

Clay mineralogy and chemistry of selected soils in Northern Cross River State, Nigeria

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Abstract

Understanding the composition and behavior of clay minerals is essential for better management of soils to perform ecosystem services. This research on clay mineralogy and chemistry of selected soils in northern Cross River State was aimed to identify the clay minerals and relate them to the chemistry of the soils for sustainable management. Fifteen soil samples were collected at designated horizons from profiles dug at four land uses; wetland, forest, grassland and farmland in the study area. X-ray diffraction (XRD) analysis of the soil was done using SIEMENS D5005 diffractometer model. The intensities of clay were obtained by using the relative intensities of individual peaks of gibbsite (4.96\AA^0), quartz (3.3\AA^0), kaolinite (7.18\AA^0), montmorillonite (10\AA^0), vermiculite (14\AA^0), and mica (18^0) shoulder. The clay minerals identified were vermiculite, montmorillonite, kaolinite, illite, polygorskite, quartz and hematite. From the results vermiculite was $> 30\%$ in wetland and forest, $15-30\%$ in grassland and farmland, montmorillonite $15-30\%$ in wetland and farmland, $7-15\%$ in forest and $< 7\%$ in grassland while kaolinite was $15-30\%$ in wetland and $> 30\%$ in forest and grassland. It was concluded that wetland soils had more 2:1 clays than other land uses and therefore will tend to hold more nutrients.

Keywords: Clay, mineralogy, chemistry, land use

INTRODUCTION

Mineralogy and chemistry of soils play crucial roles in influencing soil fertility, water retention, and nutrient availability. Clay minerals interact with organic matter and other soil constituents affecting soil structure and stability as they act as binding agents between soil particles influenced by their cohesive forces, nutrient retention and release, adsorption of pollutants and rate of mineralization of organic matter. Understanding their composition and behavior is essential for better management of soil and agricultural operations for

sustainable maintenance of soils' ability to perform ecosystem services. Clay minerals are major components of soils and are the major determinants of soil properties (Mana *et al.*, 2017). Majority of their properties including cation exchange capacity (CEC), swelling and shrinkage or plastic behavior exert great influence on soil response to several uses. They play critical roles in determining soil characteristics in agricultural and engineering applications (Gowthamy *et al.*, 2021). Clay minerals are layer silicates typically formed by weathering of other silicate minerals. Common silicate materials such as quartz, feldspars, volcanic

glasses including carbonates, non-crystalline iron oxides and primary clay minerals are transformed during diagenesis into more stable clay minerals solely by dissolution and recrystallization (Mana *et al.*, 2017). Clay minerals are formed through neoformation and alteration of primary minerals derived from the weathering product of parent materials (Essington, 2006) and are characterized by large surface area and electrical charges usually negative charge that attracts and holds positively charged ions from soil solution (Costa and Bigham 2004). This cation retention capacity has effects on soil structural stability, nutrient availability, soil pH control and soil response to fertilizers and fates of pollutants and agrochemicals in soils. In addition, some clays have the ability to attract water molecules and swell which can impact soil drainage (Foth, 2006; Liu *et al.*, 2021).

The most common phyllosilicates in humid tropical regions are vermiculite, smectite (montmorillonite), kaolinite and illites. Kaolinites group includes all the low activity layered clay minerals like kaolinite, nacrite and dickite and are 1:1 type of clay minerals. The smectite group; montmorillonite, beidellite, nantronite, saponite and hectonite are 2:1 layer alumino-silicate clay minerals while vermiculite is a hydrated magnesium aluminum ion silicate that possesses 2:1 layer (Kumari and Mohan,

2021). Illite also called mica is a group of phyllosilicate minerals with crystalline structure that are platy, flexible, clean, elastic, transparent to opaque, resilient, reflective, insulating, light weight and hydrophilic. These clay minerals, particularly the 2:1 are important because of their CEC and buffering capacities which influence the reactions or behavior of soils with regards to nutrients adsorption, absorption, availability and release. This is made possible because of their large surface area and charge characteristics.

