4 Mineralogy

The identification of the mineralogical composition of shales can be easily approached through the use of X-ray analysis.

The present chapter deals with the mineralogical composition of shales of Carboniferous age from Abu Zinema in South Sinai, Jurassic age from Al-Maghara coal mine in North Sinai, Cretaceous age from Abu Tartur phosphate mine in Western Desert, Cretaceous to Early Eocene age from Esna-Idfu at Nile Valley and of Cretaceous age from Quseir phosphate mines at the Red Sea coast.

There are simple procedures for the semi-quantitative estimation of the clay mineral content. They involve the measurement of the height of the (001) reflections above the background with different correction factors used in this study or measurements of the peak areas (Johns et al. 1954; Weaver 1958). The following is a brief description of the minerals identified by means of X-ray diffraction analyses of the clay fraction and whole rock samples.

4.1 Clay Mineralogy

4.1.1 The importance of clay minerals

Clay minerals can be used as stratigraphic markers and environmental indicators. The type of clay found in shale is a function of provenance and diagenetic history. Depositional environment had a considerable influence on the clay mineralogy through early mineral transformations in the basin of deposition (Russell 1970).

4.1.2 Structure and chemistry of clays

There are two basic building blocks common to clay mineral structures:
(i)- A sheet of silicate tetrahedra, consisting of two layers of oxygen atoms, and containing silicon in four-fold (tetrahedral) coordination.
(ii)- An octahedral sheet, consisting of two layer of oxygen atoms or hydroxyl groups, between which aluminium, magnesium or iron are bounded in six-fold coordination.
The structural units of clays therefore consists of either alternating tetrahedral and octahedral sheets (OT or 1:1 structure), as in the kaolinite group of clay minerals; a sandwich of one octahedral sheet between two tetrahedral sheets (TOT or 2:1 structure), as in illite and

smectite clay minerals or an arrangement in which the three-layer TOT units alternate with a brucite layer (2:1:1 structure) as in chlorite.

The various clay minerals can be summarized as follows:

4.1.2.1 Smectite group minerals

These have a diocthedral or a trioctahedral 2:1 layer structure. Smectites nearly always occur as fine-grained particles of clay size. The dioctahedral smectites are the phases which are often intimately associated (interlayering) with the mica-like minerals (Velde 1992). The main dioctahedral minerals are montmorillonite-beidellites (Al-rich) which are predominatly octahedrally charged, and nontronites (Fe^{3+}-rich).

4.1.2.2 Kaolinite group minerals

This group consists of uncharged, dioctahedral layer units with a 1:1 structure of 7 Å in thickness. The individual mineral species considered are:

Kaolinite, which has varying degrees of crystallinity and a distinct, platy form; Dickite, which is similar to kaolinite, but with a different stacking arrangement of the unit layers; Halloysite, which consists of a poorly ordered arrangement of kaolinite-like units, with variable amounts of water between the layers, generally between 0.6 to $4H_2O$ per formula unit, and often with a tabular form.

4.1.2.3 Chlorite group minerals

These are sometimes dioctahedral but usually trioctahedral with a 2:1:1 layer structure of 14 Å in thickness. The 2:1 layer is negatively charged because of ionic substitutions, and is balanced by a positive charge on the interlayer hydroxide sheet. Chemically, the group is extremely variable, but it should suffice to concentrate on only three types:

(i)   Mg-rich chlorite (e.g. clinochlore) which is trioctahedral.

(ii)   Fe-rich chlorite (e.g. chamosite) which is also trioctahedral.

(iii)   Al-rich chlorite (e.g. sudoite) which is mainly dioctahedral.

Chlorite and kaolinite have very different structures and geological occurrences, but they sometimes are present in natural mixtures. Chlorite has a basal series of diffraction peaks superimposed or nearly superimposed on the members of the kaolinite 001 series. High-Fe chlorites have weak odd-order reflections, so weak that the 001 peak is easily obscured or not

noticed, so the distinction between chlorite and kaolinite is most difficult when Fe-rich chlorites are involved (Duane et al. 1997).

4.1.2.4 Illite/Mica group minerals

These have a di- or trioctahedral 2:1 layer structure of 10 Å in thickness. The structure is charged due to ionic substitution in both the tetrahedral and octahedral sheets, and contains interlayer non-exchangable cations (usually K^+) that compensate for the charge deficit on the unit layers. The chemistry of the various members of the group is variable.

