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Chemical Composition of Kaolin Clay (*Nzu*) and Bentonite Clay (*Ulo*) and Consumption Prevalence among Women in Southern Nigeria

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Abstract
Food cravings are common during pregnancy, but in addition is craving and ingestion of non-food substances such as soil, and soft stones, termed 'pica'. A common form of pica is the ingestion of soil (geophagia). This study aimed at determining the chemical composition of kaolin and bentonite cla and ascertaining their consumption prevalence among women in Calabar and Onitsha – southern Nigeria. The edible clays collected were ground to fine powder and sieved for analysis. Proximate analysis was carried out using AOAC standard methods. For the determination of macro minerals, heavy metals and anti-nutrients, the samples were digested and analysed using Atomic Absorption Spectrophotometry. To assess the consumption prevalence, a structured questionnaire was designed, content-validated, pre-tested and used. Data was analysed using Microsoft Excel and Statistical Package for Social Sciences (SPSS).The results of the proximate analysis showed a high content of ash (85%) in both samples. Kaolin had significantly (P<0.05) higher content of sodium and magnesium while calcium was significantly (P<0.05) higher in bentonite. For the heavy metals, kaolin had significantly (P<0.05) higher content of lead, arsenic and aluminium. Among the respondents, about 75% admitted to consuming both clays (during and after pregnancy). The two edible clays are commonly consumed by women, irrespective of age and educational status. Both kaolin and bentonite clays contained appreciable quantities of important micronutrients but also contained some anti-nutrients and heavy metals, hence they should be consumed with caution, especially during pregnancy.

Keywords: Kaolin, bentonite, edible clays, pica, geophagia, nzu, ulo

Introduction

Pica is the craving for non-food substances such as ice, soil, and soft stones, which commonly occur during pregnancy. (Myaruhucha, 2009; Johnson, 2017). A common form of pica is the ingestion of soil; termed geophagia (Taiye *et al.*, 2013). Edible clay in Nigeria is commonly known as calabash chalk. Calabash chalk is one of such geographic materials prevalently consumed in Nigeria as well as other West African countries. It is also known in different languages/localities as 'Argile', 'Calabar stone', 'Calabash clay', also 'Poto' in English, 'La craie' in French, and 'Mabele' in Lingala of Congo (Abraham *et al.*, 2013). In South-East Nigeria, it is called 'Nzu' and 'Ulo' in Igbo and 'Ndom' in Efik/Ibibio. The naturally occurring chalks are chiefly made up of fossilized seashells, while the artificial form may be prepared from clay and mud which may be mixed with other ingredients including sand, wood ash and sometimes salt. The resulting product is moulded and then heated to produce the final product (Food Standard Agency, 2008). In Nigeria, the local white clay commonly called 'Nzu' is usually most consumed. It has been said to contain kaolin, layered silicate soft clay usually white but occasionally red, blush or brown. This clay is perceived to have benefits such as induction and acceleration of blood clothing, soothing an upset stomach and stifling hunger (Kelvin, 2012; Chen *et al.*, 2014). A picture of kaolin and bentonite clay is shown in Figure 1.

It is reported to be a remedy for morning sickness during pregnancy, and in Nigeria, pregnant and breastfeeding mothers patronize it the most (Madziva and Chinouya, 2020). These edible clays are also used as facial masks and soaps (Food Standard Agency, 2012). In countries such as Ghana and Nigeria, the mining of clay for ingestion in large volumes for sales at markets is a source of livelihood sustenance for many communities (Frazzoli *et al*., 2016) with cycles of cleaning, baking, shaping and cooking being part of the process (Henry and Cring, 2013). While most of the clay was naturally occurring before this process, there is evidence of artificial forms prepared by mixing clay with wood ash and salt, and in some cases, animal fats, followed by moulding and baking or leaving it to dry naturally (Sing and Sing, 2010). Baked clay is often shaped into blocks, tablets, small balls or sticks and sold at markets in countries such as Ghana, Nigeria, Tanzania, Congo, and Cameroon as well as ethnic minority shops in Europe (Abrahams *et al.*, 2006; Reeuwiyk *et al.*, 2013; Nyanza *et al.*, 2014).

