Determination Of Elemental Composition and Trace Elements in Limestone Deposit in Ikpeshi, Edo State, Nigeria

UMORU TITI ABDULASISI[1], SULE TUNDE USMAN NURUDEEN[2], SANNI ESHOVO BLESSING[3], EGUAOJE SAMUEL OMOKHEFE[4], OSIYOKU DADA AKANNI[5], IDIS GIMBA NURUDEEN[6], MAHMUD HAUWAU[7]

[1, 2, 3, 4, 5, 6] *Department of Petroleum and Mineral Resources Engineering Technology, Auchi Polytechnic, Auchi, Nigeria*

[7] *Department of Chemical Engineering Technology, Auchi Polytechnic, Auchi, Nigeria*

Abstract- ***The elemental composition and trace elements determination of limestone deposits in Ikpeshi, Edo State is done through qualitative analysis of the limestone, and it was aimed at determination of the major and trace elements present in the limestone from the study area. Five limestone samples were collected from the study area for qualitative analysis using X-ray fluorescence spectrometer. The result shows that the major elemental composition of the limestone in the study area is Ca (90.59%), with Si (3.33%), Al (0.92%) and Mg (1.58%) and the minor elements are S (0.66%), Sn (0.53 %), Sb (0.52 %), K (0.49 %), P (0.37%) and Mo (0.29 %). The trace elements present in the limestone are V (0.0017 %), Mn (0.0015 %), Co (0.0033 %), Ni (0.0194 %), Cu (0.0151 %), Zn (0.03 %), As (0.0005 %), W (0.0131 %), Au (0.0178 %), Ag (0.0009 %), Rb (0.0031 %), Nb (0.0016 %). The chemical relationship for purity determination between Ca/Mg ratio in the limestone from the study area is 98.40, while the Mg/Ca ratio is 0.01 and this ratio falls into the pure limestone class which revealed that the limestone in the study area is a pure limestone.***

Indexed Terms- ***Limestone, analysis, trace elements, determination, purity.***

I. INTRODUCTION

The elemental composition and trace elements determination of limestone deposits in Ikpeshi, Edo State is done through qualitative analysis of the limestone deposit from the study area. This research was conducted to determine the major and trace elements present in the limestone from the study area. Limestone is a carbonate sedimentary rock comprises of Calcium carbonate ($CaCO_3$) as the principal compound, and when the carbonate rocks contains a high percentage of the mineral dolomite, $CaMg(CO_3)_2$, it is referred to as dolostone. The United States Geological Survey [1], dolomite was referred to as magnesia limestone. Unlike other sedimentary rocks limestone composes of grains of skeletal fragments of marine organisms whose shells are made up of aragonite or calcite and it is colourless or white in its pure state and in its purest form it is called calcite. Iron and manganese carbonates are sometimes present in limestone, giving rise varieties of limestone. Limestone is an important industrial material for the production of cement, plaster of Paris, paints, drugs, ceramics and construction material. The quality of limestone is significant to its industrial application and the major elemental composition and trace elements presents in of significant to its utility, also the impurities present in it can as well hindered its usage as industrial raw material. Limestone is one of the solid mineral resources in Nigeria and it is located in various parts of the country, with the Calabar flank as the main carbonate province in Nigeria [2]. The need to investigate the major and trace elements present and the quality of the limestone in the study area for industrial production necessitated this research work.

II. THE STUDY AREA

A. Location of the study area

The study area lies in the South-South geo-political region of Nigeria and falls within latitude $7^0 06^1$N and $7^0\ 11^1$ and longitude $6^0\ 08^1$ E and $6^0\ 15^1$. It can be accessed through the Auchi-Igarra road.

