

Geochemical Discriminant for Provenance, Source Area Weathering and Paleoredox of Some Shale Deposits in Edo State, Nigeria

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Abstract

The shale samples from Uzebba, Ayoguir, and Ugbenor within Edo State, Anambra basin, southern Nigeria, were geochemically analyzed for major oxides, trace elements, and mineral content. The trace element ratios from the paleoredox inferences revealed that the shale samples were deposited in an oxic environment (Ni/Co, V/Cr, and V/V+Ni) except for V/Ni which was deposited in a dysoxic - oxic environment. The ancient climate condition of the shale was a semi-arid climate with increasing chemical maturity and the bivariate relations (SiO_2 vs. Al_2O_3) authenticating that the shale was terrestrially sourced. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ (13.48) indicates that the provenance of the shale is from a felsic source. The bivariate relationship of (SiO_2 vs. $\text{Al}_2\text{O}_3+\text{Na}_2\text{O}+\text{K}_2\text{O}$) suggests a semi-arid paleoclimate with increasing chemical maturity in a phanerozoic shale environment. The data obtained from the study, showed that the average values of the following weathering indices: the Plagioclase Index of Alteration (PIA) with a value of 91.00% (73.58-98.43), the Chemical Index of Alteration (CIA) of value 74.33% (65.18-78.25), the Chemical Index of Weathering (CIW) with a value of 93.12% (73.58-98.43) and the Mineralogical Index of Alteration (MIA) valued at 48.67% (30.36-56.50) which indicates a substantial, moderate to intense chemical weathering with a PIA average indicating a phanerozoic ancient environment. The mineralogy of the shale from the diffractogram profiles were quartz, fluorapatite, calcite and montmorillonite. The predominance of quartz again confirms the resistance of quartz to weathering conditions while the other minerals that are in trace amounts are only indications that they are less resistant to weathering and have dissolved in the solution.

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Keywords: Provenance, Paleoredox, Phanerozoic, Felsic source, Mamu shale

1. Introduction

Insight into the provenance and paleo-conditions of a sedimentary basin fill is crucial for hydrocarbon exploration/exploitation as well as other paleo conditions. Although the usefulness of the geochemistry of sedimentary rocks in the determination of provenance, maturity, and paleo-conditions has been a global subject, its application is grossly a complex function of the nature of source rock(s), weathering intensity/duration, sedimentary recycling. The geochemical attributes of elements (major and trace elements) in clastic sedimentary rocks are invaluable for construing provenance (Peters and Moldowan, 1993?). Also, the geochemical composition of elements furnishes invaluable information that is germane for paleo-climate (Ilevbare and Omodor, 2020, Cao *et al.*, 2012; Tao *et al.*, 2017) and paleo-redox (Matthew *et al.*, 2019; Mengjiao *et al.*, 2020; El-Hasan and Al-Malabeh, 2008) reconstructions.

Over the last two decades, several studies focusing on sedimentology (Tijani *et al.*, 2010; Onyekuru and Iwuagwu, 2010; Dim *et al.*, 2019) and stratigraphy (Uzoegbu *et al.*, 2013), mineralogy (Akinyemi *et al.*, 2013), palynology

(Egboka and Emejulu, 2015), reservoir characterization (Anakwuba and Onyekwelu, 2010; Okwara *et al.*, 2020), petroleum potential (Adebayo *et al.*, 2018; Ogungbesan and Adedosu, 2020), aeromagnetism, (Bello *et al.*, 2017), and gravity modeling (Obasi *et al.*, 2018; Omietimi *et al.*, 2021) have been carried out on the basin.

As a result, this study presents the inorganic geochemistry investigation for Maastrichtian shale sourced from the southern Anambra Basin, Nigeria. To decipher the provenance, maturity, source area weathering, mineral composition, and paleo-redox conditions, which will help provide more information for further exploitation of the basin.

2. Study Area

Fifteen outcrop shale samples were collected from three different communities; Uzebba, Ayoguir, and Ugbenor, and the field photographs of the outcrop are presented in Figure 1 below. In Uzebba, samples were collected from eleven (11) locations (Figure 2b) and at Ayoguir and Ugbenor Fugar (Figure 2a), all from Edo-North, Nigeria.

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Figure 1. Exposed Outcrops of Shale in the study area, Edo State, Nigeria.

