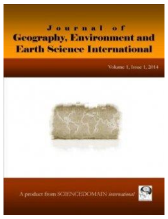

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Petrographic and Geochemical Characteristics of Metacarbonate in Northcentral Nigeria; Potential Applications in Industries

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Authors' contributions

This work was carried out in collaboration between all authors. Author JAO designed the study, wrote the protocol, and wrote the first draft of the manuscript. Authors KSA, HBH and NBB managed the analyses of the study performed and also improved the results. All authors read and approved the final manuscript.

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ABSTRACT

The mineralogical characteristics of metacarbonate from the Obajana area were determined with combine petrographic and X-ray diffraction methods. These methods revealed that the marble samples contains major proportion of calcite with minor quartz, dolomite, graphite, pyrite, olivine and phlogopite as accessory minerals. Also, analytical data from inductive coupled mass plasma spectrometry (ICPMS) showed an average SiO_2 of 2.39%, high CaO content of 54.89%, with low MgO content of 1.1% and iron oxide content of 0.33%. Trace element composition, indicated that the metacarbonate is rich in Ni, Rb, Sr and Ba compared to Co, Ga and Nb in the metacarbonate. These characteristics make the metacarbonate suitable for major industrial use especially the production of high grade precipitated calcium carbonate (PCC).

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Keywords: Metacarbonate; basement complex; marble; accessory mineral; precipitated calcium carbonate.

1. INTRODUCTION

Marbles find widespread application as raw materials in many industries depending mostly on their purity or chemical content. Therefore, prior and concise chemical characterizations are necessary before any industrial application. Nigeria is a developing nation with abundant mineral resources, especially metacarbonates which constitutes over 20% of the basement complex of the country, these metacarbonates occur in an estimated proportion of 60% dolomitic marble and 40% calcitic marble. These metacarbonate deposits usually occur within the schist belts, [1,2]. The Precambrian rocks of Nigeria occur within the Pan- African orogenic belt, [3] from the Archean to early Proterozoic. They are broadly grouped into three main subdivisions, which are, the ancient migmatite – gneiss complex, the schist belts and the Pan-African granitic series. The Nigerian schist belts are more prominent in the western half of the country and they show distinctive structural, metallogenic and petrological features [4]. The Nigerian schist belts include the Igarra, Lokoja – Jakura and Egbe-Isanlu belts in the north central Nigeria and Zungeru-Birni Gwari, Kushaka, Wonaka, Zuru in the northwest [5].

Metacarbonate rocks in the study area are utilized for the production of cement, fertilizer and tiles by local industries. Hence, the purpose of the study is to investigate the petrographic and geochemical characteristics of metacarbonate found in the north central Nigeria towards its applications in the production of PCC.

The combination of X-ray Diffraction (XRD), inductively coupled plasma mass spectrometry analysis (ICPMS), the petrographic and physical techniques were used to reveal qualitatively, the contents of the metacarbonate rock for the production of high quality precipitated calcium carbonate (PCC).

2. METHODOLOGY

Representative samples of the metacarbonate rock were collected along the trend of the marble band extending from the Southern area (Fig. 1) of the deposit towards the Northern part (N 07° 54' to N 08° 00' and longitude E 006° 25' to E 006° 30'). Optical microscopy and X-Ray Diffractrometery (XRD) obtained with Philip 1140 equipment using Cu k alpha radiation operated at 40 KV, 30 MA and 1021 per minute were used to determine the mineralogical compositions of marble samples from different locations in the study area. Also, the inductively coupled plasma mass spectrometry (ICPMS) instrument was used to conduct geochemical studies of the pulverised rock samples. The Geotechnical tests were carried out on the marbles to establish their suitability for end-product use in the PCC production. The industrial suitability of marble depends largely on physical and chemical properties. Also, physical characterization was carried out on the marble samples such as porosity, hardness, bulk density, specific gravity, pH, water absorption capacity and colour. This is in addition to tensile, compressive and shear strength of the samples. All the analytical studies were carried out according to the manufacturer's procedures in conformity to standard procedures. Also the analysis on each sample were done in multiplicity to enhance accurate presentation of the composition data, thereafter, average value were obtained to represent the composition of each component for the study site.

