Journal of Advanced Zoology
ISSN: 025a3-7214
Volume ***43*** *Issue S-* ***01 Year 2022*** *Page 486:****494***

Assessment of the environmental aspects and economic importance of the Upper Cretaceous Duwi black shales in Aswan Governorate, Egypt

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Article History	*Abstract*
	The economic significance and environmental impact of the Duwi blac in the Nile Valley district have been investigated through the examina its geochemistry and mineralogy. Smectite and kaolinite make up the m of the clay minerals, according to XRD analysis and SEM observatio average loss on ignition (LOI) values of 22.03% indicate a high concen of organic materials. The Duwi black shales exhibit significant le redox-sensitive metals such as vanadium, uranium, molybdenum, and as well as other economically valuable elements including copper, lea zinc. The presence of Zn, V, Cu, and Cr in black shale was verified t the exceptionally high CF values, which exceeded 6. The PLI readings less than one, imply that the shale is unpolluted. In general, the Duw shales are categorized as uncontaminated to moderately contaminate an I_{geo} value ranging from 0 to 1. The examined samples' organic ranges from fair to very good petroleum potential, indicating promis shales. The analysed samples exhibit HI and OI values, which indic presence of gas-oil-prone organic matter and kerogen type III. ***Keywords**: Duwi Black shale, Nile Valley, Economic implications, Environmental consequences*

1. Introduction

Black shale is a highly prospective non-conventional hydrocarbon resource. The reformation of black shale has emerged as a viable energy source for the generation of liquid hydrocarbons (Xie et al., 2020). Organic shale in China and North America has yielded hydrocarbons, particularly gas, as documented by Shao et al. (2020). Precise evaluation of the total organic carbon (TOC) content in shales facilitates the quantitative evaluation of their potential for generating hydrocarbons. The Total Organic Carbon (TOC) is frequently employed as a means to assess the quality of hydrocarbons in source rocks (Tissot and Welte, 1984). Egypt has extensive distribution of black shale resources. The black shale is extensively employed as an energy source in several industries, including cement and electric power plants. The inorganic components found in black shales consist of argillaceous minerals and carbonates. The organic component is comprised of the insoluble solid kerogen, which is found in numerous petroleum source rocks (Tissot and Welte, 1984). The presence of organic-rich sediments in Duwi mine was verified using in situ self-ignition, as documented by El Kammar et al. (1990) and El Kammar (1993). The black shale belt in Egypt is comprised of two stratigraphic rock units, namely the Duwi and Dakhla formations, which are of Campanian-Maastrichtian age. The Egyptian black shale belt has garnered the attention of numerous researchers in Egypt, such as Mostafa and Younes (2001), Ghandour et al. (2003), Temraz (2005), El Kammar (2014), Hu et al. (2017), and Abou El-Anwar et al. (2018, 2019b, 2021). However, further investigations are required to evaluate the quality of this organic shale. Additionally, the feasibility of extracting hydrocarbons from these shale formations needs to be studied. The current study aims to assess the hydrocarbon potential of the obtained samples and their economic enrichment with elements. Measurements of organic matter and total organic carbon contents, Index of Geoaccumulation (Igeo) (Muller 1979), Enrichment Factor (EF) (Sutherland 2000), Contamination Factor (CF) and

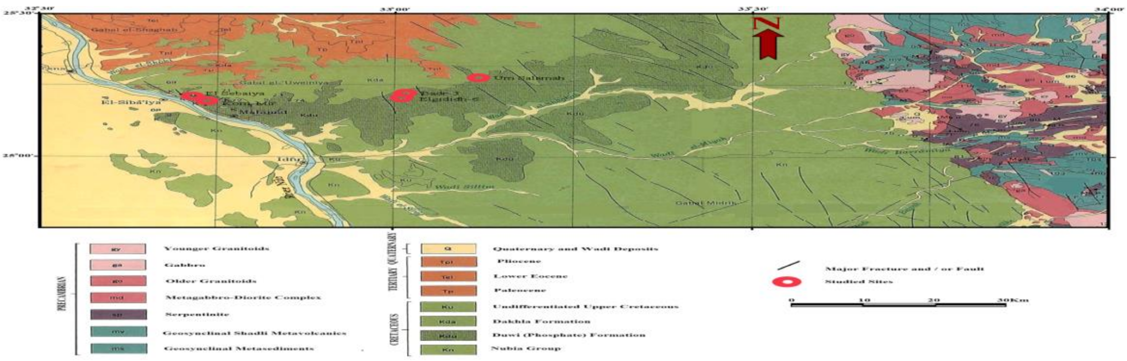
Degree of Contamination (DC) (Hakanson 1980), and Pollution Load Index (PLI) (Tomlinson et al. 1980) will be used to achieve the goals of the current study. These measurements will be made at five sites at El-Nasr company open-pit exploited phosphate mines, Nile Valley district (Kom-Mir, El Sebaiya, Um Salamah, Badr-3, Elgididh-6, Figs. 1 and 2) in Aswan Governorate, Egypt.

2. Geological setting

The study area is situated on the southwestern edge of the Nile Valley, with coordinates ranging from 32° 30′–32° 50′ E longitude and 25° 05 –25° 30′N latitude (Fig. 1). The examined rock formations consist of a sequence of sedimentary layers that date back to the Late Campanian–Early Paleocene age. The study area consists of Duwi Formation black shale (Late Campanian–Early Maastrichtian). These shale beds are found beneath the deeper marine laminated grey to black shales of the Dakhla Formation (Late Maastrichtian–Early Paleocene) (Fig. 2). The Duwi Formation comprises 3 members. The examined sequence is located in the central portion of the pre-rift section (Late Cretaceous–Middle Eocene) on the northwestern edge of the Red Sea (Said 1990). The studied succession consists of a series of interbedded shales, sandstones, and limestones from the Quseir, Duwi, Dakhla, and Esna formations, with a thickness ranging from 220 to 370 metres (Khalil and McClay 2009).

