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Provenance and Weathering History of Clays from Share-Tshonga Area, Northern Bida Basin, Nigeria

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Abstract
The claystone member of Enagi Formation exposed around Share-Tshonga, northern Bida Basin, central Nigeria was studied to unravel the provenance, paleoweathering and paleoenvironmental conditions using XRF and ICP-MS. Major oxides show enrichment in SiO_2 (60.27-79.87%), relative to Al_2O_3 (3.10-27.38 %), Fe_2O_3 (0.98-22.85%), CaO (0.01-0.03%), Na_2O (0.01-0.03%), K_2O (0.05-0.84%), MnO (0.01-0.15%), TiO_2(0.21-2.09%) and P_2O_5(0.05-0.84%). The high SiO_2/Al_2O_3 (2.20 to 22.76) with mean of 8.73 suggests higher detritus input in continental environment. Certain proxy trace elements such as Cr (64.80ppm), Th (17.42ppm) and Zr (528.80ppm) are enriched in the claystone compared to published PAAS (38.20ppm, 14.62ppm and 210.00ppm respectively) and UCC (31.00ppm, 10.70ppm and 190.00ppm respectively) data but depleted in Cu (7.03ppm), Zn (8.00ppm), Rb (12.05ppm), Sr (38.63ppm) and Ba (132.40ppm) compared to published PAAS (50.00, 85.00, 160.00, 200.00 and 650.00 respectively)ppm and UCC (25.00, 71.00, 112.00, 350.00 and 550.00 respectively)ppm. The LREE (250.15ppm) enrichment relative to HREE (23.49ppm) with $(La/Yb)_N$ of 9.67 to 11.98, negative Europium (Eu/Eu*) anomaly (0.54-0.63) and (Ce/Ce*) anomaly (0.83-1.49) suggest felsic provenance. The mean values of Al_2O_3/TiO_2 (13.17), K_2O/Al_2O_3 (0.02), LREE/HREE (10.65) coupled with discriminant plots of $\log K_2O/Na_2O$ versus SiO_2, TiO_2 versus Zr, La/Th versus Hf support dominant felsic source within passive margin tectonic settings. The ranges and mean ratio values of Cu/Zn, V/Cr and U/Th indicate oxic, semi-humid to humid climatic settings. The values of chemical indices; chemical index of alteration (CIA=96.44-99.13), chemical index of weathering (CIW=98.73-99.89), plagioclase index of alteration (PIA=98.71-99.89) compared with the values of PAAS and UCC supported by various plotting including CIW versus CIA and ICV versus CIA show that the claystone clearly depicted extremely high weathering. Relatively higher mean of index of compositional variability (ICV) values (2.03) compared to PAAS (0.74) and UCC (1.18) also indicate compositional maturity.

Keywords: *Claystone, Geochemistry, Paleoweathering, Provenance, Oxic.*

Introduction

Clays are mixtures of very fine-grained clay minerals and other minerals like quartz, heavy minerals which are situated close to the surface of the Earth (Murray, 2007). Velde (1995) also defined claystone as a clastic sedimentary rock that consists mainly of very fine particles of less than 1/256mm size, cemented and compacted into a rock with widely varied colour. Taylor and McLennan (1985) reported that fine grained clastic rocks are better in studying crustal scale processes due to homogeneity before deposition and acquisition of debris from wide area. Several research works (e,g. Dill *et al.*, 2011; Liu *et al.*, 2015; Madhavaraju *et al.*, 2016) have been published on fine-grained sedimentary rocks using bulk geochemical data (major, trace and rare earth elements) to be able to understand their geochemical signatures. Trace elements geochemistry owing to reduced mobility or inertness during sedimentary processes is also vital in the provenance study of sedimentary rocks (McLennan *et al.*, 1983 and Armstrong-Altrin *et al.*, 2004).

The present study area is located in parts of the northern Bida Basin, central Nigeria. The Bida Basin which is Campanian-Maastrichtian in age, is one of the Nigerian inland sedimentary basins, and located between Iullemmeden Basin in the northwestern part and Anambra Basin in southern part (Figure 1). On the tectonic evolution of the Basin, King (1950) and Kennedy (1965) concluded that the basin is a rift bounded tensional structure produced by faulting associated with the Benue Trough System (BTS) and drifting apart of the African and Brazilian (AB) plates during the Cretaceous. Geographically, Adeleye and Dessauvagie (1972) sub-divided Bida Basin into the northern and southern parts (Figure 2). The stratigraphic framework in the northern Bida Basin consists of four horizons; the basal Campanian-Maastrichtian Bida Formation (conglomerate and sandstone), the Sakpe Formation (ironstone), the Enagi Formation (sandstone, siltstone and claystone) and the Batati Formation (ironstone). Their lateral equivalents in the southern part of the Basin are Lokoja Formation (conglomerate, sandstone), Patti Formation (sandstone, shale, claystone) and Agbaja Formation (ironstone).

Previous geochemical studies on the source and origin of the claystone within the study area are scanty to the best knowledge of our knowledge and this might be due to the non-exploit of clay deposits in the area. Few related studies include Ojo *et al.* (2011) who evaluated geotechnical characteristics of claystone in Share and Agbaja and suggested that they composed mostly hydrated siliceous aluminosilicates with low contents of MgO and K_2O and low abundance of heavy metal. Ojo (2012) deduced fluvial processes for Bida Formation sediments around Share-Patigi area and suggested an uplifted continental block provenance within warm humid paleoclimatic conditions and short transportation history for the sub-arkose sandstone facies. Okunlola and Olubunmi (2012) revealed prominent kaolinite, dickite and illite occurrence in the Patti claystone-shale in southern Bida Basin. Alabi *et al.* (2018) reported that the clay deposit around Kutigi area in the northern Bida Basin was sourced from weathered adjoining basement complex rock material. Ohanyiri and Omotowo (2018) reported Patti claystone comprises dominantly of kaolinite with minor constituents as illite, muscovite and gorceixite. They also observed pyrite, marcasite, anatase and rutile and suggested an intermediate to felsic igneous rocks as the source. Adepoju *et al.* (2019) studied the lithofacies, pebble morphogenesis and provenance of the Bida Formation in the northern Bida Basin and concluded that the sediments within the study area were transported and deposited in a high energy fluvial setting suggested to have derived from igneous granitic and metamorphic origin. This present research present bulk inorganic geochemical compositions (major, trace and rare earth element) of selected clay in parts (Share and Shonga) of northern Bida Basin, Nigeria focusing on delineating their possible provenance and weathering history.

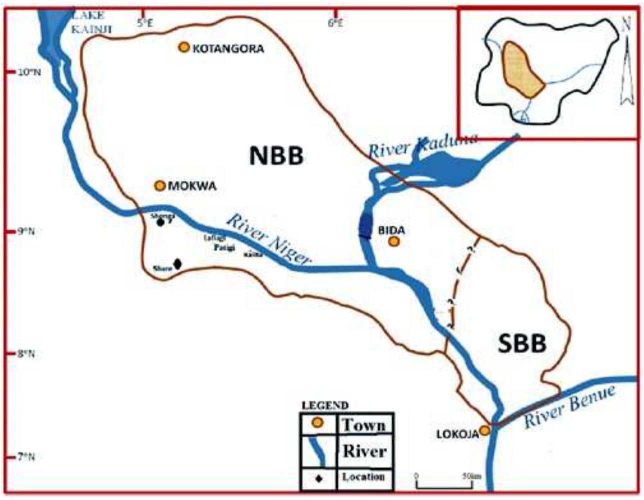
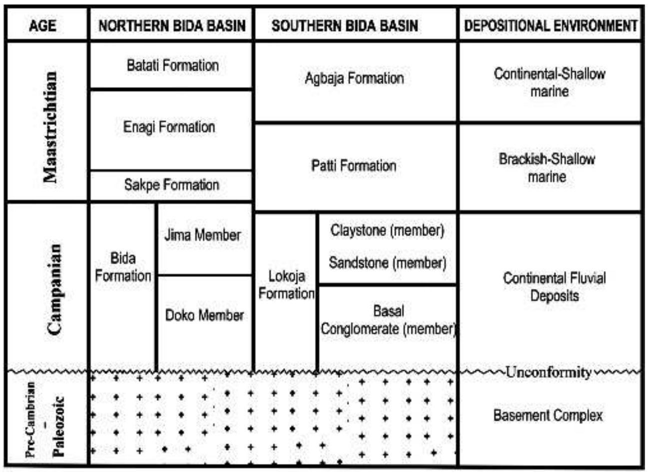


Fig. 1: Map of Bida Basin showing study locations at Share-Tshonga area (modified after Adepoju *et al.*, 2019). NBB – Northern Bida Basin, SBB – Southern Bida Basin.



