ANALYSIS OF CHEMICAL CONSTITUENTS OF ROCKY OUTCROPS IN SOLLARE, GULANI LOCAL GOVERNMENT AREA OF YOBE STATE, NIGERIA

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ABSTRACT

This research work focused on analyzing the chemical composition of the rocky outcrops in Sollare, Gulani Local Government Area of Yobe State with the aim of determining the economic importance of the rocks. The field equipment used included GPS, prismatic compass, geographic hammer and polythene bags. Three (3) fairly sizeable pieces of rocks with fresh surfaces were prepared and collected one from each site as representative samples and taken to the laboratory for geochemical analysis. Preparation of the samples involved the use of analytical balance, weighing boat and aluminum press cups- Herzurg swing mill and Herzurg press machine. XRF (X-ray Fluorescence) analysis was carried out on the 3 samples at the Laboratory of Ashaka Cement Factory. Results of the analysis showed that the average percentage of Calcium Carbonates was 96.333%. Some of the chemical constituents of the 3 samples included silica ($Si0_2$ 2.905%), aluminium oxides (Al_2O_3 1.937%), iron oxides (Fe_2O_3 1.359%), magnesium oxides (MgO_2 0.660%) and potassium oxides (K_2O, 0.115%). The outcrops covered an area of 45.56 km^2. Analysis of interview responses on the cultural values attached to the rocky outcrops showed that there were no values attached to the rocks. For time and financial constraints, chemical analysis on other rock outcrops farther away from Sollare could not be carried out. With this result, it is believed that Companies could exploit the rocks for the production of cement and other valuable products. It is also recommended that some researchers should conduct some researches on those rocks, and on rocks elsewhere in Nigeria with a view of determining their chemical composition in order to establish their economic importance.

Keywords: Analysis, Chemical, Constituents, Rocky Outcrops, Sollare

INTRODUCTION

Rock is a naturally occurring solid aggregate of one or more mineral matter and a constituent of the earth's crust Clamosa, (2020). The disposition of rocks, especially in massive forms, is explained by natural phenomena. The study area, located within the northern part of Gongola basin within the Upper-Benue Trough, comprises of one of the three major groups of rocks commonly found in northern Nigeria, namely Precambrian basement complex, Cretaceous sediments and Tertiary/Quaternary volcanic rocks of the Biu Plateau (Falconer, 1911 and Falconer & Raeburn 1923). One of the early detailed geological works including stratigraphy, Paleontology, structural aspect, economic geology and hydrogeology covering part of Gombe, Yobe, Borno and Adamawa states was carried out by Abubakar, Dike, Obaje, Wehner & Jauro (2008). In late 1980s through 1990s the basement complex of North-eastern Nigeria, and to some extend the Cretaceous sediments in the region, have been studied with respect to the structural settings, geochemistry of Uranium (U) and mineralization (Abubakar, *et al,* 2008),

Numerous low grades occur within the Gubrunde Horst (basement complex) of sedimentary rocks adjacent to Gulani. This includes Ashaka and Gongila Formations (Abubakar, *et al,* 2008), and other Uranium minerals include those of Gumti and Mika (Dada, 2006). Moreover, various workers have studied the solid minerals associated with the cretaceous and younger sediments of the Upper Benue Trough (Rahaman, 1988; Idowu and Ekweozor, 1993). Mineral deposits hosted by sediments in the region include evaporated diatomites, limestone, clays, coal and sophist. Barite have been reported in several places within the Benue trough forming a metalogenic belt extending from Abakaliki in the south east of the trough through Akwana, Arufu and Azara in the middle Benue trough.

Ayuba, Audu and Chahul (2015) carried chemical analysis of some limestone samples from the Middle Belt Zone, Nigeria and their possible industrial applications. The study found out that most of the limestone samples met some industrial specifications. The samples of the rocks were collected from different locations in the Middle Belt which could make exploitation of the limestone as raw resources difficult and uneconomical.