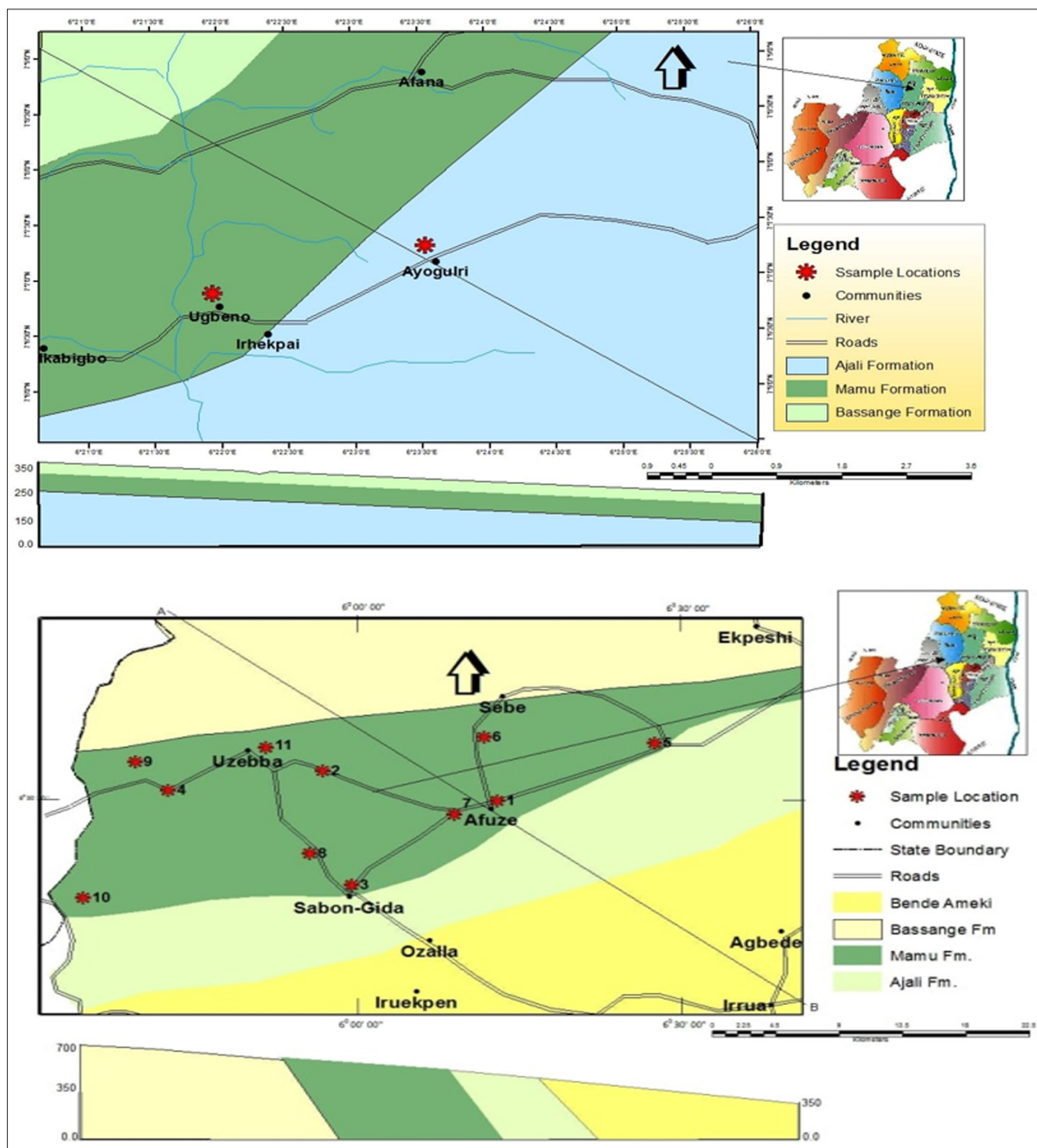


Figure 2. Location map of (a) Ugbenor and Ayogulri shale (Upper) and (b) Geologic section of Uzebba shale (down).

2. Geologic Settings of the Basin

The Anambra Basin (Figure 3 and 4) is tiered up with the southern ensemble of the Benue Trough and its genesis is closely related to the evolution of the Benue Trough, which is connected with the separation of Africa from the South American plate in the Mesozoic, which is the opening of the Atlantic Ocean (Burke *et al.*, 1971). There have been several investigations by researchers on the geochemistry of the sedimentary successions of the Anambra Basin (Ilevbare and Imasuen 2020; Ilevbare and Omodolor, 2020; Overare *et al.*, 2020; Ilevbare and Omorogieva, 2020).

Although the Formation mechanism is debatable, the majority of studies favor tensional movements that result in rifts, graben-like structures, or a dominant tectonic process of wrenching (Cratchley and Jones, 1965; Stoneley, 1966). (Benkhelil, 1989; Maurin *et al.*, 1986). Evidence supporting the rift model has been gathered through structural, geomorphic, stratigraphic, and paleontological results (Burke *et al.*, 1972; Benkhelil, 1989; Guiraud and Bellion, 1995). Following the emergence of a hotspot, it is now understood to be a folded aulacogen or a failed arm of a triple rift system (Burke and Dewey, 1974; Olade, 1975).

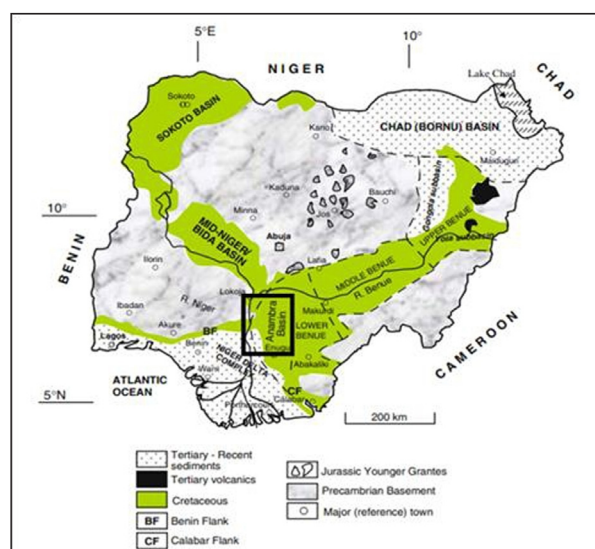


Figure 3. Generalized geological map of Nigeria showing the Anambra Basin in the thick rectangular box (modified after Obaje *et al.*, 2004).

