THE GEOCHEMICAL AND MINERALOGICAL ANALYSIS OF CLAYS FROM OKHORO FOR THE PRODUCTION OF PAINT IN SOUTHERN NIGERIA.

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Abstract Five (05) clay samples were obtained from Okhoro and Environs in Southern Nigeria and subjected to geochemical and mineralogical analysis, the aim of which is to determine if the clays are free of Volatile Organic Compounds (VOC) for the production of paint. The analysis was achieved with the aid of the X-Ray Florescence (XRF) and X-ray Diffraction (XRD) machines, respectively. Results for XRF gave values of SiO_2 (37.54-58.45wt%) with mean values of 51.05wt% and Al_2O_3 (27.49-33.60wt%) with mean values of 29.67wt%. Other major oxides include Fe_2O_3, MgO, CaO, K_2O and NaO with mean values of 7.40wt%, 0.61wt%, 0.46%, 1.14% and 0.38%, respectively. The XRD analysis shows dominant contribution from kaolinite and k-feldspar with minor amount of quartz, mica, hematite, montmorrillonite, illite and others. The clays from Okhoro area could be used for paint production subject to beneficiation with silica-rich material such as sands, quartz, quartzite to mention a few.

Keystone: clay; mineralogy; analysis; paint; geochemical

Introduction

Clay minerals are extremely fine grained materials that are less than two micrometers. It is also defined as a finely-grained material that combines one or more clay minerals with non-clay minerals which is possibly traces of quartz, metal oxides (Al_2O_3, MgO i.e. Alumina or corundum and magnesia respectively etc.) and organic matters, clay deposit are mostly composed of phyllosilicate minerals containing variable amount of water trapped in the mineral structure. Its colour varies from grey, brown, purple or red to orangey-red or orange to deep orangey red. There are two types of clay deposits; which are:

I. Primary clay deposits: they are also called residual clay deposits. These clay deposits are found in the place of origin or weathering.
II. Secondary clay deposits: they are also called transported clays. They have been transported by agents of erosion such as wind or water to a new environment or position.

Clay minerals are based on two atomic structures,

i. Alumina-magnesia octahedron; having magnesium or aluminum at the center surrounded by six equidistant oxygen (Grim, 1962).
ii. Silicon tetrahedral: with silicon surrounded by four oxygen. Figure 1 and 2 shows the two atomic structures.

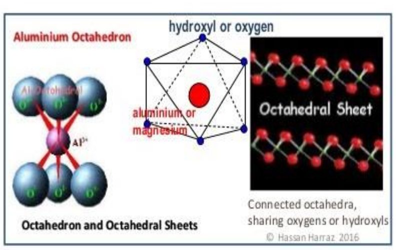

Figure 1: Alumina-magnesia octahedral sheets. (Harraz, 2016)

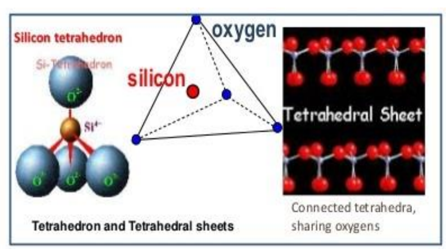

Figure 2: Silicon tetrahedral sheets (Harraz, 2016)

In the sheet structure of octahedral units, aluminum (Al), iron (Fe) or magnesium (Mg) may be seen in the coordination so that the six oxygen atoms maybe equidistant from them. If aluminum is present, two third of the possible position is filled producing a gibbsite ($Al_2(OH)_6$) structure. Where, magnesium

(Mg) is present, all the possible position is filled producing a brucite ($Mg_3(OH)_6$) structure. The tetrahedral structure forms a hexagonal network repeatedly to form a sheet composition of $Si_4O_6(OH)_4$. There are four groups of clay:

i. Kaolinite ii. Smectite (Montmorillonite) iii. Illite iv. Chlorite

Kaolinite has a formula $Al_4Si_4O_{10}(OH)_8$ with theoretical composition of 46.54% SiO_2, 39.5% Al_2O_3, and 13.96% H_2O. The structure is a combination of a the gibbsite ($Al_2(OH)_6$) and a silica tetrahedral (SiO_4) structure. It does not expand when water is added to it. It has low cation-exchange and high anion-exchange capacity. It is flaky with a white, sometimes red, brown and blue tint color. Sometimes the packing of kaolinite is disordered which can be used as refractory clays. The structure of kaolinite is seen in Figure 3.

