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GEOCHEMISTRY OF THE PALEOCENE LIMESTONES OF EWEKORO FORMATION, EASTERN DAHOMEY BASIN, SOUTHWESTERN NIGERIA: IMPLICATION ON PROVENANCE AND DEPOSITIONAL CONDITIONS.

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ABSTRACT

Thirty three limestone samples of the Paleocene Ewekoro Formation from exploratory drill cores within Ibeshe cement quarry, southwestern Nigeria were investigated for major, trace and rare earth elements abundances using inductively coupled plasma spectrometry (ICP-MS) analytical method. The aims were to investigate the depositional settings and source of rare earth element (REE). The major oxides concentration showed significant variations among the limestone facies. Higher SiO_2, Al_2O_3 and Fe_2O_3 contents were observed in the marly and sandy facies than the fossiliferous limestone, whereas the fossiliferous facies were enriched in CaO content. The trace elements content of the limestones normalized with the Post-Archean Australian Shale (PAAS) values revealed significant enrichment in Nb, Sr and U, whereas Ba, Th, Rb and other trace elements contents were depleted. The PAAS normalized REE + Y of the limestones displayed relatively uniform patterns of (i) slightly enriched LREE; (ii) positive Ce anomaly; (iii) positive Gd anomaly; (iv) positive Eu anomaly (v) high Y/Ho ratio. The characteristics non-seawater-like REE patterns, elevated ΣREE, high La_N/Yb_N ratios and high Y/Ho ratios, suggested that variations in REE contents were mainly controlled by the amount of terrigenous contaminations in the limestones. Ratios of La/Sc, La/Co, Th/Co, Th/Cr, Cr/Th and Th/Sc suggested that the terrigenous inclusions in these limestones were derived mainly from intermediate to felsic source rocks. The negative correlation of Sr with Mn and positive correlations of Eu with elements such as Zr, Y, Th and Hf suggested that the observed positive Eu anomalies in the limestones might be due to diagenetic processes. The geochemical parameters such as Ce anomaly, authigenic U, Mn*, V/(V+Ni), V/Ni ,Th/U ratios indicated that the limestones of Ewekoro Formation were deposited in restricted to open shallow marine environments under fluctuating oxidizing to anoxic conditions.

Keywords: Ewekoro Formation, Rare Earth Elements, Depositional Condition, Provenance, Dahomey Basin.

INTRODUCTION

Geochemistry of sedimentary rocks is a valuable tool to infer factors that control sediment characteristics during and after their deposition and to delineate the relationship between specific units of both clastic and carbonate strata (Nagarajan *et al.*, 2008; Armstrong-Altrin *et al.*, 2009; Frimmel, 2009; Madhavaraju and Lee, 2009). The importance of geochemistry in determining the source area of sedimentary rocks, paleo-weathering conditions as well as tectonic evolutions of sedimentary basins is well established in many literatures (Taylor and McLennan, 1985; Cullers *et al.*, 1988; McLennan *et al.*, 1990; Nagarajan *et al.*, 2007). The concentration of rare earth elements (REE) in clastic and carbonate rocks provides important information on marine depositional conditions like surface productivity variations (Toyoda *et al.*, 1990), oceanic paleo-redox conditions (Wang *et al.*, 1986; Liu *et al.*, 1988; German and Elderfield, 1990; Murray *et al.*, 1991) and diagenetic processes (Nath *et al.*, 1992; Madhavaraju and Ramasamy, 1999; Armstrong-Altrin *et al.*, 2003).

The Ewekoro Formation (Paleocene) is one of the stratigraphic units in the eastern Dahomey Basin. It is composed dominantly of limestone with subordinate thin bands of shale, marl and sand (Jones and Hockey, 1964). The limestone, which is the focus of this study, is of particular importance due to its regional industrial potential for cement manufacturing. Consequently, there are a quite number of geological studies focusing largely on stratigraphy, paleontology, petrology and geochemistry of the limestone of Ewekoro Formation (Jones and Hockey, 1964; Reyment, 1965; Adegoke *et al.*, 1971; Ogbe, 1972; Fayose and Asseez, 1972; Okosun, 1988; Oladeji, 1992; Nton, 2001; Elueze and Nton, 2004; Adekeye *et al.*, 2006;

Akaegbobi *et al.,* 2011). However no detailed study of geochemical constraints on provenance and depositional conditions has been carried out. Hence, this study focuses on the use of geochemical characteristics (including major, trace and rare earth elements geochemistry) to trace the depositional environment, to interpret the possible source of REEs, and to know the reason for variations of Eu and Ce anomalies as well as predict the paleo-redox conditions in the limestones of Ewekoro Formation.

GEOLOGY AND STRATIGRAPHY OF DAHOMEY BASIN

Dahomey Basin is an extensive coastal sedimentary basin on the margin of Gulf of Guinea. It is part of a system of West African margin basins developed during the period of the rifting associated with the separation of South American and African plates and subsequent opening of Gulf of Guinea in the late Jurassic to early Cretaceous (Burke *et al.*, 1971; Whiteman, 1982). Rifting, block faulting and subsidence accompanying opening of Gulf of Guinea led to deposition and accumulation of sediments in the basin (Whiteman, 1982). The Nigerian sector of the basin (Eastern Dahomey Basin) extends from the boundary between Benin Republic and Nigeria to Benin Hinge line. It consists of Cretaceous-Recent sedimentary formations (~3000 m thick) outcropping in an arcuate belt roughly parallel to the coastline (Whiteman, 1982; Billman, 1992) (Fig. 1). The structural setting, general geology and hydrocarbon potential of eastern Dahomey Basin have been summarized by Jones and Hockey (1964), Reyment (1965), Adegoke (1969), Omatsola and Adegoke (1981), Nwachukwu and Adedayo (1987), Ekweozor and Nwachukwu (1989), Billman (1992), Okosun (1998), Nton *et al.* (2006). Billman (1992) divided the stratigraphy of the entire basin into three chronostratigraphic packages; pre-lower Cretaceous folded sediments, Cretaceous sediments and Tertiary sediments.

The oldest dated sediments onshore are the Cretaceous sediments which rest unconformably on the crystalline Basement Complex. Further offshore, the Cretaceous sediments thicken and rest unconformably on the pre-lower Cretaceous sediments (Billman, 1992). In Nigerian sector of the basin, the Cretaceous sequence referred to as Abeokuta Group is sub-divided into three formations; Ise, Afowo and Araromi Formations (Omatsola and Adegoke, 1981). Ise Formation (Neocomian-Albian) is the oldest lithic fill and is unconformably disposed on the basement complex. It comprises of conglomerate and grit at the base, overlain by coarse grained loose sand interbedded with kaolinitic clays (Omatsola and Adegoke, 1981). Afowo Formation is the middle layer of the Cretaceous sequence. It is composed of transitional sand and sandstone with variable but thick interbedded marine shales, siltstone and claystones. The sandy facies are tar bearing, while the shales are organic-rich. The formation has been dated Turonian-Maastrichtian (Billman, 1992). Araromi Formation (Maastrichtian-Paleocene) is the uppermost unit and is made up of fine to medium grained sandstone at the base, overlain by shale and siltstone with interbeds of limestone, marl and lignite.

The Tertiary sediments consist of Ewekoro, Akinbo, Oshosun, Ilaro and Benin Formations. Ewekoro Formation (Paleocene) is composed mainly of fossiliferrous well bedded limestone with subordinate thinly banded shale, marl and sand. The limestone is traceable for a distance of about 320 km from Ghana toward the eastern margin of Dahomey Basin. Akinbo Formation (Paleocene-Eocene) consists of shale and clay units overlying Ewekoro Formation (Ogbe, 1972). Its base is defined by glauconitic band. Oshosun Formation overlies the Akinbo Formation and consists of phosphate-bearing, greenish-grey or beige clay and shale with interbeds of sandstone (Okosun, 1998). Ilaro and Benin Formations are predominantly coarse sandy estuarine, deltaic and continental beds which are difficult to identify on the field.

