

# Geochemistry and Mineralogy of Clays from Ewohimi, Northern Niger Delta Basin, Nigeria

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## ABSTRACT

*Neogene age clay samples of the Ogwashi-Asaba Formation at Ewohimi, were analysed for geochemical and mineralogical properties, using XRF, ICP-AES and XRD in order to investigate their compositional characteristics of major and trace elements. With integrated geochemical and mineralogical approach, the composition, provenance, weathering, paleo – redox and the tectonic setting under which they were formed was defined. Mineralogical analysis indicate subordinate amounts of quartz and kaolinite as the only observable clay minerals. Major oxides content of SiO<sub>2</sub> (56.03 – 72.84%) and Al<sub>2</sub>O<sub>3</sub> (13.63 – 22.92%) constitute over 84% of the bulk chemical compositions, indicating source rocks rich in quartz and silica-rich. Low occurrences of Na<sub>2</sub>O, MgO and K<sub>2</sub>O indicate the extent of weathering and transport, thus, suggest a continental granitic origin, possibly from the Oban Massif, east of the Anambra Basin. Although notable disparities exist in the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents of the clays in Ewohimi; the River Odu clay is more siliceous and less aluminous than the others whereas, the Asaboro clay is more aluminous than others confirming a high degree of weathering activities. Redox-sensitive trace element ratios (Ni/Co, V/Cr and V/V+Ni) indicate a predominantly oxic environments of deposition. The dominance of detrital kaolinite, the enrichment of chemically immobile elements (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) and high values of Chemical Index of Alteration (CIA) suggest intensive chemical*

*weathering of the source rocks under tropical to subtropical humid climatic conditions.*

## (I) INTRODUCTION

Clay is widely distributed. Besides their geological interest, they are of importance for local

Industry, abundant mineral resource of major industrial importance for an enormous variety of uses. In both value and amount of annual production, it is one of the leading minerals worldwide. In common with many geological terms, the term “clay” is ambiguous and has multiple meanings: a group of fine grained minerals — i.e., the clay minerals; a particle size (smaller than silt); and a type of rock — i.e., a sedimentary deposit of fine-grained material usually composed largely of clay minerals. In the latter definition, clay also includes fine-grained deposits of non-aluminosilicates such as shale and some argillaceous soils. Clay minerals have a wide range of particle sizes from 10’s of angstroms to millimetres (An angstrom (Å) is a unit of measure at the scale of atoms).

Globally, clay has a wide spread occurrence. In Nigeria, clay is widely distributed though not always found in sufficient quantity or suitable quality for modern industrial purposes. More than 80 clay deposits have been reported from all parts of the country (Coker et al. 1992). For instance, clay deposits occur in Abak, Akwa Ibom State, Uruove near Ughelli in Delta State, Ifon in Ondo State, Mokola in Oyo State, Sokoto in Sokoto State, Gombe in Gombe State,

Umuahia in Abia State, Dangara in Niger State, Onitsha in Anambra State and Aloji, Udane Biomi, Agbenema and Ofe jiji all in Kogi State, Ozanogogo and Ubulu-Uku in Delta State e.t.c

Few studies have been made of the clays in the Neogene Ogwashi – Asaba Formation. Thus, the present study evaluates the mineralogical and chemical characteristics of the clays at Ewohimi, as this will help to give a better understanding of the clay materials, as well as their geochemistry.

### Aim and objectives

This work is aimed at achieving the geochemistry and mineralogical composition(s) of clays within the Northern Niger Delta Basin.

### Location and Accessibility

The study area (Fig. 1) falls under Esan North East Local Government Area of Edo State Nigeria. The study plot lies approximately between latitude 6°23' and 6°30' East of the Greenwich Meridian and equally lies approximately between longitudes 6°18' and 6°22' north of the equator. It is bounded by so many towns. To the North it is bounded by Igueben, Ubiaja and Ewatto. Also, to the south it is bounded by Igbodo and Idumuje-Ugboko respectively.

Both the foot paths, old and new road were used as access path ways. Those areas that were not easily accessible was cleared using the cutlass.

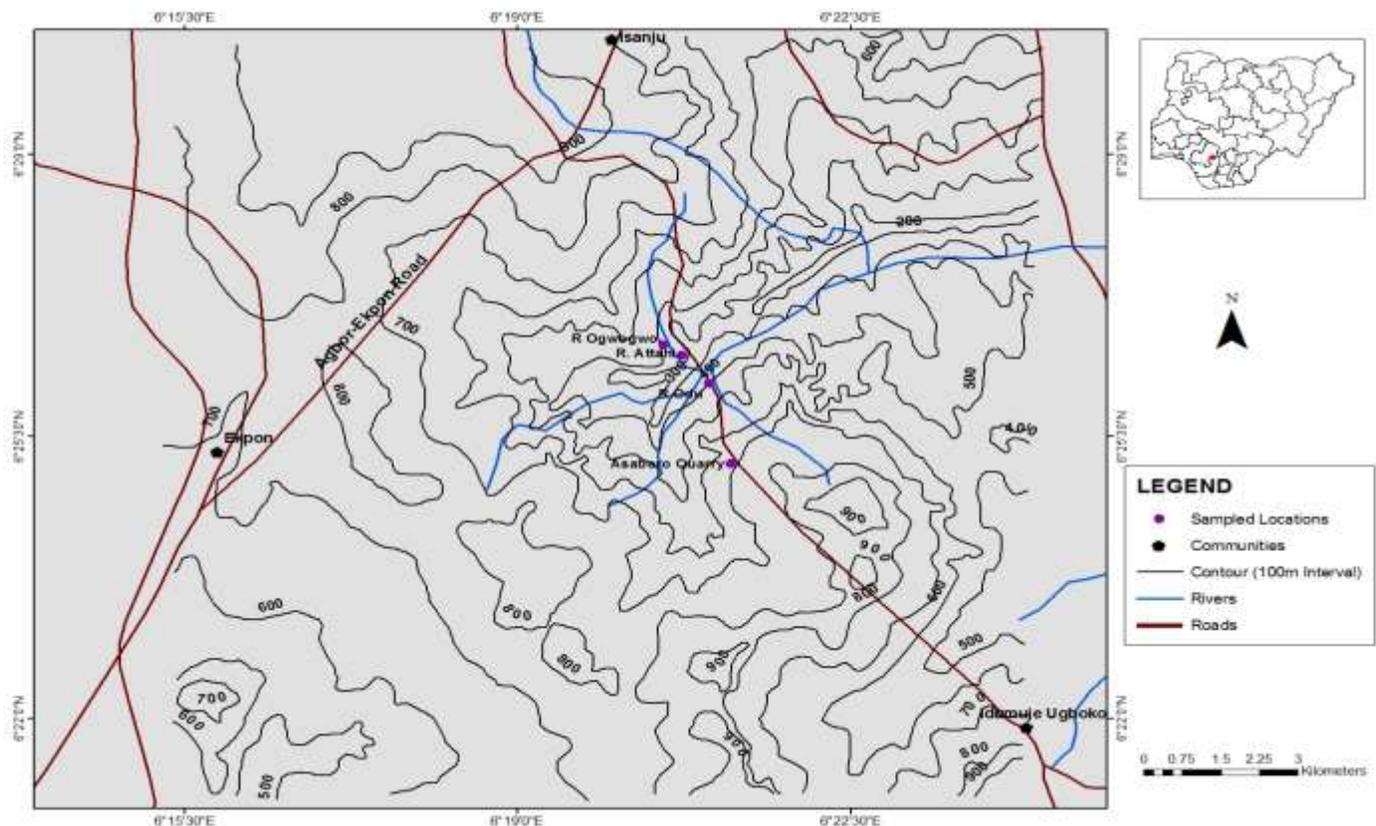


Figure 1: showing the sample locations and accessibility of the study area.

