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Potentiality of chemical weathering under arid conditions of black shales from Egypt

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The Upper Cretaceous–Lower Tertiary succession is widely distributed in Upper Egypt and consists of black shales–phosphorites–chert–dolostones association. The present work is confined to study the black shales of Dakhla (*Maastrichtian-Danian*) and Duwi (*Campanian*) Formations, from the association. Quantitative mineralogy is performed on more than 200 whole black shale samples and their clay size fractions by means of infrared spectroscopy and X-ray diffraction with the support of chemical analysis and scanning electron microscopy.

Although the prevailing climatic conditions are classed as arid proper, evidence of the extensive effect of chemical weathering is conspicuous. The weathering of the heterocompounds and asphaltine creates an acidic medium, causing acceleration of mineral and chemical changes. The breakdown of organic matter and pyrite increases fissility. The average mass loss due to chemical weathering is estimated to be about 45%, where organic matter, pyrite, dolomite, ankerite and calcite are found to be the main losses. Smectite converts into illite, passing through a smectite/illite mixed layer. This transformation requires K^+ and H^+ to liberate Na^+, Ca^{2+} and Si^{4+}. In the weathering profile the gained illite and quartz are almost equal to the smectite lost.

Distinction between the black shales of Dakhla Formation and the underlying Duwi Formation, on the basis of their clay mineralogy, is very possible and it suggests a possible readjustment of the stratigraphic boundary between the two formations.

Keywords: black shale; chemical weathering; Upper Cretaceous; Egypt; Illitization

Introduction

The Upper Cretaceous–Lower Tertiary succession is widely distributed throughout Egypt. The succession provides a good example of a sedimentary association encompassing black shales–phosphorites–chert–dolostones. The phosphorites are intercalated with, or capped by, black shales that contain considerable amounts of

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organic matter enriched by heavy metals. It is believed that by the advent of the Upper Cretaceous (*Cenomanian*), a major marine transgression took place covering most of the Egyptian territory southwards up to latitude 24°N around Aswan. The major marine transgression during the Upper Cretaceous and Lower Tertiary was interrupted by minor mild regressive pulses associated with uplifting and some tectonic pulses.

The wide geographic and stratigraphic distribution of black shales, besides wide variation in their chemical and mineral compositions, suggest a wide range of geologic settings. This assumption has long been reported by Twenhofel (1939) who concluded that black shales should not be assigned to any general condition, but that each should receive its own interpretation based on its distinct characteristics. The depositional controlling factors have recently been quantified by many authors, such as Fyffe & Pickerill (1993), Pasava *et al.* (1993), Jones & Manning (1994), Quinby-Hunt & Wilde (1994) and Piper (1994). They explained a variety of processes such as: rate of sedimentation, sea level changes, nutrient availability, fixation of specific trace elements, changes in continental climates, basin morphology and expanded oxygen-depleted zone (anoxic conditions).

A common view is that chemical weathering is not an effective agent under arid conditions due to the rarity of water. Therefore, interpretations on the genesis of sediments are regularly drawn from petrographical, mineralogical and geochemical evidence of samples collected from surface exposures. The present work, however, provides important clues on significant mineral and chemical changes occurring in black shales as a result of chemical weathering under the arid environment of the Egyptian Sahara. The major losses on mass as well as the serious changes in mineral composition impart the weathered black shale with a fissile, papery, friable and slippery nature.

Samples

The area under investigation is located in the southern part of Egypt (Dakhla–Kharga Oases, *Wadi* Qena; Nile Valley, Red Sea District, Fig. 1). More than 200 samples were collected from six representative surface sections covering the area from Dakhla Oasis (Edmonstone and Teneida), Abu Tartur, Kharga Oasis (Umm El Ghanayim), *Wadi* Qena (Abu Had) and Quseir-Safaga District (Wasif and Abu Shigiala). The black shales of such surface sections are affected, to a variable extent, by chemical weathering. Black shales, having the least possible degree of chemical weathering, were collected from three cores from Safaga (Mohamed Rabah) and Quseir (Younis and Abu Shigaila), as well as from some phosphorite mines in Safaga–Quseir and Abu Tartur. The underground phosphorite mines were the only available choice to collect fresh or least-weathered black shale samples. The depth of the mines varies from a few metres to more than 150 m, as in the Qusier and Abu Tartur areas. These black shales are denoted herein as ‘non-weathered’. The comparison between surface (weathered) and sub-surface (non-weathered) black shales is confined to those of correlated geological setting and they essentially belong to the lower Dakhla Formation. The non-weathered samples, being limited in number (only 16 samples), are excluded from the minerals correlation of the six sampled stratigraphic sections.

Methods and results

Whole black shale samples and clay size fractions were analysed by different techniques to evaluate their mineral and chemical compositions. The clay size fraction was separated by the method described by Moore & Reynolds (1989) using dilute

