Provenance Studies of Sandstone Facies Exposed Near Igbile Southwestern Nigeria: Petrographic and Geochemical Approach

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Abstract

The petrography, as well as the major, trace and rare earth element compositions of ten (10) sandstone samples of Maastrichtian Afowo Formation exposed near Igbile, Southwestern Nigeria, have been investigated to determine their provenance, source area weathering conditions, paleoclimate and tectonic setting using petrographic analysis and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

Results of the petrographic analysis revealed that quartz is the most dominant detrital mineral with (86%) followed by weathered plagioclase feldspar (5.10%) and rock fragments (10.9%). The quartz grain is sub-angular to sub-rounded in shape and the sandstones were classified as quartz arenites, sublitharenites and subarkoses based on framework composition of quartz, feldspar and rock fragment plots. This suggests a recycled orogen source for the sandstones and deposition in a humid climate, evidenced by the weathered feldspars. Eleven (11) major, seventeen (17) trace and fourteen (14) rare earth elements were obtained from the geochemical analysis. The major elements values range in concentration from 0.01%-81.39% with SiO₂ being the dominant oxide followed by Al₂O₃ and Fe₂O₃ constituting over 95% of the major oxides; K₂O, TiO₂, Na₂O, CaO, MgO and P₂O₅ made up the remaining 5%. The average ratio of SiO₂/Al₂O₃ valued 4.31 for the sandstone is appreciably high indicating that it has been heavily weathered. The trace elements range in concentration from 0.2 ppm-1651.2 ppm with Zr being the most dominant element an indication of orogenic recycling. The rare earth elements range in concentration from 0.01 ppm-163.7 ppm with Ce having the highest concentration, depicting that the sandstones were deposited in an oxidizing environment. Also, the trace element relationship illustrated from the spider plot shows chemical coherence and uniformity of the sandstones. The chondrite normalized rare earth elements (REE) plot shows enrichment in the Light REE over the heavy REE for the sediment with strong negative Eu anomaly values between (0.57–0.69) suggesting a felsic provenance derived from upper continental crust for the sandstones.

Keywords: Maastrichtian, provenance, petrographic, subarkoses, chondrite

1. Introduction

The Precambrian domain of West Africa accommodates important Phanerozoic depositional sites. Among the latter is the Dahomey basin a coastal sedimentary basin which covers much of the continental margin of the Gulf of Guinea. It extends from the Volta Delta in Ghana in the west to the Okitipupa ridge in Nigeria in the east. It is a marginal pull-apart basin (Klemme, 1975) or marginal sag basin (Kingston et al., 1983) which developed in the Mesozoic as the African and South American lithospheric plates separated and the continental margin founded (Burke et al., 1971; Whiteman, 1982). Upon deposition of sediments in a sedimentary basin, the sedimentary rocks formed retain information about previous orogenic conditions and the composition, namely, source rock composition, chemical weathering, climate, transport, burial and diagenesis. The geochemical characteristics of clastic sedimentary rocks (which include sandstones) are useful in determining the depositional setting and its associated provenance. The study of sedimentary provenance interfaces several of the mainstream geological disciplines and it includes the location and nature of sediment source areas, the pathways by which sediment is transferred from source to basin of deposition, and the factors that influence the composition of sedimentary rocks (e.g., relief, climate, tectonic setting). Information on transport history, paleoenvironment of

deposition and energy of transport medium can be deduced from mineralogical studies and the incorporation of this into data from inorganic geochemistry will ultimately result in a concise depiction of sediment provenance amongst other information.

The aim of this work is directed at carrying out comprehensive provenance studies of the sandstones near Igbile by means of a fusion of petrographic and inorganic geochemical studies with a view to determining the weathering condition of the source area, paleotectonic and palaeoclimatic settings, sediment maturity and paleoenvironment of deposition.

1.1 Local Setting

The study area is located near Igbile with coordinates 6°43'N to 6°45'N and 3°51'E to 3°53'E on the eastern flank of the Dahomey basin. Accessed by main roads and footpath (Figure 1), it is an area with lowlands and few ridges. Relative to the lowlands, the hills are very high characteristics of tropical rain forest of south western Nigeria. During the dry season a relatively high temperature of about 30 °C although the harmattan as a result of the northeasterly winds from December to February, has ameliorating effects on the dry season high temperatures. On the contrary low temperatures as low as 24 °C are experienced during the rains, especially between July and August (Akintola, 1986). The average annual rainfall is about 1500 mm promoting perennial tree growth with varying height. The area is well drained with NE-SW trending rivers such as Ogun, Ona, Shasha and Lagos lagoon. The geomorphology and the drainage pattern in the study area are probably influenced by the geology of the area.

Previous studies on the sandstones of the area include Nton (2001) and Ikhane et al. (2011).



Figure 1. Map of the study area

1.2 Regional Geology and Stratigraphy

The Dahomey Basin, a wrench modified basin, is an extensive sedimentary basin (Clifford, 1986). It is a marginal pull apart basin (Klemme, 1975) or marginal sag basin (Omatsola & Adegoke, 1981; Kingston et al., 1983) developed during the commencement of rifting, associated with the opening of the Gulf of Guinea in the Mesozoic era and it is characterized by both block and transform faulting superimposed across an extensive Paleozoic basin during the break-up of the African, North American and South American paleo continents. This led to the formation of continental margin and coastal margin which was filled up by Cretaceous and Tertiary sediments (Burke et al., 1971; Whiteman, 1982).

The Ghana ridge, presumably an offset extension of the Romanche Fracture Zone binds the basin to the west while the Benin Hinge Line, a basement escarpment separating the Okitipupa structure from the Niger-Delta binds it to the east. The Benin Hinge Line supposedly defines the continental extension of the Chain Fracture Zone. The onshore part of the basin covered a broad arc-shaped profile of about 600 km² in extent. The onshore section of the basin attains a maximum width along its N-S axis, some 130 km around the Nigerian-Republic of Benin border. The basin narrows to about 50 km on the eastern flank where the basement assumes a convex upwards outline with concomitant thinning of sediments. Jones and Hockey (1964) and Agagu (1985) from dip measurements revealed that the sedimentary successions dip only gently south or southwest at about 3°. This implies that the basin recorded only very little post depositional tectonism. Therefore, the diastrophism resulting in the horst and graben were probably predepositional.

