

CHAPTER SIX

(A): BRINE CHEMISTRY AND ORIGIN OF HYPERSALINE PANS AND PONDS, RAS SHUKEIR SABKHA, GULF OF SUEZ

(B): ORGANIC GEOCHEMISTRY OF THE STUDIED EVAPORITE CORE SAMPLES

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(A): BRINE CHEMISTRY AND ORIGIN OF HYPERSALINE

PANS AND PONDS, RAS SHUKEIR SABKHA, GULF OF SUEZ

(B): ORGANIC GEOCHEMISTRY OF THE STUDIED EVAPORITE

CORE SAMPLES

1. Introduction:

The solute chemistry and minerals of evaporite basins in both continental and marine environments have been intensely studied by many authors among of them (Jones, 1966; White *et. al*, 1963; Braitsch, 1971; Jones *et. al*, 1977; Eugster *et. al*, 1970 and Jones, 1979; Al-Droubi *et. al*, 1980; Sonnefeld, 1980; Eugster *et. al*, 1980; Harvie and Weare, 1980; Harvie *et. al*, 1980,1982,1984; Barnetley et al, 1984; white *et. al*, 1963, 1984; Sonnefeld, 1981; Last, 1989; Jankowski and Jacobson, 1989 and Wali *et. al*, 1998 an 2001).

Many fundamental geochemical problems related to chemistry and evaluations of brines in evaporite basin have been resolved (Jones, 1966; white *et. al*, 1963, Gerrals *et. al*, 1967 and Eugster *et. al*, 1970), however, some problems are still encountered including the discrepancy between predicted and observed minerals suites, the presence of non-equilibrium mineral thickness and apparent lack mass balance between solute and accumulated evaporite deposits (Alderman, 1983; Spencer *et al.*, 1985a and b).

The non-equilibrium assemblages of evaporite minerals in many marine basins provide a classic example of the discrepancies observed between predicted and observed amounts of minerals precipitation. Arguments have been raised by Lowenstein *et al* (1989) and Haride (1990). Some of these discrepancies can be attributed to variable chemistry in water source(s). Haride (1990) describes the relative depletion of magnesium sulfate in many marine evaporite

deposits in the world compared to that predict by thermodynamic models. King (1947) proposed that exchange of water between a restricted evaporating body of water and the ocean was a possible way as to produce non-equilibrium thickness and unusual mineral suites observed in many marine evaporite deposits. He add farther that the continued re-dilution of evolving brine by source water (seawater) would limit the increase in salinity and allows continual precipitation of only the more insoluble minerals. Sonnefeld (1980) has expanded this concept by developing an equation to show the salinity in restricted body of water as a function of the influx of seawater out of and into a basin undergoing evaporation. Sanford and Wood (1991) suggested that even a small amount of continual out flow from restricted evaporating body of water may significantly affected the solute concentration, brine evaluation and potential mineral precipitation.

In this part of this chapter the main concern is to deal with the Ras Shukeir brine pools chemistry, evaluation (source type of brine) through adapting the scheme of both Haride and Eugster (1970) and White and Warring (1963) and their available condition for preservation of the organic matter generated by biological activity in these brines as evaporitic hypersaline environments. The brine samples from hypersaline (solar and saline pools) of Ras Shukeir area were collected according to chosen profiles covering different depths in order to represent their aerial and vertical distribution. The brines samples were analyzed for their chemical constituents (major, minor ions, pH and salinity as well as their physical properties). The result of analyses were shown and tabulated in Table-6

2. The physical Properties:

The specific gravity, density and conductivity values of the analyzed brine samples are high and show some variation in their aerial distribution within the area from the hypersaline in south to saline pools in the north. The average values range from 1.639 g/cm³ to 1.0549g/cm³ for the specific gravity and from 1.03985 gm/ml to 1.0517 gm/ml for the density as well as it ranges

from 0.091 Mohs/cm to 0.084 Mohs/cm in average for the conductivity. The values of specific gravity, density and conductivity are changeable and fluctuates vertically with depths even if it were very shallows (10-15 cm) which suggesting that there are layering within the same water body from the surface to the bottom where the heavier occur in the top of lighter one as the depth increase (Table -6).

3. Hydrochemical Characteristics:

The measured salinity values of the analyzed brine samples from the study area range from 120,000 ppm to 1190,000 ppm with an average 770,000 ppm. This range is considered to be high salinity according to U.S. Salinity Laboratory Staff (1954). The salinity values vary between hypersaline and saline pools ranges, as well as it change vertically with depth within the same water body of the pool. The change of salinity with depth, even within very shallow depths (10-15cm), is suggesting the presence some of stratification and layering (Table-6).

The total dissolved solid (T.D.S) contents of the analyzed brine samples are high (Table-6) and displaying variation with depth as well as with, salinity. The T.D.S values range from 85,010ppm to 124,450ppm, which were categorized as hypersaline, saline and residual brines according to proposed scale of Carpenter and Millar (1969).

