CHEMICAL ASSESSMENT OF LIMESTONE DEPOSIT IN PARTS OF IJEBU MEMBER, DAHOMEY BASIN, NIGERIA

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Abstract- Fifteen rock samples were collected from some part of the Ijebu member of Ewekoro formation around Odogbolu, Southwestern Nigeria. These samples were analyzed for their elemental oxides and petrography to determine their depositional environment and rock provenance. The analysis was carried out using appropriate methods. The total organic carbon value ranges between 0.13% and 0.28% as against the threshold value of 0.30% for a good source of carbonate rock. The geochemical analysis indicates that the CaO percentage ranges from 19.12 to 52.69%, while the MgO percentage is generally low, ranging from 0.13 to 2.60%. This implies little or no dolomitization, and it indicates a good raw material for cement production. The SiO_2 percentage ranges from 5.61 to 37.03%. These could have resulted from the slight incursion of the underlying Abeokuta formation, but studies revealed that it reduces as it grades towards the upper layers. The Fe_2O_3 percentages were relatively low. Further studies revealed that the limestones contain some fossils including foraminifera, gastropods, mollusks, echinoids and algae which have been recrystallized, obliterated and refilled by calcite during the diagenetic process.

Keywords: Chemical, Gastropods, Mollusks, Limestones, Source Rock

1. INTRODUCTION

Limestone is an extremely valuable raw material, they are widely used throughout industry, although the principal consumers are the construction and manufacturing industries. Harrison (1993) explains limestone to contain mainly of Calcium carbonate ($CaCO_3$ in form of Calcite or occasionally aragonite in topical deposits. It may contain some impurities such as clay minerals, silica, organic matter and iron hydroxide minerals. It could be formed through biogenic processes, which consist of the fossils of carbonates- secreting organisms while others are formed resulting from inorganic chemical precipitation.

The research work was conducted on the limestone deposits within Ijebu member, Ewekoro formation with a total depth of 120.0 meters, at Ikise within the Southern axis of Odogbolu area of Ogun State, Southwestern Nigeria. This locality falls within the Ijebu member of the Ewekoro formation (Figure 1). Series of studies have been conducted within this basin, but not much has been done in this locality mostly the subsurface deposits. Previous research works conducted within this basin include (Akinmosin and Shoyemi, 2010; Amigun et al., 2012; Odunaike et al., 2010; Akinmosin et al., 2012 and Ikhane et al., 2012). They applied sedimentological and geophysical analysis to describe the basin. Other research studies on the study area (Jones and Hockey, 1964; Omatsola and Adegoke, 1981; Agagu, 1985; Elueze and Nton, 2004; Akinmosin et al., 2005) assess this basin using geology and stratigraphy of the Dahomey basin. The stratigraphy of the basin is mostly constituted by sand and shale alternations with minor proportion of limestone, (Agagu, 1985). The Cretaceous and Tertiary ages limestone is related with shale siltstone, and fine-grained sandstone that are often hard, gray and shelly.

The Tertiary beds sometimes contain limestone and inter-bedded marbles (RMRDC, 2001). Most of the deposits being exploited by the cement industry have varied compositions, which range from about 81% calcite ($CaCO_3$) in Sokoto to about 96% calcite ($CaCO_3$) in Mfamosing.

