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Physico-Chemical and Mineralogical Analysis of Geophagic Clays in Lubumbashi and Assessment of the Risks Associated with Geophagy

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Abstract: ***In view of the increasing local exploitation of clays used in geophagy in Lubumbashi, and with the aim of adding value to it, this work has identified and characterized three of them. Organoleptic tests showed that these clays vary in colour from brownish yellow to yellow-brown, "stick" to the tongue and are crunchy when chewed. X-ray fluorescence spectrometry (XRF) highlighted major oxides: SiO_2 (54.8- 64.7%), Al_2O_3 (20.0-24.0%), Fe_2O_3 (1.8- 5.0%), TiO_2 (1.4-2.8%) and K_2O (0.9- 2.4%). Cation exchange capacity (CEC) varied from 21.4 to 26.0 meq/100 g, loss on ignition varied from 5.1% to 13.2%, moisture content range from 2.40% to 2.96% with a swelling index from 53.57% to 55.27%, density and organic matter were too low. The pH water and pH KCl were between 4.04 and 5.96 and between 3.72 and 5.49 respectively. High levels of certain metallic elements such as As, Cd, Pb and Ni, and the presence of uranium-bearing substances, were also revealed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). This study revealed that geophagic clays were plastic based on their oxides, illites and/or chlorites, also depending on their CEC, acidic considering their pH and that they were contaminated by compounds that could be harmful to the health of geophagists.***

Keywords: Description, clay, geophagy, Lubumbashi, pregnant woman

1. Introduction

Clays are natural materials made by a combination of several mineral types, with clay minerals predominating (Liewig *et al.*, 2012), with allogenic minerals (quartz, feldspars, micas, heavy minerals) or authigenic minerals (anatase, sulphates, etc.) being associated with them. Their varied structures, physico-chemical compositions, mineralogical and geotechnical compositions, which are known thanks to the results of advances, give them a variety of applications, in several fields (Qlihaa et *al.*, 2016).

These clays are used in human and veterinary medicine (Voinot *et al.*, 2014, Pourshahrestanie *et al.*, 2016); in the pharmaceutical industry (Rautureau *et al.*, 2017, Mahamoud *et al.*, 2017); in textile, plastics and food industries (Wu & Khlangwiset, 2010); in water treatment as pollutant barriers and catalysts (Qlihaa *et al.*, 2016); in construction (Wetshondo, 2012); and even in geophagy (OKereafor *et al.*, 2016, Qlihaa *et al.,* 2016).

The term geophagy, derived from geophage (to eat the earth), describes a common behaviour observed in geographic areas, and is a part of the eating condition pica (Lambert *et al.*, 2013) Geophagists consume kaolinites, illites and smectites (Young *et al.*, 2010) against nausea and vomiting during pregnancy, and as mineral supplementation and antidote (Liewig *et al.*, 2012).

However, the risks associated with geophagy include anaemia due to martial deficiency (Young *et al.*, 2008; Mc Lean *et al.*, 2009; Nafil *et al.*, 2015), intoxication by heavy metals and radioactive substances (Winklhofer et al, 2000; Harris *et al.*, 2013; Lambert *et al.*, 2014; Mahamoud *et al.*, 2017), ionic disruption (Chaushev *et al.*, 2003, Lambert *et al.*, 2013), and, bacterial and geohelminth contamination (Kawai *et al.*, 2009; Kutalek *et al.*, 2010).

Despite the risks associated with geophagy, various soils are consumed with relish by humans on all continents of the world, particularly in Africa (Gomes *et al.*, 2007; Ngole and Ekose, 2015), and especially by pregnant women (Mikkelsen *et al.*, 2006; Brand *et al.*, 2007; Adehossi *et al.*, 2017).

Several studies have investigated the mineralogical and physicochemical characterisation of clays, identifying different clay minerals: smectite, montmorillonite, bentonite,

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illite, vermiculite, kaolinite and sepiolite, with different heavy metal absorption capacities. The chemical composition, physical and geotechnical properties were also determined to justify their use in various fields, including geophagy (Qlihaa *et al*., 2016, Okereafor *et al*., 2016).

Lubumbashi, a city within DR Congo's Haut-Katanga Province, is home to many mining companies, which contribute to environmental pollution through mine company's effluents and metal-laden smelting gases (Romain, 2018).

Saad and colleagues (2011) found cobalt-rich deposits with naturally high uranium and multiple metals from Lubumbashi to Kolwezi, confirming the carbonate, metal-oxide, silicate, and organosilicate rich soils which affect trace element mobility (Lamy et *al*., 2006). It is therefore essential to determine the physico-chemical and mineralogical profile of geophagic clays to understand their impact on the health of geophagic practitioners.

The aim of this study was to characterise three local clays used in geophagy in Lubumbashi from an organoleptic point of view, before subjecting them to a physicochemical and mineralogical study. The results obtained will allow to confirm that these products are not dangerous to utilize and to envisage using them in the pharmaceutical and cosmetic fields.

2. Material and methods

2.1 Material

An analytical study following the collection of clay samples used in geophagy. It concerns 3 samples collected in 3 areas located in the 3 communes (Katuba, Kampemba and Rwashi) of the city of Lubumbashi. The three (3) samples collected were coded so as not to confuse them according to their origin: ENw (Naweji sample), EKm (Kamasanka sample), EKl (Kalanda sample). Laboratory analyses were carried out in four laboratories: (1) Molecular and Material Chemistry Laboratory of the Polytechnic Faculty at Université de Mons (Umons) in Belgium, (2) Regional Center for Nuclear Studies of Kinshasa (CRENK) at Kinshasa, DR Congo, and (3) Office Congolais de Contrôle (OCC), Lubumbashi, DR Congo.

