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CHARACTERIZATION OF INORGANIC MATRIX AND POTENTIAL OF ORGANIC MATTER OF SOME EGYPTIAN BLACK SHALE FROM THE WESTERN DESERT, EGYPT

J.S., Basta*, S.I., Shara
Egyptian Petroleum Research Institute Nasr, City 11727, Cairo, Egypt.

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ABSTRACT

Three Egyptian black shale samples were assembled from the main producing Abu Tarture phosphate mine in the Western Desert (Egypt). The black shale rocks were analyzed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques in order to identify the minerals of black shales. It was found that the montmorillonite, smectite, quartz, calcite, gypsum, kaolinite and dolomite constitute the main bulk composition of the inorganic matrix. In addition, SEM micrographs of the black shales indicated that the montmorillonite particles can be regarded as an aggregation of a leaf shape and lameller aggregate structure addressed as papery structure. Bitumen and kerogen concentrates were extracted from the studied oil rocks. Genetic potential of organic matters in the black shales was studied by means of Rock Eval pyrolysis and Fourier Transform Infrared spectroscopy. It was suggested that all the studied samples are not oil source rock with some potentiality for gases

Keywords: Black shale, FTIR, SEM microscopy, Rock Eval pyrolysis, XRD.

INTRODUCTION

Black shale is a natural sedimentary rock containing abundant residual organic materials, which can be converted into oil and fuel [**Razvigorova *et al.*, (2008)**]. The inorganic fraction of the black shale is composed mainly of clay minerals and carbonates. Other minerals such as pyrite may be found in subordinate amounts. The black shale organic matter is composed mainlyof a soluble bitumen fraction and insoluble fraction (kerogen) [**Forsman (1963), Vandenbroucke & largeau (2007)**]. The soluble portion of the organic matter, bitumen, is composed mainly of aliphatic and aromatic hydrocarbons. [**Anabtawi & Hilal, (2004), Kattai *et al.*, (1990), Tyson (1995)**]. The inorganic matrix may contain quartz, feldspars, clay minerals, carbonates and others.

There is a trending belt of phosphate and shale bearing sediment extending from east to west and spanning the lower-middle latitudes of Egypt. The belt is well developed in three regions, namely, Quseir-Safaga region (along the Red Sea coast), Idfu region (along the Nile Valley) and the Kharga-Dakhla region (in the Western

Desert). First preliminary estimation of the oil shale potential in the Red Sea area indicated that a reserve of some billions of barrels of oil exist in place **[Truger (1987)]**. Fig. (1) illustrates the location of the studied black shale samples pertaining to the Upper Cretaceous sediments that are rich with organic materials **[Ganz & Kalkreuth (1987)]**.

In the present study, three samples were collected from black shale beds exposed at the Abu Tarture phosphate mine. Identification of the samples is given in Table (1) and Fig. (1) **[Said (1962)]**.

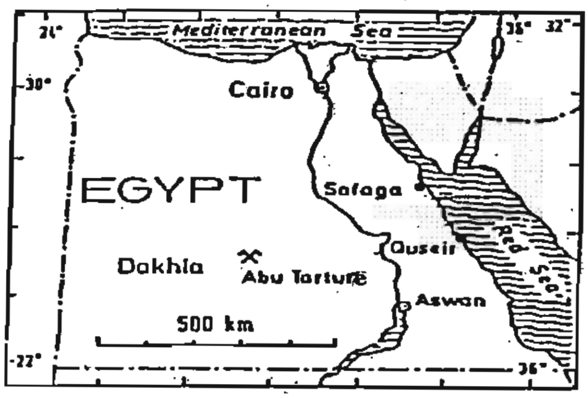

Fig. 1: The location of black shale samples

Table (1): Location and identification of the black shale samples

Sample No.	Location	Formation	Age
1 2 3	Abu Tarture	Duwi	Upper Companion to Lower Maastrichtian

EXPERIMENTAL

Preparation of Black Shale Samples:

One kilogram of black shale sample was ground in a ball mill and sieved. A portion < 200 mesh was chosen for different analyses procedures and extraction processes. An accurate weight of the sample was dried at 100°C. The dried sample was weighed and the percentage of moisture was calculated from the weight loss.

Extraction of Organic Matter:

Bitumen was extracted in a soxhelt using benzene-methanol (70:30 vol/vol) for ~ 72h. Then the solvent was removed by means of rotary evaporation at mild conditions. The solvent-free bitumen was weighed and stored for further extraction and analysis. Inorganic matrix, including carbonates and silicates, was removed from the dry black shale sample by the conventional HCl-HF acid extraction method **[Robinson (1969)]**. The kerogen obtained was weighed and stored for analytical investigation.

