Bulletin of Faculty of Science ,Zagazig University (BFSZU) ***2024***
Bulletin of Faculty of Science, Zagazig University (BFSZU)
e-ISSN: 1110-1555
Volume-2024, Issue-2, pp- 115- 125
https://bfszu.journals.ekb.eg/journal
Research Paper DOI: **10.21608/bfszu.2023.242833.1328**

==

Paleosalinity and hydrothermal characteristics of the Upper Cretaceous Duwi black shales, Aswan Governorate, Egypt

Samir M. Zaid[1], Oussama A. EL-Badry[1], Adel M. Akarish[2], Mahmoud A. Mohamed[1*]

[1]Department of Geology, Faculty of Sciences, Zagazig University, Zagazig, Egypt
[2]Department of Geological Sciences, National Research Centre, Dokki, Giza, Egypt
Corresponding author: malekmahmoud412@gmail.com

ABSTRACT : The Upper Cretaceous Duwi black shales of Nile Valley district, Aswan Governorate, Egypt, were geochemically examined to determine their paleosalinity and hydrothermal characteristics present at the time of their deposition. Elemental ratios such as strontium/barium (Sr/Ba) and TOC/S were applied for paleosalinity reconstruction. The Duwi black shales show Sr/Ba >0.5 and TOC/S <5. The values of the elemental ratio show that the Duwi black shales were deposited in a marine environment. For hydrothermal activities ratio, Sc/Cr was used and Binary diagrams TOC vs P were constructed to discriminate between normal water, mixed and hydrothermal influence. The Sc/Cr ratio was <0.120 indicating that the black shales in the Nile Valley district were deposited in a hydrothermal water environment. The binary discriminant diagram of TOC vs P shows that all the shales were influenced by hydrothermal processes during the time of their deposition.

KEYWORDS: Black shale; Duwi; Nile Valley; Paleosalinity; Hydrothermal activity.

Date of Submission: 16-10-2023 Date of acceptance: 29-11-2023

I. INTRODUCTION

Black shale deposits are found all across Egypt. Several economic plants rely on raw ingredients mined from black shale. The latter is primarily enriched in certain metals such as U, V, Cu, Ni, and Zn (Schultz 1991). Many sectors, including cement and power plants, use black shale as an energy donor. Inorganic fractions in black shales contain argillaceous minerals as well as carbonates. The organic portion is represented by the insoluble solid kerogen found in many petroleum source rocks (Tissot and Welte., 1984). The quantity of organic-rich sediments in the Duwi mine was confirmed by in-place self-ignition (El Kammar et al. 1990; El Kammar 1993). Stratigraphically, the black shale belt in Egypt is represented by two stratigraphic rock units of Campanian–Maastrichtian age (Duwi and Dakhla formations). The two formations extend along the southern escarpments of the Western Desert from Dakhla to Kharga Oasis, then south to the Sinn El-Kaddab escarpment, then west to Kom-Ombo, and then north along the Nile Valley from Idfu to Wadi Qena and the Galala plateau, as well as along the Red Sea coast between Quseir and Safaga, forming a thick belt.

The research into the role of salinity within sedimentary systems is closely related to the features of the systems, including lithology, fossils, and water bodies. These features contain major signals that, when evaluated, provide significant information on the previous salinity of the sedimentary framework, as well as the salinity that prevailed during the development of the lithology and retention of the fossils. Salinity is a chemical characteristic of water masses seen in modern aquatic systems. Within a sedimentary system, the paleoenvironmental conditions can be entirely marine (Yan et al., 2018), primarily freshwater (Qiu et al., 2015), or mixed (estuary) environments that can be made by primordial sedimentary formations. Paleosalinity research has a long history, and both geochemical and non-geochemical approaches have been extensively used. Elemental geochemical indicators have recently been proven to be a powerful tool for determining the salinity of fine-grained sedimentary deposits in sedimentary systems (Mackenzie and Garrels, 1971). Holmden et al. (1997) and Ye et al. (2016) measured paleosalinity using a combination of elemental geochemical proxies such as Mg/Ca, Sr/Ca, and Na/Ca, despite the fact that these elemental ratios are prone to diagenetic alteration.

The Egyptian black shale belt has been discussed by many authors (e.g., Mostafa and Younes, 2001; Ghandour et al., 2003; Temraz, 2005; El Kammar, 2014; Hu et al. 2017; Abou El-Anwar et al., 2018, 2019b, 2021), but further research on organic shale is needed to determine the paleosalinity and hydrothermal activity that existed during the time of shale deposition. The present study aims to clarify the paleosalinity and hydrothermal activity that occurred at the time of shale deposition via using the trace element indicators and total organic carbon contents (TOC). The main objective is to determine the chemical composition and total organic carbon contents using X-ray fluorescence (XRF) analysis for black shale samples. These samples were taken from five different places at El-Nasr Company's open-pit exploited phosphate mines in Aswan Governorate, Egypt (Kom-Mir, El Sebaiya, Um Salamah, Badr-3, Elgididh-6, Figs. 1 and 2).

