Research Article



A Review of the Carbonate Facies of the Ewekoro Formation, Nigeria: Its Origin, Diagenesis and Classification

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Abstract: Petrographic and elemental weight analyses have been found useful in the assessment of origin and paleo-conditions of sedimentary systems. In this present study, geochemical assessment of EwekoroLimestones were carried out using their elemental oxides weight percentages. A deduction of the paleoenvironment of deposition has also been carried out using an integrated approach involving microscopic studies and trace element concentrations. The samples were analysed using X-Ray Fluorescence (XRF) method. Results show that the limestone have a mean composition of major oxides in this order; CaO (49.67 wt. %), SiO₂ (4.86 wt. %), Al₂O₂ (2.54 wt. %), Fe₂O₂ (1.34 wt. %), MgO (0.88 wt. %), K₂O (0.25 wt. %), TiO₂ (0.11 wt. %) and MnO (0.01 wt. %). For this study, the increase in silica (SiO₂) content with magnesium oxide (MgO) and calcium oxide (CaO) indicates the introduction of arenaceous materials. Petrographic analysis revealed four (4) major components which are fossils, peloid, ooids and quartz. An assessment of the proportions of microscopic components shows that the limestone samples are mostly matrix-supported but with > 10% clast. Hence, most were classified as peloidalwackestones. Bioclastpackstone also occur within the formation. The trace elements were useful in deducing ancient environment of formation. Strontium (Sr) concentration ranged from 22 - 37 ppm with a mean value of 32 ppm while the manganese (Mn) concentration ranged from 129 ppm to 252 ppm with a mean value of 187 ppm. These ranges of values, together with the fine-grained carbonate materials suggest a shallow water carbonate. The Ca/Mg percentage weight ration indicated a calcitic limestone category.

Keywords: XRF, Ewekoro, Geochemical, bioclast, Depositional Environment.

INTRODUCTION

Limestone studies conducted by Jones and Hockey (1964) in the Ewekoro Formation of the Dahomey Basin were the first of its kind. At this time, sedimentological information were derived. Adegoke et al (1971) and Ogbe (1972) went further for paleontological studies after which the following facies were proposed from the limestone units; red phosphaticbiomicrite, algal biosparite, shelly biomicrite and sandy biomicrite.

The interest on the rock unit was because it is one of the few carbonate rocks occurring in Nigeria. Carbonate rocks form approximately 15% of the earth's sedimentary crust and their derived products are useful as aggregrates, glass raw material, reactive agents in sulphur oxide removal and in a variety of economic uses.

The importance of geochemical investigation cannot be overlooked as it helps to determine and measure the extent to which two variables are related. Moreover, this relationship helps in the classification of the limestone. Despite alterations that may have occurred post-diagenetically, the elemental concentrations may also serve as a tool for the interpretation of depositional environment (Ofulume, 2012).

In this study, a microscopic study of the carbonate facies has been employed. This allows for a study of its components for a proper typing. Furthermore, we have applied the use of geochemical information to determine the category of limestone and the changes that may have occurred during precipitation. A reconstruction of the environment of deposition has also been carried out.

Location of Study Area and Geology

The study areas lie within the Shagamu and Ewekoro quarry sites of West African Portland Cement Company (WAPCO), a subsidiary of LAFARGE. The area constitutes part of the eastern Dahomey basin and lies within latitudes 6⁰ 48'and 6⁰ 56'N and longitudes 3⁰ 13'E and 3⁰ 38'E (Figure 1).

The rock units of the study area have been recorded to lie within the Ewekoro Depression of south-western Nigeria which occupies a low lying marshy depression within the Dahomey Basin (Jones and Hockey, 1964). The depression is bounded in the south by the low, gently sloping dissected escarpment of the southern upland plateau. Plateau-like features attaining a maximum height of about 122 m near Ilaro have been discovered in the northern part of the basin.