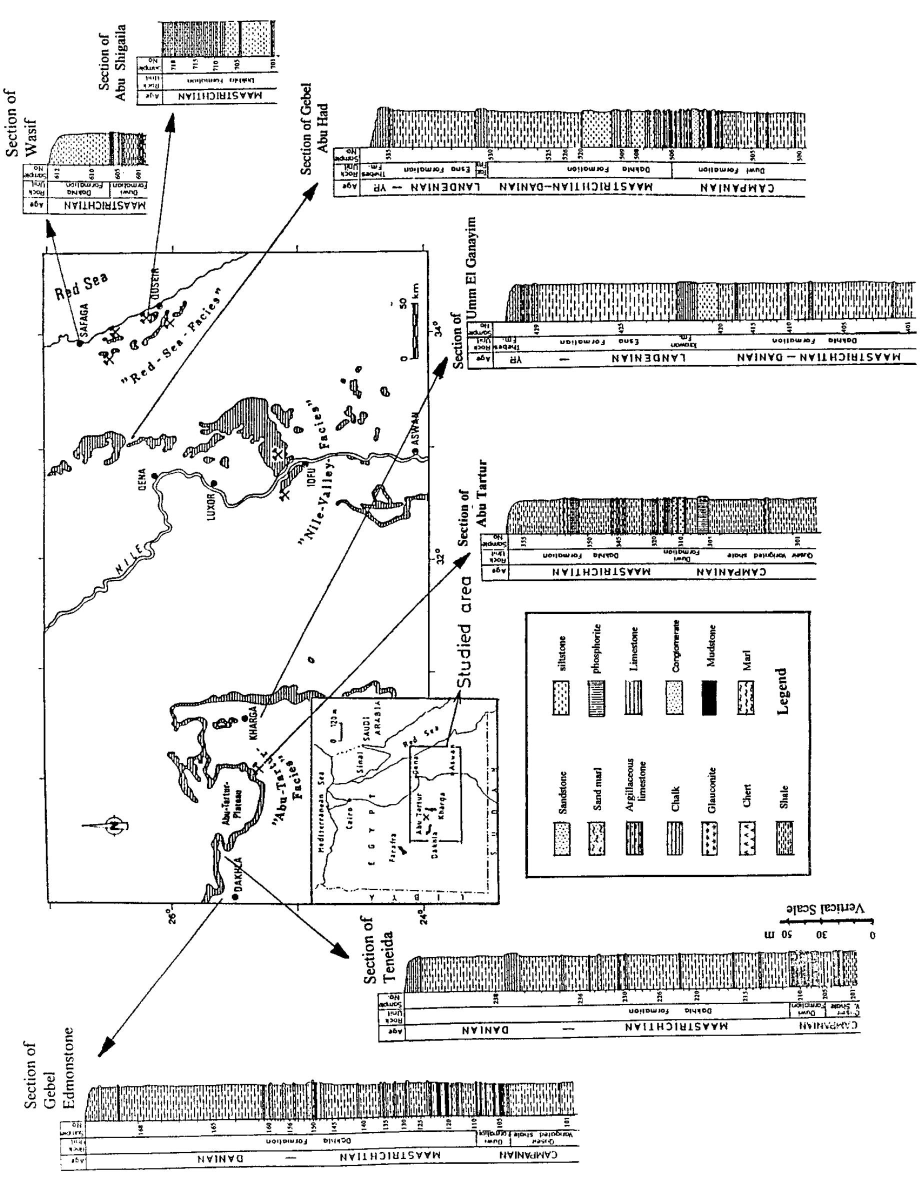


Figure 1. Sketch map showing the location of the measured and sampled stratigraphic sections, Upper Egypt.

Table 1. *Minimum, maximum and mean values of the relative abundance of clay minerals of the studied black shales as measured from X-ray diffractograms*

Clay minerals	Minimum %	Maximum %	Mean %*
Kaolinite	0	70	27
Illite	0	29	10
Smectite	27	98	62
Illite (%) in mixed layer†	5	50	19
Smectite (%) in mixed layer†	50	95	80

*Mean value of 99 samples.
†Illite (or smectite) percentage in the illite/smectite mixed layer.

chemicals. The grain size coarser than 63 μ, was then separated by sieving. The suspension was disaggregated using ultrasonic equipment, then washed until it shows turbidity (conductivity 50 ms); and then centrifuged in order to separate the clay size fraction from the silt size. The thick slurry was smeared onto a glass slide with a pipette and dried under room temperature.

(a) *X-Ray diffraction analysis (XRD).* Whole samples and clay size fractions were analysed by Ni-filtered Cu–Kα radiation (50 kV, 30 mA) from an APD 1700 X-ray diffractometer. The analysis was conducted on oriented clay size fractions as well as treated mounts using ethylene glycol and heating at 550°C for 4 h.

The peak heights under the (001) basal reflections of the identified clay minerals were used as a measure of their relative abundance, except for kaolinite where the peak height was divided by three to compensate its higher degree of crystallinity compared to other clay minerals (Thorez, 1976). The minimum, maximum and mean values of the obtained data are given in Table 1. The identification criteria given by Srodon (1980, 1984) and Moore & Reynolds (1989) were considered in the present work.

Twenty clay fraction mounts representing the various lithologies of black shales under consideration were treated by heating at 250°C for 10 h in order to identify the organic-rich smectite which is denoted as ‘organophillic’ smectite by Nemecz (1981). However, the peak area as measured from the X-ray diffractograms of the whole black shale samples were used to determine the relative abundance of the non-clay minerals. The same approach has also been adopted by many authors (e.g. Biscay, 1965; Decleer, *et al.*, 1983). The identified association of non-clay mineral in decreasing order of relative abundance: calcite, quartz, carbonate fluorapatite, dolomite (and ankerite), and pyrite (Table 2). Goethite was detected in minor amounts, both in whole and clay size samples.

(b) *Infrared spectroscopy.* This technique is sensitive to grain size and shape of the mineral particles (Serna, *et al.* 1982; Brown & Elliot, 1987; Russell, 1987), so that the grinding and homogenization of the pulverized sample to a size less than 25 μ was recommended. The pellets were prepared by mixing 30 mg of the well pulverized and homogenized sample with 270 mg KBr as an embedding medium. The homogenization of the blend was done five times by using a vibrator for 30 s each time. The homogenate was kept overnight at 110°C to prevent rehydration. Ten milligrams of the blend were added to 200 mg KBr and carefully homogenized as described before. This method was used to minimize possible errors during weighing.

In the present work IR spectroscopy was found to be a very reliable quantitative technique for measurement of mineral composition of black shales. A computer program for identification and quantification of minerals from the IR spectrograms was used. The measurement of the clay minerals and their admixtures was accomplished by matching the spectrogram of the analysed sample with a large number of mixtures having different proportions of synthetic and natural standards. Details on the quantification procedure are given by Ganz *et al.* (1990*a*).

The variation of crystallinity and chemical composition of a mineral, as well as the effect of dehydration and the preparation technique make use of IR spectroscopy in quantitative analysis easier than XRD. The results obtained from the IR analysis are graphically represented in Fig. 2.

(*c*) *Scanning electron microscope (SEM)*. Sixteen selected samples were examined by SEM to throw more light on the rock fabrics and hence genetical and diagenetical bearings.

(*d*) *Chemical analysis*. The preparation of samples for analysis was done following Ganz *et al.* (1990*a*). Total carbon (TC) and total sulfur (TS) were measured using a C/S-244 Leco Analyzer. Total organic carbon (TOC) was measured

Table 2. *Relative mineral abundance of whole black shale samples of the Dakhla Formation, as measured from X-ray diffractograms*

Sample number	Calcite	Quartz	Apatite	Dolomite	Pyrite	Remarks on clay mineral*
1	63	15	5	2	-	
2	-	100	-	-	-	+Il
3	-	100	-	-	-	+Il
4b	22	68	10	-	-	+Sm
6	58	34	5	-	2	+Sm–Il
10	-	100	-	-	-	+Il/Sm
11	-	100	-	-	-	+Il/Sm
12	-	33	-	16	7	+Kaol.–Sm
20	-	100	-	-	-	+Il/Sm
26	72	28	-	-	-	+Il/Sm
27	48	36	-	-	-	+Kaol.≅16%
29	-	100	-	-	-	+Il/Sm
30	18	82	-	-	-	+Il/Sm
31	45	55	-	-	-	+Il/Sm
32	86	14	-	-	-	
33	-	42	-	45	12	
34	88	12	-	-	-	
35	85	15	-	-	-	
36	63	10	-	-	-	+Il/Sm
37	-	78	-	-	22	+Sm–Kaol
38	63	37	-	-	-	+Kaol.–Sm
39	74	26	-	-	-	+Kaol.≅7%
49	-	63	-	-	27	–clay min.
74	52	36	-	-	12	–clay min.
75	62	38	-	-	-	–clay min.

*Il/Sm=Illite/Smectite mixed layer; Kaol.=Kaolinite.
+=major amount; –=minor amount.

