Rare Earth Elements Fingerprints: Implication For Provenance, Tectonic And Depostional Settings Of Clastic Sediments Of Lower Benue Trough, Southeastern Nigeria

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Abstracts: The study areas, Lower Benue Trough is divided into Asu River Group (ARG) and Cross River Group (CRG) and it is delimited by longitudes 7°00'E and 8°30'E and latitudes 5°00'N and 6°30'N. ARG covers Awi, Abakaliki and Mfamosing Formations while Ekenkpon, Eze-Aku, New Netim, Awgu and Agbani Formations fall within CRG. Sampling was done to cover both the Abakaliki Anticlinorium and Calabar Flank. The study aimed at using geochemical approach through rare earth elements (REE) to deduce provenance and depositional environment in a holistic manner which hitherto has not been used by any worker. A total of 56 fresh outcrop samples were obtained from the study area. The samples were subjected to detailed lithologic description by visual examination. Geochemical analysis was done using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to determine trace and rare-earth elements using lithium metaborate/tetraborate fusion method. The chondrite normalized REE plots shows enrichment in the LREE over the HREE with negative Eu anomaly for both ARG and CRG. While the (Eu/Eu*) average for ARG and CRG are 0.74 and 0.73 respectively indicating Quartzose sedimentary, Intermediate igneous and Felsic igneous provenances for the sediments. The Cerium anomaly (Ce/Ce*) values average 1.20 and 1.68 in ARG and CRG respectively indicating oxidizing and shallow marine environment. The REE pattern is consistent with that of the Upper Continental Crust (UCC).

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Introduction

The Benue Trough is a unique rift feature on the African continent in that it occupies an intracontinental position and has a thick compressionally folded Cretaceous supracrustal fill which is generally divided into Lower, Middle and Upper Benue Troughs sub-basins (Cratcheley and Jones 1965; Wright 1968; Grant 1971; Burke et al., 1971; Burke and Whiteman 1973; Nwachukwu 1972; Olade 1975). The Lower Benue Trough (LBT) has a lateral extent of about 250km in the south and includes the Anambra Basin, the Abakaliki anticlinorium and the Afikpo syncline. It is a linear, intracratonic, graben basin, tending NE-SW. Its origin is associated with the separation of the African and South American continents in the Early Cretaceous. The trough is characterized by an uplifted basement block, flanked by deep basin containing about 6km thick of sediments. The intra-continental Benue Trough was initiated during the lower Cretaceous in relation with the opening of Atlantic Ocean.

The sedimentary succession in the Lower Benue Trough is predominantly pre-Santonian in age and has been established as the Asu River Group (ARG) and Cross River Group (CRG) which sometimes are further subdivided into Eze-Aku Group and the Awgu

Group in the Abakaliki area and Awi Formation, Mfamosing Limestone, Ekenkpon Shale and New Netim Marl in the Calabar Flank (Fig. 1). A total number of fifty-Six (56) outcrop samples collected from eight (8) Formations: Awi, Abakaliki, Mfamosing Formations which constitute ARG while Ekenkpon, Eze-Aku, New Netim Marl, Awgu and Agbani Formations constitute CRG (Figs 2, 3 and 4). The collected samples were subjected to geochemical analysis so as to have a clearer picture or information about the provenance, tectonic setting and weathering history of the source area. The geochemical composition of terrigenous sedimentary rocks is a function of the complex interplay of various variables, such as provenance, weathering, transportation and diagenesis (Bhatia, 1983). Recent investigations on geochemical characteristics of ancient and modern detritus have been carried out in order to infer the source rocks, provenance and tectonic setting (Potter, 1978; Bhatia, 1983; Hiscott, 1984; Bhatia and Crook, 1986; Roser and Korsch, 1986&1988). The rare earth elements (REE, from lanthanum to lutetium) are a coherent geochemical group characterized by a single oxidation state except for cerium and europium. During the last few decades, REE have become important geochemical tracers in order to understand

and describe the chemical evolution of the earth's continental crust (Goldstein and Jacobsen, 1988; McLennan, 1989; Gaillardet, 1995; Dupre et al., 1996). Moreover, REE have been used as analogues for actinide elements, in studies related to radioactive waste disposal in order to demonstrate their general immobility in weathering environments (Wood, et al., 1979a.). Hence, this study is aimed at using the rare earth elements signatures to infer the weathering, provenance, tectonic setting as well as depositional environment in each group and holistically across the LBT in manner which hitherto has not been used by any worker (Fig. 5).