The pH value is directly proportion with salinity so it's a reflection of salinity value(s), (Wali *et al*, 1999). The pH values of the brine samples from the area of study are varies from acidic to slightly alkaline, which range from 5.5 to 8.6 as the depths increase (Table-6). The recorded variation in pH value(s) may reflect different diagenetic processes as decomposition of organic matter and mixing of different salinity water(s) and/or brine(s). The low pH values were due to the deficiency of bicarbonate ion caused by high salt content of medium (Amit and Benter, 1971).

The chemical analyses data (Table-6) of the analyzed brine samples from the study area show the following:

Sodium cation content of the samples is the predominant cation in these samples. The concentration of Na^+ shows some variation aerielly from both (eastern and western) hypersaline pans in South to solar and saline ponds in north of the area where the average concentrations change from 37,469 ppm and 5,442 ppm in both hypersaline pans to 19,707 ppm and 18,776 ppm in solar and saline ponds respectively. Also the Na^+ concentration values changed and fluctuated vertically as the depth increase even if it very shallow within the water body (Fig.41).

The average magnesium cation concentrations range from 12,594 ppm in hypersaline pans (eastern pan) to 6,898 ppm in saline ponds. This range is relatively high proportion suggesting Mg^{+2} enriched brines after deposition of gypsum, which may be due to continental water influx. As well as Na^+ concentration, Mg^{+2} concentrations varies as the depth increase within the same water body in respect to each pool at the area of study (Fig. 41). The content of potassium cation is range from 1040 ppm to 1998 ppm in average. This range is considered to be high suggesting enrichment of brine by potassium cation, which attributed to continental influx of meteoric water in origin of brines. Also potassium cation values changed vertically as the depths increased.

The calcium content is the lowest abundant cation, which may attribute to removal by precipitation of carbonate minerals by evaporation. The vertical distributions of Ca^{+2} concentration show variation with depth of brine pool. The unusual high concentration of Cr^{+2} Cation was detected suggesting a possible continental influx on origin of brines (Wali, *et al* 1990)

The chloride anion contents is the most abundant anions in all analyzed brine samples and directly proportional with sodium. The aerial distribution of Cl^- is different through the area of study where the average ranges from 96316 ppm and 13845 ppm in both hypersaline pans to 53703 ppm and 51806 ppm in solar and saline ponds respectively. The concentration of chloride anion varies vertically as the depth increase within the each pool even if it very small (Fig.41).

The Sulfate contents are high and coincidence with precipitation of gypsum. The sulfate anions have content within the area pools where the average range from 7633 ppm and 3282 ppm at both hypersaline pans in south to 7546 ppm in solar ponds to 7546 ppm in north saline pools. The concentration of SO_4^{2-} changes vertically with depth of each pool regardless to this depth. The bicarbonates anions content is the lowest abundant anions due to removal by precipitation of carbonate minerals during the evaporation process and low rainfall in the area.

4. The Hydrochemical Water Types:

The chemical composition of the analyzed samples from the study area plotted on Fig.43, which illustrates the brine/water characteristics according to Haride and Eugster (1970) of closed basin system. Haride and Eugster (1970) adopted a scheme for identifying the water and/or brine types. The scheme is based on mol% values of Cations and Anions distributed into two triangles each is divided into 19 fields furthering each field is readable according to mol% of cation and anions which constitute the type of water brines (Table-7and Fig.42). The major saline minerals of different brine types after Haride and Eugster (1970) are shown in Fig.43 and the major brine types are as the following, Table-8

- (A) Ca-Mg-Na- (K)-Cl
- (B) Na- (Ca)- SO_4 -Cl
- (C) Mg-Na- (Ca)- SO_4 .Cl
- (D) Na- CO_3 -Cl

(E) Na-Ca-SO₄-Cl

The Hydrochemical composition of the analyzed samples show slightly diversity of major cations composition but the most abundant cation is Na⁺ while the brines have single dominant Anion which is Cl⁻ with minor SO₄⁻². The correlation between the plotting of these chemical composition of the analyzed brine samples and scheme of brine classification proposed by Haride and Eugster (1970) indicate the following:

- 1- The analyzed samples compositions lies in sectors 3, 4, 7, 8 and 1, 2 and 12 (Table-8 and Fig.43)
- 2- The water brine types of these analyzed samples are:
Mg-Na- (Ca)-Cl-SO₄
Na- (Ca)-Mg-Cl- (SO₄)
Na-Mg-Cl- (SO₄)
- 3- The major saline minerals of these water types are present in Table-9, which reflect both sources of recharge and evaporation processes.

Eugster *et al*, 1970 illustrates the development of parent brine tile the present composition (Fig.44) that represents evaporation paths for nine typical waters in term of the major species. All paths begin at composition of natural waters and end at point of evaporation, which produces an ionic strength of about 5. The correlation of analyzed samples and Eugster *et al*, 1970 illustration indicate the path of these water brines is (i) path and are belong to water leaching sandstone where it starts with a low Na⁺ content and exhausts its (HCO₃⁻ + CO₃⁻²) and SO₄⁻² producing a Ca-Mg-Na-Cl water type brine based on the Following:

- 1-The reached hydrochemical composition indicates that the water brine type is Mg-Na- (Ca)-Cl-SO₄ and follow (i) path.