In studying the uses of limestone, James, Timothy and Greta (2008) indicated that when rich in calcium carbonate, have a number of uses besides cement making. For instance, calcium carbonate is an important ingredient in fertilizer making. Naturally, limestone exists as calcite and dolomite. When heated, and in some cases combined with salt, limestone is used in making many everyday products such as paper, glass, paint and varnish, soap and detergents, textiles, refractories, baking powder, and pharmaceuticals, including milk of magnesia and bicarbonate of soda (James, *et al*, 2015). Finely ground, they are used to control coal mine dust, to collect sulfur dioxide from power plant exhaust, to sweeten soils, and as ingredients in making fertilizer and stock feed (James, *et al,* 2008). Limestone is used extensively in Michigan to refine beet sugar. When burned in a kiln to drive off gases, calcite and dolomite form burnt lime. Among the uses for burnt lime are water and sewage treatment, acid waste neutralization, and road base stabilization. Crushed calcite and dolomite are used in concretes, road constructions, building materials, and as filler in asphalt Ayuba, *et al* (2015). Besides, there are other uses of limestone and they include products such as calcium supplement pills, antacid tablets, high-quality paper and white roofing granules and marble table tops (James, *et al*, 2008).

Detail analyses and accurate investigations of chemical constituents of rocks in Sollare village and its environs, the study area, were minimal. Therefore, this study provided detailed analysis of the chemical composition of the rocky outcrops at Sollare. Effort was also made in providing information on the associated cultural values of the rocks. Map of the area was produced through the application of ArcGIS software in order to locate all the rock composite units of the study area. This was followed by thorough laboratory analysis of samples of the rocks collected from the three locations of the outcrops. Questionnaire was administered to some individuals in the study area to find out whether or not the community has some cultural values attached to the rocky outcrops. Generally, the geology of the study area consists of unconformably rock ranging from northern part of Sollare to the western part of the village, and volcanic rock ranging in age from Cretaceous to Quaternary (Abubakar, *et al,* 2008).

MATERIALS AND METHODS

Study Area

Sollare village is located in Gulani L. G. A. of Yobe State and it lies between latitudes 11^0 6’ N and 11^0 30' N and longitudes 11^0 31' E and 11^0 33' E of the Greenwich Meridian as shown in Figure 1.

