Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 10, Page 3433-3447

http://www.jmaterenvironsci.com/

Characterization Based on Biomarkers Distribution of Some Crude Oils in Gulf of Suez Area – Egypt

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Received 12 Jun 2016,
Revised 12 Dec 2016,
Accepted 15 Dec 2016

Keywords

- ✓ isoprenoids,
- ✓ heavy metals,
- ✓ GC-MS,
- ✓ hopanes,
- ✓ steranes,
- ✓ thermal maturity.

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Abstract

Eight crude oil samples from the Gulf of Suez oil fields were analyzed by using GC-MS. Biomarker characteristics are used to provide information on source organic matter input, depositional environment and maturation level. Data includes normal alkanes and a cyclic isoprenoids distribution, tarpanes and steranes aliphatic biomarkers. The biomarkers are characterized by a dominance of low to medium molecular weight n-alkane compounds with significant waxy n-alkane (nC25-nC35), low pr/ph ratio (<1.0), high proportions of hopanes relative to tricyclic terpanes, Ts/Tm ratio of the oil samples ranged from (0.25 to 1.00) this together with the high sulphur contents, high values of C35/C34 and high C27 regular steranes. The biomarker parameters reflecting that the oils were derived from carbonate source rocks contain aquatic (algal and bacterial) organic matter with minor terrigenous organic matter contribution that were deposited in marine environments under reducing conditions and generated at different maturities.

1. Introduction

Biomarkers found in crude oils, rocks, and sediments show little or no changes in structures from their parent organic molecules or so-called biogenic precursors (e.g., hopanoids, sterols, and steroids) in living organisms [1]. Thus the identification and quantification of biomarker compounds have obtained great importance for recognition and classification of crude oil source [2,3] and then used as tracers for geological and environmental processes [4].

These unique characteristics of biomarkers provide chemical fingerprint about the origin, formation and environment of a geological sample [5]. Among the various types of biomarkers, triterpanes and steranes are the best target molecules for identification and quantification. The biomarker investigation of crude oil can give more detailed information needed to answer exploration questions on source input and conditions of the depositional environment of organic matter [6].

The Gulf of Suez occupies the northern end of the Red Sea rift [7]. It is a northwest-southeast fault-forming basin that provided adequate conditions for hydrocarbon generation, maturation and entrapment [8]. 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 32 % of the overall daily oil production in Egypt [9].

In the present study bulk geochemical characteristics and saturate biomarkers distributions have been determined for a collection of crude oils from the three provinces (northern, central and southern) of Gulf of Suez.

2. Experimental

Eight crude oil samples from a number of wells in the Gulf of Suez area were chosen for this study. The geographic locations of the selected oil fields are shown in Fig. (1). The American Petroleum Institute gravity or simply API gravity was determined according to ASTM D 1250.

The sulfur content of the collected crude oil samples were achieved using X-Ray Sulfur Meter (Model RX-500S, Tanaka) according to ASTM D 4294 and IP 336 methods.

Nickel and vanadium contents of the whole oil were detected by adding specific volume of sulfuric acid (4 ml) to 2 gm of crude oil samples and placed in a microwave ash (Milestone-Pyro) for 3 hr at 750^{o}C according to ASTM D 874. The residue was weighed and then dissolved in 50 ml diluted nitric acid 50%. These solutions were then taken and aspirated into flame atomic absorption spectrometer (ZEEnit, Analytikjena Co, Germany).

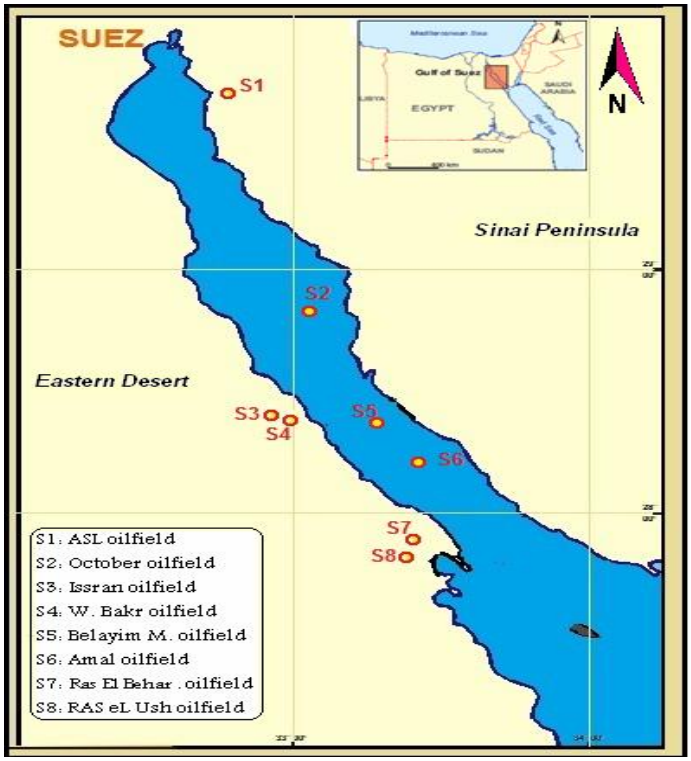


Figure 1: Location map of the studied oilfield in the Gulf of Suez, Egypt, complied after EGPC (1996) [10]

A specific volume of crude oil samples were distilled up to 200^{o}C. Asphaltenes were precipitated from the residues (above 200 ^{o}C) by n-heptane. Five grams of residue (above 200 ^{o}C) were weighed and dissolved in 30 fold n-heptane and then allowed to reflux for one hour. The solution is then stand to settle down overnight in dark place. This solution was filtered off. The filtrate included maltene was dried to constant weight in vacuum oven. The precipitate including asphaltene was sohxlet extracted with benzene and then dried till constant weight. The deasphalted crude oil samples were separated into saturated hydrocarbon, aromatic hydrocarbon and polar compound (NSO) using alumina: silica (1:1) column chromatography. The column was wetted with n-hexane, and then 0.6 g of the maltenes dissolved in the least amount of n-hexane was charged onto the column. Saturates, aromatics and resins were eluted by n-hexane, toluene, and methanol-methylene chloride mixture (1:1) respectively [11]. These fractions were identified by refractometer. The solvents were distilled off and the separated saturates, aromatics and resins were dried in vacuum oven to constant weight.

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

The saturated hydrocarbon fractions were analyzed for biomarker traces using PerkinElmer Claruss 500 GC-MS apparatus. Samples were injected onto a fused silica capillary column (30 m × 0.32 mm. id., film thickness

0.25μm) coated with HP-5 MS. Helium was the carrier gas with flow rate of 1.5 ml/min. and temperature was programmed from 80°C to 310°C at rate of 3°C/min. The mass spectrometer was operated at ionization energy of 70 ev. With scan time of 1 scan/second. The transfer line and ion source temperature were 250°C and 280°C respectively. The identification of biomarkers are obtained through, saturated hydrocarbon ratios. The relative sterane and triterpane abundance were calculated using the integrated peak areas for the relevant ion m/z 191 and m/z 217 chromatograms and comparing their retention times and mass spectra with Nist, Willey, Pfligger and MS of Geochemical Petrochemicals and Biomarkers Library for matching the spectrum and identification of biomarker compounds, In addition to the published data [12, 13].