However, it is a thing of concern whether or not all clays are considered good for consumption, particularly surface clay which may contain undesirables such as animal and human faeces and other undesired biological elements. Instead, clays are carefully selected and preferred based on appearance, texture and taste after being excavated from well-known traditional sources (Frazzoli *et al.*, 2016). Clay has also been used medicinally over the centuries for various ailments. The ancient Egyptians and Mesopotamians used it to plaster wounds and consumed it to treat various infirmities, especially those related to the gut (Starks and Slabach, 2012).

Some studies have pointed to the nutritional benefits of clay consumption, edible clays contain traces of calcium, iron, zinc, magnesium, potassium, copper and manganese (Tayie *et al.*, 2013). Nevertheless, the bioavailability of these minerals is yet to be guaranteed and hence may not be nutritionally significant (Ekosse *et al*., 2010; Taiye *et al.*, 2013). Apart from the fact that clay serves as a reservoir for mineral elements, it also contains other chemical and biological agents. Among the chemical agents are heavy metals, radioactive gasses and organic chemicals (Bisi-Johnson *et al*., 2010). These heavy metals such as lead, cadmium, and arsenic, when introduced into the body, can be toxic and detrimental to health depending on the quantities consumed. More importantly, exposure to lead during pregnancy has been associated with the development of pregnancy-induced hypertension (Kennedy *et al*., 2012). Lead and other toxic elements present in the chalks/clays have been reported to be associated with numerous gastrointestinal disorders including nausea, ulcers, and gastritis (Kennedy *et al*., 2012). Hence, this present research seeks to determine the chemical composition of kaolin clay and bentonite clay, and their consumption prevalence among women in the south-eastern part of Nigeria.

Materials and Methods

Ethics

For this study, a waiver was obtained from the Faculty Animal Research Ethics Committee (FAREC-FBMS), Faculty of Basic Medical Sciences, University of Calabar, Cross River State on the 7th of February, 2023.

Collection of Samples

Samples were purchased from Watts market, Calabar, Cross River state and transported to the Department of Human Nutrition and Dietetics laboratat the University of Calabar, Calabar. The samples were identified by the locals according to their local names. The edible clays were grinded in a mortar and pestle, and sieved with a mesh (115 µm) and packaged in air tight containers, then transported to the Department of Food Science and Technology Laboratory in University of Calabar, Calabar for chemical analyses.

Digestion of clay samples

Clay samples were digested according to Hu (2014). Accurately 5g of clay samples was weighed into 250 cm^3 conical flask and moistened with few drops of water to prevent sputtering. 3cm^3 of 30% H_2O_2 was then added and left to stand for 60 min until the vigorous reaction ceased. About 75 cm^3 of 0.5mol/dm^3 solution of HCl was added and the content heated gently at low heat on the hot plate for 2 hr. The digest was allowed to cool, and then filtered into 50 cm^3 standard flask. The content was then diluted to 50 cm^3 mark with the same acid solution. Triplicate digestions of each sample together with a blank were carried out.

Experimental Procedure

-Proximate Analysis

The proximate composition of the edible clays was determined gravimetrically using AOAC standard methods. The carbohydrate content was calculated by difference as the nitrogen-free extract (NFE), a method described by James (1995). The caloric value of the samples was obtained by multiplying the mean values of protein, fat and carbohydrate by their respective Atwater factors (4, 9 and 4 respectively) and taking the sum of the product.

-Determination of Macro-minerals and Heavy metals

A portion of the sample (0.5g) was weighed into a 500ml volumetric flask, 15ml HNO_3, and 5ml of 70% Perchloric acid ($HCIO_4$) wasadded to the flask. The flask was placed on a hot plate in the fume cupboard to digest to clarity. The solution was transferred to a 100ml volumetric flask and diluted to volume with water. Aliquots or dilutions of this sample were then aspirated into the air-acetylene flame of the WFX 320 (AAS) Atomic Absorption spectrometer to determine the elements listed above. The elements were conventionally reported through graphic extrapolations with standard pure metals. The macro minerals Mg, Ca, Na, K and heavy metals Pb, Cd, As, and Al, were determined using the Official Methods of AOAC International.

