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Trace and Rare Earth Elements Geochemistry of Oshosun Sediments of Dahomey Basin, Southwestern Nigeria

[1]T.R. Ajayi, [1]A.A. Oyawale, [2]F.Y. Islander, [3]O.I. Asubiojo, [2]D.E. Klein and [1]A.I. Adediran
[1]Department of Geology, Obafemi Awolowo University, Ile-Ife, Nigeria
[2]Nuclear Engineering Teaching Laboratory, Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States of America
[3]Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

Abstract: Geochemical data of two borehole samples that penetrated Oshosun formation in Oja-Odan area located in the western part of the Dahomey basin of SW Nigeria were studied. A total of twenty-nine elements, comprising three major, twenty trace and six rare earth elements were considered with the objective of determining the distribution pattern, source rocks and the environment of deposition of the sediments. The results showed that the mean concentrations for Fe, Na and K are 3.725, 0.073 and 0.683 wt.%, respectively. The relatively high Fe content is attributed to accumulation of goethite in the phosphatic shales of the formation. The absolute REE concentrations are in the order of clay>grey shale>black shale. On the average, the patterns indicate that the sediments were derived from granite and grey gneiss of nearby basement rocks but their accumulation was strongly controlled by mechanical and chemical processes of sedimentation. Trace element data on Cr and Co shows that the sediments of Oshosun formation are argillaceous and were deposited in a shallow oxygen poor environment consistent with the model of structural framework of a series of horst and grabens of the Dahomey basin.

Key words: Oshosun formation, trace elements, deposition, dahomey basin

INTRODUCTION

Oshosun formation is one of many sedimentary formations in the Dahomey basin (Fig. 1). Although poorly exposed, the formation stretches along a narrow east-west belt in the coastal plain of Southwest Nigeria (Ako *et al*., 1980). Oshosun formation overlies Ewekoro formation and it is partly marine and partly continental. The maximum thickness is 130 m and it is dominantly composed of pale greenish grey laminated glauconitic clays and shale (Adegoke *et al*., 1991). The sediments of Oshosun formation were deposited during the middle to late Eocene regression (Ako *et al*., 1980).

Ako *et al.* (1980) and Idowu *et al.* (1993), respectively carried out studies on the aspects of stratigraphy, the origin and significance of Oshosun formation. Despite these detailed studies, there is need for trace element geochemical studies as additional multidisciplinary approach of investigating the formation. Trace element geochemical studies of sedimentary basins are useful indicators of sulphide mineralization, depositional environment, facies and diagenetic changes (Lewis and Banderia, 1981). Rare Earth Elements (REE) are known to be more resistant to fractionation by weathering and metamorphism than any other trace elements (Nance, and Taylor, 1974). They show similar chemical characteristics except for Ce and Eu (Piper, 1974a) and exhibit limited fractionation during passage through the ocean. They therefore offer means of identifying the major source rocks of the sediments.

The distribution of major and trace elements, as well as REE patterns of the sediments of Oshosun formation were evaluated in this study to provide a better understanding of the environment of deposition as well as to determine their source rocks.

MATERIALS AND METHODS

Geologic settings: The West African coastal basins were initiated during the separation of South America and African landmasses and the subsequent opening of the Atlantic Ocean, which occurred during Jurassic to Cretaceous period. This is evidenced by sedimentary sequences in Brazil, which are similar to those of West Africa basin (Asmus and Ponte, 1973). The Nigerian sector of Dahomey basin is part of wider Dahomey Embayment, which stretches from Southeastern Ghana to the western flank of Niger Delta (Omatsola and Adegoke, 1981). The axis of the embayment and the thickest sediments occur slightly west of the border between

Corresponding Author: Oyawale Adedapo Adekunle, Department of Geology, Obafemi Awolowo University, Ile-Ife, Nigeria Tel: +234 803 331 2150

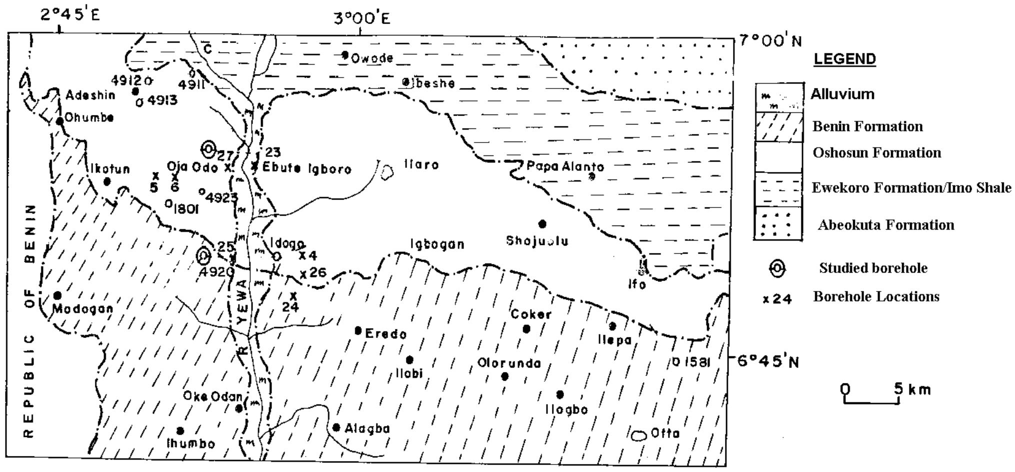

Fig. 1: Simplified Geological map of part of Southwest Nigeria showing location of boreholes 25 and 27

Nigeria and Benin Republic (Antolini, 1968). It is bounded on the west by faults and tectonic structures, which are associated with the Romanche fracture zone. On the eastern end, the Benin Hinge line-a landward extension of the Chain Fracture zone marks the limit of the embayment (Omatsola and Adegoke, 1981).

Dahomey basin's sedimentary sequence comprises of seven formations, which range in age from lower Cretaceous to Recent. The sediments of Oshosun formation in the western part of Dahomey basin are underlain by lower Cretaceous to Paleocene strata: Ise formation, Afowo formation and Araromi formation which belong to the old Abeokuta group and Ewekoro formation (Omatsola and Adegoke, 1981). Overlying Oshosun Formation are old Ilaro formation, coastal plain sands and alluvial deposits. All the sedimentary sequences lie unconformably on the crystalline Precambrian Basement Complex of southwestern Nigeria.

