# **Geochemical Properties of Kalambaina Formation: Implication on Limestone and Marlstone Qualities for Industrial Uses, Sokoto Basin, Nigeria**

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*Abstract: Six samples were collected from Bua Cement Quarry site of Kalambaina Formation with a view towards determining the geochemical properties of the lithofacies, the industrial qualities and applications of the limestone and marlstone. Field outcrop litho-log description was carried out by noting the composition, textural attributes, fossil content, structures and diagenetic effect. The samples were subjected to geochemical analysis using atomic absorption spectrometry (AAS). Field result shows that Kalambaina sequence varies at the base from sparsely fossiliferous whitish limestone, overlain by light grey fissile shale, subsequently overlain by poorly fossiliferous limestone. The shale is intercalated within the upper and lower limestone beds. The nonfossiliferous limestone is unconformably overlain by sandstone, marlstone and micaceous shale which is unconformably capped by conglomeratic ironstone. The geochemical results that for the clastic facies (sandstone and shale) have SiO2, CaO, and Al2O<sup>3</sup> average concentration values of 66.7, 24.43 and 0.03 % respectively. Carbonate sediments have average concentration values in SiO2, CaO and Al2O<sup>3</sup> with 1.26, 52.36 and 0.56 % respectively, which implies that the carbonate were marine sourced while the clastic sediments were continentally derived. The CaO and SiO<sup>2</sup> values for the limestone (52.36, 1.27 %), and marlstone (50.10, 1.26 %) are at variance due to influx of clastic material into the marine carbonate. A comparison of the Kalambaina carbonate rocks with other deposits in Nigeria shows higher CaO content and lower SiO<sup>2</sup> value except Shagamu Limestone (CaO: 59.20 % and SiO2: 5.70 %) with higher concentration values. The kalambaina Limestone has a* *moderately high CaO value of 54.61 % and low SiO<sup>2</sup> content of 1.26 % which make it suitable for cement production, and other industrial purposes.*

*Keywords: Lithofacies, Kalambaina Formation, Fossiliferous limestone, Marlstone, Suitable for cement production*

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#### **1.0 Introduction**

Kalambaina Formation was described to separate the underlying older Dange Formation from the younger overlying Gamba Formation in the Sokoto Basin, Nigeria. The Kalambaina Formation contains chiefly fossiliferous limestone, marlstone and intercalated fissile shale. Different authors have described the lithofacies sequence of the Kalambaina Formation, they include Reyment (1965), Kogbe (1973, 1976, 1979), and Dessauvagie (1975).

Kalambaina Formation seems to appear differently at different locations with some facies thinning out or downgrading within the lithosequence. Among recent researchers that have described the lithosequence of the Kalambaina Formation include Offodile (2002), Ahmed *et al*. (2018), Ola-Buraimo and Mohammed (2024), Ola-Buraimo and Meshack (2024). Kalambaina Formation belongs to the Sokoto Group, dated Paleocene age (Offodile, 2002). However,

this assertion has been criticized and voided due to differences in the depositional ages of the three formations that constitute the Sokoto Group; thereby, nullifying the stratigraphic nomenclature and the terminology Sokoto Group (Ola-Buraimo and Mohammed, 2024; Ola-Buraimo and Meshack, 2024). The Kalamaina Formation was recently dated based on pollen and spore recovery and based on foraminifera studies at Kalambaina Quarry of BUA Cement factory, Kalambaina Village to be Early Maastrichtian to Paleocene age (Ola-Buraimo and Mohammed 2024; Ola-Buraimo and Meshack, 2024).

Most of the documented geochemistry studies on the Kalambaina Formation were based on hydrogeological study (Alagbe,

2006), sedimentology and geophysical study (Emmanual *et al*., 2021), and sequence stratigraphy (Hamidu *et al*., 2024). However, there is little or no work documented on the geochemical properties and industrial uses of the Kalambaina Formation. This precipitated the concept of investigating the geochemistry of the Kalambaina Formation with emphasis on the geochemical properties of the carbonate facies and their suitability for cement production and other industrial applications.