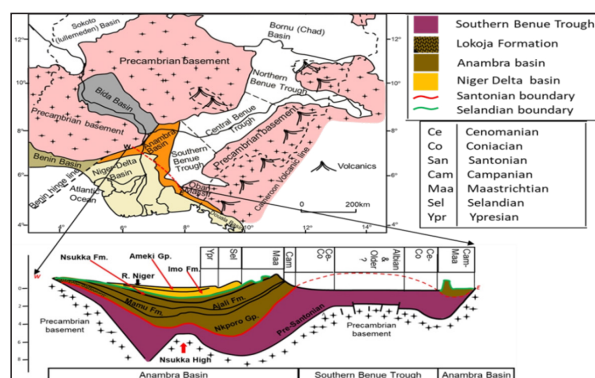


Figure 4. Map of Nigeria showing areas underlain by basement and sedimentary rocks. Below is a W-E cross-section of the Anambra Basin and Southern Benue Trough (after Edegbai *et al.*, 2019a and b).

3. Materials and Methodology

The methods of investigation involved both field study and laboratory analyses. Laboratory investigations of samples for geochemical characteristics were the 15 shale samples were immediately stored in a Ziploc polyethylene bag and preserved at room temperature. Samples were oven-dried and later disaggregated using Porcelain mortar and pestle.

3.1 XRF and LA-ICPMS Analyses

The pulverized shale samples were analyzed with the XRF technique. X-ray fluorescence spectrometry and instrumental neutron activation analysis would be used for sample preparation, as well as major and trace element analysis.

The analytical procedures for XRF are as follows:

Pulverized shale samples were analyzed for the major element using an Axios instrument with a 2.4 kWatt Rh X-ray Tube. Further, the same set of samples was also analyzed for trace elements using LA-ICPMS instrumental analysis; LA-ICP-MS is a powerful and sensitive analytical technique for multi-elemental analysis. The laser was used to vaporize the surface of the solid sample, while the vapor and any particles, were transported by the carrier gas flow to the ICP-MS (Okitor and Ighodaro, 2020). The detailed procedures for sample preparation for both analytical techniques are reported below.

- Add 10.0000 g \pm 0.0009g Claiss flux and fuse in M4 Claissfluxer for 23 minutes.
- 0.2 g of NaCO₃ was added to the mix and the sample+flux+NaCO₃ was pre-oxidized at 700°C before fusion.
- Flux type: Ultrapure Fused Anhydrous Li-Tetraborate-Li-Metaborate flux (66.67 % Li₂B₄O₇ + 32.83 % LiBO₂) and a releasing agent Li-Iodide (0.5 % LiI).

3.2 Pressed Pellet Method for Trace Element Analysis

- Weigh 8g \pm 0.05 g of milled powder
- Mix thoroughly with 3 drops of wax binder
- Press the pellet with a pill press to 15-tonne pressure in the oven at 100°C for half an hour before analyzing.

Eleven (11) major oxides were analyzed (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, MnO, CaO, Na₂O, K₂O, Cr₂O₃ and P₂O₅) as well as seven (7) trace elements ((Ba, Cu, Zn, Cr, Ni, Co, and V) using Phillips PW-1800 X-ray fluorescence (XRF) analyzer

3.3 X-ray diffraction analysis and procedures

The X-ray diffraction studies for mineral identification were conducted as described by Bundy (1993) and Murray and Keller (1993). X-ray diffraction analysis (XRD) was used to determine the mineralogical composition of these samples. Representative samples from shale outcrops were analyzed to assess their whole-rock geochemical compositions.

The analytical procedures for XRD are as follows:

Powdered samples were pelletized and sieved to 0.074mm and later taken to an aluminum alloy grid (35mm x 50mm) on a flat glass plate and covered with paper. Wearing hand gloves, the samples were compacted by gently pressing them with the hand.

Each sample was run through the Rigaku D/Max-III C X-ray diffractometer developed by the Rigaku International Corporation Tokyo, Japan, and set to produce diffractions at a scanning rate of 2°/min in the 2 to 50° at room temperature with a CuK α radiation set at 40kV and 20mA. The diffraction data (d-value and relative intensity) obtained were compared to that of the standard data of minerals from the mineral powder diffraction file ICDD, which contains and includes the standard data of more than 3000 minerals (Haque and Roy, 2019).

4. Results and Discussion

The results obtained from the geochemical analyses are presented in Table 1a and b.

For the area under study, the major oxide data (Table 1) show that (SiO₂; 58.10% for AY7 to 52.10% for UZ4 and UG4) and (Al₂O₃; 16.92% for UZ11 to 13.90% for UG4) predominate, followed by other oxides: Fe₂O₃, K₂O, MgO, CaO, TiO₂, Na₂O, P₂O₅, and MnO. There are traces of the residual oxides.

