

Paleoenvironmental Studies of Ahoko Shale, south eastern Bida basin, Nigeria: Insight from Palynomorph Assemblage and Trace Metal Proxies

Adebayo, O. F., Akinyemi, S. A., Madukwe, H. Y., Aturamu, A. O., Ojo, A. O.

Geology Department, Ekiti State University, Ado Ekiti, Nigeria, Geology Department, University of Leicester, University Road, Leicester, LE1 7RH, UK.

Abstract- Ahoko lies within the Lokoja Sub-basin of the Bida Basin in the North Central part of Nigeria. Local stratigraphy of the sediments and the field relationship show that the lithologic succession consists of dark grey shales at the base, followed by light grey shales and siltstones that are intercalated at intervals by grey to brownish, highly indurated ironstone concretion. The sediments when subjected to geochemical analysis showed ratio of Th/Cr, Cr/Th, Th/Co and Cr/Ni which suggests felsic source rocks. Geochemical results further revealed lower Mo/Al, V/Al, U/Al, Cr/Al, Ba/Al, Sr/Al, Ni/Al and Co/Al ratios which indicate the potentially 'extreme' bottom-water oxic conditions during deposition. The approximate order of enrichment relative to average shale being in the order: Zr > U > Pb > Mo > Y > Co > Cr > V > Zn > Ba > Cu > Rb > Ni > Sr and Zr > Y > U > Zn > Co > Mo > Sr > Pb > Cr > Ba > V > Cu > Ni > Rb for profile A and B respectively. Estimated Ce/Ce* ratio and Log (Ce/Ce*) show positive anomaly in studied samples which suggests well oxygenated bottom-water conditions during deposition. Trace element ratios such as U/Th, V/Cr, Ni/Co, Cu/Zn, V/Sc ratios and V/(Ni+V) indicate oxic environment of deposition. These results in conjunction with the recovery of *Echitriporites trianguliformis*, *Monocolpites marginatus*, *Retimocolpites obaensis*, *Psilatricolporites crassus*, *Longapertites marginatus*, *Proxapertites cursus*, *Acrostichum aureum*, *Cyatridites minor*, *Zlivisporites blanensis* and charred graminiae in the sediments suggest fluviodeltaic source and moderately distal oxic environment of deposition.

Index Terms- Ahoko shale, Bida basin, Trace metal, rare earth metals, paleoenvironmental conditions.

I. INTRODUCTION

The Bida basin, which is located in west central Nigeria, is perpendicular to the main axis of the Benue Trough. Due to its large areal extent and facies variation, the basin is often geographically divided into northern and southern Bida basins or what some authors prefer to refer to as Bida and Lokoja Sub-basins (1; 2; 3). Most previous geologic accounts indicate a rift related origin for the basin (4; 5; 6) that was associated with the Benue Trough system and the drifting apart of African and Brazilian plates; whilst Braide (2) advanced a wrench fault tectonics for its evolution and, thus, suggested a pull-apart origin.

Stratigraphic framework in this basin has been along the geographic subdivision of the basin into Bida and Lokoja Sub-basins. Adeleye and Dessauvage (7) and Adeleye (8) established four stratigraphic horizons in the northern Bida Sub-basin whereas three are three formations that are their lateral equivalents in the southern Lokoja Sub-basin.

Trace elements characteristically show substantial enrichment in laminated, organic-rich facies, mostly those deposited under euxinic conditions and, equally, little if any enrichment in bioturbated, organic-poor facies (9; 10; 11). The geochemical pattern of trace elements in modern organic rich fine grained sedimentary rocks (i.e. shales) and anoxic basins has often been reported in literature (12; 10; 13; 11). Redox-sensitive trace element (TE) concentrations or ratios are among the mostly broadly used indicators of redox conditions in modern and ancient sedimentary deposits (e.g., 10; 14; 15; 16; 18; 19; 20; 11).

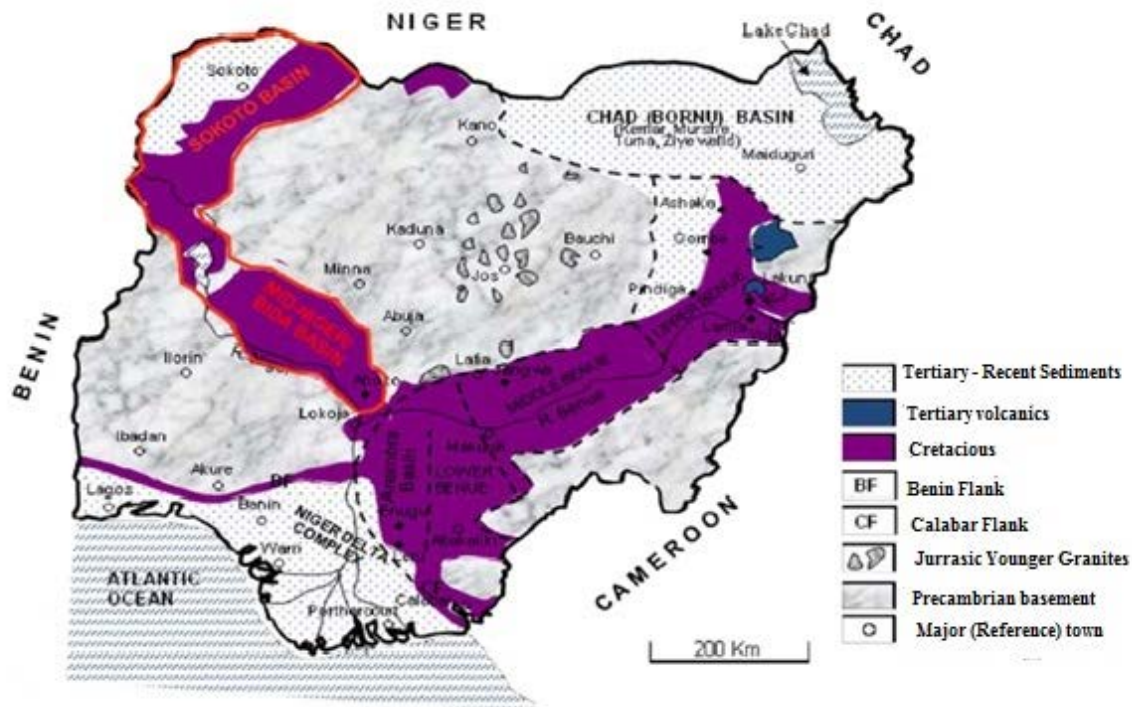
Enrichments of redox-sensitive elements can reconstruct the depositional environment of ancient organic carbon-rich sediments and sedimentary rocks and accordingly be used to reveal the likely palaeoceanographic conditions leading to their formation (21, 22; 23; 24). The degree of enrichment/depletion is typically based on the element/Al ratio in a sample, and calculated relative to the respective element/Al ratio of a common standard material, e.g. average marine shale (25). Although such comparisons have to be handled with care, as the composition of any common standard material is not necessarily representative for a certain erosional source area (26), they are uncomplicated for elements with very high degrees of enrichment/depletion and/or low concentrations in the standard material. High enrichments of redox-sensitive elements in organic carbon rich sediments have been related to anoxic bottom waters. Under reducing conditions these metals may be precipitated as sulfides, co-precipitated with iron sulfides or bound to organic matter (21; 27; 28; 12; 29; 23; 10; 24; 30).