2- The Ras Shukeir sabkha area is boarded by faulted block trending NW-SE, which enhance recharge, the pools.

5. Discussions and Evaluations:

The water brine samples, which covered profile of different vertical depths for Ras Shukeir sabkha pans and pounds, were analyzed to identify their physical, chemical composition and their water source(s). The samples were analyzed for their major cations and anions, T.D.S, pH, salinity and physical properties (specific gravity with density). The Salinity values are high and vary with depth. pH values indicate slightly acidic to slightly alkaline as the salinity increased. T.D.S values are high and categorize the water pools as hypersaline. The specific gravity, density and salinity were suggesting introducing the layering within the water body even if it very shallow as it were confirmed by hydrochemical composition. The water types are belonging to a sandstone types with a composition of Mg-Na- (Ca)-Cl- SO_4 and path (i), which represent the manner of evolution of the reached composition. The structural configuration of the area (fault) facilitates recharging the sabkha pools by seawater.

From the above consideration, we conclude that the Ras Shukeir sabkha is hypersaline environment as all hypersaline environments. These hypersaline environments are very productive in exposed surface, on the margin and water brine body as a whole (Evan and Kirkland, 1981). These organic matters that were generated in this hypersaline environment have several possible fates it may be preserved or may partly or completely destroy. The detailed analyses of water brines of Ras Shukeir sabkha approved that the destruction of the generated organic matter within the water column are inefficient due to the following:

1. The oxygenated destroyer water column is very thin and the destructive capacity is very low due to these hypersaline pans have very high salinity, which decrease the solubility of oxygen.

2. The viscous behavior of highly mineralized water brines of these hypersaline pans permits their stratification and layering within the water body even if it was very shallow, which permit the flushing the organic on the top, lighter, less saline, surface.
3. The existence of these stratification and layering prevents contact of more oxygenated destructive water with underlying sediments rich in decayed organic, which led to their preservation.
4. The alkalinity nature of brines proved the reducing environment for preservation of the originated organic matter.

For all these reasons, we can conclude that the hypersaline environment at Ras Shukeir has capability of preserving at least a part of organic matter generated by biological activity in their brines, then the further evaporitic source beds would be exist.

(B): ORGANIC GEOCHEMISTRY OF THE STUDIED EVAPORITE CORE SAMPLES

1. Introduction:

Organic geochemistry is an invaluable tool to elucidate the effective petroleum source and to provide good information about origin, migration and alteration of petroleum in earth's crust. The evaluation of source rock is depend on the determination of organic content (organic richness), the types of organic matter, the capability of the rich source rock to generate petroleum and the level of the thermal maturation required to generate and expel hydrocarbons.

This branch of has attracted many authors among of them Lopatin, 1971; Tissot *et al*, 1974; Ekweozor *et al*, 1979; Waples; Tissot and Welte, 1984; Moldowan *et al*, 1985;

Shanmugam, 1985; Peters, 1986; Bazhenova and Arefiev, 1990; Chung *et al*, 1992; El Kammar, 1995; Hunt, 1996; Damste *et al*, 1998; Hung, 2000 and Radke *et al*, 2001.

The relationship between evaporite and organic matter documented in geological record and the understanding that extremely high biological activity is associated with evaporites forming in modern setting have led to an increasing consideration of evaporite sequences as potential source rock for hydrocarbons (oil and gas), Warren, 1986; Lowenstein and Haride, 1985.

Kirkland and Evans, 1981 proposed the idea that favorable conditions for accumulation and preservations of organic matter exist in evaporite environments and that these conditions occurred repeatedly over the geological times. Two branches of study support this idea:

1- the biochemical characterization of immature organic rich rocks, sediments and oil related to evaporite system (Connan *et al*, 1986; Brassel *et al*, 1988; Ten Have *et al*, 1988; de'Leew and Sinighe damste' 1990

2- studies of types and quality of organic matter associated with evaporitic environments (Lavor, 1989; Barbe *et al*, 1990 and Grimalt *et al*, 1991).

Hofmann *et al*, 1993 studied the organic matter of the Mulhose basin, France and conclude that the evaporite sediments (anhydrite, halite and sylvite) of Mulhose basin were probably deposited in Monomictic Lake and the formation of organic matter-rich evaporite deposits was preserved by the high rate of sedimentation rates.

Benali *et al*, 1995 studied the characterization of organic matter from a restricted/ evaporative environments of late Miocene age of Lorca basin, Southeastern Spain and proposed that such regions are highly biological productivity, usually from planktonic population and there

is a strong likelihood that evaporite-related organics will accumulated and be sealed by evaporite beds themselves.

The present work is considered to clarify and/or to investigate the relationships between organic material accumulation, preservations and evaporite. The main target of this chapter is to answer whether or not the thermal and source rock evaluation of evaporite deposits through studying the recent restricted and evaporative environments (coastal sabkha and old evaporite of Miocene age) from the Gulf of Suez and Mediterranean Sea regions. In order to know if these evaporite deposits could act and measured as a source rock for hydrocarbons and the encountered potentialities to be used economically in Egypt, however, in Gulf of Suez basin, several attempts have been done to study the Miocene and Pre-Miocene source rocks, among of them Abdel Azim, 1970; Bobbit and Gallagher, 1978; Rohrbach, 1980 and 1982; Barakat, 1982; Shahin and Shehab, 1984; Shahin, 1988; Shahin *et al*, 1994 and Essam *et al*, 1995, but it still needs more comprehensive source investigation to grade targets and reduce exploration risk.