3. **Results and discussion**

3.1. *Non hydrocarbon characteristics*

3.1.1. Bulk properties of crude oils

The bulk crude oil properties and compositions for the studied oils are presented in (Table 1). The API gravity for light, intermediate, heavy, extra heavy and for biodegraded petroleum are >30°, 20-29°, 10-19° and <10° respectively [14]. The crude oils from Gulf of Suez area have a variety of API gravity values in the range of 14.29-39.87 API, classifying the oil as light crude oil (S1, S7, S8), medium (S2, S5, S6) and heavy crude oil (S3, S4), which have API gravities of (14.29, 15.31) as shown in (Table 1). Low API gravity is generally associated with either biodegraded oils or with immature sulfur-rich oil [15]. In contrast, (S1, S2, S5, S6, S7, S8) represent oil samples, which exhibit medium to high oil API gravities between 25.46 and 39.87. These oils have a variety of sulfur contents, ranging from 0.35 to 3.12 Wt% as shown in Table (1) suggesting that they have been generated from carbonate poor source rocks [16].

Table (1): Bulk geochemical properties of crude oil samples from Gulf of Suez

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**
API	39.87	25.69	15.31	14.29	25.46	33.2	35.8	36.57
S (wt%)	0.46	2.45	4.67	4.37	3.12	1.65	0.43	0.35
V (ppm)	32.25	49.33	74.42	52	48.53	37.55	30.25	26.13
Ni (ppm)	16.46	27.23	35.62	30.05	38.69	25.56	15.5	14.98
V/Ni	1.96	1.81	2.09	1.73	1.25	1.47	1.95	1.74
Asphaltene%	0.8	6.36	10.69	11.84	3.55	0.66	0.16	0.72
Sat./Arom	2.51	1.41	1.03	0.97	1.25	2.61	3.46	2.44
Pr/Ph	0.85	0.82	0.52	0.21	0.57	1.07	0.5	0.84
Pr/n-C17	0.92	0.47	0.40	0.34	0.35	0.64	0.99	0.95
Ph/n-C18	1.21	0.61	0.77	0.68	0.59	0.59	1.26	1.21
Waxiness	1.00	1.01	1.23	1.89	1.17	1.24	2.43	1.02
CPI	1.02	0.99	0.89	0.97	1.01	1.02	1.03	1.11
OER	1.02	0.91	0.83	0.96	0.95	1.04	0.97	1.06

3.1.2. Nickel and Vanadium contents

The ratio of transition metals (Vanadium and Nickel) in crude oil is useful in the determination of source rock type, depositional environment and maturation because they remain unchanged irrespective of digenetic and in-reservoir alteration effects. Absolute concentrations of vanadium and nickel can be used to classify and correlate oils, these metals are the major metals in petroleum [17].

The high values of Vanadium and sulfur content obtained in Gulf of Suez samples could be explained according to **Barwise (1990)**[18]**.** He mentioned that under low oxic conditions, sulphate-reducing bacteria generate hydrogen sulphide. High sulphide in the pore waters of anoxic sediments causes nickel ion to precipitate as nickel sulphide, leaving vanadyl ion (VO2+) to complex with the available free porphyrins. In general, oils from marine carbonates or siliciclastics show high concentrations of nickel and vanadium, and high vanadium/nickel ratios (≥1). Oils from lacustrine source rocks show moderate quantities of metals, and low

vanadium/nickel ratios (< 0.5). Oils derived from higher plant organic matter show very low metal contents. The results also indicate that trace metals are sensitive to changes in the source and depositional environment.

The investigated oils have V and Ni content values ranging from 26.13 to 74.42 ppm and from 14.98 to 38.69 ppm respectively, as revealed in (Table 1). The correlation between the total concentration of (V+Ni) and sulfur content is shown in (Fig.2). As indicated from this figure, the studied crude oil samples could be classified into three groups according to maturity, crude oil samples (S1, S7, S8) are highly mature and samples (S2, S5, S6) are more mature than (S3, S4) [19].

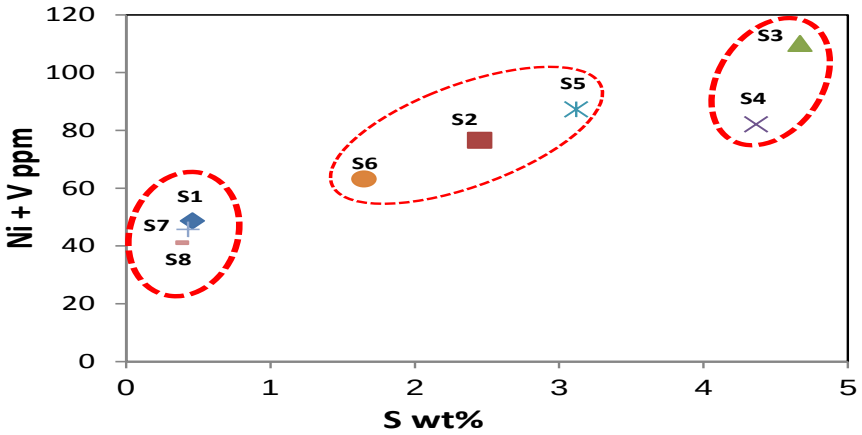


Figure 2: The correlation between the total concentration of (V+Ni) and sulfur

3.2. *Biomarker characteristics*

3.2.1. Normal alkane and isoprenoids

The gas chromatograms of saturated hydrocarbon fractions from the representative oil samples are shown in (Fig 3) and derived parameters are listed in (Table 1). The gas chromatograms of the saturated fraction of oil samples display a full range of C_{13}-C_{40} n-alkane and isoprenoid [pristane (pr) and phytane (ph)]. The n-alkane patterns of the oil samples are dominated by short (n-C_{12} - n-C_{20}) to middle-chain (n-C_{21}-n-C_{25}) n-alkanes with the presence of significant amounts of waxy alkanes (n-$_{C23+}$) thus give moderate values of CPI (0.89–1.11) [20] (Table 1). Data indicate that microbial reworked organic matter in sediments is characterized by low CPI values at low maturation stage as indicated in the oil samples (S3,S4) which have the lowest CPI values 0.89 and 0.97 respectively (Table 1). In these contexts, the crude oils in Gulf of suez area were interpreted to be drived from algae and bacterial organisms, deposited under marin conditions [21]. These are supported by the degree of waxiness Σ (n-C_{21}- n-C_{31})/Σ (n-C_{15}- n-C_{20}) [22]. The calculated ratio of Σ (n-C_{21}- n-C_{31})/Σ (n-C_{15}- n-C_{20}) for the oil samples ranges between 1.0- 2.43 (Table 1) suggesting mainly contain algal and / or bacterial organic matter with lower terigenous organic matter input [23].

The relative amounts of pristane and phytane in a crude oil, expressed as pr/ph ratio, have been used as an indicator of source depositional environment or reflect the relationship between contributing organisms and the chemistry of the environment. It is generally accepted that very low values (pr/ph <1.0) indicate anoxic conditions commonly associated with a stratified water column or hypersaline environments, whereas high values (pr/ph >3.0) are related to terrestrial organic matter input under oxidizing conditions. The pr/ph ratios of the investigated oil samples range from 0.21-1.07 (Table 1), suggesting two oil types were derived from different source rock. The type I (S1, S2, S3, S4, S5, S7 and S8) have pr/ph ratio values <1.0, whereas type II crude oil sample (S6) has moderately pr/ph ratio 1.07. The pr/ph ratio indicate that the type I oils are considered to be derived from source rocks containing mainly marine-algal-derived organic matter which was deposited in more reducing environment compared to oil sample S6 that was deposited under (sub-oxic) conditions [24]. Pristane/n-C_{17} and phytane /n-C_{18} ratios are in the range of 0.34-0.99 and 0.59-1.26, respectively. The cross plot pr/n-C_{17} versus ph/n-C_{18} suggests marine organic matter preserved under anoxic conditions, whereas the oil sample S6 reflect mixed organic matter deposited under (sub-oxic) conditions as shown in (Fig. 4) [25, 26].