Stratigraphy and Geological Setting

The intracontinental Benue Trough was initiated during the lower Cretaceous in relation with the Atlantic Ocean opening. The first stage of its evolution started in the Aptian, forming isolated basins with continental sedimentation. In the Albian times, a great delta developed in the Upper Benue Trough, while the first marine transgression coming from the opening Gulf of Guinea occurred in the south and reached the Middle Benue. The widespread Turonian transgression made the Atlantic and Tethys waters communicate through the Sahara. Niger basins and the Benue Trough. The tectonic evolution of the Benue Trough was closely controlled by transcurrent faulting through an axial fault system, developing local compressional and tensional regimes and resulting in basins and basement horsts along releasing and restraining bends of the faults. Two major compressional phases occurred in the Abakaliki area (southern Benue) during the Santonian and at the end of the Cretaceous in the Upper Benue Trough. In Abakaliki, the sedimentary infilling was severely deformed through folding and flattening, and moderate folding and fracturing occurred in the northeast. The Cretaceous magmatism was restricted to main fault zones in most of the trough but was particularly active in the Abakaliki Trough, where it has alkaline affinities. From Albian to Santonian, the magmatism was accompanied in part of the Abakaliki Trough by a low-grade metamorphism.

Asu river group

The Abakaliki-Benue Phase (Aptian-Santonian), have more than 3000m of rocks sequence comprising the Abakaliki, Eze-Aku and Awgu Formations, deposited during the first phase in the Abakaliki-Benue Basin, the Benue Valley and the Calabar Flank. Structural inversion affected the Abakaliki region and displaced the depositional axis further to the south of the Anambra Basin (Obi et al., 2001). In the Lower Benue, regression ended during the Santonian and the Abakaliki area emerged completely, however the effects of the Santonian phase are restricted to the Abakaliki anticlinorium, the Anambra syncline does not display traces of this tectonic episode (Benkhelil, 1986). ARG represents the first and the oldest cycles of the shallow marine to brackish water sediment, which were deposited in Albian and end around the Cenomanian. These sediments were deposited on the Basement Complex and consist of roughly 2000-3000m of poorly bedded shales (Abakaliki Shales), siltstone and limestone, and mudstone. The presence of Cenomanian sediments and Santonian intrusions of dykes and sill extrusions that possess important mineralization zones along the gently folded axis of the Abakaliki anticline had been reported (Fig. 3).

Cross river group

The Cross River Group as exposed within Calabar Flank is part of the continental margin of Nigeria dominated by block faults with NW-SE trending horst and graben structures, such as the Ituk high and the Ikang trough. The Calabar Flank forms that part of the southeastern continental margin lying between the Cameroon volcanic trend on the east, Ikpe platform on the west, Oban massif to the north and Calabar hinge line to the south. The Calabar Flank contains up to 4000 m of Albian to Maastrichtian marine sediments in outcrop sections. Overlying the Asu River Group is the Cross River Group comprising of Ekenkpon Formation, Eze-Aku Formation, New Netim Formation, Awgu Formation and Agbani Formation. The Eze-Aku Shale is represented by the Ekenkpon Shale which overlies the Odukpani Formation in the Calabar Flank and is underlying the Awgu Shale which is also represented by New Netim Marl and both represent the Nkalagu Formation (Fig. 4).



Fig 1: Geological map showing different basin in Nigeria, note the Benue trough (BT), Abakaliki (ARG) and Calabar Flank (CRG)

Materials and Methods

A total of Fifty (56) fresh outcrop samples were obtained from the study area; Sampling was done to cover both Asu River (ARG) and Cross River Groups (CRG) within Benue Trough. ARG covers Awi, Abakaliki and Mfamosing Formations while Ekenkpon, Eze-Aku, New Netim, Awgu and Agbani Formations fall within CRG. The study area fall within the coordinate (longitude 7°00'E and 8°35'E and latitude 5°00'N and 6°45'N) Lower Benue Trough, Southeastern Nigeria, samples were collected from Amaseri quarry, Enyingba quarry, Nigercem quarry, Setraco quarry, Ishiagu bridge, Ugwueme, and Ugwuokwute in ARG (Fig 3) while in CRG (Fig 4), samples were collected from Unicem quarry, Unicem junction, Km7 Awi, Km7 farmland, Km 7 Ekenkpon, Odukpani junction and New netim. Fifty (56) samples were subjected to detailed lithologic description by visual examination and were for rare-earth elements analysed at Acme Laboratories Limited (code: 4A4B), Vancouver, Canada. The elements were analysed by lithium metaborate/tetraborate fusion method. The sediment was at 60°C and sieved to -80 mesh (-180 μm). A 250g aliquot was riffle split and pulverized to 85%

passing 200 meshes (75 μm) in a mild-steel and puck mill before its introduction into ICP-MS machine. **Results and Discussion** Sedimentological study

