Mineralogical Profile of Geophagic Clayey Soils Sold in Selected South African Informal Markets

Okereafor G. Uchenna, Mavumengwana Vuyo and Mulaba-Bafubiandi F. Antoine

Abstract— Geophagia, the intentional ingestion of clavey soil has both useful and negative health effects on humans due to the biomass, physicochemical, mineralogical and geochemical composition of the gritty material. In a few circumstances, clayey soil is viewed as a supplement to health deficiencies resulting from a less than stellar eating routine. Geophagy has been of interest to researchers and analysts due to continued habitual, religious and cultural practices by diverse communities globally in spite of reports contraindicating its purported benefits. The gritty material remains a thing of interest considering the nature in which they are obtained, transported and stored. Six geophagic clayey soil samples were obtained from chosen casual markets in South Africa. Four of these samples were originally from around South Africa and two were originally from Nigeria. The samples were analysed and characterised utilizing XRF, XRD, pH, and electrical conductivity to survey the nutritious qualities that support the continued use by mostly females and pregnant ladies in various parts of South Africa. Results of the XRD analysis revealed that the clay materials were mainly composed of kaolinite with minor palygorskite, illite, Amesite, Gupeite, Hematite and Magnetite. Quartz was the major non-clay constituent identified. Results of the XRF analysis showed average values of major elements such as SiO2 (54.02%), Al₂O₃ (35.45%), Fe₂O₃ (6.73%), K₂O (2.76%), MgO (1.16%) with MnO, Na₂O and P₂O₅ falling below 0.5%. Titanium was a major heavy metal identified from the samples which may result in heavy metal toxicity. The potential medicinal application of these clayey soils is supported by their kaolinite contents; in contrast the trace elements are pointers of probable adverse effects on humans.

Index Terms — Clayey soils, Geophagy, Kaolinite, Mineralogy, Quartz.

I. INTRODUCTION

Clay is a naturally occurring material composed of fine-grained minerals, which are for the most part plastic at proper water contents and solidifies when dried or fired [1]. Clay possess varying chemical components depending on their physical and geographical occurrence. Characteristic clay minerals are well known to humanity from time immemorial. As a result of their affordability, abundance in diverse regions of the globe, high sorption potential for ion exchange, clay

Manuscript received August 26, 2016.

- G. U. Okereafor is with the Department of Metallurgy, University of Johannesburg P.O Box 17011 Doornfontein 2028, Johannesburg, South Africa.
- A. F. Mulaba-Bafubiandi is with the Mineral Processing and Technology Research Centre, Department of Metallurgy, School of Mining, Metallurgy and Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg P.O Box 17011 Doornfontein 2028, Johannesburg, South Africa
- V. Mavumengwana is with the Department of Biotechnology and Food Technology, Faculty of Science, University of Johannesburg P.O Box 17011 Doornfontein 2028, Johannesburg, South Africa.

minerals are applied as strong adsorbents [2].

Although clay minerals share an essential arrangement of structural and chemical characteristics, each clay mineral has its own unique properties that decide how it will associate with other synthetic species. The variation in both chemistry and structure, among the different clays prompt their applications in different fields. Often time clay minerals are classified by the differences in their layered structures. Some of the classes of clay include smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, talc, vermiculite and sepiolite [3].

Clay is principally made up of silica, alumina and water, oftentimes with considerable amounts of iron, alkalies and alkali earths [4]. Basically, there are two structural units when looking at the atomic lattices of several clay minerals; one unit comprises of firmly pressed oxygen and hydroxyls in which aluminum, iron and magnesium atoms are inserted in an octahedral mix with the goal that they are equidistant from six oxygen or hydroxyls. The second unit is made of silica tetrahedrons that are orchestrated to shape a hexagonal system that is rehashed to form $Si_4O_6(OH)_4$ [4].

Previously, geophagy used to be peculiar amongst pregnant women and children in rural communities in African countries but recently it is gaining a global adoption. The implications of consuming geophagic clays in respect to their heavy metal content are still being studied. From the South African context, efforts had been made regarding geophagy as documented in the studies of [5], [6], [7], [8], [9], [10], [11] and [12], all pointing that geophagy is prevalent within the various provinces within the country. Most of the geophagists' particularly pregnant women supported their practice on several factors, some of which include natural craving to alleviate early morning illness, reducing the threat of infection as well as the assurance of the quality and quantity of breast milk for their unborn child [13]. Further claims include its potential to agitate appetite and curb vomiting during pregnancy.

Emphatically speaking, no explanation can basically substantiate the practice of geophagy as it has great benefits as well as adverse implications. Previous studies reveal that humans and some animals engage in geophagy due to certain nutrient deficiency [14] and in some instances, in response to gastrointestinal disorders. [15]. Human geophagy is a global phenomenon that is seen amongst all races, ages, sexes, and social classes [16]. With immigrants and cross border trades amongst nations, geophagic clayey soils are sold in open markets in South Africa, rural dwellings in America, Asia and Europe [17]. Most geophagic clayey soils are highly retentive due to their fine-grained sizes, thus absorbing metal ions into their crystal lattices. The concentration levels of these elements

determine their usefulness or harm when consumed by humans.

Several techniques such as scanning electron microscope, X-ray diffraction and infrared spectrometry, atomic absorption spectroscopy were used in identifying the specific clay minerals. The principal aim of the study is to determine both the physical and chemical makeup of various geophagic clays sold in different informal markets within South Africa irrespective of their sources with the goal of ascertaining their suitability for human consumption.

