



ISSN: 0975-833X

RESEARCH ARTICLE

BULK GEOCHEMICAL CHARACTERISTICS OF CRUDE OILS FROM GULF OF SUEZ, EGYPT

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ARTICLE INFO

Article History:

Received 16th June, 2015

Received in revised form

28th July, 2015

Accepted 11th August, 2015

Published online 30th September, 2015

Key words:

Biomarkers, Suez Gulf,
Depositional environment,
GC-MS, Pristane, Phytane,

ABSTRACT

Bulk geochemical characteristics include, API gravity, sulfur content, metal contents (V and Ni), bulk composition (saturate, aromatic, polar NSO and asphaltene), normal alkanes and isoprenoids (detected from gas chromatography) were determined for the crude oil samples collected from northern, central and southern province of Gulf of Suez region. These characteristics are used to provide information about source organic matter input, depositional environment and maturation level. The obtained data indicate that these oils were derived from carbonate source rock contain aquatic (algal and bacterial) organic matter with minor terrigenous organic matter contribution that were deposited in marine environments under high reducing conditions and generated at different maturities.

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Citation: El-Sabagh, S. M., El-Naggar, A. Y., El Nady, M. M., Badr, I. H. A., Rashad, A. M., Ebiad M. A. and Abdullah, E. S., 2015. "Bulk Geochemical Characteristics of Crude Oils from Gulf of Suez, Egypt", *International Journal of Current Research*, 7, (9), 20574-20580.

INTRODUCTION

In the Exploration field of study, it is important to understand the hydrocarbon systems of the basin being explored. Defining and evaluating the successful exploration depends on understanding the type and quality of crude oils, their correlation, degree of thermal maturity and subsequent alteration. Detailed geochemical analyses of the crude oils also help in understanding the characteristics of the source rocks from which these oils were generated. The contribution has implication for the oil characterization using different parameters which have been used for this purpose (Mohamed et al., 2015). Most of these parameters are based on the analyses of American Petroleum Institute "API" gravity and sulfur compounds for the crude oil as well as saturated and aromatics hydrocarbons, pristane and phytane ratio, isoprenoids, n-alkanes and the biological markers distributions as steranes and terpanes in the crude oils (Walples, 1991). These parameters are used for comparison of oils to detect genetic relationships, depositional environments and thermal maturation. They are classified into bulk parameters including the API gravity, saturate content, concentration of the main types of hydrocarbon and asphaltene content and specific

parameters including n-alkanes and isoprenoids distribution as well as biological markers obtained by gas chromatography analysis (Walples, 1991). This present study aims to characterize crude oil samples from Gulf of Suez in terms of their bulk geochemical parameters.

MATERIALS AND METHODS

Eight crude oil samples from a number of producing 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). Physicochemical characterization of the studied oil samples such as density IP 190, API gravity ASTM D 1250. Sulfur content by X-Ray Sulfur Meter (Model RX-500S, Tanaka) according to ASTM D 4294, nickel and vanadium contents of the whole oil using microwave ash (Milestone-Pyro) for digestion then aspirated into flame atomic absorption spectrometer (ZEEnit, Analytikjena Co, Germany). The deasphalted crude oil samples were separated through column chromatography into saturated hydrocarbon, aromatic hydrocarbon and polar compound (NSO). 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, 0.32 mm in internal diameter and 0.25 µm of film thickness. The elution of

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the studied liquid was achieved with temperature programming from 80°C to 310°C at a rate of 3°C / min. Helium was used as a carrier gas flowing at a rate of 1ml / min. The injector and detector temperatures were 320°C and 350°C, respectively. The data were estimated by integration of the area under the resolved chromatographic profiles using the Chemstation software.



Figure 1. Map of Suez Gulf showing the locations of the collected crude oils

RESULTS AND DISCUSSION

Physicochemical parameters (API gravity, Sulphur content and Vanadium and Nickel contents) and bulk composition (*saturate, aromatic, Resin and asphaltene*) of the studied oil samples are given in Table 1. Isoprenoids and n-alkanes parameters (Pr/Ph, Pr / n-C17, Ph / n-C18, waxiness, carbon preference index CPI, odd/even ratio OER and terrigenous / aquatic ratio TAR of the saturated fractions are also shown in the same table. Gas chromatograms of the studied crude oil samples are shown in Figure 5.

