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Mineralogy and Geochemistry of a Marble Deposit, Owan-East, Southwestern Nigeria: Implications for Protolith and Industrial Uses

Akinola Oluwatoyin O and Adebayo Olajide Femi*

Department of Geology, Ekiti State University, 5363 Ado-Ekiti, Nigeria

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ABSTRACT

This research investigates and reports the mineralogy, geochemistry, industrial implications and protolith of a marble deposit in the basement complex of Owan-East, Edo-State, Southwestern Nigeria. Field geology revealed the marble is interbedded with calc-silicate gneiss, quartz-biotite schist, polygenetic metaconglomerate, mica schist and quartzite. The marble occurs as lenses within the gneiss and overlain by a thin gritty tropical soil. The fine-grained marble occurs in three colour varieties (white, grey, and banded). The banded type exhibits strong axial foliation which is concordant with NNE-SSW regional strike with westerly dip ranging between 68° and 82°. Petrographic investigation revealed that calcite and dolomite account for over 85% of the marble. X-ray diffraction showed the marble is composed of calcite (52%), dolomite (35%), accessory quartz (6%), biotite (4%) and feldspar (2%). Optical and X-ray results indicate the bands in the banded variety represents clay impurities in the original limestone protolith.The marble is calcitic (CaO, 51.7-60.76%; MgO, 1.42 – 2.57%) with average Mg^{2+}/Ca^{2+} ratio of 3:100. Average alkali (Na_2O + K_2O) contents (1.13%) suggest deep water, low saline (estuarine, brackish to paralic) environment of deposition for the ancient limestone. Alumina content of the marble (white, 0.5 %; grey 0.35 % and foliated 3.49 %) (total average: 1.45 %) and that of Fe_2O_3 (white, 0.19 %; grey 0.5 % and foliated 1.78) (total average: 0.82 %) exceed those of other marble deposits in southwestern Nigeria. Silica Ratio (SR) (1.28), Alumina Ratio (AR) (3.54), and Lime Saturation Factor (LSF) (537.75) suggest the marble is useful in the manufacture of cement. The marble also meets industrial specifications for fertilizer production and as refractory lime.

1. Introduction

Calcareous deposits occur abundantly in Nigeria. While limestone is found in Ogun, Edo, Imo, Abia, Cross-River, Ebonyi, Enugu, Benue, Bauchi, and Gombe States; largedeposits of marble occur in Edo, Kogi, Kwara, Nassarawa, Niger, Oyo, and the Federal Capital Territory (Fatoye and Gideon, 2013) (Figure 1). Many of these marble deposits have not been fully harnessed partly due to insufficient information about their compositional features whichultimately determine their industrial applications. The use of marble depends not only on its chemistry but also on petrographic characteristics. Mineralogy and grain sizewhich are readily observable physical features are the primary factorsinfluencing strength,aesthetics and colourof marble and its industrial use. Marble isa metamorphosed limestonethatpossess several unique features that makes it useful for different industrial applications. In fact, rocks having as many industrial applications as marble are rare. Previous researchesshow Nigeria marbles have several applications in pharmaceutical, agronomic, cosmetics, paints, and paper industries (Akinola and OlaOlorun, 2012). Marble is softer thangranite and this enhances itsworkability.Even though, it not asdurable asgranite in concrete mixing for engineering construction;however, its affordability and availability still make ita popular stone aggregate. Its beauty attracts architects and sculptors,some monumental buildings like the Taj Mahalin India, the Washington Monument and Lincoln Memorial are amongst World's notable marble buildings. Only quartz and tourmaline have more colours than marble, these different colours often produce enchanting aesthetic infloor tiles, kitchen tabletops, and top of laboratory cabinet and monumental masonries. Marble derived from the purest limestones is white, those containing iron oxide impuritiesexhibit yellow, orange, pink or red colour while serpentine tend to colour marble green.Clay minerals in the parent limestone sometimes produce array of colours range from grey to brown formingfantastic bands (Akinola and OlaOlorun, 2020). When the precursor limestone is enriched in bituminous materials, it impacts dark grey or black hue on the marble. Marble is formed when limestone or dolostone is transformed by heat and pressure to a crystalline rock.Calcite (CaCO3) and dolomite Ca,Mg(CO3)2 are the dominant carbonate minerals in marble. Previous research also revealedthat for marble to be useful for any applications, it must meet certain specifications.Among these applications aremanufacture of cement, steel, glass, chalk, chemicals, and fertilizers. Household applications include ceramics, insecticides, and toothpaste. Previous works on chemical feature of prominentmarble deposits in southwestern Nigeria include: Igbetti marble (Emofurieta and Ekuajeni, 1995;

Tele:
E-mail address: olajide.adebayo@eksu.edu.ng

Akinola and OlaOlarun, 2012); Ikpeshi marble (Obasi and Anike, 2013), Ososo marble (Emofurieta and Ekuajeni, 1995), Igue marble (Akinola and OlaOlorun, 2020); Jakura and Burum marbles (Elueze and Okunlola, 2003), and Obajana Marble (Elueze et al., 2015).Scott and Durham, (1984) identified about two hundred end uses of raw marble and their calcined products. However, in addition to petrographicand geochemical characteristics, this research presentsinformation on protolith and industrial applicationsof a marble deposit in Owan-East area of Edo-State, Nigeria.The study area forms part of Edo State which originally comprise of the Bini, Esan, Owan and Etsako people. Specifically, the vicinity of the marble deposit is occupied by the Afemai group who populate the hills and plains of the Owan East Local Government area of Edo State in Nigeria. With a Local Government Council in Afuze, the study area is surrounded by Emai, Ihievbe, Ikao, Ivbi-Mion, Ive-Ada-Obi, Otuo, and Uokha. Other economic marble deposits in Edo State are located in Ikpeshi, Okpella, Ikao, Ososo and Igarra.

