

Geochemistry of lignite associated shales in Ogwashi-Asaba Formation: Implication for paleoredox, source-area weathering, provenance and tectonic settings

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Abstract

Shale samples obtained from the Obomkpa lignite belt were analysed for geochemical attributes such as major, trace and rare earth elements using XRF, ICP-MS and ICP-OES techniques. Paleoweathering and paleoredox conditions, provenance and tectonic settings were evaluated. High CIA (97.79 – 99.00), CIW (99.92 – 99.93), and MIA (95.58 – 98.00) values indicated intense weathering in the source areas and high detrital input dominated by strong chemical weathering, which led to the formation of clay minerals by hydration and leaching of ions such as Ca²⁺, K⁺ and Na⁺ known to be present in the feldspar minerals. Cross plot of CIA vs SiO₂ shows that the mineral matter composing the shale samples have been substantially recycled in the course of weathering. Ratios of redox-sensitive trace elements (V/Cr = 0.92 av., Ni/Co = 2.8 av., and Th/U = 4.14 av.) suggests an oxic paleodepositional environment for the sediments. The strongly positive Ce anomaly (Ce/Ce*) (0.83 – 0.96) also affirms an oxic setting. Trace element ratios (La/Sc, Th/Sc, Th/Co, Th/Cr, and Cr/Th and Eu/Eu*) applied for provenance discrimination and with a range of values: 1.31 – 2.89, 0.86 – 1.04, 0.35 – 1.74, 0.11 – 0.14, 7.23 – 9.52, and 0.52 – 1.38 respectively, for the samples, compared to those of sediments derived from mafic and felsic sources. A felsic provenance was inferred for the shales after due comparison. A plot of Zr/Sc vs. SiO₂ suggested substantial reworking of the sediments. Inferences made by integrating various discrimination plots of major element concentrations (SiO₂/Al₂O₃, TiO₂, Na₂O+CaO, Al₂O₃ (Na₂O+CaO) vs. Fe₂O₃+MgO), classified the shales as Active Continental Margin (ACM) sediments.

Keywords: Lignite geochemistry, provenance, alteration, paleoredox, paleoweathering

1. Introduction

The Obomkpa area (Fig. 1) is well known geologically for exposures of the sediments of the Ogwashi-Asaba Formation. The Formation, Oligocene-miocene in age, has been studied by various authors (Reyment, 1965; Short and Stauble, 1967; Okezie and Onuogu, 1971, 1985; Dessauvage, 1974; Nwajide, 2013). The lignites of the Ogwashi-Asaba Formation were discovered by the Mineral Survey of Nigeria (1908; 1909) and are underlain and capped by shales. Within the formation, the lignites are confined to a narrow belt of about 10 miles wide and 150 miles long trending northwest-southeast from the Niger in the west to the Nigerian-Cameroun frontier, east of Calabar (Whiteman, 1982). The shales

associated with the lignites have not been exploited and are thus, the centre of focus of this study.

Generally, shales are the most abundant form of clastic sediments in sedimentary basins globally (Pettijohn, 1975). Mineralogical and chemical compositions of terrigenous sedimentary rocks are the products of several variables such as provenance, weathering conditions, sorting during transport, sedimentation and post-depositional diagenesis, climate and tectonics (McLennan, 1989; Johnson and Basu, 1993; Nesbitt and Young, 1996; Nesbitt et al. 1996). In geochemical studies, the major elements and some selected trace elements like Th, Sc, Co, Cr, Zr, Hf, Y, Ni, Co, V with rare earth elements (REEs) and

their elemental ratios are used as sensitive indicators of the provenance, paleoredox conditions, tectonic setting, paleoweathering conditions of the clastic sedimentary rocks (Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsch, 1986, 1988; McLennan and Taylor, 1991; Johnson and Basu, 1993; McLennan et al., 1993; Condie, 1993; Nesbitt et al., 1996; Fedo et al., 1997)

The major element discrimination diagrams of Bhatia (1983) has commonly been used to classify the tectonic settings of sedimentary basins as applied in this work (e.g., Armstrong-Altrin et al., 2004), although attention is drawn to their subjective usage (Armstrong-Altrin and Verma, 2005), as the diagrams are produced using the concentration of highly mobile elements including SiO₂, Na₂O, CaO and K₂O. These oxides show low enrichment or depletion of quartz, mica and plagioclase feldspars in intensely weathered sediments. As opposed to the major oxides, rare earth elements (e.g., La, Ce, Nd, Gd, Yb, Y), are most suitable for the discernment of provenance and tectonic setting since they have comparatively low mobility during sedimentary processes and their short residence times in seawater (Taylor and McLennan, 1985; Bhatia & Crook, 1986; Wronkiewicz & Condie, 1987, 1989 and 1990). Also, trace elements, because they are quantitatively transferred into sediments during sedimentary processes, reflect the signatures of the parent materials and are thus, also suitable for discerning the source rock compositions and tectonic environments of sediments (Bhatia and Crook, 1986; McLennan, 1989; Condie, 1993). Elemental ratios

including La/Sc, La/Co, Th/Sc and Zr/Cr have been established to be good discriminators between mafic and felsic source rocks (Tijani et al., 2010). Trace elements such as La, Th and Zr are said to be more concentrated in felsic igneous rocks while Co, Sc and Cr have higher concentrations in mafic rocks (Ronov et al., 1974; Wronkiewicz and Condie, 1987, 1990).

The paleoredox condition of sediments is delineated using the ratios of redox-sensitive trace elements which include V/Cr, Ni/Co and Th/U ratios (Jones and Manning, 1994). These ratios reflect depositional environments of sediments as anoxic, oxic or dysoxic. The amount of weathering undergone by sediments is studied using weathering indices like Chemical Index of Weathering (CIW), Chemical Index of Alteration (CIA), and Mineralogical Index of Alteration (MIA) (Harnois, 1988; Nesbitt and Young, 1992; Voicu et al., 1997).

Although considerable work has been carried out on the Lignite-bearing Ogwashi-Asaba Formation, especially as it relates to hydrocarbon exploration stratigraphy of the oil-rich Niger Delta Basin, very little has been achieved in understanding the paleoredox, paleoweathering, provenance and source-area weathering of the. In this work an attempt is made to establish the paleoredox, paleoweathering, provenance and source-area weathering of the lignite bounding shales in the Ogwashi Asaba Formation through inorganic signatures derived from the sediments, in order to improve and add to the geological information concerning the formation.

