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# GEOCHEMICAL ANALYSIS OF LIMESTONE FROM EWEKORO DEPOSIT, EXPOSED AT SAGAMU QUARRY, DAHOMEY BASIN, SOUTHWESTERN NIGERIA

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***Abstract:*** Limestone as a sedimentary rock is composed predominantly of carbonates of calcium ($CaCO_3$) known as calcite. The primary source of the calcite in limestone is commonly shelly marine organisms which settle out of the water and are deposited on ocean floors as pelagic ooze or alternatively in a coral reef. Based on colour and facies, eight samples were collected from the Sagamu quarry, were pulverized, pelletized to 13mm and were analyzed with PIXE (Particle Induced X-ray Emission) using 2.5 Mev proton beam issued from the Ion Beam Analysis (IBA) facility of the 1.7MV Tandem accelerator. The Lagos end of the Sagamu quarry is calcium rich compared to the Sagamu end with mean percentage concentration of 53.38±0.09 and 48.28±0.09 respectively. The overall mean percentage calcium content of the limestone in the Sagamu quarry is 48.84±0.09. The Sagamu end is silica rich compared to Lagos end with mean percentage silica of 0.26±0.05 and 0.10±0.02 respectively which suggests that the Sagamu end contains more arenaceous materials than the Lagos end. The limestone in the Sagamu quarry has a high CaO content (48.84%) when compared to that of Ewekoro quarry (about 46.01%). The result shows that the CaO content of Sagamu quarry falls below the 56% CaO content recommendation for cement production. However, the differences are not significant, can be augmented, and therefore the resources are acceptable for use in cement production.

## 1.0 Introduction

Limestone as a sedimentary rock is composed predominantly of carbonates of calcium in form of the mineral calcite ($CaCO_3$). Basically, the primary source of the calcite in limestone is the remains of shelly marine organisms which precipitate out of the water and are deposited on ocean floors as pelagic ooze or alternatively in a coral reef. Limestone especially is the chief raw material for manufacturing Portland cement, an essential component of concrete (Akpan *et al*, 2011).

Cement is the most common and extensively used adhesive in the construction industries for highways, houses, embankments, bridges, commercial establishments and flyovers (Mmemek-Abasi *et al.* 2021). The limestone deposit quarried in Sagamu serves as the source of the major raw material for cement production by Lafarge WAPCO. Portland cement is produced by the calcination of finely ground raw mix consisting of a mixture of about 75% limestone and 25% clay, at about $1450^0$C in a rotary kiln to form a calcium silicate clinker which is then ground and mixed with a small amount of gypsum which acts as a setting retardant (Bouazza *et al*, 2016)**.** The quality of the cement that is produced from this process depends solely on the chemical composition of the limestone.

Limestone can be used for different purposes which include pharmaceuticals, when the limestone is very pure, and fertilizer, when the limestone is enriched in phosphate by the chemical action of the sea. Other applications include production of lime used extensively in agriculture and glass making. Limestone that contains a minimum of 56% calcite can be used for cement production (Duff, 1994). The Ewekoro deposit has been extensively studied (Agagu, 1985; Nton, 2001; Elueze and Nton, 2004; Nwajide, 2013; Akinmosin, *et al, 2019*) but the Sagamu quarry being a later discovery is yet to be extensively studied. This takes cognizance of the fact that geological formation can experience significant variation in parameters from one location to the other. This makes it mandatory that a lot more work needs to be done in the Sagamu quarry. Therefore, this study is to determine the geochemical composition of the limestone in the Sagamu quarry of Lafarge WAPCO.

The study area is located in Ogun state along Lagos – Ikorodu expressway about 55 kilometres from Lagos, (Figure 1.1). It lies within the eastern part of Dahomey basin and lies within the Ewekoro formation (Jones and Hockey 1964).