Table 1a. Major elements and chemical weathering indices of shale deposits sourced from Uzebba, Ugbenor, and Ayoguirri communities, Anambra basin, Nigeria.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	P ₂ O ₅	K ₂ O	MnO	MgO	Na ₂ O
UZ 1	52.40	14.50	7.50	0.77	0.85	0.09	3.86	0.04	1.40	0.30
UZ 2	57.15	16.88	5.82	0.74	0.79	0.07	4.65	0.02	1.55	0.32
UZ 4	52.10	13.98	6.00	0.74	3.55	0.08	3.85	0.02	1.45	0.30
UZ 6	56.50	15.22	5.70	0.75	0.11	0.06	4.04	0.02	1.15	0.33
UZ 7	58.00	15.10	5.50	0.75	0.13	0.05	4.05	0.01	1.12	0.30
UZ 9	55.30	16.50	6.57	0.76	0.64	0.07	4.50	0.01	1.49	0.31
UZ 11	57.13	16.92	5.80	0.75	0.80	0.07	4.65	0.04	1.55	0.30
UG 4	52.10	13.90	6.05	0.79	3.55	0.07	3.80	0.03	1.45	0.31
UG 4B	56.50	15.27	5.65	0.77	0.11	0.06	4.04	0.01	1.16	0.31
UG 5	52.38	14.52	7.53	0.74	0.85	0.09	3.88	0.02	1.38	0.32
UG 7	57.16	16.87	5.80	0.76	0.79	0.07	4.65	0.02	1.55	0.32
AY 2	52.13	13.97	6.00	0.74	3.55	0.07	3.82	0.03	1.45	0.31
AY 4	56.50	15.27	5.65	0.77	0.11	0.06	4.04	0.01	1.16	0.31
AY 7	58.01	15.10	5.49	0.77	0.11	0.07	4.02	0.01	1.12	0.30
AY 8	55.31	16.49	6.59	0.76	0.63	0.07	4.51	0.01	1.49	0.31

Table 1b. Major elements and chemical weathering indices of shale deposits sourced from Uzebba, Ugbenor, and Ayoguirri communities, Anambra basin, Nigeria.

Sample	SiO ₂ /Al ₂ O ₃	Fe ₂ O ₃ /K ₂ O	Al ₂ O ₃ / TiO ₂	K ₂ O/ Al ₂ O ₃	CaO*	CIA	CIW	PIA	MIA
UZ 1	3.61	1.94	18.83	0.27	0.550	75.48	94.46	92.60	50.96
UZ 2	3.39	1.25	22.81	0.28	0.557	75.33	95.06	93.31	50.66
UZ 4	3.73	1.56	18.89	0.28	3.283	65.29	79.60	73.87	30.58
UZ 6	3.71	1.41	20.29	0.27	-0.090	78.05	98.45	97.77	56.10
UZ 7	3.84	1.36	20.13	0.27	-0.037	77.78	98.29	97.67	55.56
UZ 9	3.35	1.46	21.71	0.27	0.407	75.98	95.84	94.36	51.96
UZ 11	3.38	1.25	22.56	0.27	0.567	75.41	95.13	93.40	50.82
UG 4	3.75	1.59	17.59	0.27	3.317	65.18	79.31	73.58	30.36
UG 4B	3.70	1.40	19.83	0.26	-0.090	78.19	98.58	98.08	56.38
UG 5	3.61	1.94	19.62	0.27	0.550	75.35	94.35	92.44	50.70
UG 7	3.39	1.25	22.20	0.28	0.557	75.32	95.06	93.31	50.64
AY 2	3.73	1.57	18.88	0.27	3.317	65.23	79.39	73.68	30.46
AY 4	3.70	1.40	19.83	0.26	-0.090	78.19	98.58	98.08	56.38
AY 7	3.84	1.37	19.61	0.27	-0.123	78.25	98.84	98.43	56.50
AY 8	3.35	1.46	21.70	0.27	0.397	75.97	95.89	94.43	51.94

CIW – Chemical index of weathering, CIA – Chemical index of Alteration, PIA – plagioclase index of alteration, MIA – Mineral index of alteration

4.1 Major Elements

The SiO_2 content should be associated with the presence of quartz particles: the highest value for all samples refers to the higher sand fraction in particle size distribution analysis and higher quartz content in mineral composition. Alumina (Al_2O_3) reflects the presence of aluminosilicates. Iron (Fe_2O_3) is related to the presence of hematite while potassium (K_2O) is linked to the presence of k-feldspars (Nzeukou *et al.*, 2021).

Discussing the provenance of the shale samples since in situ weathering did not produce the majority of the shale deposits in the study area, geochemical signatures for clastic rocks were employed to determine the origin (Madharaju and Ramasamy, 2002; Armstrong-Altrin *et al.*, 2004). The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio grows from 3 to 8 for mafic igneous rocks, 8 to 21 for intermediate rocks, and 21 to 70 for felsic igneous rocks. These ratios have also been used to determine the composition of the source rock of clastic rocks (Ilevbare and Imasuen, 2020, Hayashi *et al.*, 1997). As calculated from Table 1b, the respective average ratios are as follows: 3.58, 1.07, 13.48, 0.27, and 0.871 for $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$, $\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$.

Decreasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, (3.58), MgO content (low 1.36), and increasing Fe_2O_3 content, 6.11 (Table 1) may also indicate the residual weathered Fe–Mg minerals such as olivine and/or amphibole and pyroxene, which are inherited from moderately weathered granitoids.

Girty *et al.*, (1996) stated that sediments from mafic rocks have $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio <14 while sediments from felsic rocks ranged from 19-28. Comparing the major oxides, the bivariate plot of Titanium oxide and Alumina (Figure 6), indicates that the shale samples are from felsic source rock. However, the provenance discrimination plot (Figure 7) indicates that the data points plots in both the intermediate rock field and to felsic rock field.

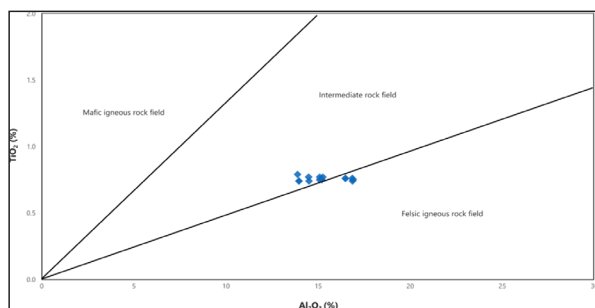


Figure 5. Titanium oxide versus Alumina for Provenance, (after Girty *et al.*, 1996).

An insight into the paleoredox, source area weathering, and paleoclimate conditions for the shale indicates that the shale is of Continental oxic environment with prevailing oxidizing conditions (Figure 5), intensive chemical weathering (Figure 6), and a semi-arid paleoclimatic condition (Figure 7).

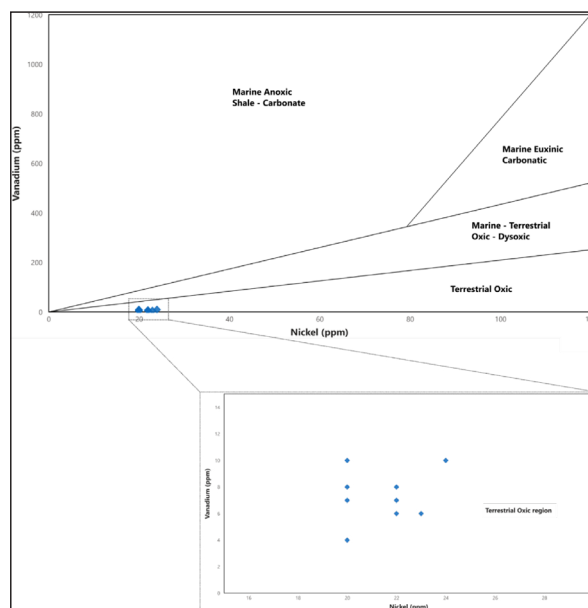


Figure 6. Vanadium versus Nickel for paleoredox discrimination, (after Girty *et al.*, 1996).

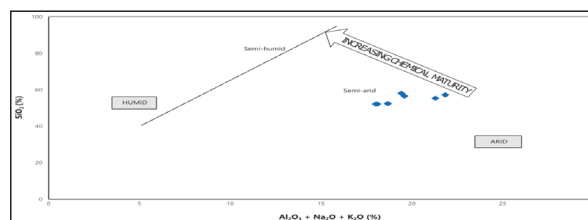


Figure 7. Silica versus Alumina showing paleoclimate, (after Girty *et al.*, 1996).

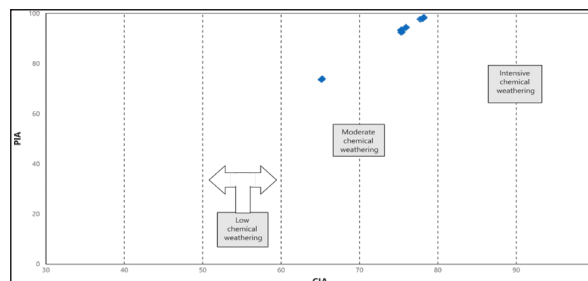


Figure 8. PIA versus CIA showing weathering conditions, (after Girty *et al.*, 1996).

4.2 Trace Elements

The relative abundance of major oxides and trace elements in sediment is controlled by sedimentation rate, terrigenous influx, biogenic influx, hydrothermal input, diagenesis and, weathering (Leventhal, 1998; Schieber and Zimmerle, 1998). Their enrichments indicate a comprehension of their paleo-depositional and paleo redox setting, as well as the paleo-climate (Vine and Tourtelot, 1970). Therefore, the concentrations of these redox-sensitive elements (Table 2), were sensitive indicators of prevalence paleoconditions (Adegoke *et al.*, 2014). The concentration of vanadium (V), and nickel (Ni) as well as their ratios provide a means of deciding the degree of anoxia during deposition (Barwise, 1990; Bechtel *et al.*, 2001; Galarraga *et al.*, 2008). Vanadium is usually enriched in comparison with Nickel in anoxic marine environments (Peters and Moldowan, 1993).