4.2 Clay minerals in the studied shale samples

Smectite, kaolinite and chlorite in addition to illite are the most abundant clay minerals encounted in the studied shale samples. The following is a discussion on the recognized clay mineral associations. Representative profiles and the semi-quantitative results obtained are shown in Appendix (Table 2 & 3 and Fig.1 to 5) and the following Table (Table 1).

Table 1: Average semi-quantitative clay mineralogy of the studied shales (by XRD)

Location	Formation	No. of samples	Smectite %	Kaolinite %	Chlorite %	Illite %
Nile Valley	Esna Shale	11	88	2	10	0
	Dakhla Shale	10	73	9	18	0
	Duwi	6	98	2	0	0
Quseire Mines	Dakhla and Duwi	11	80	20	0	0
Abu Tartur Mine	Duwi	4	100	0	0	0
Al Maghara Mine	Safa	3	traces	100	0	0
Abu Zinema Area	Ataqa	3	0	87	0	13

4.2.1 Smectite

Smectite is the dominant constituent of the clay mineral content of the studied shales in the Upper Cretaceous–Lower Tertiary sediments of Duwi Formation at Abu Tartur phosphate mine, Duwi Formation and Dakhla Shale at Quseir phosphate mines and Duwi Formation, Dakhla Shale and Esna Shale at Esna –Idfu at Nile Valley. The average content of smectite in the samples ranges from 100 % at Abu Tartur phosphate mine to 80 % at Quseir phosphate mine (Table 1); (Fig.6).
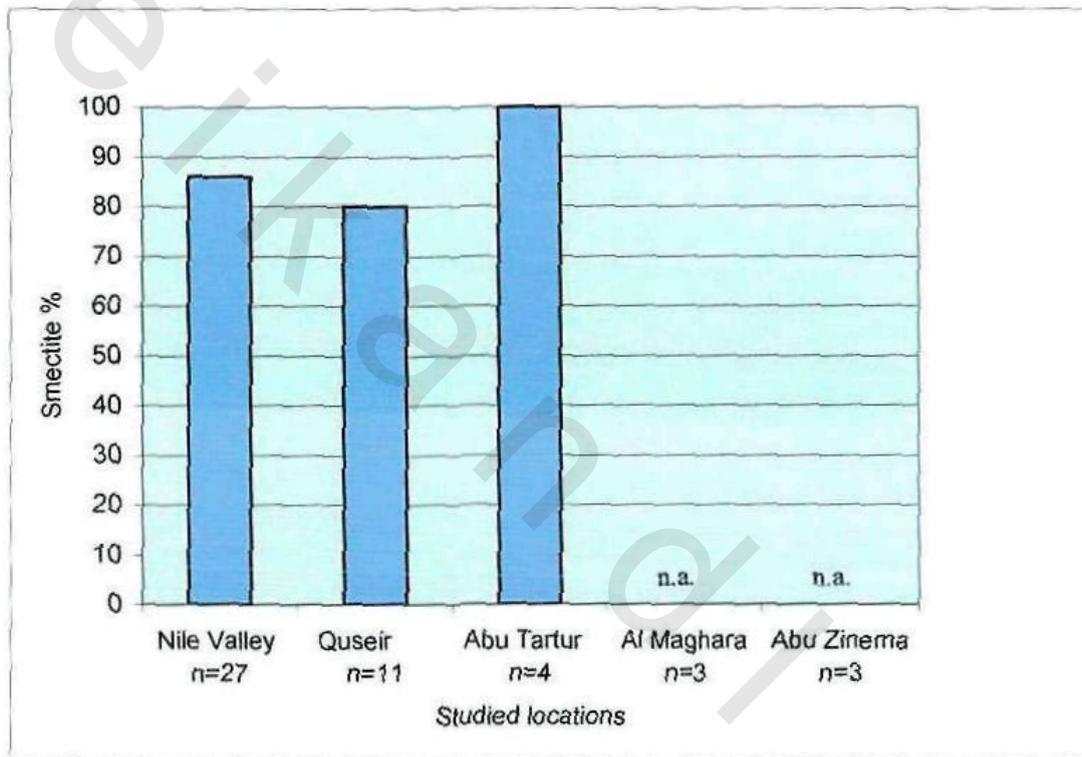