II. EXPERIMENTAL METHODS

A. Materials

The clay samples were obtained from selected informal open markets within South Africa as indicated in Table 1. The six representative samples were used as received from the vendors at the markets without any form of modification. To further enhance the surface area of the clayey soils, the samples were ground using mortar and pestle. Physical characterization of the various samples was analysed using standard methods as proposed by [18]. The samples were digested prior to chemical characterization by Atomic Absorption Spectrophotometer (AAS).

B. Digestion of Clay Samples

2g of the various samples were weighed into a Teflon crucible and moistened with 100mL of 0.5M, 1M and 2M HCl acid. The mixtures were covered and placed on a shaker for 24 hours at 130rpm. The solutions were filtered and the filtrates were stored in sterile bottles prior to being analysed for minerals using AAS.

C. Loss of Ignition

10g of each clay sample was weighed and put into a crucible before being transferred into a furnace at 1000°C for 3hours. The representative fractions were then allowed to cool in a desiccator and re-weighed. Weight lost is the loss due to ignition, usually expressed as:

 $LOI = \frac{\text{Weight loss x } 100}{\text{Weight of initial sample}}$

D. Determination of Oxides Using XRF

10g of the clay sample were pelletised using a mould at very high pressure and then placed in the sample compartment of X-ray fluorescence (XRF; Rigaku ZSX PrismusII). This was to analyse the elemental compositions of the various minerals that make up the clay.

E. Determination of The Mineral Phases Using XRD

The XRD patterns of clay were obtained on a powder X-ray Diffractometer Model Rigaku Ultima IV with $\text{CuK}\alpha$ radiation (40kV and 40mA) having a scanning speed of $0.04^{\circ}/\text{s}$. This was done at the Extractive Metallurgy Laboratory of the University of Johannesburg. The XRD aided the determination of the mineralogical composition of the material components and also qualitative and quantitative phase analysis of multiphase mixtures as described by [19]. Representative bulk samples were crushed and homogenized to fine powder at approximately $10\text{-}15\mu\text{m}$ in size. Each reflection as displayed by the X-Ray diffraction corresponds to particular mineral. With the peaks

well separated from each other, their heights are applied in the determination of the orientation of certain mineral in the mixture. The basis of clay mineral analysis by X-Ray diffraction is centred on the identification of various peaks and comparison of their relative heights. Different phase levels were identified as semi quantitative estimates based on the relative peak heights [20]. The wavelength of 1.5406 was used to calculate the diffraction angles.

F. Determination of Trace Elements Using Atomic Absorption Spectrophotometer (AAS)

The filterate from the digestion of the clay samples was analysed for elemental quantitative analysis using AAS (Win Lab32). Each metal with the exception of Si and Al that required nitrous oxide flame were analysed using air acetylene flame and deionized water as blank.

III. RESULTS AND DISCUSSION

Physico-Chemical Characterization of Geophagic Clays

The physico-chemical characteristics of the studied geophagic clayey soils which provide information on their benefits and possible deleterious effects are summarized in Tables 1 and 2. Colours ranged from yellowish orange through brownish yellow to brownish grey. The greyish colour may be attributed to the presence of finely disseminated organic matter while, the yellowish to brownish colour could be linked to the presence of iron oxides or from mixing of green clay minerals and organic matter. Clayey soil pH was in the range of 4.47 to 6.36 with an average of 5.54. Considering all six samples, GSA 1 registered the highest pH while GNG 2 recorded the lowest 4.47. Electrical conductivity values ranged from 121.5 µS/cm to 1028.5μS/cm with a mean of 671.1μS/cm. With respect to the loss of ignition (LOI) all four samples originally from South Africa (GSA 1-4) showed higher values compared to samples originally from Nigeria. There were notable textural differences, with GNG1 and GNG2 samples being sandy, whereas samples GSA 1-4 were more clayey. The latter appeared to consist of weathered shale or clay, while GNG1 and GNG2 probably represented alluvial sandy material.

TABLE I
PHYSICAL CHARACTERIZATION OF GEOPHAGIC CLAY SAMPLES

Sample Code	pH (H ₂ O)	LOI %	Electrical Conductivity
GSA 1	6.36	0.27	1028.50 μS/cm
GSA 2	5.76	0.63	908.50 μS/cm
GSA 3	5.73	0.34	822.00 μS/cm
GSA 4	6.26	0.24	974.50 μS/cm
GNG 1	4.67	0.23	121.5 μS/cm
GNG 2	4.47	0.17	171.6 μS/cm

GSA 1-4 (Clay samples originally from South Africa obtained from informal markets: Midrand, Johannesburg CBD, Limpopo, Soweto respectively), GNG 1 & 2 (Clay samples obtained from Johannesburg CBD, originally from Nigeria)

TABLE II

COLOUR AND MACROSCOPIC DESCRIPTION OF 6 GEOPHAGIC SAMPLES FROM INFORMAL MARKETS

Sample	(Hue value chroma)	Colour	Description
GSA 1	10YR6/6	Dark Yellowish Orange	Clayey sand; disperses easily but does not slake.
GSA 2	10YR8/6	Pale Yellowish Orange	Coarse blocky material, soft and decomposed; strongly variegated and patchy in color; Clayey/silty texture.
GSA3	10YR4/2	Dark Yellowish Brown	Coarse platy structure; weathered shale; clayey; dispecses easily but does not slake immediately.
GSA4	10YR4/2	Dark Yellowish Brown	Coarse platy structure; weathered shale; clayey; dispecses easily but does not slake immediately.
GNG 1	5Y5/4	Reddish Brown	Coarse blocky structure; sandy texture; contains fragments of carbonized wood; slakes immediately in water.
GNG 2	2.5Y6/2	Light Brownish Grey	Sandy material containing white inclusions and organic matter; slakes immediately in water.

