Geochemical Evaluation of Arimogija-Okeluse Limestones, Eastern Dahomey Basin, Southwestern Nigeria

Edema Abayomi [1, *], Owonipa Omoniyi Dare [2,]

[1] Department of Geological Sciences, Achievers University, Owo, Nigeria

[2] Earth Sciences Department, Kogi State University, Anyigba. Nigeria

[*]edemayomi07@yahoo.com

Abstract. 10 representative samples of limestone were collected from the Arimogija- Okeluse Axis of the Dahomey Basin and subjected to X-Ray Fluorescence analysis. Major and Trace elements were used to classify and predict the depositional environment of Arimogija-Okeluse limestone.

The results for the major oxide composition revealed that CaO content ranges from 47.6-52.31% with a mean value of 50.06%. SiO_2 concentration varies from 1.94-5.24% with an average of 3.36%. Fe_2O_3. MgO, and Al_2O_3 contents have mean values of 1.702%, 1.52%, and 1.09% respectively. Other oxides; Na_2O, P_2O_5, K_2O and TiO_2 are low in concentration. The Loss on Ignition also varies from 38.9-41.8 with a mean value of 40.43% suggesting a high carbonate content for the limestone. Standard Ca/Mg and Mg/Ca ratios varies from 25.87-37.63 and 0.03-0.04 with a mean of 33.31and 0.031 respectively. The high strontium content reveals a saline environmental condition of formation for the limestone.

The results obtained showed that the Arimogija-Okeluse limestone is a Magnesian limestone deposited in a shallow marine environment and suitable for cement production.

1. Introduction

Limestone is the most abundant commodity with a global industrial use. A wide range of products has been made from limestone and its by-products. Such products include fertilizers, refractory fillers, ceramics and paints. Limestone has been mined for cement production. The suitability of limestone for cement production is a function of its chemical characteristics, hence the reason for this work.

A knowledge of the purity status of the limestone in the Arimogija – Okeluse area will guide prospective investors and stakeholders in decision making and thus subsequent establishment of a cement factory in the zone. A good number of limestone occurrence in Nigeria has been reported; [1, 2, 3, 4, 5,]

Published works on Arimogija – Okeluse limestone are rare. Very few studies have been carried out on the Arimogija – Okeluse sub-basin. Ehinola et al [5] worked on the depositional environment, geophysical mapping and reserve estimation of the limestone deposit. Ola- Buraimo et al [7] did a Palynological Investigation of a Type Section of Early Maastrichtian Arimogija – Okeluse Shale Sequence. Unlike other research work done on the Arimogija-Okeluse Axis, little or no work has been done on the quality of the limestone. However, this work is aimed at bridging the information gap via geochemical criterion using major and trace element analysis to classify and predict the depositional environment of Arimogija-Okeluse limestone.

2. Geologic Setting

The Dahomey Basin is a sedimentary basin that extends from south-eastern Ghana in the west to the western flank of Niger Delta in Nigeria. It is bounded in the west by the Ghana ridge, which is an extension of the Romanche Fracture Zone; and on the east, by the Benin Hinge line, a basement escarpment which separates the Okitipupa Structure from the Niger Delta Basin and also marks the continental extension of the Chain Fracture Zone [8]. The Nigeria portion of the basin extends from

the boundary between Nigeria and Republic of Benin to the Benin Hinge Line. The stratigraphy of the sediments in the Nigerian sector of the Dahomey Basin is controversial. This is primarily because different stratigraphic names have been proposed for the same formation in different localities in the basin [9]. This situation can be partly blamed on the lack of good borehole coverage and adequate outcrops for detailed stratigraphic studies.

