

PETROGRAPHY, COMPOSITIONAL CHARACTERISTICS AND STABLE ISOTOPE GEOCHEMISTRY OF THE EWEKORO FORMATION FROM IBESE COREHOLE, EASTERN DAHOMEY BASIN, SOUTHWESTERN NIGERIA

M. E. NTON AND M. O. ADEYEMI

(Received 26 May 2014; Revision Accepted 10 October 2014)

ABSTRACT

Subsurface samples of the predominantly carbonate Ewekoro Formation, obtained from Ibese core hole within the Dahomey basin were used in this study. Investigations entail petrographic, elemental composition as well as stable isotopes (carbon and oxygen) geochemistry in order to deduce the different microfacies and depositional environment.

Petrographic study reveals the presence of dolomite, biomicrite, sandy biomicrite, and biosparite facies. Preserved pore types such as; intercrystalline, moldic and vuggy pores were observed as predominant conduits for fluids. The major element oxides ranges are; CaO (39.79 - 53.98wt. %), SiO₂ (1.29-25.37 wt. %), Al₂O₃ (0.43-3.77 wt. %), K₂O (0.04-0.27wt. %), Fe₂O₃ (0.74-2.35 wt. %), and Na₂O (<0.01-0.05 wt. %). Cross correlation of the major oxide contents shows that Al₂O₃, K₂O, Na₂O, TiO₂, Fe₂O₃, and P₂O₅ are associated with aluminosilicates and their low concentrations indicates that the basin was free of suspended clays and other aluminosilicates materials during carbonate sedimentation. The relatively high concentration of SiO₂ and its interrelationship with other major oxides, suggests SiO₂ has strictly influenced the sedimentation of the carbonate hence would have been contributed as free silica, probably from beaches and not as aluminosilicates.

The Mn/Sr ratio reveals an influence of diagenesis on the mineralogy of the carbonates. The Mg/Ca ratio ranges from 0.02 and 0.1(av. 0.04), with an outlier value of 0.1, indicating a strong diagenetic influence and the precipitation of dolomite in the mixing zone. The isotopic composition of δ¹³C (-1.9‰ to 0.79‰) shows a discrepancy from modern carbonate sediments. The average estimated formational temperature of the limestone is 32.5^oC. The δ¹³O versus δ¹⁸O bivariate diagram indicates that the limestone is predominantly average marine limestone with chalk and late cement. The values of depositional setting (Z), estimated from δ¹³O and δ¹⁸O composition support a diagenetic influence on the Ewekoro Formation. The U/Th ratios (~0.25 to 2.3; av. 1.2) and Ce anomaly (0.70 - 0.94, av. 0.85) indicate a predominantly oxygenated environment with little fluctuation in bottom water oxygen level.

INTRODUCTION

The Dahomey Basin extends considerably along the continental margin of the Gulf of Guinea, westward from the Volta Delta in Ghana to the Okitipupa Ridge in Nigeria (Fig. 1). It is a marginal sag basin (Kingston et al., 1983) or a marginal pull apart basin (Klemme, 1975), whose development in the Mesozoic (Jurassic – Cretaceous) is associated with the separation of the African and South American lithospheric plates (Burke et al., 1971). The basin contains over 3,000m of Cretaceous to Recent sediments, which thickens from the onshore margin to the offshore (Whiteman, 1982).

The eastern Dahomey basin has been of much geological interest as a result of reported occurrences of

bitumen, limestone, glass sands and phosphates (Nton, 2001). It is of immense importance to note that exploration activity for hydrocarbon commenced in Nigeria in this basin in 1908, near Okitipupa, east of Lagos, where bituminous sands outcrop. With the discovery of oil in the Niger Delta in 1956, focus shifted from the eastern Dahomey basin to the Niger Delta and the wells earlier drilled, were termed "dry" and later abandoned. Recently, due to increased government incentives to prospectors and re-evaluation of data gathered from such unsuccessful attempts, there is a resurgence of interest into having a better understanding of the source rock, compositional and reservoir characteristics of the basin.

M. E. Nton, Department of Geology, University of Ibadan, Ibadan, Nigeria
M. O. Adeyemi, Department of Geology, University of Ibadan, Ibadan, Nigeria

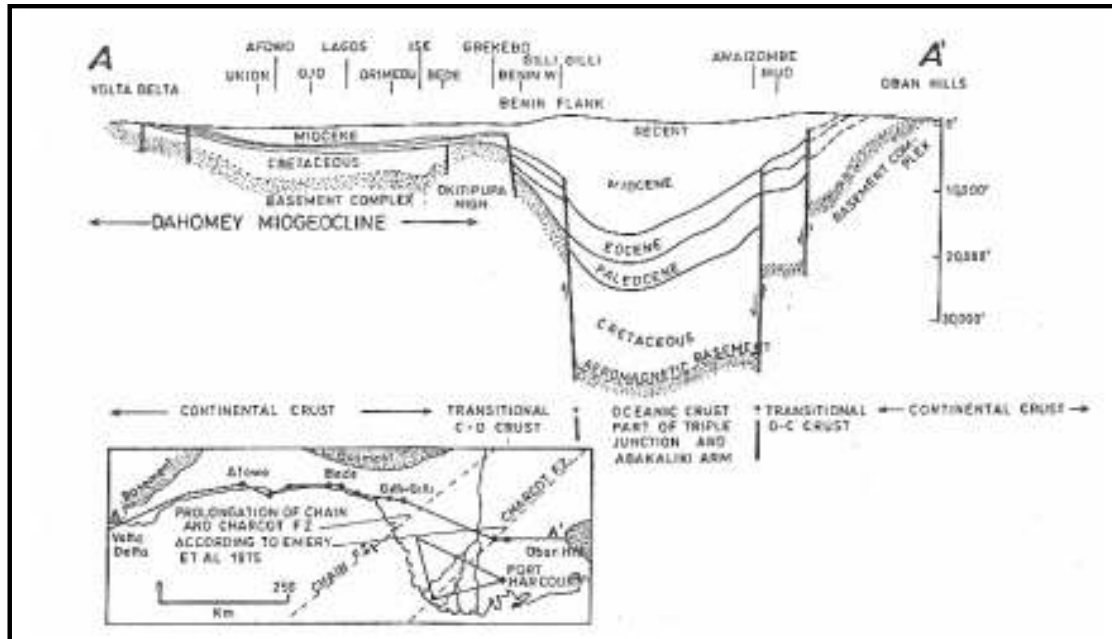


Figure 1: East-West Geological section showing the Dahomey basin and upper part of the Niger-Delta (After Whiteman, 1982)

Several authors have described microfacies of the Ewekoro Limestone on the basis of depositional properties such as texture, fabric and compositional constituents. Adegoke (1969) proposed a Paleocene age to the Formation. Elueze and Nton (2004) examined the organic geochemical characteristics of limestones and shales in the eastern Dahomey basin and reported that the fossil assemblages of the limestone are made up of coralline algae, pelecypods, echinoids, gastropods and other skeletal debris; thus inferring a shallow marine environment of deposition.

Stable isotope (carbon and oxygen) geochemistry is an important tool in the reconstruction of paleoenvironmental conditions such as paleoclimate, paleotemperature, paleosalinity as well as in evaluating rock –fluid interactions between meteoric water and limestones during diagenesis (Nagarajan et al., 2008; Armstrong-Altrin et al., 2011). Adekeye et al., (2005) while examining the carbon and oxygen isotopic composition together with petrography and paleontological studies of the Ewekoro limestone documented that it was deposited in a shallow marine inner shelf with a relatively humid climate and an

estimated formational temperature varying between 26.65°C and 32.52°C.

The present study further examines the different microfacies of the Ewekoro limestone; deduce the diagenetic history and the influence of detrital influx on the deposition of the carbonate in line with current understanding.

LOCATION OF STUDY AREA AND GEOLOGY

The studied well is located within latitudes $6^{\circ}10^1$ to $6^{\circ}40^1$ N and longitudes $2^{\circ}12^1$ and $2^{\circ}36^1$ E and lies within the eastern Dahomey basin (Fig. 2). The stratigraphy of the eastern Dahomey basin has been discussed by various workers and several classification schemes have been proposed. These notably include those of Jones and Hockey (1964); Ogbe (1972); Omatsola and Adegoke (1981); Billman (1992); Nton (2001); Elueze and Nton (2004); Nton et al. (2006) among others. In spite of all these classification schemes, there are still controversies on age assignments and nomenclatures of the different lithological units within the basin. The different classification schemes are shown in Fig. 3.