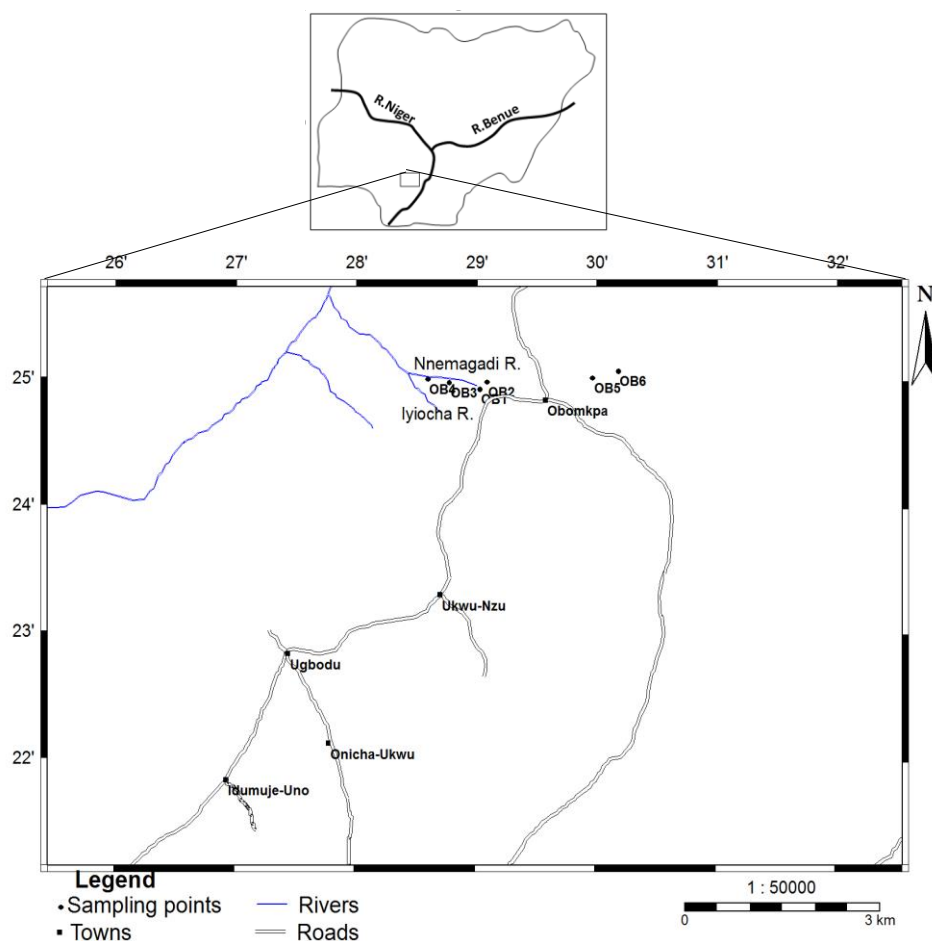


Fig 1. Location map of study area showing sample collection points in and around Obomkpa

1.1 Geology and field relation

The proximal (northern) Niger Delta is characterized by three formational units, two of which (Imo Shale and Ameki Formations) of Neogene age, hence older than the objective formation in this study (Ogwashi-Asaba Formation) (Fig. 2). In general, the lithostratigraphic units of the Niger Delta Basin has been classified into two: (i) the outcropping units found mainly in the northern depositional belt (Doust and Omatsola, 1990) and (ii) subsurface units, (Reyment, 1965; Frankl and Condry, 1967; Short and Stauble, 1967; Adegoke, 1969; Whiteman, 1982; Nwajide, 2013) which occur in the central to distal delta. The outcropping units are surface lateral equivalents of the subsurface units (Fig. 2).

Stratigraphically, the Ogwashi-Asaba Formation straddles the Paleogene-

Neogene with an age range of Oligocene-Miocene (Reyment, 1965; Short and Stauble, 1967 and Dessauvagie, 1974) (Fig. 2). Outcrops of the formation consists of interbeds of white, blue and pink clays, cross-bedded sands, carbonaceous mudstones, shales and seams of lignite (Okezie and Onuogu, 1971; Nwajide, 2013). From studies of pollen data, Okezie and Onuogu (1971, 1985) assigned the lignites to tropical and semi-tropical plants consisting mainly of palms. An upper floodplain environment of deposition was inferred for the formation from the plot of Short and Stauble (1967). The samples obtained for this study are from dark shales overlying lignite seams in and around Obomkpa town (Fig. 3), a community renowned for excellent exposures of the lignite facies of the Ogwashi-Asaba Formation.

SUBSURFACE		SURFACE OUTCROPS			BASIN
Niger Delta Basin Stratigraphy	Oldest known Age	Youngest known Age	Southern Benue Trough	Oldest known Age	
Recent Benin Formation	Oligocene	Recent	Benin Formation	Miocene	Niger Delta
Recent Agbada Formation		Miocene	Ogwashi-Asaba Formation	Oligocene	
		Eocene	Ameki Formation	Eocene	
Recent Akata Formation	Eocene	Eocene	Imo Shale Formation	Paleocene	Anambra
		Eocene	Nsukka Formation	Maastrichtian	
	Cretaceous	Campanian	Ajali Formation	Campanian	Abakaliki
		Campanian/Maastrichtian	Mamu Formation	Santonian	
		Coniacian/Santonian	Nkporo Shale	Turonian	
Unknown		Turonian	Awgu Shale	Turonian	
		Albian	Eze-Aku Shale	Albian	
			Asu River Group	Albian	

Fig. 2. Geological formations of the Niger Delta Area, Nigeria (Modified from Short and Stauble, 1967)

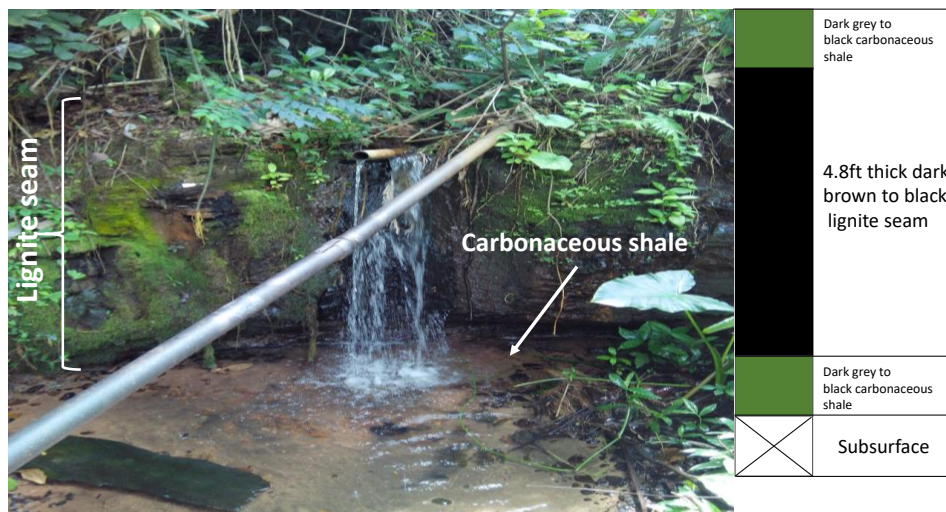


Fig. 3. Outcrop of the Ogwashi-Asaba Formation exposed in the forested woodlands around Obomkpa community, showing lignite seam bedded in dark shale.

On the right of the figure is a lithologic log of the exposure. Groundwater is seen flowing out of the rocks as springs which forms the headwaters of many streams in the area.

2. Data and methodology

The six shale samples studied were collected from shale beds overlying lignite in the study area (Fig. 3). 25 g of each sample was weighed, using a Mettler

Teledo, PL602-S balance. The weighed samples were prepared and chemically analysed for major, trace and rare earth elements (REEs) at Acme Analytical Laboratories, Vancouver BC, Canada. During preparation, the samples were dried at 60°C and pulverized to 85% passing 200 mesh (75 microns), using a mild-steel pulveriser (PUL85). After preparation, each sample (10g) was digested to complete dryness with an acid solution of

(2:2:1:1) H₂O-HF-HClO₄-HNO₃. 50% HCl was added to the residue and heated using a mixing hot block. After cooling, the solutions were transferred to test-tubes and brought to volume using dilute HCl. Sample splits of 0.25g were analysed for the concentrations of trace and rare earth elements (REEs) using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). Both analyses (ICP-OES and ICP-MS) were performed with the NexION® 300 ICP-MS instrument. Quality Assurance (QA) and Quality control (QC) were applied in the analysis of the samples using Nickel Sulphide Ore (OREAS 72b) and Geochemical Multi-acid Digestion (OREAS 45E) reference materials as standards to ensure accuracy of results.