The stratigraphy of the entire basin into three chronostratigraphic packages; they are pre - lower Cretaceous folded sediments, Cretaceous sediments and Tertiary sediments [10]. In the Nigerian portion of the basin, the Cretaceous sequence, as compiled from outcrop and borehole records, consists of the Abeokuta Group which is sub- divided into three formational units: Ise, Afowo, and Araromi Formations [11]. Ise Formation unconformably overlies the basement complex and comprises of coarse conglomeratic sediments. Afowo Formation is composed of transitional to marine sands and sandstone with variable but thick interbedded shales and siltstone. Araromi is the uppermost formation and is made up of shales and siltstone with interbeds of limestone and sands

The Tertiary sediments consist of Ewekoro, Akinbo, Oshosun, Ilaro and Benin (coastal plain sand) Formations. Ewekoro Formation is made up of fossiliferous, well-bedded limestone while Akinbo and Oshosun Formations are made up of flaggy grey and black shales. Glauconitic rock bands and phosphatic beds define the boundary between the Ewekoro and Akinbo Formations. Ilaro and Benin Formations are predominantly coarse sandy estuarine, deltaic and continental beds [12]. The shale – limestone sequence at Arimogija – Okeluse belong to the Cretaceous Abeokuta Formation which was deposited during the first marine transgressive cycle in the Dahomey basin.

The study area lies within longitude 5°33'E - 5°43'E and latitude 6°46'N - 6°51'N at the easternmost part of the Dahomey Basin with elevation range between 50 and 80 meters. (Fig. 1). The mapped area is part of the Cretaceous Abeokuta Group
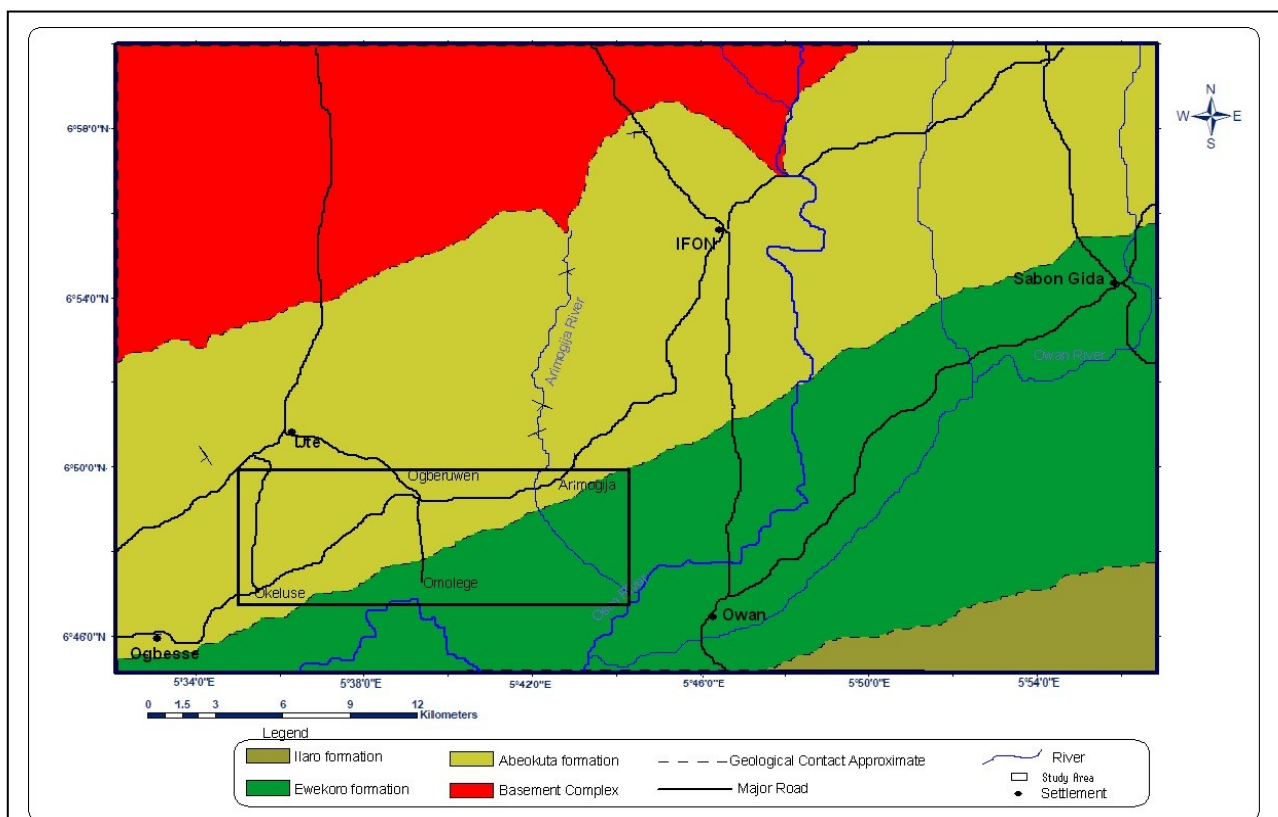

