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Geochemistry and economic potential of marble from Obajana, north central, Nigeria

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ABSTRACT

Nigeria is endowed with varieties of valuable solid minerals and rocks. These minerals/rocks are capable of boosting the economic potentials of the country if fully exploited. Marble is one of such rocks that occur prominently in Obajana area of Kogi State, North Central, Nigeria. Twenty five (25) marble samples were subjected to geochemical, petrographic and physical analyses. Geochemical data show that the marble has variable geochemical characteristics; low dolomite $CaMg(C0_3)$ (1.1-3.01%) and high calcite $CaCO_3$ (94-98%). Physical tests indicate high compressive strength (93.46-95.77MPa), shear strength (13.84-13.34MPa) and low water absorption (0.30-0.69%) respectively. Petrographical studies reveal that the marble contains calcite, dolomite, quartz, actinolite, phlogopite and graphite. Based on these characteristics, the marble from Obajana is suitable as raw materials for manufacture of lime, steel flux, drugs, toothpaste, lubricant, pesticide production, paper and paint. It is also important in the production of livestock feed, electrical insulators, flooring tiles and terrazzo chips. The marble is very suitable for cement production.

Keywords: marble, petrographical, geochemistry, variable characteristics, suitable raw materials.

INTRODUCTION

Marbles are generally metamorphic derivatives of sedimentary carbonates. They have been known to be relatively impermeable during metamorphism (Nabelek, 1991). A review of the economic utilization of carbonates therefore to some extent takes into consideration aspects of the mineralogy, physical and chemical properties of the marble deposits. The marble occur as low-lying outcrops, scattered as lenses within quartz mica schist about 4km to Obajana town. The marble in Obajana area occurs in large deposit, yet very little data are available on its chemistry. This study therefore presents data on the marble chemistry with the purpose of appraising its economic potentials and industrial applications.

MATERIALS AND METHODS

Field study
A reconnaissance survey and systematic field mapping of the marble deposits and other associated rock types was undertaken between November 2010 and February 2011 when there was dry weather and outcrops were well exposed. The marble in Obajana 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.

Petrology of Obajana area

Basement rock exposures in the Lokoja-Jakura schist belt are dominated by metasedimentary rocks, chiefly, quartz-mica schist with small occurrences of quartzite, marble and silicate facies iron-formation. These metasedimentary rocks are interbanded with meta-igneous rocks such as granite gneiss. Chemical data on major and trace elements of the sheared and unsheared varieties of quartz – mica schist from the Obajana area, reveal a composition comparable to that of semipelitic metasediment (Olobaniyi, 2003). 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.

Sample collection

Forty five (25) representative marble samples of about 550g each were collected from the studied area (Figure-1) by means of sledge hammer. Global positioning system (GPS) instrument was used to locate and determine the elevations and co-ordinates of sampled points.

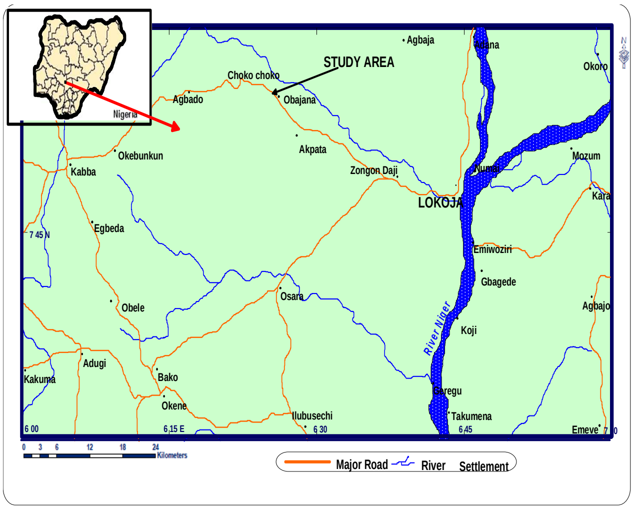

Fig.1: map of Northcentral Nigeria showing the location of the study area. (Adopted from Wikipedia)

Sample preparation

Thirteen (13) of the samples were pulverized into powder (180µm mesh) using Denver pulverize equipment. They were sent to ACME laboratory in Vancouver, Canada for major and minor oxides geochemical analyses using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) method. X-ray Diffractometer (XRD) was also carried out for three (3) pulverized marble sample in same laboratory. The whole rock CO_2 abundances were calculated following duplicate determination of $CaCO_2$ using the Carbonate-bombe method of Birch, 1981.

