



GEOCHEMICAL ANALYSIS OF MARBLE FROM UBO RIVER AREA: IMPLICATION FOR PALEO-ENVIRONMENTAL CONDITIONS



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Abstract: Twenty (20) marble samples from Ubo River area were obtained and subjected to geochemical analysis with the aim of determining the paleo-depositional environment of the original sediments using major elemental composition. The samples were pulverized into powder-form and further subjected to geochemical analysis using Atomic Absorption Spectroscopy (AAS) and Flame Photometer. The results obtained show that CaO ranges between 52.98-82.18%, Al₂O₃ ranges between 0.01-0.34%, MgO ranges between 1.64-5.32%, Na₂O ranges between 0.05-0.43%, SiO₂ ranges between 0.01-0.08%, MnO ranges between 0.01-0.03%, FeO ranges between 0.05-1.9% and K₂O ranges between 0.02-0.84%. Multivariate statistical analysis was also used to determine the relationship between the variables with CaO vs MgO having fairly high positive correlation indicating fairly high precipitation and Fe₂O₃ vs CaO having negative correlation indicating low precipitation, respectively. Findings reveal that the carbonate sediments were probably deposited in a quiet shallow marine environment and are very useful in the industrial sector.

Keywords: Marble, geochemistry, major oxides, mineralogy, paleo-environmental conditions

Introduction

Marbles are generally metamorphic derivatives of sedimentary carbonates and have been known to be relatively impermeable during metamorphism. Marble is a major raw material for industries; resulting from the metamorphism of limestone, a carbonate sedimentary rock formed in shallow marine and lakes environment which when subjected to increase in temperature ranging from 150 – 750°C and pressure leads to its formation (Mason, 1966).

During recrystallization, the resulting marble rock is typically composed of interlocking grains of crystals with the primary sedimentary structure and texture typically modified. Marble consist of swirls and veins of many coloured varieties which are due to mineral impurities which include quartz, tremolite, actinolite, chert, biotite, muscovite, forsterite, hematite, serpentite, pyrite (Phillip, 2009). Pure marbles (high calcium marble) is composed primarily of the mineral calcite or aragonite with total carbonate content of 95-97%, pure dolomite is composed of 45.7% MgCO₃ and 54.3% CaCO₃ or 30.4% lime (CaO) and 21.8% magnesia (MgO) (Boynton, 1980). Only a few marbles are predominantly dolomite-rich and such marbles comprises alternating beds or masses of calcite and dolomite, which are undesirable because the two minerals frequently differ in texture, colour, susceptibility to polish and resistance to weathering.

Marble deposits usually occur in the subsurface but in rare cases when found at the surface the overburden is removed and the marble is thus mined through various mining techniques. The present work aims at determining the major elemental composition of the Ubo marble, using multivariate statistical analysis to determine elemental relationship

between the major oxides hence, determining the paleo-environmental conditions that existed during the deposition of the sediments

Geologic setting

The study area is located in Ubo River area which is situated at Akoko Edo LGA, Edo North, South Western Nigeria and lies between latitude N07°21'10" to N07°22'28" and longitude E006° 24' 34" to E006° 28'29.4" on Auchi Sheet 266 on a scale of 1:10,000 with an area extent of 420.86 km². Marble occurs in the north-eastern part of the area and active quarries occur in several locations (Figs. 1 and 2).

The study area "Ubo" belongs to the southern basement complex of Nigeria, which is underlain by metasediments (Madhavaraju and Rahmasamy, 1999). It is associated with crystalline rocks of Precambrian basement complex. The basement rocks have undergone different stages of tectonic activities such as different episode of intrusion, folding, metamorphism etc. The rocks in the study area from the oldest to the youngest are the migmatite-gneiss complex which is overlain by quartzite, followed by the carbonate rock such as marbles with calc-gneisses closely associated with the marbles and the Younger metasediments and the Pan African rocks (Rahaman, 1988; Odeyemi, 1988; McCurry, 1976). Touret, (1977) suggested that the formation of calc-gneiss is probably a reaction between calcite derived from marl sediments or original limestone and quartz from detrital grains during metamorphism. The area experienced later phases or episodes of intrusions such as dykes, batholiths, laccoliths, etc. The major and minor igneous rocks are charnockites, porphyritic granites, aplites and pegmatites, respectively.

