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The Geochemistry of Carbonate Rocks in Igwe Igarra, Southwestern Nigeria

Jumoke Mujidat Omodeni

Department of SLT (Geology/Mining), Ekiti State University, Ado Ekiti, Nigeria
Email: omodenijumoke97@gmail.com

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Abstract

Nigeria has an abundance of valuable solid minerals and rocks which can generate revenue for the government if they are fully exploited. Carbonate rock is one of such rocks that occur prominently in Igwe Igarra area of Edo State. Five (5) carbonate rock samples (Four marble and One Calcsilicate) were subjected to geochemical analyses. A petrographic study reveals that marble and calcsilicate contain calcite, quartz, microcline, plagioclase, biotite and opaque minerals. Geochemical data shows that carbonate rocks have variable geochemical characteristics: Igwe marble is highly Calcitic (96% - 98%) and very low in dolomite $Mg(CO_3)$. Calcsilicate rock is low in CaO (27.5%) and higher in marble. The Igwe marble is pure and contains fewer impurities compared to calcsilicate rock which makes it unideal for usage. Based on these characteristics the marble from Igwe is suitable as raw materials for the productions of glass, papers, beet sugar, aggregates, lubricants and fillers.

Keywords

Carbonate Rocks, Geochemistry, Igwe Area, Photomicrograph, Southwestern Nigeria

1. Introduction

The abundance of mineral resources in Nigeria cannot be overstated. The extractive industry's mining and solid mineral sector have long been a promising field and are now receiving the recognition it deserves as the main catalyst for economic growth and revenue diversification in the country. Nigeria is endowed with a diverse range of minerals and rocks, encompassing both metallic and non-metallic resources, such as granite, charnokites, bentonite, talc, gemstones, lead, zinc, gold, and carbonates. Among these are carbonate rocks, which primarily consist of carbonate minerals such as marble and calcsilicates. Marble, a nonfoliate metamorphic rock, contains primarily recrystallized carbonate minerals, with calcite or dolomite being the most commonly occurring ones. The color of marble varies depending on the impurities present during its formation. Marble made from limestone with fewer impurities tends to be light in color, while those with impurities such as iron oxides and clay minerals can be darker. The metamorphism of impure limestone that contains chert, quartz sand, and argillaceous materials with silicate minerals results in the formation of calcsilicate rocks. In Nigeria, marble and calcsilicate rocks occur in large deposits in areas like Jakura and Ekirin Adde in Kogi state, Igbeti and Alaguntan in Oyo state; Elubu in Kwara State and Igarra in Edo State are just a few of the quantified and already being exploited locations where carbonates rocks are found (Fatoye and Gideon, 2013) [1]. Igwe is an area around Igarra in Edo state that boasts a vast deposit of carbonate rocks, including marble. Marble, being a type of carbonate rock has extensive industrial applications. It can be crushed into powder and utilized as fillers in paints, cosmetics, and papers. Moreover, it is also used for soil treatment, as a supplement in poultry feeds, and has several applications in the pharmaceutical industry. Despite the considerable attention paid to the geology of Igarra and its environs, including Igwe, there is a paucity of data concerning the geochemistry of the calcsilicates and marble deposits in this region. This study's goal is to determine the geochemistry of carbonate rock deposits that are exposed in and around the village of Igwe in order to determine their potential for industrial use.

2. Study Area

The study area is located within the Igarra schist belt. It lies within the longitude N7˚27'55" and latitude E6˚27'48" NW of Edo state Nigeria. The major highway in the area runs from Igarra-Auchi. The research area, Igwe, is located off Igarra-Auchi, 9 kilometers from Sogbe Ogbe. The area around Igwe has a decent road network connecting it to neighboring towns, including Ikao, Etsako, and Ukpilla, which are known for their marble deposits. The research area has a tropical environment with two distinct seasons: the rainy season and the dry season. The typical temperature ranges from 28˚C to 30˚C. The location has high humidity and receives enough precipitation. Samples were taken during the rainy season.

2.1. Overview of the Southwestern Basement Complex

Nigeria lies approximately between latitudes 4˚N and 14˚N and longitudes 3˚E and 14˚E within the Pan African mobile belts that lie between the West African and Congo Cratons. The geology is made up of almost equal proportion of basement and sedimentary rock units (Woakes *et al.* 1987) [2]. The basement complex of Nigeria is commonly described under three lithologic groups: Migmatite gneiss complex, the schist belt and the older granites suites.

