

Molecular Organic Geochemistry of Crude Oil from Shushan and Abu Gharadig Basins, Western Desert, Egypt

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Abstract. Eight crude oil samples recovered from eight fields located in Abu Gharadig and Shushan basins in the north Western Desert, Egypt, were geochemically assessed in order to understand their genetic relationships. Two genetic families of oil are identified in this study, namely Abu Gharadig and Shushan oil families. Bulk (API and sulphur contents), *n*-alkanes, isoprenoids, biomarkers terpanes and steranes, and dibenzothiophene and phenanthrene parameters of the oils of the two families suggest regional variations of organic facies in their source rocks. Shushan samples represent oil typically generated from clay-rich terrigenous source rocks with great higher plant input, deposited under oxic conditions. Contrary, Abu Gharadig oil samples are of marine origin, their source rocks are rich in clay content and were deposited under suboxic environment. Biomarker maturity parameters $Ts/Ts+Tm$, $\beta\beta/aa$ and $20S/(20S+20R)$ C_{29} sterane ratios indicate that the studied samples had reached the peak of the oil window, with high maturity level biased towards Abu Gharadig oil. None of the studied oils have undergone biodegradation or water washing. This explains much of the chemical and physical properties uniformity observed across individual oil samples in each basin.

Introduction

One of the key issues in petroleum exploration is the understanding of the hydrocarbon systems of the basin being explored. When defining and evaluating exploration plays, it is helpful to understand the type and quality of crude oils, their correlation, degree of thermal maturity and subsequent alteration. Detailed geochemical analyses of the crude oils also helps in understanding the characteristics of the source rocks from

which these oils were generated (paleoenvironmental conditions and lithology of the source rocks).

Geological Background

Although the Western Desert consists of a series of small rift basins (EGPC, 1992), most commercial petroleum discoveries occur in the basins located in the north parts of the desert, north of latitude 29°N. Figure 1 illustrates the Western Desert basins distribution as well as the locations of the studied oil samples that had been recovered from the vicinities of Abu Gharadig and Shushan basins. Abu Gharadig Basin is an E-W oriented asymmetric graben containing more than 35,000 ft of sediments, including 7,000 ft of Upper Cretaceous strata (EGPC 1992; Schlumberger, 1995). Shushan Basin, NW Egypt, represents a NE-SW half-graben system with a maximum thickness of 24,606 ft, mainly Jurassic, Cretaceous and Paleogene strata (EGPC 1992; Schlumberger, 1995).

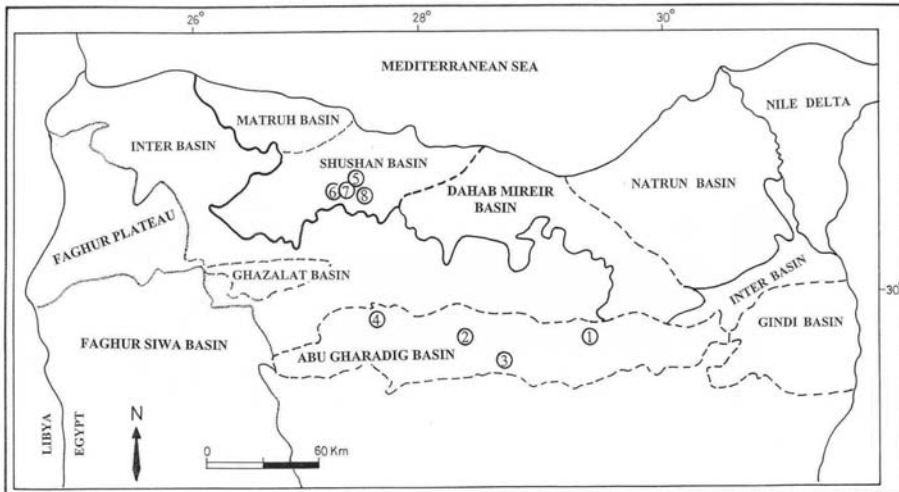


Fig. 1. Map showing the locations of the studied oil samples. Numbers of samples refer to Table 1 (after EGPC, 1992; Petro-consultant, 1997).

Adequate potential source rocks are stratigraphically and areally widespread in the Western Desert. Petroleum source rocks are common in Jurassic, Cretaceous, and Paleozoic rock units (Parker, 1982; Sultan and Halim, 1988; El Ayouty, 1990; EGPC, 1992; Dahi and Shahin, 1992; Ghanem *et al.*, 1999; Khaled, 1999; Sharaf *et al.*, 1999; El-Nadi *et al.*,

2003; and Alsharhan and Abd El-Gawad, 2008). Among the various source rocks in the north Western Desert, (Fig. 2), the Jurassic Khatatba Formation and the Turonian Abu Roash Formation are the most prolific oil and gas prone source rocks.

The occurrence of oil is closely related to the tectono-stratigraphic history of the area, which has created multiple reservoir and seal combinations. As illustrated in Fig. 2, both sandstone and carbonate of Jurassic and Cretaceous ages represent the commercial hydrocarbon bearing formations, while shales, dense limestone and dolomite beds of Jurassic, Cretaceous, Eocene, and Oligocene age make efficient seals in the north Western Desert (EGPC 1992; Schlumberger, 1995). Structural traps are the main types of petroleum traps in the north Western Desert, while stratigraphic traps are less common (El Ayouty, 1990).

Previous Work

The Western Desert of Egypt covers an area of 700,000 square kilometers and comprises almost two thirds of the whole area of Egypt (EGPC, 1992). The Western Desert still has a significant hydrocarbon potential as recent oil and gas discoveries indicate (Dolson *et al.*, 2001). There are few available literatures concerning the geochemical characterization of crude oils from the Western Desert of Egypt (Bagge *et al.*, 1988; Taher *et al.*, 1988; Zein El-Din *et al.*, 1990, 1991, 1993; Halim *et al.*, 1996; Barakat *et al.*, 1997; Mostafa *et al.*, 1998; and El-Gayar *et al.*, 2002). Based on bulk geochemical properties and aliphatic molecular markers, classification of oil types in the Western Desert has been attempted by a number of investigators over the past two decades. Zein El Din *et al.* (1990) divided the oils from the north Western Desert into two main groups: The first includes oils from Shushan-Matruh basins, that are thought to be derived from source rocks of terrestrial origin, while the second includes oils of marine origin from Abu Gharadig and Gindi basins. In a subsequent study by Mostafa *et al.* (1998), four oil types have been recognized in the north Western Desert. Oils from Shushan and Matruh basins are characterized by terrestrial waxes input, while oils from Abu Gharadig Basin are generated from marine siliciclastic source rocks, and those from Alamein Basin are seemed to be derived from mixed marine/terrigenous sources. In an extension of the previous studies, this paper presents a comprehensive

organic geochemical study utilizing representative oil samples from Abu Gharadig and Shushan basins. The principal aim is to develop a reliable classification of the oils to determine their source signature and maturity range, and to understand differences in their composition through a range of conventional hydrocarbon biomarker analyses.

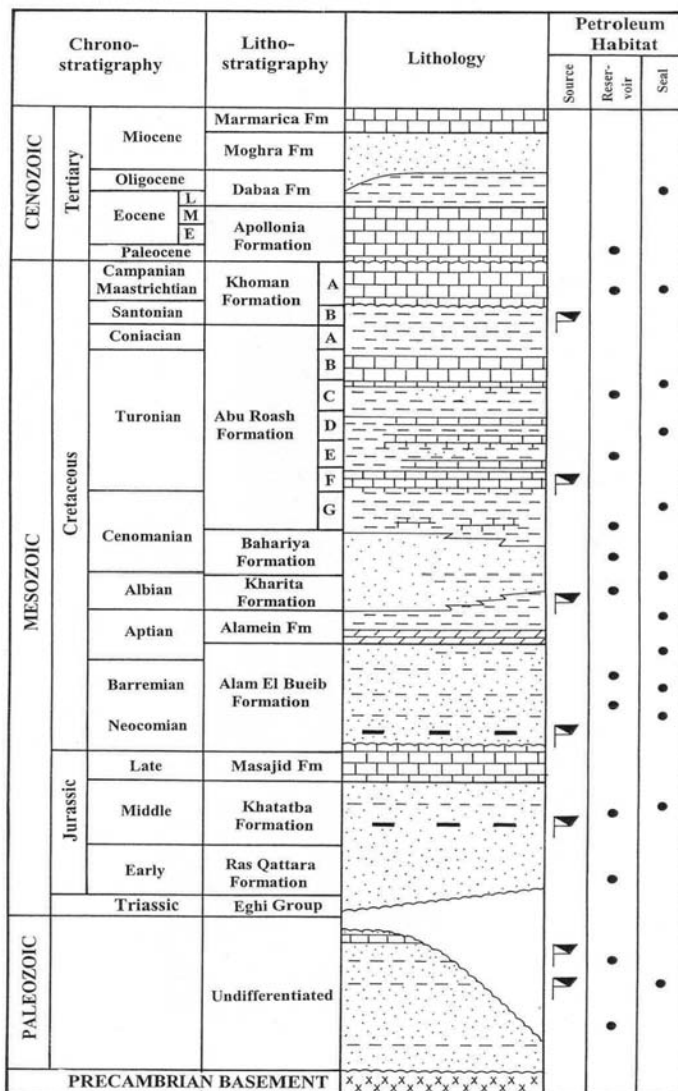


Fig. 2. Simplified stratigraphic section of the north Western Desert (after EGPC 1992; Moustafa *et al.*, 2003).

