

# Evaluations of Turonian Limestone Formation Exposed at NIGERCEM-Quarry, Nkalagu, Southeastern Nigeria: A Geochemical Approach.

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## ABSTRACT

A geochemical study of Nkalagu limestone of the Lower Benue Trough as exposed at Nigeria Cement Company (NIGERCEM) was carried out. The study aims at the determination of major oxides and trace elements of the limestone exposed in the quarry using X-Ray Fluorescence Spectrophotometer (XRF) and Atomic Absorption Spectrophotometer (AAS) respectively as well as reconstructing the depositional history of the deposit. Petrographic study was also done to enhance the determination of biogenic contents of the deposit. Results of fifteen (15) samples collected for analysis put the range major elements as follow: CaO (46.56 – 54.15%), SiO<sub>2</sub> (3.12 – 10.04%), Fe<sub>2</sub>O<sub>3</sub> (0.23 – 1.37%), MgO and Al<sub>2</sub>O<sub>3</sub> (0.72 – 1.27%) and (0.65 – 1.90%) respectively. Also, the trace elements contents expressed in ppm were found to be 1653 – 3306 for Fe, 76 – 1543 for Mn, 600 – 1035 for Sn and 4.5 – 53 for Zn. Interpretation of these results suggest a shallow marine possibly an off – shelf depositional model for the formation.

(Keywords: geochemistry, limestone, petrographic study, oxides, trace elements)

## INTRODUCTION

Nkalagu limestone is a rock unit in Nkalagu formation of the Lower Benue Trough. This formation has been found to evolve in Turonian time (Peters, 1978). Nkalagu formation type section is located at the Nkalagu limestone quarry of Nigeria, where it is well exposed in two quarry faces. These mineral (limestone) is been exploited for the production of cement. What determines the suitability of a limestone deposit for the production of cement is largely its

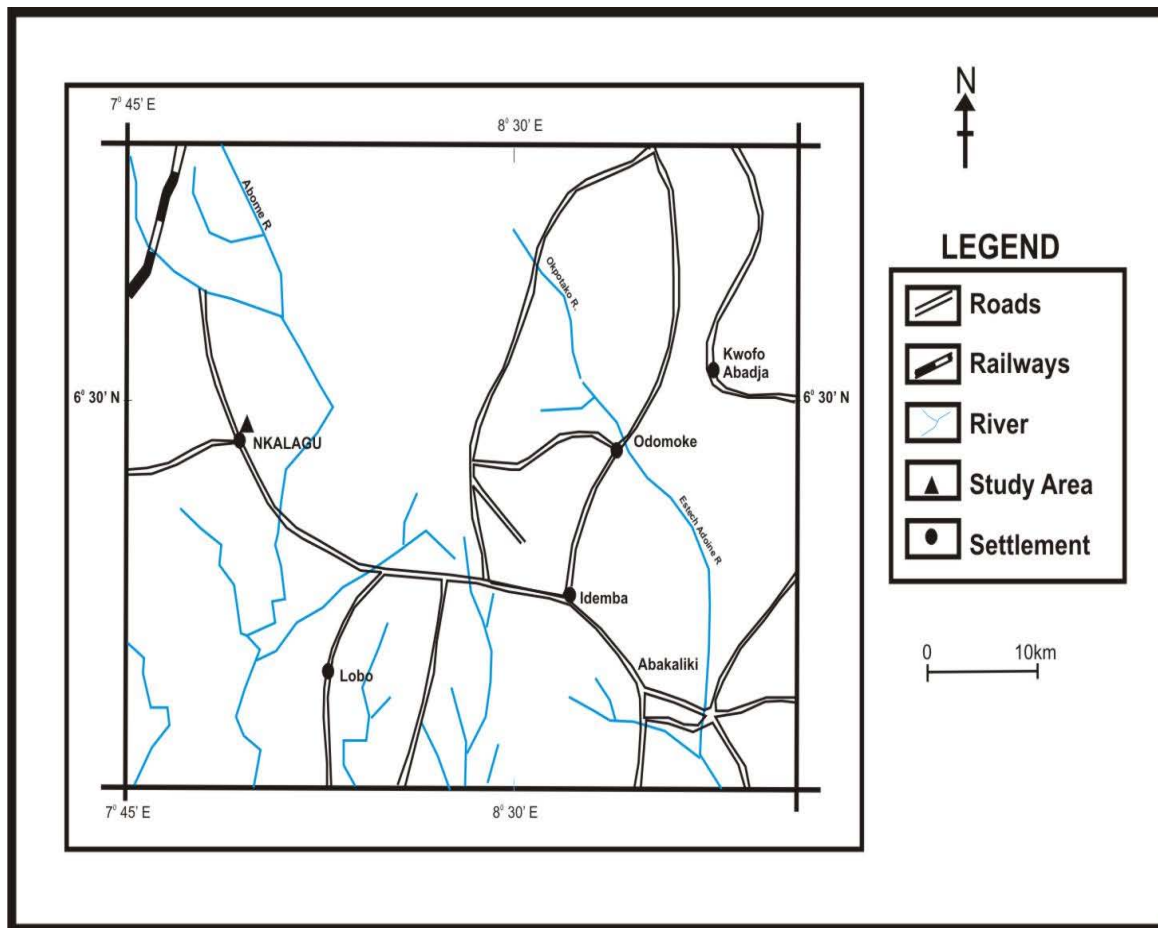
chemical characteristics, hence the justification of this study.