The removed of inorganic minerals was checked by X-ray diffraction analysis after each step of extraction.

Instrumental Techniques:

The structure parameters derived from the analytical techniques adopted could be utilized to evaluate the potential of organic species and to characterize the composition of whole rocks in the studied area.

Elemental Analysis:

Carbon, hydrogen and nitrogen contents of black shales were determined using Perkin-Elmer elemental analyzer. Total Organic Carbon (TOC) in black shale samples was determined in a carbonate-free sample using a Hochtemperature-TOC/TNb-Analysator (Liquid TOC). Total sulfur content was determined according to ASTM D-2492 standard procedures **[ASTM Standard Method D-2492]**.

Microscopic Studies:

Petrographic characteristics of black shale, as whole-rock samples, were investigated by means of scanning electron microscopy (SEM) technique. SEM analysis was carried out using a scanning electron microscope, Type S-2700, HITACHI, JAPAN. Identification of different minerals through SEM was facilitated by comparing their characteristic morphologies with those shown in SEM petrology Atlas of **[Welton (1984)]**.

X-Ray Diffraction (XRD):

The raw black shale samples and the samples obtained after HCl-HF extraction were analyzed by means of XRD powder technique using X"pent PRO X-ray diffraction system.

FTIR Spectroscopy:

The black shale samples were analyzed using Fourier Transform Infrared (FTIR) Spectroscopy. About 2 mg of sample was mixed efficiently in a mortar and pestle with 200mg of dry KBr. The fine well mixed powder was pressed into a pellet at 10,000 psi. The pellet was loaded into FTIR spectrometer, model 960 Moog, ATT Mattson infinity series and spectra were recorded to cover the region 4000-400cm^{-1}.

Rock-Eval Pyrolysis:

Rock-Eval pyrolysis of the studied black shale samples was carried out in applied Petroleum Technology A.S. in Norway using Rock Eval-6 instrument followed by NIGOGA, 4th edition procedures **[Gouda (2005)]**.

The pyrolysis measured the total hydrocarbons and other gases evolved during pyrolysis. The pyrolyzed hydrocarbons and carbon dioxide were measured as a function of temperature to give program of three peaks (S_1, S_2 and S_3). S_1 represents free hydrocarbons in the rock. S_2 represents hydrocarbons generated from pyrolysis of kerogen. S3 represents the amounts of CO_2 generated from the pyrolysis of oxygenated functions present in kerogen

RESULTS AND DISCUSSION

Results of chemical analysis of black shales are summarized in Table (2). However, the elemental analysis of the black shales is comparable with those obtained for other shales collected from the Red Sea zone or nearly areas such as Safaga, Quseir [**Ganz (1986), Mostafa *et al.*, (1964)**] and Red Sea regions [**Basta (1999)**]. The results showed that the black shale samples have percentages of sulfur contents. This may be attributed to the presence of sulfur containing minerals (gypsum and pyrite) in different amounts as a part of the inorganic matrix.

In order to evaluate the selected samples of black shale, the whole rock samples have been subjected to different analytical procedures, with the aim of characterizing the whole rock composition and studying the genetic potential of organic matter.

Table (2) : Chemical analysis of black shale samples

Analysis	Sample No.		
	(1)	(2)	(3)
Moisture %	4.6	5.2	8.0
Ash%	82.2	83.6	80.9
Total carbon%	15.2	16.4	17.3
Hydrogen%	0.90	1.07	1.10
Nitrogen%	Trace	Nil	Trace
Oxygen %	8.58	8.49	10.07
Total sulfur%	0.92	1.11	2.13
TOC%	0.61	1.12	0.72
Total minerals%	74.40	72.93	69.40

1.Composition of Inorganic Matrix:

1.1.Scanning Electron Microscopy (SEM):

SEM examination was performed for selected samples in order to diagnose and understand the microstructure and diagenetic relationships among the main constituents and the matrix of the studied samples; the SEM micrograph shown in Fig.(2) is observed on a representative sample.

The observations indicate that the smectite is the dominant clay mineral in the studied shale samples of Abu Tarture phosphate mineFig. (2). The SEM micrograph shows also that the smectite particles have expanded, flored "Cornflak" or Okal leaf" like structure. The semectite group minerals are characterized by extremely fine-grained, poorly defined particles with diffuse outlines and curled edges.

The montmorillonite particles can be regarded as an aggregation of a foliated as papery structure Fig. (2). This may be the result of expulsion of water and gas during the compaction and oxidation of organic matter **[Keller *et al.,* (1986)]**. The SEM study of the samples indicates that pyrite crystals may be present as a bright crystals by variable percents.

