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Geochemical and Mineralogical Studies of Kaolinitic Clays in Parts of Ilorin, Southwestern Basement Rock Area, Nigeria

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Abstract This study is focused on the clay deposits at Akerebiata area in Ilorin (north-central Nigeria), southwestern basement complex, Nigeria. The chemical and mineralogical compositions of the clays were investigated with the aim of determining their provenance, weathering history and most suitable use. X-Ray Diffraction (XRD) method was employed for the mineralogical analysis while X-Ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrophotometer (ICPMS) methods were used to for the determination of the bulk elemental composition. XRD analysis revealed kaolinite as the predominant clay mineral (54.2 to 90.9 wt. %) indicating intensive chemical weathering of aluminium-rich source rocks and exhaustive leaching under a warm, humid condition. Other non-clay minerals in the assemblages are quartz, rutile, anatase, microcline and plagioclase. Results of geochemical analysis show predominance of SiO_2 (47.14 to 64. 92 wt. %) and Al_2O_3 (19.47 to 29.39 wt. %) which support the kaolinitic nature of the clay and classify the clay as aluminosilicates. The relatively high mean values of the Chemical Index of Alteration (CIA) and Chemical Index of Weathering (CIW) (87.15 and 90.09) also suggest an intensive chemical weathering in the source area. Other relevant geochemical indices; plot of TiO_2, ratios of Th/Co, Th/Cr, Cr/Th and relative proportion of Ni and Cr reveal felsic igneous parent rock. The clays are characterized by light colour, fineness, low-moderate LOI, mineral assemblage and chemical composition that make them favorably compared with standards for refactory, ceramics, pottery and paints.

Keywords Akerebiata, Granite, Kaolinite, Provenance, Weathering

1. Introduction

Clays are essentially fine-grained, earthy materials that become plastic and tenacious when moist, and they become permanently hard when baked or fired [1, 2]. They may be composed of mixtures of clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. They are commonly formed either as products of the chemical weathering of pre-existing crystalline rocks and feldspar minerals, particularly in warm tropical and subtropical regions of the world or as a result of the hydrothermal alteration. Clays and clay minerals are economic minerals that have been found useful in manufacturing and environmental industries where they serve as major raw materials in the making of ceramic, paint, paper, refractory, plaster of paris and pharmaceutical products. Other applications of clays include; cure of ulcers, for cleansing purposes, detoxification, adsorption, skin emulsifiers and cure against dysentery and cholera [3].

The major geological process that affects the composition of clay and clay rich sediments is chemical weathering, even though the parent rock is altered into soils and clays by the combined effects of biological chemical and physical weathering [4, 5]. Studies have also shown that the imprints of the original composition of the source rock are often preserved in the sediments [6, 7, 8]. The immobile major and trace elements such as Al, Fe, Ti, Th, Sc, Zr , Th, Cr, Ni and Co and the rare earth element (La, Eu, Yb, Ce) provide good provenance and weathering history signatures.

The present study is on clay deposits from Akerebiata locality in Ilorin (north-central Nigeria), where for decades, the clays have been worked by the locals essentially for pottery making. Akerebiata is a locality in the northern part of Ilorin Township and situated along Ilorin-Shao road, near the Sobi Ridge. The location falls within Ilorin sheet 223NW (1:50,000) lying between longitudes 4°30' to 4°37' and latitudes 8°27' to 8°32' (Fig. 1). In spite of the abundance of this deposit and age long indigenous processing for pottery and ceramics by the local people (Fig. 2a), not much is known about the geology and geochemical characteristics of the deposit. This paper thus examines the provenance, weathering history and industrial suitability based on

chemical composition and environmental implications of the chemical constituents. Several studies that dwell on these aspects of clays in different part of Nigeria and the world are available in literature. Among these are [9, 10, 11, 12, 13]. In these studies, the chemical composition of the clays was used to characterize the clays.

