

Use of Geochemistry to Study the Provenance, Tectonic Setting, Source-Area Weathering and Maturity of Igarra Marble, Southwest, Nigeria.

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ABSTRACT: *The need to study the provenance, tectonic setting, weathering and maturity of Igarra marble forms the objectives of this research. The effects of alteration due to metamorphism and deformation are noticed by low concentration of some mobile elements. Other possible alteration effects can further be elucidated from the Harker variation diagrams where SiO_2 is compatible and correlated positively with Na_2O , K_2O , Fe_2O_3 , Al_2O_3 , and TiO_2 and negatively with CaO . Al_2O_3 value ranges between 0.16 and 0.61 wt %. Al_2O_3 correlates positively with Fe_2O_3 , and TiO_2 suggesting a possible input of clay minerals believed to have formed from weathering of ferromagnesian minerals. The Chemical Index of Alteration and the Chemical Index of Weathering have the same percentage range values of 30 -118 % with an average of 76.1 %, indicating that a low to high degree of weathering of the source materials must have taken place. The relatively low contents of K_2O (K-feldspar) and Na_2O (Na-feldspars) suggest that the source rocks may have been exposed to weathering. The sediments being generated as a result of the weathering is suggested to have been deposited in the passive continental margin. These thick continental margin deposits can only be derived if source areas are sufficiently stable to allow intense chemical weathering capable of destroying rock fragments and feldspars to take place. The tectonic discrimination parameters suggest that the tectonic settings are of both the active continental margin and passive continental margin an indication of multiple tectonic activities. Provenance studies showed that the quartz-rich materials observed within the marble domain might have been derived from the surrounding rocks of mixed origin*

Keywords: *Source-area weathering, provenance, mixed origins, passive margin.*

I. INTRODUCTION

The geochemistry, economic potential and classification of marble from Igarra have been studied (Obasi et al., 2012, Obasi, 2012). Major oxides, trace and rare earth elements ratios are used in most cases as indicators in the study of tectonic settings, and source area weathering. Bhatia, (1983); Bhatia and Crook, (1986); Roser and Korsch, (1986); Roser and Korsch, (1988); McLennan and Taylor, (1991); McLennan et al., (1993); Johnson and Basu, 1993; Condie, (1993); Nesbitt et al., (1996); Fedo, et al., (1997); Cullers and Podkovyrov, (2000); Bhatt and Ghosh, (2001) have used elemental ratios as sensitive indicators for the study of the source rocks, tectonic setting, paleo-weathering conditions and paleoclimate of sediments including the clastic sediments. The Igarra areas have diverse rocks, carbonate deposits and mineral type's particularly industrial minerals at different localities. The formation of large carbonate (marble) deposits may have resulted from heavy accumulation of marls, mud and skeletal sediments at shallow marine environment.

Igarra area is underlain by low-grade upper Precambrian metasediments (Odeyemi, 1988). These metasediments form part of the Nigerian schist belt. Hockey and Jones (1964) described the metasedimentary rocks of the Nigerian schist belt as consisting of quartzite, marble and mica schists. Rahaman (1976) grouped most of these rocks as Younger metasediments or unmixed schists, indicating low grade metasediments formed during the Pan-African Orogeny. The plots of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ in Fig. 1 collaborate with the geology of Igarra area by plotting in the sedimentary and metasedimentary field.

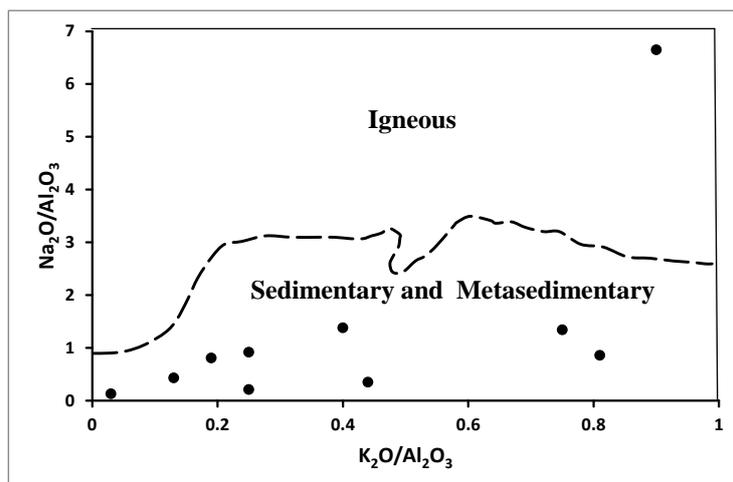


Fig. 1: Discrimination plots of Na_2O/Al_2O_3 vs. K_2O/Al_2O_3 used for Igarra Marble. Fields of Igneous and Sedimentary and Metasedimentary rocks (After Garrels and Mackenzie, 1971).