3. Samples and methodology

A total of twenty-five black shale samples from the Duwi Formation were gathered from five specific locations in the El Sebaiya district of Aswan Governorate, Egypt (Figs. 1, 2). A petrographic analysis was conducted on 10 specifically chosen samples of black shale using thin sections observed under a polarising microscope. The mineral composition of the examined samples was ascertained using X-Ray diffraction (XRD) examination. The shape of the clay minerals and the mineral composition of the shale samples were identified using Scanning Electron Microscope (SEM) examination. X-ray fluorescence (XRF) analysis was used to assess the chemical composition of all samples. The laboratories of the National Research Centre of Egypt conducted XRD, SEM, and XRF studies. The TOC content of each sample was measured using a high-temperature TOC/TNb analyzer (Liqui TOC) following decarbonation. The Rock-Eval pyrolysis analysis was conducted on each sample using a Rock-Eval 6 apparatus (Espitalie et al., 1977).



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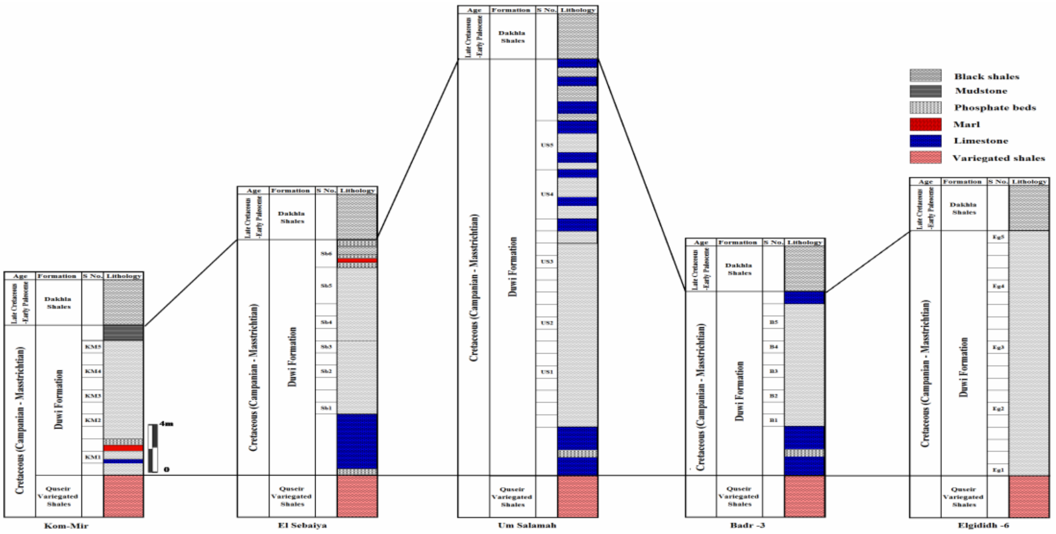

Fig. 2 Correlation chart depicting the Duwi Formation at the examined sites

4. Results and discussions

4.1 Petrography

The sedimentological investigation indicates that the shales of the Duwi Formation consist predominantly of organic matter-rich black shale. The rock is composed of quartz grains and has a greyish brown colour. The quartz grains have a size ranging from silt to sand size (Fig. 3a). The sediments undergo quick burial in an environment with reduced oxygen levels, facilitating the preservation of carbon compounds in rocks. Dark spots of iron oxides replace the argillaceous matrix (Fig. 3a). This suggests that these iron oxides are created through diagenesis, which can occur either through the alteration of minerals that contain high amounts of iron.

4.2 Mineralogy

The X-ray diffraction (XRD) examination and scanning electron microscopy (SEM) observations indicated that the clay minerals consist predominantly of smectite and kaolinite (Fig. 3b). Kaolinite is formed through terrestrial weathering in a warm and humid climate (Hallam et al., 1991). The non-clay minerals include quartz, calcite, phosphate, dolomite, and feldspar. Additionally, there are smaller amounts of gypsum, anhydrite, iron oxides, and pyrite, listed in descending order of their prevalence. The occurrence of framboidal pyrite indicates the existence of a reducing environment (Berner and Raiswell 1983).

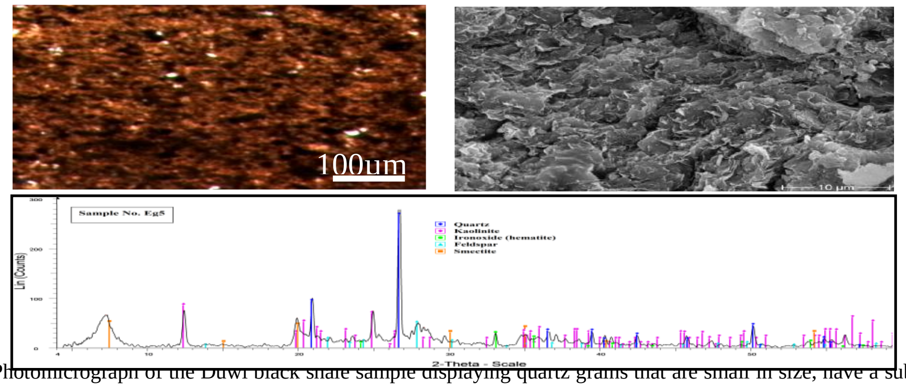

Fig. 3: a) Photomicrograph of the Duwi black shale sample displaying quartz grains that are small in size, have a subangular shape, and are not well sorted; b) Scanning Electron Microscope (SEM) image of the Duwi black shale sample revealing a foliated and lamellar smectite aggregate with a papery structure; c) X-ray diffraction pattern of the Duwi black shale sample (Eg5)