AGE	NORTHERN BIDA BASIN		SOUTHERN BIDA BASIN		DEPOSITIONAL ENVIRONMENT
Maastrichtian	Batati Formation		Agbaja Formation		Continental-Shallow marine
	Enagi Formation		Patti Formation		Brackish-Shallow marine
	Sakpe Formation				
Campanian	Bida Formation	Jima Member	Lokoja Formation	Claystone (member)	Continental Fluvial Deposits
				Sandstone (member)	
		Doko Member		Basal Conglomerate (member)	
					Unconformity
Pre-Cambrian - Paleozoic					Basement Complex

Fig. 2: Generalized stratigraphic sequence of the Bida Basin (Adapted from Akande *et al.*, 2005).

Methods

Four fresh representative claystone samples were selected among the samples collected from Share (Eastern part of Agbona ridge, latitude: 8^{0}49′28.9″, longitude: 4^{0}58′24.6″), Tsaragi (Western of Agbona ridge, latitude: 8^{0}49′32.2″, longitude: 4^{0}58′36.2″) and Tshonga (latitude: 4^{0}01′28.8″, longitude: 5^{0}08′48.1″) where good lithological sections of Enagi Formation are exposed. At each section, the sedimentary beds were studied texturally, structurally and true thickness of each bed measured with their vertical profile constructed (Figures 3, 4 and 5). Four samples (L3G, L4G, L4H and L5G) were analyzed for major, trace and rare elements analysis using X-Ray Fluorescence (XRF) and Inductively Coupled Plasma Atomic Mass Spectrometry ICP-MS at MS Analytical, Canada. The sample powders were digested with 2 mol/L concentrated HF in capped Teflon bombs on an electric hot plate (~150 °C) for 24 h. The solution was evaporated to near dryness, and re-dissolved in 2 mol/L 6 N HNO_3 in capped teflon at 150 °C for two days. The samples were then evaporated near to dryness, then 1 mol/L of 6 N $HNO_3$was added, and the solutions were further diluted for analysis.

Results

Lithologic log and description

The lithologies encountered in the studied locations are sandstone, ironstone, conglomerate and claystone. The claystone colour varies between white and dirty white (creamy) with random reddish stains probably due to leaching of iron-bearing minerals from overlying ironstone/lateritic overburden. The claystone is often capped by ironstone and ferruginized sandstone and underlain by fine to medium grained sandstone. The exposure is about 35m (Figure 3) high at the eastern flank of the E-W trending Agbona ridge in Share. The claystone of the Enagi Formation at the middle of the sedimentary section is about 4m with artificial "claystone cave" feature where artisanal mining had taken place which paved way for access to sampling (Figures 3a and 3b). Sample L3G was taken at -Eastern end of Agbona ridge at Share. At Tsaragi end of Agbona ridge, claystone samples L4G and L4H were taken (figure 4a). Figure 4b shows Enagi Claystone exposed by erosional channel. Tshonga section consists dominantly of sandstone, claystone, capped with ferruginous and highly indurated conglomerate (figure 5), L5G sample was taken at Tshonga.

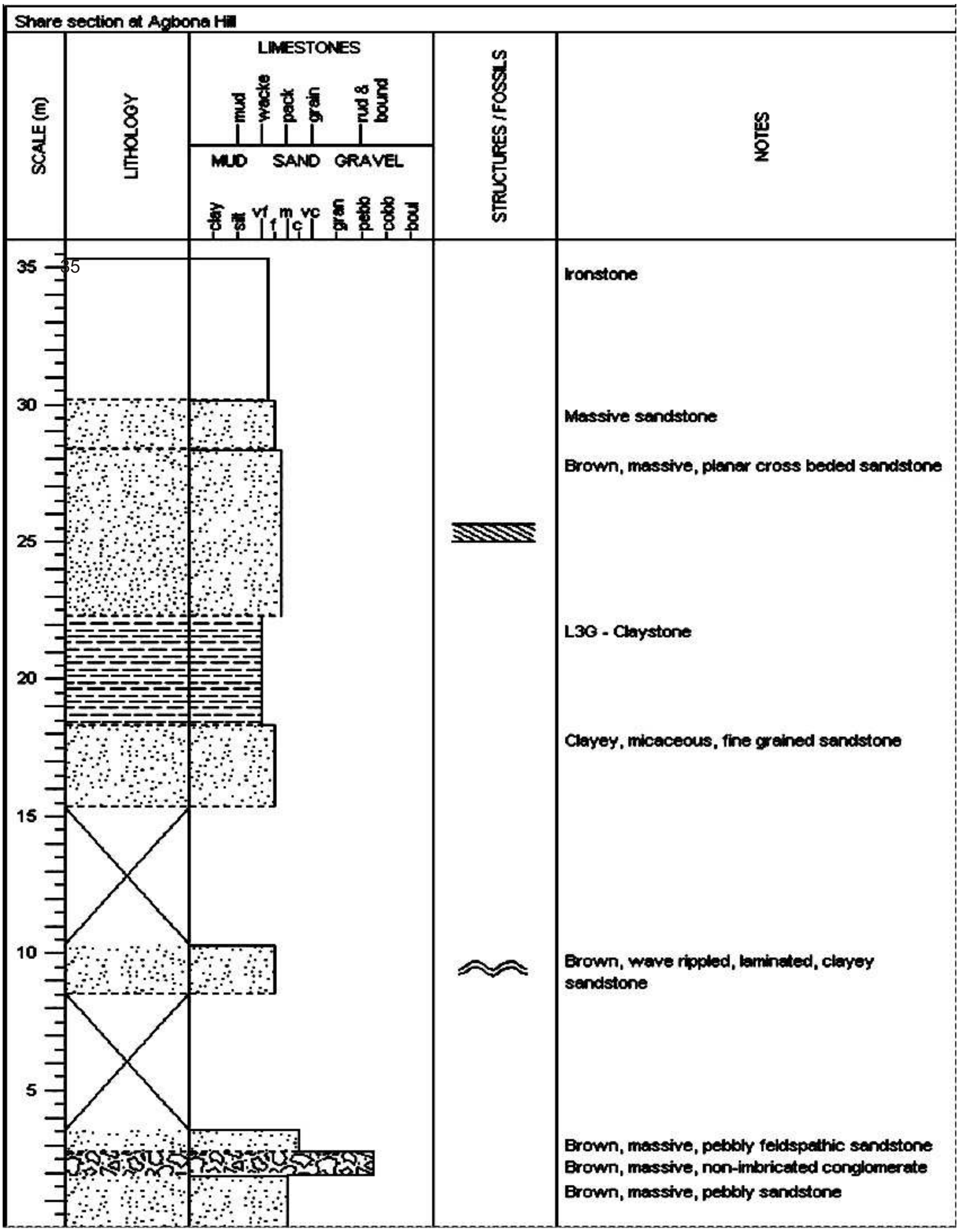


Fig. 3a: Lithologic sections at Share (Latitude: 8049′28.9”, Longitude: 4058′24.6”; Elevation: 310m).