2.2 Methods

2.2.1. Sampling and sample processing

The samples were chosen because they were harvested in Lubumbashi and following a survey of geophagists and clay sellers. The samples were taken at the production sites in order to limit the risk of sampling bias, since not all Lubumbashi's geophagic clays are not locally produced. The collected samples were subjected to four preliminary processes: cutting into pieces using a stainless-steel knife, drying in an oven for 24 hours at 80°C, crushing using a grinder and sieving using a 2mm sieve.

2.2.2. Organoleptic tests

Les tests organoleptiques se basant sur l'aspect, le goût, l'odeur, la couleur, la consistance des échantillons donnent une idée sur le type de famille minéralogique, la pureté et la composition en minéraux des argiles (Allègre, 2012).

The clays were identified by the geophagists and the research team by (i) observing them to see if they were indeed clay, (ii) placing a piece of clay on the tongue to see if it catches the tongue like a suction cup with a dry sensation in the presence of Attapulgite or Sepiolite or Smectite if the suction cup effect is accompanied by a muddy and slippery sensation, chewing the said piece reveals the presence or otherwise of sand and mica when the pasty sensation after disintegration is effective or not, if it just grabs at the beginning and accompanied by a muddy and slippery sensation to signify the presence of a Smectite; or chewing of the said piece to appreciate the presence or not of sand and mica when the pasty sensation after disintegration is effective or not; (iii) determination of the different colourings by sight with comparison to the colouring results of the Munsell soil colour booklet (2002), according to Reilly&Henry (2000) and Okereafor *et al*. (2016).

2.2.3. Physico-chemical profile

Nine (9) methods were used to characterise geophagic clays, including: measurement of pH, moisture content, density, swelling index, colloidality and loss on ignition. Determination of organic matter, cation exchange capacity (CEC) and chemical entity content using X-ray fluorescence.:

pH Determination allows the freshness of the sample to be determined and the contribution of acidity when the solid is in contact with the solution to be quantified (Amin, 2009). It was decided to characterise clays according to their ability to sorb trace metals and their oxides, as their sorption is strongly influenced by pH (Corami *et al*., 2007). Two types of pH measurement were addressed: measurement of actual acidity (pHwater) and measurement of potential acidity (pHKCl). For this, a 10% m/v clay solution was prepared with distilled water and/or 1mol/L KCl. The mixture was allowed to stand for 4 hours at 25°C to allow ions to dissolve and was homogenised using a magnetic stirrer before being read directly on a Metter Toledo pH meter. The difference between the two pH values determines the acidity reserve of the clays (Qlihaa *et al*., 2016).

Moisture content is measured by determining the mass of water removed by drying a moist material to a constant mass at a temperature of 105 ± 5°C for 24 hours. The mass of the clay sample after drying was taken as the mass of solid particles (Mp). The determination of the moisture content was calculated from the ratio of the mass in grams of water (ME) to the mass in grams of solid particles (Touhatouh *et al*., 2014). H%=Me/Mp X100 (I).

Bulk density of studied sample was measured by determining the volume of a m mass of the sample using a pycnometer (Qlihaa *et al*., 2016).

Density=(Mass of sample volume)/(Mass of distilled water volume) (II).

The swelling index was measured by suspending the clay samples in distilled water. A 100 ml graduated cylinder was

filled with 50 ml of distilled water and 0.5 g of clay sample was added. After 45 minutes, another 0.5g of clay sample was added. After 2 hours, the swelling volume was recorded. The swelling index was measured according to the formula (Qlihaa *et al.*, 2016):
Swelling index (%) = (swelling volume X 50)/(50-humidity) (III)

Colloidality measurement is used to determine whether the samples under investigation are clay materials. Colloidality is defined as the coverage of the surface of each clay particle by a double layer of water-soluble ions of opposite charge. Colloidality was measured by suspending 50g of clay and adding 0.2g of MgO to allow deflocculation. After stirring for 5 minutes, the mixture was placed in a graduated cylinder. After 24 hours, the volume V (ml) occupied by the supernatant was measured. Colloidality was measured by the formula (Qlihaa *et al.*, 2016): C (%) =100-V (IV) with C: Colloidality in % and V: volume of supernatant water in ml.

Loss on ignition, expressed in (%), is the loss in weight of a sample after calcination at 1100°C, relative to the initial weight. It is used to determine the number of products likely to decompose or volatilise during firing. The loss on ignition was measured after placing 10 g of clay, i.e. its weight of P1, in a porcelain crucible, which had been pre-treated, and placing the crucible in a kiln with a gradual temperature increase up to 1000 °C for 1 hour. The crucible was then removed and placed in a desiccator to cool and weigh it, i.e. its weight P2 (Qlihaa *et al.*, 2016).

