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The Petrography, Geochemistry and Potential Applications of Ndi-Uduma Ukwu/Ohafia-Ifigh Limestone, Ohafia, S.E. Nigeria

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Abstract The Ndi-Uduma Ukwu/Ohafia-Ifigh limestone deposit is located approximately 55km East of Umuahia and about 125km Northwest of Calabar, S.E. Nigeria. This coarse grained, light to dark grey limestone is sandwiched between two carbonaceous highly fissile shale units of the Nsukka Formation forming shale-limestone-shale sequence. Outcrop samples were utilized in the petrographic investigation and geochemical analysis using Atomic Absorption Spectrophotometer (AAS). The calcium carbonate content (% $CaCO_3$) of the limestone ranges from 65.08 to 82.41%. The samples from Ohafia-Ifigh are SO_3-free and purer while the Ndi Uduma Ukwu had MgO and SO_3 content of 3.34 and 1% respectively. Petrographic analysis of the limestone reveals a highly fossiliferous limestone infilled with chiefly sparry calcite with micrite envelope, consisting of foraminifera, ostracod, echinoid, bivalve gastropod, coralline algae suggestive of shallow marine environment. Although the limestone does not compare with that of Shapfell, UK and Mfamosing S.E. Nigeria in chemical purity to warrant lime production with it, yet it meets some industrial raw material specification such as for cement, agriculture and poultry applications.

Keywords: *Geochemistry, Lime, Limestone, Ohafia, Petrography*

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1. Introduction

Limestone is a sedimentary rock composed primarily of Calcium Carbonate ($CaCO_3$). The Precambrian limestones occur as metamorphosed crystalline marbles while the sedimentary limestones range in age from Cretaceous to Paleocene and occur in association with sands, marls and shales, and are located in almost all sedimentary basins of Nigeria. Limestone though variable in quality is an extremely valuable raw material and is widely used in a variety of ways with construction and cement industries as the principal consumers. Strategic evaluation of limestone according to [11] is far more than a basic geological appraisal and should include laboratory determination of physical, mechanical, chemical as well as comparison with national or international specifications for each potential end use. The potential applications are numerous; however Ofulume [1] noted that the ultimate utilization is mainly a function of both its chemical and technological properties.

