GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION OF MARBLE AND ITS ECONOMIC IMPORTANCE FROM IGUE AREA SOUTHERN NIGERIA

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CERTIFICATION

This is to certify that this project work was carried out by **Chukwuamaka Daniella KOSONYEME** with matriculation number **PSC1809026** of the Department of Geology, University of Benin, Benin City.

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______________________ _______________

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(Head of Department)

DEDICATION

This work is dedicated to God Almighty for his love, care and guidance all through the course of this program.

ACKNOWLEDGEMENTS

My deepest appreciation goes to God Almighty, who guided me through the stormy era of my academic pursuit at the University of Benin and during the duration of my project.

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My special thanks go to the Head of Department, Dr. S.A Salami, whose fatherly mentoring was crucial to my success, as well as his professional and moral commitment, which cannot be overemphasized.

Special thanks to my parents, Mr. and Mrs. Kosonyeme, as well as my guardians, Mr. Oladunjoye and Miss Tina Brown, and also my siblings Daniel, Victor, and Ogor, for their love, care, and guidance.

I will also like to appreciate my friends especially Otito, Seun, Asonye, Ovo, Esther, and others too numerous to mention as well my project colleagues.

ABSTRACT

Five (5) marble samples from Igue and Environs in Southern Nigeria were obtained with the aim of qualifying the marble using XRF as well as XRD techniques and determining its economic importance. The major element composition of the marble deposit shows it has a mean chemical composition of CaO (91.14 wt. %), MgO (0.64 wt. %), SiO_2 (4.17 wt. %), K_2O (0.16 wt. %), Al_2O_3 (2.57 wt. %) and Fe_2O_3 (0.40 wt. %), respectively. The modal composition of the marble is, Calcite (65.1 %), Quartz (14.74 %), Orthoclase (7.66 %), Lime (6.5 %) and Illite (5.96 %). The results of the analysis revealed that the Igue marble is highly calcitic in composition. The ternary plot tends towards CaO and $CaCO_3$ which confirms the former. Subject to beneficiation, Igue marble can be used for cement production. Igue marble is also used for sculpture, tiles, chips and decorative purposes. It is suggested that detailed trace element analysis should be carried out on the marble.

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CHAPTER ONE

INTRODUCTION

1.1 GENERAL STATEMENT

Marble is a metamorphic rock that is formed when carbonate rocks are recrystallized during metamorphism. Marble is a rock composed primarily of calcite ($CaCO_3$) and usually contains other impurities such as muscovite, biotite, pyrite, graphite and chlorite etc. (Odokuma-Alonge, 2020). Carbonate rocks can either be sedimentary (limestone) or igneous (carbonatites). It is composed mainly of recrystallized carbonates like calcite ($CaCO_3$) and dolomite ($Ca,Mg\ (CaCO_3)_2$. When carbonates (mostly sedimentary carbonates) such as limestone or dolomite are subjected to increase in temperature, it result in varying recrystallization of the original mineral grains. As this occurs, the size of the crystals in the rock increases, and the rock develops a distinct crystalline appearance (Tanko and Omosebi, 2021). Generally, marbles are the metamorphic derivatives of sedimentary carbonates.

The formation of marble usually occurs at convergent plate boundaries and begins with the deposition of calcium carbonate rich minerals in a sedimentary basin. After a long period of time, these sediments are subjected to intense heat and pressure at great depths over an extensive area which conforms to regional metamorphism. Contact metamorphism also produces marbles when hot magma intrudes and heats up an adjacent limestone or dolostone. Marbles may have colours ranging from pure white, grey, green, blue; it could be foliated when its formation is accompanied by various stress regimes. (Oluwatoyin *et al.,* 2021).

Swirls and veins in coloured marbles are caused by different mineral varieties such as iron oxides, clays, sand, or silt that were present as layers or grains in limestone; hence, pure white marble is caused by metamorphism of very pure limestone or dolostone. The chemical composition of any marble deposit will depend on the original limestone from which it was formed and the physiochemical conditions during such transformations. (Oluwatoyin *et al.,* 2021).

1.2 AIM AND OBJECTIVES

1.2.1 AIM

The aim of the study is to determine the mineralogical and geochemical characterization of marble in Igue and its economic importance.

1.2.2 OBJECTIVES

The objectives of the study are to:

a) Carry out X-Ray Fluorescence (XRF) analysis on collected samples.

b) Subject collected samples to X-ray diffraction (XRD) analysis.

c) Implement geochemical classification of the marbles.

d) Implement mineralogical classification of the marbles.

e) Ascertain the suitability of the marbles for cement production.

1.3 LOCATION OF STUDY AREA

The study area is located at Owan East Local Government of Edo state (Figure 1.1). Igue is located in the South Western part of Igarra (it runs between latitudes 7° 12’ 40” and 7° 13’ 22” North and longitudes 6° 5’ 21” and 6° 5’ 38.5”) on Auchi Sheet 266.

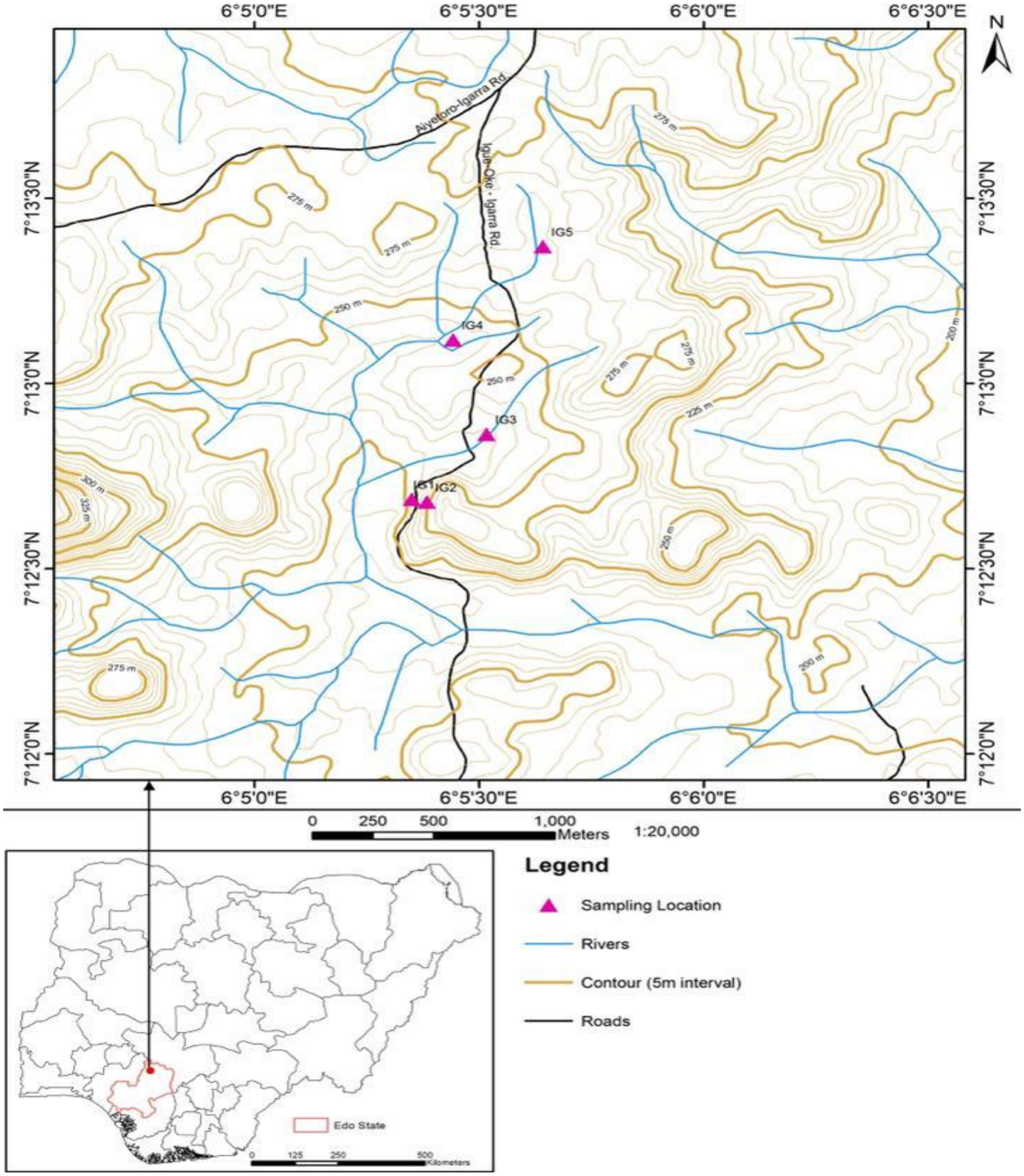

Fig 1.1: Location Map of Igue and Environs (Owan-East Local Government Area)

1.4 ACCESSIBLITY

The study area is accessible via major and minor roads, but primarily via minor and pathways.

At the time the samples were collected from the field, it was during dry season, the rocks were exposed as the bushes had dried out either by burning or by clearing, thus making the exposure easily accessible**.**

1.5 GEOGRAPHY AND GEOMORPHOLOGY

Geomorphology is the study of landforms on the earth's surface, their classification, origin, development and history. The physical characteristics of the earth are studied in geography. Igue terrain comprises of the Igarra schist belt which forms a part of the Precambrian Basement complex. The study area is made up of metamorphic and igneous rocks.

1.6 TOPOGRAPHY

The terrain is uneven and gently undulating in this location, rugged with dendritic drainage pattern. The granites are of higher elevations (highlands) than the metasediments (valleys).

1.7 CLIMATE, VEGETATION AND SOIL

The study area falls under the tropical region. The vegetation of the study area is tropical rain forest. The area is made up of rainy season and dry season. The rainy season runs from March-October while the dry season runs from November - February. Due to the fact the terrain is a basement environment, the soil is highly enriched in elements that aid plant growth.

1.8 HUMAN ACTIVITIES

The natives of this area are known for agricultural practices like farming, fishing, and hunting. Town's people are known for trading activities.

CHAPTER TWO

LITERATURE REVIEW / GEOLOGICAL SETTING

2.1 GENERAL GEOLOGY

The geology of Nigeria consists of three major litho-petrological units namely (Figure 2.1):

1. The Basement Complex
2. The Younger Granites
3. The Sedimentary Basins

The Migmatite-Gneiss Complex, Schist Belts, and Older Granites constitute the Nigerian Basement Complex. It is polycyclic hence it as undergone major orogenic cycles of deformation. It is Precambrian in age.

2.2 REGIONAL GEOLOGIC SETTING OF THE PRECAMBRIAN BASEMENT COMPLEX

2.2.1 TECTONIC SETTING

Nigeria lies approximately between latitudes 4^0N and 14^0N and Longitudes 3^0E and 15^0E and is situated with the Pan African Mobile Belt, northwest of the Congo Craton, east of West African Craton and south of the Tuareg Shield. The presence of basic to ultrabasic rocks which are characteristcs of the Ophiolite Complexes, is evidence that the Pan African belt developed by tectonic processes (Black *et al.,* 1979, Caby *et al.*, 1981) which involved the collision of passive continental margin of the West African Craton and the active margin of the Tuareg Shield about 600 mya.