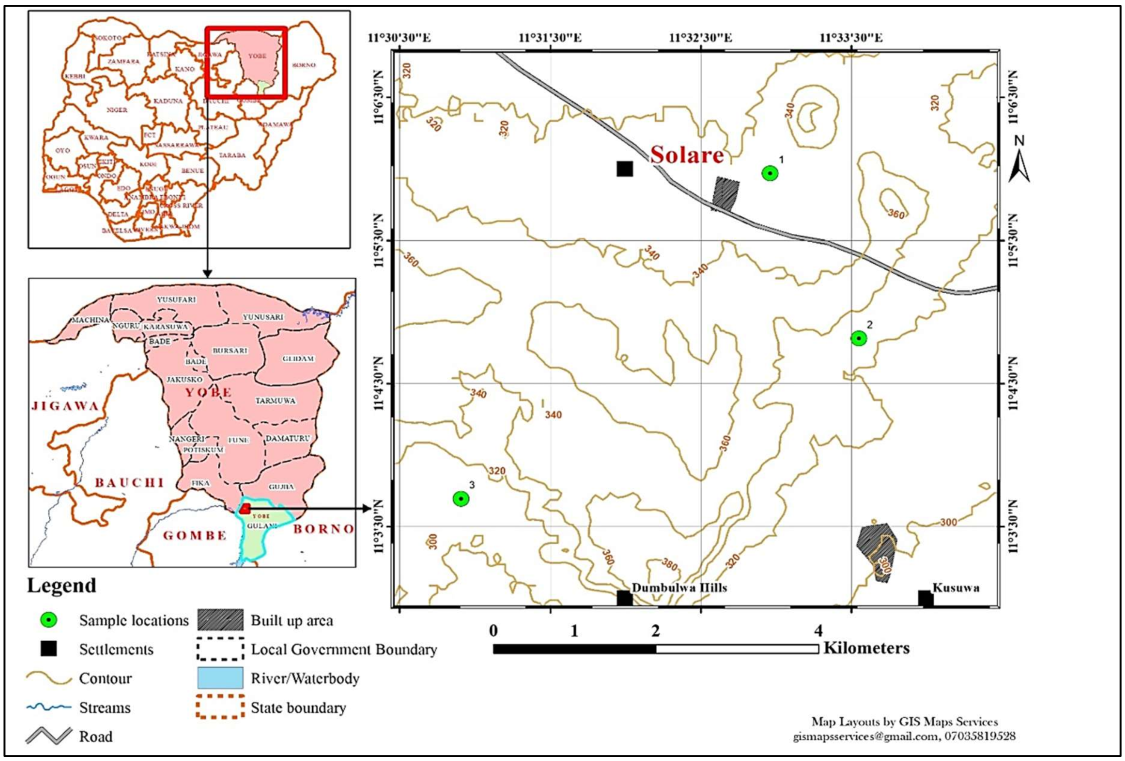

Fig. 1: Gulani L. G. A. showing Study Area and sample points
Source: Federal Ministry of Land and Survey, 2019

The geology of Gulani L. G. A. which is presented in Fig. 2 revealed that the area consists of Precambrian basement complex rocks, Cretaceous sediment and Tertiary or Quaternary Basalt of Biu Plateau. The basement complex rock is represented by diorite, porphyritic granite and coarse porphyritic biotite. The sediment includes sandstone, siltstone, shale, limestone of the Dumbulwa, Gongila, Fika, Bima, Yolde and Pindiga Formations (Benkhelil, Guiraud, Ponsard and Saugy, 1989). Epigenetic barite-copper mineralization occurs with barite vein restricted to Bima and Yolde Formations or sandstone while the copper mineralization occurs in granite. The Gongila Formation is composed of limestone.

Petro graphic study indicates that the diorite is largely composed of andesine plus hornblende and associated quartz and iron oxides. The granite on the other hand, consists essentially of quartz, microcline and orthoclase with minor biotic and iron oxides. The Bima and Yolde sandstones are composed of quartz, microcline plagioclase and accessories biotite and opaque crystals. The large quartz and microcline crystals in both granite and sandstones are fractured. The Kanawa members of the Pindiga Formation are made up of shale interblended with limestone. The limestone is interblended with both crystalline and fossiliferous types. The basalt consists of labradorites, olivine, augite and opaque types. Transmitted light petrography of the hydrothermally altered Bima and Yolde sandstones show the presence of quartz, barite and microcline. The barite occurs with pore spaces in infilling minerals between the quartz and the microcline and within the fractures of these brittle minerals.

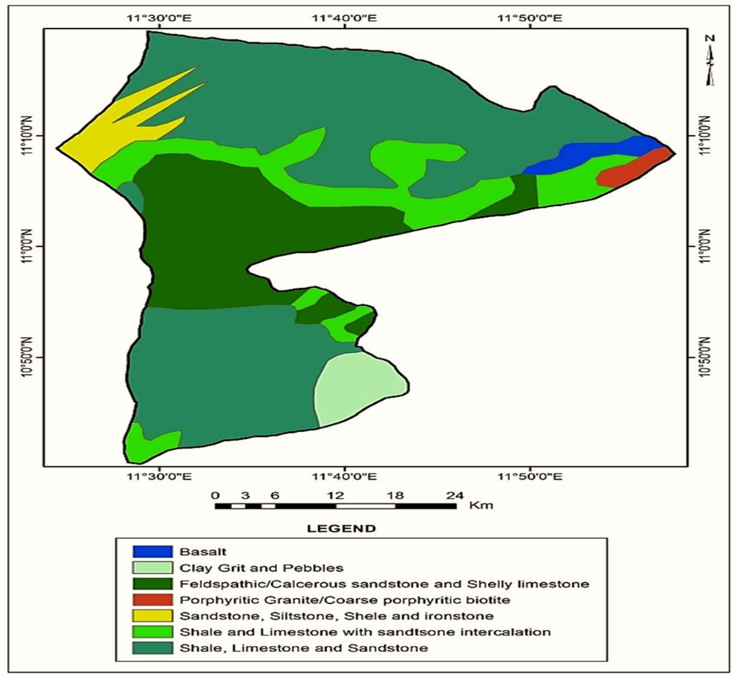

Figure 2: Geological Map of Gulani Local Government Area
Source: Nigeria Geological Survey Agency,2019

