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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 consist of SiO_2 (44.77%), Al_2O_3 (15.01%) and Fe_2O_3 (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_2 and Rb/K_2O 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_2O_3/TiO_2 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.*

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

I. 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 withTiO_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 etal,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 Yewa, 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 biomicrosparite, 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 morphometry 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.

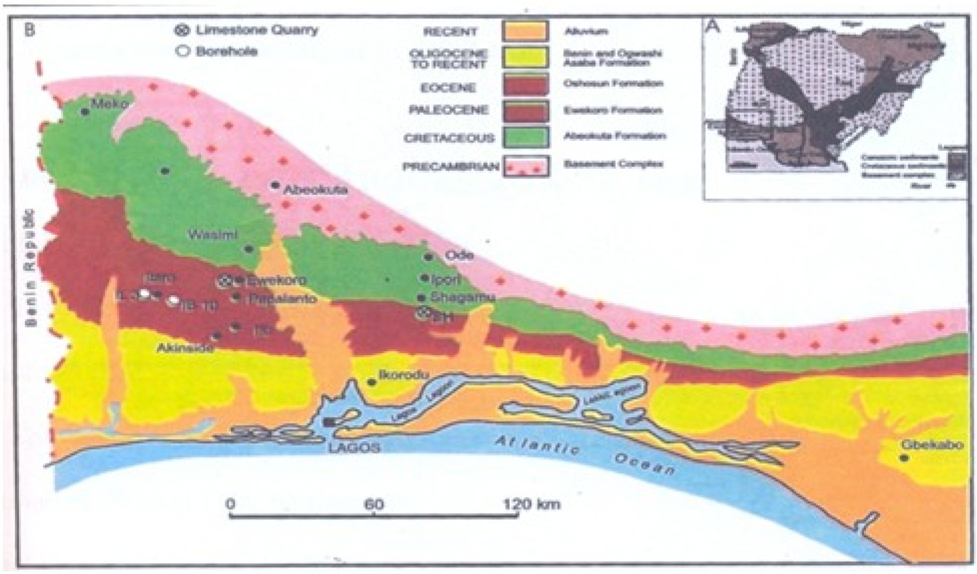


Fig 1: Generalized Geological setting of eastern Dahomey basin (Modified by Billman, 1976)

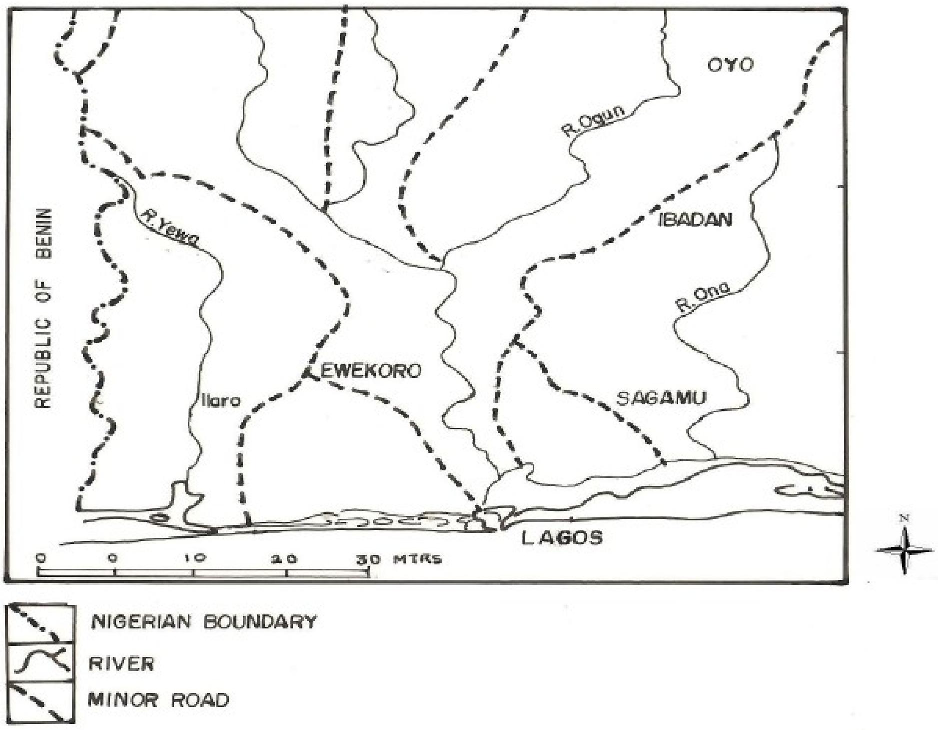
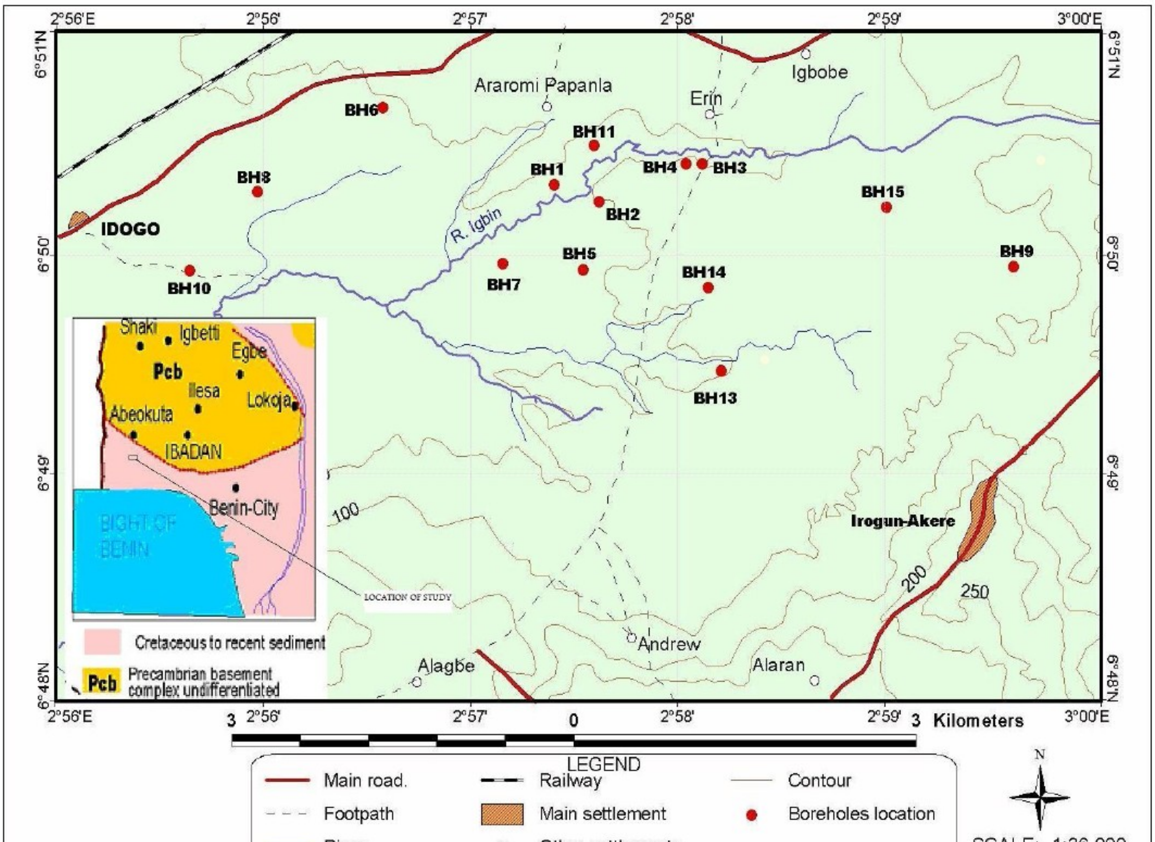


Fig 2: The principal rivers and water shed parts of South Western Nigeria (after Jones and Hockey, 1964)

Fig3: The cored points where representative limestone samples were collected

II. Methodology



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, Igbobe, Oke odan, Owode, Ado-odo, Ipokia, Idi-iroko, Ibatefin, 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^o 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 $LiBO_2/LiB_4O_7$ flux. The crucibles were placed in an oven and heated at 980^oC for 30 minutes. The cooled bead was dissolved in 5% HNO_3 (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_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5, Cr_2O_5, 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^oC for 90 minutes.