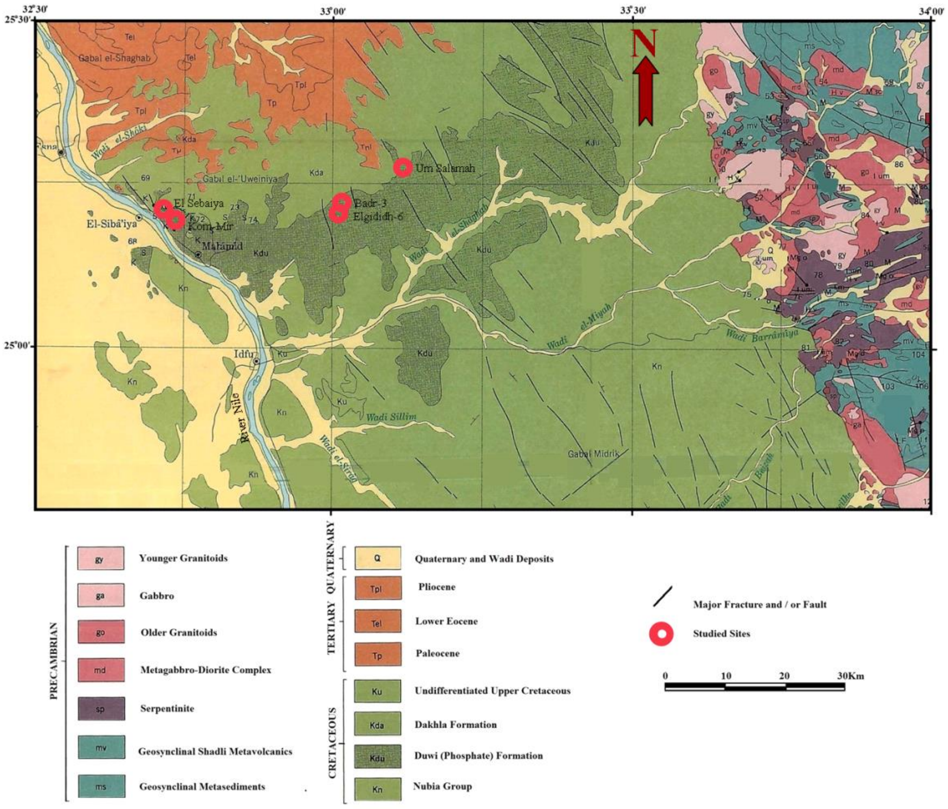

Fig. 1 Locations of studied sites (modified after Conoco 1987)

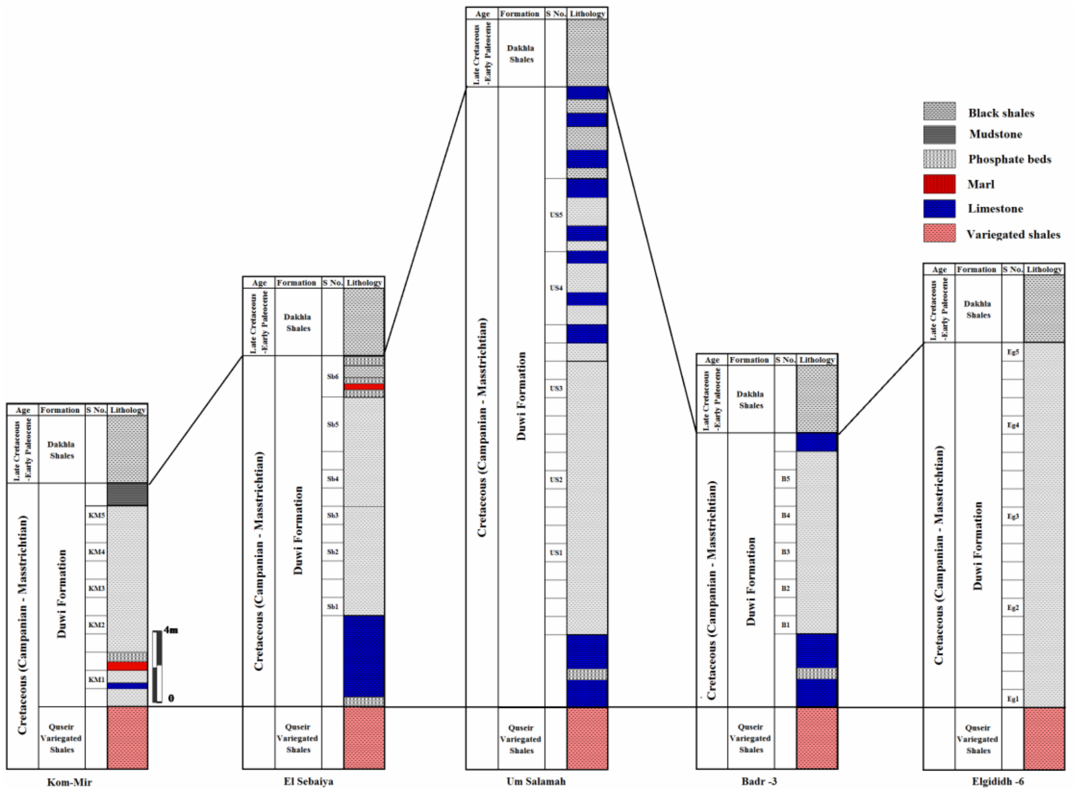

Fig. 2 Correlation chart of the Duwi Formation at the studied locations (Zaid et al., 2018)

II. GEOLOGICAL SETTING

The study area is located on the southwestern side of the Nile Valley, between longitudes 32° 30′–32° 50′ E and latitudes 25° 05 –25° 30′N (Fig. 1). The stratigraphic succession of the investigated outcrops is Late Campanian–Early Paleocene age. The succession represents a significant part of the dominated siliciclastic deposits of black and variegated shales. Obviously, this stratigraphic succession extends alongside the New Valley and Safaga–El Qusier region on the Coastal plain of the Red Sea. The study area is characterized by the abundance of black shale beds that is represented by Duwi Formation (Late Campanian–Early Maastrichtian). Duwi Formation is conformably covered by the deeper marine laminated gray to black shales of the Dakhla Formation (Late Maastrichtian–Early Paleocene) and unconformably overlie the older Nubia Formation (El-Azabi and Farouk 2010) (Fig. 2). The Duwi Formation involves three members. Both of lower and upper members are made up of intercalations of phosphorite bed with black shales thin lenses, whereas the middle member is mostly made up of black shale. The investigated succession is located in the middle section of the pre-rift phase (Late Cretaceous–Middle Eocene) in the northwestern border of the Red Sea (Said 1990). This part consists of 220–370-m-thick sequence of sandstones, limestones and shale interbeds of Quseir, Duwi, Dakhla, and Esna formations (e.g., Khalil and McClay 2009).