The main lithologic units identified in the Oshosun formation are limestone, black shale, grey shale and clay based on correlation of some borehole sections in the belt. Limestone encountered formed the top of underlying Ewekoro formation. The limestone comprises of shelly biomicrite, algal biosparite and red phosphatic biomicrite units. They are brown, coarse grained with abundant fossils and intensive recrystallisation. They have several units that display rapid but irregular facies changes at a depth of 135 m (Oladeji, 1992).

The black shale of Oshosun formation is generally fissile, well laminated and locally calcareous. The black shale probably belongs to the Imo shale member with some sand and limestone intercalations occurring at a depth of 117 m in the borehole nearest to borehole 27. Glauconite occurs sporadically in the unit.

The grey shale is moderately laminated, calcerous and glauconitic with some phosphatic nodules and limestones intervals (Okosun, 1998). It occurs at the depth of 43.8 to 52 m and at the depth of 70.8 to 97 m of sand beige intercalation. The lower boundary of the grey shale is marked by beige shale or unconsolidated sands.

The clayey unit is light grey in colour, finely laminated, soft and plastic with occasional pockets of grits (Ako *et al.*, 1980). It occurs with intercalations of other lithologies, which are of varied thickness in the top part of the two boreholes. Clay beige of about 18 m thickness caps the borehole section.

Sampling and analytical techniques: Samples were collected from boreholes drilled in 1987 by the Geological Survey of Nigeria (GSN) in Oja-Odan-Idogo areas of Ogun State, Nigeria. The boreholes were drilled during the phosphate exploration project in the area. They range in depth from 99.2 to 200 m and straddle an east-west belt of about 55 km (Fig. 1).

A total of thirty-one samples were selected at ten meters interval from the two boreholes straddling approximately north south of the study area. The boreholes were about 7 km apart covering a good part of the lithology of the study area. The boreholes reached the depth of 145 m, penetrating the top of underlying Ewekoro formation. The samples thereby represent different stratigraphic units penetrated by the boreholes. Corresponding samples collected at similar depths in the two boreholes were grouped together representing each lithologic unit.

Major elements (Na, K and Fe), trace elements and the REE were determined using Instrumental Neutron Activation Analysis technique. The analyses were carried out at the University of Texas, Austin using TRIGA MARK I reactor with a thermal neutron flux of 2×10^{12} n cm^{-2} s^{-1}. The detection system includes a high purity germanium detector connected to 4096 pulse-to-height multi-channel analyses. A local computer controlled data acquisition and reduction. Two irradiation periods were conducted. At the first period, individual samples and standards were irradiated for three minutes followed by a 5 min decay period. After 30-90 min, samples and standards were counted again for 15 min. Neutron flux variations were monitored but no correction was necessary since the maximum deviation in the thermal neutron flux was less than 2%.

The second irradiation was performed 4-8 weeks after the 3 min irradiation. Samples and standards were counted twice. The first was for 1 h each after 18-30 h to determine As, Ga, K, Na, La, Nd and Sm. The second counting was for 8 h each after 4-6 weeks to measure Ba, Ce, Co, Cr, Eu, Fe, Hf, Tb, Th, U and Zr.

RESULTS

Major elements: Potassium concentrations range from 0.061 to 0.079 wt.% with a mean of 0.084±0.017 wt.% whilst Na concentrations vary from 0.014 to 0.031 wt.% with a mean value of 0.02±0.008 wt.% in the clays (Table 1). The values of Na and K concentrations obtained for Oshosun clayey unit are comparable with mean values obtained by Ajayi *et al.* (1989) for Ifon clays, though Oshosun clay samples show comparatively lower K values. Compared with the sandy clay of Ifon area, the mean K value of Oshosun clays is similar to a mean value of 0.108 wt.% for Ifon sandy clay. The narrow Na/K ratios of Oshosun clays which range between 0.15 and 0.39 are comparable with ratios obtained for Ifon clays and this may suggest their leaching from primary source (Jerner *et al.*, 1981). The Fe content of Oshosun clays is much higher than 1.135 wt.% mean value of Fe in Ifon clays. The mean value of 2.305 wt.% for Fe in Ifon sandy-clay however is lower than that of Oshosun clay.

The K values for the grey shale of Oshosun formation range between 0.035 to 0.994 wt.% with a mean value of 0.590±0.416 wt.%. The Na values range between 0.011 to 0.075 wt.% with a mean value of 0.05±0.027 wt.%. The Fe content is between 0.281 to 7.845 wt.% with a mean value of 3.484±2.586 wt.%. The Na/K ratios range between 0.06 and 0.31 (Table 1).

Table 1: Major elements distribution of Oshosun sediments in Dahomey Basin

Lithology	Sample		K (wt.%)	Fe (wt.%)	Na (wt.%)	Na/K
Clay	B1-25		0.095	6.074	0.02	0.21
	B2-25		0.061	2.296	0.014	0.23
	B1-27		0.099	2.363	0.015	0.15
	B2-27		0.079	4.312	0.031	0.39
		Mean (n = 4)	0.084	3.761	0.02	
		Std. Dev.	±0.017	±1.803	±0.008	
		Range	0.061-0.079	2.296-6.014	0.014-0.031	
Grey shale	B3-25		0.035	0.281	0.011	0.31
	B4-25		0.129	1.967	0.035	0.27
	B5-25		0.598	7.845	0.034	0.06
	B3-27		0.890	3.885	0.069	0.08
	B4-27		0.994	4.870	0.075	0.08
	B5-27		0.891	4.239	0.074	0.08
		Mean (n = 6)	0.590	3.484	0.05	
		Std. Dev.	±0.416	±2.586	±0.027	
		Range	0.035-0.994	0.281-7.845	0.011-0.075	
Black shale	B6-25		0.898	3.498	0.037	0.04
	B7-25		0.999	3.906	0.042	0.04
	B8-25		1.164	3.829	0.067	0.06
	B9-25		0.996	3.807	0.037	0.04
	B10-25		0.841	3.288	0.069	0.08
	B11-25		0.575	2.796	0.055	0.10
	B12-25		0.726	3.918	0.444	0.61
	B13-25		0.630	4.308	0.046	0.07
	B6-27		0.905	3.725	0.061	0.07
	B7-27		0.783	3.501	0.062	0.08
	B8-27		0.703	3.950	0.067	0.10
	B9-27		0.746	2.887	0.058	0.08
	B10-27		0.815	3.376	0.059	0.07
	B11-27		0.763	4.287	0.052	0.07
	B12-27		0.863	4.599	0.081	0.09
	B13-27		0.805	6.893	0.282	0.35
		Mean (n = 16)	0.824	3.911	0.07	
		Std. Dev.	±0.145	±0.931	±0.058	
		Range	0.575-1.164	2.796-6.893	0.037-0.282	

