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**Research**

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## The Depositional Environments and Provenance Characteristics of Selected Sediments, South of Yewa River, Eastern Dahomey Basin, South Western Nigeria

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### Abstract

*An inorganic geochemical study of a clay and shale sediments sequence around Araromi and Irogun-akere (the Southern part of Yewa River), Eastern dahomey basin, south western Nigeria, was carried out to determine the sediment's depositional conditions, provenance and tectonics. Fifteen shale and clay sediment samples underwent mineralogical and geochemical analysis involving major, trace and rare earth element analysis at acme analytic laboratory, Ontario, Canada using an ICP mass spectrometer (Perkin-Elmer, Elan 6000). Mineralogical studies using X-ray diffraction analysis revealed prominent kaolinite, montmorillonite and illite peaks; accessory minerals included quartz and microcline. Major element abundance showed that the shale samples had SiO<sub>2</sub> (44.77%), Al<sub>2</sub>O<sub>3</sub> (15.01%) and Fe<sub>2</sub>O<sub>3</sub> (5.75%), constituting more than 65% of bulk chemical composition. Thirty-four elements trace metals, heavy rare earth elements and light rare earth elements analysis were quantified from the geochemical analysis. The shale sediments exhibit higher Ni, Ba, CO, Zr, Rb and Th concentrations than clay sediments, whereas clay samples are Sr-, Zn-, Pb- and U-enriched. Light rare earth element (La, Ce, Nd, Sm, Pr) were enrich in shale and clay sediment samples while, heavy rare earth elements (Tb, Yb, Lu, Gd, Dy, Ho, Tm and Eu) are depleted. High TiO<sub>2</sub> and Rb/K<sub>2</sub>O values also indicated that the shale and clay samples were matured. Geochemical parameters such as U, U/Th, Ni/Co and Cu/Zn ratios indicated that these shales were deposited in oxic conditions; the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio suggested that intermediate igneous rocks were probable source rocks for the shale, while mafic rocks were suggested as being source rocks for the claystone. However, the La/Sc, Th/Sc, Th/Co ratios and shale and clay sediment plots revealed that they came within the range given for felsic rocks as provenance, thereby suggesting mixed provenance for the sediments. A passive-margin tectonic setting was adduced for the sedimentary sequences.*

**KEY WORDS:** Trace metals, Light Rare Earth Element, Heavy Rare Earth Element, Inductively coupled mass spectrometer, X-ray diffraction analysis, provenance, tectonic setting.

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## Introduction

The inorganic geochemical study on sediments is an important tool in the determination of its provenance and environment of deposition in chemical oceanography. It also serves as major tool in the discrimination of tectonic settings. (Bhatia, 1983; Roser and Korsch, 1986) It has been established that trace elements, such as La, Y, Sc, Cr, Th, Zr, Hf and Nb, in combination with  $TiO_2$ , are best suited for provenance and tectonic setting determination studies based on their relatively low mobility during sediments deposition (McLennan *et al.*, 1983, Okunlola and Olubunmi, 2010). It is possible in principle to trace particular sediment's rare earth element concentration to its source if, the mixing and differentiating effects of sedimentation have not been too extensive. (Adekeye *et al.*, 2007) The use of mineralogical characteristics such as felsic and basic enriched rare earth elements such as La, Th, k, Sc, Cr and Co can be used as a tracer in chemical oceanography to unravel the source, origin, paleo-oxygenation and palaeo-environmental conditions of ocean sediments within and around the ocean. (Calvert and Pedersen, 1993; Jones and Manning, 1994; Nath *et al.*, 1997; Cullers, 2002; Armstrong-Altrin *et al.*, 2003; Dobrzinski *et al.*, 2004). This study was therefore aimed at identifying sequence source rock characteristics, tectonic setting, and paleo-environmental conditions of shale sediments around Idogo and araromi, Papanla, south of River, Eastern Dahomey basin in South western Nigeria using their major, trace and rare earth elements geochemistry.

## Geology and Stratigraphy

The Dahomey Basin is an extensive sedimentary basin on the continental margin of the Gulf of Guinea. It extends from south eastern Ghana through Togo and Benin Republic into western Nigeria (Slansky, 1962, Antolini 1968, Billman 1972). The basin is a marginal pull-apart basin (Klemme, 1975) which developed in the Mesozoic Era due to the separation of the African and South American lithospheric plates (Burke *et al.* 1971).

The basin contains extensive wedge of Cretaceous to Recent sediments, up to 3000 meters which thickens towards the offshore (Whiteman, 1982), Adegoke *et al.* (1970) and Ogbe (1972) provided the basic stratigraphic framework and description of the different microfacies. Fayose (1970); Jones and Hockey (1964), Reyment (1965) have attempted the reconstruction of the paleoenvironments using sedimentological and microfossil data from the onshore area. Hydrocarbon generation within the Dahomey Basin has been identified in the Abeokuta Group and the deep marine Upper Senonian-

Maastrichtian anaerobic Araromi Formation (Avbovbo, 1978).

Few studies have been conducted in the eastern Dahomey Basin in terms of hydrocarbon potential, Omatsola and Adegoke (1980) and Whiteman (1982) all worked on the age, lithology, structure, petrology and geology of the different rock units in the eastern Dahomey Basin. Reyment (1965) assigned an upper Paleocene age to the Ewekoro Formation and further established the formation as a lateral equivalent of the Imo Shale. Adegoke *et al.* (1970) subdivided the Ewekoro Formation into three microfacies units based on field evidence and petrographic studies. These are the lower sandy biomicroparite, the middle shaly biomicrite which is the thickest and most fossiliferous and an upper algal biosparite. They revealed the average thickness of 30m for the Ewekoro Limestone from studies of 21 boreholes in the vicinity of Ewekoro village. They also obtained an average of 54.45 million years from radioactive dating of glauconite within Ewekoro Formation.

Ogbe (1972) recognized another microfacies at the top of the Ewekoro Formation which he called phosphatic biomicrite algae. Omatsola and Adegoke (1980) described the tectonics and Cretaceous stratigraphy of the eastern Dahomey Basin and upgraded the Abeokuta Formation to a group status made up of Ise, Afowo and Araromi formations. According to Omatsola and Adegoke (1980), the Formations range in age from Neocomian to Paleocene. Agagu (1985) also confirmed the three members of the Abeokuta formation based on the lithological characteristics of the sediments and assigned a Neocomian to Maastrichtian to the sediment.

Ekweozor *et al.* (1989) studied the origin of the tar sands, properties and source rock evaluation of interbedded shales associated with tar sands of the eastern Dahomey Basin. They concluded that the tar sand deposits represent products of reservoir transformation of conventional oil by microorganisms. Elueze and Nton (1998) used pebble morphology to deduce that the siliclastics within the Cretaceous sequence in eastern Dahomey Basin are dominantly fluvial sediments with minor marine influences.

Elueze and Nton (2004) and Nton *et al.* 2009 suggested that the Ewekoro limestones were deposited in shallow marine setting and are predominantly gas prone organic matter with low oil prone.

