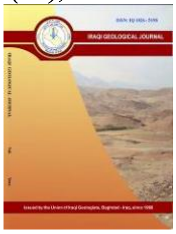
Iraqi Geological Journal

Journal homepage: https://www.igj-iraq.org



Mineralogy and Geochemistry of the Upper Cretaceous Mudrocks, Wadi Feiran Region, West-Central Sinai, Egypt

Diaa A. Saadawi[1,*], Atef M. Ibrahim[1], Harith A. AlSaad[2], Sherif A. Kamel[1] and Ahmed M. Shalaby[3]

[1] Department of Geology, Faculty of Science, Al-Azhar University, P.O. Box 11884, Cairo, Egypt
[2] Department of Geology, College of Science, University of Basrah, Basrah, Iraq
[3] Baker Hughes Petroleum Company
* **Correspondence**: deyaa_hafez@azhar.edu.eg

Received: 9 January 2023

Accepted: 11 February 2023

Published: 30 June 2023

Abstract

The present paper aims to explore the mineralogy and geochemistry of the mud rocks that have been accumulated during the Late Cretaceous in Wadi Feiran, West-Central Sinai, Egypt. The investigated section comprises three distinct lithostratigraphic units, namely the Raha, Wata, and Matulla Formations. Mineralogical examination proposes the existence of several sorts of clay minerals (e.g., kaolinite, illite, muscovite, and montmorillonite). The recognition of these clay minerals proves deposition in alkaline environmental conditions. Besides, our findings suggest that the reported clay minerals probably originated first in the form of chlorite instead of illite, as illite is likely produced from the weathering of chlorite. The overflow dispersion of both main (Al_2O_3, SiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O, P_2O_5, Cl, and SO_3) and minor (Ti, Mn, Cu, Ni, and Sr) constituents was assessed through applying chemical and physicochemical factors on the studied mudrocks. Our study concludes that reducing alkaline conditions were the limiting environmental factor in the deposition of these Upper Cretaceous rocks.

Keywords: Upper Cretaceous; Mineralogy; Geochemistry; Mudrocks; Depositional environments; Wadi Feiran; West-Central Sinai.

1. Introduction

The Sinai Peninsula constitutes a triangular area located within the extreme northeast of Egypt. This research is concerned with the Wadi Feiran area that covers about 1785 km^2 within the southwestern district of the Egyptian Sinai Peninsula. The area hosts two distinct significant lithologic associations; (1) infrastructure rocks (comprising migmatites, gneisses, and amphibolites, besides the basement complex of the Pan-African); and (2) Phanerozoic sedimentary succession of pre-rift and syn-rift stratigraphic units, which is distributed in the western and northern portions of Sinai. The investigated area lies in the western part of Sinai that has been subjected to severe tectonism during the Red Sea rifting. Noteworthy, Gabel St. Katherine, which represents the most elevated outlet in Sinai, projects upstream of the studied valley. The mountain (St. Katherine) is thought to likely originated in accompany by the broad uplift of Egypt that occurred ∼30 Ma (Meshref, 1990).

DOI: 10.46717/igj.56.1F.18ms-2023-6-26

The studied Wadi Feiran area is restricted to the northern latitudes 28o 45' and 28o 49' and the eastern longitudes 33o 20' and 33o 29’ ‘(Fig. 1). It is the biggest and widest valley within the western central Sinai and rises to 2500 m asl. The Gulf of Suez limits the Wadi Feiran eastern border, whereas the western side is limited by Gabel Hadaid. Additionally, Gabel Ekma and Gabel Nezzazat are located to the south and the northern borders of the wadi. The Upper Cretaceous rocks outcropping in the investigated Wadi Feiran range in age from Cenomanian to Maastrichtian. The Cenomanian strata (Raha Formation) are widely distributed in the studied area, and it is easily distinguished from the Lower Cretaceous Malha Formation (dominantly sandstones) forming the overlying Turonian strata by its distinct argillaceous lithology. The dominant limestone Turonian strata belong to the Wata Formation, which projects directly over the Cenomanian strata of the Raha Formation. The Coniacian–Santonian strata (Matulla Formation) are extensively represented with several exposures within the area under investigation. However, Campanian-Maastrichtian, as denoted by the Sudr Formation chalky facies, often occur in the form of detached hills distributed on the top of the typical Santonian strata (Figs. 2 and 3). The Upper Cretaceous strata constitute laterally extended and continuous belts, which facilitate the comprehensive surveying and adequate sampling of the studied sites.

Wadi Feiran and surroundings were the subjects of several studies, mainly concerned with the geology, geomorphology, hydrology, hydrogeology, and geophysics (e.g., Wachs et al., 1979; Kassem, 1981; El-Shamy et al., 1989; El Tokhi, 1992; El-Etr et al., 1993; Ghodeif, 1995; Hassan, 1997; Shendi, 1997; Geriesh, 1998; Geriesh et al., 2001; Abouelmagd, 2003; El-Shafei and Kusky, 2003; Gaber et al., 2009; Sultan et al., 2009; Abu-Alam, 2010; Massoud et al., 2010; El-Sayed et al., 2012; Kabesh et al., 2013; Seleem, 2013; Al-Rikabi et al., 2015; Mohamed et al., 2015; Arnos, 2016). Few of the aforementioned studies were targeted to explore the issues related to the mineralogy and geochemical attributes of the Upper Cretaceous strata outcropping throughout the Wadi Feiran area. Therefore, the present work tends to investigate the Upper Cretaceous stratigraphic units exposed in Wadi Feiran and discuss their lithostratigraphic setting, mineralogy, diagenesis, and geochemistry. Ultimately, this study would provide comprehensive information about the mineral composition as well as the nature of the environments under which these strata were deposited.

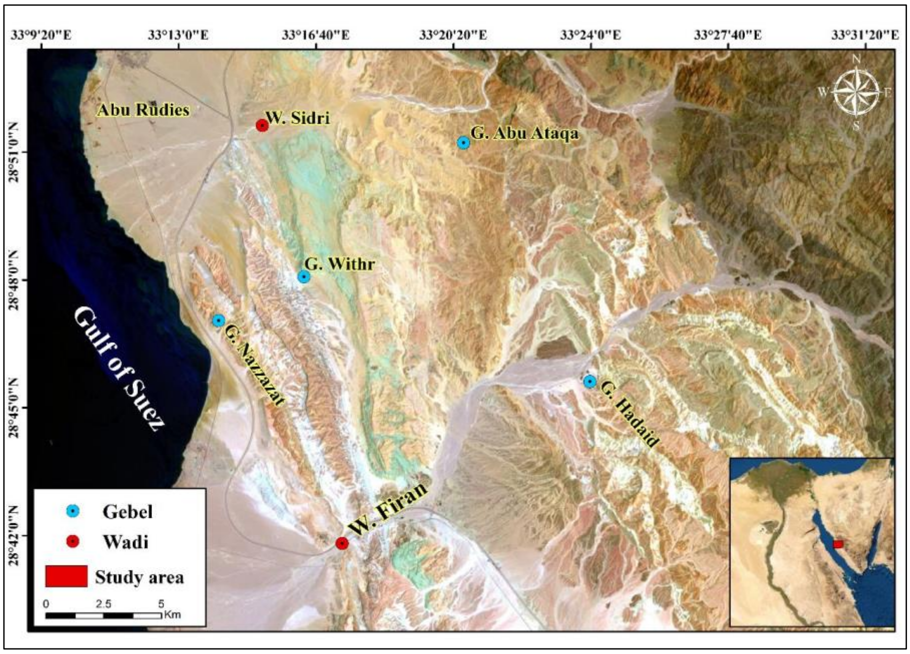


Fig.1. Locality map of the studied Wadi Feiran area.