The grey shale of Oshosun formation shows higher K mean value compared to 0.262 wt.% for Oshosun clays. The Na and Fe mean values for grey shale (0.05 and 3.484 wt.%) are also higher than Na and K values for Oshosun clays (0.02 and 3.761 wt.%). Compared with major elements (Na, K, Fe) contents of Ifon black shale, the Oshosun grey shale show higher values indicating Na, K and Fe enrichment in Oshosun grey shales. Ajayi *et al.* (1989) obtained average values of 0.14 wt.%, 0.021 wt.% and 1.265 wt.% for K, Na and Fe, respectively. On the other hand, the average value of 2.08 wt.% obtained for K in 18 H.W shale of Duncan (1981) is higher than that of Oshosun grey shale whilst 2.34 wt.% value for Fe and 0.03 wt.% value for Na are comparatively lower than those of Oshosun grey shale (Table 2).

In the black shales, the values of K range between 0.575 to 1.164 wt.% whilst Na range from 0.037 to 0.282 wt.% and Fe contents range from 2.796 to 6.893 wt.%. The Na/K ratios in the Oshosun black shale range from 0.04 to 0.61 (Table 1). The Na, K and Fe contents are higher than Na, K and Fe contents of Ifon black shales. The mean value for K in Oshosun black shale is 0.824±0.145 wt.%; Na mean value is 0.07±0.058 wt.% while Fe has a mean of 3.911±0.931 wt.%. These values are higher compared to mean values of 0.14 wt.% for K, 1.265 wt.% for Fe and 0.021 wt.% for Na obtained for Ifon black shale by Ajayi *et al.* (1989). The narrow Na/K ratio like those of Ifon clastics may suggest leaching from their primary source (Jerner *et al.*, 1981), but higher Na, Ka and Fe values indicated their enrichment in Oshosun black shale relative to Ifon black shale.

The Oshosun black shales however, show lower mean values when compared to 2.7 wt.% for K, 4.04 wt.% for Fe and 1.18 wt.% for Na obtained for average 78 Mesozoic and Cenozoic shale (Clark and Etnst, 1970). Also, Duncan (1981) reported a mean value of 2.08 wt.% for K, 2.34 wt.% for Fe and 0.034 wt.% for Na for average 18 H. W shales (Table 2). The Fe and Na mean values are relatively lower than the values for Oshosun black shale; however, K mean value is relatively higher.

Table 2: Average major element concentrations (wt.%) of Oshosun sediments compared with those of other sediments

Sample	K	Na	Fe
A	2.08	0.03	2.34
B	2.7	1.18	4.04
C	0.32	0.088	1.135
D	0.108	0.01	2.325
E	0.14	0.021	1.265
F	0.262	0.02	3.761
G	0.59	0.05	3.848
H	0.084	0.07	3.911
I	0.683	0.073	3.873

A: Arithmetic average of 18. H. W drill core samples (Duncan, 1981), B: Average of 78 Mesozoic and Cenozoic shale (Clark and Etnst, 1970), C: Ifon clays (Ajayi *et al.*, 1989), D: Ifon Sandy clays (Ajayi *et al.*, 1989), E: Ifon Black shale (Ajayi *et al.*, 1989) F: Oshosun clays (This study), G: Oshosun grey shale (This study), H: Oshosun black shale (This study), I: Average of all Oshosun sediments (This study)

Trace elements: The twenty trace elements analyzed for in Oshosun sediments are grouped as compatible and incompatible trace elements. The compatible trace elements include Cr, Ni and Zn. The remaining elements, Ba, Co, Cs, Au, Br, Ga, Zr, Ge, Hf, Rb, Sb, Sc, Se, Sr, Ta, Th and U are incompatible elements.

In clays, the mean values of Ni, Cr and Zn are 036.36±15.77 ppm, 108.37±44.84 ppm and 101.15±43.9 ppm, respectively. Ba, Co, Cs, Br, Ga, Zr, Ge, Hf and Rb show mean values of 159.29±78.01 ppm, 5.14±3.43 ppm, 2.64±1.90 ppm, 2.08±0.93 ppm, 18.52±7.12 ppm, 64.78±21.67 ppm, 0.96±0.43 ppm, 17.22±0.34 ppm and 36.58±42.82 ppm, respectively. Others show mean values of 0.30±0.1 ppm (Sb), 1.35±0.13 ppb (Au), 14.23±4.81 ppm (Sc), 190.7±267.25 ppm (Se), 166.83±154.41 ppm (Sr), 0.21±0.12 ppm (Ta), 18.68±5.12 ppm (Th) and 1.21±0.22 ppm (U) (Table 3).

Gross (1964) obtained average value of 59 ppm for Cr in varved diatomaceous clay-silt of oxygen poor environment. This value is much lower than mean value of 108.37±44.84 ppm for Cr in Oshosun clay. Cobalt mean value of 5.14±3.43 ppm in Oshosun clay is however relatively lower than corresponding value of 7 ppm in varved diatomaceous clay-silt. The U mean value of 1.21 ppm is lower than 12 ppm obtained for floor and mud of variable composition while the Th mean value of 8.68 ppm in Oshosun clay is higher than 11 ppm mean value for the floor and mud of variable composition obtained by Landergreen and Manhem (1963). This comparison suggests a near oxygen poor environment of deposition for Oshosun clays. The trace elements show a slightly uniform concentration to depletion with depth in Oshosun clays (Table 4a and b). However, Se and Ta enrichment, compared to other lithologies delineate the clayey unit.

The compatible trace element plot shows high mean values with large standard deviation for Cr and Zn, while Ni has low mean values (Table 3). In the grey shales, the mean values for the compatible trace elements range from 43.79±22.87 ppm for Ni to 124.61±95.69 ppm for Zn. Cr has a mean value of 112.48±47.89 ppm. The incompatible trace elements show mean values of 168.85±31.67 ppm (Ba), 12.02±10.88 ppm (Co), 3.60±3.06 ppm (Cs), 1.52±0.33 (Au), 1.68±0.46 ppm (Br), 14.4±11.57 ppm (Ga), 44.87±18.59 ppm (Zr), 1.5±0.86 ppm (Ge) and 11.53±5.67 ppm (Hf). Other ean values are 56.56±50.42 ppm (Rb), ppb 0.23±0.11 ppm (Sb), 39.85±26.08 ppm (Se), 120.78±55.78 ppm (Sr), 0.11±0.14 ppm (Ta), 12.49±6.19 ppm (Th) and 0.49±0.23 ppm (U) (Table 3).