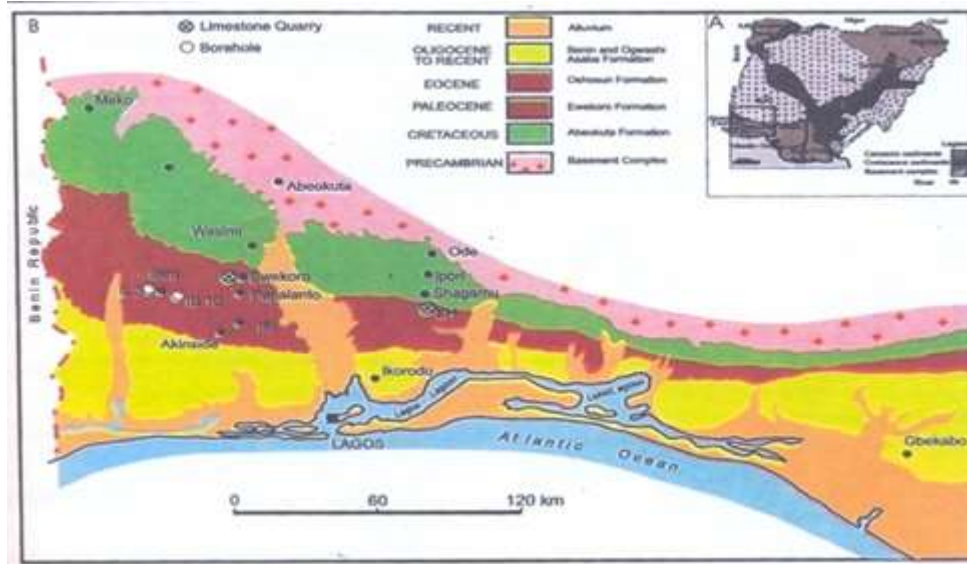


Fig 1: Generalized Geological setting of eastern Dahomey basin (Modified by Billman, 1976)

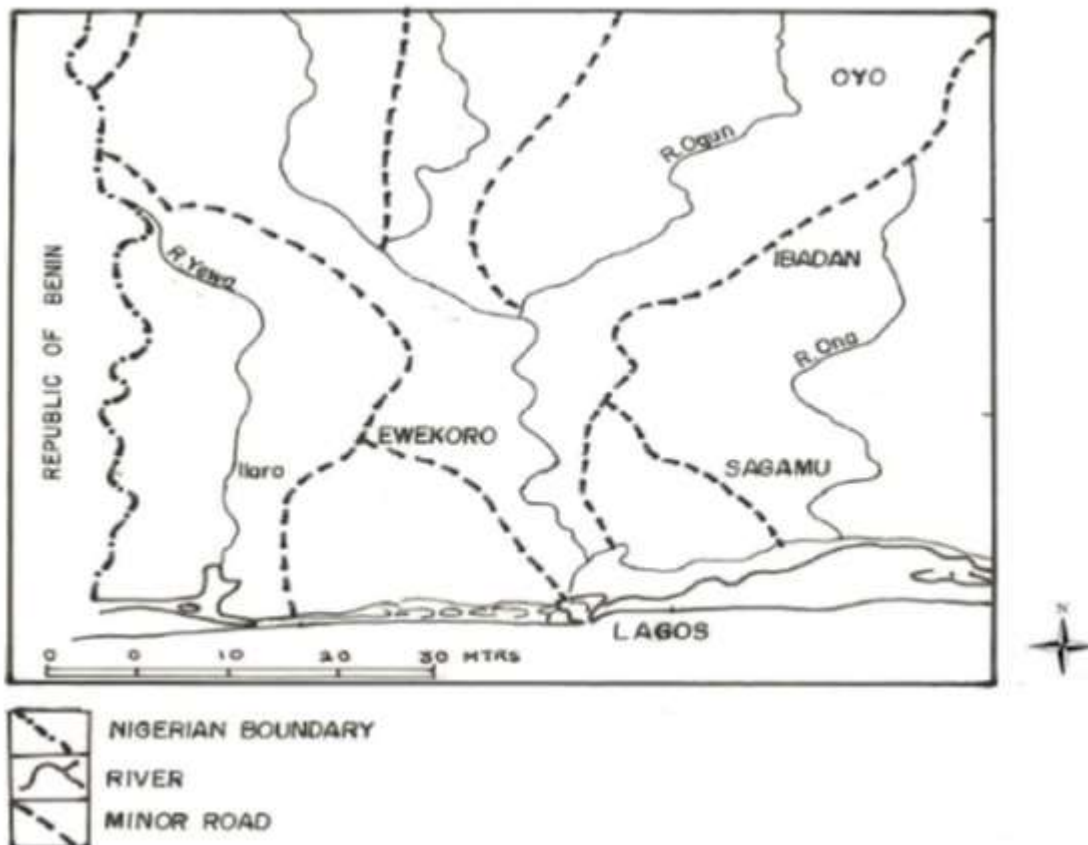
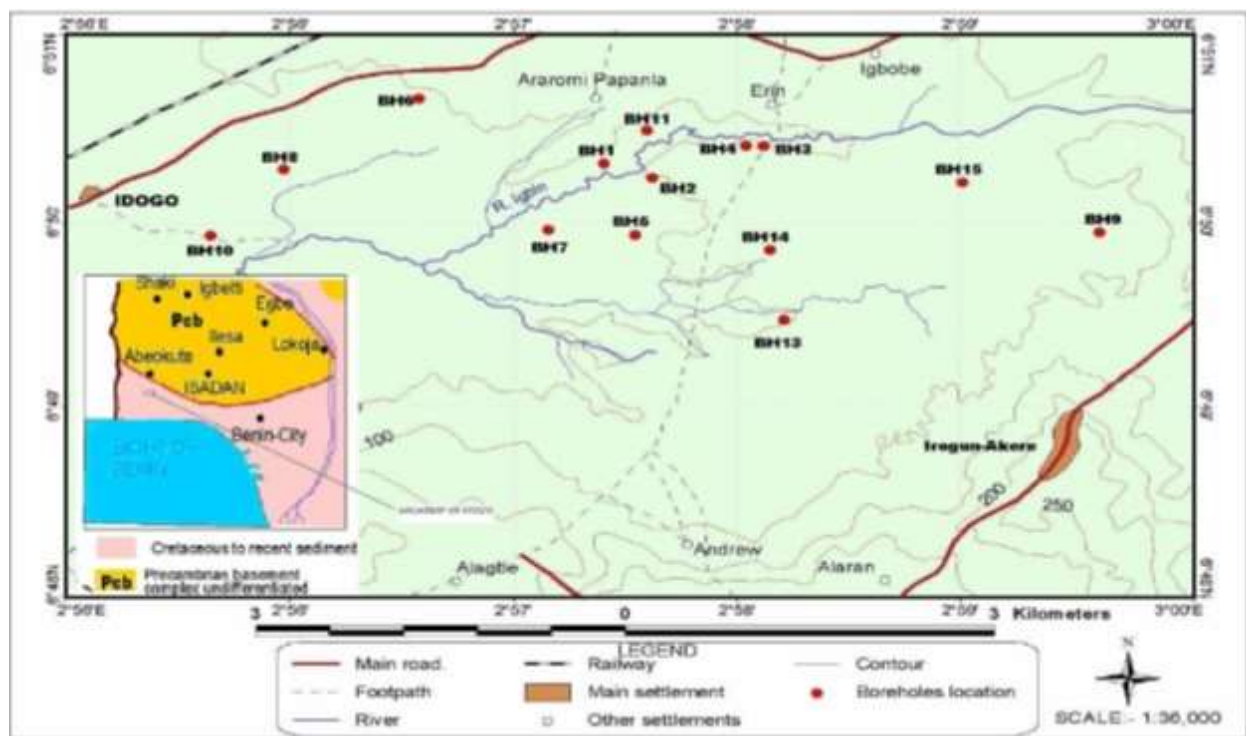


