# Mineralogical and Geochemical studies of Eocene Carbonate rocks at East El-Minia Governorate, Egypt.

Mahmoud A. El Ammawy<sup>1\*</sup>, Abdel Galil A. Hewaidy<sup>2</sup>, Bothaina M. Moussa<sup>1</sup>, Nabil A. Abd el Hafz<sup>2</sup> and El Sayed A. El Abd .

<sup>1</sup>Geology Department, Desert Research Center, Mathaf El Matariya Street, Cairo 11753, Egypt <sup>2</sup>Geology Department, Faculty of Science, Al Azhar University, Cairo 11651, Egypt \*Corresponding author's E-mail: elammawymahmoud@yahoo.com. Telephone No: 02-01017386993

Submitted date: 24/06/2022 Accepted date: 27/10/2023 Published online: 30/11/2023

#### Abstract

The present work is mainly concerned with the Mineralogical and geochemical studies on the Eocene rocks exposed at East El-Minia Ggovernorate. The study area is located on the eastern side of the Nile Valley between Maghagha City and Mallawi City. It is located between lat.  $27^{\circ}42'7''N$  and  $28^{\circ}41'30''N$  and long.  $30^{\circ}43'15''E$  and  $31^{\circ}30'E$ . The study areas, are represented by five formations namely; Minia (Lower Eocene), Samalut, Maghagha and Qarara (Middle Eocene) and El Fashn (Middle – Late Eocene) Formations. The mineral component shows that the Eocene carbonates were deposited in an alkaline environment that was close to a landmass that provided quartz and clay to the environment. Limestone chemical characters reveals that; Eocene limestones were mostly deposited under relatively warm alkaline conditions. However the pH degree of alkalinity during the Minia, Samalut and Maghagha formations (less in SiO<sub>2</sub> content) was higher than that prevailed during the El Fashn Formation times.

Keywords: Eocene, Minia, Samalut, Maghagha, Qarara, El Fashn.

#### 1. Introduction

Calcium carbonate (Limestone), as a sedimentary calcareous rock, mostly composed of calcite with some gangue minerals such as quartz, feldspar, iron oxides and mica. Limestones ore considered as a very important industrial mineral. The constituents of Limestone ore as a raw material for different industrial uses play a significant role in the cost effectiveness. The most significant constituents of limestones as above mentioned are calcium oxide (CaO), alumina ( $Al_2O_3$ ), iron oxide  $(Fe_2O_3)$ , magnesium (MgO), and silica  $(SiO_2)$ . Calcium carbonate (Limestone) rocks cover wide areas throughout Egypt map forming ridges and plateaus. Limestone purity was classified according to the weight percentage of CaCO<sub>3</sub>, CaO, MgO, SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. Deposits of limestone in the Nile Valley extent nearly from north to south along the Valley comprising five formations namely; Minia (Lower Eocene), Samalut, Maghagha and Oarara (Middle Eocene) and El Fashn (Middle – Late Eocene) Formations. The work here deals with the calcium carbonate mineral exploration for different industrial uses. The study area occupies eastern parts of the Nile bank at El Mania Governorate. It is located between lat. 27°42'7"N and 28°41'30"N and long. 30°43'15"E and 31°30'E (Fig. 1).

Limestone deposits, specifically calcium carbonate rocks, are widespread across Egypt, giving rise to extensive ridges and plateaus on the country's landscape. The Eocene succession in these areas has garnered the attention of numerous researchers over the years. Notable contributors to the study of this geological formation include Said (1960 & 1962), Bishay (1961 & 1966), Omara et al. (1977), Keheila (1978), Cronin and Khalifa. (1979), Strougo and Azab (1982), Boukhary and Abdallah (1982), Keheila (1983), Mansour and Philobbos (1983), Strougo (1986), Philobbos and Keheila (1991), Strougo and Azab (1991), Elewa (1994), AbdEl Tawab (1994), Tolba et al .(1999), El Ghar and Hussein (2005), Wahab et al. (2010), AbdEl Wahed (2013), Serry et al. (2015), Hegab et al (2015), Hegab et al .(2016), and Gaber (2017).

#### 1. Methodology

The current work aims to provide rapid

geochemical and mineral component studies of Eocene carbonate rocks in the research area. The samples were prepared and measured in the Egyptian Geologic Survey and the Nuclear Materials Authority in the following manner:

2.1 Fourteen specimens were chosen for examination, and an X-ray diffraction (XRD) analysis was conducted using a Phillips PW 3710 diffractometer, which utilized Ni-filter and Cu radiation. The analysis was performed under specific conditions, with X-ray emission set at 40KV and 55mA, at the Nuclear Materials Authority.

2.2 Eleven samples were selected for geochemical study to determine the major and trace elements. The major wet chemical analyses have been done following the methods of Shapiro and Brannock (1962). Three solutions were prepared from the powdered samples (200 mesh size). The first solution (acid mixture solution) was used to measure CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and Fe<sub>2</sub>O<sub>3</sub>. The second solution (fused by NaOH) was used to measure  $SiO_2$  and  $Al_2O_3$ . The third solution was used to measure  $SO_4$  and Cl. The  $SiO_2$ , Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> were measured using spectrophotometric techniques; the  $Fe_2O_3$ , CaO, MgO, SO<sub>4</sub> and Cl were measured using gravimetric techniques whereas the Na<sub>2</sub>O and K<sub>2</sub>O were measured using flame photometer technique. On the other hand, the trace elements Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Pb, Sr, Ga, V and Nb were measured using XRF technique (model Phillips X Unique II, PW1510 with automatic sample changer) using fused pellets. All the analyses were measured at the Egyptian Geologic Survey and the Nuclear Materials Authority.