III. 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.

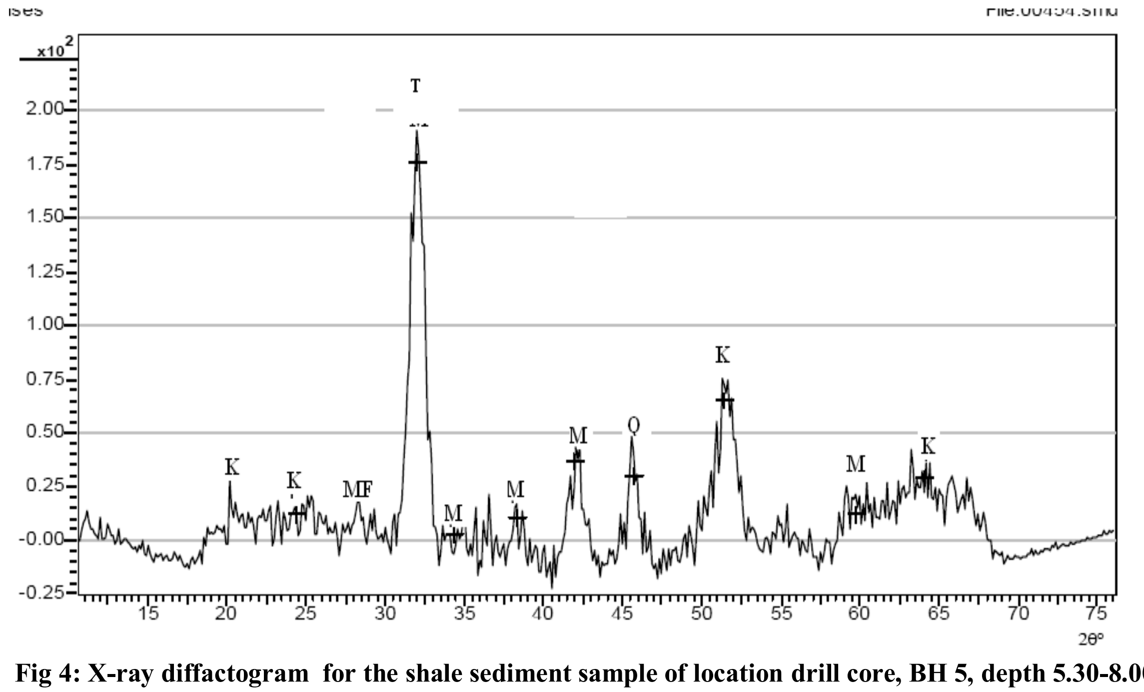


Fig 4: X-ray diffactogram for the shale sediment sample of location drill core, BH 5, depth 5.30-8.00 meters (E of River Igbin) K-kaolinite, MF-microcline feldspar, M-montmorillonite, Q-quartz,

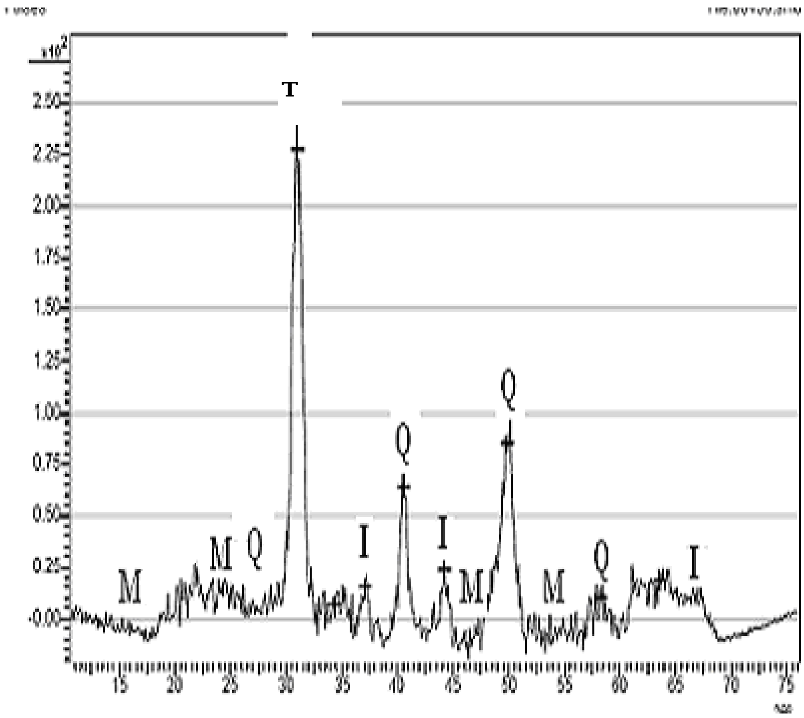


Fig 5: X-ray diffactogram for the shale sediment sample of location drill core, BH 10, depth, 3.20-4.00m South of Idogo) M montmorillonite, Q-quartz, I-illite

Plate 1-4: 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

Drillcore Number (DC)	A1	A2	A3	A4	A5	A6
SiO_2 %	48.88	47.22	48.22	39.89	45.21	39.21
Al_2O_3 %	16.74	15.89	18.00	12.33	17.24	9.87
Fe_2O_3 %	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

Table2: Other results Of The Major/Minor Elements Composition Of Shale Samples With Depth

BOREHOLE NUMBER BH)	A1	A2	A3	A4	A5	A6
Na_2O %	0.10	0.10	0.05	0.06	0.05	0.04
K_2O %	0.91	0.57	1.05	0.70	0.79	0.11
TiO_2 %	0.67	0.77	0.71	0.68	0.70	0.80
P_2O_5 %	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_2O_3 %	0.01	0.02	004	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-etal.,1987
SiO_2	39.89-48.88	44.77	69.94	44.91	58.1	64.82
TiO_2	0.67-0.80	0.72	0.52	0.65	0.6	0.8
Al_2O_3	9.87-18.0	15.01	10	15.71	15.4	17.05
Fe_2O_3	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_2O	0.04-0.10	0.06	0.4	0.42	1.3	1.13
K_2O	0.11-1.05	0.83	1.15	2.36	3.2	3.97
P_2O_5	0.07-0.47	0.08	0.17	0.46	0.2	0.15
LOI	0.01-26.0	20.14				
SiO_2/Al_2O_3	2.91	2.91				
K_2O/Na_2O	13.83	13.83				
K_2O /Al_2O_3	0.055	0.055				
Al_2O_3/TiO_2	20.84	20.84				
Cu/Zn	50.16	50.16				
NI/CO	3.32	3.32				

