

Appraisal for the environment, weathering and provenance of Upper Cretaceous-Lower Tertiary shales, Western Desert, Egypt

Abdelaziz EL SHINAWI¹, Fatma RAMADAN² and Martina ZELENAKOVA^{3*}

Authors' affiliations and addresses:

¹ The Environmental Geophysics Lab (Z EGL),
Department of Geology, Faculty of Science,
Zagazig University, Egypt
e-mail: geoabdelaziz@yahoo.com

² Department of Geology, Faculty of Science,
Zagazig University, Egypt
e-mail: fs_ramadan@hotmail.com

³ Institute of Environmental Engineering, Faculty
of Civil Engineering, Technical, University of
Kosice, 042 00 Kosice, Slovakia
e-mail: martina.zelenakova@tuke.sk

*Correspondence:

Martina Zelenakova, Institute of Environmental
Engineering, Faculty of Civil Engineering,
Technical, University of Kosice, 042 00 Kosice,
Slovakia
tel.: +421556024270
e-mail: martina.zelenakova@tuke.sk

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Abstract

The combination of the mineralogical and geochemical composition of shales is considered a key to decipher their environment evolution, weathering, climatic conditions, and provenance. The Upper Cretaceous-Lower Tertiary succession is extensively dispersed in Egypt. The present work is devoted to studying the Dakhla shales of (Maastrichtian- Danian), Duwi (Campanian) and Quseir (pre-Campanian) formations. Chemical and mineralogical analyses were conducted by using seven representative surface sections from Dakhla Oasis. Dakhla shales are dominated by Smectite and kaolinite. The average percentages of SiO₂, Al₂O₃, CaO, MgO, Na₂O and K₂O are subordinate values. In contrast, Al₂O₃ contents of Dakhla shale, TiO₂, P₂O₅ and Fe₂O₃, contents are relatively higher than common shale composition. The CIA and CIW high values due to clay minerals and the absence of feldspars. This is also confirmed by the smectite domination and subordinate kaolinite in these formations. The ICV values for Dakhla and Duwi shales are 0.59 and 0.74 (ICV < 1). The shale is mature and deposited in a quiescent environment. Whereas the ICV for Quseir shale is 1.24, it can be incidental that it is immature. The shale is wholly detrital and a product of moderate to intensive weathering. The provenance was constituted of granitic and basaltic source rocks, and the parent provenance is basalt. Consequently, the shale is deposited under fluvio-marine environments, and the prevailed condition was of alkaline chemical affinity probably passed through different environments varying from a fluvial, eolian and shallow marine.

Keywords

Depositional environment, clay minerals, weathering; Dakhla shale, thermal analyses.



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Introduction

Geochemical analysis of shale can introduce information on the environment, provenance, weathering conditions, and sediment recycling (Peng et al., 2014). Further studies (for example, Rowe et al., 2008; Ross and Bustin, 2009; Smail, 2015; Jianhua Zhao et al., 2016; and Nabih and El Shinawi, 2020) show that the main factors affecting compositions of sediments are source rock, source area weathering, sorting, tectonic setting, diagenesis, and recycling. Moreover, tectonics are organised by the uplifting rate and the landforms gradient (Pandey and Parchaa 2013). As well, the geochemistry of the sediments is very significant for considering the erosional features of the basin and record the erosional and weathering process (Moufti and Németh, 2016, El Shinawi and Naymushina, 2015 and Kramarenko et al., 2016). The geochemistry of shale is a valuable tool in the study of paleoclimatic conditions of sediments (Wronkiewicz and Condie, 1987; Feng and Kerrich, 1990) and provided constraints on the continental crust evolution through time. Furthermore, a variable studies of shales elemental composition with the goal of defining the provenance of sedimentary rocks (McLennan and Taylor, 1991; and Nesbitt, 1982). The major elements are useful in understanding the rock compositions, provenance and tectonic setting of the deposited sedimentary rocks (McLennan et al. 1991). On the other hand, major element compositions are precise by weathering, lithology, and diagenesis. Consequently, clastic sediments have a vital role in identifying the composition and environment of the source rocks (Peng et al., 2018 Peng et al., 2018 and Abdeltawab et al., 2013). The geochemistry imitates mostly the principal mineralogy of the parent rock and the overlaid belongings of pre- and post-depositional chemical weathering, well-ordered by element mobility and founding secondary phases such as clays (Philippe Négrel et al., 2021). Moreover, their mineralogical and chemical composition were influenced by factors such as weathering, source provenance, and diagenetic processes. Specifically, clay minerals provide constraints on continental weathering under different climatic conditions (Thiry, 2000; and Song et al., 2012 and Attwa, and El Shinawi, 2014). Hence, shale geochemistry is a helpful tool in studying the paleoclimatic conditions, tectonic setting, and provenance of sediments. Therefore, geochemical studies of fine sediments such as shale is the most beneficial rock attributable to their homogeneity (Christopher et al., 2017; Alqahtani and Khalil, 2019). Recent geochemical inquiries for shales are concerned with the provenance and tectonic evolution of sedimentary basins. The ratios of minor and major oxides, such as $\text{SiO}_2/\text{Al}_2\text{O}_3$, high due to enriched Al-rich clay minerals relative to quartz mineral and high $\text{SiO}_2/\text{Al}_2\text{O}_3$ are due to enrichment quartz. Additionally, used alkali oxides to reveal facts about the provenance of the clastic sediments. Furthermore, CIA and $\text{Al}_2\text{O}_3\text{-(CaO+Na}_2\text{O)-K}_2\text{O}$ (A-CN-K) ternary plots are useful geochemical parameters for study the provenance and rocks maturity (Armstrong-Altvain et al., 2004; Lee et al., 2005; Wanas and Abdelmeguid, 2006; Campos Alveraz and Roser, 2007). However, very few studies conducted geochemical data to study the depositional environments, weathering, and provenance of deposits. Consequently, clay minerals are used as paleo-climatic indicators. Clay mineralogy delivers important information regarding the characteristics of paleoclimate, provenance, and diagenetic environments. By contrast, climatic changes with eustatic sea level are regarded as the main controlling factors that detect the depositional environment (Nesbitt, 1982 & 1984 and Naymushina et al., 2010). The Clay minerals are considered as a sedimentation product and provide information for the paleoclimate, provenance, and environments. Furthermore, clay minerals are extensively dispersed in sediments and are the main indicator of the paleo-environment, the different environments well-known by the clay-mineral content (Xie et al., 2010; and Sun et al., 2019 and Abd-Elaty et al., 2020). The study area lies between Latitudes $25^\circ 10'$ and $26^\circ 00'N$ and Longitudes $26^\circ 30'$ and $29^\circ 20'E$, covers about 5625 Km^2 (Fig. 1) and is situated in the Dakhla basin, it shows lateral many facies variations (El-Azabi and El-Araby, 2000). The Dakhla Oasis is accessible through the east asphaltic road, which starts from the Kharga Oasis in the east of about 180 km. to the west. The wide extended clay deposits exposed all over the El Kharga and El Dakhla stretch give attention to the government and scientists. Among the clay deposits are the black shales, which have considerable economic importance due to their special composition. The Dakhla Formation type locality, the northern bordering the Dakhla Oasis, where its thickness reaches 250 m. The shale is accommodated chiefly in the Campanian-Maastrichtian Dakhla and Duwi formations. In the present study, the shales geochemistry and mineralogy, especially clay minerals, are used to estimate the environments and provenance. The novelty in the present study, the shale is represented different stratigraphic ages, Dakhla shales (Maastrichtian-Danian), Duwi (Campanian), and Quseir (pre-Campanian) formations and also various locations, Seven representative surface sections from Dakhla Oasis were measured, chemically and mineralogical analysed (Fig. 1).