## (II) METHODOLOGY

On the field, the rock exposures were observed and described based on their colour, texture, structural elements and mode of occurrences. From field observations, all locations within the study area consist of laterite except along newly constructed Abuja – Onitsha road and river cut where clay was identified.

As such, samples from location A, B, C and D were labelled with their coordinates respectively for easy identification. A total of four (4) clay samples weighing about 10kg, were carefully taken from the locations with the aid of a geological hammer. All samples were carefully labelled and arranged in sac bags for the laboratory analyses.

### LABORATORY ANALYSIS.

A quantitative determination of the geochemical and mineralogical properties of the Ewohimi clay samples using X-ray diffraction (XRD), X-ray fluorescence (XRF) and Inductively Coupled Plasma Atomic Electron Spectroscopy (ICP-AES) were carried out at Geoscience Laboratories (Geo Labs) Ontario, Canada.

Four (4) of the clay samples (EWH<sub>A</sub>, EWH<sub>B</sub>, EWH<sub>C</sub> and EWH<sub>D</sub>) were analysed using X-ray fluorescence (XRF) and inductively coupled plasma atomic electron spectroscopy (ICP-AES). However, only one clay sample (EWH<sub>A</sub>) was analysed using X-ray diffraction (XRD).

### X-ray fluorescence (XRF)

The four clay samples were pre-oxidized at 50°C in porcelain crucible for 5h. After cooling, the oxidized, calcined (ignited) sample (1.000 g) is normally weighed into a

borate flux (6.000 g) composed of a 49.75:49.75:0.50 mixture of lithium metaborate, lithium tetraborate and lithium iodide (“50/50” borate mix) and the samples were then melted at 120°C in Pt-Au crucible and cooled in Pt-Au disk mould. This flux mixture enables a wide range of different geological matrices to be analyzed and the lithium iodide serves as a releasing agent from the platinum crucibles. A platinum-5% gold alloy for crucibles and casting dishes is used because it is strong, stable, durable, heats and cools rapidly, does not melt at fusion temperatures and is easily washable in a 10% nitric acid solution. The automated fluxer used to create these glass disks is the Claisse M4 fluxer. The disks were analysed for the determination of Major Elements by WD-XRF Method Codes: XRF-M01 and XRF-M02 Operation of PANalytical Axios Advanced. Analytical precision was verified by the preparation and analysis of several in-house standards. Analysed major elements were SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, CaO and P<sub>2</sub>O<sub>5</sub>.

### Inductively coupled plasma atomic electron spectrometry (ICP-AES)

Also, the four clay samples were analysed for major and trace elements using inductively coupled plasma atomic electron spectrometry (ICP-AES). Multi-Acid Sample Dissolution: Method Code SOL-OT3 Open Beaker Hydrofluoric-Perchloric-Nitric Digest Acid. Acid digestions were prepared using approximately 50mg of powdered sample, peroxidised overnight with 1ml HNO<sub>3</sub> (65%) in PTFE vessels, and subsequently heated to 180°C for six hours in PTFE autoclaves (PDS-6) with 3ml HF (40%) and 3ml HClO<sub>4</sub> (70%). Acids were removed by evaporation at 180°C on hot plates, and the wet residue were re-dissolved

and re-evaporated using 3×1 ml of half concentrate HCL. After the final HCL treatment, wet residues were dissolved in 1ml HNO<sub>3</sub> (65%) and diluted to 50ml with distilled and deionised water.

At the solution preparation stage, a known amount of rhenium and ruthenium are added to the samples as internal standards. Rhenium is monitored for indications of unspiked samples or samples missed due to an auto sampler error, and data will be collected for determination of its applicability as internal standards to correct for elemental concentrations due to drifts or variances in the argon plasma.

### **X-ray diffraction (XRD)**

The EWH<sub>A</sub> clay sample was ground in a clean agate mortar to obtain minus 10µm size. The powder sample is filled and pressed in a sample stage (Reflection-Transmission Spinner PW3064/60) and pushed into the goniometer(PW3050/60) chamber of the XRD machine (XPERT-PRO). The machine was set at operating voltage of 40KV and ampere of 45mA and continuously ran at 25°C from 5.0066 to 84.98262θ with inbuilt standards, peak/width and a detector. The diffraction pattern was obtained with the aid of a computer, while the 2θ, d-values and peak intensities yielded by the powder patterns were used to identify the minerals.

### **Statistical analysis**

Statistical analysis of the geochemical results (XRF and ICP - AES) were performed using Microsoft Excel 2013, Iogas geochemical trial software (version 5.0) and statistical package for social science (SPSS) version 21. They were used to plot the data sets for the determination of major and trace elements correlation, correlation coefficient (Pearson's Correlation coefficient), provenance, source area weathering, paleo-redox conditions, tectonics. Normalization of values for major and trace elements, was done using the Iogas geochemical trial software (version 5.0).

## **(III) RESULTS AND INTERPRETATION**

### **FIELD DESCRIPTION**

River Ogwogwo Clay (EWH<sub>A</sub>) The River Ogwogwo is located about a kilometre from the water board, along Abuja-Onitsha new road that traverses Okaigben-Ewohimi. At location one (1), (N 06° 26' 37.6" and E006° 20' 31.9"), the clay is lithified into claystone. This exposure is capped by an impervious ferruginous ironstone with a thickness of about 30m, thereby serve as a barrier to percolating groundwater and a consequent subsurface lateral flow that emanates as a spring as shown in (Fig. 2 ). The clay at this location is greyish-white in colour.



**Figure 2: showing the clays at Ogwogwo River.**

**River Attahi clay (EWH<sub>B</sub>)** The River Attahi clay (N 06° 26' 29.7" and E006° 20' 43.5") is exposed at the Attahi River cut in Okaigben-Ewohimi, opposite the water board. The exposed clays are very massive and low lying and 7m thick. The clay exhibits an off-white colour with little stain of red-brown which is attributable to oxidation (lateritization).

**River Odu Clay (EWH<sub>C</sub>)** The River Odu Clay (N 06° 26' 09.0" and E006° 21' 00.6") is exposed along the road cut beside the water board just before the river Odu Bridge. The exposed clay coloration ranges from an alternating off-white at the bottom of 1.1 metres thick, mixed brown and off-white layer of 1.5 metres thick, brownish

layer of 2.4 metres thick and a lateritic capping. It is smooth but gradually changes to gritty sandy clay towards the base.

