JBAAR
Journal of Basic And Applied Research
ISSN 2413-7014

X-Ray Florescence Analysis (XRF) of Kaolin in the South Eastern Nigeria

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Received: 7-4-2016
Revised: 15-4--2016
Published: 22- 4-2016

Keywords:
Kaolinite,
Florescence,
Geophagy,
Element,
Silcate

Abstract: The analysis of Kaolin using X-ray Florence analysis was carried out to determine the elements that kaolin are made of , as well as to ascertain Kaolin's health benefits. There is variation in the concentration of Kaolin in the five South Eastern states of Nigeria. The analysis shows the presence of six (6) major elements (Mg, Ti, Na, K, Fe), six (6) minor elements (V, Mn, Cr, CZn, Rb, Ba) and Seven trace elements (As, Sm, U, Sc, Co, Cs, Th) in the five South Eastern states under studies. The concentrations of most of these elements far exceeds the daily dietary needs or permissible limits of human being and can thus make them toxic unless taken in small doses.

INTRODUCTION

Kaolin (*Bolus alba*) is a broad name given to a range of clay compound substances made up of Kaolinite (predominantly), in addition it frequently contains quartz, mica, feldspar and montmorilla. It is composed of Aluminium silicate hydroxide $Al_2Si_2O_5(OH)_4$ with approximately 46% SiO_2, 40% Al_2O_3, and 14% H_2O. There are two types of kaolin; the primary and secondary kaolin. The primary is found and originated from parent rock and have not been transferred by the force of nature, this class of kaolin is purer in nature. The secondary kaolin are kaolin that have been removed or eroded, transported and deposited as sediment from the site of their parent rock by the force of nature such as water, wind or glacial action, as transportation and deposition was going on they become contaminated with material of different origin. Kaolin is produced by the alteration of feldspathic rock caused by the process of weathering. As a compound, the composition of Kaolinite and other minerals varies from sample to sample and depending on its chemical composition, it is present as white, green, pink, grey, yellow or red in colour and has a soft plastic nature. Like all other clays, it is hydrated clay that is very stable during natural conditions and it is ranked as one of the top seven industrial minerals in the world (DME, 2005). Clay is a natural earthy fine grained inorganic material that develops plasticity when mixed with limited amount of water. Natural clay minerals are well known to mankind from the earliest days of civilization and because of their low cost, abundance in most continents of the world, high absorption characteristics and potential for ion exchange, they form a good material for absorbents (Nayak and Singh, 2007). Clay soils generally contain mostly silica (47%) and alumina (40%). Elemental analysis have shown that a great number of minor and trace metallic elements such as Sc, Cr, Cu, Ti, Ga, Zr, Mn, Mg, Sr and Pb exist in clay soil. There are several classes of clay which include; smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Nayak and Singh, 2007). The specific elemental composition of each clay material will usually depend on the amount of the element present in the host rock, the chemical association of the elements with stable and/or unstable mineral during weathering and the intensity of drainage and other polygenetic alterations associated with clay materials (Ibeanu *et al.*, 1997)

Kaolin is named after a hill in China (kao-ling) from which it was mined for centuries. Samples of Kaolin were first sent to Europe by a French Jesuit missionary around 1700 as example of the materials used by the Chinese in the manufacture of porcelain. The eating of clays or Kaolin occurs among cultural groups on every inhabited continent, a practice known as geophagy. Geophagy is the practice of eating earthy or soil-like substance such as clay, mud, ash and chalk. It exists in animals in the wild and also humans, most often in rural or preindustrial societies among children and pregnant women. Human geophagy may be related to pica a classified eating disorder characterized by abnormal cravings for non-food items. In animals, geophagy is considered to be a normal adaptive behavior that is documented among numerous animal groups including primate species. Despite its wide distribution and long documented history, human geophagy is not well understood. It is acknowledged that the behaviour is most prevalent among populations in tropical climates, and that it is possible to define high-risk groups (Abraham, 1996). Populations most likely to engage in geophagy live in rural areas, practice a traditional culture, and have little or no access to modern healthcare facilities (Corbert *et al.*, 2003; Horner *et al*., 1991). Interestingly, geophagy has been shown to be associated with micronutrient deficiencies, especially iron and zinc (Young *et al*., 2008; Wiley *et al*., 1998; Beyan *et al*., 2009; Alice, 1998). Geophagy has been linked to physiological, cultural, and socio-economic factors, adding to the complexity and mysterious nature of the behaviour. Culturally speaking, the practice amongst many of the kaolin (clay) eaters emanates from having doubtlessly watched their mothers or close relatives eat the clay (Bisi-Johnson *et al*., 2010). Many of the studies on geophagia have advanced many more other reasons for this phenomenon around the world. In southern parts of U.S.A, pregnant women who traditionally ate substances like clay, corn starch and baking soda believed that such substances helped to prevent vomiting, helped babies to thrive, cured swollen legs and ensured beautiful children(Mcloughlin,1987). In parts of Africa, rural areas of the United State and villages in India, clay consumption is correlated with pregnancy (Geophagy, 2014). In Australia, some Aborigines eat white clay for medicinal purposes (Bisi-Johnson *et al*., 2010). In Haiti, South Africa, Malawi, Zambia, Zimbabwe and Swaziland, geophagy is widespread. In South Africa, the eating of clay is mostly observed among pregnant women. In urban South Africa, young women believe that earth eating will give them a lighter colour (making them supposedly more attractive) and soften their skin (Alexander *et al*., 2002). Studies have also established that geophagia is rife among the Tanzanians and Kenyans in the eastern part of Africa, as well as, Senegal, Mali and Nigeria in West Africa, and South Asia.