Materials and Methods

Eight crude oil samples from north Western Desert have been geochemically analyzed. The studied samples are from Upper Cretaceous Abu Roash and Bahariya formations. Four oil samples are recovered from wells in WD-33, BED-4, GPT-SW, and Raml fields located in Abu Gharadig Basin. The others are from wells in A-11, M-16, M25, and M.NE-15 oil fields located in Shushan Basin (Fig. 1 and Table 1). Analytical work was carried out at the Institut für Erdöl und Organische Geochemie, Jülich, Germany. Samples were separated into aliphatic and aromatic hydrocarbons, and polar fraction (resins and asphaltenes) using an automated medium pressure liquid chromatography (MPLC) procedure. The saturated and aromatic hydrocarbons were analyzed using a Hewlett-Packard 5890 Series II gas chromatography (GC), and Finnigan MAT 95SQ mass spectrometer coupled to a HP 5890 Series II GC.

Results and Discussion

API gravity, sulphur content, Pr/Ph, waxiness, nC_{17} - nC_{19}/nC_{27} - nC_{29} , and DBT/Phen ratios of the studied oil samples are given in Table 1. Source and maturity-dependent biomarker parameters of the oils are summarized in Table 2. Hydrocarbon distributions of *n*-alkanes, pristane and phytane obtained from GCs are depicted in Fig. 3 and 4 for the studied crude oil samples. In this context, an oil family is defined as those oils that have a common composition of those compounds that are least affected by secondary alteration processes. On the basis of the detailed geochemical analyses undertaken in this study, two oil families had been recognized and designated as, Abu Gharadig and Shushan families.

Table 1. Bulk composition and geochemical characteristics of the studied crude oil samples.

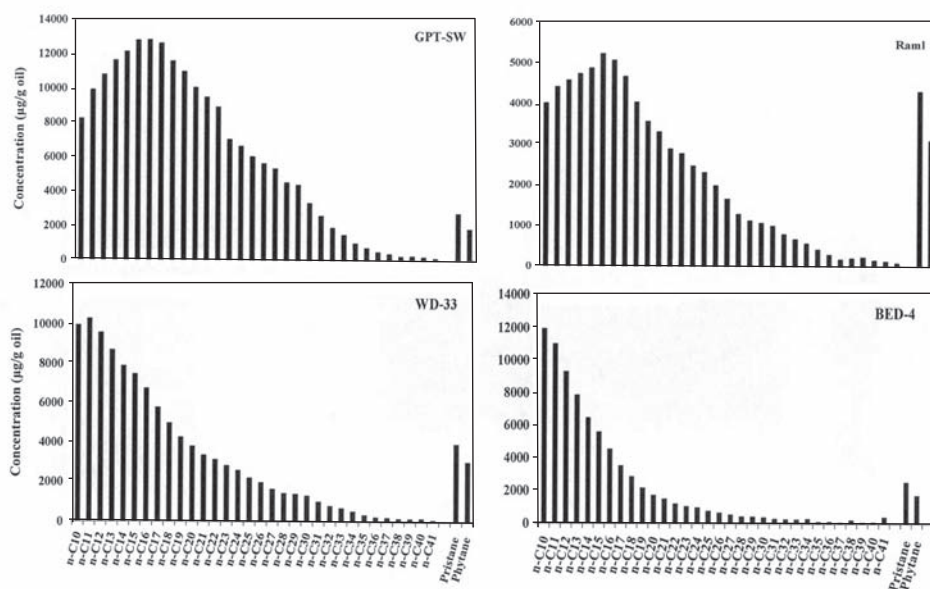
Sample no.	Oil well	Reservoir formation	Reservoir age	^a API	S% ^b	Pr/Ph ^c	Waxiness ^d	C_{17-19}/C_{27-29}	DBT/Phen ^e
1	WD-33	Abu Roash C	U. Cretaceous	39.20	0.11	1.50	0.98	2.32	0.54
2	BED-4	Abu Roash C	U. Cretaceous	42.00	0.20	1.48	0.41	6.00	0.65
3	GPT-SW	Bahariya	U. Cretaceous	39.50	0.23	1.30	0.69	3.36	0.74
4	Raml	Bahariya	U. Cretaceous	35.00	0.51	1.40	0.75	3.53	0.70
5	A-11	Bahariya	U. Cretaceous	34.50	0.08	3.91	1.54	1.21	0.19
6	M. NE-15	Bahariya	U. Cretaceous	35.10	0.07	3.61	1.51	1.23	0.16
7	M-16	Bahariya	U. Cretaceous	33.10	0.09	3.51	1.55	1.19	0.17
8	M-25	Bahariya	U. Cretaceous	34.00	0.09	3.52	1.52	1.26	0.12

API^a: API Gravity; S^b: Sulphur; Pr/Ph^c: Pristane/Phylane; Waxiness^d: $\Sigma(n-C_{21}-nC_{31})/\Sigma(n-C_{15}-nC_{20})$; DBT/Phen^e: Dibenzothiophene/Phenanthrene.

Table 2. Selected source and maturity parameters in the studied crude oil samples.

Sample no.	Oil well	Source specific parameters				Maturity specific parameters			
		HHI ^a	GI ^b	C ₂₉ Dia ^c	C ₂₉ /C ₂₇ ^d	% 20S ^e	% $\beta\beta$ ^f	Ts/(Ts+Tm) ^g	%22S ^h
1	WD-33	0.09	0.00	0.48	1.32	0.49	0.65	0.71	0.61
2	BED-4	0.09	0.00	0.29	1.29	0.49	0.63	0.53	0.60
3	GTP-SW	0.09	0.00	0.40	1.48	0.43	0.61	0.56	0.59
4	Ram1	0.09	0.00	0.18	1.54	0.39	0.64	0.47	0.58
5	A-11	0.03	0.01	1.47	2.96	0.31	0.51	0.33	0.61
6	M.NE-15	0.03	0.01	1.79	2.78	0.35	0.42	0.31	0.60
7	M-16	0.03	0.01	1.50	3.30	0.33	0.54	0.31	0.59
8	M-25	0.04	0.01	1.40	3.39	0.38	0.57	0.37	0.60

HHI^a: Homohopane index, C₃₅/(C₃₁-C₃₅) (m/z 191); GI^b: Gammacerane index, gammacerane/17 α (H), 21 β (H) - hopane (C₃₀) (m/z 191); C₂₉ Dia^c: C₂₉ diasterane/sterane (m/z 217); C₂₉/C₂₇^d: C₂₉ $\alpha\alpha\alpha$ 20R sterane/C₂₇ $\alpha\alpha\alpha$ 20R sterane (m/z 217); %20S^e: C₂₉ $\alpha\alpha\alpha$ Sterane 20S/(20S+20R) (m/z 217); % $\beta\beta$ ^f: C₂₉ $\beta\beta$ / $\beta\beta + \alpha\alpha$ (m/z 217); Ts/(Ts + Tm)^g: 18 α (H) - 22,29,30 - trisnorhopane/(18 α (H) - 22,29,30 - trisnorhopane + 17 α (H)-22,29,30 - trisnorhopane) (m/z 217); %22S^h: C₃₂ S/S + R (m/z 191).

**Fig. 3. Distribution of *n*-alkanes, and isoprenoids pristane and phytane in crude oil samples from Abu Gharadig basin.**

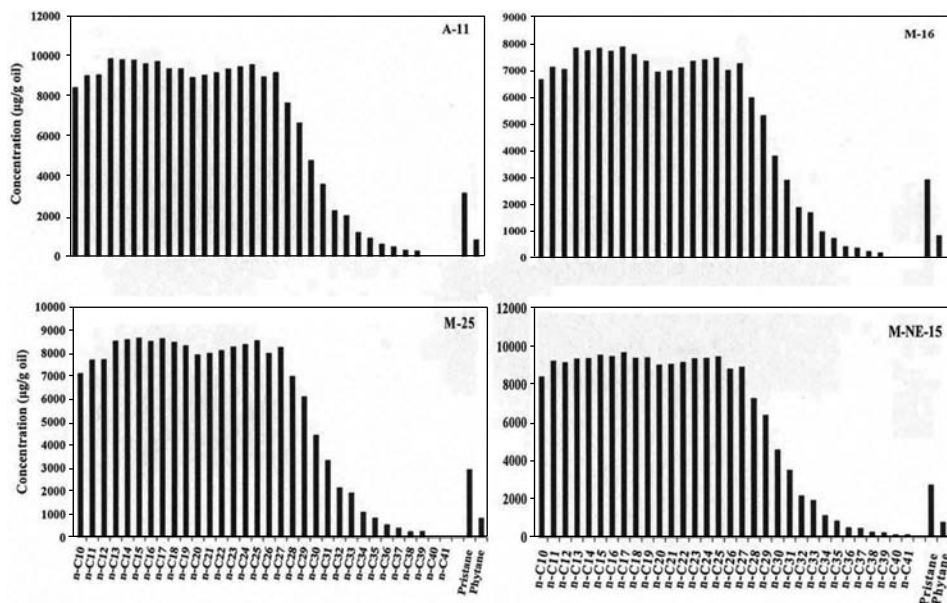


Fig. 4. Distribution of *n*-alkanes, and isoprenoids pristane and phytane in crude oil samples from Shushan basin.

