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Provenance and Weathering History of the Maastrichtian Shale Member of the Patti Formation, Southern Bida Basin, Nigeria

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Abstract: The present study is focused on the geochemical characterization and provenance of the shale member of the Maastrichtian Patti Formation which is well represented at the centre of the southern Bida Basin in Nigeria. The major element composition of the studied shales and clays compare favourably with the reference shales, however, the trace elements vary slightly. Application of binary plot of TiO_2 versus Al_2O_3 and Al_2O_3/TiO_2 ratios of the studied shale samples show mixed mafic to felsic igneous sources. The chemical composition (plot of SiO_2 versus Log (K_2O/Na_2O) indicates active to passive continental margin province, however, a minor derivation from recycled provenance is probable. Intense chemical weathering based on the high values of Chemical Index Alteration (CIA), Chemical Index of Weathering (CIW) and Zr values obtained from the shale and clay samples a warm humid condition is suggested. The high values also probably suggest predominance of clay minerals and low feldspar. This is supported by the XRD (X-Ray Diffractometer) data which indicates predominance of kaolinite in the samples.

Keywords; continental margin, humid, maturity, passive, weathering, Nigeria.

INTRODUCTION

The Bida basin is made up of about 3.5 km thick upper Cretaceous clastic rocks. The basin is a rift bounded tensional structure produced by faulting associated with the Benue trough system and drifting apart of the African and Brazilian plates during the Cretaceous (King, 1950; Kennedy, 1965). Landsat imageries analysis by Kogbe et al. (1983) indicates that the southern Bida basin is controlled by NW-SE trending faults which support a rift model. In this study, the geochemical characteristics of the shale-clay facies of the Maastrichtian Patti Formation located at Ahoko and Idu area, southern Bida Basin, Nigeria (Fig. 1) are investigated for the first time. The Patti Formation is one of the three main stratigraphic horizons, which is sandwiched between the basal Campanian Lokoja and the youngest Agbaja Formations. Patti Formation consists of both shale and sandstone members and the shale member particularly in the study area comprises of shale, claystone, siltstone and ironstone facies (Ojo and Akande, 2008).

A number of investigations on aspects related to facies analysis, palynology and source rock evaluations have been carried out on the argillaceous sediments of the Bida Basin and published in the last two decades. These include Jan du Chene et al. (1978) and Agyingi (1991), who, assigned Campanian to Maastrichtian age to the argillaceous rocks in the southern Bida Basin. Ojo and Akande (2006, 2008) proposed a more definite Maastrichtian age for the shale member of the Patti Formation based on pollen/spores and dinoflagellates. Ojo and Akande (2009) examined the sedimentological characteristics of the sandstone facies of the Patti Formation and proposed a tidal to shoreface environments.

Inspite of the good exposures and vast occurrence of the shales and clays in the study area, no published data on the weathering history and provenance of the shales exists. This paper, therefore, examines the chemical composition of the shale and the clay in the context of weathering history, provenance, paleotectonics.

LITHOLOGIC DESCRIPTION AND METHODS OF STUDY

Two exposures; quarry face at Ahoko and Idu road cut (Fig. 2) of the shale member of the Patti Formation were logged on the basis of bed to bed measurements and sampling at relevant intervals. The quarry section (about 20 m thick) at Ahoko consists of well bedded, alternating shales, siltstones, claystones and ironstones (Fig. 3). At

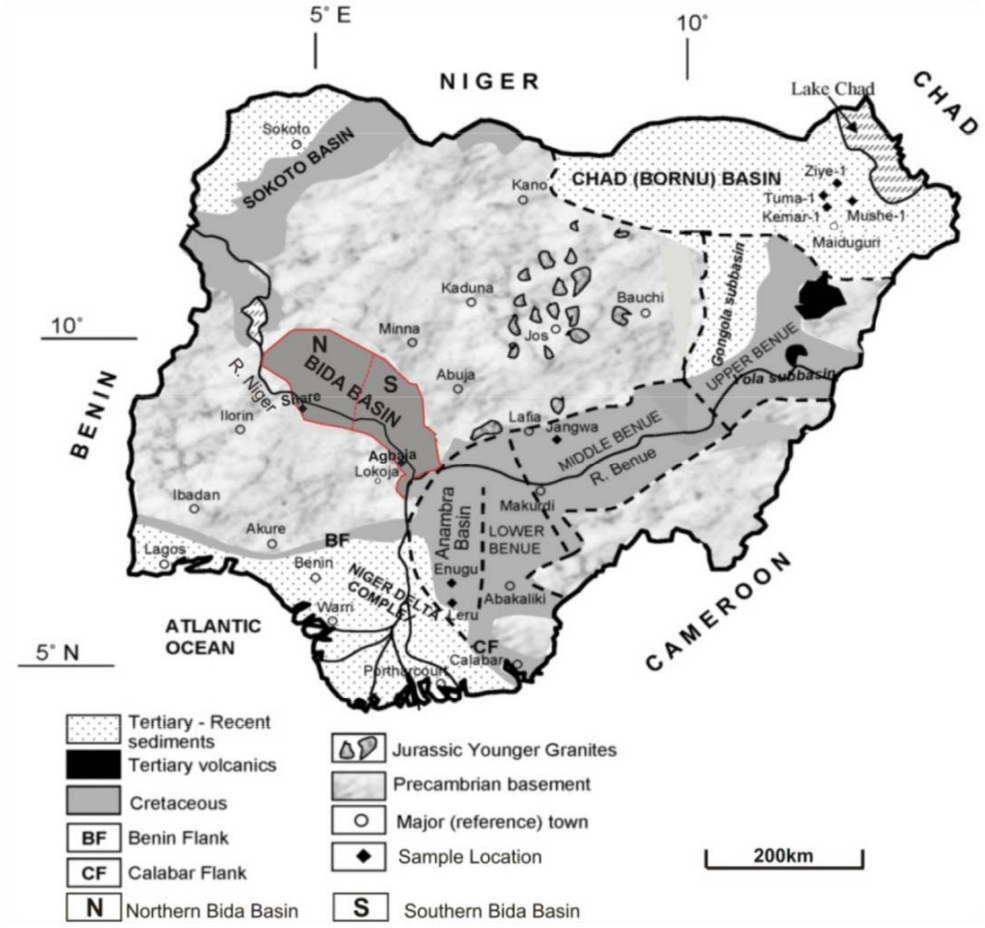


Fig.1. Geological Map of Nigeria showing the studied Bida Basin (Modified after Obaje *et al*, 2004). Note the studied part of the basin (boxed area)

