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Mineralogy and Geochemistry of Geophagic Clays from Share Area, Northern Bida Sedimentary Basin, Nigeria

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Abstract

The Share area occurs within the northern Bida sedimentary basin in Nigeria. The focus is on the geological settings, mineralogical and chemical compositions of Share geophagic clays with the aim of inferring their depositional environments, provenance and possible human health implications. The field method include collection of representative samples at appropriate clay stratum and the samples of the geophagic clays were subjected to petrographic, X-Ray fluorescence and X-Ray diffraction analyses. XRD revealed that Geophagic clays are polymineralic and the main reflections of the clay minerals identified were kaolinite, nacrite, gibbsite and dickite. The peaks of other traces are hematite, quartz and pyrite. Geochemical data indicated that geophagic clays composed of SiO_2 content ranging from 64.40% to 46.30%, Al_2O_3 values varies from 36.54% to 20.54%, Fe_2O_3 values varies from 4.71% to 1.42%, MgO content varies from 0.08% to 0.06%, CaO ranges between 1.30% and 0.03%, TiO_2 values varies from 9.17% to 0.20%, and MnO content ranges from 0.631%. to 0.09%. These values indicate that the geophagic clays are essentially siliceous aluminosilicates.

The presence of sedimentary structures typical of tidal sedimentation, low abundance of MgO and K_2O indicate lack of expandable clays, and the presence of ironstones further attests to abundant oxygen due to sub aerial exposure resulting to the oxidation of Fe^{2+} to Fe^{3+}. The presence of basal conglomerate, rootlets structures, iron capping, fining upward sequence and abundances of kaolinite indicate a fluvial (continental) sedimentation. Geophagic clays may introduce metals like Fe, Zn, Cu, Ni, Ti, and Zr to the gastro-intestinal system of consumers, causing adverse effects like increase in the gastro-intestinal pH, and the binding of plant toxins and pathogens which create a surfacial coating on the stomach with inferred pharmaceutical implications. Negative impact of ingesting geophagic clays may lead to electrolyte disturbance, intestinal obstruction, constipation, hypertension, peritonitis, eclampsia, iron deficiency, anemia, microbiological infections, helminthiasis and heavy metal poisoning while coarse sandy quartz particles in the clays could affect dental enamel and also lead to the possible rupturing of the Sigmoid colon due to the abrasive nature of the particles.

Keywords: Aluminosilicate; Kaolinite; Hematite; Quartz; Continental and Granite

Introduction

Geophagia, the deliberate ingestion of earthy material by both animals and humans [1-3]. It is practiced by women of child bearing age in developing countries of Africa [4]. Geophagia has been reported in Nigeria, Uganda, South Africa and Swaziland on the African continent [1,2]. An underlying reason for geophagic practices being sustained in developing countries is that the geophagic materials are readily available at little or no cost. Geophagic materials have varied mineralogical and chemical compositions [5]. The materials are usually soils sediments that are clayey in particle size and contain at least one clay mineral as mineralogical constituent [2,6]. Women indulge in the practice because they believe in the relieving effects resulting from soil consumption, which include supplementation of minerals and nutrients and antacid, anti-emetic, and anti-diarrheal properties [4,7,8].

Clays are composed of mixtures of finer grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Clays and clay minerals are found mainly on or near the surface of the Earth [9]. Clay minerals in the earth crust can be used as indicators of the environment during weathering, allothi- and authi-genesis in the sediments and in the study of source area of the detrital supply [10]. In Nigeria, geophagy is almost synonymous with clay consumption and geophagia was reported in Share area, Odewumi [11] and Ibadan, Asaba, Benin City and Aramoko-Ekiti [12]. There is a very limited documentation of the geology, mineralogy and geochemistry of the geophagic clays in Nigeria. This paper's primary objective is to examine the geological settings, mineralogical and chemical compositions of geophagic clays from Share area, with the aim of inferring depositional environments, provenance and possible human health implications.