The Benue trough is commonly subdivided into three main domains, the lower, the middle and the upper Benue troughs. The Upper or northern Benue Trough represents full marine incursion into the trough which occurred during Turonian –Santonian times Obaje (2009) and Mbiimbe, Tabale and Barka (2019). The Upper Benue Trough consists of Kerri-Kerri Formation, Gombe Sandstone, Gongila/Pindiga Formations, Yolde and Bima Formations Mbaya (2012); Mbiimbe, *et al*, (2019) and are shown in Fig 3.Lithologically, the formations are characterized by dark/black carbonaceous shales and limestone intercalated with pale coloured limestone, shales and minor sandstones (Mbiimbe, *et al*, 2019). The Gongila Formation is exposed in areas around Bajoga/Ashaka and has been affected by erosional processes exposing their layers at locations within the Benue Trough as can be deduced from Figure 3. The lithostratigraphic piles include shale, sandstone and some pyroclastic in a shallow marine environment during the Albian times.

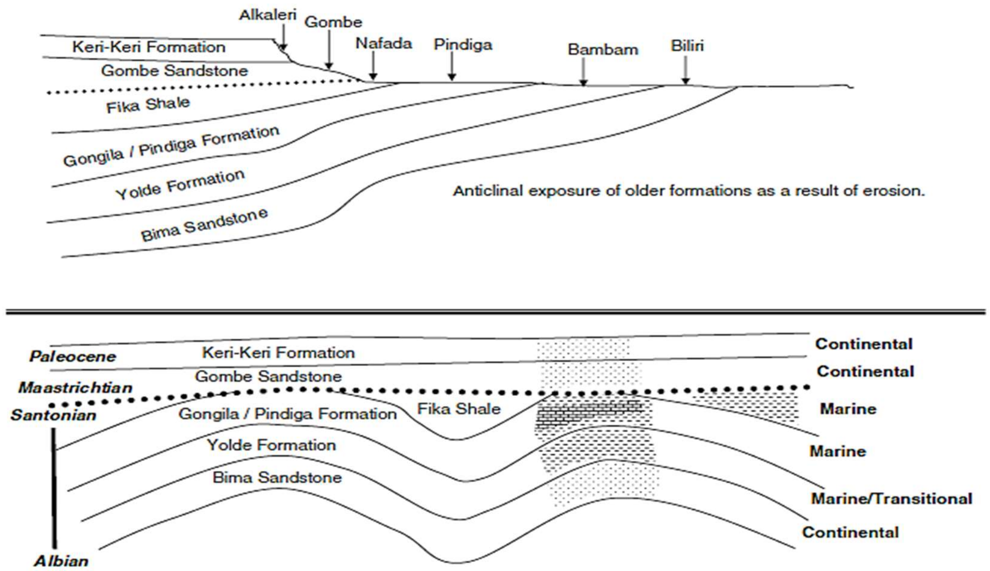

Figure 3: Stratigraphic Succession in the Gongola Area in the Upper Benue Trough (After Mbiimbe, *et al*, 2019)

Collection of rock Samples

The geographic hammer was used in blasting portions of the faces of the rocky outcrops until fairly sizeable pieces with fresh surfaces were obtained. Only three (3) fresh samples one from each site of the rocky outcrops were collected for analysis in the laboratory. Each of the samples collected was labeled using masking tape for identification and each was placed inside a separate polythene bag to protect them from contamination. The three samples were taken to Ashaka Cement Company laboratory for analysis.