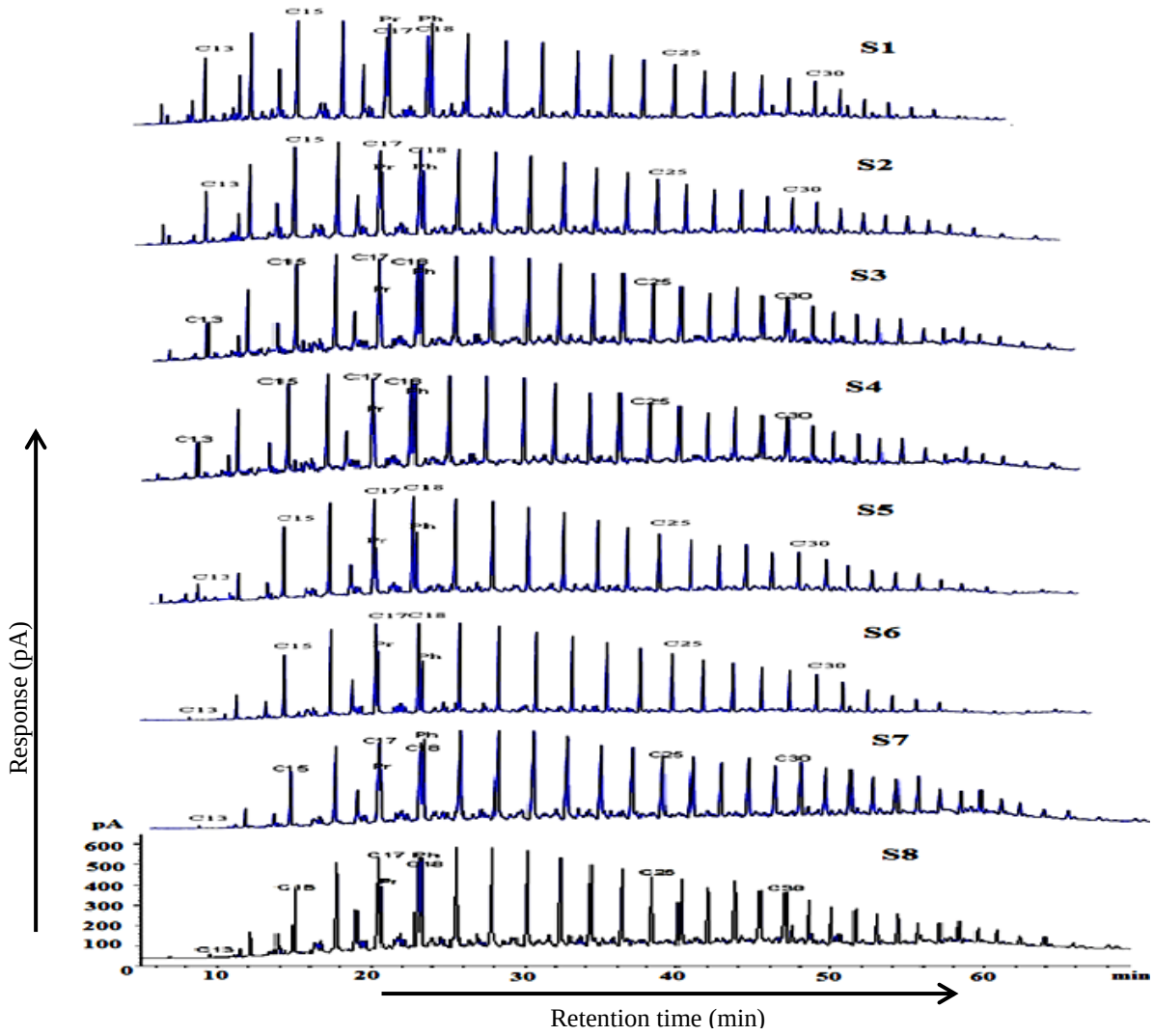


Figure 3: Gas Chromatograms of the saturate fractions of Gulf of Suez crude oil samples

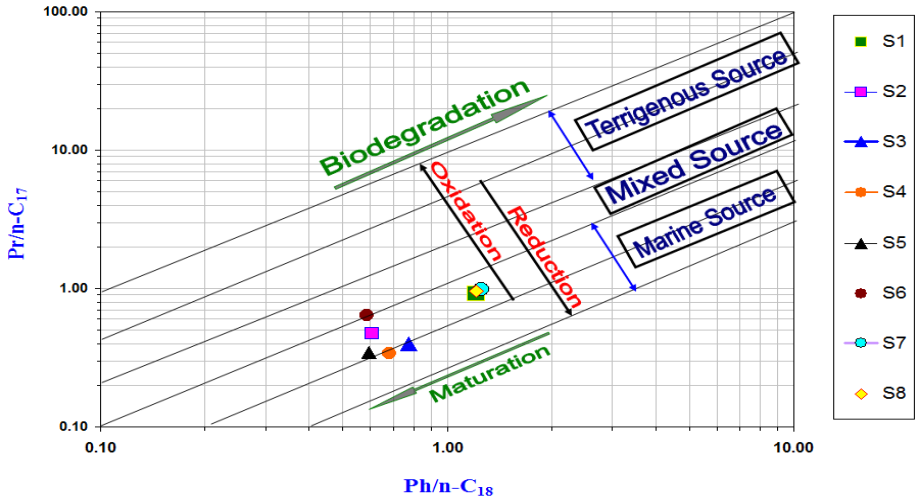
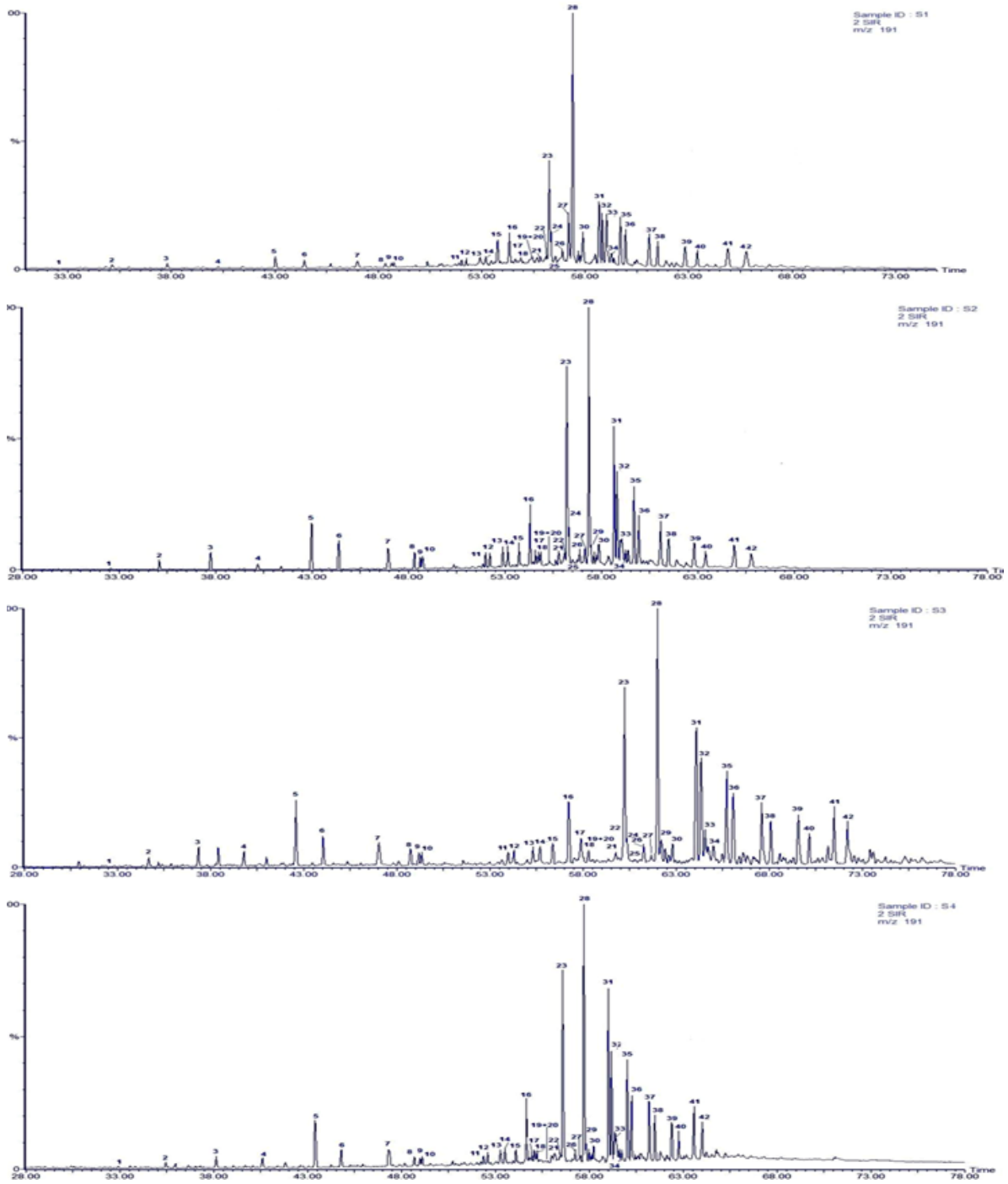


