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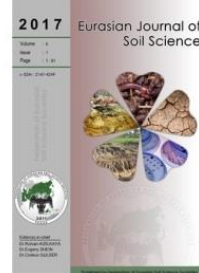
Depositional environments signatures, maturity and source weathering of Niger Delta sediments from an oil well in southeastern Delta State, Nigeria

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Abstract

Attempts have been made to classify the sediment on their degree of maturity. Compositional maturity is a reflection of intensity of weathering and a function of labile grains, unstable/stable rock fragments and stable quartz arenites. The main aim of this study is to investigate maturity and area of deposition and attempt to shed light on source area paleo-weathering conditions. Twenty one samples of shales and sandstones units were collected from a depth precisely between 1160 to 11,480m at a well in western Niger Delta, grinded, pulverized and sieved with less than 75µm. About 10g was packed and sent to Acme analytical Laboratory LTD., Vancouver, Canada. From the results, various plots and indexes inferring maturity and area of deposition were utilized. Using the A-K-F ternary plots of Englund and Jørgensen (1973), the depositional environment is transition zone. The silicate weathering indexes CIA, CIW and PIA values ranges from 45-65, on average indicates low to moderate weathering in the source area with extreme weathering of some sand fraction. Various calculated values of the weathering indices: Chemical Index of Alteration (CIA), Plagioclase Index of Alteration (PIA), Chemical Index of Weathering (CIW) and scatter plots of formulated ratios of Al/Na, K/Na, and Rb/K vs chemical index of alteration (CIA) were plotted. The moderate values below average suggest low to moderate weathering conditions in the source area or during transportation. This also inferred their recycling processes are insignificant. The clay content is low and feldspars are averagely high implying immaturity. The calculated ZTR index for the sand ranges from 36.4-75.0 from with an average mode of 55.5% implying almost all contain mineralogically immature sediments. The calculated Zircon- Tourmaline-Rutile (ZTR) index shows that majority of the sample depths have >43% ZTR index but below 75% which corresponds to generally immature sediments.

Keywords: PIA, CIW, CIA, AKF, ZTR index, weathering index, Niger delta, immature sediments, depositional environments.

Introduction

The use of geochemical composition of siliciclastic sedimentary rocks is a vital tool to know weathering and erosion dynamics (Nesbitt and Young, 1982) and post-depositional changes (Fedo et al., 1995, 1996). The extent and duration of weathering in siliciclastic sediments can be estimated by examining the relationships among alkali and alkaline earth elements (Nesbitt and Young, 1982). The use geochemical data from sediments to understand such sedimentary processes is increasing in use due to the specificity of some key trace elements in identifying minor components that are not easily recognized petrographically (Abd El-

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Rahman et al., 2009). The upper continental crust is established to be dominated by the presence of feldspars and volcanic glass (Nesbitt and Young, 1982, 1984). As a result, the dominant process during chemical weathering, transportation, deposition and soil formation is the degradation of labile feldspars from source rocks to its corresponding clay minerals. The intensity of degradation can infer its maturity, distance travelled from provenance. These and other such chemical processes are preserved and ultimately transferred to sedimentary records which gives a tenable signature for evaluating the original composition maturity and following weathering conditions (Akarish and Dessandier, 2011).

The Niger delta is situated at the intersection of an early cretaceous Atlantic and gulf of guinea triple junction. The southern and northern arms developed into Atlantic and gulf of guinea respectively as they grow into spreading events which cause separation of South-America from Africa (Ofoegbu, 1984). The third arm which is the Benue trough failed during late cretaceous to become an aulacogen. The development of cretaceous pro-deltas was terminated in the Paleocene by a major transgression. Niger Delta which stretches from Eocene to recent in age. The offshore boundary of the province is defined by the Cameroon volcanic line to the east, the eastern boundary of the Dahomey to the west, a two-kilometer sediment thickness to the south and sediment thickness greater than two kilometers to the southwest.

The Niger Delta province covers 300,000 km² and includes the geologic extent of the Tertiary Niger Delta (Akata-Agbada) Petroleum System (Kulke, 1995). First, shale diapirs formed from loading of poorly compacted, over-pressured, prodelta and delta-slope clays (Akata Fm.) by the higher density delta-front sands (Agbada Fm.). Second, slope instability occurred due to a lack of lateral, basin ward, support for the under-compacted delta-slope clays (Akata Fm). For any given depobelt, gravity tectonics were completed before deposition of the Benin Formation and are expressed in complex structures, including shale diapirs, roll-over anticlines, collapsed growth fault crests, back-to-back features, and steeply dipping, closely spaced flank faults (Evamy et al., 1978; Xiao and Suppe, 1992). The Tertiary section of the Niger Delta is divided majorly into three formations, representing prograding depositional facies that are distinguished mostly on the basis of sand-shale ratios. The three formation type are described in Short and Stäublee (1965) and Doust and Omatsola (1990). The Akata beginning in the Paleocene and through the recent was formed during lowstands when terrestrial organic matter and clays were transported to deep water areas characterized by low energy conditions and oxygen deficiency (Stacher, 1995). Little of the formation has been drilled so its estimated depth is about 7,000 meters thick (Doust and Omatsola, 1990). The formation is estimated to underlie the entire delta and it is as expected over pressurized. The deposition of the overlying reservoir; Agbada Formation which is the major petroleum- bearing unit began in the Eocene and continues into the Recent. The formation consists of parallic siliciclastics over 3700 meters thick and represents the actual deltaic portion of the sequence (Doust and Omatsola, 1990). The Agbada Formation is overlain by the third formation, the Benin Formation, a continental latest Eocene to Recent deposit of alluvial and upper coastal plain sands that are up to 2000 m thick (Avbovbo, 1978).

Weathering processes: The compositional maturity basically reflects the weathering process in source area and degree or extent of reworking/recycling and transportation. Typical compositionally immature sediments are located close to their source area or they have been rapidly transported and deposited with little reworking from a source area of limited physical and chemical weathering. The classification of sandstones and shales in this study is based on widely used but simple classification system which is a function of feldspar content, rock fragments, quartz grains and matrix after Pettijohn et al. (1972). Two percentages are used to subdivide terrigenous sandstone which is percentage of matrix (any clastic material finer than 30 microns or coarse silt). The other is its Composition of framework grains which is basically sand, quartz, feldspar, and rock fragments (lithics). These two major groups based on texture can be viewed as also being divided into whether the sandstones are composed of grains only, the arenites, or contain more than 15% matrix forming the wackes. For the arenite, quartz arenite is applied to those with 95% or more quartz grains, Arkosic arenites is a term for the arenite with more than 25% feldspar which exceeds the rock fragment content and litharenite is applied where the rock fragment exceeds 25% and is greater than feldspar. Two rock types transitional with quartz arenite are sub-arkose (5-25% feldspar and > rock fragments) and sub-litharenite (5-25% rock fragments and > feldspar). Climate in the source area can also play a major role in producing quartz arenites: tropical climate will breakdown and evacuate many of the unstable feldspar grains. A matures river channel, without steep slopes and generally undulating relief will enhance slow sedimentation rates and as such, quartz will dominate the detritus. Arkoses are known to be derived from feldspar especially orthoclase K-bearing feldspar in granites and granitoid gneiss. Climate and source area relief may also influence the production of arkoses apart from its provenance geology. Under

humid conditions, feldspars are weathered to clay minerals, so that semi-arid and glacial climates favor arkose formation. A very rapid erosion in a very high-relief environment will also favor arkose formation.

Various works has been done on the Niger delta clastic sediments but the precise area of deposition, their maturity and sediment transport has been very limited. The main aim of this study is to investigate maturity and area of deposition and attempt to shed light on source area paleo-weathering conditions using different perspective.