Analysis of Geochemical Parameters

This involved geochemical analysis of the representative samples for mineral constituents of the rocky outcrops. XRF (X-ray Fluorescence) analyses were carried out on each of the three (3) samples to determine their mineral constituents.

Pressed Pellet Preparation

0.4g of stearic acid was weighed and put into a weighing pan and 20g of each of the samples was added. The mixture was transferred into grinding vessel. The vessel was placed in position inside the swing mill machine and the clamp down was pressed.

Appropriate program for the sample was selected (from chart in the preparation room). Press the Start button of Herzurg milling machine was pressed and the programme was allowed to run to the end. The vessel was removed and and the sample poured out on a clean sheet of paper. An aluminum cup was filled to about 1/3 of its volume with stearic acid. The cup was filled to the brim with the grinded sample and the surface was carefully leveled with a spatula. Press The start button of the press machine was pressed and the plunger rose up.The cup was placed on it when it was in the up position and the plunger was allowed to take the cup down. The Die-head was inserted on the sample and screwed the fastener to hold it in position. After the pressing action was concluded, the start button was pressed and waited for 1minute. The fastener was loosened and the press button was started. The die-head, together with the pressed pellet, were lifted out. The die-head and the pellet were carefully removed and the sample ID was written in pencil on the back of the pellet (the exposed surface of pellet was avoided from contamination).

Note that if the surface of the pellet cracked, it should not be analyzed. Repeat another pellet but wait for two minutes after pressing before removing it. Clean the vessel and work area before leaving . The pellet was placed face down in the XRF computer machine and then inserted in the loading position. From the measure and analyses window of the XRF computer (Super software), the appropriate program for the sample was selected. The ID of the sample was entered and clicked 'measure'. Waited for the analysis to be completed. The result was printed out as presented in Table 1.

X-Ray Florescence Spectrometry

Wavelength Dispersive X-ray Fluorescence (WDXRF) is a none destructive analytical technique used for identification and determination of concentrations of elements' presence in solids, powdered and liquid samples at trace levels often below one part per million. It has up to 100% wide application in industries and research drives. The technique has the ability of carrying out accurate, reproducible results and at very high speed with modern computers-controlled systems. Operation is fully automated and results are typically delivered within minutes, or even seconds.

The XRF analytical method depends on the fundamental principles that are common to several other instrumental methods involving interaction between electron beams and x-ray with samples. When sample atoms are irradiated with high energy primary X-ray photons electrons are ejected in the form of photo electrons. This creates electrons "holes" in one or more of the orbital's, converting the atoms into ions which are unstable. To restore the atoms to a more stable state, the holes in inner orbital are filled by electrons from outer orbital's such transitions may be accompanied by an energy emission in the form of a secondary X-rays photons, a phenomenon known as fluorescence. The various electrons orbital are called KLMN e.t.c where K is closest to the nucleus and each corresponds to a different energy level and the energy (E) of emitted fluorescent photons is determined by the difference in energies between the initial and final orbital for the individual transition.

The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behavior of atoms when they interact with x-radiations when materials are excited with high energy, short wavelength. When radiated (e.g. x-ray), an atom becomes ionized if the energy of the radiation is sufficient to dislodge a tightly held inner electron, the atom become unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to decrease in the binding energy of inner electron orbit compared with an outer one. The emitted radiation is of lower energy that the primary incident, x-rays, is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbital in a particular element, the resulting fluorescent x-ray can be used to detect the abundance of elements that are present in the sample.

RESULTS

Results of laboratory analysis of major oxides in the rock samples are shown in Table 1 and depicted in figure 4.

Sample 1 shows the concentration of calcium oxide as 55.736%, and that of silica content is 1.788%, with iron oxide as 1.354%. Aluminum oxide has 1.695% as shown in Table 1.