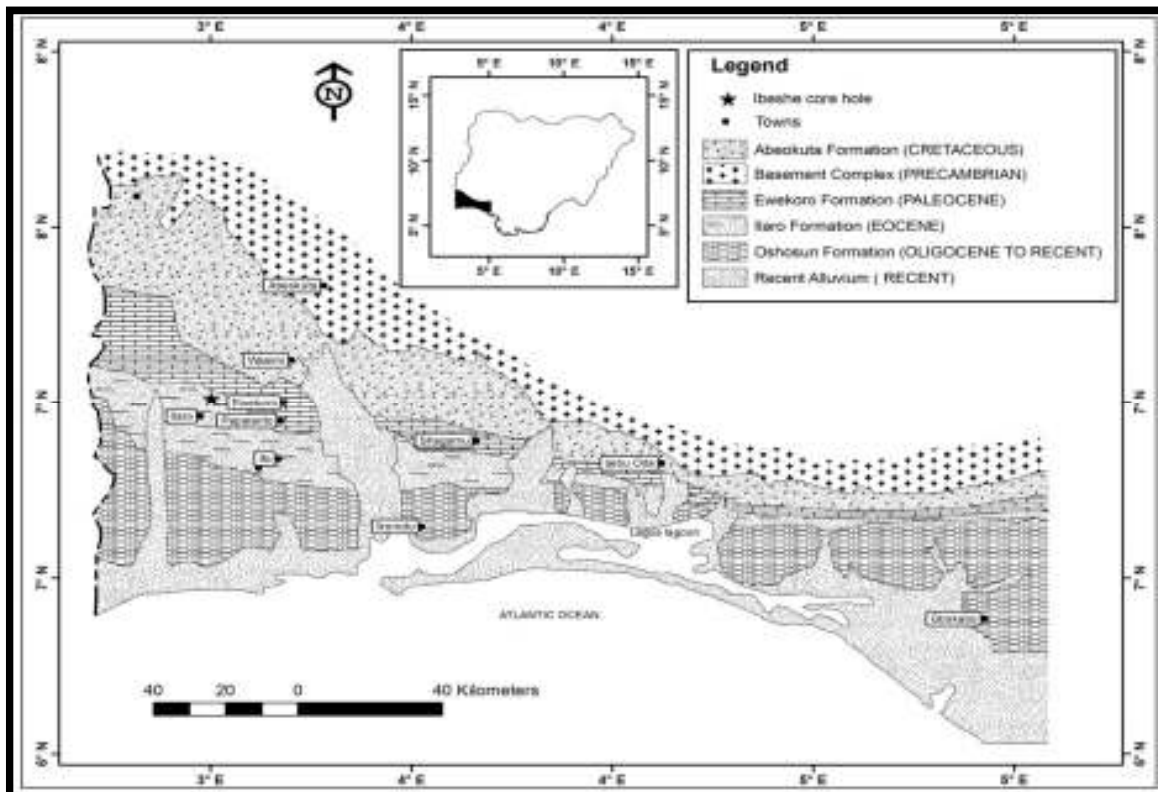


Figure 2: Geologic map of eastern Dahomey Basin showing location of study well (Modified after Bankole et. al., 2006)

Omatsola and Adegoke (1981) proposed the Cretaceous sequence in the eastern Dahomey basin as beginning with the Abeokuta Group, made up of three formations from oldest to the youngest namely; the Ise, Afowo and Araromi Formations. The Ise Formation unconformably overlies the basement complex of southwestern Nigeria and consists of conglomerates and grits at base and in turn overlain by coarse to medium grained sands with interbedded kaolinite. The conglomerates are unimbricated and at some locations, ironstones occur (Nton, 2001). The Ise formation is of non-marine origin and of age Neocomian to Albian.

Overlying the Ise Formation is the Afowo Formation, which is composed of coarse to medium grained sandstones with variable but thick interbedded shales, siltstones and claystone. The sandy facies are tar-bearing while the shales are organic - rich (Enu, 1990). The lower part of this formation is transitional with mixed brackish to marginal horizons that alternate with well sorted, sub-rounded sands indicating a littoral or estuarine near-shore environment of deposition. Using palynological assemblage, Billman (1992) assigned a Turonian age to the lower part of this formation, while the upper part ranges into the Maastrichtian.

The Araromi Formation overlies the Afowo Formation and has been described as the youngest Cretaceous sediment in the eastern Dahomey basin (Omatsola and Adegoke, 1981). It is composed of fine to medium grained sandstone at the base, overlain by shales, siltstone with interbedded limestone, marl and lignite. This Formation is highly fossiliferous containing abundant planktonic foraminifera, ostracods, pollen and spores. Omatsola and Adegoke (1981) assigned a Maastrichtian to Palaeocene age to this formation based on faunal content.

The Ewekoro Formation overlies the Araromi Formation in the eastern Dahomey basin. It is an extensive limestone body, which is traceable over a distance of about 320km from Ghana in the west, towards the eastern margin of the Dahomey basin in Nigeria (Jones and Hockey, 1964). Elueze and Nton, (2004) has reported that the limestone is of shallow marine origin owing to abundance of coralline algae, gastropods, pelecypods, echnoid fragments and other skeletal debris. It is Palaeocene in age.

Overlying the Ewekoro Formation is the Akinbo Formation, which is made up of shale and clayey sequence (Ogbe, 1972). The claystones are concretionary and are predominantly kaolinite (Nton and Elueze, 2005). The base of the Akinbo Formation is defined by the presence of glauconitic band with lenses of limestones (Ogbe, 1972; Nton, 2001). The Akinbo Formation is thought to be a deeper marine deposit, with regards to its absence of arenaceous materials and great abundance of planktonic foraminifera. The formation is Palaeocene to Eocene in age.

The Oshosun Formation overlies the Akinbo Formation and consists of greenish – grey or beige clay and shale with interbeds of sandstones. The shale is thickly laminated and glauconitic. According to Okosun (1998), the basal beds consist of the following facies; sandstones, mudstones, claystones, clay-shale or shale. This formation is phosphate-bearing (Jones and Hockey, 1964; Nton, 2001).

The Ilaro Formation overlies conformably the Oshosun Formation and consists of massive, yellowish poorly, consolidated, cross-bedded sandstones. The youngest stratigraphic sequence in the eastern Dahomey basin is the Benin Formation. It is also known as the Coastal Plain Sands (Jones and Hockey, 1964)

and consists of poorly sorted sands with lenses of clays. The sands are in parts cross-bedded and show

transitional to continental characteristics. The age is from Oligocene to Recent.

Reyment, 1965 Adegoke, 1969		Billman, 1976		Omatsola & Adegoke, 1981		Okosun, 1990	
M a a s t r i c h t i a n	Araromi Shale (Informal)	Pal	Nkporo Shale	Pal	Ewekoro Fm	Pal	Araromi Formation
		Maastr.		Maastrichtian	Araromi Formation	Maastrichtian	
	Abeakuta Formation	Senonian	Awgu Shale	Maastrichtian			
		Turonian	Abeokuta Formation	Turonian	Afowo Formation	Upper Albian - Senonian	Abeokuta Formation
		Albian	Unnamed Albian Sands	Neocomian-Albian	Ise Formation		
		Pre-Albian	Unnamed Older Folded Sediments				

Figure 3: Stratigraphic successions in the Dahomey Basin as compiled by various workers.

SAMPLES AND ANALYTICAL METHODS

Samples

Thirteen subsurface limestone samples were collected from the Ibeso corehole. With a total depth of 58m, the corehole is made up of lower limestone unit of

about 20m belonging to the Ewekoro Formation overlain by about 38m of thick shale sequence which belongs to the Akinbo Formation. The limestone is grayish and fossiliferous while the shale is grayish, fissile and partly gypsiferous (Fig. 4)

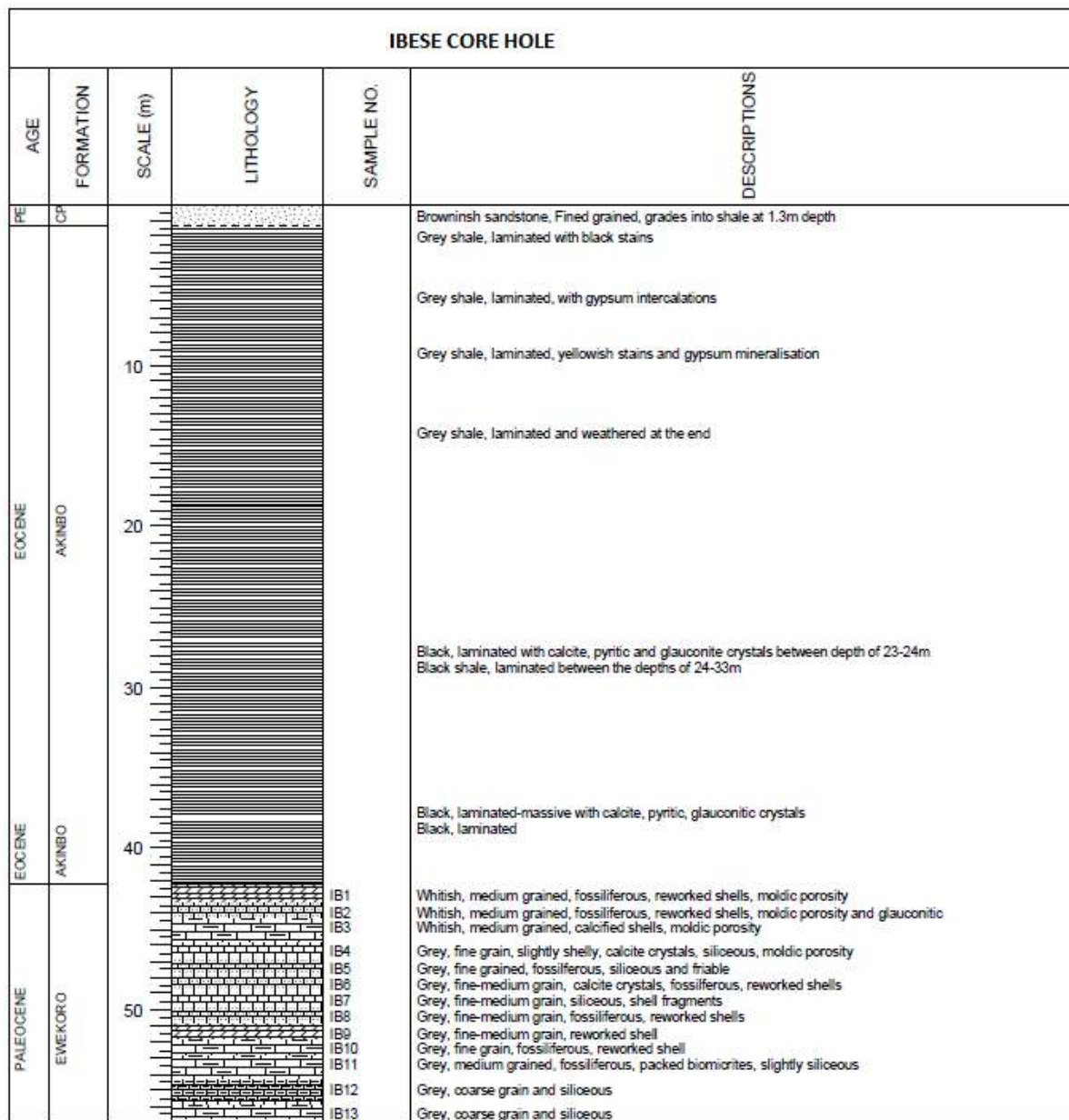


Figure 4: Lithologic profile and description of Ibesse corehole

METHOD OF ANALYSIS

Thin section petrography

Thin section preparation of the limestone was done by standard methods and the slides were observed under the flat stage of petrological microscope (Brunnel model). Photomicrographs of features of interest were taken and studied with the aid of appropriate references. The limestone was classified based on the scheme of Folk (1959). Thin section preparation and slides examination were conducted at the Department of Geology, University of Ibadan.