# 3. Lithostratigraphy

The study area is primarily composed of Eocene rocks and Quaternary sediments (Fig. 2). The Eocene strata consist primarily of limestone and chalk, with occasional layers of sandy, cherty, and clayey limestones interspersed (Bishay, 1961, Ullah et al., 2023). The formation can be categorized into five primary units: Minia (Lower Eocene), Samalut, Maghagha, and Qarara (Middle Eocene), and El Fashn (Middle – Late Eocene) Formations (Said, 1962).

3.1 Minia Formation occupies southern portion of the study area. It consists of pale white, cavernous, fossiliferous, limestone rich in Nummulites and containing dolomitic nodules, followed upward by fossiliferous and coquina limestone. It attains an average thickness of 37 meters.

3.2 The Samalut Formation overlies conformably Minia Formation. It is formed of coquina, chalky, argillaceous, fossiliferous, Nummulitic limestones, which are pale white, pale grey, pinkish white, medium to hard, cavernous and containing dolomitic nodules (40cm diameter) in the lower part of the formation. It attains an average thickness of 72 meters.

3.3 Maghagha Formation; occupies the low lands to the north of the study area. It overlies Samalut Formation and it consists of creamy, yellow to pale white, hard, fractured argillaceous limestone in the lower and middle parts of the formation, following upward by brown calcareous clay and limestone. It attains an average thickness of 89.5 meters.

3.4 Qarara Formation overlies conformably Maghagha Formation. The Qarara Formation is considered as one of the thickest Middle Eocene sequence along the Eastern side of the Nile valley between Cairo and Minia. This formation is composed of claystone, shally claystone and calcareous siltstone at its base, going upward to marl and argillaceous limestone at the top. It attains an average thickness of 100 meters.

3.5 El Fashn Formation overlies conformably Qarara Formation. It is composed mainly of snow-white crystalline limestone and fossiliferous limestone ended by reworked limestone beds with chert nodules. It attains an average thickness of 58.5 meters.

# 4. Carbonate Mineralogical Composition

The x-ray diffraction analysis has garnered significant attention due to its prominent position in the fields of mineralogy and petrography. Chillingar and Bissell (1963) noted that x-ray diffraction analysis allowed for the distinction not only between formations of the same age, but also between carbonate rocks belonging to two different eras. This was demonstrated in (Figs 3, 4, 5, and 6).

The objective of this research is to investigate the discrepancies and distinctions in the mineral composition of various Eocene carbonate sediments within the examined regions and their implications for environmental interpretation. Analysis of the bulk limestone samples through X-ray diffraction revealed a prevalence of calcite as the primary carbonate mineral, alongside noncarbonate minerals like gypsum, halite, muscovite, and clays in varying quantities. The identification of these minerals was conducted according to the ASTM standards of 1960.

The X-ray diffraction analysis recorded at Minia Formation are characterized by calcite as a predominance mineral with gypsum, apatite, halite then pyrite, dolomite and kaolinite in the middle, and muscovite and illite in the upper part of the Formation. This mineral assemblage reflecting that the Minia Formation is deposited in an inner neritic marine environment with alkaline.

Samalut Formation x-ray diffraction analysis reveals the predominance of calcite then pyrite with muscovite, anhydrite and stevensite in the upper part of the formation. This mineral assemblage reflecting that Samalut Formation is deposited in a warm, reefal shallow neritic marine environment with relatively calm water conditions with alkaline. The X-ray diffractograms of the bulk samples of the Maghagha formation reveal the predominance of calcite then halite, pyrite and gypsum followed by predominance of chlorite then calcite and muscovite. Maghagha Formation is deposited in quiet water of weak short-lived currents of outer neritic zone in the marine environment. The fore-mentioned associations reveal the prevealing of marine condition followed upward by a regressive phase (presence of halite and clay mimerals).

The X-ray diffractograms of the bulk samples of El Fashn formation reveal the predominance of calcite with halite. This mineral association indicates deposition in an inner neritic marine environment with alkaline, normal salinity and calm water characters.



Fig. 1. Location and geological maps of the study area, After Conoco, 1987



Fig. 2. Columnar Lithic Log verus geochemical characters of the Eocene Formations recorded at the study area



Fig. 3. X-ray diffraction pattern of Early Eocene Carbonate bulk samples at Minia Formation.



Fig. 4. X-ray diffraction pattern of Middle Eocene Carbonate bulk samples at Samalut Formation



Fig. 5. X-ray diffraction pattern of Middle Eocene Carbonate bulk samples at Maghagha Formation.



Fig. 6. X-ray diffraction pattern of Late Eocene Carbonate bulk samples at El Fashn Formation.