These belts consist of low to medium grade metamorphic rocks of mainly sedimentary and igneous origins and they trend in N-S direction (Elueze, 1982). Marble at Igarra was formed when limestone exposed to high temperatures and pressures recrystallised during the Pan African thermo tectonic episode about 600 ± 150 Ma (Ajibade et al, 1988). The tectonic setting, source area weathering and maturity of marble as derived from precipitated sediments of limestone are what this paper aims at studying.

II. MARBLE GEOCHEMISTRY

The geochemical characteristics of marble from Igarra have been highlighted in the early works of Obasi et al., 2012.

Table 1 Major element components of the samples and some ratios and weathering indices

	1	2	3	4	5	6	7	8	9	10
SiO ₂	1.84	2.11	1.89	2.99	4.33	4.83	1.90	3.69	3.53	4.26
Al ₂ O ₃	0.31	0.45	0.16	0.54	0.52	0.31	0.18	0.61	0.45	0.36
Fe ₂ O ₃	0.18	0.35	0.12	0.14	0.32	0.58	0.08	0.26	0.33	0.52
MnO	0.005	0.032	0.018	0.007	0.03	0.22	0.004	0.011	0.024	0.026
MgO	1.45	1.26	1.28	1.89	2.8	1.1	5.33	3.22	3.02	3.52
CaO	51.35	53.06	52.76	52.24	48.68	47.89	47.82	50.66	50.12	46.51
Na ₂ O	0.09	0.20	0.13	0.23	0.18	2.06	0.05	0.13	0.62	0.31
K ₂ O	0.05	0.11	0.03	0.07	0.23	0.28	0.01	0.15	0.18	0.29
TiO ₂	0.011	0.02	0.003	0.015	0.22	0.27	0.003	0.022	0.004	0.24
P ₂ O ₅	0.04	0.08	0.02	0.04	0.04	0.01	0.05	0.04	0.04	0.04
LOI H ₂ O,CO ₂	43.0	32.59	43.08	42.4	41.61	41.25	43.06	42.18	41.06	42.05
Total	98.38	90.26	99.49	100.6	98.8	98.34	98.46	101	99.38	98.82
Na ₂ O/K ₂ O	1.8	1.82	4.33	4.67	0.78	7.36	5.00	0.87	3.44	1.07
% CIA	60	84	30	102	105	61	37	118	88	76
% CIW	60	84	30	102	105	61	37	118	88	76

CIA: Chemical Index of Alteration

CIW: Chemical Index of Weathering

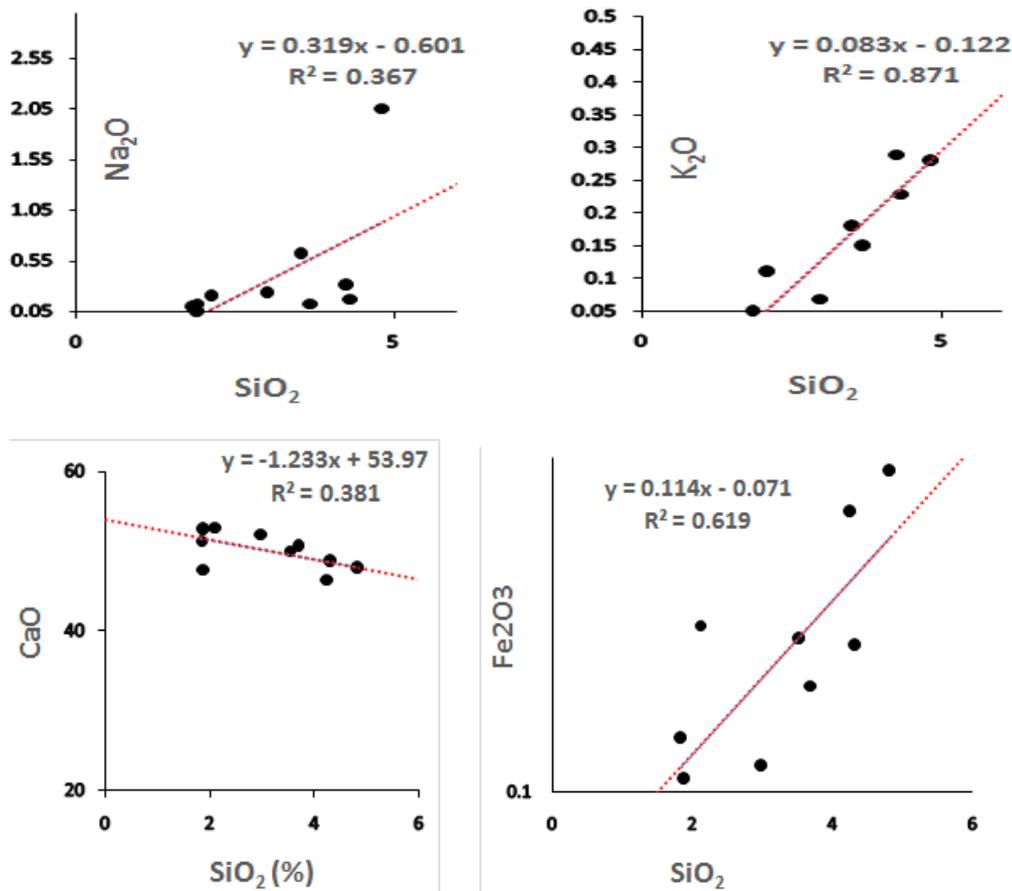
Table 1 shows the major elements and some ratios of weathering indices. SiO₂ content ranges from 1.84 to 4.83wt % , Na₂O (0.05-2.06) , K₂O (0.01-0.39),) P₂O₅ (0.01-0.04), TiO₂ (0.003-0.27) and Na₂O/K₂O (0.76- 7.36) .The low abundance of these major elements can be compared to typical values of Jakes and White,1971 that ascribed the low concentrations for calc-alkaline due to loss during alteration and metamorphism.