According to Hatch and Levantal (1992) with Kimura and Wanatabe (2001), as well as Nagarajan *et al.*, (2007), Ni/Co ratio less than 2 ppm indicate an oxic environment, while ratios between 5 to 7 ppm indicate a dysoxic environment and a value greater than 7 ppm indicates a suboxic to anoxic environment. This study has a Ni/Co value of 1.80 ppm (Table 2) which again confirms an oxic environment. Again from this study, the Ni/Co ratio is below 5, which suggests an oxidizing condition for the Mamu shale.

Similarly, a V/Cr value less than 2 ppm indicates an oxic environment, while a value of 2 to 4.25 suggests a dysoxic environment, and that greater than 4.25 ppm indicates sub-oxic to anoxic conditions. From Table 2, these samples collected have a value much less than 2 (0.38ppm) which

indicates oxidizing conditions. This again agrees with Akinyemi *et al.*, (2013) having a result of between 1.01 and 1.91. Olajubaje *et al.*, (2018) have V/Cr values which may indicate that relatively oxidizing conditions were also prevalent. Furthermore, the V/Cr ratios of the examined samples are below 2(1.142) and therefore indicate the oxic depositional setting.

The $V/(V + Ni)$ value less than 0.46 suggests an oxic environment, while that of 0.46–0.60 indicates a dysoxic environment and 0.54–0.82 indicates a suboxic to anoxic condition, and a value less than 0.84 suggests an euxinic condition (Hatch and Levantal 1992). This study gives an average value of 0.26 ppm for $V/(V + Ni)$ which again confirms an oxic environment.

Table 2. Trace elements of shale deposits sourced at Uzebba, Ugbenor and Ayoguirri communities, Anambra basin.

Sample	ppm											
	Ba	Cu	Zn	Cr	Ni	Co	V	Ni/Co	V/Ni	V/Cr	$V/(V + Ni)$	
UZ 1	882	22	12	20	22	10	6	2.20	0.27	0.30	0.21	
UZ 2	992	20	10	20	20	10	4	2.00	0.20	0.20	0.17	
UZ 4	990	23	10	22	22	10	8	2.20	0.36	0.36	0.27	
UZ 6	976	20	12	20	20	8	10	2.50	0.20	0.50	0.33	
UZ 7	980	20	10	20	23	6	6	3.80	0.26	0.30	0.21	
UZ 9	990	22	9	21	22	8	8	2.75	0.36	0.36	0.27	
UZ 11	995	24	12	18	24	10	10	2.40	0.42	0.42	0.29	
UG 4	894	22	10	20	20	8	7	2.50	0.35	0.35	0.26	
UG 4B	986	20	8	19	20	8	8	2.50	0.40	0.42	0.29	
UG 5	990	22	12	15	22	10	6	2.20	0.27	0.40	0.21	
UG 7	994	20	10	22	24	10	10	2.40	0.42	0.45	0.29	
AY 2	992	23	12	20	22	9	8	2.40	0.36	0.40	0.27	
AY 4	995	22	12	18	20	10	10	2.00	0.50	0.50	0.33	
AY 7	890	24	10	22	22	8	7	2.75	0.32	0.32	0.24	
AY 8	880	20	12	22	20	10	10	2.00	0.50	0.45	0.33	
	UZ- Uzebba			UG-Ugbenor				AY- Ayoguirri				

According to Hatch and Levantal (1992) with Kimura and Wanatabe (2001), as well as Nagarajan *et al.*, (2007), Ni/Co ratio less than 2 ppm indicate an oxic environment, while ratios between 5 to 7 ppm indicate a dysoxic environment and a value greater than 7 ppm indicates a suboxic to anoxic environment. This study has a Ni/Co value of 1.80 ppm (Table 2) which again confirms an oxic environment. Again from this study, the Ni/Co ratio is below 5, which suggests an oxidizing condition for the Mamu shale.

Similarly, a V/Cr value less than 2 ppm indicates an oxic environment, while a value of 2 to 4.25 suggests a dysoxic environment, and that greater than 4.25 ppm indicates sub-oxic to anoxic conditions. From Table 2, these samples collected have a value much less than 2 (0.38ppm) which indicates oxidizing conditions. This again agrees with Akinyemi *et al.*, (2013) having a result of between 1.01 and 1.91. Olajubaje *et al.*, (2018) have V/Cr values which may indicate that relatively oxidizing conditions were also

prevalent. Furthermore, the V/Cr ratios of the examined samples are below 2(1.142) and therefore indicate the oxic depositional setting.

The $V/(V + Ni)$ value less than 0.46 suggests an oxic environment, while that of 0.46–0.60 indicates a dysoxic environment and 0.54–0.82 indicates a suboxic to anoxic condition, and a value less than 0.84 suggests an euxinic condition Hatch and Levantal (1992) and Khoury (2014). This study gives an average value of 0.26 ppm for $V/(V + Ni)$ which again confirms an oxic environment.

