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# Mineralogical and geochemical aspects of geophagic clayey soils from the Democratic Republic of Congo

G. E. Ekosse<sup>1</sup>\*, V. M. Ngole<sup>2</sup> and B. Longo-Mbenza<sup>3</sup>

<sup>1</sup>Research Development, Walter Sisulu University, P/Bag XI Mthatha 5117, Eastern Cape, South Africa. <sup>2</sup>Faculty of Science Engineering and Technology, Walter Sisulu University, P/Bag XI Mthatha 5117, Eastern Cape, South Africa.

<sup>3</sup>Faculty of Health Sciences, Walter Sisulu University, P/Bag XI Mthatha 5117, Eastern Cape, South Africa.

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Clayey soil samples ingested by the people of the Democratic Republic of Congo (DRC) were obtained in their physical state of ingestion, from selected localities in the country. The particle size, minerals contents and geochemical composition of the samples were determined in order to establish baseline information on mineralogy and geochemistry of geophagic soils in DRC. The geophagic clayey soils were whitish, light grayish to brownish in colour and their textures were silt, silt loam, silty clay loam and silty clay. From X-ray diffractometry analysis, the following twelve minerals were identified in the samples: quartz and kaolinite being the most dominant, followed by muscovite, and others in minor to trace being talc, microcline, goethite, haematite, siderite, gibbsite, anatase, smectite and halite which is added in processed samples for taste. Concentrations of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported identified kaolinite abundance in the samples. Kaolinite, which is the main desirable mineral component of the geophagic clayey soils, was geochemically derived from surrounding granites, rhyolites and basalts. Derivation of secondary minerals contained in the geophagic clayey soils were further substantiated from values obtained for chemical index of alteration (CIA) (80.25 to 99.68) and chemical index of weathering (CIW) (95.59 to 99.94) which were supportive of intense weathering environment for the formation of the clayey soils.

Key words: Chemical index of alteration, geophagia, kaolinite, quartz, soil texture.

### INTRODUCTION

Geophagia, which occurs in almost all the continents in the world including Africa (Aufreiter et al., 1997; Young et al., 2007; Ekosse et al., 2010; Ngole et al., 2010; Woywodt and Kiss, 2002), North America (Aufreiter et al., 1997; Vermeer and Frate, 1979; Grigsby et al., 1999), Central America (Hunter and De Kleine, 1984); South America (Abrahams and Parsons, 1996), Asia (Aufreiter et al., 1997) and Europe and the Middle East (Höllriegel et al., 2007), is the involuntarily deliberate consumption of earthy material including clayey soil, especially by women and children in developing countries, and several types of animals (Abrahams, 1997; Geissler et al., 1998; Saathoff et al., 2002; Hunter, 2003; Brand et al., 2009). The triangular association of geophagia, hunger and poverty has been inferred (Von Humboldt, 1985), although there is mounting evidence pointing to the habit not being limited to the poor but cutting across socio-economic, ethnic, religious and racial divides (Ekosse and Jumbam, 2010).

The practice is therefore very common in many African countries including the Democratic Republic of Congo (DRC). The DRC (4°31'0"S, 15°32'0"E) is among the largest developing countries located in West-Central Africa covering 2,267,600 km<sup>2</sup>, and among the five most populated countries in Africa with 65.8 million inhabitants. It shares its western border with the Atlantic Ocean and the Republic of Congo; the southern border with the Central African Republic and the Sudan; the eastern border with Uganda, Rwanda, Burundi and Tanzania; and its southern border with Angola and Zambia. The land is

<sup>\*</sup>Corresponding author. E-mail: gekosse@wsu.ac.za.

Sample number	Sources and local names of samples	Geographic coordinates	Hue/value/chroma of samples	Colour of samples
1	Mabele de Kasavubu (smoked), from Kimbanseke, Kinshasa (processed)	4°05'39"S, 15°30'06"E	2.5Y/2.5/1	Black
2	Mabele de Kasavubu (non smoked), from Kimbanseke, Kinshasa (unprocessed)	4°05'39"S, 15°30'06"E	5Y/6/1	Gray
3	Mabele de Masina (smoked), Kikwit (processed)	5°2'18"S, 18°49'5"E	2.5Y/2.5/1	Black
4	Ngola de Masina		2.5YR/5/8	Red
5	Mabele ya Pemba de Masina, Kinshasa		5Y/8/1	White
6	Ngola de Kasavubu	4°18'35"S, 15°18'30"E	10R/5/8	Red
7	Mabele ya Pemba de Kasavubu	4°18'35"S, 15°18'30"E	5Y/8/1	White
8	Kasai Mbiyi-Mayi	6°09'23"S, 23°35'41"E	2.5Y/6/2	Light brownish gray
9	Kolwezi (Katanga)	10°45'56"S, 25°30'20"E	5YR/7/3	Pink
10	Fungurume (Katanga)	10°31'10"S, 26°19'30"E	2.5Y/8/1	White
11	Pemba du Katanga Likasi, with black spots (recent sediment)	10°58'53"S, 26°44'0"E	10YR/7/2	Light gray
12	Pemba du Katanga, Lubumbashi. dense dirty (distinct root remains)	11°40'33"S, 27°30'49"E	7.5YR/6/4	Light brown
13	Pemba du Katanga, Lubumbashi. light recent sediment (distinct root remains)	11°40'33"S, 27°30'40"E	7.5YR/5/6	Strong brown
14	Pemba du Katanga, Lubumbashi; porous light	11°40'33"S, 27°30'49"E	10YR/7/1	Light gray

