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MAJOR ELEMENT ANALYSIS OF EZEAKU SANDSTONES OUTCROPING AT ABINI, CROSS RIVER STATE, NIGERIA

Edirin Akpofure[a], Felix D. Akori[b]

Department of Geology, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria

[a.] edirinakpofure@yahoo.com, [b.] felixakori430@gmail.com

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Abstract: The samples from Amasiri Sandstone outcropping at Abini were studied and subjected to XRF analysis to determine the elemental constituents of the rock in order to infer maturity, degree of weathering, paleotectonic setting of the Sandstone. The elemental concentrations were presented as oxides in percentages which were used in normative calculations to achieve results. The results show that the dominant oxide in the Sandstone; CaO, along with MgO and Na_2O correlate negatively with SiO_2. This indicates CaO and MgO enrichment against SiO_2, which is corroborated by the calculated mild level of calcification for the sediment which ranges from 4.31 to 10.06 with an average of 6.39. The negative correlation of Na_2O with SiO_2, also show enrichment of Na_2O which could be predicated on the abundance of Na_2O in source rock and minimal chemical weathering due to proximity of source rock. The SiO_2/Al_2O_3 ratio of the studied sediment ranges from 1.89 – 2.89 with an average of 2.42, while that of the K_2O/Na_2O ratio for the sandstone range from 0.08 to 0.50. The maturity indices using the SiO_2/Al_2O_3 and K_2O/N_2O ratios and weathering parameters: CIA, CIW and MIA all indicate that the Sandstone is immature, formed in an arid climate and has not gone through intense weathering to enable silica enrichment and feldspars depletion. The ICV values of the sandstone are > 1; they range from 4.58 to 10.88, signifying the Sandstone is immature and is not from a cratonic basin. In the K_2O/Na_2O ratio versus SiO_2 plot, the sediments plot in the Oceanic island arc tectonic setting.

1. Introduction

The bulk chemical analysis of sandstones is a very important aspect of its geochemistry that can be used in lots of studies that include: classification, maturity, degree of weathering, paleotectonic setting, hydraulic conditions and lot more. The relative concentration of the major and trace elements are presented in their oxide forms in percentages. The enrichment and depletion of these oxides characterize peculiar sandstone classes, phases of maturity, intensity of weathering, paleotectonic setting and hydraulic conditions prevalent from source rock to depositional basin.

The Amasiri Sandstone is a member of the Ezeaku Group and occurs as series of parallel ridges in Afikpo Syncline. The Amasiri Sandstone ridge in Abini, has been classified as a calcarenaceous sandstone based on mineralogy by [1]. The bulk chemical analysis of samples from the Sandstone at Abini, in Cross river State, Nigeria was carried out by subjecting the collected samples to XRF to determine the elemental constituents of the rock to infer maturity, degree of weathering, paleotectonic setting as it affects the Sandstone.