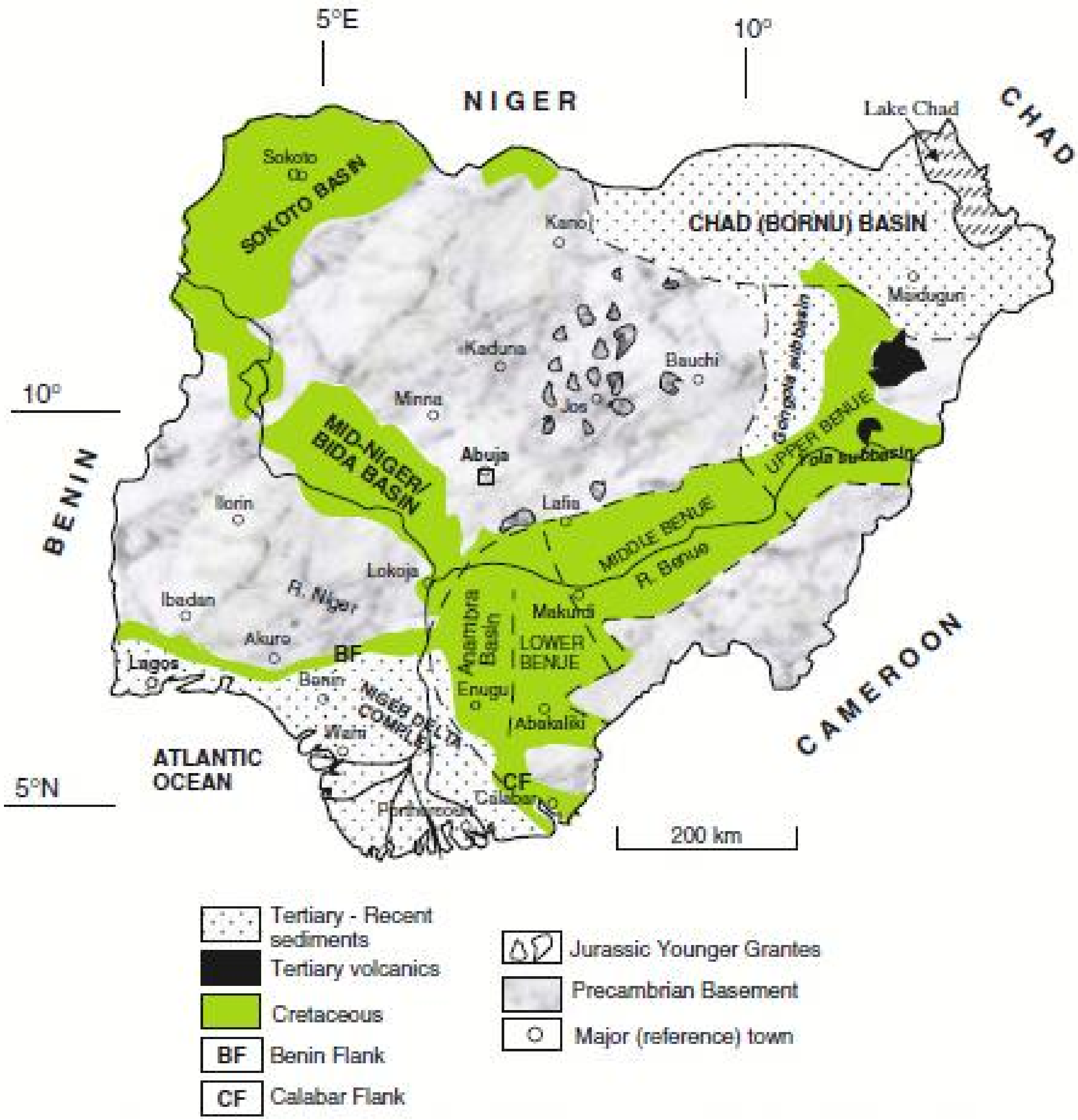

Figure 2.1: Geologic Map of Nigeria (Obaje, 2009)

The suture is marked by a string of positive gravity anomalies corresponding to the emplacement of ultrabasic and basic rocks including perhaps Ophiolites. The collision of these plate margins has been suggested to have resulted in the reactivation of the Pan African belt's interior area. Within the reactivated internal region of the Pan-African Belt is the Nigerian Basement Complex.

The Nigerian Basement Complex is polycyclic and is believed to of at least four major cycles of deformation, metamorphism and based on radiometric age dating it comprises rocks of Liberian (2700+/-200Ma), Eburnean (2000+/-200Ma), Kibaran (1100+/-150Ma) and Pan African (600+/-Ma) (Rahaman, 1976).

The first three cycles were characterized by intense deformation and isoclinal folding, as well as regional metamorphism which was followed by extensive migmatization. The Pan African deformation was accompanied by migmatization and extensive granitization which produced granites and homogeneous gneiss (Abaa, 1983).The end of the orogeny was marked by faulting and fracturing (Gandu *et al.,*1986).Based on geochronology, stratigraphy and composition, the rocks of the Nigerian Basement Complex fall into two broad groups: the Pre Pan-African crystalline rocks comprising the migmatite gneisses and ancient granites; and the Pan African crystalline rocks consisting of the Older Granites and metasedimentary series (Ominigbo,2022) . Typically, the Pan African rocks lie unconformably on the Pre Pan-African basement (Ekueme, 1990).

2.2.2 REGIONAL STRATIGRAPHIC SETTING

The basement rocks in Nigeria are exposed in five major locations namely: Northeastern Zone, Southeastern Zone, Southwestern Zone, South-southeastern zone (The Oban Massif) and the Northwestern Zone (Obiora, 2005).

The entire basement complex has been described and classified into various groups by a variety of authors amongst whom are: Oyawoye (1965), Cooray (1974), Rahaman 1976), Obiora (2005) and Dada (2006). Figure 2.2 shows the Basement Geology of Nigeria.

Oyawoye (1965) subdivided the rocks of the Basement Complex into three major groups namely:

a) The older meta-sediments consisting of calc-silicate rocks, arkosic quartzites and high grade schists.
b) The gneisses, migmatites and Older Granites.
c) The younger metasediments

Cooray (1974) recognized three major lithological units similar to those identified by Oyawoye (1965) as presented below:

a) Metasediments (older and younger)
b) Gneisses and Migmatites
c) Intrusives

Rahaman (1976) subdivide the basement complex into six major petrological group as follows:

a) Migmatite-Gneiss-Quartzite complex
b) Schist belt

c) Charnokitic, gabbroic and dioritic rocks

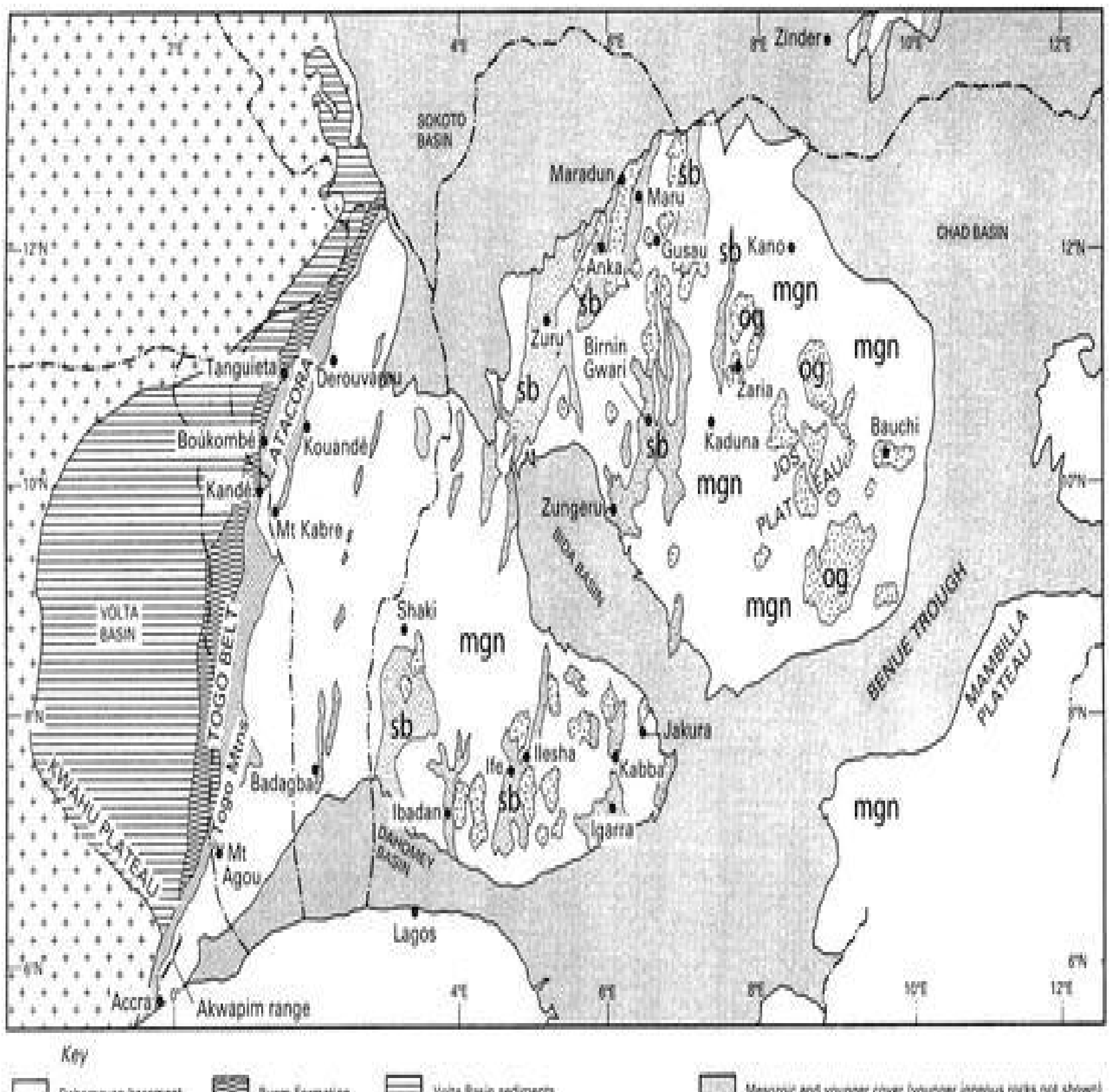

Figure 2.2: Basement Geology of Nigeria: The Migmatite Gneiss Complex (mgn), the Schist Belt (sb) and the Older Granites (og) (Obaje, 2009)

d) Rocks of the Older Granite suite

e) Metamorphosed and unmetamorphosed calc-alkaline volcanics and hyperbassal rocks

f) Unmetamorphosed dolerite dykes, syenite dykes.

Obiora (2005) subdivided the Precambrian basement complex rocks into three main groups namely:

a) Gneisses and Migmatites /Migmaite gneisses

b) Schist belts

c) Pan African (older granites)

Dada (2006) in his review of the previous works on the Basement Complex presented four distinct lithologies, namely:

a) Migmatite-Gneiss Complex

b) Schist belts

c) Pan African granitoids

d) Undeformed acid and basic dykes

Generally, the different rock types can be grouped into three and described as follows:

2.2.3 Migmatite-Gneiss Complex (MGC)

The Migmatite gneiss-quartzite complex accounts for over 60% of the basement complex (Rahaman and Ocan, 1978). These rocks are considered as Basement (*sensu stricto*) and they represent the oldest rocks in the Nigerian Basement Complex. These rocks exhibit variations in composition because of the difference in protolith and the metamorphic (P-T) conditions under which they were formed. Petrographic evidence implies that a number of the MGC's constituent minerals underwent partial melting and recrystallization as a result of the Pan-African reworking. Most of the rocks display medium to upper amphibolite facies metamorphism (Obaje, 2009). The rocks are mainly felsic and medium to coarse grained, with alternating layers of bands of dark and light colored minerals. The variably deformed rocks have dominant N-S and NNE-SSW trending foliations and lineaments (Oluwatoyin *et al*., 2021).

The unit is dominated by heterogenous assemblage of migmatites, gneisses and granite-gneisses (Obaje, 2009) that exhibit complex deformation styles attributed to its polycyclic nature. The gneissic complex is regarded as the most widespread unit (Udensi *et al*., 1986; Ogezi, 1988) and forms the country rock in most areas underlain by the basement complex. They occur as low – lying denuded masses.

Migmatites are made up of a metamorphic host (often schists and gneisses) that is streaked and veined with granitic (quartzo-feldspathic) elements characteristic of anatexis. The majority of gneisses are metasedimentary rocks, as shown by their aluminosilicate mineral components. Migmatite is typically a fine to medium grained granoblastic rock with varying structural features. Many outcrops have tortuous veins that represent high-grade regional metamorphism and tectonic deformation, while others include ptygmatic folds. These rocks record three major geological events (Rahaman and Lancelot, 1984): the earliest, at 2,500 Ma involved initiation of crust forming proceses (e.g. the banded Ibadan grey gneiss of mantle origin) and of crustal growth by sedimentation and orogeny: next came the Eburnean, 2,000 ± 200 Ma, marked by the Ibadan type granite gneisses: this was followed by ages in the range from 900 to 450 Ma which represent the imprint of the Pan-African event which not only structurally overprinted and re-set many geochronological clocks in the older rocks, but also gave rise to granite gneisses, migmatite and other similar lithological units.

2.2.4 The Schist Belts

The Schist Belts comprises low grade metasediments with narrow N-S trending belt which are best developed in the western province of The Nigerian Basement Complex (Figure 2.3). These belts are Upper Proterozoic supracrustal rocks that have infolded into the Migmatite-gneiss Complex. The schist belts' lithological varieties include coarse to fine-grained clastics, pelitic schists, phyllites, banded iron formation, carbonate rocks (marbles/dolomitic marbles), and mafic metavolcanics (amphibolites). In the southwestern Basement Complex, the belt is associated with marbles, dolomites and calc-silicate rocks (Obiora, 2005). In the northwest, there is a dominance of schists of greywacke origin comprising meta-pelites, quartzites, phylittes, mica-schists, quartzo-feldspathic schists, paragneiss, Fe-Mn rich quartzites and garnet amphibolites (Dada, 2006).

