GEOCHEMICAL AND MINERALOGICAL COMPOSITIONS OF GEOPHAGIC CLAYS FROM TERMINUS AND NEW MARKET, JOS, PLATEAU STATE, NIGERIA.

Supported by tetfund

Odewumi Shola Christopher, Dihis Chamun Istifanus and Idris Amina Abubakar
Department of Science Laboratory Technology, University of Jos, Jos, Nigeria
Corresponding author: scodewumi@gmail.com

Received: September 14, 2023 Accepted: November 28, 2023

Abstract: This research focuses on geochemical and mineralogical compositions of geophagic clays from Terminus and New Market, Jos, northcentral Nigeria. A total of four (4) geophagic clay samples were collected with two (2) samples each from Terminus and New markets. The geophagic clays were subjected to X-ray fluorescence spectrometry (XRF) and X-Ray diffraction (XRD) analyses. The elemental compositions of geophagic clays shows that Fe ranges from 3.55 to 5.18 wt%, Cr varies from 605.70 to 631.70 ppm, Sr ranges from 501.30 to 717.50 ppm, Mn varies from 0.88 to 3630.00 ppm, Rb varies from 74.80 to 164.70 ppm, Nb varies from 141.80 to 181.70 ppm, Ta ranges from 20.00 to 37.75 ppm, Th varies from 67.20 to 81.60 ppm and Sn ranges from 175.90 to 227.70 ppm respectively. Higher values of Cu (21.60 - 67.20 ppm), Zn (63.00-131.30ppm), Ni (69.50-75.30ppm), Zr (1030.00-1310.00), Pb (152.70-199.00), As (3.40-22.80) and V (1100.00-1170.00ppm) in the geophagic clays samples than the values of Cu (1.0 ppm), Zn (33 ppm), Ni (0.1 ppm), Zr (0.3 ppm), Pb (100 ppm), As (10 ppm) and V (1000 ppm) needed daily necessary for human body function of FAO/WHO indicate higher heavy metal concentrations in geophagic clays that may be detrimental to the health of the consumers. The mineralogical compositions of geophagic clays shows that quartz ranges from 58.20 to 63.30%, kaolinite ranges from 15.10 to 21.30%, orthoclase ranges from 9.30 to 12.30%, albite varies from 0.70 to 8.80 and chlorite varies from 2.50 to 6.40%, The high percentage of kaolinite suggests K-feldspar while presence of chlorite suggests biotite as part of the mineralogical compositions of the protoliths. The occurrence of chlorite and kaolinite in geophagic clays attest to hydrothermal alteration of the granitic protoliths. The high percentage of quartz, K-feldspar, orthoclase, biotite and albite in the geophagic clays could be attributed to granitic protoliths.

Keywords: clays, geophagic, protolith, provenance and granites

Introduction

Geophagia, the deliberate ingestion of earthy material by both animals and humans (Abrahams and Parsons, 1997; Ekosse et. al., 2010; Geissler et al., 1998; Odewumi, 2013). Women indulge in the practice because they believe in the relieving effects resulting from soil consumption, which include supplement of minerals and nutrients and antacid, anti-emetic, and anti-diarrheal properties (Ekosse et al., 2010; Brand et al., 2010; Kawai *et. al*., 2009). Clay and earthy substances are used by native doctors to cure various diseases in Nigeria (Bisi-Johnson et al., 2010). In Nigeria, Tiv tribe believe that craving for soil by women is a sign of pregnancy and geophagia was reported in Share area (Odewumi 2011); and Ibadan, Asaba, Benin City and Aramoko-Ekiti (Okunlola and Owoyemi, 2011).

Geophagic materials have varied mineralogical and chemical compositions (Ferrell, 2008; Ekosse *et. al*., 2010; Ngole *et. al*., 2010). Most clay minerals form where rocks are in contact with water, air or steam. The origin of clays and clay minerals is governed principally by protore rocks, climate, relief and time (Blum and Stillings, 1995; Buggle et al., 2011). The primary minerals are replaced by the secondary minerals when there is a change in the prevailing conditions subjected to the rock. The hydrothermal fluids cause hydrothermal alteration of rocks by passing hot water fluids through the rocks and changing their composition by adding, removing or redistributing components (Eberl, 1984; Konta, 1995).

