



Characterization of Ogwuta Source Clay Using Advanced Analytical Tools

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Authors' contributions

This work was carried out in collaboration among all authors. Authors OC and I-EMU designed the study and vetted the manuscript. All authors wrote the protocol and the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

One of the naturally abundant minerals with diverse industrial applications is the clay mineral. The choice of application depends on the characteristics of the clay. In this study, internal composition of the large and untapped Ogwuta clay deposit located in Afikpo, South Eastern Nigeria was further investigated as a guide to its applications. Scanning Electron Microscope (SEM), Thermogravimetric (TG), and X-ray diffraction (XRD) techniques were employed to access its composition. The scanning electron micrograph revealed that the clumping of the clay particles was due to edge-to-edge, edge-to-face or face-to-face flocculation. Thermogravimetric analysis revealed that at temperature range of 153-325°C, the observed weight percent loss (13.67%), consistent with kaolinitic clays, was due to the removal of water of crystallization of the interlayer cations. X-ray diffraction result further revealed kaolinite as the predominant mineral with the presence of quartz and polygorskite. This study has revealed the applicability of Ogwuta source clay in both industrial and manufacturing activities.

Keywords: *Characterization; SEM; TGA/DTA; XRD; kaolinite; source clay.*

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1. INTRODUCTION

According to the Clay Mineral Society, clay minerals are naturally occurring materials composed mainly of fine-grained minerals which become plastic in the presence of water and become hard when dried or fired. They are any group of hydrous aluminum silicates having diameter less than 2 μm . This inherent size of clay crystallites is as a result of the amount of crystal defects in the axes of symmetry [1], which diminishes the crystal growth and making nucleation less energy consuming. They are mainly inorganic material formed by in situ weathering of parent minerals and by hydrothermal alteration of the host rocks [2]. Non crystalline hydroxides of metals such as Al, Fe, Mg, Ni etc. are capable of co-precipitating SiO_2 from its dilute solution produced by weathering process. The concentration of SiO_2 relative to that of the cation in the weathered solution, more often determine the mineral type in the clay [3].

Basically, clays are made of complex silicates of various ions such as Al^{3+} , Fe^{2+} , Mg^{2+} etc. due to the importance of water to clay formation, they are often regarded as hydrous aluminosilicates or hydrous aluminum phyllosilicates [4]. Iron substitute for aluminum and magnesium to varying degrees and appreciable quantity of potassium, sodium and calcium are frequently present [5]. Structurally, clay minerals like all phyllosilicates are characterized by two dimensional sheets of corner sharing SiO_4 tetrahedra and/or AlO_4 octahedra. The silicon-oxygen tetrahedral consists of silicon surrounded by four oxygen atoms that unite to form the silica sheet. The aluminum or magnesium octahedron consists of aluminum surrounded by six hydroxyl units to form the gibbsite or brucite sheet, depending on any of the dominating atoms. The tetrahedral sheet has Si^{4+} surrounded by three basal oxygen atoms shared by three other nearby tetrahedral sheets. The fourth free oxygen atom (known as apical oxygen) forms bond or link with other tetrahedral or octahedral sheets [6]. The tetrahedral sheet is charge deficient due to the isomorphous substitution of Al^{3+} in place of Si^{4+} . Conversely, the predominant metal ion in the octahedral sheets are Al^{3+} and Mg^{2+} that are surrounded by six oxygen or hydroxyl group. Aluminum, with three positive valences, has only two-thirds of the sites filled. This results in the formation of a di-octahedral sheet $[\text{Al}_2(\text{OH})_6]$. If magnesium ion dominates, a tri-octahedral sheet, with unit cell formula, $\text{Mg}_2(\text{OH})_6$ is formed through the sharing

of two oxygen of each octahedral. The sheet units have the chemical composition $(\text{AlSi})_3\text{O}_4$.