The detail sedimentological description of the pre-Santonian Lower Benue Trough is given in another paper (Adeigbe and Oruene, 2012) but in summary, the study revealed the sandstones of Awi Formation to be angular to subangular, feldspathic, and generally fines upward and Amaseri are calcareous, indurated and laterally extensive. Agbani Sandstone consists of thick vertical sequences of ferruginized indurated sandstones. and The lithologies observed include sandstone, shale, marl, limestone as well as lignite. Megascopically, the sandstones are fine to medium grained, well sorted and sub-angular to sub-rounded, while the shales are organic ranging from light grey to black. Majority of the shale samples were very fissile while, others were highly indurated with laminations and specs of mica. The lignite is black in colour and could represent subbituminous to bituminous coal. It is also worthy of note that some of the sandstone samples appear reddish brown in colour as a result of ferruginisation. Observed limestone samples were fossilliferous with some of the fossil fragments visible to the naked eye.



Fig 2: Geological Map of Southeastern Nigeria Covering the Study Area (ARG, i.e Red Thin line) and (CRG, i.e Blue Thick line)



Fig. 3: Geological map of the ARG showing sample location



Fig 4: Geological map of the CRG showing sample location



Fig. 5: Correlation Chart of all Outcrops Studied showing their Locations, Formations and Groups.

Rare Earth Elements Geochemistry

Rare-earth elements (REE) are regarded as among the least soluble trace elements and are relatively immobile during low-grade metamorphism, weathering and hydrothermal alteration. They are effective indicators of sediment source when compared to Upper Continental Crust (UCC), Oceanic Crust (OC) and mantle materials. Rare earth element (La-Lu with atomic numbers 57 to 71) concentrations in rocks are usually normalized to a common reference standard, which most commonly comprises the values for chondritic meteorites (Figs 1 and 2). Chondritic meteorites were chosen because they are thought to be relatively un-fractionated samples of the solar system dating from the original nucleosynthetic event. Chondrite normalization (Figs 1 and 2) eliminates the abundance variation between even and odd atomic elements and also allows any fractionation of the REE group relative to chondrite meteorites to be identified. The normalized REE (concentrations in ppm) were then plotted against the Atomic numbers of the REE which gave a REE pattern indicating the Europium anomaly. The REE chondrite – normalizing factors used for this study are from Wakita et al., (1971). Europium anomalies may be quantified by comparing the measured

concentration with an expected concentration obtained by interpolating between the normalized values of Sm and Gd. Thus, the ratio of Eu is a measure of the Europium anomaly and a value greater than 1.0 indicates a positive Europium anomaly while the value less than 1.0 is a negative anomaly (Tables 3 and 4). Cerium anomaly (Ce/Ce*) may be used as a means of determining the environmental conditions at the time of deposition since higher values (>1.0) tentatively depict an oxidizing environment (Piper D.Z, 1974; Milodowski and Zalasiewicz, 1991; McDaniel et al., 1994) and for this study, the mean value of Ce/Ce* is greater than (1.0) for both group (Tables 3 and 4). This goes to show that the sediments were deposited in an oxidizing and shallow marine environment. Eu/Eu* anomaly which is the ratio of actual normalized Eu to interpolated normalized Eu for non-depletion or enrichment of the chondrite-normalised plots and is calculated by the following equation:

 $Eu/Eu*=\sqrt{Eu_N}/(Sm_N x Gd_N).$

 $Ce/Ce^* = 5Ce_N / [4la_N + Sm_N]$

Note: $_{\rm N}$ and * indicate chondrite normalized elements.

It can be further suggested that the distribution of rare earth element in the sediments of Awi,

Abakaliki and Mfamosing Formations sampled are controlled by the mineralogy of the parent rock which was formed as a result of the removal of feldspar from a felsic melt either by crystal fractionation or the partial melting of a rock(Adeigbe and Oruene). The removal of feldspar from the felsic melt that formed the sediments of the study area is further buttressed by ternary plot of Folk (1968) which shows that the sediments of the Awi Formation sampled from the study area falls within the subarkose region (Adeigbe and Oruene, 2012).

While, the observation of the rare earth element plots and the spider diagrams for sediments of the Awi, Abakaliki and Mfamosing Formation with respect to the pattern of the plots (Figs 6, 7 and 8) shows that the sediments are sourced from the parent rock of the Upper Continental Crust (UCC). This is also backed up by the ternary plot of Dickinson and Suczek (1979) made from the petrographic study which shows that the sandstone deposits of Awi Formation are products of a continental block provenance (Adeigbe and Oruene, 2012).

