# Reactivity of Clays Consummated in Côte d'Ivoire in Digestive Conditions: Bioavailability of Mineral Elements

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**ABSTRACT—** ***In order to evaluate the impact of clay on the body during digestion, a study of the bioavailability of elements from clay minerals from Anyama and Bingerville (Abidjan district) was performed in vitro. A simulation of the destruction of a solid matrix in the human gastrointestinal tract was undertaken. The analysis of different juices after digestion revealed the presence of numerous inorganic elements essential for biological activity. Green clay of Anyama consisting of chlorite, illite and smectite, released more elements than those of Bingerville, the mineralogy of witch being dominated by kaolinite. The concentration of some ions (Al, Co, Ca, Cu, Fe, Zn, Pb, Si) decreased during the transition from the step of the stomach (pH = 2.5) to that of the small intestine (pH ≈ 7). The proportions of zinc and copper in spite of decrease during the small intestine step, remain superior to the others. To the contrary, an increase was observed for K, Ni and P. Iron and calcium in this series were distinguished by their disappearance during the stage of the small intestine.***

**Keys word:** clay minerals, trace elements, reactivity, bioavability, geophagy.

## 1. INTRODUCTION

Clays are materials containing many elements that can be beneficial or hazardous for humans, depending on their bioavailability and their impact on metabolic processes. For millennia, clays have been used in many fields, on all continents, due to their numerous properties. Some of these properties (absorption, antiseptic, antacid, healing, etc.), provide them many therapeutic and cosmetic functions. They are used internally, mainly for gastrointestinal care, or externally (**Neli et *al.*, 2016**), mainly in dermatology (**Carretero, 2002, 2010**). Thus, very present in the pharmacopoeia of natural or traditional medicines, clays are also used in "official" medicine under the form of pharmaceutical specialties (palygorskite, kaolinite or aluminum silicate, montmorillonite, beidellite ...). In addition, ingestion of soil or geophagia, also known as pica, is observed on all continents (**Johns and Duquette, 1991; Abrahams and Parsons, 1996; Mahaney *et al.*, 2000; Tateo *et al.*, 2001; Saathoff *et al.*, 2002; Nchito *et al.*, 2004**). However, in nature clays are associated with impurities and contain heavy metals which pose a danger in human internal use. Moreover, geophagy may contribute to intestinal parasitosis (**Wong *et al.*, 1991; Holland *et al.*, 1995; Geissler *et al.*, 1998**) and mineral deficiencies (**Horner *et al.*, 1991; Moore and Sears, 1994; Trivedi, 2005**). In Côte d'Ivoire as elsewhere, some pregnant women ingest clays for preventing nauseas due to hyper-salivation, against ulcer pain and also because of the aroma it gives off. According to **Hunter, (1973); Vermeer and Ferrell, (1985**), ingestion of clay would be a remedy against diarrhea and also intestinal parasites, since ingested particles protect the gastrointestinal epithelium (**Moré *et al.*, 1987**). Clays are also used as antibacterial **(Williams, 2017).**To contribute to prevent the risks related to the use of clays without any control, a study of the bioavailability of minerals has been undertaken in vitro. In this experiment, a simulation of the destruction of a solid matrix in the human gastrointestinal tract was performed on some clays from Côte d'Ivoire. This study aims at predicting the nature and content of mineral elements that should be at the disposal of the body after digestion.

## 2. MATERIALS AND METHODS

### *2.1 Materials*

Studied materials come from Anyama and Bingerville (district of Abidjan), respectively located in the north-east and south-east of Abidjan. These locations are in a sedimentary basin containing sand and clay formations (**Tastet, 1979**). Anyama's sample (named AVA) was taken on the outcrop and air-dried as that sold on the market. Bingerville's samples

(named LBF, LRF, LVF, LMF, LJPF, and LJFF) were also collected on the deposit depending on the color and have undergone the same heat treatment as the marketed material called "Lokpo". That heat treatment consists in heating and roaster the material for 3 to 5 days in an oven built in clay and fueled with wood. This operation gives often a pleasant smell to the clay material. Different analyzes in previous studies have revealed the mineralogy. The sample of Anyama consists of chlorite (29.5%), smectite (2.5%) and illite (20.2%) (**Coulibaly *et al.*, 2013**) while those of Bingerville are mainly composed by kaolinite (41 to 84%), quartz (14 - 27%), goethite (2 - 5%) for all samples except LJFF (26%) and illite (4 -10%) associated with the rutile trace (1%) (**Coulibaly *et al.*, 2014**).