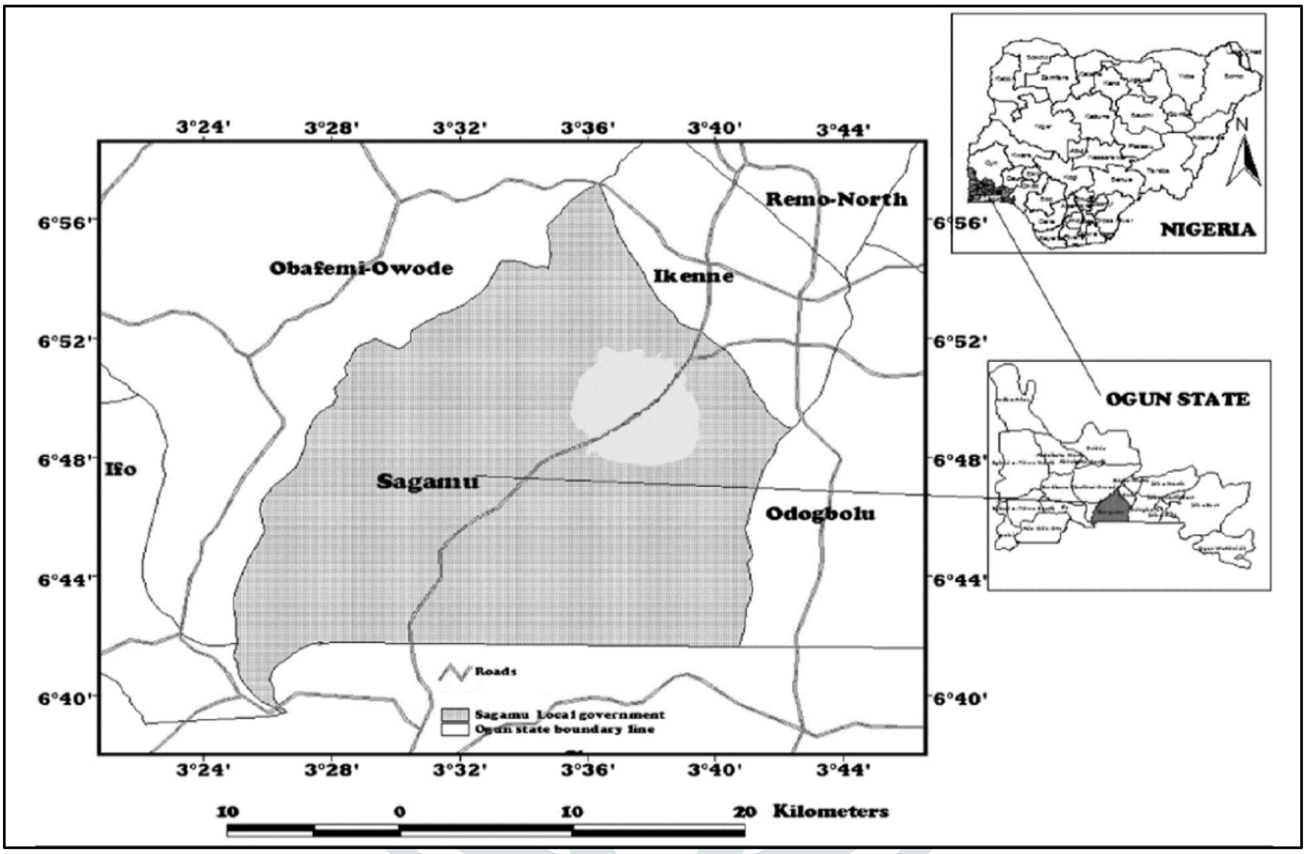



Fig.1 Location map showing the study area

## 2.0 GEOLOGIC SETTING

Sagamu quarry lies within the Eastern Dahomey Basin in the Southwestern Nigeria. Geologically, the study area is part of the Dahomey embayment, which extends from the Volta region of Accra, Ghana through Togo and Benin Republic to the southwestern part of Nigeria where it terminates against the Okitipupa ridge (Ganiyu *et al* 2021). The Nigerian portion of the Dahomey (Benin) basin extends from the boundary between Nigeria and Benin Republic (in the area of the Gulf of Guinea), eastwards and terminates at the Okitipupa Ridge/Benin Hinge Line, which is the continental extension of the Chain Fracture Zone (CFZ), a major fault structure marking the western limit of Niger Delta (Omatsola and Adegoke, 1981; Olabode and Adekoya, 2008; Olabode and Mohammed, 2016). It is also bounded in the north by the Precambrian basement rock and the Gulf of Guinea in the south (Omatsola and Adegoke, 1981). Structurally, the basin is bordered on the west by faults and other tectonic structures associated with landward extension of the Okitipupa ridge, a paleographic height and Benin hinge line, a major regional faults structure (Murat, 1970), which is probably a landward extension of the fracture zone (Omatsola and Adegoke, 1981). The basin is one of the series of West African Atlantic Margin basins (marginal pull-apart/marginal sag basin) that were initiated during the period of rifting in the late Jurassic to early Cretaceous (Omatsola and Adegoke, 1981; Whiteman, 1982; Storey, 1995; Olabode, 2006; Ehinola *et al*., 2016).

The onset of sedimentation happens before the separation of the African landmass from the South American landmass, and this justifies the similarities in the sedimentary sequence of the marginal basins of West

African coasts and most of the Brazilian basins (Omatsola and Adegoke, 1981). The sediment thickness increases from onshore to offshore and sediment thicknesses range from less than 100m onshore to more than 3000m offshore (Whiteman, 1982; Billman, 1992; Akinmosin *et al*, 2018). The review work of Omatsola and Adegoke (1981) shows that the evolution and stratigraphy of the Benin (Dahomey) basin, is subdivided into three tectono-sedimentary stages: the pre-rift (pre-transform; Precambrian to Triassic intra-cratonic rocks and Jurassic to Lower Cretaceous rocks), Syn-transform (Lower Cretaceous to Late Albian rocks), and passive margin (Post-transform; Cenomanian to Holocene). The Cretaceous sediments were further divided into three formations; Ise, Afowo and Araromi Formations, and they are altogether referred to as the Abeokuta Group. The age of the oldest sediments (Ise Formation which unconformably overlies the basement complex) is Neocomian and it is made up of conglomerates and sandstone facies. The Afowo Formation which consists of coarse to medium grained sandstone overlies the Ise Formation which is then overlain by the Araromi Formation. The Araromi Formation which is composed mainly of dark shales and fine to medium grained sandstones, siltstone with interbedded limestone, marl and lignite (Omatsola and Adegoke, 1981; Oladele *et al* 2014), ranges from Early Paleocene to Maastrichtian. Overlying the Abeokuta Group conformably is the Paleocene-Eocene Ewekoro and Akinbo Formations (Figure 2). The Ewekoro Formation is a fossiliferous shelly limestone, about 12.5m thick, which becomes sandy in the lower parts (Nwajide, 2013). The Ewekoro Formation is overlain by the intercalation of shale and sand with thin beds of limestones which is regarded as the Oshosun Formation. This is then succeeded by marine to continental Ilaro Formation which consists of massisve yellowish, poorly consolidated, cross-bedded sandstone (Oladele *et al* 2014). The upper section of the basin is occupied by poorly fossiliferous continental sandstone and siltstone deposits (Fayose, 1970; Billman, 1976; Omatsola and Adegoke 1981).

