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Evaluation of Presence of Quicklime (CaO) in Ohafia-Arochukwu Areas of Nsukka Formation, Afikpo Basin, Southeastern Nigeria

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ABSTRACT: The co-ordinates of the area studied are within latitudes 5º29ˈ to 5º51ˈN and longitudes 7º29ˈ to 8º00ˈE. The Nsukka Formation in the studied area consists of two facies associations; limestone-shale and cross bedded sandstone. The Limestone-shale facies association consists of the following lithofacies; rippled clayey sandstone, carbonaceous shale, heterolithic sandstone-shale, laminated grey shale, fossiliferous limestone, Fine grained sandstone, Silty shale, Medium grained sandstone and carbonaceous sandstone. The cross bedded sandstone facies association consists of only cross bedded sandstone. Representative samples of these rocks from Ohafia area were collected and stored in a polythene bag for further investigations. XRF analyses were carried out on these rock samples. The XRF oxide content of elements in sample OHA 1 of original rock was found to be CaO (76.00), Fe_2O_3 (8.35), SiO_2 (7.13), Al_2O_3 (2.46), SO_3 (2.29) and MgO (1.81) with other oxides in minor quantities. The shale-limestone lithofacies of OHA 2 of the same rock showed CaO (85.90), SiO_2 (5.13), MgO (2.56), Al_2O_3 (1.80), SO_3 (1.71), Fe_2O_3 (1.20) and P_2O_5 (1.02) with other oxides in minor quantities. OHA 3 of cross-bedded sandstone lithofacies contains SiO_2 (52.70), Fe_2O_3 (14.10), Al_2O_3 (14.50), MgO (3.74), CaO (9.00), TiO_2 (2.54), K_2O (1.41) and Cl (0.12) with other oxides in minor quantities. For OHA 4 through the XRF indicates Chloride (Cl), CaO and SiO_2 contains 79.60%, 0.58% and 3.52%. The samples showed that major component were SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and TiO_2. The presence of CaO was determined to be deposited on the surface of debris of rocks in the area. It was observed that the occurrence of CaO is amorphous in nature and not crystalline.

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The studied area is situated along Ohafia-Arochukwu in the Southeastern Nigeria. The coordinates of which are 5º29ˈ to 5º51ˈN and 7º29ˈ to 8º00ˈE. Limestone diagenetic records of the Late Maastrichtian to Danian Nsukka Formation in Ohafia and its environs were studied to understand the geological processes that affected the rock after its deposition. Limestone is a sedimentary rock composed largely of the mineral calcite ($CaCO_3$), which is formed either by organic or inorganic processes (Serra, 2006). It is formed either by direct crystallization from water (usually sea water) or accumulation of shell or shell fragments. Most limestones are formed with the help of living organisms. Many marine organisms such as mussels, clams, oysters and corals extract calcium carbonate from sea water to make shells or bones. Microscopic organisms such as foraminifera are also involved in limestone production. Limestones can also be formed without the aid of living organisms. If water containing calcium carbonate is evaporated; the

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calcium carbonate is left behind and will crystallize out of solution. These limestones are found in association with shales, fine grained sandstones and siltstones trend in a northwest to southeasterly direction from Onukwu to Ndi Uduma Ukwu in the north, through Ndi Okorie and Ndi Okereke to Asaga village in Southern Arochukwu which have a southward extension into the Obotme area (Ekwere *et al*., 1994) of the Calabar Flank. Reyment (1965) observed that the Nsukka Formation outcropping southwards of Okigwe consist of bands of fossiliferous limestones interbedded with sandstones, shales and sandy shales. The two major lithofacies associations observed in the area are shale-limestone and cross-bedded sandstone. The shale-limestone facies association consists of several lithofacies which include rippled clayey sandstone, carbonaceous shale, heterolithic sandstone-shale, laminated grey shale, fossiliferous limestones, fine grained sandstone, silty shale, medium grained sandstone and carbonaceous sandstone. The silt of the area as indicated show the greatest concentration of Na_2CO_3 and NaCl (Nandy and Deo, 1961). Microscopic examination of silt samples revealed the presence of rich organic remains such as algal filaments, fungal hyphae and spores, diatoms etc. (Badve *et al*., 1993). Co abundances in these samples of the more massive glasses do not reflect any appreciable inclusion of meteoritic siderophilic materials (Stroube *et al*., 1978). Because of the variability in the target rocks, the apparent increase of Cd with shock in the glasses may be no more than a reflection of target material sampling (Morgan, 1978). Diagenetic changes usually take place either in the submarine, sub aerial fresh water and subsurface environments. In Carbonate rocks the diagenetic processes consist of six main types mainly; cementation, micritization, neomorphism, dissolution, compaction and dolomitization (Saffer *et al.,* 2010). This research aims to determining the presence of quicklime (CaO) in Ohafia-Arochukwu Areas of the southeastern Nigeria.