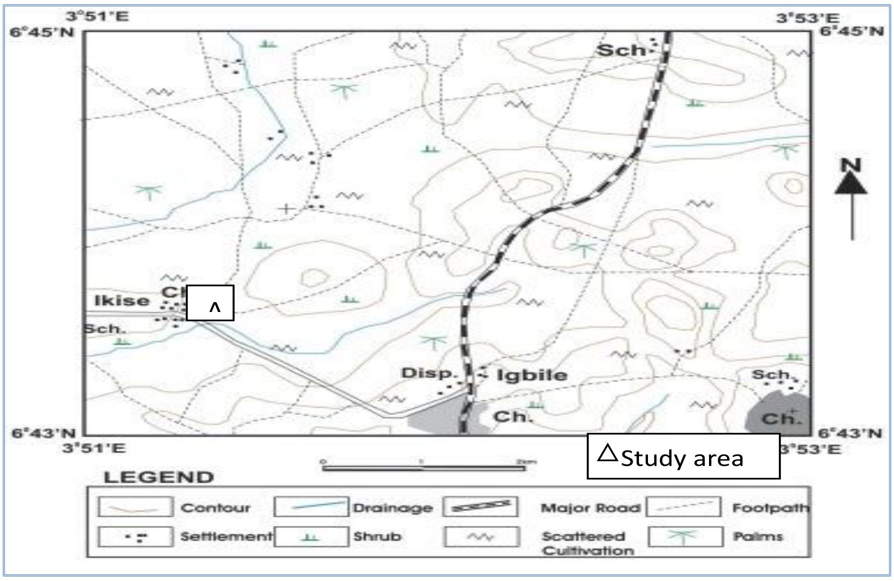


Figure 1; Map of the study area (Adapted from Ikhane et al. 2013)

2. GEOLOGICAL SETTINGS OF THE STUDY AREA

The area under study can be seen in part of the Eastern Dahomey basin, it lies withn coordinates N 06^0 44^1 and N 06^0 47^1, and E 03^0 52^1 and E 04^0 02^1 as shown in figure 1. The Dahomey Basin is a one-sided source asymmetry basin (Omatsola and Adegoke, 1981) which formed the transitional crustal zone sandwiched between thick continental crust and thin oceanic crust.