In the XRD method diffractograms were obtained with a Philip 1140 equipment using Cuk alpha radiation operated at 40KV, 30MA and 1021 per minute. Ten (10) samples were tested for their physical strength properties while another ten (10) samples were used for petrographic studies.

RESULTS AND DISCUSSION

Table-1 shows a variable geochemical characteristic of Obajana marble. SiO2 (silica) values are generally low to high ranging from 0.58% to 7.99%. High content of silica has a positive impact on the economic use of marble for cement production TiO_2, MnO, FeO_3 values are all less than 0.4%. Similarly Na_2O, K_2O are less than 0.2% in the marble.

Al_2O_3 values ranges between 0.08 – 0.31% with an average value of 0.59%. These Al_2O_3 values are comparable to that of the Ososo and Igbeti marbles, (Emofurieta, 1995), Kwakuti marble (Mcleod, 1955) and Osara marble (NSDA, 1986).

CaO values ranges between 46.90 – 58.54% with an average value of 53.89% and this value is higher when compared to the Burum marble (Okunlola, 2003), Ososo and Igbeti marbles, (Emofurieta, 1995) Igwe marble, (Okoro, 2009).

MgO values ranges from 0.18% - 2.89% with an average value of 1.1% and this value is lower when compared to the Igbeti and Ososo marbles, (Emofurieta, 1995), Ukpilla marble (GSNA Report number, 1192), Burum marble, (Okunlola, 2003), Sharpfell marble (Dowrie et al, 1982) and Igwe marble (Okoro, 1982).

The Loss on ignition (LOI) varies between 38.10-42.60 % with the highest value of (42.60%). High LOI results from loss of water from clay mineral, montmorillonite and loss of CO_2 from carbonate minerals. LOI in Obajana marble is within range for cement production.
nterpretation of XRD reveals the presence of Calcite, dolomite and quartz (fig.2)