# 5. Geochemical characterization of Limestone

In this study, the Early Eocene Minia Formation was represented by two limestone samples, while the Middle Eocene was examined through eight samples from the Samalut and Maghagha formations. Additionally, one sample from the late Eocene El Fashn Formation was included in the analysis. These samples were utilized to categorize the Eocene limestones under investigation, establish connections between facies variations, and gain insights into the distribution and prevalence of both major and trace components. Krauskopf (1979) proposed a definition of weathering as the process of approaching equilibrium in a system involving rocks, air, water, and the agents of chemical weathering, which include moisture, free oxygen, carbon dioxide, organic acids, and nitrogen acids. He further introduced a weathering index for comparing the degree of deterioration among different rock types. According to this index, as weathered material loses elements like calcium, magnesium, sodium, and potassium while gaining aluminum and iron, the index for that material will inevitably decrease.

Weathering index = 
$$\frac{\text{CaO} + \text{MgO} + \text{Na}_2 \text{ O} + \text{K}_2 \text{ O}}{\text{SiO}_2 + \text{Al}_2 \text{ O}_3 + \text{Fe}_2 \text{ O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2 \text{ O} + \text{K}_2 \text{ O}}$$

The weathering index for the Eocene carbonate sediments has been calculated and is presented in (Table 1). The weathering index values indicate a significant degree of weathering in all samples, showing that the examined rocks have been mildly impacted by weathering agents. Additionally, the clastic elements in the samples have a low content of  $SiO_{22}Al_2O_{32}$ , and  $Fe_2O_{32}$ .

Table 1	Weathering	index	values	of the	studied	Eocene	carbonates

Age	Formations	S. No.	Weathering index		
Early Eocene	Minia Fm.	M1	0.997677742		
		M5	0.993937233		
	Samalut Fm.	\$3	0.995895056		
		<b>S</b> 9	0.993431564		
		S11	0.994826048		
Middle Eocene		S15	0.992869875		
	Maghagha Fm.	Mg1	0.990215264		
		Mg9	0.995006242		
		Mg13	0.991631054		
		Mg17	0.996608354		
Late Eocene	El Fashn Fm	Gq18	0.989501779		

#### 6. Abundance and Distribution of Major Components

Tables (2) display the range and average composition of the key oxides in the various formations of the examined area. The behavior and distribution of the primary oxides in relation to lithology are illustrated in (Fig.2).

Age	Early l	Eocene		Late Eocene							
Formations	Minia	a Fm.	Samalut Fm.					Maghag	El Fashn Fm		
Sp. No. /oxides	M1	M5	S3	S9	S11	S15	Mg1	Mg9	Mg13	Mg17	Gq18
SiO <sub>2</sub>	0.11	0.28	0.19	0.33	0.23	0.28	0.45	0.23	0.39	0.16	0.51
TiO <sub>2</sub>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	0.01	0.04	0.02	0.02	0.03	0.04	0.05	0.02	0.04	0.01	0.04
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.02	0.02	0.02	0.03	0.08	0.05	0.03	0.04	0.02	0.04
CaO	55.8	55.65	55.73	55.89	55.7	55.61	55.46	55.66	55.5	55.74	55.47
MgO	0.03	0.07	0.05	0.05	0.05	0.07	0.18	0.11	0.14	0.07	0.12
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na <sub>2</sub> O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
K <sub>2</sub> O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
P <sub>2</sub> O <sub>5</sub>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cl	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
SO <sub>3</sub> -	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LOI	43.84	43.73	43.78	43.91	43.8	43.69	43.58	43.74	43.6	43.55	43.59
Total	99.87	99.86	99.86	100.3	99.85	99.84	99.84	99.86	99.8	99.62	99.84
K <sub>2</sub> O/Na <sub>2</sub> O	1	1	1	1	1	1	1	1	1	1	1
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	11.00	7.00	9.50	16.50	7.67	7.00	9.00	11.50	9.75	16.00	12.75
log SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.04	0.85	0.98	1.22	0.88	0.85	0.95	1.06	0.99	1.20	1.11
log Na <sub>2</sub> O/K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
log Fe <sub>2</sub> O <sub>3</sub> /K <sub>2</sub> O	0.00	0.30	0.30	0.30	0.48	0.90	0.70	0.48	0.00	0.30	0.60
Fe <sub>2</sub> O <sub>3</sub> +MgO	0.33	0.29	0.40	0.40	0.60	1.14	0.28	0.27	0.00	0.29	0.33

Table 2 Major oxides (XRF %) and some ratios of some representative samples

#### Silica

The Eocene limestone samples analyzed in this study exhibit notably low levels of silicate mineral oxides. Generally, a higher  $SiO_2$ concentration in limestone signifies the influence of terrigenous input during deposition, while a low  $SiO_2$  value suggests a deepening of the basin with limited delivery of terrigenous clastic sediment. The variation diagrams illustrating the relationship between  $SiO_2$  and CaO oxides for these limestones can be found in (Fig 7). The  $SiO_2$  concentration demonstrates a strong inverse correlation with CaO across all limestone categories, indicating a gradual reduction in detrital quartz and a subsequent increase in calcite content.

Corbel (1959) demonstrated an increase in  $SiO_2$  content in regions with warmer climates, while

Dekimpe et al. (1961) observed that higher pH levels corresponded to a decrease in silica content. Consequently, the Eocene limestones were predominantly deposited under relatively warm and alkaline conditions. However, the pH degree of alkalinity during the Minia and Samalut formations, characterized by lower  $SiO_2$  content, was higher than that which prevailed during the Maghagha and El Fashn formations.