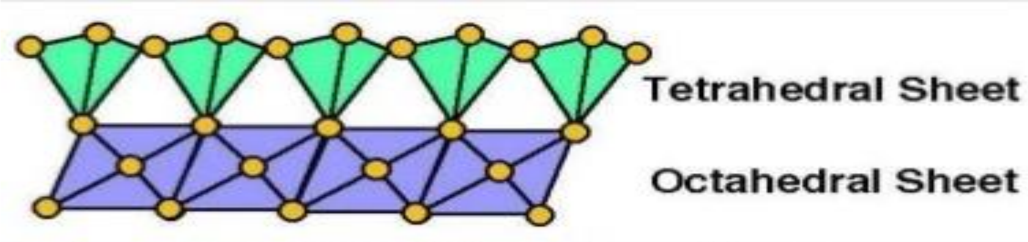

Figure 3: Kaolinite 1:1 atomic structure (Harraz, 2016)

Paint is a term used to describe a number of substances that consist of a pigment suspended in a liquid or a paste called a vehicle such as water or oil (Crowley *et al*., 2008). Paint provides an economical protection, preservation, decoration and aesthetic functionalities to structures. Paints composition largely determines its characteristics, usage and classification. By suitable variation of the various constituents, paints can be greasy, glossy flat or dry (Abidalla, 2008). Clay paint is a matt mineral and ecological paint are made from clay materials and other natural elements such as fillers, binders and solvents etc. that is eco-friendly and free of VOC's (Volatile Organic Compounds). Clay paints do not pollute the environment unlike the household paints. It does not pose a threat on the health of humans. It contains little or no plastics and attracts little or no dust. It has a natural smell and is non-toxic. Raheem and Olowu, (2013) made household paints using clay materials. The clay materials are kaolin clay from Lagos around Ikorodu and Yaba. The major aim was to produce paints free of VOC's and pocket friendly as opposed to the conventional paints which has VOC's and is harmful to humans still using this conventional paint as a control. Clays (kaolin) with or between 40-50% silica (SiO_2) and 35-40% alumina (Al_2O_3) is most preferably used. According to Ombaka (2016), the application of various clay mineral is related to their structural, physical and chemical characteristics. Onyeobi *et al*., (2013) stated that industrial potential of clays from the southern parts of Nigeria e.g. Ubiaja, Iyuku, Benin etc. are based on their physical, chemical, and geotechnical characteristics and revealed that they are suitable for paint production, making of refractory bricks and ceramics etc., depending on the appropriate processing applied. Ramaswamy and Raghavan, (2011) is of the opinion that kaolin may be accompanied by other mineral impurities such as feldspar, mica, quartz, illite, anatase, hematite, and carbonaceous materials etc. thereby reducing its industrial usefulness. Chandrasekhar, (2006) opined that brightness is a critical property in most high-value application of kaolin. The aim of this study, however, is to determine the suitability of the Okhoro clay for paint production taking into cognizance the absence of VOC's.

GEOLOGIC SETTING OF THE STUDY AREA

The study area is in Okhoro, Benin City, Egor Local Government Area, Edo State. It lies between longitudes 5º36'30''E to 5°39.0''E and latitudes 6°22'30''N to 6°23'30''N which is shown in Figure 4.

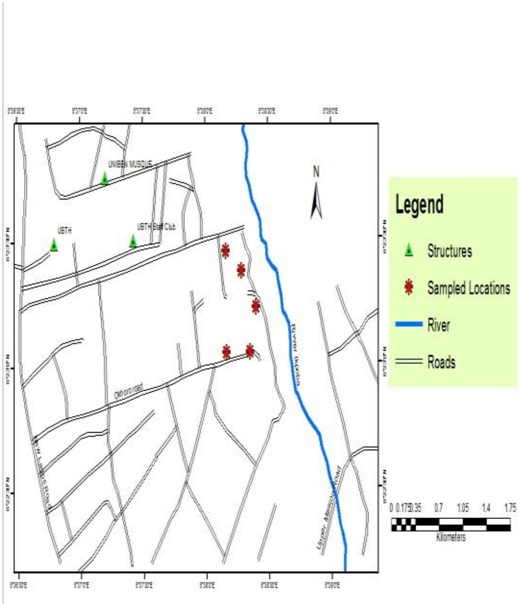

Figure 4: Location map of the study area.

