X-RAY FLUORESCENCE AND STABLE ISOTOPES ANALYSES OF IKPESHI MARBLE, SOUTH SOUTHERN NIGERIA

[1]Ikhane, Phillips Reuben; [1]Oyebolu, Olalekan Olayiwola and [1]Alaka, Afolabi Omotayo.
[1]Department of Earth Sciences, Olabisi Onabanjo University, Ago – Iwoye
Correspondence author E-mail: Ikhane.phillips@oouagoiwoye.edu.ng

ABSTRACT

Integration of X-ray fluor escence and stable isotope spectrometric techniques for quality assessment and provenance study of exposed marble deposit at Fakunle Quarry, Ikpeshi, South Western Nigeria constitute the fundamental aims of this research. Fourteen fresh (14) marble samples obtained at different localities within the quarry were subjected to geochemical and isotopic analyses to ascertain the quantitative abundance of major oxides and stable isotopes using X-Ray Fluorescence and Thermo Fisher mass spectrometer respectively. The major oxides revealed by XRF analysis of the marble samples are CaO, MgO, SiO2, Al2O3, Fe2O3 and Na2O with percentage composition ranging between 11.66 – 13.25, 7.75 – 9.65, 41.36 – 47.55, 12.36 – 15.23, 7.79 – 10.55 and 1.44 – 1.75respectively. Na2O + K2O value ranges between 1.48 and 1.78.The classification of marble in relation to percentage of calcite-dolomite indicate a percentage range of -5 to 4% and 93-103% for Calcite and Dolomite respectively. Chemical Index of Alteration (CIA) ranges from 45.16 to 51.59 % and Chemical Index of Weathering (CIW) ranges from 46.19 to 52.30 %. Stable isotope (□–180) of marble ranges from -10.50 to -7.00 with a corresponding value from 25.50 to 55.33.Interpretation of the overall results indicates an impure quartz-rich dolomitic marble; metamorphosed from a low carbonate sedimentary/meta sedimentary protolith which shallowly precipitated within a passive marginal marine environment under humid condition. The high silica impurity can however be attributed to the inordinate influx of terrigenous sediments during the precipitation process. Weathering effect is minimal on the marble deposit. Conclusively, strong correlation is apparent between the obtained geochemical result and the basement geology of the study area.

Keywords: Marble, Meta sedimentary, Stable Isotope, dolomitic, mass spectrometer
Accepted Date: 12 June 2020

INTRODUCTION

Marble is one of the industrial rocks presently gaining prominence in the manufacturing sector of the Nigerian economy (Alabi *et al*., 2013) because of its wide range of industrial and domestic applications. Scott and Durham (1984) identified about 204 end uses of raw marble and lime (the calcined form of marble).The industrial use of a marble body is largely determined by its composition, required specification, end product and tonnage of deposit. Broadly, however, the economic values of marble can be classified under six main groups namely; metallurgical, chemical, environmental, construction, refractory and agriculture (Boynton, 1979). Each of these groups requires some chemical specifications for the marble to be useful. The research is aimed at determining the composition and provenance of the marble deposit at Ikpeshi, Southwestern Nigeria using X-ray fluorescence and stable isotope analytical techniques.

LOCATION AND ACCESSIBILITY

The study area is geographically located between longitude $6^{O}5^{1}24^{11}$E to $6^{O}7^{1}12^{11}$E and latitude $7^{O}13^{1}48^{11}$N to $7^{O}16^{1}48^{11}$N, Southwestern Nigeria (Fig. 1a)and highly accessible through a network of inter connected footpaths, major and minor roads. Although area is plagued with a rugged topography the availability of favourable derived savannah vegetation provides easy accessibility to the outcrops.

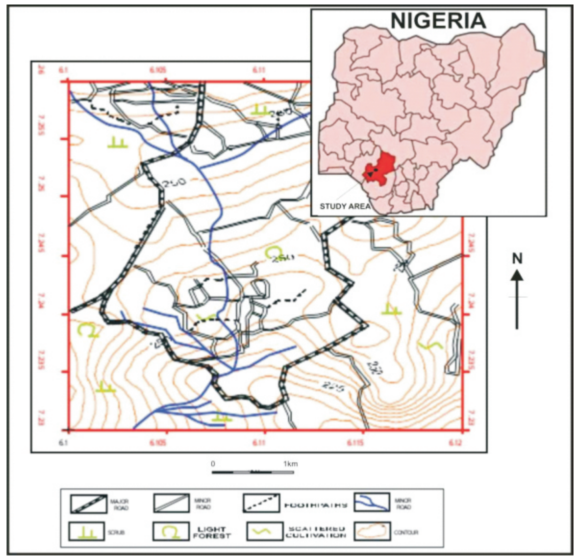


Fig. 1a: Accessibility Map of the Study Area

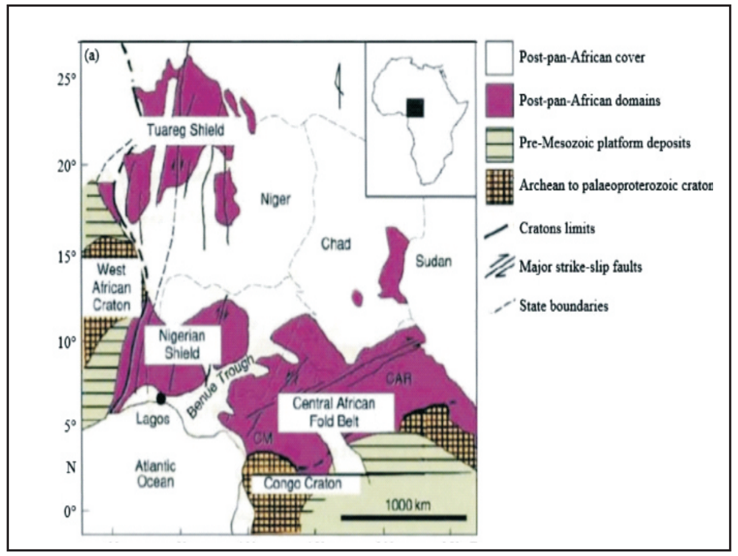


Fig. 1b: Geological sketchMap of Africa indicating Nigeria within reactivated Pan-Africandomain (Modified after Rahaman and Ocan, 1988)

LOCAL GEOLOGY

The study area constitute part of the Nigerian basement complex and schist belt in particular lying east in a mobile belt of the West African Craton affected by the Pan-African thermo tectonic events (Fig.1b). Lithologically, the study area can be divided into three major rock groups which include dolomitic marble, quartzite, gneisses with meta-sedimentary cover.