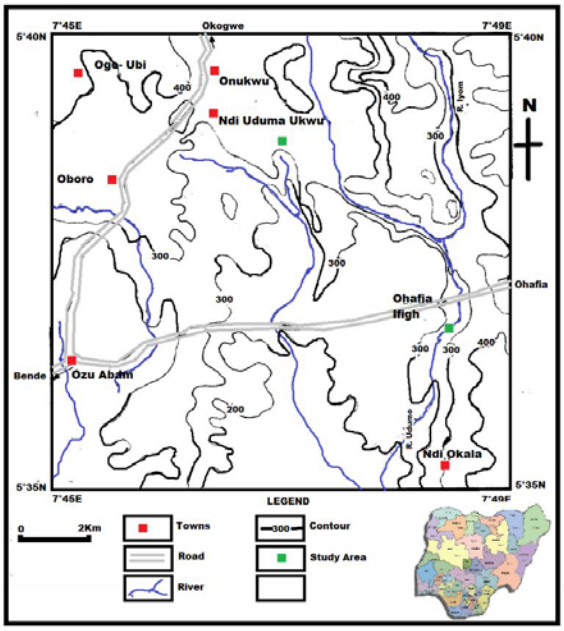

Figure 1. Topographical Map of the Study Area

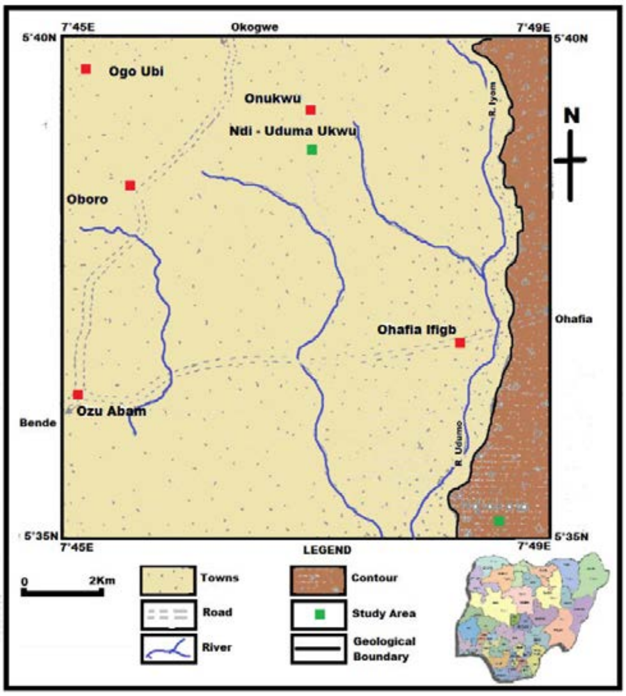

Figure 2. Geological Map of the Study Area

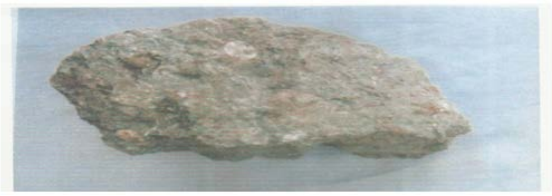

Figure 3. Ohafia-lfigh Limestone Sample (NU1)

Figure 4. Ndi Uduma Ukwu Limestone Sample (NU2)

Lime is a product of burning of limestone in a kiln at a temperature in excess of 950°C. Lime itself is probably the most important chemical in commerce having more than two hundred applications [2]. Its usage according to Ofulume et al [3] spans metallurgical, chemical, pharmaceutical, constructional, environmental, food and food bye-products, agricultural and petroleum.

The Ndi-Uduma Ukwu/Ohafia-Ifigh limestone is among the very few limestones in Nigeria that has been understudied. Petrographic and chemical examinations of the limestone have been undertaken, and the chemical composition compared with the Carboniferous limestone at Shapfell, UK, and Mfamosing limestone, S.E Nigeria well known for their purity, with the aim of recommending its potential applications where necessary.

2. General Geology

The geology of Ndi-Uduma Ukwu/Ohafia-Ifigh is part of the south eastern sedimentary basin of Nigeria within the south eastern arm of Afikpo syncline. Two lithostratigraphic units have been identified in this area. They are: Ajali Formation and Nsukka Formation.

The Ajali Formation consists of white, unconsolidated coarse-grained, moderately to poorly sorted sandstone. One of the most conspicuous features of the Ajali Sandstone is its cross-stratification. The formation is located between two well-defined Campano-Maastrichtian paralic sequences. The Ajali Formation is the main water-bearing geological formation in the area. The formation starts with a kaolin-rich unit along Ebem Ohafia road and grades into loosely-cemented sandstone with angular to sub-rounded quartz grains [4]. Analysis of the grains by Ibe [5] indicates that the Ajali sandstone has two modes in size distribution. The Ajali Sandstone in the area has two distinct units: the quartz-rich lower unit and the overlying iron-rich variety. The lower unit is cream-coloured, passing through iron-stained sandstone to the iron oxide-cement sandstone that contains glauconite. The ironstone unit underlies the foraminiferal limestone that contains glauconite. The ironstone unit underlies the foraminiferal limestone that distinguishes the Nsukka Formation in Ohafia area [6]. Maastrichtian age has been assigned to this formation.