Fig. 3b: Exposed lithological section in parts of Agbona ridge, Share showing massive claystone cave sequel to artisanal mining

Chemical composition

Major Elements

Major element distribution in clays from Share and Tshonga areas is presented in Table 2. The result shows high SiO_2 content ranging from 60.27% to 79.87% (Mean-69.18%) with relatively low Al_2O_3 and Fe_2O_3 contents that ranges from 3.10 to 27.38% (Mean-16.36%) and 0.98% to 22.85% (Mean-6.85%) respectively. CaO, Na_2O, K_2O, MgO, MnO and P_2O_5 contents are very low (less than 1.00%) and relatively similar in compositions having an average value of 0.02%, 0.02%, 0.32%, 0.04%, 0.05% and 0.13% respectively while TiO_2 contents are relatively higher (0.21-2.09%; Mean-1.26%). Higher concentrations of SiO_2 in all the clays may be attributed to abundance of sand and silt fractions, and therefore, can be classified as silico–aluminous clay type. It is also noted that sample L4H have high Fe_2O_3 content (22.85%) but lower Al_2O_3 content (3.10%) whereas other samples have low Fe_2O_3 contents (L3G-0.98%, L4G-1.31% and L5G-2.24%) but higher Al_2O_3 contents (L3G-23.83%, L4G-27.38% and L5H-11.13%). The high iron (Fe_2O_3) content with low alumina (Al_2O_3) in L4H may have resulted from ferruginization from overlying ironstone rolled down the very steep Agbona Hill. Ojo *et al.* (2011) stated that very low Na_2O and K_2O chemical compositions in the Bida Basin claystones suggest low amount of illite or K-feldspar which may indicate hydrated siliceous aluminosilicates clay type that formed from complete weathering of feldspars. Higher contents of titanium (TiO_2) in the studied claystone samples may indicate occurrence of titanium (Ti) within the clay lattices and this according to Ross and Bustin (2009) may be due to a high input of detrital materials. The chemical compositions of the studied clay are well compared to average published data (Table 1) on Share-Agbaja claystone from Ojo *et al.* (2011), Patti claystone from Okunlola and Olubunmi (2012), Upper Continental Crust from McLennan (1989) and Post Archean Australian Shales (PAAS) from McLennan (2001).

Trace elements

Trace element composition in the analyzed bulk samples are listed in Table 2. The samples exhibit higher Cr, Th and Zr relative to Cu, Zn, Sr, Ba, Rb, and Zn. An enrichment is also recorded for elements Cr, Th, U, V and Zr relative to published PAAS and UCC data while others are depleted (Table 2).

Rare Earth Elements

Rare earth element (REE) concentrations of the claystones are presented in table 3. The samples have REE concentrations range from 66.47 to 356.00 (275.03 ppm) and exhibit enrichments in the light rare earth element (LREE) with values ranges from 60.84 to 323.44 ppm (Mean-250.12 ppm) relative to the relative to heavy rare earth element (HREE) which ranges from 5.34 to 32.24 ppm (Mean-23.49 ppm). Generally, the ΣREE, ΣLREE and ΣHREE concentrations in the samples are higher compared to the PAAS (184.77 ppm; 165.08 ppm and 17.61 ppm) data and UCC (148.14 ppm; 132.80 ppm and 14.34 ppm) data. The chondrite-normalized REE spider diagram using the REE provided by Boyton (1984) confirmed LREE enrichment with almost flat HREE pattern (Figure 6). The calculated Europium anomaly (Eu/Eu*) values show negative (0.54-0.63; 0.58) which is similar to the compared published PAAS (0.71) and UCC (0.72) values. Meanwhile, the Cerium anomaly (Ce/Ce*) value (0.83-0.1.47; 1.02) is relatively lower compared to published values of PAAS (2.17) and UCC (2.12). The values of $(La/Yb)_N$ ratio (9.67-15.60) with relatively higher mean values (12.14) than the recorded for PAAS (9.43) and UCC (9.26) supports not only the REE chondrite-normalized plot but also agree with the Eu/Eu* and Ce/Ce* values.

Interpretation

Source and Tectonic Setting

Several attempts have been made by previous

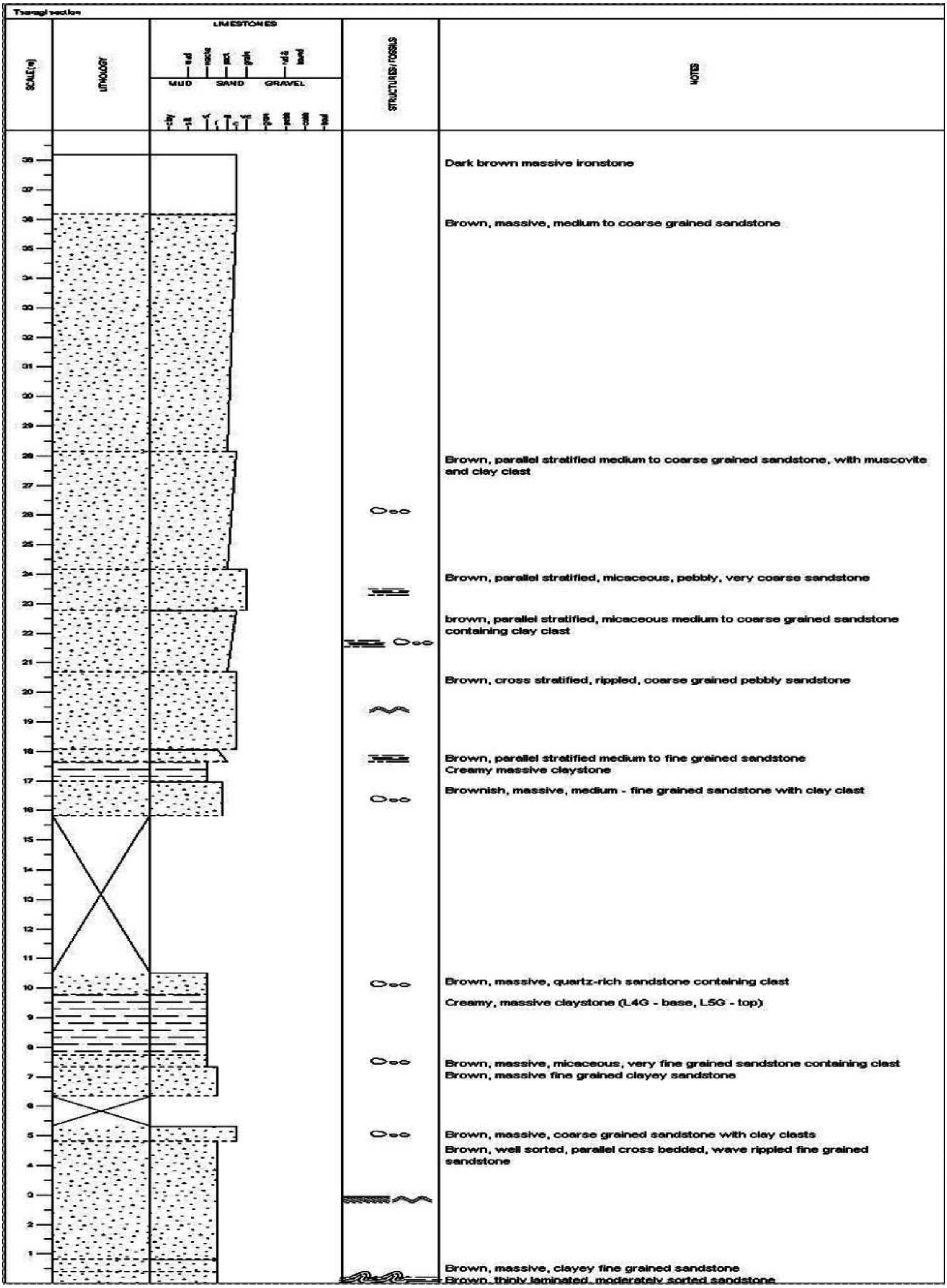


Fig. 4a: Lithologic sections at Tsaragi end of the Agbona Ridge (Latitude: 8049’32.2”, Longitude: 4058’ 36.2”; Elevation: 321m (cont’d on next page).