2. Geological Setting

2.1 Regional Geology

Nigeria lies within the Pan-African orogenic belt (Turner, 1983). Specifically, it occupies the eastern side of West Africa craton and northwest of Congo craton. Part of this belt that falls within Nigeria comprise of crystalline rocks popularly called the basement complex. The basement rocks are separated from each other by geosynclines containing Cretaceous-Recent sediments which overlie it with observable unconformities. The basement complex formsa unique topographic entity and outcrop in southwestern and northcentralNigeria while three smaller areas occur in eastern part of the country(Ekwueme, 2003; Obiora, 2005) (Fig. 2). This complex of Nigeria generally contains threepetrologic groups, these are: migmatite-gneiss complex, the schist belts, and Pan-African granite (Elueze, 2000). Migmatite-gneiss complex is the oldest lithology, its long evolutionary history (Emofurieta and Ekuajeni, 1995) revealed it has been reworked by multiple tectono-thermal activities. This Achaean-Proterozoic unit (Dada, 1998) is metamorphosed to amphibolite facies grade (Rahaman, 1988). Elueze, (1981) reported the chemical variation exhibited by the unit reflects heterogeneous antecedents. The schist belts comprise pelites and psammites, para-schists and meta-igneous rocks, calc-silicates, schistose and talc-bearing rocks that are preserved in low-grade metamorphism (Rahaman, 1988). The schist belts occur mainly as N-S trending bodies and are more prominent in the western part of Nigeria (Rahaman, 1988; Turner, 1983). Russ (1957), Oyawoye (1964) and McCurry (1976) believed the schist belts represent relics of a once widespread sedimentary cover deposited in a single basin. However, Black et al. (1979) and Elueze, (1981) emphasized that the lithologic variations indicate they developed in separate basins. Ajibade (1980) believed the schist belts have same age and origin as they all experienced same deformational episodes. The schist belts are about the most frequently reported rock in the basement because they contain gold, Banded Iron Formation (BIF) and marble. Pan-African granites intrude the migmatite gneiss complex and the schist belts. The granite suites comprise rocks of a wide range of compositions including granite, granodiorite, charnockite and pegmatite (Truswell and Cope, 1963). The minor rocks (dolerite dykes and syenite) are late-stage intrusive which represents terminal stage of the Pan-African magmatism (Elueze, 2002). The structural framework of Nigeria consists of Precambrian rocks that have been subjected to Liberian, Eburnean, Kibaran and Pan-African activities (Ajibade and Fitches, 1988). Rocks in Nigeria have experienced polycyclic deformation with Pan-African episode being the most pervasive (Odeyemi, 1977). The author believed all structural fabrics in the basement is tectonic in origin as the pre-existing primary structures have been obliterated by subsequent deformation episodes. The basement complex of southwestern Nigeria has been affected by two phases of deformation namely D1 and D2, the first phase produced tight to isoclinal folds while the second produced open folds with variable styles and large vertical NNE-SSW trending faults (Annor, 1983; Oluyide, 1988). Tectonic deformation has completely obliterated the primary structures except in few places where they survived deformation (Okonkwo, 1992).

2.2 Local Geology

The landmass of Edo-State is shared between metamorphic and sedimentary rocks. The metamorphic belt forms substantial part of the Igarra schist belt while the sedimentary domain occurs around Auchi, Ekpoma and extends eastwards into the neighbouring Delta State. The study area is underlain by the basement complex and consists of schistose assemblages, amphibolite, calc-silicate gneiss and marble which were intruded by Pan-African plutons.The marble deposit occurs at about ten kilometers southwest of Igarra and approximately 20 kilometres northwest of Auchi (Figure 3). The area is underlain in most parts by low-grade, strongly deformed Neoproterozoic metasediments (Odeyemi, 1990). The metasedimentary assemblages in the area have been described in the works of Odeyemi (1976, 1977). The author reported basal quartz-biotite schist overlain by calc-silicate gneiss and marble, metaconglomerate as well as mica schist and quartzite all resting on the ancient migmatite gneiss complex. The metasediments, together with their basement sub-structure were deformed during the Pan-African orogeny which culminated in the emplacement of Igarra, Ososo and Aroko granite plutons located at the centre of the emergent folds (Odeyemi, 1990). The geology of the study area is contained in the works of Odeyemi (1977), Rahaman and Ocan (1978), Ladipo (1986), Odeyemi (1990), Odeyemi and Rahaman (1992), Obasi and Anike (2012), Obiadi et al. (2012), Oloto and Anyanwu (2013), Ayodele and Ofuyah (2017) among others. The marble with calc-silicate gneiss occur as lenses under a thin dark brown to black humus-rich tropical soil. The marble body stretches E-W and folded concordantly with the anticlinal structures which represent regional trend of the basement. The eastern segment of the marble shows extensive fracturing while the distortion of its structure is attributable to the emplacement of the Igarra granite batholith which truncates the eastern and western margins of the marble. The marble shares contact with metaconglomerate in the north and the two became folded together around Otuo towards south of Ibillo where it is terminated against quartzite and granite. The marble is delimited in the south by muscovite schist. The beautiful alternating shades of white, brown, and grey colours gave it a resemblance of contrasting colours of zebra. This distinct feature is diagnostic as it distinguishes the marble from all known marble deposits in southwestern Nigeria. The marble is relatively close to the surface; thus, it is exploited by open mining method (Figure 4). The geological contacts between the marble and other lithologies are not exposed in most of the areas; even the mine workings do not reveal major lithological boundaries.

