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# Full Length Research Paper

# Physico-chemistry, mineralogy, and geochemistry study on the geophagic soils from Eastern Cape Province

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The consumption of soils is widely practiced in several rural communities in the world including the Eastern Cape Province of South Africa which is considered to be poor with a large rural population where culture and indigenous practices remain endemic and well entrenched. This pioneering study of geophagic soils from the province had its primary objective of understanding their physico-chemistry, mineralogy, and geochemistry, and inferring on nutrient bioaccessibilty. Geophagic soil samples obtained from selected sites were subjected to the following laboratory analyses: colour, particle size distribution (PSD), pH, cation exchange capacity (CEC), X-ray diffractometry, and X-ray fluorescence spectrometry. Results depicted values close to those obtained for other geophagic soils from different parts of the world. Elemental concentrations were used to calculate the nutrient bioavailability of the soils consumed by the individuals. The pH of the soils ranged from 4.9 - 8.3, whereas their CEC values ranged from 4.69 - 18.95 cmol (+)/kg. The samples were mainly siliceous with quartz being the dominant mineral in most of the samples. The low nutrient content of the soils raises questions about their suitability as nutrient supplements to geophagic individuals.

Key words: Geophagic individuals, kaolinite, principal component analysis, quartz.

# INTRODUCTION

Soils are significant in human health because of their role in supplying nutrients to plants. Relationship between soil chemistry, physico-chemistry, mineralogy, geochemistry and plant growth has been established. That between soil and human health is compounded by many involving variables. According to Abrahams and Parsons (1997), epidemiological evidence aimed at linking soil and clay properties with human health have seldom proved causality. Studies on soils ingested by humans could provide clues on the relationship between health of

geophagic individuals and soil geochemical, physico-chemical and mineralogical properties. Human geophagia has been practiced for centuries among different communities around the globe (Halsted, 1968; Hunter, 1973; Johns and Duquette, 1991), and especially in sub Saharan Africa (Kutalek et al., 2010). Though commonly practiced among pregnant women (Geissler et al., 1999; Prince et al., 1999), women of all ages, educational level, and social status equally engage in the habit (Halsted, 1968; Hunter, 1973; Johns and Duquette, 1991; Reid, 1992; Woywodt and Kiss, 2002; Callahan, 2003; Songca et al., 2010). The practice has been attributed to several reasons which include Fe deficiency, nutrient supplementation, detoxification of food, and alleviation of gastrointestinal disorders such as diarrhea (Wilson, 2003). According to Callahan (2003), Geissler et al. (1998) and Harvey et al. (2000), cultural beliefs and psychological, medicinal, physiological and nutritional needs are explanatory reasons justifying the practice of human geophagia.

In some communities like the Chagga of Tanzania, geophagia is considered to be sacred to women (Knudsen, 2002). South African urban women believe that ingesting soils enhances their beauty (Woywodt and Kiss, 2002). African pregnant women consume soil to facilitate smooth delivery, and enhance dark skin pigment for the baby (Anell and Lagerkrantz, 1958). Red soil is ingested in many communities to prevent or alleviate symptoms of iron (Fe) deficiency anemia because of its inferred high Fe content (Harvey et al., 2000; Dreyer et al., 2004). In Guatemala geophagia is reported to supply 17 – 55% of recommended pregnancy supplementation of calcium (Ca), magnesium (Mg), zinc (Zn), Fe, copper (Cu), manganese (Mn), selenium, (Se), potassium (K), nickel (Ni) and cobalt (Co) (Hunter and de Kleine, 1984). The Yorubas of Nigeria use clays as one of the active ingredients for the treatment of dysentery and cholera (Ademuwagun et al., 1979) highlighting their medicinal value.

The positive and negative effects of ingesting soils may vary depending on the physico-chemistry, mineralogy and geochemistry of the ingested soils which to a large extent are influenced by the soils pedogenetic development and the quantity of soil/clay ingested. Types of soils/clays ingested vary widely depending on several soil inherent properties. Preference for a particular soil has often been linked to properties like soil colour, its fineness or coarseness, and in some instances its organoleptic properties, all of which are influenced by the soil physicochemical properties including pH, and minerals content. Wilson (2003) and Young et al. (2008) indicated that physico-chemical properties may aid in the interpretation of physiological and nutritional reasons for geophagic practice but according to Mahaney and Krishnamani (2003), most geophagic materials are not properly characterized in terms of their pH, electrical conductivity (EC), CEC and texture. Studies of physico-chemical properties of geophaigic soil revealed variations in their color (Mahaney et al. 2000; Abraham (1997) and clay content (Abraham and Parsons 1997; Aufreiter et al. 1997). Though soil has been ingested to alleviate symptoms of Fe, deficiency anemia, Severance et al. (1988) have shown that geophagia has in some cases caused Fe deficiency. This was attributed to the CEC of the ingested soils (Brouillard and Rateau, 1989). The physico-chemical properties of the soils ingested may therefore play a significant role in the accessibility of nutrients contained in the ingested soils. Studies by Slamova et al. (2011), Ekosse et al. (2010), and Dominy et al. (2004) have indicated that kaolin group of minerals are the most dominant clay minerals in geophagic soils. Some of these soils could contain high concentrations of major and trace elements which could be associated with

health complications. Kutalek et al. (2010), Hooda et al. (2002), Abrahams and Parsons (1997), and Johns and Duquette (1991) have also reported varied concentrations of heavy metals in ingested soils.

