Geochemical Characterization of Shale Deposits Around Afikpo Area, Southeastern Nigeria

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Abstract

The mineralogical and geochemical composition of shale sourced from Mamu and Nkporo Formations, around Afikpo area in south-eastern Nigeria, were investigated to evaluate the source rock composition/provenance, infer paleo-redox conditions, sedimentary cycle, maturity and the intensity of source area weathering. Dominant clay mineral in both formations is kaolinite. Plots of Al_2O_3 vs. SiO_2 , TiO_2 vs. Al_2O_3 , $\text{Th}/\text{Sc}^{*100}$ vs. Zr/Sc , $\text{La} - \text{Th} - \text{Sc}$ and Cr/V vs. Y/Ni with observed light rare-earth elements (LREE) enrichment and negative Eu anomalies (Eu/Eu^* : 0.04 – 0.08 for Nkporo and 0.06 – 0.08 for Mamu Formation samples) indicates largely felsic sources provenance, supported by presence of kaolinitic mineral. The redox-sensitive trace element values (Mo, U, and V) suggest a marginal marine (oxic) environment for Mamu Formation shale but marine (oxic to anoxic) setting for Nkporo Formation, this was supported by U/Th and Ni/Co values as their ratios suggest that the depositional basin experienced oxic to anoxic depositional conditions. The characteristic moderate HREE depletion pattern with low $\text{Gd}_\text{N}/\text{Yb}_\text{N}$ ratios for the investigated Afikpo shale indicates non-monazite accumulation in the samples. The sediments are mature according to values of ICV, ratios of Th/Sc and Zr/Sc. Plots of CIA vs. SiO_2 , ICV vs. CIA with $\text{Al}_2\text{O}_3 \cdot (\text{CaO} + \text{Na}_2\text{O})/\text{K}_2\text{O}$ signpost an intense weathering in the source area. There is insignificant differences between the weathering and sediment maturity for the shale sediments of both formations from the same sedimentary basins, however, there exist disparity in their source rock/provenance and redox settings justifying the different formations.

1. Introduction

Significant information like tectonic setting, provenance, conditions of weathering and possible sediment recycling can be obtained from both mineralogical and chemical composition of shales based on their clastic nature (Roddaz et al., 2011; Armstrong-Altrin et al., 2015; Nichols, 2015; Madhavaraju et al., 2016). According to Deconinck et al. (2005) and Dera et al., (2009), clay minerals study is considered to be a powerful tool for the interpretation of weathering conditions and paleoclimate in the source area while Da-Peng et al. (2012) documented that trace and rare earth element geochemical study of fine-grained sediments, in most cases are assumed to give a clue to the average composition for the upper continental crust (UCC) more than any other sedimentary rock, because, they preserve the signature of the precursors and diagenetic history (Mondal et al., 2012; Madhavaraju et al., 2016). Some authors, although not limited to Cullers, 2000, 2002; Gupta et al, 2012; Raza et al., 2012; Armstrong-Altrin, 2009; Fatima and Khan, 2012; Madhavaraju, 2015; Ramachandran et al., 2016 have demonstrated that geochemical compositions of clastic sediments are helpful in understanding the source-area weathering conditions and provenance. Although, chemical weathering, modification in redox conditions and post-depositional diagenesis can rework the main chemical composition of the shale (Nesbitt et al., 1996; Armstrong-Altrin et al., 2015; Madhavaraju, 2015). Likewise, certain trace elements with their ratios and REE patterns of clastic sediments are believed to be an efficient tool for the reconstruction of source rock composition because during the processes of sedimentation, lithogenesis and metamorphism, they are not considerably redistributed (Fu et al., 2010; Zaid, 2012). As such, the elemental distribution pattern at any process can be used to identify the distinctions in paleo-redox conditions in both marine and continental sediments (Madhavaraju and Lee, 2009; Madhavaraju et al., 2015).

This work focused on the shale deposits of the Afikpo area, located in Nigeria's oldest sedimentary rocks of lower Cretaceous age in the Benue Trough's southern end. For this investigation, shale samples were collected from the exposed section near the towns of Owutu, Amosu, Ezi-Edda, Ndiofia-Edda, Amaigbo, Amoba, Asaga-Amangwu, Ogbu, Ekeje, Amaiyi road, Enohia, Nguzu and Ebunwana along erosion channels, watercourse and building channels (Fig. 1). Major, trace and rare earth elements were analyzed from the shale samples collected at different sections. The purpose of this study, hence, is to apply the geochemical character and signature to assess the source rock composition/provenance, infer paleo-redox conditions with sedimentary cycle, the intensity of source area weathering and maturity for the Afikpo shale deposits.

2. Geology And Stratigraphy

Three major Cretaceous lithostratigraphic units have been recognized in the Afikpo Basin, namely: the Asu-River Group, the Eze-Aku Group and the successions of the post-Santonian proto-Niger Delta (Odigi and Amajor, 2010) (Figs. 2 and 3).

Non-marine to marginal marine deposits is the oldest sedimentary rocks overlying the Precambrian Oban Basement Complex stones. Sandstones and dark shales with ammonites form the Asu-River Group. Deposits of the first transgressive regressive marine deposition period in the region are represented by the Asu-River Group (Petters, 1980).