Several researches have been carried out on clays in Jos such as mineralogical Characteristics of Nahuta Clay (Odewumi, 2016); Chemical Weathering Indices and Geochemical climofunctions of Kuba Clay, (Odewumi et al., 2016); Trace elements geochemistry of Kuba (Major porter) and Nahuta clays (Odewumi, 2015). The geological Settings and Geochemistry of Younger Granitic rocks from Jos was reported by Odewumi (2020). The preliminary Paleoclimatic Assessment and Geochemical Weathering Characteristics of Isan clays (Odewumi, 2019) and Major, trace and rare earth elements geochemistry of Isan clays (Odewumi and Adekeye, 2020) indicated that the clays were derived from granitic rocks of southwestern Nigeria (Odewumi et al., 2012)

The study area is located in Terminus Market and New Market in Jos North Local Government Area of Plateau State as shown in Figure 1. The present study focuses on geochemical and mineralogical compositions of geophagic clays from Terminus and New Markets, Jos, northcentral Nigeria.

Figure 1: Map of Plateau State showing Jos-North LGA.

Figure 2: Geophagic clay samples from terminus market.

Materials and Methods

Four (4) geophagic clay samples were collected with two (2) samples each from Terminus Market and New Market in Jos-North Local Government Area of Plateau State, Nigeria. The geophagic clay samples from terminus market are shown in Figure 2. The clay samples were dried at room temperature; it was then grinded with agate mortar and pestle. Fifty (50) grams of the samples was weighed and shipped to Nigerian Geological Survey Agency, Kaduna State. Nigeria for XRF and XRD analyses

Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer of model "Epsilon 4" by PanAlytical was used for the analysis. Twenty (20) grams of the prepared sample was weighed each into a sample cup. The cups with the contents were carefully placed in their respective measuring positions on a sample changer of the machine. The following condition sets were made as the machine was switched on: Elemental composition determination; Nature of the samples to analyzed as lose powder; The current used as 14kv for major oxides, 20kv for the trace elements/rare earth metals and Selected filters were "kapton" for major oxides, Ag/Al-thin for the trace elements/rare earth metals.

The selection of filters was guided by a given periodic table used for elemental analysis. Time of measurement for each sample was 100 seconds and the medium used was air throughout. The machine was then celebrated by the machines gain control, after which the respective samples were measured by clicking the respective positions of the sample changer.

Loss of ignition (LOI) was determined gravimetrically by heating 1g of the powdered sample in a cleaned weighed crucible at 1000^{o}C. After which the crucible and the content was weighed to get the difference in weight before and after heating. 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 0° to 70° (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. 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.

Results

The geochemical compositions of geophagic clay are presented in Table 1 and some selected elements of geophagic clays with their comparism with WHO 2001 are presented in Table 2 while Table 3 shows the mineralogical compositions of geophagic clays. Figure 3 shows mineralogical compositions of geophagic clays from New Market 1 and Figure 4 shows mineralogical compositions of geophagic clays from New Market 2 while Figure 5 shows mineralogical compositions of geophagic clays from Terminus Market 1 and Figure 6 shows mineralogical compositions of geophagic clays from Terminus Market 2