The value of the loss on ignition is given by the following relationship:
PAF=(p1-p2)/p1 X100 (V)

Organic matter, expressed as (%), is used to determine the purity of clay samples as it is the most abundant element in soils. It was determined by etching with hydrogen peroxide (Laibi *et al.*, 2017). The ratio of the difference between the initial mass of the sample mo and the mass of the sample after the reaction m1 to the initial test mass mo is the organic matter contained in the soil. Following formula gives the value of organic matter:

$$CMOC\ (\%) = \frac{mo-m1}{\text{mo}} X100\ \text{(VI)}$$

The mass m1 is obtained by weighing 100 g of the sample, placing it in a 500 ml beaker, adding 200 ml of distilled water and 20 ml of 10 vol. hydrogen peroxide, allowing the mixture to stand for 2 hours, drying in an oven at 105°C and weighing the mixture.

Cation exchange capacity (CEC), expressed in milliequivalents per 100 g (MEQ), is an essential parameter for the characterisation of clay materials by determining different mineralogical families, considering their value in milliequivalents per gram (Malkoc *et al.*, 2006).

It represents the ability of clays to reversibly bind certain cations present in the surrounding solutions and corresponds to the number of negative charges capable of binding cations. The CEC was determined using the cobaltihexamine method (Mamindy *et al.*, 2011), in which 2 g of ground clay, dried at 80 °C for 24 h, is introduced into 100 ml of a 0.045 N solution of cobaltihexamine chloride salt ($Cl_3\ [Co\ (NH_3)_6]$). After a contact time of 1 hour with intensive and discontinuous stirring, the solution was filtered, and the excess salt was determined by UV-visible spectroscopy at a wavelength of 470 nm (Balze, 2006).

The coding of the different mineralogical types according to their CEC, which is given in the literature in (mEq/100 g), is as follows: Kaolinite1-3, Illite/chlorite 10-40, Montmorillonite 80-150 and vermiculite 100-150 (Malkoc *et al.*, 2006; Qlihaa *et al.*, 2016).

Determination of oxides and chemical entities by X-ray fluorescence and ICP-AES

The chemical entities and their oxides were analysed by means of (a) an Axion X-ray fluorescence spectrometer with a wavelength dispersion of 1 kW and (b) an IRS-Intrepid II XSP ICP-AES Atomic Emission Spectrometer.

3. Results and discussion

3.1 Organoleptic parameters

Colour and texture give an idea of the purity of clays. They have a major influence on the selection of geophagic clays. The colour alone can provide a mineralogical and/or a physico-chemical characterisation of the clay soils. In addition to the results of the identification and purity tests, the results of the organoleptic tests are made up of the results of the colour analysis.

All the samples tested had a slightly sticky taste and a sludgy feel in the mouth. There was no crunching between the teeth, apart from the pasty sensation in the mouth after chewing.

Studied samples are not pure, but a mixture of several mineralogy families and other impurities, which are sand granules dispersed throughout the clay material. These results confirm those of Okereafor *et al.* (2016) on geophagic clays sold in informal markets in South Africa, which showed coarseness and sand presence.

According to several authors, geophagy prefers sandy clay soils to silkier and softer ones (Allègre, 2012; Ngole-Jeme & Ekose, 2015; Qlihaa *et al.*, 2016) Soils containing sand can cause dental lesions (Woywodt & Kiss, 2002; Ngole & Ekosse, 2010) and perforation of the sigmoid colon (Lohn *et al.*, 2000; Diko & Ekosse, 2014) in geophagous animals due to the abrasive nature of silica-rich particles.

Different colourations of samples were determined visually by comparing sample colourations with those recorded by Reilly & Henry (2000) and Okereafor *et al.* (2016) based on Munsell soil colour chart (2002).

The EKm and EKl samples have a brownish-yellow colouration corresponding to the Munsell notation of 10YR4/2, while the ENw sample has a yellowish-brown colouration corresponding to the Munsell notation of 2.5YR-7.5YR 8/6.

The brownish-yellow and yellowish-brown colourations may be associated with the presence of iron oxide or a mixture of green clay minerals and organic matter, suggesting the presence of hematite (Fe_2O_3), goethite ($FeO(OH)$) and/or iron oxyhydroxide (Young, 2008; Bain *et al*., 2011).

These results indicate that clay soils used for geophagy in Lubumbashi contain iron in ferrous oxide form, which is not easily absorbed by humans (Ekosse & Jumbam, 2010; Ngole & Ekosse, 2010).

Results of the study conducted in South Africa by Okereafor *et al*. (2016) showed that the clays are white in colour, which justifies the presence of more kaolinitic than other mineralogical families and the pale brown colouration was due to the presence of finely disseminated organic matter.

3.2 Cation exchange capacity

The cation exchange capacity (CEC) is essential for the characterisation of clay materials, as it allows the identification of the different mineralogical families or types of clays commonly encountered (illites, kaolinites, montmorillonites or smectites, etc.) (Malkoc *et al*., 2006; Qlihaa *et al*., 2016).

The CEC values of the analysed clays are presented in Table I. below.

Table I: CEC of analysed clays

Cleys samples	CEC (meq/100g)
EKm	23.04
ENw	26.04
EKl	21.44

The CEC values of the analysed geophagic clay samples presented in Table I range from 21.44 meq/100g to 23.04 meq/100g. These values are within the range associated with illite and chlorite (10-40 meq/100g) (Touhtouh *et al*., 2014; Maman *et al*., 2017). According to Fait *et al*. (2017), these clay materials have a low capacity for cations retention by their sheets.

3.3 Physical and chemical parameters of clays

Characterising clays also means describing their physical and chemical parameters. The average values of the physico-chemical parameters (pH, moisture, loss on ignition, swelling index, colloidality and organic matter) recorded for the clays analysed are given in Table II.

