Geochemical assessment of claystone deposits from the Patti Formation, Southern Bida Basin, Nigeria

Geokemična opredelitev plasti glinavca formacije Patti v južni kadunji Bide v Nigeriji

Ohanyiri C. Chiemezie*, Omotowo B. Aminat

Department of Geology, University of Ibadan, Ibadan, P.M.B. 5116, Oyo State, Nigeria
* emezieohans@gmail.com

Abstract

Geochemical studies of claystone deposits from the Patti Formation in the southern Bida Basin, north-Central Nigeria, were carried out on representative samples to determine the basin's depositional conditions, provenance and tectonic setting. The localities within the study area included Gegu, Ahoko, Ahoko-Etigi, Omu and Idu.

Semi-quantitative phase analysis using the Rietveld method and X-ray powder diffraction data revealed that the claystone samples had prominent kaolinite with other constituents such as quartz, illite–muscovite, K-feldspar, pyrite, marcasite, anatase, rutile and gorceixite.

Enrichment of Al_2O_3, Ba, Th, Sr, Cr and La suggests that these elements are primarily controlled by the dominant clay minerals.

Geochemical parameters such as U, U/Th, Ni/Co, V/Cr and Cu/Zn ratios strongly implied that these claystones were deposited in an oxidising environment. Provenance deducing ratios for felsic, mafic and basic igneous rocks were compared. Al_2O_3/TiO_2 ratio suggested intermediate to felsic rocks as the probable source rocks for the claystone samples; however, Y/Ni, Cr/V, La/Sc and Th/Sc ratios suggested a felsic progenitor. The tectonic discrimination diagram showed that the samples' plot was within the region specified for passive margin-type tectonic setting.

Key words: claystone, geochemical, tectonic, provenance, paleo-oxygenation

Povzetek

Geokemične raziskave plasti glinavca formacije Patti v južni kadunji Bida v severnem delu osrednje Nigerije smo izvedli na reprezentativnimh vzorcih z namenom ugotoviti sedimentacijske razmere v kadunji, izvor snovi in tektonsko lego. Večji kraji v proučevanem ozemlju so Gegu, Ahoko, Ahoko-Etigi, Omu in Idu.

Semikvantitativna analiza z Rietveldovo metodo in rezultati praškovne rentgenske difrakcije pričajo o prevladujočem kaolinitu v vzorcih glinavca in o prisotnosti nadaljnjih mineralov, kot so kremen, illit-muskovit, kalijev glinenec, pirit, markazit, anataz, rutil in gorceixit.

Obogatitve Al_2O_3, Ba, Th, Sr, Cr in La nakazujejo, da so vsebine teh prvin odvisne predvsem od prevladujočih glinenih mineralov.

Geokemični parametri kot U in razmerja U/Th, Ni/Co, V/Cr in Cu/Zn pričajo o tem, da so bili glinavci odloženi v oksidnem okolju. Primerjali smo razmerja, ki nakazujejo izvorne magmatske kamnine. Razmerje Al_2O_3/TiO_2 kaže, da so matične kamnine glinavcev prehodne do felzične magmatske kamnine, Y/Ni, Cr/V, La/Sc in Th/Sc pa nakazujejo felzični izvor. Vzorčne točke, nanešene v tektonskem diskriminacijskem diagramu, so na področju značilnem za tektonsko lego tipa pasivnega roba.

Ključne besede: glinavec, geokemija, tektonska lega, izvor, paleo-oksidacijske razmere

Introduction

Claystone is a fine grained, dark grey to pink sedimentary rock mainly consisting of compacted and hardened clay. According to Gary [1], if it can be determined that most of the particles of a rock (over two-thirds) are clay sized, the rock may then be called a claystone.

Geochemical parameters have been used by several authors to decipher paleo-oxygenation conditions of ancient sediments [2–7]. Redox parameters such as Cu/Zn ratio was proposed by Hallberg [8], while U/Th ratio was proposed by Jones and Manning [3]. Hayashi et al. [9] noted that Al_2O_3/TiO_2 ratio is essentially used to infer source rock composition with various ranges given for mafic, intermediate and felsic igneous rocks.

On the basis of mean crustal abundance, geological elements are classified as major, minor and trace elements based on their percentage composition by mass in rocks. Some researchers noted that major element geochemistry of sedimentary rocks is more important in discriminating tectonic setting [10–11]; however, trace elements are more useful in discriminating tectonic evolution of rocks and the provenance of clastic materials [12]. Gritty et al. [13] attributed this to their low mobility during sedimentary depositional processes.

This study aimed at identifying the depositional environment, provenance and tectonic setting of the claystones of the Patti Formation, southern Bida Basin, North-Central Nigeria, using major and trace element geochemistry as well as clay speciation analysis.

Geology and stratigraphy

The Bida Basin as depicted in Figure 1 is a linear northwest–southeast trending intracratonic sedimentary basin extending from Kontagora in the Niger State of Nigeria to areas slightly beyond Lokoja in the south and is approximately perpendicular to the Benue Trough. It is delimited in the northeast and southwest by the basement complex, while it merges with Anambra Basin (in the north) and Sokoto Basin (in the south) in sedimentary fill comprising post-orogenic molasse facies and few thin un-folded marine sediments. The basin is frequently regarded as the north-western extension of the Anambra Basin [14–16], both of which were major depocentres during the third major transgressive cycle of southern Nigeria in Late Cretaceous time.

Adeleye [17] noted that the basin is a gently downwarped trough whose genesis may be closely connected with the Santonian orogenic movements of southeastern Nigeria and the Benue valley nearby, while Whiteman [14] and Okunlola and Olubunmi [18] suggested that the basin was formed from simple cratonic sag. Agyingi [19] proposed a post-Santonian origin for the basin stating that the sediments in the basin were generally undisturbed as in the case of the post-Santonian sediment of the adjacent Sokoto Basin and Anambra Basin.

Two main rock types found in the Bida Basin include crystalline basement rock and sedimentary rock. The crystalline rock that includes gneiss, granite, marble and quartzite are of Precambrian to early Palaeozoic age [20].