Also, the CRG comprising Eze Aku, Ekenkpon, New Netim, Awgu and Agbani Formations revealed

REE pattern that shows enrichment evidences in support of LREE relative to the HREE in the Eze-Aku. This is also similar in all other formations within CRG. The REE pattern also indicates the enrichment of LREE compared to HREE (Figs 9, 10, 11, 12 and 13) while Cerium anomalies range of 1.0-3.2 (Tables 4) suggest an oxidizing environment which supports the removal of feldspar from the melts through fractional crystallization. These suggest the removal of feldspar from the melt. These evidences indicate that the enrichment in LREE relative to HREE is controlled by the hornblende in the parent source rock as proposed by (Hugh Rollinson, 1993.) especially in siliciclastic rocks within the CRG. Hence, it may be implied that the distribution of Rare earth elements in some of the formations in Awgu Shale are controlled by the mineralogy of the parent rock including pyroxene, sphene and hornblende. (After Mclennan 1989a) These suggest that the sediments of CRG were deposited in a shallower marine environment during transgressive/regressive phases in Turonian times. (Reyment, 1965; Murat, 1972 and Nwachukwu, 1975).

Table 1: Results of Chondritr normalized Rare-Earth Elements for sediments of Cross river and Asu River Groups,
Lower Benue Trough, Southeastern Nigeria

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SAMP LE	LITHOLO GY	FORMATI ON	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
			PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M	PP M
		MDL	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.0 1	0.05	0.0 2	0.03	0.0 1	0.05	0.0 1
RK 056	SANDSTO NE	AGBANI	9.3	24.5	1.6	6.2	1	0.21	0.65	0.1 1	0.64	0.1 2	0.37	0.0 6	0.38	0.0 5
RK 055	SANDSTO NE	AGBANI	3.7	7.3	1	4.9	1.32	0.32	1.33	0.2 7	1.56	0.3 1	1.06	0.1 7	1.18	0.1 6
RK 054	SANDSTO NE	AGBANI	5.2	9.1	0.98	3.2	0.53	0.14	0.42	0.0 6	0.27	0.0 8	0.19	0.0 3	0.24	0.0 3
RK 053	SANDSTO NE	AGBANI	5.1	9.6	1.1	4.2	0.61	0.12	0.52	0.0 9	0.37	0.0 8	0.24	0.0 4	0.28	0.0 5
RK 052	SANDSTO NE	AGBANI	5.9	11.7	1.25	4.3	0.78	0.12	0.57	0.0 8	0.4	0.0 8	0.21	0.0 3	0.21	0.0 4
RK 051	SANDSTO NE	AGBANI	6.2	12	1.36	5.5	0.85	0.19	0.7	0.1	0.51	0.1	0.26	0.0 5	0.27	0.0 4
RK 050	SANDSTO NE	AGBANI	6.1	11.1	1.25	4.7	0.77	0.14	0.55	0.0 8	0.36	0.0 8	0.19	0.0 3	0.22	0.0 3
RK 049	SANDSTO NE	AGBANI	3.8	6.3	0.57	2.1	0.28	0.05	0.21	0.0 3	0.21	0.0 4	0.1	0.0 2	0.13	0.0 2
RK 048	SANDSTO NE	AGBANI	4.8	8.9	1.04	3.5	0.63	0.11	0.45	0.0 6	0.25	0.0 5	0.15	0.0 3	0.21	0.0 3
RK 047	SHALE	AWGU	105	240. 4	30.8 5	123. 5	20.7 9	4.34	13.6 2	1.9 6	9.36	1.4 7	3.81	0.5 8	3.57	0.5 1
RK 046	SHALE	AWGU	59.3	124. 2	14.4 7	56.9	9.15	1.93	6.89	1.0 7	5.47	1.0 5	2.96	0.4 7	2.99	0.4 3
RK 045	MARL	NEW NETIM	30.9	5.35	1.22	4.38	0.66	3.36	0.63	1.7 5	0.26	1.6 5	0.25	2.6 1	0.57	0.2
RK 044	MARL	NEW NETIM	26.7	4.85	1.09	3.92	0.57	3.05	0.55	1.5 1	0.24	1.4 8	0.24	2.7 3	0.55	0.1
RK 043	MARL	NEW NETIM	21.5	3.62	0.88	2.86	0.46	2.48	0.43	1.3 2	0.2	1.1 5	0.19	6.1 5	0.27	0.1