3. Materials and Methods

3.1 Fieldwork and Sampling

An existing geological map of the study area (Odeyemi, 1990) provided the requisite information needed for the study. Hence, detailed systematic geological mapping was not undertaken. Point sampling technique was adopted and all textural and colour variants of the marble are considered in the random sampling procedure. As part of the methodological approach, only fresh samples were taken. Thirty fresh marble samples (10 each for the white, grey, and foliated) are obtained from the mining pits; the lumps are reduced using a sledgehammer. Samples are labelled appropriately and kept in sample bags. For traversing, a Global Positioning System (GPS) (model GARMIN GPS Map 76 CSX) was used to locate positions in the field, while a compass clinometer helps in the determination of bearings, strike and dip values. Marble samples were prepared into thin section for optical examinations.

3.2 Optical Investigation

A small piece of marble measuring approximately 22 mm x 40 mm x 10 mm was cut from the rock sample with a diamond saw. The rock chip is then glued to a glass slide with epoxy and heated on a hot plate to harden. Subsequently, the rock was allowed to cool to room temperature and the specimen sliced until approximately 250 µm thick section remained on the glass slide. The sample is then ground down to a thickness of about three hundredth of a millimetre using the lapping machine. At this thickness, every mineral in the rock become so thin that they will allow light to pass through. The resulting slides were examined on a stage of polarizing microscope to identify the minerals and structures in the rock. Petrographic analysis utilizes optical properties such as colour, relief, zoning, reaction rims, alterations, extinction angle, pleochroism, texture, crystallinity, inclusions and twinning to identify the minerals. Confirmation of the minerals was achieved by comparing features on plane polar with cross polar and modal analysis computed. Thin section preparation and their snapshots were taken on the facility at Department of Geology, University of Malaya, Kuala Lumpur, Malaysia. Photomicrographs of some sections of the thin sections are presented (Figure 5).

4. Results and Interpretation

4.1 Origin of Bands in the Marble

Marble originates from recrystallization of limestone, the temperature for this transformation is attainable only at certain depths within the earth. Rocks below the surface are under pressure due to burial, this confining pressure increases with the depth. At a point, the pressure is sufficient to initiate recrystallization along grain boundaries. When the confining pressure is equal in all directions, mineral grains do not have preferred growth direction. However, when the pressure varies in different directions, soft mineral grains align themselves perpendicular to the direction of maximum stress. Hence, recrystallizing mineral grains develop shapes that align their longest dimensions perpendicular to the direction of maximum pressure which results in a banded structure. Thus, differential stress is required to form metamorphic rock such as the foliated marble. Most often, fascinating banded structures like these are product of impurities of brown, grey or dark clay, shale or grit incorporated into the depositional basin at the time the original carbonate sediments were deposited. Tectonic forces of varying magnitudes within the sedimentary basin must have triggered contortion and folding as the sediments are squeezed during recrystallization. This tectonic activity probably accompanied emplacement of granite of batholithic dimensions around Igarra. The more the directional pressure the more intense the folding. The structure of this marble is in conformity with the basement gneisses by having N-S and NNE-SSW strike directions. Strike values within the mining pits range from 007°to 025°and dip values from 68°W to 82°W.

4.2 Petrography

The white Owan-East marble is dominated by calcite and dolomite (Figure 5a) Calcite occurs as euhedral grains with well-developed crystal faces and low refractive index.Some of the calcite appears cloudy with a characteristic low relief. The grey marble variety in addition to these two minerals contains accessory quartz (Figure 5b). Quartz grains are small, anhedral, largely unaltered andlocated in the interstices of calcite and dolomite. Dolomite has euhedral grainswith well-defined rhombohedra characterized by lamella twinning and high birefringence. Calcite and dolomite can be distinguished by the relation of the twin lamellae to the cleavage planes. Dolomite has twin lamellae set parallel to both the long and short diagonals of the cleavage rhomb.On the other hand, calcite twins are parallel to the long diagonals and the edges of the rhomb. Dolomite has a high order white interference colour; it is mostly anhedral but rhombic shape with curved crystal faces do occur. In addition to calcite and dolomite, biotite and quartz occurs as fine-grained mineral components in the foliated marble (Figure 5c).Biotite forms the main acicular mineral with laths oriented in same direction. Most of the bands are made of extremely fine-grained groundmass of biotiteand quartz. Even though, biotite is absent in the white marble variety, graphite occurs as major opaque mineral aggregate associated with the foliated marble type (Figure 5d). The modal composition of the marble (Table 1) reveals the rock is made of calcite, dolomite, quartz, biotite and graphitein decreasing order of abundance. The average modal composition of the marble compared to other known marble deposits (Table 2) indicate that the latter depositshave relatively higher calcite contents. The lower calcite may compensate for higher dolomite content. The Igbetti grey marble variety (Akinola and OlaOlorun, 2012) has additional minerals like chlorite and tremolite which are absent in the studied grey marble variety. The white Igbettimarble and white Owan-East marble have comparable mineral assemblages. The banded (foliated) Owan-East marble has a unique composition due to presence of significant amounts of biotite. The mean quartz content in the Owan-East marble (9%) is higher than the mean quartz value (4%) in Igbetti marble (Akinola and OlaOlorun, 2012). Marble specifications for many industries (Table 2) show a wide discrepancy in mineralogy and calcite requirements.

