GEOCHEMICAL AND MINERALOGICAL ANALYSIS OF MARBLE IN UBO AND IKPESHI AREAS, SOUTHWESTHERN NIGERIA.

BY

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UNIVERSITY OF BENIN,

BENIN CITY

SEPTEMBER, 2023.

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A PROJECT WORK SUBMITTED TO THE DEPARTMENT OF SCIENCE LABORATORY TECHNOLOGY, FACULTY OF LIFE SCIENCES, UNIVERSITY OF BENIN, BENIN CITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE DEGREE (B.Sc.) IN SCIENCE LABORATORY TECHNOLOGY (GEOLOGY AND MINING TECHNIQUES).

SEPTEMBER, 2023.

CERTIFICATION

This is to certify that this project work described in this work was carried out by Valerie Ibhade DANIEL-EHIGHALUA with Matriculation number **LSC1706017** in the Department of Science Laboratory Technology, Faculty of Life Sciences, University of Benin, Benin-City, Edo State, Nigeria.

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EXTERNAL EXAMINER DATE

DEDICATION

This project work is dedicated to God Almighty for unending mercies and support towards the completion of this research.

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ABSTRACT

Five (05) marble samples were obtained from Ubo and Ikpeshi areas Southwest Nigeria with the aim of identifying the chemical composition, mineralogical characteristics, and geological origin of the marble. The samples were subjected to X-ray Diffraction and X-ray Fluorescence analysis. Findings revealed the presence of Calcite (1.6-65%), Quartz (14.1-44.0%), Muscovite (3.0-37%), Orthoclase (2-30%), Anorthite and Anthophyllite with modal abundance of 8% and 18% at UB1 and UB2, respectively. The result from geochemical analysis reveals the presence of SiO_2 (3.91- 47.3wt.%), Al_2O_3(2.61-8.20wt.%), Fe_2O_3 (0.17-7.04wt.%), CaO (31.4-88.8wt.%) and MgO, MnO, K_2O, P_2O_2 having <1wt.%. The low values of the total alkali content in the marble samples from the two sites suggest that the environment of deposition of the original carbonate material that underwent metamorphosis to become marbles from both sites must have been that of a shallow, highly saline environment. The marble deposits are not good raw materials for cement production due to its relatively low value of silica and alumina. However, they are suitable for pesticide production and soil liming. Further geochemical analysis can be achieved to determine their trace elements constituents.

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CHAPTER ONE

INTRODUCTION

1.1.GENERAL STATEMENT

Marbles are generally metamorphic derivatives of sedimentary carbonates. They have been known to be relatively impermeable during metamorphism (Chaanda *et al*., 2019). The exploitation of marble deposits in regions such as Ikpeshi, Igwe, Okpella, Ubo, and Obajana, particularly around Igarra, is prevalent for the production of Portland cement, dimension stones, and construction and monumental purposes (Elueze *et al*., 2015; Jimoh *et al*., 2016).Igarra area in Edo State, Nigeria, is endowed with large marble deposit associated with biotite schists and gneisses. The marble deposits with the above phrase are been exploited and mined for many purposes. The quest for exploitation of valuable mineral resources in the earth to satisfy human wants has given rise to technological development in mining industry. This demonstrate the best mining methods that fits the geometry and the structural orientation of the deposit which is to be mined within the limits allowable safety standard, technology, and economics, with the lowest cost and return of maximum profit (Saliu and Komalafe, 2014).. Since the only practical way to extract minerals for industrial application is through mining; the impact of mining cannot be over-emphasized.

In Nigeria, marble bodies are being extensively mined and utilized as essential ingredients in various industrial products and processes. Marble exhibits a wide range of applications, making it a versatile and valuable material. It can be crushed to produce terrazzo chips, concrete aggregate, ballast, and road stone. When cut or shaped, marble finds utility as travertine for walls, flooring slabs, furniture, paving, kerbs, and building stones. Its crystals are utilized in the manufacturing of nicol prisms for petrological microscopes. Furthermore, marble is milled to harness its optical properties and pigments, including precipitated calcium carbonate (PCC), lake pigments, white wash, paints, paper fill, paper coating, plastic, rubber, linoleum, and painting links. It can be precipitated as aerosols for mine dusting, printing, and rolls, as well as used as abrasives in toothpaste, tooth powders, and polishing powders. Additionally, precipitated marble serves as fillers for cosmetics, particularly face powders, adhesives, and pharmaceuticals, including tableted goods and antibiotics (Odokuma-Alonge, 2019).

Previous investigations have focused on exploring the distribution, applications, and industrial potentials of specific deposits (RMRDC, 2010a; RMRDC, 2010b). However, a comprehensive mineralogical and geochemical investigation of marble in Ubo and Ikpeshi area is crucial to unravel the geological secrets and enhance its utilization across industries.

1.2.AIM AND OBJECTIVES OF THE STUDY

1.2.1. Aim: The aim of this research is to conduct a comprehensive geochemical and mineralogical analysis of marble deposits in the Ubo and Ikpeshi areas. The study aims to identify the chemical composition, mineralogical characteristics, and geological origins of the marble, providing valuable insights into its formation and potential industrial applications.

1.2.2. Research Objectives: The objectives include:

- To determine the major element composition of the marble samples collected from Ubo and Ikpeshi areas through geochemical analysis.
- To identify the mineralogical composition of the marble samples using X-ray diffraction (XRD).
- To contribute to the existing scientific literature on marble and update the existing geological map.

1.3.Location of Study area

The study area is located in Ubo and Ikpeshi, Southwestern Nigeria and lies between latitudes N07° 8' 47" - N07° 25' 18" and longitudes E06° 10^{1} 54^{4} – E06° 24' 35" of Auchi Sheet 266 on a scale of 1:100,000 with an area extent of 420.86km^2. (Fig 1.1)

1.4.Accessibility

The study area, Ubo and Ikpeshi, exhibits varying levels of accessibility, with some areas being moderately accessible while others pose significant challenges due to dense vegetation and uneven terrain, particularly the slopes between lowland and hills.The area is essentially made up of basement rocks and thus has a very rough and rugged topography (Ailegbo *et al.,*2021).

1.5.Topography:

The topography of the area presents the general configuration of the land surface (geomorphology). It is characterized by gentle, steep, and rugged topography with high relief. It featured mainly basement complex rocks with some of these rocks exposed as high ridges and valleys because of tectonic activities and erosion with the rocks having an important effect on the soil of the area (Odeyemi, 1976).

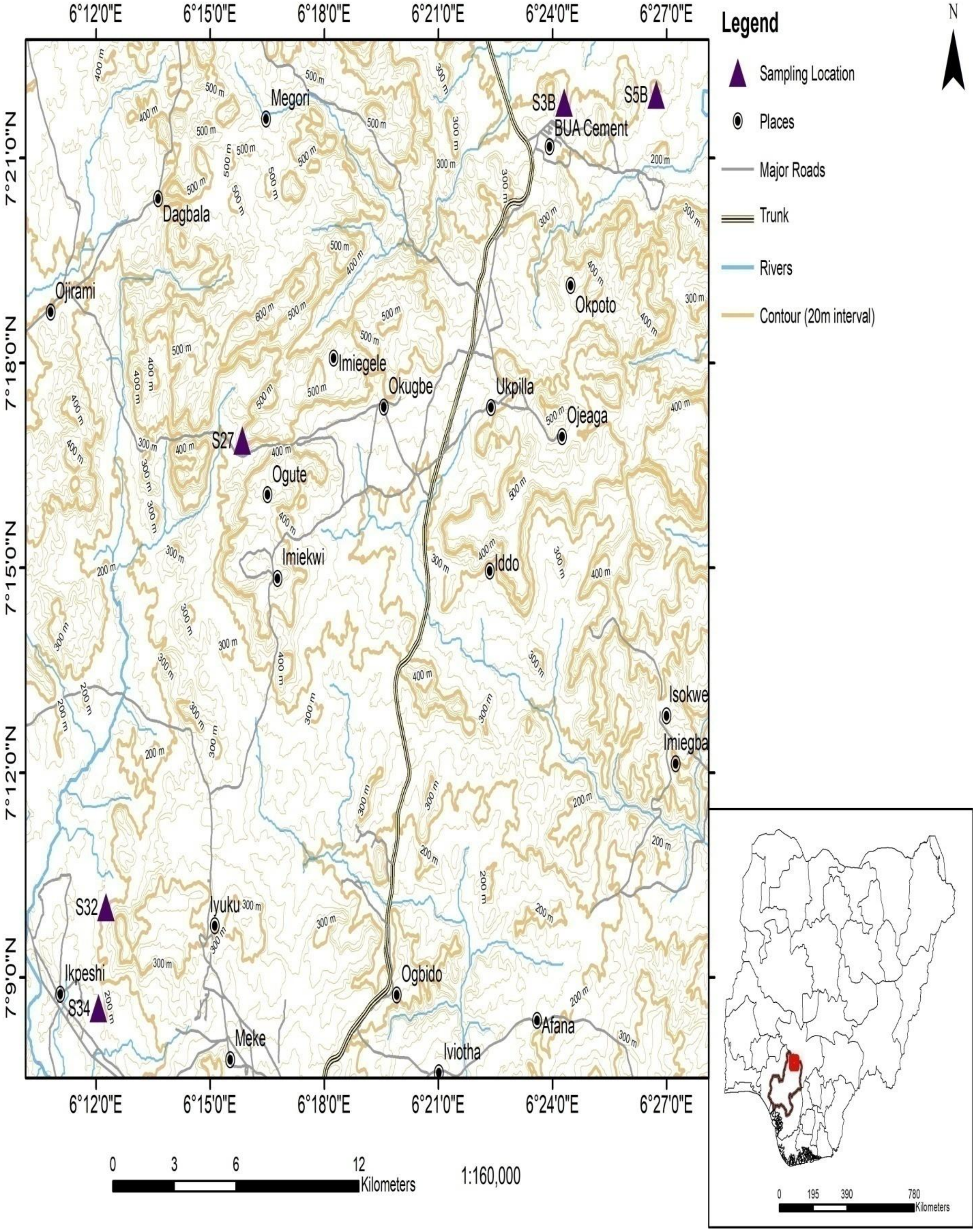


Fig.1.1: Location map of the Study Area (Source: GSN, 1974)

1.6. Climate, Vegetation, and Soil:

The region has a warm climate with little or no variation depending on the amount of rainfall. The average temperature is between 24˚C and 28˚C (Eludoyin *et al.*, 2014). Humidity is constantly high, and the area has a savannah climate that experiences both rainy and dry seasons. The rainy season usually begins with southwest winds from April to October with the peak period in July and August every year. The total amount of precipitation ranges from 1270 mm to 1790 mm (N.M.A. 2018). Furthermore, dry season begins from November to March, which marked by the northeast, cold, and dry harmattan wind usually blown from the Sahara Desert (Ileoje, 2001).

The climate and topography play an important role in the vegetation of the area. The vegetation is more dense in low-lying areas and sparse in the upland area due to abundant runoffs from crystalline rocks (Ailegbo *et al.,*2021).

1.7.Human Activities

The people of Ubo and Ikpeshi in Akoko Edo engage in various human activities that contribute to the local economy and community life. Agriculture, artisanal mining, traditional crafts, trade, and cultural festivals are prominent. Agriculture is vital, with crops, livestock farming, and cash crops. Artisanal mining involves extraction of minerals. Traditional crafts include pottery, weaving, woodcarving, and blacksmithing. Trading in local markets is active, and cultural festivals attract tourists. These activities drive economic growth, preserve cultural heritage, and foster community interactions in the region.

CHAPTER TWO

LITERATURE REVIEW/GEOLOGICAL SETTING

2.1. GENERAL GEOLOGY

The geology of Nigeria is made up of three major litho-petrological components, namely, the *Basement Complex*, *Younger Granites*, and *Sedimentary Basins* .The Basement Complex is one of the three major litho-petrological components that make up the geology of Nigeria and the rocks are truncated by the sedimentary rocks in almost equal proportions. The crystalline rocks are of two age groups, the Precambrian age and the Younger Granites of Jurassic age. The sedimentary sequences are Cretaceous to Quaternary in age and spread across five sedimentary basins (Fig. 2.1).The Precambrian rocks of southwestern Nigeria is part of the Precambrian Basement Complex of Nigeria. The Basement Complex is made up of Gneiss-migmatite Complex and the Pan African Older Granite rocks and schist rocks. These rocks have undergone polycyclic deformation thereby causing the deformation of both the macro and micro structures. Secondary structures in rocks that can be used as clues to determine the geologic history of an area include; joints, folds, fractures and foliations etc. Some of these structures are not deformational but were formed at the same time the rocks were emplaced. A lot of literatures abound on the study of Basement Geology of Nigeria and its associated structures which include (Anifowose and Borode, 2007) who noted that joints ranging from minor to major ones are found in all the rock types, some of which are filled with quartz, feldspars or a combination of both. They lie generally in the NE-SW direction.