Adeleye and Dessauvagie [21] specified that overlying the basement complex are poorly exposed basal beds of coarse conglomerate and cross-stratified sandstones with angular pebbles. Conformably, overlying these basal beds are continental sediments mainly comprising sandstones, siltstones and claystones. Often, experts working in the area have divided the basin geographically into northern and southern Bida Basin [19, 22, 23], probably due to rapid changes in facies across the basins. The southern Bida Basin comprises the basal Campanian Lokoja Formation (mainly conglomerate and sandstone), Maastrichtian Patti Formation (shale, claystone and sandstone) and the youngest Agbaja Formation (ironstone). Their lateral stratigraphic equivalents in the northern Bida Basin consist of the basal Bida Formation (conglomerate and sandstone), Enagi Formation (siltstone, claystone and sandstone) and Batati Formation (ironstone) as exemplified in Figure 2. The present study correlates with the Enagi Formation.

Prominent features and structures in the basin include unconformity surfaces (nonconformity), different forms of beddings (parallel beddings, cross beddings and graded beddings), deformation, diagenetic features and fractures.
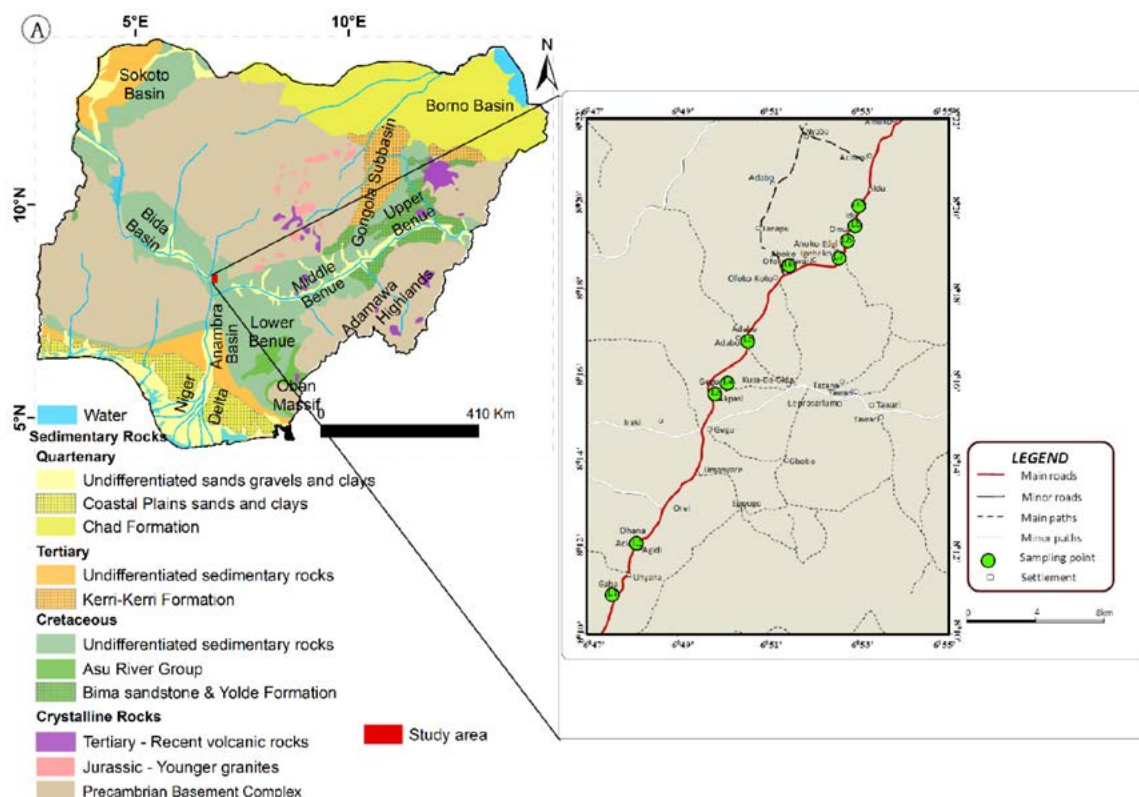
Figure 1: *Generalised geologic map of Nigeria showing sampling locations (modified after Adelana et al. [25] and Fagbohun et al. [26]).*

Figure 2: *Stratigraphic successions in the mid-Niger Basin (adapted from Akande et al. [16]).*

Initial gravity studies in the Bida Basin by Ojo [24] put the maximum thickness of the sedimentary successions at about 3.500 m in the central axis, while Agyingi [19] from aeromagnetic interpretation recorded a maximum sedimentary thickness of about 3.300 m.

Data and methods

The field investigation was carried out on exposed clay sections cut open by the Lokoja–Agbaji road with an effort made to obtain fresh samples for laboratory studies. The studied locations lie within the Patti Formation in the southern Bida Basin. A total of 23 representative samples were selected and used for this study.

Geochemical characterisation involved analysing 20 representative samples at Acme Analytical Laboratories Limited, Vancouver, Canada, for major and trace element concentrations using ultratrace inductively coupled plasma–mass spectrometer (ICP–MS; Perkin-Elmer 6000) and inductively coupled plasma–mass spectrograph.

Table 1: *Results of semi-quantitative phase analysis (wt.%).*

Mineral	Ideal formula	S1	S6a	S7a
Quartz	SiO_2	31	14	18
Kaolinite	$Al_2Si_2O_5(OH)_4$	58	80	69
Illite–Muscovite 2M1	$K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_2$–$KAl_2AlSi_3O_{10}(OH)_2$	4	2	3
K-feldspar	$KAlSi_3O_8$	4	3	7
Pyrite	FeS_2	0.3	-	-
Marcasite	FeS_2	1	-	-
Anatase	TiO_2	2	1	2
Rutile	TiO_2	-	-	1
Gorceixite	$BaAl_3(PO_4)(PO_3OH)(OH)_6$	-	-	1
Total		100	100	100

Aqua regia digestion was done by weighing 0.2 g aliquot into a graphite crucible and mixing with 1.5 g $LiBO_2/Li_2B_4O_7$ fusion. The crucibles were placed in an oven and heated at 98°C for 30 minutes. The cooled bead was dissolved in 5% HNO_3 (ACS grade nitric acid diluted with demineralised water) and then calibrated standard and reagent blanks were added to sample sequences.

