# PALEOENVIRONMENTAL INTERPRETATION OF CLAY DEPOSITS WITHIN ODUKPANI, SOUTHEASTERN NIGERIA

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## ABSTRACT

*Clay geochemical and mineralogical composition in Odukpani area, Southeastern Nigeria was analyzed from 10 different locations in order to infer its importance as paloenvironmental indicator. The results show variation in major elements and mineralogical composition. Chemical data showed the average values of silica ($SiO_2$), alumina ($Al_2O_3$) and hematite ($Fe_2O_3$) as 47.46% (46.79- 49.51)%, 34.08% (32.2-35.37) % and 2.79% (2.15-2.62)% respectively, while kaolinite being the most dominant mineralogical constituents has its average value as 88.10% (83- 89)%. The high occurrence and concentration of $SiO_2$ and $Al_2O_3$ infer terrestrial processes, while the low occurrence of $Ti0_2$ (less than 0.001%) and $P_20_5$ (0.0267%) concentration may be due to claystone associated with continental processes. The mean value of illite / kaolinite ratio is 0.069 (ranges from (0.042-0.091), with higher concentration of kaolinite over illite indicate sediments of fluvial environment and this ratio in the presence of hematite shows oxygenated environment in an arid climate. A very low concentration of CaO (0.04%), MgO (0.19%) and $K_20$ (0.61%) infer non marine influence.*

***Keywords:*** *Clay geochemical, Odukpani area, paloenvironmental, terrestrial processes, illite / kaolinite ratio*

## INTRODUCTION

Clay minerals are of great significant indicator of some of the various processes that have developed in the earth. Clay minerals and their relative abundance may record information such as climate, eustasy, burial diagenesis or reworking, (Kassim, 2006) and even provide knowledge of the source of rock (provenance) of the parent materials. The minerals are formed in limited range of geologic environments such as continental and marine sediments, soil horizons, geothermal fields, volcanic deposits, weathering and rock formations (Akinyemi *et al.*, 2014). Some of the chemical constituents of these clay minerals are diagnostic in environmental interpretation. The two/ three layers ratio in clay minerals is mainly control by climate of the environment where the occur (Churchman, 2000). These may be useful in determining warm and humid condition which favoured kaolinization or dry condition favourable for illite/smectite formation. Trindade et al 2008 uses the illite –kaolinite ratio to be directly related to aridity/ humidity ratio to describe the same paleoclimatic condition. Kaolinite is therefore formed in an acidic condition (low PH condition) and high leaching and weathering environment (Oloruntola *et al*., 2010)**.**

This study will therefore use the geochemistry and mineralogy observed from 10 clay deposits in Odukpani Southeastern, Nigeria to infer the paleoenvironmental conditions under which theses clays were formed.

## LOCATION OF THE STUDY AREA

The study area is located in Ikot Omin, in Odukpani Local Government Area of Cross River State, Southeastern Nigeria (figure 1). The geographic coordinates are on longitudes 008° 20' 40" to 008 43' 50" and latitudes 04° 42' 30" to 04 43' 50". This study area lies within the Tertiary coastal sediments of the Calabar Flank Basin (Nyong, 1995) in the Southeastern Nigeria (figure 2). According to Nyong (1995), Calabar Flank is sedimentary basin consisting of the following Cretaceous units: Awi Sandstone, Mfamosing Limestone, Ekenkpon Shale, New Netim Marl and Nkporo Shale. The unit is topped by Tertiary coastal plain sand of Benin Formation.

Areas investigated were from local mined clay samples and along river channels and adequate cares were taken not to use weathered samples. Some of the mined clays showed some iron stains coloration of reddish brown.

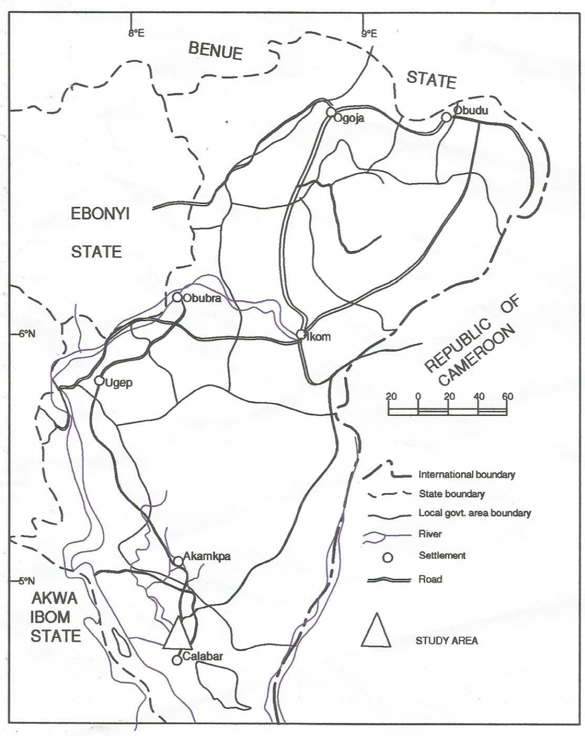


FIG. 1 : Map of Cross River State showing study area.

