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ASSESSMENT OF MINERALOGICAL AND HEAVY METAL CONSTITUENTS OF GEOPHAGIC CLAYS IN PARTS OF ANAMBRA STATE, NIGERIA

[1]Ezealaji, I.P., [1]Akudinobi, B.E.B, and [2]Lar, U.A
(1) Department of Geological Sciences, Nnamdi Azikiwe University, Awka
(2) Department of Geology, University of Jos
Corresponding Author's Email: ip.ezealaji@unizik.edu.ng

Abstract
The mineralogical and chemical composition of in-situ geophagic clays were carried out in parts of the Niger Delta Basin,with the aim of determining the types, major and trace element constituents, and public health implications of the clays. Five samples were collected and subjected to X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analyses.XRD analysis revealed kaolinite (54 to 78 wt. %),chlorite (46 to 64 wt. %), namuwite (3 to 10 wt. %), kupletskite(4 wt. %), montmorillonite (4 to 5 wt. %),palygorskite (4 wt. %), quartz (22 to 46 wt. %) and albite (7 wt. %) minerals. The constituents observed from XRF analysis include SiO_2 (60.15 to 67.25 wt. %), Al_2O_3 (7.24 to 14.23 wt. %), Fe_2O_3 (3.22 – 4.61 wt. %), TiO_2 (0.47 – 0.91 wt. %), MgO (1.57 – 6.59 wt. %), CaO (1.62 – 2.87 wt. %), Na_2O (0.32 – 2.14 wt. %), K_2O (0.61 – 1.51 wt. %) and MnO (0.03 – 0.30 wt. %). When compared with average crustal abundance values, the samples from Enugwu-Agidi had higher SiO_2, TiO_2, MgO and MnO; Igbariam higher MnO; Nteje higher TiO_2, MgO and MnO; Isinyi-Nando higher MgO and MnO. The XRF analysis also revealed the following heavy metal concentrations; Zn (61.12 to 321.11 ppm), Cu (16.03 to 36.08ppm), Pb (13.29 to 24.1 ppm), Hg (0.02 to 0.06 ppm), Co (1.81 to 5.41 ppm), Ni (29.00 to 83.27 ppm), As (3.42 to 5.20 ppm), Se (<0.01 to 20.02 ppm), Cr (43.71 to 106.20 ppm), Cd (0.06 to 0.12 ppm) and V (79.58 to 220.49 ppm). Zn, Pb, Ni, As, Cr and V were found to be higher than the joint FAO/WHO maximum daily permissible limits for heavy metals in food and vegetables. An assessment of the levels of contamination of the heavy metals using index of geo-accumulation (Igeo), shows that Zn, Cu, Pb, Hg, Co, Ni, As, Cr, Cd and V (all with Igeo< 1) did not contaminate the clays. The study suggests that a safe remediation technique be put in place before consuming these clays.
Keywords: *X-Ray Diffraction, X-Ray Fluorescence, Enugwu-Agidi, Heavy metal and Geoaccumulation*

Introduction

A clay material is any fine-grained, natural, earthy, argillaceous material (Grim, 1962). The word clay can be used in terms of a rock or particle size. They are composed essentially of a small group of extremely small crystalline particles of one or more members of a group of minerals that are commonly known as the clay minerals (Grim, 1968). Typical examples of clay minerals include kaolinite, montmorillonite, illite and chlorite. Clays originate from natural processes - mostly weathering, transportation and deposition by sedimentation within geological periods. They have the ability to adsorb other elements present in the immediate environment which can constitute pollutants with adverse health implications, particularly when it is to be ingested by humans and animals.

Nevertheless, geophagy (or geophagia) can be defined as the deliberate ingestion of earthy or soil-like materials such as clay and chalk (Crawford and Bodkin 2011). This practice is common among animals and human beings alike. It exists in rural and urban areas, among men, children and most commonly, pregnant women. Susan Allport (2002) reported cases of women from Nepal who eat red and white coloured clays, especially during pregnancy. The same geophagic clays have been used in building their mud houses. Geophagia is not limited to any particular age group, race, sex, geographic region or time period (Abraham et al., 2013), and has no connotation with one's level of education. Culturally speaking, the practice amongst many of the clay eaters emanates from having doubtlessly watched their mothers or close relatives eat the clay (Bisi-Johnson et al., 2010).According to Lar et al. (2015), the reasons for eating clays may include natural cravings, purification of stomach, reducing the risks of afterbirth complications, to safeguard the health of the unborn, to derive nutrients for the unborn – particularly calcium, to reduce vomiting and salivating during pregnancy, and to guarantee the

quality of breastmilk. However, this can constitute serious health problems for the consumers if not treated before consumption. These clays can be contaminated by heavy metals and other toxic substances. Some of these heavy metals are essential nutrients for the human body in low amounts but become toxic in high amounts. Toxic metals have proven to be a major threat to human health, mostly because of their ability to cause membrane and DNA damage, and to perturb protein function and enzyme activity. These metals disturb native proteins' functions by binding to free thiols or other functional groups, catalyzing the oxidation of amino acid side chains, perturbing protein folding, and/or displacing essential metal ions in enzymes (Witkowska et al., 2021).

In 2002, the European Union alerted the Cameroon Ministry of Public Health that kaolin carried from Cameroon to Europe had abnormally high amount of lead (Pb) at levels a hundred times higher than the maximum permissible level. This kaolin is mined from different sources and sold in several markets, some locally and others from Nigeria (Bonglaisin et al. 2011). Kelle et al., (2014) studied geophagic clays from various markets within Onitsha metropolis and noted that some samples contained relatively high amounts of lead and mercury. Odewumi, (2013) reported high levels of Cu, Zr, Zn, Ni, Fe_2O_3, TiO_2, and MnO while studying the mineralogy and geochemistry of geophagic clay deposits in Share area of Kwara State, Nigeria.

The chemical and mineralogical characteristics of edible (geophagic) clays have been studied by numerous scholars (**Odewumi, 2013; Lar, 2015;** Kelle et al., 2014; Bisi-Johnson et al., 2010) in Nigeria, but only few have placed attention on their heavy metal contents and public health implications. This paper thus seeks to relate the heavy metal constituents of in-situ geophagic clays and their public health implications in parts of Anambra State, Nigeria and provide adequate information about the type of clay deposits in the area. In-situ investigation of the clays is considered necessary since the desired properties may have been significantly altered in the course of transportation and processing, prior to marketing. This aspect has not been adequately addressed and documented, particularly in this part of Nigeria.