Material and Methods

The sampled were collected from a well in an oil field in Niger Delta. The exact coordinates is not detailed due to propriety and ownership rights of the oil well. The pictorial location of the well on regional Nigerian map is shown in figure 1.
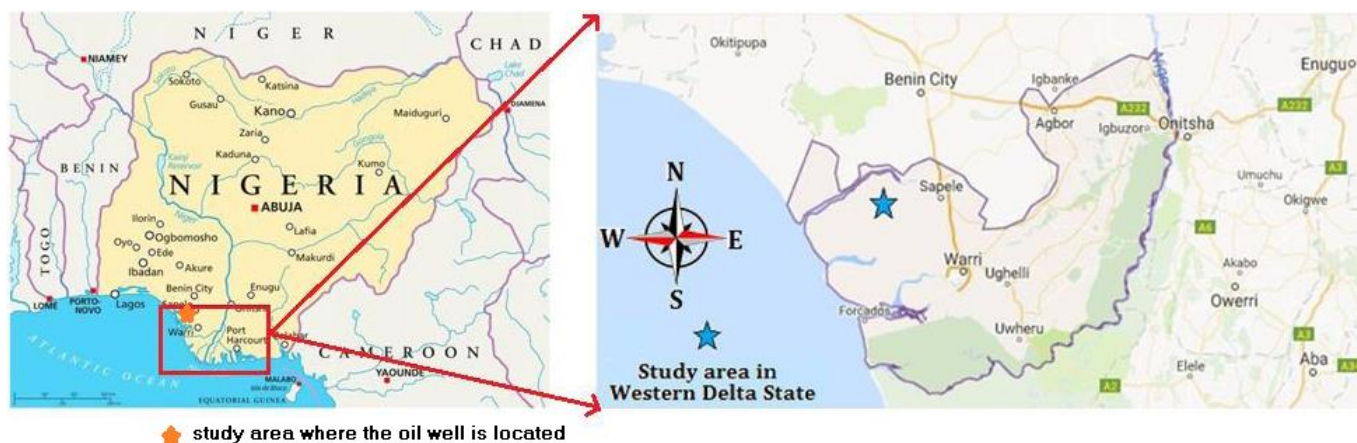

Figure 1. Pictorial location of the study area in western Niger Delta, Nigeria

The Niger delta extends from about longitudes 3°E and 9°E and latitudes 4°30N to 5°21N. It is situated at the intersection of an early cretaceous Atlantic and gulf of guinea triple junction. The low to intermediate weathering of the studied sediments may infer climate change towards arid and cold conditions that are unfavorable to weathering from situ. In this study, twenty-one core samples were collected and used for analysis. The analysis used in this project the major oxides, trace elements and heavy mineral analysis. The samples are first oven dried, washed with de-ionized water and dried again.

Major Oxides and Trace Elements

The samples were grinded and pulverized for both the major oxides and trace elements. The samples were reduced by sieving and crushing through a < 75μm. About 10g of the pulverized sample was packed in a suitable bag and sent to Acme analytical Laboratory LTD., Vancouver, Canada. The analyses were carried out by both Induced Coupled Plasma-Mass Spectrometry (ICP-MS) for trace elements and Induced Coupled Plasma-Emission Spectrometry (ICP-ES). The results of the major oxides are as illustrated in table 1 while trace elements in table 2.

Heavy Mineral Separation: Pretreatment, Setup and Procedure

Heavy mineral analysis of the sandstone sequence entails preparation of samples which includes size reduction, disaggregation and cleaning. The eight sand samples were subjected to pre-treatment by dis-aggregating about 50g 0f each of the coherent sediment samples to liberate individual mineral grains. It is followed by acid digestions which include boiling in dilute HCl for 15 minutes to remove dolomites. It was later soaked in dilute HCl for 24 hours so as to remove the carbonates and calcareous particles from the unconsolidated sediment. It also rid the grains of iron oxide coating. The samples are washed thoroughly with distilled water to decant the removed carbonate and any clay fraction present. The sample is spread on filter paper, air dried and further oven dried.

The gravity settling techniques was used for the separation of the heavy minerals. This was accomplished by the use of bromoform of specific gravity 2.80. The light mineral grains either floated or were trapped as middling within the bromoform while the heavy mineral settled into the stem of the separating funnel. 8 grams of each pre-treated sample is poured into the separating funnel (containing bromoform) and stirred thoroughly until the heavy mineral could no longer be observed to settle into the stem of these separating funnel.

Table 1. Eleven major element oxides in percentages after Oni et al. (2014)

Samples Depth (in meters)	Lithology	FeO	Fe_2O_3	CaO	P_2O_5	MgO	TiO_2	Al_2O_3	Na_2O	K_2O	MnO	SiO_2	Total
		%	%	%	%	%	%	%	%	%	%	%	%
1160-1180	Sand	0.5	0.5	1.1	bdl	0.1	0.1	1.7	0.2	0.2	bdl	95.5	100.0
1560-1580	Shale	0.4	0.5	0.6	bdl	0.1	0.1	1.5	0.4	0.3	bdl	96.0	100.0
1960-1980	Sand	1.0	1.1	0.8	bdl	0.1	0.1	1.7	0.6	0.6	bdl	93.8	100.0
2960-2980	Shale	2.2	2.4	0.4	bdl	0.2	0.3	5.1	1.8	1.7	bdl	85.8	100.0
3960-3980	Shale	4.3	4.7	0.4	bdl	0.4	0.7	11.1	2.6	3.0	bdl	72.7	100.0
4560-4580	Shale	3.9	4.4	0.4	bdl	0.4	0.7	13.5	3.3	3.1	bdl	70.1	100.0
5460-5480	Shale	3.6	4.0	0.2	bdl	0.1	0.3	3.8	4.6	2.9	bdl	80.4	100.0
5760-5780	Shale	4.7	5.2	0.2	0.1	0.1	0.8	6.5	4.5	2.9	bdl	74.9	100.0
6160-6180	Shale	3.4	3.8	0.7	0.1	0.2	0.6	11.0	3.7	2.8	bdl	73.8	100.0
7060-7080	Sand	2.9	3.2	0.7	0.2	0.1	0.3	3.1	6.0	4.3	bdl	79.2	100.0
7260-7280	Sand	2.8	3.2	0.7	0.1	0.1	0.3	4.4	6.8	4.7	bdl	76.9	100.0
7560-7580	Sand	3.2	3.6	0.6	0.1	0.2	0.3	5.4	6.0	4.5	bdl	76.0	100.0
7760-7780	Shale	4.3	4.8	0.8	0.1	0.6	0.6	9.0	1.9	3.1	bdl	74.7	100.0
7960-7980	Shale	2.8	3.1	0.8	0.1	0.2	0.3	5.4	4.7	3.9	bdl	78.6	100.0
8060-8080	Shale	2.9	3.2	1.4	bdl	0.6	0.2	3.5	1.0	1.7	bdl	85.5	100.0
8160-8180	Sand	3.0	3.4	3.1	0.1	1.6	0.3	4.8	0.7	1.7	bdl	81.2	100.0
8560-8580	Sand	3.8	4.2	1.7	0.1	0.4	0.2	3.9	1.0	1.6	bdl	82.9	100.0
8960-8980	Shale	4.7	5.2	0.9	0.1	0.4	0.8	11.7	0.9	2.5	bdl	72.7	100.0
10360-10380	Shale	2.7	3.0	0.5	0.1	0.3	0.4	6.0	1.3	2.8	bdl	82.8	100.0
11060-11080	Shale	7.7	8.6	0.7	0.2	0.9	0.8	13.5	1.2	2.7	0.1	63.6	100.0
11460-11480	Shale	6.1	6.8	0.5	0.1	0.5	0.9	14.6	1.1	2.1	0.1	67.2	100.0

*bdl values are values below detection limit at approximately 0.0.