Earlier researchers have worked extensively on the determination of the age, biostratigraphy and depositional environment(s) of the formation. Such workers include, but not limited to, Reyment (1965), Nwachukwu (1972), Dessauvagine (1974), Fayose and de Klas (1976), Offodile (1976b), Peters (1980), Amajor (1992) and Oko (2002). The source rock and reservoir potentials of the Eze – Aku shale and associated limestone have been largely discussed by Peters and Ekweozor (1982a), Unomah and Ekweozor (1986) and Nwachukwu (1988). However, this study is directed to the geochemical evaluations of the limestone deposit using the major oxides and trace elemental concentrations.

## GEOGRAPHIC LOCATION AND GEOMORPHOLOGY

The study area is a limestone deposit of Nigeria Cement Company (NIGERCEM) quarry at Nkalagu. Nkalagu town is situated along the Enugu – Abakaliki expressway, about 50km NE of Enugu. It lies on latitudes 6° 10' and 6° 40'N and longitudes 7° 35' and 7° 50'E. The area is quite accessible through a network of roads and footpaths especially during dry season, Figure 1. Nkalagu belongs to southern equatorial climate zone, characterized by very heavy rainfall and short dry seasons.

The mean annual rainfall is 150 – 186cm while annual relative humidity is over 80%, and means annual temperature exceeds 21°C. Dendritic drainage pattern is prevalent in the area.