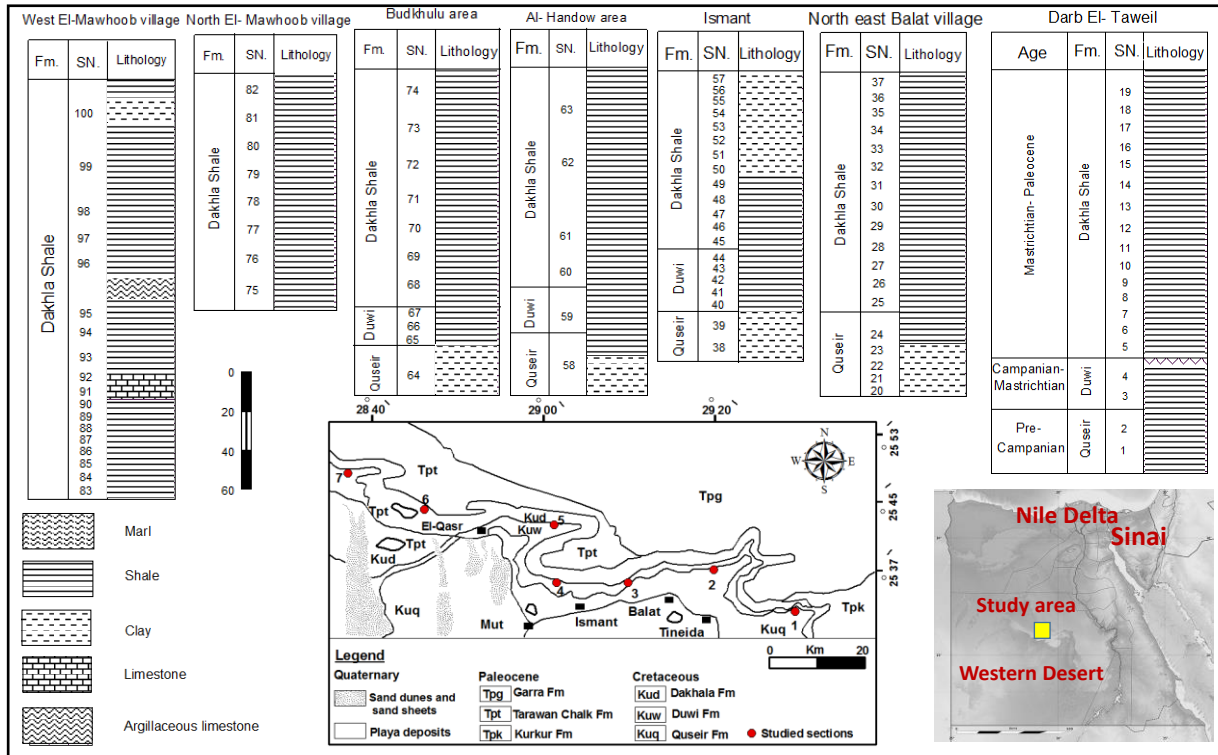


Fig.1. Sketch location map for the stratigraphic sections, Dakhla Oasis, Egypt

Geologic Settings

More researchers have been studied the study area of geology, such as (Tantawy et al., 2001), (Sediek and Amer, 2001), (Abdou and Shehata, 2007), and (Brookes, 2010). These studies are revealed that Quseir Formation founded at the succession base and composed of siltstone, variegated claystone and sandstone (Youssef, 1957). The shale of the Quseir Formation consists of shale and claystone with minor interbedded sandstone streaks and pockets. The average thickness ranges from 20-37 ms. Overlying Middle Campanian (Quseir Formation) is the Duwi Formation phosphate-bearing (Youssef, Op. Cit). It is mainly composed of alternating beds of phosphate, shale and marly limestone. The Duwi Formation is overlain conformably by a thick shale succession with mudstone interbeds of the Dakhla Formation. The Dakhla Formation is of Maastrichtian–Danian age; it and its correlative Khoman Chalk are followed upwards by the Tarawan and Esna formations, respectively. The sequence is dominated by many lithologic varieties, including shale, sandstone, claystone, limestone, phosphorite with various micro- and macrofossils assemblages. The studied sections it is composed of the argillaceous limestone at the base, followed by fissile grey shale with alternating bands of fossiliferous mudstone, wherein the upper part of the sequence is composed of grey and purple shales alternating with yellowish-brown ferruginous sandy limestone. The Dakhla Formation thickness range from 70-180 m; it marks the thickest and widespread shale unit throughout the Upper Cretaceous-Lower Tertiary sediments all over Egypt. At north and west, El-Mawhoob Village base is unexposed.

Materials and Methods

Seven sections (Darb El-Taweil; Ismant; Northeast Balat Village; El Handow; Budkhulu; North El-Mawhob Village, and West El-Mawhoob) of the pre-Campanian to Danian rocks were sampled (Fig. 1). The measured successions are mainly composed of shales and mixed siliciclastic and carbonate rocks, of which the phosphorite is dominant in the basal and middle parts of the Duwi Formation, whereas the carbonates comprise the main bulk of the upper part in the Duwi Formation (Fig.1). About 101 samples representing the different ages of study shales (10 from Quseir Formation, 11 from Duwi Formation and 80 from Dakhla Shale) were collected and chemically analysed for SiO₂, MgO, Al₂O₃, MnO, Fe₂O₃, CaO, Na₂O, K₂O, P₂O₅, Cl⁻, SO₃²⁻, TOC and TiO₂. The samples are tested, 200-300 mg of as a powder in Teflon beakers with a mixture of perchloric, hydrofluoric, and nitric acids. The mixtures were diluted by hydrochloric acid. The total iron is expressed as FeO. The limits for the analysed elements are mostly around 0.01 ppm. The range of accuracy (Analytical uncertainties) is 2 % for all major oxides except P₂O₅ and MnO, for which uncertainties can be +/-10 %. The results are compared with the Phanerozoic Shale average composition (Condie, 1993), Normal Pierre Shale (Schultz et al., 1980), (UCC) Upper Continental Crust (Taylor and McLennan, 1985), Russian Mesozoic and Cenozoic Shales (RMCS)