2.1 Chemical alteration and element mobility

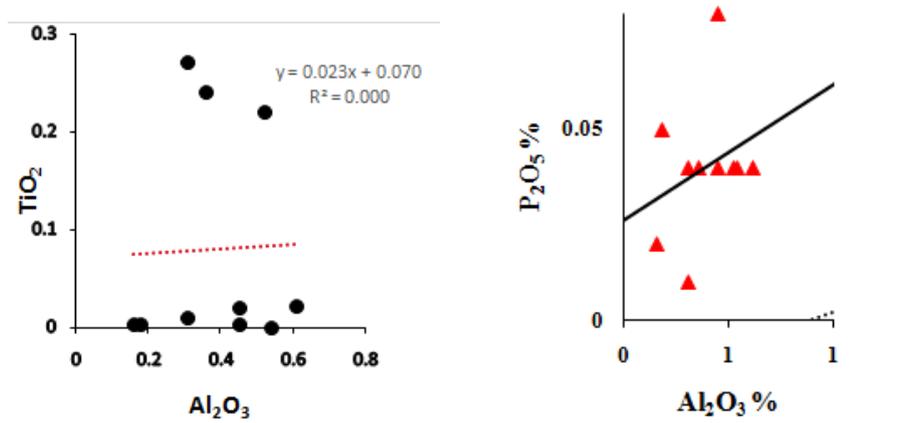
Metamorphism and deformation in any geological environment usually alter the originality of the rocks. Igarra area has been described by authors such as Odeyemi, (1988) to have been affected by low grade metamorphism and several generations of deformations. The effect of alteration is noticed by low concentration of some mobile elements as shown in Table 1. SiO₂ forms a minor impurity that was incorporated with the calcite during the low grade metamorphism and /or extensive deformation that occurred within the study area.

The possible alteration effects of metamorphism and deformation can further be elucidated from the Harker variation diagrams (Figs.2a&2b) where SiO₂ is compatible and correlated Positively with NaO₂, K₂O, Fe₂O₃, AL₂O₃, and TiO₂ and negatively with CaO. The low value of SiO₂ however may be attributed to chemical destruction under oxidizing conditions of the source-area.

Al₂O₃ value ranges between 0.16 and 0.61 wt % .AL₂O₃ correlates positively with Fe₂O₃, and TiO₂ suggesting a possible input of clay minerals believed to have formed from the weathering of ferromagnesian minerals. Again TiO₂ increasing with Al₂O₃, suggests that TiO₂ is probably associated with phyllosilicate especially with illite (Dabard, 1990). The linear negative trend of CaO versus SiO₂ implies that as CaO abundance increases within the carbonate environment the less the incorporation of SiO₂ during the re-crystallization of calcite. The lesser the SiO₂ content in the marble the more the purity and its economic applicability in the chemical industries.