Studies so far carried out in South Africa aimed at understanding the geophagic habits of individuals of selected communities in the Free State and Limpopo Provinces of the country (Songca et al., 2010), as well as physico-chemistry (Ngole et al., 2010) and the mineralogy (Ekosse et al., 2010) of the clayey soils ingested by geophagic individuals of these communities. The need to expand the study to other parts of the country and especially in the Eastern Cape Province became imperative due to pressing demographic concerns. The Eastern Cape Province is considered to be the poorest in the country with a large rural population where culture and indigenous practices remain endemic and well entrenched. In a preliminary provincial investigation of geophagic practice, it was found to be very common. Moreover, no study had been carried out to characterize the soils ingested. The basis of this research was therefore to study geophagic soils from selected communities in Eastern Cape Province with the primary objective of understanding their physicochemistry, mineralogy, and geochemistry, and to infer on nutrient bioaccessibilty.

### MATERIALS AND METHODS

# Samples collection

Through geophagic individuals from the different communities, sites from where geophagic materials are mined were located. Information on the amount of soil ingested and frequencies of ingestion were also noted. From the located sites, 18 geophagic soil samples were collected using a hand trowel that had been decontaminated by washing with tap water. The samples were then transported to the laboratory where they were air-dried and packaged for analyses.

# Physicochemical analyses

Physico-chemical properties of the geophagic soils analyzed included colour, particle size distribution (PSD), pH, and CEC. A Munsell soil colour chart was used to determine the colour of the samples (Munsell Soil Color Book 1992). Particle size analysis of the samples were conducted by initially treating with 30% H<sub>2</sub>O<sub>2</sub> and 10% HCl to remove organic matter and carbonates/iron oxides respectively, after which they were each homogenized to form a representative sample. A suspension of each homogenized sample in Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was then loaded into a Malvern Mastersizer 2000 fitted with Hydro 2000G dispersion unit. A polydisperse 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 10-20%. Scattered light data were recorded from 2000 to 5000 snapshots of 10  $\mu$ s. The correlation between the angles of light scattered from the particles in a laser beam was used to determine the size distribution of these particles. A texture Auto Lookup Software Package (TAL Version 4.2) was then used to determine the texture of each sample. The CEC and pH of each sample were determined using the ammonium acetate and



Figure 1. Particle size distribution of geophagic samples.

potentiometric techniques respectively (Ngole, 2011).

#### Minerals identification

For minerals identification, representative subsamples of each of the 18 samples collected were crushed to fine powder with a mill and homogenized to a fine powder of approximately 10  $\mu$ m -15  $\mu$ m size. A sub-sample of the powdered sample was then pressed into a shallow sample holder against a rough filter paper to ensure random orientation. Each sample was then scanned from 2° 20 to 70° 20 with Cuka radiation at a speed of 0.02° 20 teps size/0.5 second using a LYNXEYE detector and generator settings of 40 kV and 40 mA. Phase concentrations were determined as semi quantitative estimates using relative peak height/area proportions (Brime, 1985) and reference-intensity-ratio (RIR) method. Mineral phases in each scanned sample were identified with the aid of the Mineral Powder Diffraction File Data Book (MPDFDB 2001) and cross checked with data presented in International Center for Diffraction Data (ICDD) (2001).

#### **Geochemical analyses**

Total sulfur and carbon content of the samples were determined with an Eltra CS 800 Double Dual Range system calibrated with certified carbon and sulfur standards (Euronorm-CRM 484-1 Whiteheart malleable iron and Leco No 501-502). Samples for major and trace element analyses were milled and roasted at 1000°C for at least 3 hours to oxidize  $Fe^{2+}$  and S and to determine the loss on ignition (LOI). One gram (1 g) of the roasted sample and nine grams (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 which were then used for analyses of 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>, and H<sub>2</sub>O. For the analyses of trace element, 12 gm of milled sample and 3 g Hoechst wax were mixed and pressed into a powder briquette. The pressed powder pellets were then analyzed for 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. Analyses were done using a PANAlytical Axios, sequential WDXRF spectrometer. An amphibolite reference material was used for quality control of the data generated from the XRF analyses. Methods were those described in Council for Geosciences (2011) and Fitton (1997).

#### Statistical analyses

Geochemical data collected were transformed using a centered logratio (clr) by dividing the concentration of each element by the geometric mean of the element (centered) and taking the logarithm of each value (Grunsky and Smee, 2003; Drew et al., 2010). All elements with zero variance were removed from the data set which was then subjected to an RQ-mode Principal Component Analyses (Zhou et al., 2003). An RQ-mode was preferred because it facilitates display of component loadings of the samples, and the elements in the same component space. Cluster analyses using average distance between groups was carried out as a complementary analysis to PCA.

