Mineralogy and Geochemistry of Geophagic Soils in Ghana: A Review

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ABSTRACT

Geophagy is practised all over the world but it is still challenging to attest to the safety of the practitioners as the provenance and geochemistry of clays ingested are not fully understood. Clay can form over all types of rocks but the mineralogical and chemical compositions may vary. Significance of provenance and geochemical studies in Southern Africa aided in the identification of some elements and minerals which upon their ingestion affect human developments to be reduced as part of recommendations from that investigation. Published articles in geophagy in Ghana indicate lack of investigations in provenance and geochemistry into clays used in geophagia, even though the practice is nationwide and very common in rural Ghana. The variability of the geochemistry across landscape and different provenance of clays recognized elsewhere in similar geological settings motivated the review of geophagy in Ghana since similar clay occurrence can exist in similar geologic province. The after review comments by the authors is that the understanding of the provenance and geochemistry of clays used in the practice can lead to approval of removing or reducing some known toxic elements and minerals to make the practice safe and attractive and therefore recommend the investigation into provenance and geochemistry of clays to be used as geophagic materials in Ghana.

Keywords: Geophagia, Toxic elements, Geologic province, Provenance

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I. INTRODUCTION

Geophagia also known as geophagy [29] is the practice of eating earth or soil-like substances. The geophagia practice is considered normal when it occurs in non-humans but seen as an abnormal behaviour in humans. In humans, the practice is most often in rural or preindustrial societies among children and pregnant women [1]. Human geophagia is a form of pica [2]. In Ghana, there have been numerous speculations about the ingestion of clay popularly known locally as “ayilo”, “agatawe” and “shile” by the Gas, Ewes and Fantes respectively [4]. Geophagia is widely practised throughout Ghana. However, notable regions known for producing the geophagic materials are Volta, Ashanti and Upper East Regions. This clayey soil is sundried into egg-shaped balls which are then sold on the local market for all to patronize [4]. The positive or negative effects of geophagia in humans depend on the physicochemical, chemical, biological and mineralogical properties of the materials ingested [16, 20, 28]. This work seeks to review published works conducted on geophagia particularly in Ghana with some examples elsewhere based on the mineral constituents and the chemical characterisation of the geophagic clays. The intention is to establish the missing knowledge gap between geophagic practice and the health of the individual geophagic practitioners.

II. METHODOLOGY

Ten published works on geophagy across the globe were reviewed. Three of these published articles were works done in Ghana. Six were from other parts of Africa (South Africa, Cameroon, Swaziland, Botswana, Democratic Republic of Congo and Nigeria) of which the searches were primarily based on the mineralogical and chemical assessment of geophagic soils and the impact of the practice on the health of the geophagic individuals, except for one conducted in South Africa by Ekosse et al. [12] which considered the weathering intensity, trends and provenance of the geophagic soils and the effect of the practice on the health of the practitioners. Furthermore, there was one reported in the United Kingdom on trace element analysis in baked clay and the risk of human exposure to arsenic and other toxic elements from geophagy using inductively coupled plasma mass spectrometry. The researches done in Ghana were geared towards identifying the trace elements in geophagic materials and determining their concentration levels. Similar investigation was also on heavy metal assessment and potential health risk of the geophagic clays via the pathways of oral and dermal exposures on the health of the practitioners. This vividly shows that researches done on geophagy in Ghana by previous researchers were mainly on trace and heavy metals concentrations in the geophagic

materials and the effects of the practice on the health of the geophagic individuals.