Figs 2a: Harker diagrams: NaO, K₂O, CaO, Fe₂O₃ Versus SiO₂



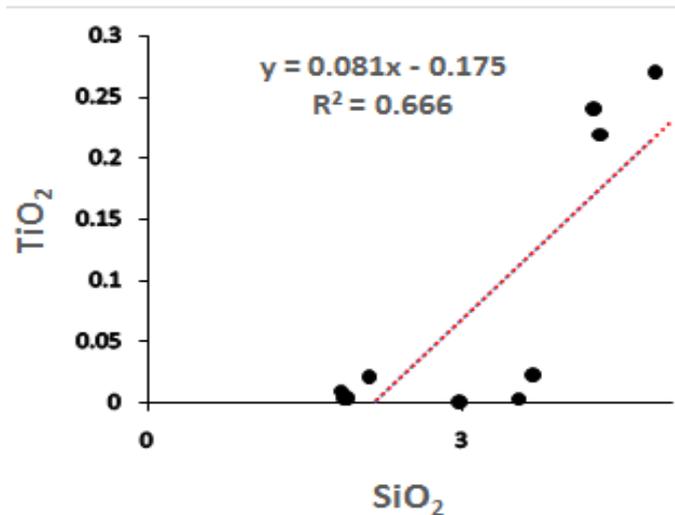


Fig. 2b: Harker variation diagrams of TiO_2 , P_2O_5 Versus Al_2O_3

III. SOURCE AREA WEATHERING

Weathering of the source rocks is affected by factors such as properties of the parent rocks and the climate. Authors such as Nesbitt and Young (1989) and Nesbitt et al., (1996) have disclosed that the chemical composition of rocks largely depends on the composition and the weathering conditions at the source rock area. Nesbitt and Young (1982) proposed the calculation of the chemical index of alteration (CIA), where CIA is equal to molar $(Al_2O_3/[Al_2O_3+CaO+Na_2O+K_2O])$ as a measure of the degree of chemical weathering/alteration of the sediments source rocks. Harnois (1988) proposed the equation for the chemical index of weathering (CIW) as $CIW = \text{molar } (Al_2O_3/ (Al_2O_3+ CaO + Na_2O))$ and this is similar to the CIA except that K_2O is removed from the equation. McLennan, et al., (1983, 1993) and Mongelli, et al., (1996) stated that the CIA and CIW are interpreted in the same way with values of 50 for un weathered upper continental crust and roughly 100 for materials that are highly weathered and whose alkali and alkaline-earth elements are completely removed. Fedo, et al. (1995) also stated that when the value of the CIA is as low as 50 or less, it might reflect cool and / or arid conditions, therefore little or low weathering. In the study area the CIA and the CIW have the same percentage range values of 30 -118 % with an average value of 76.1 %, indicating that a low to high degree of weathering of the source materials must have taken place. The relatively low contents of K_2O (K-feldspar) and Na_2O (Na-feldspars) implies that the source rocks may have been exposed to weathering. A plot of the CIA against Al_2O_3 indicates a low to high intensity of weathering in the area (Fig .3).

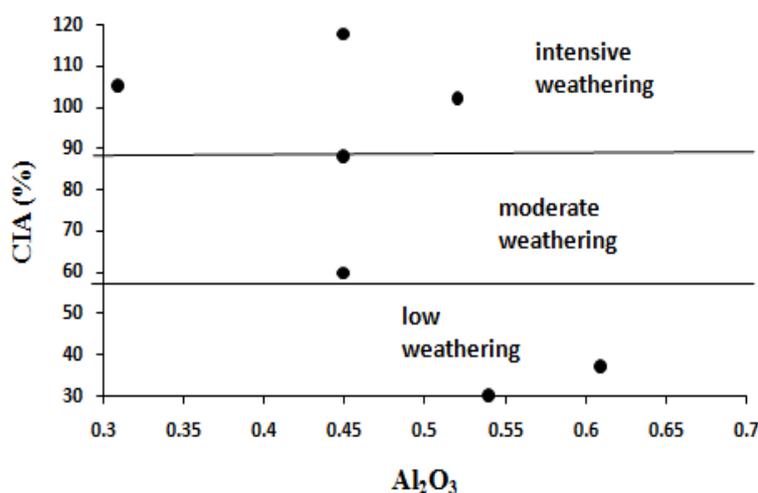


Fig .3: Plot of CIA (%) against Al_2O_3

The depletion of highly mobile K and Na elements is due to leaching during the formation of clay minerals during increased chemical weathering. A plot of K_2O against Al_2O_3 (Fig .4) shows clearly the clay minerals, feldspar and illite that are susceptible to chemical weathering .

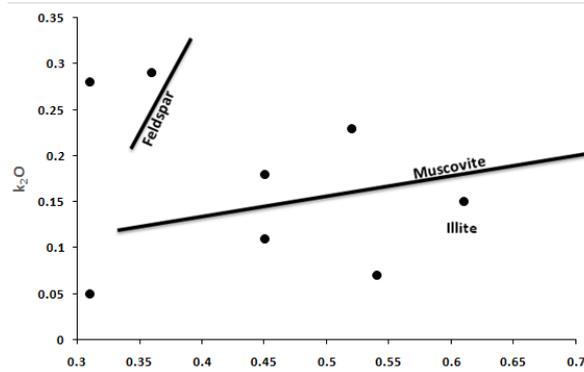


Fig. 4: Plot of K_2O versus Al_2O_3

Fig. 5 is the ternary diagram of $CaO-MgO-SiO_2$ classification system for marbles (Storey and Vos, 1981) indicating the sixteen marble divisions of which pure calcite takes prominence with pure dolomitic calcite as traces. The samples plotted sensu stricto within the field of marble.