3. DISCUSSION

3.1 The Field Relations and Mode of Occurrences Characteristics of the Mable

The Obajana marble deposit lies 13km west of Obajana town and is located between latitude N 07^0 54' to N 08^0 00' and longitude E 006^0 25' to E 006^0 30'. Notable occurrences of metacarbonate rock in lensoid form can be found around the northern to southern area of Obajana. These metacarbonate rocks are interbanded with meta-igneous rocks such as phyllite and quartz mica schist (Fig. 1). The major rock types in Obajana area are gneisses, schists, banded iron formation, quartzite and marble. Rocks in this area generally have a North-South trend and dip in a western direction.

The marble bodies are exposed along river channels. However, the contacts with the schist rocks are not exposed. They are two textural varieties of the metacarbonate rock which are fine-grained variety which sometimes has a mixed band of white and grey colour. The second is the medium to coarse-grained variety which is mostly bright white to pale white in colour. In addition to the carbonate minerals abundant in the marble samples, graphite, quartz, phlogopite, iron oxides, olivine and pyrite were also present as accessory mineral constituents. However, the distribution of these accessory minerals are not homogeneous; for instance; pyrite is enriched in the marble samples located around the northern part of the deposit while the green olivine is enriched in samples from southern areas. The marble samples further display calcite with twin lamellae and rhombohedral cleavages.