4.3 Geochemistry

The chemical analysis of the marble (Table 3) shows the different colour varieties of the marble have slightly varying chemical compositions. However, the marble generally has low percentage of silica, alumina, iron, and magnesia. The marble equally has low alkali (Na_2O and K_2O), manganese, titanium, and phosphorus. CaO contents for the white, grey, and foliated marble are 60.76%, 59.35% and 51.7% respectively. Loss on ignition value is 33.46%, 36.12% and 33.49% respectively.

4.4 Geochemical Evidence of the Protolith

4.4.1 Silica content

Most carbonate rocks inherit silica through a combination of processes, one is breakdown of silicates which is basically part of all rock forming minerals, it could also be introduced through chert nodules sourced from siliciclastic materials of nearshore origin incorporated into the depositional environment of the ancient limestone before subsequent metamorphism (Brownflow, 1996). The silica content of marble from Owan-East, Edo State (white, 2.92 %; grey 1.74 % and foliated 4.04 %) (ca. 2.9 %) is higher than Igbettimarble (white, 0.11 %, grey, 0.33 %) and Jakuramarble (ca. 0.43 %) (Table 2). The higher silica content may reflectshallow depth possibly a continental shelf or nearshore environment of deposition for the ancient limestone protolith.

4.4.2 Alkali (K_2O/Na_2O) content

The alkali (K_2O + Na_2O) content in the marble in Owan-East(white 0.47 %, grey 0.42 %, foliated 2.51 %) (ca. 1.13 %) is higher than the Ekinrin-Adde marble (<0.35 %) (Onimisi et al. 2017). Although this average compares with typical marble deposits (Table 4); however, as pointed by Clarke, (1924), the percentage of alkali in calcareous units decrease with increasing salinity and increase with depth. The high average alkali content (1.13 %) may suggest a low saline (freshwater, brackish or paralic) environment for the ancient protolith for the limestone.

4.4.3 Al_2O_3 and Fe_2O_3 content

Alumina content of the Owan-East marble (white, 0.5 %; grey 0.35 % and foliated 3.49 %) (ca. 1.45 %) and total iron content – Fe_2O_3 (white, 0.19 %; grey 0.5 % and foliated 1.78) (ca. 0.82 %) are higher than Ekinrin-Adde marble andother marble deposits in southwestern Nigeria. The unprecedented high alumina and iron contents may reflect incursion of aluminosilicate impurities into the marble,particularly the foliated variety.

4.4.4Loss on Ignition (L.O.I)

When marble is heated to a temperature of 900°C, it breaks down and part of it escapes as volatile resulting in loss of weight. This reduction is referred to as Loss on Ignition (L.O.I) and this represents volatile constituents like ($CO_2$and H_2O).The average L.O.I in the Owan-East marble deposit (white 33.46 %; grey 36.12 % and foliated 33.49 %) (ca. 34.36 %) is lower than other marble deposits from southwestern Nigeria. Even at this average, the marble deposit contains high carbonate content.

5. Industrial Applications

The industrial application of marble is diverse and the specifications for each end use varies considerably. Boynton, (1979) recognized six main economic application of marble to include construction, chemical, environmental, refractory, agriculture and metallurgical. For marble to be useful, it must meet the requirements for the application and these specification ranges from chemical to physical. The industrial uses of Owan-East marble deposit in accordance with compositional features using the British Cement Index (BCI) specification (for cement production) and the Industrial Specification of India -ISI (Bhargava, 1978) are enumerated.

5.1 Production of Cement

For carbonaceous rocks (limestone and marble) to be useful in production of cement, the CaO content of 46.65-52.46 % and $CaCO_3$ between 83.50 - 93.90% is required. The maximum tolerable limit for MgO content in cement manufacture is 2% (Table 4). According to Talbot, (1982), a higher MgO value results in the formation of periclase as an intermediate product in the manufacture of Portland cement causing sintering of limestone by alumino-silicate materials such as clay changing into nodules in the cement kiln. During this process, water combines with MgO to form Mg $(OH)_2$ resulting in corresponding volumetric disparity between the initial periclase [MgO] and brucite [Mg $(OH)_2$] to cause structural disparity which is characteristic of low-quality cement.Cement clinker is a product of mixing appropriate ratios of the chemical components: Silica Ratio (SR), Alumina Ratio (AR), and Lime Saturation Factor (LSF) to place a constraint on the composition of the clinker. The calculation of the ratios involves the oxides values of CaO, SiO_2, Al_2O_3 and Fe_2O_3. The SR, AR and LSF values for a conventional cement kiln feed for the studied marble are determined as follows:

Silica Ratio(SR) = SiO_2/ (Al_2O_3 +Fe_2O_3) = 2.9/ (1.45 +0.82) = 2.9/2.27 = 1.28

Alumina Ratio (AR) = Al_2O_3/ Fe_2O_3 = 2.9/ 0.82 = 3.54

Lime Saturation Factor (LSF) = 100*(CaO)/ [2.89 (SiO_2) + 1.2 (Al_2O_3) + 0.65 (Fe_2O_3)] = 100 (57.27)/ [2.89(2.9) + 1.2(1.45) + 0.65 (0.82)] = 5727/[8.38 + 1.74 + 0.53] = 5727/ [10.65] = 537.75

The recommended SR, AR and LSFvalues for marble as a raw material in production of cement are (1.9 - 3.2), (1.5 - 2.5)and (242- 417) respectively (Onimisi et al. 2017). The overall calculated average for SR, AR and LSF for Owan-East marble deposit are 1.28, 3.54 and 537.75, respectively. All these values fall outside the recommended range for cement production. The overall average LSF of Owan-East marble (537.75) which exceeds the upper threshold (417) limit for cement (Table4)may prove useful, if the marble can be blended in appropriate ratio with another type that can bring the values of SR up while AR and LSF are reduced. Consequently, this can be achieved by mixing with appropriate amounts of lateritic clay to improve its silica, alumina, and iron respectively (Panda, 2016).