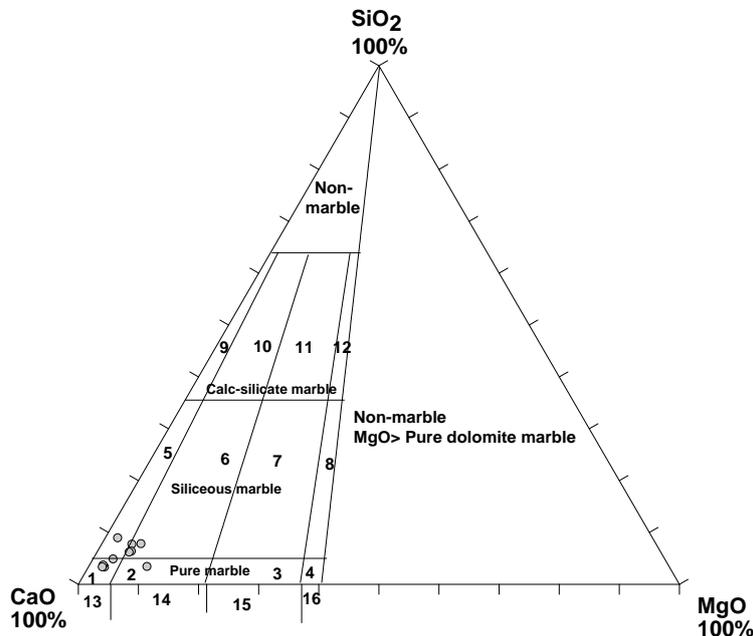


Fig 5: $CaO-MgO-SiO_2$ ternary diagram classification system for marbles (from Storey and Vos 1981).

- 1 Pure Calcite
 - 2 Pure Dolomitic Calcite
 - 3 Pure Calcitic Dolomite
 - 4 Pure Dolomite
 - 5 Siliceous Calcite
 - 6 Siliceous Dolomitic Calcite
 - 7 Siliceous Calcitic Dolomite
 - 8 Siliceous Dolomite
 - 9 Calc-Silicate Calcite
 - 10 Calc-Silicate Dolomitic Calcite
 - 11 Calc-Silicate Calcitic Dolomite
 - 12 Calc-Silicate Dolomite
 - 13 Calcite Marble
 - 14 Dolomitic Calcite Marble
 - 15 Calcitic Dolomite Marble
 - 16 Dolomite Marble
- Non – marble and $MgO >$ pure marble

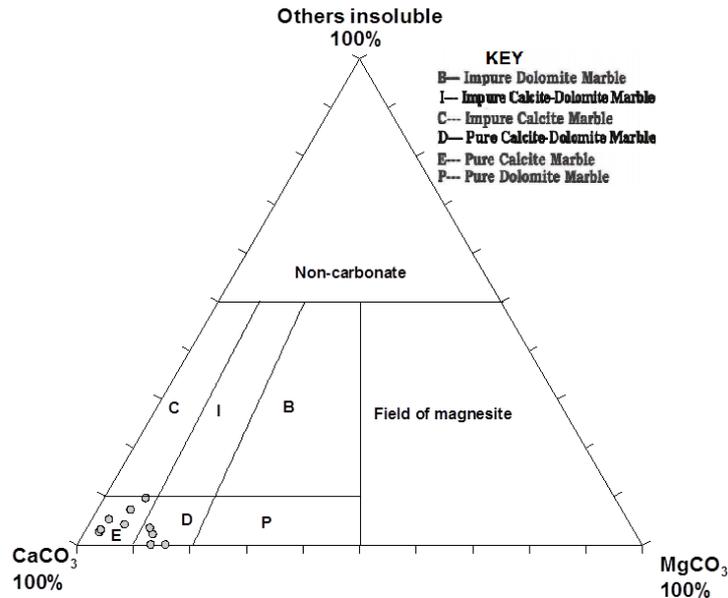


Fig.6: Classification of the Igarra Marble (After Carr & Rooney, 1983).

Fig 6 is a confirmation of the ternary diagram of Fig.5 which classified the marble into pure calcitic marble with traces of pure calcite-dolomitic marble and all belong to marble fields.