#### Alumina

Aluminium is not normally substituted as a carbonate mineral. The measure of aluminum is directly linked with the influx of detrital sediments to the depositional site (Botz et al 1988). Buckley and Cranston (1991) inferred that the variations of  $Al_2O_3$  in sediments might be associated with changes in clay mineral content or with the content of feldspars in the sediment. The  $Al_2O_3$  vs CaO plot shows an inverse correlation limestone. As alumina is considered to be the detrital influence, the precipitation product of CaCO<sub>3</sub> must have been greatly reduced at the sites of terrigenous sediment deposition. (Fig. 8)

#### Sodium oxides

The reduced levels of Na<sub>2</sub>O in the limestone could be attributed to sporadic freshwater inflow into the deposition basin and an extended diagenesis process in an environment less saline than typical seawater. The limited presence of Na<sub>2</sub>O in these limestones may suggest they were initially formed from a solution with low Na<sub>2</sub>O concentration, as suggested by Land (1973), or it could indicate recrystallization of the limestone, as proposed by Kinsman (1969) (Fig. 9). Generally, sodium content diminishes significantly over time and with increasing levels of carbonate diagenesis. This phenomenon has most profoundly impacted ancient carbonates, and even recent carbonates have experienced changes in sodium content due to diagenetic alterations such as replacement and neomorphism, as noted by Veizer et al. in 1977. The concentrations indicate a noteworthy reduction in sodium across most of the samples compared to recent marine carbonate sediments, which typically have a higher overall sodium content, as reported by Land and Hoops in 1973.

#### Potassium oxides

Potassium levels are influenced by the initial chemical composition of the interstitial water and are subject to secondary enrichment during diagenesis, primarily through the process of carbonate neomorphism, as discussed by Morton in 1985. The carbonate minerals themselves contain only trace amounts of potassium. The potassium content is relatively stable and less affected by the diagenesis of carbonate minerals; however, it does decrease with prolonged diagenetic processes. The inverse relationship observed between K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> suggests that these limestones were not linked to detrital

compounds (Fig. 10).

### Iron oxides

The presence of iron in carbonate rocks can be attributed to two factors: a) Iron becoming incorporated within calcite during the precipitation of calcite in reducing conditions of diagenetic environments, and b) The result of the input and sedimentation rate of detrital material into the depositional environment (Brand, 1989). A small amount of iron may also substitute for Ca<sup>2+</sup> in calcite or for  $Mg^{2+}$  in magnesian calcite, resulting in ferroan calcite (Fe calcite). In the current study, the Fe2O3 values range from 0.01-0.08% for limestone. The low content indicates the depletion of iron in the pore fluid during the precipitation of calcite, which is caused by a decrease in the supply of detrital materials (Brand, 1989).

# Calcium Oxides

In his 1971 study, Kukal observed that the presence of natural salts and higher temperatures lead to a decrease in the solubility of CaCO<sub>3</sub>. Additionally, an increase in the concentration of Ca<sup>2+</sup> ions from other sources also contributes to the reduced solubility of  $CaCO_3$ . In the spatial distribution pattern, the higher concentrations of CaO are seen in all samples. the higher CaCO<sub>3</sub> content seems to be due to the fact that the depth of water during deposition of all formations was not deep enough to cause a great variation in temperature and to increase the solubility of CaCO<sub>3</sub> or the amounts of the argillaceous materials derived to the site of deposition were inconsiderable leading to the relative increase in the CaCO<sub>3</sub> at the expense of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents.

#### Magnesium oxides

Magnesium, originally deposited within the skeletons of living organisms, commonly remains within the rock throughout the process of lithification and uplift. The magnesium values, varying by the diagenetic equilibration of  $CaCO_3$  with meteoric water, depend on mineralogy and other factors causing either addition or depletion of magnesium (Morrisson and Brand 1988). The Mg values are very low, indicating the prevalence of less saline and/or freshwater diagenesis by which extensive leaching can take place (Wilkinson and Given 1986), possibly during later stages of diagenesis (Given et al., 1990).

Chave, (1954) suggested that there is a direct relation between the content of MgO and temperature. Chilingar, G.V (1963) stated that the MgO content increases with salinity but is simultaneously affected by so many other factors that it cannot serve as an adequate indicator" He also noted that in carbonate sediments the Ca/Mg ratio increases seawards

with depth.

Chilingar, et al. (1967) stated that "in as mush as shallow near -shore waters are systematically warmer as a rule than deep off -shore waters; the gross Ca/Mg ratio reflects temperature -depth- distance from shore". The computed Ca/Mg ratio for the studied Eocene limestone areas are as follows Table (3) and (Fig. 11), reflecting that Minia and Samalut formations more deeper and far from shore than Maghagha and El Fashn formations.

Table 3 CaO/MgO ratio in of the studied Eocene carbonates.