Geology and Petrography

The basal conglomerate was directly on the basement complex which comprises of gneisses and metasedimentary rocks that have been intruded by granites of probable Pan African (ca. 600Ma) age. Its composition and texture are clearly indicative of little or no textural/compositional maturation as viewed around NYSC Orientation Camp Yipata, Kwara State. These beds of conglomerate are interlayered with pebbles, clast size varies from granules to pebbles. Roundness is equally variable while perfectly rounded pebbles are mixed with angular ones. The fabric is isotropic, since no imbrications or any other mode of systematic clast arrangement is apparent. The conglomerate is mixed with sand grade which can be regarded as matrix supported. The quartz occurs as colourless, transparent and shows no cleavage.

Sandstone unit was observed along the Agbonna hill, size sorting is very poor and overlying the basal conglomerates. There is an extreme

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variation in the structural composition of the crystals, although there appear to be bimodal distribution. The depositional environment of the sandstones appears to fall in a mid-fan facies setting [13]. The monocrystalline grains are invariably sharp in extinction. The polycrystalline grains show undulose extinction, with the elongate crystals usually oriented parallel to each other. The grains are generally sub-rounded, inclusions in the quartz grains are mainly microlites, muscovite and euhedral zircon. The inner layer consists of euhedral quartz crystals which have grown into a core of loose, white and fine quartz sand. The microtexture of the sandstone grains range in size from 0.2 to 1.6mm i.e. fine to very coarse with an average of 0.55mm which is coarse. Quartz grains are present with very few feldspar.

Claystone occurs on the slopes of Agbonna hill within Share town and constitute the geophagic material. It overlies coarse sandstone and consists entirely of clay with hardly any silt, as shown by the absence of any gritty feel to the teeth. Rootlet structures were also observed in the claystone unit, the secondary structure is jointing and there is a profuse permeation of both beds by short tight joints in all directions. These have given rise to intense iron staining, presents as yellow and brown patches and fridges around the joints. In petrographic studies, the claystones have sheet structures and a single perfect cleavage, they are optically negative and the slow vibration direction which invariably lies in the plane of the single perfect cleavage. Ironstone is the fourth lithological unit that directly overlying the clay stone that is kaolin rich. The ironstone serves as the capping in Share area of northern Bida sedimentary basin.

Materials and Methods

The samples of Geophagic materials were collected at appropriate clay stratum in Share area of northern Bida sedimentary Basin. Eight samples of Geophagic clays from Share area were analyzed using XRD. The procedure was by preparing a strongly oriented specimen, air drying, grinding the natural sample and sucking it onto the flat surface of a porous tile disc. Mineralogical analysis was performed at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile Ife (Nigeria). X-ray diffraction patterns were obtained with a diffractometer equipped with Ni filtered Cu-kα radiation, with automatic slit and on-line computer control. The samples were scanned from 15° to 72° (2θ). Mineral identification on the diffractograms and a semi quantitative mineralogical composition were processed using EVA software. Measurements were performed on strongly oriented powder preparation from bulk samples.

X-Ray diffraction patterns registered for all the reflections correspond to each mineral. When the peaks are sufficiently separated from each other, their heights may be used to determine the orientation of a particular mineral in the mixture. Recognition of different peaks and comparison of their relative heights form the basis of clay mineral analysis by X-Ray diffraction [14]. In the study of clays, XRD method incorporates a means of identifying the different clay minerals forming the rock materials as well as measuring their individual orientation. The wavelength of 1.5406 was used to calculate the diffraction angles. The procedure used to prepare disc specimen produces a very highly oriented structure, greatly emphasizing the basal plane reflections 001 and 002, and reducing the edge reflection 020.

Eight samples of geophagic materials collected from the area were selected and cut into thin sections in the workshop of the Department of Geology, University of Ilorin, Ilorin (Nigeria). Petrographic studies of these thin sections were carried out using the transmitted light petrological microscope. The X-Ray fluorescence analyses comprising major oxides and trace elements of eight Geophagic clay samples were carried out at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile Ife (Nigeria).

