Geochemical and petrogenetic characteristics of the marble deposit at Ikpeshi southern Nigeria

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Abstract: The marbles at Ikpeshi are granoblastic rocks of low grade metamorphism. Based on different classification schemes for marbles; Ikpeshi marbles are pure calcite marbles, pure dolomite marbles, pure dolomitic calcite and pure calcitic dolomite. The concentration of the total alkalis is very low, which indicates that the environment of deposition of the protolith was probably a shallow, saline environment. Due to the presence of both calcitic and dolomitic carbonates, the dolomites observed in the marbles were probably of precipitatory origin. The concentration of the immobile Ni and Cr in the Ikpeshi marbles is similar to the sedimentary carbonates. The Mn content is lower than that in both deep and shallow seas carbonates. This may be due to the substitution of Mn by Ca during the recrystallization at higher temperature. The Zn and Sr values of the marbles studied are however similar to that of carbonates from the deep sea. Using various trace and rare earth element ratios, the paleo-oxygenation of the protolith depostional environment is basically oxic and to a lesser extent suboxic. Bivariate tectonic discrimination plots of the Ikpeshi marbles based on major oxides, shows majority of the samples in the passive margin zone and few in the active continental margin zone.

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1. Introduction

The Carbonate rocks make up about one-fifth to one-quarter of all sedimentary rocks in the stratigraphic record. They occur in many Precambrian assemblages and in all geologic systems from the Cambrian to the Quaternary (Boggs, 2009). Pure marble is composed primarily of the minerals calcite or aragonite with total CaCO3 content of between 97 – 99%, and pure dolomite is composed of 45.7% MgCO3 and 54.3% CaCO3 or 30.4% lime (CaO) and 21.8% Magnesia (MgO), (Boynton,). A value of MgO greater than 1% in limestone suggests that the mineral dolomite is present (Brownlow, 1996). Dolomite is the dominant carbonate rock in Precambrian and Paleozoic sequences, whereas limestone is dominant in carbonate units of Mesozoic and Cenozoic age (Ronov, 1983). Carbonates have been found in mantle peridotite as interstitial grains (Culler, 1995), as globules in association with silicate glass (Dypvit, 1984, Dill, 1986) and as component of fluid inclusions (Hanson, 1980) . Carbonate has been found to occur in anhydrous olivine and garnet in upper mantle where oxygen fugacity (partial pressure) is enough to stabilize carbonate minerals of magnesite, $MgCO_3$ and dolomite, $CaMgCO_3$. Carbonate is a major component of marble. Marble is a granoblastic metamorphic rock resulting from the metamorphism of limestone or dolostone (carbonate rocks). This metamorphic process causes a complete recrystallization of the original rock into an interlocking mixture of calcite, aragonite and/or dolomite crystals. It is white in its pure form, but mineral impurities such as clay, silt, sand, iron oxides, or chert cause Marble to have diiferent colours. The major influence on the chemistry and relative purity of a marble is the original composition of the carbonate sediment. Environments of deposition of carbonate material generally occur on a large scale, suggesting that material will be consistent over a large definable area (Grant, et al., 1989).

Ikpeshi area has massive carbonate deposits and diverse minerals, particularly industrial minerals. Ikpeshi area lies within the Precambrian Basement Complex of Southwest, Nigeria. The Basement rocks are notably the migmatite gneiss complex, schist (metasediment), older granite and late intrusives (Rahaman, 1978.; Elueze, 1982). The schist occurs as a supracrustal cover on the Basement and consists of mica schist, metaconglomerate, calc-gneiss and marble and quartz biotite (Okeke and Meju, 1985; Ajibade et al., 1987; Odeyemi, 1988; Ekwere and Ekwueme, 1991; Imeokparia and Emofurieta, 1991; Ocan et al., 2003). The metasedimentary rocks at Ikpeshi areas comprise mainly quartz-biotite schist, calc silicate and marble, mica schist and granulites. Field study indicates that in most of the quarries the dolomite occurs in association with calcite in the marble deposits; texturally, the marble is medium to coarse –grained, figure 1 is a map of Ikpeshi area showing the sample locations.