III. SAMPLES AND METHODOLOGY

Twenty-five representative black shale samples of Duwi Formation were collected from five sites in El Sebaiya area, Aswan Governorate, Egypt. (Figs. 1, 2). These sites include Um Salamah, El Sebaiya, Kom-Mir, Badr-3, and Elgididh-6 (Figs. 1, 2). The shale layer ranges in thickness from 2.0- 2.5m in the excavated bit. The chemical composition of all samples was determined using X-ray fluorescence (XRF) analysis. XRF analyses were performed at the laboratories of National Research Center of, Egypt. The total organic carbon (TOC) content was determined on each sample using a Hochtemperatur- TOC/TNb-Analysator (Liqui TOC) after decarbonating. The analyses were performed at the Stratochem Service lab, Egypt.

IV. RESULTS AND DISCUSSION

4.1. Paleosalinity

Black shales in sedimentary basins have largely had their paleosalinity determined using elements including gallium, barium, strontium, total organic carbon (TOC), boron, and sulfur. The ratio between these elements identified the type of water and environmental factors present at the time the shale was deposited (Table 1).

4.1.1. Sr and Ba signatures

Sr is freed more quickly than Ba in terrestrial weathering conditions (Ding et al., 2001; Yang et al., 2004a, 2004b, 2006). Despite the comparatively low solubility of Sr-carbonates and Sr-sulfates, Sr2+ is mobile once liberated by weathering under most environmental circumstances (Brookins, 1988). Although hydrothermal Sr from mid-ocean ridges and alteration/dissolution of seafloor carbonates are significant secondary sources (Krabbenhöft et al., 2010), riverine inputs are the main source of Sr to the oceans. When compared to the oceans' 1.5 kyr mixing time, Sr's residence time in seawater (2.4 Myr) is long, indicating relatively conservative behavior (Krabbenhöft et al., 2010). Although some Sr can be removed through reaction with oceanic crust, Sr2+ substitution for Ca2+ in carbonate minerals is the main sink of Sr in the ocean (Roden et al., 2002; Krabbenhöft et al., 2010). Sr/Ba ratios of 0.20 (0.14-0.28) can be detected in current freshwater sediments, according to data published by Wei and Algeo (2020). Sr/Ba ratios in current marine sediments are 0.43 (0.24-0.82), while they are 0.44 (0.27-0.66) in brackish sediments. The Sr/Ba ratio, a gauge of paleosalinity, may be impacted by the presence of carbonate in a sediment, according to Wang et al. (2021). A sedimentological extraction of Sr and Ba before use as a paleosalinity indicator was suggested by Wang et al. (2021) due to the effect of carbonate content on the Sr and Ba concentration in some sediments. According to Liu et al. (2022), the use of the Sr/Ba ratio as a proxy for paleosalinity necessitates some caution because the presence of carbonate minerals in a sample may change the Sr/Ba ratios because Sr is susceptible to strong carbonate mineral influences and may thus occupy their lattice positions. The Sr element content of the bulk sediments must be adjusted when utilizing Sr/Ba as a paleosalinity proxy for carbonate containing rocks or carbonate rocks.

The approach utilized in this work to achieve the geochemical data eliminated the carbonate present in the shales prior to the start of the analyses, making the results feasible and appropriate for use in paleosalinity characterisation. According to Wang et al. (2021), the Sr/Ba ratios of fresh water, brackish water (delta front), salt water (pro delta), and normal marine water are as follows: <1, 1.0-3.0, 3.0-8.0, and >8.0. The Ba content of the examined shales varied from 33 to 362 ppm with an average of 156 ppm, whereas the Sr content ranged from 76 to 1597 with an average of 600 ppm. The examined shale samples' Sr/Ba ratios ranged from 0.55 to 16.8, with an average of 4.83. The values for all the facies waters cut across the majority of the samples when comparing the concentration of Ba and Sr in the studied shale samples to the dataset of Wei and Algeo (2020), making it difficult to differentiate between the salinity facies of the studied shale samples. However, when comparing the ratio of Sr/Ba, all the studied samples fall within the range of marine facies. Wei and Algeo (2020) proposed a ratio for the paleosalinity facies as Sr/Ba is 0.2 in freshwater, 0.2-0.5 in brackish, and >0.5 in marine facies after compiling numerous data and conducting a specific case study in the Paleogene brackish to marine facies of Bohai Bay Basin and northeastern China, Ordovician marine, and Triassic lacustrine facies of Ordos Basin, North China. The majority of the Duwi black shales fell under the category of marine facies, according to the values of the ratio of shales examined in the Bohai Bay Basin and Ordos Basin by Wei and Algeo (2020) (Fig. 3). According to the Sr/Ba ratio ranges for the various waters supplied by Wang et al. (2021), it is evident that most of the Duwi black shales were deposited in marine environments (Table 1).