A programmed quantity of each sample was roasted to determine the Loss on Ignition (LOI) before the XRF analysis.

The roasted sample was then fused in a platinum-gold crucible with a commercial lithium tetraborate (LiBO₄) flux. The molten material was cast in a platinum mold and the fused discs were analysed by XRF for major elements using an X-Ray Fluorescence Spectrometer. Diorite Gneiss (SY-4) reference material was used as a standard for QA and QC of analytical results.

3. Results and discussion

3.1 Major elements geochemistry

Quantitative elemental oxide values present in each analysed sample is shown in Table 1. Initial litho-geochemical classification based on major elements geochemical composition (using the plot of Fe₂O₃/K₂O vs. SiO₂/Al₂O₃), classed the samples on the Terrigenous sandstone and shale diagram of Herron (1988) as Fe-rich shales (Fig. 4).

Table 1: Major element concentrations of the samples in contrast to Post Achaean Australian Shale (PAAS) and Upper Continental Crust (UCC) (Taylor and McLennan, 1985).

Element	Detection Limit (Wt. %)	SAMPLES								UCC	PAAS
		OB1	OB2	OB3	OB4	OB5	OB6	Average			
SiO ₂	0.01	49.04	46.78	51.20	47.56	45.90	52.45	48.82	66.00	62.80	
Al ₂ O ₃	0.01	29.82	25.76	25.33	26.32	29.25	25.82	27.05	15.20	18.90	
Fe ₂ O ₃	0.01	2.76	4.09	2.45	3.25	4.20	2.85	3.27	5.00	7.23	
CaO	0.01	0.26	0.09	0.08	0.06	0.15	0.18	0.14	4.20	1.30	
MgO	0.01	0.23	0.17	0.15	0.19	0.25	0.17	0.19	2.20	2.20	
Na ₂ O	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	3.90	1.20	
K ₂ O	0.01	0.28	0.36	0.55	0.32	0.45	0.53	0.42	3.40	3.70	
MnO	0.01	0.01	<0.01	0.02	0.04	0.02	0.03	0.02	0.08	0.11	
TiO ₂	0.01	1.48	1.87	2.99	3.20	1.95	1.63	2.19	0.50	1.00	
P ₂ O ₅	0.01	0.06	0.09	0.07	0.05	0.07	0.10	0.07	ND	0.16	
Cr ₂ O ₃	0.01	0.02	0.02	0.02	0.02	0.03	0.02	0.02	ND	ND	
LOI	-	15.47	20.11	16.79	18.22	17.54	16.16	17.38	ND	ND	
SUM	-	99.43	99.35	99.64	99.24	99.82	99.95	99.57	100.48	98.60	
Al ₂ O ₃ /TiO ₂	-	20.15	13.78	8.47	8.23	15	15.84	13.58	30.40	18.90	
CIA	-	99.00	98.54	97.79	98.72	98.42	97.91	98.40	57.58	75.60	
CIW	-	99.93	99.92	99.92	99.92	99.93	99.92	99.92	66.09	88.73	
MIA	-	98.00	97.08	95.58	97.44	96.84	95.82	96.79	15.16	51.20	
Na ₂ O/K ₂ O	-	0.04	0.03	0.02	0.03	0.02	0.02	0.03	1.14	0.32	

CIA: Chemical Index of Alteration (Nesbitt and Young, 1982); CIW: Chemical index of Weathering (Harnois, 1988); MIA: Mineralogical Index of Weathering (Voicu et al. 1997).

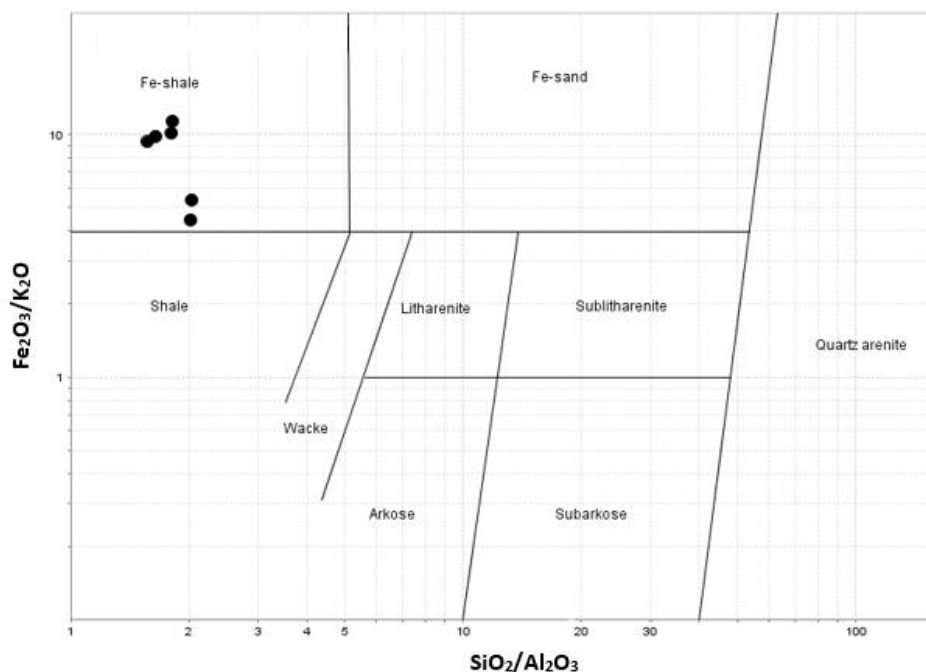


Fig. 4. Classification of Terrigenous Sandstones and Shales (after Herron, 1988).

The dominant major elements in the samples are SiO_2 , Al_2O_3 , and Fe_2O_3 (although SiO_2 is relatively enriched compared to Al_2O_3 and Fe_2O_3) (Table 3). Samples of shale from the Ogwashi-Asaba Formation at Obomkpa show a high SiO_2 wt. % (mean = 48.82 wt. %), close to the average values of the Post Achaean Australian Shale (PAAS) (62.8 wt. %) and sediments of the Upper Continental Crust (UCC) (66.0 wt. %) (Taylor & McLennan, 1985), suggesting a high detrital input characterised by intense weathering and dissolution of other minerals during transportation and subsequent formation of the shales. The samples also show a lower concentration of aluminium than silica, like PAAS and UCC, as indicated by the relatively lower Al_2O_3 wt. % (27.05 wt. % average).

Other major elements (Na_2O , K_2O , MnO , MgO , P_2O_5 , Cr_2O_3 , and CaO) are heavily depleted in the samples with very low average concentrations in comparison to PAAS and UCC except TiO_2 (av. = 2.19 wt. %). Na_2O resides in the Na-plagioclase while TiO_2 is associated with the mafic minerals. The depletion of Na_2O in all the samples (0.01 wt. %) can be attributed to the relatively lower enrichment of Na-

plagioclase in them. Thus, the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio (28 - 55) is a good indication of the dominance of K-plagioclase, illite and mica. Since Al_2O_3 is dominant in felsic rocks and TiO_2 in mafic rocks, (Mishra and Sen, 2012), the high $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of the shale samples (Table 1) suggests felsic source rocks, supported by the relatively very low amounts of MgO (0.15 - 0.23 wt. %), known to be high in mafic and ultramafic rocks. In addition, the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios of the rocks can be used as a pointer of the initial composition of primordial deposits (Nagarajan et al. 2007). The $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios range for clay minerals and feldspars are 0.0 to 0.3 and 0.3 to 0.9 respectively (Cox et al. 1995). The ratios for the study samples range approximately from 0.009 to 0.02, indicating that the samples are rich in clay minerals.