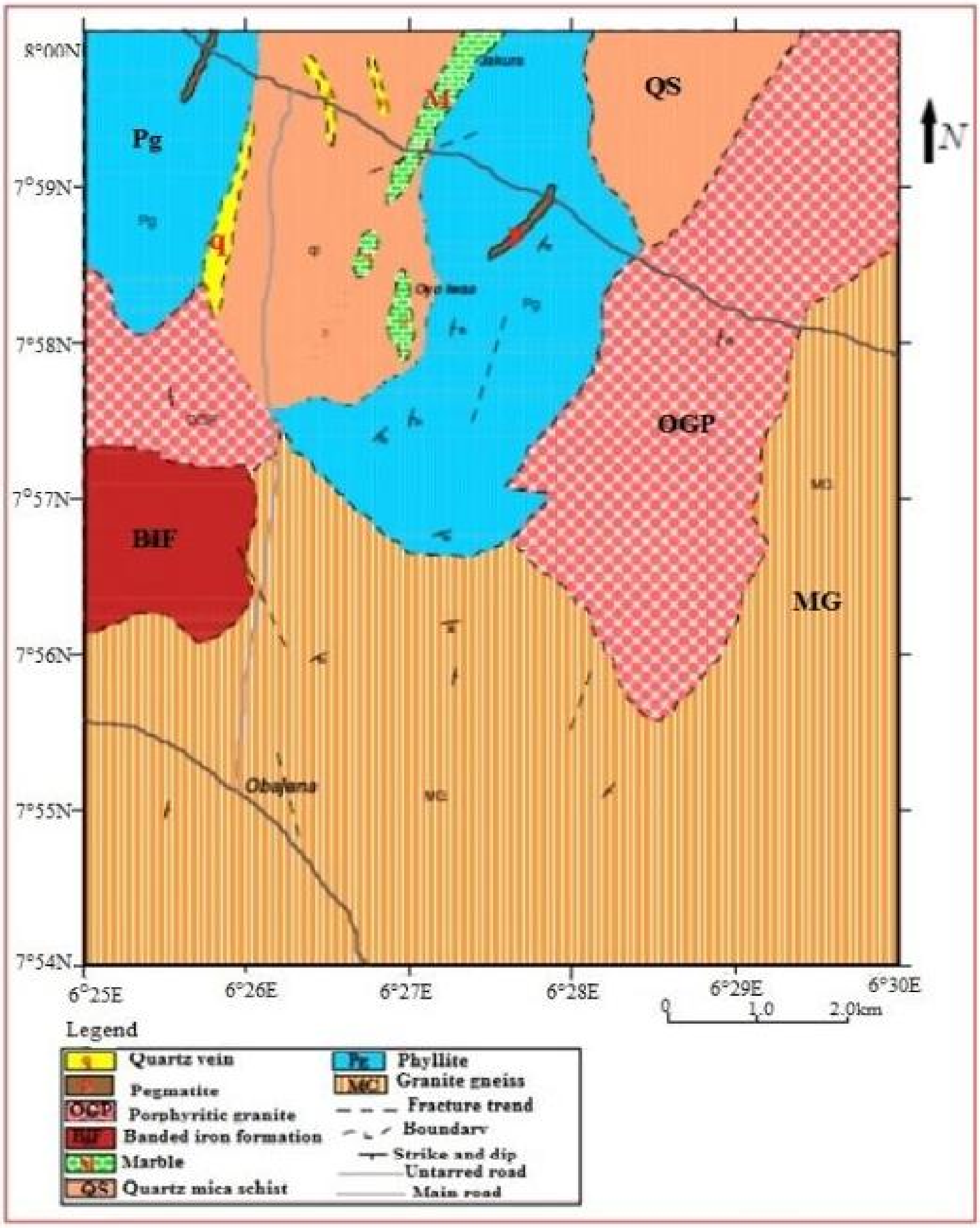


Fig. 1. Geological map of the study area (modified after [2])

3.2 Petrographic Characterization

The marbles found in the study area are two varieties texture wise, they are fine-grained and medium to coarse grained. Calcite minerals in the sample occur as equi-granular crystals, most of them showing perfect rhombohedra cleavage and twinning. The carbonate phase of these marbles is more commonly whitish to greyish white in colour. Graphite, phlogopite, quartz, olivine, pyrite, and some iron oxides were found as accessory minerals in the carbonate minerals. However, these accessory mineral modal abundance were very low. Petrographic analysis of the Obajana marble sample in Fig. 2 revealed that the primary assemblages of the marble are calcite (calcitic) + quartz + phlogopite ± olivine reflecting low to medium grade metamorphism.

Fig. 3 shows the result from XRD analysis carried out on the metacarbonates rock, from the XRD peak, it is clearly seen that calcite ($CaCO_3$) is the most abundant mineral having about (97%) of the total composition, while dolomite ($CaMgCO_3$) is relatively low and constitute about (3%). The Obajana-marble mineralogical composition points to it as low in silica, dolomite and high in calcite when compared to other marble bodies found within Nigeria.

Determination of the major and trace for geochemical analysis were carried out for some selected representative marble samples by inductively coupled plasma mass spectrometry (ICP-MS). The chemical composition of these carbonate minerals are given in Table 1. the result reveals an average low SiO_2 content of 2.39%, with very high CaO ranging from 46.90% to 56.54%, However the iron oxide present was very low in concentration (0.06% to 0.88%) with the MgO content ranging from 0.18% to 2.89%. These figures are comparable to Bee low and Melham limestone U.K [6], Barra Honda limestone Costa Rica [7], Ososo marble [8]. [9] suggested that marble with less than 6 percent $MgCO_3$ content is a low magnesium marble and is therefore referred to as calcitic. [10] stated that marble with less than 0.50% of $MgCO_3$ is calcitic; those with greater than 40% of $MgCO_3$ are dolomitic and those that falls between 5% and 40% of $MgCO_3$ are referred to as magnesian marbles. Based on this, the Obajana marble is calcitic, and therefore can be applied in various industrial applications.

