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Full Length Research Paper

Mineralogical and geochemical properties of clay deposits in parts of Southeastern Nigeria

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The rocks underlying many parts of Southeastern Nigeria had undergone extensive alterations to form considerable clay deposits. The mineralogical compositions of some of these clay deposits were evaluated with the X-Ray Diffraction (XRD) method to ascertain the suitability of the deposits as raw materials. Results of the analyses indicated that kaolinite ($Al_2Si_2O_5(OH)_4$) is the dominant clay mineral. Traces of bentonite and dickite were also observed, while the identified non-clay minerals were quartz and iron. Chemical analysis of the clays revealed the predominance of SiO_2, Al_2O_3, Fe_2O_3 and TiO with values ranging from 31.70 to 56.45%, 19.30 to 29.30%, 3.11 to 29.42% and 2.21 to 7.04%, respectively, while the compositions of CaO, MgO, Na_2O, and MnO in the analyzed samples were relatively lower with values ranging from 0.19 to 0.29%, 0.13 to 0.19%, 0.11 to 0.70% and 0.01 to 0.03%, respectively. The Al_2O_3/TiO_2 ratio (3.7 to 13.5) of the studied clays indicated a mafic to intermediate igneous rock origin. Binary plots of TiO_2 versus Al_2O_3 to distinguish between granitic and basaltic sourced clays indicated basalt-rhyolite/granite provenances. The high chemical index of alteration (95.8%), chemical index of weathering (98.3%) and low contents of alkali and alkali earth elements (averaging 0.11%) of the clay-rich sediments, is indicative of a relatively intense weathering source area. The SiO_2-K_2O/Na_2O plots suggested that the sediments in the study area were deposited between passive and active continental margins. In comparison with other reference clays and standard specifications, the clay deposits in the study area possess characteristics satisfactory for economic and some engineering purposes.

Key words: Chemical, clay, deposits, economic, mineralogical, potentials, provenance.

INTRODUCTION

Clay is usually (but not necessarily) an ultrafine-grained sediment considered to be less than 2 µm in size on standard particle size classification. Chemically, clays are hydrous aluminum silicates, ordinarily containing impurities, for example potassium, sodium, calcium, magnesium, or iron, in small amounts and are characterized by sheet-like silicate structures of composite layers stacked along the c-axis (Grim, 1968). The term can thus be applied both to materials having a particle size less than 2 µm and to the family of minerals that have similar chemical compositions and common crystal structural characteristics (Velde, 1995).

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Clay minerals are products of long periods of the gradual chemical weathering of pre-existing rocks (usually silicate-bearing), by low concentrations of carbonic acid and other diluted solvents, particularly in warm tropical and subtropical regions of the world. In addition to the weathering process, some clays are formed through hydrothermal alteration of rocks. In terms of sedimentary processes, some clays are residuals that are formed *in situ* as a result of leaching (chemical), while others undergo substantial transportation before being deposited (clastic).

Clays have slaking ability and exhibit plasticity when mixed with water in certain proportions. However, when dry, clay becomes firm and when fired in a kiln, permanent physical and chemical changes occur. These changes convert the clay into a ceramic material. Because of these properties, clay is used for making pottery, both utilitarian, decorative and construction products, such as bricks, wall and floor tiles. Different types of clays when used with different minerals and firing conditions are used to produce earthenware, stoneware and porcelain. Due to thegeometric increase in pollution indices of many towns in the developing countries, clays are being used for pollution control in engineered landfills as linings (Ibe et al., 2003). Solid heterogeneous catalysts and adsorbents derived from clay are also becoming relevant in pollution control (Okoye and Obi, 2011) as they have been associated with the removal of heavy metals.

Based on the foregoing and the high volumetric abundance of clay minerals in the study area, a thorough review of the properties of clay deposits in some parts of Southeastern Nigeria was undertaken in order to ascertain the quantity and quality of the deposits for economic purposes. In view of the current program of government to invest in the mining of mineral deposits to augment oil and gas revenues, this study aimed at ascertaining the possible utilization of the clays as raw materials will be of great value in the planning and exploitation of the identified clay resources in the Southeastern part of Nigeria.

The selected localities for the study are bounded by Latitudes 5°53' and 6°30' N and Longitudes 6°56' and 7°30' E. (Figure 1).Within this area are Uturu, Ikpankwu, Ezinnachi and Ohiya in the Okigwe-Umuahia axis and sections along the Awommama-Orlu axis Southeastern Nigeria. The towns can be accessed through the Enugu-Port Harcourt Expressway and other roads in the area.

Geology

The studied lithostratigraphic units include the Mamu Formation (Uturu and Ikpankwu), Ajali Formation (Uturu), Nsukka Formation (Ikpankwu), Imo Shale (Ezinnachi), Ameki Formation (Ohiya) and Benin Formation (Awommama and Orlu). These are the post-Santonian formations in the Anambra Basin and Niger Delta. Sediment deposition in the basin started in the Campanian with a short marine transgression followed by a regression. The Nkporo Shale and its lateral equivalents, the Enugu Shale and Owelli Sandstone (Nkporo Group), constitute the basal beds of the Campanian period. The broad shallow sea gradually became shallower because of gradual subsidence, initiating a regressive phase during the Maastrichtian that deposited deltaic foresets and flood plain sediments of the Mamu Formation (Lower Coal Measures). The Mamu Formation is overlain by the continental beds of Ajali Sandstone (False bedded Sandstone), followed by a return to partially paralic conditions and the deposition of the Nsukka Formation. The Nsukka Formation marked the onset of the Sokoto transgression and documented the return to paludal conditions (Murat, 1972). The Imo Shale that overlies the Nsukka Formation show shallow-marine shelf conditions in which foreshore and shoreface sands are occasionally preserved (Petters and Ekweozor, 1981) and consists of blue-grey clays and shales and black shales with bands of calcareous sandstone, marl and limestone (Reyment, 1965).

Regression continued throughout the Eocene (Jones and Hockey, 1964; Reyment, 1965) culminating in the deposition of Lower and Middle Eocene deposits including the clastic Ameki and Nanka Formations. The progradational Nanka Formation marks the return to regressive conditions. The prograding shoreface and river plain deposits are reflected in the subsurface deposits of the Agbada Formation in the northern depobelts of the Niger Delta, whilst the marine Imo Shale equivalent in the subsurface is termed the Akata Formation.

The uppermost lithostratigraphic units of the stratigraphic succession in the area are dominated by the Ogwashi-Asaba and the Benin Formations that are of Oligocene-Recent in age (Nwajide, 2005).

During the Miocene, the Niger Delta continued to build up and prograde seawards. There was lowering of sea level during the Pleistocene. The Niger River cut wide valleys through its own delta. These troughs are being filled today as the sea level gradually rises. The stratigraphic sequence shown in Figure 2 and graphically illustrated in Figure 3 generally show the lithic fill of the study area.

MATERIALS AND METHODS

Field work and sample collection

Detailed field mapping carried out along the N-S traverse (A-A'), through Ikpankwu, Okigwe to Ohiya in the Okigwe-Umuahia Axis was aimed at ground-truthing information on the local geology of the study area (Figure 3). A total of eighteen fresh clay samples were collected during the mapping exercise and taken to the laboratory for mineralogical and chemical analyses.