Geochemical analysis using ultratrace ICP–MS analysis consisting of the elements Co, Mn, Fe, U, Th, Sr, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W, Sc, S, Te and Ga was carried out on the claystone samples. A second 0.5 g sample split was digested in aqua regia and analysed by ICP–MS to determine Ag, Au, As, Bi, Cu, Cd, Mo, Hg, Pb, Ni, Sb, Se, Tl and Zn. An ICP emission spectrograph (Spectro Ciros Vision) was used for the determination of the basic package consisting of the following major oxides and elements: MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3, Ba, Ni, Sr, Zr, Y, Nb and Sc. Loss on ignition (LOI) was determined by heating a predetermined amount of sample at 950°C for 90 minutes.

Quantitative phase analysis using the Rietveld method and X-ray powder-diffraction data was carried out on three representative clay samples. The samples were pulverised and reduced to the optimum grain-size range for quantitative X-ray analysis (<10 mm) by grinding using ethanol in a vibratory McCrone Micronising Mill for 10 minutes. Step-scan X-ray powder diffraction data were collected over a 2θ range of 3–80° with CoKα radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident and diffracted-beam Soller slits and a LynxEye XE detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA using a take-off angle of 6°. The X-ray diffractograms were then analysed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker and refined with Rietveld program Topas 4.2 (Bruker AXS).

Results and discussion

Clay mineralogy

The mineralogy of the claystone samples was revealed by semi-quantitative phase analysis using Rietveld refinements plots (Table 1). These amounts represent the relative amounts of crystalline phases normalised to 100%. The Rietveld refinement plots are shown in Figures 3–5.

These plots revealed prominent kaolinite (average value of 66.0%) as the dominant mineral with minor amounts of quartz, illite-muscovite, K-feldspar, pyrite, marcasite, anatase, rutile and gorceixite. The relatively high proportion of kaolinite is attributable to the weathering of feldspar-rich rocks in the humid climatic
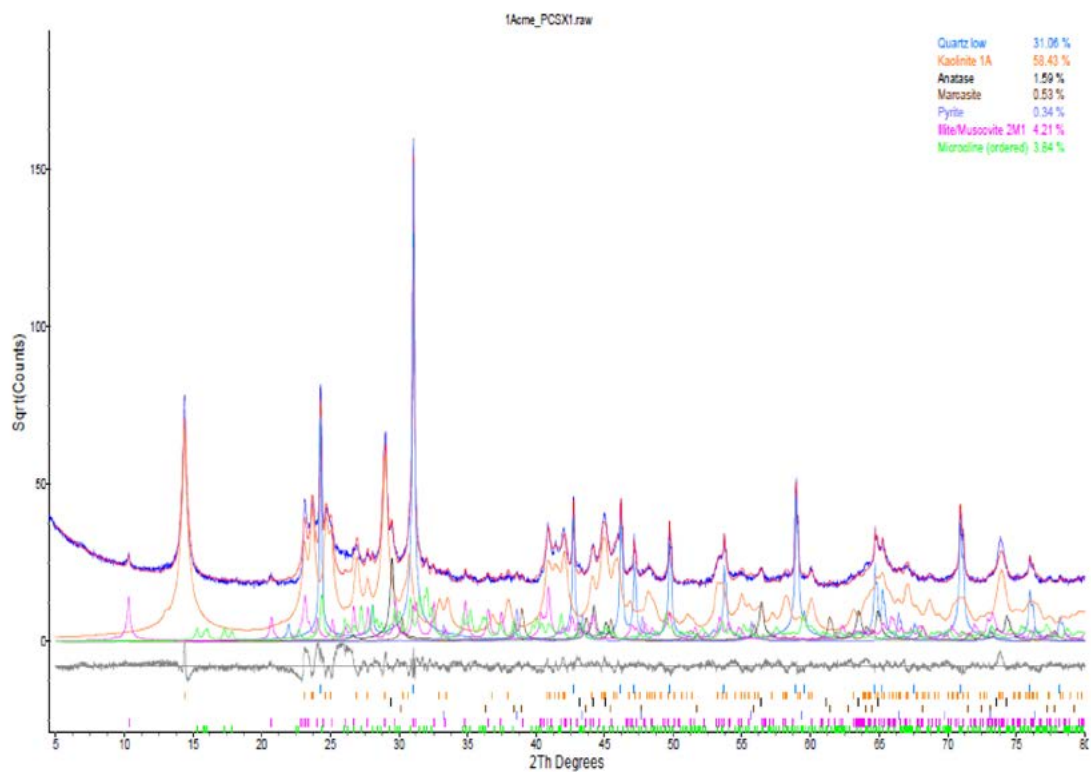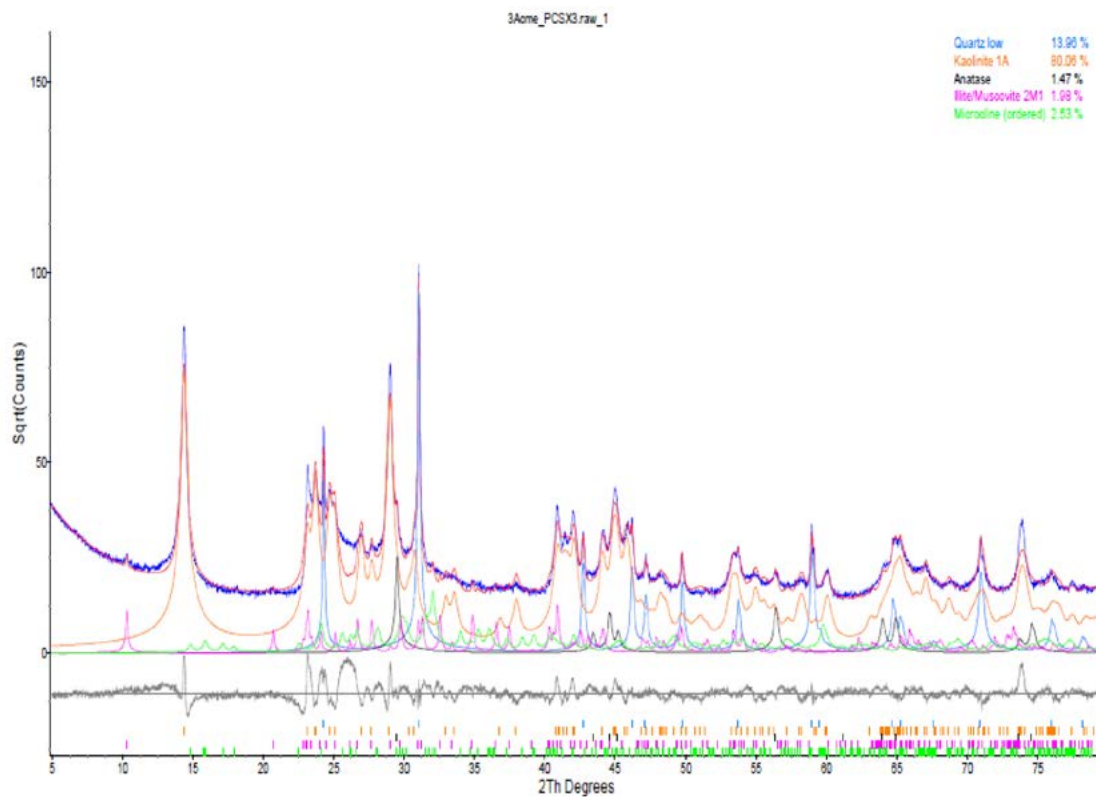
Figure 3: *X-ray diffractogram of sample S1.*