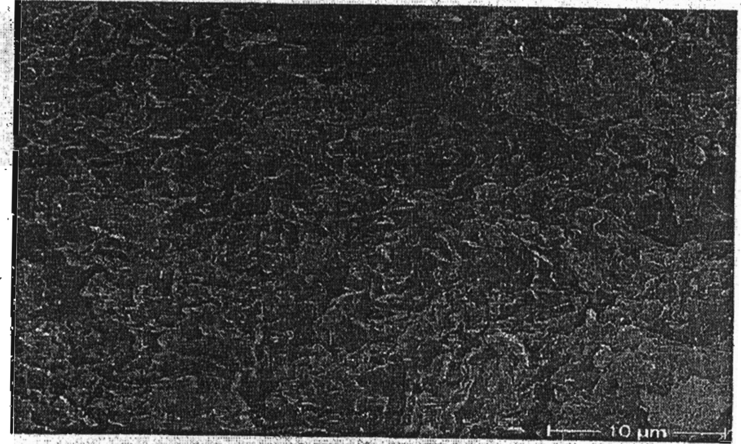

Fig. (2): SEM micrograph of black shale samples in Duwe Formation of Abu Tarture mine

1.2.Identification of Inorganic Minerals by X-Ray Diffraction (XRD):

Inorganic minerals make up about 70% of the black shale samples as revealed from the results of chemical analysis Table (2). XRD was carried out to identify minerals occuring in the black shales. The XRD diffractograms indicated that the shales contain montmorillonite, quartz, kaolinite,calcite, gypsum and dolomite, Figs. (3-6).

The removal of inorganic minerals from the black shales, in order to obtain kerogen concentrates, was checked by XRD analysis after each step of extraction and the results are shown in Figs. (4-6). Benzene-methanol treatment was performed to extract bitumen of the black shale. Evidently, the XRD Patterns of the original shale and bitumen-free (BF) shale show no differencesFigs(.3 and 4)., respectively

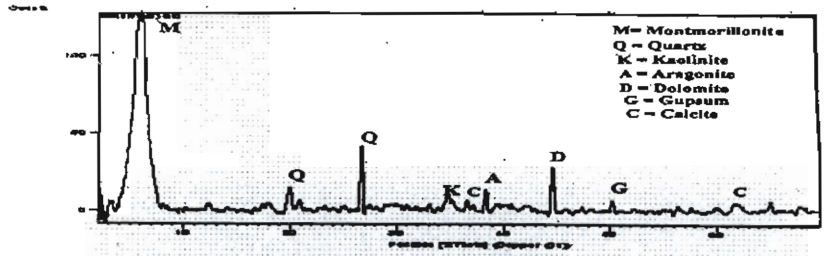

Fig. (3): X-ray diffraction pattern of original black shale

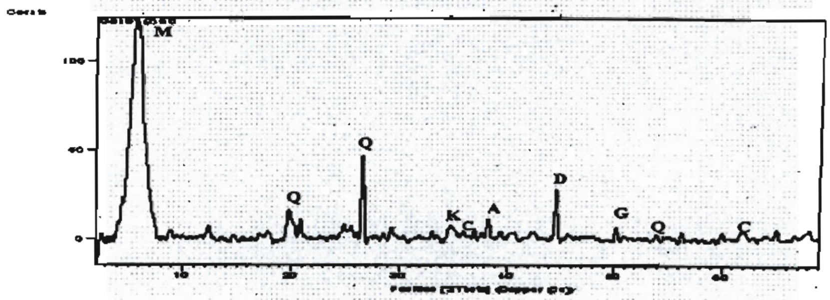

Fig. (4): X-ray diffraction pattern of bitumen-free shale

HCl treatment dissolved carbonate minerals (mainly as calcite) of the black shale. The diffractogram of the carbonate-free (CF) shale Fig. (5) contains fewer peaks than those

