Geochemical Provenance Study And Classification Of The Agbabu Soil, Ondo State, South Western Nigeria.

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***Abstract*—The geochemistry of the major elements, the provenance, tectonic setting , source area weathering, and the maturity status of the Agbabu bitumen rich area were studied. X-Ray fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) techniques were used to determine the geochemical composition of the bitumen-rich soil.SiO2 is enriched (68.23- 88.74) wt % followed by Al2O3 (3.86- 16.07) wt %, with low contents of Fe2O3 (1.12-3.76), K2O (0.37-1.61), and a strongly depleted TiO2 (0.88-1.53) . Low concentration of Fe2O3 and TiO2 is a reflection of low occurrence of Ti-bearing minerals in the soil. Other oxides such as P2O5, Na2O, MgO, MnO and CaO have low concentrations that are less than unity (1). The low contents of these oxides may be attributed to chemical destruction under oxidizing condition during weathering. The ratio of SiO2/Al2O3 (4.25 - 22.64) wt % shows high silica to alumina content but the ratio of Al_2O_3/ SiO_2 is extremely low (0.04-0.25) thus supporting quartz enrichment in the study area. The mineralogical index of alteration (MIA) ranging from -17.9 to 91.1%, indicate that the source area has intensively weathered ,thus supporting the results of the chemical index of alteration,(CIA), chemical index of weathering,(CIW) and plagioclase index of alteration, (PIA). It is possible that these aluminium silicates are parts of the source area that have undergone an intensive chemical weathering. The provenance study shows that the source area contains quartzose sedimentary rocks whose sediments were deposited in the passive continental margin (PCM) and derieved from quartz arenite,sublitharenite and arkose classes. The deposits are repository of organic matter most favourably for the generation of bitumen.**

Keywords—Geochemistry, provenance, quartzose, organic matter, bitumen

1 INTRODUCTION.

Agbabu as a community in Ondo State has been severally studied by authors such as [1,2,3] due to a large deposit of bitumen that occurs in the area. However, there are two distinct geologic regions in Ondo State, the sedimentary rocks in the south, and the Basement rocks in the north. The sedimentary rocks are mainly of the Post Cretaceous sediments and Cretaceous Abeokuta Formation. while the basement rocks are mainly of the medium gneisses. The study area belongs to the Ise Formation of the Cretaceous Abeokuta Group, the oldest group of sediment uncomformably overlying the basement [4]. The Akinbo shale is underlain by the Cretaceous sediments of the Abeokuta Group [2]. The composition of sediments is affected by several factors, such as hydraulic sizing, tectonic environment, diagenesis, weathering and transportation processes [5,6,7] .The composition equally depends on the primary chemical composition of the source rock area and the tectonic setting of the depositional basins [8,9]. 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 the sandstones has been used as sensitive indicator for provenance and weathering conditions as well as the source of sediments[10,11,12] The geochemical composition of sediments becomes an important tool in the study of provenance [13]. The Agbabu bitumen impregnated sand has been studied in the area of its environmental impact in the area of contamination and level of pollution ,but scantly or no literature exists on the study of its provenance , tectonic setting, classification, maturity, as well as its source area weathering conditions , hence this study.

2 Methods and Materials.

i Sample Preparation and geochemical analysis

Soil sediment samples were air dried at room temperature and sieved using a 75µm stainless steel mesh wire in preparation for a geochemical analysis. X-ray fluorescence (XRF) analysis was carried out on ten (10) selected samples for their major oxide composition [14] in the laboratory of Stellenbosch University, South Africa. The analysis provided data on major oxides that are used for this work. Other methods employed to analyze the data in order to determine the provenance, tectonic setting , area source weathering and classification include, chemical index alteration (CIA)= $(Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O))\times100$, Chemical index of weathering (CIW)

CIW = $(Al_2O_3/ (Al_2O_3+CaO+Na_2O)) \times100$,and Plagioclase Index of Alteration , PIA = $[(Al_2O_3-K_2O)/ (Al_2O_3+CaO + (Na_2O-K_2O)] \times100$

3 Result and Discussion

i Geochemistry of the Agbabu Soil.