2.2. Metamorphism in Carbonate Rocks

Carbonates rocks are predominantly composed of carbonate minerals, usually limestone and dolostone. They may be pure carbonate, or they may contain variable amounts of other precipitates such as hematite or chert or detrital materials like sands and clay Metamorphosed carbonates are called metacarbonates, they are metamorphosed calcareous (limestone and dolostone) rocks in which the carbonate component is predominant with granoblastic polygonal texture. Chemically the carbonates rocks are rich in CaO, CO_2, MgO and other subordinate oxides if the carbonates are impure. Metacarbonates include:

1) Marbles which are nearly pure carbonate (carbonate > 50%);

2) Calcsilicates rocks: Carbonate is subordinate (carbonate < 50%) and may be composed of Ca-Mg-Fe-Al silicate minerals, such as talc, diopside, epidote and plagioclase. We also have Skarn which are calcsilicate rocks formed by metasomatism between carbonates and silicate-rich rocks or fluids.

Metacarbonates can be divided into:

1) Pure Metacarbonates: metamorphism of pure carbonates yield calcite and/or dolomite marbles. Many marbles are composed only of calcite and/or dolomite with minor quartz and phyllosilicates, originally of detrital origin.

2) Calcitic Marble: it is produced when the calcite in limestone recrystallizes to form a rock that is a mass of interlocking calcite crystals. It has a chemical composition of $CaCO_3$.

3) Dolomitic Marble: it is produced when dolostone is subjected to heat and pressure. It is a calcium magnesium carbonate with a chemical composition of $CaMg(CO_3)_2$.

4) Impure Carbonates: calcsilicates are rocks rich in Ca-Mg silicate minerals but poor in carbonates, they form via the metamorphism of very impure calcite or dolomite limestone and they also from limy mudstones (marls).

2.3. Calcsilicate Rocks and Marble

The metamorphism of carbonates leads to the formation of calcsilicate rocks, which are typically of low to medium grade metamorphism and consistent with the metamorphic grade of the Igarra basement complex. Calcsilicate rocks are rich in Ca-Mg silicate minerals, with a small amount of carbonates present. When impure limestones containing silicate minerals undergo metamorphism, they are transformed into calcsilicate rocks. On the other hand, marble is formed from limestone subjected to the heat and pressure of metamorphism. It primarily consists of the mineral calcite ($CaCO_3$) and may contain other minerals such as clay minerals, micas, quartz, pyrite, iron oxides, and graphite.

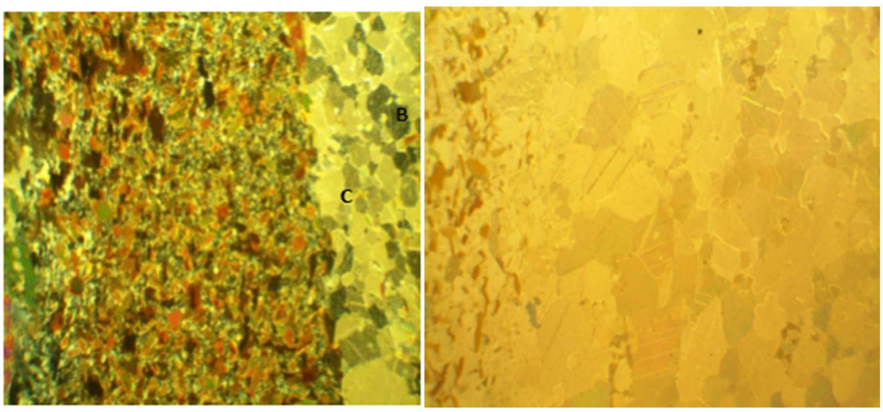
3. Materials and Methodology

During a department of Geology training exercise, rock formations were identified using topographic and geologic maps, and ten fresh samples were collected from different locations in the Igwe-Igarra area for examination. The samples included metacarbonates units such as marble and calcsilicate rocks, which varied in texture and color and occurred as low-lying outcrops. Detailed descriptions and photographs were taken to document the findings of the geological field mapping exercise. Most of the samples are foliated and can almost split along foliation plane, medium to large and equidimensional grain size, some samples have visible faint greenish coloration, and some samples are banded of felsic and mafic minerals. Some samples are highly reflective and purely felsic in nature. The identifiable minerals using hand lens are calcite, quartz and mica. For the petrographic studies, ten rock samples were subjected under plane and crossed polarized light for identification of mineral in the rock samples that were not hitherto seen with unaided eyes in the rock samples. The geochemical analysis of the sample was carried out at Activation Laboratory in Canada. The laboratory uses a package called CODE 4B where lithium metaborate/tetraborate fusion ICP method for whole rock analysis. The fusion ICP has a detection limit of 0.01% for most oxides except MnO and TiO_2 (0.001). The instrument is programmed for recalibration regularly to prevent error and enhance accuracy. The samples are fused and diluted and analyzed by Perkin-Elmer-Scienx ELAN6100.

