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Geochemical Investigation of Enugu Shale, Anambra Basin Nigeria: Implication for Provenance and Paleoenvironment

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Abstract
The shale units of the Campanian-Maastrichtian Enugu Formation were sampled from road cuts at Enugu, Anambra Basin, southeastern Nigeria. The study is focused on examining the source rock weathering history, tectonic setting and paleo-environmental conditions of deposition using a high quality bulk elemental composition data of the shale samples. Obtained geochemical data reveal that the protoliths of these shales were most probably felsic in nature based on the average values of SiO_2 (55.67%), Al_2O_3 (14.00%), K_2O (1.22%), CaO (0.38%), MgO (0.95%), K_2O (1.22%) and TiO_2 (1.39%) and other geochemical proxies. The values are relatively lower except Fe_2O_3 (10.63%) when compared to North American Shale Composite (NASC) and post-Archean Australian Average Shales (PAAS) values. The normalized REE distribution patterns which displayed relatively depleted LREE but enriched HREE coupled with small concentration of Eu/Eu* also reveal felsic protolith for the shales. The ratio of values of certain trace elements in the studied shales; La/Sc (7.27), Th/Sc (3.07), Th/Co (1.01), Th/Cr (0.65) and Cr/Th (1.67) are comparable to the published average values of the sediments derived from felsic and basic rocks (fine fraction), Upper Continental Crust (UCC) and PAAS and therefore suggest felsic provenance. The plot of Th/Co versus La/Sc and TiO_2 versus Ni is also indicative of felsic protolith for the sediments. Weathering indices (mean Chemical Index of Alteration CIA 87.65 and Chemical Index of Weathering CIW 95.21),low K_2O content (1.22% average), Th/U (7.58 average), Th (11.1ppm average), and U (1.57ppm average), and A-CN-K plot suggest these shales were derived from a source subjected to intense weathering. The geochemical parameters such as U, U/Th, V/Cr, Ni/Co and Cu/Zn values obtained suggest that the shales were deposited under oxic environment. The immobile trace element ratios and geochemical discrimination diagrams (K_2O/Na_2O vs. Si_2O; La-Th-Sc) reveals that the protoliths of the Enugu Formation were derived from a semi-humid to humid region under intense weathering.

Keywords: *Enugu, humid, geochemistry, oxic, protolith.*

Introduction

The investigated shale sections of the Maastrichtian Enugu Formation lies between latitudes 6°41'N and 7°06'N and longitudes 7°21'E and 7°54'E in the Anambra Basin, Nigeria (Fig. 1).

The Anambra Basin, one of the basins in the Benue Trough, Nigeria evolved consequent to tectonic uplifting and folding of Pre-Santonian sediments in Abakaliki-Benue Trough (Reyment, 1965; Murat, 1970; Kogbe, 1976; Whiteman, 1982; Benkhelil, 1989). Almost 9 km thick sedimentary deposits were deposited in the basin. They are mostly horizontally laid and are essentially of Campanian to Paleocene age. The flanks of the Abakaliki Anticlinorium served as major sediment source. The sedimentary successions in the Anambra Basin comprise of the Enugu Shales (Campanian), Mamu Formation (Maastritchian), Ajali Sandstone (Maastrichtian) and Nsukka Formation (upper Maastrichtian) (Simpson, 1954).

The Enugu Formation comprises of dark parallel laminated shales which is intercalated with thin beds of siltstone. According to Nwajide and Reijers (1996), they were deposited in open marine setting and the dark colour of the shales is an indication of bottom anoxia perhaps due to density stratification and poor circulation. The Mamu Formation overlies the Enugu shales and is composed of shales, siltstones, coal, sandstones and heteroliths of mud, silt and sand. It is transitional between the normal marine Enugu Shales and marginal marine (largely tidal) Ajali Sandstone. The Ajali Sandstone is made up of quarzarenitic sandstones that are friable to weakly consolidated.

Previous studies have shown that major element geochemistry is invaluable in provenance studies of sedimentary rocks, particularly shales which are abundant in most sedimentary basins worldwide (Pettijohn, 1975: Bhatia, 1983; Roser and Korsch, 1986). McLennan *et al.,* (1983) identified some certain trace elements such as La, Y, Sc, Cr, Th, Zr, Hf, Nb, and TiO_2 among other major elements that are provenance indicators and good proxies for tectonic setting determination. This is because of their relatively low mobility during sedimentary processes. In addition, a reliable assessment of the relative distribution of the immobile elements with varying concentration in granitic and basic rocks such as La and Th (enriched in felsic rocks) and Sc, Cr, and Co (enriched in basic rocks) can provide insight into relative contribution of felsic

and basic sources in shales from different tectonic environments (Wronkiewicz and Condie, 1990). The REEs and trace elements also serve as valuable tool for unravelling the paleoredox conditions in ancient marine environments and this has been found applicable in the present geochemical investigation.

The Enugu shale section has been studied by several authors with focus on biostratigrahic and hydrocarbon source rock investigations. The work of Ojo *et al*. (2009) and Akaegbobi *et al.* (2009) are notable in this regard. Inorganic geochemical study is however not available. In this article, provenance, weathering history and paleoenvironments of the Maastrichtian shales based on inorganic geochemical data are evaluated. Several relevant geochemical proxies were employed in the assessment in order to have a deep insight on the above listed objectives.

Materials and Methods

Eleven carefully selected shale samples from the logged road cut of Enugu Formation along Enugu - Onitsha highway, Enugu were analyzed for Major Oxides, Trace Elements (TE) and Rare Earth Elements (RRE) via two methods; X-ray Fluorescence (XRF) and Aqua regia ultra-trace Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis at ACME Analytical Laboratories (AcmeLabs), Canada.

About 50-100g of the whole rock samples were reduced to chips of 2 mm and pulverized in a mortal agate mill to avoid contamination. A 0.2 g aliquot was weighed into a graphite crucible and mixed with 1.50 g of $LiBO_2/Li_2B_4O_7$ flux. The crucibles were heated in a 980ºC oven for 30 minutes. The resulting bead was dissolved in 5% HNO_3 (ACS grade nitric acid diluted in demineralized water). Samples and calibrated reagent blanks were aspirated into an XRF (SpectroCiros Vision or Varian 735) to determine the set of major oxides and elements. Loss on ignition (LOI) was determined by igniting a 1.0 g sample split at 950ºC for 90 minutes, then measuring the weight loss. Total Carbon and Sulphur were determined by Leco method.