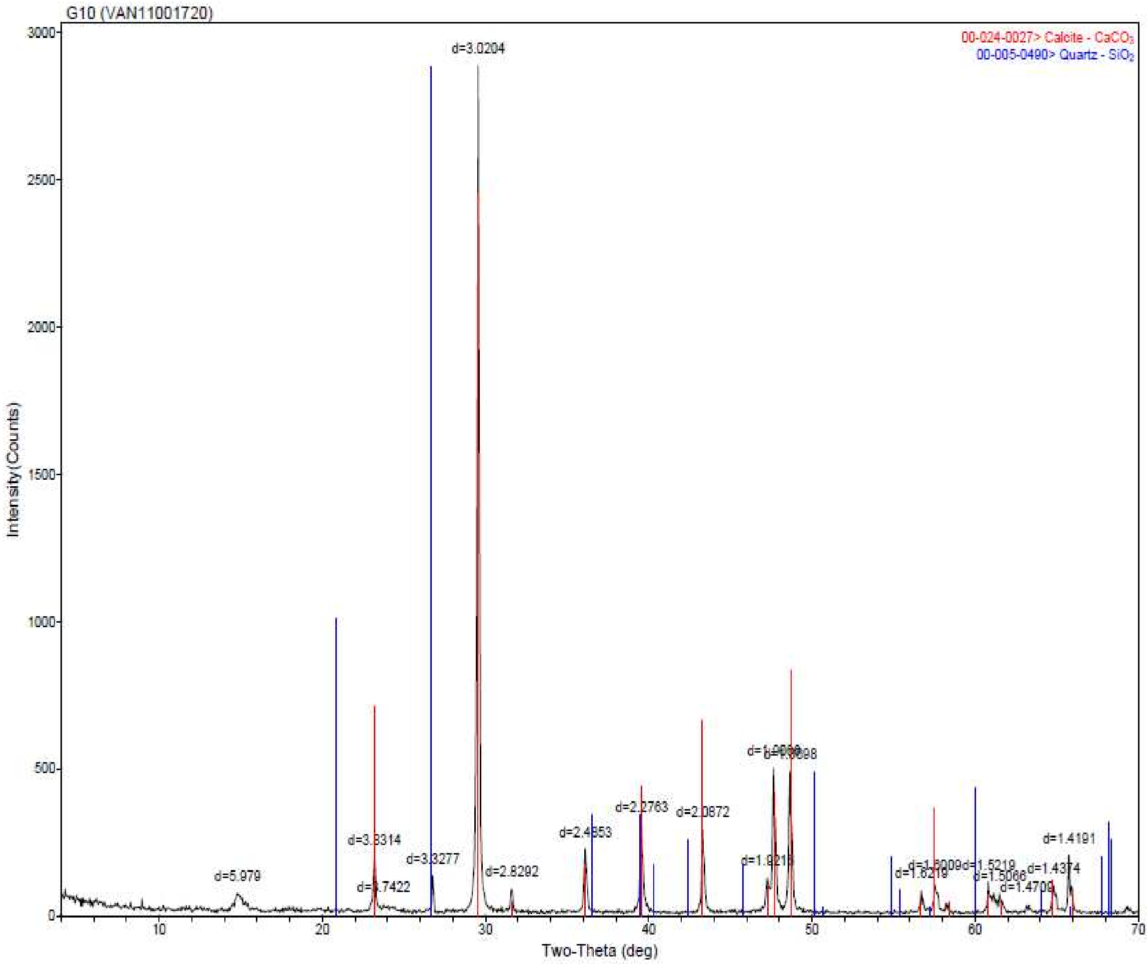

Fig: 2 X-ray diffractogram for Obajana marble sample G10 showing calcite (abundant) and quartz (very minor)

Trace elements content (Table 2) of the marble shows high Sr values which ranges from 1577 – 3673ppm with the lowest values in some impure samples. Average value is 2853.5ppm. Of all the trace element Sr is the highest which confirms its association with calcium.

Cu concentration in the samples ranges from 1.0ppm – 6.3ppm and have average value of 2.58ppm, higher values are encountered in samples where marbles form intercalation with quartz mica schist

Lead concentrations in the sample ranges from 0.3 – 1.8ppm and have an average value of 1.3ppm while zinc amount to a range from 1.0 – 10ppm and average of 2.63ppm. 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 occur as associated element in the marble deposit.

Table 1: Geochemical analytical results of the major oxides of Obajana marble samples

Oxide(wt %)	1	2	3	4	5	6	7	8	Range	Average
SiO_2	7.99	3.12	0.58	1.99	1.56	0.67	2.54	0.67	0.58-7.99	2.39
TiO_2	0.12	0.04	<0.01	0.03	0.02	<0.01	0.03	<0.01	<0.01-0.12	0.03
Al_2O_3	2.31	0.81	0.08	0.43	0.34	0.10	0.52	0.11	0.10-2.31	0.59
Fe_2O_3	0.88	0.35	0.06	0.24	0.19	0.09	0.25	0.08	0.06-0.88	0.33
Cr_2O_3	0.003	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02 -0.003	0.02
MnO	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01-0.03	0.01
MgO	2.37	0.85	0.18	2.89	0.73	0.31	1.06	0.41	0.18-2.89	1.1
CaO	46.90	52.90	57.97	51.66	54.28	58.54	53.43	55.51	46.90- 58.54	54.89
Na_2O	0.33	0.15	0.07	0.12	0.10	0.07	0.11	0.07	0.07-0.33	0.13
K_2O	0.47	0.21	0.02	0.04	0.06	0.01	0.09	0.02	0.01-0.47	0.12
P_2O_5	0.09	0.06	0.03	0.05	0.05	0.08	0.05	0.12	0.03- 0.12	0.07
LOI	38.10	41.10	40.60	42.30	42.40	39.80	41.50	42.60	38.10-42.60	41.05
Total	99.54	99.60	99.56	99.76	99.69	99.68	99.59	99.60	99.54-99.76	99.67