the lower part of the section beds of fissile, carbonaceous shale with average thickness of 0.5 m which exude sulfurous odour occur. The exposure at Idu is about 16 m thick and the lithologies are similar to those mentioned above. For mineralogy, six samples were analyzed using X-ray diffraction (XRD) method at the Department of Geology, Faculty of Natural and Agricultural Sciences, University of Pretoria, South Africa. The samples were prepared for XRD analysis using a back loading method. They were analysed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Kα radiation. From both sections, fifteen samples of the fresh carbonaceous shales and clays were sampled and selected and analyzed for bulk elemental composition; Major oxides, trace elements (TE) and rare earth elements (RRE) via two methods; X-ray Fluorescence (XRF) and Aqua regia ultra-trace Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at ACME analytical laboratories (Acme Lab), Canada. The samples splits for XRF analysis were pulverized to 85% passing 200 mesh (75 µm) in a mild-steel ring-and-puck mill at 60ºC dryness followed by pulverization via a jaw crusher to 70% passing a 10 mesh (2mm). A 0.2 g aliquot was weighed into a graphite crucible and mixed with 1.5 g

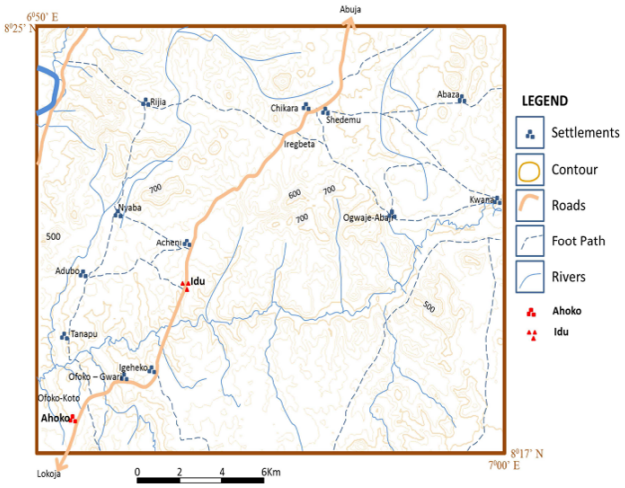


Fig.2. Topographic map of the study area showing the location of investigated outcrops.



Fig.3. (a) Shale – claystones of Patti Formation exposed at Ahoko quarry, Lokoja – Abuja highway (Longitude: 08°19'59.6"N, Latitude: 6°53'05.6"E). **(b)** Patti Formation exposed at Idu, along Lokoja – Abuja expressway (08°18'13.6"N, 6°51' 29.7"E).

of $LiBO_2/Li_2B_4O_7$ flux. The crucibles were heated at 980ºC in a oven for 30 minutes. The resulting bead was dissolved in 5% HNO_3 (ACS grade nitric acid diluted in dematerialized water). Samples and calibration and reagent blanks were aspirated into an XRF (SpectroCiros Vision or Varian 735) to determine the set of major oxides and elements. Loss on ignition (LOI) was determined by igniting a 1.0 g sample split at 950ºC for 90 minutes, then the weight loss measured. Sample splits for (ICP-MS) analysis were pulverized to 95% passing 150 mesh (100 μm) in a mild-steel ring-and-puck mill. A 0.2 g aliquot was weighed into a graphite crucible and mixed with 1.5 g of $LiBO_2/Li_2B_4O_7$ flux. The crucibles were heated in a oven at 980ºC for 30 minutes. The resulting bead was dissolved in 100mL 5% HNO_3 (ACS grade nitric acid diluted in demineralized water). An aliquot of the solution was poured into a polypropylene test tube. Samples and calibrated reagent blanks were aspirated into an ICP-MS (Perkin-Elmer Elan 6000 or 9000) and a digested split of 0.5 g in aqua regia and aspirated into an ICP-MS to determine the elements.

RESULTS AND DISCUSSION

Mineralogical Composition Identified by XRD

Mineral assemblages in some of the investigated shales included clay minerals and non-clay minerals. The clay minerals are essentially kaolinite; montmorillonite, muscovite and chlorite (Table 1). Kaolinite dominates in all the samples whereas chlorite and montmorillonite occur in few samples in trace amount (less than 6 wt.%). Other non-clay minerals include quartz which occurs in substantial amount ranging from 26.36 to 73.9 wt.% in all the samples. Microcline, anatase and rutile are generally low (less than 6.5 wt.%) in the samples. Representative X-ray diffractograms showing identified mineral peaks in the samples are shown in Fig.4.

Chemical Composition

The values of major, trace and rare earth elements obtained from the study area are presented in Tables 1 and 2. In the Ahoko samples, SiO_2 concentration ranges from 5.9 – 73.5 wt. % (average of 43.99 wt. %), Al_2O_3 contents range from 3.23 to 27.75 wt.% (averages 15.13 wt%) and Fe_2O_3 content ranges between 1.1 – 50.09 wt.% with average of 20.8 wt. % (Table 1). The ferruginous shale samples (AHK1D, AHK1E, AHK 1R and AHK 1X) and sample AHK1G which contains ferruginised mudstone concretions have high values of Fe_2O_3 ranging from 27.8 to 69.79 wt. % and low values of SiO_2 while the dark gray shale and clay have low Fe_2O_3 but high SiO_2. The CaO content ranges between 0.01 – 6.71 wt. % with an average of 0.94 wt. %. However, relatively high CaO concentrations (greater than 2.0 wt. %) were obtained for a dark grey fossiliferous shale at the basal part of the section and the ferruginous shales. MgO is also low ranging from 0.04 – 2.43 wt. % with an average of 0.82 wt. %. MnO and TiO_2 concentration ranges

Table 1. Mineralogical Composition (wt%) of Patti Formation Shale

Minerals	AHK 1A	AHK 1G	AHK 1L	AHK 1Q	AHK 1V	ID 1D
Anatase	4.65	7.8	5.13	-	1.66	8.6
Montmorillonite	5.35	-	-	-	-	-
Kaolinite	35.59	49.95	45.03	33.77	15.6	57.67
Microcline	4.84	5.61	3.98	6.22	5.55	-
Muscovite	5.59	3.59	4.43	4	2.76	6.87
Quartz	43.07	32.49	41.01	55	73.9	26.37
Rutile	0.91	0.56	0.29	-	-	0.49
Calcite	-	-	0.14	-	-	-
Zircon	-	-	-	-	0.53	-