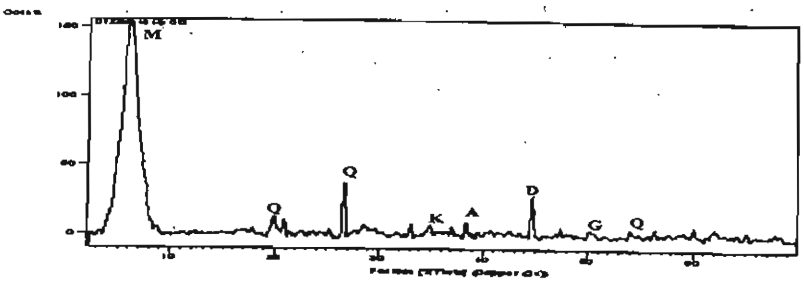

Fig. (5): X-ray diffraction pattern of carbonate-free shale

of BF shale. HF was used to dissolve silicate minerals. In the diffractorgram of silicate-free shale Fig. (6), the series of peaks attributed to complex silicate minerals are absent. We could identify the presence of α-quartz and clay minerals of the kaolinite and montmorillonite type. α-Quartz is the main constituted of silicates, since the peaks corresponding to α-quartz are the most intense in the diffractogram. HCl and HF treatments do not destroy pyrite ($2\theta^{o}$=56). The diffractogram of SF Fig.(6) contains peaks which could be identified as pyrite. These pyrite peaks are not observed in the previous diffractograms due to masking by carbonates and silicates peaks. In the diffractogram of SF Fig. (6), there is an unresolved region between 11° and 25°2θ. This region may be due to organic material which has some orientation [**Yurum *et al.*, (1985)**].

In general the XRD studies of black shale and its demineralized products showed that the mineral matrix was composed mainly of clay minerals such as

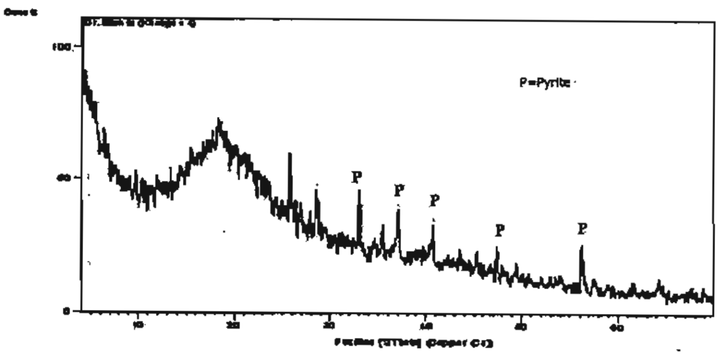

Fig. (6): X-ray diffraction pattern of silicate-free shale, kerogen

montmorillonite, calcite, α-quartz, kaolinte, dolomite and gypsum. Benzene-methanol method treatment can extract the bitumens. Carbonate and silicate minerals could be removed with acid dissolution but pyrite needs more drastic treatment with lithium aluminium hydride which cannot be found easily. From the XRD studies, the organic matter (kerogen concentrate) obtained seemed to be free of minerals.

2.Potential of Organic Matter:

A semiquantitative evaluation of the genetic potential can be achieved using Rock-Eval pyrolysis. The quantity S_1 represents the fraction of the original genetic potential, which has been effectively transformed into hydrocarbons. The quantity S_2 represents the other fraction of the genetic potential which has not yet been used to generate hydrocarbons. Thus S_1+S_2 expressed in kilograms of hydrocarbon per ton of rock) is an evaluation of oil and gas potential of the black shales. Results are given in Table (3). In view of the genetic potential values, the studied black shale samples are not considered as an oil source rock, but have some potentiality for gases [**Tissot (1984)**].

Table (3) : Results of Rock-Eval pyrolysis and FTIR spectroscopy of the studied black shale samples

Black shale sample	S_1 Kg/t	S_2 Kg/t	S_1+S_2 Kg/t	A-factor	TOC	A-factor. TOC.10
1	0.01	0.09	0.10	0.50	0.61	3.05
2	0.02	0.84	0.86	0.41	1.12	4.59
3	0.01	0.18	0.19	0.37	0.72	2.66

Evaluation of black shale potentials is determined by the application of FTIR spectroscopy together with Rock-Eval pyrolysis according to the method employed by **Ganz & Kalkreuth (1987).** In this method, distinctive absorption peaks at 2923 and $2852cm^{-1}$ of aliphatics and $1605cm^{-1}$ of aromatics were considered as in Fig. (7). The change in the intensities of the aliphatic peaks relative to the aromatic ones is expressed as A-factor. This factor is calculated from the heights of these components according to the following equation:

A-factor = ($2923cm^{-1}$ + 2852 cm^{-1}) / $2923cm^{-1}$ + $2852cm^{-1}$ + $1605cm^{-1}$).