RK 042	MARL	NEW NETIM	16.6	2.9	0.63	2.39	0.36	1.83	0.33	1	0.14	0.9 3	0.13	7.6 9	0.2	0.3
RK 041	SANDSTO NE	EZE AKU	8.8	16.3	1.9	7.7	1.25	0.43	1.06	0.1 7	0.91	0.2	0.59	0.0 9	0.57	0.0 8
RK 040	SANDSTO NE	EZE AKU	11.9	23.2	2.67	10.4	1.85	0.47	1.64	0.2	1.6	0.3 6	1.02	0.1	0.98	0.1
RK 039	LIMESTO NE	EZE AKU	5.8	11.1	1.27	4.9	0.83	0.17	0.68	0.1	0.51	0.1	0.31	0.0	0.29	0.0
RK 038	SHALE	EZE AKU	49.7	103. 1	11.5 1	44.5	7.47	1.52	6.26	0.9 8	5.47	1.0 6	2.99	0.4 8	2.9	0.4
RK 037	LIMESTO NE	EZE AKU	18.2	34	3.73	14.8	2.38	0.46	1.7	0.2 7	1.56	0.2 8	0.75	0.1	0.83	0.1
RK 036	LIMESTO NE	EZE AKU	9.9	17.6	2.11	8.2	1.47	0.37	1.41	0.2	1.31	0.2 7	0.79	0.1	0.71	0.1
RK 035	SHALE	EZE AKU	21	40.8	4.67	17.8	3.03	0.66	2.46	0.3 7	1.91	0.3 7	1.03	0.1 5	0.9	0.1 3
RK 034	SHALE	EZE AKU	15	28.4	3.32	12.6	2.16	0.48	1.74	0.2 6	1.38	0.2 6	0.75	0.1 1	0.71	0.1
RK 033	SHALE	EZE AKU	21.6	39.1	4.58	18.5	3	0.66	2.34	0.3 7	1.78	0.3 8	1.07	0.1 6	0.93	0.1 4
RK 032	LIMESTO NE	EZE AKU	32.1	68.9	8.46	36.1	8.27	2.19	9.86	1.5 9	8.22	1.5 5	3.92	0.4 9	2.68	0.3 5
RK 031	LIMESTO NE	EZE AKU	82.8	166. 1	22.0 9	107. 4	24.8	6.47	29.2 7	4.3 2	22.6 7	3.9	9.34	1.1 2	5.8	0.7 5
RK 030	SHALE	EZE AKU	52.1	100. 2	12.1 4	44.7	7.67	1.6	5.88	0.8 9	4.7	0.8 8	2.45	0.3 8	2.41	0.3 7
RK 029	SHALE	EZE AKU	50.7	95	11.6 6	45.5	7.71	1.54	6.29	0.9 4	4.9	0.8 5	2.49	0.3 7	2.38	0.3 4
RK 028	SHALE	EKENKPO N	106. 4	223	30.5 8	130. 5	25.4 3	6.01	24.4 9	4.0 2	21.4 3	3.9 3	10.6 4	1.5 3	8.62	1.1 2
RK 027	SHALE	EKENKPO N	112	311. 5	49.6 7	231. 9	49.2 7	11.0 8	43.5 4	6.4 4	32.4 7	5.4 3	13.0 4	1.5 8	7.76	0.9 3
RK 026	SHALE	EKENKPO N	42.8	87	10.7 9	44.6	7.78	1.86	7.75	1.1 8	6.64	1.2 5	3.6	0.5	3.2	0.4 7
RK 025	SHALE	EKENKPO N	48.5	92.7	11.0 7	43.6	6.61	1.32	5.18	0.8	4.21	0.7 7	2.04	0.3	2.27	0.3
RK 024	SHALE	EKENKPO N	53.3	101	11.4 9	42.1	6.07	1.09	3.98	0.5 9	3.22	0.6 7	2.19	0.3 7	2.59	0.4 1
RK 023	LIMESTO NE	EKENKPO N	122. 8	182. 2	22.7 9	98.8	18.2 7	4.58	20.8 1	3.2 3	18.9	3.9 5	11.5	1.8	11.1 4	1.6 8
RK 022	SHALE	EKENKPO N	55.5	104. 2	12.3 3	48.5	7.12	1.37	5.04	0.7 1	3.53	0.5 9	1.83	0.3 1	2	0.3
RK 021	SHALE	EKENKPO N	61.7	117. 8	14	53.4	8.2	1.56	5.65	0.8 1	3.95	0.7 1	2.08	0.3 4	2.16	0.3
RK 020	SHALE	EKENKPO N	55.8	105. 5	12.4 6	45.5	7.37	1.35	5.31	0.8	4.06	0.7 4	2.25	0.3 7	2.4	0.3 3
RK 019	SHALE	EKENKPO N	53.6	103. 7	12.4	45.5	6.97	1.37	5.4	0.7 9	3.99	0.7 3	2.29	0.3 7	2.31	0.3 4
RK 018	SHALE	EKENKPO N	58.4	113. 8	13.3 7	50.6	8.36	1.69	6.73	0.9 9	5.23	0.8 9	2.79	0.4 2	2.59	0.3 9
RK 017	SHALE	EKENKPO N	57	115. 5	13.8 5	54.9	9.02	1.89	7.36	1.1 4	5.97	1.1 1	2.99	0.4 5	2.85	0.4 4
RK 016	LIMESTO NE	MFAMOSI NG	1.5	2.2	0.26	1.1	0.17	0.06	0.26	0.0 4	0.25	0.0 5	0.16	0.0 2	0.13	0.0 2
RK 015	LIMESTO NE	MFAMOSI NG	1.1	1.7	0.2	1.1	0.14	0.03	0.13	0.0 2	0.14	0.0	0.07	0.0	0.09	0.0
RK 014	LIMESTO NE	MFAMOSI NG	2	3.3	0.39	1.3	0.29	0.07	0.32	0.0 6	0.23	0.0 7	0.16	0.0	0.14	0.0 2
RK 013	LIMESTO NE	MFAMOSI NG	3.3	5.8	0.64	2.5	0.5	0.13	0.49	0.0 9	0.5	0.1 2	0.31	0.0 5	0.31	0.0 4
RK 012	LIMESTO NE	MFAMOSI NG	2.8	4.3	0.5	1.8	0.3	0.06	0.29	0.0 5	0.31	0.0 5	0.16	0.0 2	0.15	0.0 2
RK 011	SHALE	ABAKALI KI	23.7	50.6	5.96	24.8	4.72	1.32	4.3	0.7 1	3.44	0.7	1.9	0.2 9	1.85	0.2 6
RK 010	SHALE	ABAKALI KI	58.7	121. 1	13.8 7	55.3	8.72	1.69	6.38	0.9 7	5.17	0.9 7	2.88	0.4 9	2.98	0.4 4
RK 009	SHALE	ABAKALI KI	68.2	136. 8	15.7 7	63.3	10.2 5	1.98	7.78	1.1 9	5.97	1.1 3	3.06	0.4 6	2.9	0.4 2