Elemental oxides

0.2g and 0.5g of pulverized samples were labeled, stored in air tight containers and sent for whole rock geochemical and stable isotope (carbon and oxygen) analyses respectively. The major elements were determined using ICP-emission spectrometry by

digesting 0.2g of the subsample with Lithium metaborate/tetraborate flux and fused in a furnace. A total abundance of eleven major oxides and two trace elements were reported. The trace and rare earth elements were determined by ICP-mass spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric digestion. A total of forty three trace elements were reported. The elemental analysis was carried out at Acme laboratories, Canada. The isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) of the carbonates was determined using a GVI Optima Stable Isotope Ratio Mass Spectrometer.

0.5g of each pulverized sample were reacted in 105% phosphoric acid at 90°C using an Isocarb common acid bath system and the $\delta^{13}C$ and $\delta^{18}O$ values of the resulting CO₂ gas was analyzed in dual inlet mode. All isotope Data were computed to VPDB (Vienna Pee Dee Belemnite limestone) and expressed in the notation ‰ (per mil) using NBS-19 calcite standard.

Standard precision was based on repeat analyses of an in-house calcite standard (n=6), the precision for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is $\pm 0.03\%$. The isotope analysis was conducted at the Stable Isotope Laboratory, University of California, Davis, U.S.A. Detailed analytical methods are documented in Adeyemi (2014).

RESULTS AND DISCUSSIONS

Petrography

Four microfacies of the limestones have been identified namely; sandy biomicrite, biomicrite, biosparite and dolomite (Fig. 5). The fossil constituents are mainly; gastropods, pelecypods, brachiopods, ostracods, coralline algae and foraminifera. The Sandy Biomicrite is made up of shell fragments and other detrital debris embedded in a mud supported matrix (Fig. 5A). The Biomicrite facies are highly fossiliferous and mud supported with bioclasts such as; corals, algae, gastropods and brachiopods. The bioclasts are

preserved in micrite envelopes (Fig. 5B and D). The Biosparite shows evidence of partial dissolution and recrystallisation of initial sediment- fill (micrites) with neomorphic sparry calcite (Fig. 5C). The predominant bioclasts include gastropods, ostracods and echinoids embedded in micritic groundmass. The sharp boundary, between the micrite and the sparry calcite, reflects aggrading neomorphism.

The depositional textures and features in the dolomitic facies have been completely obliterated as a result of a very high degree of recrystallization to dolomitisation as reported by Petters, (1978). The dolomitic facies, exemplified by samples 1B1 and 1B9, show uniform mosaic of dolomicrospar rhombs ($< 5\mu$) and drusy spars lining its cavities (Fig. 5E). As pointed out by Adams and Rhodes (1960), such features are typical of mixing zone of dolomite cement and the depth may define the extent to which the heavier brines near the surface move downwards as density currents in the pore system.

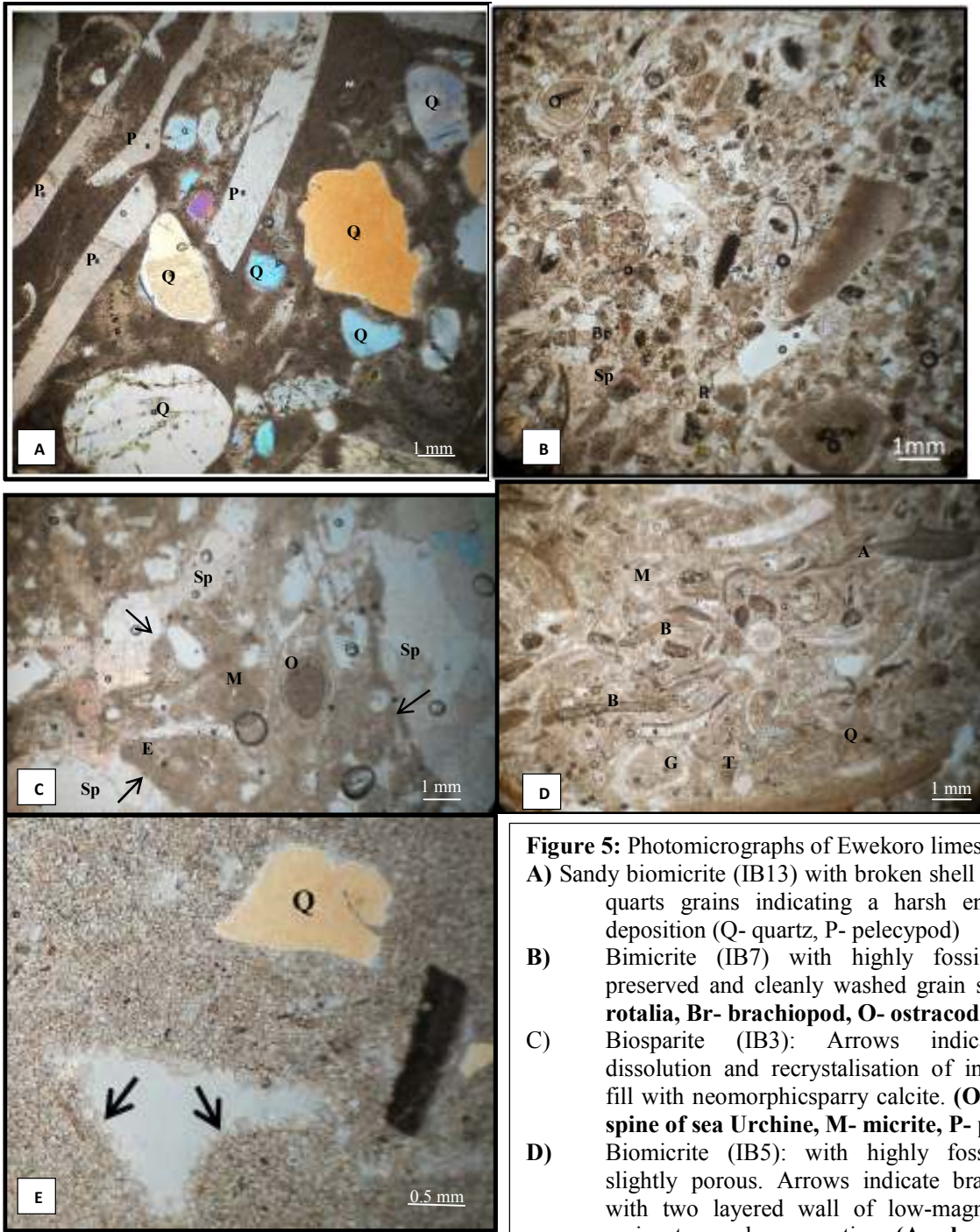


Figure 5: Photomicrographs of Ewekoro limestone.

- A)** Sandy biomicrite (IB13) with broken shell fragments and quartz grains indicating a harsh environment of deposition (Q- quartz, P- pelecypod)
- B)** Bimicrite (IB7) with highly fossiliferous, well preserved and cleanly washed grain supported. (R- rotalia, Br- brachiopod, O- ostracods)
- C)** Biosparite (IB3): Arrows indicating partial dissolution and recrystallisation of initial sediment fill with neomorphic sparry calcite. (O- ostracod, S- spine of sea Urchine, M- micrite, P- pores).
- D)** Biomicrite (IB5): with highly fossiliferous and slightly porous. Arrows indicate brachiopod shell with two layered wall of low-magnesium calcite owing to good preservation. (A- algae, B- bivalve, Br- brachiopod, T- textularia, Q- quinqueloculina, R- rotalia, M- micrite, P- pores, S- syntaxial rim)
- E)** Dolomitic (IB9): with a non-mimic fabric leaving no vestige of the original depositional. The arrows indicates drussy spar lining the cavities. (Q- quartz)

Major Element Geochemistry

The results of major elemental oxides (wt. %) in this study are presented in Table 1. CaO is most abundant of the major oxides, ranging between 39.79 and 53.98wt. % (av. 47.43 wt. %), SiO₂ ranges from 1.29 to 25.37 wt. % (av.7.18 wt. %). Other oxides are low in concentration with the following average values; 1.41 wt. %, Al₂O₃; 0.12wt. %, K₂O; 1.23 wt. %, Fe₂O₃; 0.03 wt. %, Na₂O; 0.07 wt.%, TiO₂; 0.14 wt. %, P₂O₅ ; 0.02 wt. %, MnO and 1.99 wt. % , MgO. A stratigraphic section and major oxide profiles of the Ewekoro Formation as penetrated by the corehole is presented in Fig. 6.