Fig. 4b: Enagi Claystone exposed along erosional channel at Share

researchers (e.g. Floyd and Leveridge, 1987; Floyd *et al.*, 1989; McLennan *et al.*, 1993; Okunlola and Olubunmi, 2012; Adepoju *et al.*, 2020; Liu *et al.*, 2021; Ojo *et al.*, 2021) to determine the detrital sediment's source area composition using their bulk geochemical compositions of major, trace and rare earth elements. Geochemical discrimination diagrams presented on binary and ternary plots using abundances of selected element have also been employed by previous workers including Lopez *et al.* (2005) and Pe-Piper *et al.* (2008) to infer the tectonic setting of source rocks to a clastic sedimentary basin and the amount of weathering that the detrital sediments have undergone. For example, McLennan *et al.* (1993) stated that Ti which usually concentrates in phyllosilicate minerals is less mobile compared to other major elements during sedimentary processes. Application of this proposal in the present

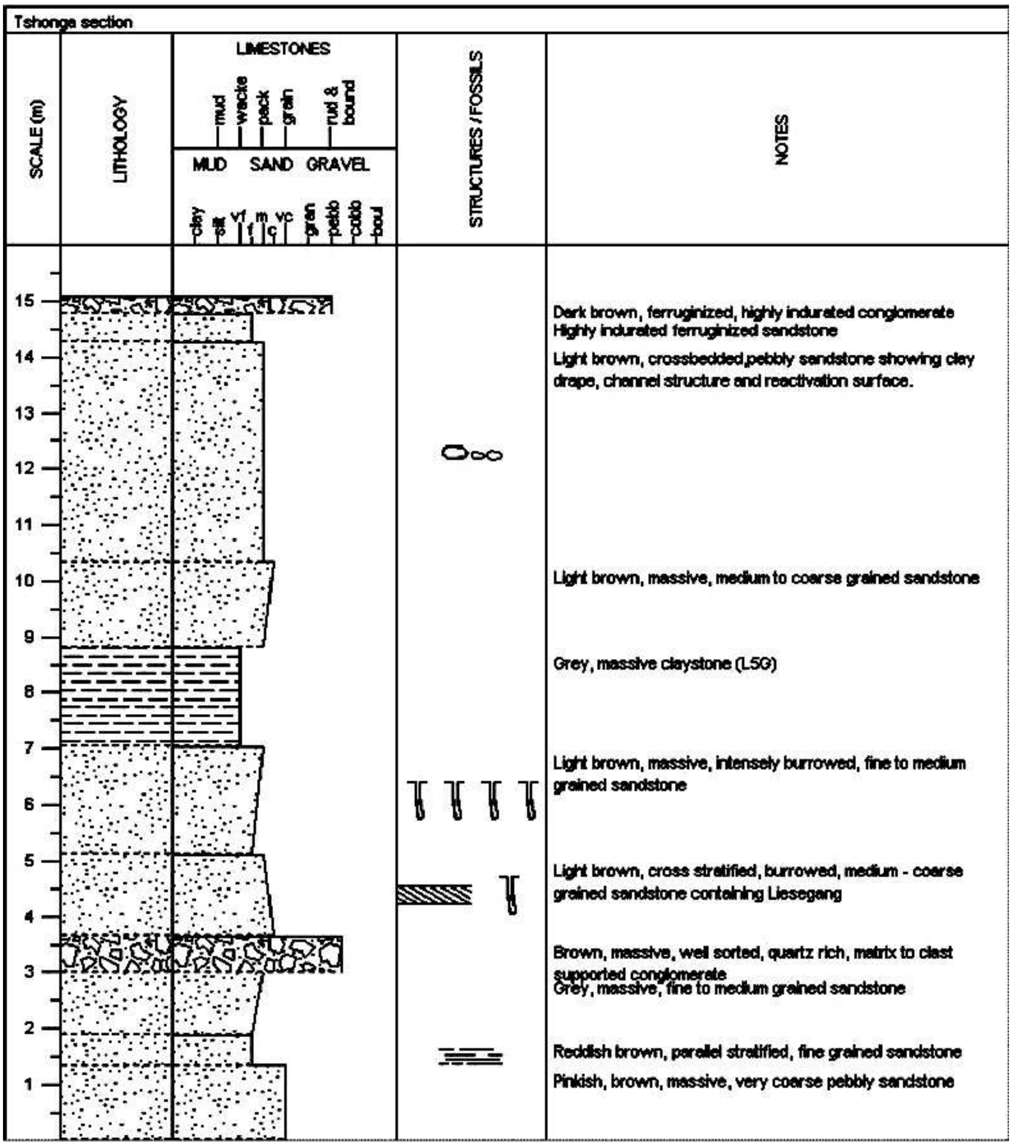
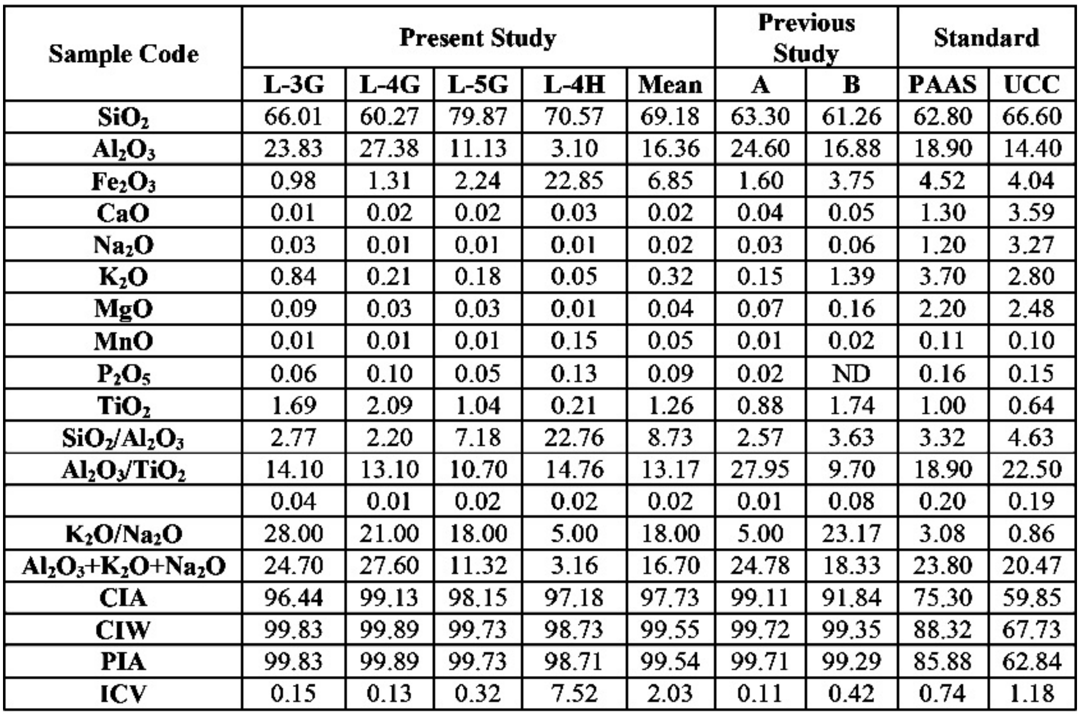


Fig. 5: Lithologic sections at Tshonga (Latitude: 4001' 28.8", Longitude: 5008' 48.1"; Elevation: 101 m).

Table 1: Major elemental composition and calculated proxies for the studied samples

