂₈ $\alpha\beta\beta$ sterane (20S)
L	C ₂₈ Bisonorhopans	L	C ₂₈ $\alpha\alpha\alpha$ sterane (20R)
M	C ₂₉ 17 α H,21 β H-Norhopanes	M	C ₂₉ $\alpha\alpha\alpha$ sterane (20S)
N	C ₂₉ 17 β H,21 α H-Normoretane	N	C ₂₉ $\alpha\beta\beta$ sterane (20R)
O	C ₃₀ 17 α H,21 β H-Hopane	O	C ₂₉ $\alpha\beta\beta$ sterane (20S)
P	C ₂₉ 17 β H,21 α H-Moretane	P	C ₂₉ $\alpha\alpha\alpha$ sterane (20R)
Q	C ₃₁ 17 α H,21 β H-Homohopane (22R)	Q	C ₃₀ $\alpha\beta\beta$ steranes (20R)
R	C ₃₀ Gammacerance	R	C ₃₀ $\alpha\beta\beta$ steranes (20S)
S	C ₃₂ 17 α H,21 β H--Homohopane (22R)	S	C ₃₀ $\alpha\alpha\alpha$ steranes (20R)
T	C ₃₃ 17 α H,21 β H--Homohopane (22R)		
U	C ₃₄ 17 α H,21 β H--Homohopane (22S)		
V	C ₃₅ 17 α H,21 β H--Homohopane (22R)		

Fig. 4: Cross plots of Pr/Ph versus waxiness $\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-C_{21})$ for the studied samples.

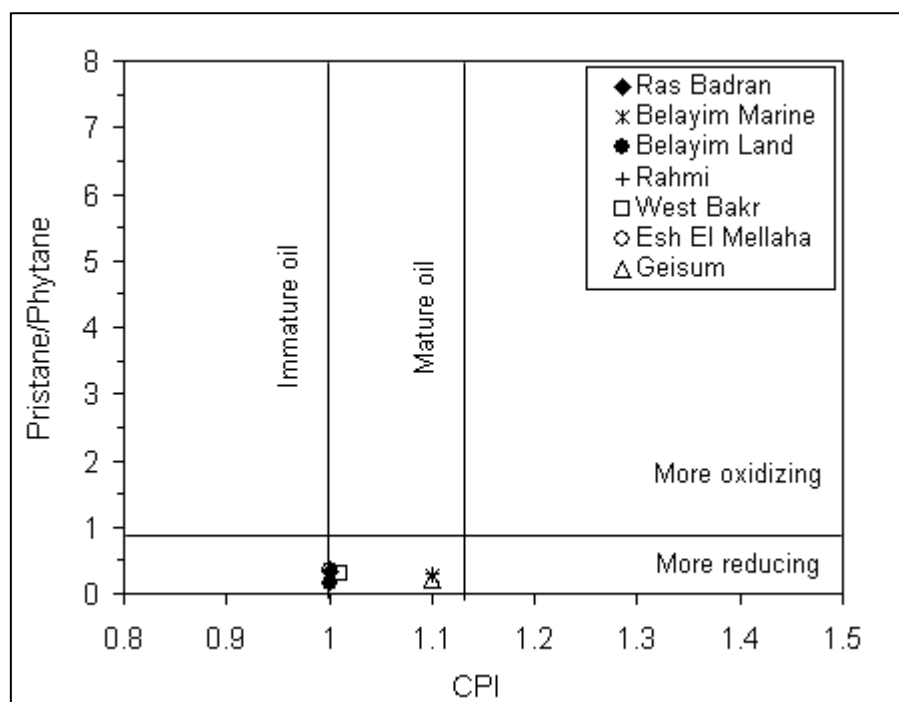


Fig. 5: Pristane/Phytane versus CPI showing the sources of studied crude oils (Akinula et al., 2007).