(Ronov and Migdisov, 1971) and (NASC) North American Shale Composite (Gromet et al., 1984). The Chemical Index of Alteration (CIA) was calculated (Nesbitt and Young, 1982). The index represents the molar ratios of $(Al_2O_3 / (Al_2O_3 + CaO + K_2O + Na_2O)) \times 100$, which has been established as a general indicator for the weathering degree (Nesbitt and Young, 1982). High values (76-100) indicate intensive chemical weathering in the source area, whereas low values of 50 or less indicate un-weathered areas. They reported a CIA value of nearly 100% for kaolinite and chlorite, and 70 to 75% for moderate or average shales, whereas Taylor and McLennan (1985) reported a CIA value of 85 to 100% for residual clays. The chemical index of weathering (CIW) is calculated $(Al_2O_3 / (Al_2O_3 + CaO + Na_2O)) \times 100$. Where, Al_2O_3 , CaO, and Na_2O are in molecular proportions. In the proposed index, Al_2O_3 is used as the immobile component. CaO and Na_2O are considered as mobile constituents because they are free leaked during weathering. Additionally, (ICV) Index compositional variation was used for sediments maturity determination (Cox et al., 1995), sediments show ICV (>1) are immature with the first cycle of sediments deposited in tectonically whereas, ICV (<1) are mature and deposited in craton environment, where the recycling of sediment is active.

Therefore, the clay portions were subjected to X-Ray diffraction analysis to identify their clay mineral composition (Carroll, 1970). Three oriented mounts were prepared from each sample: untreated, glycolated and heated at 600°C for one hour. Semi-quantitative detection of the identified clay minerals was undertaken with the method adopted by (Pierce and Siegel, 1969). X-Ray diffractograms were obtained using Philips X-Ray diffractometer model PW/1710 with a monochromator, Cu-radiation ($\lambda = 0.1542$ nm) operating at 40 KV, 30 mA. The diffraction forms are collected at 25°C with step size 0.05° per step and a dwell time of 12 s per increment. As well as, shale samples were investigated by different techniques to evaluate their mineral compositions. They were studied by using differential thermal techniques (Ramachandran et al., 2002). The thermal analyses were done by mean of MOM Derivatograph, which gives the differential thermal analysis (DTA) and the Thermal Gravimetry (TG). One gram of each powdered sample was heated by 10 Co/min up to 950 Co with $\alpha-Al_2O_3$ as reference material. DTA sensitivities and TG were set at 1/10 and 500 mg, respectively. DTA and TG are explained by the form of derivatographs. The principal thermal reactions and the approximate temperature ranges are generally considered in low temperature below 400°C: loss of adsorbed water, 400–750 °C: dehydroxylation and the creation of quasi-stable dehydroxylated phases and high temperature above 750°C up to 950°C: recrystallisation and formation of new phases.

Results and discussion

Mineralogical composition

The inspected samples of the Duwi, Quseir, and Dakhla Shale were studied using differential thermal techniques. The thermal analyses were conducted for 12 clay samples of different rock units. DTA and Thermogravimetry (TG) results are explained by the form of derivatograph (Fig. 2). The characteristic thermal manners of each mineral as follow:

Smectite

DTA curves for smectite show in variable symmetric endothermic peaks at temperature ranges from 50.8 C° – 940.3C° (Fig. 2). The total losses in weight upon heating up to 950 C° range from 12.64 % to 20.37 % of the original sample weight. All smectite yields three peaks in studied samples, the first is a peak at a low-temperature range from 50.8 C° to 100.2C° (Mackenzie, 1970; and Alejandra et al., 2017), the second is a main endothermic peak at a temperature ranging between (510.1C° - 525.1 C°) related to loss of hydroxyl water and the third is an endothermic reaction at a temperature ranging between 860.3 C° to 940 C° (Fig. 2 a, d, f and b). The formation of smectite requires the presence of Na & K (alkali metals), and silicates formed by the hydrolysis of Ca, Mg and Fe tend to combine with silica to form smectite (Millot, 1970; and Keller, 1970).

Kaolinite

It predominates in studied Dakhla shales, but it present as a minor in Quseir and Duwi shales. It exhibits two peaks on DTA curve, the first peak is the main peak of smectite at a temperature ranging between 510.1C° and 525.1 C° upon loss of structural water, and the second is at a temperature ranging between 860.3 C° and 940 C° due to structural change (Fig. 2a, c and d). The Dakhla Formation consists of kaolinite and less of a smectite/illite mixed layer than Duwi and Quseir formations. Kaolinite is considered a weathering product and soil formation of all rocks (Frederickson, 1952). These conditions involve the removal of Na, K, Mg, Ca and Fe and the addition of H (Millot, 1970 and Keller, 1970). Moreover, the end product of weathering is Kaolinite under the condition of acid soil solution and good drainage in a temperate climate (Krauskopf, 1979).

Goethite

The amorphous ferric oxide is recorded in the curves of a few samples of Quseir and Dakhla Shale. It exhibits a very small endothermic peak at a temperature range between 240C°-280C° (Fig. 2a), as mentioned by (Mackenzie, 1970). After deposition iron may be leached from clay minerals which combine with hydroxyl ion to form colloidal goethite (Ehlers et al., 1982).

Calcite

Calcite is present as a minor constituent in a few samples of Quseir and Dakhla shale. In the current study calcite, gives a single endothermic peak as mentioned by (Mackenzie, 1970) due to the decomposition of carbonate ions associated with calcium. The single endothermic peak is detected at a temperature ranging between 700°C-735 °C (Fig. 2f).

X-ray diffraction analysis

The X-ray diffraction was conducted for the oriented clay fraction (untreated). It revealed the existence of a sharp peak of 14.1 Å and a very weak 7.16 Å. When glycolated run the peak 14.1 shifts to a larger spacing peak of 17.9 Å, while with heating to 550 °C, it collapsed and sharpened at 9.8 Å peak. X-ray analysis of 35 samples revealed that smectite range from 35 % to 85 %, while kaolinite (0-75 %), consequently illite – smectite mixed layer and quartz (6.5% to 15%) other than calcite and goethite occur as minor constituents (Table 1). Goethite and calcite were detected in minor amounts in study samples. As a whole, the shale are generally composed of smectite, kaolinite and smectite/ illite mixed layer. The second dominant clay constituent is Kaolinite, besides occasional goethite and calcite. The Dakhla shale is comparatively more kaolinitic and less of a smectite and smectite/illite mixed layer than Duwi and Quseir formations.

