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RESEARCH ARTICLE

Geochemical appraisal of major elements in geophagic clays from Vhembe District, South Africa

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ABSTRACT

Geophagic clays are consumed by human beings and other members of the animal kingdom for a number of reasons such as mineral nutrient supplementation, relief of early morning sickness in pregnancy and craving. The objective of this study was to assess major elements in geophagic clays in order to know clays that were enriched or depleted in major elements of nutritional value. The major elements were determined by means of X-ray fluorescence spectrometry (XRFS). The average concentration of SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 are 42.52%, 29.20%, 12.04% and 1.26% respectively with low content of CaO (0.26%). Chemical index of alteration (CIA) values for geophagic clays ranges from 17.09 – 99.07. There are no differences in major oxides of Mg, Mn, K and P in geophagic and non-geophagic clays. Cluster analysis of the major elements showed two groups of chemical differences amongst the elements in geophagic clays, low and moderate to high degree of weathered clays. Functional analysis showed that some of the geophagic clays were enriched in SiO_2, Al_2O_3 and Fe_2O_3 and depleted in CaO, K_2O and MnO. Geophagic clays devoid of Al_2O_3, SiO_2, MgO and those that are enriched in Fe_2O_3 and CaO are ideal for human consumption because of the potential benefits that are associated with Fe_2O_3 and CaO in human metabolism.

INTRODUCTION

Geophagy or geophagia is the deliberate ingestion of earth materials (clays, sands, ant hills, termite mounds and dried up pond sediments) by human beings and other members of animal kingdom. The practice cuts across the globe, including American continents, the British Isles, Europe and Africa (Brand *et al*., 2009). The habit is prevalent in the sub-Saharan Africa and it has been documented in the following countries; South Africa, Swaziland; Nigeria, Zambia, Tanzania; Ghana; Uganda; Malawi; Zimbabwe and Cameroon (Abrahams, 1997; Ekosse and Jumban, 2010). Human beings indulge in geophagic practice for wide varieties of reasons. Some of the rationale why people crave for Earth materials are as follows; to supplement intake of available Cu, Ca, Zn and Mg by rural communities (Davies, 2008); the treatment of dysentery, cholera and the definition of feminism amongst Chagga women of Tanzania (Ngole *et al*., 2010). The use of geophagic materials as nutrient supplements may depend on several factors, these includes concentrations of nutrients in the soils, their bioaccessibility and amount of earth material that is consumed on daily basis (Ngole *et al*., 2010). Three major hypotheses put forward to explain geophagic practice are: hunger, micronutrient deficiency and protection from toxins and pathogens. The hunger hypothesis states that people consume earth materials because they don't have anything else to eat (Young *et al*., 2010). The micronutrient deficiency hypothesis posits that people with micronutrient deficiencies eat earth materials in order to increase micronutrient intake of iron (Hunter, 1973). The practice of geophagy has been shown to supply 17% - 55% of recommended pregnancy supplementation of Ca, Mg, Zn, Fe, Cu, Mn, K and Se (Brand *et al*., 2009). Calcium and Fe are the two mineral nutrients that are frequently implicated in the physiological explanation for geophagy. The daily Ca need for pregnant women increases from 800 to 1200 $mgday^{-1}$, primarily to provide the nutrient for foetal, skeletal growth and development (Selinus, 2005). There is a paucity of data on the major element geochemistry of geophagic clays in Vhembe District. It is very necessary to address the lack of knowledge about geophagic clays in this locality. The primary purpose of this study was to evaluate the major element in geophagic clays and, application of multivariate statistics (cluster and functional analysis) on the studied elements in order to know the geophagic clays that are depleted or enriched in major elements of nutritional value to humans. The geochemical characteristics of geophagic clays are compared to non-geophagic clays in the District to establish the geochemical pattern.