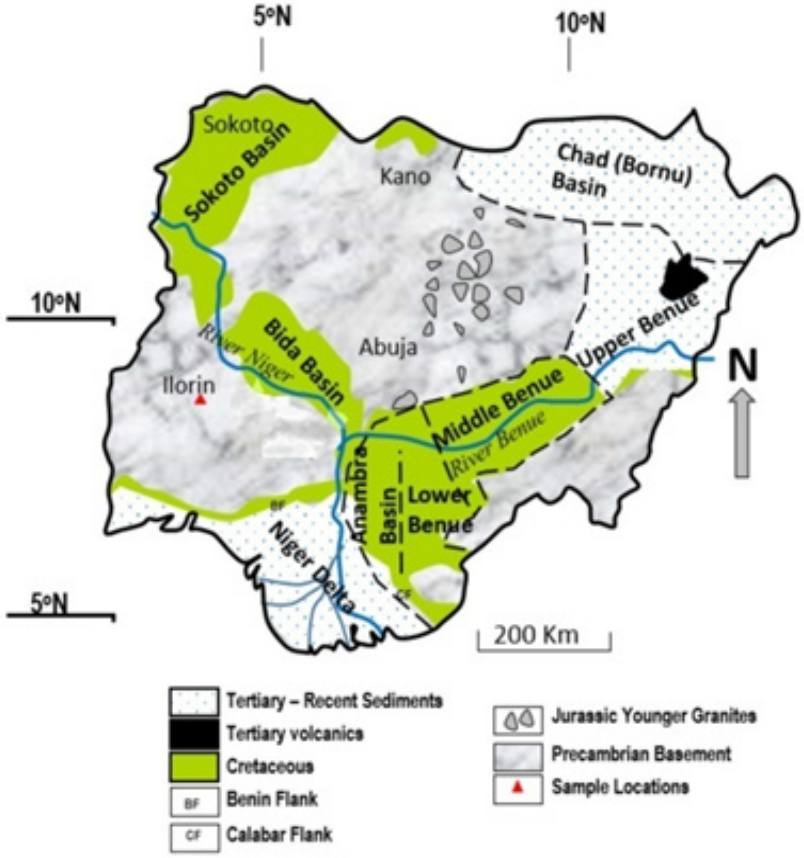


Figure 1. Geological map of Nigeria. Note the sample location



(a) (b)

Figure 2. a) A pottery maker processing the clay b) Sample pit (sample L8).

Table 1. Quantitative determination of mineral composition of the clays by the XRD methods.

Location	Sample No	Minerals	Weight (%)	3 σ error
Akerebiate/Ilorin	L4A	Anatase	3.56	0.36
		Kaolinite	79.12	1.14
		Quartz	16.02	1.02
		Rutile	1.3	0.36
	L7	Anatase	2.78	0.27
		Kaolinite	54.19	1.29
		Microcline	6.37	0.99
		Plagioclase	5.61	0.87
		Quartz	30.57	0.93
		Rutile	0.48	0.27
	L8	Anatase	3.79	0.42
		Kaolinite	90.92	0.96
		Quartz	5.29	0.9

2. Geological Setting

Ilorin is located geographically in North-Central Nigeria and the rocks belong to the southwest basement complex of Nigeria. The crystalline basement rocks of Ilorin Sheet form part of the West African Craton and the geology closely compares with that of the rest of the basement rocks of southwestern Nigeria which has been well discussed [14, 15, 16, 17]. They comprise of migmatite complex of Eburnean age (2000±200ma). Large scale magmatic activities in the area lead to emplacement of Older Granite series of Pan African age. Apart from the isolated hills (particularly the Sobi Hills), most part of the study area is covered by dark sandy or clayey loamy top soils. This is usually followed by laterites which may be as thick as 2m in places. The underlying lithologies consist of weathered to fresh crystalline basement rocks. Main crystalline rocks include; biotite hornblende gneiss with intercalated amphibolites, porphyritic granites and granite gneiss.

3. Materials and Methods

The method involves sampling of clays and bulk elemental composition and mineralogical analysis of the claystone samples. Accessibility and collection of the samples were made possible by river channel exposure and pitting (Fig. 2a). In the field, the profiles were observed and described based on their colour, texture and thickness. Fresh clay samples were taken through at different sites (Sample L4A N08°30′835″ and E004°33′442″; Sample L7 N08°30′594″ and E004°33′466″; N08°30′702″ and E004°33′123″) around Akerebiata, Ilorin. All samples were labeled and arranged in sample bags and processed in the laboratory.

A quantitative determination of the mineralogical composition of the clay samples using X-ray diffraction were carried out on three samples at University of Pretoria, South-Africa. Prior to XRD processing, about 100 g of each dried sample were gently crushed and sieved and then the clay fractions were seaparated according to Moore and Reynolds [18]. The samples were analyzed using a PANalytical X'Pert Pro powder diffractometer in θ–θ configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å). The phases were identified using X'Pert Highscore plus software. Percentage mineralogical composition was also estimated based on the relative peak intensities of the respective minerals in the XRD charts. The samples were also selected for bulk elemental composition analysis using X-Ray Fluorescence (XRF) and standard Inductively Coupled Plasma-Mass Spectrophotometer (ICP-MS) methods at Acme Laboratory Canada.