# RESULTS

#### Physico-chemistry of geophagic clayey soil samples

The particle size distribution of the samples varied as indicated in Figure 1. Most of the particles in samples



Figure 2. Texture of geophagic samples.

ECM8, ECK10, ECK12, ECK14, ECK16, and ECB27 had diameters within the silt range (2  $\mu$ m- < 50  $\mu$ m), whereas the other samples had most of their particles occurring within the sand range (50  $\mu$ m - < 2000  $\mu$ m) of particles (Figure 1).

The clay contents were  $\leq$  10% in all but one sample (Figure 1). Textural classification of the samples therefore included silt loam, sandy loam, loamy sand, and sand (Figure 2). The colors of the soil varied but majority of them had shades of brown whereas only one sample was reddish (Table 1). The pH values ranged between 4.9 (acidic) in sample ECK11 to 8.29 (slightly alkaline) in sample EN2 (Table 1). Most of the samples had pH values within the slightly alkaline range (7 and 8.3) (Table 1). The CEC of the samples were low, ranging from 4.69 cmol (+)/kg in sample ECK13 to 18.95 cmol (+)/kg in sample ECK9 (Table 1).

Majority of the samples had CEC values of between 10 cmol (+)/kg and 18.95 cmol(+)/kg (Table 1). The values of total carbon (C) content in the soils were very low with values of between 0.04 % in samples ECB18 to 3.0 in samples ECK16. The concentration of C in the other samples were, 2.37% (EN1), 0.57% (EN2), 0.53% (EN3), 1.19% (EN4), 1.54% (EN5), 1.09% (ECM6), 0.64% (ECM7), 0.10% (ECM8), 1.47% (ECK9), 0.13% (ECK10), 0.36% (ECK11), 0.37% (ECK12), 1.92% (ECK13), 0.10% (ECK14), 1.85% (ECK15), and 1.68% (ECK17). From the values of total C, the samples were inferred to have low content of organic carbon and consequently low content of organic matter. Sulfur (S) was not detected in the samples except for sample EN1 which had a very low content of S (0.02%).

# Mineralogy of geophagic clayey soil samples

Ten different mineral phases were identified in the samples (Table 2). All samples contained quartz (SiO<sub>2</sub>) and at least 50% of the samples contained plagioclase group of minerals and or kaolinite (Table 2). Except for sample ECM8 which had kaolinite as the most dominant mineral, semiquantitative analyses revealed quartz to be the most dominant mineral in all samples followed by the plagioclase group of minerals (albite (Na(Si3Al)O 8) and anorthite (Ca, Na)(AI, Si)2Si2O8)). Microcline (KAISi3O8) and muscovite (KAl2(Si3Al)O10(OH,F)2) were also present in some of the samples (Table 2). Secondary minerals identified in the samples included kaolinite (Kaolinite-1A - Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), illite (KAl2(Si3Al)O10(OH)2), smectite (montmorillonite 15A Na0.3(AI, Mg)2Si4O10(OH)2.4H2O), and hematite (Fe2O3). Calcite was identified in sample EN1 only (Table 2). A diffractogram of representative geophagic sample is presented in Figure 3.

# Geochemistry of geophagic clayey soils

#### Major elements

Except for sample ECM8 which had silica content of 42.76%, the rest of the samples could be described as being siliceous with values of SiO<sub>2</sub> ranging from 62.68% in sample ECK11 to 90.34% in sample ECM 7 (Table 3). The alumina (Al<sub>2</sub>O<sub>3</sub>) contents in the soils were also very low with a range of 4.77 to 26.48% (Table 3). Samples also had low values for the Fe oxides (1.84% in sample

Table 1. Physico-chemical properties of geophagic samples.

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S/n	Sample code	Local description of sampleP	lace of collection	Munsell notation	True colour	рн	(cmol(+)/kg)
1	EN1	Mole soil	Ndantsane	10YR 6/8	Brownish yellow	8.18	8.51
2	EN2	Yellowish soil	Ndantsane	10YR	Brownish yellow	8.17	10.30
3	EN3	Soft stone	Ndantsane	10YR	Light brownish grey	8.29	6.35
4	EN4	Termite mound soil	Ndantsane	10YR	Grayish brown	7.3	10.39
5	EN5	Mole soil (brown)	Ndantsane	10YR	Grayish brown	6.85	7.32
6	ECM6	Garden soil	Matatiele	7.5YR	Grey	7.45	8.35
7	ECM7	Garden soil	Matatiele	2.5Y	Olive brown	8.13	8.03
8	ECM8	Red soil	Matatiele	10R	Red	7.65	9.37
9	ECK9	Mole soil	Centane	7.5YR	Brown	8.03	18.95
10	ECK10	Yellow soil	Centane	10YR	Very pale brown	8.07	11.64
11	ECK11	Yellowish soil	Centane	10YR	Brownish yellow	4.9	15.56
12	ECK12	Clay soil	Centane	10YR	Yellowish brown	7.61	17.34
13	ECK13	Beetle soil	Mthatha	7.5YR	Light brown	7.05	4.69
14	ECK14	Khaki soil	Centane	5Y	White	5.75	15.91
15	ECK15	Khaki soil	Centane	5Y	White	5.74	15.10
16	ECK16	Earth worm soil	Centane	2.5Y	Olive brown	6.5	14.80
17	ECK17	Garden soil Khaki	Centane	10YR	Yellowish brown	7.16	16.02
18	ECB18	Butterworth	Butterworth	2.5 Y	Olive Yellow	7.34	14.09