Tab. 1. Semi-quantitative (wt %) mineralogical composition of the studied shales, analysed by X-ray diffractometry

Clay minerals	Minimum %	Maximum %	Mean %
Smectite	35	85	56
Kaolinite	0	75	18
Illite- Smectite	0	30	9
Quartz	6.5	15	7

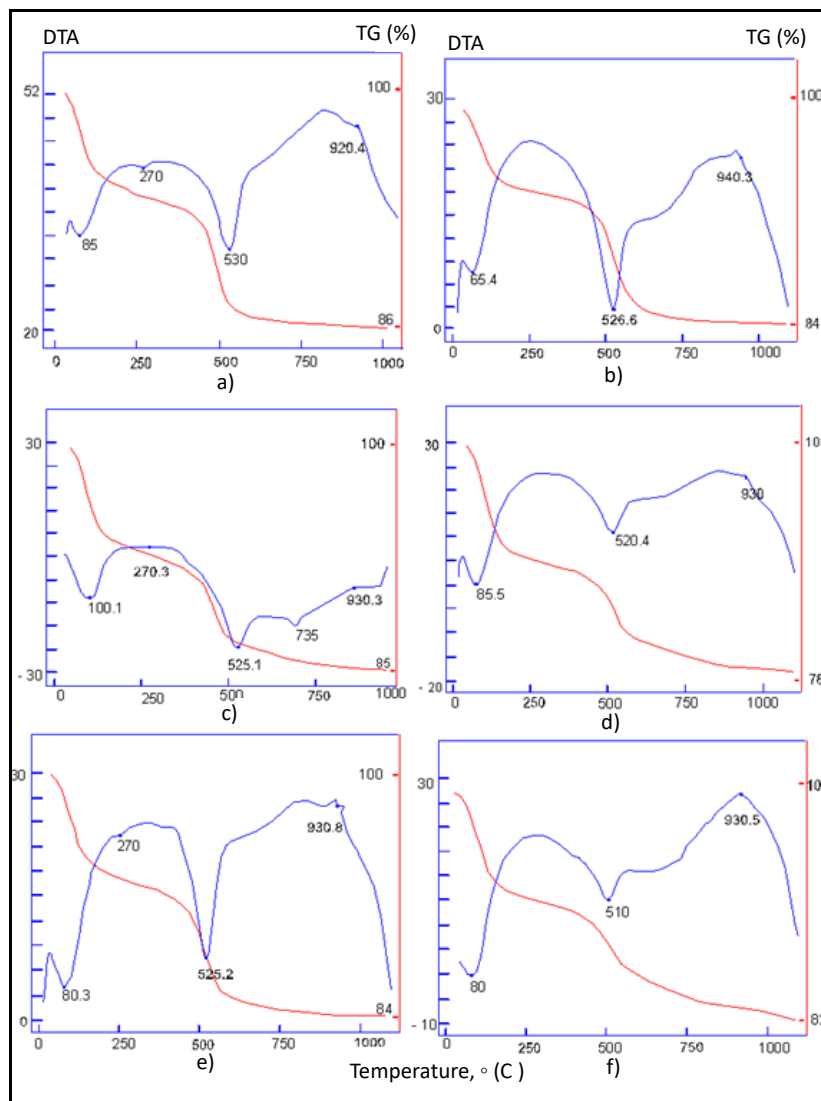


Fig.2. DTA and TG curves. Blue line for DTA and red line for TG. a, b and c for Dakhla Shales, d and e for Duwi samples and f for Quseir)

Geochemical composition

Elemental concentrations

The chemical analysis of 101 samples which are represented Qusier, Duwi and Dakhla Shale. Geochemical analysis data of these samples are shown in Tables (2, 3 and 4) and Figure 3. Al_2O_3 and SiO_2 are more common in Duwi, Qusier, and Dakhla shales averaging 55.31%, 55.59% and 47.73%, respectively (Table 1). While, the concentrations of Al_2O_3 and SiO_2 for (UC) and NASC (66 % and 64.82% for SiO_2 and 15.2 % and 16.92 % for Al_2O_3) are lower (Taylor and McLennan, 1985; and Gromet et al., 1984). Shale in Quseir and Duwi formations are slightly more enrichment in SiO_2 , and relatively around the standard average for Pettijohn, 1975 and Turekian & Wedephol, 1961 (58.10 % and 58.50 %), while the Al_2O_3 in Dakhla shale (20.57 %) are higher than published shale composition (Table 3). The samples were rich in major oxides as SiO_2 , Al_2O_3 & TiO_2 and poor in MgO , CaO , and K_2O & Na_2O (Fig. 3). These elements show discordance when compared with the known world shale; Upper Crust (Taylor and McLennan, 1985), North American Shale Composite (NASC, Gromet et al., 1984). Meanwhile, these elements relatively show concordance with Pettijohn, 1975 and Turekian & Wedephol, 1961 (Table 3). The high correlation coefficients between SiO_2 and Al_2O_3 , Fe_2O_3 , TiO_2 and MgO ($r = 0.97, 0.90, 0.96$ and 0.73 ; respectively) and moderate correlation with K_2O ($r = 0.43$) (Table 4) suggest the occurrence of these oxides in common phases, most likely clay minerals. The moderate correlations (Al_2O_3 with K_2O and Na_2O ($r = 0.37$ and 0.24 ; respectively) are explained due to minor illite concentrations and recommend that the main amount of Na and K occurs in clay minerals. CaO exhibits a strong positive relationship with TOC $r = 0.71$, Table 4), indicating that the main part of Ca exists in carbonate minerals. According to the geochemical classification, which depends on the log values of the ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ (Herron, 1988), the black shale is classified into iron–shale.