Sample splits for ICP-MS analysis were pulverized to 95% passing 150mesh (100 µm) in a mild-steel ring-and-puck mill. A 0.2 g aliquot was weighed into a graphite crucible and mixed with 1.5 g of $LiBO_2/Li_2B_4O_7$ flux. The crucibles were heated in a 980ºC oven for 30 minutes. The resulting bead was dissolved in 100mL 5% HNO_3 (ACS grade nitric acid diluted in demineralized water). An aliquot of the solution was poured into a polypropylene test tube. Samples and calibrated reagent blanks were aspirated into an ICP-MS (Perkin-Elmer Elan 6000 or 9000) and a digested split of 0.5 g in Aqua Regia and aspirated into an ICP-MS to determine the elements.

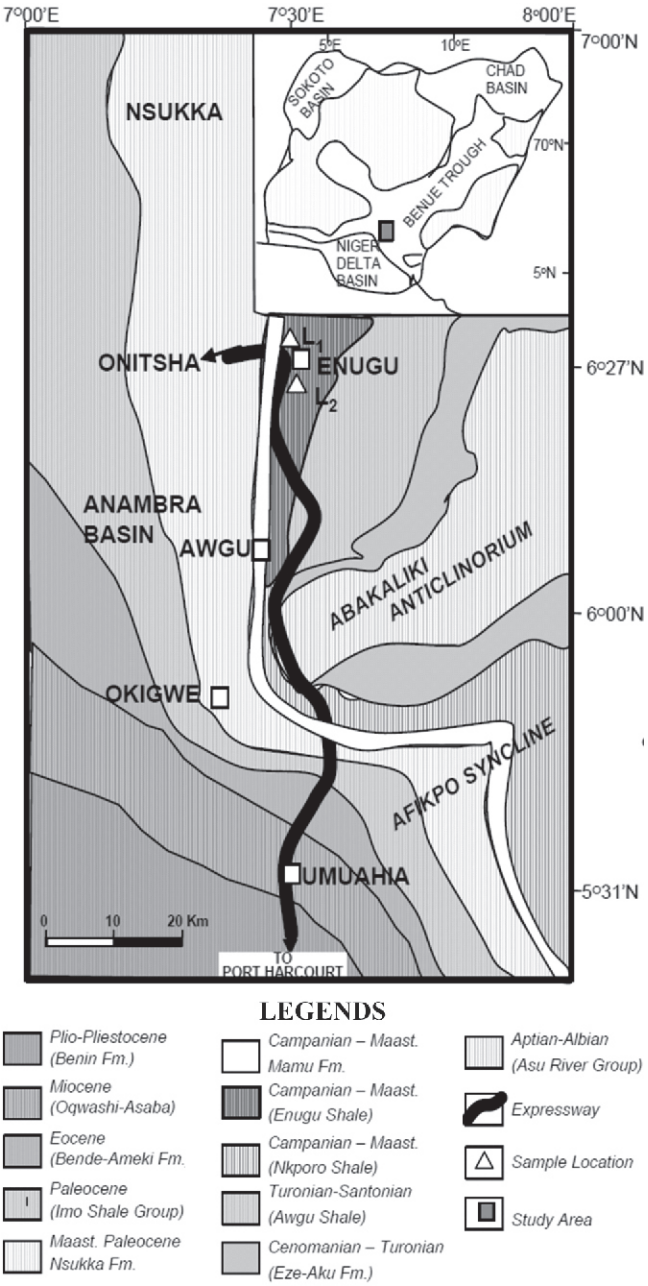


Fig. 1: Geological Map of the Anambra Basin and Adjacent Areas with inset as the Geological Map of Nigeria. Note the locations of the sections studied (Ojo et al. 2009).

Results Presentation

Chemical Composition

The values of major, trace and rare earth elements and

some important ratios as well as their distribution pattern are presented in tables 1-7. The frequencies of these elements and their discrepancies were also compared with the published shale data from Nigeria and other reference data (NASC, UCC, PAAS etc).

Major Oxides

The obtained major elemental composition of the studied Enugu shales is presented in table 1. The shale samples varied widely in content of SiO_2 (26.72-80.24% with average of 55.67%), Fe_2O_3 (1.36%-31.39%, average of 10.63%) and Al_2O_3 (7.07-17.95%, average of 14.0%). The moderately high $SiO_2$is a possible indication of the presence of silt-size detrital grains (two of the shale samples with relatively rich Fe_2O_3 content however have SiO_2 lower than 30%) while the relatively high value of Al_2O_3 may indicate a high aluminosilicate materials such as mica and kaolinite according to Besly and Clearl (1997). These shales, however, show low concentration in TiO_2, CaO, MgO, Na_2O and K_2O. Low mean concentrations of K_2O (1.22%), Na_2O (0.26%), MnO (0.09%) and TiO_2 (1.39%) in the studied shales is probably an indication of degradation of detrital feldspars and consequently low amount of illite. The mean concentrations of CaO (0.38%) and MgO (0.95%) are low, and may indicate prevalence of clastics, though one of the samples has CaO of 2.04% which may probably indicate presence of calcareous shell in the bed. The average silica/alumina ratio value (4.40) of the studied shales shows they are highly siliceous. The ratio closely compared with the values of North American Shale Composite and Post Archean Australian Shales (4.97 and 3.32 respectively) (Gromet *et al.* 1984; Taylor and McLennan, 1985). This is indicative of the detrital nature of the shale.

Table 2 presents the average major oxide data of the studied shale in comparison with those from other parts of Nigeria such as southern Bida Basin Shale (Okunlola and Idowu 2012), Auchi Shale (Akpokodje *et al*., 1991), Eze-Aku Shale (Amajor, 1987), Upper Benue (Gongila Formation) Shale (Adepoju and Ojo, 2013). Comparing the chemical composition of these shales, the studied shale samples have SiO_2 concentration closely compared with others from various part of Nigeria sedimentary basin and that of PAAS and NASC while SiO_2, Fe_2O_3, Al_2O_3 and CaO show lower concentration relative to other shales. MnO, K_2O, Na2O are comparable with shales from southern Bida Basin and the Auchi but relatively lower in content than others. TiO_2 in the investigated shales of Enugu Formation are similar to those of Auchi and southern Bida Basin but higher than those from other parts of Nigeria (Gongola and Lower Benue Trough) and other parts of the world (Average Shale-AS, NASC, PAAS).

Table 1: Major oxides concentration (%) for Enugu shales in this study compared to the similar values derived from NASC and PAAS.