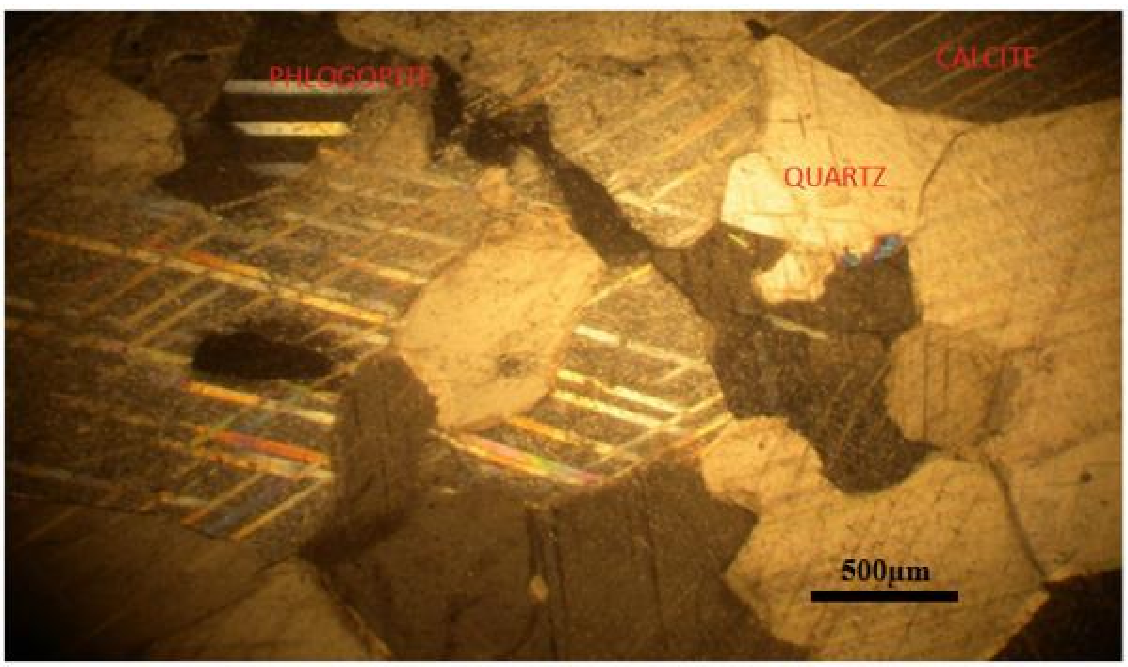


Fig. 2. Photomicrograph of the marble in transmitted light showing: Quartz, calcite, and phlogopite

Petrographic study of the metacarbonate rock reveals the metasomatism of the parent mineral assemblage. Alteration assemblage were possibly composed of Tremolite ± Phlogopite ± Calcite ± Quartz

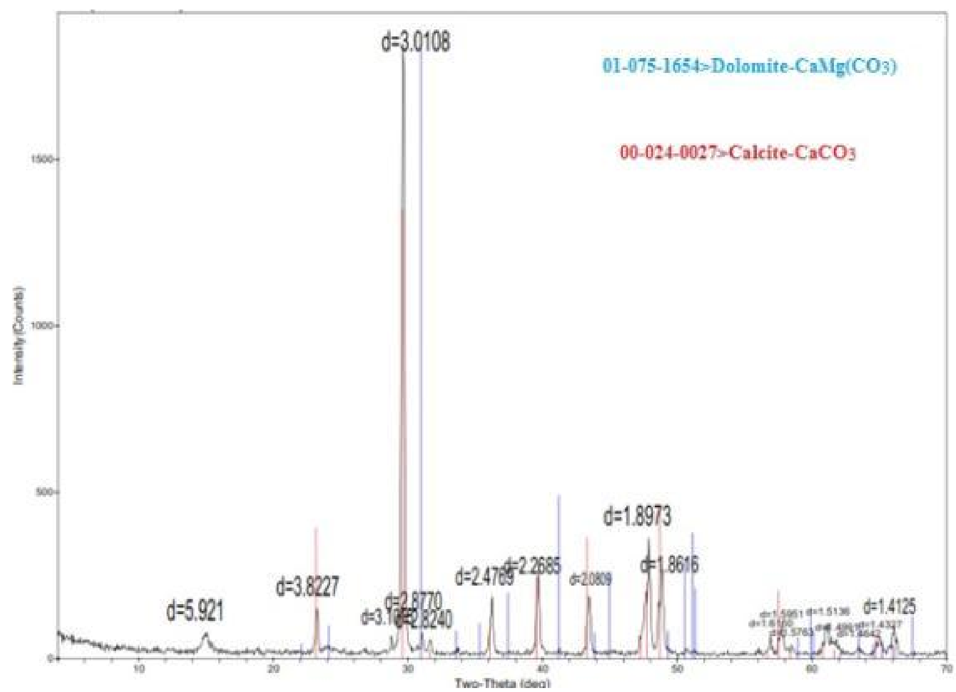
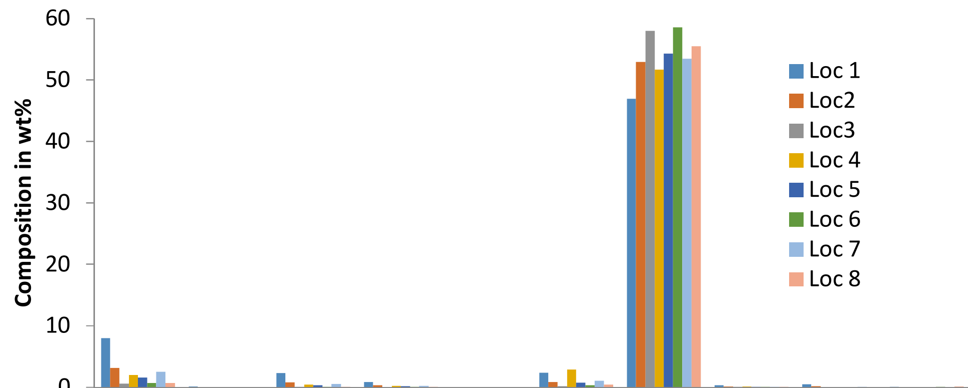


