GEOCHEMISTRY OF EKENKPON AND NKPORO SHALES, CALABAR FLANK, SE NIGERIA: IMPLICATIONS FOR PROVENANCE, TRANSPORTATION HISTORY AND DEPOSITIONAL ENVIRONMENT

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ABSTRACT

The Cretaceous Nkporo and Ekenkpon Shales within the Calabar Flank were investigated using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) and Atomic Emission Spectroscopy (ICP-AES) to deduce the provenance, transportation history and depositional environment. The results show the dominance of SiO_2 (45.27 – 46.45%; 44.50 – 54.83%), Al_2O_3 (22.27 – 23.57%; 19.20 – 20.20%) and Fe_2O_3 (8.30 – 9.04%; 5.64 – 7.30%) constituting the bulk major oxides of Nkporo and Ekenkpon Shales respectively. The Index of Chemical Variation (ICV) ranges from 0.42 – 0.56 and 0.57– 0.68 for Nkporo and Ekenkpon Shales respectively, suggesting moderate and high degree of weathering. The enrichment of Sr (124 – 350ppm; Nkporo Shale and 176 – 856ppm; Ekenkpon Shale) compared to Post Australian Archean Shale (PAAS; 14.6ppm) could be attributed to feldspars in the source area, and is easily incorporated in the clay minerals of the shales. Also the values of Th and U which are 15.00 – 17.20ppm; 14.6-23.2ppm and 3.5-4.2ppm; 1.9-6.2ppm respectively in Nkporo and Ekenkpon sediments show enrichment compared to PAAS of 14.6ppm and 3.1ppm for respective values of Th and U. The Eu anomaly of 0.04 to 0.07 suggests felsic source rocks for both formations while plots of TiO_2 vs. Al_2O_3 indicate an intermediate to dominantly felsic granodiorite source for both shales, with little input from felsic volcanic provenance plus traces of quartzose sedimentary rocks. The mobility of Na, Ca, and K due to progressive weathering of the shales is evident in the bivariate plots of Na_2O wt% vs. PIA, CaOwt% vs. PIA and K_2O vs. PIA. Values of Th/U ratios range from 3.37 – 4.91(Nkporo) and 3.10 – 7.68 (Ekenkpon), indicating moderate to high weathering and reworking of sediments. It is envisaged that the area is associated with passive to active continental margin tectonics, where sediments were mainly sourced from felsic rocks of the adjoining terrain and deposited in oxic, continental to transitional marine environment based on Al_2O_3–K_2O +CaO+MgO-Fe_2O_3+MgO; AKF plot.

KEYWORDS: Cretaceous, Calabar Flank, provenance, transportation history, depositional environment.

INTRODUCTION

The Calabar Flank is that part of the southern Nigerian sedimentary basin, bordered by the Oban Massif to the north, the Niger Delta to the south, the Cameroon volcanic ridge to the east, Ikpe platform to the west, and Afikpo syncline to the northwestern (Fig. 1; Murat, 1972).The Cretaceous – Tertiary successions in the basin represents a post -rift basin-fill, containing about 4km of fluvial-continental, marine and paralic sediments (Odumodu, 2012).

Several studies have been carried out on various lithostratigraphic units of the Calabar Flank to ascertain its geology, and economic potentials with much success recorded in the limestone, sandstone and marl bearing formations as they are raw materials for cement, sources of ground water and construction materials (Ekwueme, 1985; Reijers and Petters, 1987; Esu and Okereke, 1990; Ekwere, 1993; Ekwere et al., 1994 and Edet and Okereke, 2002) among others. Earlier geological studies were based on tectonics, field associations, biostratigraphy and sedimentological

descriptions of these Cretaceous sedimentary rocks as exposed at different outcrops locations. Such works include: Reyment (1965); Dessauvagie, (1974); Adeleye and Fayose (1978); Petters, 1980; 1982; Petters and Ekweozor (1982), Akpan, 1985; Nyong and Ramanathan, (1985) ; Petters et al. (1995) .

Organic geochemical appraisal of the associated shales and limestones within the Calabar Flank have been reported by Essien et al. (2005); Ekpo et al., (2012), Ekot et al.,(2014) ; Boboye and Okon (2014). Boboye and Okon (2014), worked on sedimentological and geochemical characterization of the sediments of Calabar Flank by using petrography, inorganic and organic geochemical studies to deduce the provenace, depositional environment, hydrocarbon potential as well as tectonic setting of the area .

However, most of the previous work within the Calabar Flank centred on aspects of lithostratigraphy, organic geochemistry, biostratigraphy and sedimentology. Detailed inorganic geochemical assessments of the sediments have not been fully examined distinctly apart from a few (Ekwueme, 1985;

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Ekwere, 1993; Elueze et al. 1999; Okon *et al.,* 2017). It is known that among sedimentary rocks, shales are considered to retain most of their mineral constituents of the source and their bulk chemistry preserved the near-original geochemical constituents of the provenance and reveal the palaeo-weathering conditions (Pettijohn, 1975). In addition, they represent the average crustal composition of the provenance much better than any other rock type. The elemental composition of shales

can therefore be used to deduce the source, tectonics, transportation history and depositional environment of such sediments (Nesbitt and Young, 1984; Bhatia, 1983; Roser and Korsch, 1988; Condie, 1993; McLennan *et al.*, 1993; Cullers, 2000).