ECM7 to 11.72% in sample ECM8) (Table 3). Contents of TiO<sub>2</sub>,  $Cr_2O_3$ , and MnO were all < 1% whereas those of the alkali and alkali earth metals (Na<sub>2</sub>O, K<sub>2</sub>O, CaO and MgO) were slightly higher (Table 3). Loss on ignition values ranged from 2.61% in sample ECM7 to 11.26 % in sample ECM8 (Table 3). Values for the sum total of major cations in the samples were between 99.60 and

101.98%. These values for the reference material used for quality control (Table 3) indicated high reliability of the data (101%).

# Trace elements

Trace element concentrations in the geophagic

soils varied but all values were within those reported for mineral soils (Alloway, 1995). The concentrations of Ba, Cr, Ce, Rb, Sr, V, Zn and Zr were highest among the trace element analyzed in the samples with most values of each of these trace metals in the soils being >75 ppm (Table 4). Arsenic, Bi, Cs, Ge, Mo, Se, Ta, U and Yp had the lowest concentrations with all values being

Sample code	Calcite	Hematite	Microcline	Plagioclase	Quartz	Kaolinite	Muscovite	Smectite	Illite
EN1	2		-	6	92	-	-	-	-
EN2	-	2	-	-	94	4	-	-	-
EN3	-	-	-	17	78	-	-	-	5
EN4	-	-	-	2	90	3	-	-	5
EN5	-	-	-	12	78	2	8	-	-
ECM 6	-	-	-	12	85	1	2	-	-
ECM 7	-	-	1	4	95	-	-	-	-
ECM 8	-	5	-	-	38	57	-	-	-
ECK 9	-	-	-	25	75	-	-	-	-
ECK 10	-	3	-	-	73	7	15	2	-
ECK 11	-	5	-	5	68	1	16	5	-
ECK 12	-	4	-	5	82	2	5	2	-
ECK 13	-	-	2	5	93	-	-	-	-
ECK 14	-	-	2	-	83	10	-	5	-
ECK 15	-	2	-	2	93	-	3	-	-
ECK 16	-	2	-	7	89	-	2	-	-
ECK 17	-	-	-	3	97	-	-	-	-
ECB18	-	-	-	14	82	1	3	-	-

Table 2. Semi-quantitative analyses of minerals (wt %) in geophagic samples.

< 10 ppm (Table 4). The concentrations of the other elements (Br, Co, Cu, Ga, Ge, Hf, La, Nb, Ni, Pb, Sc, Sm, Th and Y) were between 10 and 75 ppm (Table 4). Trace elements such as Co, Cu, Se and Zn which are of nutritional significance to humans and Ni, Pb and Cr which have lower toxicity thresholds were relatively low compared to those found in soils for agricultural purpose.

# Statistical analyses

The mean pH, CEC and total C values of the geophagic soils analyzed were 7.23, 11.82 cmol(+)/kg and 1.05%, respectively. The soils therefore had circumneutral pH with mean CEC value within the range of those reported in

kaolinite. Results of *clr* Principal Component Analyses (PCA) of the geochemical data of the samples are presented in biplots in Figure 4. The first two components of the *clr* transformed geochemical composition of geophagic samples accounted for 49.51% of the variability observed in the data. Major elements on the positive side of component 1 included Al<sub>2</sub>O<sub>3</sub>, Cr <sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> (t), MgO, TiO<sub>2</sub>, and K<sub>2</sub>O, whereas the trace elements loading positively on this component were As, Ba, Ce, Cr, Co Ga, Rb, Pb, La, Ni, Nb, Yb, Nd, Ge, Th, U, W and Y (Figure 4). Only Na<sub>2</sub>O, CaO, SiO<sub>2</sub>, Yb, Sr, Zr and Hf loaded negatively on component

1. Samples ECK10, ECK11, ECK12 ECK14, EN3, ECB18, EN4, EN5, ECK9, ECK15 and ECK18 were on the positive side of component 1 whereas samples EN1, ECM6, ECK13, ECM7, ECK16 and

ECK17 were on the negative side. Eight samples and major and trace elements loaded positively on component2 (Figure 4). Cluster analyses of the samples also revealed a similar association of samples. Four main clusters were identified. The first cluster comprised of samples ECM7, ECK13, ECK17, the second cluster of samples EN3, EN5, ECM6, ECK16 and ECK18, the third cluster of samples EN1, ECM9, EN4, ECK12, and ECK15, and the fourth cluster consisted of ECK10, ECK11, EN2, ECK14, and ECM8 (Figure 5).