Figure 4: Pr/n-C17 vs Ph/C18 for samples from Gulf

3.2.2. Terpanes biomarkers

The distributions of terpanes are commonly studied using GC-MS by monitoring the ions m/z 191 as shown in (Fig. 5). The peak assignments depicted in (Table 2) and their parameters are given in (Table 3). Biomarkers in oils are widely investigated to provide reliable information on depositional paleoenvironments, organic matter input and thermal maturity. The m/z 191 mass fragmentograms of the saturated hydrocarbon fractions of all the oil samples analyzed show high proportions of hopanes relative to tricyclic terpanes as shown in (Fig. 5).



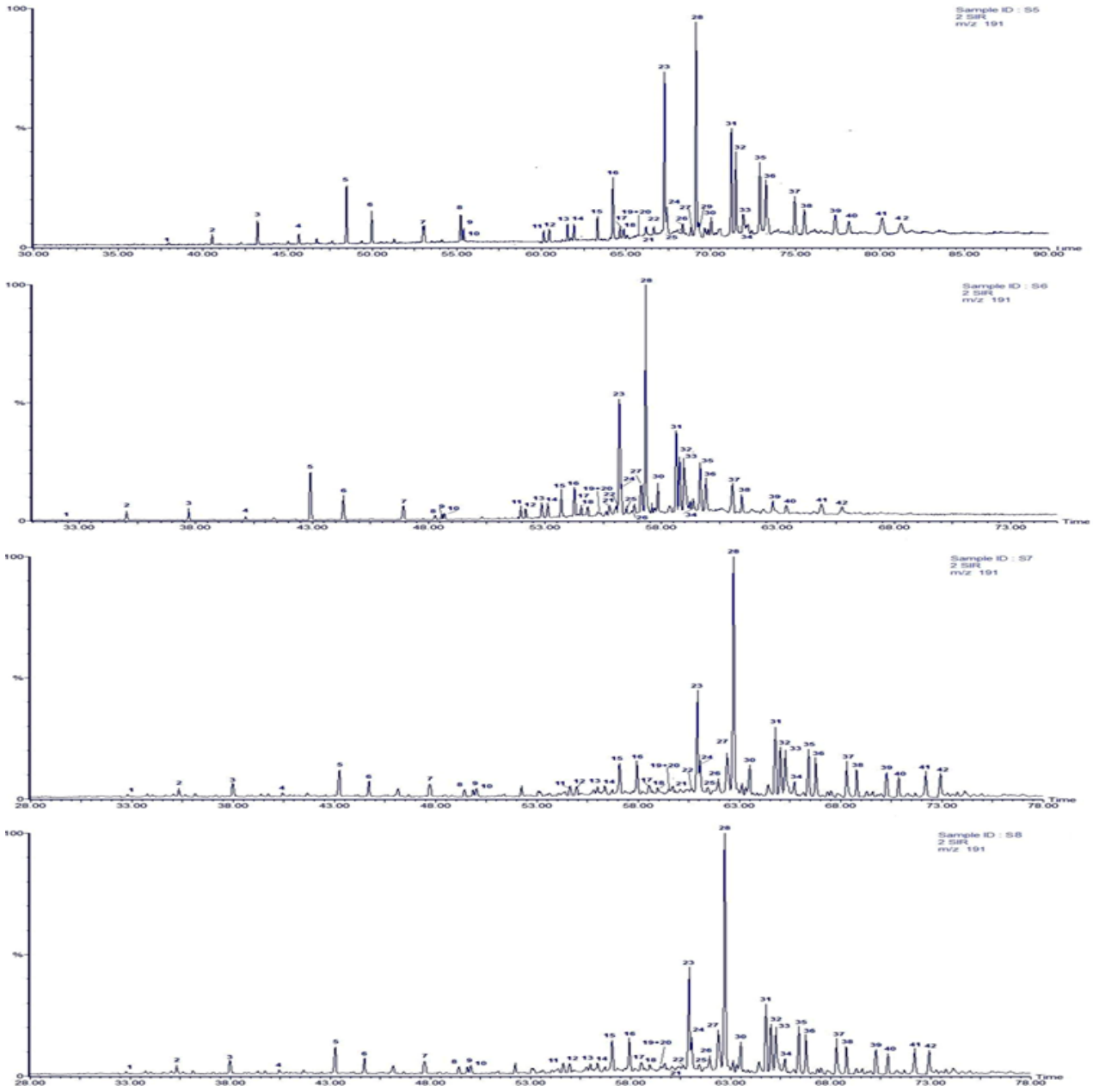


Figure 5: m/z 191 for Gulf of Suez samples

The relative abundance of C_{29} norhopane is generally less than that of C_{30} hopane in all the studied oil samples, with C29/C3017α (H) hopane ratios in the range of 0.29–0.80. Diahopane is detected in the oil samples with very low Dihopane/hopane ratios (0.00-0.03) this is consistent with their marine origin. The Ts/Tm ratios of the oil samples (S1-S8) from southern-central and northern of the Gulf of Suez area ranged from (0.25 to 1.00) (Table 3). This low value of the Ts/Tm ratio and together with the high sulfur content indicate that the oil could originate from a marine carbonate/evaporite depositional environment [13]. Mello et al., 1990 showed that Ts/Tm values below 1 imply a lacustrine/saline, marine evaporitic or marine carbonate depositional environment, whereas values above 1 indicate lacucstrine fresh-water or marine deltaic environment [27]. The abundant gammacerane detected in samples S1- S8 as shown in Table (3) is an additional indicator of carbonate or evaporite source rocks [16]. The extended hopanes or homohopanes (C_{31}-C_{35}) distribution has been used to evaluate redox conditions based on a homohopanes index. High C_{35} homohopanes are believed to be indicated as highly reducing marine conditions, whereas low C_{35} homohopane concentrations are typically observed in oxidizing water conditions.

