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SEDIMENTARY GEOCHEMICAL STUDY OF LEDIA CLAYSTONE: IMPLICATION ON PROVENANCE, PALEOENVIRONMENT OF DEPOSITION AND CLAYSTONE CLASSIFICATION, GWANDU FORMATION, SOKOTO BASIN, NORTHWESTERN, NIGERIA

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ABSTRACT

This study combines sedimentary and geochemical studies of Ledia Claystone outcrops in Argungu area, Sokoto Basin, Nigeria. The study was carried out to improve current understanding of the depositional conditions, provenance as well as the classification of the sediments. The methods employed include both field description and geochemical study using the Atomic Absorption Spectrometry and flame photometry. The lithostratigraphic section consists of a fining-upward sequence of beds, where the basal bed is made up of fine laminated herringbone structure sandstone, followed by claystone facies; intercalation of silty claystone and a massive variegated bioturbated claystone, capped by oolitic ironstone. Geochemical analytical results of the claystone revealed a quantitative concentration of SiO_2 and Al_2O_3 varying from 57.19 to 83.4 % and 3.15 to 29.5 % respectively. Relatively high concentrations of Fe_2O_3 (4.6 %) indicate ferruginization, while the CaO and P_2O values of 1.62 mg/l and 0.37 mg/l respectively are indicative of deposition in marine environment due to dissolved diagenetic calcite cement. Relatively moderate values of MgO (8.63 mg/l) and CaO (1.62 mg/l) in the samples indicated the presence of calcite. All other oxides decreased with an increase in SiO_2 (67.75 %) due to mineral dissolution with distance of deposition. In particular, the Al_2O_3/TiO_2 ratio from Samples I and 2 of Ledia Claystone had 23.64 and 22.69 values respectively: suggestive of felsic igneous rock source. However, Sample 3 with Al_2O_3/TiO_2 ratio of 3.16 is indicative of mafic igneous rock source. The low Ni content (1.034) was suggestive of a felsic provenance source, while low values in the Cu/Zn and Ni/Co ratios 4.310 and 0.301 respectively were indicative of deposition under oxidizing conditions. The Log (Fe_2O_3/K_2O) against Log (SiO_2/Al_2O_3) shows that Samples 1 and 2 are claystone while Sample 3 is sandstone, classified between sub-arkose and litharenites facies.

Keywords: *Herringbone structure, Variegated claystone, Ferruginization, Felsic, igneous rock, Oxidizing condition.*

INTRODUCTION

The Sokoto Basin sediments accumulated in multifaceted periods (Ola-Buraimo and Mohammad, 2024; Ola-Buraimo and Meshack, 2024). The Gundumi and Illo Formations made up the first phase of sedimentation; composed of grits and clays, deposited on the Crystalline Basement. The second phase of sediment accumulation constitutes the questionable Maastrichtian Rima Group, encompassing the Dukamaje, Taloka and Wurno Formations. The third phase is multiplex in deposition of the questionable Paleocene Sokoto Group. The unrecognized Sokoto Group is made up of shales in Dange, the Carboniferous Kalambaina, and Gamba Formations, dated to range from Early Maastrichtian to Middle Eocene age (Ola-Buraimo and Mohammed, 2024; Ola-Buraimo and Meshack,2024). These sediments gradually thicken and dip to the northwest, reaching a maximum thickness of over 1,200 meters close to the border with the Niger Republic (Adeleye, 1975; Okosun, 1989).

The last phase was responsible for the deposition of the Gwandu Formation, earlier dated Eocene age and posited to be deposited in continental environment (Kogbe and Sowunmi, 1975). However, Ola-Buraimo*et al*. (2018) described the Gwandu Formation to be ambiguous in lithofacies composition. The sedimentary structures were described to have formed by both syn-sedimentation and post depositional tectonic processes (Ola-Buraimo*et al*., 2018). Recent investigations by researchers show that the Gwandu Formation was deposited in various environmental settings ranging from continental to deeper marine (Ola-Buraimo*et al*., 2018; Ola-Buraimo and Haidara, 2022; Ola-Buraimo and Usman, 2022; Ola-Buraimo*et al*., 2022; Ola-Buraimo*et al*., 2023).