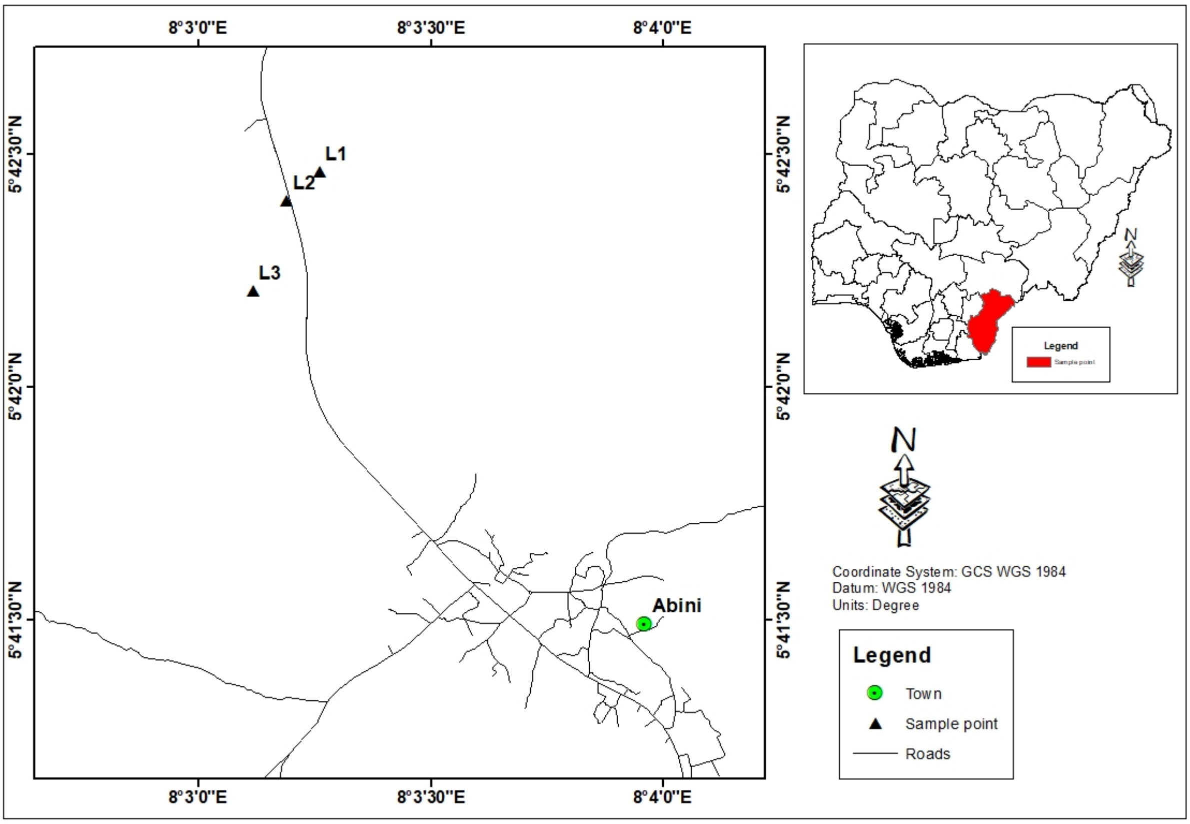


Figure 1 Location map showing study locations.

2. Literature Review

The Ezeaku Group is one of the major formations in the Afikpo Syncline and Anambra Basin. The Amasiri Sandstones is a member of the Ezeaku Group in the Afikpo Syncline, the Sandstone occurs as Northeast-Southwest trending ridges.

[2] Found that southern Nigeria has been affected by three major depositional cycles. The first was in the pre-Albian time which was confined mainly to the Benue – Abakiliki Trough. The second cycle was in the Turonian – Conacian times which filled the Anambra Basin and Afikpo Syncline. The third cycle was that of the Campanian – Maastrichtian transgression and regression which led to the deposition of the Post Santonian Proto Niger Delta sequence.

The Ezeaku Formation lies unconformably on the Aptian – Albain Asu River Group. The Ezeaku Formation is made up of calcareous and non-calcareous sandstones, shales and limestones [3]. The Ezeaku Formation is highly indurated and sedimentary structures such as ripples, swaley cross stratification, planar crossbeds and bioturbation occur. Weathering on exposed surface is also intense giving a reddish colour due to the presence of oxidized iron minerals [4].

[1] Found Ezeaku Formation ridge at Abini to be a hybrid facies, it is not a quartz arenite neither a calcareous sandstone and classified the Sandstone as calcarenaceous Sandstone based on mineralogy.

3. Stratigraphy

The Basement Complex is unconformably overlain by the Asu River Group in the Late Albian – Early Cenomanian times when the first marine transgression – regression occurred. It has a thickness of about 3000 m. The Awi Formation, Abakaliki Shale and the Awe Formation are members of the Group. They are non-marine to marginal marine deposits [5].

The second marine transgression – regression occurred in the Late Cenomanian – Early Santonian and the Ezeaku Group sediments were deposited unconformably on the Asu River Group. It is about 200 m thick and is made up of shale, limestone and sandstone ridges which strike NW- SW with dips ranging from 20^o to 68^o. The sandstone ridges are parallel to elongate features [6]. These ridges are prominent in the south eastern part of the basin and are parallel to the axis of the basin [7]. The Awgu Shales overlie the Ezeaku Group in the Anambra Basin.

The third transgressive - regressive phase in the Cretaceous is represented by the proto Niger Delta Formations: The Nkporo Group, Mamu Formation, Ajali Sandstone and the Nsukka Formation in the Campanian – Maastrichtian times (Table 1).