Bulk Composition

API gravity and sulphur content are whole oil properties as determined in the refinery. API is a property for evaluation of a prospect as it determines the oil's producibility, and can be used as a crude indicator of thermal maturity (Hunt, 1996). Sulphur content reflects to a certain extent the type of organic input to the source rock and its depositional environment (Moldowan *et al.*, 1985). High and low sulphur crude oils are derived from sulphur-rich and sulphur-poor kerogens, respectively (Gransch and Posthuma, 1974). Clay-poor marine carbonate source rocks generally have high sulphur contents and produce high sulphur crude oils, whereas source rocks deposited in siliciclastic environment usually have low sulphur contents and release low-sulphur crudes (Gransch and Posthuma, 1974). In the present study, API gravity and sulphur content might be useful for an initial grouping of the oils (Table 1). Abu Gharadig and Shushan oil samples show high API gravities (35 to 42 and 33.1 to 35.8, respectively). Sulphur contents are low, with less than 0.10 % for the Shushan oils, and between 0.11 to 0.51% for Abu Gharadig oils.

Source and Formation Environment of Crude Oil

Primary organic matter characteristics (*i.e.*, marine; terrigenous; algal; bacterial; *etc.*...) are important for oil composition. Various cross plots (Fig. 6-9, 11-12) between biomarker parameters were conducted to reflect the organic facies of source rocks of the studied oil samples, and consequently provide a good differentiation among the hydrocarbon families.

Normal Paraffin Distribution Parameters

The distribution of *n*-alkanes in crude oils can be used to indicate the organic matter source (Duan and Ma, 2001). Figures 3 and 4 display the GC distributions of the normal paraffins (*n*-alkanes) and the isoprenoids (pristane and phytane) of crude oil samples from Abu Gharadig (WD-33, BED-4, GPT-SW, and Raml) and Shushan (A-11, M-16, M25, and M.NE-15) basins, respectively. The striking molecular feature is that in each oil family, the oils are characterized by uniformity in distribution patterns, suggesting that oils in each family are related and have undergone similar histories, with no signs of water washing or biodegradation.

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 component to the oil (Hedberg, 1968). 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 $\sum (n-C_{21}-n-C_{31})/\sum (n-C_{15}-n-C_{20})$ ratios (Table 1).

All Shushan oils show extended *n*-alkane envelopes beyond *n*-C₂₆ to C₄₀, with bimodal distributions and are characterized by low percentages of $nC_{17}-nC_{19}/nC_{27}-nC_{29}$ ratios (1.19-1.26%) of *n*-alkanes in the saturate fractions (reflecting minor low molecular weight *n*-alkanes), and high waxy $\sum (n-C_{21}-n-C_{31})/\sum (n-C_{15}-n-C_{20})$ ratios (1.51-1.55) (Fig. 4, Table 1), confirming their waxy nature, and suggesting terrestrial input mainly

from higher plants (Peters and Moldowan, 1993; and Hunt 1996). This finding is further supported by the high Pr/Ph ratios $> 3.50\%$ (Table 1).

Abu Gharadig oil samples (Fig. 3) contain *n*-alkanes ranging from *n*-C₁₀ to *n*-C₄₀, with unimodal distributions and maximum from *n*-C₁₅ to *n*-C₁₇. Heavier *n*-alkanes bearing more than 20 carbon atoms are low in concentration and a steady decrease of *n*-alkanes concentration with increasing chain length is observed. Such distribution patterns are typical for crude oil of marine origin (Tissot *et al.*, 1971). Evidence of marine organic matter contribution to the analyzed Abu Gharadig crude oils is interpreted from detailed GC-MS analyses that indicate the presence of 24-*n*-propylcholestanes (derived from marine chrysophyte algae, Fig. 5a), indicating contribution from marine, algal organic matter. Alternatively, 24-*n*-propylcholestanes are absent from all Shushan oils (Fig. 5b) consistent with a non-marine source (Moldowan, 1984; Moldowan *et al.*, 1990; Summons *et al.*, 1992; and Peters and Moldowan, 1993).

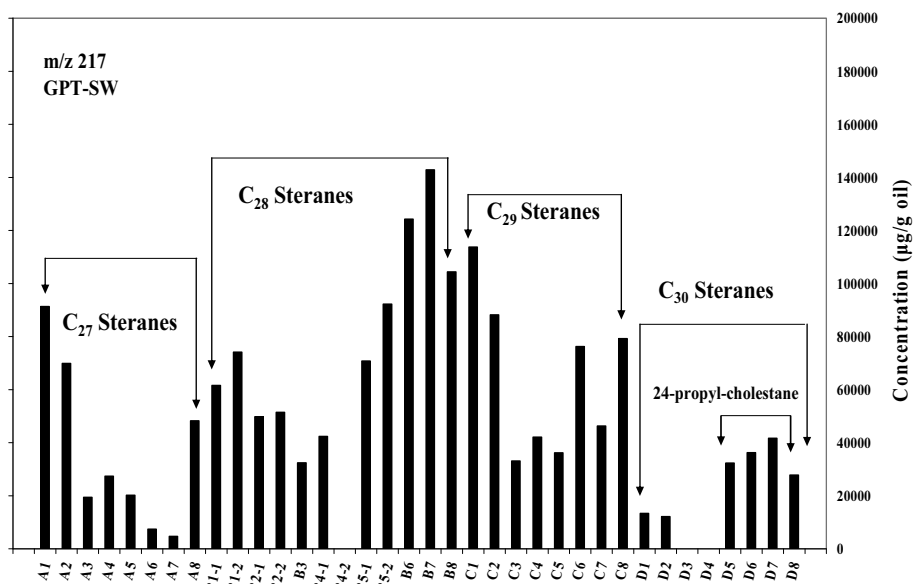


Fig. 5a. Distribution of steranes (m/z 217) in GPT-SW oil sample from Abu Gharadig Basin (Peaks identification is given in Table 3).

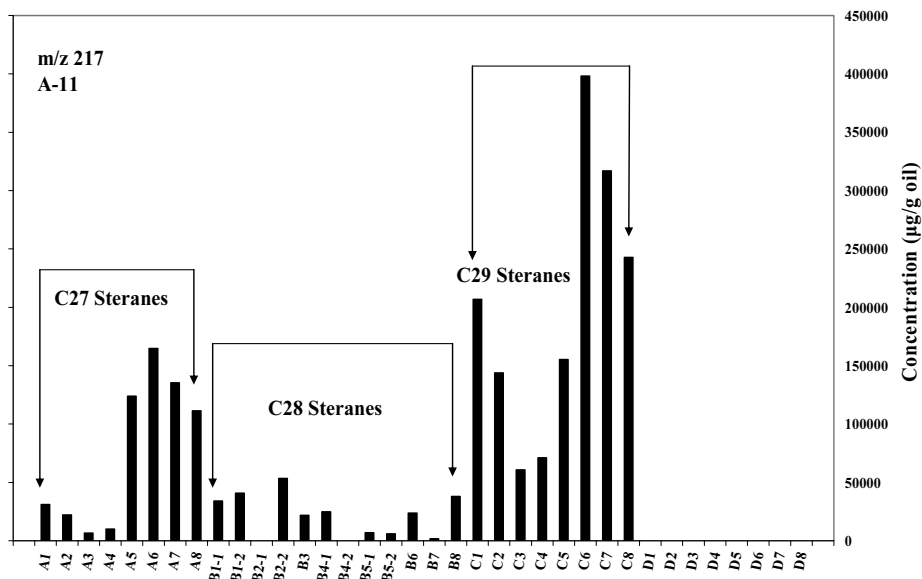


Fig. 5b. Distribution of steranes (m/z 217) in A-11 oil sample from Shushan Basin (peaks identification is given in Table 3).

Table 3. Peaks identification for steranes (Fig. 5a&b).