Table 2. Some trace element in ppm as reported from the analysis with their corresponding MDL values

Samples Depth In meters	Lithology	Mo	U	Th	Sr	Cd	Cr	W	Zr	Sn
1160-1180	Sand	1.42	0.7	3.4	59	0.05	10	3.0	43.9	1.0
1560-1580	Shale	0.63	0.6	2.6	69	0.03	7	3.1	32.4	0.6
1960-1980	Sand	1.09	0.8	3.2	68	0.07	12	5.7	44.0	0.9
2960-2980	Shale	3.50	1.6	5.5	64	0.16	36	8.2	90.4	1.7
3960-3980	Shale	3.38	2.8	9.9	123	0.19	70	13.7	163.0	2.3
4560-4580	Shale	3.31	2.8	10.4	97	0.19	80	8.6	148.0	2.8
5460-5480	Shale	6.29	0.8	3.8	34	0.19	63	17.1	93.3	1.9
5760-5780	Shale	6.70	1.2	5.8	46	0.26	82	44.8	176.5	2.6
6160-6180	Shale	3.50	1.7	6.8	252	0.20	67	6.1	154.8	2.5
7060-7080	Sand	2.85	0.5	2.6	447	0.32	61	9.4	77.8	1.8
7260-7280	Sand	3.67	1.1	1.7	247	0.33	94	9.6	100.7	2.0
7560-7580	Sand	2.90	0.8	2.2	236	0.50	125	10.4	83.6	1.8
7760-7780	Shale	2.35	1.6	6.6	225	0.14	57	8.4	115.6	2.0
7960-7980	Shale	2.94	0.7	2.2	284	0.54	166	17.4	76.3	2.1
8060-8080	Shale	3.58	1.1	3.4	183	0.17	41	26.8	69.0	1.2
8160-8180	Sand	6.37	1.5	6.4	168	0.48	51	36.5	105.2	1.5
8560-8580	Sand	2.97	0.8	3.8	162	0.53	197	58.0	53.8	1.6
8960-8980	Shale	3.34	2.3	10	193	0.45	94	11.4	156.0	2.4
10360-10380	Shale	1.57	1.1	6.6	164	0.26	46	2.8	97.6	1.1
11060-11080	Shale	2.15	1.9	10.1	168	0.21	93	2.2	182.3	3.1
11460-11480	Shale	2.67	1.9	9.0	235	0.22	96	2.8	190.8	3.1
	MDL	0.05	0.1	0.1	1	0.02	1	0.1	0.2	0.1

The mixture was then allowed to settle for about 20 minutes. The accumulated heavy minerals in the stem were allowed to pass with the bromoform into the filtering funnel by carefully opening the stop-lock. The heavy minerals were held back on the filter paper in the funnel while the bromoform drained away into the 500ml conical flask as filtrate. The re-cycled bromoform is used again. The filter paper was then removed from the measuring funnel and placed on a clean flat surface where it was mildly washed with acetone, and allowed to dry. The acetone helps to neutralize the effect of the bromoform. Separated heavy minerals were spread on the mountant which consist of a glass slide with Canada balsam. The preparation includes the splitting of the heavy mineral fractions. It also includes grain mounts in which the grains were sprinkled evenly unto the surface of a glass slide with Canada balsam. The advantage of the Canada balsam is that it has mollass-consistency which is excellent for crystal rolling. This enables the examination of grains in different orientations and thus assists greatly in the identification of difficult minerals.

The microscopic identification and grain counting which involves the use of ribbon grain counting method was employed. Five strips of masking tapes were used to cover the section of the slide on which the heavy minerals were mounted mimicking the ribbon technique after Galehouse (1971). The sample slides were thoroughly previewed in systematic transverse starting from the base. Following standards used for identification, a tally of 300-500 grains in several transverses across the slides were used to get a reasonable percentage of each mineral present. This was achieved by removing a strip of masking tape at a time and then counting from base to top of the exposed section of the slide the total number of mineral grains. After that the non-opaque minerals were identified, counted and tabulated.

Results and Discussion

Depositional Environments Signatures

Ternary plots of Englund and Jørgensen (1973) proposed that certain classification of soil samples may be employed to ascertain the depositional environment of the sediments of the basin. This employs the chemical classification on the basis of AKF [Al_2O_3-(K_2O+Na_2O+CaO)-(Fe_2O_3+MgO)] contents. The samples were plotted on the ternary diagram of the AKF plots which reveals whether the sediments are deposited in continental, transition and/or marine zone. The results show a gradual transition of the sediments of the basin from continental to marine environment, majorly falling within the transition zone as indicated in figure 2.
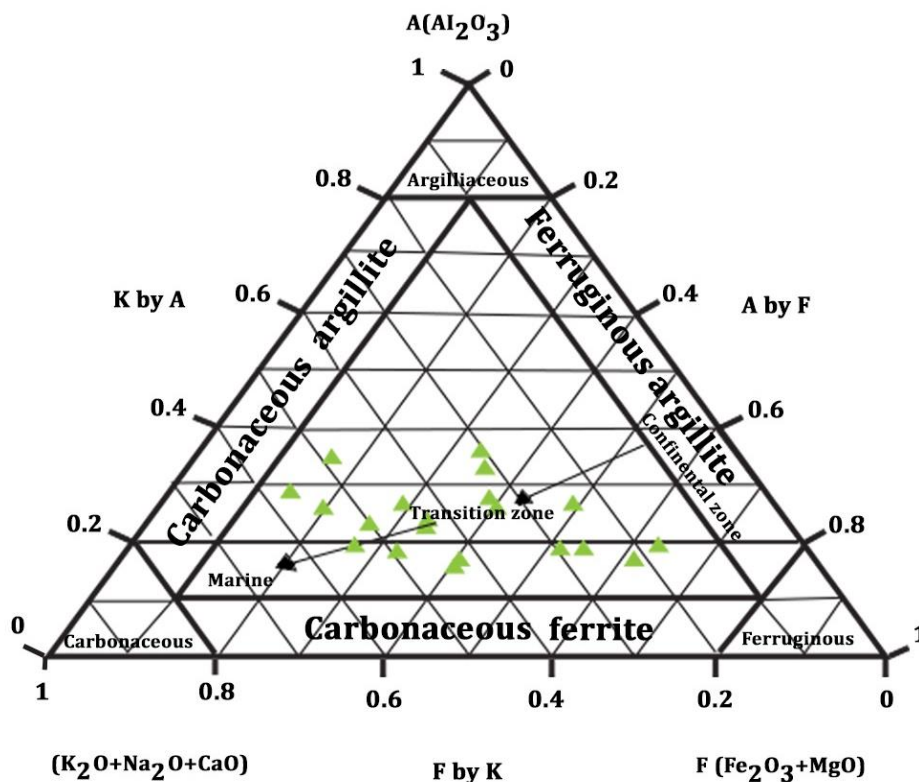

Figure 2. A-K-F plots for sediments from well "Y" after Ternary plots of Englund and Jørgensen (1973).

Maturity of Sediments

Major oxide geochemical analysis can be used to determine sediment classification and maturity conditions. The clastic sediments are considered as sodic and non-calcareous continental sands. A Low CaO oxide suggests a chemical destruction under oxidizing conditions during weathering. Sediments with little or no tertiary material have little or no MnO, P_2O_5 and relatively high Al_2O_3 values

Ratio of Quartz to Feldspar and Rock Fragments

This ratio is an index of compositional maturity, reflecting the difference between super mature quartz arenites typically white to light gray consisting almost entirely of sand-sized monocrystaline quartz grains which contains heavy minerals such as tourmaline, zircon, and rutile as well as resistant grains of chert, metaquartzite (95% - 97% SiO_2, 0.5% - 1.0% Al_2O_3), and dirty sand with lots of soft, unstable, decomposable rock fragments and feldspar. It is a ratio that zones the samples into arenites that are texturally clean, matrix free/matrix poor arenacious material or into argillaceous matrix rich wackes/dirty sandstones. Continuous weathering and recycling should ultimately generate sand residues composed of only the most resistant materials which are the quartz arenites. In these ratio plots, the quartz usually SiO_2 is used to correlate with feldspars. In terms of mineralogical maturity, a rock is immature when it contains a mix of stable (quartz arenites) and unstable (feldspar and clay) minerals, and is mature when it contains only stable (quartz) minerals. By describing sedimentary rocks in terms of their percentage of quart, feldspar, and lithic fragments (and ignoring accessory minerals), it is possible to use ratios as index markers. This implies that the ratio of feldspar to lithic fragments can serve as an index of sands provenance. If a rock has more lithic fragments relative to feldspars, then the source rock is probably resistant supracrustal rocks (like volcanics). If a rock has more feldspars to lithic fragments, then the source rock is probably less resistant subcrustal rocks (like plutons).