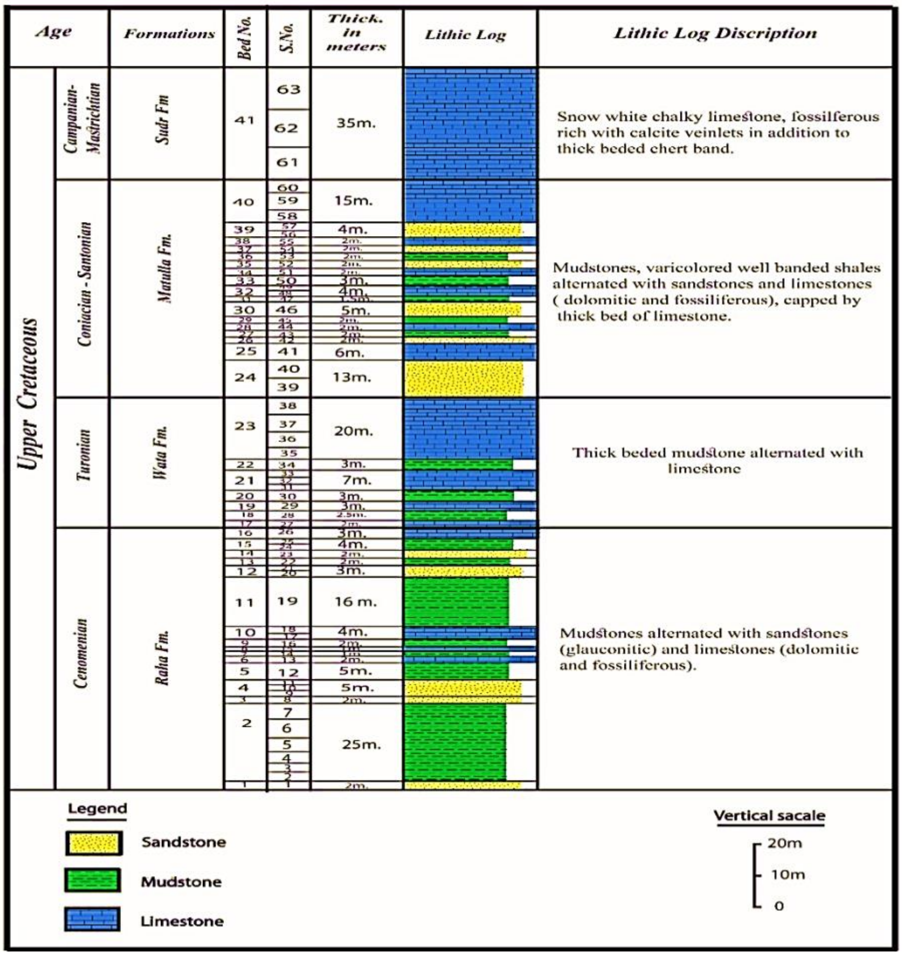


Fig. 2. Generalized graphic representation for the composite Upper Cretaceous lithological succession of the Wadi Feiran area (after Shalaby et al., 2022).

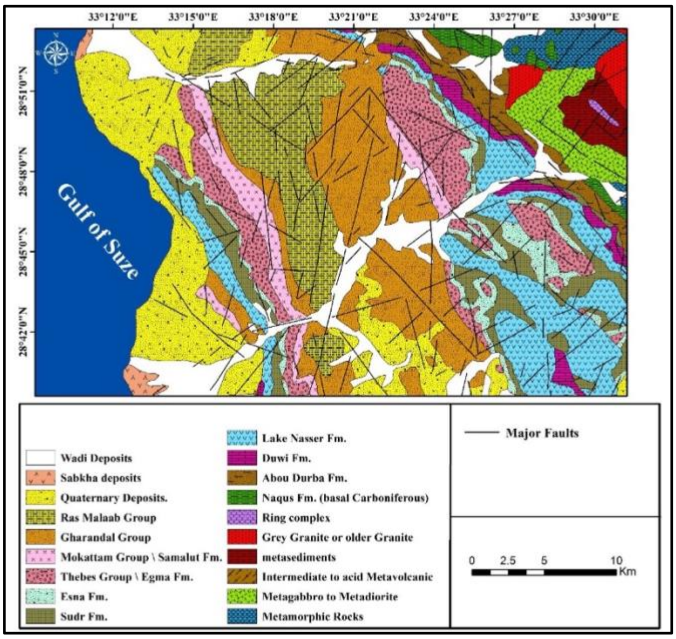


Fig.3. Geologic map of the studied Wadi Feiran area.

2. Materials and Methods

The well-developed Upper Cretaceous succession in Wadi Feiran has been studied in the field and 20 samples were gathered to conduct the present research. Usually, samples were obtained from these Upper Cretaceous outcrops at relatively regular intervals. The measured succession is divisible into four stratigraphic units. These are 79 meter-thick of the Raha Formation (Cenomanian), 40 meter-thick of the Wata Formation (Turonian), 69 meter-thick of the Matulla Formation (Coniacian – Santonian), and finally 35 meter-thick of the Sudr Formation (Campanian – Maastrichtian) with a thickness of 35 meters. A clay size fraction (particles <2 microns) is prepared following the technique described by Folk (1968); Jackson (1959) and Carver (1971), considering the precautions provided in these procedures. Oriented clay slides are prepared following the procedure given by Gibbs (1965 and 1968). X-ray diffraction (XRD) analyses were conducted at the Nuclear Materials Authority of Egypt (N.M.A.E) via the Philips X-ray diffract to a meter (Type PW/1050) with Ni-filter, Cu-radiation, λ = 1.5AA18 A° at 30 kv, 10 mA, and a regular scanning speed of 2 θ/min. The XRD was performed on six samples representative of the investigated Upper Cretaceous mudrocks. Additionally, six powdered samples were analyzed chemically using the X-ray fluorescence (XRF) technique (at NRCE Labs.) to detect the major oxides (SiO_2, CaO, Al_2O_3, K_2O, Fe_2O_3, MgO, Na_2O, P_2O_5, Cl, and SO_3), and trace elements (Ti, Zr, Sr, Mn, Rb, Cr, Pb, Cu, Ni, and Zn).

3. Results and Discussions

3.1. Mineralogical Composition

The data derived from the XRD of the examined samples are presented in Table 1 and Figs. 4 and 5. Our findings refer to the presence of several clay mineral types, including kaolinite, illite, muscovite, and montmorillonite. The existence of kaolinite and illite in studied Upper Cretaceous clays of the Wadi Feiran area likely favors accumulation under alkaline waters and further alkaline digenesis influence, and this agrees with the conclusion of Millot (1970). The occurrence of montmorillonite is owed to occur by an alkaline solution holding Ca_2^{+}, Mg_2^{+}, and Fe_2^{+}, and illite by solutions enriched with K^+ (Krauskopf, 1979). The evaluation of clay mineral assemblages detected in the Upper Cretaceous mudstones specify an alkaline depositional environment and indicates that these clays likely originated as chlorite more probably than illite. This is further complemented by knowing that illite may be ascended from the chlorite weathering (Droste et al., 1962). Krauskopf (1979) pointed out that determining clay mineral types provide clues about the environments of formation and that the nature of the originally formed clay minerals depends largely on the weathering history. Millot (1970) studied the alteration of clay minerals and proposed the following assumptions:

Illite→ Illite → vermiculite
Chlorite→ Chlorite - vermiculite
} Vermiculite- Montmorillonite
↓
Montmorillonite

3.2. Diagenesis

Clay minerals chemistry and mineralogy are highly sensitive to variations in pressure, temperature, and the chemical attributes of the environment. Clay minerals are commonly formed from previously existing minerals, particularly rock-forming silicates, through transformation and/or neoformation when these rocks are exposed to water, air, or steam (Lopez Aguayo, 1990; Gutierrez-Mas et al., 1997; Srodon, 1999; Carretero et al., 2002; Merriman, 2002).

3.2.1 Weathering

The weathering processes usually occur in sub-aerial environments. It encompasses both mechanical disaggregation and chemical degradation, which collectively result in transferring the original minerals into clays. Weathering is governed by different factors, including rock type, topographic setting, climate (temperature, chemical factor, and rainfall), and interaction of living organisms (Velde, 1992; Foley, 1999). The studied sequence generally fits in a tropical region with Mediterranean climates, which is characterized by a distinct seasonality. Under the influence of these circumstances, kaolinite accounts for the major clay mineral component. Kaolinite mixed with occasional illite could be neo-formed under a temperate climate with high precipitation.

3.2.2. Sedimentation

The clay mineral types are distributed throughout the shore till the open sea according to the following order: kaolinite-illite-smectite. Overall, clay minerals potentially replicate paleoclimate and paleorelief, besides the lithology from which the sediments were derived (source area). Kaolinite is a characteristic clay mineral produced through direct precipitation.

3.2.3 Origin of the Kaolinitic Clay Deposits

Kaolinite has different genesis; including weathering (residual kaolin) and hydrothermal activity (hydrothermal kaolin). Also, the kaolin may be found as an authigenic mineral in the sedimentary rocks. Contextually, sedimentary kaolin consists of kaolinized particles eroded from the source area, which is then transported and accumulated within coastal or continental environments. The aforementioned review of the mineralogy complements the supposition regarding the genesis of kaolinitic clay deposits. Contextually, kaolinite may be originated via neo-formation and/or transformation in rainy temperate climatic regions. The latter circumstances can act to alter biotite and muscovite into kaolinite with occasional illite.

3.3. Geochemical characteristics of mudrocks

The chemical composition, besides the data from the aforementioned mineralogical composition, would be employed to figure out and explore the distribution pattern and frequency of major and trace elements.

3.3.1 Major oxides (Frequency and Distribution)

Silica represents the principal component of shales and clays. It commonly occurs as undecomposed detrital silicates or as free silica within the clay mineral complex. The silica contents in the Cenomanian Raha Formation (Tables 2 and 3 and Fig. 6) range from 41.21 % to 46.23 % with an average of 43.14%. In the Wata (Turonian) and Matulla (Coniacian – Santonian) formations, the silica contents have averages of 23.67 % and 47.43% respectively. The vertical distribution of the average SiO_2 content in the Upper Cretaceous mudstones does not illustrate any distinct trend.

Alumina content in the Cenomanian Raha Formation (Tables 2 and 3 and Fig. 6) ranges from 8.14 % to 14.20 % with an average of 11.05 %. The Alumina contents attain an average of 7.45 % and 16.07% within the Turonian and Coniacian - Santonian rock units (Wata and Matulla formations), respectively. The distribution of the Al_2O_3 content in the examined Upper Cretaceous mudstones shows no specific trend as traced vertically. Alumina and silica behave in the same manner, where both likely tend to associate with each other in the clay minerals. However, if this does not occur, alumina remains in situ with iron, while silica is washed out to accompany magnesia and lime (Millot, 1970).