To better characterize the geophagic materials, the chemical index of alteration (CIA, $[Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)]\times 100$) and chemical index of weathering (CIW, $[Al_2O_3/(Al_2O_3+CaO+Na_2O)]\times 100$) Harnois [15], values were calculated. In the CIA index the CaO is incorporated in the silicate structure [16]. The primary provenance of the geophagic materials was inferred from TiO_2 vs Al_2O_3 segregation diagram for granite, rhyolite and basalt [17].

Results

X-Ray diffraction patterns of Share Geophagic clays are shown in figures 1-4. The mineralogical compositions of the Share geophagic clays

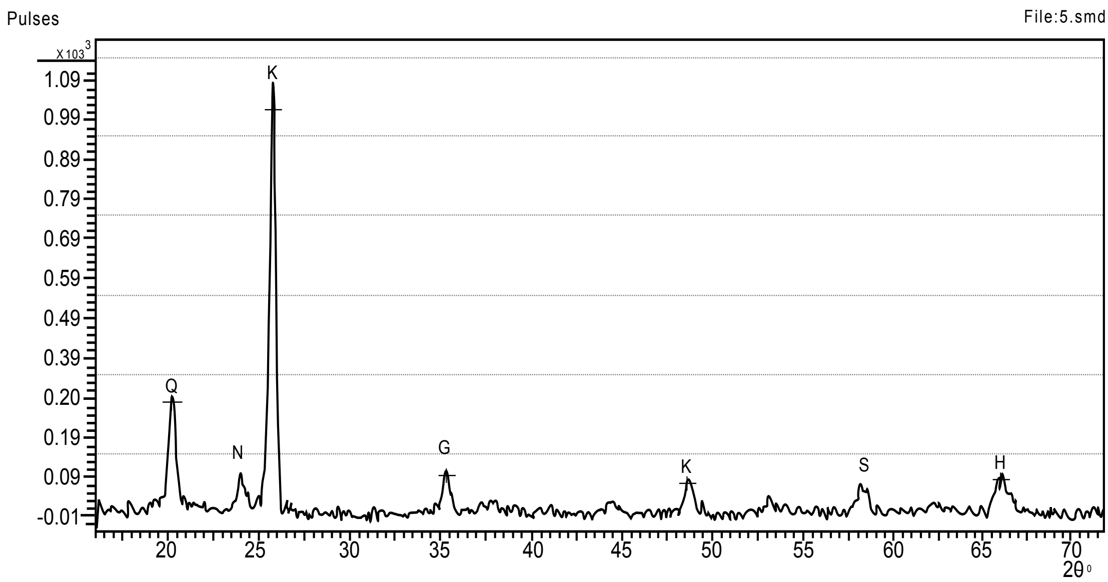

Figure 1: X-Ray diffraction traces for disc specimen of geophagic Clays (SG 1) (G=Gibbsite, K=Kaolinite, N=Nacrite, Q=Quartz, S=Sillimanite and H-Hematite).

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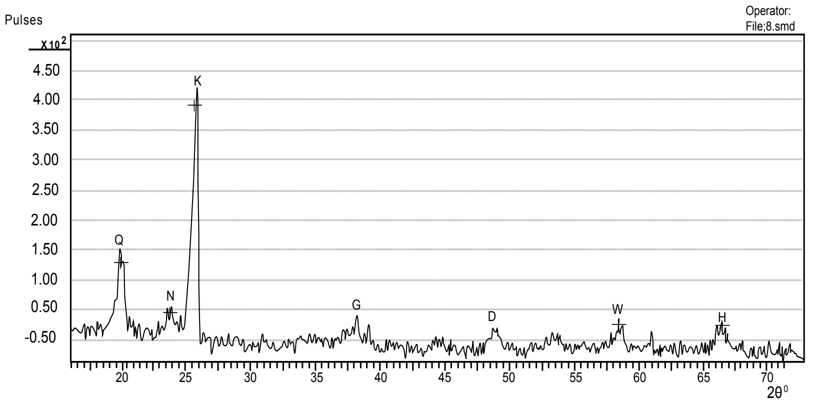

Figure 2: X-Ray diffraction traces for disc specimen of geophagic clays (SG 2) (K=Kaolinite, D=Dickite, N=Nacrite, Q=Quartz, G=Gibbsite, D=Dickite, H=Hematite and W=Wollastonite).

