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Physical Properties and Gross Composition of Crude Oils of Some Oilfields, Gulf of Suez, Egypt

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A R T I C L E   I N F O

A B S T R A C T

Background: Crude oil is a complex mixture containing a large number of closely related compounds. Which controlled initially by the nature of organic matter in the source rock. The relative amounts of normal alkanes, isoprenoid, aromatics, and sulfur compounds, are characteristic of the source and should be essentially for all oils derived from a particular source rock. Objective: The purpose of the present study was the evaluation of the geochemical characteristics for the crude oils in order to identify physical characteristics, gross composition, origin, oil classes, maturation, depositional environments and the genetic relationship between these oils. The saturated distributions have been used in an attempt to characterize the type of organo-facies, oil classes, and depositional environments of the crude oils. Results: The results revealed that, these oils have high specific gravity, high sulfur content, high concentrations of Nickel and vanadium and rich in saturated hydrocarbons .Isotopic ratios of the saturate and aromatic fractions indicate minor variation in isotopic composition of the oils. Conclusion: According to the results the studied crude oils was classified into non waxy aromatic intermediate oils derived mainly from marine sources. Gas chromatographic analyses show that the crude oils are mainly mature, derived from source rocks, deposited under marine environments deposited under suboxic conditions. And there is a close genetic relation between studied crude oils.

INTRODUCTION

Crude oil is a complex mixture containing a large number of closely related compounds. The compounds present, are controlled initially by the nature of organic matter in the source rock. The relative amounts of normal alkanes, isoprenoid, aromatics, and sulfur compounds, are characteristic of the source and should be essentially for all oils derived from a particular source rock (Waples, 1985). Geochemical characterization of crude oils increases the efficiency of petroleum exploration and exploitation programs (Demasion and Huizinga, 1991). According to Tissot and Welte (1984) the common method for determining geochemical characterization of crude oils is the measurement of API gravity, sulfur content, crude oil compositions and stable carbon isotope ratio ($\delta 13C\%o$).

The characteristics of crude oils of Gulf of Suez have been evaluated by Zein El Din et al. (1981), who reported that the oils produced from some fields within Gulf of Suez, are derived from similar marine source rocks. Rohrback (1983) suggested marine origin for oils recovered from the major producing fields allover the Gulf. Barakat et al. (1996) divided the oils of the Gulf of Suez into three types. Type I is sourced from carbonate source rocks (mainly of marine origin), Type II appears to be originated from Tertiary source rocks with contribution from high land plants, and Type III is a mixture of Types I and II. Wever (2000) stated that oils from the Gulf of Suez were derived from source rock consists of pre-Miocene marine carbonates with predominantly type II kerogen. El Nady (2001) recognized that the oils in southern Gulf derived mainly from terrestrial origin. Barakat et al. (2002) stated that there is a close genetic relation between the oils in the southern part of Gulf of Suez. More recent studies as El Nady and Harb (2005) recognized that the source of oils in the northern part in the Gulf of Suez was derived from different contributions of varies origins. El Nady (2006) stated that the crude oils in South Gulf of Suez are mature, originated mainly from marine sources and show good correlation with the Lower Miocene source rocks. El Nady et al. (2007) classified crude oil in the central Gulf of Suez into moderately mature, generated in a strongly reducing (marine) environment, and mature,

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generated from source rocks deposited under lacustrine conditions. Sharaf et al (2007) identified four oil families in the southern Gulf of Suez. Family (1) rich in type II organic matter and deposited under anoxic depositional environment. Family (2) rich in source rocks deposited under oxic depositional environment. family (3) oil is of mixed sources (marine and non marine), generated from source rock of Tertiary and / or Younger age. Family (4) oil sourced mainly from carbonate source rocks rich in clay minerals with algal and bacterial contributions. Roushdy et al.(2010) reported suggest that the crude oils are mature and derived mainly from mixed organic sources from terrestrial and marine inputs contribution to the biomass from algae and plankton in different saline environments. Harb and El Nady (2010) divided crude oils in the Gulf of Suez into 1. Heavy oils characterized by low maturation and originated mainly from terrestrial organic sources. 2. Light oils of high maturity level orginated mainly from marine organic sources. Faramawy et al., (2012) classified the crude oils into aromatic intermediate heavy oils of low waxy content characterized by high maturity level and derived from mixed organic sources; belong to the carbonate type, deposited in transitional environments under reducing-oxidizing conditions.