This study examines the elemental composition of the Ekenkpon and Nkporo shales within the Calabar Flank and attempts to constrain their provenance, transportation history and environment of deposition.
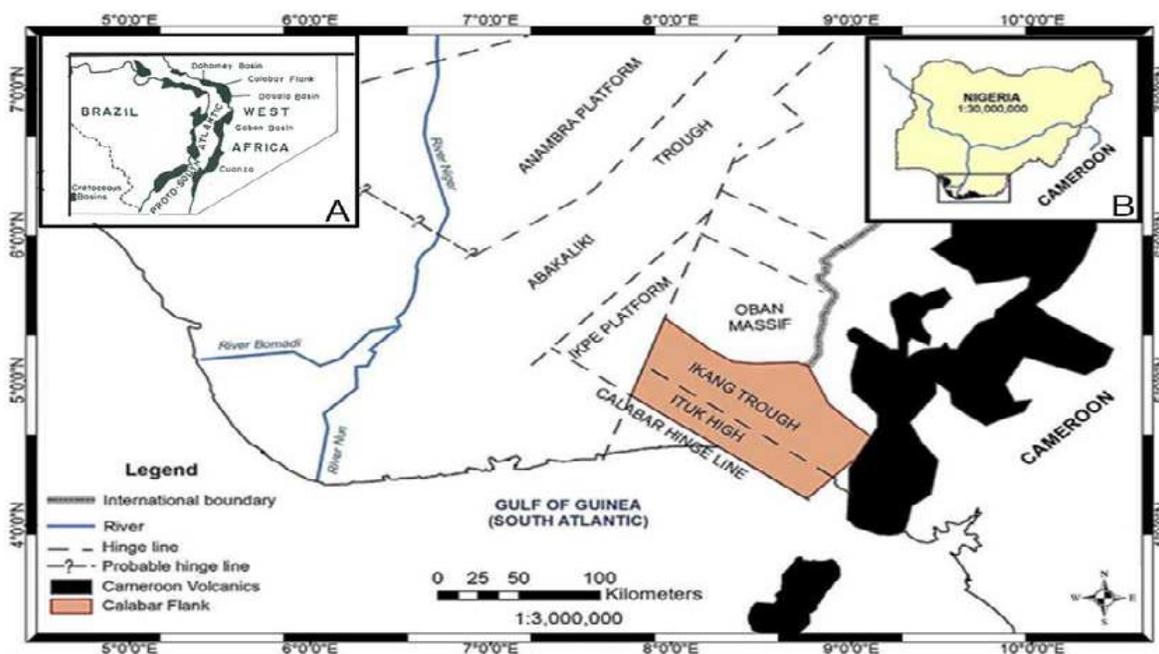
Figure 1: Map of southern Nigeria showing the location of Calabar Flank and its structural elements in relation to adjacent geological features (after Nyong and Ramanathan, 1985)

LOCATION OF STUDY AREA AND GEOLOGY

The area of study is located within Latitudes 05^0 15'08"N and $05^0$31'08"N, and Longitudes $008^0$15'08"E and $008^0$33'00"E in the Calabar Flank (Fig. 2). The Calabar Flank is part of an X-shaped, fault-controlled depression, formed in the crystalline Basement Complex of the African Craton (Short and Stäuble, 1967) whose origin is associated with the break-up of South America from Africa during the opening of the Gulf of Guinea in the Mesozoic (Fig.1). Its geologic history is associated with that of Southern Nigeria, which has been controlled by three major tectonic phases (Murat, 1972). This resulted in the displacement of the axis of the main basin, giving rise to three successive basins in which Calabar Flank is one. The major tectonic element of the Flank is a hinge zone, which consists structurally of NW-SE trending basement horsts (the Oban Massif and the Ituk high), separated by a graben – the Ikang Trough (Petters and Reijers, 1987; Fig. 3).

Different formation names have been proposed by several authors for sediments within the Calabar Flank (Reyment, 1965; Dessauvagie, 1974; Adeleye and Fayose, 1978; Petters, 1982; Petters *et al.*, 1995). The lithostratigraphic succession in the Calabar Flank is presented in Figs 2 and 4. The sedimentary sequence of the Calabar Flank begins with continental clastics,

consisting of a fluvio-deltaic sequence of cross –bedded sandstone, claystone, and shale. The unit overlies the Precambrian Oban Massif unconformably and constitute the Awi Formation of Early Cretaceous (probably Aptian age; Adeleye and Fayose, 1978; Nton, 1999). Enhanced subsidence of the faulted blocks resulted in the initiation of a series of marine transgressions. The earliest marine transgression in Middle Albian resulted in the deposition of platform carbonates (Mfamosing Limestone, Petters, 1982).

Overlying the Mfamosing Limestone is the Ekenkpon Shale Formation (Petters *et al.,* 1995) which comprised a thick sequence of black fissile shales with minor but frequent intercalation of marls, calcareous mudstones and shales. This shale sequence was deposited as a result of the second phase marine transgression which was initiated in Late Albian and continued through Turonian times with a break towards the Cenomanian (Nyong and Ramanathan, 1985).

The New Netim Formation, made up of thick marl unit with thin shale intercalations, overlies the Ekenpon Shale Formation. The Santonian and Early Campanian sediments are not encountered in the Calabar Flank as this period is regarded as a period of non deposition / or erosion. The Late Campanian to Maastrichtian sediment of the Nkporo Formation (Reyment, 1965), comprising dark-grey, carbonaceous,

friable shales with occasional thin bands of marlstones and gypsum overlies the New Netim Formation. The Nkporo Shales are overlain by Tertiary-Recent continental sands of Benin Formation.

Figure 2: Geologic map of Calabar Flank showing sample locations and stratigraphic sequences (Modified after Ekpo *et al.*, 2013)

Figure 3: Structural elements and conceptual subsurface distribution of Cretaceous Sediment in the Calabar flank (After Nyong and Ramanathan, 1985)

Figure 4: An outcrop location of Ekenkpon Shale at location E1 showing different beds within the outcrop (GPS coordinate: 008^{0}20'25"/05^{0}05'51")

METHODOLOGY

Field Sampling

Field sampling involving taking vertical profiles of the sedimentary successions and noting variations in lithology, thickness and sedimentary structure was carried out on road cut exposures along the Calabar-Ikom and Calabar –Itu Roads within the Calabar Flank. Altogether, over thirty (30) samples were collected, made up of sandstone, limestones, marl and shales but seven (7) representative shale samples, made up of four (4) from Ekenkpon and three (3) from Nkporo Formations were used in this study while others are reported elsewhere. Attempts were made at collecting fresh samples at each location. The sampling points were georeferenced and shown in Figs 2 and 4.

Geochemical analyses

The Ekenkpon and Nkporo Shales were analyzed for major oxides, trace elements and rare earth element (REE) composition. Each sample 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°C 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 was determined for the shale samples. A second 0.5g split sample was digested in Aqua Regia

and analysed by Inductively Coupled Plasma-Mass Spectrometer (Perkin-Elmer, Elan 6000) on powdered and pressed pellets to determine Au, Ag, As, Bi, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn.

The Inductively Coupled Plasma-Atomic Emission Spectrometry-(ICP-AES) was used for the major elements and some trace elements while Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to determine trace and REE concentration. The analyses were conducted at the Acme Analytical Laboratories Ltd., Canada.

RESULTS AND DISCUSSIONS

Major elements geochemistry

The results of major element analysis of the samples are shown in Table 1. The major oxide concentrations in Nkporo shale are dominated by SiO_2 (45.27% - 46.45), Al_2O_3 (22.27-23.57%) and Fe_2O_3 (8. 3-9.04wt %). Other oxides such as TiO_2, CaO, Na_2O and K_2O have respective ranges; 1.00 – 1.04; 0.08 – 1.82; 0.07 – 0.99 and 1.27 – 1.54. The Ekenkpon samples on the other hand; SiO_2 (44.5-54. 83%) and K_2O (2.76-5.43%) but depleted in Al_2O_3 (19.2 – 20.2%) and Fe_2O_3 (5.64 - 8.24wt %) compared to Nkporo Shale (Table 1).