Fig 2: The principal rivers and water shed parts of South Western Nigeria (after Jones and Hockey, 1964)



**Fig3: The cored points where representative limestone samples were collected**

### Materials and Method

The fifteen samples used for this study were taken from 14 numbers core drilling operations (BH1-14) carried out around adjoining communities of: Alagbe, Andrew, Alaran, Erin, Irogun akere, Idogo, Araromi papanla, Igboke, Oke odan, Owode, Ado-odo, Ipokia, Idi-iroko, Ibatofin, Ogun state, South of River Yewa, eastern Dahomey basin, south western Nigeria see fig 3: Representative shale sediment samples were collected from the drill core box for analysis labeled-; BH-1, BH-5, BH-7, BH-9, BH-10, BH-

13. Representative whole rock shale sediment samples using BH-5 and BH-10 samples were studied by X-ray diffraction (Phillips – PW 1011 diffractometer). The diffractograms were recorded using a 1° 2/min/cm scanning rate with Ni-filtered Fe–K alpha radiation. X-ray diffraction curves were interpreted by comparing notable intensity peaks with those for standard minerals established by Carrol (1971). Quantitative determination was made by a real method; the shale samples' fraction was not separated for speciation evaluation in this study because, initially, it was necessary to establish the shale sequence's holistic compositional features to have an unobliterated pattern of its evolution within the basin.

Geochemical characterisation involved analyses of fifteen sediments samples at the Acme Analytical Laboratories Ltd, Ontario, Canada for major, minor and trace element geochemistry using an ICP mass spectrometer (Perkin-Elmer, Elan 6000) and

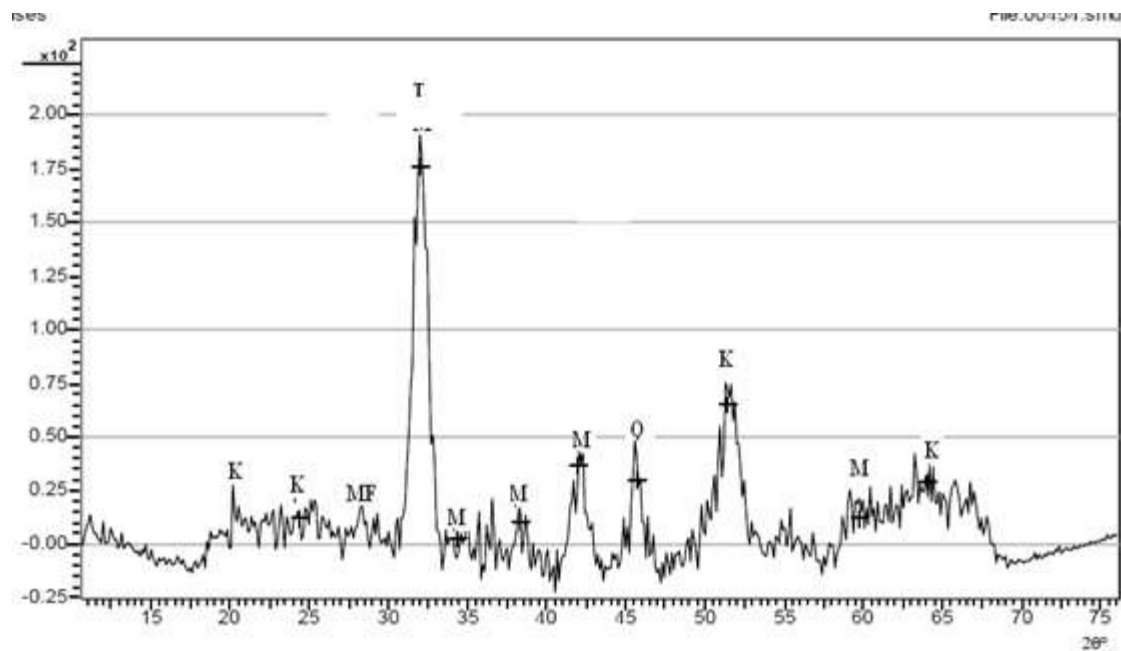
inductively coupled plasma mass spectrograph on powdered, pressed pellets prepared from 3-5g samples. It was digested by weighing 0.2g aliquot in a graphite crucible mixed with 1.5g LiBO<sub>2</sub>/LiB<sub>4</sub>O<sub>7</sub> flux. The crucibles were placed in an oven and heated at 980°C for 30 minutes. The cooled bead was dissolved in 5% HNO<sub>3</sub> (ACS grade nitric acid diluted in demineralised water). Calibration standards and reagent blanks were added to sample sequences. The basic package consisting of thirty-four elements (Ba, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Lu, etc) was determined for the shale and clay samples. A second 0.5g split sample was digested in Aqua Regia and analysed by ICP-MS to determine Au, Ag, As, Bi, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn. An ICP emission spectrograph (Spectro Ciros Vision or Varian 735) was used for determining major oxides and some trace elements (i.e. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>5</sub>, Ba, Nb, Ni, Sr, Sc, Y and Zr). Loss on ignition (LOI) was determined for both packages by measuring the weight loss after heating a 1g split sample at 95°C for 90 minutes.

### Results and Discussion

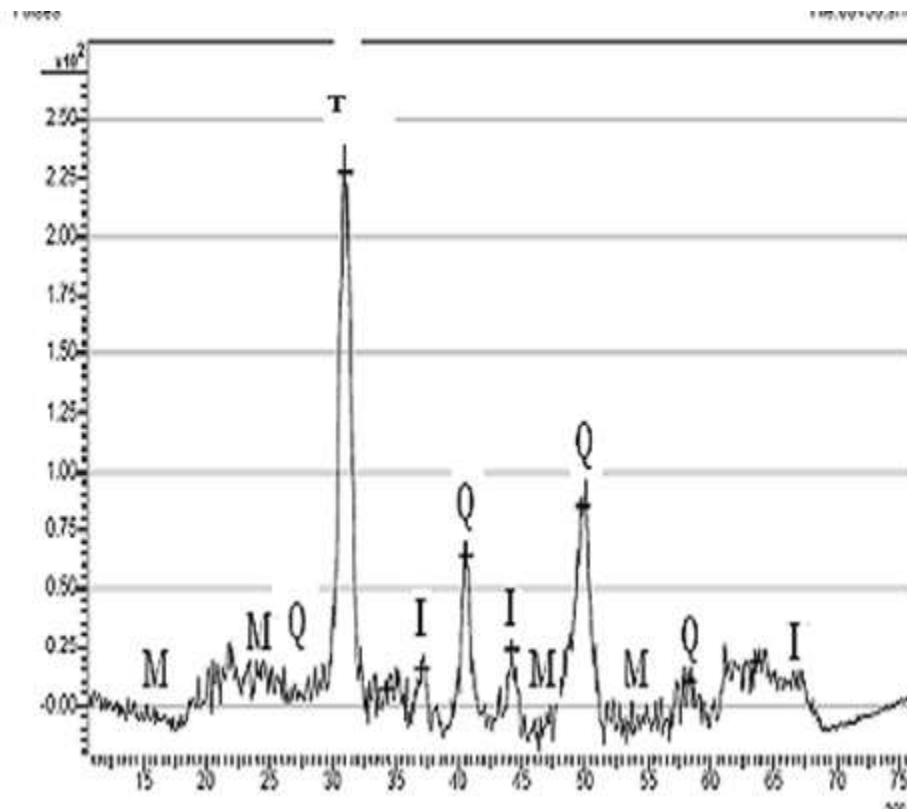
#### Mineralogy

The X-ray diffractograms (XRD) for the whole rock sediments of south of River Yewa, shale samples revealed minerals such as kaolinite (13.02%), montmorillonite (31.31%), illite (4.3%),