The correlation of alumina against the other trace elements (Figure 9) using the data set (Table 3) helps to delineate the shale type using the correlation coefficient classifies the shale to be predominately detrital shale, (Table 4) with the negatively correlated as authogenic and the positively correlated as detrital.

Table 3. The Correlation plot of Al₂O₃ against the trace elements.

Al ₂ O ₃	Al	Ba	Cu	Zn	Cr	Ni	Co	V
14.50	3.84	882	22	12	20	22	10	6
16.88	4.47	992	20	10	20	20	10	4
13.98	3.70	990	23	10	22	22	10	8
15.22	4.03	976	20	12	20	20	8	10
15.10	4.00	980	20	10	20	23	6	6
16.50	4.37	990	22	9	21	22	8	8
16.92	4.48	995	24	12	18	24	10	10
13.90	3.68	894	22	10	20	20	8	7
15.27	4.04	986	20	8	19	20	8	8
14.52	3.84	990	22	12	15	22	10	6
16.87	4.47	994	20	10	22	24	10	10
13.97	3.70	992	23	12	20	22	9	8
15.27	4.04	995	22	12	18	20	10	10
15.10	4.00	890	24	10	22	22	8	7
16.49	4.37	880	20	12	22	20	10	10

Another important consideration in the use of trace elements in palaeo-redox determination is to examine whether they are detrital or authigenic in origin. Correlation values derived from cross plots of Al versus the trace elements (Figure 9) can determine if they are detrital or authigenic in origin. The shale sediments are predominantly of a detrital origin, (Table 4). This result is consistent with the pieces of evidence from the high weathering history recorded from the shale and with the mineralogical composition that reveals that the quartz has survived been weathered and has been transported through a fairly long distance. The correlation result of Alumina (Al₂O₃) versus Cu and Zn are both authigenic.

Table 4. Interpreted correlation result of the shale.

Al vs. TE	Corr. Coef.	Interpretation
Al vs. Ba	0.212	Detrital
Al vs. Cu	-0.321	Authigenic
Al vs. Zn	-0.110	Authigenic
Al vs. Cr	0.152	Detrital
Al vs. Ni	0.185	Detrital
Al vs. Co	0.213	Detrital
Al vs. V	0.257	Detrital

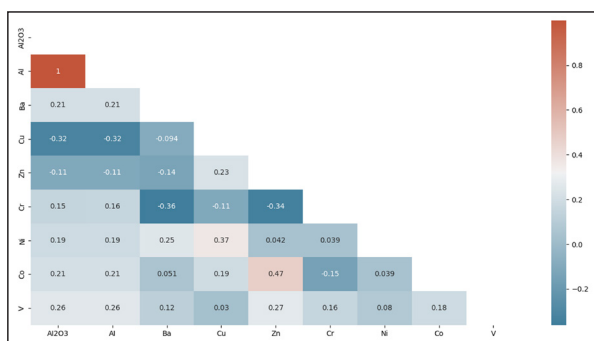


Figure 9. Correlation chart of aluminum and other trace elements.

In the diffractogram (Figure 10), for Ayoguir shale, the quartz with six observed peaks had the highest peak of 90cps with 30° which was followed by calcite with 50cps/35° with three observed peaks. Other minerals in minor quantities

and without prominent peaks are montmorillonite with four peaks and Figure fluorapatite with three observable peaks.

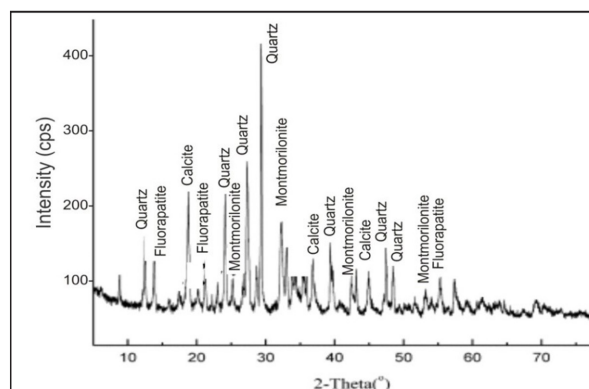


Figure 10. Diffractogram of Mamu shale in Ayoguir community, Anambra Basin.

In Ugbenor shale, quartz has 6 observed peaks with 110cps/35° being the highest. This was followed by calcite with three observed peaks with the highest being 40cps/48°; also observed were fluorapatite and montmorillonite (Figure 11).

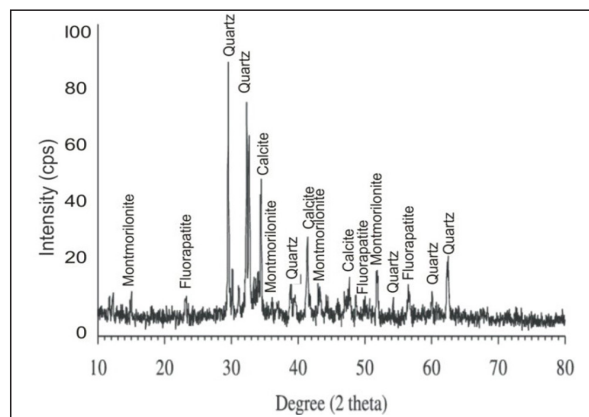


Figure 11. Diffractogram of Mamu shale in Ugbeno community, Anambra Basin.

