



## A Geochemical Appraisal of Some Marble Physiques in Ubo Area and Environs, Southwestern Nigeria

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**ABSTRACT:** Twenty (20) marble samples from Ubo and environs were analyzed both geochemically and statistically with the aim of determining their industrial applicability. The samples were subjected to AAS analysis. Findings revealed a fairly high - very high values of CaO (52.98wt% - 82.18wt %) and low values of MgO (1.64wt%-6.95wt %). Other major oxide such as SiO<sub>2</sub>, FeO/Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> had values below 2wt%. The multivariate analysis employed revealed a high correlation between CaO/Fe<sub>2</sub>O<sub>3</sub>, MgO/Al<sub>2</sub>O<sub>3</sub> and FeO/CaO which is an indication of their fairly similar valencies and ionic values. The high lime content is connected to the shallow marine environment during deposition prior to metamorphism. The marbles are classified as the high calcite group and their industrial use range from the production of Portland cement to their use for ceramics.

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Despite abundant petrological and structural studies as well as geological mapping performed over several decades in Igarra and environs by (Emofurieta, 1984; Folami and Ojo, 1991; Obasi, 2012; Onimisi *et al.*, 2015; Obasi *et al.*, 2015; Kayode and Enu, 1976), not much research and detailed geological mapping have not been done on the marble Formations in Ubo area. Marble is a major raw material for industries and results from metamorphism of limestone, a carbonate sedimentary rock formed in shallow marine and lake environments which is further subjected to change in temperature (150°-650°C) and pressure (3kb - 15kb) (Mason, 1966). This study is aimed at classifying the marble in the study area geochemically in a bid to determine its applicability in the industrial sector. Multivariate statistical analysis was also used to determine the elemental relationship between the major oxides and help to reconstruct the paleo-environmental conditions that probably existed during the deposition of the sediments. The study area is located in Ubo area Akoko-Edo LGA, SW Nigeria and lies between latitude N07° 18'10" to N07° 20' 8" and longitude E006°18' 34" to E006°27'29.4" on Auchi Sheet 266 on a scale of 1:100,000 covering an area extent of 95.58km<sup>2</sup> (Figure 1). The Nigerian Basement Complex forms part of the trans-Saharan Pan African mobile belt of neo-Proterozoic (500–750Ma) age situated between the Archean-Paleo-Proterozoic blocks of the West African Craton to the west, the east Saharan blocks to the east and the Congo Craton to the southeast. The evolution of the Nigerian basement complex took place within, at least four orogenic events viz: Liberian (2800±200Ma), Eburnean (1950±200Ma), Kibaran (1100±200Ma) and the Pan African Orogeny (600±150Ma). The Pan-African

Orogeny was the most important, evidenced by the development of the Older Granites (Oyawoye, 1964). Rahaman, (1989) identified six major rock types and they are: (1) Migmatite – gneiss – quartzite complex (2) Slightly migmatized to non-migmatized metasedimentary and meta- igneous rocks which are often referred to as Newer metasediment (Oyawoye, 1970) or the Schist belts. (3) Charnockitic, gabbroic and dioritic rocks. (4) Members of the Older granite suite. (5) Metamorphosed to unmetamorphosed calc-alkaline volcanic and hypabyssal rocks (McCurry, 1976; McCurry and Wright, 1971). (6) Unmetamorphosed dolerite dykes, basic dykes and syenite dykes etc. Furthermore, Odeyemi, (1988) divided the rocks in Igarra areas as belonging to the:- (i) Migmatites, biotite and biotite– hornblende gneisses. (ii) Low grade metasediments,(schists, calc-silicate gneisses, marbles, polymict metaconglomerates and quartzites) (iii) Syn-late tectonics porphyritic biotite and biotite hornblende granodiorites and adammellites, charnockites and gabbros, unmetamorphosed dolerites, pegmatites, aplites and syenite dykes.

The Ubo body is associated with crystalline rocks of the Precambrian basement complex including migmatites, quartzites, porphyritic granites, the granites, charnockites, calc-gneisses, pegmatites, biotite and biotite hornblende granites (Figure 2). The outcrop was mined by the then Bendel Cement Factory but remnant of the body showed it is white in colour and very coarse grained in texture. It has sharp contact with the charnockites. A pegmatitic dyke of about 30cm thick cross-cuts the body. There is a reaction zone between the charnockites and the marble body.

