

**GEOCHEMICAL, PROVENANCE TECTONIC SETTING, SOURCE- AREA WEATHERING AND MATURITY STATUS OF TAR SANDS FROM ODE AYE AREA OF ONDO STATE, SOUTHWESTERN, NIGERIA.**

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**ABSTRACT :** *The geochemistry of the major oxides, provenance and tectonic setting as well as the maturity status of the Ode Aye bitumen-impregnated sand (tar sand) are presented in this study. Silica oxide ( $\text{SiO}_2$ ) is dominant and ranges between 66.36 and 94.29 wt %. In a descending order,  $\text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{TiO}_2$ . Their association suggests a relationship with clay minerals. The results of the calculations of  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) < 1.5$  and  $\log ((\text{Fe}_2\text{O}_3+\text{MgO})/(\text{K}_2\text{O}+\text{Na}_2\text{O})) > 0$  support the classification conditions of the sediments as lithic arenites. Sediments plotted in the passive continental margin as well as granite gneiss provenance field collaborating with continental sands (lithic arenites) that are of ferromagnesian potassic type. Granite and gneisses provenance probably provided the source sediments that were deposited in the passive margin that created favourable conditions for accumulation and maturation of organic matter in the studied area. The sediments however are immature and they tend towards chemical maturity due to their formation under semi humid and humid conditions.*

**KEYWORDS:** Lithic arenite, Ferromagnesian potassic, Passive margin, Immature sediments.

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## INTRODUCTION

The experience of tar sand and bitumen in Ode -Aye area of Ondo State has created different kinds of environmental fears of degradation on their land, crops, water, and their general health welfare. Ode Aye is a community that depends on their soil, water and their farm produce for their existence. The tar sand in this community exists in several farm lands including the palm tree plantations one of which is the present study area.

Tar sands (bituminous sand) were discovered in Nigeria in the beginning of the 20th century around 1900 (Akinmosin, Osinowo and Oladunjoye, 2009). Tar sands have similar composition as the light crude. Adegoke (2000) compared the Nigerian tar sands with the large deposits in Alberta Canada and Trinidad. Tar sands generally are believed to have formed from biodegradation and water-washing of light crude due to lack of cap rock. The Nigerian Tar sands are believed to have formed in a similar process. Tar sands are impregnated sands that yield mixtures of liquid hydrocarbons, which require further processing other than mechanical blending before becoming finished petroleum products.

Ode Aye area lies between latitudes  $6^\circ 34'N$  and  $6^\circ 64'N$  and longitudes  $4^\circ 54'E$  and  $4^\circ 74'E$  of the tropical rainforest belt of Nigeria. Vast deposit of bitumen is located in one of the palm tree plantations of Ode Aye area and this flows during the hot weather and hardens when the temperature cools down. Figure 1 shows the congealed (thickened) bitumen in one of the locations in the palm plantation. Ode-Aye is underlain by the sediment of Imo shale of South East, lateral equivalent of which is the Ewekoro and Akinbo formations of South west Nigeria (Fig 2). Ewekoro formation directly overlies the Abeokuta group (Ise, Afowo and Araromi

formations) as observed from the section at Ewekoro and Sagamu quarries as well as the cored sections at Ibeshe (Omatsola and Adegoke (1981), and Agagu (1985). The Ewekoro is made up of greyish white and occasionally greenish limestone which is sandy toward the base and having a thickness that varies between 15-30m. This formation is dated to be Paleocene in age. Ise formation is the oldest formation in Abeokuta group and it unconformably overlaps the Precambrian basement complex. Afowo formation indicates the commencement of deposition in a transitional environment after the entire basal and continental Ise formation. The sediments are composed of interbedded sands, shales and clays, which range from medium to fine grains in size (Omatsola and Adegoke; 1981 and Agagu; 1985) and this has been found to be bituminous in both surface and subsurface sections. The age is Maestrichian Araromi formation represents the youngest unit of the Abeokuta group. The formation is composed of shales, fine-grained sand, thin interbeds of limestone, clay and lignite bands (Omatsola and Adegoke; 1981; Agagu; 1985).



**Figure 1. Congealed bitumen rich soil**

## **LITERATURE/THEORETICAL UNDERPINNING**

Sandstones are made up of detrital grains that form the framework of sediments, quartz being the most common mineral and the most stable. The abundance of quartz depends on its availability (source area geology), mechanical and chemical stability as well as its resistance to weathering and alteration. Rock fragments in sandstones usually give specific information on the provenance of a deposit once they can be tied to a particular source geological formation. The composition of sandstones according to Roser and Korsch, (1986, 1988), Huntsman-Mapilaa et al, 2005 has been used as sensitive indicator for provenance studies and weathering conditions at the source of sediments. The major assumption proposed for sandstone provenance studies is that each tectonic setting is made up of its own rock type, (Dickson and Suezek, 1979; Dickson, 1985). Bhatia (1983), Taylor and McLennan, (1985) and Bakkiaraj, et al. (2010) suggested also that the geochemical composition of sediments is an important tool in the study of provenance. Since Ode Aye community is a non-pristine area with weathering, heavy metals occurrence, anthropogenic, natural processes and presence of bitumen; there is



oxides such as  $K_2O$ ,  $Na_2O$ ,  $MgO$  and  $CaO$  have low concentrations and each has less than unity (1). The low values of these oxides may be attributed to chemical destruction under oxidizing condition during weathering. The ratio of  $SiO_2/Al_2O_3$  ranges from 6.055 to 41.537 showing high silica to alumina content.  $K_2O/Al_2O_3$  ratio is low (0.019-0.042) an indication of low K-bearing mineral contents in relation to alumina.  $K_2O/Na_2O$  ratio ranges between 0.0 and 11.50 supporting the low contents of K and Na bearing minerals.  $Al_2O_3/TiO_2$  ratio varies from 4.28 to 9.37 showing a slightly high alumina relative to titanium oxide.