Table. 1. XRD data of the Upper Cretaceous analyzed clay samples of Wadi Feiran.

Age	*S.No.*	*Quartz*			*Kaolinite*			*Illite*			*Muscovite*			*Dolomite*			*Calcite*			*Montmorillonite*		
		2θ	**dA⁰**	***I/Iₒ***	**2θ**	**dA⁰**	***I/Iₒ***	**2θ**	**dA⁰**	***I/Iₒ***	**2θ**	**dA⁰**	***I/Iₒ***	**2θ**	**dA⁰**	***I/Iₒ***	**2θ**	**dA⁰**	***I/Iₒ***	**2θ**	**dA⁰**	***I/Iₒ***
Coniacian-Santonian		26.61	3.35	100	12.28	7.21	16	8.77	10.08	9	-	-	-	-	-	-	-	-	-	5.90	14.97	8
	45	20.83	4.26	35.7	29.42	3.04	15	12.28	7.21	16				-	-	-	-	-	-	19.78	4.49	11
Matulla Formation		39.44	2.28	11	24.91	3.57	12	36.57	2.45	9	-	-	-	-	-	-	-	-	-	34.70	2.59	3.8
Turonian		26.40	3.38	87	12.15	7.21	5	-	-	-	-	-	-	30.63	2.92	100	29.14	3.07	14	-	-	-
	30	20.60	4.31	20	34.58	2.59	14	-	-	-	-	-	-	32.98	2.72	10	31.76	2.82	12	-	-	-
Wata Formation		39.24	2.30	4	25.53	3.50	8	-	-	-	-	-	-	36.66	2.45	7	39.24	2.30	4	-	-	-
		26.66	3.34	100	-	-	-	8.86	9.98	20	19.76	4.49	20	-	-	-	29.47	3.03	51	5.76	15.31	18
	24	20.89	4.25	22	-	-	-	39.54	2.28	15	25.26	3.53	9	-	-	-	39.54	2.28	15	34.63	2.56	16
		36.59	2.46	17	-	-	-	24.38	3.65	5	23.05	3.86	8	-	-	-	30.88	2.90	3	36.06	2.49	14
		26.65	3.34	100	-	-	-	-	-	-	-	-	-	30.85	2.90	25	-	-	-	-	-	-
	22	20.86	4.26	22	-	-	-	-	-	-	-	-	-	37.30	2.41	4	-	-	-	-	-	-
Cenomanian		36.54	2.46	6	-	-	-	-	-	-	-	-	-	34.69	2.59	5	-	-	-	-	-	-
Raha Formation		26.62	3.35	49	12.29	7.20	11	-	-	-	-	-	-	30.87	2.90	100	29.42	3.04	30	-	-	-
	9	20.87	4.26	35	24.93	3.57	9	-	-	-	-	-	-	24.11	3.69	10	39.46	2.28	10	-	-	-
		36.00	2.49	9	38.57	2.33	4	-	-	-	-	-	-	33.37	2.68	6	36.00	2.49	9	-	-	-
		26.59	3.34	100	12.36	7.16	10	8.76	10.08	18	-	-	-	-	-	-	-	-	-	-	-	-
	2	20.80	4.27	32	19.77	4.49	12	19.77	4.49	12	-	-	-	-	-	-	-	-	-	-	-	-
		36.61	2.45	14	39.46	2.28	7	30.82	2.90	59	-	-	-	-	-	-	-	-	-	-	-	-

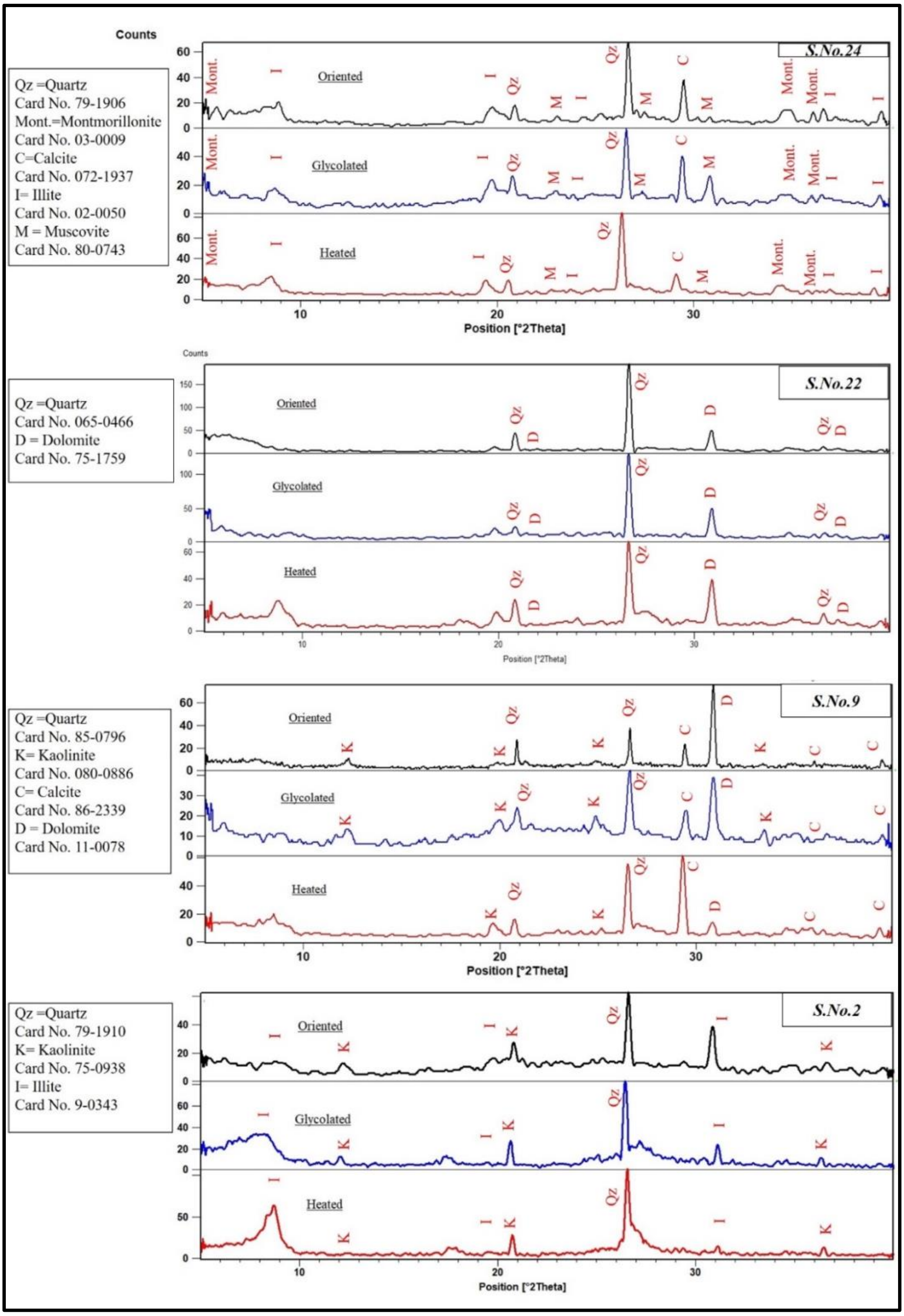


Fig.4. XRD configuration of the oriented clay samples from the Wadi Feiran Upper Cretaceous mudstones, (S. No.2, 9, 22, and 24).