The lithostratigraphic units of the Cretaceous to Tertiary sequence of the eastern Dahomey basin according to Omatsola and Adegoke (1981) is presented summarily in (Figure 2) though, there are still controversies on age assignment and nomenclature of the different litho-sections. The study area belongs to the Cretaceous Abeokuta group in which Omatsola and Adegoke (1981) recognized three formations belonging to the group based on lithologic homogeneity and similarity of origin. This group is the thickest sedimentary unit within the basin and the formations from oldest to youngest are Ise, Afowo and Araromi.



Figure 2. Stratigraphy of the Eastern Dahomey Basin (After Omatsola & Adegoke, 1981)

Ise Formation consists of conglomerate and grits at the base overlain by coarse to medium grained sands with interbedded kaolinite unconformably overlies the basement complex of Southwestern Nigeria. In some locations within the basin the conglomerates are imbricated and ironstone occurs (Nton, 2001). Based on paleontological assemblages a Neocomian-Albian age is assigned.

Afowo Formation overlies the Ise Formation and composed of coarse to medium grained sandstone with variable but thick interbedded shales, siltstone an claystone. The sandy facies are tar-bearing while the shales are organic rich (Enu, 1985). The lower part of this formation is assigned a Turonian age while the upper part ranges into Maastrichtian as deducted from palynological assemblage.

Araromi Formation is the youngest Cretaceous formation in the group and conformably overlies the Afowo Formation. It is composed of fine-medium grained sandstone at the base, overlain by shales, sitstone with interbedded limestones, marl and lignite. Based on faunal content Omatsola and Adegoke (1981) assigned a

Maastrichtian to Paleocene age to this formation.

The Abeokuta group is overlain by the Imo group comprising of Ewekoro and Akinbo Formations (Adegoke, 1977; Jones & Hockey, 1964; Ogbe, 1972), the Ososhun Formation (Jones & Hockey, 1964; Nton, 2001), Coastal plain sands and Recent Alluvium (Jones & Hockey, 1964).

2. Methods

Ten representative samples were carefully collected from the outcrop during the field mapping using spotted method of sampling. The samples were collected from bottom to the top of the sequence with only fresh rock samples taken. During the field work, visual examination of the outcrop and the megascopic analysis of the sandstone facies was carried out with the aid of a hand-lens to recognize the colour, grain-size, grain shape, sorting and roundness. The outcrop is laterally extensive and massive, vertically of about 6.05–10.52 m. It consists of mudstone and and sandstone lithological units with an average vertical thickness of 2 m. The sandstone unit is highly ferruginised with siltstone-mudstone heterolith. It has a dull appearance with a dark grey colour, and it is highly weathered and bioturbated with presence of rootlets of grasses and ichnofossils. See Figure 3.



Figure 3. Photograph of the exposure or outcrop section

2.1 Thin-section Petrography

Thin-section petrography was carried out at the geological laboratories of the University of Ibadan on the ten (10) representative samples for microscopic examination of their mineralogical composition. The unconsolidated samples were impregnated in epoxy before cutting and mounted on glass slides by means of Canada balsam. Three stages of grinding were involved in the preparation of the slides and extreme caution was taken to examine the slides between each stage of grinding to check for uniform reduction of the interference colors. The prepared slides were then labelled, and examined with the aid of transmitted light under the flat stage of the petrographic microscope using point count method according to Ingersoll et al. (1984) and Osae et al. (2006). Photomicrographs were taken and features of the mineral grains were observed based on the optical properties of the minerals.

2.2 Geochemical Analysis

Inorganic geochemical analyses carried out on the samples by Inductively Coupled Plasma-Electron Spectrometry (ICP-ES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), using lithium metaborate/tetra-borate fusion. The sediment was dried (60 °C) and sieved to -80 mesh (-180 μ m) before jaw crushing to 70% passing a 10 mesh (2 mm). A 250 g aliquot was riffle split and pulverized to 85% passing a 200 mesh (75 μ m) in a mild-steel and puck mill. A 0.2 g aliquot is weighed into a graphite crucible and mixed with 1.5 g of lithium metaborate/tetraborate flux (LiBO₂/Li₂B₄O₇). The Crucibles are placed in an oven and heated to 980 °C for 30 minutes. The cooled bead is dissolved in 5% HNO₃ (ACS grade nitric acid diluted in demineralised water). Calibration standards and reagent blanks are added to the sample sequence. To avoid contamination, all samples were washed thoroughly using de-ionized water prior to preparation for ICP analyses at Acme Laboratories, Vancouver, Canada. Where the geochemical analysis was carried out.

3. Results and Discussion

The geochemical analyses carried out on the samples yielded data for the concentration of 10 major elements (SiO₂, Al₂O₃, TiO₂, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, and MnO), 17 trace elements, (Ba, Co, Cr, Cs, Cu, Ga, Hf, Nb, Rb, Sc, Sr, Ta, U, V, Y, Zr) and 14 rare-earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) as presented in Tables 1, 2 and 3 whereas the result of the petrographic analysis on the basis of abundance of quartz, feldspar and rock fragment in the sandstone is presented in Table 4.