Fig. 2: Outcrop section in Fakunle Quarry site, Ikpeshi

MATERIALS AND METHODS

Fourteen spatially distributed marble samples within the confines of the quarry (Fig.2) were collected for analyses. Sequel to field activities, the marbles samples were prepared on a silicon carbide disc and ultrasonically purified with methanol for 10minutes and dried at 110^{0}C for at least 2hours. Larger fragments were reduced to a diameter of 1cm in a Spex shatter box, and further pulverized and transferred into the representative sample bags. Borate glass discs were then prepared for the X-ray analysis by mixing 2g of ignited sample powder with 4g lithium tetra-borate ($Li_2B_4O_7$) and labeled. In a platinum crucible, the mixture was melted together in an induction oven for several minutes. The resulting melt obtained was turned into a disc mould, and allowed to consolidate into a glass disc on which the whole rock analyses were made using an X-Ray Fluorescence spectrometer. Instrument settings were at count of 800-1000 for standards and 100seconds for major elements/oxides

Analysis of stable isotope composition for carbon and oxygen was done by using a Thermo Fisher DELTA V mass spectrometer – connected online to a Thermo Fisher Gas Bench II and a CTC Combi-Pal auto sampler. For the decomposition of the fine-grained samples (approximately 0.2mg), H_3PO_4 concentration was used in a 'He-flushed' atmosphere heated to a temperature of 700^{o}C (900^{o}C for dolomites); long-term precision turned out to be 0.06%0 for oxygen, and 0.05% for carbon, respectively.

RESULT AND DISCUSSION

The result of the X-Ray Flou rescence (XRF) and stable isotope analyses conducted on the fourteen marbles samples is depicted in Figure 3 and 4 respectively. In descending order of abundance, the major oxides revealed by XRF are SiO_2, Al_20_3, CaO, Fe_2O_3, MgO, and Na_2O, with a percentage composition range of 41.36 – 47.55, 12.36 – 15.23,11.66 – 13.25, 7.79 – 10.55,7.75 – 9.65, and 1.44 – 1.75respectively (Fig. 3). Other compounds (oxides) presents include P_2O_5 $K_2O$and TiO_2. Also stable isotope (δ–180) of the marble -10.50 to -7.00 (Fig. 4)

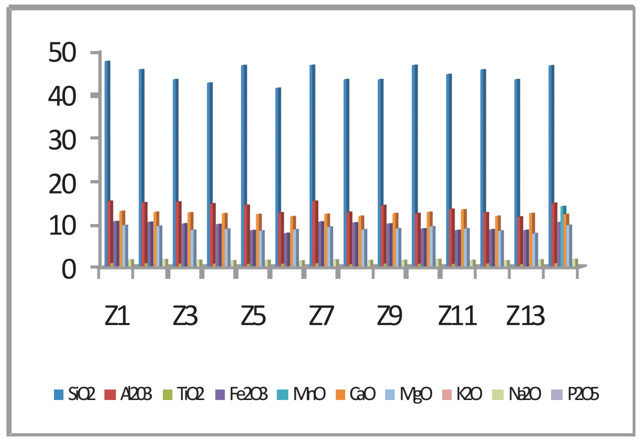


Fig. 3: Result of XRF Analysis of Ikpeshi Marbles

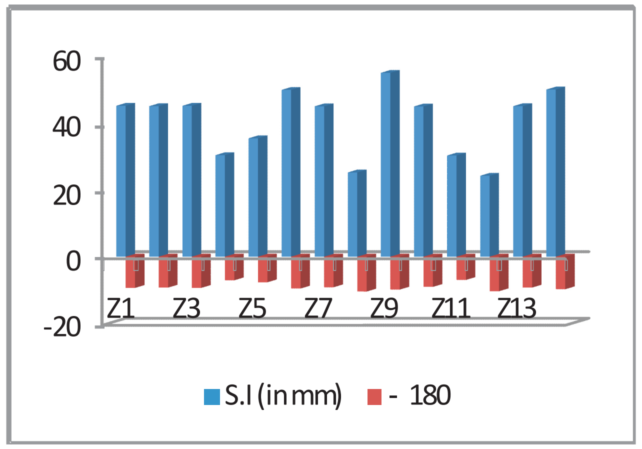


Fig. 4: Result of Stable Isotope Analysis of Ikpeshi Marbles

In consonance with the classification scheme of Goldschmidt *et. al.*, 1955, a mean value of 12.35% and 7.75% for CaO and MgO, is strongly an indication of an impure low-grade substandard dolomitic marbles. CaO/MgO of Ikpeshi marble ranges from 1.26 – 1.60, with seven out of the sample falling below the theoretical limit of 1.39 proposed by Grant, *et al.,* 1989. The average content of silica (SiO_2) in the samples is 44.8%; which can be closely connected to the periodical influx of near shore clastic sediments into shallow crystallizing environment of carbonate protolith, in response to sea level fluctuations and possibly stream rejuvenation.

According to Clarke (1924), Na and K concentration in marbles tend to decrease with increase in salinity. Concentration of the total alkalis (Na_2O+K_2O) in the sample ranges between 1.48 and 1 .78 per cent; signifying a slightly saline depositional environment at a relatively shallower depth.

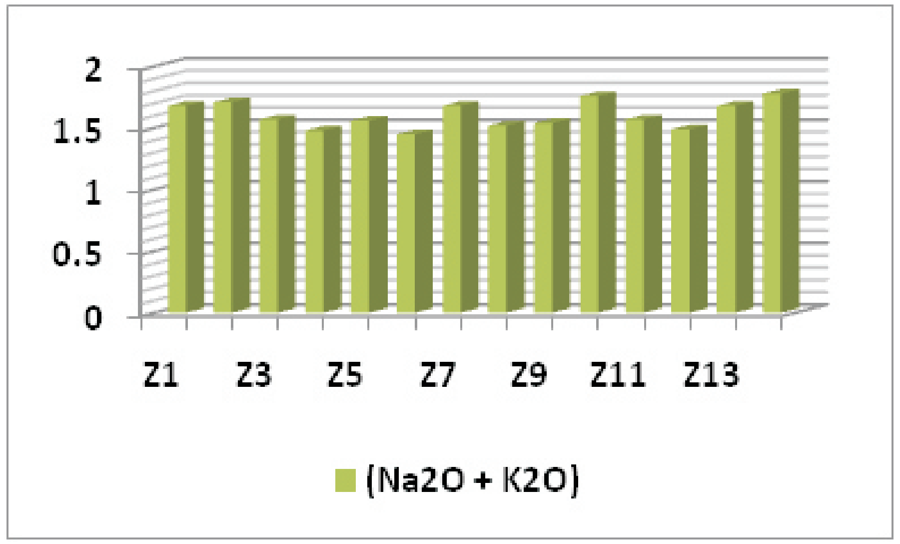


Fig. 5: Total Alkalis Concentration in the Marble Sample

Al_2O_3 and Fe_2O_3 occur substantially in the marble samples confirming its enrichment in aluminosilicates (clay minerals). Figures 6 and 7 compares the chemical composition of sampled marble with typical calcitic and dolomitic marbles in other environments respectively.