IV. Major Element Composition

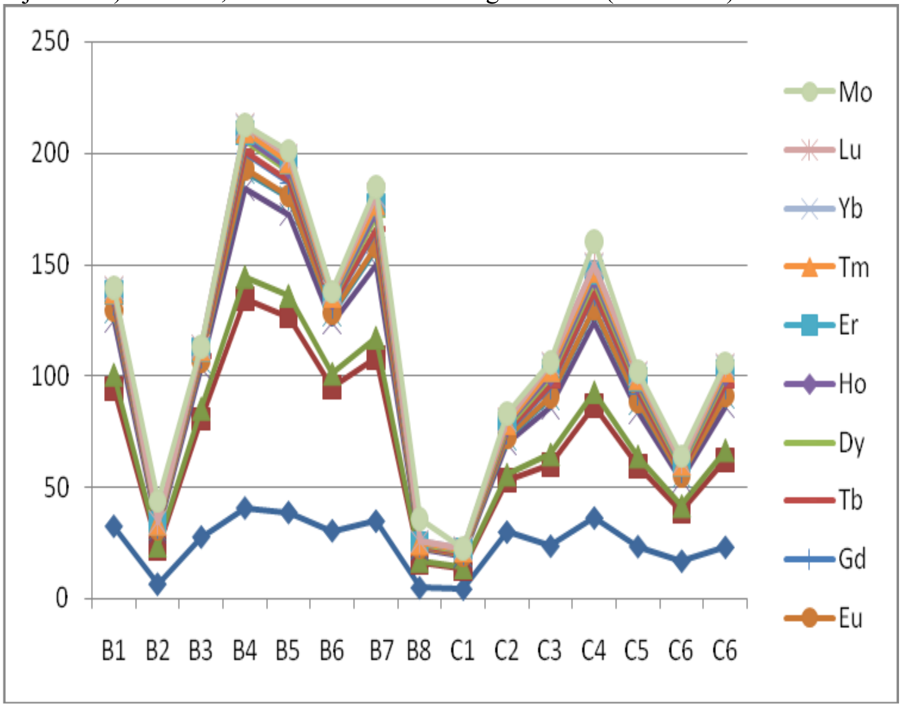
Table 1and 2 gives the major oxide analysis of six shale sediments samples; Table 3 summaries the average major element oxide (wt %) data for the samples being studied. These were compared to the average shale worldwide (Pettijohn, 1957), NASC (Gromet et al., 1984) and shales from other parts of Nigeria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

The SiO_2 (39.21-4888. %), had moderately high Al_2O_3 (9.87 -16.74%) and a small variation in Fe_2O_3 values (3.68%-5.99%); they were, however, low in TiO_2 (10.0.-17.05), CaO, (3.10-15.48) Na_2O (0.06-1.30) and K_2O (0.83-3.97).

Such low K_2O 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_2, Al_2O_3 and Fe_2O_3 content, while theTiO$_2$ is slightly higher compared to the other sedimentary shale.

The shale sample has low phosphate (P_2O_5) content; P_2O_5 depletion could have been due to the lower amount of accessory phases, such as apatite and monazite. The MgO and MnO concentration were higher than the global shale, (Pettijohn, 1957), the Na_2O 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_2) 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_2 (44.77%) and Al_2O_3 (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_2O_3 (5.75%) and TiO_2 (1.74%). The south of River Yewa formation shale sediment samples has higher

TiO_2 values than the average global shale sediments (Pettijohn, 1957). Potassium-Alumina ratio (K_2O/Al_2O_3) can be used as an indicator of ancient sediments' original composition. The K_2O/Al_2O_3 ratios for clay minerals and feldspars are different (0.0 to 0.3, 0.3 to 0.9, respectively) according to Cox et al., 1995. The average K_2O/Al_2O_3 ratio for shale varies from 0.06 to 0.1 and is 0.09 for claystone. The (0.055) K_2O /Al_2O_3 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_2.The TiO_2 concentration is higher with the exception of North American shale composite NASC (Gromet etal., 1984) while, the Alumima (Al_2O_3) and iron (Fe_2O_3) 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).



B – Shale samples, C-Clay samples

Fig 6: Rare earth element plot for shale and clay samples South of River Yewa formation

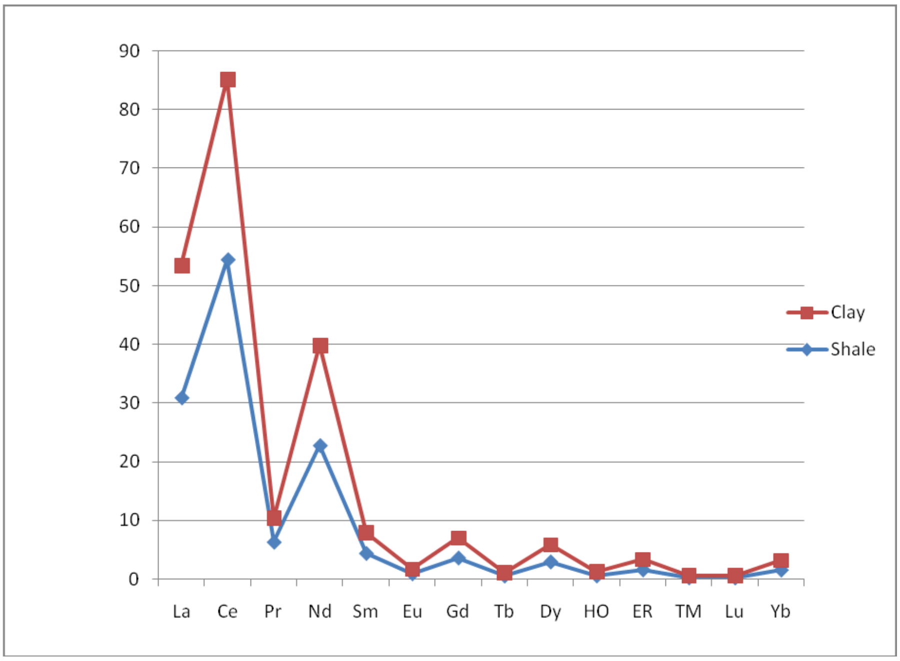


Fig 7: Average Rare Earth Elements composition of the shale samples of the study area showing a slight enrichment of LREE