Sample	ENU 1A	ENU 1C	ENU 1D	ENU 1H	ENU 1P	ENU 1Q	ENU 1S	ENU 1U	ENU 1V	ENU 2B	ENU 2E	Mean
SiO_2	52.97	47.60	59.42	55.86	57.41	26.72	59.17	80.24	76.78	35.03	61.19	55.67
Al_2O_3	17.22	13.66	16.99	15.38	16.85	8.92	15.72	7.07	10.76	13.49	17.95	14.00
Fe_2O_3	7.91	14.43	4.89	6.91	5.79	29.03	6.48	4.93	1.36	31.39	3.85	10.63
CaO	0.47	0.78	0.08	0.24	0.05	2.04	0.09	0.03	0.08	0.34	0.02	0.38
MgO	0.76	1.45	0.49	0.48	0.42	5.26	0.46	0.10	0.24	0.42	0.34	0.95
Na_2O	0.31	0.30	0.49	0.41	0.35	0.12	0.29	0.20	0.23	0.04	0.14	0.26
K_2O	1.36	1.20	1.45	1.42	1.37	0.62	1.37	1.01	1.26	0.89	1.50	1.22
MnO	0.04	0.09	0.01	0.009	0.05	0.63	0.04	0.009	0.03	0.07	0.009	0.09
TiO_2	1.37	1.13	1.58	1.70	1.63	0.84	1.54	1.29	1.54	1.11	1.52	1.39

Trace Elements

The results obtained show that Mn, Zn, Ba and V contents with average values of 667.5, 65.18, 66.73 and 34.82 ppm, respectively are relatively high among the other trace elements (Table 3). Sr, Pb, Th, Cr, Ni, Co and Cu have lower average values (11.49, 14.32, 11.1, 17.71, 16.15, 18.79 and 17.80 ppm respectively). Other important trace elements used as proxies in this study like Rb (8.37), Ga (3.27), Zr (4.20) and U (1.57) have relatively low concentrations. All the trace elements were compared with standard data e.g. PAAS and NASC and the result show that the studied shales were depleted in Ba, Cr, Ni, Rb, Sr, V, Cu and Zr but enriched in Th relative to PAAS.

Rare Earth Elements

The values of concentration of rare earth elements (REE) are listed in Table 4. The concentrations of REE are similar in all the investigated samples. There is depletion in LREE (light rare earth elements; La, Ce, Pr,

Table 2: Major oxides concentration (%) for Enugu shales in this study compared to the similar values derived from NASC and PAAS.

Sample	This Study	1	2	3	4	5	6	7	8
SiO_2	55.67	61.26	51.68	44.91	50.24	58.10	64.82	62.4	58.50
Al_2O_3	14.00	16.88	18.76	15.71	17.38	15.40	17.05	18.78	15.00
Fe_2O_3	10.63	3.75	4.67	6.24	5.95	6.90	5.70	7.18	4.72
CaO	0.38	0.05	1.90	15.42	4.42	3.10	3.51	1.29	3.10
MgO	0.95	0.16	4.39	2.58	0.81	2.40	2.83	2.19	2.50
Na_2O	0.26	0.06	0.93	0.42	0.06	1.30	1.13	1.19	1.30
K_2O	1.22	1.39	1.16	2.36	2.36	3.20	3.97	3.68	3.10
MnO	0.09	0.02	0.06	0.06	0.02	Trace	ND	ND	ND
TiO_2	1.39	1.74	1.95	0.65	0.82	0.60	0.83	0.99	0.77

1 - Southern Bida Basin Shale by Okunlola and Idowu (2012)
2 - Auchi Shale by Akpokodje et al. (1989)
3 - Eze-Aku (Lower Benue) Shale by Amajor (1987)
4 - Gongola Basin (Upper Benue) Shale by Adepoju and Ojo (2013)
5 - Average Shale (AS) by Pettijohn (1975)
6 - North American Shale Composite (NASC) by Grometet al. (1984)
7 - Post-Archean Australian Shale (PAAS) by Taylor and McLennan (1985)
8 - Turekian and Wedephol (1961)

Nd, Sm, Eu, Gd), HREE (heavy rare earth elements; Tb, Dy, Ho, Er, Tm, Tb, Lu) and total ΣREE compared to the standard values in the PAAS and NASC (Table 4). There is relative depletion in the HREEs compared to LREEs and this may point to a lower concentration of heavy minerals e.g. zircon in the sediments. A strong negative Eu-anomaly was observed in all the shale samples, ranging from 0.61 to 0.80. The Eu anomaly in sedimentary rocks is usually associated with igneous source rocks (Taylor and McLennan, 1985).

Table 3: Trace element concentrations (ppm) in Enugu Formation shales compared to the similar values derived from NASC and PAAS.

Sample	ENU 1A	ENU 1C	ENU 1D	ENU 1H	ENU 1P	ENU 1Q	ENU 1S	ENU 1U	ENU 1V	ENU 2B	ENU 2E	Mean	NASC	PAAS
Ga	3.40	3.70	3.70	4.10	3.00	2.10	3.30	2.80	2.70	3.40	3.80	3.27	-	-
Rb	11.30	9.90	8.50	8.60	7.60	4.90	7.40	4.30	4.30	7.70	17.60	8.37	-	160.0
Sr	17.80	16.90	5.70	8.20	5.60	31.40	4.00	6.60	5.80	15.80	8.60	11.49	142.0	200.0
Ba	21.50	105.90	29.60	42.20	18.10	29.50	18.30	315.50	19.00	34.60	99.80	66.73	636.0	650.0
Pb	18.29	14.39	17.07	12.48	18.3	6.22	16.11	7.30	9.65	10.26	27.46	14.32	-	20.0
Zr	3.70	4.10	4.70	5.90	4.30	3.80	4.70	3.20	6.10	3.00	2.70	4.20	200.0	210.0
Nb	0.0019	0.03	0.05	0.05	0.04	0.02	0.04	0.04	0.1	0.04	0.07	0.04	-	1.90
Th	13.30	11.60	12.70	11.10	14.30	7.00	11.90	7.40	10.70	10.90	11.20	11.10	11.12	6.00
U	1.94	1.43	1.97	1.60	2.27	1.21	1.75	0.63	0.91	1.52	2.04	1.57	-	3.10
Sc	5.40	7.80	3.40	4.20	3.90	9.90	5.50	1.40	1.80	11.00	2.40	5.15	14.07	6.67
Hf	0.11	0.12	0.14	0.15	0.13	0.10	0.14	0.06	0.11	0.08	0.11	0.11	-	-
V	28.00	36.00	22.00	39.0	25.00	46.00	29.00	23.00	17.00	93.00	25.00	34.82	130.0	150.0
Cr	20.90	21.30	14.30	21.3	14.40	18.50	17.20	13.10	14.20	26.00	13.60	17.71	85.54	55.0
Ni	20.60	26.40	11.30	13.10	20.70	24.50	27.80	4.40	12.00	12.20	4.70	16.15	58.00	55.0
Co	19.50	33.60	11.10	16.6	23.30	36.00	26.40	3.70	15.80	17.70	3.00	18.79	17.67	23.0
Cu	20.39	22.05	11.23	13.52	24.12	13.38	22.48	9.45	9.17	41.05	8.96	17.80	-	50.0
Zn	50.80	96.40	30.70	48.10	59.80	113.00	77.10	36.50	49.00	142.3	13.30	65.18	-	85.0
Mn	281.00	684.00	84.00	44.00	268.00	5002.00	224.00	46.00	189.00	500.00	20.00	667.50	-	-