MATERIALS AND METHODS

Stratigraphic Setting: The Santonian deformational process resulted in the fragmentation of the lower Benue trough (Fig. 1) into the Abakiliki syncline (Kogbe, 1976). The predominantly Albian-Cenomanian marine depositional cycles which terminated by a phase of folding (Nwachukwu, 1972; Olade, 1975) affected the Asu River Group in the area. A second transgressive – regressive of deposition in the Turonian to Santonian was again terminated by a phase of folding and faulting in the early Santonian times. This affected all the sediments deposited before the tectonism and this gave rise to the Afikpo (Abakiliki) syncline (Fig. 1). Imprint of tectonism on the sediments in the lower Benue trough were preserved by series of joints trending NW – SE. Typical depositional environments of a syncline are marine, continental and transitional environments which produced lithostratigraphic units of Asu River Group and Eze-Aku Group (Table 1) etc.

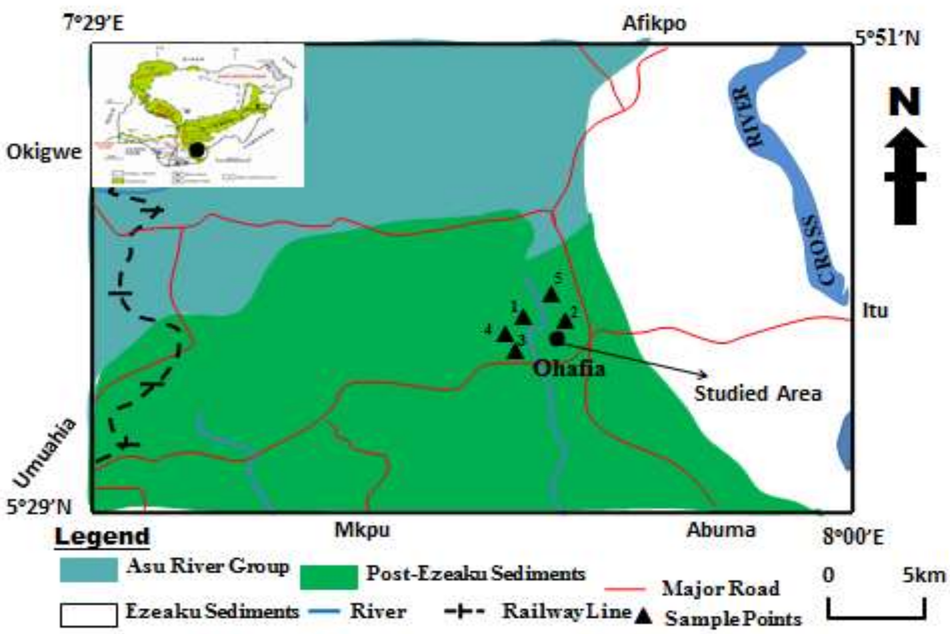

Fig. 1: Geological map of the studied area (inset: map of Nigeria showing location of the Afikpo Basin).
Table 1: Stratigraphic units of the lower Benue Trough (after Uzoegbu and Ikwuagwu, 2016b).