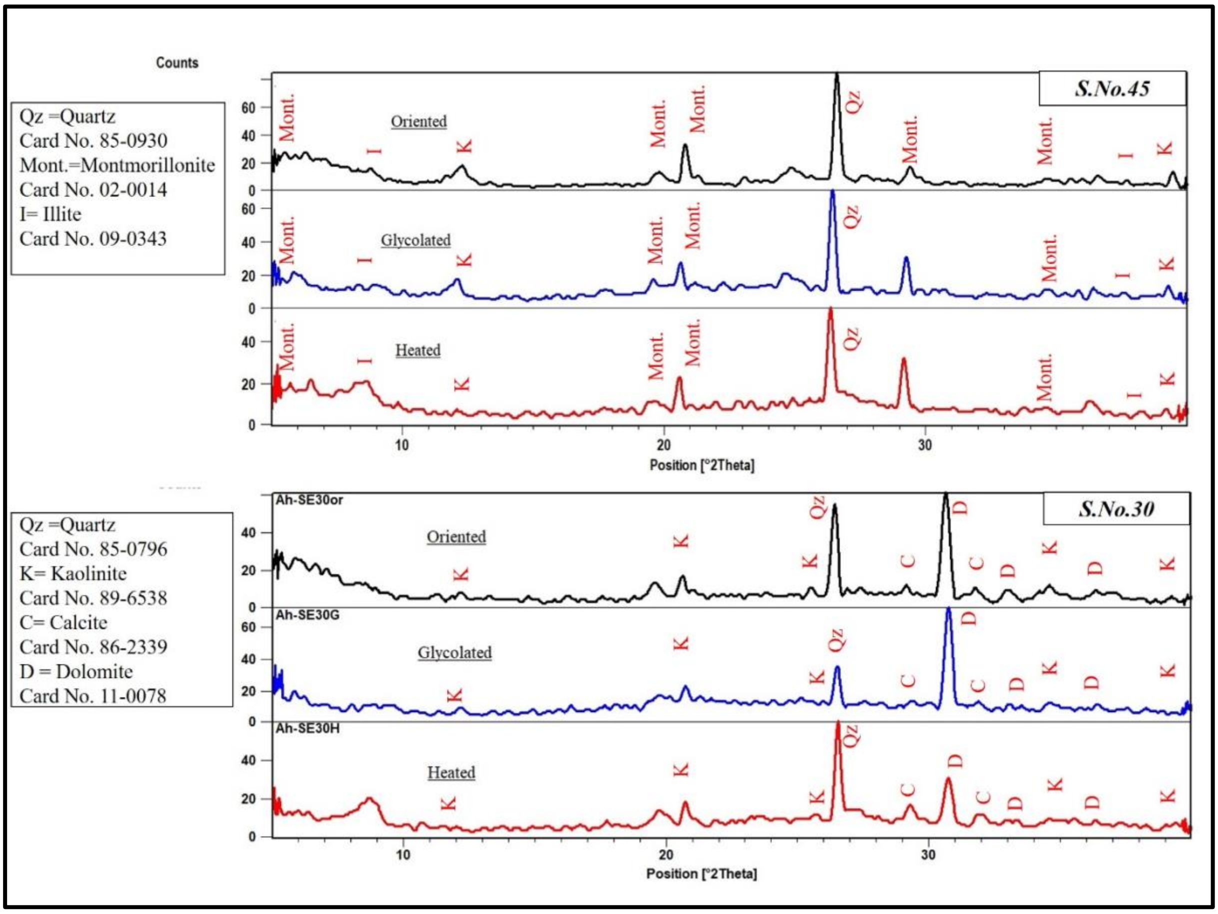


Fig.5. XRD configuration of the oriented clay samples from the Wadi Feiran Upper Cretaceous mudstones, (S. No.30 and 45).

Table. 2. The chemical composition (major oxides) of the examined Upper Cretaceous mudrocks in weight percent (wt. %).

Age	**Cenomanian Raha Formation**				**Turonian Wata Formation**	**Coniacian–Santonian Matulla Formation**
Oxides In (wt. %)	**S.No. 2**	**S. No. 9**	**S. No. 22**	**S. No. 24**	**S. No. 30**	**S.No. 45**
SiO_2	41.21	46.23	42.56	42.56	23.67	47.43
Al_2O_3	8.36	8.14	13.51	14.20	7.45	16.07
Fe_2O_3	19.69	6.27	7.03	7.63	5.76	11.42
MgO	2.20	3.29	5.36	2.59	8.21	2.84
CaO	0.55	17.10	5.59	5.15	16.34	2.96
Na_2O	4.93	4.99	1.19	3.50	0.94	1.40
K_2O	3.35	1.04	1.67	3.21	1.04	1.86
P_2O_5	0.33	0.12	0.14	0.04	2.14	0.19
SO_3	0.44	1.12	0.16	0.16	0.38	0.11
Cl^-	5.51	5.89	0.70	3.99	0.65	2.026

Table.3. The range and average concentration of the major oxides (wt. %) of the examined Upper Cretaceous mudrocks.

Age	**Cenomanian Raha Formation**			**Turonian Wata Formation**	**Coniacian–Santonian Matulla Formation**
Oxides In (wt. %)	**Min.**	**Max.**	**Aver.**	**Aver.**	**Aver.**
SiO_2	41.21	46.23	43.14	23.67	47.43
Al_2O_3	8.14	14.20	11.05	7.45	16.7
Fe_2O_3	6.27	19.69	10.16	5.76	11.42
MgO	2.20	5.36	3.36	8.21	2.84
CaO	0.55	17.10	7.10	16.34	2.96
Na_2O	1.19	4.99	3.65	0.94	1.40
K_2O	1.04	3.35	2.32	1.04	1.86
P_2O_5	0.04	0.33	0.16	2.14	0.19
SO_3	0.16	1.12	0.47	0.38	0.11
Cl	0.70	5.89	4.02	0.65	2.026

Pettijohn (1975) indicated that the silica/alumina ratio is an applicable proxy for grain size. An increase in the silica content on an expanse of alumina refers to a grain size coarsening. Among the studied Upper Cretaceous mudstones, the silica/alumina ratios (Tables 4 and Fig. 7) ascribe the mudstones of the Matulla Formation (Coniacian–Santonian) as being finer than those of the older beds, where the Cenomanian mudstones hold the coarsest sediments. This suggests that the older mudstone beds are of the sandy type (sandy mud, silica/alumina ratio equals 3.9). It seems that as the Upper Cretaceous mudstones get younger, they change from sand-size dominance to clay-size dominance through silty type and from sub-mature to immature and the younger beds were deposited in warmer climatic areas within basic alkaline conditions.

The distribution of iron oxide within the Upper Cretaceous mudstones reveals that iron oxide content in the Cenomanian (Raha Formation) rock unit (Tables 2 and 3 and Fig. 6) ranges from 6.27 % to 19.69% with an average of 10.16 %. Among the Turonian and Coniacian–Santonian (Wata and Matulla formations) mudstones, the iron oxide content has averages of 5.45 % and 11.42 % respectively.

The distribution of Fe_2O_3 within the Upper Cretaceous mudstones does not show a particular trend. This can be ascribed to its occurrence either in a free state (pigment) or in a silicate-bound state. During diagenesis, iron has a profound affinity to be incorporated within the silicate structure, which results finally in the development of glauconite and even chlorite in marine deposits (Millot, 1970).

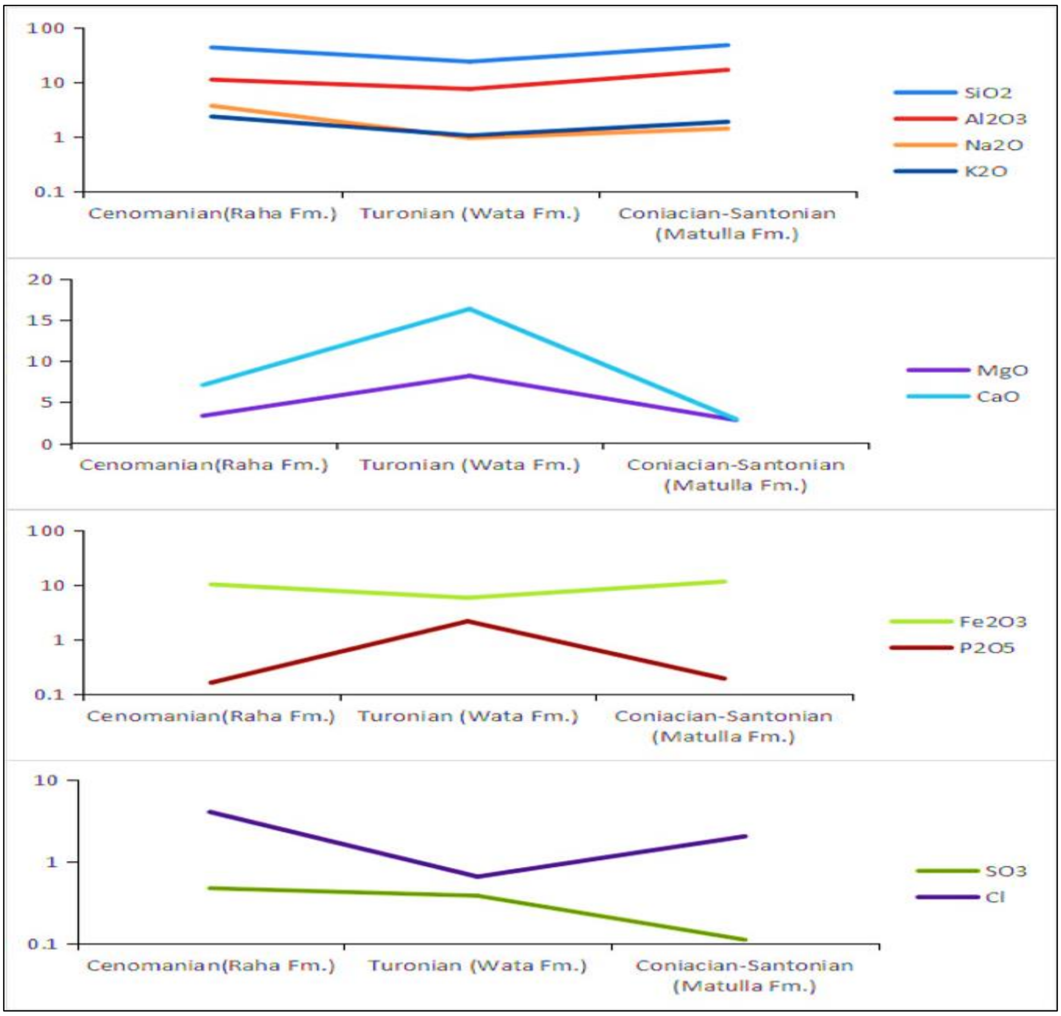


Fig. 6. Average distribution of the major oxides (wt. %) among the studied Wadi Feiran Upper Cretaceous mudrocks.