Commonly employed geochemical criteria for estimate of sedimentary maturity are the SiO_2 content as well as SiO_2/Al_2O_3 ratio (Pettijohn et al., 1972). This reflects the relative presence of clays, feldspar and quartz content. There is a more efficient method to determine chemical maturity by determining the alkali content ($Na_2O + K_2O$), which is a function of the feldspar content. Using an index of chemical maturity and the Na_2O/K_2O ratio, Pettijohn et al. (1972) proposed a classification of terrigenous sands based upon a plot of $\log (Na_2O/K_2O)$ vs $\log (SiO_2/Al_2O_3)$. The plot for the analyzed samples is as shown in figure 3. Herron (1988) modified the diagram of Pettijohn et al. (1972) using $\log (Fe_2O_3/K_2O$ along the Y-axis instead of $\log (Na_2O/K_2O)$. The SiO_2 content and SiO_2/Al_2O_3 ratio are the most commonly used geochemical criteria to determine the abundance of quartz, feldspar and clay contents and for differentiating mature and immature sediments (Potter, 1978). The ratio Fe_2O_3 (total)/K_2O allows arkoses to be more successfully classified and its mineral stability may be easily accessed. As confirmed for ferromagnesians, they tend to be less stable during weathering and this is illustrated as Fe-Shale transition to Fe-sand and finally disappearing with intense weathering in the more resilient quartz arenites. The plot is shown in figure 4. The ratio Fe_2O_3 (total)/K2O allows arkoses to be clearly illustrated.
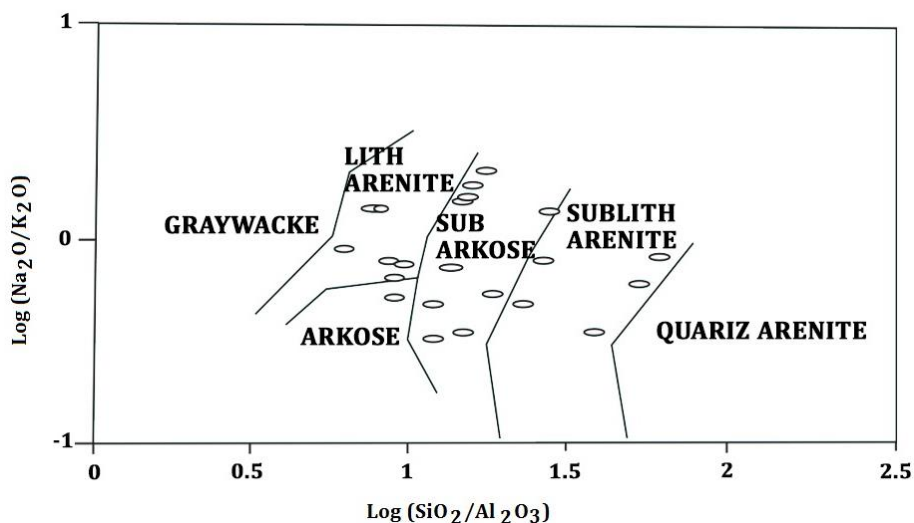

Figure 3. The classification of terrigenous sandstones using $\log (Na_2O/K_2O)$ vs $\log (SiO_2/Al_2O_3)$ from Pettijohn et al. (1972) with boundaries redrawn by Herron (1988).
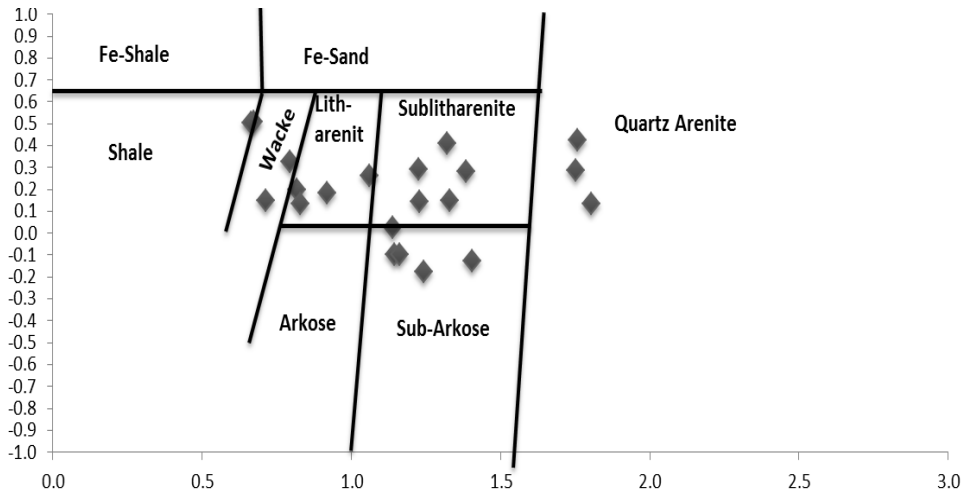
Figure 4. The classification of terrigenous sandstones and shales using log (Fe₂O₃/K₂O) vs log SiO₂/Al₂O₃) after Herron (1988).

The plot of figure 3 and figure 4 based on the basic oxides can be used to deduce the percentage of quartz, feldspars and lithic fragments. As observed from figure 3 and 4, most of the samples plotted as litharenites, sublitharenites and subarkose. Majority of the samples in litharenites implies the rock fragment exceeds 25% and is greater than feldspar. Litharenites usually contain 30-80% quartz and 25-50% lithic fragments. The compositional maturity may vary broadly depending on the nature of the lithic fragments but generally litharenite sediments are termed immature according to Folk classification system that prescribed sediments containing more than 5% clay and sand grains as poorly sorted, angular as immature. The sublitharenites implies 5-25% rock fragments and > feldspar while sub-arkose is 5-25% feldspar and > rock fragments. According to folk classification of textural maturity, a sedimentary rock is texturally immature when it contains greater than 5% clays/silt or a larger portion of unstable minerals such as feldspar, and lithic fragments. The litharenites, sublitharenites and subarkoses points to textural immaturity of the sediments

The ratio of quartz to other components (feldspar and lithic fragments combined) is an index of compositional maturity. Sediment with low proportion of quartz and a higher proportion of soft-unstable elements is an immature rock. If the sample contains a high proportion of resistant, stable quartz compared to the unstable elements it is a more mature rock. In terms of textural maturity, a rock is immature when it contains angular, poorly sorted grains, and it is mature when it contains rounded, well-sorted grains. Very few samples plotted in quartz arenites in figure 4 and none in figure 3 confirms majority of the sediments are angular and poorly sorted, probably produced from short transportation and limited reworkings. This emphasized the feldspars, lithic and angular fragments have not been broken down by mechanical weathering, wearing and abrasion to remain very stable and resilient quartz arenites.

Source Area Weathering Provenance

The concentrations of major elements can be affected by diagenesis and metamorphism, so that prior to any interpretation, their weathering from the source before mobility must be studied (McLennan, 2001). The weathering history of ancient sedimentary rocks can be evaluated in parts by examining the relationship among the alkali and alkaline earth elements (Al₂O₃, CaO, Na₂O and K₂O) (Nesbit and Young, 1989). Generally the alteration of igneous rock during weathering results in the depletion of alkali and alkaline earth elements and preferential enrichment of Al₂O₃ in the sediments. Al₂O₃ and K₂O content may relate to the presence of potassium feldspars (orthoclase and microcline), illite and mica. The source of Na₂O is principally related to plagioclase feldspar since its (Ca-Na) feldspar. MgO content is related mostly to the presence of dolomitic materials as fragments or cement. Calcite cement and rock fragments are the main source for CaO. The weathering effects are evaluated in terms of the molecular percentage of the oxide components as well as estimated mineralogical composition. A good measure of the degree of chemical weathering can be obtained by the calculation of Silicate weathering indexes such as

Chemical index of alteration CIA (Nesbit and Young, 1989).

$$\text{The CIA } = 100 \ * [(Al_2O_3 / (Al_2O_3+CaO^*+Na_2O+K_2O)]$$

CaO^* is the calcite bound in silicates. The CIA can be shown graphically with the A (Al_2O_3) – CN ($CaO+Na_2O$) – K (K_2O) composite plots generally termed A-CN-K ternary diagram, with the corresponding CIA values to the left as shown in figure 5. This values obtained from the ternary plots sharply equates the calculated values from the CIA formula given above. High CIA values reflect removal of labile cations (Ca^{2+}, Na^+, K^+) relative to stable residual constituents (Al^{3+}, Ti^{4+}) during weathering implying intensive weathering activities probably with long distance, slow sedimentation rates and humid tropical conditions. Conversely, low CIA values indicate the near absence of chemical alteration and might reflect cool and arid conditions (Fedo et al., 1995).