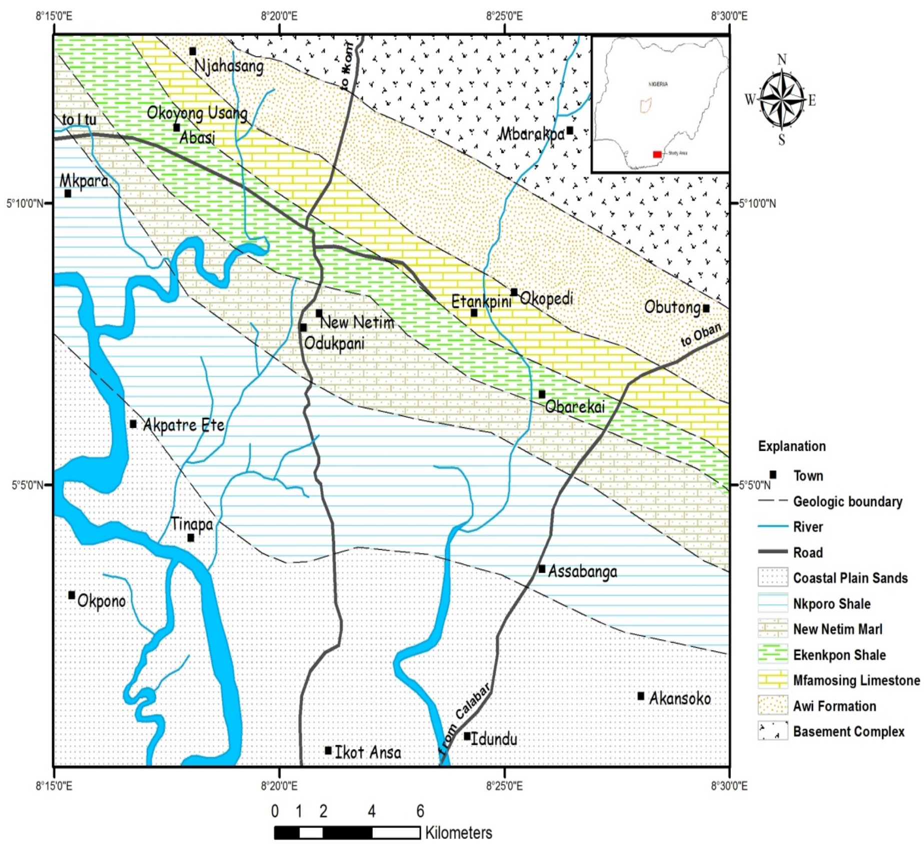


***Figure 2.*** *Geologic map of Calabar Flank, Southeastern Nigeria (After Nyong, 1995)*

## MATERIALS AND METHODOLOGY

Ten fresh clay samples were collected from ten different locations within Ikot Omin clay deposits at Odukpani, Southeastern Nigeria. About 2.0kg per sample was collected and placed in small polythene bags. 1.0kg of each sample was dried, pulverized and sieved before analysis. A sub-sample of 1.0gm each of the dried sample was digested and XRD analysis for mineralogical determination carried out. The recommended standard methods of A.O.A.C (1990) for the elemental quantitative analysis was also done. For each experimental condition 2 to 3 measurements were performed to estimate the repeataibility.The repeatability was quite good and the data presented represent the results obtained beyond the experimental error.

## RESULT AND DISCUSSIONS

Tables 1, 2 and 3 showed the results of the major and elemental composition of the clay from the study area and comparison to the average composition of China clay (Huber, 1985), NAFCON (1985) and other clays in Nigeria.