Table 4. The SiO_2/Al_2O_3 ratio within the studied Wadi Feiran Upper Cretaceous mudrocks deposits.

Age	**Cenomanian** **Raha Formation**	**Turonian** **Wata Formation**	**Coniacian – Santonian** **Matulla Formation**
SiO_2	43.14	23.67	47.43
Al_2O_3	11.05	7.45	16.7
Ratio	3.90	3.18	2.84

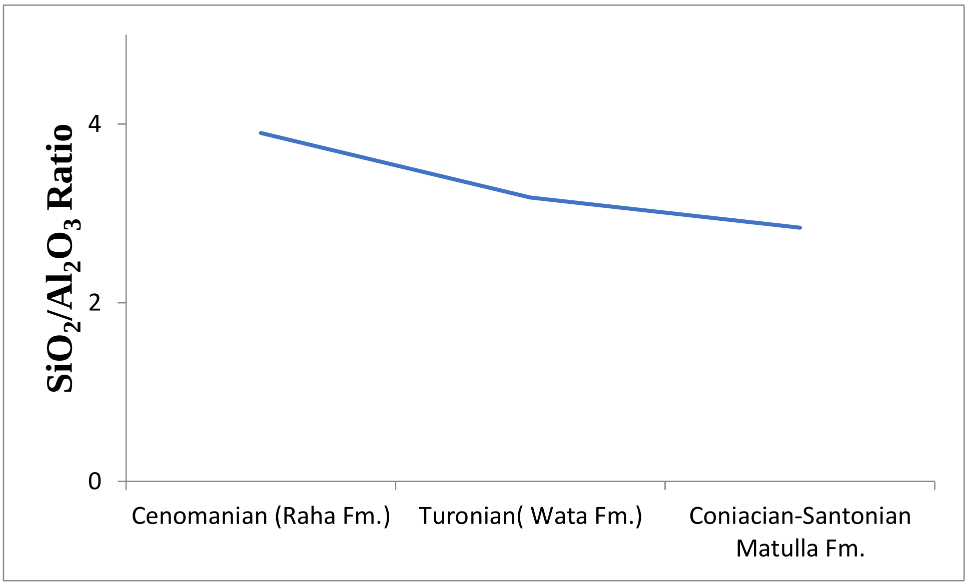


Fig. 7. The SiO_2/Al_2O_3 ratio throughout the studied Wadi Feiran Upper Cretaceous mudrocks.

The ions of calcium and magnesium relatively share the same attributes. Pettijohn (1975) indicated that lime occurs in the shales mostly as carbonate and occasionally in the form of gypsum. Besides, enormous quantities of magnesium could be wasted in the hydrosphere during the development of clays, either by a transformation of decomposed minerals or by the transformation of magnesian clay minerals (Millot, 1970). Chlorite, montmorillonite, illite, glauconite, and vermiculite are magnesian clay minerals where calcium doesn't enter into play.

In the present study, calcium oxide contents in the Cenomanian rock unit (Raha Formation) range from 0.55 % to 17.10 % with an average of 7.10 %. In the Turonian and Coniacian - Santonian rock units (Wata and Matulla formations), the iron oxide contents have averages of 16.34 % and 2.96 % respectively. The present study shows that the high values of CaO are owed to the occurrence of calcareous material.The MgO contents of the Cenomanian rock unit (Raha Formation) range from 2.20 % to 5.36 % with an average of 3.36 %. In the Turonian and Coniacian - Santonian rock units (Wata and Matulla formations), the MgO oxide contents have averages of 8.21 % and 2.84 % respectively. Furthermore, we didn't observe any distinctive trend for the distributional pattern of both calcium and magnesium oxides through the different Upper Cretaceous mudstones. According to Vinogradov and Ronov (1956), the Ca/Mg ratio of the clays and shales across the geological record proposes that the surface of the crystalline rocks (basement complex) liable for weathering had declined over time. The Ca/Mg ratio of the investigated Upper Cretaceous mudstones (Table 5 and Fig. 8) shows values comparable to that reported by Vinogradov and Ronov (1956).

Table 5. Average Ca/Mg ratio of the studied Wadi Feiran Upper Cretaceous mudrocks.

Age	Cenomanian Raha Formation	Turonian Wata Formation	Coniacian - Santonian Matulla Formation
Ca	5.07	11.68	2.12
Mg	2.03	4.95	1.71
Ratio	2.50	2.36	1.24

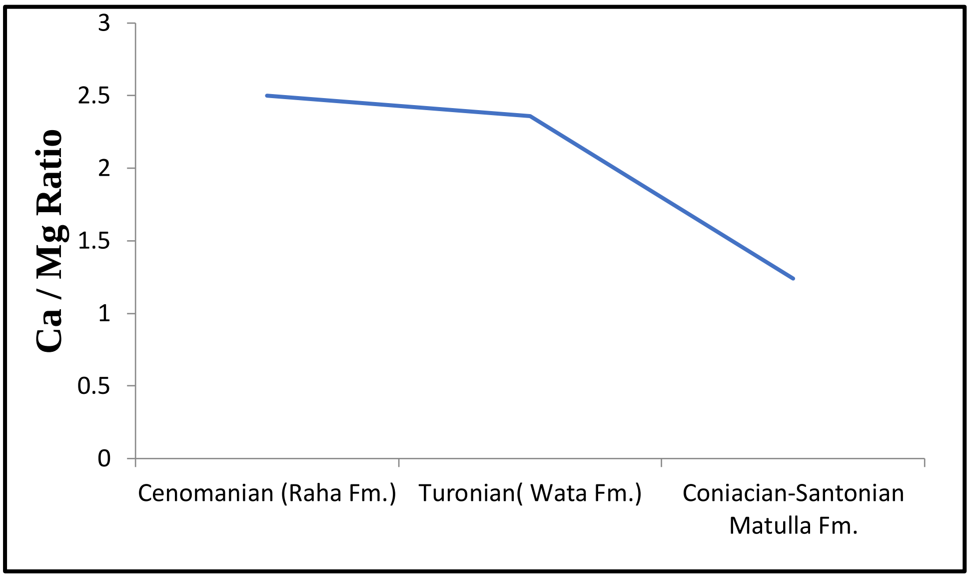


Fig. 8. Line graph demonstrating a decline in the Ca/Mg ratio through the studied Wadi Feiran Upper Cretaceous mudrocks.

The Na_2O content in the Cenomanian Raha Formation rock unit (Tables 2 and 3 and Fig. 5) ranges from 1.19 % to 4.99 %) with an average of 3.65 %. However, the Wata and Matulla formations (Turonian-Santonian) reveal reduced sodium contents with averages of 0.94 and 1.40 %, respectively.

The K_2O concentration of the Cenomanian Raha Formation ranges from 1.04 % to 3.35 % with an average of 2.32 %. The Wata and Matulla formations (Turonian-Santonian), however, demonstrate a decrease in the K_2O contents with averages of 1.04 % and 1.86 % respectively. The figures of the averages show the predominance of K_2O over Na_2O regarding their contents in each sample except those of the Cenomanian Raha Formation. Millot (1970) proposed that crystalline rocks (igneous and metamorphic) comprise relatively equal shares of both potassium and sodium. Nevertheless, the clays are commonly enriched in potassium, where the K/Na ratio approaches 2.8 (2.94 if measured as oxides; i.e.,K_2O/Na_2O).K/Na and K/Mg ratios have great significance. Where low ratios occur in montmorillonite and chlorite clay minerals, high ratios mark the clays of illite type (Garrels and Christ, 1965; Weaver, 1967). Additionally, high values of K/Na and K/Mg were proved to characterize continental rather than marine environments.

The computed ratio (Table 6 and Fig. 9) favors the following:

- Given the K/Na and K/Mg ratios almost exceed1.0, the studied mudstones are, consequently, characterized by the prevalence of clays on expanse silts. Besides, the X-ray investigation suggests the prevalence of illite (hydro mica rich in K) and the rarity of montmorillonite.
- The decreased K/Na and K/Mg ratios in the Cenomanian Raha Formation may be owed to the predominance of montmorillonite and chlorites.
- The dominance of potassium on the expanse of sodium mostly signifies long-distance transportation of the weathering products away from the source area which permits the dissolution of sodium due to hydrolysis. It could also ascribe the crystalline source rocks as being enriched in potassium aluminium-silicate minerals. Moreover, the extensive tightly chemical weathering of the crystalline source rocks led to the leaching of most sodium compared to potassium (Vinogradov and Ronov, 1956). The distributions of both sodium and potassium oxides (Tables 2 and 3 and Fig. 5) through the Upper Cretaceous mudstones do not reveal a distinct trend. The distribution of potassium and Na_2O oxides in Upper Cretaceous mudstones is consistent with that of aluminum oxide.

Table. 6. The K/Na ratios within the Wadi Feiran Upper Cretaceous mudrocks.