Fig. 3. X-ray diffractogram for Obajana marble sample showing calcite (abundant) and dolomite (minor)

Table 1. Analytical result of Obajana metacarbonate rock



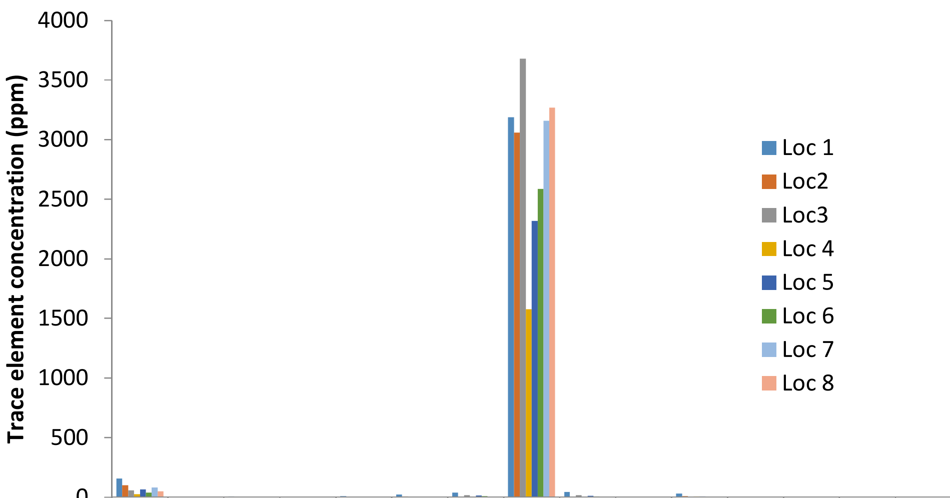
	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5
Loc 1	7.99	0.12	2.31	0.88	0.02	2.37	46.9	0.33	0.47	0.09
Loc2	3.12	0.04	0.81	0.35	0	0.85	52.9	0.15	0.21	0.06
Loc3	0.58	0	0.08	0.06	0	0.18	57.97	0.07	0.02	0.03
Loc 4	1.99	0.03	0.43	0.24	0	2.89	51.66	0.12	0.04	0.05
Loc 5	1.56	0.02	0.34	0.19	0	0.73	54.28	0.1	0.06	0.05
Loc 6	0.67	0	0.1	0.09	0	0.31	58.54	0.07	0.01	0.08
Loc 7	2.54	0.03	0.52	0.25	0	1.06	53.43	0.11	0.09	0.05
Loc 8	0.67	0	0.11	0.08	0.03	0.41	55.51	0.07	0.02	0.12

Components

High content of silica of about 7.99% in loc1 of the sample may indicate a fluid inclusions which could be evidences for syn to post metamorphic hydrothermal interactions with the metacarbonate and the host rocks. Most of the samples in Table 1 shows low values of L.O.I, this indicate the calcitic nature of the deposit, in addition to having a very low amount of Al_2O_3, MnO, K_2O, TiO_2 and Na_2O.