Clay for consumption in Nigeria is known as calabash chalk. Calabash chalk - also known according to language/ locality as Argile, Calabar stone, Calabash clay, Ebumba, Lacraie, Mabele, Ndom, Nzu, Poto and Ulo – is a generic term used for naming these in Nigeria, geophagical materials (Abrahams *et al*., 2013).

BASIC PRINCIPLE OF XRF ANALYSIS

When a high energy electron, proton or photon impinges on an atom, an electron may be excited from one of the inner shells of the atom to a higher energy level or even ejected out of the atom (ionization) into the atmosphere. The excitation or ionization of the atom creates core ‘hole’ in the inner shell of the atom. An electron from the higher energy level then moves towards the nucleus to fill the electron hole in the lower and more stable level of the atom. As a result of this downward movement, the wavelength associated with the energy difference between the shells, will be emitted in form of characteristic X-ray of the atom. X-ray fluorescence (XRF) analysis is therefore based on the excitation of the core electron and subsequent emission of the characteristic X-ray. In practice, the electron, proton or photon must have the approximate energy to make the process possible. In fact, these particle must have energy well above the threshold energy (the binding energy of the electron, E_b), to excite the electron.

A snag of the process is that a large part of the kinetic energy of these particles and photon give rise to bremsstrahlung spectrum on which the characteristic X-ray lines are superimposed. However, with the advances in XRF, radio-isotopic sources, which emit electron, proton and X-ray, are now used as exciting sources for the primary X-rays. These sources produce intensities whose magnitudes are several orders lower than the conventional X-ray intensities (Dim, 1991).

METHODOLOGY

Sample Collection

Samples were collected randomly from five south-eastern states of Nigeria in solid form, stored in clean polythene bags and transported to the laboratory for analysis.

Sample preparation

In satisfying the homogeneity condition of XRF analysis, the kaolin samples were pulverized using the pulverizer to obtain a very fine powder. Afterwards, 11.0g of each of the powdered sample was collected and weighed. The samples were then poured into the XRF machine sample cups held by the sample tray which can take 12 sample cups simultaneously. The sample analysis was performed using the Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer at the National Geological Survey Agency, Kaduna. The EDXRF spectrometer consist of a self-contained miniature x-ray tube system which includes the x-ray tube with a silver (Ag) transmission target, a beryllium window, a controller which generates all the voltages needed to operate the x-ray tube and provides both voltage(kV) and current (μA) display and control. The x-ray Detector is coupled to multichannel analyser for signal and data acquisition.

Spectral Acquisition and Analysis

The XRF machine is switch-on alongside the computer system attached to the machine. The machine is allowed to stabilize through its gain control process that takes about an hour or less depending on the last period of usage, during the same period the computer system application called “Epsilon 3” is started from the application menu. After the gain control process the machine is then ready for use. The samples position on the sample tray is then noted and identified before analysis.

The position of the peaks determines the elements present in the sample, while the height of the peaks determines the concentration.

RESULTS AND ANALYSIS

The result of X-ray fluorescence analysis showing the concentration in mg/kg of Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Ag, Pb, and Th are indicated in the table 1 below.