### *2.2 Methods*

* Physicochemical characterization

The specific surface areas of samples were determined by the BET method using nitrogen as a probe molecule to 77 K.

For the measurement of pH, 4 g of sample were placed in 100 mL of distilled water. After one hour stirring, the pH of the sample is measured directly.

The measurement of the Cation Exchange Capacity (CEC) was performed by moving the exchangeable cations by cobalt hexammonium ions $[Co(NH_3)_6]^{3+}$ which gives orange solutions ($2.5 < pH < 5.5$). This method, simple and rapid, is very reliable because the cobalt hexammonium ion has a very high power for moving the exchangeable cations off the clays (**Morel, 1957**). The cobalt hexammonium ion in the supernatant was then titrated by colorimetry using a spectrophotometer Shimadzu UV 2100, and some of the displaced ions ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and $Al^{3+}$) were analyzed by atomic absorption.

Chemical analysis of clay samples and **digestion solutions** were carried out using a Perkin Elmer Elan 5000 quantometer equipped with a plasma ICP-MS according to the procedure described by **Carignan *et al.***, (**2001**).

* Extraction Solution

The literature reveals several physiological extraction protocols in vitro (**Cabral and Small, 1989; Tateo *et al.*, 2001; Cave *et al.*, 2003**).

Among these, a modified method based on that of **Cave *et al.*, (2003)** was used, because of its simplicity and the fact that the composition of the extraction liquid is closer to the composition of human gastric juice. The steps of the stomach and the small intestine were considered.

* ***Stomach medium:***

A mixture of pepsin (1.25 g, Sigma Aldrich), sodium malate (0.50 g, Sigma Aldrich), sodium citrate (0.50 g), lactic acid (420 µL, Sigma Aldrich), acetic acid (500 µL) is completed to one liter with deionized water. The pH is adjusted to 2.5 with a concentrated solution of hydrochloric acid. Then, in a polypropylene bottle, one g of clay was contacted with 100 mL of this juice. The vials containing the mixture (simulated gastric fluid and the sample) were placed under stirring in a temperature regulated bath at 37 ° C. After one hour at 37 ° C, 25 mL were withdrawn and filtered through a cellulose filter of 0.2 micrometers (Gelman) for analysis. This filtrate is the phase of the stomach.

* ***Small Intestine medium:***

25 mL of the solution were added to the initial gastric contents of the vial containing the mixture to maintain the initial solid/solution ratio. The conditions were then modified by adding a saturated solution of sodium bicarbonate to adjust the pH to 7. Then, bile salts (175 mg, Sigma Aldrich) and pancreatin (50 mg, Sigma Aldrich) was added. The samples were placed in a stirred water bath. After two hours, 25 mL of supernatant were removed and filtered through a cellulose filter of 0.2 µm. This collection is the filtrate phase of the small intestine. Extracts collected at the two phases were then analyzed to identify and assess the proportions of different ionic species that may pass through the body.

According to **Abraham *et al.***, (**2006)**, the ratio of one g per 100 mL can maintain the stability of pH and needs 2 hours to reach equilibrium.

## 3. RESULTS

### *3.1 Characteristics of the samples*

#### *3.1.1 Chemical composition of the samples*

The sample of Anyama is poor in $Al_2O_3$ and generally richer than samples of Bingerville in $SiO_2$, $Fe_2O$, MgO and $K_2O$ (**Coulibaly *et al*; 2013, 2014**).

Chemical analysis reveals that, except LJFF, all samples of Bingerville (**Table 1**) have relatively similar chemical composition. The $SiO_2$ content range from 45.73 to 57.05%, those of $Al_2O_3$, from 25.22 to 34.41%, and trace amount of

$Fe_2O_3$, $TiO_2$, $Na_2O$, $K_2O$ and MgO are detected. Sample LJFF has high concentration of iron oxide (26.02%) and lower concentrations of silica (42.71%) and alumina (18.33%).