Geology

The study area falls within the Niger Delta Basin, southeastern Nigeria. This Basin was formed at the site of a rift triple junction related to the opening of the southern Atlantic starting in the Late Jurassic, and continuing into the Cretaceous. It began to develop proper in the Eocene, accumulating sediments of over 10 kilometers thick (Tuttle et al, 1999). Sedimentation in southern Nigeria, which began in the Early Cretaceous, was facilitated by the breakup of the African and South American continents, leading to the formation of the Benue Trough (Benkhelil, 1989). Murat (1970) identified three major tectonic phases of sedimentation in the Benue Trough, the Niger Delta Basin developed in the third phase. The basin fills of the Niger Delta Basin are the Imo Formation, Akata Formation, Ameki Group (Nanka Formation), Agbada, Ogwashi-Asaba Formation and Benin Formation. The Imo and Nanka Formations were encountered in the study area.

The geophagic clays were encountered mainly within the Imo Formation. Eneh (2021) classified geophagic clays into kaolin or calabash clay (nzu in Igbo) and bentonite clay (ulo/uro in Igbo). She noted that geophagic clays are used in early pregnancy to curb morning sickness; relieve the discomfort of heartburn, indigestion, gastro-oesophageal reflux disease and peptic ulcer disease; as appetite suppressant and weight loss regimen; for skin treatment; for healing of wounds; as contraceptives; as antidiarrhoea etc.

The Imo Formation is essentially a mudrock unit consisting mainly of dark grey to bluish grey shale, with occasional admixtures of clay, ironstone, thin sandstone bands and limestone intercalations (Nwajide, 2013). From XRD analyses, kaolinite has been made out as the principal mineral component of the Imo Shale. Montmorillonite and illite are minor, as inferred

from the generally low content of K_2O and Na_2O, and the K_2O could even be from the presence of K-feldspar (Ogbukagu, 1982; Nwajide, 2013). High percentage of SiO_2 (44 – 54%) within Imo Formation, reflects the dominance of quartz among the non-clay mineral components. There are also small amounts of carbonates, essentially calcite. Titanium oxide reflects the presence of the heavy minerals ilmenite and rutile. Iron oxide, most probably as haematite, is an ubiquitous and essential component of the shales. Trace elements are numerous, but the most common are Zr (193 – 636ppm), Cr (224 – 301ppm) and Sr (75 – 228ppm). The Ameki Group consists of the Nanka Sand, Nsugbe Formation, and Ameki Formation (Nwajide, 1979), which are laterally equivalent. Arua (1981) nominated four stratigraphic units as members of the Ameki Formation. They are Pebbly Sandstone, Argillaceous Sandstone, Shale and Clay members. The Nanka Formation is compositionally highly mature on account of the absence of feldspars and the dominance of the ultrastable heavy mineral suite – zircon, tourmaline and rutile. Kyanite and staurolite constitute the balance of the non-opaque heavies, and point to metamorphic parent rocks as the main provenance material (Nwajide, 2013).

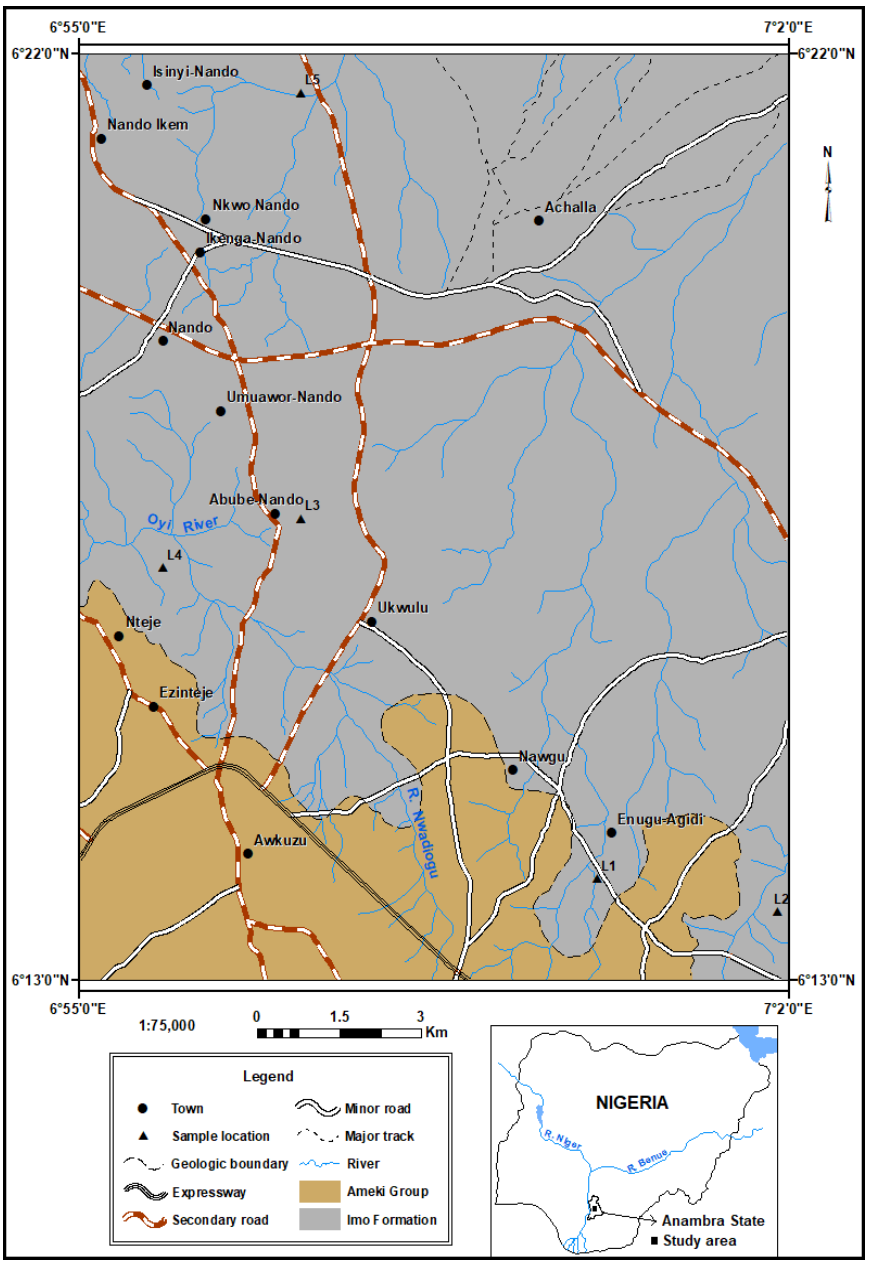


Fig 1: Geologic and location map of the study area (modified from Nwajide, 2013).