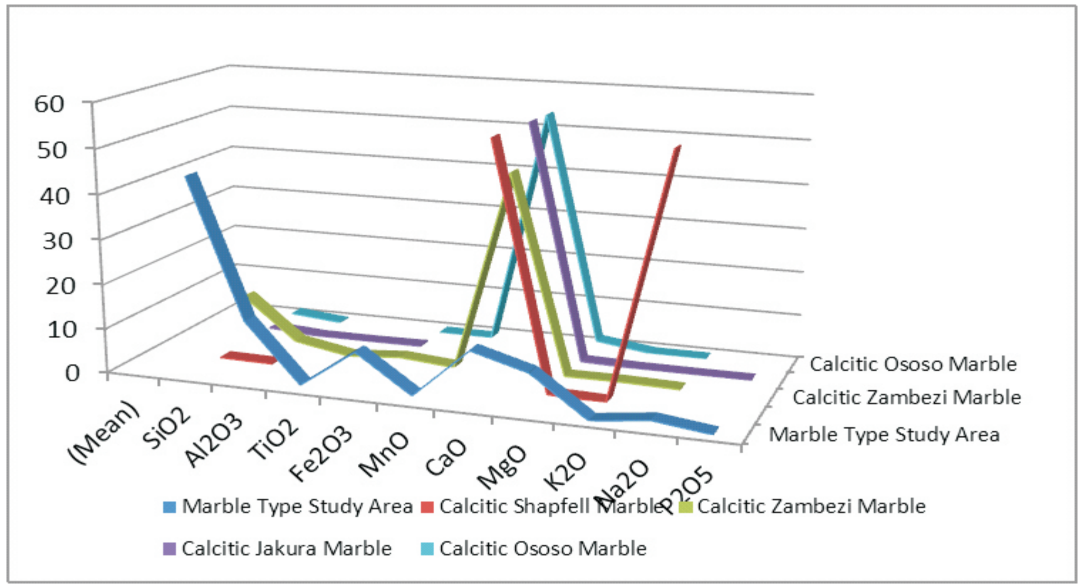


Fig.6: Comparison of Ikpeshi Marbles with Known Calcitic Marbles

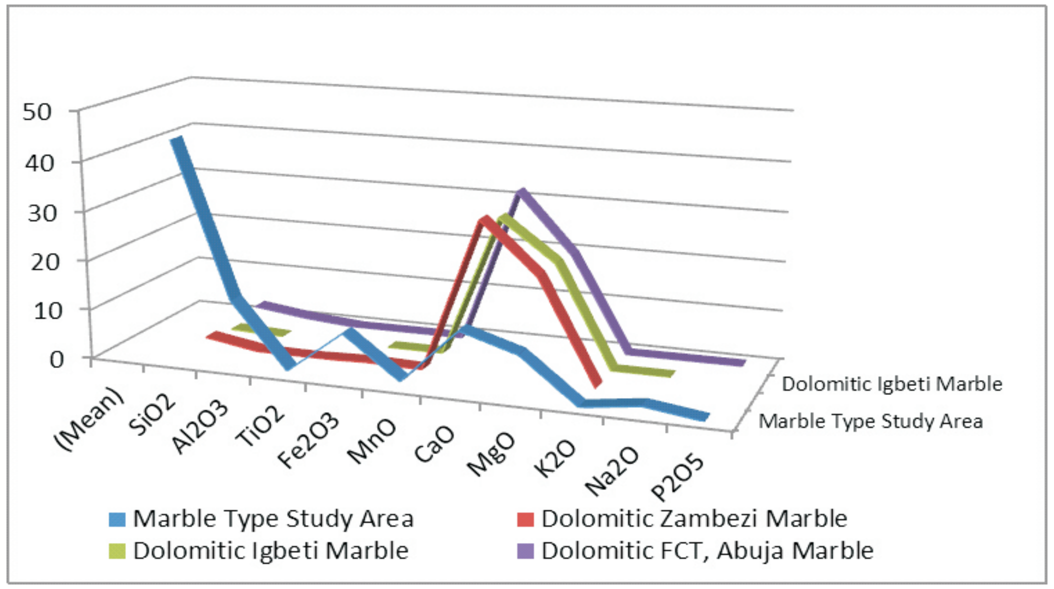


Fig.7: Comparison of Ikpeshi Marbles with Known Dolomitic Marbles

Marble Classification

The CaO/MgO ratio in the study area ranges between 1.26 and 1.60, averaging a value of 1.40. The relative percentage occurrence of calcite and dolomite in the investigated marble ranges between -5% and 4%; 93% and 103% respectively; which apparently indicate a dolomitic marble type (Gold Schmidt *et al.,* 1955).

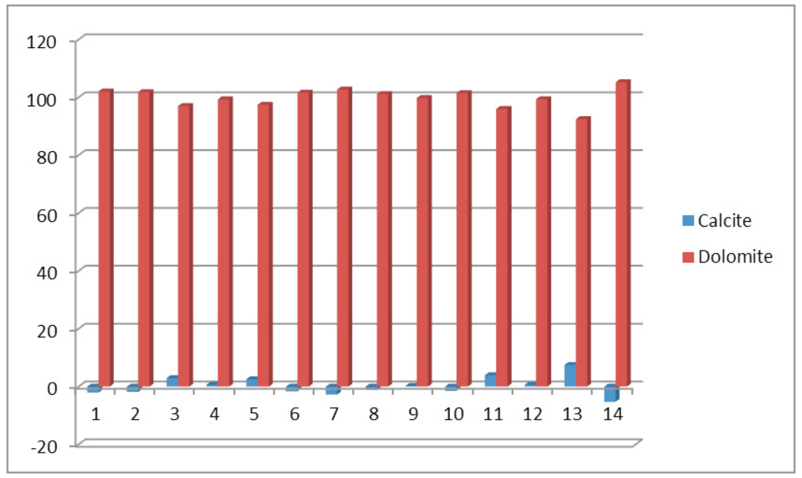


Fig. 8: Relative percentage composition of Calcite and Dolomite in the acquired samples

The ternary diagram classification scheme by Carr and Rooney (1983) for selected major oxides (CaO-MgO-SiO2) in the marble samples showed that marble sample from the study area falls within the calc-silicate group (Fig. 9a); none of the compositional plotting for the obtained samples however falls within any recognized class under the Storey and Vos grouping scheme (Fig. 9b).