Peak	Compound	Peak	Compound
A1	(20S)-13β(H), 17α(H) - Diacholestane	C1	(20S)-24-Ethyl-13β(H), 17α(H) - Diacholestane
A2	(20R)-13β(H), 17α(H) - Diacholestane	C2	(20R)-24-Ethyl-13β(H), 17α(H) - Diacholestane
A3	(20R)-13α(H), 17β(H) - Diacholestane	C3	(20R)-24-Ethyl-13α(H), 17β(H) - Diacholestane
A4	(20S)-13α(H), 17β(H) - Diacholestane	C4	(20S)-24-Ethyl-13α(H), 17β(H) - Diacholestane
A5	(20S)-5α(H), 14α(H), 17α(H) - Cholestane	C5	(20S)-24-Ethyl-5α(H), 14α(H), 17α(H) - Cholestane
A6	(20R)-5α(H), 14β(H), 17β(H) - Cholestane	C6	(20R)-24-Ethyl-5α(H), 14β(H), 17β(H) - Cholestane
A7	(20S)-5α(H), 14β(H), 17β(H) - Cholestane	C7	(20S)-24-Ethyl-5α(H), 14β(H), 17β(H) - Cholestane
A8	(20R)-5α(H), 14α(H), 17α(H) - Cholestane	C8	(20R)-24-Ethyl-5α(H), 14α(H), 17α(H) - Cholestane
B1	(20S)-24-Methyl-13β(H), 17α(H) - Diacholestane	D1	(20S)-24-Propyl-13β(H), 17α(H) - Diacholestane
B2	(20R)-24-Methyl-13β(H), 17α(H) - Diacholestane	D2	(20R)-24-Propyl-13β(H), 17α(H) - Diacholestane
B3	(20R)-24-Methyl-13α(H), 17β(H) - Diacholestane	D3	(20R)-24-Propyl-13α(H), 17β(H) - Diacholestane
B4	(20S)-24-Methyl-13α(H), 17β(H) - Diacholestane	D4	(20S)-24-Propyl-13α(H), 17β(H) - Diacholestane
B5	(20S)-24-Methyl-5α(H), 14α(H) - 17α(H) - Cholestane	D5	(20S)-24-Propyl-5α(H), 14α(H) - 17α(H) - Cholestane
B6	(20R)-24-Methyl-5α(H), 14β(H) - 17β(H) - Cholestane	D6	(20R)-24-Propyl-5α(H), 14β(H) - 17β(H) - Cholestane
B7	(20S)-24-Methyl-5α(H), 14β(H) - 17β(H) - Cholestane	D7	(20S)-24-Propyl-5α(H), 14β(H) - 17β(H) - Cholestane
B8	(20R)-24-Methyl-5α(H), 14α(H) - 17α(H) - Cholestane	D8	(20R)-24-Propyl-5α(H), 14α(H) - 17α(H) - Cholestane

Generally, processes leading to a shift in *n*-alkanes distribution from heavy to light components are attributed to a final stage of catagenesis, after the peak of hydrocarbon generation has already been surpassed. This conclusion is confirmed in the current study by the established maturity data plotted in Fig. 14 and 15, and presented in Table 2. In Abu Gharadig oils, the predominance of low molecular weight *n*-alkanes (Fig. 6) and the lack of bimodal *n*-paraffin distribution (Fig. 3) as compared to Shushan oils (Fig. 4), appear to have resulted from thermal maturity accompanied with cracking of the higher molecular weight *n*-paraffins to lighter products during maturation, hence yielding low molecular weight hydrocarbons (Powell and McKirdy, 1973; and Connan *et al.*, 1975). Such feature is evidenced from the high percentage of ratios nC_{17} - nC_{19}/nC_{27} - nC_{29} that vary from 2.32 to 6.0 (Table 1), and the high level of thermal maturity, which is supported by thermal maturation-dependent biomarkers indicators C_{29} $\alpha\alpha\alpha$ steranes (Table 2, and Fig. 7). A noteworthy feature in Abu Gharadig oils is that WD-33 oil sample contains higher waxy $\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-n-C_{20})$ ratios than other oils of this family, reflecting relatively higher concentrations of land plant derived biomarkers in this sample than the remaining Abu Gharadig oil samples (Fig. 6, Table 1).

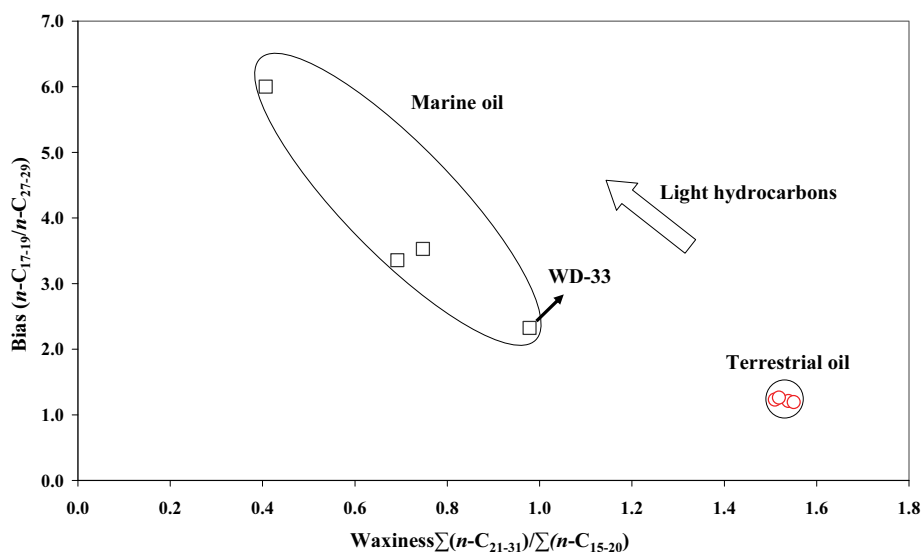


Fig. 6. Bias versus waxiness plots for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

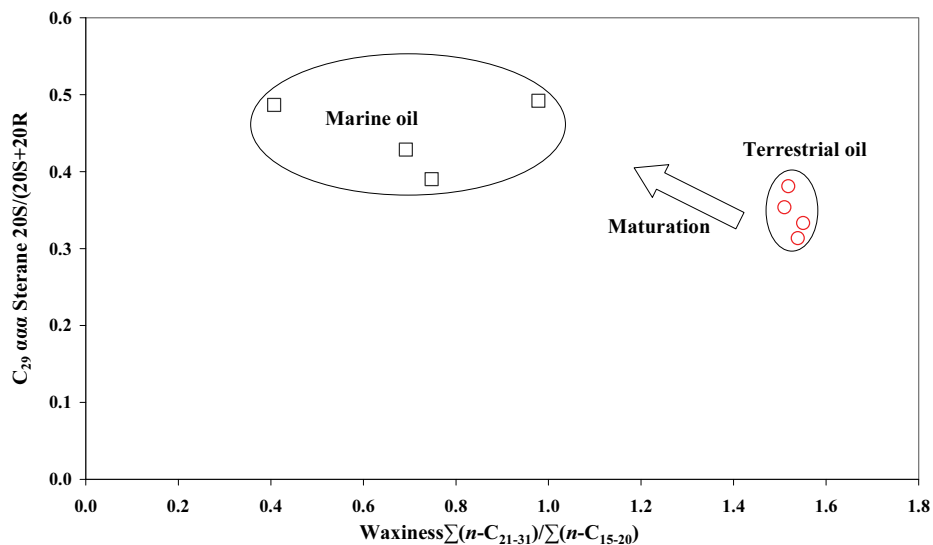


Fig. 7. Cross plots of waxiness $\sum (n-C_{21-31})/\sum (n-C_{15-20})$ versus C29 $\alpha\alpha\alpha$ Sterane 20S/(20S+20R) for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

Redox Conditions (Pristane/Phytane Ratio)

The pristane/phytane (Pr/Ph) ratio is one of the most commonly used geochemical parameters and has been widely invoked as an indicator of the redox conditions in the depositional environment and source of organic matter (Powell and McKirdy, 1973; and Didyk *et al.*, 1978). High Pr/Ph ratios have generally been inferred to indicate that the organic matter has undergone some degree of oxidation, because oxidation of the phytol side-chain of chlorophyll is believed to lead to the formation of pristane. Whereas, under reducing conditions, phytane is the favored product from diagenesis of phytol. Therefore, oils originating predominantly from terrestrial plants would be expected to contain high Pr/Ph (>3.0) because of the availability of oxygen during initial diagenesis of chlorophyll in comparison with oils and sediments containing marine organic matter (Brooks *et al.*, 1969; and Powell and McKirdy, 1973). However, it should be mentioned that multiple sources of these isoprenoids are possible. Recently, archaeobacteria have been proposed as another source of phytane (Risatti *et al.*, 1984) and pristane may also be derived from tocopherols (ten Haven *et al.*, 1987).