Samples	SST1	SST2	SST3	SST4	SST5	SST6	SST7	SST8	SST9	SST10	
UNIT	%	%	%	%	%	%	%	%	%	%	
ANALYTES											
SiO ₂	81.39	68.07	83.22	64.85	69.66	66.1	64.29	71.46	60.93	60.32	
Al ₂ O ₃	10.16	18.72	9.08	20.74	17.2	20.97	21.74	17.58	24.36	24.97	
Fe ₂ O ₃	2.41	2.76	1.97	2.65	3.91	1.76	2.08	1.2	2.24	1.97	
MgO	0.04	0.04	0.05	0.05	0.08	0.04	0.05	0.05	0.05	0.06	
CaO	0.02	0.02	0.05	0.02	0.03	0.02	0.03	0.03	0.03	0.04	
Na ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
TiO ₂	1.16	2.27	0.96	2.38	1.92	2.38	2.59	2.29	2.01	2.3	
K ₂ O	0.04	0.03	0.04	0.05	0.05	0.03	0.04	0.02	0.05	0.15	
MnO	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.02	
P_2O_5	0.03	0.07	0.03	0.08	0.05	0.08	0.05	0.1	0.06	0.06	
Cr ₂ O ₃	0.01	0.02	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02	
LOI	4.7	7.7	4.5	8.9	6.9	8.3	8.8	7	10	9.8	

Table 1. Major elements concentration

Table 2. Trace element concentration in the study area

SAMPLES	SST1	SST2	SST3	SST4	SST5	SST6	SST7	SST8	SST9	SST10
UNIT	Ppm	ppm	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
ANALYTES										
Ba	27	93	30	112	44	108	113	107	103	157
Be	1	1	1	2	1	1	1	1	3	2
Со	1.8	3.6	1.4	3.7	2.4	3.3	3.4	1.6	2.6	4.1
Cs	0.2	0.2	0.3	0.3	0.5	0.2	0.2	0.2	0.2	0.6
Ga	14.4	24.3	13	26.2	22.8	28.3	27.6	25.5	32.3	31.3
Hf	15.4	30.8	13	35.5	21.5	35.7	39.7	43.6	28.6	29.61
Nb	19.2	39.6	18.2	40.1	30.9	43.3	47.1	54.4	36.1	37.9
Rb	2.3	1.2	1.9	1.9	3.4	0.9	1.3	1.5	1.6	5.4
Sn	3	9	29	5	21	8	34	6	5	9
Sr	16.5	60	17.4	60.2	29.5	67.4	70.9	168.1	71.5	73.4
Та	1.4	3.7	1.2	2.8	1.9	2.9	3.7	3.9	2.7	3
Th	7.7	13.8	8.2	13.5	11.5	14.4	16	13.4	15.1	13.5
U	1.4	3.6	1	4.4	2.2	3.9	4	3.5	3.4	3.7
V	55	99	59	93	97	94	90	72	97	99
W	1.1	3.4	1.6	3.2	1.7	2.9	3.2	3	2.9	2.7
Zr	566.6	1206.7	517.4	1319.3	851.7	1406.5	1454.6	1651.2	1080.2	1125.4

SAMPLES	SST1	SST2	SST3	SST4	SST5	SST6	SST7	SST8	SST9	SST10
UNIT	Ppm	ppm	Ppm	ppm	ppm	Ppm	ppm	Ppm	ppm	ppm
ANALYTES										
Y	10.5	43.3	6.2	60.3	17.2	41	43.8	34	71.6	39
La	18.6	73.7	20.1	73.2	33.3	91.9	85.8	85.2	95.6	91.2
Ce	32.1	119.7	30.8	122.8	55.8	142.7	142.1	163.7	163.3	139.1
Pr	3.18	10.6	2.74	10.61	5.52	12.91	13.49	18.05	14.5	12.95
Nd	11	31.5	8.4	30.9	16	37	43.9	59.3	42.5	40.5
Sm	1.48	5.04	1.07	4.87	2.28	5.49	6.51	8.72	6.86	6.14
Eu	0.28	1.04	0.22	1.07	0.43	1.2	1.29	1.6	1.3	1.27
Gd	1.29	4.66	1.01	5.28	1.93	5.52	5.54	5.85	7.28	5.6
Tb	0.23	0.98	0.18	1.19	0.38	1.06	1.05	0.93	1.55	1.03
Dy	1.44	5.83	1.2	8.02	2.68	6.67	7.11	5.59	10.68	6.38
Ho	0.3	1.45	0.32	2.13	0.54	1.72	1.64	1.21	2.67	1.55
Er	1.15	4.72	0.76	6.98	1.87	4.97	5.41	4.58	8.66	4.42
Tm	0.19	0.7	0.12	1.04	0.26	0.81	0.79	0.6	1.28	0.69
Yb	1.42	5.44	0.92	6.99	1.9	5.27	5.46	4.58	8.66	4.42
Lu	0.23	0.69	0.13	1	0.29	0.85	0.85	0.73	1.26	0.68
Мо	0.2	0.2	0.4	0.2	0.7	0.1	0.1	0.1	0.1	0.1
Cu	10.5	0.9	5.5	0.8	8.1	1.2	0.6	1.1	2	0.7
Pb	4.1	8.6	14.1	5.2	20	6.4	6.9	4.9	3.9	12.4
Zn	1	1	2	1	4	1	1	1	1	1
Ag	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ni	0.8	0.5	0.8	0.4	2.3	0.6	0.7	0.5	0.9	0.8
As	1	0.5	0.9	0.5	1.9	0.5	0.5	0.5	0.5	0.5
Au	1.8	2	2.6	2	1.4	3.3	1	1.6	1.2	0.5
Cd	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sb	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Bi	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Hg	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ti	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Se	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table 3. Rare earth elements concentration for the sediments within the study area

3.1 Petrography

This involves the systematic study/description and evaluation of rocks by means of microscopic examination of thin-section for the purpose of determining mineralogy, textures, and composition in an attempt to classify the sandstone as well as deduce their transportation history, provenance, maturity indices, palaeoclimate and paleotectonic setting. Petrological studies revealed that the sandstones have similar mineralogical compositions as well as similar lithology types, although with some few variations. The studies revealed that quartz is the most dominant detrital mineral averaging about 75–90%. This is an indication that the sandstones are texturally mature (Folk, 1951). It also implies a high degree of mechanical and chemical stability for the sandstones. The quartz grains are large anhedral crystals that are sub-angular to sub-rounded in shape (Figure 4) suggesting that the sandstone has been transported a long distance from their source. The quartz crystals also occur as monocrystalline to polycrystalline crystals, with the polycrystalline quartz having crystals with sharp to sutured intra-grain boundaries typical of metamorphic rocks (Pettijohn et al., 1972; Blatt et al., 1972). Some of the grains show the presence of iron oxide rimming their edges, as well as the presence of inclusions and vacuoles which

could be attributed to a low temperature source such as a hydrothermal vein. The quartz also have straight to strongly undulose extinction which is as a result of strain on the crystals and the polycrystalline crystals appear slightly more in number than the monocrystalline quartz. This character of quartz revealed possible contributions from both igneous and metamorphic sources (Figures 4 and 5). Quartz is the common silicate mineral acting as cement in the analytes, although there are patches of iron-oxide cement. These cementing materials are chemically attached to the crystal lattice of existing quartz grains forming rims of cement (overgrowths). Mineral content of cement is silica and iron-oxide.