***Table 1.*** *Major elements composition from the study area*

| Oxides (%) | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 | L10 | Range | mean | H | O | U | UC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SiO2 | 49.51 | 48.17 | 46.83 | 48.2 | 46.83 | 46.79 | 46.83 | 46.97 | 46.96 | 47.53 | 46.79-49.51 | 47.462 | 46.88 | 58.09 | 42.2 | 66 |
| AlO2 | 35.37 | 34.59 | 34.02 | 34.02 | 32.32 | 35.22 | 32.32 | 34.81 | 33.52 | 34.62 | 32.32-35.37 | 34.081 | 37.65 | 21.86 | 26.2 | 15.2 |
| TiO2 | 0.001 | 0 | 0.002 | 0.001 | 0 | 0.002 | 0 | 0 | 0.001 | 0.002 | 0.00-0.002 | 0.0009 | 0 | 0.92 | -5 | 0.5 |
| Fe2O3 | 2.62 | 2.47 | 2.4 | 2.33 | 2.16 | 2.17 | 2.19 | 2.19 | 2.22 | 2.15 | 2.15-2.62 | 2.29 | 0.88 | 2.74 | 5.1 | 5 |
| MgO | 0.01 | 0.23 | 0.21 | 0.21 | 0.19 | 0.2 | 0.21 | 0.21 | 0.21 | 0.22 | 0.01-0.22 | 0.19 | 0.13 | 0.22 | 0.7 | 2.2 |
| MnO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - | 0.13 | 0.03 | 0.08 |
| CaO | 0 | 0 | 0.06 | 0.06 | 0.05 | 0.05 | 0.04 | 0.04 | 0.04 | 0.04 | 0-0.06 | 0.038 | 0.03 | 1.51 | 1.6 | 4.2 |
| Na2O | 1.62 | 0.54 | 1.32 | 2.69 | 1.62 | 2.93 | 1.62 | 1.18 | 2.18 | 2.16 | 0.54-2.93 | 1.786 | 0.21 | 0.65 | 2.9 | 3.29 |
| K2O | 0.51 | 0.39 | 0.96 | 0.77 | 0.64 | 0.32 | 0.71 | 0.58 | 0.57 | 0.6 | 0.51-.96 | 0.605 | 1.6 | 0.79 | 8.3 | 4.4 |
| P2O5 | 0.01 | 0.01 | 0.02 | 0.02 | 0.31 | 0.15 | 0.61 | 0.5 | 0.52 | 0.52 | 0.01-0.61 | 0.267 | - | - | - | - |
| LOI | 12.5 | 13 | 12 | 12 | 12.5 | 12.6 | 12.6 | 12.6 | 12 | 12 | 12.0-13 | 12.38 | - | 13.08 | - | - |
| Total | 102.151 | 99.4 | 97.822 | 100.301 | 96.62 | 100.432 | 97.13 | 99.08 | 98.221 | 99.842 | | | | | | |

*H-China Clay (Huber, 1985)*
*O-Illorin Clay (Ojo et al., 2014)*
*U-Afam Clay (Jubril and Amajor, 1991)*
*UC-Upper Continental Crust (Condie, 1993)*

***Table 2.*** *Mineralogical composition of clay derived from the study area and comparison with other clays*

| Min % | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 | L10 | Range | Mean | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kaolinite | 88 | 86 | 86 | 89 | 84 | 83 | 86 | 89 | 94 | 96 | 83-89 | 88.1 | 91 | 96 | 85 | 85 |
| Illites | 8 | 6 | 4 | 6 | 7 | 7 | 6 | 7 | 4 | 5 | 4-8 | 6 | 3 | 3 | 15 | 3 |
| Quartz | 1 | 3 | 1 | 2 | 3 | 2 | 3 | 1 | 1 | 1 | 1-3 | 1.8 | 6 | 2 | - | 4 |
| Feldspar | 1 | 2 | 3 | 3 | 3 | 4 | 3 | 2 | 1 | 0 | 0-3 | 2.2 | - | - | - | 2 |
| others | 2 | 3 | 5 | 0 | 3 | 6 | 2 | 1 | 0 | 0 | 0-6 | 2.2 | - | - | - | 8 |

*1) Average mineralogical composition of Ibadan Clays (Emofuriefa, 1988)*
*2) Average mineralogical composition of Kaduna (Kankara). Kaolin (Emufurieta, 1988)*
*3) Average mineralogical composition of the China clay (Huber, 1985)*
*4) Recommended value by NAFCON (1985 Kaolin tender document)*