Discussion

Classification of the Sediments

An attempt at the classification of the investigated shales was made in accordance to Herron (1988) by using the routine plot of log (Fe_2O_3/K_2O) against log (SiO_2/Al_2O_3) (Fig. 2). The Sand Class system plot of the studied shales, reference data from parts of Nigeria and other parts of the world such as Southern Bida Basin Shale (Okunlola and Idowu 2012), Auchi Shale (Akpokodje *et al*., 1991), Eze-Aku Shale (Amajor,

Table 4: Rare Earth Element concentrations (ppm) for Enugu Formation shales (this study) compared to the similar values derived from NASC and PAAS.

Sample	ENU 1A	ENU 1C	ENU 1D	ENU 1H	ENU 1P	ENU 1Q	ENU 1S	ENU 1U	ENU 1V	ENU 2B	ENU 2E	Mean	NASC	PAAS
La	30.2	19.8	32.3	24.7	29.9	14.00	23.3	16.7	26.9	16.9	35.3	24.55	31.10	38.20
Ce	75.7	54.5	81.4	67.4	85.3	39.5	67.1	40.4	66	43.7	91.5	64.77	67.03	345
Pr	8.48	6.24	8.74	7.13	9.19	4.60	6.9	4.43	7.24	5.1	9.75	7.07	9.10	-
Nd	38.7	31.53	38.92	31.64	42.93	23.86	31.83	19.34	32.55	24.21	44.99	32.77	30.4	128
Sm	8.15	6.63	7.39	6.69	8.28	5.7	6.26	3.63	6.91	5.2	8.18	6.64	5.98	16.2
Eu	1.72	1.55	1.67	1.55	1.82	1.49	1.46	0.68	1.3	1.24	1.82	1.48	1.25	1.31
Gd	6.22	5.61	5.59	4.98	6.8	6.74	4.46	3.04	5.22	4.39	5.91	5.36	5.50	6.12
Tb	0.69	0.69	0.6	0.61	0.69	0.76	0.51	0.3	0.61	0.57	0.71	0.61	0.85	-
Dy	3.94	3.93	3.27	3.29	3.65	5.29	2.79	1.59	3.44	3.74	3.41	3.49	5.54	3.05
Ho	0.53	0.58	0.39	0.45	0.54	0.85	0.38	0.17	0.49	0.54	0.44	0.48	1.27	-
Er	1.17	1.56	0.86	1.11	1.15	2.15	0.76	0.48	1.34	1.55	0.9	1.18	3.275	1.25
Tm	0.14	0.18	0.09	0.1	0.11	0.3	0.09	0.04	0.15	0.18	0.09	0.13	0.54	-
Yb	0.71	1.09	0.55	0.6	0.61	1.79	0.49	0.31	0.94	1.00	0.53	0.78	3.11	1.00
Lu	0.08	0.12	0.06	0.06	0.07	0.23	0.06	0.03	0.12	0.13	0.05	0.09	0.46	-
ΣREE	176.43	134.01	181.83	150.31	191.04	107.26	146.39	91.14	153.21	108.45	203.58	149.40	165.40	517.93
ΣLREE	161.23	118.70	168.75	137.56	175.60	87.66	135.39	84.50	139.60	95.11	189.72	135.80	143.61	505.20
ΣHREE	13.48	13.76	11.41	11.20	13.62	18.11	9.54	5.96	12.31	12.10	12.04	12.14	29.54	11.42
ΣLREE/ ΣHREE	11.96	8.63	14.79	12.28	12.89	4.84	14.19	14.18	11.34	7.86	15.76	11.70	4.86	44.24
Eu/Eu*	0.71	0.76	0.76	0.79	0.72	0.73	0.80	0.61	0.64	0.77	0.76	0.73	0.65	0.33

1987), Upper Benue (Gongila Formation) Shale (Adepoju and Ojo, 2013), Pettijohn (1975), Turekan and Wedephol (1961), NASC (Grometet *al.*, 1984) and PAAS (Taylor and McLennan, 1985) were plotted. Of the eleven Enugu Formation Shale samples (present study), nine plotted within the Shales and Fe-shales class while only one each fall within lith-arenite and Fe-sand class. It is interesting to note that all the shale samples investigated plotted within Shale and Fe-shale class (Fig. 2). This further indicates similarity in composition when compared with most shales in Nigeria.

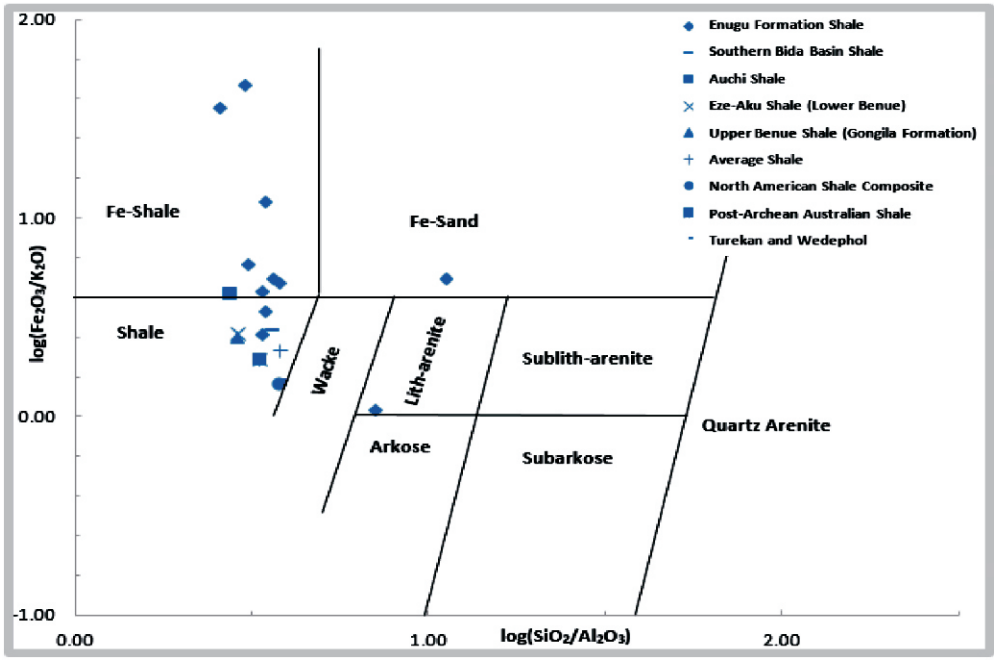


Fig. 2: SandClass scheme for the Enugu shales (after Herron, 1988). Note that most of the investigated samples and shales from various localities in Nigeria within Shale and Fe-Shale fields.