The Nsukka Formation, in most locations starts with an iron-rich, conglomeratic unit. However, at the western part of the study area, shale-limestone-shale sequence is exposed. This formation which has been reported by Wilson and Bain [7], as being similar to that of Mamu Formation, which is of strand plain marsh origin with occasional fluvial incursion. It consists of alternating sequence of laminated, very fine-grained sandstones and siltstones, brown and grey shales and mudstones with numerous coal seams at various horizons. Ironically, in this area of study, it is entirely marine in origin. This is obvious in the surface outcrops along Ebem-Ozu Abam road, about 1km from Ndi-Uduma River. At area Northeast of Ohafia-Ifigh, there are alternations of carbonaceous or greyish shales with fossiliferous limestones. In some of the locations in Ndi-Uduma, the limestone samples are seen with quartz pebbles. Ages ranging from Maastrichtian to Palaeocene have been assigned to the Nsukka Formation [6,8].

In between these two formations (Ajali Sandstone and Nsukka Formation) (Figure 2) appears a lateritic ironstone which forms the transitional zone, capping the Ajali Sandstone. Within the study area, each lithostratigrphic unit can be further divided as given below:

v Upper Shale - Fossil and carbonaceous

iv Limestone - (a) Fossiliferous limestone

(b) Fossiliferous limestone with quartz as the dominating mineral.

iii Lower Shale - Fossil and carbonaceous

ii Lateritic Ironstone - Ferruginous grits and clay ironstone

i Sandstone - Strongly cross bedded.

Unit (i) or the sandstone unit belongs to the Ajali Formation, which (ii) is the transitioned zone between the Ajali Sandstone below and the Nsukka Formation above. Units (iii), (iv) and (v) belong to the Nsukka Formation.

In general, the Ajali Formation is semi-confined, leading to the occurrence of numerous warm springs such as Muri, Obayi and Anyinta at Ebem Isiugwu and Ndi-Uduma Awoke villages respectively. All the formations within the study area are conformable, dip between 8° and 25° to the west. The Nsukka and Ajali Formations both constitute a great deal of lithologic boundary of the shale-sandstone sequence of the area [5].

2.1. Age and Correlation

In the Ohafia area, the Nsukka Formation rests conformably on the Maastrichtian Ajali Sandstone and overlain by the Paleocene Imo Shale. Simpson [8] and Reyment [6] assigned Maastritchian to Palaeocene age to the Nsukka Formation. In southern Nigeria, Reyment [6,9] and Kogbe [10] stated that the uppermost beds of Nsukka Formation contain typical Paleocene foraminifera and suggested a Danian age for this part of the formation. The foraminifera assemeblage Gravellinela Specie and Ammobaculities Specie are of the age inference, but the overall assemblage is indicative of a shallow marine environment. The presence of similar foraminifera and ostracod microfauna in both the limestone and interbedded shale, suggest that the sediments are autochthonous or Para-autochthonous.

A Maastrichtian to Recent age is assigned to the shale-limestone-shale sequence of the Nsukka Formation, based on the diagnostic index ostracoda: Butonia butonia. This indicates therefore that the Nsukka Formation cannot be older than Maastrichtian. The genius is also indicative of shallow marine environment.

The ostracod fauna includes upper Maastrichtian forms from the Araromi and Gbekebo boreholes by Reyment [6]. On the basis of the occurrence of the ostracod though of low diversity, it is inferred in line with Reyment [6] earlier suggestion for the Western Nigeria sedimentary basins, that the Nkporo Shale was deposited throughout Maastrichian time in the Afikpo syncline, and the trasitional Nsukka Formation are partly contemporaneous with the black carbonaceous shale unit, representing Nkporo Shale.

2.2. Biostratigraphy

Both macro and micro fauna exist in the Nsukka formation that led to the limestone deposit. The macro fauna consists of gastropod and fragments of bivalves. Both were discovered from the limestone deposit at Ohafia-Ifigh. The microfauna consist of ostracods and foraminifera. The microfauna are of low diversity which may be due to instability in the salinity or may be due to environmental conditions such as restricted environments. Foraminifera recovered from both shale and limestone units Ndi-Uduma Ukwu/Ohafia-Ifigh are dominated by calcareous benthic followed by arenaceous forms. The arenaceous form is restricted to the shale unit only. Planktonic forms are entirely absent [8]. Other micro and macro fauna identified, according to Simpson [8] are coralline algae, echinoids and brachiopods.