Trace elements content shown in Table 2 reveals that the marble has high Strontium values that ranges from 1577 ppm – 3673 ppm with the lowest values detected in some impure samples close to the contact with the host rock. Average value for the Strontium is 2853.5 ppm. Of all the trace element Strontium is the highest which confirms its association with high calcium content. The presence of high strontium makes it very suitable in pcc production. The elemental Cu concentration in the samples ranges from 1.0 ppm – 6.3 ppm with an average value of 2.58 ppm, higher values were encountered in samples where marbles formed intercalation with quartz mica schist. These values of Cu are acceptable for the production of pcc using British standard as show in Table 3. Lead concentrations in the sample ranges from 0.3 – 1.8 ppm with an average value of 1.3 ppm. However, zinc concentration range from 1.0 ppm – 10 ppm with an average of 2.63 ppm. Lead and zinc occur generally in close association. Most lead and zinc occurrence are confined to marble, limestone, dolomite and other calc-magnesium rich rocks. In Obajana, they occurred as associated element in the marble deposit [11]. These values are within range for the production of high grade precipitated calcium carbonate.

Table 2. Geochemical analytical results of the trace elements found in Obajana marble samples



	Ba	Co	Cu	Pb	Zn	Rb	Sn	Sr	Ta	Th	Zr	Ag	Au	Hg	Ti
Loc 1	157	1.5	6.3	4	10	21.6	37	3186	44.2	2.5	28.6	0.1	0.5	0.01	0.1
Loc2	100	0.6	1.3	1.5	3	7.8	0	3058	0.3	0.7	8.7	0.1	0.5	0.01	0.1
Loc3	57	0	1.7	0.5	0	0.8	16	3678	16.2	0.3	2.2	0.1	0.5	0.01	0.1
Loc 4	24	0.5	3.2	1.3	1	2	5	1577	5.4	0.4	7.7	0.1	0.9	0.01	0.1
Loc 5	64	0	2.3	0.7	2	2.9	15	2318	11.5	0.5	5.9	0.1	0.5	0.01	0.1
Loc 6	36	0.4	1.8	0.3	0	0.2	9	2586	7.7	0.2	1.9	0.1	0.5	0.01	0.4
Loc 7	83	0.4	2.8	1.8	2	4.1	5	3156	4.2	0.5	5.4	0.1	0.8	0.01	0.1
Loc 8	50	0	1	0.9	1	1.1	0	3269	0.3	0.3	3.4	0.2	1.6	0.02	0.1

Trace Elements

Table 3. Typical chemical specifications of a PCC product [12]

Chemical properties	
Color	Bright White
Hunter Whiteness	97 % Min.
CaCO3 % by Weight	98.5 Min.
Lead as Pb	Traces
Copper as Cu	Negligible
Arsenic as As	NIL
Sulphate as SO4	0.2 % Max.
Soluble alkali as Na2O	0.15 % Max.
Silica as SiO2	0.07 % Max.
Iron as Fe	0.01 % Max.
pH	9.0 to 10.5
Phosphate as PO4	0.05 % Max.
Chloride as Cl	Traces
Magnesium as MgO	0.7 % Max.
Flouride as F	Traces
Manganese (Mn)	0.05 Max.

3.3 Physical Characteristics

Physical property determinations in Table 4 showed that there is no marked difference in apparent porosity values for the raw marble samples (0.66%), due to these low porosity values the marble deposit aside the production of pcc can also be use by the constructions industries. The bulk density value (2.54 g/cm^3) and specific gravity value (2.72) for the samples are within the ranges for Precambrian marble generally [13]. These values are comparable to Indiana marble [13] and Cheetor marble [14]. However, these values are slightly higher compared to those for Sharpfell marble [15], Muro marble [16] and British whitening [16]. Compressive strength (93.77 Mpa), and Shear strength (13.81 Mpa) are within the range of values for marbles [13] and meets specification for use as road bases, construction stone and ornamental stones. PH value of 8.3 for the studied marble is comparable to Igbetti marble [17] and Cheetor marble [14]. This simply means that the powdered marble sample can be used to reduce soil acidity level, thereby optimizing maximum plants growth in agriculture. Most tropical soil is acidic due to high precipitation, acid rain and depletion of basic nutrients by crops and application of nitrogen fertilizers [2]. Studies by [14] revealed that aluminum ion is the prominent cation in the majority of soils with pH 5 or less. Above all, these figures are comparable to international standards for PCC production.