The results of major element composition in Table1shows an enriched SiO_2 (68.23 - 88.74) wt %, and Al_2O_3 (3.86- 16.07) wt %, with low contents of Fe_2O_3 (1.12-3.76), K_2O (0.37-1.61), and a strongly depleted TiO_2 (0.88-1.53) and MnO (0.02-0.03). Low concentration of Fe_2O_3 and TiO_2 is a reflection of low occurrence of Ti-bearing minerals such as biotite, ilmenite, titanate ahend titanferous magnete in the soil. Other oxides such as P_2O_5, Na_2O, MgO, MnO and\ CaO have low concentrations that are less than unity (1). The low contents of these oxides may be attributed to chemical destruction under oxidizing condition during weathering. The ratio of SiO_2/Al_2O_3 (4.25 - 22.64) wt % shows high silica to alumina content but the ratio of Al_2O_3/ SiO_2 is extremely low (0.04-0.25) thus confirming the quartz enrichment in the study area. K_2O/ Al_2O ratio is low (0.02-0.21) wt %, an indication of low K-bearing mineral contents in relation to alumina, while the ratio of Al_2O_3/TiO_2 (3.65 - 11.16) wt % suggests a slightly high alumina relative to titanium oxide.

Table 1. Major oxides composition of Agbabu bitumen -rich soil (Wt. %)

OXIDES	SAMPLES									
	1	2	3	4	5	6	7	8	9	10
SiO_2	84.78	88.44	86.39	79.05	81.72	81.25	88.74	73.08	68.23	88.29
Al_2O_3	5.90	3.86	4.91	9.87	8.68	7.17	3.92	12.51	16.07	4.37
K_2O	0.49	0.70	1.02	0.37	1.45	1.51	1.22	0.20	1.61	0.70
Na_2O	0.06	0.01	0.05	0.00	0.07	0.07	0.05	0.02	0.06	0.01
Fe_2O_3	2.02	1.12	1.19	2.88	2.39	2.36	1.01	4.60	3.76	1.17
MgO	0.09	0.09	0.09	0.09	0.10	0.11	0.08	0.12	0.15	0.08
P_2O_5	0.07	0.05	0.06	0.09	0.06	0.08	0.04	0.13	0.09	0.05
CaO	0.20	0.09	0.15	0.09	0.06	0.10	0.12	0.13	0.07	0.06
TiO_2	0.96	1.04	1.28	1.31	0.88	1.24	1.14	1.53	1.44	1.06
Cr_2O_3	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00
L.O.I (%)	5.06	3.90	4.91	6.17	4.43	5.62	3.01	7.59	8.22	3.42
Mno	0.03	0.03	0.03	0.02	0.02	0.05	0.03	0.03	0.02	0.02
SUM OF Conc.(%)	99.66	99.33	99.37	99.95	99.86	99.57	99.36	99.95	99.72	99.23
% CIW	95.78	97.47	96.09	99.10	98.52	97.68	95.84	98.82	99.20	98.42
% CIA	88.72	77.51	80.10	95.55	84.60	41.05	73.68	97.28	89.89	85.02
%PIA	95.41	96.93	95.11	99.06	98.23	97.08	94.08	98.80	99.11	98.13

CIA: Chemical Index of Alteration = $(Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O))\times100$

CIW: Chemical Index of Weathering = $(Al_2O_3/ (Al_2O_3+CaO+Na_2O)) \times100$

PIA: Plagioclase Index of Alteration = $[(Al_2O_3-K_2O)/ (Al_2O_3+CaO + (Na_2O-K_2O)] \times100$

ii Variation diagrams

Variation diagrams have been geologically used to condense and simplify geochemical data in order to identify the relationships between the individual rocks or elements in a rock terrain. The following plots presented in Fig 1 show the relationships between various major elements and silica (SiO_2). Silica (SiO_2) has strong negative correlation with TiO_2 ,(y = - 0.021), Al_2O_3 (y = - 0.585), MgO (y= - 0.002), K_2O (y = - 0.008) and Fe_2O_3 (y = - 0.165) implying that SiO_2 is present as quartz grains.