**Asaboro borrow pit Clay (EWH<sub>D</sub>)** The Asaboro borrow pit clay (Fig. 3), (N 06° 16' 32.2" and E006° 02' 12.6") is exposed at about 4 kilometres from Odu River, along the Onitsha-Abuja. The exposure is a borrow pit where sand is excavated. The clay unconformably overlies a sand sequence and is then overlain by channel lag deposits which is then capped by weathered lateritic sand as overburden. The area has a rolling terrain with height reaching 277m above sealevel. The clay deposit is mostly off-white with reddish, bluish and brownish stains which is attributable.



**Figure 3: Showing the occurrence of Clays at Asaboro borrow pit.**

Generally, the clay horizons exhibit a coarsening-up sequence. This attribute indicates deposition in overbank settings (Ashmore, 1991)

**Whole rock geochemistry** Tables 4 and 5 presents the results of geochemical analysis showing the different elements and oxide forms of the major elements contained in the clay samples, with a little over 87% of the samples being characterized by ten

elements. The remaining 15% of the composition is ascribed to water, trace elements and, perhaps, organic matter. For comparison, typical composition of Ubiaja clay (UBJ), Onyeobi et al. 2013, Afam clay (AFC) Jubril and Amajor, 1991, Upper Continental Crust (UCC), Rudnick and Gao, 2003, average clay-shale (AVCS), Pettijohn, 1957 and Post Achean Australian Shale (PAAS), Taylor and McLennan, 1985).

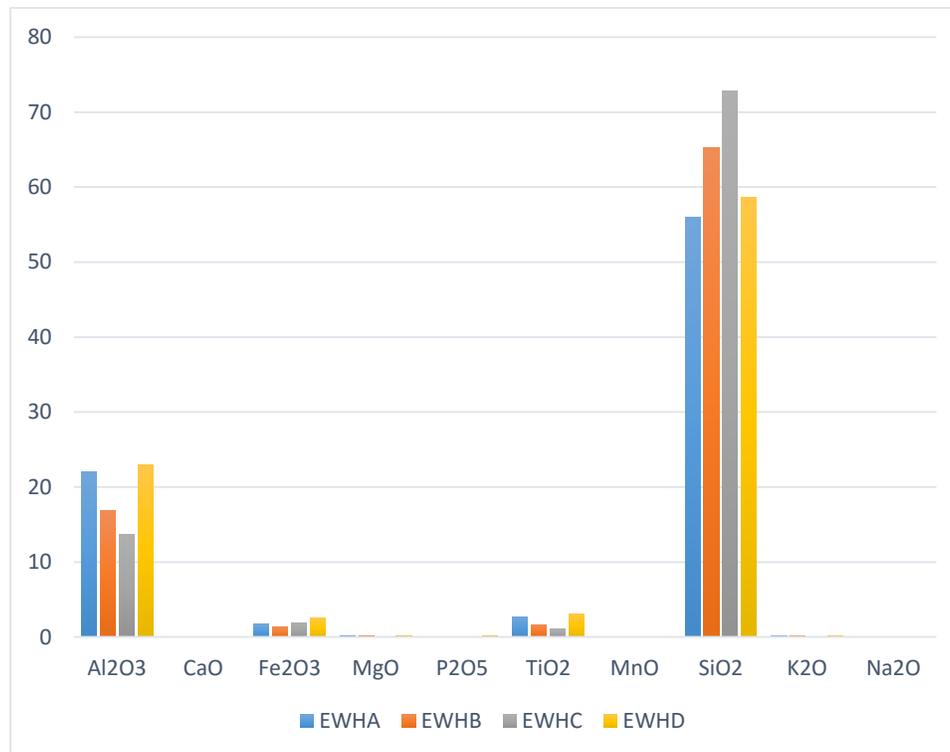
**Table 4: Major oxides of the clay samples from XRF analysis.**

Oxide	Units	Detection Lim	EWH <sub>A</sub>	EWH <sub>B</sub>	EWH <sub>C</sub>	EWH <sub>D</sub>	Average
Al <sub>2</sub> O <sub>3</sub>	Wt%	0.02	22.07	16.9	13.63	22.92	18.88
CaO	Wt%	0.006	0.043	0.025	0.025	0.024	0.029
Fe <sub>2</sub> O <sub>3</sub>	Wt%	0.01	1.72	1.3	1.91	2.55	1.87
K <sub>2</sub> O	Wt%	0.01	0.16	0.17	0.05	0.14	0.13
LOI	Wt%	0.05	16.66	14.35	8.79	11.18	12.75
MgO	Wt%	0.01	0.09	0.09	0.07	0.1	0.086
MnO	Wt%	0.002	0.012	0.008	0.006	0.014	0.01

Na <sub>2</sub> O	Wt%	0.02	<0.02	<0.02	<0.02	<0.02	-
P <sub>2</sub> O <sub>5</sub>	Wt%	0.002	0.06	0.055	0.03	0.079	0.056
SiO <sub>2</sub>	Wt%	0.04	56.03	65.28	72.84	58.7	63.21
TiO <sub>2</sub>	Wt%	0.01	2.74	1.65	1.1	3.09	2.15
Total			99.61	99.84	98.45	98.83	99.18
CIA			98.99	98.74	99.31	99.20	99.06
CIW			99.72	99.73	99.67	99.81	99.73
MIA			97.98	97.48	98.62	98.4	98.12
PIA			99.71	99.73	99.67	99.81	99.73

**Table 5: Major and trace elements distribution of the clay samples from ICP-AES.**

Elements	Units	Detection Lim	EWH <sub>A</sub>	EWH <sub>B</sub>	EWH <sub>C</sub>	EWH <sub>D</sub>	Average
Al	Ppm	20	109227	89463	71833	>110000	
Ba	Ppm	1	134	121	41	142	109.50
Ca	Ppm	25	192	79	66	69	101.50
Co	Ppm	1	<1	<1	<1	<1	1
Cu	Ppm	1	21	13	14	24	18.00
Cr	Ppm	2	109	62	62	144	94.25
Fe	Ppm	40	12696	10167	14949	19687	
K	Ppm	65	214	1448	292	1122	769
Li	Ppm	1	8	6	6	5	6.25
Mg	Ppm	20	404	329	314	383	357.50
Mn	Ppm	1	80	46	41	103	67.50
Na	Ppm	45	69	80	46	71	66.50
Ni	Ppm	2	19	12	16	18	16.25
Pb	Ppm	35	45	42	<35	59	45.25
Sc	Ppm	1	13	10	8	13	11.00
Sr	Ppm	1	81	68	31	100	70.00
Ti	Ppm	1	16308	10160	6713	>10000	
V	Ppm	1	93	87	92	159	107.75
Y	Ppm	1	20	19	8	24	17.75
Zn	Ppm	4	21	15	14	20	17.50



**Figure 4 : Major elements variation of the Clay samples**

Major oxide values in the samples (Table 4) shows a dominance of SiO<sub>2</sub> (56.03 – 72.84%), moderately high Al<sub>2</sub>O<sub>3</sub> (13.63 – 22.92%) and low amount of TiO<sub>2</sub> values (1.10 – 3.09) and Fe<sub>2</sub>O<sub>3</sub> values (1.30 – 2.55%). CaO, K<sub>2</sub>O, MgO, MnO, Na<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> presented least values. Such low K<sub>2</sub>O content indicates low amount of illite or K-feldspar in the sediments.