The Pr/Ph ratios of the studied oil samples are given in Table 1, suggesting a gradual change in the depositional conditions of the source rocks, with more reducing conditions for source rocks that generated the Abu Gharadig crude oils. Figure 8 exhibits the relationship between Pr/Ph and waxiness (Table 1), where the crude oils can be divided into two families. Abu Gharadig oil family is characterized by pristane/phytane ratios (1.30 to 1.50) and waxiness values (0.41 to 0.98), confirming that these oils have been originated from marine organic source deposited under suboxic conditions. On the other hand, Shushan oil family shows high Pr/Ph ratios (> 3.50) and high waxiness values (1.51 to 1.55), suggesting terrestrial origin mainly of higher plants, deposited under oxidizing conditions.

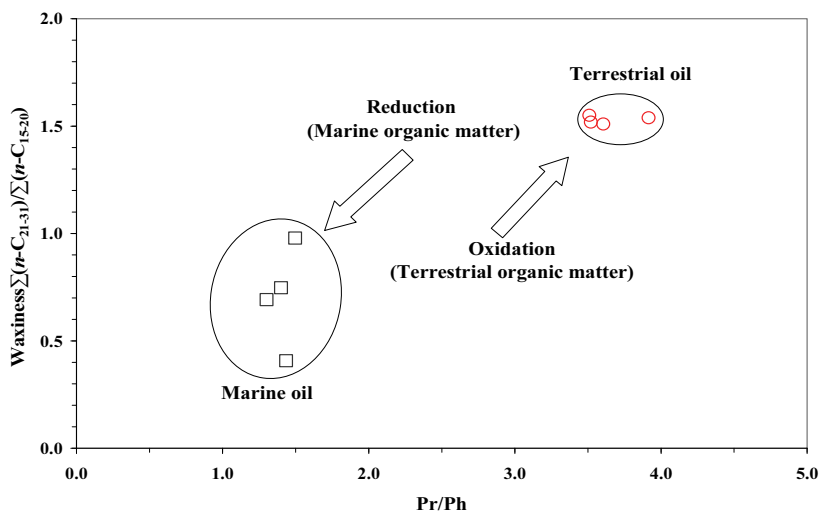


Fig. 8. Cross plots of Pr/Ph versus waxiness $\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-n-C_{20})$ for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

Lithology of Source Rocks and Paleoenvironmental Conditions

When lithology is considered, source rocks can be roughly subdivided into two categories: Clay-rich; and carbonate-rich. Clay-rich source rocks, generate in general, oil with low sulphur and high diasterane vs. regular sterane content (Peters and Moldowan, 1993). Clay minerals play a major role to catalyze the transformation of steroids to diasteranes. Metals such as iron in clays interact with sulphur (*e.g.* forming FeS_2) that might otherwise be incorporated into the organic matter and generated oil (Peters and Moldowan, 1993).

There is an increasing weight of observational evidence that the coaly intervals of the Khatatba Formation (Fig. 2) have the quality and maturity to comprise a significant oil source rock that generated oil of the Shushan family (Bagge *et al.*, 1988; Abdel Halim *et al.*, 1996; and Alsharhan and Abd El-Gawad, 2008). The Cenomanian-Turonian shales of the Abu Roash Formation (G, F and E Members) that contain marine types II kerogen (EGPC, 1992; Abdel Halim *et al.*, 1996; and Khaled, 1999) are suggested to be the main contributing source rocks for the oil and gas of Abu Gharadig Basin.

In the current work, a cross plot of dibenzothiophene/phenanthrene (DBT/PHEN) versus pristane/phytane (Pr/Ph) ratios, classified the oil samples into two environment/lithology zones (Fig. 9, Table 1). Zone 3 specifies oil generated from marine shales of type II kerogen. This zone is bounded by DBT/PHEN ratios < 1.0 , Pr/Ph ratios between > 1.0 and < 3.0 . Abu Gharadig oil samples lie within this zone. On the other hand, zone 4 includes Shushan oil samples with DBT/PHEN ratios less than 0.5 and Pr/Ph ratios more than 3.50. Hydrocarbons in zone 4 are derived from shales deposited in a variety of fluvial to deltaic environments. The kerogen in this zone is mainly of mixed marine and terrestrial origin.

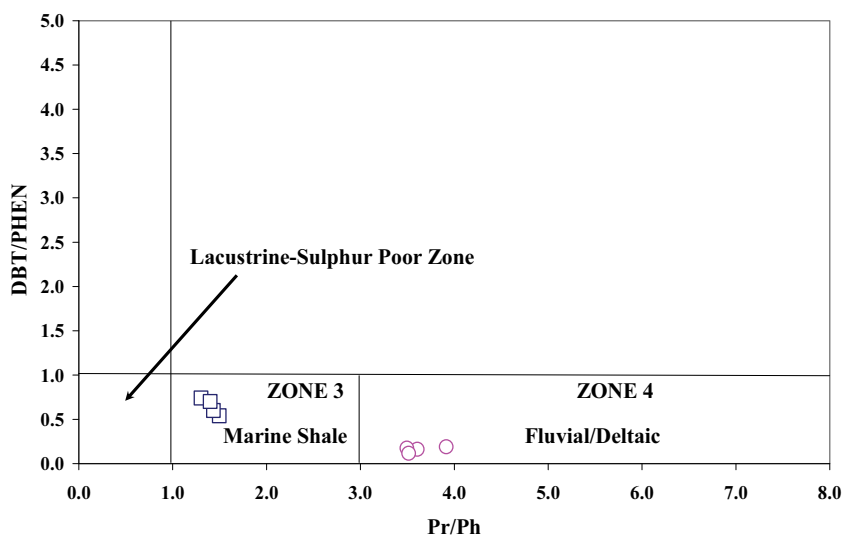


Fig. 9. Cross plots of dibenzothiophene/phenanthrene (DBT/PHEN) vs. Pr/Ph showing oil groups according to their source rock depositional environments and lithologies (squares, Abu Gharadig oils; circles, Shushan oils) (after Hughes *et al.*, 1995).

Biomarkers Terpanes (M/Z 191) Distributions

*C*₃₀-Hopane and Homohopanes (*C*₃₁-*C*₃₅)

The pentacyclic terpanes belong mostly to the 17 α (H), 21 β (H) hopane series, with molecules ranging from *C*₂₇ to *C*₃₅ (Fig. 10). Hopane-*C*₃₀-17 α (H), 21 β (H) (peak 9H) is the most abundant component, followed by norhopane- *C*₂₉-17 α (H),21 β (H) (peak 5NH-5) and a full range of *C*₃₁ to *C*₃₅ homohopanes.

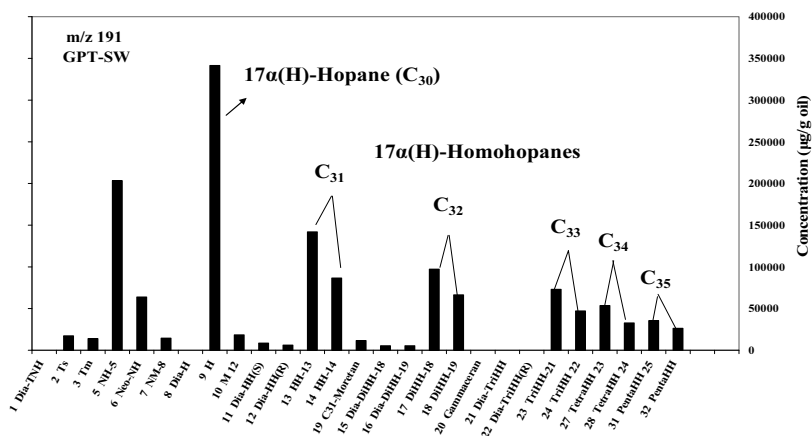


Fig. 10a. Distribution of hopanes (m/z 191) in GPT-SW oil sample from Abu Gharadig basin (peaks identification are given in Table 4).

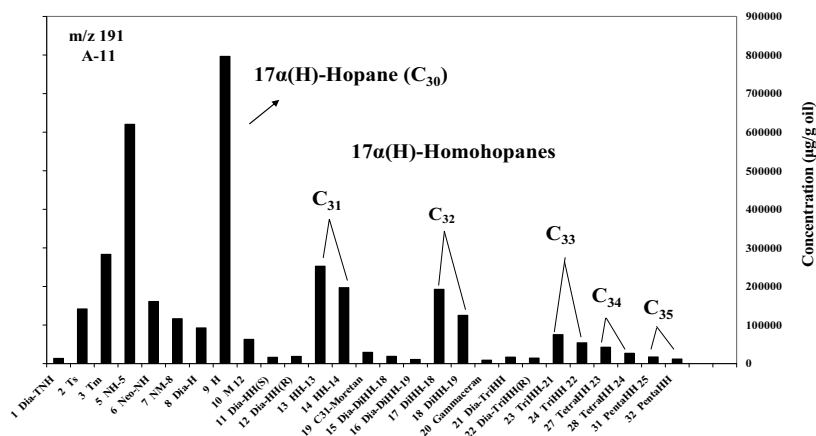


Fig. 10b. Distribution of hopanes (m/z 191) in A-11 oil sample from Shushan basin (peaks identification are given in Table 4).