The low K_2O content in Nkporo Shale indicated the low amount of illite or K-feldspar present in the source material, and/or longer transport distance/susceptibility of the source material to high degree of weathering (Akpokodje et al., 1991). Table 2

summarises the average major element oxide (wt %) data for the studied samples compare to average shales worldwide (Pettijohn, 1957). On the average, the shale samples are relatively depleted in SiO_2, MgO, CaO, Na_2O, K_2O and enriched in Al_2O_3 and Fe_2O_3 compared to average shales from other formations worldwide (Table 2).

Table 1: Major element composition of Ekenkpon Shale and Nkporo Shale sample. Where CIA= Index of Chemical Variation, CIA=Chemical Index of Alteration, PIA=Plagioclase Index of Alteration

Oxide	N5	N6	N7	E1	E2	E3	E4
SiO_2	46.45	45.27	45.59	54.83	51.30	44.50	51.60
Al_2O_3	23.57	22.27	23.31	19.66	19.20	19.60	20.20
Fe_2O_3	8.30	9.04	8.40	5.64	8.24	6.69	7.30
MgO	0.99	1.23	0.80	1.64	2.10	1.95	1.95
CaO	0.99	1.82	0.08	1.17	1.38	0.08	1.19
Na_2O	0.99	0.16	0.07	1.14	0.61	0.10	0.68
K_2O	1.30	1.53	1.27	3.27	2.76	5.43	3.27
TiO_2	1.00	1.04	1.04	0.96	0.98	1.07	0.77
P_2O_5	0.10	0.10	0.12	0.16	0.10	0.17	0.12
MnO	0.02	0.02	0.02	0.02	0.06	0.02	0.06
Cr_2O_3	0.02	0.02	0.02	0.01	0.01	0.01	0.01
Al_2O_3/TiO_2	23.57	21.41	22.41	20.48	19.59	18.32	26.23
K_2O/Al_2O_3	0.06	0.07	0.05	0.17	0.14	0.28	0.16
ICV	0.49	0.56	0.42	0.57	0.68	0.63	0.62
CIA	87.78	86.38	94.26	77.89	80.17	77.75	79.72
PIA	91.84	91.29	99.32	87.65	89.20	98.75	90.05

Table 2: Average chemical composition of the Nkporo and Ekenkpon shales compared to published average shales

Oxide	Nkporo Shale	Ekenkpon shale	Average Shale (Pettijohn, 1957)	Turekan & Wedephol (1961)	PASS (Taylor and McLennan, 1985)	NASC (Gromet et al., 1984)
SiO_2	45.77	50.56	58.1	58.5	62.40	64.82
Al_2O_3	22.72	19.67	15.4	15	18.78	17.05
Fe_2O_3	8.58	6.98	6.9	4.72	7.18	5.7
MgO	1.01	1.91	2.4	2.5	2.19	2.83
CaO	0.96	0.87	3.1	3.1	1.29	3.51
Na_2O	0.41	0.7	1.3	1.3	1.19	1.13
K_2O	1.37	3.68	3.2	3.1	3.68	3.97
TiO_2	1.03	0.95	0.6	0.77	0.99	0.8
P_2O_5	0.11	0.14	0.2	0.16	0.16	0.15
MnO	0.02	0.04	Trace	_	_	_
Cr_2O_3	0.017	0.011	Trace	_	_	_

Trace, and rare earth elements geochemistry

The trace elements results are shown in Table 3. Ranges of values are; Ba (199-284ppm) and Rb (62 - 69.8ppm) in Nkporo shale and Ba (104 –550ppm) and Rb (146 – 230ppm) in Ekenkpon shale. These may be concentrated in K-feldspars and phyllosilicates and are depleted relative to PAAS (average post-Archean Australian average shale; Condie, 1993). Strontium with values ranging from 124 - 350ppm and 176 - 856ppm respectively for Nkporo and EkenkponShalesis greatly enriched when compared with PAAS, average granite and granodiorite. Similarly, the ranges of Thorium (15.0 – 17.2ppm in Nkporo) and (14.6-23.2ppm in Ekenkpon) are enriched in both formations with respect to PAAS (14.6ppm) and on the average, almost similar to average granite (18ppm) in the Ekenkpon Shale.

It has been reported that Ti, Nb and Hf are preferentially partitioned into melts during fractional crystallization and anatexis (Feng and Kerrich, 1990) resulting in their enrichments in felsic rather than mafic rocks. In this study, Nkporo Shale exhibits nearly values; Zr (160-191), Hf (4.1-5.3), Nb (20.1-23.9) and Ti (0.3-

0.9) in comparison to Ekenkpon shale with Zr (148.8-181.5ppm), Hf (3.9-5.2), Nb (15.8-19.5) and Ti (0.2-1.5). Generally, the samples are enriched in trace elements relative to PAAS and are thus believed to have been sourced from a felsic to intermediate rocks.

The rare earth elements result is shown in Table 4. Samples from both formations are enriched in LREE (174.6-284.2ppm) compared to PAAS (166.1ppm) but are depleted in HREE (33.41-49.8ppm) relative to

322.18ppm of PAAS. The negative Eu anomalies (Eu/Eu*= 0.05-0.08 and 0.04-0.06) for Ekenkpon and Nkporo Shales respectively may be attributable to the Eu-depleted felsic igneous rocks, *i.e.* granites and granodiorite, in the source region. The Chondrite normalised REE plot (Figs. 5a and 5b) show that the Ekenkpon and Nkporo Shales are LREE enriched and have a near flat HREE pattern, with negative Eu.