Table 3: Trace Element distribution (ppm) of Oshosun sediments and Comparison with other sediments in Dahomey basin

	Clay			Grey shale			Black shale								
Element	Mean (n=4)	Std. Dev	Range	Mean (n = 6)	Std. Dev	Range	Mean (n = 16)	Std. Dev	Range	A	B	A.S	B.S1	B.S2	SH
Ba	159.29	±78.01	49.78-234.74	168.85	±31.67	108.1-192.4	225.43	±243.41	107.4-1132.3				323	450-700	580
Co	5.14	±3.43	2.09-9.87	12.02	±10.88	0.38-27.19	9.1	±5.05	2.96-17.09	7	12		26	5.5	19
Cr	108.37	±44.84	64.87-255.76	112.48	±47.89	33.36-152.1	209.09	±84.33	93.46-441.06	59	80	100	164	10-500	90
Cs	2.64	±1.90	0.76-5.29	3.6	±3.06	0.09-7.49	3.28	±1.26	2.16-4.69						
**Au	1.35	±0.13	1.2-1.5	1.52	±0.33	1.1-1.8	1.61	±0.66	1.0-3.5						
Br	2.08	±0.93	1.2-3.0	1.68	±0.46	0.93-2.16	4.41	±2.39	2.62-59.23						
Ga	18.52	±7.12	12.43-26.92	14.4	±11.57	1.51-26.18	13.69	±3.1	10.0-23.24				29		19
Zn	101.15	±43.9	63.46-165.45	124.61	±95.69	21.64-302.6	114.24	±30.1	80.82-182.13						
Zr	64.78	±21.67	41.01-91.05	44.87	±18.59	24.98-78.35	27.73	±15.36	10.22-67.95				417	100-1000	160
Ge	0.96	±0.43	0.71-1.19	1.5	±0.86	0.27-2.97	1.57	±0.48	0.83-2.43						
Hf	17.22	±0.34	8.69-23.7	11.53	±5.67	6.65-22.08	5.38	±3.62	1.6-14.92						
Ni	36.36	±15.77	22.62-53.66	43.79	±22.87	10.36-68.38	38.56	±8.99	25.43-54.29			70			
Rb	36.58	±42.82	9.91-100.56	56.56	±50.42	3.65-120.62	83.71	±23.7	58.98-133.75			56.5			
Sb	0.30	±0.1	0.17-0.45	0.23	±0.11	0.1-0.41	0.43	±0.59	0.15-2.58			0.23			
Sc	14.23	±4.81	7.85-18.1	13.64	±8.1	3.28-21.45	12.57	±2.66	8.95-19.56			13.6			
Se	190.7	±267.25	51.66-591.52	39.85	±26.08	10.75-78.48	53.25	±26.28	19.17-110.81			39.8			
Sr	166.83	±154.41	74.13-397.83	120.78	±55.57	57.7-207.43	284.26	±116.52	90.01-466.45			120			
Ta	0.21	±0.12	0.12-0.372	0.11	±0.14	0.011-0.34	0.043	±0.04	0.006-0.132			0.11			
Th	18.68	±5.12	15.52-26.32	12.49	±6.19	5.12-19.05	9.74	±2.11	6.89-14.62		11	12.5	21	12	
U	1.21	±0.22	1.05-1.55	0.49	±0.23	0.51-1.15	0.93	±0.24	0.56-1.62		12	12.5	8.4		3.7

**Au Values in ppb, A - Varved diatomaceous clay-silt (Gross, 1964), B - Floor and mud of variable composition (Landergreen and Manhem, 1963), A.S - Average of compatible elements in World's average shale (Taylor, 1964; 1966; 1969), SH- Turekian and Wedepohl's average shale (Turekia and Wedepohl, 1961), B.S1 - Black Lignitic shale of Ifon sediments (Ajayi *et al.*, 1989), B.S2- Black shale (Hawkes and Webb, 1962)

Table 4a: Trace element concentration (ppm) of oshosun sediments in BH 25 with depth in Dahomey basin

Depth (m)	Ba	Co	Cr	Cs	**Au	Br	Ga	Zn	Zr	Ge	Hf	Ni	Rb	Sb	Sc	Se	Sr	Ta	Th	U
5	176.61	5.361	137.15	2.08	1.2	2.67	26.92	88.75	72.24	1.19	19.89	45.81	17.82	0.45	18.1	62.23	96.06	0.128	26.32	1.55
15	49.78	2.09	64.87	0.76	1.3	1.2	12.43	63.46	54.78	0.71	16.59	22.62	9.91	0.17	7.85	591.5	74.13	0.372	17.08	1.05
25	108.09	0.38	33.36	0.09	1.4	0.93	1.51	21.64	45.39	0.27	13.37	10.36	3.65	0.1	3.28	10.75	57.7	0.011	5.12	0.51
35	178.75	2.84	86.82	0.81	1.3	1.88	4.27	66.28	24.98	1.47	7.57	32.39	9.16	0.18	5.85	17.14	79.55	0.013	6.15	0.61
45	168.19	5.31	101.94	1.87	2.0	1.65	6.1	302.56	78.35	1.44	22.08	31.93	56.08	0.41	10.56	31.7	92.76	0.07	10.55	1.15
55	191.86	3.55	189.46	4.29	1.5	3.03	12.84	87.63	40.89	1.79	12.29	46.7	96.38	0.34	13.7	39.04	90.01	0.006	11.7	0.92
65	141.13	3.28	187.87	3.97	1.0	2.92	11.27	80.82	53.93	1.65	14.92	25.43	109.0	0.22	11.7	40.74	131.3	0.015	10.54	1.04
75	192.52	3.85	246.98	5.28	1.7	3.96	14.25	106.11	30.84	2.26	7.02	26.47	135.7	0.29	14.76	49.07	311.9	0.006	12.59	1.22
85	161.39	4.13	262.67	4.93	1.2	3.65	15.3	87.35	32.84	1.93	8.03	33.3	121.8	0.3	15.41	43.37	114.3	0.031	11.82	0.83
95	179.93	3.87	257.89	4.19	1.5	8.1	12.87	146.14	13.7	1.74	3.81	33.38	97.63	0.43	11.56	88.94	456.2	0.08	8.75	0.83
105	157.53	2.96	314.04	2.96	1.8	10.98	10	95.04	17.95	1.26	3.32	37.85	59.83	0.3	9.09	65.83	466.4	0.042	9.14	0.88
115	175.99	8.09	399.67	3.55	1.0	3.39	13.17	87.62	16.41	2.43	3.95	34.33	71.43	0.25	11.92	46.6	219.7	0.131	9.1	0.66
125	159.13	11.78	315.86	2.63	1.0	7.43	14.64	121.19	20.4	1.47	4.66	47.05	64.99	0.56	11.97	110.8	309.2	0.038	10.15	0.78
135	99.27	12.22	109.29	2.46	1.3	3.27	9.99	75.94	13.59	1.05	2.78	28.39	43.58	0.21	8.76	34.37	92.46	0.039	6.63	0.47
145	239.74	22.73	147.77	5.48	1.3	1.66	22.5	111.21	37.52	0.98	9.54	57.19	121.6	0.27	19.99	61.61	151.5	0.007	17.35	0.47