Provenance and Tectonic Settings

The geochemical signatures of sediments are routinely used for provenance reconstruction (Taylor and McLennan, 1985; Condie *et al.,* 1992; Cullers, 1995). Cox *et al.* (1995) demonstrated application of K_2O/Al_2O_3 ratios in determining the original composition of sediments. They proposed ratio ranging from 0.0-0.3 as indicator of shale minerals whereas values from 0.3-0.9 signify feldspars contents. The calculated mean ratio of K_2O/Al_2O_3 in the Enugu shales ranges from 0.07 to 0.14, thus indicating prevalence of shale minerals. Hayashi *et al.,* (1997) stated that ratio of Al_2O_3/TiO_2 in most clastic and terrigenous sediments are essentially used to infer the source rock compositions and values of ratio ranging from 3 to 8 suggests mafic igneous rocks source, 8 to 21 signifies intermediate igneous source rocks, while values from 21 to 70 points to the felsic igneous rocks. Al_2O_3/TiO_2 ratio in the Enugu shales ranges from 5.48 to 12.57 (mean is10.19) and this essentially fits into the intermediate igneous origin (Table 5).

Ferromagnesian trace elements (Cr, Ni, Co and V), according to Feng and Kerrich (1990) are characterized by high fractionation during weathering. In the studied shales, low mean values of Cr (17.71), Ni (16.15), Co (18.79) and V (34.82) were obtained which may suggest low contribution from basic igneous source region. These values are also low compared to the published NASC and PAAS values. This is in support of an insignificant mafic rock input from the source area. It has also been shown that ratios, such as La/Co, La/Sc, Th/Sc, Th/Co, Th/Cr and Cr/Th, in terrigenous sediments can be used as provenance indicators (Cullers, 1995). We obtained these average ratios [La/Co (2.55), La/Sc (7.27), Th/Sc (3.07), Th/Co (1.10), Th/Cr (0.65) and Cr/Th (1.67)] in the studied Enugu Formation shales and these probably imply felsic igneous origin (Table 6). These therefore lend support for felsic igneous provenance for the Enugu shales.

The REEs and high field strength elements (HFSE, including Y, Zr, Ti, Nb, Ta), Th, Sc, Hf, and Co) are considered to be relatively of low mobility during weathering, transport, diagenesis, and metamorphism. These attribute make them very suitable for provenance determination. In addition, the REE pattern is also useful for reconstructing sedimentary rocks provenance. Basic rocks contain low LREE/HREE ratios and low Eu anomalies, whereas more silicic rocks usually contain higher LREE/HREE ratios and negative Eu anomalies (Cullers and Graf, 1984; Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987). Low mean values of REE (149.50ppm), LREE (135.80ppm) and HREE (12.14ppm) with slightly high mean LREE/HREE (11.70) and negative mean Europium (Eu) anomalies (0.73) for the Enugu shales (Table 4) is in support of possible intermediate to felsic granitic protolith. A depleted LREE, HREE, total ΣREE and relative high Eu anomalies recorded in this study compared to NASC and PAAS confirms felsic provenance.

The chemical index of alteration (CIA) and chemical index of weathering (CIW) are often employed for the provenance studies as they indicate sediment recycling processes (Nesbitt *et al*., 1980). Calculated values of CIA (87 to 96) and that of CIW (96 to 99) are indicative of a more felsic source. In this study, CIA from 76.23 to 91.40 (mean 87.65) and CIW from 80.51 to 99.12 (mean 95.21) were obtained for the studied shales indicating a felsic origin.

For the tectonic settings, several classifications schemes based on relevant geochemical proxies have been proposed by many authors; plots of TiO_2 *vs.* Ni after Floyd *et al.,* (1989) and Th/Co *vs.* La/Sc after Cullers (2002). Application of these discriminant functions plots in this study (figs. 3 and 4) suggest the derivation of the Enugu shales from felsic source rocks. Also, the ternary plot of end-members of the La-Th-Sc (after Bhatia and Crook, 1986) and curve model mixing of Cr/V versus Y/Ni (after Floyd and Leveridge, 1987) are employed in this study to determine the sediment sources. The former plot (Fig. 5) show that Enugu shales fall within a field closer to the PAAS and NASC and this clearly rules out the influence of mafic igneous protolith while the later (Fig. 6) also shows little or no contribution from mafic-ultramafic igneous source.

Weathering Effect

The weathering history of the studied samples was evaluated using the elemental composition as suggested by Ekosse and Ngole (2012). Ratio of SiO_2/Al_2O_3 provides an indication of transportation history and sediment maturity. In the studied shales, mean value of 4.40 was obtained which suggest high amount of quartz and therefore implying long transportation history and sediment maturity. Low K_2O content (mean value of 1.22%) was recorded in the samples suggesting low amount of detrital feldspars and mineralogical maturity. Feldspars are typically unstable and tend to decrease with increasing weathering. Also, the relationship between Th/U ratio concentrations can also be applied

Table 5: Some ratios of Major Oxides, Trace and Rare earth element concentrations (geochemical proxies) for the investigated Enugu shales compared to similar values derived from NASC and PAAS.

