



A Geochemical Approach and Industrial Utilization of Some Marble Bodies from Ubo River Area and Environs, Southwestern Nigeria

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ABSTRACT: Marble bodies occur in Ubo River Area as lenses of rocks. Seven (07) marble samples were obtained, analyzed and subjected to X-Ray Fluorescence (XRF) analysis to determine both the major and trace elemental composition of the samples. The analysis revealed high CaO values (52.23-58.10 wt. %) and moderate values for SiO₂ (7.50-10.43 wt. %), fairly low values for Al₂O₃ (2.30 – 4.21 wt. %), Fe₂O₃ (2.62 – 5.15 wt. %), MgO (0.42 – 0.7 wt. %), MnO (0.01 – 0.06 wt. %), K₂O (0.32 – 1.55 wt. %) and Na₂O (0.01 – 0.03 wt. %), respectively. Variation plots involving Na₂O/Al₂O₃ vs K₂O/Al₂O₃ reveal sedimentary progenitors for the rocks. The fairly high SiO₂ and low K₂O content is an indication of the environment of deposition and may have been in a shallow marine environment with fair input of classic sediments into the system. The relatively high CaO content, moderate SiO₂ content and fairly low Al₂O₃ and Fe₂O₃ values indicates a fair degree of purity of the parent rock, hence its suitability as a raw material in the industrial sector.

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Marble is a metamorphic rock formed when limestone is subjected to changes in heat and pressure. Marble forms under such conditions because the limestone undergoes a recrystallization process in the solid state (Gillen, 1982). Marble is a rock, composed primarily of calcite (CaCO₃) and usually contains other impurities such as muscovite, biotite, pyrite, graphite and chlorite etc. The variety of colours exhibited by marble are a consequence of minor amount of the aforementioned minerals incorporated into the system during metamorphism. Marble fizzes on contact with dilute hydrochloric acid (HCl) (Robert, 1979). Marble bodies generally form at convergent plate boundaries, where large areas of the earth's crust are exposed to regional metamorphism. Some marble bodies form by contact metamorphism when a hot magma body heats adjacent limestone or dolostone (Robert, 1979). Prior to metamorphism, the calcite in the limestone is often in the form of lithified fossils with other biological debris. During metamorphism, calcite recrystallizes and the texture of the rocks becomes massive. Marble subjected to low grade regional metamorphism, possesses fine crystals, but metamorphism progresses the crystals increase in size. Clay minerals within the marble transform to micaceous and more complex silicate mineral as metamorphism progresses (Touret, 1997). The aim of this study is to determine the

chemical composition of the marble bodies with a view to bring to the fore the probable origin of the non-calcareous materials.

Geological Setting: The study area lies approximately between longitude E006° 00'26.7" to E006° 26'20.8" and latitude N07°05'26.7" to 7°26'00" on a scale of 1:100,000 on Auchi Sheet 266. The study area forms part of the crystalline basement complex rocks (Figure 1). The Precambrian basement complex of Nigeria is polycyclic in nature (Ajibade and Fitches, 1988) as it has been affected by more than one orogenic event accompanied by deformation and metamorphism. The most prominent of these being the Pan African Orogeny which overprinted and obliterated to a large extent earlier structures of the basement rocks (Fitches *et al.*, 1985). The Precambrian basement rocks include the migmatized gneissic complex of Archean to Early Proterozoic age (Dada, 1999; Dada *et al.*, 1993; Grant *et al.*, 1972), the N-S trending Schist belts of the Upper Proterozoic age (Rahaman, 1988) and the older granitoids of the Pan African age (Fitches *et al.*, 1985). The polycyclic migmatized gneiss complex rocks are the most widespread and occupy about 60% of the total surface area of the basement rocks (Rahaman and Ocan, 1988). The Schist belts occur as synformal troughs infolded into the migmatite-gneiss complexes

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and are largely sediment dominated. The most important lithologies are pelites, banded-iron formation, quartzites, marbles and calc-silicate rocks (Turner, 1983).