The geochronology of the schist belts remains challenging, despite the fact that the ages of the intrusive cross-cutting Older Granites indicate a lower limit of Ca750 Ma.. Rb/Sr age of 1,040 ± 25 Ma, for the Maru Belt phyllites has been accepted as a metamorphic age by Ogezi (1977). Turner (1983) and Ajibade *et al*., (1987) identified and classified eleven main schist belts in the northwestern and northcentral parts of Nigeria. The eleven schist belts are the

1. Birnin Gwari Schist Belt

2. Kushaka Schist Belt

3. Wonaka Schist Belt

4. Zuru Schist Belt

5. Anka Schist Belt

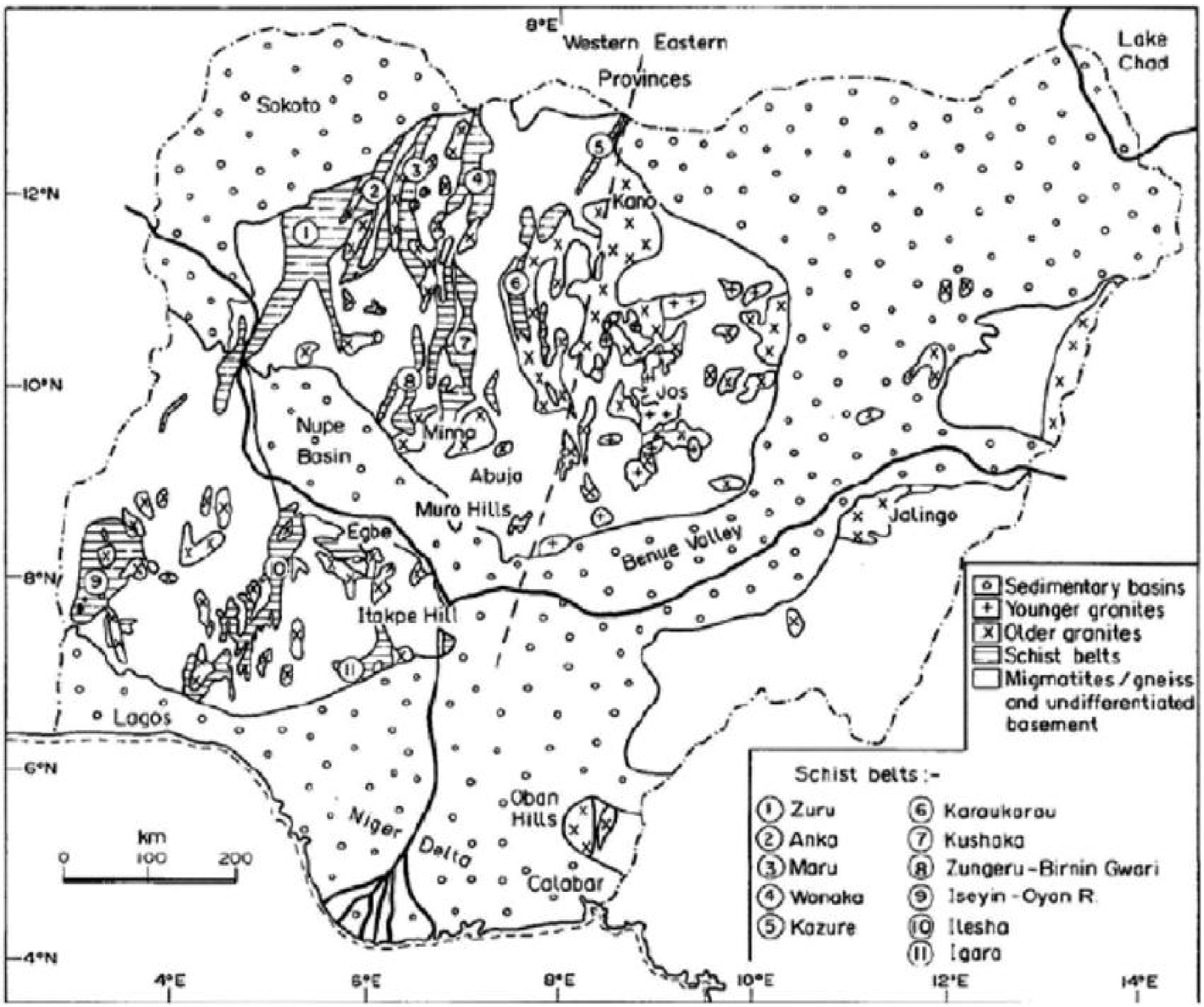

Figure 2.3: Map of the Schist Belt of Nigeria (Woakes *et al*., 1987)

6. Maru Schist Belt

7. Malumfashi Schist Belt

8. Kazaure Schist Belt

9. Ilesha Schist Belt

10. Igarra Schist

11. Isenyi-Oyan schist belts

2.2.5 The Pan-African Granites

The Pan African Granites are also known as the Older Granites. The term Older Granite was introduced by Falconer (1911) to distinguish the Older Granites from the discordant tin bearing younger granites of Nigeria. They range from plutons to batholiths in size. The Older Granites are syn and post tectonic intrusions which cut the Migmatite-gneiss complex and the Schist belt. Rocks with a variety of different compositions can be found in the Older Granites which includes: granites, granodiorites, adamellites, quartz monzonite, syenites, pegmatites. Granitic to granodioritic compositions are most common (Rahaman, 1976). The Pan-African Granites are medium-coarse grained containing both muscovite and biotite, plagioclase and microcline. Petrographically and geochemically, the Older Granites are calc-alkaline; thus they represent product of subduction/collision or mountain building event, characteristic of convergent/compressional tectonic events and are therefore orogenic granites (Obiora, 2005)

2.3 LOCAL GEOLOGY

Igue area lies within the Precambrian Basement Complex of southwest, Nigeria. According to (Odeyemi, 1981) the basement complex of Igue area comprises

1) Polycyclic crystalline complex of migmatite and gneisses
2) Younger metasedimentary succession
3) Suite of syn to late tectonic intrusive granitoids

The schist occurs as a supracrustal cover on the basement and consists of mica schist, metaconglomerate, calc-gneiss and marble and quartz biotite schist (Odeyemi, 1988).

Igue marble is associated with calc-silicate gneiss and appears as lenses atop migmatised schist and beneath polymictic metaconglomerate. It occurs as low lying herogeneneous bodies intersected at relatively shallow depths (Oluwatoyin *et al*., 2021).

Mineralogical composition shows that rocks in this area consist dominantly of calcite, quartz, k-feldspar, illite. Igue marbles are white to off white in colour exhibiting bandings which range from grey to brown (Plates 2.1 and 2.2). The area is very rugged due to its undulating topography. The marbles occur as low-lying bodies. Figure 2.4 shows the geological map of Igue and environs.

Plate 2.1: An Exposed Marble Deposit in Igue and Environs.

Plate 2.2: Banded Marbles in Igue and Environs.

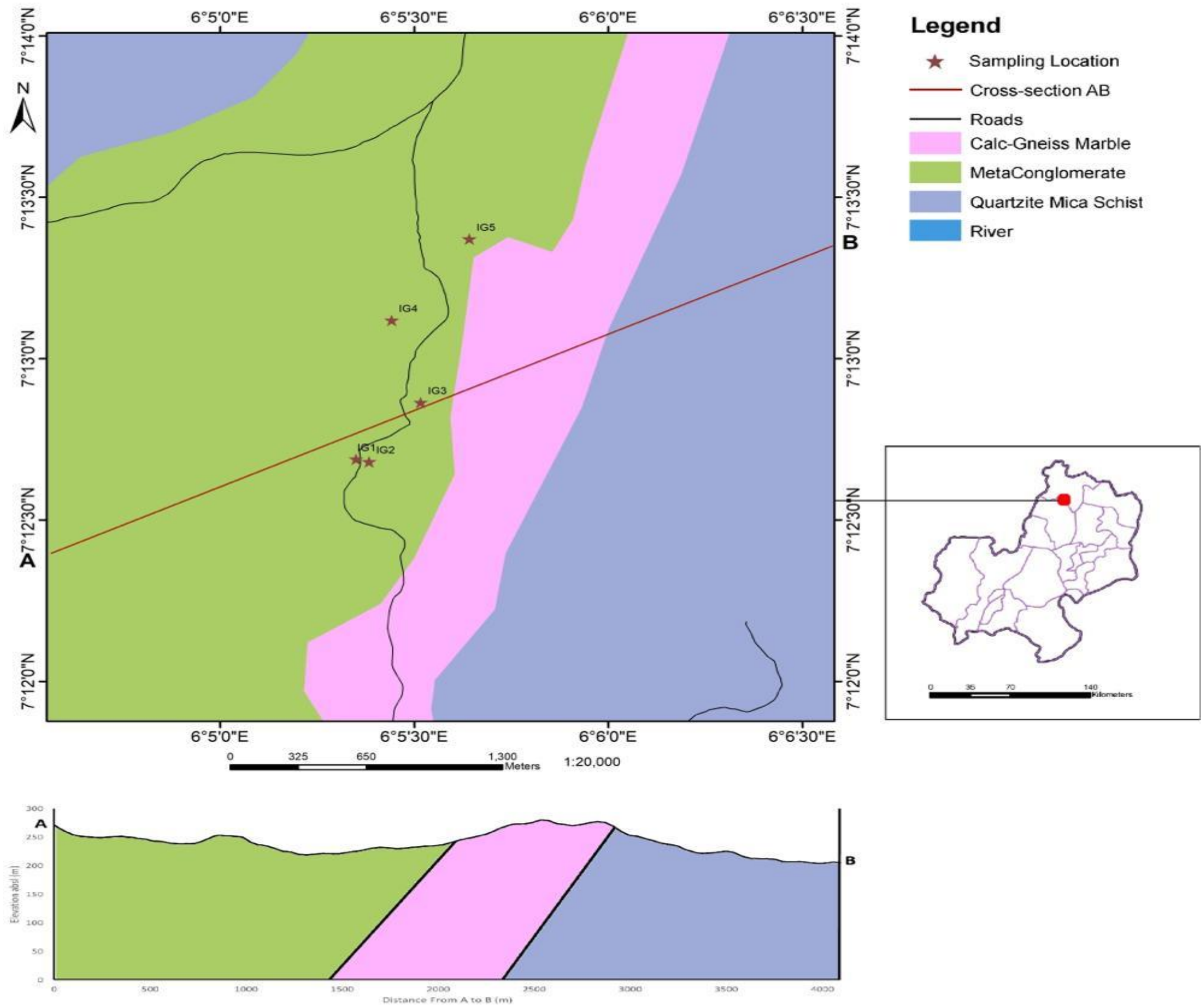

Figure 2.4: Geologic Map of Igue and Environs

2.4 PREVIOUS WORKS

Aliegbo *et al*., (2021) in "Investigation of the Geochemical composition and Paleo- Depositional Environment of Ubo and Ikpeshi marble Deposit Southwestern Nigeria" silica was used as an absicca in these plots because it shows substantial variations among the marble with the most of the linear relationship between silica and the various oxides showing negative correlations, these probably reflect the admixture of carbonates with chert.

Oluwatoyin *et al*., (2021) in "Lithological Features and Chemical Characterization of Metamorphosed Carbonate rocks in Igue Southwestern Nigeria" concluded that marble deposits from different parts of Nigeria Basement exhibits variable geochemical features that are influenced by their protoliths, mode of formation and associated lithologies and forms the basis and various economic uses.

Odokuma-Alonge *et al*., (2020) in "A Geochemical Approach and Industrial Utilization of some Marble Bodies from Ubo River Area and Environs" concluded that the marble bodies are emplaced within the schist and the marble bodies has high content of lime.

Egesi *et al*., (2019) in "Petrography, Structural Characteristics and Mineral Resources of Igue Oke Igarra Area Southwestern Nigeria" observed that the rock types presently of more economic importance in the area are marbles which are quarried in a large-scale at Ojukutu and lyuku area for aggregates.

Odokuma-Alonge (2019) in “A Geochemical Appraisal of Some Marble Physiques in Ubo Area and Environs, South Western Nigeria” revealed that the marbles are classified as the high calcite group and their industrial use range from production for Portland cement to their use for ceramics.

Ephraim *et al*., (2018) in “The Genesis of Nsofang Marble of Ikom Area of Southern Nigeria” concluded that the Cenozoic timing of the CVL coincide with the time of the dolomitization, while the extrusives provided a source of heat and additional ions for circulating sea water that drove calc- dolomite reactions of the replacement types dolomitization model.

Oluwajana *et al*., (2018) in “Subsurface mapping and geochemical investigation of a marble deposit around Igarra, Southwestern Nigeria” concluded that the snow white coloured marbles are purely calcitic to fairly dolomitic marbles while the grey to dark grey variety is highly dolomitic.

Onimisi *et al*., (2017) in “Field Occurrence, Chemical Composition and Industrial Composition of Ekirin-aade Marble deposit, Kogi State, North Central Nigeria” concluded that Ekirin –Aade marble is suitable for cement production and production of plant enhancers.