TABLE III
TRACE ELEMENT COMPOSITION OF GEOPHAGIC CLAYEY SOILS.

Trace Element	GSA1 mg/L	OSA2 mg/L	GSA3 mg/L	GSA4 mg/L	GNG1 mg/L	GNG1 mg L
Cu	0.26	0.21	0.20	0.17	0.15	0.16
Pb	0.20	0.24	0.26	0.18	0.18	0.09
Zn	0.33	0.33	0.21	0.56	0.09	0.29
Fe	81.37	63.53	37.82	39.08	5.18	1.66
Co	0.13	0.09	0.05	0.05	-0.01	0.00
Mn	6.05	6.54	5.68	5.14	1,23	1.24
Cr	0.01	0.12	0.07	0.04	0.00	0.00

IV. DISCUSSION

Colour

Colour as a physical property of clayey soils aid in describing specific characteristics, such as mineralogical composition, age and soil processes (chemical alteration, carbonate accumulation, the presence of humified organic matter, etc.). The colour and texture of the clay often have an influence on the type of soil being consumed by the geophagists [21]. White clay is mainly made up of kaolin; while yellowish and reddish clays are composed of iron, which could be a source of iron supplement [22]. However, most geophagic soils contain mainly ferrous-oxide iron which apparently is not easily absorbed by the body [6].

With the aid of a Munsell colour chat, the predominant form of iron oxide in clays could be easily determined. Thus, a deep red (5YR) on a Munsell colour chat is indicative of soils whose iron oxide mineral is hematite (Fe₂O₃), while soils having goethite [FeO(OH)] as the main iron oxide mineral are brown (2.5YR-7.5YR).yellowish Soils containing lepidocrocite, another form of iron oxyhydroxide, are a distinctive orange colour (7.5YR) [23, 24]. A previous study asserted that inclination for reddish or brownish soils is based on the supposition that such clays contain more iron [9]. In most cases, iron in heam form (Fe2+) is readily absorbed by the body unlike the non-heam form (Fe3+), with best possible uptake occurring in the duodenum [25].

The colour (hue values) of the geophagic soils ranged from yellowish (10YR) to brownish with samples GSA 1-4 being

yellowish brown suggesting the presence of Magnetite, Hematite or goethite FeO(OH) while NGN1 and NGN2 were brownish grey in appearance which could infer the presence of oxidized Fe3+ and Mn4+. The consumption of the clays for iron supplementation may be acceptable to some extent [6, 26]. Nevertheless, it is important to note that the reddish or yellowish shade of clays could be used to deduce the presence of Fe but not its quantity or bioavailability [9]. The study of [27] in Cameroon supports the consumption of samples GSA 1-4 as most brownish or reddish clays have more palatable earthy aroma that emanates from them usually after very light showers of rain, and they are less sticky.

TEXTURE

Based on previous studies, the attitude of most geophagists towards the "feel" of clay they consume revealed a preference for clays that leaves little or no undesirable sensation in the mouth [28]. Textural analyses results revealed that the soil samples were texturally dominated by clay size particle with some silt and very fine sand particles. Based on these outcomes, it suggests that the geophagic soil samples possess high surface area, which allows them to adsorb much more water; since adsorption is a function of surface area. This property therefore supports the medicinal hypotheses as they tend to curtail diarrhea and other gastrointestinal ailments.

Consumers of geophagic clays prefer those that are soft, silky and granular. Samples GNG 1 and 2 when compared to samples GSA 1-4 will not suit the pleasure of the individual due to the feel of coarseness and sand grains [27]. Geophagic clays that are gritty comprise of silt and fine sand particles of quartz and feldspars which may destroy dental enamels of an individual (via grinding, cracking, splitting and breakage during mastication); because quartz (harness 7) scratches the dental enamel, which is the main inorganic component of the human tooth and dominated by hydroxyl apatite (Ca₅(PO₄)₃(OH), (a calcium phosphate mineral), of hardness 5 on the Mohr's scale. Previous studies indicated medium sized sand (250-500 µm) to have severe dental damage in hominid species [9, 29]. Perforation of the sigmoid colon has been reported in some geophagic individuals [30]. Foreign bodies in the small intestines can cause perforation and the most important consideration of these bodies is the size, shape and nature of the object [31, 32].

pН

The taste of geophagic clays is largely influenced by their pH and dissolved salt contents. A more acidic soil generally, leaves a sour taste when consumed [33]. Women in Kenya and Nigeria ingest clay to control excessive secretion of saliva during pregnancy [34] and this application of geophagic clay during pregnancy could be linked to the sour taste of the clay [35].

The pH values of all the studied clay samples irrespective of their sources lie within the acidic to moderately acidic range as they were generally below 7, thus imparting a sour taste to the individual when consumed. The pH values of samples NGN1 and NGN2 conform to the studies of [33] based on their very strong acidic level. Hence, NGN 1 and 2 could be ingested to prevent excessive secretion of saliva as well as reduce nausea during pregnancy in women. Due to the acidity (pH = 2) of the gastric juice found within the stomach, there could be possible

chemical reactions involving clay minerals and organic matter in the geophagic clayey soil [36]. However, residence time of ingested material in the stomach, being approximately 2 hours, is insufficient for any significant reaction to occur.