Soil mineralogy plays enormous roles in the control of all reactive substances in the soil environment that in turn influences the chemistry of soil in several ways including reduction-oxidation (redox) reactions, ion mobility, soil pH, nutrients availability and organic matter decomposition. These chemical processes vary with land use and the levels of aeration in soil which is influenced by landscape positions among other factors. For instance, upland soils typically have lower organic matter content and pH compared to lowland soils and they tend to be more acidic due to leaching of basic cations and have lower fertility levels. Reduction and oxidation or redox reactions occur in almost every soil and have not been regarded or emphasized as very important soil forming processes. Redox reactions contribute to formation of plinthite and gley

horizons. Gleying is especially significant in poorly drained soils, such as paddy field/soil where inundation of the soil is a required operation for cultivation of lowland rice (Tan, 2011).

Oxidation reactions usually occur in well-drained soils. On the other hand, reduction processes are more likely to be predominant in poorly drained soils or hydromorphic condition where excess water is present. Both oxidation and reduction conditions can occur simultaneously in the pedon. The surface layers of the pedon can be in an oxidized state and the subsoil layers in a reduced condition due to fluctuating ground water level. These conditions affect the stability of iron and manganese compounds. To a certain extent, microbial activity, accumulation and decomposition of organic matter are all affected by soil redox state. As posited by Tan (2011), soils with different redox conditions may react differently upon N fertilization. In well drained soils, ammonium N is subject to nitrification and converted into nitrate (NO_3^-). However, if ammonium fertilizer is applied to a reduced soil such as lowland rice or paddy soils it remains available as ammonium (NH_4^+). The state of ions in the soil determines to a larger extent adsorption and absorption potential of the ions as well as its ability to be fixed.

Northern Cross River State due to its

diverse parent materials, climatic conditions and topography has different soil types which are put under different land uses because of the agrarian lifestyle of the people. Despite the importance of clay minerals in soil fertility and environmental management, mineralogy of soils of northern Cross River State has not been well studied or has received less attention. Knowing the types and amounts of clay in soils is important to estimate fertilizer requirements, the doses of application and the future physical and chemical degradation rates of soils and as such constitutes an essential index for soil management and conservation. However, several studies have shown that they are variations in clay mineralogy of soil with land use and the impact of land use on clay behavior (Basga *et al.*, 2018; Ouyang *et al.*, 2021). This work was aimed to identify the clay minerals of selected soils in northern Cross River State and to relate the mineralogy to the chemistry of the soils to enhance proper management.

MATERIALS AND METHODS

The study was carried out in four Local Government Areas (LGAs) of northern Cross River State. The LGAs were Ogoja, Yala, Bekwara and Obudu. Northern Cross River State lies between latitudes $6^{\circ} 20'$ and $6^{\circ} 43'$ N and longitudes $8^{\circ} 00'$ and $9^{\circ} 10'$ E. The area is bounded in the north by Benue State,

south by Ikom and Boki LGAs, west by Ebonyi State and east by the Republic of Cameroon. The area is characterized by humid to sub humid climate and falls within the tropical rainforest zone and the guinea savanna. The annual rainfall in the area ranges from 1700 to 3000mm, temperature of 19 to 37°C and relative humidity of 48 to 86% (Bulktrade, 1989). The major parent materials in the area include basement complex rocks, sandstone, shales, limestone and mudstone.

Field Method

Soil samples were collected from four profile pits dug in the four Local Government Areas based on land use. The land uses selected were rainforest at Kakum (Obudu), Farmland at Ukpah (Bekwarra), Grassland at Okuku (Yala) and wetland at Bansara (Ogoja). Profile pits were dug to standard dimensions with depth varying from 0-119 cm, 0-150 cm, 0-150 cm and 0-106 cm in Obudu, Bekwarra, Yala and Ogoja respectively. A total of fifteen soil samples were collected from the delineated horizons in the profiles into well labeled polythene bags and taken to the laboratory for preparation and analysis.

Laboratory Procedure

Mineralogical Properties

Soil samples were air dried, crushed gently with a mortar and pestle and sieved to remove fragments greater than (>) 2 mm.

X-ray diffraction (XRD) analysis of the soil samples was done using SIEMENS D5005 diffractometer model. Ten grammes (10g) of soil samples were collected and ground to fine powder and sieved with less than 10µm sieve. Ten micrometer (10µm) of air-dried soil was treated with 30% H₂O₂ and heated for 2 hours to decompose organic matter. Excess H₂O₂ was removed through centrifugation by washing three times with water and 3 ml sodium chloride (NaCl) added each time to prevent deflocculation of clay particles, and supernatant solution discarded by decantation. The pH of the soil suspension was adjusted to 10 by addition of sodium hydroxide (NaOH). Clay fraction (<2 µm) was separated by repeated sedimentation siphoning method. Two series of specimens, magnesium-saturated and glycerol solvated samples were prepared for clay mineralogy. The fine ground sample was then placed into a sample holder, smeared uniformly onto glass slide to ensure a flat upper surface. X-rays were directed at the sample and diffracted rays recorded.