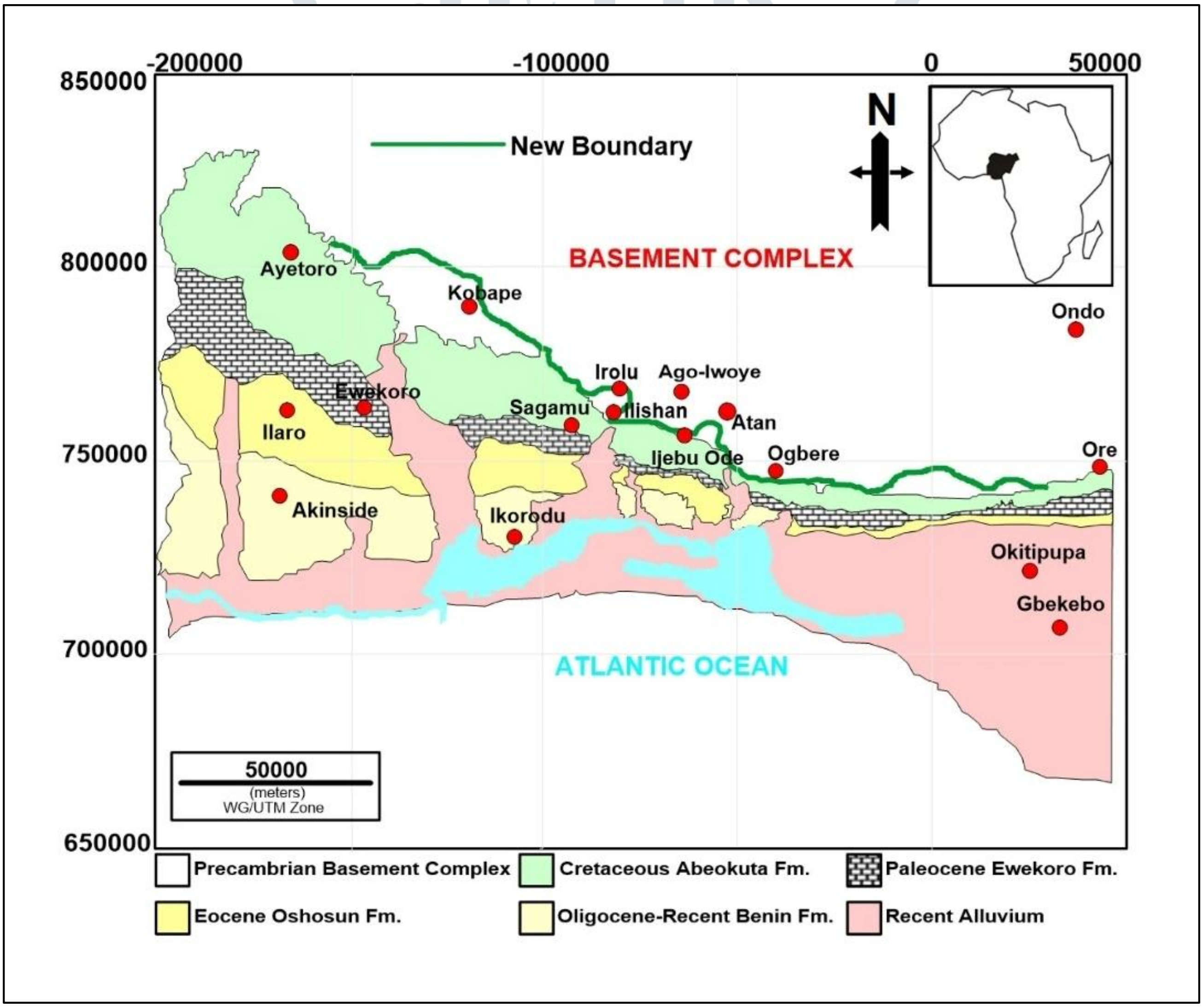



Fig.2: Geological Map of Eastern Dahomey Basin (modified by Ganiyu *et al*., 2021)

## 3.0 MATERIALS AND METHODOLOGY

Eight (8) samples were collected from the Sagamu quarry of the West African Portland Cement Company (WAPCO). Four (4) samples were collected vertically at various depth across the Lagos end and four (4) from the Sagamu end. The quarry is divided into phases because of the heterogeneous nature of the limestone in this area. These samples were also collected based on changes in colour and facies. All the samples were given identification number based on the location from which they were picked. The limestones in Sagamu quarry are generally fossiliferous and medium grained. The color of the sample ranges from brownish grey, light grey to dark grey.
The samples collected were crushed into smaller sizes. The samples to be used were often weighed in a sample dishes for Tandem Accelerator analysis. In preparation for the Ion Beam Analysis (IBA) using the Tandem Accelerator, the samples were pulverized in an electric pulverizer (rock lab) for about five (5) minutes. Thereafter, the pulverizer cup was washed with water thoroughly and later rinsed with ethanol to avoid contamination. Then, the pulverized samples were gently transferred into a clean pharmaceutical nylon and labeled accordingly.

Thereafter, ethanol was used to clean up the pellet cup in readiness for pelletizing of the samples (Fig.3a). The pulverized sample was packed into a pellet cup with a clean paper and fill to the brim. The pellet cup was gently placed under a pressing cylinder (pelletizer) ensuring that the cup was well fitted. After pressing for about fifteen to twenty presses, the sample was removed as a pellet of 13mm thick for ion beam analysis (IBA) Tandem Accelerator (Figure 3.1b & c).


Fig.3.1: Pelletizing Process of Limestone Samples

## 3.1 SAMPLE ANALYSIS

The PIXE (Particle Induced X-ray Emission) experiments were performed using 2.5 Mev proton beam issued from the ion beam analysis (IBA) facility of the 1.7 MV Tandem accelerator at the Centre for Energy Research and Development (CERD) at Obafemi Awolowo University, Ile-Ife Osun State, Nigeria. This IBA system is based on 8-10 mm diameter proton beams of a few microamps and consists of four channels, PIXE for elements from Al to Pb, PIGME for lighter elements such as F, Na, Mg and Rutherford Backscattering (RBS) for C, N, O, and Forward Recoil Analysis for Hydrogen. The four channels can operate simultaneously or separately. In this work, only the PIXE and PIGME were used. The beam spot was 8 mm in diameter and the beam current was of 4-6 μA. The irradiation was about 15 minutes. An EG&G Ortect Model SLP Si(Li) detector with the associated pulse processing electronics and a Canberra S100 MCA card interfaced to a 386 IBM/PC were used for the X-rays data acquisition while an Ortect Ge(Li) detector was used for the γ-rays. With respect to the beam direction, the sample's normal was located at $0^0$ and the Si(Li) and Ge(Li) were at $45^0$ to the left and right of the beam respectively Figure 3.2


Fig.3.2: Set Up for Ion Beam Analysis with Tandem Accelerator (a – d)