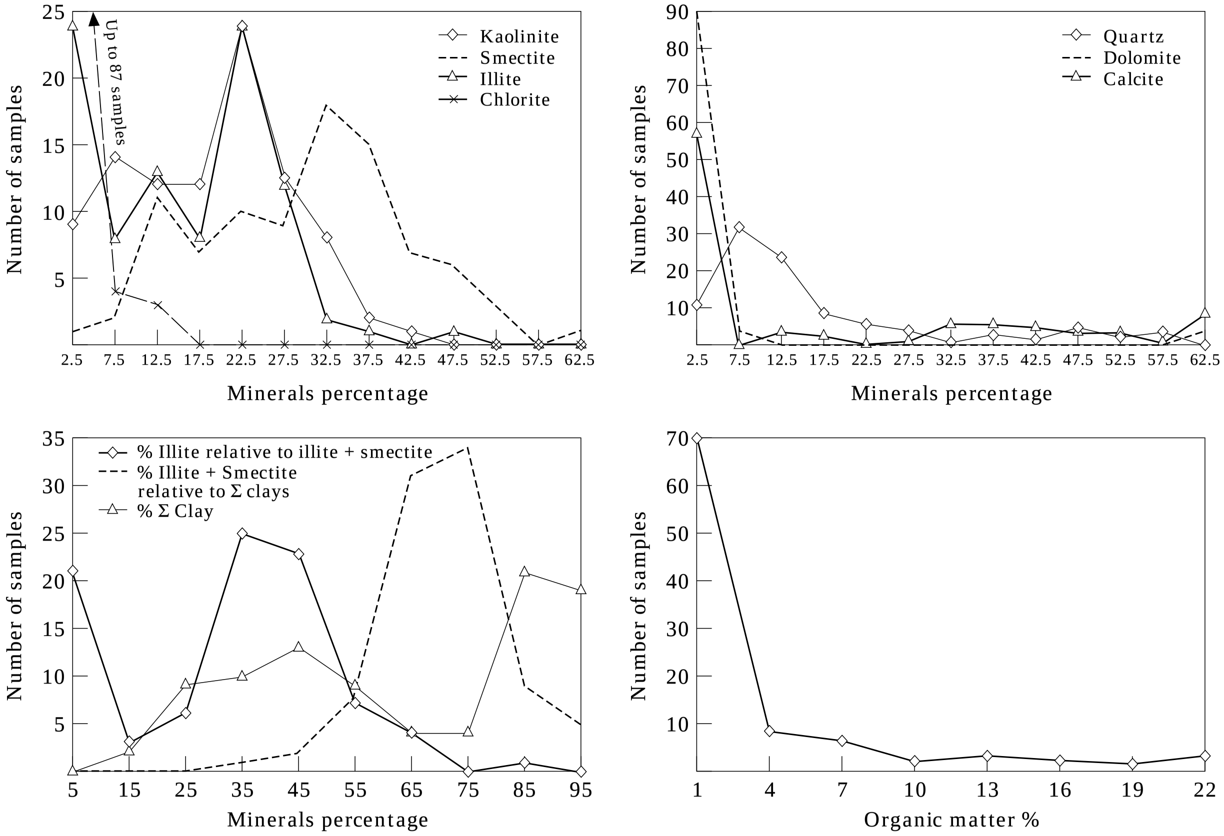


Figure 2. Frequency distribution of the main mineral constituents of black shales as measured by infrared spectrophotometry.

after complete destruction of the inorganic carbon using HCl. The inorganic carbon was calculated by difference between TC and TOC.

The major chemical composition was determined in 160 separated clay size fractions, representing both weathered and non-weathered black shales. Approximately 2 g of dehydrated (at 100°C) sample powder were ignited at 1000°C for so as to determine loss on ignition (LOI). The LOI was reduced by a factor representing the oxidation of Fe^{2+} to Fe^{3+} upon ignition, on the basis reported by Lechler & Desilets (1987). The ignited material was ground, carefully homogenized and pressed in a pellet-like form to be analysed using a Philips PW 1404/10 automatic sequential wavelength dispersive X-ray spectrometer connected to a personal computer. The analysed elements were calibrated by one program containing 45 international rock and artificial standards. The minimum, maximum and mean values of the calculated chemical formula of the clay fractions for both weathered and non-weathered black shales are given in Table 3. The chemical analysis data were used in the present work to confirm compositional changes due to weathering, but details of their significance and of the calculations procedure will be published later. The calculation was based on 22 negative charges for each unit cell ($O_{10}(OH)_2$). Samples that contain appreciable amounts of non-clay impurities were excluded from the calculations of the structural formula. The percentage of kaolinite, as estimated by IR in clay fractions, is subtracted from the chemical data.

Discussion

In general, the black shales of the Dakhla Formation are mainly composed of smectite/illite mixed layers with varying proportions of smectite to illite. Kaolinite is a second dominant clay constituent, besides occasional chlorite. In spite of that, the Dakhla

Table 3. *Average structural formulae of clay fractions separated from black shales of Dakhla and Duwi Formations*

	Dakhla Formation			Duwi Formation (*n*=16)*
Variable	Mean, all samples (*n*=75)*	Mean, non-weathered samples (*n*=13)*	Mean, weathered samples (*n*=20)*	
Ca^{2+}	0·06	0·13	0·03	0·03
Na^{+}	0·04	0·01	0·04	0·04
K^{+}	0·13	0·14	0·13	0·13
Si^{4+}	3·59	3·73	3·57	3·81
Al^{3+} Tetra.	0·41	0·27	0·43	0·19
Al^{3+} Octa.	1·36	1·41	1·36	1·42
Ti^{4+}	0·06	0·05	0·06	0·04
Fe^{3+}	0·44	0·37	0·46	0·31
Mg^{2+}	0·24	0·19	0·25	0·31
Interlayer charge	0·29	0·41	0·23	0·23
Tetrahedral charge	0·41	0·27	0·43	0·19
Octahedral charge	0·06	–0·14	0·13	–0·06
Layer charge	0·48	0·13	0·56	0·13

**n* is number of analysed samples.

Formation is comparatively more kaolinitic and less of a smectite/illite mixed layer than either the underlying Duwi Formation or the overlying Esna Formation. This variation in clay mineralogy is persistent and can easily be traced over a great sector of the country (Figs 3 and 4). The boundary that witnesses remarkable change in clay mineralogy between Dakhla and Duwi Formations matches with a conglomeratic band that best developed in the Edmonstone section (type locality of the Dakhla Formation). This band has a pervasive distribution and may reach 30 cm in thickness. Therefore, the clay mineralogy of the black shales in the studied six stratigraphic sections (non-weathered samples are excluded) indicates a rather consistent and diagnostic composition for the black shales of the Dakhla Formation relative to those of the underlying and overlying formations. The clay mineralogy, as such, may be used as a tool to enable precise correlation over the whole of Egypt. This tool can be further extended to cover a wider regional scale.