**Table 1. Major oxides composition of the Ode Aye (Wt. %)**

OXIDES	SAMPLES NUMBER							
	1	2	3	4	5	6	7	8
$SiO_2$	81.40	86.70	82.99	89.01	91.86	66.36	94.29	85.90
$Al_2O_3$	6.79	5.48	7.31	5.23	3.02	10.96	2.27	4.43
$K_2O$	0.15	0.17	0.28	0.10	0.07	0.46	0.05	0.12
$Na_2O$	0.0	0.0	0.03	0.0	0.0	0.04	0.0	0.0
$Fe_2O_3$	1.10	1.98	2.49	2.11	0.68	1.29	0.71	1.42
$MgO$	0.11	0.15	0.16	0.15	0.07	0.17	0.09	0.09
$CaO$	0.03	0.03	0.06	0.03	0.03	0.07	0.03	0.05
$TiO_2$	0.94	1.28	1.30	1.22	0.50	1.17	0.51	0.62
$MnO$	0.01	0.03	0.03	0.04	0.00	0.01	0.01	0.00
$SiO_2/Al_2O_3$	11.988	15.82	11.35	17.02	30.42	6.06	41.54	19.40
$K_2O/Al_2O_3$	0.022	0.031	0.038	0.019	0.023	0.042	0.022	0.027
$Al_2O_3/TiO_2$	7.223	4.281	5.623	4.286	6.04	9.368	4.450	7.145
$K_2O/Na_2O$	0.0	0.0	9.333	0.0	0.0	11.50	0.0	0.0
<b>CIA</b>	97.5	96.5	95.18	97.6	96.79	95.05	96.59	96.30
<b>CIW</b>	99.6	99.45	98.78	99.42	99.02	99.00	98.69	98.88
<b>MIA</b>	95	93	90	95	93	90	93	92
<b>PIA</b>	99.6	99.4	98.7	99.4	98.9	98.9	98.7	98.9

## DISCUSSIONS

Most of the oxides have been used to obtain cross plots. Figures 3 and 4 show some of the plots against  $SiO_2$  and  $Al_2O_3$  respectively. Major oxides,  $CaO$ ,  $FeO$ ,  $Fe_2O_3$ ,  $MgO$  and  $TiO_2$  correlate negatively with  $SiO_2$  except  $Al_2O_3$  which is positive and which trend upwards with  $R^2=0.007$ . The negatively correlated oxides have downward linear trend suggesting non association with  $SiO_2$ . Figure 3 indicates positive correlations between  $Fe_2O_3$  and  $Al_2O_3$  and between  $TiO_2$  and  $Al_2O_3$  implying their associations with clay. They trend upwards with  $(Fe_2O_3/Al_2O_3)$   $R^2=0.135$  and  $(TiO_2/Al_2O_3)$   $R^2=0.481$ .

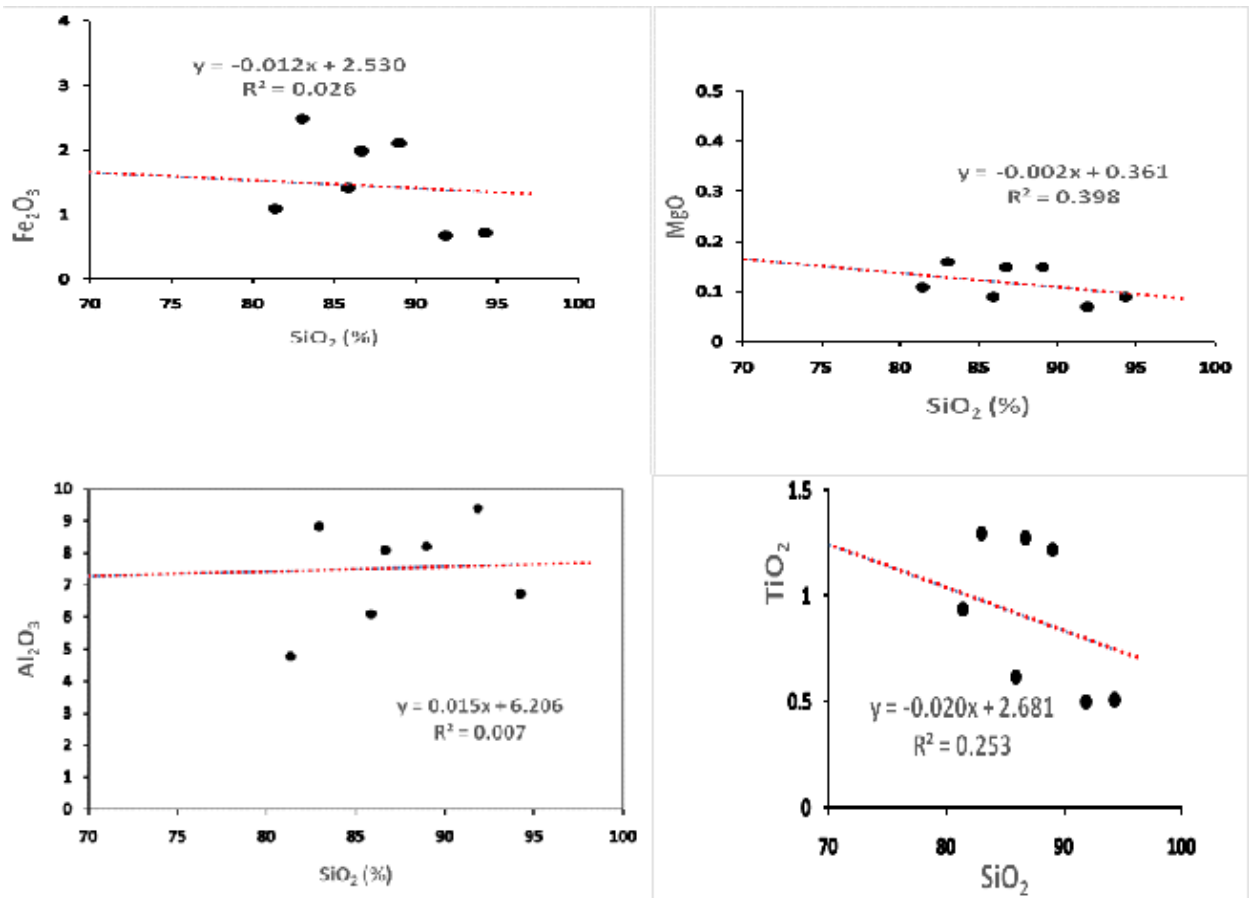
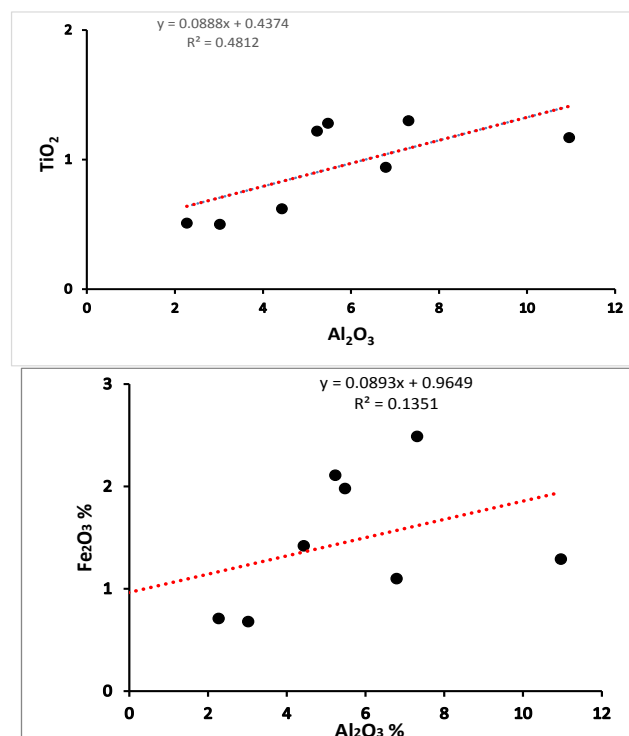