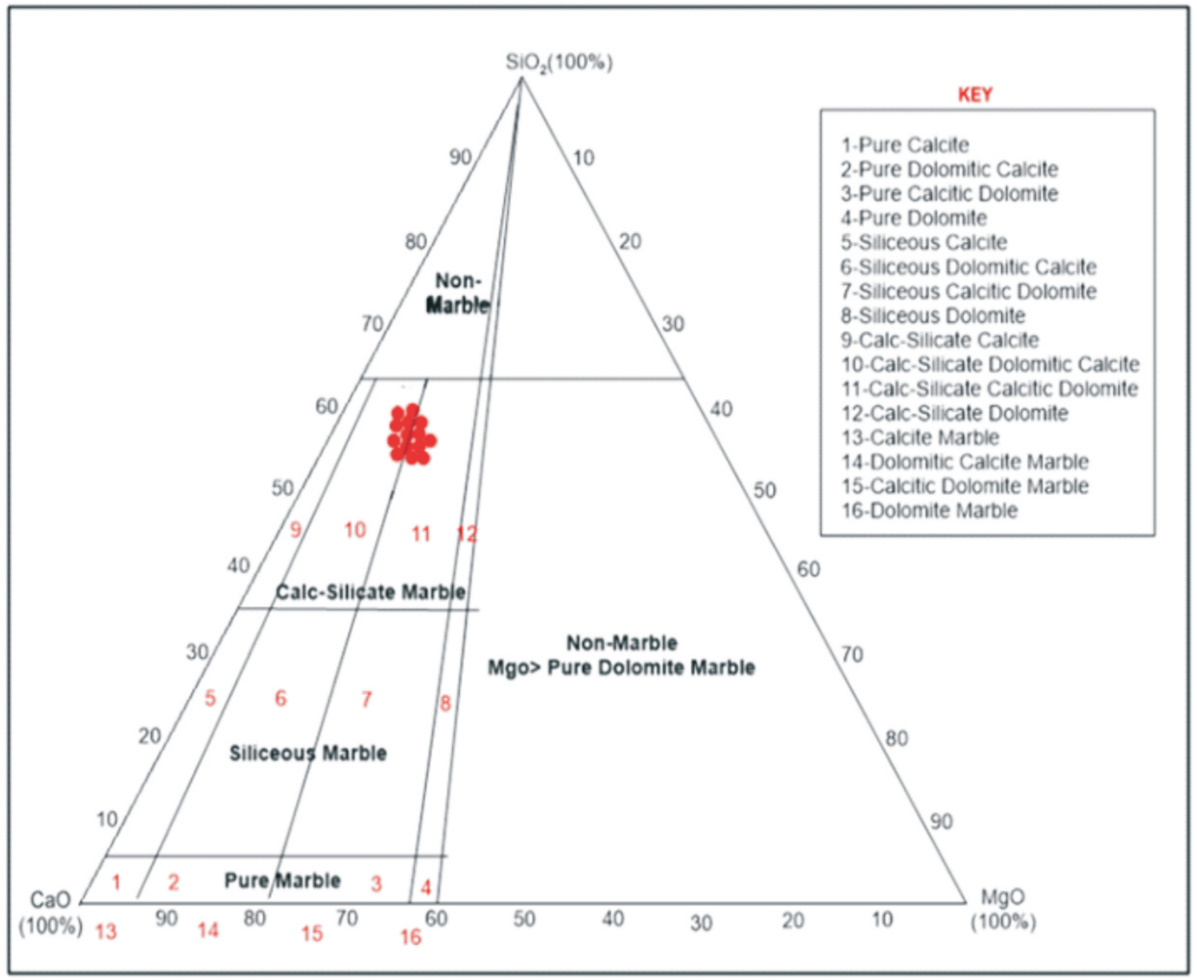


Fig.9a: CaO-MgO-SiO_2 Ternary Diagram Classification by (Carr & Rooney, 1983)

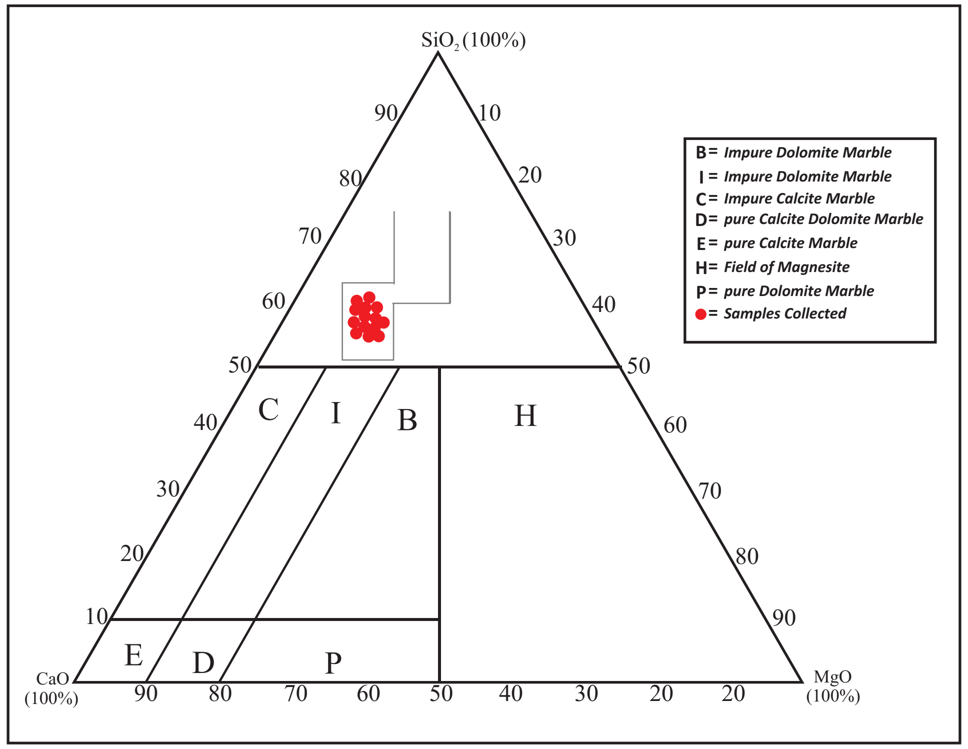


Fig.9b: CaO-MgO-SiO_2 Ternary Diagram Classification by (Storey and Vos, 1988)

Characterization of quartz content in the marble samples using the bivariate plot of Na_2O versus K_2O, and CaO versus MgO (after Crook, 1974) indicate a contradictory quartz poor and quartz rich marble disparately (Fig. 10 and 11).