Fig. 6 : Smectite average at studied locations

Terrigenous clay minerals are often transported great distances by wind and water before being deposited on the seafloor. The composition and characteristics of clay minerals in well preserved sediments record the paleoclimatic and tectonic environments of their source areas (Chamley 1989; Ehrmann et al.1992; Velde 1995). Climate has strong influence on rock alteration, and clay minerals are often the main product of this process. For example, the global pedogenic and climatic zonation is reflected in the latitudal distribution of certain clay minerals (Chamley 1989). However, other factors than climate such as assemblage, topography, transport and diagenetic changes can modify the original clay assembladge

topography, transport and diagenetic changes can modify the original clay assemblage (Yuretich et al. 1999). Clay minerals in marine sediments have been used to infer paleoenvironmental conditions (Jeong and Yoon 2001). In continental weathering environments, smectite and kaolinite are generally formed by active chemical weathering of rocks under humid temperate to tropical climates (Weaver 1989). Smectite and kaolinite occurrence in marine sediments was often ascribed to the chemical weathering in a warm humid environment. Chamley (1989) stated that in temperate arid regions the neoformation of smectite in vertisols often occurs simultaneously with negative transformations (e.g. open illite, irregular mixed-layer) and the preservation of some parent-rock minerals. In arid tropical areas smectite neoformation becomes exclusive. The pedogenic smectitization can extend over the humid intertropical zone, if the drainge conditions are poor and prevent the normal evacuation of ions. Smectite can also form diagenetically from illite, kaolinite, or chlorite (Moore and Reynolds 1989).

The dominance of smectites in the Upper Cretaceous-Lower Tertiary sediments in South Egypt has been described by Hendriks (1985, 1988), Hendriks et al. (1990), Ismael (1996) and Ahmed (1997). The dominance of smectite in the studied samples is in agreement with the obtained results from the other authors. The origin was believed by those authors to be due to continental pedogenesis as well as marine neoformation. Terrestrial smectite developed under warm and humid to seasonally humid conditions by the degradation of chlorite and illite or by crystallization from ion-enriched hydrolytic solutions in badly-drained alkaline soils. According to Moore and Reynolds (1997) there are two kinds of smectite, one produced by the kind of weathering found in soils and one by neoformation such as in the alteration of volcanic glass. Four main genetic hypotheses for the origin of smectite and mixed layer (I/S) exist: (1) reworking of soils and enrichment by differential settling, (2) alteration of volcanic material, (3) transformation of detritals, and (4) authigenesis (Chamley 1989; Thiry and Jaquin 1993). The absence of any conceivable volcanic precursor, such as tuff or glass in the studied shales indicates that smectite is mainly of a detrital origin. Smectite is the predominant clay mineral in many lacustrine settings. For example, it makes up to 100% of the shale minerals in some stratigraphic units of the Messel oil shale (Weber 1991). The author suggested a warm/humid climate proven by the smectite which corresponds with the existence of a diverse fauna and flora in south Egypt (Hendriks et al.1990). Discrete smectite and mixed-layer illite/smectite (I/S) commonly forming from the weathering of ultrabasic or very basic rocks which produce magnesium minerals (Surdam and Stanley 1979).

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The main sources of the studied shales lie in the rugged tectonic belt which forms the Precambrian basement complex and their weathering products in the South-Eastern Desert of Egypt and the northern part of Sudan. These basement rocks are mainly an association of metasediments, metavolcanics, metagabbros and serpentinites, constituting the ophiolitic melange (Shackleton et al. 1980) that is interrupted by gneisses in structural highs. This sequence is unconformably overlain by volcanics, and intruded by granite ranging in composition from quartz diorite to alkali-feldspar granite. Primarily the detrital material is carried to the shelf by streams and river system. Partially, however, aeolian transportation may have played a minor role. The detritus encountering the shelf environment undergoes further mechanical as well as chemical differentiation, and the transformation of detritus into deeper marine sediments results in further chemical and mineralogical changes.