Age	Cenomanian Raha Formation	Turonian Wata Formation	Coniacian – Santonian Matulla Formation
K	2.32	1.04	1.86
Na	3.65	0.94	1.40
K/Na	2.03	3.54	4.25

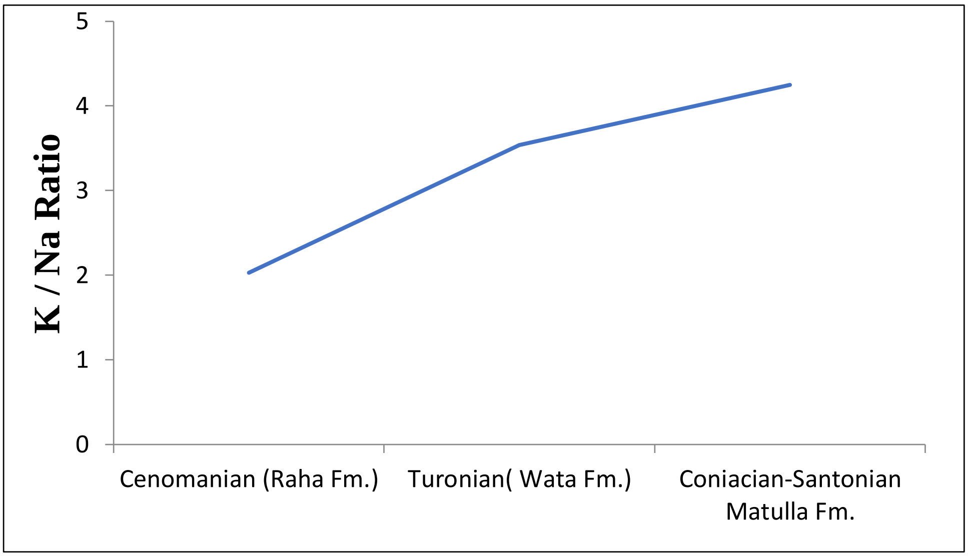


Fig. 9. Line graph demonstrating the progressively increased K/Na ratio of the studied Upper Cretaceous mudrocks.

The P_2O_5 content in the Cenomanian Raha Formation rock unit (Tables 2 and 3 and Fig. 6) ranges from 0.04 % to 0.33 % with an average of 0.16 %. In the Turonian and Coniacian-Santonian deposits (Wata and Matulla formations), the P_2O_5 contents have averages of 2.14 % and 0.19 %respectively. These values extremely exceed the background concentration of phosphorous pentoxide for shale (0.07 %; Turekian and Wedepohl, 1961). Therefore, these higher concentrations reported herein from the Wadi Feiran Upper Cretaceous mudstones could be attributed to diagenesis in oxidizing conditions, which derives further fixation of the phosphorous ions.

The sulfate (SO_3) records concentrations ranging from 0.16 % to 1.12 % with an average of 0.47 % throughout the Cenomanian Raha Formation. In the Wata (Turonian) and Matulla (Coniacian–Santonian) formations, the SO_3 whose average concentrations of 0.38 % and 0.11 % respectively. Noteworthy, these values are lower than the average value specified according to Clarke (1924) (SO3 = 0.64 %). Therefore, these relatively low contents of SO_3 indicate that the evaporation process was not active enough in enhancing the deposition of the Upper Cretaceous mudstones in a such semi-restricted environment.

The soluble chloride (Cl contents in the Cenomanian Raha Formation (Tables 2 and 3, Fig.6) range from 0.70 % to 5.89 % with an average of 4.02 %. In the Turonian and Coniacian-Santonian deposits (Wata and Matulla formations), the Cl contents have averages of 0.65 % and 2.03% respectively. The soluble chloride concentrations of the investigated Upper Cretaceous mudstones relatively violate the average predetermined value (Clarke, 1924; 180 ppm) indicating deposition in a predominately warm semi-restricted environment. Of interest, the samples containing high soluble chloride content have also high sulphate content. This favors the previously mentioned idea about the climate and environment of deposition prevailing during the Upper Cretaceous.

3.3.2 Trace elements (Frequency and Distribution)

Trace elements are normally derived during the weathering processes. Also, human activities contribute greatly to enriching the hydrosphere through trace elements (Stumm and Baccini 1978; Galloway, 1979; Nriagu et al., 1979). The severity of chemical weathering and the original mineralogical composition determine the kind of trace elements being supplied into the solution via weathering (Harris and Adams, 1966; Kronberg et al., 1979). Owing to adsorption, trace elements are mostly accompanying fine-grained clayey deposits. The pH greatly controls the adsorption process. Despite the negligibility of adsorption at reduced pH, all cations have a great tendency to be adsorbed at high pH (James and Healy, 1972b). Generally, substantial trace elements fixations directly by deposition aren't common (Krauskopf, 1979). Whereas each trace element has a distinct migration and deposition pattern, we prefer to discuss each element separately, in terms of the behavior and abundance, throughout the studied Upper Cretaceous mudrocks.

The trace elements distribution within the weathered material is essentially governed by the intensity of weathering instead of the mother rock composition. The elements Ti, Mn, Ni, Sr, Cu, and Zn tend to accumulate in a clayey-enriched weathering crust. Organic matter exerts a vital role in enhancing the Cu and Ni concentrations. According to Strakhov et al. (1956), the variability of the trace elements migration pattern is dependent on the physio-chemical circumstances that prevailed during the weathering. During migration in the colloidal and true solution state, the majority of the elements tend to be adsorbed into the clayey fractions. Subsequently, the trace elements should be preferably examined in clay fraction rather than in sand fraction (Keith and Degens, 1959) to recognize the long history of the units hosting them.

Titanium represents the most frequent trace element reported from the studied Upper Cretaceous Wadi Feiran mudstones. Ti contents of the Cenomanian Raha Formation range from 2398 ppm to 3957 ppm with an average of 3747 ppm. In the Wata Formation and Matulla formations, the Ti contents have average concentrations of 1619 ppm and 5515 ppm, respectively. The distribution of titanium (Tables 7 and 8 and Fig. 10) didn't show a particular trend for distribution. The higher titanium content reported from the Coniacian–Santonian Matulla Formation mudstones violates the average value (4,600 ppm) predetermined by Turekian and Wedepohl (1961). This can be owed to the existence of titanium in possibly authigenic anatase and rutile, which is structurally bound within iron minerals (Goldberg and Arrhenius, 1958).

Table 7. Concentrations (in ppm) of the common trace elements reported from the investigated Upper Cretaceous mudrocks of Wadi Feiran.

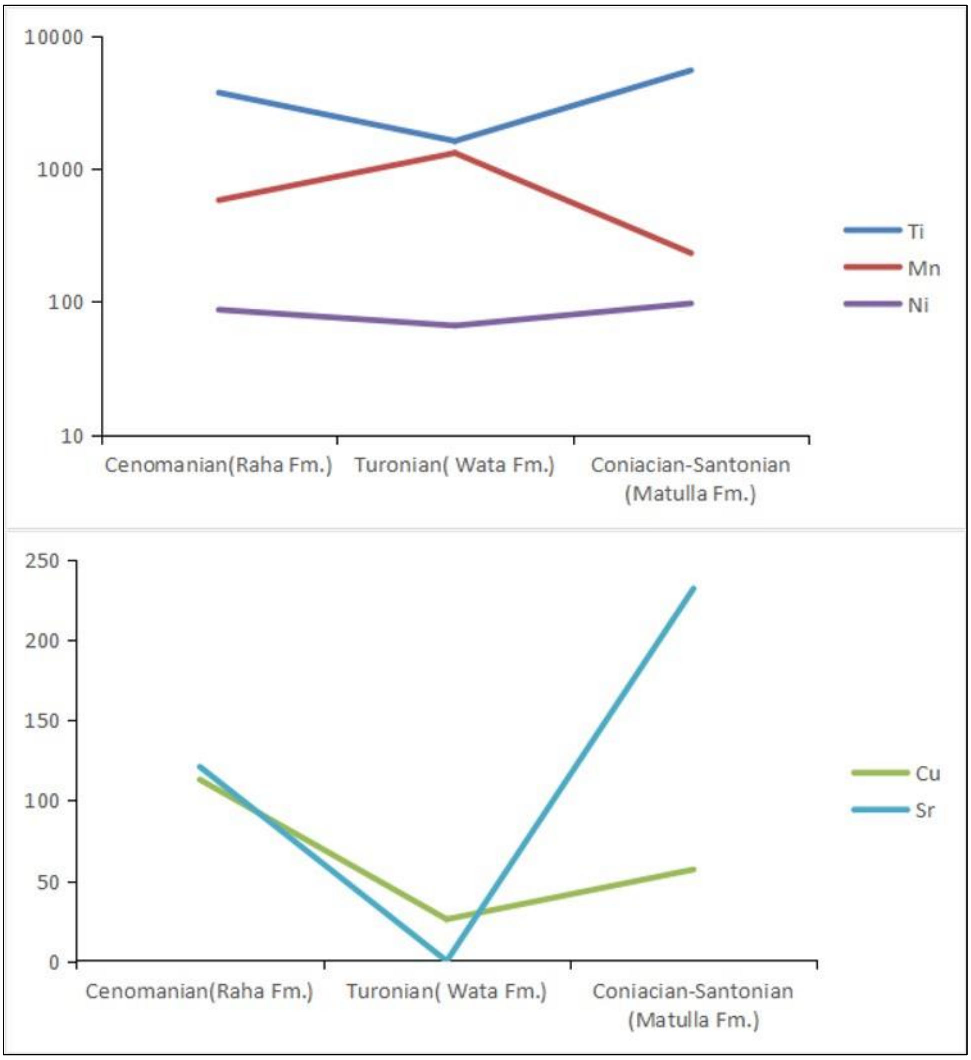
Age	Cenomanian Raha Formation				Turonian Wata Formation	Coniacian–Santonian Matulla Formation
Trace Elements (ppm)	S.No. 2	S. No. 9	S. No. 22	S. No. 24	S. No. 30	S.No. 45
Ti	3897	2398	3957	4736	1619	5515
Mn	310	1162	465	387	1317	232
Cu	--	60	23	256	26	57
Ni	85	124	80	59	66	97
Sr	88	166	49	181	--	232

Table 8. Range (min-max) and average concentrations (ppm) of the common trace elements reported from the investigated Upper Cretaceous mudrocks of Wadi Feiran.