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

Element (ppm)	1	2	3	4	5	6	7	8	Range	Average
Ba	157	100	57	24	64	36	83	50	24-157	71.38
Cu	6.3	1.3	1.7	3.2	2.3	1.8	2.8	1.0	1.0-6.3	2.26
Co	1.5	0.6	<0.2	0.5	<0.2	0.4	0.4	<0.2	<0.2-1.5	0.5
Pb	4.0	1.5	0.5	1.5	0.7	0.3	1.8	0.9	0.3-4.0	1.38
Ce	13.4	3.5	1.2	3.0	1.9	0.8	3.3	3.4	0.8 -13.4	3.81
Nb	10.4	0.6	2.7	1.6	2.7	4.1	1.5	0.4	0.4-10.4	3.0
Rb	21.6	7.8	0.8	2.0	2.9	0.2	4.1	1.1	0.2-21.6	5.0
Sn	37	<1	16	5	15	9	5	<1	<1-37	11.13
Sr	3186	3058	3678	1577	2318	2586	3156	3269	1577-3678	2853.5
Ta	44.2	0.3	16.2	5.4	11.5	7.7	4.2	0.3	0.3-44.2	11.23
Th	2.5	0.7	0.3	0.4	0.5	0.2	0.5	0.3	0.2-2.5	0.68
Zr	28.6	8.7	2.2	7.7	5.9	1.9	5.4	3.4	1.9-28.6	7.98
Y	4.1	1.5	0.4	1.3	0.9	0.3	1.1	1.0	0.3-4.1	1.33

Economic potentials

The marble has high economic values classified by 6 broad categories namely: metallurgical, chemical, environmental, construction, refractory and agriculture (Scott and Durham, 1984). Each of this group requires a specification for the marble to be useful.

Metallurgical lime production

Most of the lime produced from marble is used as steel flux, in steel manufacture lime acts as a flux use in removing of phosphorous, silica and sulphur, as calcium phosphates, silicates and sulphides in the slag which is tapped off as molten metal. Requirements for metallurgical lime (steel flux) in blast furnaces, CaMgO is required with Silica (SiO_2) less than 5% less than 2% preferred. (Al_2O_3) less than 2%, (MgO) less than 4% . Phosphorus pentoxide (P_2O_5) not more than a trace, i.e., .005ppm to .006ppm. While for steel flux (open hearth) Calcium carbonate content preferably not less than 96% lower grades occasionally accepted. Phosphorus must not exceed trace amounts. The Obajana marble meets this specification $CaCO_3$ >96% which means it can be used for both open hearth and blast furnaces in steel fluxes.

For refractory lime i.e. dead burned dolomite for open hearth lining. The requirements are Magnesium oxide (MgO) not less than 18%. Silica (SiO_2), ferric oxide (Fe_2O_3) and alumina (Al_2O_3) not to exceed 1% each, but lower grades sometimes accepted. The Obajana marble is not useful because of its low MgO (1.1%) content.

Calcium carbide and Calcium cyanimide Production

In the manufacture of calcium carbide and calcium cyanimide, sodium alkalis such as sodium carbonate, bicarbonate and hydroxide used in chemical manufacture. With the requirement of Calcium carbonate ($CaC0_3$) content must exceed 95%. Magnesium oxide (MgO) should be less than 0.5%: alumina and ferric oxides (together) less than 0.5%; silica ($Si0_2$) less than 1.2% and phosphorus less than 0.01%. Sulfur must not be present in greater than trace amount. Obajana marble meets all this specifications with $CaCO_3$ content > 96% and therefore can be used.

In the use of marble in the manufacturing of calcium carbide- a product of the electric furnace formed when lime and coke are mixed in 60% to 40% proportions respectively and heated to $2{,}000^0$C. For each ton of calcium carbide manufactured, 2 tons of limestone or 1 ton of lime is required.

Paints and fillers
In the industries for the production of paints and fillers it is required that In general the calcium carbonate content should exceed 96% but magnesian limestones containing as much as 8% magnesium oxide occasionally are tolerated—the $MgCO_3$ content generally is 1%. Other maxima are; Fe203—0.25%, SiO_2—2.0% and SO,—0.1%.

Quicklime for pulp and paper
While in the manufacturing of quicklime for pulp and paper the Calcium carbonate ($CaCO_3$) contents must be more than 96% for most manufacturers. In the paper industry, high calcium marble is required as it is suitable for making soda pulp and sulfate pulp. The marble can be reacted with sulfur dioxide to produce cooking liquor. This acidic liquor is then used to digest the constituents of the wood chips except cellulose. The Obajana marble meets these specifications for both uses as fillers in paper and in the manufacturing of paints with $CaCO_3$ content of >96% and MgO of less than 1.1%.