The elemental compositions of geophagic clays shows that V ranges from 1100.00 to 1180.00 ppm, Cr varies from 605.70 to 631.70 ppm, Cu varies from 39.00 to 67.20 ppm, Sr ranges from 501.30 to 717.50 ppm, Zr ranges from 1060.00 to 1310.00 ppm, Mn varies from 0.88 to 3630.00 ppm, Zn varies from 63.00 to 131.30 ppm, Pb varies from 152.70 to 199.00 ppm, Fe ranges from 3.55 to 5.18 wt%, Br varies from <0.001 to 13.90 ppm, As ranges from 3.40 to 22.80 ppm, and Y varies from 103.20 to 154.50 ppm. Ni ranges from 69.50 to 75.30 ppm, Rb varies from 74.80 to 164.70 ppm, Nb varies from 141.80 to 181.70 ppm, Ta ranges from 20.00 to 37.75 ppm, W varies from 5.65 to 6.70 ppm, Hf ranges from 8.00 to 52.00 ppm, Th varies from 67.20 to 81.60 ppm and Sn ranges from 175.90 to 227.70 ppm respectively (Table 1).

The values of Ce, Cs, Mo, Cd, Se, U, Sb and Ge in the geophagic clay samples were less than 0.001 ppm (Table 1). From the mineralogical compositions of geophagic clays (Table 3), the percentage composition of quartz ranges from 58.20 to 63.30%, kaolinite ranges from 15.10 to 21.30%, chlorite varies from 2.50 to 6.40%, orthoclase ranges from 9.30 to 12.30% and albite varies from 0.70 to 8.80%.

Table 1: Geochemical compositions of geophagic clays from Terminus and New Markets

Elements (ppm)	New Market 1	New Market 2	Terminus Market 1	Terminus Market 2
V	1180.00	1170.00	1130.00	1100.00
Cr	631.70	631.20	605.70	619.20
Cu	21.60	67.20	39.00	50.80
Sr	558.200	501.300	717.500	641.500
Zr	1030.00	1310.00	1060.00	1270.00
Mn	16.700	3630.00	0.88	43.30
Zn	63.00	65.30	68.80	131.30
Ce	<0.001	<0.001	<0.001	<0.001
Pb	152.70	153.60	157.10	199.00
Fe	3.74 (%)	5.18 (%)	3.55 (%)	4.71 (%)
Br	<0.001	13.90	11.20	9.90
As	11.50	22.80	11.50	3.40
Cs	<0.001	<0.001	<0.001	<0.001
Y	154.50	103.20	154.30	139.00
Ni	75.30	69.50	72.30	69.90
Rb	95.90	74.80	99.00	164.70
Mo	<0.001	<0.001	<0.001	<0.001
Cd	<0.001	<0.001	<0.001	<0.001
Nb	142.20	159.20	141.80	181.70
Ta	20.00	23.450	30.800	37.750
W	5.990	6.700	5.650	6.050
Hf	8.00	10.80	34.80	52.00
Se	<0.001	<0.001	<0.001	<0.001
U	<0.001	<0.001	<0.001	<0.001
Th	72.700	74.100	67.200	81.600
Sb	<0.001	<0.001	<0.001	<0.001
Ge	<0.001	<0.001	<0.001	<0.001
Sn	183.900	175.900	188.700	227.700

LLD = 0.001ppm

Table 2: Selected elements of geophagic clays from Terminus market and New market with their comparism with WHO 2001.

Trace elements (ppm)	New market 1	New market 2	Terminus market 1	Terminus market 2	HBC FAO/WHO 2001
Fe	3.74 (wt%)	5.18 (wt%)	3.55 (wt%)	4.71 (wt%)	3.00
Mn	16.700	3630.00	0.88	43.30	50
Cu	21.600	67.200	39.00	50.800	1.0
Zn	63.00	65.300	68.800	131.300	33
Ni	75.30	69.500	72.300	69.900	0.1
Zr	1030.00	1310.00	1060.00	1270.00	0.3
Pb	152.700	153.600	157.100	199.00	100
As	11.500	22.800	11.500	3.400	10
Cd	<0.001	<0.001	<0.001	<0.001	20
V	1180.00	1170.00	1130.00	1100.00	1000

Table 3: Mineralogical Compositions (wt.%) of Geophagic Clays from terminus and New Markets