3.2 Trace elements

Table 2 presents the PAAS-normalized (Taylor and McLennan, 1985) trace element values obtained for the samples and plotted in a multi-element diagram (Fig. 5). The PAAS-normalized configurations of trace elements of the shales show a heavy depletion of Ba, Rb,

Sr, Y, Cu and V, a moderate diminution of La, Sc, U, and Th and an enrichment of Nb, Ga, Cr, Co, Zr, Hf, Ni and Pb relative to PAAS. The average concentrations of Zr, Ni, Co, Pb, Nb, and Cr (Table 2) are 284.70ppm, 64.67ppm, 29.13ppm, 31.64ppm, 65.46ppm, and 123.67ppm respectively, and are higher compared to the values of PAAS (210ppm, 55ppm, 23ppm, 20ppm, 19ppm and 110ppm respectively). Other elements show depletion in their concentration relative to PAAS. The very low content of Ba

concentration indicates an absence of barite crystals of syn-sedimentary origin in the shales. The high Zr content may signpost recycled or fractionated sediments (Basu et al., 1982; McLennan et al., 1993) as indicated by enrichment in zircon.

None of the trace elements has a positive correlation with Al_2O_3 as the correlation co-efficient, r , between the elements and Al_2O_3 is equal to zero. This suggests that none of the trace elements is associated with the clay minerals in all the shales.

Table 2. PAAS-normalized trace elements concentration of the shale and coal samples (PASS; Taylor and McLennan, 1985)

Element	Detection Limit (ppm)	OB1	OB2	OB3	OB4	OB5	OB6	Average Obomkpa Shale	PAAS
La	0.1	15.4	42.9	39	35.21	37.54	39.51	34.93	38
Y	0.1	5.1	20.1	14.6	15.33	18.24	20.5	15.65	27
Zr	0.2	223.3	284.5	358.7	288.83	256.27	296.62	284.7	210
Ba	1	0.02	0.03	0.04	0.05	0.03	0.02	0.03	650
Hf	0.02	6.12	6.9	9.43	7.11	8.35	5.85	7.29	5
Sc	0.1	11.8	16.4	13.5	12	16.67	14.32	14.12	16
Cr	1	92	141	150	95	125	139	123.67	110
Sr	1	51	74	74	70	68	72	68.17	200
V	1	87	123	125	120	96	119	111.67	150
Ni	0.1	36.8	82.7	71	76	84	71	64.67	55
Co	0.2	5.8	43.6	26.8	32.4	37.2	28.9	29.12	23
Zn	0.2	47.5	36	97.8	55.2	71.7	85.6	65.63	85
Cu	0.02	39.21	20.64	35.33	32.63	28.22	37.24	32.21	50
Ga	0.02	38.5	33.62	35.95	39.61	32.81	37.44	36.32	20
Rb	0.1	9	16.6	56	32.54	23.14	45.11	30.4	160
Nb	0.04	56.33	57.15	76.27	62.34	73.41	67.28	65.46	19
Pb	0.02	27.05	34.56	33.17	30.22	35.24	29.61	31.64	20
Th	0.1	10.1	15.3	16.6	12.4	17.3	14.6	14.38	14.6
U	0.1	3.5	3.3	3.8	3.2	3.9	3.1	3.47	3.1
Th/U	-	2.89	4.64	4.37	3.88	4.44	4.71	4.14	4.71
V/Cr	-	0.95	0.87	0.83	1.26	0.77	0.86	0.92	1.36
Ni/Co	-	6.34	1.9	2.65	2.35	2.26	1.3	2.8	2.39
Zr/Sc	-	18.92	17.35	26.57	21.39	15.37	20.71	20.05	13.13
La/Sc	-	1.31	2.62	2.89	2.93	2.25	2.76	2.46	2.38
Th/Sc	-	0.86	0.93	1.23	1.03	1.04	1.02	1.02	0.91
Th/Co	-	1.74	0.35	0.62	0.38	0.47	0.51	0.68	0.63
Th/Cr	-	0.11	0.11	0.11	0.13	0.14	0.11	0.12	0.13
Cr/Th	-	9.11	9.22	9.04	7.66	7.23	9.52	8.63	7.53
Cr/V	-	1.06	1.15	1.20	0.79	1.30	1.17	1.11	-
Y/Ni	-	0.14	0.24	0.21	0.20	0.22	0.29	0.26	-

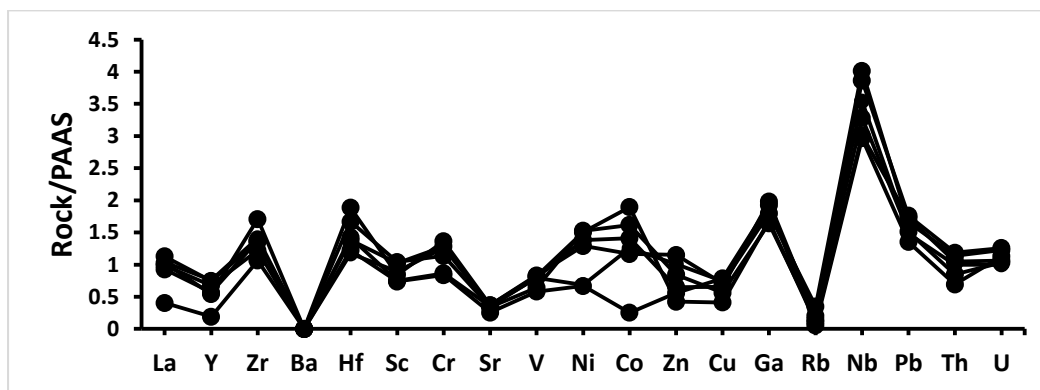


Fig. 5. Multi-element diagram showing the PAAS-normalized trace element distribution pattern of the Ogwashi-Asaba Formation shale at Obomkpa.

Rare earth elements

The chondrite-normalized REE pattern (Fig. 6) show a distribution of REEs similar to the PAAS values (Fig. 7) with an augmentation of light rare earth element (LREE), a flat high strength rare earth element (HREE) pattern and a negative Eu anomaly (av. = 0.83; Table 3). However, the analysed samples are depleted in REE abundances relative to PAAS due to the effect of quartz dilution. The shales also

show more fractionation of REEs ($La_N/Yb_N = 10.47$) than PAAS ($La_N/Yb_N = 9.15$). The negative Eu anomaly ($Eu/Eu^* = 0.83$ av.) of the shales is attributed to a cratonic source (McLennan and Taylor, 1991) comprised of Eu-depleted felsic igneous rocks e.g. granites, granodiorites etc. Gao and Wedepohl (1995) have shown that in all geologic ages, negative Eu anomalies are a common feature in shales, especially those with high CIA values.