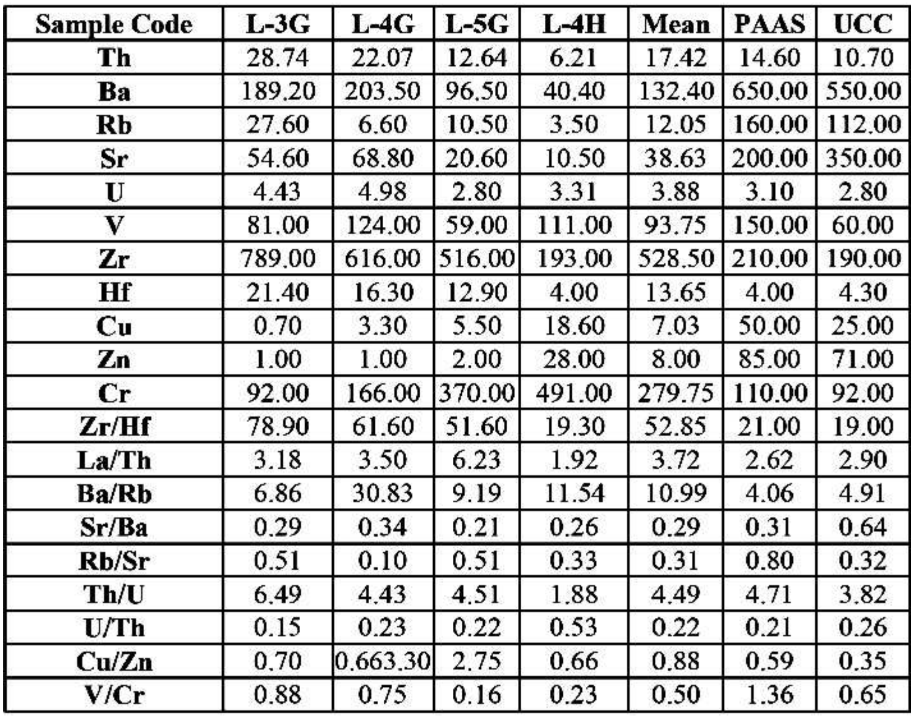


Sample Code	Present Study					Previous Study		Standard	
	L-3G	L-4G	L-5G	L-4H	Mean	A	B	PAAS	UCC
SiO_2	66.01	60.27	79.87	70.57	69.18	63.30	61.26	62.80	66.60
Al_2O_3	23.83	27.38	11.13	3.10	16.36	24.60	16.88	18.90	14.40
Fe_2O_3	0.98	1.31	2.24	22.85	6.85	1.60	3.75	4.52	4.04
CaO	0.01	0.02	0.02	0.03	0.02	0.04	0.05	1.30	3.59
Na_2O	0.03	0.01	0.01	0.01	0.02	0.03	0.06	1.20	3.27
K_2O	0.84	0.21	0.18	0.05	0.32	0.15	1.39	3.70	2.80
MgO	0.09	0.03	0.03	0.01	0.04	0.07	0.16	2.20	2.48
MnO	0.01	0.01	0.01	0.15	0.05	0.01	0.02	0.11	0.10
P_2O_5	0.06	0.10	0.05	0.13	0.09	0.02	ND	0.16	0.15
TiO_2	1.69	2.09	1.04	0.21	1.26	0.88	1.74	1.00	0.64
SiO_2/Al_2O_3	2.77	2.20	7.18	22.76	8.73	2.57	3.63	3.32	4.63
Al_2O_3/TiO_2	14.10	13.10	10.70	14.76	13.17	27.95	9.70	18.90	22.50
	0.04	0.01	0.02	0.02	0.02	0.01	0.08	0.20	0.19
K_2O/Na_2O	28.00	21.00	18.00	5.00	18.00	5.00	23.17	3.08	0.86
$Al_2O_3+K_2O+Na_2O$	24.70	27.60	11.32	3.16	16.70	24.78	18.33	23.80	20.47
CIA	96.44	99.13	98.15	97.18	97.73	99.11	91.84	75.30	59.85
CIW	99.83	99.89	99.73	98.73	99.55	99.72	99.35	88.32	67.73
PIA	99.83	99.89	99.73	98.71	99.54	99.71	99.29	85.88	62.84
ICV	0.15	0.13	0.32	7.52	2.03	0.11	0.42	0.74	1.18

A – Share-Agbaja Clay, Bida Basin (Ojo et al., 2011)

B - Patti Formation Clay-Shale member, Southern Bida Basin (Okunlola and Olubunmi, 2012)

Table 2: Trace element (ppm) distribution and calculated ratio of the analyzed claystone



Sample Code	L-3G	L-4G	L-5G	L-4H	Mean	PAAS	UCC
Th	28.74	22.07	12.64	6.21	17.42	14.60	10.70
Ba	189.20	203.50	96.50	40.40	132.40	650.00	550.00
Rb	27.60	6.60	10.50	3.50	12.05	160.00	112.00
Sr	54.60	68.80	20.60	10.50	38.63	200.00	350.00
U	4.43	4.98	2.80	3.31	3.88	3.10	2.80
V	81.00	124.00	59.00	111.00	93.75	150.00	60.00
Zr	789.00	616.00	516.00	193.00	528.50	210.00	190.00
Hf	21.40	16.30	12.90	4.00	13.65	4.00	4.30
Cu	0.70	3.30	5.50	18.60	7.03	50.00	25.00
Zn	1.00	1.00	2.00	28.00	8.00	85.00	71.00
Cr	92.00	166.00	370.00	491.00	279.75	110.00	92.00
Zr/Hf	78.90	61.60	51.60	19.30	52.85	21.00	19.00
La/Th	3.18	3.50	6.23	1.92	3.72	2.62	2.90
Ba/Rb	6.86	30.83	9.19	11.54	10.99	4.06	4.91
Sr/Ba	0.29	0.34	0.21	0.26	0.29	0.31	0.64
Rb/Sr	0.51	0.10	0.51	0.33	0.31	0.80	0.32
Th/U	6.49	4.43	4.51	1.88	4.49	4.71	3.82
U/Th	0.15	0.23	0.22	0.53	0.22	0.21	0.26
Cu/Zn	0.70	0.663.30	2.75	0.66	0.88	0.59	0.35
V/Cr	0.88	0.75	0.16	0.23	0.50	1.36	0.65

Table 3: Rare earth element (ppm) distribution of the analyzed claystone

Sample Code	L-3G	L-4G	L-5G	L-4H	Mean	PAAS	UCC
La	91.40	77.30	78.70	11.90	64.83	38.20	31.00
Ce	158.60	149.20	135.80	36.10	119.93	79.60	63.00
Pr	15.85	16.89	17.57	2.49	13.20	8.83	7.10
Nd	50.10	60.80	58.40	8.70	44.50	33.90	27.00
Sm	7.49	11.64	9.89	1.65	7.67	4.55	4.70
Eu	1.34	2.28	1.75	0.29	1.42	1.08	1.00
Gd	7.61	10.42	8.43	1.60	7.02	4.66	4.00
Tb	1.20	1.47	1.13	0.24	1.01	0.77	0.70
Dy	8.19	8.67	6.26	1.40	6.13	4.68	3.90
Ho	1.79	1.61	1.27	0.27	1.24	0.99	0.83
Er	5.35	4.43	3.62	0.79	3.55	2.85	2.30
Tm	0.81	0.65	0.52	0.09	0.52	0.41	0.30
Yb	5.45	4.35	3.40	0.83	3.51	2.82	2.00
Lu	0.82	0.64	0.54	0.12	0.53	0.43	0.31
∑REE	356.00	350.35	327.28	66.47	275.03	184.77	148.14
∑LREE	323.44	315.83	300.36	60.84	250.12	165.08	132.80
∑HREE	31.22	32.24	25.17	5.34	23.49	17.61	14.34
∑LREE/∑HREE	10.36	9.80	11.93	11.39	10.65	9.37	9.26
Eu/Eu*	0.54	0.63	0.59	0.55	0.58	0.71	0.72
Ce/Ce*	0.87	0.92	0.83	1.47	1.02	2.17	2.12
$(La/Yb)_N$	11.31	11.98	15.60	9.67	12.14	9.43	9.26

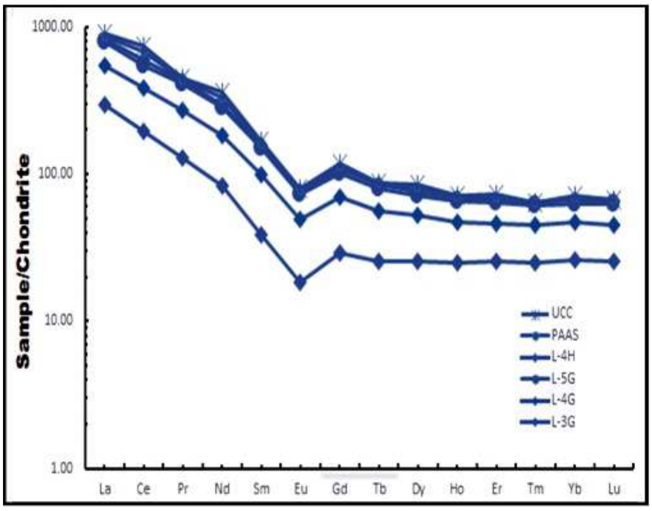


Fig. 6: Chondrite Normalized Rare Earth Elements plot of the studied claystone

study reveal that relatively similar TiO_2 concentrations (0.21-2.09 %; Mean-1.26 %) compare to the average values of PAAS (1.00 %) and UCC (0.64 %) is a strong indication in support of felsic igneous rocks contributions in the source area. Garcia *et al.* (1994) and Andersson *et al.* (2004) employed values of Al_2O_3/TiO_2 ratio as a geochemical indicator to determine and recognize the sources sedimentary rocks. Hayashi *et al.* (1997) proposed range of values for Al_2O_3/TiO_2 ratio from 3.00 to 8.00 for mafic rocks, 8.00 to 21.00 for intermediate rocks and 21.00–70.00 for felsic igneous rocks. The range of concentrations of Al_2O_3/TiO_2 ratio from 10.70 to 14.76 and the calculated mean (13.17) in the present study fits more into the intermediate igneous rock provenance. Cox *et al.* (1995) opined that K_2O/Al_2O_3 ratio in sedimentary rocks can be used to infer original composition of ancient sediments because sediments rich in clay minerals have values less than 0.30 while values in feldspars rich sediments have values between 0.30 and 0.90. The calculated values of K_2O/Al_2O_3 ratio in the present study show ranges between 0.01 and 0.04 (Table 1) which indicate dominance of clay minerals constituents in the claystone.