4.1.2. S and TOC proxy

Pyrite minerals are the primary suppliers of sulfur in depositional systems. It turns out that pyrite-containing shale has a high sulphur concentration. Pyrite formed in aquatic systems is influenced by the presence of elements like decomposed organic matter, reactive iron, and sulfate dissolved in pore water (Calvert and Karlin, 1991). Aqueous sulfate concentrations control the production of hydrogen sulfide (H2S) in sedimentary freshwater systems, whereas reactive organic matter types and quantities control H2S generation in marine systems (Pallud and Van Cappellen, 2006). The lack of aqueous sulfate in freshwater systems is partly responsible for the low concentration of sedimentary sulfur, whereas the presence of sulfate in seawater sulfate, which serves as the main source, causes a high concentration of sedimentary sulfur in a marine environment (Millero, 2011). According to data obtained by Wei and Algeo (2020), the average sulphur content of sediments deposited in a freshwater environment is 0.06%, with values ranging between 0.03 and 0.16%, while the average value of organic carbon is 2.2%, with values between 0.97 and 5.2%.

Table 1: Concentration of selected trace, major elements and TOC in ppm and their calculated ratios.

Samples	Ba	Cr	TS	Sc	Sr	TOC	P	Sc/Cr	Sr/Ba	TOC/S	TS/TOC
KM1	256	74	0.056	7	251	0.23	1.44	0.09	0.98	4.11	0.24
KM2	333	99	0.056	5	422	0.15	1.35	0.05	1.27	2.68	0.37
KM3	132	108	0.06	7	561	0.65	1.44	0.06	4.25	10.83	0.09
KM4	211	94	0.064	8	1597	0.19	1.09	0.09	7.57	2.97	0.34
KM5	139	105	0.076	5	77	0.2	0.92	0.05	0.55	2.63	0.38
Sb1	362	64	0.068	9	1200	0.14	0.92	0.14	3.31	2.06	0.49
Sb2	225	57	0.068	10	704	3.1	0.87	0.18	3.13	45.59	0.02
Sb3	88	50	0.068	12	208	0.22	1.27	0.24	2.36	3.24	0.31
Sb4	104	112	0.064	9.5	350	0.13	0.96	0.08	3.37	2.03	0.49
Sb5	120	174	0.056	7	493	0.26	1.13	0.04	4.11	4.64	0.22
US1	240	94	0.06	6	411	1.2	1.09	0.06	1.71	20.00	0.05
US2	225	100	0.052	7	860	0.92	0.96	0.07	3.82	17.69	0.06
US3	161	102	0.056	7	745	0.22	1.4	0.07	4.63	3.93	0.25
US4	237	88	0.056	7	958	0.21	1.18	0.08	4.04	3.75	0.27
US5	242	75	0.06	8	660	0.16	1.22	0.11	2.73	2.67	0.38
B1	111	35	0.064	11	953	0.23	1.25	0.31	8.59	3.59	0.28
B2	109	122	0.052	10	129	0.17	1.44	0.08	1.18	3.27	0.31
B3	99	540	0.052	7.5	644	0.24	1.13	0.01	6.51	4.62	0.22
B4	53	100	0.056	6.6	891	0.71	1	0.07	16.8	12.68	0.08
B5	88	240	0.06	8.5	1031	0.96	1.09	0.04	11.7	16.00	0.06
Eg1	93	81	0.068	8	76	0.18	1.4	0.1	0.82	2.65	0.38
Eg2	33	28	0.072	12	300	2.9	1.48	0.43	9.09	40.28	0.02
Eg3	73	377	0.056	13	474	0.28	1.22	0.03	6.49	5.00	0.20
Eg4	78	630	0.06	8	484	0.2	1.16	0.01	6.21	3.33	0.30
Eg5	91	412	0.06	9	513	0.15	1.27	0.02	5.64	2.50	0.40

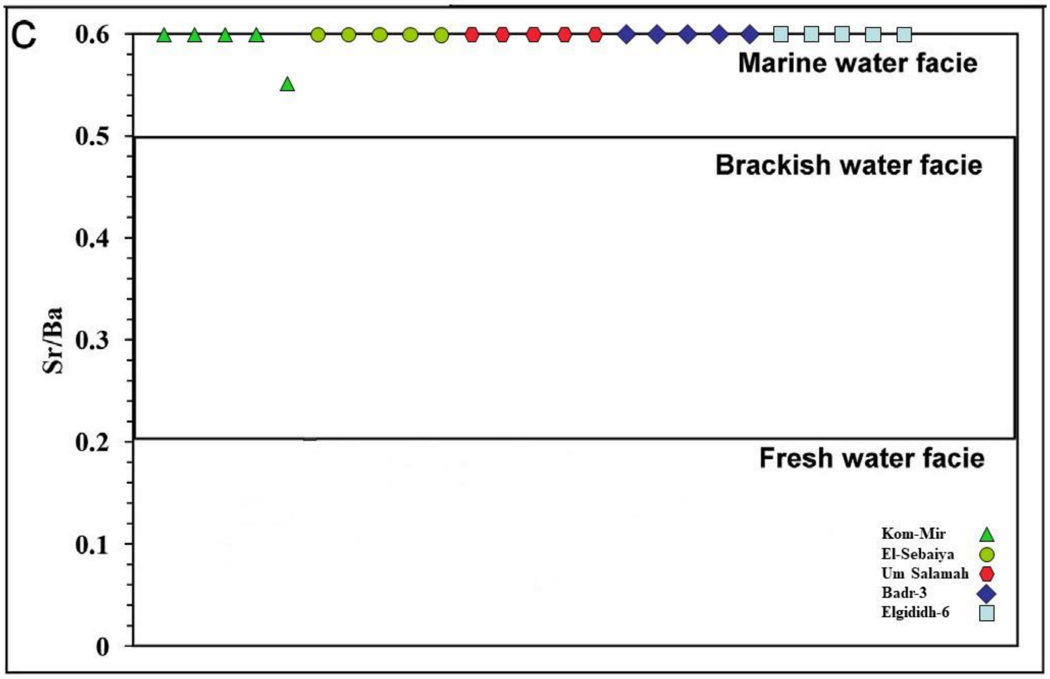

Fig. 3 Binary diagram showing Sr/Ba constructed from literature of Wei and Algeo (2020).