Furthermore, a plot of the ternary diagram in Fig. 4 for the studied marble samples using geochemical results from ICPMS confirm that it is calcitic rather than dolomitic.

Table 4. Physical (mechanical) properties of Obajana marble

Properties / description	Values
Ph	8.3
Porosity	0.61%
Bulk density	2.55 g/cm^3
Specific gravity	2.715
Shear strength	1583.33 kpa
Compressive strength	3166.66 kpa
Hardness	3.0
Water absorption	0.69%
Brightness	94%
Specific surface area	5.7 m^2/g

3.4 Potential for Precipitated Calcium Production

Table 3 shows the product specifications for high quality PCC product, however the desired properties of PCC generally varies according to its field of application. In paper industries, high quality PCCs enhances the smoothness, brightness, and opacity of paper. It also increases receptivity of the ink. In paint, $CaCO_3$ is used as the primary extender compound to reduce consumption of higher cost pigments, like TiO_3. Fine sized and narrowly ranged PCC grains provide gaps among TiO_2 particles and improves their binding power. By this extension, the opacity is improved. The usual product specifications for PCC is purity of more than 99%, density of 2.7 g/cm, particle size for filler pigments of 70% < 2 μm, and the specific surface area of about 10 m^2/g. The particle size has a significant effect on smoothness, gloss and printing characteristics of the paper [18]. Characteristics of printing are also in relation to the particle size range and particle shape of PCC, which also directly affects the consumption of chemical additives in papermaking. The brightness of the PCC filler pigments should be higher than 93%, and the pH of 1 mol of PCC in 1 L solution should be 9. Average particle size of PCCs as coating pigment should be in 0.4 to 2 μm size range, refraction index of 1.49 – 1.67 and a specific surface area of 4 – 11 m^2/g. Narrower particle size ranges and higher refraction indexes of PCCs improves light scattering of the sheets. The ISO standards for brightness of PCCs as a coating pigment is 95%, which necessitates a $CaCO_3$ source with a high purity in order to be used as a raw material [19] For PCC manufacturing industry, raw material