Table 3. Table showing the sample depth with corresponding silicate weathering indices: Ruxton ratio, CIW, PIA and CIA values

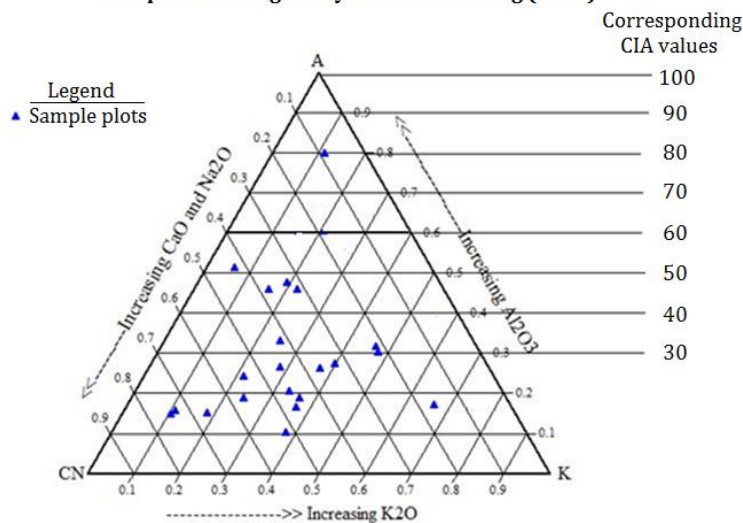| Samples Depth In meters	Lithology	RUXTON RATIO	CIW VALUES	PIA VALUES	CIA VALUES
1160-1180	Sand	57	55	52	51
1560-1580	Shale	64	59	53	52
1960-1980	Sand	56	54	43	45
2960-2980	Shale	17	70	61	56
3960-3980	Shale	7	79	73	65
4560-4580	Shale	5	79	74	67
5460-5480	Shale	21	44	16	33
5760-5780	Shale	12	58	44	46
6160-6180	Shale	7	72	65	60
7060-7080	Sand	21	32	-20	22
7260-7280	Sand	18	37	-5	26
7560-7580	Sand	14	45	12	33
7760-7780	Shale	8	77	68	60
7960-7980	Shale	15	50	21	37
8060-8080	Shale	8	60	44	47
8160-8180	Sand	17	56	45	47
8560-8580	Sand	21	60	46	48
8960-8980	Shale	6	87	84	73
10360-10380	Shale	14	76	63	56
11060-11080	Shale	5	87	85	75
11460-11480	Shale	5	90	89	80
AVERAGE		18.95	63.19	48.2	51.4

Figure 5. CIA value from the samples on plot of A-CN-K denoting (Al_2O_3-CaO&Na_2O-K_2O) as designed by Nesbit and Young (1989).

The calculation of chemical index of alteration is a useful means to describe the degree of weathering. This is because the CIA provides vital information on the relative abundance of the unweathered materials especially the feldspars which contains the labile cations (Ca^{2+}, Na^+ and K^+) (Osahe et al., 2006). The higher the CIA values, the closer the CIA value is to 100, the more weathered the rock. A CIA value of 100 suggests complete alteration of feldspar and labile to fine argillaceous aluminum rich clay weathering products, which are basically kaolinite and chlorite (with no feldspar).

Weathering indices of sedimentary rocks can provide useful information of tectonic activity and climatic conditions in the source area. According to Jacobson et al. (2003), the increase in chemical weathering intensity has been attributed to decrease in tectonic activity and/or the change of climate towards warm and humid conditions which are more favorable to chemical weathering in the source region. The low to intermediate weathering of the observed sediments may thus be linked with increase in tectonic activity and/or climate change towards arid and cold conditions that are unfavorable to weathering from situ.

A derived CIA value between 90 and 100 (near 100) implies fine argillaceous smectite or illite sediments with very minute/minimal feldspars. The rate of chemical weathering and soil formation is largely controlled by climate. Weathering intensity and chemical maturity is a function of climate and rates of tectonic uplift (Wronkiewicz and Condie, 1989). Kaolin minerals tend to develop preferentially within the tropics while chlorite and smectite tends to be preserved in artic regions. Average shale CIA value ranges around of 75. CIA and PIA (Plagioclase index of alteration PIA) between 60 and 75 indicates moderately/average intensive weathering in the source area. This two indices also helps to prove that although there was intensive weathering in the source area, the sediments as well did not travel far before been deposited. We can thus conclude a high CIA and PIA values (75-100) indicates intensive weathering in source area with little or no feldspar present whereas low values that are lesser than 50 indicates low weathering in the source area. Unweathered granite has a CIA of 50 which also the reference CIA for upper continental crust. At 50, it corresponds to upper continental crust and anything below 40 indicates that the site has consistently received sediments (with feldspars) that have undergone very little or no chemical weathering (Nesbitt and Young, 1989).

CIA is also much affected by grain size. It increases as grain size decreases. Also noteworthy is to mention that with increase in CIA, the porosity and permeability decreases. CIA values needed to be interpreted with caution. If the samples plot mostly in the upper part of the Illite /Kaolinite, it is an indication of a high degree of alteration as shown in figure 5. It will be seen most of the unweathered samples plotted near the calcium-sodium (CN) end indicate that the feldspars present are in form of plagioclase feldspars The dominance of unaltered feldspars as inferred from geochemical data suggests that the immature nature of sediments. The Niger Delta sediments probably formed from low residence times in the source region waters or river basin and quick removal of materials without continuous recycling or formed from rapid moving waters/ steep mountainous rivers (physical weathering dominates). Furthermore, deviations from ideal weathering trends can give information on the type of alteration, as for example K-metamorphism which discloses the alteration of plagioclase/K-feldspar to aluminum rich illite clay minerals to (Fedo et al., 1995)

Plagioclase index of alteration PIA (Fedo et al.,1995)

$$\text{The PIA } = 100 * [(Al_2O_3\text{-}K_2O) / (Al_2O_3+CaO+Na_2O\text{-}K_2O)]$$