Fig. 1: Geological Map of Arimogija Okeluse Axis (Adapted from Ehinola et al [5])

3. Materials and Methods

10 representative samples of limestone were collected from the Arimogija-Okeluse sub-basin. The collected samples were appropriately labelled and georeferenced. These samples were further subjected to geochemical analysis via the X-Ray Fluorescence method after being pulverised and sieved with 65μ mesh. Concentrations of the major elements were determined on fused lithium-metaborate discs by X-ray fluorescence spectrometry (Philips PW1400 Spectrometer) at Activation laboratory using an Rh tube operated at 40 kV and 70 mA. Loss on ignition (LOI) was determined by heating powdered samples for 50 min at 1000 ºC. The concentrations of Ba, Sr, Zr, were also determined on pressed pellets by X-Ray Fluorescence spectrometry at Activation Laboratory (operating conditions: Rh radiation, 70 kV, 40 mA).

4. Results and discussion

Sediment Chemistry

4.1 Major Oxides

The result of major elemental oxides (Table 1) for the analysed samples show that the concentration of CaO ranges from 47.6 – 52.31% with an average of 50.06%. The SiO_2 content varies from 1.94 – 5.24 % with a mean of 3.36% and Fe_2O_3 ranges between 1.2 – 2.54% with a mean of 1.70% while MgO and Al_2O_3 contents vary from 1.39 – 1.84% and 0.61 – 1.82% with average values of 1.52 and 1.09% respectively. Other oxides; Na_2O, P_2O_5, k_2O and TiO_2 are low in concentration with average values of 1.52, 0.90, 0.1, 0.05 and 0.08% respectively (Table 1). The Loss on Ignition also varies from 38.9 – 41.8 with a mean of 40.43 %

Table 1: Major Oxides (%) Concentrations for Arimogija-Okeluse Limestone

SAMPLE ID	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI
ARS1	4.52	1.79	2.03	1.76	48.60	0.02	0.07	0.13	1.31	0.1	39.5
ARS2	5.24	1.82	2.54	1.84	47.60	0.02	0.06	0.13	1.42	0.1	38.9
ARS3	3.89	0.97	1.89	1.43	49.20	0.02	0.06	0.12	1.29	0.1	40.2
ARS4	4.58	1.57	2.41	1.60	48.67	0.02	0.06	0.13	1.33	0.1	39.5
ARS5	4.78	1.66	2.03	1.58	47.89	0.02	0.07	0.12	1.30	0.1	39.8
OKL6	1.94	0.61	1.20	1.39	52.31	0.02	0.04	0.03	0.43	0.1	41.8
OKL7	1.96	0.61	1.22	1.40	51.98	0.02	0.04	0.03	0.47	0.1	41.2
OKL8	2.54	0.61	1.22	1.40	50.06	0.02	0.05	0.03	0.51	0.1	40.9
OKL9	1.99	0.61	1.28	1.42	52.22	0.02	0.05	0.03	0.48	0.1	41.3
OKL10	2.16	0.61	1.20	1.40	52.04	0.02	0.04	0.03	0.47	0.1	41.2
MEAN	3.36	1.09	1.70	1.52	50.06	0.02	0.05	0.07	0.90	0.1	40.4

ARS: Arimogija Limestones, **OKL:** Okeluse Limestones

CaO; Calcium Oxide and SiO_2; Silica

From the result of the major oxides, CaO is prevailing, Table 1. CaO shows an inverse relation with silica SiO_2. Relatively, high value of CaO shows a low value of MgO. Comparatively, high level of CaO and low values of silica and MgO show a high degree of purity of the limestone. This makes it fit for cement production.

The CaO at Arimogija- Okeluse compares satisfactorily with that of Olade [2]but it displays a strong low when compared to that of Sagamu (89.2 %,), Ewekoro (80.3%) and Ibeshe (75.7%) [4], Table 2. Ehinola et al [5] reported a highly fossiliferous limestone for the Arimogija Okeluse limestone and thus classify it as a bioclast wackestone. These carbonate grains are derived from the reworking of shelf carbonate allochems during transgression [13, 14].