Table 1 Sratigraphic Succession in the Lower Benue Trough

AGE	ANAMBRA BASIN	AFIKPO SYNCLINE	CALABAR AREA
Campanian - Maastrichtian	Nsukka Formation Ajali Sandstone Mamu Formation Nkporo Group = Owelli Sandstone/ Enugu Shale	Nsukka Formation Ajali Sandstone Mamu Formation Nkporo Group = Afikpo Sandstone	Nkporo Shale
Santonian			? ? ?
Coniacian	Awgu Shale =Agbani Sandstone		New Netim Marl
Turonian	Ezeaku Formation = Nkalagu Limestone	Ezeaku Formation = Amasiri Sandstone	Ekenkpon Shale
Cenomanian			
Albian	Asu River Group = Abakaliki Shale	Asu River Group	Mfamosing Limestone Awi Formation
	[8]	Unknown?	[9]

4. Methodology

Samples were collected from Ezeaku Formation ridge at Abini, in Afikpo Syncline trending 310^{o} NW – SE at location 1 with georeference: N05^{o} 42.402’, E 008^{o} 03.190’ at elevation of 9 m; location 2 with georeference N 05^{o} 42.209’, E 008^{o} 03.117’at elevation of 30 m; and location 3 with georeference of N 05^{o} 42.463’, E 008^{o} 03.260’. They were labeled and presented in the laboratories for geochemical analysis.

Bulk chemical analysis of samples from the Formation was carried out by subjecting the collected samples to XRF to determine the elemental constituents of the rock to infer maturity, degree of weathering, paleotectonic setting as it affects the Formation.

The samples received were crushed and split into two equal halves. One crushed portion was pulverized to 100% passing through 75µm sieve, split into two portions with one portion further submitted for XRF Analysis while the other half was kept as reference sample.

The pulverized aliquot was analyzed using Xenemetrix GENIUS-IF XRF Equipment. Duplicate analyses performed to obtain average values.

5. Presentation of Results

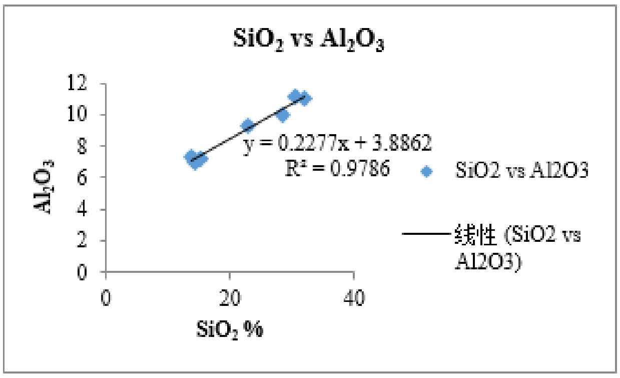
Table 2 Elemental Constituent of Ezeaku Sandstone in Abini, Afikpo Syncline In Percentages

SAMPLES	ABS -01	ABS -02	ABS -2B	ABS -3B	ABS -4B	ABS -5B	ABS - 5MC	**AVERAGE**	REMARKS
SiO_2	22.84	28.39	15.32	13.84	14.37	30.39	31.87	**22.43**	
SnO_2	0.77	0.44	0.39	0.55	0.44	0.53	0.50	**0.52**	
Ag_2O	0.02	0.03	0.01	0.02	0.02	0.03	0.03	**0.02**	
MnO	0.03	0.04	0.02	0.04	0.02	0.04	0.03	**0.03**	
Fe_2O_3	1.09	2.46	1.14	1.35	0.92	2.50	2.33	**1.68**	
K_2O	3.51	4.17	2.00	2.01	1.90	4.29	4.59	**3.21**	
Na_2O	6.99	-	17.85	-	23.53	-	-	**6.91**	
SrO	0.19	0.23	0.19	0.29	0.18	0.21	0.20	**0.21**	
BaO	0.28	0.28	0.11	0.17	0.10	0.33	0.35	**0.23**	
P_2O_5	-	-	-	-	-	-	-	**-**	
SO_3	-	1.46	0.35	-	-	0.37	0.40	**0.37**	
CaO	54.25	51.49	54.48	69.24	48.70	49.18	47.64	**53.57**	
Cl	0.39	0.38	0.28	0.31	0.26	0.39	0.39	**0.34**	
Al_2O_3	9.27	10.03	7.21	7.33	6.95	11.15	11.01	**8.99**	
Ta_2O_5	0.03	0.03	0.02	0.04	0.02	0.02	0.04	**0.03**	
TiO_2	0.22	0.42	0.24	0.18	0.18	0.42	0.41	**0.30**	
MgO	-	-	0.30	4.49	2.32	-	-	**1.02**	
ZrO_2	0.01	0.02	0.003	0.001	0.01	0.01	0.03	**0.01**	
SiO_2/Al_2O_3	2.46	2.83	2.12	1.89	2.12	2.72	2.89	**2.42**	
Al_2O_3/SiO_2	0.41	0.35	0.47	0.53	0.48	0.37	0.35	**0,42**	
$Al_2O_3 + K_2O + N_2O$	19.77	14.2	27.06	9.34	32.38	15.44	15.6	**19.11**	
K_2O/Na_2O	0.50	-	0.11	-	0.08	-	-		
Log K_2O/Na_2O	0.3	-	-0.95	-	-1.1	-	-		