-Anti-nutrient determination

To about 1g of the sample was added 75ml of 1.5N H_2SO_4 and the solution was carefully stirred using a magnetic stirrer for 1 hour before being filtered using What-man No. II filter paper; 25ml of the extract was collected and titrated when hot against 0.1N $KMnO_4$ solution to a faint pink colour end point.

Oxalate = (titre value x 0.9004) mg/g

Phenol contents in the extracts were determined by the modified Folin-Ciocalteu method as described by Kupina *et al*. (2018). An aliquot of the extract was mixed with 5 ml Folin-Ciocalteu reagent (previously diluted with water 1:10 v/v) and 4 ml (75 g/l) of sodium carbonate. The tubes were vortexed for 15 s and allowed to stand for 30 min at 40 °C for colour development. Absorbance was then measured at 765 nm using the Hewlett Packard UV-VS spectrophotometer.

Cross sectional survey

Study area

A cross-sectional study was conducted using a convenience sample of 200 pregnant women, who attended antenatal clinics in General Hospital Onitsha, Anambra State and General Hospital Calabar, Cross River State. Structured interviews were conducted in April, 2023, using an anonymous, structured, closed-ended questionnaire designed specifically for the study based on the study objectives and literature review. The questionnaire was content validated by experts in the field and it comprised three sections: Section A was on background information; Section B was designed to collect data on the respondents' knowledge, attitude and perception of geophagy while Section C was designed to ascertain the health status of respondents. A pilot study was carried out using 10 respondents who were excluded from the main study. The participants were given the consent form to read and sign after which they were co-opted into the study. Duly completed and returned copies of the questionnaires by the 200 participants, were analysed statistically.

Data analysis

Laboratory analytical results were compiled, entered into the computer, and analyzed using Microsoft Excel 2013 spreadsheet and expressed as mean ± SEM. Statistical analyses – Analysis of Variance (ANOVA) and T-tests were carried out using Statistical Package for Social Sciences (SPSS version 20.0) and significance was accepted at $p< 0.05$.

Data availability Statement

The results supporting the findings of this study are published in this article. Any additional information can be made available by the authors, on request.

Results and Discussion

Results

Proximate Composition of the edible clays

In Table 1, the proximate analysis shows that there is a significant difference between the moisture content of kaolin clay and bentonite clay (3.9 ± 0.03%; 3.18 ± 0.01%, P=0.001 respectively). No significant difference (P=0.632) was observed between the ash content of both clays (about 85%) as well as between their fat content which was quite low (about 0.5%). Bentonite clay was found to contain no fibre while kaolin clay had significantly higher (P=0.001) content of fibre (2%). The protein content of bentonite clay (3.59 ± 0.02%) was significantly (P=0.001) higher than that of kaolin clay (2.59 ± 0.05%). Similarly, the energy value of bentonite clay (48.65 ± 0.52Kcal) was also significantly higher (P=0.001) than that of kaolin clay (37.94 ± 0.28%).

Macro mineral and heavy metal content of the edible clays

The result of the macro mineral analysis (all values in mg/g) presented in Table 2, shows that the sodium (Na) content of kaolin clay (0.18 ± 0.01) is significantly higher (P=0.003) than that of bentonite clay (0.11 ± 0.01). Calcium (Ca) content of bentonite clay (2.21) was significantly higher (P=0.001) than that of kaolin clay (1.22 ± 0.01). In addition, the magnesium (Mg) content of kaolin clay (2.16) was significantly higher (P=0.001) than that of bentonite clay (1.69 ± 0.01). There was no significant difference (P=0.070) in the potassium (K) content of both clays. For the heavy metals, both clays contained the exact same amount of cadmium (Cd) while bentonite clay was found to contain no lead. The arsenic (As) and aluminium (Al) contents of kaolin clay were significantly higher (P=0.001) than those of bentonite clay.