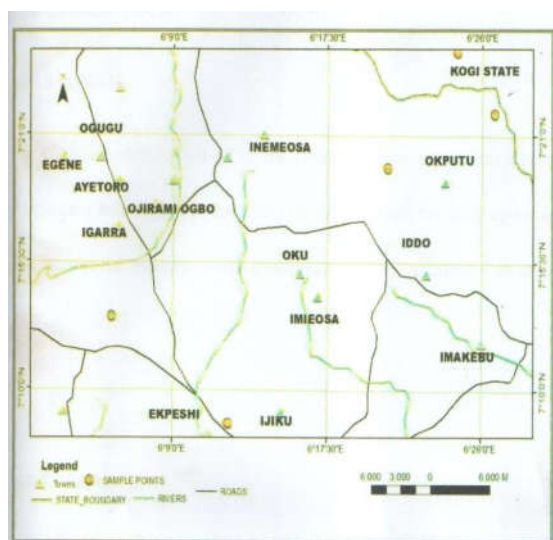


Fig 1: The location map of the study area (modified after GSN, 1974)

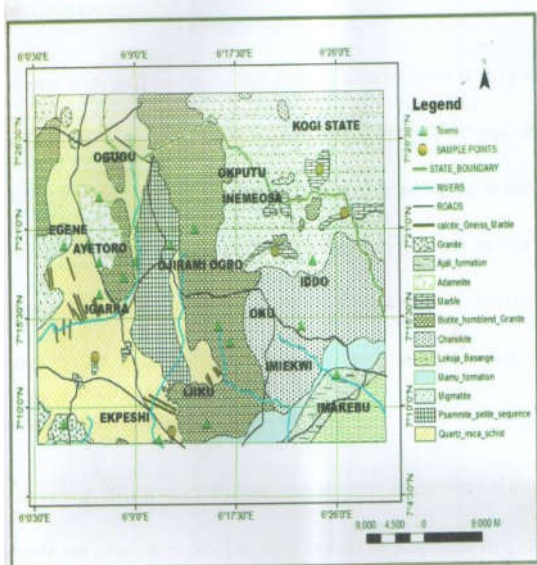


Fig 2: The geological map of the study area (modified after GSN, 1974)

The contact between the migmatite- gneiss complex rocks and the metasediments are fault bound in most cases (Odeyemi, 1988). The Older Granites represents a diverse magmatic cycle (750 ± 450 Ma) associated with the Pan African Orogeny (Woakes *et al.*, 1987). Rocks belonging to this suite vary in composition from tonalites-granodiorites-granites. Syenitic and granodiorite rocks appear to be most common (Rahaman, 1988). The marble bodies studied for this

paper are emplaced within the quartz mica schists near Ikpeshi area and the migmatites towards the north eastern axis of the area near Ubo River Area (Figure 2), respectively. A number of authors have worked on marble bodies within the basement complex such as Emofurieta and Aganbi, 2008; Obasi *et al.*, 2015; Ogungbuyi *et al.*, 2013; Onimisi *et al.*, 2013; Bassey and Obasi, 2012 to mention a few.

MATERIALS AND METHODS

A number of geological tools were employed for this study and they include the Global Positioning System (GPS), compass clinometer, the sledge hammer, sampling bag, field note books, writing material and dilute hydrochloric acid (HCl). Seven (7) rock samples (fresh) were collected using the sledge hammer from different locations of the marble bodies in the study area. The GPS was used to determine the coordinates where the samples were collected. The rock samples were labeled and kept in the sampling bag. The altitudinal measurements were determined using the compass clinometer. A drop of dilute HCl was placed on the sample and effervescence was observed. The samples were sent for geochemical analysis at National Steel Raw Material Exploration Agency (NSRMEA), Kaduna.

Pulverization of the Rock Sample: The X-ray Fluorescence technique was employed. In order to determine the chemical composition of the samples, the samples were first oven-dried at a temperature of 60°C , crushed using a disc mill to about 0.5mm grain size. They were then subjected to vibrating cup miller (Herzog model) by setting the equipment at 6-8rpm. Having obtained the powdered sample of particle size 100 mesh (0.15micron), the sample is ready for the XRF machine.