III. THE REVIEW

Arhin and Zango [4] highlighted on the fate of geophagia in Ghana by collecting and analysing thirty (30) baked clay balls with an average weight of 70 g from market centres in Kumasi, Navrongo and Anfoega. Trace elements contents were determined for their concentration levels. Out of thirty samples, 10 samples were collected from each region. The field samples were prepared by drying, pounding and sieving. The samples were sieved to $<125\ \mu\text{m}$ fraction, weighed to 100 g portion, labelled and bagged. The labelled and bagged samples were sent to the laboratory for trace element analysis using XRF analytical technique. Arhin and Zango analysed the trace element concentrations and also carried out calculation on the probable daily intake (PDI) and health risk indices (HRI), and used country averages in geophagic clays as calculated by Hunter [18] using in vitro extraction method as a reference to compare Potassium (K), Calcium (Ca) and Magnesium (Mg) of major oxides in baked clay-ball samples from the three regions. K concentration recorded in the clay balls in Volta was same as recorded in Upper East, as 2.72 mg/kg, whilst it was 2.19 mg/kg in Ashanti region. Analyses of the results showed enrichment of K in clay balls in the three regions relative to the country average concentration of 0.13 mg/kg. Higher values were obtained for Mg in the clay balls in all the three regions when values were compared to the in vitro extraction average of 0.28 mg/kg. Volta and Upper East regions recorded same values of 1.5 mg/kg whilst Ashanti had higher value of 2.29 mg/kg. On the contrary, the most cherish element such as Ca that is essential for bone building was consistently lower in all clay balls analysed in all the three regions. Equal measurements of Ca concentrations of 0.03 mg/kg were recorded for Volta and Upper East regions whereas 0.23 mg/kg in Ashanti region. Similar analyses performed by Arhin and Zango on the trace elements in the geophagic clays were Arsenic (As), Chromium (Cr), Cobalt (Co), Molybdenum (Mo), Caesium (Cs), Zirconium (Zr) and Lanthanum (La).

The concentration levels of Cr ranged from 90 to 146 mg/kg with a mean of 124 mg/kg, Co were 28 and 30 mg/kg with a mean of 29 mg/kg, and a range of 3.8 to 4.8 mg/kg with a mean of 4.3 mg/kg for Mo were reported at Anfoega. Contrastingly different concentration values were measured for Cr, Co and Mo. The results for these elements in Navrongo and Kumasi were reported as 285.5, 28.5 and 2.7 mg/kg, and were 159, 61.7 and 4.4 mg/kg, respectively. All these concentrations obtained for Cr, Co and Mo were above their accepted background concentrations of 102 mg/kg for Cr, 25 mg/kg for Co and 1.2 mg/kg for Mo. However, these three elements are known essential elements for humans only in low concentrations. Excess of these elements as have been recorded may be harmful to the consumers. For instance, in the case of Cr and Co kidney damage (Nephritis) and Heart failures may occur for uncontrolled ingestion. The As contents in the geophagic clays similarly showed relatively high average assay values of 13.4 mg/kg for Anfoega, 11.7 mg/kg for Navrongo and 10.8 mg/kg for Kumasi compared to the accepted values known in soils. Judging from the As-assay results and the fact that As is bioaccessible and can bio-

accumulate in humans suggest As-related health effects may be prevalent among the practitioners of geophagy in the three study areas with highest cases occurring at Anfoega and lowest in Kumasi. Pearson bivariate correlation of the elements concentrations showed higher Probable Daily Intake (PDI) rates for As, Cr and Co compared to the Provisional Maximum Tolerable Daily Intake (PMTDI) accepted by WHO/FAO [27]. The interplay of elements in clay balls from the three areas studied showed the coexistence of essential and harmful elements. The oral ingestions of the clay ball do not separate the essential elements from the harmful ones. Therefore, to make geophagia attractive and safe require investigations that identify elements distributions and concentrations to guide the dosage as the amount ingested has its corresponding response. The authors consent with the methods used and results obtained by Arhin and Zango but because of the variability of the elements concentration levels and distributions across the landscape, identifying the provenance of clays used for the practice can help in addressing many of the associated health consequences.