4. Results

4.1 Mineral Composition

The diffractograms obtained from the XRD analysis in the region between 2^o – 65^o revealed the dominant clay mineral as kaolinite with minor muscovite. A summary of the quantitative XRD analysis results are presented in Table 1, while the charts are shown in figure. 3. The non-clay minerals include quartz, anatase, rutile, plagioclase and microcline. High silica contents with low alumina, and less alkali, revealed by the chemical characteristics signify kaolinitic features. Quartz is inversely proportional to kaolinite in the samples analysed. The mineralogical assemblage of the clays appear similar and therefore suggesting same source and and extent of kaolinitization. Kaolinite is highest in sample L8 while plagioclase and microcline are absent. Presence of feldspars in samples suggests an incomplete alteration and formation of the clay from in situ weathering of the older crystalline rocks in the study area [19].

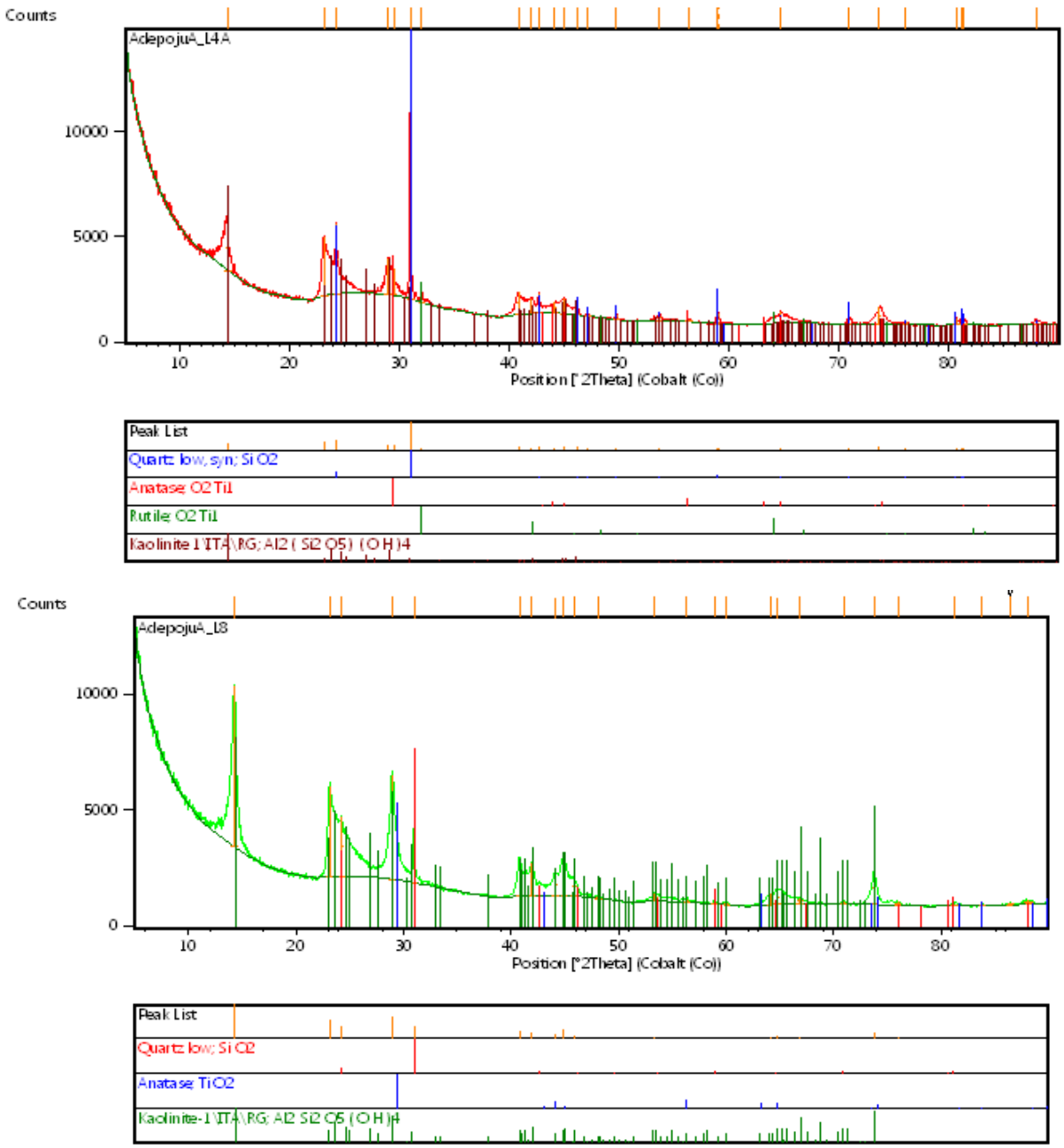


Figure 3. Diffractogram chart showing the mineralogical composition of the investigated clays

4.2. Chemical Composition

The major and trace element concentrations of the investigated clays are presented in tables 2 and 3. Major element distribution usually provides indications of provenance and suitability of the clays for industrial [7, 20, 21, 22].

4.2.1. Major Elements

The major elements of the clays in Akerebiata are dominated by SiO_2 (47.14 to 64.92 wt. % average 58.09 wt. %), Al_2O_3 (19.47 to 29.39 wt. %, average 21.86 wt. %), Fe_2O_3 (2.17 to 4.0 wt. %, average 2.74 wt. %). The oxides compare relatively with Ilorin granite, PAAS (Post Archean Australian Shales) and UCC (Upper Continental Crust). Sample L8 have major oxides composition SiO_2 and Al_2O_3 similar to that of pure kaolinite (46. 3 wt. % SiO_2 and 39.8 wt. % Al_2O_3, [23]. The data also reveal that clay sample L8 with highest kaolinite content has the highest Al_2O_3 and LOI (Loss on Ignition) concentrations. According to [12], LOI and Al_2O_3 increase as kaolinitization increases and formation of hydrated clay minerals like kaolinite occurs rather than goethite. This is observed in the present study area where clay sample L8 with highest kaolinite content has the highest Al_2O_3 and LOI concentrations. Goethite is absent in all the samples analysed. The ratio of SiO_2/Al_2O_3 ranging from 1.60 to 3.88 indicates presence of siliceous sands particularly in samples L4A and L7 and this can be attributed to high quartz