CaO + Mgo)/Al2O3	5.86	5.13	7.6	10.06	7.34	4.41	4.31	**6.39**	
Fe_2O_3/ K_2O	0.31	0.59	0.57	0.67	0.48	0.58	0.51	**0.53**	
Fe_2O_3 + MgO	1.09	2.46	1.44	5.84	3.24	2.50	2.33	**2.7**	
(Fe2O3 + Na2O + CaO + MgO + TiO2)/Al2O3 ICV	6.75	5.42	10.26	10.27	10.88	4.67	4.58	**7.55**	
CIA	12.53	15.27	8.84	9.33	8.57	17.25	17.40	**12.74**	Weak weathering
CIW	13.14	16.30	9.07	10.59	8.78	18.48	18.77	**13.59**	Weak weathering
CIA/ CIW	0.95	0.94	0.97	0.88	0.98	0.93	0.93	**0.94**	Unweathered rock
MIA	-74.94	-69.46	-81.86	-78.82	-82.44	-63.04	-62.46	**-73.29**	Onset of weathering

6. Discussion

The constituent elements of the Ezeaku Formation at Ibini are presented as oxides percentages in Table 2. One way of determining the relative enrichment or depletion of an element is by the elemental ratio. Enrichment or depletion is indicated by the following: Values >1 indicates enrichment, <1 indicates depletion, and =1 indicates no change in the relative abundance of the element. The Sandstone is enriched in the following elements: SiO_2, K_2O, Na_2O, Al_2O_3, Fe_2O_3 and CaO, while, it is depleted in the following: SnO2, Ag_2O, MnO, SrO, BaO, P_2O_5, SO_3, Cl, Ta_2O_5, TiO_2, ZrO_2 and MgO.



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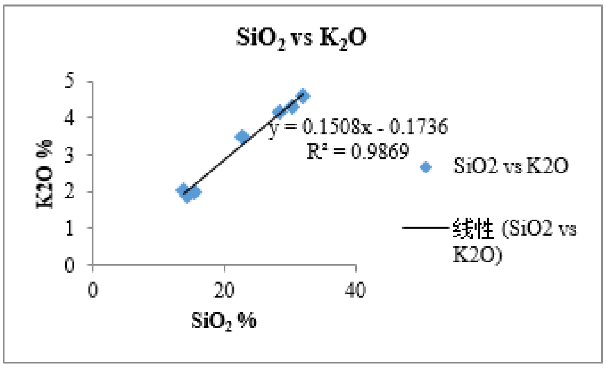