The samples show variability in average silica content (Table 4). Samples from River Ogwogwo presents the lowest SiO<sub>2</sub> values (56.03%), while samples from Odu River has the highest value of 72.84%. Al<sub>2</sub>O<sub>3</sub> content for the samples range from 13.63% - 22.92%, with a mean value of 18.88%. The variation, although discernible, is not systematic. This could be due to the

CaO dilution effect since its content is high in most samples. On the other hand, this may be attributed to their enrichment in carbonate minerals. Silica tends to decrease with an increase in carbonates. However, the Fe<sub>2</sub>O<sub>3</sub> concentrations range from as low as 1.3% for the Atarhi sample to as high as 2.55% for the Asaboro sample reflecting the higher degree of oxidation in the latter. TiO<sub>2</sub> contents are less than 4% in the Asaboro and Ogwogwo samples and less than 2% in the Atarhi and Odu clays. All samples had low P<sub>2</sub>O<sub>5</sub> content; P<sub>2</sub>O<sub>5</sub> depletion could have been due to the lower amount of accessory phases, such as apatite and monazite.

The alkalis ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ) generally occur in relatively low proportion, of which  $\text{Na}_2\text{O}$  occur in insignificant amount. The low proportion of the alkalis as well as  $\text{MnO}$ , which occur in low proportions also, are indicative of a high degree of weathering, undertropical conditions, from which the

clay bodies resulted.  $\text{MgO}$  and  $\text{CaO}$  content are low; the samples thus did not indicate associated carbonates or dolomitization. The 12.75% average loss on ignition (LOI) for the clays were high, showing potential for carbonaceous materials.

**Table 6: Comparison of the average major oxides composition of the studied clays with average chemical composition of other clay types in the Niger Delta.**

Oxide (wt%)	EWOHIMI	UBJ Onyeobi et al., 2013	AFC Jubril & Amajor, 1991	ASABA Okunola et al., 1992	BENIN Okunola et al., 1992	UBULU-UKU Emofurieta et al., 2011
$\text{Al}_2\text{O}_3$	18.88	31.62	26.20	24.94	28.31	32.70
$\text{CaO}$	0.029	0.11	1.60	0.03	0.04	–
$\text{Fe}_2\text{O}_3$	1.87	2.43	5.10	4.10	2.53	2.59
$\text{K}_2\text{O}$	0.13	0.29	8.30	0.37	0.34	0.37
$\text{MgO}$	0.09	0.17	0.70	1.0	0.15	0.15
$\text{MnO}$	0.01	0.02	0.03	0.03	<0.01	0.006
$\text{Na}_2\text{O}$	–	0.02	2.90	0.02	0.03	0.06
$\text{P}_2\text{O}_5$	0.06	0.14	–	–	–	–
$\text{SiO}_2$	63.21	50.41	42.20	47.20	52.80	50.74
$\text{TiO}_2$	2.14	2.73	–	1.55	1.58	1.99

The chemical compositions of the Ewohimi clays are compared with other Nigerian clays in Asaba, Ubiaja, Afam clay, Benin and Ubulu-Uku in Nigeria as shown in table 6. The  $\text{SiO}_2$  content of the Ewohimi clays are

higher than other clays indicating its grittiness. The values of  $\text{Al}_2\text{O}_3$  is lower in Ewohimi clays than other clays in other areas in Nigeria indicating extent of transport. Also the values of  $\text{Fe}_2\text{O}_3$  in

Ewohimi clays is lower than the values of  $\text{Fe}_2\text{O}_3$  clays in other areas (Table 6), indicating that it is least weathered of all clays. The values of other major oxides of Ewohimi clays compared well with other clays in Nigeria with little variations. The concentrations of major oxides apart from Al and Si were generally very low reflecting very intense weathering of primary minerals.

On the following, a detailed description and discussion on the geochemistry of the major and trace elements of the studied clay samples is presented below.

**Major elements** In a plot of  $\text{Al}_2\text{O}_3$  against  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$  and  $\text{P}_2\text{O}_5$  ( $r=0.876$ ,  $0.995$ ,  $0.986$  and  $0.917$ ) values show a positive correlation according to the Pearson's correlation coefficient ( $r$ ), whereas  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{K}_2\text{O}$  do not show any trend, while  $\text{SiO}_2$  ( $r = -0.968$ ) shows a negative correlation. A positive linear correlation shows that the oxide is associated with the rock during the time the rocks were formed. They also indicate that they are associated with clay minerals whereas, a negative linear correlation shows that they were introduced during the period of weathering and transportation. Thus, the negative correlation and high percentage of quartz suggests that  $\text{SiO}_2$  was introduced into the clays during transportation, while the concentration of other oxides were influenced by weathering and the silica dilution effect (Abdou, 1989). Pettijohn (1975), stated that silica is present in clays as a part of the clay minerals, as undecomposed detrital silicates and as free silica, and both detrital quartz and biochemically precipitated silica such as opal of radiolarians, diatoms, and spicules. Iron is present either in the structure of clay minerals and/or as an independent Fe-

mineral such as goethite. The enrichment of  $\text{Fe}_2\text{O}_3$  in the clays may be attributed to the information under oxidizing conditions with a high input of non-reactive iron to the basin (Ahmed 1997). This may be due to the association of  $\text{Fe}^{3+}$  with clay minerals. The strong positive correlation of  $\text{TiO}_2$  with  $\text{Al}_2\text{O}_3$  may suggest that Ti is essentially associated with clays and reflecting its terrigenous origin.  $\text{TiO}_2$  is usually disseminated within the clays as discrete minerals, e.g.

rutile and anatase, (Degens, 1965).

The above interpretations is evident when the data is compared with the Upper Continental Crust, (UCC) and Post Archaen Australian Shale, (PAAS). The  $\text{SiO}_2$  is similar to the PAAS but lower than the UCC and the  $\text{TiO}_2$  value is higher than the PAAS and UCC. Also,  $\text{Al}_2\text{O}_3$  content is similar to the PAAS, but higher than the UCC.  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CaO}$  and  $\text{K}_2\text{O}$  are depleted in all the samples, (Table 6). This shows that Ewohimi clays have been subjected to intense weathering and recycling. The major oxides in the clay samples show variation with depth.  $\text{SiO}_2$  exhibits a decreasing trend with depth, and  $\text{Al}_2\text{O}_3$  shows a general increase.  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{TiO}_2$  increase downwards and  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$  showed minimal variation.

The distribution of major oxides in the samples, therefore, indicate fractionation of the sediments in the water column and enrichment of finer sediments consisting of phyllosilicates in the deeper segments, while the upper segments are sand rich.