microcline(12.09%) and quartz (37.80%). (Figure 4&5); kaolinite was the dominant clay mineral while quartz is the dominant non clay mineral.



**Fig 4: X-ray diffractogram for the shale sediment sample of location drill core, BH 5, depth 5.30-8.00 meters (E of River Igbin) K-kaolinite, MF-microcline feldspar, M-montmorillonite, Q-quartz,**



**Fig 5:** X-ray diffractogram for the shale sediment sample of location drill core, BH 10, depth, 3.20-4.00m South of Idogo) M montmorillonite, Q-quartz, I-illite



**Fig 6-9:** X-lithological samples of marl, shale, sand and clayey-shale sediments from the study area

**TABLE1: THE RESULTS OF THE MAJOR/MINOR ELEMENTS COMPOSITION OF SHALE SAMPLES WITH DEPTH**

<b>Drillcore Number ( DC)</b>	<b>A1</b>	<b>A2</b>	<b>A3</b>	<b>A4</b>	<b>A5</b>	<b>A6</b>
SiO <sub>2</sub> %	48.88	47.22	48.22	39.89	45.21	39.21
Al <sub>2</sub> O <sub>3</sub> %	16.74	15.89	18.00	12.33	17.24	9.87
Fe <sub>2</sub> O <sub>3</sub> %	5.57	6.11	5.99	4.41	8.75	3.68
MgO %	3.41	2.91	3.51	1.86	2.52	0.66
CaO %	1.53	1.15	0.86	13.34	1.48	19.34
LOI	0.01	24.90	21.30	26.00	23.00	25.60

<b>BOREHOLE NUMBER (BH)</b>	<b>A1</b>	<b>A2</b>	<b>A3</b>	<b>A4</b>	<b>A5</b>	<b>A6</b>
Na <sub>2</sub> O %	0.10	0.10	0.05	0.06	0.05	0.04
K <sub>2</sub> O %	0.91	0.57	1.05	0.70	0.79	0.11
TiO <sub>2</sub> %	0.67	0.77	0.71	0.68	0.70	0.80
P <sub>2</sub> O <sub>5</sub> %	0.10	0.05	0.04	0.47	0.07	0.46
MnO %	0.05	0.15	0.06	0.02	0.05	0.04
Cr <sub>2</sub> O <sub>3</sub> %	0.01	0.02	0.04	0.02	0.03	0.01



**TABLE 3: AVERAGE CHEMICAL COMPOSITION OF SHALE SEDIMENTS SAMPLES OF THE STUDY AREA COMPARED TO SHALE OF OTHER SEDIMENTARY BASIN.**

OXIDE%	RANGE	STUDY AREA	ASU RIVER GROUP Amajor,1987	EZE-AKU SHALE Amajor,1987	AVERAGE SHALE PettiJohn,1957	NASC Gromet-et al.,1987
SiO <sub>2</sub>	39.89-48.88	44.77	69.94	44.91	58.1	64.82
TiO <sub>2</sub>	0.67-0.80	0.72	0.52	0.65	0.6	0.8
Al <sub>2</sub> O <sub>3</sub>	9.87-18.0	15.01	10	15.71	15.4	17.05
Fe <sub>2</sub> O <sub>3</sub>	3.68-8.75	5.75	4.04	6.24	6.9	5.7
MnO	0.02-0.06	0.06	0.04	0.06	Trace	-
MgO	0.66-3.51	2.48	0.87	2.58	2.4	2.83
CaO	1.48-19.34	6.28	3.38	15.42	3.1	3.51
Na <sub>2</sub> O	0.04-0.10	0.06	0.4	0.42	1.3	1.13
K <sub>2</sub> O	0.11-1.05	0.83	1.15	2.36	3.2	3.97
P <sub>2</sub> O <sub>5</sub>	0.07-0.47	0.08	0.17	0.46	0.2	0.15
LOI	0.01-26.0	20.14				
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.91	2.91				
K <sub>2</sub> O/Na <sub>2</sub> O	13.83	13.83				
K <sub>2</sub> O /Al <sub>2</sub> O <sub>3</sub>	0.055	0.055				
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	20.84	20.84				
Cu/Zn	50.16	50.16				
Ni/CO	3.32	3.32				

**Major Element Composition**

Table 1 and 2 gives the major oxide analysis of six shale sediments samples; Table 3 summaries the average major element oxide (wt %) data for the samples being studied. These were compared to the average shale worldwide (Pettijohn, 1957), NASC (Gromet *et al.*, 1984) and shales from other parts of Nigeria (Table 3). It was apparent that most shale samples in Table 1 varied slightly regarding.

SiO<sub>2</sub> (39.21-48.88. %), had moderately high Al<sub>2</sub>O<sub>3</sub> (9.87 -16.74%) and a small variation in Fe<sub>2</sub>O<sub>3</sub> values