The Eze-Aku beds are unconformably overlaid by the Asu-River Group and consist of shales, calcareous, and sandstone ridges, with dips ranging from 20° to 68° on average, N 40° E. The bodies of sandstone are parallel with elongated features. The Eze-Aku beds represent the second depositional transgressive period that occurred during the Upper Cretaceous (Murat, 1972). The Turonian end was marked by a regressive period that ended the Campanian-Maastrichtian transgression by a third sedimentation stage. The transgression and regression of the Campanian-Maastrichtian contributed to the deposition in the board of the post-Santonian Campanian-Maastrichtian proto-Niger Delta sequences and a gentle depression of the Afikpo Basin (Fig. 2).

The sediments of the post-Santonian (Campanian-Maastrichtian) lie unconformably over the Eze-Aku strata. These beds contain marine conglomerates, sandstones, mudstones and shales that are fluvial, shallow to deep-water, showing a NE-SW pattern (Odigi and Amajor, 2010). The Paralac Nkporo Formation, Mamu, Ajali, and Nsukka formations were deposited in the subsiding Afikpo Basin following the southwest change of the depositional axis in southern Benue Trough. Lithologically, the Campanian Nkporo Formation is encompassed by a parallel succession of Mamu Formation siltstone, shale, coal seam and sandstone units deposited in the Early Maastrichtian (Ladipo, 1986). Nton and Awarun (2011) identified the shale and coal units of the Mamu Formation as fair to rich oil/gas prone, immature source rocks of terrestrial precursor on the basis of organic geochemical and biomarker parameters. The Mamu Formation is successively superimposed on the Maastrichtian Ajali Sandstone by cross-bedded, tidal channel/fluvial deposits (Ladipo, 1986; Fig. 3).

3. Methodology

3.1 Mineralogical analysis

Ten (10) shale samples were selected for clay mineralogical study. Preparation of samples followed standard XRD procedures of Brindley and Brown, 1980; Moore and Reynolds, 1989. The mineralogical analysis was conducted using an X-ray diffractometer at the Nigeria Geological Survey Agency (NGSA), Kaduna, Nigeria. By analyzing or comparing peaks of substantial intensity with those of the Joint Committee on Powder Diffraction Standard (JCPD), 1974 and standard or ordinary shale minerals documented by Carol (1971), the obtained curves were interpreted.

3.2 Inorganic Geochemical Analysis

The collected samples were air-dried, and pulverized systematically to avoid contamination and then sieved through 75µm sieve. Thirty (30) shale samples were packed for geochemical analysis at the ACME Analytical Laboratories Ltd, Canada. Major elements composition for the shale samples were obtained via Inductively Coupled Plasma Atomic Emission (ICP-AES; Spectro Varian 735) whereas inductively coupled plasma-mass spectrometer (ICP-MS; PerkinElmer, Elan 6000) was used for the determination of trace and rare-earth elements. Loss on ignition (LOI) was evaluated for by calculating the weight loss after heating a 1 g divided sample at 95°C for 90 min. For precision, calibration standards and chemical reagent blanks were applied as applicable.

4. Results

4.1 Clay mineralogical characteristics

The bulk mineralogical composition for the Afikpo shale from both Mamu and Nkporo Formations are presented Table 1. The shales from Mamu Formation (Fig. 4A) yielded kaolinite (21.52% - 43.55%) as the dominant clay mineral. The associated non-clay minerals are quartz (54.30% - 60.70%) and anatase (13.25% - 18.20%) (Table 2). The Nkporo Formation (Fig. 4B) shows dominant kaolinite (32.30% - 39.40%) but relatively small amount of smectite (0.57% - 5.70%) as clay minerals while non-associated clay mineral includes: quartz (41.20% - 56.90%), anatase (3.15), jarosite (1.20% - 12.00%), Goethite (1.35% - 13.50%), Hematite (0.98% - 9.75%), pyrite (1.11% - 11.10%), phenate (0.97% - 9.70%) and limonite (0.88% - 8.80%) (Table 2).

Table 1
Mineral contents (in percentage) of shale in Afikpo-Edda Area

Location/SN	Formation	Quartz	Kaolinite	Anatase	Jarosite	Goethite	Hematite	Pyrite	Smectite	Phenate	Limonite
Amaiya/L1	Mamu	58.80	41.20								
Ebuwana/L9	Mamu	60.30	21.52	18.2							
Amaiya/L16	Mamu	56.45	43.55								
Nguzu/L20	Mamu	54.30	32.45	13.25							
Amangwu/L7	Nkporo	49.60	39.40	-	12.00	-	-	-	-	-	-
Amoba/L30	Nkporo	51.10	36.40			13.50					
Owutu/L40	Nkporo	51	49								
Ogbu/L41	Nkporo	51.75	38.50				9.75				
Ogbu/L43	Nkporo	41.20	32.30					11.10	5.70	9.70	
Enohia/L52	Nkporo	56.9	39.3								8.8
Average		53.14	37.36	3.15	1.20	1.35	0.98	1.11	0.57	0.97	0.88

4.2 Geochemistry

4.1.1 Major element geochemistry

The major elemental composition for the shales under investigation are presented in Table 2. The documented results revealed that the shales from Mamu Formation are somewhat enriched in SiO_2 (range 45.10 – 73.13 wt%; Av. 59.79 wt%) compared with Nkporo Formation (range: 42.67 wt%; Av. 49.71 wt%) (Table 1).