The Niger Delta Basin is also referred to as the **NIGER DELTA PROVINCE.** It is an extensional rift basin or passive margin located in the Niger Delta and Gulf of Guinea on the passive continental margin near the western coast of Nigeria with suspected or proven access to Cameroon, Equatorial Guinea and Sao Tome and principle (Tuttle *et al.*, 2015). This Basin was formed as a result of a failed rift junction during the separation of South American and African plates. The Basin is bounded by the Atlantic Ocean in the south and it is very prolific in terms of hydrocarbon. The Basin is one of the largest sub aerial Basins in Africa with about75000km², 300,000km² in total area and a sediment fill of 500,000km³ (Tuttle *et al.*,2015). The sediment fill has a depth of 9-12km. The Niger Delta Basin lies in the south western most part of the larger tectonic structure, the Benue Trough and is bound by Cameroon Volcanic Line and Transform Passive continental margin (Fatoke, 2010). The geologic map in is shown in Figure 5 and Figure 6 shows the stratigraphy of the Niger Delta Basin. The Niger Delta Basin comprises Agbada, Akata and Benin Formations.

i. Agbada Formation was formed in during the Eocene period. It is a marine or oceanic facies having both freshwater and oceanic attributes. This facies is where natural oil and gas is mainly formed. It is about 3,700meters thick (Tuttle *et al*., 2015).

ii. Akata Formation is Paleocene in age and composed of thick shales, turbidites, sands and little amount of silt and clay. Its thickness is estimated to be 7,000meters thick (Tuttle *et al*., 2015). The sediments are pressed into shale diapers in the basin and the formation is formed from being over pressured and not having access to water (Tuttle *et al*., 2015).

iii. Benin Formation is formed in Oligocene to recent times. It is estimated to have a thickness of 2000meters. It consists of Upper and Lower Deltaic Plain Sands (Tuttle *et al*., 2015).

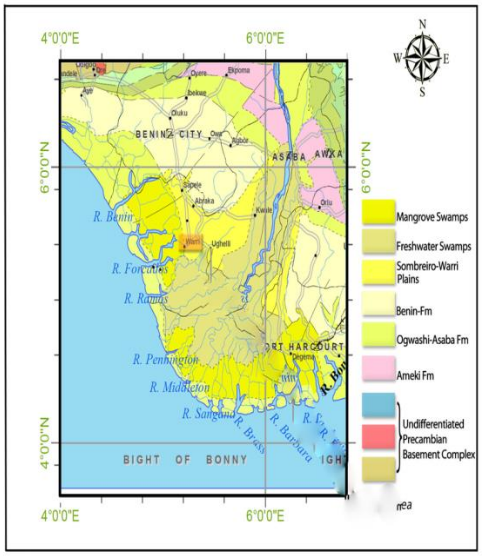

Figure 5: The geologic map of Niger Delta Basin (NGSA, 2004)

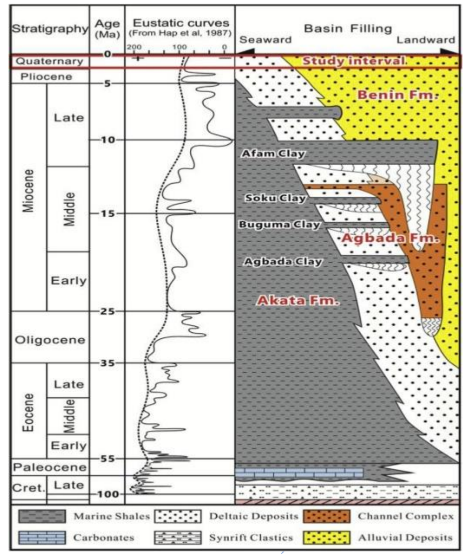

Figure 6: The stratigraphy of Niger Delta Basin (Corredor *et al*., 2005).