Materials and Methods

Sample Collection

A total of five (5) clay samples were collected from exposed outcrops at varying depths (30cm – 2m), using hammer and trowel. The hammer was used to loosen up the deposits and trowel used in collecting them into sample bags. The sampling depths depended on the thickness of the exposed overburden, at each location. Sampling was made where the clays outcrop – mostly along erosion channels, river channels and excavation sites.Efforts were made to collect fresh unweathered samples. Well labelled samples weighing about 10g each were collected, cleaned and stored in transparent polythene bags for wet samples and cloth bags for dry samples. After fieldwork and before taking the samples to the lab, they were air–dried at room temperature (25 C°) and sieved to remove debris. Both the Xray Diffraction (XRD) and XrayFloresence (XRF) were done at the National Geosciences Research Laboratories, Kaduna, Nigeria.

Analytical Methods

X-ray Floresence (XRF): This measured the oxides and elemental compositions of the clay samples. The instrument used was Epsilon 5 X-ray fluorescence model (panalytical). Glass beads were used for major elemental analyses while compressed rock powder pellets were used for trace elemental analysis. The rock samples were reduced to less than 63 microns using a Tema vibrating mill. The beads were prepared by drying the sample powder in an oven at 100^0C for 24 hours, igniting about 5.0g of the dried rock sample powder in the furnace at 100^0C for 2 to 3 hours. Each ignited rock powder was cooled and weighed to determine the weight of the calcinated impurities. Exactly 5 times of flux (spectroflux 100B) was added to 1.0g of the stored ignited rock powder. Mixing and igniting the weighed mixture was done in the pre-set furnace at 100^0C for 10 minutes to form a molten mixture. The molten mixture was cooled over a compressed stream of air while tapping the edge with a small iron slab until the glass bead formed is separated. Each glass bead was labelled and slotted into the computerized XRF for major elemental analysis. The compressed pellets were prepared by weighing about 3.0g of oven dried rock powder samples, adding 3.0g flux (cellulose-powder) as a binder and dispersive agent, and then shaking in small plastic containers for 12 min. The mixture was then compressed by applying a pressure of $1{,}500Kgm^{-2}$ using both manual and electronic compressors. The pellets were placed in the computer programmed XRF for trace elemental analysis.

X-ray Diffraction Spectrometer (XRD): This was used to determine the clay mineral types. The equipment used was the Empyrean diffractometer DY 674 (2010) with a cupper anode material manufactured by Panalytical Holland. The diffractometer consists of three basic elements: an X-ray tube, a sample holder and an X-ray detector. The clay samples were finely ground, homogenized and sieved to pass through the 75 microns. A representative portion of the powdered sample is then prepared using the sample preparation block and compressed in the flat sample holder to create a flat, smooth surface that was later mounted on the sample stage in the XRD cabinet. The sample is analysed using the reflection-transmission spinner stage using the theta-theta settings. The intensity of diffracted X-rays is continuously recorded as the sample holder and X-ray detector rotate through their respective angles on the spinner stage, and the results recorded as peak positions on a diffractogram.

Data Analysis

Calculation for the estimation of the degree of contamination

The index of geoaccumulation (Igeo) was used in estimating the degree of heavy metal contamination of the geophagic clays. This was introduced by Muller (1969) and have been corroborated by several authors. It is calculated from the formula:

$I_{geo} = \log_2 [(C_n/1.5B_n)]$

where C_n is the measured concentration of the heavy metal and B_n is the background concentration of the element using the average upper continental crust values. The factor 1.5

was introduced in this equation to minimize the effect of possible variations in the background values [B_n] due to lithogenic influence (Lar, 2015). Interpretation of Igeo values are presented in table 1.

Table 1: Interpretation of Index of Geoaccumulation of Heavy Metals by Class (after Muller (1969)

I_{geo} Value	**I_{geo} Class**	**Pollution Intensity**
> 5	6	Extremely polluted
4-5	5	Strongly to extremely polluted
3-4	4	Strongly polluted
2-3	3	Moderately to strongly polluted
1-2	2	Moderately polluted
0-1	1	Unpolluted to moderately polluted
0	0	Unpolluted

Comparison with FAO/WHO maximum permissible limits

The heavy metal concentrations in the clay samples was compared with the maximum daily permissible limits set by the joint expert committee on food additives of the Food and Agriculture Organization (FAO) and the World Health Organization (WHO, 1989).

Results and Discussion

Mineral Composition

The XRD analysis revealed that the mineral compositions of the geophagic clays varied from one locality to another. The summary of the results is presented in Table 2 while the diffractogram from the XRD is presented in figures 2 to 6 below. The clay minerals present include kaolinite, chlorite, namuwite, kupletskite, montmorillonite and palygorskite. The non-clay minerals present are quartz and albite. Kaolinite and chlorite are the dominant clay mineral while quartz is the dominant non-clay mineral in the samples. Albite indicates the presence of feldspar in the clay while chlorite indicate the presence of mica. The high abundance of kaolinite might be indicative of weathering of aluminium-rich source rocks. High silica contents with low alumina, and less alkali, revealed by the chemical characteristics signify kaolinitic features (Olusola et al, 2014).

Table 2: Quantitative determination of mineral composition of the clays by the XRD methods.