The study area is the Kalambaina Quarry site of the BUA Cement factory, located within Kalambaina Town, Wamakko Local Government, Sokoto State, Nigeria. The area lies between Latitude  $13^{\circ}$  3' 4" N to Longitude  $5^{\circ}$  9' 21" E (Fig. 1).





#### **2.0 Materials and Methods**

Fieldwork was carried out on the BUA Cement quarry site. Litho-description of the quarry mine was carried out which entailed careful observations on the rock types and tectonic deformation structure. Field observations include colour, grain size,

fossil content, diagenetic effect, structures, dip and strike. However, GPS was used for the location coordinates; collection and labelling of samples with markers, and sample bags were used for the collection of samples for onward laboratory studies. Fresh samples of selected limestones, marlstone, shale and sandstone samples were pulverized



and subjected to Atomic Absorption Spectrometry (AAS) method.

The Atomic Absorption Spectrometry (AAS) method is a very sensitive method for elemental analysis. It allows determination of metals in a variety of samples at the pictogram level. SEM instruments place the specimen in a relative high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The equipment used is PerkinElmer Analyst 400 AA Spectrometer.

# **3.0 Results and Discussion** *3.1 Field and Lithological Description*

Field observation and the lithological description of the investigated quarry mine is situated at Bua Cement Quarry site, with coordinates of Lat.  $13^{\circ}$  3' 4" N to Long.  $5^{\circ}$  9' 21" E, and an elevation of an approximate value of 260 m.

**Litho-description:** The basal bed at the mine is composed of sparsely fossiliferous, whitish- coloured limestone. The limestone facies is fairly thick and lithified. The overlying bed is light grey fissile shale. The light grey fissile shale is overlain by poorly fossilliferous limestone. The shale is intercalated between the upper and lower limestone beds. The shale is here overlain by marlstone, characterized by clastic impurities such as quartz and clay. The presence of the classic materials influx into the limestone during its formation reduces the quality of the limestone, thus, described to be of low-grade limestone in an economic sense.

The middle section of the outcrop is marked by an unconformity where the nonfossiliferous limestone is unconformably overlain by sandstone. The medium-grain sandstone is overlain by marlstone. However, the sandstone marks the top of the Maastrichtian sediment deposit and commencement of Eocene deposits that constitute the Gamba Formation. The Gamba Formation is characterized by micaceous shale, suggested to have been deposited in a relatively deeper marine setting. The micaceous shale is unconformably overlain by conglomeratic ironstone of possibly continental origin (Fig. 2).

<b>AGE</b>	<b>FORMATION</b>	LOG	<b>DESCRIPTION</b>	<b>PALEO-</b> <b>ENVIRONMENT</b>	<b>LEGEND</b>
			Ironstone	<b>CONTINENTAL</b>	
		М	<b>Micaceous Shale</b>	<b>MARINE</b>	
<b>Middle Eocene</b>	GAMBA		<b>Marlstone</b>		Iron
			<b>Sandstone</b>		<b>Micaceous</b> $M - M$ <b>Sandstone</b>
		D D O ם D O $\overline{a}$ $\mathbf{a}$ $\sim$ ם $\sigma$ $\circ$ Q	<b>White Coloured</b> <b>Fossiliferous Limestone</b>		Marl
Early Maastrichian Paleocene	KALAMBAINA		Light grey fissile Shale	<b>MARINE</b>	<b>Fossiliferous</b> QQ D
		D D Q D $\circ$ $\circ$ $\mathbf{a}$ $\overline{a}$ O D $\sim$ ᠳ O $\sigma$ $\sigma$ $\circ$	<b>Fossiliferous Limestone</b>		<b>Shale</b> Limestone

**Fig. 2: Litho-log sequence of BUA Cement Quarry at Kalambaina Village**

# **3.2** *Geochemistry of Kalambaina Limestone*



Geochemical analysis was carried out on the six samples collected from the kalambaina Quarry mine site. The samples were analyzed for heavy metals and rare earth elements (REE) as presented in Table 1. The geochemical characteristics of the kalambaina carbonates were investigated by obtaining the values of the major oxides and by determining the highest, lowest and average values of the concentrations. The major oxides determined from the analyzed samples include  $SiO<sub>2</sub>$ ,  $Al<sub>2</sub>O<sub>3</sub>$ ,  $Fe<sub>2</sub>O<sub>3</sub>$ ,  $TiO<sub>2</sub>$ , CaO, P2O5, K2O, MnO, MgO, and Na2O The results were presented in Table 1.