Age	**Cenomanian Raha Formation**			**Turonian Wata Formation**	**Coniacian–Santonian Matulla Formation**
Trace Elements (ppm)	**Min.**	**Max.**	**Aver.**	**Aver.**	**Aver.**
Ti	2398	3957	3747	1619	5515
Mn	310	1162	581	1317	232
Cu	23	256	113	26	57
Ni	59	124	87	66	97
Sr	49	181	121	--	232

The reducing environmental condition drives titanium dissolution and thus it may be adsorbed by clays (Isayeva, 1971). The prevailing circumstances favor the accumulation of titanium as hydrolysates at lower pH (alkaline) values within reducing environmental circumstances. According to Arrhenius (1954), the variable titanium concentrations within the Upper Cretaceous mudstones indicate different rates of sedimentation, which is attributed as a probable cause for the higher Ti content in the Coniacian–Santonian mudstones relative to those recorded from the Cenomanian and Turonian.

The manganese (Mn) contents in the Cenomanian deposits (Raha Formation) range from 310 ppm to 1162 ppm, where the average attains a value of 581 ppm. The average Mn content greatly increased throughout the Turonian mudstones of the Wata Formation (1317 ppm) and dropped again within the Coniacian–Santonian mudstones of the Matulla Formation (232 ppm). No specific trend was observed within the vertical distribution of manganese in the Upper Cretaceous mudstones. The manganese content is generally below the average value (850 ppm) given by Turekian and Wedepohl (1961), except within the Turonian deposits. This could further be explained by the lowered mobility of manganese under oxidizing environmental conditions (Manheim, 1961; Wedepohl, 1964 and Hartmann, 1964). Therefore, it can be concluded that the Upper Cretaceous mudstones (except during the Turonian age) were developed under reducing environments, which triggers the leaching of manganese and lessens its documented concentrations. The distribution curves of both Mn and Ti are similar to each other signifying concurrent deposition under the same conditions. The Ni contents in the Cenomanian Raha Formation range from 59 ppm to 124 ppm with an average of 87 ppm. In the Turonian and Coniacian–Santonian rock units (Wata and Matulla formations), the Ni contents attain average concentrations of 66 ppm and 97 ppm, respectively. The distribution of nickel in Upper Cretaceous mudstones does not illustrate any distinct trend. The lower Ni content within the Turonian Wata Formation, compared to the average value (80 ppm; Turekian and Wedepohl, 1961), is linked to deposition in a reducing environment. According to Landergren and Joensuu (1965), the accumulation of Ni is influenced by subsea adsorption reactions and biological practices. For the Upper Cretaceous mudstones, the coincidence between nickel and magnesium (Fig. 10) augments its linkage to magnesium distribution and proves its incorporation in the magnesian clay mineral.



.

Fig.10. Distribution curves of the trace elements (in ppm) of the examined Upper Cretaceous mudrocks of Wadi Feiran.

In addition, Kukal (1971) mentioned that "deep-sea sediments are appreciably enriched in nickel where it is confined to the finest fraction which reveals a direct relationship between nickel and both manganese and ferrous iron. He also concluded that the increased content of nickel may also occur in sediments with a larger amount of organic matter. For the studied mudstones, the relationship between Ni and both Mg and Mn proves strong correlations (Fig. 10) and supports that nickel was deposited under reducing conditions. The lowered Ni content compared to that delineated by Nicholis (1967), (Ni > 150 ppm) for deep-sea sediments, indicates that the environment of deposition of the Upper Cretaceous mudstones was shallower than 250 meters.

The copper (Cu) content in the Cenomanian Raha Formation ranges from 23 ppm to 256 ppm with an average attaining about 113 ppm. In the Turonian and Coniacian–Santonian rock units (Wata and Matulla formations), the Cu contents have average concentrations of 26 ppm and 57 ppm, respectively. The copper distribution curve in the Upper Cretaceous mudstones does not reveal any distinct trend. Moreover, the Cu average value reported in the Turonian Wata Formation is considerably below the average value (50 ppm) assumed by Turekian and Wedepohl (1961). The Cenomanian Raha Formation and the Coniacian–Santonian Matulla Formation, however, whose Cu concentrations violating the average value (50 ppm) of Turekian and Wedepohl (1961), which can be ascribed to the organic matter recorded at these units. Kukal (1971) indicated that copper inferred tends to be substantially concentrated within manganese concretions, and occasionally in sediments enriched among organic matter. The copper distributional pattern did not correlate with that of manganese in the studied mudstones (Fig. 9), supporting copper deposition accompanying organic matter under reduced conditions.

The strontium (Sr) content in the Cenomanian Raha Formation ranges from 49 ppm to 181 ppm with an average of 121 ppm. The Sr was not detected in the Turonian Wata Formation, whereas the Coniacian–Santonian Matulla Formation has an average Sr of 232 ppm. The detected strontium in the studied mudstones reveals no distinct trend of distribution. The reported lower Sr concentration, compared to the average value (400 ppm) given by Turekian and Wedepohl, (1961), can be ascribed to the decline in the supply of calcium and potassium. According to Krauskopf (1979), Sr (1.21A") can substitute both Ca^{2+} (1.08A°) and K^{+} (l.46 A°), so its trend is a compromise between the trends of these two major elements. Again, strontium is a poor salinity proxy in mudstones and is particularly associated with the carbonate phase, where it suffers the diagenetic alterations of the carbonate.

4. Conclusions

Mineralogical investigation identifies four types of clay minerals (illite, kaolinite, muscovite, and montmorillonite) from the studied Wadi Feiran Upper Cretaceous mudrocks. The occurrence of illite and kaolinite clay minerals suggests an alkaline depositional environment. Moreover, chlorite is thought to be the origin of the reported clay minerals, where weathering of chlorite could produce the illite. Diagenetic impact analyses suggest two patterns for kaolinite formation. It can be either formed by direct neo-formation or through kaolinization of muscovite and biotite in rainy temperate climatic regions. Our findings derived from chemical and mineralogical analyses suggest that the investigated mudrocks were accumulated within a reducing alkaline environment.

Acknowledgements

The authors extend their sincere gratitude to the reviewers, who provided fruitful comments enhanced the research scientific value. authors would also like to thank all those who provided support during this research.

References

Abouelmagd, A. A., 2003. Quantitative hydrogeological studies on Wadi Feiran basin, South Sinai, with emphasis on the prevailing environmental conditions. M.Sc. Thesis, Geology Department, Faculty of Science, Suez Canal University, Egypt, 252.

Abu-Alam, T S., 2010. Metamorphic and Structural Evolution of the Wadi Feiran Complex, Southwest Sinai; Doctor of Science, Doctoral School of Earth Sciences, Karl-Franzens University of Graz, 133.

Al-Rikabi, A., Elmewafey, M., Beshr, A. and Elnaggar, A. A., 2015. Using GIS based morphometry estimation of flood hazard impacts on desert roads in South Sinai, Egypt; International Journal Science Engineering Resources, 6(7) 1593–1599.

Arnos, M. O., 2016. Groundwater potentiality mapping of hard rock terrain in arid regions using geospatial modeling: Example from Wadi Feiran basin, South Sinai, Egypt; Hydrogeology Journal, 24(6) 1375–1392.

Arrhenius G., 1954. Origin and accumulation of alumo-silicates in the ocean. Tellus, Stockholm, 3, 215-220.

Carretero, M.I., Ruiz, F., Rodriguez Ramırez, A., Ca ceres, L., Rodriguez Vidal, J., Gonzalez Regalado, M.L., 2002.The use of clay minerals and microfossils in paleoenvironmental reconstructions: the Holocene littoral of Las Nuevas (Donana National Park, SW Spain). Clay Minerals v. 37, 93–103.