Table 2. Range and average major oxides concentration (in %wt) for Afikpo shale samples

	Samples from Nkporo Formation		Samples from Mamu Formation		UCC	PAAS
Major oxides	Range	Av.	Range	Average		
SiO_2	42.67-64.40	49.71	45.10-73.13	59.79	66.00	62.80
Al_2O_3	12..69	22.39	13.48-22.99	18.90	15.40	18.90
Fe_2O_3	4..14- 17.99	9.67	1.39 - 6.69	4.47	5.04	7.22
MgO	0.24 - 1.24	0.72	0.05 - 0.54	0.40	2.48	2.20
CaO	0.02 - 0.54	0.11	0.02 - 1.35	0.35	3.59	1.30
Na_2O	0.04 - 0.13	0.06	0.02 - 0.07	0.05	3.27	1.20
K_2O	0.57 - 3.09	1.17	0.18 - 1.76	1.09	2.80	3.70
TiO_2	0.80 - 1.40	1.04	0.93 - 1.53	1.19	0.64	1.00
P_2O_5	0.05 - 0.24	0.12	0.07 - 0.35	0.15	0.15	0.16
MnO	0.01 - 0.07	0.003	0.01 - 0.04	0.02	—	—
Cr_2O_3	0.013 - 0.21	0.018	0.01 - 0.017	0.014		
LOI	8.50 - 19.90	14.66	6.70 - 22.40	13.31		
Total		99.77		99.74		
SR	1..12 - 1.72	1.55	1.55 - 3.72	2.56		
AR	1.13 - 4.50	2.32	2.40 - 12.01	4.23		
$\text{MgO}+\text{CaO}$	0.26 - 1.94	0.83	0.10 - 2.08	0.75		
$\text{Al}_2\text{O}_3+\text{Na}_2\text{O}+\text{K}_2\text{O}$	15.90 - 26.40	23.6	15.10 - 23.80	1.14		
$\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$	1.81 - 19.89	8.26	3.15 - 7.72	4.10	1.80	1.95
$\text{SiO}_2/\text{Al}_2\text{O}_3$	1.89 - 4.86	2.22	2.01 - 5.27	3.16	4.29	3.32
$\text{K}_2\text{O}/\text{Na}_2\text{O}$		19.50		21.80	0.86	3.08
$\text{Al}_2\text{O}_3/\text{TiO}_2$	13.79 - 29.91	21.52	10.91 - 19.00	15.88	24.06	5.10
$\text{K}_2\text{O}/\text{Al}_2\text{O}_3$	0.02 - 0.06	0.05	0.01 - 0.04	0.06	0.18	0.20
$\text{MgO}/\text{Al}_2\text{O}_3$	0.01 - 0.06	0.03	0.01 - 0.04	0.02	0.16	0.12
CIA	90.23 - 99.41	94.35	87.16 - 98.52	92.62	52.76	70.39
PIA	95.14 - 99.76	99.21	93.76 - 99.60	97.80	53.49	79.05
CIW	79.86 - 99.75	94.79	94.00 - 98.82	94.31		
ICV	0.31 - 1.04	0.52	0.17 - 1.22	0.34	1.16	0.89

The results when also compared with PAAS (Post-Archean Australian Shales after Taylor and McLennan, 1985) and UCC (Upper Continental Crust after Rudnick and Gao, 2003), indicates that the investigated Afikpo shale samples from both Nkporo and Mamu Formations are enriched in

SiO₂, Al₂O₃ and TiO₂ but are depleted in most of the major elements, especially CaO, MgO, Na₂O, K₂O, and MnO (Table 2), thus corroborating with the mineralogical composition (Table 1).

The weathering indices; chemical index of weathering (CIW), chemical index of alteration (CIA) and plagioclase index of alteration (PIA) were calculated for the shale samples and contrasted to that of UCC and PAAS (Table 2). The values of CIA for both Formations (Nkporo: av. 94.35; Mamu: av. 92.82) are greater than that of PAAS with a recorded value of 70 and UCC with 51 and the PIA values for the investigated Afikpo shales (Nkporo Formation: av. 99.21; Mamu Formation: 97.80) are also greater than that of PAAS with a recorded value 79 (Table 2). Obtained CIW of all the investigated samples averaged 94.79 for Nkporo Formation and 94.31 for Mamu Formation, Higher than 79 recorded for PAAS and 74 for UCC (Table 2).

The shale samples were thus, classified into mafic, intermediate and felsic compositions based on the model put forward by Le Bas et. al. (1986) and Armstrong-Altrin, (2009). Using the model in Fig. 5, almost all the samples from Nkporo Formation fall into the mafic region, while samples from Mamu Formation are in the region of both intermediate and compositional field correspondingly. According to Cox et al. (1995), the K₂O/Al₂O₃ ratio can be used as a sign for original composition of ancient sediments, K₂O/Al₂O₃ ratios for clay minerals range from 0.0 to 0.3 and those for feldspars from 0.3 to 0.9. In this present investigation, K₂O/ Al₂O₃ ratios range in values from 0.02 to 0.24 for Afikpo shale samples from Nkporo Formation while from Mamu Formation, it ranged from 0.01 to 0.20, thus, suggesting presence of clay minerals, typically of kaolinite compositions as presented in table 1.