Mean SiO_2 values of 13.9% and 11.3% for Igunmale and Sokoto respectively [2]. The Silica concentration of Arimogija-Okeluse limestone (3.36%) is low relative to other limestones deposits in Nigeria. However, it is almost at par with that of Sagamu, Ewekoro and Ibeshe with mean values of 5.7%, 8.7% and 14.8% respectively, [4]. This study however established that Arimogija–Okeluse limestone is a low silica limestone, hence it is of high grade

Alumina (Al_2O_3) and Magnesium Oxides (MgO)

Relative to the concentration of CaO, Alumina and Magnesium oxide concentrations are low with mean values of 1.09 % and 1.52 % respectively [2]. The low concentration of alumina suggests a low energy environment. The skeletal debris of marine invertebrate has low magnesium with increasing level in the phyla, [15]. Arimogija – Okeluse limestone is rich in brachiopods, gastropods, bivalves, and shell fragments of echinoids and ostracods which are typical of an open shelf environment [5]. The presence of these invertebrates is suspected to be responsible for the low level of magnesium in the samples. Magnesium concentration is also a function of temperature of formation, and often low in shells living in shallow waters [16]. Consequently, shallow marine environment is therefore proposed for Arimogija – Okeluse limestone.

Table 2: Analytical Data of Other Comparable Limestones in Nigeria (%)

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI
RelativelyPure Limestone [17]	1.88	0.83	0.26	2.75	50.89	0.06	0.01	0.01	0.01	0.01	
This study	3.36	1.09	1.70	1.52	50.06	0.02	0.05	0.08	0.90	0.10	40.4
Tse-Kucha Limestone [6]	6.40	2.20	1.40	0.70	48.20	0.09	0.48	0.11	0.11	0.13	40.12
Nkalagu [18]	5.90	1.30	0.77	0.99	49.74	-	-	-	-	-	-
Middle Belt Zone [19]	0.53	0.07	0.04	1.77	52.17	0.19	0.13	0.01	-	0.07	44.97
Gboko Limestone [20]	9.78	1.48	2.20	1.99	48.88	0.05	0.01	-	-	-	36.57
Mfamosing Limestone [21]	0.25	0.35		0.15	56.12	0.01	0.03	-	-	-	-
Sagamu [4]	5.70				89.20						

Classification of Limestone

Pettijohn, [17], have classified limestone. However, the classification of limestone in the study area is made after Todd, [22]. The standard ratio; Ca/Mg ratio and its reciprocal ratio: Mg/Ca was employed by Todd [22] as a parameter for Chemical Classification of limestone. Todd [22] grouped Limestone samples with Ca/Mg ratios with a range of 1.41%-12.30% as Dolomitic Limestone, samples with Ca/Mg ratio of 12.30%-39.00% as "Magnesian Limestone" and Limestone samples having 39.00% to 100% are grouped as "Pure Limestone" Table 3.

Table 3: Chemical Classification of Limestone [22]

Descriptive term	Standard ratio Ca/Mg	Reciprocal Ratio Mg/Ca
Dolomitic Limestone	12.30 – 1.41	0.08 – 0.18
Magnesian Limestone	39.00 – 12.30	0.03 – 0.08
Pure Limestone	100.00 – 39.00	0.00 – 0.18

However, the standard Ca/Mg ratio varies from 25.87 to 37.63 while the reciprocal ratio Mg/Ca ranges from 0.03 – 0.04. This result reveals that the limestone deposit in Arimogija – Okeluse is the Magnesian limestone type (Table 4).

The Ca/Mg ratio also corresponds to stability condition during the formation of carbonate rock [23]. He pointed out that the degree of salinity increases with decrease in Ca/Mg ratio. Higher values of Ca/Mg ratio of the studied carbonate indicates comparatively less evaporation of sea water and low salinity which prevailed during the formation of limestone in general.

