COMPOSITIONAL CHARACTERISTICS AND ECONOMIC POTENTIALS OF SHALE DEPOSITS AROUND AFIKPO AREA, SOUTHEASTERN NIGERIA

BY

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CERTIFICATION

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DEDICATION

This work is dedicated to my late father Chief Bartholomew Ifeanyichukwu Onuorah Okonkwo

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ABSTRACT

Shale is an important geological material useful in the production of ceramics, building materials and other chemical products. The Mamu and Nkporo shales have been studied mainly for their stratigraphic and sedimentary significance without much attention to their compositional, mineralogical and physical characteristics necessary for determining their economic importance. Therefore, this study was designed to investigate the mineralogical, geochemical and physical compositions of the shales, in the Afikpo Area, Southeastern Nigeria.

The Afikpo area was mapped on a scale of 1:100,000. Fifty-two shale samples were purposively collected, air-dried and pulverised. Thirty representative samples were selected and analysed for major, trace and rare earth elements using inductively coupled plasma mass spectrometry. Chemical compositions of the shale samples were compared with their Standard Units. Ten samples were selected for mineralogical analysis using X-ray diffractometer. Ten samples were also analysed using Total Organic Carbon TOC-LECO C-230 Carbon Analyser to quantify the organic content of source rocks. Geotechnical tests of fourteen selected samples were performed to determine the Atterberg limits and firing tests.

The Nkporo shale was observed to be fossiliferous and highly fissile with limestone nodules and crystals of pyrite, while Mamu shale was dark-grey with some lignite bands, cross-beddings, clay and intercalated oolitic ironstones. The percentage concentrations of SiO_2, Al_2O_3, Fe_2O_3, K_2O, and TiO_2 for Nkporo shale were 42.6 – 64.4; 12.6 – 25.3; 4.1 – 18.0; 0.6 – 3.1 and 0.8 – 1.4, respectively, while Mamu shale were 45.1 - 73.1; 13.5 – 24.9; 1.4 – 6 -7; 0.18 – 1.8 and 0.9 – 1.5, respectively. The chemical compositions of the shale samples met the required industrial specifications for bricks, ceramics and refractory products. The plot of TiO_2/Al_2O_3 showed that both shale sequences were derived from granitic source. The rare earth element pattern of the shale indicated a source similar to average upper continental crust. Kaolinite was the major clay mineral, while quartz was the major non-clay mineral, with minor amounts of hematite, limonite, jarosite, goethite and smectite. The average TOC, oil generation potential and thermal maturity level of the shale samples for Mamu and Nkporo were 2.68 wt% and 1.89 wt%; 0.88 mg/g and 1.81 mg/g; 428^{o}C and 427^{o}C, respectively, indicating good organic matter concentrations, poor source rock potential and immature organic sediment. The plot of plasticity indices against Liquid Limits (26.87% and 23.86%); (62.87% and 51.66%) for Nkporo and Mamu shales, respectively indicates that both shales are mostly inorganic clay and silt, of medium to high plasticity and compressibility. The linear shrinkage and the water absorption capacity of the shale samples were moderate, as they ranged from 2.0% - 9.0% and 2.0% - 6.0%; 3.65% - 9.82% and 5.90% -10.08% for Nkporo and Mamu shales, respectively.

The shale deposits in the Afikpo area were dominated by kaolinite and met the specifications for bricks, ceramics and refractory products.

Keywords: Shale deposits, Shale economic potential, Kaolinite and High plasticity

Word counts: 485

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CHAPTER ONE

INTRODUCTION

1.1 General Statement

Shale deposits have been discovered in many parts of the world. The age ranges from Cambrian to Tertiary and have been produced in a number of coastal, mainland and lacustrine settings (Agumanu, 1989). Shales are universally characterized as sedimentary rock of fine-grained texture having organic matter that will produce measures of oil and fuel gas after refining. Shales from weathered rocks bye-products is typically those that contain clay minerals, quartz, feldspars, mica, heavy minerals. In addition, shale rocks that contain calcareous, silica and phosphatic remains of animal skeletons are mainly gray in colour, but the addition of varying quantities of minor constituents changes the rock colour (Akande et, al., 1992).

Shales are significant for manufacturing industries and household use in developed and developing nations. Their value can generate a great deal of economic development and job creations (Nton and Elueze, 2005). A source of shale by way of economic potential is naturally refered to the one, which is at or close to the earth surface to be mined through open-cast method. Shale can provide a wide range of chemical base for manufacturing products like plastics, resins and adhesives. Powdered oil shale contains calcium compounds which, when added to acidic soil, will help to increase its pH value. Ash from oil shale pulverized fuel combustion can be used in the manufacture of bricks as asphalt filler in road construction. Oil shale ash, although alkaline in reaction, can be used as an amendment for waste materials in remediation work; in particular for acid colliery waste. Shale is comparatively fragile, as far as rock fragility is concerned; therefore, it is rarely used in its raw nature for building or industrial applications. When properly processed, it may be used as associate degree additive in cement and art clay products (Okunlola, 2015). Nigeria is one of the developing countries with an affluence of mineral resources and known fossil energy sources like coal, crude oil, and natural gas (Obaje, 2009).

Afikpo shale deposit studied in this project is located in Nigeria's oldest sedimentary rocks of lower Cretaceous age in the Benue Trough's southern end. The trough formed during the separation of South America and Africa, the opening of the South Atlantic Ocean at the triple junction. Olade, 1976; Binks and Fairhead, 1992, defined the basin as a failed arm of the rift system (Aulacogen) which established progressive mantle plume activities and was followed by sedimentation. According to (Offodile, 1976), the Benue Trough consists of a longitudinal section of the sedimentary basin, stretching from the present confluence of the Niger and Benue Rivers to the Northeast, enclosed by the basement complex in the North and South of the Benue Rivers. Benkhelil, (1989), noted several cycles that resulted in the affirmation of sedimentary rocks of various compositions and ages. Mineralization in the Benue Trough is limited to Cretaceous rocks contained in about 4800 m of the trough. In addition to salts, barites and other valuable deposits, lead-zinc ore has been extracted in the trough. Galena and sphalerite are found in the Albian carbonaceous shale, the Abakaliki Shale of the Asu-River Group (Reyment, 1965 and Ehinola, 2003, 2005).

This work hinges on the shale deposits around Afikpo in terms of their mineralogical, chemical composition, physical properties and rock source characteristics and as well as using the main, trace and rare earth elements geochemistry to delineate their compositional characteristics and economic potentials of the shales.

1.2 Justification

In Nigeria, several cases of clay/shale have been studied and reported by noteworthy authors. Nevertheless, their focus were on the economic of the hydrocarbon generation potentials, mineralization potentials and stratigraghic successions of the rocks. However, pioneering studies continue to be incapacitated by the lack of application of inorganic whole rock geochemistry to shale resources which may promote the generation of a bulk mineralogy model, and hence the Total Organic Carbon (TOC) data model for an improved understanding of the paleoredox environments and give insights on relative rock brittleness. All of these are keys to understanding shale reservoirs, and a view to expeditiously exploit the local shale raw materials for sustainable economic development and job creation. This study was centred on the potentials local raw materials of the economic geology of the shale deposits around the Afikpo-Edda area, in order to compare the compositional characteristics of clay/shale deposits elsewhere and renowned standards.

1.3 Aim and Objectives

The investigation aims at evaluating the compositional characteristics and economic potential of Afikpo shale and then to determine their use as raw materials in industries. The objectives are:

i. To determine the Shales' mineralogical composition in the region
ii. To ascertain the inorganic geochemistry composition of the shale
iii. To determine the potential for hydrocarbon generation of the shale
iv. To establish the physical properties of shale using geotechnical techniques
v. To evaluate the economic potentials of the shale in the area
vi. To determine the provenance of the area

1.4 Scope of Study

This work focused on the shale/clay deposits in the Afikpo area, Southeastern part of the Nigeria. The study involves field and laboratory investigations. Fieldwork aspect involves collecting representative samples of the exposed shale in the area. The different lithological section was described in order to know the field relationship of the unit. Laboratory work will include sample preparation, mineralogical, geochemical analyses (using Inductively CoupledPlasma Mass Spectromerty (ICP-MS) and (using Inductively Coupled Plasma Atomic Emission Spectromerty (ICP-AES) to detect major, trace and rare earth elements), geotechnical (liquid limit, plastic limit, plasticity index, shrinkage limit, natural moisture content, specific gravity and firing tests), and source rock analysis. In addition, calculation of various possible parameters of the source rock, such as TOC, Tmax, S1, S2, S3, HI, OI, PI will be carried-out.

1.5 Physiographic Setting

The terrain of the study area is not a flat terrain, but an alternation of high and low land. It is mostly a succession of hills and valleys. Cultivation is active on the hills, while the surface water bodies occupy most of the valley; the hill is steep with a sudden drop to the valley below.

1.6 Study location and Accessibility

The area under investigation is situated between 7°55.30'E and 7°48'E longitude and 5°51N and 5°44'N latitudes within the Afikpo syncline of the Nigeria's Sedimentary Basins, lower southern Benue Trough (Anambra basin); Oso to the west, Nko (Cross River) to the east, Abba-Omega towards the north, and Owutu in the south end, bordering Afikpo (Fig. 1.1). The major communities within the study area include Onu-nnachi guesthouse near Government Secondary school, Asaga Amangwu, Amosu, Ezi-edda, Ndi-ofia Edda, Amaigbo, Amoba, towards Ekeje, Owutu, Ogbu, Ekeje, Amaiyi, Enohia, Nguzu, Ebuwana and Unwana road (Fig. 1.1).

Afikpo is highly accessible via Federal, State and Local Government road networks interconnected by sequence of forest paths and other footpaths. The federal highway Afikpo-Abakiliki and the federal highway Okigwe-Afikpo formed a Y-junction about 1 km from Ozara Ukwu, providing good access to the study area from these cities. The two roads joined and then connected the study area to the cross-river state.

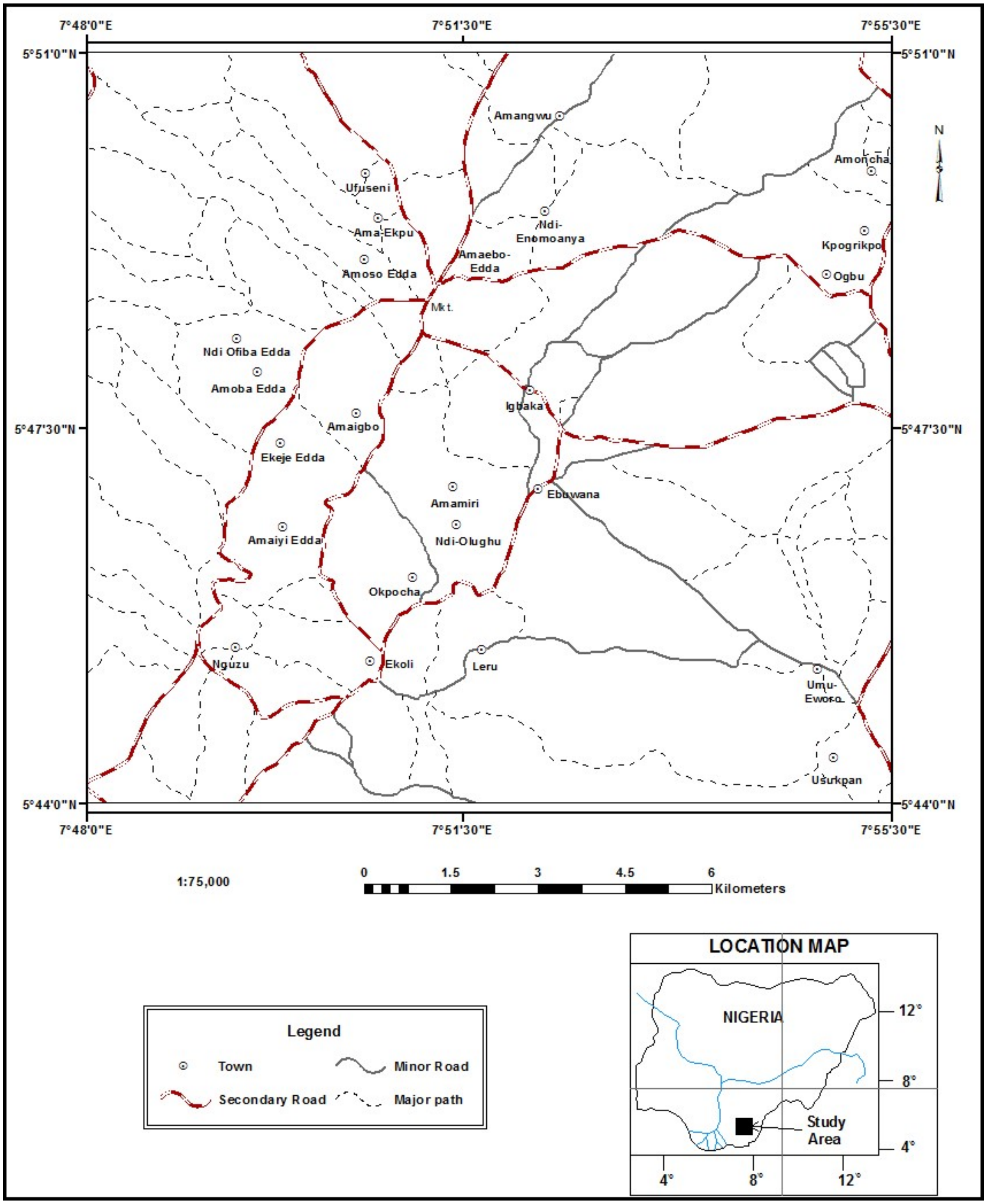


Fig. 1.1 Accessibility Map of Afikpo-Edda. (Modified from Geological and Mineral Resources Map of South-east Zone, Nigeria by NGSA 2007, First Edition)

1.7 Drainage

The drainage pattern of the sedimentary terrain is basically dendritic. Five Rivers- Asu River, Iyioka River, Uroro River, Ubei River, and Iyiogu River drain the study area. These four rivers are the main tributaries of the Cross River, the major river draining the study area. The lithological features also influence the study area's drainage pattern. It is mainly dendritic with some forms of trellis. Several rivers have their drainages, Enugu Cuesta sources with the highest altitude of approximately 214.11m. The Uroro River drains the northeastern direction of the central areas. The River Iyioka leads to the sandstone ridge of the Afikpo and drains southewards of the study area (Fig. 1.2).

1.8. Topography

The topography of the study area was mainly due to differential weathering and erosion resulting from differences in resistance of the underlying rocks. Due to low resistance to weathering and erosion, mud rocks will always form low soils. The indurated sandstone forms the ridges with the highest elevation being more resistant to weathering processes and with relatively sparse vegetation, whereas the lowland (mud rock) has more luxuriant vegetation (Fig.1.3).

1.9. Relief

The study area of Afikpo is characterized by an undulating landscape in a North-South profile that rises from about 30.5m in the Northern part to about 152.5m in the Southeast. Two major ridges that stand out from the study area distinguish the area; they are the Eze-Aku group's Amasiri sandstone member to the north and the Nkporo group shale and Afikpo sandstone member along with a dolerite intrusion to the southeast with the Afikpo sandstone being the highest of all. The Cuesta is a prominent linear asymmetric feature characterized by a smooth dip slope and a steep northward scarp slope (Fig. 1.3).

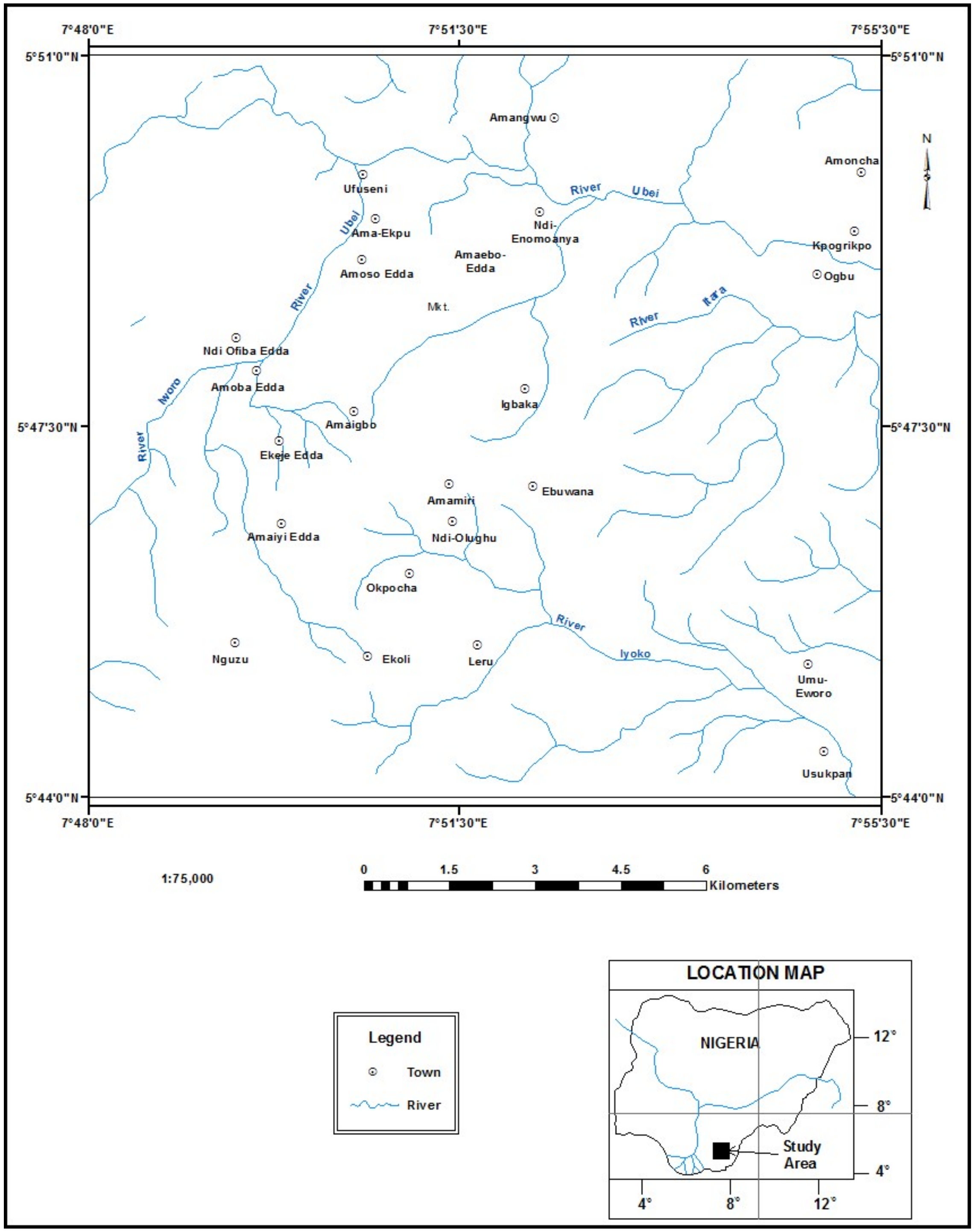


Fig. 1.2 Map of the Drainage Pattern of the Area (Modified from Geological and Mineral Resources Map of South-east Zone, Nigeria by NGSA 2007. First Edition)

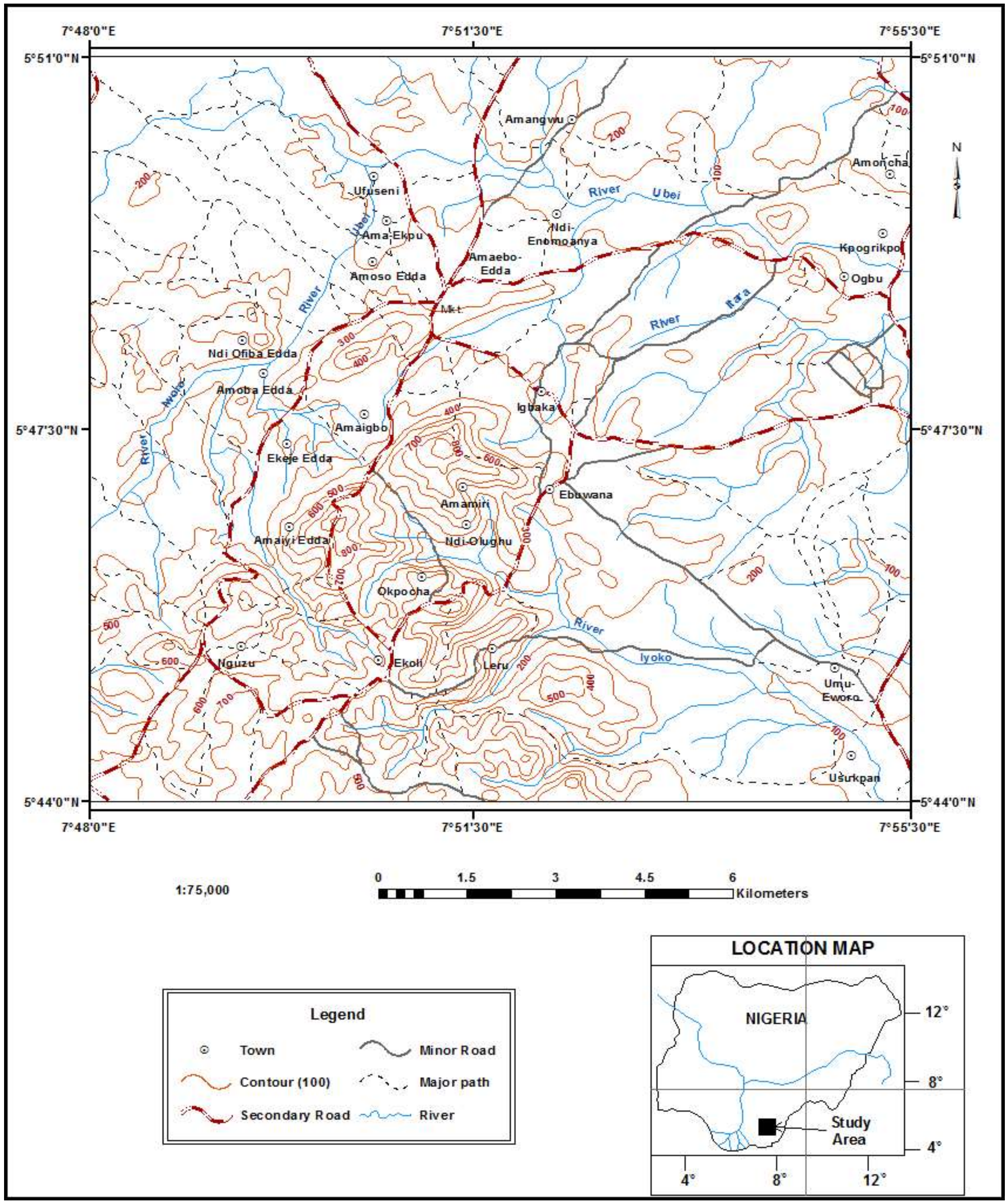


Fig. 1.3 Topographic Map of Afikpo-Edda area (Modified from Geological and Mineral Resources Map of South-east Zone, Nigeria by NGSA 2007. First Edition)

1.10 Climate and Vegetation

The climate of Afikpo Basin is warm and humid with a mean annual precipitation of about 152-203 cm corresponding to its neighboring basin (Anambra Basin). The two main seasons in Afikpo are the rainy and dry seasons. The rainy seasons usually begin in March and last until October. The temperature range between 18 ° C-32 ° C and rainfall ranges from 150cm-210 cm, with relative humidity ranging from 65% to 90% (Ehinola, 2010). The dry season is November-February, which is characterised by less rainfall and temperatures between 30 ° C and 35 ° C (Ehinola, 2010).

The study area's vegetative nature primarily involves perennial trees, grasses, stubs and climbers. Human activities, annual precipitation, topography, and other weather factors affect the vegetation. During the dry season, the grass withers and the shrubs turn yellowish while the vegetation in the valley retains its greenish color due to the shaley soil in the area that does not allow water to percolate deep into the soil, hence the availability of interrupted human activities, particularly in the lowland valley (Fig. 1.4).

The valley terrain principally causes thick vegetation because of the supply of surface water caused by the impervious nature of sedimentary rock. Whereas within the descending season, part withered grasses area unit found within the hills with occasional occurrences of shrubs and trees and therefore the depression principally contains denser vegetation. Vegetation is usually Guinea Savannah sort because of intensive deforestation.

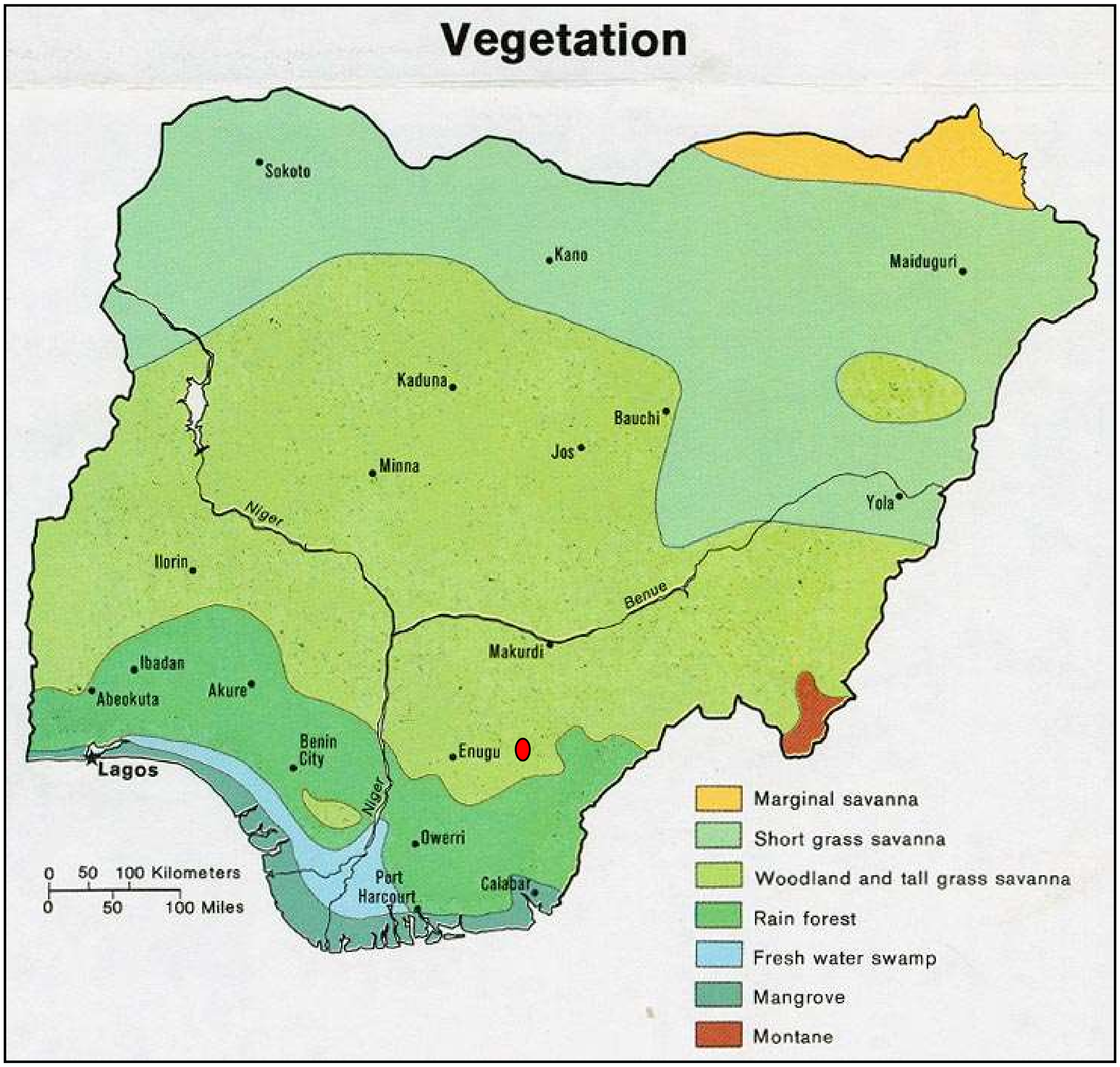


Fig. 1.4 Map of Nigeria showing the type vegetation in Afikpo-Edda Area (after Iloeje 1980)

CHAPTER TWO

LITERATURE REVIEW

2.1 Shales of South-Eastern Nigeria

Afikpo area has attracted loads of geological interests, references in several published and unpublished studies by many geologists and researchers within the past. Several studies were also done to follow up. Nkporo and Mamu formation where the study space belongs has received necessary attention.

(Okoro et al, 2012) opined that the hydrocarbon prospective and thermal maturity of Lower Benue Trough Nkporo shale indicated that the Total Organic Carbon (TOC) ranged from 0.54% to 3.01% by weight. The study concludes that these values surpassed the bare smallest worth of 0.5 wt% normally needed for hydrocarbon source rock potential. Relatively low hydrogen indicators were measured; fluctuating within the small range of 20 mg Hc / g and 153 mg Hc / g. TOC recorded organic matter of type 111 and mixed type 111/11 kerogen indicating gas-prone. Tmax and PI differ between 426 and 439 °C (average 432°C) and 0.02 and 0.08 respectively (average 0.03°C). These values have shown that the shales are actually thermally immature.

Obrike et. al., (2012), investigated the compositional and physical features of sedimentary rock (shale) from Mpu, southeastern Nigeria. In their analysis, they assessed the potential of the shale as industrial raw materials and concluded that the shale deposits can be exploited for ceramics, painting, earthenware and refractory industries based on mineralogical and chemical compositions.

Nwabineli et. al., (2013), assessed the economic potential of Clay Deposit at Akanu Ibiam Federal Polytechnic Unwana, Afikpo. The clays and shales range in age from the tertiary cretaceous to the geological time. The clays deposited throughtout the Cretaceous period are richer in quality. The study shows that Unwana clays are high in refractory (SiO_2 and Al_2O_3) with corresponding low flux (MgO, CaO, K_2O Na_2O TiO_2) making them good materials for making low-grade refractory, vitrifying and non-vitrifying structural clay products and finished ceramic product. Additionally, the high value and frequent shortage of cement and therefore the occurrence of huge deposits of clay minerals inside the Federal Polytechnic Institute Alkanu ibiam, and therefore the need for a variety of building materials, additionally require the institution of brick factories.

Ekweozo and Gormly (1983) have proved that the Campano-Maastrichtian Nkporo shale exhibit characteristics of potential hydrocarbon source system for services of oil/gas and comdensate show found within the Ajali sandstone.

Akaegbobi and Schmitt (1998) studied the organic facies, hydrocarbon source potential and reconstruction of the depositional paleoevironment of the Campano-Maastrichtian Nkporo shale. The concluded that the Nkporo shale was an example of marine source rock composed of type 111/11 kerogen, with dominance of terrestrial derived organic matter. In addition, they postulated that the oil generation threshold lies between the depth intervals of 1900-2300m based on combined parameters.

Akaegbobi et. al., (2000) studied the distribution of aromatic hydrocarbon and estimated the volume of the hydrocarbon in the post Santonian shale and coals of Nkporo and Mamu formations. They concluded that the total volume of hydrocarbon probably generated and entrapped in the Nkporo shale and Lower Coal Measures is 7790 million barrels of oil.

Obaje et. al., (2004) studied the hydrocarbon prospects of Anambra Basin based on organic geochemistry and organic petrology. The study reveals that the coal beds in Mamu formation have total organic carbon of as much as 60.8wt%. Mean hydrocarbon index of 364mgHC/gTOC, vitrrnite reflectance of 0.54-0.56%, and Tmax 440.433^{o}C. Gas chromatography and gas chromatography-mass spectrometry of the lipid extracts showed great contribution of terrestrial humic/ higher organic matter, high level of aerobic conditions as well as maturity level below the beginning of oil generation.

Adeleya et. al., (2017) studied the hydrocarbon prospect of coals and associated shale and mudstones of the Mamu formation in the Anambra basin. The studies shows that the organic matter type in the sediments are predominantly type II/III and type III kerogen with subordinate type IV kerogen which are oil and gas prone. The coals are dominated by oil and gas prone type II/III kerogen, while shale and mudstones are dominated by gas prone type III kerogen. The thermal maturity derived from Rock-Eval data indicates that the sediments are predominantly immature with respect to hydrocarbon generation and the proposed hydrocarbon can only be attained at appropriate maturity.

The above account shows that the previous investigation on hydrocarbon generation were based on Rock-Eval pyrolysis, Vitrinite Reflectance, Gas Chromatograph, Paleoevnvironments, Palynofacies/Palynomaceral methods, Mass Spectrometry method and Clay mineralogy. However, very little or non has been reported about compositional characteristics and economic potentials of the shale deposits of the Mamu and Nkporo shale of the Afikpo area.

2.2 Regional Geology of South Eastern Nigeria

Nigeria's geology consists of three major litho-petrological parts, particlarly the Basement Complex, the Younger Granites and the Sedimentary Basins. The Basement Complex, that is precambrian in age, consists of the Migmatite-Gneiss Complex, the metamorphic, Schist Belts and also the Older Granites. The Younger Granites units are comprised of a number of Jurassic period magmatic ring buildings turned around Jos and totally different items of northern focal Nigeria. They are essentially and petrolologically clear from Older Granites. The Sedimentary Basins, having silt load of Cretaceous to Tertiary ages. Nigeria is made up of seven key sedimentary basins, specifically, from the oldest, the Calabar Flank, the Benue Trough, the Chad Basin, S E Illummenden or Sokoto Basin, the Dahomey or Republic of Benin Basin, Nupe/Bida or Mid-Niger Basin and Niger Delta Basin (Fig. 2.1). Sedimentary progressions in these basins are of middle Mesozoic to Recent age. Older sedimentary deposits were not preserved most likely during the Paleozoic - early Mesozoic. However, the sedimentary successions in these basins are generally divisible into,

i. Substructural continental sandstone, siltstones and mudstones;
ii. Central oceanic shales and limestone interbedded with sandstones and siltstones;
iii. Peak sandstone order, that is continental and paralic.

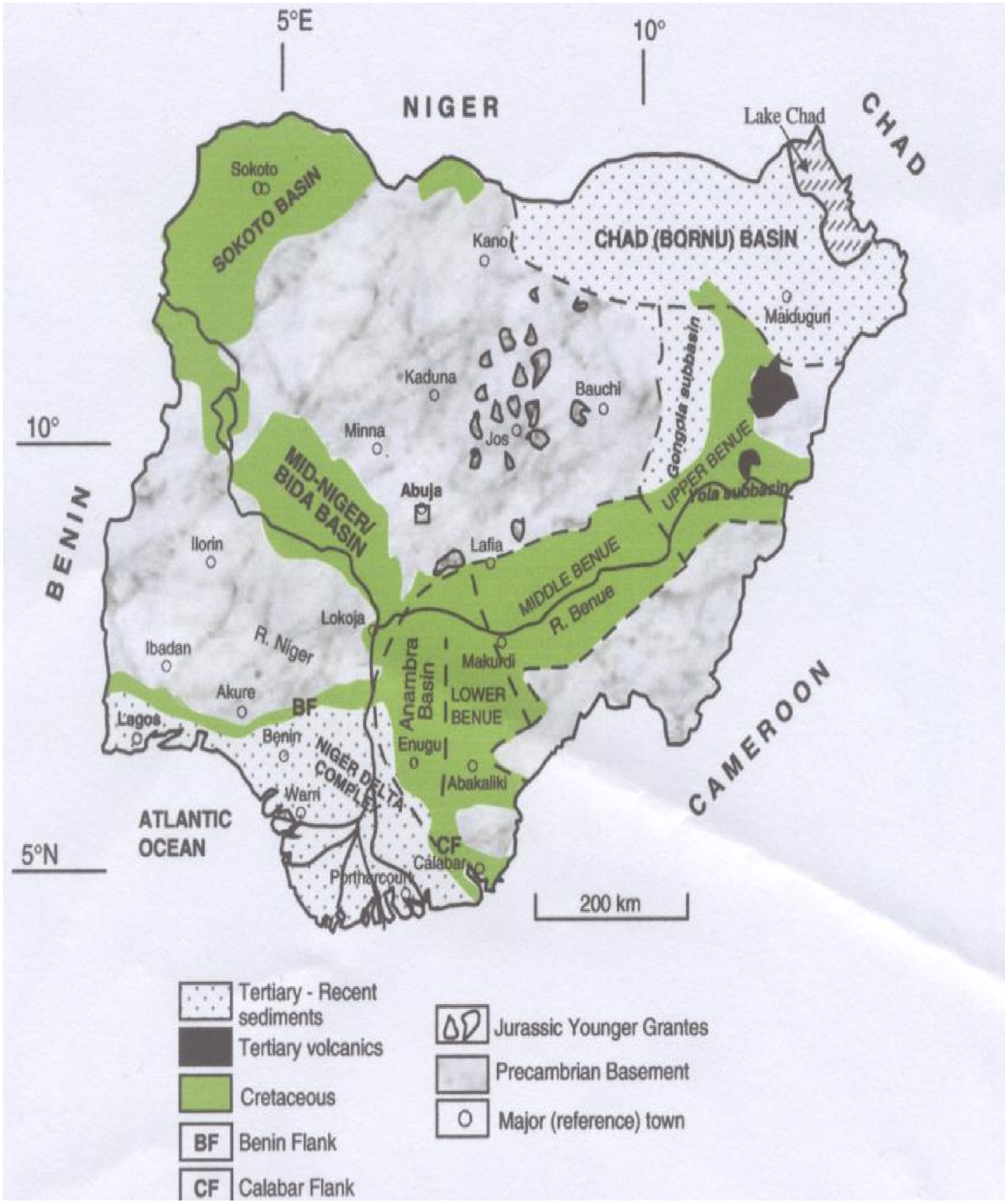


Figure 2.1 Geological sketch map of Nigeria showing the major geological components; Basement Younger Granites, and Sedimentary Basins (after Obaje, 2009)

In Southeastern Nigeria, the evolution of sedimentary basins preceded the opening of the South Atlantic and the crumble in late Jurassic times of the South American and West African plates (Olade, 1976) (Fig. 2.1). The Benue Trough's basin was unsuccessful section of a triple RRR junction that stretched to the Chad region in the NE from the northern edges of the Niger Delta Basin (Olade, 1976).