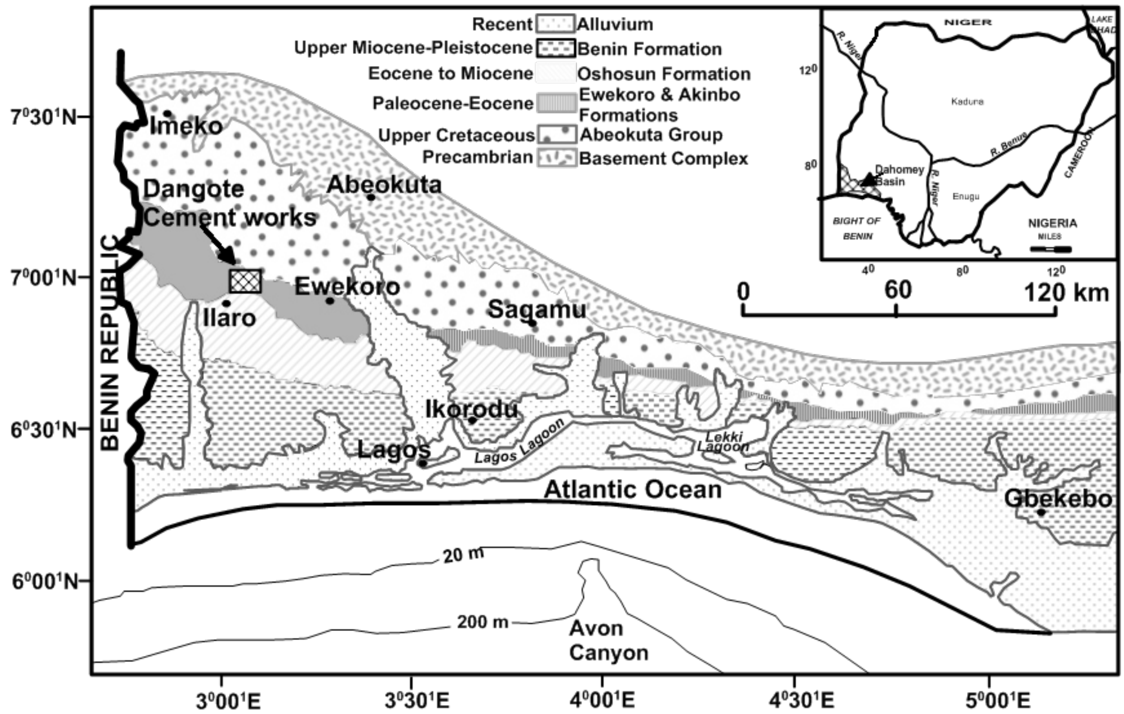

Fig. 1: Regional Geological map of Dahomey Basin showing the extent of the basin from Ghana in the west to Nigeria in the east (modified after Billman, 1992)

MATERIALS AND METHODS

Samples were collected from six exploratory drill cores within Dangote Cement Quarry near Ibeshe village, southwestern Nigeria (Fig. 1). The samples were picked from limestone intervals within the Ewekoro Formation (Fig. 2). For preliminary investigation, 20 representative samples of the limestone were cut into slabs from which thin sections were made for identification of carbonate components. These were studied under a flat stage petrographic microscope. Depositional texture, grain composition and microfossil assemblage were determined in thin sections of the samples.

Whole-rock chemical analysis for major, trace and rare earth elements concentrations in 33 limestone samples were determined using inductively coupled plasma-mass spectrometry (ICP-MS) at Acme Analytical Laboratory Limited, Vancouver, Canada. The selected samples were first wash to remove any contamination and then air dried and ground in an agate mortar. 5 g of each measured sample was placed in a well labeled white cellophane bags and send for geochemical analysis. At the laboratory, two methods of digestion were employed for this analysis; a lithium borate fusion digestion to analyzed for major oxides, rare earths (La-Lu) and refractory trace elements (Ba, Co, Cs, Hf, Nb, Rb, Sr, Ta, Th, U, V, Zr and Y) by Inductively coupled plasma emission spectrometry (ICP-ES) using a simultaneous/sequential Thermo Jarell-Ash Enviro II ICP equipment, and an aqua regia digestion to analyzed for Cu, Mo, Ni, Pb and Zn using a Varian Vista Pro Inductively Coupled Plasma Mass Spectrometer. An internationally recognized standard reference material known as SO-18 was used for reference. Replicate analyses of samples indicate errors better than 1% for major elements, whereas between ranges of 3-5% for both trace and rare earth elements. Loss on ignition (LOI) was determined by heating dried samples to 1000°C for 2 hours. The results of major, trace and rare earth elements were presented in Table 1-3. The trace and rare earth elements (REE) data were normalized relative to Post-Archean Austrialian Shale (PAAS) values of Taylor and McLennan (1985).

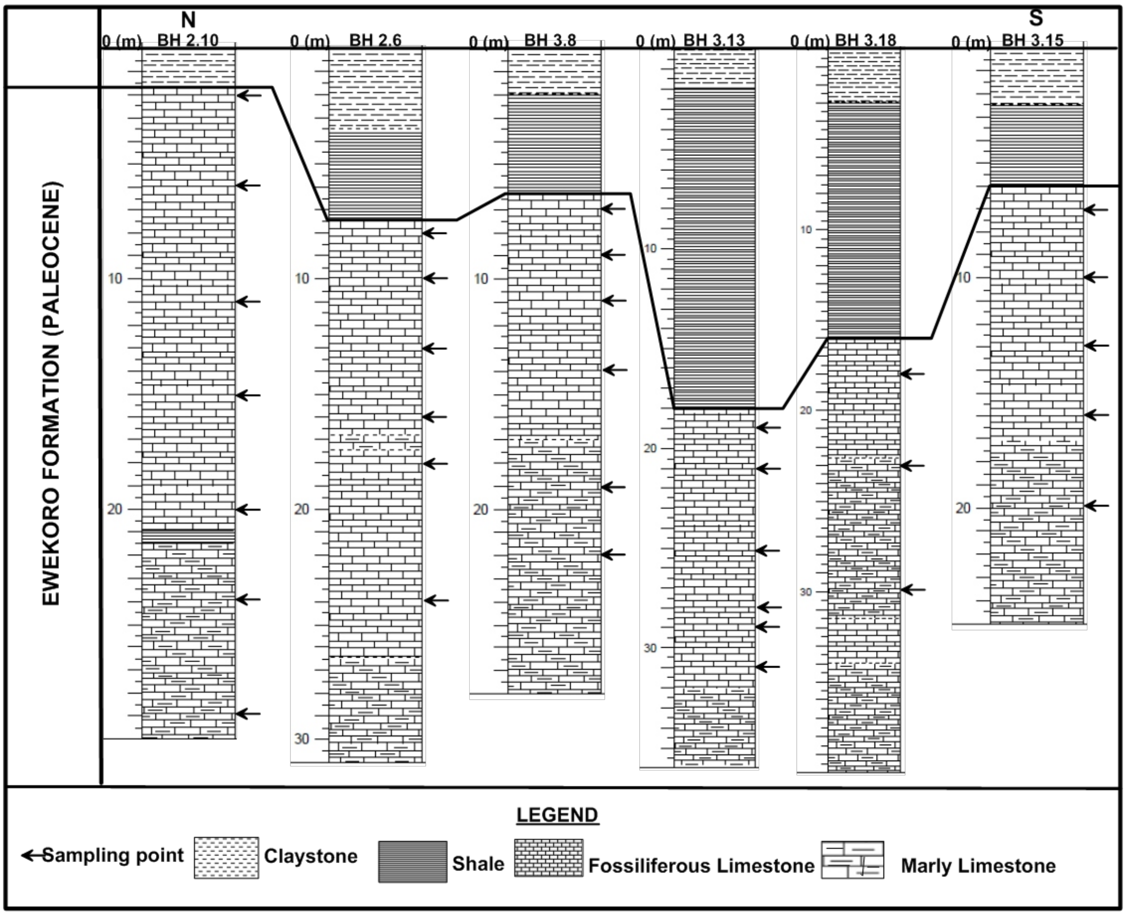

Fig. 2: Well sections of sampled boreholes (N-S) showing depth of the limestone intervals

RESULTS AND DISCUSSION

Petrography

The microscopic study revealed that the framework components of the studied limestone samples consisted of skeletal and non-skeletal grains, sparry calcite, micrite and some quartz grains (Fig. 3). Skeletal grains comprise broken and whole shells of foraminifera, bryozoa, echinodermata, ostracoda, mollusca and brachiopoda. Shell structures of foraminifera and echinoderms were generally preserved, while others had variably been replaced by calcite spar (Fig. 3a-d). Non-skeletal grains consisting mostly of peloids and ooids were identified in the studied samples. Ooids were abundant in many samples and were generally associated with bioclast surrounded with micritic matrix. The presence of ooids and peloids usually indicate low-energy, warm and shallow seas supersaturated with $CaCO_3$ and having restricted circulation. Sparry calcite was present mostly as pore-filling cements. Three generations of sparry calcite cementation were identified in the studied limestones; the earliest generation was fine crystalline rim cement around allochems (Fig. 3e), which was interpreted to have been precipitated under marine phreatic zone. The second generation was relatively large, equant and blocky crystalline cements that filled pore spaces between allochems and also the internal space in allochems (Fig. 3b&c). This was the most common in the studied samples and was interpreted to have been precipitated under meteoric phreatic-burial zone. The third generation of cements occupied fractures (Fig. 3e). Limestone microfacies include bioclastic packstone, Oolitic bioclastic packstone, bioclastic wackstone-packstone and sandy bioclastic packstone that are related to three facies belt of lagoon, shoal and open shallow marine.