The analytical procedures that were described in detail in chapter Three have been preformed on whole rock samples, insoluble organic matter (kerogen) and soluble organic matter (bitumen) for both evaporite sediments of recent coastal sabkha and evaporite cores of Miocene age found in Gulf of Suez and Mediterranean Sea.

2. Significance of Obtained Data:

2.1. Ras Shukeir Coastal Sabkha Area:

Evaporite formed in restricted-marine, marine marginal (mixed water) and continental setting (Schreiber, 1986) and the extent of organic production, preservation and destruction dictated by the physical condition of each setting. Hypersaline environments as evaporite setting

have been studied by different authors among of them Kirkland and Evan, 1985; Fridman *et al*, 1985; Hofmann *et al*, 1993 and Benali *et al*, 1995. These studies concluded that the all hypersaline environments have high biological productivity in the exposed surface on the margin and water brine body as a whole. Good preservation condition of these organics can exist in stable, high density stratified hypersaline water bodies with highly saline at bottom and shallow, moderately saline upper water body (Hofmann *et al*, 1993 and Benali *et al*, 1995). This agreement was discussed and accepted in chapter-5 (brine chemistry) of this work. This is conformable with the field observation of Ras Shukeir coastal sabkha (Chapter Two)

Ten Haven *et al*, 1985; Sinnighe Damste' *et al* 1985 and other suggested that the evaporite that were formed in different environments are rich in organics and the organics species will produce hydrocarbons if it were subjected to an appropriate thermal regime. Generally, the total organic carbon contents (TOC) of the analyzed evaporite samples from Ras Shukeir sabkha are moderately high. The values of TOC content range from 0.34 to 2.44-wt% (Table-10) suggesting marginal to good organic richness. However, some of these analyzed samples have low TOC contents suggesting lean organic richness. The low contents ranges from 0.08 to 0.16-wt% which may be attributed to the dilution of organic matter by the high rate of sedimentations of evaporite sediments (Schreiber *et al*, 1986) even if the primary productivity is high and the prevailing conditions are favorable (Hofmann *et al*, 1993).

The total organic carbon is good indicators for the organic richness while the pyrolysis analysis can be clarifies the organic type, potentialities as well as the thermal maturation level as indicated by different parameters. The S₂ values of Rocky-Eval pyrolysis for the analyzed evaporite samples from Ras Shukeir sabkha ranges from 0.45 to 11.6 mg/g suggesting poor to excellent hydrocarbon potentialities for these samples (Table-10).

The Kerogen types and its natural quality (gas or oil prone) are based mainly on the Rocky-Eval pyrolysis parameters. These parameters are: 1-the hydrogen and oxygen indices, 2- quality index (QI) and 3- pyrolyzable carbon value (Pc), where $Pc = K (S_1 + S_2)$. $K = 0.083$ (Table-10), knowing that these parameters are applied together.

The Rocky-Eval Pyrolysis data of the evaporite samples representing that the hydrogen and oxygen indices (“HI” and “OI”) values range from 132 to 559mg/g of TOC and 12 mg/g to 170mg/g of TOC respectively (Table-10). This wide range may be attributed to the change of the basin conditions. The position of these analyzed samples upon plotting on the modified Van Krevelen diagram indicate that the organic matter is characterized by kerogen content belonging to type I and II of oil prone (Fig.45). These kerogen types are believed to be deriving mainly from algal and planktonic biomass together with microbial residues that accumulated under saline to hypersaline and moderately to highly moderately reducing conditions (Ganz *et al*, 1990). These results are in agreement with observing algal mat in and around the hypersaline pans of Ras Shukeir Sabkha (Chapter Two).

The quality index (S_2/S_3) of Rocky-Eval pyrolysis is ratio represent the hydrogen to oxygen content of kerogen and can be used as guideline to predict whether or not a source rock is oil or gas. The values of quality index for the analyzed evaporite samples are generally high >5 , Table -10. These high values indicate that the kerogen is corresponding to oil and gas prone (type I and II)

The pyrolyzable carbon (Pc) parameter of Rocky-Eval can be correlated with the types of organic matter. The Pc values of the analyzed samples are high suggesting the presence of oil and gas prone kerogen as indicated by the next two parameters where the pyrolyzable carbon (Pc) values represent the 40-60% of TOC content.

The Maximum temperature of pyrolysis ($T_{\max}$) for the analyzed evaporite samples range from 348C° to 439C° demonstrating that the low degree of thermal maturity for the kerogen content of these analyzed samples (Table-10). The immaturity level is supported by the low values of production index of pyrolysis (S_1/S_2+S_3), which is known as the transformation ratio that is increase with increasing maturity as hydrocarbon generated. These low values indicate the low grade of the thermal maturity in agreement with $T_{\max}$ parameter.