The smectite-kaolinite association in the studied shales does not suggest the formation of kaolinite under the same conditions of smectite formation or the insitu formation of kaolinite by chemical precipitation. Smectite formation is compatible with alkaline reducing conditions, while kaolinite is generally thought to require acid conditions, and it may be unstable in alkaline environments. The occurrence of smectite together with kaolinite and chlorite indicates the alteration of feldspar in connection with an „arenization" (Millot 1970) of crystalline basement rocks in a warm and semi-arid climate. Hendriks et al. (1990) stated that the clay mineral associations within the sedimentary succession of southern Egypt are attributed to a terrestrial provenance. They suggest a warm and semi-arid climate on the continent.

In the Duwi Formation at Abu Tartur phosphate mine, the abundance of smectite and the low content or absence of illite and kaolinite refer to a deposition under fluvio-marine environment. The presence of pyrite rombs indicates a reducing environment. These results are in agreement with these obtained by Sediek and Amer (2001). Dakhla and Esna Shale at Nile Valley section, Quseir phosphate mines, show an association of smectite with some kaolinite and chlorite, indicating the detrital origin and deposition in open marine environments. Generally, the clay mineral associations in the studied shales at Abu Tartur, Nile valley and Quseir with its smectite dominance suggest a terrestrial provenance that had not attained intensive weathering, a warm and semi-arid climate and the resulted materials were carried by fluvial action, which finally interfered and admixed with marine environments (marginal marine, low energy and reducing conditions of Duwi Formation and open marine facies of Dakhla and Esna Shale).

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4.2.2 Kaolinite

Kaolinite is the dominant clay mineral of the studied shales of Safa Formation at Al Maghara coal mine and Abu Zinema. The average content of kaolinite in the shales of the 5 locations in Safa Formation at Al Maghara coal mine, in the Ataqa Formation at Abu Zinema, in the Duwi and Dakhla formations at Quseir phosphate mines and in the Duwi, Dahkla and Esna formations at Nile Valley varies between 0 and 100 % (Fig. 7); see also (Table 1).
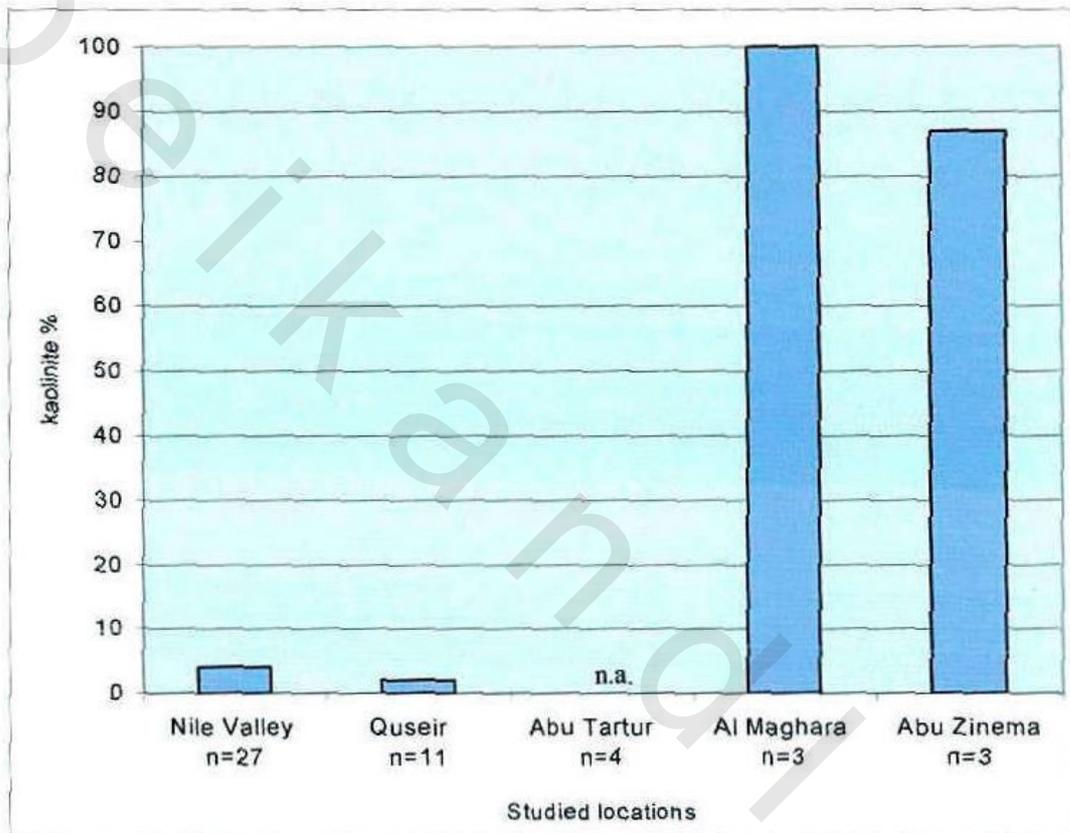

Fig. 7 : Kaolinite average at the studied locations.