An analysis of the tectonic structure of Nigeria's inland sedimentary basin revealed that the rejuvenation of existing basement fractures was indeed the Benue Trough system. Wrench activities along these faults resulted in the cracking of blocks and many sedimentary basins being formed. In the past, the Benue Trough system was easily subdivided into the lower, central and upper Benue Troughs (Ramanathan and Fayose 1990). Nevertheless, recent aeromagnetic and magnitude data across the whole system, each with its well-defined sedimentary progression and separated by optimistic anomaly areas, have shown the distinct existence of these basins. In some of these basins inside the Trough, sediment thicknesses of up to 8km have been recorded (Binks and Fairhead, 1992).

The Abakaliki, Anambra and Afikpo Basins, as well as other small basins such as the Calabar flank and Mamfe Embayment, which collectively figure the lower Benue Trough, are included in Southeastern Nigeria. The Paleogene basin was primarily affected by the transformation of later generation faults originating from the inner Atlantic ridge system and now spreading only to the Tertiary basin in the central portion of the Niger Delta basin, much of which is above the deep-sea basement, sediments have been deposited for up to 12 km.

2.3 Geology and Stratigraphic Summary of the Afikpo Basin

The Benue Trough is an intra-continental basin with linear NE-SW patterns. In the Benue Trough (Fig.2.2), the Cretaceous succession is revealed in Nigeria. The Benue Trough is about 85 to 90 km broad fault-bounded depression encompasses up to 6000 m of cretaceous sedimentary and volcanic rocks which are slightly too strongly deformed.

The sedimentary cover in the Afikpo basin is split into the Asu River Group, the Eze-Aku Group and the proto-Niger Delta succession into three tectonic-stratigraphic mega sequences (Fig. 2.2), Obaje, 2009). The oldest sedimentary rocks overlying the complex rocks of the Precambrian Basement are non-marine to marine Early-Mid-Albian sediments in Southeastern Nigeria. With siliclastic and calcareous sandstones, the Albian, Asu River Group is dominantly shale. The oldest sedimentary sequences, overlain by shales, lower and higher regressive sandstones are from a conglomerate to arkosic sandstone. (Petters and Ekweozor, 1982) consider the lower and upper sandstone bodies as Awi and Awe Formations.

The Eze Aku Group overlays the Asu River Group unconformably, while the proto-Niger Delta deposits also overlap the Eze-Aku Group. The proto-Niger Delta basin consists of post-unconformity deposits of the Campian-Maastrichtian and Paleocene sediments (Fig. 2.3).

During the three tectonic events, namely Cenomanian, Santonian and Maastrichtain periods, three mega sequences: Asu River Group, Eze-Aku Group and the proto-Niger Delta sediments were intruded by basic rocks (Odigi and Amajor, 2010).

Three major Cretaceous lithostratigraphic units have been recognized in the Afikpo Basin, namely: the Asu-River Group, the Eze-Aku Group and the successions of the post-Santonian proto-Niger Delta (Odigi and Amajor, 2010) (Fig. 2.3). The basal sediments consist of the Awi Formation and Abakaliki Shales and the Awe Formation are the 3000 m-thick Asu-River Group (Late Albian to Early Cenomanian). There are 2000m thick Late Cenomanain-Early Santonian sediments of the Eze-Aku Group unconformably overlying the Asu-River Group. The Eze-Aku Group unconformably overlies post-Santonian sediments of the pro-Niger Delta beds.

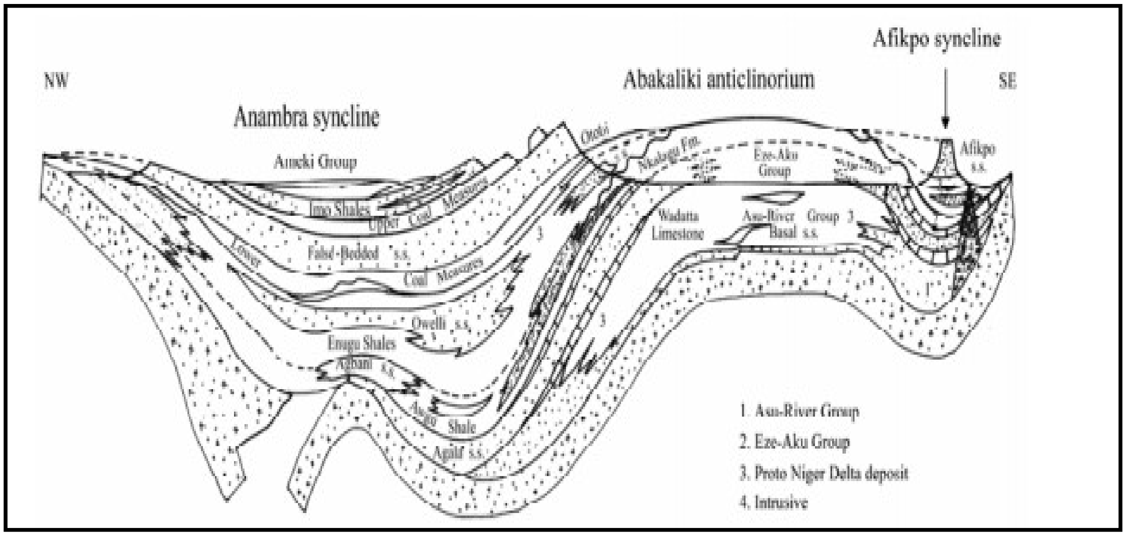


Fig. 2.2 Stratigraphic Segment across the Benue Trough in N-S trend (After Obaje, 2009)

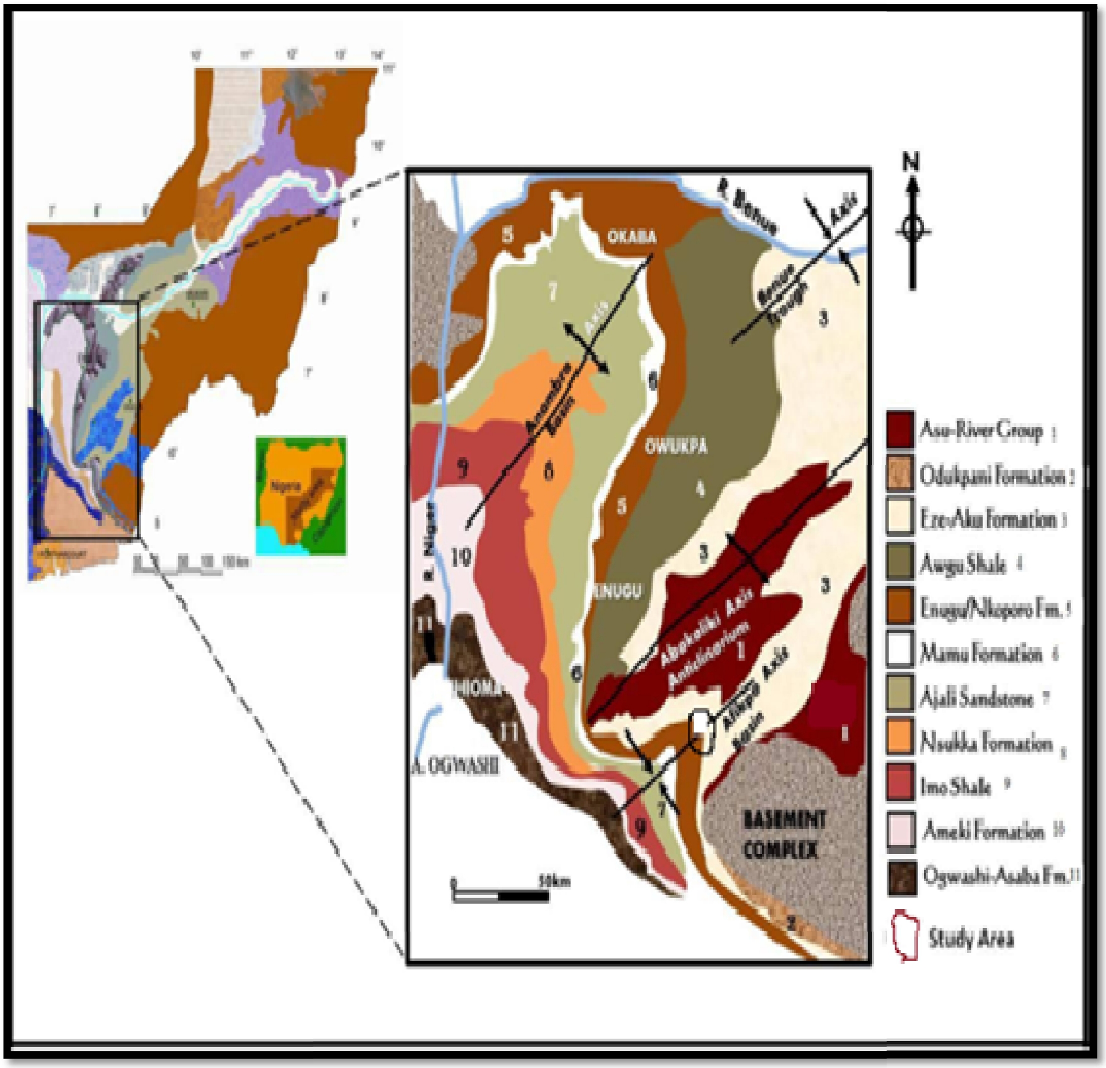


Fig. 2.3 Regional stratigraphic sequences in Southeastern Nigeria (Modified from geologic map of Nigeria, 1994)

CHAPTER THREE

METHODOLOGY

3.1 Field Activities

The Fieldwork was carried within the month of November 2016. The shale samples used for this study were taken in Afikpo South Local Governmenst Area (Edda) from the exposed shale outcrops. Using the Global Positioning System (GPS) and thus the topographic map to mark sample positions and lithological borders, mapping were carried out simeoutenousely while sampling were randomly selected from the areas of Owutu, Amosu, Ezi Edda, Ndi Ofia Edda, Amaigbo, Amoba, Asaga-Amangwu, Ogbu, Ekeje, Amaiyi road, Enohia, Nguzu and Ebunwana along erosion channels, watercourse channels, building channels (Fig. 3.1). Strong/hard samples were collected with the help of the hammer; effort was made to grab the deeper parts of the shale thus to avoid the weathered samples. The fifty-two samples were collected, placed in individual sample polythene bags, well tagged with applicable co-ordinates locations, using first the initial L followed by numeric e.g. L1 to L52, to avoid mixed up and cross contamination, (Fig. 3.1).

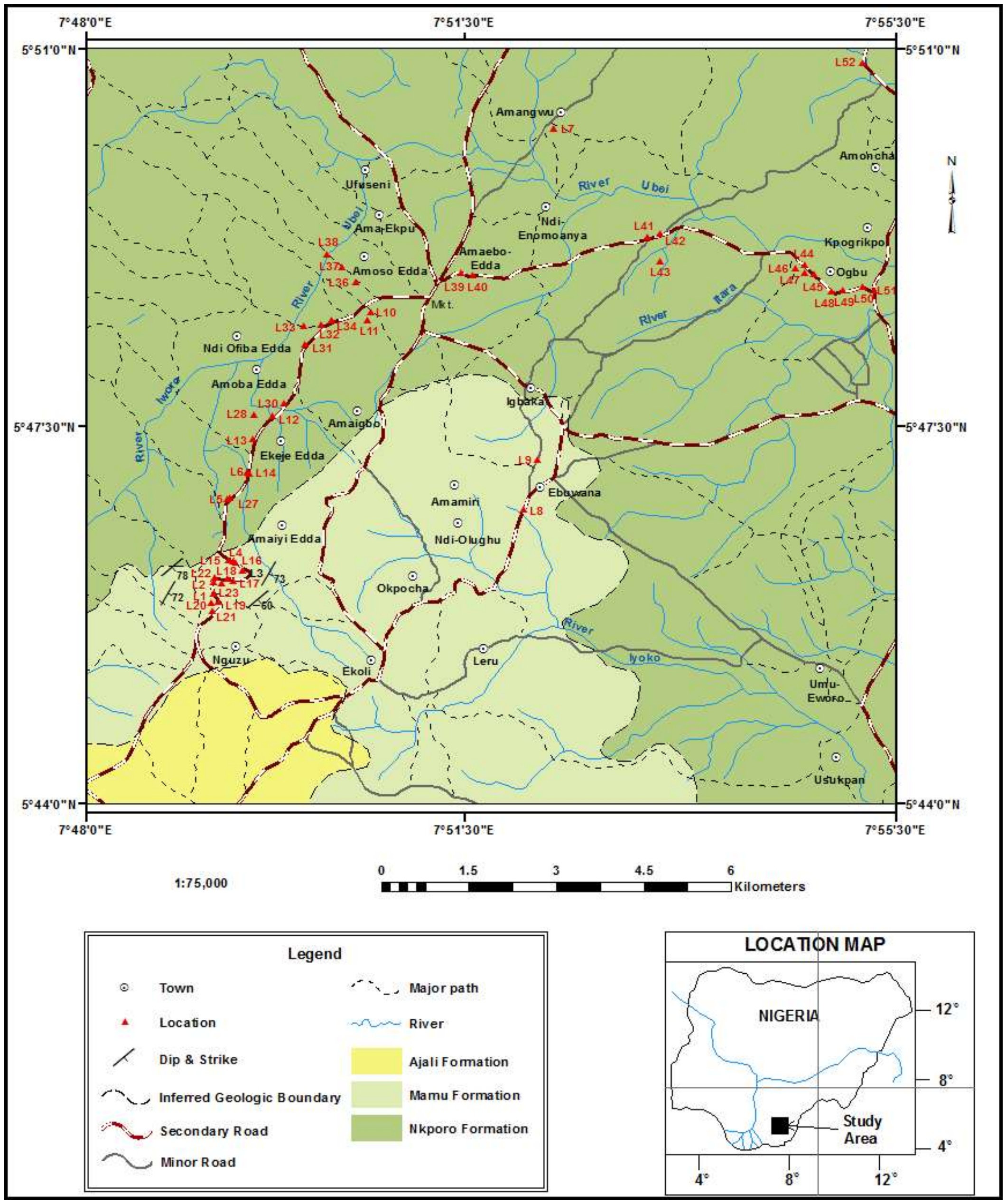


Fig. 3.1 Sampling Location Map of Afikpo-Edda area (Modified from Geological and Mineral Resources Map of South-east Zone, Nigeria by NGSA 2007. First Edition)

3.2 Sample Preparation

The collected samples were finally air-dried, and pulverized with mortar and pestle and sieved to fine grain particles. The samples were crushed systematically to avoid contamination. The mortar and the sieve were therefore cleansed after each pulverizing of sample with methylated spirit to forestall contamination with another sample before the next turn is done. Each pulverized sample is seived through 75µm sieve and then tagged in sample sachets. All these were done to prepare the samples ready for further analyses and tests. Forty samples out of fifty-two cardinal samples collected within the field was used.

3.3 Laboratory Analysis

3.3.1 Mineralogical Test

A mineralogical analysis was conducted using an X-ray diffractometer PW 1800 model on ten (10) samples of Afikpo shales at the Nigeria Geological Survey Agency (NGSA), Kaduna, Nigeria. The Diffractogram diagrams were recorded using a scanning rate 1^{o} 2/min/cm with a Ni-filtered & Fe k-alpha. Analyzing or comparing tips of substantial intensity by way of the Joint Committee of Powder Diffraction (JCPD), (1974) standard or ordinary shale minerals documented by Carol (1971) was used in interpreting of the obtained curves.

3.3.2 Inorganic Geochemical Analysis

Thirty (30) shale samples were packed for geochemical analysis, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Perkin-Elmer Elan 6000) at Acme Laboratory, Canada for basic package determination consisting of thirty four elements (e.g. Ba, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, Tl, U, V, W, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). A second sample split of 0.5g was predigested in aqua regia 3 part HCl and 1 part HNO_3) for the same period of time and temperature and analysed by ICP-MS to work out Au, Ag, As, Bi, Cd, Cu, Hg, Mo, Ni, Pb, Sb, So, Ti, and Zn.

The ICP-AES Inductively Coupled Plasma Atomic Emission Spectrometry (Spectro Ciros Vision) was used for major oxides and elements determination (SiO_2, Al_2O, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5, Cr_2O_3, Ba, Nb, Sr, Sc, Y, Zr, Ce, Co, Cu, Ta and Zn). Loss on Ignition (LOI) was assesed by quantifing the weight loss after heating a 1g split sample for 90 minutes at $95^{o}C$.

By weighing 0.2 g of aliquot into a graphite crucible, sample digestion was performed and mixed with 1.5g of flux $LiBO_2$ / $Li_2B_4O_7$. The crucibles are placed in an oven and heated for half an hour at 98°C, then the cooled bead is dissolved in 5 percent HNO_3 (ACS grade nitric acid diluted in demineralized water). For precision, calibration standards and chemical reagent blanks were applied as applicable for the same period of time and temperature.

3.3.3 Organic Geochemical Analysis

To characterize their hydrocarbon generation potential, ten shale samples fine pulverised and oven dried at temperature of 50^{o}C were subjected to geochemical analysis at Geomark Research, LTD Houston Texas USA using;

i Hawk Programmed Pyrolysis

ii Total organic carbon (TOC-LECO)

3.3.3.1 Hawk Programmed Pyrolysis

It is a technique to measure the richness/type, hydrocarbon generative potential and thermal maturity of potential source rocks. According to Espitalie et. al., (1977), Pyrolysis provides information on the quantity and thermal maturity of an associated organic matter and is defined as the heating of organic matter in the absence of oxygen to yield organic compounds.

For this study, ten shale samples were subjected to Rock- Eval pyrolsis and were analysed in the Rock- Eval analyser-6 instruments. The pulverized organic rich samples were heated in an inert environmemt to measure the yield of three groups of the free oil content, remaining generation potential and the organic carbon dioxide yield (S_1, S_2 and S_3 respectively). Approximately 70 milligrams of wached, ground (60 mesh) whole rock sample is analyzed in the Analyzer-6 instruments. Samples were heated at 300^{o}C for 3 minutes to produce the S_1 peak. Where high S_1 values were recorded large amounts of kerogen derived bitumen (for an active source rock) or the presence of migrated hydrocarbon were as a result. Temperature for heated was then increased from 300^{o}C and 650^{o}C at 25 ^{o}C /min then held at 650^{o}C for 3 minutes to obtain S_2 peak. Temperature is held here toensure accuracy of reading. The S_3 peak is measured between 300^{o}C and 400^{o}C, which is a measure of the carbon dioxide releasd thus giving an idea of the oxygen content of the rock. 'Tmax' is measured here as the measure of maturity.

3.3.3.2 Total organic carbon (TOC-LECO)

Geochemical technique that is accustomed quantifies the organic content of rocks. These are powerful techniques to spot zones with the very best potential for production and to assess the expected production of every organic interval. TOC-LECO analysis is measured employing a LECO C-230 Carbon Analyzer for speedy, precise, and reliable results. The method provides an explicit and reliable determination of organic and inorganic carbon and sulphur abundance on a variety of organic and inorganic materials: coal, coke, oil, drilling cuttings, soil, sediment and cement.

Total Organic Carbon (TOC) was recorded while holding temperature at 300^oC, for a minute then, rose to 850^oC at 20^oC/min, and held at 850^oC for 5 minutes.
Measured parameters obtained from the Rock-Eval includes,

S_1: Free oil content (Mg HC/g rock)
S_2: Remaining generation potential (Mg HC/g rock)
Tmax Temperature at maximum evolution of S2 hydrocarbon (^oC)
S_3: Organic carbon dioxide yield (Mg CO_2/g rock)
Several useful ratios are also utilized from Rock-Eval and TOC data. These are:

Hydrogn Index (HI):	S_2/TOC x 100 (in mg HC/g TOC)
Oxygen Index (OI):	S_3/TOC x 100 (in mg CO_2/g TOC)
Normalized Oil Content:	S_1/TOC x 100 (in mg HC/g TOC)
S_2/S_3:	(Mg HCl mg CO_2)
Production Index (PI):	$S_1/(S_1+S_2)$
Total Organic Carbons	(Wt %)

3.3.4 Physical Test

Physical tests were conducted on fourteen (14) shale samples at the geotechnical laboratory of Obafemi Awolowo University in the Department of Civil Engineering, Ile Ife, Osun State, Nigeria. These tests were conducted with reference to Part 2: 1990 of the British Standard Institution Code of Practice BS 1377. The physical tests carried out are discussed below:

3.3.4.1 Natural Moisture Content (Mc):

The ratio of the weight of water in the soil to the material's dry weight is the natural moisture content. The container was clean, dried and weighed (W3).

The rock sample was pulverised and placed loosely at intervals in the container and so the lid replaced. The container and its content were weighed again (W1). The lid was removed and so the container with its lid and its content was then placed within the oven and dried at 105^0C to 110^0C for 24 hours. The lid was not replaced whereas the sample was at the intervals in the oven. Once the sample is dried and cooled, the container and its content were weighed (W2). The natural wet content was then calculated as a percentage of the dry soil mass from this equation:

$Mc = (W_{1-} W_2/ W_2 - W_3) \times 100$

Where W_1 = weight of wet soil and container together

W_2 = weight of dried soil and container together

W_3 = Container's weight

$W_1 – W_2$ = weight of moisture only

$W_2 – W_3$ = Dried soil weight

3.3.4.2 Liquid Limit (LL):

The Casagrande apparatus was first adjusted so that the cup drops 10mm when raised to its maximum height. The rock sample was pulverised and placed loosely on a glass plate for thorough mixing with amount of water to create a thick paste. The cup was filled so that once it was completely resting on its base, the surface of the glue was even with the edge of the cup and thus the paste surface was levelled so that it was absolutely parallel to the bottom.

The grooving tool was used to form a groove/channel through the centre of the cup's pivot along the diameter. In order to maintain the grooving tool normal to the cup surface, care must be taken while forming the groove. The handle was rotated at a rate of two revolutions per second and the range of bumps required to close the bottom of the groove over a distance of 13 mm were counted together. (if the quantity of bumps exceeds 50, a small amount of water will be added to the soil, thoroughly mixed and the levelling method repeated together until the quantity of bumps drops below 50).

Approximately 10gm of soil from the vicinity where the groove was closed was placed in a weighing container and the water content was therefore determined. The soil remaining in the cup was returned to the soil mixture on the glass plate; additional water was poured and the soil was therefore completely mixed. The cup was then refilled, the test repeated, as the average range of bumps and water content determined.

The average water content of each specimen was plotted on a logarithmic scale against the corresponding average range of bumps and, in addition, the water content at which the groove would close after removing 25 bumps. The water content was described as the Liquid Limit.

3.3.4.3 Plastic Limit Test (P.L):

By kneading with the fingers into a small ball, about 20 grams of soil is completely mixed, which was then extended by hand on a glass plate until it became a 3 mm diameter thread. As a consequence of it being rolled, this method of kneading and rolling continued until the 3 mm thread began to crumble and the soil was then at its plastic limit. After that, the components of the thread were collected and their water content determined. At least three determinations of the plastic limit were produced and the following water content averaged jointly.

3.3.4.4 Plasticity Index (P.I) = Liquid limit – Plastic limit

The plasticity index indicates that the water content of which the soil remains plastic is indicated by the numerical distinction between the liquid limit and the plastic limit. Using both the liquid limits and therefore the plasticity index values for proper evaluation of the plasticity properties of a soil has been found fascinating. Engineering soil classification systems used these values as a basis for classifying fine-grained soil.

3.3.4.5 Linear Shrinkage/Shrinkage Limit- Test

The sample passing through 425μm check sieve was placed on a flat glass plate and thoroughly mixed using palette knives until it became a smooth consistent paste at regarding the liquid limit of the soil. The mixture was then placed in an exceedingly mould and also the mould gently jarred to get rid of any void a part of the mixture adhering to the rim of the mould removed by wiping. The mould and its content were allowed to air dry slowly until the soil shrinks far away from the walls of the mould before absolutely oven drying at a temperature of $105^{o}C$ to $110^{o}C$. The mould and soil were then cooled and the mean length of the cooled soil bar was determined. The samples were then meticulously removed from the mold as soon as they became bent during the drying process and the length of the upper and lower surfaces measured. As a consequence of the length of the oven dry sample, the median of these two lengths was taken

The linear shrinkage of the sample was then calculated from:

Linear shrinkage % = (1- L/L0) x 100

Where L0 = original length of the sample andL1 = length of the oven dry sample (mm)

3.3.4.6 Specific Gravity Test

Dried density bottle was weighed (WI) and about 25gm of the pulverised sample was transferred into it. The bottle and the content were once more weighed (W2). Distilled water was added to the sample in order that the bottle was merely covered. Its fully content was totally mixed or stirred with a glass rod to induce and eliminate any trapped air inside the sample. The bottle is then crammed to the brim to get rid of any remaining air. The bottle and thus the content were weighed once more (W3). The content of the bottle was empty, the bottle washed, of distilled water solely and weighed (W4). The specific gravity was then calculated from;:

Gs = W2 – W1/ (W4 – W1) – (W3 – W2)

Where: W1 = mass of density bottle (gm)

W2 = mass of density bottle + dry sample

W3 = mass of density bottle + dry sample + water

W4 = mass of density bottle + water only

The value of the specific gravity was to be given to the nearest 0.01 gm.

3.3.4.7 Firing Test Procedure

The samples were pulverised in Geochemistry Laboratory, University of Ibadan. The pulverised samples were taken right down to the Geotechnical Laboratory of Obafemi Awolowo University in the Department of Civil Engineering, Ile-Ife, Osun state. At the laboratory, the pulverized samples that are representative of every location were mixed with very little water and place in a cylindrical mould. The moulds were oven dried then taken to the furnace for firing at 1000^{o}C. The samples were left for soaking immediately the furnace attained 1000^{o}C so as to be stable at this temperature. The samples were brought out after about 10 hours and therefore the colour changes discovered. The fired samples were weighed to determine the weight and keep. The fired samples were soaked in water in a beaker and heated for one and half hours to determine the water absorption capacity. The weight of the soaked samples was also determined. WAC = (soaked weight - fired weight)/ fired weight x 100%.

3.3.4.8 Variation plots and Maps

Excel software was used to plot the geochemical graphs, variation plots and Origin 50 and Surfer software were used for the maps

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Results

4.1.1 Lithological Description of the Rock Samples for the Locations

By classifying or defining the rocks into their different physical properties and the geological formations they belong to, lithological analyses was carry out and were presented in Figures 4.1-4.13. Details of the lithological description considered includes: color, texture, rock shape, macrofossils present, mineralogy, calcareous or non-calcareous rocks were measured and delineated on some outcrops sections around Afikpo-Edda from different locations. Below are the observations:

Location, L1: In (Fig. 4.1) at Amaiyi/Nguzu road; The outcrop length is around 21.5 m, from the base, dark grey to black fissile, laminated shale is overlaid with oolitic iron with thicknesses ranging from 3.2-3.6 m, followed by another dark gray to black fissile, laminated shale, calcareous thinly laminated light grey fissile shale. The thicknesses of calcareous shale ranged from 4.90 – 8.00m, light brown Clay and Topsoil with little clay, firm brownish, poorly sorted, rounded with light brown sand. The thicknesses ranged from 11.4 – 21.5m. No structures found (Fig. 4.1).

Location L2: (Fig. 4.2) at Nguzu road; the outcrop is about 6.3m, no structures were observed. The lithology order are light grey fissile laminated shale with an intercalation of ironstone, dark grey fissile laminated shale bed with microfossils and reddish fissile shale with on structures found (Fig. 4.2).

At L3, (Fig. 4.3), Nguzu road; No structures found, the lithology order are; white/ pinkish, fine angular grains and well-sorted sandstone, reddish/brown fissile shale and reddish clay. The length of the outcrop is about 11.4m (Fig. 4.3).

L4 (Fig. 4.4), at Amaiyi; Some forams were noticed, brownish well sorted angular grains sandstone with forams, dark grey shale, interbedded oolitic ironstone, dark grey shale and reddish brown fissile shale (Fig. 4.4).

The outcrop is about 5.7m. Lithologic profile of Ebunwana outcrop (L9; Fig. 4.5), no geologic structure was found. Reddish brown shale with length of about 1.3m was measured.

Lithologic profile of Nguzu outcrop (L20; Fig. 4.6), has the outcrop range from 0 to 11.8m. The outcrop comprises of grey/dark fissile shale, oolitic ironstone. Whitish/pinkish coal suspected to be lignite, red laminated shale and reddish laterite.

At L22, (Fig. 4.7), Nguzu road; No structures found, the lithology order are; white/ pinkish, fine angular grains and well-sorted sandstone, reddish/brown fissile shale and reddish clay. The length of the outcrop is about 6.6m (Fig. 4.7).

Lithologic profile of Nguzu outcrop (L23; Fig 4.8), the outcrop ranges from 0 to 10.9m with interbedded oolitic ironstone, dark fissile shale and reddish grey shale.

L5 (Fig. 4.9) at Iyiesa/Amaiyi-Edda; Parallel laminated pinkish poorly sorted angular, rounded friable sandstone, reddish laminated medium indurated poorly sorted sandstone, yellowish, friable, laminated poorly sorted clay matrix, reddish, medium indurated, laminated sandstone and reddish coarse sandstone.

Lithologic profile of Asaga Amangwu outcrop (L7; Fig. 4.10) indicated dark fissile shale overlying the reddish grey fissile shale. Some structures like moulds of microfossils such as gastropods and ostracod were found in dark shale of 0 to 2.5m.

Lithologic profile of Nkelogu Ezi-Edda outcrop (L10; Fig. 4.11) showed whitish/pinkish, laminated, well-sorted and very fine-grained sandstone overlaid, brown, fine-granulared with well-sorted clay; some geological structures were noticed in the fine-grain sandstone.

At location (L11; Fig. 4.12.), lithologic profile of Ekelogu outcrop, no structure found. It has whitish, friable, poorly rounded sandstone with reddish brown coarse oolitic ironstone and light brown with reddish intercalation shale.

Lithologic profile of Ogbu outcrop (L43; Fig. 4.13); only biogenic structures are the casts and moulds of the bivalve, inoceramus labiatus occur in places. The thicknesses of calcareous shale ranged from 0.60 – 1.50m. There are pyrites concretions of varied sizes present in both lithologies. The thicknesses of marlstone ranged from 0.10 – 0.30m with dark colour due to the presence of anoxicity. A succession of consolidated interbedded papery dark gray to black calcareous shales, platy light gray marlstones with Lithofacies identified are calcareous shale facies with platy marlstone facies, ammonite and inoceramus, spheroidal and elongate ellipsoidal.