4.1.2. Trace element geochemistry

Trace element composition of the Afikpo shales were grouped into three different elemental categories for their description as presented in Table 3. Most of the shales in the study area on an average are depleted in Large ion lithophile trace elements (LILE) such as Rb, Ba, and Sr except Sr for samples from Mamu Formation enriched relative to PAAS but shale samples from both formations (Nkporo and Mamu Formations) are slightly more enriched in Th and U relative to PAAS and UCC (Table 3, Figs. 6 and 7). In table 3 and fig. 6, it could be observed that the investigated shale samples are largely enriched in all the High Field-Strength Elements (HFSE; Nb, Th, U, Zr, Hf, and Y, when compared with the PAAS and UCC compositions (Table 3, Fig. 6). The average values of transition trace elements (TTE) such as Sc, Cr, V, Ni, Co in the investigated shales to some great extent, showed wide dissimilarity to those of the PAAS and UCC, such that shale samples from Nkporo Formation is enriched in V, Sc and Cr relative to both of PAAS and UCC but showed higher values in Ni, and Zn compared to UCC while Cu, values were similar. On the other hand, samples from Mamu Formation, only Cr was enriched compared to those of PAAS and UCC but V, Ni, Cu, Zn, Sc showed higher values compared to UCC (Table 3 and Fig. 7).

Table 3: Elemental categories for the Afikpo shale

	elements	Nkporo Formation			Mamu Formation		
		Range	Average		Range	Average	
L	Ba	146	2758	423	210	1033	501
I	Sr	80.6	232	138	67.3	545.9	210.9
L	Rb	45.8	107	73	7.2	79.9	50
E	Th	15.3	46	19.9	14.8	28.5	21.7
	U	2.7	8.2	3.9	3.2	9.5	5
H	Zr	129.4	2107	383	157.4	1119.3	549.1
F	Y	15.9	42.6	25	23.5	60.3	39.5
S	Nb	17.2	32.7	25.5	19.9	40.6	28
E	Hf	3.5	53.5	9.85	4.4	27.7	13.84
T	V	107	232	190	98	157	127.6
T	Ni	20	75	30.4	20	39	27.6
E	Co	2.6	19	6.9	1.6	17.7	9.7
	Cu	8	24.3	17	3.2	36.2	19.1
	Zn	5	157	34.8	2	92	29..5
	Sc	9	20	16.91	10	21	14.71
	Cr	130	220	183.04	100	170	140
	Mo	0.3	6.2	1.4	0.2	1.4	0.6
	Pb	9.5	26.6	18	5.8	24.8	17.8
ΣLILE		90.36	3038.5	657.8	377.1	377.1	788.6
ΣHFSE		174	2226.8		205.2	1206.8	616.6
ΣTTE		249.3	644.3		243.9	484.5	338.71
Cr/Ni		2.27	9.17	6.02	3.42	7	5.07
Ni/Co		2.88	10.27	4.41	1.64	12.5	2.85
U/Th		0.17	0.24	0.2	0.19	0.33	0.23
Th/U		4.13	5.94	5.1	3	5.39	4.34
Rb/Sr		0.23	1.24	0.53	0.01	1.19	0.24
La/Sc		2.91	13.11		3.42	10.78	
Th/Sc		0.88	5.11		1.04	2.5	
Th/Co		0.87	10.54	2.88	1.14	16.5	2.24
La/Co		3.39	33.5		3.65	80.75	

4.1.3 Rare Earth Elements geochemistry

The concentrations of rare earth elements are given in Table 4. The chondrite-normalized patterns are shown in Fig. 8. The chondrite-normalized REE diagram shows that the HREEs display an almost flat pattern ($(\text{Gd}/\text{Yb})_{\text{cn}}$: 1.86 – 5.27 for Nkporo Formation samples and 1.71 – 4.47 for Mamu Formation samples), concentrations of LREE are considerably higher than that of HREE, and significant negative Eu anomalies (Eu/Eu^* : 0.04 – 0.08 for Nkporo Formation samples and 0.06 – 0.08 Mamu Formation samples). This typically describes general distribution of REEs in shales (Gromet et al., 1984; Condie, 1991). The shale samples show slight variations in ΣREE content especially within formations but large variations recorded between the two different formations (Nkporo and Mamu Formations; Table 4) suggesting that the observed distinctions may be owing to compositional inconsistency and environment of deposition.

Table 4. Range and average rare earth element distribution (ppm) of Afikpo shale samples, Southeastern Nigeria

	Nkporo			Mamu		
	Range		Ave	Range		Av
La	46.6	118	64.1	61.4	68.3	64.1
Ce	85.6	235.9	131.6	113.1	134	131.6
Pr	8.7	26.6	14.7	11.8	15.3	14.7
Nd	29.7	100.5	53	40.7	57.7	53
Sm	4.2	16.6	9	6.6	11	9
Eu	0.92	2.49	1.7	1.28	2.13	1.7
Gd	3.17	13.05	7	5.22	7.73	7
Tb	0.48	1.55	0.93	0.75	1	0.93
Dy	2.92	8.34	5.17	4.43	5.48	5.17
Ho	0.56	1.43	0.95	0.84	1.11	0.95
Er	1.78	4.3	2.69	2.27	3.28	2.69
Tm	0.27	0.62	0.38	0.32	0.46	0.38
Yb	1.75	4.25	2.55	2.27	3.22	2.55
Lu	0.25	0.73	0.38	0.32	0.45	0.38
Sc	9	20	17	16	20	17
Y	15.9	42.6	25	21.2	32.9	25
Eu*	0.04	0.08	0.07	0.06	0.07	0.07
La/Yb	6.03	35.12	7.15	6.03	8.56	7.15
Gd/Yb	1.7	5.27	2.22	1.7	2.75	2.22
Σ REE	216.8	585.35	336.15	300.73	337.45	336.15