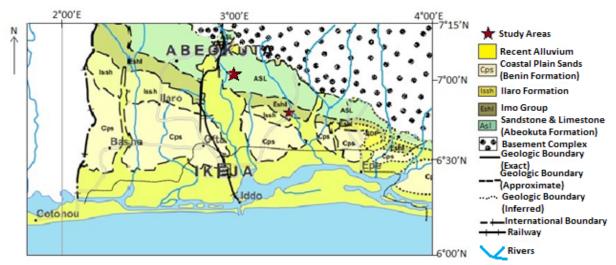


Fig1. Geologic map and location of study area

In most parts of the basin, monotonous sand and shale alternations with only minor proportions of limestone and clays dominate the stratigraphy (Adegoke, 1977). General rock formations by different workers is shown in figure 1. The Ewekoro Formation is regarded as the rock unit lying above the Cretaceous strata of the eastern Dahomey basin. The formation consists of limestone which is glauconitic in some places. It is traceable over a distance of 320 km continually from Ghana to the Eastern margin of Dahomey basin in Nigeria. It is the broadest and most extensive carbonate deposit in South Western Nigeria. It finally becomes finer grained, grading into the dominantly shaleyAraromi formation, which pinches out against the western flank of Okitipupa ridge (Adegoke, 1977).

The lithologies exposed at the Shagamu quarry is made up of limestone, shale, marl and the usual lateritic top soil. The lithology at the Shagamu quarry site is mainly of three (3) sections namely the Lagos end, the Main phase and the Sagamu end. The reason why the quarry is divided into phases is because of the heterogeneous nature of the limestone in this area. At the Ewekoro quarry, the lithologies exposed is made up of light brown sandy bed, limestone and siltstone. The samples are all of varying colours.

METHODS OF FIELD AND LABORATORY STUDIES

Field Studies

Field study involved the collection of eight (8) samples from the Shagamu quarry and ten (10) samples from the Ewekoro quarry, all belonging to the West African Portland Cement Company. All the samples were given

identification number based on the spot from which they were picked. The limestone is generally fossiliferous. The colours possessed by the rocks ranged from brownish to light and dark grey (Figures 2-4).

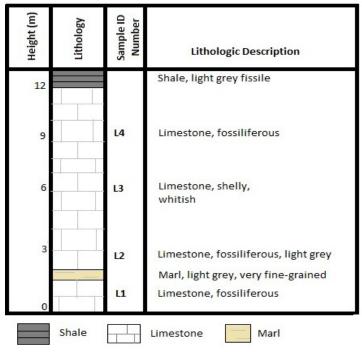


Fig2. Lithostratigraphic log from the Lagos end of the Shagamu quarry

Figure 4 shows the lower shelly limestone bed grading upward to a brown, light and brittle limestone bed and of course the overburden. The next figure 5 is a photo image of the location where mining is currently taking place at the Ewekoro quarry.

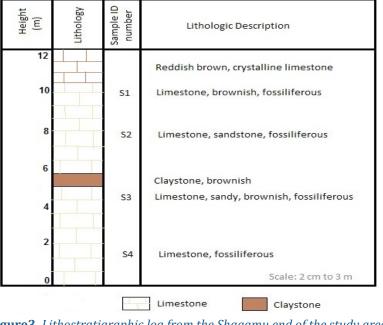


Figure3. Lithostratigraphic log from the Shagamu end of the study area



Fig4. Photo-image of representative outcrop of the Ewekoro Formation as exposed at the Ewekoro Quarry.



Fig5. Photo-image of quarrying activities at the Ewekoro quarry.

Laboratory Analysis

The samples were, thereafter, taken for laboratory analysis where they were first of all crushed into smaller units with the use of a rubber hammer. Iron hammer was avoided to prevent the introduction of iron into the samples.For the samples taken at the Shagamu quarry, the already prepared pellets were introduced into the X-Ray Fluorescence (XRF) analysis chamber at the XRF Laboratory of the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife.

For those sampled at the Ewekoro quarry, Energy Dispersive X-ray fluorescence (EDXRF) spectrometer of model "Minipal 4" was used for the analysisat the Quality Control Department of Lafarge Cement Factory Ewekoro, Ogun state.

The weighing balance, crusher, ethylene glycol (Pills), milling machine, sample rings and pressing machine were theapparatus used for the sample preparation before geochemical analysis. In the X-Ray Fluorescence analysis (XRF) field, it may fairly be said that sample preparation can be the largest factor that cause analysis error. When more precise analysis is required, it is recommended to analyze the sample after pulverization to eliminate the grain size effect and segregation as much as possible.