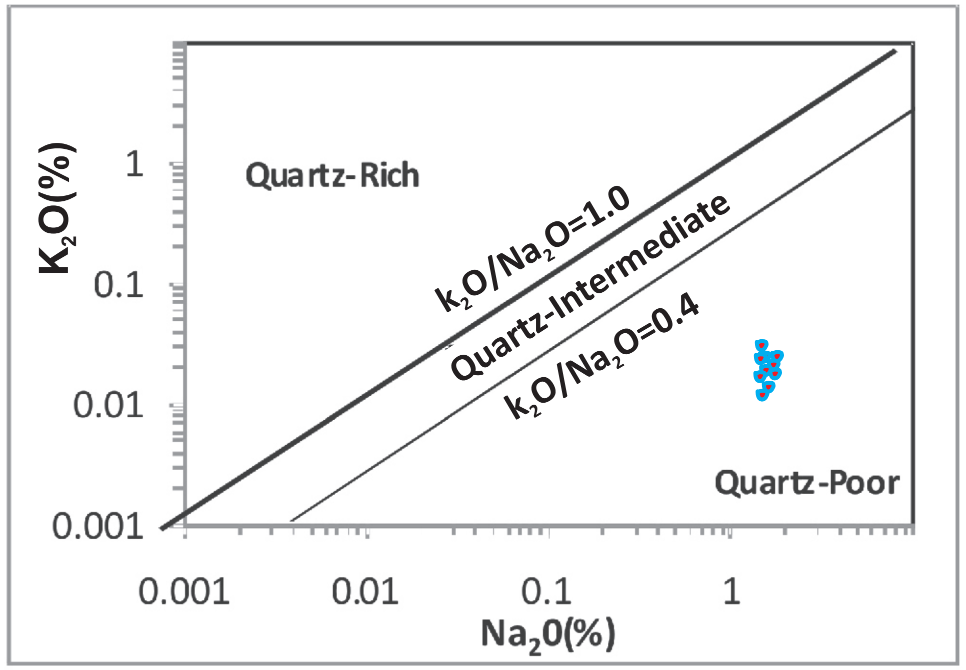


Fig 10: Quartz Content Bivariate Plot of Na_2O versus K_2O.

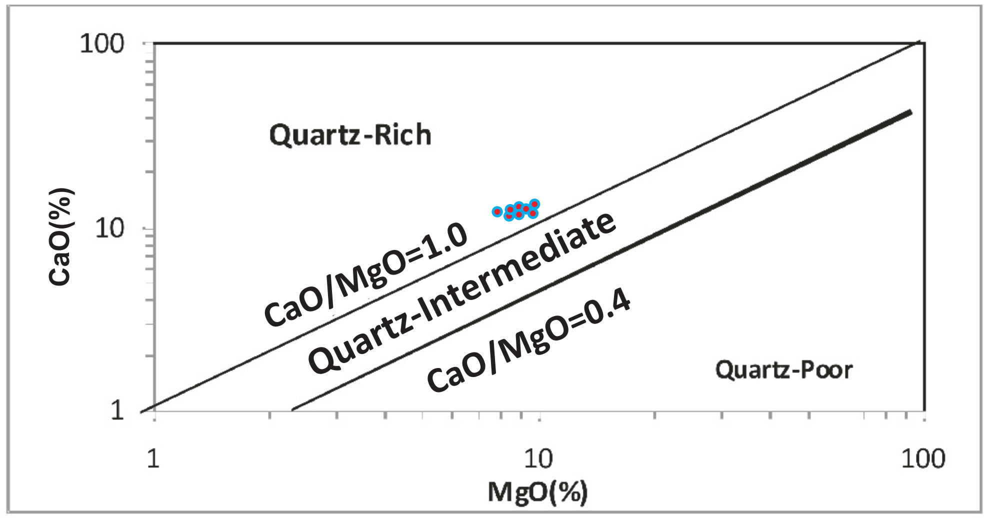


Fig 11: Quartz Content Bivariate Plot of CaO versus MgO

A discriminant plot of Na_2O/Al_2O_3 vs. K_2O/Al_2O_3ratio of the examined marbles (Fig. 12) suggests aprotolith of meta-sedimentary origin, which strongly correlates with the field observations (marble crystallinity, deformed bedding planes, specks of dotted dark colouration of burnt organic matter).

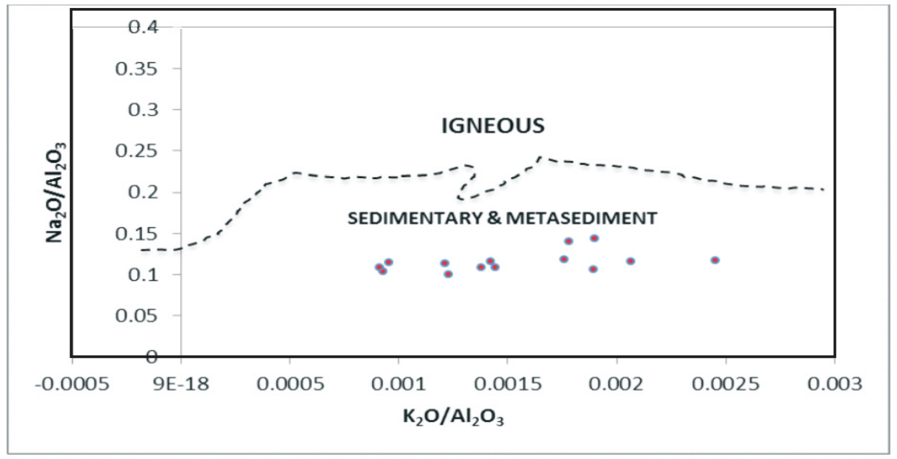


Fig 12: Nature of Protolith (Na_2O/Al_2O_3 vs. K_2O/Al_2O_3)

A bivariate tectonic discrimination plot of K_2O/Na_2O against SiO_2(after Roser and Korsch, 1986)specified the formation of marble protolith along a passive continental margin, away from the plate boundaries.

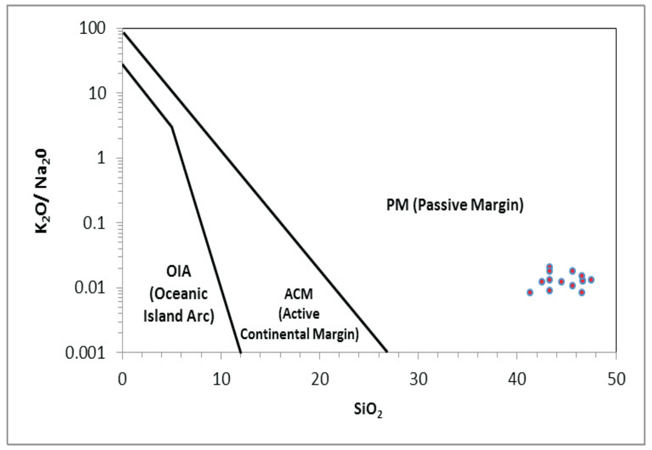


Fig. 14: Tectonic discrimination plot (after Roser and Korsch, 1986).

