GEOCHEMICAL PROPERTIES AND ECONOMIC POTENTIALS OF OGISO AND OKHORO CLAY DEPOSITS, BENIN CITY, SOUTHERN NIGERIA

BY

Eguasa Samson AGBONGIAGUE

(PG/PSC1513867)

B.Sc. Hons, (University of Benin)
MINERAL EXPLORATION (OPTION)

DEPARTMENT OF GEOLOGY
FACULTY OF PHYSICAL SCIENCES
UNIVERSITY OF BENIN, EDO STATE

DECEMBER, 2019

GEOCHEMICAL PROPERTIES AND ECONOMIC POTENTIALS OF OGISO AND OKHORO CLAY DEPOSITS, BENIN CITY, SOUTHERN NIGERIA

BY

Eguasa Samson AGBONGIAGUE
(PG/PSC1513867)
B.Sc. Hons, (University of Benin)

A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, UNIVERSITY OF BENIN, EDO STATE

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (MSC) GEOLOGY (MINERAL EXPLORATION OPTION)

DECEMBER, 2019

CERTIFICATION

This is to certify that this project was carried out by Eguasa Samson AGBONGIAGUE of the Department of Geology, Faculty of Physical Sciences, University of Benin, Benin City, Edo State.

________________________ ________________________

Prof. I. O Imasuen Date

Project Supervisor

________________________ ________________________

Prof. I. O Imasuen Date

Head of Department

DEDICATION

I dedicate this work to Almighty God for the strength and grace for me to be able to complete this project and also to my dear mother.

ACKNOWLEDGEMENTS

I will first of all thank God Almighty for giving me the grace and capacity to carry out this project work. This project work was made possible by the assistance of several people, I would therefore like to offer my sincere thanks to them all.

I would like to specially acknowledge my esteemed supervisor, Professor O.I.S. Imasuen for his supervisory role well played during the course of this research, his constructive criticism as well as correction of write-ups and suggestions that made this research work a success. My special appreciation to the Head of Department, Professor C.N Akujieze and also Prof. F.A Lucas, they always call me their friend but they are my fathers. I will not forget to thank Dr S.A. Salami for his wonderful contributions. My appreciation also goes to Dr. M. Omorogieva, what a wonderful elder brother you are, thank you. I also am not forgetting Dr. A. Ogbamikhumi, Dr. J. Edegbai and Dr. (Mrs.) G. E. Maju-Oyovwikowhe for their supports.

I will also like to express my special thanks to Dr (Mrs.) O. Alonge who played a wonderful role as well as her willingness to render assistance when necessary. May God continue to bless you Mama.

My special appreciation to my good friends and brothers Mr. H. Omodolor, Mr Ayamezimi Ehinlaiye, Mr. Joseph Omobude-idiado , Ojo Solomon, Mr. Efosa K. Obanor, Mr. N.S. Igbinigie, Mr. Fredrick E. Chegwe, Mr. Johnson Otu, Mr. Edward Emenemiaye, Mr. J. Odia-Oseghale, Mr. Dan Omoruyi for their valuable information during the period of this work.

My gratitude also to my sectional head Mr. Binitie Vincent for his fatherly role right from when I started this work. I will not forget to thank my big mummy Mrs. Joan Wogheren for her special support.

I thank and appreciate my loving Mother, my brother Destiny Benson, my Aunt Finefine , Kehinde Aghama and my special Whitney.O. Imagbe for their moral and spiritual support.

I would also like to thank in a very special way High Priest Harrison Okao for his support.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF PLATES

LIST OF TABLES

ABSTRACT

There has recently been an increase for the usage of clay minerals. Hence, the driving force for this research work which was carried out to determine the chemical composition and basic geotechnical and physical characteristics of Ogiso and Okhoro clay deposits in Edo State, Southern Nigeria. In this study, ten (10) fresh clay samples were randomly collected, three(3) from Okhoro and seven(7) from Ogiso and were subjected to X-ray-Diffraction (XRD), X-ray-Fluorescence (XRF) and geotechnical analysis to determine their mineralogy, chemical composition and engineering behaviour so as to evaluate their economic potential. The XRD analysis revealed that the basic mineralogy of the samples studied is made up of kaolinite, quartz and hematite with traces of zircon, illite and anatase occurring in minor amounts in some of the samples. The XRF analysis revealed the occurrence of 10 elemental oxides and 10 elemental trace elements. The major elemental oxides include SiO_2 with a range of 55.82 – 61.41wt %, Al_2O_3 with a range of 21.12 – 24.42% and Fe_2O_3 with a range of 6.05 – 9.06% while the major elemental trace elements are zircon with a range of 0.89 – 1.78wt%, zinc with a range of 0 – 1.51%, copper with a range of 0 – 1.39wt% and chromium with a range of 0.01 – 0.11wt%. The geotechnical analysis revealed that the samples are of low to medium plastic inorganic clay with percentage fines fraction of 76.84 – 78.45%. The high chemical index of alteration (CIA) values, high chemical index of weathering (CIW) values and moderate ratio of TiO_2/Zr suggest an intense weathering source area. The mineralogical composition, the elemental trace element, main element discrimination diagram and elemental ratios of these samples such as TiO_2/Al_2O_3 suggest a provenance mainly of intermediate source. The results from my analysis further indicate the clay samples from the study areas are mainly kaolinitic clay and categorized as commercial ball clays. It is a fairly good construction material based on the moderate plasticity index.

CHAPTER ONE

INTRODUCTION

1.1 GENERAL STATEMENT

Clay and clay minerals has been indispensable in architecture, in industry and agriculture. Today they are among the most essential mineral used as raw materials for manufacturing and environmental studies.

Clay is formed from common geological processes such as weathering which takes place daily everywhere in the world. Weathering breaks up rocks and enables water to wash away soluble soda, potash or lime parts of the feldspar. One of the commonest processes of clay formation is chemical decomposition of feldspar (Clews, 1969).

Clay mineral are referred to as hydrous aluminosilicate sometimes with variable amount of iron, magnesium, alkaline metals, alkaline earth metals and other cations.

Clay has a wide spread occurrence in the world, Clay is largely distributed though not always found to be enough or suitable quality for modern industrial purposes in Nigeria. It occurs both as sedimentary and residual clay. Clay is a common name for a number of fine grained, earthy materials that become permanently hard when baked or fired. Velde, (1995), classified clay as materials having a particles size less than 2 micrometers and to the family of minerals that has a similar chemical compositions and common crystal structural characteristics. Other minerals associated with clay minerals may include quatz and feldspar, Grim (1968), as well as detrital materials that were eroded from the earth's surface.

The nature of clay and its composition determine not only its quality and commercial value but also to a large extent, its engineering behavior. Among the characteristics of clays that influence their engineering performance is clay mineral composition, physical properties such as particle size distribution, non- clay mineral composition, organic matter content and geologic history (Grim, 1968).

This work will attempt to address the nature, composition and basic geotechnical and physical characteristics of Ogiso and Okhoro clay deposit in Edo state Nigeria, with a view of their engineering behavior and evaluating their economic potentials as a contribution to the nation's industrial raw material data base

1.2 LOCATION OF STUDY AREA

The study was carried out at Ogiso and Okhoro Communities in Benin City, Southern Nigeria as indicated in Figure 1. The study area lies within latitude 6°20'20" & longitude 5°36'10" and latitude 6°18'10" & longitude 5°41'50". Both clays are units of the Benin Formation in the Niger Delta Basin.

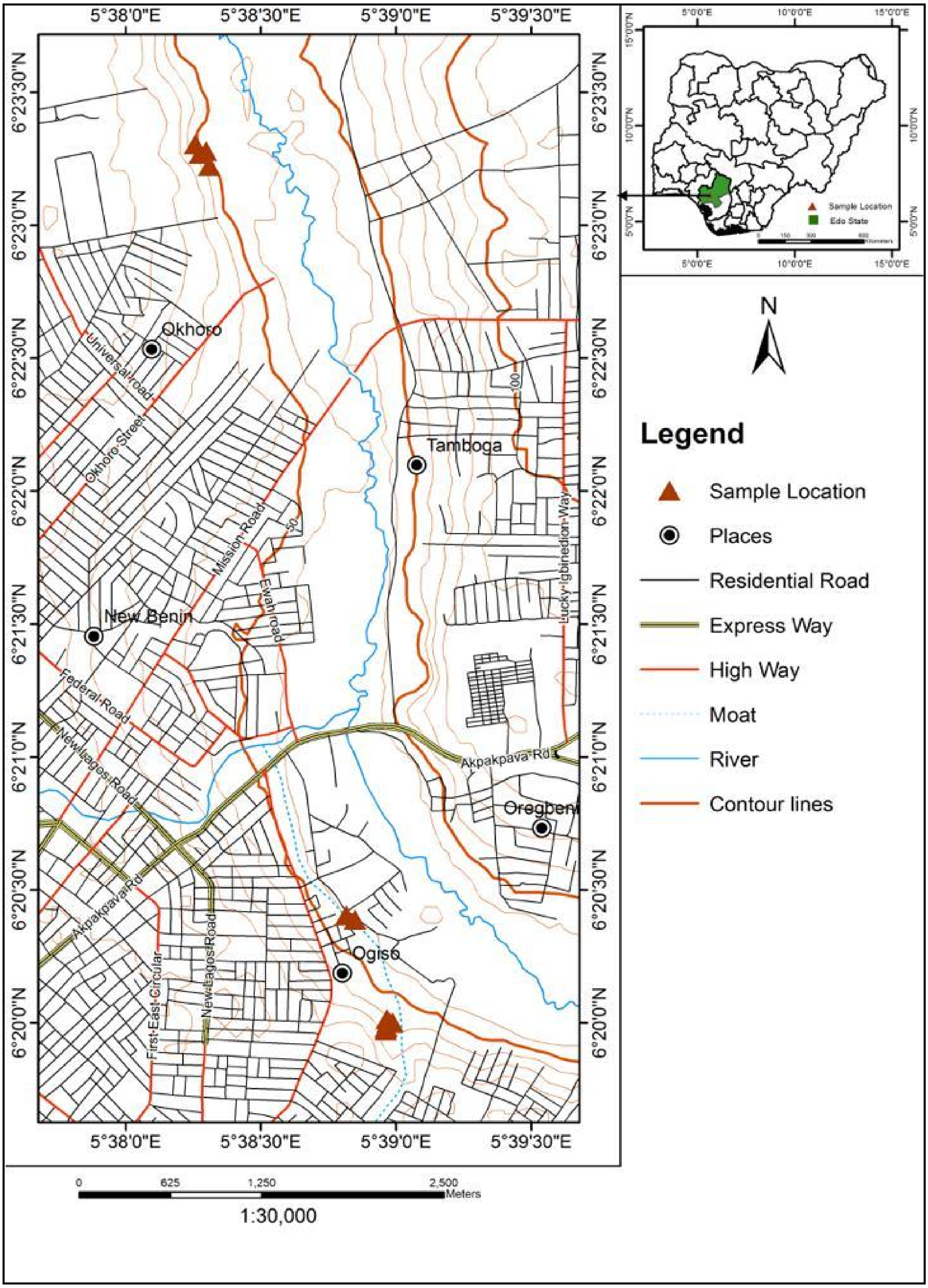

Figure 1. 1: Location Map of the Study Area modified from Akujieze 2004

1.3 AIM AND OBJECTIVES

The aim of this work is to address the nature, chemical composition and basic geotechnical and physical characteristics of Ogiso and Okhoro clay deposit in Edo State, Southern Nigeria.

The objectives include:

- Characterization of clay to infer its mineralogy
- Highlighting the Geochemistry of the clay mineral
- Geotechnical testing such as atterberg limit test and particle size distribution.
- To predict their engineering behavior and evaluate the economic potential associated with clay deposits.

1.4 SCOPE OF STUDY

- Results from X-Ray Diffraction analysis will be used
- Major oxides and trace element was determined using X-ray fluorescence
- Geotechnical properties: Atterberg limit test will be determined as well as physical properties will also be determined.

1.5 VEGETATION

Both locations are densely populated with tall trees and shrubs suggestive to be of the tropical rain forest zone. The top soil ranges from brownish to reddish sand.

1.6 OCCUPATION

The common occupations of the inhabitants include farming and trading.

1.7 ACESSIBILITY

The study area was accessible by (major and minor roads) and footpaths. The areas has good road network. Most places are built up areas, and there are foot-paths to the various outcrops.

CHAPTER TWO

LITERATURE REVIEW

2.1 REGIONAL GEOLOGY OF THE STUDY AREA

The geology setting of the sampled areas lies within the sedimentary basin of the south southern Nigeria and it is of the Benin Formation in the Niger Delta Basin.

2.2 REGIONAL STRATIGRAPHIC SETTING OF THE NIGER DELTA BASIN

The Niger Delta stratigraphic sequence comprises an upward-coarsening regressive association of Tertiary clastics up to 12 km thick. It is informally divided into three gross lithofacies: (i) marine claystones and shales of unknown thickness, at the base; (ii) alternation of sandstones, siltstones and claystones, in which the sand percentage increases upwards; (iii) alluvial sands, at the top (Doust, 1990). Three lithostratigraphic units have been recognized in the subsurface of the Niger Delta (Short and Stauble, 1965; Frankl and Cordy, 1967 and Avbovbo, 1978). These are from the oldest to the youngest, the Akata, Agbada and Benin Formations all of which are strongly diachronous.

2.2.1 AKATA FORMATION (MARINE SHALES)

The Akata Formation is the oldest lithostratigraphic unit in the Niger Delta. The Akata Formation (Paleocene) is a marine sedimentary succession that is laid in front of the advancing delta and ranges from 1,968 ft to 19,680 ft in thickness. It consists of mainly uniform under-compacted shales, clays, and silts at the base of the known delta sequence with lenses of sandstone of abnormally high pressure at the top (Avbovbo, 1978). These streaks of sand are possibly of turbidite origin, and were deposited in holomarine (delta-front to deeper marine) environments. The shales are rich in both planktonic and benthonic foraminifera and were deposited in shallow to deep marine environments (Short and Stauble, 1967). Marine shales form the base of the sequence in each depobelt and range from Paleocene to Holocene in age. They crop out offshore in diapirs along the continental slope, and onshore in the northeastern part of the delta, where they are known as the Imo Shale.

2.2.2 AGBADA FORMATION (PARALIC CLASTICS)

The Agbada Formation (Eocene-Recent) is characterized by paralic interbedded sandstone and shale with a thickness of over 3,000m (Reijers, 1996). These paralic clastics are the truly deltaic portion of the sequence and were deposited in a number of delta-front, delta-topset, and fluvio-deltaic environments. The top of Agbada Formation is defined as the first occurrence of shale with marine fauna that coincides with the base of the continental-transitional lithofacies (Adesida and Ehirim, 1988). The base is a significant sandstone body that coincides with the top of the Akata Formation (Short and Stauble, 1965). Some shales of the Agbada Formation were thought to be the source rocks, however; Ejedawe et al. (1984) deduced that the main source rocks of the Niger Delta are the shales of the Akata Formation. The Agbada Formation forms the hydrocarbon-prospective sequence in the Niger Delta. As with the marine shales, the paralic sequence is present in all depobelts, and ranges in age from Eocene to Pleistocene. Most exploration wells in the Niger delta have bottomed in this lithofacies.

Clay is formed from common geological processes such as weathering which takes place daily everywhere in the world. Weathering breaks up rocks and enables water to wash away soluble soda, potash or lime parts of the feldspar. One of the commonest processes of clay formation is chemical decomposition of feldspar (Clews,1969).

Detailed information on clay mineralogy and chemistry is provided notably by Grim (1968), Brindley and Brown (1980), Caillere *et al.*, (1982), Veld, (1985), Barshad, (1966), Biscaye, (1965), Moore and Reynolds, (1997).

Adeleye and Dessauvagie,(1972) identified clays in the Middle Niger Basin or the Nupe sandstone now renamed the Nupe Group. They studied the Stratigraphic succession in the area and reported the direct overlying of the Basement by a coarse conglomerate, clay sandstone admixture, boulders etc are of sedimentary origin.

Adeleye and Parker (1975) analysis on clay minerals from shale of the sedimentary area of Eastern Nigeria showed that the marine shale of such area contained relatively high proportion of montmorillonite, illite, and mixed layered clay of both.

The Ibese clay-shale deposit which is situated 9Km North of Ilaro-Abeakuta road has been studied extensively in the past by various workers such as Adegoke and Dessauvagie (1970), Fayose and Assez (1972), have been involved in determining the stratigraphy relationship, the depositional characteristics and environment of deposition of the clay-shale and underlying limestone deposit of the area.

Sedimentary kaolin deposit are known to occur in Nigeria mainly as beds, lenses or bands within the Cretaceous and Tertiary sedimentary sequences in the Sokoto, Benue, Chad and particularly the Niger Delta Basins.

Emofurieta *et al.*, (1995) described the mineralogy and the geochemistry of lateritic clays derived from weathered biotite gneiss in Ile-Ife Southwestern Nigeria. They observed that the clay assemblage is dominated by kaolinite, montmorilonite, vermiculite and illite.

Some of the basement rocks have been greatly weathered to form residual clays in the southwestern Nigeria, extensive occurrences and utilization of such residual bodies have been reported by various scientists, Emofurieta *et al.,* (1995) . Based on the evaluation of the chemical compositions, thermal properties and colour, the residual clays in Abeokuta were found to be of great economic importance according to Bolarinwa (2001). Elueze and Bolarinwa (1995) presented the industrial applications of some of the clay deposits in southwestern Nigeria clay deposit.

Interestingly, many researchers have looked at some of the clays from different angles. For example, Ajayi and Agagu, (1981) carried out mineralogical analyses of primary clay deposit from seven localities representing different rocks in the Nigerian basement complex and found that the deposits that weathered from Granites,gneisses, pegmatites and schist consisted mainly of Kaoline and trace proportions of montmorillonite and illite while deposits weathered from calc-silicate rocks contained high proportions of montmorillonite. Many sedimentary deposits have also been investigated in detail e.g the Iguoga clay and Sokoto clay Ola,(1987) and the Ubulu-Uku clay Ola,(1987).

Onyeobi *et al.*, (2013) describes Iyuku clays as clearly autochthonous, being the product of in-situ weathering of igneous rocks within the Nigeria Basement complex mainly granite and pegmatite.

2.2.3 BENIN FORMATION (CONTINENTAL SANDS).

The Benin Formation is the youngest lithostratigraphic unit in the Niger Delta. It is Miocene – Recent in age with a minimum thickness of more than 6,000 ft and made up of continental sands and sandstones (>90%) with few shale intercalations. The shallowest part of the sequence is composed almost entirely of nonmarine sand. The sands and sandstones are coarse-grained, sub-angular to well-rounded and are very poorly sorted. It was deposited in alluvial or upper coastal plain environments following a southward shift of deltaic deposition into a new depobelt. The oldest continental sands are probably Oligocene, although they lack fauna and are impossible to date directly. Offshore, they become thinner and disappear near the shelf edge.

2.3 FORMATION OF CLAY

Clay minerals are typically formed over long period of time by the gradual chemical weathering of rocks, usually silicate-bearing minerals, by low concentrations of carbonic acid and other diluted solvent. These solvents, usually acidic, migrates through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed in place as a residual deposit, but thick deposits usually are formed as a result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation.

One of the common processes of clay formation is the chemical decomposition of feldspars. Clay deposits are typically associated with very low energy depositional environment such as large lakes and marine deposits. Primary clays, also known as kaolins are located at the site of formation. Secondary clays have been moved by erosion and water from their primary location chemically, the clay minerals are hyrous aluminium silicates but could also contain minor amount of magnesium, iron, calcium and alkali. Actually, compositions show variations in si/Al ratio, H_20 and considerable amount of Mg, Fe, Ca and alkali.

2.4 GROUP OF CLAYS

Clay minerals can be classified as 1:1or 2:1, this originates because they are fundamentally built of tetrahedral silicate sheets and octahedral hydroxide sheets.1:1 clay would consist of one tetrahedral sheet and one octahedral sheet, and examples would be kaolinite and serpentine. 2:1 clay consist of an octahedral sheet sandwiched between two tetrahedral sheets, and examples are talc, vermiculite and montmorillonite.

Clay minerals includes the following groups:

2.4.1 KANDITE GROUP

They include kaolinite, Dickite, Nacrite, Halloysite and others. Minerals of these groups are 1:1 layer silicates and their basic unit of structure consist of tetrahedral and octahedral sheets in which the anions at the exposed surface of the octahedral sheet are hydroxyls. A typical species of this group is kaolinite, with an ideal structural formula of $Al_2Si_20_5 (OH)_4$. Dickite and nacrite are polytypic varieties of kaolinite. Halloysite also has a composition close to that of kaolinite but with addition of a layer of water $Al_2Si_20_5 (OH)_4 . 2H_20$.

2.4.2 MICA MINERAL GROUP

Mica minerals have a basic structural unit of the 2:1 layer type like pyrophyllite talc, but some of the silicon atoms (ideally one-fourth) are always replaced by those of aluminium. The result in a charge deficiency that is balanced by potassium ions between the unit layers. Typical examples are muscovite, for dioctahedral species, phogophite and biotite, for trioctahedral species and those similar to muscovite are called illite and generally occur in sediments. The illites are different from muscovite in that the amount of substitution of aluminium for silicon is less; sometimes only one-sixth of the silicon ions are replaced. As a result, the illite have lower potassium content than the muscovites. Celadonite and glauconite are ferric iron-rich species of dioctahedral micas.

2.4.3 VERMICULITE

The vermiculite unit structure consists of sheets of trioctahedral mica or talc separated by layers of water molecules; these layers occupy a space about two water molecules thick. Heating vermiculite to temperatures (depending on its crystal size) as high as 500° C drives the water out from between the mica layers, but the mineral quickly rehydrates at room temperature to maintain its normal basal spacing of approximately 14 to 15Å if potassium or ammonium ions are not present in the interlayer sites.

2.4.4 SMECTITE

The structural units of smectite can be derived from the structures of pyrophyllite and talc. The 2:1 silicate layers of smectite have a slight negative charge owing to ionic substitutions in the octahedral and tetrahedral sheets. The distinguishing feature of the smectite structure is that water and other polar molecules (in the form of certain organic substances) can, enter between the unit layers, cause the structure to expand in the direction normal to the basal plane. Examples of smectites are called montmorillonite and beidellite. In the latter type smectite, those in which ferric iron is a dominant cation in the octahedral sheet instead of the aluminum and magnesium are called nontronite zinc dominant species are called sauconite. Other examples of smectite minerals are saponite, stevenite, hectorite, beidellite and volkonskoite respectively.

2.4.5 CHLORITE

The structure of the chlorite minerals consist of alternate mica-like layers and brucite-like hydroxide sheets about 14Å thick.structural formulas of most trioctahedral chlorite may be expressed by four end-member compositions: clinochlore, chamosite, pennantite, nimite.

Chlorite with a muscovite-like silicate layer and an aluminum hydroxide sheet are called donbassite. In many cases, the octahedral aluminum ions are partially replace by magnesium, as in magnesium-rich aluminum dioctahedral chlorites called sudiote. Cookeite is another type of dioctahedral chlorite, in which lithium substitutes for aluminum in the octahedral sheets. Chlorite structure are relatively thermally stable compare to kaolinite, vermiculite, and smectite minerals and are thus resistant to high temperatures.