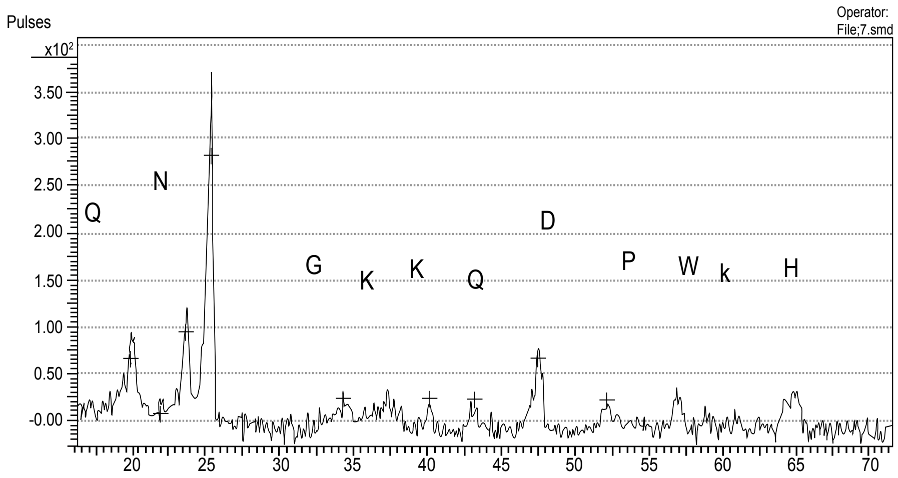

Figure 3: X-Ray diffraction traces for disc specimen of geophagic clay (SG 3) (K=Kaolinite, N=Nacrite, W=Wollastonite, Q=Quartz, P=Pyrite, D=Dickite, H=Hematite, G=Gibbsite and P=Pyrite).

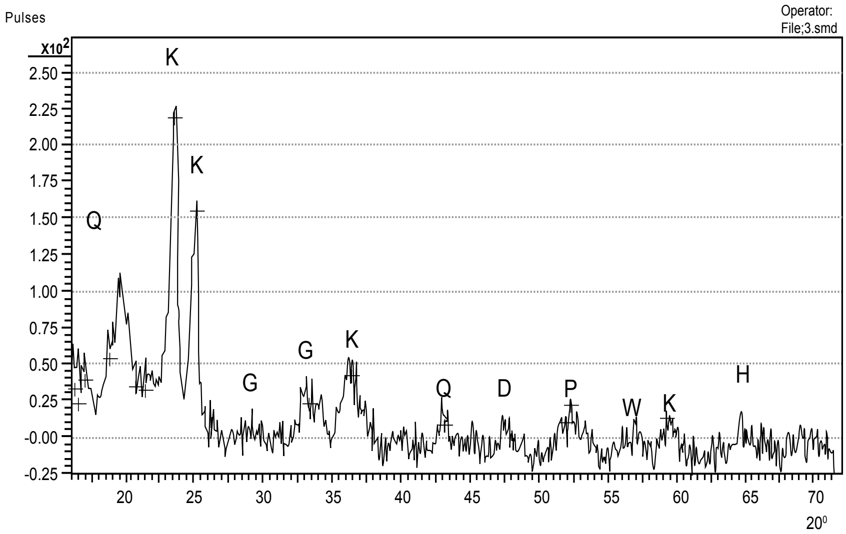

Figure 4: X-Ray diffraction traces for disc specimen of geophagic clay (SG 4) (K=Kaolinite, N=Nacrite, W=Wollastonite, Q=Quartz, P=Pyrite, D=Dickite, H=Hematite, G=Gibbsite and P=Pyrite).

is rather homogeneous and is mainly kaolinite associated with gibbsite, nacrite, dickite and quartz with small amounts of pyrite, sillimanite, wollastonite and hematite. The results in wt% of semi quantitative analysis of minerals identified in Share geophagic clays are shown in table 3. Iron in the geophagic clays is in the form of pyrite and/or hematite.