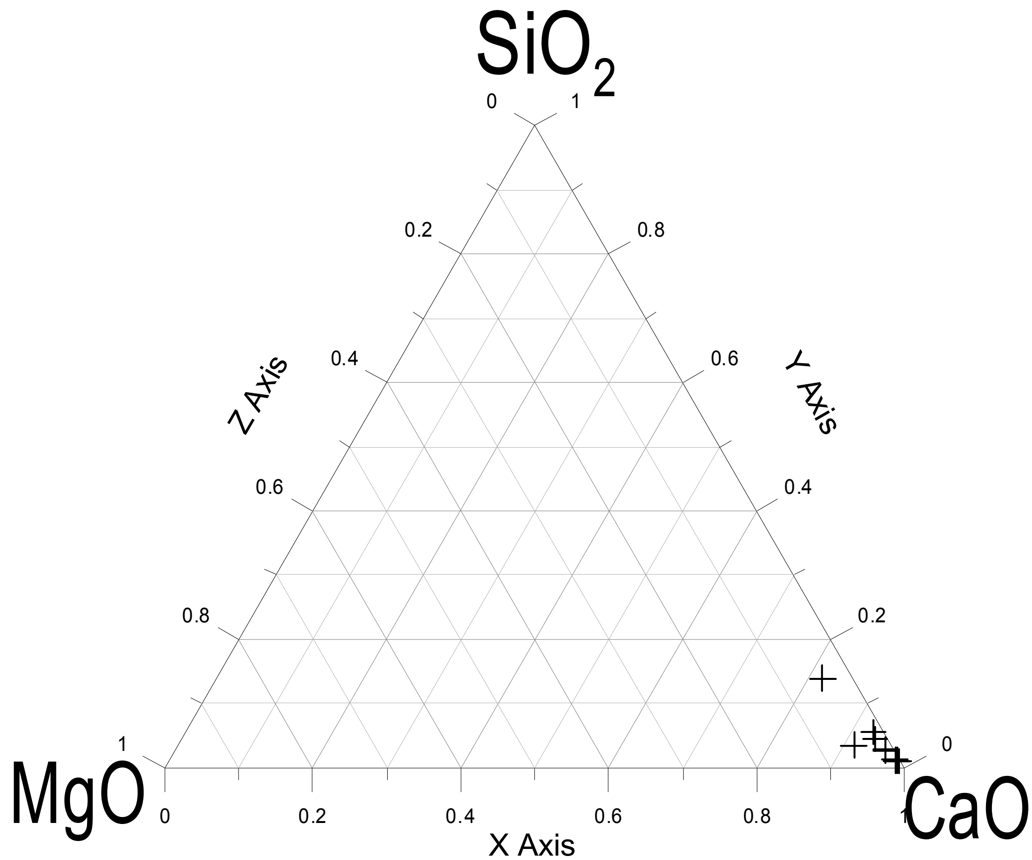


Fig. 4. Showing ternary diagram of Obajana marble deposit

should contain low manganese and iron as mineral impurities because these elements have detrimental effects on the brightness of the product [19].

Study by [4] reveals that marble with less than 0.50% of $MgCO_3$ is calcitic, those with greater than 40% of $MgCO_3$ are dolomitic and those that falls in-between 5% and 40% of $MgCO_3$ are referred to as magnesia marble. Based on this, the Obajana marble is calcitic and therefore can be applied in a variety of precipitated calcium carbonate industries.

Obajana marble deposit has a considerable high content of calcium carbonate that makes it suitable in several industrial applications such as fertilizer, cement production, production of lime for both steel industries and water treatment. Although, the Obajana marble is being utilized for some of the mention applications. However, the production of high grade precipitated calcium carbonate (PCC) is being neglected due to inadequate information. Therefore, the importation of the PCC from Asia and Europe for use in most developing nations like Nigeria prevails. The PCC, an value added product (in high demand) from the marble rock following its characteristic compositions has received wide applications in paper, paint, textile and detergents, among others [20-23]. Industrially, PCC is synthesized from limestones [24] and from high purity calcium carbonate resources. The availability of the active ingredients CaO (46.9 – 58.54 wt%) in high percentage makes the deposit a natural raw material for the production of PCC. Similarly, [25] reported the industrial PCC manufacturing process from naturally available carbonate rocks following three successive steps: (1) calcination process where quicklime (calcium oxide, CaO) is produced by heating limestone ore, (2) conversion of CaO into slaked lime (calcium hydroxide, $Ca(OH)_2$ through the hydration process and (3) synthesis of PCC by bubbling CO or adding aqueous solutions of carbonate salts such as sodium carbonate through $Ca(OH)_2$.

Consequently, the compositions of the marble rock samples stand to justify the economic potential of the marble rock deposit in the study area as suitable source for high quality PCC production.

4. CONCLUSION

The metacarbonate deposits of Obajana occur in beds intercalated by schist, phyllite, and granite gneiss. The mineralogy and the petrography of the metacarbonate samples have been examined. Calcite is found to be the major mineral in the marbles. Quartz appears as the minor mineral in almost all varieties of Obajana marbles. Other minerals present are graphite, olivene, pyrite and very low content of dolomite. In term of texture, the recognized field samples are of two varieties termed fine-grained that sometimes has a mixed bands of white and grey colour. The second is the medium to coarsed-grained veriety which is mostly bright white to pale white in colour. Results from XRD analyses and petrographic investigation suggests that the appearance of quartz depends on the availability of silica in the limestone precursor prior to regional metamorphism. The geochemical analysis of pulverized the marble sample shows that CaO content varies from 46.90 to 58.54%. Other impurities includes: Fe_2O_3, Al_2O_3, MgO and SiO_2. Only the latter two have an average content higher than 1%. All these characteristics makes the deposit highly suitable for most industrial use especially precipitated calcium carbonate production (PCC).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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