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Petrography, Geochemistry and Industrial Applications of Limestone Deposits around Jana Area, in Yobe State

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Abstract:
This study confers detailed petrographic and chemical compositional characteristic of limestone for possible industrial application. The study area falls within the Gongola basin, North-Eastern Nigeria. Eight of this fine grained, grey to dark brown limestone were selected for petrographic and geochemical analysis(X-Ray Fluorescence).Mineralogical data obtained from petrographic studies revealed that the limestone samples consists mainly of calcite and dolomite with subordinate quartz, plagioclase, and opaque minerals in form of iron oxide and limonite. Trace amounts of colorlessrecrystallized fossils remains were also noted in the thin sections. The results obtained from XRF, shows a range of values of; SiO_2 3.57-20.81wt%, Al_2O_3 1.65-7.62wt%, Fe2O3 2.27-6.76wt%, CaO 32.20-53.71wt%, MgO 0.14-0.60wt%, K2O 0.23-0.67wt%, TiO 0.17-0.81wt%, MnO 0.45-1.78wt%, P2O5 0.08-0.98wt%, loss on ignition 29.01-38.40. The study revealed that the limestone around Jana area satisfies the chemical consideration for the manufacture of cement, asphalt filler and can be utilized in agricultural soil conditioning.

***Key Words**: Petrography, Geochemistry, Limestone, Stratigraphy, Gongola arm, Gulani, Jana area.*

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I. Introduction

Mineral resources play an essential part in the economy of any nation, especially in a developing country like Nigeria. Limestone is a sedimentary rock with greater than 50% calcium carbonate (calcite – $CaCO_3$). Limestone can as well contain other minerals such as dolomite and many non-carbonate components as impurities (Brennan et al., 2013, El-Magd et al., 2018, Konecny et al., 2017, Noiriel et al., 2009 and Rao et al.,2011). Limestone is used in many aspects of our life; manufacture of cements, as base in road construction, serve as petroleum reservoirs, agriculture, pharmaceutical, construction, chemical and metallurgical studies, sculpture making, as additives in toothpaste, paper and plastic making,; hence, it plays a vital role in the well-being of mankind. Limestone has been of economic importance in the family of industrial minerals it plays an important role in the economic development of any industrialized nation.

The demand for limestone has increased due to increase in population. It may be precipitated from water (non-clastic, chemical or inorganic limestone), secreted by marine organisms including algae and coral (biochemical limestone), or can shape from the shells of lifeless sea creatures (bioclastic limestone). Some limestones form from the cementation of sand and/or mud by way of calcite (clastic limestone), and these often have the appearance of sandstone or mudstone. As calcite is the precept mineral component of limestone, it will fizz in dilute hydrochloric acid. This study presents the petrographic and chemical composition of limestone around Jana area to determine its purity and desirability for industrial applications.

II. Regional Geology

The study area forms parts of the Gongola arm of the Upper Benue Trough (Fig. 1). The Benue trough is a major NE-SW striking rift basin which extends for greater than 1000 km, starting from the northern tip of the Niger Delta in the south to the southern tip of the Chad Basin in the north. Its width ranges from 50-150 Km made up of up to 6000 M of Cretaceous-Tertiary sediments (Carter et al., 1963). It is geographically dividedinto three major subdivisions namely; the southern, central and northern Benue Trough (Nwajide, 2013).