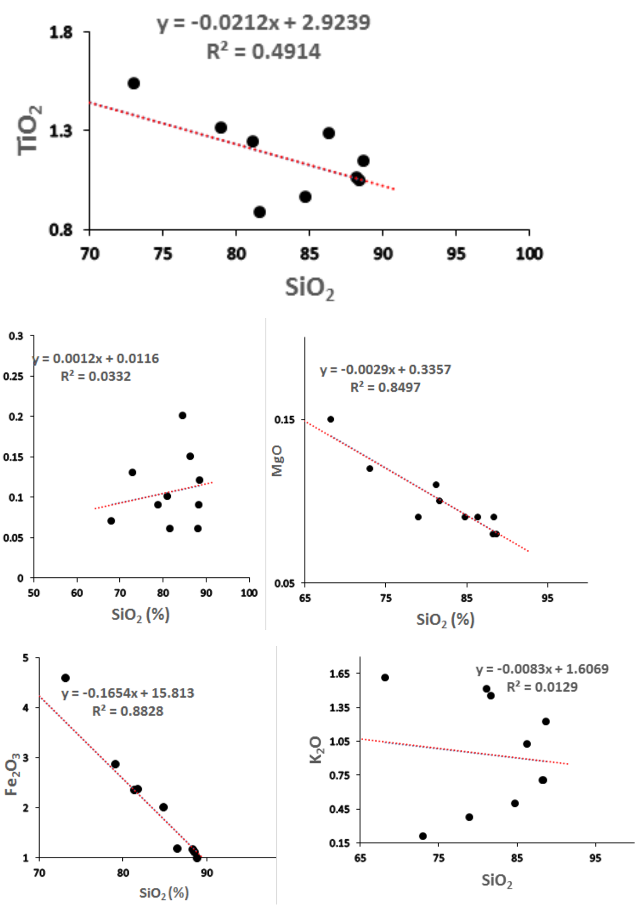

Fig.1 Plots of major elements vs SiO_2

The increasing trend of quartz (SiO_2) and decreasing oxides of iron, magnesium, potassium, aluminium, and titanium in Fig 1 indicating a strong negative geochemical coherence between them and quartz suggest an underlying processes, but the positive correlation with calcium, means there is a mixing of chemical components that contributed to the composition of the soil being studied.

iii Geochemical Classification

Several geochemical classification schemes have been adopted by scholars such as [15,16,17,18,19] . The plot of log ratios of Fe_2O_3/K_2O against SiO_2/Al_2O_3 shows that the Agbabu soil samples fall within the quartz arenite and a few on the litharenite and subarkose fields Fig. 2

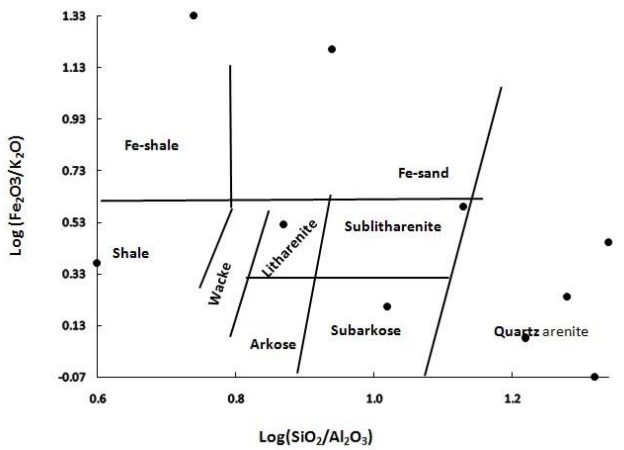

Fig. 2: Chemical classification of the Agbabu soil samples based on log (SiO2/Al2O3) *vs.* log (Fe2O3/K2O) [18].

There are four conditions that govern the geochemical classification of sandstone into quartz arenite, graywacke, arkose and lithic arenite [19]. The ratio of log (SiO_2/Al_2O_3) ranges between 0.63 and 1.37 while log (K_2O/Na_2O) varies from -0.07 to 1.33 hence satisfying the groupings into quartz arenite and arkose groups.

SiO_2 content and SiO_2/Al_2O_3 log ratio are commonly used as geochemical criteria for mineralogical maturity [20] , reflecting the quantity or abundance of quartz, clay and feldspar contents in a soil. Fe_2O_3/K_2O ratio makes provision for arkoses to be classified as well as show mineralogical stability since ferromagnesian minerals tend to be less stable during weathering.

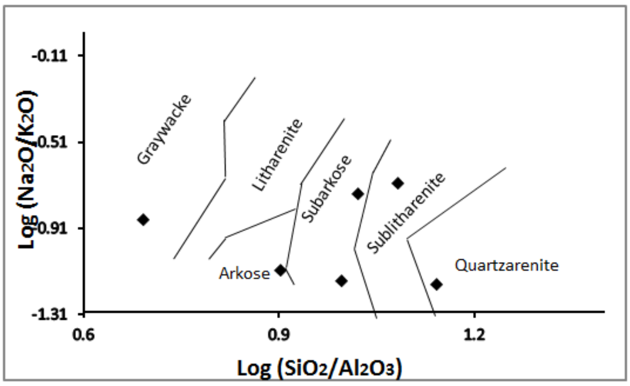

Fig 3: Chemical classification of Agbabu sandstones based on [15] .