The PIA values can also be shown pictorially with the ternary plot of (Al_2O-K_2O)-CaO-Na_2O diagram. And just like CIA, the values given by the ternary plot is the same as the values calculated from the formula above. The combination of CIA and PIA avoids misleading interpretation of too low CIA values and reveals a more realistic degree of chemical weathering. The PIA was determined following Fedo et al. (1995). The PIA generally reports higher values than CIA in K-metasomatized rocks. From the studied samples results, it is shown in table 6 that PIA is lesser (48.2) than CIA in table 5 (51.4). It is very correct to infer that the provenance of Niger Delta clastic sediments were more of plagioclaise (NaO, CaO) than orthoclase (K-metasomatized) rocks. Integrating the CIA and PIA values of both sand and shales, it seems that the Niger Delta sediments were derived from the different zones of weathering, and likely from rapid erosion of fast rising recycled orogens. The values obtained from the PIA are very similar to the CIA and their inference or interpretations are the same.
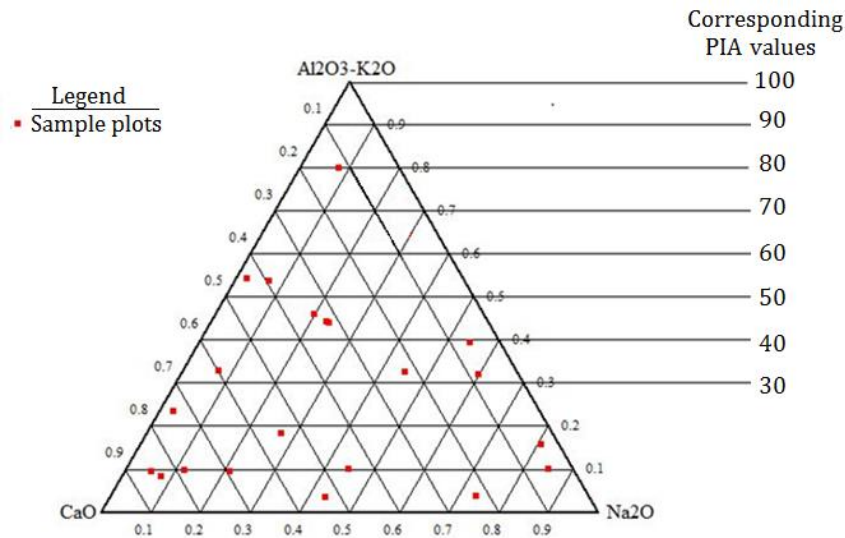
Figure 6. The values of the $(Al_2O_3-K_2O)-C_aO-Na_2O$ and the corresponding PIA values after Fedo et al. (1995).

Chemical index of weathering CIW (Harnois, 1988)

The CIW = $100 * [(Al_2O_3) / (Al_2O_3+CaO+Na_2O)]$

The role of chemical and mineralogical weathering indices is essentially to quantify the degree of depletion of mobile components relative to immobile components during weathering (Harnois, 1988). According to Harnois (1988), a CIW between 0-40 is classified as low weathered, 40-65 as intermediate or moderately weathered and greater than 70 as highly weathered sediments. From table 2, the average CIW is derived as 63.19, which made the sediments to be interpreted as moderately weathered.

Ruxton ratio: The ruxton ratio RR is given by RR = (SIO_2/AL_2O_3)

Ruxton (1968) prescribed the Ruxtion ratio of a digit (0-9) as intense chemical weathering, 10-30 as intermediate or moderate weathering while greater than 30 is interpreted as very weak chemical weathering. RR value greater than 30 suggests weak chemical weathering while those with one digit value (0-9) indicate high level of chemical weathering. From the RR results obtained, it is observed that majority of the samples have two digit value >10 implying low to medium level of weathering. However the instability or the alternation between high and low RR values is a clear indication of the highly weathered shale and less weathered (poorly sorted, immature) sand sediments.

Maturity in terms of feldspar/quartz and argillaceous sediments

Colin et al. (1994) identified that sediments that evolved from increased physical and chemical weathering as characterized by sediments deposited during the cretaceous is observed to have a decrease smectite (illite-chlorite) ratio. It implies that there is more of chlorite than illite with increasing intensity of weathering. As long as feldspars persist, the sediments will remain compositionally immature (Nesbitt and Young, 1996). In line with Medaris et al. (2003), absence of feldspar in sediments and sedimentary rocks is a characteristic feature of super mature sedimentary rocks. This agrees with Fedo et al. (1996) that if the source rocks experienced intense chemical weathering, feldspars present in the source rock would be altered totally as aluminous clay. Repeated cycles of weathering and abrasion during transport eventually result in destruction of feldspars and formation of clay minerals (Nesbitt and Young, 1996). As such decrease in smectite (illite-chlorite) ratio or increase in magnitude of samples plotting near the chlorite/kaolinite end which is at the top of the triangle is an indication of supermature, feldspar free sediment/sedimentary rock. However the presence of feldspars in the samples of this study as inferred from CIA and PIA plot suggest their derivation by physical and/or moderate chemical weathering.

Large-ion lithophile elements (Rb, Sr, K, and Na) in relation to CIA values and chemical weathering.

It is established that in chemical weathering intensity rapidly leaches Sr compared to Rb (Nesbitt and Young, 1982); implying that Rb/Sr ratio increases with increasing weathering and consequently increasing CIA values (Ma et al., 2000). In the same manner, K will shows rapid depletion against Rb also implying

Rb/K values varies directly with weathering intensity and CIA as well (Wronkiewicz and Condie, 1989). Rb has been studied and considered to be primarily fixed in weathering residues and less reactive than Ca, Na, and Sr (Woyski and Harris, 1963). Rb/Sr ratios in the illite minerals are usually greater than 1 (Chaudhuri and Brookings, 1979). None up to 1 in the studied samples as shown in table 11. It has a maximum value of 0.46 implying that the sediments had not suffered intense chemical weathering and is low in alumina/clay. This is confirmed by the low CIA value averaging 51.4 as well as the samples plotting below the Illite level (90). The Rb/Sr ratios of sediments and sedimentary rocks can thus be used to monitor the degree of source rock weathering (McLennan et al., 1993). The Rb/Sr, Rb/K ratios of studied sediment samples are as shown in table 4.

Table 4. Some analysed elemental ratios of trace elements in the samples.

Samples Depth	Lithology	AL/NA	K/NA	Rb/Sr	Rb/K
1160-1180	Sand	5.06	0.98	0.23	80.00
1560-1580	Shale	2.48	0.87	0.20	50.00
1960-1980	Sand	1.88	1.04	0.30	41.63
2960-2980	Shale	2.01	1.08	0.46	20.41
3960-3980	Shale	3.08	1.32	0.39	18.92
4560-4580	Shale	2.94	1.06	0.40	15.06
5460-5480	Shale	0.58	0.69	0.45	6.50
5760-5780	Shale	1.04	0.72	0.32	6.22
6160-6180	Shale	2.12	0.85	0.14	14.79
7060-7080	Sand	0.37	0.79	0.06	7.20
7260-7280	Sand	0.46	0.78	0.09	5.41
7560-7580	Sand	0.64	0.83	0.12	7.86
7760-7780	Shale	3.31	1.80	0.20	17.42
7960-7980	Shale	0.83	0.94	0.09	7.94
8060-8080	Shale	2.59	1.93	0.17	22.16
8160-8180	Sand	5.09	2.85	0.20	23.99
8560-8580	Sand	2.83	1.84	0.15	17.50
8960-8980	Shale	9.16	3.05	0.24	22.23
10360-10380	Shale	3.25	2.40	0.30	20.72
11060-11080	Shale	7.82	2.41	0.27	20.36
11460-11480	Shale	9.52	2.18	0.18	11.81

Scatter plot of Al/Na ratio versus chemical index of alteration (CIA): This is another way to show the silicate weathering extent at glance is to plot the Al/Na against CIA values as shown in fig 8. From the scatter plot of Al/Na ratio versus chemical index of alteration (CIA) it is observed that there is a very strong correlation between both indexes, which reflects the silicate weathering intensity. The Al/Na ratio expresses the abundance and increase of intensely weathered Alumina and or clay particles (Al_2O_3) over unweathered arenacious arenites and wackes; especially feldspars. As the Al/Na ratio increases, the Alumina, weathering intensity and CIA values increases and the feldspar decreases.