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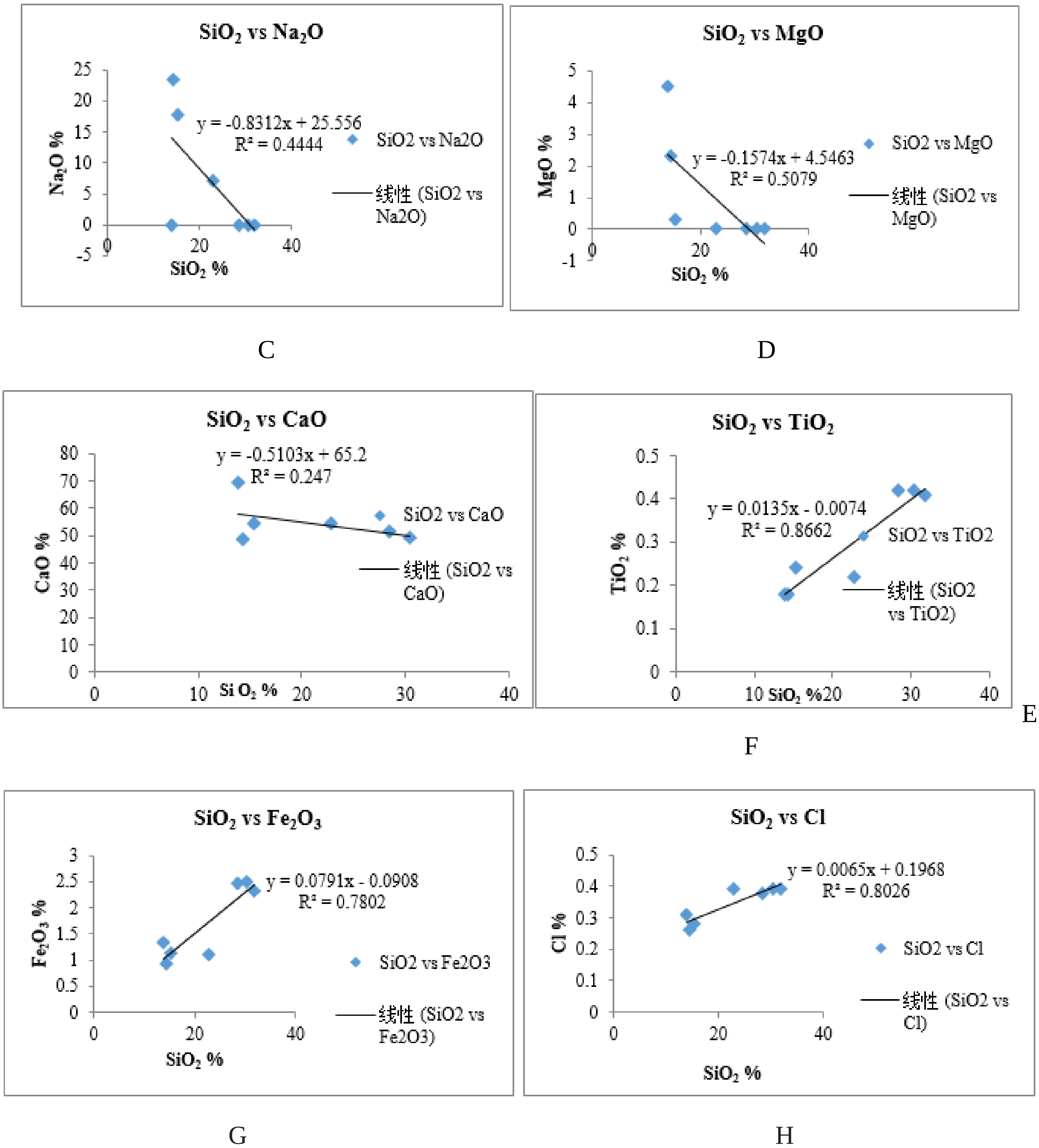

Figure 2 Harker diagrams of SiO2 versus Al2O3, K2O, Na2O, MgO, CaO, TiO2, Fe2O3 and Cl.

The dominant elements are as follows: SiO_2 ranges from 13.84% – 31.87% with an average of 22.43%. K_2O ranges from 1.90% – 8.35%, with an average of 3.21%; Na_2O ranges from 6.99% – 23.53%, some samples lack Na_2O; Fe_2O_3 ranges from 0.64% – 2.46%, with an average of 1.68%; MgO ranges from 0.30% – 4.49%, with an average of 1.02%; CaO ranges from 48.70% – 69.24%, with an average of 53.57%; and $Al_2O_{3\%}$ ranges from 7.21% – 16.66%, with an average of 8.99%.

The relatively low values of Fe_2O_3 and MgO with paucity of MgO in some sediments is attributed to the chemistry of source rock. SiO2 correlates positively with Al_2O_3, Fe_2O_3, K_2O, TiO_2 and Cl which may be in relation to the formation of clay minerals and iron minerals in the rock. Also, SiO_2 has negative correlation with CaO, Mgo and Na_2O (Figure 2A-H). The negative correlation of SiO_2 with CaO may be due to the diagenetic replacement, corrosion and cementation of quartz grains by calcite, leading to the enrichment of CaO [1]. That of MgO is also attributed to the presence and enrichment of carbonates especially dolomite. The negative correlation of Na_2O with SiO_2 shows enrichment of Na_2O with respect to SiO_2, despite the paucity of Na_2O in some sediment. This may be due to the abundance of plagioclase in the source rock and low chemical weathering.