According to the Missouri Department of Natural Resources, (2011), Ca/Mg ratio can be used to identify the mineral composition of the limestone with the

assumption that it is made up of only calcite and dolomite [Ca/Mg>59.37 (high calcium limestone), 28.99-59.36 (magnesian limestone), 4.69-28.98 (dolomitic limestone), 1.99-4.68 (calcitic dolomite), 1.66-1.99 (dolomite)]. The Ca/Mg (wt. %) ratio of the Ewekoro limestone vary from 9.73 to 65.89 (av. 35.63). The Ewekoro limestone was estimated to be made up of about 7.6% of High calcium limestone, 53.9% is magnesian limestone and 38.5% is dolomitic limestone. Also, the Ewekoro limestone show low Mg/Ca ratios varying between 0.02 and 0.1 (av. 0.037) with sample IB9 (51meters within corehole) having a distinct value of 0.1 indicating the precipitation of dolomite. This assertion has been corroborated by the petrographic studies (Figure 5E).

Table 1: Major oxide composition of the Ewekoro limestone

Samples	IB1	IB2	IB3	IB4	IB5	IB6	IB7	IB8	IB9	IB10	IB11	IB12	IB13	Mean
Depth (m)	39.5	40.5	42	43.5	45	46.5	48	49.5	51	52.5	54	55.5	57	
SiO ₂	2.84	2.19	1.29	5.48	4.16	9.22	4.36	4.44	3.54	9.00	18.82	2.68	25.37	7.18
Al ₂ O ₃	0.84	0.72	0.43	2.02	1.56	3.77	1.56	1.58	1.28	2.58	0.73	0.84	0.47	1.41
Fe ₂ O ₃	1.01	0.94	1.01	0.95	1.13	1.59	1.25	1.39	1.96	2.35	0.76	0.95	0.74	1.23
MgO	3.20	2.63	0.97	1.48	1.59	1.55	1.78	2.05	5.49	1.91	1.13	1.26	0.84	1.99
CaO	48.84	50.18	53.98	48.47	49.16	43.88	49.18	48.90	45.11	44.74	42.88	51.48	39.79	47.43
Na ₂ O	0.02	0.02	0.02	0.03	0.03	0.05	0.04	0.04	0.02	0.03	0.01	<0.01	0.01	0.03
K ₂ O	0.15	0.12	0.06	0.15	0.11	0.27	0.11	0.11	0.09	0.18	0.07	0.04	0.05	0.12
TiO ₂	0.03	0.02	0.02	0.10	0.06	0.16	0.07	0.06	0.05	0.10	0.08	0.03	0.12	0.07
P ₂ O ₅	0.18	0.14	0.10	0.09	0.14	0.20	0.17	0.17	0.11	0.19	0.13	0.10	0.15	0.14
MnO	0.04	0.04	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.02	0.01	0.02	0.02
Cr ₂ O ₃	0.009	0.008	0.013	0.006	0.007	0.011	0.008	0.008	0.007	0.016	0.007	0.005	0.005	0.01
LOI	42.80	42.90	42.00	41.10	41.90	39.10	41.30	41.10	42.20	38.70	35.30	42.50	32.30	40.25

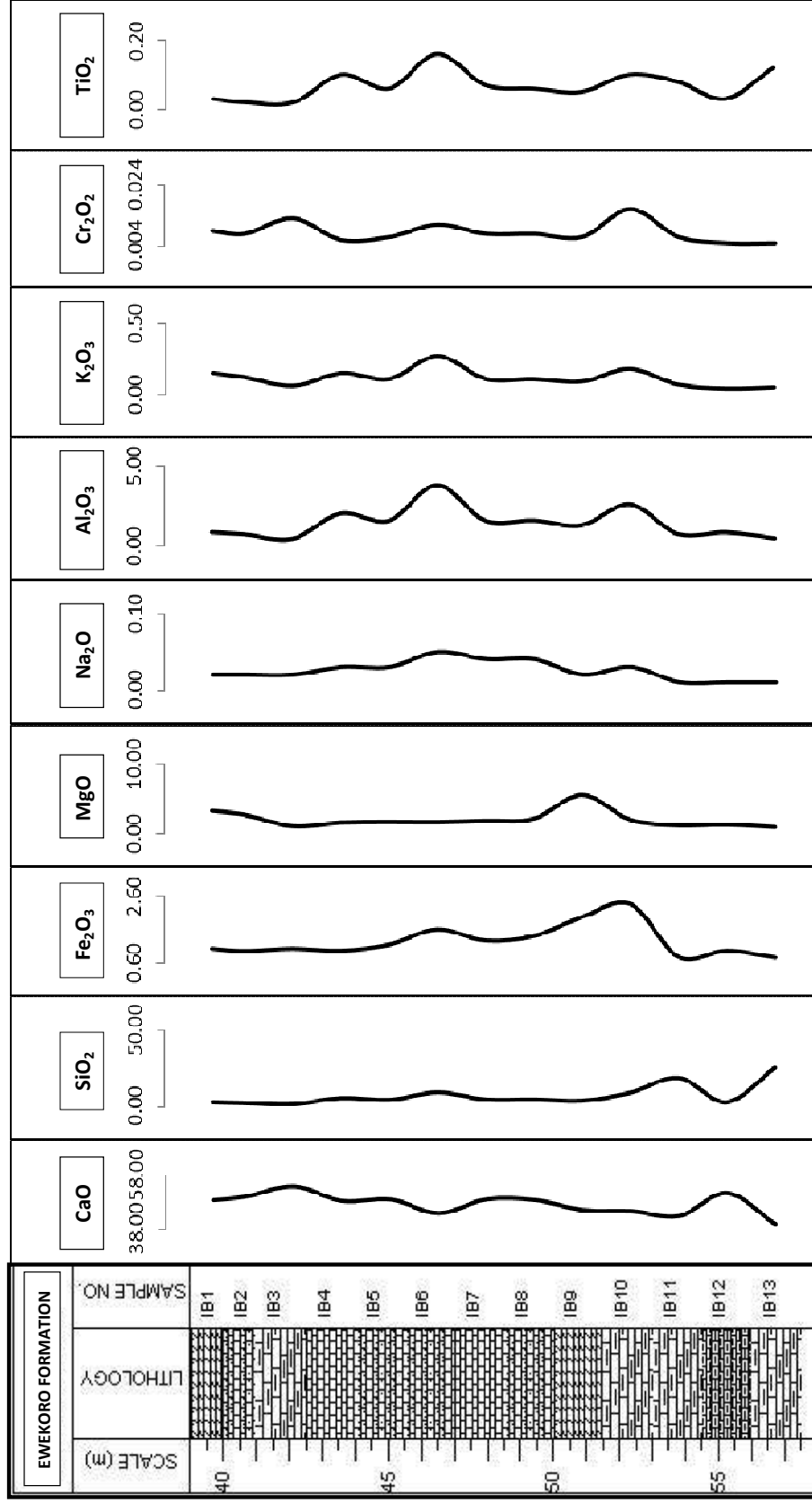


Figure 6: Stratigraphic section and major oxide profiles of the Ewekoro formation (contents in wt. %)

Trace Element Geochemistry

Results of the trace elements composition of the limestone as presented in Table 2, shows that Strontium (Sr) is the most abundant (371.3 - 966.4ppm, av. 640.2ppm). This is similar to that of lithosphere carbonates (Sr = 610 ppm, Turekian and Wedepohl, 1961). The average abundance (in ppm) of the other trace elements are ; Zn (38.77), Zr (26.59), Ce (26.59),

V (17.42), Nd (13.79), Ba (11.15), Y (7.74), Ni (7.19), Sn (6.00), Ta (4.70), Rb (4.57), Nb (4.12), Pb (3.68), Pr (3.42), W(3.0), Th (2.25), U (2.24), Sm (2.24), Cu (2.21), Gd (1.95), Co (1.62), Ga (1.54), Mo (1.48), Dy (1.40), Be (1.00), Hf (0.81), Er (0.72), Yb (0.60), Bi (0.55), Eu (0.53), Cs (0.43). Other trace elements all have concentrations below their various detection limits.