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The orientation of the Ubo marble is within west of NNS-NE-EW trends with dip values of 26°-90°.

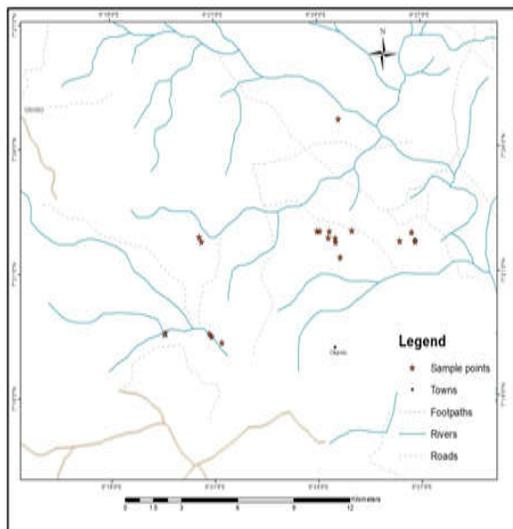


Fig.1: Map of study area showing sample locations

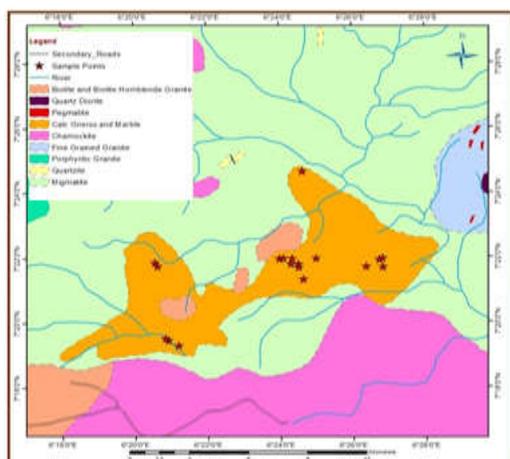


Fig.2: Geologic map of study area (GSN, 2015)

## MATERIALS AND METHODS

**Sample Collection:** Twenty (20) samples were collected from different locations within the study area using a sledge hammer.

**Sample Preparation and Analysis:** The samples, well labeled, were pulverized using a disc mill to reduce the size and increase the surface area during digestion. The reagents used were all of analytical grade (Adler, 1971). 1gm of the sample was weighed into a teflon crucible. 5ml, of concentrated HF was added to the powdered sample. Effervescence occurred and the teflon crucible was placed in the sand-bath which was heated to a temperature of 120°C for 30 minutes. 5ml of concentrated HClO<sub>3</sub> was added and placed in the sand-bath for another 10-30 minutes until the substance was molten. The crucible was brought down to cool slightly and 5ml of concentrated HCl was finally added. The sample was allowed to cool and

made up to 250ml with de-ionized water and finally poured into well labeled sampled bottles in preparation for further geochemical analysis (25ml for dilution factor of 100) (Thompson and Wood, 1981). The alkali metals K<sup>+</sup> and Na<sup>+</sup> were analyzed using a flame photometer. The instrument was switched on and allowed to stand for 1 hour to be stabilized. It was calibrated with the highest and lowest standard series to obtain a linear range (working range). The standard series of the order 0, 2, 4, 6, 8, 10ppm were determined with the resultant values recorded. The Atomic Absorption Spectrophotometer (AAS) was used to determine the other major elements.

## RESULTS AND DISCUSSION

Table 1 shows the major elements of the marble from the area of study. The Na<sub>2</sub>O values range of 0.03-0.43%, K<sub>2</sub>O from 0.02-0.84%, CaO from 52.98-82.18%, MgO from 1.11-6.95% SiO<sub>2</sub> from 0.01-0.03% MnO<sub>2</sub> from 0.01 – 0.04% Al<sub>2</sub>O<sub>3</sub> from 0.01-0.34%, Fe<sub>2</sub>O<sub>3</sub> from 0.03-1.31% and FeO from 0.05-1.52%. The mean values for the major oxides range between 0.02% - 63.82% for MnO<sub>2</sub> and CaO, respectively. All the samples in this study had MgO values < 6% except sample 5 which suggests they are low magnesium marble (Brown, 2007). 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 Ca<sup>2+</sup> with Mg<sup>2+</sup> and also probably contribution of magnesium rich organic matter in low temperature environments (Pettijohn, 1975).