Before Arhin and Zango [4] investigation, Nkansah et al. [23] had carried out a similar survey. Their study was on heavy metal contents and potential health risk of geophagic white clay from Kumasi Metropolis in Ghana. The aim of that study was to determine the levels of heavy metals in the geophagic white clay ingested by the geophagist, the potential risks associated with the heavy metals as well as the cumulative carcinogenic and non-carcinogenic risks through the pathways of oral and dermal exposure on the health of the geophagic practitioners. Three (3) samples each of white clay samples were collected from ten major markets at Abuakwa, Asafo, Asuoyeboah, Ayigya, Bantama, Central Market, Kwame Nkrumah University of Science and Technology (KNUST), Kwadaso, Santasi and Tanoso in the Kumasi Metropolis in the Ashanti Region. Thermo scientific Niton XRF Analyser (Mobile Test S, NDT-3t-XL3t-86956, com24) was used to analyse the heavy metals content in the clay samples. Metal bioaccessibility and average daily intake (ADI) of the samples were calculated. Both essential and toxic metals levels in the clay samples were determined using ICP-MS analyses. The PMTDI of the metals was calculated based on the Standard Provisional Maximum Tolerable Daily Intake as estimated by WHO and FAO. Health risk assessment of the measured elements was examined and calculated. The threshold values raised by USEPA were used as standards to assess the potential health effects on the geophagic practitioners. The chronic daily intake (CDI) was also calculated for different heavy metals that were analysed in the samples. The hazard Quotient (non-carcinogenic) and cancer risk (carcinogenic) of the different metals in the samples were calculated. Arsenic levels within the clay samples from some selected markets, from ICP-MS results were compared. Four of the samples showed approximately the same concentrations whilst there was inconsistency in the results for two samples. The results from their study showed As concentration level in the samples ranging from 8.11 to 14.18 ppm. This was identified to be higher than the mean exposure level (3.0 $\mu\text{g/kg BW/day}$) set by the Joint FAO/WHO Expert Committee on Food Additives. Likewise, Pb concentration was in the range of 549.34 to 622.92 μg , which is thrice the required daily intake for a 60 kg weight

adult. Outcome of the study showed that consuming the clayey samples over a long time can lead to serious health problems of which dysfunctioning of kidney, liver and heart of the geophagic individual; cardiovascular, renal, gastrointestinal and haematological effects are possible to occur. The samples showed no concentration of Cd and Mercury (Hg) because their concentrations were below detection limit. Other essential metals that were present in the samples and in high concentrations were Potassium and Iron. Calcium concentrations were below the accepted level of 1000 ppm referenced from WHO/FAO. The PMTDI values recorded from selected samples showed values higher than the 180 µg value required for a 60 kg adult, and the highest was recorded in samples from the Kumasi Central Market. Their work revealed that As and Cd had the potential of causing both carcinogenic and non-carcinogenic risk whilst Pb has the potential of causing only non-carcinogenic risk. The calculated cancer risk value for As was higher than the permissible level, hence As appeared to be the main metal with the potential of causing cancer, with its dominating exposure route being ingestion (oral). The elements bio-accessibility missing in Arhin and Zango's work was considered by Nkansah et al. but failed also to investigate the provenance of the white clay which may relate to different rock types. The gap in knowledge still remains as the geological makeup of the clay is useful in suggesting the type of elements contained in the geophagic clay consumed by the practitioners.

Though provenance studies on clays for geophagy has not been done in Ghana but Ekosse et al. [12] has carried out that study at Free State Province in South Africa. Their study aimed to understand the mineralogy and elemental composition, weathering intensity, trends and provenance of geophagic soils, and to infer on the health implications on the geophagic individuals. Particle size distribution (PSD) of the samples using laser diffraction technique described by Van Reeuwijk [26] was employed. Mineralogical analysis using X-ray diffractometry technique, and PANalytical Axios WDXRF spectrometer for geochemical analysis as described by Fitton [14] and by the Council for Geosciences [6]. Ekosse's team further analysed the bioaccessibility of heavy metals in the samples using physiologically based extraction test which involved chemical environment stimulation in the human gastrointestinal tract (GIT) to determine the ions in the GIT. The revelation of the PSD studies indicated the samples to contain clay, silt and sand particles. The mineralogical analysis identified the samples to contain quartz, kaolinite, montmorillonite, muscovite, microcline, plagioclase (albite identified) and goethite. The abundant non-clay mineral was quartz with smectite being the dominant clay mineral. Next to these were kaolinite and muscovite, both of which occurred in minor quantities though muscovite was absent in one of the samples. Microcline, plagioclase and goethite occurred in trace amounts with muscovite absent in one, plagioclase absent in four of the samples and goethite occurring in only two of the samples. These results obtained attested to the mineral constituents of the geophagic soils and clays from Guinea, Ivory Coast and Senegal [19], Cameroon and Nigeria [9], Democratic Republic of Congo [11], and Swaziland [10].