Table 4: Chemical classification of Arimogija - Okeluse Limestone

SAMPLE ID	MgO	CaO	Ca/Mg	Mg/Ca	Remarks
ARS1	1.76	48.60	27.61	0.0362	Magnesian Limestone
ARS2	1.84	47.60	25.87	0.0387	Magnesian Limestone
ARS3	1.43	49.20	34.41	0.0291	Magnesian Limestone
ARS4	1.60	48.67	30.42	0.0329	Magnesian Limestone
ARS5	1.58	47.89	30.31	0.0330	Magnesian Limestone
OKL6	1.39	52.31	37.63	0.0266	Magnesian Limestone
OKL7	1.40	51.98	37.13	0.0269	Magnesian Limestone
OKL8	1.40	50.06	35.76	0.0280	Magnesian Limestone
OKL9	1.42	52.22	36.78	0.0272	Magnesian Limestone
OKL10	1.40	52.04	37.17	0.0269	Magnesian Limestone
MEAN	1.52	50.06	33.31	0.0315	

ARS: Arimogija Limestones, **OKL:** Okeluse Limestones

4.2 Loss on Ignition (L.O.I)

L.O.I reveals the content of volatiles present in the limestone deposit. The L.O.I value in the study area averages 40.4 .High L.O.I value is indicative of high volatile content and this suggests a high carbonate content since it is synonymous with the evolvement of carbon dioxide after heating at 1000 ºC [24]. The fluctuation (increase or decrease) in Fe_2O_3 content may have a relationship with the terrigenous influx associated with high Iron bearing solutions. Higher amount of Fe_2O_3 in carbonate rocks reduces the absorption capacity which in turn lowers the rate of ignition of the samples

4.3 Trace Element Geochemistry

The trace elemental composition reported in ppm (Table 5) has the concentration of Sr ranging from 409 – 516 ppm with an average of 460 ppm. Zr and Ba vary from 8-36 ppm and 10 – 25 ppm with mean values of 22 ppm and 18.3 ppm respectively.

Trace elements analysis has been used in describing the conditions at deposition in specific depositional environment. It is a veritable tool used in the differentiation of shallow water and deep water limestones. Strontium and Manganese are markedly enriched in carbonate sediments. Hence, the enrichment of strontium in limestone is accounted for by the fact that Sr^{2+} substitutes readily for the very similar ion $Ca^{2+.}$ The smaller but appreciable concentration of manganese in carbonates is probably also attributable to similarity in ionic size.

Strontium

Flugel and Wedepohl, [25] reported relatively low Sr values (100-400 ppm) for shallow marine and relatively high Sr content (Oberalm limestone) for deeper water carbonates. Bausch [26, 27] also reported a high value of Sr (500-3000 ppm) which depicts a deep marine environment. Shallow water and deep water carbonates also have relatively low Sr (100-400 ppm) and high Sr values respectively [28]. The strontium (Sr) concentration in Arimogija-Okeluse Limestone indicates that the formation of the limestone under higher saline environmental conditions.

Table 5: Trace Element Concentration (ppm) of Arimogija-Okeluse Limestone

SAMPLE ID	Ba	Sr	Zr
ARS1	23	505	35
ARS2	25	516	35
ARS3	20	502	36
ARS4	24	504	35
ARS5	25	510	36
OKL6	10	420	8
OKL7	12	415	9
OKL8	15	410	9
OKL9	14	417	9
OKL10	15	409	8
MEAN	18.3	460.8	22

ARS: Arimogija Limestones, **OKL:** Okeluse Limestones

5. Summary and Conclusion

Limestone remains one of the industrial minerals with global use. Limestone is quarried for cement production in some part of Nigeria. However, the suitability of limestone production depends on its chemistry. This helps in the prediction of its purity.

The geochemical investigation of the Arimogija-Okeluse limestone was carried out to accomplish a chemical classification with respect to its chemical composition. It was revealed that CaO shows an inverse relationship with SiO_2. The prevailing concentration of CaO with respect to SiO_2 depicts its suitability for cement production.

The Todd chemical classification revealed that the Arimogija Okeluse limestone is the Magnesian type; with Ca/Mg standard ratio range of 25.87-37.63 and a reciprocal ratio Mg/Ca range of 0.03-0.04. The relationship between Alumina (Al_2O_3) and MgO depicts a shallow marine environment for the Arimogija Okeluse limestone. The Trace element geochemistry also predicts the formation of limestone in shallow waters.

In general, the results obtained, however revealed that the Arimogija-Okeluse limestone is a Magnesian limestone type deposited in a shallow marine environment and suitable for cement production.

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