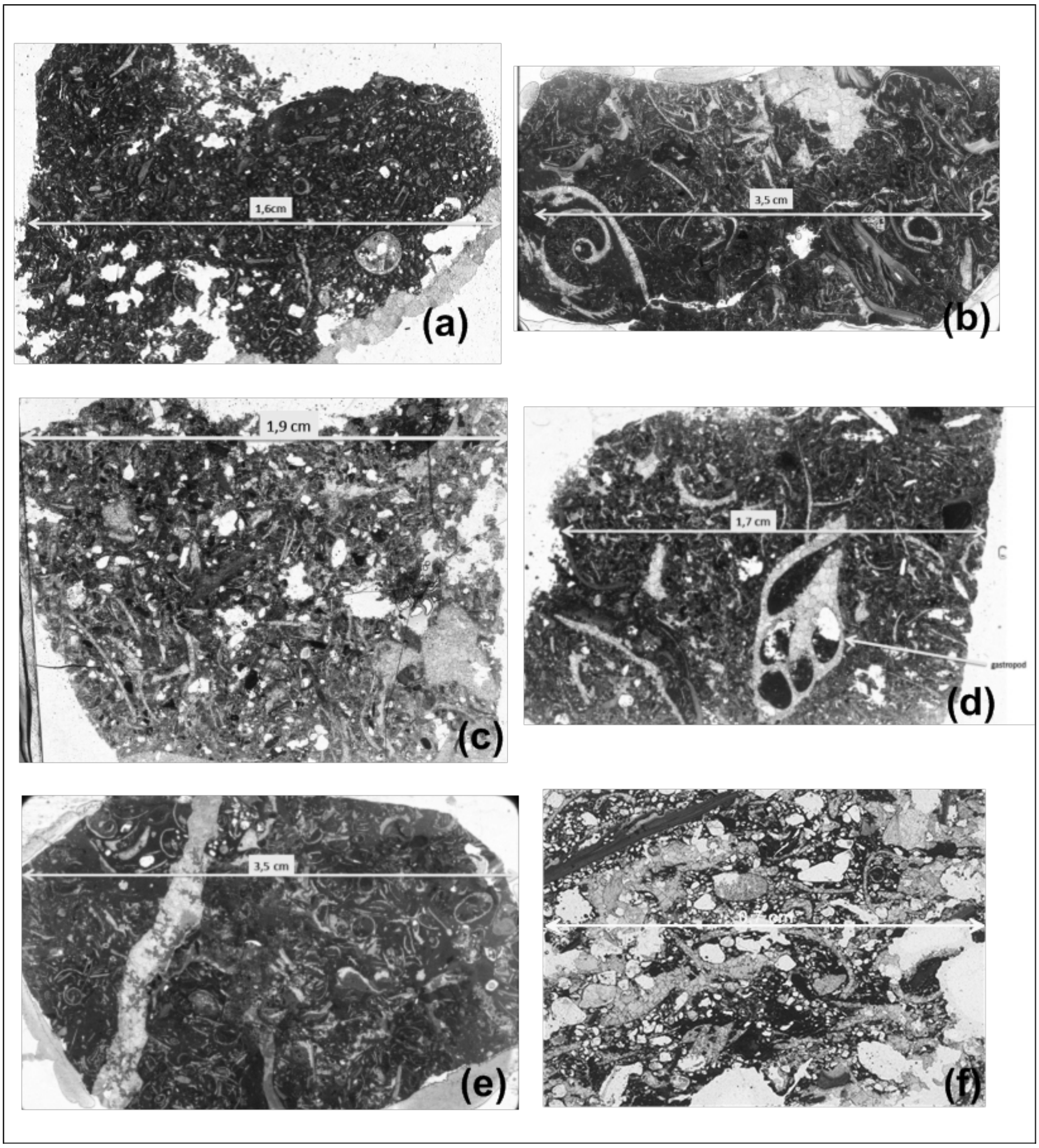

Fig. 3: Thin section photographs of limestone microfacies of the Ewekoro Formation. (a)–Bioclastic packstone containing abundant fragments of echinoderm, molluscan (bivalves and gastropods) and foraminifera floating in micritic matrix. (b)-Oolitic bioclastic packstone containing corals, bivalves gastropods bryozoans, echinoderms, peloids and ooids floating in micritc matrix with some sparite. (c)–Bioclastic wackstone-packstone with abundant fragments of recrystallized molluscs, echinoderms and altered ooids. (d)–Bioclastic packstone with abundant echinoderms, foraminferas, peloids and recrystallized gastropods. (e)–Bioclastic packstone containing ostracods, bryozoans, molluscs, echinoderms and sparite in micrite matrix. (d)–Sandy bioclastic packstone containing sandy quartz grains, bioclasts, few sparite and micrite matrix.

Geochemistry

Major and Trace Elements

The concentrations of major oxides and trace elements in the analyzed limestone samples were presented in Tables 1 & 2 respectively. High variations were observed in the major oxides contents of the analyzed limestones. SiO_2 concentration varied from 1.76 to 48.96%. High SiO_2 contents (~10 - 48%) were observed in marly and sandy limestones, whereas low concentration was found in fossiliferous limestones. The contents of Al_2O_3 (0.37–8.55%) and Fe_2O_3 (0.47–7.06%) showed similar trends in the samples. The CaO content varied from 14.1 to 52.95%. Fossilifeous limestone samples showed higher concentration in CaO than marly and sandy facies. The contents of K_2O, TiO_2, P_2O_5, MnO and Cr_2O_3 were low in all the analyzed samples (Table 1). CaO showed distinct negative correlation with other major elements (statistically significant at

0.01 level), which probably suggested that CaO exhibits different mode of origin. The positive correlations of Al_2O_3 with SiO_2, Fe_2O_3, MgO, K_2O, TiO_2, P_2O_5, MnO and Cr_2O_3 (r = 0.49, 0.81, 0.52, 0.82, 0.92, 0.65, 0.42 and 0.74 respectively) indicated that these elements were associated with detrital phase (Nagarajan *et al.*, 2007).

The PAAS-normalized trace elements concentrations showed significant variations in transition trace elements (TTE: Sc, Co, Cu, Ni, V, Zn, Cr and Mn) and high field strength elements (HFSE: Zr, Hf and Nb) (Fig. 4). Overall, PAAS-normalized patterns of the limestones showed significant enrichment in Nb, Sr and U, whereas Pb, Ba, Th, Rb were lower than PAAS. The Sr content (~119-587 ppm) was lower than the average value of the lithosphere carbonates (610 ppm; Turekian and Wedepohl, 1961). The low Sr content suggested diagenetic alteration due to meteoric water rock interaction.