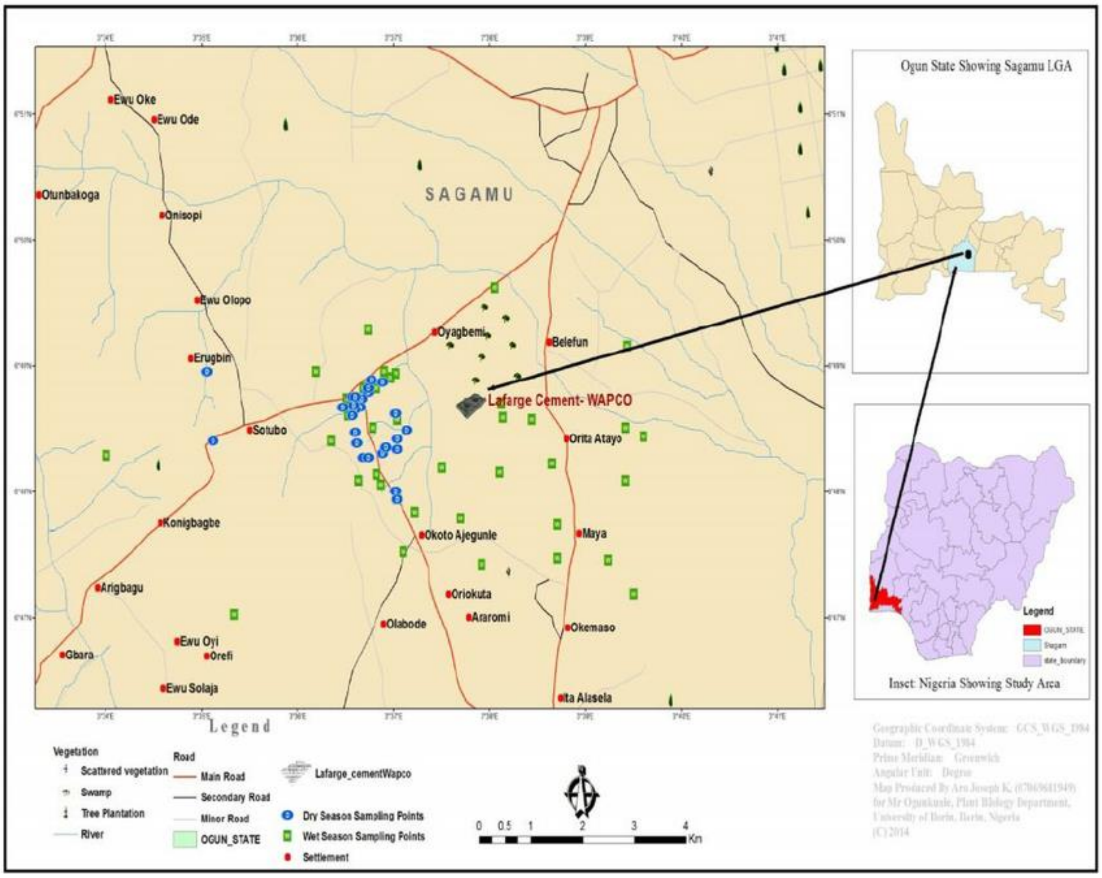



Fig.3.3 Map of Sagamu showing quarry site of Lafarge WAPCO

## 4.0 PRESENTATION AND INTERPRETATION OF RESULT

The quarry site is divided into phases because of the heterogeneous nature of the limestone in the area (Fig.4.1). So, basically, there is Lagos end, the Sagamu end and the Main phase. Samples were collected along the Lagos end and the Sagamu end because these are the major production phases. The Lagos end is composed of medium grained fossiliferous light grey limestone (Table 4.1) while the Sagamu end is composed of medium grained fossiliferous brownish grey limestone (Table 4.2). All the samples were given identification number based on the location from which they were picked.

Table 4.1 Sample description from the Lagos end of Sagamu quarry

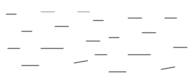
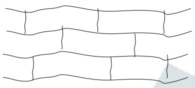
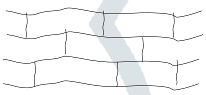
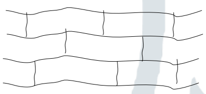
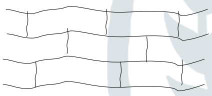
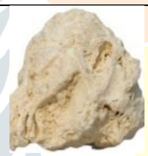
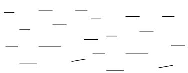
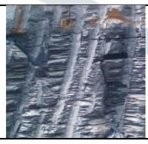
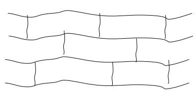
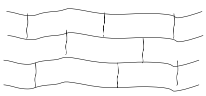
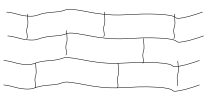
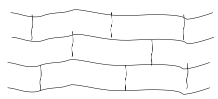
| Lithology | Outcrop Sample | Depth (m) | Sample ID | Description |
|---|---|---|---|---|
|  |  | 2.4 | No sample | |
|  |  | 4.5 | $LG_1$ | Light grey fossiliferous, medium grained limestone |
|  |  | 6.0 | $LG_2$ | Light grey fossiliferous, medium grained limestone |
|  |  | 7.3 | $LG_3$ | Light grey fossiliferous, medium grained limestone |
|  |  | 9.2 | $LG_4$ | Light grey fossiliferous, medium grained limestone |

Table 4.2 Sample description from the Sagamu end of Sagamu quarry

| Lithology | Outcrop Sample | Depth (m) | Sample ID | Description |
|---|---|---|---|---|
|  |  | 2.6 | No sample | |
|  |  | 4.3 | $SG_1$ | Brownish grey, fossiliferous, medium grained limestone**.** |
|  |  | 6.5 | $SG_2$ | Brownish grey, fossiliferous, medium grained limestone |
|  |  | 7.2 | $SG_3$ | Brownish grey, fossiliferous, medium grained limestone |

| | | | | |
|---|---|---|---|---|
|  |  | 8.5 | $SG_4$ | Brownish grey, fossiliferous, medium grained limestone |

The results of the geochemical analysis of the Sagamu limestone are shown in Table 1. The results revealed that the Lagos end of the Sagamu limestone has a calcium (Ca) content that ranges from 41.02% to 53.38% with a mean value of 49.40%. The manganese (Mn) content ranges from 0.02% to 0.05% with a mean value of 0.03%. The Silicon (Si) content ranges from 0.00% to 0.40% with a mean value of 0.10%. The Iron (Fe) content ranges from 0.27% to 0.45% with a mean value of 0.38%. The strontium (Sr) content ranges from 0.00% to 0.02% with a mean value of 0.005 %.)