Nutrient content of the edible clays

From the results shown in Table 3, the oxalate concentration of bentonite clay was higher, though not significantly different from that of kaolin clay (0.65 ± 0.48 mg/g and 0.29 ± 0.01 mg/g, respectively, P=0.487). The phenol concentration of kaolin clay (16.89 ± 0.01 mg/g) was also significantly higher (P=0.000) than that of bentonite clay (5.18 ± 0.01 mg/g).

Socio-demographic characteristics of the respondents

Table 4 shows the socio-demographic characteristics of the respondents. Almost 90% of the women were pregnant, with almost 60% of them being aged below 40 years. The Majority of them (77.5 %) were married while 6.5% were separated from their spouses. Many of the respondents (72%) had a Tertiary Education and above. Most of them (71.0%) were working in the Private sector and 51.0 % revealed that their monthly income ranged between ₦50,000.00 and ₦ 149,000.00. Out of the 200 respondents in this study, 174 of them lived in 2-6 person households.

General responses on the consumption of edible clays by respondents

This section presents the general responses on the consumption of 'Nzu' (kaolin clay) and 'Ulo' (bentonite clay). From the findings (Table 5), a greater percentage of the respondents (over 50%) admitted that they sometimes consume 'Nzu' and 'Ulo', some said they consumed it only during pregnancy, while others consumed it at other times. Only 6% of the respondents admitted to consuming 'Nzu' and 'Ulo' daily, while 41.0% of them revealed that they consume both 'Nzu' and 'Ulo' up to three times a week. For those who consumed the edible clays, 'neighborhood' and 'their hometown' were the major places of obtaining these substances, with 57.5% reporting consuming small sizes of the substances.

Discussion

According to Willey *et al.* (2008), moisture content above 15% is considered conducive to microbial growth. The low moisture of these clays may explain why they can be stored for a longer time without spoilage. Some women carry them around in handbags and purses for weeks without any spoilage. The ash content of both edible clays was found to be high and this was in agreement with the earlier report of Ejike and Ogugua (2017) who revealed a high ash content in 'Nzu' and 'Ulo'. According to Ndife *et al.* (2019), ash content is an indication of the mineral content of a food/substance. Thus, both edible clays had a considerable ash content indicating high inorganic composition (mineral content). The protein and fat content of both kaolin and bentonite clay was very low (being non-food substances). The macro minerals - sodium, potassium, magnesium and calcium, were present in moderate concentrations and they were in line with earlier reports of Umudi (2017) and Ejike and Ogugua (2017). Calcium is an important mineral required for bone formation and neurological function. The calcium content was low in both samples considering the WHO/FAO recommended intake of 400-500 mg per day of calcium for adults and 1200 mg per day for children. Magnesium was present in significant quantities in both samples. Considering the adult required daily allowance (RDA) of 250 mg/day (FNB/IOM, 2002), it cannot be regarded as a rich source of magnesium to the body. The sodium and potassium content were also not high with potassium being slightly higher than sodium in both samples (as recommended by WHO).

In addition, both edible clays were found to contain some non-nutrients such as heavy metals and anti-nutrients. Heavy metals have a toxic impact, but detrimental impacts become apparent only when long-term consumption of large quantities occurs. Due to the fact that clay is not the only dietary source of heavy metals, certain groups of consumers such as the elderly with cardiovascular and kidney problems, who ingest these substances over time, need to be cautious as they are more susceptible to toxicities. The heavy metal analysis results showed the presence of lead (Pb), cadmium (Cd), arsenic (As) and aluminium (Al) in both clays with bentonite clay not containing lead. The mean concentrations of most of the metals were below the safe limits recommended by FAO and WHO; kaolin clay recorded the highest mean concentrations in all the heavy metals and this is similar to the report of Ejike and Ogugua (2017). The most commonly noted toxic complication of pica is lead poisoning (Ali, 2001). Lead has the tendency to displace calcium in mineralizing tissues. There is also a likelihood of congenital intoxication with lead poisoning. High exposure to lead can cause problems in the synthesis of haemoglobin, and damage to the kidney, gastrointestinal tract, joints, reproductive system and the nervous system (Zhuk and Kist, 1993). This has important public health implications as Pb poisoning can affect both the foetus and neonates because is excreted through the placenta and breast milk. Miscarriage, stillbirth, and premature birth are among the complications reported in mothers due to Pb poisoning.