The low Al<sub>2</sub>O<sub>3</sub> (0.01-0.34%) could be attributed to the absence of aluminosilicates or probably due to the low energy environment of the area at the time of deposition. Alkali content of the rock is known to be < 1%. Clarke (1924) is of the opinion that alkali content decreases in marbles with increase in salinity. The alkali content of Ubo marble could be considered to have formed in a relatively deep shallow environment with very little input from salty brine water in the basin (Onimisi et al., 2015; Olatunji, 1989). The fairly high - high value of CaO, (58.98-82.18%) is an indication that the marble in study area are calcitic in composition and the CaO/MgO ratio range from 9 - 40. Sample 5 had a CaO/MgO of 9.10 owing to the high MgO content of 6.95% while sample 9 had a CaO/MgO of 40 owing to the very high value of CaO (82.18%) and low value of MgO (2.05%). The high CaO content in sample 9, 16 and 19 can be attributed to large amount of Ca-rich mineral (calcite) in the environment. The inter-elemental association was determined statistically with the aim of determining the relationships between variables and their relevance to the actual problem being studied. For this study, Pearson's correlation matrix was used to determine a linear relationship between two variables (Webbs and Howarth, 1979). Table 2 shows the correlation matrix for the major oxides in the study. It was observed that there is a very strong positive correlation between M<sub>2</sub>O

vs Al<sub>2</sub>O<sub>3</sub> (+0.838), FeO vs Fe<sub>2</sub>O<sub>3</sub> (+0.999), CaO vs Fe<sub>2</sub>O<sub>3</sub> (+0.803), FeO vs CaO, (+0.793) and a fairly strong positive correlation between MgO vs CaO (+0.634), SiO<sub>2</sub> vs K<sub>2</sub>O (+0.650) and Al<sub>2</sub>O<sub>3</sub> vs CaO (+0.479). The strong positive correlation between CaO

vs Fe<sub>2</sub>O<sub>3</sub>, FeO vs CaO and MgO vs CaO can be attributed to their similar valencies owing to the easy substitution and replacement of CaO for Fe<sub>2</sub>O<sub>3</sub>, FeO and MgO.

**Table 1:** The chemical composition of the samples in the study area

S/No	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	SiO <sub>2</sub>	MnO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO
1.	0.14	0.05	67.03	2.05	0.07	0.01	0.05	0.14	0.20
2.	0.08	0.02	58.82	3.27	0.08	-	0.10	0.03	0.05
3.	0.07	0.36	58.28	2.45	0.08	0.02	0.06	0.16	0.24
4.	0.43	0.54	67.03	2.86	0.03	0.08	1.05	1.52	
5.	0.05	0.02	63.25	6.95	0.07	-	0.02	0.26	0.38
6.	0.08	0.34	65.14	2.05	0.02	-	0.01	0.74	1.07
7.	0.08	0.02	69.83	4.09	0.02	-	0.01	0.17	0.25
8.	0.05	0.02	63.25	2.86	-	-	0.03	0.21	0.32
9.	0.24	0.07	82.18	2.05	-	0.01	0.08	0.40	0.58
10.	0.16	0.10	65.14	1.64	0.02	-	0.06	0.09	0.12
11.	0.24	0.43	67.04	2.86	-	-	0.08	1.31	1.90
12.	0.25	0.19	58.39	1.64	0.03	-	0.05	0.14	0.19
13.	0.32	0.84	58.39	4.19	-	0.02	0.34	0.41	0.62
14.	0.30	0.10	63.8	1.64	0.01	0.03	0.02	0.25	0.37
15.	0.24	0.10	61.36	2.86	0.04	0.01	0.10	0.12	0.16
16.	0.08	0.02	78.4	5.32	0.02	0.01	0.17	0.31	0.45
17.	0.08	0.05	62.44	3.68	0.02	0.03	0.12	0.08	0.12
18.	0.11	0.02	59.82	3.27	0.04	0.04	0.10	0.06	0.09
19.	0.22	0.08	70.29	2.86	0.02	0.02	0.14	0.25	0.36
20.	0.08	0.02	52.98	2.05	0.01	0.01	0.11	0.07	0.10
Mean	0.15	0.09	63.82	2.91	0.03	0.02	0.11	0.16	0.23
SD.	0.09	0.11	7.42	1.11	0.03	0.01	0.04	0.09	0.13