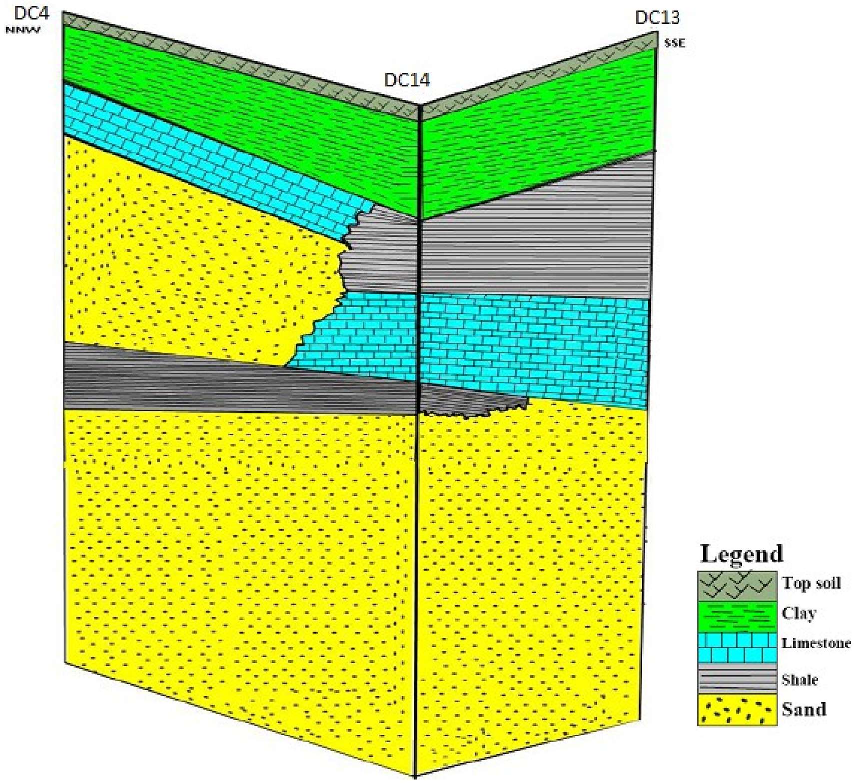


Fig 8: Correllation of Drillcore (Borehole) 4, 14 & 13 (NOT TO SCALE)

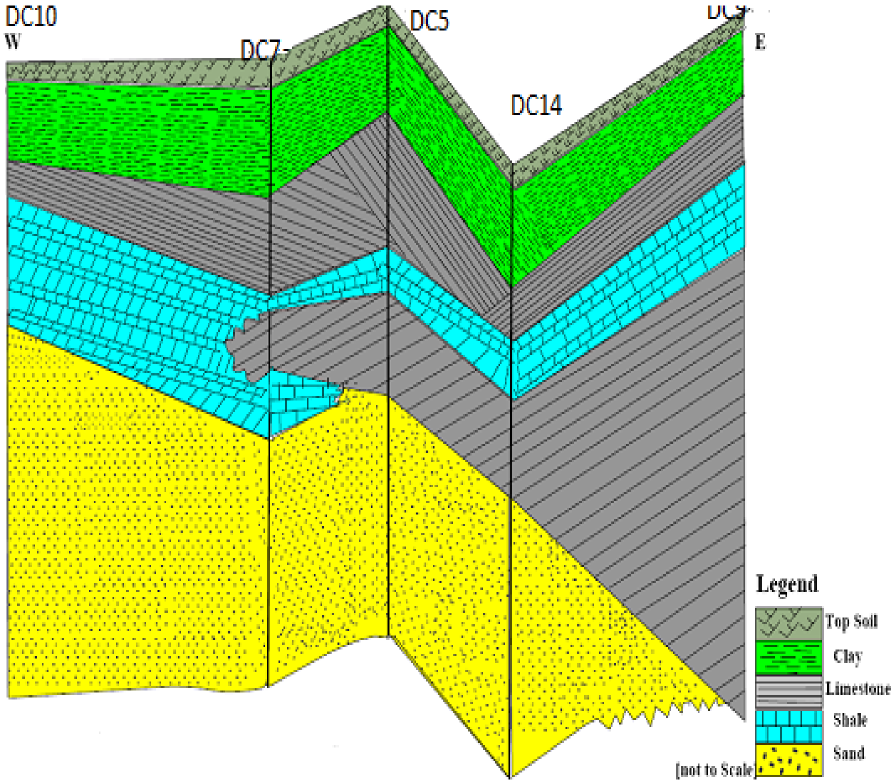


Fig 9: Correllation of drllcore DC(Borehole) 10,7, 5 ,14 & 9 (NOT TO SCALE)

Table 4: 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 etal.,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_2O	44.53	-					
U/Th	0.17	3.61					

Table 5: 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 6: 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
Th/Sc	**0.63**	**0.95**	**0.91**	**0.73**	**0.93**	**0.84**	**1.00**	**0.60**
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
Th/CO	**0.77**	**0.66**	**0.72**	**0.42**	**1.54**	**0.91**	**0.82**	**0.6**
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
La/Sc	**20.3**	**3.3**	**1.9**	**2.39**	**3.22**	**2.03**	**3.48**	**2.5**

Table 7: 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
Th/Sc	**0.9**	**1.6**	**1.35**	**1.03**	**0.045**	**0.043**	**0.053**
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
Th/CO	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
La/Sc	**0.28**	**14.95**	**1.69**	**2.12**	**1.95**	**1.15**	**2.31**

Table 8: Elemental Ratio Of Shale In The Study Area

Elemental ratio	Shale	Clay	Felsic sediments range	Mafic sediments range	Upper continental crust	Post archean sediments
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

V. 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 el 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 8). These comparisons also indicated that such ratios came within the range of felsic source rocks.

Table 7&8 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 (Figure7) showed that shale and clays samples from the South of RiverYewa were LREE enriched and a 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 etal., 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 4), 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.

VI. Conclusions

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., South 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 include 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_2 (44.77%), Al_2O_3 (15.01%) and Fe_2O_3 (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_2O_3/TiO_2 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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APPENDIX

The trace elements composition of shale samples with depth

Borehole Number	B1	B2	B3	B4	B5	B6	B7	B8
Sc	16.00	2.00	14.00	17.00	12.00	15.00	10.00	2.00
Ba	227.00	21.00	284.00	477.00	116.00	102.00	144.00	2.00
Be	3.00	1.00	2.00	3.00	2.00	2.00	2.00	1.00
Co	13.10	2.90	17.60	29.60	7.20	13.80	12.20	2.00
Cs	7.00	0.70	4.40	7.30	2.60	5.60	1.20	0.40
Ga	22.90	3.30	22.70	25.10	16.10	23.30	12.70	2.60
Hf	3.90	0.70	4.20	4.10	5.00	5.20	9.70	0.40
Nb	18.30	3.70	25.30	19.70	20.60	23.80	21.90	2.40
Rb	58.10	6.60	36.30	65.40	36.30	47.40	8.60	5.00
Sn	3.00	1.00	3.00	4.00	3.00	3.00	3.00	1.00
Sr	100.60	220.30	90.70	104.10	351.90	100.00	105.60	207.20
Ta	1.20	0.20	1.50	1.30	1.20	1.40	1.60	0.20
Th	10.10	1.90	12.70	12.40	11.10	12.60	10.00	1.20
U	1.40	1.00	1.10	1.40	2.50	1.30	3.50	0.6
V	111.00	54.00	141.00	135.00	260.00	130.00	84.00	41.00
W	1.30	0.50	1.30	1.40	1.20	1.80	1.50	0.50
Zr	134.60	25.20	154.70	152.20	185.20	171.00	325.80	18.50
Y	12.90	4.20	7.20	25.20	24.20	10.00	39.80	3.50