content. [18, 24] have proposed that quartz (SiO_2) may occur as fine disseminated crystalline particles in kaolinite or deposited with tiny flasks of the clay minerals, so, the mean values of SiO_2 content of the clays which is in excess of 50 %, implies that quartz is the main constituent of the clay samples. The relatively high percentage of alumina (Al_2O_3) is probably related to the clay minerals and feldspar in the deposit. The relatively low Fe_2O_3 may be responsible for non detection of iron oxide minerals haematite or goethite from the XRD analysis of the clays.

Low CaO, MgO, K_2O and Na_2O suggest the clays are most probably non expandable/swelling and low feldspar content. According to [25], the composition suggests that the clay samples are hydrated siliceous aluminosilicates. TiO_2 values range from 0.67 to 1.33 wt. % average of 0.92 wt. %. The value is probably too low in sample L8 to form rutile. Presence of TiO_2 in the clay sediments may reflect the incorporation of Titanium with detrital minerals such as rutile or and anatase particularly those of terrestrial origin such as kaolinite [18, 26]. The values of TiO_2 samples L4A and L7 in the study area suggest the dissemination of the discrete minerals such as rutile and anatase in the clays.

The LOI which is a measure of organic matter content and other combustible fractions, chemically combined water and CO_2 have mean percentage of 13.08%. This low-moderate value could be attributed to the absence of carbonates rock.

4.2.2 Trace Elements

The relative abundance of the trace elements; Cu, Pb, Zn, Ag, Ni, Co, Sr, Cd, Ba, Cr, Mo, and Mn when compared with that of PAAS, UCC, NASC (North American Shale Composite) and Ilorin granite, a wide variation was observed (Table 3). It is also noted that some elements (e.g. Cr, Cu, Mn, Co and Ni) are higher in the Akerebiata clay than those from sedimentary areas [13]. However, there is no much variation in the trace elements of the samples analysed. Distribution of trace elements in clays and sediments are influenced by weathering processes and nature of the parent rocks [27, 28, 29, 30]. The investigated clays are depleted in Zn, V, Cu, Cr, Rb and Sr compared to UCC, NASC, but similar to that of the proxy source, the Ilorin Granite. The probable reason for their depletion may be their low abundance in the parent rock. Sc, Y, U, Hf and Th are similar in content to those in UCC, NASC and PAAS. This may be due to their association with zircon which is heavy mineral that is highly resistant to weathering. The samples are more enriched in Ba (average 232ppm) than that of Sr (25.3ppm). This can be attributed to relative abundance of plagioclase and potassium feldspar at the source and relative stability of the feldspars [31].