Pelletization of the sample: The powdered sample is mixed with a binder, usually sodium/lithium tetraborate (Borax). The ratio of the binder to the sample to be analyzed is about 4:1 grams. This ratio of binder to sample is evenly mixed using Herzog vibrating cup miller at 8rpm. The mixture is loaded onto a cup of size 22mm by 40mm made of aluminum material. The pelletizing machine is operated and the pressing force is set at 240Newtons and the movement stroke is set at 6rp. The pellet is formed ready for the XRF analysis.

Analyzing the sample using XRF: Pressure values are set at 16Pa (Paschal), the recommended voltage level is 45V and the current level is 40A. The equipment is allowed to run for 4-5 hours to enable the standards

and other features responsible for analysis to stabilize (Fitton, 1997).

RESULTS AND DISCUSSION

The results from the XRF analysis is shown on Table 1. CaO ranges from 52.23 – 58.10wt%, MgO ranges from 0.42 – 0.74 wt%, but was not detected in sample G, SiO₂ ranges from 7.50 – 10.43wt%, Fe₂O₃ ranges from 2.62 – 5.15wt%, Al₂O₃ from 2.30 – 3.40wt%,

MnO, from 0.01 – 0.09wt%, K₂O from 0.32 – 1.55wt% and Na₂O from 0.01 – 0.03wt%. The low MnO values indicates warm and humid climate during deposition of the carbonate sediments (Kotoky and Katakya, 1993). Table 2 shows the Silica Ratio (SR), Alumina Ratio (AR) and Lime Saturation Factor (LSF) of the results. The importance of this table is to determine the industrial use of the rock for the production Portland cement.

Table 1: Chemical Composition of Major Oxides from the study area (wt. %)

Elemental Oxides	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	i	ii	iii	
CaO	55.27	58.10	54.77	54.33	56.08	52.23	55.10	5.87	52.46	49.80	51.55
SiO ₂	9.36	9.20	10.43	10.00	7.50	8.06	10.43	2.93	3.76	6.75	4.91
Fe ₂ O ₃	3.23	2.70	4.35	3.33	2.62	5.15	4.56	2.53	0.66	1.47	0.66
Al ₂ O ₃	3.20	2.36	3.40	2.50	2.30	4.21	2.45	1.91	1.10	0.71	1.28
MnO	0.06	ND	0.09	ND	0.01	ND	ND	0.08			
K ₂ O	0.34	0.50	1.05	0.41	0.32	1.55	0.45	1.23	0.18	Tr	Tr
Na ₂ O	0.02	0.01	0.02	0.01	0.01	0.03	0.01	0.02	0.22	Tr	Tr
MgO	0.42	0.61	0.74	0.51	0.43	0.67	ND	0.32	1.23	1.48	0.63
SO ₃	0.13	0.18	0.53	0.30	0.21	0.40	0.41	0.40			
BaO	0.08	0.14	0.23	ND	0.12	0.35	0.30	0.27			
TiO ₂	1.72	1.43	1.30	0.45	0.16	0.30	ND	1.56			
Ta ₂ O ₅	0.04	ND	0.80	0.02	ND	0.10	0.03	0.78			
Eu ₂ O ₃	ND	0.01	0.05	ND	ND	ND	ND	0.04			
V ₂ O ₅	0.01	0.01	0.03	ND	0.03	0.02	ND	0.02			
HgO	ND	0.45	0.70	0.33	ND	0.30	ND	0.40			
CuO	ND	0.01	0.02	ND	0.04	ND	0.01	0.03			
Cr ₂ O ₃	0.02	ND	0.02	0.01	0.04	0.01	0.03	0.03			
Ag ₂ O	ND	0.04	0.02	ND	0.07	ND	0.03	0.05			
In ₂ O ₃	ND	0.01	0.02	0.01	0.04	ND	ND	0.03			
NiO	0.01	ND	0.01	ND	ND	0.01	ND	0.01			
LOI	27.20	24.20	23.13	27.80	30.01	26.78	25.93	5.81	40.38	39.65	40.76