3. Petrography

3.1. Under Plane Polarized Light

The biogenic composition at Ndi-Uduma Ukwu/Ohafia-Ifigh limestone consists of Ostracods, foraminifera, bivalves, gastropods coralline algae, echinoids. Low relief mineral of fine grained quartz as detrital, sub rounded are found disseminated in the ground mass of calcite (Figure 5 and Figure 7) and high relief mineral (apatite), in some places collaphane instead of apatite (Figure 8c) are visible. The gastropod, bivalves, foraminifera and brachiopods are filled with calcite (Figure 5 and Figure 7).

Fossil fragments like gastropod in long section (Figure 5 and Figure 7) preserved drusy sparite, since the shell was originally composed of aragonite and this must have dissolved leaving void. Most chambers are filled with micrite envelope. The majority of gastropod traces have shell remains of aragonite with similar internal structure of bivalves. The external microstructure of fossil gastropods were not seen since the original aragonite has mostly been replaced by calcite (Figure 5A and Figure 5B). Bivalve fragments present are labeled as "B" in the diagrams. They are seen as elongated with micrite envelope found around their fragments. The internal structure of the bivalves could not be preserved since the shell is filled with drusy sparite (calcite). The bivalves possess micrite envelope which in several cases are fractured as a result of compaction (Figure 5A, Figure 7B and Figure 7C). Foraminifera are very common in the microscopic section. They dominate the percentage of the fossil present labeled as "C". They are of very diverse shapes but under the microscope many common foraminifers forms are circular to subcircular with chambers. The text wall is microgranular in the thin-walled type (Figure 6, Figure 5A and Figure 5C) and fibrous in larger thicker species. Foraminifera at times are filled with phosphatic matters (Figure 7A and Figure 7C).

Brachiopod shells in thin section are similar to those of bivalves in shape and size. The common structure is very thin, outer layer of calcite fibers oriented normal to the shell surface, and a much thicker inner layer of oblique fiber (Figure 5C, Figure 6B and Figure 7A).

Ostracod labeled as "D" is refilled with micrite with the two valves or lobes attached to each other at the hinge (Figure 5A, Figure 5B and Figure 6A). It is also in-filled in some sections with dolomites and sparites (Figure 7C).

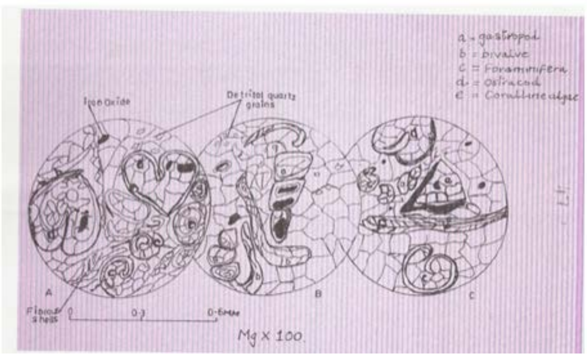

Figure 5. Thin Section Diagram of NU1 Sample under PPL

3.2. Under Crossed Polars

The quartz is seen schistozed, probably of metamorphic origin (Figure 9B). Coarse crystalline calcite cement known as sparite fills pore spaces. Little glauconite, fossil remains, calcareous algae (coralline) with cellular structure, probably calcareous and cryptocrystalline calcite, precipitated within and between the cell walls (Figure 9), spherical to irregular algal balls also occur in carbonate cemented conglomerates (Figure 9B) coralline algae are filled with sparites (Figure 9B). Cracks are associated with fibrous shells (Figure 8). The shell fragments have in some places a micritized veneer. Individual calcite grains are observed to increase in size and decrease in number away from the allochems (Figure 8 and Figure 9). Variation in size of the coarse sparite cement in the slides is that certain amount might be neomorphic. A mixed origin is suspected.