Ledia Claystone, which is the subject of this research, is well exposed in Ledia Village in Argungu (Figure 1). It occurs within the Gwandu Formation of the Sokoto Basin. Furthermore, the need for an improved understanding of sedimentary geochemistry Ledia Claystone has necessitated this study. The geochemical perspective is imperative towards propping the mineralogical composition, depositional processes, sediment maturity, paleoenvironment of deposition and sediment classification.

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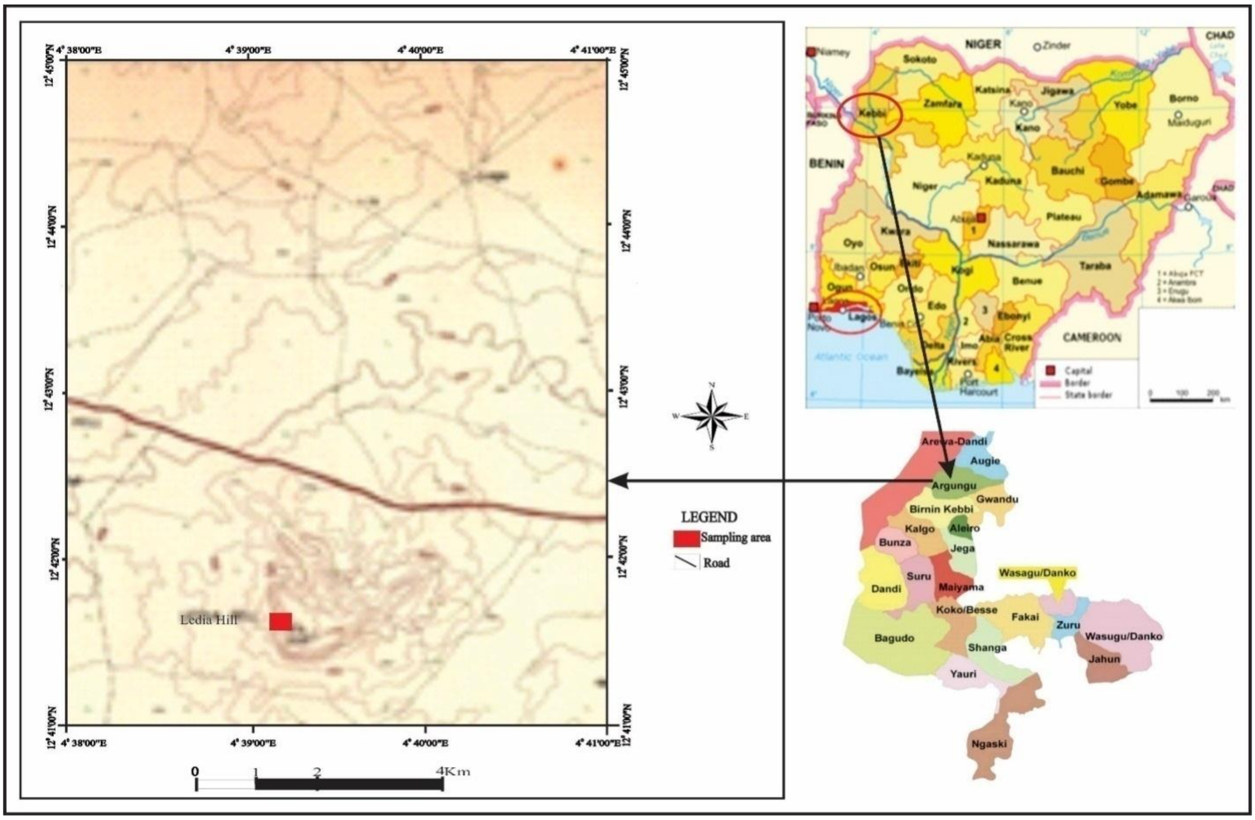

Figure 1: Location map of the study area

METHODOLOGY

Field study was carried out for detailed observations such as colour, grain size, textural parameters, fossil content, diagenetic effect, and structures. Fresh samples of the selected claystone samples were pulverized and analysed with Atomic Absorption Spectrometry (AAS) method.