2.4.6 SEPIOLITE AND PALYGORSKITE

Sepiolite and palygorskite are papyrus-like or fibrous hydrated magnesium silicate minerals and are included in the phyllosilicate group because they contain a continuous two-dimensional tetrahedral sheet of composition Si_2O_5. They differ, however, from the other Layers silicates because they lack continuous octahedral sheets. The structures of sepiolite and palygorskite are like and can be regarded as consisting of narrow strips or ribbons of 2:1

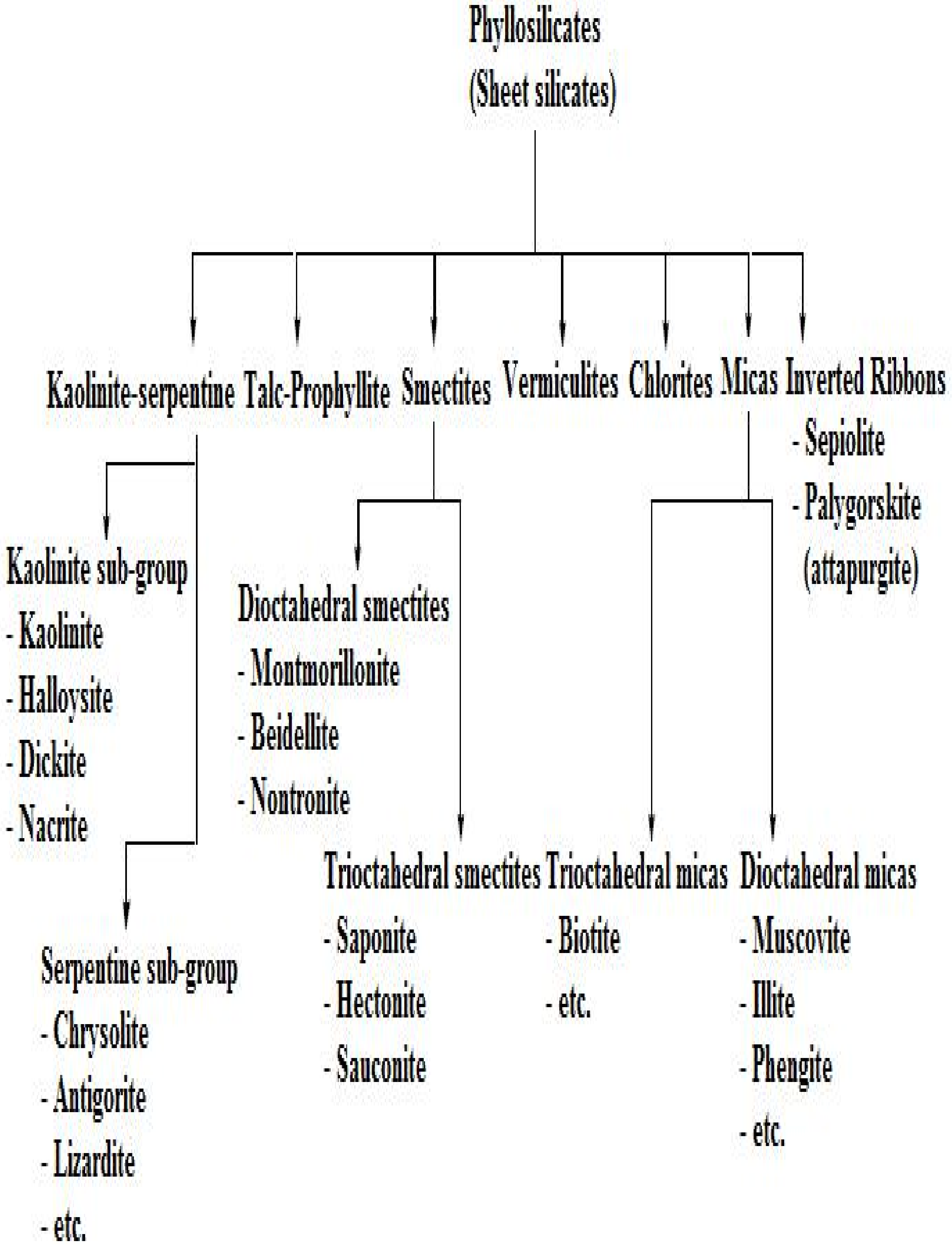

Figure 2. 1: Classification of Clays as Phyllosilicates

2.5 INDUSTRIAL APPLICATION OF CLAY MINRALS

Clay minerals are some of the most important, if not the most important, of our industrial minerals. Millions of tons are utilized annually in a large variety of applications. The important characteristics relating to the application of clay minerals are particle size and shape, surface chemistry, surface area, surface charge, and other properties specific to particular application, including viscosity, colour, plasticity, green, dry and fire strength, absorption and adsorption, abrasion and pH.

Below is a brief discussion on the industrial raw material applications of clays in construction, agricultural, textile, paper, pharmaceutical, ceramic, electrical, nuclear energy, and petroleum industries, respectively, etc.

2.5.1 Construction Industry

Clays and bricks are used as construction raw materials. Bricks are made up of 100% earth materials which include shales, clays, and fine-grained lateritic soils. Clay minerals in the natural lime rock or in the clay or shale mixed the limestone would contribute SiO_2, Al_2O_3 and possibly Fe, alkalis, and alkaline earths depending on the identity of clay minerals for the manufacture of Portland cement. Kaolinite is best suitable for the manufacture of white Portland cement **.**

2.5.2 Pharmaceutical Industry

Clays, especially kaolinites, have been used for centuries in pharmaceutical preparations of intestinal adsorbent drugs and other therapeutically useful applications. Clays such as montmorillonite, kaolinite and attapulgite are used in the preparation of pastes, ointments and body lotions. These clays are used in cosmetic formulations because of their properties such as softness, dispersion, gelling, emulsifying, adsorption, etc.

2.5.3 Petroleum Industry

Bentonites, halloysite and kaolinite clays are used as catalysts in the thermal cracking of heavy petroleum fractions to gasoline.

Bentonite clays are also used as drilling muds in the oil and gas industry. In addition, bentonites and kaolinite are used in compounding rubber to provide desirable reinforcement and stiffening properties in rubber products. Kaolinite clays are extensively used to produce reinforced polyester resins and other reinforced plastics.

2.5.4 Paint Production

Various kinds of kaolinite clays are used in the manufacture of paints to improve their brushability, body or film surface (glossy or flat) properties

2.5.5 Agricultural Industry

(a) Fertilizers

Phlogopite, illite, and glauconite clays are used as agromineral additive to enhance soil fertility for crop production because of their high content of potassium. Also, clays are used as diluents in chemical fertilizers to provide the optimum relative concentration of the elements.

(b) Pesticides

Clays composed of montmorillonites and kaolinites are used in pesticide preparations as diluents to enhance the even dispersion of the toxicant and the retention of the pesticide by plants.

(c) Animal Feed Additives

Vermiculites and montmorillonite clays are used as feed additives for poultry, cattle and other animals.

2.5.6 Ceramic Industry

Clays are very valuable prime raw materials in the manufacture of several ceramic products, namely:

(i) Ceramic building materials (bricks, tiles, stoneware pipes, domestic sanitary wares, and fittings for sewage and drainage).

(ii) Domestic ceramics (table wares, dinner ware, flower vases, dental wares, e.g. artificial teeth, etc.).

(iii) Chemical and technical ceramics (chemical engineering apparatus/equipments, hospital equipments and acid resistant tiles and sinks, etc.).

(iv) Specialized laboratory and engineering ceramics (jet nozzles, crucible, pestle mortars, rocket motors, and spark plugs).

(v) Ceramic in electrical industry (electrical insulators, motor brushes and battery carbons).

2.5.7 Textile and Paper Industry

Clays are used for filling, sizing and backing textiles of various kinds. Very fine-grained kaolinite clays with particle sizes from 2-5µm are best suitable fillers for textiles and papers.

2.5.8 Clarification of Water

In clarification of portable water, colloidal matter is removed by filtration and/or sedimentation processes. Alum is usually used to flocculate the colloidal materials to enhance its settling and filtration rate. In some cases, the alum alone is not completely effective, and it may be desirable to add highly colloidal, easily dispersible clay to the water prior to the addition of alum. Alum flocculates the clay which serves to gather up and collect all the colloidal matter in the water that would not have otherwise settle at the base of the water container. Research studies have shown that bentonite clays are best suitable for water clarification purpose because they possess the essential dispersion and adsorptive properties. Weir [28] documented that in water treatment, clays can be used to reduce and remove bad odor and taste in water and for softening of water

2.5.9 Clarification of Wines, Cider, Beer, etc.

The colloidal impurities in wine have been reported to carry positive charges, and therefore, they can be coagulated and removed by stirring a small amount of negatively charged clay material into the wine, cider or beer for clarification Bentonites are best suited for this application.

2.5.10 Atomic (Radioactive) Waste Disposal

The disposal of waste waters and solutions carrying radioactive materials of high biological toxicity is a vital problem in the development of nuclear energy. Clays are used in disposal of highly radioactive (nuclear) wastes by adsorbing the ions and then fixing them against leaching by calcifying to temperature in excess of 1000°C which would be adequate to vitrify the clay and thereby to tie up the radioactive material in insoluble state. The liquid waste is thus converted into a solid form which can be buried without fear that the radioactive materials will ever be dissolved and mobilized into the ground water resources.

2.6 LOCAL GEOLOGY

The Benin Region is underlain by sedimentary formation of the South Sedimentary Basin. The geology is generally marked by top reddish earth, composed of ferruginized or literalized clay sand. The term Benin sand was first used to describe the reddish earth underlain by sands, sandy clays and ferruginized sandstone that mark the Paleo-Coastal environment of Paleocene-Pleistocene age. These sediments spread across the southern fringes of the Anambra Basin and marking the upper fancies off-flaps of the Niger Delta. The name Coastal plain sands is used to describe the formation of red earth underlain by sands and clays that mark an ancient coastal plain environment now exposed in Calabar, Owerri, Onitsha and the Benin Region with the age Oligocene-Pleistocene. However the name Benin Formation was reinstated to identify the reddish-brown-yellow generally white sand soften with clayey and pebbly horizons with type-locality around Benin. This is also referenced at Calabar and other parts of South Eastern Nigeria. The formation was further established by well logging of Etete 1, well drilled on-shore east of River Niger by Shell Nigeria. Petroleum Development Company (SPDC) and described the formation as about 1830 m thick at the seashore but thins landwards. The sedimentary suits of the Benin Formation dip 2˚ - 8˚ south. Geologically, the Benin Region comprises:

1) Drift/top soil and
2) Alluvium;
3) Benin Formation
4) Azagba-Ogwashi Formation

Ogiso clay deposit shows intercalations of clays and reddish sand (lateritic) as shown in Plate 1.1 and 1.2 while Okhoro shows a light grey with brownish patches clay overlying with reddish sand respectively as shown in plate 1.3 and 1.4. The brownish and reddish colouration in Ogiso and Okhoro can be attributable to oxidation.

Plate 1. 1: Sample location at Ogiso Moat showing clay deposit

Plate 1. 2: A location at Ogiso Moat

Plate 1. 3: Sample location at Okhoro showing clay deposit

Plate 1. 3: Sample location at Okhoro showing clay deposit

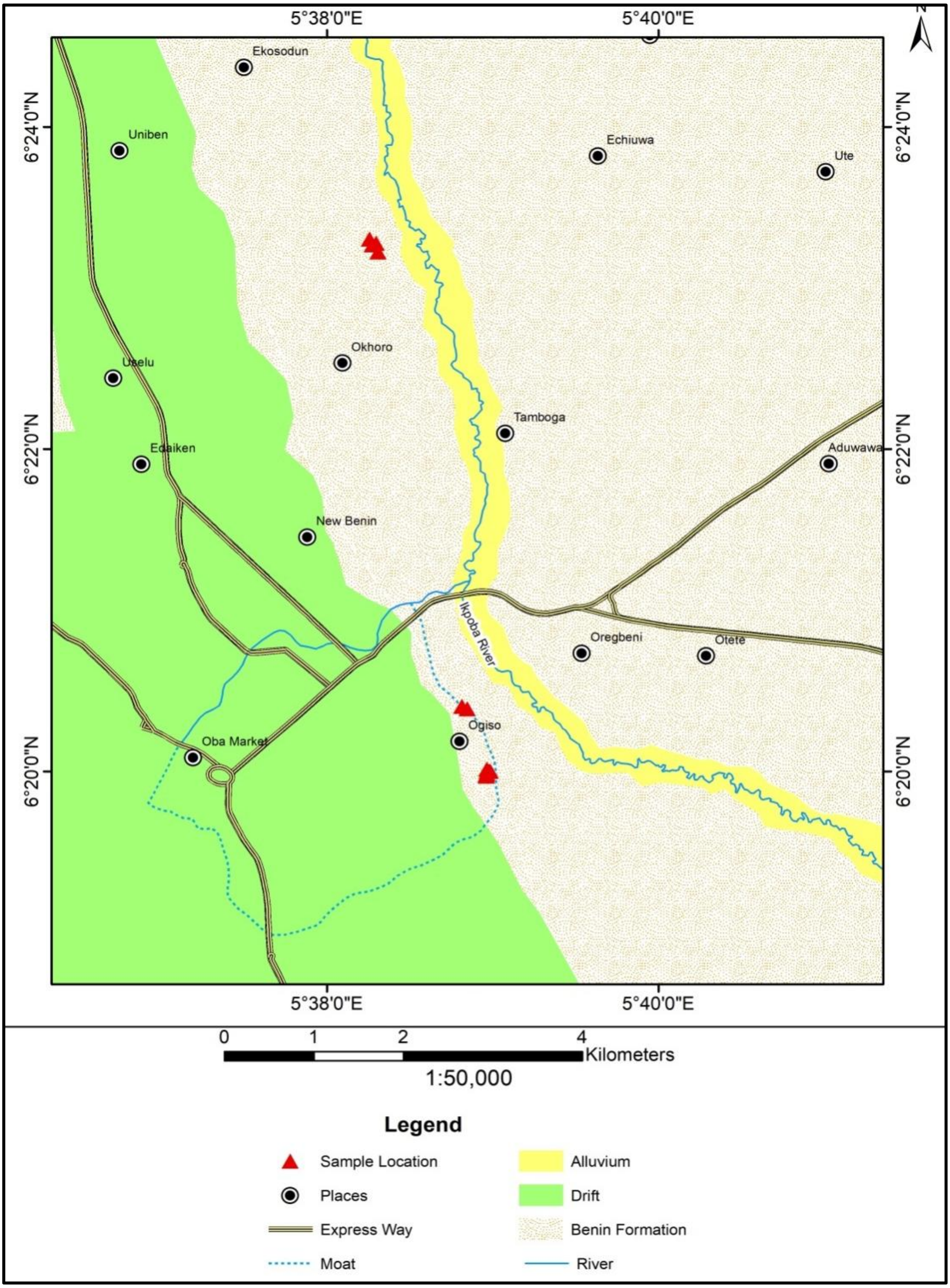

Figure 2. 1: Geologic Map of the study area showing sample location, modified after NGSA, 2006

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 MATERIALS

Ten (10) soil samples were collected from two locations namely Ogiso and Okhoro. Seven soil samples were collected from Ogiso while three soil samples were collected from Okhoro. Geochemical and mineralogical analysis was carried out on the samples.

In this study, several methods were applied to determine the mineralogy, geochemical composition and geotechnical characteristics of the clay deposits. Some of the method include; X-ray diffraction analysis for the determination of the clay mineralogy and, X-ray fluorescence analysis for the determination of the geochemical composition and geotechnical test which includes: particule size analysis, atterberg limit test (plastic limit, liquid limit, shrinkage limit, plasticity index), specific gravity, natural moisture content and linear shrinkage.

3.2 METHODOLOGY

3.2.1 SAMPLING AND ANALYTICAL METHODS

A total of ten (10) fresh samples were collected randomly from fresh clay deposits, seven (7) from Ogiso and three (3) from Okhoro communities. The samples were place in a sealed polythene bags to prevent contamination and loss of moisture, and then taken to the laboratory for testing.

3.2.2 MINERALOGICAL ANALYSIS

A quantitative determination of the mineralogical properties of the clay samples using x-ray Diffraction machine /X-ray Diffractometer were carried out at Natural Steel and Raw Material Exploration Agency, Kaduna. Powdered samples were pelletized and sieved to 0.074mm. These were later taken in an aluminium alloy grid (35mm×50mm) on a flat glass plate and covered with a paper. Wearing hand gloves, the samples were compacted by gently pressing them with the hand. Each sample was run through the Rigaku D/Max-IIIC X-ray diffractometer developed by the Rigaku Int.corp. Tokyo, Japan equipped with an x-ray tube capable of producing a beam of monochromatic x-ray,a sample holder, inbuilt standards, Peak/width goniometer and x-ray detector and, set to produce diffractions at scanning rate of 2°/min in the 2 to 50° at room temperature with a cuka radiation set at 40kv and 2mA. The angles and intensities of diffractions for each mineral are recorded electronically using a detector. After the scan of the sample the x-ray intensity can be plotted against angle 2ϴ to produce a chart. The angle 2ϴ for each diffracted peak can be converted to d-relative intensity) obtained was compared to that of the standard data of minerals established by Brown (1951), Carrol (1971) and the JCPDS (joint Committee on powder Diffraction Standard) the mineral powder diffraction file (1980), which contained and includes the standard data of more than 3000 minerals.

3.2.3 CHEMICAL ANALYSIS

X-ray Fluorescence is a rapid, relatively non-destructive process that produces chemical analysis of rocks. Its purpose is to identify the element abundances of the sample i.e. Identification of both major and trace elements. The samples were analyzed for major element oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, MnO, P_2O_5 and Ti_2O) in percentages while Ba, Cd, Zn, Sr, Cu, Ni and Pb were analyzed in parts per million using a Philips PW1606 X-ray Fluorescence Spectrometer.

3.2.3a PULVERIZATION AND PELETIZATION OF SAMPLE

1. The samples were using oven at temperature of 60°C for 30mins.
2. Each sample were with a jaw crusher and then pulverized for 60 seconds using Herzog Gyro-mill (Simatic C7-621) at 6-8pm.The powder is then fused and pressed into a will adequately absorb the primary X-rays.

3. Pellets were prepared from the pulverized sample, first by grinding 20g of each sample with 0.4g of stearic acid for 60 seconds. After each grinding the Gyro-mill was cleansed to avoid contamination.
4. 1g of stearic acid was weighed into an aluminium cup to act as binding agent and the cup was subsequently filled with sample to the level point.
5. The cup then taken to Herzog pelletizing equipment when it was passed at a pressure of 200KN for 60 seconds.
6. The 2mm pellets were added into a sample holder of the x-ray equipment (Phillips PW-1800) for analysis.

3.2.3b PROCEDURE FOR XRF TECHNIQUE

The samples were exposed to the entire spectrum of photons consisting of primary radiation emitted from a standard X-ray tube. This specimen irradiated causing the elements in it to emit secondary fluorescence with their characteristics x-ray line spectra. The energies and intensities of the emitted lines were determined by the detection system. This is made up of two units; the primary channel simultaneous wavelength dispersive spectrometer and the personal computer for control and data processing.

The intensities of the individual wavelength are measured in a mass gas flow at peak and background position. The output signals from the detector were fed into the analyzer, where the photon counts were stored in the computer memories. The count rate was calibrated for each element pre-determined composition.

The spectra line energies of wavelengths of the emitted line were used in the quantitative analysis of the element in the specimen.

3.2.4 GEOTECHNICAL TESTS

A determination of the geotechnical properties of the clay samples was carried out at Engineering geology laboratory, University of Benin, Benin City Edo State Nigeria. The various analysis carried out include the determination of moisture content, Atterberg limit(liquid limit, plastic limit and plasticity index) and particle size distribution, specific gravity, natural moisture content and linear shrinkage. These laboratory analysis were carried out according to British Standard Methods of test for soils. (BS1377: part 2:1990).The liquid limit, plastic limit and plasticity index of clay soils are used extensively, to correlate with engineering behavior such as compressibility, permeability, compactibility, shrink swell and shear strength and to specify the end product material.

3.2.4.1 ATTERBERG LIMITS

The following moisture conditions – liquid limit, plastic limit, along with shrinkage limit are referred to as the "Atterberg limits". It is also called consistency test. Depending on the water content of the soil, it may appear in four states: solid, semi-solid, plastic and liquid. In each state, the consistency and behavior of the soil is different and consequently so also are its engineering properties. Thus, the boundary between each state can be defined base on a change in the soil's behavior.

3.2.4.2 LIQUID LIMIT TEST PROCEDURE

The liquid limit is defined as the moisture content at which soil begins to behave as a liquid material and begins to flow. The liquid limit is determined in the laboratory as the moisture content at which the two sides of a groove formed in a sample come together and touch for a distance of ½ inch after 25 blows. Since it is very difficult to get this to occur exactly, the test is repeated until the groove closes ½ inch with over 25 blows and under 25 blows. The results are plotted as blow count versus moisture content.

3.2.4.2a APPARATUS FOR LIQUID LIMIT TEST

Liquid limit mechanical device which consist of a brass cup suspended from a carriage designed to control its drop onto a hard rubber base. The device may be operated by either a hand crank or electric motor.

- Cup brass with mass (including cup hanger) of 185 to 215g.
- Cam designed to raise the cup smoothly and continuously to its maximum height, over a distance of at least 180° of cam rotation, without developing an upward or downward velocity of the cup when the cam follower leaves the cam.
- Flat grooving tool made up of plastic or non-corroding metal having specified dimensions.
- A metal gage block for adjusting the height of the drop of the cup to 10mm.
- Pulverizing apparatus –morta and rubber covered pestle
- U.S. No. 40(0.425mm) sieve.
- Spatula, about 3 inch.(75mm) long and approximately ¾ inch (19mm) wide.
- Watering bottle, with distilled, demineralized or tap water
- Clay sample.

3.2.5 PREPARATION OF SAMPLE

- It is preferable that soils used for liquid limit determination be in their natural or moist state, because drying may alter the natural characteristics of some soils. Organic soils in particular undergo changes as a result of over-drying or even extended air-drying. Clay may agglomerate, lose absorbed water which is not completely regained on rewetting, or be subjected to some chemical change.
- If it is determined that the soil is organic or fine-grained, containing no plus No. 40 (0.425mm) material, the liquid limit shall be run on the sample in its natural state.
- If the soil contains sand or large size particles, provision must be made to separation the minus No. 40 (0.425mm) material for testing despite the possibility that drying may alter the characteristics of some soils. The fine fraction of granular soil is normally free organic matter or contains a minimal amount which does not affect the

liquid and plastic limit results. The soil shall be thoroughly dried in an oven at a temperature not exceeding 230±9°F (110±5°C). The pulverizing apparatus and the No. 40 (0.425mm) sieve shall then be utilized for separation of the minus No. 40 (0.425mm) fraction.

- Care should be exercised to insure that the pulverizing apparatus does not reduce the natural size of the individual grains. If the sample contains brittle particles, the pulverizing operation shall be done carefully and with just enough pressure to free the finer material adhering to the coarser particles. The ground soil shall then be separated into two fractions by means of No. 40 (0.425mm) sieve. The plus No. 40 (0.425mm) component shall be reground as before. When repeated grinding produces only a minimal quantity of minus No. 40 (0.425mm) soil, the material retained on the No. 40 (0.425mm) sieve shall be discarded and further pulverization of this fraction should be suspended.
- The material passing through the No. 40 (0.425mm) sieve obtained from the grinding and sieving operation described above shall be thoroughly mixed together and set aside for use in performing the physical test. Approximately 0.3 1b. (100g) would generally suffice for the liquid limit test.

3.2.5.1 PROCEDURE FOR PREPARTATION OF SAMPLE

- About 100g of dry sample sieved through 0.425mm (keeping a couple of tablespoons of dry soil aside) was thoroughly mixed with water in a metal mixing bowl until it was in plastic condition.
- A portion was transferred into a brass cup of the liquid limit machine (Cassagrande apparatus). The sample was then squeezed and spread into position with a few strokes of

the spatula as possible. Care was taken to prevent the entrapment of air bubbles within the mass.