Tab. 2. Ranges of the major elements concentration in studied shales

Age	Formation	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl-	SO_3^{--}	TOC	TiO_2
Maastrichtian - Paleocene	Dakhla N=(92)	1.4- 69.51	0.4- 25.55	0.93- 9.94	0.00 7- 2.13	0- 3	0.19- 51.5	0.12- 19.29	0.08- 1.69	0.07 - 1.75	0- 2.09	0- 5.01	0- 41.6	0.03- 21.24
		47.16	20.57	6.43	0.88	0.49	2.1	1.69	0.71	0.75	0.2	1.38	4.26	12.81
Campanian - Maastrichtian	Duwi N=(11)	46.25 - 73.61	7.78- 17.87	2.65- 8.28	0.02 - 8.28	0-1.3	0.01- 3.32	0-4.68	0.14- 1.99	0.09 - 1.67	0.02 - 1.39	0.06- 2.87	0.15- 11.7	1.1- 17.17
		55.59	14.85	5	1.42	0.24	1.7	1.55	1.16	0.96	0.41	1.45	2.4	11.78
Pre-Campanian	Qusier N=(10)	36.91 - 70.45	9.68- 17.62	3.5- 9.8	0.49 - 1.95	0.01- 0.27	0.14- 10.52	0.38- 10.05	0.33- 3.72	0.41 - 4.69	0.03 - 0.29	0.21- 1.83	0- 0.05	7.52- 22.21
		55.31	12.75	6.76	1.07	0.08	2.79	0.18	1.07	2.31	0.18	0.54	0.19	13.83

Mean values are listed between brackets – N is the number of analysed samples

Tab. 3. Comparison of the average composition of the studied shales with published average shales (N is the number of samples)

Composition	Present Study			UC	NASC	Pettijohn	Turekian and
	Dakhla Shale N=80	Duwi N=11	Quseir N=10	(Taylor and McLennan, 1985)	(Gromet et al., 1984)	(1975)	Wedephol, (1961)
SiO_2	47.73	55.59	55.31	66.00	64.82	58.10	58.50
Al_2O_3	20.57	14.85	12.75	15.20	16.90	15.4	15.00
Fe_2O_3	6.43	5.00	6.76	5.00	5.65	n.a.	0.77
MnO	0.88	1.42	1.07	0.08	0.06	4.02	4.72
MgO	0.49	0.24	0.08	2.20	2.86	2.44	2.50
CaO	2.10	1.70	2.79	4.20	3.63	3.11	3.10
Na_2O	1.69	1.55	2.35	3.90	1.14	1.30	1.30
K_2O	0.71	1.16	1.07	3.40	3.97	3.24	3.10
P_2O_5	0.75	0.96	2.31	-	0.13	n.a.	0.16
Cl-	0.20	0.41	0.18	-	-	-	-
SO_3^-	1.38	1.45	0.54	-	-	-	-
TOC	4.26	2.40	0.19	-	-	-	-
TiO_2	12.81	11.78	13.83	0.50	0.80	n.a.	0.77

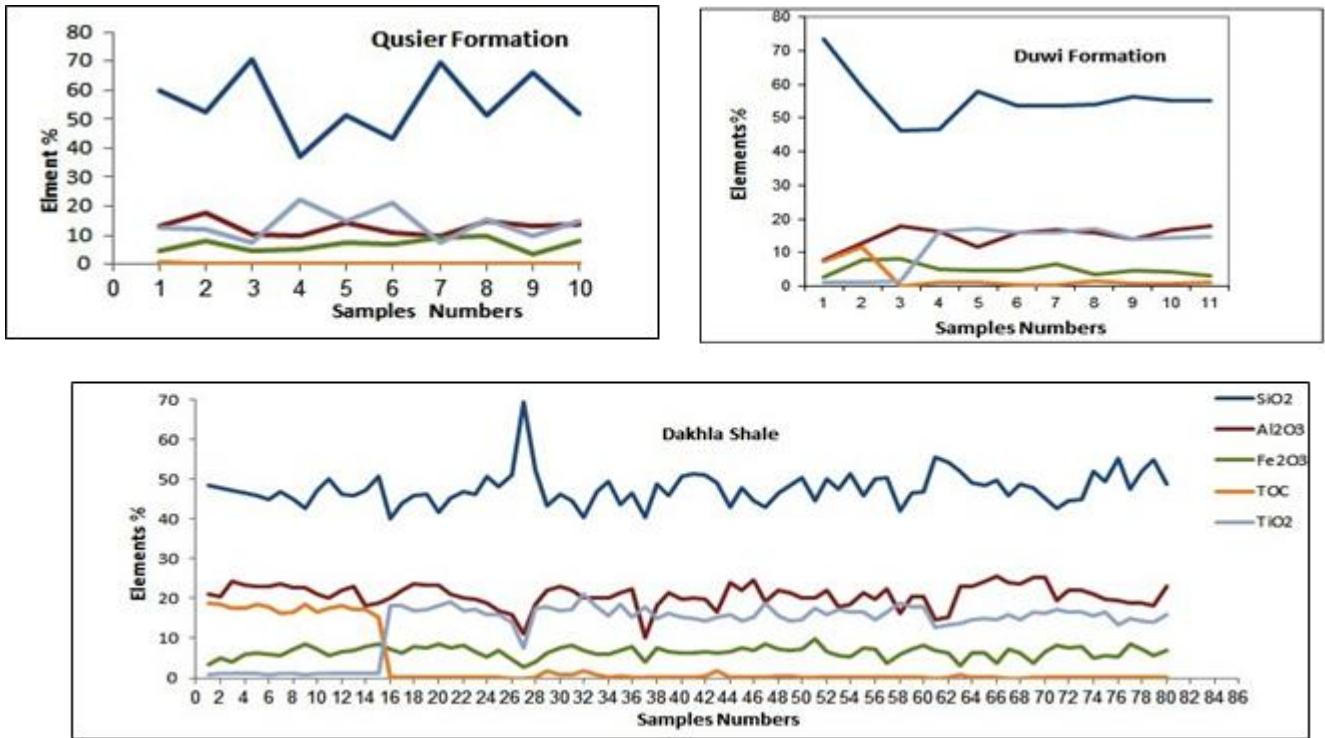


Fig. 3. Geochemical composition of studied shales

Tab. 4. Correlation coefficients of the major elements

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cl ⁻	SO ₃ ⁻	TOC
SiO ₂	1												
Al ₂ O ₃	0.97	1											
Fe ₂ O ₃	0.90	0.96	1										
TiO ₂	0.96	0.95	0.87	1									
MnO	0.54	0.53	0.61	0.60	1								
MgO	0.73	0.77	0.83	0.73	0.46	1							
CaO	-0.18	-0.17	-0.13	-0.17	-0.09	0.31	1						
Na ₂ O	0.44	0.24	0.78	0.79	0.36	0.65	0.03	1					
K ₂ O	0.43	0.37	0.87	0.89	0.64	0.69	-0.01	0.8	1				
P ₂ O ₅	0.27	0.28	0.07	0.26	-0.02	-0.06	-0.06	0.45	0.19	1			
Cl ⁻	0.58	0.46	0.46	0.46	0.14	0.39	-0.01	0.42	0.62	-0.09	1		
SO ₃ ⁻	0.18	0.18	0.02	0.16	-0.01	0.21	0.61	0.47	0.23	0.72	0.07	1	
TOC	0.55	0.57	0.55	0.54	0.31	0.82	0.71	0.60	0.63	0.12	0.39	0.62	1