For freshwater sediments, the calculated ratio content of S/TOC showed an average value of 0.02 with values ranging between 0.01 and 0.06. Sulfur concentration for sediments deposited in brackish water environments ranged from 0.28 to 1.53% with an average of 0.69%, whereas total organic carbon content had an average of 4.4% with values ranging from 2.8 to 5.7%. The S/TOC ratio reveals an average content value of 0.18 and a total content value that ranges from 0.07 to 0.35. Sediments deposited in marine environments have S/TOC ratio values ranging from 0.17 to 0.47, with an average ratio value of 0.26, according to Wei and Algeo (2020). The average amount of total organic matter in marine sediments was 4.1%, with values ranging from 1.7 to 6.7%, whereas the average amount of sulphur was 1.18% with values ranging from 0.48 to 1.69%. The Duwi black shale has a sulphur concentration that ranges from 0.052 to 0.076, with an average of 0.06. With an average value of 0.56, the range of the total organic carbon content values was 0.13 to 3.1. The S/TOC ratio in this study has values ranging from 0.02 to 0.49, with an average of 0.25. Due to these widespread problems, it is clear that the majority of the samples fall between the brackish and marine environment when examining the environment's salinity characteristics based on the sulphur, total organic content, and S/TOC ratio above and comparing them to those of the study shales. A based line for calculating salinity using the S/TOC ratio was put up by Wei and Algeo (2020). For them, a S/TOC ratio of less than 0.1 indicates the features of freshwater, whereas TS/TOC ratios more than 0.1 indicate the brackish and marine environments. According to Wei and Algeo (2020), the TS/TOC was ineffective at differentiating between brackish environment characteristics and marine characteristics. This is possibly because the reduction of microbial sulfate in both brackish and marine environments is restricted to organic carbon rather than just sulfate. According to the Wei and Algeo (2020) results and the ratio values shown in Table 1, the majority of the analyzed samples belong to the marine and brackish water environments, with only a small number belonging to the freshwater environment.

Researchers like Berner and Raiswell (1984), Mao et al. (2021), and Liu et al. (2021) applied the proxy of TOC/TS in an inverse form as TS/TOC to characterize the paleosalinity of sediments while displaying some factors like diagenesis and sedimentological characteristics that may significantly affect the burial of carbon and sulphur and thus alter this proxy as a useful tool for determining paleosalinity. Liu et al. (2022) claim that variables including depositional events and biogenic methane can change the proportion of carbon to sulphur (C/S), which will affect how accurate they are as paleosalinity proxies. It is suggested by Liu et al. (2022) to take other proxies into account when employing the C/S ratio for paleosalinity distinction. They advise combining Sr/Ba ratio and paleoecological paleosalinity data, if possible, in order to reduce biased sedimentary facies description.

According to Berner and Raiswell (1984), the sediments must meet the following requirements for the TOC/S proxy to be used for paleosalinity studies: (a) the sedimentary rock must contain organic carbon (>1% C by dry weight), eliminating clastic rocks like conglomerate and the majority of sandstones; and (b) it should not be used for pure carbonate rocks with a low proportion of Fe minerals that may influence pyrite formation. As stated by Berner and Raiswell (1984), long-term diagenesis has no effect on the C/S ratio of either marine or freshwater sediment, making it a useful tool for distinguishing between the two types of sediment. According to them, freshwater rocks have high TOC/S values (>10) and marine rocks have low TOC/S values (0.5–5). According to Liu et al. (2021), a TOC/S ratio of <2.8 indicates a marine environment, while a value of >2.8 indicates a freshwater environment. Due to their TOC/S ratio (Table 1) and plotting from the created binary diagram (Fig. 4), the Duwi black shales were deposited in a marine environment, supporting the claim made above by Berner and Raiswell (1984).

4.2. Hydrothermal activity signature

In order to characterize and assess the black shales of the Niutitang Formation's hydrothermal strength during deposition, Xue et al. (2020) investigated them using the Sc/Cr ratio. The values of the Sc/Cr ratio in the Niutitang Formation ranged between 0.144 and 0.120, according to Xue et al. (2020). They interpret values of the Sc/Cr ratio as shale deposits prone to hydrothermal deposition when they are less than 0.120 and as shale deposits in normal water when they are larger than 0.144. Sediments that have undergone both hydrothermal activity and normal water deposition are identified by a Sc/Cr ratio value between lower than 0.120 and greater than 0.144. The Duwi black shales have values of the Sc/Cr ratio that vary from 0.01 to 0.43, with an average of 0.1. Nearly all of the samples are shown to fall within the range of hydrothermal deposition in the binary diagram created using the research of Xue et al. (2020) (Fig. 5).

The hydrothermal fluid supply during shale deposition was calculated by Xue et al. (2020) using the link between P and TOC enrichment. They view the P element content and organic matter content of normal water deposition as being low. In shales, hydrothermal fluid influence raises the TOC content while increasing the P content in conditions of mixed hydrothermal and normal water deposition, according to Xue et al. (2020). The binary diagram of TOC vs. P (Xue et al., 2020) shows that the majority of the samples fall within the zone of hydrothermal activity (Fig. 6).