Table 3: Trace element (ppm) composition of Ekenkpon and Nkporo Shale, and Post Archaean Australian Shale (PAAS; Taylor and McLennan, 1985)

Element	N5	N6	N7	E1	E2	E3	E4	PAAS
Pb	14.9	16.4	16.9	14.2	19.3	78.0	10.7	16.00
Zn	201	101	168	49	81	21	56	650
Be	4	1	<1	5	4	8	3	23
Cs	5.5	4.3	5.6	9.2	11.3	20.3	12.5	5.0
Ga	28.8	26.6	26.0	29.1	24.8	29.8	26.8	1.9
Sn	4	3	3	4	4	6	3	1.6
Sr	124.3	350.1	170.3	176.9	393.4	856.6	403.5	14.6
Ta	1.6	1.3	1.5	1.4	0.9	1.7	0.9	3.1
W	1.2	1.2	1.1	1.5	1.2	2.1	1.1	150
Mo	3.8	2.5	4.6	0.5	0.3	7.3	0.4	210.0
As	18.3	20.0	23.0	4.6	8.4	4.2	10.9	10.0
Cd	6.2	1.9	50.6	3.5	0.2	0.1	0.6	55
Ni	48.6	36.3	61.0	23.4	30.9	56.8	25.8	
Sc	19	18	22	14	17	21	16	
Ba	203	199	284	550	564	104	316	_
Co	18.1	14.4	18.9	12.0	18.3	30.9	16.9	_
Hf	5.3	4.1	4.9	5.2	3.9	4.6	4.3	_
Nb	23.9	20.4	20.1	17.9	19.1	19.5	15.8	_
Rb	69.8	64.8	62.0	146.0	146.8	230.3	157.8	_
Th	15.6	17.2	15.0	23.2	18.7	19.2	14.6	14.6
U	3.7	3.5	4.2	4.3	3.3	6.2	1.9	3.1
V	267	191	289	109	122	138	131	_
Zr	191.2	138.6	160.0	181.5	143.8	148.8	162.4	
Cu	24.7	23.9	39.4	27.0	33.8	193.3	26.9	_
Sb	0.2	0.1	0.3	<0.1	<0.1	<0.1	<0.1	_
Bi	0.3	0.3	0.3	0.4	0.4	0.7	0.4	_
Au	1.0	0.8	2.1	1.7	2.0	1.2	1.4	_
Hg	0.03	0.03	0.03	<0.01	<0.01	0.01	<0.01	_
Tl	0.5	0.3	0.9	0.2	0.2	1.5	0.2	_
Se	5.2	2.1	5.1	<0.5	<0.5	<0.5	<0.5	_

Table 4: Rare element composition of Ekenkpon Shale, Nkporo Shale, and Post Archaean Australian Shale (PAAS; Taylor and McLennan, 1985)

REE	N5	N6	N7	E1	E2	E3	E4	PAAS
La	51.9	53.6	53.0	43.7	59.5	63.0	44.5	38.2
Ce	108.5	116.2	126.0	82.3	118.7	135.6	82.2	79.6
Pr	12.07	13.08	15.19	9.95	13.47	15.71	9.02	8.83
Nd	46.5	49.1	60.2	36.2	52.0	59.6	33.1	33.9
Sm	8.60	8.72	11.56	6.68	8.62	10.31	5.81	5.6
Sum LREE	227.6	240.7	266.0	178.8	252.3	284.2	174.6	166.1
Eu	1.80	1.71	2.39	1.22	1.70	1.93	1.02	1.1
Gd	6.99	6.92	8.72	4.90	7.24	7.37	4.56	4.7
Tb	1.08	1.07	1.21	0.77	1.01	0.95	0.71	0.8
Dy	5.62	5.33	5.17	4.00	5.61	3.91	3.86	4.7
Ho	1.10	1.09	0.91	0.71	1.00	0.71	0.77	1.0
Er	3.13	3.02	2.50	2.10	2.77	1.83	2.24	2.9
Tm	0.43	0.43	0.36	0.32	0.44	0.31	0.33	0.41
Yb	2.73	2.78	2.33	2.25	2.40	2.14	2.17	2.82
Lu	0.42	0.41	0.35	0.34	0.34	0.29	0.34	0.43
Y	26.5	25.2	18.5	15.8	26.6	16.1	19.6	
Sum HREE	49.80	47.96	42.44	32.41	49.11	35.54	35.60	322.18
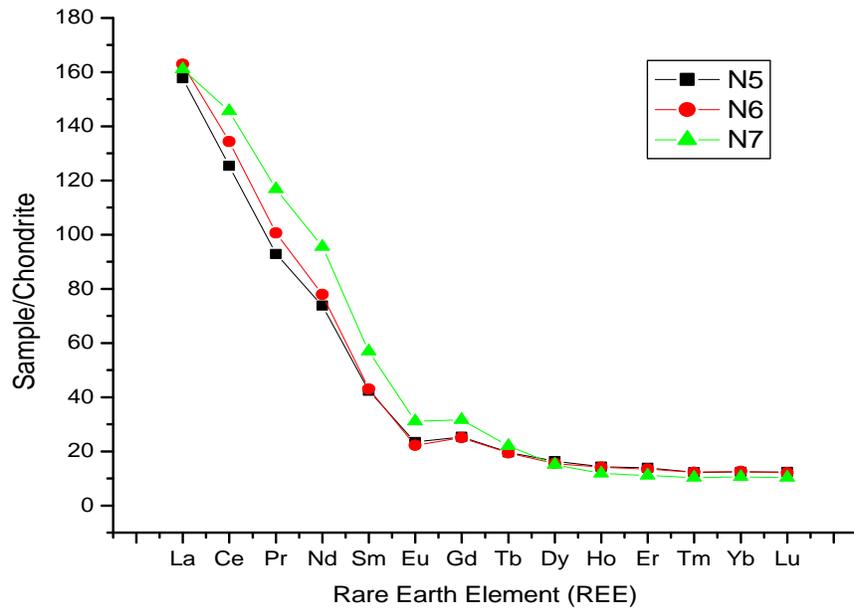
Figure 5a: Plots of Chondrite normalized REE plots for Nkporo shale (After White, 2013)
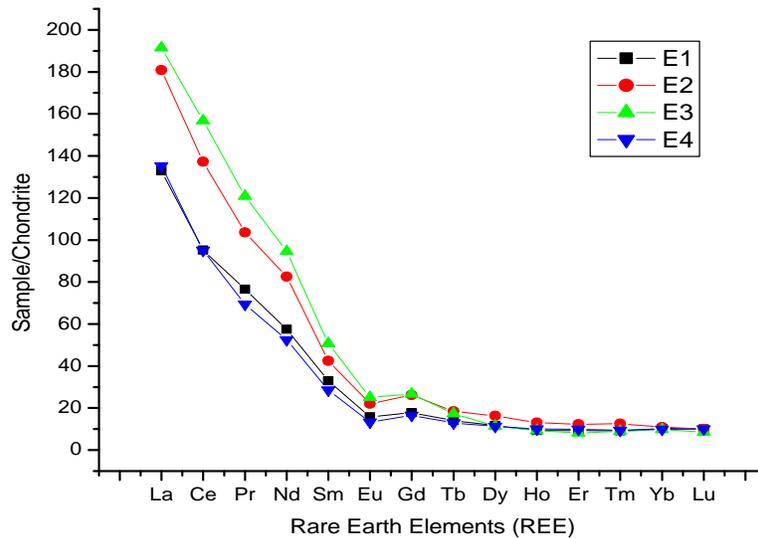
Figure 5b: Plots of Chondrite normalized REE plots for Ekenkpon shale (After White, 2013)