4.3 Major and trace elements

The black shale samples are rich in SiO_2, Al_2O_3, Fe_2O_3t, CaO, and P_2O_5, with average concentrations of 41.69%, 12.12%, 10.93%, 5.89%, and 2.83%, respectively (Table 1). The presence of a large amount of SiO_2 and Al_2O_3 suggests the existence of a humid-warm environment (Armstrong-Altrin 2015). The loss on ignition values (LOI) vary from 17.13% to 23.34% (average 22.03%), indicating a significant presence of organic matter (Sarah, 2011). The black shale is abundant in most trace elements and has low levels of Hf and Cs concentration. The chemical weathering intensity of the shale under investigation can be determined using the chemical index of alteration (CIA) values. CIA is calculated using the formula $CIA = (Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)) \times 100$. The CIA (Chemical Index of Alteration) exhibits a range of values from 81.57% to 86.1% (with an average of 84.26%, Table 1), indicating a significant degree of chemical weathering.

4.4 Pollution indices and environmental aspects

The environmental aspects of the shale under study can be evaluated using several calculations: the Index of Geoaccumulation (I_{geo}), the Enrichment Factor (EF), the Contamination Factor (CF), the Degree of Contamination (DC), and the Pollution Load Index (PLI)= $\sqrt[n]{CF1 * CF2 * \ldots * CFn}$. These calculations are based on formulas developed by Muller (1979), Sutherland (2000), Hakanson (1980), and Tomlinson et al. (1980). The concentration of the target element (Cm) is measured, while the concentration of the target element in the Upper Continental Crust (Bm) is provided by Taylor and McLennan (1985). The concentrations of Sr, Ba, V, Ni, Cr, Zn, Cu, and Rb are given as 320 ppm, 628 ppm, 97 ppm, 47 ppm, 92 ppm, 67 ppm, 28 ppm, and 84 ppm, respectively. Rs represents the content of the reference element in the examined samples, while Rc represents the content of the reference element in the Upper Continental Crust.

Table 1 Major (wt%) and trace (ppm) element composition of studied Duwi black shales

Location	Kom-Mir					El Sebaiya					Um Salamah					Badr-3					Elgididh-6					av	Std
	KM1	KM2	KM3	KM4	KM5	Sb1	Sb2	Sb3	Sb4	Sb5	US1	US2	US3	US4	US5	B1	B2	B3	B4	B5	Eg1	Eg2	Eg3	Eg4	Eg5		
SiO_2	43.1	43.3	44.2	42.4	45.4	41.41	43.2	42.5	44.5	42.02	45.1	41.55	42.7	42.27	42.30	41.80	40.3	40.9	43.5	42.7	40.38	40.62	42.30	41.80	41.40	41.69	1.00
Al_2O_3	12.8	12.9	13.8	13.1	13.2	13.9	14.8	12.7	13.91	12.8	13.3	14.3	13.4	12.10	12.30	12.96	11.3	11.7	13.07	11.81	12.7	11.6	12.20	11.80	11.90	12.12	0.55
CaO	5.8	6.3	5.1	4.1	4.2	4.5	5.3	4.1	4.9	4.2	5.3	4.6	4.4	5.40	5.30	5.40	7.3	8.1	4.3	4.5	6.4	6.3	5.63	6.00	6.00	5.89	1.07
MgO	1.6	1.2	1.4	1.3	1.9	1.3	1.4	1.1	1.3	1.5	1.3	1.1	1.5	1.60	1.57	1.58	1.7	1.4	1.4	1.7	1.6	1.7	1.56	1.56	1.58	1.58	0.10
$Fe_2O_3^*$	11.1	11.1	9.2	12.1	11.3	12.2	12	11.7	11.6	11.6	11.7	12.5	11.4	10.80	11.20	10.48	10.9	9.9	10.8	10.8	11.4	11.7	11.00	10.70	11.50	10.93	0.48
TiO_2	0.9	1.3	0.9	1.1	1	1	0.9	0.91	1.1	1	0.96	0.45	0.27	0.57	0.55	0.56	0.4	0.4	0.7	0.6	0.5	0.4	0.55	0.53	0.54	0.53	0.09
P_2O_5	3.3	3.1	3.3	2.5	2.1	2.1	2	2.9	2.2	2.6	2.5	2.2	3.2	2.70	2.80	2.86	3.3	2.6	2.3	2.5	3.2	3.4	2.80	2.65	2.90	2.83	0.33
Na_2O	0.9	0.9	0.8	0.8	0.9	0.88	1.1	0.8	0.86	0.8	0.8	0.8	0.7	0.60	0.60	0.66	0.7	0.7	0.6	0.5	0.8	0.6	0.63	0.62	0.70	0.64	0.08
K_2O	1.7	2	1.8	1.9	1.9	1.8	2	1.6	1.5	1.6	1.7	1.6	1.5	1.53	1.54	1.60	1.7	1.7	1.5	1.4	1.9	1.6	1.59	1.57	1.70	1.61	0.13
SO_3	0.14	0.14	0.15	0.16	0.19	0.17	0.17	0.17	0.16	0.14	0.15	0.13	0.14	0.14	0.15	0.16	0.13	0.13	0.14	0.15	0.17	0.18	0.14	0.15	0.15	0.15	0.02
LOI	18.66	17.76	19.35	20.54	17.91	20.74	17.13	21.52	17.97	21.74	17.19	20.77	20.79	22.29	21.69	21.94	22.27	22.47	21.69	23.34	20.95	21.9	21.60	22.62	21.63	22.03	0.61
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100.0	0.00
CIA	83.04	81.57	84.08	82.84	82.43	83.76	82.60	84.03	85.42	84.14	84.11	85.56	85.84	84.97	85.12	85.09	82.41	82.91	86.10	86.09	82.40	84.00	84.55	84.29	83.15	84.26	1.31