Physicochemical parameters

API gravity and sulphur content are whole oil properties as determined in the refinery. API gravity is a bulk physical property of oils that can be used as a crude indicator of thermal maturity, thus during thermal maturation, the heavy components in oil, NSO compounds, asphaltenes, and heavy saturated and aromatic compounds undergo increased cracking, resulting in increased API gravity (Peters *et al.*, 2005). The API gravity for light, intermediate, heavy, extra heavy and for biodegraded petroleum are >30°, 20-29°, 10-19° and <10° respectively (Fazeelat *et al.*, 2007; Arif Nazir, 2013). 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, 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, 1974). In the present study Crude oil samples (S1, S6, S7 and S8) from northern and southern province of Suez gulf are light oils with high API gravities (33.2 to 39.87). Medium API gravity was observed for offshore samples from central province while onshore sample show low API gravity. Sulphur contents are low for the northern oils S1 and the onshore southern oils S7 and S8 while high sulfur contents were observed for central and offshore southern sample ranging from 1.65 to 4.67 wt%. Cross plot of API gravity and sulfur content has been used for initial grouping of crude oils Fig (2).

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 diagenetic 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 (Udo, 1992). The high values of Vanadium and sulfur content obtained in Gulf of Suez samples could be

Table 1. Bulk Geochemical Parameters of the Studied Crude Oils

	S1	S2	S3	S4	S5	S6	S7	S8
Location	Northern Province of Gulf of Suez Basin (Onshore)	Central Province of Gulf of Suez Basin (Offshore)	Central Province of Gulf of Suez Basin (Onshore)	Central Province of Gulf of Suez Basin (Onshore)	Central Province of Gulf of Suez Basin (Offshore)	Southern Province of Gulf of Suez Basin (Offshore)	Southern Province of Gulf of Suez Basin (Onshore)	Southern Province of Gulf of Suez Basin (Onshore)
API °	39.87	25.69	15.311	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
Ni ppm	16.46	27.23	35.62	30.05	38.69	25.56	15.5	14.98
V ppm	32.25	49.33	74.42	52	48.53	37.55	30.25	26.13
V/Ni	1.96	1.81	2.09	1.73	1.25	1.47	1.95	1.74
Saturate %	59.19	46.69	33.74	33.02	47.26	61.93	71.17	59.22
Aromatic %	23.54	33.18	32.68	34.04	37.68	23.75	20.57	24.22
Resin %	16.47	13.76	22.89	21.1	11.51	13.65	8.1	15.84
Asphalten%	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	0.63	0.57	1.07	0.50	0.84
Pr / n-C17	0.92	0.47	0.40	0.70	0.35	0.64	0.99	0.95
Ph / n-C18	1.21	0.61	0.77	0.48	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
TAR	0.37	0.37	0.49	0.84	0.48	0.53	0.72	0.59

$$\text{Waxiness} = \frac{\sum nC_{21}-nC_{31}}{\sum nC_{15}-nC_{20}}$$

$$\text{CPI} = \frac{1}{2} \left[\frac{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})} + \frac{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})} \right] \text{ (Bray and Evans, 1961)}$$

$$\text{OER} = \frac{(C_{25}+6 \cdot C_{27}+C_{29})}{(4 \cdot C_{26}+4 \cdot C_{28})} \text{ (Scalan and Smith, 1970)}$$

$$\text{TAR} = \frac{C_{27}+C_{29}+C_{31}}{C_{15}+C_{17}+C_{19}} \text{ (Bourbonniere and Meyers, 1996)}$$

explained according to Barwise (1990). He mentioned that under low oxic conditions, sulphate-reducing bacteria generate hydrogen sulphide (Barwise, 1990). High sulphide in the pore waters of anoxic sediments causes nickel ion to precipitate as nickel sulphide, leaving vanadyl ion (VO_2^+) 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).

Non-marine oils derived from higher plant organic matter show and 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 74.42ppm 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.3). 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) (Wenger *et al.*, 2002).