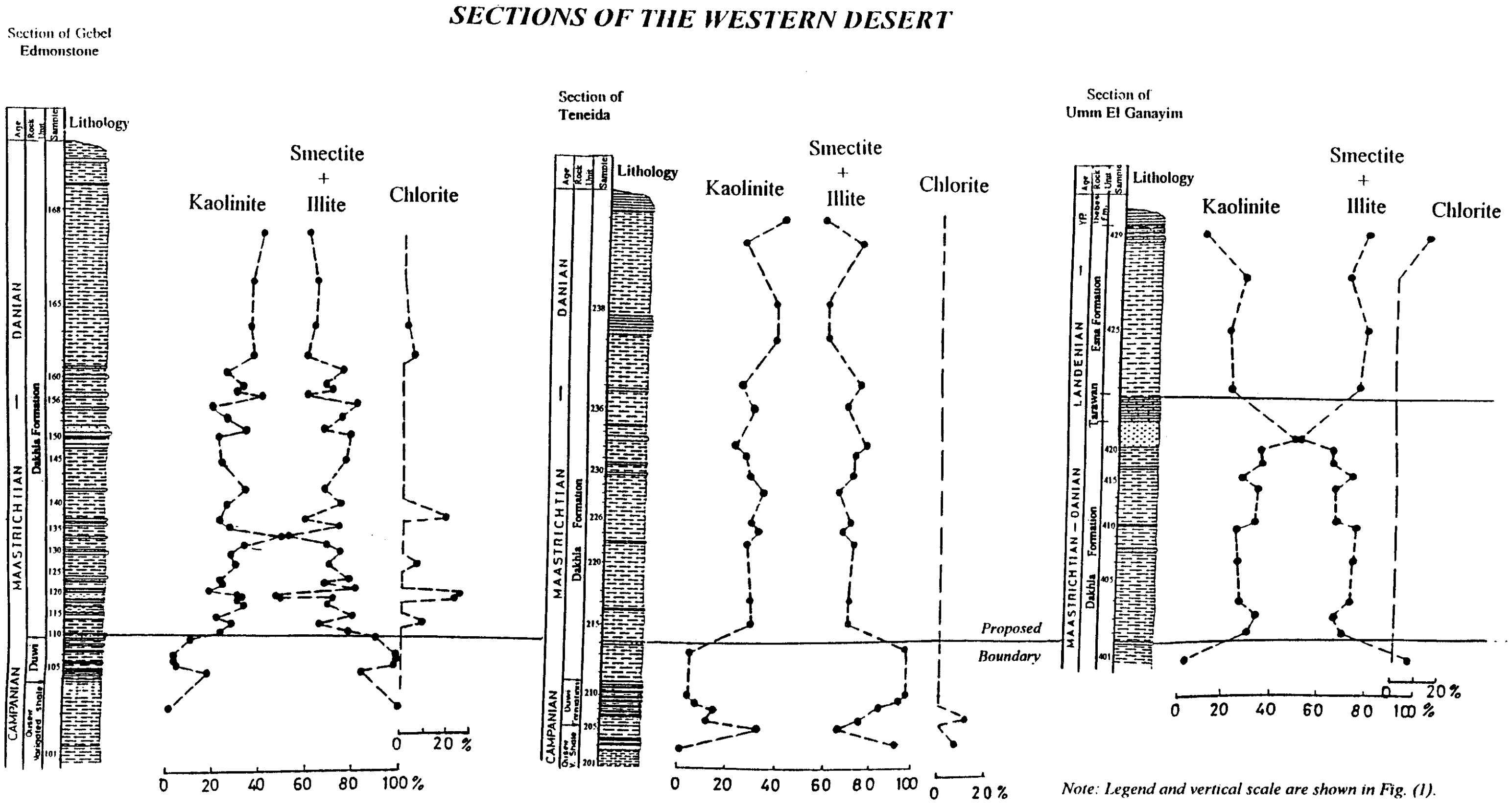
The vertical distribution of the clay minerals over the Dakhla Formation reflects general upward increase in the content of kaolinite together with increase in the carbonate content (calcite and dolomite). This can be interpreted as related to gradual upward change towards shallower conditions.

The distribution of the clay to non-clay ratio in the black shales of the Dakhla Formation shows marked but gradual eastward decrease where carbonates increase at the expense of the argillaceous materials. The black shales of Abu Had (Nile Valley) and Wasif and Abu Shigaila (Red Sea District) are generally less argillaceous and more calcareous than those of the Western Desert. It can be assumed that the depositional basin forming during the sedimentation of the Dakhla Formation was gradually deepening towards the eastern direction. The black shale of the Dakhla Formation remains always smectite/illite-poor and kaolinite-rich compared with that of the underlying Duwi or the overlying Esna Formations, irrespective of the clay to non-clay ratio (Figs 3 and 4).

Chemical weathering

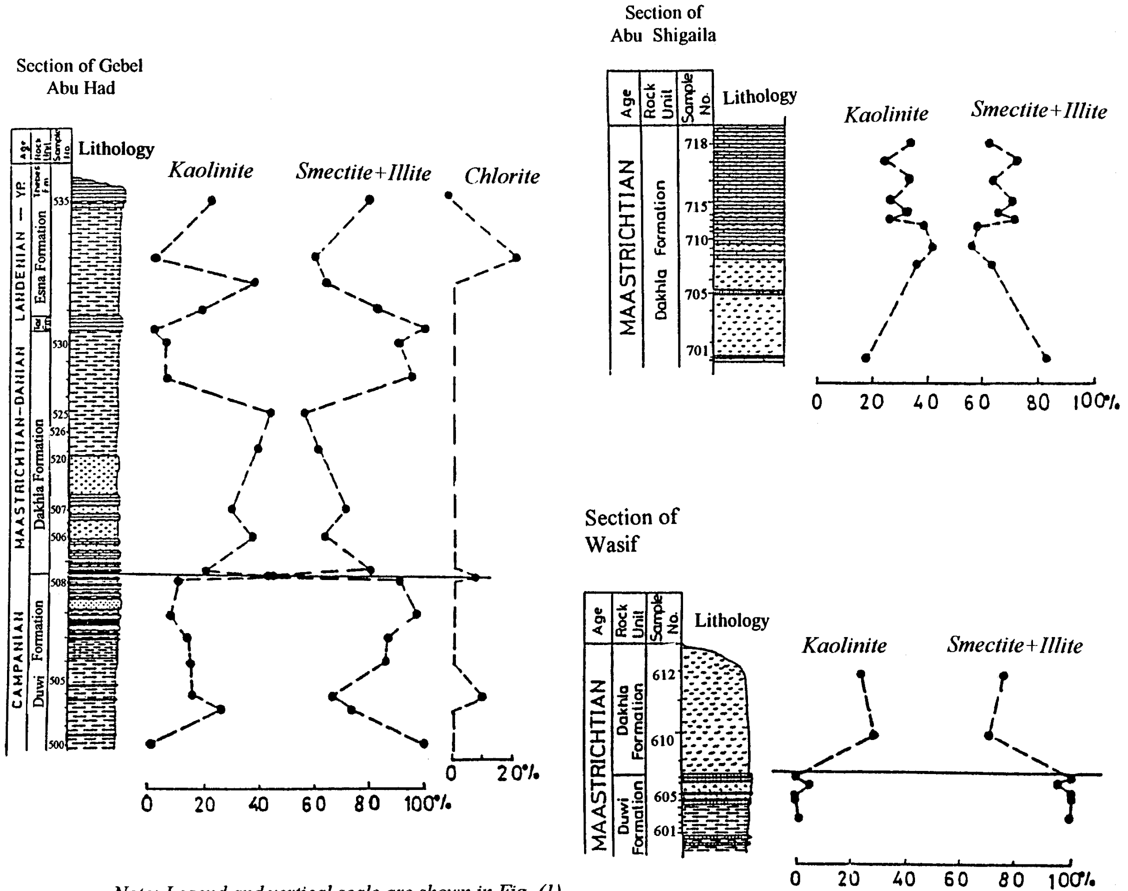
Krauskopf (1979) stated that 'dry air causes rock to decay only very slowly, as attested by the marvellous preservation of carved inscriptions dating from three and four thousand years ago in arid climate of Egypt'. This statement is undoubtedly true when we talk about colours made of minerals ultra-stable to weathering such as hematite, 'limonite', pyrolusite, malachite and gypsum; which were customarily used by ancient Egyptians. This argument becomes an over-statement when a system of organic matter-rich black shale is subjected to weathering for a geological lapse of time, even under arid climatic conditions. Although the climate in the Egyptian Sahara is generally arid, the Dakhla black shales seem to be significantly affected by chemical weathering. The comparisons of the mineral composition (Fig. 5) of the weathered and non-weathered shales, of correlated stratigraphic position, suggest the following inferences:

1. The average content of the total organic matter (TOC) diminishes from 7·05% to 0·04% upon weathering. The destruction of the organic matter seems to be responsible for improving fissility in the weathered black shales. However, Weaver (1989) assumes that the loss of water via dehydration of rock containing swelling phyllosilates commonly develop the fissility. The SEM photomicrographs (Fig. 6) show clear displacement of clay flakes as a result of expulsion of gas during decaying organic matter and oxidation of pyrite.
2. Pyrite, which occurs mostly as framboids, is extensively pseudomorphosed into goethite and/or hematite. As the intensity of weathering increases, the oxidation products of pyrite are leached (Fig. 7). The pseudomorphism of pyrite requires oxygenated water, while the removal



Note: Legend and vertical scale are shown in Fig. (1).

Figure 3. The contact between Dakhla and Duwi Formations can easily be traced depending on their clay mineralogy.



Note: Legend and vertical scale are shown in Fig. (1).

Figure 4. Clay mineral distribution in the studied sections of the Eastern Desert.

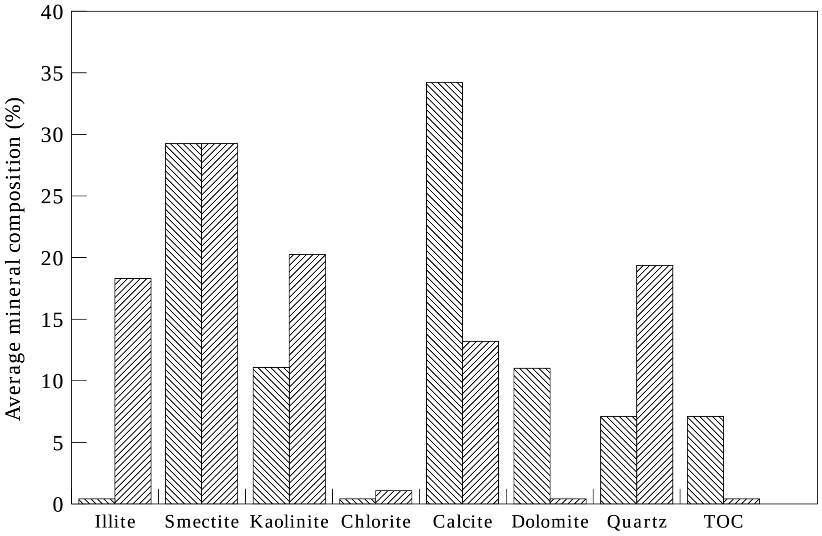


Figure 5. Average mineral composition of weathered and non-weathered black shales of Dakhla Formation. (▧ = non-weathered; ▨ = weathered).

of the pyritic iron probably needs a high concentration of CO_2 that is evolved from decaying organic matter under subaerial conditions. However, the sulfates produced from weathered pyrite concentrate along bedding planes or joints as gypsiferous thin bands or streaks can easily be seen in every weathering profile.

(3) Dolomite, which is essentially of the ferroan type (ankerite), seems to be almost entirely destroyed upon weathering. According to Frank (1981) and El Kammar (1983), the ferroan variety of dolomite is easily collapsed during weathering due to the oxidation of Fe^{2+} to Fe^{3+}. The latter is expelled from the lattice along cleavage planes or crystal boundaries as ferruginous material.

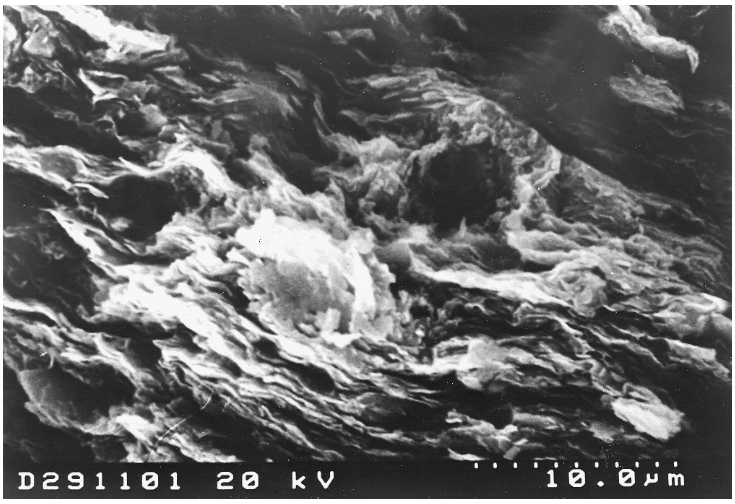


Figure 6. SEM photomicrograph showing the development of the papery texture as a result of expulsion of gases during the destruction of the organic matter.