The origin of kaolinite in the studied shales has been interpreted for a long time as to be a product of chemical weathering of feldspars. Kaolinite formation is favoured under tropical to suptropical humid climatic conditions (Chamley 1989, Hallam et al. 1991). In addition to a detrital origin, kaolinite may also develop by diagenetic processes due to the circulation of acid solutions (Ghandour et al.2003).

The dominance of kaolinite in the studied shales of Safa Formation at Al Maghara coal mine of Jurassic age immediately beneath the coal bed and the dominance of kaolinite also in the bituminous black shale at Attaqa Formation at Abu Zinema area of Carboniferous age are in

agreement with the results obtained by El-Anbaawy and Youssef (1989), Abd El Hameed 1997) and Ghandour et al. (2003). The kaolinite in Safa Formation at Al Maghara coal mine is interpreted to have been deposited in lakes or lagoons adjacent to the coastline (Said 1990). Kaolinite formed as a result of extensive chemical weathering and leaching of rocks which occur in the exposed granite-metamorphic basement area (granite intrusions ranging in composition from quartzdiorite to alkali-feldspar granite) of South Sinai. Mostafa and Younes (2001) stated that shales of Safa Formation at Al Maghara coal mine are generally immature for oil generation. Generally, mudstones which are immature for oil generation contain discrete minerals predominantly of detrital origin reflecting largely the character of parent rocks (Lindgreen and Surlyk 2000). During diagenesis, the morphology of kaolinite changes from vermicular or aggregates of books to individual blockier crystals (Ehrenberg et al. 1993). However, there is no SEM observation evidence for the role of diagenesis in the formation of kaolinite in Safa Formation Ataqa Formation of Abu Zinema, i.e. the kaolinite is of primary or detrital origin.

The origin of kaolinite in the Upper Cretaceous-Lower Tertiary sediments of southern Egypt also was attributed by Gindy (1983) to the extensive chemical weathering and leaching of rocks which occur especially in the exposed granite-metamorphic basement areas in the south of Egypt and in northern Sudan. In the opinion of Hendriks et al. (1990) kaolinite in the marine deposits of Upper Cretaceous-Lower Tertiary age are products of terrestrial weathering and represent continental products of a warm and at least seasonally humid climate, being eroded and transported toward the sea by rivers.

The amount of kaolinite in the shales of Upper Cretaceous-Lower Tertiary age Dakhla and Esna Shale in the Nile Valley section and also in Duwi and Dakhla Shale at Quseir phosphate mine is in agreement with the results obtained by Hendriks et al. (1990), Ismael (1996) and Ahmed (1997). This kaolinite represents a continental weathering product at a warm and at least seasonally humid climate, being eroded and transported towards the sea by rivers.