Heavy Mineral Analysis

Apart from major, trace and rare earth elements, heavy mineral studies of the sedimentary rocks are a powerful tool in identifying provenance (Morton, 1985). The term heavy mineral applies to minor assessory mineral constituents of rocks having ordinarily specific gravities higher than 2.89g/dm^{3}. This high density accessory mineral constituents of siliciclastic sediments are separated using liquids with densities of 2.89 (bromoform) or 2.96 (tetrabromoethane) in which they sink hence the name heavy minerals. Heavy minerals in their parent rock they are present either as essential rock forming minerals (e.g. amphiboles, pyroxenes, micas) or as accessory components such as zircon, apatite, tourmaline, occurring in a variety of rock types. Having a good knowledge of the mineral characteristics in surface and diagenetic environments can be used to deduce sedimentary processes and factors operating in depositional environments. This is because crystallization of minerals begins during the petrogenesis of the rock when the properties of the crystal such as structure, morphology, color, twinning and many others are formed. The effects of transport, climate, alluvial storage, sedimentary reworking and redeposition, burial diagenesis and recycling are

mostly preserved within the structural properties and surface textures of a particular heavy mineral grain. The recognizing of these chemical and physical signatures enables the critical assessment and interpretation of the prevalent conditions and the paleo-environment under which the sediments are deposited. The chemical stability of a particular heavy mineral can be determined from the pH of the geochemical environment. A heavy mineral assemblage seems to respond differently to extremes of acid environments (such as typical lateritic or humid–tropical weathering conditions) and alkaline environments (as typical in desert soils or saline brines associated with hydrocarbon reservoirs).
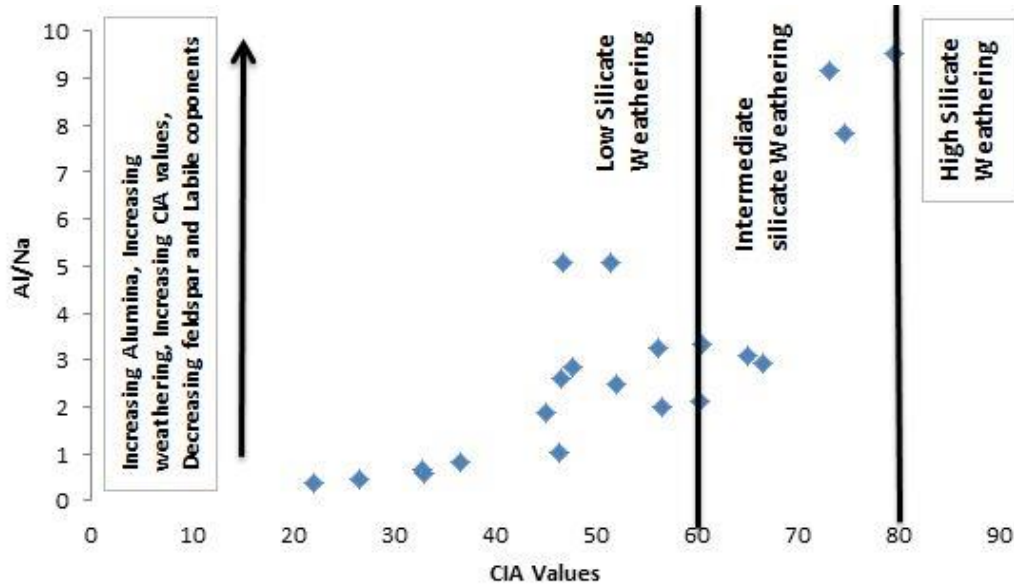

Figure 7. Scatter plot of Al/Na ratio versus chemical index of alteration (CIA)

Table 5. Table showing the stable and ultrastable elements as observed by grain count under the microscope.

Sample Depth in meters	Zr	Ru	To	Ga	Ap	Ep	Mu	St	Total Opaque	Total Non Opaque	Z+T+R	Z%	R%	T%	ZTR INDEX
1160-1180	11	10	6	5	8	5	5	2	64	36.0	27.0	40.7	37.0	22.2	75.0
1960-1980	13	8	8	12	4	3	2	2	93	46.0	29.0	44.8	27.6	27.6	63.0
7060-7080	15	11	13	9	2	-	4	5	55	58.0	39.0	38.5	28.2	33.3	67.2
7260-7280	9	5	6	7	2	2	7	4	69	55.0	20.0	45.0	25.0	30.0	36.4
7560-7580	11	6	5	11	3	2	4	1	80	51.0	22.0	50.0	27.3	22.7	43.1
8160-8180	10	7	6	9	4	1	2	1	72	52.0	23.0	43.5	30.4	26.1	44.2
8560-8580	9	10	3	13	3	2	6	1	43	37.0	22.0	40.9	45.5	13.6	59.5
Average	11.1	8.1	6.7	9.4	3.7	2.1	4.3	1.0	68	47.9	26.0	43.3	31.6	25.1	55.5

Key
Zr   Zircon   Ru   Rutile
To   Tourmaline   Ga   Garnet
Ap   Apatite   Ep   Epidote
Mu   Monazite   St   Staurolite
ZTR   Zircon Tourmaline Rutile Index

ZTR Index

Heavy mineral suites may also be used as an index of maturity using the ZTR index. The ZTR index is a method of determining how weathered, both chemically and mechanically a sediment (or a corresponding sedimentary rock) is. The letters in ZTR stand for 3 common minerals found in ultra-weathered sediments: zircon, tourmaline, and rutile. Other minerals that can be used along the ZTR index are garnet, magnetite, sphene, and other minerals from local provenance sources. The ZTR index is commonly high in beach or littoral zone depositional environments due to the long transport distances from the source and the high energy of the environment. These minerals are found in abundance due to their high specific gravity and resistance to weathering. The ZTR index can also be used as a scale for the estimation of the degree of modification or maturity of the entire heavy mineral assemblage.
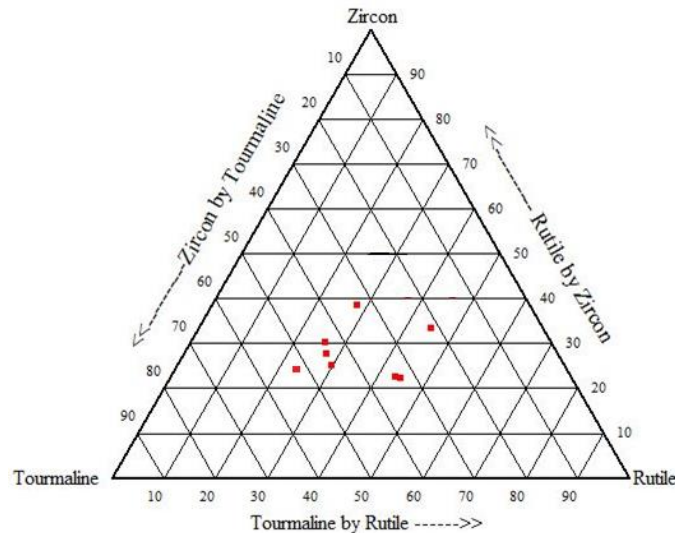
Figure 8. The ZTR ternary diagram of the eight sand samples

Statistics indicates that zircon of most sandstone are represented predominantly by rounded grains or angular fragments. Zircon is common heavy mineral, derived from granitic, volcanic, and metamorphic recycled sources. Kaolin deposits display a mature to super-mature assemblage of heavy minerals, represented dominantly by zircon. The lower zircon content (most samples plotted relatively far from Zircon end) for the plotted samples is an indication of immaturity, absence of Kaolin and presence of feldspars.

Rutile grains were yellowish to reddish brown, showed adamantine luster in reflected light and occurred mostly in small prismatic crystals. Rutile is an ultrastable mineral and is one of the three index species (ZTR), which are used to characterize the mineralogical maturity of a heavy mineral suite. Rutile is widespread accessory metamorphic mineral and mostly from high grade metamorphic rocks, particularly in schist, gneisses and amphibolite. The relatively higher rutile proportion indicates recycled metamorphic origin (Hubert, 1962).

Tourmalines are widespread in all types of detrital sediments and are ultrastable both mechanically and chemically. Tourmaline has proven particularly useful as a provenance mineral due to its presence in many rock types, chemical responsiveness to environment of formation, complex and variable chemical and mechanical weathering, and stability through digenesis and metamorphism. Tourmalines hardness and chemical stability make it extremely durable in sedimentary cycle. The heavy mineral assemblage (relatively higher concentrations) of tourmaline of rutile and zircon may indicate both igneous and metamorphic origin.

The opaque mineral species exceeded the non-opaque minerals (table 5). The large amount of heavy opaque minerals suggests oxic (oxygen-rich) environments of deposition (Odumoso et al. 2013). The heavy mineral garnets indicate a high grade metamorphic source while tourmaline, rutile and zircon indicate both igneous and metamorphic origin (Feo-Codecido, 1956).