Figure 4: *X-ray diffractogram of sample S6a.*

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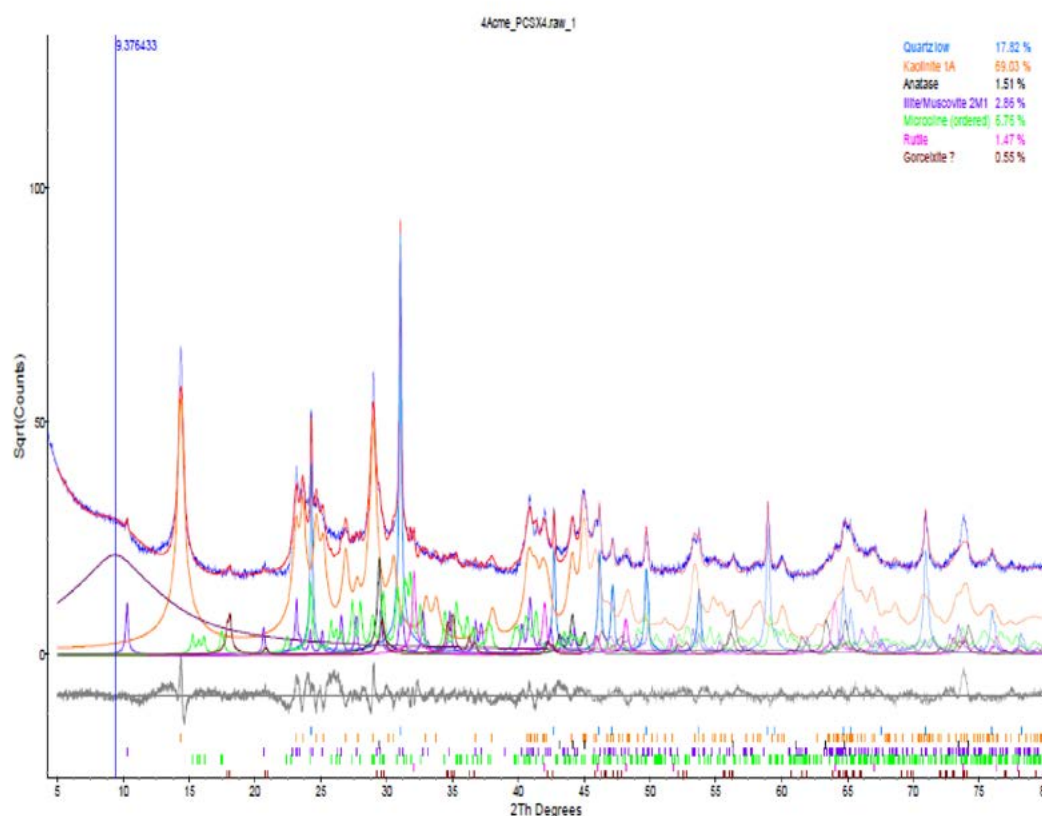
Figure 5: *X-ray diffractogram of sample S7a.*

setting [27]. The presence of kaolinite also suggests that the sediments were deposited in a continental or nearshore environment [28].

The blue lines in Figures 3–5 indicate the observed intensity at each step, red lines indicate calculated pattern, solid grey lines below indicate the difference between observed and calculated intensities and vertical bars indicate positions of all Bragg reflections. Coloured lines are the individual diffraction patterns of all phases.

Geochemistry

Major elements

Results of the major oxide analysis are summarised in Table 2. The claystones are rich in SiO_2, Al_2O_3 and Fe_2O_3 compared to K_2O, CaO, MgO, TiO_2 and Na_2O. The low concentration of K_2O (0.86%) indicates the low amount of illite or K-feldspar present [29], while the low content of CaO (0.05%) may be attributed to the absence of marine carbonate facies

in the associated sedimentary sequence [30]. Low Fe_2O_3+TiO_2+MgO value (average value of 1.23%) implies that the clays are chemically inert and non-corrosive [31]; therefore, they may offer good quality kaolin.

The K_2O/Al_2O_3 ratio of sediments can be used as an indicator of the original composition of ancient sediments. According to Cox et al. [32], K_2O/Al_2O_3 ratios for clay minerals and feldspars are different with values of 0.0–0.3 and 0.3–0.9, respectively. In this study, the K_2O/Al_2O_3 ratios for the claystones vary from 0.01 to 0.06, which are close to the lower limit of the clay mineral range.