When alkalis (Na and K) replace calcium in calcareous rocks like limestone or marble, it increases the setting rate of cement when it encounters air or humidity. This is because alkalis are more reactive than alkali earths. However, the chemical reaction that allows this transformation requires that Ca^{2+} is replaced by $2Na^{+1}$ or $2K^{+1}$, or $Na^{+1}$and K^{+1} to preserve the electrical neutrality. Talbot, (1982) indicated that alkalis react with active silica which results in the disintegration of some concretes. Therefore, total alkali contents in calcareous material for cement manufacture must be sufficiently low. The total alkali content in the marble is 0.34%, which is comparable to the upper limit (0.35%) accepted for cement production. Overall average value of Al_2O_3, Fe_2O_3 and SiO_2 in the marble are 1.45 %, 0.82 % and 2.90 % respectively. The first two values fall within the recommended values for cement production (Table 4). However, the third is marginally lower than the recommended average. Sulphur and phosphorus when present in substantial amount (>1 %) are undesirable to the quality of cement as they slow down the setting time. However, while sulphur was not captured in the analysis of Owan-East marble, the phosphorus content represented as P_2O_5 in the marble does not pose problem to the industrial application for cement manufacturing as it is 0.1% and far below 1%.

5.2 Chemical Applications

5.2.1 Manufacture of Sodium Alkalis

The use of raw marble as major ingredient in the production of lime is one of the commonest applications in the chemical industry. Among the lime products are sodium carbonate, bicarbonate, and their hydroxides. In the Solvay process, it is useful for producing ammonia (or ammonium soda). For raw marble to be useful for this application, the total carbonate contents ($CaCO_3$, $MgCO_3$) must exceed 70%. This specification is met by the studied marble as it has a higher total carbonate content.

5.2.2 Manufacture of Calcium Carbide

When Calcium carbide (CaC_2) reacts with water, its product is useful in oxyacetylene flame for the weldingof iron. In the manufacture of this product, acetylene and quicklime (CaO) are mixed with coke (C) and heated to 2000°C. Molten carbide is extracted and disaggregated after it become solid. It is then crushed for use.In the production of calcium carbide, the industrial requirement ishigh calcium (CaO> 90%) content, low SiO_2 (< 3%), low P (< 0.02%) and MgO < 0.5%. Based on these specifications, the Owan-East marble does not meet the requirements for the manufacture of calcium carbide as it contains MgO > 0.5% even though the average SiO_2 (2.9%) content is within acceptable limit.

5.2.3 Manufacture of Bleaching Powder

When dry hydrated lime absorbs chlorine, it results in the production of bleaching powder. For effective performance, the amount of water in the hydrated lime must fall within a narrow limit and must not exceed 2%. When iron and manganese exceed certain limits, they pose problems and become unsuitable for use as iron oxide reduces the effectiveness of the bleaching powder by reducing the colour quality of the bleached material. Silica disrupts the settling of bleaching powder and so, must contain a low percentage of SiO_2. The industrial specification for use of marble in the manufacture of bleaching powder is (CaO) > 95%, (Fe_2O_3 + Al_2O_3 + MnO_2) < 2%, MgO < 2%, SiO_2< 1.5%. Based on these specifications, the Owan-East marble deposit is unsuitable for the manufacture of bleaching powder as itsCaO< 95% and SiO_2> 1.5 %.

5.2.4 Pesticide Production

Calcium arsenate which is a product of reacting arsenic acid with a milk of lime is a chemical ingredient that is essential in the production of pesticide. In the industrial production of pesticide from marble, a CaO content which exceeds 65% is required. Based on this specification, the Owan-East marble is not a suitable raw material for the manufacture of Pesticide as the white grey and foliated marble contain 60.76%, 59.35 % and 51.7 % respectively. All the marble varieties under consideration contain CaO values that are lower than the recommended 65 %.

5.2.5 Glass production

In industrial application of marble for glass production, a high calcium content in the form of $CaCO_3$ more than 94.5 % is required. Iron and other materials that has colouring effects such as carbon is objectionable, therefore chemical criteria include Fe_2O_3 should not exceed 0.2%. For the glass to be colourless, the marble should contain $CaCO_3$ (> 98.5%), Fe_2O_3 should have a maximum value of 0.04%. Based on the above specification, the Owan-East marble is not suitable for the manufacture of glass as it contains high contents of Fe_2O_3(> 0.2%) and SiO_2> 2.5%.

5.2.6 Sugar production

The sugar industry requires lime to clarify juice cane. The industrial specification for this purpose according to India (1SI: 3204-1978) is that the marble must contain CaO> 50 %, SiO_2< 2%, MgO <1%, (Al_2O_3 + Fe_2O_3) < 1.5%. Because sugar is edible and useful in food processing, the specification of marble for its manufacture must be strictas it could have some health consequences. Due to the colouring effects, it is preferred that iron is totally absent, or if present at all, it should be negligible. The evaluation of Owan-East marble on these parameters indicates the deposit is unsuitable for the manufacture of sugar as its overall contents of silica (3 %), MgO (1.87 %) and Al_2O_3 + Fe_2O_3 (2.27%) exceeded the recommended limits.