***Table 3.*** *Elemental composition of clay of the study area*

| Element (%) | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 | L10 | Range | Mean | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | 55.35 | 56.42 | 56.43 | 61.11 | 60.26 | 57.59 | 58.24 | 60.22 | 59.22 | 58.37 | 55.35-61.11 | 58.321 | 583.21 |
| Al | 31.12 | 32.35 | 30.14 | 39.11 | 30.54 | 27.48 | 27.06 | 28.29 | 29.16 | 28.17 | 27.06-39.11 | 30.342 | 303.42 |
| Ti | 10.41 | 9.12 | 11.11 | 8.1 | 4.94 | 9.31 | 7.76 | 7 | 6.08 | 7.35 | 4.94-11.11 | 8.118 | 81.18 |
| K | 2 | 0.11 | 0.11 | 0.42 | 1.21 | 3.09 | 3.84 | 2.38 | 3.09 | 3.36 | 0.11-3.84 | 1.961 | 19.61 |
| Ca | 1.12 | 2.21 | 1.26 | 3.05 | 2.53 | 2.11 | 2.75 | 2.21 | 3.09 | 2.85 | 1.12-3.09 | 2.318 | 23.18 |
| Na | 0 | 0.0045 | 0.0046 | 0.0035 | 0.0027 | 0.0028 | 0.0039 | 0.0029 | 0.003 | 0.0036 | 0-0.0046 | 0.00315 | 0.0315 |
| P | 0.6 | 0.2 | 1.6 | 1 | 0.6 | 0.8 | 0.6 | 0.8 | 1 | 1.5 | 0.2-1 | 0.87 | 8.7 |
| Mg | 0.0003 | 0.0003 | 0.0004 | 0.0002 | 0.0004 | 0.1303 | 0.1204 | 0.1001 | 0.1118 | 0.1213 | 0.0002-0.1303 | 0.05855 | 0.5855 |
| Mn | 0.0006 | 0.1402 | 0.1281 | 0.1265 | 0.1129 | 0.1205 | 0.1254 | 0.1254 | 0.126 | 0.1233 | 0.0006-.01281 | 0.11289 | 1.1289 |
| | 0.0003 | 0.0004 | 0.0005 | 0.0002 | 0.0003 | 0.0003 | 0.0012 | 0.0004 | 0.0005 | 0.0004 | 0.0002-0.012 | 0.00045 | 0.0045 |

These clays are found within sedimentary rocks of Calabar Flank and are therefore sedimentary origin (Attah, 2008). From the analyses silica ($SiO_2$) and alumina ($Al_20_3$) are the predominant major oxides and constituting over 80% of the major elements. Their average and range values are 47.46%, 34.08% (46.79-49.5) % and (32.32-35.37) % respectively. The silica value falls within the China clay value while the alumina is correlated with other clays in Nigeria. This make the clay sample to be qualified as siliceous alumino - silicate minerals (Emufrieta *et al.*, 1992, Nton and Elueze, 2005, and Ojo *et al*., 2011).

There are a lot of variations in the chemical composition of this clay. According to Folk (1974) residual clays form in place has characters depending on the climate, drainage and parent rock material. From the analysis the high occurrence of $Al_20_3$ and a low or impoverished lime (CaO = 0.038%), magnesia (MgO =0.19%) and alkaline earth elements (Ca=0.00315%, Mg=0.11% and Mn=less than 0.01%) infer humid condition in the study area. Kaolinite formation is favoured by weathering or hydrothermal alteration of aluminosilicates minerals especially in rocks rich in feldspar minerals (Odoma *et al*.,2013).For kaolinite to formed ions of alkali and alkaline earth elements like K, Na, Ca, Mg and Fe must be leached away by weathering or alteration process (Odoma *et al.,* 2013). This leaching is highly favored in an acidic condition (low pH). The low concentrations of these elements (table 3), total average value less than 14%, indicate deposition of this clay under investigation in acidic environment. The low concentration of lime, which is less than 0.079 in the investigated area indicates absence of marine processes. Also the low abundance of MgO and $K_2O$ infer absence of expandable clay which may be either illite or montmorillonite in the studied area. The LOI which according to Olusola *et al* (2014) is a measure of organic matter content and other combustible fractions, chemically combined water and $CO_2$, from this study area have mean percentage of 12.38%. This low-moderate value could be attributed to the absence of carbonates rock or absence of marine influence.

High occurrence of illite is seen in temperate to semi-arid setting, while montmorillonite indicates, temperate weathering environment (Folk, 1974), these were absent in the study area and infer non temperate to semi-arid environmental influences**.**

The low occurrence of $Ti0_2$ (less than 0.001%) and $P_20_5$ (0.0267%) concentrations may be due to claystone associated with continental processes, while Imeokparia and Onyeobi (2007) reported a higher concentration of these oxides in northern Bida Basin as influence of transgresive shallow marine.

According to Trindade *et al* (2008), high illite/Kaolinie ratio with the presence of hematite shows oxygenated environment and arid climate, where physical weathering of the source rock was the main processes for clay production, while low illite/kaolinite ratio, infer terrigenous character, shown by high quartz and less oxygenated condition by the presence of goethite. This low ratio infer a corresponding decrease in aridity/ humidity condition (Trindade *et al* 2008) and indicate wet and humid condition from the study area. This study has revealed a very low illite/kaolinite ratio of mean value 0.069 (ranges from (0.042-0.091) with kaolinite mean value of 88.1%, which may infer terrigenous or continental conditions operating in the area.

The high presence of kaolinite minerals among the mineralolgical composition of the studied clay samples, suggest acidic, an approximately low $_P$H conditions in the basin of deposition. According to Weaver (1960),

Kaolinite is dominant in sediments of fluviatile environments as indicated in the clay samples of Odukpani environments.

## CONCLUSION

The geochemical study of ten clay samples investigated in Odukpani environs in southeastern Nigeria, show that the variation in the clay chemical composition is a good diagnostic factor of paleoenvironmental interpretation.

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