2.2. Ras Gemsa Area:

The Total organic carbon content (TOC) of the evaporite core samples from wells numbers Gs-89-02, 03,04,05 and 06 from Ras Gemsa area are generally moderately high (Table-10). The values of TOC contents range from 0.42 to 5.95wt% which suggesting fair to excellent organic richness; however, some of these analyzed core samples from these different wells have low TOC contents, which indicate poor organic richness. The observed low values of TOC content explain the variation in the sedimentation rates of evaporite sediments, where the high sedimentation rates of evaporite dilute the organic matter of the sediments (Schreiber *et al*, 1986 and Hofmann *et al*, 1995).

The total organic carbon is a good indicator for the organic richness while the pyrolysis analysis can be clarifies the organic type, potentialities as well as the thermal maturation level as indicated by different parameters. The S_2 values of Rocky-Eval pyrolysis for these analyzed evaporite core samples from the wells belong to Ras Gemsa are generally low. They yield a rang from 0.27 mg/g to 1.36 mg/g (Table-10) that suggesting poor source rock potentials, however, the samples intervals of depths (370.2m, 405.2m, 234.7m and 211.8m) from well numbers Gs-89-02, 03,05 and 06 respectively have high S_2 values. These S_2 values yield from range 3.88 mg/g to 11.66 mg/g (Table-10), which indicate well to excellent hydrocarbon potentials.

Kerogen is usually examined by two ways in order to evaluate its quality and proneness. The evaluation of kerogen quality determined by microscopic examination, while the proneness by plotting the elemental ratios or pyrolysis (Tissot and Welte, 1984) or by IR Spectra (A and C factors, Ganz, 1987). For Ras Gemsa area the kerogen types and its quality are based mainly on the Rocky-Eval pyrolysis, IR spectra and gas chromatograph analysis for bitumen extracts.

The position hydrogen indices (HI) and oxygen indices (OI) of Rocky-Eval pyrolysis parameters for analyzed core samples from Ras Gemsa area in modified Van Krevelen diagram (Fig. 46) indicate that the characteristic kerogen contents belong to type I and II with significant amount of type II/III and III, which are supported by both quality index and the pyrolyzable carbon parameters of Rocky-Eval pyrolysis (Table-10).

The available IR data on the evaporite core samples from well numbers Gs-89-02, 03,04,05 and 06 belong Ras Gemsa area provide evidences on the origin matter as well as the kerogen types. The results derived from IR analysis of kerogen indicate a variation in contributions of autochthonous and allochthonous organic matters in evaporite sediments, where the main kerogen types are type I, II and III (Fig.47) as indicated by Rocky-Eval pyrolysis data. The kerogen type I and II are oil prone and derived mainly from algal and planktonic biomass together with bacterial residues accumulated under saline to hypersaline and moderately to moderately high reducing condition and Kerogen type II/III derived mainly from oxidation during the deposition (Ganz *et al*, 1990) but the type III derived mainly from land derived materials or terrestrial origin (Tissot *et al*, 1984). These samples have the most potential for hydrocarbons (yields oil) as indicated by their high A-factor and TOC (Table-11) where A-factor of IR-analysis could also be used to defined the hydrocarbon potentials of organic rich rocks (Ganz *et al*, 1990).

The source of organic matter content of these evaporite samples is confirmed by the results of gas chromatograph for extracts. The n-alkane distribution pattern provides several parameters to differentiate the source of the organic matter, the level of maturity and the environment of deposition. The gaschromtograph analyses of extracts show (Figs. 48A, 48B and 48C): 1-a predominance of acyclic isoprenoids and n-alkane in region of C_{15} - C_{28} with no marked odd or even predominance which indicates significant contribution of algal/bacterial organic matter to the evaporite deposited in hypersaline environments with lack of terrestrial derived organic debris (Philip, 1985 and Ducan *et al*, 1988), 2-a relative abundance of phytane and low pristane/phytane ratios (<1), which were attributed to the highly reducing (anoxic) condition and/or bacterial biosynthesis (Maxwell *et al*, 1972 and Didyk *et al*, 1981) (Table-12) and 3- a relative enrichment ratios of $Pr/n-C_{17}$ and $Ph/n-C_{18}$ (<1) supports the marine origin and contribution of the archaeobacterial input to highly reducing environment of deposition (Table-12). The land derived organic debris input to the organic matter of these evaporite deposits is indicated by the presence of n-alkane $> C_{23}$ of typical higher plant waxy (Waples, 1985 and Simoneit, 1986) and bimodal distribution of the n-alkane of extracts.