Samples having C_{35}/C_{34} value range (1.08-1.49) (Table 3), suggesting a higher contribution of bacterial biomass to the sediments, and reflecting a highly saline reducing carbonate environment of deposition with no available free oxygen [28] and this is consistent with the observed values > 0.8 represent marine carbonate evaporates postulated by [21]. Further, in support is a relatively high homohopane index for the studied oil samples in the range (0.102-0.176) (Table 3). The highest homohopane index in samples S1and S8 while the lowest one in S6 which can be used to evaluate the strength of the reducing conditions.

In contrast to hopanes, moretanes seem to be abundant in organic materials of terrestrial origin [29]. The lower abundance of moretane relative to hopane may reflect a weak terrigenous input. The ratio of 17β(H), 21α(H) -mortane to corresponding 17α(H), 21β(H)-hopane (βα- mortane/αβ-hopane) rise from 0.075 to 0.159 (Table 3). These relatively low ratios reflect an open sea with minimal contributions from terrestrial material.

Table (2): Main terpanes and hopanes identified in the fragmentograms

1	TR19	C_{19} Tricyclic Terpane	22	NOR25H	C_{29}-17α(H), 21β(H)-25 –dinorhopane
2	TR20	C_{20} Tricyclic Terpane	23	H29	17α(H),21β(H)-30-norhopane
3	TR21	C_{21} Tricyclic Terpane	24	C29Ts	C_{29}-18α(H) norneohopane (29Ts)
4	TR22	C_{22} Tricyclic Terpane	25	DH30	C_{30}-15 α-Methyl-17α(H)- 27 norhopane (diahopne)
5	TR23	C_{23}Tricyclic Terpane	26	M29	C_{29}-17α(H), 21α(H)-30- norhopane (normoretane)
6	TR24	C_{24} Tricyclic Terpane	27	OL	18α(H) and 18β(H)-oleanane
7	TR25A + TR25B	C_{25} Tricyclic Terpan (R+S)	28	H30	C_{30}-17α(H), 21β(H)-hopane
8	TET24	C_{24} Tetracyclic Terpane	29	NOR30H	17α(H)-30-nor-29-homohopane
9	TR26A	C_{26}Tricyclic Terpane (22R)	30	M30	C_{30}-17 β (H), 21α(H)-moretane
10	TR26B	C_{26}Tricyclic Terpane (22S)	31	H31S	C_{31}-17α(H), 21β(H)-30 homohopne (22S)
11	TR28A	C_{28}Tricyclic Terpane (22R)	32	H31R	C_{31}-17α(H), 21β(H)-30 homohopne (22R)
12	TR28B	C_{28}Tricyclic Terpane (22S)	33	GAM	C_{30} Gammacerane
13	TR29A	C_{29}Tricyclic Terpane (22R)	34		C_{31}-17β(H), 21α(H)-30 homohopne
14	TR29B	C_{29}Tricyclic Terpane (22S)	35	H32S	C_{32}-17α(H), 21β(H)-30 bishomohopne (22S)
15	Ts	C_{27} 18α(H)-22, 29, 30-trisnorneohopane (Ts)	36	H32R	C_{32}-17α(H), 21β(H)-30 bishomohopne (22R)
16	Tm	C_{27} 17α(H)-22, 29, 30-trisnorneohopane (Tm)	37	H33S	C_{33}-17α(H), 21β(H)-30 trishomohopne (22S)
17	TR30A	C_{30}Tricyclic Terpane (22R)	38	H33R	C_{33}-17α(H), 21β(H)-30 trishomohopne (22R)
18	TR30B	C_{30}Tricyclic Terpane (22S)	39	H34S	C_{34}-17α(H), 21β(H)-30 tetrakishomohopne (22S)
19	TR31A	C_{31}Tricyclic Terpane (22R)	40	H34R	C_{34}-17α(H), 21β(H)-30 tetrakishomohopne (22R)
20	TR31B	C_{31}Tricyclic Terpane (22S)	41	H35S	C_{35}-17α(H), 21β(H)-30 pentakishomohopne (22S)
21	H28	C_{28}-17α(H), 21β(H)-28,30-dinorhopane	42	H35R	C_{35}-17α(H), 21β(H)-30 pentakishomohopne (22R)

Tricyclic terpanes are usually common in marine environment and are believed to have their origin from algae and bacteria [30]. Tricyclic terpane also may represent a marker for highly saline depositional environments [31] which are present in oils in different concentrations relative to pentacyclic terpanes.

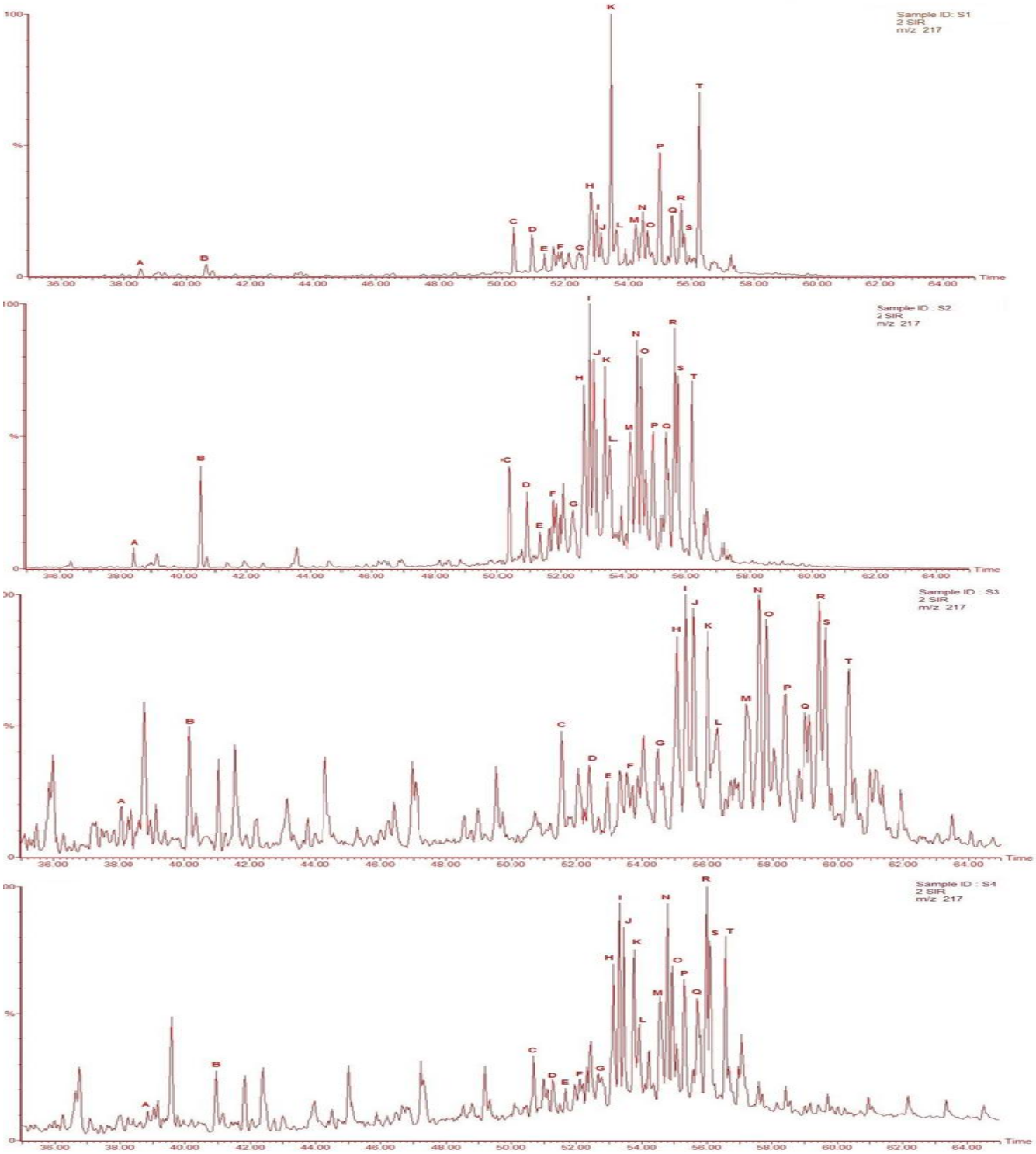
Short-chain tricyclic terpanes are believed to be related to bacterial organic matter [32]. The ratios of various tricyclic terpanes give some insight into the source organic material [33]. The oil samples from Gulf of Suez area contain significant amount, of tricyclic terpanes, as indicated by saturated biomarker data (Table 3 and Fig 5), including tricyclic terpane distribution with the predominance of C_{23} tricyclic terpane relative to C_{19} tricyclic terpane C_{19}/C_{23} tricyclic terpane ratios (0.011-0.189). The oil samples have relatively high tricyclic terpenes compared to tetracyclic terpanes and low values of C_{24} tetracyclic terpane to C_{26} tricyclic terpane ratio ranges between 0.389 and 0.787 (Table 3). This is consistent with high contribution from marine organic matter. The relative amount of C_{26} tricyclic terpane to C_{25} tricyclic terpane can be used to differentiate marine from lacustrine source rock [34]. In almost all of the samples from Gulf of Suez area the C_{26} tricyclic terpane is less abundant than the C_{25} tricyclic terpane, C_{25}/C_{26} ratios < 1, the oils have high C_{23} tricyclic terpane/C_{24} tetracyclic terpane ratios (Table 3). This is indicating marine environment and believed to have their origin from algae and bacteria except sample S6 which have a lower value of C_{23} tricyclic terpane /C_{24} tetracyclic terpane ratio, this reflect mixed organic matter input as revealed in Fig. 3.