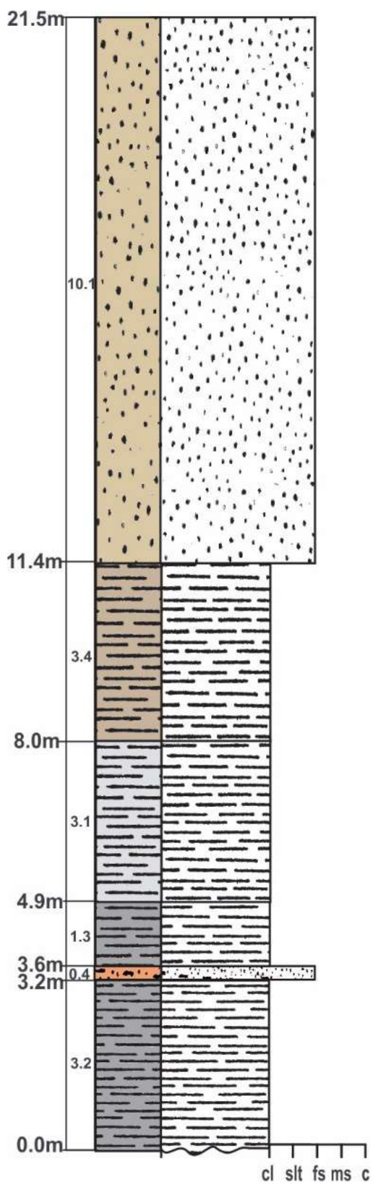
Lithology	Location	Structures	Description
	L1 Amaiyi N5°45 966’ E7°49 174’	No structures found	Topsoil with little clay, firm brownish, poorly sorted, rounded with light brown sand. The thicknesses ranged from 11.4 – 21.5m. Firmly light brown Clay Calcareous thinly laminated light grey fissile, shale. The thicknesses of calcareous shale ranged from 4.90 – 8.00m. Dark gray to black fissile, laminated shale Oolitic Ironstone bed. The thicknesses range from 3.2-3.6m Dark gray to black fissile, laminated shale

Fig. 4.1 Lithologic Profile of Amaiyi Outcrop (L1) in Mamu Formation

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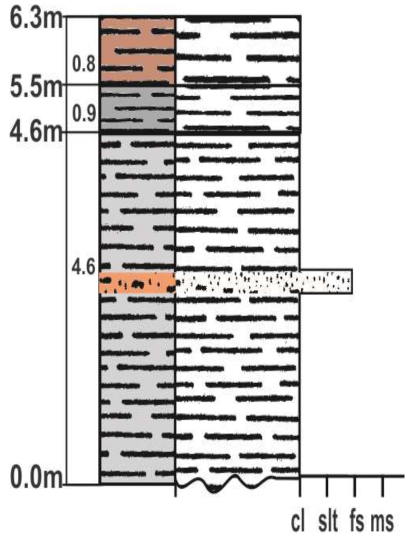
Lithology	Location	Structures	Descriptions
	L2 Nguzu N5°46 023' E7°49 186'	No structures found	Reddish fissile shale Dark grey fissile laminated shale bed with microfossils Light grey fissile laminated shale with an intercalation of ironstone

Fig. 4.2 Lithologic Profile of Nguzu Outcrop (L2) in Mamu Formation

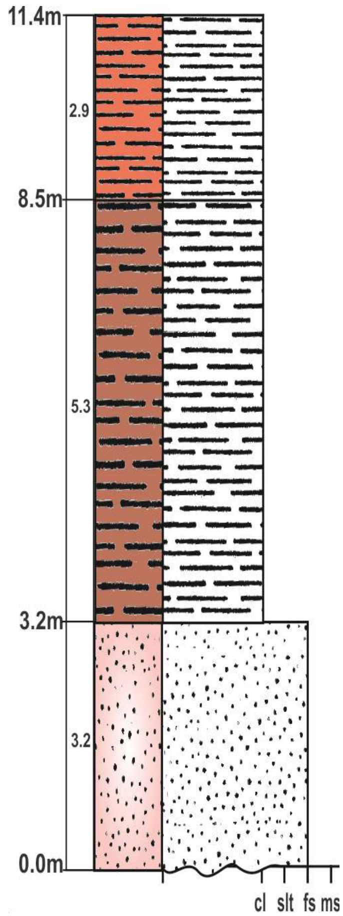
Lithology	Location	Structures	Descriptions
	L3 Nguzu N5°46 131’ E7°49 453’	No structures found	Reddish clay Reddish/brown fissile shale White/ pinkish, fine angular grains and well-sorted sandstone

Fig. 4.3 Lithologic Profile of Nguzu Outcrop (L3) in Mamu Formation

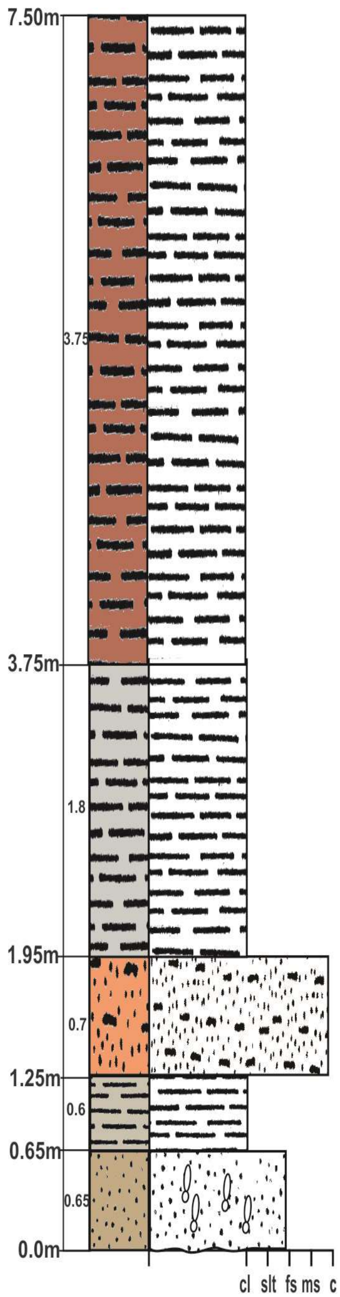
Lithology	Location	Structures	Descriptions
	L4 Ekeje N5°46 214’ E7°49 369’	Some geologic structures are noticed (microfauna).	Reddish brown fissile shale Dark grey shale Interbedded oolitic ironstone Dark grey shale Brownish well sorted angular grains sandstone with forams

Fig. 4.4 Lithologic Profile of Amaiyi Outcrop (L4) in Mamu Formation

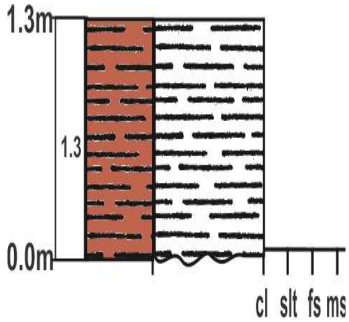
Lithology	Location	Structures	Descriptions
	L9 Ebunwana N5°47 161' E7°52 183'	No structures found	Reddish brown shale

Fig. 4.5 Lithologic Profile of Ebunwana Outcrop (L9) in Mamu Formation

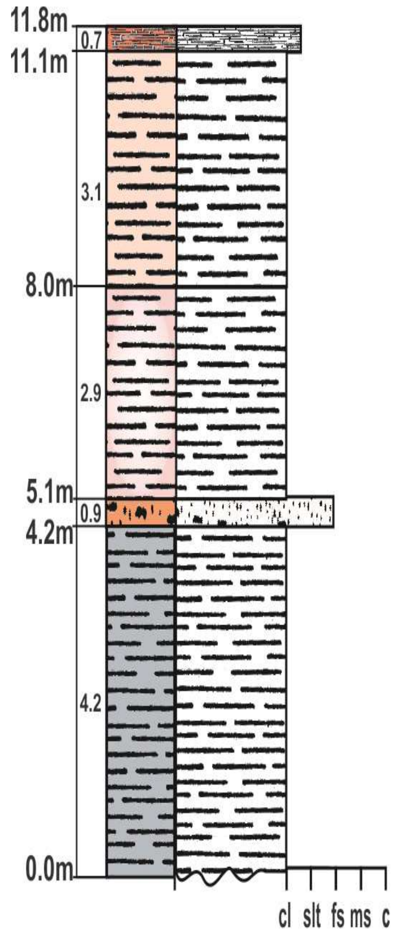
Lithology	Location	Structures	Descriptions
	L20 Amaiyi/Nguzu N5°45 937’ E7°49 173’	No structures found	Reddish laterite Reddish laminated shale Whitish/pinkish coal Oolitic ironstone Grey/dark fissile shale

Fig. 4. 6. Lithologic Profile of Amaiyi/Nguzu Outcrop (L20) in Mamu Formation

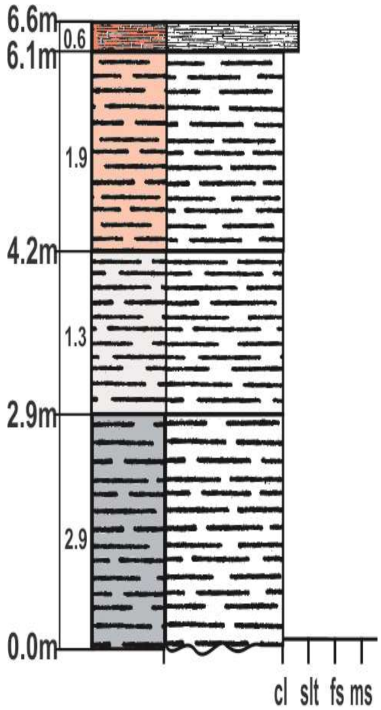
Lithology	Location	Structures	Descriptions
	L22 Nguzu N5°46 076' E7°49 174'	No structures found	Reddish laterite Reddish grey, fissile shale Light grey shale Dark grey fissile shale

Fig. 4.7 Lithologic Profile of Nguzu Outcrop (L22) in Mamu Formation

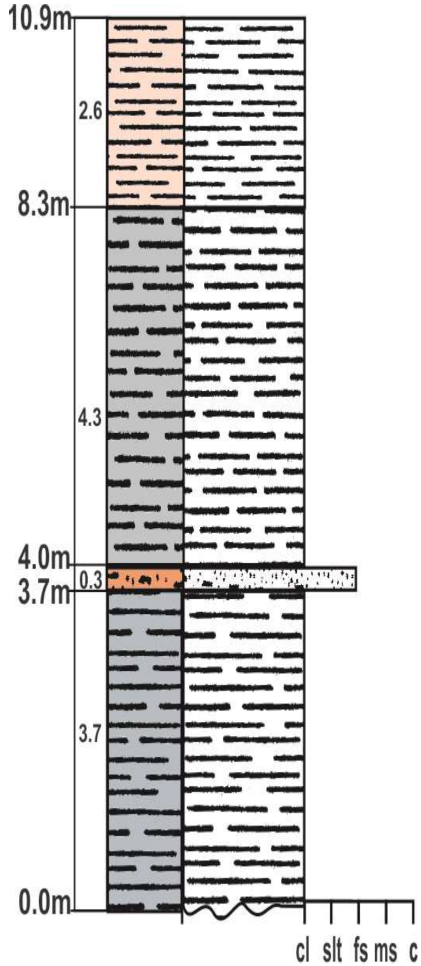
Lithology	Location	Structures	Descriptions
	L23 Iyiesa-Amaiyi N5°46 052’ E7°49 240’	No structures found	Reddish grey fissile shale Dark fissile shale Interbedded oolitic ironstone Dark fissile shale

Fig. 4.8. Lithologic Profile of Nguzu Outcrop (L23) in Mamu Formation

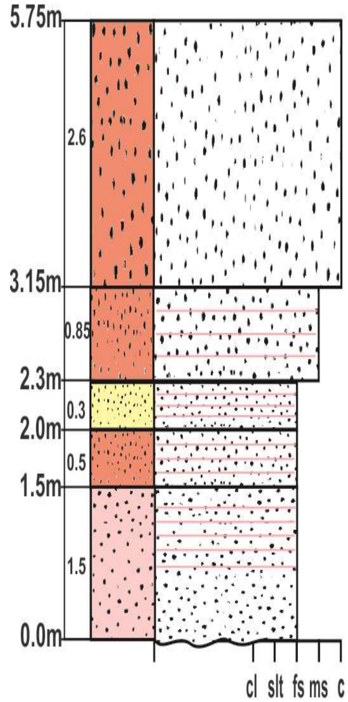
Lithology	Location	Structures	Descriptions
	L5 Ekeje N5°46 797’ E7°49 314’	No structures found	Reddish coarse sandstone Reddish, medium indurated, laminated sandstone Yellowish, friable, laminated poorly sorted clay matrix Reddish laminated medium indurated poorly sorted sandstone Parallel laminated pinkish poorly sorted angular, rounded friable sandstone

Fig. 4.9 Lithologic Profile of Ekeje Edda outcrop (L5) in Nkporo Formation

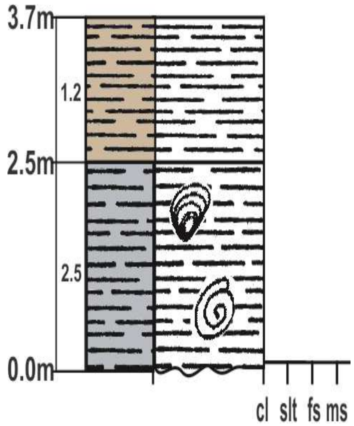
Lithology	Location	Structures	Descriptions
	L7 Asaga-Amangwu N5°50 246' E7°52 329'	Some structures like moulds of microfossils such as gastropods and ostracod were found	Reddish grey fissile shale Dark fissile shale

Fig. 4.10. Lithologic Profile of Asaga Amangwu Outcrop (L7) in Nkporo Formation

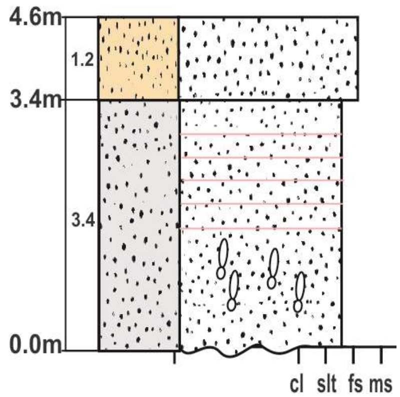
Lithology	Location	Structures	Descriptions
	L10 Nkelogu Ezi-Edda N5°48 551' E7°50 641'	Some structures found (microfauna)	Brown, fine-grained and well-sorted sandstone/clay Whitish/pinkish, laminated, well sorted and very fine-grained sandstone

Fig. 4.11. Lithologic Profile of Nkelogu Ezi-Edda Outcrop (L10) in Nkporo Unit

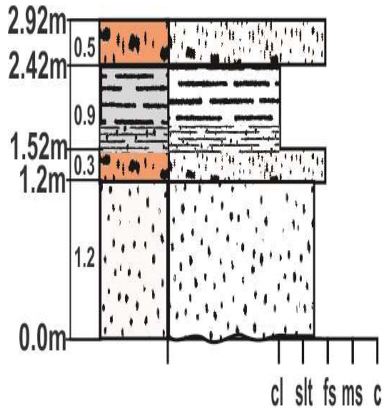
<table>
<tr><th>Lithology</th><th>Location</th><th>Structures</th><th>Descriptions</th></tr>
<tr><td>
</td><td>L11
Ekelogu
N5°48 551’
E7°50 641’</td><td>No structures found</td><td>Brown, coarse oolitic ironstone
Light brown with reddish intercalation shale
Reddish/brown, coarse oolitic ironstone
Whitish, friable, poorly sorted rounded sandstone</td></tr>
</table>

Fig. 4.12. Lithologic Profile of Nkelogu Outcrop (L11) in Nkporo Formation

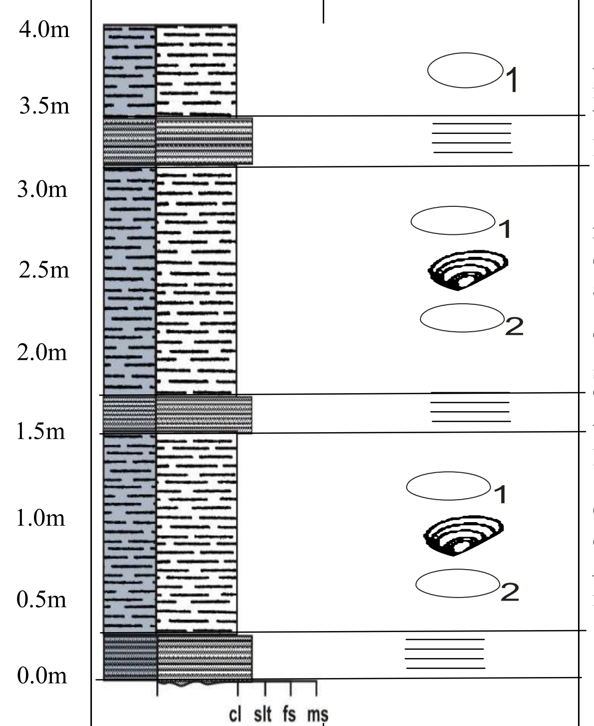
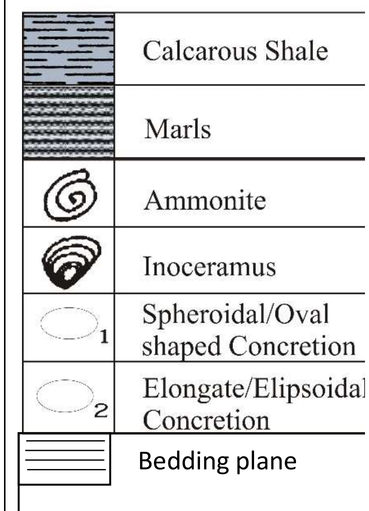
Thickness	Lithology	Structure/Fossils	Description	Location	Lithofacies	Interpretation
			A succession of consolidated interbedded papery dark grey to black calcareous shales and platy light grey marlstones. The thicknesses of marlstone ranged from 0.10 – 0.30m. Dark colour due to the presence of anoxicity. The thicknesses of calcareous shale ranged from 0.60 – 1.50m. There are pyrite concretions of varying sizes present in both lithologies. Only biogenic structures are the casts and moulds of the bivalve, *Inoceramus labiatus* which occur in places.	L43 Iyiesa-Amaiyi N5°49 007' E7°54 608'	Lithofacies identified are calcareous shale facies and platy marlstone facies	Oscillating sedimentation flux. Low energy, shallow marine, anoxic environment. **LEGEND** 

Fig. 4.13 Lithologic Profile of Ogbu Outcrop (L43) in Nkporo Formation

4.2 Geology of the Study Area

The geology of the Afikpo-Edda area is shown in Figure 4.14. It is observed that it made up of the Nkporo and Mamu formations. Figs. 4.1 - 4.13 reveals the dominant rock varieties presence are, sands/sandstone, carbonate/evaporites and mudstone/shale. Majority of the shale outcrop sections at Afikpo area are laid by oolitic ironstone or lateritic cap rock. Communities within the study area are Asaga-Amangwu, Amosu, Ezi-Edda, Ndi-ofia Edda, Amaigbo, Amoba, Owutu, Ogbu, Ekeje, Amaiyi, Enohia, Nguzu, Ebuwana and Unwana road were, underlain by sedimentary rocks of Southeastern Nigeria.

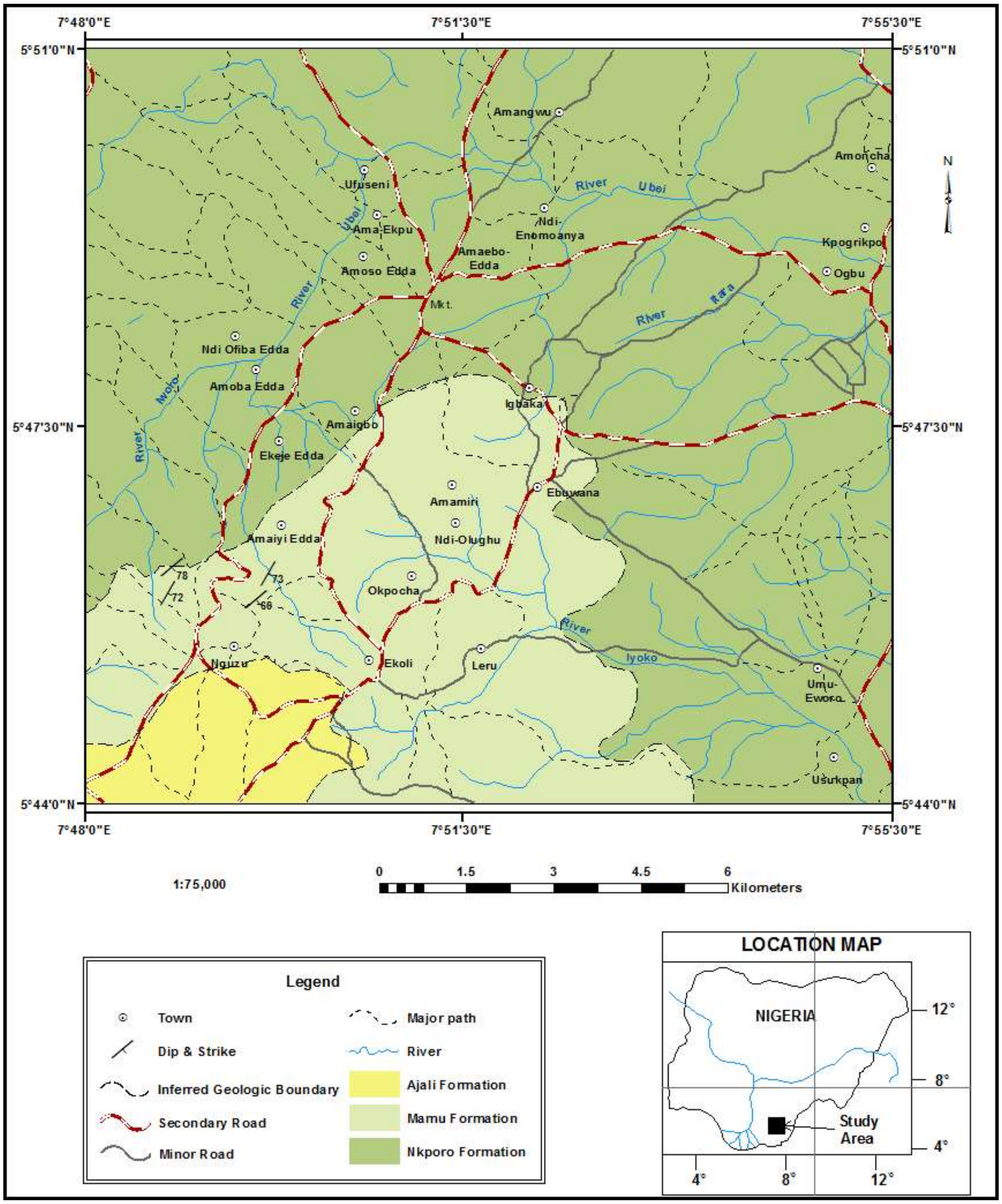


Fig. 4.14 Geological Map of Afikpo-Edda area (Modified from Geological and Mineral Resources Map of South-east Zone, Nigeria by NGSA 2007. First Edition)

4.2.1 Nkporo Formation:

Nkporo shale of Late Campanian age is the basal facies of the late Cretaceous sedimentary cycle within the Anambra basin (Reyment, 1948). Exposures in the study area are poor, with coarsening upward deltaic sequences of shale and sands interbedded (Murat, 1972; Obi, 2000; Obi). The vertical association of distributaries channel sands (basal Mamu Formation) supports this interpretation (Figure 15). The sediments are normally associated with siderites and pyrites of Ogbu road (L43), which are early diagenetic minerals. Sedimentary structures of the channel sand exposed at Asaga Amangwu (L7), for instance demonstrates possible tidal processes aswell as a few ostracod and gastropod shells, suggesting marine incursions into these distributaries channel systems.

4.2.2 Mamu Formation:

The Mamu Formation (Lower Maastrichtian) previously, the Lower Coal Measures (Simpson, 1954; Reyment, 1948) overlies the Nkporo/Enugu Shales without indication of a break in sedimentation.

Mamu Formation overlies the upper Campanian lateral facies associations delineated above. The age ranges from lower to middle Maastrichtian from south to north. Both vertical and lateral facies changes were observed, with formation thickness and height ranging from 100m to 1000m, 3m to 22m respectively across the basin. The lithology includes shales and sandstones, with some limestone nodules within the south and coal seams/lignite bands ascertained around Amaiyi/Nguzu road (Figure 15). Depositional environments include distributaries/estuarine channels, barrier foot, swamp and tidal flat.

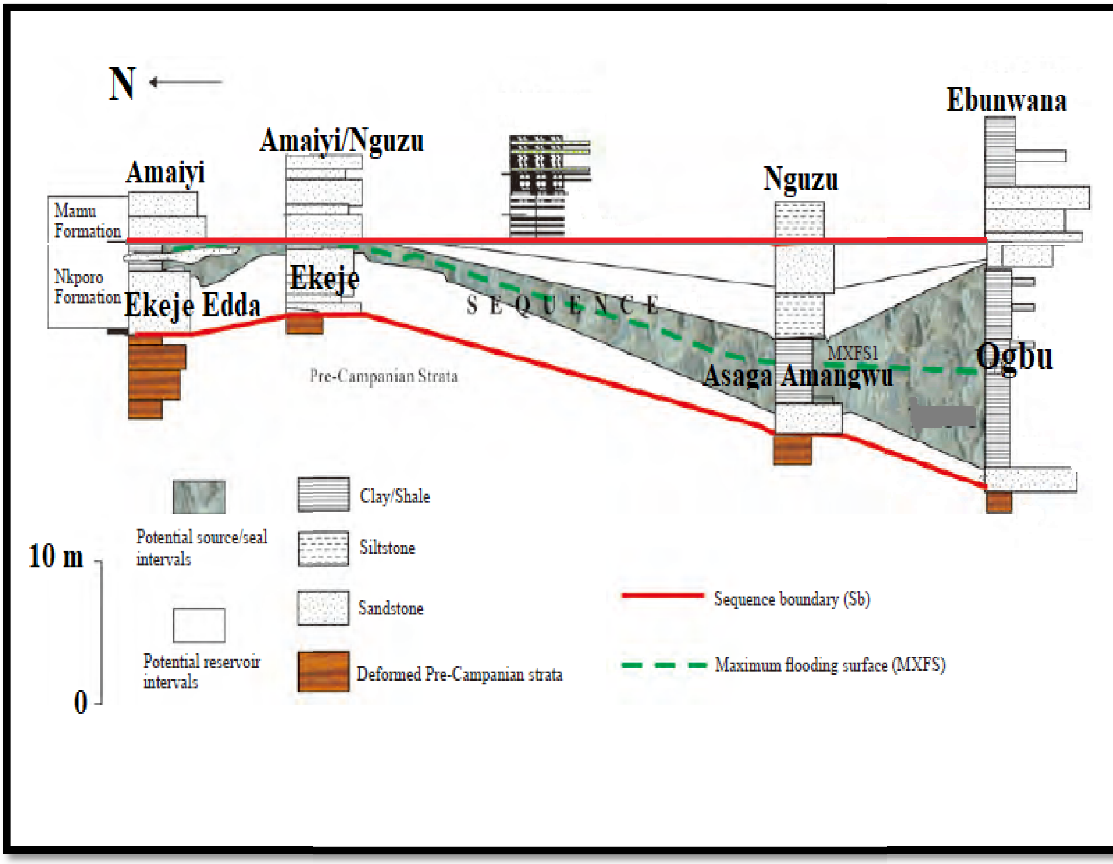


Fig. 4.15. Litho-Stratigraphic Correlation across the Anambra Basin base on Mamu and Nkporo Formation (modified after Odnuze and Obi, 2013)

Table 4.1 Rock Descriptions (Hand specimen) Texture, Mineralogy and Sample Locations of Mamau Formation

Sample code	Co-ordinates	Location	Texture	Mineralogy	Rock type
L1	Lat.5°45´97´´N Long.7°49´17´´E	Amaiyi	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale, lignite & oolitic ironstone
L2	Lat. 5°46´02´´N Long.7°49´19´E	Nguzu	Fine grained	Quartz, kaolinite	Reddish shale, dark grey shale &oolitic ironstone
L3	Lat. 5°46´13´´N Long.7°49´45´´E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, brown shale, clay and oolitic ironstone
L4	Lat. 5° 46´21´´N Long.7°49´40´´E	Ekeje	Fine grained	Quartz, kaolinite	Fossil Sandstone, dark grey shale and oolitic ironstone
L5	Lat. 5° 46´80´´N Long.7°49´31´´E	Amaiyi	Fine grained	Quartz, kaolinite	Sandstone and clay matrix
L8	Lat. 5° 46´70´´N Long.7°52´05´´E	Ebunwana	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L9	Lat.5°47´16´´N Long.7°52´18´´E	Ebunwana	Fine grained	Quartz, kaolinite and anatase	Reddish brown shale
L 15	Lat. 5° 46´23´´N Long.7°49´33´´E	Amaiyi-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L16	Lat. 5° 46´22´´N Long.7°49´27´´E	Amaiyi-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L17	Lat.5°46´04´´N Long.7°49´36´´E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L18	Lat. 5°46´06´´N Long.7°49´34´E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L19	Lat. 5°45´92´´N Long.7°49´18´´E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone

Continuation of Rock Descriptions (Hand specimen) and Sample Locations of Mamu Formation

Sample code	Co-ordinates	Location	Texture	Mineralogy	Rock type
L20	Lat. 5°45′94′′N Long.7°49′17′′E	Nguzu	Fine grained	Quartz, kaolinite and anatase	Sandstone, dark grey shale and oolitic ironstone
L21	Lat. 5° 45′98′′N Long.7°49′17′′E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L22	Lat. 5° 46′08′′N Long.7°49′17′′E	Nguzu	Fine grained	Quartz, kaolinite	Reddish laterite clay, dark grey shale and ironstone
L 23	Lat. 5° 46′05′′N Long.7°49′24′′E	Nguzu	Fine grained	Quartz, kaolinite	Dark grey shale& oolitic ironstone
L25	Lat.5°46′20′′N Long.7°49′37′′E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L26	Lat. 5°46′26′′N Long.7°49′27′E	Nguzu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone

4.2 Rock Descriptions (Hand specimen) Texture, Mineralogy and Sample Locations of Nkporo Formation

Sample code	Co-ordinates	Location	Texture	Mineralogy	Rock type
L6	Lat. 5° 47´05´´N Long.7°49´49´´E	Ekeje	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L 7	Lat. 5° 50´25´´N Long.7°52´32´´E	Amangwu	Fine grained	Quartz, kaolinite, jarosite	Dark fissile shale and reddish grey shale
L10	Lat. 5°48´55´´N Long.7°50´64´E	Nkelogu	Fine grained	Quartz, kaolinite	Fossilferous andstone and clay
L11	Lat. 5°48´50´´N Long.7°50´61´´E	Nkelogu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L12	Lat. 5° 47´60´´N Long.7°49´74´´E	Amoba	Fine grained	Quartz, kaolinite	Sandstone, dark shale oolitic ironstone
L13	Lat. 5° 47´36´´N Long.7°49´55´´E	Ekeje-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L14	Lat. 5° 47´04´´N Long.7°49´49´´E	Ekeje-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L27	Lat. 5°46´83´´N Long.7°49´34´´E	Ekeje	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L28	Lat. 5° 47´58´´N Long.7°49´56´´E	Ekeje	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L29	Lat. 5° 47´60´´N Long.7°49´76´´E	Amoba	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L30	Lat. 5° 47´69´´N Long.7°49´84´´E	Amoba	Fine grained	Quartz, kaolinite and goethite	Sandstone, dark grey shale and oolitic ironstone
L 31	Lat. 5° 48´25´´N Long.7°50´03´´E	Ndi-Ofiba	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone

Continuation of Rock Descriptions (Hand specimen) of Nkporo Formation

Sample code	Co-ordinates	Location	Texture	Mineralogy	Rock type
L32	Lat. 5° 48´42´´N Long.7°50´19´´E	Ndiba-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L33	Lat.5°48´40´´N Long.7°50´02´´E	Ndiba-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L34	Lat. 5°48´45´´N Long.7°50´45´E	Amaigbo	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L35	Lat. 5°48´47´´N Long.7°50´36´´E	Ezi-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L36	Lat. 5° 48´83´´N Long.7°50´51´´E	Amosu-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L37	Lat. 5° 48´95´´N Long.7°50´37´´E	Amosu-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L38	Lat. 5° 49´08´´N Long.7°50´24´´E	Amosu-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L 39	Lat. 5° 48´89´´N Long.7°51´49´´E	Owutu-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L40	Lat. 5° 48´89´´N Long.7°51´59´´E	Owutu-Edda	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L41	Lat.5°49´23´´N Long.7°53´20´´E	Ogbu	Fine grained	Quartz, kaolinite and hematite	Sandstone, dark grey shale and oolitic ironstone

Continuation of Rock Descriptions (Hand specimen) of Nkporo Formation

Sample code	Co-ordinates	Location	Texture	Mineralogy	Rock type
L42	Lat. 5°49´26´´N Long.7°53´31´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L43	Lat. 5°49´01´´N Long.7°54´61´´E	Ogbu	Fine grained	Quartz, kaolinite, pyrite, siderite, and phenate	Calcareous dark shale and marlstone
L44	Lat. 5° 48´98´´N Long.7°54´65´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L45	Lat. 5° 48´89´´N Long.7°54´65´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L46	Lat. 5° 48´96´´N Long.7°54´68'´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L 47	Lat. 5° 48´84´´N Long.7°54´79´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L48	Lat. 5° 48´74´´N Long.7°54´90´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L49	Lat.5°48´74´´N Long.7°55´01´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L50	Lat. 5°48´78´´N Long.7°55´19´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L51	Lat. 5°48´73´´N Long.7°55´29´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L52	Lat. 5° 50´85´´N Long.7°55´19´´E	Enohia	Fine grained	Quartz, kaolinite, and limonite	Sandstone, dark grey shale and oolitic ironstone

Continuation of Rock Descriptions (Hand specimen) and Nkporo Sample Locations

Sample code	Co-ordinates	Location	Texture	Mineralogy	Rock type
L46	Lat. 5° 48´96´´N Long.7°54´68’´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L 47	Lat. 5° 48´84´´N Long.7°54´79´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L48	Lat. 5° 48´74´´N Long.7°54´90´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L49	Lat.5°48´74´´N Long.7°55´01´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L50	Lat. 5°48´78´´N Long.7°55´19´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L51	Lat. 5°48´73´´N Long.7°55´29´´E	Ogbu	Fine grained	Quartz, kaolinite	Sandstone, dark grey shale and oolitic ironstone
L52	Lat. 5° 50´85´´N Long.7°55´19´´E	Enohia	Fine grained	Quartz, kaolinite, and limonite	Sandstone, dark grey shale and oolitic ironstone

4.3 X-Ray Diffraction Results

The relative proportions of clay minerals in a sample, however, can be estimated from the relative intensities of the peaks on an X-ray diffraction pattern (Gillott, 1969).

The classic x-ray diffractogram of Afikpo-Edda samples are shown in Figs 4.16-4.25 and Tables 4.3a-4.3b shows modal mineralogical values. These diffractograms were comparing among the recognised level also be viewed in relation to Joint Committee on Powder Diffraction Standards (1974) and that of clay minerals recognized by (Carol, 1971). Area methodology was employed in calculating relative proportions of the known minerals as shown below (Fig 4.16- 4.25).

As shown by the diffractogram (Figs. 4.16 – 4.25), shales in Afikpo are typically composed of varying quantities of trace and minor minerals containing clay minerals (kaolinite and smectite), anatase, jarosite, goethite, hematite, pyrite, phenate and limonite, with quartz as the dominant non clay mineral. The standard shale color obtainable from the hand-specimen is gray, but the color of the rock varies with the addition of varying quantities of minor constituents. Some colour changes in shale are indicative of the presence of ferric oxide minerals for example hematite alters to red colouration; iron hydroxide mineral like goethite changes the rock to brown colour while limonite changes the colour to yellow, or micaceous minerals change the colour to green (Jubril and Amajor, 1991; Herbert, 1996).

Black shales that form in anoxic circumstances contain compacted free carbon at the side of ferrous iron (Fe^{2+}) and sulphur (S^{2-}) (Blatt et. al., 1996). In this work, pyrite and jarosite produce the black colourations whereas phenate modify the colour of the rock to purple. In terms of industrial applications, some samples of shale could pose a threat to their industrial exploit for paper and elastic synthetic substance manufacturing, considering the existence of certain minerals containing ferric oxides. This is often as a result of iron oxide which produces colouration effect on finishes product.