Elueze *et al*., (2015) “Compositional Composition Characteristics and Functional Application of Obajana Marble Deposit in the Precambrian Basement of Complex of Central, Nigeria” suggested that the marble in the study area find suitable environmental application in water treatment, owing to its high PH value and very low cobalt content. While in sewage management, it can be utilized in silica phosphate removal from sewage effluents as well as its application in agricultural soil.

Onimisi *et al*., 2014 in “Geochemistry and economic potential of marble from Obajana, North - Central Nigeria” concluded that the Obajana marble indicate variable characteristics of high calcite and low dolomite and that an economic appraisal of the marble shows that they serve as raw materials for a variety of products.

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 MATERIALS

A field mapping exercise was carried out to assess the marble occurrence at Igue and environs. The marble bodies were mapped and samples were taken for mineralogical and geochemical analysis.

The materials used to carry out the field exercise include: field map, the global positioning system (GPS), sledge hammer, camera, field notebook, sample bag, compass clinometer, Hydrochloric acid and others.

The geologic map was used to establish locations on the map, and also to measure elevations of the observed outcrops.

3.2 METHODOLOGY

Five (05) marble samples were taken from the field and taken to the laboratory, Chemical and Mineralogical analysis was carried out in National Steel Raw Materials Exploration Agency (NSRMEA) Kaduna, Nigeria. The Chemical analysis was carried out using X-Ray Fluorescence (XRF) technique while mineralogical analysis was carried out using X-Ray Diffraction (XRD) technique.

The XRF technique is a non-destructive elemental analysis method used to determine the chemical composition of solids and liquids. The fluorescent X-rays are in general measured by two types of detection systems:

1) Wavelength dispersive detection (WDXRF)

2) Energy dispersive detection (EDXRF)

To excite a sample, the WDXRF analyzer employs an x-ray source. X-rays with wavelengths characteristic of the elements in the sample are emitted, and they propagate in all directions along with scattered source x-rays. A crystal or other diffraction device deflects the sample's x-rays. An x-ray detector is positioned to detect x-rays that have diffracted and been scattered off the crystal.

Specific wavelengths focused at the detector can be changed by adjusting the spacing between the crystal lattice's atoms (the diffractive device) and its angle in reference to the sample and detector. To test elements sequentially, the angle can be changed, or numerous crystals and detectors can be placed around a sample for simultaneous examination.

The EDXRF analyzer also uses an x-ray source to excite the sample, but it can be configured in one of two ways. Direct excitation is the first method, where the sample is directly exposed to the x-ray beam. To raise the excitation of the target element or decrease background in the region of interest, a filter made up of different elements can be positioned between the source and the sample. The second approach makes use of a secondary target, in which the source is directed toward the target element, which is excited and fluoresces, and the target fluorescence is then used to excite the sample. A detector is placed to detect fluorescence and scattered x-rays from the sample, and a multichannel analyzer and software assigns an energy value to each detector pulse, producing a spectrum.

The XRF method has a significant restriction in that components lighter than sodium (Na) cannot be examined. Plate 3.1 shows Xenemetrix benchtop EDXRF Spectrometer, Genius IF.

X-ray diffraction (XRD) is a technique for determining the crystallographic structure of a substance. The process of XRD involves blasting a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that escape. The spatial structure of crystalline materials is shown by the XRD method. Only crystalline substances (or the crystalline components of a combination) can be analyzed using XRD to offer information on their structures, phases, preferred crystal orientations (texture), and other structural features.

In X-ray diffraction, the constructive interference of monochromatic X-rays with a crystalline substance is widely employed. Each crystalline substance has a unique three-dimensional atom arrangement, which results in a unique X-ray diffraction pattern. Diffraction patterns can serve as "fingerprints" for identifying crystalline phases. X-ray diffraction tests are performed by exposing a crystalline sample to an X-ray beam The X-rays are diffracted from the atomic planes after interacting with the substance. Only photons released in specified directions survive due to interference (constructive interference). The remaining beams are destroyed by destructive interference. Plate 3.2 shows an X-ray diffractometer.

The most common application of X-ray powder diffraction (XRPD) is the identification of unknown crystalline materials (e.g., minerals, inorganic compounds). According to (Bunaciu *et al*., 2015) the limitations of the XRPD are:

1. Homogeneous and single-phase materials are excellent for identifying unknowns.

2. Access to an inorganic compound standard reference file is necessary.

3. The material must be pounded into a powder in tenths of a gram increments.

4. The detection limit for mixed compounds is greater than 2% of the sample.

5. Pattern indexing for non-isometric crystal systems is difficult for unit cell determinations.

Plate 3.1: Xenemetrix Benchtop EDXRF Spectrometer, Genius IF.

Plate 3.2: X-ray Diffractometer, Rigaku Miniflex XRD

3.2.1 SAMPLE PREPARATION

Proper sample preparation was necessary to acquire the best results from the XRF and XRD techniques: The more precise the analytical results, the better the sample preparation. Sample preparation for the XRF approach entails pulverizing 100g of each collected sample with a motorized agate mortar such that the grains of the pulverized fine powder pass through the mesh sieve. Each powder sample was homogenized in an agate mortar with 1g of stearic acid. The mixture was placed in a 40mm diameter hardened steel disk and hydraulically crushed into a pellet at a pressure of 25tons. XRF was then used to evaluate the pellets.

Powders must be extremely fine-grained for XRD analysis to produce a good signal-to-noise ratio (and reduce intensity fluctuation), avoid spottiness, and decrease preferred orientation. Powder reduction to fine particles ensures adequate particle participation in the diffraction process. The most suitable size range is 1-5 mm (Klug and Alexander, 1974), especially if phase quantification is desired. Using an agate mortar and pestle, grind solid materials to a fine talc-like powder. Transfer the powdered sample to a glass bottle with a suitable label. Choose between steel and plastic sample holders. Push the powder carefully until it is flush with the sample holder using a glass slide. The powder must have a smooth surface. Before placing the sample holder into the appropriate XRD slot, remove any extra powder from its edges.

3.2.2 PRINCIPLE AND TECHNIQUE

X-ray diffraction is a common technique for examining crystal structures and atomic spacing. The underlying mechanism behind X-ray diffraction is the monochromatic X-rays' constructive interference with a crystalline substance. A cathode ray tube generates these X-rays, which are subsequently focused by collimation, created as monochromatic radiation, and directed onto the sample. When the incident rays contact with the sample, they produce constructive interference (and a diffracted ray) if the following requirements are met:

$$n\lambda = 2d\sin\theta \qquad \text{Equation 1}$$

Where n is an integer

λ is the wavelength of the X-rays,

d is the interplanar spacing generating the diffraction

θ is the diffraction angle.

This law explains how the lattice spacing and diffraction angle of a crystalline sample relate to the wavelength of electromagnetic radiation. The diffracted X-rays are then found, processed, and totaled. Each compound has a different set of d-spacings, so converting the diffraction peaks to d-spacings allows identification of the compound. Because the powdered material is randomly oriented, all potential lattice diffraction directions should be obtained by scanning the sample through a range of 2 angles. This is typically accomplished by comparing d-spacings to established reference patterns (Bunaciu *et al.*, 2015).

An X-ray tube, a sample holder, and an X-ray detector are the three fundamental components of an X-ray diffractometer. In a cathode ray tube, X-rays are produced by heating a filament to produce electrons, then accelerating those electrons toward a target by applying voltage and bombarding that target material with them. When the electrons have enough energy to knock out the inner shell electrons of the target material, distinctive X-ray spectra are produced. These spectra consist of several components, the most common being Ka and Kb (Bunaciu *et al*., 2015).

The sample rotates at an angle of relative to the collimated X-ray beam in an X-ray diffractometer, while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. A goniometer is the instrument used to maintain the angle and spin the sample. Figure 3.3 shows the schematic diagram of a diffractometer.

In XRF, X- rays produced by a source irradiate the sample. The wavelength of X-rays are in the range 0.01 to 10nm, which correlates with energies in the range from 0.125 to 125keV. X-ray wavelengths are inversely proportional to their energies. This is illustrated as

$$E * \lambda = hc \quad \text{———— Equation 2}$$

Where E is the energy in keV

λ is the wave wavelength in nm

hc is the product of Planck's constant and the velocity of light.

There are three main interactions when X-rays contact matter: Fluorescence, Compton scatter and Rayleigh scatter. When a sample place on a slab material is exposed to beam of X-ray photons, a fraction of the wave is scattered back, a fraction will be transmitted through, and a fraction is absorbed producing fluorescent radiation (Figure3.4). The loss of energy can occur from scattering other times, there is no loss of energy. The former is called Compton scatter, while the latter is called

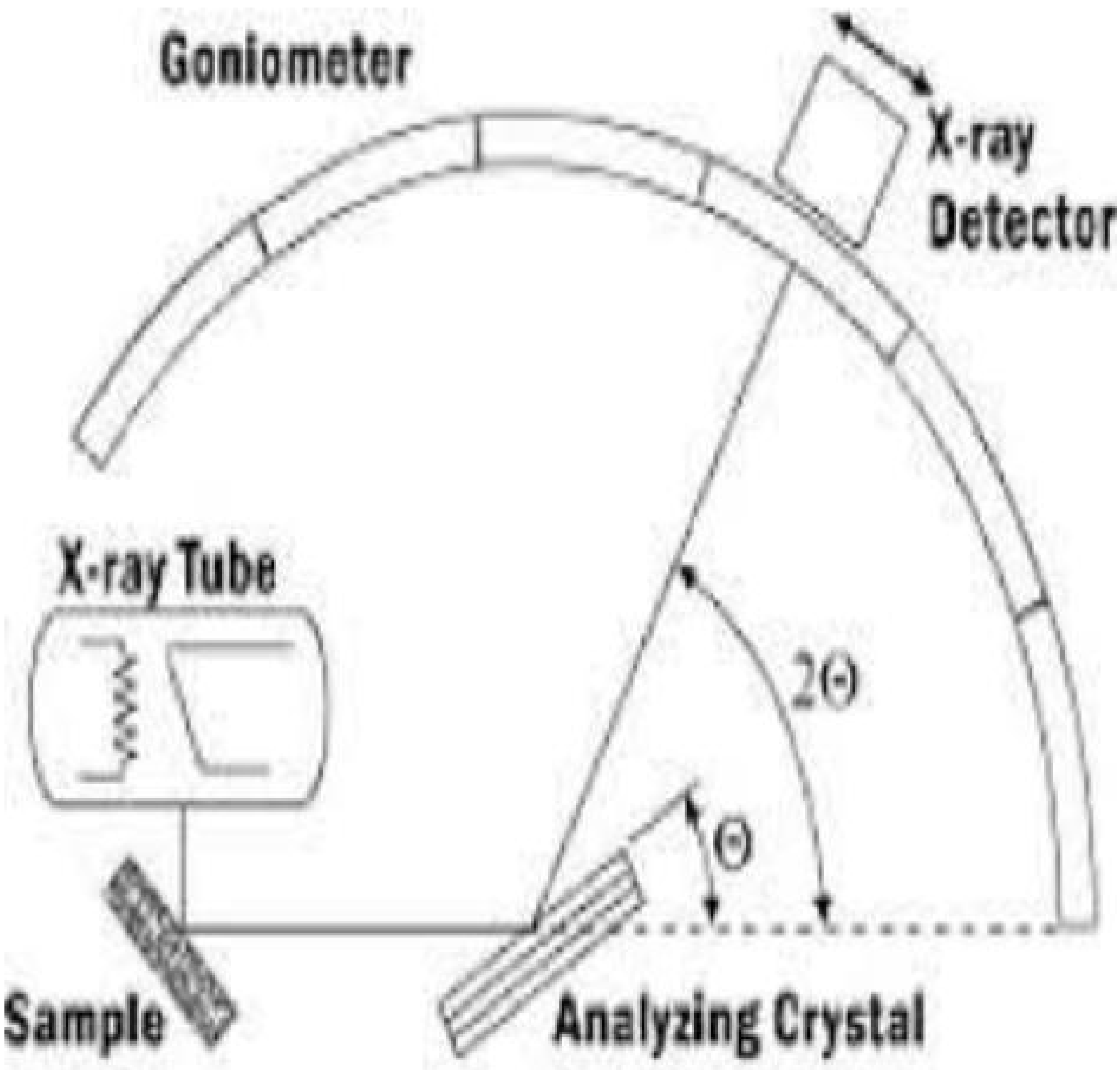

Figure 3.3: Schematic Diagram of a Diffractometer.

