CHAPTER FOUR

SAMPLING AND APPLIED TECHNIQUES

This chapter summarizes the sampling and all executed analysis for the collected brine and rock samples. Analytical pathway and procedure of treatment(s) are shown on the flow chart (Fig. 35 and Table-1), while the detailed laboratory procedures and techniques are given as follows:

1. Sampling:

1.1. Brine Sampling:

The brine samples were collected from different hypersalline pools of Ras Shukeir area. The brine samples covering different profiles across each pool with respect to their depths and salinities were followed in a systematic way. The depths of the pools were measured and found with a range between 15 cm up to 7.5m .The gradient of the collected samples (24 in number) were given on the table-6. The samples were collected using vertical diving device and the depth profile is seen in figure-40. The collected brine samples were subjected to determining their chemical characteristics through determining their major cations and anions (K^+, Na^+, Ca^{++}, Mg^{++}, Cl^-, $HCO3^-$, $SO4^-$, $CO3^-$, pH, salinity and T.D.S) in addition to identification of their physical properties (Resistively, conductivity, density and specific gravity) by using different geological techniques

1.2. Core sampling:

Core samples from off shore and on shore wells of Miocene evaporites from Gulf of Suez and Mediterranean Sea as well as shallow deep cores from Ras Shukeir recent sabkha area were selected representing different macro- and micro-lithofacies. The subsurface shallow deep cores at Ras Shukeir area were drilled along profile C1, C3, C4, C5 and C6 (Fig.23) covering the encountered defined facies as described in the previous Chapter. The shallow deep cores from

the recent sabkha were collected through hammering plastic rigid tube down to average depth of 100 cm and then the sealed and pulled out. The pipes were opened and slapped for detailed description and processing to elucidate the relative distribution of clastic, evaporite and organic component. The cores samples were subjected to petrographical, mineralogical, inorganic and organic geochemistry analysis by using the following different geological techniques.

2. Applied Techniques:

2.1. Microscopic Technique:

Microscopic technique was used to study the petrography of different lithofacies in order to determine their mineral constituents, diagensis, mode of occurrences and distribution of organic material. The selected samples were prepared to study them under the petrographic polarized microscope. More than 120 thin-sections representing the described different evaporite lithofacies in the studied subsurface cores from the recent sabkha and the different wells from different areas and were prepared following the procedure described by Miller (1988).

2.2. Scanning Electron Microscope and EDX Techniques:

SEM with EDX technique was used to study and to examine the structure textured of the rock constituent, diagenitic sequence and the form of the present organic material, particularly in rich organic sediments.

a. Selection of samples:

SEM is a technique applied to illustrate the micro-fabric relation(s) of the examined samples as well as their textural (original and obliterated). Also the specimens are unlikely to be totally representative of the sample from which they are prepared. It for this reasons that it was not felt necessary to examine every sample using SEM

b. Sample preparation.

Mounting: A cube of rock 0.5 Cm was cut from the center of sample. The cube was split in half. Each half was mounted; fracture surface upper most, on aluminum stubs with Durafir glue. When the glue had hardened, the sample is then placed on the stub and stored in desiccators till father processing and/or examination after coating. The slides of each specimen were painted with silver paint.

Pre-coating: Preventing of Electrostatic charge charging the surface layer of the specimens occurs when electron unable to conducted away. A charged region is seen brightly glowing area in which eventually images loose all details. Before coating, loose particles were removed from the fracture surface by sharply tapping the stubs. Bust particles were removed by application of electrostatic charge.

Coating: The specimens were given a thin electrically conducting coating under vacuum using a sputter coater.

- SEM equipment

The used instrument in this study was a Joel sm 5300 with link energy dispersive X-ray analyzer and CL. Cathodluminescencead scattered detectors. The secondary electron image resolution is 4.5mm (SEI, 30kv, wd =8mm), accelerating voltage is 0.5 to 3kv, 0.1kv/step (26 steps) and 5 to30kv; 5kv/step (6 steps) linked with objective lens hysteresis eliminating function for selecting accelerating voltage. Electron gun filament represented by hairpin filament cartridge type; gun bias: Auto; for high accelerating voltage (2.1 to 30kv and for low Acc.V. (0.5 to 2kv), magnification display: x15 to 200.000, specimen size maximum 150mm, observation CRT: green, 9 inch for observation and photography, frame size: 135X180 mm (TV). Scanning speed: 0.27, 0.58, 2.88, 9.6 sec/frame, TV scan for observation and28.8, 86.4 sec/frame (50HZ) 24, 72 sec/frame (60HZ) for photographing and fully automated system.