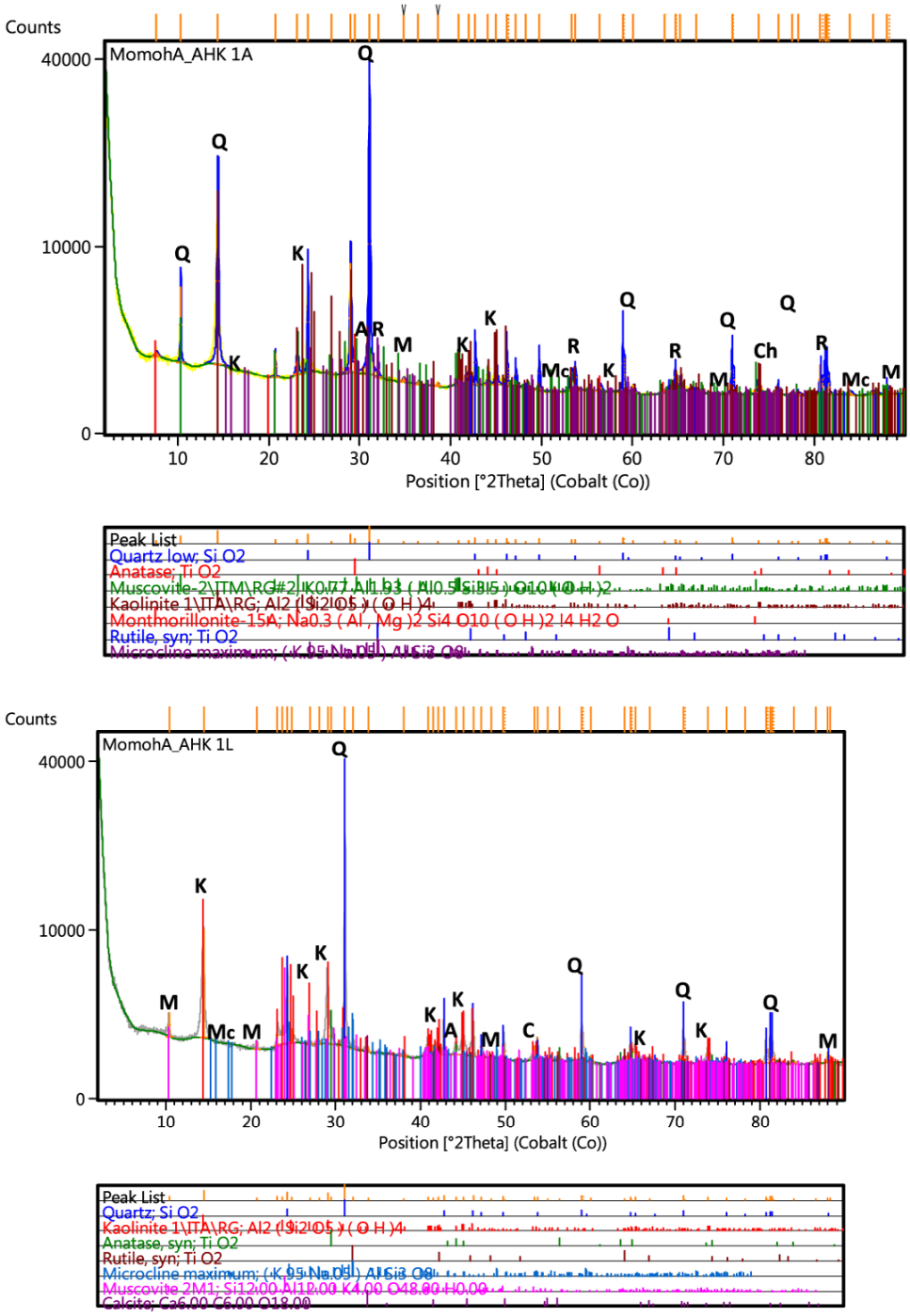


Fig.4. Representative XRray Diffractogram of investigated shales (AHK 1A and AHK 1L). Note: Q-Quartz; K-Kaolinite; A-Anatase; R-Rutile; C-Calcite; Microcline; Mc-Muscovite and Ch-Chlorite.

from 0.01 – 0.95 wt% and 0.17 – 2.93 wt% with an average of 0.23 and 1.49 wt. % respectively. The contents of P_2O_5 and Cr_2O_3 are relatively low except in samples AHK1G and AHK1X with 3.65 and 1.02 wt % respectively (Table 1).

According to Braide (1993), high content of CaO (>4%) indicates a calcareous shale. The Ahoko and Idu shales have relatively low CaO content (0.9 and 0.02 wt. % average) indicating a non-marine shale except the dark grey fossiliferous shale unit and ferruginous shales at Ahoko with relatively high CaO (1.59 - 6.71wt. %) suggesting they are calcareous and probably marine. Ojo and Akande (2009) reported the shales as rich in marine fossils such as gastropod and bivalve shells. High CaO value indicates presence of calcite (a non silicate phase). The generally low

CaO in the Ahoko shales is probably due to the scarcity of calcic minerals (Dabard, 1990) which is reflected in the low carbonate content and therefore indicating predominance of fresh water conditions. The samples with high CaO also contain relatively high MgO (1. 54 - 2.43wt. %). This may be attributed to influence of marine water reworking.

The Na_2O and K_2O contents range from 0.01 to 0.06 wt. % (average of 0.03 wt %) and 0.10 to 1.41wt. % (average of 0.81wt. %) respectively. Few samples of the dark gray shales have K_2O above 1 wt. % and remarkably, the values correlate positively with high SiO_2. According to Rahaman and Suzuki (2007) and Ogbukagu (1982) low amounts of K_2O and Na_2O may be due to low feldspar content and presence of little or no expandable clay mineral.