It is indisputable that the reliability of the predictions of the paleoenvironments of deposition, source and reservoir rocks and mineral prospect of this basin will depend on adequate and detail reconstruction of the provenance and the depositional history of the sediments (31). This can be best achieved through an integrated study of the freshly exposed and thick clastic road-cut outcrop sequences along Lokoja - Abuja road. The aims of this paper are to determine the provenance, redox conditions of bottom water condition during deposition, and element enrichments of the Maastrichtian shale sequence around Ahoko, along Lokoja - Abuja

highway. The objectives of this paper is to combine palynomorph assemblage and trace metal proxies (i.e. Ni/Co, V/Sc, V/Cr, Cu/Zn, U/Th and V/(Ni+V)) to reconstruct paleogeography and paleoceanographic conditions during deposition.

II. GEOLOGICAL SETTING OF MIDDLE NIGER (BIDA) BASIN

The Middle Niger (Bida) Basin is a linear intracratonic sedimentary basin situated in central Nigeria. It trends NW – SE and roughly perpendicular to the Benue Trough. It is separated from the basal continental bed of the Sokoto Basin by a narrow outcrop of the crystalline basement rocks in the west and it is adjacent to the Anambra Basin in the east (Fig.1). The basin occupies a gently downwarped trough (32). The epeirogenesis responsible for the basin genesis appears closely connected with the Santonian tectonic crustal movements which mainly affected the Benue Basin and SE Nigeria. The underlain basement complex perhaps has a high relief (1) and the thick sedimentary successions is approximately 2000 metres as shown by gravity survey (33), comprised of unfolded post-tectonic molasse facies and thin marine strata. Borehole logs, Landsat images interpretation, and Geophysical data across the basin suggest that it is bounded by a NW-SE trending system of linear faults (34). Gravity survey studies also corroborate central positive anomalies flanked by negative anomalies (35; 6). This trend agreed with rift structures as observed in the adjacent Benue Trough/Basin. A detailed study of the facies indicates rapid basin-wide changes from various alluvial fan facies through flood-basin and deltaic facies to lacustrine facies (3). Consequently, a simple sag and rift origin earlier suggested may not account for the basin's evolution (32). Braide (2) paleogeographic reconstruction suggests lacustrine environments were widespread and elongate.



Lacustrine environments occurred at the basin's axis and close to the margins. This suggests that the depocenter must have migrated during the basin's depositional history and subsided rapidly to accommodate the 3.5 km thick sedimentary fill (32).

The sedimentary sequences are Late Cretaceous (Campanian – Maastrichtian) in age and were named the Nupe Sandstone by Russ (37). Adeleye (38) upgraded Nupe Sandstone to Nupe Group and subdivided it into four formations: Bida Sandstone (oldest), Sakpe Ironstone, Enagi Siltstone and Batati Ironstone (youngest). A lateral facies variation occurs in the southern part of the basin. Around Lokoja, the basal sequence is usually referred to as the Lokoja Sandstone. Nonetheless, the sandstone is only partly equivalent to the (Bida) Sandstone (39) and is overlain by Patti Formation and Agbaja Ironstones respectively (32). The Bida area and Lokoja area are usually considered separately as the stratigraphy are slightly different. The Lokoja Formation consists of pebbly clayey grit and sandstone, coarse-grained cross bedded sandstone, and few thin oolitic iron stones. A basal conglomerate of well-rounded quartz pebbles in a matrix of white clay is rarely exposed. Its thickness depends on the relief of the underlying Basement Complex floor and varies between 100 and 300 metres (40). The Patti Formation is a sequence of fine to medium-grained, grey and white sandstones, carbonaceous siltstone, claystone, shale and oolitic ironstone. Thin coal seams may be present and white gritty clays are common. The maximum exposed thickness is 70 m (1), while the oolitic ironstones range from 7-16 m thick. The strata yielded a few non-diagnostic plant remains (38). A Maastrichtian (and possibly Senonian) age was thus assigned to it based mainly on correlation with other formations e.g Enugu Shale. Dessauvagie (39) showed that Patti Formation yielded fossil plants (from the carbonaceous beds) and dates the formation as Campanian - Maastrichtian.

III. MATERIALS AND METHOD OF STUDY

The location of study lies between longitude $06^{\circ} 54' E$ and latitude $078^{\circ} 22' N$ (Fig. 2). Samples for this study were taken from two profiles at the exposed road-cut at Ahoko along Lokoja- Abuja road. Eleven samples representing the Lokoja and the Patti formations were studied on the basis of bed to bed measurements and systemic sampling of relevant intervals.

3.1 XRF AND LA-ICPMS ANALYSES

The pulverized shale samples were analysed with XRF and LA-ICPMS technique. The elemental data for this work have been acquired using X-ray fluorescence (XRF) and Laser Ablation inductively coupled plasma spectrometry (LA-ICPMS) analyses. The analytical procedures are as follows;

Pulverised shale samples were analysed for major element using Axios instrument (PANalytical) with a 2.4 kWatt Rh X-ray Tube. Further, the same set of samples were analysed for trace element using LA-ICPMS instrumental analysis. LA-ICP-MS is a powerful and sensitive analytical technique for multi-elemental analysis. The laser was used to vaporize the surface of the solid sample, while the vapour, and any particles, were then transported by the carrier gas flow to the ICP-MS. The detailed procedures for sample preparation for both analytical techniques are reported below.

3.2.1. Fusion bead method for Major element analysis

- Weigh $1.0000 \text{ g} \pm 0.0009 \text{ g}$ of milled sample
- Place in oven at 110°C for 1 hour to determine $\text{H}_2\text{O}+$
- Place in oven at 1000°C for 1 hour to determine LOI
- Add $10.0000 \text{ g} \pm 0.0009 \text{ g}$ Claisse flux and fuse in M4 Claisse fluxer for 23 minutes.
- 0.2 g of NaCO_3 was added to the mix and the sample+flux+ NaCO_3 was pre-oxidized at 700°C before fusion.
- Flux type: Ultrapure Fused Anhydrous Li-Tetraborate-Li-Metaborate flux ($66.67 \% \text{ Li}_2\text{B}_4\text{O}_7 + 32.83 \% \text{ LiBO}_2$) and a releasing agent Li-Iodide ($0.5 \% \text{ LiI}$).

3.2.2. Pressed pellet method for Trace element analysis

- Weigh $8 \text{ g} \pm 0.05 \text{ g}$ of milled powder
- Mix thoroughly with 3 drops of Mowiol wax binder
- Press pellet with pill press to 15 ton pressure
- Dry in oven at 100°C for half an hour before analysing.

These analytical methods yielded data for eleven major elements, reported as oxide percent by weight [$\text{SiO}_2, \text{TiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{MgO}, \text{MnO}, \text{CaO}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{Cr}_2\text{O}_3$ and P_2O_5] and 21 trace elements [Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Co, V, Pb, Th, U, Ti, Cr, Ba, La, Ce, Nd and P] reported as mg/kg (ppm).