The  $SiO<sub>2</sub>$  content of the carbonate samples ranges between 1.25 to 1.26 % with an average (1.25 %). This is very low when compared to clastic sediment that overlain it, having a silica range between 62.25 to 71.15 %. However, the silica content in the carbonate facie tend to be higher slightly in the marlstone sample compared to the limestone sample. This increase in SiO<sup>2</sup> resulted from the influx of clastic materials such as clay and sand particles into the initially developing carbonate material in the marine, consequently the clastic influx resulted to the formation of the marlstone.

**Table 1. Geochemistry results of Major and Rare Earth Elements (REE)**

riement	HUBI		HUMI HUMZ HUMS		HUTI "HUTZ" "HIghest" "Eowest " Ave HQM3 and HQT <sub>2</sub> were devined from the
SiO <sub>2</sub>	1.250	62.25	1.265	71.15	committee carbonation property in the 150 carbon
$Al_2O_3$	0.549	27.4	0.590	21.47	croses can de calculation of the case of the case of the case of the case of the cross
Fe <sub>2</sub> O <sub>3</sub>	1.10	1.10	1.67	2.74	lof8 marine72envirdement. The10 magnestion
TiO <sub>2</sub>	0.01	0.01	0.01	0.01	Ooxide coult thas updefinite pattern between
CaO	54.60	0.03	54.63	0.03	5the Clastic and carbonate rock with a range of
$P_2O_5$	0.04	0.05	0.02	.	$\cdot$ 1.74 to 3.2 % ( $\frac{\mathcal{A}}{\mathcal{D}}$ 52.47 %). Compared $\frac{0.32}{0.3}$
$K_2O$	0.14	5.22	0.04	0.02	$^{0.03}_{0.04}$ clastic material with 2.42 $^{0.03}_{0.04}$ 3.30 % $^{2.23}_{0.04}$ $^{0.01}_{0.1}$
MnO	0.01	0.01	0.01	0.01	$\frac{0.01}{2.86}$ .
MgO	3.02	2.70	1.74	3.30	1.74 $. \, 0.5.$ 3.30. 2.42
Na <sub>2</sub> O	0.64	1.23	1.53	1.27	$\frac{1}{1.54}$ highest value of magnesium $oxide$
LOI	33.66	32.25	29.02	27.22	$2g$ gegended $25\frac{1}{4}$ the $33\frac{8}{4}$ distong $5\frac{1}{4}$ acies. $\gamma$ <sub>b</sub>
Pb	0.746	0.138	2.320	0.250	3patassium 3qque sontent of the samples 44
Ni	1.033	1.025	1.020	1.032	1909.08 %) for 1920 1020 1030.14 % (ay20.08 %) for
Zn	0.430	0.443	0.230	0.250	<b>Oborth</b> the constationate under and olaratic rock by

The variation in silica content of the clastic samples as found in the shale and sandstone indicated that the sandstone facies have a higher silica content of 71. % compared with



The very low value of alumina in the carbonate may be a result of a deficiency of clay materials within the limestone sediment. This as well may indicate that the marlstone sediment had the sand and clay particles washed perhaps from the lagoon environment into the marine setting. The TiO2 and MnO contents of both the carbonate and clastic sediment have a constant value of 0.01 % which suggests a non-impact of titanium oxide on the stratigraphic sequence of the Kalambaina Formation. The CaO concentration value of all the samples vary from one another, carbonate samples recorded the highest values which range between 50.10 to 54.63 % (av. 52.36 %) with the highest value of calcium oxide recorded in the limestone facie than calcium oxide recorded in marlstone sample (Tab. 2). However, the calcium oxide values in the clastic sediments are very low with a constant value of 0.03. This low value of calcium