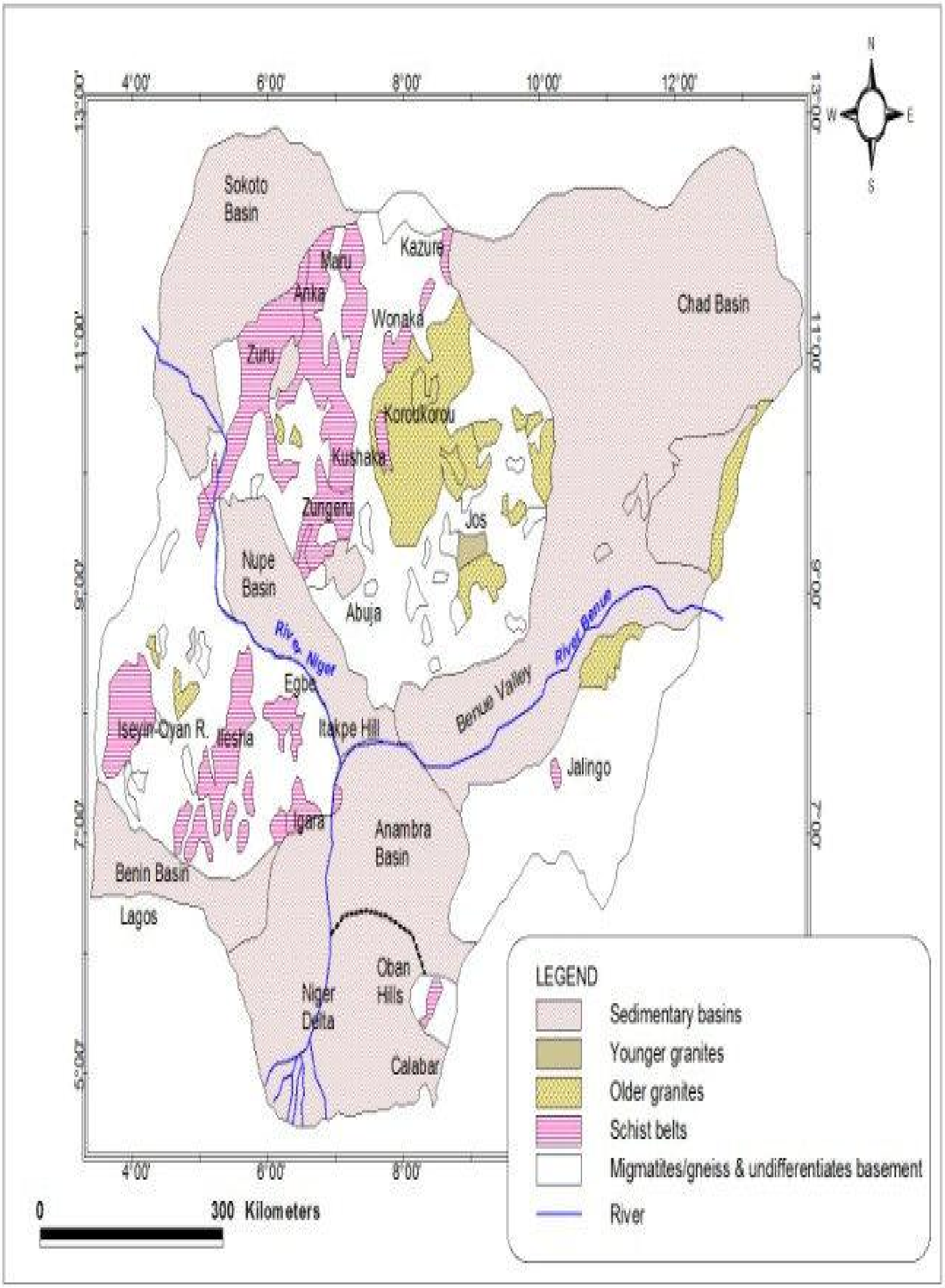


Fig 2.1: Generalized Geological Map of Nigeria showing the Basement Complex (Akinola *et al.,* 2014)

Within the Basement Complex of Nigeria four major petro-lithological units are distinguishable as identified by Dada, (2006).

1. The Migmatite – Gneiss Complex (MGC)
2. The Schist Belt (Metasedimentary and Metavolcanic Rocks)
3. The Older Granites (Pan African Granitoids)
4. Undeformed Acid and Basic Dykes

2.1a. The Migmatite – Gneiss Complex (MGC)

The Migmatite – Gneiss Complex is generally considered as the Basement Complex *sensustricto* (Rahaman, 1988; Dada, 2006) and it is the most widespread of the component units in the Nigerian basement. It has a heterogeneous assemblage comprising migmatites, orthogneises, paragneisses, and a series of basic and ultrabasic metamorphosed rocks.

2.1b. The Schist Belt (Metasedimentary and Metavolcanic Rocks)

The Schist Belts comprise low grade, metasediment-dominated belts trending N–S which are best developed in the western half of Nigeria .These belts are considered to be Upper Proterozoic supracrustal rocks which have been infolded into the migmatite-gneiss-quartzite complex. The lithological variations of the schist belts include coarse to fine grained clastics, pelitic schists, phyllites, banded iron formation, carbonate rocks (marbles / dolomitic marbles) and mafic metavolcanics (amphibolites). Some may include fragments of ocean floor material from small back-arc basins. Rahaman (1976) and Grant (1978) for example suggest that there were several basins of deposition whereas Oyawoye (1972) and McCurry (1976) consider the schists belts as relicts of a single supracrustal cover. Olade and Elueze(1979) however consider the schist belts to be fault-controlled rift-like structures.

2.1c. The Older Granites (Pan African Granitoids)

The term "Older Granite" was introduced by Falconer (1911) to distinguish the deep-seated, often concordant or semi-concordant granites of the Basement Complex from the high-level, highly discordant tin-bearing granites of Northern Nigeria. The Older Granites are believed to be pre-, syn- and post-tectonic rocks which cut both the migmatite-gneiss-quartzite complex and the schist belts(Wilson, 1989)

2.1d. Undeformed Acid and Basic Dykes:

The undeformed acid and basic dykes are late to post-tectonic Pan African. They cross-cut the Migmatite-Gneiss Complex, the Schist Belts and the Older Granites (Dada, 2006). The undeformed acid and basic dykes.

a. Felsic dykes that are associated with Pan African granitoids on the terrain such as the muscovite, tourmaline and beryl bearing pegmatites, microgranites, aplites and syenite dykes etc. (Dada, 2006).

b. Basic dykes that are generally regarded as the youngest units in the Nigerian basement such as dolerite, dykes and the less common basaltic, felsite and lamprophytic dykes also occur.

2.2. LOCAL GEOLOGY

The study area Ubo and Ikpeshi belongs to the Southern Basement Complex of Nigeria which is underlain by rocks of the Precambrian Basement Complex. About four major groups have been observed within this area. These are the migmatite-gneiss complex, the metasediments (schists, calc-silicate rock, quartzites, marble, metaconglomerates) and the porphyritic Older Granite which have discordant, non metamorphosedsyenite dyke (Odeyemi, 1976).

Touret, (1977) suggested that the formation of calc-gneiss is probably a reaction between calcite derived from marl sediments or original limestone and quartz from detrital grains during metamorphism. The area experienced later phases or episodes of intrusions resulting in dykes, batholiths, laccoliths and discordant dykes. The major and minor igneous rocks are charnockites, porphyritic granites, aplites and pegmatites, respectively.

Rocks around Ikpeshi in the Igarra schist belt consist of a highly deformed metamorphic suite, which have been intruded by igneous plutons of Pan-African age (Aguomo and Egesi, 2016).The granite in the area has dome-shaped range with white coloured phenocrysts. The rocks are fairly well exposed with the level of exposure approaching sixty percent in some places. These like the Igarra plutons are dome-shaped and contain small whitish phenocrysts intruding basically schist and rarely metaconglomerate and calc-silicate rocks.

The area is underlain by metasediments known as the Igarra Schist Belt, which Rahaman (1988) describes as "metamorphosed pelitic to semi-pelitic rocks, Granite polymict." Metaconglomerate, calcareous rocks, malfic to ultramafic rocks with a tiny quantity of Greywacke, and acid to moderate volcanic rocks are all present.

The region comprises a diverse geological assemblage, including a variety of rocks, with the Igarra metasediments being a significant component. These metasediments consist of several rock types, such as quartz-biotite schist, paragneiss, marble, calc-silicate gneiss, polymictmeta conglomerate, mica schist, phyllite, and quartzite (Odeyemi, 1977, 1988; Obasi and Anike, 2012; Jimoh *et al.,* 2016).

One essential rock type within the metasediments is marble. Marble is a metamorphic rock that forms from the recrystallization of limestone under high temperature and pressure conditions. In the Igarra region, limestone deposits likely underwent metamorphism due to tectonic forces and geological processes over millions of years, resulting in the formation of marble. The presence of marble alongside other rocks like schist, gneiss, metaconglomerate, and others indicates a complex geological history for the region. The metamorphism and deformation of these different rock types suggest a dynamic geological environment during their formation.

The intrusion of rocks (porphyritic granite, granodiorite, syenite, pegmatite, and aplite) of Pan-African age (600 + 150 Ma), suggests that during the Pan-African orogeny around 600 million years ago, molten magma intruded into the pre-existing rocks of the Igarra region. These intrusive rocks are younger than the metasediments and likely played a role in the further metamorphism and alteration of the surrounding rocks, including marble.

Additionally, the minor basic rocks like dolerite and lamprophyre as intrusives in the Igarra Schist Belt indicates later volcanic activities in the region. These basic rocks have intruded the existing metasediments and contributed to the geological complexity of the area.

Figure 2.3 shows the rocks in the study area from the oldest to the youngest are the migmatite-gneiss complex which is overlain by quartzite, followed by the carbonate rock such as marbles with calc-gneisses closely associated with the marbles and the Younger metasediments and the Pan African rocks (Rahaman, 1988; Odeyemi, 1988);

Plates 2.1 -2.4 shows boulders and outcrops of calcite marble at Freedom quarry in the study area. Marble is found in the north- eastern part of the area and active quarries are observed in many parts (Ailegbo *et al.,*2021). The marble in Ikpeshi as seen in Plate 2 varies in colour from whitish, pinkish to grey, while the texture ranges from fine, medium to coarse which are generally known as non-foliated rocks although some are foliated.

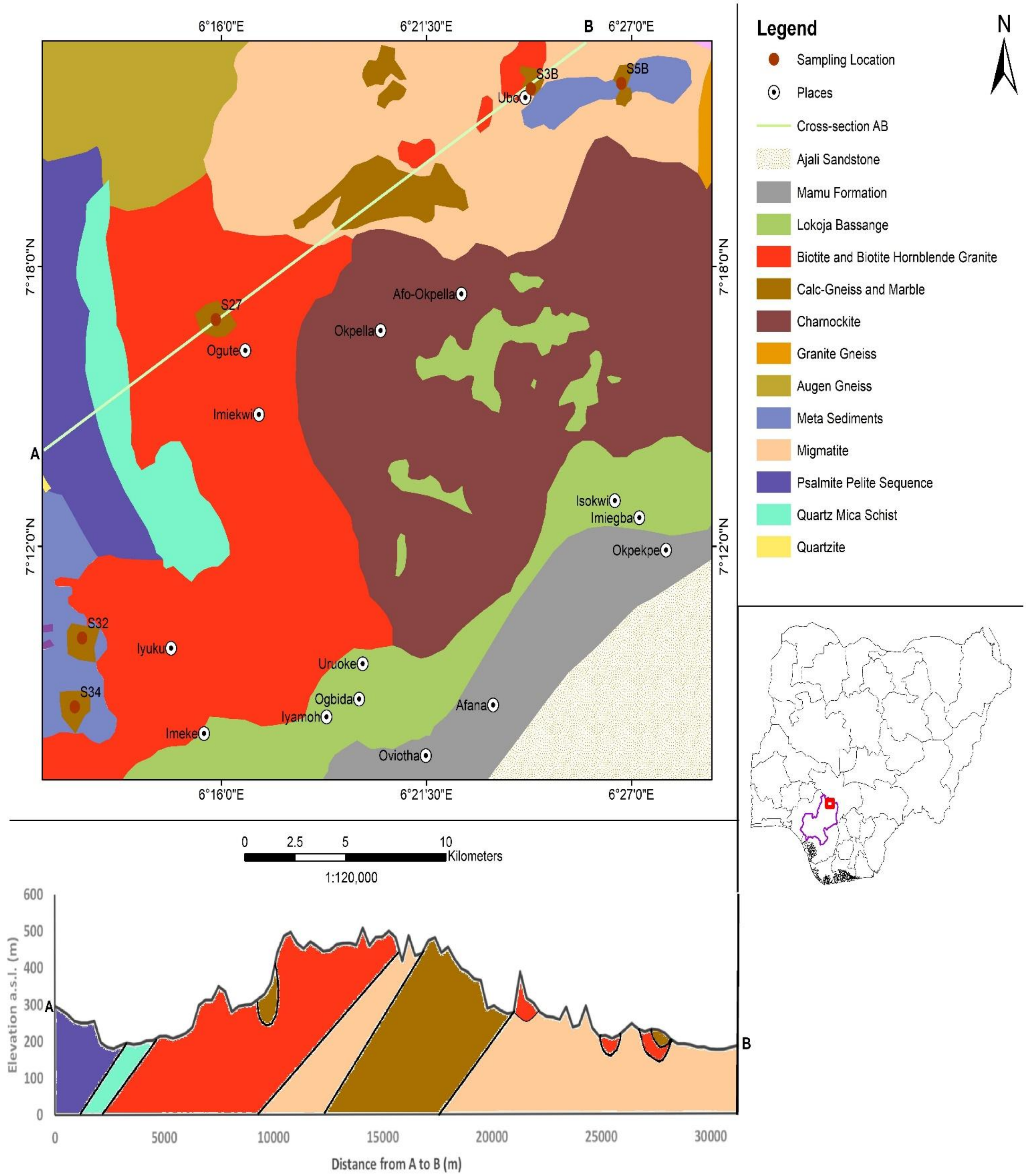


Figure 2.3: Geological Map of Ikpeshi and Ubo Areas (Source, NGSA, 2015):

Plate 2. 1: Boulders of Calcite Marble at Freedom Quarry Ikpeshi.