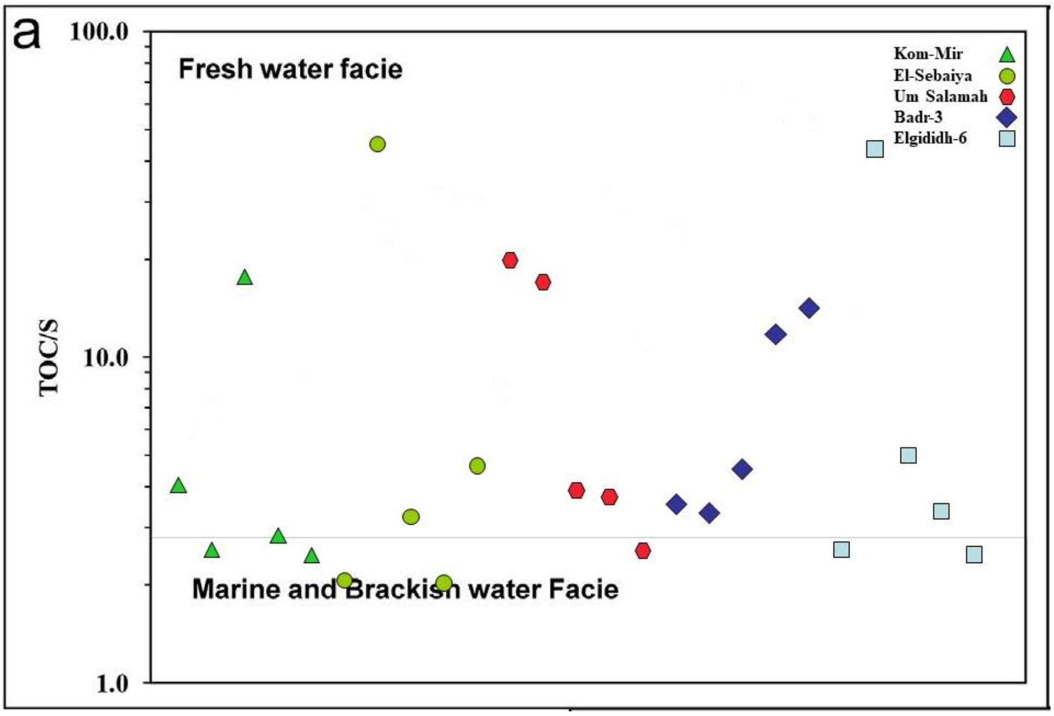

Fig. 4 Binary diagram showing TOC/S constructed from literature of Berner and Raiswell (1984).

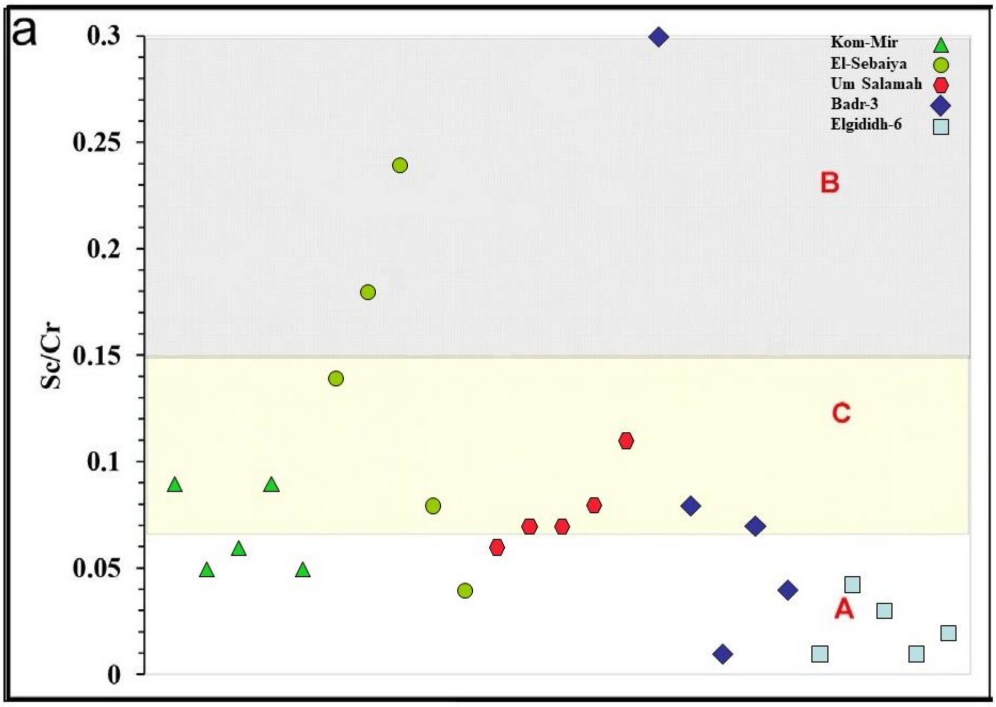

Fig. 5 Binary plot of Sc/Cr (Xue et al., 2020), The A-domain signifies hydrothermal activity; B-domain signifies normal water deposition; C-domain signifies mixed hydrothermal and normal water deposition shale.