7. Maturity

Mineralogical maturity in sediments is expressed in the constituent amount of quartz in the sediment. The more the quartz content, the more mature the sediment is. This is because quartz is one mineral that is very stable and resistant to weathering. Maturity can be determined by using SiO_2/Al_2O_3 ratio which gives a measure of silica enrichment. The duration and intensity of weathering and sediment recycling can also be derived from it. High values of the ratio indicate maturity of the sandstone [10]. According to [11], any value higher than 5.0 shows progressive maturity as the average ratio range in unaltered igneous rocks is from ~ 3.0 (basic rocks) to ~ 5.0 (acidic rocks). The SiO_2/Al_2O_3 ratio of the studied sediment ranges from 1.89 – 2.89 with an average of 2.42. The low values of the ratios indicate immaturity in the sandstone. The Sandstone has not gone through intense weathering and long distance of transport to have enabled silica enrichment. The K_2O/N_2O ratio is another index for mineralogical maturity of sandstone; it is a measure of the concentrations of alkalis in the sediment. Abundant feldspars (Na_2O and K_2O) are indicative of immature sandstones. There is paucity of Na_2O for some of the samples, only those with values for Na_2O are used for the ratio. The K_2O/Na_2O values for the sandstone range from 0.08% to 0.50%. The ratio indicates predominance of Na_2O where it occurs. According to Lindsey (1972), log (K2O/ Na2O) for tuffaceous sandstones, is < 0; for nontuffaceous sandstones, > 0. The log (K2O/ Na2O) ratio of the studied sandstone is < 0 and it implies a tuffaceous igneous source rock. The high feldsparthic content of the sediment indicates proximity to source area and short distance of transport which has reduced the intensity of weathering, thereby making the Sandstone immature. The occurrences of alkali – feldspars characterize more acidic source rock, while plagioclases characterize basic igneous rocks. Both alkali feldspars and plagioclases occur in remarkable quantities in the Sandstone, which may be interpreted to mean more than one source rock.

Figure 3 [12], gives the plot of SiO_2 (%) versus $Al_2O_3 + K_2O + N_2O$ (%) and it shows that the Sandstone is immature with low SiO_2, was formed in an arid climate, where chemical weathering was inhibited and proximity to source area, probably high relief contributed.

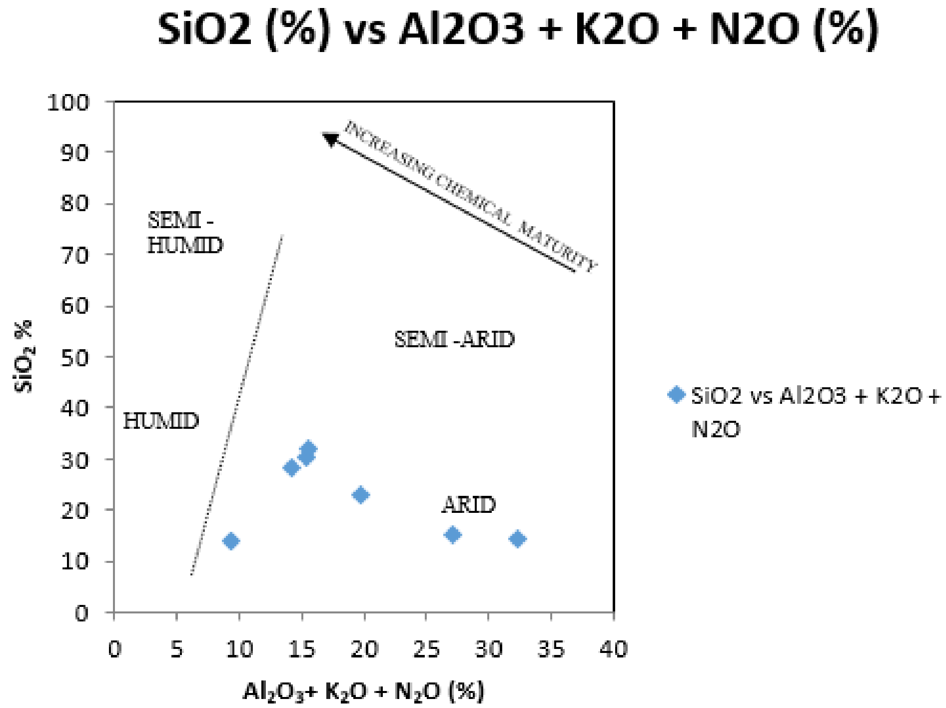

Figure 3 SiO2 (%) versus (Al2O3 + K2O + N2O) (%) [10]

Calcite is the most abundant mineral in the Sandstone. It occurs as skeletal grain, replacement for quartz and as sparry calcite cement [1]. To determine the level of calcification of the Sandstone according to [13], (CaO + Mgo)/Al_2O_3 molecular weight ratio was applied. The ratio for the sediments ranges from 4.31 to 10.06 with an average of 6.39, indicative of mild calcification of the Sandstone. According to [1], the Ezeaku Sandstone occurring at Abini is classified as a calcarenaceous Sandstone, a hybrid facie between quartz arenite and calcareous sandstone.

The sediments have a low SiO_2/ Al_2O_3 ratio, with a range of 1.89 – 2.89, and >1 value for the Fe_2O_3/ K_2O. The values range from 0.31 – 0.67. This implies immaturity in the sediments. As a result, the Sandstone will be mineralogically unstable and very prone to reaction. This alludes to the CaO enrichment observed in the Sandstone.