Location	**Sample No**	**Coordinates**	**Minerals**	**Weight (%)**
Enugwu-Agidi	L1	6° 13' 59.20"N 7° 00' 06.40"E	Kaolinite	78
			Quartz	22
	L2	6° 13' 39.88"N 7° 01' 52.97"E	Chlorite	64
			Quartz	33
			Namuwite	3
Igbariam	L3	6° 17' 29.07"N 6° 57' 11.07"E	Kaolinite	54
			Quartz	38
			Kupletskite	4
			Montmorillonite	4
Nteje	L4	6° 17' 0.22"N 6° 55' 49.59"E	Kaolinite	78
			Namuwite	10
			Albite	7
			Montmorillonite	5
Isinyi-Nando	L5	6° 21' 38.52"N 6° 55' 41.76"E	Chlorite	46
			Quartz	46
			Montmorillonite	4
			Palygorskite	4

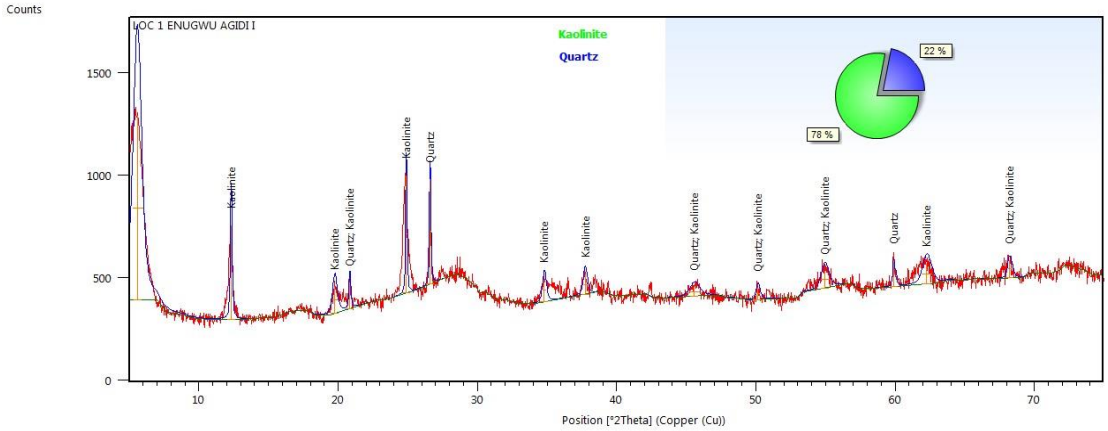


Fig. 2: X-Ray Diffractogram of L1 (Enugwu-Agidi) Sample

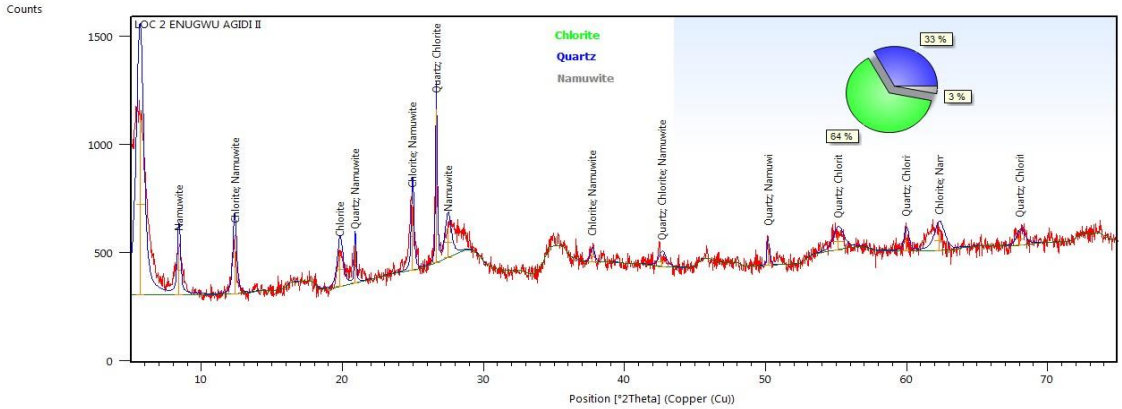


Fig. 3: X-Ray Diffractogram of L2 (Enugwu-Agidi) Sample

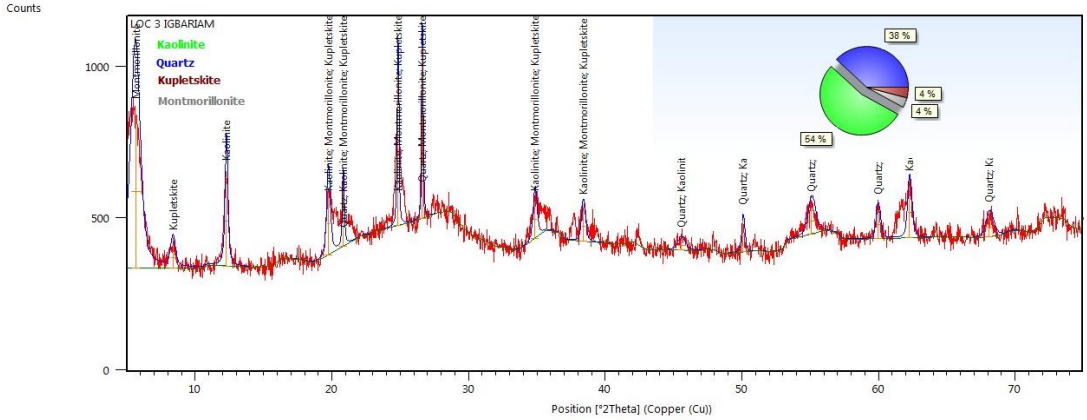


Fig. 4: X-Ray Diffractogram of L3 (Igbariam) Sample

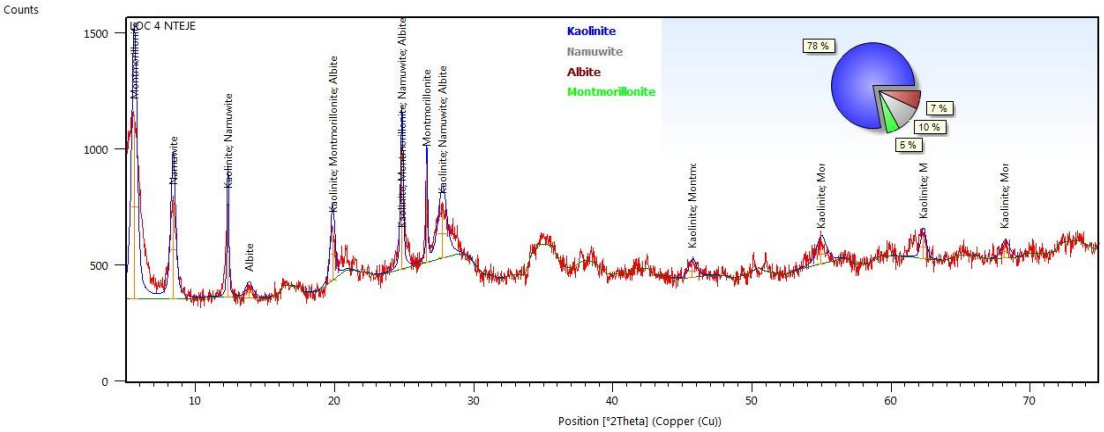


Fig. 5: X-Ray Diffractogram of L4 (Nteje) Sample

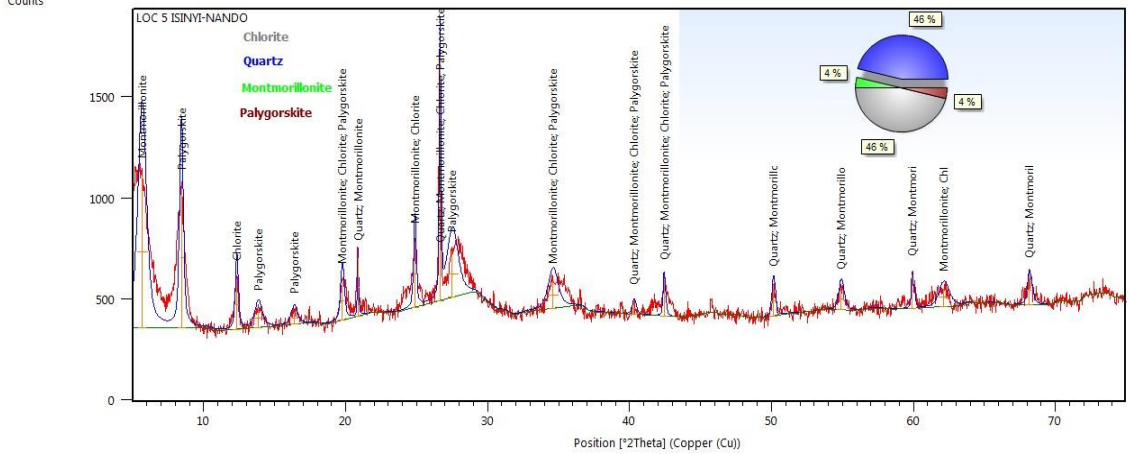


Fig. 6: X-Ray Diffractogram of L5 (Isinyi-Nando) Sample

Chemical Composition

This involves the major and trace constituents of the investigated clays as revealed by the XRF analysis. Tables 3 and 4 show the major and trace constituents of the clay samples analyzed.

Major elements

The major constituents (oxides) of the samples (in wt.%) include SiO_2 (60.15 – 67.25), $A1_2O_3$ (7.24 – 14.23),Fe_2O_3 (3.22 – 4.61), TiO_2 (0.47 – 0.91), MgO (1.57 – 6.59), CaO (1.62 – 2.87), Na_2O (0.32 – 2.14), K_2O (0.61 – 1.51) and MnO (0.03 – 0.30). When compared with the upper crust concentrations by Rudnick and Gao (2003), SiO_2 was higher in sample L1; TiO_2 higher in L1 and L4; MgO higher in L2, L4 and L5 and MnO higher in L2, L3, L4 and L5.

The SiO_2 content of the clays is in excess of 60 %, with other detected major constituents making up the remaining 40%. This implies that quartz is the major constituent element of the clay samples. The relatively low percentage of alumina (Al_2O_3) is probably related to the low feldspar in the deposit. The relatively low Fe_2O_3 may be responsible for non-detection of iron oxide minerals (haematite or goethite) from