RK 008	SHALE	ABAKALI KI	67.6	124. 8	15.2 4	58.5	10.3 1	2.02	7.63	1.0 9	5.49	1	2.8	0.4 4	2.45	0.3 7
RK 007	SHALE	ABAKALI KI	64	115	12.9 3	47.3	6.93	1.38	5.98	0.9 8	5.3	0.9 5	2.85	0.4 3	2.47	0.3 7
RK 006	SHALE	ABAKALI KI	66.3	115. 6	12.9 1	44.8	7.24	1.45	6.38	1.1 2	6.15	1.1	2.93	0.4 6	2.74	0.3 7
RK 005	SANDSTO NE	AWI	20.3	37.7	4.59	16.5	3.21	0.66	2.51	0.3 1	1.57	0.3	0.85	0.1 3	0.92	0.1 3
RK 004	SANDSTO NE	AWI	13.9	27.3	3.52	13.4	3.03	0.65	2.8	0.3 9	2.18	0.4 1	1.13	0.1 8	1.07	0.1 6
RK 003	SANDSTO NE	AWI	15.5	31.2	3.69	15	2.73	0.45	1.95	0.2 8	1.55	0.3	0.93	0.1 5	1.18	0.1 9
RK 002	LIGNITE	AWI	45.5	88	9.93	37.5	6.25	1.03	4.07	0.5 4	2.68	0.4 8	1.57	0.2 4	1.59	0.2 5
RK 001	SANDSTO NE	AWI	30.8	59	6.75	25.1	4.16	0.66	2.72	0.3 7	2	0.4	1.23	0.1 9	1.28	0.1 9

Sample No: (1-16) – Asu River Group

Sample (17-56) – Cross River Group

Table 2: Summary of Chondrite normalized REE for clastic sediments of the Lower Benue Trough (A) ARG (B) CRG

Δ	REE	Minimum	Maximum	Average					
~	La	1.1	68.2	30.3					
	Ce	1.7	136.8	57.8					
	Pr	0.2	15.97	6.69					
	Nd	1.1	63.3	25.6					
	Sm	0.14	10.25	4.3					
	Eu	0.03	2.02	0.85					
	Gd	0.13	7.78	3.37					
	Tb	0.02	1.19	0.51					
	Dy	0.14	6.15	2.68					
	Ho	0.03	1.13	0.50					
	Er	0.07	3.06	1.43					
	Tm	0.01	0.49	0.22					
	Yb	0.09	2.98	1.39					
	Lu	0.01	0.44	0.2					
]	Eu/Eu*	0.6	1.15	0.73					

	Ce/Ce*	1.01	1.62	1.20
D	REE	Minimum	Maximum	Average
В	La	3.7	122.8	38
	Ce	2.9	312	71
	Pr	0.57	49.7	9.1
	Nd	2.1	232	37.4
	Sm	0.28	49.27	6.78
	Eu	0.05	11.08	1.76
	Gd	0.21	43.54	5.99
	Tb	0.03	6.44	1.04
	Dy	0.14	32.47	4.77
	Ho	0.04	5.43	0.99
	Er	0.1	13.04	2.38
	Tm	0.02	7.69	0.82
	Yb	0.13	11.14	2.08
	Lu	0.02	1.68	0.3
	Eu/Eu*	0.6	0.8	0.74
	Ce/Ce*	1.0	4.3	1.75