**Element HQB1 HQM1 HQM2 HQM3 HQT1 CHAPPLE HQT1 HQM1 HQM3** and HQT<sub>2</sub> were derived from the  $\textbf{SiO}_2$  1.250 62.25 1.265 71.15 1.2993 fune the environment while the carbonate  $\mathbf{Al}_2\mathbf{O}_3$  0.549 27.4 0.590 21.47 0.598 can be described to be a superfunctionships,  $Fe<sub>2</sub>O<sub>3</sub>$  1.10 1.10 1.67 2.74 1 $\alpha$ 68 mari $\alpha$  environment. The 0 magnesing the magnesi **TiO<sup>2</sup>** 0.01 0.01 0.01 0.01 0.01 0.01 0.1 0.1 0.1 oxide content has no definite pattern between  $CaO$  54.60 0.03 54.63 0.03 5the Clastic and carbonate rock with a range of **P2O<sup>5</sup>** 0.04 0.05 0.02 ….. ….. ….. 0.05 0.02 0.035 **Na<sub>2</sub>O**  $0.64$   $1.23$   $1.53$   $1.27$   $1.54$   $1$ **LOI** 33.66 32.25 29.02 27.22 28.99rded 25.774 the sandstone facies. The  $\frac{2648}{P}$  0.746 0.138 2.320 0.250 3.2488 3.3438 0.3488 6.90 at 6.044 content of the samples 4.42 **Ni** 1.033 1.025 1.020 1.032 1**99309**rally low 0.02 to 39.14 % (av20.08 %) for 5  $Zn$  0.430 0.443 0.230 0.250 0.220 0.250 and class and class tic rock but 5 1.74 to 3.2 % ( $\frac{10052.47}{90}$  %) compared to clastic material with 2.42 to 3.30 %  $\chi$ av.  $0.0160$ . exceedingly relatively high in the shale, with

a value of 5.22 %. This indicates that the type of feldspar mineral which decomposed to shale is k-feldspar, which is more dominant in shale formation than sand and carbonate



formations (Tab. 2). The sodium content value is almost the same in all the samples (carbonate and clastic sediments) with values ranging from 1.23 to 1.27 % (av. 1.25 %) with the lowest value of 0.64 recorded in the basal limestone bed. There is a relative increase of sodium oxide content upward within the carbonate rock. The loss on ignition (LOI) varies from one sample to another. It is highest in limestone (33.66 %), moderate in shale with (32.25%), and lowest in sandstone (27.22 %).

The geochemical composition of the Kalambaina carbonate rocks of this study is presented in Tables 1, 2 and 3. The mean CaO of the limestone and that of the marlstone (52.36 %) in the study area compare favourably and higher than those of Tse-Kusha Limestone (48.88 %) and Nkalagu Limestone (49.74 %) (Ikhane *et al*., 2009), but the mean CaO of Agoi Ibami Limestone is very low compare to Etono Limestone (Odey *et al*., 1985). The relatively pure limestone of Olaide





(1988) with CaO content of 50.89 is in tandem with the result obtained with the marlstone in the Kalambaina Formation. The CaO content in Kalambaina Limestone (54.61 %) is very close in concentration value to Efamosing Limestone (55.30 %) (Ekwueme, 1985). However, it is only Shagamu Limestone with CaO of 59.20 (Brand, 1983) which has a higher CaO content than Kalambaina Limestone and Marlstone (Tab. 3). However, the average  $SiO<sub>2</sub>$  concentration value  $(1.26 \%)$  is relatively low compared to other limestone deposits in Nigeria, except those of Efamosing Limestone (0.38 %) (Ekwueme 1983), Middle Belt zone (0.53 %) (Petters, 1980), and Shapfell Limestone (0.71) (Downie *et al*., 1982).

The high  $SiO<sub>2</sub>$  content in the limestone of other places in Nigeria is greater than those of Kalambaina carbonate rocks possibly due to the influx of clastic materials during their formation. The low concentration of alumina suggests a low-energy environment for the carbonate sediment compared to a relatively higher-energy environment attributable to the clastic sediments (sand and shale). The skeletal debris of marine invertebrate has low MgO with increasing level in the phyla (Chave, 1954). The Kalambaina Limestone is fairly rich in Gastropods and Echinoderm which are typical of open shelve environment (Ehinola *et al*., 2012). The presence of these invertebrates is attributable to low levels of magnesium in the shallow marine environment (Odey *et al.,* 2021).