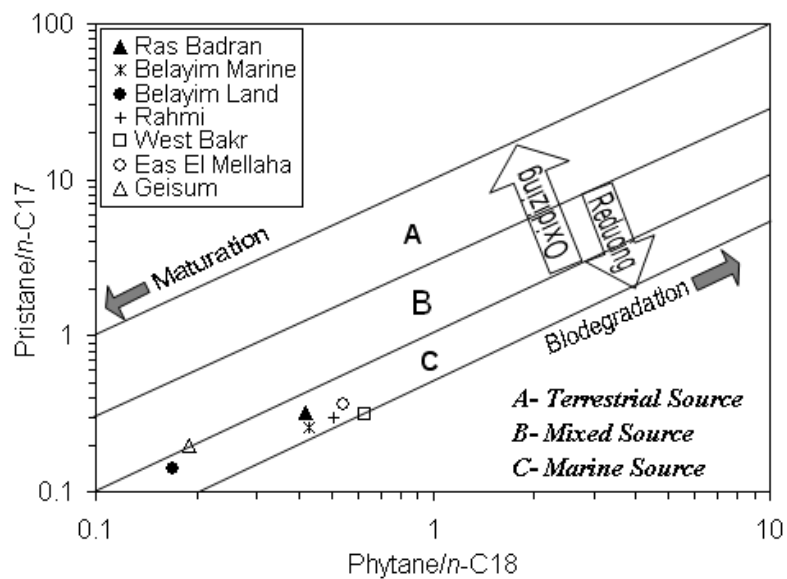


Fig. 6. Plot of pristane/ n -C₁₇ versus phytane/ n -C₁₈ (Shanmugam, 1985), showing the organic sources and maturation of studied oil samples.