Trace elements composition of shale samples with depth

Borehole Number	B1	B2	B3	B4	B5	B6	B7	B8
La	32.50	6.60	27.70	40.70	38.70	30.50	34.80	5.00
Ce	61.60	15.80	52.60	93.70	87.60	64.30	73.20	11.00
Pr	6.62	1.67	5.23	10.18	9.77	6.36	9.30	1.36
Nd	23.80	5.90	17.70	39.30	36.30	22.30	32.30	4.60
Sm	4.12	1.23	2.95	7.61	7.04	4.14	7.14	0.95
Eu	0.86	0.25	0.59	1.68	1.49	0.79	1.48	0.20
Gd	3.00	0.98	2.03	6.55	5.79	2.92	6.86	0.82
Tb	0.49	0.16	0.32	1.03	0.93	0.47	0.92	0.11

Dy	2.51	0.76	1.54	5.14	4.65	2.25	6.08	0.66
Ho	0.48	0.14	0.31	0.93	0.87	0.42	1.29	0.13
Er	1.47	0.42	0.89	2.50	2.45	1.28	3.47	0.33
Tm	0.21	0.07	0.15	0.40	0.36	0.19	0.47	0.05
Yb	1.42	0.42	1.00	2.48	2.15	1.41	3.29	0.28
Lu	0.21	0.06	0.14	0.35	0.31	0.20	0.52	0.07
Mo	0.18	9.64	0.06	0.13	2.68	0.38	3.60	10.40
Cu	0.02	0.22	0.03	0.42	0.02	2.71	0.03	0.13
Pb	4.30	1.10	10.80	9.50	5.20	7.70	8.40	0.90

Trace elements composition of shale samples with depth

Borehole Number	B1	B2	B3	B4	B5	B6	B7	B8
Zn	33.00	15.00	40.00	48.00	65.00	56.00	33.00	11.00
Ni	12.10	4.90	30.70	39.40	21.50	16.80	14.80	3.10
As	0.50	1.80	0.50	0.50	0.50	2.40	0.80	0.50
Cd	0.30	0.20	0.10	0.40	6.50	0.40	2.80	0.10
Sb	0.10	0.10	0.10	0.10	0.10	1.10	0.10	0.10
Bi	0.10	0.10	0.10	0.20	0.10	0.20	0.10	0.10
Ag	0.10	0.10	0.10	0.10	0.90	0.10	0.10	0.10
Au	1.30	0.60	0.70	1.40	1.00	1.10	0.50	0.50
Hg	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.01
Ti	0.50	0.40	2.20	0.30	0.20	0.40	0.10	0.10
Se	0.50	0.50	0.50	0.90	7.40	0.90	0.50	0.60

The trace elements composition of clay samples with depth

Borehole Number	C1	C2	C3	C4	C5	C6	C7
Ni	20.0	21.00	20.00	145.00	20.00	20.00	20.00
Sc	1.00	1.00	2.00	3.00	51.00	51.00	51.00
Ba	80.0	42.00	54.00	48.00	51.00	51.00	51.00
Be	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Co	3.80	7.10	3.20	10.00	4.70	11.70	4.30
Cs	0.30	0.50	0.40	0.60	0.40	0.50	0.40
Ga	1.70	1.60	1.60	3.2222 0.7 5	1.90	2.60	1.60
Hf	0.40	0.40	1.20	1.50	1.00	1.30	1.30
Nb	1.90	11.50	3.80	9.90	4.80	49.9	4.90
Rb	2.30	6.50	7.40	13.90	6.80	6.80	6.80
Sn	1.00	2.00	1.00	1.00	1.00	2.00	1.00
Sr	155.10	451.50	275.10	467.50	279.30	271.30	289.30
Ta	0.10	1.40	0.30	2.10	0.30	0.50	0.30
Th	0.90	1.60	2.70	3.10	2.30	2.20	2.70
U	2.10	8.30	1.60	36.30	1.70	4.20	1.70
V	360.00	71.0	28.00	279.00	28.00	48.00	28.00
W	1.20	1.60	1.00	0.50	0.90	0.90	0.60

The trace elements composition of clay samples with depth

Borehole Number	C1	C2	C3	C4	C5	C6	C7
Zr	13.7	25.80	43.40	51.6	41.10	59.80	50.80
Y	4.70	15.90	28.70	41.7	26.10	12.00	26.20
La	4.40	29.90	23.60	36.20	23.40	16.90	23.10
Ce	8.80	22.90	36.50	50.10	36.00	22.10	38.80
P4	1.08	3.11	4.85	6.57	4.67	2.84	4.91
Nd	4.40	13.50	20.80	30.80	19.60	11.00	19.10
Sm	0.89	2.54	4.21	5.75	3.91	2.20	4.34
Eu	0.19	0.52	0.89	1.23	0.82	0.44	0.88
Gd	0.80	2.45	4.13	5.83	3.79	1.90	4.18
Tb	0.13	0.38	0.64	0.88	0.61	0.31	0.66
Dy	0.65	1.97	3.80	5.36	3.24	1.52	3.44
Ho	0.15	0.42	0.78	1.09	0.70	0.34	0.76
Er	0.41	1.17	2.28	2.89	1.94	0.93	2.11
Tm	0.06	0.18	0.34	0.43	0.29	0.14	0.31
Yb	0.34	0.99	2.15	2.49	1.85	0.91	1.91
Lu	0.06	0.14	0.30	0.40	0.26	0.13	0.29
Mo	0.30	2.90	0.80	10.30	0.90	2.60	1.00

The trace elements composition of clay samples with depth

Borehole Number	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Cu	1.90	7.80	3.50	9.60	4.00	3.10	3.50
Pb	3.50	119.00	32.90	87.00	35.90	155.80	67.10
Zn	9.00	56.00	31.00	69.00	34.00	72.00	42.00
Ni	8.80	15.70	4.70	116.10	4.10	7.80	5.50
As	2.8.00	8.60	0.50	47.10	0.50	5.90	0.50
Cd	1.10	1.60	3.50	3.60	3.20	0.90	3.50
Sb	0.20	1.40	0.20	9.40	0.20	0.80	0.20
Bi	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Ag	0.10	0.10	0.10	0.20	0.10	0.10	0.20
Au	0.10	0.10	0.10	0.20	0.10	0.10	0.20
Hg	0.01	0.01	0.01	0.1	0.02	0.02	0.03
Ti	0.50	0.40	2.20	0.30	0.20	0.40	0.10
Se	0.50	0.50	0.50	0.90	7.40	0.90	0.50
Hg	0.01	0.01	0.01	0.01	0.02	0.02	0.03
Ti	0.50	0.40	2.20	0.30	0.20	0.40	0.10

Major and trace elements of the BOREHOLE (BH) with depth

Major element of shale A	**BH5**. 5.3 - 8.0m A1	**BH7** .5.4 - 6.0m A2	**BH7** .6.2 - 10.m A3	**BH9**. 6.1- 9.8 A4	**BH9**. 16.5- 30.0m A5	**BH10**. 3.2- 4.0	**BHC10**. 3.2-4.0m	
Trace element of shale B	**BH5** .5.3-8.0m B1	**BH5**. 11.9- 14.1m B2	**BH7**. 5.4- 6.0m B3	**BH7** .6.2-10m B4	**BH9.** 6.10 – 9.80 B5	**BH.9**.16.5 – 30.0 B6	**BH10**.3.20 – 4.00 B7	**BH.10** 8.00 – 12.00 B8
Trace elements of clay C	**BH.4** 1.60 – 4.00m C1	**BH5.** .8.00 – 10.30 C2	**BH.7.** 6.00 – 6.20 C3	**BH.7.** 10.00 – 12.80 C4	**BH.9.** 9.80 – 11.50 C5	**BH.10.** 4.00 – 7.00 C6	**BH13**. 12.20 – 16.10 C7	