Sample	ENU 1A	ENU 1C	ENU 1D	ENU 1H	ENU 1P	ENU 1Q	ENU 1S	ENU 1U	ENU 1V	ENU 2B	ENU 2E	Mean	NASC	PAAS
SiO_2/Al_2O_3	3.08	3.48	3.50	3.63	3.41	3.00	3.76	11.35	7.14	2.60	3.41	4.40	4.97	3.32
K_2O/Na_2O	4.39	4.00	2.96	3.46	3.91	5.17	4.72	5.05	5.48	22.25	10.71	6.55	3.51	3.09
K_2O/Al_2O_3	0.08	0.09	0.09	0.09	0.08	0.07	0.09	0.14	0.12	0.07	0.08	0.09	0.23	0.20
Al_2O_3/TiO_2	12.57	12.09	10.75	9.05	10.34	10.62	10.21	5.48	6.99	12.15	11.81	10.19	20.54	18.97
Ga/Rb	0.3	0.37	0.44	0.48	0.39	0.43	0.45	0.65	0.63	0.44	0.22	0.44	-	-
Rb/Sr	0.63	0.59	1.49	1.05	1.36	0.16	1.85	0.65	0.74	0.49	2.05	1.01	-	0.80
Sr/Ba	0.83	0.16	0.19	0.19	0.31	1.06	0.22	0.02	0.31	0.46	0.09	0.35	0.22	0.31
Sr/Cu	0.87	0.77	0.51	0.61	0.23	2.35	0.18	0.70	0.63	0.38	0.96	0.74	-	4.0
La/Sc	5.59	2.54	9.50	5.88	7.67	1.41	4.24	11.93	14.94	1.54	14.71	7.27	2.21	5.55
Th/Sc	2.46	1.49	3.74	2.64	3.67	0.71	2.16	5.29	5.94	0.99	4.67	3.07	0.79	0.90
Th/U	6.86	8.11	6.45	6.94	6.30	5.79	6.80	11.75	11.76	7.17	5.49	7.58	-	1.94
La/Th	2.27	1.71	2.54	2.23	2.09	2.00	1.96	2.26	2.51	1.55	3.15	2.21	2.80	6.19
Cr/Ni	1.01	0.81	1.27	1.63	0.70	0.76	0.62	2.98	1.18	2.13	2.89	1.45	1.47	1.00
Cr/Th	1.57	1.84	1.13	1.92	1.01	2.65	1.45	1.77	1.33	2.39	1.21	1.67	7.69	9.17
Th/Co	0.68	0.35	1.14	0.67	0.61	0.19	0.45	2.00	0.68	0.62	3.73	1.10	0.63	0.26
Th/Cr	0.64	0.54	0.89	0.52	0.99	0.38	0.69	0.56	0.75	0.42	0.82	0.65	0.13	0.11
U/Th	0.15	0.12	0.16	0.14	0.16	0.17	0.15	0.09	0.09	0.14	0.18	0.14	-	0.52
V/Cr	1.34	1.69	1.54	1.83	1.74	2.49	1.69	1.76	1.20	3.58	1.84	1.88	1.52	2.73
V/Ni	1.36	1.36	1.95	2.98	1.21	1.88	1.04	5.23	1.42	7.62	5.32	2.85	2.24	2.73
Ni/Co	1.06	0.79	1.02	0.79	0.89	0.68	1.05	1.19	0.76	0.69	1.57	0.95	3.28	2.39
La/Co	1.55	0.59	2.91	1.49	1.28	0.39	0.88	4.51	1.70	0.95	11.77	2.55	1.76	1.61
Cu/Zn	0.40	0.23	0.37	0.28	0.40	0.19	0.29	0.26	0.19	0.29	0.67	0.32	-	0.59
U-(Th/3)	-2.49	-2.44	-2.26	-2.10	-2.50	-1.12	-2.22	-1.84	-2.66	-2.11	-1.69	-23.43	-2.13	-
CIA	88.94	85.70	89.37	88.14	90.49	76.23	89.98	85.08	87.27	91.40	91.53	87.65	-	-
CIW	95.67	92.67	96.75	95.95	97.68	80.51	97.64	96.85	97.20	97.26	99.12	95.21	-	-

Table 6: Ratios and logarithm values of some major oxide element concentrations of the investigated Enugu Formation shales compared to some standard shale values.

Sample	ENU 1A	ENU 1C	ENU 1D	ENU 1H	ENU 1P	ENU 1Q	ENU 1S	ENU 1U	ENU 1V	ENU 2B	ENU 2E	1	2	3	4	5	6	7	8
Fe_2O_3/K_2O	5.82	12.03	3.37	4.87	4.23	46.82	4.73	4.88	1.08	35.27	2.57	2.70	4.03	2.64	2.52	2.16	1.44	1.95	1.52
Sio_2/Al_2O_3	3.08	3.48	3.50	3.63	3.40	3.00	3.76	11.35	7.14	2.60	3.41	3.63	2.75	2.86	2.89	3.77	3.80	3.32	3.90
log Fe_2O_3/K_2O	0.76	1.08	0.53	0.69	0.63	1.67	0.67	0.69	0.03	1.55	0.41	0.43	0.61	0.42	0.4	0.33	0.16	0.29	0.18
log Sio_2/Al_2O_3	0.49	0.54	0.54	0.56	0.53	0.48	0.58	1.05	0.85	0.41	0.53	0.56	0.44	0.46	0.46	0.58	0.58	0.52	0.59

*** See Table 2 above for 1-8.**

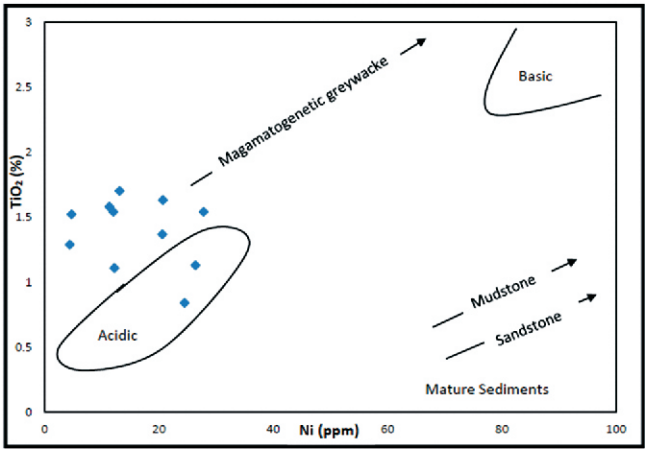


Fig. 3: TiO_2 versus Ni provenance discrimination plot for the Enugu shales (after Floyd *et al.*, 1989). Note the shale samples plot near and within acidic source field provenance.

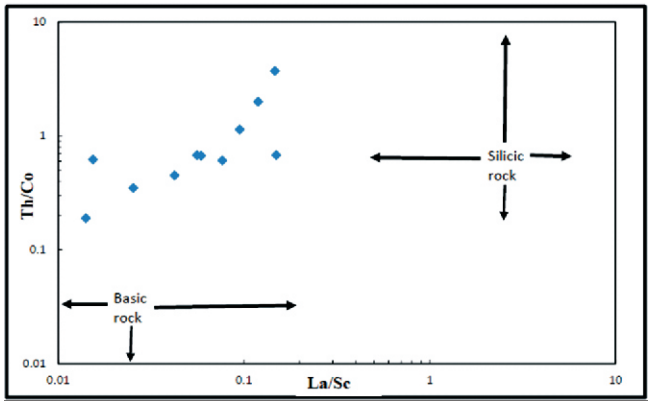


Fig. 4: Th/Co versus La/Sc provenance discrimination plot for the Enugu shales (after Cullers, 2002). Note the shale samples plot near silicic rock source field provenance.

as an estimate of the degree of weathering in sedimentary rocks. According to McLennan and Taylor (1993), sedimentary rocks with Th/U values higher than 4.0 indicate intense weathering in the source areas or sediment recycling, while values below 3.5