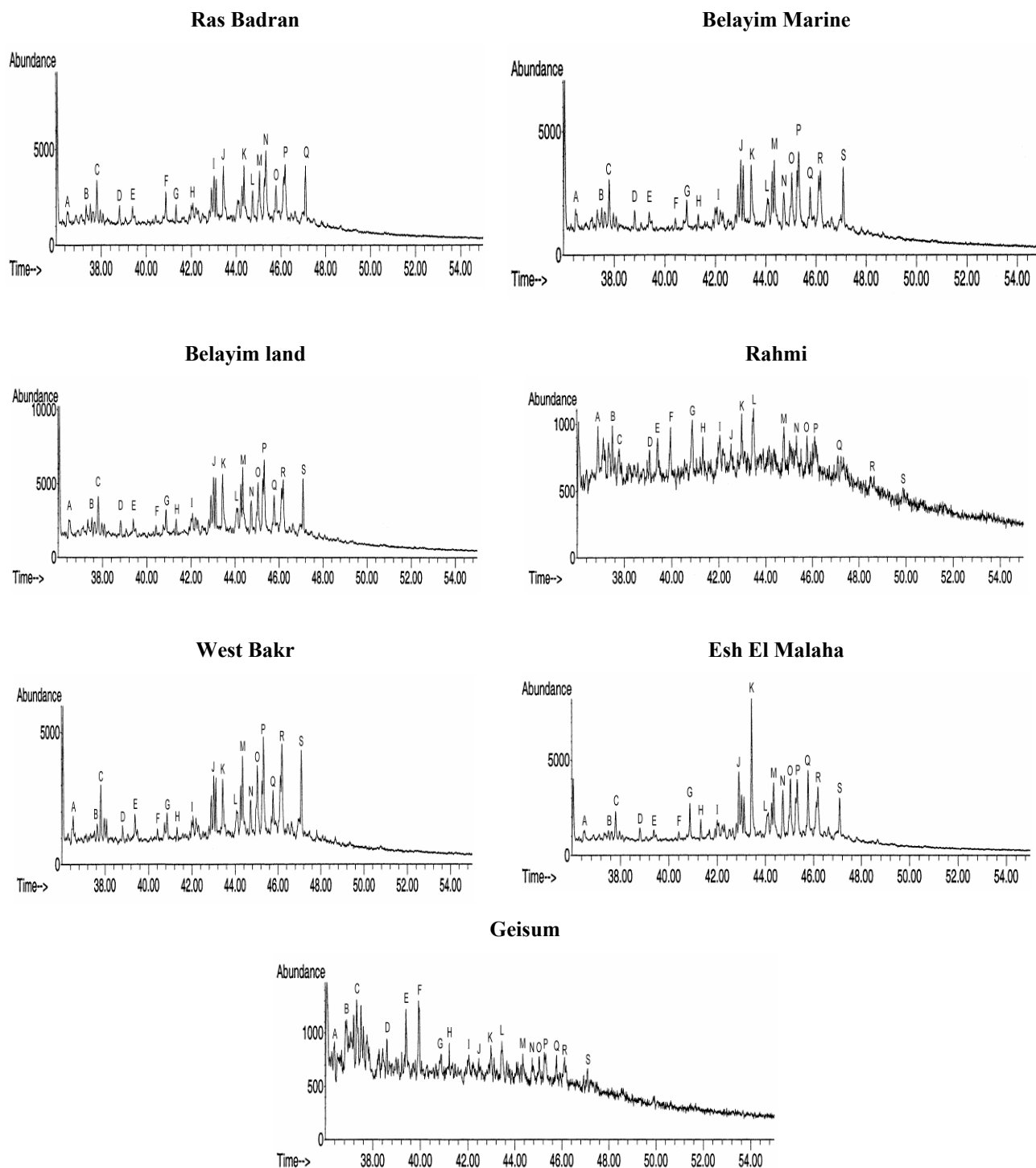


Fig. 7. Ion fragmentgrams (m/z 217) steranes of saturated hydrocarbons of the studied oil samples in the Gulf of Suez, Egypt

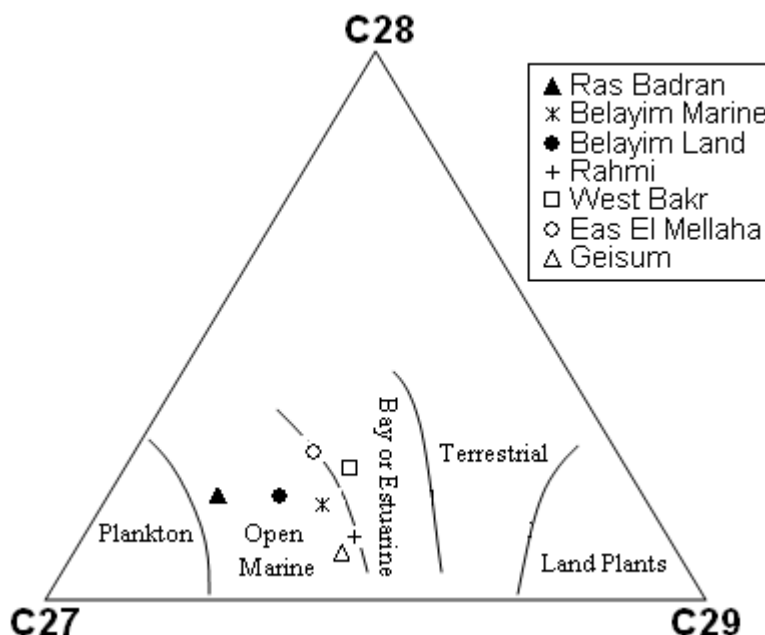


Fig. 8. Distribution of C_{27} , C_{28} , and C_{29} regular steranes (Huang and Meinschein, 1979), showing organic facies of the crude oils in the Gulf of Suez, Egypt.

mature and sourced mainly from carbonate source rocks. On the other hand, C_{21} , C_{23} to C_{28} tricyclic terpanes peaks A, C to I are generally of low detection levels in the studied oils indicating that these oils have some inputs derived from terrestrial organic material (Hunt, 1996). This confirms with the conclusion of steranes biomarkers.