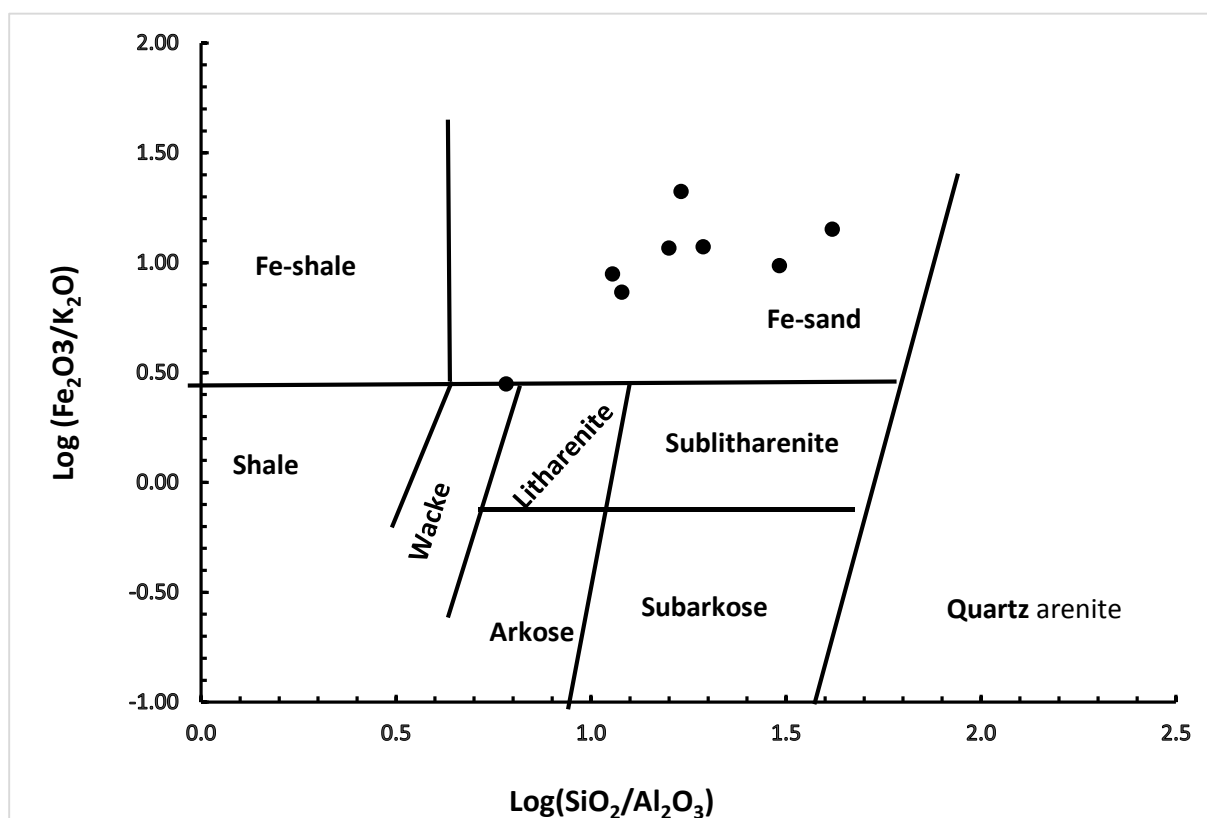
Figure 3. Cross plots of major oxides against SiO<sub>2</sub> showing correlation





**Figure 4. Cross plots of major oxides versus Al<sub>2</sub>O<sub>3</sub> showing correlations.**

Several geochemical classification schemes have been adopted by scholars such as Pettijohn et al, (1972), Blatt et al,(1972), Folk, (1974), Heron, (1988) and Lindsey, (1999). The plot of log ratios of Fe<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O against SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> shows that the Ode Aye tar sand sediments fall within the iron sand (Fe-sand) field (Fig 5).