**Au Values in ppb

Table 4b: Trace element concentration (ppm) of Oshosun sediments in BH 27 with depth in Dahomey basin

Depth	Ba	Co	Cr	Cs	**Au	Br	Ga	Zn	Zr	Ge	Hf	Ni	Rb	Sb	Sc	Se	Sr	Ta	Th	U
5	234.74	3.24	75.68	2.42	1.40	3.10	12.77	86.20	91.05	0.91	23.70	23.33	17.99	0.31	13.11	51.66	99.30	0.156	15.77	1.16
15	176.01	9.87	155.76	5.29	1.50	1.32	21.95	165.45	41.01	1.17	8.69	53.66	100.56	0.25	17.84	57.36	397.83	0.192	15.52	1.07
25	194.91	14.93	152.08	5.41	1.80	1.40	23.47	120.17	42.74	2.97	10.19	54.35	73.93	0.23	19.68	65.05	129.02	0.340	19.05	0.80
35	192.36	27.19	149.60	5.91	1.50	2.16	24.89	115.74	47.06	1.53	9.34	68.58	120.62	0.25	20.96	75.48	158.19	0.135	18.81	0.96
45	170.80	21.45	151.10	7.49	1.10	2.06	26.18	121.28	30.67	1.34	6.65	65.80	115.93	0.23	21.45	48.97	207.43	0.080	15.66	0.85
55	210.12	15.38	170.10	6.29	3.50	3.60	23.24	120.22	27.24	1.82	6.30	52.08	94.46	0.28	19.56	71.25	223.34	0.132	14.62	1.17
65	107.40	11.01	158.21	3.82	1.50	4.98	13.26	119.56	10.22	1.44	2.43	33.71	75.43	0.18	10.65	95.01	234.04	0.059	7.03	0.79
75	130.80	14.30	93.46	2.82	1.20	2.62	10.49	182.13	21.85	0.84	3.60	43.38	60.91	0.15	8.95	25.92	327.88	0.045	6.89	0.67
85	206.19	10.01	105.70	3.30	1.00	2.74	12.58	85.29	14.94	1.03	3.24	48.12	69.03	0.18	10.14	24.60	242.54	0.027	7.26	0.76
95	167.40	13.93	150.35	3.63	2.40	2.65	13.60	103.58	22.10	2.29	4.06	28.27	66.92	0.22	11.94	39.19	292.50	0.033	9.29	0.91
105	150.17	14.77	143.91	3.75	1.60	2.64	15.44	117.69	23.91	0.83	3.36	35.93	91.69	0.20	12.56	46.48	298.66	0.025	9.12	0.81
115	143.45	17.09	141.76	3.62	1.60	3.45	15.58	170.61	26.85	1.36	4.08	54.29	65.90	0.24	12.31	46.00	438.20	0.012	9.26	0.97
125	1132.36	7.66	207.67	2.16	2.30	4.46	10.56	116.85	67.95	1.25	1.60	36.65	58.98	2.58	14.90	19.17	391.54	0.008	8.53	1.62
135	295.68	3.38	52.14	0.63	4.20	59.23	3.17	256.73	45.58	1.81	0.81	88.96	51.59	19.22	0.93	28.91	1236.72	0.020	0.85	1.55
145	434.63	9.63	161.16	1.48	2.10	55.75	5.05	236.26	11.34	0.68	1.57	47.15	82.68	0.29	5.09	12.72	106.13	0.004	0.91	1.15

**Au Values in pp

The Co mean value of 12.02 ppm for the grey shale is comparable to 7 ppm mean value for varved diatomaceous clay-silt of Gross (1964), but the Cr value of 59 ppm of the diatomaceous clay-silt is lower. This suggests anoxygen-poor environment obtained mean values of 580 ppm for Ba, 19 ppm for Co, 90 ppm for Cr, 160 ppm for Zr and 3.7 ppm for U. These averages are higher than corresponding averages for Oshosun grey shale (Table 3). However, the Thorium mean value is comparable. Table 3 shows wide variations in concentration of compatible trace elements. Zinc and Cr show higher mean values than Ni.

Compared with averages of compatible trace elements in world average shale of Taylor (1964; 1966; 1969), Oshosun grey shales show higher mean values of 112.48 ppm and 124.61ppm for Cr and Zn, respectively. These values are however, comparable with mean value of 100 ppm for world average shale for both elements. The

Table 5: Absolute concentration (Ab) of REE (ppm) and Chondrite-normalized values (CN) in the Sediments of Oshosun formation