Homohopanes

The homohopanes (C_{31} to C_{34}) are believed to be derived from bacteriopolyhopanol of prokaryotic cell membrane. C_{35} homohopane may be related to extensive bacterial activity in the depositional environment (Ourisson et al., 1984). The distribution of $17\alpha,21\beta(H)$ -29-homohopanes $22R+22S$ $C_{35}/(C_{31}-C_{35})$ (or simply homohopane index) in crude oils can be used as an indicator of the associated organic matter type, as it can also be used to evaluate the oxic/anoxic conditions of source during and immediately after deposition of the source sediments (Peters and Moldowan, 1991). Low C_{35} homohopanes is an indicator of highly reducing marine conditions during deposition, whereas high C_{35} homohopane concentrations are generally observed in oxidizing water conditions during deposition, consistent with the oxic conditions as suggested by high pristane/phytane ratios (Peters and Moldowan, 1991).

The studied crude oils have low concentrations of C_{31} - C_{35} homohopanes (20S and 20R) (peaks S to V Fig. 8, Table 2) which are more significant to hypersaline marine oils. The homohopane indices

values 0.21 to 0.98 (Table 1) confirms the above conclusion.

Gammacerane

Gammacerane, is associated with environments of increasing salinity, both marine and lacustrine (Waples and Machihara, 1991; and Peters and Moldowan, 1993). Gammacerane (peak R, see peaks identifications in Table 2, Fig. 8) is only detected in relatively low amount in the studied oils indicating input of marine organic matter in different saline environments, e.g. lakes, lacustrine, ponds, ... etc .

Ts/Tm

The ratio of Ts (trisnorneohopane) to Tm (trisinorhopane) more than (0.5) increases as the portion of shale in calcareous facies increases (Hunt, 1996). Also, this ratio was proved to be useful in paleofacies predictions, though not as decisive as mature parameters. Van Grass (1990) stated that Ts/Tm ratios begin to decrease quite late during maturation, but Waples and Machihara, (1991) reported that Ts/Tm ratio does not appear to be appropriate for quantitative estimation of maturity. In the present study we show that the Ts/Tm ratios range from 0.53 to 0.65 for the studied oils (Table 1). These relatively high ratios suggest that the studied oils were generated mainly from calcareous facies.

C_{29}/C_{30} hopanes ratios

C_{29}/C_{30} hopanes ratios are generally high (>1) in oils generated from organic rich carbonates and evaporates (Connan et al., 1986). The majority