Fe₂O₃ as Total Fe; ND = not detected; Reference Limestone Samples (i) – (iii) are from Cement Technology Course Volume (JAO-Geotect, 1987)

Table 2: Comparison of the industrial utilization of samples

Sample	A	B	C	D	E	F	G	i	ii	iii
SR	2.93	3.90	3.07	4.00	3.26	1.91	4.26	2.53	2.01	1.90-2.51
AR	0.99	0.87	0.78	0.75	0.88	0.82	0.54	1.94	5.56	1.50 – 2.50
LSF%	852	710	910	724	739	1106	753	320	307	242 – 417
CaO/MgO	131.59	95.25	74.01	106.53	130.42	77.96	-	81.88	171.00	

Sample A-G = Samples from study area; Reference limestone samples (i) & (ii) are from Cement Technology Course Volume (JAO-Geotect, 1987). Standard values (iii) from Cement Course Volume (JAO-Geotect, 1987)).

The SR values for the studied samples are higher than the reference samples (i) & (ii) but the AR of the studied samples are less than those of the reference samples (Table 2). The LSF values for the studied samples are higher than those of the reference samples. This is probably due to the high Al₂O₃ content of the reference samples. The very high values of LSF of the studied samples may also be due to the fair values of Fe₂O₃ and SiO₂ in the samples. The high values of Al₂O₃, Fe₂O₃ and SiO₂ content in the study area may be connected to the associated rocks namely, migmatites, in the area. The general standard values for SR, AR and LSF are 2.51, 2.31 and 242 – 417, respectively (JAO-Geotect, 1987). In order to achieve the above values, appropriate portions of raw materials rich in shale, laterite and silica-rich materials must be

added to the mix to boost the AR and SR values in other to meet the requirement for the production of Portland cement. The high CaO/MgO ratio is an indication of the low salinity condition during the formation of carbonate rocks (Marshner, 1968) prior to metamorphism. It is also an indication of the closeness to the shoreline during the period of deposition (Bora et al., 2013). The high CaO/MgO values (74.01 – 131.59) is an indication that the marble in the study area are calcite dominated, hence the marble can be characterized as pure marble or high quality marble (Todd, 1966). The CaO/MgO values are high and comparable to those of Mfamosing limestone, Jakura and Akure marble, Southwestern Nigeria (Ekwueme, 1995; Ofulume, 1993; Emofurieta and Ekuajemi, 1995). The metasedimentary

succession of the non-carbonate sediments indicates that the sediment possess sedimentary progenitors. This is revealed by the plot of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ versus $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ (Figure 3) according to Garrel and Mackenzie, (1971).

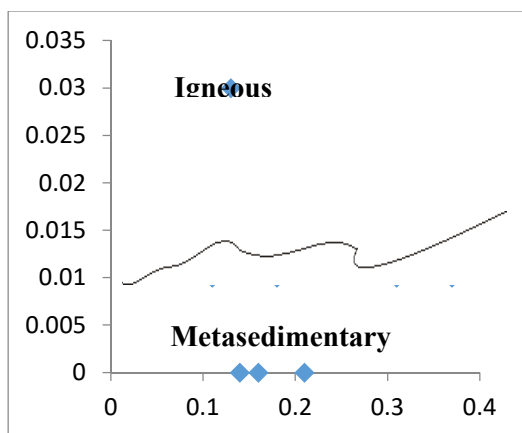


Fig 3: The metasedimentary plot of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ vs $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ (modified after Garrel and Mackenzie, 1971)

Figures 4 to 7 shows the relationship between CaO and SiO_2 , Fe_2O_3 , Al_2O_3 and MgO. In Figure 4, the plot shows a very weak positive relationship between CaO and SiO_2 . This is a reflection of the presence of siliceous materials probably from the incursion of remains of lower plants and animals during deposition (Baishya and Mahanta, 1994). The relationship between CaO and Fe_2O_3 , Al_2O_3 and MgO as shown in Figure 5, 6 and 7 is a strong but negative one which reveals that as CaO increases, Fe^{2+} , Al^{3+} and Mg^{2+} decreases (Bora, 2013). The bivalent plot between CaO and Fe_2O_3 indicates a slightly reducing environment (Wolf et al., 1967). It probably also depends on the availability of the materials in the basin, the chemistry of the ions and the effect of the environmental conditions that played out during deposition (Bora et al., 2013; Odokuma-Alonge and Amadin, 2018).