Approximate mineral contents of the clay fractions were estimated based on the relative peak intensities in the pattern as described by Moocher (2004). Identification and estimation of mineralogical composition of the clay fractions were carried out using X-ray diffraction method (XRD). The intensities of clay were obtained by using the

relative intensities of individual peaks of Gibbsite (4.96\AA^0), quartz (3.3\AA^0), kaolinite (7.18\AA^0), montmorillonite (10\AA^0), vermiculite (14\AA^0), and mica (18^0) shoulder.

RESULTS AND DISCUSSION

The clay minerals identified in the study area and their relative abundance in each pedogenic horizon are presented in Tables 1 and 2 while the diffractograms are shown in figures 1, 2, 3 and 4. The dominant phyllosilicate in the soils were kaolinite and vermiculite. Vermiculite, kaolinite, montmorillonite, palygorskite, illite and kaolinite-montmorillonite were the major phyllosilicate identified in soils of the area with lesser percentages of quartz and oxide of iron(hematite)(Tables 1 and 2, Figures 1, 2, 3 and 4). Vermiculite was the dominant clay in soils of Ogoja and greater than 30 % in all the horizons followed by montmorillonite (15 – 30 %) in Ap and Bt horizons. In Obudu, both quartz, kaolinite and vermiculite (>30 %) occurred in the Ap horizon, quartz and vermiculite (>30 %) in the Bt horizon while montmorillonite was low (7-15%) in lower horizon. In contrast to clay horizon distribution in Ogoja and Obudu, kaolinite and vermiculite dominated the first three horizons of the soil in concentrations > 30 % and 15-30 % accordingly while illite and montmorillonite were found in trace amounts in the Ap or upper horizon in Yala. Kaolinite and quartz were found (>30 %) in Ap horizon

while vermiculite and montmorillonite were obtained (15-30 %) in subsurface horizon probably due to translocation since they are smaller in sizes than kaolinite and quartz (Table 2) in Bekwarra. Throughout the soils of all the land uses, the intensities of the diffractogram peaks that depict clay quantity were higher and sharper in the top and lowest horizons than middle horizons and similar trend was observed for the d spacing (Figs 1, 2, 3 and 4). Like in this study, Irmak *et al.* (2007) in their study obtained lower clay content in upper horizon than subsurface horizons and attributed it to leaching of clay from surface to subsoils.

Kaolinite

Kaolinite was identified in all the land uses but at different quantities and was identified at 7.1\AA^0 in all the soils (Figures 1, 2, 3 and 4). It has relative abundance of > 30 % in Yala (grassland), Bekwarra (farmland) and Obudu (forest) while in Ogoja (wetland) kaolinite amount varied from 15 to 30 % and also with kaolinite-montmorillonite interstratification of 15 to 30 % in forest (Obudu). Kaolinite is a phyllosilicate with one tetrahedral sheet bonded by hydrogen-hydrogen linkage to an octahedral sheet. Due to its inability to expand, CEC is very low and restricted to the surfaces of the particles. Isomorphous substitution of aluminium for silicon in the tetrahedral sheet is low or absent. The specific surface area is low ($10\text{--}60\text{ m}^2\text{g}^{-1}$). The

implication of the low CEC in kaolinite explains the inability of this clay mineral to adsorb or hold on to nutrients. As a result, soils dominated by kaolinite in the study area will be low in nutrients than those with abundance of 2:1 clay mineral like montmorillonite and vermiculite (Tan, 2011). In line with this present study, Afu *et al.* (2018) in a related study on land use in the area (northern Cross River State) reported that soils developed on wetland had higher fertility levels when compared with those of grassland, farmland and forest. They attributed this difference to the reduction-oxidation (redox) reactions, ion mobility, soil pH, nutrient availability and organic matter decomposition. Redox reactions in wetlands brings about consumption of acid ion (H^+) thereby making more nutrients available for plant uptake.