The following condition sets were made as the machine was switched on:

- I. Elemental composition determination
- II. Nature of the samples to analyzed as press powder (pellet)
- III. The current used as 14kv for major oxides, 20kv for the trace elements/rare earth metals.
- IV. Selected filters were "kapton" for major oxides, Ag/Al-thin for the trace elements/rare earth metals.

The selection of filters was guided by a given periodic table used for elemental analysis. Time of measurement for each sample was 100 seconds and the medium used was AIR throughout, when the sample is placed on the normal position on the sampler changer on the XRF machine, it was acted upon by an electromagnetic radiation and become excited by an external energy source, the sample will emit X-ray photons of a characteristics energy or wave length. By counting the number of photons of each energy emitted from a sample, the element present may be identified and quantitated. The X-ray obeys the laws of electromagnetic radiation which states that a body surface can absorb incident radiation and reflect the incident radiation as a mirror with spherical symmetry which can transmit incident radiation and emit the radiations. The machine was then controlled by the machine's gain control, after which each respective sample was measured by clicking the respective positions of the sample changer.

Thin Section Preparation

The thin section analysis method involves, foremost, thin section preparation and polished section preparation as well as the calculation of the modal analysis of limestone rock unit. Thin section analysis was carried out at the Geology Laboratory of the Federal University of Technology, Akure (F.U.T.A).

Ten samples were selected for petrographic analysis. For proper identification of the materials constituents, the samples were made into thin sections. In the preparation of thin section of the samples the following materials and equipment were used; rock cutter, lapping machine, grinding machine, hot plate, araldite, silicon carbide (carborundum), Canada balsam, cover slide, glass plate, mountain needle and methylated spirit. Steps taken in the preparation of petrographic thin section including;cutting, trimming, lapping, mounting, re-lapping, covering, washing and labeling.

Microscopic studies involved determining the average mineral composition under plain polarized light (PPL) and crossed nicols (CN) at a magnification of ×40. Minerals like biotite and hornblende were observed under PPL. Under CN, minerals like quartz, plagioclase, microcline and orthoclase were observed.

RESULTS AND DISCUSSIONS

Results of geochemical analysis of the limestone samples are shown in table 1. The trend and the relationships of the elemental oxide parameters have been studies using scatter plots. The percentage correlation of the elemental oxides have also been illustrated in a pie chart (Figure 6). The calcium oxide content ranges between 38.69 and 63.13 wt. % with an overall mean of 49.67%, while the magnesium oxide content ranges from 0.15 to 1.65 wt. % with an overall mean of 0.88%.

Elemental Oxides Correlation

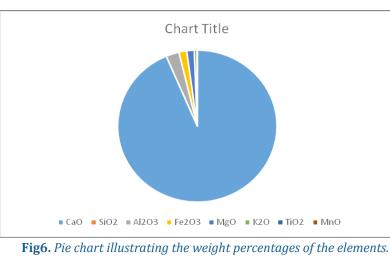
The oxides that are highly associated are identified more clearly by the mutual correlation between them. Those with a negative correlation (y = -mx + c) indicate that an increase in one of the variables will result in a decrease in the other while positive correlation (y = mx + c) implies that an increase in one variable will lead to an increase in the other.

CaO – Fe2O3

The concentration of CaO (Calcium Oxide) versus Fe_2O_3 (iron oxide) shows a negative correlation (Fig 7). This indicate that the proportion of CaO increases with a subsequent leaching of iron oxide.