The maturity evaluations of the analyzed samples are based on the vitrinite reflectance equivalent, maximum temperature (T_{max}) of Rocky-Eval pyrolysis and GC results of the extracts for Ras Gemsa area. The vitrinite reflectance equivalents of all analyzed evaporite samples from Ras Gemsa area confirm the low degree of thermal maturity where it range from 0.28 $R_0\%$ to 0.38 $R_0\%$ (Table-11). This immaturity state is supported by the low T_{max} values of the Rocky-Eval pyrolysis (range from 340C° to 430C°, Table-10. The n-alkane distribution patterns of the extracts indicate the immature state for all analyzed samples in agreement with IR analysis on kerogen and Rocky-Eval pyrolysis by the relative abundance of phytane over pristane ($Pr/Ph <1$) and low $pr/n-C_{17}$ and $ph/n-C_{18}$ ratios, where these ratios decrease significantly with increasing the maturity (Powell and Mackirdy, 1973 and Tissot *et al* 1971). The low grade of thermal

maturity is also indicated by the relative presence of n-alkane $< C_{23}$. The most of above-mentioned results were represented in geochemical log (Figs. 49, 50, 51 and 52).

2. 3.Southeast Zeit Area:

The total organic carbon content (TOC) of analyzed evaporite core samples from well number Gs-89-07 belong the Southeast Zeit area is generally lean (range from 0.08wt% to 0.17wt%) which suggesting poor organic richness, however, the samples from depths (87.2m and 101.5m) have high TOC contents (range from 2.19 wt% to 3.01wt%) which indicates good organic richness to be excellent source rock (Table-10). The low TOC content of the most evaporite is explained by the variation in sedimentation rate where the high rate of sedimentation of evaporite sediments over any type of sediments as a diagnostic features for evaporite dilute the organic matter even if the primary productivity is high and the prevailing conditions are favorable (Schreiber, 1986 and Hofmann *et al*, 1995).

The pyrolysis analysis can be clarifies the organic type, potentialities as well as the thermal maturation level as indicated by different parameters. The S_2 values of Rocky-Eval pyrolysis for all analyzed evaporite core samples are generally low yields which suggesting poor source rock potentials for hydrocarbon generation. This low generation may be attributed to the poor preservation or oxidation of organics after deposition by subaerial exposure due to the tectonic up lift that characterized the Gulf region.

The Kerogen types and its quality nature (gas or oil prone) for the analyzed core samples from well: Gs-89-07 of this area is based mainly on the Rocky-Eval pyrolysis parameters. These parameters that used together are: 1-the hydrogen and oxygen indices, 2- quality index (QI) and 3- pyrolyzable carbon value (Pc), where $Pc = K (S_1 + S_2)$. $K = 0.083$ (Table-10). The characteristic kerogen of evaporite sediments from this area is type II and/or II/III with presence of type III as

indicated from the position of their hydrogen and oxygen indices in modified Van Krevelen diagram (Fig.53). This result is supported by low values of quality index and pyrolyzable carbon (<2.5), which indicate the presence of gas prone kerogen (type II/III); derived mainly from the oxidation during the deposition, while type III is mainly from terrestrial origin (Simoneit, 1986 and Ganz *et al*, 1990). The low values of the maximum temperature of pyrolysis (T_{max}) confirm the low degree of thermal maturity for all analyzed evaporite samples where its range is from 284C° to 371 C° (Table-10). The above-described results are represented in the geochemical log (Fig. 54).

2.4. Ras Dib Area:

The total organic carbon contents (TOC) of the analyzed evaporite core samples of well numbers Gs-89-08, 09,10,11,12,13 and 14 from Ras Dib area are range from 0.12wt% to 1.0wt%, which suggesting lean to fair organic richness to source rock for hydrocarbons, however, some evaporite core intervals (120.1m, 67.9,68.2m, 52.2m and 84.8m) from well numbers Gs-89-08, 09,12,13 and 14 respectively have TOC content range from 1.62wt% to 2.44 wt% which indicate good to excellent organic richness to be source for hydrocarbons (Table-10). The low organic richness of these evaporite samples explained to the dilution of organic matter by the high sedimentations rate of evaporite sediments (Schreiber *et al*, 1986) even if the primary productivity is high and the prevailing conditions are favorable (Hofmann *et al*, 1993).

The hydrocarbons potentialities of the analyzed evaporite core samples from Ras Dib area are generally poor to fair yield for hydrocarbon generation as indicated from the S_2 values of Rocky-Eval pyrolysis data (Table-10). The evaporite core samples of depths 102.1m and 67.9m from well numbers Gs-89-08 and 09 have very high S_2 yields values (12.48 and 13.66 mg/g of TOC) which suggesting excellent potential for hydrocarbon generation.

The IR analysis of kerogen indicates that the organic matter characterized by kerogen types I and II of mostly oil and gas prone. This result is confirmed by the Rocky-Eval pyrolysis data, where the position of hydrogen and oxygen indices for the analyzed evaporite samples in modified Van Krevelen diagram suggesting the kerogen content are belonging to types I and II with presence of type II/III and III, (Figs. 55 and 56). The types I and II of kerogen are believed to be derived mainly from algal and planktonic population together with microbial residues accumulated under saline to hypersaline and moderately to moderately high reducing (anoxic) conditions while the type III of kerogen derived mainly from land derived organic debris and the presence of kerogen of type II/III indicates the oxidation during the deposition (Ganz *et al*, 1990).