Mineralogy of soils influences their redox potentials by determining the availability of electron donors and acceptors. For instance, minerals like hematite, goethite and other metallic oxides can serve as electron acceptors, influencing redox reactions in soil. Mineral composition of soils is key for predicting their redox behavior and potential impacts on nutrients availability. Dayo-Olagbende *et al.* (2022) reported that redox potential caused changes in chemical properties of soil and observed that exchangeable cations were lowest in soils

under highly reduced condition. Redox reactions are crucial aspect of soil chemistry that change the speciation and solubility of many nutrient elements, create new compounds thereby changing soil chemical conditions. These processes differentiate wetland from upland soils chemically. Upland soils like Yala (grassland), Bekwarra (farmland) and Obudu (forest) are said to be more acidic with lower organic matter content due to the faster rate of decomposition caused by higher temperatures and activities of microorganisms and high rate of erosion and leaching of organic matter and basic cations from surface soil. The various inorganic redox reactions that occur in soil and sediments become unstable at critical redox potentials. Sequentially, following flooding, oxygen is reduced first, followed by nitrate and oxidized manganese compounds and then ferric iron compounds. After the reduction of ferric iron, the next redox compound to become unstable is sulphate followed by the reduction of carbon dioxide to methane (Delaune and Reddy, 2005). The measured redox potential in soil is generally a mixed potential which reflects a weighted average of the potentials present. Due to continuous addition of organic matter which oxidizes and serves as an electron donor, a redox equilibrium is almost never attained in a natural system. NO_3^- is reduced to N_2 , Fe^{+3} to Fe^{2+} , SO_4^{2-} to S^{2-} or HS

(depending upon pH) and accumulation of acetic acids that are produced by microbial metabolism.

In upland soils, redox reaction involves the transfer of electrons between different chemical species. In anaerobic conditions, iron and manganese exist in their oxidized forms (Fe^{+3} and Mn^{4+}) but in anaerobic conditions, they are reduced to their oxidation states (Fe^{2+} and Mn^{2+}). These redox transformations influence nutrient cycling, soil fertility and overall health of upland ecosystems.

Smectites (montmorillonite)

Smectite (montmorillonite) was dictated at 10\AA and 18\AA levels and has abundance of 15 to 30% in wetland land use in Bansara (Ogoja) and 7 to 15 % in forest of Kakum (Obudu) while Okuku (grassland) and Bekwara (farmland) montmorillonite level was less than 7% (Table 2). Wetland soils in Ogoja (Bansara) are characteristically formed from shales. The abundance of montmorillonite at 15-30 % supports literatures that their occurrence is more prevalent in wet environment. Furthermore, Foth (2006) reported that shale parent material is composed of 25 % clay minerals.

Montmorillonite has been reported to have high cation exchange capacity (80 to 120 cmol/kg) with corresponding specific

surface area of approximately 700 to 800 m^2/g (Tan, 2011). The basal spacing ranges from 9.6 to 18\AA or more. These together with the weak oxygen-oxygen bond (linkage) allow for the expansion of this clay mineral on absorption of water. Also, montmorillonite is a 2:1 clay that has Mg^{2+} and Fe^{2+} (ferrous) ion in octahedral position (Tan, 2011; Essington, 2006) which can be released into the soil solution upon weathering and transformation. The presence of montmorillonite in the soils of northern Cross River State implies that the cation exchange capacity of the soils will be high reflecting the fertility of the soils. However, because of the expansion and shrinking of soils dominated by montmorillonite, basic cations like K^+ and NH_4^+ can easily be fixed in the interlayer spaces of the clays making these ions limited in the soils for plants to utilize. The cumulative effects of mineralogy and chemistry influence nutrient dynamics which in through protonation can increase acidity of soils that can have implication in nutrient solubility and in turn affect the growth and yield of crops in an area.

Vermiculite

The abundance of vermiculite in wetland (Bansara) soils developed on shale stone parent material and forest (Kakum) soil developed on basement complex was $> 30\%$. In soils derived from sandstone in grassland

in Okuku and farmland in Ukpah vermiculite was 15-30 % dominant. In a related study, Ouyang *et al.* (2021) obtained 13 % vermiculite in shale parent material and stated that its presence was the least among the identified clays which contradicts this present study. However, the study of Ouyang *et al.* (2021) was on upland soils. The dominance of vermiculite in wetland and forest in Ogoja and Obudu means that the soils are or initially rich in mica. The loss of interlayer K^+ from mica resulting in development of negative charges coupled with repulsion of adjacent layers may have resulted in formation of vermiculite (Foth, 2006). Mica in soils apparently weather to vermiculite via direct simple transformation which is the generally accepted mode of trioctahedral vermiculite formation in soils (Essington, 2006). Biotite and phlogopite can also chemically weather to vermiculite. Trioctahedral vermiculite is considered to be an unstable intermediate phase particularly in acid soils (Douglas, 1989) but its occurrence and stability in calcareous and silica-rich soil has not been documented