Sample	Quartz	Kaolinite	Chlorite	Orthoclase	Albite
Terminus Market 1	60.40	21.30	6.40	12.00	0.70
Terminus Market 2	62.80	19.80	5.70	9.30	3.00
New Market 1	58.20	21.20	2.50	9.70	8.80
New Market 2	63.30	15.10	2.80	12.30	7.04

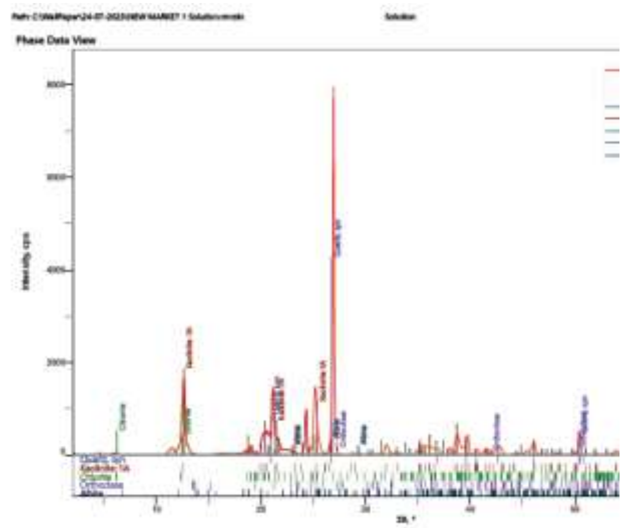

Figure 3: Mineralogical compositions of geophagic clays from New Market 1

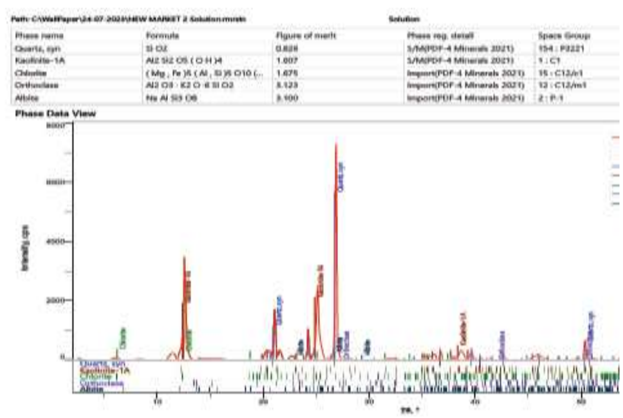

Figure 4: Mineralogical compositions of geophagic clays from New Market 2

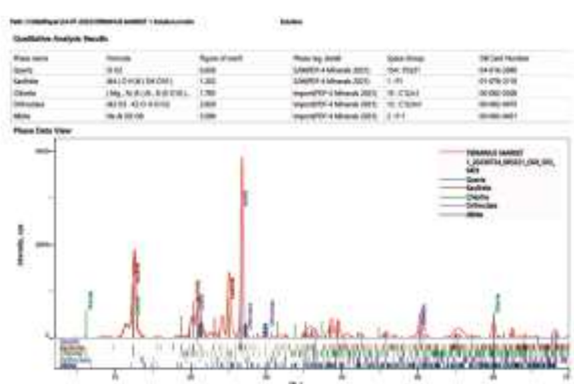

Figure 5: Mineralogical compositions of geophagic clays from Terminus Market 1

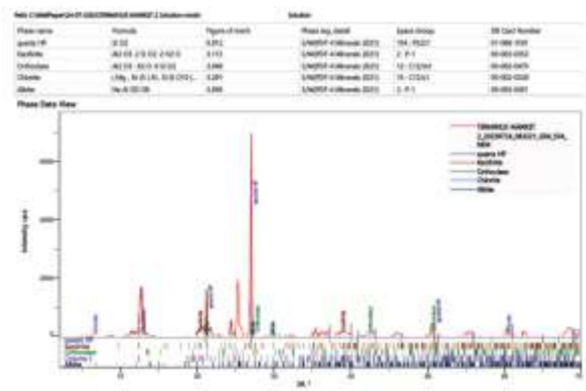

Figure 6: Mineralogical compositions of geophagic clays from Terminus Market 2

Discussion

The heavy metal concentrations of geophagic clays were compared with permissible limits of FAO/WHO 2001 as presented in Table 2. The Cu content in the geophagic clays have a range of 21.60 to 67.20 ppm while daily intake necessary for human body function is 1.0 ppm. The value of Zn in geophagic clays ranges from 63.00 to 131.30 ppm while daily intake necessary for human body function is 33 ppm, Ni content in geophagic clays varies from 69.50 to 75.30 ppm while daily intake necessary for human body function is 0.1 ppm, Zr value in geophagic clay varies from 1030.00 to 1310.00 ppm while daily intake necessary for human body function is 0.3 ppm.

The Pb value in geophagic clay ranges from 152.700 to 199.00 ppm while daily intake necessary for human body function is 100 ppm, As content in geophagic clay ranges from 3.40 to 22.80 ppm while daily intake necessary for human body function is 10 ppm, the V value of geophagic clay ranges from 1100.00 to 1170.00 ppm while daily intake necessary for human body function is 1000 ppm and Cd value in geophagic clay is <0.001ppm while daily intake necessary for human body function is 20 ppm. The Fe (3.55 to 5.18%) and Mn (0.88 to 3630.00) values in geophagic clays were higher than daily intake necessary for human body function of Fe (3.00pp) and Mn (50ppm) respectively.

Higher values of Fe (3.55 - 5.18%), Mn (0.88 - 3630.00), Cu (21.60 - 67.20 ppm), Zn (63.00 - 131.300ppm), Ni (69.50 - 75.30ppm), Zr (1030.00 - 1310.00), Pb (152.70 - 199.00), As (3.40 - 22.80) and V (1100.00 - 1170.00ppm) in the geophagic clays samples than the values of Fe (3.00ppm), Mn (50ppm), Cu (1.0ppm), Zn (33ppm), Ni (0.1ppm), Zr (0.3ppm), Pb (100ppm), As (10ppm) and V (1000ppm) that were needed daily necessary for human body function indicate higher heavy metal concentrations in geophagic clays that may be detrimental to the health of the consumers. The geophagic clays may introduce metals like Fe, Mn, Cu, Zn, Ni, Zr, Pb, As and V to the gastro-intestinal system of consumers causing adverse effects.