The calculated ZTR index for the sand samples range from 36.4-75.0

ZTR Index = [(Z + T + R)/ Total non-opaque] * 100

Z = Zircon, T = Tourmaline, R = Rutile, ZTR Index = 55.5

The detrital epidote-group minerals, garnet and titanite in some of the samples indicate a major contribution from metamorphic sources. It is high (like 10%) in some samples while it is like 1-1.5% in some other samples. This variation probably is the result of influences from different sources for the different sediments. The variation could be produced by fluvial systems which change tracks through time, or that the sediments were fed by partly different fluvial systems. Further, it might mirror different tectonic activity in the source regions of the sediments.

According to Hubert (1962), the non-opaque or transparent non-micaceous heavy mineral assemblage of the quartz are predominantly zircon, tourmaline and rutile and these grains are ultimately concentrated in sands by prolonged abrasion. According to modification of heavy mineral association and provenance by Feo-Codecido (1956) the presence of zircon, rutile and tourmaline indicates an acid (felsic) igneous rock source of the sediments. The possibility of the source rock being basic igneous rock is very low because augite, diopside, hypersthene or olivine are largely absent from the heavy mineral assemblage. Instead Staurolite, Rutile and garnet occur in relatively fairly large quantities with respect to Epidote and Sillimanite, which are indicative of dynamo thermal metamorphic rock source.
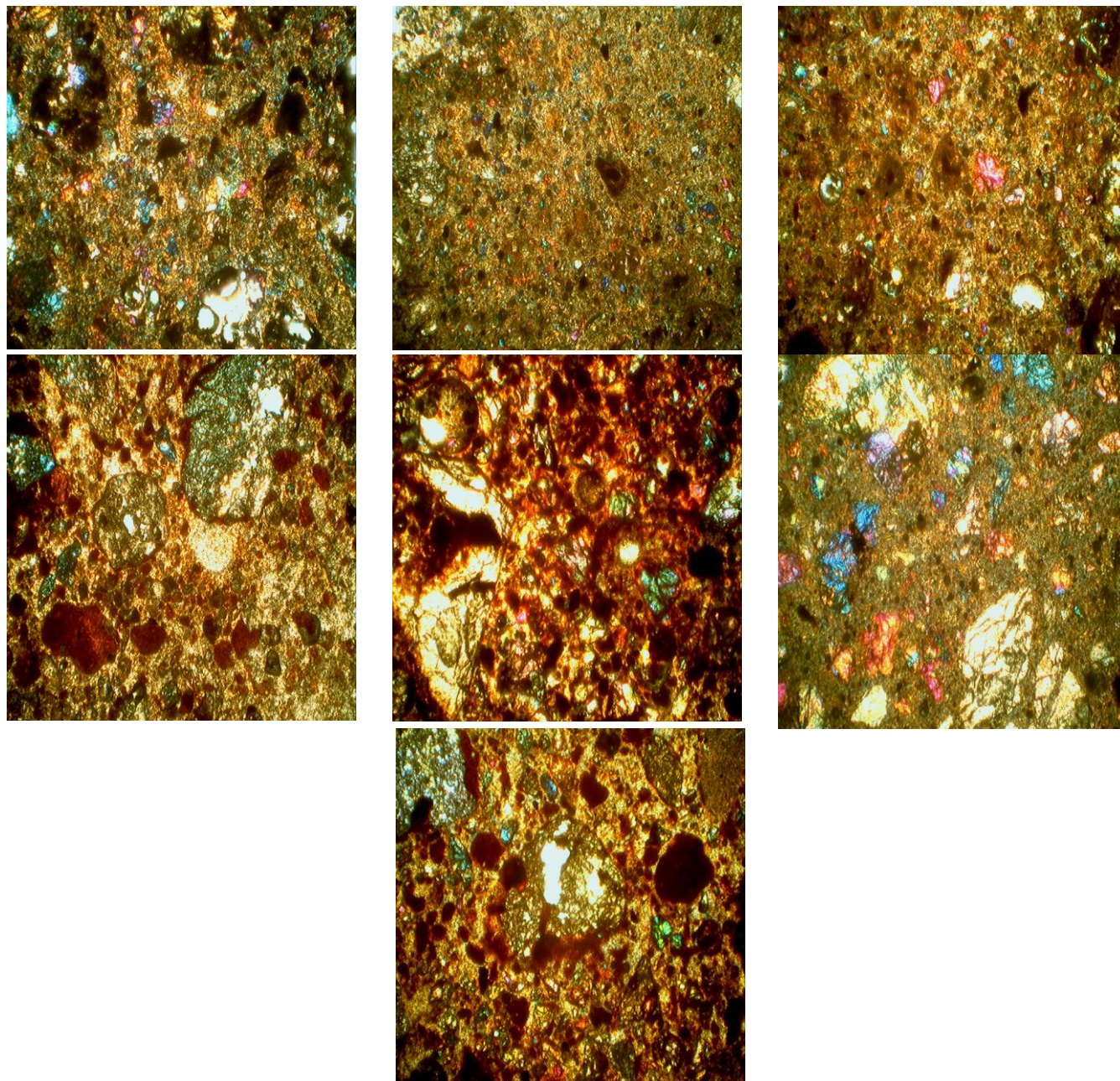

Figure 9. The photomicrograph of some of the samples

Conclusion

It is very obvious that the sediments are not matured. From the classification of terrigenous sandstone and shale based on Herron (1988) and Pettijohn et al. (1972), most of the samples plotted in litharenite, sublitharenite to sub-arkose and arkose. There is presence of matrix, while the grain shape sub-angular to sub rounded and only very few plotted in Quartz Arenite portion in Herron's diagram of figure 4. All this infer moderately mature sediment. From the CIA, PIA CIW and RR value obtained, it can be concluded that the trough has consistently received sediments (with feldspars) that have undergone very little or no

chemical weathering and minimized sediment reworkings. The dominance of unaltered feldspars as inferred from geochemical data emphasize the immature nature of sediments. The less than 50 CIA and PIA average values, coupled with poor sorting, alternating values of Ruxtion ratio and angular fragments is an indication of the immaturity of the sediment. Repeated cycles of weathering and abrasion during transport will eventually result in destruction of feldspars and formation of clay minerals and since feldspars persist, the sediments are compositionally immature.

From the A-K-F ternary plot, it is very clear that the depositional environment is a transition zone between continental and marine zones. The AKF plots show a gradual transition of the sediments of the basin from continental to marine environment.

The heavy mineral analysis prescribes a granitic-metamorphic origin of these sediments. Comparisons of specific indicator heavy minerals, such as garnet and tourmaline also strongly support this conclusion. Tourmalines indicate granitic and low-grade metamorphic provenances. Garnets are indicator of granitic and metamorphic, reflecting the fact that probably the granite suffered from regional metamorphism on a large scale. A metamorphic origin for the angular and euhedral pink to green tourmaline can also be inferred by its association with garnet and staurolite. The concentration of garnet in sediments can be due to increase erosion of metamorphic rocks. The angular to sub-angular shape of the sandstone is an indication of a short distance of transportation or closeness to the source area. The appreciable concentration of feldspar, the dominance of sub-angular to angular shape and the poorly sorted nature of the sandstones of the study area infer textural and mineralogical immaturity. Z.T.R. averaging 55.5% equally corresponds to immature sediments. The opaque mineral more than non-opaque is indicative of oxic paleoenvironment. The occurrences of zircon, tourmaline, apatite, and sphene suggest a felsic igneous source (Oni et al., 2014). Thus the provenance or source of the sediments is acidic or felsic igneous rock. The results of the geochemical analysis revealed that the Niger Delta sandstones consist of relatively high SiO_2, Al_2O_3, Na_2O, K_2O, and CaO and these suggest a quartz and feldspar-rich source area. From all the analysis above, we can conclude that the sediments are immature to moderately matured and of felsic/acidic igneous (probably granitic) and/or metamorphic provenance.

Acknowledgements

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