Incidentally that of Ghana has not been researched into or unavailable. This thus makes the review relevant as it

explicitly shows the gap that has to be filled. The authors therefore consent to some parts of Ekosse's et al. work particularly the aspect on mineralogy and geochemistry to identify the provenance of clays at the three areas earmarked for the study. A stronger argument to fill this knowledge gap is work by Diko and Ekosse [7] that characterised geophagic soils using the physico-chemical and mineralogical compositions to determine possible health implications on the geophagic individuals. In this work, soil samples were collected from in situ geophagic materials at mining sites in Moko for geochemical analysis of all contained elements.

Munsell Soil Colour chart following procedures discussed in Diko et al. [8] was used for the soil colour determination. Particle size distribution (PSD) was determined with a Malvern Mastersizer Hydro 2000 Mu laser particle size analyser, following discussions in Fitzsimmons et al. [15]. The plasticity index (PI) was calculated from liquid limit (LL) and plastic limit (PL) as $PI = LL - PL$, and was determined using a Cassagrande apparatus for fine mortar fraction of the samples. pH and EC were determined with a pH meter (Hi 9321 Micro Processor) and Metler Toledo EC meter [24]; and XRD for bulk kaolin was carried out. From the results, the physico-chemical properties of the analysed geophagic colour range from yellowish through brownish yellow to pinkish grey. The samples were generally silty. The LL had a mean value of 55.7 mass % and a mean value of 41.8 mass % for PL, given an average PI value of 13.8 mass %. Soil pH recorded an average of 4.9, and 8.7 µS/cm for the EC. From the mineralogical analysis, the mineral phases identified were kaolinite + quartz + mica + microcline + goethite + anatase ± smectite ± hematite ± gibbsite. The XRD patterns were depicted by weak first order kaolinite peaks and the absence of the second order and 110 kaolinite peaks in all samples. From the study, the physico-chemistry and mineralogy of the geophagic soils were evaluated and their possible health effects discovered. Quartz and feldspar found in the samples were noted to affect the health of the geophagic individuals due to their gritty texture. The outcome from the study was that the soil qualifies to be used as remedy to relieve nausea and to curb salivating among pregnant women because the soils possessed high plasticity and was acidic. The quantity of kaolinite found in the samples rendered it suitable in ionic reactions such as isomorphous substitution and release of nutrients to the geophagic individuals. Beneficiation to reduce and to do away with quartz content was recommended. The quartz in the geophagic clays if not identified in the study could pierce the large colons to cause stomach health issues during ingestion by the geophagy practitioners. There were significant health concerns associated with the quartz content but because of the considerable good geophagic properties in the soils mechanism to reduce the quartz content thereby making the ingestion of the material less problematic was developed.

Some earlier work by Arhin and Zango [3] carried out geological and geochemical assessment on geophagia in Ghana with the objective of identifying the effects of the practice on human health. The analysed clay samples were taken from markets at Navrongo in the Upper East, Kumasi in the Ashanti and Anfoega in the Volta region; and hair samples from some geophagic individuals to assess the consequences of Arsenic concentration in the body. The study