Age	Early	Eocene		Late Eocene							
Formations	Min	ia Fm.	Samalut Fm.					Magha	El Fashn Fm		
Sp. No. /oxides	M1	M5	S3	S9	S11	S15	Mg1	Mg9	Mg13	Mg17	Gq18
CaO	55.8	55.65	55.73	55.9	55.69	55.6	55.5	55.66	55.53	55.74	55.47
MgO	0.03	0.07	0.05	0.05	0.05	0.07	0.18	0.11	0.14	0.07	0.12
CaO/Mgo	1860	795	1115	1118	1114	794	308	506	396.64	796.29	462.25



Fig. 7. SiO<sub>2</sub> / CaO diagram of the studied rocks



Fig. 8. Al<sub>2</sub>O<sub>3</sub>versus CaO diagram of the studied rocks.



Fig. 9. Distribution curve of average CaO oxides and Na<sub>2</sub>O oxides of samples.



Fig. 10. Distribution curve of average Al2O3oxides and K2O oxides of samples.



Fig. 11. Variation of Ca/ Mg average ratio in the Eocene Carbonate rocks

# 7. Abundance and Distribution of Trace Elements

Stumm, Baccini, Nriagu, et al., and Galloway (1979) state that trace elements can originate from the weathering of rocks or be introduced into the hydrosphere through alternative mechanisms. Weathering can cause a particular trace element to dissolve. depending on the mineral it is found in and the extent of chemical weathering. The studies conducted by Kronberg et al. in 1979 and Harris & Adams in 1966. Adsorption is negligible at extremely low pH levels, while all cations are heavily adsorbed at high pH levels. James and Healy (1972b) conducted the study. Suarez and Longmuir (1976) found that copper (Cu), titanium (Ti), chromium (Cr), strontium (Sr), nickel (Ni), zinc (Zn), manganese (Mn), vanadium (V), barium (Ba), phosphorus (P),

and lead (Pb) in Pennsylvania soil were primarily present in manganese and iron oxide phases. Additional mechanisms that contribute to the distribution of elements in sediments include precipitation subsequent to oxidation or reduction, as described by Garrels and Christ (1965), as well as different interactions involving organic matter. Sholkovitz conducted research in 1967 and 1973.

Typically, the occurrence of trace element concentrations solely generated by sedimentary processes is uncommon. Krauskopf's work in 1979. The migration and deposition of elements in the Eocene carbonate sediments of the examined area result in varying abundance and behaviour for each element. This information can be found in (Tables 4 and Fig.12).

Age	Age Early			Late									
	Eocene												
Formations	Minia Fm.		Samalut Fm.					El Fashn					
									Fm				
Sp. No.	M1	M5	S3	S9	S11	S15	Mg1	Mg9	Mg13	Mg17	Gq18		
/elements										L C	-		
Cr	22	26	16	18	17	17	33	19	25	20	39		
Ni	8	10	15	7	13	12	18	16	14	10	15		
Cu	24	20	18	25	20	79	22	68	45	174	25		
Zn	18	18	25	23	23	88	20	78	25	188	30		
Zr	51	60	67	68	57	133	133	126	130	87	74		
Rb	7	12	10	4	9	7	5	9	13	10	6		
Y	u.d	3	2	2	2	2	5	2	4	2	3		
Ba	12	18	10	15	10	37	29	19	32	16	35		
Pb	u.d	u.d	u.d	2	u.d	4	3	4	u.d	10	u.d		
Sr	159	214	186	272	203	430	440	424	415	296	159		
Ga	8	12	13	u.d	29	2	2	6	9	5	4		
V	2	5	8	12	13	13	17	4	15	9	14		
Nb	u.d	u.d	u.d	u.d	u.d	u.d	u.d	u.d	u.d	u.d	u.d		
n.m= means not measured					u	u.d= means under detection limit which is 2 ppm							

Table 4 Trace elements (ppm) of some representative samples from section



Fig. 12. Trace elements varition diagram of the studied rocks in the study area.

Chow and Goldberg (1960) noted that the concentration of barium is influenced by pressure and temperature in the environment where it is deposited. The rise in barium concentration can be partially attributed to the generation of sulphate ions through biological processes. Kukal (1971) asserted that the correlation between strontium and barium, as well as their relationship to salinity, has been extensively debated. The Ba/Sr ratio of the analysed carbonate was calculated and depicted in (Fig. 13), as commonly accepted.



Fig. 13. Ba-Sr elements variation diagram of the studied rocks in the study area.

## Strontium

Typically, it is well accepted that the Sr concentration of a carbonate rock falls as the degree of modification by continental water increases. The average strontium concentration in ancient marine limestone ranges from 400 to 700 parts per million (ppm) (Bausch 1965).

The calcite that formed in balance with seawater contains an approximate concentration of thousands of parts per million of strontium (Kinsman 1969). In contemporary settings, the calcium carbonate varieties that precipitate directly from seawater and high-Mg calcite exhibit strontium (Sr) concentrations ranging from 400-1000 ppm (Land and Goreau 1970) to 5000 ppm, while aragonite typically contains an average Sr content of approximately 9800 ppm (Kinsman 1969). Brand and Veizer (1980) state that the final concentration of Sr in a carbonate rock, which has undergone diagenesis with meteoric waters, is influenced by various factors including the initial mineral composition of the carbonate, the ratio of water to rock, and the chemical composition of the infiltrating meteoric water. Therefore, the low concentration of Sr observed in this study suggests that diagenesis has influenced the formation of these limestones, whereas high Sr levels indicate minimal change. The Sr content in all limestone samples varies from 159 to 440 parts per million (ppm). Morrow and Mayers (1978) proposed that multiple instances of solutionreprecipitation can originate from early diagenesis. Nevertheless, they suggested that Sr values below 400 ppm are improbable to be attained during the initial diagenetic phase