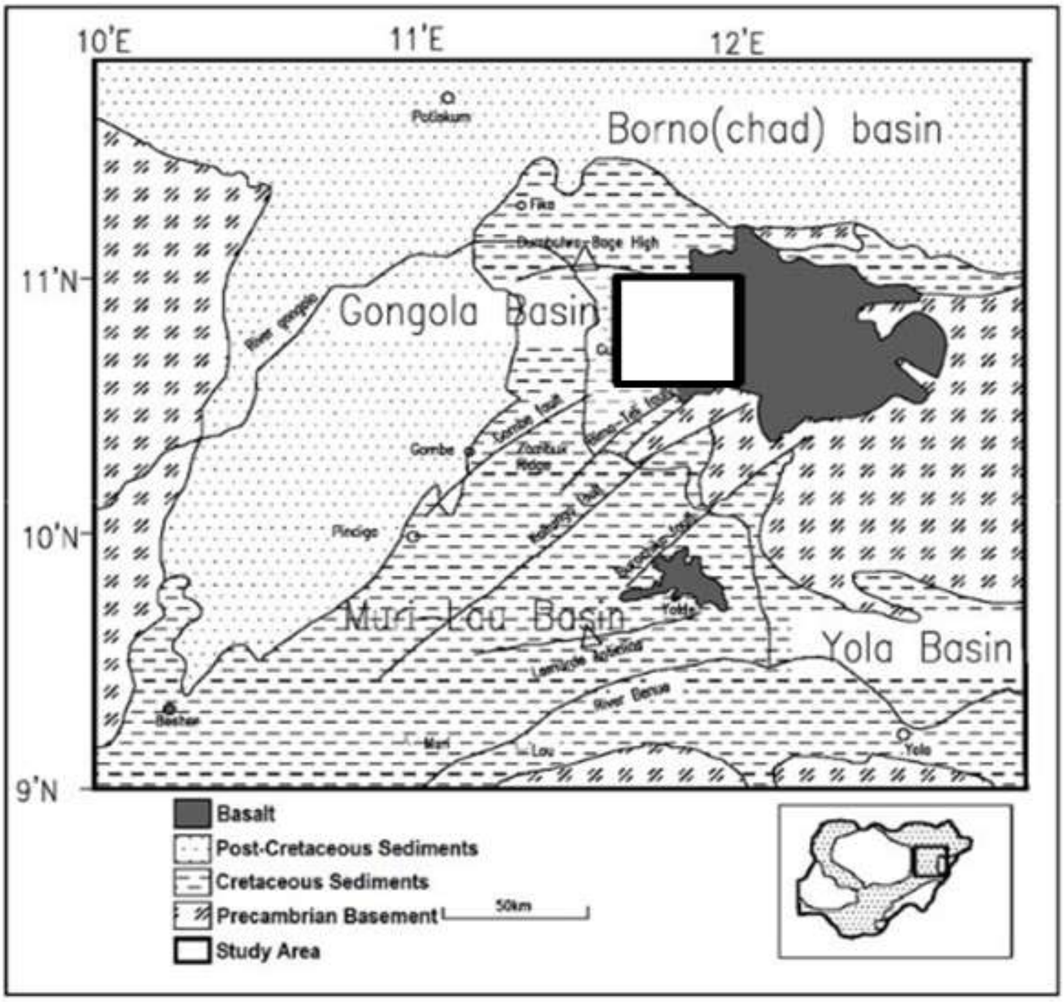

Figure *1*: Regional geological map of the Gongola arm of the Upper Benue Trough showing the study area. (Modified from Zaborski et al 1997).

The limestone unit studied in this work forms part of the Kanawa Member which outcrops over a large part of the study area (Fig. 1) mainly forming flat featureless topography. The Unit is made up of grey shale interbedded with thin often fossiliferous limestones. The Kanawa Member gives rise to black to dark grey clay soils often with limestone regolith.

Previous work in the region indicates that, the CaO content of the limestone ranges from 43.04% to 53.04% shows that the limestone is of moderate quality Baba et al., (1995). The purest limestone documented in Nigeria is that of Mfamosing with a Cao content of 52 to 56% and a carbonate content 99% (Ekwueme, 1987).

The trough is believed to have evolved from the extensional forces of the African and South American Plates which happened during the early Jurassic to early Cretaceous (Nwajide 2013). The Y shaped geological entity of the Northern Benue Trough is made up of three arms namely the NE-SW trending Muri-Lau basin, the E-W trending Yola arm and the N-S trending Gongola arm (Dike 2002). In the Gongola arm, the Aptian-AlbianBima Group which is of continental origin represents the base of the succession, which uncomformably lies on the Precambrian basement and consists largely of sandstones and clays series.CenomanianYolde formation lies conformably on the Bima group and represents the onset of marine incursion into the Gongola sub basin, and consists of varieties of sandstones and shales. The Yolde is conformably overlain by the Pindiga formation which comprise of the Kanawa, Gulani, Deba Fulani, Dumbulwa and Fika Members (Zaborski et al., 1997, Nwajide 2013). The Pindiga Formation is overlain by lacustrine Gombe sandstones and Kerri=karri Formations both of which outcropped at the western part of the sub Basin.

III. Methodology

A total number of eight limestone samples were provided the samples were chipped to small pieces with geological hammer. The surface of the chipped sample was polished on a glass lap with the help of abrasive powder and water starting with 90 grades followed by 120 grades after which a uniform surface of the samples, polishing was continued with various grades of the abrasive powder then finally 800 grades of the abrasive powders were used in polishing the sample for the slide. Both polished sample and glass slide were placed on the on the hot plate at about 80-90 degree Celsius, the mixed araldite with the wooden stirrer were smeared on the polished surface of the glass slide while still on the hot plate for about 5-10 minutes and then were removed from the hot plate to cold plate to cool down to a room temperature.