also placed emphasis on the amount of clay ingested within a time frame whilst working out the sources of the arsenic in the geophagic individuals. Wet digestion method was adopted to analyse the clay samples for As, Pb, Ca, K, Mg, Zn, Fe, Cu, Mn and Se whereas the solution obtained from the hair samples were analysed using a high resolution ICP-MS. The results revealed insignificant concentrations of Pb and K, of which K had values ranging from 1.2 to 1.3 wt.% and showed relatively high concentrations of Ca as 17.3 to 26.1 wt.% and As as 14.5 to 20.9 ppm. The Arsenic concentrations recorded averages 21 ppm, 19 ppm and 15 ppm in the samples from Kumasi, Anfoega and Navrongo, respectively. The Arsenic concentrations of samples from Kumasi and Navrongo were compared to two perceived selected major elements, K and Ca, considered essential elements, which are needed by geophagists within permissible level of concentrations. The study unfolded for the first time the risk assessment studies that the sun-baked clay (locally known as “Hyire”) consumed mostly by women in Ghana can be a source of the As-related-diseases reported at the health centres. They teased out the need for chemical assessment of the geophagic materials and proposed the need to standardized quantities to be ingested daily for safe practice.

Further investigations were conducted by Ekosse and Anyangwe [13]. This investigation was based on studies carried out on geophagic practice in South Africa and Swaziland to establish the mineralogical and particulate morphological characterization of geophagic clays from Botswana. Samples of geophagic clays were purchased from roadside vendors in the following towns Gaborone, Kanye, Francis town, Palapye, Selebi and Phikwe. The samples were subjected to four different forms of examination and analyses: clayey soil colour; X-ray powder diffractometry (XRD) tests for minerals identification and quantification; optical research for morphology of sand/silt particles; and environmental scanning electron microscopy (ESEM) for morphology of the clay size particles in the samples. The identifiable colours were white, light grey, yellow, and light yellow brown to dark greyish brown, which were similar to samples analysed from South Africa and Swaziland by different researchers. Both clay minerals kaolinite, calcite, microcline, smectite, talc, mica, hematite and dolomite and non-clay mineral quartz were identified from the mineralogical analysis. The dominant mineral was quartz with concentrations ranging from 70 wt. % to 80 wt. %. Feldspar occurred in the form of microcline, and smectite as sodium montmorillonite. A typical kaolinite morphology was dominant considering the clay size particle morphology. The particle size of most of the samples clearly reflected pseudo-hexagonal platelets of kaolinite, and these particles identified on the pseudo-hexagonal platelets were pointed out as smectite particles. The quartz identified in the samples were very angular in shape and coarse grained. The study realized the ability of quartz to easily damage the dental enamel as well as eroding the walls of the gastro-intestinal tract. The need for conducting beneficiation exercise to reduce the coarse angular sandy and silt particles contained in these geophagic soils was recommended so as to render geophagic clayey soils safe for human consumption after the geophagic clay morphological studies. Ekosse and Ngole [10]

further examined the mineralogical and chemical composition of geophagic soils from Swaziland to deduce the possible human health effects. Their results were intended to establish baseline mineralogical and chemical characterization of geophagic soils in Swaziland where the habit is mostly practiced. Twelve geophagic soils from different areas and markets from the Middle Veldt Region of the country were sampled. Among the collected samples are field samples that were obtained from the Mahlanya and Ezulwini traditional mining sites using a hand trowel, and portion of the samples were bought from open markets in Mbabane. Colour determination, particle size analysis, mineral identification and chemical composition were determined. The samples were mounted and the colour properties were obtained by visually comparing them with colours of standard soils as recorded in the Munsell Soil Colour Book [22]. A Malvern Mastersizer 2000 fitted Hydro 2000G dispersion unit was used in the determination of the particle sizes of the soils. X-ray diffractometry using both Qualitative and semi-quantitative mineralogical analyses approach as described by Bish and Reynolds [5], Moore and Reynolds [21], and Council for Geosciences [6] were done on the samples. For the chemical analysis, samples were analysed for major oxides and trace elements concentrations using fusion beads and pressured powder pellets with a PANalytical Axios WDXRF Spectrometer as described by Fitton [14] and by the Council for Geosciences [6]. The chemical index of alteration (CIA) and chemical index of weathering (CIW) values were calculated to better characterize the geophagic clay samples. From the results, with the colour determination, five different colour varieties which were as a result of possible staining by goethite and hematite were observed in the samples. With the particle size analysis, silt dominated in all the samples. The minerals quartz, plagioclase, kaolinite, microcline, goethite, muscovite, and/or hematite, and illite-smectite were present in the geophagic soil samples. All the minerals except for plagioclase were present in minor to trace quantities and/or occurred in only few samples. Plagioclase was however present in only five of the twelve samples having abundance range of trace to 37 wt%, a significance of incomplete alteration and an indication of the soils possibly formed from surrounding granitic rocks. The major oxides and trace element concentrations of the samples were compared to the average upper continental crust (UCC) [25], the average Post-Archaean Australian Shale (PAAS) [25] and the average Swazi Granite (SG) [17]. The results revealed 95% confidence level for $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Fe}_2\text{O}_3$, $\text{SiO}_2/\text{K}_2\text{O}$, $\text{TiO}_2/\text{Fe}_2\text{O}_3$, MgO/MnO , $\text{P}_2\text{O}_5/\text{CaO}$ when the oxides were correlated. $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Fe}_2\text{O}_3$ demonstrated negative correlation which signifies that soils having high Si content contain low Al and Fe whilst the result for positive correlation for $\text{SiO}_2/\text{K}_2\text{O}$, $\text{TiO}_2/\text{Fe}_2\text{O}_3$, MgO/MnO and $\text{P}_2\text{O}_5/\text{CaO}$ implied an increase in concentrations of Si with K, Ti with Fe, Mg with Mn, and P with Ca. Apart from Al and Si which dominated from the chemical analysis results, the concentrations of the other major oxides were generally very low which signifies very intense weathering of primary minerals. The samples had very high CIA and CIW values, with the CIA values being an indication of the samples having low concentrations of essential chemical constituents. The