# DISCUSSION

The brownish shade of colors of the samples from the studied area differed from those reported by



Figure 3. X-ray diffractograms of representative geophagic clayey soil samples analyzed (Note: H = hematite, K = k aolinite, Q = quartz).

Songca et al. (2010) in soil ingested in other Provinces in South Africa which were mainly whitish and grayish (described as khaki by geophagic individuals). This observation further strengthens the variations in geophagic habits and preference for material ingested even in the same country. The textures of the samples were more coarse compared to those reported in geophagic material from other parts of South Africa and Swaziland (Ngole et al., 2010), Thailand, Uganda, and Zaire (Abrahams and Parsons 1997), Turkey, Mississippi, and Georgia (Minnich et al., 1968). Ingesting coarse textured soils may present some health risks. Damage of dental enamel during mastication (King et al., 1999) could occur because of the differences in the hardness of quartz (7 on the Mohr hardness scale) which is the main component of sand that constitutes the greater percentage of particles in the geophagic soils; and hydroxylapatite (5 on the Mohr hardness scale) which makes up dental enamel. Dental damage in hominid species as a result of ingesting medium sized sand has also been reported by King et al. (1999). In addition, the

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe2O3(t)	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P2O5	Cr2O3	LOI	Total
EN1	77.68	1.11	5.39	5.87	0.06	0.44	2.1	0.53	0.76	0.1	0.02	5.91	99.96
EN2	64.55	1.1	11.54	15.37	0.04	0.35	0.01	0.09	0.62	0.04	0.07	6.53	100.3
EN3	73.16	0.52	11.68	5.62	0.05	0.56	1.18	1.81	1.51	0.05	0.01	3.67	99.83
EN4	74.14	1.01	11.13	4.77	0.05	0.61	0.17	0.37	1.31	0.04	0.01	6.54	100.15
EN5	69.26	0.56	12.8	6.15	0.08	1	0.78	1.33	2.44	0.15	0.01	5.8	100.36
ECM6	77.17	0.51	10.03	3.34	0.04	0.46	1.13	1.58	1.15	0.08	0.01	4.94	100.43
ECM7	90.34	0.51	4.77	1.84	0.05	0.2	0.34	0.4	0.87	0.04	0.01	2.61	101.98
ECM8	42.76	1.41	26.48	17.2	0.05	0.48	0.03	0.02	0.39	0.04	0.04	11.26	100.15
ECM9	71.71	1.78	8.96	6.86	0.14	1.41	2.53	1.05	0.92	0.1	0.03	4.95	100.43
ECK10	63.69	0.72	18.55	7.08	0.07	1.29	0.03	0.1	2.74	0.06	0.01	5.97	100.32
ECK11	62.68	0.86	19.07	6.98	0.08	0.94	<0.01	0.13	3.55	0.06	0.01	6.13	100.45
ECK12	66.81	0.8	14.09	9.55	0.05	0.81	0.21	0.38	1.68	0.08	0.02	5.85	100.32
ECK13	86.09	0.38	4.64	2.42	0.05	0.17	0.24	0.79	0.96	0.07	0.01	4.54	100.34
ECK14	72.23	0.93	16.71	2.65	0.01	0.38	<0.01	0.01	2.29	0.04	0.01	4.98	100.22
ECK15	71.41	1.05	10	7.29	0.06	0.63	0.28	0.28	1.35	0.41	0.02	7.03	99.81
ECK16	75.14	0.85	8.72	3.92	0.08	0.58	0.85	0.92	1.27	0.12	0.02	8.14	100.62
ECK17	83.38	1.39	5.72	4.11	0.05	0.29	0.11	0.23	0.69	0.03	0.01	4.62	100.64
ECB27	66.6	0.87	15.05	5.57	0.06	1.51	0.89	2.3	1.64	0.03	0.02	5.07	99.6
Certified													
sample	45.78	1.52	16.52	9.79	0.18	8.04	10.87	3.58	0.68	0.26	0.07	2.61	99.89
Results	45.07	1.54	16.69	9.8	0.18	8.34	10.97	3.69	0.68	0.25	0.08	2.63	99.93