IV. RESULTS AND DISCUSSION

4.1 LITHOLOGICAL DESCRIPTION

At Felele along Okene-Lokoja road, the Lokoja Formation is composed of a fining upward sequence of conglomerates, sandstones and claystones (Figs. 3&4). The basal clast-supported conglomerates (0.4 m thick) consist of angular to sub-rounded quartz pebbles, feldspars and rock fragments. A slightly stratified, ferruginized and pebbly sandstone unit (0.6m thick), separates the basal conglomerates from the overlying matrix-supported conglomeratic facies that grades into another weakly stratified pebbly sandstones and medium to coarse grained sandstones in the middle. The sequence is finally capped by massive sandy claystone and the argillaceous units of the Patti Formation are well exposed on both sides of the road due to a road-cut (Fig. 2). The approximately 30 m thick sequence consists predominantly of shales and siltstones which are rhythmically interbedded with concretionary to massive ironstones, the ironstones are sometimes bioturbated. The basal part of the section consists of dark to dark-grey shales strata with an average bed thickness of 0.5 m. The shales are carbonaceous and fissile with several joints that are in-filled with ferruginized siltstones. The silty shale unit overburden rocks. At the outcrop section at Ahoko, along Lokoja - Abuja expressway (Fig.2) within the interval 5.5-8.0 m at the upper section contains abundant woody fragments

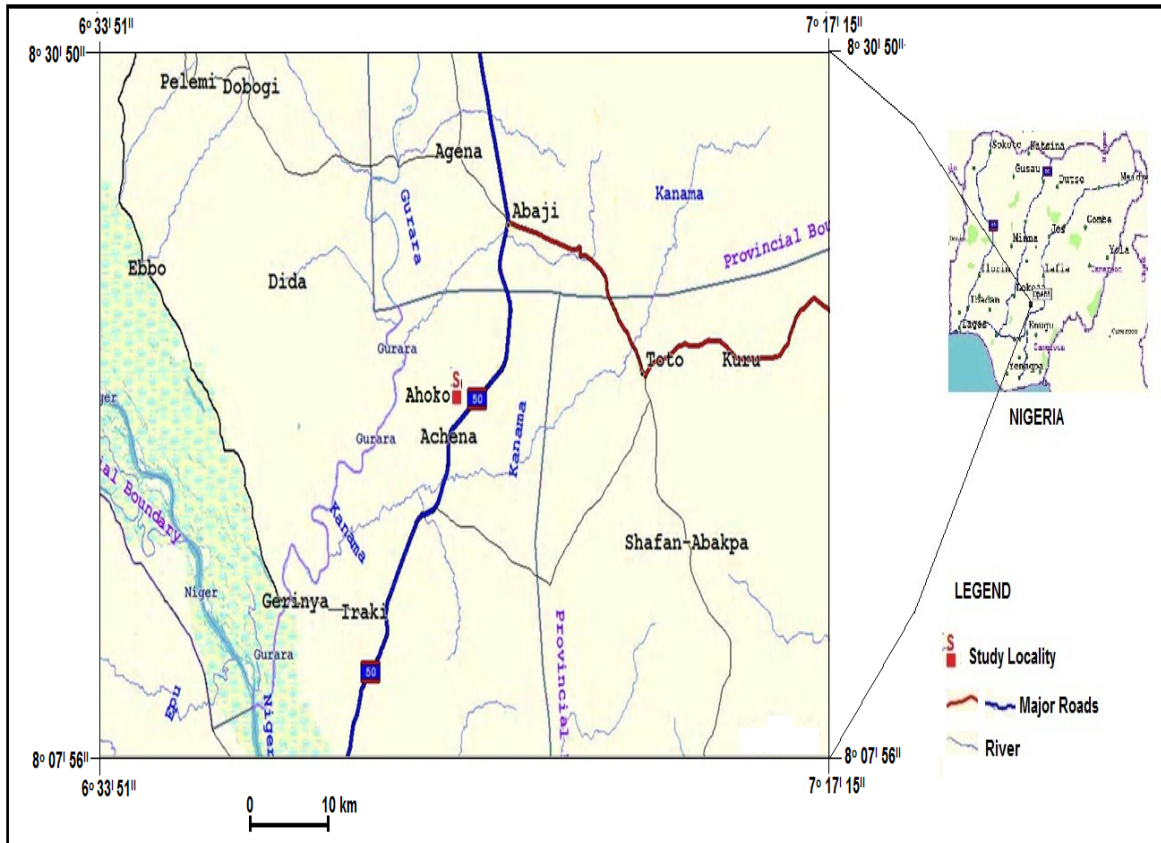


Fig. 2: Location map of exposed Ahoko shale along Lokoja-Abuja Road.

and plant remains. Silty shales and siltstones become more pronounced towards the upper part of the section where they are interbedded with ironstones. The ironstones have an average thickness of 0.2 m and are mainly concretionary, although some of the beds are massive and contain vertical and horizontal burrows (40).

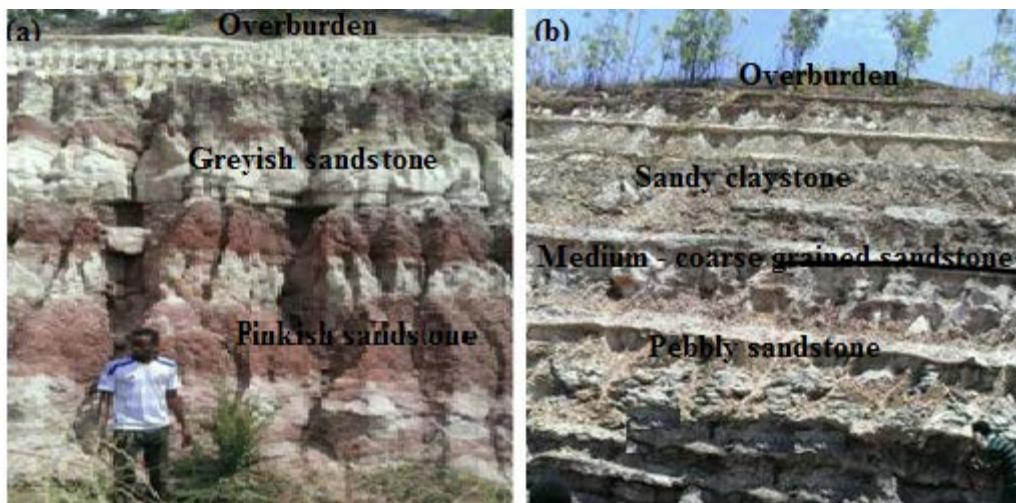


Fig. 3: (a) Lokoja Formation at Felele Junction and (b) Patti Formation at Ahoko, Lokoja-Abuja Road.