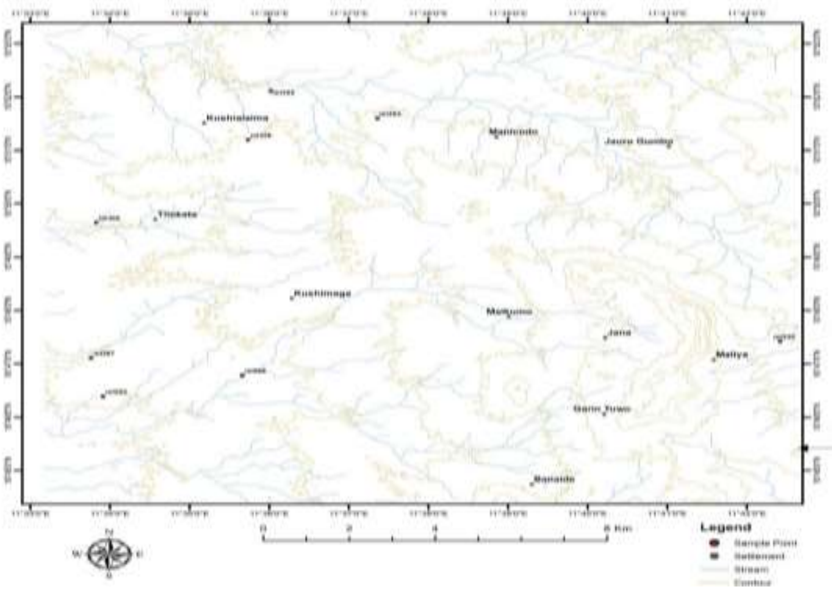

Figure 2: Topographic map of the study area showing sample locations.

The cutting machine was used to reduce the sample size leaving about60 microns thick of the sample, polishing with the abrasive powder on the glass slide is continued until a thickness of 30 microns is achieved, the 30 microns is realized when the quartz and feldspar material in the samples turns grey to white of the first order interference color, blade is used to scrape offthe overflow of the epoxy around the thin slice. The prepared slide was placed on the hot plate at 80-90 degree Celsius and a drop of Canada balsam was added then the cover slip was placed over itto gently remove the gas and the excess of Canada balsam and in particular to increase the relief of the sample. After keeping on the hot plate for like 5-10 minutes. The excess of the balsam was stripped using organic solvent and finally detergent and were ready for use. Finally, the slides were used for microscopic observation using optical microscope for composition.

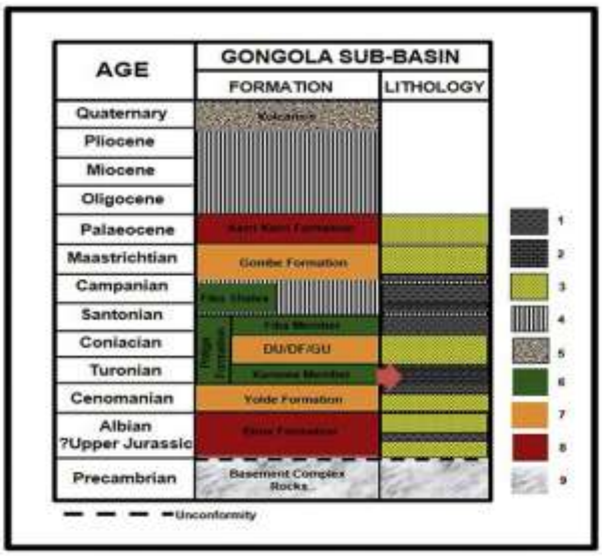

Figure 3: Stratigraphy of the Gongola basin modified from Zaborski et al., (1997). 1- Mudstone, 2-Limestone, 3 - Sandstone, 4 - Hiatus, 5 - Basalt, 6 - Marine sediments, 7- Transitional marine sediments, 8- Continental sediments, 9- Basement complex, (DU-Dumbulwa Member, DF- Deba Fulani Member, GU- Gulani Member).