Comparison of the average chemical compositions of the investigated clay samples with other known characterised clays showed that the Abraka clay [33] has higher SiO_2 (61.92%) values but lower Al_2O_3 (20.62%) values (Tables 3). Plastic fire clay, St. Louis [34], and Isan clay [35] have lower SiO_2 and higher Fe_2O_3 values. The investigated Fe_2O_3 concentration is generally low relative to the reference samples. The present

Table 2: *Major element composition for some of the claystone samples.*

	S1	S3b	S3c	S4a	S5a	S5c	S6a	S6b	S7a	S7b	Average
SiO_2	58.89	66.29	66.91	57.38	59.15	83.95	51.06	63.53	52.75	50.13	61.00
Al_2O_3	24.48	20.39	19.88	25.83	26.25	9.34	31.70	20.86	27.49	29.54	23.57
Fe_2O_3	3.27	1.17	1.26	1.16	1.25	0.57	1.37	1.60	2.99	3.05	1.77
MgO	0.11	0.11	0.14	0.13	0.10	0.05	0.11	0.22	0.55	0.49	0.20
CaO	0.04	0.08	0.06	0.16	0.06	0.01	0.02	0.02	0.03	0.03	0.05
Na_2O	0.03	0.06	0.04	0.05	0.05	0.04	0.02	0.06	0.05	0.04	0.04
K_2O	0.48	1.30	0.80	1.11	0.43	0.31	0.40	1.26	1.33	1.23	0.86
TiO_2	1.95	2.00	2.09	1.19	1.73	1.42	1.29	2.94	1.30	1.23	1.71
P_2O_5	0.08	0.07	0.04	0.38	0.04	0.04	0.05	0.07	0.24	0.18	0.12
MnO	0.01	0.02	0.01	0.01	<0.01	0.01	<0.01	0.01	0.01	<0.01	0.01
Cr_2O_3	0.016	0.012	0.012	0.018	0.015	0.007	0.015	0.016	0.019	0.023	0.02
LOI	1.4	8.2	8.6	11.5	10.7	3.8	13.9	9.2	13.0	13.9	10.32
Sum	99.76	99.70	99.84	98.92	99.79	99.55	99.95	99.79	99.76	99.85	99.70

LOI represents loss on ignition.

Table 3: *Average major element composition of the claystones compared to published works.*

Oxides	Present study on claystone	Abraka clay [33]	Plastic fire clay, St. Louis [34]	Isan clay [35]
SiO_2	61.00	61.92	57.67	60.47
Al_2O_3	23.57	20.62	24.00	17.77
Fe_2O_3	1.77	5.00	3.23	8.18
MgO	0.20	0.71	0.30	1.26
CaO	0.05	0.02	0.70	0.47
Na_2O	0.04	0.14	0.20	0.44
K_2O	0.86	0.63	0.50	1.17
TiO_2	1.71	3.20	-	-
P_2O_5	0.12	-	0.61	-
MnO	0.01	0.11	-	0.03
H_2O	-	10.69	-	9.72

study's Al_2O_3, MgO and K_2O values are comparable to plastic fire clay's values. The average SiO_2 (61.00%) and Al_2O_3 (23.57%) chemical composition in the clay samples constitutes about 84.57% of the samples' total composition. This shows that claystones are highly siliceous.

Provenance

Gritty et al. [13] noted that the low mobility of rare earth elements during weathering, transportation, diagenesis and metamorphism makes them suitable for determining provenance and tectonic setting. The trace element

Table 4: *Trace element distribution for some of the claystones from the study area (in ppm).*

	S1	S3b	S3c	S4a	S5a	S5c	S6a	S6b	S7a	S7b
Mo	0.14	0.26	<0.01	0.39	0.11	0.12	0.05	0.06	0.06	0.06
Cu	10.04	7.94	7.63	23.44	24.29	3.11	34.51	6.04	15.06	19.74
Pb	17.34	20.21	11.72	23.31	17.91	13.11	36.99	25.83	14.05	17.67
Zn	2.8	4.7	3.6	6.2	3.3	1.0	4.7	12.4	20.7	16.2
Ni	0.4	0.4	0.6	0.7	0.6	0.4	1.0	1.3	3.3	2.6
Co	0.2	0.4	0.5	0.4	0.2	0.2	0.4	0.9	2.4	1.8
Mn	7	15	8	15	2	4	7	11	33	19
U	4.2	1.3	2.3	8.1	5.7	2.0	3.1	1.6	3.0	5.5
Th	21.2	20.5	10.8	29.8	24.0	21.0	21.3	12.7	9.3	20.8
Sr	22.6	9..0	11.0	84.7	14.6	4.8	25.4	25.1	173.5	69.4
Sb	0.07	0.02	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Bi	0.27	0.18	0.19	0.35	0.23	0.05	0.35	0.25	0.25	0.32
V	37	5	9	12	20	7	5	13	30	26
La	36.9	27.9	18.7	71.4	34.7	32.1	31.1	22.1	30.0	42.8
Cr	27.0	11.9	10.9	29.3	24.1	4.0	24.6	14.2	26.7	29.9
Ba	51.0	22.0	23.8	260.2	18.1	23.1	33.3	45.8	225.3	164.2
B	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Sc	7.4	2.7	2.2	11.7	7.8	3.7	8.8	2.4	8.8	13.8
Tl	0.04	0.04	0.04	0.03	0.03	<0.02	0.11	0.03	0.09	0.11
Se	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ga	5.2	3.1	2.7	4.9	4.4	1.3	6.0	3.4	6.8	6.7
As	1.3	<0.1	0.3	0.1	<0.1	0.2	<0.1	0.3	0.7	1.2

composition of the claystones is shown in Table 4.

Provenance can also be confirmed using Y/Ni and Cr/V ratios. McLennan et al. [36] observed that high Cr/V (>10) ratio and low Y/Ni ratio (<0.5) depict ultramafic source rocks, whereas felsic source rocks show lower Cr/V (<10) ratio and higher Y/Ni ratios (>0.5). In this study, the Cr/V ratio ranges from 0.57 to 4.92, while Y/Ni ratio ranges from 0.81 to 4.25, as shown in Table 5. This assumes a felsic source rock for the studied sections.

Furthermore, for most clastic rocks, the Al_2O_3/TiO_2 ratio is used to infer source rock composition. Al_2O_3/TiO_2 ratio ranges of 3–8 are given for mafic igneous rocks, 8–21 are given for intermediate rocks and 21–70 are given for felsic igneous rocks [9].

In this study, the Al_2O_3/TiO_2 ratio ranges from 6.57 to 24.57, suggesting intermediate to felsic igneous rocks as the probable source rocks for the claystone samples.