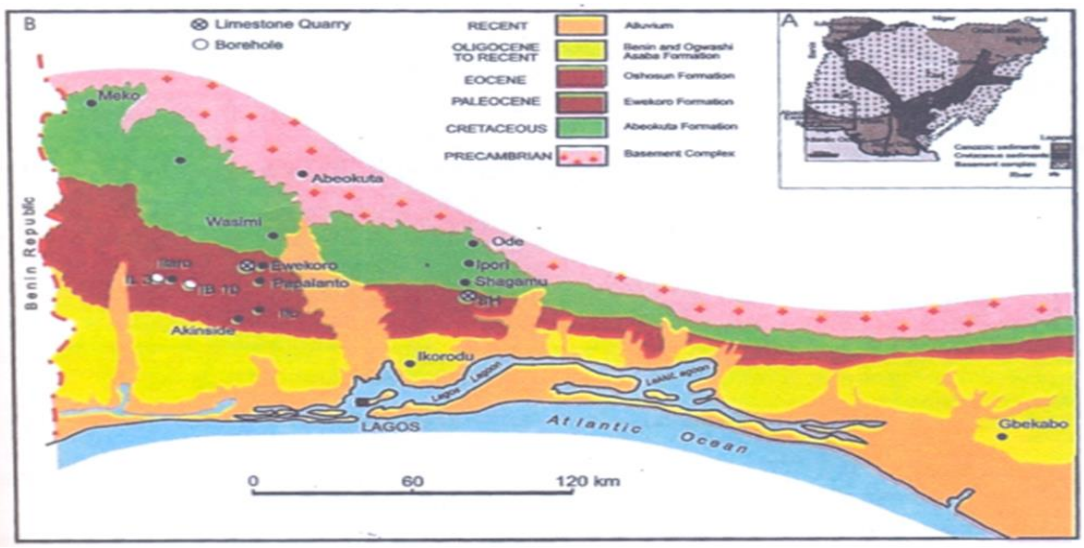


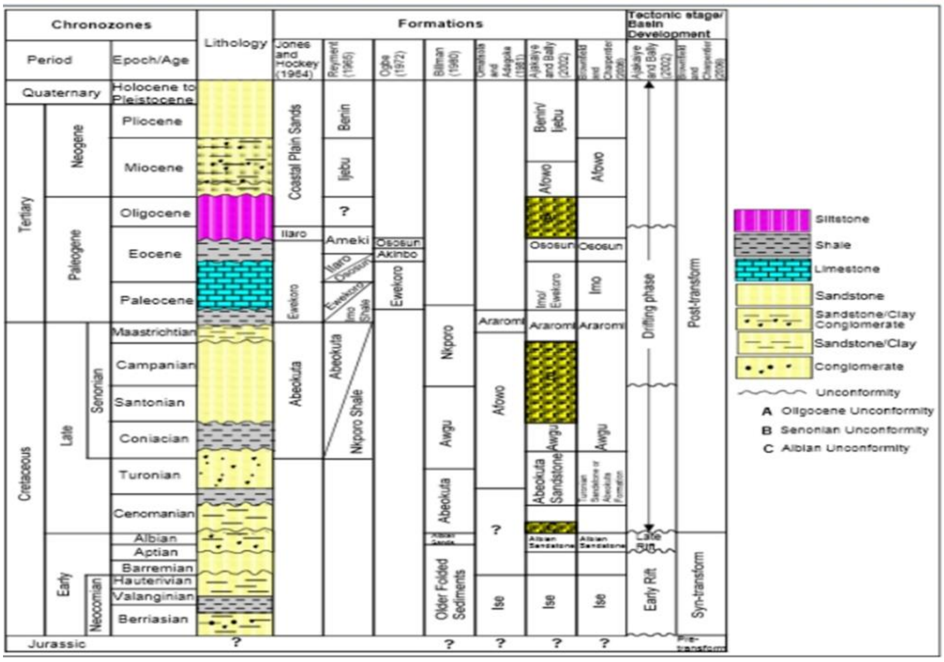
Fig.2: Eastern Dahomey Basin Geological map showing the study area (Billman, 1992)

This Evolved due to the series of opening up of the Central and South Atlantic in the Middle Jurassic and Cretaceous. Deposition was originated in the fault controlled structural depression (Omatsola and Adegoke, 1981) on the basement complexes during early Cretaceous. This was followed with subsidence that led to the deposition of a very thick (over 1400m) sequence of continental grits and gravelly sands over the entire basin, covering most of Southwestern Nigeria, the Benin Republic, Togo and Ghana.

During the Santonian, another episode of major tectonic movement occurred in the basin which led to the tilting and block –faulted into sequence of horst and graben (Bodashe Horst, Ilepaw Horst, Afowo Graben, Ojo Platforms, Orimedu Graben and Ise graben (Omatsola and Adegoke, 1981) that are still active till date. Sediment accumulation in the basin varies in thickness on the on-shore coastal section from 100m to 1,400 m along strike and well over 2,000 m in the offshore part of the basin.

The architectural stratigraphy (Table 1) of Dahomey basin was well discussed from the research studies of Jones and Hockey (1964); Omatsola and Adegoke (1981); Agagu (1985); Enu (1990), Nton et al., (2006). Agagu (1985) opined that the eastern Dahomey basin stratigraphy from surface to subsurface data, showed that in most section, the stratigraphy is dominated by repetition of sand and shale alternations. This Limestone under study occur within the Sedimentary Basin of Dahomey. The earliest work in this basin was conducted by the Mineral Survey of Southern Nigeria between 1905 and 1908. A detailed description of the Ewekoro formation was given by Jones and Hockey (1964), he assigned a lower palaeocene age to the formation based on biostratigraphic studies.

Table 1: Generalized stratigraphic column showing age, lithology, and sequence of the formations and tectonic stage of basin development in the Nigerian sector of the basin. Olabode, (2016)



The stratigraphy of the basin was delineated resulting in creating the boundary between the Ewekoro formation and the underlying Abeokuta formation. Adegoke (1981), studied twenty-one boreholes within Ewekoro formation, he observed an average thickness of 16m of Ewekoro limestone and an average age of 54.45/+2.7millions from radioactive dating of the glauconite within the Ewekoro formation was assigned to the rock. He subdivided the limestone into three microfacies units, using field evidence and petrographic studies. In his research study, Ogbe (1972), observed a discontinuous topmost unit of the limestone which he referred to as a red phosphatic biomicrite.