- The drop height of the liquid limit device was adjusted to 1cm using the block end of the grooving tool. With the spatula, the clay sample was leveled and at the same time trims it to a depth of 0.3937inch. (10mm) at the point of maximum thickness. The excess sample was returned to the evaporating dish.
- The clay sample in the cup was divided equally by a firm stroke of the grooving tool along diameter through the center line of the cam follower so that a clean, sharp groove of the proper dimensions will be formed. To avoid tearing of the sides of the or slipping of the clay cake on the cup, up to six strokes, from front to back, or from back to front counting as one stroke, is permitted. The depth of the groove should be increased with each stroke and only the last stroke should scrape the bottom of the cup.
- At this point the crank was turned at a rate of 2 turns per second until the two halves of the sample flow together and come in contact at the bottom of the groove along a distance of ½ inch (12.7mm), Keeping track of the blow count. The number of dropsm require to close the groove is recorded and moisture content was gotten by removing a slice of clay sample approximately the width of the spatula, extending from edge to edge of the soil cake at right angles to the groove and including that portion of the groove in which the sample flowed together.
- If the blow count is greater than 25 blows, add some water and repeat. If less than 25 blows were obtained, add dry soil, mix extremely well, and repeat. The liquid limit is the water content at which it will takes 25 blows to close the groove over a distance of 13mm (1/2inch).
- The procedure was repeated for other samples and the moisture content was taken each time.

3.2.5.2 APPARATUS FOR PREPARATION OF SAMPLE

- Pulverizing apparatus – mortar and rubber covered pestle
- Evaporating dishes – porcelain or similar mixing dishes approximately 4½ inch (114mm) in diameter.
- No. 40 (0.425mm) sieve.
- Spatula, about 3 in. (75mm) long and approximately ¾ in.(19mm) wide
- Watering bottle, with distilled water, demineralized or tap water
- Surface for rolling: A round glass plate or piece of glazed or unglazed paper on which to roll the clay sample
- A 1/8in. (3mm) diameter rod may be used as a guide to help the estimate the thread size.
- Clay sample.

3.2.5.3 PROCEDURE

- About 15g of sample was mixed with water in an evaporating dish until it becomes plastic to be handled easily.
- The mass was rolled between fingers or palm of hand and the ground glass plate with just sufficient pressure to form the mass into a thread of uniform diameter.
- When the diameter of the thread becomes 1/8 in. (3mm), the thread is broken into six or eight pieces. The pieces are then squeezed together between the thumbs and fingers into a uniform mass roughly ellipsoidal in shape, and are rerolled again.

- Alternate rolling to a thread 1/8 in. (3mm) in diameter and gathering together, kneading and rerolling continues until the thread crumbles under the pressure required for rolling and the clay soil can no longer be rolled into a thread.
- Crumbling may occur when the thread has a diameter greater than 1/8 in. (3mm). The shall be considered a satisfactory end point, provided the soil has been previously rolled into a thread 1/8 in. (3mm) in diameter.

3.2.6 DETERMINATION OF PLASTICITY INDEX

The moisture content determination for the liquid limit (LL) and plastic limit (PL) test were used to compute the plasticity index, PI. The difference between the LL and PL gave the PI for each of the clays, to the nearest whole number (table 3.1).

Plasticity Index = Liquid Limit Plastic Limit

PI= LL PL

Soils with medium to high plasticity index tend to be clay, those with lower plasticity index to be silt, and those with plasticity of zero (0) i.e. non plastic tends to have little or no silt or clay.

Table 3. 1: Degree of expansion after Chen (1988)

Plasticity index	Degree of expansion After Chen (1988)
Low plastic	0-15
Medium plastic	10-35
High plastic	20-55
Very high	>55

3.2.7 NATURAL MOISTURE CONTENT DETERMINATION

Moisture content is determined by loss on drying techniques and this method is used to determine the percentage of water in a sample by drying the sample to a constant weight. The natural water content also called the natural moisture content is the ratio of the weight of water to the solid in a given mass of soil. This ratio is usually expressed as percentage and this testing conforms to ASTM D2216-90. The natural moisture content will give an idea of the state of soil in the field.

3.2.7.1 APPARATUS FOR MOISTURE CONTENT DETERMINATION

- Non-corrodible air-tight container
- Electric oven, (temperature between 105 C to 115C). Desiccators
- Sensitive balance.
- Clay sample

3.2.7.2 PROCEDURE FOR MOISTURE CONTENT DETERMINATION

- The container with lid was cleaned, dried and weighed. They was recorded as (w1).
- The moisture sample was weighed immediately in the container and record as the wet weight of sample (w2).
- The container was kept in the lid removed. The clay sample was dried to constant weight maintaining the temperature between 105°C to 110°C for a period of 16 hours
- The sample was allowed to cool.
- The final constant weight (w3) of the container with dried soil sample was recorded.

3.2.7.3 CALCULATION FOR MOISTURE CONTENT

The moisture content of the sample is calculation using the following equation:

W%= × 100

Where: W% = Percentage of moisture in the sample

W1 = Weight of can.

W2 = Weight of can + wet sample.

W3 = Weight of can + dry sample

3.2.8 DETERMINATION OF LINEAR SHRINKAGE

Linear shrinkage is the decrease in length of a soil sample when oven-dried, starting with a moisture content of the sample at liquid limit.

3.2.8.1 SPECIAL APPARATUS FOR LINEAR SHRINKAGE

- 100mm spatula
- Shrinkage moulds
- A 300mm steel rule graduated in mm
- Enamel, plastic, glass, or porcelain mixing bowl of about 150mm diameter.
- A liquid limit machine
- A grooving tool
- Drying oven capable of maintaining from 105°C to 110°C.
- Petroleum jelly (Vaseline) or silicone grease.
- Wash bottle containing deionised water.

3.2.8.2 PREPARATION OF SAMPL FOR LINEAR SHRINKAGE

A sample weighing 150g from thoroughly mixed portion of the bulk material passing 425 micron sieve is prepared. This sample is placed in the mixing bowl and thoroughly mixed with deionised water using the spatula, until the mass becomes a thick homogeneous paste. Sufficient water is added to bring it to a consistency equal to or slightly wetter than the liquid limit. When the sample is tested in the liquid limit machine, the groove should close with between 15 and 25 blows.

3.2.8.3 PROCEDURE FOR LINEAR SHRINKAGE DETERMINATION

- The mould is thoroughly cleaned and a thin film of grease is applied to its inner walls.
- The thoroughly mixed soil-water paste is placed in the mould such that it is slightly above the sides of the mould, taking care to thoroughly remove all air bubbles from each layer by lightly tapping the base of the mould slightly, the mould overfilled and then the excess materials leveled off with the spatula. All soil adhering to the rim of the mould was removed.
- Then the mould with the soil paste is dried in the oven maintained at a temperature of 105°C to 110°C.
- After complete drying, the mould and soil is cooled and the mean length of the soil bar is measured

3.2.8.4 CALCULATION FOR LINEAR SHRINKAGE

Calculation the percentage linear shrinkage (LS) of the specimen. Table 3.2 shows

$$LS\% =$$

Where:

L= Length of the mould (mm) or initial length of specimen

L_S= Longitudinal shrinkage of the samples (mm) or length of oven dried specimen

Table 3. 3: Degree of expansion after Altmeyer (1955)

Linear shrinkage	Degree of expansion After Altmeyer (1955)
<5	Non-critical
5-8	Marginal

>8	Critical

3.2.9 DETERMINATION OF SPECIFIC GRAVITY OF THE SAMPLE

This test is done to determine the specific gravity of fine-grained soil by density bottle method as per IS: 2720 (part III/Sec) 1980. The test to determine the specific gravity of solid will be used to assist in the hydrometer-analysis test. Specific gravity is the ratio of the weight in air of a given volume of a material at a standard temperature to the weight in air of an equal volume of distilled water at the same stated temperature.

The apparatus used:

- Two density bottles of approximately 50ml capacity along with stoppers
- Constant water temperature bath (27° + 0.2°C)
- Vacuum desiccators
- Oven capable of maintaining a temperature of 105° to 110°C
- Weighing balance, with an accuracy of 0.001g
- Spatula

3.2.9.1 PREPARATION OF SAMPLE FOR SPECIFIC GRAVITY

The clay soil sample (50g) was ground to pass through a 2mm IS sieve. 10g of sub-sample was obtained by riffling and oven-drying at a temperature of 105 to 110°C

3.2.9.2 PRECEDURE FOR DETERMINATION OF THE SPECIFIC GRAVITY

1. The density bottle along with the stopper, was dried at a temperature of 105 to 110°C, cooled in the desiccators and weighed to the nearest 0.001g (w1).
2. The sub-sample, which has been oven-dried was then transferred to the density bottle directly from the desiccators in which it was cooled. The bottle and the contents together with the stopper were weighed to the nearest 0.001g (w2).

3. Distilled water from the glass wash bottle was added to the density bottle and allowed to stay for a period of 2 to 3 hours for soaking. Water was then added to fill the bottle to about half.
4. The entrapped air can be removed by heating the density bottle on a water bath.
5. The bottle without the stopper was kept in a vacuum desiccators for about 1 to 2 hours until there is no further loss of air.
6. The soil in the density bottle was gently stirred with a glass rod, carefully wash off the adhering particles from the rod with drops of distilled water and see that no more soil particles are lost
7. The constant temperature in the bottle was observed and recorded.
8. The stopper in the density bottle was then inserted, wiped and weighed (w3).
9. Lastly, the density bottle was emptied, cleaned thoroughly and filled with distilled water at the same temperature. The stopper in th bottle was then, wiped dried from the outside and weigh (w4).

3.2.9.3 CALULATIONS FOR SPECIFIC GRAVITY

The specific gravity G

The specific gravity should be calculation at a temperature of 27°C and reported to the nearest 0.01. If the room temperature is different from 27°C, the following correction should be done:

G’

Where: G’ 27°C

G

k

Relation density of water at various temperature is taken from a standard table

3.2.10 METHOD FOR THE PARTICLE SIZE ANALYSIS OF SOILS BY HYDROMETER METHOD

This method was used to determine the particle size distribution for sample and the process took about 25 hour when testing a single specimen, Because more than one sample is been analyzed, multiple hydrometer tests was carried out simultaneously in order to save time.

3.2.10.1 APPARATUS FOR PARTICLE SIZE ANALYSIS

1. Sedimentation Cylinder: A cylinder made of glass, approximately 18 in (450mm) in height and 2.5 in (60mm) in diameter, marked for a volume of 1.1 qt (1000ml).
2. Hydrometer
3. Plunger
4. Milkshake mixer and dispersion cup (metal milkshake cup)
5. Stopwatch
6. Thermometer
7. Weigh scale
8. Weigh boat
9. Two beakers, one at least 500ml
10. Calgon dispersing agent
11. Spoon/stir sticks (for transferring solid and stirring)
12. 2mm sieve
13. Amyl Acid and pipette

3.2.10.2 PROCEDURE FOR PARTICLE SIZE ANALYSIS

1. All fragments of the clay sample were separation out using a 2mm sieve
2. About 50g of your fine-textured sample was weight out

3. The 50g sample was added to a 500ml beaker, and then 250ml of distilled water was also added
4. 5g (of calgon dispersing agent was poured into a separate beaker, and then distilled water added to 50ml, and it was stirred together until the calgon was dissolved.(because particle-size analysisnis being done for multiple samples, calgon solution was mixed up with all of the sample simultaneously.
5. Add the calgon solution and the soil the solution to a dispersion cup (metal milkshake cup), If some of the sample remains in the beaker, which it often does, pour some water from the dispersion cup into the beaker, swirl it around, and quickly dump it back into the dispersion cup. Continue doing this until the entire sample is in the dispersion cup.
6. The dispersion cup was placed in the milkshake mixer and stirred for 15 minutes.
7. The soil suspensions were transferred to a sedimentation cylinder and water was added to the 1L mark. (Getting the sand out of the dispersion cup can be difficult. After the initial pour into the cylinder, continue adding water im small amount to the dispersion cup, swirling it around and dumping it into the cylinder. This was done until no sediment was remaining in the dispersion cup.
8. Take a temperature reading of the water- it should be approximately room temperature. If not, cover the cylinder and allow the temperature to equilibrate overnight.
9. Use a plunger to stir the suspension for 2 minutes, moving it up and down through the cylinder (25-30 plunges).
10. Remove the plunger and quickly, lower the hydrometer into the suspension. This should occur simultaneously with step 11 but care was taken.

11. Start your stopwatch immediately upon removal of the plunger from the cylinder. Reading of the hydrometer was taken at 20 seconds, 2minutes, 7minutes, and 30minutes and again after 1 hour, because multiple samples measured at the same time, the hydrometer was rinsed between readings of the different samples.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PRESENTATION OF RESULTS

X-ray Fluorescence and X-ray Diffraction was employed for the characterization and identification of the soil samples with particular emphasis on clay fractions on which the behaviour of the soils depends to a large extent. The identity of the minerals that make up the soil clays are hidden and unknown as the minerals usually occur in very finely divided fragments that their identification by ordinary optical and chemical methods was not practicable. X-ray diffractogram (XRD) analysis was used to determine the mineralogy of the clays from which the percentage compositions of the clay types were calculated, while X-ray Fluorescence (XRF) analysis was used to determine the elemental composition of the clays from which the inherent constituents of the clays were determined.

Geotechnical properties of the clay samples such as specific gravity, particle size analysis, Atterberg's Tests, etc where also determined. Below are the presentations of these results.

Table 4. 1: Results for the Geochemical Analysis

ELEMENTAL OXIDES	SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	TiO_2	MgO	Na_2O	MnO	P_2O_5	LOI
OG 1	55.82	23.77	0.08	5.03	2.95	1.13	0.08	0.9	0.07	0.05	6.1
OG 2	63.46	23.34	0.16	6.16	0.52	1.25	0.18	0.9	0.08	0	10.4
OG 3	56.91	28.62	0.03	7.16	0.21	1.23	0.17	0.02	0.08	0.05	7.8
OG 4	60.57	23.84	0.09	8.14	0.21	1.17	0.19	0.8	0.06	0.04	10.42
OG 5	62.35	25.77	0.09	6.05	0.2	1.21	0.18	0.7	0.07	0.05	6.95
OG 6	61.96	24.63	0.08	9.06	0.25	1.83	0.09	0.03	0.08	0.04	6.5
OG 7	59.8	27.34	0.14	8.17	0.17	1.3	0.2	0.06	0.09	0	8.02
OK 1	59.99	27.78	0.08	6.36	0.12	1.34	0.2	0.05	0.09	0	9.92
OK 2	62.19	25.47	0.24	7.31	0.04	1.2	0.19	0.9	0.06	0.05	9.11
OK 3	62.57	26.44	0.09	7.34	0.16	1.25	0.18	0.85	0.08	0.05	8.77