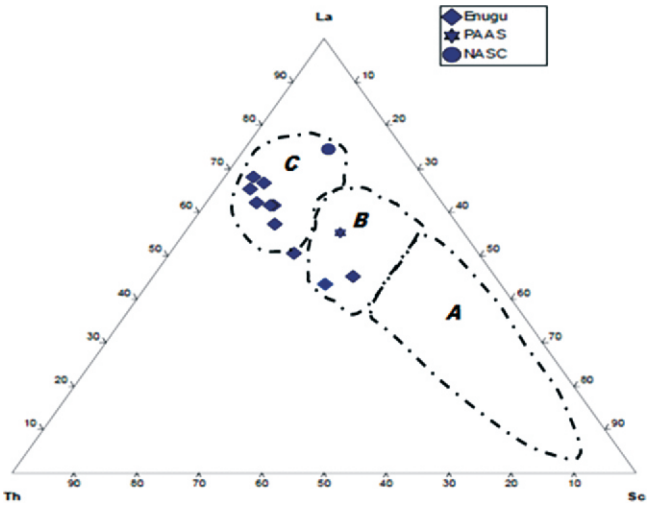


Fig. 5: La-Th-Sc provenance discrimination plot for the Enugu shales (after Bhatia and Crook, 1986). The fields are: A, Oceanic island-arc; B, continental island-arc; C, active continental margin; D, passive margin. Note that samples show a strong trend to continental island-arc, active continental margin and passive margin source rock.

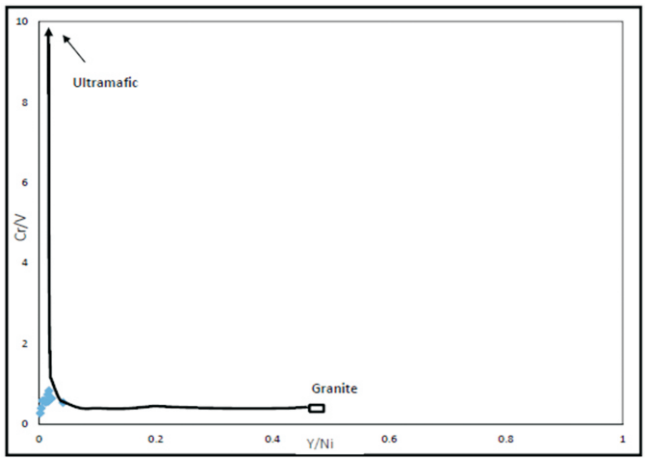


Fig. 6: Binary plot of Cr/V versus Y/Ni for provenance discrimination for the Enugu Shale (Floyd and Leveridge, 1987).

accompanied by low Th and U contents is interpreted as indication of low weathering in the source areas. In this investigated samples, the mean values of Th/U (7.58), Th (11.1), and U (1.57) obtained are in the range indicative of intense weathering in the source area.

Nesbitt and Young (1982) proposed Chemical Index of Alteration (CIA) as an indicator of progressive alteration of primary feldspars to clay minerals. They suggested high values between 76 and 100 as an indication for intensive chemical weathering in the source area and low values of less than 50 as an indication for unweathered areas. The CIA values for the Enugu shales (Table 4) range from76.23 to 91.40 (mean-87.65) indicating high chemical weathering. Also, Chemical Index of Weathering (CIW) values which was proposed by Depetris and Probst (1998) when less than 50, is an indication of chemically unweathered source rock, while values ranges between 51 and 75 and greater than 75 indicate moderate and strong weathering respectively. The calculated CIW obtained for the Enugu shales ranges from 80.51 to 99.12 (mean-95.21) which are higher than those of NASC (21.67) and PAAS (21.11) and thus indicates that the studied shales had experienced strong chemical weathering at the source area and long transportation.

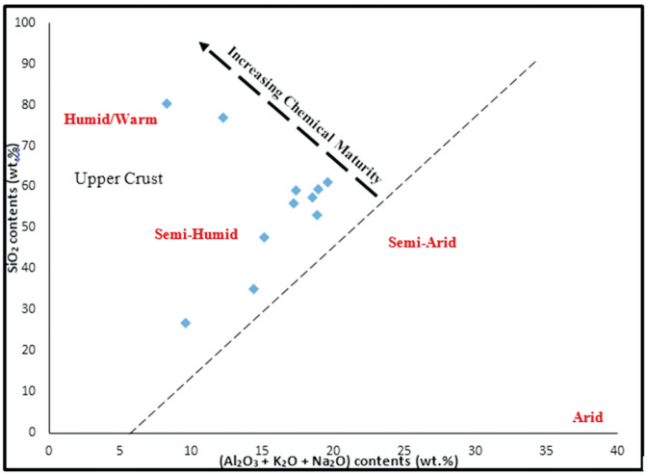


Fig. 7: SiO2 versus (Al_2O_3+K_2O+Na_2O) plot showing the paleoweathering and maturity trend for the Enugu shale (after Suttner and Dutta, 1986).

The bivariant plot of SiO_2 against total (Al_2O_3+K_2O+Na_2O) proposed by Suttner and Dutta (1986) is employed in this study for determination of the sediments maturity and climate. The plot reveals the prevalence of semi-humid to humid weathering conditions for the Enugu shales (Fig. 7). The ternary plot of Al_2O_3-(CaO+Na_2O)-K_2O (A-CN-K) also shows an advanced weathering from the source for the investigated shale samples as they plot mostly within the kaolinite-illite region. A similar trend is shown by the fact that the samples did fall close to the plagioclase-k-feldspar (Fig. 8).

Paleo-Redox, Paleo-Water Salinity and Paleoclimate Conditions

The Paleo-redox condition during sedimentation of the Enugu Formation shale was also evaluated using the trace elements data (see Table 3). Many studies interested in paleoenvironment analysis have used certain geochemical proxies as tools. Tribovillard *et al.,* (2006) pointed out that manganese (Mn) forms highly insoluble hydroxides or oxides in form of Mn^{3+} or Mn^{4+} under oxidizing conditions, while form soluble cations like Mn^{2+} or $MnCl^{+}$ in the reducing conditions. Algeo and Maynard (2004) also concluded that the dissolved