Table 1 Concentration of Elements in Kaolin (Nzu) samples in mg/kg.

ELEMENT	EBONYI	IMO	ABIA	ENUGU	ANAMBRA
Mg	3200	3459	3504	0	4917
Al	167400	143200	132300	140600	188400
Ti	12200	2642	12010	10190	12130
V	114	180	234	259	139
Mn	136.2	15	29	21	30
Na	330	6037	716	7125	519
K	5913	3305	2029	2596	2377
As	3.15	2.6	4.7	5	2.9
Sm	10.44	14.45	10.67	12.63	13.39
U	3.4	3.1	4	3.1	3.4
Sc	22.3	15.45	13.45	14.42	18.64
Cr	123	155	140	133	151
Fe	18400	8537	7809	10260	15350
Co	8.2	2.2	2.2	2.5	3.7
Zn	37	55	0	0	0
Rb	54	26	0	0	0
Cs	5.1	3.6	1.7	1.9	2.2
Ba	213	205	173	161	129
Th	23.9	21.5	24.8	21.9	26.1

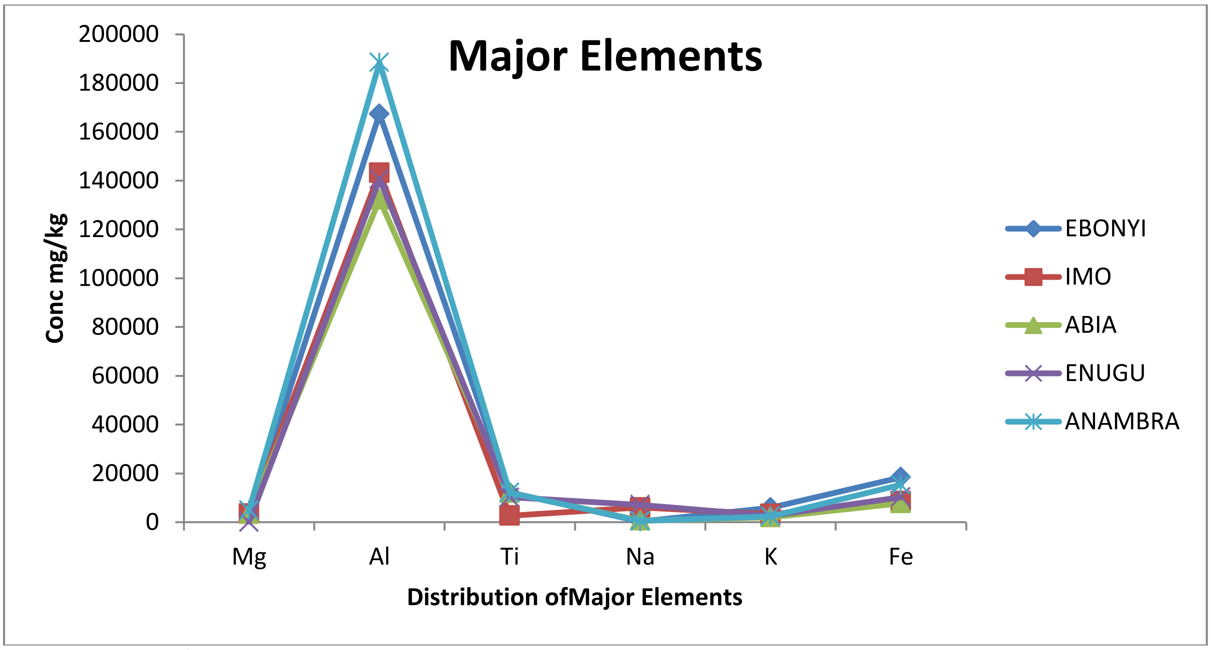

Fig.1 Distribution of Major Elements in Kaolin Sample

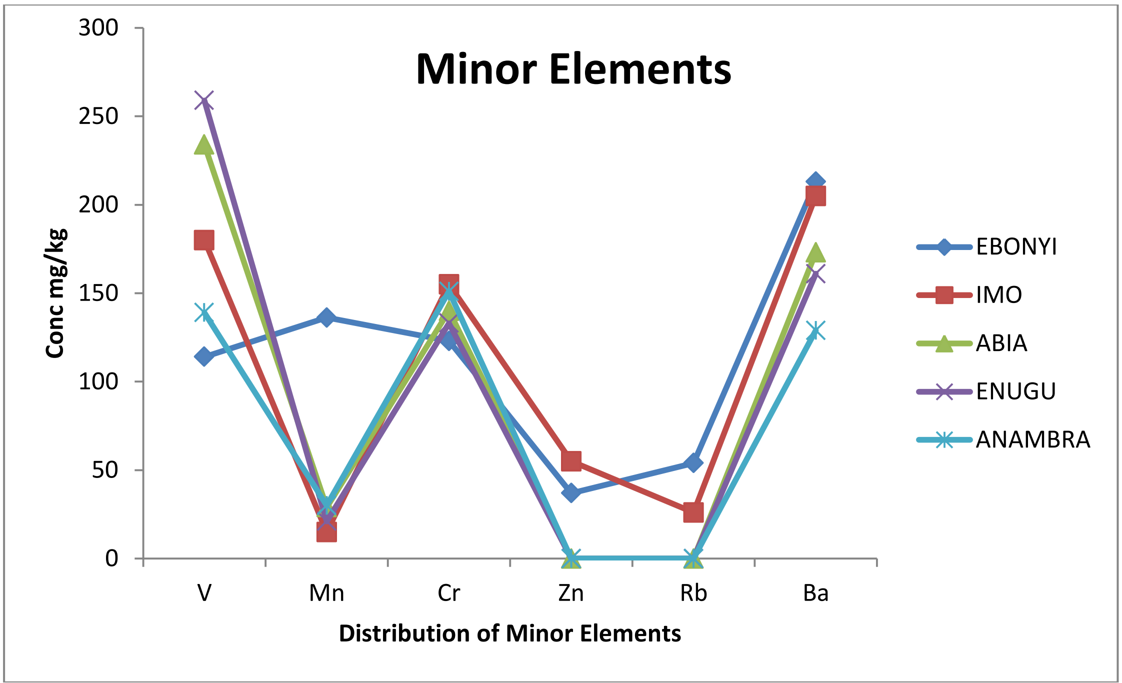

Fig.2 Distribution of Minor Elements in Kaolin Sample

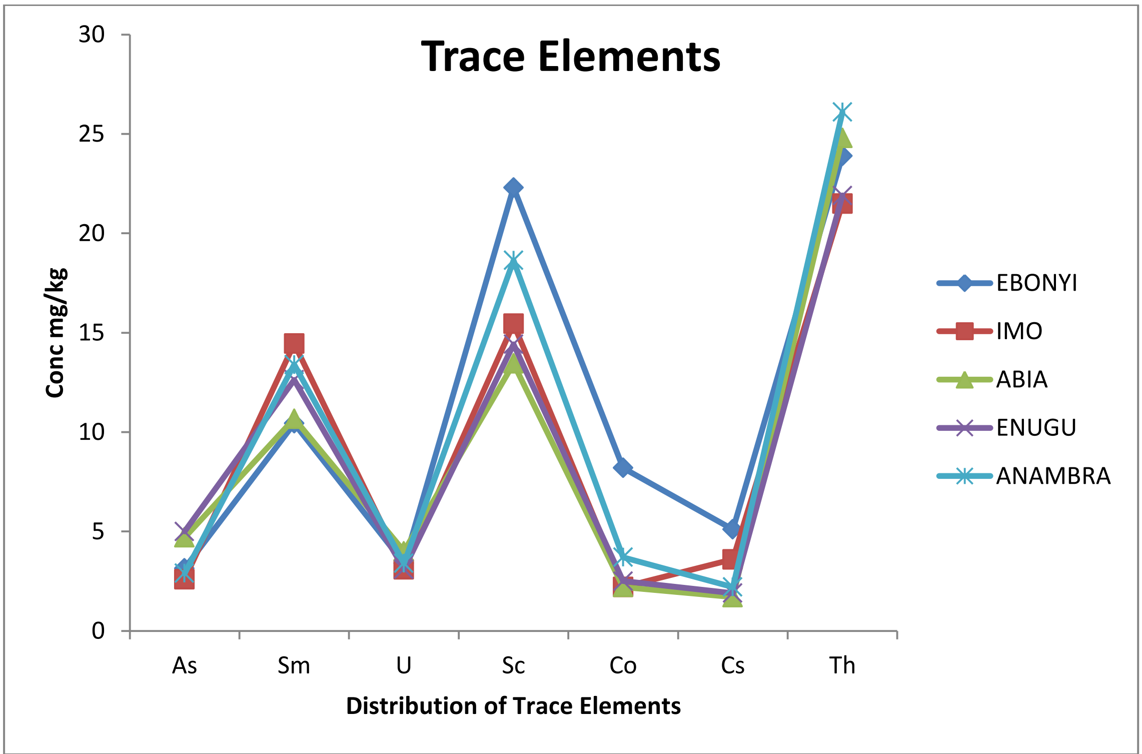

Fig.3 Distribution of Trace Elements in the Kaolin Sample

From the above table and figures, it is clearly evident that there is a variation in the concentration of kaolin sample in all the five states. Iron, Fe, having a concentration range of 5622.32mg/kg in Abia to 9119.88mg/kg in Ebonyi has the highest concentration in the sample.

Enugu has the highest concentration of Ag with 1082.95mg/kg, Imo is next with 1118.15mg/kg, Abia has 1116.5mg/kg, Anambra has 730.51mg/kg and finally Ebonyi having the least concentration with 529.54mg/kg. Silver when combined with sulfadiazine, becomes a topical antibacterial agent for the treatment of burns. (Modak *et al.*, 1998). However, long term inhalation or ingestion of silver compounds may cause argyria and/or argyrosis (Gulbranson *et al.*, 2000). Argyria or Argyrosis is an irreversible pigmentation of the skin (argyria) and/or eyes (argyrosis). The affected area becomes bluish-gray or ash-gray and is most prominent in areas of the body exposed to sunlight.