Table II: Mean values of analysed samples physico-chemical parameters

Parameters	Samples	Mean±SD
pHEau	EKm	5,957±0,0056^{a,b}
	ENw	6,909±0,0120^{a}
	Ekl	4,050±0,0174^{b}
pHKCl	EKm	5,093±0,0005^{a}
	ENw	5,491±0,0012^{a}
	Ekl	3,714±0,0125^{b}
ΔpH	EKm	0,864±0,0060^{a}
	ENw	1,418±0,0111^{b}
	Ekl	0,336±0,0296^{c}
TxH (%)	EKm	2,405±0,0057^{a}
	ENw	2,411±0,0020^{a}
	Ekl	2,964±0,0076^{a}
IG(%)	EKm	53,573±0,0351^{a}
	ENw	53,587±0,0153^{a}
	Ekl	55,274±0,0012^{a}
PF(%)	EKm	5,714±0,00147^{a}
	ENw	13,197±0,0063^{b}
	Ekl	11,291±0,0053^{b}

For each parameter, the mean values of the samples with the same superscript did not show a significant difference ($p = 0.05$).

The pH values mean (pHEau and pHKCl) are acidic (4.05 - 5.96) according to results in Table II. This acidity is due either to the presence of ferrous and aluminous ions or to impurities in the humic matter contained in the clays (Wetshondo, 2012), based on the range of variation in soil pH (Chaignon *et al*., 2003). The difference between the two pHs, which provides information on the variability of the reserve acidity of the soil samples (Mathieu *et al*., 2003), was small, i.e. 0.87±0.45, ranging from 0.6<difference<1 to >1.

The EKl materials had statistically higher mean values than the EKm materials and higher values than the ENw materials, although not statistically significant.

The taste of clays used in geophagy is influenced by their pH and dissolved mineral content. A more acidic geophagic clay gives a bitter taste when consumed (Diko & Ekose, 2014; Okereafor *et al*., 2016), controls excessive salivation and reduces nausea (Ibeanu *et al*., 2014). The acidic pH makes these clays suitable for treating pregnancy-related nausea and hypersalivation (Eigbike *et al*., 2013; Okereafor *et al*., 2016).

The moisture content depends on the nature of the adsorbed ions and corresponds to the amount of water in the interlayers between the silicate layers. The moisture content found in this study was too low, averaging (2.59 ±0.32) %, and did not show a significant statistical difference between them. In the literature, this type of soil is classified as fersial, alisolic or gleyisolic, which are the driest, as opposed to vertisolic and calcimagnesic soils, which are more or less humid (Touhtouh *et al*., 2014; Romain, 2018).

These clays are poorly hydrated, they are not able to fix water in the plates and they are not very porous; their hydration characteristics are different from those that characterise smectites (Touhtouh *et al*., 2014). These results are consistent with those of (Wetshondo, 2012; Qlihaa *et al*., 2016; Bakouan, 2018) and contradict those of other authors (Amirouche, 2011; Touhtouh *et al*., 2014).

The swelling index was highly variable, averaging 54.14±0.8%, and did not differ between clays at the p=0.05 threshold. It is not sufficient to classify these clays as swelling clays such as smectites, but rather as low swelling clays such as illites, chlorites and kaolinites (Shackelford *et al*., 2000). The results of the swelling index are not in agreement with the work of others who have found higher or lower values (Rowe *et al*., 2009; Qlihaa *et al*., 2016; Nacéreddine, 2017).

Colloidality was low, averaging (9.36±0.4)%, and showed a statistically significant difference between clays; this can be explained by the absence of negative charges on the surface of the grains or by low ionisation of the clay particles (Qlihaa *et al.*, 2016), these clays would be free of impurities (Nacéreddine, 2017).

Organic matter had a low percentage of (1.20±0.5)% and showed a statistically significant difference between the clays. Clays are characteristic of soils with low humus content and are considered geotechnically as inorganic soils (Guerraoui *et al.*, 2008). These soils prevent sulphate reduction and favour the formation of insoluble, potentially toxic complexes that prevent pathogenic and saprophytic microorganisms from multiplying (Barour, 2015).

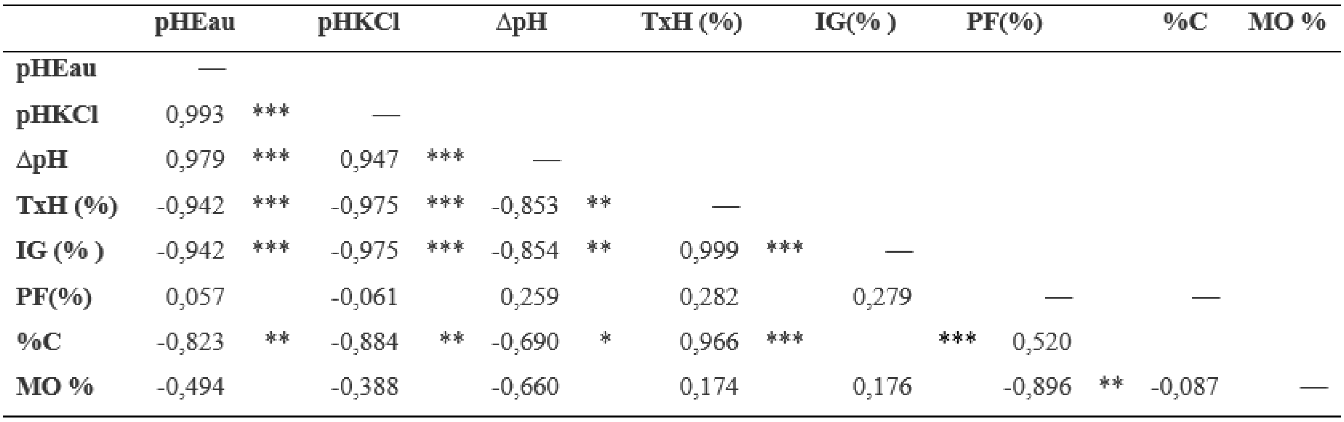
These results confirm those of several researchers (Guerraoui *et al.*, 2008; Maman *et al.*, 2014; Touhouh *et al.*, 2014; Bentahar, 2016).