5.3 Metallurgical Applications

Metallurgical industry forms one of the several areas where raw marble and its derivatives find applications. In particular, the greatest use is as flux in steel manufacture and foundry industry. A fluxing agent is a chemical substance for cleaning metals prior to soldering or oxides on the metal to aid good bond. According to O'Driscoll (1988), about 88% of the world total lime production is being used as steel flux. In the blast furnace, to reduce energy cost for melting in the production process, marble is used to lower the melting temperature, it equally forms $CaSiO_3$ by reacting with silica in the ore of iron and released as slag. For it to be useful as metallurgical lime, the CaO must exceed 65%, SiO_2 must range between 1-1.5%, and SO_3 between 0.05 – 1% (Onimisi, et al. 2017). This lime can equally function as refractory lime in metallurgical application for lining open hearth systems. The requirement for this application is like those for fluxes but the SiO_2 content range is between 2 and 4%.

Following the specifications enumerated above, the Owan-East marble deposit is not suitable for applications as steel flux due to higher SiO_2 content (white, 2.92%; grey, 1.74% and foliated 4.04%) which exceeded the upper acceptable limit (1.5%). However, like the Ekinrin-Adde marble in Kogi State, the Owan-East marble meets the specification for use as refractory lime as its silica content (3.14%) falls within the accepted range of 2-4%. Blending the different colour brands of the marble in same ratio also results in an overall average of 2.90% which still falls within the limit for refractory lime.

5.4 Environmental Applications

5.4.1 Water treatment

Two prominent areas where raw marble finds application in environmental use are in the purification of water and neutralization of sewage. This application greatly influences community health and prevention of epidemic. Lime is useful in water treatment. Sometimes the chemical characteristic of water depends on the rock type that bore it, or it flows through. Water produced in limestone environment often exhibits hardness which sometimes reflect in its taste and colour. Hard water appears cloudy due to some dissolved rock constituents. Marble in the form of lime helps in treating temporary hardness of water by softening it through removal of bicarbonates. It equally helps to adjust the pH and prevents dissolution of unwanted materials from the piping system. During purification of water, lime is retained in reservoir tanks for 24 - 48 hours to cause precipitation of unwanted turbid and contaminants similar to when alum $[KAl(SO_4)_2.12H_2O]$ is added to water. High alkalinity is produced by lime which helps to eliminate bacteria like Ecoli (Boynton and Gutshick, 1975). For lime to be useful for water purification, the carbonate rock must contain $CaCO_3$> 80%, MgO < 2%, SiO_2< 0.01%. The Owan-East marble is not suitable for water treatment due to its higher overall SiO_2 content (2.9%) which exceeds the recommended 0.01%.

5.4.2 Neutralization of sewage

The use of lime extends further into sewage treatment, treatment of acid water, and removal of silica and phosphate fromsewage discharges. Sewage by its nature are liquid wastes that are deleterious and could produce several health consequences within the environment. For carbonaceous material like lime to be useful for sewage neutralization, the specifications are like those for water softening and purification. To be applicable for water treatment as filtering gravel, the lime must contain $CaCO_3$which exceed 95%, CaO value greater than 53.2%, and SiO_2 less than 1%. The Owan-East marble is not applicable in this regard as it has $CaCO_3$< 95%, CaO< 53.2% and SiO_2 greater than 1%.

5.4.3 Agronomic Application

Soil amelioration with quicklime or hydrated lime is one of the oldest applications of marble (Ojo et al. 1998). Lime neutralizes acidic soils by enhancing soil fertility. To be useful as acid neutralizers, the carbonate must show low grit content.Marble also finds agronomic application in manufacture of poultry feed. For this application, the marble may not be considered on stringent purity. However, Al_2O_3 content must be lower than 1.5%. Considering this specification, Owan-East marblesatisfies thecondition for use in poultry feed as it contains an average Al_2O_3 content of 1.45%.

In recent times, limestone and marble are playing a new agronomic role in the manufacture of fertilizers such as calcium ammonium nitrate. Majority of calcium ammonium nitrate is used as fertilizer which roughly contains 8% calcium and 21-27% nitrogen. Calcium Ammonium Nitrate (CAN) is desired on acidic soils as it acidifies soil less than many common nitrogen fertilizers. Calcium ammonium nitrate fertilizer including nitrogen and quick-acting calcium has hygroscopic characteristics and deteriorates easily over time particularly in humid environments. To be useful for this purpose, the marble should contain $CaCO_3$ more than 85%, a CaO value greater than 47.6 %, SiO_2 value that is less than 5%. Because of this specification, the Owan-East marble can be a raw material in the manufacture of fertilizer as its average values of $CaCO_3$ (91. 24 %), CaO (57.27%), SiO_2 (2.90%) fall within the recommended limits.

5.4.4 Filler/Extender

In addition to their application in the manufacture of rubber, plastics and toothpaste, fillers and extenders are valuable in other areas like paint, paper, animal feed, and pharmaceuticals. The requirements for this application include CaO value that exceeds 52 %, Al_2O_3 value below 0.2 %, Fe_2O_3 below 0.2%. Silica and magnesia must be lower than 3 %,SO_3< 0.2% and P_2O_5< 0.15%.