SECTION	SAMPLE NO	CaOwt%	K ₂ O	TiO ₂	MnOwt%	Fe ₂ 0 ₃	Al ₂ O ₃ wt%	MgOwt%	SiO ₂ wt%
SAGAMU END	S1	60.31	0.35	0.02	0.02	1.02	1.72	0.99	0.00
OF THE SHAGAMU	S2	58.94	0.28	0.02	0.02	0.00	1.23	0.89	0.51
QUARRY	S3	59.19	0.35	0.02	0.02	0.78	2.44	0.57	1.03
· ·	S4	63.14	0.38	0.02	0.02	0.16	0.47	0.75	0.67
	MEAN	60.40	0.34	0.02	0.02	0.49	1.47	0.80	0.55
LAGOS END OF	L1	51.94	0.34	0.02	0.03	1.19	1.24	0.45	0.00
THE SHAGAMU	L2	47.71	0.27	0.03	0.03	0.54	0.84	0.45	0.00
QUARRY	L3	47.74	0.24	0.03	0.03	1.26	3.40	0.71	0.86
	L4	44.91	0.26	0.02	0.03	0.16	0.51	0.55	0.00
	MEAN	48.08	0.28	0.03	0.03	0.79	1.50	0.54	0.22
	E1	45.66	0.19	0.19	0.00	2.59	3.49	1.23	8.56
	E2	49.67	0.08	0.10	0.00	0.96	2.05	0.84	5.02
	E3	46.69	0.15	0.30	0.00	2.42	3.33	1.49	7.86
	E4	51.13	0.04	0.13	0.00	1.05	1.33	0.79	2.90
	E5	45.03	0.26	0.29	0.00	2.44	3.85	1.65	9.21
EWEKORO	E6	39.03	0.30	0.20	0.00	2.99	5.53	1.47	13.25
	E7	44.68	0.09	0.08	0.00	1.51	3.80	0.79	9.77
	E8	38.69	0.73	0.35	0.00	2.41	6.62	0.92	17.17
	E9	49.61	0.07	0.04	0.00	1.46	2.17	0.54	5.48
	E10	49.92	0.09	0.08	0.00	1.19	1.67	0.67	5.19
	MEAN	46.01	0.23	0.18	0.00	1.90	3.38	1.04	7.92





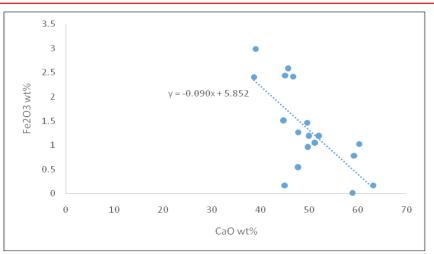


Fig7. Scatter plot of CaOversus Fe2O3showing the mutual relationship between them

SiO2-MgO-CaO

An obvious relationship exists between Silica (SiO_2) and magnesium oxide (MgO) as shown in their concentration (Fig. 8). The dependence between them is as a result of the influx of arenaceous and foreign particles. The remarkable positive correlation (Figure 9) existing between MgO and CaO, especially in Shagamu section, has been as a result of re-precipitation of calcium and introduction of magnesium-rich Textularia (Foraminifera) and also Echinoderms whose agglutinated tests and ossicles have been constructed from foreign particles (See plates and appendix for fossil occurrences). According to Boggs (2009), echinoderms are composed of high-magnesian calcite and foraminifera are composed of low- to high-magnesian calcite. The positive correlation between SiO₂ and CaO (Fig 10a) also shows that the silica found in this carbonate rock abound in some sections, acting as the nuclei for the coated carbonate grains. In the Ewekoro section (Figure 10b), an increase in SiO₂ depicts a decrease in calcium oxide and vice-versa. It should be noted that Akinmosun*et al.* (2005) indicated that the Ewekoro Limestone belong to the class of grainstone, as a result of this.

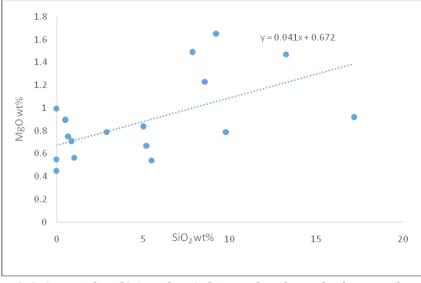


Fig8. Scatter plot of SiO2 and MgO showing the relationship between them

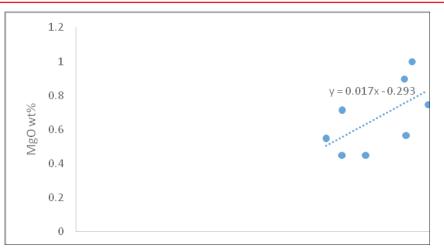
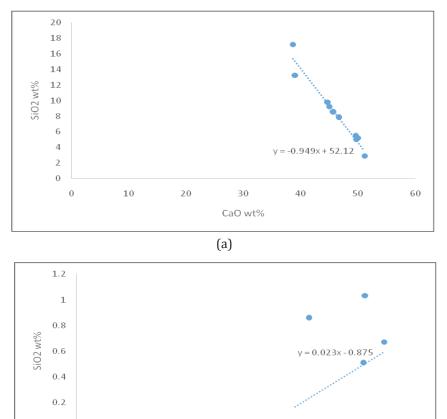