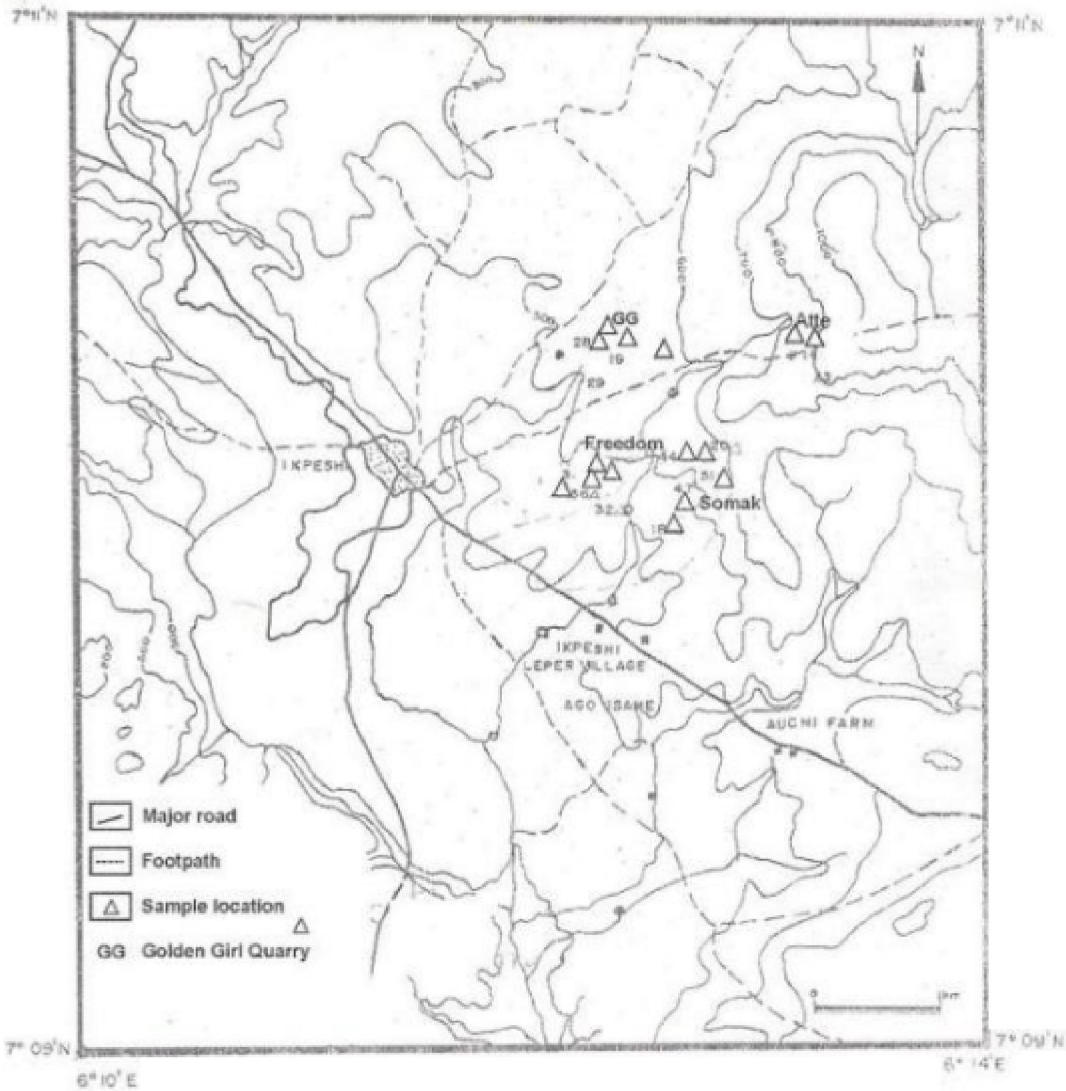

Figure 1. Topographic map of Ikpeshi area showing sample locations. (Adopted from GSMN Auchi N.W. sheet 226).

Marbles associated with metasediments and metavolcanics are usually fine grained, grey in colour, and have fine dark and light grey laminations, while marble that has been intruded by igneous bodies is normally coarse grained, and varies from white with shades of blue, to green, orange, or grey (Grant, et al., 1989). This marble according to Grant, et al. (1989) is characterized by an absence of planar structures, with the exception of flow foliation. This study seeks to determine the geochemical characteristics, classification, paleoenvironment and the possible origin of the marble of the Ikpeshi.

2. Material and Methods

Ten marble samples were collected from different quarry pits and analysed for trace and rare earth elements using the Inductively Coupled Plasma-Mass Spectrometer machine (ICP-MS)at the Actvation laboratory (ACTLAB) in Ontario Canada. The details of the ICP-MS method are seen in Nath et al., (1997), Nesbitt, et al., (1980). X- Ray Fluorescence (XRF) analysis was used to determine the major oxides composition of the marble samples. The marble in Ikpeshi varies in colour from whitish, pinkish to grey while the texture ranges from fine, medium to coarse. In places, the marble is associated with banded calc-gneiss within the schist rock unit.

3. Results and discussion

The data for the major oxides, trace elements, rare earth elements and the values of $CaCO_3$, $MgCO_3$, of the Ikpeshi marble are presented in table 1. There are different methods of classifying calcium carbonate rocks the marbles inclusive. Within the marble group, classification may be further subdivided on the basis of texture, colour, type of metamorphism, and geochemistry. A geochemical classification method generally applied to all types of calcium carbonate rocks uses the ratio of CaO to MgO (CaO/MgO). The theoretical limits of CaO/MgO range from 1.39 (the ratio of ideal calcite to ideal dolomite) to infinity (Grant, et al., 1989). The ratio of CaO to MgO can be converted to percent calcite and percent dolomite using the following equations (Grant, et al., 1989):

The CaO/MgO ratio of the Ikpeshi marbles range between 1.70 and 23.71 with an average of 15.08. The percentage of calcite is between 10.80 and 89.71 (average = 71.22%), while dolomite range from 10.29 to 89.20 (28.78%). Based on figure 2, most of the Ikpeshi marbles classified as dolomitic calcite marble, while two are calcitic dolomite marbles. According to Gold Schmidt et al., (1955), calcitic marble have CaO usually in the range of 50 – 54% while MgO is less than 15%, while dolomitic marbles have CaO values in the range of 28-31% and MgO values in the range of 15-21%. The samples have CaO in the order of 33.64-53.02% and the MgO is less than 15% with only two greater than 15%. Table 2 is a comparison of the chemical composition of Ikpeshi marble with typical calcitic and dolomitic marbles; the Ikpeshi marble samples is comparable to typical calcitic marbles from different environments, the reduced CaO value and the elevated MgO value of the Ikpeshi samples is due to two dolomitic samples. Figure 3 is a ternary diagram classification system for marbles by Storey and Vos (1981) that presents the Ikpeshi marbles as pure calcite and pure dolomitic calcite with two samples plotting between pure calcitic dolomite and pure dolomite. Carr & Rooney (1983) used another marble classification scheme (fig. 4); this scheme categorized most of the Ikpeshi samples as pure calcite marbles with two plotting as pure dolomite marble. According to Lippman (1973), pure carbonates should have a total carbonate content of 70% and above while impure carbonates have between 40 – 70%.