**Figure 1:** Location Map of the Area.

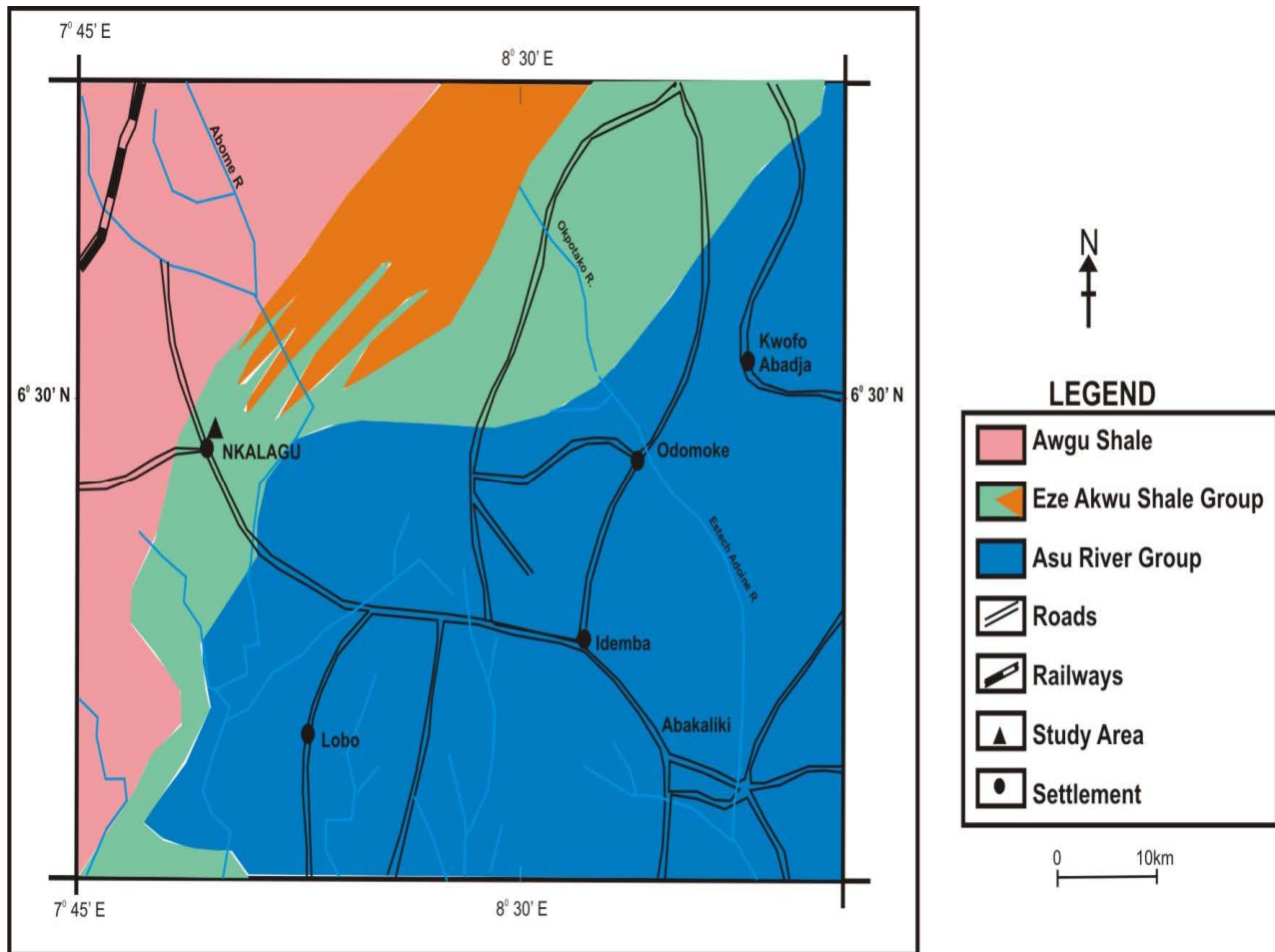
The land is covered with tall grasses of savannah and tropical bush and it support agriculture of various types.

### THE STRATIGRAPHY OF LOWER BENUE TROUGH

The study area falls within the Lower Benue Trough. The stratigraphic succession in the Lower Benue Trough has been discussed by several authors (Reyment, 1965; Murat, 1972, Peters 1978a, Agagu, 1978 and Agagu et al., 1985). The Sedimentation in the Benue Trough was controlled by two dominant factors namely: the progressive eustatic rise in sea level from Albian and the consequent widespread drowning of the continental margins, and the creation of vast interior seaways during the Cenomanian and Turonian times and local diastrophism. Both processes resulted in the transgressive –

regressive cycles that characterized depositional pattern.