The Atomic Absorption Spectrometry method was used for elemental analysis. It allows determination of metals in a variety of samples at the pictogram level. The methods adopted followed standard procedure as in Welz and Spelling (2008) as well as Garcia and Báez (2012). All the samples were of an appropriate size to fit in the specimen chamber and were generally mounted rigidly on a specimen holder called a specimen stub. The atomic absorption phenomenon involves measurement of the intensity of optical radiation subsequent to its passage through a cell containing gaseous atoms. Modern instrumentation for AAS typically consists of a light source called a hollow cathode lamp (HCL), which emits specific wavelengths of light that are ideally only absorbable by the analyte.

RESULT AND INTERPRETATION

The study area, Ledia was investigated for both field observation and sample collections for laboratory geochemistry analysis. Three outcrop samples were collected from different locations for geochemical studies. Outcrop sedimentary structures have been partially to completely obliterated due to prolong weathering and human activities in some cases. Descriptions of geologic features observed in the field were discussed in detail below.

Field and Lithological Description

Location; Ledia

Coordinate: 12° 42'12"N and 4° 40' 11" E.

Elevation: 290 m

Description: The Ledia outcrop is composed of herringbone structure fine sandstone associated with bioturbation at the bottom, overlain successively silty claystone, bioturbated claystone and ferruginized ironstone (Figure 2).

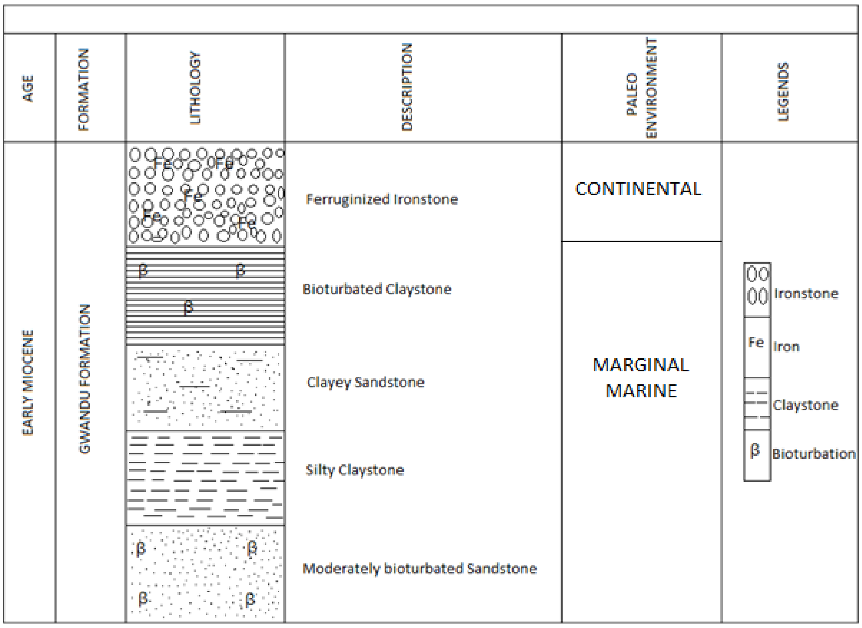

Figure 2. Litho-log description of exposed section of Ledia outcrop (12° 42'12"N and 4° 40' 11" E.)

Some of the sedimentary structures encountered are herringbone structure, lamination, bioturbation and loadcast structure (Plates. 1-4). They are similar to those reported in the works of Ola-Buraimo *et al*. (2018), Ola-Buraimo and Usman (2022) and Ola-Buraimo *et al*. (2023b). The structures suggest the transportation and depositional processes and current energy; it also indicate the post depositional processes, effects and the degree of weathering.