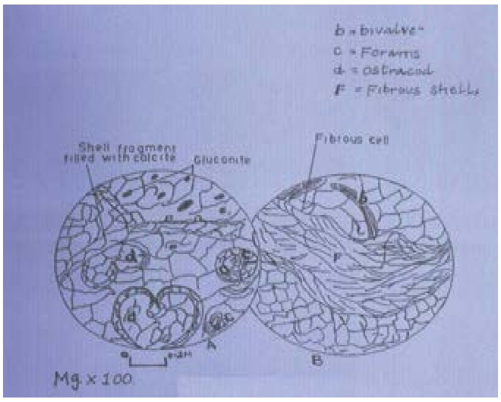

Figure 6. Thin Section Diagram of NU1 Sample under PPL

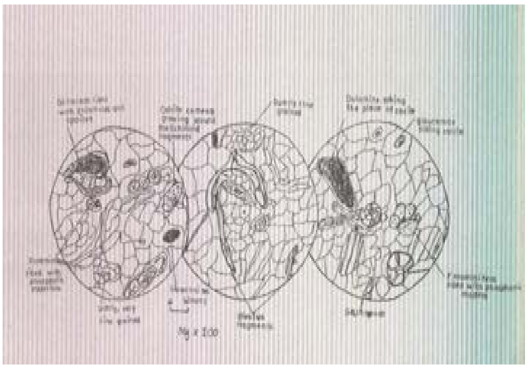

Figure 7. Thin Section Diagram of NU1 Sample under PPL

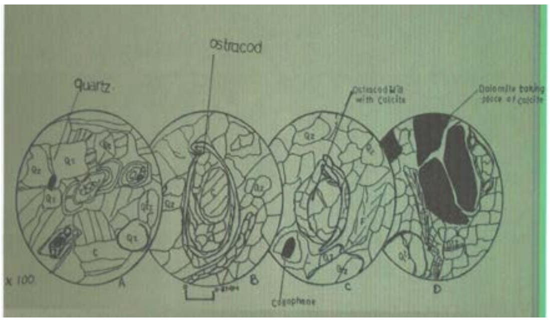

Figure 8. Thin Section Diagram of NU2 Sample under XPL

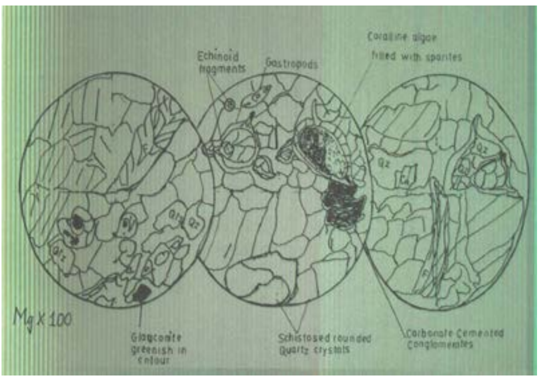

Figure 9. Thin Section Diagram of NU2 Sample under XPL

4. Geochemistry

The major elements abundance in the representative samples of the limestone were determined using Atomic Absorption Spetrophotometry (AAS). After digestion of the samples the concentration of Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, and S in the limestone samples were measured with a single element light source. Calibration for each element was achieved using four AAS standard solutions of known concentrations. Elemental values were recalculated to oxides using appropriate conversion factors. Summary of the chemical results is presented in Table 1. CaO expectedly constitutes the dominant component of the limestone and ranges in value from average 36.35% of Ndi-Uduma Ukwu to average 46.15% of Ohafia-Ifigh. This is very much in agreement with [5] which asserted that limestone units at Ohafia have relatively high CaO content (41-53%) with most samples having CaO values of over 45% and with a few having less than 45%. SiO_2 (Silica) is the chief source of impurity and measured up to average 8.05% in the Ndi-Uduma Ukwu samples. It is also noteworthy that Ohafia sample is sulphur free while measuring up to average 1% in Ndi-Udima Ukwu limestone. MgO in Ohafia samples averages 0.05% and at 3.34% ranks next to silica as source of impurity in the Ndi-Uduma Ukwu limestone. Dolomitization could be responsible for this relatively high percentage content. The Ohafia-Ifigh limestone though purer (82.41%$CaCO_3$) does not compare favourably with either the Mfamosing limestone (96.68%$CaCO_3$) regarded as high purity limestones used for fluxing application steal making (Table 1).