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Report Date: July 17, 2009

Page: 2 of 2 Part 1

CERTIFICATE OF ANALYSIS VAN09002542.1

Method		4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B
Analyte		SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	Cr2O3	Ni	Sc	LOI	Sum	Ba	Be	Co	Cs	Ga
Unit		%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm
MDL		0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.002	20	1	-5.1	0.01	1	1	0.2	0.1	0.5
ILB01	Core Pulp	3.71	1.10	1.78	0.85	50.20	<0.01	0.05	0.07	0.13	0.34	<0.002	<20	1	41.7	99.95	80	<1	3.8	0.3	1.7
ILB02	Core Pulp	4.32	0.84	2.02	1.30	48.74	0.07	0.17	0.59	1.10	0.19	0.015	21	1	40.5	99.86	42	<1	7.1	0.5	1.6
ILB03	Core Pulp	40.53	1.02	1.42	0.38	29.97	0.06	0.20	0.36	1.32	0.14	0.007	<20	2	24.5	99.92	54	<1	3.2	0.4	1.6
ILB04	Core Pulp	6.93	1.89	7.32	1.67	43.84	0.20	0.35	0.37	7.67	0.52	0.024	145	3	29.0	99.78	48	1	10.0	0.6	3.6
ILB05	Core Pulp	40.26	1.01	1.35	0.39	30.04	0.06	0.19	0.51	1.27	0.14	0.007	<20	2	24.7	99.91	53	<1	4.7	0.4	1.9
ILB06	Core Pulp	8.52	1.46	1.47	0.84	45.97	0.05	0.17	1.09	0.49	0.22	0.014	<20	1	39.6	99.90	31	<1	11.7	0.5	2.6
ILB07	Core Pulp	40.05	1.00	1.32	0.38	30.16	0.05	0.19	0.50	1.29	0.14	0.007	<20	2	24.8	99.91	51	<1	4.3	0.4	1.6
ILB08	Core Pulp	48.88	16.74	5.57	3.41	1.53	0.10	0.91	0.67	0.10	0.05	0.016	43	16	21.9	99.83	227	3	13.1	7.0	22.9
ILB09	Core Pulp	8.22	2.20	3.09	15.25	28.38	0.02	0.14	0.12	0.04	0.26	0.005	<20	2	42.0	99.71	21	<1	2.9	0.7	3.3
ILB10	Core Pulp	47.22	15.89	6.11	2.91	1.15	0.10	0.57	0.77	0.05	0.15	0.027	52	14	24.9	99.82	284	2	17.6	4.4	22.7
ILB11	Core Pulp	48.22	18.00	5.99	3.51	0.86	0.05	1.05	0.71	0.04	0.06	0.015	78	17	21.3	99.79	477	3	29.6	7.3	25.1
ILB12	Core Pulp	39.89	12.33	4.41	1.86	13.34	0.06	0.70	0.68	0.47	0.02	0.043	36	12	26.0	99.79	116	2	7.2	2.6	16.1
ILB13	Core Pulp	45.21	17.24	8.75	2.52	1.48	0.05	0.79	0.70	0.07	0.05	0.024	42	15	23.0	99.84	102	2	13.8	5.6	23.3
ILB14	Core Pulp	39.21	9.87	3.68	0.66	19.34	0.04	0.11	0.80	0.46	0.04	0.018	33	10	25.6	99.87	144	2	12.2	1.2	12.7
ILB15	Core Pulp	5.95	1.62	2.44	15.53	30.61	0.02	0.11	0.09	0.04	0.25	0.004	<20	2	43.0	99.70	20	<1	2.0	0.4	2.6

This report supersedes all previous preliminary and final reports with this file number dated prior to the date on this certificate. Signature indicates final approval; preliminary reports are unsigned and should be used for reference only.

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Client: **University of Ibadan**
Department of Geology
Ibadan Nigeria

Project: None Given
Report Date: July 17, 2009

Page: 2 of 2 Part 2

CERTIFICATE OF ANALYSIS VAN09002542.1

Analyte		Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Method		4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B
Unit		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MDL		0.1	0.1	0.1	1	0.5	0.1	0.2	0.1	8	0.5	0.1	0.1	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01
ILB01	Core Pulp	0.4	1.9	2.3	<1	155.1	0.1	0.9	2.1	36	1.2	13.7	4.7	4.4	8.8	1.08	4.4	0.89	0.19	0.80	0.13
ILB02	Core Pulp	0.6	11.5	6.5	2	451.5	1.4	1.6	8.3	71	1.6	25.8	15.9	29.9	22.9	3.11	13.5	2.54	0.52	2.45	0.38
ILB03	Core Pulp	1.2	3.8	7.4	<1	275.1	0.3	2.7	1.6	28	1.0	43.4	28.7	23.6	36.5	4.85	20.8	4.21	0.89	4.13	0.64
ILB04	Core Pulp	1.5	9.9	13.9	1	467.5	2.1	3.1	36.3	279	<0.5	51.6	41.7	36.2	50.1	6.57	30.8	5.75	1.23	5.83	0.88
ILB05	Core Pulp	1.0	4.8	6.8	1	279.3	0.3	2.3	1.7	28	0.9	41.1	26.1	23.4	36.0	4.67	19.6	3.91	0.82	3.79	0.61
ILB06	Core Pulp	1.3	9.9	6.8	2	271.9	0.5	2.2	4.2	48	0.9	59.8	12.0	16.9	22.1	2.84	11.0	2.20	0.44	1.90	0.31
ILB07	Core Pulp	1.3	4.9	6.8	<1	289.1	0.3	2.7	1.7	28	0.6	50.8	26.2	23.1	38.8	4.91	19.1	4.34	0.88	4.18	0.66
ILB08	Core Pulp	3.9	18.3	58.1	3	100.6	1.2	10.1	1.4	111	1.3	134.6	12.9	32.5	61.6	6.62	23.8	4.12	0.86	3.00	0.49
ILB09	Core Pulp	0.7	3.7	6.6	<1	220.3	0.2	1.9	1.0	54	<0.5	25.2	4.2	6.6	15.8	1.67	5.9	1.23	0.25	0.98	0.16
ILB10	Core Pulp	4.2	25.3	36.3	3	90.7	1.5	12.7	1.1	141	1.3	154.7	7.2	27.7	52.6	5.23	17.7	2.95	0.59	2.03	0.32
ILB11	Core Pulp	4.1	19.7	65.4	4	104.1	1.3	12.4	1.4	135	1.4	152.2	25.2	40.7	93.7	10.18	39.3	7.61	1.68	6.55	1.03
ILB12	Core Pulp	5.0	20.6	36.3	3	351.9	1.2	11.1	2.5	260	1.2	185.2	24.2	38.7	87.6	9.77	36.3	7.04	1.49	5.79	0.93
ILB13	Core Pulp	5.2	23.8	47.4	3	100.0	1.4	12.6	1.3	130	1.8	171.0	10.0	30.5	64.3	6.36	22.3	4.14	0.79	2.92	0.47
ILB14	Core Pulp	9.7	21.9	8.6	3	105.6	1.6	10.0	3.5	84	1.5	325.8	39.8	34.8	73.2	9.30	32.3	7.14	1.48	6.86	0.92
ILB15	Core Pulp	0.4	2.4	5.0	<1	207.2	0.2	1.2	0.6	41	<0.5	18.5	3.5	5.0	11.0	1.36	4.6	0.95	0.20	0.82	0.11