**Table 3.** Concentrations of major oxides in the geophagic samples.

**Table 4.** Trace element concentrations (ppm) in geophagic clayey soil samples.

Sample	EN1	EN2	EN3	EN4	EN5	ECM6	ECM7	ECM8	ECM9	ECK10	ECK11	ECK12 E	ECK13 E	ECK14 E	CK15 E	CK16 E	CK17 EC	B27 Certi	ified sample I	Results
H <sub>2</sub> O-	1.3	1.7	0.9	1.5	1.3	1.0	0.8	2.0	2.7	1.4	1.8	1.5	0.8	2.0	1.5	1.7	0.9	1.6	0.2	0.1
As	8.8	17.0	11.0	13.0	7.4	7.7	4.5	4.0	4.0	4.4	27.0	34.0	4.0	14.0	4.0	4.5	4.3	17.0	4.0	4.0
Ва	387.0	283.0	631.0	456.0	625.0	422.0	341.0	137.0	439.0	599.0	682.0	487.0	333.0	352.0	402.0	426.0	291.0	386.0	266.4	334.0
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	3.0	3.0	3.0	3.0	3.0	3.0
Br	45.0	32.0	8.1	20.0	9.8	18.0	4.7	2.6	29.0	4.9	5.4	7.5	4.5	2.0	8.6	15.0	15.0	46.0	2.0	2.0
Ce	62.0	58.0	55.0	60.0	75.0	60.0	42.0	53.0	67.0	68.0	55.0	54.0	39.0	116.0	62.0	54.0	54.0	86.0	44.4	42.0
Co	15.0	24.0	15.0	13.0	18.0	12.0	10.0	6.5	33.0	32.0	23.0	19.0	6.5	9.2	18.0	18.0	10.0	13.0	35.5	40.0
Cr	109.0	360.0	57.0	65.0	64.0	50.0	60.0	253.0	177.0	75.0	75.0	104.0	60.0	49.0	113.0	110.0	69.0	92.0	511.7	503.0
Cs	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Cu	37.0	31.0	15.0	17.0	19.0	8.5	8.8	82.0	43.0	23.0	22.0	23.0	10.0	15.0	22.0	25.0	12.0	5.6	7.8	6.2

Table 4. Contd.

Ga	8.3	17.0	17.0	15.0	17.0	12.0	5.2	30.0	11.0	25.0	23.0	18.0	4.9	21.0	14.0	9.9	7.4	20.0	17.8	19.0
Ge	1.0	1.1	1.1	1.0	1.1	1.0	1.0	1.8	1.0	1.2	1.2	1.0	1.1	1.5	1.1	1.0	1.2	1.0	1.0	1.0
Hf	18.0	12.0	3.0	9.7	7.6	9.2	9.0	3.1	11.0	3.0	3.0	6.7	12.0	15.0	11.0	11.0	15.0	3.0	4.4	<3.0
La	26.0	23.0	40.0	32.0	36.0	24.0	22.0	32.0	31.0	24.0	29.0	30.0	19.0	58.0	31.0	30.0	28.0	47.0	24.2	37.0
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	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Nb	11.0	17.0	12.0	17.0	12.0	8.1	9.6	10.0	20.0	15.0	16.0	15.0	6.1	20.0	17.0	11.0	19.0	12.0	31.3	33.0
Nd	20.0	16.0	33.0	27.0	26.0	19.0	19.0	23.0	20.0	19.0	25.0	23.0	15.0	51.0	21.0	24.0	21.0	43.0	26.4	22.0
Ni	16.0	26.0	22.0	16.0	19.0	11.0	8.9	25.0	40.0	33.0	19.0	20.0	6.1	16.0	21.0	26.0	8.8	36.0	99.1	103.0
Pb	81.0	28.0	23.0	23.0	41.0	25.0	12.0	14.0	36.0	28.0	37.0	27.0	12.0	52.0	26.0	16.0	14.0	9.0	6.2	6.9
Rb	43.0	46.0	107.0	79.0	115.0	59.0	40.0	20.0	41.0	148.0	153.0	83.0	38.0	138.0	94.0	52.0	49.0	65.0	20.9	21.0
Sc	8.8	18.0	13.0	13.0	12.0	9.4	6.9	91.0	13.0	18.0	19.0	17.0	7.2	13.0	14.0	13.0	8.7	17.0	38.6	35.0
Se	1.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sm	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Sr	119.0	16.0	244.0	49.0	154.0	260.0	34.0	10.0	122.0	37.0	14.0	53.0	67.0	33.0	49.0	92.0	35.0	116.0	332.3	337.0
Та	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	2.0	2.0	2.0	2.0	2.0	2.5	2.0
Th	5.8	11.0	13.0	12.0	13.0	7.6	5.9	4.3	6.3	13.0	17.0	14.0	4.6	22.0	11.0	6.0	8.4	19.0	3.8	3.0
TI	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.00	3.0	3.0	3.0	3.0	3.00	3.0	3.0	3.0	3.0	3.0	3.0
U	2.0	3.4	3.0	4.5	2.3	3.2	2.0	2.7	2.0	2.9	4.3	3.1	2.0	5.7	2.3	2.1	2.4	3.8	2.2	2.0
V	128.0	315.0	94.0	95.0	87.0	60.0	44.0	210.0	143.0	110.0	110.0	157.0	43.0	77.0	140.0	86.0	90.0	135.0	259.4	276.0
W	3.0	4.1	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	3.0	3.00	3.6	3.0
Y	15.0	19.0	26.0	23.0	21.0	15.0	19.0	15.0	19.0	23.0	30.0	20.0	11.0	89.0	20.0	18.0	19.0	25.0	27.0	29.0
Yb	3.0	3.0	3.4	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.9	7.9	3.0	3.0	3.0	3.4	4.2	3.8
Zn	116.0	40.0	68.0	56.0	124.0	52.0	23.0	43.0	143.0	97.0	62.0	61.0	24.0	55.0	127.0	57.0	28.0	66.0	87.8	88.0
Zr	752.0	473.0	258.0	408.0	299.0	466.0	370.0	140.0	406.0	143.0	206.0	302.0	498.0	564.0	395.0	502.0	615.0	244.0	121.6	123.0