Lubricants
For the manufacturing of lubricants (greases) Calcium oxide not less than 72.6%, magnesium oxide not more than 1 %, maximum silica plus iron plus alumina, 1.5%, maximum carbon dioxide (at point of manufacture) 1%.The Obajana marble meets this specifications due to its high calcium oxide and low magnesium oxide contents.

Textile dye
In production of lime for textile dyeing the Calcium carbonate ($CaCO_3$) not less than 94%, alumina - iron not more than 2%, silica not more than 2.5% and magnesia not more than 3%. Obajana marble meets these specification thus it can be used in dye manufacture.

Pesticide production
In pesticide production, calcium arsenate, arsenic acid is reacted with a milk of lime forming calcium arsenate, CaO> 60% is required, also for varnish the marble must be very low in iron and magnesium oxide. Obajana marble can be used for both varnish and pesticide production.

Beet-sugar
For the manufacturing of beet-sugar the Silica (SiO_2) content not more than 2%. Magnesia not more than 4% is required. At some plants ferric oxide (Fe_20_3) must not exceed 0.5%. The high calcium limes when finely powdered can be employed in refining beet and cane sugar by carbonization. This is because the pure marble from Obajana would not impart a sour taste to sugar. Since carbon-dioxide as well as lime is required in beet sugar refining, the raw marble may be burned at the refinery. The lime precipitates impurities from the juices/syrup from impure solutions. Obajana marble meets these specifications and thus can be useful in the beet sugar manufacturing.

Glass manufacturing
In glass manufacturing Ferric oxide (Fe_2O_3) not more than 0.05, preferably not more than 0.02% for colorless glass, rock having up to 0.1 % Fe_2O_3 is sometimes accepted for colored container glass. Calcium carbonate ($CaCO_3$) should exceed 96% in case of marble, or 96% calcium-magnesium carbonate in case of dolomite. Amounts of silica, alumina, magnesia etc., must not vary from shipment to shipment. Obajana marble meets these specifications and thus can be used in glass manufacturing.

Portland cement production
In Portland cement production, the major requirements are Magnesium oxide (MgO) not more than 3%, preferably not more than 2%. Total alkalies not more than 0.5%. Minimum calcium carbonate ($CaCO_3$) content varies from plant to plant depending upon availability of other raw materials, but generally is more than 82%. Obajana marble meets these specification thus it is suitable for the production of Portland cement.

Water treatment
Environmental usage, especially in water treatment where a high pH of about 10-11 is needed for water softening. The ability of Obajana marble to do this is not in doubt as it will kill most types of bacteria (Boynton, 1975) when added to water retention tanks. Absence of Cobalt, mercury and lead is a major requirement and Obajana marble has none of these earlier mention elements either in trace or minor amounts.

Sewage treatment
Their lime products will be useful in sewage treatment, neutralization of acid water, silica and phosphate removal from sewage effluents. These specifications are quite similar to that for water softening and purification. If processed quite well, the Obajana marble lime products should be useful in sewage water treatments.

Construction
For concrete aggregate, ballast, road metal, road base. General requirements are Concrete aggregate should be low in alkalies and free from surface organic matter. Presence of opaline silica is highly undesirable in concrete aggregate. Other aggregate suitability is based chiefly on durability, particularly toughness and of low porosity. CaO, MgO of about 70%, CO_2 < 50% (ASTM, 1976). In terms of fitness, it must leave little or no residue. Compressive strength of > 20Mpa, tensile strength > 2Mpa and shear strength > 7Mpa. Obajana marble meets these specifications and could as well be used as road stabilizers, aggregates, ornamental stones and building blocks.

Agriculture
Soil liming is one of the oldest uses of raw and calcined marble (Ojo et al, 1998). The marble function as a neutralizer of acids and soil enhancer, the requirements are pH>8 with low grittiness and Obajana marble having (pH=8.3) meets this requirements and thus is useful as soil ameliorants and nutrients status enhancer.

CONCLUSION

Geochemical data of Obajana marble indicate variable characteristics; high calcite and low dolomite. An economic appraisal of the marble and its associated minerals show that they serve as raw materials for a variety of products such as fillers, glass, papers, lime, pesticide and sewage treatment. They also find applications in decorative construction, monuments, paint making and most of all very suitable for cement production.

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