MATERIALS AND METHODS

Study site and sample collection

Vhembe District is located at the north-western tip of South Africa in the Limpopo Province. It is made up of former Venda home land and part of Ganzakulu Republic. The area is mainly covered by soils derived from quartzite and sandstones which are generally shallow, gravely and acidic in nature (Mucina and Rutheford, 2006). Soils within the District are silty sandy soils, sandy and clayey soils which are found within the river valleys. The basement of Vhembe District is made up of Archean granulite gneiss, overlain by pink massive quartzite before the deposition of Karoo sediments. Numerous

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dolerite dykes and sills of diabase are within the District (Taylor, 1986). The sills were emplaced along the interface of shale and quartzite within the locality. Geophagic clays were purchased from retail outlets in local markets, shops and mining sites in the District. These materials were already in a consumable state without further processing before consumption. Four types of Earth materials totalling 35 geophagic clays were collected from the area of study. The first group of geophagic clays is reddish brown termite mounds found on the bark of trees, the second group is yellowish silty sandy material found in horizon A soil profile, the third group is grey smooth natural clays available in local markets and retail shops across the District, while the fourth group is a whitish silty sandy material. Three non geophagic samples were also sampled close to geophagic sites for comparative purposes.

Sample preparation and analyses

Geophagic clays were air-dried in a clean laboratory at a room temperature. Thereafter, the samples were crushed and grounded to < 75µm in a tungsten carbide milling vessel. They were roasted at 1000 °C to determine loss on ignition value, 1 g of sample was added to 6 g of $Li_2B_4O_7$ fused into a glass bead. The major elements (SiO_2, Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, Na_2O, MgO, MnO, SO_3, K2O and CaO) analyses were performed on the fused bead using the ARL 9400 XP X-ray fluorescence spectrometer. Quality control of the preparation and instrumental performances were checked using a blank and certified reference material analysed with each batch of samples. A comparison between the certified values of the reference materials and those found in this study indicated that the recoveries were within a very close range.

Statistical analyses

Multivariate statistical method was applied on major oxides data (wt %) in geophagic clays using IBM SPSS 19.0 statistical software. Varimax rotated factor analysis was performed on correlation matrix of rearranged data for 35 geophagic samples. The variance, cumulative and extraction sum of square loadings of the variables with Eigen values were computed. Rotation of the axis defined by factor analysis produced a new set of factors each one involving primarily a subset of the original variables with a little overlap as possible, so that the original variables were divided into groups. The factor analysis of the present dataset further sorted by the contribution of less significant variables (<0.4 factor score). A Varimax rotation (raw) of the different varifactors of Eigen value greater than 1, were further cleaned up by this technique (Akinyemi *et al*., 2011). Liu *et al*., (2003) classified the factor loading as “strong,” “moderate” and “weak” corresponding to absolute loading values of > 0.75, 0.75 - 0.50 and 0.50 - 0.40, respectively. Factor and cluster analyses were combined to assess the degree of major component matrix dissolution and determination of chemical processes. Hierarchical agglomerative clustering was performed on data normalised to zero mean and unit variance using squared Euclidean distances as the measure of similarity (Massart *et al*., 2003). Wards method was selected because it possesses a small space distorting effect, uses more information on cluster contents than other methods and has proven to be an extremely powerful grouping mechanism.

RESULTS AND DISCUSSION

Major oxides geochemistry

The results of major oxides in geophagic clays and control samples are shown in Table 1. Mean total contents of SiO_2, Al_2O_3 and Fe_2O_3 in geophagic clays were 42.52%, 29.20% and 12.04% respectively. LOI-loss on ignition, SD- standard deviation, C1-C3: Non geophagic control samples, Cert Ref – Certified reference Mean values of other oxides in geophagic clays from the area were as follows; TiO_2 1.26%; P_2O_5 0.09%; Na_2O 0.29%; MgO 2.47%; MnO 0.12%; SO_3 0.03%; K_20 4.20%; CaO 0.26% and LOI 7.8%. The concentration of the following oxides; Mn, Na, P, S, Ca were less than 1%. Geophagic samples had lower mean concentration of SiO_2 and Fe_2O_3 than control samples.