**Table 1:** Chemical content in major elements in weight percent (n.d = not determined). (**Coulibaly *et al*; 2013, 2014**)

| Samples | Colour | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AVA** | Green | 61.58 | 17.21 | 7.42 | 0.08 | 3.84 | 0.04 | 0.46 | 2.38 | 0.75 | n.d | 5.74 |
| **LBF** | White | 52.83 | 29.74 | 2.34 | n.d | 0.29 | n.d | 0.11 | 1.17 | 1.06 | 0.08 | 12.03 |
| **LRF** | Red | 51.06 | 30.18 | 4.48 | 0.00 | 0.22 | n.d | 0.11 | 1.16 | 1.13 | 0.06 | 11.97 |
| **LMF** | Brown | 56.55 | 25.44 | 4.25 | 0.01 | 0.36 | n.d | 0.08 | 1.01 | 1.10 | 0.08 | 11.46 |
| **LVF** | Purple | 45.73 | 34.41 | 4.92 | n.d | 0.07 | n.d | 0.06 | 0.57 | 1.12 | 0.09 | 13.12 |
| **LJPF** | Yellow | 55.33 | 27.81 | 3.97 | 0.00 | 0.24 | n.d | 0.06 | 0.77 | 0.94 | 0.21 | 11.40 |
| **LJFF** | Dark-yellow | 42.71 | 18.33 | 26.02 | n.d | 0.14 | n.d | 0.05 | 0.63 | 0.87 | 0.12 | 11.69 |

The elements identified as trace represent the majority of heavy metals, lanthanides and actinides. Samples contain some other heavy metals (cobalt, copper, molybdenum, zinc) (**Coulibaly *et al*; 2013, 2014**).

### *3.1.2 Mineralogical and physicochemical characteristics*

The total surface area was 5.4 $m^2/g$ for the sample of Anyama, while those of Bingerville ranged from 26.8 to 43.0 $m^2/g$ (**Table 2**). These values are consistent with those reported in the literature (**Guyo, 1969; Liétard, 1977**). Except for samples LRF and LVF of Bingerville, the specific surface increases with the content of iron oxide (goethite), what is usual (**Borggaard, 1982**). Moreover, the pH measured ranged from 4.6 to 5.4, reflecting the acidity of the samples.

**Table 2**: Mineralogical and physicochemical characteristics of the samples (**Coulibaly *et al*; 2013, 2014**)

| Samples | Physicochemical properties | | Mineralogical composition (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | pH | $S_{BET}$ ($m^2.g^{-1}$) | Kaolinite | Illite | Chlorite | Smectite | Quartz | Goethite | Rutile |
| **AVA** | 5.4 | 5.4 | - | 20.17 | 29.53 | 2.5 | 40.53 | - | 1.00 |
| **LBF** | 4.8 | 35.7 | 66.79 | 9.73 | - | - | 17.06 | 2.34 | 1.06 |
| **LRF** | 5 | 35.05 | 67.98 | 9.66 | - | - | 14.77 | 4.48 | 1.13 |
| **LVF** | 4.6 | 26.8 | 83.61 | 4.74 | - | - | 4.3 | 4.92 | 1.12 |
| **LMF** | 4.7 | 39.8 | 57.06 | 8.38 | - | - | 25.96 | 4.25 | 1.10 |
| **LJFF** | 4.8 | 43 | 41.86 | 5.28 | - | - | 20.67 | 26.02 | 1.00 |
| **LJPF** | 4.7 | 35.8 | 65.02 | 6.44 | - | - | 21.87 | 3.97 | 1.00 |

The CEC values were determined both from the cobalt hexammonium consumption and from the sum of the cations released in the solution. Thus, in the absence of other phenomena, the CEC values deduced from the two methods would have to be close each others. The obtained results are given in **table 3**. Two points must be pointed out:

(i) In most of the cases, (except for sample AVA), the CEC determined by adsorption of cobalt hexammomium ions is greater than the sum of ions titrated in the solution, what suggested that, other ions that those analyzed assume a significant part of the ionic compensation (e.g. Mn, Fe…) ;

(ii) (ii) Compensation in samples LBF, LRF, LVF, LMF, LJFF, and LJPF, is mainly provided by aluminum, whereas for the sample AVA, CEC is supported by Mg and Al. Aluminum released could be, in part, attributed to the dissolution of poorly crystalline aluminum hydroxide, as noticed by **Andji *et al.*, (2009)** for outcrop clays from the same neighborhood. The high mobility of aluminum indicates that the lateritic weathering profile is not at equilibrium.