The Geochemical (wavelength dispersive X-ray fluorescence (WDXRF) analysis was carried out at the Centre for Dry land Agriculture, Bayero University Kano, North Central Nigeria. The fused beads were carried out through regrinding the core samples to <60 ohms meter, drying raw with more than o.5 percent moisture for 1 hour at a temperature of about 100 degree Celsius, weighing 2g of the sample into crucible and igniting in the furnace at 950 degree Celsius was carried out reweighing the ignited samples and calculating the loss on ignition (LIO). The samples were carefully crushed inside the crucible with the help of a spatula, 1g of the ignited sample was weighed into a dry fusion crucible, 8g added of flux and thoroughly mixed together, 1ml of 25 percent of LiBr solution using 1ml pipette was added but the samples were not mixed after the addition of the substance, the crucibles were placed on a fusion machine holder, where recipe F was selected, pressing ad holding the start button for about 10 seconds and releasing when it was complete, the machine automatically ignited and the fusion process is carried out by the machine, at the end of the process the machine indicates fusion complete, labeling the beads while still in mould on the outer surface were carried out and the glass disk was used in removing and transferring the bead into pellet cup but the surface was in contact with the mould. The core samples were grounded by means of pulverizes agate mortar to less than 200 mesh size. Boric acid and dilatants are the mixed to get a simultaneous mixture and pellets were made. These were inserted into spectrometer for analysis. The elements determined include Si, Al, Fe, Ca,Mg, S, Na, K, Ti, P, Mn and LOI.

IV. Results and Discussion

4.1 Petrography of Jana limestone

The limestone is grey to brownish with a composition dominated by calcite and dolomite to some extent. Petrified ammonites of the *Vascocerascostattum* (Fig. 4a) and fragments of mollusks are common in the hand specimen. Trace amounts of recrystallized fossils and also macro remain of organism dominantly calcite are also present. Trace to minor amounts of clastic material made up of quartz and feldspars grains were recorded. Traces of opaque high relief iron oxide minerals present with some of it disseminated in form of limonite. The limestone generally fall into the micrite, biomicrite and intramicrite classes of Folk 1963. The limestone studied has not undergone significant diagenetic transformation.

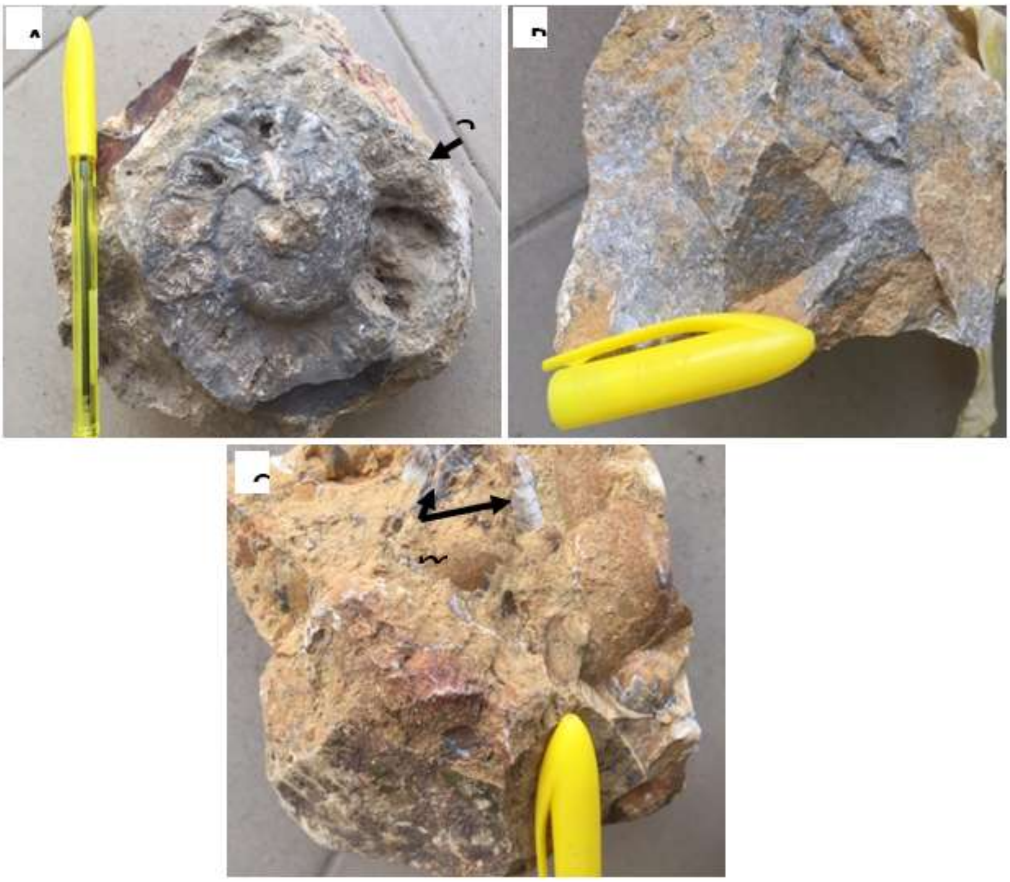

Figure 4.Fragments of Jana limestone (A) showing ammonite of the *vascocerascostattum* (B)grey massive (C) brown showing fragments of mollusks).