On the triangular (A-Si-CM) Al₂O₃, SiO₂, and CaO+ MgO; the studied samples can be classified as silty shales (Fig.4). The sediments plot relative coincides with Pettijohn (1975) and Turekian & Wedephol (1961) standards. The major element analyses of the studied samples compared to (UC) Taylor and McLennan (1985) and (NASC) Gromet et al. (1984); Pettijohn (1975) and Turekian and Wedephol (1961) Table (3). This table shows variation in the major element content for all analysed samples. For example, the SiO₂ contents range from 47.16 to 55.59 wt%, the TiO₂ content from 11.78 to 13.83wt%, the Al₂O₃ content from 12.75 to 20.57 wt%, and the Fe₂O₃ content ranges from 5 to 6.76 wt%. The contents of MgO, CaO, and MnO are low. The Na₂O and K₂O contents range from 1.39 to 2.35 wt % and from 0.71 to 1.16 wt%, respectively. Nesbitt and Young (1982, 1984, 1989 & 1996) and Nesbitt et al. (1996) used the ternary diagrams (Fig. 5) Al₂O₃-(CaO + Na₂O)-K₂O (A-CN-K) and Fe₂O₃ + MgO-(CaO + Na₂O + K₂O)-Al₂O₃ (A-CNK-FM) to deduce weathering trends. On both the A-CN-K triangular diagram (Fig. 6) and the A-CNK-FM diagram (Fig. 7), high Al₂O₃ contents, intensive weathering history. Weathering has occurred when the alkali elements decreased or detached from the sediments.

Weathering conditions

The CIA is calculated, [(CIA = 100 × (Al₂O₃/(Al₂O₃ + CaO + Na₂O + K₂O))] according to Harnois (1988) has been established as a general indicator for the weathering degree in a provenance region (Nesbitt and Young,

1982). The CIA of the sediments ranges from 59.23 % to 94.83%. However, the average value for (Qusier Formation) is 74.68 %, 77.13 % for Duwi Formation and for Dakhla Shale is 84.57 % (Table 4), which is high compared to UC, and NASC, indicating a moderate to high weathering degree. The studied Dakhla Shale was founded on intensive weathering than Duwi and Quseir formations. The CIW is calculated, $[(CIW = (Al_2O_3 / (Al_2O_3 + CaO + Na_2O)) \times 100]$. In studied shales, CIW averages 80.36 %, 81.97 % and 87.83 % for Qusier, Duwi and Dakhla Shales, respectively (Table 4). It is high equivalent to standard average percentages, suggesting moderate to intensive chemical weathering. The CIA and CIW high values (Table 4) imitates the presence of clay minerals and the absence of feldspars. This is also confirmed by the smectite dominance and subordinate kaolinite in these formations.

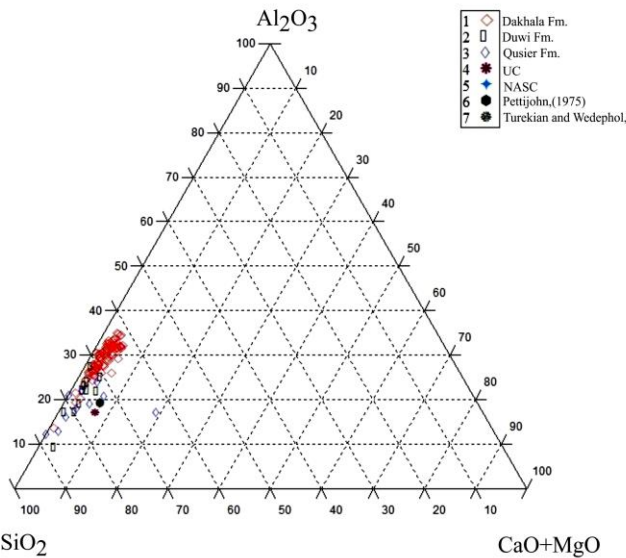


Fig. 4. A-Si-CM Triangular showing plot of studied samples and standards sediment samples

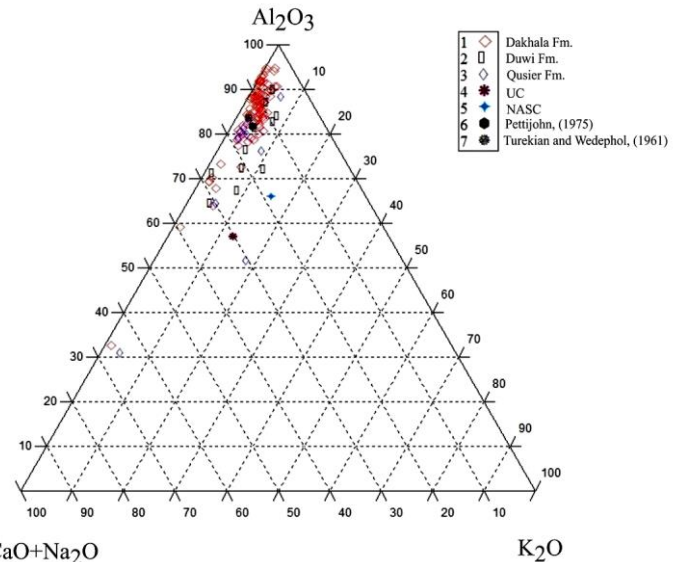


Fig. 5. A-CN-K Triangular showing plot of studied samples and standards sediment samples

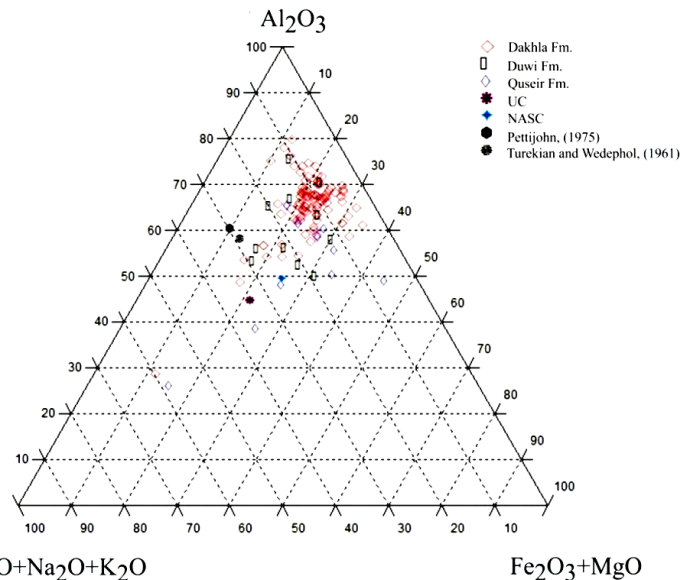


Fig. 6. A-CN-K-FM Triangular showing plot of studied samples and standards sediment samples