Calcareous shales were deposited in the structural depressions during transgressive phase while shoal carbonates developed on submerged structural highs (platforms, horsts) protected from clastic influx. Extensive deltaic sediments, filling the subsiding basin and by predominantly fine clastics (shallow marine shales) deposits over the structural highs dominated the regressive phases. Agagu (1978) recognized five repetitive cycles depositing marine shales and limestones and fluvio-deltaic sandstones and shales in the Upper Cretaceous sequence while the Tertiary have only one cycle. The local geology is made-up of a cyclic sequence of fossiliferous upward fining shales and limestone beds. The limestone beds thicken southwards and grade laterally into shale (Umeji, 1984), Figure 2.



**Figure 2:** Geological Map of Nkalagu Area (Modified After Amajor, 1992).

## METHODOLOGY

A reconnaissance survey where detail lithological description of the outcrop at each location, taking into consideration the color, texture, bedding characteristics, prominent sedimentary structures, composition and stratigraphic sequence, was conducted. The average thickness of each bed on the profile was measured and recorded. A total of fifteen (15) limestone samples were collected at different stratigraphic succession along the column as shown in Figure 3.

The samples collected were taken to laboratory for treatment and standard laboratory preparation prior to analysis and thin section preparation. Geochemical analysis of major elements was done using an X-Ray Fluorescence Spectrophotometer (XRF) at the Portland Cement Company Laboratory, Sagamu.

Many authors agree to the efficiency of this method for major oxide determination (Al – Jaboury and McCann, 2008). The trace element analysis was carried out with Atomic Absorption Spectrophotometer (AAS) in the Central Laboratory of Obafemi Awolowo University, Ile-Ife, Nigeria. The thin section was equally prepared in a standard laboratory for modal analysis study.

## RESULTS AND DISCUSSION

### Major Oxides

The result of the major elemental oxides shown in Table 1 indicates that the calcium oxide CaO concentrations range between 46.56 – 54.15 % with mean value of 49.74 %.

AGE	FORMATION	THICKNESS (m)	LITHOLOGY SECTION	SAMPLE CODE	LITHOLOGICAL DESCRIPTION
TURONIAN	NKALAGU FORMATION, PETERS & EKWEZOR, 1982	3.0		NK LST15	Thick clay overburden
				NK LST14	Light to dark grey fossiliferous fine grained limestone.
		5.1		NK S4 NK S3 NK S2	The shale is grey, fissile and micaceous, with thin limestone stringers, fossiliferous.
		9.3		NK LST13 NK LST12	Light grey-brownish thin marl.
				NK LST11 NK LST10 NK LST9	Massive dense shaly limestone light to dark grey, fairly fossiliferous limestone with intercalations of marl lamina, which is silty and friable and thin shale stringers. Ammonite and pelecypod common macro fossil.
		15.3		NK LST8	Fissile laminated black shale with abundant inoceramic remains, several thin (< 5cm) bands of marls present.
		20		NK S1	Hard and fossiliferous highly indurated.
		19.1		NK LST7 NK LST6 NK LST5 NK LST4	Dark grey highly fossiliferous micritic limestone. The limestone consist of bioclasts of whole and broken fossils with silty friable thin marls.
				NK LST3	Limestone consist of clasts of various sizes, mostly fossil fragments. Pelecypods and gastropods are common macro fossils.
		21.6		NK LST2 NK LST1	Limestone consist of clasts of various sizes, mostly fossil fragments. Pelecypods and gastropods are common macro fossils.

Figure 3: A Composite Lithologic Section Showing Sampling Points at NIGERCEM Quarry Nkalaku.

The silica  $\text{SiO}_2$  contents range between 3.12 – 10.04 % with a mean value of 5.9% and  $\text{Fe}_2\text{O}_3$  between 0.23 – 1.37% with mean of 0.77%, MgO and  $\text{Al}_2\text{O}_3$  contents vary between 0.72 – 1.27% and 0.65 – 1.90% with mean values of 0.99% and 1.30%, respectively.