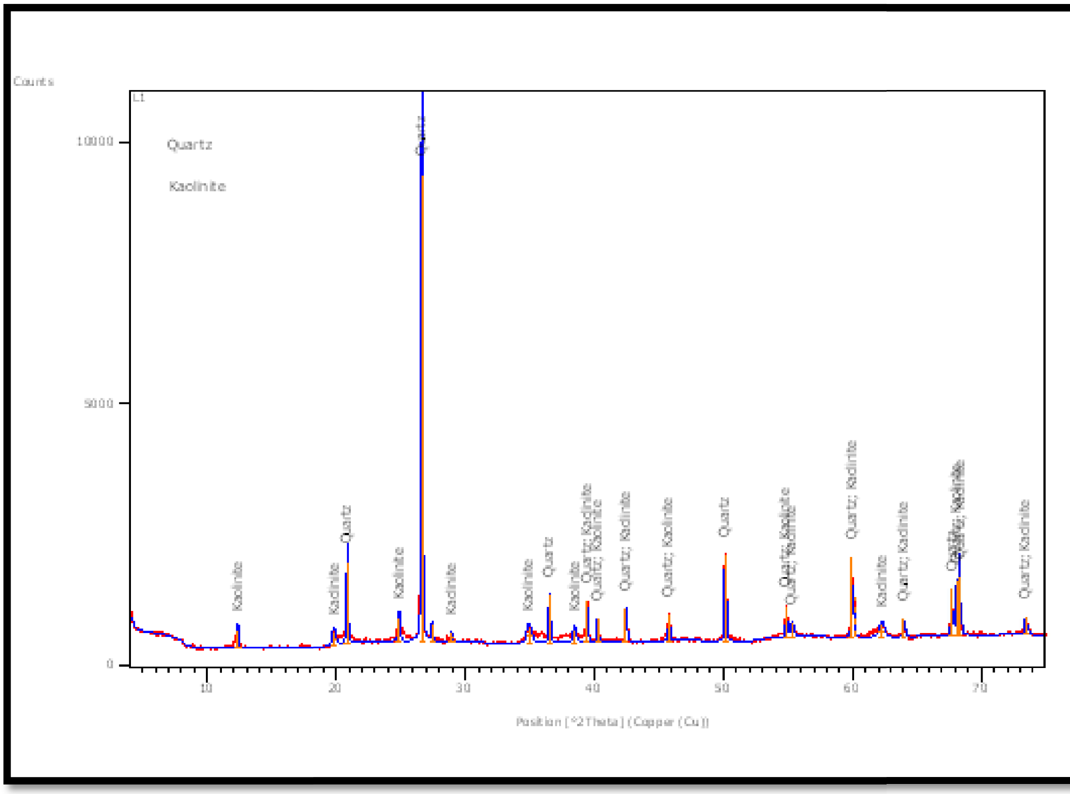


Figure 4.16. X-ray diffractogram for the L1 Mamu shale sample

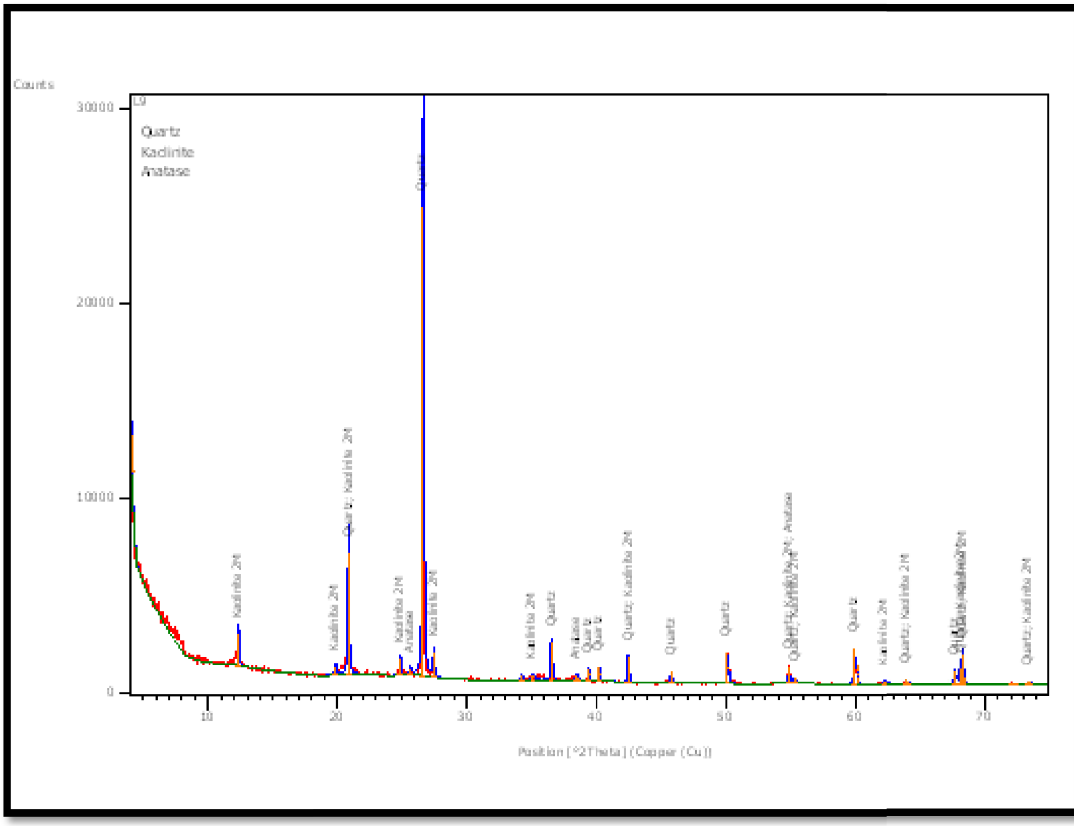


Figure 4.17. X-ray diffractogram for the L9 Mamu shale sample

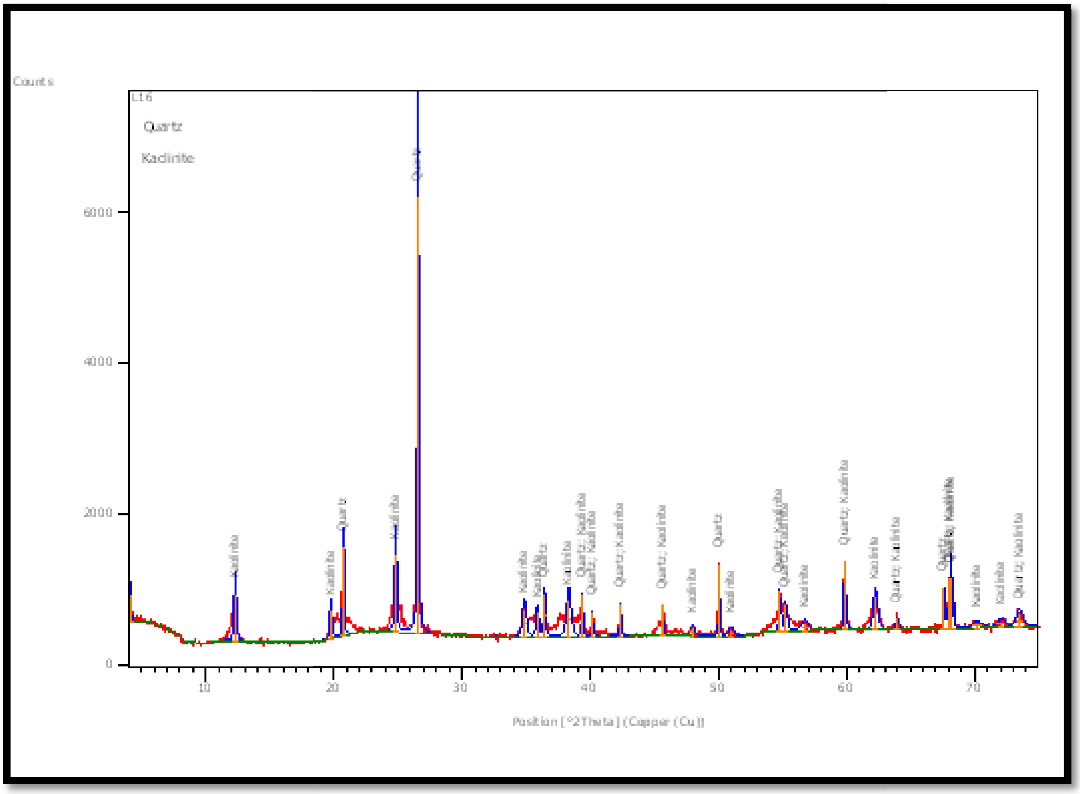
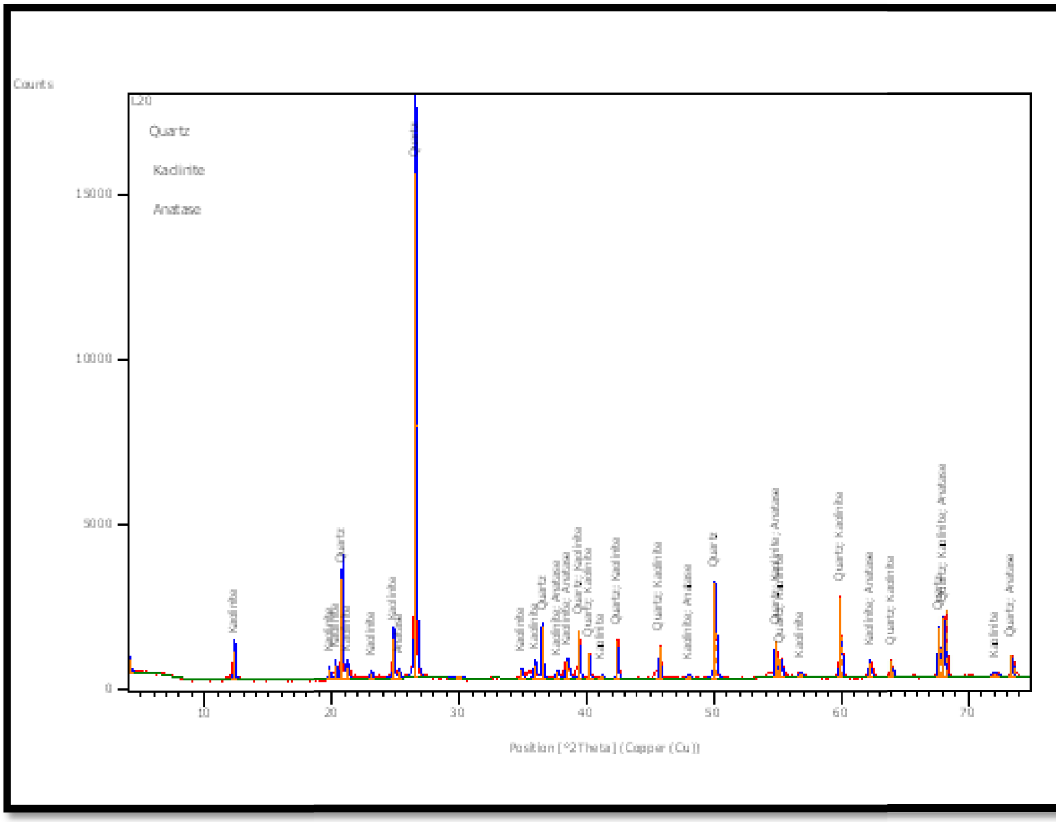


Figure 4.18. X-ray diffractogram for the L16 Mamu shale sample



Figrue 4.19. X-ray diffractogram for the L20 Mamu shale sample

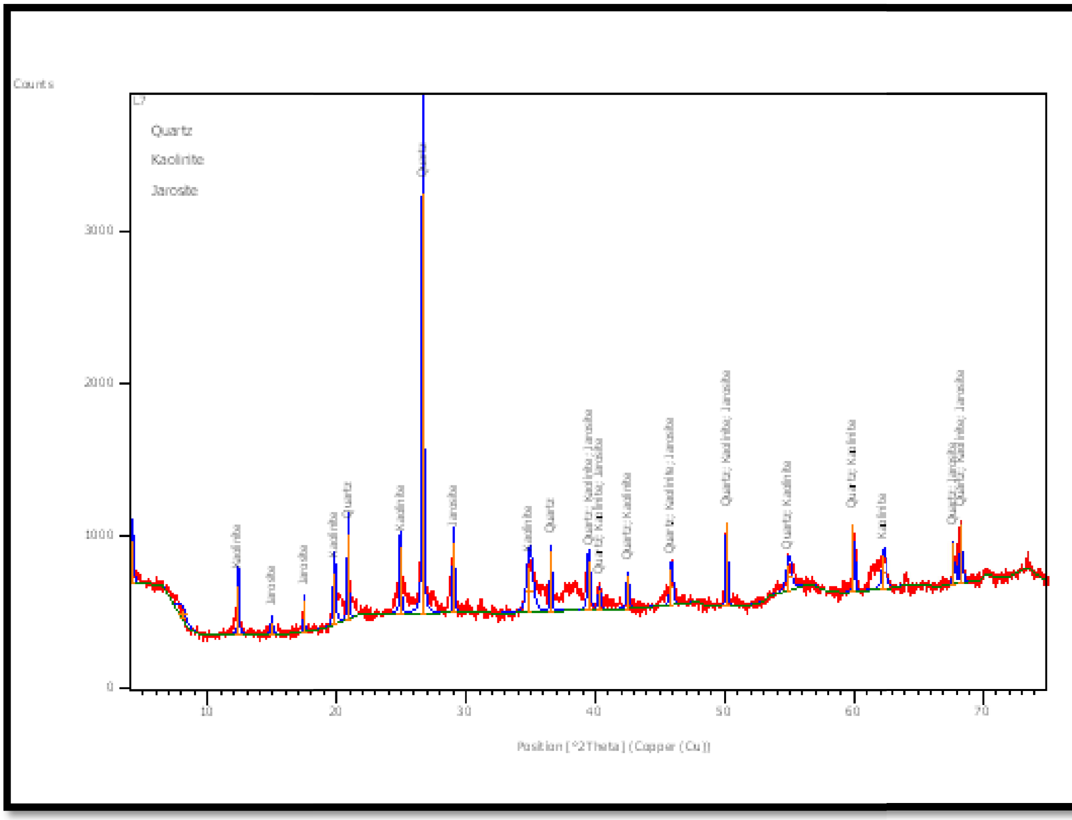


Figure 4.20. X-ray diffractogram for the L7 Nkporo shale sample

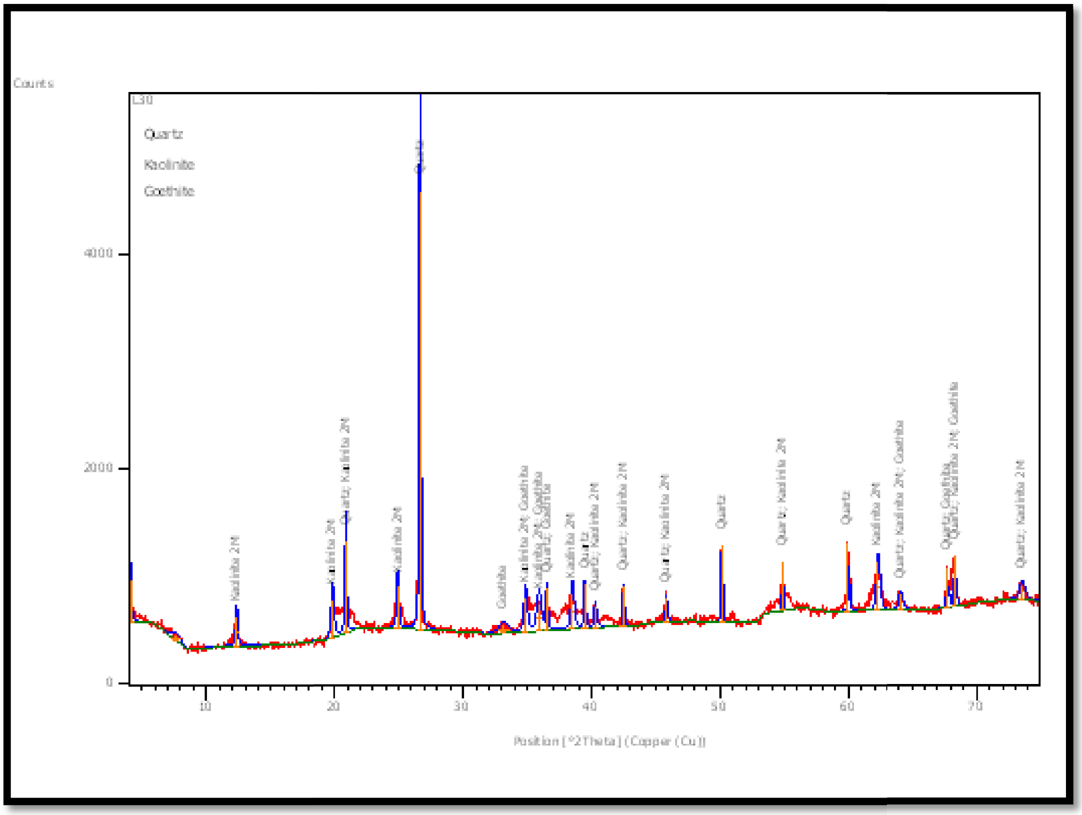


Figure 4.21. X-ray diffractogram for the L30 Nkporo shale sample

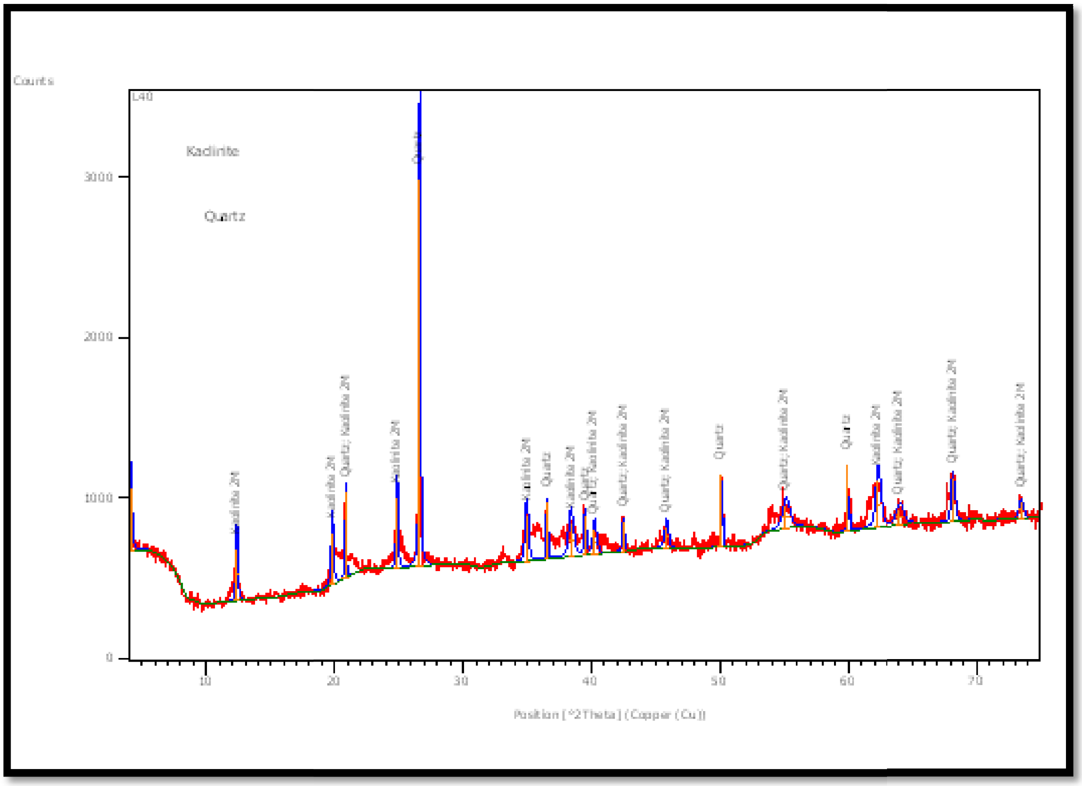


Figure 4.22. X-ray diffractogram for the L40 Nkporo shale sample

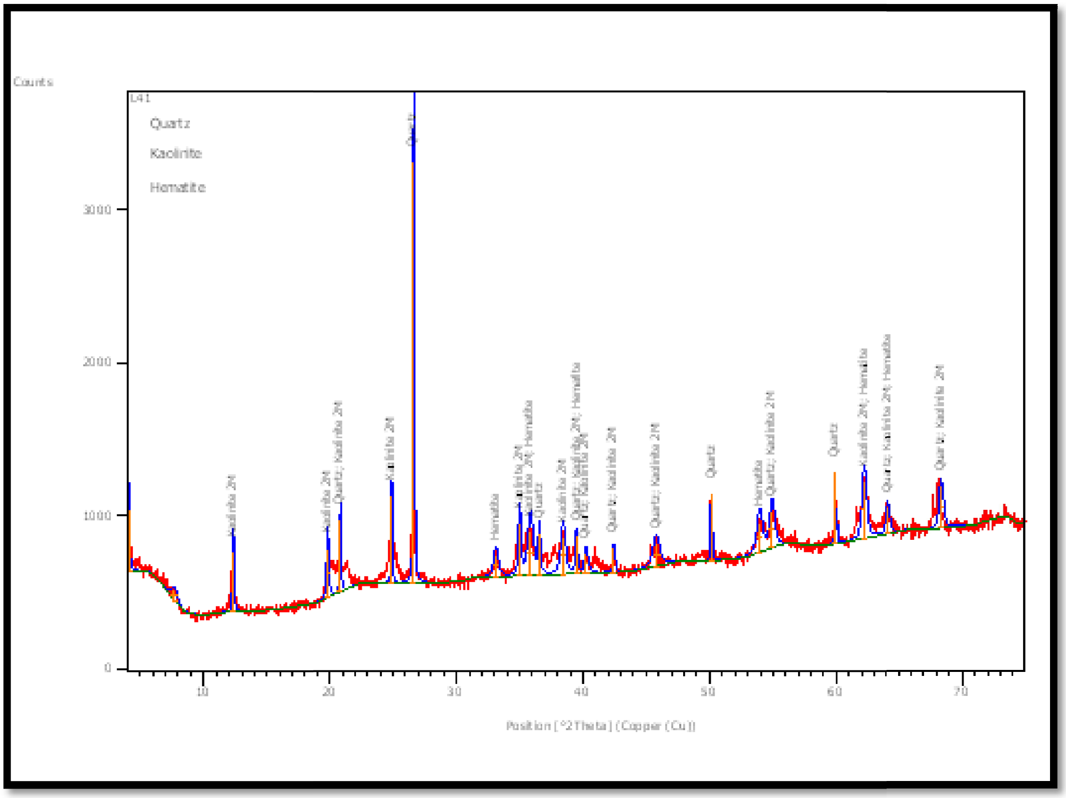


Figure 4.23. X-ray diffractogram for the L41 Nkporo shale sample

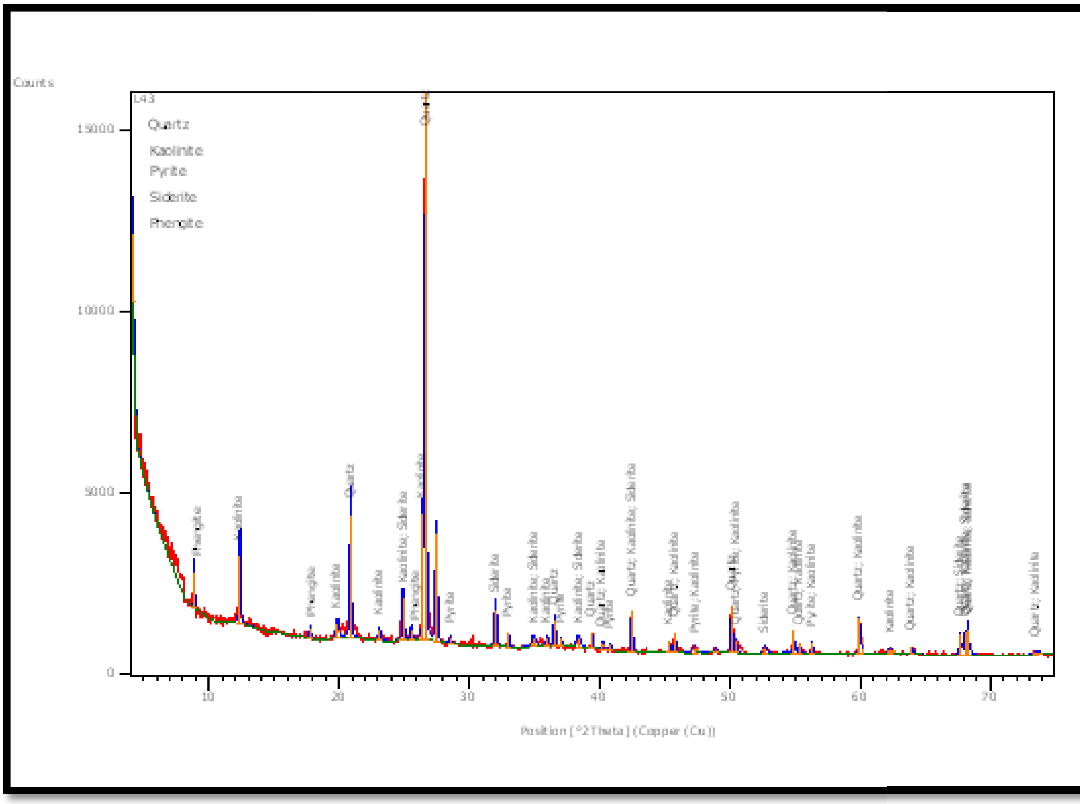


Figure 4.24. X-ray diffractogram for the L43 Nkporo shale sample

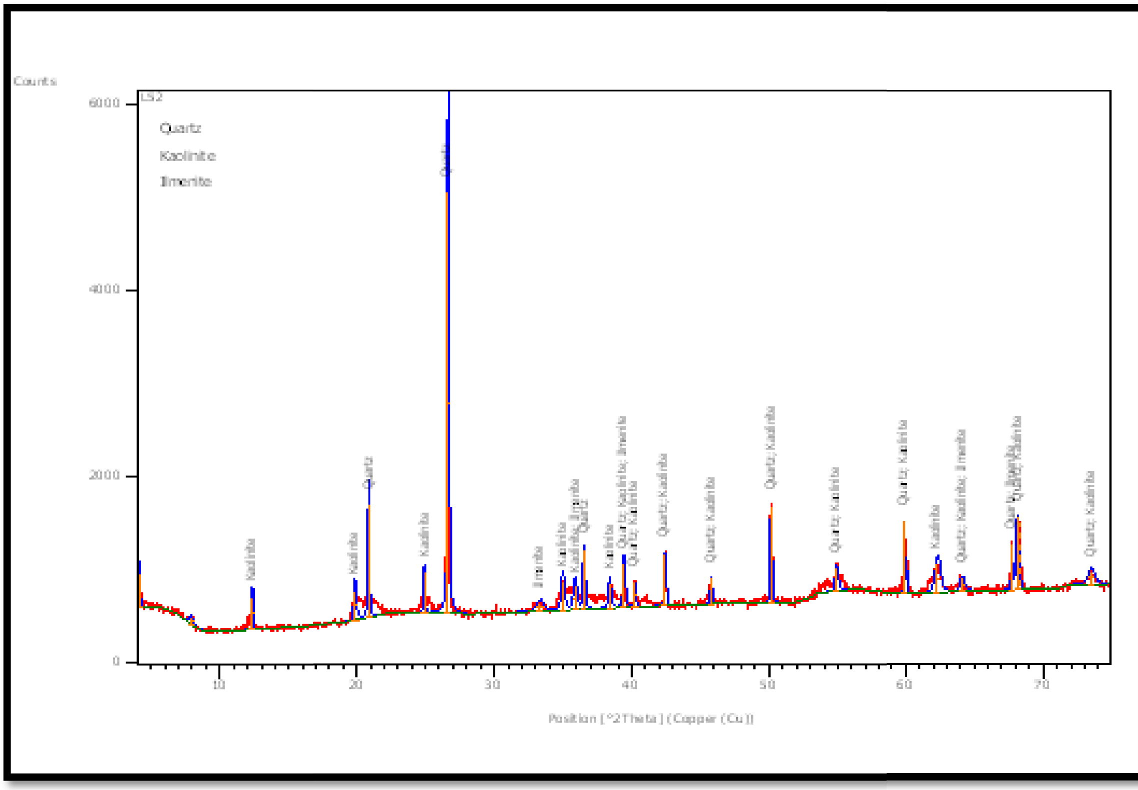


Figure 4.25. X-ray diffractogram for the L52 Nkporo shale sample

4.3.1 Mineralogical Characteristics

The X-Ray diffraction results signified that the shale group consists of Quartz, Kaolinite, Jarosite, Anatase, Goethite, Hematite, Pyrite, Smectite, Siderites Phenate and Limonite. In L1 (Fig. 4.16), the minerals identified are mainly quartz and kaolinite. Quartz is the dominant non-clay mineral constituting about 58.80% of the total mineral present, whereas the average of the clay minerals (kaolinite and smectite) found are between 41.20% and 5.7% (Table 4.3b), respectively. In addition, the XRD findings for the shale in position L7 (Fig. 4.20) indicate the prevalence of minerals such as kaolinite, quartz, and jarosite. The percentage of the kaolinite and smectite group clay minerals within the shale in this location is 39.40% and 0.57% (Table 4.3b). The large and sharp peaks, which are signs of moderate to well crystalline minerals, show the prominent basal reflections of quartz (Figs. 4.16 - 4.25). Quartz is common and dominant that constitute of about 49.60% of the mineral present whereas jarosite the last mineral present within the location may be a sulphate mineral formed in ore deposits by the oxidisation of iron sulphides constitutes about 12.0% of total mineral composition in sample from location L7 (Table 4.3b).

The XRD results for shale in locality of L9 (Fig. 4.17) exposed quartz with the level of about 60.30%, kaolinite of about 21.50% while Anatase, one of the minerals that form titanium, is about 18.2%. Virtually, similar range of minerals in location L1 was also observed within the X-ray diffractogram in shale sample from L16 (Fig. 4.18) that constituting quartz and kaolinite. As shown by the diffractogram, the shale mineral assemblage from sample L20 (Fig. 4.19) consists of kaolinite, anatase, and quartz as the predominant non-clay mineral. Here like others quartz has the highest proportion of about 61.30%, kaolinite constitutes about 32.45% and anatase about 6.25% (Table 4.3a). The X-ray diffractogram result of L30 (Fig. 4.21) showed that kaolinite, quartz and goethite are the mineral assemblage present. The major dominant and commonly distributed clay minerals are 36.40 percent (kaolinite), 13.50 percent (goethite) and quartz is 50.10 percent average dominant non-clay mineral (Table 4.3b).

The obtained XRD result of L40 (Fig. 4.22) reveals distinct peaks of quartz and kaolinite. The kaolinite and quartz in this sample have the same proportion of 50% each (Table 4.3a). The shale mineral assemblage as evident by the diffractogram in location L41 (Fig. 4.23) includes kaolinite, quartz and hematite. The result indicates mean percentage of the kaolinite is 38.50 percent, hematite about 9.75% and quartz about 51.75% (Table 4.3b). Location L43 (Fig. 4.24) consists of kaolinite, quartz, pyrite and smectites. Smectite is another clay mineral. Phenate, any salt or ester of phenol (when considered as an acid). Most dominant minerals are quartz and kaolinite with the percentage of 41.2% and 32.3%, pyrite constitutes of about 11.10%, siderite consists of about 5.70% while phenate about 9.7% (Table 4.3b). The XRD of sample L52 (Fig. 4.25) revealed the presence of kaolinite, quartz as the predominant non-clay mineral and limonite. Limonite is an iron ore composed of a mixture of hydro-iron (III) oxides of different compositions. The proportion of clay mineral (kaolinite) is 39.3%, quartz, non-clay mineral is about 51.90% and limonite is 8.8% (Table 4.3b).

In conclution, Fig 3a of Mamu formation comprises of only three minerals includes; Quartz, kaolinite and anatase (titanium content) while Fig 3b of Nkporo Formation made up of quartz, kaolinite and smectite, jarosite, goethite, hematite, pyrite, phenate and limonite (mainly ferric oxide minerals).

Table 4.3a Mineral Contents (in percentage) of Mamu Shale in Afikpo-EddaArea.

Location/SN	Formation	Quartz	Kaolinite	Anatase	Jarosite	Goethite	Hematite	Pyrite	Smectite	Phenate	Limonite
Amaiyi/L1	Mamu	58.80	41.20	_	_	_	_	_	_	_	_
Ebuwana/L 9	Mamu	60.30	21.52	18.20	_	_	_	_	_	_	_
Amaiyi/L16	Mamu	56.45	43.55	_	_	_	_	_	_	_	_
Nguzu/L20	Mamu	54.30	32.45	13.25	_	_	_	_	_	_	_
	Average	**57.46**	**34.68**	**7.86**	**-**	**-**	**-**	**-**	**-**		

Table 4.3b Mineral Contents (percentage) of Nkporo Shale in Afikpo-Edda Area

Location/SN	Formation	Quartz	Kaolinite	Anatase	Jarosite	Goethite	Hematite	Pyrite	Smectite	Phenate	Limonite
Amangwu/L7	Nkporo	49.60	39.40	-	12.00	-	-	-	-	-	-
Amoba/L30	Nkporo	51.10	36.40	_	_	13.50	_	_	_	_	_
Owutu/L40	Nkporo	51.00	49.00	_	_	_	_	_	_	_	_
Ogbu/L41	Nkporo	51.75	38.50	_	_	_	9.75	_	_	_	_
Ogbu/L43	Nkporo	41.20	32.30	_	_	_	_	11.10	5.70	9.70	_
Enohia/L52	Nkporo	56.90	39.30	_	_	_	_	_	_	_	8.80
Average		**50.26**	**39.15**		**1.20**	**1.35**	**0.98**	**1.11**	**0.57**	**0.97**	**0.88**

4.4 Inorganic Geochemistry Results

4.4.1 Major Oxide Results

Major oxide analyses of thirty shale samples results are shown in Tables 4.4a and 4.4b. The mean for the major oxides (wt %) data for the samples understudy is summarised in Table 4.45. These are contrasted with the average shales of the globe; (Pettijjohn, 1957), North American Shale Composite (NASC) (Gromet et. al., 1984; Turekan and Wedephol 1961) and Nigerias' other shales (Table 4.7). The chemical analysis result revealed the predominance of SiO_2 ranging from (42.67 - 64.40%) for Nkporo and (45.10% - 73.13%) for Mamu shale. The Al_2O_3 content for Nkporo shale which is moderately high ranges from (12.69% – 25.26%) with the average of (22.39%) while for the Mamu shale is between 13.48% – 24.87% with the average of (18.90%). The average silica /alumina ratios for the shale are 1.55% and 2.32% correspondingly for Nkporo, while 2.56% and 4.23% for Mamu shale (Table 4.4a and 4.4b). These results clearly define the shale in Nkporo to be slightly low siliceous and highly aluminous, whereas Mamu shale is highly siliceous with low aluminous content. This determines the potential relative proportions of aluminate and ferrite phases in the rock, which shows that there are proportionally more aluminate and less ferrite in the rock. The average SiO_2 content of Nkporo and Mamu shales are 49.71% and 59.79% respectively while the average of Al_2O_3 is 22.39% and 18.90% respectively (Tables 4.4a and 4.4b). This means that the shales are of refractory varieties of low grade. In general, the higher the amount of alumina indicates the higher the refractory product quality. In Tables 4.4a and 4.4b, silica ratio (SR) and alumina ratio (AR) of examined shales ranges from 1.55 to 4.04 and 2.40 to 12.01 for Mamu shale, with averages of 2.56 and 4.23 in that order. These quotients are the SR: 1.5 to 4.00 and AR: 1.4 to 3.50, which are favorable for the shale in making of constructional products and refractory materials (Abatan et al., 1993). The mass (71.91% and 68.07%) of the chemical compositions are these two oxides; SiO_2 and Al_2O_3.

With an average of 9.67% and 4.47%, the chemical impurities of Fe_2O_3 within the Nkporo and Mamu shales respectively, indicated by the presence of hematite (iron ore) in L41. Limonite that is currently recognized as a mixture of associated minerals of hydrated iron oxide (Northrop, 1959), including goethite and jarosite (L7) (Table

4.4a). However, after other minerals such as pyrite, there are limonite pseudomorphs, as in L43 of mineralogical characteristics (Table 4.4a).

For TiO_2 average in both shales are 1.04% and 0.19% (Tables 4.4a and 4.4b). The comparatively high prevalence of iron oxide in the analyzed samples resulted in the light brown color during the firing process. Fired colour is objectionable into paper as well as a few ceramic objects manufacturing however be appropriate in production of inferior floor covering, constructional commodities like roofing tiles, wall bricks, paints and earthenware.

Other significant chemical impurities include MgO which ranging from (0.24% – 1.24%) with the average of 0.72 in Nkporo shale and from 0.055% – 0.73% with the average of 0.40% in Mamu shale, whereas K_2O in Nkporo and Mamu ranges from (0.57 – 3.09%), average (1.17%) and (0.18% - 1.76%), average (1.09%) severally. In TiO_2, it varies from (0.80% - 1.40%). average (1.04%) in Nkporo and (0.93% - 1.53%), an average of 1.19% in Mamu shale whereas CaO, Na_2O, P_2O_5, MnO, Cr_2O_3 and MgO are <1%. With a usually low MgO and CaO content, K_2O and TiO_2 are > 1 percent, suggesting no related carbonates or dolomitisation phase in the study area (Obrike et al, 2012; Tables 4.4a and 4.4b). Abakaliki, Afikpo and Ngbo have been found associated with carbonates and dolomitisation of portions of Afikpo shale (Agunmanu, 1989). An indicator of the presence of illite is the comparatively high K_2O value in Afikpo shales (Akpokodje et. al., 1991; Tables 4.4a and 4.4b). In comparison, the low Na_2O values are most likely due to the comparatively low prevalence of sodium feldspar and sodium-rich clay in the samples analyzed.

Also, the high significance of TiO_2 in Mamu area reveals the presence of ilmenite, rutile and anatase (Winkler, 2003), as indicated in L9 and L20 mineralogical characteristics. Paints and varnishes, as well as paper and plastics, other pigment applications such as printing inks, fibres, rubbers, and beauty products are the most important application areas. The shale at Nkporo, serve as crude materials in the production of ceramics and refractory materials and poor quality bricks, then coloured paper, rubber and paint due to iron oxide contents.

The substandard quality of bricks, then white or plain paper, rubber and pigment can be updated by blending in with unadulterated alumina content or screening of the shale to limit the iron oxide, titanium and quartz contents by chemical treatment. This later treatment can in any case, increment the bricks production.

Table 4. 4a Major Oxides Concentration (in %) for Shale Samples of Nkporo Formation.