IV. Maturity And Paleoclimate During Sedimentation

The plot of SiO₂ versus Al₂O₃+K₂O+Na₂O in Fig.7 shows that the samples plotted in the humid/semi-humid climatic zone. The paleoclimatic condition displaying wet condition accelerates weathering process and speeds up the chemical maturity.

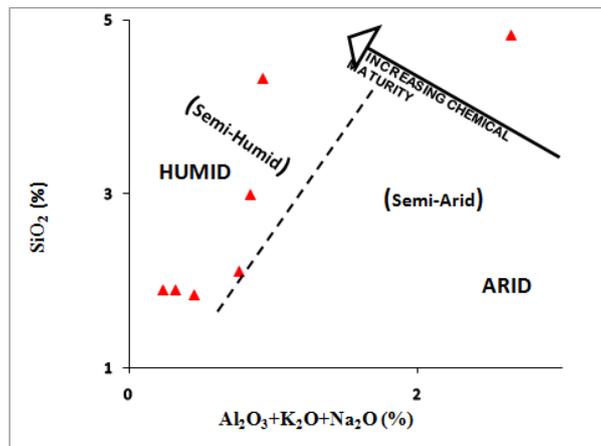


Fig.7 : SiO₂ versus Al₂O₃+K₂O+Na₂O.

SiO₂/Al₂O₃ index is used to measure the maturity of sandstones (Potter, 1978) in terms of mineralogical maturity. Maturity is reflected best in quartz, rock fragments, feldspars and grain size. SiO₂/Al₂O₃ ratios of clastic rocks are sensitive to sediment recycling and weathering process and these are indicators of sediment maturity. However, the quartz contents in the marble can be used in reference to the increasing sediment maturity, because quartz survives preferentially to feldspars, mafic minerals and lithics (Roser and Korsch, 1986; Roser et al., 1996). The average SiO₂/Al₂O₃ ratios in unaltered igneous rocks range from ~ 3.0 (basic rocks) to ~ 5.0 (acidic rocks). Values of SiO₂/Al₂O₃ ratio > 5.0 in sandstones are an indication of progressive maturity (Roser et al., 1996). Low values of SiO₂/Al₂O₃ ratios and low values of K₂O/Na₂O together indicate mineralogically immature sediment. The Igarra marble samples have SiO₂/Al₂O₃ ratios (4.68 - 15.58) greater than 5.0 and therefore show the tendency for increasing mineralogical maturity with a low degree of clayness as depicted in the low K₂O/Na₂O ratios of 0.14- 1.28 (Pettijohn et al., 1972; Roser and Korsch, 1986; Fedo et al., 1995; Paikaraj et al., 2008).

The $\text{Al}_2\text{O}_3/(\text{CaO}+\text{MgO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$ ratio can be used in determining the stability of mobile oxides as proposed by Gill and Yemane (1996). The values obtained are in the range of 0.003 to 0.011 and positive implying that there are stable mobile oxides in the marble. The index of compositional variability (ICV) defined by Cox et al.,(1995) as $(\text{Fe}_2\text{O}_3+\text{Na}_2\text{O}+\text{CaO}+\text{MgO}+\text{TiO}_2)/\text{Al}_2\text{O}_3$ can be used to assess the variable compositions in marble. Calculated values show a very high range of 100.38 -345.50 suggesting variability of marble composition as sourced from mixed origins especially during the formation of the parent rock.

The various source compositions of marble can further be elucidated by using the bivariate plot of Na_2O versus K_2O showing a spread of the samples from quartz intermediate to quartz-rich again suggesting mixed sources of materials (Fig.8). The bivariate plots of CaO against MgO also confirms the quartz-rich nature of the local marble surrounding rocks (Fig.9). Bivariate Plot of CaCO_3 versus MgCO_3 of the studied samples showed quartz content that is rich in the marble environment.(Fig.10). However the richness of quartz in marble environment is relative because its utility depends on its applicability .