Plate 2.2: Overview Showing the Massive Nature of the Body at Freedom Quarry Ikpeshi

Plate 2.3: "Large Calcitic Marble at Ikpeshi Freedom Quarry.

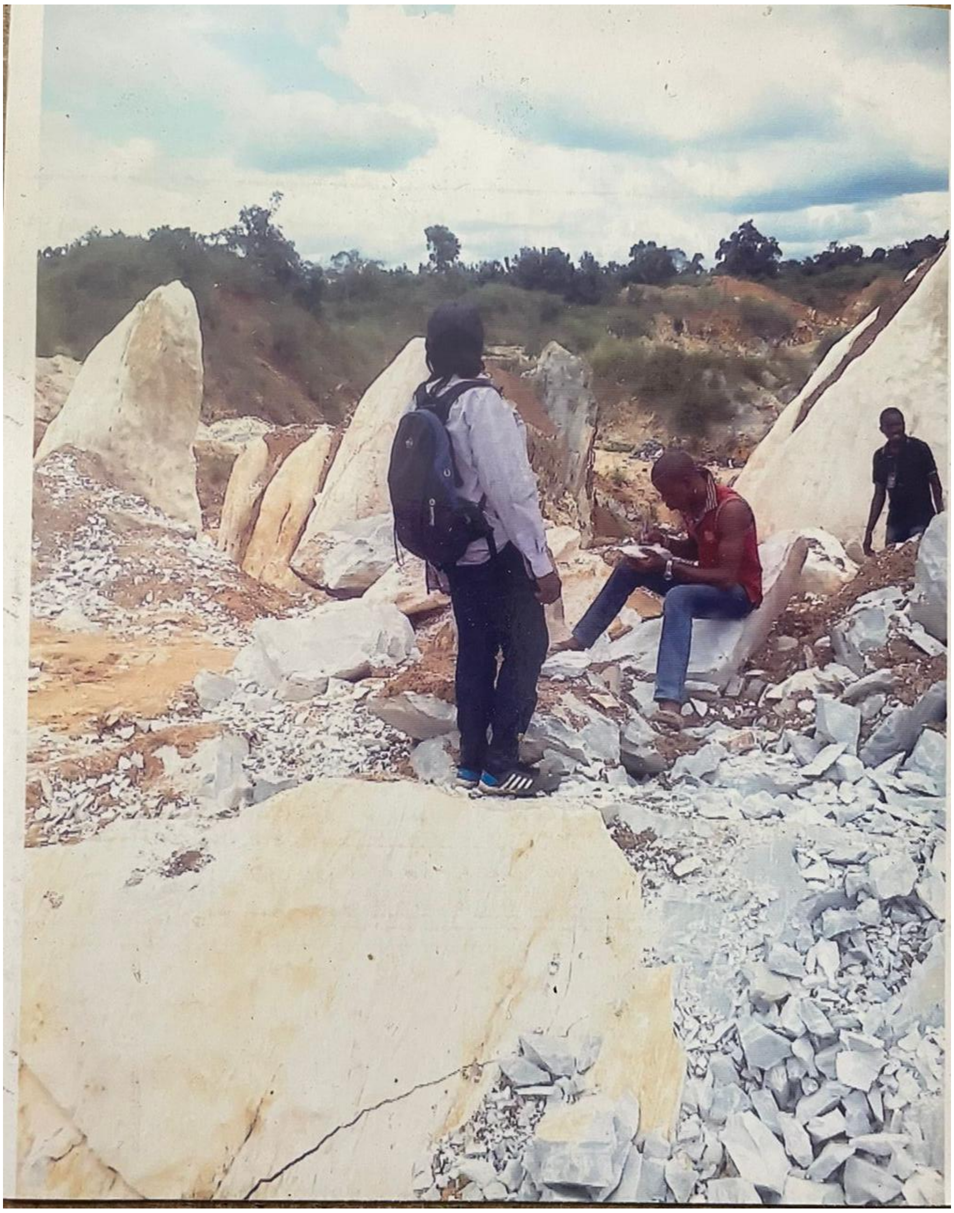


Plate 2.4: Outcrops of Marble at Ikpeshi Freedom Quarry

In some places, the marble is associated with banded calc-gneiss within the schist rock unit. As reported by (Obasi and Isife, 2012), the marble covers about 16km^2 of the total land mass in the study area and 6% of the general rock type. A number of companies are involved in mining the marble in the area e.g. Geo-Works Limited Quarry and also Freedom Group of Quarry located in Ikpeshi.

2.3. PREVIOUS WORK

- Omodeni, (2023), In "The Geochemistry of Carbonate Rocks in Igwe Igarra, Southwestern Nigeria" analyzed five carbonate rock samples from the Igwe Igarra area of Edo State, Nigeria. The Petrographic analysis revealed that the samples contained calcite, quartz, microcline, plagioclase, biotite, and opaque minerals. Geochemical data showed that the Igwe marble had a high calcite content (96% - 98%) and low dolomite content, while the calcsilicate rock had lower CaO (27.5%) and higher marble content. The Igwe marble was found to be pure with fewer impurities compared to the calcsilicate rock, making it suitable for various industrial applications such as glass, paper, beet sugar, aggregates, lubricants, and fillers.
- Taiwo and Omotehinse, (2022) In "The economic potential of some metacarbonate rocks in Akoko-Edo, Edo state Nigeria" examined metacarbonate rocks from Enwan, Bekuma, and Ekpedo deposits in Akoko Edo, Nigeria. Modal petrographic analysis and XRS-FP quantitative analysis were used to determine their mineralogical and chemical properties. Results showed that the metacarbonate rocks from Enwan, Ekpedo, and Bekuma contained average $CaCO_3$ percentages of 96.4%, 58.5%, and 77.35%, respectively, and MgO percentages of 3.6%, 41.5%, and 13.1%, respectively. The main constituents were calcite, dolomite, quartz, plagioclase, and muscovite, with calcite being the dominant mineral. The low quartz content and mineral composition make these metacarbonate

rocks suitable for applications in calcium carbonate industries, such as paint, factory lime, pesticide and animal feed production, construction materials, and the chemical industry.

- Ailegbo *et al.,*(2021) in " Investigation of the Geochemical Composition and Paleo-Depositional Environment of Ubo and Ikpeshi Marble Deposit, Southwestern Nigeria"discovered significant differences between Ubo and Ikpeshi marbles in terms of CaO, MgO, Na_2O, $MgCO_3$, Cu, and Ni content, with Ni being highly significant. The Ubo marble deposit was found to be a lensoid body within a younger metasedimentary sequence. Chemical analysis showed that both marbles are calcitic composition, indicating a shallow, highly saline depositional environment. The plots of $Na_2O + K_2O$ vs. SiO_2 demonstrated variations in salinity between the marbles from both locations.
- Akinola and Olaorun (2021) in "Lithological features and chemical characterization of metamorphosed carbonate rocks in Igue, Southwestern Nigeria" revealed that the marble appears as lenses between different rock blocks and comes in three color variants: white, grey, and foliated. Chemical investigation revealed that the rock is calcitic, with varied SiO_2, CaO, and MgO concentrations. The chemical properties of the marble are similar to those of other surrounding rock types, however it differs dramatically from the dolomitic Igbeti marble deposit. These differences in geochemical characteristics are impacted by protoliths, formation processes, and adjacent lithologies, which contribute to the region's different commercial applications of marble deposits.
- Omoseebi and Tanko, (2021) in "Geochemistry and Determination of Mineral Properties of Dolomite Deposit in Ikpeshi Southern, Nigeria". This work focused on the geochemistry and determination of the mineral properties' distribution of dolomite deposit from Ikpeshi, using variogram analysis, Samples collected from the study area were subjected to laboratory analysis to determine the porosity, water content and geochemical properties. Variograms maps were constructed and fitted to the model. The

results of the variogram analysis were used in plotting of predictive maps which show the property distribution of the dolomite. The porosity varies between 0.68%–3.24% and the Water Content varies between 0.1–1.65%. The geochemical analyses reveal that the average concentration of the elemental oxides is 1.790, 0.461, 0.299, 0.045, 20.380 and 46.130 forSiO_2, Al_2O_3, Fe_2O_3, MnO, MgO and CaO, respectively. CaO and MgO are more abundant when compared with other major elements; the predictive maps of the distribution and directions of the mineral properties and the distribution are not uniform in all directions which indicates that the mineral properties of the dolomite deposit are anisotropic.

- Aderogbin and Isibor, (2020) in "Petrographic and Geochemical Studies of IGBETI Marble Southwestern Nigeria in Relation to It's Economic Potential' revealed its composition as calcite (88.49%vol), dolomite (4.71%vol), pyrite (1.97%vol), muscovite (1.44%vol), tremolite (0.78%vol), quartz, and albite (2.81%vol). Geochemical analysis showed low levels of SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, and P_2O_5, while MgO, CaO,were relatively high. The marble's silica and alumina ratios fell below the recommended values for cement production, indicating it is not suitable as a raw material. However, it can be upgraded to meet the required composition for cement production.
- Chaanda *et al.,* (2019) In "Environmental Geochemistry of Igarra Marble Mining District, Southwestern Nigeria" showed high levels of Cd, Co, Cu, Ni, Pb, and Zn are present in the marble. Water samples from streams, taps, and wells contained high concentrations of Cd, Co, Cu, Ni, Pb, and Zn, with lead showing levels exceeding acceptable limits. Lead, nickel, and cadmium were found to be present in high concentrations in both surface and underground water, indicating the need for water treatment before use. The implementation of mining regulations and corporate social responsibility measures should be prioritized to protect the health and well-being of the local population.

- Odokuma-Alonge, (2019) in "A Geochemical Appraisal of Some Marble Physiques in Ubo Area and Environs, Southwestern Nigeria" discovered that high levels of CaO (ranging from 52.98wt% to 82.18wt%) and low levels of MgO (ranging from 1.64wt% to 6.95wt%). Other major oxides, including SiO_2, FeO/Fe_2O_3, Na_2O, K_2O, Al_2O_3, and MnO_2, were below 2wt%. The multivariate analysis showed a strong correlation between CaO/Fe_2O_3, MgO/Al_2O_3, and FeO/CaO, indicating similar valencies and ionic values. The high lime content suggests deposition in a shallow marine environment before metamorphism. The marbles belong to the high calcite group and have various industrial uses, such as for the production of Portland cement and ceramics.
- Madukwe and Obasi, (2016). In "Geochemical and petrogenetic characteristics of the marble deposit at Ikpeshi southern Nigeria" concluded that Ikpeshi marbles are low-grade metamorphic granoblastic rocks. Pure calcite marbles, pure dolomite marbles, pure dolomitic calcite, and pure calcitic dolomite are among them. The protolith was most likely deposited in a shallow, saline environment. The dolomites found in the marbles are most likely of precipitatory origin. The immobile Ni and Cr concentrations are comparable to sedimentary carbonates, while the Mn content is reduced, probably due to recrystallization at higher temperatures. The protolithdepositionional environment's paleo-oxygenation is generally oxic, with occasional suboxic conditions.
- Onimisi *et al.,* (2013) in "The geochemical investigations of the marble deposit in Itobe, Kogi state, central Nigeria" revealed the presence of Mg in the marble and suggested co-precipitation with Ca from hyper-saline waters under anoxic conditions, influenced by microfauna and flora. Metamorphic carbonate rocks like Itobe marble are commonly found in continental environments affected by crustal distension. The association of the marble deposit with other rock types indicates deposition in a rift environment with rapid

subsidence and contemporaneous magmatism, followed by subsequent deformation of the sediments.