Table 1: Result of XRF analysis of the 3 samples (Ashaka Cement Laboratory)

Compound	Sample I (%)	Sample II (%)	Sample III (%)	Average (%)
$Si0_2$	1.788	3.756	3.171	2.905
Al_2O_3	1.695	2.097	2.020	1.937
Fe_2O_3	1.354	1.397	1.326	1.359
CaO_2	55.736	53.005	53.182	53.974
MgO_2	0.485	0.706	0.790	0.660
SO_3	0.605	0.617	0.620	0.614
K_2O	0.038	0.165	0.142	0.115
Na_2O	0.075	0.079	0.089	0.081
P_2O_5	0.070	0.105	0.228	0.134
Mn_2O_3	0.135	0.500	0.543	0.393
TiO_2	0.095	0.109	0.106	1.103
$CaCO_3$	99.478	94.603	94.919	96.333

Source: Authors' fieldwork at Ashaka Cement Laboratory, 2019

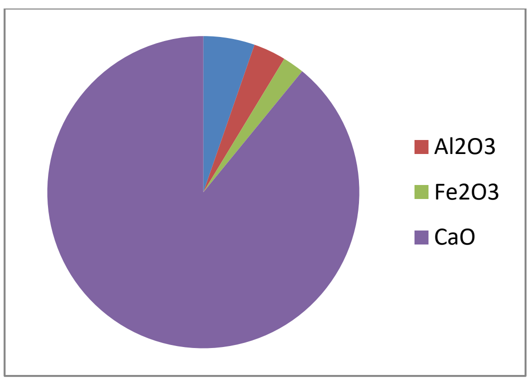

Figure 4: Major Chemical Constituents in Sample 1.

Source: Authors' fieldwork, 2019

The analysis of Sample 2 shows that the result of silica oxide is 3.756, with Aluminum Oxide of 2.097 and iron oxide of 1.397 with concentration of calcium carbonate 53.005 as shown in Figure 5.

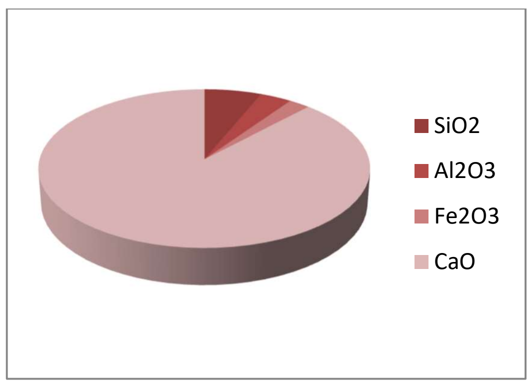

Figure 5: Major Chemical Constituents in Sample 2

Source: Authors' Laboratory Analysis, 2019

The analysis of Sample 3 shows that the concentration of Calcium Carbonate is higher than what was obtained in Samples 1 and 2 shown in Figure 6.