Table 1: Major oxide concentration (%) for limestones of the Ewekoro Formation

Well ID/Sample No	Depth (m)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Sum
BH2.10/1	3	6.12	1.36	1.25	0.36	49.61	BDL	0.03	0.09	0.22	40.70	99.89
BH2.10/2	7	2.45	0.90	0.47	0.42	52.95	BDL	0.04	0.04	0.13	42.60	99.92
BH2.10/3	11	3.46	0.79	1.50	0.48	51.58	BDL	0.03	0.03	0.21	41.80	99.89
BH2.10/4	15	29.03	0.37	0.96	0.17	38.93	BDL	0.05	0.09	0.43	29.90	99.95
BH2.10/5	20	34.48	4.01	4.76	0.72	28.52	0.04	0.33	0.33	1.69	24.90	99.83
BH2.10/6	24	34.41	8.55	3.29	1.20	25.05	0.03	0.61	0.43	0.63	25.60	99.84
BH2.10/7	29	19.48	0.62	0.92	0.67	42.32	0.01	0.05	0.07	0.12	35.60	99.89
BH2.6/1	8	48.96	5.17	7.06	2.59	14.10	0.01	1.30	0.27	0.89	19.40	99.87
BH2.6/2	10	18.98	4.87	4.52	12.24	21.64	0.03	0.82	0.24	0.71	35.40	99.71
BH2.6/3	13	20.94	2.63	2.43	1.77	37.49	0.02	0.27	0.17	0.36	33.80	99.89
BH2.6/4	16	5.48	1.43	0.90	0.92	49.08	0.02	0.09	0.07	0.24	41.70	99.91
BH2.6/5	18	5.80	1.78	0.74	1.48	48.48	0.02	0.12	0.07	0.23	41.10	99.88
BH2.6/6	24	8.38	1.87	2.79	5.93	40.59	0.01	0.10	0.06	0.18	39.90	99.80
BH3.18/1	18	2.09	0.66	0.80	2.18	50.91	0.02	0.09	0.03	0.19	42.90	99.91
BH3.18/2	24	2.57	0.82	0.73	1.27	51.68	0.02	0.12	0.03	0.15	42.50	99.91
BH3.18/3	30	2.74	0.84	0.74	1.31	51.75	0.02	0.08	0.05	0.13	42.20	99.9
BH3.8/1	7	1.76	0.70	1.09	0.46	52.81	0.02	0.04	0.03	0.10	42.80	99.91
BH3.8/2	9	5.04	0.96	1.71	0.37	50.83	0.01	0.05	0.05	0.20	40.60	99.89
BH3.8/3	11	17.32	0.41	0.61	0.24	44.97	0.02	0.04	0.05	0.31	35.90	99.94
BH3.8/4	14	23.48	1.18	1.62	0.26	39.56	0.05	0.12	0.10	0.18	33.30	99.95
BH3.8/5	19	13.20	0.74	1.48	0.26	46.54	0.02	0.05	0.04	0.33	37.20	99.93
BH3.8/6	22	23.34	0.64	1.18	0.25	40.53	0.01	0.05	0.05	0.11	33.70	99.88
BH3.13/1	19	12.14	1.60	1.46	1.71	45.35	0.02	0.07	0.06	0.26	37.20	99.86
BH3.13/2	21	19.80	2.09	1.96	1.24	40.80	0.02	0.12	0.07	0.22	33.50	99.89
BH3.13/3	25	15.21	1.61	1.42	1.55	43.29	0.03	0.09	0.06	0.30	36.30	99.89
BH3.13/4	28	32.49	0.79	1.15	1.02	35.89	0.02	0.07	0.12	0.29	28.10	99.92
BH3.13/5	29	32.87	0.56	0.81	0.87	35.61	BDL	0.05	0.12	0.18	28.80	99.93
BH3.13/6	31	27.32	0.52	0.66	0.71	38.52	BDL	0.03	0.07	0.16	31.90	99.94
BH3.15/1	7	25.70	5.51	5.31	10.30	19.66	BDL	0.98	0.30	0.69	31.10	99.74
BH3.15/2	10	10.95	1.97	1.99	1.84	43.70	BDL	0.30	0.10	0.50	38.50	99.89
BH3.15/3	13	2.66	0.86	0.88	0.70	51.85	BDL	0.09	0.03	0.34	42.50	99.92
BH3.15/4	16	3.43	1.19	1.04	0.76	51.09	0.02	0.16	0.04	0.13	42.00	99.91
BH3.15/5	20	6.92	1.91	2.06	1.33	47.11	0.03	0.13	0.06	0.23	40.00	99.87

BDL – Below detention Limit

Table 2: Trace elements concentrations (ppm) for limestones of the Ewekoro Formation, eastern Dahomey Basin.

Well ID/Sample No	Depth (m)	Sc	Co	Cu	Ni	V	Zn	Cr	Mn	Zr	Cs	Hf	Nb	Rb	Sr	Th	U	Ba	Pb
BH2.10/1	3	1	11.3	6.6	7.0	27	11	34.2	1316.6	30.0	0.2	0.7	2.1	1.7	235.5	1.6	1.0	232	3.3
BH2.10/2	7	1	-	3.5	-	10	10	34.2	232.3	11.3	0.1	0.3	1.1	1.8	318.4	1.2	1.4	3	2.9
BH2.10/3	11	2	1.5	2.7	4.5	29	51	68.4	232.3	4.1	-	0.3	-	2.6	411.2	2.4	1.9	5	2.3
BH2.10/4	15	1	1.1	4.0	1.6	23	25	27.4	232.3	44.4	-	1.0	1.2	2.4	119.7	1.1	2.1	4	1.8
BH2.10/5	20	7	7.3	2.9	13.5	47	82	123.2	387.2	214.1	1.0	5.7	4.4	16.4	428.6	3.8	12.0	33	6.4
BH2.10/6	24	8	10.0	5.3	16.6	68	69	116.3	309.8	127.3	2.3	3.4	8.7	26.4	387.5	9.0	3.4	47	8.8
BH2.10/7	29	1	2.2	2.8	3.2	14	16	27.4	387.2	135.5	0.2	3.2	1.1	2.2	429.6	1.2	2.0	28	2.1
BH2.6/1	8	5	22.0	4.1	17.9	108	44	335.3	619.6	102.0	1.5	2.8	6.8	44.7	153.3	4.8	7.1	85	9.9
BH2.6/2	10	4	11.1	4.3	17.8	68	50	164.2	1858.7	46.7	1.6	1.2	6.3	30.2	329.7	4.0	3.3	61	4.0
BH2.6/3	13	3	6.2	6.6	8.2	41	23	88.9	309.8	85.6	0.6	2.1	3.4	10.4	333.8	3.2	5.7	36	5.2
BH2.6/4	16	1	1.5	3.1	2.9	23	24	47.9	154.9	26.9	0.6	0.8	1.5	4.6	456.8	1.4	3.3	15	3.3
BH2.6/5	18	2	1.0	2.2	3.3	20	26	61.6	-	18.2	0.6	0.5	1.2	5.5	550.1	2.2	2.7	19	2.9
BH2.6/6	24	2	3.2	1.7	11.6	17	98	95.8	154.9	12.7	0.3	0.3	0.5	5.0	441.4	3.2	2.6	17	3.2
BH3.18/1	16	1	0.4	1.6	-	24	9	34.2	464.7	6.1	0.4	0.4	1.6	5.3	377.3	1.5	7.5	20	1.2
BH3.18/2	20	-	-	1.4	0.5	18	12	54.7	232.3	7.3	0.1	0.4	3.6	4.6	384.7	1.6	2.6	6	2.2
BH3.18/3	22	-	3.5	1.7	6.5	19	18	41.1	154.9	22.9	0.4	0.7	2.8	4.7	430.1	0.8	3.5	22	1.5
BH3.8/1	7	-	5.8	2.0	3.8	15	55	27.4	464.7	7.0	0.2	-	0.2	1.5	382.4	0.9	2.6	95	1.4
BH3.8/2	9	2	2.5	2.0	9.1	29	39	61.6	309.8	21.1	0.3	0.7	13.0	2.4	373.5	1.2	2.4	12	3.5
BH3.8/3	11	1	0.3	2.3	3.2	15	21	47.9	309.8	39.8	-	1.0	-	1.9	235.2	1.6	2.4	7	2.4
BH3.8/4	14	3	1.5	3.4	8.9	14	37	47.9	387.2	41.9	0.2	1.2	0.9	4.4	137.0	1.4	2.3	11	3.4
BH3.8/5	19	2	2.3	2.6	5.7	20	38	27.4	619.6	47.4	0.1	0.9	0.2	2.0	183.8	2.4	1.7	12	4.6
BH3.8/6	22	1	2.2	2.6	4.3	19	23	47.9	542.1	73.0	0.5	2.3	88.1	2.4	199.5	1.2	1.8	12	3.5
BH3.13/1	19	2	2.2	1.9	6.6	13	60	68.4	77.4	14.8	0.3	0.4	0.8	4.2	681.3	2.6	3.0	15	3.5
BH3.13/2	21	2	3.5	1.9	10.9	30	68	102.6	77.4	22.6	0.4	0.5	1.0	5.6	542.0	2.7	2.5	16	4.0
BH3.13/3	25	2	2.1	2.2	9.0	12	69	61.6	77.4	14.0	0.3	0.2	0.5	4.1	587.6	2.4	2.9	16	3.4
BH3.13/4	28	2	1.9	1.3	7.7	-	49	47.9	154.9	130.3	0.2	3.7	1.1	3.2	362.0	1.6	4.1	12	2.1
BH3.13/5	29	-	0.4	0.8	0.3	-	20	41.1	232.3	107.4	-	2.7	1.0	2.2	317.4	1.1	1.7	10	1.5
BH3.13/6	31	-	0.6	1.1	0.6	-	19	34.2	232.3	41.4	0.1	1.2	0.5	1.9	347.8	0.7	1.5	10	1.4
BH3.15/1	7	5	8.5	9.9	15.2	81	49	205.3	1471.5	58.3	1.3	1.5	7.7	31.1	251.9	4.2	3.1	49	5.6
BH3.15/2	10	2	4.6	3.5	6.3	33	17	82.1	542.1	23.2	0.6	0.7	2.6	10.3	338.9	1.9	4.3	26	3.0
BH3.15/3	13	-	1.1	3.1	3.9	17	13	27.4	232.3	6.5	0.3	-	0.6	3.6	351.8	0.9	8.7	5	2.1
BH3.15/4	16	1	1.3	2.3	2.4	28	24	75.3	154.9	9.8	0.6	0.5	0.4	6.1	378.7	2.3	1.6	16	4.2
BH3.15/5	20	3	2.7	2.4	11.9	30	82	116.3	154.9	22.0	0.4	1.0	0.5	5.5	490.0	3.9	3.4	21	3.1