The composition of Owan-East marble reveals the following: CaO (57%), Al_2O_3 (1.45%), Fe_2O_3 (0.82%), SiO_2 (2.90%); and P_2O_5 (0.10%), while SO_3 was not determined. Even though, the marble does not meet all the necessary conditions for use as filler/extender, it met some e.g. CaO, SiO_2 and P_2O_5 are within the acceptable limits. On this basis, the Owan-East marble may be blended in certain proportion with other marble to generate the desired chemistry for it to be used as fillers and extenders.

6. Conclusions

The marble deposit occurs as lenses in Owan-East area of the Igarra schist belt, southwestern Nigeria. The marble is associated with muscovite schist, polymictic metaconglomerate, calc-gneiss and quartzite, and occurs in three compositional varieties (the white, grey, and banded). The strong foliation in the banded marble is related to the stress regime associated with the emplacement of Igarra granite in the vicinity of the marble deposit.

Mineralogically, the marble contains lower percentage of calcite compared to most other marble in the basement complex of Nigeria. The dominant minerals in the marble are calcite and dolomite while other minerals (quartz, feldspar, and biotite) occur in traces.

The ancient protolith (limestone) for the marble deposit in Owan-East was formed in a low saline (freshwater, brackish or paralic) environment.The high silica content reflects shallow depth, possibly a continental shelf or nearshore environment of deposition.The unprecedented high alumina and iron contents in the marble probably indicate incursion of aluminosilicate impurities into the original limestone, particularly the foliated variety prior to metamorphism.

The assessment of industrial suitabilityof the marble reveals that the silica Ratio (SR), the Alumina ratio (AR) and Lime Saturated Factor (LSF) fallsoutside the recommended range for cement production.Equally, it does not satisfy the requirements for production of calcium carbide, bleaching powder, water treatment, pesticide, sewage neutralizer, sugar or glass. However, the marble is useful as raw material in the manufacture of metallurgical refractory material, poultry feeds, sodium alkalis and to some extent as fillers and extenders.

References

Ajibade AC (1980).Geotectonic evolution of the Zungeru region, Nigeria. Ph.D. Thesis, University of Wales (Aberystwyth) 303p.

Ajibade AC, Fitches WR (1988).The Nigerian Precambrian and thePan-African Orogeny.Precambrian Geology of Nigeria 1:45-53.

Akinola OO, OlaOlorun OA (2012). Lithogeochemistry and Industrial Appraisal of Igbetti Marble, Southwestern Nigeria. *African Journal of Sci.Technology Innovation and Development* 4(2): 173-187.

Akinola OO, OlaOlorun OA (2020). Lithological features and chemical characterization ofmetamorphosed carbonate rocks in Igue, SouthwesternNigeria. *Journal of Geology and Mining Research* 8(2): 1-10.

Annor AE (1983).Metamorphism of pelitic rocks in relation to deformation episodes around Okenne, Nigeria. *Nigerian Journal of Mining and Geology* 20(1 & 2): 17-24.

Ayodele MO, Ofuyah W (2017).The Geology of Eshiawa in Igarra Area, Southwestern Nigeria. International Journal of Research 4(6) : 1265-1275.

Bhargava DN (1987). Report of expert group on classification of minerals with regard to their possibleoptimum “industrial uses”: Government of India, Ministry of Steel and Mines, Department of Mines, Delhi, India: 42p.

Black R, Caby R, Moussine-Pouchkine A, Bayer R., Bertrand JM et al. (1979).Evidence for Late Precambrian plate tectonics in West African. *Nature*, 278: 223-226.

Boynton RS, Gutshick KA (1975).Chemistry and Technology of Lime and Limestone. John Wiley and Sons Inc., New York: 578p.

Brownflow AH (1996).Geochemistry (2nd Ed). Prentice Hall: 350-351.

Clarke FN (1924).The Data of Geochemistry (2nd Ed). Washington Government Printing Office: 782p.

Dada SS (1998).Crust-Forming ages and Proterozoic Crustal Evolution of Nigeria: a Reappraisal of Current Interpretations. *Precamb. Res*. 87: 65-74.

Davou DD, Ashano EC (2009). The Geochemical characteristics of the marble deposit east of the Federal Capital Territory (F.C.T), Nigeria. *Global Journal of Geological Sciences* 7(2): 189-198.

Ekwueme BN(2003).*The Precambrian Geology and Evolution of the South Eastern Nigerian Basement Complex*. University of Calabar Press: 240p.

Elueze AA (1981).Geochemistry and petrotectonic setting of metasedimentary rocks of the Schist Belt of Ilesha area, Southwestern Nigeria. *Journal of Miningand Geology* 19(1): 194-197.

Elueze AA (2000). Compositional appraisal and petrotectonic significance of Imelu banded ferruginous rock in the Ilesha Schist Belt, Southwestern Nigeria. *Journalof Mining and Geology* 36(1): 9-18.

Elueze AA (2002). *Compositional Character: Veritable Tool in the Appraisal of Geomaterials.* An Inaugural Lecture, University of Ibadan, Ibadan, Nigeria: 43p.

Elueze AA, Okunlola OA (2003).Petrochemical and petrogenetic characteristics of metas-edimentary rocks of Lokoja-Jakura Schist Belt, central Nigeria. *Journal of Mining and Geology* 39(1): 21-27.