With a pH of about 8 in the duodenal and intestinal section of the gastrointestinal tract (GIT) [36], notable chemical alterations may occur within some of the clay-size particles when consumed. However, with the silica dominated silt and sand-sized particles, alteration may not occur. These unaltered silt and sand-sized particles could seep through the GIT and possibly be stuck in the diverticulitis of the sigmoid colon, as was seen and reported in a boy after extended consumption of sandy material [37]. Due to the abrasive nature of these silica-rich particles, possible lacerations, and eventual rupturing of the colon may occur; (perforation of the sigmoid colon).

The solubility of Fe and other cations in the GIT increases with a decrease in pH [24]. With most of the studied clays being acidic, their ingestion has higher tendencies of preventing the stomach pH from falling to levels that are favorable for the dissolution of Fe thus reducing their bioavailability to the geophagic individual even when there is a high concentration of Fe in the ingested soil.

ELECTRICAL CONDUCTIVITY (EC)

The quantity of dissolved salts in soils could be determined based on electrical conductivity (EC) [38]. All the studied geophagic soil samples exhibited very high EC, indicating that the amount of dissolved salts contained in them is high. This is a possible pointer that the taste of the samples could in addition to pH have been influenced by the salt content. These higher values will result in the clays absorbing diarrhea-causing enterotoxins while also protecting the gastrointestinal epithelium. Studies conducted by [39], revealed that there is a relationship between flocculation, soil pH and salts. The flocculation of geophagic soil could influence their ability to coat and create a shield in intestinal mucosa thus protecting the intestines from the acidic gastric juice [40]. The observed high dissolved salts in the studied geophagic soil samples are however, likely to influence the degree of flocculation that may occur.

LOSS OF IGNITION (LOI)

The loss on ignition values is indicative that the clayey soil samples had lower carbonaceous matter and higher mineral matter contents. The degree of organic matter in the samples were basically low, inferring a low pathogen load, thus, the danger of bacterial infection including those like *Escherichia coli, Entamoeba histolytica*, and helminthes infection such as those of *Ascaris lumbricoides* and *Strongyloides stercoralis* as a result of consuming the clays is slim. Nutrient scarcity due to low organic matter will result in diarrhea-causing pathogen not surviving.

From a toxicity or nutritional stand point, not all trace elements analyzed are of biological significance, but were all reported for the sake of completeness. Trace elements of interest based on human nutrition, Copper (Cu), Manganese (Mn), Lead (Pb) and Zinc (Zn), were in varying compositions ranging from moderate to high when compared with the usual range in mineral soils. The same is true of trace elements such as Chromium (Cr) and Pb, which are often linked with toxicity.

The level of Zn was highest in GSA4 with 0.56 ppm and lowest in sample from Nigeria – GNG1 with 0.09 ppm. The level of Cu, Pb and Mn were lower than the values found for mineral soils as reported by [41]. The amount of Pb in all the samples exceeded the recommended EPA (Environmental Protection Agency) standard levels of about 0.01 mg/L.

Results of major element analysis (Table 3.) revealed that the average SiO_2 values ranged from 49.77% - 61.67% with the GNG 1 samples recording the highest value while GSA 1 and GSA 2 both shared lowest value. Mean Al_2O_3 values also ranged from 31.02% in the GNG 2 samples to 33.55% in both GSA 1 and 2 samples respectively. GNG 2 showed the lowest Fe_2O_3 content of 1.90% while GSA 4 had the highest of 8.32%. CaO concentrations in all the samples were less than 0.4%. Average TiO_2 values were in the range of 0.69% - 1.72%. On the other hand NGN 1 and 2 both showed lower concentrations of K_2O with GSA 4 having the highest of 4.27%. Na_2O content was highest (1.28%) in GNG 2 samples. There were trace amounts of both MgO and K_2O in the clays.

PHYSICO-CHEMICAL CHARACTERIZATION

Lower amount of MgO and K_2O in the samples may point to lack of expandable clays [42]. The various concentrations are indicative that the clays are hydrated siliceous aluminosilicate. From the investigations, most of the oxides infer that bulks of the samples were containing more of Silica oxide and alumina with other minerals occurring in trace amounts. The relatively high Fe_2O_3 could be attributed to superficial oxidation while the low concentrations of Ti in the various clays may result in the inability to mineralize into neither anatase nor rutile. The TiO_2 in the sampled clays have the tendencies of occurring as free Ti-oxides [43]. In the octahedral sheet of kaolinite, some Ti may have substituted for Al since no Al_{3+} substitution in the tetrahedral sheet would take place due to the Al_2O_3 values in the clays (31.02 - 33.55 wt.%) being below that of pure kaolinite which is 39.49 wt.% [44].

The concentrations of aluminum within the studied samples were in the range of (16.42 – 17.75 wt. %), whereas a daily recommended values for Aluminium is 0.03pmm [45]. The amount of major oxides such as Fe₂O₃, TiO₂ and MnO exceed the required values for human body function. The samples originally from South Africa (GSA1-4), however, were more iron-rich than any of the samples, with ferric oxide ranging from 8.32 to 9.46%. There is a strong likelihood of the geophagic clays introducing heavy metals such as Fe, Zn, Pb, Cu, Titanium (Ti) and Mn in the gastro-intestinal system of the geophagists. This might impact negatively on the consumer by increasing the pH of the gastro-intestinal tract [46].