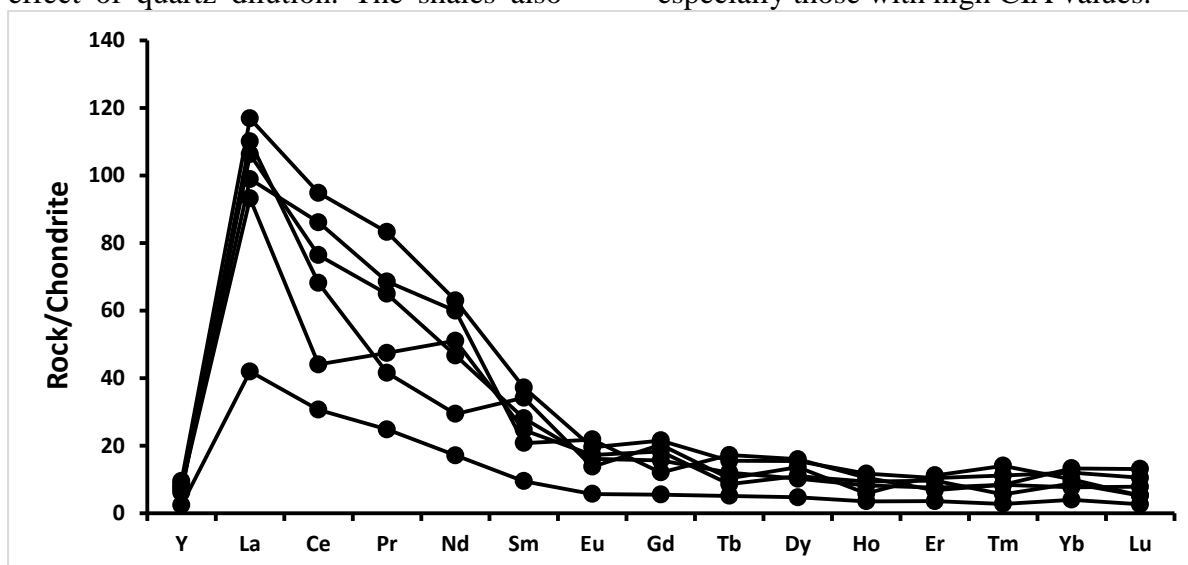


Fig. 6. Multi-element diagram showing the chondrite-normalized Rare Earth Element (REE) distribution pattern of the Obomkpa shales

Table 3. Normalized REE Concentrations of study Samples and Chondrite Values of each Element (Taylor and McLennan, 1985).

Element	Detection Limit (ppm)	SAMPLES							Average	Chondrite values	PAAS
		OB1	OB2	OB3	OB4	OB5	OB6				
Y	0.1	5.10	20.10	14.6	16.35	18.10	12.82	14.51	2.10	27.00	
La	0.1	15.40	42.90	39.00	34.20	36.30	40.40	34.70	0.367	38.20	
Ce	0.02	29.32	90.75	73.13	42.61	82.43	65.23	63.91	0.957	80.00	
Pr	0.1	3.40	11.40	8.90	6.50	9.40	5.70	7.55	0.137	8.83	
Nd	0.1	12.2	44.80	33.2	36.30	42.60	20.9	31.67	0.711	32.00	
Sm	0.1	2.20	8.60	6.50	5.70	4.80	7.90	5.95	0.231	5.55	
Eu	0.1	0.50	1.70	1.40	1.50	1.90	1.20	1.37	0.087	1.08	
Gd	0.1	1.70	6.60	4.80	5.60	3.70	6.20	4.77	0.306	4.66	
Tb	0.1	0.30	0.90	0.70	0.50	1.00	0.60	0.67	0.058	0.77	
Dy	0.1	1.80	5.90	3.90	4.20	6.10	5.20	4.52	0.381	4.68	
Ho	0.1	0.30	1.00	0.70	0.80	0.90	0.50	0.70	0.0851	0.99	
Er	0.1	0.90	2.60	1.90	2.40	1.70	2.80	2.05	0.249	2.85	
Tm	0.1	0.10	0.40	0.30	0.20	0.30	0.50	0.30	0.0356	0.41	
Yb	0.1	1.00	3.00	1.90	2.20	3.30	2.50	2.32	0.248	2.82	
Lu	0.1	0.10	0.40	0.30	0.20	0.50	0.20	0.28	0.0381	0.43	
LREE	-	63.02	200.15	162.13	126.81	177.43	141.33	145.15	2.49	165.66	
HREE	-	6.20	20.80	14.50	16.10	17.50	18.5	15.60	1.40	17.61	
LREE/HREE	-	10.16	9.62	11.18	7.88	10.14	7.64	9.44	-	9.41	
Eu/Eu*	-	0.79	0.69	0.77	0.81	1.38	0.52	0.83	-	0.65	
Ce/Ce*	-	0.95	0.96	0.92	0.67	1.05	1.01	0.93	-	1.02	
La _N /Yb _N	-	10.41	9.66	13.87	10.51	7.43	10.92	10.47	-	9.15	

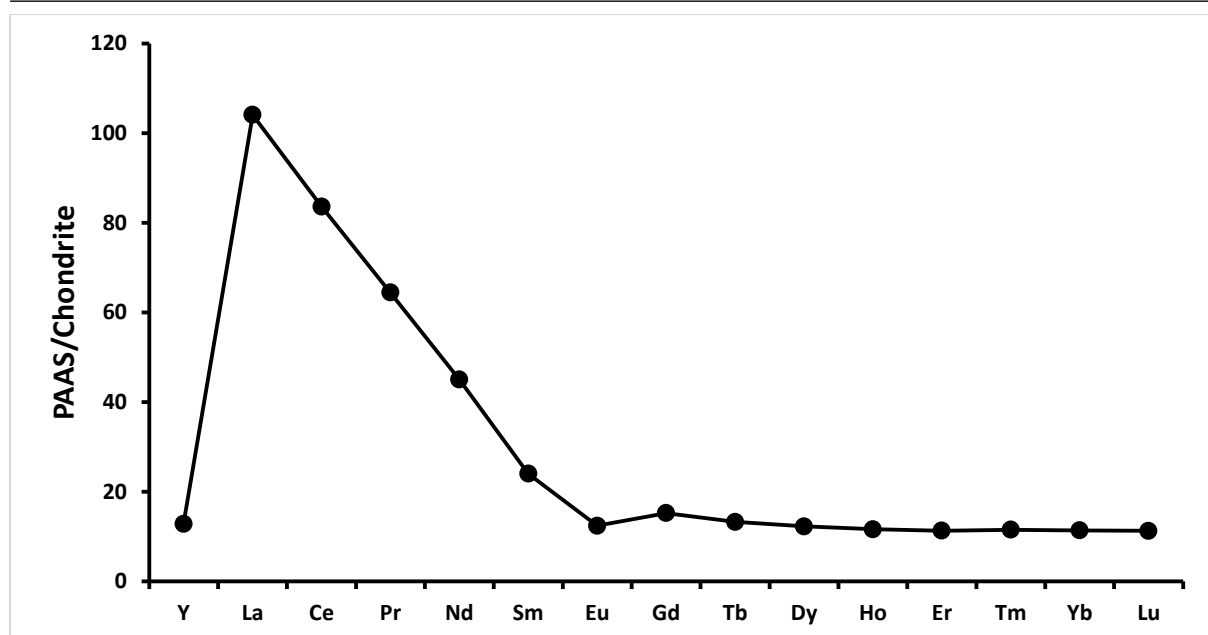


Fig. 7: Multi-element diagram showing the chondrite-normalized Rare Earth Element (REE) distribution pattern of the Post-Archean Australian Shale PAAS (Taylor and McLennan, 1985)