**Figure 5. Chemical classification of the Ode Aye sediments based on log (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) vs. log (Fe<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O) diagram of Herron (1988).**

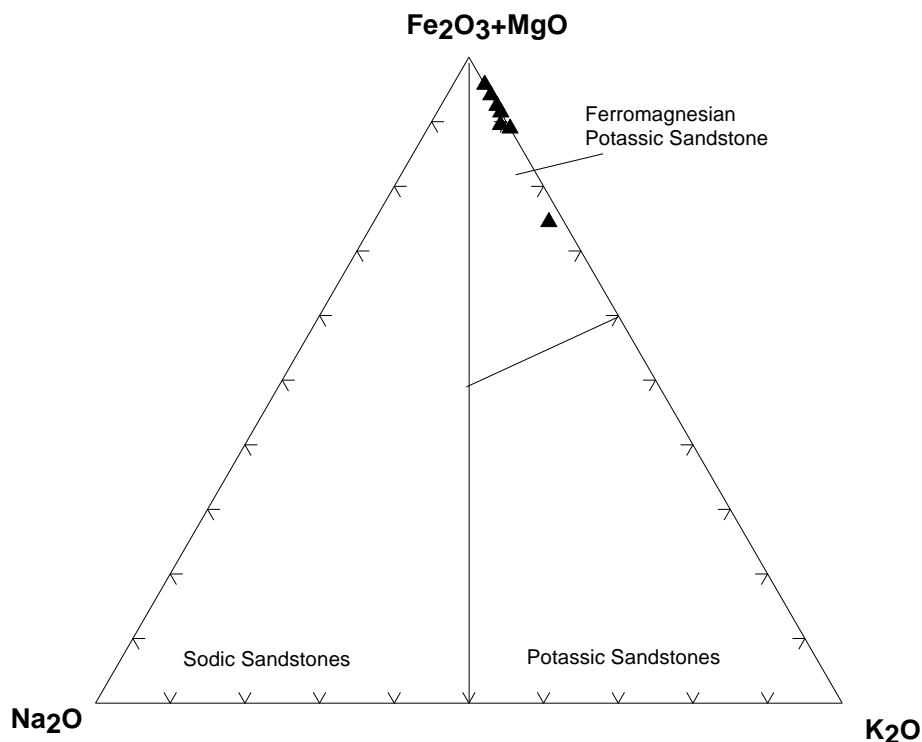
Using the guidelines as proposed by Lindsey, (1999) for chemical classification of sandstone, four reference sets are as shown below ;

- 1) Quartz arenite:  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) \geq 1.5$
- 2) Graywacke:  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) < 1$  and  $\log (\text{K}_2\text{O}/\text{Na}_2\text{O}) < 0$
- 3) Arkose (includes subarkose):  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) < 1.5$  and  $\log (\text{K}_2\text{O}/\text{Na}_2\text{O}) \geq 0$  and  $\log ((\text{Fe}_2\text{O}_3+\text{MgO})/(\text{K}_2\text{O}+\text{Na}_2\text{O})) < 0$
- 4) Lithic arenite (subgraywacke, includes protoquartzite):  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) < 1.5$  and either  $\log (\text{K}_2\text{O}/\text{Na}_2\text{O}) < 0$  or  $\log ((\text{Fe}_2\text{O}_3+\text{MgO})/(\text{K}_2\text{O}+\text{Na}_2\text{O})) > 0$ .

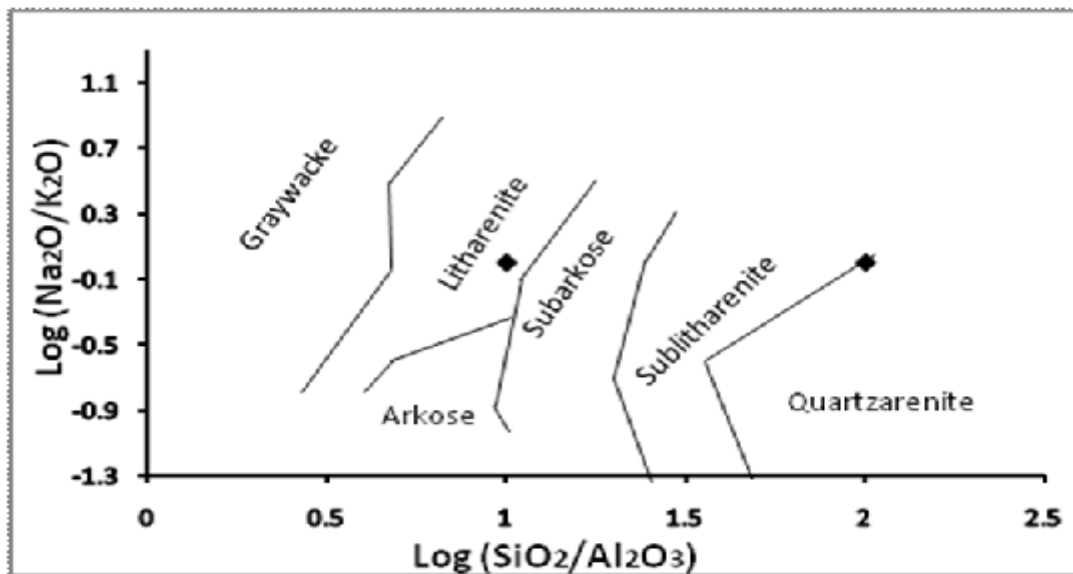
Based on these sets, the value of  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) \geq 1.5$  for the Ode Aye sediment is 1.34 and therefore falls short of quartz arenite. The average value of  $\log (\text{K}_2\text{O}/\text{Na}_2\text{O}) < 0$  for the sampled area is 0.25, therefore condition 2 does not hold since it is higher than zero. In