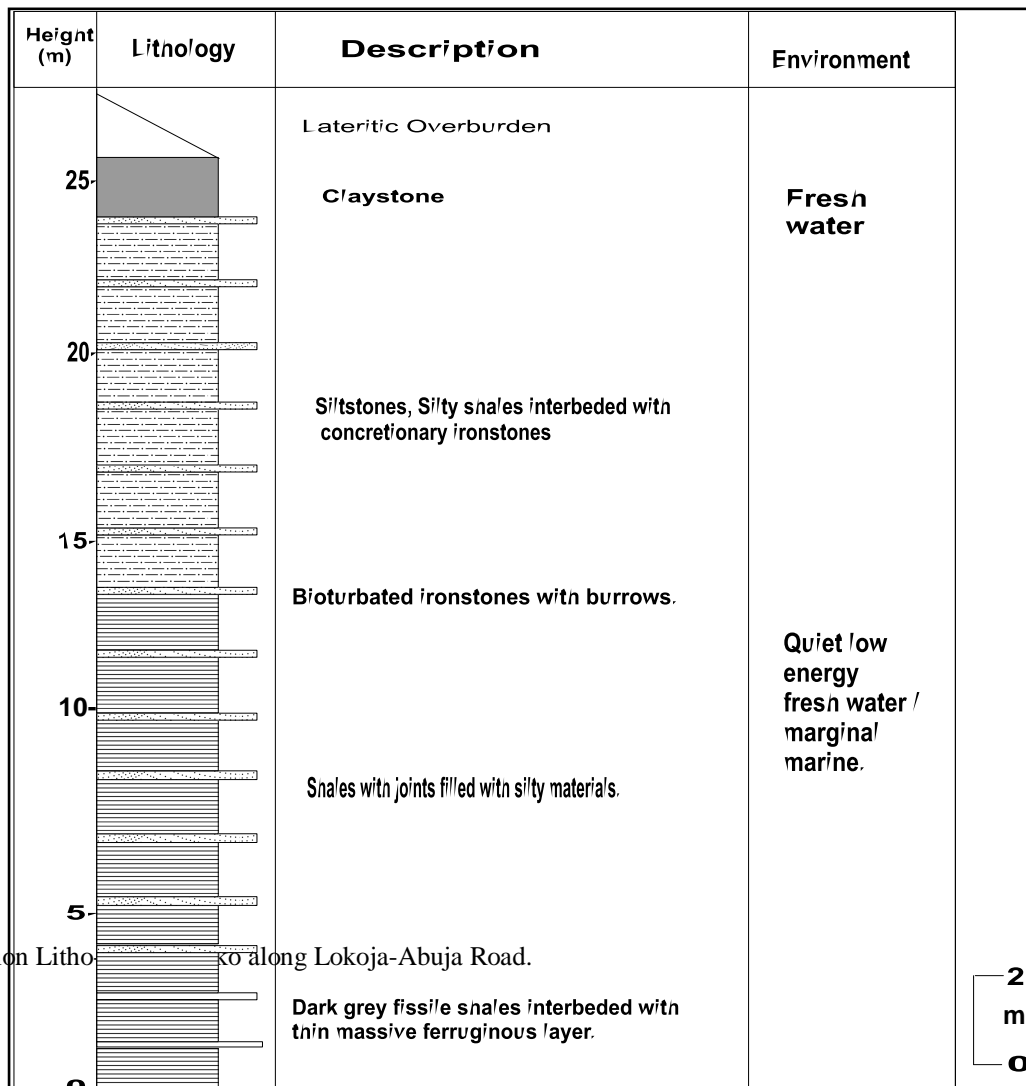


Fig. 4: Patti Formation Lithology along Lokoja-Abuja Road.

4.2 PALYNOMORPH ASSEMBLAGE

According to a work done by the first author (31), the biostratigraphical assemblage consists of well preserved palynomorphs dominated by angiospermous pollen and pteridophytic spores. Some of these are *Echitriporites trianguliformis*, *Monocolpites marginatus*, *Retimocolpites obaensis*, *Psilatricolporites crassus*, *Longapertites marginatus*, *Proxapertites cursus*, *Acrostichum aureum*, *Cyatridites minor* and *Zlivisporites blanensis*. Some charred gramineae were also recovered in the sediments. The presence of pteridophytic spores (*Acrostichum aureum*, *Cyatridites minor*, *Zlivisporites blanensis*) have been attributed to vegetation growing on wetland (41; 42) whilst the recovery of charred gramineae in addition suggest a marginal dysoxic-anoxic source to mud-dominated oxic shelf environment of deposition (43).

4.3. TRACE ELEMENT/AL RATIOS AND ENRICHMENTS

The enrichment factor (EF) is equal to (Element/Al) / (Element/Al) shale, where the ratio in the numerator is that for the shale in question, and the ratio in the denominator is that for a ‘‘typical’’ shale (using data from 9 & 44). This approach has been used by various authors to evaluate trace-element enrichments in modern and ancient sediments (e.g., 10; 45; 46). Generally, comparisons of V/Al ratios in the Ahoko shale samples with average shale (Wedepohl, 1971) show clear enrichments in the samples code-named profile A (Ahk_{3PA}) and profile B (Ahk_{1PB} and Ahk_{2PB}) (Tables 1&2). Mo/Al ratios in the studied samples compared with average shale show obvious enrichments in samples from both profiles with exception of sample code-named Ahk_{2PA} from profile A. Lower Mo/Al and V/Al ratios in studied samples from both profiles indicates the potentially ‘extreme’ bottom-water oxic conditions during deposition. The Ni/Al ratio in the studied shales compared to average shale does not show noticeable enrichments in profile A and B. Whereas, Co/Al show clear enrichment in the samples code-named profile A (Ahk_{1PA}, Ahk_{2PA}, Ahk_{3PA} and Ahk_{5PA}) (Tables 1&2). Lower Ni/Al and Co/Al ratios in the samples suggest higher oxygen regime during deposition.

U/Al ratio compared with average shale show clear enrichment in all studied samples from both profiles A and B. Conversely, Cr/Al ratio compared with average shale show evidence of enrichment in shale samples with the exception of sample code-named profile A (Ahk_{5PA} and Ahk_{6PA}) and profile B (Ahk_{3PB}). Lower U/Al and Cr/Al ratios suggest oxic bottom water condition during deposition. Ba/Al and Sr/Al ratios in the Ahoko shale compared with average shale do not show evidence of enrichments but clear enrichment was observed in profile B. Furthermore, lower Ba/Al and Sr/Al ratios suggest well oxygenated bottom water condition during deposition.

The Cu/Al ratio compared with average shale in Ahoko shales show clear enrichment in code-named sample profile A (Ahk_{6PA} and Ahk_{2PA}). Zn/Al ratio in studied shales compared with average shale show evidence of enrichment in sample code-named profile A (Ahk_{3PA}) and B (Ahk_{2PB}). Lower Cu/Al ratio is obtained from both profiles A and B. Conversely, higher Zn/Al ratio is observed in the samples code-named profile A (Ahk_{3PA}) and profile B (Ahk_{2PB}). The Pb/Al ratio in the studied shale samples compared with average shale show clear enrichments with the exception of samples code-named profile A (Ahk_{6PA}). In addition, lower Pb/Al ratio is observed in the Ahoko shales obtained from both profiles. Rb/Al ratio in the samples compared with averaged shale does not show evidence of enrichments. Higher Rb/Al ratio is recorded in the samples collected from profile B code-named Ahk_{1PB}, Ahk_{3PB}, Ahk_{4PB} and Ahk_{5PB}. On the other hand, lower Rb/Al ratio is observed in the samples obtained from profile A. The Y/Al and Zr/Al ratios in the samples compared with averaged shale showed clear enrichments in both profiles A and B with the exception of enrichment factor of Y in the sample code-named profile B (Ahk_{1PB}).