Table 1. Source, geographic coordinates and colour of geophagic clayey soil samples from Democratic Republic of Congo.

topographically characterized by plateaus merging into savannas in the south, mountainous terraces in the west, dense grasslands in the north, higher glaciated and volcanic mountains of the Great Rift Valley in the east and visible peaks of the Shaba Plateau in the southeast. Civil wars and political instability has for the last 20 years plagued DRC; and has led to widespread poverty, food shortage and augmented sicknesses and diseases. These circumstances have caused increased consumption of geophagic clayey soils in the country with noticeable pre-ingestion beneficiation efforts to apparently improve on health quality.

Several reasons have been advanced to justify the practice; some of which are cultural and others medicinal (Carretero, 2002; Ekosse et al., 2010; Tateo et al., 2001). The ingested geophagic clayey soils could supplement nutrients and minerals, and serve as homeopathic remedy for common ailments (Gomes and Silva, 2007;

Halsted, 1968; Reilly and Henry, 2000). The consumption of geophagic clavey soils also has drawbacks which impact negatively on human health, and some of which include anaemia, microbial infections, helminthiasis, intestinal obstruction, dental abrasion and heavy metal poisoning (Geissler et al., 1998; Kawai et al., 2009). Though, the consumption of geophagic clayey soil is very prevalent in the developing countries, including DRC, there is however very limited documentation of research on the minerals contents and chemical compositions of the soils which are being consumed. The focus of this study was therefore to mineralogically and geochemically analyse geophagic clayey soils from DRC in the physical state in which they are ingested, in order to determine their sediment provenance. It is anticipated that the findings of the study could establish baseline mineralogical and chemical characterisation of geophagic clayey soils in DRC; and contribute to the renewed and recently rekindled research interests (Williams and Haydel, 2010), and intellectual debates on geophagic practice within the broader scientific community (Finkelman et al., 2005; Sheppard, 1998).

#### MATERIALS AND METHODS

Samples of geophagic clayey soils commonly ingested by individuals in DRC were obtained from different areas of the country as indicated in Table 1. The samples were the true representatives of the different geophagic clayey soils available in DRC, based on visual examination by colour and feel. The samples were either processed or unprocessed. For the processed oven lining samples, salt (NaCI) was added and then molded into pencil-like forms, baked, burned and boiled to render them more palatable and sterile. The unprocessed samples comprised of alluvium clay from dried village ponds and earth from different traditional clay mines. Laboratory tests were carried out on the geophagic clayey soil samples to determine colour, particle size distribution, minerals' identification and chemical composition. The samples were initially oven-dried at 105°C to eliminate moisture content in them. Where aggregates were present in the samples, they were separated to single particles using a mortar and pestle. With a spatula, the samples were mounted on white cardboard sheets provided by the Munsell Color Company Inc., MD 21218, USA (Mpuchane et al., 2008). The colour descriptions, which comprised the hue, value/chroma and colour of the mounted samples, were obtained by visually comparing them to colours of standard soils recorded in the Munsell Soil Color Book (1992).

The Hue, value, chroma and colour of the geophagic clayey soil samples were determined using the method in the Munsell Soil Color Book (1992).

The particle sizes of the geophagic clayey soil samples were determined using a Malvern Mastersizer 2000 fitted with Hydro 2000G dispersion unit. The method used was based on the correlation between the angles of light scattered from the particles in a laser beam with the size distribution of these particles. Geophagic clayey soil samples were treated with 30% H<sub>2</sub>O<sub>2</sub> and 10% HCI to remove organic matter and carbonates/iron oxides, respectively. The disaggregated samples were then homogenized to form a representative sample. A suspension of each sample in Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was then loaded into the laser particle analyzer. Scattered light data were recorded from 2000 to 5000 snapshots at 10 µs. A poly disperse mode of analysis and a refractive index of 1.53 with an adsorption of 0.1 were chosen. Size data collection was performed at constant obscuration in the range of 10 to 20%. With the aid of a Texture Auto Lookup Software Package (TAL Version 4.2), the results obtained from the PSA were used to determine the texture of each sample.

Qualitative and semi quantitative mineralogical analyses were done using the technique of X-ray spectrometry as described by these studies (Council for Geosciences, 2011; Bish and Reynolds, 1989; Moore and Reynolds, 1997). Bulk samples which constituted representative samples of the geophagic clayey soils were crushed, milled and homogenized to fine powder at approximately 10 to 15 µm in size. Sub-samples were pressed into shallow sample holders against rough filter paper in order to ensure random orientation. The mounted samples were scanned from 2 to 70° 2 $\theta$  Cu<sub>Ka</sub> radiation at a speed of 0.02° 20 steps size/0.5 s, using a LYNXEYE detector and generator settings of 40 kV and 40 mA. Diagnostic peaks for the identification of the minerals together with the Mineral Powder Diffraction File Data Book (MPDFDB, 2001) reference numbers, and the crystal system, d-values, peak intensity and Miller indices of the minerals in the samples presented were cross checked with data reported (ICDD, 2001). Phase concentrations were determined as semi quantitative estimates, using relative peak heights/areas proportions (Brime, 1985).