The result of the geochemical analysis as shown in table 1 indicate that the geophagic clays composed of SiO_2 content of 46.30% to 64.40%; Al_2O_3 values of 20.54% to 36.57%; $Fe_2O_{3(T)}$ values of 1.42 to 4.71%; MgO content of 0.06% to 0.08%; CaO values of 0.03 to 1.30%; TiO_2 values of 0.20 to 1.30%; K_2O values of 0.01 to 0.03%; MnO values of 0.09 to 0.631%. These concentrations suggest that the clays are hydrated siliceous aluminosilicate [18]. The relatively high Fe_2O_3 is probably due to superficial oxidation and contamination by the Fe-rich percolating water from the highly ferruginous facies capping the ridge. Low abundance of MgO and K_2O indicate lack of expandable clays.

Major Oxides (%)	SG 1	SG 2	SG 3	SG 4	HBC	PAAS	UC
SiO_2	60.30	64.40	62.88	46.30	-	62.80	66.00
Al_2O_3	21.62	20.54	22.60	36.57	-	18.90	15.20
$Fe_2O_{3(T)}$	4.71	1.42	2.57	1.56	3.00	6.5	4.5
MgO	0.06	0.06	0.07	0.08	-	2.2	2.2
CaO	1.30	0.03	0.04	0.07	0.10	1.3	4.2
TiO_2	0.20	1.31	0.30	0.92	0.20	1.0	0.5
K_2O	0.03	0.01	0.03	0.02	-	3.7	3.4
Na_2O	0.02	0.04	0.05	0.03	-	1.20	3.90
MnO	0.47	0.16	0.63	0.09	0.05	0.11	0.08
CIA	94.12	99.61	99.47	99.67	-	75.30	56.93
CIW	94.25	99.66	99.60	99.73	-	88.32	65.24
K_2O/ Na_2O	1.5	0.25	0.6	0.67	-	3.08	0.87
SiO_2/Al_2O_3	2.79	3.14	2.78	1.27	-	3.32	4.34
Trace Elements (ppm)							
Cu	3.0	7.0	6.0	8.0	1.0	-	-
Zn	31	89	104	157	33	85.0	71.0
Ni	39	98	26	124	0.1	55.0	20.0
Zr	210	411	185	610	0.3	21.0	190.0

SG1-4= Share Geophagic clays; HBC=Human Body content (FAO/WHO, 2001): PAAS=Post Archean Australian Shale and (UC) Upper Continental Crust [22].

Table 1: Chemical compositions of geophagic clays from Share area.

The chemical compositions of geophagic clays in Share area are compared with chemical compositions of Nigerian clays in Asaba, Aramoko-Ekiti, Ibadan and Benin [12]; Itakpe [19]; Isan Ekiti and Ara-Ijero [20]; Itu area [21]; Ubulu-Uku and Awo-Omama [18] in Nigeria as shown in table 2. The SiO_2 content of the Geophagic clays in Share area is higher than the SiO_2 content of clays in Asaba, Aramoko-Ekiti, Ibadan, Benin, Ubulu-Uku, Awo-Omama and Itakpe areas but lower than the SiO_2 content of clays in Ara Ijero and Itu areas. The values of Al_2O_3 is higher in Share Geophagic clays than clays from Isan-Ekiti, Ara-Ijero and Itu area but lower than the values of Al_2O_3 in other areas in Nigeria. The values of $Fe_2O_{3(T)}$ in Share geophagic clays is higher than the values of $Fe_2O_{3(T)}$ in Aramoko, Ibadan, Benin and Awo-Omama clays but lower than the values of $Fe_2O_{3(T)}$ of clays in other areas (Table 2). The values of other major oxides of Geophagic clays in Share area compared well with other clays in Nigeria with little variations.