#### Calcium Oxide (CaO) and Silica ( $\text{SiO}_2$ )

From the result of major oxides, CaO from calcite is dominant. Petrographic studies also indicate that the limestone is essentially biomicritic and calcite, in form of grain, matrix and cement constitutes the carbonate component suggested to be precipitated from solution by organisms and

skeletal remains of these organisms such as pelycypods, brachiopods, Bryozoans, Mollusc (Gastropods) and echinoderms as the dominant bioclasts of the limestone in the study.

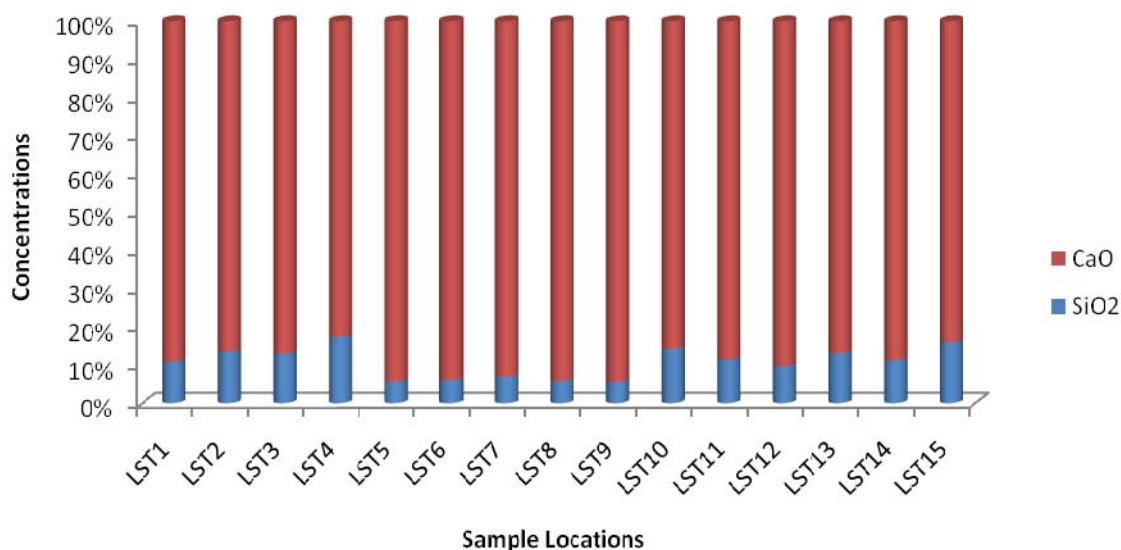
The relatively high level of CaO and low values of silica and MgO, Figure 4, show a high degree of purity of the limestone hence its suitability as raw material for cement. The CaO compares favorably with that of Olade (1988) put at 45.2% but far lower than that of Sagamu, Ewekoro and

Ibeshe having mean values of 89.2%, 80.3% and 75.7% respectively, Akinmosin *et al* (2005).

Silica concentrations of Nkalagu is low (3.12% - 10.04%) compared with other limestone deposit in Nigeria; such as Ewekoro (19.9%), Igunmale (13.9%), Sokoto (11.3%), Olade (1988), but almost at par with that of Sagamu, Ewekoro and Ibeshe with mean values of 5.7%, 8.7% and 14.8% respectively, Akinmosin *et al*. (2005).

**Table 1:** Elemental Composition of Nkalagu Limestone.

Sample Code	CaO %	MgO %	Al <sub>2</sub> O <sub>3</sub> %	Si <sub>2</sub> O %	Fe <sub>2</sub> O <sub>3</sub> %
LST1	54.15	0.95	0.65	6.62	0.48
LST2	48.56	0.74	1.22	7.6	0.47
LST3	47.27	0.79	1.57	7.05	0.95
LST4	47.58	0.9	1.27	10.04	0.23
LST5	52.49	1.13	1.08	3.16	0.93
LST6	52.5	0.72	1.01	3.38	0.8
LST7	52.52	0.9	0.9	3.91	0.7
LST8	50.09	0.9	0.87	3.09	0.68
LST9	52.79	0.9	0.82	3.12	0.4
LST10	46.96	1.35	1.9	7.79	0.97
LST11	47.69	1.21	1.9	6.16	0.58
LST12	50.5	1.07	1.42	5.4	0.96
LST13	49.17	1.27	1.73	7.42	0.78
LST14	46.56	0.92	1.31	5.9	1.37
LST15	47.17	1.15	1.83	8.93	1.37