- Odewumi *et al.,* (2012) In "Geological Settings, Geochemical Characteristics And Signatures Of Elebu, Okunrun And Okoloke Marble Deposits, Southwestern Nigeria,concluded that geochemical data found discrepancies in the SiO_2/Al_2O_3 and Ca^{2+}/Mg^{2+} ratios, with Okunrun and Elebu having lower values and Elebu having higher values. The Mn/Sr ratio revealed that carbonate rocks were kept differently in each place, with Okoloke being highly preserved, Elebu being partially affected, and Okunrun being mildly damaged by post-depositional activities. These differences indicate that the marble deposits in the three areas are in different geological settings and depositional basins
- Davou and Ashano, (2009) in "The geochemical chararateristics of the marble deposits east of Federal Capital Territory (FCT), Nigeria" discovered that the marbles have fine to medium calcite and dolomite grains, accounting for 97.00% to 99.78% of the rocks. The marbles are dolomitic, with an average Mg/Ca ratio of 2:3, implying a shallow marine depositional environment rich in Mg and Ca, impacted by microbial activity.

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1. MATERIALS

The following materials and equipment were used for the project. They include:

3.1.1. Field Materials

- Geological Hammer
- Hand Lens
- Field Notebook
- GPS Device
- Sample Bags
- Compass Clinometer
- Chisel and Pry Bar
- Camera
- Measuring Tape/Ruler
- Pulverizer
- Petrographic Microscope
- X-ray Diffraction (XRD) Analyzer
- Laboratory Glassware
- Analytical Reagents
- Safety Equipment:

3.1.2. Preparation of Samples

The samples after collection were labeled UB1,UB2,UB3,IKP4, and IKP5. The samples are then pulverized using a disc mill to reduce the size and increase the surface area before analysis. The samples were air-dried to remove moisture and then sent to Natural Steal Raw

Materials Exploration Agency (NSMREA) Laboratory in Kaduna State for X-ray diffraction and X-ray fluorescence analysis.

3.2. METHODOLOGY

3.2.1. X-RAY DIFFRACTOMETER

X-ray diffraction (XRD) is a powerful analytical technique used to determine the atomic and molecular structure of a crystalline material. It provides valuable information about the arrangement of atoms within a crystal lattice, crystallographic orientation, and the presence of defects or impurities (Lamas *et al.,* 2017). The methodology for X-ray diffraction involves several key steps, which are outlined below.

a. **Sample Preparation**: The first step in X-ray diffraction methodology is the preparation of a suitable sample. The sample must be in the form of a crystalline material, which can be a single crystal or a powdered sample. Powders are commonly used in XRD analysis as they provide a more representative average of the crystal structure.

b. **X-ray Source**: X-rays are generated using an X-ray source, typically an X-ray tube. The X-ray source emits a beam of X-rays with a specific wavelength, typically in the range of 0.01 to 10 nanometers (nm).

c. **Sample Alignment:** The sample is mounted on a goniometer, which allows precise rotation and tilting of the sample. Proper alignment is crucial to ensure accurate diffraction patterns. The sample is often placed in a sample holder, such as a glass capillary or a thin film, to ensure uniform exposure to X-rays.

d. **X-ray Diffraction**: The X-ray beam is directed towards the sample, and the interaction of the X-rays with the crystal lattice leads to constructive and destructive interference, resulting in a diffraction pattern. The diffracted X-rays form a series of spots or peaks on a detector, which can be recorded as a diffraction pattern.

e. **Data Collection**: The diffraction pattern is collected by a detector, such as a photographic film, an image plate, or a modern electronic detector. The detector records the position and intensity of the diffracted X-rays.

f. **Data Analysis**: The collected diffraction pattern is then analyzed to extract information about the crystal structure. This involves measuring the angles and intensities of the diffracted spots. The angles provide information about the spacing of atomic planes within the crystal lattice, while the intensities give insights into the arrangement of atoms and their electron density.

3.2.1a. Fundamental Principles of X-ray Diffraction:

The fundamental principles underlying X-ray diffraction are based on Bragg's law and the wave nature of X-rays. Bragg's law states that for constructive interference to occur, the path difference between X-rays scattered by adjacent atomic planes in a crystal lattice must be equal to an integer multiple of the X-ray wavelength.

The wave nature of X-rays causes them to behave as waves and exhibit diffraction phenomena when interacting with a crystal. The diffracted X-rays interfere constructively or destructively, depending on the path difference and the angle of incidence (Fang *et al.*, 2019). By analyzing the resulting diffraction pattern, researchers can determine the crystal structure, lattice spacing, and other properties.

3.2.1b. How Does X-ray Diffraction Work:

X-ray diffraction works by exposing a crystalline material to a beam of X-rays and analyzing the resulting diffraction pattern. When the X-ray beam interacts with the crystal lattice, the X-rays are diffracted by the atoms in the lattice, resulting in constructive interference at specific angles. The diffracted X-rays form a pattern of spots or peaks, which can be recorded and analyzed.

The diffraction pattern provides information about the crystal structure, such as the arrangement of atoms and the spacing between atomic planes. The angles and intensities of the diffracted spots in the pattern are measured and used to determine the crystallographic parameters of the material (Nergis *et al*., 2020).

By comparing the experimental diffraction pattern with known crystal structures or using advanced analysis techniques, researchers can identify the crystal structure of the sample, quantify the presence of impurities or defects, and investigate various properties such as crystal orientation, phase transitions, and crystallite size

3.2.1c. Applications in Geological Processes:

X-ray diffraction has various applications in studying geological processes, aiding in the characterization and analysis of geological materials. Some key applications include:

a.Mineral Identification: XRD is widely used for mineral identification in geological samples. Each mineral has a unique diffraction pattern, allowing scientists to identify and quantify the mineral composition of rocks and sediments.

b.Phase Analysis: XRD helps in determining the phase composition of geological materials. It can identify different polymorphs (variations in crystal structure) and detect minor phases that may influence the behavior of rocks and minerals.

c.Structural Analysis: XRD provides valuable insights into the crystal structure of minerals and their relationship to geological processes. It helps in understanding the bonding, coordination, and arrangements of atoms within minerals, shedding light on their formation and transformation mechanisms.

d.Quantitative Analysis: XRD can quantify the amount of different minerals present in geological samples. This information is crucial for assessing the geological history, identifying mineral resources, and predicting the behavior of rocks under different conditions.

3.2.5. Strengths and Limitations of X-ray Diffraction:

X-ray diffraction offers several strengths that contribute to its widespread use, but it also has some limitations to consider:

Strengths:

a. **Non-destructive**: XRD is a non-destructive technique, allowing for the analysis of valuable samples without altering their composition.
b. **High Resolution**: XRD can provide high-resolution structural information, enabling the determination of atomic positions and small structural changes.
c. **Wide Applicability**: XRD can be applied to a broad range of materials, including minerals, metals, ceramics, and complex organic compounds.
d. **Quantitative Analysis**: XRD can provide quantitative information about mineral phases, allowing for precise compositional analysis.

Limitations:

a. **Sample Requirements**: XRD requires crystalline samples, limiting its applicability to crystalline materials.
b. **Time-consuming**: Obtaining accurate results from XRD analysis may take time, as the technique involves precise measurements and data processing.
c. **Surface Sensitivity**: XRD is primarily surface-sensitive, which means it may not accurately represent the bulk properties of a material without proper sample preparation.

d. **Amorphous Materials**: XRD is less effective in analyzing amorphous materials lacking a long-range order.

3.2.2. X-Ray Fluorescence Spectroscopy (XRF Analysis):

A non-destructive analytical method used to ascertain the elemental makeup of diverse materials is called X-ray fluorescence spectroscopy (XRF). It is based on the idea that when a sample is subjected to high-energy X-rays, its atoms absorb the energy and release the distinctive X-rays that are associated with that energy. To identify and measure the elements contained in the sample, these emitted X-rays are detected and examined. The following steps are commonly included

a.Sample Preparation: The sample must first be ready for analysis in the first stage. The sample could be a solid, liquid, or powder. For solid samples to assure homogeneity and representativeness, they are frequently ground into a fine powder. To attain the desired consistency, liquid samples may need to be diluted or dried before being examined.

b.Instrumentation: XRF analysis requires a specialized instrument known as an X-ray fluorescence spectrometer. This instrument consists of an X-ray tube that generates high-energy X-rays and a detector system to measure the emitted characteristic X-rays from the sample.

c. X-ray Emission: Following the removal of the inner-shell electrons, outer-shell electrons descend to replace the empty spaces. This process results in the emission of distinctive X-rays with energy unique to each element. The X-rays that were released will be examined.

d. X-ray Detection and Analysis:

The spectrometer's detector system picks up the emitted X-rays. A spectrum that depicts the intensity of various X-ray energies is produced by the detector. Specific elements in the sample are represented by the characteristic peaks in the spectrum.

e. Data Analysis: The obtained X-ray spectrum is then processed using software that compares the peaks' positions and intensities with a database of known standards. The software identifies the elements present in the sample and quantifies their concentrations based on the X-ray intensities.

3.2.2a Fundamental Principles of XRF Analysis:

X-ray fluorescence spectroscopy principle that when activated by high-energy X-rays, each element in the periodic table has a distinct electron structure that results in distinctive characteristic X-ray energies. This characteristic enables XRF to recognize and count the elements in a sample.

The concentration of the elements in the sample directly relates to the intensity of the distinctive X-rays that are released. Using typical reference materials as a benchmark, XRF can pinpoint the precise elemental makeup and concentration of the sample.

3.2.2b. Applications of XRF Analysis:

XRF analysis is a versatile technique widely used in various industries and research fields. Some of its primary applications include:

a. **Mining and Geology:**

Mineral exploration and resource assessment are made easier by using XRF to examine the elemental composition of geological materials. It facilitates the discovery of precious minerals and guarantees effective mining operations.

b. **Environmental Monitoring:**
c. For the purpose of locating and calculating pollutants and contaminants such heavy metals, XRF may evaluate samples of soil, sediment, and water. This is crucial for determining environmental effect and ensuring that rules are followed.
d. **Archaeology and Art Conservation:**

XRF helps determine the elemental composition of artifacts, paintings, and historical objects, aiding in dating, authentication, and preservation efforts.

e. **Forensics:**

XRF is used in forensic analysis to identify trace elements and compounds in evidence materials, aiding in criminal investigations.

CHAPTER FOUR

PRESENTATION AND DISCUSSION OF RESULTS

4.1. PRESENTATION OF RESULTS

The summary of the mineralogical and geochemical results is presented in Tables 1 and 2 and Figure 4.1a, 4.1b to 4.5a, 4.5b shows X-ray diffractograms and pie charts of the mineral distribution of the samples.