condition 3 the values obtained for  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) < 1.5$  and  $\log (\text{K}_2\text{O}/\text{Na}_2\text{O}) \geq 0$  are 1.34 and 0.25 respectively while the average  $\log ((\text{Fe}_2\text{O}_3+\text{MgO})/(\text{K}_2\text{O}+\text{Na}_2\text{O})) < 0$  value is 1.25 . Going by this the sediments cannot be classified as arkose. The values obtained match  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3) < 1.5$  and  $\log ((\text{Fe}_2\text{O}_3+\text{MgO})/(\text{K}_2\text{O}+\text{Na}_2\text{O})) > 0$  of condition 4 thus supporting the chemical classification of the sediments as lithic arenites. The calculation for  $\log (\text{Fe}_2\text{O}_3+\text{MgO})/(\text{K}_2\text{O}+\text{Na}_2\text{O}) > 0$  shows also that the value 1.13 is greater than zero and therefore supports the lithic arenite conditions . Lithic arenites usually contain 30-80% quartz and 5-50% lithic fragments. The compositional maturity can vary broadly depending on the nature of the lithic fragments while the textures commonly range from sub -mature to mature. These statements can be corroborated from the immature nature of the sediments as obtained from the proposals of Michael, et al. (1998).

Using the ternary diagram proposed by Blatt et al., (1972), the Ode Aye tar sands plotted mainly in ferromagnesian potassic sandstones field. (Fig 6).The ternary diagram by Blatt et al., (1972) omitted sandstones with less than 5%  $\text{Al}_2\text{O}_3$ , consequently, quartz arenites is missing. Based on the work by Lindsey (1999) using data from Pettijohn (1963; 1975), average lithic arenites plotted in the ferromagnesian Potassic sandstones field, whereas average greywacke would plot in the sodic sandstone field while average arkose would appear in the potassic sandstones field. Figure 7 indicates that the sediments fall on litharenite field and in the boundary of quartz arenite and sublitharenite.



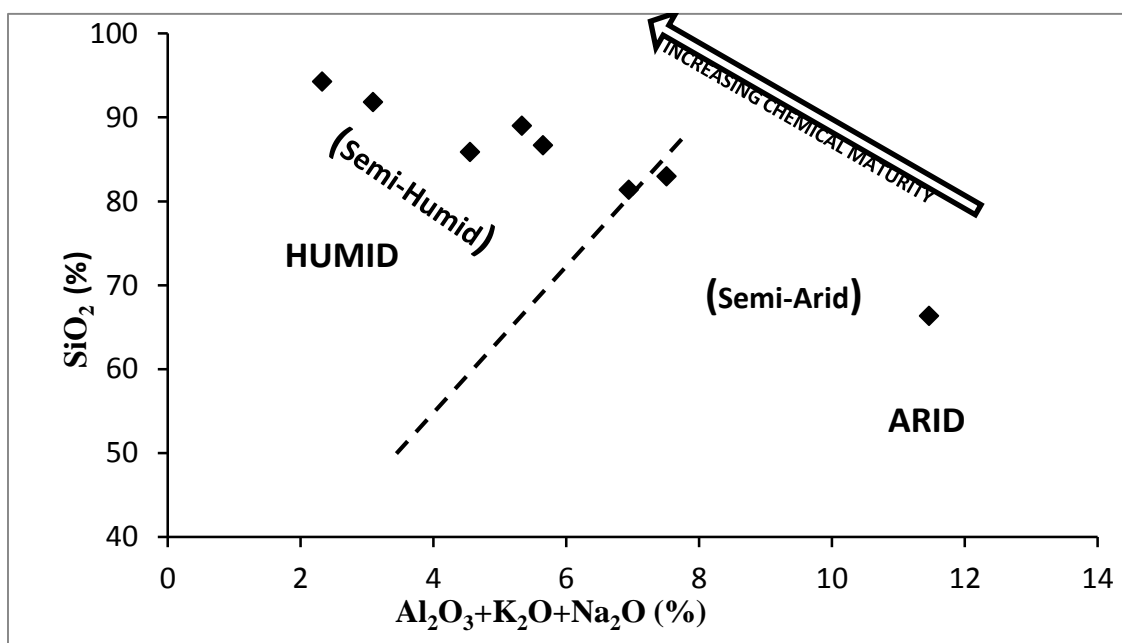
**Figure 6. Ternary diagram of  $\text{Fe}_2\text{O}_3+\text{MgO}-\text{Na}_2\text{O}-\text{K}_2\text{O}$  of Ode Aye tar sand from Blatt et al. (1972).**



**Figure 7.** The plot of  $\log \text{Na}_2\text{O}/\text{K}_2\text{O}$  versus  $\log (\text{SiO}_2/\text{Al}_2\text{O}_3)$ .

Maturity of sediments describes the composition and texture of grains in clastic rocks especially sandstones. Texture is a reflection of the grain sizes, how sorted the sample is while composition reflects how much the composition of rock fragments, clay contents and other are. A mature sediment is more uniform in appearance and exhibits little compositional variation while an immature sediment contains/ more angular grains, diverse grain sizes, and is compositionally diverse (Boggs, 2006). Maturity is reflected best in quartz, rock fragments, feldspars and grain size.

The values of the  $\log (\text{K}_2\text{O}/\text{Na}_2\text{O})$  ratio shows a range of between 0.97 and 1.06 with a mean value of 0.25. This indicates that the tar sands are immature. It implies also that potassium is absent in the sediments. Figure 8 shows that majority of the sands tend towards increasing chemical maturity because they formed under Semi- humid/humid conditions.