3.3 Discussion

3.3.1 Paleoredox condition

Redox-sensitive trace element ratios (Ni/Co, V/Cr and Th/U) (Table 2) are usually considered powerful geochemical indicators for paleoenvironmental discrimination (Jones and Manning, 1994; Hoffman et al. 1998; Rimmer et al. 2004; Algeo and Maynard, 2004; Johnson et al. 2010; Saez et al. 2011). Jones and Manning (1994) used <5 Ni/Co ratios to deduce oxic conditions, 5–7 dysoxic conditions and >7 suboxic to anoxic conditions. They also used <2 V/Cr ratios to infer oxic conditions, 2 – 4.25 for dysoxic conditions and >4.25 for suboxic to anoxic conditions. The V/Cr vs Ni/Co plot (Fig 8) shows that all the samples fall

within the oxic domain. An oxic depositional environment is thus inferred for the formation of the sediments. Also, extensive application of Th and U contents and the Th/U ratio as proxies to evaluate redox conditions in the depositional environment have been carried out by Jones and Manning, (1994), and has been proven generally to be a more consistent redox indicator than Cr/V and Ni/Co ratios. A relative enrichment of Th to U is an indication of oxic conditions. Thus, high Th/U value indicates oxicity. The Th/U values (Table 4) for the samples range between 2.89 – 4.71, suggesting a relative abundance of Th to U in the samples, further affirming that the deposits were formed in an oxic environment.

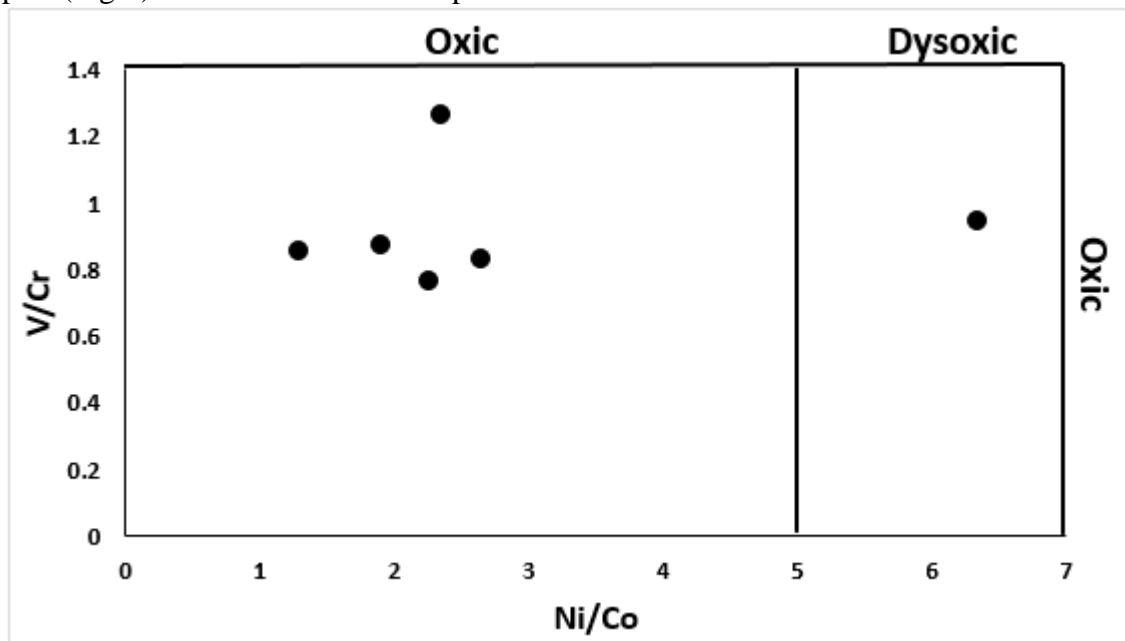


Fig. 8. Cross plot of redox-sensitive trace element ratios V/Cr versus Ni/Co. Ranges are from Jones and Manning (1994).

3.3.2 Paleo-weathering

A good quantitation of the extent of chemical weathering was determined by calculating three different weathering indices including the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982); Chemical Index of Weathering (CIW; Harnois, 1988) and Mineralogical Index of Alteration (MIA; Bock et al. 1998) was assumed. In this respect, the CaO values were accepted and used in the chemical index of alteration (CIA) is defined as $CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$; $CaO > Na_2O$, it was assumed that the the chemical index of weathering (CIW) as $CIW = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)] \times 100$ and the mineralogical index of alteration (MIA) as $MIA = 2[CIA - 50]$. In the equations given above, CaO* and

is the amount of CaO incorporated in the silicate minerals of the studied samples (Fedotko et al. 1995). Correction for CaO from carbonate input was not done for the sediments as there was no CO_2 data. Therefore, to calculate for CaO* from the silicate portion, the conjecture proposed by Bock et al. (1998) was assumed. In this respect, the CaO values were accepted and used in the chemical index of alteration (CIA) is defined as equations only if $CaO \leq Na_2O$; accordingly, when $CaO > Na_2O$, it was assumed that the the chemical index of weathering (CIW) as CIW concentration of CaO equals that of Na_2O (Bock et al. 1998). Kaolinite has a CIA value of 100 and represents the highest degree of

weathering. Illite is between 75 and 90, muscovite at 75, and the feldspars at 50. Fresh basalts have values between 30 and 45, while fresh granites and granodiorites of 45 to 55 (Nesbitt and Young, 1982; Fedo et al., 1995). The plot of CIA versus SiO_2 (Fig. 9) suggests that the Obomkpa samples and sediments of the Post-Achaean Australian Shale (PASS) have

been intensely weathered as they fall within the region of kaolinite and muscovite unlike the upper continental crust (UCC) which falls slightly above the region of feldspars and has relatively not undergone intense weathering. The high concentration of SiO_2 in the shales sample, suggests a high amount of reworking of these sediments.

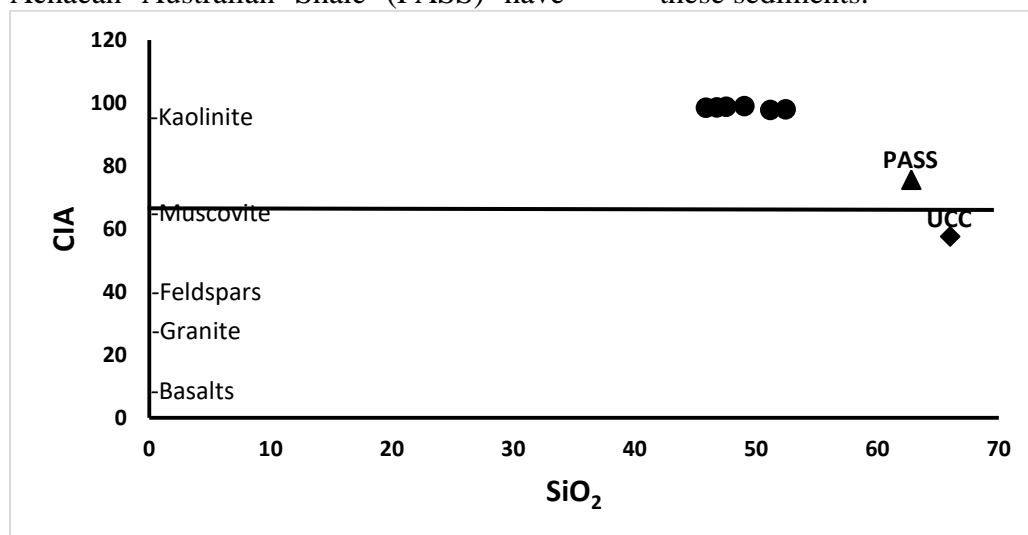


Fig. 10: A plot of CIA versus SiO_2 (After Nesbitt & Young, 1982).