Elueze AA, Jimoh AO, Aromolaran OK (2015). Compositional Characteristics and Functional Application of Obajana Marble Deposit in the Precambrian basement complex of central Nigeria.*Ife Journal of Science* 17(3) : 591-603.

Emofurieta WO Ekuajemi VO (1995). Lime products and economic aspects of Igbeti, Ososo and Jakura marble deposits in Southwestern Nigeria. *Journal of Miningand Geology* 31(1): 89-97.

Erhuero JB (1986).Installed Capacity Utilization in the Nigeria Cement Industry: the case of Bendel Cement Company Limited. Unpublish M. Sc Dissertation, University of Benin, Nigeria: 128p.

Fatoye FB, Gideon YB (2013). Geology, and Occurrence of Limestone and Marble in Nigeria, *Journal of Natural Sciences Research* 3(11): 60-65.

Ladipo K (1986).Tidal Shelf depositional Environment for the adjourning sandstone in the Igarra schist belt, Southern Nigeria.Journ. of Science 2(3): 25-30.

McCurry P (1976). The geology of the Precambrian to Lower Palaeozoic rocks of northern Nigeria: A review. In: Kogbe, C.A. (Ed.), *Geology of Nigeria*. Elizabethan Publishing Co. Lagos: 15-39.

Obasi RA Anike OL (2012).Geochemistry and appraisal of the economic potentials of Calc-gneiss and marble from Igarra, Edo State, Southwest Nigeria.*ARPN Journal of Scienceand Technology* 2(10): 1018-1021.

Obiadi II, Anike OL, Ajaegwu NE, Anakwuba EK, Akpunomu EO, Ezim EO (2012).Imaging Subsurface Fracture Characteristics using 2D electrical Resistivity Tomography. *International Research Journal of Engineering Science Technology and Innovation* 1(4) : 103-110.

Obiora SC (2005).*Field Descriptions of Hard Rocks with examples from the Nigerian Basement Complex (1st Edition)*. Snap Press (Nig.) Ltd. Enugu: 14p.

Odeyemi IB (1976). Preliminary report in the relationships of the Basement complex rocks around Igarra, Mid-west. In: Geology of Nigeria by C.A (Ed) Elizabethan Publ. Lagos: 59-63.

Odeyemi IB (1977). On the Petrology of the Basement complex rocks of Bendel State of Nigeria, Ph. D. Thesis, Unpublished. University of Ibadan Nigeria: 223p

Odeyemi IB (1990). The Petrology of a Pan-African pluton in Igarra area, Southwestern Nigeria, *Nigerian Journal of Sciences*, 24,(142). Pp. 181-193.

Odeyemi IB Rahaman MA (1992).The petrology of a composite syenite dyke in Igarra, southwestern Nigeria. *Journal of Minning and Geology*. 28 (2): 255-263.

O' Driscoll M (1988).Burnt lime/dolime: Seeking markets green. Industrial Minerals; *AIME;*22: 1- 10.

Ojo AM, Abimbola AF, Okunlola OA Oguntoyinbo FI (1998). Agro-geological studies of limestone, phosphate and gypsum occurrences in Dahomey basin southwestern Nigeria in relation to soil acidity amelioration. Book of Abstracts, 35th

Okonkwo CT (1992).Structural geology of basement rock of Jebba area, Nigeria. *Journal of Mining and Geology* 28(2): 203-209.

Oloto IN, Anyanwu DE (2013).Petrology of Ibillo-Mangongo area of Igarra, Edo State, Nigeria. *Adv. Appl. Sci. Res*. *4*(3): 140-145.

Oluyide PO (1988).“Structural Trends in the Nigerian Basement Complex”. In: P.O. Oluyide.

Precambrian Geology of Nigeria.Geological Survey of Nigeria, Lagos Nigeria: 93-98.

Onimisi M, Ojonimi IT,Kolawole MS, Ibimode TB (2017). Field occurrence, chemical composition and Industrial Application of Ekinrin-Adde Marble Deposit Kogi State, Northcentral Nigeria.*Confluence Journal of Environmental Studies* 11(2): 37-46.

Oyawoye MO (1964). The geology of the Nigerian Basement Complex- A survey of our present Knowledge of them. *J. Niger. Min. Geol. Metall. Soc.* 1: 87-103.

Panda H (2016). The Complete Technology Book on Asbestos, Cement, Ceramics and Limestone. Asia Pacific Business Inc.: 592p.

Rahaman MA, Ocan O (1978).On Relationship in the Precambrian Migmatitic Gneiss of Nigeria. *J. Min. Geol.* 15: 23-32.

Rahaman MA (1988). Recent advances in the study of the basement complex of Nigeria. *In: Geological Survey of Nigeria (Ed). Precambrian Geol. Nigeria*: 11–43.

Russ W (1957).The Geology of parts Niger, Zaria and Sokoto provinces, with special reference to the occurrence of gold. *Bull Geol. Survey Nigeria* 27: 22– 27.

Scott TW, Durham AC (1984).Problems in the evaluation of limestones for diverse market. *Sixth Industrial Mineral International Congress,* Toronto: 21p.

Talbot C (1982). Cement and the Geologist: In Course Note on Rocks as Construction Material. AGID Headquarters, Bangkok, Thailand: 120p.

Truswell JF, Cope RN (1963).The Geology of parts of Niger and Zaria Provinces, Northern Nigeria. *Geol. Surv. Nigeria Bull.* 29: 52.

Turner DC (1983). Upper Proterozoic Schist Belts in the Nigerian sector of the Pan-African Province of West Africa. *Precambrian Research* 21: 55-79.