Age		Anambra basin	Afikpo basin	Calabar flank
Tertiary	Oligocene Eocene Paleocene	Ogwashi-Asaba Fm Ameki Group Imo Shale	Ogwashi-Asaba Fm Ameki Group Imo Shale	
Cretaceous	Maastrichtian	Nsukka Formation Ajali Sandstone Mamu Formation	Nsukka Formation Ajali Sandstone Mamu Formation	Nkporo Shale
	Campanian	Nkporo Shale Enugu Shale	Nkporo Shale Enugu Shale Afikpo Sandstone	
	Santonian Coniacian	Agwu Shale	Agwu Shale	
	Turonian	Eze-Aku Group	Eze-Aku Group	New Netim Marl
	Cenomanian			Ekenkpon Shales
	Albian		Asu-River Group	Mfamosing Limestone
	Aptian			Awi Formation
		Precambrian	**Basement**	**Complex**

The first marine transgression in Nigeria occurred during the middle Albian. Albian sediments unnamed and undifferentiated constitute the Asu River Group and its equivalents (Ojoh, 1999).

Ukaegbu and Akpabio (2009) have differentiated the Asu River Group northeast of the Afikpo Basin as consisting of alternating shale, siltstone with occurrence of sandstone. The maximum thickness of the Asu River Group is 1000m, Albian in age and rich in ammonites as well as foraminifera, radiolarian and pollens. The shales are also characterized by species of monticeras and elobiceras ammonites (Offodile, 1976).

The regressive phase of the first marine transgression led to the deposition of the Cenomanian sediments. This is found in the southeastern part of the basin around Calabar. These beds have been assigned as Odukpani Formation (Reyment, 1965). It was deposited under shallow water conditions (Kogbe, 1976).

The basal beds comprised of arkosic followed by quartzose –felspathic and siltstone facies while shales predominate in the upper part of the formation (Reyment, 1965).

The type locality of the Eze-Aku Group is found at the Eze-Aku River valley in the southeast of Eze-Aku. The formation comprised of hard grey to black shale and siltstone.

The thickness varies but may attain 100m locally. The Eze-Aku shale represents shallow marine deposits. The fossil contents indicate a basal Turonian age (Carter *et al*., 1963; Ukaegbu and Akpabio, 2009).

Sample Collection and Pretreatment: Representative rock samples from both lithofacies (shale-limestone and cross-bedded sandstones) were collected to study the chemical phenomena.

Most of these rocks are found to be covered by a thin layer of unknown composition; images are shown in Plate 1. The rocks were sent for XRF analysis and then the weight and volume was taken to calculate the density of the rocks and dimensions were also taken (Table 2). Rocks were taken for samples OHA 1 and OHA 2 (Tables 4 and 5). Similarly, the rocks from other locations were collected and sent for XRF analysis (Tables 6, 7 and 8).

Sample Analysis: The rocks samples collected in a polythene bag, before sending for XRF analysis, the layered part was scraped with a finger nail and also by pointed biceps to remove the salt, but were not scraped.

Hence were sent for XRF analysis. The dimension of the rocks was taken and noted down. After this, the rocks were weighted on a standard balance and the weights were noted down, the volume was taken by a measuring cylinder of borosilicate make by displacement method of water. Both the rocks were immersed in water to take volume, and when the rocks were taken out of the water, it was observed that the color of the rocks was seen to be gray similar to cement color. Afterwards, when the rocks were dried, the original white color had appeared. Density was calculated by using the formula m/v g/cc (Table 2).

Plate 1: Outcrops of the Nsukka Limestones at (a) &(b) Ogbugbandu Plantation, Ndi Oji (c) Akoli River, Ndianku, (d) Ogbueke stream, Ndi Okorie (e) Ndianku village (f), (g) & (h) Ohafia-Ozu Abam road, (i) Akoli River, Ndi Uduma (j) Oboro village (k) Ndi Uduma Ukwu (l) Ndi Uduma Ukwu (m) Eziafor village (n) &(o) Akoli River forest.