La/Sc and Th/Sc ratios are significantly different in felsic and basic rocks and may lead to constraints on average provenance composition [32, 37, 38]. They gave Th/Sc and La/Sc ranges between (0.84–20.5) and (2.5–16.3), respectively, for felsic source rocks. Comparison

Table 5: *Elemental ratios for some of the claystones in the study area.*

	Th/Sc	La/Sc	Y/Ni	La/Th	Cr/V	V/Cr	Ni/Co	Cu/Zn	Zr\10	U/Th
S1	2.86	4.99	2.78	1.74	0.73	1.36	2.00	3.59	120.0	0.20
S3b	7.59	1.33	3.70	1.36	2.38	0.42	1.00	1.69	186.0	0.06
S3c	4.91	8.50	2.25	1.73	1.21	0.82	1.20	2.12	71.1	0.21
S4a	2.56	6.10	3.90	2.40	2.44	0.41	1.75	3.78	135.7	0.27
S5a	3.08	4.45	2.61	1.45	1.21	0.82	3.00	7.36	88.2	0.24
S5c	5.68	8.66	4.25	1.53	0.57	1.75	2.00	3.11	312.0	0.10
S6a	2.42	3.53	0.81	1.46	4.92	0.20	2.50	7.34	31.3	0.15
S6b	5.29	9.21	2.60	1.74	1.09	0.92	1.44	0.49	71.8	0.13
S7a	1.06	3.41	1.45	3.23	0.89	1.12	1.38	0.73	28.4	0.32
S7b	1.51	3.10	1.56	2.06	1.15	0.89	1.44	1.22	24.5	0.26
Average	3.69	6.22	2.59	1.87	1.65	0.87	1.79	3.14	106.9	0.19

of La/Sc and Th/Sc ratios for the claystone samples from this study (Table 5) with this model also indicated that such ratios came within the range of felsic source rocks.

Paleo-oxygenation condition

Barnes and Cochran [39] illustrated that uranium oxidation exerts a strong influence on marine geochemistry. Low content of uranium is generally found in sediments deposited in marine environment under oxygenated conditions [40, 41], while high uranium contents are found in sediments from oxygen-depleted zones [4, 40, 42, 43]. The claystone samples show a low content of uranium (in the range of 1.3–8.1).

Cu/Zn ratio has been put forward as a redox parameter [8]. According to Hallberg [8], a high Cu/Zn ratio indicates reducing depositional conditions, while a low Cu/Zn ratio suggests oxidising conditions. In this study, the clay samples have a range of 0.49–7.36 Cu/Zn ratios (Table 5); this indicates more oxidising conditions. The U/Th ratio may be used as a redox indicator, with this ratio being higher in organic-rich mudstones [3]. The U/Th ratio below 1.25 suggests oxic deposition conditions, whereas values above 1.25 suggest suboxic and anoxic conditions [4]. In this study, the clay samples' U/Th ratio had a range of 0.06–0.32, indicating that they were deposited in an oxidising environment.

Jones and Manning [3] also suggested that Ni/Co ratios below 5 indicate oxic environments, whereas ratios above 5 indicate suboxic and anoxic environments. Thus, the low Ni/Co (1.00–3.00) ratio for the clay samples indicates that they were deposited in well-oxidising conditions.

In addition, Ernst [44], Bjorlykke [45] and Dill et al. [46] used V/Cr ratio as an index of paleo-oxygenation in various studies. Bjorlykke [45] observed that Cr is mainly incorporated in the detrital fraction of sediment and so may substitute for Al in the clay structure, whereas Shaw et al. [47] noted that V is generally found in sediments deposited in reducing environments. According to Jones and Manning [3], ratios above 2 indicate anoxic conditions, while ratios below 2 suggest oxidising conditions. In the present study, the V/Cr ratios were in the range of 0.20–1.75, which indicates that the claystones were deposited in an oxidising environment.

Tectonic setting

Bhatia and Crook [48] identified La, Th, Zr, Nb, Y, Sc, Co and Ti as being the most useful elements in discriminating different tectonic settings. Four distinct environments, oceanic island
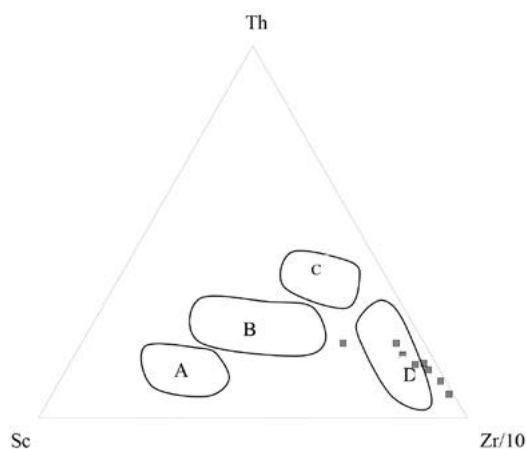
Figure 6: *Th–Sc–Zr/10 greywackes discrimination diagram [48]. The fields are as follows: A – oceanic island arc, B – continental island arc, C – active continental margin and D – passive margin.*

arc, continental island arc, active continental margin and passive margin, are recognised on La–Th–Sc and Th–Sc–Zr/10 trivariate plots. Using the Th–Sc–Zr/10 greywackes discriminant diagram of Bhatia and Crook [48], the tectonic setting for this study was adduced to be passive margin type as the claystone samples' plot was within the region specified for passive margin-type tectonic setting (Figure 6).

Passive–massive-type sandstone is generally enriched in SiO_2 and depleted in Na_2O, TiO_2 and CaO, suggesting their highly recycled and mature nature according to Bhatia [10]. The analysis of the major elements of the studied claystone samples revealed that they were also enriched in SiO_2 and depleted in Na_2O, TiO_2 and CaO (Table 3).

Conclusions

Mineralogical and geochemical analyses of the claystone samples were used to deduce compositional attributes, provenance, tectonic setting and paleo-oxygenation condition. Major element abundance showed that the claystone samples have average composition of SiO_2 (61.00%), Al_2O_3 (23.57%), Fe_2O_3 (1.77%) and TiO_2 (1.71%), constituting about 98% of the bulk chemical composition.