The anti-nutrients analysed in this study were oxalate and phenols. Anti-nutrients at high concentrations may cause reduced nutrient bioavailability. Most of the anti-nutritional factors become ineffective by simple processing methods such as heating, soaking, germination or autoclaving. Anti-nutrients in foods are known to inhibit the proper absorption and utilization of essential nutrients thereby decreasing bioavailability. In sensitive people, small amounts of oxalates can result in burning in the eyes, ears, mouth, and throat; large amounts may cause abdominal pain, muscle weakness, nausea, and diarrhoea (Popova & Mihaylova, 2019). Oxalates reduce calcium and magnesium utilization by binding them and making them indigestible although the negative effect of oxalates on humans depends on the levels (Nguyen *et al*., 2018).

The results of the survey show that most of the respondents, mostly married women, consume both kaolin and bentonite clay up to three times a week and this indicates that both edible clays are commonly consumed among women in Anambra State and Cross River State, Nigeria. The results of this study support the earlier report of Ekenedo and Okereke (2018), who reported a high prevalence of geophagy in Owerri, Imo state. This finding raises concern considering the health implications of the practice as have been revealed by experts. Various types of geophagic materials are available, and people opt for a particular type at a time (especially pregnant women as a result of pica). In this study, 'Nzu' (kaolin clay) was reported to be consumed more than "Ulo" (bentonite clay) and again this agrees with the report of Ekenedo and Okereke (2018), which showed a higher consumption rate of "Nzu" compared to other clay types. Reasons behind such choice may include craving, taste, cultural practices and supposed nutritional value (Arikan-Saltik *et al*, 2013). Similarly, Simelane (2008) found that in South Africa, soil is preferred to other geophagic materials. Respondents aged below 40 years were the highest consumers of geophagia materials. This is similar to the findings of Njiru *et al.* (2011), which showed that the prevalence of geophagy was higher among school children and pregnant women in Africa. In parts of Africa, clay consumption is commonly associated with pregnant women who consume earth materials to alleviate the symptoms of morning sickness and is not affected by age, race, economic status or physiological state, though today the practice is most common amongst the world's poorer or more tribally oriented people (Abrahams *et al.*, 2013). In suggesting how pica may be managed, it was argued that intrusive treatment approaches are necessary when an individual's pica is considered life-threatening (Stiegler, 2005).

Limitation of the Study: The main limitation of this study was insufficient funds for further analysis of the edible clays (especially the anti-nutrients). Also, the lack of research assistants in other locations for data collection limited our sample area and size.

Conclusion

Consequent to the above findings, it was concluded that the consumption of both kaolin clay and bentonite clay are a common practice among women (especially pregnant ones) in Onitsha and Calabar, irrespective of age, educational status and location of residence. The results of the chemical analyses of the edible clay samples showed a very high ash content for both clays and a low content of other nutrients with bentonite clay having a significantly higher energy value. Subsequently, looking at the non-nutritive content of the edible clays, the results showed both contained significant amounts of heavy metals and anti-nutrients which may affect the bioavailability of the lowly-concentrated nutrients. This implies that they contain toxic substances which could be considered to be relatively unsafe for consumption at certain levels. Hence, high consumption of these clays could be a risk factor for some diet-related deficiency diseases and may be harmful to both pregnant mothers and babies. Therefore, edible clay consumption should be with caution, especially during pregnancy.