LOCAL GEOLOGY OF THE STUDY AREA (OKHORO AREA)

Benin Formation is found within the surface and surface of the Basin. The surface formation is seen from the west across to the east of the Basin. It is made up of:

- More than 90% sand and sandstone.
- Discontinuous intercalations of clay beds. It is generally poorly bedded; it may contain quartz bed, friable, loose ranging from fine, medium and coarse grained sediments. (Generally pebbly to gravelly at the base). It is most times poorly sorted i.e. the sand grains vary from sub angular to well-rounded. This Formation is studied through the use of well logging on shore (Short and Stauble, 1967).

Benin Formation is having a top reddish earth, mainly clayey sands capping highly, pebbly loose sands/sandstones and local thin clays in shales, thought to be from braided river origin. The colour varies from reddish brown, red, pink, and orangey-red for the sandstone to gray or white or purple for the clay. It was assigned the ages Oligocene to Recent. Figure 7 shows the geologic map of the study area.

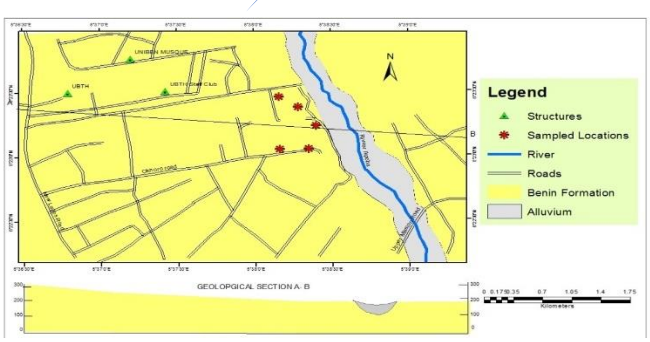

Figure 7: Local Geological Map of the Study Area

Okhoro and its environs is situated in Egor Local Government Area. It comprises mainly sand and clay intercalations as shown in Plate 1 and 2.

1  2 

Plate 1 and 2: Sands and clay intercalations and Concretions in Okhoro Clay Body.

MATERIALS AND METHODS

Five (05) samples were obtained from Okhoro and Environs with the aid of a peak hammer, placed in well labeled sample bags and subjected to further geochemical pretreatment processes. The samples were pelletized and further subjected to the X-Ray Florescence and X-Ray Diffractometer, Schmadzu 6000 Model, in National Steel Raw Materials Exploration Agency (NSRMEA), Kaduna, Nigeria.

PRESENTATION AND DISCUSSION OF RESULTS

The result of the elemental compositions is presented in Table 1. Table 2 shows the mineralogical composition of OKH 1 to 5 clay samples. Table 3 shows the comparison of the major oxides found in the study area with Raheem and Olowu, (2013), Paynes (1961) and WHO, (2005), respectively. Figures 8 and 9 show the mineralogical composition of each location.

GEOCHEMICAL ANALYSIS OF THE CLAY SAMPLES.

Table 1 shows the chemical composition of the five (05) clay samples (OKH1-5) from the central part of the study area. The major oxides found in the study area include SiO_2 which ranges from (37.54-58.48) wt.% with a mean value of 51.05wt.%. This value is in accordance with WHO, (2005) which states that the silica content of paints should be ≤65% so as not to cause fibrosis, silicosis and lung cancer. Al_2O_3 in all the clay samples ranges from 27.78-33.60 wt.% with a mean value of 29.69wt.%. Fe-oxide varies irregularly from (2.76-24.11) wt.% with a mean value of 7.40 wt.%. This is probably as a result of the organic matter in the sediments (Odigi, 1986). This also impacts a brownish or purplish colouration on the clay samples. Titania (TiO_2) ranges from 4.12-5.19% with average values of 4.65%. The Na_2O ranges from 0.22-0.44 wt.% with a mean value of 0.38wt%. The CaO ranges from 0.40-0.56 wt.% with a mean value of 0.46%. CaO is seen in three locations only, OKH1, OKH3 and OKH 5. K_2O has a range of 0.59-1.37 wt. % with a mean value of 1.14wt% while MgO ranges from 0.48-0.78 wt.% with a mean of 0.61wt%. Sulphur (S), zircon (Zr), and niobium (Nb) occur in trace amounts in OKH1-OKH5 but vanadium (V) occurs only in OKH1.The subordinate amount of S, Zr, and Nb would not impact colouration to the paint when produced (Emofurieta *et al*., 2008). The SiO_2/Al_2O_3 show that locations (OKH1-OKH5) has values of 3.20, 2.63, 3.60, 2.25, and 2.88, respectively, making OKH2, OKH4, and OKH5 probably kaolinitic and OKH1 and OKH3 being montmorillonitic in composition owing to the <3 values for the SiO_2/Al_2O_3 ratio (Emofurieta *et al*., 1999; Anozie *et al*., 1993).