Mineralogical analysis

The mineralogical analysis of clay samples using X-Ray Diffraction

Age	Basin	Stratigraphic Units						
Oligocene-Recent	Niger Delta	Ogwashi-Asaba Fm	Benin Formation					
Eocene		Ameki/Nanka Fm/Nsugbe Sandstone (Ameki Group)	Agbada Formation					
Thanetian		Imo Formation	Akata Formation					
Danian	Anambra Basin	Nsukka Formation						
Maastrichtian		Ajali Formation						
		Mamu Formation						
Campanian		Nkporo Fm	Nkporo Shale	Enugu Fm	Owelli Ss	Afikpo Ss	Otobi Ss	Lafia Ss
Santonian	Southern Benue Trough	Agwu Formation						

Figure 1. Generalized stratigraphic sequence in Anambra Basin.
Source: Modified from Nwajide (2005).

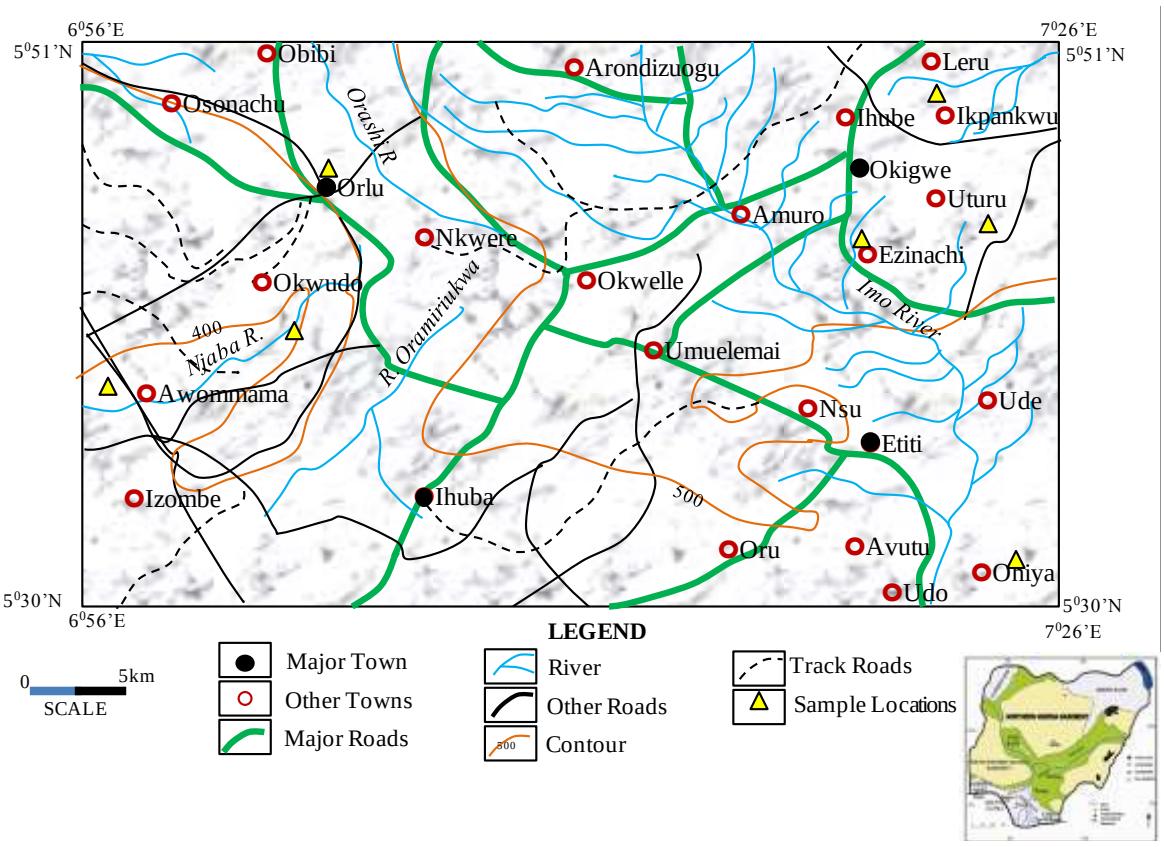

Figure 2. Section map of Nigeria showing the study area.