The studied shales exhibit different degrees of trace-element enrichment, with the approximate order of enrichment relative to average shale being in the order: Zr > U > Pb > Mo > Y > Co > Cr > V > Zn > Ba > Cu > Rb > Ni > Sr in the profile A. On the other hand, the approximate order of enrichment of Zr > Y > U > Zn > Co > Mo > Sr > Pb > Cr > Ba > V > Cu > Ni > Rb is obtained in the shale samples from profile B.

4.4. RARE EARTH ELEMENT GEOCHEMISTRY

Standards that are commonly used (Table 4) include the World Shale Average (WSA), as calculated by (24) from published analyses (47 and 48); the North American Shale Composite (NASC), analyzed by (49); the Upper Continental Crust (UCC), with several slightly different values reported by numerous individuals (e.g., 50; 51; 52), but with quite similar interelement concentrations; Post Archean Australian Shale (PAAS), advanced by (53); and lastly an average of chondrites (54).

Table 1: Trace element/Al ratios and enrichments in the profile A compared to World Average Shale (WSA) (9)

Element	WSA	Ahk _{1PA}	Ahk _{2 PA}	Ahk _{3PA}	Ahk _{4PA}	Ahk _{5PA}	Ahk _{6PA}
Ni (ppm)	68	26.03	19.85	46.35	19.28	28.86	20.51
(Ni/Al)*10 ⁴	7.7	2.69	1.94	4.01	2.40	2.58	1.89
EF		0.35	0.25	0.52	0.31	0.33	0.70
Co (ppm)	19	75.12	8.12	49.47	9.21	34.68	21.39
(Co/Al)*10 ⁴	2.1	7.75	0.79	4.28	1.15	3.10	1.97
EF		3.69	0.38	2.04	0.55	1.48	0.25
Cu (ppm)	45	14.83	16.16	18.23	19.21	31.71	24.43
(Cu/Al)*10 ⁴	5.1	1.53	1.58	1.58	2.40	2.83	2.25
EF		0.30	0.31	0.31	0.47	0.56	1.47
Zn (ppm)	95	76.44	51.93	263.24	46.37	80.88	38.12
(Zn/Al)*10 ⁴	11	7.89	5.07	22.75	5.78	7.23	3.51
EF		0.72	0.46	2.07	0.53	0.66	0.44
V (ppm)	130	95.52	147.93	215.55	95.46	122.20	94.50
(V/Al)*10 ⁴	15	9.86	14.43	18.63	11.90	10.92	8.70
EF		0.66	0.96	1.24	0.79	0.73	0.88
Cr (ppm)	90	105.17	117.99	133.82	86.57	107.37	98.56
(Cr/Al)*10 ⁴	10.2	10.86	11.51	11.57	10.79	9.59	9.08
EF		1.06	1.13	1.13	1.06	0.94	0.84
Ba (ppm)	580	408.90	486.44	473.47	415.19	401.99	398.67
(Ba/Al)*10 ⁴	66	42.21	47.46	40.92	51.76	35.91	36.72
EF		0.64	0.72	0.62	0.78	0.54	0.87
Rb (ppm)	140	43.70	51.24	50.48	52.89	43.03	47.83
(Rb/Al)*10 ⁴	16	4.51	5.00	4.36	6.59	3.84	4.41
EF		0.28	0.31	0.27	0.41	0.24	0.98
Sr (ppm)	300	59.36	73.26	132.15	61.17	66.79	65.22
(Sr/Al)*10 ⁴	34	6.13	7.15	11.42	7.63	5.97	6.01
EF		0.18	0.21	0.34	0.22	0.18	0.98
Zr (ppm)	160	1413.48	1049.23	1007.92	1308.83	1299.68	1784.71
(Zr/Al)*10 ⁴	18	145.93	102.36	87.11	163.18	116.10	164.40
EF		8.11	5.69	4.84	9.07	6.45	1.13
Pb (ppm)	22	44.17	55.43	51.91	53.46	49.54	45.28
(Pb/Al)*10 ⁴	2.5	4.56	5.41	4.49	6.67	4.43	4.17
EF		1.82	2.16	1.79	2.67	1.77	0.91
U (ppm)	3.7	11.95	9.84	19.08	12.02	18.01	17.18
(U/Al)*10 ⁴	0.42	1.23	0.96	1.65	1.50	1.61	1.58
EF		2.94	2.28	3.93	3.57	3.83	1.28
Mo (ppm)	1	2.55	0.99	2.10	1.25	2.21	1.65
(Mo/Al)*10 ⁴	0.1	0.263	0.097	0.181	0.155	0.197	0.152
EF		2.63	0.97	1.81	1.55	1.97	0.58
Y (ppm)	41	77.55	64.09	81.12	70.61	77.95	88.32
(Y/Al)*10 ⁴	4.6	8.01	6.25	7.01	8.80	6.96	8.14
EF		1.74	1.36	1.52	1.91	1.51	1.02

Table 2: Trace element ratios and enrichments in the profile B compared to World Average Shale (WSA) (9)

Element	WSA	Ahk _{1PB}	Ahk _{2PB}	Ahk _{3PB}	Ahk _{4PB}	Ahk _{5PB}
Ni (ppm)	68	59.28	17.83	17.15	11.36	28.38
(Ni/Al)*10 ⁴	7.7	5.30	7.20	2.15	1.36	3.05
EF		0.69	0.93	0.28	0.18	0.40
Co (ppm)	19	23.07	22.47	33.55	3.73	83.08
(Co/Al)*10 ⁴	2.1	2.06	9.07	4.21	0.45	8.92
EF		0.98	4.32	2.00	0.21	4.25
Cu (ppm)	45	38.81	14.69	16.34	5.77	26.49
(Cu/Al)*10 ⁴	5.1	3.47	5.93	2.05	0.69	2.84
EF		0.68	1.16	0.40	0.14	0.56
Zn (ppm)	95	111.05	298.93	32.01	30.71	34.21
(Zn/Al)*10 ⁴	11	9.93	120.67	4.02	3.68	3.67
EF		0.90	10.97	0.37	0.33	0.33
V (ppm)	130	183.43	50.51	74.42	93.33	90.55
(V/Al)*10 ⁴	15	16.40	20.39	9.34	11.18	9.72
EF		1.09	1.36	0.62	0.75	0.65
Cr (ppm)	90	138.58	25.48	79.12	96.86	95.42
(Cr/Al)*10 ⁴	10.2	12.39	10.28	9.92	11.60	10.24
EF		1.21	1.01	0.97	1.14	1.00
Ba (ppm)	580	378.97	420.72	429.12	409.99	393.77
(Ba/Al)*10 ⁴	66	33.88	169.84	53.83	49.12	42.27
EF		0.51	2.57	0.82	0.74	0.64
Rb (ppm)	140	59.99	8.54	50.69	51.18	44.33
(Rb/Al)*10 ⁴	16	5.36	3.45	6.36	6.13	4.76
EF		0.34	0.22	0.40	0.38	0.30
Sr (ppm)	300	79.76	851.63	57.67	63.08	75.66
(Sr/Al)*10 ⁴	34	7.13	343.80	7.23	7.56	8.12
EF		0.21	10.11	0.21	0.22	0.24
Zr (ppm)	160	703.95	88.65	1831.38	1454.35	1622.73
(Zr/Al)*10 ⁴	18	62.92	35.79	229.74	174.23	174.19
EF		3.50	1.99	12.76	9.68	9.68
Pb (ppm)	22	46.65	9.88	43.80	25.67	46.94
(Pb/Al)*10 ⁴	2.5	4.17	3.99	5.49	3.08	5.04
EF		1.67	1.59	2.20	1.23	2.02
U (ppm)	3.7	11.72	5.21	11.51	12.75	10.58
(U/Al)*10 ⁴	0.42	1.05	2.10	1.44	1.53	1.14
EF		2.49	5.00	3.44	3.64	2.70
Mo (ppm)	1	1.45	0.77	2.58	1.01	2.63
(Mo/Al)*10 ⁴	0.1	0.130	0.310	0.324	0.121	0.282
EF		1.30	3.10	3.24	1.21	2.82
Y (ppm)	41	48.46	274.65	87.38	73.25	83.33
(Y/Al)*10 ⁴	4.6	4.33	110.87	10.96	8.77	8.94
EF		0.94	24.10	2.38	1.91	1.94