The feldspars observed is mainly plagioclase which has been significantly weathered giving it a brown coloration. They constitute about 5.1% (Table 4) and exhibits simple twinning (Figure 5). The occurrence of very little feldspar suggests lower source relief, moderately to long transportation distance and probably slow sedimentation rate. This can be ascertained from the quartz content (75–90%) that is more stable to weathering. As earlier stated, feldspars occur as plagioclase which is more abundant and the most resistant or best preserved feldspar in rocks derived from chemical and mechanical weathering.

The rock fragments or lithic constituents averages about 20.4% (Table 4) which are most likely derived from supra-crustal rather than plutonic sources, due to its fine grained nature. Majority of the samples contain varying proportions of mica and muscovite is more abundant than biotite since it is more resistant to weathering. The matrix is about 12% of the detrital fraction and consists of fine silty particles that appear brownish in some samples. This brownish coloration coupled with presence of iron oxide is a strong indication of weathering and ferruginisation or probably be as a result of percolation from the lateritic cover. Also, the reduction or oxidation process of the iron oxide may be responsible for this. The Q, F, RF modes was determined by plotting on the composition diagram after Folk (1968); Dickinson and Suczek (1979); Suttner et al. (1981) see (Figures 6, 7 and 8). Rocks derived from similar parent rock type in similar climate are compositionally unique. Studies have shown that sand generated from plutonic rocks in humid climate have average quartz, feldspar, and rock fragments content of 60%, 27%, 13% respectively, whereas in semi-arid climate the average modal composition is 27%, 39%, and 34% respectively. Metamorphic derived sands are put at 74%, 6% and 20% (humid) as seen in (Folks, 1951) (Table 4). Judging from the ternary diagram, climatic condition of the sandstone are of metamorphic humid and metamorphic arid with most of the sandstones concentrated in metamorphic humid (Suttner et al., 1981) (Figure 8). From the ternary plot (Figure 7), the sandstone can be classified as a product of recycled orogen for which sources are deformed and uplifted strata sequences in subduction zones, along collision orogens, or within foreland fold- thrust belts (Dickinson & Suczek, 1981), Terrigenous sediments derived from recycled orogens are more felsic which explains the reason why quartz minerals are more dominant. Classifications based on Quartz, Feldspar and rock fragment (after Folk, 1968) classified the rock into two different rock types which are sublitharenite and litharenite (Figure 6).

SAMPLES	QUARTZ (%)	FELDSPAR (%)	ROCK FRAGMENTS (%)
Sst1	68	3	18
Sst2	64	0	26
Sst3	62	5	14
Sst4	63	4	37
Sst5	80	8	20
Sst6	78	10	30
Sst7	88	8	12
Sst8	70	0	30
Sst9	74	11	26
Sst10	87	2	13
AVERAGE	74.5	5.1	20.4

Table 4. Abundance of quartz, feldspar and rock fragment in the sandstone samples



Figure 4. Thin section and modal composition of the studied sample (lower bed/layer)



Figure 5. Thin section and modal composition of the studied sample. (upperbed/topbed/layer)



Figure 6. Ternary plot for classification of sandstone within the study area using Q-F-RF (after Folk, 1968)



Figure 7. Ternary plot for Palaeotectonic provenance of the sandstone within the study area using Q-F-RF (after Dickinson & Suczek, 1979)



Figure 8. Paleoclimatic setting of the sediments within the study area using Q-F-RF (after Suttner et al., 1981)

3.2 Major Element Geochemistry

The geochemical composition of terrigenous sedimentary rocks is a function of the complex inter-play of various variables, such as provenance, weathering, transportation and diagenesis. Unlike many igneous rocks, it is difficult to find a simple relationship between the mineralogy of sandstones and their chemical composition. For this reason, the geochemical classification of sandstones does not mimic the conventional mineralogical classification of sandstones based on quartz-feldspar-lithic fragments, rather it differentiates between mature and immature sediments. However, it can be used partly to determine the degree of alteration of the source material (Nesbitt & Young, 1982; Fedo et al., 1995; Von Eynatten et al., 2003). It is also a helpful tool when contemplating certain trends in the general composition of rocks and to decipher the weathering profile of rocks (Boles & Franks, 1979; Nesbitt & Young, 1982; Nesbitt et al., 1996).

Observation from the result of major element of the analyzed samples indicated that the sandstones are extremely rich in SiO₂ (silica) ranging from 60.32% to 81.39% with an average of 69.03%, this is higher than the average of 66% by weight for upper continental crust (UCC) by (Taylor & McLennan, 1985). The average content of Al_2O_3 for sandstone is moderately high (about 18.55%) ranging from (9.08 to 24.36%). The very low values of K₂O/Al₂O₃ (0.01–0.07) suggest probably sedimentary recycling or increase in the degree of source area weathering (Bauluz et al., 2000). This can be backed-up by the increase in the value of Al_2O_3 and Fe₂O₃ (See Table 5) which is an indication of weathering and alteration (Akarish & El Gohary, 2008).