Pregnant women from the city of Johannesburg may suffer from liver damage due to high concentration of iron in all the studied samples. Despite Fe providing supplement for those who lack iron in their blood, a high level of Fe in the blood could result in hemochromatosis and possible death [45]. Besides, the consumption of iron rich lateric soils may influence negatively on the utilization of copper, zinc and selenium in the body [47].

The highest concentration of Cr was recorded in sample GSA2 as shown in Table 4 (0.12mg/L) which is above the World Health Organization (WHO) recommended value of

0.05ppm [45]. Chromium has been reported to be responsible for lung cancer and death [48].

Sample GSA3 had the highest concentration of Pb with 0.26mg/L while GNG2 had the lowest concentration of 0.09mg/L. Daily recommended value for lead (Pb) is 0.01ppm [45]. The presence of Pb in the samples poses a problem as there is no prescribed limit for its consumption due to its extreme toxic nature. Previous study revealed that exposure to Lead may cause intelligence decline in children and as well as cancer in adults [49]. Consumption of these clayey samples over a long time may result in serious health effects such as coma, seizure, the dysfunctioning of the kidney, liver and heart of the consumers [50]. Lead targets multiple organs in the human body due to its systemic toxicity which can lead to cardiovascular, renal, gastro-intestinal and haematological effects [50]. Neurotoxicity, carcinogenicity and reproductive failures in adults are some of the effects of exposure to Lead (Pb) as contained in the data from the European Food Safety Authority (EFSA) [51].

Zinc (Zn) concentration in the studied samples was highest in sample GSA4 with 0.56mg/L Zn in the clay. A minimal concentration of 0.29mg/L was observed in sample GNG2. Having a recommended value for Zinc (Zn) as 0.01 [45], excessive consumption of these clays may lead to unusual drowsiness, nausea/vomiting, diarrhea and growth retardation of an unborn baby [52]. Zinc plays a vital role in cellular metabolism and is a major component of body tissues and fluids [53]. Most catalytic activities of enzymes require Zinc. Also, it is required during immune function, wound healing, protein synthesis, DNA synthesis and cell division. Zinc ions are effective antimicrobial agents even at low concentrations [54]. Zinc is required for proper sense of taste and smell and supports normal growth and development during pregnancy, childhood, and adolescence [55]. There are claims of Zinc having antioxidant properties, which may protect against accelerated aging and helps speed up the healing process after an injury; however, studies differ as to its effectiveness [54].

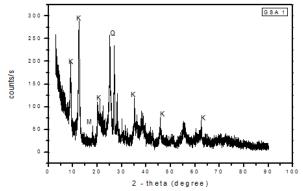


Fig1 X-ray diffractogram of geophagic soil (GSA1) indicating mineral peaks (Note: K = Kaolinite, Q = Quartz, M = Muscovite)

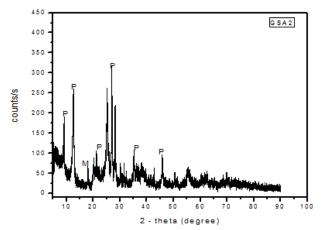


Fig. 2 X-ray diffractogram of geophagic soil (GSA2) indicating mineral peaks (Note: P = Plagioclase M = Muscovite)

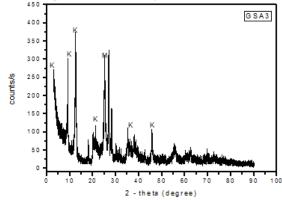


Fig.3: X-ray diffractogram of geophagic soil (GSA3) indicating mineral peaks (Note: K =Kaolinite M = Muscovite)

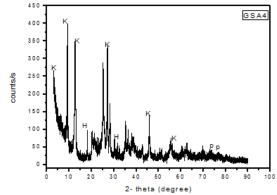


Fig 4 X-ray diffractogram of geophagic soil (GSA4) indicating mineral peaks (Note: K=Kaolinite H=Hypothetical silica p= Pseudobrookite)

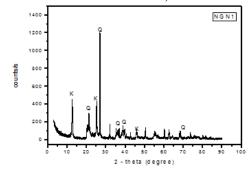


Fig. 5 X-ray diffractogram of geophagic soil (GNG1) indicating mineral peak (Note: K = Kaolinite Q = Quartz)

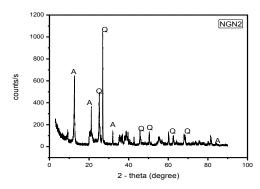


Fig. 6 X-ray diffractogram of geophagic soil (GNG2) indicating mineral peaks (Note: A = Amesite Q = Quartz)

There was a degree of consistency from the results of the bulk chemical analysis with those of the mineral analyses of the bulk soils (Table 5). The identification of minerals based on diagnostic peaks was aided by the International Centre for Diffraction Data (ICDD) reference numbers and the crystals system, d-values, and peak intensity of the various minerals. The X- Ray diffraction analysis of the different geophagic clays revealed Kaolinite as the major clay mineral alongside muscovite, Amesite and Fayalite.