Table 4. Peaks identification for hopanes (Fig. 10).

Peak	Compound	Formula
1 Dia-TNH	Diatrinorhopane	C27H46
2 Ts	18 α (H)-22,29,30-Trinorneohopane	C27H46
3 Tm	17 α (H)-22,29,30-Ttinorhopane	C27H46
5 NH-5	17 α (H),21 β (H)-30-Norhopane	C29H50
6 Neo-NH	18 α (H)-Norneohopane	C29H50
7 NM-8	17 β (H),21 α (H)-30-Norhopane (Normoretane)	C29H50
8 Dia-H	Diahopane	C30H52
9 H	17 α (H),21 β (H)-Hopane	C30H52
10 M 12	17 β (H),21 α (H)-Hopane (Moretane)	C30H52
11 Dia-HH(S)	(22S)-Diahomohopane	C31H54
12 Dia-HH(R)	(22R)-Diahomohopane	C31H54
13 HH-13	(22S)-17 α (H),21 β (H)-29-Homohopane	C31H54
14 HH-14	(22R)-17 α (H),21 β (H)-29-Homohopane	C31H54
19 C31-Moretan	17 β (H),21 α (H)-Homohopane (Homomoretane)	C31H54
15 Dia-DiHH-18	(22S)-Diadihomohopane	C32H56
16 Dia-DiHH-19	(22R)-Diadihomohopane	C32H56
17 DiHH-18	(22S)-17 α (H),21 β (H)-29-Dihomohopane	C32H56
18 DiHH-19	(22R)-17 α (H),21 β (H)-29-Dihomohopane	C32H56
20 Gammaceran	Gammacerane	C30H52
21 Dia-TriHH	(22S)-Diatrihomohopane	C33H58
22 Dia-TriHH(R)	(22R)-Diatrihomohopane	C33H58
23 TriHH-21	(22S)-17 α (H),21 β (H)-29-Trihomohopane	C33H58
24 TriHH 22	(22R)-17 α (H),21 β (H)-29-Trihomohopane	C33H58
27 TetraHH 23	(22S)-17 α (H),21 β (H)-29-Tetrahomohopane	C34H60
28 TetraHH 24	(22R)-17 α (H),21 β (H)-29-Tetrahomohopane	C34H60
31 PentaHH 25	(22S)-17 α (H),21 β (H)-29-Pentahomohopane	C35H62
32 PentaHH	22R)-17 α (H),21 β (H)-29-Pentahomohopane	C35H62

The homohopanes (C₃₁ to C₃₄) are believed to be derived from bacteriopolyhopanol of prokaryotic cell membrane, abundant C₃₅ homohopane may be related to extensive bacterial activity in the depositional environment (Ourisson *et al.*, 1979, 1984). The distribution of 17 α ,21 β (H)-29-homohopanes 22R+22S C₃₅/(C₃₁-C₃₅) [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). High C₃₅ homohopanes is an indicator of highly reducing (low Eh) marine

conditions during deposition, whereas low C_{35} homohopane concentrations are generally observed in oxidizing (high Eh) water conditions during deposition, consistent with the oxic conditions as suggested by high pristane/phytane ratios (Peters and Moldowan, 1991).

The data given in Table 2 and displayed in Fig. 11 show variations in homohopane index ratios among the Shushan and Abu Gharadig oil samples, and are most likely caused by subtle source input changes in each basin. The Abu Gharadig oil samples are characterized by high C_{35} -homohopane indices and have low Pr/Ph ratios as compared to Shushan oils (Fig. 11, Table 2), suggesting that these oils were generated from marine sources influenced by suboxic conditions of the depositional environment. On the other hand, the resulting very small homohopane indices ($C_{35}/C_{31-C_{35}}$) in Shushan oils (Fig. 11, Table 2), suggest that anoxic conditions did not occur during the time of deposition of their relevant source rocks. Visual examination of $C_{31-C_{35}}$ homohopanes on m/z 191 chromatograms depicted in Figure 10 displays a smooth decrease in the homohopanes ($C_{31-C_{35}}$) profile with increasing carbon number. This profile feature is typical for all the investigated oils, and the patterns are characterized by a regular stair-step progression of the C_{31} to C_{35} homologues. Such declining pattern of the extended hopanes is normally seen in clastic, low saline or freshwater environments contrary to carbonate or evaporate source rocks, which often have pronounced C_{33} or C_{35} hopane contents (Waples and Machihara, 1991).

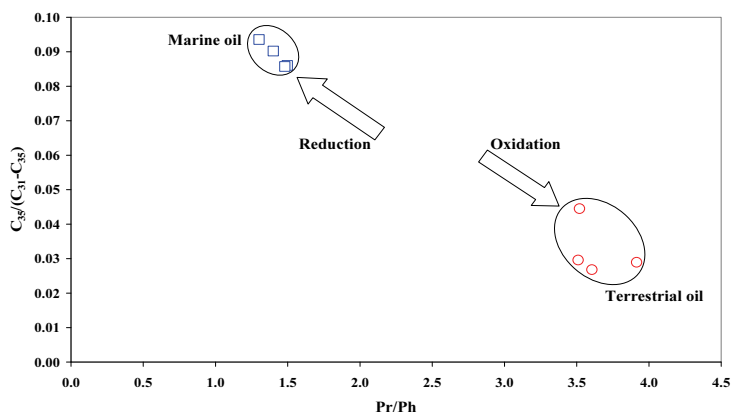


Fig. 11. Cross plots of $C_{35}/(C_{31}-C_{35})$ homohopanes and Pr/Ph ratios for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

Gammacerane

Gammacerane, a pentacyclic triterpanes, made up of six-membered ring, formula $C_{30}H_{52}$, is a facies-controlled triterpane, generally associated with environments of increasing salinity, both marine and lacustrine (Waples and Machihara, 1991; and Peters and Moldowan, 1993). The biomarker analyses in this study show that all the Shushan crude oils contained low concentrations of gammacerane (peak 20, Fig. 10b), which is absent in all the Abu Gharadig oil samples. The abundance of gammacerane compared with $17\alpha(H)$, $21\beta(H)$ -hopane (C_{30}) expresses as percent, is called the Gammacerane Index (Table 2), with low to very low values indicating a shaly source rock.

$17\alpha(H)$ -Diahopane & $18\alpha(H)$ -Nornehopane (C_{30}^* & $C_{29}Ts$)

C_{30}^* $17\alpha(H)$ -diahopane compound has been regarded as a possible terrestrial marker because of its presence in coals and terrestrially sourced oils (Philip and Gilbert, 1986). In this study, C_{30}^* -diahopane compound is absent from Abu Gharadig oils, while all Shushan oils contain this C_{30}^* diahopane compound (peak 8 Dia-H in Fig. 10b), which further support terrestrial organic matter input. The $18\alpha(H)$ -nornehopane ($C_{29}Ts$) compound eluting immediately after $C_{29}17\alpha(H)$ -norhopane, has been identified in many oils sourced from terrestrial organic matter in Australia (Philip and Gilbert, 1986). This compound, is present in both Shushan and Abu Gharadig crude oil samples (peak 6 Neo-NH in Fig. 10), suggesting that Abu Gharadig oils have contribution from terrestrial organic matter.

Biomarkers Steranes (M/Z 217) Distributions

$C_{29}aaa\ 20R\ Sterane/C_{27}aaa\ 20R\ Sterane$

Steranes are thought to be mainly sourced from eukaryotic organisms in sedimentary organic matter (Ourisson *et al.*, 1979). Generally, sterane distributions reflect variation in algal input to source rocks and can be used as effective source facies discriminators to group oils in a region on the basis of genetic relationships. Petroleum generated from kerogens containing organic matter derived from higher plants often display enhanced amounts of C_{29} relative to C_{27} steranes (Mackenzie *et al.*, 1982; and Czochanska *et al.*, 1988), and by analogy, C_{29} steranes are

often used as indicators of land-plant-derived organic matter in source rocks and oils.

All Shushan oils are dominated by C_{29} regular steranes, especially the $\alpha\alpha\alpha 20R$ epimers, with high concentrations relative to the C_{27} regular steranes (Table 2). High concentrations of C_{29} steranes is linked with a terrestrial contribution of organic matter to sediments and crude oils (Robinson, 1987). However, it was subsequently noted that certain marine organisms contribute to C_{29} regular steranes (Volkman, 1988). In addition, Nichols *et al.* (1990) noted that large amounts of C_{29} sterols are produced by marine diatoms during the spring bloom in cold Antarctic waters.