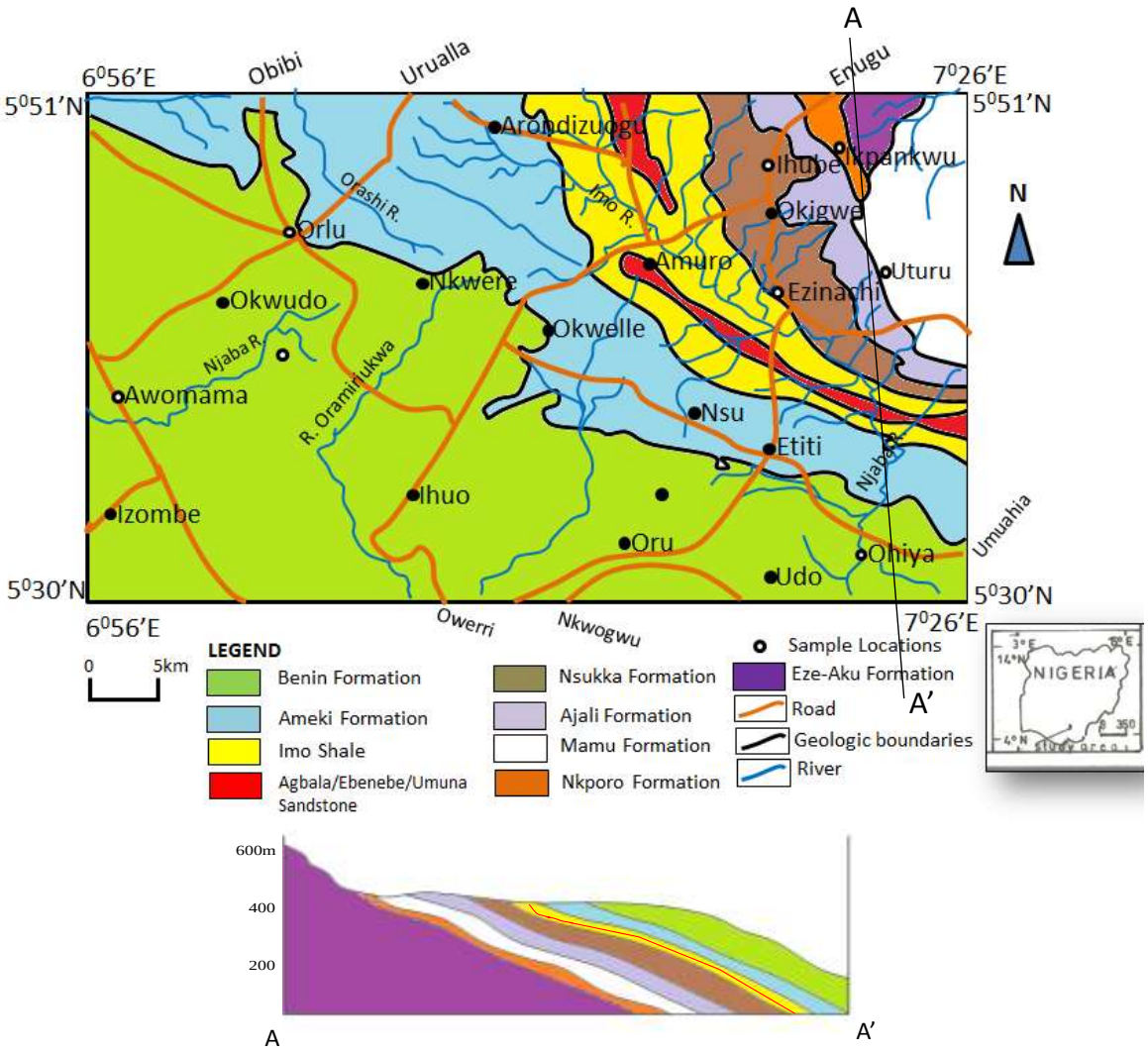

Figure 3. Geological map and section A-A' of the study area.

(XRD) was carried out in the Nigerian Geological Research Laboratory, Kaduna. Sample preparation for the analysis commenced with the samples being finely ground, homogenized and average bulk composition determined. The powdered sample was further prepared using the preparation block and compressed in a sample holder to create a flat and smooth surface which later, was mounted on the sample stage in the XRD cabinet.

The sample was then analyzed using the reflection-transmission spinner stage with theta-theta (θ - θ) settings. The -Theta starting and ending positions during the analysis were 0.00483 and 75.000, respectively. The positions were associated with two-theta steps of 0.026 at 3.57 s per step. The current and tension in the tube were set at 40 mA and 45 VA, respectively, with a fixed divergent slit size of 1° and a goniometer radius of 240 mm used.

The intensity of diffracted X-rays is continuously recorded as the sample and detector rotate through their respective angles. A peak intensity occurs when the mineral contains lattice planes with d-spacing appropriate to diffract X-rays at that value of θ (reflection angle). Although each peak consists of two separate reflections ($K\alpha_1$ and $K\alpha_2$), at small values of 2θ, the peaks overlap with $K\alpha_2$ appearing as a hump on the side of $K\alpha_1$. Greater separation occurs at higher values of θ. Typically, these combined peaks are treated as one. The 2λ position of the diffraction peak is typically measured as the center of the peak at 80% peak height.

Results are commonly presented as peak positions at 2θ and X-ray counts (intensity) in the form of a table or an x-y plot. Intensity (*I*) is either reported as peak height intensity, which is intensity above background or as integrated intensity, the area under the peak. The relative intensity is recorded as the ratio of the peak intensity to that of the most intense peak (relative intensity = $I/I_1 \times 100$).

The d-spacing of each peak was obtained by solution of the Bragg equation for the appropriate value of λ. Once all the d-spacing have been determined, automated search/match routines compared the d-spacing of the unknown to those of known materials. Because each mineral has a unique set of d-spacing, matching these d-spacing provided an identification of the unknown sample. A systematic procedure is used by ordering the d-spacing in terms of their intensity beginning with the most intense peak. Files of d-spacing for hundreds of thousands of inorganic compounds are available from the International Centre for Diffraction Data (ICDD) as the Powder Diffraction File (PDF). The peaks obtained from the analyses were matched with the minerals from ICDD database which is attached to the software of the machine.

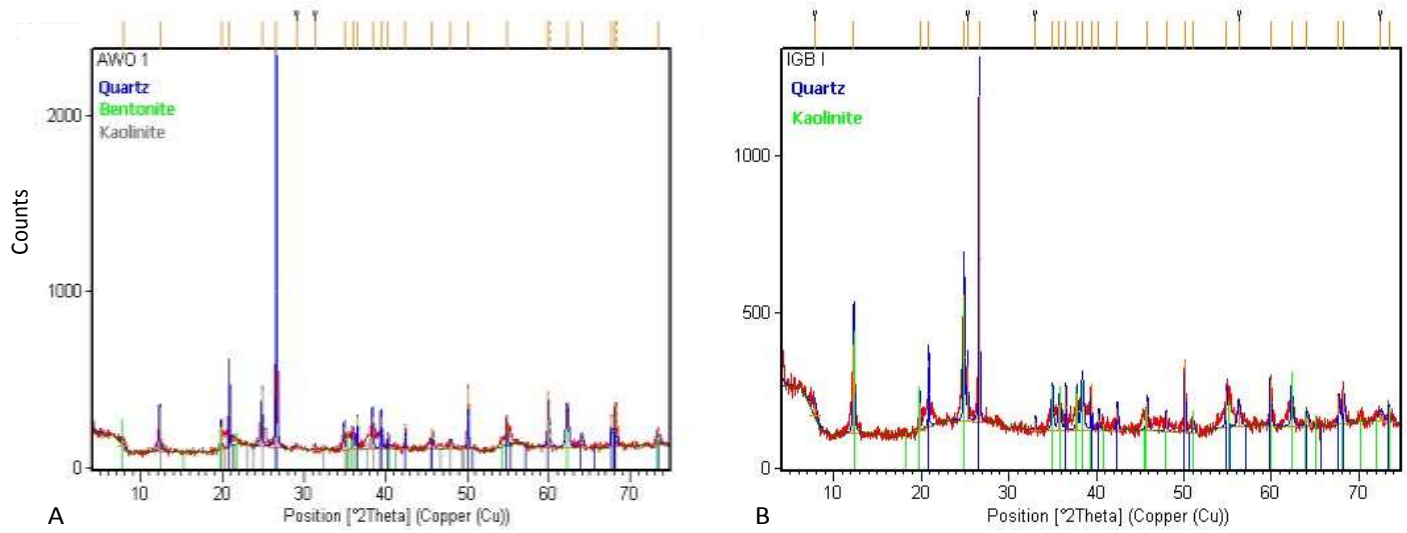

Figure 4. Representative X-Ray diffractions showing the major peaks in the clay deposits in (A) Awommama and (B) Ikpankwu sections.