Table 2: Trace elemental composition of the Ewekoro limestone

Samples	IB1	IB2	IB3	IB4	IB5	IB6	IB7	IB8	IB9	IB10	IB11	IB12	IB13	Mean
Depth (m)	39.5	40.5	42	43.5	45	46.5	48	49.5	51	52.5	54	55.5	57	
Ba	19	5	6	15	13	23	12	11	8	15	6	5	7	11.15
Co	0.2	0.6	1	2	1.7	2.9	1.8	1.6	1	5.4	0.8	0.8	1.2	1.62
Cs	0.4	0.3	0.2	0.6	0.4	1.1	0.4	0.4	0.4	0.7	0.3	0.2	0.2	0.43
Ga	0.8	<0.5	<0.5	1.7	1.2	2.9	1.1	1.2	0.9	2.5	<0.5	<0.5	<0.5	1.54
Hf	0.2	0.2	<0.1	0.9	0.3	0.7	0.4	0.5	0.2	1.1	2.4	0.2	2.6	0.81
Nb	2.1	1.9	1.6	1.6	1.2	2.5	1.5	1	1.2	1.8	4.5	1.4	31.3	4.12
Rb	5.4	4.1	2	6.6	4.9	11.4	4.3	4.3	3.3	7.3	2.4	1.7	1.7	4.57
Sr	371.3	418.3	532.5	840.8	881.6	870.5	966.4	893.1	593.2	768.7	378.2	448.9	359.6	640.24
Ta	3.3	5.9	5.1	1.2	1.2	0.9	1.4	1.4	1.6	0.9	10.5	5.6	22.1	4.7
Th	1.8	1.5	2	2.2	2.8	4.5	2.8	3.1	1.8	3.7	1	1	1	2.25
U	3	3.3	0.5	1.8	2.8	2.9	2.7	2.4	2.4	2.4	1.5	2.3	1.1	2.24
V	21	19	23	12	18	21	15	17	14	31	8	10	<8	17.42
Zr	5.5	4.2	3.4	28.1	10.3	26.1	14.1	14.7	8.4	37.8	90.9	4.3	97.9	26.59
Y	9.8	7.6	8.6	5.6	6.8	9.5	6.5	8.2	5.3	12.2	9.2	4.1	7.2	7.74
Mo	<0.1	0.5	0.2	1.5	2.4	4.1	2.2	2.3	1.2	2.7	0.2	0.4	0.1	1.48
Cu	5.2	1.6	1.4	2	2.5	3.7	2.1	2.2	1.6	2.7	1.2	1.3	1.2	2.21
Pb	2.5	2.4	3.8	3.5	5.2	7	5.4	4.8	2.5	5.5	1.8	1.7	1.7	3.68
Zn	19	19	23	20	40	45	50	53	40	121	20	30	24	38.77
Ni	3.1	4.3	2.2	5.6	8	12.9	8.3	9.2	6.9	22.6	2.8	2.5	5.1	7.19
As	2.3	4.2	4	5.2	9.7	9.1	8.6	7.2	6	16.2	1.4	4.4	1.9	6.17
Au	3.8	2.5	86.8	4.4	2.4	2.5	2.1	2.1	<0.5	1	1.4	4.1	1	9.51
Cd	0.7	0.7	0.5	0.3	0.5	0.5	0.6	0.5	0.3	0.9	0.2	0.3	0.2	0.48
Sb	0.1	0.1	0.2	<0.1	0.3	0.1	0.3	0.2	0.2	0.3	<0.1	0.2	<0.1	0.2
Bi	0.5	0.7	0.8	0.3	0.2	0.2	0.2	0.3	0.2	0.2	0.9	0.8	1.8	0.55
Se	<0.5	1	0.9	0.7	1.7	1.5	1.7	1.3	0.9	2.3	<0.5	0.6	<0.5	1.26
La	10.3	8.6	11.6	12.5	14.8	23.3	15.8	16.5	10.5	22.7	10	8.7	10.2	13.5
Ce	16.7	13.4	18.1	24.6	30.9	48.9	32.8	35.4	23.1	48.3	16.1	19	18.4	26.59
Pr	2.47	1.96	2.85	2.95	3.86	6.2	3.98	4.39	2.86	6.11	2.39	2.35	2.58	3.46
Nd	8.6	7.9	11	11	17.3	23.9	16.2	17.6	10.8	24.2	10.4	10.5	9.9	13.79
Sm	1.86	1.48	2.39	1.85	2.61	4.09	2.73	2.98	1.89	4.29	1.78	1.46	1.8	2.4
Eu	0.47	0.4	0.54	0.4	0.56	0.84	0.58	0.57	0.35	0.94	0.42	0.33	0.43	0.53
Gd	2.08	1.45	2.26	1.44	2.06	3.14	1.89	2.12	1.45	3.09	1.72	1.16	1.53	1.95
Tb	0.29	0.22	0.31	0.21	0.26	0.42	0.27	0.29	0.2	0.44	0.25	0.15	0.23	0.27
Dy	1.55	1.16	1.5	1.07	1.41	1.74	1.46	1.51	1	2.26	1.59	0.71	1.27	1.4
Ho	0.3	0.21	0.29	0.16	0.25	0.32	0.21	0.22	0.18	0.43	0.27	0.14	0.21	0.25
Er	0.82	0.61	0.88	0.57	0.62	0.94	0.59	0.76	0.48	1.21	0.8	0.34	0.73	0.72
Tm	0.11	0.08	0.11	0.07	0.09	0.13	0.09	0.1	0.06	0.16	0.11	0.04	0.1	0.1
Yb	0.63	0.5	0.65	0.46	0.61	0.82	0.49	0.57	0.45	0.91	0.7	0.34	0.68	0.6
Lu	0.09	0.07	0.08	0.06	0.07	0.1	0.07	0.07	0.05	0.13	0.11	0.04	0.08	0.08

Carbonate Depositional Environment

A combination study of texture, composition and fossil assemblage, together with the evaluation of the elemental and isotopic results, were used to interpret the depositional environment and deduce the paleoredox condition of the Ewekoro limestone. The presence of biomicrites, with associated gastropods, coralline algae, echinoid spines in the Ewekoro Formation suggest a shallow marine environment.

The sandy biomicrities are composed of unsorted broken shells and grains of calcite. Some of the visible quartz grains are monocrystalline and non undulatory under petrographic study (Fig. 5A). The texture and composition indicates a textural inversion caused by the mixing of the products of two energy levels. It is probable that the quartz grains were washed into the lagoon from beaches or streams with indications that a high energy environment has moved across the shoal down to low energy settings in the lagoon, possibly in the middle shelf environment (Folk, 1974). The absence of varieties of bioclasts and abundance of shell fragments reflects a harsh environment unsuitable for a wide variety of open marine biota. The biomicrite

facies are highly fossiliferous (Fig. 5C, D). The fossil assemblages of gastropods, ostracods and species of benthic foraminifera that belongs to the suborders *Textularina*, *Miliolina* and *Rotalia* population in addition to the abundance of lime mud suggest a restricted shallow, shelf marine environment during the Maastrichtian to Paleocene transgression into the eastern Dahomey Basin. This corroborates the findings of Reijers and Petters (1987). A barrier might have isolated the lagoon from the open sea except during storm surges. The lagoon reached hypersaline conditions during episodes of reduced inflow of surface meteoric water, which probably was the case during deposition.

Oxygen isotope composition for this study varies from -5.42‰ to -2.13‰ PDB and the carbon isotope composition ranges between -1.9‰ and 0.79‰. The Ewekoro limestone shows a strong positive excursion of $\delta^{13}\text{C}$ (Table 3) which indicates high bioactivity and in turn suggests an oxygenated environment. The negative excursion of $\delta^{13}\text{C}$ at the upper and basal parts of the formation is as a result of diagenesis.

Table 3: Carbon and Oxygen isotopic data for Ewekoro limestone

Samples	Depth(m)	$\delta^{13}\text{C}$ (VPDB)	$\delta^{18}\text{O}$ (VPDB)	$\delta^{18}\text{O}$ (SMOW)*	Z	T (°C)
IB1	39.5	-0.3	-3.83	26.91	126	32.87
IB2	40.5	-0.37	-4.26	26.47	124	34.89
IB3	42	0.53	-5.06	25.65	126	38.69
IB4	43.5	0.5	-3.41	27.35	125	30.87
IB5	45	0.33	-3.28	27.48	126	30.24
IB6	46.5	0.79	-2.13	28.66	128	24.91
IB7	48	0.55	-2.78	27.99	127	27.93
IB8	49.5	0.31	-3.03	27.74	126	29.09
IB9	51	-0.48	-3.62	27.13	125	31.86
IB10	52.5	0.38	-2.64	28.14	127	27.28
IB11	54	0.06	-4.12	26.61	125	34.23
IB12	55.5	-1.99	-5.42	25.27	121	40.46
IB13	57	-0.81	-5.01	25.69	123	38.49
Study sample (Ewekoro Formation)						
Average		-0.04	-3.74	27	125	32.45
Range		-1.99 to 0.79	-5.42 to -2.13	25.27 - 28.66	121- 128	24.76 - 39.56
Adekeye (2005)						
Range		-3.41 to -7.68	1.01 to -2.44	-	-	26.65 - 32.52
Tertiary Sea Water Carbonates						
Average		0.05	-2.33	-	-	-
* $\delta^{18}\text{O}_{\text{calcite}}(\text{SMOW}) = 1.03086 \text{ }^{18}\text{O}(\text{PDB}) + 30.86$ (Friedman and O'Neil, 1977)						

The paleotemperature was estimated based on the concept of Pollack et al., (2009) and shown in the equation below;

$$T = 16.998 - 4.52(\delta_c^{18}\text{O} - \delta_w^{18}\text{O}) + 0.003(\delta_c^{18}\text{O} - \delta_w^{18}\text{O})^2$$

Where:

T =paleotemperature in °C

$\delta_c^{18}\text{O}$ = oxygen isotopic composition of the limestone (V-PDB)

$\delta_w^{18}\text{O}$ = oxygen isotopic composition of sea water during limestone precipitation (SMOW)

The paleotemperature (T), estimated from the stable oxygen isotope analysis varies between 24.76 and 39.56 °C (av. 0.32 °C; Table 3) and suggests a warm climatic setting during the Paleocene. Crossplot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ (Hudson, 1977) reveals that the Ewekoro limestone is predominantly of average marine

limestone with chalk and late cements (Fig.7). Using the depositional setting (Z) model proposed by Nelson et al., (1996) as inferred by the equation below;

$$Z = a(\delta_c^{13}C + 50) + b(\delta_w^{18}O + 50)$$

Where:

$$a = 2.048, b = 0.498$$

$\delta_c^{18}O$ = oxygen isotopic composition of the limestone (V-PDB)

$\delta_c^{18}C$ = carbon isotopic composition of the limestone (V-PDB),

they proposed that Depositional setting parameter, $Z > 120$ is marine type; $Z < 120$ (freshwater type) and $Z \approx 120$ (intermediate). It can be revealed that the Ewekoro limestone is predominantly marine type with marginal influence of freshwater diagenesis in samples IB12 and IB13, having respective values of 121 and 123