The concentrations of the REE in these standards represent two compositional extremes of siliciclastic-source-rocks the one felsic (WSA, UCC, PAAS, NASC) and the second ultramafic (chondrites) (55). The Ce anomaly may possibly be quantified by comparing the measured concentration (Ce) with an expected concentration (Ce*) obtained by interpolating between the values of the neighboring elements. Ce anomalies in shales of the anoxic facieses attributed to eustatic sea level changes (56). Similar to Mn, Ce⁴⁺ is less soluble under oxic conditions, whereas under anoxic conditions it will be mobilized, leading to depletion in Ce in anoxic sediments relative to those deposited under oxic conditions. A negative Ce anomaly would result.

Table 3: Ce anomaly for Ahoko shale samples (Two quantification approaches are given).

Profile A							
	Equations	Ahk _{1PA}	Ahk _{2PA}	Ahk _{3PA}	Ahk _{4PA}	Ahk _{5PA}	Ahk _{6PA}
Taylor and McLennan (1985)	Ce* = SQRT(La*Pr)	35.45	30.63	78.27	30.89	49.10	42.70
	Ce/Ce*	4.13	4.04	4.63	4.12	4.26	4.24
Wilde et al. (1996)	Ce* = (La + Pr)/2	85.46	78.71	170.12	73.43	121.93	104.44
	Log (Ce/Ce*)	0.23	0.20	0.33	0.24	0.23	0.24
Profile B							
	Equations	Ahk _{1PB}	Ahk _{2PB}	Ahk _{3PB}	Ahk _{4PB}	Ahk _{5PB}	
Taylor and McLennan (1985)	Ce* = SQRT(La*Pr)	40.09	48.48	34.62	30.71	27.76	
	Ce/Ce*	4.57	3.97	4.08	4.06	3.93	
Wilde et al. (1996)	Ce* = (La + Pr)/2	93.42	137.12	84.04	73.92	69.35	
	Log (Ce/Ce*)	0.29	0.15	0.23	0.23	0.20	

Table 3 shows two different values given for the Ce anomaly, which are based on different calculations. Taylor and McLennan (57) recommended use of the geometric mean $Ce^* = \sqrt{La \cdot Pr}$. The ratio Ce/Ce* is then a measure of the anomaly, with values greater than unity being termed positive. Wilde et al. (56) support use of the arithmetic mean $Ce^* = (La + Pr)/2$ and calculated the logarithm of the ratio Ce/Ce*. Both calculations lead to essentially the same values for Ce*, with the most positive anomaly in Ahoko shale samples. Therefore, the Ahoko shales were deposited under oxic conditions.

4.5. PROVENANCE AND PALEO-ENVIRONMENTAL CONDITIONS

Armstrong-Altrin et al. (58) reveals low concentration levels of Cr indicates a felsic provenance, and elevated contents of Cr and Ni are primarily found in sediments derived from ultramafic rocks. Chromium and nickel concentrations are lower in the studied Ahoko shale samples compared with average shale (Tables 5, 6 & 7). Consequently, the low Cr/Ni ratios in both profile A (i.e. 2.89-5.95) and profile B (i.e. 1.43 – 8.53) indicate that felsic components were the main components among the basement complex source rocks. A few number of authors showed that ratios such as La/Sc, Th/Sc, Th/Co, and Th/Cr are significantly different in felsic and basic rocks and may allow constraints on the average provenance composition (59; 60; 61). The ratios of Th/Cr (profile A = ~0.23 – 0.40 and profile B = ~0.16-0.39), Cr/Th (profile A = ~2.47 - 4.32 profile B = ~2.58 - 6.45), Th/Co (profile A = ~0.32- 3.58 and profile B = ~0.18 – 8.34) and Cr/Ni (profile A = ~2.89 – 5.95 and profile B = ~1.43 – 8.53) suggests that the Ahoko shale sequence were derived from felsic source rocks (62; 63; 64; 59; 65).

Trace element ratios such as Ni/Co, V/Cr, Cu/Zn and U/Th have been used to evaluate paleoredox conditions (66; 14). The ratio of uranium to thorium may be used as a redox indicator with U/Th ratio being higher in organic rich mudstones (14). U/Th ratios below 1.25 suggest oxic conditions of deposition, whereas values above 1.25 indicate suboxic and anoxic conditions (14; 69). The studied shale samples show low U/Th ratio (profile A = ~0.34 – 0.51 and profile B = ~0.29 – 1.32) (Tables 5, 6 & 7), which indicate that Ahoko shale sequence were deposited in an oxic environment.

Some authors have used V/Cr ratio as an index of paleoxygenation (70; 71; 65). The incorporation of Cr in the detrital fraction of sediments and its possible substitution for Al in the clay structure (73). Vanadium may be bound to organic matter by the incorporation of V⁴⁺ into porphyrins, and is generally found in sediments deposited in reducing environments (73). The V/Cr ratios above 2 indicate anoxic conditions, whereas values below 2 suggest more oxidizing conditions (14). Therefore, the V/Cr ratios of Ahoko shale sequence vary between (i.e. profile A = 0.91 and 1.61 and profile B = 0.94 and 1.98) (Tables 5, 6 & 7) which indicates that they were deposited in an oxic bottom water condition. Several authors have used the Ni/Co ratios as a redox indicator (74; 70; 65). The Ni/Co ratios below 5 indicate oxic environments, whereas ratios above 5 suggest suboxic and anoxic environments (14). The Ni/Co ratios vary between (i.e. profile A = ~0.35-2.45 and profile B = ~0.34 – 3.05) (Tables 5, 6 & 7) suggesting that Ahoko shale were deposited in a well oxygenated environment. The Cu/Zn ratio is also used as a redox parameter (66).

High Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidizing conditions (66). Consequently, the low Cu/Zn ratios (profile A = $\sim 0.07 - 0.64$ and profile B = $\sim 0.05 - 0.77$) in the studied Ahoko shale (Tables 5, 6 & 7) indicate that they were deposited under oxic conditions. The V/(Ni+V) ratios below 0.46 indicate oxic environments, but ratios above 0.54 to 0.82 suggest suboxic and anoxic environments (23). The V/(Ni + V) ratios in the studied shale sequence vary between (profile A = ~ 0.74 and 0.89 and profile B = $\sim 0.74 - 0.89$) which indicate suboxic to anoxic environment of deposition. The V/Sc ratios below 9.1 indicate oxic environment of deposition (75). Therefore, the V/Sc ratios in the studied shale samples indicate oxic environment of deposition. Conversely, shale sample code-named Ahk₁ shows V/Sc ratio above 9.1 (Tables 5, 6 & 7).

V. CONCLUSIONS

The lithologic succession consists of dark grey shales at the base, followed by light grey shales and siltstones that are intercalated at intervals by grey to brownish, highly indurated ironstone concretion. Geochemical analysis showed ratios of Th/Cr, Cr/Th, Th/Co and Cr/Ni suggests that the studied samples were derived from felsic source rocks.

Geochemical results further revealed lower Mo/Al, V/Al, U/Al, Cr/Al, Ba/Al, Sr/Al, Ni/Al and Co/Al ratios which indicate the potentially 'extreme' bottom-water oxic conditions during deposition. The estimated order of enrichment relative to world average shale (WSA) being in the order: Zr > U > Pb > Mo > Y > Co > Cr > V > Zn > Ba > Cu > Rb > Ni > Sr and Zr > Y > U > Zn > Co > Mo > Sr > Pb > Cr > Ba > V > Cu > Ni > Rb for profile A and B respectively. Ratio of Ce/Ce* and Log (Ce/Ce*) values showed positive anomaly which indicates well oxygenated bottom-water conditions during deposition.

Redox sensitive element ratios such as U/Th, V/Cr, Ni/Co, Cu/Zn, V/Sc ratios and V/(Ni+V) suggests oxic environment of deposition. The identified palynomorph assemblage such as *Echitriporites trianguliformis*, *Monocolpites marginatus*, *Retimocolpites obaensis*, *Psilatricolporites crassus*, *Longapertites marginatus*, *Proxapertites cursus*, *Acrostichum aureum*, *Cyatridites minor*, *Zlivisporites blanensis* and charred graminiae in the sediments suggest fluviodeltaic source and moderately distal oxic environment of deposition.

Table 4: Rare earth elemental composition of studied samples and rock standards-World Shale Average (WSA), North American Shale Composite (NASC), Upper Continental Crust (UCC), Post Archean Australian Shale (PAAS), and Average chondrites.

Ahoko shale profile A											
Element	WSA	UCC	PAAS	NASC	Aver. Chondrites	Ahk _{1PA}	Ahk _{2PA}	Ahk _{3PA}	Ahk _{4PA}	Ahk _{5PA}	Ahk _{6PA}
La	41	30	38.2	31.1	0.32	77.33	72.22	149.65	66.23	111.08	94.83
Ce	83	64	79.6	66.7	0.9	146.27	123.84	362.74	127.33	209.08	181.08
Pr	10.1	7.1	8.83	7.7	0.13	16.26	13.00	40.94	14.41	21.70	19.23
Nd	38	26	33.9	27.4	0.57	59.35	44.32	152.66	52.99	78.86	69.90
Sm	75	4.5	5.55	5.59	0.21	11.26	8.29	26.27	10.46	14.73	13.77
Eu	1.61	0.88	1.08	1.18	0.074	1.98	1.51	4.76	1.61	2.59	2.09
Gd	6.35	3.8	4.66	4.9	0.31	10.76	7.97	19.07	9.61	13.30	12.64
Tb	1.23	0.64	0.774	0.85	0.051	1.76	1.46	2.90	1.68	2.09	2.16
Dy	5.5	3.5	4.68	4.17	0.3	12.64	10.09	16.43	11.44	14.15	14.36
Ho	1.34	0.8	0.991	1.02	0.074	2.70	2.38	3.25	2.63	2.96	3.29
Er	3.75	2.3	2.85	2.84	0.21	8.45	7.16	8.88	7.94	8.94	10.04
Tm	0.63	0.33	0.405	0.84	0.032	1.28	1.15	1.27	1.16	1.30	1.52
Tb	3.53	2.2	2.82	3.06	0.18	1.76	1.46	2.90	1.68	2.09	2.16
Lu	0.61	0.32	0.433	0.46	0.032	1.36	1.26	1.23	1.27	1.44	1.59
Ahoko shale profile B											
Element	WSA	UCC	PAAS	NASC	Aver. Chondrites	Ahk _{1PB}	Ahk _{2PB}	Ahk _{3PB}	Ahk _{4PB}	Ahk _{5PB}	
La	41	30	38.2	31.1	0.32	83.83	127.94	76.17	66.87	63.26	
Ce	83	64	79.6	66.7	0.9	183.06	192.53	141.30	124.56	109.06	
Pr	10.1	7.1	8.83	7.7	0.13	19.17	18.37	15.74	14.11	12.19	
Nd	38	26	33.9	27.4	0.57	70.22	78.57	58.16	52.11	44.83	
Sm	75	4.5	5.55	5.59	0.21	12.60	15.91	11.14	9.84	8.53	
Eu	1.61	0.88	1.08	1.18	0.074	2.39	4.33	1.58	1.75	1.29	
Gd	6.35	3.8	4.66	4.9	0.31	10.08	25.21	10.65	10.06	8.96	
Tb	1.23	0.64	0.774	0.85	0.051	1.51	3.82	1.94	1.67	1.70	
Dy	5.5	3.5	4.68	4.17	0.3	9.29	26.63	13.47	12.28	12.77	
Ho	1.34	0.8	0.991	1.02	0.074	1.90	6.42	3.08	2.68	2.95	
Er	3.75	2.3	2.85	2.84	0.21	5.55	18.73	9.76	8.08	9.16	
Tm	0.63	0.33	0.405	0.84	0.032	0.80	2.45	1.49	1.21	1.43	
Tb	3.53	2.2	2.82	3.06	0.18	1.51	3.82	1.94	1.67	1.70	
Lu	0.61	0.32	0.433	0.46	0.032	0.91	2.08	1.62	1.37	1.55	

WSA (24; 9, 44; 76; 77; 78); UCC (50; 52; 51); PAAS (53); NASC (49); Average Chondrites (54).