Sample Code	L5	L6	L7	L13	L27	L28	L30	L31	L32	L33	L34	L36	L38	L39	L40	L41	L43	L44	L47	L48	L50	L51	L52	**Average**
Location	Ekeje	Ekeje	Amagwu	Ekeje	Amiyi	Ekeje	Amoba	Ndi-Ofiba	Ndiba	Ndiba	Amaigbo	Amoso	R. Ubei	Amaebo	Owutu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Enohia	
SiO_2	45.60	46.42	50.29	46.51	47.24	47.37	52.98	49.84	49.07	45.24	42.67	54.33	54.26	50.68	45.36	46.55	61.68	64.40	47.85	46.69	48.63	45.98	53.76	49.71
Al_2O_3	23.38	24.53	21.72	23.57	22.25	24.73	23.53	23.07	24.11	21.97	20.25	21.76	23.65	20.51	21.28	24.14	12.69	18.64	24.12	24.77	25.26	24.61	20.33	22.39
Fe_2O_3	6.83	6.38	7.61	7.33	7.96	10.41	7.73	9.51	9.15	16.11	17.99	8.57	5.46	10.27	14.29	11.93	8.91	4.14	9.99	10.52	8.52	11.89	10.97	9.67
MgO	1.07	0.81	1.05	0.74	1.24	0.53	0.41	0.88	0.79	0.63	0.84	0.54	0.69	0.94	0.82	0.59	0.63	0.24	0.74	0.73	0.60	0.57	0.44	0.72
CaO	0.54	0.04	0.08	0.07	0.70	0.03	0.02	0.04	0.02	0.02	0.04	0.02	0.14	0.02	0.11	0.03	0.38	0.02	0.05	0.02	0.02	0.02	0.02	0.11
Na_2O	0.13	0.08	0.07	0.11	0.13	0.04	0.04	0.05	0.05	0.04	0.06	0.03	0.04	0.05	0.04	0.04	0.11	0.09	0.05	0.05	0.04	0.04	0.03	0.06
K_2O	1.38	1.40	2.20	1.26	1.43	0.78	0.57	1.46	1.15	0.81	1.29	0.63	1.00	1.37	1.00	1.00	3.09	2.29	1.21	1.18	1.05	0.98	0.78	1.17
TiO_2	0.80	0.82	0.92	1.21	0.83	1.40	1.15	1.05	0.98	1.04	0.87	0.98	1.17	0.99	0.99	1.20	0.92	1.04	1.03	0.96	1.31	1.20	1.06	1.04
P_2O_5	0.11	0.10	0.24	0.19	0.12	0.09	0.05	0.14	0.09	0.07	0.42	0.07	0.13	0.12	0.12	0.10	0.21	0.08	0.05	0.08	0.06	0.07	0.10	0.12
MnO	0.01	-	-	-	0.02	-	-	-	-	-	-	-	-	-	-	-	0.07	-	-	-	-	-	-	0.003
Cr_2O_3	0.017	0.017	0.017	0.018	0.017	0.020	0.016	0.020	0.018	0.022	0.017	0.019	0.017	0.019	0.02	0.022	0.015	0.013	0.019	0.019	0.021	0.021	0.017	0.018

Continuation of Major Oxides Concentration (in %) for Shale Samples of Nkporo Formation.

Sample code	L5	L6	L7	L13	L27	L28	L30	L31	L32	L33	L34	L36	L38	L39	L40	L41	L43	L44	L47	L48	L50	L51	L52	Average
Location	Ekeje	Ekeje	Amagwu	Ekeje	Amiyi	Ekeje	Amoba	Ndi-Ofiba	Ndiba	Ndiba	Amaigbo	Amoso	R. Ubei	Amaebo	Owutu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Enohia	
LOI	19.9	19.2	15.6	18.8	17.9	14.4	13.3	13.7	14.4	13.9	15.4	12.9	13.2	14.8	15.8	14.2	10.8	8.5	14.6	14.8	14.3	14.4	12.3	14.66
Total	99.77	99.8	99.80	99.8	99.84	99.80	99.80	99.76	99.83	99.85	99.85	99.85	99.76	99.77	99.83	99.80	99.51	99.45	99.71	99.82	99.81	99.78	99.81	99.77
SR	1.51	1.50	1.71	1.51	1.56	1.35	1.69	1.53	1.48	1.19	1.12	1.79	1.86	1.65	1.28	1.29	2.86	2.83	1.40	1.32	1.44	1.26	1.72	1.55
AR	3.42	3.84	2.85	3.22	2.80	2.38	2.60	2.43	2.63	1.36	1.13	2.54	4.33	2.00	1.49	2.02	1.42	4.50	2.41	2.35	2.96	3.58	1.85	2.32
MgO,+CaO	1.61	0.85	1.13	0.81	1.94	0.56	0.43	0.92	0.81	0.65	0.88	0.56	0.83	0.96	0.93	0.62	1.01	0.26	0.79	0.75	0.62	0.59	0.46	0.83
Al_2O_3+Na2O+K_2O	24.9	26.0	24.0	24.9	23.8	25.6	24.1	24.6	25.3	22.8	21.6	22.4	24.7	21.9	22.3	25.2	15.9	21.0	25.4	26.0	26.4	25.6	21.1	23.6

Table 4.4b Major Oxides Concentration in Rocks Samples of Mamu Formation (%).

Sample Number	L1	L9	L16	L19	L20	L22	L24	Average
Location	Amaiyi	Ebuwana	Amaiyi	Nguzu	Nguzu	Nguzu	Nguzu	
Co-odinate	N5°45 966’ E7°49 174’	N5°47 161’ E7°52 183’	N5°46 219’ E7°49 365’	N5°45 937’ E7°49 173’	N5°45 916’ E7°49 180’	N5°46 076’ E7°49 174’	N5°45 065’ E7°49 320’	
SiO_2	64.46	71.03	56.58	57.61	73.13	45.10	50.61	59.79
Al_2O_3	15.16	13.48	24.87	22.99	16.69	22.39	16.70	18.90
Fe_2O_3	5.55	5.62	3.28	3.05	1.39	6.69	5.72	4.47
MgO	0.54	0.17	0.29	0.30	0.05	0.73	0.70	0.40
CaO	0.11	0.02	0.02	0.07	0.05	1.35	0.86	0.35
Na_2O	0.06	0.07	0.04	0.02	0.02	0.05	0.06	0.05
K_2O	1.76	1.55	0.68	0.55	0.18	1.35	1.54	1.09
TiO_2	1.17	0.93	1.52	1.21	1.53	0.93	1.07	1.19
P_2O_5	0.09	0.07	0.07	0.32	0.35	0.09	0.09	0.15
MnO	0.01	-	-	0.01	-	0.04	0.05	0.02
Cr_2O_3	0.012	0.01	0.015	0.017	0.017	0.017	0.013	0.014
LOI	10.9	6.7	12.4	13.5	6.2	21.1	22.4	13.31
Total	99.82	99.65	99.77	99.65	99.61	99.84	99.81	99.74
SR	3.11	3.72	2.01	2.21	4.04	1.55	2.26	2.56
AR	2.73	2.40	7.58	7.54	12.01	3.35	2.92	4.23
MgO,+CaO	0.56	0.19	0.31	0.37	0.10	2.08	1.56	0.75
$Al_2O_3+Na_2O+K_2O$	17.0	15.1	25.6	23.6	16.9	23.8	18.3	1.14

Table 4.5, present the relationship between the average chemical composition of the Nkporo and Mamu shales at Afikpo with the chemical composition of some published shale samples and industrial specifications. According to Anon, (1972), the two shales have preferred specification for refractory. However, the iron oxide is much higher than the specification in each studied shales (average of 9.67 percent and 4.47 percent respectively). The Brick clay industrial specification: (Murray, 1960) correlates favourably with the chemical composition of Nkporo and Mamu shales studied, except that the soda, magnesia and quick limes of the studied shales are less than the specification. Generally, because of the higher ferric oxide content within the studied shales, each shale does not comply with the desired pharmaceutical, rubber, textile, paper and agricultural specifications, but they can simply be consider of favorably for glass ceramics that their SiO_2 (silica) and alumina fall short of the requirements. The average concentration of the studied region's SiO_2, MgO, CaO, Na_2O.and K_2O content compares favorably with what is expected in the agricultural specification.

Comparing the different shales of the study region with some other notable samples of shale in Nigeria. It has been shown that Nkporo shale correlates rather closely with shale in Itu Mbonuso/Iwere (Okunlola and Egbulem, 2015) and Auchi shale (Emofurieta, 1994) just that Nkporo shale contains more Alumina and Ferric but less Magnesia than the shale in Itu-Mbonuso/Iwere (Table 4.5). In alternative terms, the Nkporo shale contrasts with the Auchi shale, which is higher in Al_2O_3 and Fe_2O_3, and lower in MgO and CaO. Mamu shale is part of the shale correlation in Mpu (Obrika et al., 2012). There is a general conformity simply that Mamu has abundant higher ferric oxide with Mpu shale and lower Alumina, while they contrasted very closely with Ifon shale except that Mamu contained higher Fe_2O_3 and K_2O but lower SiO_2 (Table 4.5).

Table 4.5 Comparison of Average Shale Values in the Area with Some Shales in Nigeria.

	Afikpo-Edda Shales, study area							
	A1	A2	B	C	D	E	F	G
Oxides (%)	Nkporo Shale	Mamu Shale	Itu-Mbonuso / Iwere Shale	Auchi Shale	Ezeaku Shale	Mpu Shale	Okada Shale	Ifon Shale
SiO_2	49.71	59.79	49.92	51.68	44.91	59.45	55.76	63.3
Al_2O_3	22.39	18.90	18.15	18.76	15.71	21.70	20.60	18.47
Fe_2O_3	9.67	4.47	6.63	4.67	6..24	2.00	0.70	1.26
MgO	0.72	0.40	3.73	4.39	2.58	0.36	0.20	0.82
CaO	0.11	0.35	0.48	1.90	15.42	0.23	0.30	0.09
Na_2O	0.06	0.05	0.09	0.93	0.42	0.34	2.00	0.42
K_2O	1.17	1.09	0.94	1.16	2.36	1.74	0.30	2.36
TiO_2	1.04	1.19	1.49	1.95	0.65	1.52	1.15	1.02
P_2O_5	0.12	0.15	0.10	0.25	0.46	0.03	0.012	0.46
MnO	0.003	0.02	0.08	0.06	0.06	0.04	0.02	0.01
Cr_2O_3	0.018	0.014	0.02	-	-	-	-	-

Reference Samples

A1 = Mamu shale (Present study).

A2 = Nkporo shale (Present study).

B = Itu-Mbonuso/Iwere (Okunlola and Egbulem, 2015).

C = Auchi shale (Emofurieta, 1994).

D = Ezeaku shale (Amajor, 1987).

E = Mpu shale (Obrika, 2012).

F = Shales from Okada (Obrika et al., 2007).

G = Ifon shale (Ajayi et al, 1989).

Table 4.6a Trace Element Distribution of Shale Samples of Nkporo Formation (ppm).

Sample Code	L5	L6	L7	L13	L27	L28	L30	L31	L32	L33	L34	L36	L38	L39	L40	L41	L43	L44	L47	L48	L50	L51	L52	Mean
Location	Ekeje	Ekeje	Amagwu	Ekeje	Amiyi	Ekeje	Amoba	Ndi-Ofiba	Ndiba	Ndiba	Amaigbo	Amoso	R. Ubei	Amaebo	Owutu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Enohia	
Ba	235	248	304	226	253	208	193	660	298	175	242	146	245	371	257	293	798	2758	893	289	248	233	156	423
Sr	110.7	100.2	91.6	160.7	94.5	146.2	85	185	167	135	92.3	115	232	159	145	209	162.7	169	88.2	178	80.6	81.3	193	138
Ni	75	53	41	28	47	23	24	22	48	24	<20	29	25	21	26	28	32	<20	27	26	24	23	<20	30.4
Co	19	15.5	8.8	8.2	15.7	4.5	5.6	4.4	4.7	3..9	4.1	4.9	3.4	4.4	4.4	5.8	11.1	2.6	6.0	6.2	5.4	5.7	3.3	6.9
Cu	24.3	17.0	17.0	12.9	22.8	18.1	15.5	16.0	17.9	14.1	21.8	13.5	20.4	15.4	17.3	13.4	8.0	16.3	14.3	20.1	19.7	21.1	13.5	17.0
Zn	157	107	47	37	103	9	11	10	14	9	39	18	8	7	11	8	139	12	8	9	5	8	24	34.8
V	181	184	151	209	166	217	174	201	193	232	229	207	228	199	201	208	107	153	184	169	196	186	198	190
Y	27.7	23.2	22.3	19.1	26	22.9	29.6	22.5	24.2	18.8	15.9	26.6	28	20.7	18.7	21.8	42.6	34.8	21	21.2	28.7	25	32.9	25
Zr	167.3	129.4	311	155.7	295	205.9	388	261	183	229	159	417	312	255	214	307	2107	976	321.8	199	319	412	477	383
Mo	3.9	1.6	0.8	1.1	1.1	0.6	0.8	0.8	0.7	0.8	6.2	1.4	2.5	0.9	1	1	1.4	0.3	0.4	0.6	1	1.4	1.5	1.4
Nb	17.2	17.9	19.8	27.5	17.8	30.4	25.7	21.4	21.7	26.9	17.9	23.3	32.7	20.7	20.7	26.9	23.7	22.8	23.2	20.1	29.7	27.6	24	25.5
Pb	15.1	20.5	24.4	19.2	15.1	16.3	18.5	18.8	17.5	17.4	26.6	17.9	18.2	17.4	16.8	18.8	9.5	13.2	15.4	16.7	17.8	20.1	23.9	18.0

Continuation of the Trace Element Distribution of Shale Samples of Nkporo Formation (ppm).

Sample Code	L5	L6	L7	L13	L27	L28	L30	L31	L32	L33	L34	L36	L38	L39	L40	L41	L43	L44	L47	L48	L50	L51	L52	Mean
Location	Ekeje	Ekeje	Amagwu	Ekeje	Amiyi	Ekeje	Amoba	Ndi-Ofiba	Ndiba	Ndiba	Amaigbo	Amoso	R. Ubei	Amaebo	Owutu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Enohia	
Rb	85.6	91.5	107	99.2	83.8	65.8	45.8	80.2	65.3	53.4	76.9	48.6	57.9	69.8	61.3	67.1	99.2	78.9	71.9	74	62.3	57.3	76.2	73
Th	16.5	16	17.9	16.8	21	19.3	19.7	17	15.9	17.9	15.3	16.9	19	16.4	17.7	19.2	46	27.4	18.9	19	21.1	19.7	23.2	19.9
U	4	3.3	3.4	3	4	3.5	4.2	2.9	3	3.4	2.7	3.8	4.1	3.4	3.7	3.7	8.2	5.2	3.5	3.2	4.7	4.4	5.2	3.9

Table 4.6b Trace Element Distribution of Shale Samples of Mamu Formation.

Sample code	L1	L9	L16	L19	L20	L22	L24	Average
Location	Amaiyi	Ebuwana	Amaiyi	Nguzu	Nguzu	Nguzu	Nguzu	
Co-odinate	N5°45 966’ E7°49 174’	N5°47 161’ E7°52 183’	N5°46 219’ E7°49 365’	N5°45 937’ E7°49 173’	N5°45 916’ E7°49 180’	N5°46 076’ E7°49 174’	N5°45 065’ E7°49 320’	
Unit	Ppm	Ppm	Ppm	Ppm	Ppm	Ppm	Ppm	Ppm
Ba	364	551	240	1033	790	210	319	501
Sr	76.4	161.3	86.4	451.9	545.9	67.3	86.8	210.9
Ni	<20	<20	32	29	<20	39	38	27.6
Co	10.6	2.2	5.6	17.7	1.6	14.5	15.9	9.7
Cu	13.7	9.7	36.2	24.5	3.2	23	23.5	19.1
Zn	35	4	6	9	2	71	92	29..5
V	132	98	132	157	99	151	124	127.6
Y	32.2	31.7	39.5	60.3	54.5	23.5	34.7	39.5
Zr	577.8	1119.3	508	415.9	677	157.4	388.1	549.1
Mo	0.6	0.3	-	0.2	0.6	1.4	1.1	0.6
Nb	24.5	28.1	40.6	23.9	33.5	19.9	25.4	28.0
Pb	24.8	13.9	21.6	17.1	5.8	23.5	18.2	17.8
Rb	74.1	50.9	32.7	41.4	7.2	79.9	60.5	50
Th	14.8	25	28.5	22.3	26.4	16.6	18.1	21.7
U	3.2	5.1	9.5	4.5	4.9	3.3	4.2	5.0
Ta	1.7	1.8	3.0	1.8	2.5	1.3	1.7	2.00

4.4.2. Trace Element Results

All the trace element concentrations for Nkporo and Mamu shale at Afikpo is listed in Tables 4.6a and 4.6b. The shales show moderate to high enrichment in Ba, Sr, V, Zr and Rb. The Mamu shale show higher abundance in averages of Ba, Sr and Zr than Nkporo shale, however, Nkporo show higher abundance in V, Rb, Ni, Mo and Pb than Mamu shale. Each shale show exceptional enrichment in Ba and Zr contents ranging (~ 156 – 2758ppm) with the average of 423 and (~ 80.6 – 233ppm) with the average of 138ppm respectively for Nkporo shale, whereas that of Mamu is ranging (~ 210 – 1033ppm), with the average of 501 and (~ 67.3 – 545.9ppm) with the average of 210ppm respectively. However, there is depletion in their Mo contents ranging in Nkporo from (0.3 - 6.2ppm) with the average of 1.4ppm, and Mamu from (.0.2 - 1.4ppm) with the average of 0.6-ppm compare to other trace elements. There are slight depletion in some elements in both shales like in Ni Nb and Y contents.

Table 4.7. Comparison of Average Trace Element Composition of Shales in the Study Area with some Shale from Other Sedimentary Basins

	Afikpo-Edda Shales, area		**References Samples**					
	A1	A2	B	C	D	E	F	G
Elements (ppm)	Nkporo Shale	Mamu Shale	Levinson (1974)	Vine & Tourtelot (1970)	Turekian & Widepohl (1990)	*PAAS	*NASC (Gromet et al, (1984)	Taylor and McLennan (1981)
Ba	423	501	300	700	600	650	636	700
Sr	138	210.9	200	300	400	200	142	350
Ni	30.4	27.6	50	70	80	55	58	-
Co	6.9	9.7	10	20	20	23	n.a	-
Cu	17.0	19.1	70	50	50	50	n.a	-
Zn	34.8	37.4	300	100	90	85	n.a	-
V	190	127.6	150	130	130	150	130	60
Y	25	39.5	30	25	35	-	n.a	22
Zr	383	549.1	70	160	180	210	200	240
Mo	1.4	0.6	10	3.0	2.0	-	n.a	-
Nb	25.5	28.0	20	20.0	n.a	1.90	n.a	25
Pb	18.0	17.8	20	n.a	20	20	n.a	-
Rb	73	50	140	n.a	140	160	n.a	110
Th	19.9	21.7	12	n.a	12	14.60	n.a	10.5
U	3.9	5.0	4	n.a	3.5	3.10	n.a	2.5
Cu/Zn	0.49	0.51	0.23	0.5	0.56	0.58	-	-
Ni/Co	4.41	2.85	5.00	3.50	4.00	3.39	-	-
Rb/K_2O	62.39	45.87	-	-	-	-	-	-
U/Th	0.20	0.23	0.33	-	0.29	0.21	-	0.24

***PAAS- Post Archean Austrialian Average Shale** and ***NASC - North American Shale Composite Average**

The calculated averages of the shale proportions in Nkporo and Mamu were compared with some shales in sedimentary basins such as (Vine and Tourtelot, 1970; Gromet et. al., North American Shale Composite (NASC) 1984 and Turekian and Widepohl, 1990) and Post Archean Austrialian Average Shale (PAAS) (Tables 4.7). The Nkporo shale average for Barium is comparable to that of (Levinson, 1974) although slightly higher. As the associated degree measure of detrital influx, Ba enrichment in sedimentary rocks can be considered. Sr content in Nkporo shale may be comparable to (NASC) (Gromet et al., 1984), whereas Mamu shale may also be comparable to (Levinson, 1974) and (PAAS). The content of Co in Mamu shale can be compared with (Levinson, 1974). Nkporo shale's vanadium content is higher than the reference samples, while (Vine, 1970), NASC by (Gromet et al, 1984; 'D', Turekian, 1990) can be contrasted with Mamu shale. The Y enrichment in Nkporo shale can be compared with (Vine and Tourtelot 1970) while Y for Mamu shale can be compared with (Turekian and Widepohl 1990). Both shales for Niobium can be compared with (Taylor and McLennan, 1981) while both shales also can be compared with (Levinson, 1974; Turekian and Widepohl 1990) and PAAS. Mo in Nkporo can be compared with (Turekian, 1990) (Table 4.7). The Zr and Th have very higher enrichment than the reference samples while Ni, Rb, Cu and Zn average contents in the shales show depletion, very low than the reference samples. The Mo and Uranium contents of Nkporo shale can be comparable with the (Turekian and Widepohl 1990). The average Uranium contents in both shale samples (Nkporo and Mamu) are very low at 3.9 and 5.0 respectively (Tables 4.6a, 4.6b and 4.7).

Uranium oxidation has a strong effect on marine geochemistry (Barnes and Cochran, 1990). Low uranium content is generally found in oxygenated conditions in the marine environment (Somayajulu et al., 1994), while higher uranium content is found in oxygen-minimum zone sediments (Barnes, 1990 and Nath et al., 1997). This obtained result (Tables 4.6a and 4.5b) suggest oxygenated condition for the Afikpo shale deposit.

4.4.3. Rare Earth Element Geochemistry

The rare earth element (REE) concentration in the Nkporo and Mamu shale understudy is shown in Tables 4.8a and 4.8b. Concentrations of rare earth elements were statistically compared between the two shale samples. In REE content there are some variations within the concentrations of elements in each shale, however Mamu shale shows higher enrichments in all the listed elements except scandium, which has the average of 17ppm in Nkporo shale and 14.7ppm in Mamu shale, however Mamu shale samples shows more variability than in the Nkporo shale samples. Despite REE concentrations in Mamu shale samples tend to be more variable than in Nkporo shale samples (e.g. La, Pr Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y; Figs. 4.18 and4.19).

Table 4.8a Rare Earth Element Distribution (ppm) of Shale Samples of Nkporo Formation.

Sample Code	L5	L6	L7	L13	L27	L28	L30	L31	L32	L33	L34	L36	L38	L39	L40	L41	L43	L44	L47	L48	L50	L51	L52	Mean
Location	Ekeje	Ekeje	Amagwu	Ekeje	Amiyi	Ekeje	Amoba	Ndi-Ofiba	Ndiba	Ndiba	Amaigbo	Amoso	R. Ubei	Amaebo	Owutu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Ogbu	Enohia	
Ppm																								
La	64.5	69.2	68.6	65.9	66.4	70.1	55.6	68.9	60	59.9	46.6	57	69.2	63.5	67.4	71.5	118	87.1	52.5	68.3	68.3	61.9	61.4	64.1
Ce	138.9	150	135.7	123.1	132	135.9	108.4	141.4	126	115.8	85.6	113.6	144.4	126	135.8	130	235.9	172.6	88.8	134	126.1	113.7	113.1	131.6
Pr	16.4	17.6	15.0	12.9	15.1	15.4	12.9	16.2	14.7	12.3	8.7	12.8	16.3	13.6	15.1	13.9	26.6	19.2	9.8	15.3	13.9	12.7	11.8	14.7
Nd	62.3	67.8	47.1	41.9	57	54.4	48.7	59.3	54.9	42.1	29.7	47.2	62.2	48.1	51.2	47.7	100.5	69	34.1	57.7	50.6	45.8	40.7	53
Sm	11.2	11.4	7.5	5.8	10.1	8.8	9.3	11.0	9.2	6.0	4.2	8.4	11.8	8.4	8.1	8.3	16.6	11.0	5.8	11.0	8.4	7.8	6.6	9.0
Eu	2.4	2.2	1.4	1.15	1.97	1.83	1.82	2.33	1.92	1.13	0.92	1.79	2.49	1.71	1.63	1.74	1.88	1.9	1.13	2.13	1.7	1.64	1.28	1.7
Gd	9.17	8.69	5.62	4.37	7.77	6.6	7.58	8.94	7.17	4.33	3.17	6.93	9.45	6.76	5.7	6.7	13.05	8.01	4.66	7.73	6.78	6.13	5.22	7.0
Tb	1.23	0.99	0.77	0.59	1.06	0.86	1.08	1.17	0.98	0.59	0.48	0.96	1.22	0.89	0.76	0.87	1.55	1.11	0.66	1	0.97	0.88	0.75	0.93
Dy	6.65	5.26	4.35	3.72	5.68	4.96	6.38	5.81	5.29	3.43	2.92	5.43	6.66	4.63	3.96	4.81	8.34	6.39	4.18	4.87	5.48	5.3	4.43	5.17
Ho	1.14	0.88	0.85	0.75	1.01	0.84	1.15	0.93	0.88	0.69	0.56	1.4	1.06	0.83	0.76	0.85	1.43	1.3	0.78	0.84	1.11	0.94	0.85	0.95
Er	3.02	2.5	2.46	2.23	3.1	2.6	3.7	2.55	2.55	2.03	1.78	2.92	3.1	2.3	1.84	2.35	4.3	3.93	2.35	2.27	3.28	2.8	2.51	2.69

Continuation of the Rare Earth Element Distribution (ppm) of Shale Samples of Nkporo Formation.

Tm	0.41	0.33	0.35	0.31	0.39	0.34	0.46	0.33	0.35	0.29	0.27	0.4	0.42	0.31	0.28	0.32	0.62	0.57	0.35	0.32	0.46	0.42	0.36	0.38
Yb	2.57	2.24	2.44	2.12	2.57	2.28	3.39	2.03	2.31	2.01	1.75	2.6	2.85	2.15	1.92	2.28	4.25	3.91	2.28	2.27	3.22	2.81	2.42	2.55
Lu	0.38	0.31	0.36	0.31	0.37	0.31	0.51	0.3	0.35	0.29	0.25	0.37	0.41	0.31	0.27	0.34	0.73	0.59	0.36	0.32	0.45	0.41	0.41	0.38
Sc	18	17	18	14	17	18	18	17	18	16	14	18	17	17	19	18	9	15	18	19	18	20	16	17
Y	27.7	23.2	22.3	19.1	26	22.9	29.6	22.5	24.2	18.8	15.9	26.6	28	20.7	18.7	21.8	42.6	34.8	21	21.2	28.7	25	32.9	25

Table 4.8b Rare Earth Element Distribution (ppm) of Shale Samples of Mamu Formation.

Sample code	L1	L9	L16	L19	L20	L22	L24	Average
Location	Amaiyi	Ebuwana	Amaiyi	Nguzu	Nguzu	Nguzu	Nguzu	
Co-odinate	N5°45 966' E7°49 174'	N5°47 161' E7°52 183'	N5°46 219' E7°49 365'	N5°45 937' E7°49 173'	N5°45 916' E7°49 180'	N5°46 076' E7°49 174'	N5°45 065' E7°49 320'	
La	56.2	72.2	64.9	87.1	129.3	57.7	58.1	75.1
Ce	113.9	141.4	126.2	188.6	300.5	113.7	119.8	157.7
Pr	12.5	16.4	15.5	23.3	38.0	13.2	13.4	18.9
Nd	45.7	64.4	62	89	158.2	48.9	50.1	74.0
Sm	8.31	11.8	11.6	16.0	31.5	8.5	9.42	18.9
Eu	1.72	1.64	2.31	3.43	7.56	1.81	1.91	2.91
Gd	7.12	8.72	9.57	13.84	28.26	6.51	8.14	11.74
Tb	0.99	1.09	1.36	1.98	3.58	0.93	1.14	1.58
Dy	6.12	5.58	8.04	11.21	17.16	5.07	6.58	8.54
Ho	1.1	1.13	1.5	2.1	2.57	0.88	1.28	1.51
Er	3.53	3.3	4.54	6.27	6.17	2.53	3.72	4.29
Tm	0.47	0.5	0.65	0.85	0.78	0.34	0.51	0.59
Yb	3.35	3.39	4.47	5.43	5.1	2.27	3.41	3.92
Lu	0.52	0.55	0.71	0.81	0.67	0.34	0.53	0.59
Sc	11	10	19	21	12	16	14	14.7
Y	32.2	31.7	39.5	60.3	54.5	23.5	34.7	39.5

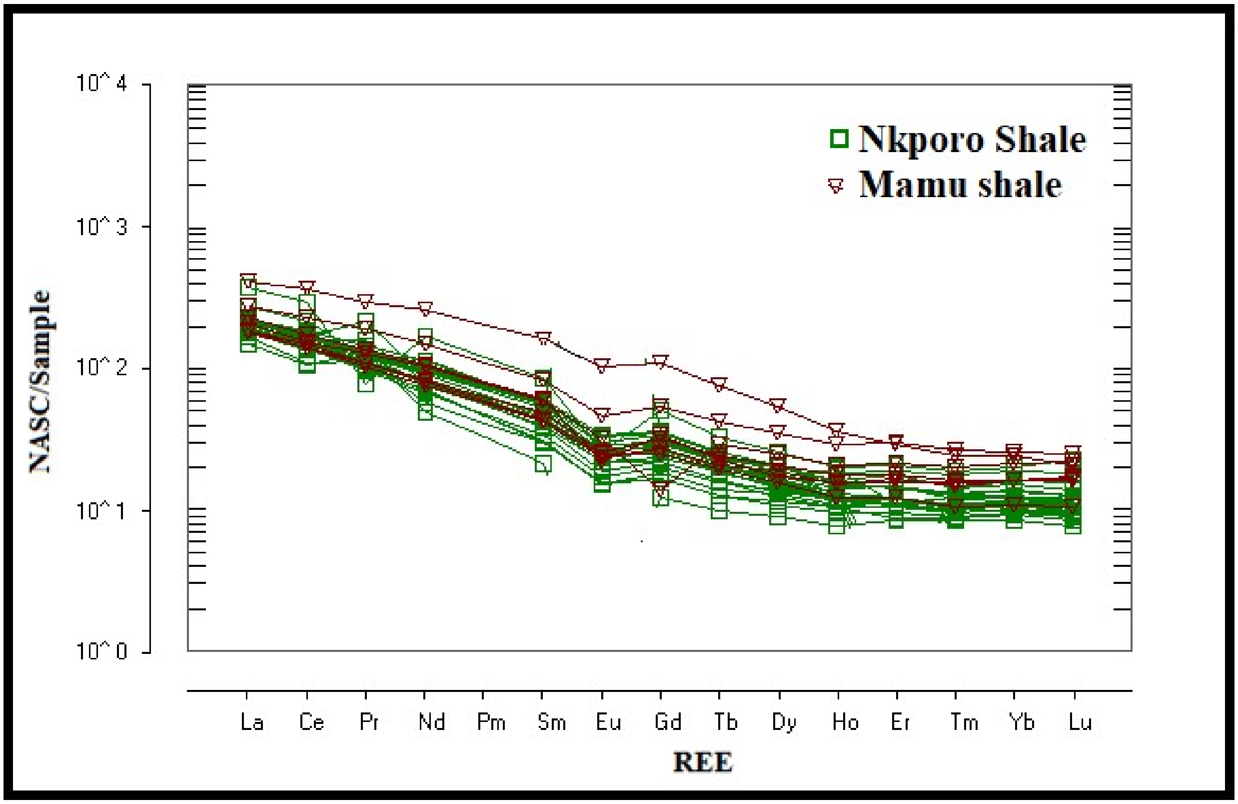


Fig. 4.26 NASC-Chondrite normalised Rare Elements plot for the Shale Samples under Investigation (After Boynton 1984).

4.4.4 Provenance

Major and trace elements concentrations in the minerals that make up the sediments are derived from very different physico-chemical processes that define the aqueous geochemistry of the individual elements, e.g. origin, diagenesis and transport, transformation and sorting of sediments. The Rare Earth elements, in addition to supporting analysis of major elements that are invariably in their oxides and to an extent Th, Sc, Cr and Co, are most helpful for provenance studies. They are immobile and believed to be exclusively transported as clastic components and they show the indents of transportation. Trace elements ratios may be the basic ratios, are so regarded as best methods to determine the provenance of long travelled clastic sediments over time. (McLennan et. al, 1993) used Th/Sc - Zr/Sc ratios in (Fig.4.28) as associate in nurturing the index of the majority composition of the provenance.

The TiO_2 vs Al_2O_3 binary plot in Fig. 4.27 as proposed by Perri, (2014) to categorise granitic from basaltic rocks, suggest an intermediary to granite rock origin for the shale deposits. From the discriminative diagram of Fig. 4.27, the investigated samples plot inbetween the granodiorite and granite, revealing a granitic source for the shale deposits.

According to Cullers' (1994), the diagram in (Fig. 4.29) which distinguishes felsic and basic provenance, the shale data falls within a predominantly felsic region. (Vital e.t al., 1999) Th - Co - Zr/10 diagram was also used for provenance determination. The diagram reveals, that the samples are low in Co and enriched in Th indicating felsic source.

From the observed characteristic enriched LREEs and low with nearly flat HREE patterns tending towards negative Eu and Tm anomalies (Tables 4.8a and 4.8b, Fig. 4.26). This suggests that the original precursor was felsic and that the negative Eu anomaly is taken as proof from a discriminated, granitic source (McLennan et al., 1993). The REE result shows a small enrichment within the light rare earth elements, however a major depletion in heavy rare earth elements similar to seawater (marine) derived shale (Haskin et al., 1996); (Tables 4.8a and 4.8b). This signifies that the shale precursors are granitic rocks meaning that the provenance of Afikpo Edda is heterogeneous. It is to signal that the samples are depleting in Er, Tm, Yb, and Lu.

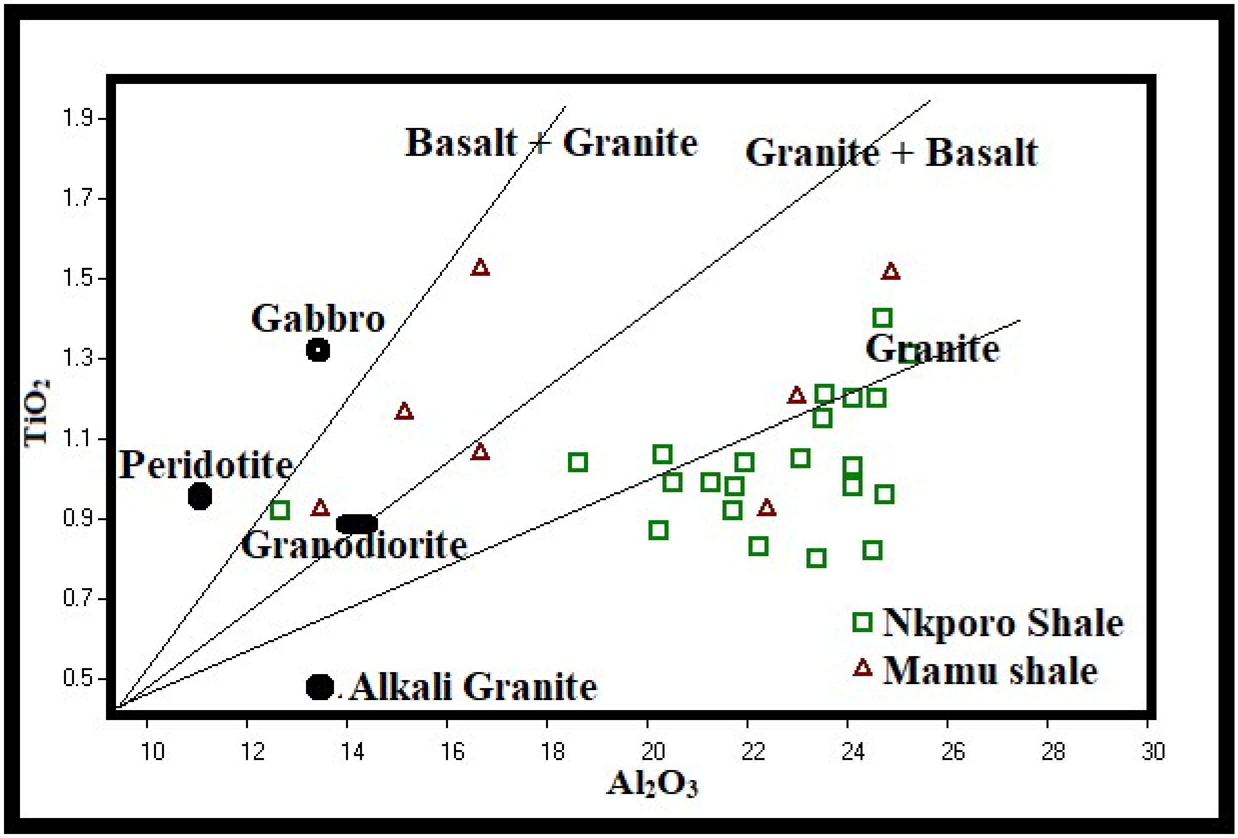


Fig. 4.27 TiO_2 vs Al_2O_3 Binary Plot of the studied Afikpo Shale Samples (After Perri, 2014).