The log plot of Na_2O/K_2O versus SiO_2/Al_2O_3 in Fig 3 shows that some samples fall on quartz arenites and arkose groups. This chemical classification suggests a collaboration of chemically mixed components in the Agbabu soil.

Using the compositional fields for the same classification as proposed by [19] Agbabu sandstones plotted majorly in the quartz arenite. (Fig 4).

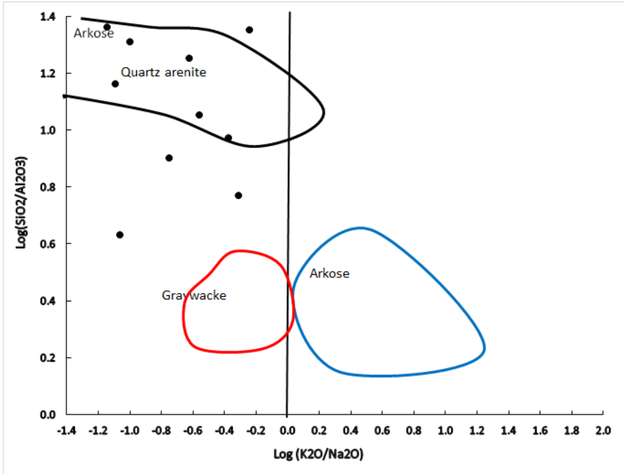

Fig 4: Compositional fields for major classes of sandstones ; ($\log(SiO_2/Al_2O_3)$versus(K_2O/Na_2O). [19] .

iv. Maturity

Maturity can be reflected in finer grain sizes; however it is actually clay content that is more directly related to lack of maturity. Maturity is reflected best in quartz, rock fragments, feldspars and grain size. As the percentage of quartz increases the mineralogical maturity also increases.[21].Log (K_2O/Na_2O) ratio has been used in determining the maturity of the Agbabu soil samples. [21] suggest that;

when the ratio of log (K_2O/Na_2O) is less than (<) 0, it indicates maturity and presence of potassium,when the ratio of log (K_2O/Na_2O) is greater than (>) 0, it indicates immaturity and when the ratio of log (K_2O/Na_2O) is 0, it indicates there is absence of potassium in the sediment.

The log ratio of (K_2O/Na_2O) ranges between 0.00 and 1.85 indicating that the ratio is greater than zero, thus satisfying the condition that when the ratio of log (K_2O/Na_2O) is greater than (>) 0, the soil is regarded as immature . However, Fig 5 indicates that majority of the soil samples tend towards increasing chemical maturity because they formed under semi-humid/semi arid conditions. Semi-humid environment is an environment that has undergone moderate chemical weathering and semi-arid is also an environment of moderate physical weathering. This indicates that the soil samples have undergone moderate chemical and physical weathering.

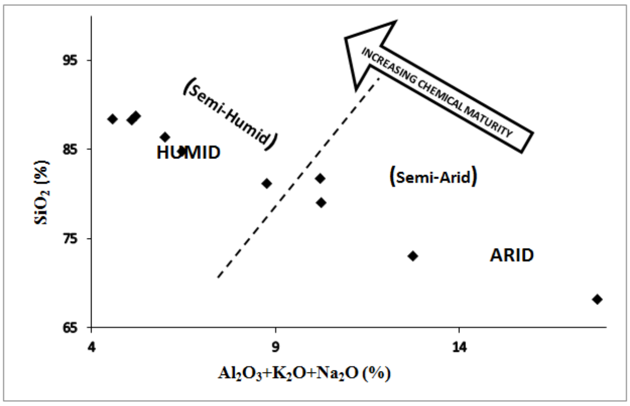

Fig 5. Chemical maturity of the Agbabu soil components expressed by bivariate plot of SiO_2 Vs Al_2O_3 + K_2O+Na_2O [22] .

V. Source Area Weathering

The properties of the parent rocks be it mineralogical, chemical, structural as well as other factors like climate affect the susceptibility of such rocks to weathering. [23] documented some factors controlling the chemical composition of siliciclastic sedimentary rocks that affect the degree of weathering of the source area and their tectonic setting. [24,25] suggested that the chemical composition largely depends on the composition and the weathering conditions at the source rock area. [26] demonstrated a measure of the degree of chemical weathering/alteration of the sediments source rocks by calculating the chemical index of alteration (CIA), where CIA=molar(Al_2O_3/[Al_2O_3+CaO+Na_2O+K_2O]). [27] proposed the chemical index of weathering (CIW) similar to the CIA except that K_2O is not in the equation stated as, CIW = molar (Al_2O_3/(Al_2O_3+ CaO + Na_2O)). The CIA and CIW are interpreted in similar ways with values of 50 for unweathered upper continental crust and roughly 100 for highly weathered materials, with complete removal of alkali and alkaline-earth elements [28,29,30]. Low CIA values (i.e. 50 or less) also might reflect cool and / or arid conditions [31] .