Geochemically, samples were analyzed for the following major elements concentrations SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>(t), MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>O<sub>3</sub> as well as trace elements concentrations ranging from V to Ce using the PANalytical Axios WDXRF spectrometer in accordance with the method described by the Council for Geosciences (2011) and Fitton (1997). Analysis for the following major elements were conducted on glass disks: SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>(t), MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, LOI and H<sub>2</sub>O. On the other hand, analysis for the following trace elements was done on pressed powder pellets: As, Ba, Bi, Br, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, La, Mo, Nb, Nd, Ni, Pb, Rb, Sc, Se, Sm, Sr, Ta, Th, Tl, U, V, W, Y, Yb, Zn and Zr. The major and minor elements were analysed on glass disks to eliminate matrix effects. Milled samples with grain size of <75 µm were roasted at 1000°C for 3 h to oxidise Fe<sup>2+</sup> and S and to determine the loss of ignition (LOI). One gram of roasted sample and 9 g of flux consisting of 34% LiBO<sub>2</sub> and 66% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> were fused at 1050°C to form stable glass disks. For trace element analysis, 12 g of milled sample and 3

g Hoechst wax was mixed and pressed into powder briquette by hydraulic press with an applied pressure of 25 ton.

To better elucidate on geophagic clayey soil formation, the chemical index of alteration (CIA) which is based on the assumption that the dominant process during chemical weathering is the degradation of feldspar and the formation of clay minerals (Goldberg and Humayun, 2010), and chemical index of weathering (CIW) values were calculated. The CIA =  $[Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$ , where CaO considered is that which is incorporated into silicate structure (Nesbitt and Young, 1982). The CIW =  $[Al_2O_3/(Al_2O_3 + CaO + Na_2O)] \times 100$  (Harnois, 1988). Provenance of sediments was inferred from TiO<sub>2</sub> versus  $Al_2O_3$  segregation diagram for their concentrations in granite, rhyolite and basalt (Ekosse, 2001).

#### **RESULTS AND DISCUSSION**

## General observations, particle sizes and their classification

Nine different colour shades were observed in the geophagic clayey soils from DRC (Table 1). The colours were reflective of possible tinting from colour imparting minerals, such as goethite and haematite, and smoke due to processing. Considering the fact that the colours are of light shade, only very small quantities of the colour imparting minerals are assumed from visual observations to be present in the geophagic clayey soil samples. Most of the samples felt gritty, though few were either soapy or silky. The ranges of values for the different fractions in the samples were as follows: sand = 0.01 to 37.53 wt%, silt = 41.41 to 98.21 wt% and clay = 1.63 to 57.37 wt% (Figure 1).

Silt was the most dominant soil fraction in all the samples. The textural classification of the geophagic clayey samples was as follows: silt = five samples, silt loam = three samples, silty clay loam = one sample and silty clay = five samples (Figure 2). The five silty clay samples were the samples which were light brown to red in colour (Table 1).

## Minerals contents of the studied geophagic clayey soils

Twelve minerals were identified in the geophagic clayey soil samples: quartz (SiO<sub>2</sub>), kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), halite (NaCl), microcline (KAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>), muscovite (KAlSi<sub>3</sub>O<sub>8</sub>), goethite (FeO.OH) and/or haematite (Fe<sub>2</sub>O<sub>3</sub>), siderite (FeCO<sub>3</sub>), gibbsite (Al(OH)<sub>3</sub>), anatase (TiO<sub>2</sub>), talc (Mg<sub>3</sub>(OH)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>) and smectite (Na<sub>0.3</sub>(Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>-(OH)<sub>2</sub>.xH<sub>2</sub>O). Table 2 gives a summary of results of the semi quantitative analysis of identified minerals in the samples and Figure 3 is a representative diffractogram of analysed samples. Quartz and kaolinite were the two most dominant mineral phases contained in the samples. Both triclinic and monoclinic kaloinites were identified in the geophagic clayey soil samples. Kaolinite peaks identified for six of the samples were similar to those



Figure 1. Particle size distribution of geophagic clayey soil samples from Democratic Republic of Congo.



Figure 2. Textural triangle showing the textures of geophagic clayey soil samples from Democratic Republic of Congo.

Sample	Siderite	Halite	Gibbsite	Goethite/Hematite	Anatase	Microcline	Quartz	Kaolinite	Muscovite	Talc	Smectite
1	-	4	-	-	-	1	38	53	3	-	2
2	-	-	-	-	-	1	38	54	3	-	4
3	-	3	5	-	-	-	29	59	1	-	2
4	-	-	-	3	1	-	21	61	14	-	-
5	-	-	-	-	3	-	55	43	-	-	-
6	-	-	-	3	-	1	22	59	15	-	-
7	-	-	-	-	3	-	41	46	10	-	-
8	6	-	-	2	2	-	8	82	-	-	-
9	-	-	-	1	-	5	77	12	5	-	-
10	-	-	-	-	-	-	-	-	-	99	1
11	4	-	-	1	4	-	6	86	-	-	-
12	-	-	-	-	3	5	59	28	-	-	4
13	-	-	-	2	4	-	35	59	-	-	-
14	-	-	-	-	-	-	12	88	-	-	-