Samples	SST1	SST2	SST3	SST4	SST5	SST6	SST7	SST8	SST9	SST10	AVERAGE
UNIT	%	%	%	%	%	%	%	%	%	%	
ANALYT	ES										
SiO ₂	81.39	68.07	83.22	64.85	69.66	66.1	64.29	71.46	60.93	60.32	69.03
Al ₂ O ₃	10.16	18.72	9.08	20.74	17.2	20.97	21.74	17.58	24.36	24.97	18.55
Fe ₂ O ₃	2.41	2.76	1.97	2.65	3.91	1.76	2.08	1.2	2.24	1.97	2.3
MgO	0.04	0.04	0.05	0.05	0.08	0.04	0.05	0.05	0.05	0.06	0.05
CaO	0.02	0.02	0.05	0.02	0.03	0.02	0.03	0.03	0.03	0.04	0.03
Na ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TiO ₂	1.16	2.27	0.96	2.38	1.92	2.38	2.59	2.29	2.01	2.3	2.03
K ₂ O	0.04	0.03	0.04	0.05	0.05	0.03	0.04	0.02	0.05	0.15	0.05
MnO	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02
P_2O_5	0.03	0.07	0.03	0.08	0.05	0.08	0.05	0.1	0.06	0.06	0.06
Cr_2O_3	0.01	0.02	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02
LOI	4.7	7.7	4.5	8.9	6.9	8.3	8.8	7	10	9.8	7.66
TOTAL	99.99	99.73	99.93	99.77	99.84	99.73	99.72	99.77	99.78	99.72	99.8
CIW	99.7	99.8	99.3	99.9	99.8	99.9	99.8	99.8	99.8	99.8	99.76
CIA	99.3	99.7	98.9	99.6	99.5	99.7	99.6	99.7	99.6	99.2	99.48
PIA	99.7	99.8	99.4	99.9	99.8	99.9	99.8	99.8	99.8	99.8	99.76

Table 5. Major oxide concentration for the sediments within the study area

TiO₂ increases slightly with Al₂O₃, suggesting that TiO₂ is probably associated with Phyllosilicate especially with illite (Dabard, 1990), this is also statistically suggested by the strong positive correlation between TiO₂(%) and Al₂O₃(%) (Figure 9). However the correlation values for Fe₂O₃, and Na₂O, with Al₂O₃ are negative suggesting their non association with phyllosilicates which implies probably other source of input (Figures 10 and 11). The correlation values with K₂O (R² = 0.08) (Figure 12) are also positive suggesting the input of aluminosilicate and feldspar (Akarish & El Gohary, 2008). Negative correlation is shown by SiO₂ due to most of the silica being sequestered in quartz as indicated by Osman (1996) (Figure 13). The relatively high values of K₂O/Na₂O average ratios(Table 5) is attributed to the presence of albitic plagioclase, K-feldspar, mica and illite (Pettijonh et al., 1963; McLennan et al., 1983; Nath et al., 2000; Osae et al., 2006). Compared to other major

elements, the concentration of Fe₂O₃ and TiO₂ indicates the probably presence of iron-titanium minerals (haematite and anatase rutiles) (Pearse et al., 1999). The low average value of Al₂O₃/SiO₂ (Table 5) for the sandstones (0.28) is also an indication of quartz enrichment (Bhatia, 1983), this is in contrast with the high average ratio of SiO₂/Al₂O₃ for sandstones (4.31). This ratio is an indication of the weathering profile and from the high average for sandstone, because most of the feldspar content has been weathered away. Also the values of the ratio TiO₂/Al₂O₃ (0.08–0.13) and Na₂O/K₂O (0.06–0.45) suggest that the sediments are moderately chemically mature (Jenner et al., 1981). The trend of decreasing K₂O with increasing SiO₂ is sensitive to grain size, probably due to the decrease of clay content in the coarser sediments. Also correlation with MgO, MnO and CaO are negative and their values are insignificant. The positive correlation between K₂O and Al₂O₃ (Figure 14b) (R² = 0.08) suggest that the concentration of the K-bearing minerals have significant influence on the distribution of Al and suggests that the abundance of these elements is primarily controlled by the content of clay minerals (McLennan et al., 1983).

Also, the standard plot of Herron (1988) using log (Fe_2O_3/K_2O) against log (SiO_2/Al_2O_3) which is a modified version of Pettijohn et al. (1972) was employed to classify the sediments of the study area. From these plots (Figure 14), it is indicated that the sediments from the study area plotted within the Fe sand, sublitharenite and wacke fields. The Fe-sand field is an indication of the presence of ferruginised sandstone within the Formation under study which further suggests an incursion of fluvial current. This is consistent with the presence of reddish or brownish (iron coated) sandstone beds, observed in the field.



Figure 9. Positive correlation chart of TiO₂ versus Al₂O₃



Figure 10. Negative correlation chart of Fe₂O₃ against Al₂O₃



Figure 11. Correlation chart of Na₂O against Al₂O₃



Figure 12. Positive correlation chart of K₂O against Al₂O₃



Figure 13. Negative correlation chart of SiO₂ against Al₂O₃



Figure 14. Classification of terrigenous sandstone within the study area (after Herron, 1988)

3.3 Trace Element Geochemistry

Trace element geochemistry is very useful particularly for the purpose of carrying out provenance studies (McLennan et al., 1990; 1993). They can also be used to deduce the palaeotectonic setting of sedimentary successions (Bhatia & Crook, 1986; Floyd & Leveridge, 1987; McLennan, 1989a; 2001). They are also most suited for provenance and tectonic setting determinations because of their relatively low mobility during sedimentary processes and their low residence time in sea water (Holland, 1978). These elements are transported quantitatively into clastic sedimentary rocks during weathering and transportation and thus would reflect the signature of the parent materials (McLennan, 1989b). Ajayi et al. (2006) grouped trace elements into compatible and incompatible types. According to him, Cr, Ni and Zn fall into the first group, while, Ba, Co, Cs, Au, Br, Ga, Zr, Ge, Hf, Rb, Se, Sc, Ta, Th and U belong to the second type. Trace element concentrations (in ppm) are shown in (Table 2). Bauluz et al. (2000) and Lopez et al. (2005) have also created classification scheme for representing trace element abundances and distribution relative to the Upper Continental Crust (UCC). These are the large ion Lithophile elements (LILE), Sr and Ba; the High Field Strength Elements (HSFE), Zr, Y and Nb; and the Transition Trace Element (TTE) Cr, Ni, and Sc.