The ratio of SiO_2/Al_2O_3 is low for the samples (average of 1.86 wt %) (Table 3) indicating low silt content and kaolinitization under humid condition (Ekosse and Ngole, 2012). The concentration of the major elements (mean values) of the shale and clays are compared with those of the UC (the upper Crust, according to Taylor and McLennan, 1985), NASC (North America Shale Composite, Gromer et al., 1984), PASS (Post-Archean Shale, Taylor and McLennan, 1985) and Wedepohl (1971). The SiO_2 and Al_2O_3 content of the shales closely comparable with reference (PAAS, NASC and UC) samples (Table 4). However, the composition of the ferruginous shales from the study area is different from the reference samples. The SiO_2 is lower while the Fe_2O_3 is higher than the average values of the reference samples.

The average V content of the Ahoko shale (122.5) is slightly lower than the published average for shales while those of the Idu shales (167.5) is higher than the published average for shales. According to Ernst (1970) higher enrichment is supposed to occur in marine shales which may reflect their organic matter content. This may further indicate more influence of continental contributions than marine. In most of the shale samples, Ce is 100ppm, and higher than average for UC, PAAS. In fact, Ce is extremely high in samples AHK1G and AHK1L (345 and 394ppm respectively). Generally, the trace element composition of the Maastrichtian shales varies slightly from the average values of PAAS, NASC, and UC. The values of V and Cr are comparable to PAAS but slightly below NASC and UC. Cu and Ni in the studied shales are less than UC, PAAS and NASC while Zn is greater. Relatively high values of the trace metal are recorded in some samples. Zn is exceptional high (greater than 500 ppm) in samples AHK1G, GH1L and AHK 1J while Pb is relatively high in AHK1A, AHK1E, AHK1L (Table 2).

Among the samples, AHK 1G and AHK 2A have the highest Ce values (345 and 177.2 ppm respectively), while Idu shales have the lowest Ce value (127.2 ppm). The enrichment of Ce indicates that the Ahoko shales at the lower part might have undergone some degree of phosphatization leading to precipitation of phosphate minerals as discussed by Trappe (1998). Interestingly this sample also shows relative high P_2O_5.

Ba content of the studied shales is lower than average of the PAAS, UC and NASC except in samples AHK1A and AHK1E and Sr is extremely high in ferruginous shale samples AHK1E, AHK1G (462 and 360.3 respectively). Other samples have lower values than average recorded for the reference samples.

The values of the REE are illustrated in Fig.5 and all analyzed samples have similar concentrations of REEs. The REE patterns of the investigated samples are similar to those of NASC and PAAS but differ in the HREE content compared to the UC. The chondrite-normalized La/Yb ratio ranges from 7.47 to 35.6, with most sediment having slightly higher values than those of PAAS and UC.

Table 2 Values (wt. %) of major elements of the shales and clays in the study area

Sample	S_iO_2	T_iO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	LOI	Sum
AHK 1A	59.6	2.88	20.13	2.61	0.04	0.28	0.06	0.93	0.03	0.18	12.91	99.65
AHK 1E	73.5	2.93	13.07	1.76	0.03	0.18	0.1	1.15	0.04	0.32	6.35	99.43
AHK 1D	17.5	0.75	5.07	50.09	1.07	1.54	1.68	0.31	<0.01	0.34	21.3	99.65
AHK 1G	5.9	0.17	3.23	49.86	0.95	2.25	6.71	0.1	0.04	3.65	26.19	99.05
AHK 1J	50.2	1.49	27.75	3.56	0.03	0.49	0.07	0.99	0.02	0.13	15.52	99.25
AHK 1L	61.3	2.11	21.59	2.3	0.02	0.25	0.03	0.93	0.02	0.11	11.16	99.82
AHK 1N	15.1	0.5	5.07	47.1	0.42	2.43	2.28	0.38	0.01	0.15	26.27	99.71
AHK 1Q	64.8	1.86	15.03	3.22	0.02	0.16	0.05	1.37	0.06	0.06	13.52	100.15
AHK 1R	22.1	0.81	7.1	41.91	0.6	1.85	1.59	0.45	0.01	0.14	23.41	99.97
AHK 1S	64.3	2.27	17.54	2.15	0.03	0.13	0.05	1.24	0.04	0.09	11.85	99.69
AHK 1T	11.7	0.34	5.71	50.15	0.23	2.35	2.25	0.22	0.01	0.23	26.82	100.01
AHK 1V	81.3	1.83	10.47	1.1	0.03	0.07	0.02	1.41	0.04	0.06	3.5	99.03
AHK1X	14.4	0.61	5.88	69.79	0.22	0.16	0.04	0.25	0.03	1.02	8.19	100.59
AHK 2A	56.1	2.16	27.51	2.29	0.01	0.22	0.12	0.87	0.02	0.14	10.74	100.18
ID 1A	54	1.87	28.99	1.87	0.01	0.28	0.02	1.09	0.02	0.11	11.71	99.97
ID 1D	52.1	1.32	27.89	3.47	0.01	0.55	0.02	1.3	0.03	0.21	12	98.9
Total	703.9	23.9	242.03	333.23	3.72	13.19	15.09	12.99	0.42	6.94	241.44	
Mean	43.99	1.49	15.13	20.83	0.23	0.82	0.94	0.81	0.03	0.43	15.09	

Table 3. Values (ppm) of trace and rare earth elements of the shale and clay samples