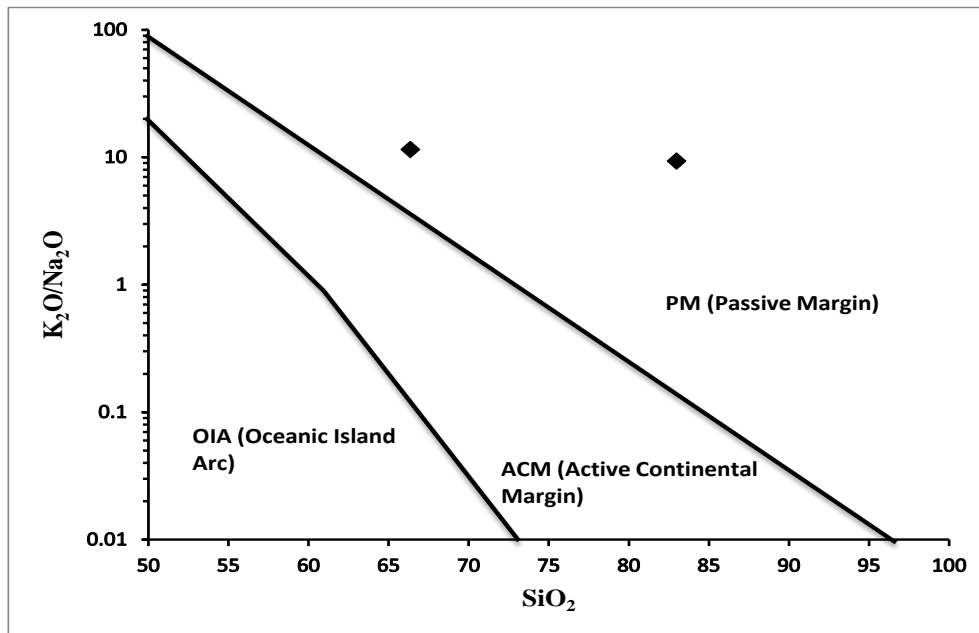


**Figure 8. Chemical maturity of the Ode Aye tar sand components expressed by bivariate plot of SiO<sub>2</sub> Vs Al<sub>2</sub>O<sub>3</sub> +K<sub>2</sub>O+Na<sub>2</sub>O (After Suttner and Dutta, 1986)**

The chemical composition of any rock be it sedimentary depends majorly on the composition and weathering conditions of the source rock areas, (Nesbitt and Young (1989) and Nesbitt et al. 1996). Nesbitt and Young (1982) evaluated the degree of chemical weathering/alteration by using the chemical index of alteration (CIA), where  $CIA = \text{molar } (Al_2O_3/[Al_2O_3+CaO+Na_2O+K_2O])$ . This index expresses well when Ca, Na, and K are decreasing while the intensity of weathering is increasing (Duzgoren-Aydin et al. 2002). Another index is the Chemical index of weathering (CIW) proposed by Harnois, (1988). CIA and CIW have similar formulae except that K<sub>2</sub>O is not in the equation for CIW.  $CIW = \text{molar } (Al_2O_3/(Al_2O_3+ CaO + Na_2O))$ . Their interpretations are equally similar with values of 50 for unweathered upper continental crust and roughly 100 for highly weathered materials with complete removal of alkali and alkaline-earth (McLennan et al. 1983; McLennan, 1993;

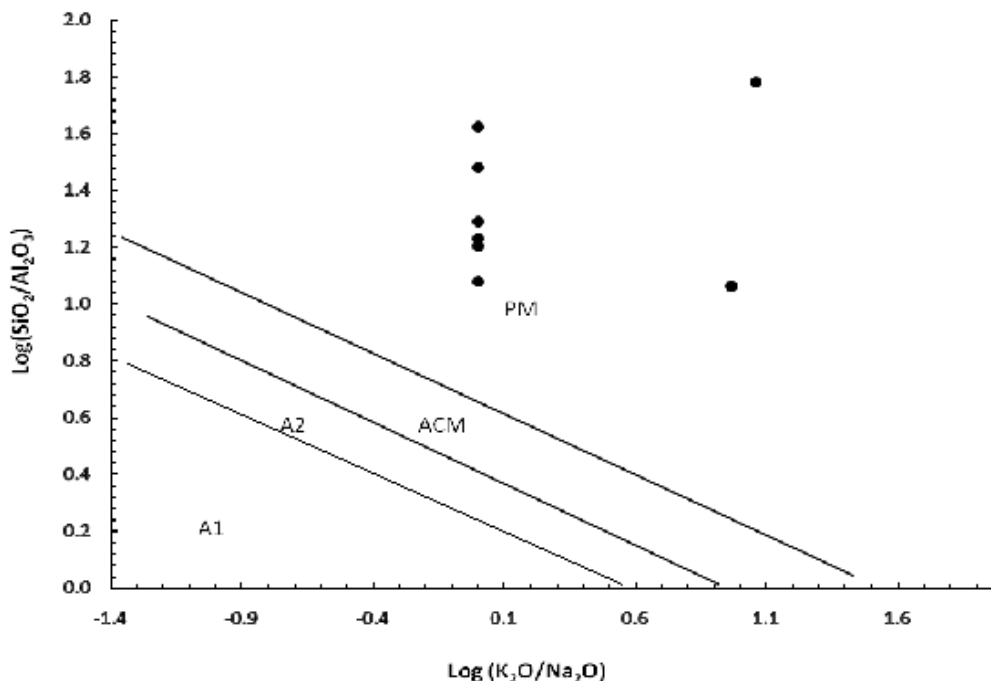
Mongelli et al. 1996). This implies that when CIA has Low values as much as 50% or less, it reflects cool and / or arid conditions (Fedo et al. 1995), and when the value is more than 50 it grades from moderate to high degree of weathering of the source rock areas. The CIA ranges between 95 and 97% (Av.96 %), while CIW ranges from 98.8 to 99.6 % with an average of 99. % an indication of a very high degree of weathering of the source materials. The plagioclase Index of Alteration (PIA) can be used to measure the intensity of the chemical weathering using the molecular proportion:  $PIA = [(Al_2O_3-K_2O)/(Al_2O_3 +CaO -Na_2O)] \times 100$  where CaO\* is the CaO residing only in the silicate fraction.( Fedo et al.1995). Unweathered plagioclase has the PIA value of 50 while Phanerozoic shales have PIA value of 79. The PIA values in the tar sands range between 98.7% and 99.6% suggesting a high degree of weathering. The Mineralogical Index of Alteration (MIA) has also been used as a parameter to indicate the extent of weathering in a rock (Voicu et al.1997). The MIA is calculated as  $MIA = (MIA-50) \times 2$ . When the values of MIA lie between 0 and 20%, it is designated as incipient meaning just started; between 20 and 40% it means weak weathering ; 40-60% (moderate) and between 60 and 100% extreme degree of weathering. Extreme value of 100% indicates complete weathering of the primary rock material into its equivalent weathered product (Voicu and Bardoux, 2002). MIA values for the Ode Aye tar sands range from 90 to 95% an expression of the very high intensity of the weathering in agreement with the CIA, CIW and PIA respectively. It should be noted that Na, K and Ca are highly mobile elements and their depletion in the rocks implies heavy leaching due to an enhanced chemical weathering. In the present study, the ranges of Na<sub>2</sub>O (00-0.04), K<sub>2</sub>O (0.07 -0.46) and CaO (0.03-0.07) exhibit impoverished contents, thus synchronizing with an increased chemical weathering as confirmed earlier by CIA,CIW,PIA and MIA respectively.