Carver, R.E., 1971. Procedures in sedimentary petrology New York-Wiley, 653.
Clark, F. H., 1924. The data of geochemistry, 5th ed. U. S. Geol. Surv. Bull. 770- 841.
Droste, J.B.J Bhattacharya, H. and Sunderman, J.A., 1962. Clay mineral alteration in some Indiana soils, clays and clay minerals (9th Nat. Conf. 1960), 329-343.
El Tokhi, M., 1992. Petrographical, geochemical and experimental studies on the migmatite rocks of Wadi Feiran, Southern Sinai, Egypt; Ph.D. Thesis, Univ. Karlsruhe, Germany.
El-Etr, H. A., Saleh, A. S. and Abdel Tawab, S., 1993. Mitigation of flash flood hazards of Wadi Feiran basin, Western Sinai, Egypt; Proc. Inter. Conf. 30 Years Cooper, 309–333.
El-Sayed, M. H., Abo El-Fadl, M. M. and Shawky, H. A., 2012. Impact of hydrochemical processes on groundwater quality, Wadi Feiran, South Sinai, Egypt; Australian Journal Basic Applied Science, 6(3) 638–654.
El-Shafei, M. K. and Kusky, T. M., 2003. Structural and tectonic evolution of the Neoproterozoic Feiran–Solaf metamorphic belt, Sinai Peninsula: Implications for the closure of the Mozambique Ocean; Precamb. Res. 123 269–293.
Foley, N.K., 1999. Environmental characteristics of clays and clay mineral deposits. USGS Information Handout, 4.
Folk, R.L., 1968. Petrology of Sedimentary Rocks, Hemphill's Austin, Texas, 170.
Gaber, A., Ghoneim, E., Khalaf, F. and El-Baz, F., 2009. Delineation of paleolakes in the Sinai Peninsula, Egypt, using remote sensing and GIS; J. Arid Environ. 73 127–134.
Galloway, J.K., 1979. Alteration of trace metal geochemical cycles due to the marine discharge of Wastewater, Geochem. Casmochim, Acta, 43, 207-218.
Garrels, E.M., Christ, C.L., 1965. Solutions, Minerals and Equilibria, Harper and Raw, New York, N.Y., 450.
Geriesh, M. H., 1998. Artificial recharge as an effective tool for augmenting the groundwater resources of Saint Katherine area, South Sinai, Egypt; Proc. 5th Conf. Geol. Sinai Develop., Ismailia, Egypt, 47–67.
Geriesh, M. H., El-Shamy, I. Z. and Abouelmagd, A. A., 2001. Flash flood mitigation and groundwater augmentating in Wadi Feiran basin, South Sinai, Egypt; Proc. 6th Conf. Geology of Sinai Develop., Ismailia, 303–319.
Ghodeif, K. O., 1995. Hydrogeological studies on east St. Katherine environ, south-central Sinai, Egypt; M.Sc. Thesis, Suez Canal University, Ismailia, Egypt.
Gibbs, R.J., 1965. Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques, Am. Mineralogist y, 50,741-751.
Gibbs, R.J., 1968. Clay mineral mounting techniques for x-ray diffraction analysis Jour. Sod. Petrol, 38. 242-244.
Goldberg, E.D., and Arrhenius, G.O.S., 1958. Chemistry of pacific pelagic sediments. Geochim. Cosmochim. Acta, 131-153.
Gutierrez-Mas, J.M., Lopez Galindo, A., Lopez Aguayo, F., 1997. Clay minerals of Miocene– Pliocene materials at the Vera basin, Almerı´a, Spain. Geological interpretation. Mineralogica et Petrographica Acta 29A, 259–266.
Harriss, R.C., Adams, J.A.S., 1966. Geochemical and mineralogical studies on the weathering of granitic rocks American Journal of Science, 264, 146-173.
Hartmann, M., 1964. Zur Geochemie von Mangan und Eisen in der Ostsee, Meyniana 14, 3.
Hassan, E. A., 1997. Geomorphology and hydrogeology of Wadi Feiran area and its surroundings, Sinai-Egypt; M.Sc. Thesis, Geol. Dept., Fac. Sci. Cairo Univ., Beni Suef Branch, 242.
Isayeva, B.A., 1977. Relation between titanium and iron in the sediments of the Indian Ocean, Geokhimiya, 3, 310-317.
Kabesh, M., Asran, M. A. and Abdel Rahman, E., 2013. Mineral chemistry of banded migmatites from Hafafit and Feiran areas, Egypt; Arab. J. Geosci. 6 3669–3681.
Kassem, M., 1981. Hydrogeological studies in Wadi Feiran, Southwestern Sinai; M.Sc. Thesis, Geology Department, Faculty of Science, Suez Canal University, Egypt, 181.
Keith, M.L. and Degens, E.T., 1959. Geochemical indicators of marine and fresh water sediments. In research in Geochemistry, J. Wiley & Sons, New York, 38.

Krauskopf, K.B., 1979. Introduction to Geochemistry, Me-Graw-Hill, New York, 617.
Kronberg, B.I., Fyfe, W.S., Leonardos, JR., Santos, A.M., 1979. The chemistry of some Brazilian soils, elements mobility during intense weathering, Chem. Geol. 24, 211-229.
Kukal, Z., 1971. Geology recent sediments, Academic press, London, New York, 490.
Lopez Aguayo, F., 1990. Aplicacion de la mineralogia de arcillas al ana´ lisis de cuencas. In: Galan, E., Ortega Huertas, M. (Eds.), IX y X Reuniones Cientificas. Sociedad Espanola de. Arcillas. Universidad de Granada, Spain, 69–86.
Manheim, F., 1961. A geochemical profile in the Baltic Sea, Geochim. Cosmochim. Acta, 25, 52.
Massoud, U., Santos, F., El Qady, G., Atya, M. and Soliman, M., 2010. Identification of the shallow subsurface succession and investigation of the seawater invasion to the Quaternary aquifer at the northern part of El Qaa plain, Southern Sinai, Egypt by transient electromagnetic data; Geophysics Prospecting, 58 267–277.
Merriman, R.J., 2002. Contrasting clay mineral assemblages in British Lower Paleozoic slate belts: the influence of geotectonic setting. Clay Minerals 37, 207–219.
Millot T.G., 1970. Geology of clays.Keathering, sedimentology Geochemistry. C.R. Acad. Sci. Fr., Chapman Hall, London, 429.
Mohamed, L., Sultan, M., Ahmed, M., Zaki, A., Sauck, W., Soliman, F., Yan, E., Elkadiri, R. and Abouelmaged, A., 2015. Structural controls on groundwater flow in basement terrains: Geophysical, remote sensing, and field investigations in Sinai; Surv. Geophys. 36(5) 717–742.
Nicholis C.D., 1967. Trace elements in sediments: an assessment of their possible utility as depth indicators, Mar. Geol., 5, 539-555.
Nriagu, J.O., Kemp, A.L.W., Wong, H.T.K., Harper, N., 1979. Sedimentary record of heavy metal pollution in Lake Erie, Geochim. Cosmochim. Acts, 43, 247-258.
Pettijohn, F. J., Fetter, P.E., Siever, R., 1975. Sedimentary Rocks. Harper and Row, New York, 630.
Seleem, T. A., 2013. Analysis and tectonic implication of DEM-derived structural lineaments, Sinai Peninsula, Egypt; Int. J. Geosci. 4 183–201.
Shalaby A.M., Saadawi D.A., Kamel S.A. and Ibrahim A.M., 2022. Facies analysis and geochemistry of Upper Cretaceous carbonate rocks, Wadi Feiran District, West Central Sinai, Egypt. Iraqi Geological Journal, 55 (1F), 1-19.
Shendi, E. H., 1997. On the effectiveness of the VLF-EM method for groundwater prospecting in the basement terrains, Sinai, Egypt; Qatar University Science, 17(1) 143–152.
Srodon, J., 1999. Use of clay minerals in reconstructing geological processes: recent advances and some perspectives. Clay Minerals 34, 27–37.
Strakhov, N.M., Zalmanzon, E.S. and Glagoleva, M.A., 1956. Types of distribution of dispersed amounts of elements in sediments of the humid zones. Geochemistry (U.S. S.R.) (English Transl.), 6, 560-569.
Stumm, W., Baccini, P., 1978. Man-made perturbation of lakes. Lakes-chemistry: Geology, physics, ed. A. Leman, Springer-Verlag, New York, 91-126.
Sultan, S. A., Mohameden, M. I. and Santos, F. M., 2009. Hydro geophysical study of the El Qaa Plain, Sinai, Egypt; Bull. Eng. Geol. Environ. 68 525–537.
Turekian, K.K., Wedepohl, K.h., 1961. Distribution of elements in some major units of earth's crust, Geol. Soc. Amer. Bull., 72, 175-192.
Velde, B., 1992. Introduction to Clay Minerals. Chemistry, Origins, Uses and Environmental Significance. 198. London, Glasgow, New York, Tokyo, Melbourne, Madras: Chapman & Hall. Price £14.95 (paperback). ISBN 0 412 37030 1.
Vinogradov, A.P. and Renov, A.B., 1956. Evolution of the chemical composition of clays of the Russian platform Geochemistry. The Geoch. Soc. Ann.-Artor, Mich.2, 123-139.
Wachs, D., Arad, A. and Olshina, A., 1979. Locating groundwater in the Santa Catherina area using geophysical methods; Ground Water 17(3) 258–263.
Weaver, C.E., 1967. Potassium, illite, and the Ocean, Geochim. cosmochim. Acta, 31, 281-296.
Wedepohl, K.H., 1964. Unters uchungen am kupferschiefer in Nordwestdevtschland; ein Beitrag zur Deutung der Genese bitumiooser sedimente, Geochim. Cosmochim. Acta, 28, 305.