Feng and Kerrich (1990) stated that ferromagnesian trace elements (e.g. Cr and V) are characterized by high fractionation and this is reflected in this study as the claystone possess higher values of Cr (92.00-491.00) and V (59.00-124.00) which indicate contribution from felsic than basic igneous source region. The ratio of trace element like Cr/V play important role in differentiating felsic from mafic sources and according to McLennan *et al.* (1993), the ratio less than 8.00 signify felsic source while ratio above 8.00 signify mafic source. In the present study, the Cr/V ratio which ranges from 1.14 to 6.27, therefore, indicates felsic source. Several standard geochemical plots that employed major and trace elements compositions and their ratios including binary plots of TiO_2 versus Zr after Hayashi *et al.* (1997) and Hf versus La/Th after Floyd and Leveridge (1987) were considered to discriminate the provenance of the studied claystone. It is interested to note that all the diagrams show plots clustering close to the felsic igneous rock provenance field (Figures 7a and b). Rare earth elements (REE) can also be employed as a geochemical fingerprint in the determination of sedimentary rocks provenance according to Cullers (1994, 1995, 2002), Armstrong-Altrin *et al.* (2004, 2013), Roy *et al.* (2008), Liu *et al.* (2015) and Madhavaraju *et al.* (2016). Cullers (1994) concluded that in mafic igneous rocks, the ratio of LREE/HREE is usually low with positive Eu anomalies whereas higher values with negative Eu anomalies characterize the felsic igneous rocks. In this study**,** the high LREE/HREE ratio (9.80-11.93) with negative values of Eu anomaly (0.54-0.63) supports the felsic source rock provenances for the studied claystone.

Provenance of sedimentary claystone depends mostly on tectonic setting, weathering index, mobility elements during weathering and transportation of sediments from source rock (Bhatia, 1983). Bhatia (1983) concluded that sedimentary rocks from passive-margin tectonic setting are generally rich in SiO_2 and depleted in CaO, K_2O, Na_2O and TiO_2. In this study, the geochemical data reveal enrichment of SiO_2 relative to K_2O, Na_2O, CaO and TiO_2 (Table 1) and this may indicate a passive-margin tectonic setting in the source area. The standard binary plot of log(K_2O/Na_2O) versus SiO_2 after Roser and Korsch (1986) was also employed to discriminate the paleotectonic settings, and the plot presented in the figure 7c reveal that the claystones were sourced from passive margin tectonic settings.

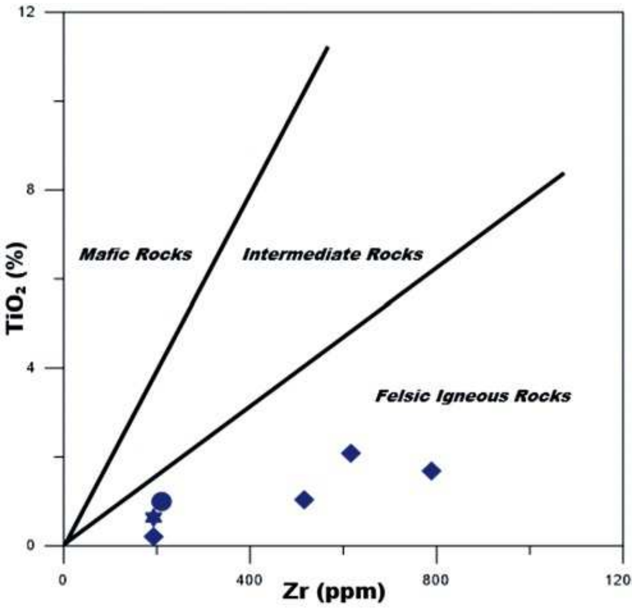


Fig. 7a: Plot of TiO_2 versus Zr after Hayashi *et al*. (1997).

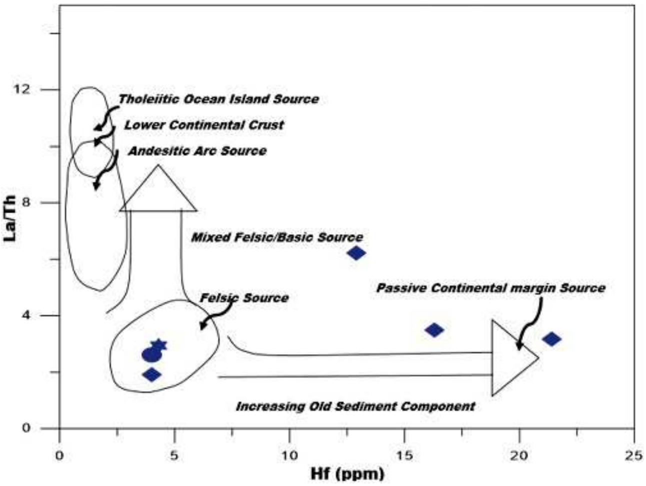


Fig. 7b: Binary plot of Hf versus La/Th after Floyd and Leveridge (1987) showing the studied claystone clustering near Felsic Field.

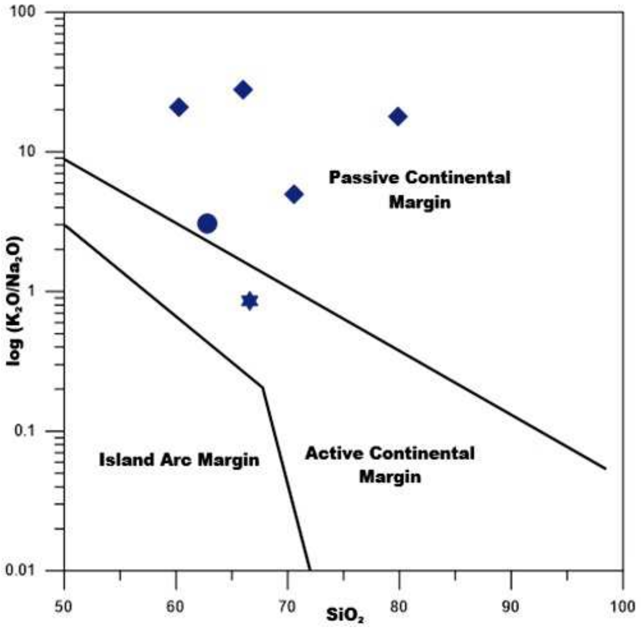


Fig. 7c: Binary plot of log(K_2O/Na_2O) versus SiO_2 after Roser and Korsch (1986) showing Passive Continental Margin.