The chemical index of alteration (CIA) ranges from 45.16- 52.26% while the chemical index of weathering (CIW) ranges between 45.20 and 52.30%; both indicating weak to moderate degree of chemical decomposition and weathering of the source materials respectively. The dot and line plot for CIA and CIW is shown in figures14 and 15in that order.

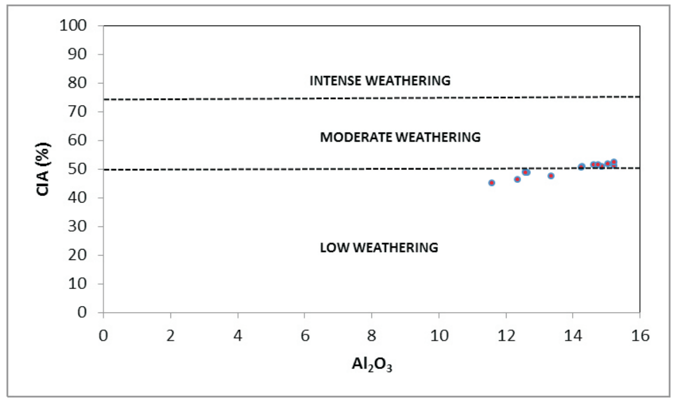


Fig 14:Dot plot of CIA against $Al_2O_3$of Ikpeshi Marble

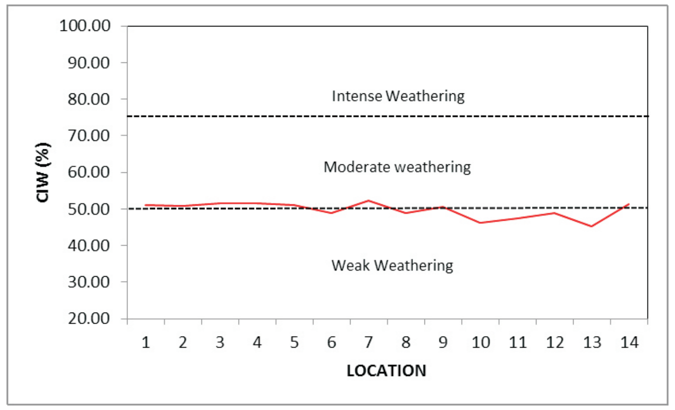


Fig. 15: Line plot of CIW of Ikpeshi Marble

Furthermore, the leaching of the highly mobile elements during active chemical weathering depleted Na and K contents in the samples but conversely enhanced the partial transformation of the source rock to clay minerals. A plot of K_2O against Al_2O_3 in figure17a below depicts more clearly the preponderance of illite in the impure marble samples –a consequence of chemical susceptibility of source area.

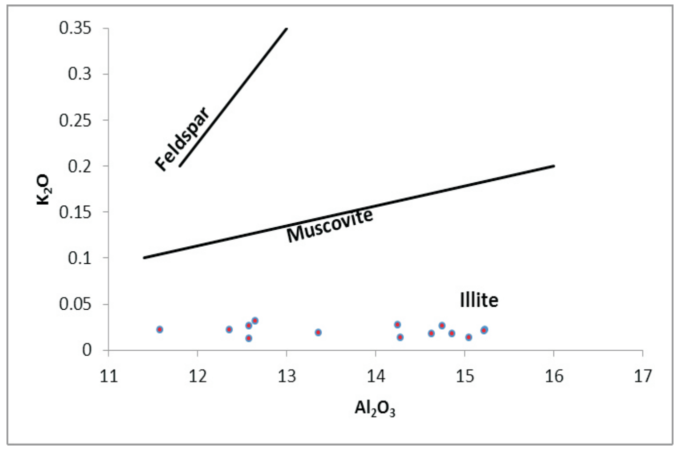


Fig. 17a: Plot of K_2O against Al_2O_3.