5. Discussion

5.1 Source area weathering conditions

The intensity of weathering in the sedimentary rocks can be investigated by using the alkali and alkaline earth elements' association (Nesbitt and Young, 1982). According to Nesbitt *et al.* (1980), labile elements such as: Na, Ca, and Sr are mostly leached away during weathering with insoluble elements such as: Al, Ba and Rb left behind. These changes in chemistry of the sedimentary rock are preserved which in turn provides a useful information for source area weathering conditions' study. (Nesbitt and Young 1982).

A chemical index generally used in the degree of source area weathering evaluation is the Chemical Index of Alteration, (CIA; Nesbitt and Young, 1982). According to Nesbitt and Young, 1982 and supported by Fedo *et al.* (1995); Srivastava *et al.* (2013) and Újvári *et al.* (2013) conclude that higher CIA values ranging from 76 to 100% in sedimentary rocks suggest an intense chemical weathering in the source region whereas low values of 50% and below indicates close or absence of chemical weathering but reflect cool and arid conditions.

The CIA values of shales from both formations (Nkporo and Mamu) of Afikpo Southeastern, Nigeria are documented in Table 2. The samples from Mamu Formation recorded a range in CIA values from 89.06% - 97.29% while Nkporo Formation's shale samples ranged from 90.23% - 99.4%. The obtained CIA values for the present study are relatively higher than both the average UCC value of 52.76 (Rudnick and Gao, 2003) and typical PAAS shale values of 79.05 (Taylor and McLennan, 1985). Therefore, the calculated CIA for the investigated shales (Table 2) indicates that their source rocks have undergone a high degree of weathering (Young, 2002).

Plagioclase Index of Alteration (PIA: Fedo *et al.*, 1995), was used to determine the degree of chemical weathering for sediments and sedimentary rocks. The PIA values for the investigated shale samples from Mamu Formation ranged from 93.76 – 99.75% while those of Nkporo Formation ranged from 93.76% - 99.75% (Table 2). These values are higher than those of UCC (53.49%) and PAAS (79.05%) but consistent with CIA values thus supporting that these shales suffered high intensity of chemical weathering.

Also, the A-CN-K ($\text{Al}_2\text{O}_3 - (\text{CaO} + \text{Na}_2\text{O}) - \text{K}_2\text{O}$) diagram (Fig. 9a) of Nesbitt and Young, (1982) supported by Fedo *et al.* (1996) which allows the study into the differentiation of compositional distinctions connected with chemical weathering and/or source rock composition (Deepthi *et al.*, 2012; Ghosh *et al.*, 2012; Madhavaraju *et al.*, 2016), was used to demonstrate the weathering history for the Nkporo and Mamu Formation shales. The shale samples plot close to high Al_2O_3 contents (A-Apex), thus reflecting a high degree of weathering to a stage where there is the release of significant amounts of alkali and alkali earth elements from the sediments. The degree of weathering in the source area was relatively higher than that of UCC and PAAS (Fig. 9a (see supplementary file); Madhavaraju *et al.*, 2016). A similar trend was observed in the plot of CIA vs. SiO_2 (Fig. 9b; see supplementary file) with the samples plotting mostly in the upper part between illite and kaolinite, indicating a high degree of weathering.

In addition, an index of compositional variability put forward by Cox *et al.* (1995) was used as a means to evaluate the shales' compositional maturity. The ICV provides information on the abundances of alumina comparative to other major cations in a rock or mineral. The ICV values (Table 3) for the Afikpo shales under investigation ranged from 0.17 to 1.17 for samples from Mamu Formation while 0.36 to 1.00 for samples from Nkporo Formation, of which most samples are < 0.89 (Value for PAAS) (Fig. 9c; see supplementary file), this typically indicates minerals such as kaolinite, illite, and muscovite, but greater than that expected in rock-forming minerals (>0.89) such as plagioclase, K-feldspar, amphiboles, and pyroxenes. This suggest typical clay rich mature sediments related to either a tectonically inactive or intra-cratonic environment, where sediment recycling is active (Cox *et al.*, 1995) or from highly weathered source rock/crystalline basements, evident from the diagram in Fig. 8c as proposed by Long *et al.* (2012) as a tool to evaluate sediment maturity and weathering intensity.

The weathering indices (CIA, PIA and ICV) suggest that the shales were under the same climatic conditions, although they were obtained from different formations within the same basin.

5.2 Source rock composition/provenance

Composition of trace elements in sedimentary rocks could possibly be a source of information to the evaluation of source rocks. The high field strength elements Zr, Hf, Y and Nb are quite immobile in sedimentary settings; just like Al and Ti, consequently they give clue into provenance composition (Taylor and McLennan, 1985).