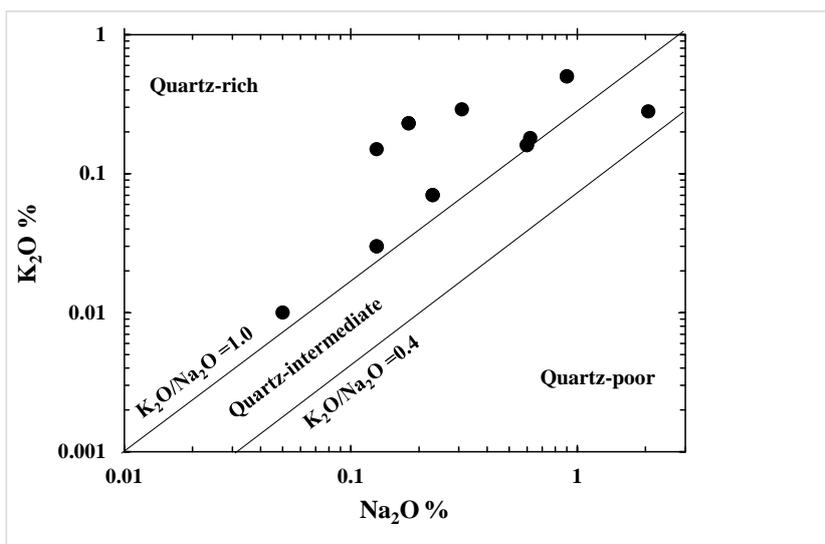


Fig. 8: A bivariate plot of Na_2O versus K_2O of the studied samples showing quartz content, after Crook (1974)

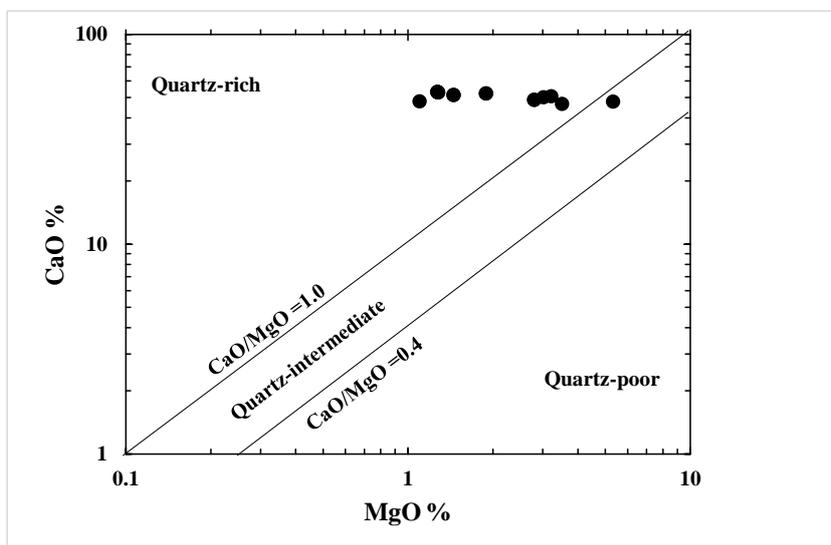


Fig.9: Bivariate Plot of CaO versus MgO of the studied samples showing quartz content, modified from Crook (1974).

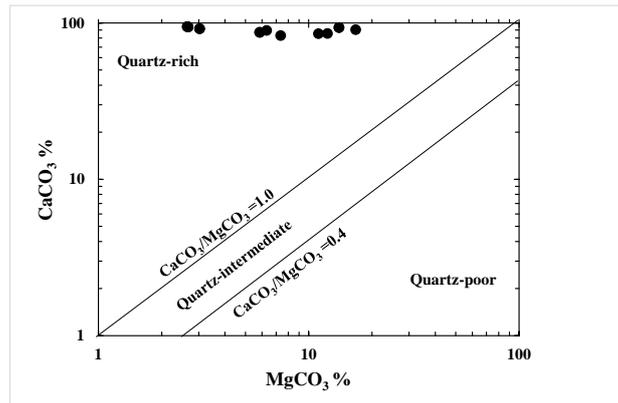


Fig. 10: Bivariate Plot of CaCO_3 versus MgCO_3 of the studied samples showing quartz content, modified from Crook (1974).

V. TECTONIC SETTING

Roser and Korsch (1986) created a tectonic discrimination diagram using $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio versus SiO_2 in Fig.11 to determine the tectonic setting of sedimentary rocks. The plot has been used to discriminate between sediments deposited in the Passive Continental Margin, Active Continental Margin and the Oceanic Island Arc. The studied samples plotted in both the active continental margin and the passive margin (PM) tectonic settings suggesting sedimentation on an ancient rift that marked the boundary between oceanic and continental margins. Roser and Korsch (1986), proposed that passive margin sediments are largely quartz-rich sediments derived from plate interiors or stable continental areas and deposited in stable intracratonic basins or on passive continental margins. Details of passive and active continental margins can be found in Bhatia (1983). The plotting on both margins goes to confirm the varied sources of material input. Samples in Figs 12 and 13 plotted in Fields D, C, and A representing the passive margin, active continental margin and oceanic island arc respectively confirming the earlier results of multiple sources.