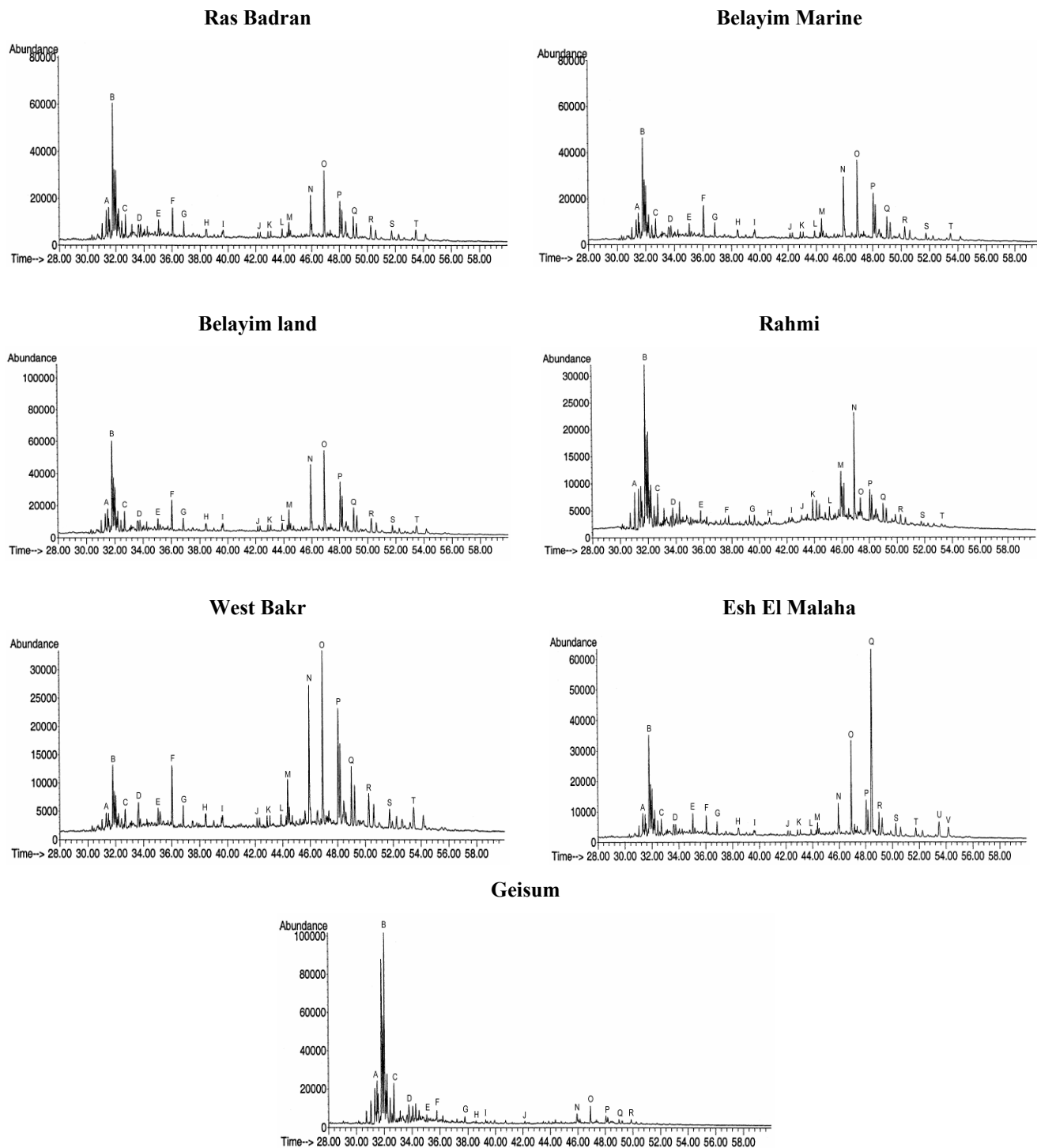


Fig. 9. Ion fragmentgrams (m/z 191) triterpanes of saturated hydrocarbons of the studied oil samples in the Gulf of Suez, Egypt

studied oil samples, having higher concentrations of C_{29} than C_{30} hopane, peaks O and Q respectively with high C_{29}/C_{30} hopane ratios range from 1.01 to 1.40 (Table 1), except oils from wells Esh El Mellaha and Geisum which have lower concentrations of C_{29} than C_{30} hopane (Fig. 8), with low values of C_{29}/C_{30} hopanes (0.04 to 0.07, Table 1). These data illustrate that the oil samples might be sourced from source rocks rich in carbonaceous organic matters. This assumption is confirmed by the low abundance of C_{29} moretane (peak P), gammacerane (peak R) and slightly higher concentration of C_{28} bisnorhopanes (peak L), Philp (1985); Riediger et al. (1990) and Waples and Machihara, (1991).

Steranes/ 17α (H)-hopanes ratio

The regular steranes / 17α (H)-hopanes ratio reflects input of eukaryotic (mainly algae and higher plants) versus prokaryotic (bacteria) organisms to the source rock (Noriyuki et al,1996). The sterane/hopane ratio is relatively high in marine organic matter, with values generally approaching unity or even higher. In contrast, low steranes and sterane/hopane ratios are more indicative of terrigenous and/or microbially reworked organic matter (Noriyuki et al,1996). From steranes/hopanes ratio of the studied crude oils range 1.25 to 2.00 of wells Ras Badran, Belayim marine, Belayim Land, Rahmi, and West Bakr and 0.57 and 0.82 Esh El Mellaha and Geisum crude oils (Table 1). This indicates that the majority of the studied crude oils can be considered generated from high marine organic matter source (marine and lacustrine algae) These results show an agreement with the data obtained from the relationship of Pr/nC_{17} versus Ph/nC_{18} (Fig. 6).