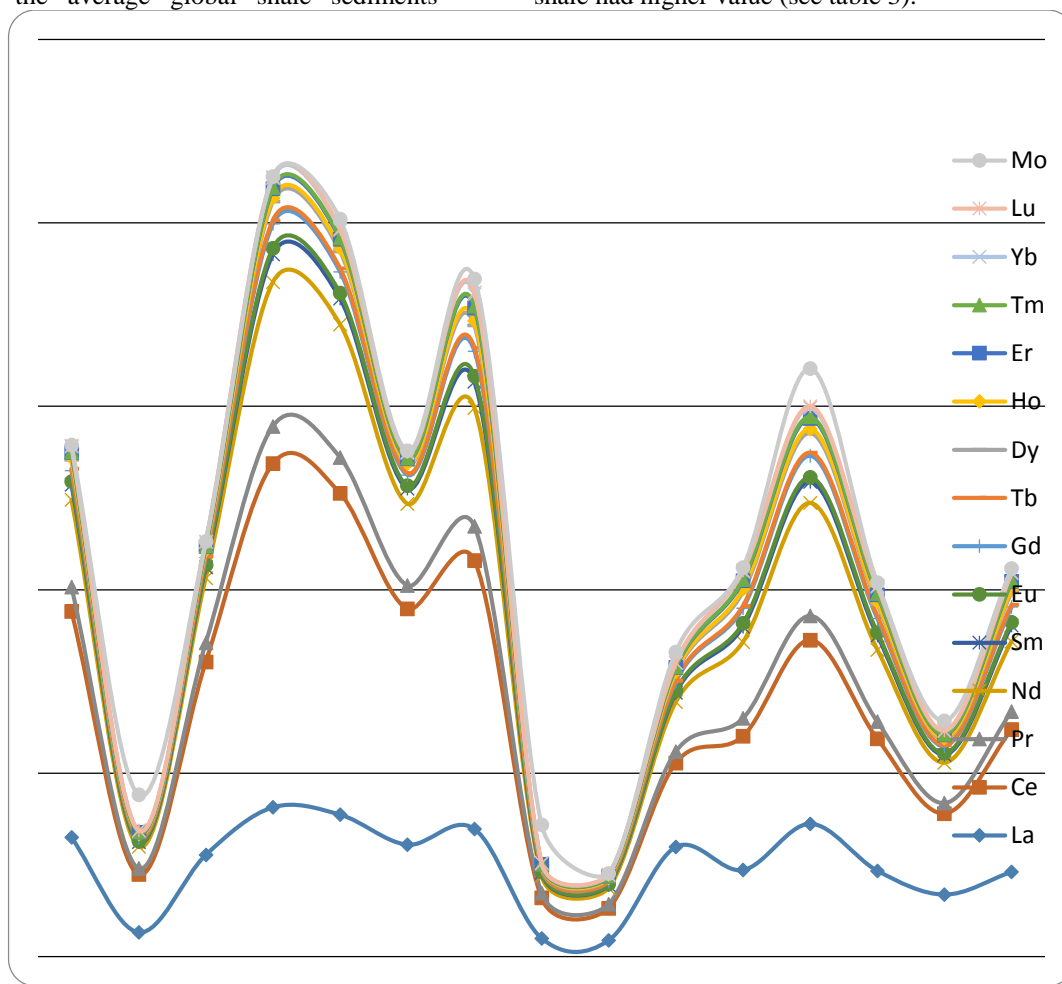
(3.68%-5.99%); they were, however, low in TiO<sub>2</sub> (10-17.05), CaO, (3.1-15.48) Na<sub>2</sub>O (0.06-1.3) and K<sub>2</sub>O (0.83-3.97).

Such low K<sub>2</sub>O content indicated the low amount of illite or K-feldspar present in the shale sediment samples (Akpokodje *et al.*, 1991). The shale sediment was relatively low in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> content, while the TiO<sub>2</sub> is slightly higher compared to the other sedimentary shale.

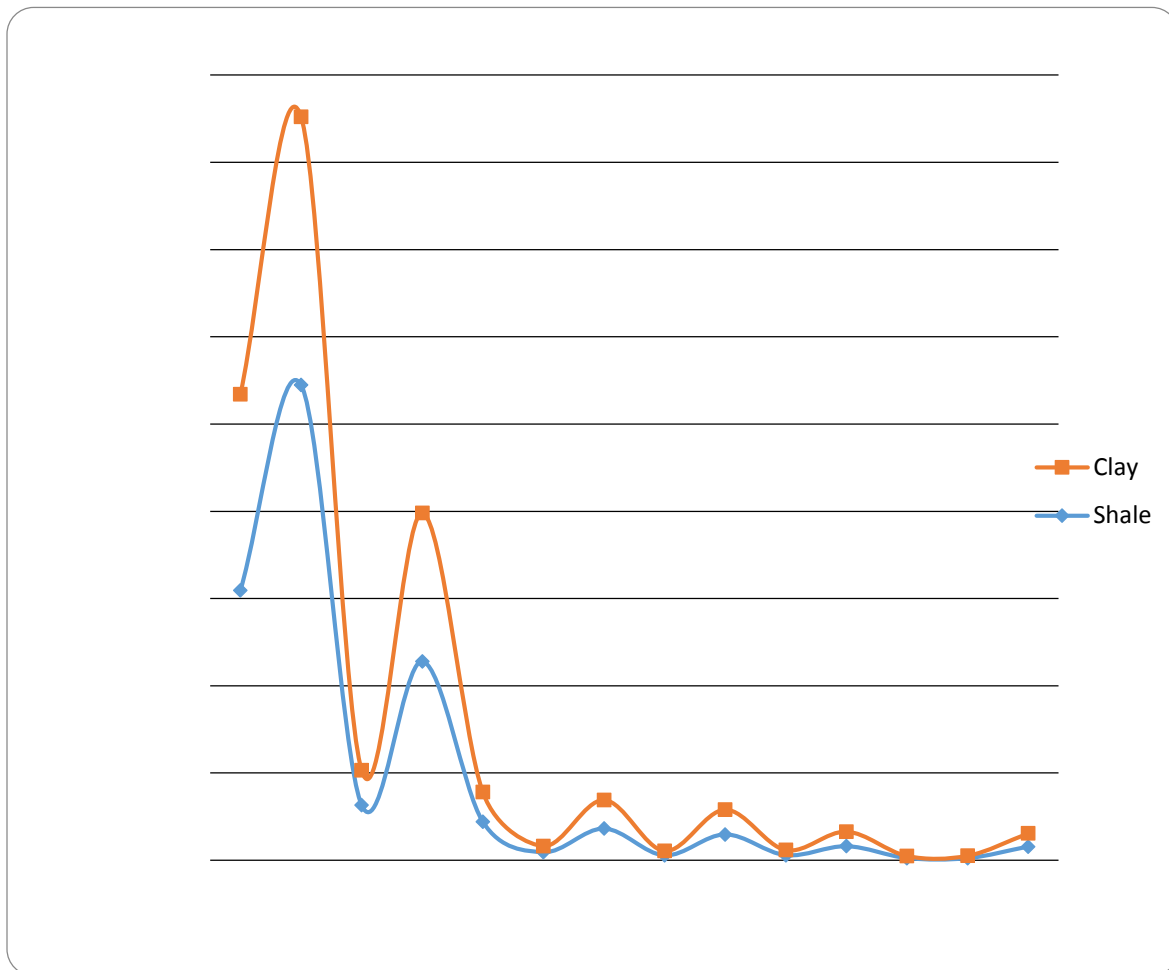
The shale sample has low phosphate (P<sub>2</sub>O<sub>5</sub>) content; P<sub>2</sub>O<sub>5</sub> depletion could have been due to the lower

amount of accessory phases, such as apatite and monazite. The MgO and MnO content values were higher than the global shale, (Pettijohn, 1957), the Na<sub>2</sub>O content of the study area is low collectively only accounting for less than 0.1%. The high value of the MgO and CaO content indicate associated carbonates or dolomitisation.. The shale and alumina to silica ratio was high (2.91), thereby indicating that the shale sediments of the study area are highly siliceous and occur in association with quartz minerals (SiO<sub>2</sub>) and sand. The average loss on ignition (LOI) of 20.14 for shale was high, showing great shale potential for carbonaceous compounds. The average SiO<sub>2</sub> (44.77%) and Al<sub>2</sub>O<sub>3</sub> (15.01%) chemical composition in shale constituted about 60% of the samples' total chemical composition. The other chemical impurities in shale samples from the Patti formation were Fe<sub>2</sub>O<sub>3</sub> (5.75%) and TiO<sub>2</sub> (1.74%). The south of River Yewa formation shale sediment samples have higher TiO<sub>2</sub> values than the average global shale sediments