Geochemical ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ in sedimentary rocks like the shale under investigation are considered as a useful tool to study different source rocks (Andersson *et al.*, 2004; Madhavaraju *et al.*, (2016). Ratio < 14 of $\text{Al}_2\text{O}_3/\text{TiO}_2$ in sediments indicates mafic origin, whereas ratios between 19 to 28 points towards felsic origin. $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios for the Afikpo shales ranged from 13.79 to 25.80 (Table 2) for Nkporo Formation while Mamu Formation shale samples varied from 10.91 to 19.00. The obtained values suggest that the Afikpo shales were chiefly derivative of felsic source rocks. This was supported with the binary plot; TiO_2 vs Al_2O_3 in fig. 10A as proposed by Perri (2014) to differentiate granitic from basaltic rocks, the plot suggest an intermediate to granite rock origin for the shale deposits. Also, from the discriminative diagram of McLennan *et al.* (1993) (Fig. 10B), the investigated Afikpo shale samples plot in between the granodiorite and granite, revealing a dominantly granitic source for the shale deposits. In addition, from Cullers' 1994a diagram (Fig. 10C) to distinguish felsic and basic provenance, the shale data falls within a predominantly felsic region, this also corroborates the mineralogical characteristic with presence of dominant kaolinite in the shale samples as presented in table 2.

For source-rock/provenance determination, stable trace elements (Ni and Cr) with their respective ratios (Cr/V and Y/Ni) are good tools that can be considered. Enriched in felsic rocks are Th and La while elements like Co, Sc and Cr are supposedly enriched in rocks of mafic source. Depending on the content of Cr and Ni in siliciclastic sedimentary rocks make them useful pointers for evaluation of provenance. With reference to the study of Armstrong - Altrin *et al.* (2004), he opined that high Cr and Ni contents suggest that the sediments are derivative of ultramafic rocks but low Cr and Ni contents implies, felsic rock source. Supporting the above assertion, Garver *et al.* (1996) proposed that ultramafic rocks are described by Cr values > 150 ppm and Ni > 100 ppm with relatively small Cr/Ni ratios of 1.3 to 1.5. The obtained values in this present investigation showed Cr to vary from 100 to 170ppm for the samples from Mamu Formation while Nkporo Formation's shales recorded Cr value of 130 to 220ppm but for the Ni composition, samples from Mamu Formation recorded 20 to 132ppm while Nkporo Formation recorded 20 to 75 ppm of Ni respectively with characterize Cr/Ni of greater than 2 (Table 3).

The Ni and Cr composition with their ratios as illustrated, imply a more felsic composition for the shale deposit under investigation.

Also, geochemical ratios of relatively stable elements, according to Cullers, (2000); Cullers and Podkovyrov, (2000) like; Th/Co, La/Sc, Cr/Th and Th/Sc have proven to be useful in the evaluation of source rock. For the present investigation, some of these ratios were used to construct binary plots of which most of the Afikpo shales plot within felsic source, although, mafic contribution cannot be ruled out (Figs. 11 A-D).

More also, from the observed characteristic enriched LREEs and low with nearly flat HREE patterns tending towards negative Eu anomalies (Eu/Eu^* : 0.04 – 0.08 for Nkporo Formation samples and 0.06 – 0.08 Mamu Formation samples; Table 4; Fig. 8). This suggest that the original precursor was felsic and that the negative Eu anomaly is taken as proof from a discriminated, granitic source (McLennan *et al.*, 1993).

5.3 Multi-proxy trace element patterns

The multi-elements proxies are appropriate tools to evaluate paleo-redox conditions than just a single elemental proxy (Tribovillard *et al.*, 2006). According to Tribovillard *et al.* (2006), trace elements such as Mo, U and V can be used due to their least vulnerability to primary and secondary complexities. The redox-sensitive trace element values (Mo, U, and V) as shown in Table 4, showed a low Mo composition (0.20-1.40), slightly high U (3.30 – 9.50), and V (98 – 157) for Afikpo shale samples from Mamu Formation, this suggest that the shale samples from Mamu Formation were deposited under a marginal marine environment or under oxygenated conditions while Shale samples from Nkporo Formation recorded a low to high Mo (0.30 – 6.20), slightly high U (2.90 – 8.20) and V (107 – 228), this reveals that the shale experienced a suboxic/anoxic condition (i.e more of marine setting) at the bottom of the water during its deposition (Somayajulu *et al.*, 1994, Nath *et al.*, 1997, and Crusius *et al.*, 1996). These values were relatively higher than that those of PAAS and UCC (Table 3).

Calculated geochemical ratios like U/Th and Ni/Co for marine sediments can be used as a dependable proxies to evaluate oxygenation conditions of a depositional environment (Dypvik, 1984; Jones and Manning, 1994 and Madhavaraju *et al.*, 2016). According to Jones and Manning, (1994), low U/Th ratio (< 0.75) indicates oxic conditions, while high U/Th ratio (> 1.25) suggest anoxic conditions. The shales from Afikpo area of southern Nigeria recorded U/Th value of 0.17 to 0.24 for samples from Nkporo Formation and 0.19 to 0.23 for samples from Mamu Formation (Table 3). Thus, the observed values in U/Th ratio for both formations suggest that the shales were deposited in an oxic conditions.