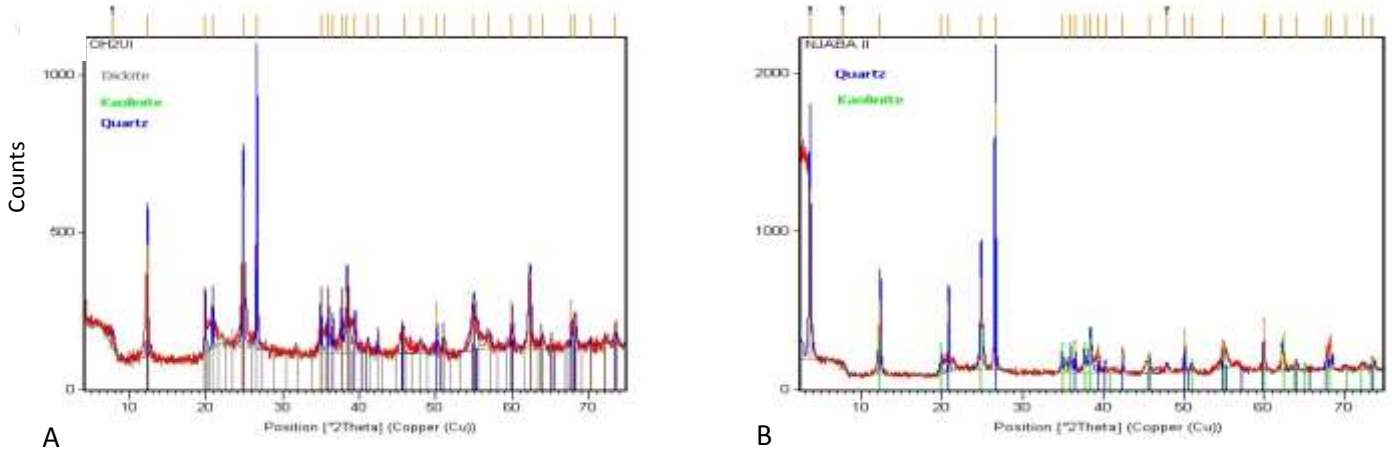

Figure 5. Representative diffractogarams showing brooding of kaolinite reflection at (A) Ohiya 2 and (B) Njaba II clay samples.

Chemical analysis

Chemical analysis was performed in the Geochemistry Laboratory of the Nigerian Geological Survey Agency, Kaduna. The main analytical equipment used for the analysis were the Energy Dispersive X-Ray Fluorescence (EDXRF) and Atomic Absorption Spectrometer (AAS).

Sample preparation for XRF involved the pulverization of about 100 g from each of the collected clay samples with a motorized agate mortar so that the grains of the pulverized fine powder would pass the 300 (53 µm) mesh sieve. 10 g each of the powdered samples was mixed with 1 g of stearic acid (binder) and thoroughly homogenized in an agate mortar. The mixture was then transferred into a hardened-steel disc with a diameter of 40 mm and pressed into a pellet at a pressure of 25 tons using hydraulic pressure press. The pellets were then used for XRF analysis.

About 0.5 g of the powdered samples was placed in a Teflon beaker and digested with 10 ml of hydrofluoric acid and 4 ml of perchloric acid before being subjected to sand bathing to near dryness in a fume cupboard. The digested sample was filtered using Whatman filter paper 541 into a 100 ml volumetric flask, which was later filled up to mark with distilled water. The obtained solution was analyzed using the Schimazu AA-7000 Atomic Absorption Spectrometer. Standard solutions of sodium and magnesium were prepared from stock solutions for instrument calibration.

RESULTS

The result of the diffraction analysis is presented as X-Ray diffractograms (Figures 4 and 5). For purposes of enhancement so that other clay minerals present in the samples could be recognized, the “stick pattern” of

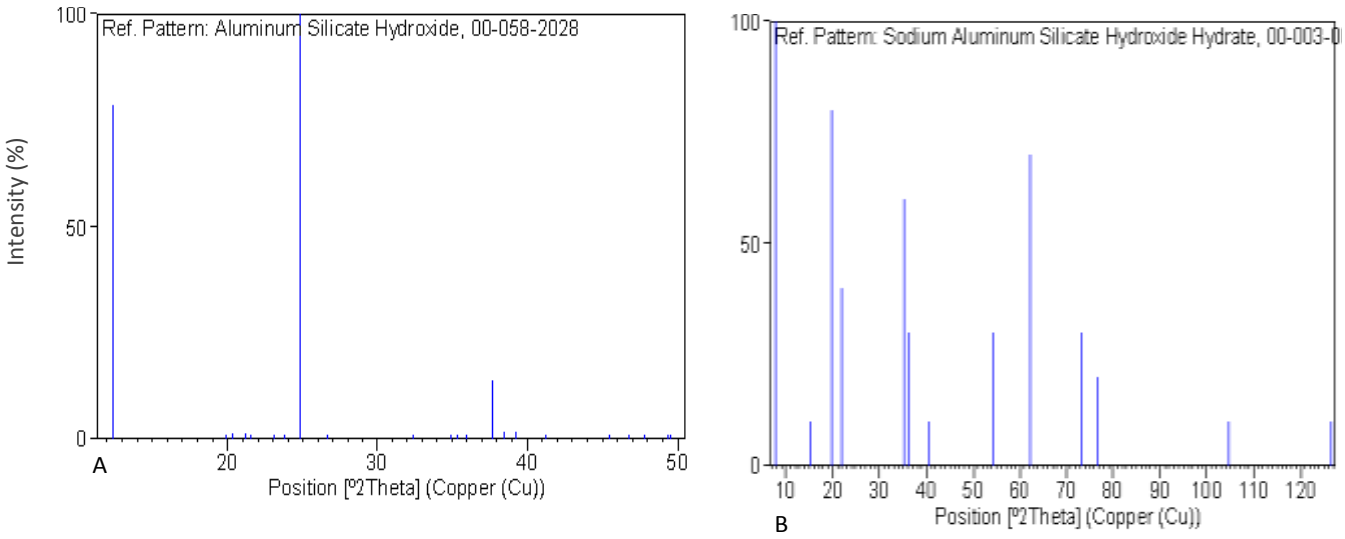

Figure 6. Representative stick patterns showing peaks of (A) Kaolinite and (B) Bentonite in clay samples.

diffraction signature was utilized to highlight the presence of iron, bentonite and dickite in some of the deposits (Figure 6).

The diffractograms revealed that only kaolinite, bentonite and dickite constitute the principal clay minerals while some iron minerals variants (fersilicate, hematite and bixbyite) are also present. Quartz was identified in all the diffractograms at basal reflections of 4.263, 3.348, 2.46 and 2.28 A°.

The results showing the major element oxide compositions and calculated Weathering Indices of the clay samples in the study area are as shown in Tables 1 and 2. Quartz (SiO_2) is the most abundant and ranged between 56.45 and 31.70%, in samples from Orlu and Ikpankwu, respectively. The tables also showed that the major oxides apart from SiO_2, include Al_2O_3 and TiO_3 while MnO, MgO, CaO, Na_2O, K_2O, and N_2O_5 were present in the clays only in small amounts. Iron as Fe_2O_3 is greater than 2% while the values of K_2O varied from 0.374 to 2.040% of the sample.

DISCUSSION

Mineralogy

Quartz was identified in all the samples indicating that it is the dominant mineral in the clay deposits in the study area. Its high dominance clearly explained its grittiness and suggestive that the clays could be of residual origin (Akhirevbulu et al., 2010).