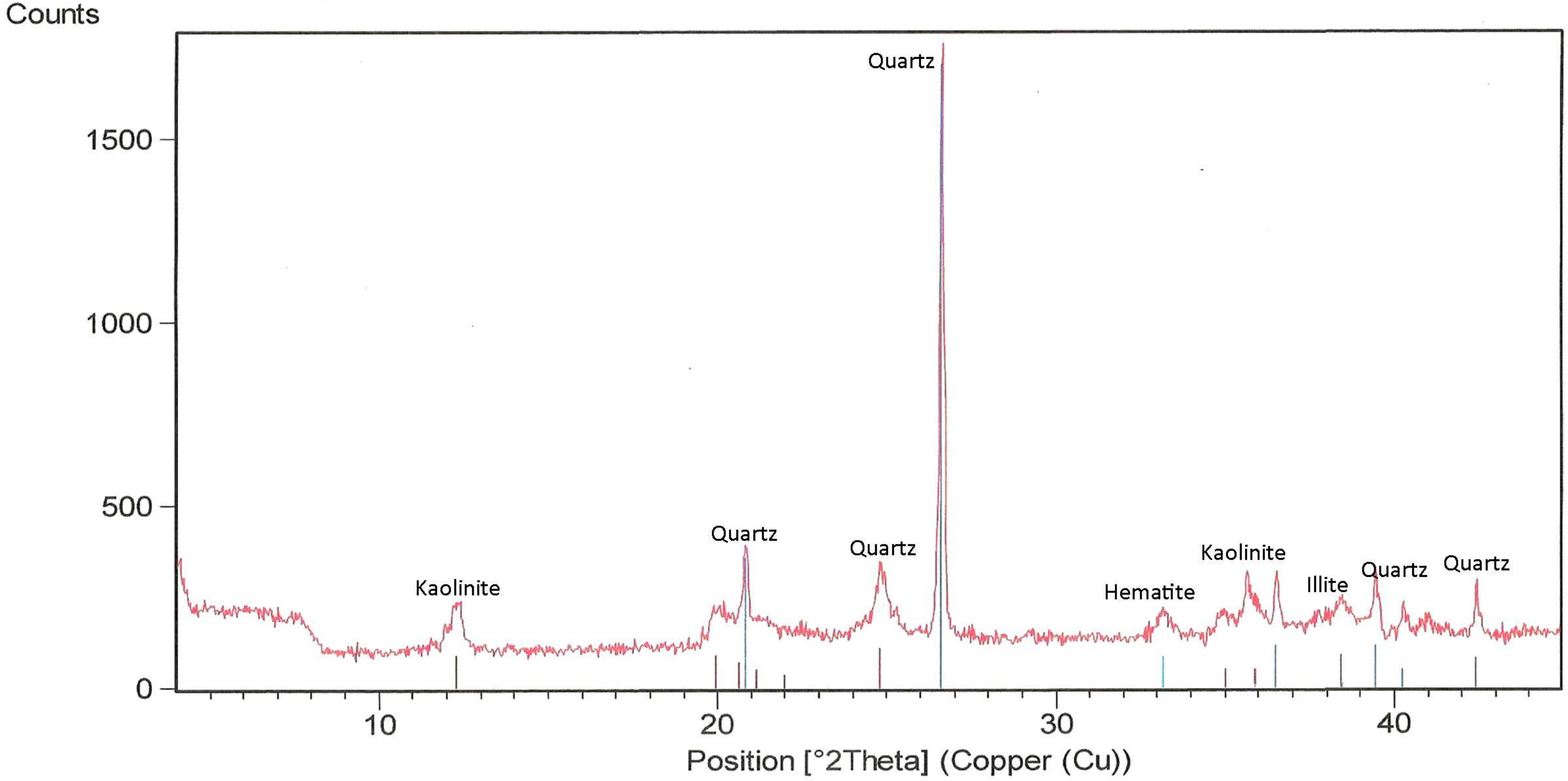

Figure 4. 1: X-ray diffraction patterns and modal composition of Ogiso sample 1

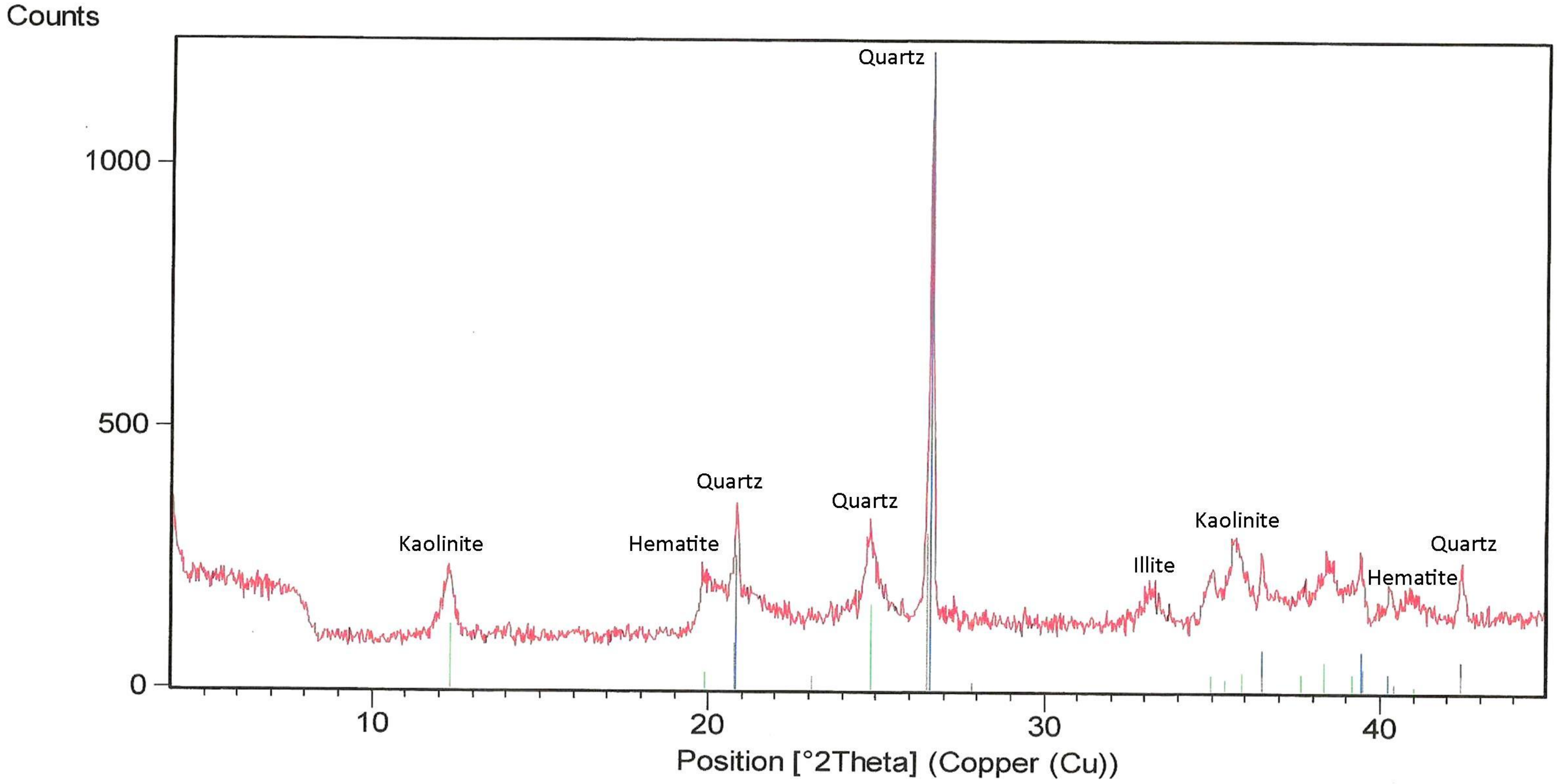

Figure 4. 2: X-ray diffraction patterns and modal composition of Ogiso sample 2

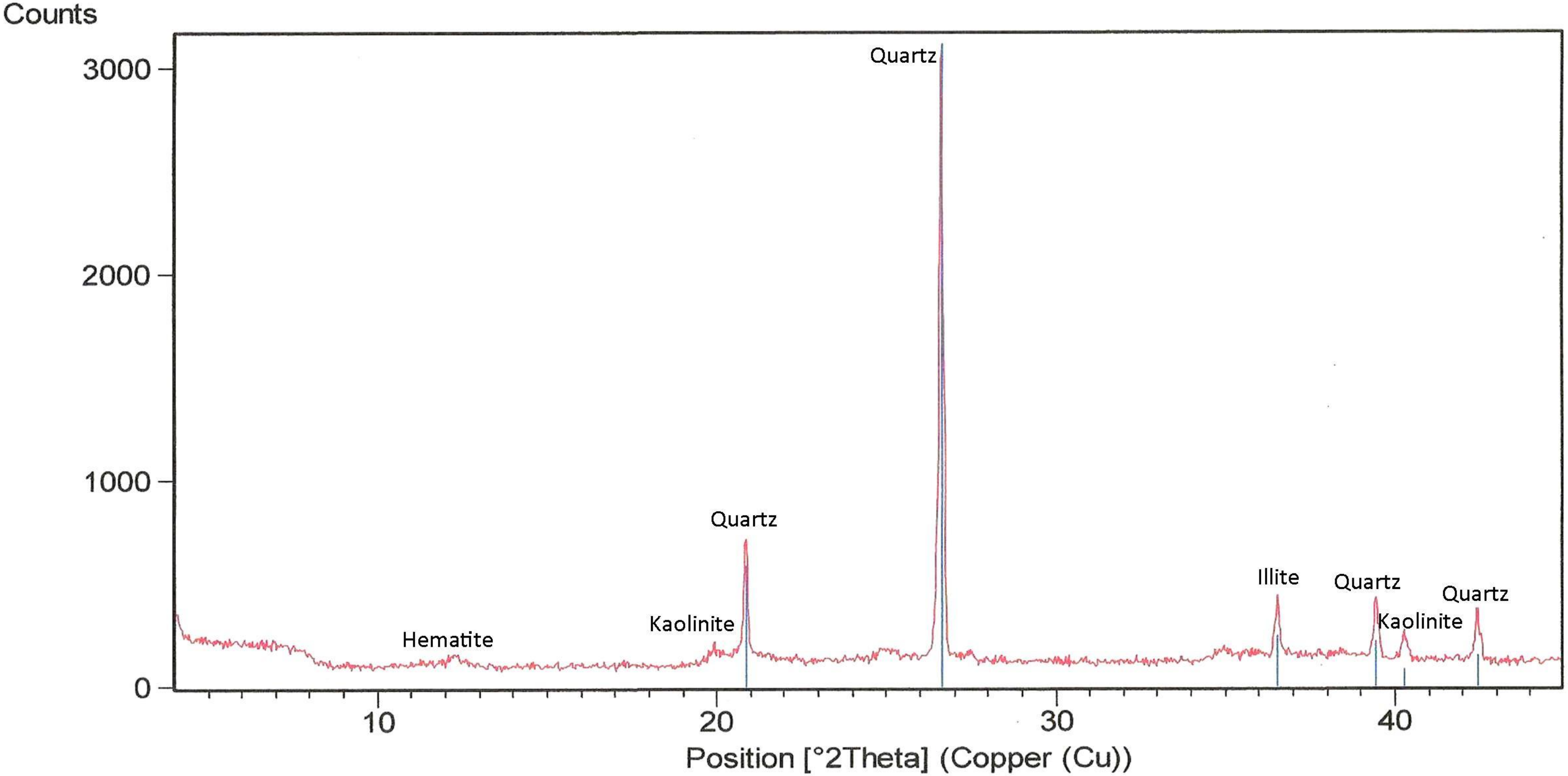

Figure 4. 3: X-ray diffraction patterns and modal composition of Ogiso sample 3

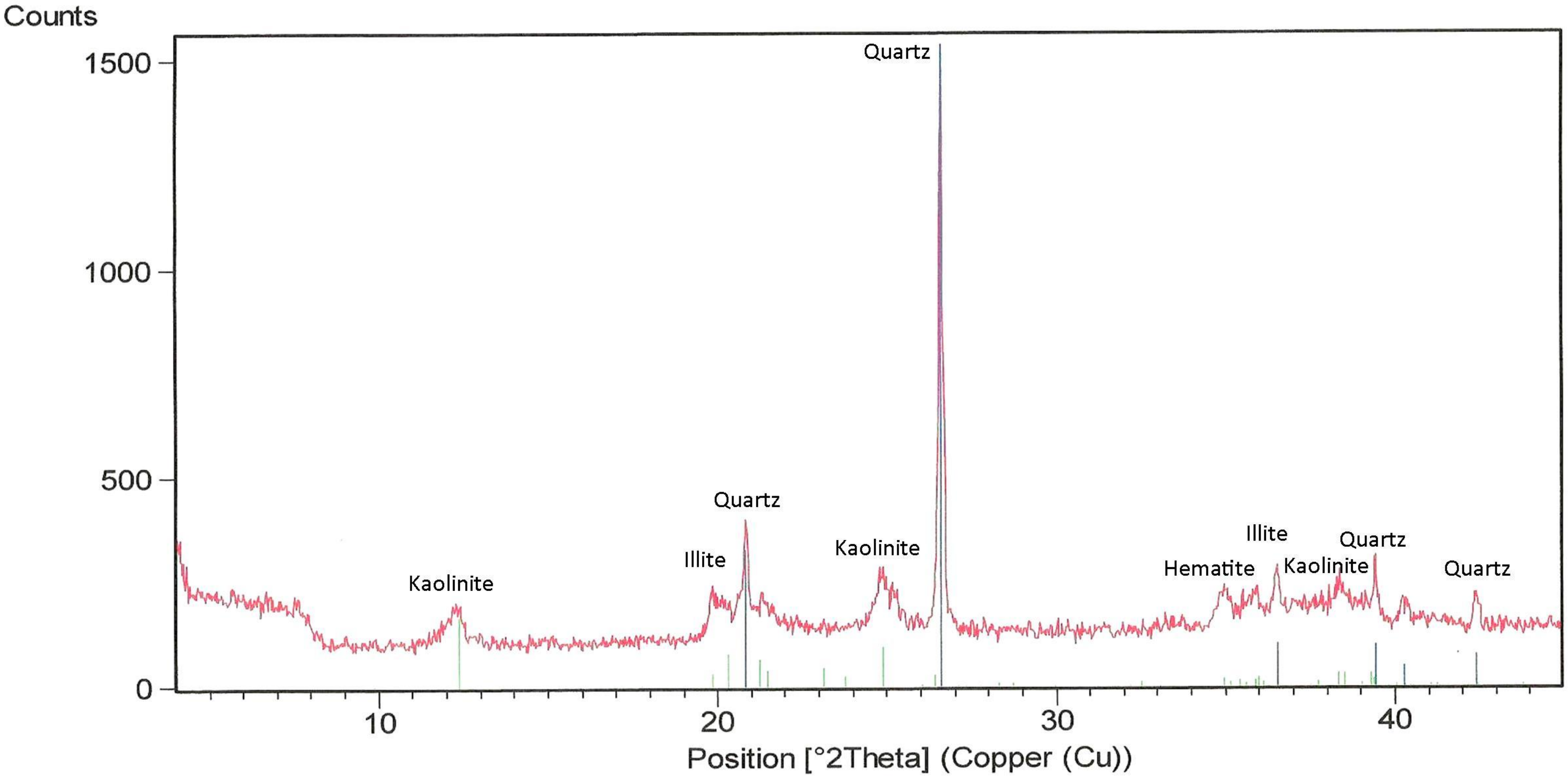

Figure 4. 4: X-ray diffraction patterns and modal composition of Ogiso sample 4

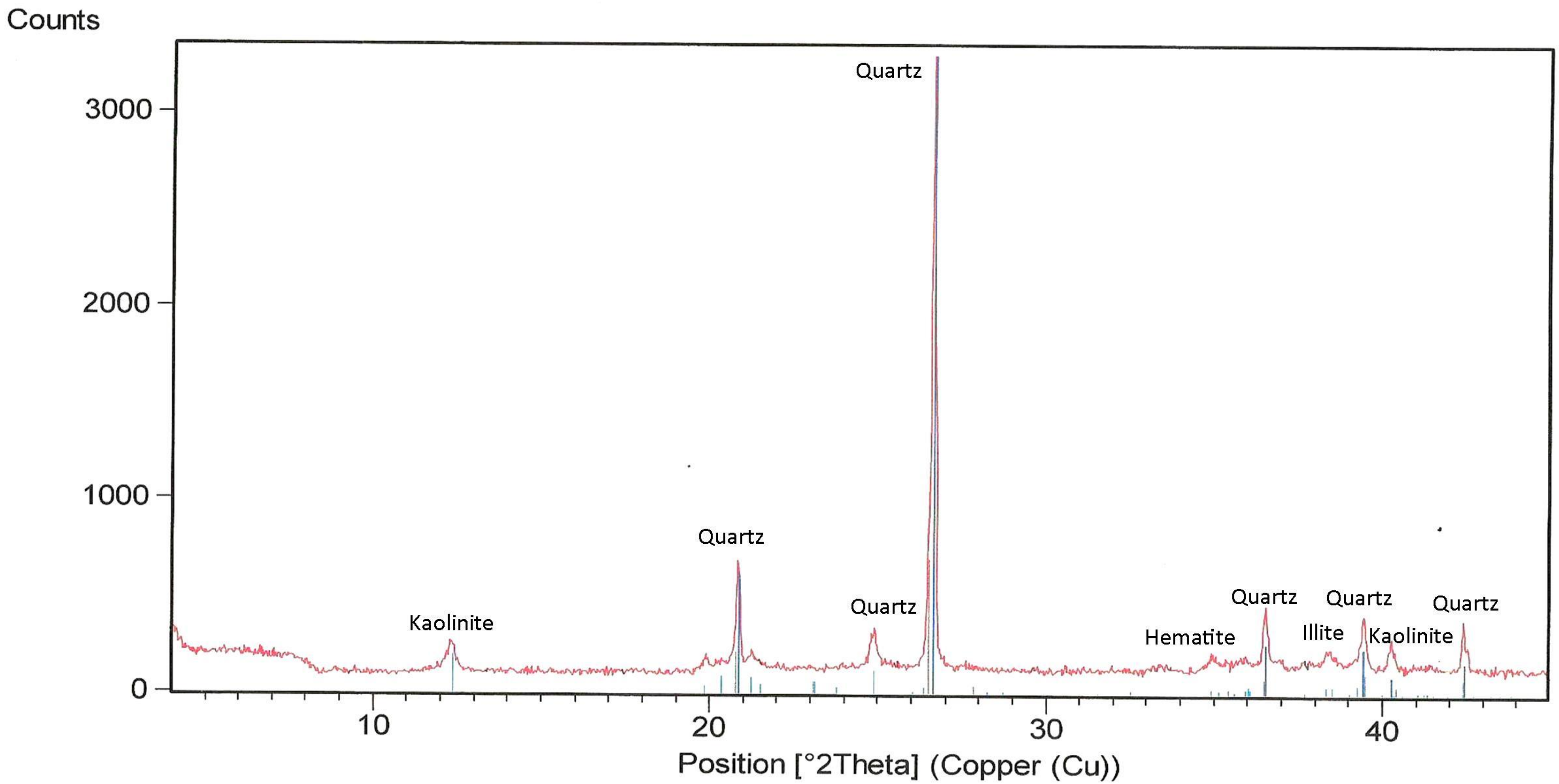

Figure 4. 5: X-ray diffraction patterns and modal composition of Ogiso sample 5

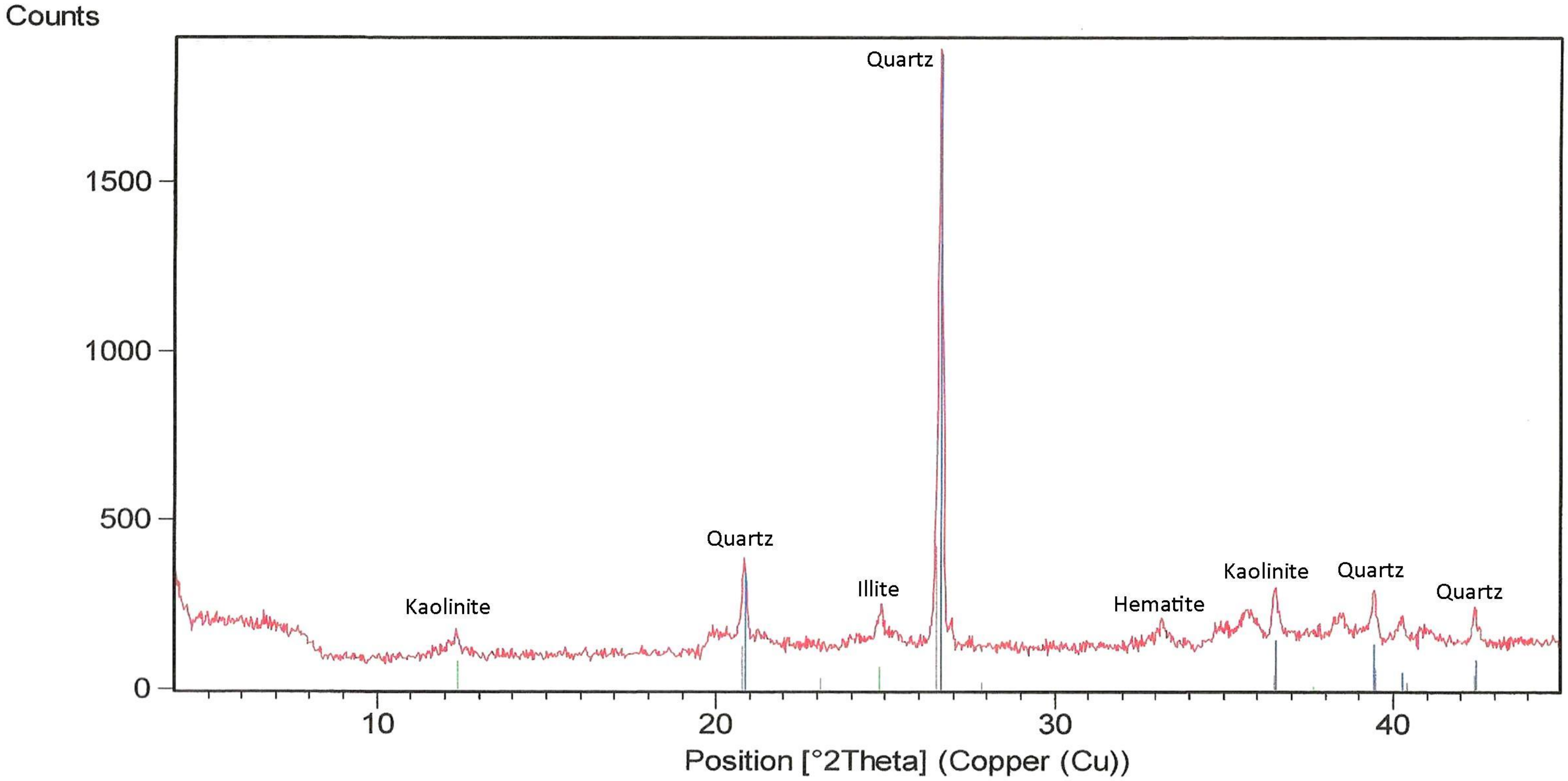

Figure 4. 6: X-ray diffraction patterns and modal composition of Ogiso sample 6

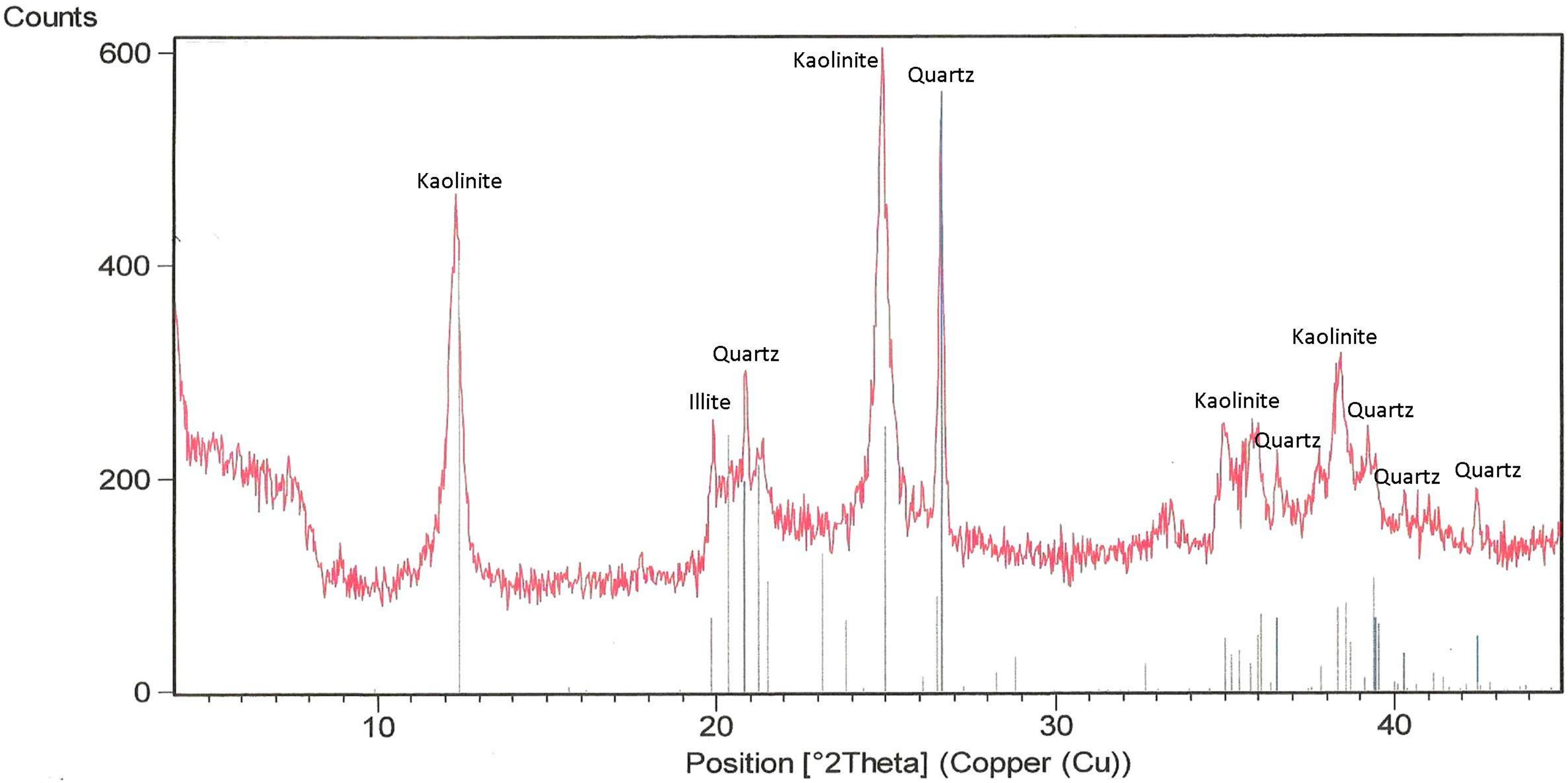

Figure 4. 7: X-ray diffraction patterns and modal composition of Ogiso sample 7

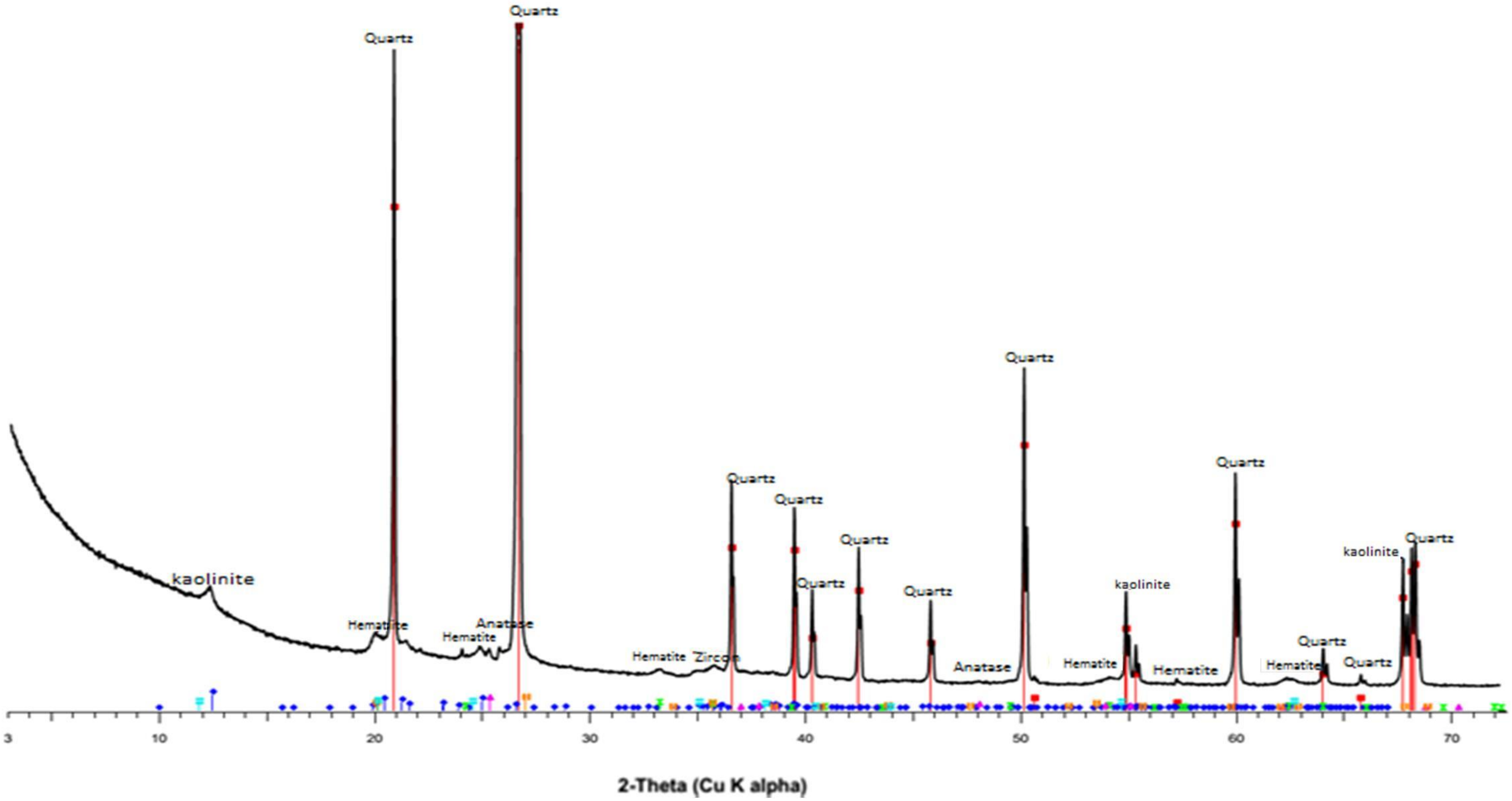

Figure 4. 8: X-ray diffraction patterns and modal composition of Okhoro sample 1

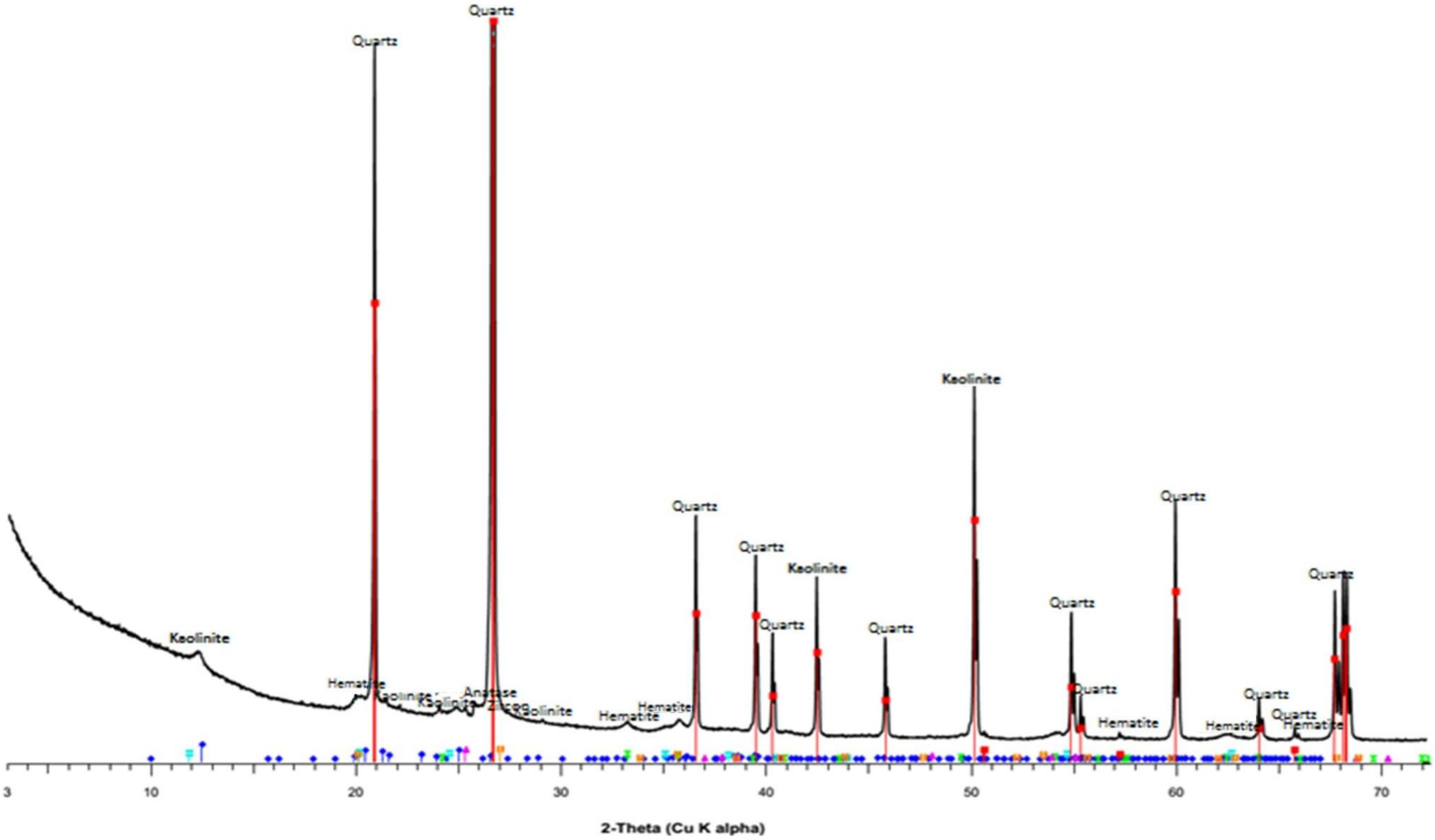

Figure 4. 9: X-ray diffraction patterns and modal composition of Okhoro sample 2

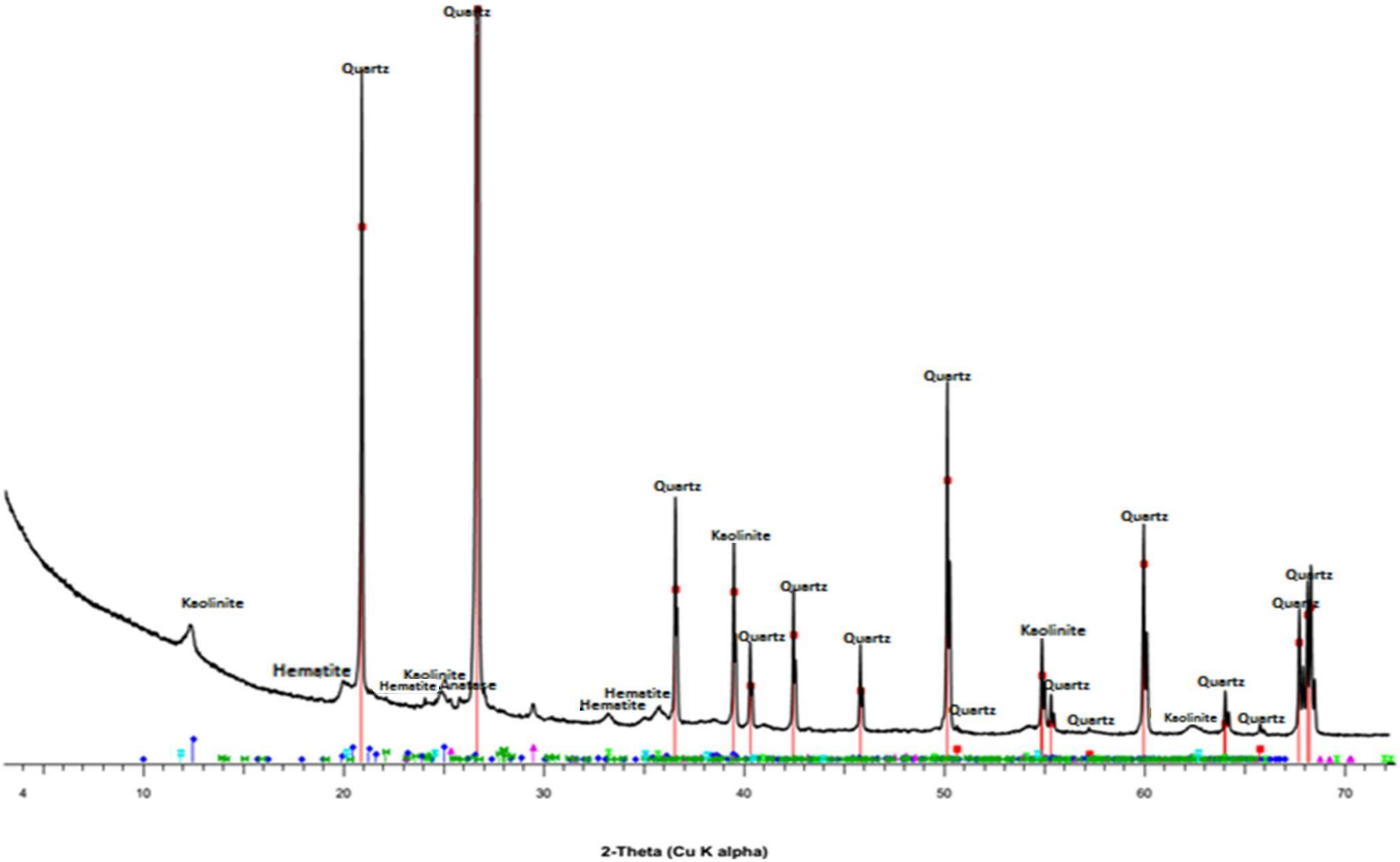

Figure 4. 10: X-ray diffraction patterns and modal composition of Okhoro sample 3

Table 4. 2: Chemical analysis of the clay sample (Elemental oxides in percentage)

ELEMENTAL OXIDES %	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	OG 7	OK 1	OK 2	OK 3
SiO_2	**55.82**	**61.41**	58.91	57.07	61.35	60.96	59.8	59.99	58.19	59.57
Al_2O_3	23.77	21.34	**24.42**	22.84	23.07	**21.13**	22.14	21.68	22.47	21.44
K_2O	0.08	0.16	0.03	0.09	0.09	0.08	0.14	0.08	0.24	0.09
Fe_2O_3	8.03	6.16	7.16	8.14	**6.05**	**9.06**	8.17	6.36	7.31	7.34
CaO	2.95	0.52	0.21	0.21	0.2	0.25	0.17	0.12	0.04	0.16
TiO_2	1.13	1.25	1.23	1.17	1.21	1.83	1.3	1.34	1.2	1.25
MgO	0.08	0.18	0.17	0.19	0.18	0.09	0.2	0.2	0.19	0.18
Na_2O	0.9	0.9	0.02	0.8	0.7	0.03	0.06	0.05	0.9	0.85
MnO	0.07	0.08	0.08	0.06	0.07	0.08	0.09	0.09	0.06	0.08
P_2O_5	0.05	0	0.05	0.04	0.05	0.04	0	0	0.05	0.05
LOI	7.1	8.04	7.8	9.42	6.95	6.5	8.02	9.92	9.11	8.77

Table 4. 3: Chemical analysis of the clay sample (Trace Element concentration in ppm)

Elemental Trace Element	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	OG 7	OKH 8	OKH 9	OKH 10
Sr	0.01	0.03	0.03	0.02	0.04	0.03	0.03	0.06	0.03	**0.07**
Ba	**0.04**	0.02	0.00	0.03	0.01	**0.04**	0.00	0.03	0.00	**0.04**
Cu	**1.39**	0.00	0.06	0.08	0.05	0.04	0.07	0.03	0.06	0.08
Ni	**0.03**	0.00	0.00	0.00	**0.03**	0.02	0.01	0.00	0.00	0.01
Pb	**0.02**	0.01	0.01	**0.02**	0.01	0.01	**0.02**	0.01	0.01	**0.02**
Co	0.01	**0.02**	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Cd	0.04	0.06	0.05	0.00	0.05	0.06	0.06	**0.07**	0.05	0.05
Zn	1.02	0.01	0.00	0.01	0.01	0.00	0.01	1.38	**1.51**	0.00
Cr	0.05	0.06	0.04	0.01	**0.11**	0.02	0.04	0.05	0.05	**0.11**
Zn	**1.02**	1.12	0.90	1.01	0.89	0.91	1.10	1.56	1.66	1.78

Table 4. 4: Comparison of the average chemical composition of the studied clays with average chemical composition of other types of clays