$$\%\text{calcite} = \frac{100\frac{CaO}{MgO} - 139}{1.17 + \frac{CaO}{MgO}} \qquad \textbf{\% dolomite = 100 - \% calcite}$$

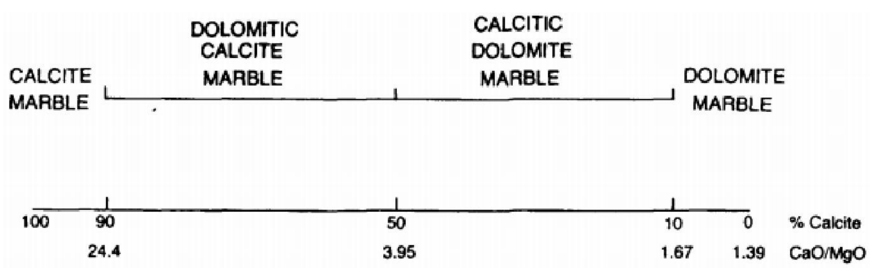

Figure 2. Marble classification systems based on % calcite and CaO/MgO ratio as used by Storey and Vos (1981).

Based on his work on limestone formations at Tangayinka, Oates (1933) observed a steady decrease in dolomite from the Precambrian marble to its complete nonexistence in recent limestone. According to McKenzie (1991), despite its thermodynamic stability and abundance in ancient rock records, dolomites are rarely found in Holocene environments. The absence of dolomite in recently formed limestone has led to a common inference that the presence of dolomite in marbles is by replacement of Ca by Mg during metamorphism. However, the discovery of a recently formed dolomite deposit by Vasconceles and McKenzie (1997) in a shallow water, isolated coastal lagoon, east of Rio de Janerio has added a new dimension to the controversy because they concluded that under anoxic conditions, Mg co-precipitates with Ca. Due to the presence of both calcitic and dolomitic carbonates in the Ikpeshi marbles, the dolomites observed in the marbles were probably of precipitatory origin rather than replacement.

Other oxides are regarded as impurities and are usually less than 1 percent. The Ikpeshi marbles have non carbonates ranging between 0.83 to 6.2% with an average of 3.25%. Table 3 is a comparison of Ikpeshi marbles with those of other sedimentary carbonate rocks, the values shows that the studied samples are similar in constituents to the relative pure limestones. Figure 5A and 5B are adaptations, which shows that the Ikpeshi marbles are quartz-rich.

Table 1: Major oxides (%), trace and rare earth elements (ppm) geochemical data of Ikpeshi marble.

Oxide	1	2	3	4	5	6	7	8	9	10	MEAN
SiO_2	1.94	1.94	1.43	0.44	1.94	1.18	1.9	1.88	1.4	1.96	1.60
Al_2O_3	1.76	0.31	0.02	0.11	1.04	0.48	1.8	0.33	1.08	0.39	0.73
Fe_2O_3	1.23	0.18	0.03	0.08	0.05	0.26	0.77	0.16	0.47	0.36	0.36
MnO	0.04	0.05	0.01	0.02	0.01	0.01	0.01	0.08	0.01	0.09	0.03
MgO	3.67	2.45	19.81	19.79	2.14	3.54	3.56	2.04	2.65	2.59	6.22
CaO	48.05	51.35	33.95	33.64	50.08	50.3	45.83	48.36	53.02	49.59	46.42
Na_2O	0.4	0.09	0.01	0.03	0.06	0.01	0.28	0.58	0.2	0.01	0.17
K_2O	0.62	0.05	0.05	0.07	0.05	0.63	0.6	0.08	0.29	0.01	0.25
TiO_2	0.15	0.02	0.02	0.03	0.01	0.01	0.1	0.01	0.05	0.03	0.04
P_2O_5	0.06	0.06	0.02	0.05	0.04	0.17	0.04	0.08	0.13	0.03	0.07
LOI	41.98	43.5	44.66	45.75	44.53	43.32	45.3	45.61	40.7	44.23	43.96
$CaCO_3$	86.74	92.63	61.58	61.03	90.36	90.76	82.78	87.29	95.61	89.49	83.83
$MgCO_3$	7.67	5.12	41.42	41.38	4.48	7.4	7.44	4.26	5.54	5.42	13.01
CaO/MgO	13.09	20.96	1.71	1.70	23.40	14.21	12.87	23.71	20.01	19.15	15.08
% calcite	82.05	88.43	11.23	10.80	89.58	83.35	81.77	89.71	87.91	87.40	71.22
%dolomite	17.95	11.57	88.77	89.20	10.42	16.65	18.23	10.29	12.09	12.60	28.78
V	24	4.8	4.9	4.95	4.92	4.85	13	8	19	4.95	9.34
Ba	121	58	13	14	102	116	157	40	140	16	77.70
Sr	1858	1968	343	259	1623	2613	2693	2612	2648	1429	1804.60
Y	1.85	1.9	1.88	1.9	1.92	1.95	1.94	2.95	3	1.95	2.12
Zr	36	12	4	3.95	3.9	4	24	4	12	3.95	10.78
Cr	20	19.95	19.85	19.9	19.98	19.85	19.9	19.99	19.99	19.95	19.94
Co	0.3	0.92	0.85	0.9	0.95	0.85	2	0.9	0.85	0.95	0.95
Ni	19.85	19.9	19.85	19.95	19.92	19.84	19.95	19.85	19.9	19.9	19.89
Cu	20	9.85	9.8	9.85	9.95	9.92	10	20	20	9.85	12.92
Zn	50	29.85	29.8	29.9	29.95	29.9	29.85	29.85	90	29.9	37.90
Rb	24	3	1.9	1.92	1.95	1.95	30	1.95	14	1.95	8.26
Ag	0.42	0.46	0.4	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.44
Sc	3	0.04	0.04	0.04	0.04	2	1	0.04	0.04	0.04	0.63
Cs	2.1	0.45	0.45	0.45	0.45	0.45	0.45	3.4	1.5	0.45	0.96
La	7.8	0.5	0.4	0.5	0.7	4.9	1.1	0.7	3.2	1.4	2.12
Ce	13.9	1.4	0.6	0.9	1.4	9.1	1.9	2 1.8	6.2	2.5	4.21
Pr	1.67	0.08	0.07	0.11	0.16	1.05	0.21	0.12	0.7	0.28	0.45
Nd	6.2	0.6	0.2	0.4	0.6	4	0.7	0.6	2.6	0.9	1.68
Sm	1.3	0.1	0.1	0.1	0.1	0.9	0.2	0.1	0.6	0.2	0.37
Eu	0.37	0.05	0.05	0.05	0.05	0.14	0.05	0.05	1.13	0.05	0.20
Gd	1.2	0.1	0.1	0.1	0.1	0.8	0.2	0.1	0.6	0.2	0.35
Tb	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.11
Dy	1.2	0.1	0.1	0.1	0.1	0.7	0.2	0.1	0.6	0.2	0.34
Ho	0.2	0.001	0.001	0.001	0.001	0.001	0.1	0.001	0.1	0.001	0.04
Er	0.6	0.1	0.1	0.1	0.1	0.4	0.1	0.1	0.3	0.1	0.20
Tm	0.09	0.04	0.04	0.03	0.04	0.04	0.06	0.04	0.04	0.04	0.05
Yb	0.6	0.08	0.08	0.08	0.08	0.08	0.4	0.08	0.08	0.3	0.19
Lu	0.09	0.03	0.14	0.02	0.03	0.03	0.06	0.03	0.03	0.03	0.05
Pb	24	5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	6.50
Th	2.4	0.4	0.001	0.1	0.2	1.8	1.3	1.3	0.2	0.1	0.78
U	1.8	1.2	0.6	0.2	1.5	1.3	1.3	1.7	0.2	0.6	1.13