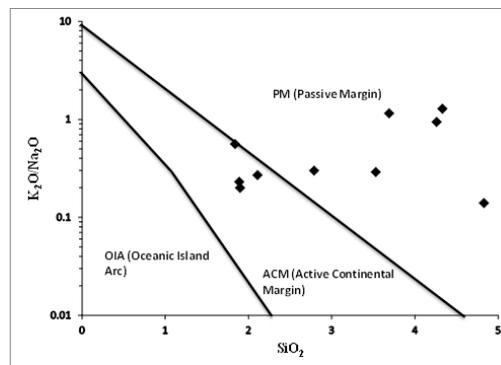


Fig.11: Tectonic discrimination plot for the Igarra marble (after Roser and Korsch, 1986).

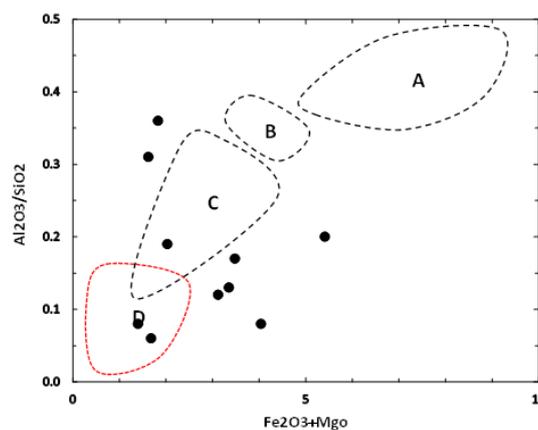


Fig. 12: Tectonic setting discrimination plot of TiO_2 versus $\text{Fe}_2\text{O}_3 + \text{MgO}$ of the studied samples. Dashed lines denote the major fields representing various tectonic settings (after Bhatia 1983).

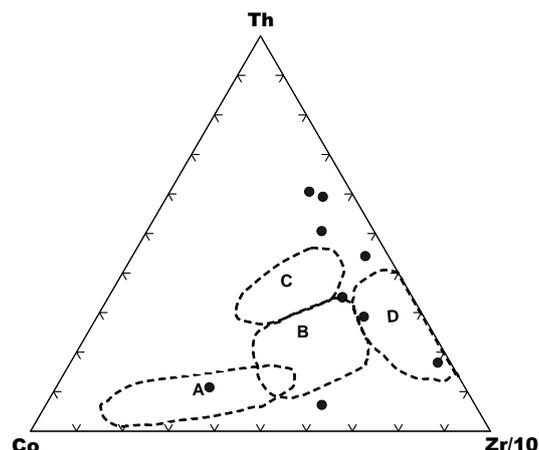


Fig- 13 : Th - Co - Zr/10 tectonic discrimination plot. All fields from Bhatia and Cook (1986): A = oceanic island arc; B = continental island arc; C = active continental margin; D = passive margin.

Fig. 14 shows the plots between Fe_2O_3 versus MgO indicating marine and non-marine depositions of quartz. The plotting exhibits both fields thus expressing the transitional nature of the marble samples between the continents and ocean margins prior to deposition into the rifted passive basin.

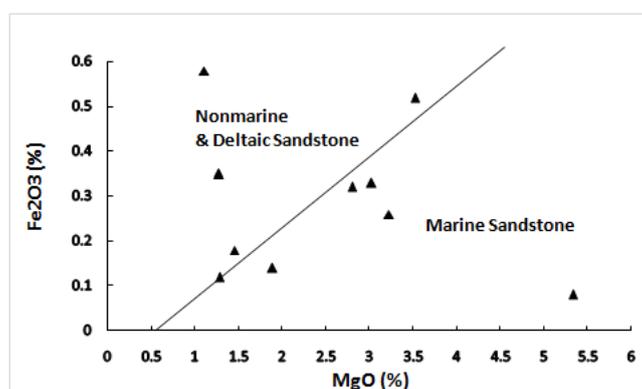


Fig.14. A plot of Fe_2O_3 versus MgO

VI. CONCLUSION

The study shows that CIA and CIW have the same percentage range values of 30 -118 % with an average of 76.1 %, indicating that a low to high degree of weathering of the source materials must have taken place. The relatively low contents of K_2O (K -feldspar) and Na_2O (Na-feldspars) imply that the source rocks may have been exposed to weathering. A plot of the CIA against Al_2O_3 shows a low to high intensity of weathering in the area and all other weathering indices indicate that the source area experienced same low to high weathering conditions.

The paleoclimatic condition during deposition indicates the humid/semi-humid climate. The prevalent wet condition accelerates weathering process and thus expedites chemical maturity while the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio indicates progressive maturity. The $\text{Al}_2\text{O}_3/(\text{CaO}+\text{MgO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$ ratio indicates that there are stable mobile oxides in the marble samples. Provenance studies suggest derivation from surrounding rocks of mixed origin while the tectonic discrimination parameters suggest that the tectonic settings are of both the active continental margin and passive continental margin an indication of multiple tectonic activities.

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