The CIA (41.05 -97.28%) ,Av= 81.34 %, and CIW (95.00 - 99.20%), Av = 97.70%) contents for the Agbabu soil samples yielded almost the same values indicating a high degree of weathering of the source materials.The results of the major elements geochemistry of the study area showed high values of SiO_2 above 80%, and relatively low quantity of K_2O (K-feldspar) and Na_2O (Na-feldspars) suggesting that the source rocks may have been exposed to weathering. A plot of the CIA against Al_2O_3 shows a minor to high intensity of weathering in the area (Fig 6).

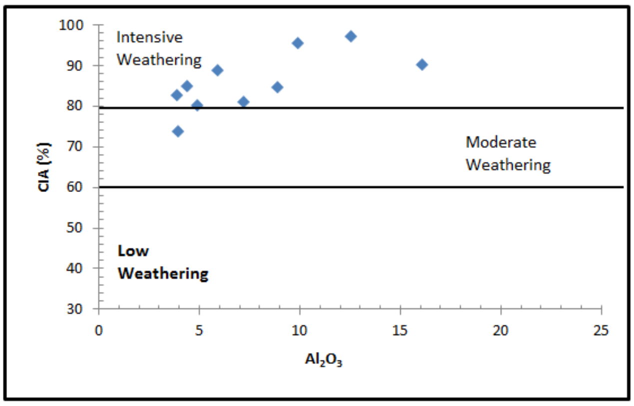

Fig 6: Plot of CIA(%) against Al_2O_3 [26]

The intensity of the chemical weathering can also be estimated using the Plagioclase Index of Alteration (PIA) in molecular proportions: PIA = [(Al_2O-K_2O)/(Al_2O_3 + CaO^* + Na_2O-K_2O)] × 100 where CaO^* is the CaO residing only in the silicate fraction [31] In this study, the PIA values range from 94.08 to 99.11%, indicating high degree of weathering. The sediments being generated as a result of the weathering of probably the quartzose sedimentary terrain and transported by water may have been deposited in the continental passive margin. which now domiciled the bitumen.[32] also proposed the Mineralogical Index of Alteration (MIA) as a weathering parameter calculated as: MIA = 2*(CIA-50). [33] to further find the various degrees of MIA showed that when MIA values varies between 0 and 20% ,weathering is said to be starting, if it is between 20-40% (weak); 40-60% (moderate) and from 60 to 100%, it is regarded that intense to extreme degree of weathering has occured. The extreme value of 100% indicates complete weathering of a primary material. The MIA values obtained from the study area range between -17.9 and 91.1%, indicating that the source material has been subjected to weathering up to intensive level,thus confirming the earlier results of the CIA, CIW and PIA. A ternary diagram of A-CN-K (Fig 7) was used to determine the types of minerals that were involved in the weathering process. Plottings on the ternary diagram showed the weathering trend that was parallel to the A-CN line. All the plots concentrated in a line directed towards the apex where clay minerals, kaolinites and illites were dominant (Fig 7). It is suggested that these aluminum silicates may have being parts of the source rocks that were susceptible to an intensive chemical weathering.

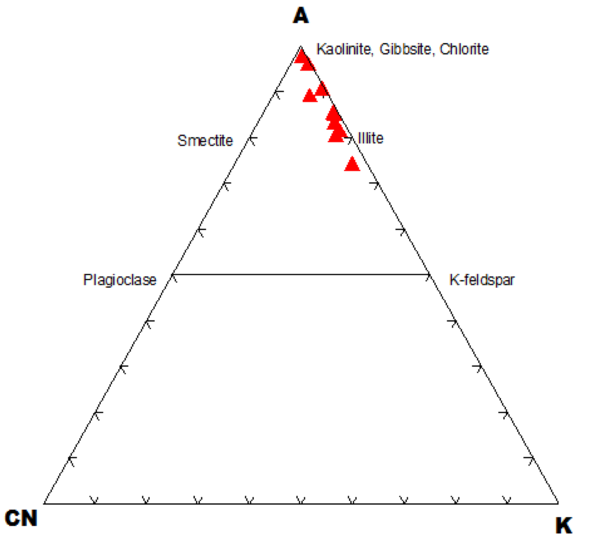

Fig 7: Ternary diagram showing the weathering trend of soil

(Al_2O_3-Cao+Na_2O-K_2O) (A- CN-K) (from Gu et al., (2002)