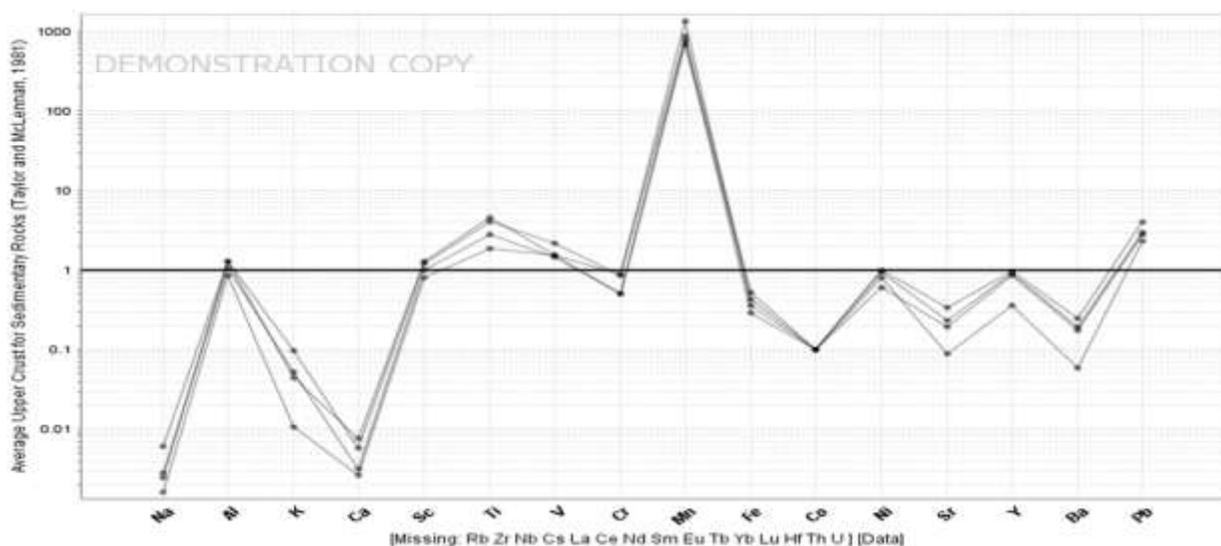
The major elements have been employed in chemical classification of sedimentary rocks and also, to differentiate between mature and immature sediments. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio,

(Potter, 1978), reflects the abundance of quartz as well as clay and feldspar content. The  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratio, (Pettijohn et al.1972), is an index of chemical maturity while the  $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$  ratio, (Herron, 1988), allows better classification of arkoses and is also a measure of mineral stability.

These parameters are used for the Ewohimi clays and are plotted in the geochemical classification diagram of Pettijohn et al. (1972) and Herron (1988).

In Herron (1988) it is identified as Fe-shale (Fig. 7). The Herron's classification can also be applied to modern unconsolidated sediments, both fine and coarse grained (Vital and Stattegar, 2000).

The Ewohimi sediments normalized to UCC (Taylor and McLennan, 1981) is plotted in Fig. 8. The pattern shows an overall similarity for elements. However, some significant differences between the elemental abundances of the study area and that of the UCC emerged. The sediments are strongly depleted in K, Sr, Na and Ca, due to their mobility, resulting in depletion in the solid materials, (Cullers et al. 1988; Nath et al. 2000). These elements are lithogenic except for Fe, which could also be anthropogenic.



**Figure 7: Ewohimi sediment normalized to Upper Continental Crust (UCC) and are plotted on spider diagrams for comparison.**

**Trace elements** Trace element distribution in Ewohimi samples follow the trend of sand and clay-rich fractions with Ni, Cu, and Pb showing enrichment in fine-grained fractions indicating their association with phyllosilicates. Zn enrichment decreases with depth in sand-rich samples indicating its non-association with quartz-rich sediments. Sr content show anomalous

distribution with respect to Ca concentrations in the samples (Table 5). With the exception of  $\text{TiO}_2$ , the Ewohimi sediments show no enrichment in the elements compared to the PAAS. On average, Ewohimi sediments have no similar values in elemental compositions (Table 6).

The transition elements, Ni, Zn, Cr, Cu, V, show depletion with silica enrichment suggesting a silica dilution effect.

Vanadium concentration ranges from 92 ppm to 159 ppm with an average concentration of 107.8 ppm. The average vanadium content in the studied clay samples is lower than those of the Post Archean Australian Shale (150 ppm) of Taylor and McLennan (1985). This is due to the oxidation and weathering of organic matter in these samples and subsequent mobilization and concentration of vanadium. Vanadium shows a positive correlation with some of the other trace elements, such as Ni, and

Cr ( $r=0.444$  and  $0.856$ ), (Fig.20). This association is considered to be typical of organic matter (Krauskopf, 1956; Gulbrandsen, 1966; Cook, 1972). Nickel shows strong positive correlation with Cr and Zn ( $r = 0.736$  and  $0.782$ ). Like chromium, zinc shows a positive correlation with the Ni element ( $r = 0.782$ ), which may be explained as related to organic matter. With its ionic radius of  $0.83 \text{ \AA}$ , Zn is liable to replace bivalent cations, such as Ca, Mg and Fe. Zn is reported to induce aragonite formation (Angus et al. 1979), but 20 to 140 ppm of Zn could also co-precipitate with calcite (Pomeroy, 1984). Zn is adsorbed on clay minerals and iron manganese oxides.

## DISCUSSION

### Weathering effects in the source area

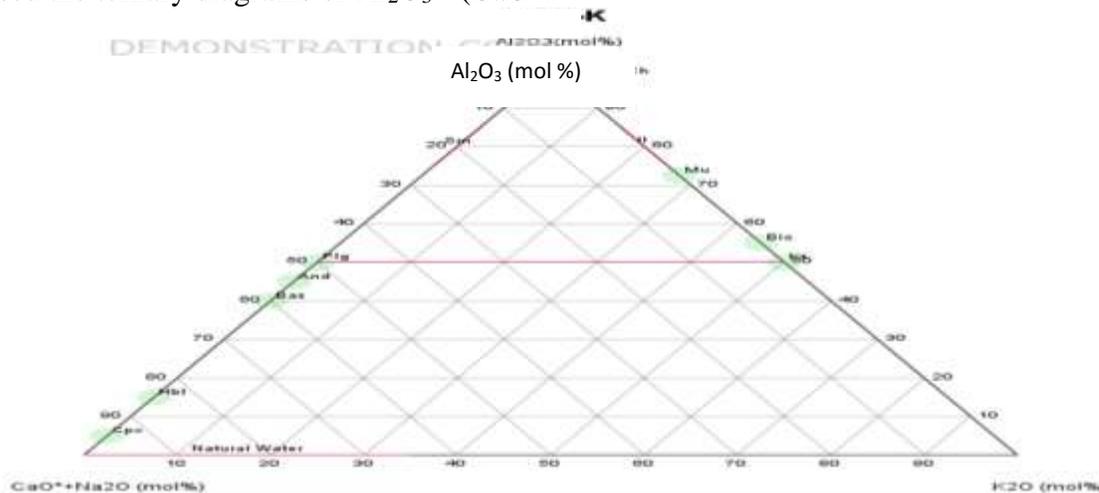
The extent of weathering at the source area can also be determined by plagioclase index of alteration (PIA), (Fedo et al. 1995), which is calculated by the following equation (molecular proportions):  $\text{PIA} = [(\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} - \text{K}_2\text{O})] * 100$ . The average PIA in Ewohimi clay sample is 99.73 and are consistent with the CIA and CIW values in the clay sample (Table 4). The high CIA, PIA, and CIW indices obtained reveal high detrital input dominated by strong chemical weathering, which leads to the formation of clay minerals by hydration and leaching of all major cations, such as  $\text{Ca}^{+2}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  present in feldspar minerals (Gertsch et al. 2011). The mineralogical index of alteration indicates the degree of weathering for each analysed sample, independent of the depth of sampling. The calculation of the mineralogical index of alteration (MIA), according to Voicu et al. (1997) is:  $\text{MIA} = 2 * (\text{CIA} - 50)$ . These ranges of MIA values indicate incipient (0-20%), weak (20-40%), moderate (40-60%), and intense to extreme (60-100%) weathering. The value of 100 % means complete weathering of a primary material into its equivalent weathered product (Voicu and Bardoux, 2002). The average MIA value for the analysed clays is 98.12.