**Table 3**: Cation Exchange Capacities (CEC) expressed in meq/100g of solid.

| Sample | Na | K | Ca | Mg | Al | CEC, sum of released cations | CEC, cobalt hexammonium |
|---|---|---|---|---|---|---|---|
| **AVA** | 0.08 | 0.27 | 0.73 | 3.55 | 2.63 | 7.26 | 7.06 |
| **LBF** | 0.06 | 0.17 | 0.24 | 0.24 | 5.86 | 6.57 | 9.66 |
| **LRF** | 0.10 | 0.14 | 0.25 | 0.19 | 3.45 | 4.13 | 9.78 |
| **LVF** | 0.07 | 0.05 | 0.14 | 0.07 | 2.95 | 3.28 | 6.92 |
| **LMF** | 0.11 | 0.30 | 0.38 | 0.38 | 6.65 | 7.82 | 10.96 |
| **LJFF** | 0.05 | 0.12 | 0.12 | 0.12 | 1.80 | 2.21 | 3.45 |
| **LJPF** | 0.08 | 0.18 | 0.15 | 0.15 | 5.09 | 5.65 | 8.6 |

### *3.2. Reactivity in digestive conditions*

Many ions are involved in human metabolism (**Table 4**). The concentrations of various chemical species extracted after the two stages of digestion were measured (**Table 5)**.

**Table 4**: Specific functions of essential minerals and trace elements (mainly from **Gomes and Silva, 2007**)

| Element | Specific functions |
|---|---|
| **Ca** | Essential for developing and maintaining healthy bones and teeth; assists in blood clotting, muscle contraction and nerve transmission; helps reduce risk of osteoporosis. |
| **Mg** | Activates over 100 enzymes and helps nerves and muscles function. |
| **K** | Regulates heartbeat, maintains fluid balance and helps muscles contraction, has an important role in nervous transmission. |
| **Fe** | Essential for red blood cells formation and function; important for brain function. |
| **Cr** | Aids in glucose metabolism and regulates blood sugar, is an acute cytotoxic poison under its hexavalent form. |
| **Co** | Promotes the formation of red-blood cells. |
| **Cu** | Promotes the formation of red blood cells and connective tissue ; acts as a catalyst to store and release iron to help form haemoglobin ; contributes to central nervous system function. In excess can be poisonous and lead to steatosis in chronic poisoning. |
| **P** | Works with Ca to develop and maintain strong bones and teeth; enhances the use of other nutrients. |
| **Zn** | Essential component of more than 200 enzymes involved in digestion, metabolism, reproduction and wound healing. |
| **Si** | Essential for normal bone growth, and for proper integrity of the skin. |
| **Al** | Cytotoxic and suspected to be involved in Alzeimer's desease. |

**Table 5**: Chemical analysis (mg/L) of the digestion solutions of the two steps: stomach (pH = 2.5) and small intestine (pH = 7)