However, the presence of vermiculite (15-30% and > 30 %) in the soils will exert a lot of influence on the soil chemical properties. This is because the mineral has high negative charges which translate to the high CEC that is largest among the inorganic colloids. This implies that Bansara and

Kakum soils with vermiculite > 30 % will be more fertile than Ukpah and Okuku soil with vermiculite at the level of 15-30 %. Vermiculite is a magnesium aluminosilicate with magnesium occupying the octahedral position between two silica tetrahedral sheets (Kolay, 2000; Essington, 2006; Tan, 2011). The CEC of vermiculite is approximately 150 cmol/kg and exceeds that of smectite. According to Tan (2011), soils of the southern region in the United States, often characterized by low CEC, exhibited higher CEC values after small admixtures of vermiculite or hydroxy-aluminum interlayer vermiculite (HIVs) in their clay fraction. Because of high selectivity for fixation of K^+ and NH_4^+ , soils with high abundance of vermiculite will slightly tend to be deficient in potassium and ammonium nitrogen. Nevertheless, fixation is not entirely seen as a negative phenomenon as fixed nutrients are released back into soil solution with time. The high K^+ and NH_4^+ fixation in vermiculite can be attributed to high negative charges in the interlayer spaces of this mineral and the metal-oxygen bonding that permits large opening of the tetrahedral and the octahedral interlayer spaces. However, the high CEC and expansion of this clay mineral and its high specific surface area is the reason for high fertility in soils dominated by it. Organic particles can also get entrapped in the spaces forming organo-mineral

complexes that adsorb nutrients and also release same for plants absorption. Organo-mineral complexes and/or chelates formed by this interaction are vital in supplying critical micronutrient to plants depending on their solubility and stability.

Quartz and hematite

Quartz was absent in wetland (Ogoja) but very dominant (> 30 %) in soils of forest (Obudu), farmland (Bekwarra) and grassland (Okuku)(Table 2). Higher quantity of quartz in the soil may be due to the fact that they are formed from sandstone and basement complex parent materials. This agrees with Foth (2006) that about 66.8 % of sandstone parent material is made up of quartz. Quartz minerals are composed entirely of silica (SiO_4) tetrahedra (Kolay, 2000; Rossman and VanOss, 2002). They occur extensively in nature and are frequently an important constituent of the clay fractions of soils. By virtue of their size (<2 μm), the fine silica particles are found mostly in the silt and sand fractions (Tan, 2011).

Structurally, quartz minerals do not belong to the phyllosilicates characterized by sheet structures, but are distinguished as minerals with framework structures or tectosilicates. Kolay, 2000; Essington, 2006). They are highly stable and very resistant to weathering due their crystallization at low temperature and lack of basic cations in their

structure. The silica minerals are generally considered inert or chemically inactive material with slight effect on chemical properties of soils and because of their low chemical activity, they are perhaps of importance only as diluents to the more active clay and humic substances. Their surface area is very small and amounts to only 2 to 3 m^2/g depending on the shape of the particles (Tan, 2011). Soils with clay fractions dominated by quartz are usually non plastic and have a small shrink-swell capacity as well as a small water holding capacity. The corresponding small CEC and anion exchange capacity are attributable to the Si-O broken bonds and Si-OH groups on particle edges. Soils dominated by quartz are low in fertility levels but can be ameliorated by addition of adequate organic matter. Higher levels of quartz in soils of Bekwarra, Obudu and Yala means that they are less fertile than their Ogoja counterpart.