Table 2: A comparison of the chemical composition of Ikpeshi marble with typical calcitic and dolomitic marbles

Major Oxides	Ikpeshi Marbles (Mean)	Typical Calcitic Marbles				Typical Dolomitic Marbles		
		1	2	3	4	5	6	7
SiO_2	1.6	0.71	11.9	0.9	1.18	1.98	0.49	2.4
Al_2O_3	0.73	0.52	2.3	0.07	0.08	0.13	0.02	0.92
Fe_2O_3	0.36	0.34	1.04	0.18	0.07	0.36	0.06	0.04
MnO	0.03	-	0.03	-	0.03	0.03	0.03	0.009
MgO	6.22	0.35	0.67	0.42	1.75	20.84	20.7	19.6
CaO	46.42	54.75	45	54.01	53.64	31.04	28.94	31.82
Na_2O	0.17	0.01	0.39	0.02	0.01	-	0.01	0.05
K_2O	0.25	0.01	0.7	0.08	0.02	0.07	0.01	0.007
TiO_2	0.04	-	0.13	0.02	-	0.01	-	0.01
P_2O_5	0.07	-	-	0.02	-	-	-	0.045
LOI	43.96	42.01	-	43.72	-	-	-	-
$CaCO_3$	83.83	97.71	-	-	95.72	-	51.69	-
$MgCO_3$	13.01	0.78	-	-	3.67	-	43.34	44.09

1. Shapfell marble (Calcitic), (Dowrie et al., 1982)
2. Zambezi belt marble (Calcitic)
3. Jakura marble (Calcitic), (Okunlola, 2001)
4. Ososo marble (Calcite), (Emofurieta et al., 1995)
5. Zambezi belt marble (Dolomitic), (Munyanyiwa and Hanson, 1988)
6. Igbeti marble (Dolomitic), (Emofurieta et al., 1995)
7. FCT, Abuja marble (Dolomitic), (Davou and Ashano, 2009