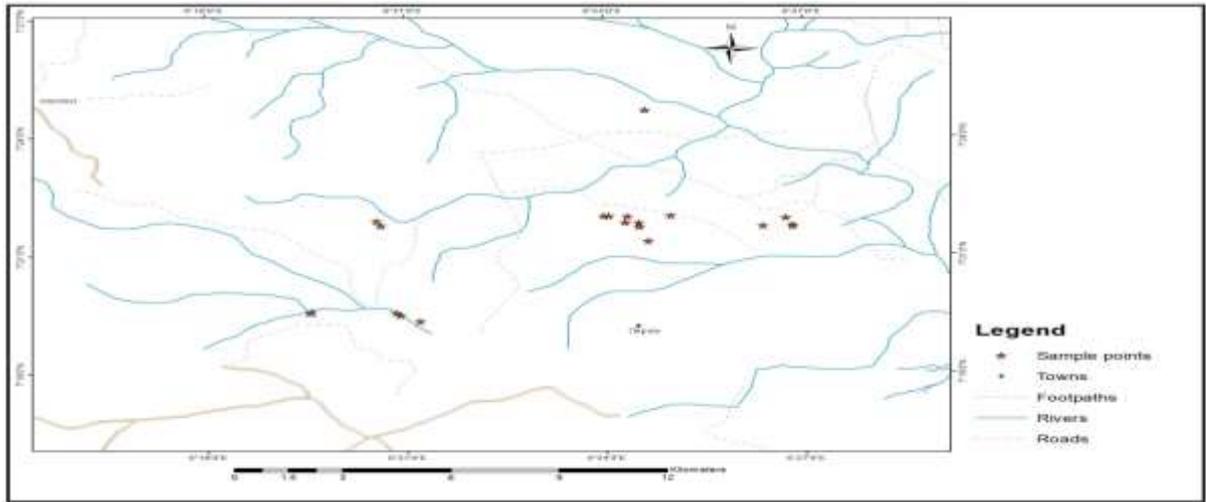


Fig. 1: Map of study area showing sample location

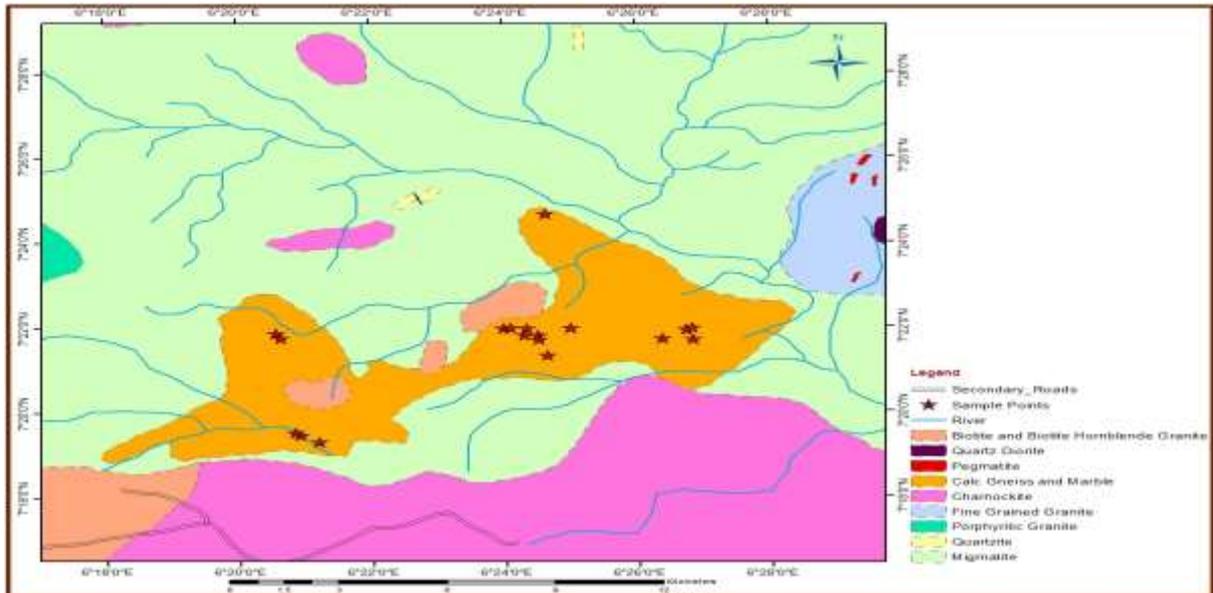


Fig. 2: Geology map of study area (GSN, 2015)

