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Characterization of Ogwuta Source Clay Using Advanced Analytical Tools

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 industries.

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Keywords: Characterization, SEM, TGA/DTA, XRD, kaolinite, source clay

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 alumino-silicates 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

38 surrounded by six hydroxyl units to form the gibbsite or brucite sheet, depending on any of
39 the dominating atoms. The tetrahedral sheet has Si^{4+} surrounded by three basal oxygen
40 atoms shared by three other nearby tetrahedral sheets. The fourth free oxygen atom (known
41 as apical oxygen) forms bond or link with other tetrahedral or octahedral sheets [6].
42 The tetrahedral sheet is charge deficient due to the isomorphous substitution of Al^{3+} in place
43 of Si^{4+} . Conversely, the predominant metal ion in the octahedral sheets are Al^{3+} and Mg^{2+}
44 that are surrounded by six oxygen or hydroxyl group. Aluminum, with three positive
45 valences, has only two-thirds of the sites filled. This results in the formation of a
46 di-octahedral sheet $[\text{Al}_2(\text{OH})_6]$. If magnesium ion dominates, a tri-octahedral sheet, with unit
47 cell formula, $\text{Mg}_2(\text{OH})_6$ is formed through the sharing of two oxygen of each octahedral.
48 The sheet units have the chemical composition $(\text{AlSi})_3\text{O}_4$.

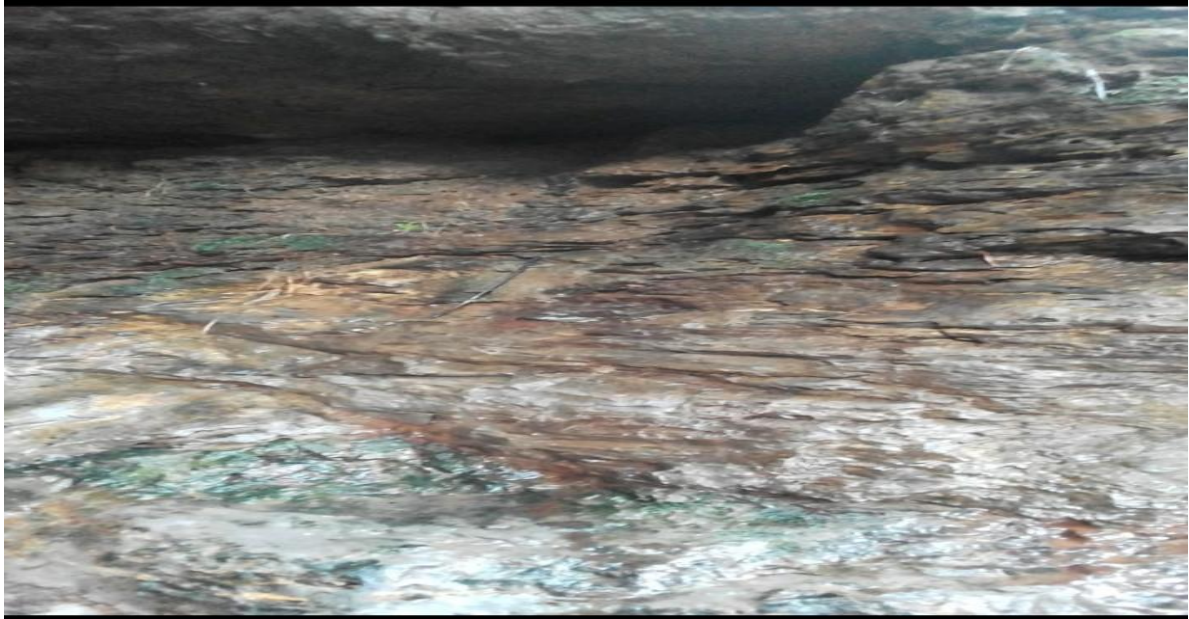
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50 Different clays have different ways these layers of sheets are packed or arranged.
51 Consequently, clays are categorized depending on the tetrahedral-octahedral sheet
52 sequence. If there is only one tetrahedral and one octahedral in each layer,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

56
57 Based on their structures and chemical compositions, the clay minerals can be divided into
58 four main classes of kaolinite, smectites, illites and micas [4]. However, Sarkar *et al.* [7] and
59 Walter [8] refer to two or three classes of clays since illites are sometimes referred to as a
60 2:1 layer and not a 2:1:1. Also, illites/micas are sometimes grouped with smectites.
61 Clays are distinguished from other fine-grained particles such as silt by their plasticity
62 properties. Most clay particles are characterized by high swelling capacity, large specific
63 surface area and high cation exchange capacity [9]. Kaolinites on the other hand have low
64 shrink-swell capacity and a low cation exchange capacity (1-15 meq/100g) with a triclinic
65 crystal system and specific gravity of 2.16-2.68.