Strontium is selectively retained in the solution, which initially has a strontium to calcite ratio that is equivalent to that of aragonite. Within a closed diagenetic system, the ratio of strontium to calcium in the solution increases as the process of dissolutionreprecipitation advances, and simultaneously, the ratio in the calcite also increases. Over time, the concentration of strontium to calcium in the solution increases to the point where the calcite being formed has the same ratio as the aragonite being dissolved. Conversely, in an open system, strontium has the potential to be released from the site of transformation, resulting in calcites that may have lower levels of strontium compared to calcites in closed systems (Pingitore 1978). The Sr concentration in marine carbonates diminishes progressively as modification intensifies.

## Barium

Barium concentration ranges from 10 to 37 ppm in limestones. Its content in marine limestones is lower (<60 ppm) but is higher in the fresh water limestone (Rao and Naqvi 1977). The Ba concentration of the samples in the study area is much lower (<60 ppm) concentration suggested for marine carbonates. The presence of high content of Ba is due to the presence of clay minerals which play a role in the distribution of Ba. The bulk of this barium is present either adsorbed on to detrital clay or as BaSo4 precipitated during diagenesis.

## 7. Conclusions

Based on the XRF and XRD investigations, it is evident that the calcite mineral is the most abundant mineral in the limestone ore. The results of this investigation can be succinctly described as follows:

1. The study area contains a significant outcrop of high purity CaCO3 (99.65%), making it suitable for mining and various industrial uses. They can be utilized in a variety of chemical plants, including paper, paint, and the manufacturing of lime, which is used for a variety of chemical purposes.

2. Most Minia Formation samples, as well as some Maghagha and Qarara Formation samples, are used in building.

3. Calcium carbonate is a good filler for paper pigment because it has a brightness reading that ranges from 91 to 93.5% and is ground into an incredibly fine powder with a particle size range of 2 to 10 m for use in the paper filler and coating industries. Gaber (2017).

4. Geotechnical studies carried out after Abed Tawab (1994) indicate that the area covered by the Samlut formation is unsuitable for use as a foundation or for building.

## Authors' Contribution

First Author Mahmoud El Ammawav. have finished the lab work and formal analysis, writing and revision in addition his contribution to the completion of fieldwork. Finishing the Manuscript and send it to the Journal for the publication. Abdel Galil A. Hewaidy, has wide contribution in validation and Visualization in addition review editing Bothaina M. Moussa, has made important contributions to review editing, visualization, and validation. Corporate authors proofread and conducted a technical evaluation of the document before to submission. Nabil A. Abd el Hafz has wide contribution in validation and Visualization in addition review editing. El Sayed A. El Abd, helps in field data collection and review/editing.

## Acknowledgement

The authors are grateful to the editor and two anonymous reviewers for their instructive comments and suggestions. We also thank the Desert Research Center, Egypt for providing logistical support for travel and fieldwork.

# **Conflict of Interest**

The authors declare that the current manuscript has no conflict of interest.

# 9. References

- Abd El-Wahed A.G.M. 2013, Sedimentology and assessment of the middle Eocene El-Minya clay deposits for ceramic industries on the light of their chemical, mineral and microstructure characteristics. Unpublished thesis, Department of Geology, Faculty of Science, Mansoura University, Egypt.
- Abdel Tawab, S. 1994. A Geotechnical Evaluation of Minia-Maghagha Area, Upper Egypt. Earth Sciences, 7(1).
- American Society of Testing Material (A.S.T.M.), 1960, Index to the powder diffraction file. A.S.T.M., special technical pub., (Alphabetical and grouped numerical index.).

- Bausch, W. M. 1968. Outlines of distribution of strontium in marine limestones. In Recent developments in carbonate sedimentology in Central Europe (pp. 106-115). Springer, Berlin, Heidelberg.
- Bishay, Y., 1961, Biostratigraphic study of the Eocene in the Eastern Desertb e t w e e n Samalut and Assiut by the large foraminifera". 3 rd Arab. Pet.C o n g r . Alexandria, 7 p
- Bishay, Y. 1966. Studies on the larger Foraminifera of the Eocene of the NileValley between Assiut, Cairo and SW Sinai. Ph. D. Thesis, Alexandria Univ.
- Boukhary, M. A., and Abdallah, A. Y. 1982. Stratigraphy and mi-crofacies of the Eocene limestones atBeni Hassan, Nile Valley, Egypt. N. Jb. Geol. Palaeont., Mh, 151-152.
- Botz, R., Stoffers, P., Faber, E., and Tietze, K. 1988. Isotope geochemistry of carbonate sediments from lake Kivu (East-Central Africa). Chemical Geology, 69(3-4), 299-308.
- Brand, U. 1989. Aragonite-calcite transformation based on Pennsylvanian molluscs. Geological Society of America Bulletin, 101(3), 377-390
- Brand, U., and Veizer, J. 1980. Chemical diagenesis of a multicomponent carbonate system; 1, Trace elements. Journal of Sedimentary Research, 50(4), 1219-1236.
- Buckley, D. E., and Cranston, R. E. 1991. The use of grain size information in marine geochemistry.Principles, Methods and Applications of particle size analysis, Syvitski, JM (Ed.), Cambridge Univ. Press, New York. Geol. Survey of Canada Contrib, 12689, 311-331
- Chave, K.E. 1954. Aspects of the biochemistry of magnesium calcareous sediments and rocks. Jour, Geol. Chicago V. 62, pp. 587-599.
- Chilingar, G. V. 1962: Dependence on temperature of Ca/Mg ratio of skeletal structures of organismsa n d d i r e c t precipitates out of sea water. Bull. S. Calif. Acad. Sci., V. 61, pp. 45–60.
- Chillingar, G.V. and Bissell, H.J. 1963. Is dolomite formation favoured by high or low pH?Sedimentology, V. 2, pp. 171-172
- Chilingar, G.V. and Fairbridge, R.W. Editors 1967. Carbonate rocks: Origin, occurrence