Table 1. Mean, standard deviation and major element analyses in geophagic and control samples from Vhembe District (wt %)

Sample	SiO_2	Al_2O_3	FeO_3	TiO_2	P_2O_5	Na_2O	MgO	MnO	SO_3	K_2O	CaO	LOI
1	39.14	32.03	10.56	0.83	0.06	0.37	1.17	0.13	0	4.73	0.12	10.05
2	42.48	21.83	23.98	3.34	0.15	0.10	0.45	0.19	0	1.04	0.87	5.31
3	39.65	25.76	16.32	2.24	0.05	0.07	1.41	0.02	0	9.27	0	5.18
4	31.81	24.49	27.17	3.08	0.16	0.03	0.67	0.07	0	0.05	0	12.18
5	40.85	27.24	14.7	1.93	0.04	0.12	1.1	0.01	0	8.39	0	5.67
6	34.81	23.03	23.47	3.54	0.15	0.09	0.85	0.03	0	8.49	0	5.53
7	39.05	33.55	9.27	0.72	0.06	0.44	2.02	0.11	0	4.11	0.17	10.46
8	39.21	32.86	9.67	0.67	0.04	0.42	2.32	0.13	0	4.75	0.19	9.70
9	39.62	31.79	10.29	0.81	0.06	0.38	2.02	0.15	0	5.03	0.09	9.62
10	38.68	31.89	9.68	0.77	0.05	0.35	1.90	0.12	0	4.81	0.08	11.47
11	38.37	30.56	11.19	0.77	0.06	0.48	2.28	0.17	0	5.19	0.19	10.51
12	39.14	33.68	9.50	0.73	0.05	0.49	1.72	0.14	0	4.26	0.11	10.52
13	39.06	33.57	9.12	0.70	0.06	0.50	2.00	0.10	0	4.28	0.16	10.40
14	39.17	32.21	9.97	0.72	0.05	0.45	1.91	0.14	0	4.74	0.10	10.38
15	38.54	31.68	10.25	0.74	0.06	0.45	1.93	0.13	0	4.79	0.13	11.11
16	43.34	28.42	11.78	1.43	0.07	0.29	1.19	0.3	0	3.58	0.14	9.28
17	38.98	33.68	8.27	0.66	0.04	0.42	1.99	0.1	0	4.48	0.06	11.28
18	38.87	32.27	9.87	0.12	0.76	0.53	1.73	0.12	0	4.33	0.15	11.13
19	39.7	32.00	9.77	0.77	0.05	0.45	1.81	0.16	0	4.70	0.11	10.28
20	38.14	32.72	10.3	0.83	0.07	0.43	1.59	0.12	0	3.99	0.16	11.39
21	50.57	34.48	7.42	0.48	0.08	0.40	1.10	0.12	0.13	4.62	0.33	1.20
22	52.16	38.02	5.67	0.86	0.04	0.12	0.01	0.02	0.11	2.57	0.15	1.10
23	37.22	31.07	26.97	3.24	0.19	0.01	0.01	0.37	0.2	0.16	0.14	1.30
24	56.44	23.73	9.68	1.31	0.02	0.09	1.21	0.03	0.02	7.07	0.02	1.52
25	39.27	30.54	25.26	2.82	0.2	0.11	0.01	0.28	0.23	2	0.5	1.63
26	42.58	29.35	22.08	2.59	0.19	0.29	0.43	0.26	0.21	0.68	0.94	1.22
27	50.78	36.49	6.51	0.47	0.04	0.39	0.65	0.09	0.14	3.97	0.23	1.43
28	51.23	35.29	6.77	0.5	0.04	0.39	0.84	0.1	0.12	4.26	0.24	1.5
29	50.58	35.96	6.86	0.48	0.03	0.39	0.8	0.09	0.12	4.2	0.25	1.53
30	50.62	35.89	6.98	0.48	0.06	0.39	0.78	0.09	0.1	4.1	0.28	1.6