provenance of the soils was predominantly from acidic rocks (granite/rhyolite) except for two of the samples that were on the boundary between granite/rhyolite and granite/rhyolite + basalt fields as inferred from the TiO_2 vs Al_2O_3 diagram. With the trace and rare elements concentrations of the samples, Co, Ni, Rb, Sc, V, and Zn as compared with PAAS and UCC had corresponding or lower concentrations whereas Cr recorded corresponding or higher concentrations. Ba, As, Cs, and Zr had similar or concentrations slightly above that of UCC. Five of the samples had La concentrations lower than PAAS and UCC values, and all samples except two showed a drop in Ce concentrations. Nd concentrations for four of the samples were above that of PAAS and UCC. The outcome from the study was that, the trace and rare earth elements recorded low concentrations, and as such, may not pose any serious toxicity risk when ingested. However, key health concern demonstrated from the study were dental damage of the geophagic practitioners, abrasion of the gastro-intestinal tract and rupturing of the colon of the geophagic individuals in Swaziland. Similar study was conducted [11] at Democratic Republic of Congo (DRC). The results showed predominance of quartz and kaolinite in the samples. The major element concentrations were also compared to average upper continental crust (UCC) and average Post-Archaean Australian Shale (PAAS) by Taylor and McLennan [25]. SiO_2 concentrations in the sample were from 43.95 to 61.02 wt% and had a mean concentration of 54.18 wt%. Al_2O_3 concentrations were in range of 18.98 to 36.20 wt% with a mean of 26.25 wt%. MgO values were between 0.02 and 1.00 wt%, except for one sample mineralogically identified as talc, which had 32.64 wt%. Na_2O , K_2O and CaO recorded low concentrations. Fe_2O_3 concentrations were from 0.40 wt% for the sample containing talc to 13.12 wt% for the goethite containing sample. The samples recorded much lower concentrations of Na, Ca and K as compared to their concentrations in UCC and PAAS, signifying intense chemical weathering. The trace and rare earth elements in the samples were grouped into elemental enrichment (As, La, Nd, Sc and Sm), slight elemental enrichment (Cs, W, Yb and Zr), no changes in elemental concentrations (Ce, Cr, Ta and Th), both elemental enrichment and depletion (Hf and Rb), slight elemental depletion (Ba) and elemental depletion (Co, Ni, U and Zn) based on their concentrations in the UCC and PAAS. CIA values were in the range of 80.25 to 99.68% which depicted intense weathering except for one sample which contained no kaolinite. The CIW values were between 95.59 and 99.94%. Both CIA and CIW values recorded were higher than PAAS and UCC values. Provenance analysis was carried out using TiO_2 versus Al_2O_3 relation to chemically characterize the sediments. Five of the samples were of granite/rhyolite + basalt provenances and eight were predominantly from granite/rhyolite except for one sample which recorded very low TiO_2 and Al_2O_3 . Quartz and kaolinite were the dominant mineral phases present in the samples except for one sample in which talc dominated. The chemical constituents of the samples were SiO_2 and Al_2O_3 dominant. The source rocks identified were granite, rhyolite and basalt based on the high CIA and CIW values.