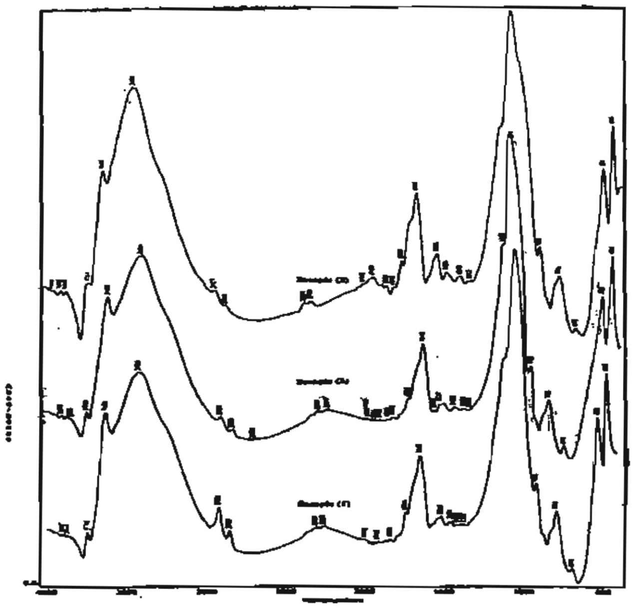

Fig. (7): FTIR spectra of black shale samples in Duwi Formation of Abu Tartour mine.

The results including A-factor and TOC are also given in Table (3). The amount of aliphatic moieties in kerogen can be used to define the hydrocarbon potentials of organic-rich rocks. This is illustrated in Fig. (8), where the A-factor multiplied by the total organic carbon content times 10 is shown to correlate well with results of gas and oil potentials obtained from Rock-Eval pyrolysis. The classification of the kerogens into oil and gas prones can also be clarified from this plot. The locations of the studied samples in the plot indicate that kerogens are gas prone in nature.

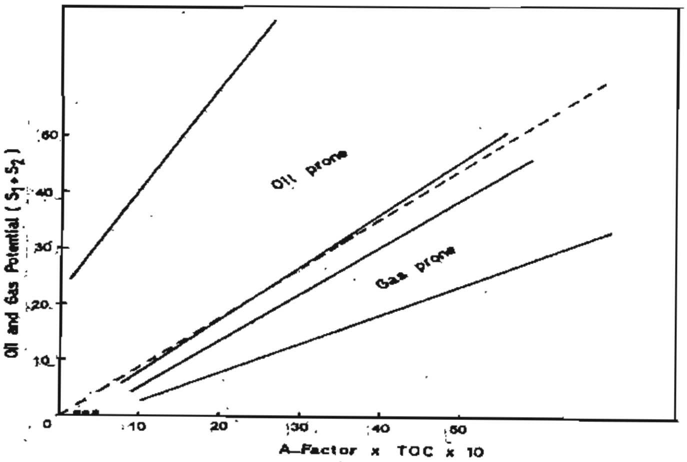

Fig.(8): Plot of A-Factor against Oil and Gas Potential.
(according to Ganz 1986)

CONCLUSIONS

From the results obtained, one may conclude the following:

- The inorganic matrix is composed of montmorillonite, smectite quartz, kaolinite, calcite, gypsum and dolomite. In addition, SEM of the black shale samples indicated that the montmorillonite minerals can be regarded as an aggregation of foliated and lameller aggregate structure.
- Rock-Eval pyrolysis indicated that the black shale samples are not an oil source rock but have some potential for gas.
- Correlation of the gas and oil potential (S_1+S_2) with the aliphatic and aromatic moieties (A-factor) gave information about classification of the kerogens. The kerogens have affinities of gas-prone in nature.

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الملخص العربى

توصيف القالب الغير عضوى وتحديد القدرة الذاتية لانتاج مواد عضوية لبعض عينات من الطفلة السوداء المصرية بمنطقة الصحراء الغربية

جانيت سعد بسطا - سامية ابراهيم شرع
قسم التحليل والتقييم - معهد بحوث البترول - حى الزهور - مدينة نصر - القاهرة

تم تجميع ثلاث عينات من الطفلة السوداء بمنطقة فوسفات ابو طرطور بالصحراء الغربية بمصر، وثم تحليل العينات بالأشعة السينية والميكروسكوب الإلكترونى وذلك للتعرف على المعادن الموجودة بالطفلة السوداء وقد وجد أن القالب الغير عضوى يحتوى على المونتمور يلونيت والسميكتيت والكوارتز والكالسيت والجبسيوم والكاولينيت والدولميت وقد أظهر الميكرو سكوب الإلكترونى أن جزيئات المونتمور يلونيت تظهر كتجمع من اوراق شجرية متعرجة وقد تم استخلاص البتيومين والكيروجين من الطفلة السوداء وبالفحص عن طريق التكسير الحرارى والأشعة المطيافية تحت الحمراء أمكن دراسة القدرة الذاتية لإنتاج مواد عضوية من عينات الطفلة السوداء وقد أظهرت النتائج أن العينات كانت ذات قدرة لإنتاج غازات وليس لها أى قابلية لإنتاج زيت.