The Sagamu end has a calcium (Ca) content that ranges from 35.21% to 54.81% with a mean value of 48.28%. The Manganese (Mn) content ranges from 0.04% to 0.07% with a mean value of 0.05%. The Silicon (Si) content ranges from 0.00% to 0.48% with a mean value of 0.26%. The Iron (Fe) content ranges from 0.51% to 1.11% with a mean value of 0.70%. The Strontium (Sr) content ranges from 0.00% to 0.03% with a mean value of 0.02%. Therefore, the overall percentage mean composition of the elements in the limestone are; Ca is 48.84%, Mn is 0.04%, Si is 0.18%, Fe is 0.54% and Sr is 0.01%.

From the result, it can be inferred that the Lagos end of the Sagamu deposit has more calcium and less of iron content than the Sagamu end of the deposit. Meanwhile, both Lagos end and Sagamu end fall short of the standard 56% calcium set by Duff (1994).

Table 4.3: Result of Geochemical Analysis of Limestone at Sagamu Quarry

| SECTION | DEPTH (m) | Ca (%) | Mn (%) | Si (%) | Fe (%) | Sr (%) |
|---|---|---|---|---|---|---|
| LAGOS END | 4.5 | 49.94±0.09 | 0.03±0.01 | 0.00±0.00 | 0.37±0.01 | 0.02±0.01 |
| | 6 | 41.02±0.08 | 0.02±0.01 | 0.00±0.00 | 0.27±0.01 | 0.00±0.00 |
| | 7.3 | 53.24±0.09 | 0.05±0.09 | 0.40±0.07 | 0.45±0.02 | 0.00±0.00 |
| | 9.2 | 53.38±0.09 | 0.03±0.01 | 0.00±0.00 | 0.42±0.02 | 0.00±0.00 |
| RANGE | | 41.02-53.38 | 0.02-0.05 | 0.00-0.40 | 0.27-0.45 | 0.00-0.02 |
| MEAN | | 49.40±0.09 | 0.03±0.03 | 0.10±0.02 | 0.38±0.02 | 0.005±0.003 |
| SAGAMU END | 4.3 | 54.81±0.09 | 0.07±0.01 | 0.00±0.00 | 0.63±0.02 | 0.03±0.01 |
| | 6.5 | 51.20±0.09 | 0.04±0.01 | 0.24±0.07 | 0.54±0.02 | 0.03±0.01 |
| | 7.2 | 51.90±0.09 | 0.04±0.01 | 0.48±0.07 | 1.11±0.02 | 0.03±0.01 |
| | 8.5 | 35.21±0.08 | 0.04±0.01 | 0.31±0.06 | 0.51±0.02 | 0.00±0.00 |
| RANGE | | 35.21-54.81 | 0.04-0.07 | 0.00-0.48 | 0.51-1.11 | 0.00-0.03 |
| MEAN | | 48.28±0.09 | 0.05±0.01 | 0.26±0.05 | 0.70±0.02 | 0.02±0.008 |
| OVERALL RANGE | | 35.21-54.81 | 0.02-0.07 | 0.00-0.48 | 0.27-1.11 | 0.00-0.03 |
| OVERALL MEAN | | 48.84±0.09 | 0.04±0.02 | 0.18±0.03 | 0.54±0.02 | 0.01±0.01 |

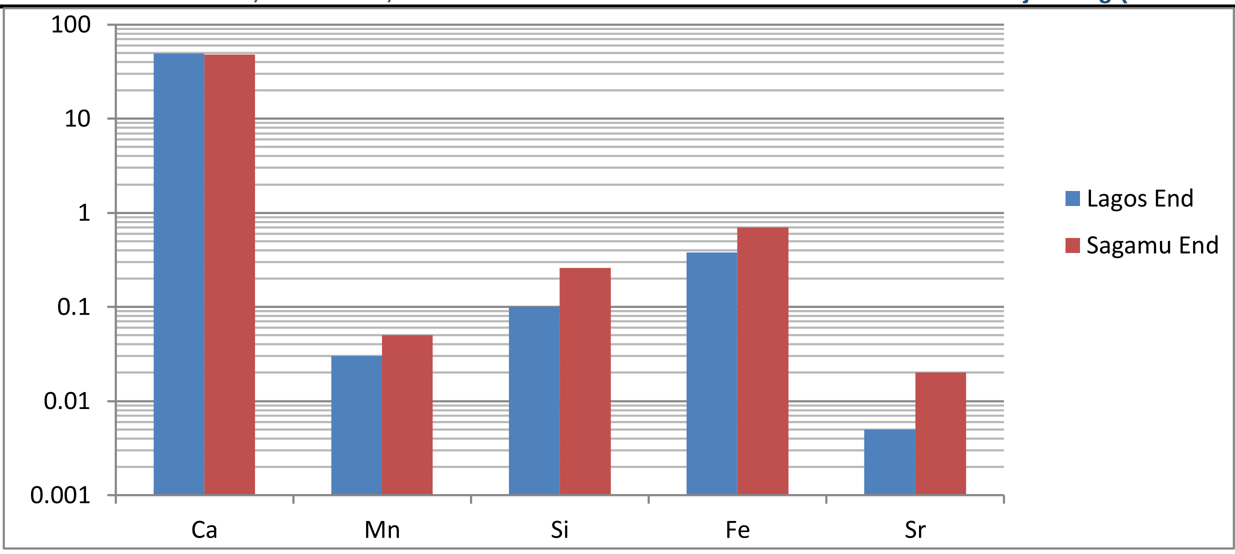



Figure 4.2a: Chart of (%) Concentration of Elements in Lagos and Sagamu Ends of the Quarry