Sr	251	422	561	1597	277	1200	704	208	351	493	411	860	811.67	1025	660	953	129	644	891	1031	76	300	474	484	513	613	365
Ba	256	333	132	211	139	362	225	88	104	120	240	225	161	237	242	111	109	99	53	88	93	33	73	78	91	156	88
V	191	199	244	200	255	158	157	155	258	260	211	214	233	204	190	121	156	1452	209	412	111	144	377	3050	2677	474	766
Ni	29	39	31	35	38	32	31	32	29	32	30	35	25	32	31	30	30	147	38	60	81	48	126	188	154	55.3	46.3
Co	5	4	5	5	4	6	4	5	4	5	5	4	5	5	4	5	5	12	7	8	16	9	18	18	19	7.5	4.9
Cr	74	99	108	94	105	64	57	50	112	174	94	100	102	88	75	35	122	540	100	240	81	28	177	630	412	150	152
Zn	71	99	43	42	66	65	53	40	61	82	71	61	50	58	61	40	133	1041	121	63	69	36	1246	1600	1110	255	452
Cu	26	31	21	21	51	10	10	9	22	34	26	24	31	27	24	9	24	156	10	33	27	9	156	243	177	48	62
Zr	299	344	234	374	221	40	40	40	70	100	292	317	276	212	100	39	144	106	41	54	138	39	109	93	98	153	110
Cs	1.0	8.0	7.0	6.0	7.0	1.0	4.0	7.0	7.5	8.0	5.0	7.0	7.0	5.0	4.0	1.0	0.0	1.0	0.0	0.0	7.0	1.0	8.0	7.0	7.0	4.7	3.0
Cd	3.0	0.0	1.0	4.0	7.0	4.0	4.0	4.0	2.5	1.0	1.0	2.0	4.0	5.0	5.0	0.0	4.0	4.0	7.0	0.0	1.0	0.0	4.0	7.0	7.0	3.3	2.3
Mo	3.0	4.0	4.0	1.0	5.0	4.0	4.0	4.0	4.0	4.0	4.0	3.0	3.0	3.0	4.0	1.0	4.0	30.0	4.0	4.0	4.0	9.0	21.0	7.0	25.0	6.5	7.4
U	14.0	5.0	5.0	4.0	7.0	51.0	27.5	4.0	4.5	5.0	5.0	5.0	4.0	20.0	28.0	24.0	9.0	44.0	27.0	11.0	4.0	27.0	52.0	41.0	34.0	18.5	16.0
Th	18.0	10.0	10.0	9.0	14.0	1.0	5.0	9.0	9.5	10.0	10.0	10.0	11.0	8.0	5.0	1.0	10.0	9.0	1.0	10.0	9	1	8	9	8	8.2	4.0
Pb	14.0	63.0	15.0	13.0	12.0	14.0	13.5	13.0	13.5	14.0	31.0	30.0	13.0	13.0	13.0	13.0	12.0	30.0	15.0	13.0	14	15	33	20	29	19.2	11.5
Sc	7.0	5.0	7.0	8.0	5.0	9.0	10.5	12.0	9.5	7.0	6.0	7.0	7.0	7.0	8.0	11.0	10.0	7.5	6.6	8.5	8.0	12.0	13.0	8.0	9.0	8.3	2.1
Hf	1.2	1.4	1.5	1.2	1.4	1.2	1.2	1.3	1.3	1.3	1.6	1.7	1.3	1.5	1.3	2.0	1.8	1.7	1.2	1.6	1.0	1.2	1.6	1.3	1.5	1.4	0.2
Rb	28.0	29.0	44.0	41.0	46.0	9.0	9.5	10.0	22.5	35.0	34.0	38.0	60.0	48.0	38.0	10.0	33.0	41.0	10.0	19.0	28	10	32	31	30	29.4	14.1
La	24.6	26.5	7.3	25.4	11.2	30.0	18.6	14.3	30.2	16.3	9.6	17.2	0.1	10.3	3.0	19.1	34.3	0.2	20.6	6.0	17.7	21.9	8.7	10.4	8.2	8.3	2.1

4.4.1 Enrichment Factor; EF

The Enrichment Factor (EF) values derived in Table 2 reveal that the examined samples show a depletion to low enrichment of Ba and Rb (EF < 2, Table 2). The studied samples show minimal to significant enrichment in Strontium, Nickel, Chromium, and Copper, with EF values ranging from 2 to less than 20. The concentration of zinc in the examined samples ranges from low to very high, with EF values between 2 and 40. In general, the black shale samples exhibit varying degrees of Vanadium enrichment, ranging from minimal to very high levels.

4.4.2 Contamination Factor; CF

The computed contamination factor (CF) indicates that the majority of shale samples had minimal levels of contamination with Ba and Rb (CF < 1, Table 2). The CF value of V is predominantly moderate (1 ≤ CF < 3), with the exception of 5 samples that are considered to be large to extremely high. The concentration of Ni is predominantly low (CF < 1), with just 7 samples exhibiting a moderate to significant value. Regarding chromium (Cr), most of the samples that were examined exhibit low to moderate contamination factor (CF), except for three samples which display significant to extremely high CF values. The CF values of Zn and Cu fall within the low to moderate range in the majority of the samples examined. The presence of significant amounts of Zn, V, Cu, and Cr (with a CF >6) indicates that the examined black shale has a high economic value due to the potential extraction of these elements.