The marine source of the organic matter contents with significant contribution from terrestrial source and their environmental deposition of these evaporite samples were confirmed also by the gas chromatograph results. The low Pr/Ph ratio (<1), the relative predominance of phytane over the $n\text{-C}_{18}$ ($\text{Ph}/n\text{-C}_{18} >1$) and the presence of gammacerane indicates a marine algal and bacterial source mixed with higher plant derived organic debris deposited under highly reducing (anoxic) and hypersaline conditions (Waples, 1985 and Ping'an *et al*, 1991), (Table-12 and Figs. 57 and 58). The type III of kerogen is attested by the presence of heavier n -alkane and bimodal distribution pattern of extracts.

The vitrinite reflectance equivalent for the all analyzed samples from this area are low (range from 0.29 $R_0\%$ to 0.4 $R_0\%$, Table-11 and Fig.55) that indicate the low degree of thermal maturity of organic matter, which is supported by the low of the maximum temperature (T_{max}) of pyrolysis (its range from 274 $^{\circ}\text{C}$ to 421 $^{\circ}\text{C}$, Table-10). This immaturity state is indicated by the n -alkane distribution pattern of extracts. The predominance of phytane, the high $\text{Ph}/n\text{-C}_{18}$ ratio (>1), the abundance of phytane over pristane ($\text{Pr}/\text{Ph} <1$) and the presence of naphthene bulge

between C₂₅-C₃₂ all confirm the low degree of thermal maturity, Fig. 57B. (Tissot, 1971 and Powell and Mckirdy, 1973). In general the kerogen data coupled with both GC and pyrolysis analyses, which confirm that the organic matter derived from marine algal and bacterial, mixed with terrestrial origin accumulated under saline to hypersaline and highly anoxic condition, mostly immature with high potential for oil and/or gas that indicated by their high A-factors and TOC content (Table-11). Some of the data were summarized in the geochemical logs, figures 59 and 60.

2.5. Shagar Area:

The total organic carbon contents (TOC) of the analyzed evaporite core samples from Wells numbers Gs-89 15A and 16 belong to Shagar area range from 0.17wt% to 0.39wt% (Table-10). The TOC values demonstrate lean to fair organic richness to be source rock for hydrocarbons. The high sedimentation rate of evaporite over other sediments dilutes the organic matter, which cause lowering the TOC values of the evaporite samples (Hofmann *et al*, 1995).

The S₂ parameter of Rocky-Eval pyrolysis indicates that the potentialities of the analyzed evaporite samples for hydrocarbons generation are generally poor, where the S₂ values yields less than 2mg/g of TOC (Table-10).

IR analysis on kerogen provided that the kerogen contents of all analyzed evaporite samples are belonging to types II and/or II/III of oil or gas prone nature, indicating the organic matter of marine source mixed with terrigenous derived organic debris, while the type II/III indicates the oxidation during the depositions. The marine source of the organic matter is supported by Rocky-Eval pyrolysis where the position for hydrogen and oxygen indices (HI and OI) for the analyzed evaporite samples in modified Van Krevelen diagram indicate that the organic matter characterized by type II and II/III with the presence of type III that indicate the

terrigenous influx (Figs.61 and 62). The type and the source of these organic matter contents are confirmed by gas chromatograph analysis for selected samples (Fig.63)

The immaturity level of the organic matter is confirmed by the low values of maximum temperature (T_{max}) of pyrolysis (it range from 213C° to 220C°). This low degree of thermal maturity is indicated by the low value of vitrinite reflectance equivalent grids. (Fig.62). The geochemical logs, figs.65 and 66, summarized the geochemical data.

2.6. Gubal Island:

The total organic carbon of the analyzed evaporite core samples from Well numbers Gs-90-17 and 18 ranges from 0.18wt% to 0.95wt% (Table-10) which suggesting lean to fair organic richness to be source rock for hydrocarbon generation. These low values of the TOC is belived to be due to the dilution of organic matter by the high rate of sedimentation of evaporite sediment over than the other sediment as a diagnostic feature of evaporite sedimentation (Schreiber, 1980 and Hofmann *et al*, 1993).

The potentialities for hydrocarbon generation are generally low for all analyzed evaporite samples as indicated by the low values of S_2 of Rocky-Eval pyrolysis data (range from 0.15 to 0.99 mg/g of TOC), Table-10. The low potential for hydrocarbon is explained by the dilution of organic matter or poor preservation due to tectonic influence affected the whole area.

The Rocky-Eval pyrolysis data of the evaporite core samples representing that the hydrogen and oxygen indices (HI and OI) values range from 183 to 636 mg/g of TOC and 8 to 39mg/g of TOC respectively. This wide range reflect the change the basin condition and /or the organic contribution. The position of these analyzed samples in modified Van Krevelen diagram indicate that the organic matter is characterized by kerogen content belong to type I, II and III.

II/III (Fig. 67). These types of kerogen indicate the marine algal and planktonic biomass together with microbial or bacterial source accumulated under saline to hypersaline and moderately high reducing conditions (anoxic), while the presences of type II/III indicate the oxidation during the deposition. The IR analysis on kerogen from the selected samples confirms the origin of the organic matter (Fig. 62).