Strontium concentration in the kaolin (nzu) sample ranges from 58.85mg/kg to 174.57mg/kg. Strontium is not an essential nutrient and it displaces calcium in the bone (Nielsen, 2004). It has gained attention for bone mineralization in part because it increases bone density as measured by X-ray test (Blake and Fogelman, 2007). Oral intake of 2mg/day of strontium renalate have improved bone strength and reduce fracture rates in women with osteoporosis, but there are reports of increased risk of venous blood clots and memory loss (Blake and Fogelman, 2005). Strontium also accumulates in the body and remains there long term. Therefore, strontium may need more evaluation before it becomes a routine treatment for osteoporosis.

The levels of Nickel were highest in Ebonyi with 23.87mg/kg and lowest in Abia with 15.4mg/kg. Meanwhile, Nickel concentration was not detected in Enugu. The recommended daily amount of Nickel is not fixed, but it is suggested that it is enough to take about 100µg/day. However, some studies show that it can be consumed daily about 200µg/d. Nickel aid in Fe absorption; it also plays a role in adrenaline and glucose metabolism. Excess intake into the body is associated with high incidence of heart disease, cancer and thyroid disease.

Copper concentration was observed to be highest in Imo with 12.54mg/kg and lowest in Anambra with 10.12mg/kg. None was detected in Ebonyi and Enugu states. The health benefit of copper includes proper growth, utilization of iron, enzymatic reactions, connective tissue, hair, eyes and energy production. The recommended dietary allowance of copper is 1mg/day and 1.3mg/d (DRI, 2001) for pregnant and lactating women respectively. However, excess intake can result in nausea, vomiting, stomach cramps or diarrhea.