Hematite was identified only in soil of Okuku (Yala). It is an iron oxide compound that occurs as coating on phyllosilicates. The presence of hematite in soil is an indication of high intensity of weathering. It constitutes 5.6 % and 1.8 % of shale and sandstone accordingly (Foth, 2006)

Classification of clay

The clay minerals identified and their classification are presented in Table 3. The

clays were classified into division (layer type), group, subgroup and species levels (Essington, 2006). The minerals identified were phyllosilicates except quartz (tectosilicate) and hematite (accessory mineral or oxide of iron). Kaolinite was the only 1:1 clay in the soil while montmorillonite, vermiculite, illite and polygorskite were 2:1 layer minerals. Nonetheless, an interstratification of kaolinite-montmorillonite was also identified in forest soils developed from basement complex in Obudu. Classification of the clay minerals into subgroup was based on the occupation of octahedral and tetrahedral sheets. The minerals identified, only vermiculite and polygorskite have their octahedral positions fully occupied by magnesium and iron (trioctahedral minerals) while others have their octahedral sheets half occupied by either Al^{3+} and Mg^{2+} , Al^{3+} or Mg^{2+} and Fe^{2+} ions and are termed dioctahedral (Table 3). When all the octahedral positions are occupied by Mg^{2+} or Mg^{2+} and Fe^{2+} , the mineral is trioctahedral while when the octahedral positions are half occupied with Al^{3+} , Al^{3+} and Mg^{2+} or Mg^{2+} and Fe^{2+} , it is dioctahedral mineral (Kolay 2000; Essington, 2006). Following this, polygorskite, $((\text{Mg}, \text{Al})_5(\text{SiAl})_5\text{O}_2)(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and vermiculite $(22\text{Mg} \cdot 0.5\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 4\text{OH}_2\text{O})$ are the trioctahedral minerals in the study area while the rest were dioctahedral except quartz

and hematite.

CONCLUSION

This study highlights the occurrence, abundance, composition and arrangement (crystallography) of the soil minerals and elucidates the behavior of the soil as conditioned by the mineralogy for the overall fertility for plant growth and yield. Understanding of this connectivity is vital for proper soil management. The study also revealed that wetland soil of Bansara (Ogoja) has more 2:1 expanding types of clay minerals (montmorillonite and vermiculite) than forest soil of Kakum (Obudu), grassland soil of Okuku (Yala) and farmland soil of Ukpah (Bekwarra) in this order. Expanding 2:1 clay minerals with higher CEC will have positive implication in soil fertility than 1:1 and non-expanding 2:1 clays that have lower CEC. It is therefore recommended that for better crop yield and sustainable soil uses, the study of clay mineralogy should be a vital component of soil fertility and nutrient management program.

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Table 1: Clay Minerals in the Study Area

S/N	Land use	Chemical formula	Mineral name
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1	Wetland (Bansara)	AlSi ₂ O ₅ (OH) ₄ NaO.3(AlMg) ₂ Si ₄ O ₁₀ (OH) ₂ .8H ₂ O 22MgO, 5Al ₂ O ₃ , Fe ₂ O ₃ .22SiO ₂ .40H ₂ O SiO ₂	Kaolinite Montmorillonite Vermiculite Quartz
2	Grass land (Okuku)	AlSi ₂ O ₅ (OH) ₄ (Mg, Al) ₅ (Si, Al) ₈ O ₂₀ (OH) ₂ .8H ₂ O 22MgO, 5Al ₂ O ₃ , Fe ₂ O ₃ .22SiO ₂ .40H ₂ O NaO.3(Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ .H ₂ O Fe ₂ O ₃ Al ₂ SiO ₅ (OH) ₄ SiO ₂	Kaolinite Palygorskite Vermiculite Montmorillonite Hematite Illite (Halloysite) Quartz
3	Farmland (Ukpah)	(K, H ₃ O) Al ₂ Si ₃ AlO ₁₀ (OH) ₂ CaO ₂ (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ .4H ₂ O KMgAlSiO ₂ .H ₂ O 22MgO, 5Al ₂ O ₃ , Fe ₂ O ₃ .22SiO ₂ .40H ₂ O SiO ₂	Illite Montmorillonite Kaolinite Vermiculite Quartz
4	Forest (Kakum)	SiO ₂ Al ₂ SiO ₅ (OH) ₄ NaO.3Al ₄ Si ₆ O ₁₅ (OH) ₆ .4H ₂ O (K, H ₃ O) Al ₂ Si ₃ AlO ₁₀ (OH) ₂ CaO ₂ (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ .4H ₂ O 22MgO, 5Al ₂ O ₃ , Fe ₂ O ₃ .22SiO ₂ .40H ₂ O	Quartz Kaolinite Kaolinite-montmorillonite Illite Montmorillonite Vermiculite