Fig9. Scatter plot of MgO and CaO showing the mutual relationship between them

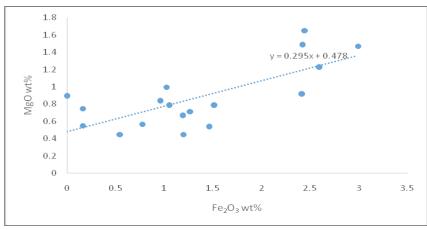


0 10 20 30 40 50 60 70 CaO wt%

Fig10. Scatter plots of SiO2 and CaO within the Shagamu (a) and Ewekoro (b) quarries showing the mutual correlation between them

Fe2o3 – Mgo

The positive correlation between Fe_2O_3 and MgO reveals that the iron oxide present formed during carbonate diagenesis. Even at that, there is an increasing state of oxidation as most samples show concentration greater than 1.0 %. This is responsible for the brownish state observed in some parts of the Shagamu end. This is even more pronounced within the outcrop exposed at Ewekoro quarry as the colour depicts light to yellowish brown. Nevertheless, this does not affect the purity as the clay content is negligible.





Geochemical Classification

Various classification schemes have been proposed for carbonate rocks (Todd, 1966, Neendorf et al, 2005) which involve the usage of ratios of percentage weights of calcium and magnesium, and the mineral composition of their oxides. These led to different kinds of limestones such as calcitic limestone (High calcium limestone and Magnesian limestone) and dolomitic limestone. Ca/Mg, Mg/Ca and CaO/MgO ratios have been used in this study to classify the Ewekoro Limestone (Table 2). The data from the present study indicates that the limestone from Ewekoro Formation falls within the high calcium/pure limestone and magnesian limestone category, with the majority falling in the range of pure limestone that is, Ca/Mg ratio range of 100 – 39 and Mg/Ca ratio range of 0.003 – 0.03 (Todd, 1966).

Paleo-Salinity Condition

According to Marshner (1968), standard Ca/Mg ratio and its reciprocal Mg/Ca are useful in the deduction of paleo-salinity conditions as at the time a carbonate rock was deposited. A high Ca/Mg ratio indicate less evaporation of sea water and low paleo-salinity condition. 83% of the samples are classified as a high calcium and pure limestone as indicated from the higher ratio range. Considering this and its reciprocal ratio, it can be concluded for the Ewekoro limestone that there was a low salinity condition and sea water evaporation resulting in the deposition of a bulk of the pure limestones.

Sample Number	Ca/Mg wt% ratio	Mg/Ca wt% ratio	CaO/MgO	Remarks
S1	71.83	0.01	66.6	High Calcium/Pure Limestone (After Todd, 1966)
S2	78	0.01	65.74	High Calcium/Pure Limestone (After Todd, 1966)
S 3	124.4	0.08	104.94	High Calcium Limestone (Neendorf et al, 2005)
S4	100	0.01	84.63	Pure Limestone (Todd, 1966)

Table2. Geochemical classification of Samples from Shagamu Quarry of Ewekoro Formation

L1	137	0.07	115.93	High Calcium Limestone (Neendorf et al, 2005)
L2	126.3	0.08	106.5	High Calcium Limestone (Neendorf et al, 2005)
L3	79.35	0.01	66.96	Pure Limestone (Todd, 1966)
L4	97.27	0.01	82.11	Pure Limestone (Todd, 1966)
E1	44.09	0.02	37.12	Pure Limestone (Todd, 1966)
E2	69.61	0.01	59.13	Pure Limestone
E3	37.08	0.03	31.35	Magnesian/Pure Limestone
E4	76.12	0.01	64.72	Pure Limestone
E5	32.34	0.03	27.29	Magnesian
E6	31.34	0.03	26.55	Magnesian
E7	66.52	0.02	56.56	Pure Limestone
E8	50.27	0.02	37.77	Pure Limestone
E9	107.45	0.009	49.07	Pure Limestone
E10	89.2	0.01	74.50	Pure Limestone

Interpretation of Trace Element Analysis

Table three (3) shows the concentrations of Mn, Sr, Se, Zr, Cr and Ni in ppm. Trace element concentration of carbonate rocks give important information on their origin, diagenesis and paleoenvironmental settings (Wedepohl, 1970; Tucker, 1973). Trace element data have been useful in differentiation of shallow marine limestones from deeper marine limestones using their manganese (Mn) and strontium (Sr) contents. These trace elements are linked with the carbonate phase.