| Clay sample | Digestion solutions | Element concentration, mg/L | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **Co** | **Cr** | **Cu** | **Ni** | **Pb** | **U** | **Zn** | **Al** | **Si** | **Fe** | **Mn** | **Mg** | **Ca** | **K** | **p** |
| **AVA** | **Stomach** | 0.18 | 0.06 | 0.79 | 0.04 | 0.01 | - | 0.34 | 5.20 | 0.71 | 1.60 | 0.18 | 6.66 | 8.65 | 6.08 | 5.66 |
| | **Small intestine** | 0.15 | 0.18 | 0.40 | 0.03 | - | - | 0.13 | 20.40 | 1.20 | - | 0.13 | 4.56 | - | 10.30 | 5.42 |
| **LBF** | **Stomach** | 0.01 | 0.04 | 0.12 | - | - | - | 0.14 | 8.40 | 1.06 | 0.50 | 0.01 | 1.31 | 2.52 | 5.40 | 3.60 |
| | **Small intestine** | - | 0.11 | 0.17 | 0.01 | - | - | 0.10 | 1.60 | 0.66 | - | 0,01 | 1.31 | - | 8.23 | 3.73 |
| **LRF** | **Stomach** | 0.01 | 0.03 | 1.69 | - | - | - | 0.12 | 8.00 | 1.58 | 0.40 | 0,01 | 1.32 | 2.25 | 5.29 | 3.27 |
| | **Small intestine** | 0.01 | - | 1.02 | 0.01 | - | - | 0.08 | 2.43 | 0.91 | - | 0,01 | 0.87 | - | 6.81 | 4.65 |
| **LJPF** | **Stomach** | - | 0.03 | 0.11 | - | - | - | 0.13 | 7.30 | 1.37 | 0.40 | 0,01 | 1.50 | 3.94 | 5.26 | 3.10 |
| | **Small intestine** | - | - | 0.08 | 0.02 | - | - | 0.12 | 1.65 | 0.68 | - | 0,01 | 1.27 | - | 7.51 | 3.88 |
| **LJFF** | **Stomach** | 0.01 | 0.03 | 0.22 | - | - | - | 0.15 | 6.60 | 3.16 | 1.60 | 0,01 | 1.16 | 2.21 | 5.22 | 1.14 |
| | **Small intestine** | - | - | 0.18 | 0.01 | - | 0.01 | 0.09 | 1.55 | 1.50 | - | - | - | - | 7.43 | 3.62 |
| **LMF** | **Stomach** | 0.01 | 0.03 | 0.12 | 0.01 | - | - | 0.16 | 8.40 | 1.00 | 0.50 | - | 1.48 | 2.58 | 5.66 | 3.19 |
| | **Small intestine** | - | - | 0.13 | 0.01 | - | - | 0.10 | 2.72 | 0.55 | - | - | 0.99 | - | 6.99 | 5.02 |
| **LVF** | **Stomach** | 0.01 | 0.03 | 0.19 | - | 0.01 | - | 0.72 | 6.10 | 1.59 | 0.20 | - | 1.06 | 1.80 | 6.75 | 3.23 |
| | **Small intestine** | 0.01 | - | 0.10 | - | - | - | 0.10 | 1.57 | 1.03 | - | - | 1.3 | - | 9.55 | 5.01 |

### *3.2.1 Analysis of digestion solutions of the stomach*

In the stomach environment, the digestion of clays leads to the release of many mineral elements whose content varies from one clay to another. Thus, more generally the elements Al (5.15 to 8.38 mg/L), Si (0.71 to 3.16 mg/L), Fe (0.18 to 1.63 mg/L), Mg (1.06 - 6.66 mg/L), Ca (1.8 to 8.65 mg/L), K (5.22 to 6.08 mg/L) and P (1.14 to 5.66 mg/L) were released in significant amounts in the stomach digestion solutions, the contents of other elements such as Cr (0.03 to 0.06 mg/L), Zn (0.12 to 0.72 mg/L) and Mn (0 to 0.18 mg/L) were quite low. The concentrations of Co, Ni, Pb and U were practically zero. They can be considered as not being bioavailable in this environment model.

The maximum observed for Fe, Mn, Mg, Ca, K and P were in the sample AVA dominated by chlorite and illite. For the elements Al, Si, Zn and Cu, the high levels were observed in samples of Bingerville dominated by kaolinite.

### *3.2.2 Analysis of digestion solutions of the small intestine*

The digestion of clays in the small intestine juice leads to the release of Al (1.55 – 20.43 mg/L), Si (0.55 – 1.5 mg/L), Mg (0-4.56 mg/L), K (6.81-10.3 mg/L) et P (3.62-5.42 mg/L) and low concentrations of Cu (0.08-0.5 mg/L) et Zn (0.08-0.13 mg/L).

Furthermore, the material balance of the two digestion steps indicated that precipitation phenomena of Al, Si, Ca, and Mg occur in small intestine digestion solutions of all Bingerville clays, while the amount of aluminum released from AVA sample was about four fold that of stomach digestion solution. Likewise, Cr concentration was three higher in the intestine digestion solutions of the samples AVA. The precipitation reactions concern also Ca in AVA sample and Fe in all clays.

Co, Cr, Pb, U, Fe, Mn and Ca where the concentrations were practically nil, may be considered as not bioavailable in this medium.

High levels of Cu, Zn, Al, Mg, K and P, were observed in the sample AVA while for Si element, the maximum was observed in the sample LJFF from Bingerville.

### *3.3.3 Comparative study of bioavailability of elements in the two models and environments in the two localities studied clays.*

In general, the mineral elements released by Bingerville samples in the medium of the stomach were more important than those relaesed in the medium of the small intestine, with the exception of elements K and P (**figure 1**).

For the AVA sample, this exception extended to the elements Si and Al in addition to elements K and P. Indeed, the rate of Al released by this sample in the middle of the small intestine model is 4 times greater than that released into the medium model of the stomach while for Si, this factor is of the order of 2.