4. Conclusions

Utilizing the GC and GC/MS technique made it possible to arrive at a clear characterization and classification of crude oils according to their sources. This has been achieved from the acyclic isoprenoids, steranes and terpanes biomarkers. Geochemical parameters based upon these components coupled with bulk geochemical parameters did indicate whether the crude oils are of marine, terrestrial or mixed marine-terrestrial origin.

Biomarkers analyses of crude oils from the Gulf of Suez, suggest the following: oils are more mature and derived mainly from mixed organic sources from terrestrial and marine inputs contribution to the biomass from algae and plankton in different saline environments.

The few discrepancies that appear between the results obtained by using the different parameters can be related to the alteration caused by the number

of processes (physical, chemical and/or biological) affecting part of the source related biomarkers pattern of the oil after generation and/or primary migration from the source rock.

Corresponding author

H. R. Ali

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

*hugochem@yahoo.com

5. References:

1. Abdel Azim, M. F. (1970): Crude oil composition-a clue to its migration in the Gulf of Suez region. 7th Arab Petrol. Congr, Kuwait, No. 37(b-2), 7p.
2. Akinlua, A. Ajayi, T. R. and Adeleke, B. B. (2007) Organic and inorganic geochemistry of northwestern Niger Delta oils. *Geochemical Journal*, 41, 271 to 281.
3. Alsharhan A. S. and Salah M. G. 1997. Lithostratigraphy, Sedimentology and Hydrocarbon Habitat of the Pre-Cenomanian Nubian Sandstone in the Gulf of Suez Oil Province, Egypt. *GeoArabia*, Vol. 2, No.4, pp385-400.
4. Andrew,D.H.,Bradley,D.R.,David,Z.J.,Moldowan ,M., Ulderico, B., 2001. upper Oligocene lacustrine source rocks and petroleum systems of the northern qaidan basin, North West China. *Bulletin of the American Association of petroleum Geologists* 85,601-619.
5. Aquino Neto, F.R., Trendel, J.M., Restle, A., Connan, J. and Albrecht, P.A. (1983). occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum. In: M.BjorØy, et al. (Editors), *Advances in organic geochemistry 1981*, Wiley, chichester, pp.659-667.
6. Barakat A. O., Mostafa, A. R., Qian, Y., and Kim, M., 2002. Geochemical fingerprinting of oil seeps in the southern part of the Gulf of Suez and its geological and archaeological implications. *Inter. Petrol. Confer. and Exhibit*, p16.
7. Barakat, A. O.; Mostafa, A. R.; El-Gayar, M. S. and Omar, M. F. (1996): Source input and paleoenvironmental assessments using molecular biomarker indicators of crude oils from southern part of the Gulf of Suez, Egypt. 13th Petrol. Explor. Seminar ,Cairo, pp. 475-488.
8. Chowdhary,L.R. and Taha, S.(1987). Geology and habitat of oil in Ras Budran field, Gulf of Suez, Egypt. *Bulletin of the American Association of petroleum Geologists*. 71:1274-1293.
9. Connan, J., Bouroullec,J., Dessort,D. and Albrecht,P.(1986). The microbial input in