Sample	Ba	Be	Co	Cs	Ga	Hf	Cr	Nb	Rb	Sn	Sr	Ta	Th	U	V	Zr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
AHK 1A	656	7	22.4	2.8	26.4	17.6	0.014	66.1	41.3	7	246.9	5.2	27.1	15.2	140	646.9	62.8	82.7	169.4	18.9	73.3	13.56	2.78	12.52
AHK 1E	1258	2	6.2	1.9	19.6	26.3	0.012	66.4	38.1	8	462	5.5	17.7	11.5	113	865.3	59.9	59.2	124	13.09	51.2	9.08	1.75	8.54
AHK 1D	178	7	22.4	0.9	6.4	5.7	0.007	16.3	11.7	2	87.1	1.6	7.6	3.9	48	209.8	22.2	19.9	44.8	4.73	20.6	3.68	0.78	3.69
AHK 1G	267	13	20.3	0.5	5.4	1	0.019	3.5	6.5	1	360.3	0.3	5	18.9	114	37.1	201.9	118.1	345	41.34	175	40.11	9.33	39.63
AHK 1J	278	6	25	5.5	38	5.5	0.019	31.3	60.7	5	100.7	2.6	17.9	7.4	165	213.2	27.1	65.7	129.2	14.27	54.2	9.28	1.94	7.33
AHK 1L	324	5	14	4	30.8	9.8	0.022	43.6	46.8	6	98.5	3.2	18	10.8	157	387.3	36.9	74.4	151.9	16.29	57	11.2	2.32	9.13
AHK 1N	204	5	29.6	0.9	7.9	6.3	0.004	14.5	14	2	95	1.2	7.6	4.1	52	245.7	28.2	23.3	46.4	5.32	21.6	3.76	0.79	4.19
AHK 1Q	333	2	9.5	2	19.8	41.1	0.014	47.8	47.2	9	51.9	4.4	25.6	10.9	72	1511.3	67.9	69.9	137.7	15.4	51.3	10.19	1.61	9.55
AHK 1R	232	4	15.6	0.8	11.3	15.6	0.01	22.9	15.7	4	74.6	1.8	12.5	5.5	49	543.7	48.5	37.8	74.2	8.56	32.5	6.61	1.35	7.26
AHK 1S	354	4	18.3	2.3	24.3	41.3	0.015	59.3	40.3	10	63.4	5.5	24.6	17.4	87	1395.7	72.5	75	146.2	16.57	61.1	11.56	1.99	10.41
AHK 1T	204	<1.0	14.4	0.8	7.8	6.4	0.006	10	9.7	2	130.8	0.9	9.9	7.7	78	243.8	121.2	48.6	106.6	12.35	52.1	12.14	3.09	15.98
AHK 1V	340	<1.0	2.1	1.2	15.2	80.3	0.006	48.9	42.7	8	43.9	4.5	39.5	12	45	2988.3	97.9	78.1	149.4	16.47	58.4	11.52	1.28	11.94
AHK1X	87	5	12.3	1	7.7	5	0.01	16.1	9.8	2	16	1.1	11.6	14.5	42	204.7	17.9	9.6	12.2	1.59	6	1.34	0.36	2.08
AHK 2A	365	<1.0	6.1	3.9	34.7	11.8	0.017	51.9	45.7	10	160.6	3.8	21.8	8.3	132	441.2	43.1	88.4	177.2	18.5	62.1	8.12	1.58	6.68
ID 1A	377	<1.0	5.7	5	41.5	10.5	0.028	40.9	54.8	7	122.8	2.8	19.6	9	156	374.4	30.7	68.6	127.2	12.77	40.9	8.15	1.62	6.89
ID 1D	483	5	8	6.3	38.9	5.4	0.022	27.6	77.1	4	288.4	1.9	15.2	5.1	179	237.4	30.8	57.9	113.2	12.51	45.2	9.03	1.82	7.24
Total	5940	65	231.9	39.8	335.7	289.6	0.225	567.1	562.1	87	2402.9	46.3	281.2	162.2	1629	10545.8	969.5	977.2	2054.6	228.66	862.5	169.33	34.39	163.06
Mean	371.25	5.42	14.49	2.49	20.98	18.1	0.01	35.44	35.13	5.44	150.18	2.89	17.58	10.14	101.81	659.11	60.59	61.08	128.41	14.29	53.91	10.58	2.15	10.19

Table 3 Contd.

Sample	Tb	Dy	Ho	Er	Tm	Yb	Lu	Cu	Pb	Zn	Ni	Sb	Tl
AHK 1A	1.97	11.73	2.44	6.9	1.04	7.09	1.03	23.5	33.7	83	21.7	<0.1	0.2
AHK 1E	1.6	10.19	2.31	6.94	1.12	7.6	1.16	5.1	39.5	27	4.5	<0.1	0.1
AHK 1D	0.64	3.58	0.82	2.62	0.37	2.75	0.41	5.5	14	124	18.7	0.1	0.1
AHK 1G	6.5	36.42	7.67	20.34	2.79	16.75	2.36	15.9	10.7	552	27.2	0.1	<0.1
AHK 1J	1.11	5.38	1.07	3.15	0.48	3.25	0.48	25.2	22.2	110	19.6	<0.1	0.1
AHK 1L	1.45	7.66	1.51	4.6	0.64	4.56	0.71	10.7	38.4	39	9.1	<0.1	<0.1
AHK 1N	0.7	4.46	0.99	3.05	0.47	3.31	0.5	6	8.6	45	15.5	<0.1	<0.1
AHK 1Q	1.76	11.87	2.65	8.36	1.25	9.24	1.32	10.1	25.6	39	6.1	<0.1	0.4
AHK 1R	1.25	7.31	1.69	5.1	0.75	4.45	0.72	6.2	10.6	80	10	<0.1	0.1
AHK 1S	1.91	11.86	2.74	8.58	1.25	8.91	1.46	17	20.9	37	12.2	<0.1	<0.1
AHK 1T	2.94	17.78	4.05	11.94	1.68	9.73	1.51	4.2	9.8	97	13.6	<0.1	0.1
AHK 1V	2.28	15.34	3.7	11.62	1.72	12.4	1.93	3.7	22.2	4	1.1	<0.1	<0.1
AHK1X	0.42	3.1	0.68	2.03	0.3	2.07	0.29	17.2	7.3	60	6	<0.1	<0.1
AHK 2A	1.23	7.31	1.51	4.99	0.72	5.02	0.78	10.1	23.4	12	3.1	<0.1	<0.1
ID 1A	1.09	5.76	1.36	4.03	0.57	3.86	0.6	15.1	17.2	10	2.3	<0.1	<0.1
ID 1D	1.1	6.32	1.22	3.46	0.52	3.93	0.52	13.2	15.7	26	5.3	<0.1	0.1
Total	27.95	166.07	36.41	107.71	15.67	104.92	15.78	188.7	319.8	1345	176	0.2	1.2
Mean	1.75	10.38	2.28	6.73	0.98	6.56	0.99	11.79	19.99	84.06	11	0.1	0.15