Losses on ignition correspond to the dehydroxylation and decarboxylation of clay minerals and provide information about the mineralogical composition of clays. After XRF analysis (Qlihaa *et al.*, 2016), they averaged 10.07±31%. ENw had statistically higher values than the others. This percentage indicates the presence of kaolinites, iron oxides, a low organic matter content and therefore a low pathogen load (Wetshondo, 2012). There is a low risk of infection with Escherichia coli, Entamoeba histolytica and helminth infections such as Ascaris lombricoides and Stronyloide stercoralis during geophagy (Sagbo *et al.*, 2015; Okereafor *et al.*, 2016).

Some of the physico-chemical parameters that have been analysed show correlations between them. These correlations, expressed in terms of the Pearson's coefficient, are presented in Table III.

On the one hand, there is a strong positive correlation between pHwater, pHKCl and ΔpH, as well as TxH AND IG, where an increase in pHwater leads to a decrease in pHKCl and an increase in TxH is accompanied by an increase in IG. On the other hand, there is a strong negative correlation between pHwater, TxH and IG, where one does not influence the other.

Table III: Correlation between investigated physico-chemical parameters



	pHEau		pHKCl		ΔpH		TxH (%)		IG(%)		PF(%)		%C	MO %
pHEau	—													
pHKCl	0,993	***	—											
ΔpH	0,979	***	0,947	***	—									
TxH (%)	-0,942	***	-0,975	***	-0,853	**	—							
IG (%)	-0,942	***	-0,975	***	-0,854	**	0,999	***	—					
PF(%)	0,057		-0,061		0,259		0,282		0,279		—		—	
%C	-0,823	**	-0,884	**	-0,690	*	0,966	***		***	0,520			
MO %	-0,494		-0,388		-0,660		0,174		0,176		-0,896	**	-0,087	—

Note : Coefficient de corrélation de Pearson. * p < 0,5, ** p < 0,1, *** p < 0,01

3.4 Oxides in the clays analysed

Clays are characterised by their oxides. The average oxide content of the samples analysed is shown in Table IV.

Table IV: Average oxide content of clays used in geophagy in Lubumbashi

Samples	ENw	Ekl	Ekm
SiO_2	54.9 ± 0.251^a	58.5 ± 0.0208^a	64.8 ± 0.108^b
Al_2O_3	23.9 ± 0.0945^a	20.1 ± 0.0208^b	23.9 ± 0.205^a
Fe_2O_3	$3.49 \pm 0.100^{a.b}$	5.39 ± 0.0015^a	1.85 ± 0.0850^b
P_2O_5	0.0633 ± 0.0153^a	0.0400 ± 0.0026^a	0.0667 ± 0.0252^a
K_2O	0.917 ± 0.0252^a	2.50 ± 0.0173^b	0.953 ± 0.0473^a
MgO	0.433 ± 0.0153^a	0.972 ± 0.0237^b	0.487 ± 0.0321^a
Na_2O	0.0287 ± 0.0013^a	0.996 ± 0.0059^b	0.0134 ± 0.0007^a
TiO_2	2.94 ± 0.0351^a	1.40 ± 0.0078^b	2.78 ± 0.0404^a
Al_2O_3 /SiO_2	0.435 ± 0.0008^a	0.344 ± 0.0004^b	$0.369 \pm 0.0030^{a,b}$
SiO_2/Al_2O_3	2.30 ± 0.00446^a	2.91 ± 0.00364^a	2.71 ± 0.0221^a
CEC	26.0 ± 0.0681^a	21.5 ± 0.273^b	23.0 ± 0.0416^b

For each parameter, the mean values of samples with the same superscript letters showed no significant difference (at the p=0.05).

Analysis of Table IV shows that the predominant constituents are silicon, aluminium, iron and titanium in oxide form. The other constituents are present in trace amounts. In order of mass percentage of oxides, silica was the most abundant, followed by alumina, sesquioxides and titanium oxides.

The silica content, which is silicon oxide (SiO_2), ranged from 54.9% for ENw to 64.8% for EKm. EKl had a content of 58.5%. This relatively high silica content means that the samples analysed can be classified as plastic (Ngon Ngon, 2007).

The alumina or aluminium oxide (Al_2O_3) content ranged from 20.1% for EKl to 23.9% for EKm. ENw had a content of 23.9%. These are lower than 39.49%, which is the characteristic content of pure kaolinite (Okereafor *et al.*, 2016), indicating that the samples analysed were composed of a mixture of mineralogical families. Several studies have shown that clay materials have a higher percentage of silica than alumina, sesquioxide, titanium oxide, etc. (Wetshondo, 2012; Gourouza *et al.*, 2013; Ouahabi, 2013; Qlihaa *et al.*, 2016).