Provenance

The geochemical signatures of clastic sediments have been used to ascertain the provenance characteristics of such sediments (Taylor and McLennan, 1985; Armstrong-Altrin *et al.*, 2004). It has been reported that the Al_2O_3/TiO_2 ratio, increases from 3 to 8 for mafic igneous rocks, 8 to 21 for intermediate rocks, and 21 to 70 for felsic igneous rocks (Hayashi *et al.,* 1997). The Nkporo Shale has Al_2O_3/TiO_2 ranges from 21.41 to 23.57 (av. 22.47) while that for Ekenkpon Shale ranges from 18.36 to 26.23 (av. 21.05). These ratios suggest intermediate to felsic source rock.

McLennan *et al.*(1980), have utilised bivariate plot of Al_2O_3 vs. TiO_2 to constrain provenance of silliciclastic rocks. In this study, values from such plots, trend towards granodiorite line; especially at the high side extreme of the Al_2O_3 axis (Fig. 6). Armstrong-Altrin *et al.*, (2004) and Wrafter and Graham (1989) have reported high Ni content to be associated mainly with ultramafic rock-derived sediments while low Ni concentration indicates felsic provenance. The Ni values for this study range from 23.4 to 56.8ppm in Ekenkpon Shale and 36.3 to 61.0ppm in Nkporo Shale, suggesting a felsic source rock. Also, comparing the Th/Co, Th/Sc and La/Sc ratios of these samples with those obtained from felsic and basic rocks-derived sediments of upper continental crust (UCC) and PAAS (Culler et al., 1988), it can be deduced that the sediments of Ekenkpon and Nkporo were sourced mainly from felsic rocks (Table 5).

Rare earth patterns can provide information on the pre-metamorphic history of a rock and their patterns have been used to identify the provenance of sedimentary rocks as they remain unchanged even during metamorphism. The europium anomaly in the sedimentary rocks provides important clues regarding the source rock characteristics as well (Taylor and McLennan, 1985). As earlier pointed out, negative Eu anomalies are generally associated with felsic rocks, whereas the mafic rocks exhibit little or no Eu anomalies (Cullers, 1994). The europium anomaly (calculated from the formula: Eu/Eu* where Eu*= Sm x Gd) indicate that the analysed samples exhibit negative Eu anomaly (0.05 - 0.08; Ekenkpon and 0.04 - 0.06; Nkporo) and further support a felsic source rock (Culler, 1994).

Arising from Th/Sc–Zr/Sc diagram of McLennan et al, (1993), Condie, (1993), samples from both formations were sourced from felsic volcanic rocks with some contribution from granodioritic rocks (Fig. 7).
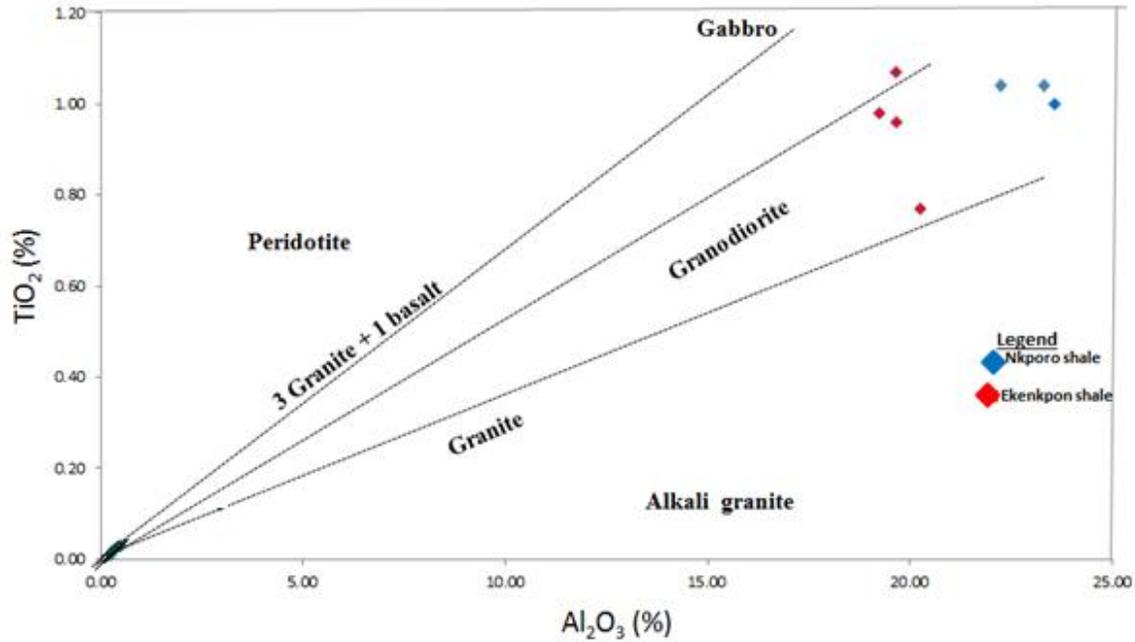
Figure 6: TiO$_2$ wt. % vs. Al$_2$O$_3$ wt. % bivariate diagram Nkporo shale and Ekenkpon shale (McLennan *et al.*, 1980)

Table 5: Range of shale elemental ratios in this study compared to ratios for similar fractions derived from felsic rocks, mafic rocks, upper continental crust and Post-Archean Australia Shale (PAAS)