Table 2: Physical Properties of rocks in Ohafia.

		Sample Numbers	
S/N	**Parameter**	**Rock OHA 1**	**Rock OHA 2**
1.	Weight in gms	27.00	133.00
2.	Volume in ml	9.10	44.00
3.	Density in g/ce	3.01	2.90
4.	Dimensions	4.0 x 2.3 x 2.0	5.1 x 4.0 x 3.9
5.	Surface feature	One side original rock, the other side covered by a white layer of CaO.	One side original rock, the other side covered by a white layer of CaO.
6.	Shape	The white side flattened and the original rock tapered	Irregular
7.	Colour	Original rock black one side, the other side deposition of white layer of CaO.	Original rock light brown one side, the other side deposition of white layer of CaO.
8.	Thickness of CaO layer	Thin layer seen on the surface.	Thick layer seen on the surface.

RESULTS AND DISCUSSION

The results obtained from XRF analyses of both lithofacies i.e., the shale-limestone and cross-bedded sandstones were observed that 16 elements and their oxides have been detected. In original rock (OHA 1), the major components in descending order are SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, TiO_2, K_2O and Cl and in layered part (OHA 2), the major components in descending order are CaO, SiO_2, MgO, Al_2O_3, SO_3, Fe_2O_3, and P_2O_5 and others in minor quantities (Tables 4 and 5). The weight taken on a standard balance, the volume taken and the density was calculated and was found to be 3.03g/cc for OHA 1 (shale-limestone facies) and 2.95 g/cc for OHA 2 (cross bedded sandstone facies) (Table 2). The dimensions were also taken, (Table 3). The results of salts by XRF (Table 6) and the physicochemical analysis are shown in table 3 respectively.

Table 3: Physicochemical analysis of salt from Ohiafia area.

S/N	**Parameters**	**Results**	**Units**
1.	pH	10.22	%
2.	Carbonate as Na_2CO_3	31.77	%
3.	Calcium Carbonate ($CaCO_3$)	0.37	%
4.	Chloride	31.68	%

The XRF result analysis showed that the oxide content of elements in sample OHA 1 of original rock was found to be CaO (76.00), Fe_2O_3 (8.35), SiO_2 (7.13), Al_2O_3 (2.46), SO_3 (2.29) and MgO (1.81) with other oxides in minor quantities (Table 4). Similarly, the shale-limestone lithofacies of OHA 2 of the same rock showed CaO (85.90), SiO_2 (5.13), MgO (2.56), Al_2O_3

(1.80), SO_3 (1.71), Fe_2O_3 (1.20) and P_2O_5 (1.02) with other oxides in minor quantities (Tables 5). In sample OHA 3 of cross-bedded sandstone lithofacies contains SiO_2 (52.70), Fe_2O_3 (14.10), Al_2O_3 (14.50), MgO (3.74), CaO (9.00), TiO_2 (2.54), K_2O (1.41) and Cl (0.12) with other oxides in minor quantities, (Table 6). The result of the analysis from salt OHA 4 (Table 7) through the XRF indicates Chloride (Cl), CaO and SiO_2 contains 79.60%, 0.58% and 3.52% respectively. To observe an area of high content of CaO deposition, rocks of shale-limestone facies and soil were analyzed by XRF which shows CaO values to be similar to that found in cross bedded sandstone facies in Tables 6 and 7. The soil sample OHA 5 analyzed by XRF shows CaO values 12.70 oxide content (Table 8). Nandi and Deo mentioned in their papers that lastly, nowhere in their region was the occurrence of limestone noticed nor struck in bore holes nor was the silts recovered high in CaO (Nandy and Deo, 1961). But from this study it is seen that the rocks were found to be encapsulated or coated by Calcium oxide salts (CaO) or in other words it can be said that CaO salts were deposited on the rocks. As per the images in plate 1a and 1b, one side is the shale-limestone facies and the other side covered by CaO salts of white nature. Cross bedded sandstone facies covered by white coating were found to be of SiO_2 origin (Son and Koeberl, 2007).