Al-Rmalli et al. [2] performed arsenic speciation analysis using HPLC (GP50 – 2 pump, Dionex, USA) coupled to an ICP-MS (Argilent Technologies, UK) on eight bags of sikor

samples originating from Bangladesh. The samples were openly sold in native Bangladeshi shops in the United Kingdom, and were bought from Birmingham, Leicester and Luton to analyse for As, Pb, Cd, Mn, Fe, and Zn concentrations. The speciation analysis of As from sikor samples by HPLC-ICP-MS showed that samples consist primarily of inorganic Arsenic with recoveries ranging from 31 to 37%, and that, this low recovery could be due to high Fe content in the samples, as Fe binds As strongly, which prevented its release under the extraction conditions. The relatively modest level of daily sikor intake alone recorded, not considering Arsenic intake from water and foods, was beyond the PMTDI for inorganic As by almost 1.9 times. The ICP-MS analysis of the sikor samples revealed the presence of a mixture of toxic elements (As, Cd and Pb). Sikor, from the outcome of the study, can be a significant source of As, Cd and Pb for the Bangladesh population consuming large quantities of this material, a particular concern raised on pregnant women practicing geophagy who were concurrently exposed to As contaminated drinking water. However, no work was done on the bioavailability of As and other elements from sikor and the impact of the sikor on human health.

Ekosse and Jumbam [9] randomly selected representative clay samples from Cameroon and Nigeria to identify the mineralogical makeup by both qualitative and quantitative means, analyse for some elements possibly associated with clay minerals, and to find out the toxicity potential in the geophagic clay samples in order to conclude on their possible effects on human health. Twelve samples were selected in all from markets in Bamenda, Kumba, Tiko, Limbe and Yaounde in Cameroon; and in Nigeria, from Ibadan and Lagos. Nine samples were selected from Cameroon and three from Nigeria. The samples were prepared before they were sent to the laboratory for analysis. X-ray diffractometry was used to identify the clay minerals in the samples except for one sample that XRPD analysis was employed because the sample was very small. The elemental analysis was carried out using ICP-MS on Rb, Ba, Sr, Sc, V, Cr, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Th and Pb. From the mineralogical analysis, six minerals comprising of three primary minerals and three secondary minerals were identified. The primary minerals were quartz, K-feldspar and mica (possibly muscovite), and secondary minerals: goethite, montmorillonitic smectite and kaolinite. Quartz and kaolinite dominated, having mean values of 63.6 wt% and 21.0 wt%, respectively for the samples from Cameroon; and from Nigeria were 65.3 wt% quartz and 30.0 wt% kaolinite. Based on the ICP-MS analysis, Rb recorded 1 ppm as the lowest and the highest was 136 ppm, with an average concentration of 50 ppm. With the alkali earth metals, Barium concentrations for the samples from Cameroon were between 480 and 950 ppm, with all the samples from Nigeria below 200 ppm, and all having mean concentration of 330 ppm. Strontium had concentrations between 66 and 98 ppm except for three samples which had less than 2 ppm, and with average concentration of 64 ppm. With the transition metals, Sc recorded lowest concentration of 6 ppm and highest of 28 ppm with a mean concentration of 18 ppm. Vanadium lowest and highest concentration in the samples were 81 and 176 ppm, respectively, with a mean of 84 ppm although Vanadium was absent in one. Cr and Co had