Roser and Korsch (1986) proposed a tectonic discrimination diagram using K<sub>2</sub>O/Na<sub>2</sub>O ratio versus SiO<sub>2</sub> (Fig. 9) to determine the tectonic setting of clastic rocks. The cross plot is used to discriminate between sediments deposited in the Passive Continental Margin, Active Continental Margin and the Oceanic Island Arc. The studied samples plotted in the Passive Continental Margin (PM) tectonic settings.



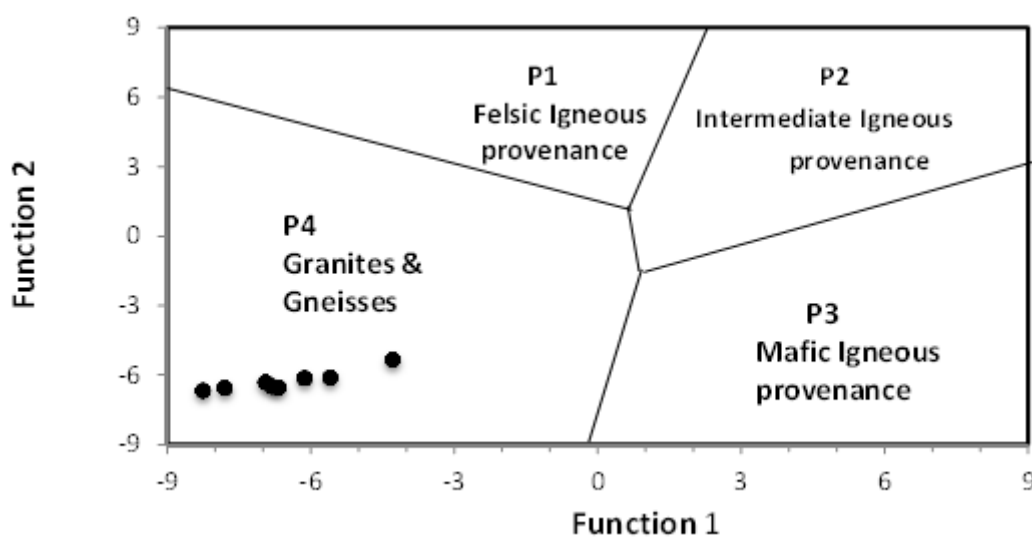
**Figure 9. Tectonic discrimination plot for the tar sand (After Roser and Korsch, 1986).**

The plot of  $\log \text{SiO}_2/\text{Al}_2\text{O}_3$  against  $\log \text{K}_2\text{O}/\text{Na}_2\text{O}$  in Fig 10 supports that the sediments in the studied area were deposited in the Passive deposited in the continental margin (PM). Passive margins are areas of economic importance as they form reservoirs of petroleum. Mann, et al. (2001) classified 592 giant oil fields into six basins and tectonic-setting categories, and noted that continental passive margins account for 31% of giant oil fields. Continental rifts which are likely to evolve into passive margins with time contain another 30% of the world's giant oil fields. Basins associated with collision zones and subduction zone are where most of the remaining giant oil fields are found. Passive margins are petroleum storehouses because these are associated with favourable conditions for accumulation and maturation of organic matter.



**Figure 10. Plot of  $\text{Log}(\text{SiO}_2/\text{Al}_2\text{O}_3)$  versus  $\text{Log}(\text{K}_2\text{O}/\text{Na}_2\text{O})$  (after Maynard et al.1982).  
A1=arc setting and andesitic detritus; A2= evolved arc setting; felsic pluton detritus;  
ACM= Active continental margin; Pm= Passive margin.**

Authors such as Blatt et al., (1980); Bhatia, (1983); Bhatia and Crook (1986); Roser and Korsch, (1986, 1988), have related sandstone geochemistry to specific tectonic environment. Roser and Korsch (1988) used the discriminant function plot of (Fig. 11) to define four (4) main provenances: mafic igneous provenance; intermediate igneous provenance; felsic igneous provenance; and granite gneiss provenance. The Ode Aye tar sand sediments plot converged in the granite gneisses provenance field suggesting that the granite gneiss might have been the source area that provided the sediments that were deposited in the passive margin. Granite gneiss forms part of the basement complex in line with the rocks of the studied area.



**Figure 11. Discriminant function plot with major elements for provenance signatures.  
(After Roser and Korsch, 1988)**

Figures 12 and 13 confirm that the tar sands of Ode Aye are continental sands since the sediments plotted in the non-marine & deltaic sandstone fields of the binary diagram of Ratcliffe et al. (2007).