Quartz was the major non-clay mineral identified. With the high quartz content in the clays, a possible formation of kaolinite could have been via the alteration of feldspathic sandstones rich in quartz [7]. The significant level of quartz in the soils may pose a threat to the health of the geophagic individual. This is because quartz is harder than dental enamel which could be easily destroyed during mastication of clays. Another problem linked with the quartz is that when ingested, it passes through the gastrointestinal tract unaltered and get deposited in the colon. Due to the abrasive nature of the materials, laceration or rupturing of the colon may occur thus leading to perforation.

V. CONCLUSION

This study has established the chemical and mineralogical compositions of geophagic clayey soils sold in selected South African informal markets. XRD results of the analysis established that the clay materials are mainly composed of kaolinite with minor palygorskite, illite, Amesite, Gupeite, Hematite and Magnetite. Quartz was the major non-clay constituent identified which poses a threat to human dental enamel. Titanium was a major heavy metal identified from the samples which may result in heavy metal toxicity. The oxidation state of the iron which was 3 indicates that the iron and aluminium are major components of the clay matrix. Excessive consumption of these clays will result in constipation. Nevertheless, the potential medicinal application of these clayey soils is supported by the kaolinite contents, magnesium, potassium etc. in contrast; the trace elements are pointers of probable adverse effects on humans.

ACKNOWLEDGMENT

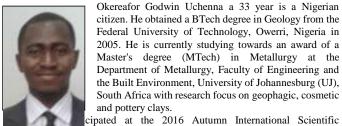
The authors thank the University of Johannesburg for providing facilities used for the XRD, XRF and AAS analysis.

REFERENCES

- P. S. Nayak and B. Singh, "Instrumental characterization of clay by XRF, XRD and FTIR," *Bulletin of Materials Science*, vol. 30, pp. 235-238, 2007
 - https://doi.org/10.1007/s12034-007-0042-5.
- [2] S. Guggenheim and R. Martin, "Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees," *Clays and clay minerals*, vol. 43, pp. 255-256, 1995. https://doi.org/10.1346/CCMN.1995.0430213
- [3] R. E. Grim, "Clay mineralogy: New York," New York: McGrawHill Book Company, 1968.
- [4] T. Shichi and K. Takagi, "Clay minerals as photochemical reaction fields," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 1, pp. 113-130, 2000. https://doi.org/10.1016/S1389-5567(00)00008-3
- [5] E. G.-I. Ekosse and N. D. Jumbam, "Geophagic clays: Their mineralogy, chemistry and possible human health effects," *African Journal of Biotechnology*, vol. 9, pp. 6755-6767, 2010.
- [6] L. Mogongoa, C. Brand, L. De Jager, and G. Ekosse, "Haematological and iron status of Qwa Qwa women in South Africa who ingest clays," *Medical Technology SA*, vol. 25, pp. 33-37, 2011.
- [7] G. E. Ekosse, L. De Jager, and V. Ngole, "Traditional mining and mineralogy of geophagic clays from Limpopo and Free State provinces, South Africa," *African Journal of Biotechnology*, vol. 9, pp. 8058-8067, 2010.
 - https://doi.org/10.5897/AJB10.296
- [8] S. F. Mpuchane, G.-I. E. Ekosse, B. A. Gashe, I. Morobe, and S. H. Coetzee, "Microbiological characterisation of southern African medicinal and cosmetic clays," *International journal of environmental health research*, vol. 20, pp. 27-41, 2010. https://doi.org/10.1080/09603120903254025
- [9] V. Ngole, G. Ekosse, L. De Jager, and S. Songca, "Physicochemical characteristics of geophagic clayey soils from South Africa and Swaziland," *African Journal of Biotechnology*, vol. 9, 2010.
- [10] V. Ngole and G. Ekosse, "Physico-chemistry, mineralogy, geochemistry and nutrient bioaccessibility of geophagic soils from Eastern Cape, South Africa," *Scientific Research and Essays*, vol. 7, pp. 1319-1331, 2012. https://doi.org/10.5897/SRE11.1556
- [11] E. Saathoff, A. Olsen, J. D. Kvalsvig, and P. W. Geissler, "Geophagy and its association with geohelminth infection in rural schoolchildren from northern KwaZulu-Natal, South Africa," *Transactions of the Royal Society of Tropical Medicine and Hygiene*, vol. 96, pp. 485-490, 2002. https://doi.org/10.1016/S0035-9203(02)90413-X
- [12] S. Songca, V. Ngole, G. Ekosse, and L. De Jager, "Demographic characteristics associated with consumption of geophagic clays among ethnic groups in the Free State and Limpopo provinces," *Indilinga:* African Journal of Indigenous Knowledge Systems, vol. 9, pp. 110-123, 2010.
- [13] T. Johns and M. Duquette, "Detoxification and mineral supplementation as functions of geophagy," *The American journal of clinical nutrition*, vol. 53, pp. 448-456, 1991.
- [14] S. L. Young, "Pica in pregnancy: new ideas about an old condition," Annual Review of Nutrition, vol. 30, pp. 403-422, 2010. https://doi.org/10.1146/annurev.nutr.012809.104713
- [15] D. Mitchell, W. Winter, and C. M. Morisaki, "Conditioned taste aversions accompanied by geophagia: evidence for the occurrence of" psychological" factors in the etiology of pica," *Psychosomatic medicine*, vol. 39, pp. 402-412, 1977. https://doi.org/10.1097/00006842-197711000-00004
- [16] J. M. Hunter, "Macroterme geophagy and pregnancy clays in southern Africa," *Journal of Cultural Geography*, vol. 14, pp. 69-92, 1993. https://doi.org/10.1080/08873639309478381
- [17] L. Crawford and K. Bodkin, "Health and social impacts of geophagy in Panama," MSURJ, vol. 6, pp. 31-37, 2011.