The high concentration of quartz (58.20 - 63.30%), orthoclase (9.30 - 12.30%) and albite (0.70 - 8.80%) in the geophagic clays suggest provenance that could thus be attributed to the granitic rocks from Jos Plateau. This is similar to the report of Odewumi (2016) on Nahuta clay in Jos where the presence of kaolinite, illite, quartz and albite indicate felsic rocks as the predominant protoliths of Nahuta clay.

Kaolinite could be derived through hydrothermal alteration and/or weathering of K-feldspar in the protoliths. Kaolinites are formed in warm, moist regions as a residual weathering product or by hydrothermal alteration of feldspars (Duane and Robert, 1997). Kaolinite (15.10 - 21.30%) in the geophagic clays suggests that geophagic clays were either formed from weathering or hydrothermal alteration of feldspars and this indicates that kaolinite are derived from K-feldspar content of granitic rocks (Nesbitt and Young, 1982, 1984; Konta, 1995). Kaolinite occurs in all the geophagic clay samples with percentage compositions of 15.10 to 21.30% indicates that kaolinite in geophagic clay are derived from K-feldspar of granitic rocks.

The occurrence of chlorite (2.50 - 6.40%) in geophagic clays further attests to hydrothermal alteration of the protoliths because chlorites are produced only through metamorphism or hydrothermal alterations (Duane and Robert, 1997). The presence of chlorite is an indication that biotite was contained in the mineralogical composition of the protoliths which could be attributed to granitic rocks

The presence of quartz, orthoclase, albite and kaolinite indicate felsic sources of geophagic clays. The high percentage of kaolinite (15.10 - 21.30%) and orthoclase (9.30 - 12.30%) in mineralogical composition of geophagic clays indicate high percentage of K-feldspar in the protoliths which is a major characteristic of the granitic protoliths. According to Odewumi (2016) on Nahuta clays, the percentage composition of illite indicates abundance of muscovite and/or K-feldspar

The black clay in the Sabon Gida mine was reported to have originated from the feldspars in the biotite granite of the Jos-Bukuru granite Complex by chemical weathering of minerals containing Al and Si, chiefly feldspar (Kogbe, 1979; Antolimi, 1967).