Tab. 5. Chemical index of weathering (CIW), chemical indices of alterations (CIA) and discrimination functions (F1 and F2) calculated for the studied shale samples

Age	Formation	CIW	CIA	F1	F2
Maastrichtian - Paleocene	Dakhla N=(80)	64.60-96.83	59.23 -94.83	-1.94 -10.72	-8.82-30.33
		87.83	84.57	6.97	2.9
Campanian - Maastrichtian	Duwi N=(11)	67.38-93.53	64.41-89.79	-4.54 -3.87	-5.06-9.49
		81.97	77.13	1.64	2.52
Pre-Campanian	Quseir N=(10)	62.69-94.16	64.39-88.25	-0.43-8.88	-3.42-23.12

Interelement relations

The Most significant observations are:

1. SiO₂ show a strong correlation with Al₂O₃ (r = 0.97), indicating free silica presence (Fig. 7).
2. A strong correlation between Fe₂O₃ and Al₂O₃ (r = 0.96) in most studied shales (Fig. 8) may reflect the source of Fe₂O₃ content is detected by clay minerals and/or micas (Mishra and Sen, 2012). Both Mg and Fe contents are controlled by nonaluminous phases such as black mafic-ultramafic rock fragments and/or accessory oxide minerals. Meanwhile, major studied samples have excess sodium content related to alkali clay minerals (Fig. 9).

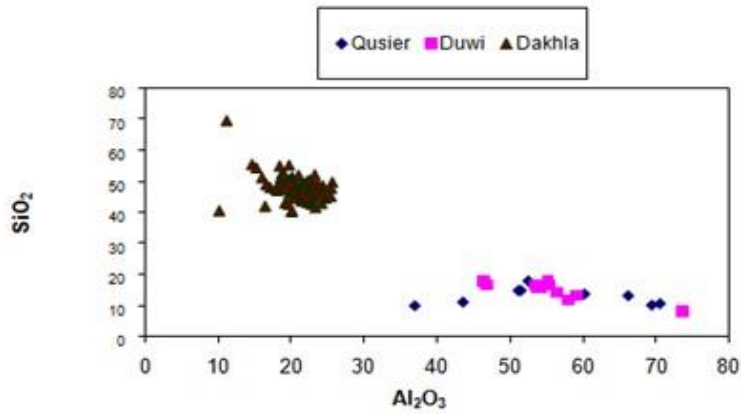


Fig. 7. Bivariant diagram of SiO₂ and Al₂O₃

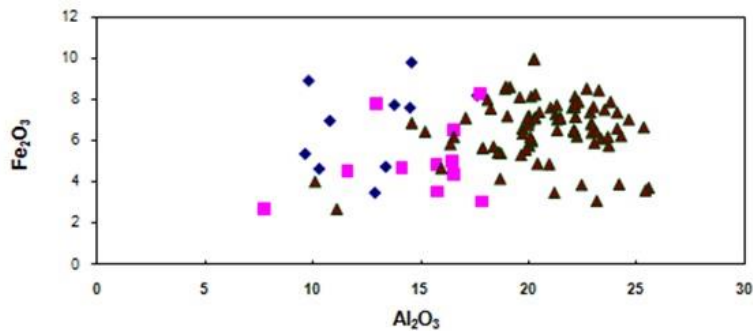


Fig. 8. Bivariant diagram of Fe₂O₃ and Al₂O₃

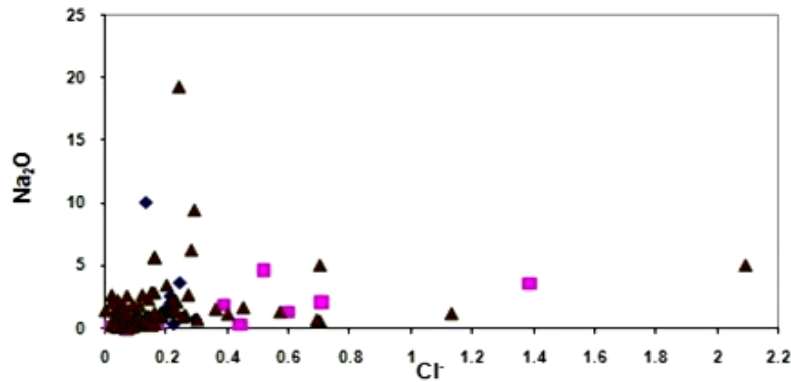


Fig. 9. Bivariate diagram of Na_2O % and Cl^- %

Sediment Maturity and climatic conditions

The maturity and original properties of sediments, in addition to the prevailed climatic conditions be able to determine by calculating the (ICV). The ICV tends to be highest in intensive weathering minerals and lowest in steady (less weathered) minerals (Cox et al., 1995). It decreases in the smectite and lowest in the kaolinite. Additionally, more mature shale lean to low ICV values (< 1.0) and shales with $\text{ICV} > 1$ are formed in tectonically active settings, with the initial cycle of immature sediments deposited. For the studied shales, the ICV values for Dakhla and Duwi shales are 0.59 and 0.74, respectively ($\text{ICV} < 1$) and 1.24. The shales are compositionally mature and deposited in the tectonically quiescent or cratonic environment. Whereas the Qusier shale ($\text{ICV} > 1$) can be incidental that are immature composition (Cox et al., 1995). To restrain the climatic condition, the proposed plot of SiO_2 against $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})$. Suttner and Dutta, 1986 was used to classifying the maturity of shales for climate detection. Shales are incidental that are compositionally in arid to semi-arid climatic conditions.