Plate 1. Herringbone structure

Plate 2. Fracture

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Plate 3. Bioturbation

Plate 4. Loadcast

Geochemistry of Ledia Claystone

The chemical composition and concentration of Ledia Claystone are in major oxides expressed in percentages (%), while the trace and rare earth elements (REE) are expressed in parts per million (ppm) as presented in Table 1. The concentration values of the major and trace elements analyzed for the three claystone samples were later compared to average shales worldwide (Pettijohn,1957), NASC (Gromet *et al.*, 1984), Turekan and Wedephol (1961) and shales from other parts of Nigeria.

The concentration values show that the claystone is relatively rich in Al_2O_3, MgO and SiO_2. The claystone has a high variation in Al_2O_3 content (3.15-29.5). The samples had low P_2O_5 content; P_2O_5 depletion could have been due to the lower amount of accessory phases such as apatite and monazite compared to PAAS (Ramasamy *et al.*, 2007; Okunlola and Idowu, 2012). The MnO, Na_2O and K_2O content values are very low in all the samples, which collectively accounted for about 3%. The claystone concentration values for MgO (8.63) and CaO (1.62) are relatively high, which indicates presence of carbonates but no dolomitisation (Table 1).

The alumina to silica ratio of 67.75:19.55 is high and they constituted about 88% of the sample total chemical composition (Table 1). The other chemical impurities in the clay sample from the Gwandu Formation are Fe_2O_3 (4.6%) and TiO_2 (1.13%). The Gwandu Formation Claystone samples have higher TiO_2 values than post-Archean Australian average shale (PAAS; Taylor and Mclennan, 1985).

Table 1. Major and Trace elements concentrations in Ledia

ELEMENTS	LD1	LD2	LD3	Highest value	Lowest value	Average value
SiO_2	62.65	57.19	83.4	83.4	57.19	67.75
TiO_2	1.1	1.3	1.00	1.3	1.00	1.13
Al_2O_3	26.00	29.5	3.15	29.5	3.15	19.55
Fe_2O_3	4.5	4.6	4.7	4.7	4.5	4.6
MnO	0.05	0.06	0.05	0.06	0.05	0.13
MgO	3.5	3.8	4.00	4.00	3.5	8.63
CaO	1.5	1.6	1.75	1.75	1.5	1.62
Na_2O	0.6	0.75	1.00	1.00	0.6	1.68
K_2O	0.75	1.00	0.75	1.00	0.75	0.83
P_2O_5	0.1	0.2	0.2	0.2	0.1	0.37
Pb	3.120	1.530	2.260	2.260	1.530	2.303

Ni	1.025	1.038	1.040	1.040	1.025	1.034
Zn	0.120	0.630	0.040	0.630	0.040	0.263
Ba	2.133	2.240	2.279	2.279	2.133	2.217
Cu	1.10	1.22	1.15	1.22	1.10	1.157
As	0.024	0.430	0.070	0.430	0.024	0.175
Ce	0.010	0.010	0.016	0.016	0.010	0.012
Co	3.250	3.430	3.620	3.620	3.250	3.433
Nb	0.022	0.030	0.012	0.030	0.012	0.0213
Y	0.050	0.042	0.029	0.050	0.029	0.040
Rb	0.030	0.040	0.020	0.040	0.020	0.03
Zr	0.006	0.004	0.024	0.024	0.004	0.011
Sr	0.010	0.010	0.008	0.010	0.008	0.009
V	0.020	0.030	0.026	0.030	0.020	0.025

Claystone samples from the study area compared favorably with shales from other parts of Nigeria. This reveals that the claystone samples are relatively rich in SiO_2, Al_2O_3, Tio_2 and Fe_2O_3 (Table2). The claystone samples were also compared with the black lignite and shale from Ifon and Auchi areas (Apokodje *et al*., 1991). The samples richness in SiO_2, Al_2O_3 and TiO_2were also compared with Eze-Aku Shales (Table2). The comparison shows a close relationship in their concentration values, except that the Eze-Aku Shale shows higher concentration values in Fe_2O_3 and CaO.