Lithology	Sample	Values	La	Ce	Nd	Sm	Eu	Tb	SREE	La_N/Sm_N
Clay	B1-25	Ab	78.66	152.5	34.81	6.21	1.18	0.65	274.01	
		CN	231.35	167.58	54.39	31.85	16.16	13.83		7.26
	B2-25	Ab	50.72	97.4	28.46	0.23	0.58	0.37	176.76	
		CN	149.18	107.03	44.47	1.18	7.95	7.87		126.42
	B1-27	Ab	56.07	102.4	42.13	8.89	1.42	0.92	211.83	
		CN	164.91	112.53	65.83	45.59	19.45	19.57		3.62
	B2-27	Ab	80.81	197.9	75.48	16.6	2.52	1.00	374.31	
		CN	237.68	217.47	117.94	85.13	34.52	21.28		2.79
	Average	Ab	65.57(4)	137.55(4)	45.22(4)	7.98(4)	1.43(4)	0.74(4)	258.49	
		CN	192.85	151.15	70.66	40.94	19.52	15.64		4.71
Grey shale	B3-25	Ab	34.92	94.80	27.51	4.34	0.63	0.31	162.51	
		CN	102.71	104.18	42.98	22.26	8.63	6.60		4.61
	B4-25	Ab	24.29	56.60	25.62	3.70	0.78	0.46	111.45	
		CN	71.44	62.20	40.03	18.97	10.68	9.79		3.77
	B5-25	Ab	28.63	80.70	34.90	9.87	2.14	1.23	157.47	
		CN	84.21	88.68	54.53	50.62	29.32	26.17		1.66
	B3-27	Ab	77.08	154.60	42.76	12.40	2.41	1.37	290.62	
		CN	226.71	169.89	66.80	63.59	33.01	36.60		3.57
	B4-27	Ab	85.49	183.40	57.74	15.71	2.85	1.72	347.91	
		CN	251.44	201.54	91.78	80.56	39.06	35.60		3.12
	B5-27	Ab	70.52	146.20	52.40	11.92	2.24	1.11	284.39	
		CN	207.41	160.66	81.88	61.13	30.68	23.62		3.39
	Average	Ab	53.49(6)	119.38(6)	40.32(6)	9.66(6)	1.84(6)	1.03(6)	225.72	
		CN	157.32	131.18	63.0	49.54	25.21	21.91		3.18
Black shale	B6-25	Ab	41.08	86.3	32.75	7.09	1.44	0.78	169.44	
		CN	120.82	94.84	51.17	36.36	19.73	16.60		3.32
	B7-25	Ab	38.29	85.6	41.38	7.91	1.67	0.91	175.76	
		CN	112.62	94.07	64.66	40.56	22.88	19.36		2.78
	B8-25	Ab	54.35	121.8	41.17	9.91	2.10	1.12	230.45	
		CN	159.85	133.85	64.33	50.82	28.77	23.83		3.15
	B9-25	Ab	48.24	90.2	32.30	5.73	1.17	0.61	178.25	
		CN	141.88	99.12	50.47	29.39	16.03	12.98		4.83
	B10-25	Ab	38.00	76.7	28.77	5.20	1.15	0.57	150.39	
		CN	111.77	84.29	44.95	26.67	15.75	12.13		4.19
	B11-25	Ab	33.48	73.0	27.51	6.31	1.25	0.75	142.3	
		CN	98.47	80.22	42.98	32.36	17.12	15.96		3.04
	B12-25	Ab	39.52	75.0	39.12	6.55	1.19	0.76	162.14	
		CN	116.24	82.42	61.13	33.59	16.30	16.17		3.46
	B13-25	Ab	38.64	74.0	32.75	5.81	1.15	0.57	152.92	
		CN	113.65	81.32	51.17	29.79	15.75	12.13		3.82
	B6-27	Ab	65.55	137.6	47.12	11.59	2.12	1.09	265.01	
		CN	192.79	151.21	73.63	59.44	29.04	23.19		3.24
	B7-27	Ab	30.95	60.1	29.21	5.03	1.00	0.53	126.83	
		CN	91.03	66.04	45.64	25.80	13.70	11.28		3.53
	B8-27	Ab	44.01	93.3	33.78	8.34	1.70	0.89	182.02	
		CN	129.44	102.53	52.78	42.77	23.29	18.94		3.03
	B9-27	Ab	31.37	63.3	20.92	5.80	1.11	0.61	123.61	
		CN	93.74	69.56	32.69	29.74	15.21	12.98		3.15
	B10-27	Ab	37.37	77.0	30.02	6.40	1.22	0.68	152.69	
		CN	109.91	84.62	46.91	32.82	16.71	14.47		3.35
	B11-27	Ab	41.59	85.3	37.22	7.43	1.42	0.75	17371.00	
		CN	122.32	93.74	58.16	38.10	19.45	15.96		3.21
	B12-27	Ab	68.36	179.9	77.41	18.54	3.51	2.03	349.75	
		CN	201.06	197.69	120.95	95.08	48.08	43.19		2.12
	B13-27	Ab	53.30	95.6	51.19	8.91	1.97	1.49	212.46	
		CN	156.76	105.05	79.98	45.69	26.99	31.70	3.43	
	Average	Ab	44.04(16)	92.17(16)	37.66(16)	7.91(16)	1.57(16)	0.88(16)	184.2316)	
		CN	129.52	101.29	58.84	40.56	21.51	18.72		3.19
Chondrite values			0.34	0.91	0.64	0.195	0.073	0.047		

* Numbers in parenthesis indicate number of samples used to calculate average values, ** Chondrite values obtained from Laul and Rancitelli (1977)

mean value of 43.79 ppm for Ni is much lower than the value of 70 ppm obtained for the world average shale. Depletion of trace elements with depth marks the grey shale beds on the trace element concentration of Oshosun sediments (Table 4a). But in borehole 27, no depletion in element concentration is shown in Table 4b.

Also in the black shale, average values of compatible trace element are 209.09±84.33 ppm for Cr, 114.24±30.1 ppm for Zn and 38.56±8.99 ppm for Ni. The incompatible trace elements show mean values of 225.43±243.41 ppm for Ba, 9.1±5.05 ppm for Co, 3.28±1.26 ppm for Cs, 1.61±0.66 ppb for Au and 4.41±2.39 ppm for Br. Ga has an average of 13.69±3.1 ppm; Ge has a mean value of 1.57±0.48 ppm, while Hf has a mean value of 5.38±3.62 ppm. Other incompatible trace elements show mean values of 83.71±23.71 ppm for Rb, 0.43±0.59 ppm for Sb, 12.57±2.66 ppm for Sc, 53.25±26.28 ppm for Se, 284.26±116.52 ppm for Sr, 0.043±0.04 ppm for Ta, 9.74±2.11 ppm for Th and 0.93±0.24 ppm for U (Table 3).

Compared with diatomaceous clay-silt of oxygen poor environment of Gross (1964), the Co mean value of 7 ppm is similar, but the black shale shows a relatively higher Cr value. The Th value of 11 ppm in the floor and mud of variable composition is comparable but the U value of 12 ppm is much higher than that in Oshosun black shale.

Based on this, oxygen poor environment is inferred for Oshosun black shale. Compared to black shale of Hawkes and Webb (1962), Oshosun black shale has higher Co mean value but a lower Zr mean value, while Ba and Cr mean values are comparable (Table 3). Ajayi *et al.* (1989), obtained mean values of 323, 417, 26, 29, 21 and 88.48 ppm for Ba, Zr, Co, Ga, Th and U, respectively for black shale of Ifon sediments. These are higher than corresponding values in Oshosun black shale but the mean Cr value is higher in Oshosun black shale.