The basin tapers to about 50 km (Akinmosun et al., 2005) towards the eastern end causing the basement to adopt a convex upwards outline with associated thinning of sediments. Towards the northeastern margin of the basin is situated the Okitipupa high (Nwachukwu and Ekweozor, 1989). The limestone is made of shallow marine origin (Elueze and Nton, 2004) resulted from concentration of coralline algae, gastropods, pelecypods, echnoid fragments and other fossil remains. The colour ranges from grayish white to seldom greenish consists of sand toward the base, with a thickness between 15 and 30m. Paleocene age was assigned for his formation. Three chronostratigraphic units were observed some research works: (i) pre-Lower Cretaceous folded sequence, (ii) Cretaceous sequence, and (iii) Tertiary sequence (Omatsola and Adegoke, 1981; Billman 1992).

2.2 Cretaceous Successions

The basin stratigraphically made of Abeokuta Group which is sub-separated into units, namely; Ise, Afowo, and Araromi (Omatsola and Adegoke, 1981). This was overlain by the oldest Tertiary sequence of the Ewekoro Formation. The Ewekoro Formation is uncomformably overlain by the predominantly shaley formation Ogbe (1972) named it Akinbo Formation. This formation rest uncomformably on the Afowo Formation where ewekoro formation is missing (Bilman, 1992).

The Akinbo Formation grade into the overlying mudstones and claystones of the Oshosun Formation. The presence of glauconites, phosphates and abundant planktic foraminifera in the Oshosun Formation indicates deposition in a fairly deep marine environment, probably in the bathyal zone. Overlying this Formation, is the Ilaro Formation, described by Jones and Hockey (1964) in shallow boreholes drilled at the Akinside and Ifo areas. The Ilaro Formation is composed of coarse, angular and poorly sorted sand with substantial clay layers and few existences of shale. The Coastal Plain capped all the formation (Jones and Hockey, 1964) within this basin. It comprises of yellow and white, occasionally cross-bedded sand, pebbly beds and clay deposits with some sandy clay lenses. Its thickness is unknown except in the Niger Delta where it measures about 2000 m.

3. MATERIALS AND METHODS

3.1 Field Sampling

The selected Thirty-six ditch cuttings samples were collected at interval of 3.0 meters depth each from the borehole within Ijebu member, Ewekoro formation, after careful selection based on lithology, colour, fossil content, texture, rock type etc., fifteen samples were prepared for geochemical analysis. Diluted HCI acid was applied on the samples to ascertain the cementing materials. They were carefully packed in Ziploc sample bags and well labelled. The lithologic descriptions are shown in Figure 3.