ELEMENTAL OXIDES	Ogiso	Okhoro	i	ii	iii	iv	v	vi
SiO_2	59.33	59.25	60.42	46.88	66	58.1	64.45	57.67
Al_2O_3	22.67	21.86	18.62	37.65	26.87	15.4	20.28	24
K_2O	0.10	0.14	1.33	1.06	-	3.24	0.42	0.5
Fe_2O_3	7.54	7.00	3.42	0.88	0.99	4.24	0.63	3.23
CaO	0.64	0.11	0.38	0.03	-	3.1	0.28	0.7
TiO_2	1.30	1.26	1.16	0.09	1.45		0.84	-
MgO	0.16	0.19	1.28	0.13	-	2.44	0.12	0.3
Na_2O	0.49	0.6	0.35	0.21	-	-	0.18	0.2
MnO	0.08	0.08	0.02	-	-	-	0.01	-
P_2O_5	0.03	0.03	0.03	-	-	-	-	-

(i) Okija Clay(Anambra state) Onyeobi *et al.*,(2013)
(ii) China Clay GTY (Huber,1985)
(iii) Kutigi Clay (Niger state) Akhirevbulu *et al.*,(2011)
(iv) Average Clay-shale(Pettijohn,1957) AVCS
(v) Iyuku Clay (Edo state) Onyeobi *et al.*,(2013)
(vi) Plastic fire Clay St Louis Huber, (1985) PFC

Table 4. 5: Major element oxides of the studied clays compared with chemical industrial specification

ELEMENTAL OXIDES	Ogiso	Okhoro	Refractory bricks (Parker 1967)	Rubber Keller, (1964)	Ceramics (Singer and Sonjai, 1964)	Brick clay (Murray 1960)	Paper (ANON,1972) As Coating and Fillers		Payne, 1961 Paint (additives)
SiO_2	59.33	59.25	51-70	44.9	67.5	38.67	47.8	48.7	48.68
AL_2O_3	22.67	21.86	25-44	32.35	26.5	9.45	37	36	9.45
$K_2 O$	0.10	0.14	-	0.28	1.10-3.10	2.76	1.1	2.12	2.76
$Fe_2 O_3$	7.54	7.00	0.5-2.40	0.43	0.5-1.20	2.7	0.58	0.82	2.7
CaO	0.64	0.11	0.1-0.2	Tr	0.18-0.30	15.84	0.04	0.06	15.84
Ti_2O	1.30	1.26	1.0-2.80	1.8	0.10-1.0	-	0.03	0.05	-
MgO	0.16	0.19	0.2-0.7	Tr	0.1-0.19	8.5	0.16	0.25	8.5
Na_2O	0.49	0.6	0.8-3.50	0.18	0.20-1.5	2.76	0.1	0.1	2.76
MnO	0.08	0.08	-	0.01	-	-	-	-	-
P_2O_5	0.03	0.03	-	-	-	-	-	-	-

Table 4. 6: Modal composition of clay minerals observed in the XRD results using peak area method, Carol (1971)

	OG1	OG2	OG3	OG4	OG5	OG6	OG7	OK1	OK2	OK3
Kaolinite	7.68	17.27	3.72	18.25	18.38	5.68	72.41	0.98	1.48	9.42
Hematite	2.49	3.77	0.53	2.68	2.94	2.62		0.16	1.48	1.45
Quartz	87.14	73.47	90.96	74.78	74.26	89.08	26.89	98.04	96.91	88.6
Illite	2.69	5.49	4.79	4.29	4.41	2.62	0.69			
Anatase								0.16		0.48
Zircon								0.33	0.12	
Total	100	100	100	100	99.99	100	99.99	99.67	99.99	99.95

Table 4. 7: Geotechnical Characteristics

Clay Samples	Natural Moisture Content %	Specific Gravity	Linear Shrinkage %	Swelling %
OG1	21.56	2.45	12.56	41.3
OG2	21.96	2.45	12.01	39.48
OG3	21.38	2.43	11.69	38.43
OG4	17.95	2.04	11.96	39.32
OG5	21.29	2.42	12.23	40.21
OG6	21.38	2.43	11.55	37.97
OG7	21.47	2.44	12.87	42.31
OK1	19.71	2.24	11.01	36.2
OK2	19.62	2.23	12.76	41.95
OK3	19.92	2.24	12.54	41.23

Table 4. 8: Sieve Analysis and Atterberg's Geotechnical Results

Clay samples	Clay size distribution			Atterberg's limit		
	Sand %	Silt %	Clay %	LL	PL	PI
OG1	50.24	31.75	18.01	56.99	20.62	36.37
OG2	44.11	34.78	21.11	47.21	15.76	31.45
OG3	43.11	35.41	21.48	53.99	20.19	33.8
OG4	41.66	36.33	22.01	55.99	14.98	41.01
OG5	46.75	28.95	24.3	52	14.11	37.89
OG6	36.19	42.8	21.01	56	20.85	35.15
OG7	45.51	33.89	20.6	52.99	21.5	31.49
OK1	49.77	27.13	23.1	56.97	15.48	41.49
OK2	47.33	30.55	22.12	62	20.62	41.38
OK3	49.44	27.66	22.9	59.99	13.73	46.26