- Quantitative X-Ray analysis:

When the electron beam strikes the specimen the electrons penetrate the specimen and exit the atoms comprising specimen. Amongst other phenomena, this result in the generation of X-ray, which have wavelengths characteristics of particular excited atoms?. The X-ray can be detected and analyzed. This kind of analysis can only be qualitative because the rough surface of the specimen result in spurious X-ray generated by back scattering and because of differential absorption by specimen of X-ray of different wavelength. X-ray from elements lighter than sodium are so strongly adsorbed that they are not detected. The analyses are obtained from individual particles by spot.

2.3. XRD Technique:

XRD for the selected bulk samples were used to identify the minerals and supplemented the identification of minerals in thin section and SEM. X-ray diffraction (XRD) analysis was carried out using Phillips X-ray diffraction. The minerals identifications were according to their principal characteristics diffracted peaks. Semi-quantitative of minerals were carried on according to peaks intensity.

2.4. ICP Techniques:

The major Cations and Anions of the water brine samples from the studied area were measured by titration, flamphotometer and Inductively Coupled Argon Plasma optical emission spectroscopy (ICP). The obtained results including the phsical and chemical properities were listed in Table-6 . The The resuts of chmeical analysis were evaluated by using statistical and geological computer programs (e.g. SPSS, Rock work, Hydro Chem).

a- Instrument

The instrument used in this study SpectroFlame Modula ICP by spectroanalytical instrument, Germany (*Slickers, K., 1993*).

b- Method of Determing of cations and anions Concentration and Operating Conditions

(ASTMD1976-91). For exampe Calcium concenteration was detrmined as follows

1. The instrument was first calibrated on a calcium line (315.887 nm) using two different known concentrations of standard calcium solution. (Fig. 36).

2. A series of standard calcium solutions of concentrations ranging from 0 to 60 ppm were prepared.

3. Intensity of each standard was determined at the same wavelength by ICP.

4. Calibration curve was constructed using the instrument software (Fig.37).

The unknown samples were then introduced and calcium ion concentrations were determined by means of these calibration curves. All operating conditions were given in Table-2

2.5. Organic Geochemistry Techniques:

The executed organic geochemistry techniques include: 1- Leco Carbon analyzer, 2- Rocky-Eval Pyrolysis and 3- Gas chromatography and Infrared Spectrometer. These techniques were used to determining and measuring the TOC content, the thermal maturity and hydrocarbon potentialities of the selected core samples after preparation to conduct these analyses as follows. All these techniques were carried out in SCS Service Company.

- Sample Preparation:

Representative samples from shallow deep cores from Ras Shukeir area and conventional cores of offshore and onshore well from the studied fields are assigned a number, which is entered into a computer system to monitor sample selection and progress. Preparation techniques are directed towards obtaining clean samples, free from drilling mud and mud additives.

Washing with cold water is standard but further washing with solvent (dichloromethane, DCM) is carried out if oil based mud is present. After washing samples are dried then rough crushed to approximately pea-sized for kerogen preparation or finely milled for chemical analysis.

2.5.1. Total organic Carbon Content (TOC) technique:

Organic carbon values are obtained by treating 0.1 g of sample with hot concentrated HCl to remove carbonates. The washed residue is filtered on to a glass fiber pad and ignited in a Leco Carbon Analyzer C/S-12. For screening purposes, samples are analyzed singly but where further analysis, such as pyrolysis or solvent extractions are anticipated a duplicated sample is run. Blank and standards are run as routine and where values from duplicated samples don't concur within accuracy limits. Where samples are heavily stained with oil, either from natural deposits or drilling mud, TOC is repeated on the drilled, solvent extracted sample. TOC measurement is fundamental in assessing source rock quality since when combined with kerogen types and maturity; a full description of potential to generate oil may be given. It's found in practice that the sediments containing less 0.3% TOC are unlikely to have any source potential, those containing between 0.3 and 1% may be marginal source but better quality sources contain more than 1% TOC.

2.5.2. Rocky-Eval Pyrolysis:

Pyrolysis data are obtained using the IFP-Fina Rocky-Eval apparatus. 100mg of crushed whole rock is weighted accurately into crucible and introduced into a furnace at $250C^\circ$. Free hydrocarbons (roughly equivalent to solvent extractable hydrocarbons) are volatilized and quantified by flame ionization detector (FID) to give peak1 (S_1, ppm). The furnace temperature is increased to $550C^\circ$ at $25C^\circ$/minute and within this range kerogen crack to give hydrocarbons measured by FID to give peak 2 (S_2, ppm) and Carbon dioxide measured by thermal conductivity detector (TCD) to give peak 3 (S_3,ppm). The temperature at maximum rate of evolution of

cracked volatiles (T_{max}) is measured automatically but can also monitored visually. The instrument is calibrated daily using standards both at beginning of work period and at regular intervals thereafter and crucible blanks are run as routine. The tabulated data in this Thesis comprise the following parameters:

T_{max} C°: Temperature of maximum rate of peak 2 hydrocarbon evolution.