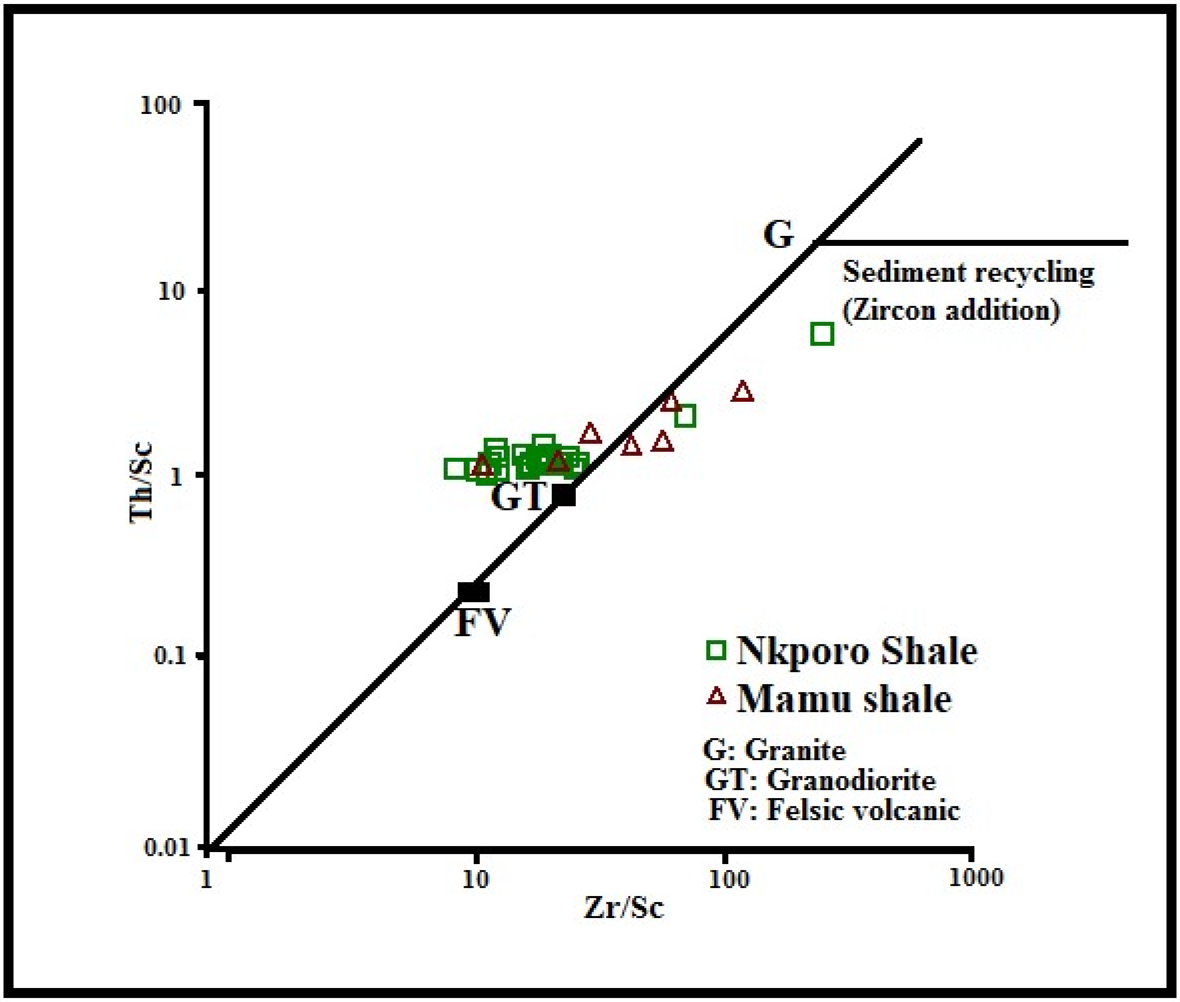


Fig. 4.28 Th/Sc–Zr/Sc diagram showing the investigated shale samples in between granite and granodiorite composition (afterMcLennan *et al.,* 1993). Granite-G, Granodiorite- GT and Felsics volcanic - FV (after Condie, 1993).

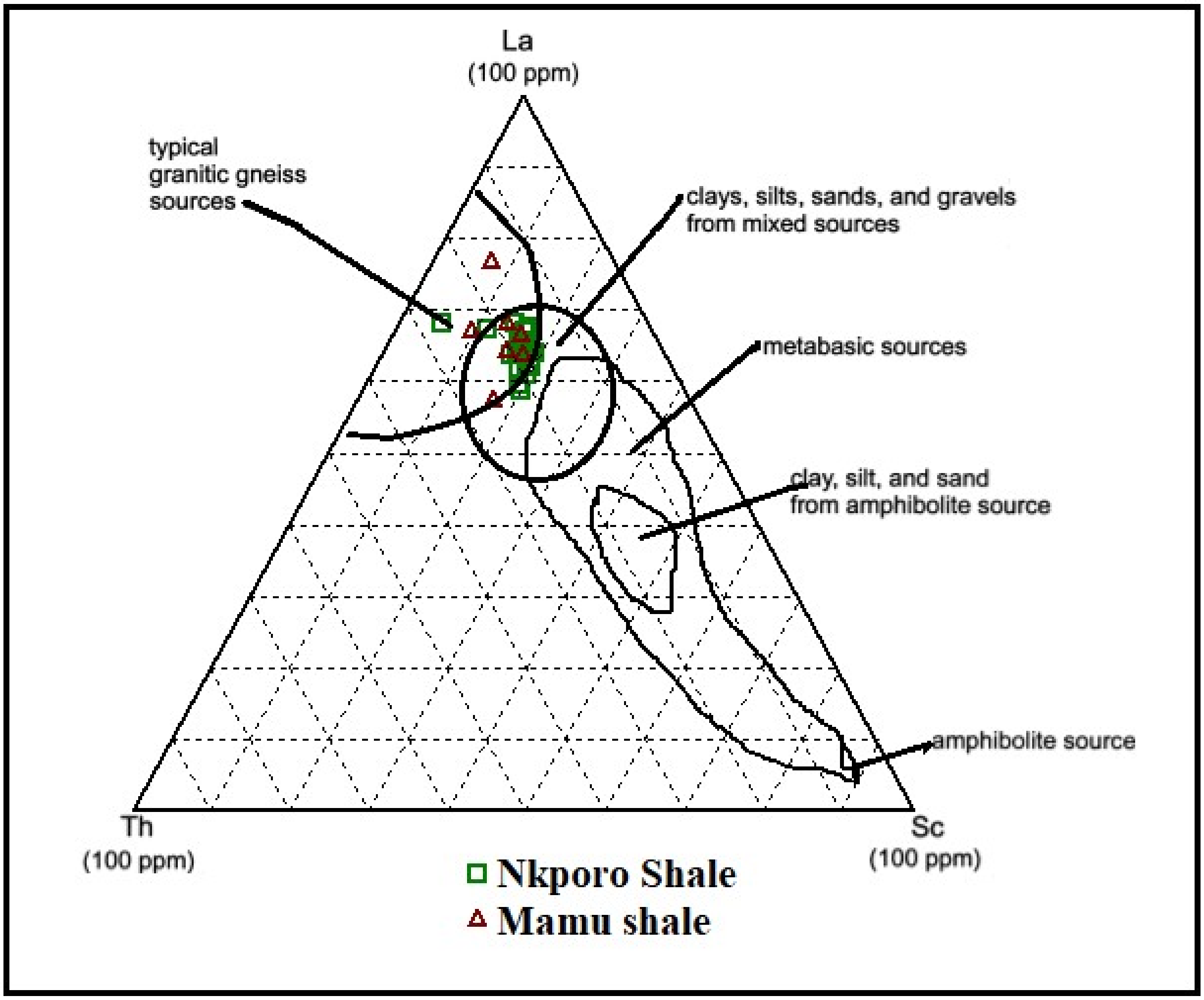


Fig. 4.29 Ternary Plot of La - Th - Sc after Cullers (1994a) for the Afikpo Shale Samples

4.4.5 Tectonic Setting

The discriminatory diagrams, as shown in Fig. 4.30, $LogK_2O/Na_2O$ versus SiO_2 (After Roser and Korsch, 1986), show the tectonic setting of the exposed shale unit of Afikpo to be of Passive Margin as all the studied samples plotted within the Passive Margin region.

The major oxide elemental analysis of the investigated shale samples are quartz - rich (>45 wt%) but low in Na_2O (<2 wt%), CaO (<1 wt% and TiO_2 (<2 wt%). Tables 4.4a and 4.4b suggests the alleviating of affirmation by Roser and Korsch, (1986) that is passive-margin type shale-clay deposits are chiefly quartz-rich. (Fig. 4.30), Th - Co - Zr/10, Bhatia and Crook, (1986) also favours Passive Margin setting as most of the samples plotted within Passive margin and Continental Island. Thus, it means that the shale samples were deposited in an intracratonic basin (Fig 4.31).

4.4.6 Petrogenesis of Afikpo Shales

Petrogenesis is the mechanism by which indirect sources of evidence from scientifically relevant deductions, originating from principles relating to structure, chemical analysis, textural characteristics and contact relationships, are observed in the field to establish the origin and source of rocks.

The origin of Nkporo and Mamu shale of Afikpo could also be regarded as being within a sedimentary terrain. Chemical results and indices provide the best answer due to the nature of the precursors of rocks particularly those that are more restricted in composition. Mostly, petrochemical variation once associated with the geological environment is significantly dependable in ascertaining the regimes of crustal evolution (Elueze, 1980).

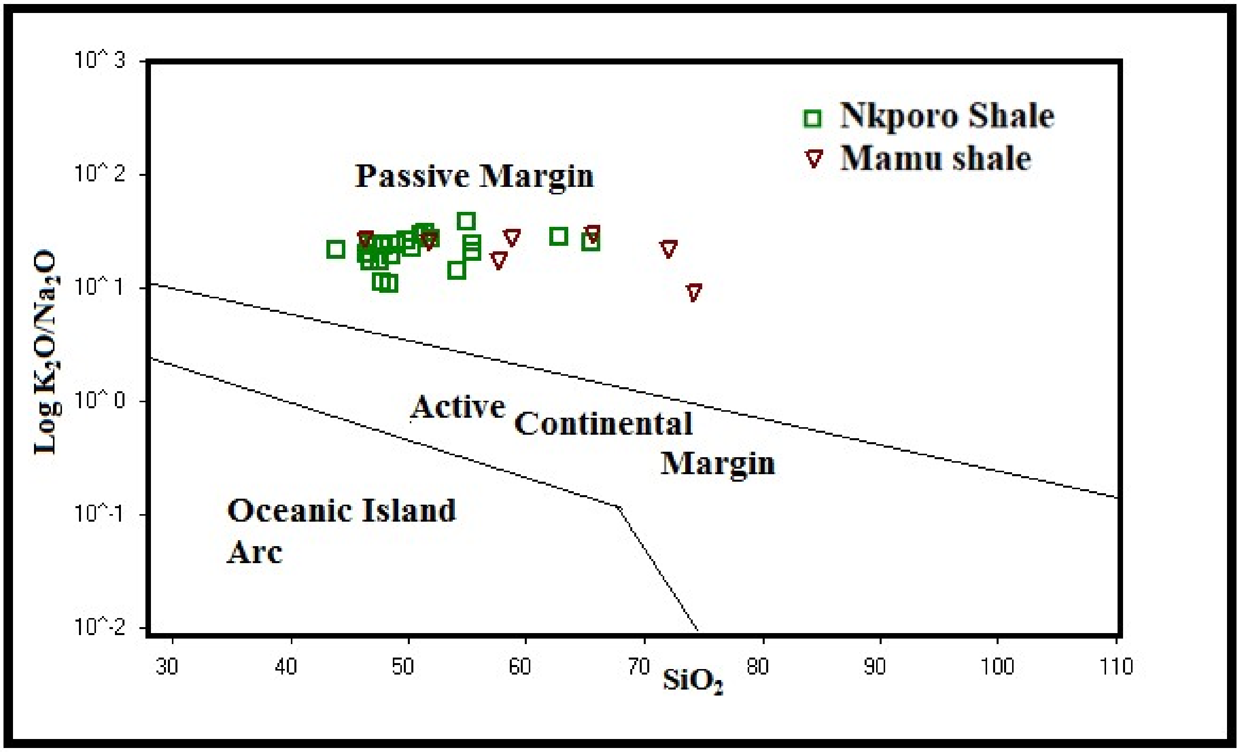


Fig. 4.30 Tectonic Discriminant Diagram for the studied Shale Deposits (After Roser and Korsch, 1986).

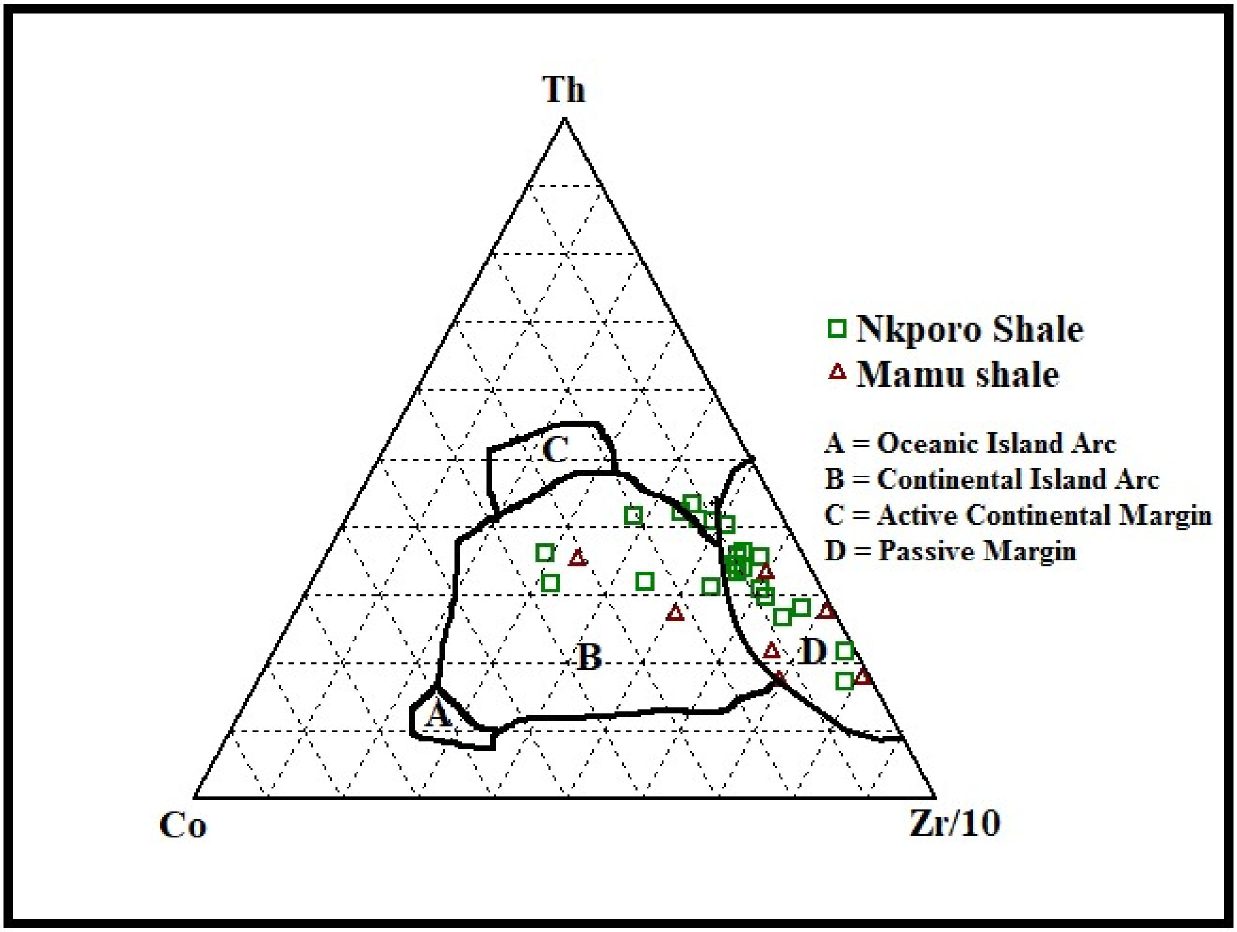


Fig. 4.31. Ternary plot of Th - Co - Zr/10 after (Bhatia and Crook, 1986) for the Shale Samples.

4.4.7 Environment of Deposition

Depositional environment is also regarded as a natural geologic entity in which sediments accumulate and can be inferred based on geological and geochemical information obtained from these areas; geochemical (major elements) data, the ratio of SiO_2/Al_2O_3 is relatively low indicating a low silt content and therefore a tendency towards a marine condition. High Fe_2O_3 in each Nkporo and Mamu shale samples designates the presence of iron-bearing minerals hematite, siderite and limonite that contains pyrite and sulphide minerals, suggesting that sediments have been deposited in a reduced environment and in addition, confirming the preservation of organic matter within sediments which may reflect on the humid condition of the area. The lithology of clastic sediment is a function of the environment within which the sediments were deposited, its transportation history, and therefore the types of rocks from which it had been derived. For instance, the meta-stable heavy mineral assemblages of the sediments indicate the provenance to be that of a mixed terrain, as within the K_2O versus Na_2O discriminating diagram of (Middleton, 1960), most of the shales are plot within the field of eugeosynclinal (Fig. 4.32).

Depositional environment is of fundamental importance in evaluating the reasons of metal enrichment or depletion within the shales. The presence of abundant, thinly laminated black to brownish-black shales in most of the samples suggests that anaerobic conditions could have predominated during most of the depositional history of the varied shale deposits (Imeokparia and Onyeobi, 2007). Plot of Na_2O versus K_2O (Figs 4.27 & 4.33) show that the shale sample in both Nkporo and Mamu formation are plotted within the field of greyweckes, which is an indication that both shales are of sedimentary origin (after Pettijohn, 1975).

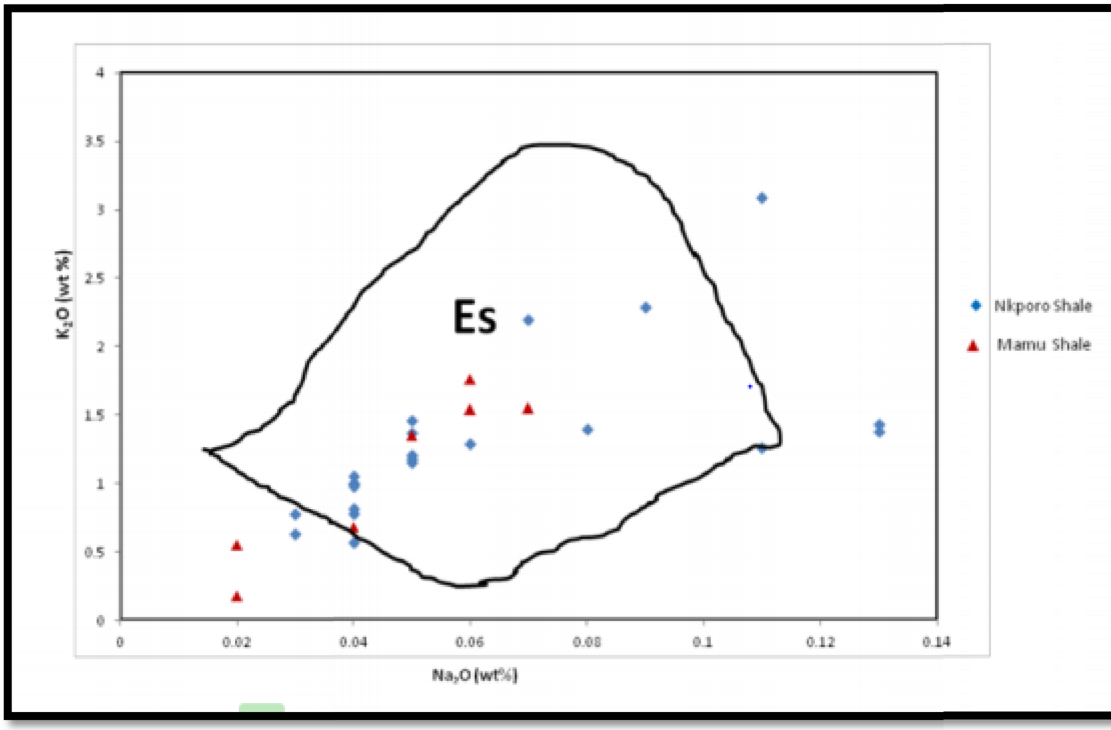


Fig. 4.32. Plot of K_2O (wt%) vs Na_2O (wt%) (Middleton, 1960)

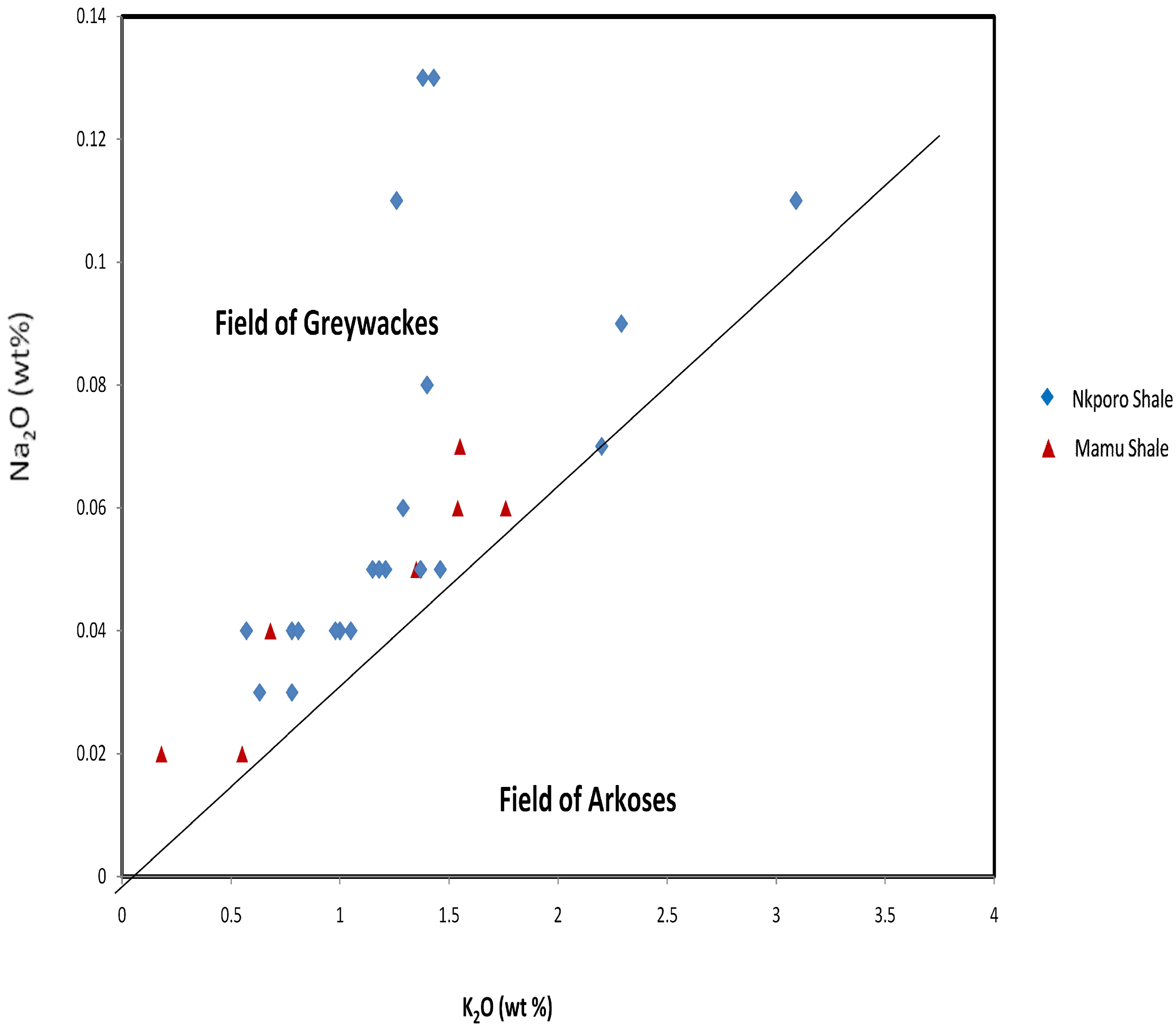


Fig. 4.33. Plot of Na_2O (wt%) versus K_2O (wt%)(after Pettijohn, 1975)

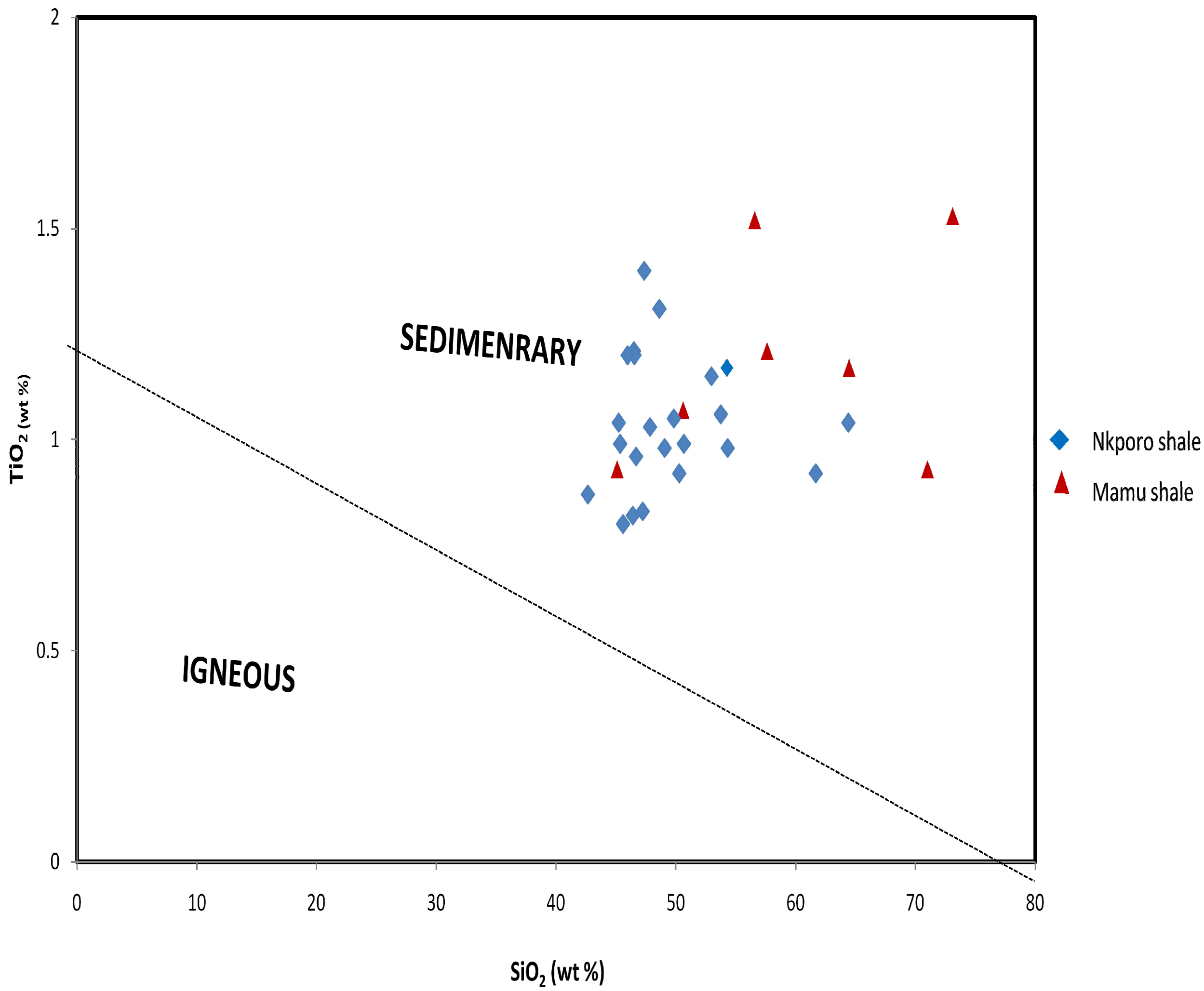


Fig. 4.34. Plot of TiO_2 (wt%) versus SiO_2 (wt%)(after Pettijohn, 1975)

With relation to elements such as V, Nb, Zr, but lower in other elements, the shales appear similar to metalliferous black shales like the Kufferchiefer. This indicates that, during a transgressive shallow marine environment with strong biogenetic production, these shales were most likely deposited (Imeokparia and Onyeobi, 2007).

Strontium is a very significant paleoenvironmental measure, more stable than Ca during weathering, which suggests that it is more related to clay minerals. Owing to the lack of feldspars within the sediments, Sr's concentration within the sample is low (Imeokparia and Onyeobi, 2007).

4.4.8. Maturity

The quartz/feldspar, the K_2O/Na_2O and $M\text{-}(K_2O+Al_2O_3)/(Na_2O+MgO)$ ratios measure maturity in clastic sediments. The highest values are linked to mature samples enriched with weather-resistant minerals (Bjorlykke, 1974). The Rb/K_2O ratio (Fig. 4.35), with high values suggests matured samples (Dyprik, 1984). High TiO_2 content characterised by low Cr concentrations (Dyprik, 1984) indicates maturity; although in maturity ratio there is an obvious variation/concentration that may reflect the provenance and or diagenetic processes (Imeokparia and Onyeobi, 2007).

Stratigraphic relations indicate the Nkporo shale samples L43, L6, L38 and L31 have the highest cerium values (235.9, 150, 144.4 and 141.4ppm respectively, Table 4.4a) while Mamu shale samples L20, L19 and L9 also have the highest cerium values of (300.3, 188.6, and 141.4ppm respectively, Table 4.4b) which may define the highest zones of possible phosphate mineral concentration. High cerium value in Afikpo shales indicates the zone of high phosphate mineral concentration in the study area (Imeokparia and Onyeobi, 2007). Fig. 4.35 indicates that the shale samples tend towards increasing chemical maturity.

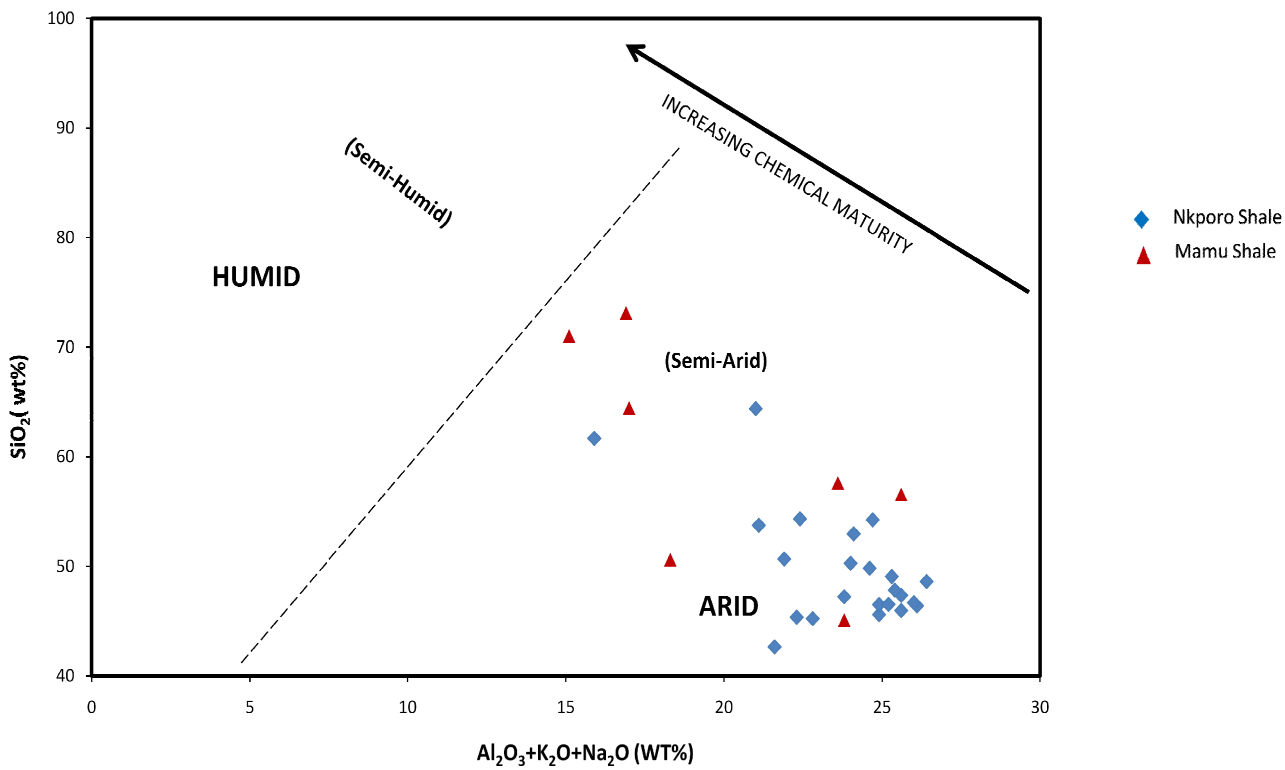


Fig. 4.35 Plot of SiO_2 (wt%) against $Al_2O_3 + K_2O + Na_2O$ (Suttner and Dutta, 1986).

4.5 Organic Geochemistry Results

The Source Rock results of the Afikpo-Edda shale are presented in Tables 4.9 and 4.10. The tables showed the parameters which give information on the quality and quantity of organic matter, hydrocarbon generating capacity, type of organic matter and thermal maturity of ten (10) samples of the Nkporo Formation and Mamu Formations. Organic geochemistry products include the Total Organic Carbon (TOC) and HAWK pyrolysis data.

4.5.1 Quality and Amount of Organic Matter

A calculation of the organic material of sedimentary rocks (Jarvie, 1991) may be the sum of organic matter expressed as total organic carbon. In other words, the measurement of the number of organic matter present in rock is articulated as TOC value in weight percent of the dry rock. The organic carbon richness of the rock samples (TOC %), is very important in the analysis of sediments as a source of petroleum. Tissot and Welte 1984; Peters and Cassa, 1994 and Peters, 1986 bestowed a scale for the assessment of source rocks potentiality, based on the TOC % and Rock-Eval pyrolysis data, such like S1 and S2 (Table 4.14a and 4.14b).