the XRD analysis of the clays. The fairly low values of CaO, K_2O and Na_2O suggests a high degree of weathering under tropical conditions, from which the clay bodies were formed. It also indicates that the clays may probably be non-expandable/swelling, with low feldspar content. According to Olusola et al (2014), the composition suggests that the clay samples are hydrated siliceous aluminosilicates.The loss of ignition (LOI) which is a measure of organic matter content and other combustible fractions, chemically combined water and CO_2 have mean percentage of 14.74%. This low-moderate value could be attributed to the absence of carbonate rocks (Olusola et al, 2014).

Table 3: Results of XRF Analysis of (in weight % oxide) in comparison with published Upper Crust Concentrations (in weight % oxide)

Oxides (%)	**L1 (Enugwu-Agidi)**	**L2 (Enugwu-Agidi)**	**L3 (Igbariam)**	**L4 (Nteje)**	**L5 (Isinyi-Nando)**	**A**
SiO_2	67.25	63.73	66.06	60.15	63.17	66.62
$A1_2O_3$	8.24	7.24	8.30	14.23	5.19	15.40
Fe_2O_3	3.65	4.61	3.23	3.22	4.14	5.04
TiO_2	0.91	0.47	0.62	0.71	0.58	0.64
MgO	1.57	6.04	2.46	2.51	6.59	2.48
CaO	2.87	1.62	1.90	2.07	2.43	3.59
Na_2O	0.44	0.32	2.14	0.92	0.66	3.27
K_2O	0.98	0.61	1.24	1.51	0.83	2.80
MnO	0.03	0.24	0.11	0.23	0.30	0.10
LOI	14.06	15.12	13.94	14.45	16.11	

A: Rudnick and Gao (2003)

Trace elements

Heavy metals such as Zn, Cu, Pb, Hg, Co, Ni, As, Se, Cr, Cd and V recorded mean concentrations (ppm) of 169.23, 23.84, 20.10, 0.04, 3.58, 51.96, 4.57, 4.02, 72.52, 0.086 and 155.47 respectively, with maximum values of 321.11, 36.08, 24.1, 0.06, 5.41, 83.27, 5.20, 20.02, 106.20, 0.12 and 220.49 respectively. Comparison of concentrations of these heavy metals with the FAO/WHO general standard for contaminants and toxins in food and feed showed that zinc is higher in samples L2, L3 and L4; lead higher in all the samples; nickel higher in samples L2 and L5, arsenic higher in all the samples; chromium higher in all the samples and vanadium higher in all the samples. Copper, mercury, cobalt, selenium and cadmium all fall within the daily permissible limits (figs 7 to 17).