Table 4 Ratio of some major and trace elements in the studied samples

Ratios	AHK 1A	AHK 1E	AHK 1D	AHK 1G	AHK 1J	AHK 1L	AHK 1N	AHK 1Q	AHK 1R	AHK 1S	AHK 1T	AHK 1V	AHK 1X	AHK 2A	ID 1A	ID 1D	TOTAL	Mean
Mn/Ti	0.014	0.01	1.43	5.58	0.2	0.009	0.84	0.01	0.74	0.013	0.68	0.016	0.36	0.004	0.005	0.007	9.918	0.62
V/Ni	6.45	25.11	2.57	4.19	8.42	17.25	3.35	11.8	4.9	7.13	5.73	40.9	7	45.58	67.8	33.77	291.95	18.2
Sr/Ba	0.37	0.37	0.49	1.35	0.36	0.3	0.47	0.15	0.32	0.18	0.64	0.12	0.18	0.44	0.33	0.59	6.66	0.4
K_2O/Na_2O	31	28.75	31	2.5	49.5	46.5	38	22.8	45	31	22	35.25	8.33	43.5	54.5	43.33	532.96	33.31
$\log(K_2O/Na_2O)$	1.49	1.46	1.49	0.4	1.69	1.67	1.58	1.36	1.65	1.49	1.34	1.55	0.92	1.64	1.74	1.64	23.11	1.44
Al_2O_3/SiO_2	0.34	0.18	0.29	0.6	0.55	0.35	0.35	0.23	0.32	0.27	0.49	0.13	0.41	0.49	0.54	0.53	6.07	0.38
$Fe_2O_3 + MgO$	2.89	1.94	51.63	52.11	4.05	2.55	49.53	3.38	43.76	2.28	52.5	1.17	69.95	2.51	2.15	4.02	346.42	21.65
Al_2O_3/TiO_2	6.99	4.46	6.76	20.88	18.62	10.23	10.14	8.08	8.76	7.73	16.84	5.72	9.64	12.74	15.5	21.12	184.21	11.51
SiO_2/Al_2O_3	2.96	5.62	3.45	1.66	1.81	2.84	2.98	4.31	3.11	3.66	2.05	7.76	2.45	2.04	1.86	1.86	50.42	3.15
La/Th	3.05	3.34	2.62	23.62	3.67	4.13	3.06	2.73	3.02	3.05	4.9	1.98	0.83	4.05	1.56	2.03	67.64	4.23
Th/U	1.78	1.54	1.95	0.26	2.4	1.67	1.85	2.35	2.27	1.4	1.28	3.3	0.8	2.63	2.18	3	30.66	1.92
Rb/Sr	0.17	0.08	0.13	0.02	0.6	0.47	0.15	0.91	0.21	0.64	0.07	0.97	0.612	0.28	0.45	0.27	6.032	0.377
Cr(ppm)	140	120	70	190	190	220	40	140	100	150	60	60	100	170	280	220	2250	140.62
Cr/Ni	6.45	26.67	3.74	6.98	9.69	24.17	2.58	22.95	10	24.59	4.41	54.54	16.67	54.8	121.7	41.51	431.45	26.96
V/Cr	1	0.94	0.68	0.6	0.87	0.7	1.3	0.5	0.49	0.58	1.3	0.75	0.42	0.78	0.56	0.81	12.28	0.76
U/Th	0.56	0.65	0.51	3.78	0.41	0.6	0.54	0.42	0.44	0.71	0.78	0.3	1.25	0.38	0.46	0.33	12.12	0.76
Th/3	9	5.9	2.53	1.67	5.96	6	2.53	8.53	4.17	8.2	3.3	13.17	3.87	7.26	6.53	5.1	93.72	5.85
U-Th/3	6.2	3.7	1.37	17.23	1.58	4.8	1.57	2.37	1.33	9.2	4.4	-1.17	10.63	1.04	2.47		66.72	4.45
Ni/Co	0.96	0.72	0.83	1.34	0.78	0.65	0.52	0.64	0.64	0.67	0.94	0.52	0.49	0.51	0.4	0.66	11.27	0.70
Cu/Zn	0.28	0.19	0.04	0.03	0.23	0.27	0.13	0.26	0.08	0.46	0.04	0.9	0.29	2	1.5	0.51	7.21	0.45
Th/Co	1.21	2.85	0.34	0.25	0.72	1.28	0.26	2.69	2.69	1.34	1.34	0.68	0.94	3.57	3.44	1.9	25.5	1.6
Th/Cr	0.19	0.15	0.11	0.03	0.09	0.08	0.19	0.18	0.125	0.16	0.16	0.66	0.12	0.12	0.07	14.2	16.635	1.04
Cr/Th	5.17	6.78	9.21	38	10.61	12.22	5.26	5.47	8	6.1	6.06	1.52	8.62	7.8	0.07	14.5	145.39	9.08
$\log(K_2O/Al_2O_3)$	-1.33	-1.05	-1.21	-1.5	-1.45	-1.4	-1.12	-1.04	-1.2	-1.15	-1.41	-0.87	-1.4	-1.5	-1.42	-1.33	-20.38	-1.27
$\log(MgO/Al_2O_3)$	-1.86	-1.86	-0.52	-0.15	-1.75	-1.9	0.07	-1.97	0.58	-2.13	-0.4	-2.17	-1.56	-2.09	-2.01	-1.7	-21.42	-1.34

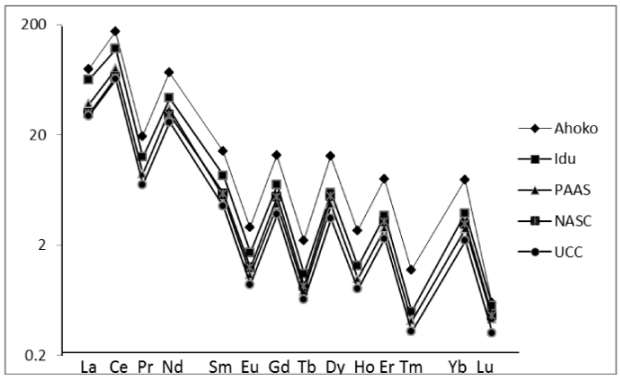


Fig.5. Chondrite normalized rare earth elements plots for the Ahoko and Idu shales in comparison with PAAS, NASC and UCC