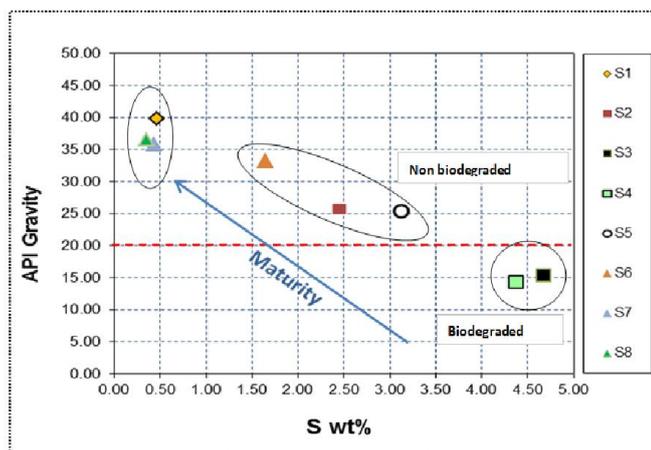


Figure 2. Cross plot of API gravity and sulfur contents

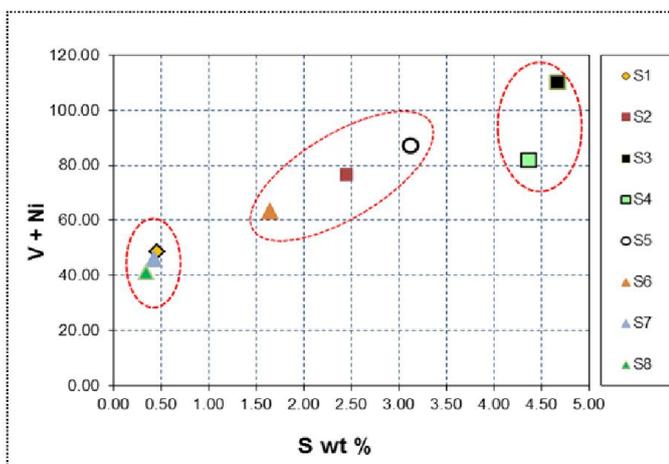


Figure 3. Cross plot of total concentration of (V+Ni) and sulfur contents

Bulk Composition "Types of Crude Oils"

The relative percentages of saturates, aromatics, NSOs (nitrogen, sulfur, oxygen containing compounds) and asphaltenes (Table 1) were used to distinguish various types of crude oils. The samples show higher relative percentages of saturates compared to other compound classes i.e. aromatics and NSOs & asphaltenes. The location of samples from northern and southern province on ternary diagram (Fig. 4) (Arif Nazir, 2013; Tissot and Welte, 1984) is close shows that the crude oils are paraffinic in nature while S2 and S5 (offshore central samples) shows a little difference being more aromatic oil type. S3 and S3 show represent heavy little biodegraded oils. A similar trend is observed of saturate/aromatic ratios of crude oils.

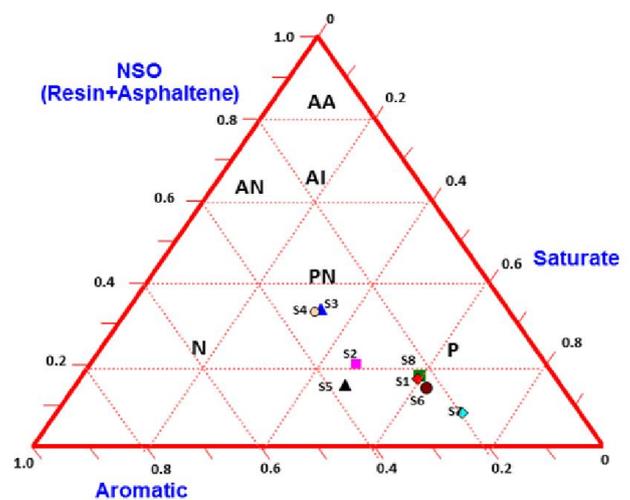


Figure 4. Ternary diagram between saturates, aromatics and NSO + asphaltenes showing types of crude oils in Gulf of Suez. P: Paraffinic; PN: Paraffinic Naphthenic; N: Naphthenic; AA: Aromatic Asphaltic; AI: Aromatic Intermediate and AN: Aromatic Naphthenic. Normal Paraffins Distribution and Isoprenoids (Pristane [Pr] and Phytan [Ph]) Parameters

Normal Alkanes

The relative abundance of *n*-alkanes is indicative of paleoenvironments and organic matter input (Cranwell, 1982; Grimalt, 1985; Duan and Ma, 2001; Mohamed, 2009). *N-Alkanes* are derived from algal, microbial and higher plant sources. The relative abundances of certain *n*-alkanes are commonly used to deduce the source of organic matter (Philp, 1985). The amorphous organic matters which derived from marine origin have maximum concentrations at *n*-C15 to *n*-C29. The humic organic matters which originated from mixed organic sources characterized by maximum concentration of *n*-C25 to *n*-C29 (Mohamed *et al.*, 2015; Waples, 1985; Peters and, 1993). Figure 5 shows gas chromatograms of the studied crude oil samples. The *n*alkanes are present in the C13-C40 range. The saturated gas chromatogram of the oil samples displays a full range of C13-C40 *n*-alkane and isoprenoid [pristane (pr) and phytane (ph)]. The *n*-alkane patterns of the oil samples are dominated by short (*n*-C12 - *n*-C20) to middle-chain (*n*-C21-*n*-C25) *n*-alkanes with the presence of significant amount of waxy alkanes (*n*-C23 +) thus give moderate values of CPI (0.89–1.11) (Table 1).