Materials and Methods

A reconnaissance survey and systematic field mapping of the marble deposits and other associated rock types was undertaken. Fieldwork accomplished in the study area with samples obtained in locations from exposed outcrops. Twenty (20) samples were obtained from different locations from the study area with the aid of a sledge hammer. Global Positioning System (GPS) was employed to locate and determine the elevations and co-ordinates of sampled points. The well-labeled samples were further placed in sample bags with care taken to avoid contamination. The samples were pulverized with the pulverizer, to reduce larger size of the sample to smaller sizes (less than 1 mm) due to inhomogeneity and to increase the surface area so that there would be a better reaction between the sample and acid when added to it. Various chemicals reagent of analytical grade and instrument were used for the digestion of the samples of appropriate high purity. The samples were analyzed using Atomic Absorption Spectroscopy (AAS) and Flame photometer for the major oxides.

Results and Discussion

The result from the analysis is shown in Tables 1 and 2. The results reveal the presence of the following major oxides and their volume in weight percentages:- CaO, 52.98-78.40; MgO, 1.64-6.95; Na₂O, 0.05-0.43; K₂O, 0.02-0.84; SiO₂, 0.01-0.08; MnO₂, 0.01-0.03; Al₂O₃, 0.01-0.17; Fe₂O₃, 0.03-1.31 and FeO, 0.05-1.52. The high CaO content is probably due to the high volume of calcareous and/or carbonate sediments in the area. This is also a reflection of the introduction of CaO from bones of dead organisms and also from precipitates. The low content of MgO indicates very little contributions of high vertebrate organisms in the the sediments prior to metamorphism (Odokuma-Alonge and Amadin, 2018). The very low MgO of less than 7% makes the marble to be classified as calcitic ones (Brown, 2007). The other major oxides occur in minor amounts. This is similar to works of other authors from other areas where marble occurs in the basement complex (Onimisi *et al.*, 2015; Obasi *et al.*, 2015; Ikoru *et al.*, 2012).

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

Sample No.	Na ₂ O	K ₂ O	CaO	MgO	SiO ₂	MnO ₂	Al ₂ O ₃	Fe ₂ O ₃	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	63.80	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	78.40	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
Std. dev.	0.09	0.11	7.42	1.11	0.03	0.01	0.04	0.09	0.13

CaO, Fe₂O₃ and SiO₂

CaO has an average value of 63.82%. Variation in CaO content with other oxides from chemical analysis is attributed to the fluctuation in the physio-chemical condition throughout the deposition of the parent rock (limestone) before metamorphism. Higher percentage of CaO with the presence of low Fe₂O₃ having an average value of 0.16% indicates a basin under reducing environment (Brown, 2007).

SiO₂ in carbonate rocks has contribution from both silicate minerals such as chert nodules, silica-rich bones from the influx of near shore materials into the basin of deposition of the original parent rock prior to metamorphism (Brownflow, 1980). The silica content in Ubo marble range from 0.01-0.08% and has an average mean of 0.03%. The relative high value of CaO and low Fe₂O₃ and SiO₂ indicates a high degree of purity of the parent rock hence its suitability of raw material for cement. The low Fe₂O₃ and FeO values in the oxide facies is a reflection of the little amount of hematite and limonite content of the rock.

K₂O + Na₂O

The alkali content such as Na and K which are indicative of salinity has been useful for interpreting the depositional environment of parent rock of Ubo marble prior to metamorphism (Land and Hopp, 1973). The concentration of the alkali content (K₂O + Na₂O) is very low, generally less than 1%. According to Clarke, (1924), Na and K concentration in marbles tend to increase with increase in salinity and vice versa. The low values of alkali content in

Ubo marble indicates that the environment of deposition of the original carbonate materials that was metamorphosed to marbles in the Ubo area must have been a relatively shallow environment with little input of salty brine water in the basin (Olatunji, 1989)

MgO + Al₂O₃

The percentage of MgO and Al₂O₃ are low 1.64 – 6.95% and 0.01 – 0.17%, respectively. Low MgO in marble translates low dolomite content and low concentration of alumina indicates low energy environment. Magnesium content in the rock may be due to the introduction of Mg²⁺ in water flowing into the basin leading to conversion of the calcite into dolomite and also from contribution of magnesium rich organic matter at low temperature environments (Pettijohn, 1975).