Zinc (Zn) is generally considered to be non-toxic, but can cause vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea, dizziness diarrhea and growth retardation of the unborn baby (Scherz and Kirchhoff, 2006). Lead (Pb) exposure can cause intelligence decline in children and cause cancer in adults (Wang et al., 2009). Nickel is an essential micronutrient mineral. It is a common trace element in multiple vitamins which increases iron absorption in blood and osteoporosis treatment. In large amounts, nickel can be carcinogenic, and may cause dermatitis, eczema, vertigo and dyspnoea to exposed human population. Chromium is a micronutrient essential for carbohydrate metabolism in animals, it is carcinogenic to the respiratory organs. (Ekosse and Jumbam, 2010). Arsenic is considered carcinogenic and is related mainly to lung, kidney, bladder, and skin disorders. High exposure to Vanadium can cause nausea, vomiting, abdominal pain and greenish discoloration of the tongue.

Table 4: Results of XRF Analysis of Trace Elements (in ppm) in comparison with FAO/WHO general standard for contaminants and toxins in food and feed (in ppm).

Element (ppm)	**L1 (Enugwu-Agidi)**	**L2 (Enugwu-Agidi)**	**L3 (Igbariam)**	**L4 (Nteje)**	**L5 (Isinyi-Nando)**	**B**
Zn	61.12	230.64.	164.66	321.11	68.55	99.4
Cu	16.03	36.08	20.18	29.64	17.26	73.3
Pb	24.1	19.22	13.29	24.08	19.82	0.3
Hg	0.06	0.02	0.05	0.02	0.03	0.1
Co	5.41	4.86	3.39	2.41	1.81	50
Ni	36.41	83.27	34.63	29.00	76.51	67.9
As	5.11	4.51	5.20	4.62	3.42	0.5
Se	0.01	0.01	20.02	<0.01	0.03	27
Cr	64.22	106.20	56.45	43.71	92.04	2.3
Cd	0.06	0.09	0.07	0.09	0.12	0.2
V	158.4	122.48	220.49	196.42	79.58	0.5

B: FAO/WHO general standard for contaminants in food and feed.