Major oxide and trace element concentrations of the geophagic clays from Share area are compared to the average upper continental crust (UC) Taylor and McLennan [22] and the average Post-Archean Australian Shale (PAAS) Taylor and McLennan [22] as shown in table 1. Chemical composition of the Share geophagic clays, PAAS and UC showed predominance of SiO_2 and Al_2O_3; the value of SiO_2/Al_2O_3 ratio in Share geophagic clays ranges between 1.27 to 3.14 which is lower than SiO_2/Al_2O_3 ratio in PAAS (3.32) and UC (4.34). Geophagic clays showed high SiO_2/Al_2O_3 ratio which is also related to high quartz content. The concentrations of major oxides apart from Al and Si were generally very low reflecting very intense weathering of primary minerals [23].

Discussion

The CIA values obtained from the Share geophagic clays ranges from 94.12 to 99.67 (Table 1) and were higher than CIA values of 45 to 55 according to Depetris and Probst [24] are indicative of lack of weathering Samples with very high CIA values in the study area also have high kaolinite content (Figures 1-4). These CIA values are compared to the CIA value for the upper continental crust (56.93) and the CIA value for the Post Archean Australia Shale (75.30). This signifies occurrence of weathering in Share area. The CIW values of the geophagic clay samples ranges between 94.25 and 99.73 which were slightly higher than the CIW values of PAAS (88.32), but significantly

Oxides	SG	A	B	C	D	E	F	G	H	I	J	K
SiO_2	58.47	47.20	56.20	53.20	52.80	52.65	55.49	60.47	60.70	70.82	50.74	51.25
Al_2O_3	25.33	24.94	26.67	25.44	28.31	27.24	18.63	17.77	17.75	13.11	32.70	32.32
$Fe_2O_{3(T)}$	2.57	4.10	2.11	2.09	2.53	3.01	9.67	8.18	6.04	2.81	2.59	2.21
Na_2O	0.04	0.02	<0.01	0.28	0.03	0.37	0.46	0.44	0.23	0.07	0.06	0.06
K_2O	0.02	0.37	0.36	0.40	0.34	1.44	1.84	1.17	1.40	0.34	0.37	0.27
CaO	0.11	0.03	0.05	0.02	0.04	0.19	0.77	0.47	0.83	0.64	Tr	Tr
MgO	0.07	1.0	0.19	0.13	0.15	0.38	1.25	1.26	1.22	0.16	0.15	0.12
MnO	0.34	0.03	0.01	<0.01	<0.01	-	0.04	0.03	0.03	-	0.006	0.005
TiO_2	3.42	1.55	1.50	1.84	1.58	-	-	-	-	-	1.99	1.20

SG=Share area (average of 4 samples); A=Asaba, B=Aramoko, C=Ibadan, D=Benin Okunlola and Owoyemi [12]; E=Itakpe Okunlola [19]; F=Isan (Brown); G=Isan (Red); H=Ara Ijero Elueze and Bolarinwa [20]; I=Itu Elueze et al.[21]; J=Ubulu-Uku, K=Awo Omama Emofurieta et al. [18]

Table 2: Chemical compositions of Share Geophagic clays compared to some other clays in Nigeria.

Sample	hematite	nacrite	dickite	Quartz	Kaolinite	Gibbsite	sillimanite	wollastonite	Pyrite
SG1	2	Trace	-	25	70	3	Trace	-	-
SG2	5	4	9	20	60	2	-	Trace	-
SG3	5	13	12	18	45	2	-	3	2
SG4	2	2	25	20	45	6	-	Trace	trace

Table 3: Mineralogical compositions (wt.%) of semi quantitative analysis of Share geophagic clays.

higher than the CIW values of UC (65.24). Kaolinite is form in warm, moist regions as a residual weathering product or by hydrothermal alteration of feldspars while dickite and nacrite are normally restricted to hydrothermal occurrences [25]. Kaolinite, dickite and nacrite were identified in Share area and this indicates that the process of formation of geophagic clays could be by weathering and/or hydrothermal alteration.