3.4 The Large Ion Lithophile Elements (LILE)

The positive correlation of Sr and Ba with Al_2O_3 ($R^2 = 0.67$ and 0.89) suggests that their distribution is mainly controlled by phyllosilicates (Lopez et al., 2005). The Sr content (4.7–189.7) of the samples is variable because of the many influences on Sr in warm temperature depositional environments (Fairbridge, 1972). For instance, the distribution of Sr can be affected by the presence of Ca, additional Sr can be incorporated in diagenetic carbonate and fractionation of Sr can result from the weathering of feldspars, particularly plagioclase. The significant positive correlation ($R^2 = 0.52$) between Ba and K₂O suggests that Ba is mainly associated with a feldspar component as it is an alkaline earth metal.

3.5 The High Field Strength Elements (HSFE)

Preferentially, Zr, Y, Hf, Nb are portioned into melts during crystallization and anatexis (Feng & Kerrich, 1990) and as a result, these elements are enriched in felsic rather than in mafic minerals. Additionally they are thought to reflect provenance composition as a result of their immobile behavior (Taylor & McLennan, 1985). The high field strength elements (Zr, Nb, Hf and Y) generally show consistent inter-relationships as do the ferromagnesian trace elements (Ni, V, Co and Sc). These trace element relationships illustrate the chemical coherence and uniformity of the sandstones. The Zr/Y values for the analyzed sandstones range from (25.94–171.11). This suggests that Zr is controlled by several depositions of weathered and transported fragments of the source rocks in the sedimentary basin.

3.6 The Transition Trace Elements (TTE)

The transition trace elements are positively correlated with Al_2O_3 . The high correlation values of Ni (0.50) and Sc (0.86) indicates that they are mainly concentrated with phyllosilicates.

3.7 Rare Earth Elements Geochemistry

Rare-earth elements are regarded as among the least soluble trace elements and are relatively immobile during low-grade metamorphism, weathering and hydrothermal alteration. They are effective indicators of sediment source when compared to Upper Continental Crust (UCC), Oceanic Crust (OC) and mantle materials.

The pathways followed by elements during weathering (either from continent and or oceanic) of rocks and subsequent deposition as sediments on the ocean floor are best understood by the behaviors of REE in authigenic and biogenic sedimentary phases and seawater. Their behavior often reveals their source but more importantly the chemical property of the depositional environment that may control their accumulation. The distribution of REE in different masses of seawater strongly reflects their fractionation in sediments. Whereas the relative concentration of REE in rivers reveal their removal from seawater by authigenic and biogenic phases resulting in decrease of their total concentration, depletion of Ce and an enrichment of heavy REE relative to light REE (Piper, 1974). It is also worthy of note that REE patterns are used widely for provenance characterization (Taylor & McLennan, 1985; McLennan, 1989). Also the concentration of REE's in sediments (Table 3) results from the competing influences of the provenance, weathering, diagenesis, sediment sorting and the aqueous geochemistry of the individual elements (Nesbitt et al., 1980). The REE chondrite – normalizing factors used for this study are from Wakita et al. (1971). Besides the normalized plots, other parameters used to characterize the REE abundance in rocks include:

1: ΣREE

2: HREE (Gd/Yb)_N

3: LREE (La/Yb)_N

4: ($\Sigma LREE/\Sigma HREE$) the ratio of the sum of light rare earth elements to the sum of heavy rare earth elements

5: Total REE (La/Yb)_N

6: Eu/Eu* anomaly which is the ratio of actual normalized Eu to interpolated normalized Eu for non-depletion or enrichment of the chondrite-normalised plots and is calculated by the following equation:

 $Eu/Eu^* = \sqrt{EuN} / (SmN \times GdN).$

7: $Ce/Ce^* = 5CeN/[4LaN+SmN]$

Note: N and * indicate chondrite normalized elements.

In this study, the concentration of the rare-earth elements is highly variable with appreciable enrichment in the LREE (La-Nd) over the HREE (Er-Lu) as can be observed from the chondrite normalized values (Figure 20). The middle REE's are the least enriched with its sharp concave shape. The sediments of the study area point to a distinctively mean negative anomaly (0.65). Eu/Eu* is a parameter used to evaluate the abundances of plagioclase in an igneous or its sedimentary derivative (McLennan et al., 1990). Thus the ratio Eu/Eu* is a measure of the europium anomaly and a value greater than 1.0 indicates a positive anomaly whilst a value less than 1.0 is a negative anomaly (Taylor & McLennan, 1985). Higher LREE/HREE ratios, and negative Eu anomalies denotes felsic source rock (Taylor & McLennan, 1985; Wronkiewicz & Condie, 1989). The value of 0.65 in this study coincides with the range of sediments from felsic sources (0.40-0.94) according to Cullers et al. (1988); Cullers (1994); Cullers and Podkovyrov (2000).



Figure 15. Normalized Rare earth element abundance of the sediments within the study area (after Wakita et al., 1971)



Figure 16. Chondrite normalised spider diagrams for rare earth elements (after Saunders & Tarney, 1984)

Also the negative anomaly also implies a less fractionated source probably of andesitic origin. In tectonic settings where plagioclase is not found, there is no evidence of systematic Eu enrichment in sediments over co-existing muds (Nathan, 1976; Bhatia, 1985). This accounts for the depletion of Eu especially in sands that have been re-worked. This can be said to be true from the enrichment of Eu in shales and its depletion in sandstones.