This is indicative of intense to extreme weathering of mineralogical component of the detrital materials from the source areas. The  $\text{Al}_2\text{O}_3$ , CaO,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  constituents in sediments are related to the CIA. The values showed no variation between

samples, reflecting same climatic zones or rates of tectonic uplift in source areas. Furthermore the depletion of Na and Ca demonstrates an intense chemical weathering of the source rocks.

Also, Nesbitt and Young (1984 & 1989), used the ternary diagrams of  $Al_2O_3$  - (CaO +

$Na_2O$ )- $K_2O$  (the A-CN-K), and  $Fe_2O_3$  +  $MgO$ -(CaO +  $Na_2O$  +  $K_2O$ )- $Al_2O_3$  (the A-CN-K-FM) diagram to deduce weathering trends. On the A-CN-K diagram (Fig. 9), all the sediments displayed an intense weathering history.



**Figure 8: Ternary Plot of  $Al_2O_3$ -(CaO +  $Na_2O$ )- $K_2O$  depicting weathering trends of the Ewohimi clay samples.**

The sediments plot exclusively in the Ka, Gi and Ch fields clearly indicating high intensity of weathering (Fig. 9).

Weathering has proceeded to a stage at which significant amounts of the alkali and alkali earth elements were removed from the sediments. Albite was not identified in the samples, indicating that the sediments have reached maturity.

### Paleo - redox condition

Redox-sensitive trace element ratios (Ni/Co, V/Cr and V/V+Ni) are usually considered powerful geochemical indicators for environmental discrimination (Lewan, 1984; Hatch and Leventhal, 1992; Jones and Manning, 1994; Hoffman et al. 1998; Rimmer, 2004; Rimmer et al. 2004; Algeo

and Maynard, 2004; Johnson et al. 2010; Saez et al. 2011). Jones and Manning (1994) suggested that  $< 5$  Ni/Co ratios inferred oxic conditions, 5-7 dysoxic conditions and  $> 7$  suboxic to anoxic conditions. They also used  $< 2$  V/Cr ratios to infer oxic conditions, 2-4.25 for dysoxic conditions and  $> 4.25$  for suboxic to anoxic conditions. Lewan (1984) showed that V/V+Ni should be greater than 0.5 for organic matter accumulated in euxinic conditions.

Hatch and Leventhal (1992), compared V/V+Ni ratios to other geochemical redox indicators, including degree of pyritization, and suggested that ratios greater than 0.84 showed euxinic conditions, 0.54-0.82 anoxic water and 0.46-0.60 for dysoxic conditions.

According to Hallberg (1976) high Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidizing conditions.

The V/Cr ratio has been used as an index of paleo – oxygenation in many studies (Ernst, 1970; Bjorlykke, 1974; Dill, 1986; Dill et al. 1988). Cr is mainly incorporated in the detrital fraction of sediments and it may substitute for Al in the clay structure (Bjorlykke, 1974).

**Table 7: show the average ratios of transition elements.**

	V/Cr	Ni/Co	Cu/Zn	V/V+Ni	Cr/Ni
EWH <sub>A</sub>	0.85	19	1.0	0.17	5.74
EWH <sub>B</sub>	1.40	12	0.87	0.88	5.17
EWH <sub>C</sub>	1.48	16	1.0	0.85	3.88
EWH <sub>D</sub>	1.10	18	1.2	0.90	8.00
Average	1.21	16.25	1.02	0.70	5.70

All the samples analysed and shown on the V/Cr vs Ni/Co and V/V+Ni vs Ni/Co cross plots of redox-sensitive trace metal ratios (Fig. 22), plotted within the oxic ranges and suboxic ranges for the four redox-sensitive trace element ratios proposed by Jones and Manning, (1994) and Hatch and Leventhal, (1992).

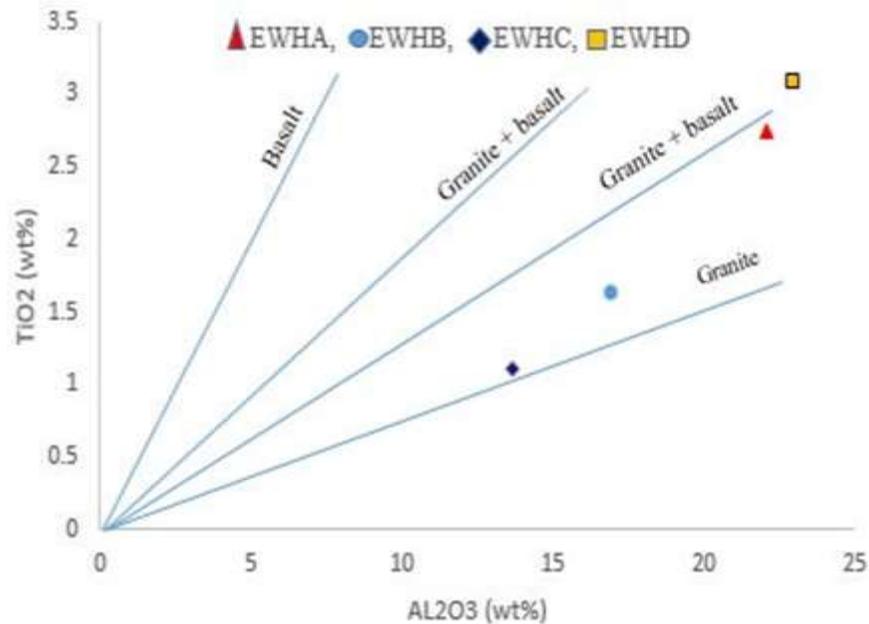
According to Jones and Manning, (1994) and Hallberg, (1976), using V/Cr and Cu/Zn average ratios from table 8, it is evident to conclude that the samples were deposited in oxic water condition. Therefore, the plot of Hatch and Leventhal, (1992) does not fit in determining the paleo – redox condition that prevailed when the Ewohimi clays were deposited.