and classification. Elsevier Amsterdam, 471 p.

- Corbel J. 1959: Vitesse de l'erosion. Zeitschrf. Geomorphologie, N.F., Bd.3.pp. 1-28, Gottingen
- Cronin, T. M., and Khalifa, H. 1979. Middle and Late Eocene Ostracoda from Gebel El Mereir, Nile Valley, Egypt. Micropaleontology, 397411
- Dekimpe C.R. Gastuch, M .C. and Brindley, G.W. 1961. Ionic coordination in aluminasilicategels inrelation to clay mineral formation. Am. Mineral., v.460, pp. 1370-1381.
- Elewa, A. M., and Ishizaki, K. 1994. Ostracodes from Eocene rocks of the El Sheikh Fadl-Ras Gharib stretch, the Eastern Desert, Egypt. Earth Science (Chikyu Kagaku), 4 8 (2), 1 4 3 - 1 5 7.
- El Ghar, M. A., and Hussein, A. W. 2005. Postdepositional changes of the lower-middle Eocenelimestones of the area between Assiut and Minia, West of the Nile Valley, Egypt. In Proceedings of the first international conference on the geology of the Tethys (pp. 224 248). Cairo University Press.
- Gaber, M. W. 2017. Characterizations of El Minia limestone for manufacturing paper filler and coating.Egyptian Journal of Petroleum.
- Galloway, J. N. 1979. Alteration of trace metal geochemical cycles due to the marine discharge of wastewater. Geochimica et Cosmochimica Acta, 43(2), 207-218.
- Garrels, R. M., Christ, C. L., Solutions, M., and Equilibria, H. 1965. Row. New York, 46.
- Harris, R. C., and Adams, J. A. S. 1966. Geochemical and mineralogical studies on the abundances of the rare earths. Origin and Distributio of the Elements. New York, Pergamon, 889-912.
- Hegab, O. A., Serry, M. A., Anan, T. I., and El-Wahed, A. G. A. 2016. Facies analysis, glauconite distribution and sequence stratigraphy of the middle Eocene Qarara Formation, El-Minya area, Egypt. Egyptian Journal of Basic and Applied Sciences, 3(1), 71-84.
- Hegab, O. A., Serry, M. A., and El-Wahed, A. G. A. 2015. Mineralogy and geochemistry of the MiddleEocene(Lutetian) El-Minya clay, Egypt. Clay Science, 19(2), 23-37.

- James, R. O., and Healy, T. W. 1972. Adsorption of hydrolyzable metal ions at the oxide waterinterface. II. Charge reversal of SiO2 and TiO2 colloids by adsorbed Co (II), La (III), and Th (IV) as model systems. Journal of Colloid and Interface Science, 40(1), 53-64.
- Keheila, E. A. 1978. Geological studies on the area southeast of Minia (Doctoral dissertation, M. Sc. Thesis, Faculty of Science, Assiut University, Egypt).
- Keheila, E. A. 1983. Sedimentology and stratigraphy of the carbonate rocks in the area north of Assiut (Doctoral dissertation, Ph. D. Thesis, Assiut University. Google Scholar).
- Kinsman, D. J. 1969. Interpretation of Sr (super+ 2) concentrations in carbonate minerals and rocks. Journal of Sedimentary Research, 39(2), 486-508.
- Krauskopf, K.B. 1979. introduction to Geochemistry.Mc- Graw- Hill, New York, 617p.
- Kronberg, B. I., Fyfe, W. S., Leonardos Jr, O. H., and Santos, A. M. 1979. The chemistry of some Brazilian soils: element mobility during intense weathering. Chemical Geology, 24(3-4), 211-229
- Kukal, Z. 1971. Geology of recent sediments, Academie press London New York, 490p.
- Land, L. S., and Hoops, G. K. 1973. Sodium in carbonate sediments and rocks; a possible index to the salinity of diagenetic solutions. Journal of Sedimentary Research, 43 (3), 614-617
- Mansour, H. H., and Philobbos, E. R. 1983. Lithostratigraphic classification of the surface Eocenecarbonates oft h e N i l e Valley, Egypt: A review. Bull. Fac. Sci. Assiut Uni, 12(2), 129-151.
- Morrison, J. O., and Brand, U. 1988. An evaluation of diagenesis and chemostratigraphy of Upper Cretaceous molluscs from the Canadian Interior Seaway. Chemical Geology: Isotope Geoscience section, 72(3),235-248
- Morrow, D. W., and Mayers, I. R. 1978. Simulation of limestone diagenesis a model based on strontiumd e p l e t i o n . Canadian Journal of Earth Sciences, 15(3), 376-396.
- Morton, A. C. 1985. Heavy minerals in provenance studies. In Provenance of

arenites (pp. 249-277). Springer, Dordrecht.