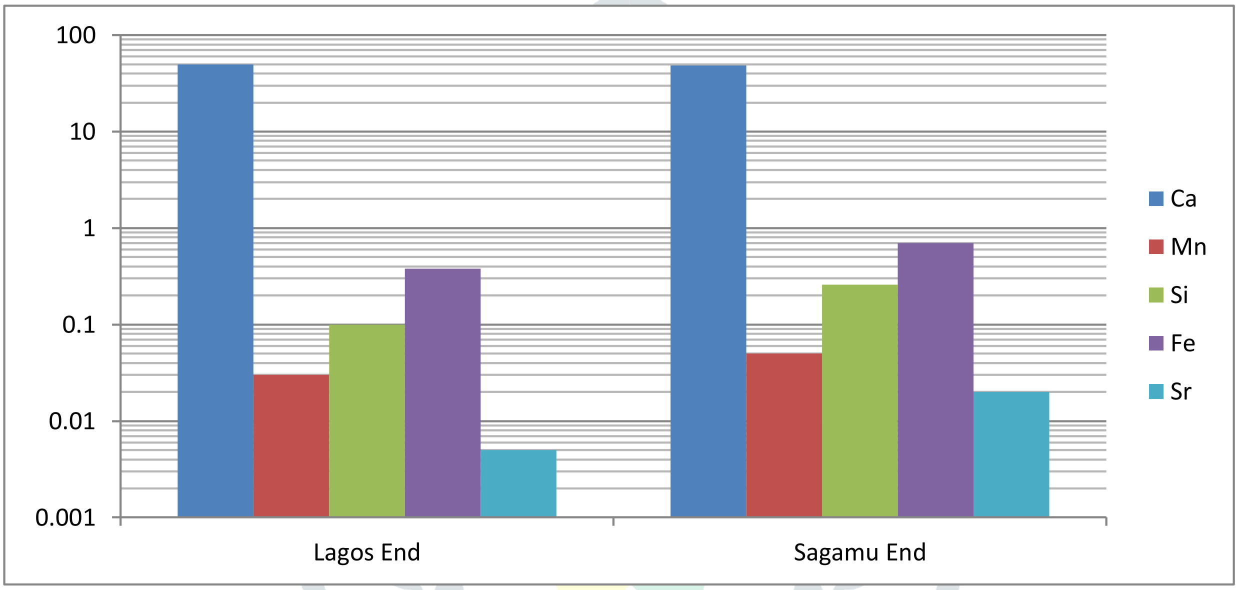



Figure 4.2b: Chart of (%) Concentration of Elements in Lagos and Sagamu Ends of the Quarry

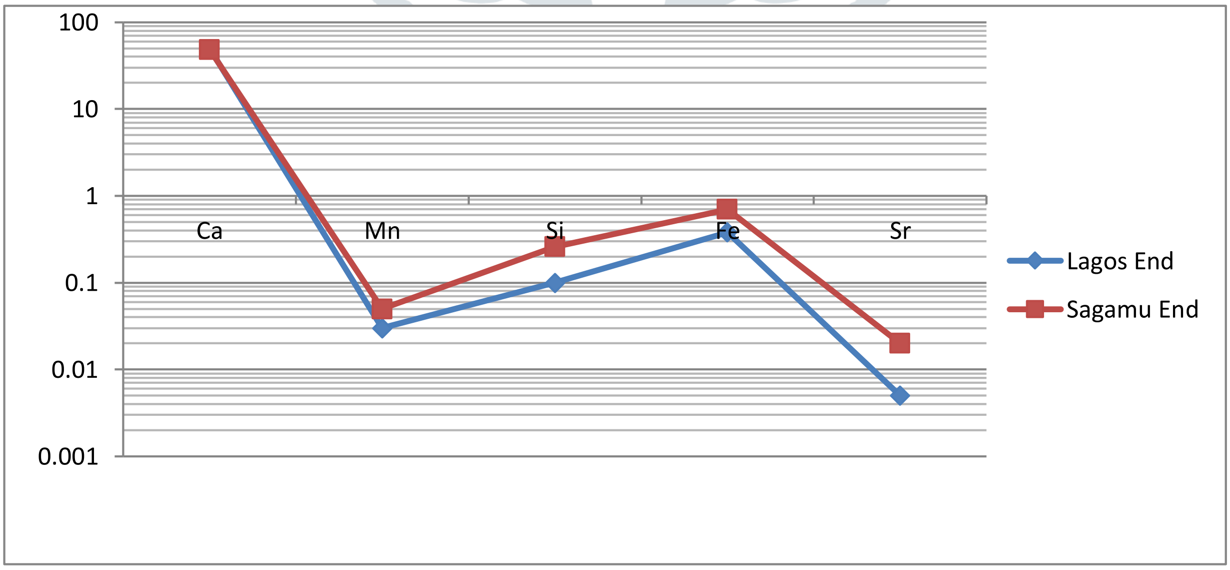



Figure 4.2c: Line Chart of (%) Concentration of Elements in Lagos and Sagamu Ends of the Quarry

# 5.0 DISCUSSION, CONCLUSION AND RECOMMENDATION

## 5.1 DISCUSSION

From the result of the geochemical analysis, it can be inferred that the Lagos end is richer in calcium than the Sagamu end with mean percentage content of 53.38±0.09 and 48.28±0.09 respectively. The Sagamu end is richer in silica than the Lagos end with mean percentage silica of 0.26±0.05 and 0.10±0.02 which suggests that there are more arenaceous materials in Sagamu end than Lagos end. This result is corroborated by the report of the percentage lime concentration of the limestone at Sagamu quarry as reported by Odundun (2019) to be ranging from 48.08% to 60.40%. Odundun (2019) reported further that percentage CaO content of limestone deposit of the Ewekoro Formation ranged from 38.69% to 63.13% with mean percentage CaO of 49.67%. Furthermore, it was reported that the limestone deposit in Sagamu is more Ca-rich than that of Ewekoro which has a mean CaO of 46.01% (Odundun, 2019). These reports are in tandem with the results of this research. Therefore, in line with Duff (1994), the Ewekoro limestone requires upgrading for it to be applicable to cement production. It is believed that since the difference in the CaO content of the Sagamu end and the Lagos end is not significant, they could be applied to the same use. In the same vein, the Ewekoro and Sagamu deposits could be applied to cement production with slight enrichment of the Ewekoro deposit. It is further inferred from the CaO and arenaceous contents, that the basin was most likely receiving materials from the Sagamu end during the time of deposition. The significant differences in the Fe (%) for both Lagos end and Sagamu end may not have deleterious effect on cement production as they are still within the tolerable level (Mahaboob *et al* 2023).