4.4.3 Degree of Contamination; DC and Pollution load index PLI

The computed degree of contamination (DC) values (Table 2) reveal that the majority of the analysed samples (21 samples) had low to moderate contamination levels. The Pollution Load Index (PLI) values are computed and presented in Table 2. The majority of the analysed samples (20 in total) exhibit PLI values below one, suggesting that the black shale under investigation is not contaminated (PLI < 1).

4.4.4 Geoaccumulation index I_{geo}

The geoaccumulation index values for Ba and Rb have been determined (Table 2). All samples are found to be uncontaminated, as shown by Igeo ≤ 0 (Table 2). Regarding Sr, the majority of samples exhibit low to moderate contamination levels (0≤ Igeo <1). The geoaccumulation index values for Vanadium indicate that the bulk of the samples (20 samples) are either uncontaminated or moderately contaminated (0< Igeo <1), while only 5 samples are moderately to substantially contaminated (1< Igeo <5). In addition, 19 samples are free from contamination by Cr and Zn. The analysis indicates that the black shales under study can be classed as usually uncontaminated to highly contaminated, with an I_{geo} value ranging from 0 to 1. The Duwi black shales have significant economic significance due to their potential as oil-producing rocks and as a source of certain trace elements (Hu et al., 2017; Eric et al., 2019). The Duwi black shales have significant accumulations of redox-sensitive metals such as vanadium (V), uranium (U), molybdenum (Mo), and nickel (Ni), as well as other economically valuable elements including copper (Cu), lead (Pb), and zinc (Zn) (Abou El-Anwar et al., 2021). Furthermore, when comparing the estimated indices, it was seen that the examined shale samples exhibited higher levels of some trace elements, particularly Sr, V, and Zn, compared to the world black shale (Table 3).

Table 2 Values of the investigated black shales' pollution indices

SN	Enrichment factor (EF)								Contamination Factor (CF)								Geoaccumulation index (Igeo)								Degree of Contamination (DC)	Pollution load index (PLI)
	Sr	Ba	V	Ni	Cr	Zn	Cu	Rb	Sr	Ba	V	Ni	Cr	Zn	Cu	Rb	Sr	Ba	V	Ni	Cr	Zn	Cu	Rb		
KM1	0.5	0.25	1.27	0.39	0.51	0.68	0.59	0.21	0.78	0.4	1.96	0.61	0.8	1.05	0.92	0.33	-0	-1	0.	-1	-0	-0	-0	-2	6.85	0.74
KM2	0.73	0.29	1.15	0.46	0.6	0.82	0.61	0.19	1.31	0.53	2.05	0.82	1.07	1.47	1.1	0.34	-0	-1	0.	-0	-0	-0	-0	-2	8.69	0.95
KM3	1.44	0.17	2.07	0.53	0.96	0.52	0.61	0.42	1.75	0.21	2.51	0.65	1.17	0.64	0.75	0.52	0.	-2	0.	-1	-0	-1	-1	-1	8.2	0.8