Table 4: Elements and Oxide composition of rocks around Ohiafia area by XRF in mass % OHA 1.

S/N	Element↓	Mass (%)	Formula	Oxide Content
1.	Ca	54.31	CaO	76.00
2.	Fe	5.80	Fe_2O_3	8.40
3.	Si	3.33	SiO_2	7.13
4.	Al	1.30	Al_2O_3	2.50
5.	S	0.92	SO_3	2.30
6.	Mg	1.10	MgO	1.80
7.	P	0.33	P_2O_5	0.80
8.	Ti	0.31	TiO_2	0.51
9.	Sr	0.21	SrO	0.30
10.	Cl	0.24	Cl	0.24
11.	Mn	0.08	MnO	0.10
12.	Zr	0.05	ZrO_2	0.06
13.	Ba	0.03	BaO	0.03
14.	Cu	0.02	CuO	0.02
15.	Zn	0.01	ZnO	0.02
16.	O	31.95		
	Total	100.00		100.01

From the analysis of shale-limestone facies for the representative samples of rocks by XRF, it is observed that the result is showing a high percentage of CaO. The deposition of CaO can be attributed to be of amorphous in nature because of the presence of deposited CaO seen on cross bedded sandstone by silica (SiO_2) (Jadhav and Mali, 2018a). If it had been for crystalline nature of silica, the deposited CaO on the surface would not be possible.

Table 5: Elements and Oxide composition of rocks around Ohiafia area by XRF in mass % OHA 2.

S/N	Element↓	Mass (%)	Formula	Oxide Content
1.	Ca	61.39	CaO	85.90
2.	Si	2.40	SiO_2	5.13
3.	Mg	1.54	MgO	2.56
4.	Al	0.95	Al_2O_3	1.80
5.	S	0.70	SO_3	1.70
6.	Fe	0.84	Fe_2O_3	1.20
7.	P	0.45	P_2O_5	1.02
8.	Sr	0.31	SrO	0.36
9.	Cl	0.15	Cl	0.15
10.	Ti	0.02	TiO_2	0.04
11.	Mn	0.03	MnO	0.40
12.	Ba	0.02	BaO	0.02
13.	Cu	0.01	CuO	0.01
14.	Zn	0.01	ZnO	0.01
15.	Mo	0.01	MoO_2	0.01
16.	O	31.19		
	Total	100.00		99.97

Table 6: Composition of cross bedded sandstone facies from Ohafia (OHA 3) area by XRF in %.

S/N	Element↓	Mass (%)	Formula	Oxide Content
1.	Si	24.63	SiO_2	52.70
2.	Al	7.67	Al_2O_3	14.50
3.	Fe	9.93	Fe_2O_3	14.10
4.	Ca	6.43	CaO	9.00
5.	Mg	2.26	MgO	3.74
6.	Ti	1.52	TiO_2	2.54
7.	K	1.17	K_2O	1.41
8.	S	0.32	SO_3	0.80
9.	P	0.34	P_2O_5	0.77
10.	Mn	0.12	MnO	0.16
11.	Cl	0.12	Cl	0.12
12.	V	0.04	V_2O_5	0.06
13.	Cu	0.04	CuO	0.05
14.	Co	0.03	Co_2O_3	0.04
15.	Zr	0.02	ZrO_2	0.03
16.	Sr	0.02	SrO	0.02
17	O	45.42		
	Total	100.07		100.03

Table 7: Analysis of salt from Ohafia (OHA 4) area by XRF in mass %.