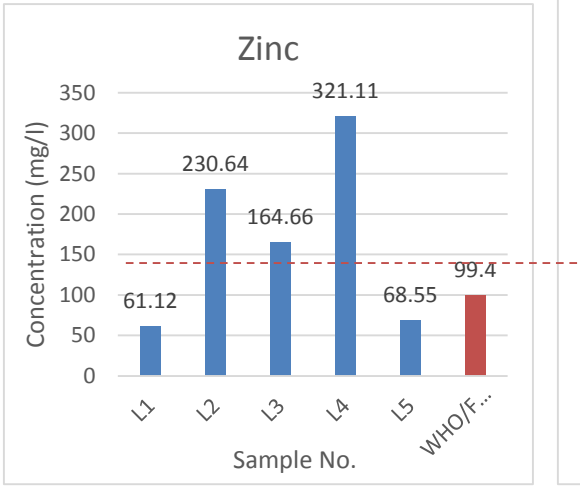


Fig. 7: Comparing Zn values with FAO/WHO

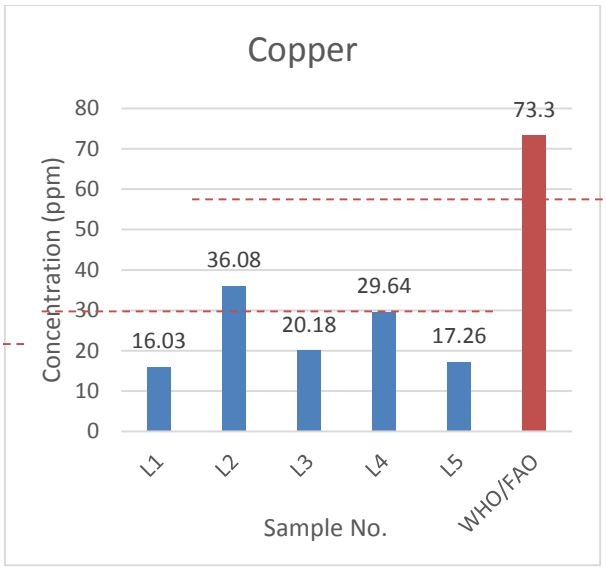


Fig. 8: Comparing Cu valueswith FAO/WHO

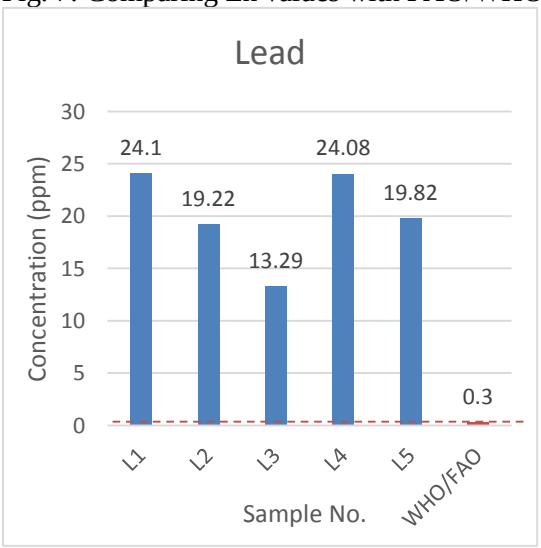


Fig. 9: Comparing Pbvalues with FAO/WHO

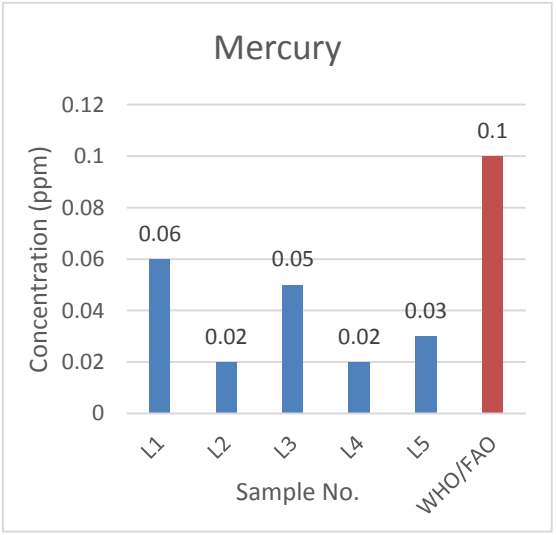
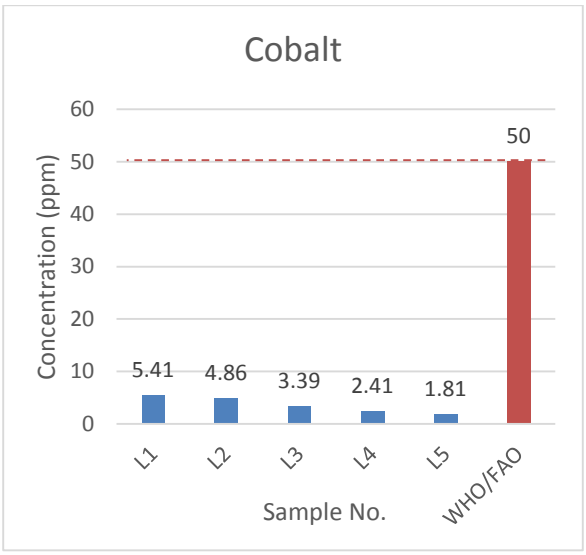


Fig.10: Comparing Hg values with FAO/WHO



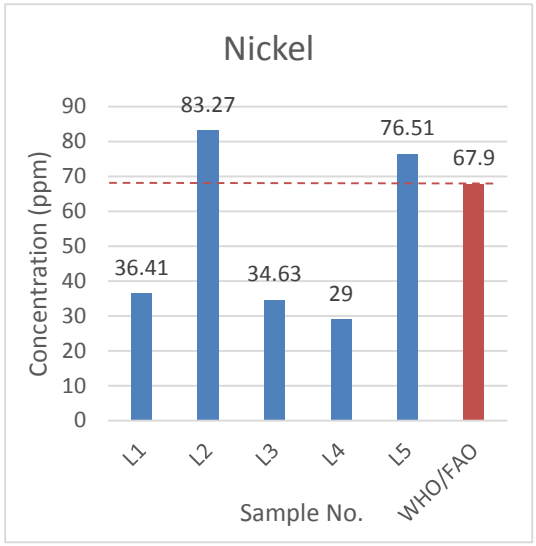
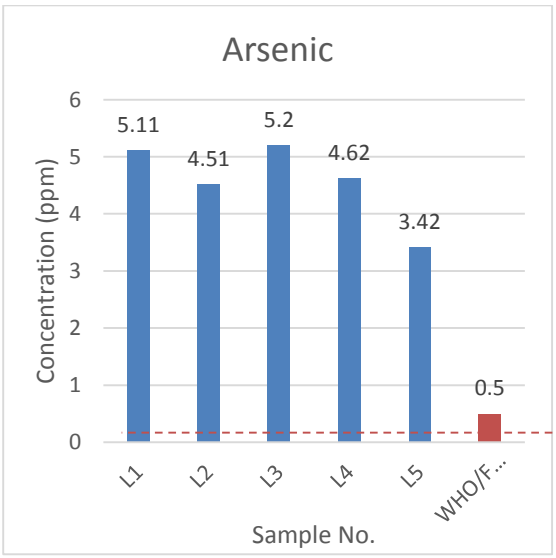


Fig. 11: Comparing Co values with FAO/WHOFig. 12: Comparing Ni values with FAO/WHO



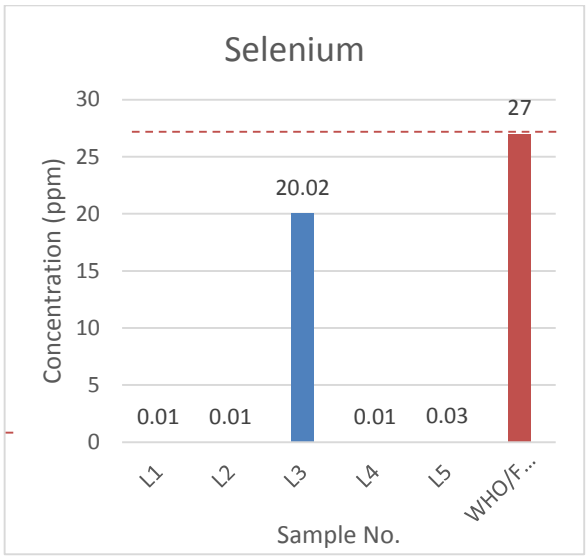
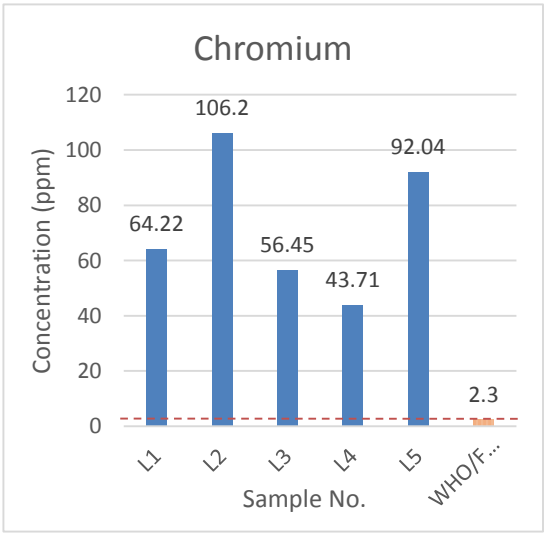


Fig. 13: Comparing As values with FAO/WHO Fig. 14: Comparing Se values with FAO/WHO