Table (3): Relation of hopanes and steranes of crude oil samples from Gulf of Suez

		S1	S2	S3	S4	S5	S6	S7	S8
C_{29}/C_{30} 17α (H) hopane		0.299	0.604	0.801	0.609	0.639	0.418	0.466	0.437
Diahopane / Hopane		0.03	0.021	0.008	0.00	0.012	0.025	0.023	0.034
Ts / Tm		0.917	0.494	0.372	0.255	0.393	0.753	0.875	1.005
homohopane index		0.176	0.128	0.149	0.15	0.132	0.102	0.138	0.171
C_{19} / C_{23} Tricyclic terpane		0.073	0.023	0.016	0.044	0.056	0.189	0.011	0.12
C_{25} / C_{26} Tricyclic terpane		1.188	1.427	1.661	1.948	2.808	1.724	1.634	1.105
C_{23} tri/ C_{24} tet cyclic terpane		1.659	1.917	2.456	2.717	1.794	0.052	2.652	1.824
C_{24} Tetracyclic/C_{26} Tricyclic		0.516	0.787	0.776	0.642	0.538	0.389	0.446	0.438
C_{35}/C_{34}		1.289	1.183	1.183	1.499	1.263	1.081	1.086	1.315
Moretane/Hopane		0.132	0.114	0.092	0.075	0.086	0.111	0.159	0.14
R. (steranes)	**C_{27} %**	43.32	42.16	43.34	36.89	43.19	40.67	46.7	43.21
	C_{28} %	24.22	18.58	19.81	20.28	24.09	20.38	20.94	25.27
	C_{29} %	32.46	39.26	36.85	42.82	32.72	38.95	32.36	31.52
Diasterane/sterane		0.252	0.429	0.479	0.308	0.249	0.321	0.204	0.315
Gammcerane/Hopane		0.309	0.197	0.152	0.22	0.147	0.375	0.33	0.22
Hopanes/Steranes		0.79	1.78	4.3	2.12	2.13	1.47	0.74	0.62
Olenane/hopane		0.27	0.072	0.045	0.039	0.047	0.13	0.239	0.224
20S/(20S+20R)C_{29} sterane		0.275	0.418	0.395	0.396	0.418	0.331	0.305	0.293
C_{32} 22S/(22S+22R) hopane		0.546	0.582	0.559	0.582	0.54	0.617	0.559	0.545

3.2.3. Steranes

The distributions of steranes are commonly studied using GC-MS by monitoring the ions m/z 217 as shown in (Fig. 6). The peak assignments depicted in (Table 4) and their parameters are given in (Table 3). The steranes are important biomarkers, which are derived from sterols that are found in higher plant and algae but rare or absent in prokaryotic organisms. The steranes composition could be used to give indication of source differences [35]. Huang and Meinschein 1979 proposed that a dominance of C_{27} steranes meinly derive from algae, while the C_{29} sterols are more typically associated with land plant, they also proposed that microalgae or cyanobacteria can also be important source of C29 sterol [36].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m/z 217
Time