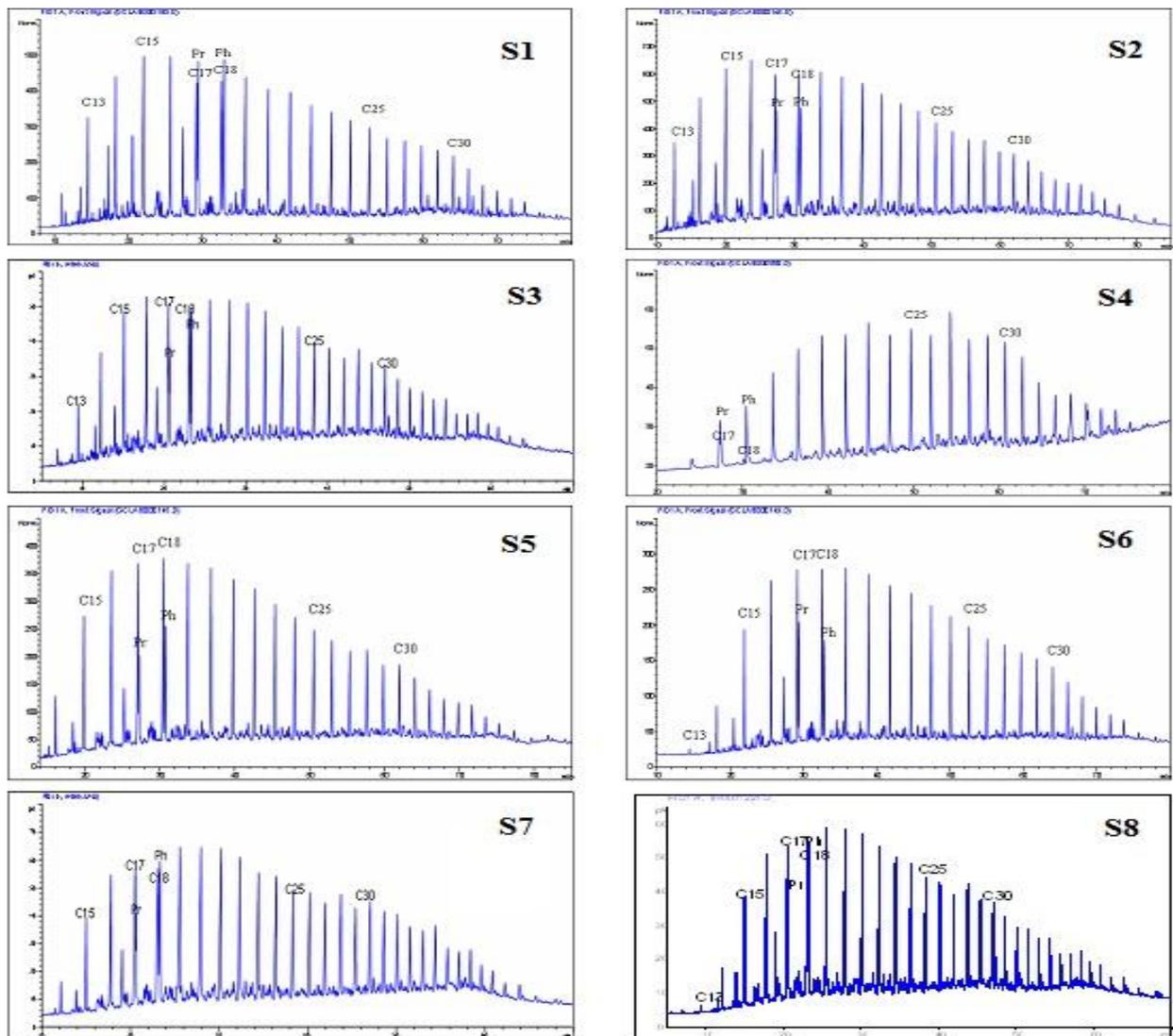


Figure 5. N-Paraffin Distribution of the saturated fractions of Gulf of Suez Samples