Index of Compositional Variability (ICV) by [14] helps to assess the detrital mineralogy of sediments. It is defined as: $(Fe_2O_3+Na_2O+CaO+MgO+TiO_2)/Al_2O_3$. According to [14], mature sandstone have lower ICV values that are less than 1.0 and such sandstones are said to originate from a cratonic basin. The ICV values of the sandstone are > 1. They range from 4.58 to 10.88, signifying they are immature and are not from a cratonic basin

8. Source Area Weathering

The degree of weathering in the provenance was calculated using: [15] scheme for chemical index of alteration CIA = $100[Al_2O_3/(Al_2O_3 + CaO + NaO + K_2O]$, [16], chemical index for weathering CIW = $100[AI_2O_3/(Al_2O_3 + CaO + Na_2O)]$. Also, [17] scheme for mineralogical index of alteration MIA was used as a weathering parameter. MIA= 2(CIA - 50). CIA/ CIW equal or less than 50% indicates unweathered rock while, CIA/CIW values between 76-100% indicates intense weathering. CIA= Chemical index of alteration ie 0-50(weak), 50-75(moderate), 76-100(intense); CIA and CIW are interpreted in a similar way. MIA values 0-20% = onset of weathering, values 20-

40% = weak weathering, values 40- 60% = moderate weathering while values 60-100 = intense weathering. The sediment CIA, CIW, CIA/CIW and MIA values are listed in Table 2, The values of CIA and CIW indicate onset of weathering, the ratio of CIA/CIW, is interpreted as unweathered sediment, while that of MIA indicate the onset of weathering. All information put together, indicate that the sediments have low intensity of weathering which conforms to the maturity index of the Sandstone.

9. Tectonic Setting

K_2O/Na_2O ratio versus SiO_2 was used to determine tectonic setting of the sediment as proposed by [10]. The plot is used to discriminate three tectonic setting, which are: Oceanic Island Arc, Passive Continental Margin and the Active Continental Margin. The sediments plot in the oceanic island arc tectonic setting.

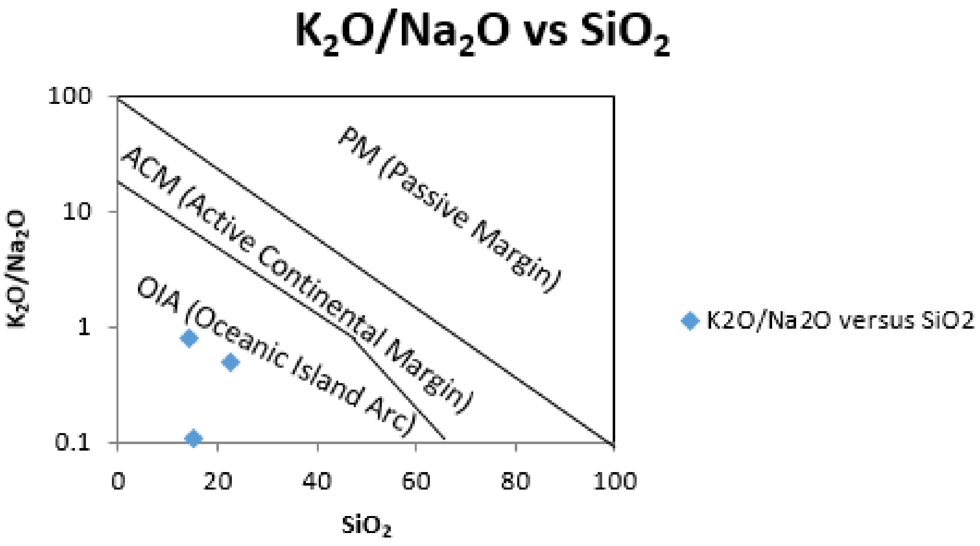

Figure 4 Plot of K2O/Na2O ratio versus SiO2

10. Conclusion

The sediments of the Amasiri Sandstone ridge outcropping in Abini is enriched in the following oxides: CaO, SiO_2, Al_2O_3, Na_2O, K_2O, Fe_2O_3 with CaO as the most dominant oxide. The Sandstone is depleted in SnO2, Ag_2O, MnO, SrO, BaO, P_2O_5, SO_3, Cl, Ta_2O_5, TiO_2, ZrO_2 and MgO as presented in Table 2. The study shows that the Sandstone is immature and has undergone minimal weathering due to lack of silica enrichment and abundance of feldspars. The (CaO + Mgo)/Al_2O_3 molecular weight ratio for the sediments ranges from 4.31 to 10.06 with an average of 6.39, and is indicative of mild calcification of the Sandstone. Index of Compositional Variability (ICV) values of the sandstone are > 1 it ranges from 4.58 to 10.88, implying immature sandstone that is not from a cratonic basin. The paleoclimatic environment implied by the plot of SiO_2 (%) versus (Al_2O_3 + K_2O + N_2O) (%) is arid climate, which corroborates the minimal chemical weathering undergone by the Sandstone. Oceanic island arc tectonic setting was implied for the sandstone as determined from the plot of K_2O/Na_2O ratio versus SiO_2.