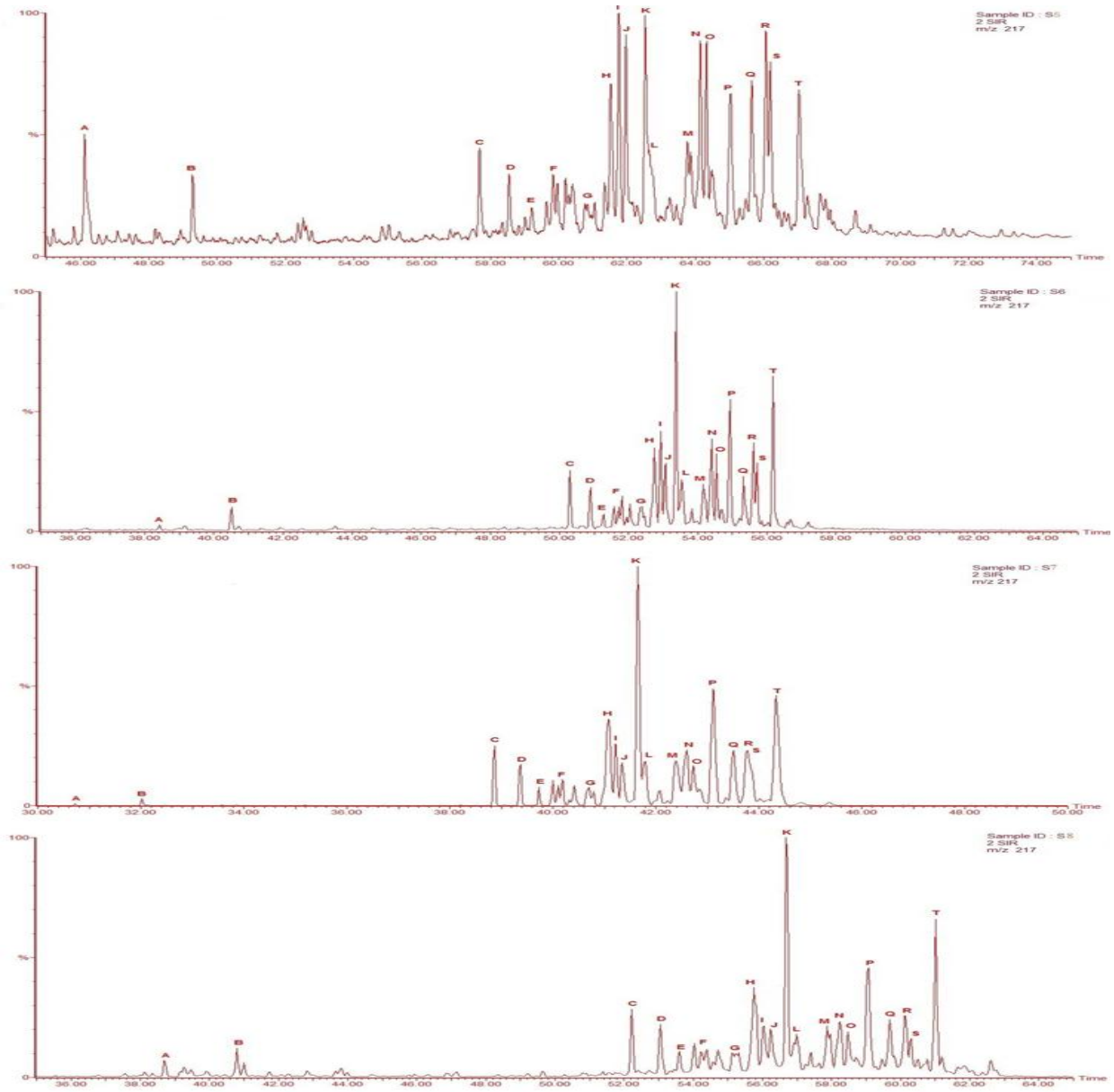

Figure 6: m/z 217 for Gulf of Suez samples

As indicated by the relative distribution of C_{27}-C_{29} regular steranes in the Gulf of Sues crude oil samples (Table 4). The high abundance of C_{27} (36.89-46.70%) regular steranes compared with C_{29} (31.52-42.82%) and C_{28}(18.58-25.27%) steranes, as shown in a ternary diagram (Fig. 7) indicates a carbonate marine source rock with high contribution of aquatic planktonic bacterial organic matter [25]. Hopane /Sterane ratios ranged from 0.62 to 4.30. Accordingly, we can classify our Samples to two types S1, S7 and S8 less than unity 0.79, 0.74 and 0.62 respectively represent a marker for highly saline marine reducing depositional environments than samples S2, S3, S4, S5 and S6 more than unity 1.78, 4.30, 2.12, 2.13 and 1.47 respectively as shown in Table 3.

Diasterane / sterane ratios are commonly used to distinguish carbonate from clay-rich source rocks. Low disterane / sterane ratios designate anoxic clay-poor source rocks e.g. carbonates while high values reveal oxic and clay-rich environment of organic matter like marine and deltaic sediments (Peters et al., 2005). The disterane / sterane ratio for the crude oil samples ranges from 0.20 to 0.47 (Table 3 and Fig. 8) the low values for disterane / sterane ratios indicate that these crude oils were generated by source rocks lean in clay minerals [37].

Table (4): Main steranes, diasteranes and steroids identified in the fragmentograms

A	S21	C21 sterane
B	S22	C22 sterane
C	DIA27S	C27 13β(H) 17α(H) Diacholestane (20S)
D	DIA27R	C27 13β(H) 17α(H) Diacholestane (20R)
E	DIA27S2	C27 13α(H) 17β(H) Diacholestane (20R)
F	DIA28SA	C28 βαDiacholestane (20S)
F	DIA28SB	
G	DIA28RA	C28 βαDiacholestane (20R)
G	DIA28RB	
H	C27S	C27 5α(H) 14α(H) 17α(H) cholestane (20S)
I	C27βββR	C27 5α(H) 14β(H) 17β(H) cholestane (20R)
J	C27βββS	C27 5α(H) 14β(H) 17β(H) cholestane (20S)
K	C27R	C27 5α(H) 14α(H) 17α(H) cholestane (20R)
L	DIA29R	C29 24Ethyl, 13β(H) 17α(H) Diacholestane (20R)
M	C28S	C28 5α(H) 14α(H) 17α(H) ergostane (20S)
N	C28βββR	C28 5α(H) 14β(H) 17β(H) cholestane (20R)
O	C28βββS	C28 5α(H) 14β(H) 17β(H) cholestane (20S)
P	C28R	C28 5α(H) 14α(H) 17α(H) ergostane (20R)
Q	C29S	C29 5α(H) 14α(H) 17α(H) stigmastane (20S)
R	C29βββR	C29 5α(H) 14β(H) 17β(H) stigmastane (20R)
S	C29βββS	C29 5α(H) 14β(H) 17β(H) stigmastane (20S)
T	C29R	C29 5α(H) 14α(H) 17α(H) stigmastane (20R)

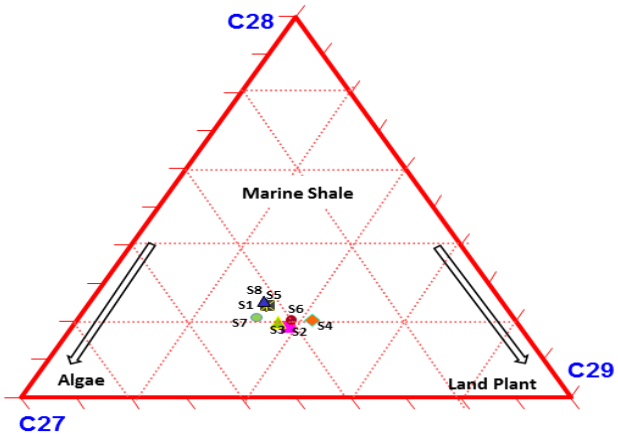

Figure 7: Ternary diagram of regular steranes (C27–C29), which shows the relationship between sterane composition and source organic matter input

3.2.3. Thermal maturity of crude oils

The components in oil, NSO compounds, Asphaltenes, saturated and aromatic hydrocarbons undergo increased cracking during thermal maturation. A variety of oil characteristics have been used to evaluate the level of thermal maturity of the investigated oils; these include biomarker and non-biomarker parameters. The biomarker and non-biomarker parameters are listed in (Tables 1, 3 and 5). From gas chromatography-mass spectrometry (GC-MS), biomarker maturation parameters such as Ts/(Ts+Tm)ratio C_{32} 22S/(22S+22R) homohopane, mortane/hopane and 20S(20S+20R) and β β/(β β+ α α) C_{29} sterane ratios were used as maturity indicators [38].

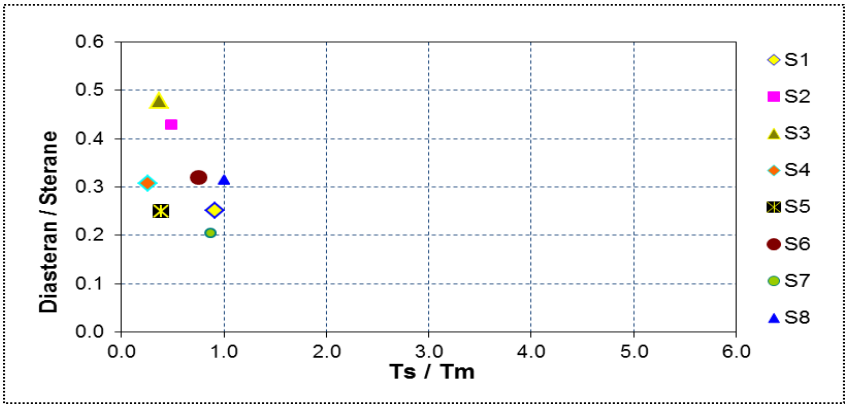

Figure 8: The relationship between the Diasterane/sterane ratio and Ts/Tm ratio

The Ts/(Tm+Ts) ratio is controlled to some degree by lithology oxicity of the depositional environment; the ratio is also maturity dependent. Ts is more stable to thermal maturation than Tm. The Ts/(Ts+Tm) ratios increase with increasing maturity as indicated in Figure (9), which shows the Ts (Ts+Tm) ratios with C_{29} sterane, 20S/(20S+20R) ratio at C_{20} in the C_{29} 5 α (H), 14 α (H), 17 α (H) sterane is a maturity indicator, this ratio rises from 0 to about 0.5 (0.52-0.55= equilibrium) with increasing maturity, this change in the ratio may be due to isomerization and or the greater stability of the 20S epimer compared to the 20R [39]. This ratio reaches the equilibrium value at or before the peak of the oil-generative window, whereas the Ts / (Ts+Tm) ratio reaches the endpoint value around the end of the oil-generative window [25]. Therefore, after the peak of the oil- generative window, the 20S/ (20S+20R) ratio remains constant at the equilibrium value and only Ts/(Ts+Tm) ratio increases with increasing maturity.