Element ratio	Ekenkpon Shale	Nkporo shale	Felsic rocks derived-sediment (Cullers, 1994, 2000; Cullers et al., 1988)	Mafic rocks derived-sediment (Cullers,1994, 2000; Cullers et al., 1988)	Upper Continental Crust (UCC)	Post-Archean average shale (PAAS)
Th/Sc	0.62 – 1.93	0.79 – 1.19	0.84 – 20.5	0.05 – 0.22	0.79	0.9
Th/Co	0.91 – 1.66	0.68 – 0.96	0.67 – 19.4	0.04 – 1.0	0.63	0.63
La/Sc	2.80 – 3.5	2.4 – 3.0	2.5 – 16.3	0.43 – 0.86	2.21	2.4
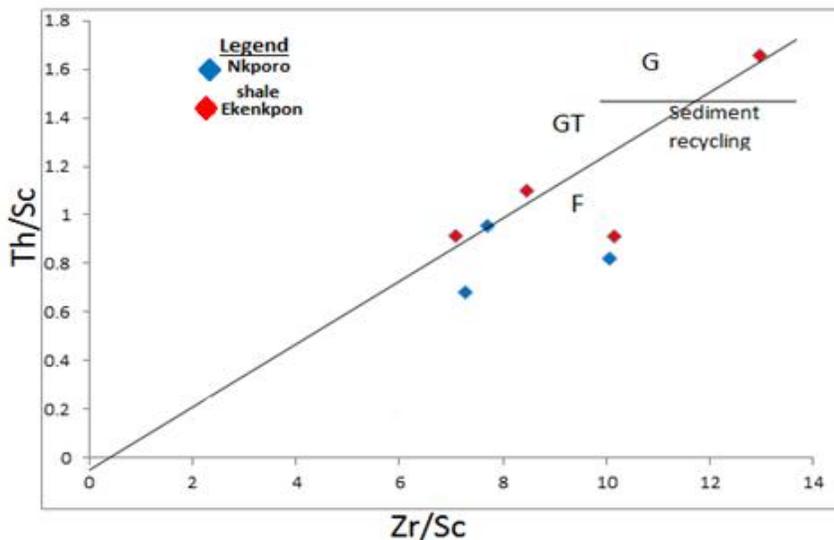
Figure 7: Th/Sc–Zr/Sc diagram for Nkporo and Ekenkpon Formation. G: granite, GT: granodiorite and F: felsic volcanic (After McLennan et al., 1993; Condie, 1993)

Weathering, paleoclimate and transportation history

Climate exerts a major control on weathering processes affecting the upper continental crust and

evidences of past weathering conditions can be obtained from the products of weathering (Cox *et al.*, 1995). The values of K$_2$O/Al$_2$O$_3$ for the Nkporo Shale

ranges from 0.05 to 0.07 and that for Ekenkpon Shales are from 0.14 to 0.17. These indicate preponderance of clay minerals over K-bearing minerals such as K-feldspars and micas or minimal alkali feldspar in the original shale as proposed by Cox et al., (1995). This clay fraction appears more in the Nkporo shale than the Ekenkpon shale.

The Index of Compositional Variation (ICV; Cox et al., 1995) where ICV = $(Fe_2O_3+K_2O+Na_2O+CaO+MgO+MnO)/Al_2O_3$ can also be used to ascertain the transportational history and the dominant products of weathering. Values of Index of Compositional Variation (ICV) of Nkporo Shale range from 0.42-0.56 while that of Ekenkpon Shale varies from 0.57-0.68. Values for the study shales are < 1, and typical of minerals such as kaolinite, illite, plagioclase and muscovite, and also, lower than higher values (>1) expected in rock forming minerals such as biotite, K-feldspar, amphiboles and pyroxenes (Cox et al., 1995). The values for the shales are still within the clay range. Non-clay minerals have a higher ratio of the major cations such as Fe, K, Na, Ca, Mg, and Mn to Al than clay minerals, making the non-clay minerals have a higher ICV. For example, the ICV decreases in the order, pyroxene and amphibole (10–100), biotite (8), alkali feldspar (0.8–1), plagioclase (0.6), muscovite and illite (0.3), montmorillonite (0.15–0.3) and kaolinite (0.03–0.05) as proposed by Cox et al.(1995). Immature shales with a high percent of non-clay silicate minerals will have ICV > 1 while mature ones have lower ICV values < 1 (Cox et al., 1995). The ICV values for the study samples suggest that the shales are compositionally mature and would have experienced longer transport and/or recycling effects.

Weathering indices of sedimentary rocks can provide useful information on climatic conditions at the source region. Increase in degree of chemical weathering may reflect the decrease in tectonic activity and/or change in climate towards warm and humid conditions (Suttner and Dutta, 1986).The degree of source rock weathering is quantified with different indices. Various known indices of weathering/alteration used in this study and their calculations are; Chemical Index of Alteration (CIA = {Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)} x 100; Nesbitt and Young, 1982), Plagioclase Index of Alteration (PIA = {(Al_2O_3 – K_2O) / ((Al_2O_3 - K_2O) + CaO + Na_2O)} x 100; Fedo et al., 1995) while Chemical Index of Weathering is represented as : (CIW* = {Al_2O_3 / (Al_2O_3 + Na_2O)} x 100; Harnois, 1988). The respective values of CIA are; 77.75 – 80.17 and 86.38 – 94.26 for Ekenkpon and Nkporo Shales; indicative of intensive weathering in the source area. The respective PIA ranges for Ekenkpon and Nkporo Shales are: 87.65 to 98.75 and 91.29 to 99.32 ; suggesting intense destruction of feldspars during the

course of source weathering, fluvial transport, sedimentation and diagenesis (Fedo et al., 1995).. During the initial stages of weathering of feldspar-bearing source material, Ca is leached rapidly than Na and K. With increasing weathering, total alkali content (K_2O+Na_2O) decreases with increase in K_2O/Na_2O ratio as evidenced in this study. This is due to destruction of feldspars where plagioclase is preferentially removed than K-feldspars (Nesbitt and Young, 1984).

In sedimentary rocks, Th/U values > 4.0, may indicate intense weathering in the source areas or recycling. The Th/U value of 3.10 to 7.68 (av. 5.46) for Ekenkpon Shale and 3.37 to 4.91 (av. 4.23) for Nkporo Shale portray moderate to high weathering. These support the findings of Adeigbe and Jimoh (2013).

Palaeoenvironment of deposition

Palaeo-redox conditions during sedimentation of siliciclastic rocks can be evaluated based on their chemical constituents. Typically redox-sensitive elements, such as V, Cr and U, provide a means to determining the degree of anoxia during deposition (Madhavaraju and Ramasamy, 1999). Low U concentration is generally associated with sediments deposited in oxygenated marine realm (Madhavaraju and Ramasamy, 1999). The U/Th ratio 1.9 to 6.2 (av. 3.85) for the shales indicate deposition in oxic marine setting.