Prominent basal reflections, strong and sharp peaks are indicators of moderate to well-formed crystalline mineral components (Jubril and Amajor, 1991; Obrike et al., 2007). Some of the samples studied (e.g. those from Njaba, Ohiya II and Orlu) showed brooding of kaolinite reflection (Figure 6) suggesting the presence of poorly ordered kaolinite (Grim, 1968). Significant quantities of bentonite were observed in samples from Awo-Omanma and Orlu. The presence of bentonite in these samples indicates that ceramic products derived from such clay types would have difficulties during drying due to the slaking properties of bentonites. Clays often contain considerable amounts of organic matter which also influences their firing properties (Robbins, 1984). Baylis et al. (1965) reported the widespread presence of dickite associated with kaolinite and illite as was observed in Ohiya II where dickite occurred with kaolinite (Figure 5).

The presence of non-clay minerals and high proportions of kaolinite suggests that the clays in the study area originated from the weathering of silicate minerals of Basement Complex rocks probably the nearby rocks of the Oban Massif under acidic condition (Odigi, 1989).

Geochemistry

Iron as Fe_2O_3 is one of the major oxides in the clay deposits in the study area. Its high values (>2%) in the samples from Uturu and Ikpankwu is probably responsible for the extreme changes in color of the clays from pink, yellow to red and the deposition of iron minerals as cementing materials that formed the concretions common in the Uturu and Ikpankwu sections. Other factors could contribute to color variations in clays (Kreimeyer, 1987), including the presence of some other constituents such as CaO, MgO, MnO and TiO_2, relative amounts of Al_2O_3, the temperature of firing and the furnace conditions all play important roles in the

Table 1. Result of the major element oxide composition and calculated weathering indices.

Sample (%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Sc_2O_3	Cao	Mgo	Na_2O	K_2O	MnO	V_2O_5	Cr_2O_3	CuO	ZnO	NiO	Ga_2O_3	Ta_2O_5	Bi_2O_3	L.O.I.	CIA%	CIW%
UT_1	40.30	4.01	25.90	13.89	0.005	0.19	0.131	0.11	0.437	0.018	0.23	0.047	0.02	-	-	-	-	3.00	11.60	97.2	98.9
UT_2	40.08	4.16	25.80	14.41	-	0.18	0.13	0.10	0.417	0.01	0.21	0.053	0.034	-	0.02	-	0.086	2.70	11.70	97.4	98.9
UT_3	48.79	6.26	28.62	3.11	-	0.25	0.21	0.10	0.467	0.030	0.28	0.040	0.02	-	0.01	-	-	1.12	10.60	97.2	98.8
$Orlu_2$	56.45	5.53	25.20	1.79	0.006	0.25	0.20	0.133	0.637	0.030	0.25	0.034	0.021	-	0.031	0.042	-	-	9.40	96.1	98.5
$Orlu_I$	47.75	7.04	25.40	1.80	0.002	0.26	0.21	0.14	0.638	0.02	0.30	0.049	0.026	-	0.025	0.041	-	-	16.30	96.1	98.4
AWO_2	55.42	3.98	27.00	1.10	0.003	0.290	0.181	0.130	0.524	0.033	0.21	0.044	0.026	-	0.019	0.030	-	-	11.00	96.6	98.5
AWO_I	56.44	4.68	25.70	1.15	-	0.23	0.17	0.12	0.374	0.030	0.22	0.035	0.024	-	0.02	-	-	-	10.80	97.3	98.7
EZ_1	54.25	3.60	22.00	2.14	0.004	0.28	0.21	0.70	2.04	0.026	0.23	0.083	0.033	0.066	0.059	-	-	-	14.20	87.9	95.7
NJ_1	54.10	5.57	26.20	1.71	0.005	0.23	0.19	0.22	0.607	0.030	0.27	0.045	0.019	-	0.01	0.01	-	-	10.80	96.1	98.3
																				95.8	98.3

Table 2. Result of the major element oxide composition and calculated weathering indices.

Sample (%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Sc_2O_3	P_2O_5	SO_3	CaO	MgO	Na_2O	K_2O	MnO	V_2O_5	Cr_2O_3	CuO	ZnO	NiO	Ga_2O_3	L.O.I.	CIA%	CIW%
NJ_2	54.44	5.37	26.50	1.68	0.002	-	-	0.238	0.20	0.18	0.571	0.01	0.28	0.059	0.022	0.003	0.020	0.02	10.40	96.4	98.4
IKP_4	38.90	3.81	20.02	23.85	-	-	-	0.16	0.10	0.281	0.720	-	0.17	0.055	-	-	0.032	-	11.90	94.5	97.8
IKP_3	31.70	3.03	19.20	29.43	0.004	0.73	-	0.25	0.195	0.42	1.02	-	0.16	0.051	0.041	0.04	0.029	-	13.70	91.9	96.6
IKP_2	48.80	5.25	28.50	1.94	0.003	0.63	0.15	0.23	0.182	0.28	0.677	0.017	0.26	0.078	0.025	-	0.026	0.053	12.90	96	98.2
IKP_1	45.69	5.01	22.60	3.40	0.007	-	3.09	0.27	0.21	0.46	1.83	-	0.29	0.076	0.027	0.01	0.046	0.048	16.93	89.8	96.9
OH_1U_1	48.89	2.16	28.20	1.97	0.003	-	0.64	0.22	0.19	0.25	0.902	-	0.21	0.061	0.035	0.01	0.039	0.03	16.20	95.4	98.4
OH_1U_2	50.77	2.16	29.30	1.24	-	-	-	0.275	0.24	0.18	0.934	0.031	0.21	0.050	0.028	0.03	0.019	0.03	14.50	95.5	98.5
OH_2U_2	48.59	2.21	27.70	2.01	0.007	-	0.72	0.290	0.20	0.13	0.810	0.029	0.20	0.062	0.042	0.01	0.037	0.045	16.90	95.7	98.5
OH_2U_1	51.35	2.47	27.60	1.57	0.006	-	-	0.268	0.21	0.15	0.797	0.032	0.21	0.068	0.042	0.006	0.02	-	15.20	95.8	98.5
																				95.8	98.3

development of color in the fired clay products (Fischer, 1984). The presence of iron minerals in the clays could also constitute a challenge to their use as industrial raw materials for paper and rubber productions (Obrike, 2012). Low iron content in samples from Ezinnachi, Njaba, Ohiya I and II potentially makes the dominant kaolin mineral useful in white body production (Murray, 2007).

The low values of K_2O that varied from 0.374 to 2.040% could be related to the absence of illite in most of the clay deposits. MgO values were also low and thus explained why smectite was absent in the deposits. Generally, the low amounts of MgO and CaO caused the absence of associated carbonate or dolomitization processes in the study area.

Provenance

The clay deposits in the study area are mainly clastics and not the product of *in situ* weathering, hence, the geochemical signatures used to identify provenance were those used for clastic rocks (Madharaju and Ramasamy, 2002; Armstrong-Altrin et al., 2004). The ratios of most

Table 3. Recalculated oxide ratios and parameters used in plotting some of the discriminating diagrams.