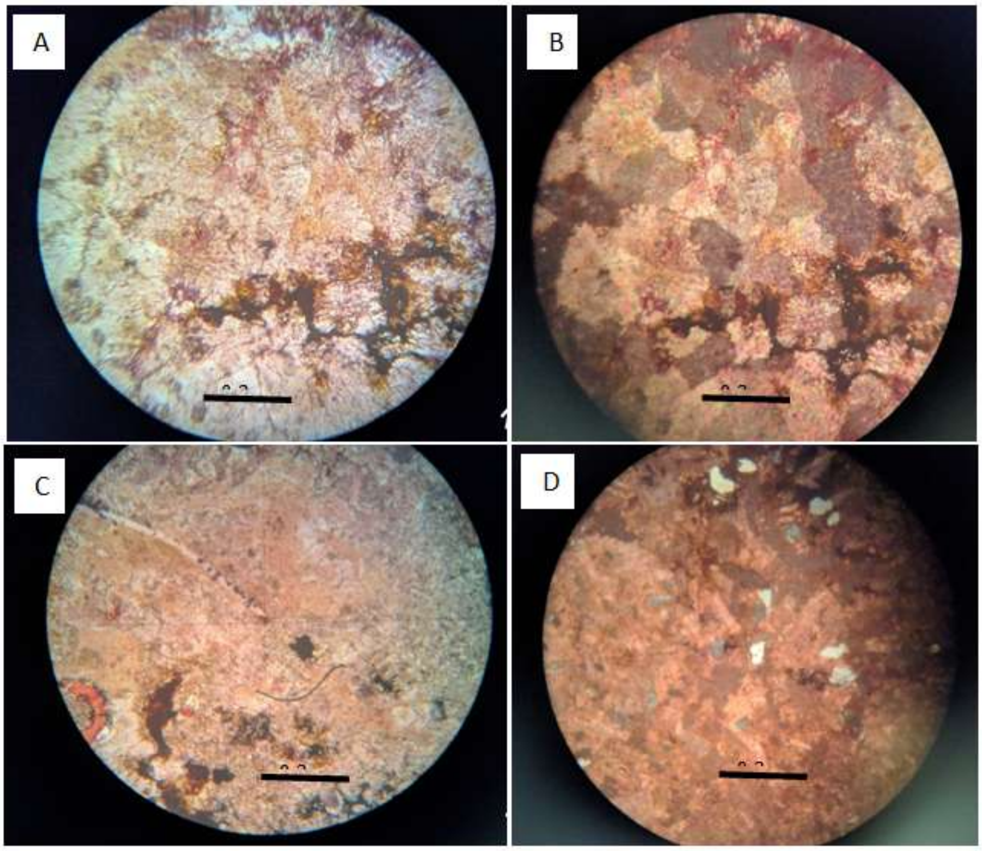

Figure 5: Thin section photomicrograph of grey to brown micritic limestone showing (A) mudstone texture with iron oxide (B) more coarser texture and C) recrystallized bioclastic materials and (D) mudstone texture with silt size quartz crystals.

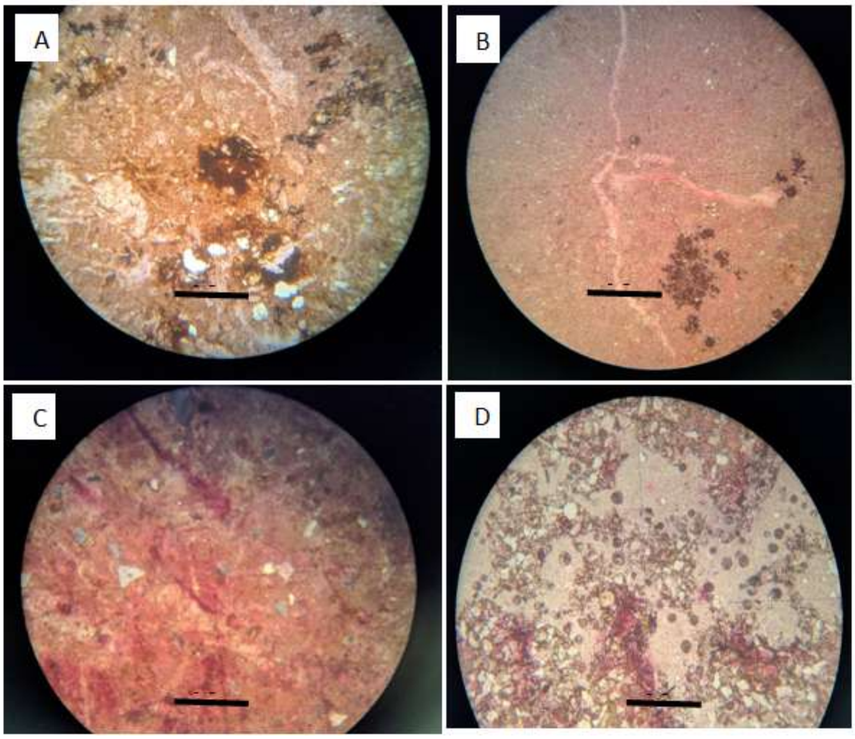

Figure 6: Photomicrograph of Jana limestone (A) showing fossil fragments (B) massive with calcite vein (C and D) showing siliciclasticgrains.