The Asu River Group has higher SiO_2, and CaO values but lower TiO_2 and Fe_2O_3 values compared to the Ledia Claystone samples from the Gwandu Formation (Table2). When compared with shales from other parts of the world, the Ledia Claystone has similar average value to those reported by Pettijohn, (1984), Turekian and Wadephol, (1961) and NASC of Gromet *et al.* (1984) in terms of SiO_2, Al_2O_3, and TiO_2 (Table3). Ledia Claystone also has average values that are relatively rich in SiO_2, Al_2O_3, TiO_2 and P_2O_5 in comparison with values obtained from PAAS and NASC (Gromet *et al*., 1984). Furthermore, the Ledia Claytone has depleted MnO, Na_2O_3, and K_2O values compared to world shale average. This depletion is suggested to be due to intense weathering on the Lidia Claystone outcrops (Tables 2 and 3).

Table2. Average chemical composition of Ledia Claystone compared to shale from other sedimentary basins in Nigeria

Oxide	Ledia Claystone (This study)	Asu River group (Amajor ,1987)	Ezeaku Shale (Amajor, 1987)	Auchi Shale (Amajor 1987)	Ifon Shale (Ajayi*et al.*, 1989)
SiO_2	67.75	69.94	44.91	51.68	63.3
TiO_2	1.13	0.52	0.65	1.95	1.02
Al_2O_3	19.55	10	15.71	18.76	18.47
Fe_2O_3	4.6	4.04	6.24	4.67	1.26
MnO	0.13	0.04	0.06	0.06	0.01
MgO	8.63	0.87	2.58	4.39	0.82
CaO	1.62	3.38	15.42	1.9	0.09
Na_2O	1.68	0.4	0.42	0.93	0.42
K_2O	0.83	1.15	2.36	1.16	2.36
P_2O_5	0.37	0.17	0.46	0.25	0.46
Total	106.29	99.69	99.91	99.87	99.81

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Table 3. Comparison of chemical composition of the Ledia Claystone (This study) to world published average shale.

Oxide	Average Ledia Claystone	Average Shale (Pettijohn, 19578.5)	Turekan &Wedephol (1961)	PAAS	NASC (Gromet *et al.*,1984)
SiO_2	67.75	58.1	58.5	62.40	64.82
TiO_2	1.13	0.6	0.77	0.99	0.8
Al_2O_3	19.55	15.4	15	18.78	17.05
Fe_2O_3	4.6	6.9	4.72	7.18	5.7
MnO	0.13	Trace	-	-	-
MgO	8.63	2.4	2.5	2.19	2.83
CaO	1.62	3.1	3.1	1.29	3.51
Na_2O	1.68	1.3	1.3	1.19	1.13
K_2O	0.83	3.2	3.1	3.68	3.97
P_2O_5	0.37	0.2	0.16	0.16	0.15
SiO_2/Al_2O_3	3.47				
K_2O/Na_2O	0.49				
K_2O/Al_2O_3	0.042				
Al_2O_3/TiO_2	17.30				
Cu/Zn	4.310				
Ni/Co	0.30				

Cr and Ni abundance in siliciclastic sediments was considered a useful provenance tool. Wrafter and Graham (1989) advanced that a low Cr concentration value indicates felsic provenance, and a high Ni content is indicative of ultramafic rock-derived sediments. However, the Ni content in this studied claystone is low with an average value of 1.034, thus, suggestive of felsic rock provenance for the Lidia Claystone (Table 4).

The very low value of Ni recorded in the samples could be attributable to intense weathering and leaching of the elements because of the tropical climatic condition compared to other parts of the world that have temperate climatic condition. This same factor was responsible for other trace elements with low contents in the Lidia Claystone compared with shale samples from other parts of the world (Table 4).