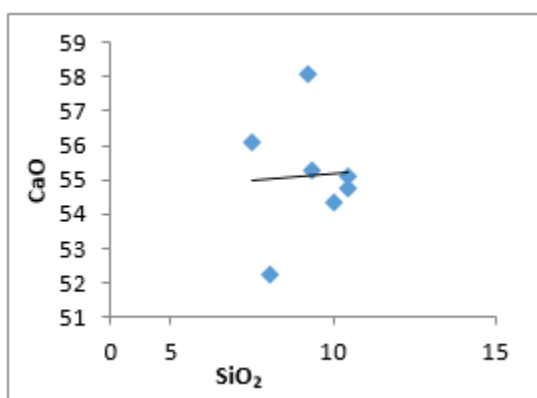


Fig 4: A plot of CaO vs SiO_2 showing a weak

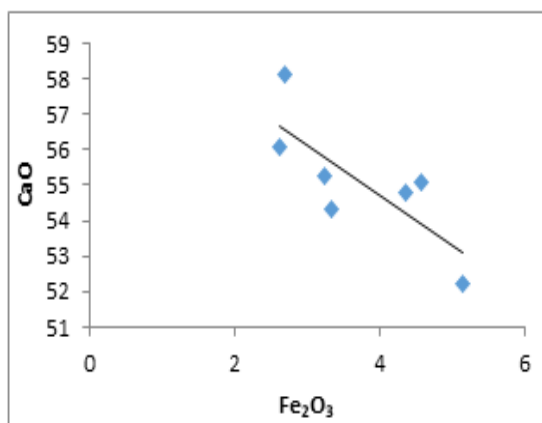


Fig 5: A plot of CaO vs Fe_2O_3 showing a positive relationship. Strong negative relationship

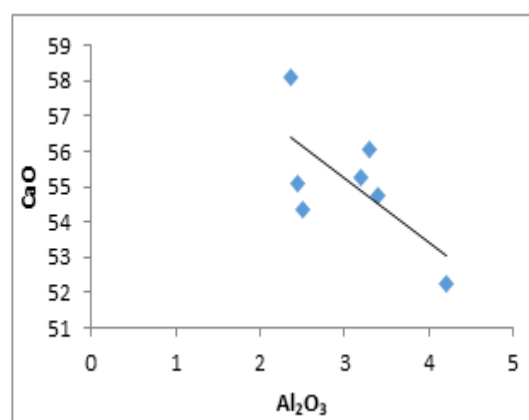


Fig 6: A plot of CaO vs Al_2O_3 showing a strong

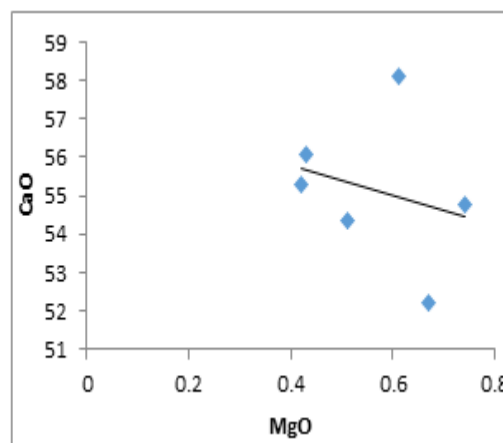


Fig 7: A plot of CaO vs MgO showing a negative relationship fairly strong negative relationship

Conclusion: The study area reveals that the marble bodies are emplaced within the schists in the western axis (Ikpeshi) and the migmatites towards the northeastern axis (Ubo River Area). Determination of the major oxides in the samples shows a high content of lime in the area. The metasedimentary succession agrees with the assertion that the non-calcareous

sediments have sedimentary progenitors. The very high CaO/MgO ratios and the high content of CaO in the rocks makes these marble to be considered as very good raw materials for the industrial sector.

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