References

[1] Akpofure, E. and Egai, A.O. (2022) Ezeaku Formation Calcarenaceous Sandstone Facies At Ibini, Cross River State. European Journal of Environment and Earth Sciences, ISSN (Online): 2684-446X (under production)

[2] Short, K.C. and Stauble, A.J. (1967) Outline of Geology of Niger Delta. Bulletin, American Association of Petroleum Geologists, Vol. 54, no. 5, p. 761-779.

[3] Umeji, O.P. (1984) Ammonite Palaeoecology of the Ezeaku Formation, Southeastern Nigeria. Journal of Mining and Geology.,v.21, pp. 55-59.

[4] Akpofure, E. and Didei, I. (2018) Sedimentology of the Turonian Ezeaku Sandstone in the Afikpo Basin, Nigeria. International Journal Geology and Mining 4(2): 211-223.

[5] Petters, S.W. (1980) Biostratigraphy of Upper Cretaceous Foraminifera of the Benue Trough, Nigeria. Journ. Forams. Research, 10, 191 – 204

[6] Murat, R.C. (1972) Stratigraphy and Paleogeography of Cretaceous Lower Tertiary in Southern Nig. African Geol. T.F.J. Dessauvagie and M.D. Whiteman (Ed), university of Ibadan press 251-268.

[7] Amajor, L.C. (1987) The Eze-Aku Sandstone Ridges (Turonian) of Southeastern Nigeria: A re- interpretation of their Depositional Origin. Nigerian Journal of mining and Geology, 23 (1&2), 19-26

[8] Nwajide, C.S. (2013) Geology of Nigeria's Sedimentary Basins. Lagos: CSS Press.

[9] Peters, S.W., Nyong, E.E., Akpan, E.B., and Essien, N.U. Lithostratigraphic Revision for the Calabar Flank, SE Nigeria. In Proc. of the 31st Ann. Conf. of NMGS

[10] Roser, B. P. and Korsch, R. J. (1986) Determination of Tectonic Setting of Sandstone-Mudstone Suites Using SiO2 Content and K2O/Na2O ratio: Journal of Geology, v. 94, no. 5, p. 635-650.

[11] Roser, B.P., Cooper, R.A., Nathan, S. and Tulloch, A .J. (1996) Reconnaissance Sandstone Geochemistry, Provenance, and Tectonic Setting of the Lower Paleozoic Terrains of the West Coast and Nelson, New Zealand. New Zealand. J. Geol. Geophys., 39: 1-16

[12] Suttner, L.J. and Dutta, P.K. (1986) Alluvial Sandstone Composition and Paleoclimate. L. Framework mineralogy. Journal of Sedimentary Petrology, Vol. 56: p. 329-345. http://dx.doi.org/10.1306/212f8909-2b24- 11d7-8648000102c1865d

[13] Gill, S. and Yemane, K. (1996) Implications of a Lower Pennsylvanian Ultisol for Equatorial Pangean Climates and Early, Oligotrophic, Forest Ecosystems. Geology, Vol. 24: No. 10, p. 905-908.

[14] Cox, R., Lowe, D.R., and Cullers, R.L. (1995) The Influence of Sediment Recycling and Basement Composition on Evolution of Mudrock Chemistry in the Southwestern United States: Geochimica et Cosmochimica Acta, Vol. 59, 2919–2940.

[15] Nesbitt, H.W. and Young, G.M. (1982) Early Proterozoic Climates and Plate Motions Inferred from Major Element Chemistry of Lutites. Nature 299, 7 1 5 -7 17.

[16] Harnois, L. (1988) The CIW index: A New Chemical Index of Weathering. Sedimentary Geology 55, 3 19-322.

[17] Voicu, G., Bardoux, M., Harnois, L, and Grepeau, R. (1997) Lithological and Geochemical Environment of Igneous and Sedimentary Rocks at Omai Gold Mine, Guyana, South America. Exploration and Mining Geology, 6: pp.153-170.