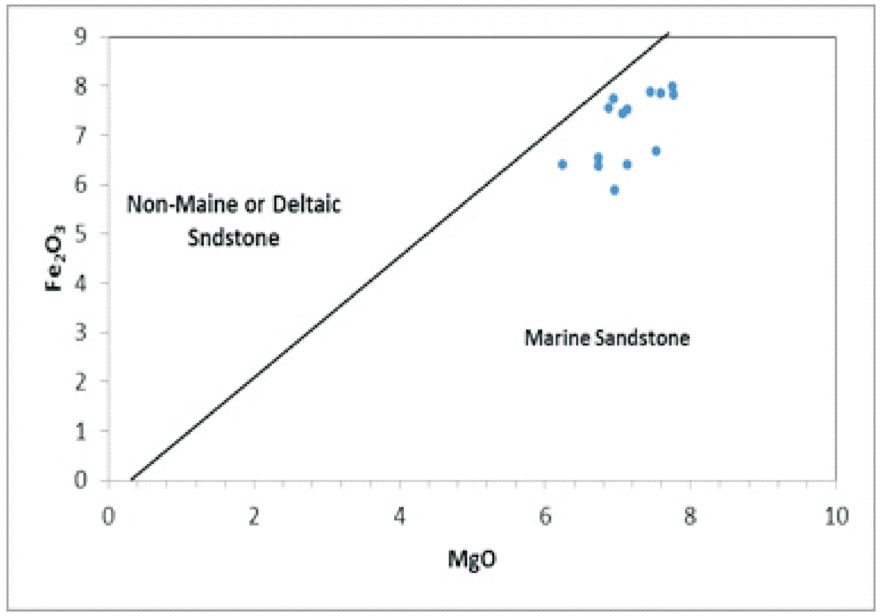


Fig. 17b: Plot of Fe_2O_3 versus MgO for Environment of Deposition

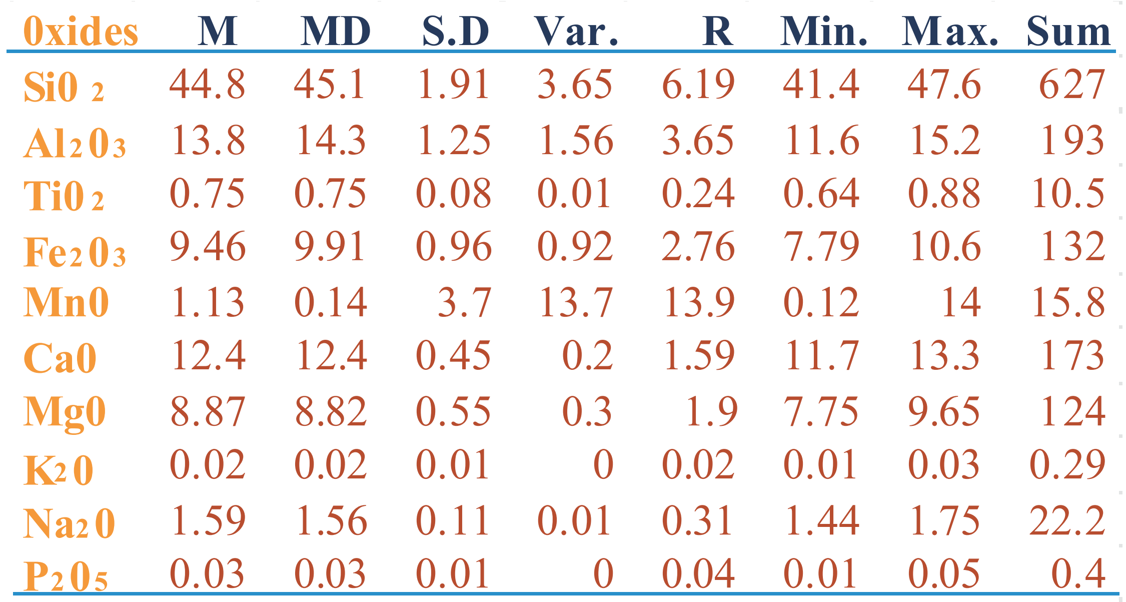
The plot of the Fe_2O_3 against MgO predicts a marginal marine depositional environment for the marble protolith as shown in figure 17b above.

DESCRIPTIVE STATISTIC OF THE ANALYSED RESULT

Analyzed statistical parameters aremean, median, standarddeviation, variance andrange. The mean value of SiO_2, Al_2O_3,CaO,Fe_2O_3,MgO,Na_2O,MnO,K_2O and$P_2O_5$are 44.80, 13.81,12.35,9.46,8.87,1.59, 1.13,0.75,0.03, and 0.02 respectively. Table 1shows the descriptive statistic of the analyzed oxides.

Table 1: Descriptive Statistics of Analyzed oxides*M_Mean *MD_Median *SD_Standard Deviation *Var_Variance *R_Range *Min_Minimum *Max_Maximum

Table 1: Descriptive Statistics of Analyzed oxides*M_Mean *MD_Median *SD_Standard Deviation *Var_Variance *R_Range *Min_Minimum *Max_Maximum



0xides	M	MD	S.D	Var.	R	Min.	Max.	Sum
$Si0_2$	44.8	45.1	1.91	3.65	6.19	41.4	47.6	627
Al_20_3	13.8	14.3	1.25	1.56	3.65	11.6	15.2	193
$Ti0_2$	0.75	0.75	0.08	0.01	0.24	0.64	0.88	10.5
Fe_20_3	9.46	9.91	0.96	0.92	2.76	7.79	10.6	132
Mn0	1.13	0.14	3.7	13.7	13.9	0.12	14	15.8
Ca0	12.4	12.4	0.45	0.2	1.59	11.7	13.3	173
Mg0	8.87	8.82	0.55	0.3	1.9	7.75	9.65	124
K_20	0.02	0.02	0.01	0	0.02	0.01	0.03	0.29
Na_20	1.59	1.56	0.11	0.01	0.31	1.44	1.75	22.2
P_20_5	0.03	0.03	0.01	0	0.04	0.01	0.05	0.4

Correlation was incorporated into the analysis to highlight the relationship among metals, and similarities in their geochemical behavior. The analysis revealed a wide range of variation in the correlation values as both positive and negative correlation was established between some compounds. The different range of correlation and its indication is shown in Table 2.Strong correlation between two oxides assertively suggests the derivation of materials from same source but weak correlation on the contrary is indicative of derivation of heterogeneous source or derivation from different source area

Table 2: Pearson correlation of the major oxides analyzed

Oxides	SiO_2	Al_20_3	$Ti0_2$	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_20	P_20_5
SiO_2	1									
Al_20_3	0.36	1								
$Ti0_2$	0.49	0.76	1							
Fe_2O_3	0.31	0.72	0.65	1						
MnO	0.26	0.22	0.36	0.27	1					
CaO	0.33	0.32	0.17	0.17	-0.1	1				
MgO	0.56	0.59	0.71	0.61	0.41	0.36	1			
K_2O	0.17	-0.2	0.02	0.41	0.27	-0.2	0.15	1		
Na_20	0.68	0.21	0.39	0.36	0.45	0.46	0.56	0.14	1	
P_20_5	0.15	-0.2	-0.1	-0.2	0.04	0.18	-0.3	0.2	0.16	1

Figure 18 is a correlation plot of TiO_2 and Al_2O_3 with a correlation coefficient of 0.5762.