Hydrogen Index (HI): S_2/TOC (mg/g) or ratio of released hydrocarbon to organic carbon content. This is a measure of the hydrocarbon generating potential remaining in the kerogen as opposed to that of the whole rock.

Oxygen Index: S_3/TOC (mg/g) or ratio of released Carbon dioxide to organic carbon content

Production Index: S_1/S_1+S_2 or ratio of amount of hydrocarbons released in the first stage of heating to the total amount of hydrocarbons released and cracked during pyrolysis.

Potential Yield: S_2 (ppm) or total hydrocarbons released during cracking of kerogen compared to original weight of rock.

T_{max}, HI and OI are each functions of both maturity and kerogen type. Using published and empirical data, it has been possible to assemble a model to show the relationships of these factors to maturity as measured by IR and vitrinite reflectance for selection pure kerogen types. The kerogen types used are algal sappropel (type I), Waxy sappropel (type II), Vitrinite (Type IIIA) and inertinite (type IIIB) and a computer program has been devised by which the amounts of these components may be calculated from HI, OI, Tmax and maturity data for any sample. These are values expressed in the kerogen composition by calculation (column tabulated) in this work.

2.5.3. Bitumen Extraction:

Traditional soxhlet extraction with CH_2CL_2 is time consuming (24-48 hrs) and large amount of organic solvent must be evaporated. This often causes losses of the light *n*-alkanes. Also, asphaltene/non-asphalene fractionation and column chromatograph are very time-

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consuming methods. These processes have been replaced CH_2CL_2 extraction by ultrasonic agitation and centrifuging. A few grams of the pulverized (dust) samples (depend on the TOC) content) are ultrasonically treated with 30ml of CH_2Cl_2 for 10 minute. After centrifuging for 4 minute at 4000 cm^{-1} and decanting of the solvent, the treatment is repeated at least times to remove all soluble bitumen until the liquid remain clear. The bitumen is collected in lab beakers slightly covered with aluminum foil and placed under hood in order allow slow evaporation of solvent. The extracted sediment is transferred in 100 ml plastic tubes of centrifuge and is ready for HCl/HF treatment of kerogen isolation. After drying, the beakers re-weighted in order to calculate the weight of extracted bitumen, and then the extracted bitumen is transferred to small 5ml vessel for analysis.

2.5.4. Kerogen Isolation:

The residue, after extraction of bitumen, is transferred into plastic tubes, some drops of methanol are added in order enhance their wettability. The residues were treated with (HCl and HF) as described by Foreman and Hunt, 1958 and Ganz et al 1990. The residue treated with HCl (10%) in order to destruct carbonates. The solution is decanted after centrifuging and the sample is treated with conc. HF (about 15ml/40%). In order a good suspension, the mixture is stirred carefully. The plastic tubes are placed in water bath at 70C° for about 3 days, each day the tubes are filled up with additional HF. The solution is decanted after centrifuging and treated with hot HCl (20%) to remove fluorides that might have formed during the solution of minerals. After HCl treatment, the samples are washed twice with hot distilled water and dried after decantation at 60C° in an ordinary laboratory oven. Ganz, 1986 indicates that the hot acid treatment and drying at elevated temperatures for limited times doesn't influence the composition of kerogen. After drying, the kerogen is ground by hand in an agate for 2 minutes. The kerogen is ready now for IR analysis.

2.5.5. IR-Analysis:

Infrared Spectroscopy (IR) is applicable method to kerogen study example (Robin et al 1977; Rouxhet et al, 1980). Also the evolution of kerogen structure during burial is reflected in the infrared spectrum (Tissot et al, 1978). In this work the IR used to determine and evaluated the kerogen types was carried out insitu. The pellets are prepared by mixing 0.4-0.5mg of isolated kerogen with 200mg KBr and carefully homogenized. The pellets are dried under vacuum at 90C° for 4 hrs in oven to insure their complete dehydration before analysis then scanned. The spectral display distinctive peaks at 2860 and2930 cm^{-1} (CH$_2$ and CH$_3$ aliphatic groups respectively) and at 1710 cm^{-1} (Carboxyl and Carbonyl group) and at 1630 cm^{-1}(aromatic C=C bands). With increasing maturation, aliphatic peaks initially decrease while there is no apparent change in the peaks representing the aromatic C=C bands (Ganz et al, 1987). The relative intensities of aliphatic, carbonyl, carboxyl and aromatic peaks (A and C factors) were used to classify the kerogen (ganz, 1978) into different types on cross plot similar to van krevelen diagram (Tissot and wellte, 1984; Ganz and Robison, 1985, Ganz, 1986) where A and C-factors are replaced the pyrolysis hydrogen index (HI) and oxygen index (OI).