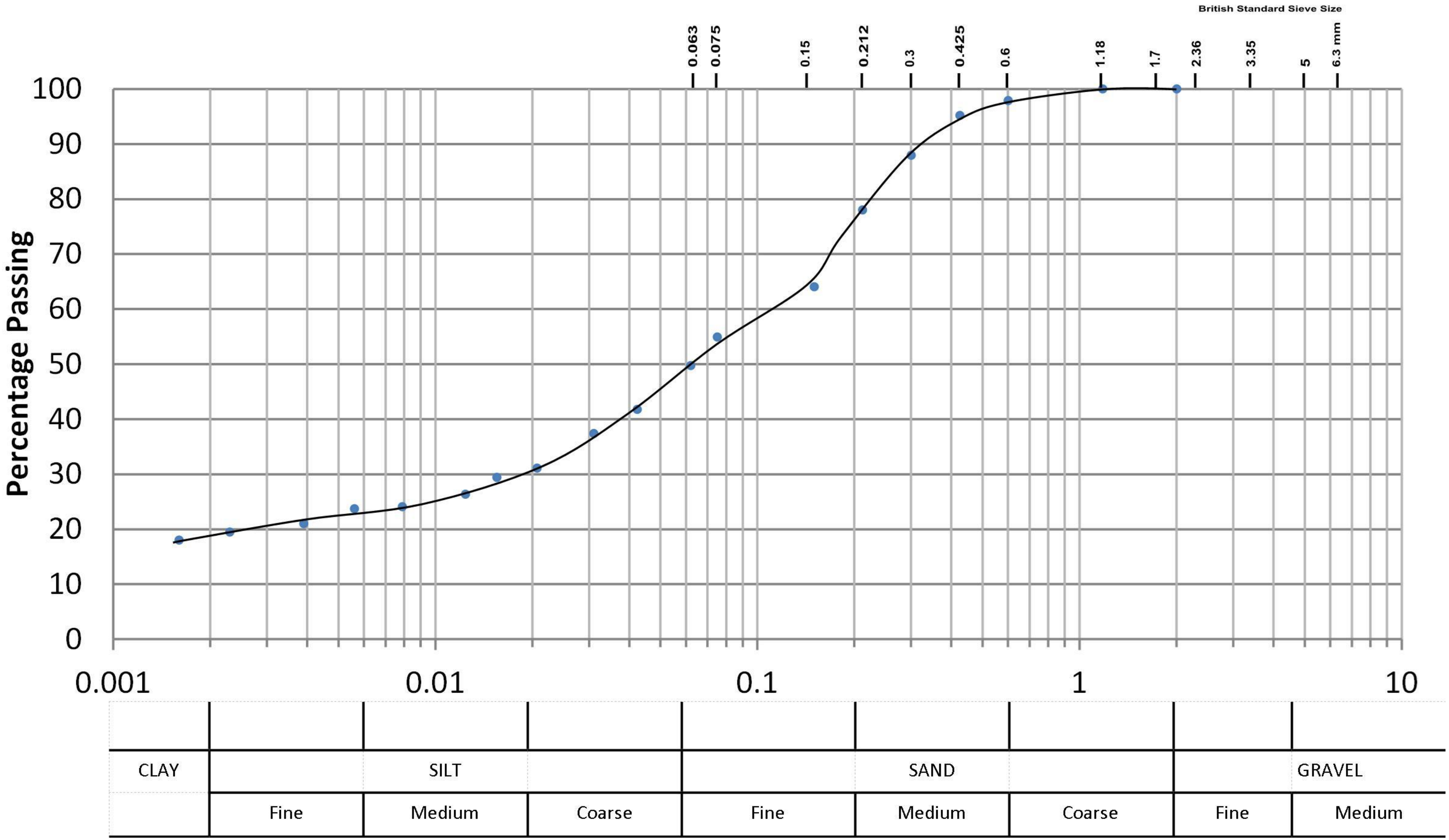

Figure 4. 11: Grainsize plot of Ogiso Sample 1

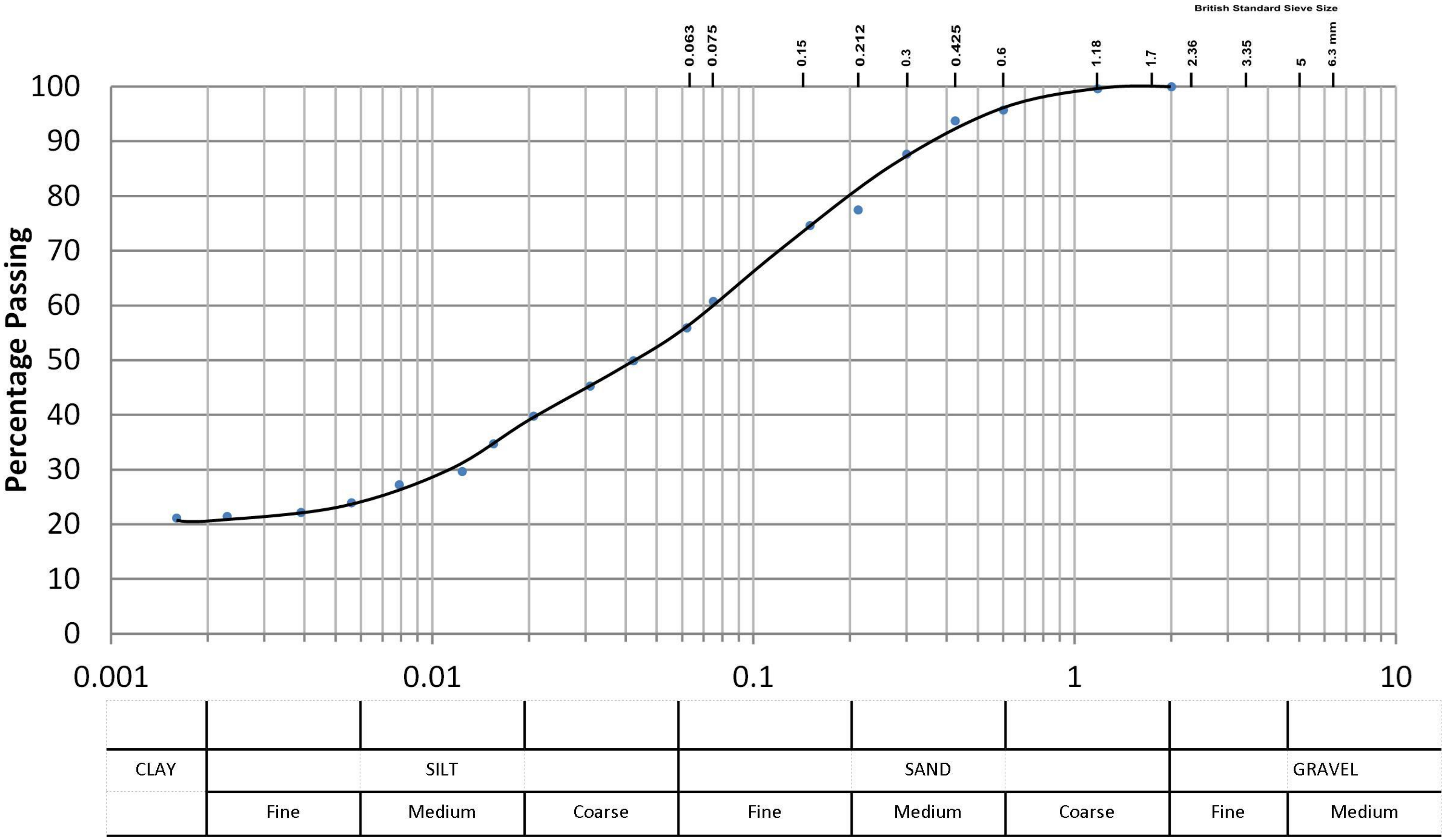

Figure 4. 12: Grainsize plot of Ogiso Sample 2

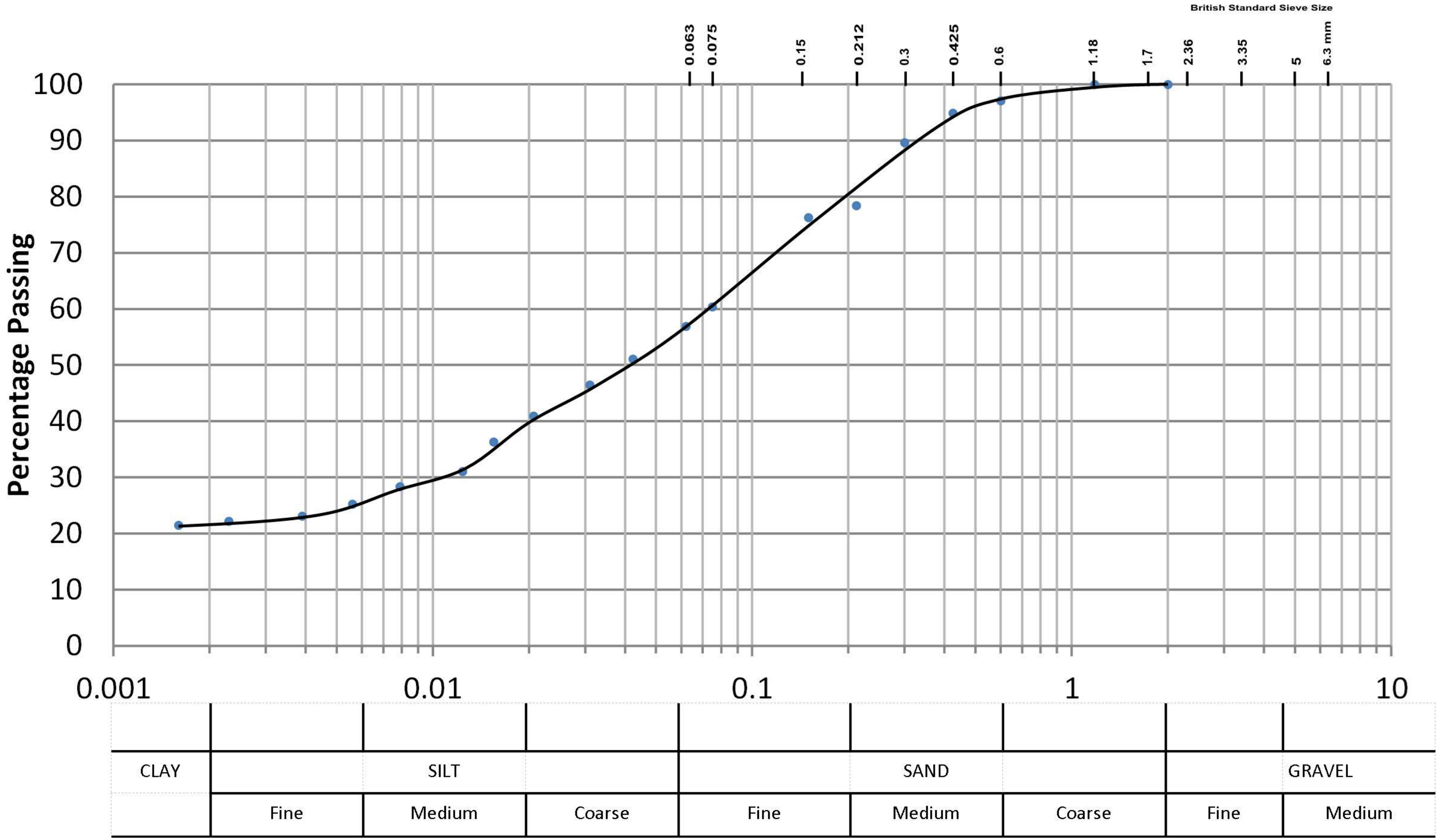

Figure 4. 13: Grainsize plot of Ogiso Sample 3

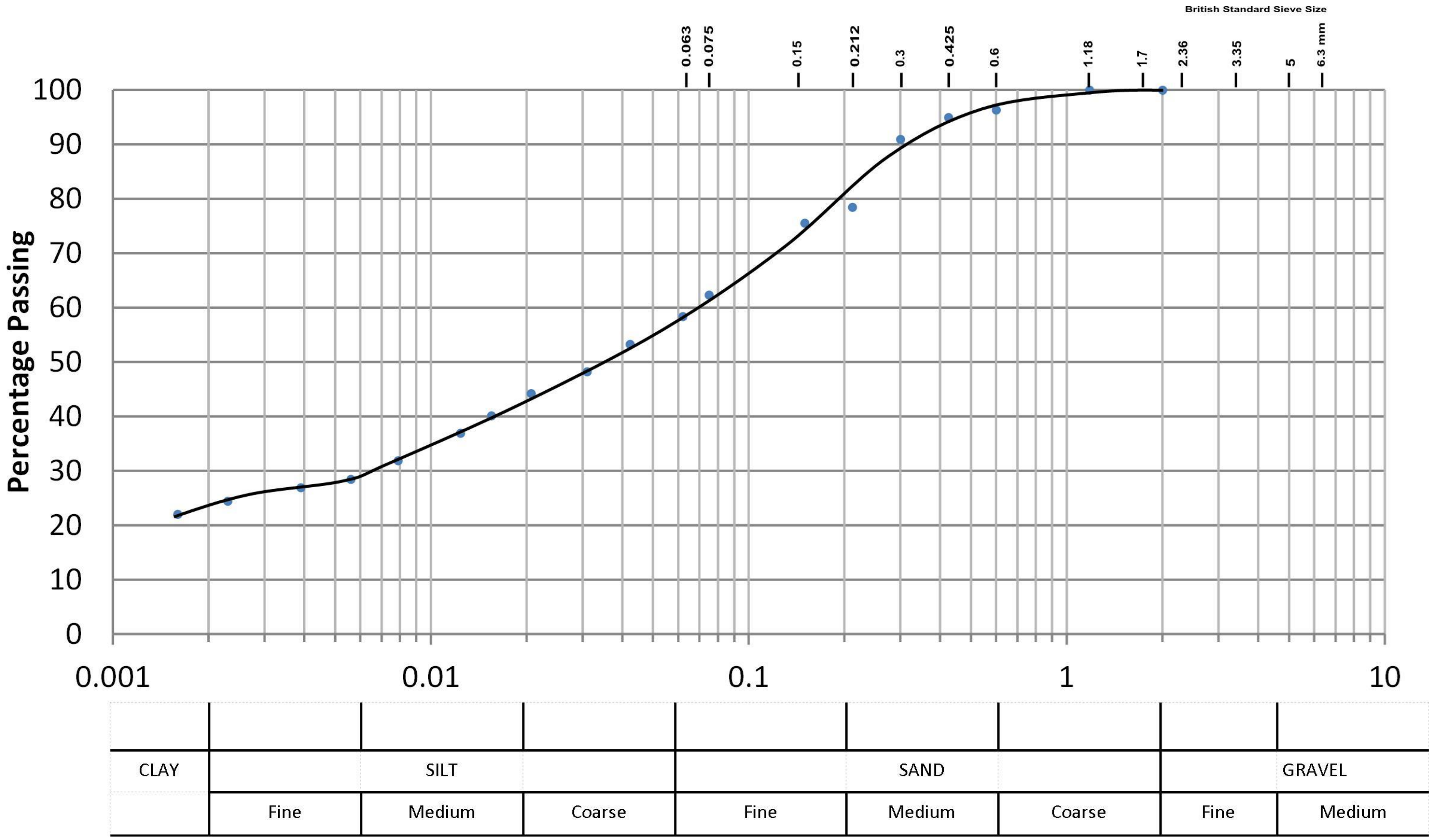

Figure 4. 14: Grainsize plot of Ogiso Sample 4

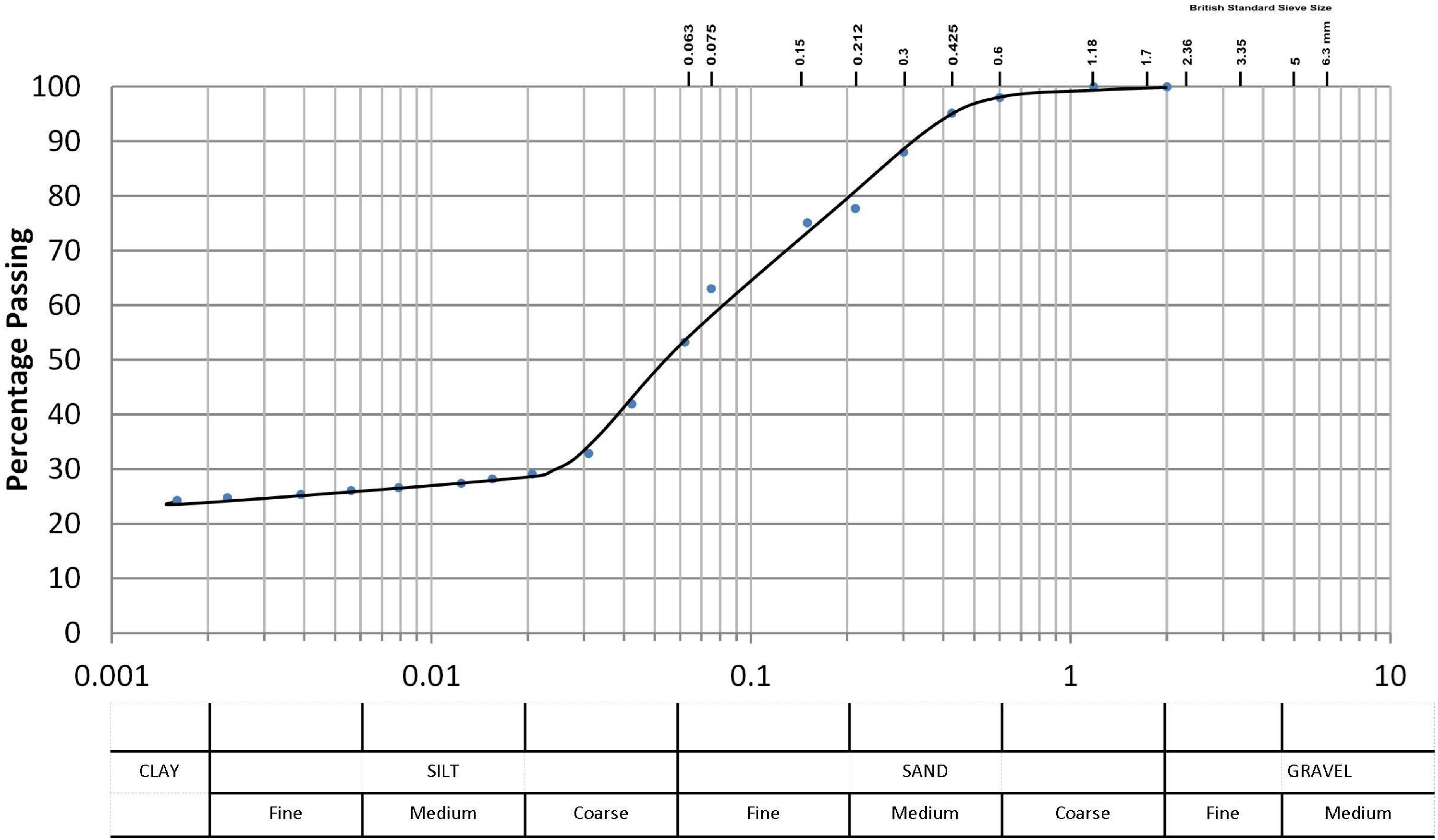

Figure 4. 15: Grainsize plot of Ogiso Sample 5

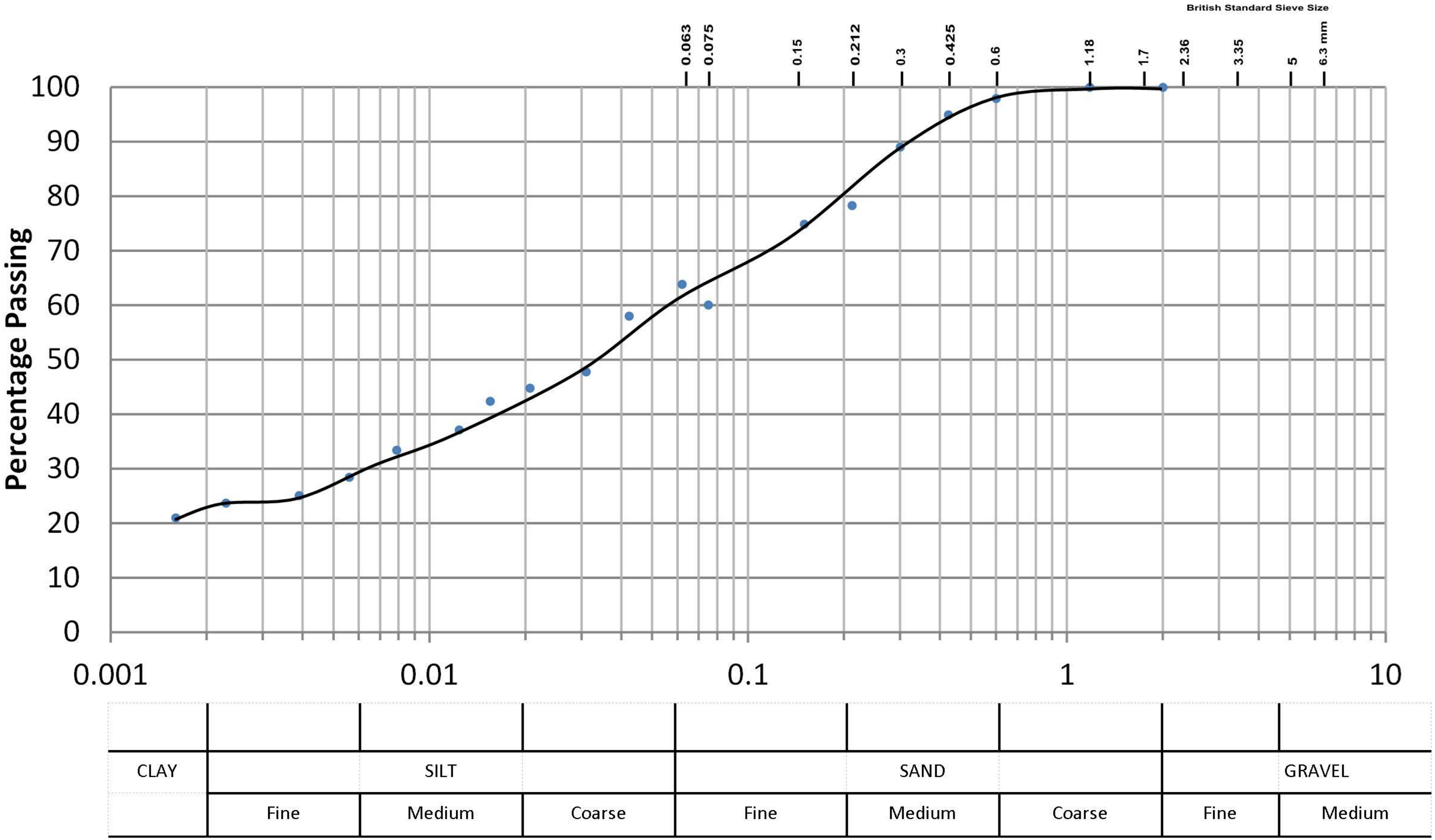

Figure 4. 16: Grainsize plot of Ogiso Sample 6

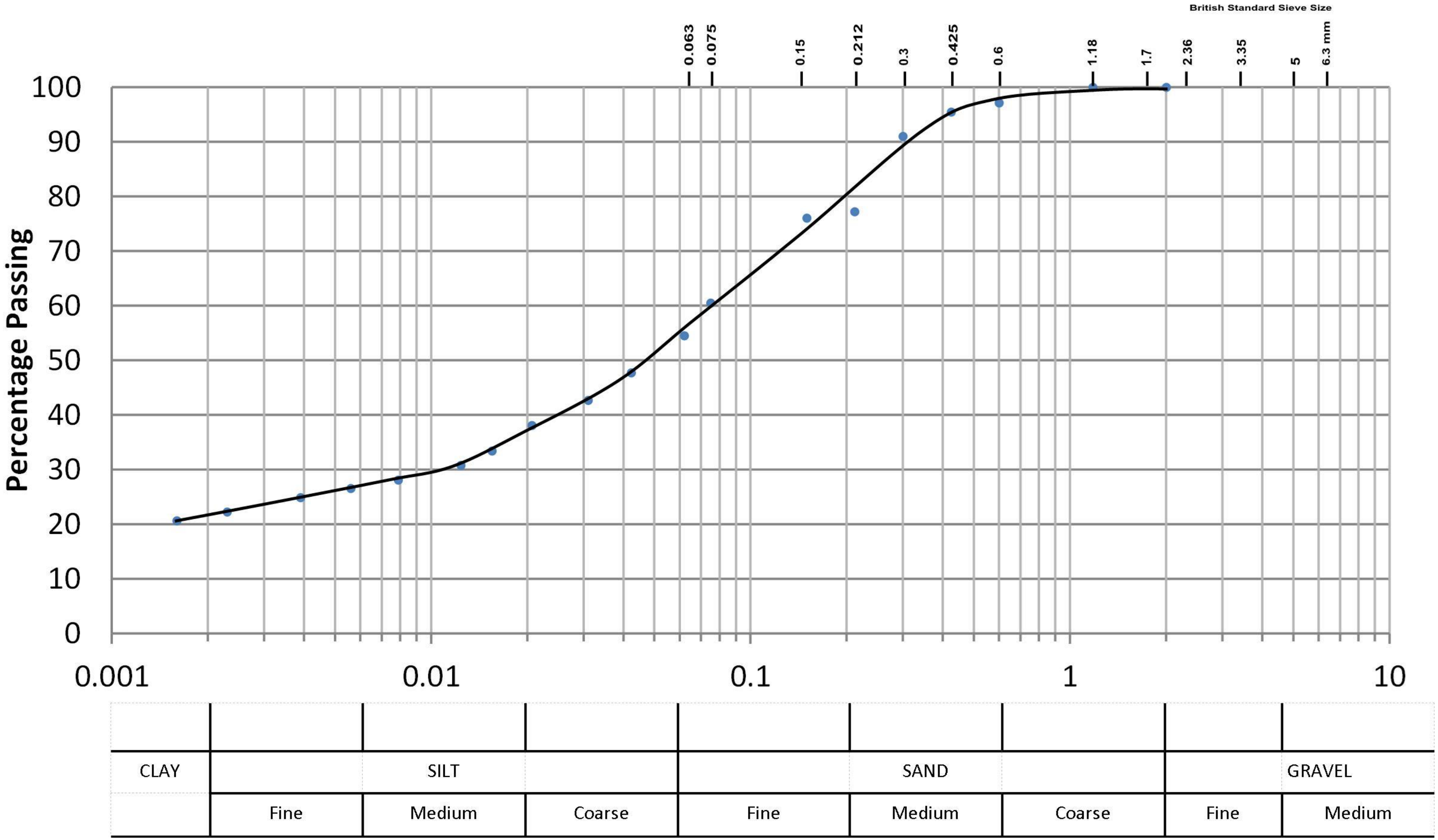

Figure 4. 17: Grainsize plot of Ogiso Sample 7

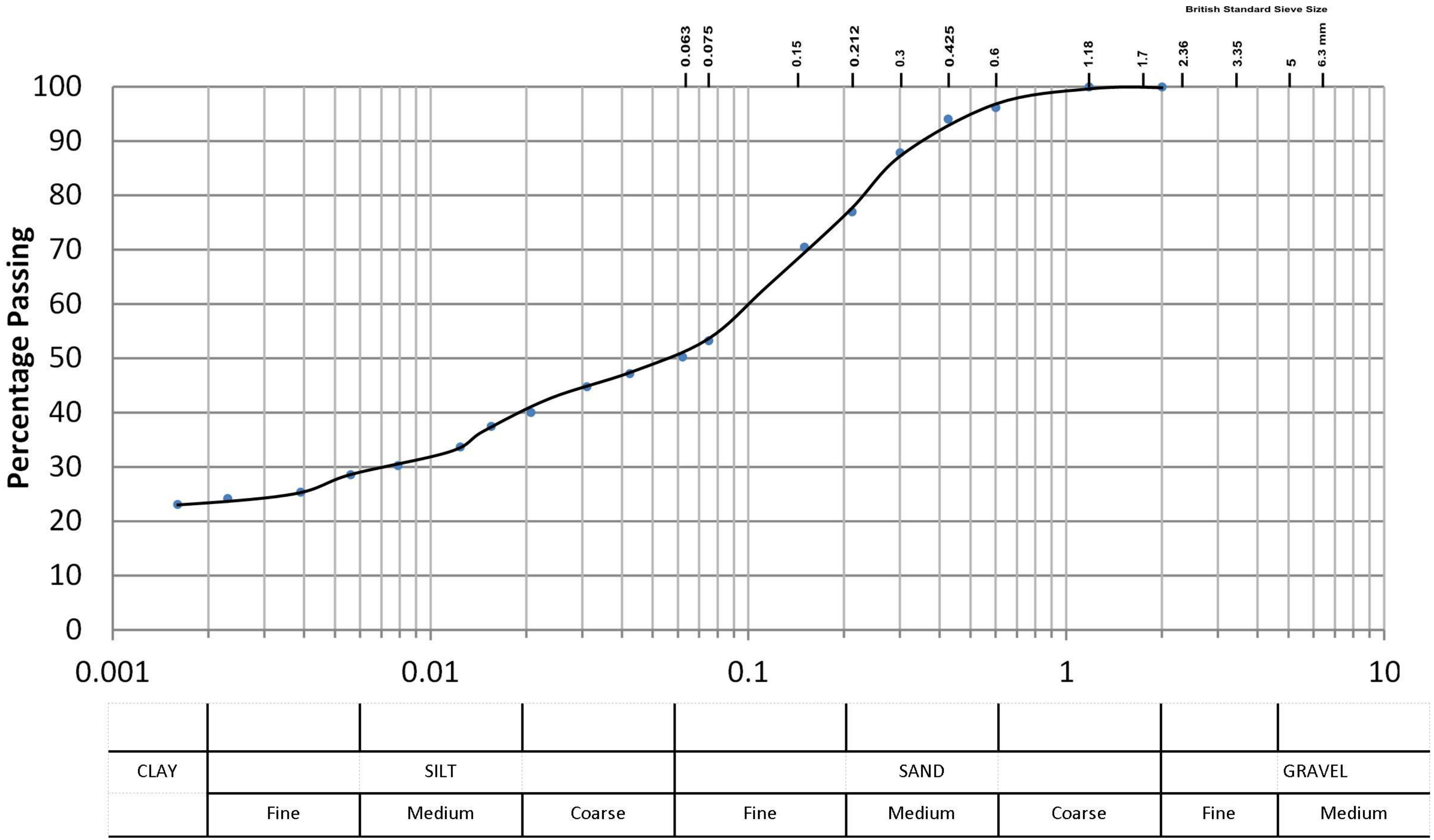

Figure 4. 18: Grainsize plot of Okhoro Sample 1

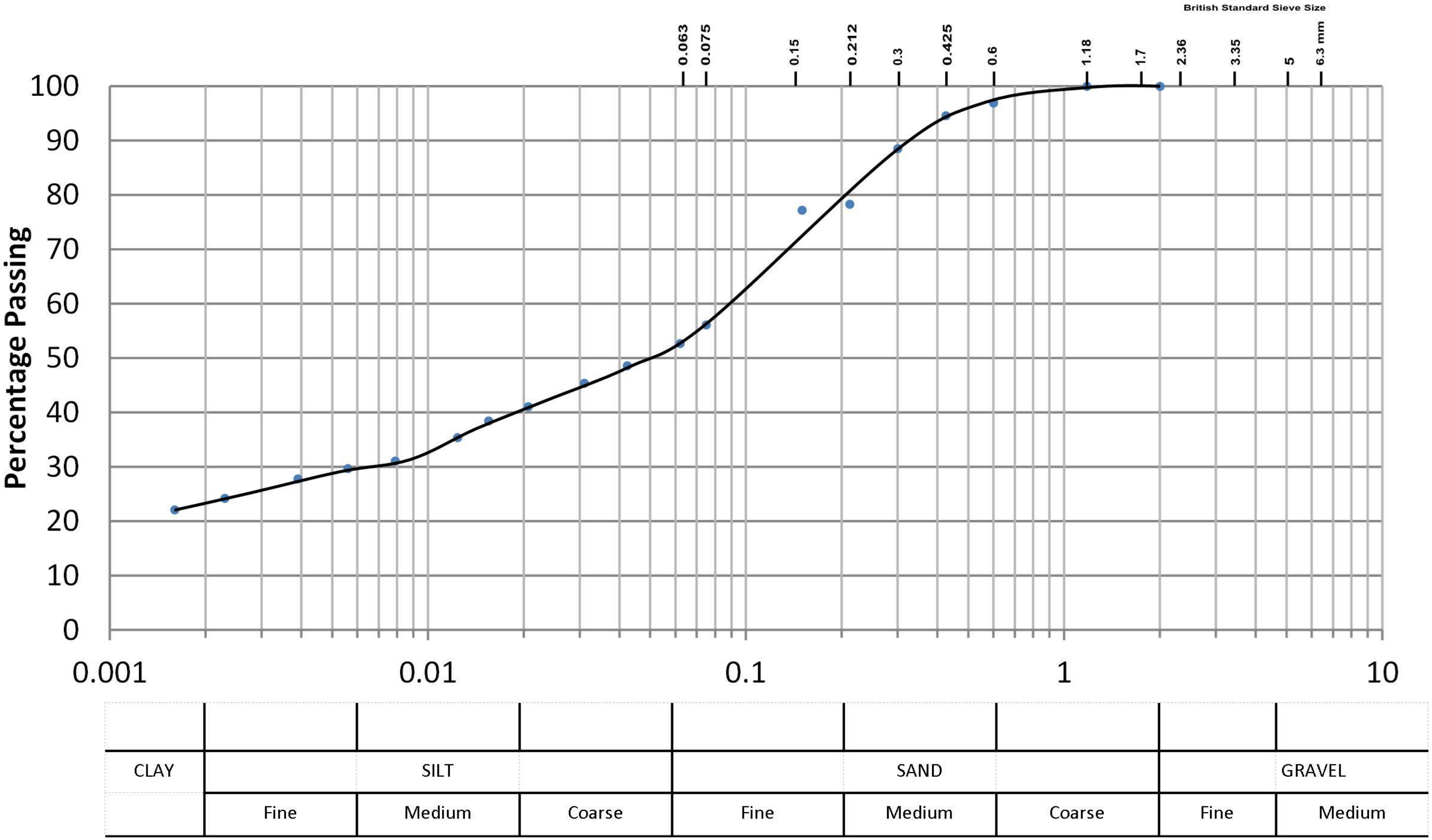

Figure 4. 19: Grainsize plot of Okhoro Sample 2

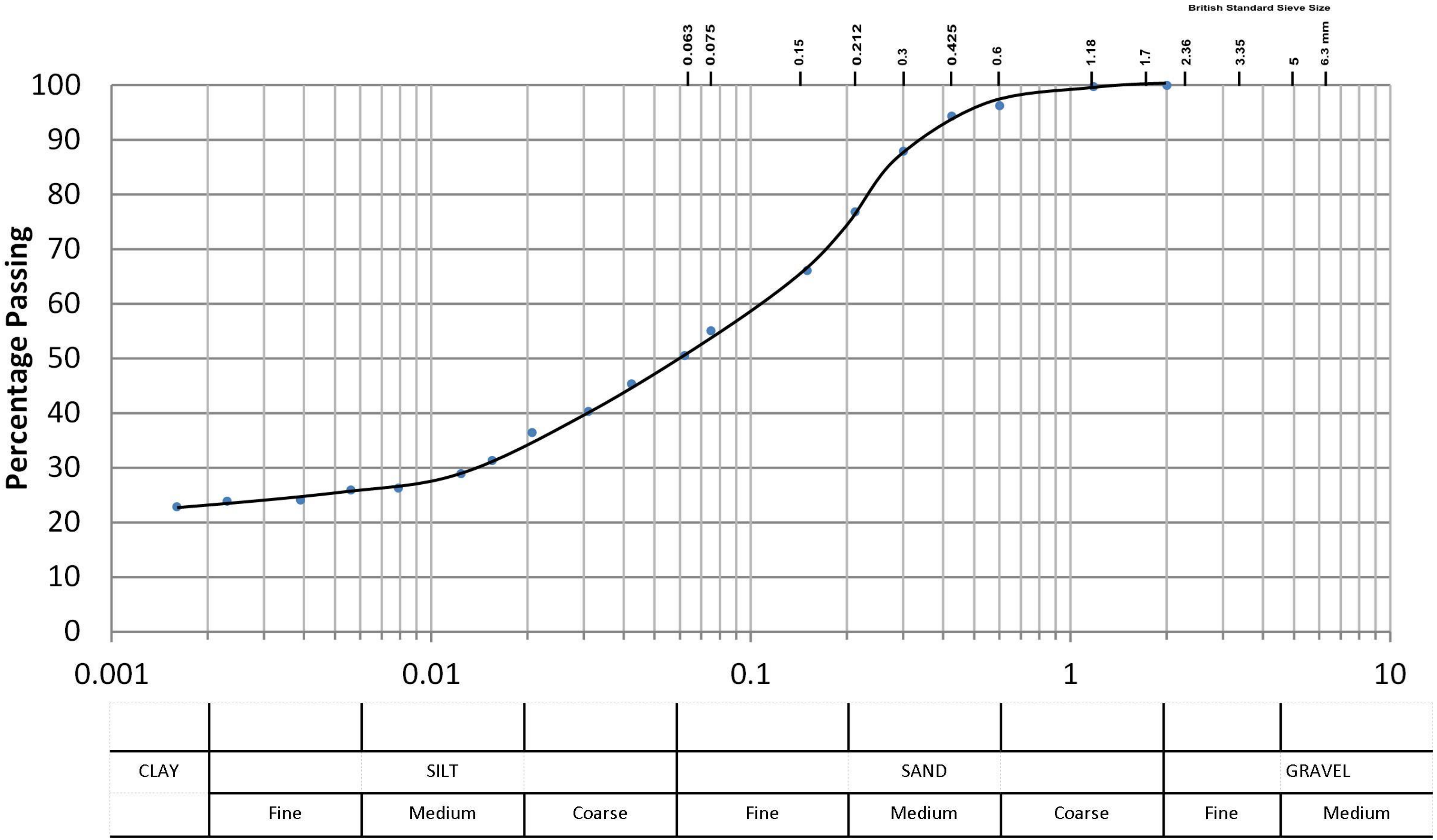

Figure 4. 20: Grainsize plot of Okhoro Sample 3

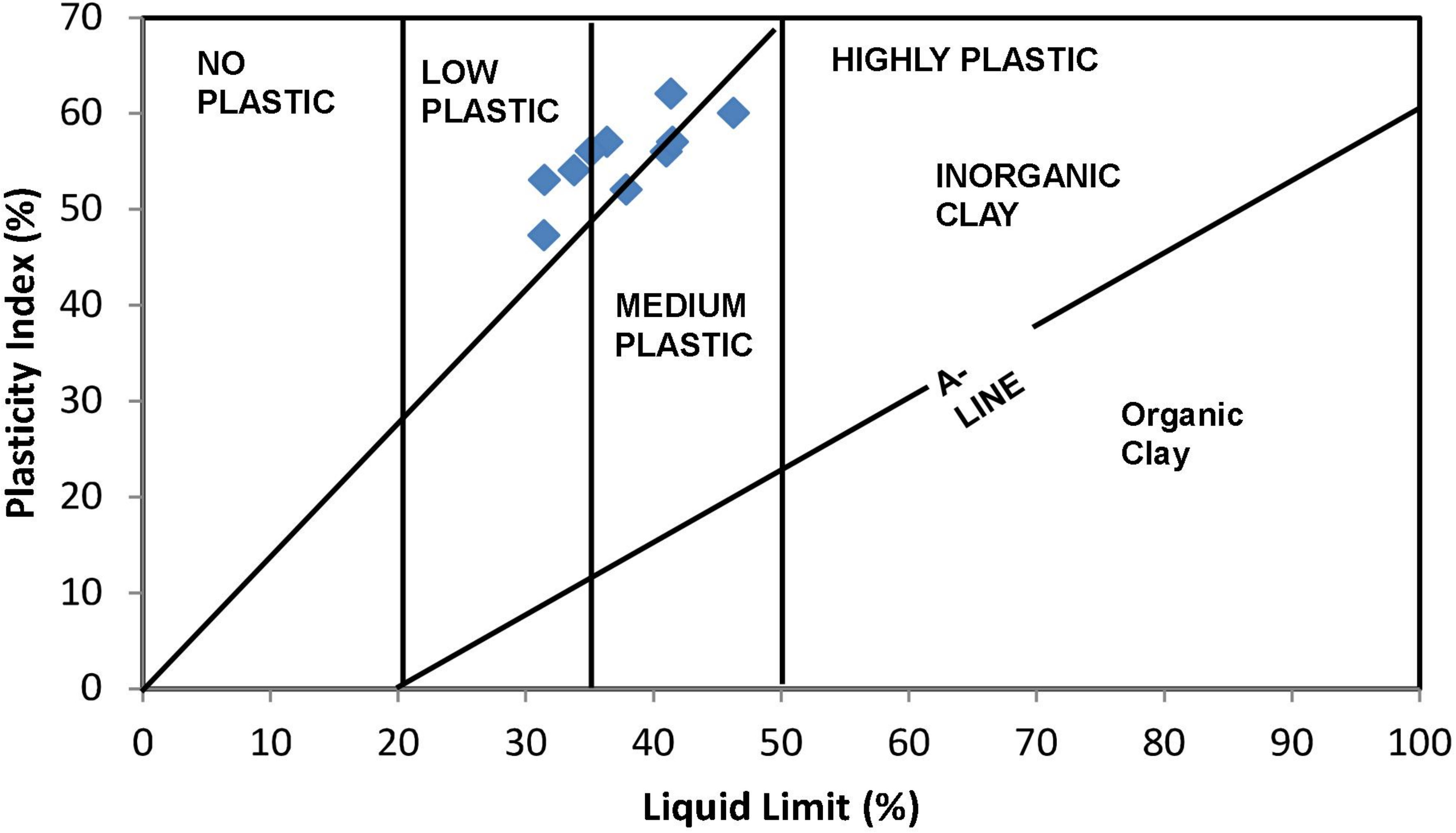

Figure 4. 21: Character of Clay samples on a typical Casagrande's Plot.

4.2 DISCUSSION OF RESULTS

4.2.1 GEO-CHEMICAL COMPOSITION

From the result obtained in table 4.1, it is evident that silica (which has the highest presence and constitute 55.82 to 63.46 %,), alumina (23.34 to 28.62 %) and iron oxides (5.03 to 9.06 %) dominate the soil's chemical composition. Others are in minor traces. When arranged in ascending order, the trend is silica>alumina>iron oxide.

4.2.2 MINERALOGICAL COMPOSITION

XRD Analysis result revealed the major minerals present to be Quarts, kaolinite and hematite. The presence of kaolinite as major clay minerals is found in all the soil samples studied and exists mainly as inorganic fractions (aluminum silicate hydroxide) as shown by the diffractograms presented in figures 4.1- 4.10.

4.2.3 GEOTECHNICAL COMPOSITION

Grains size analysis (Figure 4.11-4.20) show that the samples are predominantly clay while Atterberg's test (Figure 4.21) reveals low to medium plasticity which is typical of silt and clay. Moisture content and Specific gravity ranged from 17.95 – 21.96 % and 2.04 – 2.45 respectively. Linear Shrinkage and Swelling ranged from 11.01 – 12.87 and 36.2 – 42.31 respectively. The swelling and linear shrinkage implies that the samples may not be a useful material in the construction of roads, embankment and dams.

Below is a ternary diagram of Sio$_2$ Al$_2$O$_3$ and fe$_2$O$_3$ by schellman 1986. The results of the samples from the study area were plotted and its shows that the samples tends towards Sio$_2$ indicating that they became more richer in Sio$_2$ and less in Al$_2$O$_3$ and fe$_2$O$_3$ which are the major elemental composition of linearization. This shows that the chemical weathering were not prolong hence weak laterization.