Table 3: Europium and Cerium Anomaly values for ARG Sediments

Rock No	LITHOLOGY	FORMATION	GROUP	Eu/Eu*	Ce/Ce*	MEAN VALUE FOR Eu/Eu*	MEAN VALUE FOR Ce/Ce*		
RK016	LIMESTONE	MFAMOSING	ARG	0.63	1.06				
RK015	LIMESTONE	MFAMOSING	ARG	0.81	1.13				
RK014	LIMESTONE	MFAMOSING	ARG	0.71	1.08	0.74	1.06		
RK013	LIMESTONE	MFAMOSING	ARG	0.69	1.04				
RK012	LIMESTONE	MFAMOSING	ARG	0.88	1.01				
RK011	SHALE	ABAKALIKI	ARG	0.66	1.17				
RK010	SHALE	ABAKALIKI	ARG	0.66	1.20		1.26		
RK009	SHALE	ABAKALIKI	ARG	0.70	1.18	0.72			
RK008	SHALE	ABAKALIKI	ARG	0.68	1.26	0.72			
RK007	SHALE	ABAKALIKI	ARG	0.69	1.29				
RK006	SHALE	ABAKALIKI	ARG	0.90	1.43				
RK005	SANDSTONE	AWI	ARG	0.60	1.24				
RK004	SANDSTONE	AWI	ARG	1.15	1.16				
RK003	SANDSTONE	AWI	ARG	0.72	1.17	0.74	1.29		
RK002	LIGNITE	AWI	ARG	0.63	1.62				
RK001	SANDSTONE	AWI	ARG	0.61	1.23				

Table 4: Europium and Cerium Anomaly values for CRG Sediments

Rock No	LITHOLOGY	FORMATION	GROUP	Eu/Eu*	Ce/Ce*	Mean value for	Mean value
RK056	SANDSTONE	AGBANI	CRG	0.8	12	Eu/Eu	
RK055	SANDSTONE	AGBANI	CRG	0.7	4.1		
RK054	SANDSTONE	AGBANI	CRG	0.9	3.4		
RK053	SANDSTONE	AGBANI	CRG	0.7	3.4		
RK052	SANDSTONE	AGBANI	CRG	0.6	3.1	0.71	3.2
RK051	SANDSTONE	AGBANI	CRG	0.8	3		
RK050	SANDSTONE	AGBANI	CRG	0.7	3		
RK049	SANDSTONE	AGBANI	CRG	0.6	4.3		
RK048	SANDSTONE	AGBANI	CRG	0.6	3.6		
RK047	SHALE	AWGU	CRG	0.8	1.1		
RK046	SHALE	AGWU	CRG	0.7	1.1	0.75	1.1
RK045	MARL	NEW NETIM	CRG	0.8	1.3		
RK044	MARL	NEW NETIM	CRG	0.8	1.4	0.70	1.5
RK043	MARL	NEW NETIM	CRG	0.8	1.5	0.78	1.5
RK042	MARL	NEW NETIM	CRG	0.7	1.6		
RK041	SANDSTONE	EZE-AKU	CRG	1.2	1.0		
RK040	SANDSTONE	EZE-AKU	CRG	0.8	2.0		
RK039	LIMESTONE	EZE-AKU	CRG	0.7	3.1		
RK038	SHALE	EZE-AKU	CRG	0.7	1.2		
RK037	LIMESTONE	EZE-AKU	CRG	0.7	1.6	0.79	1.7
RK036	LIMESTONE	EZE-AKU	CRG	0.8	2.1		
RK035	SHALE	EZE-AKU	CRG	0.6	1.5		
RK 034	SHALE	EZE-AKU	CRG	0.8	1.7		
RK 033	SHALE	EZE-AKU	CRG	0.8	1.4		
RK028	LIMESTONE	EKENKPON	CRG	0.7	1.0		
RK027	LIMESTONE	EKENKPON	CRG	0.7	1.2	0.70	1.0
RK023	LIMESTONE	EKENKPON	CRG	0.7	0.8		
RK032	SHALE	EKENKPON	CRG	0.7	1.3		
RK031	SHALE	EKENKPON	CRG	0.7	1.0		
RK029	SHALE	EKENKPON	CRG	0.7	1.1		
RK029	SHALE	EKENKPON	CRG	0.7	1.1		
RK026	SHALE	EKENKPON	CRG	0.7	1.2		
RK025	SHALE	EKENKPON	CRG	0.7	1.1		
RK024	SHALE	EKENKPON	CRG	0.7	1.1	0.70	1.1
RK022	SHALE	EKENKPON	CRG	0.7	1.1		
RK021	SHALE	EKENKPON	CRG	0.7	1.1		
RK020	SHALE	EKENKPON	CRG	0.7	1.1		
RK019	SHALE	EKENKPON	CRG	0.7	1.1		
RK018	SHALE	EKENKPON	CRG	0.7	1.1		
RK017	SHALE	EKENKPON	CRG	0.7	1.1		