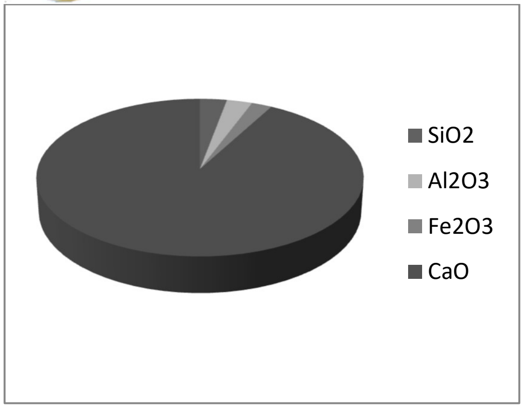

Figure 6: Major Chemical Constituents in Sample 3

Source: Authors' Laboratory Analysis, 2019

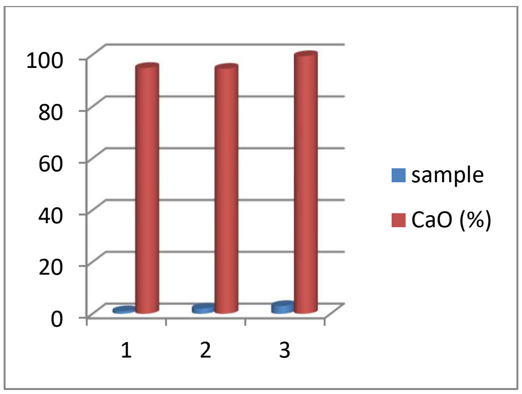

Figure 7: Proportion of CaO_2 in relation to other oxides

Source: Authors' Laboratory analysis, 2019

The result obtained from the laboratory was subjected to Analysis of Variance (ANOVA) in determining whether or not there were variations in the concentration and composition of chemical constituents of the rocky outcrops in the three locations in Sollare and its environs. In addition, tables and pie charts were used in presenting the results of the research. Questionnaire was administered to 55 community members in order to find out cultural values attached to the rocky outcrops in Sollare community.

Study Area Coverage

The study area covered 45.56 km^2 (Centre for GIS and Remote Sensing Jos, 2019). The area covered has high concentration of calcium carbonate (limestone). In addition, the distance between Ashaka Cement Factory and the study area is about 35 km by road which means that it is within easy reach of the factory when compared with the distance to the company's alternative source of energy (coal) at Maiganga west of Kumo which is being conveyed by tracts to the factory covering over 120 km).

Table 2: Analysis of Variance (ANOVA)

Variance	Sum of Squares	Df	Mean Squares	Siq.
Samples	1.084	2	0.542	0.999
Error	30356.71	33	919.9	
Total	30357.79	35		

Source: Authors' fieldwork, 2019

Demographic Characteristics of Respondents

Elements of demographic characteristics of respondents considered were tribal, sex and occupation. Cultural values attached to the rocky outcrops were also considered and presented in Tables 3, 4, 5 and 6.

Table 3: Tribal Composition of Sollare

Tribe	Frequency	Percentages (%)
Bolewa	24	43.7
Fulani	26	47.2
Babur	2	3.6
Kare-Kare	3	5.5
Kanuri	0	0
Total	**55**	**100**

Source: Author's fieldwork, 2019

Table 4: Sex composition of Respondents

Respondents	Frequency	Percentage (%)
Male	41	74.55
Female	14	25.45
Total	55	100

Source: Authors' fieldwork, 2019

Table 5: Occupational Status of People in Sollare

Occupation	Frequency	Percentage (%)
Civil servant	5	9.09
Farmers	38	69.09
Others	12	21.8
Total	55	100

Source: Authors' fieldwork, 2019

Table 6: Cultural Values attachment to Sollare Rocky Outcrops

Responses	Yes	No	Total
Knowledge about rocks	54	1	55
Rocks have Cultural value	0	55	55
Accepted mining of rocks	44	11	55

Source: Authors' fieldwork, 2019

DISCUSSION

The physical nature of the rocky outcrops at Sollare and its environs, their shapes and structure describe the environment of limestone. The colour of the rocks is brown to yellowish–brown. Soils are clayey and covered by blossom vegetation especially during the rainy season. Other common features in the environment are the presence of dotted sinking holes which depicts karst topography.

The concentration of calcium oxide (CaO_2) in the three rock samples determined the proportion of calcium carbonate ($CaCO_3$) in the samples. Considering the concentrations of Calcium Carbonates in the samples in relation to other oxides, carbonates constitute the major chemical constituents of the rocky outcrops while the other oxides made up small percentages as depicted in Fig. 7. The mean value of carbonates in the three representative samples of the rocky outcrops is 96.333% (99.478 +94.603+94.919) and it shows that the rocky outcrops at Sollare and its environs is a limestone that consists of high concentration of calcium carbonate and a small mean percentage of other oxides as pictorially shown in Fig. 7. This is in line with the observation that large amount of limestone is found in Nafada and Funakaye LGAs in Gombe State (Maina, 2019) which are bordering Gulani LGA with Sollare located at about 35 km by road to Ashaka Cement Factory. Limestone is described as "A rock made from calcium carbonate and most limestone rock contains significant amounts of magnesium, silicates, manganese, iron, titanium, aluminium, sodium, potassium, sulfur (as sulphides or sulphates Murray, Miller and Kryc (2000), and Ayuba, Audu and Chahul (2018). The limestone at the three locations at Sollare is a high grate in terms of quality which can be used for cement making or for any industrial applications in which calcium carbonate is required. Meanwhile, Ashaka cement industry can look over this area as additional limestone reserve for future exploitation.