Titanium concentration in geophagic clay samples ranges between 0.02 and 1.31wt%, this compared well with Titanium values of PAAS (1.00 wt.%) and UC (0.36 wt%). These concentrations of Ti in the geophagic clays were minute, would not be able to mineralize into neither anatase nor rutile (Table 1). Most of the TiO_2 in the geophagic clays could possibly be in the form of free Ti-oxides [26]. Some Ti may have substituted for Al in the octahedral sheet of kaolinite, knowing that no Al^{3+} substitution in the tetrahedral sheet would occur because the Al_2O_3 values in the geophagic clays (20.54 to 36.57 wt.%) is below the Al_2O_3 value for pure kaolinite 39.49 wt.%, [17].

The Share geophagic samples (SG 1-4) have a lower concentrations of Al_2O_3 (20.54-36.57 wt.%) than Al_2O_3 content (39.49 wt.%) of pure kaolinite while the SiO_2 content in the geophagic clays in Share area (54.55-64.44wt%) are higher than SiO_2 content (46.3 wt.%) of pure kaolinite. The Al_2O_3 and SiO_2 contents in this sample are not comparable to that of pure kaolinite. And this is indicative that during kaolinitization which involves the formation of hydrated minerals, predominantly kaolinite, quartz and other minerals were also incorporated from the weathering of underlying basement rocks.

The elemental composition of Geophagic clays in Share area are compared to the adequate daily intake of trace elements in the human body (as shown in Table 1), the trace element content of the geophagic clays in Share area is relatively high. The Cu content in the geophagic clays have a range of 3.0 to 8.0ppm while daily intake necessary for human body function is only 1.0ppm. The values of other trace elements like Zr (610-185ppm), Zn (31-157ppm) and Ni (26-124ppm) are higher than the values for daily intake necessary for human body function of Zr (0.3ppm), Zn (33ppm) and Ni (0.1ppm) respectively. The values of major oxides like $Fe_2O_{3(T)}$,TiO_2 and MnO are higher than the values needed for human body function (table 1). Share geophagic clays may introduce heavy metals like Fe, Zn, Cu, Mn, Ni, Ti, and Zr to the gastro-intestinal system of consumers, causing adverse effects like increase in the gastro-intestinal pH and the binding of plant toxins and pathogens which create a surfacial coating on the stomach with inferred pharmaceutical implications. This is similar to the report given by Ekosse et al. [27] on the Geophagia clays and soils from southern Africa.

This Geophagic clays may impact positively or negatively on human health when ingested. Kaolin (kaolinite, nacrite, gibbsite and dickite) can be used to treat diarrhea, gastritis, colitis, enhancement bio-activities and maintenance of normal intestinal flora. Negative impact may lead to electrolyte disturbance, intestinal obstruction, constipation, hypertension, peritonitis, eclampsia, iron deficiency, anemia, microbiological infections, helminthiasis and heavy metal poisoning [1,9]. The coarse sandy quartz particles in geophagic clays could affect dental enamel and also lead to the possible rupturing of the Sigmoid colon due to the abrasive nature of the particles [10].

The presence of sedimentary structures typical of tidal sedimentation, the presence of ironstones further attests to abundant oxygen due to sub-aerial exposure resulting to the oxidation of Fe^{2+} to Fe^{3+}. The presence of basal conglomerate, rootlets structures, iron capping, fining upward sequence and abundances of kaolinite indicate a fluvial (continental) sedimentation [28-30]. Similar kaolinite clay minerals were also reported by Mucke et al. [31], in Lokoja area of Middle Niger Embayment (southern Buda basin) indicating that the environment is not fully marine.