66
67 These properties make clay minerals find wide applications. They are useful as an annular
68 seal or plug for water wells and as protective liner for landfills. Other uses include as an
69 anti-caking agent in animal feed. In paper making, they are mixed with cellulose fiber to give
70 it body, opacity and printability. In the oil and gas industry, montmorillonite is a major
71 component of the drilling mud which helps in keeping the drill bit cool and removing drilled
72 solids (Stanisa *et al.* [10]). The endothermic dehydration of kaolinites produces disordered
73 metakaolin which is a complex amorphous compound that when added to concrete mix,
74 accelerates the hydration of Portland cement [11]. Bhattacharyya and Gupta [12] added that
75 they are effective as an adsorbent for the removal of heavy metals. This is possible because
76 clay minerals have a net negative charge due to the isomorphous substitution of silicon ion
77 by aluminum ion in the tetrahedral layers or likely substitution of aluminum ion by
78 magnesium ion.

79
80 There are several clay deposits in Nigeria ranging from the North to the East (both identified
81 and unidentified). It is therefore imperative that these clay minerals be x-rayed in physical,
82 chemical, thermal, refractory properties and documented for immediate and future use.
83 Hence, the need for this analytical exploration on the Ogwuta clay sample located at Afikpo,
84 Ebonyi State.

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87 **Plate 1.**Ogwuta clay deposit
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89 Previous work by Obi and Agha [13] on the clay deposit has revealed the clay mineral of
90 dominance was kaolinite. The researchers also recommend that based on the
91 physicochemical properties of clay obtained, it can be refined, modified and packaged for
92 various industrial applications ranging from catalysis, paint production, building, and pottery
93 to pollution control.
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95 In this study, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and
96 Thermogravimetric analysis (TGA) were further employed in order to expand the knowledge
97 of the composition of the Ogwuta natural clay for additional applications.
98

99 **2. MATERIAL AND METHODS**

100 **2.1 Materials**

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102 The clay sample was collected from its natural deposit 12 cm below earth surface in
103 Unwana, a community in Afikpo North Local Government Area of Ebonyi State, South
104 Eastern Nigeria (N 5° 47' 38.154", E 7° 55' 56.538"). The sample was sun-dried for three (3)
105 days and further oven-dried at 105°C for 2 hrs using BTOV 1423 oven, crushed with an iron
106 roller to fine particle sizes. Then, clay particles were sieved through 63 µm sized mesh
107 and stored in a glass bottle.
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110 111 112 113 114 **2.2 Methods**

115 **2.4 Sample Characterization**

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

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124 SEM for the clay samples was done according to the method reported by Rajkumar *et al.*
125 [14].
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2.4.2 Thermogravimetric Analysis

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129 The thermal analysis of the clay sample was done using a simultaneous TGA-DTA (Pekin
130 Elmer TGA 4000) analyzer. Approximately 11.209 mg of powder sample was loaded into the
131 platinum sample pan and heated from ambient temperature to 950°C at a heating rate of
132 10°C/min under air purge gas drawn at 20 ml/min and pressure of 2.5 bars. Traces were
133 recorded as percentage weight loss versus temperature.
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2.4.3 X-ray Diffraction (XRD) Analysis

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137 The XRD analysis on the natural clay sample was done according to the method reported by
138 Obi *et al.* [15].
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3. RESULTS AND DISCUSSION

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3.1 Scanning Electron Microscope (SEM)