S/N	Element↓	Mass (%)	Formula	Oxide Content
1.	Cl	79.60	Cl	79.60
2.	S	3.32	SO_3	8.30
3.	Al	3.10	Al_2O_3	5.84
4.	Si	1.65	SiO_2	3.52
5.	K	0.96	K_2O	1.20
6.	Br	0.64	Br	0.64
7.	Ca	0.41	CaO	0.58
8.	Fe	0.25	Fe_2O_3	0.36
9.	Cu	0.01	CuO	0.02
10.	Zn	0.01	ZnO	0.02
11.	Ba	0.01	BaO	0.01
12.	Zr	0.01	ZrO_2	0.01
13.	Ni	0.01	NiO	0.01
14.	O	10.05		
	Total	100.00		100.03

It is of amorphous nature of SiO_2 that makes CaO to be deposited or coated on the rocks (Jadhav and Mali, 2018b). NaCl (sea salt/common salt) is not found to be deposited on the rocks, though it is in highest percentage. This may be because NaCl is in a crystalline form of sea salt, common salt in nature (Jadhav and Mali, 2019). It is not amorphous. The above two salts i.e., SiO_2 and CaO are amorphous in nature which are found to be deposited on the rocks, whereas NaCl is not amorphous, but crystalline and hence it is not found to be deposited on the rocks. Hence the coating of silica was possible. Chemtob also reported silica coating on basaltic rocks at Hawaiian volcanic islands (Chemtob, 2013). The percentage of CaO being highest as per XRF analysis can be attributed to $CaCO_3$ (Limestones). Due to heat factor (i.e., hydrothermal and geothermal processes), $CaCO_3$ may have been dissociated to CaO and CO_2, which is the only possibility of CaO to be precipitated and deposited on the rocks. The hydrothermal process after meteorite impact has been mentioned by Hagerty and Newsom (2003). The existence of limestones [calcium carbonate ($CaCO_3$)] below the basalts has been postulated by V. Ball in his theory as mentioned by Nandi and Deo (1961).

Analysis of rock samples, soil sample and salt sample did not show high content as that found deposited on the rocks. From this, it can be inferred that the only possibility of CaO depositing on the rocks can be through $CaCO_3$ (Limestone's) buried below cross bedded sandstone facies as per theory put forward by V. Ball mentioned by Nandi and Deo, (1961). The heat generated due to the impact of a meteorite or due to heating (hydrothermal process) $CaCO_3$ to its temperature of dissociation. This $CaCO_3$ dissociated to CaO and CO_2. CaO which deposited on the rocks as can be seen today reflected on these rocks.

Table 8: Analysis of soil sample from Ohafia (OHA 5) area by XRF in mass %.

S/N	Element↓	Mass (%)	Formula	Oxide Content
1.	Si	18.88	SiO_2	40.40
2.	Cl	13.90	Cl	13.90
3.	Ca	9.08	CaO	12.70
4.	Al	5.29	Al_2O_3	10.00
5.	S	3.68	SO_3	9.19
6.	Fe	6.15	Fe_2O_3	8.79
7.	P	1.05	P_2O_5	2.41
8.	Ti	0.73	TiO_2	1.22
9.	K	0.85	K_2O	1.02
`10.	Mn	0.10	MnO	0.13
11.	Br	0.08	Br	0.10
12.	Cu	0.06	CuO	0.08
13.	Sr	0.03	SrO	0.04
14.	Zr	0.02	ZrO_2	0.03
15.	Zn	0.02	ZnO	0.02
16.	O	40.08		
	Total	100.00		99.99

All forms of calcium (carbonates, bicarbonates, oxide) or source of all forms of calcium from zoo planktons and phytoplankton sedimentary rocks always contain higher pH with water which is in amorphous form found to be deposited on the rocks submerged in the water body (Jadhav and Mali, 2018c). Depositions of calcium on these rocks are by coating of the rock but not metamorphic change. The physical and chemical characteristics remain the same. The rocks are only encapsulated by calcium salts but the original state of the rocks inside still intact.

Conclusion: The images in the plate showed the original rocks (shale-limestone and cross-bedded sandstones) covered with white layer. It can be conclude that the host rock for $CaCO_3$ (limestone) rocks within the area or rocks of lameta series as per V. Ball are being leached out, supplementing high alkalinity to the waters. The result of it is the deposition of CaO on rocks as found in the area. The presence of CaO (Lime) from the sampled lithologies indicates that within the basin limestones of carbonate nature may be present.

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