Total organic carbon in an exceedingly source rock comprises three basic components;

(a) Organic carbon in preserved hydrocarbons as obtained by the laboratory;

(b) Organic carbon which can be regenerated to hydrocarbon, referred to as changeable carbon (Jarvie, 1991) or impulse or labile carbon;

(c) A carbonaceous organic residue that may not yield petroleum as a result of deficiencies in Hydrogen unremarkably noted to as inert carbon (Jarvie, 1984)

Table 4.9 Results of Organic Geochemical Analysis of Mamu Shale

S/N	Location	FM	Sample Horizon	Percentage Carbonate (wt%)	Leco TOC (wt%)	HAWK S1 (mg Hc/g)	HAWK S2 (mg HC/g)	HAWK S3 (mg CO2/g)	HAWK Tmax (°C)	Calc % Ro (RE Tmax)	Hydrogen Index (HI)	Oxygen Index (OI)	S2/S3 (Mg HClmgCO^2)	Bituminous Index, (Mg Hc/g)/(wt%)	S1+S2 (mg Hc/ g)	P I [SI/(S1+S2)]
L1	Amaiyi, N5°45 966' E7°49 174'	Mamu	Outcrop	2.38	1.11	0.04	0.45	0.42	431	0.60	41	38	1	0.04	0.49	0.08
L3	Nguzu, N5°45 131' E7°49 453'	Mamu	Outcrop	3.90	3.44	0.11	1.83	0.82	419	0.38	53	24	2	0.03	1.94	0.06
L16	Amaiyi, N5°46 219' E7°49 365'	Mamu	Outcrop	2.43	2.73	0.08	2.40	0.50	433	0.63	88	18	5	0.03	2.48	0.03
L19	Nguzu, N5°45 916' E7°49 180'	Mamu	Outcrop	2.64	0.66	0.03	0.11	0.35	422	0.44	17	53	0	0.05	0.14	0.21
L24	Nguzu, N5°46 065' E7°49 320'	Mamu	Outcrop	8.10	5.51	0.11	4.26	1.27	422	0.44	77	23	3	0.02	4.37	0.03
L26	Amaiyi, N5°46 260' E7°49 267'	Mamu	Outcrop	8.62	2.64	0.05	1.41	0.82	436	0.69	53	31	2	0.02	1.46	0.03

Table 4.10 Results of Source Rock/Geochemical Analysis of Nkporo Shale

Sample no./Location	FM	Sample Horizon	Percentage Carbonate (wt%)	Leco TOC (wt%)	HAWK S1 (mg Hc/g)	HAWK S2 (mg HC/g)	HAWK S3 (mg CO_2/g)	HAWK Tmax (°C)	Calc % Ro (RE Tmax)	Hydrogen Index (HI)	Oxygen Iindex (OI)	S2/S3 Conc. (Mg HClmgCO^2)	Bituminous Index, (Mg Hc/g)/(wt%)	Generating Pot.,S1+S2 (Mg Hc/ g)	Prod. Index [SI/(S1+S2)]
L4/Ekeje, N5°45 214’ E7°49 369’	Nkporo	Outcrop	4.10	2.12	0.04	1.23	0.50	429	0.56	58	24	2	0.02	1.27	0.03
L5/Ekeje, N5°46 797’ E7°49 314’	Nkporo	Outcrop	7.48	1.10	0.03	0.30	0.28	422	0.44	27	25	1	0.03	0.0;kkk6	0.09
L6/Ekeje, N5° 47 48’ E7 49 490°	Nkporo	Outcrop	4.63	1.38	0.04	0.40	0.26	428	0.54	29	19	2	0.03	0.08	0.09
L14/Ekeje N5°47 044’ E7°49 493’	Nkporo	Outcrop	2.28	2.95	0.05	2.05	0.72	433	0.63	69	24	3	0.02	2.1	0.02

The Total Organic Carbon (TOC) of the Mamu Formation shale samples varies from 0.66 to 5.51 percent wt with an average of 2.68 percent wt, suggesting a strong concentration of organic matter, while the samples of the Nkporo Shale vary from 1.10 to 2.95 percent wt, with an average of 1.89 percent wt (Tables 4.14a and 4.14b). This average value suggests a very strong concentration of organic matter (Peters and Cassa, 1994). The Total Organic Carbon (TOC) value of 0.5wt percent is the threshold value needed for hydrocarbon production from a potential rock source.

The plot of S1 versus TOC in figure 4.35 confired, this conclusion that might be used to discriminate between allochthonous and autochthonous (Ghori and Haines, 2007). The relationship shows that the studied samples for the Mamu and Nkporo Shale were characterised by autochthonous hydrocarbons indicating that the organic matters made was buried in-situ.

Table 4.11 Geochemical parameters describing amount and quality of organic matter (after Peters and Cassa, 1994)

Quantity	TOC (Wt%)	Rock-Eval Pyrolysis	
		S_1	S_2
Poor	< 0.5	0-0.5	0-2.5
Fair	0.5-1.0	0.5-1.0	2.5-5.0
Good	1.0-2.0	1.0-2.0	5.0-10.0
Very Good	2.0-4.0	2.0-4.0	10.0-20.0
Excellent	> 4.0	>4.0	> 20.0

Table 4.12a Total Organic Carbon Result of Mamu Shale

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Leco TOC (wt%)
L1	Amaiyi	N5°45 966’ E7°49 174’	Mamu Shale	Outcrop	1.11
L3	Nguzu,	N5°45 131’ E7°49 453’	Mamu Shale	Outcrop	3.44
L16	Amaiyi,	N5°46 219’ E7°49 365’	Mamu Shale	Outcrop	2.73
L19	Nguzu,	N5°45 916’ E7°49 180’	Mamu Shale	Outcrop	0.66
L24	Nguzu,	N5°46 065’ E7°49 320’	Mamu Shale	Outcrop	5.51
L26	Amaiyi,	N5°46 260’ E7°49 267’	Mamu Shale	Outcrop	2.64
			Mamu Shale	**Average**	**2.68**

Table 4.12b Total Organic Carbon Result of Nkporo Shale

Sample No.	Location	Co ordinate	Formation	Sample Horizon	Leco TOC (wt%)
L4	Ekeje	N5°46 238’ E7°49 387’	Nkporo Shale	Outcrop	2.12
L5	Ekeje	N5°46 797’ E7°49 314’	Nkporo Shale	Outcrop	1.10
L6	Ekeje	N5°47 048’ E7°49 490’	Nkporo Shale	Outcrop	1.38
L14	Ekeje	N5°47 044’ E7°49 493’	Nkporo Shale	Outcrop	2.95
				Average	**1.89**

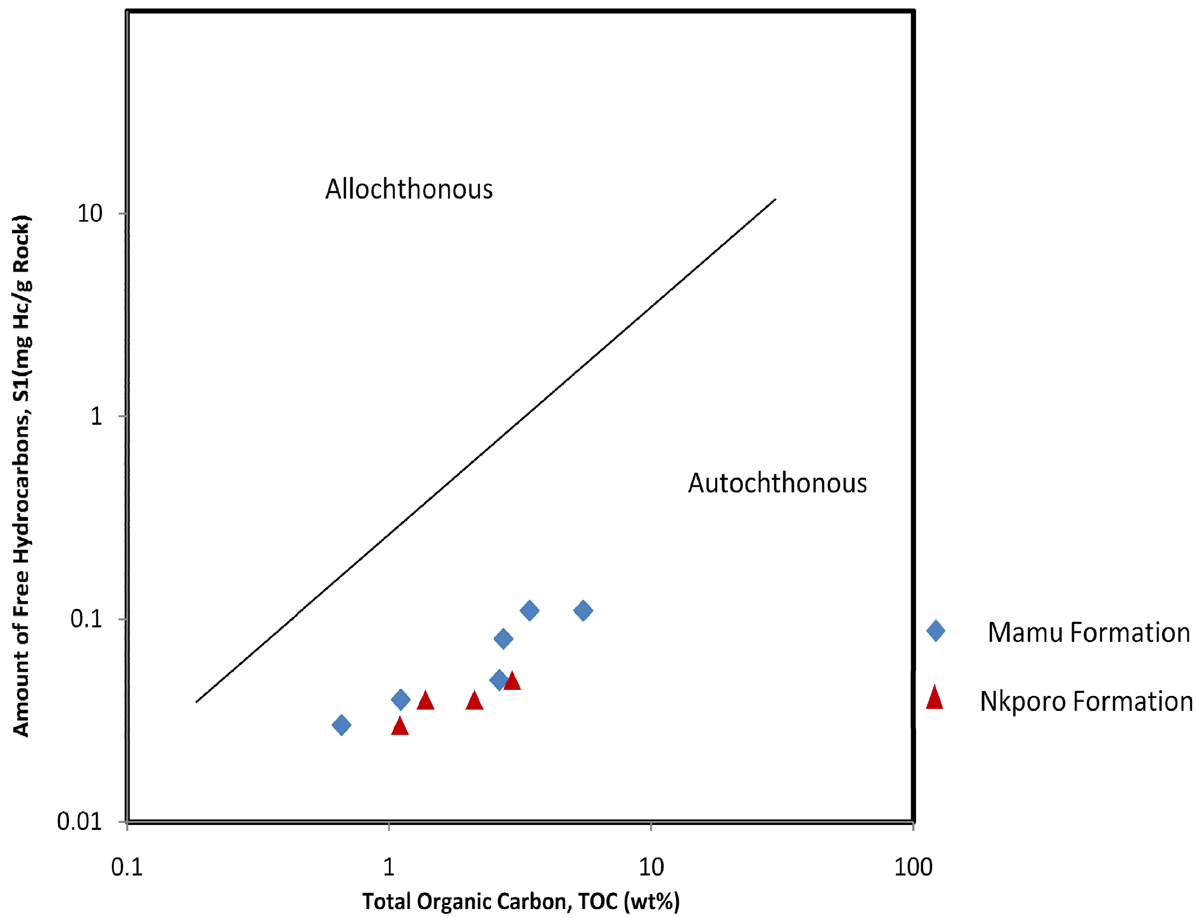


Fig. 4.36 Plot of S1 (Amount of Free Hydrocarbon) versus TOC (Total Organic Carbon) (after Ghori and Haines, 2007)

4.5.2. Hydrocarbon Generating Potentials

The findings in pyrolysis analysis are used to know the generation potential of a source rock. The generation potential (GP) is the sum of the S1 and S2 total values. According to Hunt (1996), source rocks with a GP<2 indicate poor, 2 to 5 indicate fair, 5 to 10 indicate good and >10 indicate very good potential for generation (Table 4.13a and 4.13b and Fig. 4.37). The relationship between (S1 + S2) and TOC (wt percent) shows that the samples of the Mamu Formation and even the Nkporo Shale are considered low to medium source potential (Table 4.13a, 4.13b and Fig. 4.37). On the contrary, the TOC (wt percent) plot against HI mg/g (Fig. 4.38) shows that samples of Cretaceous rocks from the Mamu Formation and the Nkporo Shale are gas to gas/oil source rocks, respectively.

Table 4.13: Genetic Potential Value and their Comparable Source Rock Quality (After Hunt 1996)

Source potential	Genetic potential value
Poor	<2 mg/g
Fair	2–5 mg/g
Good	5-10mg/g
Very Good	>10 mg/g

Table 4.14a. Results of TOC, Hydrogen Index, HI and Generation Potentials for Mamu Formation

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Leco TOC (wt%)	Hydrogen Index, HI	GP S1 + S2
L1	Amaiyi	N5°45 966’ E7°49 174’	Mamu Shale	Outcrop	1.11	41	0.49
L3	Nguzu	N5°46 131’ E7°49 453’	Mamu Shale	Outcrop	3.44	53	1.94
L16	Amaiyi	N5°46 219’ E7°49 365’	Mamu Shale	Outcrop	2.73	88	2.48
L19	Nguzu	N5°45 916’ E7°49 180’	Mamu Shale	Outcrop	0.66	17	0.14
L24	Nguzu	N5°46 064’ E7°49 320’	Mamu Shale	Outcrop	5.51	77	4.37
L26	Amaiyi	N5°46 260’ E7°49 267’	Mamu Shale	Outcrop	2.64	53	1.46
				Average	**2.68**	**54.83**	**1.81**

Table 4.14b Results of TOC, Hydrogen Index, HI and Generation Potentials for Nkporo Formation

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Leco TOC (wt%)	Hydrogen Index, HI	GP S1 + S2
L4	Ekeje	N5°46 238' E7°49 387'	Nkporo Shale	Outcrop	2.12	58	1.27
L5	Ekeje	N5°46 797' E7°49 314'	Nkporo Shale	Outcrop	1.10	27	0.06
L6	Ekeje	N5°47 048' E7°49 490'	Nkporo Shale	Outcrop	1.38	29	0.08
L14	Ekeje	N5°47 044' E7°49 493'	Nkporo Shale	Outcrop	2.95	69	2.1
				Average	**1.89**	**45.75**	**0.88**

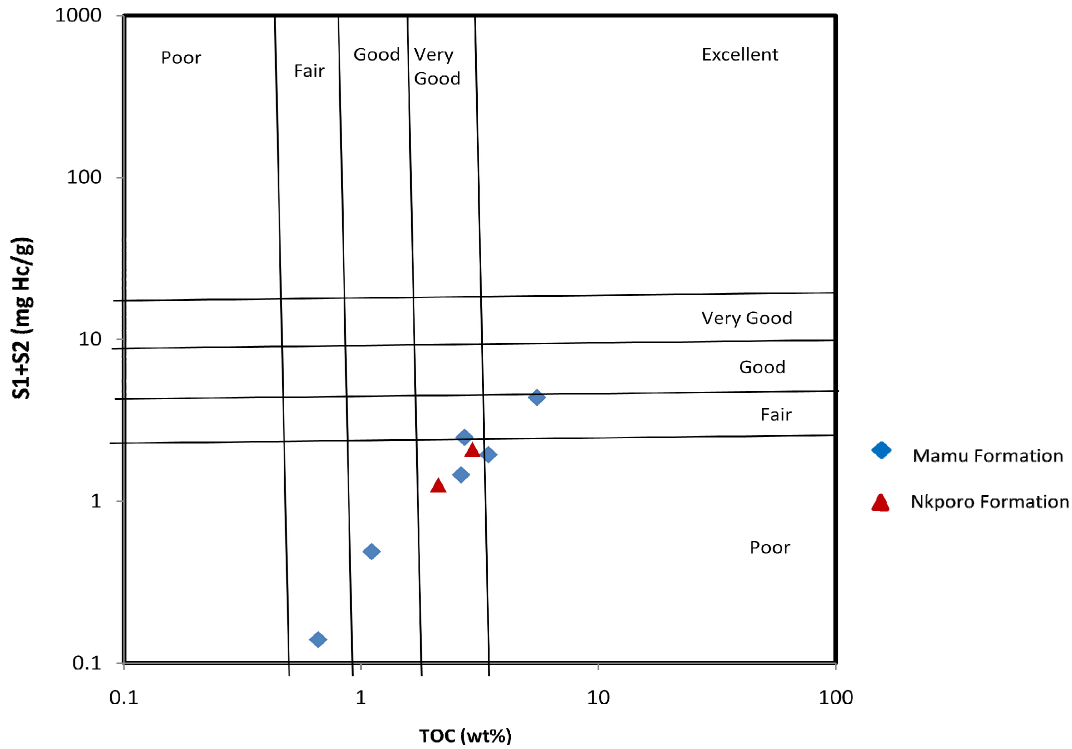


Fig. 4.37. Plot of GP (S1 +S2) versus TOC (wt%) (After Hunt (1996)

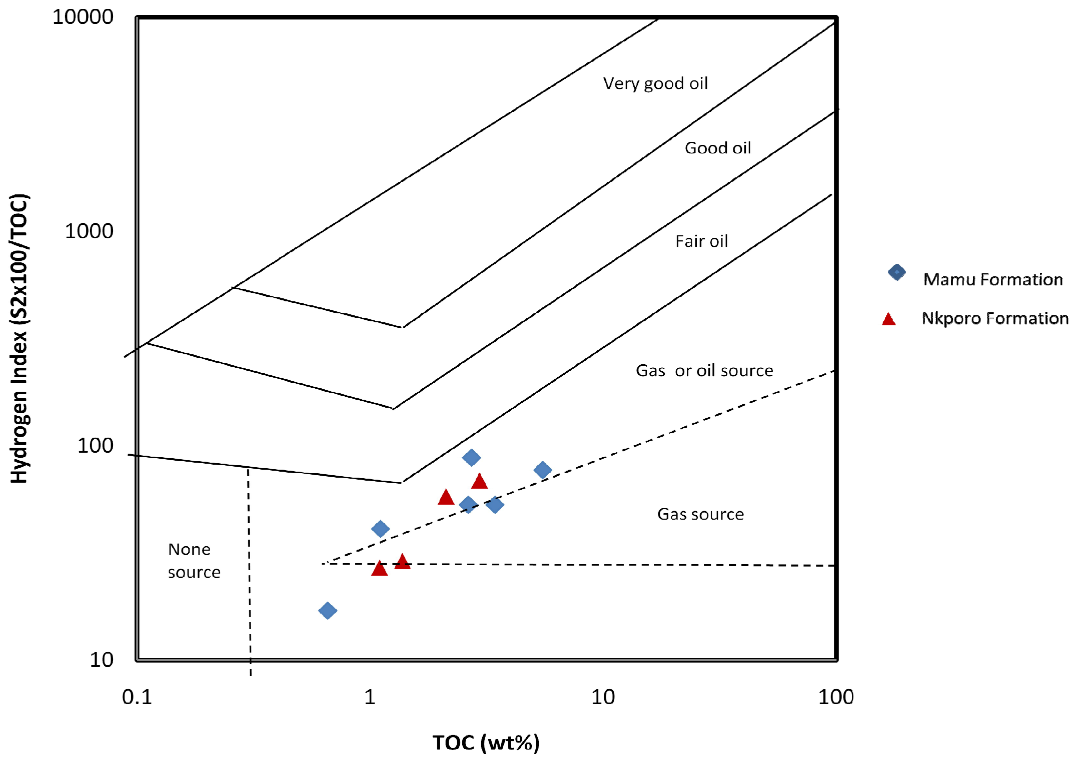


Fig. 4.38 Plot of Hydrogen Index (HI) versus TOC (After Hunt 1996)

4.5.3 Types of Organic Matter

Prediction of oil and gas potential, genetic nature of organic matter of a selected source rock is essential. The hydrogen index values (HI) were used by (Peters and Cassa 1994) to distinguish among the forms of organic matter. Hydrogen indices <50 mg HC/g show a possible cause of inert (mainly type IV kerogen) generation. Hydrogen indices of 50 to 200 mg HC/g produce kerogen of type III and are therefore capable of producing gas. Hydrogen indices involving from 200 and 300 mg HC/g produce a great deal of type III kerogen relative to type II and are thus capable of producing mixed gas and oil. Hydrogen indices between 300 and 600 mg HC/g contain a significant quantity of Type II kerogen and are therefore considered to have strong source potential for oil production in the marine environment. Hydrogen indices of >600 mg HC/g often consist of type I kerogen and therefore have an excellent potential for producing oil in the lacustrine environment (Table 4.15).

In this study, kerogen style illustration by Langford & Blanc-Valleron, 1990, representing the S2 versus TOC plot (Fig. 4.39) was used. This diagram shows that the samples analyzed for the Mamu Formation unit are characterized by type III kerogen are mostly atomic H/C between 0.7 and 1.0 (Table 4.16b; Fig. 4.39), while the Nkporo Formation unit is mainly characterized by type III and type IV with atomic H/C < 0.7 (Table 4.16b; Fig. 4.39). The Hydrogen index (HI) versus Oxygen index (OI) used to assess the form of kerogen is used on the basis of pyrolysis data for the classification of kerogen diagrams. The results indicate that the analyzed type III and IV kerogen area units of Nkporo Formation samples are mainly inert, while the analyzed type III kerogen area of Mamu Formation samples is gas-prone (Tables 4.16a and 4.16b, Fig. 4.40).

Table 4.15. Geochemical factors describing Kerogen Type (Quality) and the Character of products (after Peters & Cassa, 1994)

Kerogen Type	Hydrogen index mg HC/g TOC	S_2/S_3	Atomic H/C	Main Product at Peak Maturity
I	Greater than 600	Greater than 15	Greater than 1.5	Oil
II	300-600	10-15	1.2-1.5	Oil
II/III	200-300	5-10	1.0-1.2	Mixed Oil/Gas
III	50-200	1-5	0.7-1.0	Gas
IV	Less than 50	Less than 1	Less than 0.7	None(Inert)

Table 4.16a Results of TOC, Hydrogen Index, HI and Oxygen Index, OI for Mamu Formation

Sap. No.	Location	Co-ordinate	Formation	Sample Horizon	Leco TOC (wt %)	Hydrogen Index (HI)	Oxygen Index (OI)
L1	Amaiyi	N5°45 966’ E7°49 174’	Mamu Shale	Outcrop	1.11	41	38
L3	Nguzu	N5°46 131’ E7°49 453’	Mamu Shale	Outcrop	3.44	53	24
L16	Amaiyi	N5°46 219’ E7°49 365’	Mamu Shale	Outcrop	2.73	88	18
L19	Nguzu	N5°45 916’ E7°49 180’	Mamu Shale	Outcrop	0.66	17	53
L24	Nguzu	N5°46 064’ E7°49 320’	Mamu Shale	Outcrop	5.51	77	23
L26	Amaiyi	N5°46 260’ E7°49 267’	Mamu Shale	Outcrop	2.64	53	31
				Average	**2.68**	**54.83**	**31.17**

Table 4.16b: Results of TOC, Hydrogen Index, HI and Oxygen Index, OI for Nkporo Formation

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Leco TOC (wt%)	Hydrogen Index (HI)	Oxygen Index (OI)
L4	Ekeje	N5°46 238' E7°49 387'	Nkporo Shale	Outcrop	2.12	58	24
L5	Ekeje	N5°46 797' E7°49 314'	Nkporo Shale	Outcrop	1.10	27	25
L6	Ekeje	N5°47 048' E7°49 490'	Nkporo Shale	Outcrop	1.38	29	19
L14	Ekeje	N5°47 044' E7°49 493'	Nkporo Shale	Outcrop	2.95	69	24
				Average	**1.89**	**45.75**	**23.00**

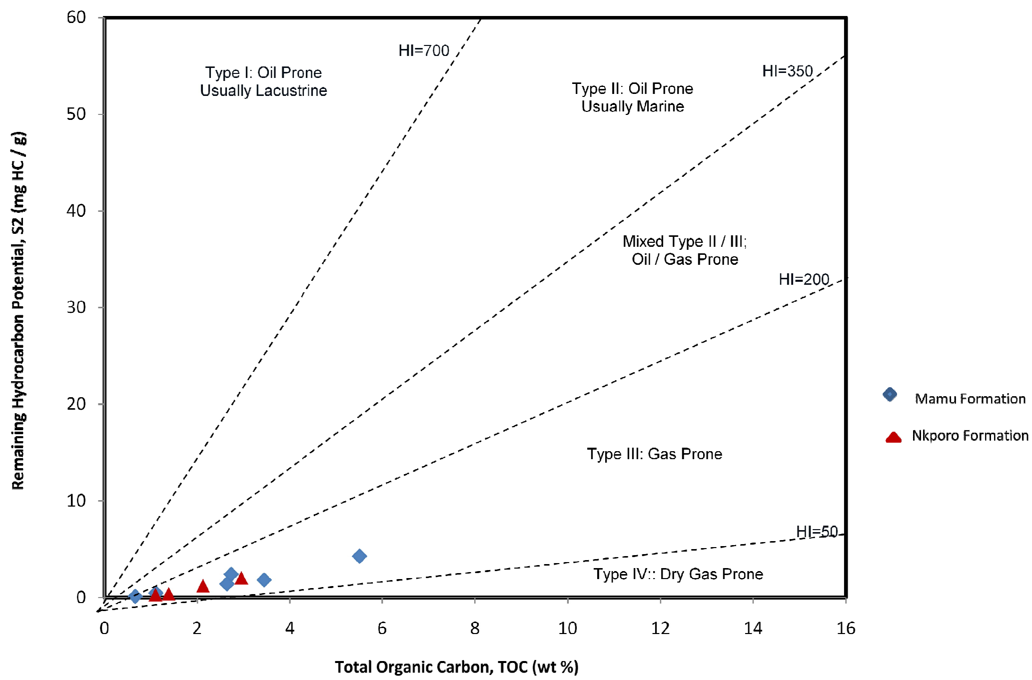


Fig. 4.39. Plot of Remaining Hydrocarbon Potential, S2 against Total Organic Carbon, TOC (Langford & Blanc-Valleron, 1990)

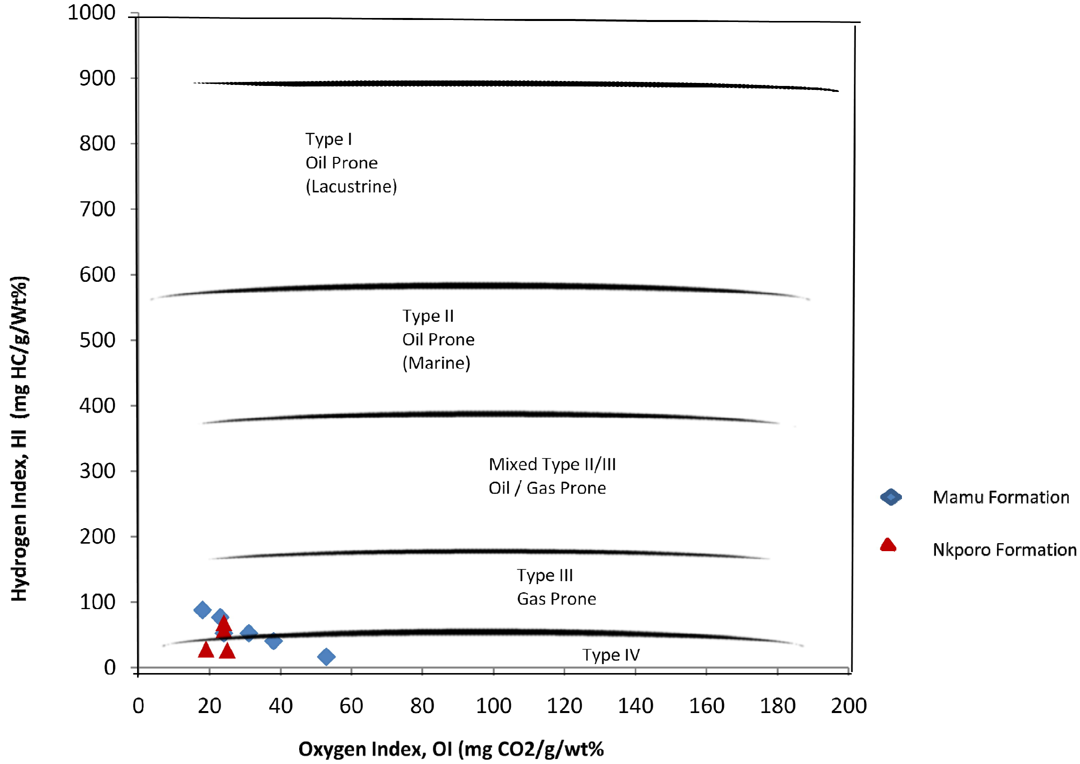


Fig. 4.40 Plot of Hydrogen Index (HI) Against Oxygen Index (Langford & Blanc-Valleron, 1990)

4.5.4 Thermal Maturity of Organic Matter

The generation of crude oil from the organic matter throughout its burial history may be a part of the overall method of thermal metamorphism process of organic matter (Tissot and Welte, 1984). The concentration and distribution of hydrocarbons contained during a particular source rely on each of the type of the organic matter and its degree of thermal alteration (Tissot and Welte, 1984; Longford and Blanc-Valleron, 1990). Within the current study, the thermal maturity level of the source rocks has been evaluated by the study of the geochemical parameters as Rock-Eval temperature pyrolysis (Table 4.17) ‘‘Tmax’’, production index ‘‘PI’’ (Hunt, 1996). Peters and Cassa, 1994 found that oil generation from source rocks starts at Tmax between 435–470 ^{o}C, and production index ‘‘PI’’ between 0.10 to > 0.25, the organic matters are in immature stage once ‘‘Tmax’’ features a value less than 435^{o}C, and ‘‘PI’’ less than 0.10 therefore the gas generation from source rocks starts at ‘‘Tmax’’ greater than 470^{o}C.

Based on pyrolysis details from kerogen classification diagrams using the Hydrogen Index, HI versus Tmax plot and Hydrogen Index, HI versus measured vitrinite reflectance as applied by Espitalie et al, 1985. The results show that the Nkporo Formation samples analyzed range from the immature to the mature zone of type III and type IV kerogen (Table 4.18a, Fig. 4.41), while the Mamu formation samples analyzed for the studied area range from the mature stage of the oil window to the type III kerogen (Table 4.18b, Fig. 4.41). The plot of the Hydrogen Index, HI versus the measured vitrinite reflectance, shows that the Nkporo Formation samples contain kerogens of type III and type IV. Some of the samples from Type III kerogens dropped into the oil window (Fig. 4.42), while the Mamu Shale samples from the study region were taken in combination with Type III kerogens and fell into the oil window (Fig. 4.42). The plot of the Production Index, PI vs. Tmax diagram (Peters, 1986; Waples, 1985) shows that almost all of the Nkporo Formation samples are immature source rocks (Fig. 4.43a), while the Mamu Shale samples are mature source rocks excluding those of the sample locations L3 and L24 that are slightly mature (Fig. 4.43a). The plot of the Production Index, PI against calculated Vitrinite Reflectance, percentage Ro shows that the studied Nkporo samples fall within the immature zone, except that the sample L14 is within the oil window, while the majority of the samples taken from the Mamu Shale jointly range from immature to the oil window (Fig. 4.43b)

Table 4.17 Parameters Describing the Amount of Thermal Maturation (After Peters and Cassa, 1994)

Phase of Thermal Maturity for Oil		Maturation			Generation
		R_0 (%)	**Tmax (^{0}C)**	**TAI**	**PI**
Immature		0.2- 0.6	< 435	1.5-2.5	< 0.10
Mature	Early	0.6- 0.65	435- 445	2.5-2.7	0.10-0.15
	Apex	0.65- 0.90	445- 450	2.7-2.9	0.15-0.25
	Late	0.9- 1.35	450- 470	2.9-3.3	> 0.25
Post-mature		> 1.35	> 470	> 3.3	---

Table 4.18a: Results of Hydrogen Index, Tmax and Production Index, PI for Mamu Formation

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Hydrogen Index, HI	Tmax	Production Index, PI
L1	Amaiyi	N5°45 966’ E7°49 174’	Mamu Shale	Outcrop	41	431	0.08
L3	Nguzu	N5°46 131’ E7°49 453’	Mamu Shale	Outcrop	53	419	0.06
L16	;Amaiyi	N5°46 219’ E7°49 365’	Mamu Shale	Outcrop	88	433	0.03
L19	Nguzu	N5°45 916’ E7°49 180’	Mamu Shale	Outcrop	17	422	0.21
L24	Nguzu	N5°46 064’ E7°49 320’	Mamu Shale	Outcrop	77	422	0.03
L26	Amaiyi	N5°46 260’ E7°49 267’	Mamu Shale	Outcrop	53	436	0.03
				Average	**54.83**	**427.17**	**0.073**

Table 4.18b: Results of Hydrogen Index, Tmax and Production Index, PI for Nkporo Formation

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Hydrogen Index, HI	Tmax (^oC)	Production Index, PI
L4	Ekeje	N5°46 238’ E7°49 387’	Nkporo Shale	Outcrop	58	429	0.03
L5	Ekeje	N5°46 797’ E7°49 314’	Nkporo Shale	Outcrop	27	422	0.09
L6	Ekeje	N5°47 048’ E7°49 490’	Nkporo Shale	Outcrop	29	428	0.09
L14	Ekeje	N5°47 044’ E7°49 493’	Nkporo Shale	Outcrop	69	433	0.02
				Average	**45.75**	**428**	**0.06**

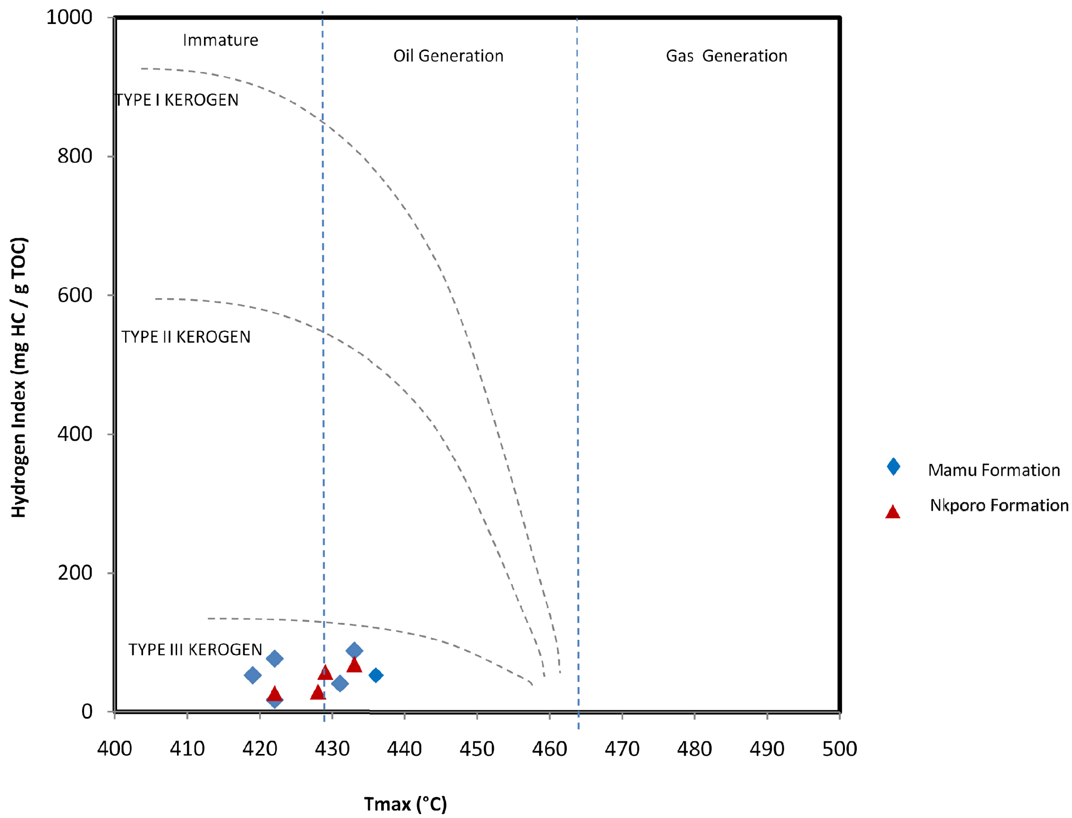


Fig. 4.41. Plot of Hydrogen Index (HI) versus Tmax (°C) (After Espitalie et al, 1985)

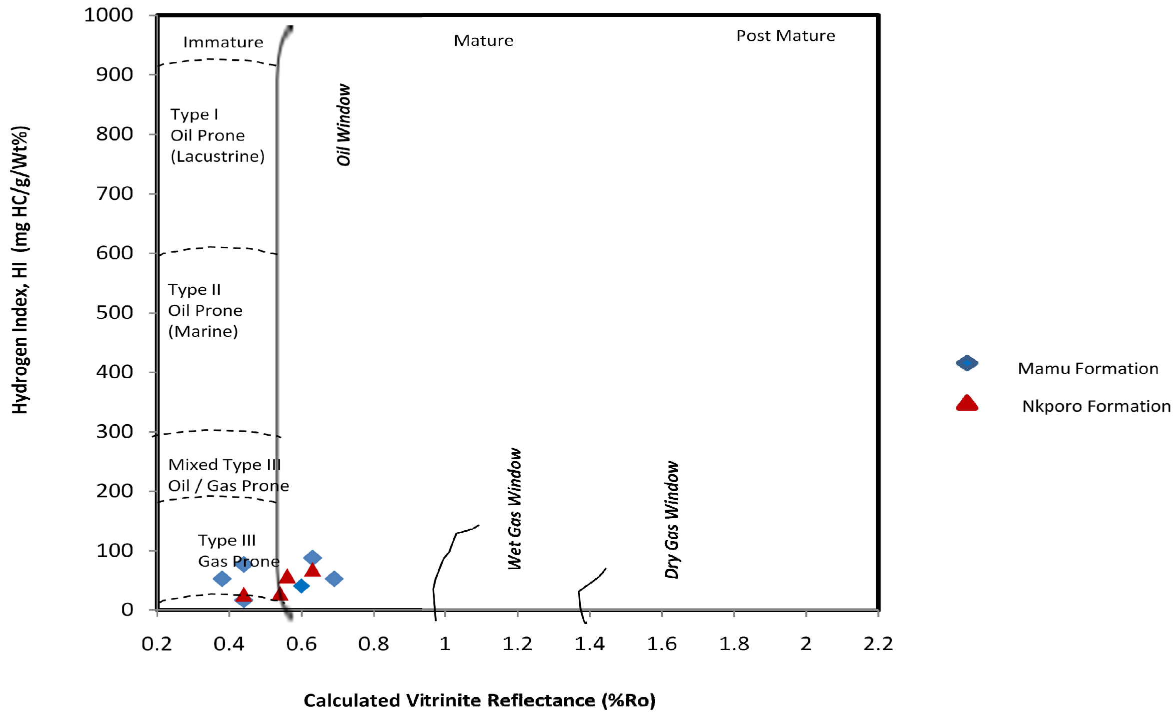


Fig. 4.42.. Plot of Hydrogen Index (HI) versus Calculated Vitrinite Reflectance (%Ro) (After Espitalie et al, 1985)