Sample No.	SiO_3	Al_2O_3	Al_2O_3/TiO_3	K_2O/Na_2O	SiO_2/Al_2O_3	T_x	DF1	DF2
UT_1	47.4	15.2	6.459	3.97	1.556	11	3.806	-1.721
UT_2	47	15.1	6.202	4.17	1.553	11.4	3.943	-1.872
UT_3	55.6	16.3	4.572	4.67	1.705	5.92	13.38	7.737
$Orlu_2$	62.6	14	4.557	4.79	2.24	4.73	14.34	9.172
$Orlu_I$	57.4	15.3	3.608	4.56	1.88	6.06	18.18	11.51
AWO_2	62.5	15.2	6.784	4.03	2.053	3.5	9.676	6.285
AWO_1	63.5	14.5	5.491	3.12	2.196	3.78	11.95	7.5
EZ_1	63.7	12.9	6.111	2.91	2.466	5.26	11.35	10.61
NJ_1	60.9	14.7	4.704	2.76	2.065	4.8	13.78	8.817
NJ_2	61	14.9	4.935	3.17	2.054	4.62	13.12	8.316
IKP_4	44.3	11.4	5.255	2.56	1.943	16.5	-2.147	-11.2
IKP_3	37.2	11.3	6.337	2.43	1.651	20.1	-8.745	-18.23
IKP_2	56.8	16.6	5.429	2.42	1.712	4.98	11.67	7.468
IKP_I	57.5	14.2	4.511	3.98	2.022	7.03	14.45	11.27
OH_1U_2	59.1	17	13.06	3.61	1.734	3.44	4.737	3.566
OH_1U_1	59.7	17.2	13.56	5.19	1.733	2.95	4.934	3.823
OH_2U_2	59.3	16.9	12.53	6.23	1.754	3.45	4.934	3.481
OH_2U_1	60.8	16.3	11.17	5.31	1.861	3.24	5.778	4.126

T_x= TiO_2 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O SiO_2 = 100 wt.%; DF1 = 56.50TiO_2 – 10.879Fe_2O_3 + 30.875Mgo – 5.404Na_2O + 11.112K_2O/Al_2O_3 – 3.89Al_2O_3 = 50 wt.%. DF2 = 30.638TiO_2 – 12.541Fe_2O_3 + 7.32Mgo + 12.031Na_2O + 35.402K_2O/AL_2O_3 – 6.382 Tx = 50 wt.%.

clastic rocks have also been used to infer the source rock composition: Al_2O_3/TiO_2 ratio increases from 3 to 8 for mafic igneous rocks, 8 to 21 for intermediate rocks and 21 to 70 for felsic igneous rocks (Hayashi et al., 1997). The application of these hypotheses in the analyzed clay samples deposited in the study area, showed that the calculated Al_2O_3/TiO_2 ratios ranged from 3.6 to 13.5, which is indicative that the clays originated from mafic to intermediate igneous rocks.

Ekosse (2001) also used of TiO_2 versus Al_2O_3 binary plots to distinguish between granitic and basaltic source rocks. Application of this plot using the recalculated oxide ratios for the discrimination of provenance of clays in the study area (Table 3) suggested that the deposits originated from basalt + rhyolite/granite provenances (Figure 7).

Again, the discrimination diagram for sedimentary provenances by Roser and Kosch (1988), showed that the sediments from the study area were derived from mafic igneous and quartzose provenances (Figure 8).

Tectonic settings

Plate tectonic processes impact distinctive mineralogical and geochemical signatures to sediments and as such clastic sedimentary rocks and sedimentary basins can be classified according to plate tectonic settings (Roser and Korsch, 1986). The SiO_2 versus K_2O/Na_2O diagram was therefore used for the discrimination of tectonic settings at the time when the claystone suites were formed in the study area. The SiO_2-K_2O/Na_2O diagram suggested that the sediments in the study area were deposited between passive and active continental margins (Figure 9).

The weathering indices of sedimentary rocks can also provide useful information of tectonic activity and climatic conditions in the source area. As demonstrated by Nesbit et al. (1982), a measure of the degree of chemical weathering alteration of sediments was constrained by calculating the Chemical Index of Alteration (CIA):

CIA = Molars [$Al_20_3/(Al_2O_3$+CaO*+Na_2O+K_2O)],

where CaO* represents the amount of CaO in silicate minerals only (that is, excluding those of carbonates).

The proposed Chemical Index of Weathering (CIW) of Harnois (1988) was also evaluated with the formular:

CIW = Molars [$Al_20_3/(Al_2O_3$+CaO*+Na_2O)]

Nesbitt et al. (1982) reported a CIA value of nearly 100 for kaolinite and chlorite and 70 to 75 for average studies whereas Taylor and McLennan (1985) reported a CIA value of 85 to 100 for residual clays. Condie (1993) reported that most post-Archean Shales show moderate losses of Ca, Na, and Sr from source weathering with CIW values of 80 to 95. The CIA and CIW of the sediments in the study area are both higher than those of

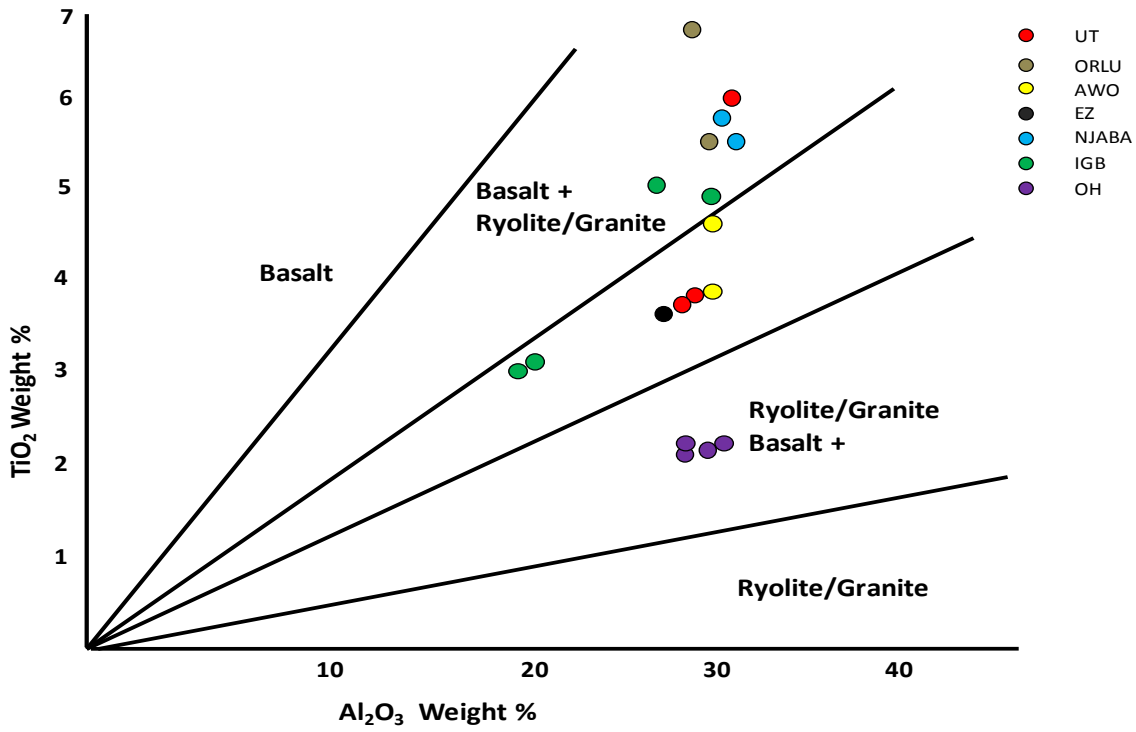

Figure 7. TiO_2/Al_2O_3 binary plots of some clays in the study area.
Source: Modified after Ekosse (2001).