Different clays have different ways these layers of sheets are packed or arranged. Consequently, clays are categorized depending on the tetrahedral-octahedral sheet sequence. If there is only one tetrahedral and one octahedral in each layer, the clay is known as a 1:1 (T-O) clay. The other composition known as 2:1 (T-O-T) clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing toward each other and forming each side of the octahedral sheet.

Based on their structures and chemical compositions, the clay minerals can be divided into four main classes of kaolinite, smectites, illites and micas [4]. However, Sarkar et al. [7] and Walter [8] refer to two or three classes of clays since illites are sometimes referred to as a 2:1 layer and not a 2:1:1. Also, illites/micas are sometimes grouped with smectites. Clays are distinguished from other fine-grained particles such as silt by their plasticity properties. Most clay particles are characterized by high swelling capacity, large specific surface area and high cation exchange capacity [9]. Kaolinites on the other hand have low shrink-swell capacity and a low cation exchange capacity (1-15 meq/100g) with a triclinic crystal system and specific gravity of 2.16-2.68.

These properties make clay minerals find wide applications. They are useful as an annular seal or plug for water wells and as protective liner for landfills. Other uses include as an anti-caking agent in animal feed. In paper making, they are mixed with cellulose fiber to give it body, opacity and printability. In the oil and gas industry, montmorillonite is a major component of the drilling mud which helps in keeping the drill bit cool and removing drilled solids [10]. The endothermic dehydration of kaolinites produces disordered metakaolin which is a complex amorphous compound that when added to concrete mix, accelerates the hydration of Portland cement [11]. Bhattacharyya and Gupta [12] added that they are effective as an adsorbent for the removal of heavy metals. This is possible because clay minerals have a net negative charge due to the isomorphous substitution of silicon ion by aluminum ion in the tetrahedral layers or likely substitution of aluminum ion by magnesium ion.

There are several clay deposits in Nigeria ranging from the North to the East (both identified and unidentified). It is therefore