- Nriagu, J. O., Kemp, A. L. W., Wong, H. K. T., and Harper, N. 1979. Sedimentary record of heavy metal pollution in Lake Erie. Geochimica et Cosmochimica Acta, 43(2), 247-258.
- Omara, S., Mansour, H. H., Youssef, M., and Khalifa, H. 1977. Stratigraphy, paleoenvironment and structural features of the area east of Beni Mazar, Upper Egypt. Bulletin of Faculty of Science, Assiut University, 6(3), 171-197.
- Philobbos, E. R., and Keheila, E. A. 1991. Development of regressive transgressive facies of the LowerMiddleEocene in the area, NE of Assiut, Eastern Desert, Egypt. Annal. Geol. Surv., Egypt, 17, 153-171.
- Pingitore, N. E. 1978. The behavior of Zn 2+ and Mn 2+ during carbonate diagenesis; theory and applications. Journal of Sedimentary Research, 48(3), 799-814.
- Said, R. 1960. Planktonic foraminifera from the Thebes formation, Luxor, Egypt. Micropaleontology,6(3), 277 286.
- Said, R., 1962, The Geology of Egypt: El Sevier, 377 p.
- Serry, M. A., Hegab, O. A., and El-Wahed, A. G. A. 2015. Egyptian Smectite-rich clays for lightweight and heavy clay products. Periodico di Mineralogia, 84(2), 351-371.
- Shapiro, L. M., and Brannock, W. W. 1962. Rapid analysis of silicate, carbonate and phosphate rocks (No. 1144). US Government Printing Office
- Sholkovitz, E. 1973. Interstitial water chemistry of the Santa Barbara Basin sediments. Geochimica etCosmochimica Acta, 37(9), 2043-2073
- Sholkovitz, E. R. 1976. Flocculation of dissolved organic and inorganicm at t e r during the mixing of river water and seawater. Geochimica et Cosmochimica Acta, 40(7), 831-845.
- Strougo, A. 1986. Mokattamian stratigraphy of eastern Maghagha-El-Fashn district. Mid. East Res. Cent. Ain Shams Univ., Sci. Res. Ser, 6, 3358.
- Strougo, A., and Azab, M. M. 1982. Middle Eocene Mollusca from the basal beds of Gebel Qarara (UpperEgypt), with remarks on the depositional environments of these beds. Neues Jahrbuch für Geologie und

Paläontologie Monatshefte, 11, 667-678.

- Strougo, A., and Azab, M. M. 1991. Bivalve molluscs from a lower Mokattamian (Middle Eocene) shellbed at the base of the Midawara Formation of Gebel el Mehasham, Magahaga area. Middle East Research Center Ain Shams University Earth Science Series, 5, 95119
- Stumm, W., and Baccini, P. 1978. Man-made chemical perturbation of lakes. In Lakes (pp. 91-126).Springer, NewYork, NY
- Suarez, D. L. and D. Longmuir 1976. Heavy metal relationships in Pennsylvania Soil. Geochim.Cosmochim.Acta, 40, pp. 589-598.
- Tolba, A. M., Hassan A. S., Hassan H. M., Farnry B. and Esmat A. k. 1999. stratigraphical and sedimentological evolution of the Eocene sequence on the eastern side of the Nile River between Minia and Ben-Suef. Unpublished thesis, Department of Geology, Faculty of Science, Assiut University, Egypt.
- Ullah, S., Hanif, M., Radwan, A. E., Luo, C., Rehman, N. U., Ahmad, S., & Ashraf, U. 2023. Depositional and diagenetic modeling of the Margala Hill Limestone, Hazara area (Pakistan): Implications for reservoir characterization using outcrop analogues. Geoenergy Science and Engineering, 224, 211584.
- Veizer, J., Compston, W., Clauer, N., and Schidlowski, M. (983. 87Sr86Sr in Late Proterozoic carbonates: evidence for a "mantle" event at~ 900 Ma ago. Geochimica et Cosmochimica Acta, 47(2),295-302.
- Veizer, J., Hoefs, J., Lowe, D. R., and Thurston, P. C. 1989. Geochemistry of Precambrian carbonates:II. Archean greenstone belts and Archean sea water. Geochimica et Cosmochimica Acta, 53(4),859-871.
- Wahab, M. A., Rasheed, M. A., and Youssef, R.
  A. 2010. Degradation hazard assessment of some soilsnorth Nile Delta, Egypt.
  Journal of American Science, 6(6), 156-161.
- Wilkinson, B. H., and Given, R. K. 1986.Secular variation in abiotic marine carbonates: constraints on Phanerozoic atmospheric carbon dioxide contents and oceanic Mg/Ca ratios. The Journal of Geology, 94(3), 321-33