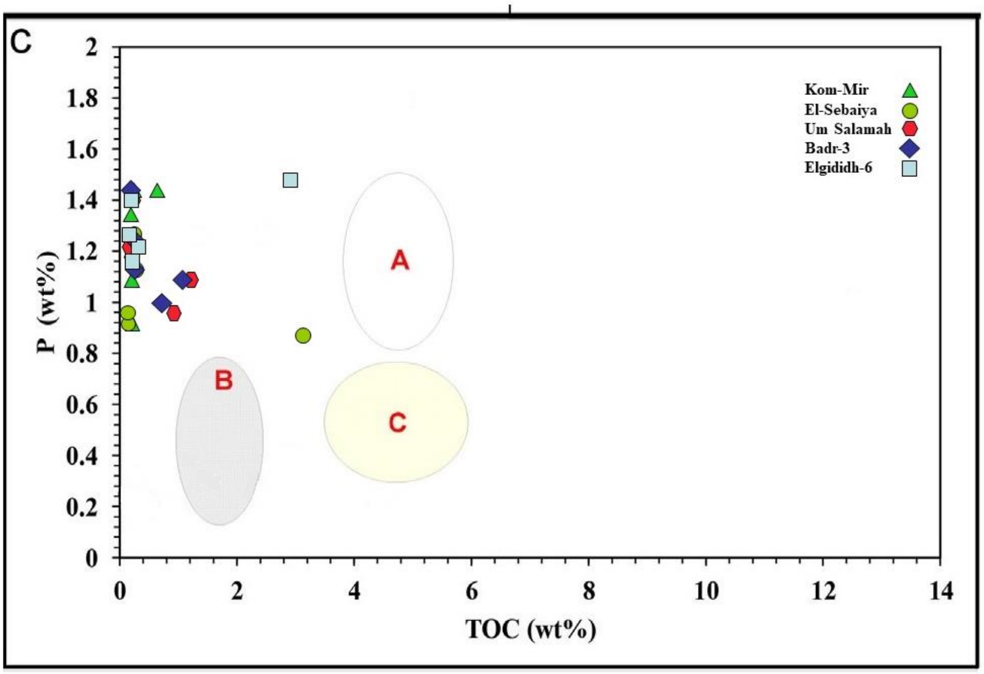

Fig. 6 Binary plot of P vs TOC (Xue et al., 2020), The A-domain signifies hydrothermal activity; B-domain signifies normal water deposition; C-domain signifies mixed hydrothermal and normal water deposition shale

V. CONCLUSIONS

For the purpose of identifying the paleosalinity and hydrothermal characteristics prevalent at the time of their deposition, the Upper Cretaceous Duwi black shales of the Nile Valley district, Aswan Governorate, Egypt, underwent geochemical analysis. To estimate the paleosalinity of black shales in sedimentary basins, a number of elements have been used, primarily barium, strontium, total organic carbon (TOC), phosphorus, and sulfur. It was possible to determine the type of water and environmental conditions at the time the shale was deposited by comparing the ratios between these elements. All of the Duwi black shale samples fell under the category of marine facies, according to Sr/Ba ratios that are >0.5. Due to their TOC/S ratio and plotting from the created binary diagram, the Duwi black shales were deposited in a marine environment. The Duwi black shales have values of the Sc/Cr ratio that vary from 0.01 to 0.43, with an average of 0.1. Nearly all of the samples are shown to fall within the range of hydrothermal deposition in the binary plot of Sc/Cr. Also, the binary diagram of TOC vs. P shows that the majority of the samples fall within the zone of hydrothermal activity.

REFERENCES

Abou El -Anwar EA, Mekky HS, Abdel Wahab W (2019b) Geochemistry, mineralogy and depositional environment of black shales of the Duwi Formation, Qusseir area, Red Sea coast, Egypt. Carbonates and Evaporites 34: 883-892

Abou El-Anwar EA, Salman S, Mousa D, Aita S, Makled W, Gentzis T (2021) Organic Petrographic and Geochemical Evaluation of the Black Shale of the Duwi Formation, El Sebaiya, Nile Valley, Egypt. Minerals, 11, 1416

Abou El-Anwar EA, Samy YM, Salman SA (2018) Heavy metals hazard in Rosetta Branch sediments, Egypt. J Mater Environ Sci 9(7): 2142-2152

Berner RA, Raiswell R (1984) C/S method for distinguishing freshwater from marine sedimentary rocks. Geology 12: 365-368

Brookins DG (1988) Seawater 87Sr/86Sr from the Late Permian Delaware Basin evaporites (New Mexico, USA). Chem. Geol. 69: 209-214

Calvert SE, Karlin RE (1991) Relationships between sulphur, organic carbon, and iron in the modern sediments of the Black Sea. Geochim. Cosmochim. Acta 55 (9): 248

Conoco (1987) Geological map of Egypt, scale (1:500,000), NG 36 SE Gebel Hamata

Ding ZL, Sun JM, Yang SL, Liu TS (2001) Geochemistry of the Pliocene red clay formation in the Chinese Loess Plateau and implications for its origin, source provenance and paleoclimate change. Geochim. Cosmochim. Acta 65 (6): 901-913

El-Azabi MH, Farouk S (2010) High resolution sequence stratigraphy of the Massstrichtian—Ypresian succession along the eastern scarp face of Kharga Oasis, southern Western Desert, Egypt. Sedimentology: 1-35

El Kammar AM (2014) Oil shale resources in Egypt: the present status and future vision. Arabian Geo-Forntiers, 1: 1-34

El Kammar AM, Darwish M, Phillip G, El Kammar MM (1990) Composition and origin of black shales from Quseir area, Red Sea coast, Egypt. J Univ Kuwait (Sci) 17: 177-190

El Kammar MM (1993) Organic and inorganic components of the Upper Cretaceous-Lower Tertiary black shales from Egypt and their hydrocarbon potentialities. Ph.D.Thesis, Cairo Univ., Egypt, 227p

Ghandour IM, Harue M, Wataru M (2003) Mineralogical and chemical characteristics of Bajocian-Bathonian shales, G. Al-Maghara, North Sinai, Egypt: Climatic and environmental significance. Geochemical J 37: 87-108

Holmden, C., Creaser, R.A., Muehlenbachs, K., 1997. Paleosalinities in ancient brackish water systems determined by 87Sr/86Sr ratios in carbonate fossils: a case study from the Western Canada Sedimentary Basin. Geochim. Cosmochim. Acta 61 (10): 2105-2121