The sediments from the three formations under the ARG and he five in CRG points to a distinctively mean negative europium anomaly (Eu/Eu*) of 0.70-0.79 (Tables 3 and 4) with higher LREE/HREE ratios (Figs 6-13). The negative Eu/Eu* anormalies denotes felsic source rock (Taylor and Mclennan, 1985). This goes to show that the sediments of the ARG and CRG tend towards felsic sources as confirmed by the europium anomaly while the mean value of Ce/Ce* for the all the formations ranges from 1.0-3.2 (Table 3 and 4) which is an evidence suggesting an oxidizing condition and characteristic shallow marine environment since cerium anomaly value is greater than 1.



Fig: 6: Plots of Chondrite normalized REE plots for Awi Formation



Fig 7: Plots of Chondrite normalized REE plot for Abakaliki Formation.



Fig 8: Plots of Chondrite normalized REE plot for Mfamosing Formation.



Fig 9: Plots of Chondrite normalized REE Plot for Ekenkpon Formation.



Fig. 10: Plots of Chondrite normalized REE plot for Eze-Aku Formation



Fig 11: Plots of REE Pattern for New Netim Marl Formation



Fig 12: REE Pattern for Awgu Formation



Fig 13: REE Pattern for Agbani Sandstone.

Multi-elements geochemistry

The Multi Elements geochemistry (Spider diagrams) was also employed to confirm the observation made from the rare earth element results and to compare the patterns from both with standard plots. The spider diagrams for sediments of Asu River Group and Cross River Group revealed a pattern that shows that the sediments are sourced from the Upper Continental Crust (UCC) (Figs 14, 15, 16, 17, 18, 19, 20, and 21).



Fig. 14: Spider diagram for Awi Formation (MORB = Mid Oceanic Ridge Basalt normalization).



Fig. 15: Spider diagram for Abakaliki Formation (MORB = Mid Oceanic Ridge Basalt normalization).



Fig. 16: Spider diagram for Mfamosing Formation (MORB = Mid Oceanic Ridge Basalt normalization).



Fig 17: Spider diagram for Ekenkpon Formation (Primitive MORB)



Fig 18: Spider diagram for Eze Aku Formation (Primitive MORB)



Fig 19: Spider diagram for New Netim Marl Formation (Primitive MORB)



Fig 20: Spider diagram for Awgu Formation (Primitive MORB)



Fig. 21: Spider diagram for Agbani Formation (primitive MORB)

Conclusions

The chondrite normalized values for the rare earth elements of the three Formations making up the Asu River Group revealed an appreciable enrichment in the LREE (La-Nd) over the HREE (Er-Lu). The average europium anomaly (Eu/Eu*) value of the three Formations is 0.73 and this coincides with the range of sediments from a felsic sources. While the cerium anomaly (Ce/Ce*) value of 1.20 shows that the sediments were deposited in an oxidizing environment and confirms even more the fact that the sediments of the Asu River Group tend towards felsic sources as earlier confirmed by the europium anomaly. The distribution of the rare earth element in the sediments of Awi Formation, Abakaliki Formation and Mfamosing Formation of the Asu River Group sediments sampled are controlled by the mineralogy of the parent rock were formed as a result of the removal of feldspar from a felsic melt. While the rare earth element pattern of the three formations conforms to that of sediments sourced from the upper continental crust. The spider diagrams normalized to that of Mid Oceanic Ridge Basalt (MORB) shows a

pattern which conforms to that of the Upper Continental Crust (UCC).

The rare earth elements of Cross River Group also revealed a mineralogical controlled process by the mineralogical composition of the parent rock. The REE pattern shows an enrichment of LREE and depletion of HRE and indicates negative europium anomaly which is similar to sediments of ARG. The enrichment in LREE can be ascribed to the high level content of hornblende in the parent rock. Evidences from Spider diagram also indicated that the sediments that the Eze Aku, Ekenkpon, New Netim Marl, Awgu and Agbani Formations have the characteristics pattern of Upper Continental Crust. Evidences from the cerium anomalies with values >1 indicate an oxidizing environments and that the sediments of Eze Aku, Ekenkpon, New Netim Marl, Awgu and Agbani Formations were deposited in a shallow marine environment.

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