Table 1: The Modern Composition of Minerals of the Samples in the Study Area(%)

Mineral name	Formula	UB1	UB2	UB3	IKP4	1KP5
Calcite	$CaCO_3$	----	1.60	61.00	58.00	65.00
Quartz	SiO_2	44.00	` 29.00	27.00	14.10	20.00
Muscovite	$KAl(Si_4O_{10})\ (OH_1F)_2$	4.00	37.00	5.00	8.00	3.00
Orthoclase	$KAlSiO_3$	30.00	2.00	2.00	6.70	2.00
Albite	$NaAlSiO_3$	5.00	9.00	2.00	2.00	5.00
Lime	CaO	9.00	3.70	1.90	11.10	4.70
Anorthite	$CaAl_2Si_2O_8$	8.00	----	----	----	----
Anthophyllite	$Mg_2Mg_5Si_8\,O_{22}(OH)_2$	---	18.00	----	----	---
Others		---	---	1.10	0.10	0.30
TOTAL		100.00	100.30	98.00	99.90	99.70

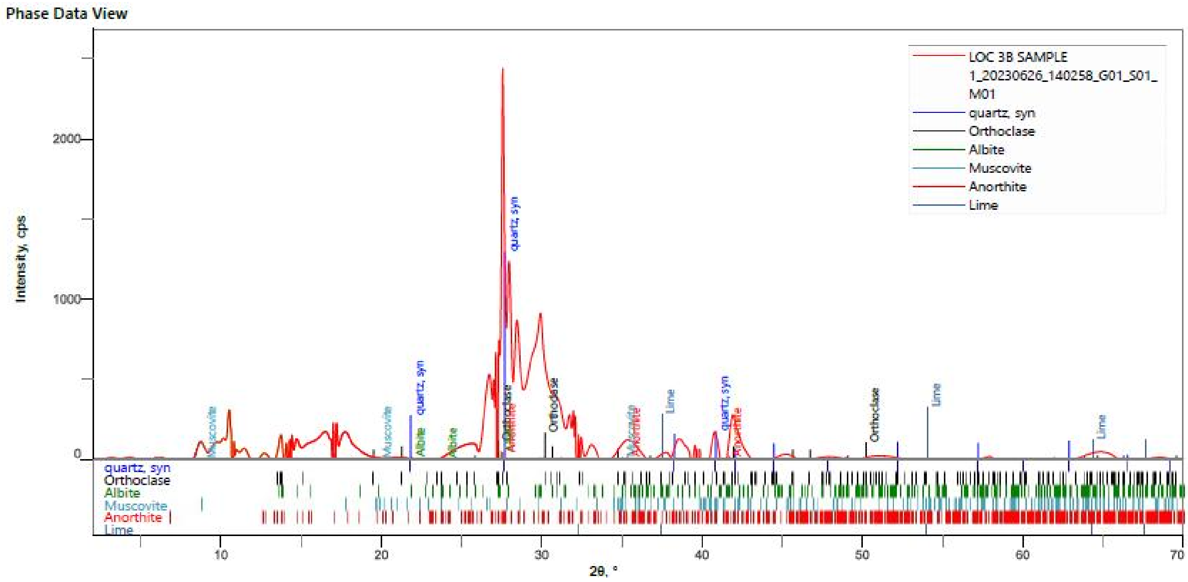
Table 2: The Chemical Composition of the Major Oxides of Samples in the Study Area (wt%)

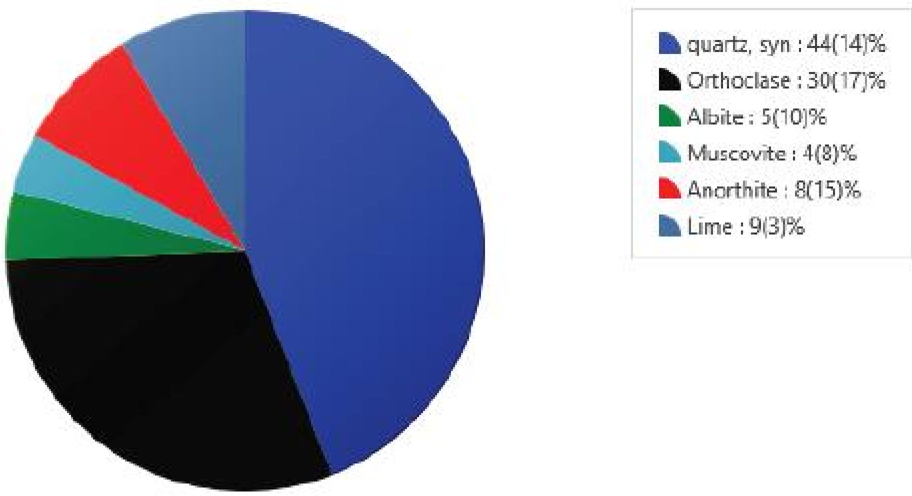
Major Oxides	**UB1**	**UB2**	**UB3**	**IKP4**	**1KP5**
SiO_2	47.30	39.10	9.22	5.43	3.95
Al_2O_3	8.20	5.93	3.53	2.81	2.61
Fe_2O_3/ FeO	4.63	7.04	1.92	0.60	0.17
CaO	31.40	37.10	82.40	88.80	79.00
MgO	N.D.	5.95	ND	ND	12.90
MnO	0.16	0.23	0.09	0.02	0.01
K_2O	3.69	0.46	0.87	0.38	0.21
P_2O_5	0.16	0.02	---	---	---
NaO	---	----	-----	-----	-----
TOTAL	95.54	95.82	98.03	98.04	98.85

UBO= UBO

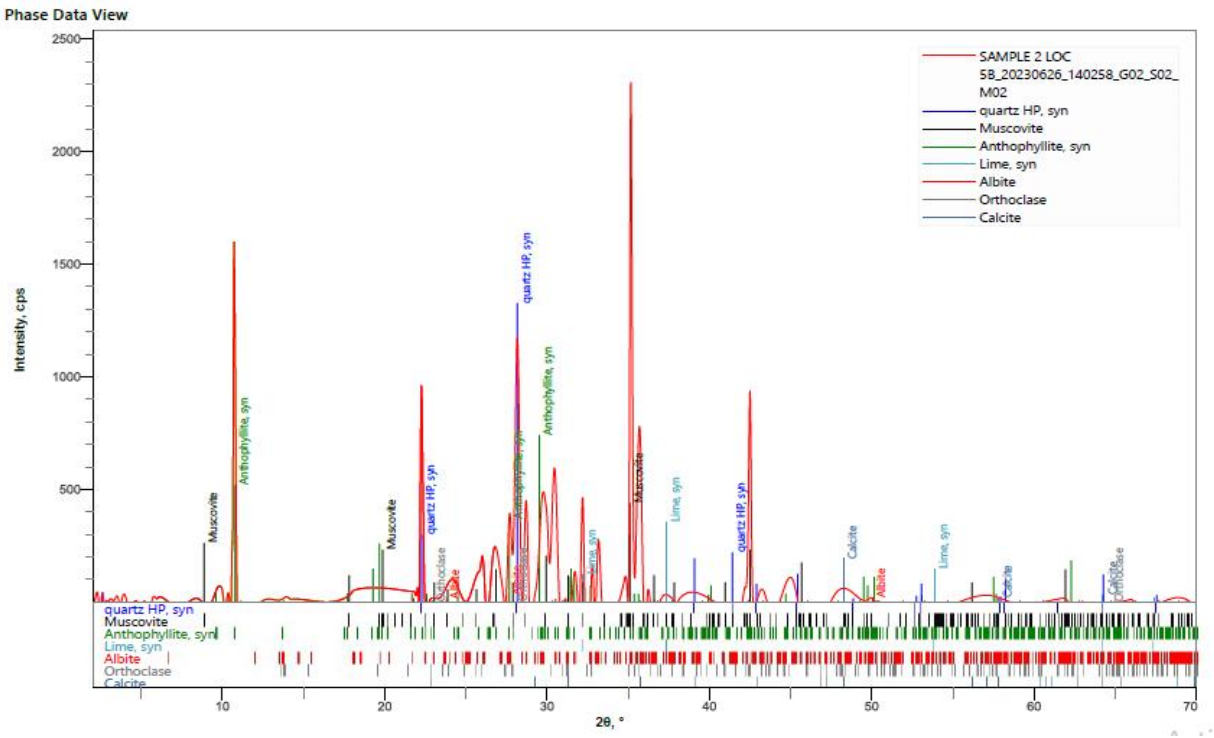
IKP = IKPESHI

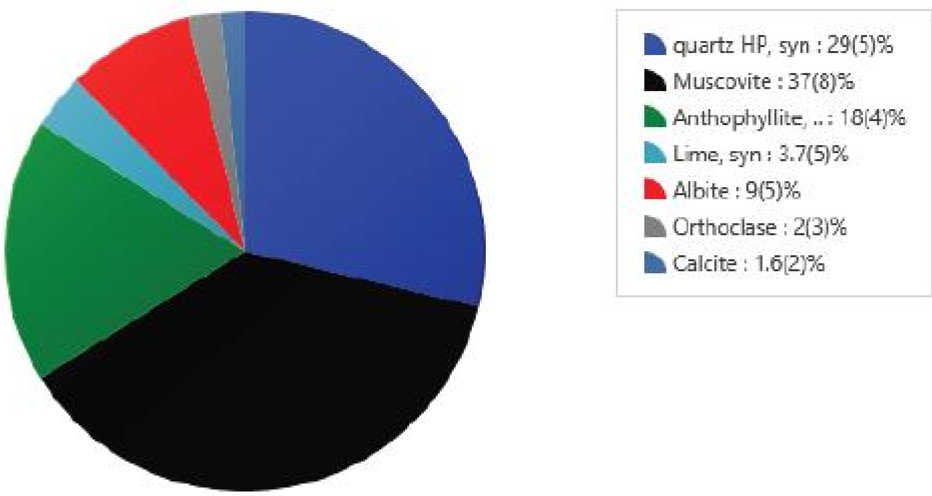
ND= Not Detected



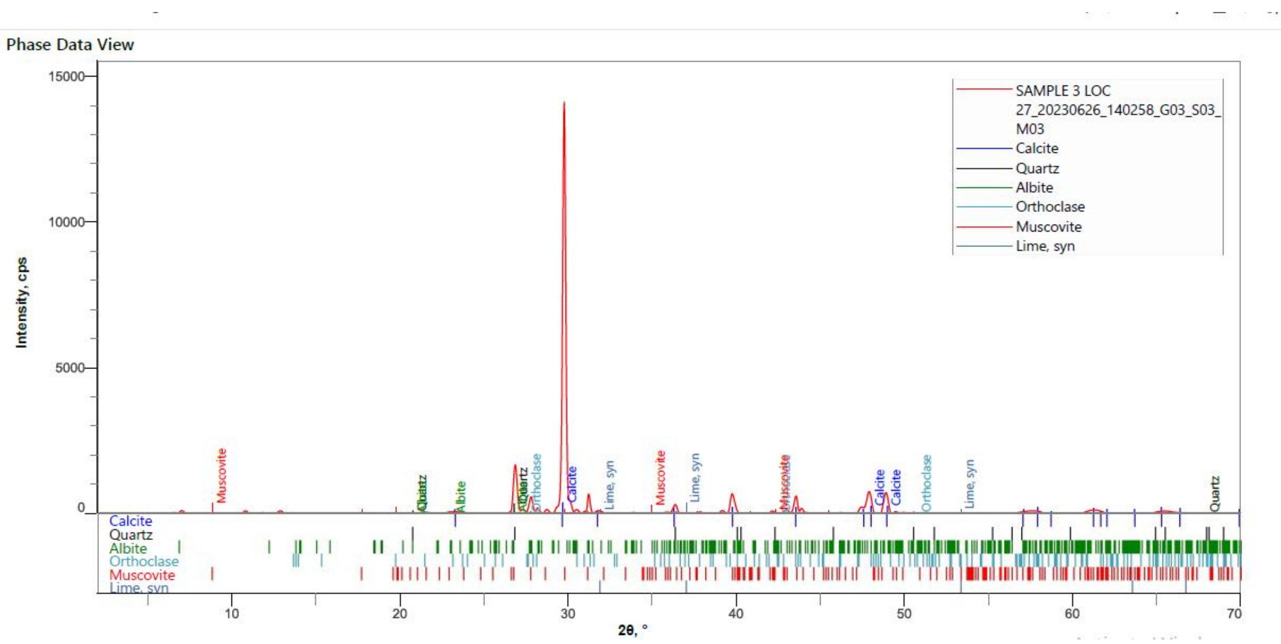


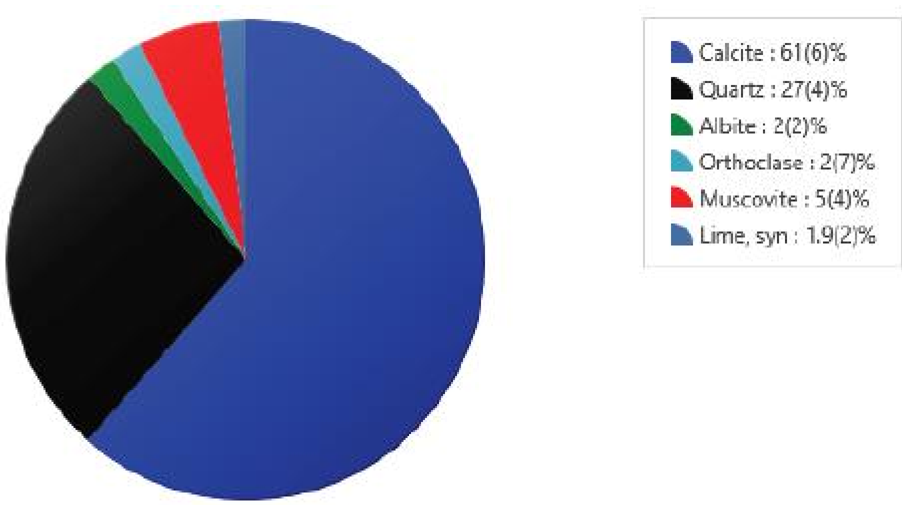
Figures 4.1a and 4.1b: An X-ray Diffraction Spectra and Pie Chart showing Mineral Distribution in UB1