**Provenance** Provenance of a rock could be determined from both major and trace element composition. Table 4 shows the major element concentration in the clay sample. In the studied clay samples, the average Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios is 8.8. Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>

ratios of most clastic rocks are essentially used to infer the source rock compositions, because the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio increases from 3 to 8 for mafic igneous rocks, from 8 - 21 for intermediate rocks, and from 21 - 70 for felsic igneous rocks (Hayashi et al. 1997). The average Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios (8.80) obtained suggest intermediate igneous rocks as the probable source rocks for the studied clay sample samples. The Ewohimi clays have SiO<sub>2</sub> content as the highest (Fig. 16) in elemental composition and averaging 63.21wt% but, as expected; the clays have higher SiO<sub>2</sub> and correspondingly lower Al<sub>2</sub>O<sub>3</sub>. The average of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of the Ewohimi clay sample is 3.35 and show detrital influx dominated by large extent of weathering. Generally, the low average values of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio (0.30) indicate quartz enrichment in the sample. The average of Na<sub>2</sub>O/K<sub>2</sub>O ratios of the clay sample is 0.15. The large quantity of alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) characterizes immature clays whereas the ratios of Na<sub>2</sub>O/K<sub>2</sub>O could

be used to establish both the provenance and diagenesis of clay deposit (Akinmosin and

Osinowo, 2008; Ibe and Akaolisa, 2010).



**Figure 9:TiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> binary plot showing the provenance composition of the studied clay samples(Mclennan, 1979).**

Mlennan, (1979) and Amajor, (1987) utilized the TiO<sub>2</sub> versus Al<sub>2</sub>O<sub>3</sub> binary plot to distinguish between granitic and basaltic source rocks. In figure 11 the TiO<sub>2</sub> versus Al<sub>2</sub>O<sub>3</sub> binary diagram for the studied samples, it is demonstrated that the provenance material is predominantly granitic.

The abundance of Cr and Ni in siliciclastic sediments are considered as a useful indicator in provenance studies. Trace elements such as Cr, Ni, Co, and V have been used to determine mafic and ultramafic sources (Wronkiewicz and Condie, 1987; Huntsman-Mapila et al. 2005). High levels of Cr and Ni and strong positive correlations between the two elements have been used by various authors (Hiscott 1984; Wrafter and

Graham 1989 and Garver et al. 1994, 1996) to infer a mafic to ultramafic provenance of the sedimentary rocks. Chromium and Nickel concentrations are high in the clays (Table 6). According to Wrafter and Graham (1989) a low concentration of Cr indicates a felsic provenance, and high contents of Cr and Ni are mainly found in sediments derived from mafic - ultramafic rocks (Armstrong- Altrin et al.2004).

However, the Cr/Ni ratio of the Ewohimi clays (5.7) is higher than in PAAS (Cr/Ni = 2). The level of Cr enrichment in the studied clay (weight average 94.3 ppm), its strong positive correlation with Ni (r = 0.736) and the high Cr/Ni ratios of about 5.7 indicate that mafic to ultramafic components were

part of the main components among the basement complex source rocks.

### **Chemical effect**

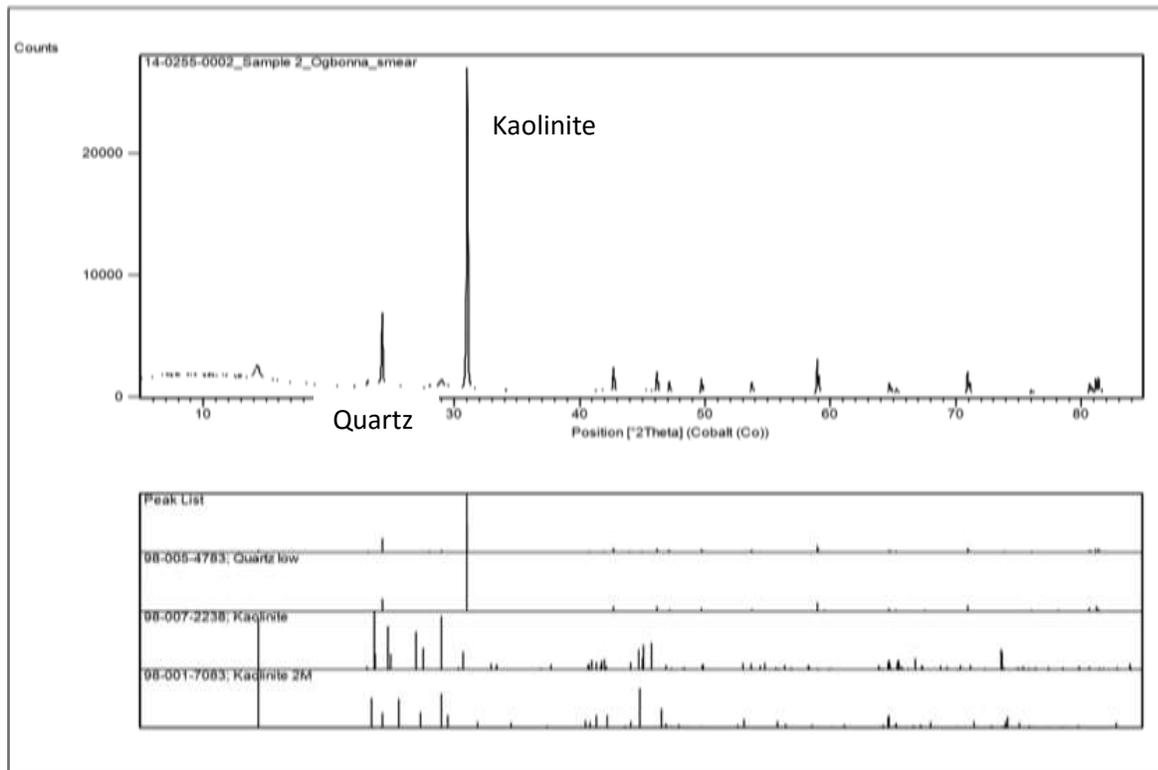
Elemental concentrations in sediments result from the competing influences of provenance, weathering, sorting, and sediment diagenesis (Quinby-Hunt et al. 1991). When comparing the chemical composition of the shale composites, the studied clay show generally enrichment of elements that are chemically immobile and are associated with terrigenous influx, such as Al, Ti and Zn. Al and Ti which can survive throughout intensive chemical weathering and diagenesis (Cullers, 2000). Their concentration in sediments is used as a measure of detrital input. The major constituents of the studied clay samples do not vary greatly from one location to another. The  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  tend to form together the main constituents of the studied clays.  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  are well correlated in all samples. This indicates that the major

oxides ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) of the Ewohimi clay samples are dominantly terrigenous in origin.  $\text{SiO}_2$  shows a negative correlation, indicating that it is not associated with the clay, rather they were introduced as detrital.