KM 4	2.58	0.17	1.06	0.38	0.52	0.32	0.38	0.24	4.99	0.33	2.06	0.74	1.02	0.62	0.75	0.48	1.	-2	0.4	-1	-0	-1	-1	-1	10.99	0.93
KM 5	0.75	0.19	2.29	0.7	1	0.85	1.59	0.47	0.86	0.22	2.62	0.8	1.14	0.98	1.82	0.54	-0	-2	0.8	-0	-0	-0	0.2	-1	8.98	0.9
Sb1	18.75	2.85	8.1	3.4	3.45	4.85	1.75	0.5	3.75	0.57	1.62	0.68	0.69	0.97	0.35	0.1	1.3	-1	0.1	-1	-1	-0	-2	-3	8.73	0.69
Sb2	11	1.75	8.05	3.25	3.05	3..95	1.75	0.55	2.2	0.35	1.61	0.65	0.61	0.79	0.35	0.11	0.5	-2	0.1	-1	-1	-0	-2	-3	6.67	0.59
Sb3	3.25	0.7	7.95	3.4	2.7	2.95	1.6	0.55	0.65	0.14	1.59	0.68	0.54	0.59	0.32	0.11	-1	-3	0.0	-1	-1	-1	-2	-3	4.62	0.42
Sb4	3.02	0.44	7.36	1.69	3.36	2.52	2.16	0.72	1.09	0.16	2.65	0.61	1.21	0.91	0.78	0.26	-0	-3	0.8	-1	-0	-0	-0	-2	7.67	0.7
Sb5	3.01	0.37	5.25	1.33	3.7	2.39	2.37	0.8	1.54	0.19	2.68	0.68	1.89	1.22	1.21	0.41	0.0	-2	0.8	-1	0.3	-0	-0	-1	9.82	0.94
US 1	0.84	0.25	1.43	0.41	0.67	0.69	0.6	0.26	1.28	0.38	2.17	0.63	1.02	1.05	0.92	0.4	-0	-1	0.5	-1	-0	-0	-0	-1	7.85	0.84
US 2	1.63	0.21	1.34	0.45	0.65	0.55	0.51	0.27	2.68	0.35	2.2	0.74	1.08	0.91	0.85	0.45	0.8	-2	0.5	-1	-0	-0	-0	-1	9.26	0.93
US 3	1.76	0.17	1.67	0.37	0.76	0.51	0.76	0.49	2.53	0.25	2.4	0.53	1.01	0.74	1.1	0.71	0.7	-2	0.0	-1	-0	-1	-0	-1	9.27	0.9
US 4	2.93	0.33	1.92	0.62	0.87	0.78	0.88	0.52	3.2	0.37	2.1	0.68	0.95	0.86	0.96	0.57	1.0	-1	0.4	-1	-0	-0	-0	-1	9.69	0.96
US 5	4.03	0.74	3.82	1.27	1.58	1.78	1.66	0.88	2.06	0.38	1.95	0.65	0.81	0.91	0.85	0.45	0.4	-1	0.3	-1	-0	-0	-0	-1	8.06	0.85
B1	14.85	0.85	6.2	3.15	1.9	2.95	1.6	0.55	2.97	0.17	1.24	0.63	0.38	0.59	0.32	0.11	0.9	-3	-0	-1	-1	-1	-2	-3	6.41	0.48
B2	0.54	0.22	2.16	0.85	1.78	2.67	1.14	0.52	0.4	0.17	1.6	0.63	1.32	1.98	0.85	0.39	-1	-3	0.1	-1	-0	0.4	-0	-1	7.34	0.7
B3	3.72	0.27	27.7	5.77	10.85	28.75	10.31	0.88	2.01	0.15	14.96	3.12	5.86	15.53	5.57	0.48	0.4	-3	3.3	1.0	1.9	3.3	1.8	-1	47.68	2.76
B4	13.23	0.38	10.23	3.8	5.14	8.57	1.66	0.52	2.78	0.08	2.15	0.8	1.08	1.8	0.35	0.11	0.8	-4	0.5	-0	-0	0.2	-2	-3	9.15	0.64
B5	11.92	0.51	15.7	4.7	9.62	3.48	4.33	0.81	3.22	0.14	4.24	1.27	2.6	0.94	1.17	0.22	1.1	-3	1.5	-0	0.7	-0	-0	-2	13.8	1.05
Eg1	0.32	0.19	1.6	2.42	1.23	1.43	1.35	0.46	0.23	0.14	1.14	1.72	0.88	1.02	0.96	0.33	-2	-3	-0	0.2	-0	-0	-0	-2	6.42	0.6
Eg2	4.65	0.25	7.4	5.1	1.5	2.65	1.6	0.55	0.93	0.05	1.48	1.02	0.3	0.53	0.32	0.11	-0	-4	-0	-0	-2	-1	-2	-3	4.74	0.37
Eg3	2.64	0.19	6.92	4.78	3.42	33.19	9.94	0.67	1.48	0.11	3.88	2.68	1.92	18.59	5.57	0.38	-0	-3	1.3	0.8	0.3	3.0	1.8	-1	34.61	1.83
Eg4	3.14	0.25	65.5	8.33	14.25	49.75	18.06	0.79	1.51	0.12	31.44	4	6.84	23.88	8.67	0.36	0.0	-3	4.3	1.4	2.1	3.9	2.5	-2	76.82	3.22
Eg5	3.2	0.28	55.18	6.54	8.94	33.12	12.64	0.7	1.6	0.14	27.59	3.27	4.47	16.56	6.32	0.35	0.0	-3	4.2	1.1	1.5	3.4	2.0	-2	60.3	2.75

Table 3 Comparative analysis of the present study and global shale deposits (parts per million)

Element	Current study	UCC[a]	North American Shale Composite (NASC)[b]	Average shale[c]	Black shales US And Canada[d]	Black shales worldwide (median)[e]
Sr	76-1597	320	142	300	200	190
Ba	33-362	628	636	580	300	500
V	111-3050	97	__	130	150	205
Ni	25-188	47	58	68	50	70
Cr	28-630	92	124.5	90	100	96
Zn	36-1600	67	__	95	< 300	130
Cu	9-243	28	__	45	70	70
Rb	9-60	84	125	140	__	74

[a] Rudnick and Gao (2014), [b] Gromet et al. (1984), [c] Turekian and Wedepohl (1961), [d] Vine and Tourtelot (1970), [e] Ketris and Yudovich (2009)

4.5 Organic matter distribution

Black shales are primarily associated with the mid-Cretaceous period, during which the majority of our current petroleum reserves were formed (Abou El-Anwar et al., 2018; Eric et al., 2022). Geological evidence suggests that black shales were capable of being deposited in an open shelf until the early Paleozoic period, but subsequently, they could only be deposited in a basin that was isolated from water flow. The shift in geological age is ascribed to the development of benthic organisms and bacteria (Klemme and Ulmishek 1991) and/or the rise in dissolved oxygen levels in the ocean (Hu et al. 2017).

An elevated concentration of organic materials in sediments is also a determining factor in recognising oil and gas source rocks. Several recent reviews have been published on the preservation of organic-rich source beds, including studies by Heydari et al. (1997), El Kammar (2014), and Eric et al. (2019). The quantity of organic matter (OM) varies from one site to another, depending on the type of shale and its specific properties. The Cretaceous Duwi Formation contains black shale that is connected to phosphate beds owned by the El Nasr mining business. These phosphate beds are known as Kom-Mir, El Sebaiya, Um Salamah, Badr-3, and Elgididh-6. They are located in the Aswan Governorate, specifically in the Nile Valley district (Table 4). The organic matter (OM) content ranges from 0.2 to 2.71 weight percent, with the exception of three samples which have OM contents of 3.44, 5.65, and 6.31 weight percent, respectively. The low organic matter (OM) percentages found in the shale formations in the Nile Valley district can be seen as exploratory indicators suggesting that the examined shales contain a significant amount of potential organic matter (El Kammar, 2014). In Sarah's method of determining organic matter, the samples are subjected to ignition for 12 and 16 hours, and then weighed after each ignition period. The ignition times for both experiments are provided in Table 4. The recommended method for determining total organic matter is to ignite it for