Figures 12 and 13 illustrate the relationships between the ratios C_{29} $\alpha\alpha\alpha 20R$ sterane/ C_{27} $\alpha\alpha\alpha 20R$ sterane (Table 2) and the ratios $\sum (n-C_{21}-n-C_{31})/\sum (n-C_{15}-n-C_{20})$ and Pr/Ph (Table 1), respectively for the studied oil samples. These figures clearly verify the predominance of C_{29} steranes in Shushan over Abu Gharadig oils, with high values held to be diagnostic of a greater contribution of higher plant matter deposited in oxidizing environment. However, the quite abundance of C_{29} over C_{27} steranes in the marine Abu Gharadig oils (Table 2) could be attributed to synthesis of C_{29} sterols from some marine phytoplankton as previously noted by Volkman (1988).

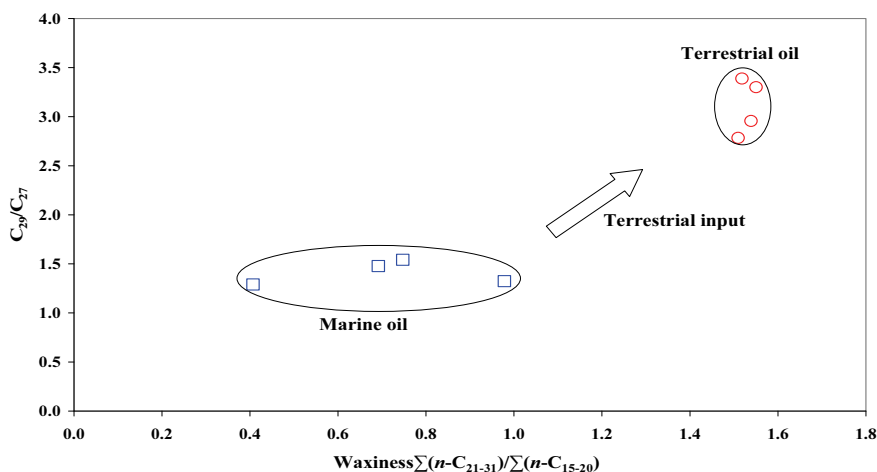


Fig. 12. Cross plots of waxiness $\sum(n-C_{21}-n-C_{31})/\sum (n-C_{15}-n-C_{20})$ and C_{29} $\alpha\alpha\alpha 20R$ sterane/ C_{27} $\alpha\alpha\alpha 20R$ sterane ratio for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

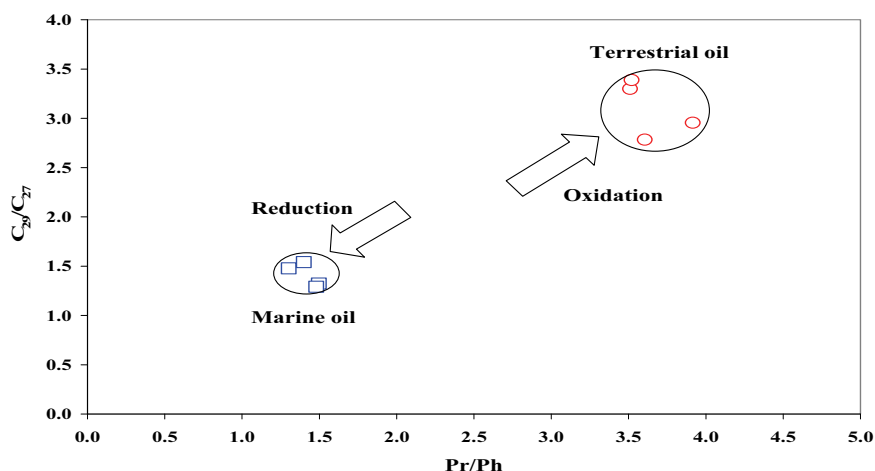


Fig. 13. Cross plots of $C_{29} \alpha\alpha 20R$ sterane/ $C_{27} \alpha\alpha 20R$ sterane and Pr/Ph ratios for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

Crude Oil Maturation

Maturation of crude oil is an important parameter for understanding their thermal history and is generally determined by several biomarker parameters (Seifert and Moldowan, 1978; and Peters *et al.*, 1999). In the current study, several hopanes and steranes biomarker parameters have been examined to estimate the relative thermal maturities of the oil (Table 2), and to assess whether oil-oil correlations would be significantly affected by maturation effects.

Steranes Maturity Parameters

$\beta\beta/\alpha\alpha$ Ratio

$C_{29}\beta\beta/\alpha\alpha$ parameter is widely applied owing to its operation beyond the start of the oil window, and employs the greater thermal stability of the $\alpha\beta\beta$ sterane isomers [$14\beta(H)$, $17\beta(H)$] as compared to the biologically-derived [$14\alpha(H)$, $17\alpha(H)$] forms. The $\alpha\alpha$ form gradually converts to a mixture of $\alpha\alpha$ and $\beta\beta$. This transformation involves changes of two hydrogen atoms from alpha positions to beta, and the ratio ($\beta\beta/(\beta\beta + \alpha\alpha)$) increases from non-zero values to about 0.7 (0.67 to 0.71 = equilibrium; Seifert and Moldowan, 1986). The $\beta\beta/\alpha\alpha$ ratio ranges from

0.61 to 0.65 in Abu Gharadig oils, and from 0.42 to 0.57 in the Shushan oils (Table 2). Overall, these values (0.42-0.65) suggest that all the studied oil samples had reached the peak of oil generation (approximately 0.6-0.9% R_o , after Peters and Moldowan, 1993). However, Abu Gharadig oils are, generally, more mature than Shushan oils.

The $\beta\beta$ ratio may be affected by reaction of steroids with minerals or sulphur during early diagenesis (ten Haven *et al.*, 1986; and Rullkötter and Marzi, 1988), resulting in generation of higher amounts of the $\beta\beta$ molecules than would be expected due solely to burial heating; however, this effect would result in overestimation rather than underestimation of the thermal maturity. The low $\beta\beta$ ratios for Shushan oils (Table 2) thus are probably due to the low thermal maturity of these oils rather than a mineral matrix or other diagenetic effect, which would tend to increase, rather than decrease, the amounts of the $\beta\beta$ components.

20S/(20S+20R) C₂₉ Sterane

The % 20S parameter (usually measured using the C₂₉ $\alpha\alpha\alpha$ steranes) is one of the most widely applied molecular maturity parameters in petroleum geochemistry, and is based on the relative enrichment of the 20S isomer compared with the biologically-inherited 20R stereochemistry, to reach an equilibrium value of 50% (Peters and Moldowan, 1993).

The C₂₉ $\alpha\alpha\alpha$ steranes range from 0.39 to 0.49 in Abu Gharadig oils, and from 0.31 to 0.38 in Shushan oils (Table 2). These 20S/(20S+20R) epimer ratios have not reached the typical end-point value of 0.50 in the Shushan oil samples (Table 2). One possible explanation is that coal matrix in their source rocks (Khatatba Formation) plays important roles in sterane isomerization as noted by Strachan *et al.* (1989). In this study, the low isomerization ratios in the Shushan oils are consistent with other findings that indicate relatively low levels of thermal stress. 20S/20R ratios are plotted in Fig. 14 against $\beta\beta/\alpha\alpha$ ratios to aid in estimating maturity. The values and relationships of these C₂₉ sterane isomers support a higher maturity level for the Abu Gharadig oils as compared to oils from Shushan Basin.

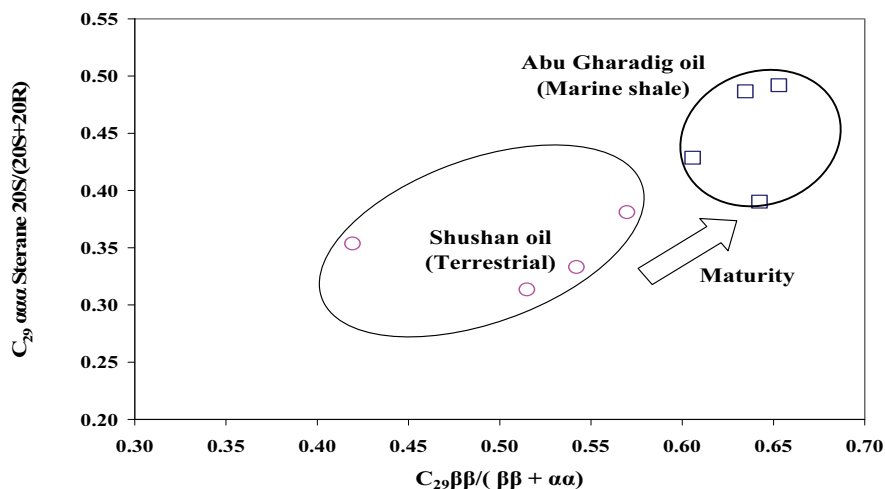


Fig. 14. Oil samples show a range of thermal maturity based on two maturity-related biomarker parameters [$C_{29} \alpha\alpha$ Sterane $20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta + \alpha\alpha)$], for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

Hopanes Maturity Parameters

$T_s/T_s + T_m$

All the Shushan oils have a predominance of $17\alpha(H)22,29,30$ -trisorhopane (T_m) over $18\alpha(H)22,29,30$ -trisorhopane (T_s). This feature is displayed by the m/z 191 chromatogram depicted in Fig. 10b for a representative A-11 oil sample. Contrary, the predominance of T_m over T_s is less pronounced in the Abu Gharadig oils (represented here by GPT-SW oil sample, Fig. 10a). Obviously, T_s/T_s+T_m ratios display maturity trends similar to the maturity indicators, C_{29} regular steranes $S/(S + R)$ and $\beta\beta/(\alpha\alpha + \beta\beta)$ ratios. Figure 15 illustrates the relationship between two maturity parameters, the $C_{29} \beta\beta/\alpha\alpha$ ratio sterane and the T_s/T_s+T_m hopane ratios of the studied oil samples. Abu Gharadig oils have higher T_s/T_s+T_m ratios (from 0.47 to 0.71), while Shushan oils exhibit lower values ranging from 0.31 to 0.37, consistent with an interpretation of low thermal history for the Shushan oils as compared to Abu Gharadig oils.