morphologies of the particles could contribute to abrasion of the gastrointestinal tract on ingestion, increasing the risk of perforation of the sigmoid colon. Lohn et al. (2000) have reported cases of sigmoid colon perforation due to ingestion of coarse sediments.

Geophagic samples ECM8, ECK10, ECK11, ECK12, ECK15 containing hematite and Mg bearing silicate minerals such as smectite were associated with components that loaded highly on those elements common in Fe oxides and Fe-Mg silicate minerals and also formed the same cluster. According to Drew et al. (2010) and Grunsky and Smee, (2003), major and trace elements including Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, Ba, Be, Ce, La, Nb, Th, Rb, Pb, and Zr are associated with feldspathic clays and mafic volcanic rocks whereas MgO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O, CaO, Cd, Cr, Co, Mg, Ni, Sc, Cu, and V are usually associated with felsic volcanic rocks and Fe oxides and Fe-Mg silicate minerals. Samples with high amounts of plagioclase including EN3,

EN5, ECM6, ECK16 and ECB18 also showed a relationship with elements contained in feldspathic minerals and formed another cluster. Similarly, samples ECM7, ECK13 and ECK 17 had the highest amount of quartz and clustered together (Figure 5). Other samples including EN1, ECM9, EN4, ECK12, and ECK15 had more than two types of minerals and also clustered together. The geophagic soils had inverse relationship between SiO<sub>2</sub> and Al<sub>2</sub>O <sub>3</sub>, and LOI and Fe<sub>2</sub>O<sub>3</sub>. Samples associated with SiO<sub>2</sub> (ECK17, ECM7, ECK13, and



**Figure 4.** First and Second principal components of geochemical composition of geophagic soils.



Figure 5. Cluster of samples based on log transformed data.

Table 5. Nutrients intake due to soil ingestion.

		Z U	Z	Z	Z .	Z	Nutrient	taken ir	n by geo	phagic i	ndividua	l /day wh	en 5 gm	are inge	ested				
Element	RDA			,	_											ECK 15	EC K16	ECK17	ECB 27
Co (µg/day)	1	0.58	0.92	0.58	0.50	0.69	0.46	0.38	0.25	1.27	1.23	0.88	0.73	0.25	0.35	0.69	0.69	0.38	0.50
Cr (µg/day)	25	4.19	13.85	2.19	2.50	2.46	1.92	2.31	9.73	6.81	2.88	2.88	4.00	2.31	1.88	4.35	4.23	2.65	3.54
Cu (µg/day)	900	1.42	1.19	0.58	0.65	0.73	0.33	0.34	3.15	1.65	0.88	0.85	0.88	0.38	0.58	0.85	0.96	0.46	0.22
Mo (µg/day)	45	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Se (µg/day)	55	0.04	0.06	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Zn (mg/da)	8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
	$\Sigma$ $\Sigma$ $\Sigma$ Nutrient taken in by geophagic individual /day when 30 gm are ingested $\Sigma$ $\Sigma$ $\Sigma$ Nutrient taken in by geophagic individual /day when 30 gm are ingested $\Sigma$															<b>-</b>			
Element	RDA															EN 15	ШZ÷	ШХト	2 0 1
Co (µg/day)	1	3.46	5.54	3.46	3.00	4.15	2.77	2.31	1.50	7.62	7.38	5.31	4.38	1.50	2.12	4.15	4.15	2.31	6.00
Cr (µg/day)	25	25.15	83.08	13.15	15.00	14.77	11.54	13.85	58.38	40.85	17.31	17.31	24.00	13.85	11.31	26.08	25.38	15.92	42.46
Cu (µg/day)	900	8.54	7.15	3.46	3.92	4.38	1.96	2.03	18.92	9.92	5.31	5.08	5.31	2.31	3.46	5.08	5.77	2.77	2.58
Mo (µg/day)	45	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.92
Se (µg/day)	55	0.23	0.35	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.46
Zn (mg/da)	8	0.03	0.01	0.02	<0.01	0.03	<0.01	<0.01	<0.01	0.03	0.02	<0.01	<0.01	<0.01	<0.01	0.03	0.01	0.01	0.03

Brody (1994).