MINERALOGICAL ANALYSIS OF THE CLAY SAMPLES.

Results of the mineralogical analysis shown in Table 2 reveal that kaolinite, quartz, and /or illite are the dominant minerals in all the samples (OKH1-OKH5) with hematite, montmorillonite, orthoclase, and mica occurring in minor amount in some locations. Hematite, mica, and montmorillonite occur in trace amount. These values are derived from the evaluation of the peaks according to Carol, (1971). The diffractograms of OKH1 and OKH2 are presented in Figures 8 and 9, respectively.

Table 1: Elemental Compositions of the Clay Samples from the Study Area

ELEMENTAL OXIDES		percentage weight concentration in (%) for major elements and in ppm for trace elements					
		0KH1	*OKH2*	*OKH3*	*OKH4*	*OKH5*	*MEAN*
Si	SiO_2	53.99	52.14	58.48	37.54	53.11	51.05
Al	Al_2O_3	27.78	33.60	27.49	28.25	31.27	29.67
Ti	TiO_2	4.98	4.27	4.12	5.19	4.72	4.65
Fe	Fe_2O_3	5.59	4.57	2.76	24.11	5.59	8.52
K	K_2O	1.21	1.28	1.37	0.59	1.26	1.14
Ca	CaO	0.43	---	0.56	---	0.40	0.46
Na	Na_2O	0.44	0.22	0.43	0.39	0.43	0.38
Mg	MgO	0.78	0.64	0.54	0.63	0.48	0.61
P	P_2O_5	1.29	0. 26	---	0.77	0.8	0.78
S	S	6.8	6.8	8.5	9.9	6.0	7.6
Zr	Zr_2O	7.7	11.7	22.5	----	3.6	11.4
Nb	Nb_2O	14.2	11.5	11.9	15.4	9.8	12.6
V	V_2O_5	6.2	---	-----	---	---	6.2
SiO_2/Al_2O_3		3.20	2.63	3.60	2.25	2.88	
TOTAL		99.13	99.98	100.04	100	100	

From figures 8-12, Kaolinite with highest peaks ranging from 3.65Å- 3.75Å are seen in OKH2-5. OKH1 has a how peak of 2.26Å, the reason is that Orthoclase has the highest peak of 3.63Å making it immature i.e. it is still undergoing decomposition to form kaolinite. The montmorillonite found in this location could be as a result of transportation through erosion to this present location from its previous environment. Quartz, being the second dominant mineral is a non-clay mineral is resistant to weathering compared to the other minerals found in this study area. It ranges from (4.06- 14.71%) in clay fraction with peaks ranging from 1.60Å-2.43Å on the diffractograms. Illite ranges in abundance from (9.12-12.04%), hematite, montmorillonite, mica and orthoclase ranges from 3.04-5.23%, 3.80-6.94%, 1.88-12.04%, and 4.64-96%, respectively. Three (03) clay samples possess montmorillonite (OKH1, OKH2 and OKH3) and are probably swelling clays. The mineralogical composition of the clay samples shows that OKH2, OKH3, OKH4 and OKH5 can be used for paint production because they are kaolinitic clays. OKH1 may not be suitable for paint production because the mineralogical abundance possess very low kaolinite content with trace amount of montmorillonite.