Multivariate statistical analysis

Multivariate statistical analysis was carried out to examine the inter-element relationship between the major elements in the marble using descriptive statistic such as mean, standard deviation and correlation matrix (Davis, 1973). The correlation matrix is presented on Table 3. The correlation between CaO vs MgO ; SiO₂ vs K₂O ; Al₂O₃ vs MgO ; Fe₂O₃ vs CaO and FeO vs CaO are 0.634, 0.630, 0.838, 0.803 and 0.793 respectively. This relationship shows a fairly strong to very strong positive correlation, which deals with their similar valences and ionic bonds (Odokuma-Alonge and Amadin, 2018).

Table 3: Correlation matrix for major elements of study area

	NaO	K ₂ O	CaO	MgO	SiO ₂	MnO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO
Na ₂ O	1.000								
K ₂ O	0.057	1.000							
CaO	0.126	-0.260	1.000						
MgO	-0.436	-0.282	0.634	1.000					
SiO ₂	-0.268	0.630	-0.128	-0.190	1.000				
MnO ₂	0.079	0.000	-0.210	-0.042	-0.131	1.000			
Al ₂ O ₃	-0.377	-0.398	0.479	0.838	-0.371	-0.193	1.000		
Fe ₂ O ₃	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

A series of plots are presented in Figs. 7 – 14. Figs. 7 and 10 shows a plot of Na₂O vs. K₂O and SiO₂ vs. K₂O and reveals a slightly strong positive correlation of $r = +0.057$ and $+0.630$ between them. Clarke (1924) is of the opinion that Na and K concentration in marbles tend to increase with increase in salinity and decreases with decrease in salinity. Hence, its low alkali content may be due to the low salinity content and energy of the environment (Bora *et al.*, 2012). The low alkali content in the marble indicates that the environment of deposition of the original carbonate-rich material may have been in a relatively shallow environment with little input of salty brine water. Low salinity content in the basin and rarity of silicate mineral in the surrounding rocks may also be responsible for the low alkali and silica content (Olatunji, 1989).