Compared with world average, the compatible trace elements of Oshosun black shale show higher mean value of Zn and Cr, but a lower Ni mean value. Table 3 shows range of values for compatible trace elements in black shale of Oshosun formation. Trace element distribution in the black shale in both boreholes 25 and 27 show little significant variation with depth (Table 4a and 4b). However, Ta shows intermittent enrichment and depletion with depth in borehole 25.

Rare earth elements: The total REE abundance in the clays ranges from 176.76 to 374.31 ppm with an average value of 258.49 ppm. The La_N/Sm_N ratios range between 2.79 to 126.42 (Table 5). The samples show similar REE pattern of depleted Light Rare Earth Element (LREE) to flat Medium Rear Earth Element (MREE).

Total REE concentrations in the grey shale range between 111.45 to 347.91 ppm (Table 5). The La_N/Sm_N ratios fall within a narrow range of 1.66 to 4.61 with a mean value of 3.18. This indicates limited fractionation of LREE (Ajayi *et al.*, 1989). The REE patterns of the samples are very similar showing depleted LREE-especially La and Ce and flat MREE.

In the black shale, the total REE concentrations vary from 123.61 to 349.75 ppm. La_N/Sm_N ratios range between 2.12 and 4.83 (Table 5). The REE plots of the samples are very similar showing depleted to flat LREE and flat MREE. The narrow range of La_N/Sm_N ratios indicate limited fractionation of LREE (Ajayi *et al.*, 1989). On the average, the REE pattern of the black shale is similar to that of the grey shale.

DISCUSSION

Lithological study of Oshosun sediments show that they are dominantly pale greenish grey to black laminated phosphatic shales representing transitional deposits in an oxygen poor environment (Ako *et al.*, 1980). Odigi and Brown-Awala (1992) recorded a high abundance of ferromagnesian mineral goethite, which constitutes about 60-65% of Oshosun phosphates. The Fe content of the phosphates however ranges from 0.21 to 0.96 wt.%. The transitional oxygen poor environment might be responsible for the goethite accumulation and this may account for the high Fe content in Oshosun formation.

There are variations in the REE abundance of the different lithologies of Oshosun formation, yet they show similarities in their REE patterns. This suggests that they are of similar origin. The REE plots of the samples of each sediment type show great similarities despite varying absolute concentrations. This is due to efficiency of mechanical mixing in the sedimentary processes (Nance and Taylor, 1974).

The source of the sediments can be deduced by comparing their REE pattern with that of nearby Basement Complex rocks. Table 6 shows the comparison of average REE concentration in Oshosun sediments with other sediments in other basins and gneisses from parts of basememt complex whilst Fig. 2 shows the comparison of

Table 6: Average REE concentrations (ppm) in Oshosun sediments compared with sediments in other basins and gneisses from parts of basement complex of SW Nigeria

Element	1	2	3	4	5	6
La	65.57(4)	53.49(6)	44.04(16)	32	96.6	95.0
Ce	137.55(4)	119.38(6)	92.17(16)	70	196	170
Pr				7.9		
Nd	45.22(4)	40.32(6)	37.60(16)	31.0	89.9	126.0
Sm	7.98(4)	9.66(6)	5.47(16)	5.7	11.5	13.5
Eu	1.43(4)	1.84(6)	1.07(16)	1.24	2.08	2.31
Gd				5.2	11.5	13.5
Tb	0.74(4)	1.03(6)	0.69(16)	0.85	1.74	1.93
Dy				5.0		
Ho				1.04		
Yb				3.1	3.87	2.78
Lu				0.53	0.68	0.58
REE	258.49(4)	225.72(6)	184.23(16)			

1: Average of Oshosun clays – This study, 2: Average of Oshosun grey shale – This study, 3: Average of Oshosun black shale – This study, 4: Composite of 40 North American shales (NAS) (Haskin *et al.*, 1966), 5: Average of grey gneiss from parts of S. W Nigeria (Rahaman *et al.*, 1983), 6: Average of Ife-Ilesha granite gneiss (Ajayi and Asubiojo, 1983)

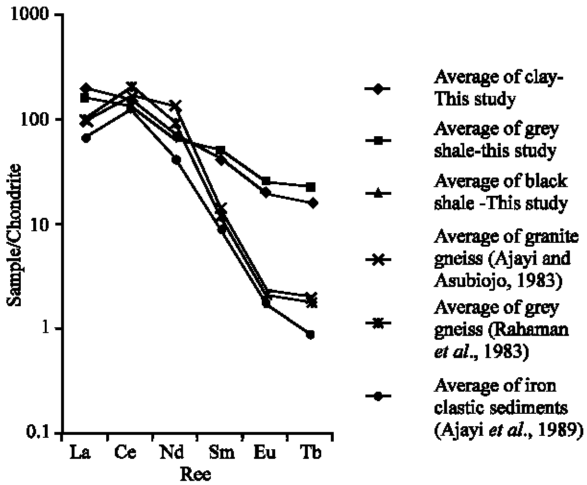

Fig. 2: REE parttern of Oshosun sediments compared with average parttern of Basement rocks and Ifon sediments

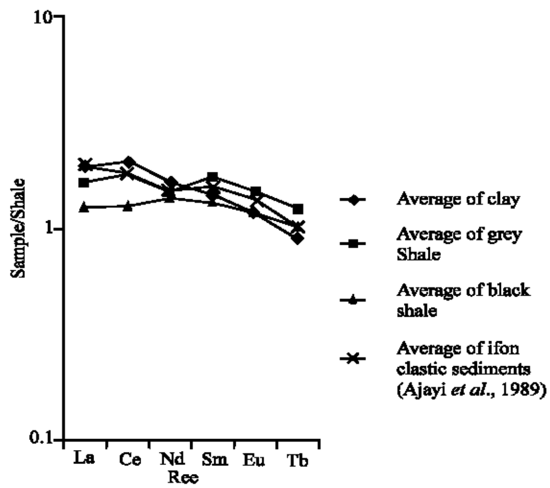

Fig. 3: Average shale-normalised REE parttern of Oshosun sediments

REE pattern of Oshosun sediments with the REE pattern of average grey gneiss (Rahaman *et al*., 1983) and average granite gneiss (Ajayi and Asubiojo, 1983). These are members of migmatite-gneiss-quartzite complex of southwestern Nigeria (Rahaman, 1976). The sediments of Oshosun formation show similar REE patterns except for the positive Ce anomaly in the basement gneisses. In the Oshosun sediments, no Ce anomaly is observed and this is due to its occurrence in +3 oxidation state like other REE in continental sedimentary rocks (Piper, 1974b). The similarities in the REE pattern of Oshosun sediments and those of granite and grey gneisses strongly suggests the derivation of Oshosun sediment from the granite and grey gneisses of the Basement Complex of SW Nigeria.