The clays at Ewohimi are enriched in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and Fe and depleted in the marine indicators CaO and MgO. This seems to indicate that the clays have been deposited under oxidizing conditions with non-calcareous planktons input or under continental conditions. This is confirmed by their association with detrital kaolinite from mineralogy.

### **Mineralogical composition**

Result of the mineralogical analysis is presented in Figure 12 which show that most of the material is either kaolinite ( $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ ) or quartz ( $\text{SiO}_2$ ). Although quantitative analysis was not carried out, the diffractograms indicate that kaolinite preponderates over quartz.



**Figure 10: X-ray diffractogram of Ewohimi clay sample.**

The results of the mineralogical composition of the clay show that the dominant minerals present are kaolinite and quartz, while other minerals occur as traces. Of all the minerals present, kaolinite covered about 80%, Quartz about 18% and others about 2%. However, result of the investigated clay deposits differ significantly from those of some well-known kaolin deposits in terms of mineralogical compositions. The kaolinite content of Ewohimi clay (80%) is lower than that of Ibadan (91%), China clay (85%), Kaduna (96%), Oza-Nagogo (86%) and NAFCON recommended value (85%). Whereas the quartz content of Ewohimi clay (18%) is far higher than those of Ibadan (6%), Oza-Nagogo (14%), Kaduna (2%), China-clay (traces) and NAFCON recommended value (4%).

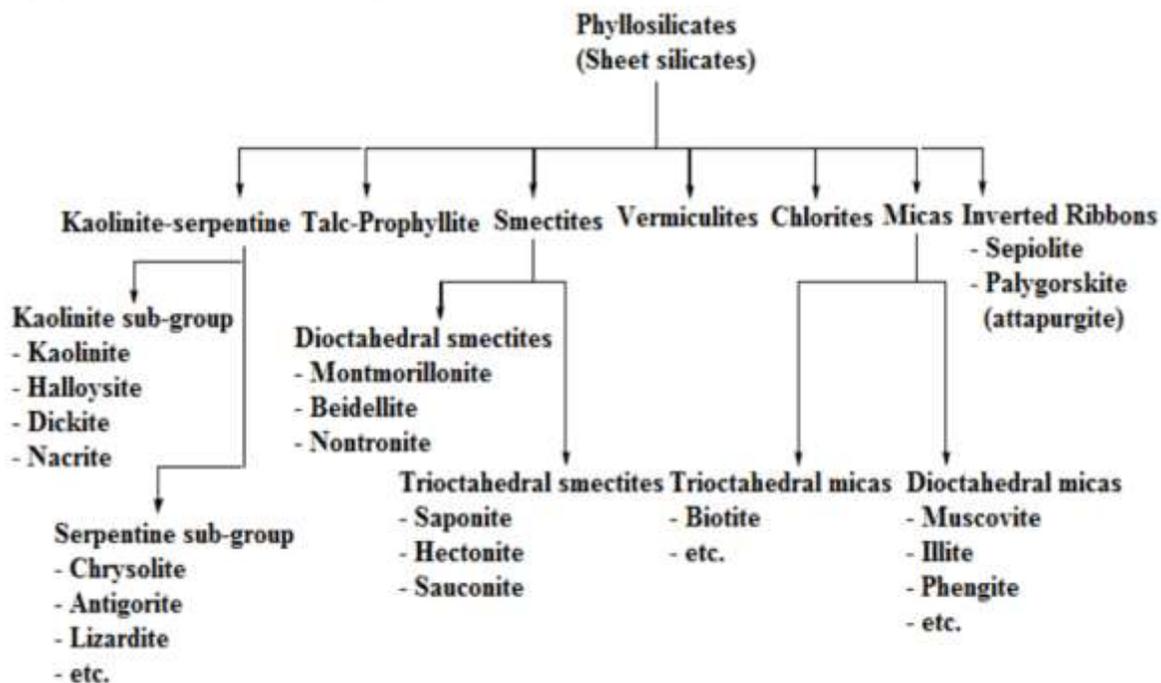
Kaolinite is believed to form by weathering or hydrothermal alteration of aluminosilicate minerals. Thus, rocks rich in feldspar commonly weather to kaolinite. Kaolinites are indicators for their detrital origin in continental sediments (Kassim, 2006). Furthermore, Weaver (1960) stated that kaolinite is dominant in sediments of fluvial environments. Kaolinite is known to be concentrated in many near-shore sediments and to decrease in abundance with distance from the shoreline as other clay minerals increase (Parham, 1966). Robert and Kennett (1994) reported that increased kaolinite contents in marine sediments resulted either from increased runoff, which could be caused by sea level falls, or from increased rainfall. Berner and Berner (1996) in their study established that kaolinite is

formed under a good drainage system where the water travel-distance was much greater, less rapid flushing of sediments and less removal of silica.

### Classification of clays

Bailey and Reider, (1998) classified clays into seven phyllosilicate groups, namely: kaolinite- serpentine, talc-prophyllite, smectites, vermiculites, chlorites, micas and the inverted ribbons groups, respectively. Minerals of the kaolinite sub-group have compositions corresponding to the formula  $Al_4Si_4O_{10}(OH)_8$ , and structures of  $Si_4O_{10}$  sheet alternating with gibbsite-type sheets. The smectite group has structures similar to prophyllite, but with exchangeable cations

and a variable number of water molecules between the layers, which results in swelling when these minerals are immersed in water. Clay mica is essentially fine-grained muscovite, often intimately mixed or inter-layered with montmorillonite. Chlorite in clays is always mixed with other clay minerals and it is often difficult to detect. Allophane clay minerals are those constituents of clay materials which are amorphous to X-ray diffraction (Grim 1962, 1968). Figure 26 below shows classification of phyllosilicates. According to Carlson (2004), polytypism in clay mineral structure is defined in respect of the different stacking arrangement of identical layers, which may be regular or random.



**Figure 11: Classification of clays as phyllosilicates (after Reider et al. 1998)**

From the above classifications, according to Lvov, (1959) Ewohimi clay is considered to be exogenous with respect to the results of the geochemical and mineralogical analysis and structural chemistry is said to be

diocahedral (gibbsite type layers). Also, based on Reiders and Bailey (1998) it is classified as Kaolinite – Serpentine.

### CONCLUSION

Conclusively, the Ewohimi clays display an intense weathering history of the source rock from the geochemical and mineralogical analyses. Weathering proceeded to a stage where a major part of the alkali and alkali earth elements were removed. The low CaO contents in sediments indicate their maturity. Ewohimi clays plot in a region clearly suggesting different relative contents in Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O and plot closer to high (Ka, Gi and Ch fields) Al<sub>2</sub>O<sub>3</sub> contents (Fig. 21), which is suggestive of a relatively high intensity of weathering. The presence of basal conglomerate, rootlet structures, iron capping, fining upward sequence, abundances of kaolinite, low abundance of MgO and K<sub>2</sub>O and sedimentary structures typical of tidal sedimentation indicate non-marine depositional environment. The presence of ironstones further attests to abundant oxygen due to sub-aerial exposure resulting to the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. This is typical of fluvial (continental) sedimentation

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