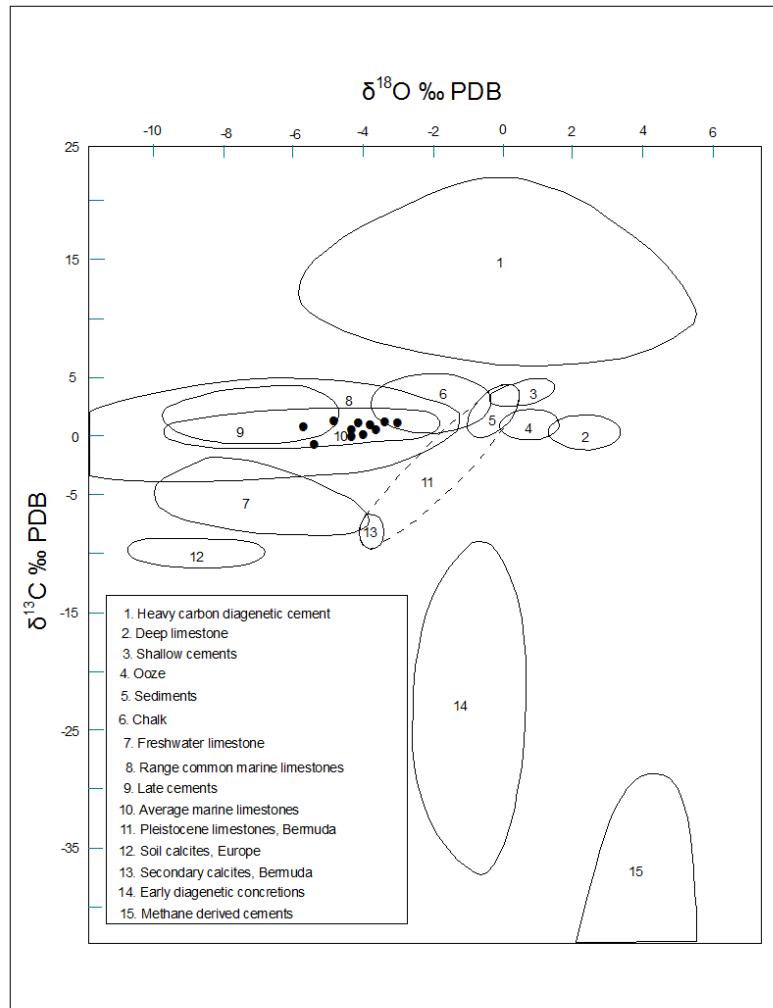


Figure 7: Cross-plot of $\delta^{18}O$ and $\delta^{13}C$ showing isotope fields for Ewekoro limestone (After Hudson, 1977)

Paleoredox Conditions

Several geochemical indices have been proposed as proxies for the oxidation state of the oceans during sedimentary processes. Geochemical indices for the Ewekoro limestone are presented in

Table 4. The U/Th ratio and Ce anomaly have been compared to examine the paleoredox setting of the Ewekoro limestone. A palaeo-oxygenation profile has been developed for the studied core hole and presented in Fig. 8.

Table 4: Geochemical indices of Ibesse corehole

Samples	IB1	IB2	IB3	IB4	IB5	IB6	IB7	IB8	IB9	IB10	IB11	IB12	IB13
Depth (m)	39.5	40.5	42	43.5	45	46.5	48	49.5	51	52.5	54	55.5	57
Mn/Sr	0.80	0.70	0.20	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.40	0.20	0.40
Sr/Ca	10.60	11.70	13.80	24.30	25.10	27.80	27.50	25.60	18.40	24.00	12.30	12.20	12.60
Rb/Sr	0.02	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01
Mg/Ca	0.06	0.04	0.02	0.03	0.03	0.03	0.03	0.04	0.10	0.04	0.02	0.02	0.02
Ca/Mg	18.09	22.61	65.95	38.81	36.64	33.55	32.74	28.27	9.74	27.76	44.97	48.42	56.13
U/Th	1.67	2.20	0.25	0.82	1.00	0.64	0.96	0.77	1.33	0.65	1.50	2.30	1.10
Ce/Ce*	0.74	0.73	0.70	0.90	0.91	0.91	0.92	0.93	0.94	0.91	0.73	0.94	0.80

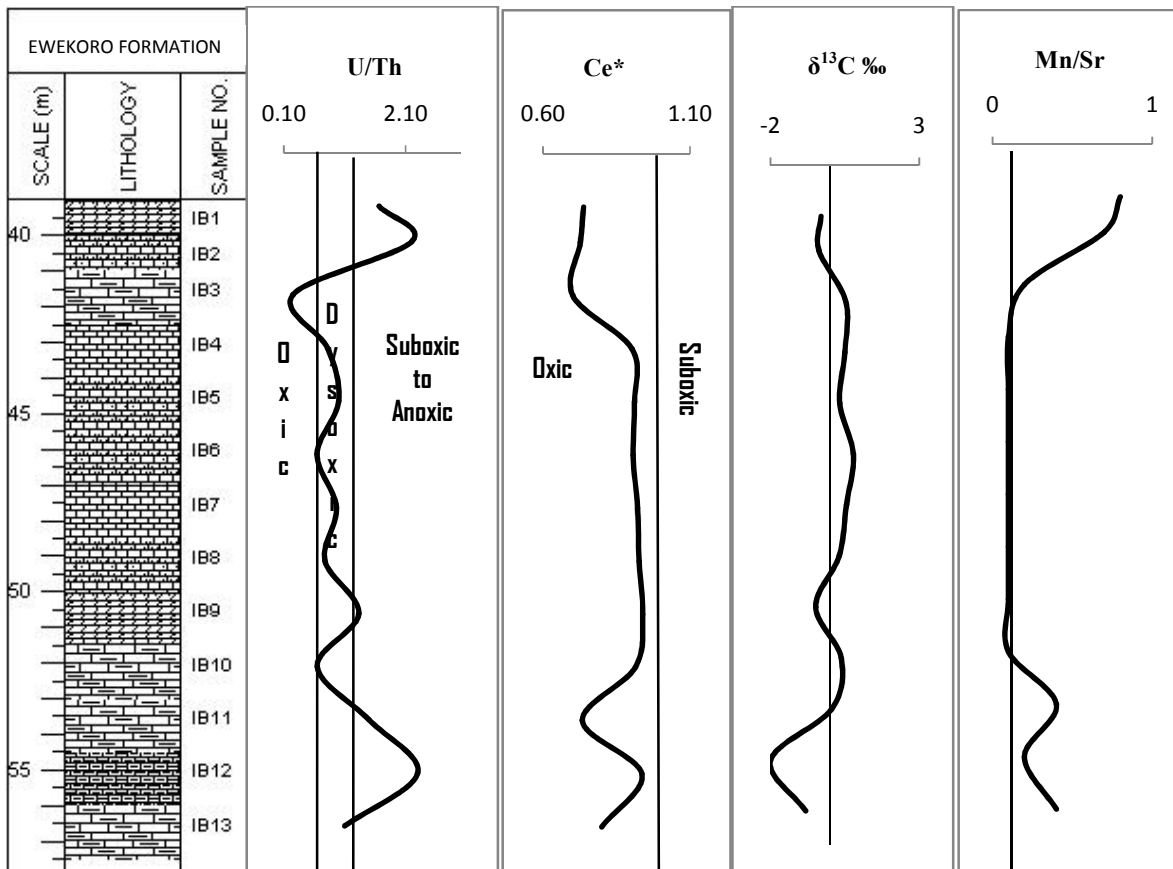


Figure 8: Stratigraphic section and Geochemical profile of Ewekoro limestone

Arising from the concept of Jones and Manning (1994), it can be shown that about 23% of the rocks have U/Th ratio < 1.25 (oxic), 46% ranges from 0.75 to 1.25 (dysoxic) while 31% shows anoxic depositional setting. These values suggest that the carbonates were deposited in an oxic setting with a strong anoxic influence. However, due to effects of post-depositional uranium mobility on U/Th ratios during events involving oxygenated fluids, direct measurements of U/Th ratios are often misleading (Pollack, 2008). Modern marine authigenic carbonates incorporate seawater rare earth element (REE) patterns, which display enrichments in heavy REE and a pronounced relative depletion in cerium and a negative cerium anomaly.

The Ce anomaly is calculated using the following equation: $Ce/Ce^* = Ce_n / (La_n \cdot Pr_n)^2$

Where n = normalized value according to (Taylor and McLennan, 1985)

Ce/Ce* values > 1 indicates a positive Ce anomaly whereas values < 1 indicates a negative Ce anomaly. The Ce anomaly (negative, < 1) for the studied samples suggests that they were deposited in oxygenated environment. In addition, the moderate variation in the values, ranging between 0.70 and 0.94 (Av. 0.85) imply they there were not much fluctuations in bottom water oxygen level.

The absolute and relative concentrations of trace elements such as; Sr, Mg, Fe and Mn the

carbonates have been used as tools in evaluating diagenetic alteration as well to reconstruct the paleoenvironment (Owen and Bruce, 1983; Brand and Veizer, 1980). Several geochemical parameters have been proposed for the evaluation of primary chemical signatures in carbonate rocks by different authors (Asmerom et al. 1991; Derry et al., 1989; Fairchild et al. 2000; Kaufman et al. 1993).

Sources of detrital influx and post-depositional studies

To study the interrelationships between the geochemical constituents of the limestone, the geochemical data have been statistically treated and the correlation coefficients of major oxides and selected elements are separately presented in Tables 5 and 6. Most of the major oxides such as K_2O , Na_2O , TiO_2 , Fe_2O_3 and P_2O_5 show positive strength of association with Al_2O_3 with respective correlation coefficient (r); 0.89, 0.82, 0.71, 0.62 and 0.53. However, SiO_2 concentration has negative correlation with the other major oxides with

the exception of TiO_2 ($r= 0.62$, $n=13$), indicating that SiO_2 might have been contributed from aluminosilicates as well as inflow recycled sediments such as those of streams or beaches. The distinct concentration of SiO_2 , particularly the relatively higher percentages in samples IB11 (18.82%) and IB13 (25.37%) corroborates with findings from petrographic examination (Fig. 5A). The strong contrast in variation between the concentration of CaO and SiO_2 ($r= -0.86$, $n=13$) shows the carbonate sedimentation is influenced by SiO_2 contribution among other factors (Graf, 1960). Whereas, the negative linear correlation coefficient between CaO and MgO ($r= -0.241$, -0.002 , $n=13$) suggest low and negative strengths of association, indicating that they were not only associated with the detrital phases but also with the carbonate and post depositional rock-fluid interaction phase. Also, the low concentrations of the major oxides associated with the aluminosilicates reflect that the basin is free of suspended clays and other siliciclastic materials which can discourage the growth of carbonate building organisms.