EN1) had the highest amount of quartz among the geophagic samples studied and loaded negatively, whereas those with high amounts of Al<sub>2</sub>O<sub>3</sub> (ECM8, EN3, ECK10, ECK11, ECK12, and ECK 18) loaded positively on component 1. This inverse relationship can be attributed to weathering of the minerals especially because the samples associated with Al<sub>2</sub>O<sub>3</sub> contained feldspar, anorthite, and secondary minerals (illite and kaolinite) which were possibly altered from the primary minerals. According to Marques et al. (2004), loss on ignition (LOI) is influenced by the presence of hydroxyl-rich secondary minerals which are usually present in the clay fraction of soils. Higher LOI values in ECK18, ECK12, EN2,

EN4, ECM8, ECK10 ECK16, and ECK15 could be attributed to the presence of kaoilinite and smectite in the samples which are able to retain water.

The associations between samples and geochemical associations as revealed by PCA and cluster analyses therefore revealed no anomalies. The geochemical and mineralogical constitutions of these soils are likely to have an implication on the health of the geophagic individuals. Samples ECK8 and ECK14 with relatively higher amounts of kaolin and samples ECK01, ECK11, ECK12 with a combination of kaolin and smectite minerals could contribute to the alleviation of gastrointestinal discomfort

related to diarrhea and the elimination of toxins in geophagic individuals. Slamova et al. (2011) highlighted the use of kaolin (for binding of toxins in the gastrointestinal tract) and smectites (treatment of infectious diarrhea) in many countries. According to Fontes et al. (2005) oxides of Fe would result in different colour pigment in soils including brownish, and yellowish colours. Most of the studied samples were brownish and yellowish and hematite was identified in some of the samples. This may be attributed to the presence of Fe-bearing mineral (Table 2) and Fe oxides in the soils (Table 3). Geophagic individuals from these communities indicated that they ingested the soils for health and pregnancy related reasons. Some soils may supply nutrient including Ca, Co, Cu, Fe, K, Mg, Mn, Na, P and Zn to humans upon ingestion. But the availability of these nutrients to the individual could depend on several other factors including the CEC, and the pH of the soil and its buffering capacity (Young 2008; Ngole et al., 2010; Brouillard and Rateau 1989). The CEC of the geophagic samples were relatively low and reflected the mineralogy and inferred low organic matter content. These soils are not likely to absorb nutrients already present in the GI.

The amount of bioaccessible element in soils varies with several factors that may include the soil matrix itself, chemical form of the element in question, soil, stomach and intestinal pH, and the soil:solution ratio (Kutalek et al., 2010). Abrahams et al. (2006) for example reported that Pb bioaccessibility in geophagic soils from United Kingdom vary between 3 - 83% whereas that of Hg varies with its chemical form. In this study we assume 50% bioaccesibility of the metals Co, Cu, Cr, Mo, Se and Zn studied. Geophagic individuals from the area indicated that the ingested between 5 g to 30 g of soils daily. Using a 50% bioaccessibility and an average weight of 65 kg for an adult female in the Eastern Cape, ingesting 5 g of these soils daily, supply significant amounts of Co and Cr whereas less than 1% of the recommended daily allowance (RDA) of Cu, Mo, Se and Zn is supplied (Table 4). Where up to 30 g of these soils are ingested daily, significant contributions are made towards the RDA for Co, Cr and Mo (Table 5). The RDAs for the different soils calculated from the total elemental concentrations are generally lower than those of the bioaccessible fraction of similar nutrients in geophagic clayey soils from Thailand, Uganda and Zaire as reported by Abrahams and Parsons (1997). By inference, the bioaccessible fraction of these elements in the studied geophagic soils makes little contribution to the nutrient demands of a geophagic female adult. Ingesting these soils to alleviate symptoms related to Fe deficiency anemia may provide little comfort to the geophagic individuals as the samples had low amounts of Fe bearing minerals and concentration of Fe<sub>2</sub>O<sub>3</sub>. However, their prolonged ingestion may present health risks due to bioaccumulation of some of these elements in body tissues.

# Conclusion

Results obtained in this research indicated that the geophagic soils varied in color and were classified as silt loam, sandy loam, loamy sand, or sand. They had pH values ranging from 4.9 - 8.3 with most of them being neutral to slightly alkaline. The CEC of the soils were from 4.69 - 18.95 cmol(+)/kg with CEC values for most being between 10 - 18.95 cmol(+)/kg. Mineral phases identified in the soils included quartz (most dominant) kaolinite, plagioclase (albite and anorthite), hematite, microcline, muscovite, illite and smectite. The soils constituted of SiO<sub>2</sub> followed by Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> (t).

Contents of TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and MnO were all < 1% whereas those of the alkali and alkali earth metals were slightly higher. The concentrations of the trace element in the studied soils were similar to those obtained for other geophagic clayey soils from different parts of the world. The findings based on calculations of nutrient bioaccessibility depicted that the elements in the soils could negligibly contribute to the nutrient demands of the geophagic individuals. Iron content in the geophagic clayey soils was low, and thus the ingestion of these soils to alleviate symptoms related to Fe deficiency anemia may provide little comfort to the need to carry out further studies to understand the reason for this behavior in man.

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