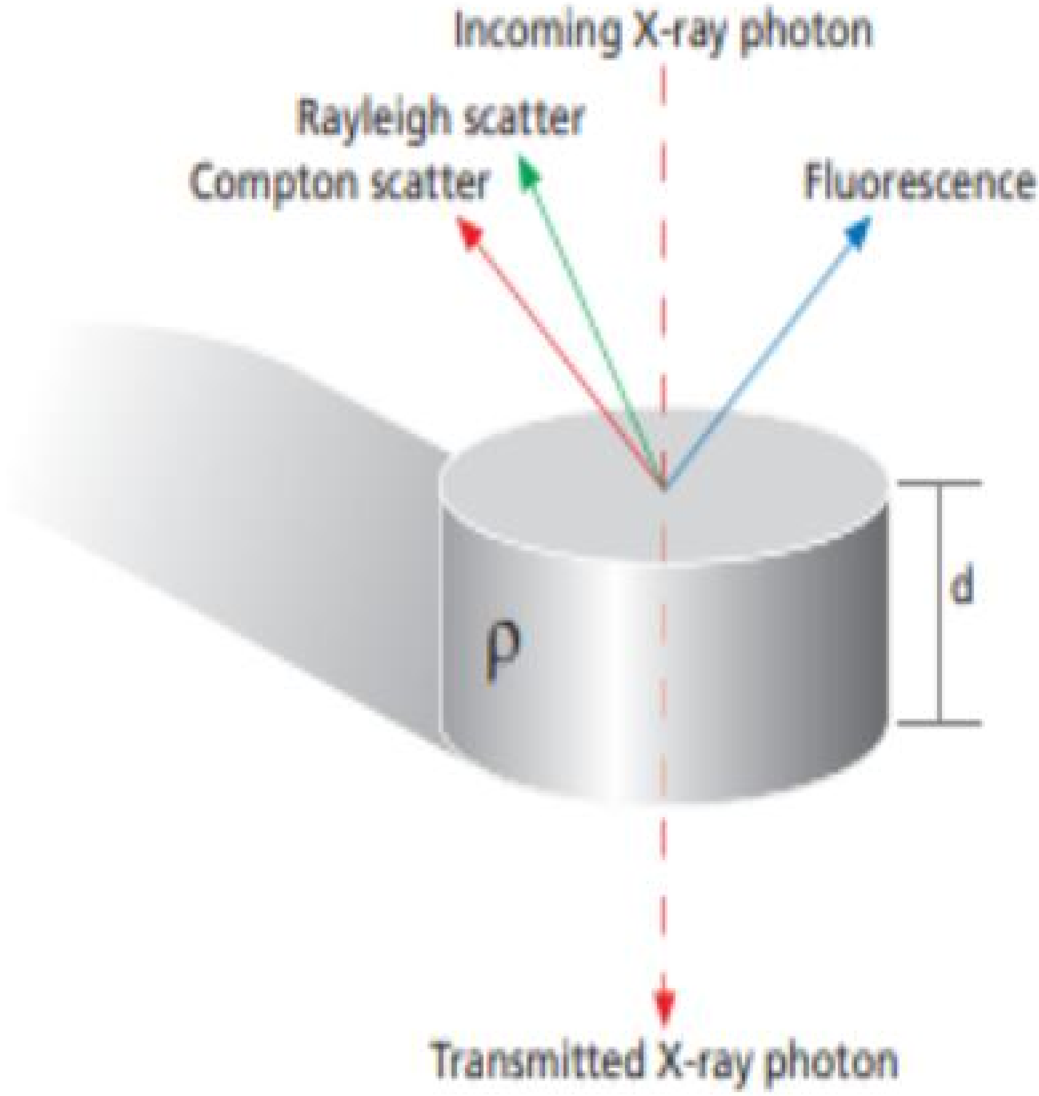

Figure 3.4: X-ray Interaction (Brouwer, 2010)

Rayleigh scatter. The fluorescence and the scatter depend on the thickness (d), density and composition of the material, and on the energy of the X-rays. . The radiation's energy, the atoms' passed-through path lengths, and the sample density all affect how much radiation is absorbed in absorption interactions. Absorption increases as the path length, density and atomic number of the elements in the layer increase, and as the energy of the radiation decreases.

The level of absorption may be so great that deep-lying elements in the sample are not exposed to incoming radiation or that distinctive radiation is no longer able to penetrate the sample. This indicates that only substances near the surface will be measured. The characteristics of radiation emitted by the atoms in the sample bombarded by X-rays (primary fluorescence), is also X-ray (secondary fluorescence). The other elements in the sample's other components can also lose electrons thanks to these fluorescent X-rays. It is challenging to distinguish between the primary and secondary contributions when using a spectrometer to quantify the total amount of fluorescence.

Apart from absorption, some of the incoming X-rays is also scattered by the sampleThis happens when a photon strikes an electron and bounces off of it. In Compton (incoherent) scatter, the photon losses some energy, which is taken in by the electron. In Rayleigh (coherent) scatter, the elements collide with strongly bound electrons. Although they continue to be in the shell, the electrons begin to oscillate at the frequency of the incoming radiation.

The incoming radiation is therefore perceived as being reflected by the atom because the electrons release radiation at the same frequency as the entering radiation. Samples with high elements give rise to high Compton scatter and low Rayleigh scatter because they have many loosely bound electrons. When the elements get heavier, the scatter reduces. For the heavy elements, the Compton scatter disappears completely and only Rayleigh scatter remains (Brouwer, 2010).

Different types of detectors are used in XRF. EDXRF mainly uses solid-state detectors while WDXRF uses gas-filled detectors scintillation detectors. All these detectors produce an electrical pulse when an X-ray photon enters the detector, and the height of this pulse is proportional to the energy of the incoming photon. The pulses are amplified and then counted by a multi-channel analyzer. A detector is effective, if it has good resolution, sensitivity and dispersion.

3.2.3 ELEMENT IDENTIFICATION

The sample's constituent elements will emit fluorescent X-ray radiation with distinct energy (corresponding to colors in optical light) that are unique to them. The equivalent of a different color is a different energy. The elements present can be identified by measuring the energy of the radiation the sample emits. This step is called qualitative analysis. By measuring the intensities of the emitted energies (colors) it is possible to determine how much of each element is present in the sample. This step is the quantitative analysis.

3.2.4 MINERAL IDENTIFICATION

Powdered samples were pelletized and sieved to 0.074mm. These were later taken in an aluminum alloy grid (35mm x 50mm) on a flat glass plate and covered with a paper. Wearing hand gloves, the samples were compacted by 27 gently pressing them with the hand. Each sample was run through the Rigaku D/Max-lllC X-ray diffractometer developed by the Rigaku Int. Corp. Tokyo, Japan and set to produce diffractions at scanning rate of 2 0 /min in the 2 to 500 at room temperature with a Cu-Ka radiation set at 40kV and 20mA. The diffraction data (d value and relative intensity) obtained was compared to that of the standard data of minerals from the mineral powder diffraction file, ICDD which contained and includes the standard data of more than 3000 minerals. Similar diffraction data means the same minerals to standard minerals which exist in the samples.

CHAPTER FOUR

PRESENTATION AND DISCUSSION OF RESULTS

4.1 PRESENTATION OF RESULTS

The results of the geochemical composition in the marble samples are shown in Table 4.1:

Table 4.1: Major element composition from XRF analysis in the marble samples (wt. %):

Major Oxides	**IG1**	**IG2**	**IG3**	**IG4**	**IG5**	**Average**
SiO_2	10.36	1.59	2.65	2.96	3.28	4.17
Al_2O_3	2.95	2.28	2.75	2.61	2.25	2.57
Fe_2O_3	0.52	0.11	0.63	0.20	0.51	0.40
CaO	84.65	94.64	92.58	92.18	91.67	91.14
K_2O	0.16	0.02	0.17	0.08	0.32	0.16
Na_2O	-	-	-	-	-	-
MnO	0.06	0.01	0.06	0.03	0.33	0.10
MgO	-	-	-	0.71	0.56	0.64
TiO_2	0.12	0.04	0.17	0.05	0.21	0.19
Total	98.82	98.69	99.01	98.11	99.13	99.29

4.2 DISCUSSION OF RESULTS

4.2.1 GEOCHEMISTRY

Based on the analytical results from the XRF analysis of Igue marble in Table 4.1, the results reveal the presence of the following major oxides and their volume in weight percentages: SiO_2 ranges from 2.65 – 10.36wt. %, MnO from 0.01- 0.33wt. %, K_2O ranges from 0.02- 0.32wt. %, CaO ranges from 84.65 – 94.65wt. %, Al_2O_3 ranges from 2.25 - 2.95wt. %, the average values for the oxides ranges from 0.10 -91.14wt. %.

4.2.2 CaO/MgO CONTENT

CaO content from the analysis has an average value of 91.14%. This can be attributed to the high amounts of CaO from all the respective samples. The high content of the samples is as a result of large amount of Ca-rich minerals deposited in the environment. Variation in CaO content with other oxides is as a result of fluctuation in the physio-chemical conditions throughout the deposition of the protolith before metamorphism.

In calcitic marble, CaO is usually in the order 50 – 54% while MgO is < 15%. Dolomitic marble on the other hand, have CaO values generally in the range of 28 – 31% and MgO values in the range of 15 – 21% (Goldschmidt *et al.*, 1955). Hence, Igue marble is a highly calcitic marble because its CaO content is 91.14%. MgO content has an average value of 0.64%. Low MgO content in marble is indicative of low dolomite content.

4.2.3 SiO_2 CONTENT

SiO_2 in carbonate rocks comes from both silicate minerals and chert nodules resulting from the influx of near shore silici-clastic materials into the basin of the original limestone deposit which was metamorphosed into marble (Brownflow, 1996). SiO_2 content has an average composition of 4.17% which is indicative that the basin of deposition of the protolith was probably near to the shore (Onimisi, 2017).

4.2.4 Fe_2O_3 AND Al_2O_3 CONTENT

The Fe_2O_3 content is very low, having a mean value of 0.40% which is an indication that the basin of deposition was probably a reducing environment (Brown, 2007). The Al_2O_3 content is low and low concentration of alumina indicates low energy environment (Odokuma-Alonge, 2019).

4.2.5 ALKALI CONTENT

Alkali content refers to the amount of Na_2O and K_2O in the marble. The average alkali content is 0.16%. According to (Clarke, 1924) alkali content decreases in marble with increase in salinity. The very low alkali content is indicative of shallow, saline environment of deposition of the limestone protolith. Table 4.2 compares the samples from this study with calcitic and dolomitic marbles from previous works.

Table 4.2: A comparison of the chemical composition of Igue marble with calcitic and dolomitic marbles

MAJOR OXIDES	THIS STUDY	CALCITIC MARBLES			DOLOMITIC MARBLES	
		1	2	3	4	5
SiO_2	4.17	3.60	2.92	3.49	1.98	2.4
Al_2O_3	2.57	1.02	0.50	1.76	0.13	0.92
Fe_2O_3	0.40	0.57	0.19	3.72	0.36	0.04
CaO	91.17	51.08	60.76	71.99	31.04	31.82
MgO	0.64	1.56	1.62	7.11	20.84	19.6
Na_2O	-	0.19	0.11	0.48	-	0.05
K_2O	0.40	0.15	0.27	0.43	0.07	-
P_2O_5	-	0.06	0.40	-	0.045	-

1 - Ekirin –aade marble (Onimisi, 2017)

2 - Ikpeshi marble (Odokuma-Alonge *et al*., 2021)

3 - Igue-oke marble (Oluwatoyin *et al*., 2021)

4 - Zambezi belt marble (Munyanyiwa and Hanson, 1988)

5 - Abuja marble (Davou and Ashano, 2009)

When compared with typical calcitic and dolomitic types, Table 4.2 shows that Igue marble possesses very high amount of CaO of about 91.1wt. % which is an indication that Igue marble is highly calcitic in composition. The MgO content is high in (4) and (5) which may be as a result of introduction of Mg^{2+} in water leading to the conversion of calcite into dolomite and also from magnesium rich organic matter (Pettjohn,1975) This also implies that marbles (4) and (5) are dolomitic marbles.

The presence of aluminosilicates or the high energy environment of the area at the time of deposition could explain the high percentage of Al_2O_3 in this study, which was 2.57% compared to other calcitic and dolomitic marble types in Table 4.2.

The SiO_2 content is also high when compared to other marble types in Table 4.2 this indicates the contribution of siliciclastic materials into the basin of deposition (Brownflow, 1996).

4.3 IGUE MARBLE FOR CONSTRUCTION PURPOSES

4.3.1 CEMENT PRODUCTION

For limestone and marble to be useful in manufacture of cement, the CaO range of 46.65%-52.46% and $CaCO_3$ range of 83.50%-93.90% is needed. A higher MgO value results in the formation of periclase as an intermediate product in the manufacture of Portland cement causing sintering of limestone by alumino-silicate materials such as clay changing into nodules in the cement kiln (Talbot, 1982). Table 4.3 shows the mean chemical composition of Igue marble and some reference samples of some limestone and marble used for cement production.