31	58.98	19.91	8.47	1.07	0.01	0.32	2.12	0.05	0	5.35	0	4.56
32	60.31	19.05	9.35	1.74	0.17	0.01	3.62	0.22	0	4.94	0.37	1.28
33	51.38	17.77	17.04	2.37	0.1	0.09	2.15	0.07	0	4.39	0.84	4.52
34	49.8	28.99	6.49	0.49	0.05	0.63	1.37	0.09	0	3.87	0	9.08
35	7.72	0.4	0.83	0.07	0.01	0	39.29	0.02	0	0.06	1.88	49.76
Mean	45.52	29.2	12.04	1.26	0.09	0.29	2.47	0.12	0.03	4.2	0.26	7.84
SD	1.57	1.21	1.11	0.16	0.02	0.03	1.09	0.01	0.01	0.36	0.06	1.41
Cert Ref	65.8	14.67	3.75	0.68	0.28	3.57	2.3	0.06	0.01	4.56	2.5	1.32
Control 1	63.64	26.46	4.47	0.61	0.01	0.03	0.76	0.02	0.04	0.01	0.01	5.3
Control 2	38.31	30.35	26.09	3.16	0.21	0.04	0.01	0.03	0.04	0.27	0.23	1.78
Control 3	50.91	14.33	14.27	1.15	0.08	0.22	3.26	0.11	0	3.69	3.32	9.06
Mean	50.93	23.71	14.97	1.64	0.1	0.09	1.34	0.05	0.01	0.36	0.06	1.41
SD	12.66	8.35	10.82	1.34	0.1	0.1	1.7	0.04	0.02	2.05	1.85	3.64

Table 2. Chemical index of alteration values for geophagic clays from Vhembe District

Group I from Dendrogram cluster analysis													
Site	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	Na_2O	MgO	MnO	SO_3	K_2O	CaO	LOI	CIA
Cly 29	50.58	35.96	6.86	0.48	0.03	0.39	0.8	0.09	0.12	4.20	0.25	1.53	88.14
Cly 30	50.62	35.89	6.98	0.48	0.06	0.39	0.78	0.09	0.10	4.10	0.28	1.60	88.27
Cly 27	50.78	36.49	6.51	0.47	0.04	0.39	0.65	0.09	0.14	3.97	0.23	1.43	88.83
Cly 28	51.23	35.29	6.77	0.5	0.04	0.39	0.84	0.10	0.12	4.26	0.24	1.50	87.83
Cly 21	50.57	34.48	7.42	0.48	0.08	0.40	1.10	0.12	0.13	4.62	0.33	1.20	86.56
Cly 22	52.16	38.02	5.67	0.86	0.04	0.12	0.01	0.02	0.11	2.57	0.15	1.10	93.05
Cly 31	58.98	19.91	8.47	1.07	0.01	0.32	2.12	0.05	0.00	5.35	0.00	4.56	77.83
Cly 33	51.38	17.77	17.04	2.37	0.10	0.09	2.15	0.07	0.00	4.39	0.84	4.52	76.96
Group II from Dendrogram cluster analysis													
Site	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	Na_2O	MgO	MnO	SO_3	K_2O	CaO	LOI	CIA
Cly 1	39.14	32.03	10.56	0.83	0.06	0.37	1.17	0.13	0.00	4.73	0.12	10.05	85.99
Cly 2	42.48	21.83	23.98	3.34	0.15	0.10	0.45	0.19	0.00	1.04	0.87	5.31	91.57
Cly 3	39.65	25.76	16.32	2.24	0.05	0.07	1.41	0.02	0.00	9.27	0.00	5.18	73.09
Cly 4	31.81	24.49	27.17	3.08	0.16	0.03	0.67	0.07	0.00	0.05	0.15	12.18	99.07
Cly 5	40.85	27.24	14.7	1.93	0.04	0.12	1.10	0.01	0.00	8.39	0.00	5.67	76.20
Cly 6	34.81	23.03	23.47	3.54	0.15	0.09	0.85	0.03	0.00	8.49	0.00	5.53	72.86
Cly 7	39.05	33.55	9.27	0.72	0.06	0.44	2.02	0.11	0.00	4.11	0.17	10.46	87.67
Cly 8	39.21	32.86	9.67	0.67	0.04	0.42	2.32	0.13	0.00	4.75	0.19	9.70	85.98
Cly 9	39.62	31.79	10.29	0.81	0.06	0.38	2.02	0.15	0.00	5.03	0.09	9.62	85.25
Cly 10	38.68	31.89	9.68	0.77	0.05	0.35	1.90	0.12	0.00	4.81	0.08	11.47	85.89
Cly 11	38.37	30.56	11.19	0.77	0.06	0.48	2.28	0.17	0.00	5.19	0.19	10.51	83.91
Cly 12	39.14	33.68	9.50	0.73	0.05	0.49	1.72	0.14	0.00	4.26	0.11	10.52	87.39
Cly 13	39.06	33.57	9.12	0.70	0.06	0.50	2.00	0.10	0.00	4.28	0.16	10.40	87.17
Cly 14	39.17	32.21	9.97	0.72	0.05	0.45	1.97	0.14	0.00	4.74	0.10	10.38	85.89
Cly 15	38.54	31.68	10.25	0.74	0.06	0.45	1.93	0.13	0.00	4.79	0.13	11.11	85.51
Cly 16	43.34	28.42	11.78	1.43	0.07	0.29	1.19	0.10	0.00	4.48	0.06	11.28	87.16
Cly 17	38.98	33.68	8.27	0.66	0.04	0.42	1.99	0.10	0.00	4.48	0.06	11.28	87.16
Cly 18	38.87	32.27	9.87	0.12	0.76	0.53	1.73	0.12	0.00	4.33	0.15	11.13	86.56
Cly 19	39.70	32.00	9.77	0.77	0.05	0.45	1.81	0.16	0.00	4.70	0.11	10.28	85.88
Cly 20	38.14	32.72	10.30	0.83	0.07	0.43	1.59	0.12	0.00	3.99	0.16	11.39	87.72
Cly 23	37.22	31.07	26.97	3.24	0.19	0.01	0.01	0.37	0.20	0.16	0.14	1.30	99.01
Cly 25	39.27	30.54	25.26	2.82	0.20	0.11	0.01	0.28	0.23	2.00	0.50	1.63	92.13
Cly 26	42.58	29.35	22.08	2.59	0.19	0.29	0.43	0.26	0.21	0.68	0.94	1.22	93.89
Cly 34	49.80	28.99	6.49	0.49	0.05	0.63	1.37	0.09	0.00	3.87	0.00	9.08	86.56
Cly 35	7.72	0.40	0.83	0.07	0.01	0.00	39.29	0.02	0.00	0.06	1.88	49.76	17.09