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Report Date: July 17, 2009

Page: 2 of 2 Part 4

CERTIFICATE OF ANALYSIS VAN09002542.1

	Method	1DX	1DX
	Analyte	Tl	Se
	Unit	ppm	ppm
	MDL	0.1	0.5
ILB01	Core Pulp	<0.1	<0.5
ILB02	Core Pulp	17.9	4.9
ILB03	Core Pulp	6.5	2.4
ILB04	Core Pulp	13.2	42.4
ILB05	Core Pulp	5.9	2.3
ILB06	Core Pulp	50.8	1.3
ILB07	Core Pulp	13.0	2.5
ILB08	Core Pulp	0.5	<0.5
ILB09	Core Pulp	0.4	0.5
ILB10	Core Pulp	2.2	<0.5
ILB11	Core Pulp	0.3	0.9
ILB12	Core Pulp	0.2	7.4
ILB13	Core Pulp	0.4	0.9
ILB14	Core Pulp	<0.1	<0.5
ILB15	Core Pulp	<0.1	0.6

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Page: 1 of 2 Part 1

QUALITY CONTROL REPORT VAN09002542.1

	Method	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B
	Analyte	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	Cr2O3	Ni	Sc	LOI	Sum	Ba	Be	Co	Cs	Ga
	Unit	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm
	MDL	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.002	20	1	-5.1	0.01	1	1	0.2	0.1	0.5
Pulp Duplicates																					
ILB09	Core Pulp	8.22	2.20	3.09	15.25	28.38	0.02	0.14	0.12	0.04	0.26	0.005	<20	2	42.0	99.71	21	<1	2.9	0.7	3.3
REP ILB09	QC																				
ILB15	Core Pulp	5.95	1.62	2.44	15.53	30.61	0.02	0.11	0.09	0.04	0.25	0.004	<20	2	43.0	99.70	20	<1	2.0	0.4	2.6
REP ILB15	QC	5.98	1.64	2.47	15.54	30.53	0.02	0.11	0.09	0.04	0.25	0.004	<20	2	43.0	99.70	18	<1	1.3	0.6	2.3
Reference Materials																					
STD CSC	Standard																				
STD CSC	Standard																				
STD DS7	Standard																				
STD DS7	Standard																				
STD DS7	Standard																				
STD DS7	Standard																				
STD OREAS76A	Standard																				
STD OREAS76A	Standard																				
STD SO-18	Standard	58.09	14.13	7.61	3.34	6.37	3.69	2.16	0.69	0.83	0.39	0.550	44	26	1.9	99.75	490	<1	26.0	6.8	17.0
STD SO-18	Standard	58.09	14.11	7.61	3.33	6.37	3.69	2.16	0.69	0.83	0.39	0.550	45	26	1.9	99.71	494	<1	26.6	6.8	17.2
STD SO-18	Standard	58.10	14.11	7.61	3.33	6.37	3.69	2.16	0.69	0.83	0.39	0.550	45	26	1.9	99.72	494	<1	26.6	6.9	17.0
STD SO-18	Standard	58.08	14.12	7.61	3.33	6.37	3.68	2.16	0.69	0.83	0.39	0.550	44	27	1.9	99.72	501	<1	27.1	6.9	17.0
STD SO-18	Standard	58.03	14.15	7.61	3.33	6.37	3.69	2.15	0.69	0.82	0.39	0.550	42	25	1.9	99.69	516	<1	26.6	6.8	17.4
STD SO-18	Standard	58.07	14.13	7.60	3.33	6.37	3.68	2.15	0.69	0.82	0.39	0.549	45	25	1.9	99.70	502	<1	26.8	6.9	17.3
STD CSC Expected																					
STD OREAS76A Expected																					
STD DS7 Expected																					
STD SO-18 Expected		58.47	14.23	7.67	3.35	6.42	3.71	2.17	0.69	0.83	0.39	0.55	44	25			514		26.2	7.1	17.6
BLK	Blank																				
BLK	Blank																				
BLK	Blank																				
BLK	Blank	<0.01	<0.01	<0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.002	<20	<1	0.0	<0.01	<1	<1	<0.2	<0.1	<0.5
BLK	Blank																				

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Ibadan Nigeria

Project: None Given

Report Date: July 17, 2009

Page: 1 of 2 Part 2

QUALITY CONTROL REPORT VAN09002542.1

	Method	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B
	Analyte	Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
	Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	MDL	0.1	0.1	0.1	1	0.5	0.1	0.2	0.1	8	0.5	0.1	0.1	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01
Pulp Duplicates																					
ILB09	Core Pulp	0.7	3.7	6.6	<1	220.3	0.2	1.9	1.0	54	<0.5	25.2	4.2	6.6	15.8	1.67	5.9	1.23	0.25	0.98	0.16
REP ILB09	QC																				
ILB15	Core Pulp	0.4	2.4	5.0	<1	207.2	0.2	1.2	0.6	41	<0.5	18.5	3.5	5.0	11.0	1.36	4.6	0.95	0.20	0.82	0.11
REP ILB15	QC	0.7	2.4	5.2	<1	207.4	0.1	1.2	0.8	37	<0.5	19.2	3.6	5.1	11.1	1.33	4.6	0.91	0.18	0.77	0.11
Reference Materials																					
STD CSC	Standard																				
STD CSC	Standard																				
STD DS7	Standard																				
STD DS7	Standard																				
STD DS7	Standard																				
STD DS7	Standard																				
STD OREAS76A	Standard																				
STD OREAS76A	Standard																				
STD SO-18	Standard	9.3	20.9	27.9	15	397.9	7.2	9.9	16.1	198	14.6	279.3	30.7	11.6	26.3	3.37	13.9	2.80	0.84	2.83	0.39
STD SO-18	Standard	9.5	20.7	28.1	15	397.9	7.2	9.6	16.0	197	14.9	280.6	30.8	11.7	26.3	3.37	13.7	2.85	0.84	2.80	0.41
STD SO-18	Standard	9.6	21.1	28.1	14	402.5	7.1	10.1	16.2	205	15.1	280.5	31.3	12.1	27.3	3.40	13.8	2.91	0.86	2.88	0.51
STD SO-18	Standard	9.6	21.2	28.2	15	407.9	7.1	9.8	16.2	205	14.7	283.5	31.5	12.2	27.7	3.41	13.9	2.87	0.87	2.91	0.51
STD SO-18	Standard	9.6	20.9	28.0	15	401.5	6.0	9.7	16.1	205	14.5	284.1	31.4	11.9	26.7	3.40	13.8	2.85	0.86	2.86	0.50
STD SO-18	Standard	9.4	21.0	28.1	15	403.1	7.2	10.0	16.0	203	14.7	282.6	31.3	11.9	26.7	3.40	13.9	2.88	0.86	2.86	0.50
STD CSC Expected																					
STD OREAS76A Expected																					
STD DS7 Expected																					
STD SO-18 Expected		9.8	20.9	28.7	15	407.4	7.4	9.9	16.4	200	15.1	280	33	12.3	27.1	3.45	14	3	0.89	2.93	0.53
BLK	Blank																				
BLK	Blank																				
BLK	Blank																				
BLK	Blank	<0.1	<0.1	<0.1	<1	<0.5	<0.1	<0.2	<0.1	<8	<0.5	<0.1	<0.1	<0.1	<0.1	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01
BLK	Blank																				

This report supersedes all previous preliminary and final reports with this file number dated prior to the date on this certificate. Signature indicates final approval; preliminary reports are unsigned and should be used for reference only.