Table 5: Correlation of Major oxides

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	LOI
SiO_2	1.00											
Al_2O_3	-0.07	1.00										
Fe_2O_3	-0.22	0.62	1.00									
MgO	-0.39	0.00	0.48	1.00								
CaO	-0.86	-0.25	-0.18	-0.02	1.00							
Na_2O	-0.41	0.82	0.44	-0.06	0.21	1.00						
K_2O	-0.13	0.89	0.50	0.10	-0.19	0.72	1.00					
TiO_2	0.62	0.71	0.24	-0.30	-0.74	0.39	0.57	1.00				
P_2O_5	0.17	0.53	0.41	0.00	-0.37	0.50	0.64	0.44	1.00			
MnO	-0.17	-0.42	-0.49	0.06	0.23	-0.14	0.31	-0.40	0.34	1.00		
Cr_2O_3	-0.21	0.41	.625*	-0.03	0.11	0.28	0.49	0.10	0.45	-0.08	1.00	
LOI	-0.99	0.02	0.16	0.44	0.84	0.36	0.11	-0.65	-0.20	0.23	0.10	1.00

Table 6: Cross correlation coefficients of selected elements of the Ewekoro limestone

	Mg	Ca	Si	Al	Fe	Mn	Na	K	Ti	P	Ba	Co	Cs	Hf	Nb	Rb	Sr	Ta	Th	U	V	Zr	Zn	Ni	Tree	
Mg	1.00																									
Ca	-0.02	1.00																								
Si	-0.39	-0.86	1.00																							
Al	-0.01	-0.25	-0.07	1.00																						
Fe	0.48	-0.18	-0.22	0.62	1.00																					
Mn	0.06	0.07	0.08	-0.58	-0.50	1.00																				
Na	-0.18	-0.09	-0.09	0.83	0.37	-0.57	1.00																			
K	0.08	-0.19	-0.12	0.89	0.50	-0.15	0.70	1.00																		
Ti	-0.31	-0.74	0.62	0.71	0.24	-0.42	0.60	0.57	1.00																	
P	0.00	-0.36	0.17	0.52	0.41	0.04	0.58	0.65	0.43	1.00																
Ba	0.06	-0.17	-0.11	0.79	0.38	-0.21	0.67	0.88	0.55	0.64	1.00															
Co	-0.17	-0.28	0.10	0.75	0.74	-0.54	0.52	0.59	0.58	0.47	0.47	1.00														
Cs	0.04	-0.30	-0.03	0.97	0.56	-0.39	0.76	0.95	0.72	0.55	0.84	0.67	1.00													
Hf	-0.43	-0.81	0.98	-0.10	-0.25	0.08	-0.13	-0.15	0.57	0.09	-0.15	0.12	-0.06	1.00												
Nb	-0.31	-0.64	0.82	-0.30	-0.34	0.22	-0.24	-0.31	0.39	0.05	-0.22	-0.10	-0.27	0.73	1.00											
Rb	0.04	-0.19	-0.13	0.93	0.49	-0.27	0.74	0.99	0.62	0.59	0.90	0.62	0.97	-0.15	-0.31	1.00										
Sr	-0.06	0.13	-0.31	0.72	0.46	-0.75	0.85	0.50	0.38	0.28	0.52	0.57	0.58	-0.30	-0.40	0.58	1.00									
Ta	-0.36	-0.51	0.80	-0.56	-0.55	0.42	-0.49	-0.52	0.15	-0.13	-0.49	-0.33	-0.50	0.75	0.91	-0.55	-0.67	1.00								
Th	-0.02	-0.04	-0.23	0.90	0.66	-0.51	0.87	0.83	0.51	0.64	0.76	0.74	0.84	-0.27	-0.36	0.85	0.81	-0.64	1.00							
U	0.45	0.09	-0.43	0.40	0.31	0.00	0.36	0.52	-0.06	0.50	0.44	0.10	0.40	-0.47	-0.44	0.50	0.29	-0.53	0.37	1.00						
V	0.19	0.39	-0.59	0.45	0.63	-0.02	0.29	0.59	-0.14	0.42	0.45	0.54	0.46	-0.57	-0.64	0.54	0.36	-0.71	0.66	0.36	1.00					
Zr	-0.41	-0.82	0.98	-0.11	-0.24	0.09	-0.14	-0.16	0.57	0.09	-0.15	0.10	-0.06	1.00	0.74	-0.17	-0.31	0.76	-0.27	-0.48	-0.57	1.00				
Zn	0.05	-0.19	-0.02	0.56	0.85	-0.50	0.40	0.40	0.31	0.53	0.31	0.90	0.45	-0.02	-0.18	0.40	0.49	-0.37	0.65	0.21	0.59	-0.03	1.00			
Ni	0.04	-0.33	0.05	0.76	0.84	-0.49	0.56	0.64	0.53	0.63	0.51	0.95	0.68	0.04	-0.13	0.64	0.57	-0.38	0.79	0.30	0.58	0.03	0.94	1.00		
Tree	-0.12	-0.23	0.00	0.89	0.72	-0.596	0.82	0.74	0.63	0.67	0.67	0.87	0.81	-0.04	-0.21	0.77	0.74	-0.48	0.94	0.27	0.57	-0.05	0.91	0.80	1.00	

According to Vine and Tourtelot (1970) elements in sedimentary rocks may be classified as carbonate (Ca, Mg, Mn, Sr) the ones associated with organic matter (Ag, Mo, Zn, Ni, Cu, Cr, V) and the elements indicative of land derived fractions of the sediments (Al, Ti, Ga, Zr, Sc). Land derived elements such as Th, Ti, and Zn are usually associated with heavy minerals such as ilmenite, rutile, zircon, and augite. The correlation coefficients developed from the cross correlation exercise of all the elements shows that most elements show a positive strength of association with Al (Table 6). Ba, Cs, Ga, Rb, Sr, Th, La, Ce, Mo, Ni and TREE all show very high strength of association values with Al ($r > 0.75$) whereas, Si, Ca, Mg, Mn, Hf, Nb, Ta and Z are the only elements that show a negative strength of association with Al. Elements having strongly correlated values with Al ($r > 0.75$) probably share siliciclastic origin with Al and their fluctuations can be linked to the variation in the detrital influx. However, the poor correlation coefficient together with relatively high concentration of Si with respect to the other aluminosilicates associated elements suggest that most of the silicon are present as free silica and has not been added as aluminosilicates (Sackett and Arrhenius, 1962). The strong variational contrast between Si and Ca ($r = -0.86$) also shows that the influx of the free silica strictly determined the carbonate sedimentation of Ewekoro limestone.

The Mn/Sr ratio has been broadly accepted to be more reliable in evaluating the degree of preservation as well as the post-depositional alteration in carbonate-bearing rocks (Nagarajan et al., 2008 and Bassey, 2012). According to the concept of Jacobsen and Kaufman (1999), Mn/Sr < 0.2, Sr values between 150 and 2,500 ppm and $\delta^{18}\text{O}$ between -5 and -10‰, have been utilized to deduce post depositional changes. In this study, a negative correlation between the concentrations of Sr and Mn ($r = -0.75$, $n=13$) could be the consequence of diagenetic alteration, where Mn from meteoric fluids replaces Sr in the carbonate system. These views have been expressed by Veizer (1983). Values from the Mn/Sr ratio imply that the carbonates are predominantly pristine, with localized alterations. The alterations may reflect rock-fluid interaction between the formation and Mn-rich meteoric fluids from the adjacent predominantly clastic formations.

SUMMARY AND CONCLUSIONS

Petrography and geochemical studies of Ibese corehole limestone of the Ewekoro Formation in eastern Dahomey basin shows the limestone is made of sandy biomicrite, biosparite, biomicrite and dolomitic facies. Cementation and recrystallisation of micrite to sparite are the important diagenetic processes that were observed in the carbonates. The limestone is rich in CaO with SiO_2 having a relatively higher concentration than the other aluminosilicates associated oxides. The low concentrations of these of Al_2O_3 , K_2O , Na_2O , TiO_2 , Fe_2O_3 , and P_2O_5 reflect that the basin was free of suspended clays and other siliciclastic materials during carbonate sedimentation. The strong variational contrast

between Si and Ca ($r = -0.86$) also shows that the influx of the free silica strictly determined the carbonate sedimentation of Ewekoro limestone. It has been deduced that the Ewekoro Limestone was deposited in an oxic setting with marginal diagenetic influence. The Ce anomaly (negative, <1) suggests that the limestone was deposited in an oxygenated environment. In addition, the moderate variation in the values ranging between 0.70 and 0.94 (av. 0.85) suggests that there were not much fluctuation in the bottom water oxygen level. The empirical formational temperatures from the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic composition vary between 24.76 - 39.56 °C, suggesting a period of warm climate during the deposition of the carbonates. Also, the estimated depositional setting indicates the limestone to be predominantly marine type with a marginal influence of fresh water diagenesis from the adjacent terrigenous formations.

ACKNOWLEDGEMENTS

The authors are grateful to the staff and management of Acme Laboratory, Canada, as well as that of the Stable Isotope Laboratory of the University of California, for laboratory analyses. We also acknowledge with thanks the useful comment of the reviewers.