Ce/Ce* may be used as a means of determing the environmental conditions at the time of deposition since higher values than one tentatively depict an oxidizing environment (McDaniel et al., 1994; Milodowski & Zalasiewicz, 1991) and in this case the mean value of Ce/Ce* is greater than one (2.39). This goes to show that the sediments were deposited in an oxidizing environment. There is also a prominent trend of general decrease, of HREE/LREE ratio with the increase of Σ REE. The enrichment of LREE and moderately negative Eu anomaly reflect their relative abundance in the crust (Goldschmidt, 1954), while the depletion of the HREE is due to their ability to form soluble complexes in seawater (Goldberg et al., 1963). The REE have to a large extent are diagenetically incorporated into the sediments. The enrichment of the REE's especially in sandstones could be caused by addition of heavy minerals especially zircon. Finally, the large spread of La/Sc ratios clearly points to different source compositions as the sediments comprise high La/Sc ratios (1.10–9.50) with an average of 3.82 (UCC after McLennan et al., 2006), (2.22). This is true as can be seen from the sediments that exhibit quartzose sedimentary provenance, intermediate igneous provenance and felsic igneous provenance from the discriminant function plots (Figure 18). But the negative Eu anomaly and higher LREE/HREE supports felsic sources. This goes to show that the sandstones are not dominated by one source area alone but a blend of various sources probably as a result of one or more sedimentary cycles, although, they tend towards felsic sources.

3.8 Source Area Weathering

The weathering history of ancient sedimentary rocks can be evaluated in part by examining relationships among the alkali and alkaline earth elements. (Nesbitt & Young, 1982). This is because alteration of igneous rocks

during weathering results in depletion of alkali and alkaline earth elements and preferential enrichment of Al_2O_3 in sediments. The most widely used indices for quantitative estimation of the degree of chemical weathering undergone by the rocks of the provenance area of clastic sediments, include; the Chemical Index of Alteration (CIA) proposed by Nesbitt and Young (1982), and Plagioclase index of Alteration (PIA) by (Fedo et al., 1995). High CIA and PIA values (75–100) indicate intensive weathering in the source area whereas low values (≤ 60) indicate low weathering in the source area (Osae et al., 2006). Other indices also used are the Chemical Index of Weathering (CIW) (Harnois, 1988). Summary of CIA, PIA and PIW values are shown in (Table 5).

The CIA=100[Al₂O₃ / (Al₂O₃ + CAO + Na₂O + K₂O)] The PIA=100[(Al₂O₃ - K₂O) / (Al₂O₃ + CaO + Na₂O - K₂O] The CIW=100[Al₂O₃ / (Al₂O₃ + CaO + NA₂O)]

These values are slightly variable within a narrow range and may be due to low concentrations of the alkalis and alkaline earth elements in the source area. Nevertheless, majority of the samples show CIA, PIA and CIW values greater than 60% indicating moderate to high (intensive) weathering either at the source or during transport before deposition (McLennan, 1993; Fedo et al., 1995). From the observed sub-angular to sub-rounded shapes of the quartz grains as seen from the petrographic studies and their high quartz percentage (75–90%) as well as their high alteration indices, indicating intensive weathering. It can be inferred that the sediments are compositionally mature. Also, the relationship between Th/U ratio and Th concentration can also be applied as an estimate of the degree of weathering in sedimentary rocks (McLennan et al., 1993). Both Th and U are relatively immobile during weathering, although, U may change its redox state during reworking under aerobic conditions and it is thus more readily removed from the system thereby increasing the Th/U ratio above upper crust igneous values. The Th/U ratio in most upper continental rocks is typically between 3.5–4.0 (McLennan et al., 1993). In sedimentary rocks, Th/U values higher than 4.0 may indicate intense weathering in the source areas or sedimentary recycling. Th/U ratios of the sediments range from 3.1–8.2 with an average of 4.54. This is an indication of intense weathering in the source areas or sediment recycling. Low Th/U ratios are commonly seen in active margin settings where rapid accumulation and burial of sediments can occur.

3.9 Provenance Signatures

The depositional environments for sediments within the study area were classified using the geochemical classification of (Herron, 1988). Here sediments plotted within the Fe sand, wacke to sublitharenite fields. Thus, it can be seen that the sandstones have undergone ferruginisation and this corresponds to their lithologic description and petrographic studies.

Several classifications have been proposed to discriminate from various tectonic settings (Maynard et al., 1982; Bhatia, 1983; Bhatia & Crook, 1986; Roser & Korsch, 1986). The provenance signature study employed for this study helps distinguish the sources of the sediments into four provenance zones, mafic, intermediate or felsic, igneous and quartzose sedimentary. This discriminant function diagram proposed by Roser and Korsch (1986) makes use of the oxides of Ti, Al, Fe, Mg, Ca, Na and K to effectively differentiate the sediments into four provenance zones. They also noted that biogenic CaO and SiO₂ in provenance determination could be eliminated by a plot in which the discriminant functions are based upon the ratios of individual TiO₂, Fe₂O₃, MgO and K₂O to Al₂O₃ which is more reliable and effective than the one based upon the raw oxides. The discriminant functions for the two plots used to discriminate the sediments within the study area are as follows:

The formula for raw oxides is given as:

Discriminant Function (DF1) = -1.773TiO₂ + 0.607Al₂O₃ + 0.76Fe₂O_{3 (T)} - 1.5MgO + 0.616CaO + 0.509Na₂O - 1.224K₂O - 9.09

Discriminant Function (DF2) = 0.445TiO₂ + 0.07Al₂O₃ - 0.25Fe₂O_{3 (T)} - 1.42MgO + 0.438CaO + 1.475Na₂O + 1.426K₂O - 6.861.

While that of the ratio plot is given as:

Discriminant Function (DF1) = $30.638 \text{ TiO}_2/\text{Al}_2\text{O}_3 - 12.541 \text{ Fe}_2\text{O}_3 \text{ }_{(T)}/\text{Al}_2\text{O}_3 + 7.329 \text{ MgO}/\text{Al}_2\text{O}_3 + 12.031 \text{ Na}_2\text{O}/\text{Al}_2\text{O}_3 + 35.402 \text{ K}_2\text{O}/\text{Al}_2\text{O}_3 - 6.382$

Discriminant Function (DF2) =56.500TiO₂/Al₂O₃ - 10.879 FeO (T) /Al₂O₃ + 30.875 MgO/Al₂O₃ - 5.404 Na₂O/Al₂O₃ + 11.112 K₂O Al₂O₃ - 3.89.