The alumina/silica ratio provides information on the permeability of the material to moisture and loss on ignition. The higher the ratio, the higher the permeability (Jarraya *et al*., 2010; Sadki *et al*., 2014; Qlihaa *et al*., 2016). In the case of this work, this ratio is between 0.34 for EKl and 0.44 for ENw. The narrowness of this ratio is consistent with low moisture and ignition loss (see Table I) (Okereafor *et al.*, 2016).

The Silica/Alumina ratio, which provides information on the substitution of silicon ions by aluminium ions, varies from 2.29 to 2.91. These values prove the presence of Quartz in the samples analysed (Gourouza *et al.*, 2013; Qlihaa *et al.*, 2016).

The ferric sesquioxide (Fe_2O_3) content ranged from 1.85% in the EKm sample to 5.39% in the EKl sample. These results confirm the brownish-yellow and yellowish-brown discolourations with the associated Munsell mentions (Young, 2008), which are linked to the presence of iron sesquioxides. The composition of the other oxides (P_2O_5, K_2O, Na_2O and TiO_2) varies from 9.38% to 17.73%, which shows that the samples analysed were not pure clays (Maman *et al*., 2013; Qlihaa *et al*., 2016).

Oxide levels are correlated with each other. These correlations between the oxide contents of the samples analysed are shown in the correlation circle below.

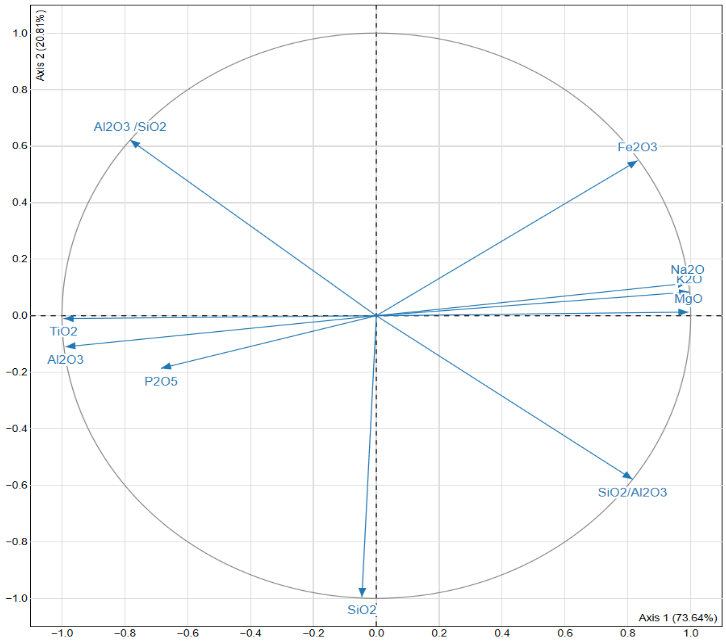


Figure 1: Correlations between the different oxides.

Figure 1 shows that the analysed samples have correlated TiO_2, Al_2O_3 and P_2O_5 contents. The Na_2O, MgO and K_2O contents are also close. These 2 groups of oxides characterise the first dimension of our samples, which are rich in them. The second dimension is characterised by the low SiO_2 content.

3.5 Analysis of Trace Metallic elements

The results of average ETM content obtained by ICP-AES for each sample are presented in Table V.

Table V: Average TME content of samples expressed in mg/g

ETM	Samples	Mean±SD
Co	EKM	0.1452 ± 0.00432^{a}
	Ekl	0.0555 ± 0.01066^{b}
	Enw	$0.0797 \pm 0.00160^{b, c}$
Cu	EKM	0.0398 ± 0.00280^{a}
	Ekl	0.1062 ± 0.01307^{b}
	Enw	0.0251 ± 0.00370^{a}
Fe	EKM	282743 ± 0.03985^{a}
	Ekl	208970 ± 0.19893^{b}
	Enw	$315510 \pm 0.04118^{c, a}$
Mn	EKM	0.0602 ± 0.00171^{a}
	Ekl	0.1372 ± 0.01607^{b}
	Enw	0.0717 ± 0.00617^{a}
Ca	EKM	0.4200 ± 0.00258^{a}
	Ekl	11153 ± 0.01957^{b}
	Enw	0.5483 ± 0.01295^{a}
Cr	EKM	0.0358 ± 0.00299^{a}
	Ekl	0.4167 ± 0.00634^{b}
	Enw	$0.5363 \pm 0.01343^{c, b}$
Zn	EKM	0.2762 ± 0.00457^{a}
	Ekl	$0.3035 \pm 0.00635^{b, a}$
	Enw	0.2080 ± 0.01049^{c}
Se	EKM	0.9163 ± 0.00512^{a}
	Ekl	21260 ± 0.01968^{b}
	Enw	20257 ± 0.04951^{b}
As	EKM	12888±0.00838
	Ekl	23462±0.01742
	Enw	33678±0.05827
Cd	EKM	0.0292 ± 0.00144^{a}
	Ekl	0.1425 ± 0.00289^{b}
	Enw	0.0262 ± 0.01132^{a}
Pb	EKM	0.3055 ± 0.00755^{a}
	Ekl	14660 ± 0.01013^{b}
	Enw	0.4157 ± 0.00608^{a}