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Ibadan Nigeria

Project: None Given
Report Date: July 17, 2009

Page: 1 of 2 Part 3

QUALITY CONTROL REPORT VAN09002542.1

	Method	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	2A Leco	2A Leco	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX
	Analyte	Dy	Ho	Er	Tm	Yb	Lu	TOT/C	TOT/S	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag	Au	Hg
	Unit	ppm	ppm	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm
	MDL	0.05	0.02	0.03	0.01	0.05	0.01	0.02	0.02	0.1	0.1	0.1	1	0.1	0.5	0.1	0.1	0.1	0.1	0.5	0.01
Pulp Duplicates																					
ILB09	Core Pulp	0.76	0.14	0.42	0.07	0.42	0.06	9.64	0.22	0.3	1.2	1.1	15	4.9	1.8	0.2	<0.1	<0.1	<0.1	0.6	<0.01
REP ILB09	QC							9.81	0.23												
ILB15	Core Pulp	0.66	0.13	0.33	0.05	0.28	0.07	10.40	0.13	0.2	0.9	0.9	11	3.1	0.5	<0.1	<0.1	<0.1	<0.1	<0.5	<0.01
REP ILB15	QC	0.61	0.12	0.32	0.04	0.29	0.06	10.41	0.10												
Reference Materials																					
STD CSC	Standard							2.98	4.23												
STD CSC	Standard							2.87	4.20												
STD DS7	Standard									18.7	96.0	68.1	389	51.6	47.4	5.8	4.2	4.4	0.8	51.7	0.19
STD DS7	Standard									16.6	100.2	62.5	375	51.4	51.0	5.8	4.0	4.3	0.7	44.8	0.18
STD DS7	Standard									19.1	108.6	67.3	376	51.4	50.3	6.5	4.1	4.8	0.7	78.8	0.18
STD DS7	Standard									21.3	111.7	75.1	400	53.6	51.2	7.0	4.7	5.0	0.8	52.8	0.19
STD OREAS76A	Standard							0.14	17.62												
STD OREAS76A	Standard							0.15	17.99												
STD SO-18	Standard	2.85	0.58	1.73	0.22	1.68	0.26														
STD SO-18	Standard	2.85	0.59	1.72	0.22	1.70	0.26														
STD SO-18	Standard	2.95	0.61	1.77	0.28	1.79	0.27														
STD SO-18	Standard	2.99	0.61	1.80	0.28	1.72	0.27														
STD SO-18	Standard	2.86	0.61	1.79	0.28	1.77	0.26														
STD SO-18	Standard	2.87	0.60	1.77	0.28	1.73	0.26														
STD CSC Expected								2.94	4.25												
STD OREAS76A Expected								0.16	18												
STD DS7 Expected										20.5	109	70.6	411	56	48.2	6.4	4.6	4.5	0.9	70	0.2
STD SO-18 Expected		3	0.62	1.84	0.29	1.79	0.27														
BLK	Blank							<0.02	<0.02												
BLK	Blank							<0.02	<0.02												
BLK	Blank									<0.1	<0.1	<0.1	<1	<0.1	<0.5	<0.1	<0.1	<0.1	<0.1	<0.5	<0.01
BLK	Blank	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01														
BLK	Blank									<0.1	<0.1	<0.1	<1	<0.1	<0.5	<0.1	<0.1	<0.1	<0.1	<0.5	<0.01

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Client: **University of Ibadan**
Department of Geology
Ibadan Nigeria

Project: None Given
Report Date: July 17, 2009

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QUALITY CONTROL REPORT VAN09002542.1

	Method	1DX	1DX
	Analyte	Tl	Se
	Unit	ppm	ppm
	MDL	0.1	0.5
Pulp Duplicates			
ILB09	Core Pulp	0.4	0.5
REP ILB09	QC		
ILB15	Core Pulp	<0.1	0.6
REP ILB15	QC		
Reference Materials			
STD CSC	Standard		
STD CSC	Standard		
STD DS7	Standard	4.0	3.2
STD DS7	Standard	4.0	3.5
STD DS7	Standard	3.9	3.2
STD DS7	Standard	4.2	3.8
STD OREAS76A	Standard		
STD OREAS76A	Standard		
STD SO-18	Standard		
STD SO-18	Standard		
STD SO-18	Standard		
STD SO-18	Standard		
STD SO-18	Standard		
STD SO-18	Standard		
STD CSC Expected			
STD OREAS76A Expected			
STD DS7 Expected		4.2	3.5
STD SO-18 Expected			
BLK	Blank		
BLK	Blank		
BLK	Blank	<0.1	<0.5
BLK	Blank		
BLK	Blank	<0.1	<0.5

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QUALITY CONTROL REPORT VAN09002542.1

		4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B
		SIO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TIO2	P2O5	MnO	Cr2O3	NI	Sc	LOI	Sum	Ba	Be	Co	Cs	Ga
		%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm
		0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.002	20	1	-5.1	0.01	1	1	0.2	0.1	0.5
BLK	Blank	<0.01	<0.01	<0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.002	<20	<1	0.0	<0.01	<1	<1	<0.2	<0.1	<0.5
BLK	Blank	<0.01	<0.01	<0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.002	<20	<1	0.0	<0.01	<1	<1	<0.2	<0.1	<0.5

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QUALITY CONTROL REPORT VAN09002542.1

		4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B
		Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
		0.1	0.1	0.1	1	0.5	0.1	0.2	0.1	8	0.5	0.1	0.1	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01
BLK	Blank	<0.1	<0.1	<0.1	<1	<0.5	<0.1	<0.2	<0.1	<8	<0.5	<0.1	<0.1	<0.1	<0.1	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01
BLK	Blank	<0.1	<0.1	<0.1	<1	<0.5	<0.1	<0.2	<0.1	<8	<0.5	1.0	<0.1	<0.1	<0.1	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01

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QUALITY CONTROL REPORT VAN09002542.1

		4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	4A-4B	2A Leco	2A Leco	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX	1DX
		Dy	Ho	Er	Tm	Yb	Lu	TOT/C	TOT/S	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag	Au	Hg
		ppm	ppm	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm
		0.05	0.02	0.03	0.01	0.05	0.01	0.02	0.02	0.1	0.1	0.1	1	0.1	0.5	0.1	0.1	0.1	0.1	0.5	0.01
BLK	Blank	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01														
BLK	Blank	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01														

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		1DX	1DX
		Tl	Se
		ppm	ppm
		0.1	0.5
BLK	Blank		
BLK	Blank		