The concentration of the chemical constituents in the three rock samples was subjected to analysis of variance (ANOVA) to test whether or not there is difference in the concentrations of chemical constituents with the formulation of the following hypothesis:

H_o: There is no difference in the concentrations of chemical compounds across the three locations.

H_1: There is difference in the concentrations of chemical compounds across the three locations.

Since p-value (0.999) is greater than 0.5 (level of significance) as shown in Table 2, we accept H_O that there is no significant difference in the concentrations of chemical constituents between and among the three samples and therefore conclude that there is no difference in the chemical composition of compounds in the rocky outcrops across the three locations in Sollare and its environs. Analysis of sex composition of the respondents showed that 74.55% were males who were aged 45-55 years while females made up 25.45% of the same age group as shown in Table 4. Exposure of males to participation in gainful activities than females accounted for the higher responses from them. This indicates that the males were more engaged in the community than females, a situation that is attributable to culture and religious factors which hinder adult females from participation in the day-to-day activity of the community.

Considering the occupational status of the respondent's shows that majority of the inhabitants of Sollare were engaged in farming (69.09%) and civil servants made up 9.09% while other occupations made up 21.8% as reflected in Table 5. Cultural value attachment such as religion and/or tradition to hills, forests or some other natural features within the vicinity of settlements of some communities in Africa, and in Nigeria in particular, is a common phenomenon. This research considered whether or not there is any cultural value attached to the rocky outcrops around Sollare village. Some members of the community, who were predominantly Bolewa and Fulani, were interviewed and the responses gathered are presented in Table 3. Fulani, the larger tribal group, made up 47.2% of the people living in Sollare while Bolewa constituted 43.7%. Kare-Kare and Babur constituted 5.5% and 3.6% respectively of the people in Sollare as shown in Table 2. Although Kanuri is a dominant tribe in Yobe State, group discussions with some members of the community revealed that no Kanuri was living in Sollare as at the time of the study. With regards to whether or not the rocky outcrops around Sollare village have cultural value(s) to the community, analysis of responses from the people interviewed showed that none (0) of the respondents indicated that the community has religious and/or traditional value attached to the rocks (Table 6). Responses as to whether or not the rocky outcrops would be accepted by the community to be mined indicated that 80% of the respondents were positive that the rocks could be accepted to be mined. However, 20% disagreed to mining the rocks. This view point could be associated with their awareness of the negative impact of mining, such as land degradation, pollution of water and air, as well as noise pollution all of which could cause hardship and unpleasant consequences to their community. This is in line with Kittipongvise's (2017) observation of environmental impact of limestone quarrying operations in Thailand which he opined that mining operations should ensure prevention and reduction of pollution in order to keep all safe and healthy.

CONCLUSION

The physical nature of the rocky outcrops, that is their shapes, structure, colour of the rocks, clayey soils and the presence of dotted sinking holes, describes the environment of limestone. These, and couple with the high concentration of calcium carbonate (96.333%) enable drawing a conclusion that the rocky outcrops in Sollare and its environs are limestone. Since all of the respondents indicated that the rocky outcrops have no cultural values attached to them, they could be mined with little or no resistance by members of the community.

Recommendations

The chemical composition of the rocky outcrops in Sollare and its environs is hugely limestone. Since the mineral (limestone) has a number of wide uses, it is recommended that firms and companies should take advantage of the mineral in the three locations in Sollare and exploit them for making some products that can be made out of it as there is market for them in Nigeria and in Africa. Government at the federal, state and local levels should create conducive environment for the utilization of the raw material which will serve as a large employer of labour. It is also recommended that composition and concentrations of rocks elsewhere in Nigeria should be analyzed with a view of finding out their economic values. The research report is recommended as a reference material for similar studies in other parts of Nigeria.

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