Another geochemical ratio of utmost important that can be used as redox indicator is Ni/Co (Jones and Manning, 1994 and Madhavaraju *et al.*, 2016). According to (Jones and Manning, 1994), ratios of Ni/Co <5 indicate oxic settings while ratios > 5 proposes suboxic and anoxic settings. Substantial disparities were observed in nickel and cobalt contents in the shale samples from different formation, most especially, the Nkporo Formation (Table 3). Nkporo Formation recorded 2.99 to 10.27 with an average of 4.4 while 1.64 to 12.50 with an average of 2.39 was recorded for samples from Mamu Formation (Table 3). This implies that the variation in the ratios of Ni/Co was controlled principally by the oxygenation level in the environment where these shales were deposited (oxic → anoxic settings).

5.4. Maturity and sediment recycling

The Afikpo shales from Mamu and Nkporo Formations were investigated using their chemistry to ascertain their maturity (Garzanti and Sergio, 2019). According to Cox *et al.* (1995), the index of compositional variation (ICV) can be used as a tool to infer maturity of sediments. As proposed by Cox *et al.* (1995), sediments with ICV > 1 suggest that the sediment is immature, while, ICV < 1 implies mature sediments. Immature sediments point towards an active tectonic environment while mature sedimentary rocks are products recycled older sedimentary rocks or that has undergone extensive transportation (Cox *et al.*, 1995; Cullers and Berendsen, 1998).

This study recorded an ICV values ranging from 0.31 to 1.04 (averaging 0.34) for samples from Mamu Formation and 0.31 to 1.04 (Av. 0.52) for samples from Nkporo Formation (Table 3), thus inferring that the shale samples are compositionally mature. This is comparable to ICV values for PAAS (Table 3).

According to Haifeng *et al.* (2015), during weathering, sedimentary recycling in oxidizing conditions results in the fractionation of Th and U due to U^{4+} which readily oxidizes to U^{6+} . Though, they could be removed from the system, Th remains immobile. Therefore, ratios of Th/U increase due to uninterrupted weathering and successions of re-deposition (Long *et al.*, 2008). The value of Th/U ratio obtained in this investigation ranged from 3.00 to 5.39 (Av. 4.34) for shale samples from Mamu Formation and 4.13 to 5.94 (Av. 4.41) for Nkporo samples. The obtained average for both formations relatively compared to UCC (Av. 3.82: McLennan, 1985), indicates very little oxic weathering (Haifeng *et al.*, 2015).

According to Seriwat *et al.* (2015), the existence of zircon in sedimentary rocks can be evaluated.

Recycled sediments show Zr/Sc ratios that are significantly dissimilar with little variation associated Th/Sc (Seriwat *et al.*, 2015), owing to the nature of the source rock, first-cycle sediments imply a positive association between Th/Sc and Zr/Sc, thus, indicating the buildup of zircon due to obliteration of other minerals through sediment recycling. The studied shales from both formations show no correlation between ratios of Th/Sc and Zr/Sc (Fig. 12A), relatively low to high ratios of Th/Sc (0.90 – 5.11 for Nkporo and 1.04 – 2.20 Mamu Formations respectively) and Zr/Sc (7.61 – 234.11; Av. 23.00 for samples from Nkporo and 19.80 – 111.93; Av. 43.57 for Mamu samples), the obtained average for the two formations with Nkporo Formation's sample less than 32 for UCC (McLennan *et al.*, 1993) but Mamu Formation's samples showed higher values, thus implying that, the sediments are not first cycle sediments, and are quite mature.

Presence of Monzonites in siliclastic sedimentary rocks portrays a characteristic very steep chondrite-normalised HREE pattern, high REE abundances, and significant increases in the chondrite normalised Gd_N/Yb_N ratio (McLennan *et al.*, 1993). The characteristic moderate HREE depletion pattern (Fig. 8) with low Gd_N/Yb_N ratios (Table 3, Fig. 12B) for the investigated Afikpo shale indicates non- monazite accumulation in the samples.

Conclusion

The mineralogical and geochemical compositions of Afikpo Shale sourced from Mamu and Nkporo Formations, south-eastern Nigeria, were investigated to evaluate the intensity of source area weathering, source rock composition/provenance, paleo-redox conditions sedimentary cycle

and maturity. Obtained dominant clay mineral is kaolinite for both Formations. The obtained values of CIA and PIA values and positions of samples on the A-CN-K diagram indicate that these shale samples were generated from a source rocks of the upper continental crust affected by intense chemical weathering, evident from the mineralogical composition. The characteristic Th/Co, Th/Sc and La/Sc indicated that the Afikpo shales were derivative of felsic composition source rocks. This was supported by similarity of REE patterns to that of PAAS, LREE enrichment, slightly flat HREE and negative Eu anomalies and plots of Al_2O_3 vs. SiO_2 , TiO_2 vs. Al_2O_3 , Th/Sc^{*100} vs. Zr/Sc , $\text{La} - \text{Th} - \text{Sc}$ and Cr/V vs. Y/Ni . The redox-sensitive trace element values (Mo, U, and V) suggest a marginal marine (oxic) environment for Mamu Formation shale but marine (oxic to anoxic) setting for Nkporo Formation, this was supported by U/Th and Ni/Co values as their ratios suggest that the depositional basin experienced oxic to anoxic depositional conditions. Binary plots of Zr/Sc and Th/Sc combine with Th/U and $\text{Gd}_\text{N}/\text{Yb}_\text{N}$ ratios with ICV values demonstrates that the Afikpo shales are matured and are probably not first cycle sediments that lacks heavy mineral enrichment. Thus, the observed record present an insignificant differences between the weathering and sediment maturity for the shale sediments of both formations from the same sedimentary basins, however, there exist slight disparity in their source rock/provenance and redox settings.