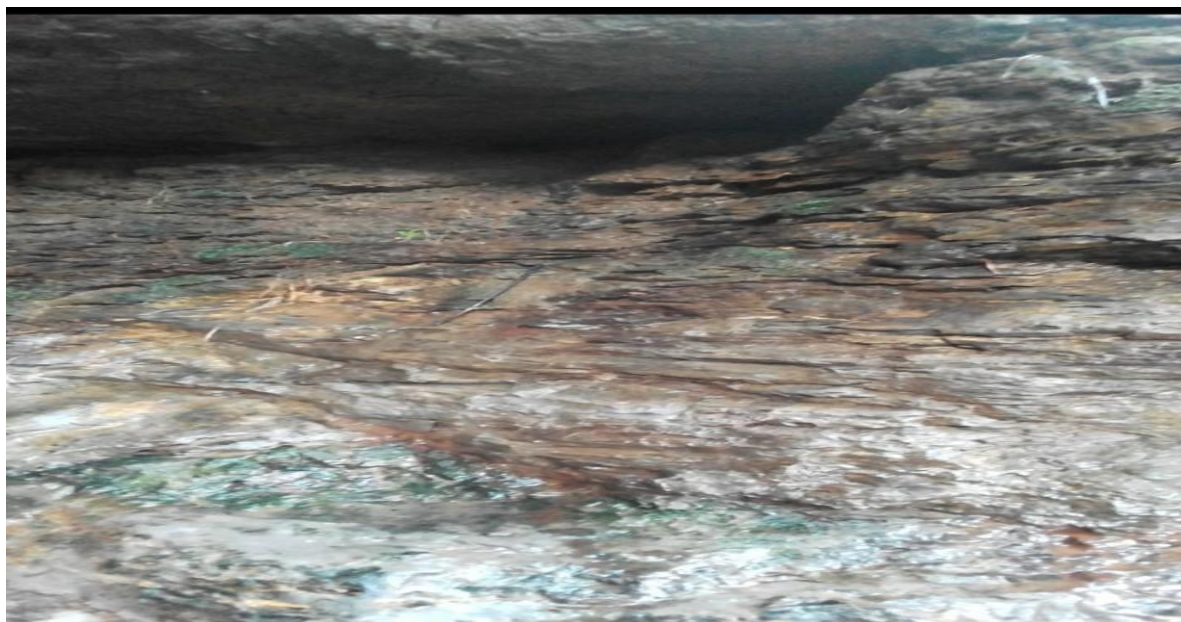


Plate 1. Ogwuta clay deposit

imperative that these clay minerals be x-rayed in physical, chemical, thermal, refractory properties and documented for immediate and future use. Hence, the need for this analytical exploration on the Ogwuta clay sample located at Afikpo, Ebonyi State.

Previous work by Obi and Agha [13] on the clay deposit has revealed the clay mineral of dominance was kaolinite. The researchers also recommend that based on the physicochemical properties of clay obtained, it can be refined, modified and packaged for various industrial applications ranging from catalysis, paint production, building, and pottery to pollution control.

In this study, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and Thermogravimetric analysis (TGA) were further employed in order to expand the knowledge of the composition of the Ogwuta natural clay for additional applications.

2. MATERIAL AND METHODS

2.1 Materials

The clay sample was collected from its natural deposit 12 cm below earth surface in Unwana, a community in Afikpo North Local Government Area of Ebonyi State, South Eastern Nigeria (N 5° 47' 38.154", E 7° 55' 56.538"). The sample was sun-dried for three (3) days and further oven-

dried at 105°C for 2 hrs using BTOV 1423 oven, crushed with an iron roller to fine particle sizes. Then, clay particles were sieved through 63 µm sized mesh and stored in a glass bottle.

2.2 Methods

2.2.1 Sample characterization

Previous characterization on the clay sample with respect to pH, surface area, specific gravity, total pore volume, cation exchange capacity (CEC), metal oxide composition, and vibrational band analysis has been carried out by Obi and Agha [13].

2.2.1.1 Scanning Electron Microscope (SEM)

SEM for the clay samples was done according to the method reported by Rajkumar et al. [14].

2.2.1.2 Thermogravimetric analysis

The thermal analysis of the clay sample was done using a simultaneous TGA-DTA (Pekin Elmer TGA 4000) analyzer. Approximately 11.209 mg of powder sample was loaded into the platinum sample pan and heated from ambient temperature to 950°C at a heating rate of 10°C/min under air purge gas drawn at 20 ml/min and pressure of 2.5 bars. Traces were recorded as percentage weight loss versus temperature.

2.2.1.3 X-ray Diffraction (XRD) analysis

The XRD analysis on the natural clay sample was done according to the method reported by Obi et al. [15].

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscope (SEM)

The scanning electron micrograph of the clay, as presented in Fig. 1 revealed particles formed by large agglomerates of irregular sizes and shapes. The agglomeration arose from the tendency by the clay particles to repel each other electrostatically, depending on the ion density and inter-granular distance [16]. However, Mitchell and Soga [17] noted that breaking of the clay material can expose hydroxyl group, leading to the existence of hydrogen bond. This will ultimately bring about clumping of particles which can be seen as edge-to-edge, edge-to-face or face-to-face flocculation. The micrograph also displays the micro-porosity of the clay mineral.

3.2 Thermal Analysis

The thermal behavior of the clay sample, as presented in Fig. 2 showed thermal behavior similar to most kaolinitic clay samples in literature

[18,19]. It showed initial exothermic weight gain that peaked at 39.84°C. This might be attributed to hygroscopic behavior of the samples enhanced by not using very dried air [20]. However, all gained weight was lost completely at 45.51°C. Also, the sample exhibited characteristic exothermic weight loss (2%) around 100-150°C. This could be associated with the physically adsorbed water [21]. From 153-325°C, the observed weight percent loss (13.67%), consistent with kaolinitic clays, was due to the removal of water of crystallization of the interlayer cations [22]. The last step of weight loss was observed between 532°C and 776°C which, according to Conconi et al. [19] was due to the dehydroxylation of the hydroxyl group of the natural clay sample.