Moreover, the rates of the elements Al, Si, Fe, Mn, Mg, Ca, K and P released by the AVA sample were higher than those of Bingerville samples. So AVA sample may be considered as a micronutrient and macronutrient provider.

For copper, the highest rate was that of sample LRF despite the fact that LMF and LJFF clays contain more copper. While for zinc, the highest amount was observed for sample LVF of Bingerville.

The concentrations released for Co, Cr, Ni, Pb, U and Mn in both the stomach and in the small intestine were negligible.

The sample LJFF which was richer in iron (26% $Fe_2O_3$) released the same amount of Fe as the sample AVA of Anyama. The lowest rate was in the sample LVF. These observations lead to assume that the iron released is a part of structure of the clay and not of iron oxyhydroxides such as goethite observed in large quantities in the sample LJFF.

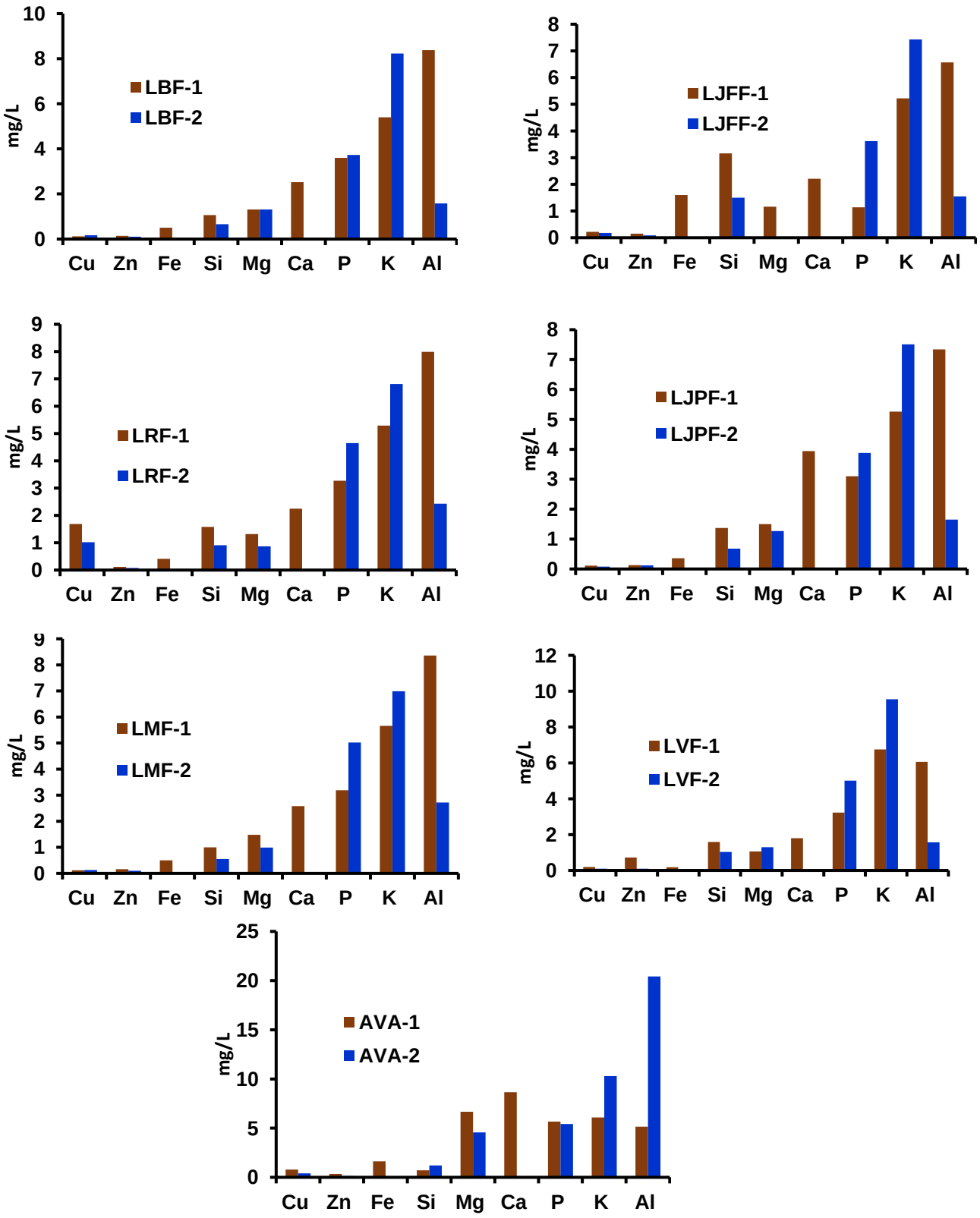


**Figure 1:** Comparative study of bioavailability in the medium of stomach and small intestine
Stomach; : Small intestine