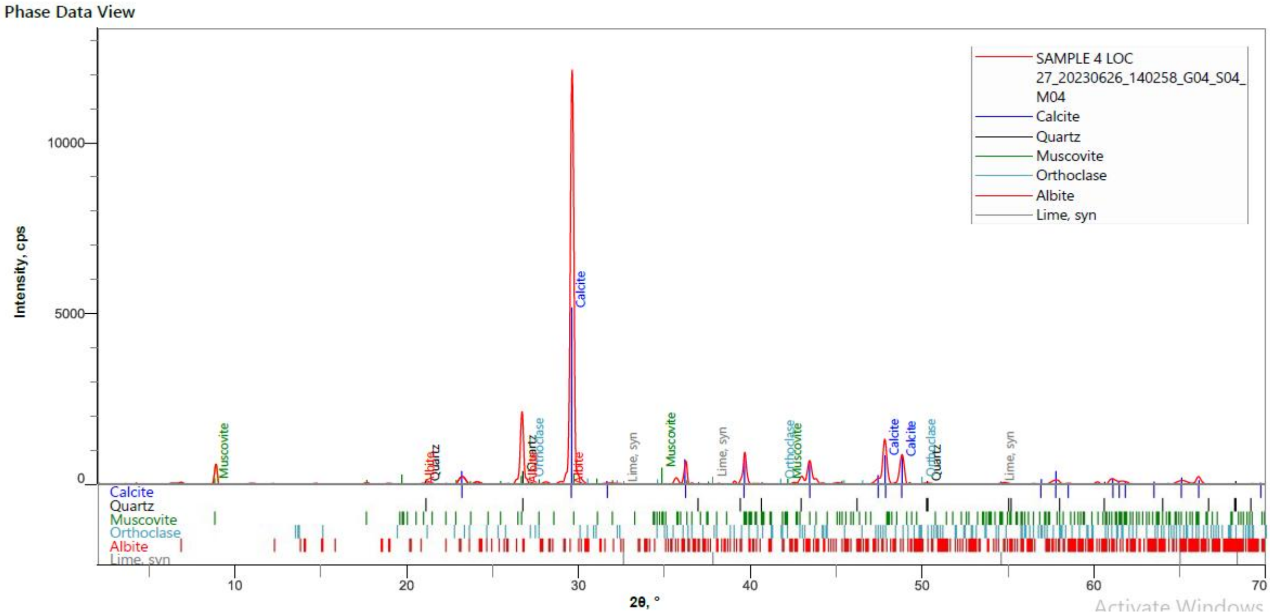


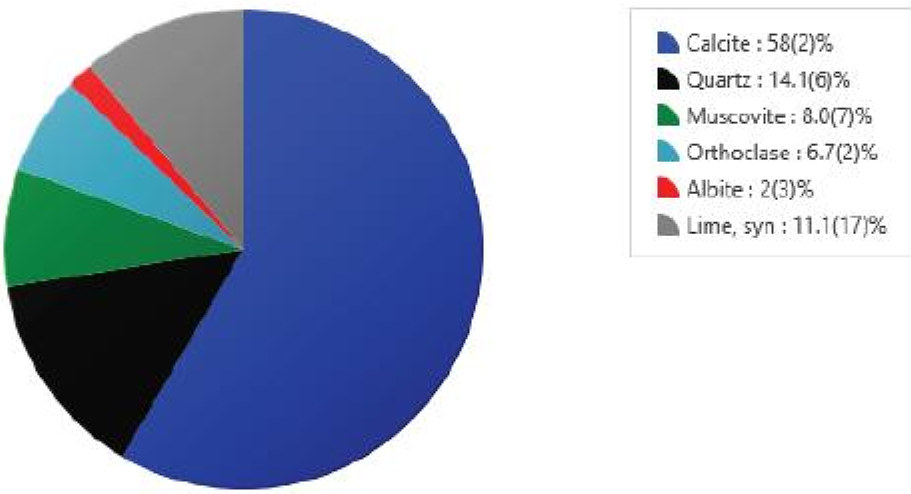
Figures 4.2a and 4.2b: An X-ray Diffraction Spectra and Pie Chart showing Mineral Distribution in UB2



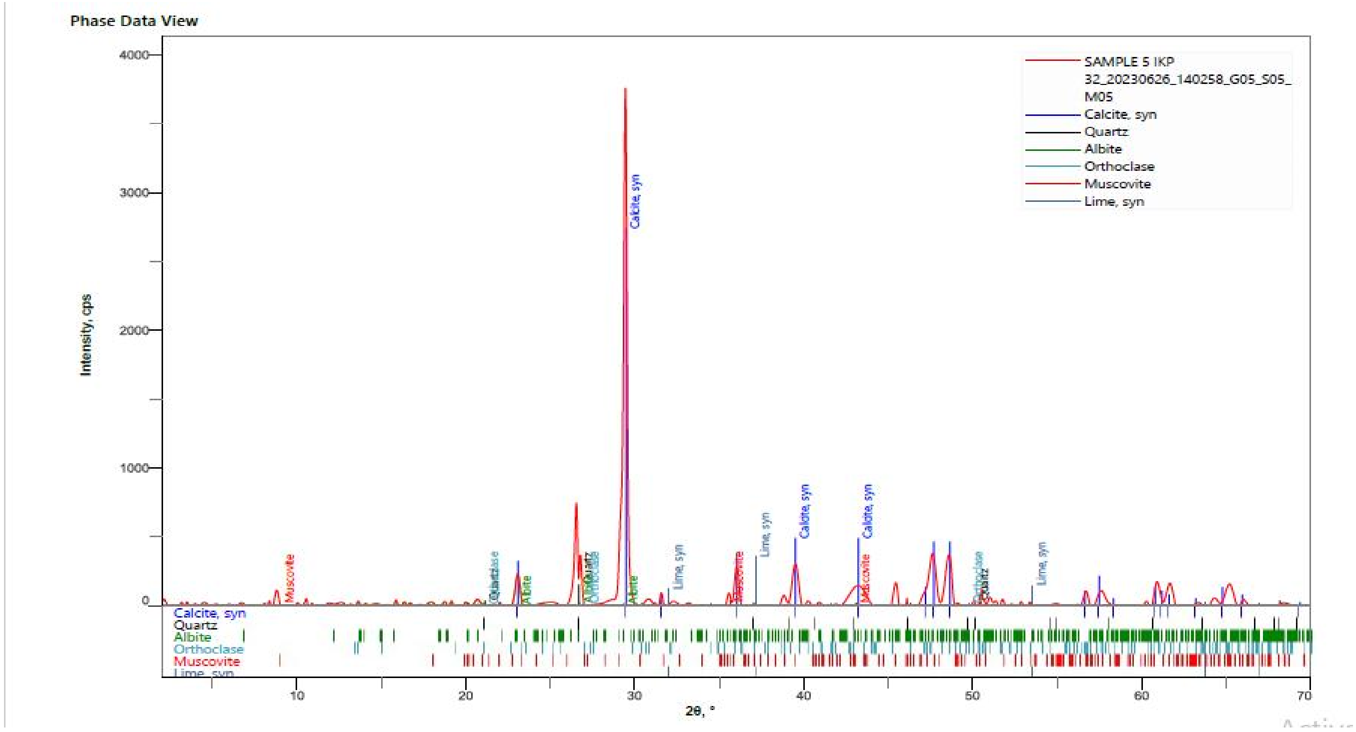


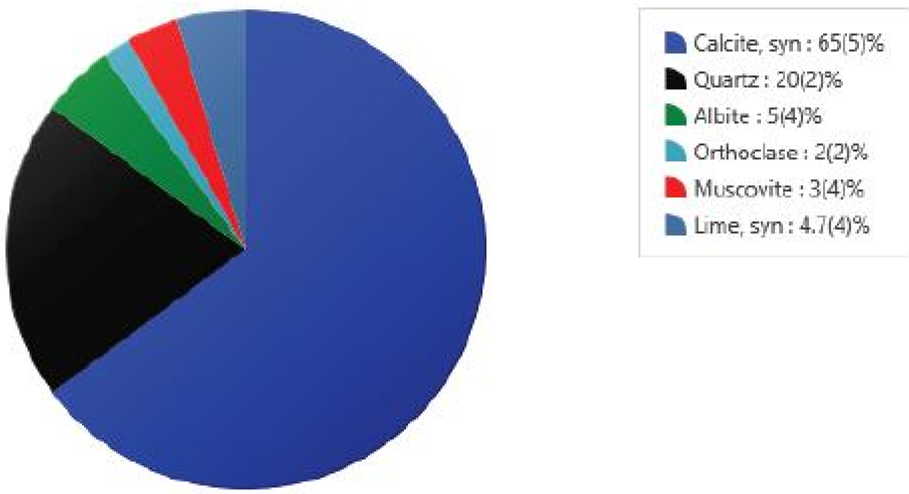
Figures 4.3a and 4.3b: An X-ray Diffraction Spectra and Pie Chart showing Mineral Distribution in UB3





Figures 4.4a and 4.4b: An X-ray Diffraction Spectra and Pie Chart showing Mineral Distribution in IKP4





Figures 4.5a and 4.5b: An X-ray Diffraction Spectra and Pie Chart showing Mineral Distribution in IKP5

4.2. DISCUSSION OF RESULTS

The presented mineralogical and geochemical results for the samples from different locations of the study area, showing the major minerals and oxides with variable characteristics are discussed below.

4.2.1. RESULTS FROM MINERALOGICAL ANALYSIS

Table 1 presents the mineral composition of the marble samples collected from the Ubo and

.Ikpeshi study areas, expressed as percentages (%).

4.2.1a. Calcite($CaCO_3$):

Calcite is the most common carbonate, it can occur in practically all types of sediments and rocks, in the latter either as a primary or secondary mineral. It has a rhombohedral cleavage with a hardness of 2.5 on Mohs scale. Some of the common forms of calcite crystal are white calcite, black calcite, red calcite, pink calcite. The calcite in the study area shows varying compositions among the samples. Notably, samples UB3, IKP4, and 1KP5 exhibit relatively higher calcite contents (61%, 58%, and 65%, respectively), indicating a dominant calcite presence in these rocks. However, sample UB2 deviates with a lower content of 1.6%. The lack of calcite at UB1 could be related to potential experimental errors during the sampling, preparation, analysis, or data recording processes.

As stated by (Onimisi *et al*., 2013) pure carbonates are believed to have a total carbonate content ($CaCO_3$) of 70% and above while impure carbonates have between 40 – 70%. Other oxides like SiO_2, MnO, and Na_2O are usually less than 1%, and are regarded as constituting impurities (Lippman, 1973).

The high calcite content suggests that these marble deposits could be valuable for industries such as cement production, ceramics, glass manufacturing, and construction materials (Akinola and Olaorun, 2021; Odokuma-Alonge, 2019).

4.2.1b. Quartz(SiO_2):

A variety of notable physical and optical features can be found in quartz, a crystalline form of silicon dioxide (SiO_2). It has a hardness rating of 7 on the Mohs scale, a high melting point, and a hexagonal crystal structure. Since quartz is clear to translucent and has anisotropic optical properties, including birefringence, it is a valuable component in a variety of optical and electronic applications. It exhibits pyroelectric and piezoelectric properties, which transform mechanical stress and temperature changes into electric impulses, separately.

Quartz content ranges from 14.1% in sample IKP4 to 44% in sample UB1. The variations in quartz content suggest the influence of different mineral sources during marble formation. The paucity of calcite in the UB1 sample may be due to the amount of quartz and its interaction with silicate minerals, which may have prevented all of the original minerals from completely converting into calcite during metamorphism.

The low silica, indicates the low presence of quartz and feldspars in the area (Oyinloye, 2012).

4.2.1c. Muscovite: $KAl(Si_4O_{10})\ (OH_1F)_2$

The mica mineral species muscovite has unique physical and visual characteristics. It has a monoclinic crystal structure with flawless basal cleavage into light-weight, malleable sheets. Muscovite ranges from transparent to translucent, and it frequently exhibits a vitreous or pearly sheen. It displays pleochroism, changing hue depending on the angle from which it is seen, and has substantial birefringence because of its anisotropic makeup

Muscovite rarely contributes significantly to the production or major change of marble, it is normally regarded as a minor component. Instead, calcite or dolomite dominate the mineral composition of marble, giving the rock its distinctive makeup and look .Muscovite content varies significantly across the samples, ranging from 3% in sample 1KP5 to 37% in sample

UB2. This variability could be attributed to the presence of different parent rocks or variations in metamorphic conditions during marble formation.