Table 5: Trace elements (as mg/kg) and redox-sensitive elements in the studied samples from profile A and World Shale Average (WSA)

Element	WSA	Ahk ₁	Ahk _{1PA}	Ahk _{2 PA}	Ahk _{3PA}	Ahk _{4PA}	Ahk _{5PA}	Ahk _{6PA}	WSA	Ahk _{1PA}	Ahk _{2 PA}	Ahk _{3PA}	Ahk _{4PA}	Ahk _{5PA}	Ahk _{6PA}
As	10	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	Mn	850	142	138	232	143.39	155	142
Ni	68	26.03	19.85	46.35	19.28	28.86	20.51	Sc	<i>nd</i>	19.14	24.69	35.07	19.14	29.03	23.56
Cu	45	14.83	16.16	18.23	19.21	31.71	24.43	Cs	<i>nd</i>	2.47	2.81	3.10	2.56	2.74	2.60
Zn	95	76.44	51.93	263.24	46.37	80.88	38.12	U	3.7	11.95	9.84	19.08	12.02	18.01	17.18
Pb	22	44.17	55.43	51.91	53.46	49.54	45.28	Mo	1	2.55	0.99	2.10	1.25	2.21	1.65
Rb	140	43.70	51.24	50.48	52.89	43.03	47.83	V	130	95.52	147.93	215.55	95.46	122.20	94.50
Sr	300	59.36	73.26	132.15	61.17	66.79	65.22	Cr	90	105.17	117.99	133.82	86.57	107.37	98.56
Y	41	77.55	64.09	81.12	70.61	77.95	88.32	Co	19	75.12	8.12	49.47	9.21	34.68	21.39
Zr	160	1413.48	1049.23	1007.92	1308.83	1299.68	1784.71	Ba	580	408.90	486.44	473.47	415.19	401.99	398.67
Nb	<i>nd</i>	67.07	68.17	53.26	58.86	52.85	60.68	Th	<i>nd</i>	24.36	29.09	37.91	23.37	40.63	39.84
La	41	77.33	72.22	149.65	66.23	111.08	94.83	Hf	<i>nd</i>	41.77	29.70	27.79	39.23	37.45	54.70
Ni/Co	3.58	0.35	2.45	0.94	2.09	0.83	0.96	Ta	<i>nd</i>	5.62	5.30	4.01	5.01	4.37	5.17
V/Cr	1.50	0.91	1.25	1.61	1.10	1.14	0.96	Cr/Th	28	4.32	4.06	3.53	3.71	2.64	2.47
U/Th	<i>nd</i>	0.49	0.34	0.50	0.51	0.44	0.43	Th/Co	0.006	0.32	3.58	0.77	2.54	1.17	1.86
Cr/Ni	1.32	4.04	5.95	2.89	4.49	3.72	4.81	Th/Cr	0.036	0.23	0.25	0.28	0.27	0.38	0.40
V/Sc	<i>nd</i>	4.99	5.99	6.15	4.99	4.21	4.01	Cu/Zn	0.053	0.19	0.31	0.07	0.41	0.39	0.64
La/Sc	<i>nd</i>	4.04	2.93	4.27	3.46	3.83	4.02	Th/Sc	<i>nd</i>	1.27	1.18	1.08	1.22	1.40	1.69
V/Ni	1.91	3.67	7.45	4.65	4.95	4.23	4.61	V/(Ni+V)	0.66	0.79	0.88	0.82	0.83	0.81	0.82

Table 6: Trace elements (as mg/kg) and redox-sensitive elements in the studied samples from profile B and World Shale Average (WSA)

Element	WSA	Ahk _{1PB}	Ahk _{2PB}	Ahk _{3PB}	Ahk _{4PB}	Ahk _{5PB}	Element	WSA	Ahk _{1PB}	Ahk _{2PB}	Ahk _{3PB}	Ahk _{4PB}	Ahk _{5PB}
As	10	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	Mn	850	137.907	7977.35	140.45	154.90	145.33
Ni	68	59.28	17.83	17.15	11.36	28.38	Sc	<i>nd</i>	20.08	16.27	20.06	21.50	22.05
Cu	45	38.81	14.69	16.34	5.77	26.49	Cs	<i>nd</i>	3.72	0.65	2.16	2.16	2.13
Zn	95	111.05	298.93	32.01	30.71	34.21	U	3.7	11.72	5.21	11.51	12.75	10.58
Pb	22	46.65	9.88	43.80	25.67	46.94	Mo	1	1.45	0.77	2.58	1.01	2.63
Rb	140	59.99	8.54	50.69	51.18	44.33	V	130	183.43	50.51	74.42	93.33	90.55
Sr	300	79.76	851.63	57.67	63.08	75.66	Cr	90	138.58	25.48	79.12	96.86	95.42
Y	41	48.46	274.65	87.38	73.25	83.33	Co	19	23.07	22.47	33.55	3.73	83.08
Zr	160	703.95	88.65	1831.38	1454.35	1622.73	Ba	580	378.97	420.72	429.12	409.99	393.77
Nb	<i>nd</i>	49.41	6.11	56.28	61.79	72.47	Th	<i>nd</i>	28.82	3.95	28.07	31.07	37.03
La	41	83.83	127.94	76.17	66.87	63.26	Hf	<i>nd</i>	19.95	2.09	56.11	41.31	50.13
Ni/Co	3.58	2.57	0.79	0.51	3.05	0.34	Ta	<i>nd</i>	5.37	0.88	4.96	5.05	6.23
V/Cr	1.50	1.32	1.98	0.94	0.96	0.95	Cr/Th	28	4.81	6.45	2.82	3.12	2.58
U/Th	<i>nd</i>	0.41	1.32	0.41	0.41	0.29	Th/Co	0.006	1.25	0.18	0.84	8.34	0.45
Cr/Ni	1.32	2.34	1.43	4.61	8.53	3.36	Th/Cr	0.036	0.21	0.16	0.35	0.32	0.39
V/Sc	<i>nd</i>	9.14	3.11	3.71	4.34	4.11	Cu/Zn	0.053	0.35	0.05	0.51	0.19	0.77
La/Sc	<i>nd</i>	4.18	7.87	3.80	3.11	2.87	Th/Sc	<i>nd</i>	1.44	0.24	1.40	1.45	1.68
V/Ni	1.91	3.09	2.83	4.34	8.22	3.19	V/(Ni+V)	0.66	0.76	0.74	0.81	0.89	0.76

Table 7: Some trace element ratios to evaluate paleoredox conditions

Element ratios	Oxic	Dysoxic	Suboxic to Anoxic	Euxinic
Ni/Co ¹	< 5	5 to 7	> 7	
V/Cr ¹	< 2	2 to 4.25	> 4.25	
U/Th ¹	< 0.75	0.75 - 1.25	> 1.25	
V/(Ni+V) ²	< 0.46	0.46 - 0.60	0.54 - 0.82	> 0.84
V/Sc ³	< 9.1			

¹(14); ²(23); ³(76).

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AUTHORS

First Author – Adebayo, O. F, Geology Department, Ekiti State University, Ado Ekiti, Nigeria, Geology Department, University of Leicester, University Road, Leicester, LE1 7RH, UK., Email: adebayo.olajide@eksu.edu.ng

Second Author – Akinyemi, S. A, Geology Department, Ekiti State University, Ado Ekiti, Nigeria, Geology Department, University of Leicester, University Road, Leicester, LE1 7RH, UK., Email: akinyemi70@gmail.com

Third Author – Madukwe, H. Y, Geology Department, Ekiti State University, Ado Ekiti, Nigeria, Geology Department, University of Leicester, University Road, Leicester, LE1 7RH, UK.

Fourth Author – Aturamu, A. O, Geology Department, Ekiti State University, Ado Ekiti, Nigeria, Geology Department, University of Leicester, University Road, Leicester, LE1 7RH, UK.

Fifth Author – Ojo, A. O, Geology Department, Ekiti State University, Ado Ekiti, Nigeria, Geology Department, University of Leicester, University Road, Leicester, LE1 7RH, UK.