The shale-normalized plot of REE patterns of Oshosun sediments (Fig. 3) shows a general flat to depleted REE pattern. Both the chondrite normalized and the shale normalized REE patterns show no Eu anomaly, which occurs normally due to reduction of Eu3+ to Eu2+ in igneous processes (Piper, 1974b). This reduction does not occur in the sedimentary environment and so, Eu remains in +3 oxidation state and behaves similarly like other REE trivalent members (Piper, 1974b). The strong similarities of REE patterns of Oshosun sediments with those of Ifon clastics and the gneisses strongly indicated similar source from the Basement Complex.

To determine the environment of deposition of any sedimentary sequences, trace element data on Cr, Mn, Co, U, B and organic matter are essential (Ajayi *et al*., 1989). However, for Oshosun sediments, only Cr, U and Co were determined. Hence a conclusive statement might not be made on the depositional environment. Table 3 shows concentration range of compatible trace elements Cr, Ni and Zn in Oshosun formation. Data on Cr and Co of Oshosun sediments show comparable values with varved diatomaceous clay silt (Gross, 1964) and floor and mud of variable composition (Landergreen and Manhem, 1963) of oxygen poor environment (Table 3). In addition, Odigi and Brown-Awala (1992) indicated that the presence of glauconite in Oshosun phosphates suggests oxygen deficient bathyal and shelf sedimentation. Omatsola and Adegoke (1981) proposed that Dahomey basin contains series of horsts and grabens and one of such grabens provided the restricted oxygen poor environment for Tertiary sediments of the basin.

On the studies of the organic matter of Oshosun formation, Idowu *et al.* (1993) showed that the contribution of organic matter was for marine biota and this was diluted by deposition of terrigenous organic mater. This is shown by low sulphur content (less than 1%) in Oshosun sediments. As a result of this, it is concluded that organic sedimentation was effected in marine dominated transitional paleoenvironment. Based on the findings presented above, it can be inferred that Oshosun sediments were deposited in shallow oxygen-poor environment similar to Ifon clastics of eastern parts of Dahomey basin.

Table 4a and 4b show trace element variation with depth. Uranium and Thorium vary slightly with depth. Most of the trace elements do not show remarkable variation in their concentrations with depth except for Se, Co, La, Ga Ta and Zn, which show little variations in their concentration with depth (Table 4a). The relatively constant variation of concentrations of the elements with depth suggests a constant geochemical condition for the deposition of the sedimentary sequence.

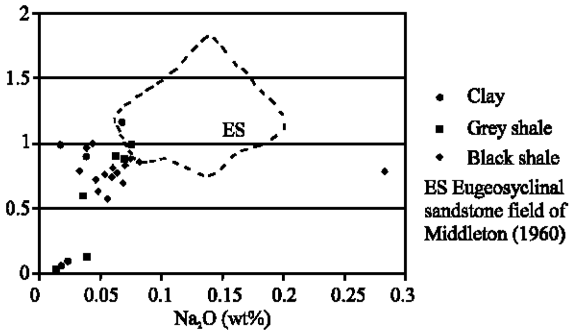

Fig. 4: K vs Na plot of Oshosun sediments

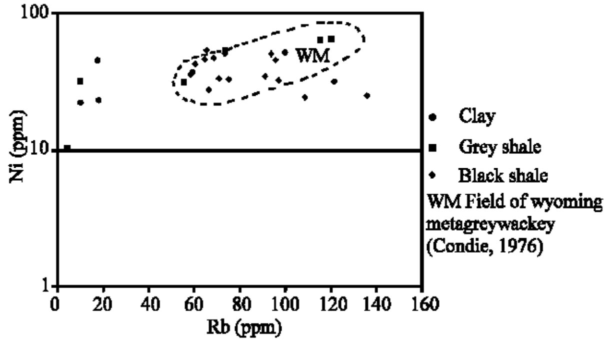

Fig. 5: Ni vs Rb plot of Oshosun sediments

Figure 4 shows the plot of K_2O versus Na_2O of Oshosun sediments. Only three samples fall in the region of eugeosynclinal sandstone of Middleton (1960), suggesting that the Oshosun sediments do not belong to the arenaceous sandstone field. The Ni versus Rb plot (Fig. 5) showed that most of the samples fall within the field of mainly argillaceous Wyoming Archean metagreywackey (Condie, 1976). The argillaceous nature of Oshosun sediments suggests a quiet shallow marine environment of deposition. This is in agreement with the results of Idowu *et al.* (1993).

The Oshosun sediments show similarities with Ifon clastic sediments, which lie in the eastern part of the Dahomey basin in their trace element distribution and REE patterns. Therefore, sedimentation probably occurred under similar conditions in shallow oxygen poor environment of horsts and grabens. This restricted depositional environment was provided by the structural framework that extends from the west to the eastern part of the basin. The source of the sediments in both areas are the granite and grey gneisses of the nearby Basement Complex. This is evident by the similarities in REE patterns of sediments of both areas with REE patterns of the gneisses. Oshosun sediments like Ifon clastics show similar REE patterns between samples, which indicates efficient mechanical mixing of sediments from wide provenance. The dominant lithologies in Oshosun and Ifon sedimentary environments are clays and shales with interbedding limestone, mudstone, sands and sandstone.

On the other hand, Fe contents of Oshosun sediments are higher than those of Ifon clastics. This is attributed to high goethite content and formation of phosphates in Oshosun sediments.

CONCLUSIONS

The Tertiary Oshosun sediments were accumulated from a wide provenance covering large parts of SW Nigeria. REE absolute concentrations off individual samples vary widely, yet similar REE patterns were shown indicating efficient mechanical mixing mechanism. The sediments show REE pattern similar to those of average granite and grey gneisses thus indicating their derivation from the gneisses. The narrow range of La_N/Sm_N ratios reflect limited fractionation of LREE. Available trace element data suggest oxygen poor environment of deposition.

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