3.2 Geochemical Analysis

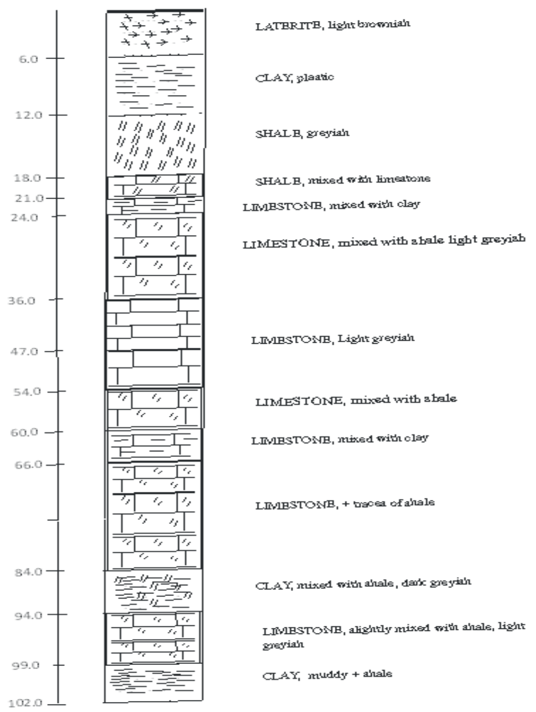
A representative of 15 samples were prepared for pulverization using mechanical pulverizer (mortar and pestle) until it could pass through the 150_{um} sieve. 25g of each sample was put in a drying dish and dried in an oven at 110^{O} C -120^{O} C for 25minutes and was subjected to cooling in desiccator. 0.8g of stearic acid was added to 20g of the sample in weighing dish. The sample was spread with the aid of spatula in the grinding puck and ring for grinding in the gyratory mill. This is used to reduce the samples to very fine powder within 2 minutes. Each of the samples was pressed with the aid of T-40 Automatic Hydraulic press in a pellet cup containing 1g of stearic acid. This was pre-set to exert 12tons of load for 25 seconds. The 40mm pressed pellet was mounted on a sample holder for analysis using X-Ray Fluorescence (XRF). The results were subjected to interpretation.

4. RESULTS AND DISCUSSION

Based on the field and laboratory analyses conducted, the lithologic description and the results are presented below:

4.1 Lithologic Description

The color of the limestone ranges from light grayish to deep greyish as increased with depth. It is fine grained, slightly friable to compacted and slightly sandy at the top indicating that the sand is uncomfortably underlying the fine grained sand on top of it. The presence of sand in this section makes the limestone to be slightly siliceous and poorly sorted (Table 1). The limestone is fossiliferous with the presence of fossilized ostracods and echinoid remains within the samples, which is indicative of its deposition in a marine environment.



(a)

Depth Range (M)	Sample Number	Lithology	Description
18.0-21.0	IJ1	Limestone	Light grey-white, sandy fossiliferous, poorly soted.
21.0-24.0	IJ2	Limestone	Milky white, fossiliferous, well compacted
24.0- 27.0	IJ3	Limestone	Milky white, fossiliferous, well compacted.
27.0-33.0	IJ4	Limestone	Milky white, fossiliferous, well compacted.
33.0-36.0	IJ5	Limestone	Milky white, fossiliferous, well compacted.
36.0-39.0	IJ6	Limestone	Milky white, fossiliferous, well compacted.
39.0-45.0	IJ7	Limestone	Milky white, fossiliferous, well compacted
45.0-48.0	IJ8	Limestone	Milky white, fossiliferous, well compacted
48.0-54.0	IJ9	Limestone	Milky white, fossiliferous, well compacted
54.0—60.0	IJ10	Claystone	Grey, fine grained well sorted, friable.
60.0-66.0	IJ11	Limestone	Grey, fossiliferous, well compacted
66.0-72.0	IJ12	Limestone	Grey, fossiliferous, well compacted

(b)

Figure 3: Lithostratigraphic Description of samples from the study area (b) Table 2: Lithologic description of the Limestone section of Ijebu member

4.2 Geochemical result

In the course of this study, twelve samples were considered for geochemical analysis to determine the major elemental compositions, the data obtained is presented in Table 3.
From the samples under study, the SiO_2 ranges from 5.61-37.03 wt % with an average value of 16.2wt%, while other elemental oxides show that Al_2O_3 varies from 0.01to18.4 (2.5wt%), CaO varies from 19.12-52.69 wt% (43.3wt%), K_2O varies from 0.03 to 0.95wt%, (0.2wt%), Na_2O

varies from 0.19 to 0.25wt% (0.2wt%), MgO varies from 0.13 to 2.55wt% (1.0wt%) and Fe_2O_3 varies from 0.95 to 9.37wt% (0.2wt%) with their wt% respectively.