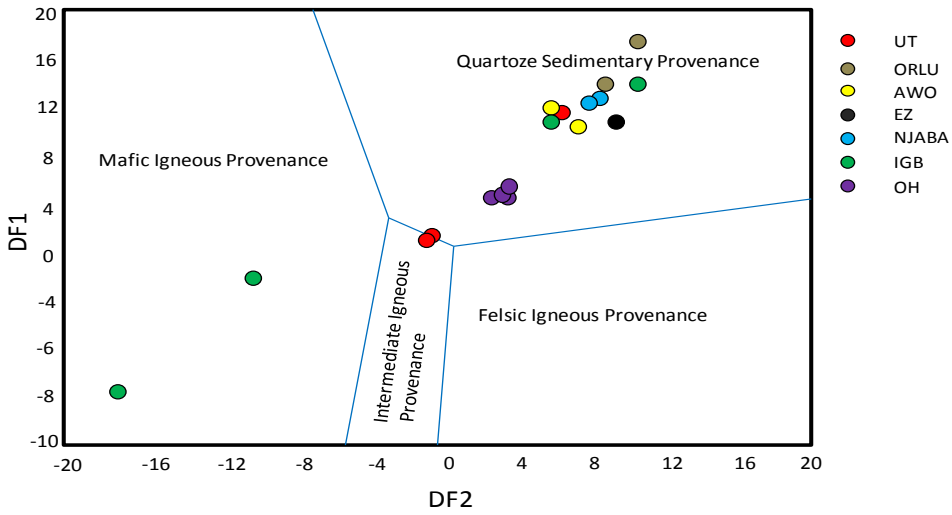

Figure 8. Discriminatory diagram for sedimentary provenance of sediments in the study area.
Source: Modified after Roser and Korsch (1988).

the average shales (95.8 and 98.3), respectively suggesting relatively intense weathering of the source area, probably corroborating the presence of clay minerals and absence of detrital feldspar (Tables 3 and 4) suggesting chemical maturity of the sediments.

Potential industrial value of the clay deposits

The assessment of the clay deposits as potential raw materials was achieved by a comparative analysis of the chemical composition of the clay deposits in the study

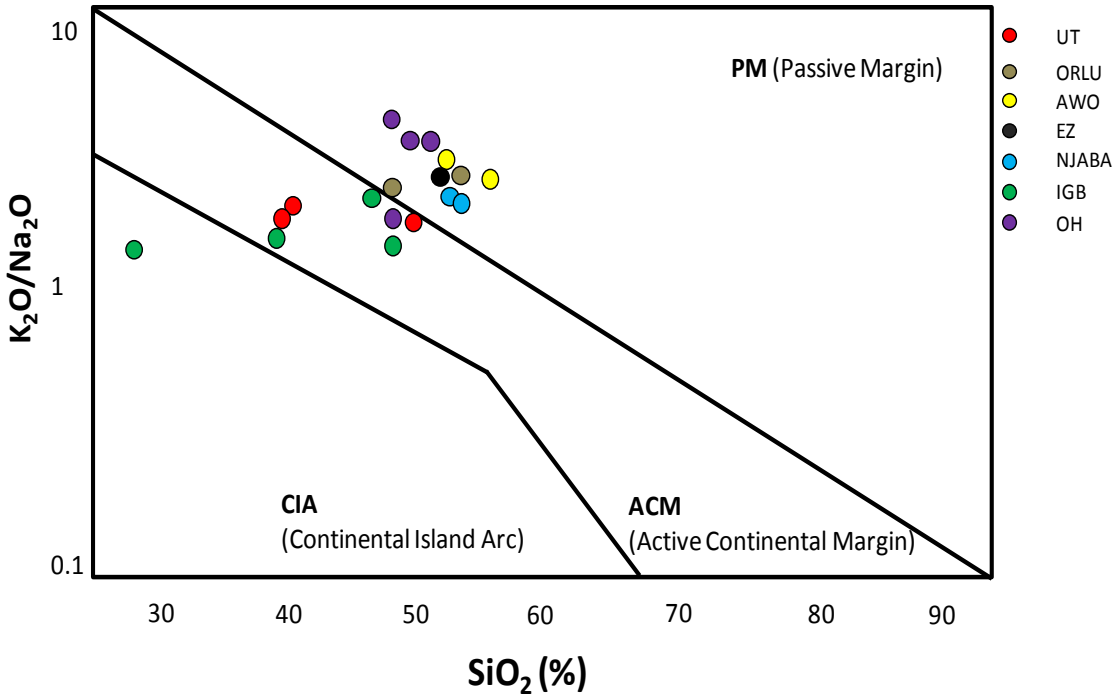

Figure 9. K_2O/Na_2O versus SiO_2 plot of Clays in the study area.
Source: Modified after Roser and Korsch (1986).

Table 4. Chemical Composition of some known reference clay samples.

Oxides (%)	Afikpo Shale (Arua and Onyeoku, 1978)	Afam Clay (Jubril and Amajor, 1991)	Plastic Fire clay of St Louis (Huber, 1985)	Florida active Kaolinite (Huber, 1985)	Maastrichtian Clay in Bida Basin (Olusola et al. (2011)	Dukku Clay Kebbi State (Salihu and Suleiman, 2018)
SiO_2	59.81	42.20	57.67	5.00	63.3	55.59
Al_2O_3	21.76	26.20	24.00	2.92	24.6	35.5
Fe_2O_3	3.02	5.10	3.23	9.42	1.60	4.5
MgO	1.45	0.70	0.30	3.65	0.06	1.9
CaO	1.32	1.60	0.70	0.08	0.04	2.10
Na_2O	0.47	2.90	0.20	1.91	0.07	-
K_2O	0.87	8.30	0.50	0.03	0.32	-
TiO_2	0.92	-	-	0.98	1.75	0.02
P_2O_5	-	-	-	1.18	0.07	-
MnO	n.d	0.03	-	0.02	0.01	-
H_2O	-	-	10.50	10.19	-	-

area with those of some notable clays and industrial specifications of some clays in other areas (Tables 3 and 4). It was observed that the average chemical compositions of the studied clay deposits were similar to the Afam clay as reported by Jubril and Amajor (1991) and plastic fire clay of St Louis (Huber, 1985), but for higher Fe_2O_3 content in the Uturu and Ikpankwu clays (Table 4).

The clay deposits in the study area were also compared with the Maastrichtian clay from the Bida Basin as reported by Olusola et al. (2011). The Bida Basin clay was observed to be more enriched in silica than those from the study area. The Fe_2O_3 with a value of 1.6 compared favorably with some of the clays in the study area, although in some locations like Ikpankwu and Uturu, the clays from the study area showed very high Fe_2O_3 content. The Bida Basin clay was observed to be depleted in MgO and CaO. The Al_2O_3 and alkali contents however showed similar value with clays from the study area (Table 4). The clay from the study area also

Table 5. Standard specifications of the concentrations (in %) of oxides in clays for various industrial uses.