Table 2. Major Elemental Composition values (%) of the Akerebiata clays and comparison with some standard values.

Samples	L4A	L7	L8	AVERAGE				
Oxides				This Study	Ilorin Granite	UCC	NASC	PAAS
SiO_2	62.21	64.92	47.14	58.09	69.49	66.00	64.82	62.80
Al_2O_3	19.47	16.71	29.39	21.86	14.11	15.20	16.90	18.90
Fe_2O_3	2.05	2.17	4.00	2.74	4.22	5.00	5.65	7.22
CaO	2.67	1.49	0.38	1.51	1.66	4.20	3.63	1.30
MgO	0.25	0.21	0.21	0.22	0.04	2.20	2.68	2.20
Na_2O	1.26	0.67	0.06	0.66	3.09	3.90	1.14	1.20
K_2O	1.22	0.79	0.35	0.79	5.61	3.40	3.97	3.70
MnO	0.12	0.27	0.01	0.13	0.55	0.08	0.06	0.11
TiO_2	1.33	0.77	0.67	0.92	0.59	0.50	0.70	1.00
LOI	9.69	11.78	17.78	13.08	0.22	-	-	-
SiO_2/Fe_2O_3	30.35	29.92	11.79	24.02	21.20	13.20	11.47	8.70
$CaO+Na_2O$	3.93	2.16	0.44	2.18	4.05	8.10	4.77	2.50
$CaO+Na_2O+K_2O$	5.15	2.95	0.79	2.96	10.36	11.5	8.74	6.20
Fe_2O_3+MgO	2.30	2.38	4.21	2.96	4.26	7.20	8.33	9.42
CIA	79.08	84.99	97.38	87.15	-	56.93	65.91	75.30
CIW	83.21	88.55	98.52	90.09	-	65.24	77.99	88.32

Table 3. Trace elements concentration (ppm) of Akerebiata clays and comparison with some standard values.

Samples	L4A	L7	L8	AVERAGE				
Trace Elements				This Study	Ilorin Granite	UCC	NASC	PAAS
Cu	7.15	20.88	6.76	11.6	6.0	62.80	52.0	50.0
Pb	5.93	11.07	4.99	7.33	33.0	-	-	20
Zn	7.50	4.40	6.60	6.20	93.0	71.0	471.0	85.0
Zr	0.6	0.6	0.6	0.6	-	193	200	210
Ag	18.00	30.00	9.00	19.00	-	-	-	-
Ni	4.80	8.60	2.70	5.40	7.0	20.0	58.0	55.0
Co	5.80	19.80	2.10	9.20	29.0	-	-	23.0
Sr	26.40	23.00	26.5	25.30	190.0	320.0	142.0	200.0
V	13.00	25.00	21.00	19.70	52.0	-	407.0	150.0
Ba	155.80	459.60	81.80	232.4	107.3	628.0	636.0	650.0
Sc	1.60	1.10	3.20	1.97	-	-	-	-
Y	8.42	14.44	7.63	10.16	-	21.0	-	-
Rb	4.70	3.50	3.50	3.80	221.0	82.0	-	160.0
Cr	7.80	6.00	10.30	8.03	51.0	-	-	-
Mn	867.00	2135.0	74.00	1025.3	-	-	-	-
Th	3.1	2.2	3.7	3.0	54.0	-	-	14.6
Th/Co	0.53	0.11	1.76	0.8	1.86	-	-	--
Th/Cr	0.40	0.37	0.36	0.38	1.06	-	-	-
Cr/Th	2.52	2.72	2.78	2.67	0.94	-	-	-

5. Discussion

5.1. Paleoenvironment and Paleoclimate

Many authors have shown that environments of deposition, to a large extent, determine both mineralogical and chemical characteristics of clays and clay types [32, 33]. It was pointed out that the sedimentary clays contain 90-95% kaolinite with quartz, ilmenite and quartz constituting the main impurities [34]. Also, according to [35], clays deposited in continental environments are characteristically whitish, but sometimes light coloured, and contain mainly kaolinite (80-100%). The mineralogical composition of the Akerebiata clays compares positively with continental deposit (Fig. 3a & b). The process of kaolinitization is associated with the removal of alkali and alkali earth metals such as Na, K, Ca and Mg [36]. Thus, the presence and high abundance of kaolinite in these sediments indicate rigorous weathering of aluminium-rich source rocks with steep relief and exhaustive leaching of weathered materials under a warm, humid and acidic medium. High amount of kaolinite minerals also indicate continental setting.