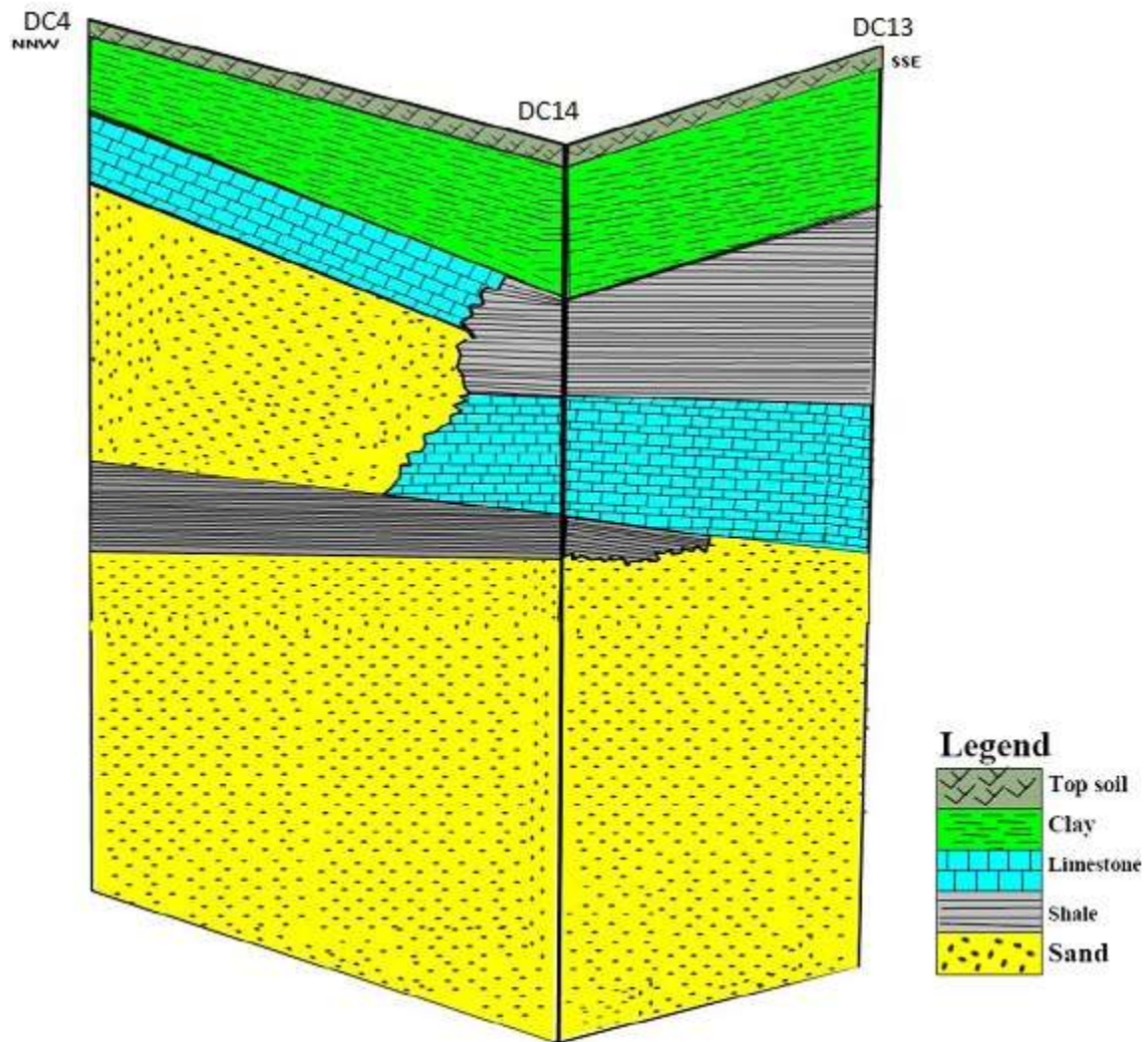
(Pettijohn, 1957). Potassium-Alumina ratio (K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>) can be used as an indicator of ancient sediments' original composition. The K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios for clay minerals and feldspars are different (0.0 to 0.3, 0.3 to 0.9, respectively) according to Cox (Cox *et al.*, 1995). The average K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio for shale varies from 0.06 to 0.1 and is 0.09 for claystone. The (0.055)K<sub>2</sub>O /Al<sub>2</sub>O<sub>3</sub> of the study area ratios were closer to the lower shale mineral range limit. Comparing the chemical composition of the shale sediment samples from the South of River Yewa ,eastern Dahomey basin with that of shales from other parts of Nigeria revealed that the shale and samples were relatively low in SiO<sub>2</sub>.The TiO<sub>2</sub> concentration is higher with the exception of North American shale composite NASC (Gromet *etal.*, 1984) while, the Alumina (Al<sub>2</sub>O<sub>3</sub>) and iron (Fe<sub>2</sub>O<sub>3</sub>) content are lower. The present study's CaO and MnO values also had values comparable with Eze-Aku shale (Amajor 1987) however, the Ezeaku shale had higher value (see table 3).



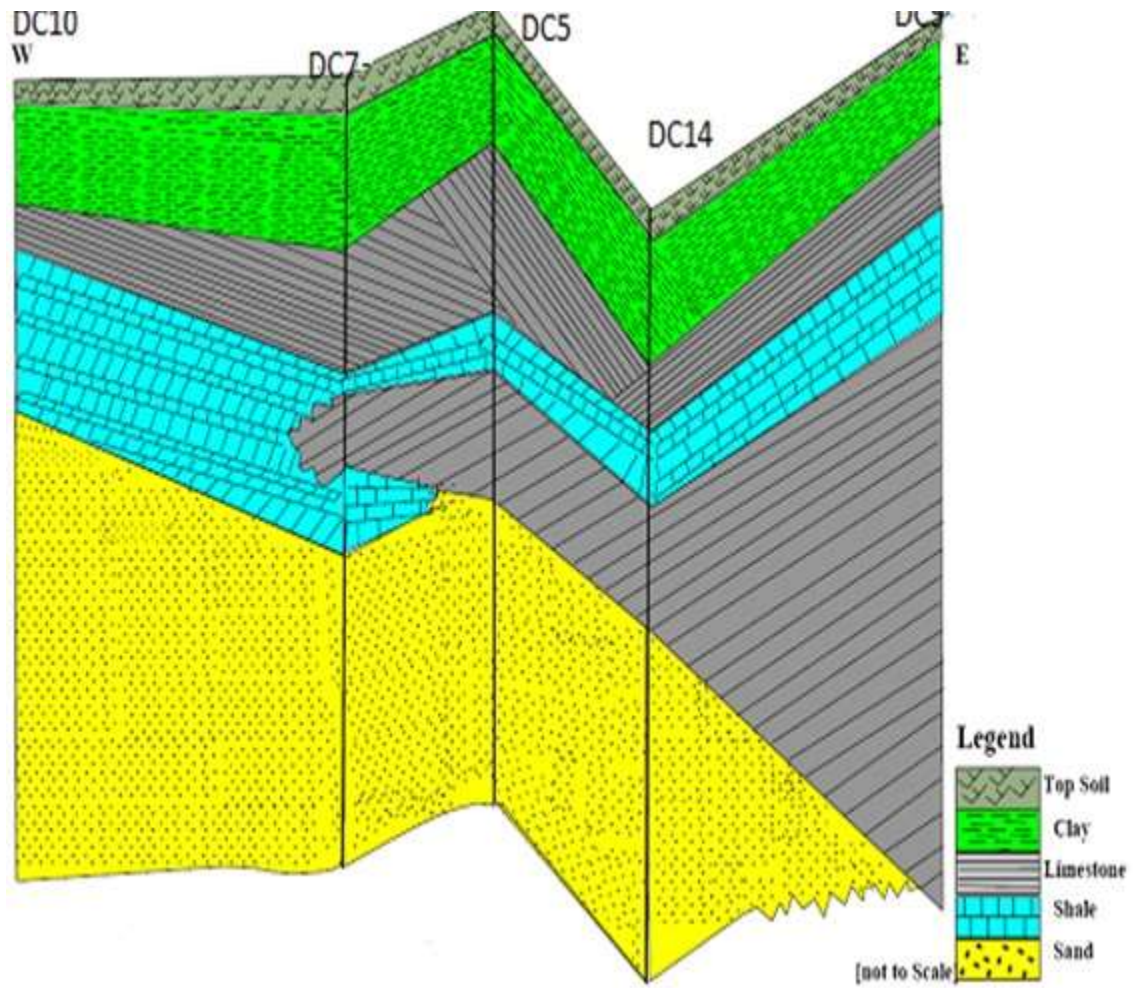
**Fig 10:** Rare earth element plot for shale and clay samples from the Patti formation