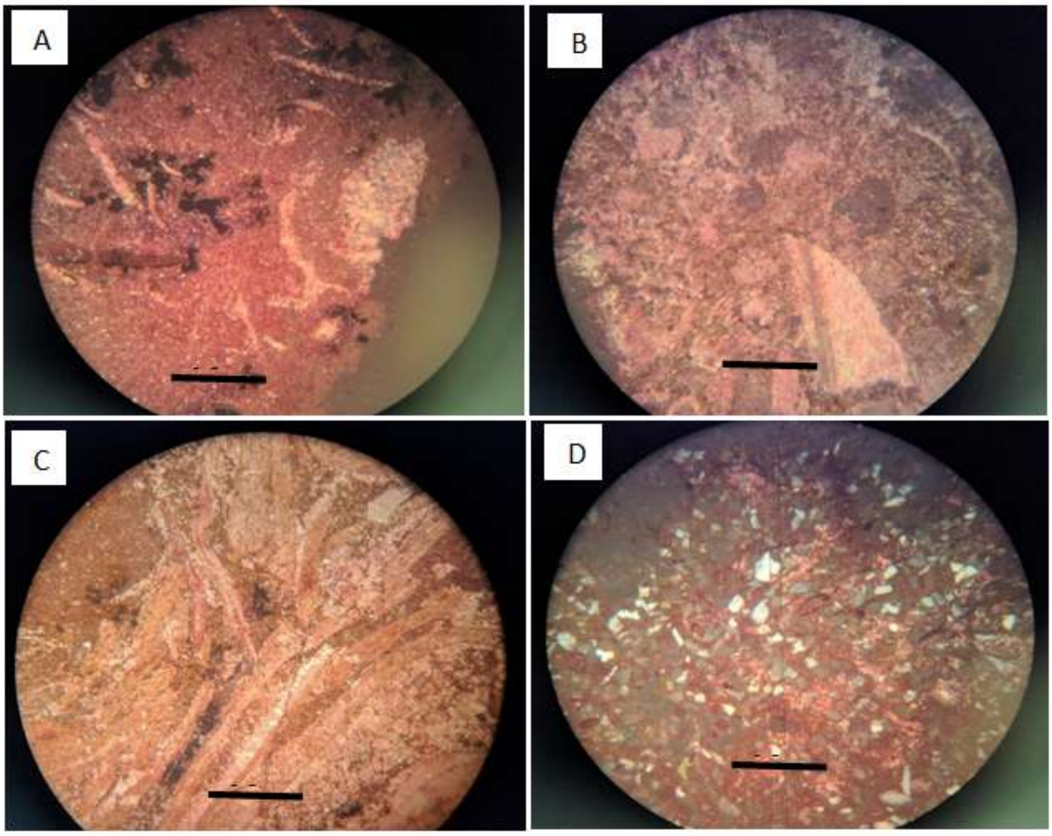

Figure 7: Thin section photomicrograph of grey to brown biomicritic limestone showing (A) mudstone texture with bioclast (B) and(C) argillaceous texture, and (D) micrite with glauconitic grain (g) and recrystallized bioclastic materials.

Geochemistry of Jana limestone

The analytical results of the Geochemical analysis of major oxides, loss on ignition (LOI) and some trace elements analysed inthe Jana limestone is presented in table 1

Table N0 1: Major Oxides and some Trace elements composition of Jana limeston**e**
NOTE: Samples 1 – 8 = Jana limestones -Notdetermined