Table 4. Average trace element chemical compositions of Ledia Claystone compared with shale from other sedimentary basins of the world.

Trace Elements	Ledia Claystone (This study)	Levinson (1974)	Vine and Tourtelot (1970)	Turekan and Wedephol (1961)	PAAS	NASC (Gromet *et al.*, 1984)
Ba	2.217	300	700	580	650	636
Sr	0.009	200	300	300	200	142
Ni	1.034	50	70	68	55	58
Co	3.433	10	20	-	23	n.a
Cu	1.157	70	50	45	50	n.a
Zn	0.263	300	100	95	85	n.a
V	0.025	150	130	130	150	130
Y	0.040	30	25	-	-	n.a
Zr	0.011	70	160	160	210	200
Mo	-	10	3	-	-	n.a

Nb	0.0213	20	20	n.a	1.90	n.a
Pb	2.303	20	n.a	n.a	20	n.a
Rb	0.03	140	n.a	n.a	160	n.a
Th	-	12	n.a	n.a	14.60	n.a
U	-	4	n.a	n.a	3.10	n.a
Cu/Zn	4.310					
(Cu+Mo)/Zn	-					
Ni/Co	0.301					
Rb/K2O	0.036					
U/Th	-					

Paleo-oxygenation condition

The ratio of Cu/Zn and (Cu+Mo)/Zn ratio have been put forward by Hallberg, (1976) as redox parameters. According to Hallberg (1976), high Cu/Zn ratio indicates reducing depositional conditions, while low Cu/Zn ratios suggest oxidizing conditions. In this present study, the claystone samples are low in Cu/Zn ratio with values ranging from 1.94 to 28.75. This suggests that the Cu/Zn ratio for Ledia Claystones were deposited in oxidizing depositional condition.

Dypvik (1984) and Dill (1986) have used the Ni/Co ratio as a redox indicator. Jones and Manning (1994) have suggested that Ni/Co ratios below 5 indicate oxic environment, whereas ratios above 5 indicate sub-oxic and anoxic environment. Thus, the low Ni/Co ratio (0.29-0.315) for Ledia Claystone in Gwandu Formation is also indicative of oxidizing conditional deposit

Provenance and Depositional environment.

In determining the provenance of the Lidia Claystone, geochemical signatures of clastic sediments have been used to ascertain its provenance characteristics after the works of Taylor and McLennan (1985), Condie *et al.* (1992), and Armstong-Altrin *et al*. (2004). The ratio of Al_2O_3/TiO_2 ratios for clastic rocks are essentially used to infer source rock composition because Al_2O_3/TiO_2 ratio increases from 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks, and from 21 to 70 for felsic igneous rocks (Hayashi *et al.*, 1997). Therefore, the Al_2O_3/TiO_2 ratio for Samples I and 2 of the Ledia Claystone have 23.64 and 22.69 values respectively, which are indicative of felsic igneous rock source (Table 4). However, Sample 3 has 3.16 Al_2O_3/TiO_2 ratio which is indicative of mafic igneous rock (Table 4).

Table 5. Elemental ratio for provenance and paleoenvironment of deposition.

Elemental Ratio	LD1	LD2	LD3	Highest value	Lowest value	Average value
SiO_2/Al_2O_3	2.41	1.94	26.39	26.39	1.94	10.25
Al_2O_3/TiO_2	23.64	22.69	3.16	23.64	3.16	16.410
Cu/Zn	9.17	1.94	28.75	28.75	1.94	20.69
Ni/Co	0.315	0.30	0.29	0.315	0.29	0.712

Classification of the study samples

The classification scheme used was the geochemical classification diagram of Herron (1988) where the Log (Fe_2O_3/K_2O) against Log (SiO_2/Al_2O_3) shows that Samples 1 and 2 plotted in the shale segment, while Sample 3 plots in litharenite segment (Figure 3). This inferred that the Sample 3 analysed for this study is not a claystone, rather it is a sandstone facies rich in rock fragments (Figure 3).