5.2. Weathering Effect

There are several parameters defined by the chemical composition of the studied clays that can be used as weathering indicators. These parameters include the high kaolinite content, enrichment of chemically immobile elements (e.g. Al_2O_3, TiO_2, Zr and Sc), the depletion of other mobile elements and relatively high values of the Chemical Index of Alteration (CIA). These parameters suggest intensive chemical weathering of the source rock. High mean value of Al_2O_3 (21.86%) for the clays and relatively high mean value of TiO_2 (0.92%) could also be attributed to the effect of chemical weathering. As precipitation and chemical weathering increases, kaolinitization is enhanced.

A Chemical Index of Alteration (CIA) value of nearly 100 was proposed for for kaolinite [4]. [10] recorded high CIA values (87 to 96) and low contents of alkali elements from kaolinite rich sediments from Central Uganda and related these high values to the intensive weathering of source rock. The CIA values of the studied clays range from 79 to 97.38 (average 87.15) (see table 3). CIA values of 45-55 were proposed by [37] as indicative of lack of weathering compared to 47 which is the value of upper continental crust. The values recorded in the present study area are higher and therefore reflect higher presence of clay minerals and absence of detrital feldspars and consequently high degree of chemical weathering. The sample with the highest kaolinite and lack of feldspar shows the highest CIA.

Also, the mean Chemical Index of Weathering (CIW) for the investigated clay (90.09) is very high, higher than that of PAAS and UC and therefore supporting intense weathering at the source area indicated by CIA (see table 2).

[4, 7] also used the ternary diagrams Al_2O_3-(CaO+Na_2O)-K_2O (the A-CN-K), diagram to deduce weathering trends. In figure 4, the samples plot in regions that clearly indicate variations in the concentration of Al_2O_3, CaO, Na_2O, and K_2O from the Ilorin granite, UCC, PASS and NASC. The investigated clay samples however plotted in a region closer to high Al_2O_3 contents (kaolinite boundary), which is suggestive of a relatively high and intensive weathering at the source. It also observed that Sr, Cr, V, and Cu were rapidly lost due to intense weathering when the values of the present study are compared with that of Ilorin Granite.

5.3. Provenance

The provenance of the clay in the study area is assessed based on the combination of the major trace and rare earth elements. [38, 39] inferred the provenance of the sedimentary rocks using the concentration of Chromium (Cr) and Nickel (Ni). A low concentration of Cr indicates a felsic provenance because it reflects the incorporation of low Cr and Ni ions to clay particles during the weathering of rocks containing Cr and Ni-bearing minerals [36] whereas high concentration of Cr and Ni are mainly found in sediments derived from ultramafic rocks.

[39] suggested that elevated Cr (>150ppm) and Ni (>100ppm) are diagnostic of ultramafic rocks in source region. In the investigated clays, Cr concentration ranges from 6 – 10.3ppm (avg. 8.03ppm) and Ni ranges from 2.7 – 8.6ppm (avg. 5.4ppm). This comparison rules out the existence of ultramafic rocks in the source region. Ratios such as Th/Co, Th/Cr and Cr/Th are significantly different in felsic and basic rocks and may allow constraints on the average provenance composition [8, 40, 41]. Th/Co, Th/Cr and Cr/Th ratios of the clay samples positively compared with those of sediments derived from felsic rocks (Table 4). This comparison suggests that the clays are within the range of felsic rocks. Higher amount of Ba relatively to Sr which were probably fractionated from K feldspar also support felsic source. [23, 42] utilized the TiO_2 versus Al_2O_3 binary plot to distinguish between granitic and basaltic source rocks. This type of binary plot was adopted for the studied clays and it reveals that the clays were sourced predominantly from granitic rocks (fig 5.) The CIA values which vary from 79.08 to 97.38, and the CIW values (83.21 to 98.52) point towards felsic igneous source [7].