**Fig 11:** *Rare Earth Elements composition of the shale samples of the study area showing a slight enrichment of LREE*



*Fig 12: Correllation of Drillcore DC4, 14 & 13 (NOT TO SCALE)*



*Fig 13: Correllation of drllcore DC 10,7, 5 ,14 & 9 (NOT TO SCALE)*

**TABLE 5: TRACE ELEMENTAL RATIO RESULTS OF SHALE SAMPLES OF THE STUDY AREA**

Element	Present study area Average Shale sediments	Present study area Average Clayey-shale	Vine & Tourtelot 1970	Levinson 1974	PAAS	Turetan & Wedepol 1961	NASC (Gromet et al.,1984)
Ni	40.50	38.00	70.00	50.00	55.00	68.00	58
Ba	171.63	53.86	700.0	300.0	650.0	580.0	636.0
Sr	160.04	312.73	300.0	200.0	200.0	300.0	142.0
CO	12.30	6.4	20.00	10.00	23.00	-	.n.a
Zn	37.63	44.72	100.0	300.0	85.00	95.00	n.a
Cu	0.45	4.77	50.00	70.00	50.00	45.00	n.a
Y	15.88	22.19	25.00	30.00	-	-	n.a
V	119.5	120.29	130.0	150.0	150.0	130.0	130
MO	3.38	2.69	3.000	10.00	-	-	n.a
Zr	145.9	40.88	160.0	70.00	210.0	160.0	200.0
Nb	16.96	12.38	20.00	20.00	1.90.0	n.a	n.a
Pb	5.98	71.6	n.a	20.00	1.90.0	n.a	n.a
Rb	32.96	10.17	n.a	140.0	160.0	n.a	n.a
Th	9.00	2.21	n.a	12.00	14.60	n.a	n.a
U	1.60	7.98	n.a	14.00	3.100	n.a	n.a
(Cu+MO)Zn	144.12	0.16					
Cu/Zn	0.012	0.106					
Ni/CO	3.29	0.59					
Rb/K <sub>2</sub> O	44.53	-					
U/Th	0.17	3.61					

**TABLE 6: AVERAGE SHALE RARE EARTH ELEMENTAL RATIO RESULTS OF SHALE SAMPLES OF THE STUDY AREA**

Rare earth elements	Present study Average shale sediments	Present study Average clay-shale sediments	DMMAS 16-1	PAAS	Codo shale	Average shale, Levinson, 1994
La	30.92	22.50	13.92	38.2	29.7	121
Ce	54.48	30.74	27.0	79.6	63.4	50
Pr	6.31	4.00	-	8.83	--	-
Nd	22.78	17.02	13.0	33.9	27.9	24.0
Sm	4.40	3.40	4.0	5.55		
Eu	0.92	0.71	1.3	1.08	-	-
Gd	3.62	3.29	-	4.66	--	
Tb	0.55	0.52	0.6	0.744	-	-
Dy	2.95	2.85	-	4.68	-	-
HO	0.57	0.60	-	0.991	-	-
ER	1.60	1.68	-	2.85		
TM	0.24	0.25	-	0.405	-	-
Lu	0.23	0.29	-	0.433		
Yb	1.56	1.52	3.8	-	-	-

**TABLE 7: ELEMENTAL RATIO OF SHALE IN THE STUDY AREA**

Element	B1	B2	B3	B4	B5	B6	B7	B8
Th	10.1	1.9	12.7	12.4	11.1	12.6	10.0	1.2
Sc	16	2	14	17	12	15	10	2
<b>Th/Sc</b>	<b>0.63</b>	<b>0.95</b>	<b>0.91</b>	<b>0.73</b>	<b>0.93</b>	<b>0.84</b>	<b>1.00</b>	<b>0.60</b>
Th	10.1	1.9	12.7	12.4	11.1	12.6	10.0	1.2
CO	13.1	2.9	17.6	29.6	7.2	13.8	12.2	2.0
<b>Th/CO</b>	<b>0.77</b>	<b>0.66</b>	<b>0.72</b>	<b>0.42</b>	<b>1.54</b>	<b>0.91</b>	<b>0.82</b>	<b>0.6</b>
La	32.5	6.6	27.7	40.7	38.7	30.5	34.8	5
Sc	16	2	14	17	12	15	10	2
<b>La/Sc</b>	<b>20.3</b>	<b>3.3</b>	<b>1.9</b>	<b>2.39</b>	<b>3.22</b>	<b>2.03</b>	<b>3.48</b>	<b>2.5</b>

**TABLE 8: ELEMENTAL RATIO OF CLAY IN THE STUDY AREA**

Element	C1	C2	C3	C4	C5	C6	C7
Th	0.9	1.6	2.7	3.1	2.3	2.2	2.7
Sc	1	1	2	3	51	51	51
<b>Th/Sc</b>	<b>0.9</b>	<b>1.6</b>	<b>1.35</b>	<b>1.03</b>	<b>0.045</b>	<b>0.043</b>	<b>0.053</b>
Th	0.9	1.6	2.7	3.1	2.3	2.2	2.7
CO	3.8	7.1	3.2	10	4.7	11.7	4.3
<b>Th/CO</b>	0.24	0.23	0.84	0.31	0.48	0.18	0.63
La	4.4	29.9	23.6	36.2	23.4	16.9	23.1
Sc	16	2	14	17	12	15	10
<b>La/Sc</b>	<b>0.28</b>	<b>14.95</b>	<b>1.69</b>	<b>2.12</b>	<b>1.95</b>	<b>1.15</b>	<b>2.31</b>