SD = standard deviation

**Table 2:** Correlation matrix for major elements of study area

	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	SiO <sub>2</sub>	MnO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO
Na <sub>2</sub> O	1.000								
K <sub>2</sub> O	0.057	1.000							
CaO	0.126	-0.260	1.000						
MgO	-0.436	-0.282	0.634	1.000					
SiO <sub>2</sub>	-0.268	0.630	-0.128	-0.190	1.000				
MnO <sub>2</sub>	0.079	0.000	-0.210	-0.042	-0.131	1.000			
Al <sub>2</sub> O <sub>3</sub>	-0.377	-0.398	0.479	0.838	-0.371	-0.193	1.000		
Fe <sub>2</sub> O <sub>3</sub>	0.359	0.083	0.803	0.302	-0.206	-0.235	0.188	1.000	
FeO	0.337	0.100	0.793	0.297	-0.203	-0.203	-0.171	0.999	1.000

The CaO/MgO ratio range from 9.10 in sample 5 to 40.08 in sample 9 is a reflection of abundance of calcite in the area. The MgO content in the sample is < 6.95% hence can be considered to be classified as pure marble (Cherneva et al., 2009; Basse, 2011) due to the low MgO content. The low silica, alumina and potash values indicate the low presence of quartz and feldspars in the area (Oyinloye, 2012). Where the CaO/MgO content > 12, the marbles are considered to be high calcite marble, where they occur between 4-12, they are considered to be high magnesian marble and where < 4 are considered to be dolomitic in composition (Cherneva et al., 2015). From this study all the samples indicate they belong to high calcite varieties except two samples (5 and 13) which gave values of 9.10 and 11.89, hence are high magnesian in composition. The marble in the study area are very useful for the production of cement when mixed with

clays. CaO content ranges between 52.98- 82.91wt% far above the basic requirement of CaO (≥ 35%) for cement production. Chips can also be crushed and used as terrazzo chips, concrete aggregate, ballast, road stone; massive or cut to shape and used for travertine for walls, floors slabs for shops and furniture, paving, kerbs and building stones; Cut, their crystals are used for nicol prisms in petrological microscopes; Milled for their optical properties and pigments such as paris white precipitated calcium carbonate (PCC), lake pigments white wash, paints, paper fill, paper coating plastic, rubber, linoleum, painting links; Precipitated as aerosols for mine dusting, printing and rolls, precipitated as abrasives for toothpaste, tooth powders, polishing powders; precipitated as fillers for cosmetics especially face powders, adhesives, pharmaceuticals including tableted goods and antibiotics. The naturally fine-grained varieties are used as sources of mineral

nutrient for preparata in bread and animal feeds stuffs. They could also be used as neutralizing in agriculture, pharmacies, water treatment, acid trade effluents and fermentation industries. When subjected to thermal treatments burnt lime (CaO) is hydrated Ca(OH)<sub>2</sub> and used for the manufacture of bleaching powder, ammonia, calcium carbide (CaC<sub>2</sub>), fertilizer, wood alcohol, soap, glycerin, glue, glass pottery and sugar; In tanneries are used in sewage, wool scouring, textiles and dyes; as budding lime in mortars, cements, pozzuolanas etc. as insecticides and fungicides; In lime – silica reaction products. When lime is reacted with silica can be used for flux in smelting operations, especially steel forming blast furnace slag, ceramics and glass (Robertson, 1960).

**Conclusion:** The marble in the study area are high calcite in classification with CaO/MgO > 12. Statistically, the high positive correlation of CaO vs Fe<sub>2</sub>O<sub>3</sub>, MgO vs Al<sub>2</sub>O<sub>3</sub>, FeO vs CaO and fairly high values of MgO vs CaO, SiO<sub>2</sub> vs K<sub>2</sub>O is attributable to the similar valencies of Fe, Ca, Mg and quite close ionic values of Al, Si, and K, respectively.

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