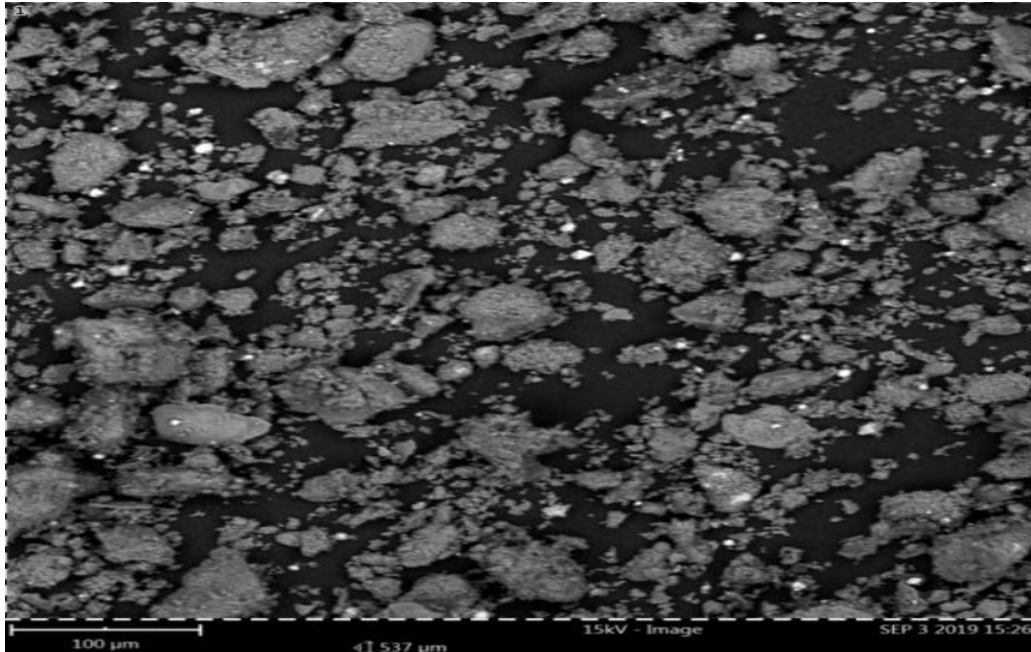
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143 The scanning electron micrograph of the clay, as presented in Figure 1 revealed particles
144 formed by large agglomerates of irregular sizes and shapes. The agglomeration arose from
145 the tendency by the clay particles to repel each other electrostatically,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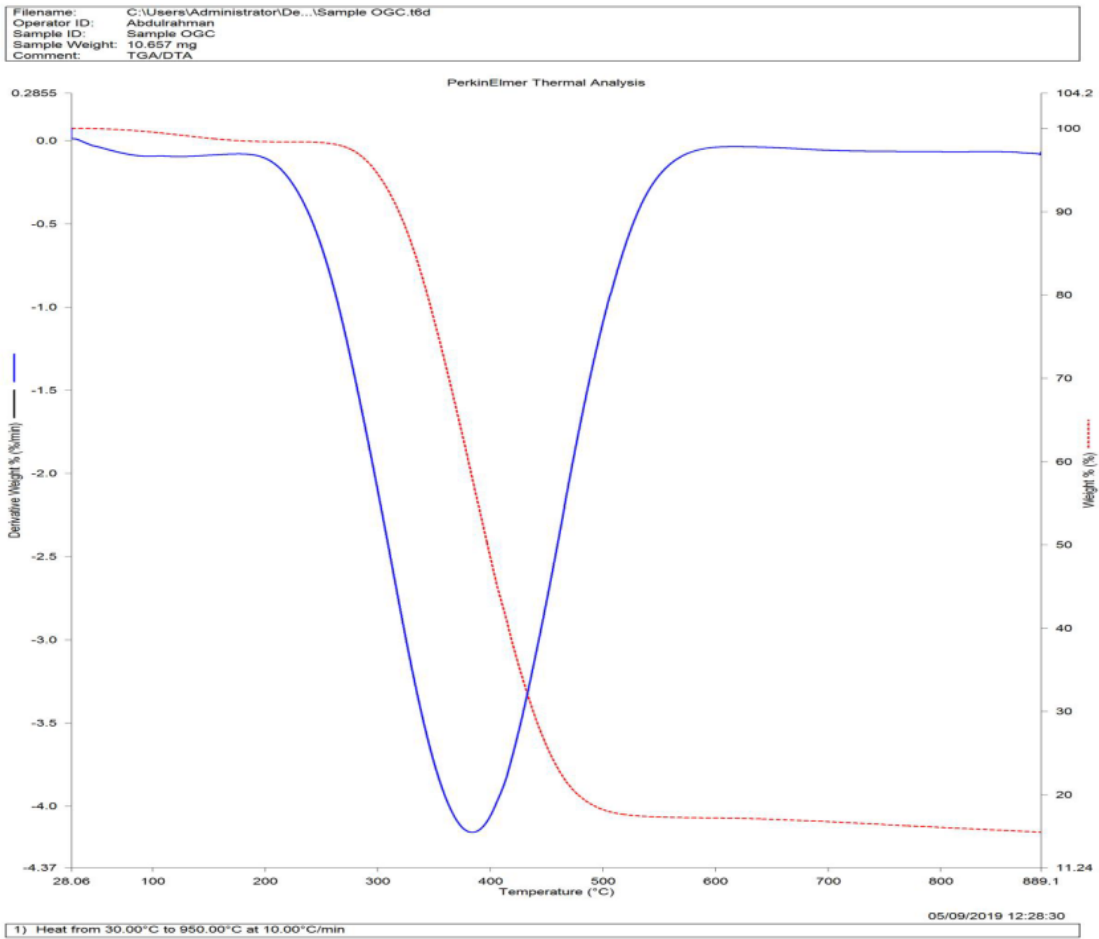