T_s/T_s+T_m is also sensitive to source deposition characteristics (Seifert and Moldowan, 1978; and Rullkötter and Marzi, 1988). An increase in the $T_s/(T_s + T_m)$ ratio, although typically attributed to increasing source maturity, may also increase with increasing shale content of the source (McKirby *et al.*, 1983), as is the case here for Abu

Gharadig oil samples (Table 2). T_s is sensitive to catalysis by clay minerals (Waples and Machichara, 1991). The low T_s contents in the Shushan oils may result from the lack of catalysis by clay minerals.

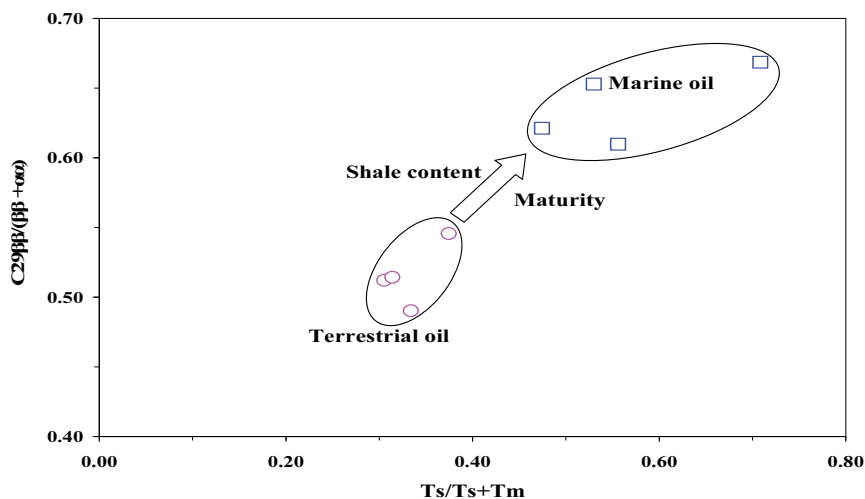


Fig. 15. Oil samples show a range of thermal maturity based on two maturity-related biomarker parameters [$C_{29}\beta\beta/(\beta\beta + \alpha\alpha)$ and $T_s/(T_s+T_m)$], for the studied samples (squares, Abu Gharadig oils; circles, Shushan oils).

Isomerisation at C-22: $22S/(22S+22R)$ (%)

The % 22S parameter is probably the most widely applied of the hopane maturity parameters. It records the relative enrichment of the more thermally stable 22S isomer (Kolaczowska *et al.*, 1990) compared to the biologically-derived 22R stereochemistry. This parameter is usually measured using the C_{31} homohopanes, however in this study, the C_{32} homologues are employed due to the possible co-elution of gammacerane with the former. As indicated by the almost identical C_{32} S/S+R ratios (0.58-0.63), the isomerizations of homohopanes have reached equilibrium values in all the oil samples indicating the characteristics of mature oil. The maturity as expressed by hopane isomerization ratios ($22S/22S+22R$) of all the studied oil samples are around 0.60 (Table 2), showing an “equilibrium value” which is known to be reached at peak oil generation (0.85% R_o) and thus indicating that oil window has been reached (Seifert and Moldowan, 1978; and Peters *et al.*, 2005).

Conclusions

Various crude oil composition parameters have been described in detail for the studied oil samples. Their potential use as indicators for thermal maturation, organic inputs and depositional environments of petroleum source rocks has been examined. The samples include four oils recovered from wells in WD-33, BED-4, GPT-SW, and Raml fields located in Abu Gharadig Basin, and four others that are from wells in A-11, M-16, M25, and M.NE-15 fields located in Shushan Basin. Two oil families designated as Abu Gharadig and Shushan families have been recognized on the basis of source-related geochemical parameters. The results of bulk property, saturated and aromatic molecular biomarker analyses of crude oils of the two families suggest the following key points:

– None of the studied crude oils have undergone postemplacement alteration in the reservoir; therefore, all the geochemical parameters are used to interpret organic matter type, depositional setting and maturity of the source rocks.

– Shushan oils have bimodal *n*-alkane profiles and are characterized by: high abundance of waxy *n*-alkanes $\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-n-C_{20})$ ratio (> 1.50), very low sulphur (< 0.10), high Pr/Ph ratios (> 3.50), low dibenzothiophene/phenanthrene ratios (< 0.20), homohopane contents are relatively low, low C_{29} tricyclic terpanes $Ts/Ts+Tm$ ratios, C_{29} steranes and diasteranes are present in greater abundance than the corresponding C_{27} . This compositional feature is associated with the occurrence of C_{30}^* 17 α (H)-diahopane, presence in small amounts of gammacerane, relatively low amounts of extended hopanes, especially the higher homologues (C_{33} , C_{34} , and C_{35}), high relative concentrations of 18 α (H)-30-norneohopane, and absence of 24-*n*-propyl- C_{30} steranes. All these features are considered typical of oil generated from clay-rich terrigenous source rocks that received greater higher plant input, and are likely generated from type III-II sources deposited under oxic conditions.

– The oils within Abu Gharadig Basin have closest affinity with the biomarker signatures of Type II source that contains primarily algal organic matter. As compared to Shushan, Abu Gharadig oil family has a nonwaxy, unimodal *n*-alkane profile, lowest pristane/phytane, highest dibenzothiophene/phenanthrene ratios, highest $Ts/(Ts+Tm)$, in addition to the existence of the marine algal biomarker, 24-*n*-propylcholestane. Collectively, these geochemical parameters are pointing towards marine

origin for Abu Gharadig oils, and indicate that the source for these oils is shale rocks deposited in suboxic environment.

– Maturity estimates based on biomarker maturity parameters indicate that all oils had reached the peak of the oil window, with higher maturity level biased towards Abu Gharadig oils.

– Overall, the results of this study emphasize the importance of utilizing a range of hydrocarbon parameters when assessing source and thermal maturity in sedimentary basins.

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جيوكيمياء عضوية جزئية لعينات زيت نطف من حوضي شوشان وأبو الغراديق في شمال الصحراء الغربية بمصر

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المستخلص. شملت هذه الدراسة عدد ثمانية عينات زيت نطف تم تجميعها من ثمانية حقول في نطاقي حوضي شوشان وأبو الغراديق، تم تحليلها جيوكيميائيا من أجل معرفة نشأتها ودرجة نضوجها وبيئة ترسيبها.

وتم تقطير عينات زيت النطف إلى مكوناتها الأليفاتية والأروماتية والثقيلة، باستخدام جهاز السائل الكروماتوجرافي ذي الضغط المتوسط، وتم تحليل كل من المكونات الأليفاتية والأروماتية باستخدام تقنيتي التحليل الكروماتوجرافي الغازي والتحليل الكروماتوجرافي الغازي المتصل بمقياس الطيف الكتلي.

وقسمت عينات زيت النطف محل الدراسة إلى عائلتي أبو الغراديق وشوشان، فبينما يتفق بترول العائلتين في تقارب الكثافة (API) وقلة نسبة الكبريت، نجد تميز زيت بترول شوشان بصفات شمعية لا تتواجد في زيت أبو الغراديق.

باستخدام دلالة البصمة لعينات زيت النطف، أفاد البحث بأن زيت أبو الغراديق أكثر نضوجاً حرارياً من زيت شوشان. وأفادت الدراسة أيضاً إلى أن زيت أبو الغراديق قد نشأ من مواد عضوية بحرية في سحنات غنية بالطفلة، وفي بيئة ترسيبية قليلة الأوكسجين، بينما نشأ زيت شوشان من مواد عضوية نباتية في سحنات تتصف بوجود الفحم، وفي بيئة ترسيبية غنية بالأوكسجين.