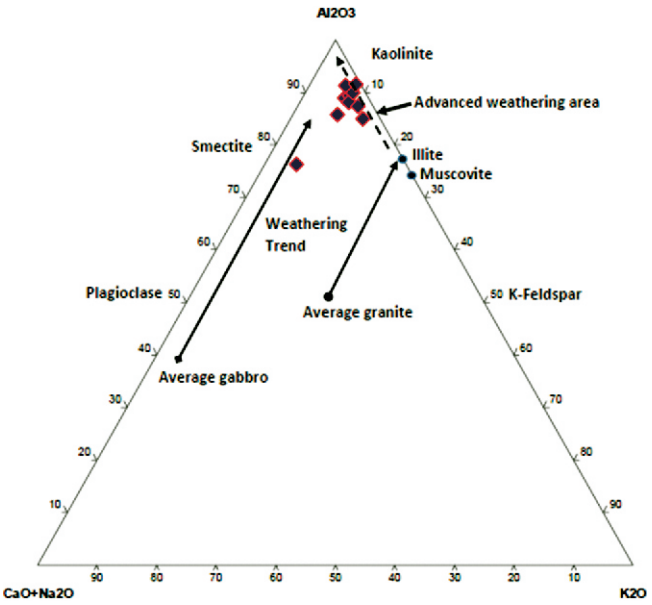


Fig. 8: A-CN-K [Al2O3-(CaO+Na2O)-K2O] diagram (after Nesbitt and Young, 1982) to demonstrate a possible weathering trendstatus and source rock for the Enugu shale.

cations like Mn^{2+} or $MnCl^{+}$ forms within bottom sediments and diffuse into the overlying anoxic water column, so that manganese concentrations in the seawater are depleted. Quinby-Hunt and Wilde (1994) proposed that low manganese contents with an average of 75 ppm are regarded as an indicator of highly reducing conditions. Therefore, low to high manganese concentrations the Enugu shales (see Table 3) serves as an evidence in support of deposition under suboxic to oxic conditions.

The Vanadium (V) and Nickel (Ni) contents which are also considered an important indicator for the redox conditions during deposition were examined in this investigation. Usually V is enriched in comparison with Ni in anoxic marine environments because V is enriched in organic rich shales that are deposited under reducing conditions (Ernst, 1970; Barwise, 1990; Peters and Moldowan, 1993; Galarraga *et al.,* 2008). Ernst (1970) and Barwise (1990) opined that values of V/Ni ratio greater than 3 indicate sediments deposition in a reducing environment, while V/Ni ratios ranging from 1.0 to 3 indicate suboxic-oxic conditions. V/Cr ratio is also applicable as a proxy for paleo-redox conditions. According to Dill *et al.,* (1988), values of V/Cr greater than 2.0 are interpreted as indicative of anoxic conditions, whereas values less than 2.0 point to more oxicity. The studied shales have mean value of the V/Ni and V/Cr ratios (2.85 and 1.84 respectively) indicating deposition under relatively oxidizing conditions. Trace elements such as V, Ni and Cr in sediments are sensitive indicators for paleo-redox conditions (Algeo and Maynard, 2004; Tribovillard *et al.,* 2006; Fu *et al.,* 2011). On the other hand, trace elements such as Ba, Sr, Cu, Rb and Ga may suggest more effect of seawater than freshwater (Reimann and de-Caritat, 1998) and humid paleoclimate conditions (Lerman, 1989; Wang *et al.,* 1997; Roy and Roser, 2013).

The ratio of uranium to thorium (U/Th) was also employed as a redox indicator according to Wedephol (1978) and Jones and Manning (1994). Nath*et al*., (1997), proposed U/Th ratio less than 1.25, as indicative of oxidizing conditions of deposition, whereas the values above 1.25 indicate anoxic conditions. In this study, Enugu shales show low U/Th ratio (0.14) which indicates that the shales were deposited in oxidizing environment. Also, the authigenic uranium content (total U-Th/3) is considered as an index of bottom water condition in ancient sedimentary sequences (Wignall and Myers, 1988). The authors proposed values less than 5 as representative of oxic depositional conditions, while values above 5 as indicative of suboxic and anoxic conditions. The calculated mean of authigenic uranium contents is low (-2.13ppm) in the samples analyzed, thus supporting that Enugu shales were deposited in an oxidizing environment. This position is further affirmed by the low mean value of Cu/Zn (0.32) ratio obtained for the shale samples. Hallberg (1976) used the Cu/Zn ratio as a redox parameter and posited that high Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidizing conditions.

Strontium (Sr) and Barium (Ba) are two elements regarded as empirical paleo-salinity indicators; a high Sr/Ba ratio reflects high salinity, and vice versa (Wang, 1996). Also, Chunrui *et al*. (2007) employed Sr/Ba ratio for the paleo-environmental discrimination, with 1.0 ppm been the boundary between the fresh water and salt water marine environment. The analyzed Enugu Formation shales ranges from 0.02 to 1.06ppm (mean-0.35ppm), indicating low saline water during deposition.

The ratio of trace elements like strontium (Sr) / copper (Cu) is an important indicator of paleoclimate conditions (Lerman, 1989; Wang *et al.*, 1997), because Sr and Cu concentrations are influenced by basin morphology and the water depth (Jia *et al.*, 2013). Lerman (1989) and Wang *et al.* (1997) suggested that Sr/Cu ratio ranging between 1.3 and 5.0 indicates a warm-humid climate, whereas ratio above 5.0 points to a hot-arid climate. Relatively low Sr/Cu values (0.18–2.35, see Table 5) were obtained from the

investigated shales indicating a warm-humid climate conditions during deposition. The warm to humid paleoclimatic conditions is also inferred from the Ga/Rb versus (K_2O/Al_2O_3) (Fig. 9) after Roy and Roser (2013). This is consistent with the discrimination plot in figure 7 which also indicates semi-arid/warm to humid warm climatic conditions.

Conclusions

The majority of the Enugu shale samples are classified as Shales and Fe-shales SandClass system. This makes them similar to reference Shale samples in Nigeria and other parts of the world.

High concentration of SiO_2, Al_2O_3, $Fe_2O_3$with low contents of K_2O, Zr, Th, U, V, Cr and La were recorded in the samples indicating intensive weathering and sediments maturity. The silica-alumina (SiO_2/Al_2O_3), CIA, CIW, Th/U ratios are also high. This combined with indications from the A-CN-K diagram are in support of the deduction that the samples have been highly weathered and had long transportation history. Relatively high values of the Chemical Index of Alteration (CIA) and depletion of mobile elements observed in the study suggest intensive chemical weathering in the source area, which is most probable and enhanced under humid warm climate.

The REE concentration and other geochemical parameters such as; HREE/LREE, negative Eu anomalies, La/Sc, La/Co,Th/Co, Th/Cr, Cr/Th, and Th/Sc ratios indicate substantial contribution from felsic igneous rocks. Various discriminant function applied in the study offer credence to this thought.

Values of geochemical proxies such V/Ni, V/Cr, U/Th, Ni/Co, Sr/Ba, Cu/Zn and Sr/Ba ratios obtained in this study suggest that the shales were deposited in an oxic environment.

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