The three crude oil samples S1, S7 and S8 have highest Ts/Ts+Tm value, whereas, the oil samples S3, S4 has lower Ts/Ts+Tm ratio as shown in Fig. (9). This may be due to differences in the source organic matter or depositional conditions [40].

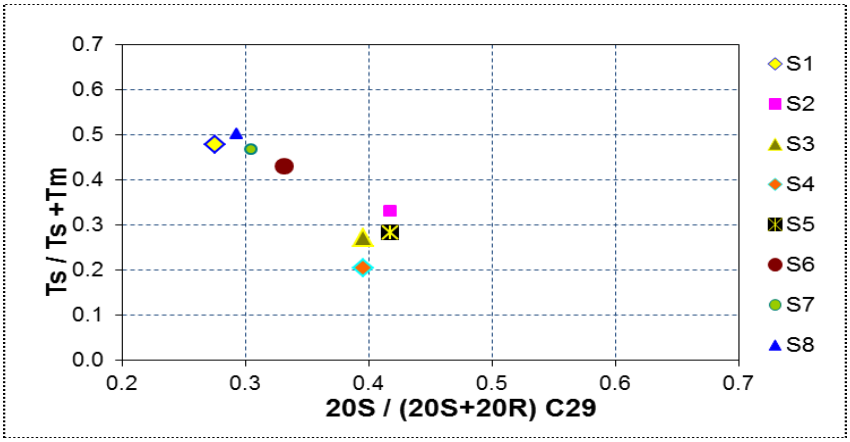

Figure 9: The relation between Ts / Ts +Tm and C_{29}20S / (20S +20R)

A widely used biomarker maturity parameter is the C_{32}22S / (22S+22R) hopane ratio. The value increases from 0 to about 0.6 at equilibrium during maturation. Values in the range 0.50-0.54 have entered oil generation. Most of the oil samples have C_{32} 22S/(22S+22R) values in the range of 0.54 - 0.617, suggesting that they have reached equilibrium and have a high maturity (Fig. 10).

Although, oleanane is specific to the higher plant input of Cretaceous or younger age, the oleanane/hopane ratio is also maturity dependent. The ratios increase from low values in immature oils to a maximum at the top of the oil generative window. The studied oil samples no. (S1, S7, S8) show the highest oleanane/hopane ratios 0.27, 0.23 and 0.22 respectively as shown in Table (3), these samples also have the highest diahopane/C30 hopane ratios. Molecular mechanic calculations, indicate that 17 α (H) - diahopane is more stable than the 17 α (H) -

hopane. Moreover, these oils have the highest Ts/ (Ts+Tm) ratios in all oil samples (Fig. 9). These results suggest that the oils no. S1, S7 and S8 are the most thermally mature oils in this study. In contrast the oil samples no. S3 and S4 have the lowest ratios of oleanane /hopane, diahopane /C30 hopane and Ts/Ts+Tm values as indicated in (Table 3). These data suggest that the two oils (S3, S4) were the least mature oils as indicated from API gravity (Table 1).

Non-biomarker parameters such as API gravity, sulfur and metal contents have also been used to evaluate the level of thermal maturity of the investigated oils. The concentrations of Ni and V varied strongly with the maturity of oils, and high maturity crude oils contained only small amounts of Ni and V elements content [18]. This is consistent with the observed low Ni and V content of samples (S1, S7 and S8) compared to the oil samples S3 and S4 (Table 1).

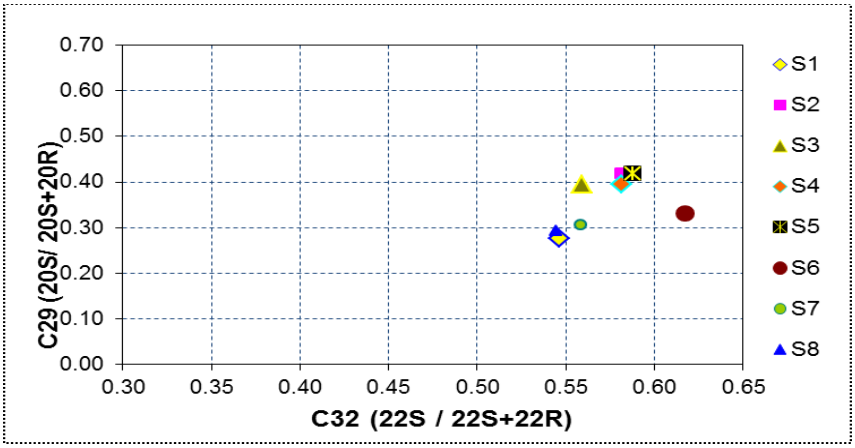

Figure 10: The relation between C_{29} (20S/ 20S+20R) and C_{32} (22S / 22S+22R)

Conclusion

Geochemical characterization based on biomarker components was used to clearly characterize the crude oils in certain oil fields in the Gulf of Suez area. The chromatograms indicate that the aliphatic hydrocarbons are dominated by n-alkanes, C_{13}–C_{40}, while branched and cyclic alkanes are less important constituents. The presence of n-alkanes as the most abundant constituents in series which extends to C_{40} is indicative of no or low levels of biodegradation. The differences in the distribution patterns of n-alkanes suggest that the investigated oils are derived from different types of organic matter. The n-alkane distributions of crude samples (S1, S2 and S5) from the Gulf of Suez are typical of marine organic matter from algae and/or bacteria. This is evident from the unimodal hydrocarbon distribution with strong predominance of n-alkanes in the C_{14}–C_{18} range.

The concentrations of Ni and V varied strongly with the maturity of oils, and high maturity crude oils contained only small amounts of Ni and V elements content. This is consistent with the observed low Ni and V content of samples (S1, S7 and S8) compared to the oil samples S3 and S4. Furthermore, the biomarker parameters (hopanes/streans), classify the samples to two types S1, S7 and S8 less than unity 0.79, 0.74 and 0.62, respectively, represent a marker for highly saline marine reducing depositional environments than samples S2, S3, S4, S5 and S6 more than unity 1.78, 4.30, 2.12, 2.13 and 1.47. Most of the oil samples have C_{32} 22S/(22S + 22R) values in the range of 0.54 - 0.61, suggesting that they have reached equilibrium and have high maturity. These results suggest that the oils no. S1, S7 and S8 are the most thermally mature oils due to their having the highest Ts/(Ts+Tm). In contrast the oil samples no. S3 and S4 have the lowest ratios of oleanane /hopane, diahopane /C_{30} hopane and Ts/Ts+Tm values, suggesting that the two oils (S3, S4) were the least mature oils as indicated from API gravity.

Acknowledgments-The authors are pleased to acknowledge the financial support of the Science &Technology Development Fund in Egypt (STDF) for funding this project(Grand number:4822) .

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