**TABLE 9: ELEMENTAL RATIO OF SHALE IN THE STUDY AREA**

<b>Elemental ratio</b>	<b>Shale</b>	<b>Clay</b>	<b>Felsic sediments range</b>	<b>Mafic sediments range</b>	<b>Upper continental crust</b>	<b>Post archean sediments</b>
Th/Sc	0.60-1.00	0.043-1.60	0.84-20.5	0.05-0.22	0.79	0.9
Th/CO	0.42-1.54	0.18-0.84	0.67-19.4	0.04-1	0.63	0.63
La/Sc	1.9-20.3	0.28-14.95	2.5-16.3	0.43-0.86	2.21	2.4



### **Provenance Tectonic Setting and Depositional Environment**

The geochemical signatures of clastic sediments have been used to ascertain provenance characteristics (Taylor and McLennan, 1985; Condie *et al.*, 1992; Cullers, 1995; Armstrong-Altrin *et al.*, 2004). Most clastic rocks'  $Al_2O_3/TiO_2$  ratios are essentially used to infer source rock composition because  $Al_2O_3/TiO_2$  ratios range of 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks and from 21 to 70 for felsic igneous rocks (Hayashi *et al.*, 1997). The  $Al_2O_3/TiO_2$  ranged from 12.34 to 25.35 in the shale of the South River Yewa ; hence, this  $Al_2O_3/TiO_2$  ratio suggested intermediate to felsic rocks as being probable source rocks for the shale samples .

CO and Ni abundance in siliciclastic sediments was considered a useful provenance tool. Ni/CO concentration of 3.29 and 0.59 were low in the shale and clay samples; a low CO and Cr concentration indicates felsic provenance, according to Wrafter and Graham (1989), and high Cr and Ni content is mainly found in ultramafic rock-derived sediment (Armstrong-Altrin *et al.*, 2004). The Nickel content in the clay sample range from 5.50-116.0, therefore suggesting felsic- ultramafic provenance.

Ratios such as La/Sc, Th/Sc and Th/Co are significantly different in felsic and basic rocks and may lead to constraints on average provenance composition (Wronkiewicz and Condie, 1990; Cox *et al.*, 1995; Cullers, 1995). The Th/Co, Th/Sc and La/Sc ratios for shale and claystone samples from this study were compared. (see table 7). These comparisons also indicated that such ratios came within the range of felsic source rocks.

Table 6 shows the shale and clays sediment samples' rare earth element (REE) concentration; a slight variation in REE content was observed between the shale (0.23 to 54.48) and clay samples (0.25 to 30.74). Bulks REE normally reside in the fine fraction (silt or clay) and it has also been inferred that trivalent REE is readily accommodated in most clay minerals enriched with alumina and ferric iron (Cullers *et al.*, 1987, 1988). The REE plot (Figure 5) showed that shale and clays samples from the South of River Yewa were LREE enriched and had an d low HREE pattern, with depleted Eu and Tm anomalies. This further attest that the shale sediments precursor are granitic with large proportions of alkali feldspars (felsic) and low proportions of plagioclase feldspars (mafic) Adekeye *et al.*, 2007.

The sedimentary rocks' REE pattern and Eu anomaly also help in providing important clues regarding source rock characteristics (Taylor and McLennan, 1985). Higher LREE (La, Ce, Nd, Sm) ratios and depleted Eu anomalies are generally found in felsic rocks, whereas mafic rocks have lower HREE (Tb, Yb,

Lu) ratios and no or small Eu anomalies (Cullers, 1995). The Higher LREE/HREE ratios and depleted Eu anomalies further confirmed the felsic source rock characteristics of the shale and clay sediment samples on the South of River Yewa sediments.

Passive-margin type sandstone is generally enriched in  $SiO_2$  and depleted in  $Na_2O$ , CaO and  $TiO_2$ , suggesting their highly recycled and mature nature (Bhatia, 1983, Okunlola and Idowu, 2012). Major element analysis of the studied shale and clay sediment samples confirmed this, as the samples were also enriched in  $SiO_2$  but depleted in  $Na_2O$ , CaO and  $TiO_2$ , (see table 3).

### **Paleo-oxygenation Condition**

Cu/Zn and (Cu+Mo)/Zn ratios have been put forward by Hallberg (1976) as redox parameters. According to Hallberg (1976), high Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidising conditions; he showed that high values should indicate more reducing conditions in the depositional basins than lower values, which may indicate more oxidising conditions. In this present study, the shale and clay sediments samples had 0.012 and 0.106 Cu/Zn ratios, respectively (Table 5), indicates more oxidising conditions. Wedephol (1968) noted that average shales reflect shallow marine sediments accumulating in oxidising conditions. The U/Th ratio may be used as a redox indicator with U/Th ratio being higher in organic-rich mudstones (Jones and Manning, 1994). A U/Th ratio below 1.25 suggests oxic deposition conditions whereas values above 1.25 suggest suboxic and anoxic conditions (Nath *et al.*, 1997). In this study, the shale samples had U/Th ratios of 0.17, indicating that both shale and clay samples were deposited in an oxic environment.

Dypvik (1984) and Dill (1986) have used the Ni/Co ratio as a redox indicator. Jones and Manning (1994) have suggested that Ni/Co ratios below 5 indicate oxic environments, whereas ratios above 5 indicate suboxic and anoxic environments. Thus, the low Ni/Co ratio for shale (3.29) and clay (0.59) samples indicate that south of River Yewa shale was deposited in well-oxidising conditions.

### **Conclusion**

Field studies have indicated that the shale from the study area were selected from core samples around Idogo, Araromi, Papanla, Erin, Igbobe, North of Irogun-Akere, Andrew and Alaran., North of River Yewa (Yelwa South Local Government). The shale occur alongside siltstones, clay and sandstone inter-bedded with bioturbated ironstone.

The mineralogical composition of the whole rock shale samples based on X-ray diffraction analysis identified clay mineral constituents as probably being kaolinite (dominant clay minerals), montmorillonite

and microcline while quartz is the dominant non clay mineral. Detailed clay fraction determination is needed to further confirm this. Other non-clay minerals included microcline, zircon, pyrite and hematite. The proportions of minerals identified in the shale and claystone samples varied.

The South of River Yewa's (Akinbo formation) clay and shale sediment samples showed considerable variation regarding their major, trace and rare earth elements. Major element abundance showed that shale samples had SiO<sub>2</sub> (44.77%), Al<sub>2</sub>O<sub>3</sub> (15.01%) and Fe<sub>2</sub>O<sub>3</sub> (5.75%), constituting more than 65% of the bulk chemical composition. There was close correlation between the rare earth element composition of shale and clay sediment samples in the South of River Yewa. Higher Ni, Ba, CO, Zr, Rb and Th concentrations were observed in shale than clay, whereas clay samples were more Sr-, Zn-, Pb- and U-enriched than the shale samples. LREE (La, Ce, Nd, Sm, Pr) were enriched in both samples, while Tb, Yb, Lu, Gd, Dy, Ho, Tm and Eu (HREE) are depleted. This further confirms felsic origin of the source rock. The tectonic setting of the shale sediments of the study area's interpretations using the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio indicated a passive-margin type (Bhatia, 1983, Okunlola and Idowu, 2007). Geochemical parameters like U, U/Th, Ni/Co and Cu/Zn ratios strongly implied that these shales were deposited in an oxic environment.

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