- carbonate-anhydrite facies of sabkha palaeoenvironment from Guatemala. A molecular approach. In: D. Leythaeuser and J. Rullkötter (Editors), advances in organic geochemistry 1985. org. geochem., 10: 29-50.
10. Connan, J. and Cassou, A.M. (1980). Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels, *Geoch. et Cosmoch. Acta*, 44:1-23.
 11. Didyk, B.M., Simoneit B.R.T., Brassell, S.C., Eglinton, G. (1978). *Nature (London)* 271:216.
 12. Duan, Y., Ma, L.H. (2001). Lipid geochemistry in a sediment core from Ruergai Marsh deposit (Eastern Qinghai-Tibet Plateau, China). *Organic Geochemistry* 32:1429-1442.
 13. EL Nady, M. M. 2001. Evaluation of geochemical characteristics of petroleum from some oil fields within Gulf of Suez, Egypt. *Zagazic Univ, Science Bull* 23 (2): 43-69,
 14. EL Nady, M. M. 2006. The hydrocarbon potential of Miocene source rocks for oil generation in the South Gulf of Suez, Egypt. *J. Petroleum Science and Technology*, 24(5): 539-561.
 15. EL Nady, M. M and Harb F. M. 2005. Evaluation of organic matters and crude oil as insight from pyrolysis, infrared spectrometric and biomarker analyses of some wells in the North Gulf of Suez, Egypt. *J. Egyptian Applied Science* 20(1): 39-61
 16. El Nady M. M, A. Barakat A. M and Harb F.M. 2007. Crude oil geochemistry and timing of petroleum generation in the Central Gulf of Suez, Egypt. *Egypt. J. Petrol.*, 16 (2): 137-155.
 17. Faramawy A. S., El-Naggar A. Y., El-Nady M. M, El-Sabagh, S. M. and F. Harb F. M. 2010. Organic Geochemical Characterization of Crude oils from El Hamd and Bakr Oil Fields in the Gulf of Suez, Egypt. Accepted in *Energy Sources*.
 18. Ficken, K.J., Li, B., Swain, D.L., Eglinton, G. (2000). A n-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Organic geochemistry* 31:745-749.
 19. Ficken, K.J., Woller, M.J., Swain, D.L. (2002). reconstruction of a subalpine grass-dominated ecosystem, lake rutundu, mount Kenya: a novel multi-proxy approach. *Pales* 177:137-149.
 20. Hammad, M. M. and Barakat, M. A. (2000): Specific geochemical parameters of Gulf of Suez crude oils in relation to maturation, origin and their source rock depositional environments. *Jour. of Environ. Sci.*, V. 19, pp.75-92.
 21. Harb and El Nady 2010 Physico-Chemical Properties, Environmental Sources, Specifications and Maturation of Crude Oils, Gulf of Suez, Egypt. Accepted for *Egypt. J. Petrol.*, V (19), No 1, pp. 83, 91.
 22. Huang, W. Y., and Meinschein, W. G. (1979). Sterols as ecological indicators. *Geochim et Cosmochim Acta*. 43. 739-745.
 23. Hunt, J.H., 1996. petroleum geochemistry and geology. 2nd ed freeman and company, New York. 743 p.
 24. Köket, M. Letoffe, J. M. Claudy, P. Martin, D. Garcin, M. and Volle J. L. 1997. Thermal characteristics of crude oils treated with rheology modifiers, *J. of Thermal Analysis and Calorimetry*, 49(2): 727-736.
 25. Lijmbach, G.W. (1975). On the origin of petroleum :proceedings of the 9th world petroleum congress. Applied science publishers, London 2:357-369.
 26. Moldowan, J. M., Dahl, J., Huizinga, B. J., Fago, F. J., Hickey, L. J., Peakman, T. M., and Taylor, D. W., 1994, The molecular fossil record of oleanane and its relation to angiosperms: *Science*, v. 265, p. 768-771.
 27. Mostafa, A. R. and Ganze, H. (1990): Source rock evaluation of a well in Abu Rudies area, Gulf of Suez. *Berliner geowiss. Abh.*, V.120, No. 2, pp.1002-1040
 28. Mostafa, M. E. and Khaled, K. A. (1988): Characters of crude oil from the Gulf of Suez extracted by factor analysis of geochemical data. *Egypt Jour. Geol.* V. 32, pp.134-157.
 29. Nagaty, M. (1992). red sea oil shows attract attention to Miocene salt, post-salt sequence. *Oil&gas Journal* 90(Des.7), 46:48-50.
 30. Noriyuki Suzuki, Masaru Suzuki, Kuniaki Takayama (1996). Biomarker distributions in oils from the Akita and Niigata Basins, Japan, Alexander Chekhmakhchey. *Chemical geology* 133:1-14.
 31. Ourisson, G., Albrecht, P., Rohmer, M., 1984. the microbial origin of fossil fuels. *Scientific American* 251,44-51.
 32. Peters, K.E. and Moldowan, J.M. (1993). the biomarker Guide. Interpreting molecular fossils in petroleum and ancient sediments. Prentice hall, Englewood cliffs, NJ, 363 pp.
 33. Peters, K.E. and Moldowan, J.M. (1991). Effects of source, thermal maturity and biodegradation on the distribution and isomerization of homohopanes in petroleum. *Organic geochemistry*. 17:47-61.
 34. Peters, K.E., Moldowan, J.W., Schoell, M. and Hemphkins, W.B. (1986). Petroleum isotopic and biomarker composition related to source rock organic matter and depositional environment. In advances in organic geochemistry 1985, eds D.Leythaeuser and J. Rullkötter. *Organic Geochemistry*. 10: 17-27. Pergamon, oxford.