4.2.3 Chlorite

Chlorite is the second most abundant clay mineral in the samples of Dakhla and Esna Shale at the Nile valley section. The average content of chlorite is 14 %. Chlorite varies between 0 and 14 % (Fig. 8); (see also Table 1). Chlorite has been interpreted to originate from the physical weathering of sedimentary, metamorphic and basic source rocks under cold climates (Ehrmann et al. 1992; Jeong and Yoon 2001).
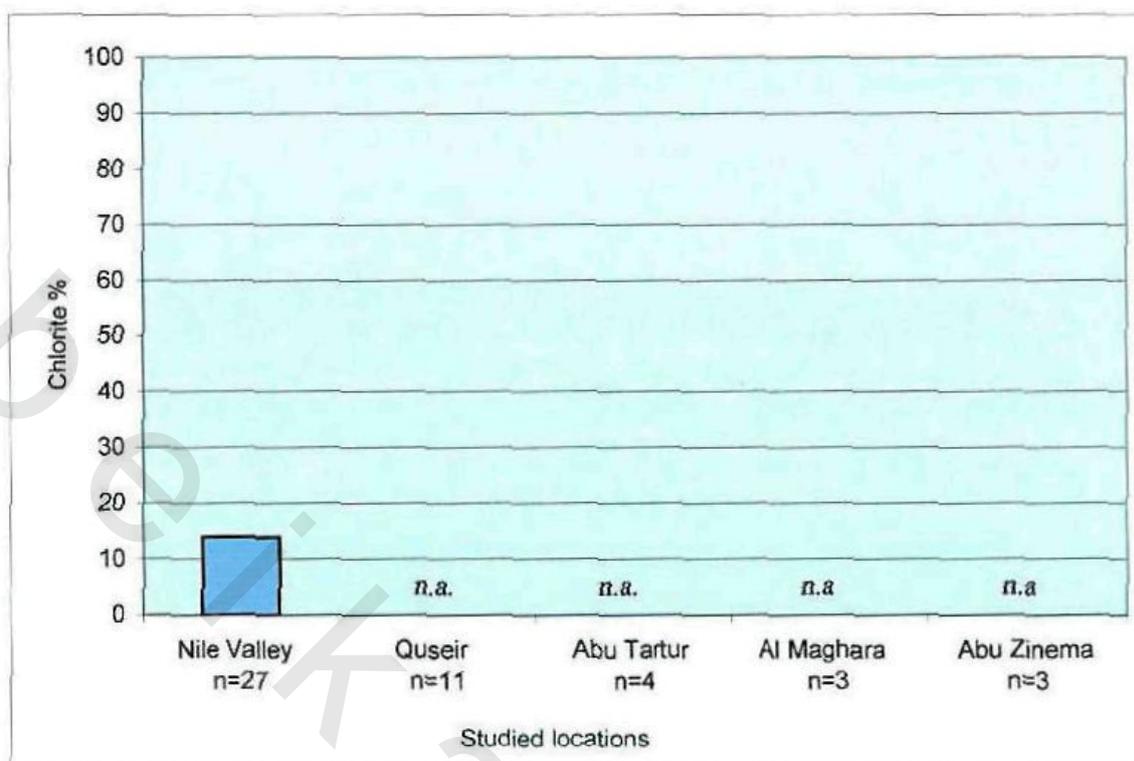
Fig. 8 : Chlorite average at the studied locations.

Chlorite reacts very sensitively in continental chemical alteration processes and is easily transformed into smectite (Millot 1970). Walker (1993) concluded that most chlorites form diagentically with burial especially in Mg-rich water in shales and slates, or can form directly at temperatures well below 200°C .

The origin of chlorite in South Egypt was attributed by Hendriks et al. (1990) to be exclusively of marine origin. The small amounts of chlorite in Dakhla and Esna Shale at Nile Valley, which are rich in Ca and Mg and characterized by the dominance of smectite, may indicate the neoformation of chlorite or may be formed by physical weathering. The main sources of chlorite in the studied shales lie in the Precambrian basement complex in the South-Eastern Desert of Egypt and the northern part of Sudan.