Oxides wt%	1	2	3	4	5	6	7	8	Range	Average	Ashaka limestone (After AQL, 2017)	Kushimaga limestone(Usman et. al., 2017)	Yelwa limestone(Kamale et. al., 2019)
SiO2	7.90	9.49	6.00	20.81	8.19	8.83	6.30	3.57	3.57 – 20.81	7.78	18.09	17.66	6.34
Al2O3	3.11	3.84	2.49	7.62	3.39	3.94	3.12	1.65	1.65 – 7.62	3.65	5.33	5.61	2.00
Fe2O3	2.27	4.42	5.01	5.03	6.01	6.76	2.72	5.21	2.27 – 6.76	4.68	1.99	2.07	2.20
CaO	53.71	45.29	47.54	32.20	41.82	45.07	47.17	48.02	32.20 - 53.71	45.10	38.99	40.05	47.78
MgO	0.5	0.6	0.14	0.40	0.02	0.60	0.20	0.25	0.14 – 0.6	0.36	0.18	0.63	0.59
K2O	0.67	0.52	0.41	2.42	0.48	0.62	0.57	0.23	0.23 – 0.67	0.74	0.89	0.87	0.02
TiO2	0.47	0.37	0.35	0.81	0.43	0.40	0.42	0.17	0.17 – 0.81	0.43	0.34	0.38	0.10
MnO	0.48	1.60	0.80	1.11	1.78	0.65	0.59	1.08	0.48 – 1.78	1.01	0.32	0.32	0.62
P2O5	-	0.08	-	-	0.43	0.12	0.50	0.98	0.08 – 0.98	0.26	0.30	0.32	0.19
LIO	31.11	34.02	37.01	29.01	37.02	33.14	38.02	38.47					
Ba	-	-	-	1254.5	1344.2	268.8	-	1433.8	268.8– 1433.8	1075.3	-	-	2477
Sr	-	423	592.2	253.8	-	423	846	423	253.8 – 846	493.5	-	-	404.98
Rb	-	-	-	182.8	-	91.4	-	-	91.4 – 182.8	137.2	-	-	7.74
Zr	-	148.0	-	74.2	-	74.0	-	-	74.0 – 148.0	74.11	-	-	32.68
S	320	480	520	640	560	520	360	880	320 - 880	535	-	-	2,477
Cl	1100	1200	1200	1500	1200	1300	1200	1300	1100 – 1500	1250	-	-	-

The result of silica (SiO_2) content carried out on the Jana limestone (n=8) varies from 3.57 - 28.81 wt%, with an average value of 7.78wt%. This value is much lower than the average value obtained from Ashaka limestone having average value of 18.09wt% and Kushimaga limestone near Gulani with an average value of 17.66wt% as reported by AQL (2017) and Usman et al. (2011) butslightly higher than the Yelwa limestone with an average value of 6.34wt% located in the Yola arm of the Upper Benue Trough as reported by Kamale et al. (2019). Indicating that the Jana limestone having low silica which is of better quality limestone thanKushimaga limestone.

The **Alumina** (Al_2O_3) content in the limestone samples obtained from Jana area vary from 1.67 – 7.62wt% with an average value of 3.65wt%. This average value is lower than that of Ashaka limestone (5.33wt5%) and Kushimaga limestone (5.61wt. %) but slightly lower than 2.00wt% for the Yelwa limestone.
Iron (Fe_2O_3) content of the Jana limestone samples range from 2.27 – 6.76wt% with an average value of 4.68wt%. This average value is high compared to the average values 1.99wt%, 2,02wt% and 2.20wt% for Ashaka, Kushimaga and Yelwa limestone respectively.
Lime (CaO) values of the Jana limestone range from 32.20 – 53.71wt%, with an average value of 45.10wt%. This average value higher than the average value of Ashaka limestone 38.99wt% and Kushimaga limestone 40.05wt% respectively and slightly lower than that of Yelwa limestone.
Magnesian (MgO) content in the Jana limestone samples range from 0.14 – 0.6wt% with an average value of 0.36wt%. This average value is higher than that of Ashaka limestone 0.18wt% and somehow lower than (0.63wt%) for Kushimaga limestone and slightly higher (0.59wt%) than that Yelwa limestone respectively.
Potash (K_2O) value in Jana limestone samples range from 0.23 – 0.67wt% with an average value of 0.74wt% which is higher than the average values 0.28wt% and 0.02wt% for the Ashaka and Yelwa limestones respectively. However the average value is slightly lower than that of Kushimaga limestone with a value of 0.87wt%.
Titania(TiO_2)value of the Jana limestone values varies from 0.17 – 0.81wt% with an average value of 0.43wt%. The average value is higher than those of Ashaka, Kushimaga and Yelwa limestones with an average values of 0.34wt%, 0.38wt% and 0.10wt% respectively.
MnO content in the limestone sample from Jana range from 0.48wt% - 1.78wt% with an average value of 1.01wt%. The average value is lower than the average values(0.32wt%, 0.32wt% and 0.12wt%) for the Ashaka, Kushimaga and Yelwa limestone as reported by (AQL, 2017; Usman et al., 2018 and Kamale et al., 2019) respectively.
Phosphoruspentoxide (P_2O_5) in the limestone sample of Jana area range from 0.08wt% - 0.98wt% with an average value of 0.26wt%. The average value is slightly lower than the average value 0.30wt% of the Ashaka limestone and 0.32wt% for the Kushimaga limestone but somehow higher than 0.19wt% for the Yelwa limestones.
Sulphur in the limestone sample of Jana area range from 320 – 880ppm with an average value of 535ppm, this average value is considerably higher compared to the low average value in Yelwa limestone reported by Kamale et al. (2019)
Strontium in the limestone sample of Jana area range from 253.8 – 846ppm with an average value of 493.5ppm and the value is lower than the average value (404.98ppm) for the Yelwa limestone.
Zirconium content in the limestone sample of Jana area ranges from 74.02 – 148.04ppm with an average value of 74.11ppm and the value seem to be lower than the average value 32.68ppm for the Yelwa limestone.
Barium content in the limestone sample of Jana area range from 268.83 – 1433.76ppm with an average value of 1075.31ppm and the value is abnormally lower than the average value 2477ppm for the Yelwa limestone.
Rubidium content in the limestone sample of Jana area varies from 91.41 – 182.82ppm with an average value of 137.15ppm and the value is abnormally higher than the average value 7.74ppm analyzed for the Yelwa limestone.