## 5.2 CONCLUSION

The limestone in Sagamu quarry is useful in the production of cement, in spite of its low CaO content (48.84%). Since there is decrease in the percentage concentration of calcium with increase in depth in the Sagamu End there is likely going to be reduction in the quality of the limestone thereby making it not suitable for cement production over time. The depositional environment is a marine environment due to the presence of fossilized materials as evident on the collected samples.

## 5.3 RECOMMENDATION

1. More research should be carried out on the limestone deposit at Sagamu quarry to establish the reason for the trend in the Cao content between the Lagos end and the Sagamu end as well as between Ewekoro deposit and Sagamu deposit.
2. In the same vein, further research should be carried out on the range in Fe (%) between the Sagamu end and the Lagos end.
3. A check on the level of beneficiation that should be done to improve or upgrade the Calcium Oxide (CaO) content of the limestone to at least 56% (Duff's recommendation for pure limestone) as well as reduce the Fe (%) in order to make the deposits more suitable for cement production.

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## APPENDIX

**Sample ID :** LD-1

**Result Collated on :** 23 Nov 2013 ,Time :23:12:03

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| CaK | 499405.6 | ±898.93 | 506.1 | Y |
| MnK | 341.2 | ±77.11 | 122.5 | ? |
| FeK | 3651.0 | ±143.85 | 79.4 | Y |
| SrK | 285.6 | ±110.13 | 164.3 | ? |

**Sample ID :** LD-2

**Result Collated on :** 23 Nov 2013 ,Time :23:12:09

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| CaK | 410156.3 | ±820.31 | 427.7 | Y |
| MnK | 217.7 | ±79.22 | 138.9 | ? |
| FeK | 2737.2 | ±131.11 | 66.1 | Y |

**Sample ID :** LD-3

**Result Collated on :** 23 Nov 2013 ,Time :23:12:13

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| SiK | 3986.2 | ±678.05 | 1126.2 | ? |
| CaK | 532427.6 | ±958.37 | 543.9 | Y |
| MnK | 414.6 | ±87.40 | 122.5 | ? |
| FeK | 4485.2 | ±160.57 | 112.3 | Y |

**Sample ID :** LD-4

**Result Collated on :** 23 Nov 2013 ,Time :23:12:16

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| CaK | 533800.8 | ±907.46 | 517.2 | Y |
| MnK | 247.1 | ±92.66 | 163.8 | ? |
| FeK | 4211.5 | ±152.88 | 82.4 | Y |

**Sample ID :** SD-1

**Result Collated on :** 23 Nov 2013 ,Time :23:12:19

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| CaK | 548062.6 | ±931.71 | 516.1 | Y |
| MnK | 704.7 | ±70.89 | 72.3 | Y |
| FeK | 6335.5 | ±186.90 | 126.9 | Y |
| SrK | 334.4 | ±99.42 | 106.5 | ? |

**Sample ID :** SD-2

**Result Collated on :** 23 Nov 2013 ,Time :23:12:23

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| SiK | 2425.0 | ±675.61 | 1134.5 | ? |
| CaK | 512033.3 | ±921.66 | 481.0 | Y |
| MnK | 408.8 | ±80.74 | 92.0 | Y |
| FeK | 5391.1 | ±170.90 | 109.1 | Y |
| SrK | 316.9 | ±119.44 | 174.1 | ? |

**Sample ID :** SD-3

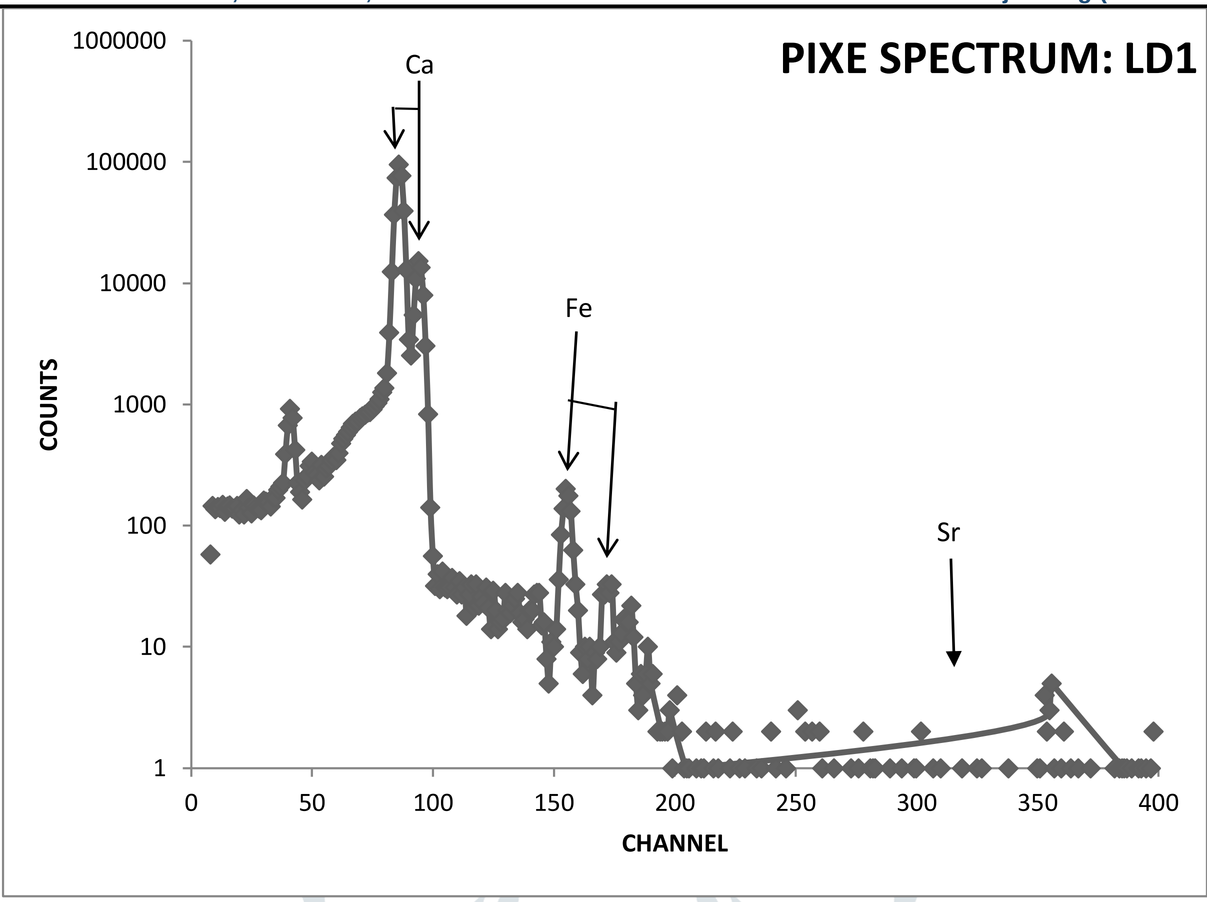
**Result Collated on :** 23 Nov 2013 ,Time :23:12:25