Intense weathering of the samples is also supported by the high CIW values which ranges between 99.92–99.93 and are consistent with the high CIA values (97.79–99). Furthermore, the classification of weathering profiles (Nesbitt and Young, 1985; 1989), displayed on the A-CN-K ternary diagram (Fig. 10) shows that the samples fall in the region of kaolinite, gibbsite and chlorite in the plot. This further affirms that the samples have been subjected to intense weathering. The mineralogical index of alteration (MIA), suggested by Voicu et al. (1997), appraises

the grade of mineralogical weathering, i.e. the alteration ratio of a primary mineral into its comparable alteration mineral. MIA produces values between 0 and 100, and reveals early ($\text{MIA} < 20$), transitional ($\text{MIA} = 20 - 60$), and late to extreme ($\text{MIA} > 60$) mineralogical conversion. The value of 100 means whole conversion of a primary mineral into its correspondent alteration product. Average MIA value (96.72) of the samples suggests an intense weathering and chemical alteration of the minerals.

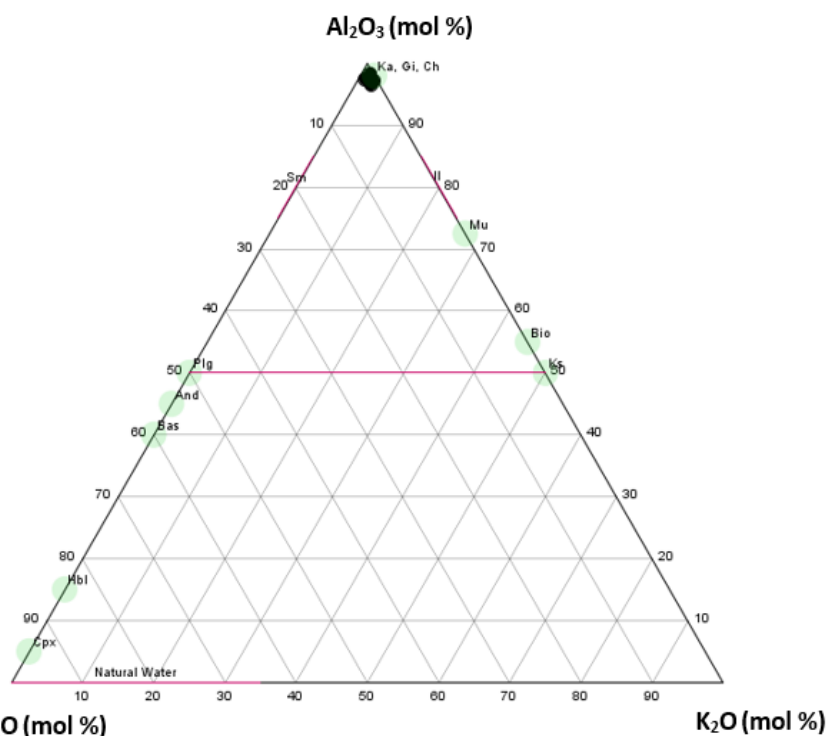


Fig. 10: Ternary plot of A-CN-K ($\text{Al}_2\text{O}_3\text{-CaO+Na}_2\text{O-K}_2\text{O}$) showing weathering profiles of the samples (After Nesbitt & Young, 1984; 1989). Ka-kaolinite, Ch-chlorite, Ill-illite, Sm-Smectite, Cpx-Clinopyroxene, Hbl-Hornblende, Plg-Plagioclase, Mu-muscovite, Bio-biotite, Ks-potassium feldspar, Gi-gibbsite, Bas-basalt, And-andesite.

3.3.3 Provenance

The geochemical signatures of clastic sediments have been used to deduce and establish provenance (Taylor and McLennan, 1985; Condie et al., 1992; Cullers, 1995; Madhavaraju and Ramasamy, 2002; Armstrong-Altrin et al., 2004). The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of most clastic rocks are essentially used to infer the source rock compositions, since the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio intensifies from 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks, and from 21 to 70 for felsic igneous rocks (Hayashi et al., 1997). In the Obomkpa shale samples, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio ranges from 8.23 to 20.15 (Table 1). On initial assessment, the ratio suggests an intermediate source rock for the samples. However, trace elements such as Cr, Ni, Co, and V have been used to define mafic and ultramafic sources (Wronkiewicz and Condie, 1987; Huntsman-Mapila et al., 2005) while Ba, Sr, Y, and Zr are used in constraining felsic sources. Felsic source rocks frequently have lower concentrations of Cr, Ni, Co, and V and higher concentrations of Ba, Sr, Y, and Zr than

mafic and intermediate source rocks (Wronkiewicz and Condie, 1987; Spalletti et al., 2008). The average concentrations of Cr, Ni, Co, and V are 123.67ppm, 64.67ppm, 29.12ppm and 111.67ppm respectively (Table 2). While Ba (0.03ppm) and Y (15.65ppm) have lower average concentrations, while Zr (284.70ppm) and Sr (68.67ppm) show relatively higher concentrations. The higher concentrations of Zr and Sr are indicative of a felsic source.

Ratios such as Eu/Eu^* , La/Sc , Th/Sc , Th/Co , and Th/Cr (Table 4) are considerably dissimilar in felsic and basic rocks and may allow constraints on the average provenance composition (Wronkiewicz and Condie, 1990; Cox et al., 1995; Cullers, 1995; Armstrong-Altrin et al., 2004). Table 5 shows the range of values of these for both felsic and mafic source rocks (Cullers 1994, 2000; Cullers and Podkovyrov, 2000; Cullers et al. 1988) compared to the values for the Obomkpa shales, UCC and PAAS (Taylor and McLennan, 1985). The range of values for Eu/Eu^* , La/Sc , Th/Sc , Th/Co , and Th/Cr ratios of the samples correspond with

those of the sediments derived from a felsic source. The average values for the samples – La/Sc (2.46ppm), Th/Sc (1.02ppm), Th/Co (0.68ppm), Th/Cr (0.12ppm), and Cr/Th (8.63ppm) – are also

similar to those of PAAS (Table 3). The probable felsic sources of the shales are the Pan-African (Older) and Younger Granites of northern and south-western Nigeria.

Table 4: Range of elemental ratios of the shales in this study compared to the ratios in similar fractions derived from felsic rocks, mafic rocks, upper continental crust (UCC), and Post-Archean Australian shale (PAAS).

Elemental Ratio	Range for	Range for Sediments ²		Average UCC ²	Average PAAS ³
	Obomkpa Shales ¹ (ppm)	Felsic Source	Mafic Source		
Th/Sc	0.86 – 1.04	0.84 – 20.5	0.05 – 0.22	0.79	0.90
Th/Co	0.35 – 1.74	0.67 – 19.4	0.04 – 1.4	0.63	0.63
Th/Cr	0.11 – 0.14	0.13 – 2.7	0.018 – 0.046	0.13	0.13
Cr/Th	7.23 – 9.52	4.00 – 15	25 – 500	7.76	7.53
La/Sc	1.31 – 2.89	2.5 – 16.3	0.43 – 0.86	2.21	2.40
Eu/Eu*	0.52 – 1.38	0.40–0.94	0.71–0.95	0.63	0.65

¹This study, Cullers (1994, 2000); ²Cullers and Podkovyrov (2000); Cullers et al. (1988); ³Taylor and McLennan (1985).