Cly = Clay

Average Al oxide concentration in geophagic samples was greater than the control samples (Table 1). The non-geophagic samples were very siliceous compared to geophagic samples.

Chemical alteration of geophagic clays

According to Nesbit and Young (1982), a good measure of the degree of weathering can be obtained by calculation of the chemical index of alteration (CIA) using molecular proportions. CIA = [Al_2O_3/ (Al_2O_3 + CaO + Na_2O + K_2O)] × 100 As a result, the chemical index of alteration (CIA) was calculated for the geophagic clays from Vhembe District. The CIA values for geophagic clays ranges from 17.09 – 99.07 (Table 2). Two major groups of geophagic clays emerged from Dendrogram cluster analyses of geophagic clays. Those geophagic clays whose SiO_2 (wt %) relationship with CIA were greater than 50%, are moderate to high degree of weathered clays (Fig. 1),

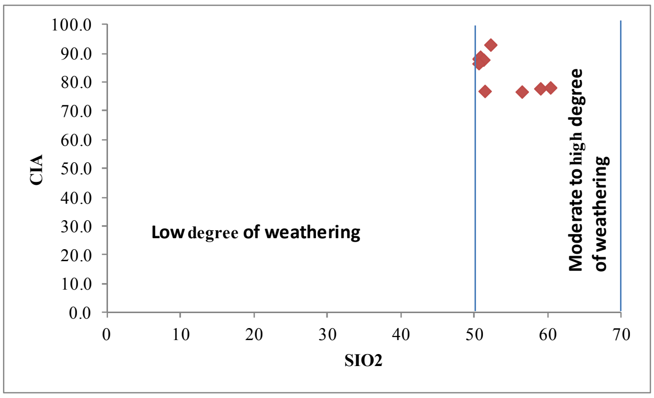

Figure 1. Relationship between SiO2 (wt %) and Chemical Index of Alteration (CIA) from Group I in the Dendrogram cluster analysis of clay samples from Vhembe District.

While those whose SiO_2 (wt %) relationship with CIA were less than 50% are referred to as clays of low degree of weathering (Fig. 2). Only one of the geophagic clay had a CIA value of less than 50%. This sample is believed to be magnesite, though mineralogical data is not reported in this study (Table 2).