Aim of Study:

The purpose of the present study was is the evaluation of the geochemical characteristics for the crude oils in order to identify physical characteristics, gross composition, origin, oil classes, maturation, depositional environments and the genetic relationship between these oils. The saturated distributions have been used in an attempt to characterize the type of organo-facies, oil classes, and depositional environments of the crude oils. These achieved through the geochemical analyses of oil samples, including sulfur content, API gravity, nickel and vanadium, Carbon isotope, and C15+ saturated obtained from gas chromatography.

Samples:

Five crude oil samples were collected from productive wells from GS 277-1, July 6, GH376-1, GS 392-2, and GH 452-1A oilfields in the South Gulf of Suez (Fig. 1). Most of the produced oils of these wells were mainly from Rudies reservoir of Early Miocene age, Kareem reservoir of Middle Miocene and Belayim reservoir of Upper Miocene age. The geologic informations of these samples are summarized in Table (1). These samples supplied to the authors after Gulf of Suez Petroleum Company (GUPCO).

Experimental:

1. API gravity: is a measure of crude oils density at $15.6^{o}C$ ($60^{o}F$) and is related by equation:

$$°API = \frac{141.5}{Specific\ gravity} - 131.5$$

2. Sulfur content: was determined by X-ray sulfur meter model RX-500 S according to ASTM D-42914 procedure, and the results expressed as weight percent.

3. Nickel and vanadium content were carried out using the Flam-Spectrophotometer, at wavelengths of 352.5 and 550mu respectively. Their concentrations were calculated from the calibrated curves of their prepared standard solutions against the galvanometers readings of the Flam-Spectrophotometer.

4. Carbon isotope values are obtained by converting the sample to $CO2$ in atmosphere of oxygen at $86^{o}C$, then by using a mass spectrometer the relative amount of ^{13}C and ^{12}C in the sample is measured and compared with those in Peedee Belemnite standard (PDB limestone). The results are expressed as per-mil deviation ($δ\%o$) and are calculated using the following equation:

$$δ\ ^{13}C = \left(\frac{(^{13}C/^{12}C)\ sample}{(^{13}C/^{12}C)\ s\tan dard} - 1 \right) x1000$$

5. The deasphalted residue of crude oils was separated by column chromatography. The column was packed with 1:1 (by weight) alumina overlying silica gel. Successive elution with n-heptane, toluene and chloroform yielded saturates aromatics and resins fractions, respectively.

6. Saturated fractions for oils were analyzed by gas chromatography using Perkin Elmer Instrument Model 8700, (Agilent Technologies, Inc., Wilmington, DE)) provided with a flame ionization detector (FID). Oven temperature was programmed for 100 to $320^{o}C$ at $5^{o}C/min$.

These analyses were carried out by Baker Hughs international, Robertson Research International (RRI), and Amoco Research Center in Tulsa, Oklahoma (TRC) in the USA.
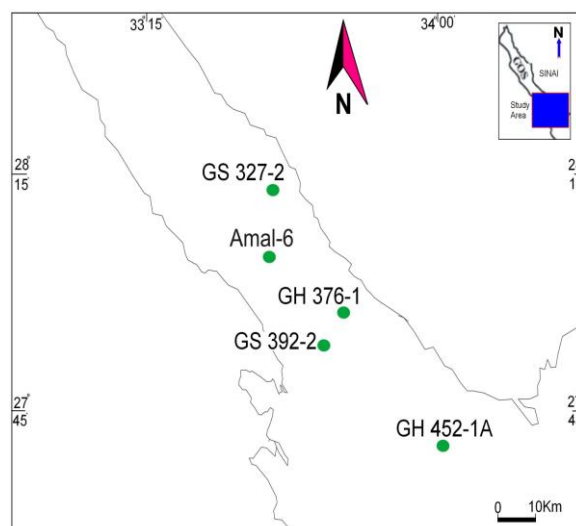
Fig. 1: Location map of the studied wells, Gulf of Suez, Egypt.