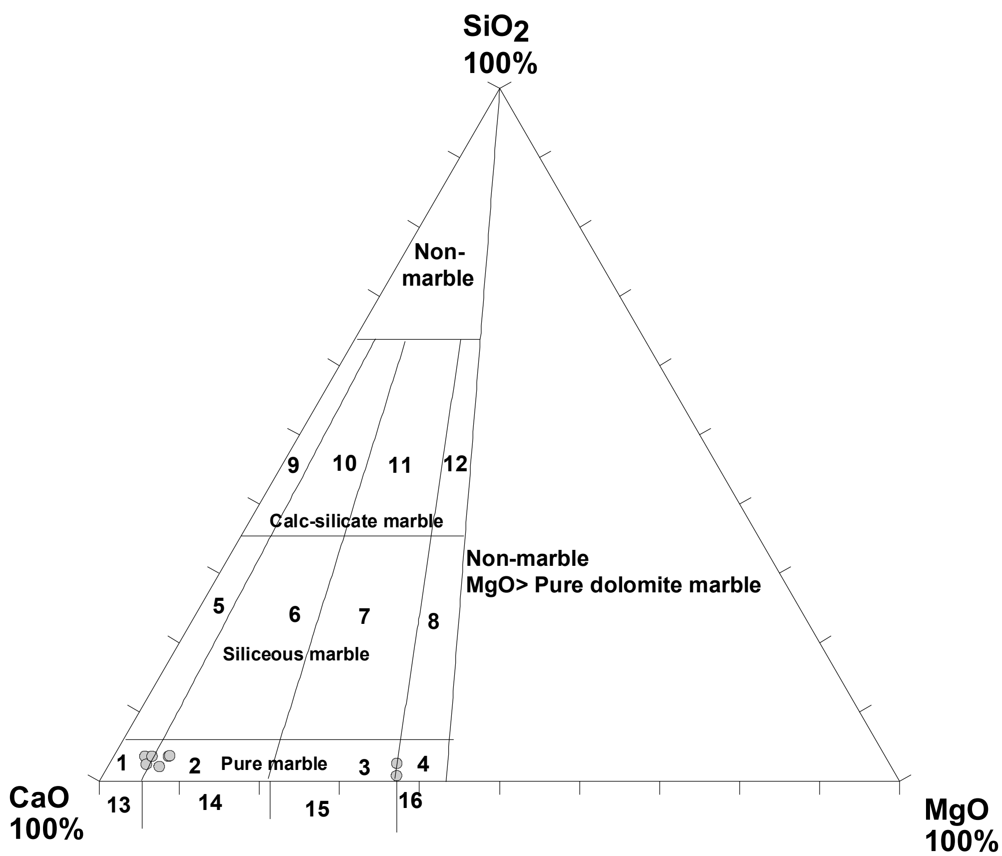

Figure 3. CaO-MgO-SiO2 ternary diagram classification system for marbles (from Storey and Vos 1981).

KEY

1. Pure Calcite	9. Calc-Silicate Calcite
2. Pure Dolomitic Calcite	10. Calc-Silicate Dolomitic Calcite
3. Pure Calcitic Dolomite	11. Calc-Silicate Calcitic Dolomite
4. Pure Dolomite	12. Calc-Silicate Dolomite
5. Siliceous Calcite	13. Calcite Marble
6. Siliceous Dolomitic Calcite	14. Dolomitic Calcite Marble
7. Siliceous Calcitic Dolomite	15. Calcitic Dolomite Marble
8. Siliceous Dolomite	16. Dolomite Marble

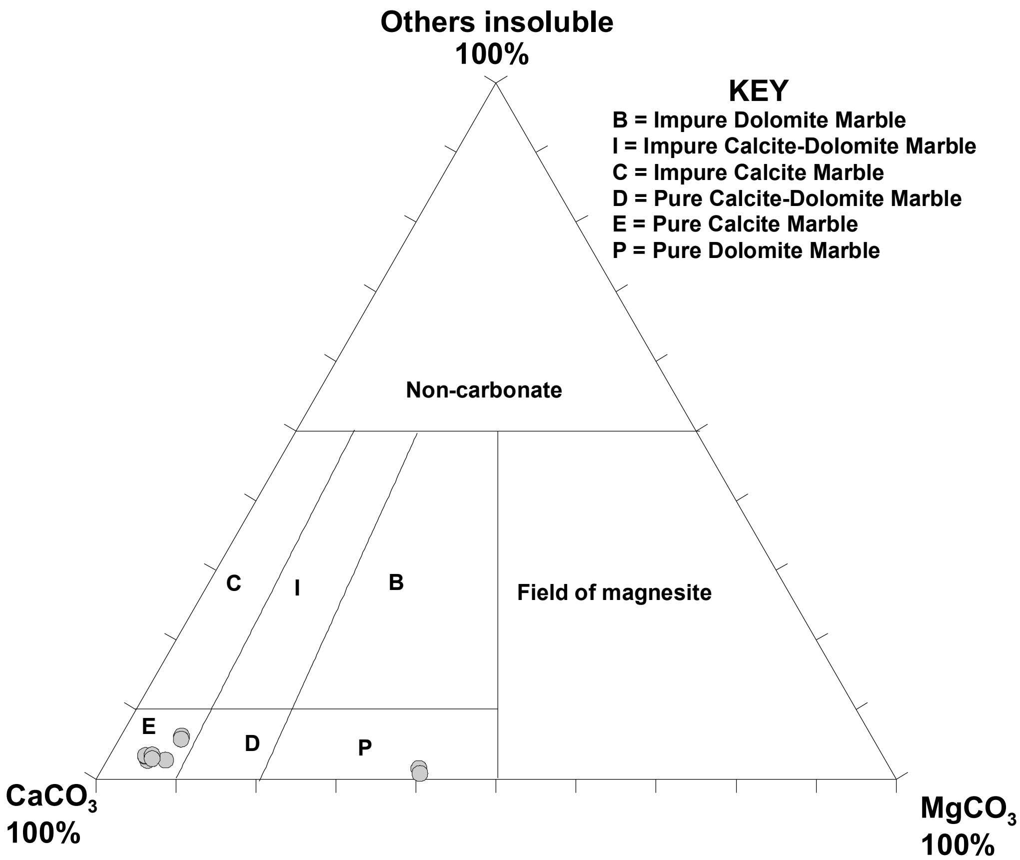

Figure. 4: Classification of the Ikpeshi Marbles (After Carr & Rooney, 1983)

Table 3: Constituents of Ikpeshi Marbles compared with constituents of sedimentary carbonate rocks