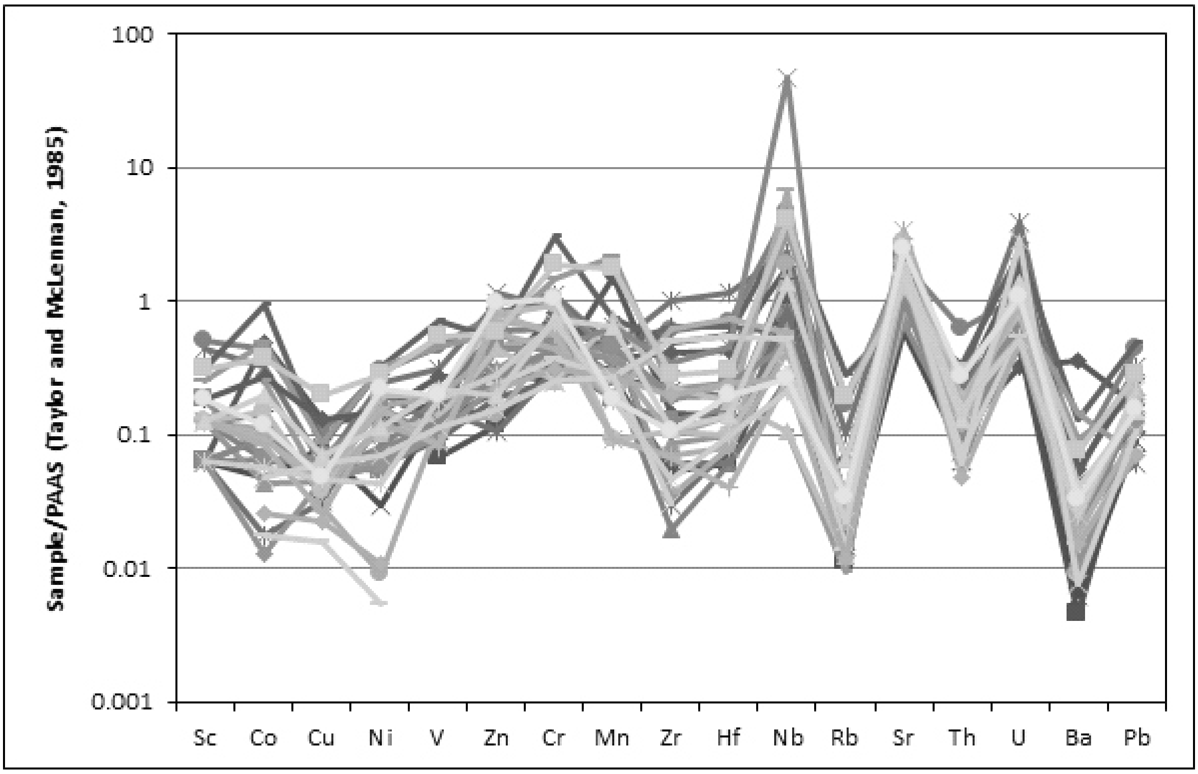

Fig. 4: PAAS-normalized trace elements distribution of limestone samples from Ewekoro Formation.

Rare Earth Elements (REE)

The REE concentrations of the analyzed limestones were presented in Table 3. ΣREE contents (41.4-390.8 ppm; average = 125.1 ppm; n=33) showed significant variations among the samples. The ΣREE contents of the studied limestones were higher than the range for marine carbonates (0.04-14 ppm; Turekian and Wedepohl, 1961) and average typical marine carbonates (~ 28 ppm; Bellanca *et al.*, 1997). The concentration of REE was less in samples with higher CaO content. The positive correlations of SiO_2 and Al_2O_3 with ΣREE content, and negative correlation of CaO with ΣREE content (Fig. 5a-c) supported the observation that ΣREE content in carbonates is mainly controlled by the amount of detrital clays and heavy minerals (Piper, 1974). The PAAS-normalized REE+Y patterns of the limestones (Fig. 6) exhibited a non-seawater like REE+Y pattern with enriched LREE [$(Nd/Yb)_{SN}$: 0.97 to 2.26], variable Ce/Ce* anomalies (0.65 to 1.14), more positive Gd_{SN}/Gd* anomalies and high Y/Ho ratio (27.2-45.0).

Table 3: Rare earth elements concentrations (ppm) for limestones of the Ewekoro Formation, eastern Dahomey Basin.