5. Utilization

5.1. Cement Production

Cement is made by calcining silicate clinker which is then ground and mixed with a small amount of gypsum which acts as a setting retardant [11]. Impurities in the raw material which may affect the quality of cement include magnesium, fluorine, phosphorous, lead, zinc, alkalis and sulphides. Most national specification for ordinary Portland cement require that the cement should contain less than 6% MgO, other chemical specification may limit SO_3 and P_2O_5 to less tan 1% and total alkalis to less than 0.6% [11]. The Ohafia-Ifigh limestone with $CaCO_3$% of 82.41% fits into [12] class of marly lime and is suitable for the manufacture of water lime and could be utilized in the manufacture of cement. On the other hand the Ndi-Uduma Ukwu limestone having 65.08% $CaCO_3$ belongs to the class of limey marl and suitable for manufacture of Raman lime.

5.2. Dimension Stone

According to [13] several parameters including cement type and grain size directly affect building stone durability. Thus fine micritic limestones are less durable than coarse spar-cemented limestone. It is therefore evident that from the petrographic analyses of the limestones within the study area that they fit into the coarse spar-cemented limestones and therefore can be used as building stone.

5.3. Flue Gas Desulphurization

Limestone is becoming widely used to reduce emission of sulphur dioxide from gaseous combustion products in power generating plants. The limestone gypsum process involves passing the flue gases through circulating slurry of limestone and water. Sulphur dioxide dissolves and reacts with the limestone to form calcium sulphate which is then oxidized to gypsum. The gypsum thus may be a useful by-product. There are lower limits of quality required of the limestone. This is represented by a minimum $CaCO_3$% content of 80% and limitations on certain impurities. The Ohafia limestone meets this $CaCO_3$% content requirement.

Table 1. CHEMICAL COMPOSITION OF OHAFIA-IFIGH AND NDI-UDUMA UKWU LIMESTONE

COMPONENTS %	NU1 (a)	NU1 (b)	NU1 (average)	NU2 (a)	NU2 (b)	NU2 (average)
SiO_2	4.18	4.32	4.25	8.02	8.08	8.05
Al_2O_3	0.09	0.13	0.11	0.16	0.10	0.13
CaO	47.21	45.09	46.15	36.56	36.34	36.45
Fe_2O_3	0.49	0.43	0.46	1.57	1.87	1.72
MgO	1.03	0.89	0.96	3.64	3.04	3.34
MnO	0.09	0.13	0.11	0.38	0.34	0.36
Na2O	0.10	0.08	0.09	1.22	1.42	1.32
K2O	0.15	0.11	0.13	0.21	0.15	0.18
SO_3	0.00	0.01	0.00	0.98	1.02	1.00
P_2O_5	0.14	0.18	0.16	0.29	0.25	0.27
$CaCO_3$	84.30	80.51	82.41	65.28	64.89	65.08

NU1 = Limestone sample from Ohafia-Ifigh
NU2 = Limestone sample from Ndi-Uduma Ukwu

Table 2. CHEMICAL COMPOSITION OF OHAFIA LIMESTONE (NU1 AND NU2) WITH SHAPFELL LIMESTONE UK, AND MFAMOSING LIMESTONE S.E. NIGERIA

COMPONENTS %	1 SHAPFELL	2 MFAMOSING	3 NU1	4 NU2
CaO	54.72	54.15	46.15	36.45
MgO	0.35	0.45	0.96	3.34
SiO_2	0.71	0.89	4.25	8.05
Al_2O_3	0.52	0.28	0.11	0.13
Fe_2O_3	0.34	0.05	0.46	0.72
SO_3	0.025	0.13	0.00	1.00
$CaCO_3$	97.71	96.69	82.41	65.08