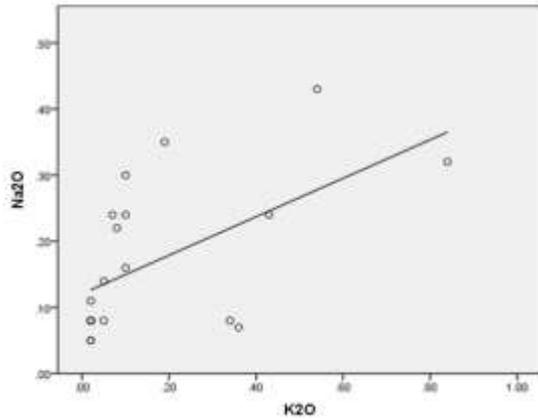


Fig. 7: Plot of Na₂O vs. K₂O

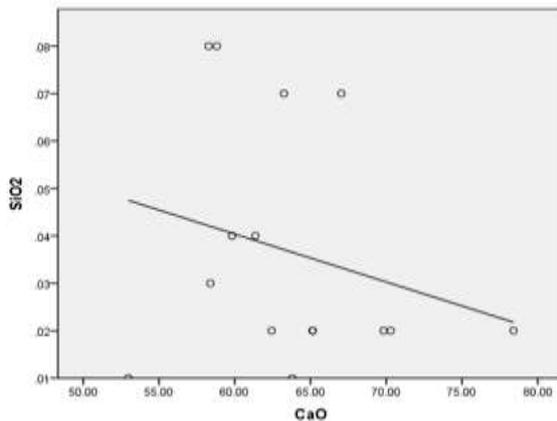


Fig. 8: Plot of SiO₂ vs. CaO

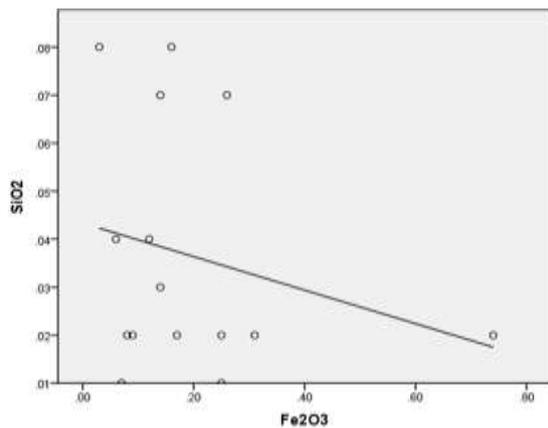


Fig. 9: Plot of SiO₂ vs. Fe₂O₃

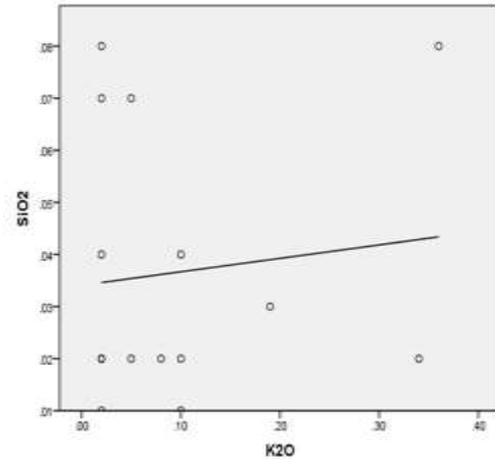


Fig. 10: Plot of SiO₂ vs. K₂O

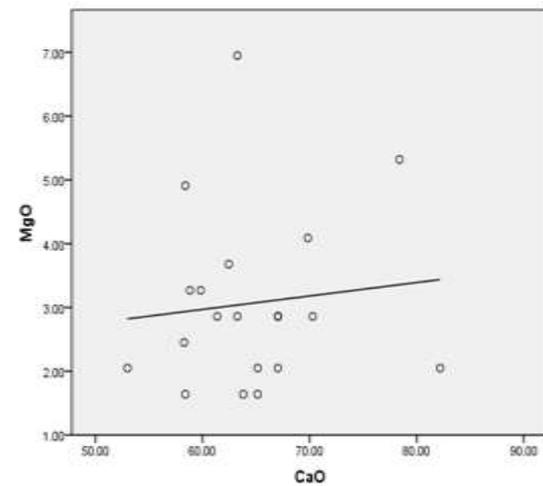


Fig. 11: Plot of MgO vs. CaO

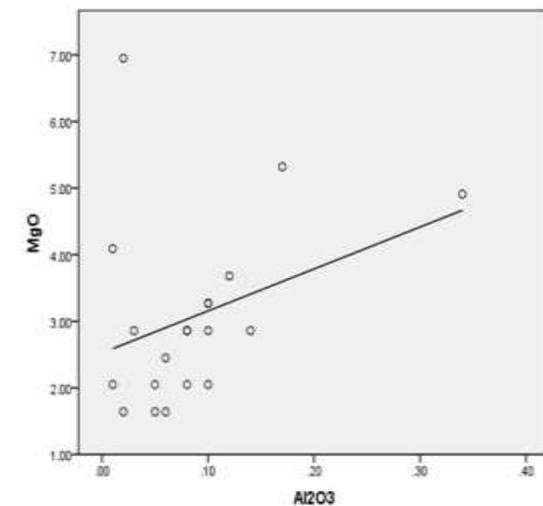


Fig. 12: Plot of MgO vs. Al₂O₃

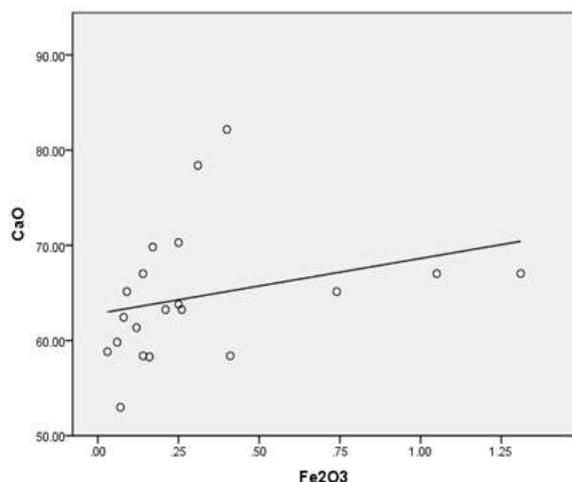


Fig. 13: Plot of CaO vs. Fe₂O₃

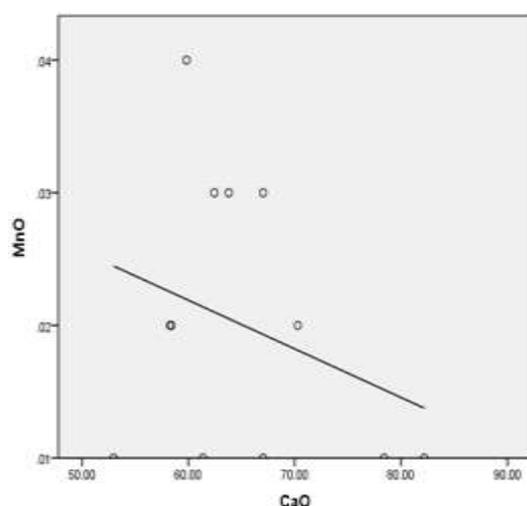


Fig. 14: Plot of MnO vs. CaO

Figure 8 shows a downhill relationship between the two variables (CaO vs SiO₂) which probably indicates that during deposition of the parent marble body, as CaO increased SiO₂ decreased. The points are scattered in a wider bands, showing a linear relationship. The low negative correlation between CaO vs SiO₂ ($r = -0.128$) reveals that silica would have been probably precipitated from brine flux in shallow basins or from low input of deltaic influx from nearby source due to climate change with high precipitation of calcite from dissolve material, transported from previously deposited biogenic material and or precipitates (Dunham, 1962). Similarly, Fig. 9 shows Fe₂O₃ vs. SiO₂ which also reveals the weak negative correlation ($r = -0.206$) of the oxides. This implies that as Fe₂O₃ increases, SiO₂ decreases and vice versa. The presence of Fe₂O₃ indicates a slightly oxidizing environment. During the influx of continental sediments into the ocean, most probably free oxygen in shallow environment tend to oxidize the iron content leading to faster precipitation of iron content (insoluble in sea water) relative to silica (Clarke, 1924). The fairly high positive correlation of MgO vs. CaO ($r = +0.634$) and very high positive correlation of MgO