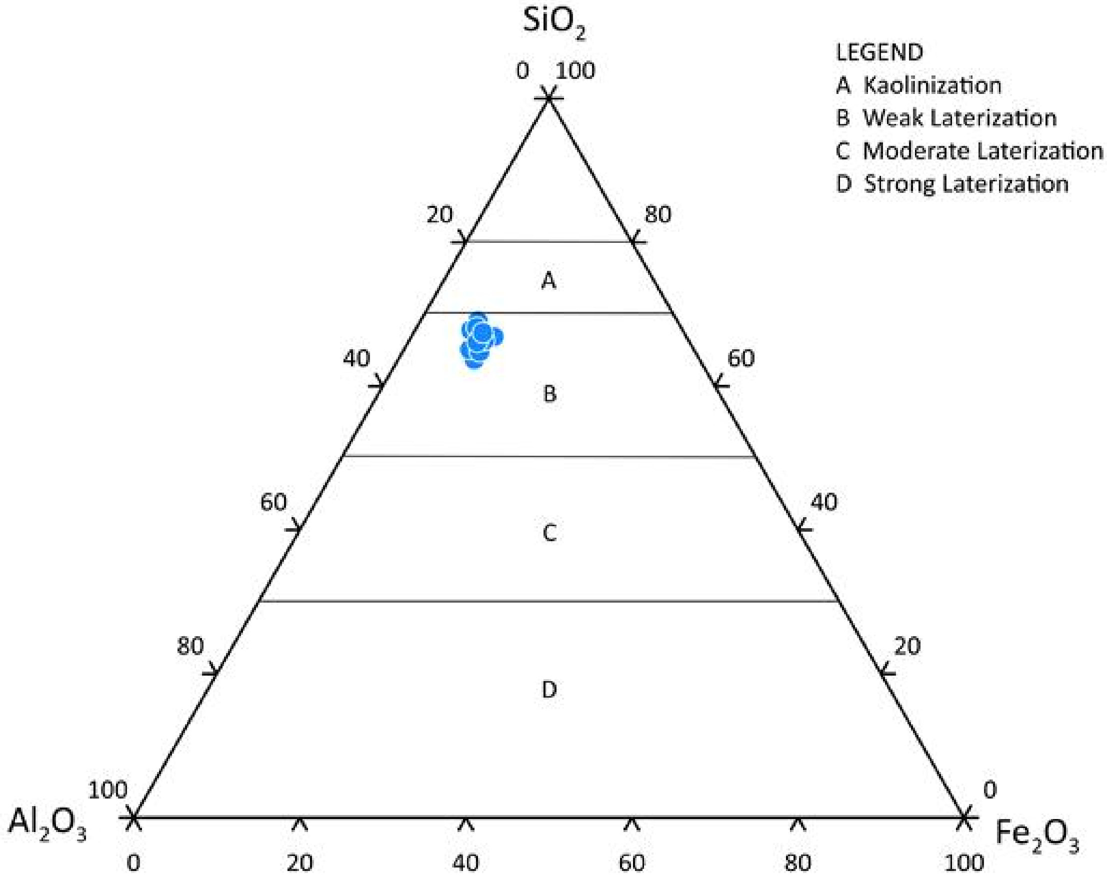

Figure 4. 22: Ternary diagram of SiO_2-Al_2O_3-Fe_2O_3 (After Schellmann, 1986) for samples from the study area.

According to the Al_2O_3–Fe_2O_3–SiO_2 ternary diagram of Schellmann (1986), the Clay samples generally define a trend with gradual change from Al_2O_3-rich to SiO_2-rich compositions (Figure 4.22). The samples indicate that the Clay deposits were products of weak lateritization.

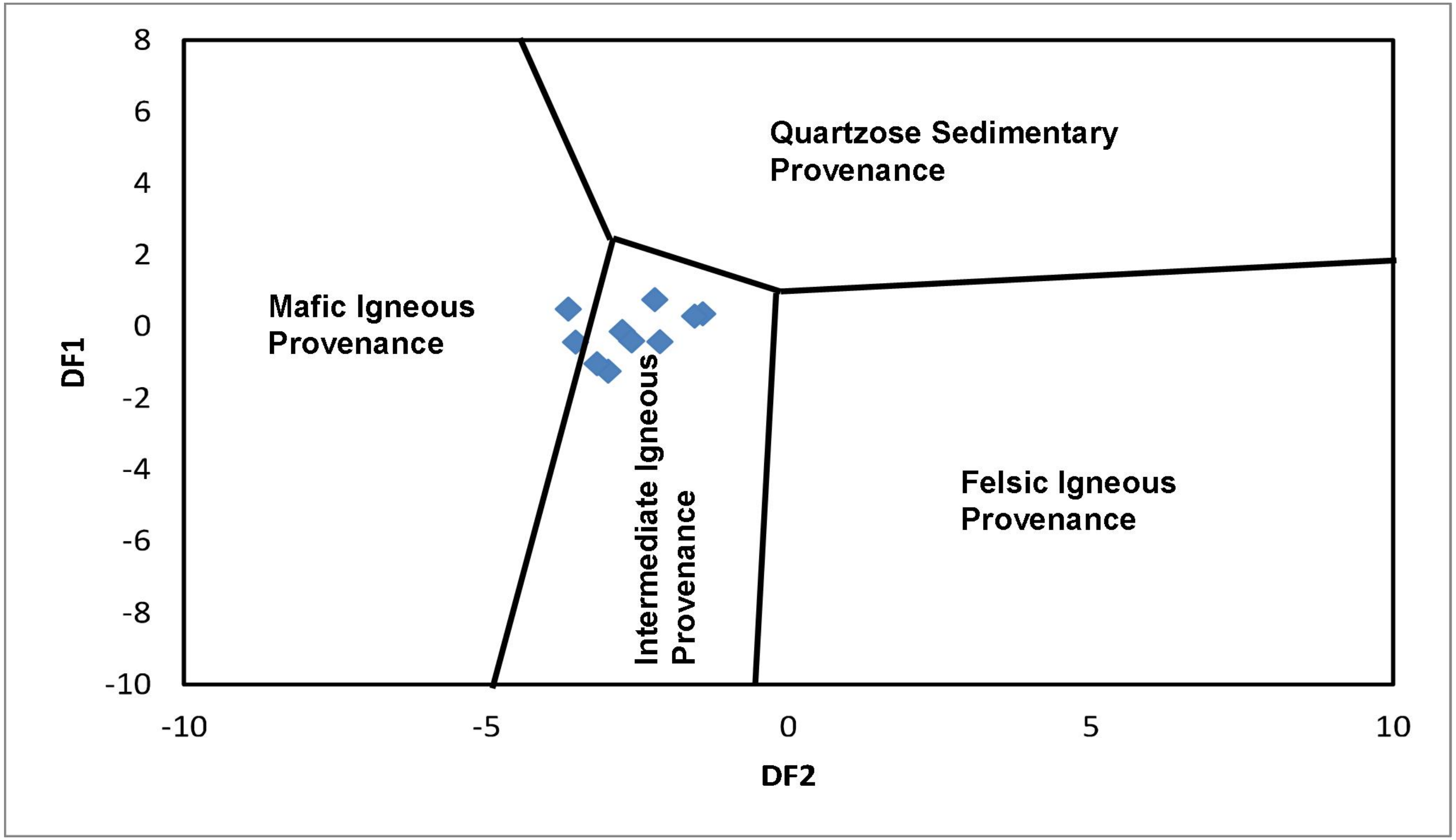

Figure 4. 23: Discriminant Diagram for Sedimentary provenance of study area (after Roser and Korsch, 1988). DFI = (56.50TiO_2 – 10.879Fe_2O_3(total) + 30.875MgO – 5.404Na_2O + 11.112K_2O)/Al_2O_3 – 3.89. DF2 = (30.638TiO_2 – 12.541Fe_2O_3 (total) + 7.32MgO + 12.031Na_2O + 35.402K_2O)/Al_2O_3 – 6.382.

The discriminant plot (Figure 4.23) shows that the samples plot mainly in the intermediate igneous province field. This characteristics indicate that the original source area was both felsic and mafic and the negative anomaly is regarded as evidence for a differentiated source, similar to granite (McLennan, 1989; Taylor and McLennan, 1985, 1995)

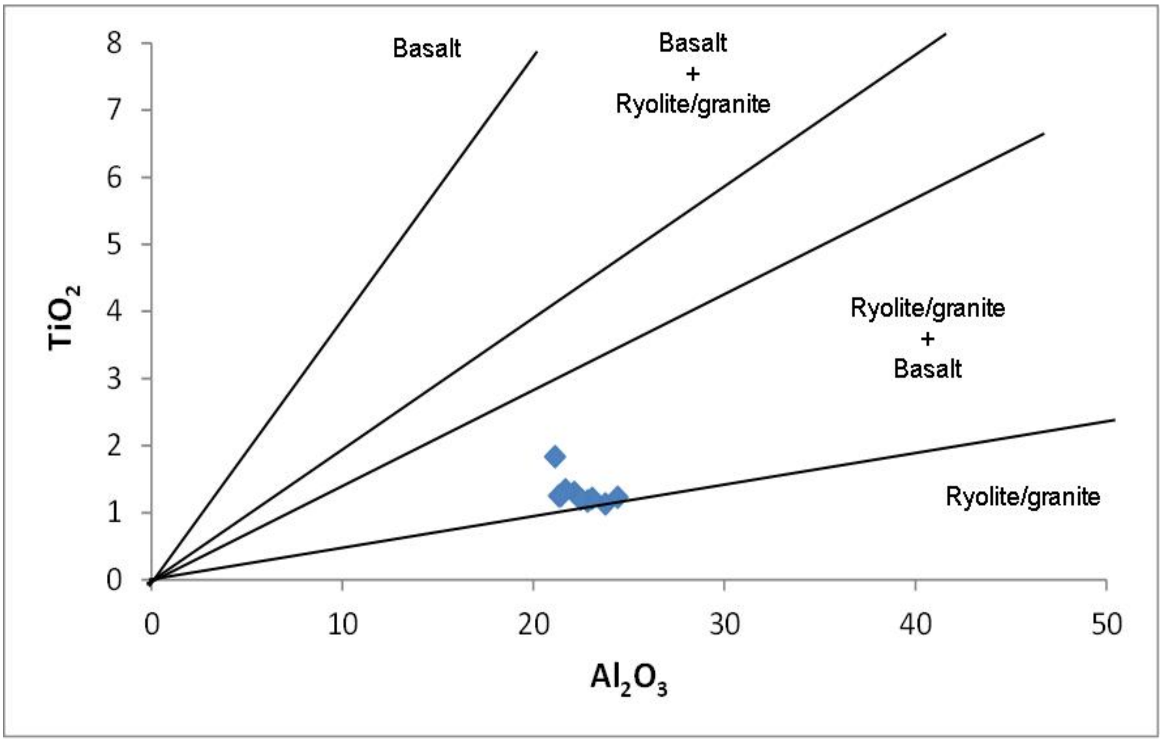

Figure 4. 25: Position of Clay deposit samples from the study area on TiO_2/Al_2O_3 binary diagram suggested by Ekosse, 2001. He suggested that the ration of TiO_2/Al_2O_3 as a province indicator. From the figure above, the plot indicates provenance of materials from predominantly granite-rhyolite.

Ekosse, 2001 suggested that the ration of TiO_2/Al_2O_3 as a province indicator. From the figure above, the plot indicates provenance of materials from predominantly granite-rhyolite.

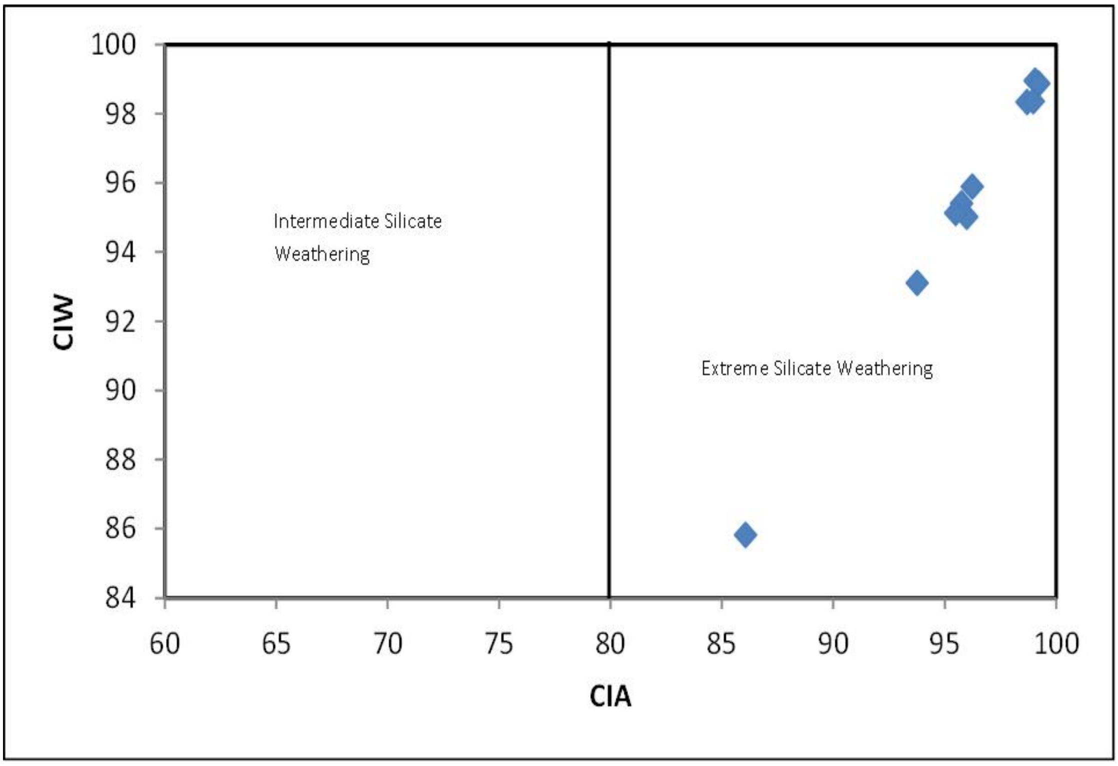

Figure 4. 26: X-ray diffraction patterns and modal composition of Okhoro sample 3 After Nesbitt *et al*., 1982

The Chemical Index of Alteration (CIA) is based on the assumption that the dominant process during chemical weathering is the degradation of feldspar and the formation of clay minerals. Values of CIA (85.81–98.95) and CIW (Chemical Index of Weathering) (86.06–99.22) of the clays sample suggest extreme silicate weathering (Figure 4.26). The values are also indicative of low to depleted oxides particularly those of K, Ca, and Na in the soils. CIW = $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O)]*100$ while CIA = $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]*100$.