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4.2.4 Illite

Illite was found to be a trace constituent only in the studied samples of Ataqa Formation which is of Carboniferous age (at Abu Zinema area, south-west Sinai). Illite average content is varies between 0 and 100 % (Fig. 9); see also (Table 1).
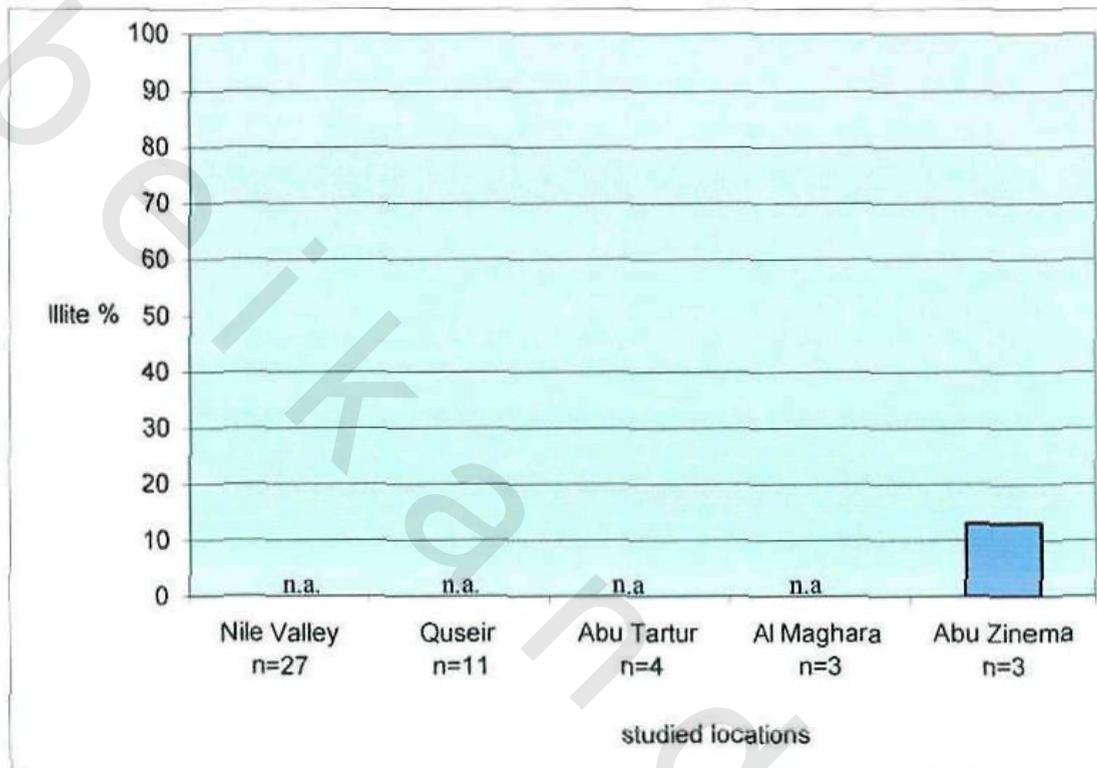

Fig. 9 : Illite average at the studied locations.

Illite typically forms under conditions completely different from those under which kaolinite and smectite are formed. Illite forms in soils with little chemical weathering, in cold and/or dry climates, and in areas of high relief where physical erosion is predominant (Ghandour et al. 2003).

In the present study the presence of illite in the Ataqa Formation of Carboniferous age (South Sinai) suggests the presence of mica in the source area. Mica have originated from felsic rocks from south of Sinai.

4.3 Whole rock samples

The peak height of the identified minerals in bulk samples are measured from x-ray diffractograms. The identified non-clay minerals are as follows:

4.3.1 Quartz

Quartz was found as an important non-clay mineral in all samples. Quartz varies from zero in samples N59, N35 and Q6 to 86% in sample AZ1 in Appendix (Table 3).

4.3.2 Carbonates

The carbonate minerals detected by XRD are calcite and dolomite. Calcite was found in most Nile Valley samples. It ranges from 0.0 % in black shale of Abu Tartur phosphate mine, Al-Maghara coal mine and Abu Zinema samples to about 88 % in the Tarawan Chalk in Nile Valley, sample N49. On the other hand dolomite was detected in a number of samples. It reaches up to 81% sample N59. The presence of calcite and dolomite in the studied samples from Duwi Formation, Dakhla and Esna Shale at both Quseir phosphate mines and Esna-Idfu at Nile Valley in addition to the presence of foraminifers' fossils may indicate the deposition of these formations in a marine environment.

4.3.3 Sulphates

Anhydrite was found in most samples of the Nile valley section. It is absent in the samples of Quseir phosphate mines, Abu Tartur phosphate mine, Al Maghara coal mine and Abu Zinema area. The anhydrite content reaches up to 94% on sample N52. It was identified in the XRD diffractograms by its characteristic lines at 3.50 Å and 2.85 Å.
Gypsum was identified in a number of samples by its characteristic lines at 7.56 Å, 3.06 Å and 4.27 Å. It reaches a maximum value of 47% in sample Q6.

The evaporites form from saline-rich fluids–brines. Brines may be generated by concentration of sea water, by evaporation or freezing, or as residual connate fluids in the subsurface (Selley 1988). Secondary brines can form where meteoric groundwater dissolves previously formed evaporites.