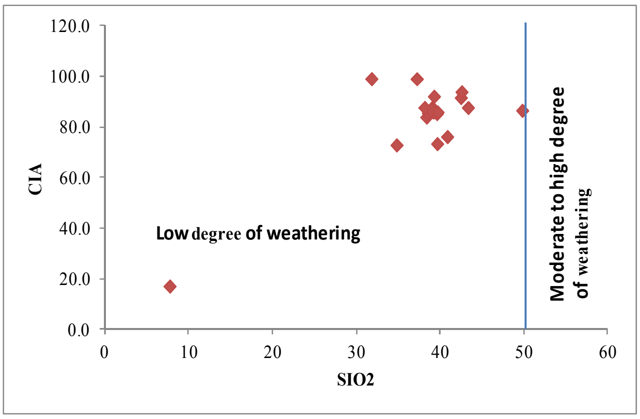

Figure 2. Relationship between SiO2 (wt %) and Chemical Index of Alteration (CIA) from Group II in the dendrogram cluster analysis of clay samples from Vhembe District.

Statistical analyses

Cluster analyses

The relationship among the geophagic clays obtained through cluster analyses synthesised by dendrogram plots (distance cluster combination) is shown in Figure 3. Statistical evaluation of the data based on dendrogram cluster analyses using the major elements SiO_2, Al_2O_3, Fe_2O_3, P_2O_5, Na_2O, MgO, MnO, SO_3, K_2O, CaO and LOI as variables classified the geophagic clays into four groups (Fig. 3). Group I consisted of samples 21, 22, 24, 27, 28, 29, 30, 31, 32 and 33; group II consist of samples 10, 11, 15, 16, 18, 20, 23, 25, 26 and 34; group III is made up of samples 1,7, 8, 9, 10, 11, 12, 13,14, 15, 16, 18 19 and 20; while group IV consisted of samples 2, 4, 6, 8, 9, 10,11, 16, 19, 20, 23, 25, 26 and 34 respectively. The discriminant function analysis performed by comparing structure matrix to functional group centroid showed strong association of SiO_2 with group I, moderate association of Al_2O_3 with group I and weak association of K_2O with group I. The following oxides, TiO_2 and Fe_2O_3 showed strong association with group II. In group III, SO_3 showed strong association, while MnO showed moderate association with it. The groups were 100% different from each other. The dendrogram plot reflects a sequence in the association displaying the phase as a degree of chemical weathering amongst the geophagic clays. The dendrogram plot broadly categorized the geophagic clays into two major groups, i.e. moderate to high degree of weathered clays and low degree of weathered clays (Fig. 3).