Well ID/Sample No	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE
BH2.10/1	3	40.4	56.2	9.7	38.4	7.1	1.5	6.7	0.7	4.5	28.7	0.7	1.7	0.2	1.3	0.2	198.0
BH2.10/2	7	13.7	21.1	3.1	13.9	2.5	0.6	2.9	0.4	2.5	19.8	0.4	1.3	0.2	1.0	0.1	83.6
BH2.10/3	11	18.7	38.6	4.8	23.4	3.4	0.7	3.0	0.3	2.0	11.1	0.3	1.0	0.1	0.7	0.1	108.1
BH2.10/4	15	18.4	31.6	4.6	20.6	4.0	0.9	4.0	0.5	3.3	20.6	0.5	1.3	0.2	1.2	0.2	111.8
BH2.10/5	20	68.8	133.5	17.0	68.2	12.9	3.0	11.9	1.5	9.0	49.2	1.5	4.2	0.5	3.7	0.4	385.2
BH2.10/6	24	64.1	131.7	16.9	68.0	13.9	3.1	13.9	1.6	10.9	55.4	1.7	4.6	0.7	3.9	0.5	390.9
BH2.10/7	29	14.1	23.4	3.4	14.4	2.9	0.7	2.8	0.3	2.4	16.0	0.4	1.1	0.2	1.0	0.2	83.1
BH2.6/1	8	38.5	97.1	10.0	43.2	8.3	1.9	7.5	1.1	5.6	33.1	1.1	2.7	0.4	2.3	0.3	252.9
BH2.6/2	10	27.4	64.0	7.0	27.9	5.4	1.2	5.3	0.7	3.5	24.9	0.8	2.0	0.3	1.8	0.2	172.4
BH2.6/3	13	19.9	40.1	5.1	17.9	3.9	0.7	3.7	0.5	2.6	14.9	0.5	1.2	0.2	1.1	0.2	112.4
BH2.6/4	16	11.4	21.2	2.6	11.1	1.9	0.4	1.8	0.2	1.3	9.4	0.3	0.7	0.1	0.6	0.1	63.0
BH2.6/5	18	17.5	42.1	4.8	18.5	3.1	0.6	2.5	0.3	1.8	9.0	0.3	0.7	0.1	0.6	0.1	101.8
BH2.6/6	24	23.0	50.1	6.0	21.9	4.1	0.9	3.5	0.5	2.6	13.7	0.4	1.0	0.2	0.8	0.1	128.6
BH3.18/1	18	9.2	12.7	2.2	7.6	1.7	0.4	1.7	0.3	1.2	7.3	0.3	0.7	0.1	0.5	0.1	46.0
BH3.18/2	24	11.9	19.5	2.7	8.9	2.1	0.5	2.0	0.3	1.5	9.6	0.3	0.6	0.1	0.7	0.1	60.8
BH3.18/3	30	10.0	14.2	2.1	12.6	1.7	0.4	1.9	0.2	1.2	8.0	0.3	0.6	0.1	0.5	0.1	53.8
BH3.8/1	7	14.0	24.1	3.1	10.4	2.2	0.5	2.3	0.3	1.8	12.7	0.3	0.8	0.1	0.6	0.1	73.2
BH3.8/2	9	15.4	26.6	3.4	13.2	2.4	0.5	2.5	0.3	2.0	12.3	0.3	0.9	0.1	0.9	0.2	81.0
BH3.8/3	11	20.9	38.1	5.7	23.0	4.1	1.0	4.1	0.5	3.0	19.4	0.6	1.6	0.2	1.2	0.2	123.5
BH3.8/4	14	14.8	27.9	3.8	14.8	3.1	0.7	2.6	0.4	2.3	12.6	0.4	0.9	0.2	0.8	0.1	85.3
BH3.8/5	19	36.3	69.3	8.5	35.5	6.4	1.2	5.5	0.7	4.1	23.2	0.7	1.8	0.3	1.4	0.2	195.1
BH3.8/6	22	16.6	26.4	4.0	17.4	3.1	0.7	3.0	0.4	2.5	17.0	0.5	1.2	0.2	1.2	0.2	94.2
BH3.13/1	19	18.5	39.9	5.1	19.8	3.3	0.8	2.8	0.4	2.0	12.5	0.5	1.2	0.2	1.0	0.1	107.9
BH3.13/2	21	16.4	37.5	4.5	19.8	3.1	0.7	2.6	0.4	1.7	10.9	0.4	1.0	0.1	0.8	0.1	100.0
BH3.13/3	25	15.8	38.4	4.4	15.3	3.3	0.7	2.5	0.4	1.8	10.6	0.4	0.8	0.1	0.6	0.1	95.0
BH3.13/4	28	15.7	30.8	4.0	16.8	3.2	0.8	3.0	0.5	2.6	16.0	0.5	1.4	0.2	1.1	0.2	96.8
BH3.13/5	29	9.6	17.1	2.3	8.5	1.9	0.4	1.9	0.3	1.6	11.2	0.3	1.0	0.1	0.7	0.1	57.1
BH3.13/6	31	7.3	12.6	1.9	7.1	1.5	0.3	1.3	0.2	1.0	6.6	0.2	0.6	0.1	0.5	0.1	41.1
BH3.15/1	7	33.2	66.9	8.4	32.7	6.9	1.5	6.4	0.7	5.2	30.3	0.7	2.2	0.3	1.6	0.2	197.2
BH3.15/2	10	17.2	60.1	4.5	17.9	3.4	0.7	3.2	0.4	2.5	14.5	0.4	1.1	0.1	0.9	0.1	127.0
BH3.15/3	13	14.8	23.2	3.2	12.8	2.3	0.5	2.1	0.3	1.9	11.1	0.3	0.7	0.1	0.6	0.1	73.9
BH3.15/4	16	13.5	23.5	3.3	11.4	2.4	0.7	2.4	0.3	1.7	11.9	0.3	0.9	0.1	0.6	0.1	73.2
BH3.15/5	20	27.3	57.7	7.1	27.3	5.2	1.1	4.0	0.6	3.0	16.3	0.5	1.4	0.2	1.2	0.2	153.1

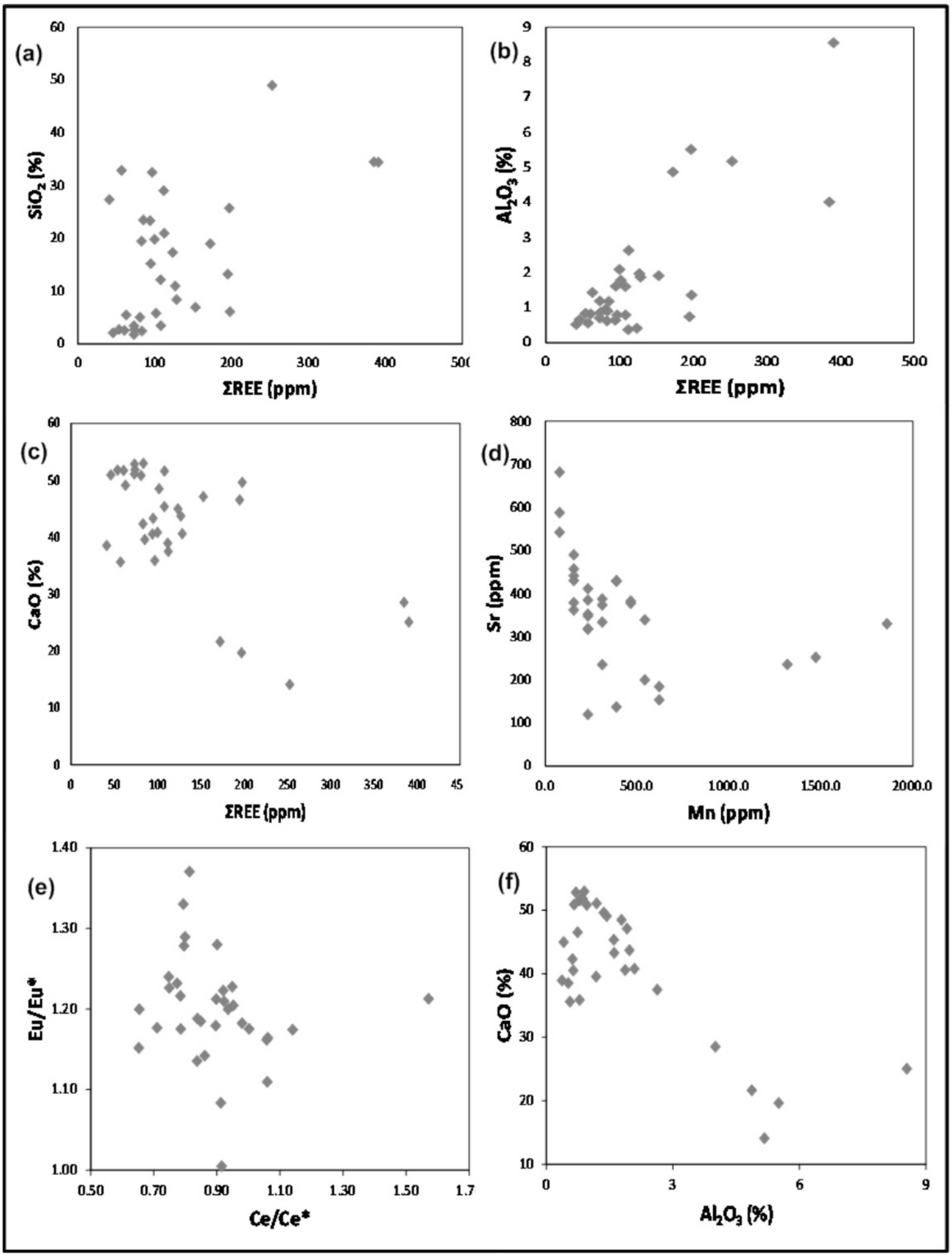

Fig. 5: Bivariate plots showing the relationship between ΣREE vs SiO_2, ΣREE vs Al_2O_3, ΣREE vs CaO, Mn vs Sr, Ce/Ce* vs Eu/Eu* and Al_2O_3 vs CaO contents for limestones of Ewekoro Formation