B. Local Geology

The study area lies between the Southwestern basement complex and the Anambra Basin in Nigeria. The geological framework of Nigeria lies inside the Pan – African Orogeny of the West African craton which was the major tectonic event that happened about 600million years ago [3]. The Geology of Nigeria is made up of two major units; the Precambrian and the sedimentary rocks and the two units occur in equal proportions [4]. The basement complex comprises of migmatitie-gneiss complex, older granites, schist, charnocktic rocks and unmetamorphosed dolerite dykes. The fig. 1 shows limestone occurrences in Nigeria.

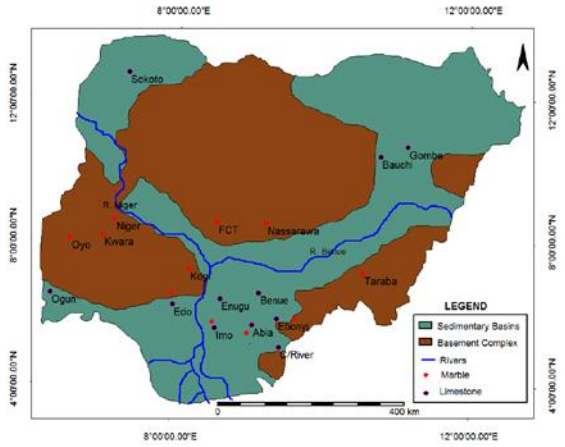

Fig. 1: Geology map of Nigeria

The Anambra Basin belongs exclusively to Nigeria [5] and it is a structural depression located at the south-western of the Benue trough with its lithology is shown in table I.

Table I: Lithological Sequence of Anambra Basin [5]

SN	Stratigraphic Units	Lithology
1	Nsukka Formation	Shale, sandy shale, ferruginized reddish clay and sandstone, silts and clay stones, Upper Coal Measure
2	Ajali Formation	Sandstone
3	Mamu Formation	Shale, sandy shale, Carbonaceous shale, Lower Coal Measure
4	Nkporo Formation	Shale, inter-bedded sand and mud

C. Geomorphology of the area

The study area have a gently undulating topography with climate commonly changing between dry and rainy seasons, as the two principal seasons, rainy season is from March to November with short break in August, while the dry season starts in November and ends in March, and harmattan occurs between December and February. The vegetation of the area falls within the guinea savannah. The mean temperature is between 28º C to 35º C, which is very intense around March to April and lowest in August [6].

III. METHODOLOGY

The qualitative analysis of limestone was conducted to determine its elemental chemical composition of using X-ray fluorescence (XRF) spectrometer. Five limestone samples were collected from the study area for qualitative analysis, the sample were crushed and pulverized into fine grain and then pelletized before testing. The analysis of elements in the limestone samples by XRF was made possible by the behavior of atoms when they interact with x radiation. The samples were illuminated by an intense X-ray beam (incident beam) and the samples were excited, some of the energy were scattered, but some were also absorbed within the sample in a manner that depends on its chemistry. The excited samples in turn emit X-ray along a spectrum of wavelength characteristics of the types of atoms present in the sample. The elements analyzed were Calcium (Ca), Magnesium (Mg), Aluminum (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Potassium (K), Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Cobalt (Co), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Lead (Pb), Tungsten (W), Gold (Au), Silver

(Ag), Rubidium (Rb), Cadmium (Cd), Niobium (Nb), Molybdenum (Mo), Tin (Sn) and Antimony (Sb).

IV. RESULTS AND DISCUSSION

The table II shows the statistical summary of XRF analytical results of the limestone samples from the study area in part per million (ppm).

Table II: Statistical summary of XRF result of limestone samples from the study area