almost similar concentrations of below 10 ppm per sample except for two samples which recorded 28 and 78 ppm for both elements, with mean concentration of 1.5 ppm. Nickel concentrations at its highest were recorded in two of the samples as 120 and 159 ppm, respectively; and Cu, 58 and 49 ppm, respectively. Zn recorded lowest and highest concentrations of 50 ppm and 250 ppm, respectively, with mean concentration of 110 ppm. Y had lowest concentration of 18 ppm and 78 ppm was highest, and 49 ppm was its mean concentration. Zr concentrations in seven of the samples were 200 ppm each although recorded lowest concentration of 100 ppm whilst three samples recorded highest concentrations between 1100 ppm and 1160 ppm. The mean concentration was 436 ppm. The three samples of highest concentration values for Zr also had highest Nb concentrations of 180, 170 and 208 ppm. The lowest concentration was 18 ppm with mean concentration of 101 ppm. Molybdenum concentrations were in general very low, recording lowest and highest concentrations of 0.2 and 5.5 ppm, with a mean concentration of 3 ppm. The concentrations of Pb and Th were generally low and similar, having lowest concentration of 15 ppm and highest 30 ppm, with same mean concentration of 24 ppm. Based on the mineralogy results, the geophagic clays were concluded to be from secondary minerals of sedimentary origin. The mean elemental concentrations were generally low, which was referenced to the origin of the samples. The particle sizes of the studied clay was concluded to make them apt to form coatings in the gastro-intestinal tract when ingested, although the clay has some medicinal and nutritional values. However, not all were beneficial, other associated elements in the clay balls could lead to allied human health risks.

IV. THE MOTIVATION FOR REVIEW

Elements distributions and concentrations vary across the landscape and the geochemical affinities of the elements at a location under suitable temperature and pressure support the formation of rocks. Meanwhile, Arhin and Zango [4] consider rock as an aggregate of one or more minerals. This highlights the significance of knowing the provenance of the clays used as geophagic material. Clay can form from all rock types through the processes of chemical weathering. Reflection of minerals and elements in the underlying rocks will have relationship with the *in situ* clay with some elements introduction from the landscape positions of where the geophagic clays are taken from. Conversely, the transported clays may have different elements originating from diverse sources. However, as noted by Arhin and Zango [4], some of these elements are nutritionally important at certain concentration while others are not essential for human physiological functioning and development. There are some that are generally toxic to humans. These toxic elements are the causes of most health problems associated with geologic materials that are unknowingly used in geophagia [3, 4]. Most importantly, the toxicities or nutritional significance of elements in geophagic materials are dependent on the chemical composition, elements concentrations and mineralogical makeups. As noted by Mahaney et al. [20]; Hooda [16] and Wilson [28] is the health risks arising from the geophagic soils are a function of their geochemistry and mineralogy in the parent material. Geophagy is widely

practised in Ghana particularly in rural Ghana and most of the products are obtained from Mfensi-Adankwame. Most of the published articles on geophagy in Ghana look at the trace and heavy metal presence in relation to possible health consequences. None of the articles investigated the provenance and geochemistry of clays used in geophagia. Though, the mineralogical makeup and the chemical composition of the consumed materials are understood to have direct chemical relationship to the underlying rocks. Provenance studies carried out in other jurisdiction [9, 10, 11] led to recommendations of removing/reducing the presence of unwanted elements from the geophagic materials in order to make their ingestion safe for the practitioners. This review thus intends to promote similar investigations on provenance and geochemical studies in order to breakeven between the benefits and banes of geophagia and thus make the practice safe and attractive.

V. CONCLUSION

On the basis of the review outcome, the authors are suggesting the need to analyse the mineral contents and elemental constituents of geophagic materials from Mfensi-Adankwame in order to determine the provenance of the clay materials that are sundried moulded into balls and sold to the geophagist. Knowledge of the geochemistry of clays being used can aid to infer the likely adverse health effects that may develop on ingestion due to the concentration levels of the distributed elements in the geophagic materials on the geophagic individuals. The understanding of the provenance and geochemistry of clays used in the practice can lead to recommendation of removing or reducing some known toxic elements and minerals to make the practice safe and attractive.

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