- [18] D. Nwosu, P. Ejikeme, and M. Ejikeme Ebere, "Physio-Chemical Characterization of 'NGWO'White Clay for Industrial Use," *Int J Multi Sci Eng*, vol. 4, pp. 11-14, 2013.
- [19] D. M. Moore and R. C. Reynolds, X-ray Diffraction and the Identification and Analysis of Clay Minerals vol. 378: Oxford university press Oxford, 1989.
- [20] C. Brime, "The accuracy of X-ray diffraction methods for determining mineral mixtures," *Mineralogical Magazine*, vol. 49, pp. 531-538, 1985. https://doi.org/10.1180/minmag.1985.049.353.06
- [21] C. Reilly and J. Henry, "Geophagia: why do humans consume soil?," Nutrition Bulletin, vol. 25, pp. 141-144, 2000. https://doi.org/10.1046/j.1467-3010.2000.00032.x
- [22] P. W. Abrahams and J. A. Parsons, "Geophagy in the tropics: An appraisal of three geophagical materials," *Environmental Geochemistry* and Health, vol. 19, pp. 0-0, 1997.
- [23] J. Fernández-Caliani and M. Cantano, "Intensive kaolinization during a lateritic weathering event in South-West Spain: mineralogical and geochemical inferences from a relict paleosol," *Catena*, vol. 80, pp. 23-33, 2010. https://doi.org/10.1016/j.catena.2009.08.005
- [24] S. L. Young, M. J. Wilson, D. Miller, and S. Hillier, "Toward a comprehensive approach to the collection and analysis of pica substances, with emphasis on geophagic materials," *Plos One*, vol. 3, p. e3147, 2008. https://doi.org/10.1371/journal.pone.0003147
- [25] B. J. Bain, I. Bates, M. A. Laffan, and S. M. Lewis, Dacie and Lewis Practical Haematology: Expert Consult: Online and Print: Elsevier Health Sciences, 2011.
- [26] G. L. Seim, E. Tako, C. Ahn, R. P. Glahn, and S. L. Young, "A Novel in Vivo Model for Assessing the Impact of Geophagic Earth on Iron Status," *Nutrients*, vol. 8, p. 362, 2016. https://doi.org/10.3390/nu8060362
- [27] C. Diko and M. Diko, "Geophagia among female adolescents as a culturally driven practice," *Indilinga: African Journal of Indigenous Knowledge Systems*, vol. 12, pp. 242-251, 2013.
- [28] A. Van Onselen, C. Walsh, F. Veldman, and C. Brand, "The Impact of Geophagia on the Iron Status of Black South African Women," World Academy of Science, Engineering and Technology, International Journal of Biological, Biomolecular, Agricultural, Food and Biotechnological Engineering, vol. 9, pp. 797-802, 2015.
- [29] V. M. Ngole-Jeme and G.-I. E. Ekosse, "A Comparative Analyses of Granulometry, Mineral Composition and Major and Trace Element Concentrations in Soils Commonly Ingested by Humans," *International journal of environmental research and public health*, vol. 12, pp. 8933-8955, 2015. https://doi.org/10.3390/ijerph120808933
- [30] A. Woywodt and A. Kiss, "Geophagia: the history of earth-eating," Journal of the Royal Society of Medicine, vol. 95, pp. 143-146, 2002. https://doi.org/10.1258/jrsm.95.3.143
- [31] J. Lohn, R. Austin, and M. Winslet, "Unusual causes of small-bowel obstruction," *Journal of the Royal Society of Medicine*, vol. 93, p. 365, 2000.
- [32] B. Nfor, I. Imasuen, and C. Eigbike, "Physico Chemical Investigations and Health Implications of Geophagial Clays of Edo State, Mid-Western Nigeria," *Journal of Geology & Geosciences*, vol. 2014, 2014.
- [33] M. Diko and G. Ekosse, "Soil Ingestion and Associated Health Implications: A Physicochemical and Mineralogical Appraisal of Geophagic Soils from Moko, Cameroon," STUDIES ON ETHNO-MEDICINE, vol. 8, pp. 83-88, 2014.
- [34] I. Ibeanu, L. Dim, S. Mallam, T. Akpa, and J. Munyithya, "Non-destructive XRF analysis of Nigerian and Kenyan clays," *Journal of radioanalytical and nuclear chemistry*, vol. 221, pp. 207-209, 1997. https://doi.org/10.1007/BF02035268
- [35] M. Diko and C. Diko, "Physico-chemistry of geophagic soils ingested to relief nausea and vomiting during pregnancy," *African Journal of Traditional, Complementary and Alternative Medicines*, vol. 11, pp. 21-24, 2014. https://doi.org/10.4314/ajtcam.v11i3.4
- [36] A. G. Oomen, A. J. Sips, J. P. Groten, D. T. Sijm, and J. Tolls, "Mobilization of PCBs and lindane from soil during in vitro digestion and their distribution among bile salt micelles and proteins of human