Elements	Mean value	Std. dev.	Max. value	Min. value	% of elements
Ca	63.7191	3.4799	66.7721	59.4156	90.59492
Mg	0.647575	0.1084	0.7212	0.4863	0.920713
Al	1.1099	0.6701	1.8441	0.3438	1.57804
Si	2.340275	1.5405	3.8914	0.9372	3.32737
P	0.260625	0.0093	0.2732	0.2516	0.370553
S	0.465875	0.1704	0.6936	0.2827	0.662375
K	0.346225	0.2328	0.5041	0.0000	0.492258
Ti	0.0000	0.0000	0.0000	0.0000	0.0000
V	0.001225	0.0009	0.0014	0.0000	0.001742
Cr	0.0000	0.0000	0.0000	0.0000	0.0000
Mn	0.00105	0.0003	0.0012	0.0006	0.001493
Co	0.00235	0.0009	0.0028	0.001	0.003341
Fe	0.430275	0.2886	0.721	0.178	0.611759
Ni	0.013675	0.0013	0.0156	0.0127	0.019443
Cu	0.01065	0.0025	0.014	0.0081	0.015142
Zn	0.0222	0.0036	0.0274	0.019	0.031564
As	0.000375	0.0003	0.0005	0.0000	0.000533
Pb	0.0000	0.0000	0.0000	0.0000	0.0000
W	0.009175	0.0030	0.0118	0.0066	0.013045
Au	0.012525	0.0051	0.0124	0.0067	0.017808
Ag	0.00065	0.0008	0.0013	0.0000	0.000924
Rb	0.00215	0.0014	0.0031	0.0001	0.003057
Cd	0.0000	0.0000	0.0000	0.0000	0.0000
Nb	0.00115	0.0014	0.0029	0.0000	0.001635
Mo	0.203925	0.0357	0.2378	0.1530	0.289938
Sn	0.37115	0.0723	0.4782	0.3261	0.527696
Sb	0.361975	0.0579	0.4469	0.3170	0.514651

*Test Time – 100 seconds, Voltage – 40.0 KV, Current – 350 μA. Std. dev. – standard deviation, max – maximum, mim – minimum, % - percentage

Fig. 2 shows the various elements concentration in the limestone from the study area.