16 hours, gradually increasing the temperature over time. However, the results obtained from igniting it for 2 hours are favourable for exploring the possible presence of organic matter in shale. The sampled shales of the Duwi Formation in the Nile Valley district exhibit encouraging levels of organic content. The data were conducive to estimating the total organic carbon content in order to assess the sampled shales as a potential energy source (Abou El-Anwar et al., 2021). Peters and Cassa (1994) defined total organic carbon (TOC) weight percent as a measure of the petroleum potential of black shale. There are a total of five classes. The petroleum potential is categorised as poor when the total organic carbon (TOC) content falls between 0 – 0.5 weight percent. It is considered fair when the TOC content is between 0.5 – 1 weight percent, and good when the TOC content is between 1 – 2 weight percent. TOC (Total Organic Carbon) content ranges from 2 to 4 wt %, indicating a very good petroleum potential. However, TOC content beyond 4 wt % indicates an excellent petroleum potential. The total organic carbon (TOC) of seven selected shale samples with the highest organic matter percentage (OM%) is determined and presented in Table 5. The analysed samples exhibit a spectrum of organic richness, ranging from moderate to excellent total organic carbon content (Table 5). This characteristic suggests that these samples hold significant potential as oil shales (Abou El-Anwar et al., 2021).

4.6 Rock-Eval pyrolysis

Rock-Eval pyrolysis yields data regarding the abundance, composition, and thermal maturity of the organic matter present, in addition to its hydrocarbon potential. Analytical procedures have been developed based on the methodologies proposed by Espitalie et al. (1977), Tissot and Welte (1984), and Peters et al. (1986). The Rock-Eval pyrolysis results for 7 bulk rock samples may be found in Table 6. All the examined samples exhibit indigenous origin (Fig. 4a). The primary factor that determines the generating potential of source rock is the S2 value. According to Peters and Cassa (1994), most of the analysed samples have S2 levels below 1.2 mg/g, which suggests a low likelihood of hydrocarbon generation. The limited generative potentiality is also shown by the low GP and PI values (< 1.2) in all samples. The S2 value can be utilised in conjunction with TOC to determine the kerogen type, as demonstrated in Figure 4b. In this case, the kerogen type is identified as type III.

Table 4 The weight percentage of organic matter (OM) after 2, 12, and 16 hours.

Locality	Fm.	S. No.	O. M. wt. % after (2) hours	O. M. wt. % after (12) hours	O. M. wt. % after (16) hours
Kom-Mir	Duwi	KM1	0.427	0.80	0.85
		KM2	0.2	0.47	0.47
		KM3	1.6	3.12	3.12
		KM4	0.83	2.53	2.55
		KM5	1.02	2.77	2.77
El-Sebaiya		Sb1	1.04	2.82	2.97
		Sb2	5.65	11.03	11.03
		Sb3	0.76	1.48	1.51
		Sb4	0.79	1.93	1.93
		Sb5	0.96	1.82	1.82
Um Salamah		US1	3.44	6.97	6.97
		US2	2.71	5.61	5.66
		US3	1.44	2.47	2.47
		US4	1.2	2.28	2.32
		US5	1.27	2.52	2.52
Badr-3		B1	0.64	1.78	1.78
		B2	1.05	2.02	2.07
		B3	1.02	2.36	2.42
		B4	1.41	3.01	3.01
		B5	1.74	3.3	3.3
Elgididh-6		Eg1	1.24	2.41	2.5
		Eg2	6.31	12.89	12.89
		Eg3	0.48	1.18	1.2
		Eg4	1.32	2.68	2.68
		Eg5	1.06	2.82	2.82

Table 5 The total organic carbon concentration in seven shale specimens

S. No.	TC wt.%	TOC wt.%	Petroleum potential
KM3	0.98	0.65	Fair
Sb2	5.89	3.1	Very Good
US1	2.1	1.2	Good
US2	1.33	0.92	Fair
B4	0.71	0.71	Fair
B5	1.46	0.96	Fair
Eg2	4.96	2.9	Very Good

Table 6 Pyrolysis results from Rock-Eval analysis of the samples under investigation

S. No.	TOC	S1	S2	S3	Tmax	HI	OI	GP	PI	S2/ S3
	wt.%	mg/g	mg/g	mg/g						

KM3	0.65	0.03	0.25	0.43	424	38	66	0.28	0.11	0.58
Sb2	3.1	0.05	1.12	1.56	425	36	50	1.17	0.04	0.72
US1	1.2	0.03	1.1	0.21	412	92	18	1.13	0.03	5.24
US2	0.92	0.03	1.09	0.22	412	118	24	1.12	0.03	4.95
B4	0.71	0.01	0.18	0.49	418	25	69	0.19	0.05	0.37
B5	0.96	0.03	1.1	0.21	412	115	22	1.13	0.03	5.24
Eg2	2.9	0.05	1.09	1.44	425	38	50	1.14	0.04	0.76

TOC = Total organic carbon, wt %; S1: Free hydrocarbons content, mg HC/g rock; S2: Remaining hydrocarbons generative potential, mg HC/g rock; S3: Carbon dioxide yield, mg CO_2/g rock; HI: Hydrogen index = 100×S2/ TOC (mg HC/TOC); OI: Oxygen index =S3×100/ TOC, mg CO2/g TOC; Tmax = Temperature at maximum of S2 peak; GP: Generative potential = S1+S2; PI: Production index = S1 / (S1+S2).