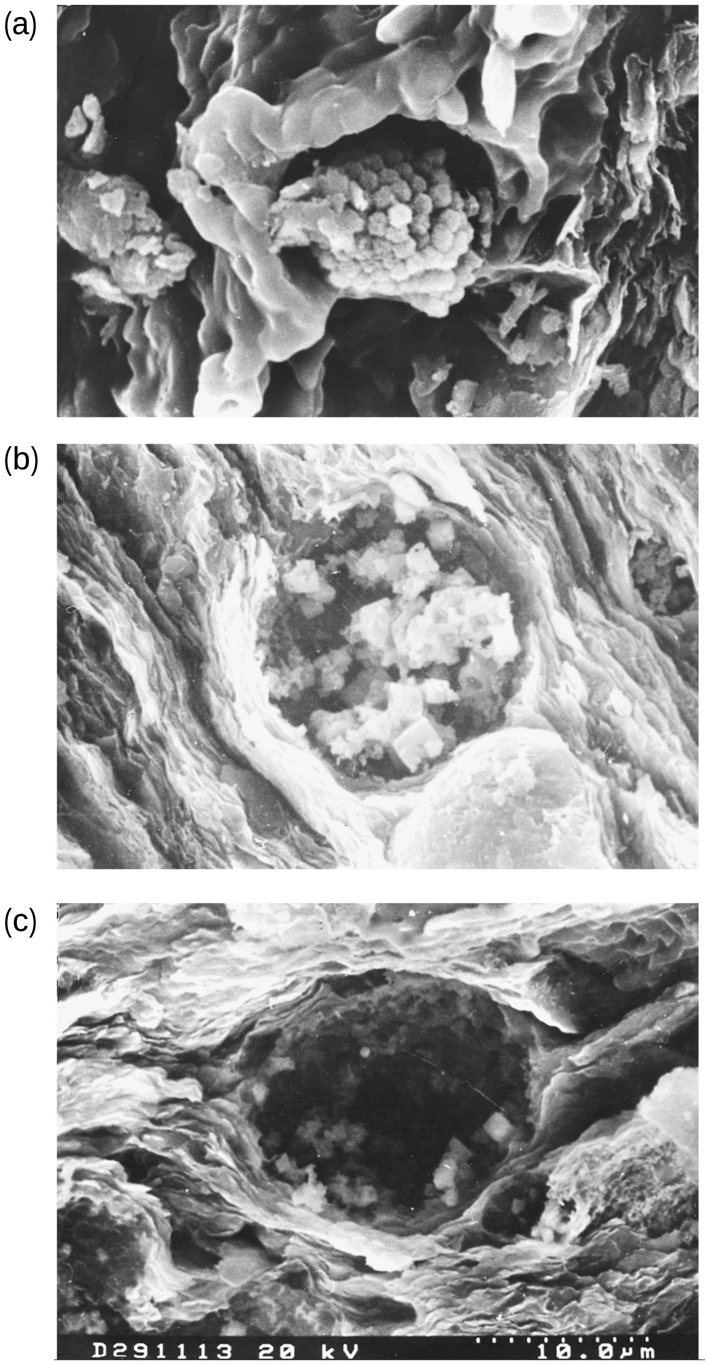


Figure 7. SEM microphotograph showing different weathering stages of pyrite framboids. (a) Framboidal pyrite, pseudomorphosed into goethite-hematite, (b) partial leaching, and (c) almost complete leaching of pyrite precursor.

(4) The content of calcite decreases from 29·53% in the non-weathered samples to 11·78% in the weathered ones. In other words, about 60% of calcite is lost upon weathering, according to the well-known equilibrium reaction of calcite with carbonic acid: $CaCO_3 + H_2CO_3$)*$Ca(HCO_3)_2$.
The authors believe that a good deal of carbonic acid is produced from CO_2 resulting from the decay of the organic matter during weathering rather than from atmosphere. Littke *et al.* (1991) tried to quantify losses of calcite, pyrite and organic matter during weathering. They observed that the resultant loss is 23–26% of the original carbonate content, 82–83% of the original pyrite content and 16–22% of the original organic matter content.

(5) The content of the clay admixture in the surface samples is higher than in that of samples collected from subsurface mines or cores. Such apparent increase in the clay content is probably a result of the sharp depletion in the carbonate and organic matter contents due to weathering.

(6) The ‘organophilic’ variety of smectite (Nemecz, 1981) has only been detected in the non-weathered black shales, suggesting an effective chemical weathering agent even to the interstratified organic matter.

(7) The most conspicuous change occurring due to weathering is the remarkable transformation of smectite into illite passing through smectite/illite mixed layer. The comparison between average quantitative mineral composition of the weathered black shales and their stratigraphically equivalent non-weathered ones (Table 4 and Fig. 5) indicates that illite is formed at the expense of smectite in the weathered samples. On average, the content of illite increases from 1% in the non-weathered to 26% in the weathered ones, while the summation of illite and smectite remains

Table 4. *Mean values of mineral composition of the weathered and non-weathered black shales of the Dakhla Formation (Range of values give in parentheses)*

Minerals	Non-weathered (n=13)	Weathered (n=20)
Illite %	0·25 (0–5)*	18 (0–46)
Smectite %	29 (0–63)	29 (5–50)
Kaolinite %	11 (0–23)	20 (0–44)
Chloite %	0·45 (0–10)	0·95 (0–12)
Calcite %	34 (0–66)	13 (0–77)
Dolomite %	11 (0–91)	0·23 (0–8)
Quartz %	7 (0–16)	19 (0–59)
TOC % (Total Organic Carbon)	7 (1–23)	0·04 (0–1)
Carbonate’s carbon	6 (1–11)	1·54 (0–10)
Illite % to $\sum$ smectite+illite.	1·25 (0–25)	38 (0–80)

almost the same in both varieties. A similar conclusion has also been reported by El Kammar & Basta (1983) in Abu Tartur clays, Western Desert, Egypt. They assume that the introduction of Al^{3+} and K^+ into the clays liberates Mg^{2+}, Fe^{2+} and Si^{4+}. In fact, the writers believe that such a transformation mechanism cannot satisfy electrical neutrality.

The mean values of the calculated chemical formula of clay fractions separated from weathered and non-weathered black shales (Table 3) suggest the following observations:

(1) The interlayer cations, such as Na^+ and Ca^{2+} are seriously depleted in the weathered clays. It can be assumed that the decrease in the content of such cations could be compensated by the H^+ of the weathering medium. The transformation mechanism can be then postulated as follows:

$$\mathrm{Smectite} + 2H^+ + K^+ + Al^{3+})^{*}\mathrm{Illite} + Na^+ + \tfrac{1}{2}Ca^{2+} + Si^{4+}$$

Therefore, the decrease in the interlayer charge, as a result of illite formation due to weathering, is accompanied with a decisive decrease of the tetrahedral charge and of the total layer charge, at the expense of the octahedral charge (Fig. 8).

(2) The release of silica from the tetrahedral sheet and the introduction of alumina instead, is demonstrated by the obtained formula for weathered clays:

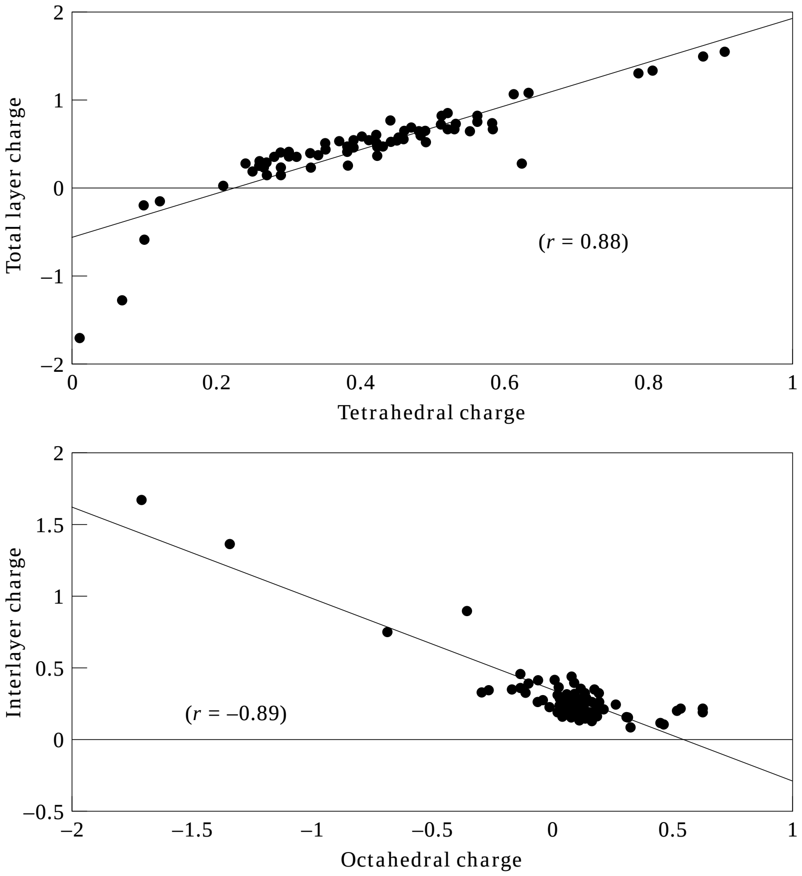


Figure 8. Relationships between lattice charges of clays separated from the black of Dakhla Formation.