Paleoweathering Condition

Major element composition of sedimentary rocks can be strongly influenced by the weathering intensity in the source area according to Nesbitt and Young (1982) and McLennan *et al.* (1993). According to Nesbitt and Young (1982), the mobile elements (e.g. Na and Ca) can be used to evaluate the chemical weathering intensity and characterize the paleoclimatic conditions in source area during deposition. Nesbitt and Young (1984) reported that weathering history of sediments and sedimentary rocks can be evaluated by the ratios of immobile oxides (e.g. Al_2O_3) to mobile components (e.g. CaO, Na_2O and K_2O). Geochemical indices that are customarily utilized by various researchers to evaluate the weathering intensity of sedimentary rocks include; chemical index of alteration (CIA) proposed by Nesbitt and Young (1982), chemical index of weathering (CIW) proposed by Depetris and Probst (1998) and plagioclase index of alteration (PIA) proposed by Fedo *et al.* (1995). Nesbitt and Young (1982) concluded that CIA is a geochemical indicator to monitor progressive alteration of primary feldspars to clay minerals, he proposed calculated values from 76 to 100 as an intense chemical weathering in the source area whereas values from 50 to 76 and less than 50 indicate moderate weathering and chemically unweathered source sediments respectively. Depetris and Probst (1998) stated that to measure the rate of CIW of sedimentary rocks, values less than 50 indicate chemically unweathered source rock, while values ranging between 51 and 75 and greater than 75 indicate moderate weathering and strong weathering respectively. In this study, the calculated values of CIA, CIW and PIA ranges from 96.44 to 99.13%, 98.73 to 99.89% and 98.71 to 99.89% respectively (Table 1) indicate intense weathering at the source area or long transportation history for the claystone. Application of the binary plots of PIA versus CIA (Figure 8a) after Abedini and Calagari (2017) and the ternary A-CN-K [(Al_2O_3-($CaO+Na_2O$)-K_2O)] plot (Figure 8b) after Nebsitt and Young (1982) show an advanced weathering from the source for the investigated claystones.

The relationship between Thorium (Th) and Uranium (U) and the concentration of their ratio (Th/U) can also be employed as an estimator of the degree of weathering in sedimentary rocks Taylor and McLennan (1985). McLennan *et al.* (1993, 1995) and Gu *et al.* (2002) employed the Th/U ratio to interpret weathering history of sedimentary rocks due to the oxidation and loss of uranium during the weathering process. According to McLennan and Taylor (1991), sedimentary rocks with Th/U values higher than 4.0 indicate intense weathering in the source areas or sediment recycling, while values below 3.5 is interpreted as indication of low weathering in the source areas. In this study, the calculated Th/U values for the claystones ranges from 1.88 to 6.49 and this is an indicative of progressive weathering from low to an intense weathering in the source area.

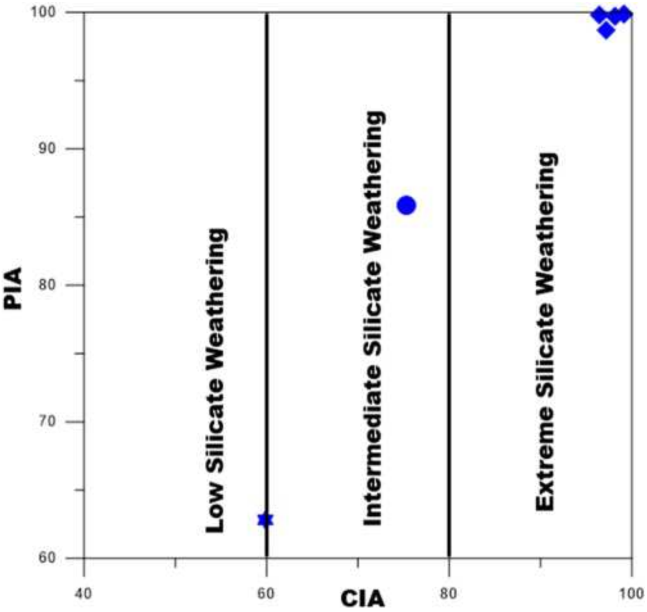


Fig. 7a: Binary plot of PIA versus CIA after Abedini and Calagari (2017) showing intense weathering for the studied claystone.

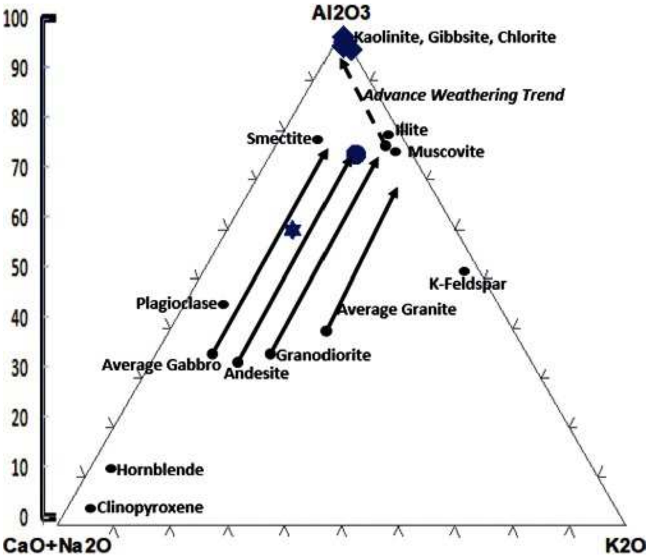


Fig. 8b: Ternary plot of Al_2O_3-$CaO+Na_2O$-K_2O diagram after Nebsitt and Young (1982) showing (modify diagram).

Paleo-Redox and Paleoenvironmental Conditions

The paleo-redox conditions during deposition of sediments can be assessed according to Wignall and Myers (1988), Tribovillard *et al.* (2006) and Yang *et al.* (2011) using some trace element proxies including Cu/Zn, V/Cr, V/(V+Ni), U and U/Th. Hallberg (1976) and Nagarajan *et al.* (2007) stated that high and low values of Cu/Zn ratios indicate reducing and oxidizing conditions of depositional environments respectively. The calculated Cu/Zn ratios (Table 3) for the studied claystones are low (0.66-3.30), indicating oxic conditions of the depositional environment. Jones and Manning (1994) concluded that V/Cr ratios of less than 2.00, 2.00-4.25 and greater than 4.25 are regarded respectively as oxic, dysoxic, and suboxic-anoxic paleo-redox conditions. The V/Cr ratios in this study (0.16-0.88) as presented in table 3 indicate prevalence of oxic conditions during the deposition of the studied claystones. Nath *et al.* (1997) concluded U/Th ratios with the values less than 1.25 are suggested for oxic paleo-depositional conditions whereas values greater than 1.25 are indicative of anoxic to suboxic conditions. The calculated U/Th value in this study (0.15-0.53) indicates that the studied claystones were deposited mainly under oxic paleo-depositional conditions. Also, application of V/Cr versus U/Th plot proposed by Jones and Manning (1994) was also employed in this study and the diagram presented in figure 9a shows that the studied claystones were deposited during oxic condition.

Strontium (Sr) and Barium (Ba) are used as empirical paleo-salinity indicators and according to Wang (1996), high Sr/Ba ratio reflects high salinity whereas low values indicate low salinity. Chunrui *et al.* (2007) employed Sr/Ba ratio for the paleo-environmental discrimination, with 1.0 ppm been the boundary between the fresh water and salt water marine environment. The calculated Sr/Ba values in this study vary from 0.21 to 0.34 which is greater than 1.00, therefore, indicating fresh water environment of deposition. Generally, non-marine clay minerals are differentiated from marine clay minerals by their low concentration of MgO with relative high concentration of SiO_2 and Fe_2O_3 while marine clay minerals have high concentration of MgO with the relative low concentration of SiO_2 and Fe_2O_3. Binary plots of $\log(K_2O/Al_2O_3)$ versus $\log(MgO/Al_2O_3)$ proposed by Roaldest (1978), Fe_2O_3 versus MgO and ternary plot of Fe_2O_3-MgO-SiO_2/Al_2O_3 proposed by Ratcliffe *et al.* (2007) were employed in this study and the diagrams indicate non-marine environment as the source of the studied clay (Figures 9b, c and d). The binary plots of SiO_2 versus $Al_2O_3+Na_2O+K_2O$ and K_2O/Na_2O versus CIA proposed by Suttner and Dutta (1986) and reveal that the studied claystones were sourced within semi-humid to humid/warm paleoclimatic condition (Figures 9e and f).