RESULTS AND DISCUSSION

API gravity:

Tissot and Welte (1984) recognized that, crude oils have API gravities less than 20o are immature, and above 20° are mature oils. Waples (1985) reported that, the normal crude oils have API gravity range form 20° to 45°, less than 20° are usually biodegraded and above 45° are condensates oil. Martinez et al. (1984) classified the crude oil into heavy, medium and light as the API gravity is less than 27.3, and from 27.3 to 31.1 and then greater than 31.1 respectively. Therefore the studied crude oil samples have API garvities range from 21.7^o to 37.6^o (Table 1) reflecting a mature light normal oils.

Table 1: Geological information and Geochemical analyses of oil samples of the studied oilfields, Gulf of Suez, Egypt.

Geochemical Data	Well Name				
	GS 327-2	Amal-6	GH 376-1	GS 392-2	GH 452-1A
Depth (ft)	5,720	7,058	8,589	9,011	4,606
Reservoirs	Rudies	Rudies	Rudies	Kareem	Belayim
Age	M. Miocene	M. Miocene	M. Miocene	E. Miocene	U. Miocene
API gravity	21.7	34.2	24.5	37.6	35.3
Sulfur %	03.7	01.8	03.3	00.7	01.1
Nickel (Ni)	30.0	33.0	52.0	25.0	36.0
Vanadium (V)	40.0	52.0	28.0	41.0	26.0
V/V+Ni	0.57	0.61	0.35	0.62	0.42
Pr/Ph	0.83	0.91	0.72	0.87	0.94
ΣC21C31/ΣC15-C20	0.70	0.80	0.70	0.65	0.95
Pr/n-C17	0.37	0.25	0.19	0.21	0.16
Ph/n-C18	0.78	0.60	0.55	0.65	0.88
CPI	0.89	0.88	0.91	0.95	0.93
δ13Saturates%	-28.9	-28.5	-29.1	-25.7	-25.7
δ13Aromatics%	-28.6	-28.2	-29.4	-24.9	-25.4
CV	-2.03	-2.15	-3.30	-1.91	-3.02

Sulfur Content:

Sulfur content was used by Moldowan et al. (1985) as an indicator of source origin; as oils of marine origin has more than 0.5 % sulfur and those originated from non marine origin have sulfur (less than 0.5 % S). It is obvious that the studied crude oil characterized by high sulfur content ranging from 0.7% in GS392 well to 3.7% in GS327-2 well. (Table 1) indicating moderately mature derived from marine source. Tissot and Welte (1984) suggested that, oils with low sulfur content less than one belong to paraffinic, paraffinic-naphthenic or naphthenic classes with high waxy content, while oils of high sulfur content more than one belong to the aromatic-intermediate class with low wax content. These data indicate that the studied crude oils are classified as aromatic intermediate oils (Tissot and Welte, 1984). Thus, there is a correlation between the studied oil samples based on the oAPI and sulfur (Fig. 2). This conclusion indicates a close genetic relation between studied crude oils.
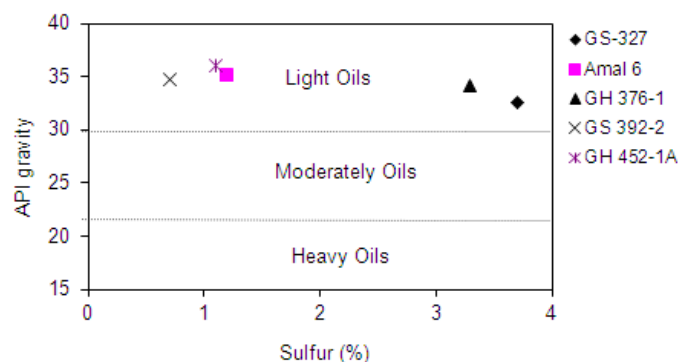
Fig. 2: A relation between API gravity and sulfur content of the studied crude oils of oilfields, Gulf of Suez, Egypt.

Nickel and Vanadium:

The concentrations of nickel (Ni) and vanadium (V) have been noted in various crude oils, although it is generally believed that they entered at the time of their formation. These metals are the major in petroleum (Lewan, 1984) and exist in petroleum largely as porphyrin complexes. Barwise (1990) recognized that the oils from marine carbonate high concentrations of nickel and vanadium, and vanadium/vanadium + nickel ratios value of 1 or less. Oils from lacustrine source rocks show low quantities of metals (<20ppm), and have higher vanadium/vanadium + nickel ratios (>2). Therefore, the studied crude oils have high concentrations of nickel content ranging from 25ppm to 52ppm and vanadium content ranging from 26ppm to 52ppm, Table 1), as well as, vanadium/vanadium + nickel ratios range from 0.38 to 0.65 (<1, Table 1) reflecting oil generated from marine carbonate origin.