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Figure 3. Chemical classification of Ledia Claystone based on log (SiO_2 / Al_2O_3) Vs (Fe_2O_3 / K_2O) diagram of Herron (1988).

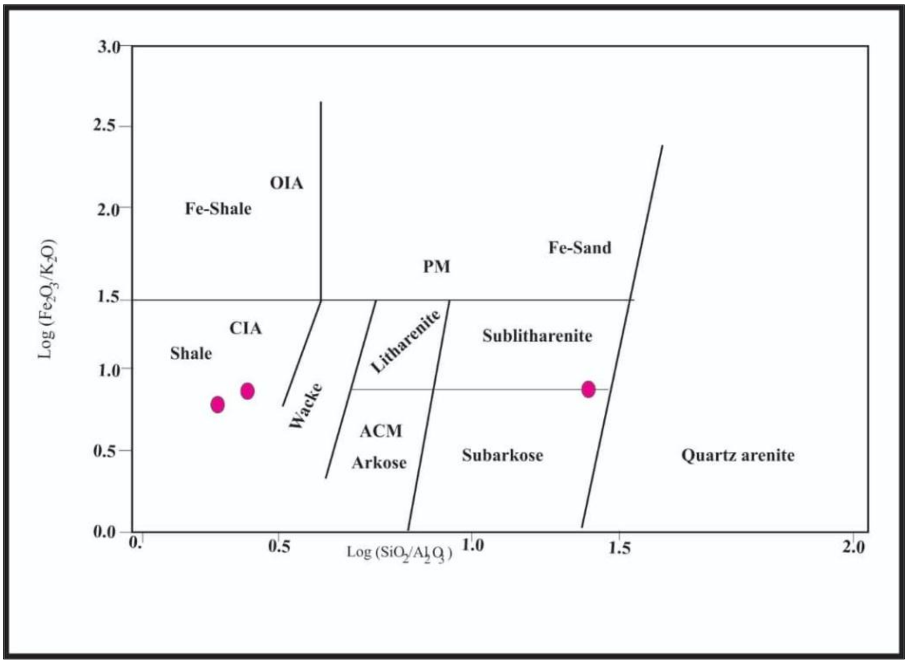

Figure 3. Chemical classification of Ledia Claystone

CONCLUSION

Gwandu Formation sequence exposed in Ledia varies at the base from fine laminated herringbone structure sandstone which fines upward to a claystone facies; intercalation of silty claystone and massive variegated claystone with bioturbation; capped by oolitic ironstone at the top. Geochemical analysis results of the claystone revealed a quantitative concentration of SiO_2 and Al_2O_3 varying from 57.19 to 83.4 % and 3.15 to 29.5 % respectively. The other heavy metals, trace and rare earth elements (REE) are very low in concentration. Relative high concentrations of Fe_2O_3 indicate ferruginisation while the CaO and P_2O are indicative of deposition in marine environment due to dissolved diagenetic calcite cement.

Relative moderate values of MgO and CaO in the samples indicate the presence of calcite and dolomitisation. All other oxides decrease with increase in SiO_2 due to mineral dissolution with distance of deposition. The Al_2O_3/TiO_2 ratio from Samples I and 2 of Ledia Claystone had 23.64 and 22.69 values respectively; suggestive of felsic igneous rock source. However, sample 3 with Al_2O_3/TiO_2 ratio of 3.16; indicative of mafic igneous rock. The low Ni content was suggestive of felsic provenance source, while low values in the Cu/Zn and Ni/Co ratios were indicative deposition under oxidizing condition. The Log (Fe_2O_3/K_2O) against Log (SiO_2/Al_2O_3) shows that Samples 1 and 2 are claystones while Sample 3 is a sandstone plotting between subarkose and litharenite facies.

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