Hu F, Liu Z, Meng Q, Song Q, Xie W (2017) Characteristics and comprehensive utilization of oil shale of the Upper Cretaceous Qingshankou Formation in the southern songliao basin, NE China. Oil Shale 34(4): 312-335

Khalil SM, McCLay KR (2009) Structural control syn-rift sedimentation, north west Red Sea margin, Egypt. Mar Pet Geol 26:1018-1034

Krabbenhöft A, Eisenhauer A, Böhm F, Vollstaedt H, Fietzke J, Liebetrau V, Augustin N, Peucker-Ehrenbrink B, Müller MN, Horn C, Hansen BT (2010) Constraining the marine strontium budget with natural strontium isotope fractionations (87Sr/86Sr*, d88/86Sr) of carbonates, hydrothermal solutions and river waters. Geochim. Cosmochim. Acta 74 (14): 4097-4109

Liu XT, Zhang MY, Li AC, Fan DD, Dong J, Jiao CQ, Chang X, Gu Y, Zhang KD, Wang HJ (2021) Depositional control on carbon and sulphur preservation onshore and offshore the Oujiang Estuary: implications for the C/S ratio as a salinity indicator. Cont. Shelf Res. 227: 104510

Liu X, Zhang M, Li A, Dong J, Zhang K, Gu Y, et al. (2022) Sedimentary pyrites and C/S ratios of mud sediments on the East China Sea inner shelf indicate late Pleistocene-Holocene environmental evolution. Marine Geology. 450: 106854

Mackenzie FT, Garrels RM (1971) Evolution of sedimentary rocks. In: Mackenzie, F.T. (Ed.), Sediments, Diagenesis, and SedimentaryRocks, Treatise on Geochemistry, vol. 7. Elsevier Pergamon, Oxford, U.K., pp. 369-407

Mao XM, Feng XL, Liu XT, Li JR, Wei JG (2021) Effects of methane seepage activity on the morphology and geochemistry of authigenic pyrite. Mar. Pet. Geol. 133: 105231

Millero FJ (2011) Chemical Oceanography, 4th ed. CRC Press, Boca Raton, Florida, p. 571

Mostafa AR, Younes MA (2001) Significance of organic matter in recording paleoenvironmental conditions of the Safa Formation coal sequence, Maghara area, North Sinai, Egypt. Intern. J. Coal Geol. 47: 9-21

Pallud C, Van Cappellen P (2006) Kinetics of microbial sulfate reduction in estuarine sediments. Geochim. Cosmochim. Acta 70 (5): 1148-1162

Qiu XW, Liu CY, Wang FF, Deng Y, Mao GZ (2015) Trace and rare earth element geochemistry of the Upper Triassic mudstones in the southern Ordos Basin, Central China. Geol. J. 50 (4): 399-413.

Roden EE, Leonardo MR, Ferris FG (2002) Immobilization of strontium during iron biomineralization coupled to dissimilatory hydrous ferric oxide reduction. Geochim. Cosmochim. Acta 66 (16): 2823-2839

Said R (1990) The geology of Egypt. A.A. Balkema, Rotterdam 734p

Schultz RB (1991) Geochemical characterization of black shale types in the Midcontinent Pennsylvanian. PhD dissertation. Univ. Cincinnati, Ohio, 229p

Temraz MG (2005) Mineralogical and Geochemical Studies of Carbonaceous Shale Deposits from Egypt. M.Sc. Thesis, Department of Civil Engineering and Applied Geoscience, Technical University of Berlin, Berlin, Germany

Tissot BP, Welte DH (1984) Petroleum Formation and Occurrence 2nd (Ed.) Springer-Verlag, New York, 699p

Wang A,Wang Z, Liu J, Xu N, Li H (2021) The Sr/Ba ratio response to salinity in clastic sediments of the Yangtze River Delta. Chem. Geol. 559: 119923

Wei W, Algeo TJ (2020) Elemental proxies for paleosalinity analysis of ancient shales and mudrocks. Geochem. Cosmochim. Acta 4: 26

Xue Y, Lei Y, Zhang J, Chen S, Chen L, Zhong K, He L, Li D, Wu Q (2020) Depositional environment of shales and enrichment of organic matters of the Lower Cambrian Niutitang Formation in the Upper Yangtze Region. Nat. Gas Ind. (5): 14

Yan C, Jin Z, Zhao J, Du W, Liu Q (2018) Influence of sedimentary environment on organic matter enrichment in shale: a case study of the Wufeng and Longmaxi Formations of the Sichuan Basin, China. Mar. Pet. Geol. 92: 880-894

Yang SY, Jung HS, Li C (2004b) Two unique weathering regimes in the Changjiang and Huanghe drainage Basins: geochemical evidence from river sediments. Sed. Geol. 164 (1): 19-34

Yang SY, Li C, Cai J (2006) Geochemical compositions of core sediments in eastern China: implication for Late Cenozoic palaeoenvironmental changes. Palaeogeogr. Palaeoclimatol. Palaeoecol. 229 (4): 287-302

Yang SY, Li CX, Yang DY, Li XS (2004a) Chemical weathering of the loess deposits in the lower Changjiang Valley, China, and paleoclimatic implications. Quat. Int. 117 (1): 27-34

Ye C, Yang Y, Fang X, Zhang W (2016) Late Eocene clay boron-derived paleosalinity in the Qaidam Basin and its implications for regional tectonics and climate. Sed. Geol. 346: 49-59

Zaid SM, EL-Badry OA, Akarish AM, Mohamed MA (2018) Provenance, weathering, and paleoenvironment of the Upper Cretaceous Duwi black shales, Aswan Governorate, Egypt. Arab J Geosci 11, 147