3.3 X-Ray Diffractogram

The result of d_{001} peak displacements in Fig. 3 showed a basal spacing of 7.13 Å at a 2θ angle of 14.115° . This also shows that clay sample has a well-defined characteristic of most clay [23]. The stick pattern shown in Fig. 4 also reflects that the clay mineral is kaolinitic in nature. The result further reveals that the source clay was amorphous having crystallinity less than 20%.

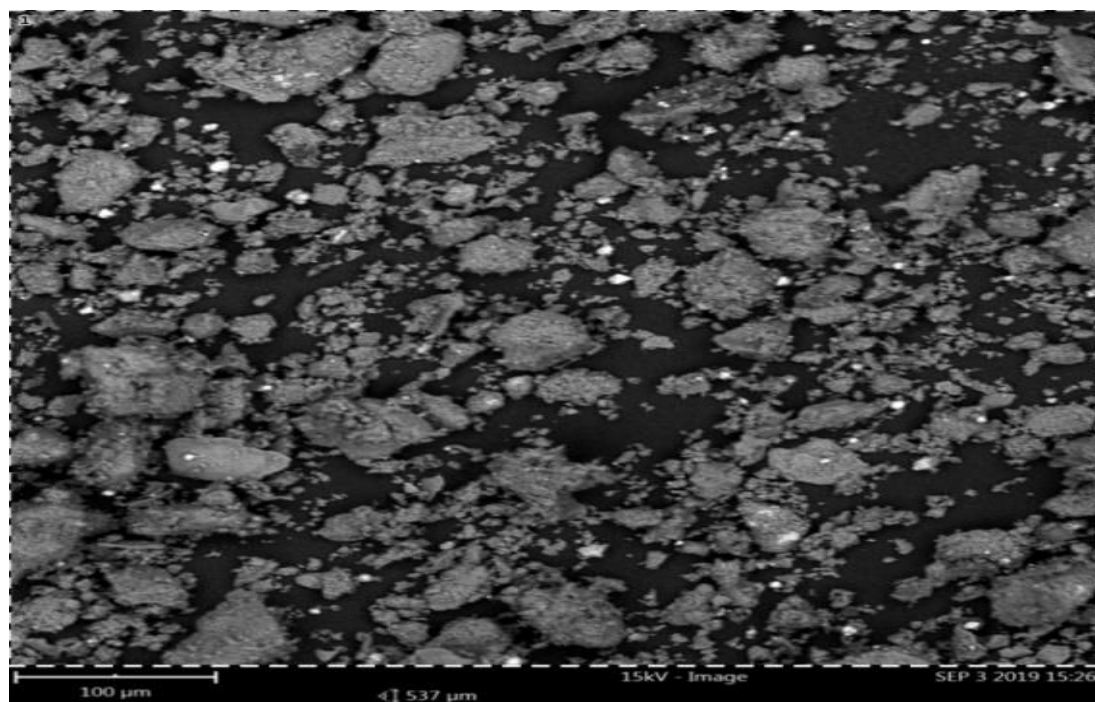


Fig. 1. SEM image of natural clay

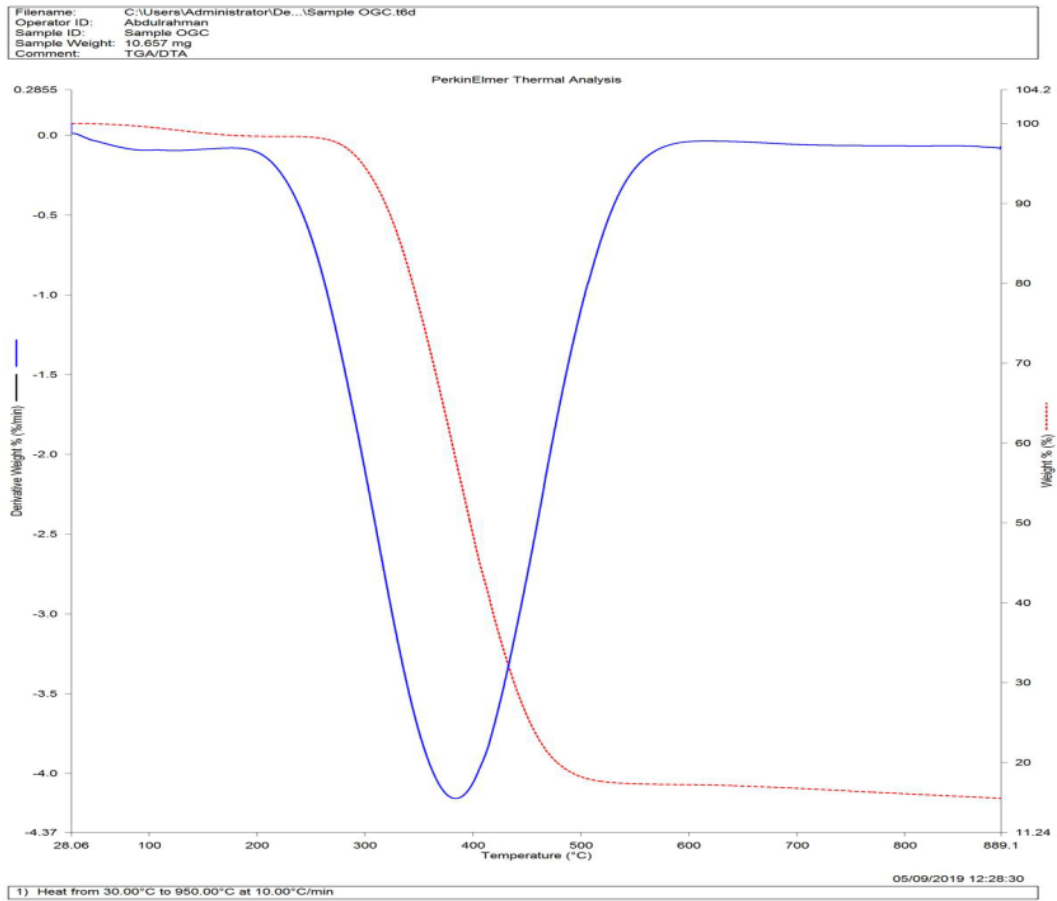