Conclusion

The high percentage of kaolinite and orthoclase in mineralogical composition of geophagic clays indicate high percentage of K-feldspar in the protoliths which is a major characteristic of the granitic protoliths. The high concentration of quartz, kaolinite, orthoclase and albite in the geophagic clays suggest provenance that could be attributed to granitic rocks

Higher values of Fe, Mn, Cu, Zn, Ni, Zr, Pb, As and V in the geophagic clays samples than the values needed daily for human body function indicate higher concentrations of heavy metals in geophagic clays that may be detrimental to the health of the consumers and geophagic clays may introduce metals like Fe, Mn, Cu, Zn, Ni, Zr, Pb, As and V to the gastro-intestinal system of consumers causing adverse effects.

Refference

Abrahams, P.W. and Parsons, J.A., (1997). Geophagy in the tropic: an appraisal of three Geophagic materials. *Environmental Geochemistry and Health*, 19: 19–22.

Antolimi, P. (1967). Report on a preliminary investigation of clay on the Plateau. Geological Survey of Nigeria. Unpub. Report, No. 145.

Bisi-Johnson, M.A., Obi, C.L. and Ekosse, G.E. (2010). Microbiological and health related Perspectives of geophagia: an overview. *African Journal of Biotechnology*, 9(19): 5784-5791.

Blum, A. E. and Stillings, L. L. (1995). Feldspar dissolution kinetics. *In Chemical Weathering Rates of Silicate Minerals (ed. A. F. White and S. L. Brantley), Mineral. Soc. Amer,* 31, 291–346.

Brand, C.E., de Jager, L. and Ekosse, G.E. (2010). Possible health effects associated with Human geophagic practice: an overview. *South African Medical Technology*, 23(1): 11–13.

Buggle, B., Glaser, B., Hambach, U., Gerasimenko, N. and Markovič, S.B. (2011). An Evaluation of geochemical weathering indices in loess-paleosol studies. *Quaternary International*, 240, 12–21

Duane, M.M. and Robert, C.R. Jr. (1997). X-Ray Diffraction and the Identification and Analysis of Clay Minerals (eds). *Oxford New York, Oxford University Press*, 138-155.

Eberl, D.D. (1984). Clay mineral formation and transformation in rocks and soils. *Philosophical Transactions of the Royal Society of London*, A31, 241-257,

Ekosse, G.E., de Jager, L. and Ngole, V.M. (2010). Traditional mining and mineralogy of Geophagic clays from Limpopo and Free State Provinces, South Africa. *African Journal of Biotechnology*, 9(47): 8058–8067.

Ferrell Jr., R.E. (2008). Medicinal clay and spiritual healing. *Clays and Clay Minerals*, 56(6): 751–760.

Food and Agricultural Organization/World Health Organization (2001). Food additives and contaminants. *Joint FAO/WHO Food Standards Programme Alinorm,(*01/12A): 1-289.

Geissler, P.W., Mwaniki, D., Thiong O, F. and Friis, H. (1998). Geophagy as a risk factor for geohelminth infections: a longitudinal study of Kenyan primary schoolchildren. *Transactions of the Royal Society of Tropical Medicine and Hygiene*, 92(1): 7–11

Kawai, K., Saathoff, E., Antelman, G., Msamanga, G. and Fawzi, W.W. (2009). Geophagy (soil-eating) in relation to anemia and helminth infection among HIV-infected pregnant women in Tanzania. *The American Journal of Tropical Medicine and Hygiene,* 80 (1): 36–43.