Table 4.3: Mean chemical composition of Igue marble and reference of limestone and marble used for cement production.

OXIDES	IGUE MARBLE	REFERENCE SAMPLES			
		I	ii	iii	RANGES
SiO_2	4.17	3.76	6.75	4.91	3.76 – 8.53
TiO_2	0.12	-	-	-	-
P_2O_5	-	-	-	-	-
Fe_2O_3	0.40	0.66	1.47	0.66	0.66 – 2.07
Al_2O_3	2.57	1.10	0.71	1.28	0.71 – 2.74
MgO	0.64	1.23	1.48	0.63	0.30 – 1.48
CaO	91.17	52.46	49.80	51.55	46.65 – 52.46
Na_2O	-	0.22	TR	TR	TR – 0.06
K_2O	0.40	0.18	TR	TR	TR – 0.06
LOI	-	40.38	39.65	40.76	39.65 – 40.86
$CaCO_3$	68	93.90	89.14	92.27	83.50 – 93.90
$MgCO_3$	-	2.57	3.09	1.32	0.63 – 2.57
TC	-	96.47	92.23	93.59	56.63 – 96.47
S/R	1.05	2.14	3.10	2.53	1.77 – 3.10
A/R	1.43	1.67	0.48	1.94	0.48 – 5.66
LSF	610.96	417	242	320	160 – 417

TR – Trace

i - Limestone sample

ii - Marble sample

iii - Limestone sample

Reference limestone samples are obtained from Cement Technology Course Volume (Blue Circle Industries, 1987)

Cement clinker is made by combining proper ratios of the chemical components: Silica Ratio (SR), Alumina Ratio (AR), and Lime Saturation Factor (LSF) to regulate the clinker's composition. The ratios are calculated using the oxide values CaO, SiO_2, Al_2O_3, and Fe_2O_3. The following are the SR, AR, and LSF values for the conventional cement kiln feed for the marble samples:

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad \text{——— Equation 3}$$

$$= \frac{4.17}{2.57 + 0.40} = 1.05$$

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad \text{——— Equation 4}$$

$$= \frac{2.57}{0.40} = 1.43$$

$$LSF = \frac{100(CaO)}{2.8(SiO_2) + 1.2(Al_2O_3) + 0.65(Fe_2O_3)} \quad \text{——— Equation 5}$$

$$= \frac{100(91.40)}{2.8(4.17) + 1.2\ (2.57) + 0.65\ (0.40)}$$

$$= 610.96$$

The recommended SR, AR and LSF values for marbles in production of cement are 1.9 – 3.2, 1.5 – 2.5 and 242 – 417 respectively (Onimisi *et al*., 2017). The calculated SR, AR and LSF values for Igue marble are 1.05, 1.43 and 610.96 respectively. The SR and LSF do not meet the recommended range. The LSF exceeds the permissible limit of 417, but the Igue marble can still be used if the LSF value is modified to fall within the approved range for cement manufacturing. This can be achieved by mixing with appropriate amounts of lateritic clay to improve its silica, alumina and iron respectively (Panda, 2016).

4.4 TERNARY PLOT OF GEOCHEMICAL SAMPLES

Figure 4.1 is a ternary plot of CaO-SiO_2-Fe_2O_3 which illustrates that all samples are plotting towards CaO indicating extremely high amounts of CaO. Low percentages of iron oxides indicate lack of Iron bearing minerals such as siderite, magnetite, limonite, hematite etc.

From the plot IG1 has higher amount of SiO_2 (10.36 wt. %) which is an indication that SiO_2 in carbonate rocks comes from both silicate minerals and chert nodules resulting from the influx of near shore siliciclastic materials into the basin of the original limestone deposit which was metamorphosed into marble (Brownflow, 1996).

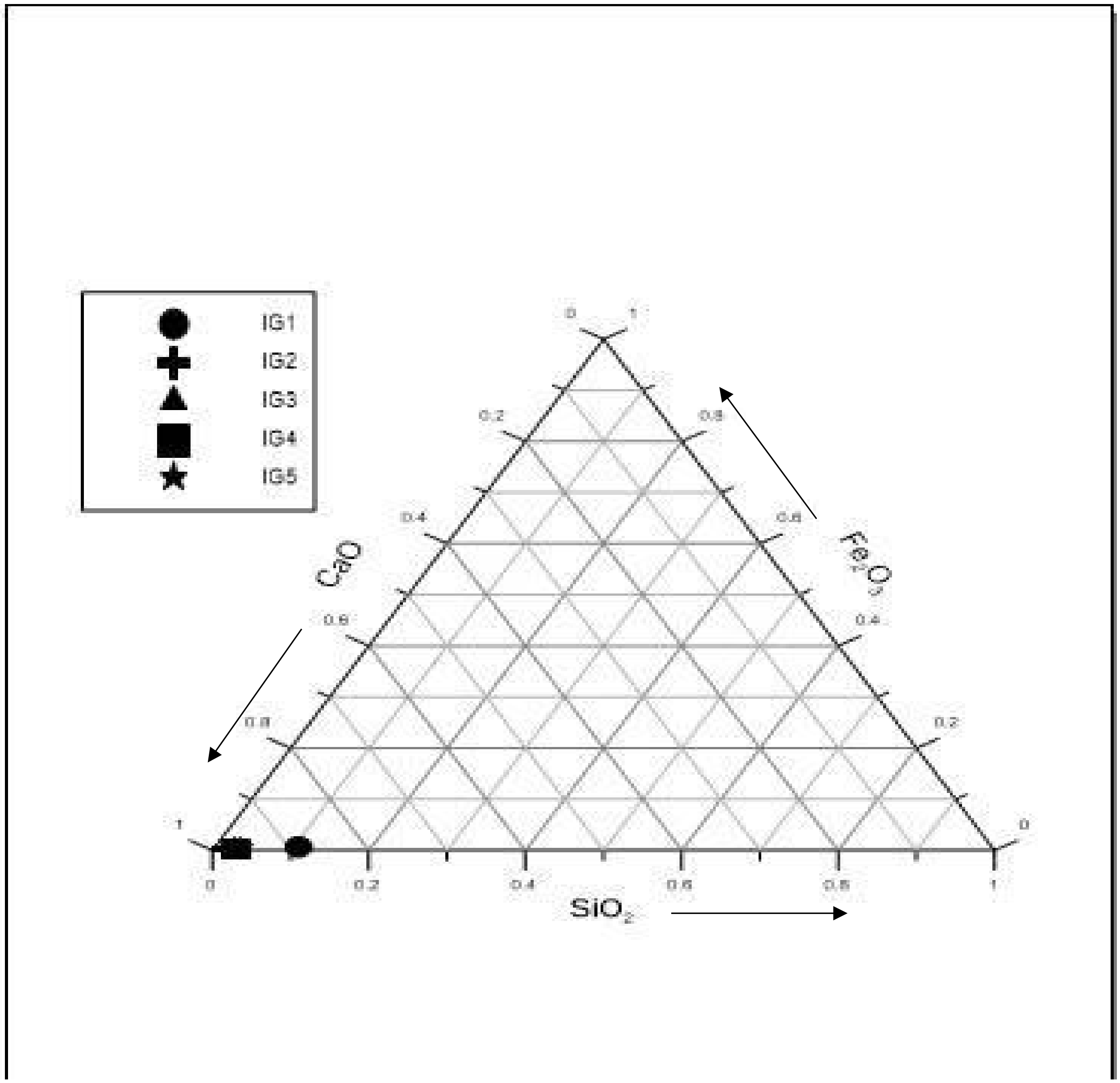

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Figure 4.1: The Ternary Plot of CaO-SiO_2-Fe_2O_3 Showing Positions of the Igue samples.

4.5 MINERALOGY

Table 4.4 shows the modal composition of minerals obtained from the XRD analysis.

Table 4.4: Modal composition of minerals from Igue area (wt. %).

Mineral	Formula	IG1	IG2	IG3	IG4	IG5
Calcite	$CaCO_3$	60.0	67.0	64.0	66.5	68.0
Quartz	SiO_2	20.7	13.0	17.0	8.0	15.0
Orthoclase	$KAlSi_3O_8$	6.6	2.0	8.3	14.0	7.4
Lime	CaO	4.5	7.0	8.7	5.9	6.4
Illite	$(KH_3O)Al_2Si_3AlO_{10}(OH)_2$	8.0	11.0	2.0	5.6	3.2
Others		0.20	0.00	0.00	0.00	0.00
Total		100.0	100.0	100.0	100.0	100.0

Calcite occurs in the five (05) location ranges (60-68%), quartz ranges from (8-20.7%), orthoclase occurrence is from (2.0-14%), lime ranges from (4.5 -8.7%), illite occurrence is from (2-11%), according to the analytical results of the XRF analysis on Igue marble in Table 4.4. Calcite has the highest mineral composition, while lime has the lowest mineral composition. The relationship between calcite and lime is that lime is a product of calcite. Hence, lime probably formed during metamorphism as a result of heat. The samples primarily consist of calcite, quartz, orthoclase, and lime. Weathering of orthoclase probably results in the formation of illite. Quartz is the second most abundant mineral which tallies with the geochemical analysis.

From the diffractograms, IG2 and IG5 have the highest calcite values with 67 and 68 %, respectively. IG1 has calcite value of 60%. However, Dolomite content is not present in the sample because there is no presence of magnesium minerals. The presence of fine grained clay mineral (illite) in the marble supports the evidence that the original limestone which metamorphosed were probably marine sediments of marls, clay and arkose particles.

The formation and presence of illite is probably from the weathering of feldspars which is in line with the kind of feldspar present (orthoclase).

Calcite is an indication of influx of Ca- rich minerals into the basin of deposition before metamorphism occurred. It was discovered that the Igue-Oke marble is used for the production of antacids which cures of stomach ache (Obasi and Isife, 2012). Igue-Oke marble is also used for sculpture, tiles, chips, decorative uses and for construction etc. (Odokuma-Alonge *et al*., 2019)

4.6 TERNARY PLOT OF MINERALOGICAL SAMPLES.

Figure 4.2 shows the ternary plot of $CaCO_3$-SiO_2-$KAlSi_3O_8$ which proves that the Igue marble are largely calcitic marbles with a reasonable amount of quartz and low percentages of orthoclase. This is indicative of influx of Ca- rich minerals into the basin of deposition and this makes Igue marble suitable for several industrial applications such as cement production, fertilizers as well as lime production and sewage treatment.

The presence of quartz indicates that the original composition of the rock (calcareous sedimentary rock) had presence of quartz before it was metamorphosed into marble. The high amount of calcite implies that the rock could be used in enhancing soil pH.

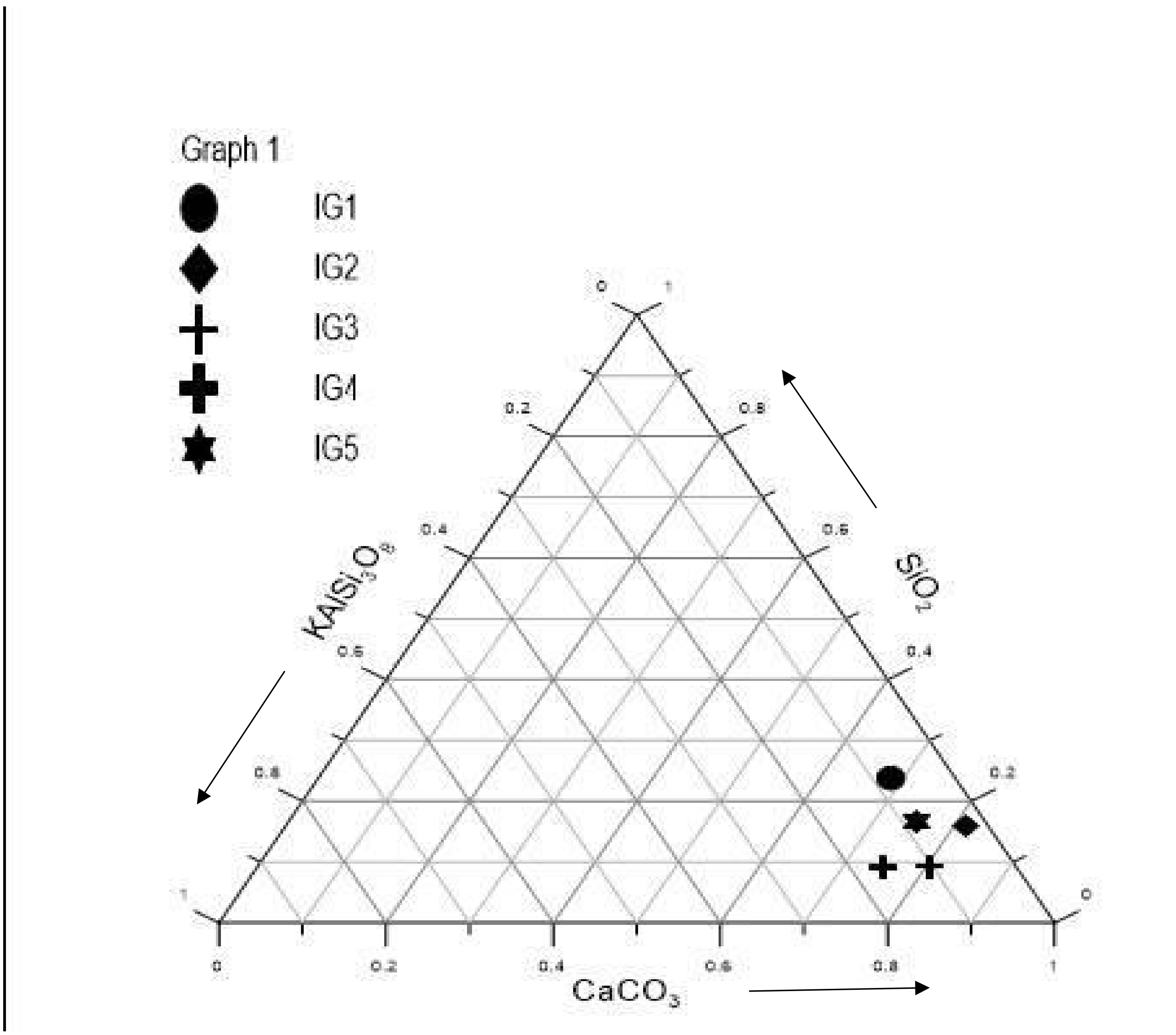


Figure 4.2: The Ternary Plot of $CaCO_3$-SiO_2-$KAlSi_3O_8$ Showing Positions of the Igue Samples.