According to Jones and Manning (1994) values of Ni/Co ratio < 5 indicate an oxic environment, whereas values > 5, suggest suboxic and anoxic environment. The Ni/Co values for Nkporo Shale ranges between 2.75 and 4.49 while that of Ekenkpon Shale is between 2.25 and 2.30; . indicating deposition in oxic environment for the samples. Wilde et al. (1996) linked Ce anomalies in shales of the anoxic facies to eustatic sea level changes. Similar to Mn, Ce^{4+} is less soluble under oxic conditions, whereas under anoxic conditions it is mobilized, leading to depletion in Ce in anoxic sediments relative to those deposited under oxic conditions. Taylor and McLennan (1985) recommended use of the geometric mean;

$Ce* = (La + Pr)^{1/2}$.

The ratio Ce/Ce* is then a measure of the anomaly, with values less than unity, termed negative and greater than unity, positive. Values of this ratio (Table 4) are less than unity: (0.27 – 0.4 for Ekenkpon and 0.31 – 0.35 for Nkporo) shales, show negative Ce anomaly, and support an oxic marine condition . Also, on the AKF; (Al_2O_3)-(K_2O+ Na_2O+CaO)-(Fe_2O_3+MgO) plot (Fig. 8), the sediments were deposited in continental to transitional zone (Fig. 8; Englung and Jorgensen, 1973).
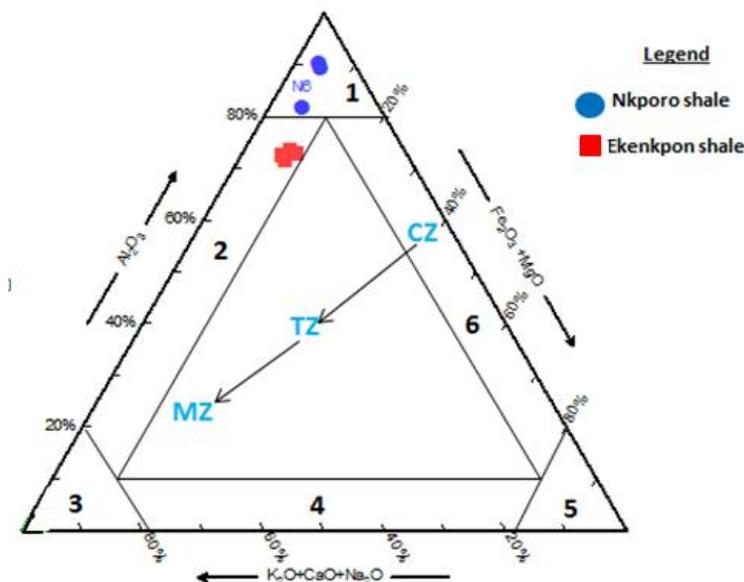
Figure 8: Al_2O_3 - $(K_2O+CaO+MgO)$ - (Fe_2O_3+MgO) [AKF] Ternary plots for Nkporo shale and Ekenkpon shale. **1**- argillaceous, **2**- carbonaceous argillites, **3**- carbonaceous, **4**-carbonaceous ferrite, **5**- ferruginous, **6**- ferruginous argillite, **CZ** = Continental Zone, **TZ** = Transition Zone and **MZ** = Marine Zone (after Englung and Jorgensen, 1973)

Tectonic setting

Several authors have described the usefulness of major, trace and rare earth elements geochemistry of siliciclastic rocks to infer tectonic settings based on discriminant diagrams plots (Bhatia, 1983; Roser and Korsch, 1986). As reported by Oni *et al.,* (2014), plate tectonic processes impart distinctive geochemical signatures to sediments in two parts; tectonic environments have distinctive provenance characteristics and are characterised by distinctive sedimentary processes. Discrimination diagram using log ratios of K_2O/Na_2O against SiO_2 (Fig. 9) based on Roser and Korsch (1986) points to active continental margin for the study samples. Such a setting, according to Roser and Korsch (1986), is characterised by intermediate quartz or SiO_2 content as seen in this study. Using Th-Co-Zr/10 and Th-Sc-Zr/10 and La-Th-Sc, ternary plots (Figs. 10 a-c), the samples from the study area plot in the continental island arc terrain and passive continental margin.