4. Discussions of Results

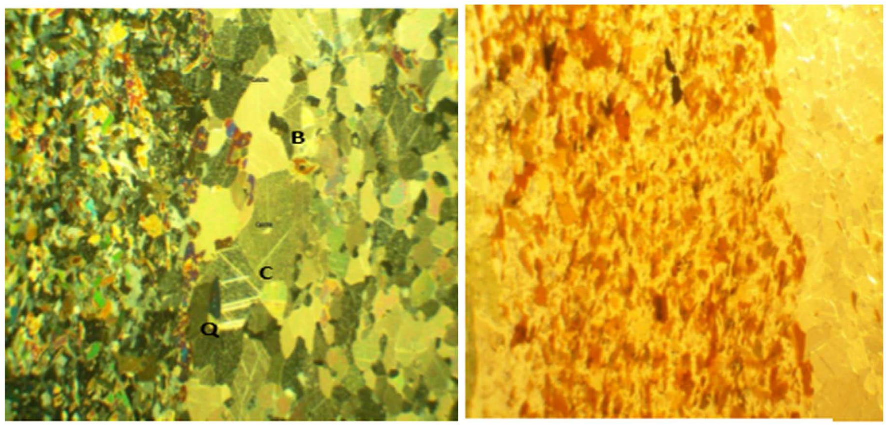
The thin section of marble and calcsilicate rock revealed the presence of minerals, with calcite, quartz, biotite, microcline, plagioclase, muscovite and opaque minerals being the most abundant. The mineral alignments in the rocks were poorly developed, and calcite and quartz were identified as large crystals, while biotite and calcite occurred in disoriented masses. Minor components include muscovite, microcline, plagioclase, while others are the opaque minerals. Quartz, biotite and calcite constitute about 90% of the rock in the thin section. The minerals identified under plane and crossed polarized light include calcite (C) which appeared, biotite (B), microcline (M), and plagioclase (P) as shown in the five different plates below (Plates 1-5).

Calcite appeared as bright, clear grains, while biotite showed pleochroism, appearing brown under crossed polarized light. Microcline and plagioclase



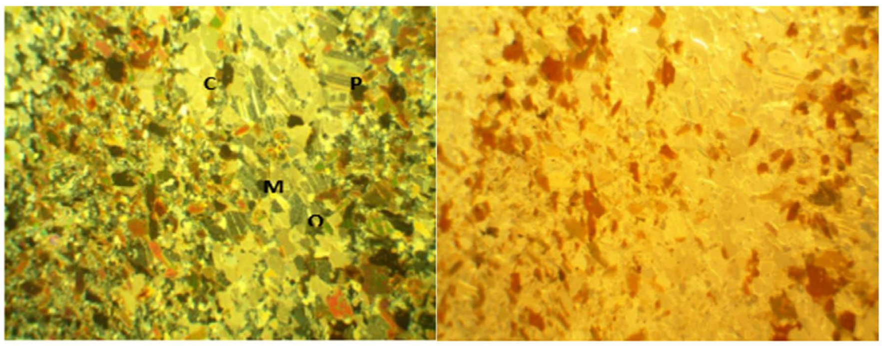
(a) (b)

Plate 1. (a) Photomicrograph of sample M2 under Crossed polarized light; (b) Photomicrograph of sample M2 under Plane polarized light.



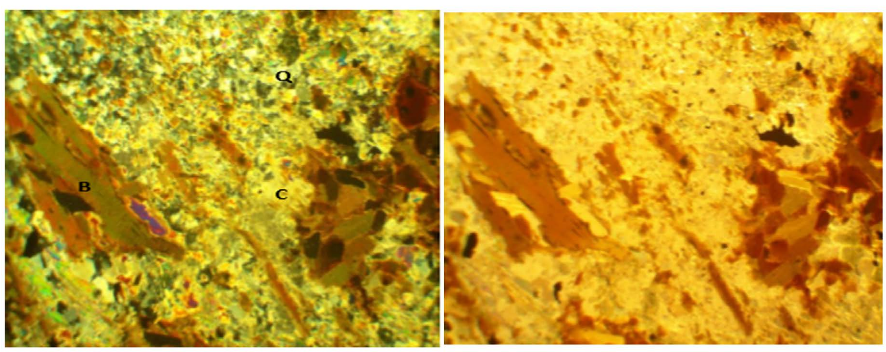
(a) (b)

Plate 2. (a) Photomicrograph of sample M3 under Crossed polarized light; (b) Photomicrograph of sample M3 under Plane polarized light.