35. Peters, K.E., Walters, C.C. and Moldowan, J.N. (2005). *The biomarker Guide*, 2nd edition: Cambridge university press, New York.
36. Petersen, H.I., Andsbjerg, J., Bojesen-Koefoed, J.A., Nytoft, H.P., 2000. Coal-generated oil: source rock evaluation and petroleum geochemistry of the Iulita oil field, Danish North Sea. *Petroleum geology* 23, 55-99.
37. Philp, R.P. (1985). *Fossil fuel biomarkers- applications and spectra*. Elsevier, Amsterdam.
38. Riediger, C.L., Fowler, M.G., Brooks, P.W., Snowdon, L.R. (1990). Triassic oils and potential Mesozoic source rocks, Peace River arch area, western Canada Basin. *Organic Geochemistry*, 16:295-305.
39. Rohrback, B. G. (1983): Crude oil geochemistry of the Gulf of Suez. In M. Bjoroy et al. (Eds.), *Advances in Organic Geochemistry*, 1981, John Wiley and Sons, N.Y., pp.39-48
40. Shahin, A.N. and Shehab, M.M. (1984). Petroleum generation, migration and occurrence in the Gulf of Suez offshore of South Sinai. *Proceedings of the 7th petroleum exploration seminar*, pp. 126-151. EGPC, Cairo.
41. Shaltute, E. M.; Zein El Din, M. Y.; Abou El Fetouh, M. and Ebaid, A. R. (1998): Abundance and distribution of porphyrins in some Gulf of Suez crude oils produced from strata ranging in age from Carboniferous to Middle Miocene. *Egypt Jour. Geol.*, V. 29, pp. 11-28.
42. Shanmugam, G. 1985. Significance of coniferous rain forest and related organic matter in generating commercial quantities of oil, Gippsland basin, Australia. *AAPG Bull.*, 69:1241-1254.
43. Sharaf, L. M. (1998): Characterization, maturation, and source environment of oils from October and Abu Rudies fields, Gulf of Suez, Egypt. M.E.R.C. Ain Shams Univ., Earth Sci., Ser. V.12, pp.65-80.
44. ten Haven, H.L., de Leeuw, J.W., Rulkötter, J., Sinnighe Damsté, J.S. (1987). *Nature* 330 641.
45. Tissot, P.B. and Welte, D.H. (1984). *Petroleum formation and occurrence* 2nd, Springer verlag, Berlin, 699pp.
46. Van Graas, G.W. (1990). Biomarker maturity parameters for high maturities: calibration of the working range up to the oil/condensate threshold. *Organic Geochemistry*. 16:1025-1032.
47. Walples, D.W., and Machihara, T. (1991). Biomarkers for geologists American association of petroleum geologists methods in exploration series, no. 9, 91pp
48. Zein El Din, M. Y.; Abou El Fetouh, M. and Shaltut, E. M. (1981): Geochemical correlation based on n-paraffins distribution of crude oils from some fields, Gulf of Suez, Egypt. *Ain Shams Sci. Bull.*, V. 23, pp.149-165.

10/10/2010