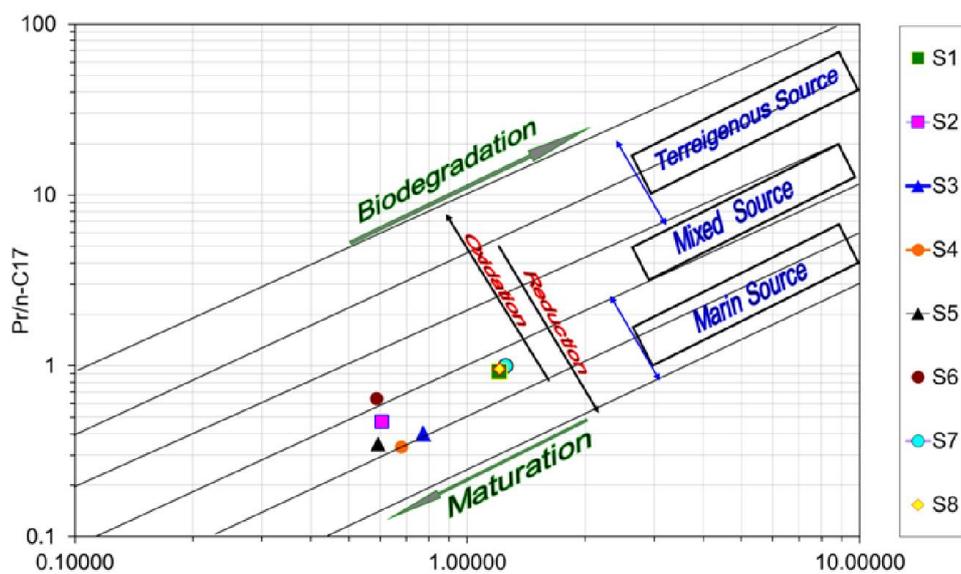


Figure 6. Cross plot of Ph/n-C18 vs Pr/n-C17 of the studied oil samples

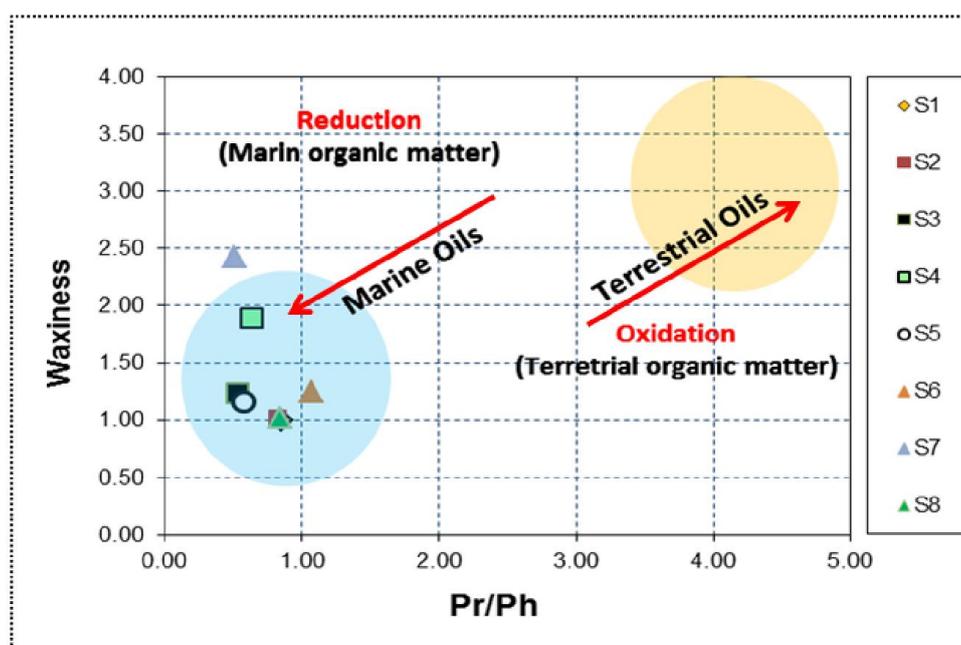


Figure 7. Cross plot of Pr/Ph vs. Waxiness of the studied oil samples

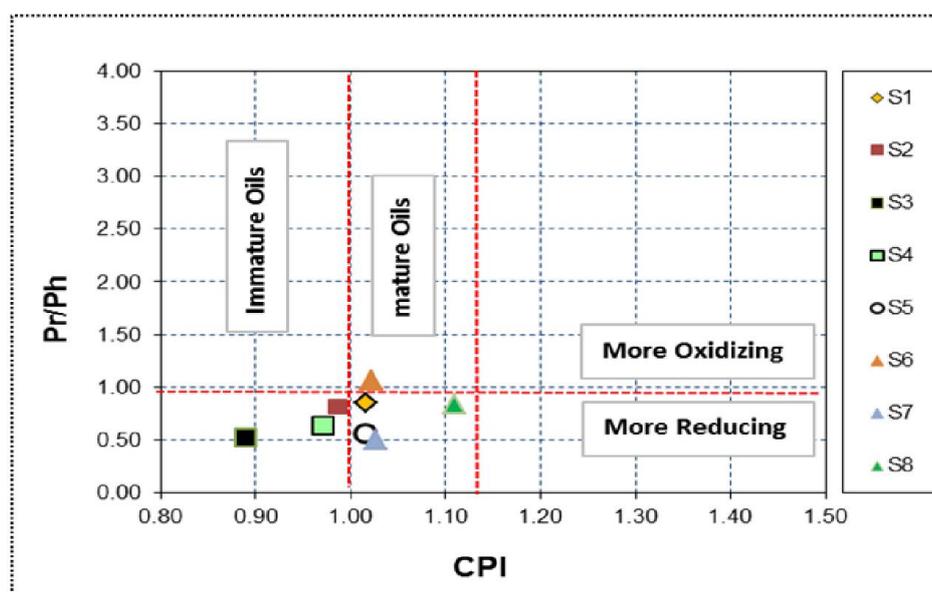


Figure 8. Cross plot of CPI vs. Pr/Ph of the studied oil samples

Data indicated 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 derived from algae and bacterial organisms, deposited under marine conditions (Peters *et al.*, 2005). These are supported by the degree of waxiness $\Sigma (n-C21- n-C31)/\Sigma (n-C15- n-C20)$ (Johns, 1986). The calculated ratio of $\Sigma (n-C21- n-C31)/\Sigma (n-C15- n-C20)$ for the oil samples ranges between 1.0- 2.43 (Table 1) suggesting mainly contain algal and / or bacterial organic matter with lower terrigenous organic matter input (Tissot and Welte, 1984).

The terrigenous to aquatic (TAR) ratio is useful to assess relative contribution of land plant versus aquatic organic matter

input however this ratio is influenced by maturity (Bourbonniere and Meyers, 1996; Peters *et al.*, 2005; Fazeelat *et al.*, 2009). The TAR values for the samples lie in the range of 0.06 to 0.87 (Table 1). The TAR value >1 indicates greater land plant input. The crude oil samples show TAR values <1 indicating that major contribution of organic matter is not from greater land plants. These low values are consistent with aquatic source of organic matter.

Isoprenoids: Redox Conditions (Pr/Ph Ratio)

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 ratio 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 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 was deposited under (sub-oxic) conditions.

Isoprenoids/n-alkanes