Lead concentrations were detected in the kaolin sample across all the five south-east states. The permissible limit for lead in food substances by FAO/WHO is 0.2µg/g and 0.3µg/g respectively (FAO/WHO, 1999/2001). The concentration of Pb in all the kaolin samples was higher than the permissible limit for lead as can be seen in table 1. Anambra has the highest concentration with 43.01mg/kg, while Ebonyi has the least concentration with 15.4mg/kg. Lead (Pb) affects every organ in the body. It is absorbed into the body and distributed to the soft tissues and bones. The central nervous system is the most vulnerable to lead (Pb) toxicity particularly in developing children (Berthelson *et al.,* 1995). A case study is the lead poisoning that killed over 400 children in Zamfara State, Nigeria as a result of illegal mining activities (Galadima and Garba; 2012)

However, the concentration of most of these elements far exceeds the daily dietary needs or permissible limits of humans and can thus make them toxic unless taken in small doses.

CONCLUSION

Based on this study, the south-east kaolin (nzu) is characterized with exceptionally high concentration of Fe, K, Al, and Mg. This implies that geophagic individuals consuming these clays may benefit from their possible medicinal and nutritional values. However, some elements were also present in high concentration far above the daily dietary need of humans; hence continuous consumption of this clay can result to bioaccumulation of these elements and thus, can pose serious health threat to its consumers

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