The chemical composition of sedimentary rocks is also influenced by weathering; thus, the hydraulic concentration of weathering-resistant phases such as zircon, Cr-spinel, monazite, and apatite may yield asymmetrical chemical variations in some trace elements (Cullers et al. 1979). The relative enrichment of Zr to Sc, shown by

high Zr/Sc ratios (Table 3), and abundance of SiO₂ in the sediments is a good indicator of sediment reworking and/or sorting (Cingolani et al. 2003). As shown in the plot (Fig. 11), the shale samples and PASS have been substantially reworked, suggesting a long distance from provenance.

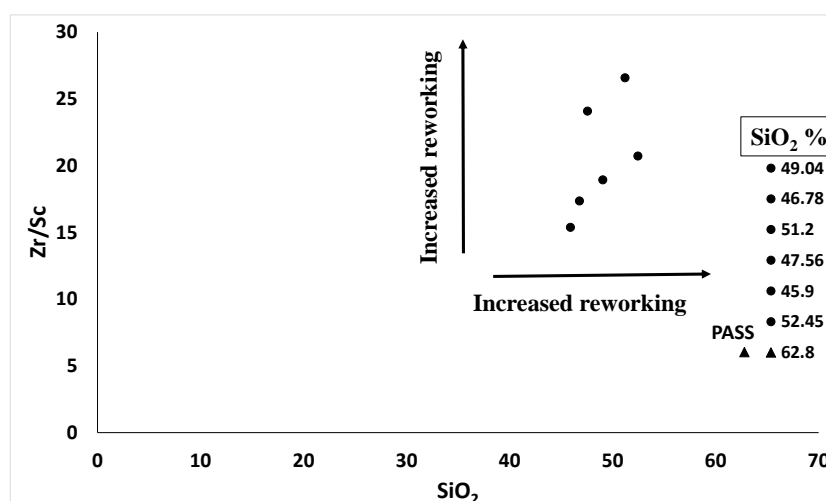


Fig. 11: A Plot of Zr/Sc versus SiO₂ indicating the extent of reworking of sediment. (Modified after Cingolani et al. 2003).

3.3.4 Tectonic setting

Various workers (e.g. Bhatia, 1983; Roser and Korsch, 1986; McLennan et al., 1990)

have used the chemical compositions of sediments to discriminate tectonic settings. The ratio of Na₂O/K₂O has been used to

constrain tectonic settings of sedimentary basins (e.g. Roser & Korsch, 1986) and data from modern deep sea turbidites signpost that sediments from volcanically active tectonic settings generally have $\text{Na}_2\text{O}/\text{K}_2\text{O} < 1$, whereas sediments from trailing edge margins display ratios higher than 1 (McLennan et al. 1990). The average ratio of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ for the shale samples is 0.03 (Table 1) suggesting a volcanically active tectonic setting.

Four tectonic settings: passive continental margin (PM), active continental margin (ACM), oceanic island-arc (OIA) and continental island arc (CIA), are recognized on the various tectonic discrimination plots of Bhatia (1983) (Fig. 12). The fields are based on primordial sandstone-mudstone pairs, substantiated against modern sediments from known tectonic locations. The Obomkpa shales fall within the field of ACM in the plots (Fig. 12a-d). The “Older Granites” (a term introduced by Falconer, 1911) are thought to be pre-, syn- and post-tectonic rocks (Obaje, 2009), formed during the Pan-

African orogenic event. McCurry (1973) classified the granites into two main groups – the first “syntectonic” group comprised elongate batholithic sheets that are partly concordant, and foliated. The second group “late tectonic” are composed of poorly foliated discordant bodies, rich in mafic xenoliths and having a lower proportion of potash feldspar. The Younger Granites, however, were deposited as ring complexes along NE-SW trending lineaments of incipient rifts during the alkaline anorogenic magmatism of the Mesozoic. The activities (both tectonic and magmatic) involved in the emplacement of the Older and Younger Granites are synonymous with those common in Active Continental Margins (ACMs). However, these tectonic settings are sometimes conspicuously unjustifiable as their discrimination involves the use of very mobile elements including SiO_2 , Na_2O , CaO and K_2O that are easily affected by weathering. Thus, the application of the discrimination plots be done with caveat.

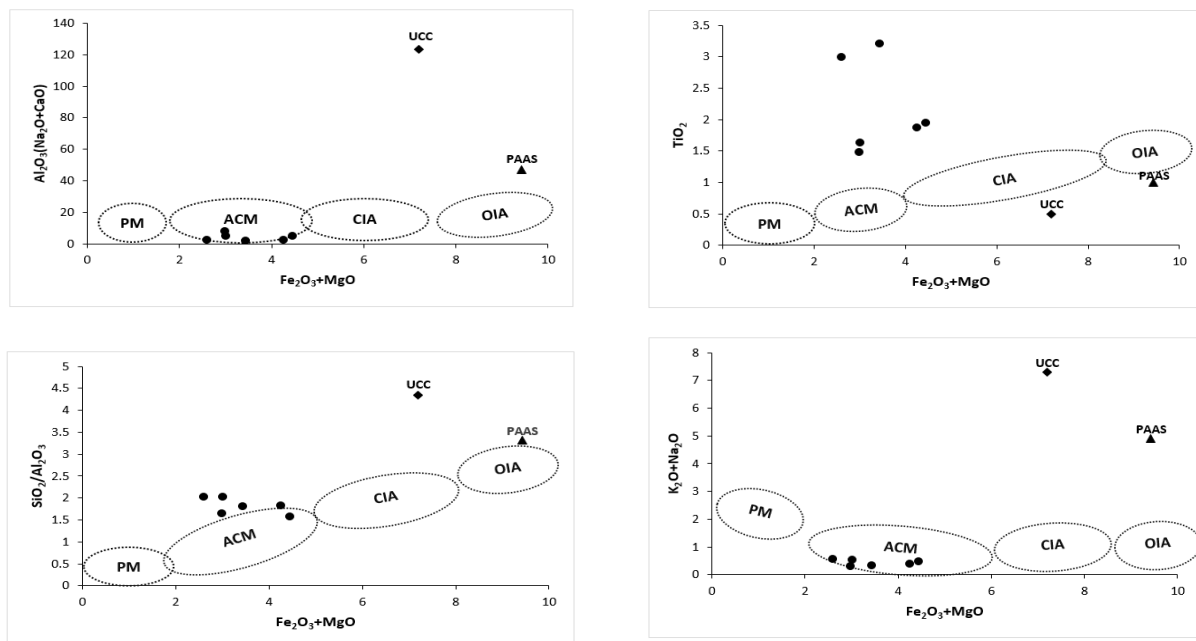


Fig. 12a-d: Tectonic setting discrimination diagrams of samples (after Bhatia, 1983). PM: passive margin; ACM: active continental margin; CIA: continental island arc; OIA: oceanic island arc.

Conclusion

Geochemical proxies obtained from the analysed samples have been to infer and affirm ancient geological conditions and domains under which the rocks in the area of study were formed, hence add to the geological information on the Ogwashi-Asaba Formation, as trace element ratios – (V/Cr, Ni/Co, Th/U) – and the near positive Ce anomaly of the analysed samples suggests an oxic depositional environment. Intense source-area chemical weathering of the rocks and their constituent minerals is indicated by major oxide signatures. This weathering scenario is also inferred to have also occurred during transportation and diagenetic processes. Trace element-based provenance discrimination indicated a felsic and mafic sources for the sediments from probably, the older and younger granites of northern Nigeria, while an Active Continental Margin (ACM) tectonic setting domain is indicated for the sediment by major elements discriminant plots.

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