**Figure 4:** Percentage Plot of Nkalagu CaO and SiO<sub>2</sub>.

## MAGNESIUM AND ALUMINA OXIDES - MgO AND Al<sub>2</sub>O<sub>3</sub>

The percentages of MgO and Al<sub>2</sub>O<sub>3</sub> are low 0.72 – 1.27% and 0.65 – 1.90%, respectively. Magnesium could be added by dolomitization process which is completely absent in this deposit. Also, Chave (1954 a) stated that marine invertebrate skeletal debris has low magnesium with increasing level in the phyla. Nkalagu limestone is very rich in bivalves, bryozoans and gastropods – higher invertebrates – which are 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 (Pettijohn, 1984). Thus shallow marine environment is proposed for Nkalagu limestone based on this. The aragonitic shells are usually magnesium deficient and such fossil shells like bivalves, a shallow marine dweller are common in the deposit. The low concentration of alumina is also an indicative of low energy environment. Al<sub>2</sub>O<sub>3</sub> values greater than 1% occur within units overlain by marl or shale.

## TRACE ELEMENT GEOCHEMISTRY, MINERALOGY COMPOSITIONS AND FOSSIL CONTENTS

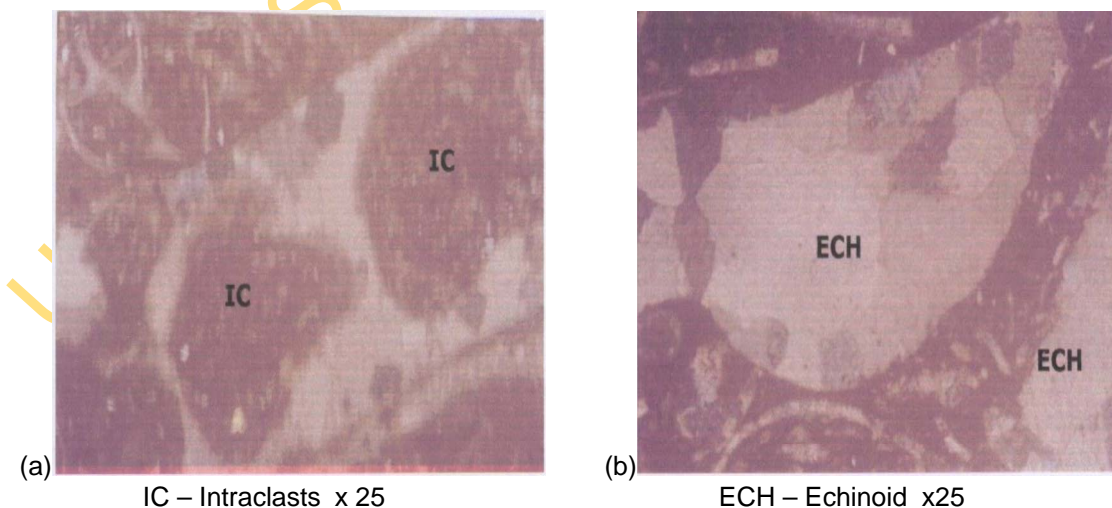
Trace element concentrations of the Nkalagu Limestone are given in the table below. The elements are Fe, Mn, Sr, and Zn. The basal lithoclastic floatstone facies appears to have trace element distributions which discriminate it from the overlying lime mud facies.