Major Oxides (Wt %)	Ikpeshi Marbles (Mean)	Relatively pure limestone (Pettijohn, 1975)	Impure limestone (Pettijohn, 1975)	Dolostones (Pettijohn, 1975)
SiO_2	1.6	1.88	10.61	3.98
Al_2O_3	0.73	0.83	4.3	0.78
Fe_2O_3T	0.36	0.26	2.97	0.64
MnO	0.03	0.01	0.22	0.02
MgO	6.22	2.75	2.01	20.26
CaO	46.42	50.89	41.9	29.09
Na_2O	0.17	0.06	1.38	0.14
K_2O	0.25	0.01	0.56	0.04
TiO_2	0.04	0.01	0.07	0.04
P_2O_5	0.07	0.01	0.21	0.32

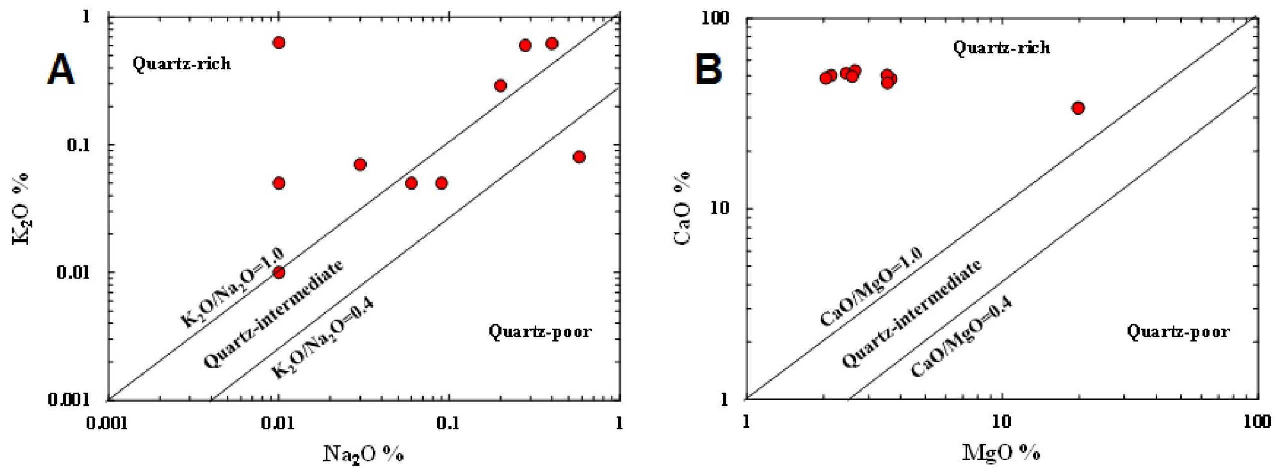

Figure 5. (A) Bivariate Plot of Na_2O versus K_2O of the studied samples showing quartz content (after Crook, 1974), and (B) MgO versus CaO (adapted from Crook, 1974).

Determination of LOI is used for the assessment of the content of organic matter in sediments . In case of carbonate rocks, it is the loss of volatile inorganic substances (CO_2, H_2O) present in the rocks. According to Olatunji (1989), high LOI means high carbonate content since it is synonymous with the evolvement of carbon dioxide after heating at 900ºC.

A discriminant plot of Na_2O/Al_2O_3 vs. K_2O/Al_2O_3 (Garrels and Mckenzie, 1971) of the Ikpeshi marbles (Fig. 6) shows them plotting in the field of sedimentary and metasedimentary rocks; only one sample plotted in the igneous zone. Na and K concentration in marbles tend to decrease with increase in salinity (Clarke, 1924). According to Land and Hopp (1973), alkalis are indicative of salinity levels and is useful in interpreting depositional and lithification conditions prior to metamorphism of carbonate rocks. The concentration of the total alkalis in the studied samples is low, which indicates that the environment of deposition of the protolith was probably a shallow, saline environment. Table 4 compares some diagnostic trace elements of Ikpeshi Marbles with that of sedimentary carbonate rocks in deep and shallow seas. The concentration of the immobile Ni and Cr in the Ikpeshi marbles is similar to the sedimentary carbonates. The Mn content in Ikpeshi marble is lower than that in both deep and shallow seas sedimentary carbonates. This may be due to the substitution of Mn by Ca during the recrystallization at higher temperature. The Zn and Sr values of the marbles studied are however similar to that of carbonates from the deep sea. According to Hallberg (1976), Cu/Zn ratios can be used as redox parameters; high Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidising conditions. The Cu/Zn ratios for the Ikpeshi marbles range from 0.22 to 0.67, indicating more oxidising conditions. The ratio of uranium to thorium has been used as a redox indicator with U/Th ratio being higher in organic rich mudstones (Jones and Manning, 1994). U/Th ratios below 1.25 suggest oxic conditions, whereas values above 1.25 indicate suboxic and anoxic conditions of deposition (Jones and Manning, 1994; Dill et al., 1988). The studied samples exhibits a varying U/Th ratio (0.75 – 7.50), which indicate deposition in oxic, suboxic and anoxic environments. Some workers have used V/Cr ratio as an index of paleo-oxygenation (Bjorlykke, 1974; Shaw, 1990; Nagarajan, 2007). The V/Cr ratios above 2 indicate anoxic conditions, whereas values below 2 suggest oxidizing conditions (Jones and Manning, 1994). The V/Cr ratios of Ikpeshi marbles vary between 0.24 and 1.20, which indicates deposition under an oxic condition. The V/(Ni+V) ratios below 0.46 indicate oxic environments, but ratios above 0.54 to 0.82 suggest suboxic and anoxic environments (Hatch and Leventhal, 1992). The V/(Ni + V) ratios for Ikpeshi marbles range between 0.19 and 0.55, which indicate oxic to suboxic environment of deposition. A V/Sc ratios below 9.1 indicate oxic environment of deposition (Hetzel, et al., 2009). The V/Sc ratios in the Ikpeshi samples range from 2.43 to 225. Only two samples reflect oxic environment of deposition, the rest shows V/Sc ratio above 9.1.