Table 2. Results in wt% of semi quantitative analysis of minerals identified in geophagic clayey soil samples.

for kaolinite-1A from Scalby, Yorkshire, England which is triclinic (MPDFDB, 2001) (Figure 3). The other seven samples containing kaolinite had peaks similar to Pugu kaolinite from Tanzania (kaolinite-1Md) which is monoclinic (MPDFDB, 2001) (Figure 4). Sample 10 had 99 wt% talc and neither kaolinite nor quartz was present in it (Figure 5). Geochemically, talc is associated with low grade metamorphic environments with asbestos minerals, such as chrysotile and lizardite (Evans, 2007), which could be deleterious to human health. Samples with high kaolinite had relatively low quartz content (Figure 6). Muscovite was identified in the samples in minor quantities. Other minerals contained in the samples were in very minor to trace quantities.

## Geochemistry and provenance of the studied geophagic clayey soils

Major element concentrations of the geophagic

clayey soil samples as compared to average upper continental crust (UC) and average Post-Archaean Australian Shale (PAAS) (Taylor and McLennan, 1985) are presented in Table 3. The SiO<sub>2</sub> concentration in the geophagic clayey soils ranged from 43.95 to 61.02 wt% with a mean of 54.18 wt%, whereas Al<sub>2</sub>O<sub>3</sub> values were 18.98 to 36.20 wt% with its mean being 26.25 wt%. Sample 10 which was mineralogically identified as talc contained only 0.65 wt% Al<sub>2</sub>O<sub>3</sub> but had 32.64 wt% MgO, whereas values for MgO in the other samples ranged from only 0.02 to 1.00 wt% (Table 3). Other low concentrations of oxides of major elements in the samples were those of Na<sub>2</sub>O, K<sub>2</sub>O and CaO. The Fe<sub>2</sub>O<sub>3(t)</sub> content in the samples were from 0.40 wt% for the talc containing sample to 13.12 wt% which contained aoethite.

Product moment correlation coefficients among oxides of major elements in samples revealed six association classes: very weak negative (<-0.5),

weak negative (>-0.5<-0.75), strong negative (>-0.75<-0.99), very weak positive (<0.5), weak positive (>0.5<0.75), very strong positive (>0.75<0.99) (Table 4). Significant associations are presented in the table as bold and underlined. Three of the associations were correlated as weak negative and these were Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, MgO/TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>/MgO; and four of the associations were weak positive  $(AI_2O_3/TiO_2, MnO/Fe_2O_{3(t)}, P_2O_5/MnO$  and  $Cr_2O_3/TiO_2$ ). There were two very strong negative associations which had their correlation significant at the 0.01 level (MgO/Al<sub>2</sub>O<sub>3</sub> and LOI/SiO<sub>2</sub>); and two very strong positive associations with their correlation significant at the 0.01 level ( $P_2O_5/Fe_2O_{3(t)}$  and LOI/Al<sub>2</sub>O<sub>3</sub>) (Table 4).

Based on geochemical analysis (Table 3), the behavior of concentrations of trace and rare earth elements in the samples as compared to concentrations of corresponding elements in the UC and PAAS could be grouped into elemental



Figure 3. Representative diffractogram of geophagic clayey soil (sample 5) with identified peaks (K=triclinic kaolinite, Q=quartz).



Figure 4. Representative diffractogram of geophagic clayey soil (sample 14) with identified peaks (K=monoclinic kaolinite, Q=quartz).



Figure 5. Non representative diffractogram of geophagic clayey soil (sample 10) with identified peaks (T=talc).



Figure 6. Scatter plot diagram of quartz versus kaolinite of the geophagic clayey soil samples.

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) (Figure 7). Similar enrichment and depletion have been recorded for kaolinitic soils and sediments (Compton et al., 2003; Nyakairu et al., 2001). The geophagic clayey soils were generally much depleted of Na, Ca and K relative to their concentrations in PAAS and UC. This depletion is indicative of intense chemical weathering with amounts lost being proportional to degree of weathering (Condie, 1993). Values obtained for the CIA (80.25 to 99.68) confirmed the very high degree of weathering as compared to CIA values are 45 to 55, which is indicative of no weathering (Depetris and Probst, 1998). Excluding sample 10 because it contained no kaolinite, the CIA values of the geophagic clayey samples plotted to kaolinite abundances did not reveal any unusual weathering pattern from that which was expected (Figure 8). Samples with very high CIA values were also high in kaolinite abundance. Particularly exemplified sample is 14 which contained 88 wt% kaolinite and had a CIA of 99.37. The CIW (95.59 to 99.94) values were in general, higher than those for CIA in same samples. Both the CIA and CIW values of the samples were higher than those of PSSA and UC (Table 3). Increase in values of CIW corresponded with increase in degree of weathering (Harnois, 1988; Price and Velbel, 2003).