> $M^{+}_{0{\cdot}05}Mg_{0{\cdot}09}\ Ca_{0{\cdot}04}K_{0{\cdot}13}Na_{0{\cdot}04}\ (Si_{3{\cdot}77}Al_{0{\cdot}23})(Al_{1{\cdot}35}\ Ti_{0{\cdot}04}Fe_{0{\cdot}38}Mg_{0{\cdot}23})\ O_{10}(OH)_2$
>
> Moreover the release of silica from the tetrahedral sheet can also be indicated from its relative decrease in the clays of the weathered black shales, as seen in Table 3. The SEM examination shows that such released silica may occupy voids or concentrate along fissility in the weathered shales (Fig. 9).

The transformation of smectite into illite as a result of weathering in the Egyptian arid desert is believed to be accelerated by the action of carbonic acid as well as of other acids resulting from the oxidation of organic matter. The weathering of the heterocompounds and asphaltine, which are substantial organic compounds in the studied black shales, should cause a decisive drop in pH due to creation of sulfate and nitrate besides organic acids. The lack of an easy percolation of water under the given climatic conditions impedes rapid dilution of the formed acids. Newman & Brown (1987) are of the opinion that the reaction

$$\text{Smectite} + K^{+} + Al^{3+} \rightarrow \text{Illite} + Si^{4+}$$

occurs during burial metamorphism of argillaceous sediments but during weathering the reverse occurs. However, this does not seem to be true for weathering under the Sahara climate.

Losses and gains due to weathering

It can be stated that significant mineral changes do occur due to chemical weathering of the black shales, even under arid conditions. The changes include development of new mineral phases such as illite and quartz at the expense of smectite (Table 5). There is absolutely no evidence of formation of kaolinite in the weathering profile. In fact, the conditions required for the formation of kaolinite cannot be maintained in the

Figure 9. SEM microphotograph showing secondary quartz filling between clay layers of weathered black shale from Wasif area, Red Sea Coast.

Table 5. *Losses and gains of minerals due to weathering of black shales of Dakhla Formation*

Mineral	Average composition (%), non-weathered*	Average composition (%), weathered*	Weathered normalized to kaolinite†	% losses and gains‡
Illite	0·25	17·96	9·93	+9·68
Smectite	29·09	28·94	15·99	–13·10
Kaolinite	11·03	19·96	11·03	0·00
Chlorite	0·45	0·95	0·53	+0·12
Calcite	34·10	1·97	7·17	–26·93
Dolomite	11·03	0·23	0·13	–10.90
Quartz	7·02	18·96	10·48	+3·46
TOC	7·02	0·04	0·02	–7·00
Total	100·00	100·00	52·28	∑–44·67

*Average mineral composition of non-weathered and weathered black shales, respectively, as given in Table 3, but recalculated to 100%.

†The average mineral composition of weathered black shales of column 2, multiplied by factor 11·03/19·96, which represents the kaolinite in non-weathered black shales relative to weathered ones.

‡Losses and gains calculated by subtracting the value in column 3 from that of non-weathered black shales in column 1.

prevailing climatic conditions, as percolating fresh or acid water is needed (Bjorlykke *et al.*, 1980). On the other hand, kaolinite is traditionally known as a mineral stable to chemical weathering. Therefore, the belief that the content of kaolinite did not suffer appreciable change as a result of prevailing weathering is not an arbitrary assumption.

Accordingly, the apparent increase in the content of kaolinite in the weathered shales is most probably a direct response to the loss of mass during weathering. Such apparent increase in kaolinite can justify mass losses and gains of individual minerals upon weathering. Quantitatively, the mass losses and gains can be obtained by normalizing the mean mineral composition of the weathered black shales by the apparent increase in kaolinite, as is readily illustrated in Table 5.

The calculations suggest that the black shales loose smectite, calcite, dolomite (and ankerite) and total organic matter, but gain illite and quartz. The summation of the gained illite plus quartz equals to the loss in smectite (≅13%). The formation of chlorite, although in minor amounts, is rather astonishing, as it is metastable under weathering conditions. However, it is believed by Hower *et al.* (1975) that chlorite can be formed by a by-product in the conversion of smectite into illite during burial metamorphism. Also, Boles & Franks (1979) confirmed the above assumption and proposed the following reaction:

$$\text{Smectite} + \text{K}^{+})^{*}\ \text{Illite} + \text{Chlorite} + \text{Quartz} + \text{H}^{+}$$

It can be assumed that the local high potential of Mg^{2+} resulting from the breakdown of dolomite (or ankerite) in the weathering profile may satisfy the Mg-potential required for the formation of chlorite. The total mass loss of minerals due to the chemical weathering of the studied black shales of the Dakhla Formation is estimated to be about 45%, on average.

Genetic bearings of clay minerals

The various shales belonging to the Upper Cretaceous–Lower Tertiary of Egypt can be distinguished on basis of their gross mineralogy, in general, and their clay mineralogy, in particular. Easily distinguishable change in the clay mineral composition marks the boundary between Dakhla and Duwi Formations. This mineral change has a pervasive distribution everywhere in Upper Egypt, from Qusier-Safaga due east to Dakhla Oasis due to east (Figs 3 and 4). The variation of this mineral can presumably be interpreted as consistent change in the depositional environments on a regional scale.

The clay mineral abundance and its distribution in the Dakhla Formation in the Western Desert is constructed in three sedimentary sections, namely, from west to east, Edmonstone, Teneida and Umm El Ghanyim. In these sections, the Dakhla Formation consists of variable proportions of smectite/illite mixed layer and kaolinite with sporadic chlorite. The black shales of the Duwi Formation are smectite-rich and kaolinite-poor compared with those of the overlying Dakhla Formation. The variation boundary of the clay mineral fits with an easily field-distinguishable conglomeratic band that has a wide distribution in the study area. The affirmative recognition between the Dakhla and Duwi Formations, besides the presence of the conglomeratic band, may suggest some modification in the stratigraphic boundary between the two formations. Stratigraphically, the Duwi Formation ends with its uppermost phosphate bed. However, the lowermost few meters of the Dakhla Formation bear clay mineralogical characteristics of Duwi proper. The authors, therefore believe that the boundary should accordingly be shifted upwardly to the conglomeratic band which separates, without discrepancy, the smectite-rich Duwi Formation from the relatively kaolinite-rich Dakhla Formation. It can be assumed that such changes in clay mineralogy cannot solely be interpreted to variation in depth of the depositional sea as advocated by Ganz *et al.* (1990*b*). The formation of smectite-rich and kaolinite-poor black shales of the Duwi Formation most probably has to do with the deposition of the phosphorites. The formation of the latter consumes large amounts of Ca^{2+} and consequently leads to a decisive increase in the Mg^{2+}/Ca^{2+} ratio that may prevent phosphorite from continuing to deposit (Lucas, 1979). The formation of clays relatively rich in Mg^{2+} seems, therefore, to be necessary in order to normalize the Mg^{2+} increment in the depositional sea. This may explain why smectite-rich shale continued after the deposition of the last phosphate bed and until the conglomeratic band. The shale between the last phosphate bed and the conglomeratic band should accordingly be included within the Duwi Formation, as it was deposited under its semi-restricted conditions. No doubt that the assumption of the boundary readjustment between Dakhla and Duwi Formations, as appraised above, will stimulate thought and argument, even rage amongst the lithostratigraphers.