The loss on ignition reveals the presence of volatility in the limestone deposit, whereby, the relatively low LOI value in this study compared to the limestone deposit of the other parts of Nigeria indicates a lower volatile content. The  $Fe<sub>2</sub>O<sub>3</sub>$  content in the Kalambaina Formation is higher in the clastic



sediment than the carbonate rocks and this may suggest a high influx of iron-bearing solutions in the terrigeneous rocks compared to Kalambaina carbonate rocks. The  $Fe<sub>2</sub>O<sub>3</sub>$ content in the Kalambaina carbonate rocks is relatively low compared to some limestone deposits in other parts of Nigeria. This is indicative of the high quality of the Kalambaina carbonate rock to having higher absorption capacity, which invariably increases the rate of ignition of the samples.

## **3.3** *Quality Implications*

The geochemical analysis result from Table 1 suggests that the Kalambaina carbonate rocks can best be classified as limestone, because of the low percentage of silica, magnesium oxide and high calcium oxide which also

indicate a moderately high degree of purity of the limestone. It is therefore suggested that the limestone is suitable as raw materials for cement production as being presently utilized by BUA Cement Company, Sokoto, Nigeria. Impurities which may affect the quality of cement production such as magnesium, fluorine, phosphorous, lead, zinc, alkalis and sulphide are in relatively very low concentrations (Tab. 1). Other chemical specifications limit silica and phosphorous to less than 1 % and total alkalis to less than 0.6 % (Harrison *et al*., 1990). It is, therefore, evident that the Kalambaina Marlstone fit into coarse sparse cemented limestone which can be used as building stone (Odey *et al* 2021).





Further advances in many uses of limestone powders are essential in carpet backing, asphalt and coal mine dust which do not require pure limestone. Therefore, the Kalambaina marlstone and limestone can be used for cement production and can as well be used as fillers respectively. The Kalambaina limestone would be useful for agricultural purpose by reducing soil acidity when added to the soil, thereby, increasing the level of calcium or magnesium in the soil.

#### **4.0 Conclusion**



This study assessed the concentrations of heavy metals in soil samples from three distinct locations around the University of Abuja Teaching Hospital and compared them to a control site and established WHO/USEPA standards. The heavy metals analyzed included lead, cadmium, chromium, and nickel. The findings revealed significant variations in heavy metal concentrations across the sites, with the highest levels recorded at SI, indicating substantial contamination. The concentrations of lead, cadmium, chromium, and nickel at SI were 120.5 mg/kg, 3.2 mg/kg, 90.3 mg/kg, and 45.8 mg/kg, respectively. In comparison, the control site had the lowest levels, with 15.2 mg/kg for lead, 0.5 mg/kg for cadmium, 10.2 mg/kg for chromium, and 5.1 mg/kg for nickel. Sites SII and SIII also showed elevated levels, with SII having 95.4 mg/kg of lead, 2.1 mg/kg of cadmium, 75.8 mg/kg of chromium, and 40.7 mg/kg of nickel, while SIII had 82.3 mg/kg of lead, 1.8 mg/kg of cadmium, 68.9 mg/kg of chromium, and 38.2 mg/kg of nickel. These concentrations exceeded the WHO/USEPA permissible limits, indicating a potential environmental and public health risk. The study concluded that anthropogenic activities, particularly industrial and hospital waste disposal practices, are major contributors to the elevated heavy metal levels in the soils. The comprehensive risk assessment highlighted the high potential for adverse health effects, underscoring the need for immediate remedial actions. The study recommended continuous monitoring of soil quality, stringent regulatory frameworks to manage soil pollution, and the implementation of sustainable soil management practices to mitigate the contamination and protect public health.

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- **Compliance with Ethical Standards Declaration Ethical Approval**

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## **Availability of data and materials**

Data would be made available on request.

## **Authors Contribution**



The first author contributed 60 %, second author 40 %