In further, chemically characterizing the sediments, provenance analysis was done. Figure 9 depicts the  $TiO_2$  versus  $Al_2O_3$  relation which is reflective of provenance of the geophagic clayey soils. Sample 10 contained very

low TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and that is a characteristic of talc which is generally formed in low grade metamorphic terrains. Eight of the samples were predominantly from granite/rhyolite, and five were of granite/rhyolite + basalt provenances. The sediment provenance could thus be attributed to granites, rhyolites and basalts occurring close to where samples were obtained. Kaolinite, being the most dominant mineral apart from quartz, was formed in a very slightly acidic milieu developing from carbonic waters as depicted in Reactions 1 and 2 as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$
  
2KAISi<sub>3</sub>O<sub>8</sub> + H<sub>2</sub>CO<sub>3</sub>  $\rightarrow$  Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> + 4SiO<sub>2</sub> + 3CO<sub>2</sub> + 2K(OH)  
K-feldspar kaolinite (2)

The kaolinite was thus formed from the weathering profiles of the source rocks. The formed kaolinite was combined with other constituents of unaltered mineral fractions of quartz and microcline, and eventually goethite/haematite, muscovite and anatase to comprise mineral components of the geophagic clayey soils.

### Conclusion

Geophagic clayey soils from the DRC were mineralogically and geochemically analyzed in order to understand their provenance and provide baseline data for geophagia in the country. The geophagic clayey soils were whitish, light grayish to brownish in colour, and their textures were silt, silt loam, silty clay loam and silty clay. Quartz and kaolinite were the most abundant mineral phases present in the clayey soils, although talc dominated

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	PAAS	UC
SiO <sub>2</sub>	54.74	53.94	51.48	53.76	72.29	54.11	61.02	43.95	60.91	60.47	44.07	53.92	46.46	47.42	62.8	66.0
TiO <sub>2</sub>	0.81	0.80	0.89	1.29	1.08	1.30	1.18	1.41	1.43	0.07	1.69	2.57	1.31	1.33	1.0	0.5
$AI_2O_3$	28.09	29.32	30.21	23.04	18.98	23.42	26.70	32.94	22.13	0.65	35.60	27.25	32.97	36.20	18.9	15.2
$Fe_2O_3(t)$	1.35	1.64	1.09	13.12	0.48	12.45	0.72	7.70	4.50	0.40	4.32	3.76	6.41	1.53	6.5	4.5
MnO	0.007	0.007	0.006	0.021	0.003	0.02	0.001	0.015	0.004	0.02	0.010	0.011	0.017	0.007	0.11	0.08
MgO	0.76	0.89	0.71	0.02	0.08	0.05	0.74	0.11	1.00	32.64	0.15	0.61	0.18	0.28	2.2	2.2
CaO	0.02	0.04	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.04	0.01	0.01	1.3	4.2
Na <sub>2</sub> O	1.13	0.01	1.02	0.01	0.01	0.01	0.01	0.01	0.36	0.01	0.01	0.01	0.01	0.01	1.2	3.9
K <sub>2</sub> Ō	1.02	1.19	0.79	0.92	0.04	0.95	1.74	0.14	2.43	0.13	0.05	1.01	0.23	0.21	3.7	3.4
$P_2O_5$	0.07	0.08	0.06	0.20	0.05	0.21	0.02	0.059	0.03	0.02	0.042	0.060	0.084	0.061	-	-
$Cr_2O_3$	0.008	0.009	0.008	0.02	0.007	0.02	0.02	0.016	0.02	0.001	0.019	0.014	0.012	0.010	-	-
L.O.I.	12.42	12.44	13.27	7.76	7.57	7.79	8.38	14.04	7.62	4.95	14.75	10.87	13.04	14.53	-	-
Total	100.43	100.26	99.57	100.04	100.42	100.20	100.41	100.25	100.45	98.99	100.56	99.99	100.56	101.45	97.7	100.0
$H_2O^-$	2.69	3.09	2.08	0.54	0.44	0.61	0.88	1.51	3.78	0.44	1.51	2.50	1.52	1.63	-	
As	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	5.7	4.0	4.0	4.0	4.0	4.0	-	1.5
Ва	239.0	263.0	197.0	929.0	113.0	1 074.0	186.0	78.0	286.0	5.0	46.0	245.0	170.0	159.0	650.0	550.0
Bi	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	-	-
Br	4.4	2.0	2.6.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.8	2.0	2.0	-	-
Ce	72.0	81.0	84.0	172.0	113.0	169.0	49.0	61.0	112.0	10.0	46.0	151.0	75.0	48.0	80.0	64.0
Co	4.3	5.3	3.5	7.7	1.4	6.9	1.7	6.3	17.0	1.6	5.3	22.0	5.7	3.8	23.0	10.0
Cr	52.0	51.0	44.0	115.0	55.0	113.0	150.0	107.0	104.0	3.4	119.0	85.0	72.0	60.0	110.0	35.0
Cs	5.0	7.0	5.0	5.0	5.0	5.0	5.0	5.0	7.1	5.0	5.0	10.0	5.0	5.0	15.0	3.7
Cu	12.0	14.0	7.5	32.0	8.5	30.0	2.9	32.0	20.0	2.2	27.0	116.0	23.0	20.0	-	-
Ga	35.0	36.0	38.0	34.0	22.0	35.0	39.0	41.0	33.0	1.3	44.0	38.0	41.0	45.0	-	-
Ge	1.4	1.0	1.3	1.0	1.0	1.0	1.0	1.0	1.9	1.0	1.4.0	2.4	1.0	1.0	-	-
Hf	4.6	4.5	6.4	3.0	6.0	3.8	11.0	7.6	12.0	3.0	10.0	15.0	5.3	5.4	5.0	5.8
La	56.0	57.0	55.0	100.0	72.0	99.0	28.0	41.0	58.0	10.0	35.0	68.0	37.0	32.0	38.0	30.0
Мо	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	32.02	-	-
Nb	19.0	19.0	21.0	27.0	14.0	27.0	26.0	39.0	28.0	1.0	46.0	71.0	35.0	38.0	-	-
Nd	35.0	39.0	39.0	125.0	76.0	128.0	20.0	14.0	56.0	10.0	12.0	68.0	25.0	19.0	32.0	26.0
Ni	15.0	17.0	14.0	8.1	5.2	7.3	11.0	18.0	38.0	2.0	20.0	67.0	15.0	15.0	55.0	20.0
Pb	38.0	45.0	42.0	44.0	37.0	43.0	17.0	27.0	9.7	31.0	22.0	20.0	27.0	28.0	-	-
Rb	66.0	79.0	47.0	34.0	2.2	35.0	67.0	10.0	194.0	5.4	3.8.0	123.0	14.0	15.0	16.0	112.0
Sc	10.0	9.6	8.3	27.0	11.0	24.0	18.0	22.0	22.0	3.0	20.0	26.0	21.0	17.0	16.0	11.0
Se	1.1	1.5	1.0	1.0	1.0	1.0	1.0	1.7	1.0	1.0	1.3.	1.0	1.2	1.0	-	-
Sm	10.0	10.0	10.0	25.0	10.0	29.0	10.0	10.0	10.0	10.0	10.0	12.0	10.0	10.0	5.6	4.5
Sr	30.0	31.0	33.0	137.0	21.0	150.0	10.0	14.0	9.9	2.0	11.0	18.0	28.0	29.0	-	-
	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	4.6	2.1	2.0	-	2.2
ih Ti	9.9	11.0	11.0	18.0	4.7	17.0	16.0	15.0	15.0	3.0	16.0	22.0	14.0	15.0	14.6	10.7
	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	-	-
U	2.4	2.6	2.0	3.5	2.0	2.0	4.2	2.0	6.4	2.0	2.0	7.0	2.0	2.0	3.1	2.8
V	65.0	76.0	62.0	221.0	/8.0	228.0	214.0	1/5.0	181.0	9.8	162.0	150.0	156.0	111.0	-	-
VV	3.0	3.0	3.0	3.0	3.0	5.3	3.0	3.0	6.2	3.0	3.0	5.3	3.0	3.0	2.7	2.0