Carbon Isotope:

The carbon isotope values for the saturates and aromatics fraction of the oil samples under consideration range from -25.7 to -28.9 and -24.9 to -29.4 respectively (Table 1). These values indicate minor variation in isotopic composition of the oils, due to the maturation level between the oil samples (Peters et al., 2000). This indicates that the oils within the study area were derived mainly from marine origin (Fig. 3).

On the other hand, the isotope composition of oil fractions (saturates and aromatics) can be used to distinguish between marine and terrigenous oils by applying a mathematical relation known as canonical variable (CV, Sofer 1984). The relation between the canonical variable (CV) and the isotope composition of the saturate and aromatic hydrocarbons is given by the following equation (Sofer, 1984).

$$CV = -2.53 \, \delta^{13}C_{saturates} + 2.22 \, \delta^{13}C_{aromatics} - 11.65$$

The oil sample with CV value lower than 0.47 is classified as marine oil and that with CV more than 0.47 classified as terrigenous oil. The calculated (CV) values of the crude oil samples under study revealed that the oil samples have CV values range from (-1.91 to -3.30, Table 1) which indicates non-waxy oil rich in marine organic matter.
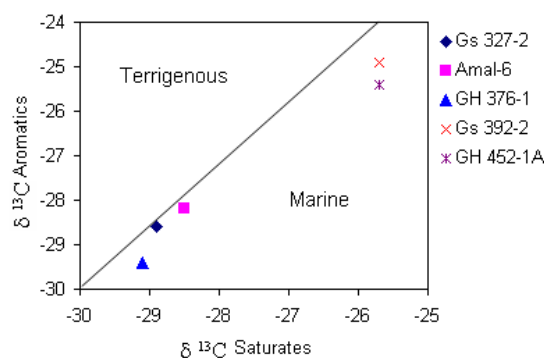

Fig. 3: A Relation between carbon isotope of saturates and aromatics fraction of crude oil of oilfields, Gulf of Suez, Egypt

Normal alkanes:

The distribution of n-alkanes in crude oils can be used to indicate the organic matter source (Duan and Ma, 2001). Figures 4 show the fingerprints of gas chromatography for the saturated hydrocarbons of the studied crude oil samples. These figures show that the studied oils appear to be mature, based on the abundance of n-alkanes in the range n-C15 to n-C20, slightly even carbon preference and moderately to low concentration of

heavy normal alkanes. The increase in the n-C15 to n-C20, suggests marine organic matters with contribution to the biomass from algae and plankton (Peters and Moldowan, 1993). The striking molecular feature of oils are characterized by uniformity in distribution patterns, suggesting that oils are related and have undergone similar histories, with no signs of water washing or biodegradation (Duan and Ma, 2001).

Degree of Waxiness:

The degree of waxiness in this study is expressed by the $\Sigma C21-C31/\Sigma C15-C20$, ratios. It is used to categorizing the amount of land-derived organic material in an oil. This method assumes that terrigenous material contributes a high molecular-weight normal paraffin components to the oil (Köket al., 1997).

The studied oils are characterized by high abundance of of n-C15to n-C20 n-alkanes in the saturate fractions reflecting high molecular weight of low waxy (Moldowan et al., 1994). The degre of waxness ($\Sigma C21-C31/\Sigma C15-C20$ ratios) ranging from 0.65 to 0.95 (Table 1) confirm low waxy nature and suggest marine organic sources mainly of higher plants, deposited under reducing condition (Peters and Moldowan, 1993).

Pristane/phytane:

The pristane/phytane (pr/ph) ratio is one of the most commonly used geochemical parameters and has been used as an indicator of depositional environment with low specificity due to the interferences by thermal maturity and source inputs (Peters et al., 2005). ten Haven et al. (1987) stressed that high pr/ph (>3.0) indicates terrigenous input under oxic conditions and low pr/ph (<0.8) indicates anoxic/hypersaline or carbonate environments. The studied oil samples are characterized by pristane/phytane ratios ranging from 0.72 to 0.94 (Table 1), confirming that these oils have been originated from marine organic source deposited under suboxic conditions.
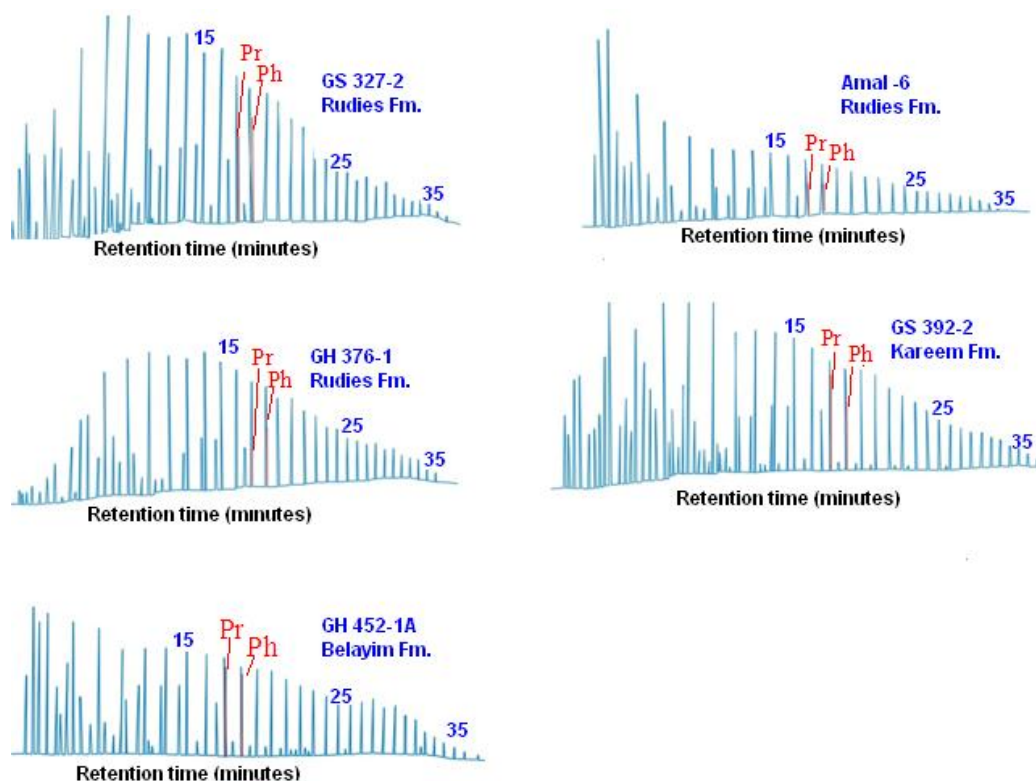

Fig. 4: Gaschromatography of saturated hydrocarbons of the studied oil samples, Gulf of Suez, Egypt.

The pristane/phytane ratios of oil show some kind of correlation with the canonical variable (CV) values (Sofer, 1984 and Chung et al., 1994). They are found that, low pristane/phytane ratio <1 and CV <0.47 associates with carbonate oils, rich in marine organic matter and more than one of pristane/phytane ratio and CV >0.47 indicates deltaic oils, derived from contribution of terrestrial and detrital sediments. Thus most of oil samples have pristane/phytane ratios range from 0.72 to 0.94 (<1) and CV of -1.91 to -3.30 (Table 1), indicating marine oils. Furthermore, the relation between isoprenoids (pr/ph) and sulfur percent (Fig. 5) suggests no variation in the salinity levels of their depositional environment (ten Haven et al., 1987) and confirms the previous conclusions.

On the other hand, the studied oil samples are characterized by pristane/phytane ratios (0.72 to 0.94) and waxiness values (0.65 to 0.95, Table 1), confirming that these oils have been originated from marine organic source deposited under suboxic conditions. Figure 6 exhibiting the relationship between pr/ph and waxiness of crude oils confirms this conclusion.
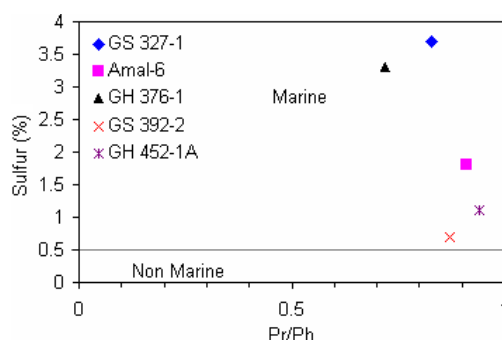