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Kaolin clay (*Nzu*) Bentonite clay (*Ulo*)

Figure 1: Pictures of both edible clays
Source: Internet

Table 1: Proximate composition of Kaolin clay 'Nzu' and Bentonite clay 'Ulo'

	Moisture (%)	Ash (%)	Fat (%)	Fibre (%)	CHO (%)	Proteins (%)	Energy (kCal)
Kaolin clay	3.94 ±0.03	85.20 ±0.10	0.50 ±0.00	2.00 ±0.00	5.78 ±0.11	2.59 ±0.05	37.94 ±0.28
Bentonite clay	3.18 ±0.01*	85.29 ±0.14	0.52 ±0.02	0.00 ±0.00*	7.57 ±0.10*	3.54 ±0.02*	48.65 ±0.52*
T-test	0.001	0.632	0.374	0.001	0.001	0.001	0.001

***** indicates values that are significantly different from Kaolin clay values at p<0.05***

Table 2: Mineral composition of Kaolin clay and bentonite clay

	Na (mg/g)	K (mg/g)	Ca (mg/g)	Mg (mg/g)	Pb (mg/g)	Cd (mg/g)	As (mg/g)	Al (mg/g)
Kaolin clay	0.18 ±0.01	0.21 ±0.01	1.22 ±0.01	2.16 ±0.00	0.09 ±0.01	0.02 ±0.00	0.02 ±0.00	0.28 ±0.01
Bentonite clay	0.11 ±0.01*	0.17 ±0.02	2.21 ±0.00*	1.69 ±0.01*	±0.00 ±0.00*	0.02 ±0.00	0.01 ±0.00*	0.18 ±0.01*
T-test	0.003	0.070	0.001	0.001	0.001	0.725	0.001	0.001

***** indicates values that are significantly different from kaolin clay values at p<0.05***

Table 3: Anti-nutrients composition of 'Nzu' and 'Ulo'

Edible clay	Oxalate (mg/g)	Phenols (mg/g)
Kaolin	0.29 ± 0.01	16.89 ± 0.01
Bentonite	0.65 ± 0.48	5.18 ± 0.01*
T-test	0.487	0.000

***** shows a significant difference from kaolin clay at p<0.05***

Table 4: Socio - demographic data of respondents

Variable	Sub-variable	n	%
Physiologic state	Pregnant	179	89.5
	Not pregnant	21	10.5
Age group (years)	18-29	46	23.0
	30-39	70	35.0
	40-49	56	28.0
	50-59	26	13.0
	>60	2	1.0
Ethnicity	Igbo	42	21.0
	Hausa	30	15.0
	Yoruba	71	35.5
	Others	57	28.5
Marital status	Single	26	13.0
	Married	155	77.5
	Separated	13	6.5
	Widow	6	3.0
Education	No Formal Education	3	1.5
	Primary	2	1.0
	Secondary	50	25.0
	Tertiary	71	35.5
	Post Grad Education	74	37.0
Income	<50,000 naira	13	6.5
	50,000-149,000 naira	102	51.0
	150,000-299,000 naira	77	38.5
	>300,000 naira	8	4.0
Occupation	Public Sector	43	21.5
	Private sector	142	71.0
	Company	13	6.5
	Informal	2	1.0
Household size	Staying alone	17	8.5
	2-3 persons	120	60.0
	4-6 persons	54	27.0
	>6 persons	9	4.5
	Total	200	100.0

Table 5: Consumption of edible clays by respondents

Variable	Sub-variable	n	%
Do you consume 'Nzu'?	Never	49	24.5
	Sometimes	114	57.0
	Only during pregnancy	37	18.5
Do you consume 'Ulo'?	Never	57	28.5
	Sometimes	104	52.0
	Only during pregnancy	39	19.5
	Don't consume	57	28.5
How often do you eat 'Nzu' and/ or 'Ulo'	< 3 times a week	82	41.0
	3-6 times a week	49	24.5
	Daily	12	6.0
How do you obtain the 'Nzu' and 'Ulo' you consume	Neighborhood	109	27.7
	Supermarkets / Shops	56	14.2
	My home town	115	29.2
	Local market	64	16.2
	Others	50	12.7
	Total	394	100.0
What size of Nzu' and 'Ulo' do you think consume	Small	115	57.5
	Medium	80	40
	Large	5	2.5