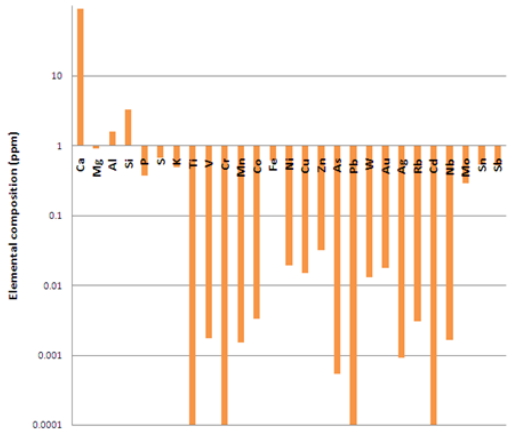

Fig. 2: Elemental composition in limestone from the study area

The elemental analysis of limestone from the study area (table 1) shows that the concentration of Ca is 63.7191±3.4799 ppm, and it is 90.59 % of the limestone. The concentration of Mg is 0.6476±0.1084 ppm, and it is 0.92 % of the limestone, Al has a concentration of 1.1099±0.6701 ppm and it is 1.58 % of the limestone, Si has a concentration of 2.3403±1.5405 ppm and it is 3.33 % of the limestone, P has a concentration of 0.2606±0.0093 ppm and it is 0.3706 % of the limestone, S has a concentration of 0.4659±0.1704 ppm and it is 0.6624 % of the limestone, K has a concentration of 0.3462±0.2328 ppm and it is 0.49 % of the limestone, V has a concentration of 0.0012±0.0009 ppm and it is 0.0017 % of the limestone, Mn has a concentration of 0.0011±0.0003 ppm and it is 0.0015 % of the limestone, Co has a concentration of 0.0024±0.0009 ppm and it is 0.0033 % of the limestone, Fe has a concentration of 0.4303±0.2886 ppm and it is 0.61 % of the limestone, Ni has a concentration of 0.0137±0.0013 ppm and it is 0.0194 % of the limestone, Cu has a concentration of 0.0107±0.0025 ppm and it is 0.0151 % of the limestone, Zn has a concentration of 0.0222±0.0036 ppm and it is 0.03 % of the limestone, As has a concentration of 0.0004±0.0003 ppm and it is 0.0005 % of the limestone, W has a concentration of 0.0092±0.0030 ppm and it is 0.0131 % of the limestone, Au has a concentration of 0.0125±0.0051 ppm and it is 0.0178 % of the limestone, Ag has a concentration of 0.0007±0.0008 ppm and it is 0.0009 % of the limestone, Rb has a concentration of 0.0022±0.0014 ppm and it is 0.0031 % of the limestone, Nb has a concentration of 0.0012±0.0014 ppm and it is 0.0016 % of the limestone, Mo has a concentration of 0.2039±0.0357 ppm and it is 0.29 % of the limestone, Sn has a concentration of 0.3712±0.0723 ppm and it is 0.53 % of the limestone, Sb has a concentration of 0.3620±0.0579 ppm and it is 0.52 % of the limestone. The result shows that the major elemental composition of the limestone in the study area is Ca (90.59%), with Si (3.33%), Mg (1.58%), Al (0.92%) and Fe (0.61 %). The minor elements are S (0.66%), Sn (0.53 %), Sb (0.52 %), K (0.49 %), P (0.37%) and Mo (0.29 %). The trace elements present in the limestone are V (0.0017 %), Mn (0.0015 %), Co (0.0033 %), Ni (0.0194 %), Cu (0.0151 %), Zn (0.03 %), As (0.0005 %), W (0.0131 %), Au (0.0178 %), Ag (0.0009 %), Rb (0.0031 %), Nb (0.0016 %). Fig. 3 shows the trace elements present in limestone from the study area.

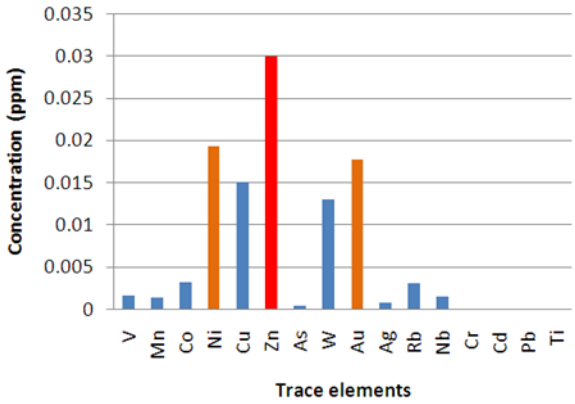

Fig. 3: Trace elements in limestone from the study area

In determining the mineral in the limestone, a triangle plot of Ca, Mg and Fe composition of carbonate minerals stable at the low temperatures near the earth's surface for classifying the limestone type in the study area was done. Fig. 4 shows the triangle plot of carbonate minerals stable at the low temperatures and the Ca/Mg/Fe proportion in limestone from the study area was plotted on it, in order to classifying the limestone type in the study area. The plot reveals that the mineral Calcite (or Aragonite) comprises the limestone.

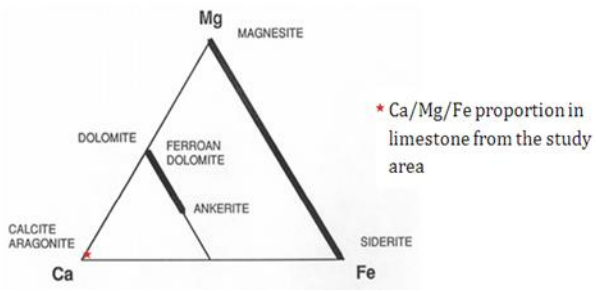

Fig. 4: Triangle plot of Ca, Mg and Fe composition of carbonate minerals stable at the low temperatures near the earth's surface

Todd (1966) set parameter for chemical classification of limestone in terms of Ca/Mg and its reciprocal Mg/Ca ratios (table III).