Provenance and Paleotectonics

The elemental composition of clastic sediments has been frequently used to assess their provenance characteristics. Al_2O_3/TiO_2 ratios of most clastic rocks are useful for determining the source rock composition. According to Hayashi et al. (1997), the Al_2O_3/TiO_2 ratio range of 3 – 8 wt. % is diagnostic of mafic igneous rocks, 8 – 21 wt. % for intermediate rocks and 21 – 70 wt. % indicates felsic igneous rocks. In the Ahoko shales, the Al_2O_3/TiO_2 ranges from 4 – 21wt. % (Table 3) suggesting that the source rocks of shales in Ahoko varies from mafic to intermediate igneous rocks while those at Idu has 15 – 21wt. % indicating intermediate rocks as the main source. This is also supported by plots of TiO_2 versus Al_2O_3 (Fig. 6). Amajor (1987) applied the TiO_2 versus Al_2O_3 binary plot to distinguish between granitic and basaltic source rocks. Application of this plot to the studied shale and clay samples in Ahoko and Idu shows that the samples are within varied fields of mafic and intermediate igneous rocks. Brooks (1973) and Spears and Kanaris (1976) found that the Carboniferous sediments in England have high TiO_2/Al_2O_3 ratios reflecting a strong correlation to the ratios ofthe parent basalt. To further constrain the source, the discriminant functions F1 and F2 were also plotted using

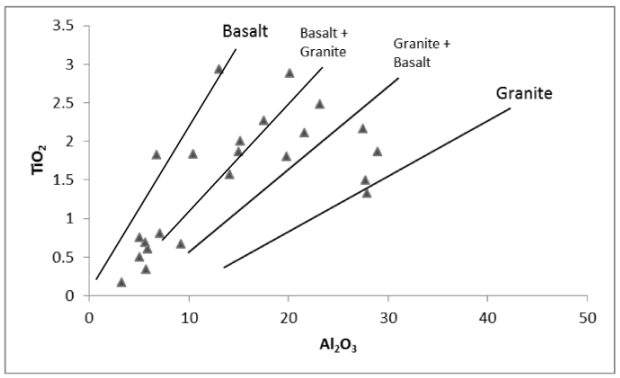
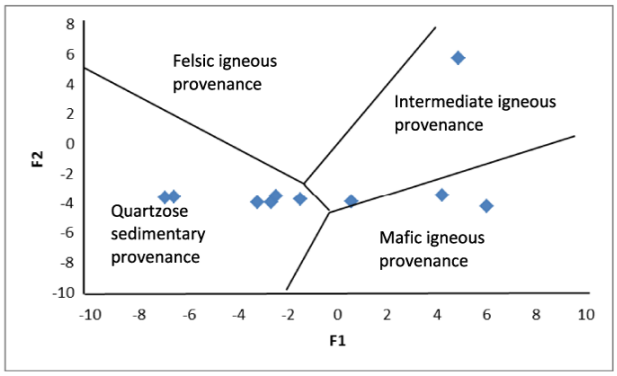


Fig.6. TiO_2 versus Al_2O_3 binary plot (after Amajor, 1987)



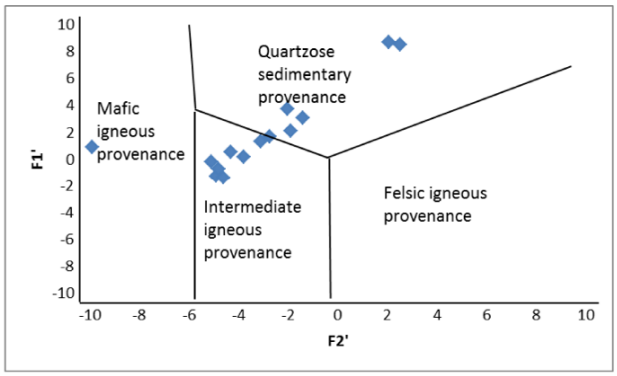


Fig.7. Plot of discriminant functions F1 and F2 for the Ahoko and Idu shales from the Patti Formation after Roser and Korsch (1988). (Samples with high CaO content excluded)

Roser and Korsch (1988). The plots show, however, possible contribution from quartzose and intermediate felsic igneous rocks (Fig. 7).

Garver et al (1996) suggested that elevated Cr (>150 ppm) and Ni (>100 ppm) are diagnostic of ultramafic rocks in source region. In comparison, Cr concentration in Ahoko shales ranges from 120 – 220 ppm (average of 165 ppm) and Ni ranges from 3.1 – 27.2 ppm (average 12.9 ppm). The shales in Idu have Cr concentration of 220 – 280 ppm (average 250 ppm) and Ni of 2.3 – 5.3 ppm (average 3.8 ppm). This comparison rules out the existence of ultramafic rocks in the source region. Garver et al. (1996) proposed a ratio of Cr/Ni between 1.3 – 1.5 ppm as diagnostic of ultramafic source rocks. The Cr/Ni ratio in Ahoko and Idu shales are greater than 2.0 ppm (Table 3) indicating lack of ultramafic rocks in the source region.

Ratios such as Th/Co, Th/Cr and Cr/Th are significantly different in felsic and basic rocks and may constrain on the average composition of provenance (Wronkiewicz and Condie, 1990; Cox et al., 1995; Cullers, 1995). Th/Co, Th/Cr and Cr/Th ratios of shales from this study are compared with those of sediments derived from felsic and basic rocks as well as the upper continental crust (UCC) and post-Archean Australian average shale (PAAS) values

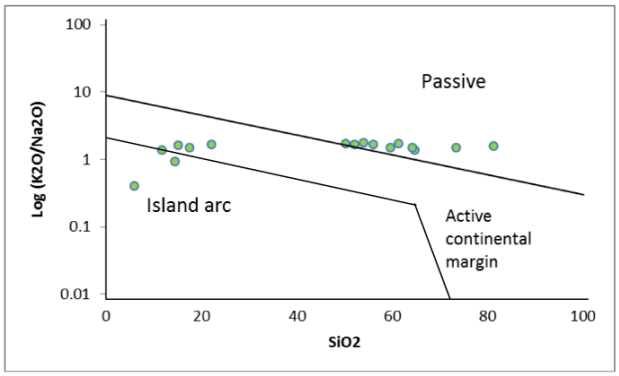


Fig.8. Tectonic setting discrimination diagram for shales from the Ahoko and Idu shales. Boundaries are after Roser and Korsch (1986).

(Table 5). This comparison suggests that the shales and clays correspond to felsic source rocks.

The plot of SiO_2 content versus ratio of log (K_2O / Na_2O) of the Ahoko and Idu shales was used to decipher their tectonic settings according to Roser and Korsch (1986). All the samples from Ahoko and Idu plot in the continental and passive margin (Fig. 8).