Conclusion

Based on the studies of bulk inorganic elemental compositions of major, trace and rare earth elements of claystone member of the Enagi Formation in the Northern Bida Basin, North central Nigeria, the following conclusions are drawn:

(1) The major elements geochemical proxies' signatures are consistent with felsic provenance source rocks. Relatively high TiO_2 contents

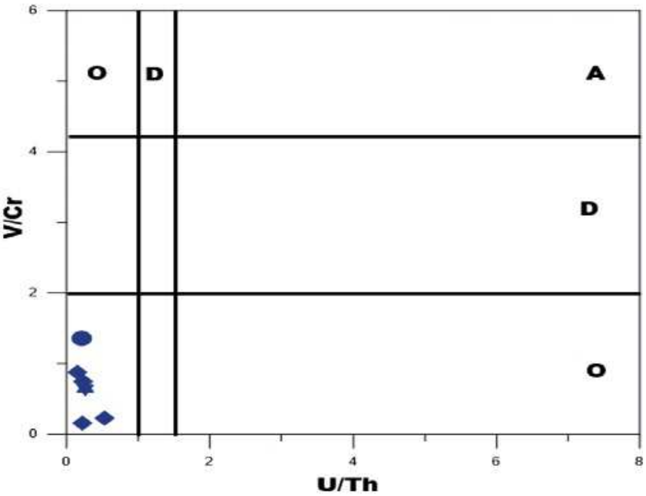


Fig. 9a: Cross plot of V/Cr versus U/Th ratio of study clays used as paleo-oxic proxies after Jones and Manning (1994). NB: O – Oxic, D –Dysoxic, A – Anoxic

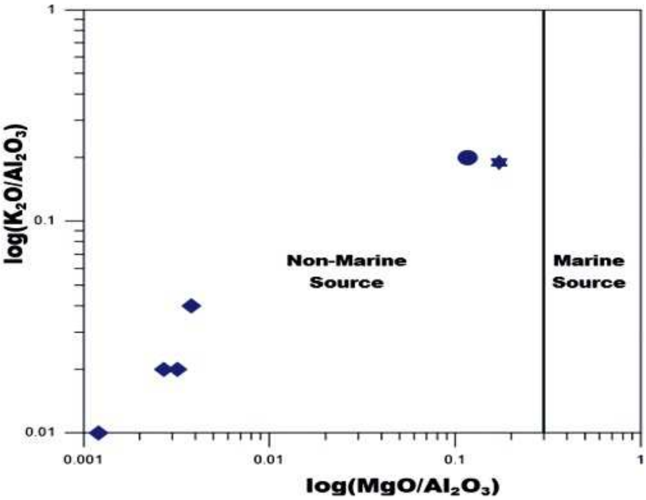


Fig. 9b: Depositional environment of Enagi Claystones after Roaldest (1978).

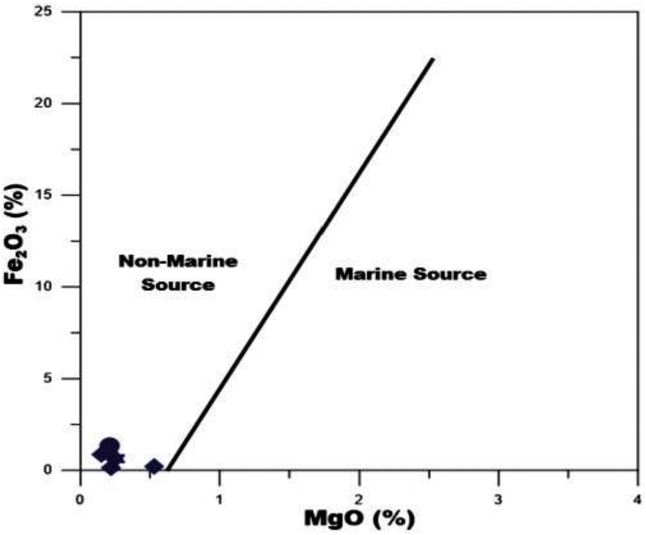


Fig. 9c: Binary diagram of depositional environment discrimination after Ratcliffe et al. (2007).

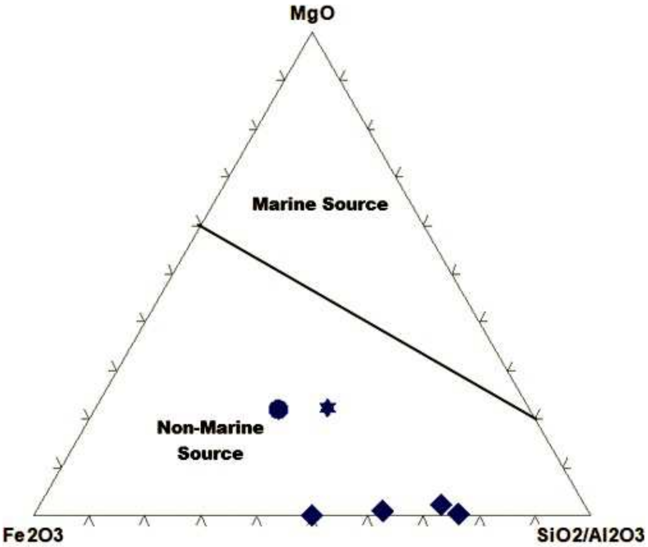


Fig. 9d: Ternary diagram of depositional discrimination after Ratcliffe *et al.* (2007).

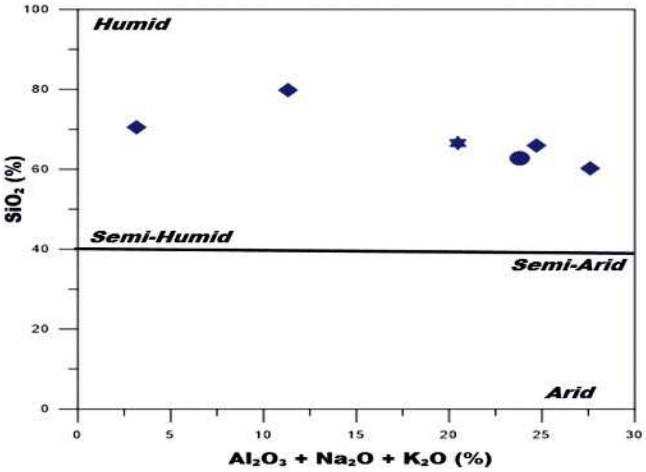


Fig. 9e: Plot of SiO_2 versus (Al_2O_3+K_2O+Na_2O) after Suttner and Dutta (1986).

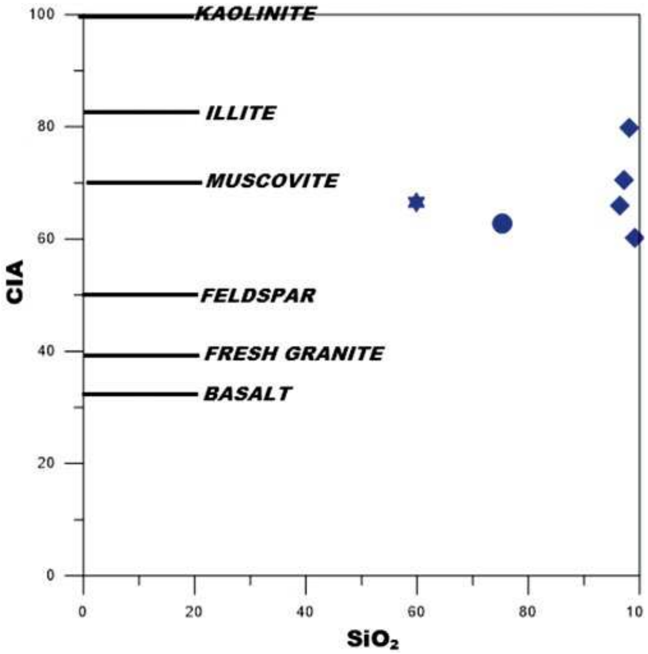


Fig. 9f: Plot of SiO_2 versus CIA after Suttner and Dutta (1986).

with other trace elements ratios and their plots also support felsic source rocks from a passive continental margin.

(2) High weathering index values including CIA, PIA and CIW and paleo-weathering diagrams indicate sediments' intense alteration/ weathering in tropical humid setting.

(3) The investigated claystones were deposited in non-marine depositional settings and oxic conditions.

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