Fig. 5: A Relation between pristane/phytane ratios and sulfur content of the studied crude oils of oilfields, Gulf of Suez, Egypt.
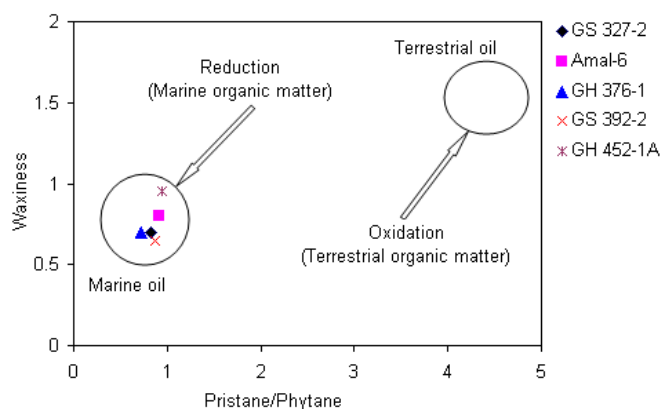

Fig. 6: Cross plots of Pr/Ph versus degree of waxiness ($\sum$C21-C31/$\sum$C15-C21) of the studied of oilfields, Gulf of Suez, Egypt.

Isoprenoids:

In crude oil studies, the ratios of isoprenoids to n-alkanes are widely used since they provide informations on maturation and biodegradation as well as source (Hunt, 1996). The isoprenoids/n-alkanes ratios (pr/n-C17 and ph/n-C18, are shown in Table 1).

The studied crude oil samples have pristane/n-C17 and phytane/n-C18 ratios range from 0.16 to 0.37 and 0.55 to 0.88 respectively (Table 1). These ratios indicate that, the crude oils were derived mainly from marine organic matter deposited under reducing environments (Fig. 7, Waver, 2000) Also, this figure also shows that with increasing the maturity, n-alkanes are generated faster than isoprenoids resulting in a decrease of isoprenoids/ n-alkanes ratio and regression along the line toward the origin. It is clear that, all the crude oil samples take the direction of increasing maturity far from the direction of biodegradation.

Carbon Preference Index:

Carbon preference index (CPI) is a measure of the strength of the odd carbon predominance in normal alkanes, and calculated as follows:

$$CPI = \frac{odd\,carbon\,atoms}{even\,carbon\,atoms} \qquad (Waples, 1985)$$

Carbon preference index obtained from the distribution of n-alkanes is affected by both source and maturity of crude oils (Tissot and Welte, 1984). The CPI values of the studied crude oils are listed in Table (1). It is clear that the oils have CPI values close to unity, ranging from 0.89 to 0.95. These values indicate that, these oils are mainly mature and most probably generated from marine organic sources (Waples, 1985).
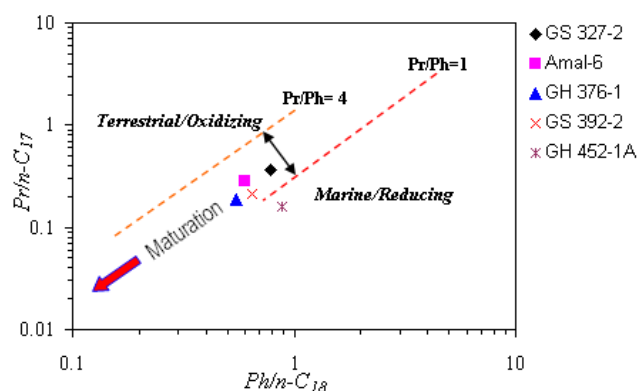
Fig. 7: Pristane/n-C17 vs. phytane/n-C18 plot of studied crude oil samples of oilfields, Gulf of Suez, Egypt.

Conclusions:

From the evaluation of the geochemical characteristics of five crude oil samples which collected from the main producing horizons of five oil wells in the Gulf of Suez revealed the following:

1. API gravities and sulfur contents are classified of crude oils as aromatic intermediate oils, characterized by low waxy and high sulfur content.

2. Carbon isotopic ratios of the saturate and aromatic fractions of the crude oils, classified of crude oils into non waxy oils derived mainly from marine sources

3. Gas chromatographic analyses indicate that, most of the studied oils are mainly mature, derived from sources rocks, deposited under marine environments.

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