### *3.3.4 Discussion*

The extracts contain Cr, Cu, Fe, Zn, Co, Mn (trace elements), Ca, K, Mg, P (macronutrients) and other ions such as Pb, U, which could be a source of nutrients or danger for the human body, depending on their concentration. In vitro studies (**Abrahams *et al.*, 2006; Johns and Duquette, 1991; Hooda *et al.*, 2002, 2004; Smith *et al.*, 2000; Owumi and Oyelere, 2015)** used to assess the release in the gastrointestinal juice of certain elements such as Ca, Cu, Fe, Mg, Mn and Zn. Similarly, **Mascolo *et al.*, (1999, 2004)** during experiments in vivo performed on rats fed with clays, toxic elements were detected in the urine and in various organs (kidney, liver, heart, brain). They concluded that the presence of these elements in the urine indicated that the absorption process occurred after ingestion of clay, causing a gradual increase of metals in urine and blood. Ion concentration is generally higher in the stomach extracts. This has been observed by many authors (**Abrahams *et al.*, 2006; Wragg and Cave, 2003; Ruby *et al.*, 1996, Smith *et al.*, 2000**) who attributed it to several factors namely:

- the effect of complex formation with pancreatic / bile salts,

- the particle size and mineralogy,

- the kinetics of dissolution,

- the pH of the medium.

According to **Ruby *et al*., (1999)**, the mobilization of the elements was higher in the stomach and thus represented the maximum amount of ions that can be absorbed. The fact that the ions are therefore more released in the stomach environment (pH = 2.5), than in the small intestine could be explained by the acidic environment of the stomach, more efficient for mineral solubilization under cationic forms. The transition from the stomach to the small intestine is accompanied by an increase in pH (pH ≈7). According to **Ruby *et al.*, (1992, 1996), Oomen *et al.*, (2003**), following the increase in pH, precipitation reactions occur. Those reactions lead to lower rates of dissolved and available elements for absorption during their transition through the intestinal epithelium. This phenomenon was stronger for Fe and Ca in the medium of the small intestine. According to **Ruby *et al.*, (1999) and Schroder *et al.*, (2003**), the cations were more affected by the rise in pH in the small intestine than the anions. In fact, in neutral or weakly alkaline conditions, iron and/or calcium hydroxides were formed, making the corresponding ions unavailable. A study of clay samples (high pH and CEC) showed retention of ions already available in the gastrointestinal juice (**Hooda *et al.*, 2002**). Samples of this study had a low pH and low CEC. It is therefore difficult to conclude on the bioavailability of these two ions since other factors such as the physiological conditions of the individual (age, fatness, nutritional status…) act on the gastrointestinal pH. However, the concentrations of these ions were higher in the gastric juice, accessibility were high therefore potentially bioavailable because, according to **William, (1999)**, the ions detected in the gastric juice are bioavailable as potentially absorbable. According to **Oomen *et al.*, 2002**, the human gastrointestinal tract is made up of a number of compartments where the ingested soil undergoes a series of reactions in which the time, the composition of the fluid and the pH of the reaction vary. Fe ions and Ca may be bioavailable if the step of the intestine was held at a pH lower than that of the experiment. The concentrations of Cu and Zn were distinguished from other ionic species; this reflects that both the ions were more bioavailable than others in different samples. The concentrations of Cu and Zn in the different samples were generally 0.1 mg/L minimum. Regarding other trace elements (Cr and Co) only two samples (LBF, AVA) released more than 0.1 mg/L. Other samples except LJFF and LJPF have released a few tens of µg/L. AVA extracts contain the highest concentrations of the various ionic species which can be explained by the mineralogical composition that consists mainly of chlorite and smectite, the mineral chemistry of which is more complicated. Indeed, compared to kaolinite, chlorite and smectites are more easily dissolved in an acid medium. K concentration ranging from 5.7 to 6.1 mg/L was the highest but was not dangerous because it was lower than toxicity limit (12 mg/L- European standards) in water intended for human consumption. The hypothesis that the ingestion of clay could provide micronutrients has also been demonstrated in numerous studies (**Abrahams and Parsons, 1997, John and Duquette, 1991, Smith *et al.*, 2000)**. However, even if the geophagia causes the release of nutrients potentially available to the body, it also carries risks. **Gelfand *et al.*, (1975)** found in five patients hyperkalemia (excess of potassium) due to excessive ingestion of clay. Moreover **Hooda *et al.*, 2004** showed that the ingestion of clay could cause a reduction in the absorption of nutrients already bioavailable, especially micronutrients such as Fe, Cu and Zn. **Trivedi *et al.*, (2005)** reported a case of hypokalemia in a pregnant woman after ingestion of clay. Cases of iron deficiency trained by geophagia have been reported by various studies (**Garnier *et al.*, 2008; Minnich *et al.*, 1968; Nchito *et al.*, 2004**). According to the limits set by the World Health Organization (WHO), the concentrations of different elements were not dangerous for the human body as their amounts were too low.