Table 3. Results of major (wt%) and trace (ppm) elements analysis of samples.

#### Table 3. Contd.

V	22.0	25.0	20.0	18.0	7 /	10.0	21.0	11.0	50.0	3.1	11.0	70.0	12.0	10.0		
ı Vh	22.0	20.0	20.0	40.0	7.4	49.0	21.0	2.0	10	3.1	2.0	70.0	12.0	2.0	20	-
	3.0	3.0	3.0	5.0	3.0	3.0	4.5	3.0	4.9	5.0	3.0	0.0.0	3.0	3.0	2.0	2.2
Zn	40.0	47.0	35.0	15.0	9.1	17.0	16.0	37.0	26.0	72.0	42.0	40.0	30.0	30.0	85.0	71.0
Zr	178.0	170.0	182.0	225.0	197.0	230.0	380.0	220.0	297.0	14.0	259.0	471.0	215.0	202.0	21.0	190.0
CIA	92.83	95.94	94.26	96.08	99.68	96.02	93.82	99.52	88.77	80.25	97.08	96.26	99.25	99.37	75.30	56.93
CIW	96.07	99.83	96.64	99.91	99.89	99.91	99.93	99.88	92.67	95.59	99.94	99.82	99.94	99.94	88.32	65.24
K <sub>2</sub> O/Na <sub>2</sub> O	0.90	119.00	0.77	92.00	4.00	95.00	174.00	14.00	6.75	13.00	5.00	101.00	23.00	21.00	3.08	0.87
$SiO_2/AI_2O_3$	1.95	1.84	1.70	2.33	3.81	2.31	2.29	1.33	2.75	93.03	1.24	1.98	1.41	1.31	3.32	4.34
La/Sc	5.60	5.93	6.62	3.70	6.54	4.12	1.56	1.86	2.63	3.33	1.75	2.61	1.76	1.88	2.38	2.72
La/Th	5.66	5.18	5.00	5.56	15.32	5.82	1.75	2.73	3.87	3.33	2.19	3.09	2.64	2.13	2.60	2.80
Th/Sc	0.99	1.15	1.33	0.67	0.43	0.70	0.89	0.68	0.68	1.00	0.80	0.85	0.67	0.88	0.91	0.97

UC=Average upper continental crust (Taylor and McLennan, 1985); PAAS=Average Post-Archaean Australian Shale (Taylor and McLennan, 1985).

Table 4. Pearson correlation test for major elements oxides in geophagic clayey soil samples.