ETM	Samples	Mean±SD
U	EKM	0.0630 ± 0.00283^{a}
	Ekl	0.2740 ± 0.00638^{b}
	Enw	$0.0509 \pm 2.52e\text{-}4^{a}$
Ni	EKM	0.2492 ± 0.01153^{a}
	Ekl	0.2053 ± 0.01059^{a}
	Enw	0.2147 ± 0.06808^{a}
Mg	EKM	56780 ± 0.07984^{a}
	Ekl	24268 ± 0.00685^{b}
	Enw	58327 ± 0.05930^{a}
Na	EKM	84690 ± 0.05156^{a}
	Ekl	118492 ± 0.06112^{b}
	Enw	93163 ± 0.07504^{a}
K	EKM	211865 ± 0.01279^{a}
	Ekl	91875 ± 0.00998^{b}
	Enw	202948 ± 0.22223^{a}
Ga	EKM	0.5258 ± 0.00222^{a}
	Ekl	0.9160 ± 0.01074^{b}
	Enw	0.4858 ± 0.00714^{a}

For each MTE, the mean values of samples with the same superscript letters were not significantly different (at the p=0.05).

An analysis of the results presented in Table V shows that the concentrations of fifteen chemical elements vary, being sometimes high, sometimes normal and sometimes below the threshold recommended in the literature. The so-called essential elements (Ingersoll *et al*., 2000), in particular cobalt (Co), copper (Cu), manganese (Mn), sodium (Na), potassium (K) and zinc (Zn), had concentrations below the threshold limits, while iron (Fe), selenium (Se), magnesium (Mg) and chromium (Cr) were above. The non-essential elements (Mench and Blaise, 2004), in particular arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni) and uranium, were present in different concentrations.

Although low and below 0.50 mg/g (Young *et al*., 2008; Mankubasi, 2015) for cobalt, i.e. 0.145 mg/g, 0.079 mg/g and 0.055 mg/g for EKm, ENw and AKl respectively. Differently from the other clays, the EKm clays showed more significant concentrations. Geophages are therefore spared respiratory pathologies (rhinitis and asthma), cardiomyopathies and polyglobulias associated with cobalt abuse (Bismuth, 2000).

Copper concentrations ranged from 0.025 mg/g for ENw to 0.106 mg/g for EKl. The latter showed statistically significant differences in concentration compared to the others, and none of the three values showed a lethal concentration of 0.35 mg/g, which can lead to nausea, gastrointestinal disorders (Koumoulou *et al*., 2012), Wilson's disease or liver disease (Poujois *et al*. 20-21) and a reduction in the expression of mRNA and other receptors, in particular atylic hydrocarbons and andostane receptors, which affect the expression of CYP1A and CYP2C isoforms (Gaetke *et al*, 2014). Copper and cobalt levels found in this study are similar to Mankubasi (2015).

Concerning manganese, the EKl clays showed a statistically significant difference compared to the other two, and the concentrations found ranged from 0.060 mg/g for EKm to 0.137 mg/g for EKl, below the threshold of 0.15 mg/g that can cause cirrhosis of the liver, pneumonia and neurological problems, especially if inhaled (Plumlee & Ziegler, 2003).

The sodium values, ranging from 8.49 mg/g for EKm to 11.84 mg/g for EKl, and the potassium values, ranging from 9.18 mg/g for EKl to 21.18 mg/g for EKm, showed significant differences between the clays analysed.

Zinc levels found in the samples analysed ranged from 0.208 mg/g for ENw to 0.303 mg/g for EKl and none of the samples reached the lethal level, which is between 0.5 mg/g and 5 mg/g, likely to cause hepatic toxicity characterised by altered mitochondrial metabolism with reduced ATP production in liver cells (Lemire *et al*., 2011).

The results obtained by Kalonda *et al.* (2015) on the trace element profiles of food crops commonly consumed in Lubumbashi contradict those obtained in this study. The zinc levels found were well above the standards set. The results of the work by Kalonda *et al.* (2015) on the trace element profile of food plants commonly consumed in Lubumbashi disagree with those of this work. The zinc levels found were well above the standards set.

Iron levels ranged from 28.27 mg/g for EKm to 31.55 mg/g for ENw. These values exceed the WHO/FAO recommended threshold of 0.3g/kg (Shanker & Venkateswarlu, 2011) and the iron concentrations in the ENw clays are statistically higher than those in the other clays. This high blood level can lead to haemochromatosis and death (Ekosse & Mulaba-Bafibiandi, 2008). A study using animal models has shown that hepatic iron overload deregulates the urea cycle, alters fatty acid oxidation and alters the methylation cycle (Pietrangelo, 2016). Liver diseases caused by the high iron concentrations in the clays studied can be induced by geophages. These results are in support of the findings of Okereafor *et al.* (2016) on geophagic clays for sale in informal markets in South Africa.

The average content of selenium in clay soils ranges from 0.8 to 2 mg/kg (Bisson *et al*., 2009), although selenium is an essential component of scleroproteins and plays a key role in many biological functions (Mangiapane *et al*., 2014).