The results of gas chromatograph for the extracts reveal significant indication of the origin, thermal maturity and the environmental deposition. The low Pr/Ph ratios (<1), Table-12, indicate the moderately high reducing condition and a high population of archaebacterial during sedimentation of evaporite sediments (Didyk *et al*, 1978 and Michaels and Albrech, 1979). The unimodal distribution pattern of n-alkane and high ratios of $\text{Ph}/\text{n-C}_{18} >1$ (Fig. 68 and Table -12) indicates a marine source of the organic matter mixed with significant terrestrial influx during the deposition. The relative abundance of n-C₁₇ where $\text{Pr}/\text{n-C}_{17} <1$, confirm the marine planktonic and algal source of the organic matter, Table-12, Venkatesan *et al*, 1982. The low maturity level was indicated by the predominance of phytane, the low Pr/Ph ratios, the abundance of phytane relative to n-C₁₈ ($\text{Ph}/\text{n-C}_{18} >1$) where these ratios decrease significantly with increasing the maturity and the presence n-alkane bulge under C₂₃-C₃₁, fig.68B. The low values of maximum temperature (T_{max}) of pyrolysis (range from 219 C° to 428 C°) and low vitrinite reflectance equivalent $R_0\%$ (range from 0.28 $R_0\%$ to 0.29 $R_0\%$) supported the low degree of thermal maturity of these analyzed samples (Table-11). The above-mentioned data represented in geochemical logs, figs. 69 and 70.

2.7. Esh El-Malaha Area:

The analyzed evaporite core samples from different Wells belong to Esh El-Malaha area is characterized by low to moderate TOC contents. The TOC contents range from 0.12wt% to 0.82 wt%, which suggesting lean to fair organic richness. The S_2 values of pyrolysis are generally low

for all analyzed samples. The values of S_2 parameter of Rocky-Eval pyrolysis range from 0.0 to 0.66mg/g of TOC yield which suggesting poor hydrocarbon generation, Table-10.

The organic matters of the analyzed samples characterized by kerogen types belong to type II and/or II/III as indicated by IR analysis on kerogen, Figure. 62. The Rocky-Eval pyrolysis and GC support this result (Fig. 64). The position of the analyzed samples on Van Krevelen diagram indicate that the characteristics kerogen is type II/III, i.e. marine origin derived from bacterial and algal source and oxidized during the deposition (high oxygen and low hydrogen indices), Ganz, 1990, Fig. 71.

The GC analysis of the extracts show: 1- the high ratios of Pr/ n-C₁₇ and Ph/n-C₁₈ (>1) which indicate marine source, 2- the relative predominance of pristane relative to n-C₁₇ indicate marine organic matter derived from planktonic populations, 3- low ratios of Pr/Ph, (Pr/Ph <1) indicates the highly reducing conditions, and 4- the presence of gammacerane and predominance of acyclic isoprenoids indicates that the sediments deposited under hypersaline conditions (Waples, 1985 and Ping'an *et al*, 1991), Table-12 and Fig. 64

The organic matter in all studied samples generally immature as indicated from; 1- the vitrinite reflectance equivalent, 2- the predominance of phytane and pristane relative to n-C₁₈ and n-C₁₇, 3- the abundance of phytane, 4- Pr/Ph <1 and 5- the low maximum temperature of pyrolysis (T_{max}).

2.8. North Sinai:

The tentative available core samples from different Wells (No. 88-15, 26, 34 and 44) belong to North Sinai area, Mediterranean Sea, is characterized by its low total organic carbon content (TOC). The TOC contents of the analyzed evaporite samples range from 0.09 wt% to 0.26wt%,

which suggesting lean to marginal source rock. This low range is attributed to the dilution of organic matter by the high rate of evaporite sedimentation over than other sediments (Schreiber *et al*, 1986), Table-10.

The S_2 values of the Rocky-Eval pyrolysis for the analyzed samples are low yields than the potential of the samples from the Gulf of Suez. It ranges from 0.08 to 0.2mg/g, yields which suggesting poor hydrocarbon potentialities for these samples. The Rock-Eval pyrolysis data show that the evaporites have hydrogen and oxygen indices (HI and OI) range from 69 to 138 mg/g of TOC and 46 to 200 mg/g of TOC respectively. Their position o modified Van Krevelen diagram indicates that the organic matter characterized by kerogen belong to kerogen types II and/or II-III. The II of kerogen are derived manly from marine source (algal and planktonic population together with microbial residues, (Ganz, 1990) mixed with terrigenous source, while the type II-III of kerogen is belived to be due to the oxidation during the deposition (Fig. 72).

The type and the quality nature (gas prone) of kerogen content of the organic matter are indicated by the low the quality index (<5) and pyrolyzable carbon value of Rocky-Eval pyrolysis, Table-11. The maximum temperature (T_{max}) of pyrolysis is very low. It ranges from 322 C° to 420C° that indicates the low degree of thermal maturity of these analyzed samples. This immaturity state is supported by the low values of production index of pyrolysis (S_1/S_2+S_3), which is known as the transformation ratio that is increase with increasing maturity as hydrocarbon generated. These low values indicate the low grade of the thermal maturity in agreement with T_{max} parameter.