V. Geochemical Classification

The standard ratio of Ca/Mg and Mg/Ca utilized by Todd(1966) for pure limestone is within the range of 100-39.0 and 0-0.3 respectively, for magnesian limestone these two ratios are 38.0-12.3 and 0.03-0.08 respectively and 12.30-1.41 and0.08-0.18 for dolomitic limestones. The distribution of Ca/Mg and its reciprocal Mg/Ca in the limestone of the study area are found to vary from 75.12 to as high as 2091 and 0.00 to 0.01 respectively (Table 2). Based on those ratios and parameters utilized by Todd(1966). The Ca/Mg ratio corresponds to the stability condition during the formation of the carbonate rock.Mashner(1968) pointed out that the degree of salinity increases with decrease of Ca/Mg ratio. Higher values of Ca/Mg ratio of the studied carbonates indicates comparatively less evaporation of sea water and low salinity that prevailed in the general formation of limestone. But some of the samples of Jana area fall out of the standard used by Todd(1966).

Table No 2:*Chemical Classification of Jana Limestone Using Todd's Classification of Limestone.*

S/N	CaO	Mg	Ca/Mg	Mg/Ca	Name
1	53.71	0.5	107.42	0.009	Pure limestone
2	45.29	0.6	75.483	0.013	Pure limestone
3	47.54	0.14	339..571	0.003	Pure limestone
4	32.20	0.40	80.50	0.012	Pure limestone
5	41.82	0.02	2091	0.000	Pure limestone
6	45.07	0.60	75.12	0.013	Pure limestone
7	47.17	0.20	235.85	0.004	Pure limestone
8	48.02	0.25	192.00	0.005	Pure limestone

VI. Application

Based on the above results of the geochemical analysis the Jana limestone is found applicable in the following;

Portland cement: Limestone is a primary raw material used in the manufacture of Portland cement (Kennedy et al., 1958). The chemical specification should contain less than 3% magnesia Phosphorous pentaoxide should be less than 0.5% and sulfur should be low. Jana limestone falls under the above specification but needs some beneficiation to reduce the sulfur content, so that it can suite well to the requirement.

***Asphalt filler**:* limestone used for asphalt should contain considerably higher calcium to magnesian ratio (Cadigan, 1942). From the geochemical analysis obtained Jana limestone seem to contain more calcium to magnesium, making most of the samples falling under pure limestone subdivision given by Todd classification scheme (Todd et al., 1966).

Agriculture: limestones is applied to soil to correct soil acidity, soil structure and maintain or promote conditions favorable for the utilization of soil nutrients by plants and for the growth of desirable soil organisms. Also termed as liming in other words.

VII. Conclusion

The limestone deposits are grey to brownish, composed dominantly of calcite minerals and are fine in texture.

Petrographic studies have concluded that the presence of micro and macro carbonate producing organisms in the limestone suggests that the environment of deposition is shallow marine.

The results of the geochemical analysis in the study shows the limestone deposit is enriched in CaO and SiO while depleted in the rest of the oxides and most of the samples are limestones according to Todd classification scheme 1996.

The chemical composition of the limestone deposit in the study area satisfies the requirement for the manufacture of cement, asphalt filler and for agricultural soil conditioning, as a result of significant amount of CaO and to some extent SiO.

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