The modal below was used to compare with the chemical composition of commercial kaolins and ball clays after plotting the result from the clay samples in the study area, its shows that the clay sample falls within the commercial ball clays section. Which further suggest that the chemical composition of the sample is similar with that of commercial ball clay. Hence the clay samples can be used industrially for the production of ceramics.

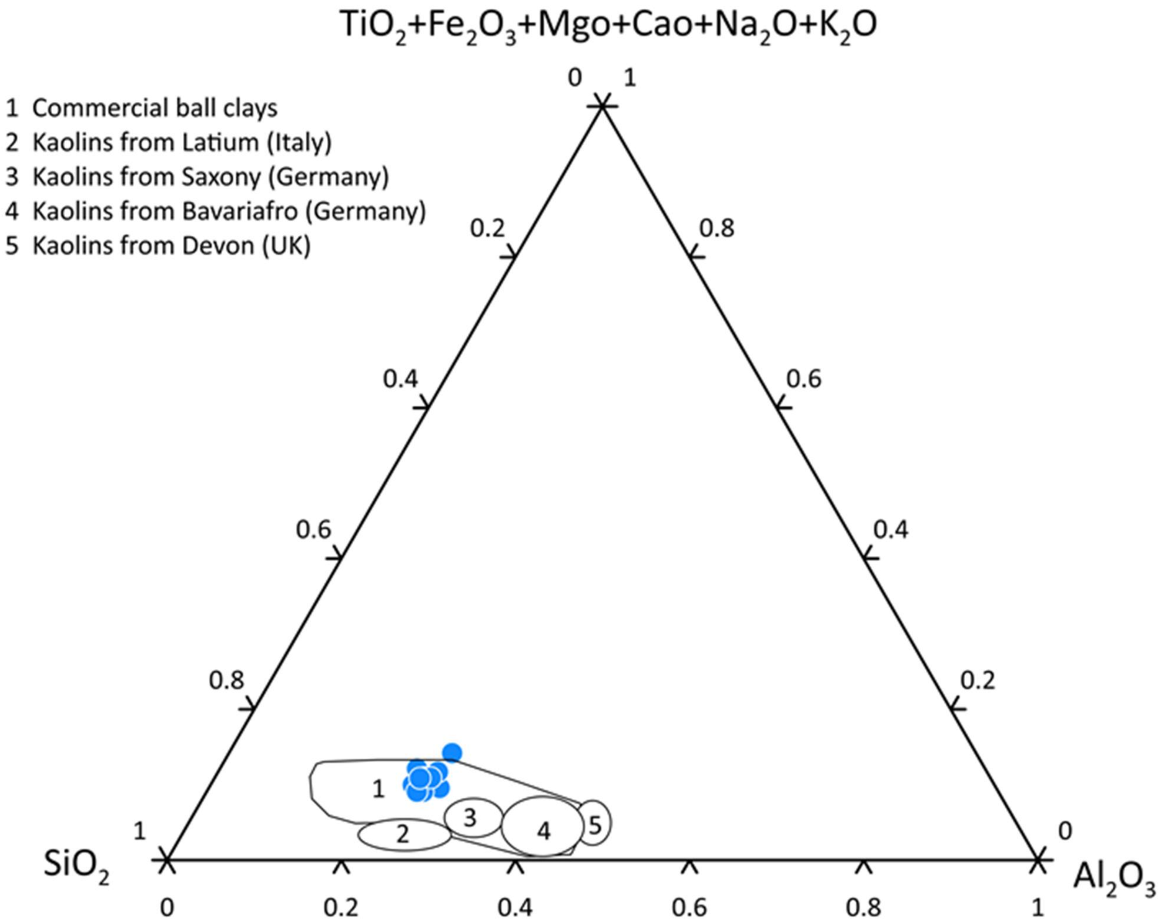

Figure 4. 27: Ternary diagram SiO_2-Al_2O_3-Other oxides of the Clay samples and comparison with the chemical composition of commercial kaolins (Ligas *et al.*, 1997) and ball clays (after Fabbri and Fiori, 1985)

Clay samples from the study area fall within the section 1 which are Commercial ball clays.

The ternary diagram below shows the major composition of Kaolin $Al_2H_4O_9Si_2$ which is Aluminum and Silical from the plot of the samples it's shows that its tends towards Alimina and Silica.

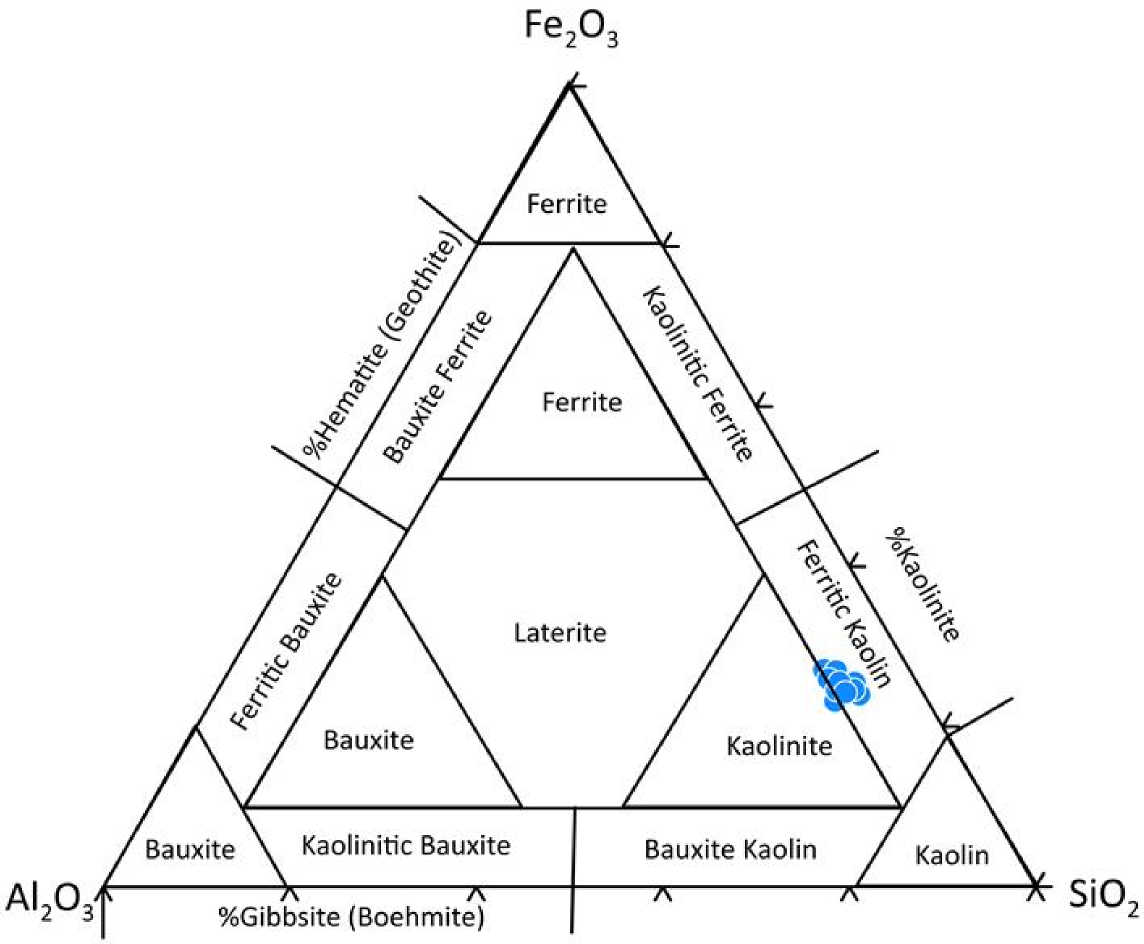

Figure 4. 28: Ternary diagram SiO_2-Al_2O_3-Fe_2O_3 (After Aleva, 1994) For Clay samples in the study area.

Figure 4.28 shows that clay samples from the study area are majorly Kaolinite.

The most dominant clay mineral in the samples is kaolinite and halloysite, which is regarded as a hydrated kaolinite phase (Weaver and Pollard, 1973). They both have the same theoretical SiO_2/Al_2O_3 ratio but with higher water content in the halloysite (Huang, 1975). It occurs mostly in association with kaolinite, sepiolite and montmorillonite. While kaolinite and halloysite occurred in association in most of the samples, there is a lower concentration of the kaolinite in some of the samples because of the hydrous nature of the clay minerals (Brindly and Brown, 1980). From the percentage composition of the minerals in the clays, the kaolinite and halloysite composition ranged between 13% and about 65% of the minerals in the samples. The other clay mineral components were mainly montmorillonite of 10% to about 30%, mignisite up to about 16% in some of the samples, illite up to about 15%, Sepiolite, which is a hydrous magnesium silicate, was also present in all the samples up to about 10% of the samples analysed, indicating an enrichment of magnesium oxide in the parent material. Quartz content in the samples was up to 25% in some samples.

Elemental analysis of the clay samples showed major and minor oxides of varying composition. The major oxides found in the samples analyzed include SiO_2, Al_2O_3, K_2O, Fe_2O_3, MgO, Ni_2O, and CaO. SiO_2 had the highest composition in the samples with an average percentage composition of about 63%. Al_2O_3 had an average composition of about 28%. The composition of Fe_2O_3 in the samples may be due to leaching and oxidation of iron rich materials within the sampled areas especially from the river sources around the area. Iron may occur in both the octahedral and tetrahedral sheets of 1:1 and 2:1 clay minerals, and, iron can also exist as a compensating ion on the clay mineral exchange complex (Diamant *et al.,* 1982). The other oxides in the samples occurred in minor and trace concentrations.

Montmorillonite found in some samples, may have indicated a marine and lacustrine environment of formation. Its 'swelling' nature gives it a high applicability in many industries. Antigorite requires that there be a deficiency of octahedral cations and anions with respect to the tetrahedral sheet, which may indicate its low concentration in the samples because of the tetrahedral: octahedral relationship of the other major clay minerals in the samples. The presence and abundance of the quartz minerals in the samples may be due to the abundance of silica in residual soils or due to contamination of the samples by surface sediments either by erosional processes or during sample collection.

From Table 4.2, major elemental oxides found in the samples from both locations showed that Silica content was highest at OG 2 and lowest at OG 1, Alumina oxide was highest at OG 3 and lowest at OG 6, while Iron oxide has highest content in OG 6 and lowest at OG 5, as shown by the bold values in the table.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

A detailed mineralogical, geochemical and geotechnical properties of Ogiso and Okhoro clay deposits shows that they are predominantly kaolinitic with variable amount of quartz, hematite and traces of zircon , illite , anatase were observe.

Geochemically, SiO2 Al203 and Fe203 were the predominant oxides with some trace element such as zircon, zinc and copper.

The geotechnical analysis review the clays are of low to medium plasticity with percentage of fine fractions.

Provenance shows that the samples are predominant granite rhyolite and intermediate igneous provenance. Further analysis shows that the clays samples suggest extreme silicate weathering.

Comparison of the clay sample characteristics with industrial specification shows that the clay samples can be used as commercial ball clays and can be used for other purpose if beneficiation and processing are carried out.

5.2 RECOMMENDATIONS

The cluster value of the deposits should be ascertain to know the quantity so that registered miners can explore for industrial and commercial benefits.

Also the clay deposits in the study areas should undergo processing and beneficiation to make them useful for other industrial purposes.

REFERENCES

Adegoke, O.S. (1979). Eocene Stratigraphy of Southern Nigeria.Mem.BRGMW69 pp 23-49.

Adeleye, D. R. and Parker, A. (1975). Diagnostic value of clay minerals in Upper Cretaceous sediments of South-Eastern Nigeria. Jour. West African Science Association, Vol.20, pp. 47-52.

Adeleye, D. R., and Dessauvagie, T. F. J. (1972). Stratigraphy of the Niger Embayment near Bida, Nigeria. *In*: Africa Geol. T. F. J. Press, (1970), pp.181-186.

Aderibigbe, D. A. and Chukwuogo, C. E. B. (1984). Potential of some Nigeria Clay Deposits as Refractory Materials for Steel Industry. Conf. Proc. Nig. Soc. of Engineers, pp. 129-145.

Ajayi, J. O., and Agagu, O. K. (1981). Mineralogy of primary clay deposits in the Basement Complex of Nigeria. Jour. of Mining and Geology, 18(1), 27-30.

Ajibade, A. C. and Fitches W. R. (1988).The Nigerian Precambrian and the Pan-African Orogeny, Precambrian Geology of Nigeria, pp.45-53.

Akujieze, C. N. (2004). Effects of Anthropogenic Activities (Sand Quarrying and Waste Disposal) on Urban Groundwater System and Aquifer Vulnerability Assessment in Benin City, Edo State, Nigeria. PhD Thesis, University of Benin, Benin City, Nigeria.

Aleva, (1994). Concentrations of Useful Elements and Residual Mineralization Indices in the Weathering Products Derived from Mineralized Rocks in Meïganga (Central Cameroon). *Journal of Geosciences and Geomatics*. 2019; 7(3):112-133. doi: 10.12691/jgg-7-3-3.

Allege, T. S., Idakwo, S. O. and Gideon, Y. B. (2014). Geology, Mineralogy and Geochemistry of Clay Occurrence within the Northern Anambra Basin, Nigeria. British Journal of Applied Science and Technology 4 (5); 841-852.

Allege, T. S., Idakwo., S. O. and Gideon, Y. B., Alege, K. E. (2013). Paleoclimate Reconstruction during Mamu Formations (Cretaceous) Based on Clay Mineral Distribution in Northern Anambra Basin, Nigeria. International Journal of Science and Technology, Vol.12, pp 879-885.

Anonymous, (1955). Kaolin Clay’s and their industrial Uses, J.M. Huber Corp., New York.

Anonymous, (1972). Kaolin the UK, English China clay deposits on its lead in world paper. Industrial Minerals, 53, pp 9-15.

Avbovbo, A. A. (1978). Tertiary lithostratigraphy of Niger Delta. American Association of Petroleum Geologists Bulletin, Tulsa, Oklahoma, pp 96-200.

Barshard, I. (1966). The Effect of Variation in Precipitation on the Nature of Clay Mineral Formation in Soils from Acid and Basic Igneous Rocks.Proc.Int. Clay Conf. (Jerusalem), 1, 167-173.

Brindley, G. W. and Brown, G. (1980). Crystal Structures of Clay Minerals and Their X-Ray Identification. Mineralogical Society, London, Monograph No. 5 pp. 495.

Brindley, G. W. and Kurtossy, S. S. (1961). Quantitative determination of Kaolinite by X-ray diffraction. Am. Min., 46, 1208-1215.

British Standards Institution – BS 1377 (1990). Methods of Tests for soils for civil engineering purposes.

Brown, G. (1951). The X-Ray Identification and Crystal Structures of Clay Minerals. Min. Soc. London, pp. 489-516.

Carrol, D. (1971). Clay minerals: A guide to their X-ray identification. Geol. Soc. Am. Special paper 126.

Cassagrande, (1932). Researches on the Atterberg limit of soils public roads, newyork, 13 (8): pp 121-136.

Chen, F. H. (1975). Foundations on expansive soils. Amsterdam, Oxford, New York: Elsevier Scientific Pub. Com.

Clews, F. H (1969). Heavy Clay Technology. 2nd Edition. New York: Academic press.

Coker, S.A.,(1986). The Mineralogy and Geochemistry of Two Clay Deposits from Southern Nigeria. Unpub. M.Sc. Thesis, University of Ife, Nigeria.

Diamant, A., Pasternak, M., Banin, A., (1982): Characterization of adsorbed iron in montmorillonite by Mossbauer spectroscopy. Clay Mineralogy. 30, 63–66.

Ehinola, O. A., Oladunjoye, M. A. and Gbadamosi, T. O., (2009). Chemical composition, geophysical mapping and reserve estimation of clay deposit from parts of Southwestern Nigeria, Journal of Geology and Mining Research, Vol. 1 (3), pp. 057-066.

Elueze, A. A. and Bolarinwa, A. T. (1995). Assessment of functional applications of lateritic clay bodies in Ekiti environs, southwestern Nigeria. Journal of Mining and Geology, 31(1), 79-87.

Emofurieta, W. O. (1987). Geochemistry, mineralogy and Economic Potentials of a Pegmatite Residual Soil Profile in SW-Nigeria.Journ.Sc.22 (1/2):91-98.

Emofurieta, W. O., Aladesawe, A. I., and Ogunseiju, P. (1995). Secondary geochemical and mineralogical dispersion patterns associated with lateralization process in Ile-Ife SW Nigeria. *Journal of Mining and Geology, 31*(1), 39-51.

Emofurieta, W. O., Kayode, A. A. and Coker, S. A. (1992). Mineralogy, geochemistry and economic evaluation of the Kaolin deposits near Ubulu-Uku, Awo-Omama and Buan in Southern Nigeria. Jour. of Mining and Geology, 28 (2).

Enu, E. I. and Adegoke, O. S. (1986). Industrial Potential of the Ifon Clay Belt, Southwest Nigeria. Jour.. Geoscience vol II, No.1 pp29-39.

Fabbri, B. and Flori, C. (1985). Clays and complementary raw materials for stoneware tiles. Mineralogica Petrographica Acta, 29A: 535-545.

Fabbri, B. and Flori, C., 1985. Clays and complementary raw materials for stoneware tiles. Mineralogica Petrographica Acta, 29A: 535-545.

Faseke, O. O. (1981). Investigation of a clay deposit and the determination of its possible industrial utilization –A case study of the Ibule

Frankl, E. J. and Cordy, E. A. (1967). The Niger Delta oil province: Recent developments onshore and offshore. Seventh world petroleum congress proceedings, Mexico, 2: pp 195-209.

Garvey, C. C. (1995). Kaolin Resources of the United States and their Industrial Utilization. In: Proceedings of the 1993 UN Workshop for Industrial Minerals Development in Asia and the Pacific. Vol. 8. Pp 252-265.

Grim, R. E. (1962). Applied Clay Mineralogy: New York: McGraw-Hill.

Grim, R. E. (1968). Clay Mineralogy. London: McGraw Hill.

Guggenheim, S. and Martin, R. T. (1995). Definition of Clay and Clay mineral: Joint Report of the AIPEA Nomenclature and CMS Nomenclature Committees. *Clay and Clay Minerals*, 43**:** 25-256.

Huang, W. H. (1975): Stabilities of Kaolinite and halloysite in relation to wreathing of feldspars and nepheline in aqueous solution. American. Miner. 59 pp. 365-371.

Huber, J. M. (1985). Kalolin Clays). Georgia, USA: Huber Corporation (Clay Division), p.64

Ligas, P., Uras, I., Dondi, M. and Marsigli, M. (1997). Kaolinitic materials from Romana (North-West Sardinia), Italy and their ceramic properties. Applied Clay Sci., 12, pp. 145-163.

Ligas, P., Uras, I., Dondi, M. and Marsigli, M., 1997. Kaolinitic materials from Romana (North-West Sardinia), Italy and their ceramic properties. Applied Clay Sci., 12: 145-163.

Mermut, A. R. and Cano, A. F., (2001). Baseline Studies of the Clay Minerals society source clay: chemical Analysis of Major Elements, Clays and Clay mineral, Vol 49, (5), pp. 381-386.

Moore, D. M. and Reynold, R. C. (1997). X-ray Diffraction and Identification and Analysis of Clay Minerals. Oxford, UK: Oxford University press.

Murat, R. C. (1972). Stratigraphy and Palegeography of Lower Tertiary, Southern Nigeria, *In:* Dessavagie, T. P. J., and Whiteman (Eds.), Afrigeol. University of Ibadan, Nigeria. 425 p.

Murray, H. H. (1960). Clay, industrial minerals and rocks (pp. 159-284). New York: American Institute of Mining, Metallurgy and Petroleum Engineers.

Murray, H. H. (1984). Clays in: Paper Coating Pigments (R.W. Hagemeyer, editor) Pp. 25-41.

Murray, H. H. (1991). Overview- Clay mineral applications. Appl. Clay Sci., 5, 378-395.

Murray, H. H. (1995). Clays in Industry and the environment. Proc. 10th Int. Clay conference, Adelaide, 49-55.

Murray, H. H. (1999). Applied Clay Mineralogy Today and Tomorrow. Clay Minerals, 34:39-49.

Nesbitt,(1982) , Judging the predictors of one's own mood: Accuracy and the use of shared theories. Journal Volume 18, Issue 6, November 1982, Pages 537-556

Nordell, E. (1951). Water treatment for industrial and other uses, Reinhold Pub. Corp., Inc., New York.

Nwajide, C. S. (1990). Cretaceous Sedimentation and Paleogeography of the Central Benue Though. In: Ofoegbe, C.O; (Ed), The Benue Tough structure and Evolution International Monograph Series, Braunschweig, pp. 19-38.

Nwajide, C. S. and Reijers, T. J. A. (1996). Geology of the Sourthern Anambra Basin. *In*: Reijers, T. J. A. (Ed), selected chapters on Geology, SPDC, Warri, pp. 133-148.

Obaje, S. O., Omada, J. I. and Dambatta, U. A. (2013). Clays and their Industrial Applications: Synoptic Review. International Journal of Science and Technology, Vol. 3.No. 5, pp 264-270.

Onyeobi, T. U. S, Imeokparia, E. G., Ilegieuno, O. A. and Egbuniwe, I. G. (2013). Compositional, Geotechnical and Industrial Characteristic of some Clay Bodies in Southern Nigeria. Journal of Geography and Geology. 5 (2): 73-84.

Oyawoye, M. O. (1964). The geology of the Nigerian Basement Complex-A survey of our present knowledge of them. J. Niger. Min. Geol. Metal. Soc., 1, pp. 87-103.

Oyawoye, M. O. (1965). Review of Nigerian Pre-cretaceous. In: Rayment, R. A., Aspect of the geology of Nigeria, University of Ibadan Press, pp. 16-21.

Parker, E. R. (1967). Materials data book for engineers and scientists (p. 283). New York: Publ McGraw Hill Book Co. 8-90.

Payne H. F. (1961). Organic coating technology, vol. II: pigments and pigmented coatings: John Wiley and Sons, Inc. New York, 796p.

Rahaman, M. A, (1976). Review of the Basement Geology of South Western Nigeria. *In*: Kogbe, C. A. (ed) Geology of South Western Nigeria. In:

Rahaman, M. A. (1971): classification of rocks in the Nigeria Precambrian Basement Complex. Paper read at annual conference of Nigeria Mining, Geological and Matallurgical Society Dec. 1971 Kaduna.

Rahaman, M. A., (1988). Precambrian Geology of Nigeria. International Conference on Proterozoic Gold and Tectonics of High-Grade Terrain, Ile-Ife, Nigeria.

Roser, B.P. and Korsch, R.J. (1988) Provenance Signature of Sandstone Mudstone .Chemical Geology, 67, 119-139.

Schellmann, W., (1986). A new definition of laterite. In: Lateritisation Processes, IGCP-127. Geological Survey of India, Memoirs, 120, 1-7.

Velde, B. (ed.) 1995. *Origin and Mineralogy of Clays. Clays and the Environment.*

Schellmann, W., 1986. A new definition of laterite. In: Lateritisation Processes, IGCP-127. Geological Survey of India, Memoirs, 120, 1-7.

Weaver, C. E. and Pollard, L. D. (1973). The Chemistry of Clay Minerals. Developments in Sedimentology, Elsevier, Amsterdam, Vol. 15, 213p.