4.2.1d. Orthoclase ($KAlSiO_3$):

A typical feldspar mineral found in both igneous and metamorphic rocks is orthoclase. On the cleavage surfaces, it exhibits hues like pink, white, gray, or colorless with a pearly shine. It cleaves along two planes at right angles and has a Mohs hardness of 6. Orthoclase is a member of the monoclinic crystal system and has a density of roughly 2.56-2.58 g/cm3. The occurrence of orthoclase in marble reflects a complicated geological past that involved mixing of several rock types, maybe as a result of geological events like faulting or intrusion of igneous rocks.

Orthoclase and albite exhibit relatively lower variations among the samples. Sample UB1 stands out with a higher orthoclase content of 30%, while the other samples range from 2% to 6.7%. Albite content remains relatively consistent between 2% and 9%. The low silica, alumina and potash values indicate the low presence of quartz and feldspar in the area. (Oyinloye, 2012)

4.2.1e. Albite ($NaAlSiO_3$)

Albite is a feldspar mineral frequently white, gray, or pale pink in color and has a vitreous to pearly sheen. It cleaves along two planes at right angles and has a Mohs hardness rating of 6 to 6.5. The triclinic crystal structure is home to albite, which has a density of roughly 2.62-2.65 g/cm3. The presence of albite in marble also shows sophisticated geological processes during formation, which may have involved hydrothermal alteration or intricate rock interactions.

4.2.1f. Lime (CaO):

Lime content shows a range from 1.9% in sample UB3 to 11.1% in sample IKP4. The higher lime content in sample IKP4 might suggest specific mineralogical reactions or localized geological conditions during metamorphism.

Through a process known as calcination, lime can be produced from the mineral calcite, which is made up of calcium carbonate ($CaCO_3$). Calcination is a chemical breakdown reaction that takes place at high temperatures and removes carbon dioxide (CO_2) from calcium carbonate, leaving behind calcium oxide, sometimes known as lime.

$CaCO_3 \rightarrow CO_2 + CaO$

Lime is produced using this method for a variety of uses in the construction, agricultural, and manufacturing sectors.

Lime Saturation Factor

In cement chemistry, the term "lime saturation factor" (LSF) refers to the mass ratio of lime (calcium oxide, or CaO) to the total mass of silica, alumina, and ferric oxide, which together make up the majority of the raw materials needed to make cement. When establishing the composition of the clinker, an intermediate product in the manufacture of cement, LSF is a crucial metric. The L.S.F. is the ratio of the actual amount of lime in raw meal/clinker to the theoretical lime required by the major oxides (SiO_2, Al_2O_3 and Fe_2O_3) in the raw mix or clinker.

Lime Saturation Factor is:

$$\text{L.S.F.} = \frac{100(\text{CaO})}{2.8(SiO_2\,\%) + 1.2\,(Al_2O_3\%) + 0.65\,(Fe_2O_3\%)} \quad \text{...............Equation 1}$$

Table 3: Calculated L.S.F. Values for Samples UB1 – UB5

Sample Name	UB1	UB2	UB3	IKP4	IKP5
L.S.F. Values	23.07	39.90	101.62	205.00	133.00

The recommended L.S.F. values for marble used in cement production are 242-417 respectively (Onimisi *et al.,*2017) The calculated L.S.F. for the marble deposit are 23.07, 39.90, 101.62, 205.00 and 133.00 respectively. None of these samples fall within the recommended range used in cement production. However, the L.S.F value of the marble can be adjusted to fall within the recommended range required for a typical cement kiln by blending the marble with suitable proportions of clay and laterite to supply SiO_2 and Al_2O_3; and Fe_2O_3 respectively (Panda, 2016)

Other uses of Ubo and Ikpeshi marbles are highlighted in Table 4 below:

Table 4: Other Uses of Ubo and Ikpeshi Marbles

S/N	**Uses**	**Specifications**	**Conclusion**
1	Paints and Filter	CaO>96.0% SiO_2>1% FeO> 0.25%	Not Suitable
2.	Pesticide Production	CaO>60%	Suitable (Except UB1 and UB2)
3.	Fertilizer	CaO>47.6% SiO_2<5%	Not Suitable.
4.	Glass Use	CaO>94.5% FeO<0.2%	Not Suitable
5.	Soil Liming	CaO>52.0%	Suitable (Except UB1 and UB2)

4.2.1.g. Anorthite ($CaAl_2Si_2O_8$.)

Plagioclase feldspar is a category of minerals that includes the calcium aluminum silicate mineral known as anorthite. It is distinguished by its intermediate position between albite and anorthite, two end members of the plagioclase group, and has the chemical formula $CaAl_2Si_2O_8$. Basalt and andesite are examples of volcanic rocks that frequently contain anorthite, as well as several metamorphic rocks. Comparatively speaking to albite and other plagioclase feldspars, it has a comparatively high calcium concentration.The sample UB1 contains 8% Anorthite indicating the incorporation of original feldspar-rich minerals from the protolith during the metamorphic process.

As earlier stated by (Selvin *et al*., 2017), Anorthite can alter marble's mineral makeup, potentially changing its color, texture, and other physical characteristics.

4.2.1.h. Anthophyllite: $Mg_2\,Mg_5Si_8O_{22}(OH)_2$

Anthophyllite is a mineral belonging to the amphibole family with a complicated chemical make-up that is mostly made up of magnesium, silicon, and oxygen. Long, thin prismatic crystals of anthophyllite are common, and it can also form fibrous aggregates. Its normal hue ranges from gray to green, and its hardness on the Mohs scale is between 5.5 and 6.Anthophyllite in marble may be a sign that the original rock had amphiboles, a mineral that is frequently found in metamorphic rocks. All samples lack Anthophyllite except sample UB2 with 18% indicating the presence of Amphiboles.

(Bloise *et al*, 2021) clearly stated that minerals, like anthophyllite, are recognized carcinogens, their presence in marble may present health risks due to the possibility of dangerous fibers being released if the marble is cut or otherwise disturbed. In order to maintain the safety of handling and usage, the presence of anthophyllite in marble should be carefully assessed and handled.

4.2.2. RESULTS FROM GEOCHEMICAL ANALYSIS

Table 2 shows the results from geochemical analysis for the samples from different locations of the study area.

4.2.2a. SiO_2 (Silicon Dioxide):

SiO_2 content varies across the samples, with UB1 having the highest (47.3wt%) and 1KP5 the lowest (3.95wt%). This variation in SiO_2 content is consistent with findings from Akinola and Olaorun (2021), where different lithologies were attributed to variations in protoliths and formation processes. The relatively high SiO_2 content in UB1 and UB2 might suggest a potential influence of impurities or siliciclastic input during deposition. However, the low SiO_2 content in 1KP5 aligns with the general nature of marble deposits, which are typically composed of calcium carbonate minerals.

4.2.2.b. Al_2O_3 (Alumina):

The Al_2O_3 content shows variations, with UB1 having the highest (8.20wt%) and 1KP5 the lowest (2.61wt%). These values are generally low, indicating the dominance of calcitic and dolomitic minerals in the marble samples. This aligns with the findings of Madukwe and Obasi (2016) and Aderogbin and Isibor (2020), where calcite and dolomite were reported as the primary constituents of marble deposits.

As earlier stated by Odokuma-Alonge(2019) the lack of aluminosilicates or low energy conditions during deposition may be responsible for the marble's low alumina content in the study area. The variations in Al_2O_3 content might reflect the presence of minor impurities or variations in mineralogical compositions due to geological factors.

4.2.2.c. Fe_2O_3/FeO (Iron Oxides)

The Fe_2O_3/FeO ratios vary across the samples, with UB2 having the highest (7.04wt%) and IKP4 the lowest (0.17wt%). This values slightly differs from the work of (Ailegbo., *et al*

2021) who also investigated the geochemical composition of marbles at Ubo and Ikpeshi. The presence of iron oxides is generally low in our samples, which is consistent with the carbonate-rich nature of marble deposits.

The low Fe_2O_3/FeO ratios in our samples suggest minimal iron mineral contributions to the overall composition. Fe_2O_3 occurs as an impurity in the marble and the higher the value, the more deteriorated or weathered the marble samples are (Ogunsola *et al*., 2019)

4.2.2.d. CaO (Calcium Oxide)

Calcium oxide content is relatively high in all samples, ranging from 31.4wt% to 88.8wt%. These values are also in correlation with the work of Odokuma-Alonge(2019) and Akinola and Olaorun (2021) who also investigated the gecochemical features of marble at Ubo..

CaO is one of the most important oxides in carbonates of most metamorphic rocks. CaO in Calcitic marble is usually in the order 50-54wt%. Hence, the high CaO values are consistent with the dominant presence of calcite and dolomite minerals in the marbles. The high percentage of CaO in this study and that of Odokuma-Alonge (2019) is an indication that the marble is Calcitic in nature.

The high CaO content makes these marbles potentially suitable for various industrial applications, as highlighted by Taiwo and Omotehinse (2022). The variations in CaO content among samples might be indicative of different degrees of diagenesis, metamorphism, or varying depositional conditions.

MgO (Magnesium Oxide)

Magnesium oxide is absent in all samples except at UB2 and IKP5 where it is 5.95wt% and 12.9wt% respectively. The presence of MgO in both samples might be attributed to the occurrence of dolomite, as observed by (Madukwe and Obasi (2016).

The MgO content in the sample is <6.95wt% hence can be considered to be classified as pure marble (Cherneva *et al*., 2009; Bassey, 2011) due to the low MgO content.

The low MgO in the area could be mainly due to low dolomite content in the rock which is probably as a result of slight replacement of $Ca2^+$ with $Mg2^+$ and also probably contribution of magnesium rich organic matter in low temperature environments (Pettijohn,1975).

4.2.2.e. MnO (Manganese Oxide):

Manganese oxide content is generally low in all samples. This aligns with the results of Ailegbo *et al*., (2021) and Aderogbin and Isibor (2020), where manganese content in marble deposits was reported to be relatively minor. The low MnO content suggests that manganese-bearing minerals are not prominent in these marbles, indicating a calcitic mineralogy.

4.2.2.f. K_2O (Potassium Oxide):

K_2O content varies among samples, with UB1 having the highest (3.69wt%) and UB2 the lowest (0.46wt%). These variations might reflect localized changes in depositional conditions or mineralogical differences.

According to Clarke (1911), Na and K concentration in marbles tend to decrease with increase in salinity, but tend to increase with depth. Hence, the environment of the deposition of the original materials that were metamorphosed to marble must have been a shallow, highly saline environment.

4.2.2.g. Alkali (NaO + K_2O) Content:

In interpreting the depositional and lithification circumstances prior to the metamorphism of carbonates, alkali elements like Na and K that are indicative of saline levels have proved particularly helpful (Land and Hopp, 1973). The research area's low total alkali content findings suggest that a shallow, very saline environment must have been present during the deposition of the original carbonate minerals that eventually transformed into marbles.

CHAPTER FIVE

SUMMARY CONCLUSION AND SUGGESTION FOR FURTHER STUDIES

5.1. SUMMARY

Five (5) marble samples from Ubo and Ikpeshi located in Akoko Edo L.G.A. Southwestern Nigeria were obtained. The result of the mineralogical analysis using X-ray diffractometer reveals the presence of Calcite (1.6-65%), Quartz (14.1-44.0%), Muscovite (3.0-37%), Orthoclase (2-30%), Anorthite and Anthopyllite: 8 and 18 at UB1 and UB2 respectively. The result from geochemical analysis reveals the presence of SiO_2 (3.91-47.3wt%), Al_2O_3(2.61-8.20), Fe_2O_3 (0.17-7.04wt%), CaO (31.4-88.8wt%), MgO, MnO, K_2O, P_2O_2 < 1wt%.

The major element composition of the Ubo and Ikpeshi marble shows it is similar in composition to calcitic marble. The calculated L.S.F. for the marble deposit are 23.07, 39.90, 101.62, 205.00 and 133.00 respectively. None of these samples fall within the recommended range used in cement production. However, they are suitable for pesticide production and soil lining as determined from the L.S.F. values.

5.2. CONCLUSION

The Ubo and Ikpeshi marble's principal constituent makeup reveals that it is composed primarily to calcitic. The low values of the total alkali content in the samples of marble from the two sites suggest that the environment for the deposition of the original carbonate materials that underwent metamorphosis to become marble from both sites must have been from a shallow, highly saline environment with probably little influx of salty brine water in the basin.

It can also be said that the Ikpeshi and Ubo marble deposits are not good raw material for cement production due to its relatively low value of silica and alumina.

5.3. SUGGESTION FOR FURTHER STUDIES

Detailed studies of the marble in Ubo and Ikpeshi were carried out by determining the mineralogical and geochemical composition using x- ray diffraction and x-ray fluorescence techniques.