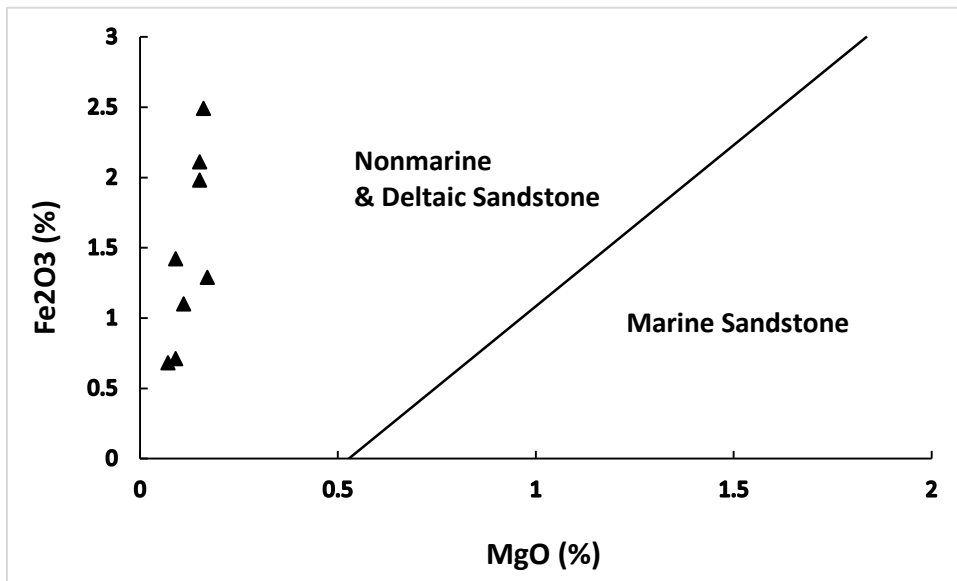


Figure 12. Binary diagrams showing characterization and differentiation of marine from non-marine tar sand (after Ratcliffe et al. 2007).

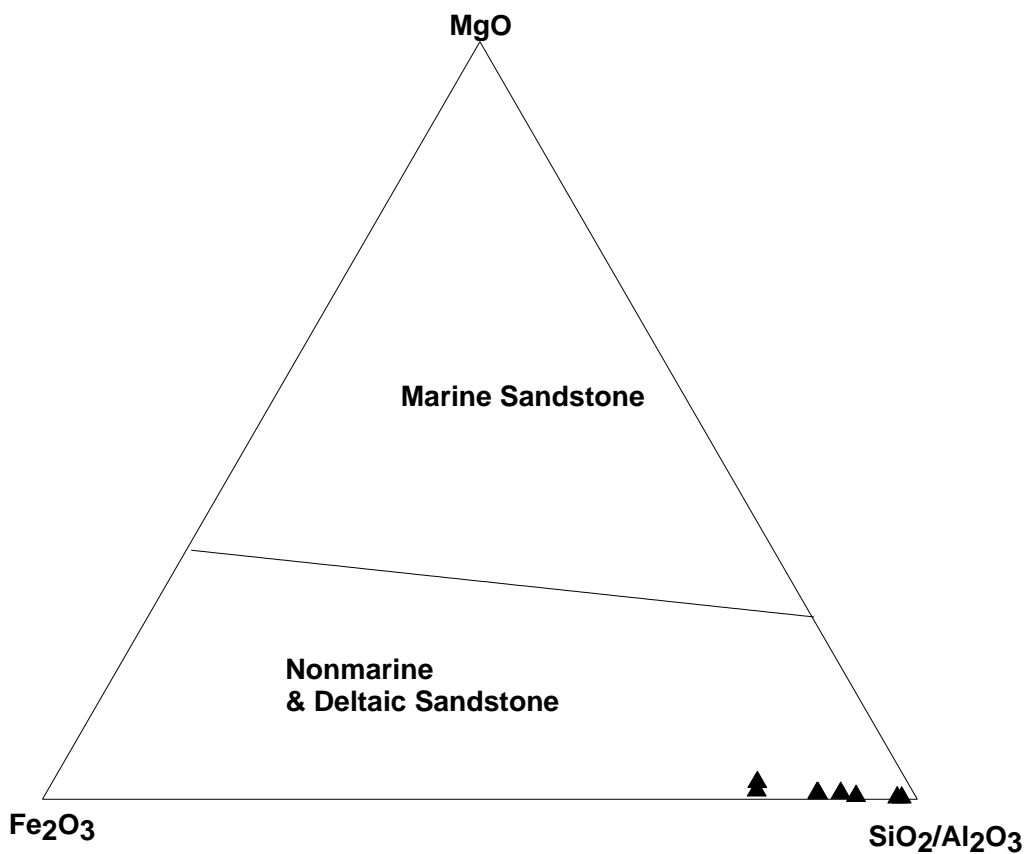


Figure 13. Ternary diagram showing characterization and differentiation of marine from non-marine tar sand (after Ratcliffe et al. 2007).

## CONCLUSION

The provenance, tectonic setting and maturity status of Ode Aye bitumen- rich sand were studied using the result of major oxides. The result indicates that the silica content ranges from 66.36 to 94.29 wt % showing its dominance.

Various plots of SiO<sub>2</sub> show negative correlation with Fe<sub>2</sub>O<sub>3</sub>, MgO and TiO<sub>2</sub> and positive correlation with Al<sub>2</sub>O<sub>3</sub>, an indication of its association and abundance with clay materials. The classification of Pettijohn et al. 1972, Blatt et al. 1975 and Heron, 1988 used for plotting show that the sediments plotted in the Fe- sand field.

However, the use of Lindsey, 1999 chemical classification guidelines classified the tar sand sediments as lithic arenites which in maturity rating is immature and tend towards increasing chemical maturity having formed under semi-humid and humid conditions. Sediments of the tar sand were deposited in the passive continental margin which are places known around the world as areas that house economic reservoirs of petroleum.

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