The Mn concentrations (ppm) in this study range from 129 ppm to 252 ppm, with a mean value of 187 ppm indicating a low Mn value. This value is expected of a shallow water carbonate. Mn values ranging between 300 ppm and 4400 ppm have been reported for deep sea carbonate sediments (Thompson, 1972). The Sr content in this work ranges from 22 to 37 ppm. The low range of strontium (Sr) concentration for this study may indicate the formation of the limestone under low salinity. The depletion of Sr in carbonate rocks has been linked with low water salinity (Wolf et al., 1967) and hence a relatively shallower environment.

Sample No	Mn	Sr	Se	Zr	Cr	Ni
S1	132	36	22	122	5.3	58
S2	129	37	22	121	5.1	51
S 3	141	36	22	123	4.7	56
S4	135	34	22	120	4.9	58
L1	234	32	20	117	6.7	41
L2	241	33	25	119	6	57
L3	252	26	21	102	4	46
L4	231	22	17	93	6.4	35

Table3. Trace elements concentrations (ppm) of Ewekoro Limestone (Shagamu Quarry)

Petrographic Analysis

Assessment of the proportions of carbonate mud and larger fragments provides an indication of the environment of deposition: A high proportion of fine-grained carbonate material suggest a relatively low-energy setting, whereas an absence of mud characterizes higher-energy environments. Higher concentration of ooids is also observable, indicating a shallow, wave-dominated coastal setting.

Plate 2 shows the presence of brachiopods with their foliated bioclasts. Degree to which shelly materials are broken up also reflects the amount of transport and re-working of sediments. In plate 3, grains consists of more originally separated particles that have been bound and cemented together forming sub-rounded to

rounded lumps. Fine-grained carbonate particles (micrite) abound in plate 4. Here, their formation resulted from partial dissolution and recrystallization. Moreover, micritization could also be constructive or destructive. A constructive development could arise from organisms that lived on or attached to the rocks while destructive micritization is related to the activities of microboring organisms (Boggs, 2009).

Larger grain-sized clasts occur in plates 6 and 7. The surrounding micrite and ooids constitute the matrix. These may have been transformed and recrystallized resulting in an increase in size. Hence, the birefringence colour of the limestone being bluish red and green under cross-polars.

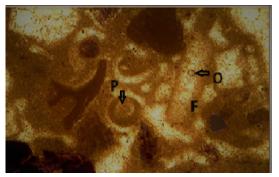


Plate1. *Photomicrograph showing cementation within the wackestone resulting in calcite cement filling (mag x40)*

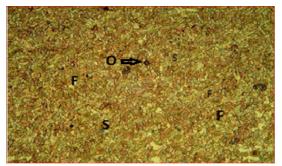


Plate3. Photomicrograph showing microgranularbioclasts from reworked foraminifera tests (mag x40)



Plate5. Photomicrograph (in cross nicol) showing cementation within the wackestone resulting in calcite cement filling (mag x40)

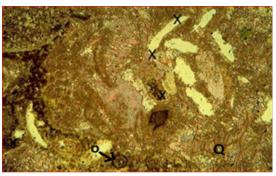


Plate2. Photomicrograph showing micrite within fossil chambers (mag ×40)

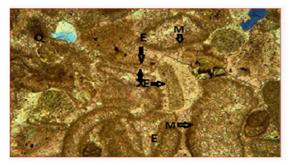


Plate4. Photomicrograph of micrite envelopes which developed around echinoderms and other fossil fragments (mag x40) Rock: grain-supported packstone

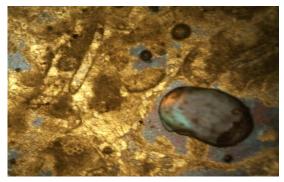


Plate 6. Photomicrograph showing (in crosspolars) larger grain-sized clasts developed within peloidalwackestone (mag x40)



Plate7. Photomicrograph showing larger grain-sized clasts surrounded by peloids and micritedeveloped within peloidalwackestone (mag x40)