Table 3: Percentage Elemental Oxides of Samples Analyzed

S/ N	IJ1	IJ2	IJ3	IJ4	IJ5	IJ6	IJ7	IJ8	IJ9	IJ10	IJ11	Mz	RANGE
Na_20 %	0.24	0.24	0.24	0.24	0.23	0.24	0.23	0.23	0.23	0.19	0.22	0.2	0.19-0.24
Mg0 %	0.14	0.13	0.15	0.3	0.51	0.38	1.05	1.82	1.62	2.55	2.6	1.0	0.13-2.55
Al_20_3 %	0.01	0.49	0.69	1.17	1.3	0.82	1.03	1.05	0.79	18.4	1.96	2.5	0.01-18.4
SiO_2 %	5.61	8.66	8.33	10.98	11.5	15.86	33.73	14.4	19.7	37.03	11.83	16.2	5.61-37.03
SO_3 %	0.09	0.09	0.09	0.09	0.12	0.09	0.11	0.13	0.25	0.62	0.31	0.2	0.09-0.63
K_20 %	0.04	0.03	0.05	0.08	0.08	0.06	0.04	0.1	0.07	0.95	0.16	0.2	0.03-0.95
CaO %	52.69	50.03	49.51	46.87	47.1	45.71	38.54	43.7	41.6	19.12	41.37	43.3	19.12-52.69
Fe_2O_3%	0.95	1.04	1.18	1.62	1.34	1.15	1.73	1.65	1.86	9.37	2.95	2.3	0.95-9.37
LOI	39.63	39.29	39.76	39,65	37.2	35.69	23.54	36.9	33.9	11.76	38.6	33.6	11.76-39.76
K2O/AL2O3	4.0	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1-0.4
SIO2/AL2O3	561.0	17.7	12.1	9.4	8.8	19.3	32.7	13.7	25.0	2.0	6.0	6.4	2.0-561
Log(SiO2/Al2O3)	2.7	1.2	1.1	1.0	0.9	1.3	1.5	1.1	1.4	0.3	0.8	0.8	0.3-2.7
Fe2O3/K2O	23.8	34.7	23.6	20.3	16.8	19.2	43.3	16.5	26.6	9.9	18.4	15.0	9.9-43.3
Log(Fe2O3/K2O)	1.4	1.5	1.4	1.3	1.2	1.3	1.6	1.2	1.4	1.0	1.3	1.2	1.0-1.6
K2O/Na2O	0.2	0.1	0.2	0.3	0.3	0.3	0.2	0.4	0.3	5.0	0.7	0.7	0.1-0.7

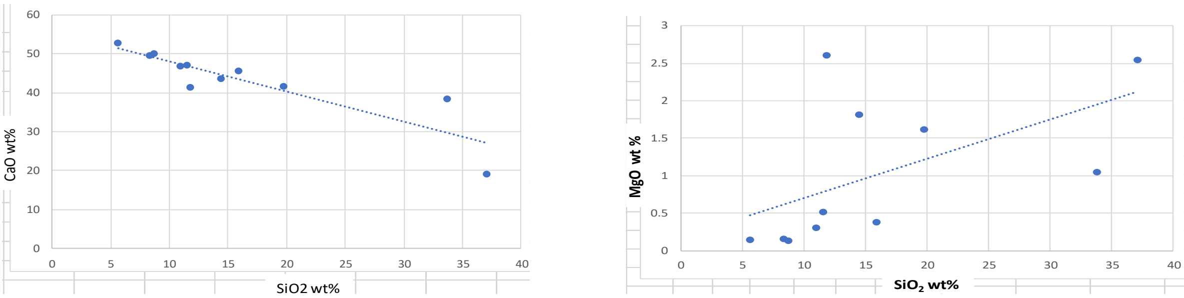
The high concentration of CaO was observed in all the samples except sample IJ10 that was slightly low. The high concentration observed might possibly resulted from the traces of fossil remains present in the samples, while the low CaO occurrence in IJ10 could be related to non- calcareous deposits. The MgO content is relatively low which an indication of little or no dolomitization. The $Si0_2$ contents is averagely high, this is indicative of the siliceous nature of the sample. The Fe_20_3 and Al_20_3 percentages are low ranging from 0.95% to 2.95%, and 0.01 to 0.49% respectively. An exception to this is average weight % of sample IJ10 with (9.37), F_20_3 and (18.41) Al_20_3. The Na_20, K_2O and $S0_3$ are very low. This could be attributable to the effects of weathering and erosion on feldspars resulting to its destruction during transportation and diagenesis (Onakomaya et al., 1992).