Weathering

The dynamics and mechanism of trace element with respect to sedimentary processes such as weathering, source area geology, sorting and diagenesis have been explained by many (Garrels and Mackenzie, 1971; Nesbitt et al, 1980; Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987). McLennan (1983) considered the Rb/Sr ratios of sediments as an indicator of the degree of source rock weathering. He considered the values of 0.32 and 0.8 ppm

Table 5 Values of major elements in the samples compared with the published data

Composition	Studied samples	1	2	3	4
SiO_2 %	43.99	64.82	62.80	64.80	66.00
Al_2O_3 %	15.12	17.05	18.90	16.90	15.20
TiO_2 %	1.49	0.8	0.5	0.7	0.50
Fe_2O_3 %	20.82	5.7	7.22	5.65	5.00
MgO %	0.82	2.83	2.20	2.86	2.20
CaO %	0.94	3.51	1.30	3.63	4.20
Na_2O %	0.028	1.13	1.20	1.14	3.90
K_2O %	0.81	3.97	3.70	3.97	3.40
P_2O_5 %	0.43	0.15	0.16	0.13	n.a
Sr ppm	150.2	142	200	142	350
Ba ppm	371.25	636	650	636	550
V	101.8	130	150	130	60.0
Ni	11	58	55	58	20.0
Cr	140.62	125	110	125	35.0
Zn	84.06	n.a	85.0	n.a	71.0
Cu	11.79	n.a	50	n.a	25
Zr	659.11	200	210	200	190

n.a = not available

1. Turekian and Wedephol (1961); 2. PAAS (Taylor and McLennan, 1985). 3. NASC (Gromet et al., 1984); 4. Upper Continental Crust (Taylor and McLennan, 1985)

indicate upper continental crust (UCC) and post Archean Australian shales (PAAS) respectively. The Rb/Sr values for the Ahoko shales are in the range of 0.02 – 0.9 ppm while that of Idu ranges from 0.2 – 0.45 ppm (Table 3) indicating strong weathering of the source area.

Zr is among the least soluble trace element and is relatively immobile during chemical weathering and diagenesis. They are believed to be transported exclusively in the terrigenous component of the sediments and therefore would reflect the chemistry of the source rock (Rollinson, 1993). All the sediments in Ahoko and Idu are enriched in Zr with an average of 687 and 305.9 ppm respectively except for AHK 1G. These values are higher than those of all the published shales (Table 4). Zr is generally transported with terrigenous influx in the form of heavy mineral (zircon). In addition to the enrichment of Zr during chemical weathering, sediment recycling is also responsible for such enrichments.

Th/U in sedimentary rocks is of interest with respect to degree of weathering. As weathering increases, there is progressive loss of U leading to increase in Th/U ratio. The Th/U ratio in most upper crustal rocks is typically between 3.5 and 4.0ppm (McLennan et al., 1993). In sedimentary rocks, Th/U values higher than 4.0 may indicate intense weathering in source areas or sediment recycling. The Th/U ratio in the Ahoko samples ranges from 0.26 – 2.63 ppm with an average of 1.75 ppm while those of Idu (Table 4) ranges between 2.18 – 3 ppm with an average of 2.6 ppm indicating moderate weathering at the source and that the derivation of these sediments might not be from the recycling of the crust.

The chemical index of alteration (CIA) values has been established as a general indicator of the degree of weathering in any provenance region (Nesbitt and Young, 1982). High values (76 – 100) indicate intensive chemical weathering in the source areas whereas low values of 50 or less indicate unweathered areas. They reported a CIA value of nearly 100 for kaolinite and chlorite, and 70 – 75 for average shales whereas Taylor and Mclennan (1985) reported a CIA value of 85 – 100 for residual clays (Table 6). CIA values vary from 91.0 to 96.25 with an average of 86.57wt. % for Ahoko shales, while the Idu shale has an average of 95.81wt. %. This indicates that the degree of chemical weathering varies considerably in the study area. CIA values <61 reflects

Table 6. Range of elemental ratios of samples in this study compared to the ratios in similar fractions derived from felsic rocks, mafic rocks, Upper Continental Crust (UCC) and Post-Archean Australian Shale (PAAS)

Elemental ratio	Present study	**Range of sediments		UCC*	PAAS*
		Felsic rocks	Mafic rocks		
Th/Co	0.25-3.57	0.67 – 19.4	0.04 – 1.4	0.63	0.63
Th/Cr	0.03-14.2	0.13 -2.7	0.018 – 0.046	0.13	0.13
Cr/Th	0.07-38	4.00 – 15	25 – 500	7.76	7.53

This study; **Cullers (1994, 2000); **Cullers and Podkovyrov (2000); Cullers *et al*. (1988); *Taylor and McLennan (1985) *n* = number of samples

samples enriched in calcite which is typical of AHK 1G (34.13wt. %). The high CIA values in the studied shale probably reflect the presence of clay minerals and low content of detrital feldspars (Nyakiru and Koeberl, 2001). The Chemical Index of Weathering (CIW) values in the Ahoko shales ranges between 98.94 – 99.67wt. % with an average of 91.33wt.% while Idu shales have an average of 97.9wt. % (Table 6). The CIA and CIW are both high, suggesting relatively intense weathering of source area.

CONCLUSIONS

The geochemical characteristics of the Maastrichtian shales in Ahoko and Idu area in southern Bida basin were investigated using XRD, XRF and ICP MS chemical analyses. The elemental compositions of the investigated shales compare favourably with that of NASC, PAAS and UCC. REE (Rare Earth Element) content and ratios of Al_2O_3/TiO_2, Cr/Ni, Th/Co, Cr/Th in the shales suggest that the sediments were derived from mixed mafic and felsic igneous rocks.

Tectonic setting discrimination diagrams based on major elements suggest intermediate to felsic provenance in passive continental margins. As indicated by the high CIW index (Chemical Index of Weathering) values of the shales and the low feldspar content, the source probably had undergone intense chemical weathering in a warm humid climate. The shales are enriched in Zr higher than those of the published shales. The clay minerals in the shales are dominated by kaolinite.

A few relatively high CaO indicate more marine influence at that interval. The CaO and MgO are definitely not from silicate phase and this is significant because other previous palynologic data by Ojo and Akande (2006) identified these as representing the maximum flooding surface in the study area.

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