Further geochemical studies using, Inductively Coupled Plasma Mass Spectrometer (ICPMS) should be done alongside petrographic interpretations to further investigate determine the geochemical composition. Additionally, a thorough petrographic examination could reveal microstructural characteristics and fluid-rock interactions that took place during metamorphism.

REFERENCES

Aderogbin, J.A. and Isibor, R.A. (2020). Petrographic and Geochemical Studies of Igbeti Marble Southwestern Nigeria in Relation to it's Economic Potential. *IJIRT* **6**(12):234-237.

Agomuo M. S and Egesi N. (2016). Petrology and Structural Geology of Ikpeshi and It's Environ Of Igarra Schist Belt Southwestern Nigeria. *International Journal of Science Inventions Today IJSIT*, **5**(4): 303-319.

Ailegbo, J, Ehinlaiye, A.O, Bassey, P and Odia-Oseghale, J.O. (2021). Investigation of the Geochemical Composition and Paleo-Depositional Environment of Ubo and Ikpeshi Marble Deposit, Southwestern Nigeria: A Comparative Study. *J. Appl. Sci. Environ. Manage***25**(3): 377-383

Akinola, O.O. and Olaorun, A.O. (2021). "Lithological features and chemical characterization of metamorphosed carbonate rocks in Igue, Southwestern Nigeria"*Journal of Geology and Mining Rsearch,***13**(1): 11-20.

Akinola, A.O., Akinyemi, S.O., Ogunniyi, A.O., Momoh, A. and Gitari, W.M. (2014). Mineralogy, physiochemical characteristics and Industrial Potential of some residual Clay deposits within Ekiti State, Southwestern Nigeria. Journal of Environment and Earth Sciences, **4**(17): 246-249.

Anifowose, A.Y.B. and Borode, A.M. (2007). Photogeological study of the fold structure in Okemesi area, southwestern Nigeria. *Journal of Mining and Geology*. **43** (2):125-130.

Bloise, A., Ricchiutic, C., Navara, R. and Punturo, R. (2021). Natural occurrence of asbestos in serpentinite quarries from Southern Spain. Environmental Geochemistry and Health 43: 2965-2983.

Clarke, F.N. (1924). *The Data of Geochemistry* (2nd ed.) Washington Government Printing Office; 782p

Chaanda, M.S., Izeze, O. and Osaze, I.T.(2019). "Environmental Geochemistry of Igarra Marble Mining District, Southwestern Nigeria" *Journal of Environmental Protection*, 10, 722-737.

Dada, S.S. (2006). Proterozoic evolution of Nigeria. In: Oshi O (ed) The basement complex of Nigeria and its mineral resources (A Tribute to Prof. M. A. O. Rahaman). Akin Jinad & Co. Ibadan, pp 29–44.

Davou and Ashano, (2009). The geochemical charateristics of the marble deposits east of Federal Capital Territory (FCT), Nigeria. *Global Journal of Geological Science*, **7**(2): 234-240.

Eludoyin, O.M., Adeleke, I.O., Webster, R. and Eludoyin, A.O. (2014). Air Temperature, Relative Humidity, Climate Regionalization and Thermal Comfort of Nigeria. *International Journal of Climatology,* **34**, 2000-2018.

Elueze, A. A., Jimoh, A. O. and Aromolaran, O. K. (2015). Compositional Characteristics and Functional Applications of Obajana Marble Deposit in the Precambrian Basement Complex of Central Nigeria. *Ife J. Sci.*, **17**(3): 591-603.

Falconer, J.D. (1911). The geology and geography of Northern Nigeria. Macmillan, London, 135pp

Fang, S., Xu, L., Wu, H., Xu, Y., Wang, Z., Shu, K. and Longhua, X. (**2019**). Influence of surface dissolution on sodium oleate adsorption on ilmenite and its gangue minerals by ultrasonic treatment. *Appl. Surf. Sci.*, *500*, 144038

Geological Survey of Nigeria (1974): *Publ. 111-125 Geological Survey of Nigeria, (GSN), Auchi Sheet 266, scale1:100,000.*

Gong, X. Jiang, W., Hu, S.; Yang, Z., Liu, X. and Fan, Z. (2021). Comprehensive utilization of foundry dust: Coal powder and clay minerals separation by ultrasonic-assisted flotation. *J. Hazard. Mater.* 2021, *402*, 124124.

Grant, N.K.(1978). Structural distinction between a metasedimentary cover and an underlying basement in the 600 my old Pan-African domain of Northwestern Nigeria. Geol Soc Am Bull89:50–58.

Holt, R.W.**(1982)**. The Geotectonic Evolution of the Anka Belt in the Precambrian Basement Complexof N.W. Nigeria. Unpublished Ph.D. Thesis, The Open University

Ileoje, N.P. (2001). A New Geography of Nigeria, New Revised Edition. Longman Publishers, Ibadan, 200

Jimoh, O. A., Ariffin, K. S., Hussin, H. B., Habeeb, A. A. (2016). Characterization and assessment of OkpellaMetacarbonate deposit in Nigeria. *Carbonates Evaporites*, pp. 1-12.

Land, L.S. and Hopp, G.K. (1973)*Journ. Sed. Pet.*, **1973**, 43, 614- 617

Lamas, D.G., Neto, M.D.O., Kellermann, G. and Craievich, A.F.(**2017**). X-ray Diffraction and Scattering by Nanomaterials. In *Nanocharacterization Techniques*; William Andrew Publishing: Oxford, UK, 2017; Chapter 5; pp. 111–182.

Lipmann, F. (1973). *Sedimentary carbonate minerals*. Springer verlag. Berlin Heidelberg. New York, 229p

Madukwe, H. and Obasi, R. (2016). "Geochemical and petrogenetic characteristics of the marble deposit at Ikpeshi southern Nigeria" *Nature and Science;* **14**(9): 23-32.

Madhavaraju, J. and Ramasamy, S.(1999). Rare earth elements in limestones of Kallankurichchi formation of Ariyalur group, Tiruchirapalli Cretaceous Tamill Nadu. *J. Geol.Soc. India.,* 291-301.

McCurry, P. **(1976).** The geology of the Precambrian to Lower Palaeozoic Rocks of Northern Nigeria – A Review. In: Kogbe CA (ed) Geology of Nigeria. Elizabethan Publishers, Lagos,pp 15–39

Nergis, D.D., Abdullah, M.M.A.B., Sandu, A.V. and Vizureanu, P. (**2020**). XRD and TG-DTA Study of New Alkali Activated Materials Based on Fly Ash with Sand and Glass Powder. *Materials* **13**, 343.

Nigerian Geological Survey Agency (NGSA) (2015): *Geological Survey of Nigeria, (NGSA), Auchi, Sheet 266, scale 1:100,000.*

Nigerian Meteorological Agency (2018). Seasonal Rainfall Report and Prediction Report, 2018.https://fscluster.org/nigeria/document/nigerian-meteorological-agency-nimet

Obasi, R. and Isife, F.(2012). Geochemistry and Economic potential of Marble Fromikpeshi, south-west, Nigeria. *ARPN Journal of Engineering and Applied Sciences*,**7**(6): 432-436

Obasi, R.A. and Anike, O.L (2012). Geochemical and economic application of marble from Igarra and Ikpeshi Areas, S.W Nigeria. *International Journal of Engineering and Technology,***2.** 173-1727

Odewumi, S.O., Ojo, O.J. and Adekeye, J.I.D. (2012). Geological Settings, Geochemical Characteristics And Signatures Of Elebu, Okunrun And Okoloke Marble Deposits, Southwestern Nigeria. *African Journal of Natural Sciences (AJNS)* 15(2)1119-1104

Odeyemi, I.B. (1988). Lithostratigraphy and structural relationships of the Upper Precambrian metasediments in Igarra area, southwestern Nigeria. *Precambrian Geologyof Nigeria*, **1:** 111-125.

Odeyemi, I.B. (1976). Preliminary Report on the Field Relationship of the Basement Complex around Igarra, Midwest Nigeria . In: Kogbe, C.A., Ed., *Geology of Nigeria,* Elizabethan Press, Lagos, 365-369.

Odokuma-Alonge, O. (2019). A Geochemical Appraisal of Some Marble Physiques in Ubo Area and Environs, Southwestern Nigeria. *J. Appl. Sci. Environ. Manage.* **23**(6) 1189-1193.

Ogunsola, N.O., Lawal1, A.I. and Saliu, M.A. (2019). Variations Of Physico Mechanical, Mineralogical And Geochemical Properties Of Marble Under The Influence Of Weathering. *Mining of Mineral Deposits***13**(1) :95-102.

Olade, M.A. and Elueze,A.A.(1979). Petrochemistry of the Ilesha amphibolite and Precambrian crustal evolution in the Pan-African domain of SW Nigeria. *Precambrian Res* 8:303–318

Oluwatoyin O.A., Bolarinwa, A.T. and Ademilua, O.L. (2014); LithologicFeatures and Petrochemical Characteristics of Metasedimentary Rocks of Igbetti Area, Southwestern Nigeria

Omodeni, J.M. (2023). "The Geochemistry of Carbonate Rocks in IgweIgarra, Southwestern Nigeria" *International Journal of Geosciences* (*I.J.G*), **14**(6): 124-129.

Omoseebi, A.O. and Tanko, I.Y.(2021). Geochemistry and Determination of Mineral Properties of Dolomite Deposit in Ikpeshi Southern, Nigeria. *European Journal of Environmental and Earth Science (JEES),* **2**(5): 345-356.

Onimisi, M., Obaje N. G. and Ashano, D. (2013). Geochemical and petrogenetic characteristics of the marble deposit in Itobearea, Kogi state, Central *Nigeria Advances in Applied Science Research*, 4(5):44-57

Onimisi, I., Ojonimi, I.T., Kolawole, M.S.1 and Ibimode, T.B. (2017). Field Occurrence, Chemical Composition and Industrial Application of Ekinrin-Adde Marble Deposit, Kogi State, North Central Nigeria. *Confluence Journal Of Environmental Studies.***11**(2): 234-239.

Oyawoye, M.O. (1972). The basement complex of Nigeria. In: Dessauvagie TFJ, Whiteman AJ (eds)African geology. Ibadan University Press, pp 66–102

Oyinloye, AO (2012). Geology and geotectonic setting of the Basement Complex rocks in southwestern Nigeria: Implications on provenance and evolution. *Earth. Environ. Sci.* (5), 98-117.

Panda, H. (2016). The Complete Technology Book on Asbestos, Cement, Ceramics and Limestone. Asia Pacific Business Inc., 592p.

Pettijohn, F.J. (1975). Sedimentary Rocks (3rd Edition)Warper and Row, New York, 628p.

Rahaman, M.A.(1976). Review of the basement geology of South-Western Nigeria. In: Kogbe CA(ed) Geology of Nigeria, 2nd edn, Elizabethan Publishers, Lagos, pp 41–58

Rahaman, M.A.(1988). Recent advances in the study of the basement complex of Nigeria. In: Geological Survey of Nigeria (ed) Precambrian Geol Nigeria, pp 11–43

Raw Materials Research and Development Council (RMRDC). 2010a. Non-Metallic Mineral Endowments of Nigeria, RMRDC Publication, Federal Ministry of Science and Technology, Abuja, Nigeria, 105p.

Raw Materials Research and Development Council (RMRDC). 2010b. Steel Raw Materials in Nigeria, RMRDC Publication(Ibrahim, H.D. and Biliaminu, K.O., Eds),Federal Ministry of Science and Technology, Abuja, Nigeria, 85p.

Saliu, M.A. and Komolafe, K. (2014). Investigating the Effect of Dolomite Exploitation on Groundwater Condition of Ikpeshi, Akoko-Edo, Edo State, Nigeria. *Journal of Earth Sciences and Geotechnical Engineering,* **4**, 137-147

Selvin, Y., Cakin. M. and Ergu, H. (2017). Usage of marble wastes in traditional artistic stoneware clay body. *Ceramics International Journal.* **43(12): 8912-8921.**

Taiwo, B.O., and Omotehinse, A.O. (2022). The economic potential of some metacarbonate rocks in Akoko-Edo, Edo state *Nigeria Journal of Applied Earth sciences*131(3): 123-128.

Touret, J. (1997). The Significance of Fluid Inclusions in Metamorphic Rocks. DG Fraser (ed) Thermodynamics in geology, Reided, Dordrecht, pp. 27-203

Turner, D. C.(1983). Upper Proterozoic schist belts in the Nigerian sector of the Pan-African Province of West Africa. *Precambrian Res* 21:55–

Wilson, M. (1989). Igneous Petrogenesis. UnwinHeyman: London.