- digestive fluid and the soil," *Environmental science & technology*, vol. 34, pp. 297-303, 2000. https://doi.org/10.1021/es990446j
- [37] A. Jahanshahee, M. H. Pipelzadeh, and M. Ahmadinejad, "A case report of colon and rectum obstruction because of sand in a three-year-old boy," *Arch Iranian Med*, vol. 7, pp. 66-7, 2004.
- [38] V. Ngole, S. Mpuchane, and O. Totolo, "Survival of faecal coliforms in four different types of sludge-amended soils in Botswana," *European journal of soil biology*, vol. 42, pp. 208-218, 2006. https://doi.org/10.1016/j.ejsobi.2006.03.004
- [39] S. Goldberg and H. Forster, "Flocculation of reference clays and arid-zone soil clays," *Soil Science Society of America Journal*, vol. 54, pp. 714-718, 1990. https://doi.org/10.2136/sssaj1990.03615995005400030014x
- [40] W. C. Mahaney, R. G. Hancock, S. Aufreiter, M. W. Milner, and J. Voros, "Bornean orangutan geophagy: analysis of ingested and control soils," *Environmental geochemistry and health*, vol. 38, pp. 51-64, 2016. https://doi.org/10.1007/s10653-015-9678-z
- [41] A. Kabata-Pendias, Trace elements in soils and plants: CRC press, 2010.
- [42] S. Odewumi, "Mineralogy and Geochemistry of Geophagic Clays from Share Area, Northern Bida Sedimentary Basin, Nigeria," *Journal of Geology & Geosciences*, vol. 2013, 2012.
- [43] D. Dolcater, J. Syers, and M. Jackson, "Titanium as free oxide and substituted forms in kaolinites and other soil minerals," *Clays and Clay Minerals*, vol. 18, p. 7, 1970. https://doi.org/10.1346/CCMN.1970.0180202
- [44] G. Ekosse, "Provenance of the Kgwakgwe kaolin deposit in southeastern Botswana and its possible utilization," *Applied Clay Science*, vol. 20, pp. 137-152, 2001. https://doi.org/10.1016/S0169-1317(01)00064-3
- [45] W. H. Organization, "Guidelines for drinking-water quality [electronic resource]: Incorporating 1st and 2nd addenda, Vol. 1, Recommendations, Third editions," ed, 2008.
- [46] G.-I. E. Ekosse and A. Mulaba-Bafibiandi, "Granulometric evaluation of continental bentonites and kaolin for ceramic applications," *Journal of Applied Sciences*, vol. 8, pp. 1021-1027, 2008. https://doi.org/10.3923/jas.2008.1021.1027
- [47] C. E. Brand, L. De Jager, and G.-I. E. Ekosse, "Possible health effects associated with human geophagic practise: an overview," *Medical Technology SA*, vol. 23, pp. 11-13, 2009.
- [48] A. Shanker and B. Venkateswarlu, "Chromium: environmental pollution, health effects and mode of action," *Encyclopedia of environmental health*, pp. 650-659, 2011.
- [49] Q. Wang, H. Zhao, J. Chen, K. Gu, Y. Zhang, Y. Zhu, et al., "Adverse health effects of lead exposure on children and exploration to internal lead indicator," *Science of the Total Environment*, vol. 407, pp. 5986-5992, 2009.
 - https://doi.org/10.1016/j.scitotenv.2009.08.038
- [50] M. A. Nkansah, M. Korankye, G. Darko, and M. Dodd, "Heavy metal content and potential health risk of geophagic white clay from the Kumasi Metropolis in Ghana," *Toxicology Reports*, vol. 3, pp. 644-651, 2016. https://doi.org/10.1016/j.toxrep.2016.08.005
- [51] M. Herreros, S. Iñigo-Nuñez, E. Sanchez-Perez, T. Encinas, and A. Gonzalez-Bulnes, "Contribution of fish consumption to heavy metals exposure in women of childbearing age from a Mediterranean country (Spain)," *Food and chemical toxicology*, vol. 46, pp. 1591-1595, 2008. https://doi.org/10.1016/j.fct.2007.12.024
- [52] H. Scherz and E. Kirchhoff, "Trace elements in foods: zinc contents of raw foods—a comparison of data originating from different geographical regions of the world," *Journal of Food Composition and Analysis*, vol. 19, pp. 420-433, 2006. https://doi.org/10.1016/j.jfca.2005.10.004
- [53] K. Soetan, C. Olaiya, and O. Oyewole, "The importance of mineral elements for humans, domestic animals and plants-A review," *African Journal of Food Science*, vol. 4, pp. 200-222, 2010.
- [54] J. Osredkar, "Copper and zinc, biological role and significance of copper/zinc imbalance," *Journal of Clinical Toxicology*, vol. 2013, 2012.
- [55] P. T. Bhattacharya, S. R. Misra, and M. Hussain, "Nutritional Aspects of Essential Trace Elements in Oral Health and Disease: An Extensive Review," *Scientifica*, vol. 2016, 2016.



Okereafor Godwin Uchenna a 33 year is a Nigerian citizen. He obtained a BTech degree in Geology from the Federal University of Technology, Owerri, Nigeria in 2005. He is currently studying towards an award of a Master's degree (MTech) in Metallurgy at the Department of Metallurgy, Faculty of Engineering and the Built Environment, University of Johannesburg (UJ), South Africa with research focus on geophagic, cosmetic and pottery clays.

Conference on Food Safety and Security, Johannesburg, South Africa. Mr Okereafor aims at study further with interest in medical geology, environmental and human health related matters.