1. Carboniferous limestone of Shapfell, UK
Source: Downie et al, [14]
2. Mfamosing limestone, S.E. Nigeria
Source: Ofulume, 2008
3. Limestone sample of Ohafia-Ifigh, Ohafia Southeastern Nigeria
4. Limestone Sample for Ndi-Uduma Ukwu, Ohafia Southeastern Nigeria

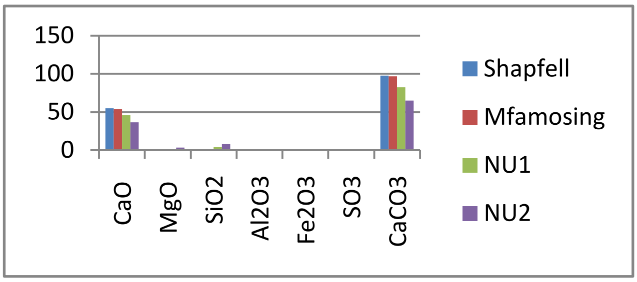

Figure 10. Histogram plot of major oxide composition of the samples compared with Shapefell and Mfamosing

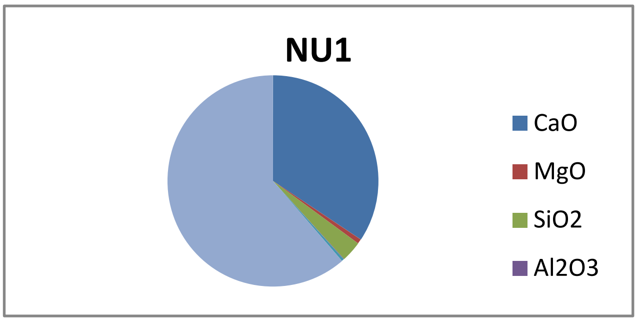

Figure 11. Pie chart showing major oxide composition of NU1 sample

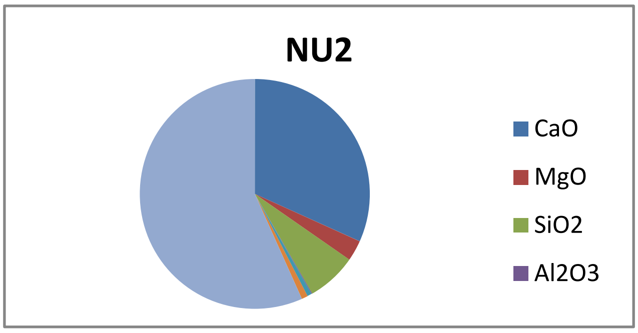

Figure 12. Pie chart showing major oxide composition of NU2 sample

5.4. Filler Application

Many uses of limestone powders such as in carpet backing, asphalt and coal mine dust do not require pure limestone (95% $CaCO_3$). Consequently the limestones under reference may be utilized for such purposes as fillers.

5.5. Agricultural

Requirements for agricultural limestone are not very rigid. The main function is to reduce soil acidity, although it may also be used to increase levels of calcium or magnesium in the soil.

6. Conclusion

Based on petrographic and geochemical analyses conducted on the Ohafia limestone samples, the following conclusion can be deduced:

1. The Ohafia limestone was deposited within Nsukka Formation during Maastrichtian to Paleocene in a shallow marine environment.
2. The presence of carbonate-producing organism such as Ostracod, foraminifera, echinoid in the limestone, as well as coralline algae are suggestive of shallow marine environment.

3. The presence of quartz pebbles in the limestone is indicative of short period of transgressive and regressive phases.
4. The Ohafia limestone can be classified based on the comprising mineralogical, chemical and biogenic compositions.
5. The quality of the limestone increases South-westerly (Ohafia-Ifigh) but decreases North-westerly (Ndi-Uduma Ukwu) with higher clastic influx.
6. The limestone fits into some industrial raw material standards for cement, agriculture, dimension and some other filler applications.

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