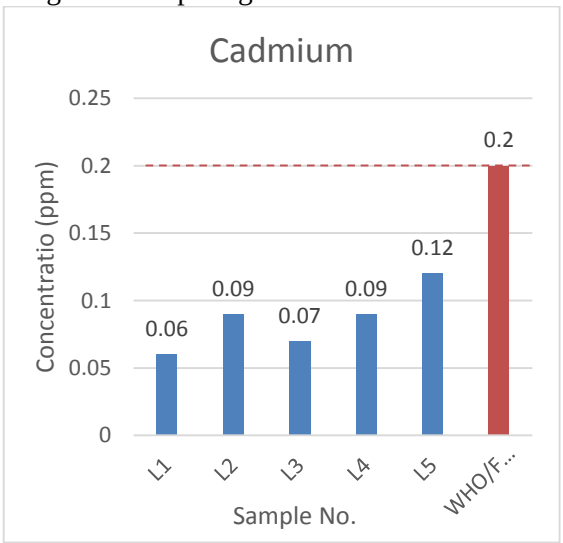


Fig. 15: Comparing Cr values with FAO/WHO Fig. 16: Comparing Cd values with FAO/WHO

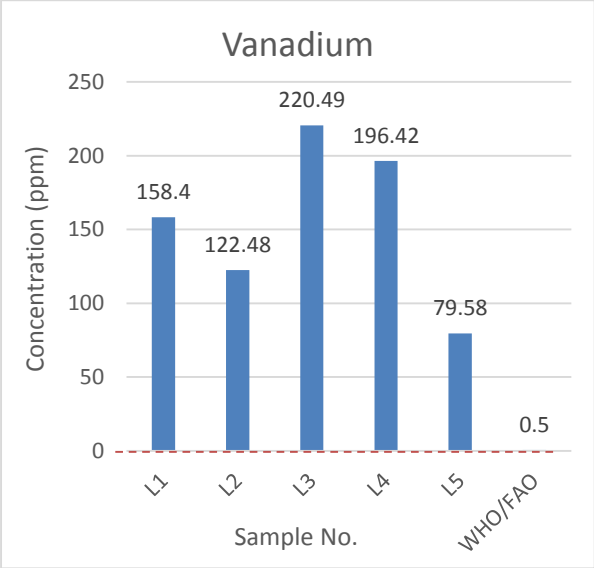


Fig. 17: Comparing V values with FAO/WHO

The degrees of contamination (Igeo) of these clays show that the values of these elements are less than 1 in most samples (Table 5). This shows that majority of the clays are unpolluted to moderately polluted (fig. 18). However, the clay from Igbariam (sample L3), showed the Igeo values of Selenium to be 44.64, which implies that it is extremely polluted and further consumption of clays from this area should be discouraged. High amounts of selenium in the human body can lead to bad breath, fever, nausea and in extreme cases - liver, kidney and heart problems (WebMD 2023).

Table 5: Calculated Index of Geoaccummulation Values for the Study Area

I_{geo}	Zn	Cu	Pb	Hg	Co	Ni	As	Se	Cr	Cd	V
L1	0.18	0.11	0.28	0.24	0.06	0.16	0.21	0.02	0.14	0.13	0.33
L2	0.69	0.26	0.23	0.08	0.06	0.36	0.19	0.02	0.23	0.20	0.25
L3	0.49	0.14	0.16	0.20	0.04	0.15	0.22	44.64	0.12	0.16	0.46
L4	0.96	0.21	0.28	0.08	0.03	0.12	0.19	<0.02	0.10	0.20	0.41
L5	0.21	0.12	0.23	0.12	0.02	0.33	0.14	0.07	0.20	0.27	0.16

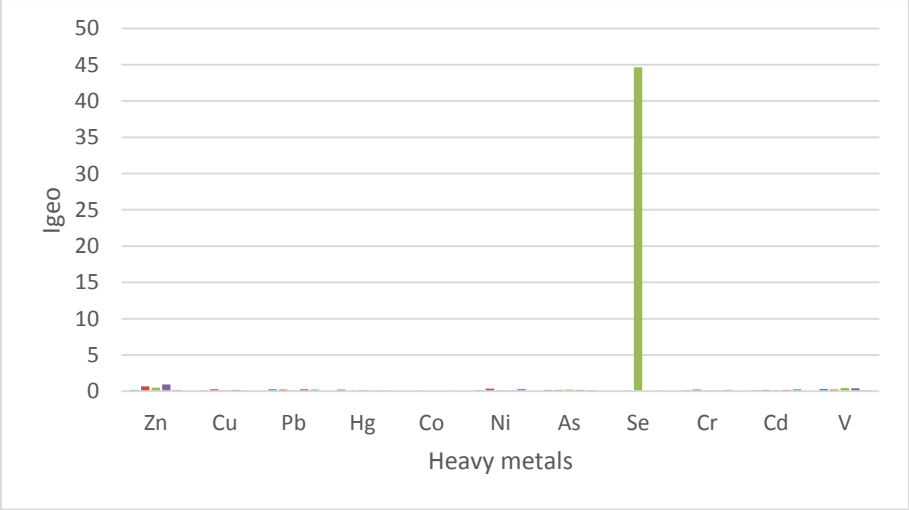


Fig. 18: Igeo values of heavy metals in the study area

Conclusion

This study has established the mineralogical and chemical compositions of geophagic clays fromparts of Anambra State, Nigeria, through XRD and XRF analysis. The XRD revealed kaolinite, chlorite, namuwite, kupletskite, montmorillonite, palygorskite and phlogopite as the clay minerals present in the geophagic clay samples in the study area. XRF revealed selected elemental compositions of the clay samples, which were classified under major and trace elements. When compared, some of the major oxides (SiO_2, TiO_2, MgO, MnO) present in the samples were above the upper crust concentration values (in ppm) given by Rudnick and Gao (2003). Some of the trace elements (Zn, Pb, Ni, As, Cr, V) were equally higher than the joint FAO/WHO maximum daily permissible limits for ingestion of heavy metals in food and vegetables. The degree of contamination (Igeo) of these clays, using crustal abundance values, show that they are not polluted at the moment, except at Igbariam, which is extremely polluted by selenium. Though consumption of these clays may not be of serious health concerns at the moment, continued contamination from natural and anthropogenic sources may increase the risks associated with their consumption. Remediation may require more than the usual firing, which merely removes moisture and organic impurities. Consumption of edible clays from Enugwu-Agidi, Igbariam, Nteje and Nando mining sites should be discouraged untilan adequate remediation techniqueis available.

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