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Figures

Figure 1
Geological Map of Afikpo-Edda area

Figure 2
Stratigraphic sections across the Benue Trough in N-S direction (After Obaje, 2009).

BASIN	TIME SCALE	LITHOSTRATIGRAPHIC UNIT		BRIEF LITHOLOGIC DESCRIPTION
NIGER DELTA BASIN	Pleistocene	Benin Formation		Coastal plains sands; cross-bedded, coarse, pebbly continental sands, with clay lenses and lignites; has marine shale breaks with foraminifera, ostracods, and molluscs
	Pliocene			
	Miocene	Ogwashi-Asaba Formation		Clays, silts, sands with thin to thick lignite seams
	Oligocene			
	Eocene	AMEKI GROUP	Nsugbe Formation Nanka Formation Amekei Formation	Mainly sands with some conglomerate bands, calcareous clays, and silts with thin shelly limestone, rich in foraminifera, minor silt, and clay intercalations
	Paleocene	IMO FORMATION	Ebenebe Sandstone Umuna Sandstone Igbaku Sandstone	Blue-grey shales with sand lenses, marls, and fossiliferous limestones, sandstone members: Ebenebe, Umuna, and Igbaku sandstones; shales with foraminifera and ostracods
ANAMBRA BASIN	Maastrichtian	COAL MEASURES	Nsukka Formation	Mainly sandstones, mudrocks (some with dark grey coal seams), and limestone often occurring as alternations or in an interfingering relationship.
			Ajali Formation	Mainly sandstones/sands, friable to semi-consolidated. Minor occurrence of mudrock break or sand/silt/clay heteroliths. Cross bedding is distinctively well developed in the sandstones
			Mamu Formation	Shales, sandy shales, carbonaceous shales, coal, and sandstones
	Campanian	NKPORO GROUP	Nkporo Fm/Enugu Fm/Owelli Fm	Nkporo Fm: Shales and mudstones with occasionally thin beds of sandy shale, fine sandstone, and marl with coatings of sulphur, rare thin bands of shelly limestone are present. Abundance of benthic foraminifera Enugu Fm: Mainly shales (with ironstone nodules), siltstone interbeds which becomes finely interlaminated with shale to form heteroliths. Otobi and Okpaya sandstone members Owelli Fm: Texturally immature (Kaolinitic), but largely compositionally mature sandstone (quartz arenite with minor feldspar content). Interbeds of marine, dark grey, micaceous, pyritic, calcareous, and occasionally glauconitic shales.
	Santonian	S a n t o n i a n		U n c o n f o r m i t y
SOUTHERN BENUE TROUGH	Coniancian	Awgu Formation / Agbani Sandstone.		Awgu Fm: Shales, sandstones, and limestones. Agbani Sst: Sandstones. Interbeds of brown laminated clays and carbonaceous shales.
	Turonian	EZE AKU GROUP	Amaseri Sandstone Nkalagu Lst Eze-Aku Shale	Consists of sandstones, siltstones, shales, limestones, and rare conglomerates.
	Cenomanian	Mfamosing Formation		Shelly limestones (with pelecypods, gastropods, and foraminifera as well as fragmentary crinoids and algae), alternation of limestones and shales, sandy shales with sandstone bands and calcareous sandstones with presence of ammonites.
	Albian	ASU RIVER GROUP	Abakaliki Formation Awi Fm / Mamfe Fm Ogoja Sst	Abakaliki Fm: Consists of folded lead zinc mineralized shales, with lenses of sandstones and limestones. It is locally rich in ammonites Mamfe Fm: Arkosic sandstones, with intercalations of marls, sandy limestones, and shales. Awi Fm: Basal, non-calcareous, sandy conglomeratic unit of the Asu River Group. Ogoja Sandstone: Basal conglomerates and arkosic sandstones.
	Aptian			
Precambrian		Basement complex		Basement complex

Figure 3

Stratigraphic framework of south-eastern Nigeria and outcropping post-Santonian Campanian- Maastrichtian proto-Niger Delta sequences and a gentle depression of the Afikpo Basin sediments (Modified from Nwajide, 2013; Ekwenye et al., 2015; Nzekwe and Okoro, 2016).

Figure 4
X-ray diffractogram for A) L1 and B) L7 representative shales sample

Figure 5

Plot of Al_2O_3/TiO_2 vs. SiO_2 (After Le Bas et al., 1986).

Figure 6

A) UCC and B) PAAS-normalized trace elements diagram for Afikpo shales of the Nkporo Formation, Southeastern, Nigeria.

Figure 7
A) UCC and B) PAAS-normalized trace elements diagram for Afikpo shales of the Mamu Formation, Southeastern, Nigeria.

Figure 8
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NASC-Chondrite normalised rare elements plot for the shale samples under investigation (After Boynton 1984).

Supplementary Files

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