The absence of any marine fossils and clay minerals like illite, smectite, montmorrillonite and chlorite which were not identified in the mineralogical composition of geophagic clays. According to Fagel et al. [32], these clay minerals will correspond to trends register in most marine sediments. This further attest to non-marine depositional environment in Share area. Mineralogically, non-marine clays are characteristically less altered during diagenesis and they lack magnesia, lime and alkalies as observed in the area.

Thus, information on provenance of geophagic clays could provide clues on type of parent materials from which they were derived. The TiO_2 vs Al_2O_3 diagram figure 5; Ekosse [17] indicated that the provenance of the Share geophagic clays were predominantly from acidic rocks, as they plot in the granite/rhyolite field. The sediment provenance could thus be attributed to the granitic rocks from Share area which constitutes part of the Precambrian basement complex of southwestern Nigeria [11].

Conclusion

Geophagic clays in the area are polymineralic and the patterns of the clay minerals identified could be attributed to kaolinite, nacrite, gibbsite and dickite. The presence of basal conglomerate, rootlets structures, iron capping, fining upward sequence, abundances of kaolinite, low abundance of MgO and K_2O, the presence of hematite, pyrite and sedimentary structures typical of tidal sedimentation indicate non-marine depositional environment. The presence of ironstones further attests to abundant oxygen due to sub-aerial exposure resulting to the oxidation of Fe^{2+} to Fe^{3+}. This is typical of fluvial (continental) sedimentation.

The CIA values obtained from the Share geophagic clays were very high, ranges between 94.12 to 99.67 and exceeds the CIA values of 45-55 that indicate lack of weathering. The CIW values of the geophagic clay samples ranges between 94.25.99 to 99.73 which were slightly higher than the CIW values of PAAS (88.32), but significantly higher

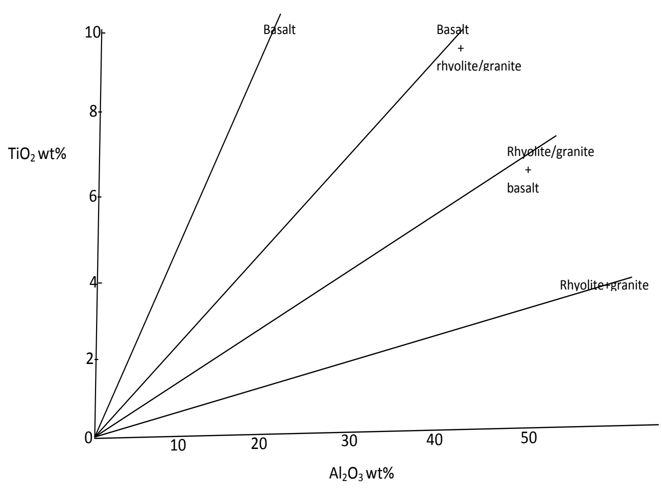

Figure 5: TiO_2 vs Al_2O_3 binary plot of geophagic clay samples from Share area Ekosse [17].

than the CIW values of UC (65.24). This is indicative that the process of formation of geophagic clays in Share area could be by weathering and/or hydrothermal alteration. The provenance of the Share geophagic clays indicated that they were derived predominantly from acidic rocks (granite/rhyolite). The sediment provenance could thus be attributed to the granitic rocks from Share area which constitutes part of the Precambrian Basement Complex of southwestern Nigeria.

The geophagic clays could be beneficial or harmful, kaolin can be used to treat diarrhea, gastritis, colitis, enhancement of bio-activities and maintenance of normal intestinal flora. Harmful effects may lead to electrolyte disturbance, intestinal obstruction, constipation, hypertension, peritonitis, dental damage, eclampsia and iron deficiency. These geophagic clays may introduce metals like Fe, Zn, Cu, Mn, Ni, Ti, and Zr to the gastro-intestinal system of consumers causing adverse effects like increasing the gastro-intestinal pH and the binding of plant toxins and pathogens, and creating a surfacial coating on the stomach with inferred pharmaceutical implications.

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