Fig. 2. TGA/DTA of natural clay sample

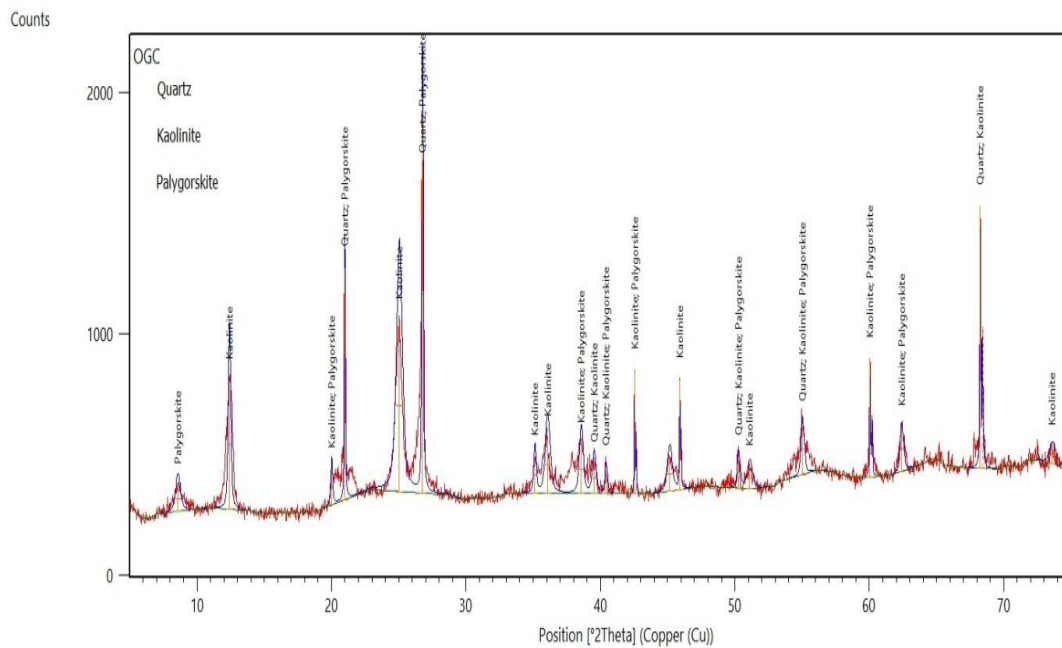


Fig. 3. XRD spectrum of natural clay sample

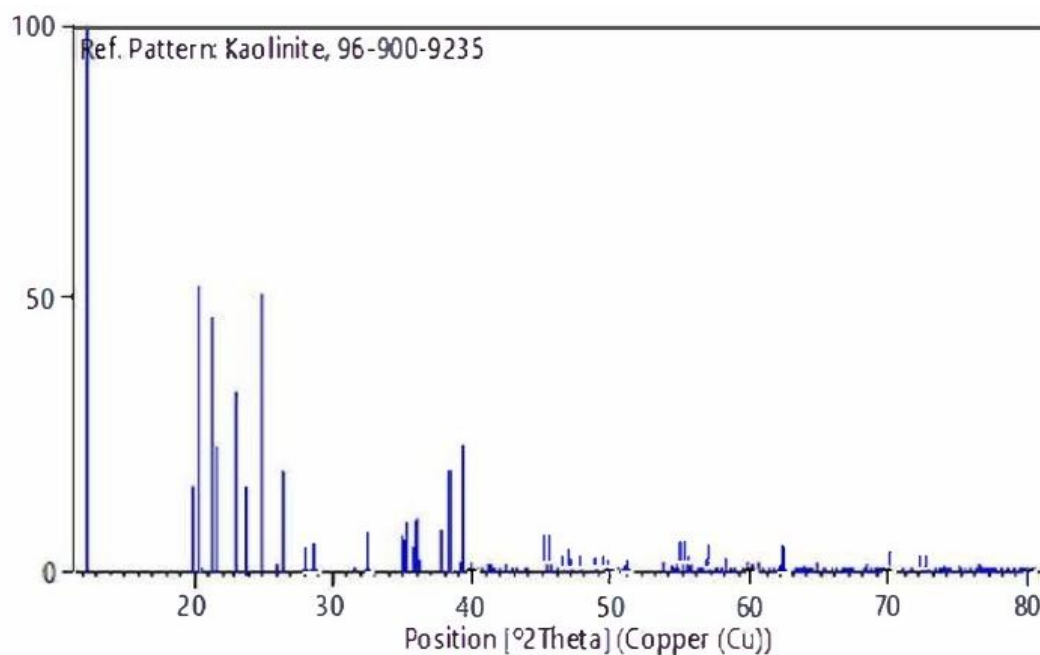


Fig. 4. XRD Stick Pattern for clay kaolinite mineral

4. CONCLUSION

Local clay sample was sourced from its vast natural deposit and characterized for proper classification and determination for possible application. Spectroscopic techniques were employed for the analysis. The XRD analysis confirmed kaolinite as the predominant mineral, with the presence of polyhgorskite and quartz. The temperature behavior of the clay as shown by the thermogravimetric result further confirmed kaolin as the dominant argillaceous mineral in the form of hydrated alumino silicate given the 13.69% water of crystallization. This study has clearly demonstrated that Ogwuta clay is a veritable precursor for application in various processes such as industrial, domestic, manufacturing, social works, etc.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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