**Table 2:** Trace Elemental Concentrations of Nkalagu Limestone.

Sample Code	Fe (ppm)	Mn (ppm)	Sr (ppm)	Zn (ppm)
NK/LST 15	3306	1543	1035	7.8
NK/LST 13	2463	214	667	11
NK/LST 11	2013	147	623	53
NK/LST 09	1828	93	600	4.5
NK/LST 02	1653	76	603	7.0

Petrographic studies of each slide from the sample were enhanced by point-count method for each mineral and individual percentages of modal analysis reveal that fossil calcareous components dominate the entire rock (Figure 5); others include quartz, and feldspar (Table 3).

The distribution of Fe, Mn, Sr and Zn could be used to delineate the various lithofacies of the study area. For example, the basal lithoclastic floatstone facies appears to have trace element distribution different from the overlying lime mud facies. Brand (1983) proposed that trace element signatures can be useful tools in interpretation of depositional environment despite post diagenetic alterations. Thus Fe, Mn, Mg and Zn, in this study show diagnostic distributions that differentiate the pelagic fine micritic limestone facies from the basal coarser wackestone facies. The trace elements show higher concentrations in the former than in the latter. Also, higher amount of Mn, Fe, in some cases Sr, are usually associated with deep sea carbonates (Frank 1975). All these features strongly suggest possibly an off-shelf depositional model for the Nkalagu formation.



**Figure 5:** Photomicrographs from Some of the Slides.

Mineralogical phases as indicated by petrographic studies put CaO as most abundant and quartz, and iron minerals. The quartz is least in the purer basal limestone.

## CONCLUSIONS

Geochemical studies of the Turonian Nkalagu limestone have been vividly carried out and the result of both major oxides and trace elemental concentrations, supported by petrographic analysis, have given some insights to the deposit

under studied. Trace elements distribution can and has been successfully used, in conjunction with other methods, to discriminate between shelf and deep sea carbonate. A shallow marine possibly an off-shelf depositional model has been postulated for the Nkalagu formation based on geochemical studies merged with the fossil contents.

Seismic exploration could be integrated with the available geochemical data to have a broader perspective on structural aspect of the petroleum potentials of the area.

**Table 3:** Estimated Modal Analysis for Nkalagu Limestone in % (After Folk, 1959).

Sample Code	Fossil Fragments	Micrite	Sparite	Intraclast	Oolites/Ooids	Litho Elist	Iron Mineral	Quartz	Pellets	Remarks Fossil
LST 1	60	30	5	5	-	-	-	-	-	Echinoid, bivalve and gastropod embedded in micrite matrix
LST 2	50	30	10	10	-	-	-	-	-	Shell of bivalves and echnoids
LST 3	60	25	10	5	-	-	-	-	-	Calcite-invaded Gastropods, micrite undergoes neomorphism to sparite. Biosparite
LST 4	45	15	15	5	-	15	-	-	-	Bryozoan and Bivalve fragment embedded in micrite matrix
LST 5	60	25	10	3	-	-	2	-	-	High micrite contents
LST 6	60	35	4	-	-	-	1	-	-	Gastropods and Shelly biomicrite
LST 7	55	30	10	-	-	-	3	2	-	Abundant shell fragments and shelly biomicrite
LST 8	50	30	10	-	8	-	-	2	-	Echinoid spine, bivalves, broken ooids and shelly biomicrite
LST 9	30	60	10	-	-	-	--	-	-	Whole shell and fragments of Gastropods and echinoids. Shelly biomicrite
LST 10	60	25	10	-	-	-	-	5	-	Calcite-invaded Gastropods, micrite undergoes neomorphism to sparite. Biosparite
LST 11	45	15	25	5	5	-	-	5	5	Echinoids and Bivalves embedded in grayish micrite
LST 12	60	25	5	5	-	-	-	5	-	High micrite. Biomicrite
LST 13	60	35	3	1	-	-	-	1	-	High micrite. Echinoids fragments and Biomicrite
LST 14	25	60	10	5	-	-	-	-	-	Low fossil contents. Biomicrite

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