In crude oil studies, the ratios of isoprenoids to n-alkanes are widely used since they provide information's on maturation and biodegradation as well as source (Ficken *et al.*, 2002). In the present study, Pristane/n-C17 and phytan /n-C18 ratios are in the range of 0.34-0.99 and 0.59-1.26, respectively. The cross plot pr/n-C17 versus ph/n-C18 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. 6) (Johns, 1986; Hakimi *et al.*, 2011).

Isoprenoids correlation with Waxiness and CPI

Cross plot of Pristane/Phytane ratio vs. waxiness is shown in Figure 7. The relation between the Pr/Ph ratio and waxiness shows that the studied oil samples have been originated from marine organic source deposited under reducing conditions. On other hand, the cross plot of Pr/Ph ratio versus CPI (Fig. 8) shows that the oils fall in the field of more reducing zone and are closed to reach the maturity means that these oils are marginally mature or moderately mature oils except S3 and S4 oil samples which show low maturity level.

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 results revealed the following:

- The determined physicochemical parameters (API°, S wt%, V & Ni ppm) reflected that the crude oils are of different source rock types and show variation in the maturity levels which led to primary classification into three groups as shown in Figures 2 and 3.
- Bulk crude oils compositions indicated that those oils are paraffinic in nature except S3 and S4 which are intermediate aromatic.
- Normal alkanes and isoprenoid parameters give clear evidence that the organic matter input is marine organic matter preserved under anoxic conditions for whole oil samples except S6 which reflect mixed organic matter deposited under (sub-oxic) conditions. These parameters also show the variety of the maturity levels of the studied oil samples.

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