A-Factor = 2930+2860 cm^{-1}/2930+2860+1630 cm^{-1}

C-Factor=1710 cm^{-1}/1710+1630 cm^{-1}

IR-diagram (Fig.38) was developed in order to determine thermal maturity by means of vitrinite reflectance equivalent which allows precise determination of Ro% Ganz et al, 1987. A-factor, measured from IR-spectrogram, had also used to define the hydrocarbon potential of the organic rich rocks by means of A-Factor X TOC X 10.

2.5.6. Gas-Chromatography (GC):

"GC" is a common technique used to separate and identify compounds in bitumen and petroleum. This technique used in this study and carried out in SCS service Company. The

samples were injected into the column under stream of carrier gas (example helium), partitioning occur between the gas and hydrocarbon gases. As molecules pass out of other end of the column, they are detected. Samples were injected into Perkin Elmer GC 3A chromatographs equipped with a fused silica capillary column coated with RSL-150 (30m length, 0.5mm I.D. and 0.25μm film thickness) and temperature programmed from 80-300C° at 20 C°/min. Injection was preformed in the split mode and injector and detector temperature were held at 320C°.

C_{15}^+ chromatograms are inspected for the distribution of n-alkanes and the presence and absence of isoprenoids (particularly pristine and phytane), steranes and triterpanes and unresolved envelops of naphthenic compounds. The ratios pristine: phytane and pristine: $n-C_{17}$ with phytane: $n-C_{18}$ is calculated. Carbon preference index (CPI) values quoted at those as defined by Philippi as the ratio $2C_{29}$ to $(C_{28}+C_{30})$ unless otherwise stated. Chromatography may reveal information about the kerogen type of the source rock, its maturity and condition of deposition and if migrant oil is present, whether this has been water flushed or biodegraded. Contaminant drilling mud additives may be identified.

2.6. Fluid Inclusion Analysis Technique:

During crystal growth, small droplets of mother solutions were trapped intracrystalline cavities of the crystal: It called fluid inclusion. The study of these fluid inclusions gives significant indication of salinity and chemical characteristics of the mother inclusion and also hydrocarbons presence.

For fluid inclusion study in this present work, millimeter size fragments of Evaporites (Gypsum, Anhydrite and Halite) were obtained by cleaving the crystals along the perfect (010) cleavage plane, the Petrographic characteristics of fluid inclusion (size, shape, abundance and distribution) within the cleavage fragments of evaporites were studied under the Petrographic Microscope prior to analysis by using magnification 400X.

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Micro thermometer was used the freezing/hearing behavior of the fluid inclusions. Melting temperatures of the solid phases can help the determination of the chemical composition and salinity of the liquid trapped in aqueous inclusion (Roeder, 1972and 1984; Hans, 1985). The freezing/melting behavior of fluid inclusions in millimeter-size cleavage fragments of Gypsum, Anhydrite and Halite crystals were observed using a Fluid Inclusion unit adapted USGS Gas flow heating/Freezing stage mounted to a Petrographic Microscope. This analysis was carried out in Cairo University. Observations were made at magnification of 400Xunder Microscope. One-phase (liquid) inclusions and two-phase (liquid and solid) inclusions were recognized. Putting the sample in a refrigerator for a week produced vapor bubbles in single-phase aqueous inclusions. The volume increase up on freezing caused the inclusions to stretch, leading to formation of a vapor bubble that persisted at room temperature as well as during subsequent freezing runs. Vapor bubbles formed in this way by stretching ensure equilibrium behavior during melting of frozen inclusions and avoid errors in determine ice melting temperatures due to metastable superheated ice and "over expanded liquid" (Roedder 1984, P.295-302 for full discussion). Super cooling to temperatures between 60C ° to 90C° then froze fluid inclusions. The frozen inclusions were then heated 1-2C° per minute and the melting temperatures of solid phases formed during freezing were recorded. Slower heating rates, approximately 0.3C° per minute, were used near temperatures of phase disappearance. The first melting temperature of fluid inclusions (Te) and the final melting temperature of ice (Ti) were recorded. The final ice melting temperatures enable calculation of fluid inclusions salinities and hence parent brine salinities using equation of Potter et al (1978). The final melting temperature of ice was recorded to within 0.1C° and was reproducible to within ±0.2C°, thermocouple accuracy was±0.1C° over the interval investigated (0C° to-40C°).

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