Selenium levels range from 0.91g/mg for EKm to 2.12g/mg for EKl, the latter being statistically significantly higher than EKm and insignificantly lower than ENw. These levels are higher than those recommended for normal dietary intake of 0.01 to 0.04 parts per million (ppm), which is similar to typical soil levels (0.05 ppm) (Muntau *et al*., 2002; Gonzalez *et al*., 2006).

Consumers of these clays are exposed to selenium poisoning, which is characterised by gastrointestinal disorders, hair loss, nail abnormalities, dermatitis, peripheral neuropathy, irritability and garlic-smelling breath (Kise *et al.*, 2024; Hadrup *et al.*, 2020).

Although kidneys excrete excess dietary magnesium, a daily dose of more than 6 mg/kg can cause diarrhoea, vomiting, vertigo, low blood pressure, respiratory depression and cardiac arrest (Kutsal *et al*., 2007; Van Dijk *et al*., 2016). The high values found in the clays range from 2.42 mg/g for EKl to 5.67 mg/g for EKm. The difference in the magnesium content between the different clays is statistically significant.

As for the chromium content, the ENw clays have statistically higher values than the EKm clays. The chromium concentrations are 0.035 mg/g for EKm and 0.536 mg/g for ENw. In comparison with the limit values (0.2 mg/g) and 0.05 ppm (Wang *et al*., 2009), the ENw sample has high chromium values. These results are in contradiction with those of Mankubasi (2015) and Okereafor *et al.* (2016). High chromium levels expose geophysicists to lung cancer, skin and mucous membrane lesions with damage to the nervous system (Bismuth, 2000) and the onset of apoptosis of liver cells (Ben Hamida *et al.*, 2016; Jin *et al*., 2022).

The natural arsenic content in soil ranges from 2-15 mg/kg (Mandal & Suzuki, 2002; Dictor *et al.*, 2004), whereas the arsenic content in the samples ranged from 1.288 mg/g for EKm to 3.367 mg/g for ENw. The arsenic content in the analysed samples was lower than the natural content in the soil, but higher than the limit set for human consumption, which is 0.00l mg/g (Smith & Smith, 2004; Salvarredy, 2008). Geophages of these clays are exposed to chronic poisoning (Moore *et al.*, 2002) and liver damage (Santra *et al*., 2000; Islam *et al.*, 2011).

High levels of cadmium, ranging from 0.029 mg/g for EKm to 0.142 mg/g for EKl, were found in the samples analysed. These values are higher than the WHO recommended threshold of 0.2ppm (Mankubasi, 2015) and the Swiss indicative values for polluted sites (0.8ppm) (Tremel-Schaub & Feix, 2005). It should be noted that EKl clays gave statistically higher concentrations than the others. Consumption of these clays exposes geophagists to kidney problems and increased blood pressure (Plumlee & Ziegler, 2003; De Burbure *et al*., 2006).

Investigated animal showed the occurrence of direct hepatocellular damage based on mitochondrial dysfunction and endothelial cell damage from hepatic ischaemia (Ren *et al.*, 2019; Niture *et al.*, 2021).

Lead concentrations were 0.305 mg/g for EKm and 1.466 mg/g for EKl. The EKl clays had statistically higher values than the others, although all values were excessive compared to the limits recommended in the literature for human consumption, which are 1mg/g or 0.001ppm (Gichumbi *et al*., 2011; Mankubasi, 2015).

The work of Mankubasi (2015) and Okereafor *et al.* (2016) is consistent with this work. The devastating effects of lead reported in the literature, particularly anaemia, digestive disorders and damage to the nervous system through encephalopathies and neuropathies (Goyer & Clarkson, 2001; Murato *et al*., 2015), may affect geophagous animals. Liver damage associated with decreased enzyme activity has also been reported in lead poisoning (Dongres *et al.*, 2013; Firoozichahak *et al*., 2022).

For nickel, the limit for human consumption is 0.2 mg/g. All clays have high concentrations, ranging from 0.205 mg/g for EKl to 0.249 mg/g for EKm. There was no significant difference between the different concentrations. These high concentrations subject geophysicists to the collateral effects of nickel poisoning described in the literature, particularly inflammatory liver lesions due to mitochondrial lesions and ferroptosis, an iron-dependent cell death (Mihali *et al*., 2012; Wei *et al*., 2022).

The presence of uranium in the samples, with values ranging from 0.050 mg/g for ENw to 0.2274 mg/g for EKl, is justified by the fact that it has the same detrital origin and is always found near clays due to their binding capacity (Amin *et al*., 2009; Liewig *et al*., 2012) and that the composition of clays at pH below 7 in silica, iron oxide, aluminium oxide, organic ligands and/or inorganic ligands is favourable to the sorption of uranium in natural settings (Bonin & Blanc, 2001).

The harmful effects of radioactivity can be present at any dose, although most of the uranium that enters the body is not absorbed and is excreted in the faeces (Kalonda *et al*., 2015). These effects are numerous and are known for ionising radiation from alpha, beta and gamma particles. However, the levels are below the threshold of 0.3 ppm (Lake *et al.*, 2011; Kalonda *et al*., 2015).

4. Conclusion

This study shows that the geophagic clays produced and consumed in Lubumbashi are plastic. They contain minerals in the form of illites and chlorites. Main oxides are aluminium, silicon, iron and titanium. They are acidic and contaminated with trace metals and uranium, which can be harmful to the health of consumers. The study is essential and paves the way for the development of decontamination methods for the safe use of these types of clays in the pharmaceutical and cosmetic industries.

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