Table 2: Average Modal Composition of the Minerals

	AVERAGE MODAL COMPOSITION (%)				
MINERALS	*OKH1*	*OKH2*	*OKH3*	*OKH4*	*OKH5*
Kaolinite	3.04	83.39	78.36	70.34	59.03
Quartz	7.60	14.71	5.40	4.06	13.84
Mica	3.42	1.88	5.40	4.64	12.04
K-Feldspar(Orthoclase)	69.96	-----	-----	4.64	-----
Hematite	3.04	-----	3.86	5.23	3.01
Montmorillonite	3.80	-----	6.94	-----	-----
Illite	9.12	-----	-----	11.04	12.04
Others	0.01	0.02	0.08	0.05	0.04
TOTAL	99.99	99.98	100.04	100	100

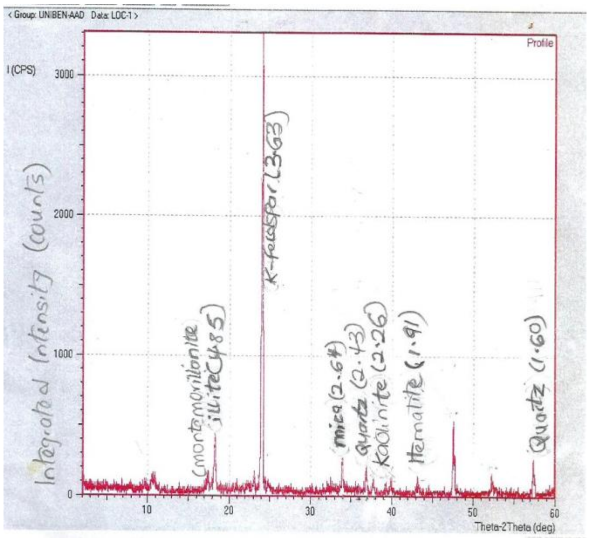

Figure 8: Diffractogram of OKH 1

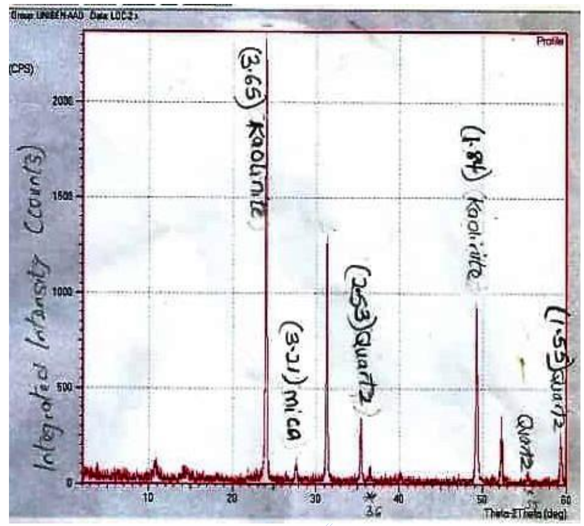

Figure 9: Diffractogram of OKH 2

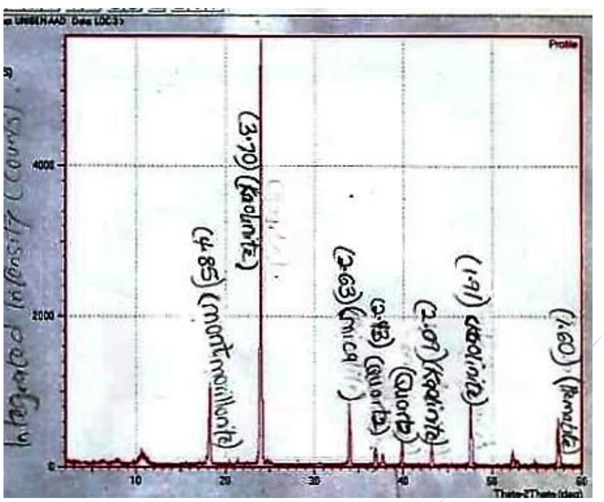

Figure 10: Diffractogram of OKH 3

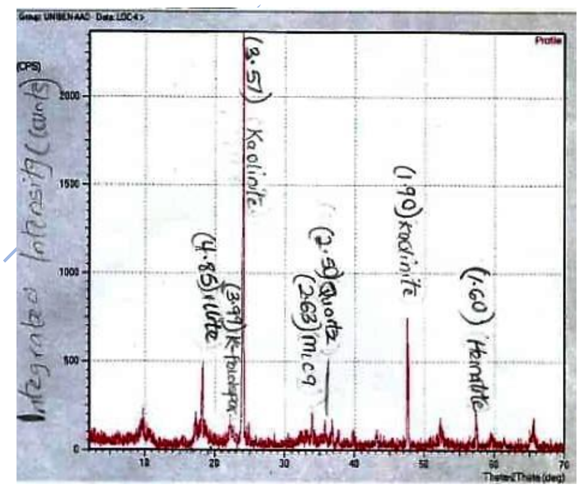

Figure 11: Diffractogram of OKH 4

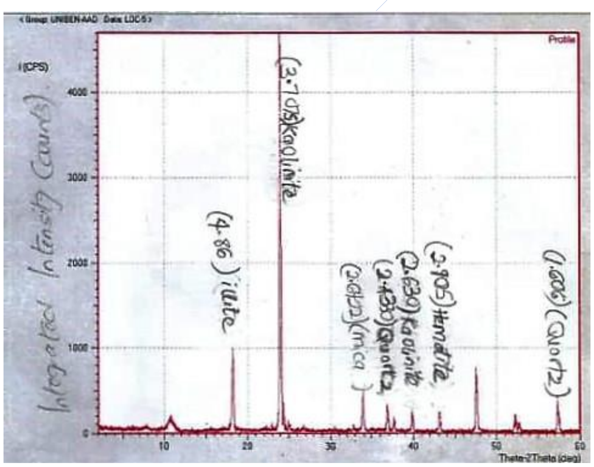

Figure 12: Diffractogram of OKH 5

In Figures 8 and 9, kaolinite with the highest peak ranges from 3.65Å- 3.75Å and is observed in OKH2, OKH3, OKH4 and OKH5 and OKH1 has low peak of 2.26Å. Orthoclase has its highest peak of 3.63Å in OKH1, hence, is considered to be immature sediments i.e. it is still undergoing decomposition to form kaolinite. The montmorillonite found in this location could probably be as a result of transportation by erosion to this present location from its previous environment. Quartz, being the second dominant mineral is a non-clay mineral, though is very fine-grained (clay-sized particles), and is resistant to weathering compared to the other minerals found in this study area. It ranges from 4.06- 14.71% with peaks ranging from 1.60Å-2.43Å on the diffractograms. While illite ranges in relative modal abundance from 9.12-12.04%, hematite, montmorillonite, mica and orthoclase ranges from 3.04-5.23%, 3.80-6.94%, 1.88-12.04%, and 4.64-69.96% in modal composition, respectively. OKH1 and OKH3 contain swelling clays because of the presence of montmorillonite probably transported to this present location. The mineralogical composition of the clay samples shows that OKH2, OKH4 and OKH5 can be used for paint production because they are kaolinitic in composition, while OKH1 and OKH3 cannot be used because they are montmorillonitic in composition.