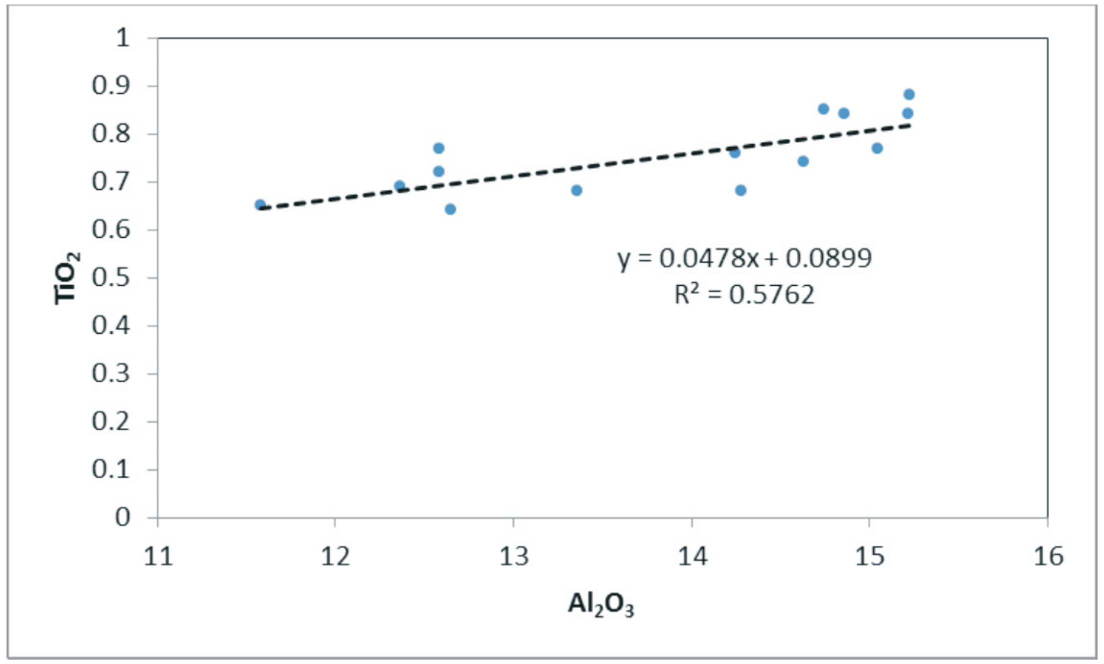


Fig. 18: Correlation plot of TiO_2 against Al_2O_3

Component Matrix Analysis

Table 3 shows Varimax rotated factor matrix of the linearly uncorrelated components of the fourteen marble samples in the study area. Component 1,2 and 3 accounts for 13.13%, 16.13%, 14.46% of variance, and 40.84%, 56.96% and 71.41% of the total cumulative percentage of the analyzed samples respectively. Predominant oxides are: TiO_2, Al_2O_3, MgO, Fe_2O_3 and Na_2O (Component 1); P_2O_5 and K_2O (Component 2) and CaO (Component 3).

Table 3: Varimax rotated factor matrix of the linearly uncorrelated components

Oxides	Component			Percentage	
	1	2	3	% Var.	Cum. %
SiO_2	0.71	0.36	0.2	40.83	40.83
Al_20_3	0.75	-0.49	0.12	16.13	56.96
$Ti0_2$	0.84	-0.25	-0.07	14.46	71.41
Fe_2O_3	0.77	-0.2	-0.33	8.7	80.12
MnO	0.5	0.28	-0.43	7.43	87.54
CaO	0.41	0.13	0.74	5.44	92.99
MgO	0.88	-0.1	-0.03	3.06	96.05
K_2O	0.19	0.53	-0.66	2.46	98.51
Na_20	0.7	0.47	0.22	1.35	99.86
P_20_5	-0.08	0.73	0.24	0.14	100
%Var.	40.83	16.13	14.46		
Cum. %	40.83	56.96	71.41		

CONCLUSION

The XRF and stable isotope analyses of the fourteen marble samples obtained from the study area clearly revealed the predominance of SiO_2 (41.36 - 47.55), Al_2O_3 (12.36 -15.23), TiO_2 (0.64 - 0.88), Fe_2O_3(7.79 -10.55), MnO (0.12-0.15), CaO (11.66 - 13.25), MgO (7.75 - 9.65), K_2O (0.012 - 0.3), Na_2O (1.44 - 1.75) and P_2O_5 (0.01 - 0.05). All the sampled marble are almost entirely dolomitic, with a relative percentage range of -5% – 4% for CaO and 93%-103% for MgO. However, comparison of these samples with other known marble environments a bruptly signifiesa rather lower CaO and MgO content but with high SiO_2anomaly.All the marble sample falls within the calc-silicate group and are poorly dolomitic. Bivariate plot of K_2O against Na_2O, and also CaO against MgO (after Crook, 1974) disparately indicates 'quartz poor' and 'quartz rich' marble. The discriminant plot of Na_2O/Al_2O_3 vs. K_2O/Al_2O_3 ratio asserts a sedimentary origin of the marble (limestone) protolith. From the bivariate tectonic discrimination plots of K_2O/Na_2O against SiO_2, it can be deduced that the protolith was precipitated along a passive continental margin. The CIA and CIW values ranges between 45.16 and 52.26%;45.20 and 52.30%; indicating weak to moderate degree of weathering and alteration. Plot of Fe_2O_3vs. MgO predicts a marginal marine depositional environmental of the protolith. Strong correlation exists between Na_2O - SiO_2 (0.68), Al_2O_3 - TiO_2 (0.76), Al_2O_3-Fe_2O_3 (0.72), TiO_2 - MgO (0.71) indicative of same source derivation; however, between SiO_2 - K_2O (0.17), SiO_2 - P_2O_5 (0.15), TiO_2 - CaO (0.17), TiO_2 - K_2O (0.02), Fe_2O_3 - CaO (0.17), CaO - P_2O_5 (0.18), MgO - Na_2O (0.56), K_2O - Na_2O, K_2O - P_2O_5, Na_2O - P_2O_5 (0.16) very weak correlation exists, symptomatic of derivation from diverse source area. XRF and stable isotope analytical results of the study conclusively deduced a poor quality marble with high silica impurity, derived from a hybrid sedimentary protolith precipitated under a tropical humid condition within a shallow marine environment along a passive continental margin.

REFERENCES

Alabi A. B., Olatunji S., Babalola O. A., Nwankwo L. I., Johnson L. M., Odutayo J. O. & Alabi A. (2013): Structural and qualitative analysis of solid minerals (marble) in selected locations in Nigeria, *Nigerian Journal of Physics* 24: 68-76.

Boynton, S.(1980): Chemistry and technology of limestone. John Wiley and Sons Inc. New York, 300.

Carr, D. D. & Rooney, L.F. (1983): Limestone and dolomite. In: Lefond, S. Y. (Ed.) Industrial minerals and rocks (5th edition). New York: *America Inst. Met. And Petr. Engr. Inc*; 833- 868.

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

Crook K.A.W. (1974):Lithogenesis and geotectonics: The significance of compositional variation in flysch arenites (greywackes). Soc. of Eco. Paleo. & Min. Special Publications. 19: 304-310.

Goldschmidth, J.R., Graff L. & Joensu, O.I. (1955):The occurrence of magnesium calcite in nature.

Geochim Cosmochim in Acta, 1: 212-230.

Grant, W. F, Papertzian, V. C.& Kingston, P. W. (1989): Geochemistry of Grenville marble in southeastern Ontario; *Ontario Geological Survey, Mineral Deposit Circular* 28: 266.

Roser, B. P. & Korsch, R. J.(1986): Determination of tectonic setting of sandstone-mudstone suites using SiO_2 content and K_2O/Na_2O ratio. *J. Geol.*, 94: 635-650.

Scott, P. W.& Dunham, A. C. (1984): Problems in the evaluation of limestone for divers market. 6th Indian MIN. *Intl Congress, Toronto*, 1-21.

Storey, C.C. & Vos, M.A. (1988): Industrial Minerals of the Pembroke-Renfrew Area, Part 1: Marble; *Ontario Geological Survey, Mineral Deposits Circular* 21: 132.