The Mn* value is a significant paleochemical indicator of the redox conditions of the depositional environment (Bellanca et al., 1996; Cullers, 2002; Machhour et al., 1994).

The expression for calculating Mn* value is $Mn^* = \log[(Mn_{sample}/Mn_{shales})/(Fe_{sample}/Fe_{shales})]$, where the values used for the Mn_{shales} and Fe_{shales} are 600×10^{-6} and 46150×10^{-6}, respectively (Wedepohl, 1978). The reduced iron and manganese form different solubilities of compounds across a redox boundary, while manganese tends to accumulate in more oxygenated conditions above the redox boundary (Bellanca et al., 1996). The Ilaro sanstone has Mn* values ranging from -0.22 to 1.36 with an average of +0.69. This suggests that the sandstones may have been deposited in oxic to suboxic conditions.

Table 4: Comparison of some trace elements of Ikpeshi Marbles and that of average sedimentary carbonate rocks

Trace elements (ppm)	**Ikpeshi Marble (mean)**	**Carbonate rocks (Turekian and Wedepohl, 1961)**	
		Shallow Sea	**Deep Sea**
Ni	19.89	20	20
Cr	19.94	11	11
Zn	37.9	20	35
Sr	1804.6	610	2000
Mn	300	1100	1000

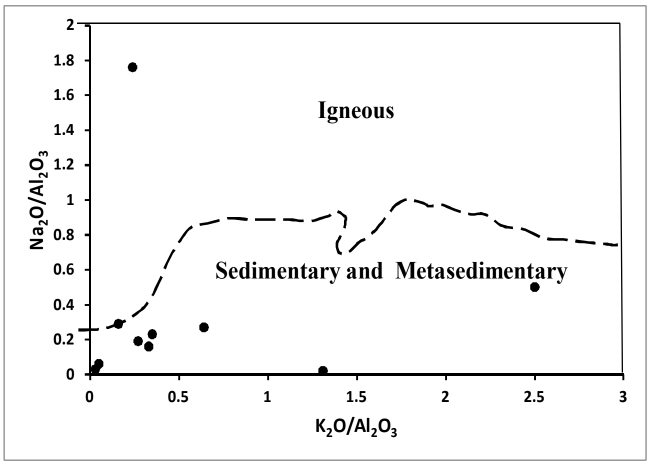

Figure 6: Na_2O/Al_2O_3 vs. K_2O/Al_2O_3 discriminant diagram of the Ikpeshi Marble (after Garrels and Mackenzie, 1971)

Figure 7A and 7B are bivariate tectonic discrimination plots of the Ikpeshi marbles based on major oxides, both shows majority of the samples in the passive margin zone and few in the active continental margin zone. Figure 8 (A, B and C) are ternary tectonic discrimination plots of the Ikpeshi marbles based on trace and rare earth elements. The variation plot for the Ikpeshi marble (fig.9A) shows a weak positive correlation between SiO_2 and Na_2O+K_2O. SiO_2 vs CaO (fig. 9B) shows a positive correlation while SiO_2 vs of MgO (fig. 10B) indicates negative correlation. This may be due to introduction of detrital and siliceous materials into the calcitic limestone. The bivariate plot of CaO vs MgO (Fig. 11) indicates strong negative correlation and an inverse relationship. This may be as a result of the converse relationship in the proportion of calcite to dolomite in themarble.

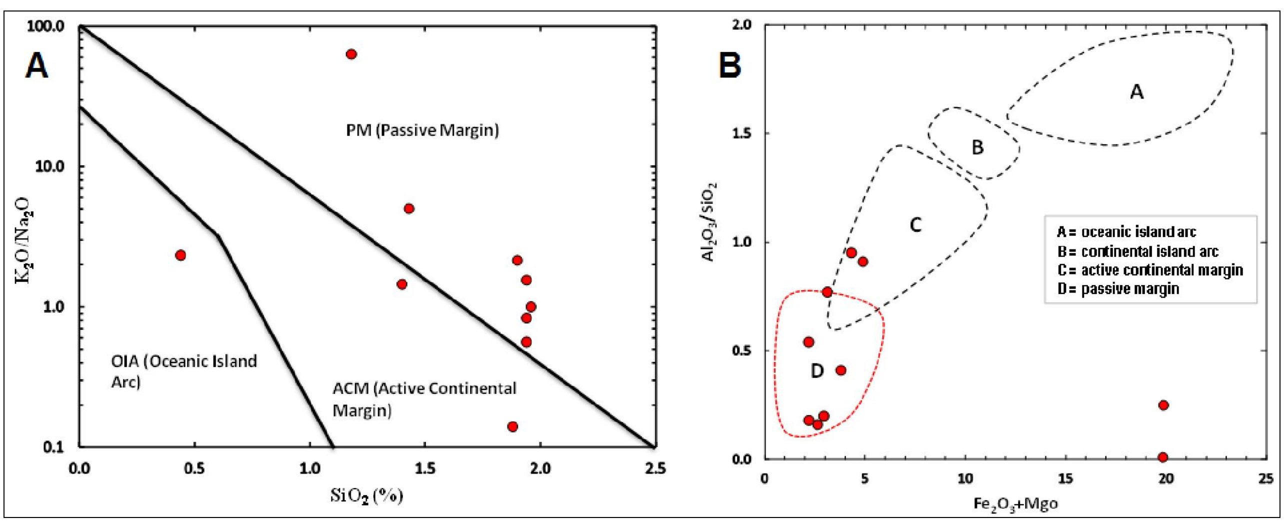

Figure 7 (A): Tectonic discrimination plot for the Ikpeshi marbles (after Roser and Korsch, 1986). (B): Tectonic setting discrimination plot (after Bhatia, 1983).