Mineralogical composition of the claystone sample-based Rietveld refinement plots revealed the dominant clay mineral as kaolinite

with minor constituents as illite–muscovite and gorceixite. The non-clay minerals had quartz predominating with minor constituents as K-feldspar, pyrite, marcasite, anatase and rutile. The provenance indicated intermediate to felsic igneous rocks as the probable source rocks for the claystone samples. Paleo-oxygenation studies using geochemical parameters such as U, Cu/Zn, U/Th, Ni/Co and V/Cr ratios suggested that these claystones were deposited in an oxidising environment.

The tectonic setting was inferred using the Th–Sc–Zr/10 greywackes discrimination diagram [48], which distinguished the tectonic setting as passive margin type.

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References

[1] Gary, N. (2009): *Sedimentology and Stratigraphy*, 2nd edition, United Kingdom: Wiley Blackwell, p.21.

[2] Calvert, S.E., Pedersen, T.F. (1993): Geochemistry of Recent toxic and anoxic marine sediments, implications for the geological records. *Marine Geology*, 113(1–2), pp. 67–88.

[3] Jones, B., Manning, D.C. (1994): Comparison of geochemical indices used for the interpretation of paleo-redox conditions in Ancient mudstones. *Chemical Geology*, 11(1–4), pp. 111–129.

[4] Nath, B.N., Bau, M., Ramalingeswara, B., Rao, C.M. (1997): Trace and rare earth elemental variation in Arabian Sea sediments through a transect across the oxygen minimum zone. *Geochimica et Cosmochimica Acta*, 61(12), pp. 2375–2388.

[5] Cullers, R.L. (2002): Implications of elemental concentrations for provenance, redox conditions and metamorphic studies of shales and limestones near Pueblo, Colorado, USA. *Chemical Geology*, 19(4), pp. 305–327.

[6] Armstrong-Altrin, J.S., Verma, S.P., Madhavaraju, J., Lee, Y.I., Ramasamy, S. (2003): Geochemistry of Late

Miocene Kudankulam Limestones, South India. *International Geology Review*, 45(1), pp. 16–26.

[7] Dobrzinski, N., Bahlburg, H., Strauss, H., Zhang, Q.R. (2004): Geochemical climate proxies applied to the Neoproterozoic glacial succession on the Yangtze Platform, South China. In: Jenkins, G. *et al.* (Eds.). *American Geophysical Union Monograph Series*, 146, pp. 13–32.

[8] Hallberg, R.O. (1976): A geochemical method for investigation of palaeoredox conditions in sediments. *Ambio Special Report*, 4, pp. 139–147.

[9] Hayashi, K., Fujisawa, H., Holland, H., Ohmoto, H. (1997): Geochemistry of ~1.9Ga sedimentary rocks from north eastern Labrador, Canada. *Geochimica et Cosmochimica Acta,* 61(19), pp. 4115–4137.

[10] Bhatia, M.R. (1983): Plate tectonics and geochemical composition of sandstones. *Journal of Geology*, 91, pp. 611–627.

[11] Roser, B.P., Korsch, R.J. (1986): Determination of tectonic setting of sandstone mudstone suites using SiO_2 content and K_2O/Na_2O ratio. *Journal of Geology*, 94, pp. 635–650.

[12] Lopez de Luchi, M.E., Hoffmann, A.S., Wemmer, K., Steeken, A. (2003): Temporal constraints on the polyphase evolution of the Sierra de San Luis Preliminary report based on biotite and muscovite cooling ages. In: Calabar, N., Libraries, E., Lopez de Luchi, M.G., Ostera, Panarello, H. (Eds.). *Actas 15*[th] *Congreso Geologico Argentiso*, I, pp. 309–315.

[13] Gritty, G.H., Hason, A.D., Knaack, C., Johnson, D. (1994): Provenance determined by REE. In: Sc analyses of metasedimentary rocks, boy den cave roof pendant, central Sierria Neveda, Carlifornia. *Journal of sedimentary research,* 64, pp. 68–73.

[14] Whiteman, A.J. (1982): *Nigeria; Its Petroleum Geology, Resources and Potential*. London: Graham and Trotman, 399 p.

[15] Ladipo, K.O., Akande, S.O., Mucke, A. (1994): Genesis of ironstones from Middle Niger sedimentary basin, evidence form sedimentological ore microscopic and geochemical studies. *Journal of Mining and Geology*, 30, pp. 161–168.

[16] Akande, S.O., Ojo, O.J., Ladipo, K.O. (2005): *Upper Cretaceous sequences in the southern Bida Basin, Nigeria*. A field guide book (Nigerian Association of Petroleum Explorationists), 60 p.

[17] Adeleye, D.R. (1975): A fauna from the ironstones of the middle Niger valley, Nigeria. *Journal of Mining Geology*, 8, pp. 45–48.

[18] Okunlola, O.A., Olubunmi, I. (2012): The geochemistry of claystone-shale deposits from the Maastrichtian Patti formation, Southern Bida basin, Nigeria. *Earth Sciences Research Journal,* 16(2), pp. 57–67.

[19] Agyingi, C.M. (1991): *Geology of Upper Cretaceous rocks in the eastern Bida, Nigeria*. Ph.D. Thesis. Ibadan: University of Ibadan 1991; 501 p.

[20] Oyawoye, M.O. (1972): *The basement complex of Nigeria*. In: African geology, Dessauvagie, T.F.J., Whiteman, A.J. (eds.). Ibadan University Press, pp. 66–102.

[21] Adeleye, D.R., Dessauvagie, T.F.G. (1972): *Stratigraphy of the Niger embayment near Bida, Nigeria*. In: African Geology, Dessauvagie, T.F.G., Whiteman, A.J. (eds.). University of Ibadan Press, pp. 181–186.

[22] Adeleye, D.R. (1971): *Stratigraphy and sedimentation of the Upper Cretaceous strata around Bida, Nigeria*. Ph.D. Thesis. Ibadan: University of Ibadan 1971; 297 p.

[23] Akande, S.O., Ojo, O.J. (2002): Organic Petrology and Rock-Eval studies on source rock facies of Champion-Maastrichtian Patti Formation, southern Bida basin, Nigeria. *Nigerian Association of Petroleum Explorationists Bulletin,* 16, pp. 21–39.