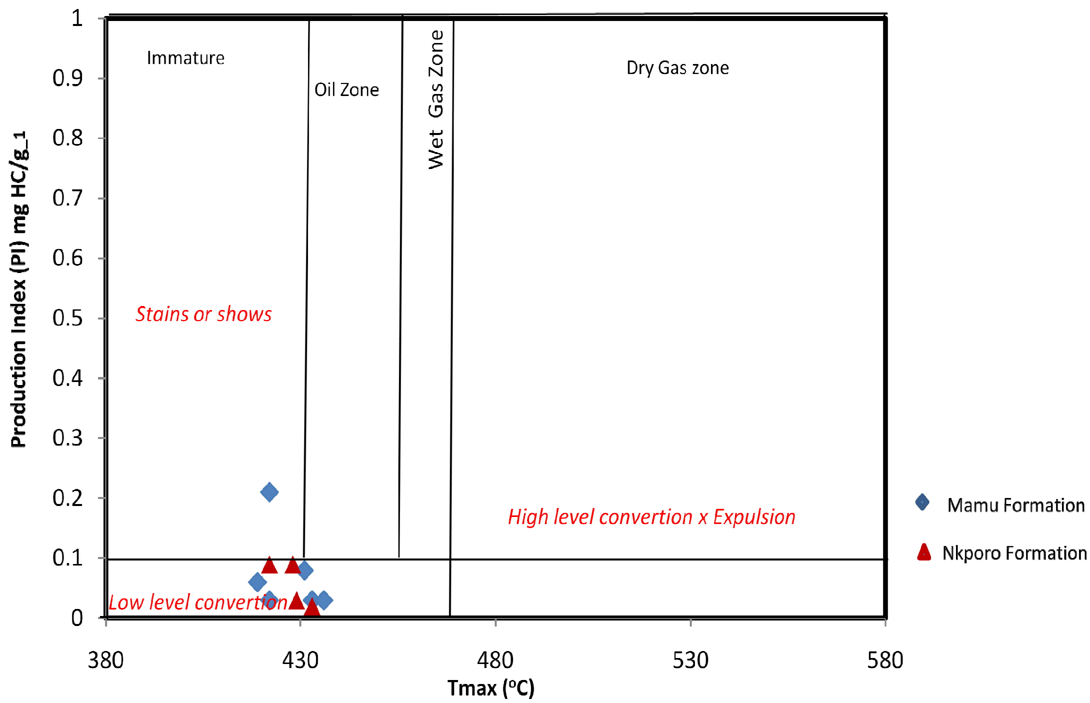


Figure 4.43a. Plot of Production Index (PI) versus Tmax (°C) Peters, 1986; Waples, 1985

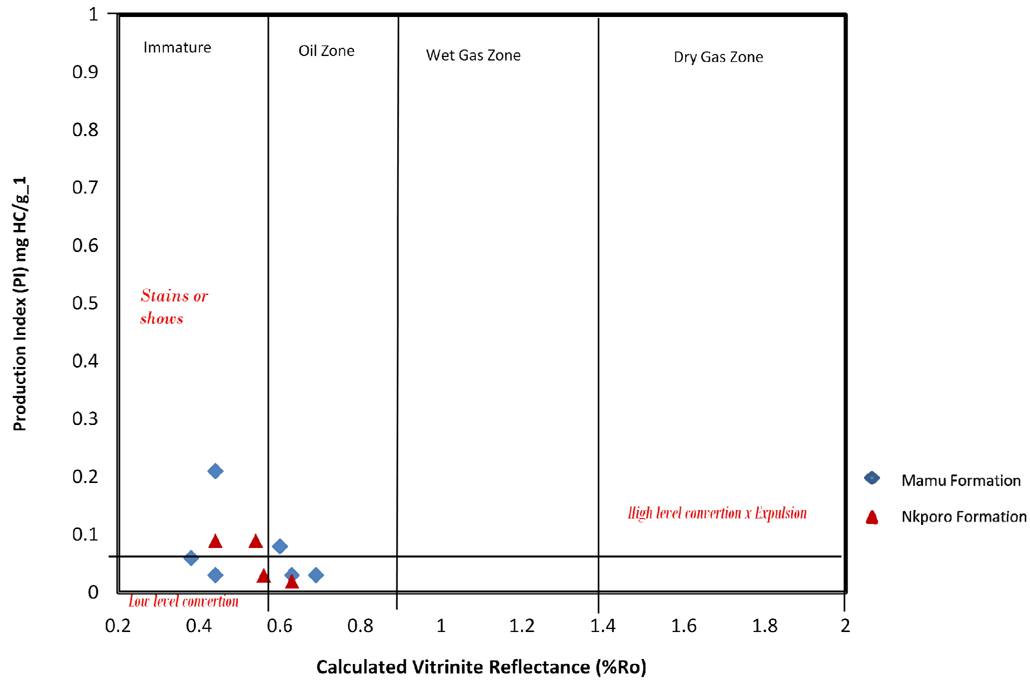


Figure 4 .43b. Plot of Production Index (PI) versus Calculated Vitrinite Reflectance (%Ro) (Peters, 1986)

4.5.5. Expulsion Potential

The capacity for expulsion is the quantity of oil expelled in organic matter. It additionally includes the quantity of hydrocarbon generated or migrated. The volume of liberated hydrocarbons within the sample (S1) over the Total Organic Carbon (TOC) defines the "Bituminous Index" (Table 4.19a and 4.19b).

The maturity, at which the value of the Bituminous Index (BI) (S1/TOC) starts to diminish, represents the start of an economical oil window or demonstrates productive expulsion of oil (Peters, et al, 2006). At a value of approximately within (0.6-0.7 percent Ro) and within (0.9-1.1 percent Ro), Tmax at intervals (433-440^{o}C Tmax) and within (442-460^{o}C Tmax) depending on the form of organic matter, the highest BI is produced. Bitumen or substantial crude oil are presumed to be the compounds formed in the early stages that subsequently form lighter oils at higher maturity by partial decomposition (Lewan, 1997). S2 is incessantly decomposing during maturity, causing a decline in S2 and an increase in free hydrocarbons (S1), and an increase in BI. The sharp rise in BI that occurs at a Tmax of 420-440 ^{o}C (or 0.45-0.73 percent Ro) marks the beginning of the generation of crude oil. S1 yields are terribly poor at 1.8 percent %Ro, the petroleum generation threshold was found at 0.5-0.6 percent %Ro, and liquid petroleum build-up shows between 0.5 and 0.85 percent Ro (Petersen, 2002 and Sykes and Snowdon, 2002).

In this research (Table 4.19a & 4.19b, and Fig. 4.44), and in line with above discussions, the hydrocarbon available in Nkporo Formation and Mamu Shale has a high degree of maturation. However, since most of the organic matter ranges from immature to the margin of the mature, it cannot be produced from a similar rock or migrated from another source rock.

Table 4.19a: Results of Bituminous Index, BI, Tmax ºC and Calc. Vitrinite Reflectance (%Ro) for Mamu Formation.

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Bituminous Index, BI	Tmax	Calc. VR %Ro
L1	Amaiyi	N5°45 966’ E7°49 174’	Mamu Shale	Outcrop	0.04	431	0.60
L3	Nguzu	N5°46 131’ E7°49 453’	Mamu Shale	Outcrop	0.03	419	0.38
L16	Amaiyi	N5°46 219’ E7°49 365’	Mamu Shale	Outcrop	0.03	433	0.63
L19	Nguzu	N5°45 916’ E7°49 180’	Mamu Shale	Outcrop	0.05	422	0.44
L24	Nguzu	N5°46 064’ E7°49 320’	Mamu Shale	Outcrop	0.02	422	0.44
L26	Amaiyi	N5°46 260’ E7°49 267’	Mamu Shale	Outcrop	0.02	436	0.69
				Average	**0.03**	**427.2**	**0.53**

Table 4.19b: Results of Bituminous Index, BI, Tmax ºC and Calc. Vitrinite Reflectance (%Ro) for Nkporo Formation.

Sample No.	Location	Co-ordinate	Formation	Sample Horizon	Bituminous Index, BI	Tmax	Calc. VR %Ro
L4	Ekeje	N5°46 238’ E7°49 387’	Nkporo Shale	Outcrop	0.02	429	0.56
L5	Ekeje	N5°46 797’ E7°49 314’	Nkporo Shale	Outcrop	0.03	422	0.44
L6	Ekeje	N5°47 048’ E7°49 490’	Nkporo Shale	Outcrop	0.03	428	0.54
L14	Ekeje	N5°47 044’ E7°49 493’	Nkporo Shale	Outcrop	0.02	433	0.63
				Average	**0.03**	**428**	**0.54**

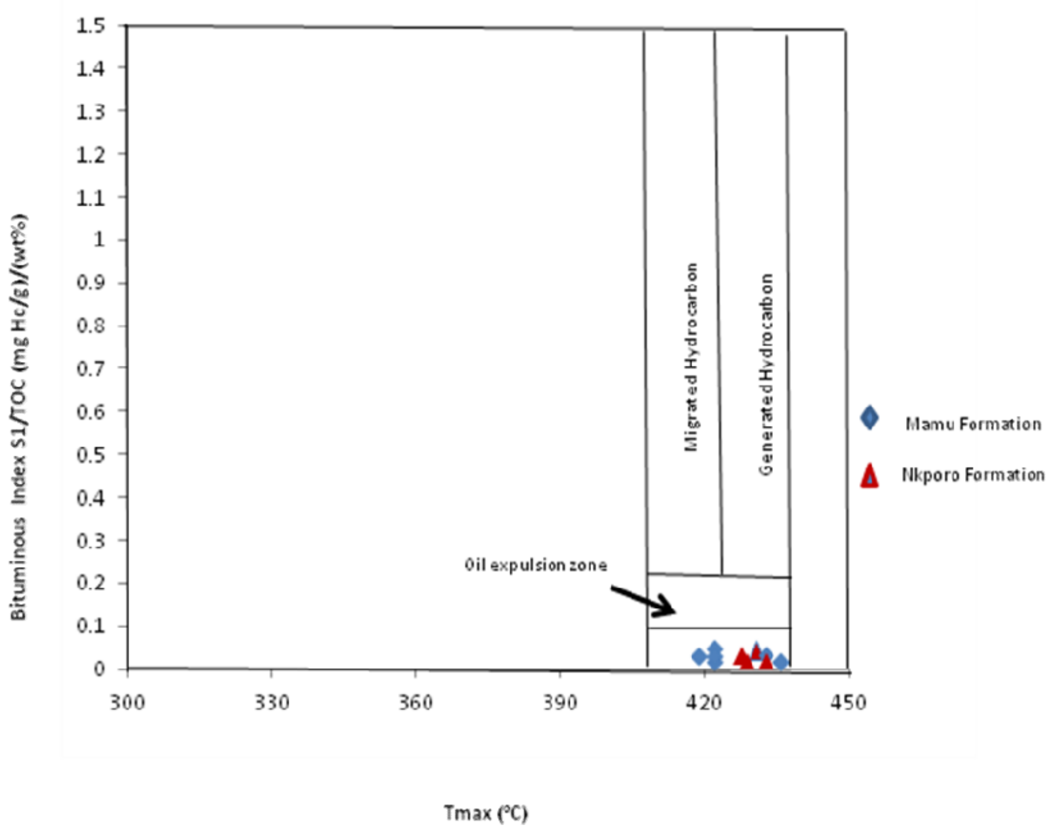


Fig. 4.44. Plot of Bituminous Index (BI) versus Tmax ºC(Peter, et al., 2006)

4.6 Geotechnical Characteristics

Tables 4.20 and 4.21a and 4.21b, show the results of the geotechnical test performed on the shales in the study area. Typically, the Nkporo and Mamu shales at Afikpo are yellow-gray to dark gray in colour in the hand specimen and turn greyish orange to reddish brown during firing. The outcomes of these experiment illustrated that the plasticity index of Mamu and Nkporo shales varies from (16.32 – 28.42 per cent and 17.82 – 38.07 per cent) with averages of (23.86 per cent and 26.87 per cent respectively. While the plastic limits for Mamu and Nkporo shale range from (23.80 – 30.51 per cent) to (17.18 – 52.93 per cent) with averages of (27.80 per cent and 36.10 per cent). The liquid limit for Mamu and Nkporo also ranged from (40.12% - 57.50 and 35.00 – 82.01%) with the average of (51.66% and 62.87%), while the linear shrinkage of Mamu and Nkporo shale ranges from (2.0 – 6.0% and 2.0 - 9.0%) with the averages of (4.0% and 5.73%) respectively. Soils having high values of liquid and plastic limits are considered generally poor as foundation materials (Cassangrande, 1948; Tables 4.20, 4.21a and 4.21b). These results showed that shales of Mamu and Nkporo Formations have slight variation in liquid, plastic limits and plastic indices, this slight variation in the range is the result of the difference in mineralogy within the samples, deficiency of smectites, and the proportion of clay and non-clay mineralsis shown in (Table 4.20). When sample L20 of Mamu shale is compared to sample L31 of Nkporo shale, this can be obvious that, there is an absence of smectites in both shales, but L20 of Mamu shale has 40.12 percent in terms of their liquid limits, while L31 of Nkporo shale has 82.01 percent. The shales fall within intermediate to high plasticity, based on the concept of plastic limits (Fig. 4.45). Grimshaw, 1971, demonstrated that for clay used for ceramic manufacturing, plasticity maximums of 10 to 60 percent of clay resources will be appropriate. This demonstrates that the shales examined are ideal for ceramics production (Table 4.19; Akpokodje et al., 1991).

According to (Casangrande's, 1948) graph, the plot of plasticity indices against Liquid Limits (Fig. 4.45) showed that Nkporo shale and Mamu shales are primarily inorganic clay and silt. Nkporo shale is medium to high in plasticity and compressibility, while Mamu shale is medium in plasticity and compressibility. Based on the liquid limit rating, Nkporo shale implies intermediary 35 to 50, high 50 to 70 and extremely high 70 to 90 plasticity, whereas the Mamu shale is moderate (35-50) to high (50-70) plasticity (Tables 4.21a, 4.20b and 4.22)

Table 4.20: Atterberg Limit Tests Gradings for Shale Samples in Afikpo

Sample's Tag No	Location	Co-ordinate	Formation	Liquid limit (%)	Plastic limit(%)	Plasticity index (%)	Specific gravity test
L 1	Amaiyi	N5°45 966' E7°49 174'	Mamu	57.50	29.08	28.42	2.55
L 9	Ebunwana	N5°47 161' E7°52 183'	Mamu	57.35	30.51	26.84	2.55
L 20	Nguzu	N5°45 937' E7°49 173'	Mamu	40.12	23.80	16.32	2.50
		Average		**51.66**	**27.80**	**Average**	**2.53**
L6	Ekeje	N5°47 048' E7°49 490'	Nkporo	68.96	39.62	29.34	2.50
L7	Amangwu	N5°50 246' E7°52 329'	Nkporo	58.29	36.06	22.23	2.55
L 30	Amoba	N5°47 692' E7°49 841'	Nkporo	75.65	37.58	38.07	2.50
L 31	Ndi-Ofiba	N5°48 252' E7°50 029'	Nkporo	82.01	47.79	35.22	2.50
L 33	Ndiba	N5°48 401' E7°50 022'	Nkporo	79.00	52.93	26.07	2.55
L 34	Amaigbo	N5°48 454' E7°50 284'	Nkporo	60.00	34.34	25.66	2.55
L 36	Amoso	N5°48 827' E7°50 507'	Nkporo	51.00	26.87	24.13	2.55
L 41	Ogbu	N5°49 228' E7°53 203'	Nkporo	74.36	43.26	31.10	2.50
L 43	Ogbu	N5°45 007' E7°54 608'	Nkporo	35.00	17.18	17.82	2.60
L 44	Ogbu	N5°48 982' E7°54 654'	Nkporo	53.75	28.78	24.99	2.60
L 52	Enohia	N5°50 854' E7°55 193'	Nkporo	53.55	32.64	20.92	2.55
		Average		**62.87**	**36.10**	**26.87**	**2.54**

Table 4.21a Mean and Range of Shales from Nkporo Formation

Properties	Formation	Mean	Range
Liquid limit	Nkporo	62.87	35.00 - 82.01
Plastic limit	Nkporo	36.10	17.18 - 52.93
Plasticity Index	Nkporo	26.87	17.82 - 38.07

Table 4.21b. Mean and range of shales from Mamu Formation

Properties	Formation	Mean	Range
Liquid limit	Mamu	51.66	40.12 - 57.50
Plastic limit	Mamu	27.80	23.80 - 30.51
Plasticity Index	Mamu	23.86	16.32 - 28.42

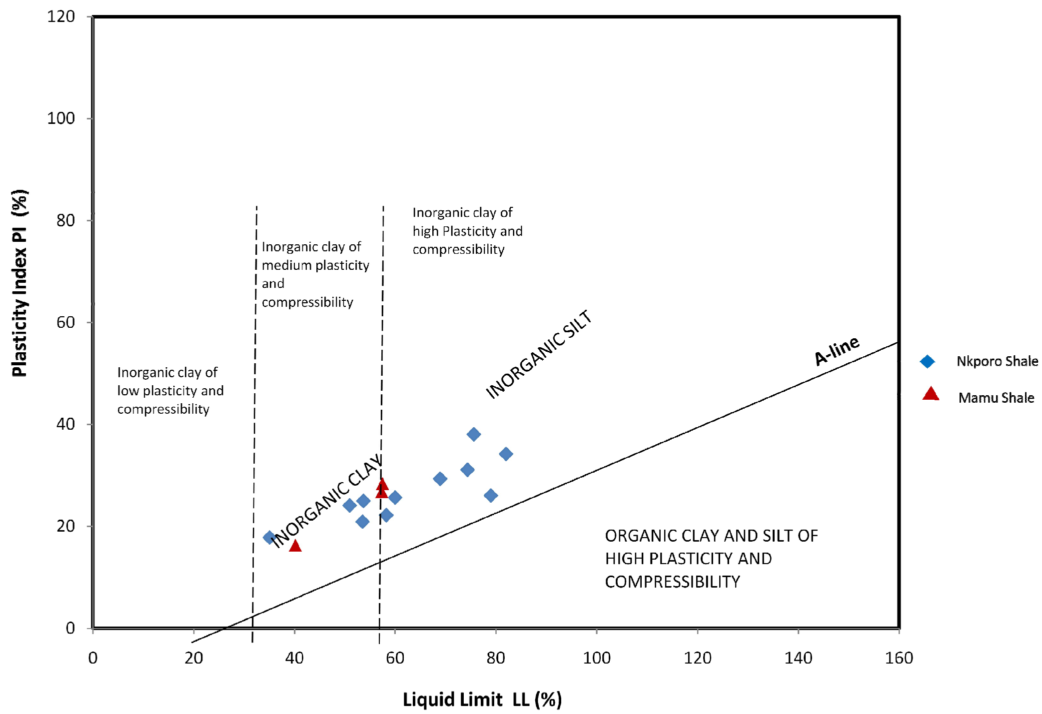


Fig. 4.45. Graphic Representation of Plasticity of Clay-Shale Bodies (after Casagrande, 1948)

Table 4.23, provides a comparison of the findings of the plasticity test of the Afikpo shale of Mamu and Nkporo shales with other reference clay and shale samples in Nigeria. By way of exemption of the Udubu clays of the Kerri-Kerri arrangement within the southern portion of Udubu, all the studied and reference samples are highly plastic (LL>50 percent). Mamu shale (4.0 percent) and Nkporo shale (5.75 percent) are advanced than the normal values for Auchi that is 2.49 percent and Gombe (3.49 percent), lesser than the common principles for Ewekoro (6.10 percent) and Okada shale (8.50 percent). Clay mineral presence (Obrike et. al., 2007) may be responsible for the high shrinkage. These physical test values make Afikpo shale an acceptable unrefined substance for the manufacture of earthenwares.

4.6.1 Firing Characteristics

The results of the fire test are shown. Shrinkage proportion and fire colours are essential features that affirm the appropriateness for wide range of industrial applications of clay/shale material. The intensity of contraction at firing is relies on the mineral structure and entirely different corporal constraints.

4.6.2 Fired Colour

The colour of the fired clay is greyish to reddish depending on the amount of iron and titanium oxides. In general, (Akpokodje et. al., 1991) 2-3% of iron oxide clay/shale can fire from pinkish to brownish. In both samples, the chemical test demonstrated that iron oxide arranges from 4.14-17.99 (ppm) with an average of 9.67 (ppm) for the Nkporo shale and from 1.39-6.69 (ppm) with an average of 4.47 (ppm) for the Mamu shale, which could be responsible for the firing colour of the representative samples (Table 4.22). The creamy, whitish-fired colors are favored in some ceramic, paper and tint productions, as opposed to the brownish colors that are most common in the earthenware and brick manufacturings. The fired colour of clay-shale renders it unsuited in favour of paper processing. The occurrence of different mixtures of mobile oxides such as hematite and limonite induces the colours (Nton and Elueze, 2005). The cost of production can be significantly increased by bleaching the clay-shale to create polish colour for papermaking.

4.6.3 Fired Shrinkage

Shrinkage fired experiments disclosed that in Nkporo shale the line of shrinkage is reasonable between 2.0-6.0% and 2.0-9.0% (Table 4.22). This can be due to the absence of smectites and the low coarse fraction within the clays and shale resulting from intermediate to lofty plasticity, resultant of inner fracture of the completed products. Such faults can lead to a decrease in the compressing potency of brick and earthenware refined commodities. The samples should intermingle with inconsistency polish sand within a reasonable proportion to reduce the fired shrinkage. Robert, (1994) has made clear that most techniques are ideal for clay bulk that meets up all the needs of a worker and contracsts not further than twelve percent. This has shown that the Afikpo shales are ideal for shrinkage-based ceramics and structural bricks.

4.6.4 Water Absorption Capacity

The principles of shales' absorption potential were also moderate, ranging from 5.90-10.08% for Mamu shale and 3.65-9.82% for Nkporo shale (Table 4.22). The presence of internal cracking was thus disclosed. Equivalent factors are affected by both linear shrinkage and water absorption ability. The higher the plastic limit the greater the potential of linear shrinkage and water absorption capacity. Nkporo shale is of medium to high plasticity and compressibility with respect to the plasticity plot, whereas Mamu shale is of medium plasticity and compressibility with significant toughness. In the form of organic matter, the high shrinkage value can be due to the volatile organic matter content.

Table 4.22. Results of the Geotechnical tests of Studied Afikpo-Edda Shales

Sample Tag No	Formation	Location	Water absorption Test (%)	Bulk density Test(g/cm^3)	Linear Shrinkage (%)	Natural Moisture Content (%)	Colour before firing	Colour after firing	Fireability
L 1	Mamu	Amaiyi	5.90	1.98	6.0	2.48	Dark grey	Reddish brown	Good
L 9	Mamu	Ebunwana	8.14	1.89	4.0	3.16	Yellow grey	Greyish orange	Good
L 20	Mamu	Nguzu	10.08	1.89	2.0	1.90	Medium grey	Light brown	Good
	Average		**8.04**	**Average**	**4.0**	**2.51**			
L6	Nkporo	Ekeje	7.34	1.92	8.0	3.36	Dark grey	Reddish brown	Good
L7	Nkporo	Amangwu	9.82	1.97	4.0	1.98	Dark grey	Reddish brown	Good
L 30	Nkporo	Amoba	7.91	1.96	9.0	4.21	Yellow grey	Greyish orange	Good
L 31	Nkporo	Ndi-Ofiba	6.29	2.17	8.0	3.42	Yellow grey	Greyish orange	Good
L 33	Nkporo	Ndiba	4.11	1.90	6.0	2.84	Yellow grey	Greyish orange	Good
L 34	Nkporo	Amaigbo	8.22	1.92	4.0	2.13	Medium grey	Light brown	Good
L 36	Nkporo	Amoso	3.65	1.93	5.0	2.25	Yellow grey	Greyish orange	Good
L 41	Nkporo	Ogbu	7.46	1.91	7.0	3.72	Dark grey	Reddish brown	Good
L 43	Nkporo	Ogbu	6.70	1.99	2.0	2.22	Dark grey	Reddish brown	Good
L 44	Nkporo	Ogbu	4.51	1.98	5.0	3.02	Medium grey	Light brown	Good
L 52	Nkporo	Enohia	4.23	1.91	5.0	2.19	Yellow grey	Greyish orange	Good
	Average		**6.39**	**1.96**	**5.73**	**2.85**	-	-	-

Table 4.23. Plasticity Test Result of Mamu and Nkporo Shales Compared with Other Shales/Clay

	Afikpo Edda shales, study area						
Reference	A1	A2	B	C	D	E	F
	Mamu shale	Nkporo shale	Auchi shale	Gombe shale	Okada shale	Ewekoro shale	Itu-Mbonuso/Iwere Shale
Plastic limit	27.8 (23.8-30.5)	36.1 (17.2-52.9)	27 (26.2-29.5)	27 (25.2-29.0)	68 (67.0-68.0)	29 (28.0-30.0)	41.7 (31.05-77.7)
Liquid limit	51.66 (40.1-57.5)	62.87 (35.0-82.0)	54 (51.5-59.0)	66 (64.4-67.0)	146 (142-152)	53.5 (53.0-54.0)	92.7 (47.7-194)
Plasticity index	23.86 (16.3-28.4)	26.87 (17.8-38.1)	26 (23.0-29.5)	36 (33.8-38.0)	78 (74.0-85.0)	24.5 (24.0-25.0)	51.0 (16.7-116.3)
% Shrinkage	4.0 (2.0-6.0)	5.73 (2.0-9.0)	2.49 (0.49-5.50)	3.49 (2.72-4.25)	8.50 (8.3-8.7)	6.10 (6.0-6.20)	7.67 (4.8-10.0)

Reference Samples

A1 and A2 = Mamu shale and Nkporo shale of Afikpo-Edda correspondingly.

B = Auchi shale: Emofurieta, (1994).

C = Gombe shale: Emofurieta, (1994).

D = Okada shale: Obrika, et al., (2007).

E = Ewekoro shale: Nton, and Elueze, (2005).

F = Itu-Mbonuso/Iwere: Okunlola, and Egbulem, , (2015).

Table 4.24. Chemical Compositions of Afikpo Shales Compared with some UK Industrial Specifications

	Study Area		Industrial Specification							
Refs.	A1 Nkporo	A2 Mamu	B	C	D	E	F	G	H	I
SiO_2	49.71	59.79	67.50	47.00	44.90	45.00	45.90	48.67	40-48	49.88
Al_2O_3	22.39	18.90	26.50	40.00	32.35	38.10	33.5-36	9.45	20-40	37.65
Fe_2O_3	9.67	4.47	0.5-1.20	-	0.43	0.60	0.30-.60	2.70	1-4	0.88
MgO	0.72	0.40	0.1-0.19	-	Trace	-	-	8.5	<5	0.13
CaO	0.11	0.35	0.18-0.30	-	Trace	-	0.0-.50	15.84	<5	0.03
Na_2O	0.06	0.05	0.20-1.50	-	0.14	-	0.0-1.6	2.76	<3	0.21
K_2O	1.17	1.09	1.10-3.10	-	0.28	-	0.0-1.6	2.76	<3	1.60
TiO_2	1.04	1.19	0.10-1.0	-	1.80	1.70	0.0-1.70	-	-	0.09
P_2O_5	0.12	0.15	-	-	-	-	-	-	-	-
MnO	0.003	0.02	-	-	-	-	-	-	-	-
Cr_2O_3	0.018	0.014	-	-	-	-	-	-	-	-

A1 and A2 -This study.

B - (Ceramics; After Singer and Sonja, 1971).

C - (Pharmaceutical; After Todd, 1985).

D - (Rubber; After Keller, 1964).

E - (Textile; After Keller, 1964).

F - (Paper; After Keller, 1964).

G - (Brick; After Murray, 1960).

H - (Refractory; Afer Anon 1972).

I - (Agricultural; Huber, 1985).

Table 4.25. Specification of some industrial Clays/Shale in Nigeria (Jongs et. al., 2018; Daspan et. al., 2009)

Oxide%	Nkporo	Mamu	Plastics	Paints	Rubber, Paper Texile	Ceramics	Refractory Bricks	Brick Clay	Tiles	Sanitary wares	Table wares
SiO_2	49.71	59.79	45.78	45.30-47.90	44.90	45.90	67.50	51-70.00	70.00	54.00	46.00
Al_2O_3	22.39	18.90	36.46	37.90-38.40	32.35	33.50-36.10	26.00	25.44	19.00	30.00	31.00
Fe_2O_3	9.67	4.47	0.28	13.40-13.80	0.43	0.60	0.50-1.20	2.40	1.60	1.40	1.10
TiO_2	1.04	1.19	-	13.80	-	0.03	-	-	1.60	1.20	0.90
Na_2O	0.06	0.05	0.25	0.20-0.35	0.14	1.60	1.50	3.50	0.50	0.50	0.40
K_2O	1.17	1.09	0.25	0.40-1.00	0.28	1.60	1.10-3.10	-	2.00	3.10	2.20
CaO	0.11	0.35	0.50	0.03-0.25	Tr	0.50	0.30	0.20	0.20	0.30	0.40
MgO	0.72	0.40	0.04	0.20-0.30	Tr	0.40	0.19	0.70	0.40	0.40	0.40
LOI	-	-	-	-	-	12.40	-	-	5.40	8.80	-

4.7 Economic Evaluation of Afikpo Shale

The criteria apply in analysing the consistency of the deliberate samples to be used in various applications such as mineralogical, chemical composition, source rock and physical properties. The Nkporo and Mamu shale at Afikpo may possibly be used as unrefined substance for the production of ceramic objects (Singer and Sonja, 1971), refractory bricks (Parker, 1967) and stoneware development (Arua and Onyeoku, 1978) from a comparison of some industrial requirements (Table 4.24). Within the Afikpo samples, the considerable level of Fe_2O_3 could pose a threat for the paper and rubber processing. Oxides of iron have a colouring effect on completed substances. The specification of some industrial clays/shale in Nigeria shown in Table 4.25, based on these characteristics, the shale were detected to be potentially suitable for the creation of ceramic, tiles, refractory wares (sanitary and table wares) then paper, rubber, and texile needed minimal processing to increase their potentials to meet the requirements with the specifications.

Research into the chemical components of clay shale has shown that clay/shale accumulations can provide as first-rate basis of unprocessed substances for cheap heat-resistant bricks. However, by selecting the untreated material to get rid of silica in the variety of quartz as well as alternate non-clay portions, the refractory product quality can be upgraded. By lightening with caustic or magnetic removal of iron oxide and titanium flaw, further upgrading can also be improved (Hughes, 1982). Lofty flux content can however, have an impact on the temperature of vitrification. Additional improvement can be added by combining the unprocessed objects requested with massive alumina or unpolluted aluminium oxide clay.

Further study of chemical components (S.R and A.R) (Tables 4.4a and 4.4b) also suggested that the shale is ideal for the production of refractory bricks of fine quality. Along with the plasticity limits (its malleability), the S.R and A.R divulge the shale fit for constructional such as roofing terrazzo, evacuation conduits with sanitized products.

Hydrocarbon source rock analysis of samples from the research was used on the basis of HAWK pyrolysis details and Total Organic Carbon (TOC) (Tables 4.12a and 4.12b) to determine the quantity of organic matter, organic richness and degree of maturation. The average total organic carbon content for the Mamu and Nkporo shales is 2.68wt percent and I.89wt percent. This means that they meet the minimum threshold value (0.5wt percent) for good organic substance concentrations. Autochthonous organic matter were characterized in the studied rock samples for the Mamu Formation and Nkporo Shale, suggesting that the organic materials formed was buried in or is indigenous to the site. The values obtained for the Hydrogen Index (HI) signify that the Nkporo Formation samples analyzed are type III and IV kerogens, which are mainly inert, while the Mamu Formation samples analyzed are type III kerogens, which are gas prone. The degree of maturity of the hydrocarbon-supply sediment was calculated by using geochemical parameters such as the Rock-Eval temperature pyrolysis "Tmax',' the production index "PI'.' The standard Tmax and PI values for the samples studied do not surpass the threshold (Table 4.18a and 4.18b). Therefore, the samples are immature to mature with respect to hydrocarbon generation.

Shale is also appropriate unprocessed substance for manufacturing of ceramic objects bricks and stoneware. The intermediate-to-lofty plasticity of the clay-shale samples crafts findings possible. Grimshaw's (1971) approval of clay products amid plasticity maximum of 10 to 60 percent suggested that the shale satisfies the ceramic requirement. Early vitrification would be favoured by the elevated accumulation of fluxes in the shale, resulting in power preservation in the business. Extra benefits of lowering the vitrification heat ensures that the goods do not become brittle also do not become glassy and broken when cooled (Robert, 1994).

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATION

5.1 Summary

Results of research conducted on the Mamu and Nkporo shale as exposed in the region of Afikpo indicate that the shale fragments mineralogically have kaolinite as the principal clay mineral with previous components like hematite, goethite, siderite with quartz as the core non clay mineral.

Chemical wise, shale displays significant subsequent oxide component concentrations; over 90 percent are SiO_2, Al_2O_3, Fe_2O_3, K_2O and TiO_2, whereas comparatively low values are MgO, CaO, Na_2O, P_2O_5, MnO, and Cr_2O_3.

Evaluation of the results of source rock analysis supported by Hawk-pyrolysis and total organic carbon (TOC) data reveals the standard and amount of organic matter, generation potential, and types of organic matter, thermal maturity of organic matter and expulsion potential of the studied area.

The findings of the Nkporo shale at Afikpo, according to reported industrial requirements, prove that it can be employ as unrefined materials in the production of earthenware and alumina content in paints (average 22.39% and 18.90% for Nkporo and Mamu shale indicated that they can also be exploited for substandard refractory building block (Aron, 1972). Nevertheless, shales could undergo refinement inorder to satisfy the specifications for agricultural, pharmaceutical and textile industries.

5.2 Conclusion

The study therefore indicates that, due to poor rock source capacity and immature sediment, the Afikpo shale is not suitable for hydrocarbon, but might used for earthenware, paint, ceramic objects and low-grade heat-respistant objects.

5.3 Recommendation

Further research is recommended with a view to figuring out if there is a solution to the inorganic geochemical characteristics, with the regards to the reduction of high impurities of alumina, iron oxide and titanium oxide in the shales, in order to make them appropriate for the production of high-grade bricks. Situations of proper blending, which remedy and provide acceptable assistance with lime water for purification procedures. Also, it would be affordable to consider other trends as alternative characteristics of sedimentary rocks as indices therefore, to understand petrological processes of shale within the area.

5.4 Contribution to Knowledge

Afikpo shale samples give bits of knowledge on relative rock fragility, which are all keys to understanding shale reservoirs, and a view to speedily exploit shale crude materials for feasible economic development and job creation. It also upheld as contrast between the compositional attributes of shale deposits of the area and other shales somewhere else and their renowned standards. Consequently, the shale at Afikpo, serve as raw materials in the creation of ceramics, pottery, and in paints production.

This study therefore indicates that, the shale in the area can frequently utilize for poor quality refractory wares, paper and rubber. The substandard quality can be updated by blending in with unadulterated alumina content or screening of the shale to limit the iron oxide and quartz contents by chemical treatment. This later treatment can in any case, increment the bricks production.

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