REFERENCES

- Adams, J. E and Rhodes, M. L., 1960. Dolomitization by seepage refluxion. AAPG Bulletin 44.12 , 1912-1920.
- Adegoke, O. S., 1969. Eocene stratigraphy of southwestern Nigeria. Bur. Rech. Geol. Min. Mem., 69, 23-43.
- Adekeye, O. A., Akande, O. S., Bale, R. B and Erdtmann, B. D., 2005. Carbon and Oxygen isotopic compositions and diagenesis of the Ewekoro Formation in the eastern Dahomey Basin south western Nigeria. Journal of Mining and Geology, 41, (10): 87-95.
- Adeyemi, M. O., 2014. Petrography, Compositional Characteristics And Stable Isotope Geochemistry Of The Paleocene Ewekoro Formation, Eastern Dahomey Basin, Southwestern Nigeria. Unpublished M.Sc. Thesis, University of Ibadan, Ibadan.
- Armstrong-Altrin, J. S., Madhavaraju, J., Sial, A. N., Kasper-Zubillaga, J. J., Nagarajan, R., Flores-Castro, k and Rodriguez, J. I., 2011. Petrography and Stable isotope Geochemistry of the Cretaceous El Abra Limestones (Actopan), Mexico: Implication on diagenesis. Journal of the Geological Society of India, 77, (4): 349-359.
- Asmerom, Y., Jacobsen, S. B., Knoll, A. H., Butterfield, N. J and Swett, K., 1991. Strontium isotopic variations of Neoproterozoic seawater: implications of crustal evolution. *Geochemica et Cosmochimica Acta*, 55, (10): 2883-2894.

- Bankole, S. I., Shrank, E., Erdtmann, B. D and Akande, S. O., 2006. Palynostratigraphic Age and Paleoenvironments of newly exposed section of the Oshosun Formation in the Sagamu quarry, Dahomey Basin Southwestern, Nigeria. Nigerian Association of Petroleum Explorationists Bulletin, 19, (1): 25-34.
- Bassey, E. E., 2012. Investigation of the signatures and conditions of formation of metacarbonate rocks occurring within the Mamfe embayment of south-east Nigeria. Earth Sci. Res.SJ. 16, (2): 39-56.
- Billman, H. G., 1992. Offshore stratigraphy and paleontology of the Dahomey Embayment, West Africa. Nigeria Association of Petroleum Exploration, bulletin, 7, (2): 121-131.
- Brad, U and Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system: 1. Trace elements: Journal of Sedimentary Petrology, 50, 1219-1236.
- Burke, K., Dessauvage, T. G. F and Whiteman, A. J., 1971. The opening of the Gulf of Guinea and geological history of the Benue depression and Niger Delta. Nature Phys. Sci., 253, 51-55.
- Derry, L. A., Kaufman, A. J and Jacobsen, S. B., 1992. Sedimentary recycling and environmental change in the late Proterozoic: evidence from stable and radiogenic isotopes. Geochim.Cosmochim.Acta 56:1317 – 1329.
- Elueze, A. A and Nton, M. E., 2004. Organic geochemical appraisal of limestones and shales in part of eastern Dahomey basin, southwestern Nigeria. Journal of mining and Geology. 40, (1): 29-40.
- Enu, E. I and Adegoke, O. S., 1988. Microfacies of shallow marine carbonates (Paleocene) in the eastern Dahomey basin, southwestern Nigeria. J. Min Geol. 24, (1 & 2): 51-56.
- Fairchild, I. J and Spiro, B., 1987. Petrological and isotopic implications of some contrasting Late Precambrian carbonates. NESpitsbergen. Sedimentology 34, 973-989
- Folk, R. A., 1959. Practical petrographic classification of limestone. Bull. Assoc. Pet. Geologists, 43, (1): 1-38.
- Friedman, I and O'Neil. 1977. Compilation of stable isotope fractionation factors geochemical interest. 440. USGPO.
- Graf, D. L., 1960. Geochemistry of carbonate sediments and sedimentary carbonate rocks: pt. II, Sedimentary Carbonate Rocks. Information circular/Illinois State Geological Survey; (no. 298).
- Hatch, J. R and Leventhal, J. S., 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U.S.A. Chemical Geology, 99, 65-82.
- Hudson, J. D., 1977. Stable isotopes and limestone lithification. J. Geol. Soc. London, 133, 637-660.
- Jacobsen, S. B and Kaufman, A. J., 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. Chem. Geol., 161, 37±57.
- Jones, B and Manning, D. A. C., 1994. Comparison of geological indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chemical Geology 111, 111-129.
- Jones, H. A and Hockey, R. D., 1964. The Geology of parts of Southwestern Nigeria. Geological Survey of Nigeria Bulletin, 31, 87.
- Kaufman, A. J., Jacobsen, S. B and Knoll, A. H., 1993. The Vendian record of Sr and C variations in seawater: Implications for tectonics and paleoclimate: Earth and Planetary Science Letters, 120, (3-4): 409-430.
- Kingston, D. H., Dishroon, C. P and William, P. A., 1983. Global basin classification system. American Association of Petroleum Geologist. Bulletin 67, 2175-2193.
- Klemme, H. D., 1975. Geothermal gradient, heatflow and hydrocarbon recovery. In: A.G. Fischer and S.Judson (eds), Petroleum and global tectonics. Princeton, New Jersey, Princeton Univ. Press, 251-304.
- Missouri Department of Natural Resources., 2011. Mineral and chemical composition of Pure Limestone, Division of Geology and land Survey.
- Nagarayan, R., Sial, A. N., Armstrong-Atrin, J. S., Madhavaraju, J and Nagendra, R., 2008. Carbon and Oxygen isotope geochemistry of Neoproterozoic limestones of the Shahabad Formation, Bhima basin, Karnataka, southern India. Revista Mexicana de ciencias geologicas, 25, (2): 225-235.
- Nelson, C. S. and Smith, A. M., 1996. Stable oxygen and carbon isotope compositional fields for skeletal diagenetic components in New Zealand Cenozoic nontropical carbonates and limestone: a synthesis and review. Newzealand Jourl. Of Geology and Geophysics. 39, 93-107.
- Nton, M. E and Elueze, A. A., 2005. Compositional characteristics and industrial assessment of sedimentary clay bodies in parts of eastern

- Dahomey Basin, south western Nigeria. *Journal of Mining and Geology* 41, (21): 175-184.
- Nton, M. E and Otoha, O. W., 2011. Lithofacies and Organic geochemical studies of Akinside 1582 well, eastern Dahomey Basin southwestern Nigeria. *Nigerian Association of Petroleum Explorationist*. 23, (1): 107-117.
- Nton, M. E., 2001. Sedimentological and geochemical studies of rock units in eastern Dahomey basin, south western Nigeria. Ph.D Thesis, University of Ibadan, Ibadan. 315p.
- Ogbe, F. G. A., 1970. Stratigraphy of strata exposed in the Ewekoro quarry western Nigeria. In: T.F.J. Dessauvagie and A.J. Whitemann (eds.). *African Geology*, University of Ibadan Press, 305-324.
- Okosun, E. A., 1990. A review of the Cretaceous Stratigraphy of Dahomey Embayment West Africa. *Cret. Res.*, Vol. 11, 17-27.
- Omatsola, M. E and Adegoke, O. S., 1981. Tectonic evolution Cretaceous stratigraphy of the Dahomey Basin. *Journal of Mining and Geology*, 18, (1): 130-137.
- Owen, R. M and Wilkinson, B. H., 1983. Mineralogy and biological controls of the Fe/Ca and Mn/Ca ratios of lacustrine carbonate allochems. *Chemical geology*, Vol. 38, (1): 175-181.
- Peters, S.W., 1978. Dolomitisation of the Ewekoro limestone. *J. Mining and Geol.*, 15, 130-137.
- Pollack, G. D., 2008. Timing and characterization of the changes in the state of Uranium in Precambrian Surface Environments: A Proxy of Oxidation State of the Atmosphere. *Geoscience Dissertation paper 3*
- Pollack, G. D., Krogstad, E. J and Beaker, A., 2009. U-Th-REE Systematics of Organic Shales from the Ca 2.15 Ga Sengoma Argillite Formation, Botswana: Evidence for oxidative continental weathering during the Great Oxidation Event. *Chemical Geology* 260, 172-185.
- Reijers T. J. A and Petters S. W., 1987. Depositional environments and diagenesis of Albian Carbonates on Calabar Flank, S.E Nigeria, *J. Petrol. Geol.* 10, 283-294
- Sackett, W and Arrhenius, G., 1962. Distribution of Aluminium species in the hydrosphere-Aluminium in the ocean. *Geochemical et Cosmochemica Acta*, 26, (9): 955-968.
- Taylor, S. R and McLennan, S. M., 1985. The continental crust: its composition and evolution.
- Turekian, K. K and Wedepohl, K. H., 1961. Distribution of elements in some major units of earth's crust. *Geological Society of America Bulletin*, 72, 175-192.
- Veizer J., 1983. Chemical diagenesis of carbonates: theory and application of trace element technique. In: Arthur M.A., Anderson T.F., Kaplan I.R., Veizer J. and Land L.S. (eds.) *Stable isotopes in sedimentary geology*. Soc. Eco. Petrol. Mineral. Short Course Notes 10, Tulsa, 3.1-3.100
- Vine, J. D and Tourtelot, E. B., 1970. Geochemistry of black shale deposits a summary report. *Economic Geology*. 65, (3): 253-272.
- Whiteman, A. J., 1962. Nigeria: Its Petroleum Geology, Resources and Potential. 1&2 Graham and Troitian. London 394p.
- Williamson, C. R., 1972. Carbonate Petrology of Green River Formation (Eocene), Uinta basin, Utha and Colorado. M.Sc. thesis. University of Utah.