Oxides (%)	A	B	C	D	E	F
SiO_2	51.70	67.50	44.90	45.90-48.5	38.67	68.478
Al_2O_3	25.44	26.50	32.35	33.5-36.1	9.45	14.942
Fe_2O_3	0.5-1.20	0.5-1.20	0.43	0.30-0.60	2.70	8.96
MgO	0.2-0.70	0.1-0.19	Tr	-	8.5	1.143
CaO	0.1-0.20	0.18-0.30	Tr	0.0-0.50	15.84	1.615
Na_2O	0.8-3.50	0.20-1.50	0.14	0.0-1.6	2.76	0.034
K_2O	-	1.10-3.10	0.28	0.0-1.6	2.76	2.045
TiO_2	1.0-2.80	0.10-1.0	1.80	0.0-1.70	-	-
P_2O_5	-	-	-	-	-	-
MnO	-	-	-	-	-	-
H_2O	-	-	-	-	3.04	-

(A) Refractory bricks (Parker, 1967); (B) Ceramics (Singer and Sunja, 1971); (C) Rubby (Keller, 1964); (D) Paper (Keller, 1964); (E) Brick Clay (Murray, 1960); (F) Refractory bricks and Ceramics (Malu et al., 2013).

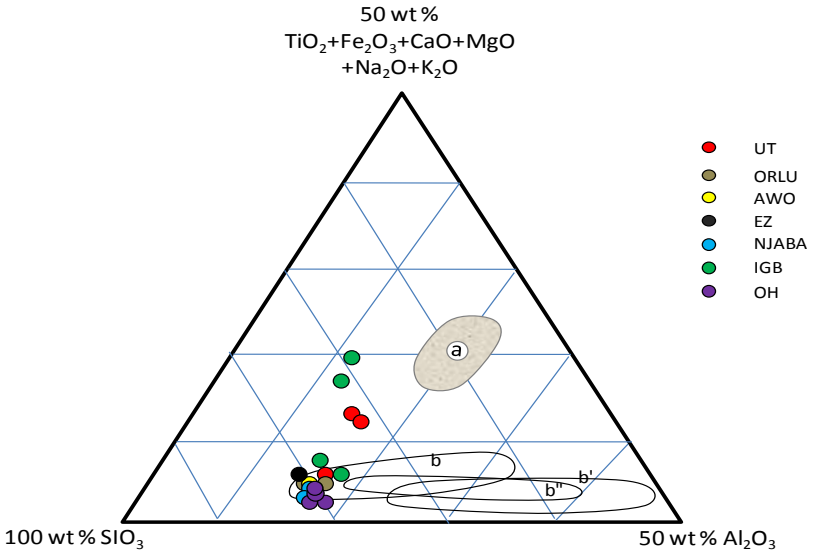

Figure 10. Tenary diagram of clays in the study area: *SiO_2/Al_2O_3*Total oxides are plotted. a = red stoneware (Italy); b, b', b'' = white stoneware in Germany, English and French industries, respectively.
Source: Fabbri and Fiori (1985).

compared similarly with Dukku clay from Kebbi State as reported by Salihu and Suleiman (2018), however, the Al_2O_3 and CaO were higher. The Dukku clay was also depleted in TiO_2. In comparison with standard chemical specifications for the requirements of kaolin to be used for refractory bricks (Parker, 1967), the average chemical compositions of the sampled clay deposits in parts of Southeastern Nigeria are suitable for refractory bricks production (Table 5).

The chemical data from the clay deposits in the study area were also plotted into the tenary diagram of Fabbri and Fiori (1985) for the classification of raw materials and industrial ceramic bodies. The plots gave ceramic compositional fields and reflected the overall chemical composition of the clays in parts of southeastern Nigeria (Figure 10). Considering the ideal composition for an optimum white body product: SiO_2 = 72 wt.%, Al_2O_3 and total oxide = 8 wt.% (Fabbri and Fiori, 1985), samples outside this specification would need processing in order to moderate iron oxide and quartz contents. It is based on these standard chemical compositions that clays could be considered as raw materials for use in structural ceramic products (Konta, 1995).

The analyses have thus shown that the clay deposits in

the study area could be used as raw materials for the production of refractory bricks (Parker, 1967; Malu et al., 2013) and pottery (Jubril and Amajor, 1991; Huber, 1985).

Iron oxide (Fe_2O_3) would be a limitation to their use in paper, rubber and white body production especially the samples from Uturu and Ikpankwu. Appreciable amounts of oxides of sodium, calcium and magnesium recorded in the deposits would also lower the vitrification of the clays (Obrike, 2012). High alumina-iron ratio in the clays will render them less suitable for the production of good quality cement except for samples from Uturu and Ikpankwu, where the alumina-iron ratio is low. An alumina-iron ratio range of 1.71 to 2.45 for clay or shale is suitable for the manufacture of good quality cement (Abatan et al., 1993).

Conclusion

Mineralogical and chemical parameters of clays have been assessed and used in this study to ascertain the industrial potentials and provenance of clays from parts of Southeastern Nigeria.

Mineralogical analysis showed the presence of kaolinite, bentonite, dickite, quartz and iron minerals in the clay deposits. Kaolinite and quartz were the most dominant minerals as they occurred in all the samples. Bentonite occurred only in samples from Awomamma and Orlu indicating a possible source from the adjoining Cameroun volcanics. The presence of bentonite in samples from Awo-Omamma and Orlu with slaking properties would render a ceramic body prone to difficulties during drying. Dickite occurred in association with kaolinite, showing progressive replacement in the Ohiya II clay unit, while iron minerals were common in clays from Ikpankwu and Uturu sections. The iron minerals caused the occurrence of concretions and extreme coloration of clays from both sections and could ensure color effects on finished products. The presence of iron minerals in these clays would constitute huge challenges for their usage in industries, especially for paper and rubber production. On the other hand, low iron content in clays from Njaba, Ohiya I and II would potentially make the dominant kaolin mineral useful in white body production.

The geochemical analysis revealed that the samples from the study area are rich in alumina Al_2O_3 which corresponds with the kaolinite clays with major oxides like SiO_2, Fe_2O_3, TiO_3, MnO, MgO and CaO.

Comparison with some industrial specifications, the clay deposits in the study area would be used as raw materials for the production of pottery, bricks, ceramics, refractories, paper, earthenware and paints. The low alumina-iron ratio in the samples from Uturu and Ikpankwu deposits would render the clays suitable for the production of good quality cement.

RECOMMENDATION

Though the results from the studied samples show wide range of industrial applications, most of them are not comparable to commercially marketed European and Asian counterparts. It is therefore recommended that elaborate treatments should be carried out by a centralized clay mineral dressing and preparation plant, remediation process by proper blending, beneficiation with lime and refining processes. It is expected that processing will help overcome compositional deficiencies.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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