Table III: Chemical Classification of Carbonates [7]

Expressive Name	Average Proportion Calcium/Magnesium	Mutual Proportion Magnesium /Calcium
Pure Limestone	100.00 – 39.00	0.00 – 0.03
Magnesian Limestone	39.00 – 12.30	0.03 – 0.08
Dolomitic Limestone	12.30 – 1.41	0.08 – 0.18

Table IV shows the chemical relationship between Ca/Mg and Mg/Ca ratios in the limestone from the study area.

Element	Contents (%)	Mean	Std Dev
Ca	90.5949	63.7191	3.4799
Mg	0.9207	0.6476	0.1084
Ca/Mg ratio	98.40		
Mg/Ca ratio	0.01		

The investigation of elemental composition and trace elements present in the limestone from the study area was conducted to determine the elements present in the limestone, which comprises of Calcium carbonate ($CaCO_3$). The elemental chemical analysis was done of by X-ray fluorescence spectrometer. The result shows that the major elemental composition of the limestone in the study area is Ca (90.59%), with Si (3.33%), Al (0.92%) and Mg (1.58%) and the minor elements are S (0.66%), Sn (0.53 %), Sb (0.52 %), K (0.49 %), P (0.37%) and Mo (0.29 %). The rest of the elements were present as trace elements. The chemical relationship between Calcium and Magnesium ratio in the limestone was done to classify the limestone. The chemical relationship between Ca/Mg ratio in the limestone from the study area is 98.40, while the Mg/Ca ratio is 0.01 and this ratios falls into the pure limestone class [7] which revealed that the limestone in the study area is a pure limestone. The limestone from the study area is suitable for cement production and other industrial purposes.

CONCLUSION

The investigation of elemental composition and trace elements present in the limestone from the study area was conducted to determine the elements present in the limestone, which comprises of Calcium carbonate ($CaCO_3$). The elemental chemical analysis was done of by X-ray fluorescence spectrometer. The result shows that the major elemental composition of the limestone in the study area is Ca (90.59%), with Si (3.33%), Al (0.92%) and Mg (1.58%) and the minor elements are S (0.66%), Sn (0.53 %), Sb (0.52 %), K (0.49 %), P (0.37%) and Mo (0.29 %). The rest of the elements were present as trace elements. The chemical relationship between Calcium and Magnesium ratio in the limestone was done to classify the limestone. The chemical relationship between Ca/Mg ratio in the limestone from the study area is 98.40, while the Mg/Ca ratio is 0.01 and this ratios falls into the pure limestone class (Todd, 1966) which revealed that the limestone in the study area is a pure limestone. The limestone from the study area is suitable for cement production and other industrial purposes.

REFERENCES

[1] United State Geological Survey, –United State Geological Survey Year book, 1990. US. 1990 Government Printing Office, United State, 1990.

[2] Reijers, T. J. A. & Nwajide, C. S, – Geology of the Southern Anambra Basin. Unpublished Report for Chevron Nigerian Limited. Field Course Note, pp 66, 1998.

[3] Obaje Nuhu George, – Geology and Mineral Resources of Nigeria. London, New York: Springer Dordrecht Heidelberg, 2009.

[4] Woakes, M., Ajibade C. A., Rahaman, M. A, – Some metallogenic features of the Nigerian Basement, 1987. In: Akindele, O. O (Ed.), *Geology and geotectonic setting of the Basement Complex rocks in south western Nigeria: Implications on provenance and evolution*. Retri eved from https://cdn.intechopen.com/pdfs-wm/24552.pdf

[5] Okogbue, C. O., – Hydrocarbon Potential of the Anambra Basin: Geology, Geochemistry and Geochemistry Perspectives, Proceeding of the First Seminar Organized by the Petroleum Technology Development Fund (PTDF), University of Nigeria, Nsukka, 2005.

[6] Nigeria Metrological Agency, – NIMET annual report on Rainfall and flood prediction in Nigeria, 2010.

[7] Todd T. W., – Petrogenetic Classification of Carbonate Rocks. Journal of Sedimentary Petrology, vol. 36, pp 317 – 340, 1966.