(a) (b)

Plate 3. (a) Photomicrograph of sample M4 under Crossed polarized light; (b) Photomicrograph of sample M4 under Plane polarized light.



(a) (b)

Plate 4. Photomicrograph of sample M5 under Crossed polarized light; (b) Photomicrograph of sample M5 under plane polarized light.

showed similar properties under polarized light, with both minerals showing twinning and appearing in shades of gray. The mineralogical characteristics of the marble rock samples are high in calcite with range of 57.2% - 99.9% but lower in calcsilicate with 47.2%. Sample M10 is extremely high in calcite with 99.9% (Table 1).

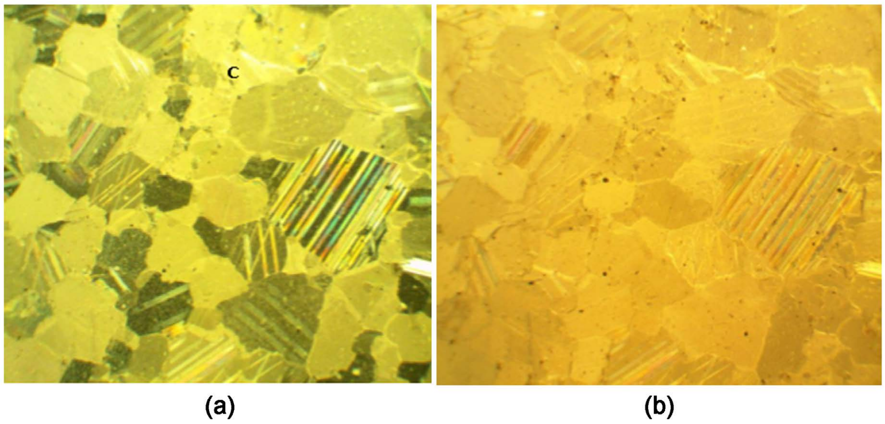


Plate 5. (a) Photomicrograph of sample M10 under Crossed polarized light; (b) Photomicrograph of sample M10 under Plane polarized light.

Table 1. Showing the modal analysis of minerals in the rock samples.

SAMPLE ID	ROCK TYPE	MINERALS (%)							
		Q	C	PLAG	MIC	B	M	OPQ	TOTAL
M2	MARBLE	14.1	64.4	0.3	7.2	14.1	0	0	100
M3	MARBLE	6.9	72.8	0	10.3	9.1	0	0.9	100
M4	MARBLE	15.6	57.2	6.6	6.3	14.4	0	0	100
M8	CALC	15.0	47.2	7.5	6.6	22.8	0.3	0.6	100
M10	MARBLE	0	99.9	0	0	0.9	0	0	100

5. Geochemistry

The geochemical characteristics of the Igwe carbonates were further investigated by obtaining the average percentile for major oxides such as a S102, Al_2O_3, Fe_2O_3 (T), CaO, MgO, MnO using the fusion ICP method of atomic absorption spectroscopy technique. The results presented in Table 2 show varieties of varying geochemical characteristics of Igwe carbonates. The SiO_2 (silica) values are generally low ranging from 1.22% - 6.55% but higher in calcsilicate with a percentage of 31.33. The cost-effectiveness of using marble for the manufacture of cement is positively impacted by its high silica concentration.

TiO_2, MnO, and P_2O_5 values are all less than 0.6%. Similarly, Na_2O, and K_2O are less than 0.2% in marble and less than 2.9% in the calcsilicate sample. The Al_2O_3 values ranged between 0.26% and 1.02%, with an average value of 1.87%. CaO had the highest concentration, ranging from 50.21% to 54.28%, with a relative mean of 51.96% for M5, M7, M9, and M10. However, the CaO value was lower in M8, with a value of 27.23%. The MgO value ranged from 0.6% to 0.97%, with an average value of 0.77%. The concentration of MgO was higher in M8, with a value of 6.23%. The Fe_2O_3 value ranged from 0.12% to 0.49% in M5, M7, M9, and M10, while the concentration was higher in M8, with a value of 4.33%.

Table 2. Geochemical analytical results of the major oxides of selected Igwe carbonate.