The high levels of aluminum and silicon observed in the different samples reflect the release of these elements from the octahedral and tetrahedral layers after acid attack (**Cabrera and Talibudeen, 1978; 1979**). This high aluminum content can be dangerous because, according to **Roig *et al.* (2006)**, the aluminum would be the cause of certain diseases, such as Alzheimer's disease. However, the aluminum released, pass into the small intestine where it can:

- Either precipitate as aluminum hydroxide by the action of gastric juices;

- Either bind to organic molecules. In the model environment of the small intestine, the reduction of the aluminum content is due to the increase of pH. Indeed, the increase in pH in the gut to earlier studies in rats (**Cochran *et al.*, 1993; Cunat *et al.*, 2000**), leads to the precipitation of aluminum dissolved by the pancreatic and biliary secretions in different forms such as aluminum hydroxide**.** According to **Owumi and Oyelere (2015)**, ingestion of clay would be a danger to pregnant women and their fetuses because of the high levels of aluminum. This is only partly true, because, under high pH conditions alumunium hydroxide is formed. Thus, the formation of hydroxide reduces the level of bioavailable aluminum.The presence of silicon can cause the formation of metastable aluminosilicates which are then excreted in the feces; this would limit the toxicity of aluminum (**Powell and Thompson, 1993**). During a study on rats fed with kaolinite, **Chaumande (2011)**, observed the absorption of aluminum in the small intestine. According **Powell and Thompson (1993)**, part of the dissolved aluminum, may bind to organic molecules of gastric juices and become soluble. Then, soluble aluminum is absorbable in small quantities in the intestinal wall. Aluminum absorbed into the systemic circulation is bound to transport proteins such as transferrin and albumin (**Cochran *et al.*, 1993; Powell *et al.*, 1994**). This fixing of aluminum leads to anemia observed in individuals practicing Geophagy (**Geissler *et al.*, 1998**).

## 4. CONCLUSION

The specific surface areas determined for samples from Bingerville (26-43 $m^2/g$) are large enough, then these samples might have a high adsorption capacity. They can be used in the treatment of diarrhea or cases of poisoning; to the contrary they would not be associated with drugs because clays could alter their active ingredients. The sample of Anyama has a surface area of $5m^2/g$. The CEC of the samples is between 3.45 and 10.96 meq/100g. The compensation is usually provided by aluminum, depicting a high mobility of this element. The presence of oxides in the samples influences the mobility of certain ionic species. In addition to the microbiological studies to be undertaken, it is necessary to perform a sieve before internal use to extract possible coarse particles including quartz grains. Moreover, the experiments in this study allow forecasting the potential bioavailability of different elements. Element concentrations released from the sample AVA are higher than those released by the samples from Bingerville. Levels are relatively more important for Al, Si, Fe, Mn, Mg, Ca, K and P. In samples from Bingerville, the elements released Co, Cu, Zn, Pb, Fe and Ca, have a high mobility in the stomach and almost zero in the small intestine. An increase in pH in the small intestine caused the formation of iron and/or calcium hydroxide or a re-adsorption of elements. Their mobility strongly depends on the pH of the medium. Mobility of toxic elements such as Pb and U is very low, not exceeding one µg per gram of clay, thus ingestion of different samples has no danger.

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