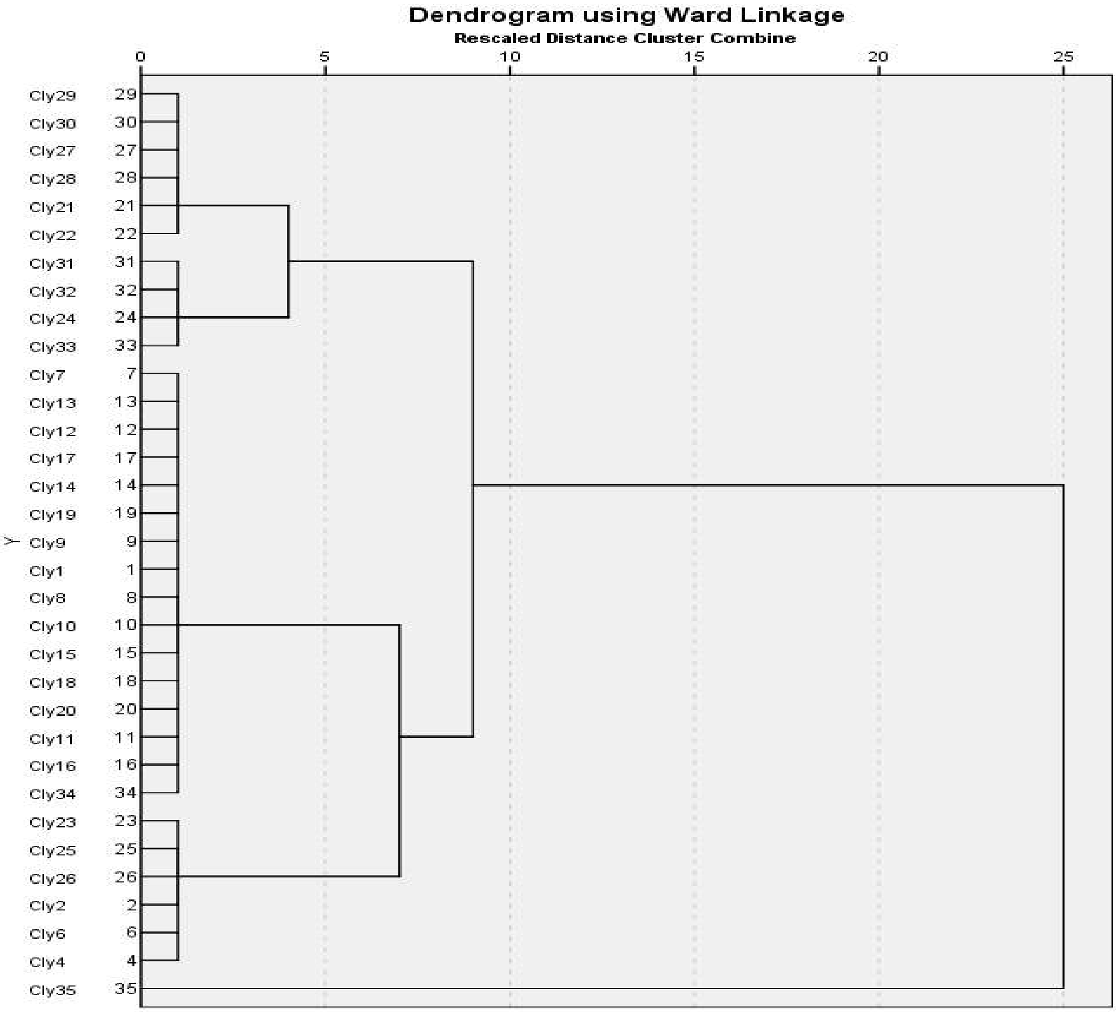

Figure 3. Dendrogram cluster analysis of clay samples using major elements reported as oxides (wt %) and loss on ignition as variables.

Functional analysis

The functional analysis of the major elements reported as oxides using rotated component matrix showed 4 components (Table 4).

Table 4. Varimax Rotated Factor Loadings Matrix and Communalities obtained from Principal component analysis for the studied major elements in geophagic clays from Vhembe District

Variables	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Communality
MgO	-0.95				0.96
LOI	-0.94				0.98
SiO2	0.80			-0.41	0.81
CaO	-0.78				0.83
Al2O3	0.68	-0.57			0.89
TiO2		0.90			0.96
Na2O		-0.87			0.87
FeO3		0.74		0.55	0.93
SO3			0.89		0.86
K2O	0.47		-0.70		0.79
MnO			0.56	0.52	0.63
P2O5				0.71	0.51
EV	3.9	2.6	1.9	1.6	
VAR (%)	32.4	22.0	16.0	13.0	
CVAR (%)	32.418	54.46	70.49	83.451	

NB. EV= Eigen value, VAR= explained variance, CVAR= cumulative variance explained

Component 1 represents 39.82% of total variance, which was found to be depleted in elements such as MgO, CaO, LOI but showed enrichment in SiO_2, Al_2O_3 and K_2O; component II represents 26.36% of total variance which was associated with TiO_2, Fe_2O_3 but was depleted in Al_2O_3 and Na_2O; component III represent 19.17% of total variance, which was associated with SO_3, MnO but depleted in K_2O and component IV represents 15.57% of total variance, which was associated with Fe_2O_3, MnO, P_2O_5 and depleted in SiO_2. The depletion of MgO and CaO in component I, Al_2O_3 and Na_2O in component IV coincide with samples taken from termite mounds, anthills and horizon A soil profile. Depletion of Al_2O_3 and Na_2O in component II coincides with termite mound, magnesite rich material and SiO_2 in component III coincides with samples from horizon A soil profile. Component IV that was deficient in SiO_2 coincides with magnesite. The depletion and enrichment trends could be due to degree of weathering and origin of formation of geophagic clays.
The geophagic clays have variable chemical compositions. There was no notable difference between total Na and P content of geophagic clays and control samples. This is consistent with the geophagic soils in Udawale National Park in Sri Lanka (Chandrajith *et al*., 2009).