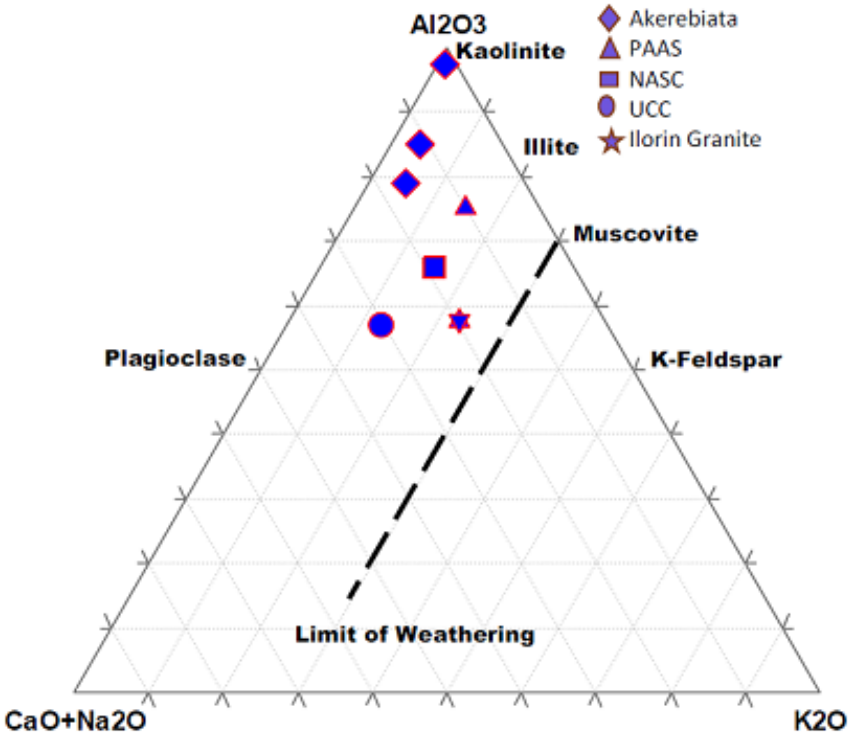


Figure 4. Al2O3-(CaO+Na2O)-K2O (A-CN-K) plot of clay samples (after Nesbitt et al., 1996). Comparinson with the standard samples shows the weathering trend of the sediments.

Table 4. Range of elemental ratios in the investigated clays compared to the ratios derived from felsic rocks, mafic rocks, upper continental crust and Post-Archean Australian Shale.

Elemental ratio	Present study	**Range of sediments		UCC*	PAAS*
		Felsic rocks	Mafic rocks		
Th/Co	0.25-10.5	0.67 – 19.4	0.04 – 1.4	0.63	0.63
Th/Cr	0.07-14.2	0.13 -2.7	0.018 – 0.046	0.13	0.13
Cr/Th	0.07-14.5	4.00 – 15	25 – 500	7.76	7.53