In Uzebba shale, the quartz with seven observable peaks had 400cps/30° followed by calcite with 200cps/20°. With four observable peaks, montmorillonite also had a significant peak here in this sample with 180cps/32°. Fluorapatite had three observed peaks with no sharp peaks, (Figure 12).

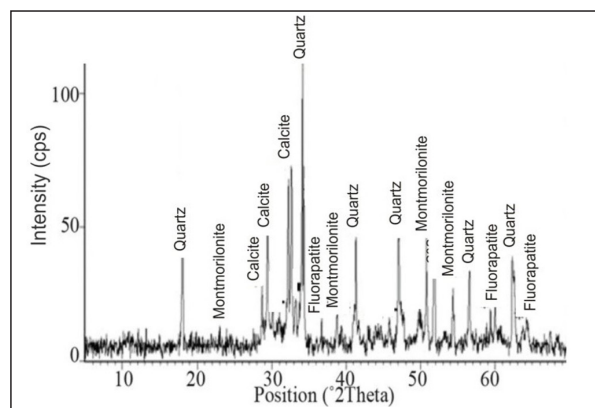


Figure 12. Diffractogram of Mamu shale in Uzebba community, Anambra Basin.

4.3 Chemical Weathering Index

Chemical weathering indices are often employed to quantify changes brought on by chemical weathering in different materials (Birkeland, 1999; Darmody et al., 2005; Ruxton, 1968; Harnois, 1988; Habboush and Jarrar, 2009). The indices are based on the idea that as leaching advances, the ratio between concentrations of mobile (e.g. SiO₂, CaO, MgO, and Na₂O) and immobile (e.g. Al₂O₃, Fe₂O₃, and TiO₂) elements will progressively plummet. Calculating the Chemical Index of Alteration (CIA), where CIA = molar (Al₂O₃/[Al₂O₃+CaO+Na₂O+K₂O]) x 100, can help understand the extent of chemical weathering of the sediments' source rocks, according to Nesbitt and Young (1982). The CIA monitors the progressive transformation of potassium feldspars and plagioclase into clay minerals (Rahman and Suzuki, 2007). When Ca, Na, and K drop as weathering severity increases, (Duzgoren-Aydin et al., 2002). The only difference between the CIA and the Chemical Index of Weathering (CIW) proposed by Harnois, (1988) is the omission of K₂O from the equation: CIW = molar (Al₂O₃ / (Al₂O₃+ CaO + Na₂O) x 100.

From the results of (Table 1), the Chemical Index of Alteration (CIA) gives an average value of 74.33% (65.18-78.25), while the Chemical Index of Weathering (CIW) has an average value of 93.12% (73.58-98.43). The Plagioclase index of alteration gives an average value of 91.00% (73.58-98.43) and the Mineralogical Index of Alteration measures 48.67% (30.36-56.50) on average.

According to McLennan, (1983), McLennan, (1993), and Mongelli et al., (1996), the results of CIA and CIW are similar, with values of 50 for the unweathered upper continental crust and approximately 100 for heavily weathered materials. Low CIA values (i.e. 50 or less) also might reflect cool and/or arid conditions. Nesbitt and Young (1982) classified the CIA values as very slightly weathered (50 to 60), slightly weathered (60 to 70), moderately weathered (70 to 80), highly weathered (80 to 90), and extremely weathered (90 to 100). This study (Table 1) indicates between slightly

weathered and moderately weathered environments (65.18-78.25). For the CIA, weathering at the incipient stage, CIA (30-55), weathering at the intermediate stage, CIA (51-85), and weathering at the advanced stage CIA >85. An average value of 74.33 from this study implies that the weathering is at an intermediate stage.

Chemical Index of Weathering (CIW) values range from 50 for unweathered upper continental crust to roughly 100 for materials that have undergone substantial weathering, with the full elimination of alkali and alkaline-earth elements (McLennan et al., (1983), McLennan (1993)). The CIW value of 93.12% (ave.) applies the shale has undergone substantial weathering.

To evaluate MIA values, it is helpful to consider the following ranges: incipient (0–20%), weak (20–40%), moderate (40–60%), and intense to extreme (60–100%) degree of weathering. The MIA of this study is 48.67 (range 30.36-56.50%) illustrates an environment with moderate weathering.

5. Conclusions

Based on the analysis of the geochemical discriminant, mineralogy and geochemical paleo redox indicators for the Maastrichtian shales of Mamu formation, Southern Nigeria the following conclusions may be drawn:

From the correlation results, the shale is of detrital origin, this explains also why the source area weathering indicated a substantial, intense to extreme chemical weathering of the phanerozoic shale.

The metallic oxide ratios indicated the provenance of the shale are of a felsic source rock in a semi-arid to arid paleoclimatic condition.

The paleoredox studies reveal that the shale was deposited in an oxic environment from the weathering indices (Ni/Co, V/Cr, and V/V+Ni) except for V/Ni which was deposited in a dysoxic - Oxic environment.

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