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| SiK | 4784.3 | ±702.81 | 1139.0 | Y |
| CaK | 519002.2 | ±934.20 | 512.2 | Y |
| MnK | 398.4 | ±76.77 | 120.5 | ? |
| FeK | 11087.5 | ±235.06 | 141.3 | Y |
| SrK | 337.6 | ±106.28 | 167.7 | ? |

**Sample ID :** SD-4

**Result Collated on :** 23 Nov 2013 ,Time :23:12:28

| Symbol | Conc (ppm) | Conc Error | LOD | Present |
|---|---|---|---|---|
| SiK | 3060.5 | ±603.22 | 994.0 | ? |
| CaK | 352135.5 | ±774.70 | 384.2 | Y |
| MnK | 357.9 | ±64.82 | 93.4 | ? |
| FeK | 5062.4 | ±167.06 | 67.3 | Y |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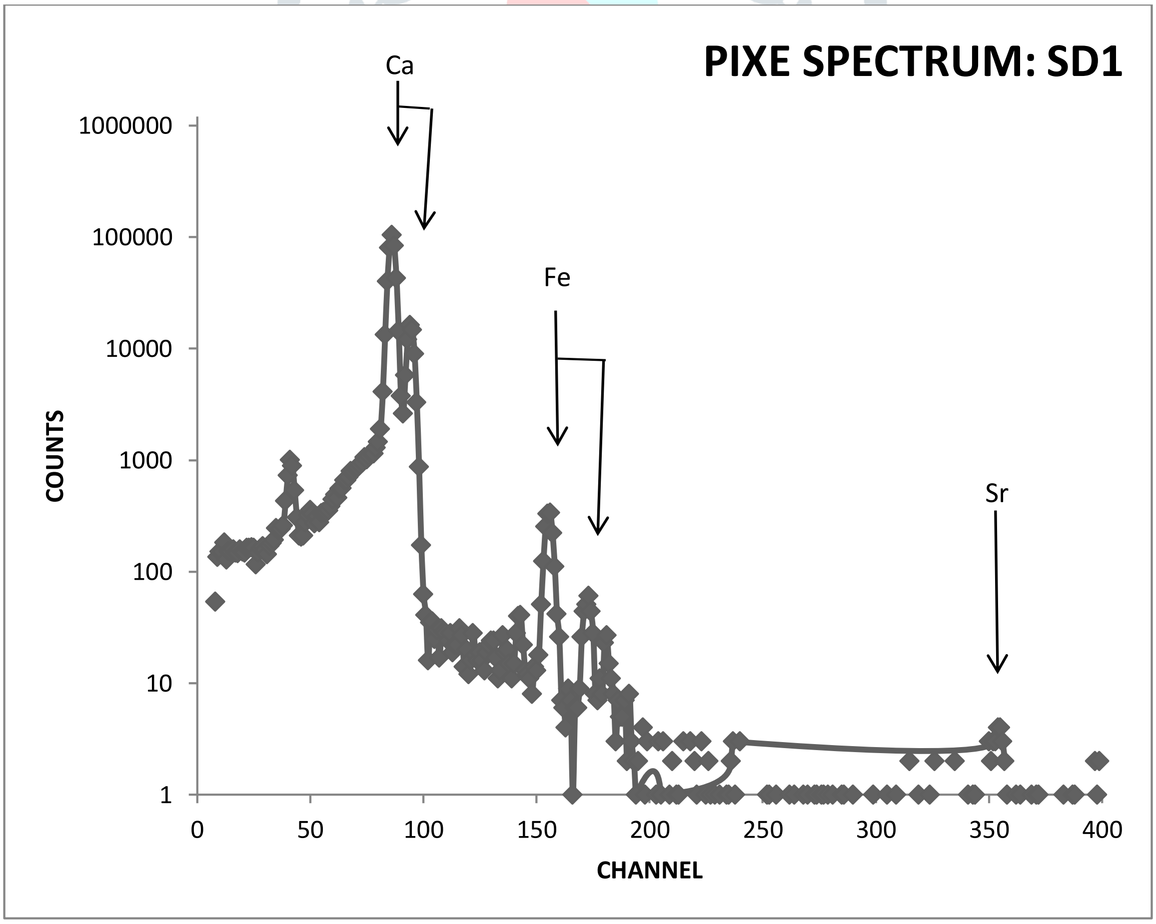
PIXE SPECTRUM: SD1
COUNTS
CHANNEL
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Sr
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1
0
50
100
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200
250
300
350
400

Staff of Lafarge WAPCO with us at the quarry site for sampling