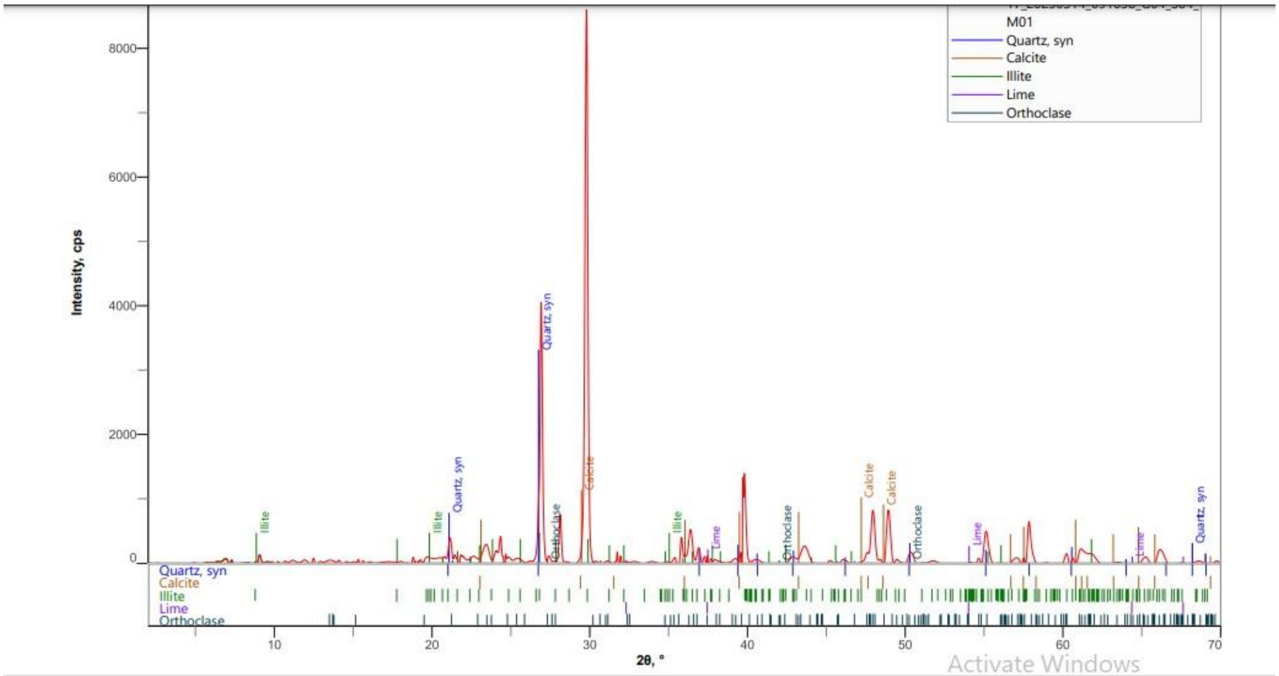
4.7 D – SPACING AND 2θ VALUES.

D-spacing is the interplanar spacing in a crystal lattice that represents the distance between consecutive planes of atoms within a crystal. The d-spacing is of utmost importance because these values are unique to the orders of the calcite. The 2θ value relays its relative abundance and intensity of the mineral. Table 4.5 illustrates the d-spacing and 2θ values of the dominant minerals. The unit of d-spacing is Angstrom units – 10^{-8} cm.

Table 4.5: D-spacing and 2θ values of the dominant minerals.

ORDERS	**IG1**	**IG2**	**IG3**	**IG4**	**IG5**
2θ (calcite)					
First order	29.75	31.08	29.70	29.70	29.72
Second order	43.56	43.48	47.87	47.42	47.50
Third order	47.93	47.42	48.84	47.78	47.89
D-spacing (Å)					
First order	2.99	2.86	3.00	3.01	3.00
Second order	2.08	2.07	1.89	1.91	1.91
Third order	1.89	1.92	1.86	1.90	1.89
2θ (quartz)					
First order	26.89	25.89	26.79	26.84	26.76
Second order	24.32	48.80	23.37	23.34	23.79
Third order	66.10	65.96	57.78	51.04	51.00
D-spacing (Å)					
First order	3.65	3.31	3.80	3.81	3.81
Second order	3.31	1.86	3.32	3.31	3.32
Third order	3.18	1.42	1.59	1.54	1.59

The results of the mineralogical analysis showing the diffractograms and pie charts are presented in Figures 4.3a – 4.7b



Path: C:\WallPaper\14-03-2023\KOSONYEME DANIELLA\SAMPLE IG (1) 17 Solution.rmrsln

Solution

Plot of results

SAMPLE IG (1) 1720230314_091638_G04_S04_M01

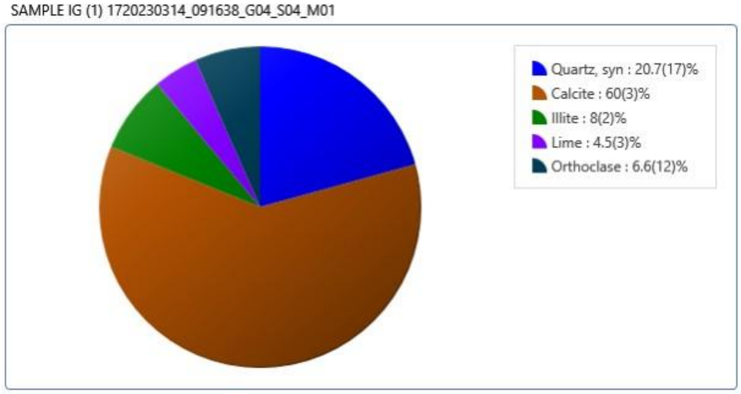
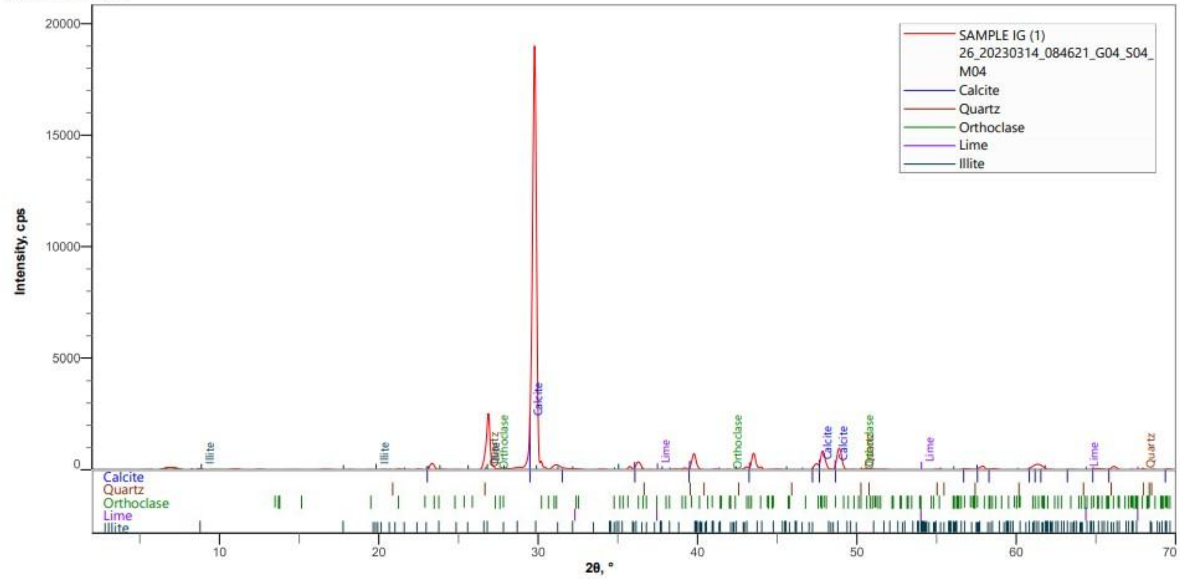


Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Quartz, syn	Calcite	Illite	Lime	Orthoclase
SAMPLE IG (1) 17_20230314_09...	0	20.7(17)	60(3)	8(2)	4.5(3)	6.6(12)

Figures 4.3a and 4.3b: X-ray Diffractogram and Pie Chart for IG1

Phase Data View



Plot of results

SAMPLE IG (1) 2620230314_084621_G04_S04_M04

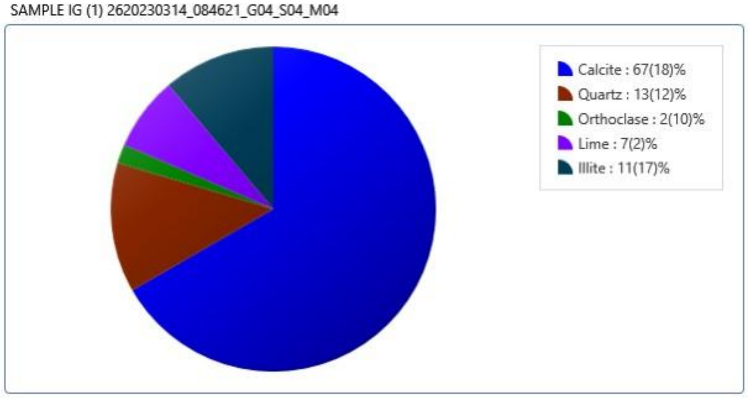
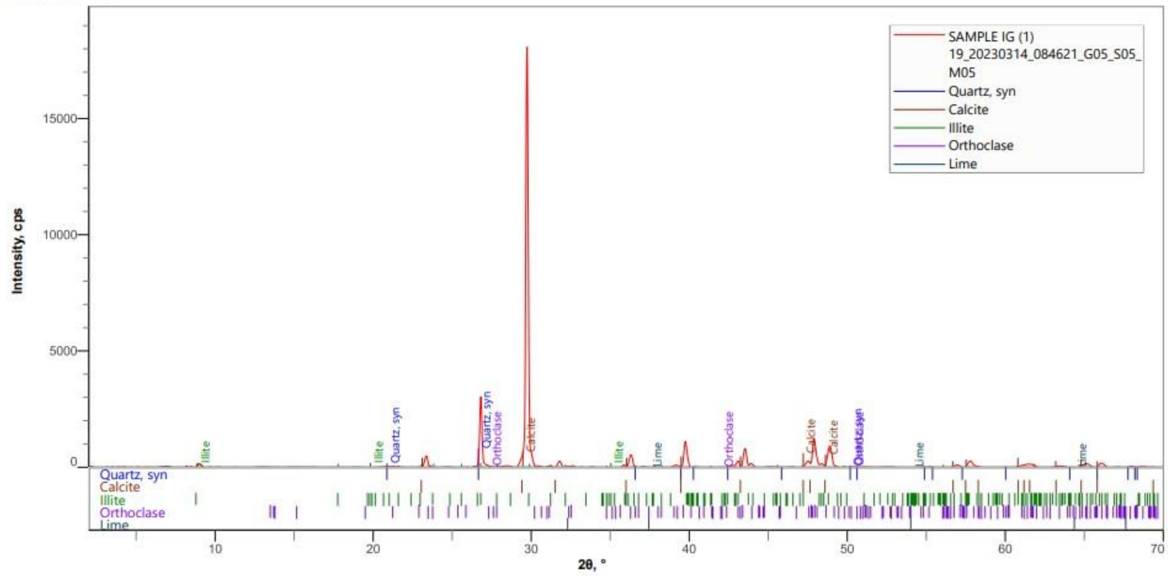


Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Calcite	Quartz	Orthoclase	Lime	Illite
SAMPLE IG (1) 26_20230314_08...	0	67(18)	13(12)	2(10)	7(2)	11(17)

Figures 4.4a and 4.4b: X-ray Diffractogram and Pie Chart for IG2

Phase Data View



Path: C:\WallPaper\14-03-2023\KOSONYEME DANIELLA\SAMPLE IG (1) 19 Solution.rmrsln

Solution

Plot of results

SAMPLE IG (1) 1920230314_084621_G05_S05_M05

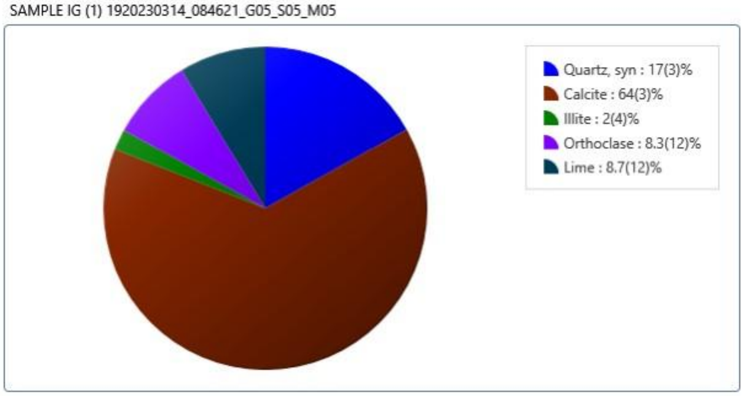
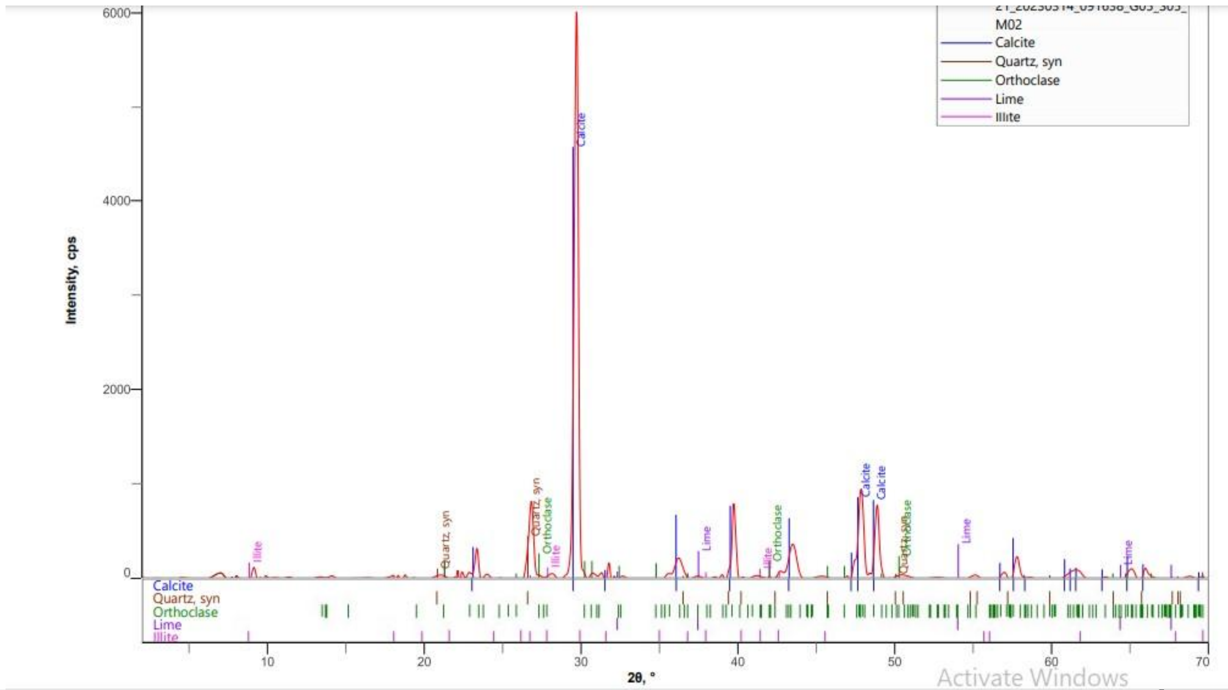


Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Quartz, syn	Calcite	Illite	Orthoclase	Lime
SAMPLE IG (1) 19_20230314_08...	0	17(3)	64(3)	2(4)	8.3(12)	8.7(12)

Figures 4.5a and 4.5b: X-ray Diffractogram and Pie Chart for IG3



Path: C:\WallPaper\14-03-2023\KOSONYEME DANIELLA\SAMPLE IG (1) 21 Solution.rmrsln

Solution

Plot of results

SAMPLE IG (1) 2120230314_091638_G05_S05_M02

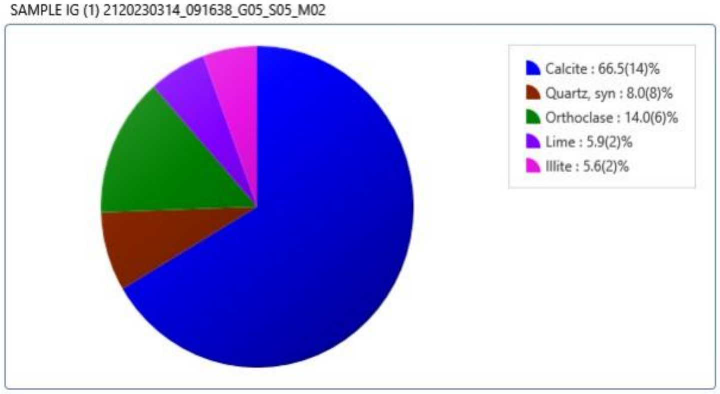
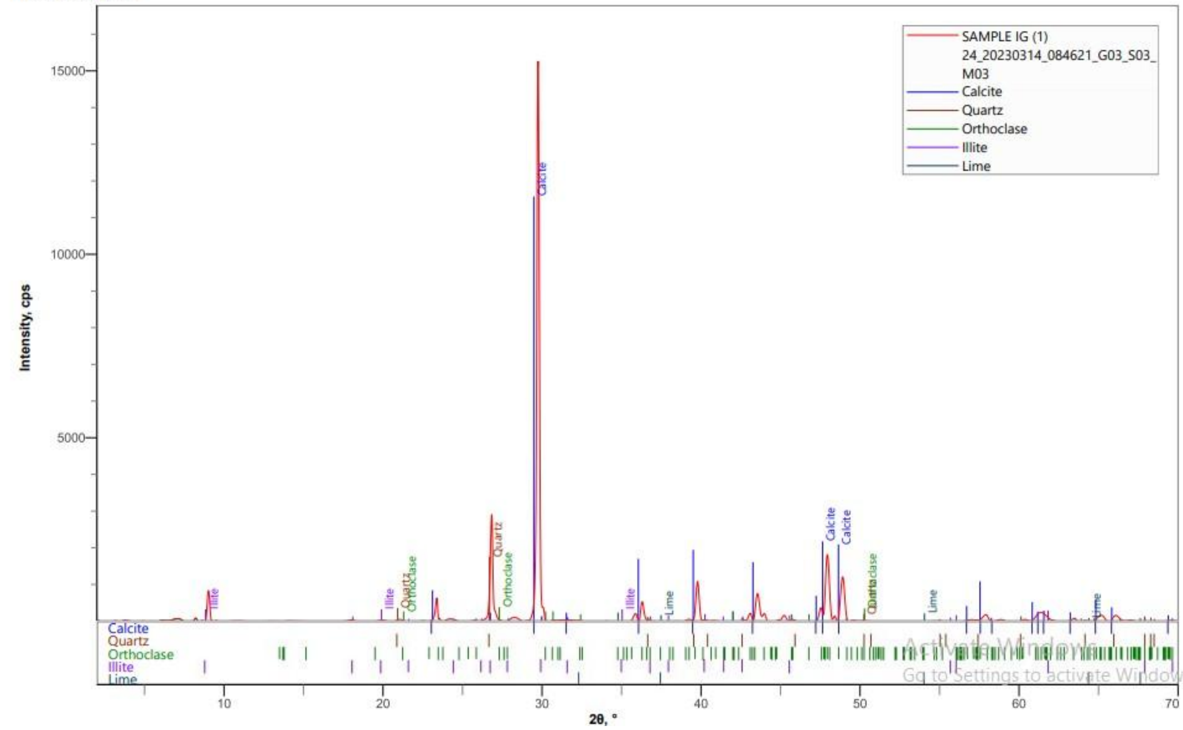


Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Calcite	Quartz, syn	Orthoclase	Lime	Illite
SAMPLE IG (1) 21_20230314_09...	0	66.5(14)	8.0(8)	14.0(6)	5.9(2)	5.6(2)

Figures 4.6a and 4.6b: X-ray Diffractogram and Pie Chart for IG4

Phase Data View



Path: C:\WallPaper\14-03-2023\KOSONYEME DANIELLA\SAMPLE IG (1) 24 Solution.rmrsln

Solution

Plot of results

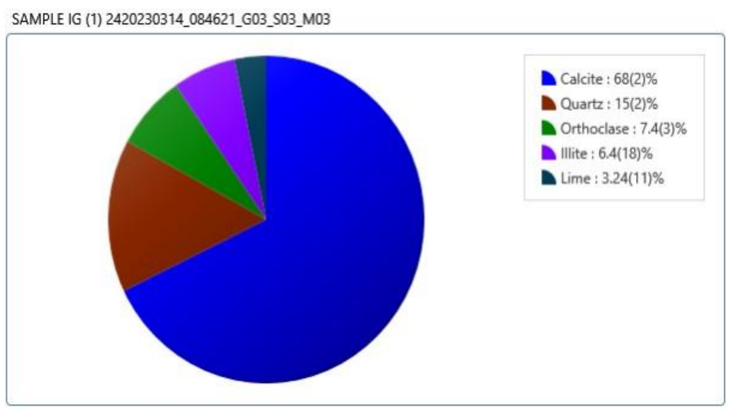


Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Calcite	Quartz	Orthoclase	Illite	Lime
SAMPLE IG (1) 24_20230314_08...	0	68(2)	15(2)	7.4(3)	6.4(18)	3.24(11)

Figures 4.7a and 4.7b: X-ray Diffractogram and Pie Chart for IG5

CHAPTER 5

SUMMARY, CONCLUSION AND SUGGESTIONS FOR FURTHER STUDIES.

5.1 SUMMARY

Marble samples were collected from Owan East Local Government area of Edo State with the aim of qualifying the marbles using geochemical and mineralogical properties utilizing XRD and XRF techniques and determining its economic importance. The analysis carried out in the laboratory revealed that the Igue marbles are calcitic marbles. Table 4.1 shows major element composition from XRF analysis in the marble samples. Table 4.2 is a comparison of the chemical composition of Igue marble with calcitic and dolomitic marbles. Table 4.3 portrays the mean chemical composition of Igue marble and reference of limestone and marble used for cement production. The calculated SR, AR and LSF values for Igue marble are 1.05, 1.43 and 610.96 respectively. The LSF exceeds the permissible limit of 417, but the Igue marble can still be used if the LSF value is modified to fall within the approved range for cement manufacturing. Figure 4.1 and 4.2 illustrates the ternary plot of minerals showing positions of the samples. Table 4.4 portrays the modal composition of minerals from Igue area. Figures 4.3a-4.7b shows X-ray diffractograms and pie charts of the minerals. The d-spacing and 2θ values portrays the reactivity of the orders of minerals and also their relative abundance.

5.2 CONCLUSION

The Igue marble form a part of the Igarra Schist belt which is intruded by the Pan African Granites. The marble varieties at Igue and environs are highly calcitic and comprises rocks that were formed at low- medium grade metamorphism. Igue marble also do not meet the permissible limit for cement production because the LSF values exceeded the permissible limit but can be used if subjected to beneficiation. From the XRD analysis, calcite is the most abundant mineral (60% - 68%). Dolomite is not present in the sample, hence the Igue marble is a calcitic marble. Igue marble is used for the production of antacids, sculptures, tiles, chips and decorative uses.

5.3 SUGGESTIONS FOR FURTHER STUDIES.

1. Further geochemical analysis using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) can be used to discover trace elemental composition for effective characterization.
2. Further studies should be carried out to determine the appropriate amounts of lateritic clay to improve its silica, alumina and iron respectively on the marbles.

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