Anhydrite and gypsum in the studied shales were probably precipitated primarily as metal sulphides under reducing conditions when the shales were deposited. After the compaction of shales and oxidation of sulphides to sulphates as a result, at least in part, of the biological activity, the produced sulfates react with the calcic cement produced by weathering of carbonate to form gypsum. These dissolved sulfates will be expelled by solution due to the compaction of clays and concentrate along bedding planes as gypsiferous bands or streaks which can be easily seen in the field.

4.3.4 Pyrite

Pyrite was only detected in the black shales of the Duwi Formation in Abu Tartur phosphate mine. It reaches up to 6% in sample Tw.4. It was identified in the diffractograms by its characteristic lines at 1.63 Å, 2.71 Å and 2.42 Å.

The presence of pyrite spheres and framboids as seen by the SEM (6.3) in Duwi Formation indicate the prevalence of a reducing environment during the deposition. The presence of pyrite spheres may be an indicator of shallow water, such as found on submarine swells or in areas of nutrient upwelling in shelf settings (Schieber and Baird 2001). Pyrite forms in sediments as a consequence of the bacterial reduction of sea water sulphate (Berner 1982). Thus, the highly pyritic shales must have formed under euxinic conditions where H_2S exists above or at least at the sediment-water interface. The presence of H_2S in turn will react with Fe^{2+} which was probably delivered into the basin as colloidal material adsorbed on clay minerals to form iron sulphide. By increasing activity of the hydrogen sulphide in presence of iron and organic matter, a hydrophobic sulphide gel might have been formed (El-Dahhar 1987).

4.3.5 Carbonate fluorapatite

The phosphate minerals encountered in Quseir Safaga area, Abu Tartur mine and Nile valley section are carbonate fluorapatite, which are traditionally called francolite. This mineral is always the sole constituent of phosphorites in unweathered or only slightly weathered sedimentary deposits, whatever their age or location (Prevot et al. 1989). The peak area under the 2.79 Å is taken as the relative abundance of francolite. The amount of francolite ranges from very high (about 78 % sample N.20) to low in others (about 14 % sample Q.4).

The Upper Cretaceous–Lower Tertiary boundary in Egypt, like in many other countries, is a good example of the sedimentary association black shale – phosphate – chert – dolostone. The contacts between these facies are either gradual or abrupt. This sedimentary succession is believed to be deposited during the Late Cretaceous transgression of North Africa (Issawi 1972; Ward and McDonald 1979; Richerdson 1982).

The presence of francolite, calcite and dolomite in the shales at Nile Valley, Quseir phosphate mines and Abu Tartur phosphate mine indicate their deposition in a marine environment. The precipitation of phosphorites relates to the upwelling of nutrient-rich water (Selley 1988). Germann et al. (1987) concluded that the origin of the Egyptian phosphorites can be attributed to four distinct genetic phases, namely: primary enrichment, secondary concentration, lithification and weathering. The primary enrichment phase under suboxic to anoxic oxygen facies, during transgression produces phosphatic black shales. The secondary concentration phase under oxic facies, but during regression produces phosphatic sands and black shales. The lithification phase in an oxic/anoxic facies controlled by permeability, chemistry of the host rocks and pore fluids, is producing calcareous, siliceous, clayey, phosphatic phosphorites, and organic-rich clay-and siltstone. The weathering phase controlled by oxic, warm-humid climate and produce limonitic, gypsiferous phosphorites with Fe-phosphates and organic-poor clay-and siltstone.

The apatite formed under euxinic conditions at very low sedimentation rates that enabled anaerobic microorganisms, present in pore water, to attack the organic matter and thus to release PO_4^{3-}. This acidic medium, in turn, will dissolve the enclosing sediments and as a result, the soluble cations (e.g. Ca^{2+}, Mg^{2+}...etc) will be concentrated within the pore waters. The presence of PO_4^{3-}, in turn, will react with Ca^{2+} and Mg^{2+} to form primarily the less stable mineral Staruvite ($PO_4(Mg)NH_4$).This transitory mineral is unstable under such conditions and, thus, the produced solutions are normally rich in Mg. The Mg ions will participate in the formation of more stable phases such as dolomite or high magnesian clays. The conditions will thus become favourable for the formation of apatite in the low magnesium pore waters (Prevot et al.1989).