The plots using the raw oxides (Figure 17) revealed that the sediments within the study area were probably sourced mainly from both felsic igneous provenance and Intermediate igneous provenance while the ratio plots (Figure 18) also indicated felsic igneous provenance and quartzose sedimentary provenance. Recycled sources

represent quartzose sediments of mature continental provenance and the derivation of the sediments could be from a highly weathered granite-gneiss terrain and/or from a pre-existing sedimentary terrain, Roser and Korsch (1986). Also recycled sediments and sedimentary rocks allow expected enrichment of Zr, reflecting zircon addition as seen from the trace element study (McLennan et al., 1990; Zimmerman & Bahlburg, 2003). This is true as most of the sediments fell within the recycled mature polycyclic quartzose detritus otherwise known as quartzose sedimentary field as well as the intermediate igneous provenance with few falling in the felsic igneous provenance field from the raw oxides.



Figure 17. Discriminant function diagram for the provenance signature of sandstones using raw oxide (based on Roser & Korsch, 1988)



Figure 18. Discriminant function diagram for the provenance signature of Igbile using ratio plots (based on Roser & Korsch, 1988)

The intermediate igneous provenance cannot be ruled out as a large number of sediments also fall in that field. In this case, the sediments could have been sourced from pre-existing syenites or diorites. The felsic input must have come from pre-existing sedimentary terrain. This assertion also agrees with the palaeotectonic setting of the analyzed samples (after Dickinson & Suczek, 1979) where the sediments fell within the recycled orogen

provenance as well as continental block provenance. This is also in agreement with petrographic studies of sandstones where the sediments are predominantly made up of quartz with few inputs from rock fragments as well as feldspar.

3.10 Provenance and Tectonic Setting

Discriminant bivariate plot of first and second discriminant functions of major element analysis of the sediment within the study area (after Bhatia, 1983) where plotted to delineate the tectonic setting. From the plot it could be noted that the sediment plotted within the Oceanic Island arc (Figure 19).



Figure 19. Discriminant chart for sandstone within the study area (after Bhatia, 1983) showing the Oceanic island arc tectonic setting of the sediment

The discriminant function is as follows:

Discriminant function 1 = $-0.0447 \text{ SiO}_2 - 0.972 \text{ TiO}_2 + 0.008 \text{ Al}_2\text{O}_3 - 0.267 \text{ Fe}_2\text{O}_3 + 0.208 \text{ FeO} - 3.082 \text{ MnO} + 0.140 \text{ MgO} + 0.195 \text{ CaO} + 0.719 \text{ Na}_2\text{O} - 0.032 \text{ K}_2\text{O} + 7.510\text{P}_2\text{O}_5 + 0.303$

Discriminant function 2 = -0.421 SiO₂ + 1.988 TiO₂ - 0.526 Al₂O₃ - 0.551 Fe₂O₃ - 1.610 FeO + 2.720 MnO - 0.907 CaO-0.177 Na₂O - 1.840 K₂O + 7.244 P₂O₅ + 43.57

4. Conclusion

The petrography has helped to ascertain the composition and chemical maturity of the sandstones in the study area as well as establishing the provenance, tectonic setting, weathering conditions as well as transportation history from the source to the environment of deposition. Also the various aspects of the geochemistry employed contributed in no small measure to shed more light and corroborate the findings of the petrographic study.

The petrographic studies revealed multiple compositions for the sediments with quartz being the most dominant followed by low-grade sedimentary and metamorphic rock fragments, with little or no feldspar. The quartz grains are sub-angular to sub-rounded in shape, consisting of both monocrystalline and polycrystalline grains pointing to medium to high levels of transportation evidenced by the highly reduced feldspar grains that have been severely chemically altered, this is seen from Suttner's paleoclimatic settings classification where the sediments were plotted in the humid fields (Figure 8). The sandstones, based on framework composition were dominantly classified as litharenite and sub-litharenites according to Folk's classification scheme. This further ascertains the high levels of weathering and transportation of the sediments.

The bulk geochemical studies of the sediments revealed that SiO_2 is the dominant oxide followed by Al_2O_3 and Fe_2O_3 which constitutes over 95% while others like K_2O , TiO_2 , Na_2O , CaO, MgO and P_2O_5 constitute the rest. The SiO_2/Al_2O_3 ratios for the sediments are appreciably high indicating that the samples have been heavily weathered evidenced from the enrichment of quartz and depletion of feldspars. Also, the relatively high concentration of Fe_2O_3 and TiO_2 is an indication of iron-titanium minerals such as haematite and anatase rutiles, whereas the high K_2O/Na_2O ratios is attributed to the presence of plagioclase. The high values of Al_2O_3 may also

indicate a high kaolinite/illite ratio. The application of source area weathering using CIA, CIW and PIA values revealed that the sediments have been subjected to intense weathering at the source area as well as high levels of chemical weathering and transportation as evidenced from the thin-section studies. The use of Herron's model, classified the sediments as Fe sand, wacke and sublitharenite authenticating Folk's classification and buttressing the fact that the sediment have been chemically altered. Furthermore, the discriminant function plots of Roser and Korsch for the provenance signature revealed dominantly intermediate igneous provenance with inputs from felsic igneous, as well as quartzose sedimentary provenances. This is in consonance with petrologic study.

Discriminant plot for the tectonic of the sediments shows that the sediment under study is sourced from the oceanic island arc. It therefore implies that the sediments were deposited in plate interiors at a stable or in an intracratonic basin. Thus, the source of the sediments under study was from a stable cratonic and/or quartzose sedimentary organic terrain provenance. The negative correlation and high positive correlation of oxides against Al_2O_3 is a pointer to the fact that the sediments input are predominantly sourced from felsic igneous rocks of the southwestern basement complex and this is backed up by the negative Eu anormaly as seen from the flat diagram.

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