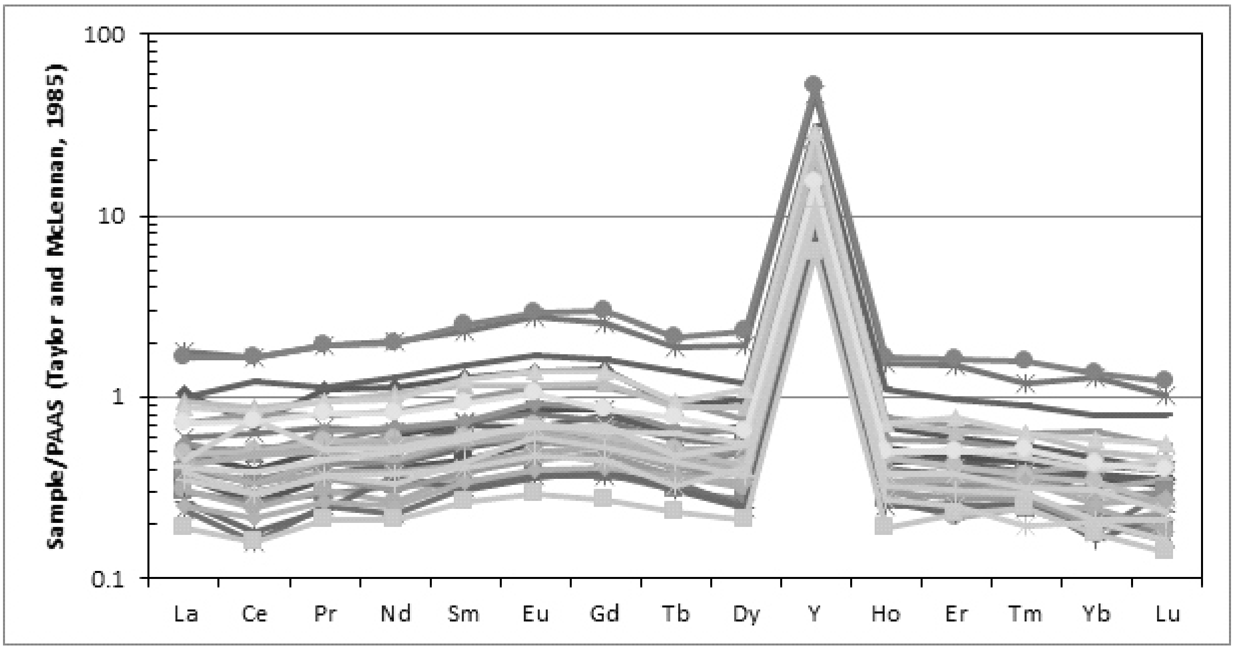

Fig. 6: PAAS-normalized rare earth elements distribution of limestone samples of the Ewekoro Formation.

Possible Source of REE

The non-seawater like pattern of chemical sediments is attributed to high REE concentration due to contamination either with silicates from terrestrial particulate matter (Elderfield *et al.*, 1990); Fe-Mn oxides (Bau *et al.*, 1996) or phosphates and sulphides derived from post-depositional diagenetic process of chemical leaching (German and Elderfield, 1990; Byrne *et al.*, 1996; Zhao *et al.,* 2009; Frimmel, 2009). Al_2O_3 and HFSEs (such as Sc, Th, Hf, Zr and Y) are higher in terrestrial sediments than seawater; hence, can be used to investigate the amount of contamination by terrestrial materials in limestones (Webb and Kamber, 2000). The significant positive correlations of ΣREE with Al_2O_3, TiO_2, Sc, Th, Hf, Zr, Y (r = 0.80, 0.84, 0.88, 0.82, 0.60, 0.62, 0.96 respectively) and negative correlations with CaO (r = -0.63) confirm that the variations of ΣREE in these limestones are associated with detrital input.

The Er/Nd ratio in normal seawater is about 0.27 (De Baar *et al.*, 1988). High Er/Nd ratio in limestone effectively reveals the seawater signature retained by marine carbonate. Addition of detrital material or diagenesis may reduce the Er/Nd ratio to less than 0.1 due to preferential concentration of Nd relative to Er (Bellanca *et al.,* 1997; German and Elderfield, 1989). The Er/Nd ratio of the studied limestones ranging from 0.04-0.12 (average =0.07) support the detrital influence on REE concentration. The detrital contaminations of the studied limestones are further supported by negative and weak correlations between ΣREE content and diagenetic proxies. The weak negative correlations of ΣREE vs Sr (r = -0.13), Ce/Ce* vs Eu/Eu* (r = -0.20), Ce/Ce* vs Y/Ho (r = -0.20) suggest that the influence of diagenetic process on REE concentration is limited.

The La/Sc, La/Co, Th/Sc, Th/Co and Th/Cr ratios showed significant variations in felsic and mafic rocks and are widely used to investigate the source area composition (Wronkiewicz and Condie, 1990; Cox *et al.,* 1995; Cullers, 1995; Armstrong-Altrin *et al.,* 2004; Armstrong-Altrin, 2009). La/Sc, La/Co, Th/Sc, Th/Co and Th/Cr ratios of the limestones of Ewekoro Formation compared with those of sediments derived from felsic and mafic rocks (fine fractions) as well as to average values of upper continental crust (UCC) and PAAS values (Table 4) suggested that the terrigenous inclusions in the these limestones were derived from intermediate to felsic source rocks.

Table 4: Range of elemental ratios of limestone samples in this study compared to the ratios in sediments derived from felsic rocks, mafic rocks, Upper Continental Crust (UCC) and Post-Archean Australian shale (PAAS).

Elemental ratio	Range for limestones of Ewekoro Formation[1]		Range of sediments[2]		UCC[3]	PAAS[3]
	Min	Max	Felsic rocks	Mafic rocks		
Eu/Eu*	1.00	1.37	0.40-0.94	0.71-0.95	0.63	0.66
La/Sc	4.93	40.40	2.50-16.30	0.43-0.86	2.21	2.40
La/Co	1.75	69.67	1.80-13.80	0.14-0.38	1.76	1.65
Th/Sc	0.47	2.30	0.84-20.50	0.25-0.22	0.79	0.90
Th/Co	0.14	5.33	0.67-19.40	0.04-1.40	0.63	0.63
Th/Cr	0.01	0.09	0.13-2.70	0.02-0.05	0.13	0.13
Cr/Th	11.4	69.85	4.00-15.00	25-500	7.76	7.53

[1]Present study, n = 33. [2]Cullers (1994, 2000); Cullers and Podkovyrov (2000); Cullers *et al.* (1988); [3]Taylor and McLennan (1985)

Y/Ho Ratio

Yttrium is inserted between Ho and Dy in the REE pattern (REE+Y) due to its identical charge and similar radii with Ho (Bau, 1996). Y/Ho ratio has been considered as a proxy of seawater composition. Seawater displays high Y/Ho ratio (~44 - 74), whereas terrigenous materials and volcanic ash have constant chondritic Y/Ho values of ~28 (Bau *et al.*, 1995; Nozaki *et al.*, 1997). In this study, the limestone samples showed wide variation in Y/Ho ratio (27.2 – 45.0; average=35.1). Most samples show Y/Ho ratios greater than chondritic value (~28) but less than superchondritic Y/Ho value of seawater. This observed variation in Y/Ho ratio suggested that the limestones of Ewekoro Formation preserved the seawater signature, though contaminated by the influence of terrigenous materials.