Table 4: Pearson correlation coefficients of the major Elemental Oxides of Samples from the study area

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3	LOI
Na_2O	1								
MgO	-0.816	1							
Al_2O_3	-0.922	0.576	1						
SiO_2	-0.725	0.558	0.687	1					
SO_3	-0.966	0.803	0.913	0.645	1				
K_2O	-0.933	0.612	0.997	0.658	0.93	1			
CaO	0.946	-0.761	-0.91	-0.883	-0.911	-0.906	1		
Fe_2O_3	-0.96	0.685	0.987	0.703	0.959	0.991	-0.939	1	
LOI	0.824	-0.52	-0.852	-0.954	-0.755	-0.826	0.933	-0.848	1

The concentrations of CaO, SiO_2 and Al_2O_3 in the sample under study indicate the incursion of sediments from clastic sediment source area of the limestones. Also, the availability of Fe_2O_3 in the samples suggest that the iron content might have been formed with calcite (Gary, 2009), mostly during primary precipitation in reducing condition (Harrison, 1993) during sedimentation processes. Bivariate plots of some major elements were conducted to determine the provenance of the limestones under study (Figure 4a and b). The SiO_2 versus CaO was positively correlated which suggested a terrigenous material (Braithwaite, 2005) transgressing into the basin. Based on the Pearson correlation coefficient table, the correlation pattern of SiO_2 against MgO, Na_2O and SO_3 diagrams (Table 4) all suggest the association of sulfur, magnesium and sodium possibly with the detrital components. From the correlation table, it was observed CaO versus Al_2O_3, MgO and SO_3 appears positively correlated whereas CaO vs. K_2O were negatively correlated an indication that $CaCO_3$ content possibly increased at the sites of fossiliferous sediment deposition.

It was further observed that the Al_2O_3 versus Fe_2O_3 and SiO_2 have negative correlation while Al_2O_3 versus MgO, Na_2O and SO_3 exhibits positive trend indicating that the limestone of the study area might have been derived from the fossil's sources (Tucker, 2001)



Figures 4a & b: bivariate plots of SiO_2 versus CaO and MgO showing postive and negative correlation patterns

5. CONCLUSION AND RECOMMENDATION

The percentage oxides of CaO contents range from 20 – 55%. This results from the high constituent of this oxide at the upper units resulting from the high fossil content, while the reduction in this was due to its trending nature to the sandy Abeokuta formation. The high oxides of CaO contents in the samples shows their calcitic nature, this makes it available for possible cement production while the reduced MgO in it is indicative of low dolomite. The $Si0_2$ content ranges from 5.61 – 37.03%. It is relatively high towards Abeokuta formation, while the Al_2O_3 and K_2O contents are low, this is attributed to the possibility of feldspars destruction during transportation and digenesis processes that occurred during burial. The silica present in the limestone from the study area would also aid the production of cement,

Finally, based on the chemical composition and other parameters, the limestone is suitable for cement and fertilizer production. It will require technical approach for exploitation. It is therefore recommended that detailed subsurface geological and geophysical studies of these areas be carried out to obtain substantial information about the subsurface geology and the probability of discovery of hydrocarbon deposits.

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