Table 3 below shows the comparison of the major oxides in the study area with other specifications. This is done to show if the clay samples are in line with clay paint specifications and hence, suitable for the production of paints.

Table 3: Comparison of the major oxides from the study area and other industrial clay specifications

MAJOR OXIDES	THIS STUDY (MEAN)	RAHEEM AND OLOWU (2013)	WHO(2005)	PAYNES (1961)
SiO_2	51.05	46.31	≥65	45.78-47.90
Al_2O_3	29.67	37.02		37.90-38.40
K_2O	1.14	0.47		0.10-0.40
MgO	0.61	0.15		0.20-0.30
Na_2O	0.38	0.32		O.20-0.30
Fe_2O_3	7.40	0.66		13.40-38.40
CaO	0.46	0.12		0.25-0.30

WHO's specification is made the standard benchmark for the production of paint as its silica ratio is ≤65%. WHO, (2005) states that for paint produced organically or inorganically, its silica content should be ≤65%. But in comparing with Paynes (1961) and Raheem and Olowu (2013), the silica content of the study area is 51.05% and is higher than Paynes (47.90%) and Raheem and Olowu, (46.31%), respectively. The low Al_2O_3, Fe-oxides and alkalis can be corrected by proper beneficiation processes such as the introduction of shale-rich materials and laterites etc. (Odokuma-Alonge and Amadin, 2018.

CONCLUSION

Five (05) clay samples from Okhoro area in Southwestern Nigeria were obtained and subjected to geochemical and mineralogical analysis, the aim of which was to determine if suitble for paint production. It was observed that of the five samples, three (03) were found to meet the WHO, (2005) specification for use for the production of paint.

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