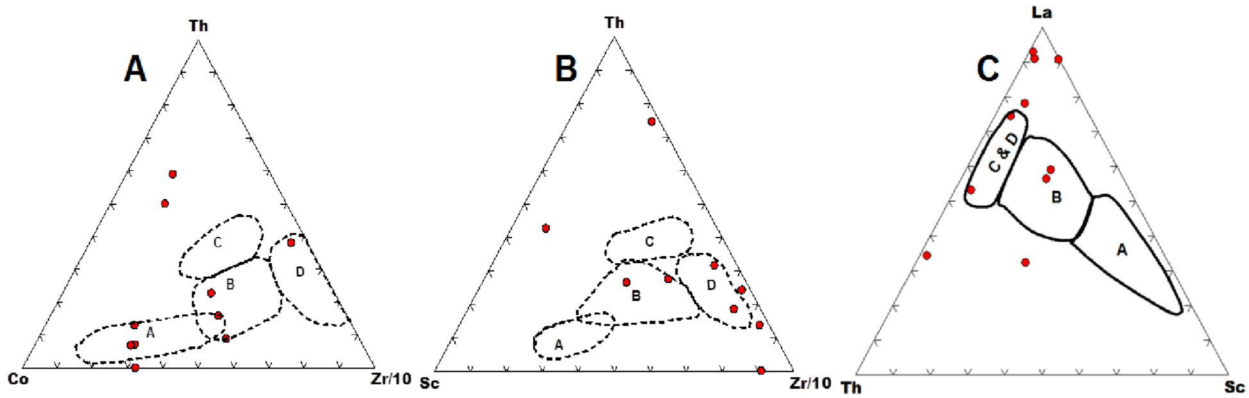

Figure 8: (a) Th - Co - Zr/10 plot; (b) Th - Sc - Zr/10 plot; and (c) La - Th - Sc plot. All fields from Bhatia and Cook (1986): A = oceanic island arc; B = continental island arc; C = active continental margin; D = passive margin.

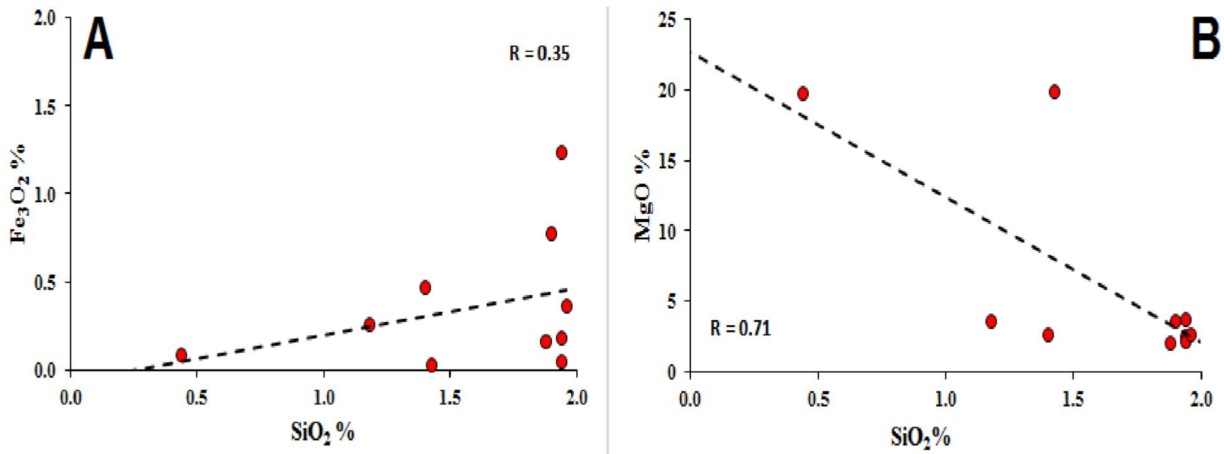

Figure 10 (A): Plot of SiO_2 vs of Fe_2O_2 vs and (B) SiO_2 vs of MgO for the Ikpeshi marbles

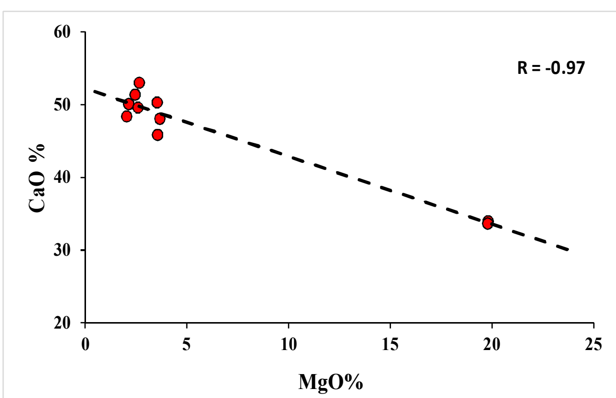

Figure 11: Plot of MgO vs. CaO for the studied marbles

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