	SiO <sub>2</sub>	TiO₂	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> (t)	MnO	MgO	CaO	Na₂O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	LOI
SiO <sub>2</sub>	1											
TiO <sub>2</sub>	-0.295	1										
Al <sub>2</sub> O <sub>3</sub>	-0.673**	0.537*	1									
Fe <sub>2</sub> O <sub>3(t)</sub>	-0.340	0.316	0.113	1								
MnO	-0.273	-0.161	-0.408	0.628*	1							
MgO	0.243	-0.609*	-0.821**	-0.282	0.496	1						
CaO	-0.003	0.037	0.007	-0.355	-0.138	0.052	1					
Na <sub>2</sub> O	0.007	-0.262	0.101	-0.295	-0.335	-0.112	0.264	1				
K <sub>2</sub> O	0.312	0.128	-0.046	0.028	-0.374	-0.234	0.175	0.243	1			
$P_2O_5$	-0.167	0.108	0.067	0.850**	0.534 <sup>*</sup>	-0.299	-0.123	-0.109	0.022	1		
$Cr_2O_3$	-0.215	0.615*	0.439	0.456	-0.188	-0.566*	-0.372	-0.247	0.486	0.175	1	
LOI	-0.781**	0.311	0.882**	-0.111	-0.290	-0.511	0.177	0.216	-0.322	-0.147	0.070	1

\*\*Correlation is significant at the 0.01 level (2-tailed); \*Correlation is significant at the 0.05 level (2-tailed).

the mineralogy of one sample. Other minerals identified included muscovite, microcline, goethite, haematite, siderite, gibbsite, anatase, smectite and halite (added in processed samples for taste). The chemical compositions of the geophagic clayey soils were dominated by  $SiO_2$  and  $Al_2O_3$ which could be related to quartz and kaolinite abundances contained in them. Increase in  $Al_2O_3$ concentration directly corresponded to kaolinite abundance, which was favoured by decrease in concentrations of oxides of major elements. Kaolinitisation of the sediments were further supported by high CIA and CIW values, and pointed to source rocks being granite, rhyolite and basalt.



Figure 7. Trace and rare earth elements concentrations in geophagic clayey soil samples from the Democratic Republic of Congo as compared to the corresponding elemental concentrations in UC and PAAS (Taylor and McLennan, 1985). x-axis = sample numbers and y-axis = log concentrations of elements.



Figure 8. Scatter plot diagram of kaolinite abundance versus chemical index of alteration of the geophagic clayey soils.



Figure 9. TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> binary plot of geophagic clayey soil samples from Democratic Republic of Congo (Ekosse, 2001).

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#### REFERENCES

Abrahams PW (1997). Geophagy (soil consumption) and iron

supplementation in Uganda. Trop. Med. Int. Health, 2(7): 617-623.

- Abrahams PW, Parsons JA (1996). Geophagy in the tropics: a literature review. Geogr. J., 162 (1): 63-72.
- Aufreiter S, Hancock RGV, Mahaney WC, Stambolic RA, Sanmugadas K (1997). Geochemistry and Mineralogy of soils eaten by humans. Int J. Food Sci. Nutr., 48(5): 293-305.
- Bish DL, Reynolds RC Jr (1989). Sample preparation for X-ray diffraction; in: Bish DL, Post JE (Eds) Reviews in Mineralogy: Modern powder diffraction; Mineralogical Society America, Washington, DC 20: 73-99.
- Brand CE, de Jager L, Ekosse GE (2009). Possible health effects associated with human geophagic practice: An overview. SA Med. Technol., 23 (1): 11-13.
- Brime C (1985). The accuracy of X-ray diffraction methods for determining mineral mixtures. Mineral. Mag., 49: 531-538.
- Carretero MI (2002) Clay minerals and their beneficial effects upon human health. A review. Appl. Clay. Sci., 21: 155-163.