**Cullers (1994, 2000); **Cullers and Podkovyrov (2000); *Taylor and McLennan (1985)

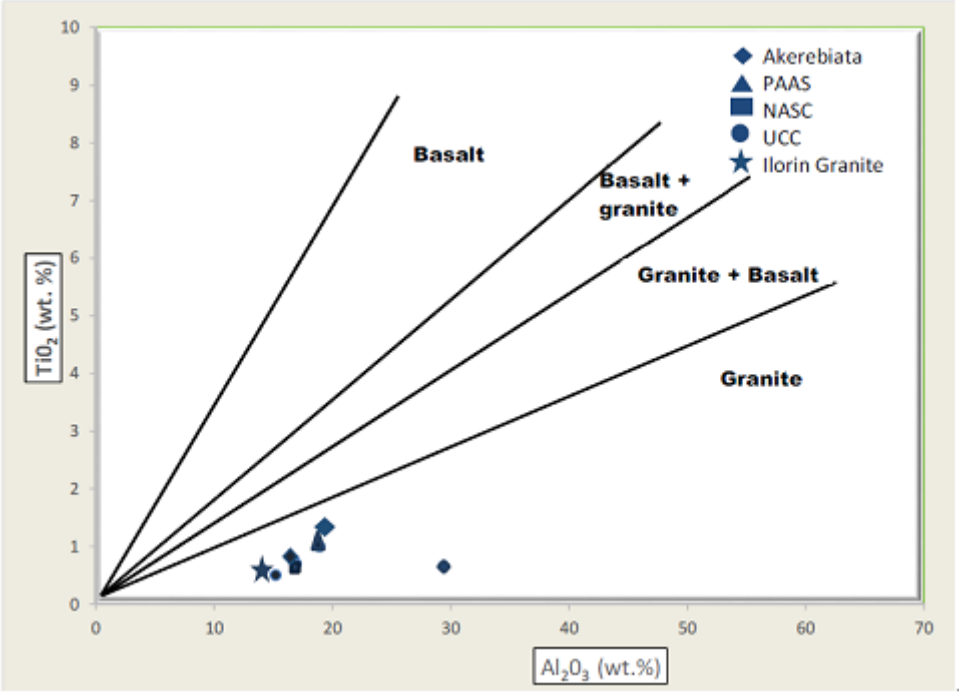


Figure 5. TiO_2/Al_2O_3 binary plot for the investigated samples. Note the granitic source of the samples (After Amajor, 1987).

Table 5. Comparison of chemical compositions of the Akerebiata Clays with some Industrial reference clays.

Oxides	Akerebiata/ Ilorin	References							
		A	B	C	D	E	F	G	H
SiO_2	58.69	47.80	48.70	48.00	45.3-47.9	67.50	51.0-70.0	46.07	49.88
Al_2O_3	21.86	37.00	36.00	37.00	38.4-39.9	26.50	25.0-44.0	38.07	37.65
Fe_2O_3	2.74	0.58	0.82	0.60	13.4-13.8	0.50-1.20	0.50-2.40	0.33	0.88
CaO	1.51	0.40	0.06	0.10	0.03-0.25	0.18-0.30	0.10-0.20	0.38	0.03
MgO	0.22	0.16	0.25	0.30	0.20-0.30	0.10-0.19	0.20-0.70	0.01	0.13
Na_2O	0.66	0.10	0.10	0.10	0.20-0.35	0.20-1.50	0.80-3.50	0.27	0.21
K_2O	0.79	1.10	2.12	1.60	0.10-0.40	1.10-3.10	-	0.43	1.60
TiO_2	0.92	0.03	0.05	0.03	0.10-1.00	0.1-1.2	1.0-2.8	0.50	0.09
LOI	13.08	13.10	11.90	12.40	12.00	-	-	13.47	12.43

(A) Paper Coating (Annon, 1972) (D) Paints (Payne, 1961) (G) Fertilizer, (NAFCON, 1985) (B) Paper Filler (Annon, 1972) (E) Ceramics (Singer and Sonja, 1971) (H) Agricultural (Hubber, 1985) (C) Porcelain (Annon, 1972) (F) Refractory Bricks (Parker, 1967)

5.4. Resource Potential

Grain size, mineralogical composition and chemical characteristics are employed in this study to assess the industrial potential of the clays. Fine particle size distribution of the kaolin along with colour is the property which makes kaolin commercially valuable [21]. Kaolintic clay is perhaps the major raw material in the ceramic industries, especially in the manufacture of sanitary wares, wall tiles, floor tiles, electrical and industrial porcelain insulators [43]. Grain size distribution of the clays shows high percentage of fines and low silts. This makes them suitable as fillers and coating materials in paint and paper industries.

Chemical composition of clay is compared with industrial specifications for refractory and ceramic clays. The elemental compositions of the clay samples from the study area are quite consistent with some standard obtained from other kaolin deposits locally and internationally (Table 5). Generally, the chemical composition is within the range specified by [44] for refractory clays. The high SiO_2, Al_2O_3 and LOI in the studied clays compare favourably with the standards for ceramics and refractory bricks [45, 46]. High kaolinite with low non-clay mineral contents, in addition to high silica, low alumina, Fe, base metal and alkalies content best appropriates the clays as Ball clay [20].

6. Conclusions

The clay in Akerebiata, Ilorin is dominated by kaolinite while goethite is probably absent. The enrichments of the kaolinitic clay with chemically immobile major elements and the high CIA and CIW values reflect a strong chemical weathering in the source area.

The major and trace element composition indicate possible derivation mainly from felsic sources. Kaolinitization process might have occurred under tropical and subtropical humid climatic conditions.

The abundance of kaolinite, the absence of swelling clay and very low accessory non-clay mineral contents, their light colours coupled with the fineness (>90%), low content of Fe_2O_3 and TiO_2 and moderate LOI in the clays suggest their suitability for ceramics, refractory and sanitary wares.

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