4.7 Organic matter (kerogen) types

Kerogen, also known as insoluble organic matter, refers to the organic material present in sedimentary rocks that cannot be dissolved by organic solvents. The composition of kerogen in organic materials significantly influences the production of hydrocarbons. The chemical composition of organic matter leads to the existence of various forms of kerogen (Tissot and Welte, 1984). The Rock-Eval 6 analyzer utilises many criteria to ascertain the kerogen type, degree of thermal maturation, and oxygen content. The hydrogen index (HI) and oxygen index (OI) can be derived from these factors. In their study, Peters and Cassa (1994) categorised the HI value into three groups: HI <150 indicating gas-prone organic matter, HI values between 150 and 300 indicating gas-oil-prone organic matter, and HI >300 indicating oil-prone organic matter. The HI values of all the analysed samples vary from 25 to 118, which is considered low (<150). This suggests the presence of gas-oil-prone organic matter, as shown by Peters and Cassa (1994). The analyzed samples' HI values display low values. On the other hand, the OI values range from 18 to 69, indicating high values. These results suggest the presence of kerogen type III, as shown in Table 7 and Figure 4c. The S2/S3 values of all analysed samples vary from 1 to 5, showing the presence of Gas brone and kerogen type III (Tables 6, 7).

4.8 Thermal maturation

The parameters Tmax and production index (PI) obtained from Rock-Eval pyrolysis are utilised to indicate the thermal maturation of organic matter (Peters and Cassa, 1994). The analysed samples have a PI value ranging from 0.03 to 0.11, as shown in (Table 6). This range implies that the samples are at an immature to early mature stage, as stated in (Table 8). Research has shown that Tmax values can be correlated with the vitrinite reflectance of Type-III kerogen and humic coal (Tissot et al., 1987). The Tmax values for the samples under study range from 412-425°C (Table 6), indicating an immature stage (Table 8).

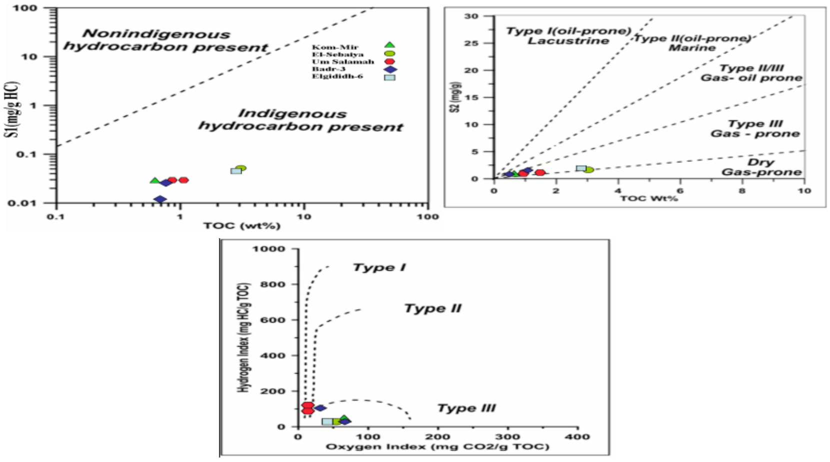

Fig. 4: (a) Comparison of total organic carbon (TOC) and S1 analysis was conducted by Hunt in 1995. (b) Dahl et al. (2004) compared TOC and S2 analysis. (c) The examined samples were analysed for hydrogen index (HI) and oxygen index (OI) by Espitalie et al. in 1977.

Table 7 The geochemical characteristics that characterise the type of kerogen and the nature of the substances released (Peters and Cassa, 1994)

Kerogen Type	S2/S3	Main expelled at peak maturity
I	> 15	Oil
II	10-15	Oil
II/III	5-10	Mixed oil+gas
III	1-5	Gas
IV	< 1	None

Table 8 Geochemical parameters that quantify the degree of thermal maturation (Peters and Cassa, 1994).

Stage of thermal maturation	Maturation Tmax (°C)	Generation PI [S1/ (S1+S2)]

Immature		<435	<0.05
Mature	**Early**	435- 445	0.10-0.15
	Peak	445- 450	0.25-0.40
	Late	450- 470	-
	Postmature	<470	-

Conclusions

Oil shale is a highly promising and abundant energy source found in many regions of Egypt. This study aimed to examine the hydrocarbon potential and environmental impact of the Upper Cretaceous Duwi black shales in the Nile Valley district of Aswan Governorate, Egypt. The Duwi black shales are primarily composed of smectite and kaolinite from a mineralogical standpoint. The non-clay minerals in this context are primarily composed of quartz, calcite, phosphate, dolomite, and feldspar, with smaller amounts of gypsum, anhydrite, iron oxides, and pyrite. The presence of Zn, V, Cu, and Cr in black shale was verified by the exceptionally high CF value, which exceeded 6. The PLI findings suggest that the examined black shale samples are devoid of contamination. Based on the derived geoaccumulation index, it can be inferred that the black shales under study are generally classed as having low to moderate contamination levels. The occurrence is ascribed to the inherent erosion of the original rocks rather than any human influence. The extraction of Zn, V, Cu, and Cr from the investigated black shale contributes to its economic value. The organic content of the samples analysed varies from moderate to excellent, indicating a significant potential for petroleum production. These samples can be classified as highly promising oil shales. The total organic carbon (TOC) concentration of the samples ranges from 0.65 to 3.1 weight percent, suggesting that they may be suitable for petroleum exploration. The analysed samples exhibit HI and OI values, which indicate the presence of gas-oil-prone organic matter and kerogen type III.

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