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Fig. 1. SEM image of natural clay

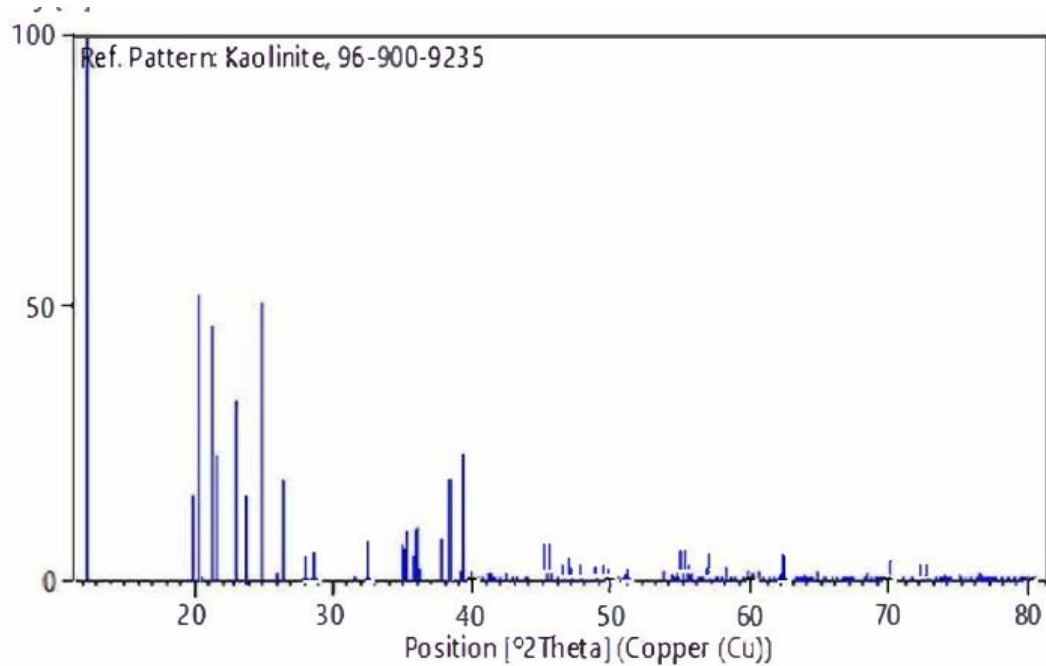
3.2 Thermal Analysis

The thermal behavior of the clay sample, as presented in Figure 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.



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Fig. 2. TG/DTA of natural clay sample



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215 **Fig. 4.** XRD Stick Pattern for clay kaolinite mineral

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217 **4.0 CONCLUSION**

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

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229 **COMPETING INTERESTS**

230

231 Author has declared that no competing interests exist.

232

233 **AUTHORS' CONTRIBUTIONS**

234

235 Authors OC and I-EMU designed the study and vetted the manuscript. Author All wrote the
236 protocol, and the first draft of the manuscript. All authors read and approved the final
237 manuscript.

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