Boboye and Okon (2014) deduced a passive to active continental margin tectonic settings for the sediments of Calabar Flank while Okon *et al.*, (2017) reported mainly passive to active continental margins for the Awi Formation. In a related study in southeastern part of the Niger Delta, Oni *et al.*, (2014) characterised the sediments as belonging to active continental margin tectonic setting. They associated such a setting with actively opening of a failed arm of a triple junction as part of the Cretaceous rift system of West and Central Africa. These may also be associated with the setting in this study. Chin *et al.,* (2013) have opined that the composition of magma in continental arc is a product of mixing between igneous differentiation of mafic magmas and felsic or silica crust melting.
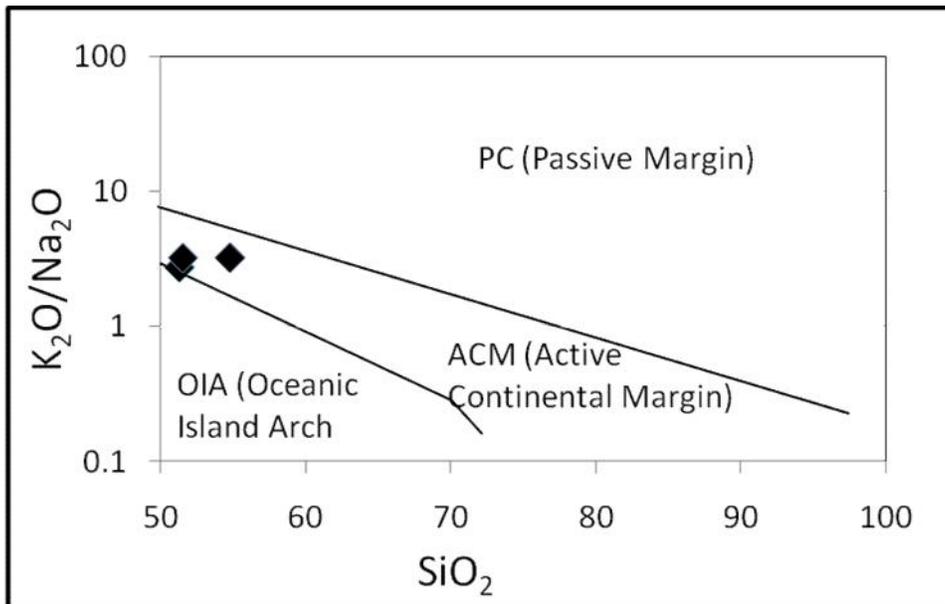
Fig. 9: Tectonic discrimination using the log ratios of K_2O/Na_2O vs SiO_2 for study samples (after Roser and Korsch, 1986)
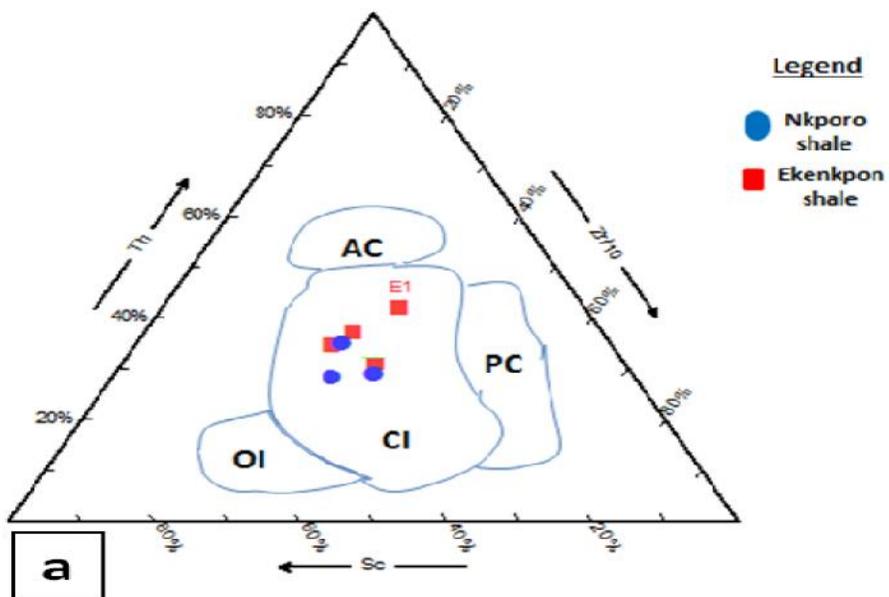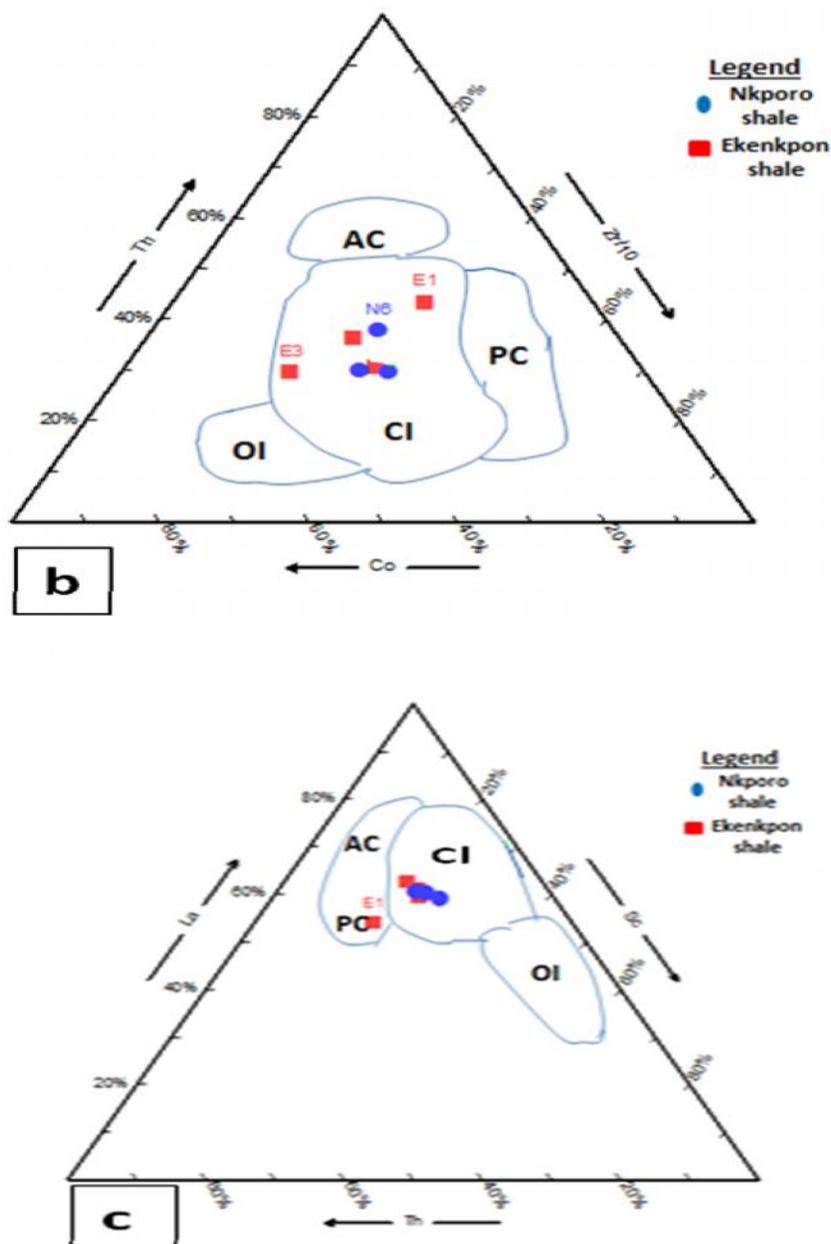
Fig 10a. Th-Sc-Zr/10 Plots for Nkporo Shale, Ekenkpon Shale and Mfamosing Limestone (After Bhatia and Crook, 1986); **b.** Th-Co-Zr/10 Plots for determination of tectonic settingfor Nkporo shale and Ekenkpon shale (After Bhatia and Crook, 1986); **c.** La-Th-Sc Plots for determination of tectonic setting for Nkporo shale and Ekenkpon shale (After Bhatia and Crook, 1986). **OI**= Oceanic Island Arc **CI**= Continental Island Arc, **AC**=Active Continental Margin, **PC** = Passive Margin

CONCLUSIONS

The geochemistry (bivariant plots of Al_2O_3 vs TiO_2; ratios of Th/Sc, Th/Co and La/Sc compared to PAAS as well as negative Eu anomalies) of Ekpenkpon and Nkporo Shales in the Calabar Flank shows that the sediments were derived mainly from felsic rocks. The shales would have suffered intense weathering, where feldspars could have been destroyed, resulting in preponderance of clay minerals in the Nkporo Shale than in the Ekenkpon Shale. It is envisaged that the sediments were formed from passive to active tectonic setting and deposited in oxic , continental to transitional marine environment. The tectonic setting is active continental margin and associated passive margin type. Integration of petrology and other chemical proxies from other lithotypes within the area, could further strengthen the deductions of the tectonic evolution of the area.

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