Provenance and depositional environment

Geochemical limits are used to identify the provenance of the studied samples. (Amajor, 1987) utilised the TiO_2 versus Al_2O_3 plot to differentiate between granitic and basaltic source rocks parent is basalt (Fig. 10) and plotting on the provenance discrimination function diagram of (Roser and Korsch 1988), illustrated in (table 5). Discriminant function I = $-1.773 \text{TiO}_2 + 0.607 \text{Al}_2\text{O}_3 + 0.76 \text{Fe}_2\text{O}_3$ (total) $- 1.5 \text{MgO} + 0.616 \text{CaO} + 0.509 \text{Na}_2\text{O} - 1.224 \text{K}_2\text{O} - 9.09$; Discriminant function II = $0.445 \text{TiO}_2 + 0.07 \text{Al}_2\text{O}_3 - 0.25 \text{Fe}_2\text{O}_3$ (total) $- 1.142 \text{MgO} + 0.438 \text{CaO} + 1.475 \text{Na}_2\text{O} + 1.426 \text{K}_2\text{O} - 6.861$ (Khader and McQueen, 2005). this plot on The diagram showed that predominance of considered samples fell within the P2 (intermediate igneous provenance) field of the diagram, and the rest of the samples (Darb El-Taweil section) fell within the P1 field, indicating mafic igneous provenances other than few samples fell within reworked older quartzose sediments field (Fig. 11). Furthermore, the low ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3$ for investigated shales indicates nearly arid climatic condition Migdisove (1960). The relationship between SiO_2 and $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})$ was revealed that the samples are plot in the semi-arid climate field (Fig. 12). Consequently, the combined mineralogical data, the main characters of studied shales, was formed by fluvial action, which sometimes interfered and admixed with the marine environment to create alkaline, quiet and reduced conditions. Smectite may be formed under different climatic conditions. Illite is interpreted to form in a relatively cold or dry climate, while a hot and humid climate leads to a stronger chemical weathering favouring the formation of kaolinite. Moreover, the weathering could cause a widespread and high-degree variation in clay minerals (Song et al., 2012). Consequently, it can be concluded that the abundances of smectite and, to lesser extent kaolinite in shales of the Qusier and Duwi formations sections are related to warmer with different chemical environments. Meanwhile, the abundance of kaolinite expansion of smectite indicates the end of weathering under the condition of acid soil solution and good drainage in a temperate climate. In conclusion, it is suggested that the shales deposited under fluvio-marine environments and the prevailed condition was of alkaline chemical affinity probably passed through different environments varying from the fluvial, eolian and shallow marine.

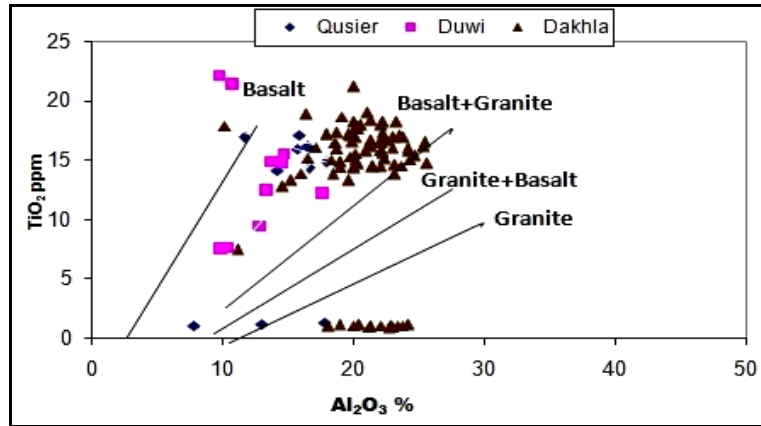


Fig. 10. TiO_2 versus Al_2O_3 binary plot for studied shales (Amajor, 1987)

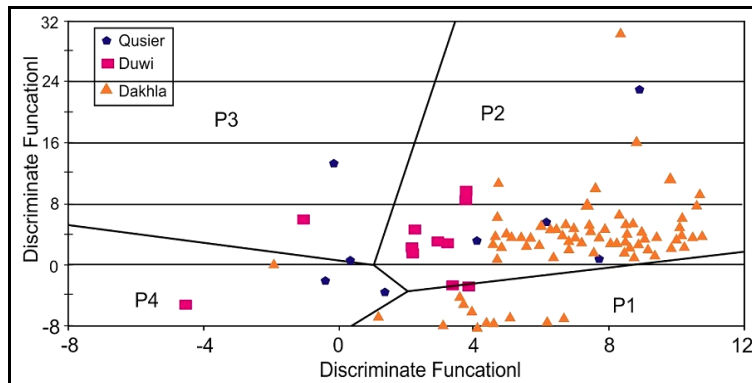


Fig. 11. Provenance-discrimination functions diagram of studied shales (after Roser and Korsch, 1988). P1 Mafic igneous provenance, P2 Intermediate igneous provenance, P3 Felsic igneous provenance and P4 Quartzose sedimentary provenance

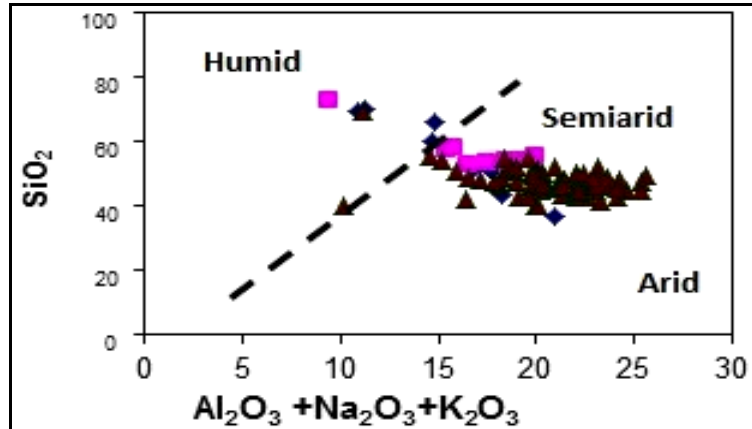


Fig. 12. SiO_2 versus $Al_2O_3 + Na_2O + K_2O$ binary plot on the diagram constructed by Suttner and Dutta (1986)

Conclusion

The studied samples are mainly composed of smectite, kaolinite, goethite and calcite. The Dakhla shale is comparatively more kaolinitic and less of smectite than the Duwi and Quseir formations. The shales were rich in SiO_2 , Al_2O_3 & TiO_2 and poor in MgO , CaO , K_2O & Na_2O . A strong correlation between $Fe_2O_3 + MgO$ and Al_2O_3 implied that both Mg and Fe are in part controlled by micas and/or clay minerals. The high equivalent to standard average percentages, suggesting moderate to intensive chemical weathering. The CIW and CIA high values perhaps due to the presence of clay minerals and the absence of feldspars. This is also confirmed by the smectite dominance and subordinate kaolinite in these formations. The ICV values for Dakhla and Duwi shales are 0.59 and 0.74, respectively ($ICV < 1$) and 1.24. The shales are compositionally mature and deposited in the tectonically quiescent or cratonic environment. Whereas the Qusier shale ($ICV > 1$) can be incidental that are compositionally immature. The plotting of SiO_2 against $(Al_2O_3 + K_2O + Na_2O)$ was used the whole shales maturity for climate detection and are incidental compositionally in arid to semi-arid climatic conditions. The majority of shale samples distinguish between granitic and basaltic source rocks, and the parent provenances is

basalt. Consequently, the shales are deposited under fluvio-marine environments, and the prevailed condition was of alkaline chemical affinity probably passed through different environments varying from the fluvial, eolian and shallow marine. From the economic point of view, Qusier, Duwi and Dakhla shales in the study region retain optimal conditions to be used in raw material for cement production due to the high TOC contents, low magnesium and sulphides values. Further studies are recommended on these shales exposures, such as physical and petrophysical properties, to assess the probability of their use for many industries (production of cement and ceramics).

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