SAMPLE	M5	M7	M9	M10	AVERAGE (M5, M7, M9, M10)	M8	RANGE (M5, M7, M9, M10)
SiO_2	3.79	1.22	6.55	5.57	9.692	31.33	1.22 - 6.55
Al_2O_3	0.85	0.26	0.90	1.873	1.873	6.57	0.26 - 1.02
Fe_2O_3	0.39	0.12	0.35	0.49	1.136	4.33	0.12 - 0.49
MnO	0.029	0.016	0.022	0.021	0.0308	0.066	0.016 - 0.029
MgO	0.65	0.61	0.97	0.86	1.864	6.23	0.61 - 0.97
CaO	53.1	54.28	50.21	50.25	51.96	27.23	50.21 - 54.28
Na_2O	0.17	0.09	0.28	0.17	0.396	1.27	0.09 - 0.28
K_2O	0.12	0.05	0.1	0.23	0.692	2.96	0.05 - 0.23
TiO_2	0.04	0.008	0.029	0.055	0.0922	0.329	0.04 - 0.08
P_2O_5	0.07	0.05	0.06	0.02	0.164	0.62	0.02 - 0.07
LOI	43.32	43.08	40.29	40.4	41.77	19.46	40.29 - 43.32
TOTAL%	100.5	99.78	99.76	99.1	99.90	100.4	52.67 - 64.04

6. Economic Potential and Applications

Carbonates rocks especially marble have high economic values depending on the specific usage. The supply of marble to industries depends on the its physical, chemical properties as well as purity thus the economic values of marble would be discussed for which the specifications for the marble to be useful would be stated below:

CEMENT PRODUCTION: The major standard for cement production in carbonate rocks are; SiO_2 not more than 22.0%, Al_2O_3 not more than 6%, Fe_2O_3 not less than 3.0% MgO not more than 3%, CaO not more than 63.0%, LOI not more than 1.5% total alkalis not more than 0.5%, $CaCO_3$ should be more than 82% (Ragput 2018). The Igwe marble does not meet these specifications therefore cannot be used in cement production except if subjected to beneficiation processes. The calcsilicate unit cannot be applied because it contains higher percentage of MgO and alkalis.

PAINTS MANUFACTURING: Paint manufacturing is required to meet specific physical and chemical standards for marble. Marble is to either be white marble or pink marble with small particle sizes. Chemically Al_2O_3 should be >2% and MgO + SiO_2 = 75%. The Igwe marble meets the physical requirement for the production of paints but does not meet the chemical requirement and thus is unsuitable for the production of paints.

PAPER PRODUCTION AND FILLERS: White Calcitic marble dust which is serves as good fillers, extenders and coating pigment. They stabilize the paint and act as a weather resistant. As paper filler, it imparts high brightness to the sheets and provides surface smoothness.

CONSTRUCTION: For concrete aggregate, road base, ballast, general requirements are concrete aggregate should be low in alkalis and free from surface organic matter, other aggregate suitability chiefly depends on mechanical and physical properties. Igwe marble chemically meets this requirement and thus can be used as road stabilizers and building blocks.

LUBRICANTS: For the manufacture of lubricants/greases Calcium oxide not less than 72.6%, magnesium oxide not more than 1%, maximum silica plus alumina 1.5% are required. The Igwe marble does not entirely meets the standard specified even though it is very low in Magnesium. However, paint manufacturers have their individual specifications as long as their products satisfy quality and in conformity with regulations.

BEET-SUGAR: For the production of beet sugar the SiO_2 content must be less than 2%, magnesia less than 4%, and ferric oxide must not exceed 0.5%. The high calcium lime when finely powdered can be employed in refining beet and sugar cane by carbonization. The pure marble from Igwe would not impact a sour taste to the sugar thus its usefulness.

Igwe marble meets this requirement and can be used in beet sugar manufacturing.

GLASS MANUFACTURING In glass manufacturing ferric oxide (Fe_2O_3) should not be more than 0.05% and 0.2% for colorless glass, rocks having up to 0.1% ferric oxide can be accepted sometimes for colored glass. $CaCO_3$ should be more than 96%, Igwe marble does not meet these specifications because it is higher in Fe_2O_3 and cannot be used in glass manufacturing unless specifically stated for use by companies.

7. Conclusion

This study's objective is to do an economic evaluation of the carbonate rocks deposit in the Igwe area by classifying the rocks on the basis of their chemical and mineralogical composition and comparing them to standards. The result of the geochemical analysis of the carbonate samples from Igwe area suggests that the rocks can be used for a variety of products such as glass, paper, beet sugar, lubricants and fillers. They can also be used as construction aggregates. The rocks can be used for the production of cement if subjected to a beneficiation process [3]-[21].

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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