[24] Ojo, S.B. (1984): Middle Niger Basin Revisited, Magnetic constraints on gravity interpretations. Nigerian Mining and Geosciences Society Conference, Nsukka, Nigeria, Abstract, pp. 52–53.

[25] Adelana, S.M.A., Olasehinde, P.I., Bale, R.B., Vrbka, P., Goni, I.B., Edet, A.E. (2008): *An overview of the geology and hydrogeology of Nigeria*. In: Applied Groundwater Studies in Africa. IAH Selected Papers on Hydrogeology, Adelana, S.M.A., MacDonald, A.M. (eds.). London: CRC Press Balkema,13, pp. 71–197.

[26] Fagbohun, B.J., Adeoti, B., Aladejana, O.O. (2017): Litho-structural analysis of eastern part of Ilesha schist belt, Southwestern Nigeria. *Journal of African Earth Sciences*, *133 p.* Available on: <http://doi.org/10.1016/j.jafrearsci.2017.05.017>.

[27] Nton, M.E. (1999): Sedimentology and depositional environment of Awi Formation, Calabar Flank, southeastern Nigeria. *Journal of Mining and Geology*, 35(1), pp. 23–36.

[28] David, J.W., Roger, M.S. (1977): Late Quarternary and clay-minerals distribution on the eastern continental margin of Canada. *Journal of the Geological Society of America*, 88(2), pp. 267–272.

[29] Akpokodje, E.G., Etu-Efeotor, J.O., Olorunfemi, B.N. (1991): The composition and physical properties of some ceramic and pottery clays of southeastern Nigeria. *Journal of Mining and Geology*, 27, pp. 9–15.

[30] Imeokparia, E.G., Onyeobi, T.U.S. (2007): Geochemical and depositional characteristics of Maastrichtian

shales in parts of southwestern, Nigeria. *Journal of Mining and Geology*, 43, pp. 167–174.

[31] Ojo, O.J., Suraj, A.A., Temitope, M.A., Aminat, O.A. (2011): Sedimentological and geochemical studies of Maastrichtian clays in Bida Basin, Nigeria: Implication for resource potential. *Centrepoint Journal (Science edition)*, 17(2), pp. 78–79.

[32] Cox, R., Lowe, D.R., Cullers, R.L. (1995): The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United states. *Geochimica et Cosmochimica Acta*, 59(14), pp. 2919–2940.

[33] Emofurieta, W.O., Ogundimu, T.O., Imeokparia, F.C. (1994): Mineralogical, Geochemical and Economic Appraisal of some Clay and Shale Deposits in Southwestern and Northeastern Nigeria. *Journal of Mining and Geology,* 30, pp. 151–159.

[34] Huber, J.M. (1985): *Kaolin Clays*. Huber Corporation (Clay Division), Georgia, U.S.A.

[35] Elueze, A.A., Bolarinwa, A.T. (1995): Assessment of functional application of lateritic clay bodies in Ekiti environs, Southwestern Nigeria. *Journal of Mining and Geology*, 31, pp. 79–87.

[36] McLennan, S.M., Hemming, S., McDaniel, D.K., Hanson, G.N. (1993): *Geochemical approaches to sedimentation, provenance and tectonics. Processes controlling the composition of clastic sediments.* In: *Geological Society of America Special Paper,* Johnson, M.J., Basu, A. (eds.)*,* 284, pp. 21–40.

[37] Wronkiewicz, D.J., Condie, K.C. (1990): Geochemistry and mineralogy of sediments from the Ventersdorp and Transvaal Supergroups, South Africa: Cratonic evolution during the early Proterozoic: *Geochimica et Cosmochimica Acta*, 54(2), pp. 343–354.

[38] Cullers, R.L. (1995): The controls on the major and trace element evolution of shales, siltstones and sandstones of Ordovician to Tertiary age in the Wet Mountain region, Colorado, U.S.A: *Chemical Geology,* 123(1–4), pp. 107–131.

[39] Barnes, U.C., Cochran, J.R. (1990): Uranium removal in oceanic sediments and the oceanic U balance. *Earth and Planetary Science Letters*, 97(1–2), pp. 94–101.

[40] Somayajulu, B.L.K., Yadav, D.N., Sarin, M.M. (1994): Recent sedimentary records from the Arabian Sea. *Sedimentology Proceedings of the Indian Academy of Sciences*, 103(2), pp. 315–327.

[41] Madhavaraju, J., Ramasamy, S. (1999): Rare earth elements in limestones of Kallankurichchi Formation of Ariyalur Group, Tiruchirapalli Cretaceous, Tamil Nadu. *Journal of the Geological Society of India*, 54, pp. 291–301.

[42] Klinkhammer, G.P., Palmer, M.R. (1991): Uranium in the oceans: where it goes and why? *Geochimica et Cosmochimica Acta*, 55(7), pp. 1799–1806.

[43] Sarkar, A., Battacharya, S.K., Sarin, M.M. (1993): Geochemical evidence for anoxic deep water in the Arabian Sea during the last glaciation. *Geochimica et Cosmochimica Acta*, 57(5), pp. 1009–1016.

[44] Ernst, T.W. (1970): *Geochemical facies analysis*, Amsterdam: Elsevier, 152 p.

[45] Bjorlykke, K. (1974): Geochemical and mineralogical influence of Ordovician island arcs on epicontinental clastic sedimentation: a study of Lower Paleozoic sedimentation in the Oslo region, Norway. *Sedimentology*, 21(2), pp. 251–272.

[46] Dill, H., Teshner, M., Wehner, H. (1988): Petrography, inorganic and organic geochemistry of Lower Permian Carboniferous fan sequences (Brandschiefer Series) FRG: constraints to their paleogeography and assessment of their source rock potential. *Chemical Geology*, 67(3–4), pp. 307–325.

[47] Shaw, T.J., Geiskes, J.M., Jahnk, R.A. (1990): Early diagenesis in differing depositional environments: the response of transition metals in pore water. *Geochimica et Cosmochimica Acta*, 54(5), pp. 1233–1246.

[48] Bhatia, M.R., Crook, A.W. (1986): Trace element characteristics of greywackes and tectonic setting discrimination of sedimentary basins. *Contributions to Mineralogy and Petrology,* 92, pp. 181–193.