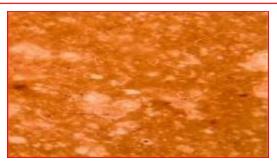


Plate8. *Photomicrograph indicating a matrixsupported limestone (mag x40)*

X – Brachiopods; M – Micrite; F or S – Fossil fragments; Q – Quartz; P – Peloids; E – Echinoderms skeletal grains

CONCLUSION

Limestone samples from the Ewekoro and Shagamu Quarries of the Ewekoro Formation is successfully classified, geochemically, as a high calcium limestone. This was based on their elemental oxide ratio and their ranges of values. Of a great importance, is the relationship between calcium oxide and magnesium oxide which describes the influence of foreign and arenaceous particles on the geochemistry of Ewekoro Limestone. Petrographically and within the framework of this study, majority of the limestone has been classified as PeloidalWackestone and bio-clast packstone.

Iron oxides as non-carbonate materials within the limestone samples were formed during carbonate diagenesis. On the other hand, depletion of Sr and values derived from Ca/Mg ratio in the carbonate rocks of Ewekoro Formation show a linkage with a low rate of evaporation of sea water and less salinity at the time of deposition of this calcitic limestone.

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APPENDIX

Minerals / View 1

Minerals/ View	1	2	3	Total	Percentage
Brachiopoda grains	4	5	5	14	16.1
Other Fossils	16	6	10	32	36.8
Ooids	4	6	5	15	17.2
Quartz	9	11	6	26	29.8
Total				87	99.9

Table A.2. Modal Analysis of sample E2

Minerals/ View	1	2	3	Total	Percentage
Brachiopoda grains	5	12	8	25	25.3
Fossils	4	4	6	14	14.1
Ooids	10	13	12	35	35.3
Quartz	10	10	5	25	25.2
Total				99	99.9

Table A.3. Modal Analysis of sample E3

Minerals/ View	1	2	3	Total	Percentage
Foraminifera grains	5	10	8	23	27.8
Other Fossils	3	4	6	13	13.4
Ooids	9	9	11	29	39.2
Quartz	9	9	6	24	19.5
Total				89	99.9

Table A.4. Modal Analysis of sample E4

Minerals/ View	1	2	3	Total	Percentage
Foraminifera grains	7	12	8	27	27.8
Fossils	3	4	6	13	13.4
Ooids	13	13	12	38	39.2
Quartz	7	9	4	20	19.5
Total				98	99.9

Table A.5. Modal Analysis of sample E5

Minerals/ View	1	2	3	Total	Percentage
Fossil	4	5	5	14	17.3
Quartz	8	6	6	20	31.6
Peloids	4	6	4	14	15.3
echinoderm skeletal grain	8	10	8	26	26.5
Total				78	99.9

Table A.6. Modal Analysis of sample E6

Minerals/ View	1	2	3	Total	Percentage
fossil	4	6	8	18	17.3
Quartz	10	8	11	29	31.6
Peloids	6	6	5	17	15.3
echinoderm skeletal grain	7	9	8	24	26.5
Total				88	99.9

Table A.7. Modal Analysis of sample E7

Minerals/ View	1	2	3	Total	Percentage
fossil	3	6	7	16	18.6
Quartz	12	8	10	30	34.7
Peloids	4	6	5	15	17.5
echinoderm skeletal grain	8	10	7	25	29.1
Total				86	99.9

Table A.8. Modal Analysis of sample E8

Minerals/ View	1	2	3	Total	Percentage
Fossil	5	6	6	17	18.9
Quartz	12	8	11	31	34.4
Peloids	4	7	5	16	17.7
ecinoderm skeletal grain	7	10	9	26	28.9
Total				90	99.9

Table A.9. Modal Analysis of sample E9

Minerals/ View	1	2	3	Total	Percentage
Fossil	4	7	6	17	18.6
Quartz	11	8	11	30	32.9
Peloids	4	6	8	18	19.8
echinoderm skeletal grain	8	10	8	26	28.6
Total				91	99.9

 Table A.10. Modal Analysis of sample E10

Minerals/ View	1	2	3	Total	Percentage
Fossil	4	6	5	15	17.3
Quartz	12	8	10	30	31.6
peloids	4	6	5	15	15.3
echinoderm skeletal grain	8	10	8	26	26.5
Total				86	99.9

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