vs. Al₂O₃ ($r = +0.838$) and CaO and Fe₂O₃ ($r = +0.803$) as shown in Figs. 11, 12 and 13, respectively, is an indication of similarities of their valencies and ionic radii (Odokuma-Alonge and Amadin, 2018). The very low values of Al₂O₃ and Fe₂O₃ may be due to the low energy environment at the time of deposition. Fig. 14

shows a weak downhill linear relationship which indicates increase in one variable leads to decrease in the other. The poor correlation of MnO with CaO may be due to different structures of Fe or the partial entry of Mn²⁺ into carbonate rocks. It has been suggested that Mn exist in dolomite crystals (Parker, 1986) but Fruth and Scherreiks (1975) are of the opinion that the presence of Mn²⁺ in carbonate rocks are mainly controlled by the influx of continental clay.

Conclusion

Marbles in the study area are rich in CaO content (52.98-78.4 wt%) with minor amount of other major oxides such as MgO and FeO. The low values of silica and the alkalis indicates that there was probably little influx of sediments and salty brine water into the basin while the high values of CaO indicates that the basin was probably formed in a relatively deep-shallow marine environment with high precipitation and low solubility of CaO and low circulation of MgO and Al₂O₃. It can also be said that the Ubo marble deposits due to the relatively low value of silica and high value of CaO, can serve as a source of raw material for CaO - manufacturing industries. The very low values of SiO₂, the alkalis, Al₂O₃ and Fe₂O₃/FeO may not only be due to the quiet shallow marine environment but also as a result of inter-relationship of the structure of the cations.

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Conflict of Interest

Authors declare that there is no conflict of interest.

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