Certain geophagic clays were deficient in Ca (< 0.2 % CaO). The geophagic clays were characterized by high Si, indicating a high amount of quartz, of which sand was the most significant fraction. According to Ngole *et al*., (2010) significant quantity of Si in geophagic clays may result in various medical conditions. These include dental enamel destruction and perforation of the sigmoid colon (Lohn *et al*., 2000). The concentrations of the following oxides; Ti, K, Mn, P, Na and S were low. This study confirms the results of several other studies carried out in Thailand, Zaire, Swaziland and Uganda (Abrahams, 1997; Ngole *et al*., 2010). Ferric content of geophagic clays from this locality was higher than those of other clays from Nigeria (Okunlola and Owoyemi, 2011). The geophagic clays were rich in Fe_2O_3 and are similar to geophagic soils from Zanzibar in Tanzania (Young *et al*., 2010). One notable feature of many geophagic soils is high Fe content, which was perceived by geophagists to relieve iron deficiencies as suggested by several researches (Abrahams, 1997; Aufrieter, 1997). The geophagic clays from this area showed high Fe concentration as well. Tough, the control samples were deficient in Fe content. Major oxides of Mn and P are variable in the geophagic clays. The values of the different oxides of Ti, K, Mn, P and S in each of the samples fell within the range of values reported in geophagic soils from Turkey, Swaziland, Mississippi, Georgia and Zanzibar (Young *et al*., 2010). According to Ekosse and Ngole (2012), Titanium oxide in geophagic soils could possibly be in the form of free Ti oxides and some may have substituted for Al in the octahedral sheet of kaolinite. High values (> 75) of Chemical Index of Alteration (CIA) indicate intensive chemical weathering in the source areas whereas low values (50 or less) indicate un-weathered source areas (Ekosse and Ngole, 2012). These high values of CIA suggests low amount of essential constituents (Ca, Mg, Fe and P) in geophagic materials. The CIA of geophagic clays from this locality showed low, moderate to high degree of weathering respectively. This is consistent with CIA values of clays from Surma Group (Depetris and Probst, 1998). Very high values (> 88) for CIA of geophagic soils from Democratic Republic of Congo (DRC), Cameroon and Nigeria confirmed extremely high degree of weathering compared to CIA Values of 45-55 which were indicative of no weathering (Depetris and Probst, 1998). Chemical index of alteration (CIA) values for geophagic clays from this locality were consistent with CIA of geophagic clays from these countries except for one sample which has a very weak CIA value of less than 20. This could be due to environment of deposition of this geophagic clay in Vhembe District. The climate is sub tropical and is similar to the climatic condition of countries like Nigeria, Cameroon and DRC where the intensity of rainfall is very high. There is scanty of data on major element geochemistry using PCA in sub-Saharan Africa geophagic clays to compare the present results, except Chandrajith *et al*. (2009) which conducted a study on geophagic soils in Udawale National Park, Sri Lanka. Component I was similar to the first component identified by these researchers. This component was largely enriched in Al_2O_3-SiO_2 and was known to be kaolinitic-quartz in terms of clay mineralogy. Most of the major elements in component I show weak loadings, only two elements, Al_2O_3 and Na_2O in component II, K_2O in component III and SiO_2 in component IV showed weak loadings, respectively.

Conclusions

The findings of this study serve as the basis for making the following conclusions. The dominant major elements in the geophagic clays were Al_2O_3, SiO_2 and Fe_2O_3. Oxides of Ti, P, Na, Mn and Ca in the geophagic clays and control samples were less significant and variable in composition. Relationship between SiO_2 and CIA revealed that the geophagic clays were of low degree, moderate to high degree of weathering. Relative enrichment and depletion trends of major elements in geophagic clays could be due to the intensity of weathering and environment where these geophagic clays were formed. Siliceous geophagic clays could be detrimental to the health of geophagists because of gradual wearing of mucosal wall and perforation of sigmoid colon. Geophagic clays in group I from Dendrogram cluster analyses are rated to be very rich in quartz and these could pose significant risk to the health of geophagic practitioners in this locality.

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