Table 2: Relative abundance of Clay minerals in the representative Land use

Profile	Horizon	Depth	>30%	15-30%	7-15%	<7%
Og/Ban	Og1	0-19	Ver,	Mont, Kao		
Og/Ban	Og2	19-119	Ver,	Mont		
Og/Ban	Og3	119+	Ver			
Ob/Kak	Ob1	0-17	Qz, Kao, Ver			
Ob/Kak	Ob2	17-60	Ver, Qz			
Ob/Kak	Ob3	60-108			Mont	
Ob/Kak	Ob4	108-150	Kao			
Ya/Oku	Ok1	0-20	Kao	Ver	Illi	Mont
Ya/Oku	Ok2	20-48	Kao	Ver		
Ya/Oku	Ok3	48-94	Kao	Ver		
Ya/Oku	Ok4	94-150	Qz			
Bk/Ukp	Bk1	0-12	Qz, Kao			
Bk/Ukp	Bk1	12-60		Mont		
Bk/Ukp	Bk1	60-106	Qz	Ver		
Bk/Ukp	Bk1	106+				

Og/Ban=Ogoja/Bansara, Ob/Kak=Obudu/Kakum, Ya/Ok=Yala/Okuku, Bk/Ukp=Bekwarra/Ukpa, Ver=vermiculite, Mont=montmorillonite, Kao=kaolinite, Qz=quartz, Illi=illite. >30%=Very abundant, 15-30% =Abundant, 7-15% =Represented, <7% =Poorly represented.

Table 3: Classification of clay from the land uses

Layer Type	Group	Subgroup	Species
1:1	Kaolinite	Kaolinite (dioctahedral)	Kaolinite/dickite
2:1	Smectite	Dioctahedral smectite	Montmorillonite
	Kaolinite/ Montmorillonite	Montmorillonite (dioctahedral)	Kaolinite/ Montmorillonite
	Vermiculite	Trioctahedral	Trioctahedral Vermiculite
	Illite	Illite	Dioctahedral Illite
	Smectite	Palygorskite	Trioctahedral Palygorskite

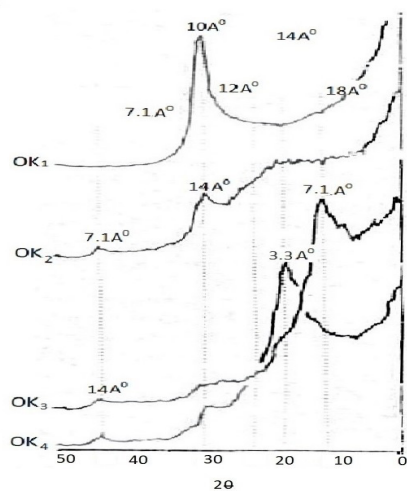


Fig. 1. X-ray diffractogram for Cu target samples Yala (Okuku)

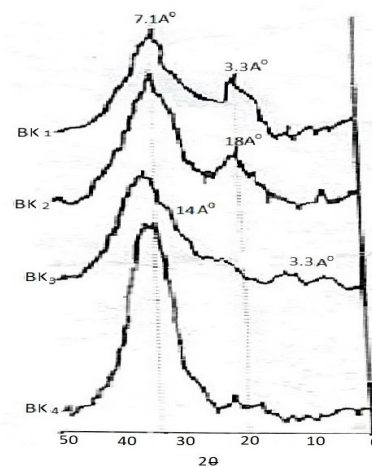


Fig. 2. X-ray diffractogram for Cu target samples Bekwarra (ukpah)

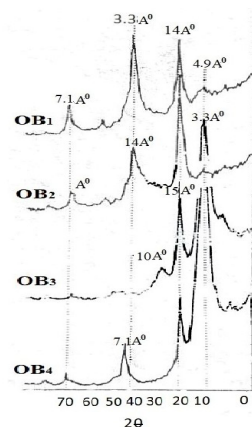


Fig. 4. X-ray diffractogram for Cu-target samples Obudu (Kakum)

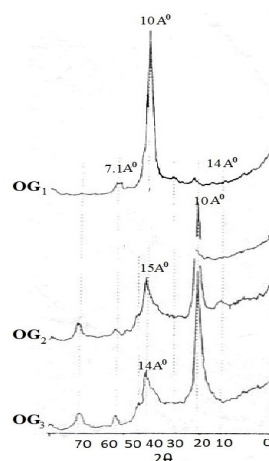


Fig. 3. X-ray diffractogram for Cu-target samples Ogoja (Bansara)