- Compton JS, White RA, Smith M (2003). Rare earth element behavior in soils and salt pan sediments of a semi-arid granitic terrain in the Western Cape, South Africa. Chem Geol., 201: 239-255.
- Condie KC (1993). Chemical composition and evolution of the upper continental crust: contrasting results from surface samples and shales. Chem. Geol., 104: I-37.
- Council for Geosciences (2011). Guide to the Services of the CGS Analytical Laboratory. http://196.33.85.14/cgs\_inter/images/stories/Lab\_Guide/Services\_of\_ the\_CGS\_Analytical\_Laboratory.pdf; p.39.
- Depetris PJ, Probst JL (1998). Variability of the chemical index of alteration (CIA) in the Paranfi River suspended load. Mineral Mag., 62A: 366-367.
- Ekosse G (2001). Provenance of the Kgwakgwe kaolin deposit in south eastern Botswana and its possible utilization. Appl. Clay Sci., 20 (3): 137–152.
- Ekosse G-IE, de Jager L, Ngole V (2010). Traditional mining and mineralogy of geophagic clays from Limpopo and Free State Provinces, South Africa. Afr. J. Biotechnol., 9(47): 8058–8067.
- Ekosse GE, Jumbam DN (2010). Geophagic clays: their mineralogy, chemistry and possible human health effects. Afr. J. Biotechnol., 9 (40): 6755-6767.
- Evans BW (2007). The Serpentinite Multisystem Revisited: Chrysotile Is Metastable. Int. Geol. Rev., 46 (6): 479-506.
- Finkelman RB, Centeno JA, Selinus O (2005). The Emerging Medical and Geological Association. T. Am. Clin. Climatol. Assoc., 116: 155-165.
- Fitton G (1997). X-ray fluorescence spectrometry. In: Gill R. (Ed) Modern analytical geochemistry: an introduction to quantitative chemical analysis techniques for earth, environmental and material sciences pp 135-153. Addison Wesley Longman, Harlow, England.
- Geissler PW, Mwaniki D, Thiong'O F, Friis H (1998). Geophagy as a risk factor for geohelminth infections: a longitudinal study of Kenyan primary schoolchildren. T Roy Soc. Trop. Med. H., 92 (1): 7-11.
- Goldberg K, Humayun M (2010). The applicability of the Chemical Index of Alteration as a paleoclimatic indicator: An example from the Permian of the Paraná Basin, Brazil. Palaeogeogr. Palaeocl., 293 (1-3): 175-183.
- Gomes CSF, Silva JBP (2007). Minerals and clay minerals in medical geology. Appl. Clay Sci., 36 (1-3): 4-21.
- Grigsby RK, Thyer BA, Waller RJ, Johnston GA Jr (1999). Chalk eating in middle Georgia: a culture-bound syndrome of pica? Southern Med. J., 92: 190–192.
- Halsted JA (1968). Geophagia in Man: Its Nature and Nutritional Effects. Am. J. Clin. Nutr., 21(12): 1384-1391.
- Harnois L (1988). The CIW index: A new chemical index of weathering. Sediment. Geol., 55 (3-4): 319-322.
- Höllriegel V, Greiter M, Giussani A, Gerstman U, Michalke B, Roth P, Oeh U (2007). Observation of changes in urinary excretion of thorium in humans following ingestion of a therapeutic soil. J. Environ. Radioactiv, 95: 149-160.
- Hunter DR (1991). The geology of Swaziland. Swaziland Geological Survey and Mines Department, Mbabane, Reprint, p.104.
- Hunter JM, De Kleine R (1984). Geophagy in Central America. Geogr. Rev., 74: 157–169.
- ICDD (2001). International Center for Diffraction Data Mineral powder diffraction file data book, International Center for Diffraction Data, Newton Square, PA, p. 942.
- Kawai K, Saathoff E, Antelman G, Msamanga G, Fawzi WW (2009). Geophagy (Soil-eating) in Relation to Anemia and Helminth Infection among HIV–Infected Pregnant Women in Tanzania. Am. J. Trop. Med. Hyg., 80(1): 36-43.
- MPDF DB (2001). The Mineral Powder Diffraction File Data Base. ICDD, Newton Square, PA, p. 942.
- Moore DM, Reynolds RC Jr (1997). X-ray diffraction and the identification and analysis of clay minerals. 2nd edition, p.378, Oxford University Press, New York.

- Mpuchane SF, Ekosse G, Gashe BA, Morobe I, Coetzee SH (2008). Mineralogy of Southern Africa medicinal and cosmetic clays and their effects on the growth of selected test microorganisms. Fresen. Environ. Bull., 17 (5): 547-557.
- Munsell Soil Colour Book (1992). The Munsell soil colour book. Colour charts. Munsell Colour Company Inc., MD 2128, USA.
- Nesbitt HW, Young GM (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of luttites. Nature, 291: 715-717.
- Ngole VM, Ekosse GE, de Jager L, Songca SP (2010). Physicochemical characteristics of geophagic clayey soils from South Africa and Swaziland. Afr. J. Biotechnol., 9 (36): 5929-5937.
- Nyakairu GWA, Koeberl C, Kurzweil H (2001). The Buwambo kaolin deposit in central Uganda: Mineralogical and chemical composition. Geochem. J., 35(4): 245 256
- Price JR, Velbel MA (2003). Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks. Chem. Geol., 202 (3-4): 397-416.
- Reilly C, Henry J (2000). Geophagia: why do humans consume soil? Nutr.Bull., 25(2): 141-144.
- Saathoff E, Olsen A, Kvalsvig JD, Geissler PW (2002). Geophagy and its association with geohelminths infection in rural schoolchildren from northern Kwazulu-Natal, South Africa. T Roy/ Soc/ Trop/ Med. H., 96: 485-490.
- Sheppard SC (1998). Geophagy: who eats soil and where do possible contaminants go? Environ. Geol., 33(2-3): 109-114.
- Tateo F, Summa V, Bonelli GC, Bentivenga G (2001). Mineralogy and geochemistry of herbalist's clays for internal use: simulation of the digestive process. Appl. Clay Sci., 20: 97-109.
- Taylor SR, McLennan SM (1985). The Continental Crust: Its Composition and Evolution. Blackwell, Oxford.
- Vermeer DE, Frate DA (1979). Geophagia in rural Mississippi: environmental and cultural contexts and nutritional implications. Am. J. Clin. Nutr., 32: 2129–2135.
- Von Humboldt A (1985). Vom Orinokko zum Amazonas. Wiesbaden: FA Brockhaus, p. 341.
- Williams LB, Haydel SE (2010). Evaluation of the medicinal use of clay minerals as antibacterial agents. Int. Geol. Rev., 52 (7-8): 745-770.
- Woywodt A, Kiss A (2002). Geophagia: the history of earth-eating. J Roy Soc. Med., 95: 143-146.
- Young SL, Goodman D, Farag TH, Ali SM, Khatib MR, Khalfan SS, Tielsch JM, Stoltzfus RJ (2007). Geophagia is not associated with *Trichuris* or hookworm transmission in Zanzibar, Tanzania. T. Roy. Soc. Trop. Med. H., 101 (8):\_766-772.