Ce Anomaly and Paleo-oxygenation conditions

The Ce anomalies (Ce/Ce*) in marine carbonates have been considered useful as indicators for understanding paleo-redox conditions (Liu *et al.,* 1988; German and Elderfield, 1990). Negative Ce anomaly in marine sediments reveals inclusion of REE directly from seawater or pore water under oxic condition (German and Elderfield, 1990; Bellanca *et al.*, 1997), whereas positive Ce anomaly could be attributed to enrichment of Ce relative to other REE through remobilization of Ce as Ce^{3+} and release to water column in suboxic to reducing condition (De Baar, 1991). The Ce/Ce* values in the studied limestones ranged from 0.65 to 1.57 (average 0.89±0.17, *n* = 33. Over 80% of the analyzed samples had Ce/Ce* values <1. The values for marine waters range from <0.1 to 0.4 (Elderfield and Greaves, 1982; Piepgras and Jacobsen, 1992) whereas the average shales Ce/Ce* is 1 (Murray *et al.*, 1992). Therefore, it appears that the Ce/Ce* values in the studied limestones were influenced by the relative proportions of precipitates from both seawater and clastic contaminations (Murray *et al.*, 1992) in oxic to suboxic depositional condition. However, the interpretation of Ce anomalies from Ce/Ce* values may be complicated due to variable La content and possible by tetrad effect. Sometimes negative Ce anomaly may be overestimated if La is enriched (Bau and Dulski, 1996; Shields and Stille, 2001). The 'true' Ce anomalies and the extent of La enrichment can be assessed using the Pr/Pr* vs Ce/Ce* discriminant diagram (Fig. 7) proposed by Bau and Dulski (1996) modified by Webb and Kamber (2000). Apparently, most of the studied samples showed positive Ce and La anomalies. This indicated that the studied limestones did not have a 'true' negative Ce anomalies as expressed by the Ce/Ce* values. The existence of a 'true' negative Ce anomaly should give Pr/Pr* ≥ 1 (Nagarajan *et al.*, 2011). The Pr/Pr* values (mostly < 1) of samples suggest that the anomalous La enrichment must be the main cause of the negative Ce anomaly.

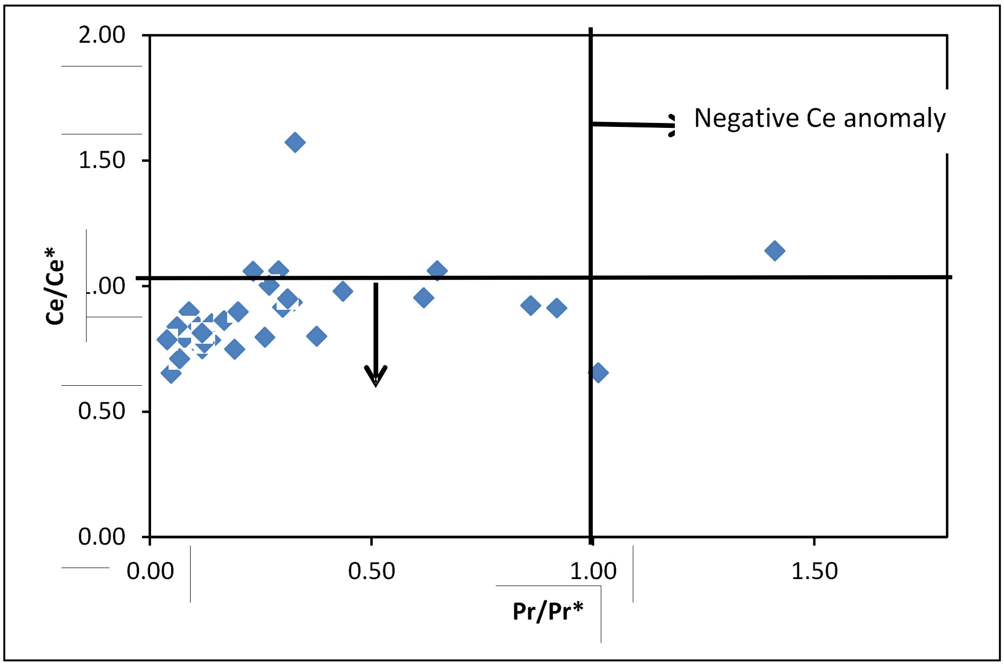

Fig. 7: Plot of PAAS-normalized Pr/Pr* vs Ce/Ce* (modified after Bau and Dulksi, 1996)

Positive Ce anomaly may occur due to detrital and diagenesis inputs (Nath *et al.*, 1997; Madhavaraju and Ramasamy, 1999; Armstrong-Altrin *et al.*, 2003), scavenging process (Masuzawa and Koyama, 1989) and anoxic condition (Liu *et al.*, 1988; German and Elderfield, 1990). Settling particles of deep marine environments will have distinct positive Ce anomaly due to scavenging of Ce over remaining REE. In the studied limestones, Ce/Ce* values did not correlate with scavenging-type particle reactive elements (e.g. Ce/Ce* vs Mn: r=0.09, Ce/Ce* vs Fe: r=0.43, Ce/Ce* vs Pb: r=0.34), but in agreement with shallow marine depositional environments, where scavenging processes were negligible when compared to deep marine environments.

The observed positive Ce anomaly whether influenced by paleo-redox changes can be tested by using other redox sensitive geochemical parameters. Machhour *et al.* (1994) and Bellanca *et al.* (1997) proposed the relation: Mn* = log $\{(Mn_{sample}/Mn_{shale})/(Fe_{sample}/Fe_{shale})\}$ to find out redox condition of the depositional environment of ancient sediments. The mean values for Mn_{shale} and Fe_{shale} to calculate Mn* are 600 and 46,150 ppm respectively (Wedepohl, 1978). Mn* values of the studied limestones range from -0.36 to 1.06. These suggest that the limestones were deposited under reducing to oxidizing conditions.

The V/Ni ratio and the proportionality of vanadium to nickel expressed as V/(V+Ni) have commonly been used to find out information on redox conditions in depositional environments (Lewan and Maynard, 1982; Breit and Wanty, 1991; Galarraga *et al.*, 2008). Galarraga *et al.* (2008) suggested that V/Ni ratio of sediment greater than 3 indicates reducing condition, while V/Ni ratios of 1.9 to 3 and below 1.9 indicate deposition under suboxic and oxic conditions respectively. The V/Ni ratios of the studied samples vary from 1.4 to 36.0 (average = 5.2) implying that these limestones were deposited under variable redox conditions of oxic to anoxic. The V/(V+Ni) values of the studied limestones (0.6 to 1.0) were higher than those for normal marine systems (≤ 0.05; Lewan, 1984). This strongly supported suboxic/anoxic conditions for the limestones. The V/(V+Ni) values greater than 0.8 of many samples (n=23), implied presence of significantly dissolved H_2S in highly reducing bottom water of marine environment in Dahomey Basin during the deposition of Ewekoro Formation.

The Th/U ratio could also be used as a redox indicator with Th/U ratios below 2 indicating anoxic marine conditions, whereas 2-7 and above 7 suggesting oxic and intensely oxic terrestrial environments respectively (Wignall and Twitcher, 1996). In the present study, the Th/U ratios of the analyzed samples varied from 0.1 to 2.6 (average =0.8) implying precipitation of the limestones in suboxic to anoxic conditions. In addition, values of authigenic uranium (authigenic U=Total U-Th/3) is also considered as index of paleo-redox conditions of marine environments (Wignall and Myers, 1988). Values of authigenic U below 2 is considered as to represent oxic depositional conditions, whereas values above 2 are indicative of suboxic and anoxic conditions. Authigenic U content of the studied limestone ranges from 0.4 to 10.7 ppm (average = 2.6), which suggest that these limestones were deposited under oxic to anoxic conditions

CONCLUSION

The Paleocene limestones of the Ewekoro Formation showed significant variations in major, trace and rare elements concentrations. The PAAS-normalized REE+Y patterns of the limestones exhibit non-seawater like REE+Y pattern with enriched LREE, positive Gd_{SN}/Gd^* anomaly Er/Nd and high Y/Ho ratios, suggesting that the REE concentration was mainly influenced by detrital contamination. Geochemical ratios such as La/Sc, La/Co, Th/Sc, Th/Co and Th/Cr suggested that these detrital inclusions were derived mainly from intermediate to felsic source rocks. The strong positive correlations of Eu with Zr, Y, Th and Hf as well as negative correlation of Mn with Sr suggested that the positive Eu anomalies in the limestones may be due to diagenetic processes. The geochemical parameters like Ce anomalies, Mn*, authigenic U, V(V+Ni), V/Ni and Th/U ratios strongly implied that these limestones were deposited in restricted to open shallow marine environments in fluctuating oxic to anoxic conditions.

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