Kogbe, C.A. (1979). Mineralogical analysis of the Greyish-Black Clay in Sabon Gida Mine (Jos -Plateau). *Journal of Mining and Geology,* 15, 20-27

Konta, J. (1995). Clay and Man: Clay raw materials in the service of man. *Applied Clay Science,* 10, 275-335

Nesbitt, H.W. and Young, G.M. (1982). Early Proterozoic climates and plate motions Inferred from major element chemistry of luttites. *Nature,* 291 : 715–717.

Nesbitt, H. W. and Young, G. M. (1984). Prediction of some weathering trends of Plutonic and Volcanic rocks based on thermodynamic and kinetic considerations. *Geochimica et Cosmochimica Acta*, 48, 1523-1534.

Ngole, V.M., Ekosse, G.E., de Jager, L. and Songca, S.P. (2010). Physicochemical characteristics of geophagic clayey soils from South Africa and Swaziland. African.*Journal of Biotechnology,* 9(36): 5929–5937

Odewumi, S.C. (2011). Mineralogical Characterization of Clays and Clay Mineral in Share area, Bida Sedimentary Basin Nigeria. *In Ekosse G-I E, de Jager L and Ngole V.M (Editors). An innovative Perspective on the role of Clays and clay minerals in Africa. Book of Conference Proceedings. Central University of Technology, Bloemfontein, South Africa,* 72-79

Odewumi, S. C., Adekeye, J. I. D. and Ojo, O. J. (2012). Petrogenesis and geotectonic settings of the granitic rocks of Idofin-Osi-Eruku area, southwestern Nigeria using trace element and rare earth element geochemistry. *African Journal of Natural Sciences*. 15: 39-51.

Odewumi, S. C. (2013). Mineralogy and Geochemistry of Geophagic Clays from Share area, Northern Bida Sedimentary Basin, Nigeria. *African Journal of Natural Sciences.* 16: 87-98.

Odewumi, S. C., Adekeye, J. I. D. and Ojo, O. J. (2015). Trace and rare earth elements geochemistry of Kuba (Major porter) and Nahuta clays, Jos Plateau, northcentral Nigeria: Implications for Provenance. *Journal of Mining and Geology*, 51 (1): 71-82.

Odewumi, S. C. (2016). Mineralogical Characteristics of Nahuta Clay, Jos Plateau, Northcentral Nigeria: Implications for Hydrothermal Alterations. *Journal of Environmental Sciences,* 17 (1 & 2): 87-96.

Odewumi, S. C., Ojo, O. J. and Adekeye, J. I. D. (2016). Chemical Weathering Indices and Geochemical climofunctions of Kuba Clay, Jos Plateau, northcentral Nigeria: Implications for Paleoclimatic Proxy. *Journal of Mining and Geology,* 52 (1): 19-27.

Odewumi, S. C. (2019). A Preliminary Paleoclimatic Assessment and Geochemical Weathering Characteristics of Isan clays southwestern Nigeria: Implications for Palaeoweathering Proxy. *African Journal of Natural Sciences*, 22: 41-56.

Odewumi, S. C. and Adekeye, J. I. D. (2020). Major, trace and rare earth elements geochemistry of Isan clay, southwestern Nigeria: Implications for Provenance. *Journal of Mining and Geology*, 56 (2): 223-230.

Odewumi, S. C. (2020). Geological Settings and Geochemistry of Younger Granitic rocks from Kuba area, Ropp Complex, northcentral Nigeria. *FUPRE Journal of Scientific and Industrial Research,* 4 (2): 9-21.

Okunlola, O.A. and Owoyemi, K.A.(2011). Compositional characteristics of Geophagic clays of southern Nigeria. In Ekosse G-I E, de Jager L and Ngole V.M (Editors). *An innovative Perspective on the role of Clays and clay minerals in Africa. Book of Conference Proceedings. Central University of Technology, Bloemfontein, South Africa*, 290-303