During the deposition of the Duwi Formation, the depositional basin was semi-restricted, so that the high Mg^{2+}/Ca^{2+} cannot be easily normalized. Several hypotheses have been postulated to explain the mechanism by which Mg^{2+} was consumed, either during a dolomitization process (Burnett, 1977) or by the formation of Mg^{2+}-rich shales (Riggs, 1979). In the present case, it seems more likely that the consumption of the excessively increasing Mg^{2+} could be through enhancement inside a smectite lattice. The data of the structural formula (Table 3) supports such a belief, as the clays of the Duwi Formation contain more Mg^{2+} in their lattice than those of the Dakhla Formation. At the very beginning of the deposition of the Dakhla Formation, the basin was not restricted any further and it was receiving significant terrestrial influx. The conglomeratic band expresses such change in the depositional environments.

The basin during the deposition of the Dakhla Formation in Edmonstone and Umm El Ghanayim was receiving a pronounced terrestrial supply compared to the equivalent stratigraphic position in Teneida. The mutual distribution of quartz (Fig. 10) supports the belief that the depositional basin of the lower part of the Dakhla Formation was relatively deeper in Teneida, compared to others in its neighborhood.

During the course of the deposition of the lower part of the Dakhla Formation, the

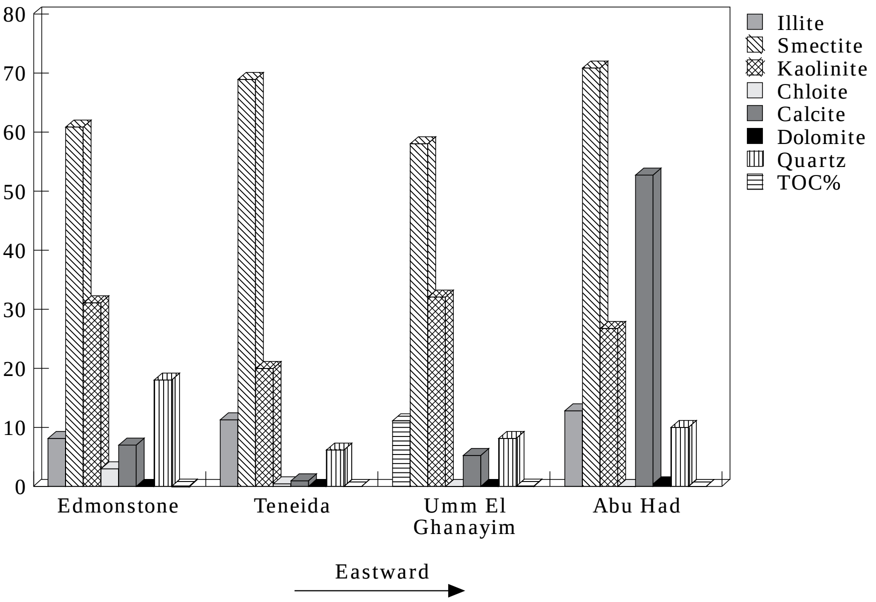


Figure 10. Average mineral composition of black shales of Dakhla Formation in different sections.

basin was sporadically receiving excessive terrigenous material in the form of siltstone bands. The influence of the continent continued until the deposition of the *Exogyra* bed, almost at the middle of the formation. Gradual transgression of the depositional sea began where conditions became more favorable for deposition of proper black shales.

Generally speaking, the clay mineral composition of the Dakhla Formation, whether in its lower or upper parts, does not display any particular variabilities in the main clay mineral composition, either on horizontal or vertical scales. The only consistent gradual variation can be traced in the upper part, where kaolinite and quartz contents increase (Fig. 4) suggesting gradual sea regression which ultimately led to the deposition of Tarawan Chalk (e.g. in Umm El Ghanayim) and its equivalent Kurkur Formation (e.g. in Abu Tartur).

In Abu Had (Nile Valley), midway between Safaga and Kharga Oasis, the shales of the Dakhla Formation are markedly more calcareous. The mutual distributions of the clay minerals display sharp and sudden change due to changing facies. The content of kaolinite as well as the illitization ratio are obviously higher in the upper part of the Dakhla Formation.

Conclusions

The Upper Cretaceous–Lower Tertiary black shales, which are mostly encompassed in Duwi and Dakhla Formations, are widely exposed throughout southern Egypt. They were formed during the major Upper Cretaceous (*Cenomanian*) marine transgression.

At the surface exposures, the black shales are grey in colour, contain abundant gypsiferous streaks, papery, fissile, slippery and preferentially eroded, suggesting an effective chemical weathering mechanism. This has inspired the authors to quantify the possible mineral and chemical changes which have occurred due to chemical weathering, although the prevailing environments in the Egyptian Sahara are arid proper.

More than 200 samples were collected to represent the various lithologies of the exposed Upper Cretaceous–Lower Tertiary black shale in Egypt. Subsurface samples were collected from phosphorite mines of the Safaga, Quseir and Abu Tartur areas. These subsurface samples are considered to be least weathered and are roughly denoted as ‘non-weathered’. The comparison between weathered and non-weathered black shales is based on samples of closely similar stratigraphic positions.

Quantitative mineral analysis was performed by using a computerized infrared spectrometric technique corroborated by X-ray diffraction and scanning electron microscope. Chemical analysis of both organic and inorganic constituents was done for 160 clay size fractions separated from weathered and non-weathered black shales.

The lateral clay mineral distribution throughout the country suggests that the black shales of Dakhla Formation are diagnostically enriched in kaolinite and depleted in a smectite/illite mixed layer, compared to those of the underlying Duwi Formation and the overlying Esna Formation. The clay mineral composition can, therefore, be used for correlation of such monotonous black sediments. The present study proposes a possible readjustment of the already known stratigraphic boundary between Duwi and Dakhla Formations.

During the sedimentation of the Dakhla Formation the depositional basin was gradually deepening towards the eastern direction. The basin was semi-restricted during the deposition of the Duwi Formation and the formation of high Mg-clays was necessary in order to normalize the increase in Mg after the sedimentation of phosphorites.

The prolonged exposure and the organic-rich nature of the black shales favour effective chemical weathering, even under arid environments. The changes occurred include:

(1) Destruction of organic matters, even those interstratified within phyllosilicates.
(2) Pseudomorphism and breakdown of framboidal pyrite.
(3) Breakdown of dolomite in general and ankerite in particular.
(4) Major loss on the content of calcite (about 60%) as a result of its dissolution by acid water.
(5) Remarkable transformation of smectite into illite passing through smectite/illite mixed layer. This process is accompanied with removal of interlayer cations such as Na^+ and Ca^{2+}. Moreover, the transformation process increases the content of alumina at the expense of the tetrahedral silica.
(6) The total mass loss of black shales upon chemical weathering under arid environments is estimated to be about 45%, on average.

The apparent increase in the content of clays, especially kaolinite, is due to the relatively high loss on some phases such as carbonates, organic matter and pyrite.

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