VI. Provenance and Tectonic Settings

[10] proposed three tectonic settings, the passive continental margin, active continental margin and the oceanic island arc that can be plotted on discrimination diagram using K_2O/Na_2O versus SiO_2. The studied samples plotted in the Passive Continental Margin (PCM) tectonic settings.(Fig 8). Plots on the ternary diagram (Fig 9) also aligns themselves on the passive continental margin . Further plots of log (SiO_2/Al_2O_3) versus log (K_2O/Na_2O) also indicated a PCM field(Fig 10). These Figures, 8,9 and 10 elucidated and supported the fact that the weathered materials were deposited in the environment full of organic matters that biodegraded to bitumen.

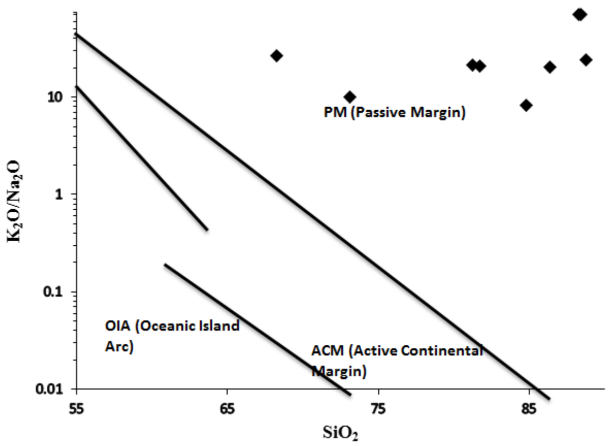

Fig 8: Plot of K_2O/Na_2O versus SiO_2 for Agbabu sandstone[11].

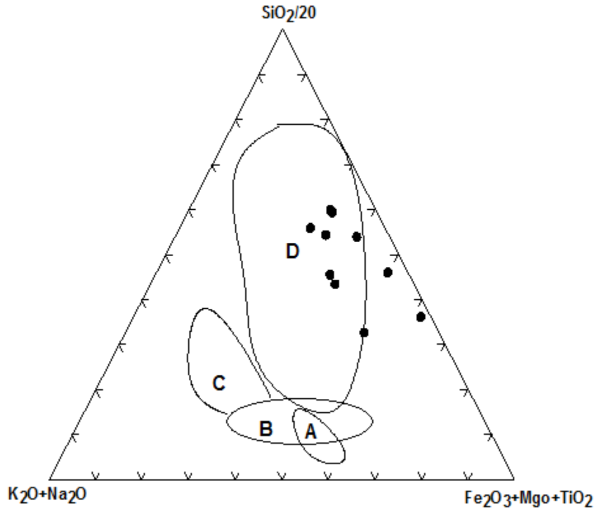

Fig 9: Ternary diagram A= Oceanic Island Arc ,B= Continental Island Arc, C= Active Continental Margin D= Passive Margin

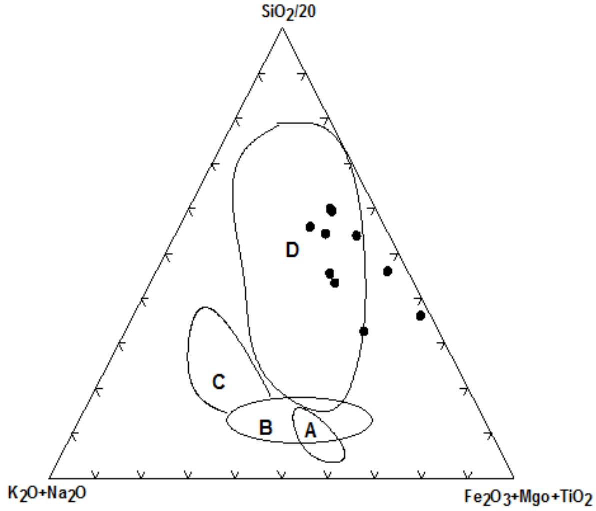

Fig 10: Plot of log (SiO_2/Al_2O_3) versus log (K_2O/Na_2O).

Discriminant plot of functions 1 and 2 as presented in (Fig 11), define four (4) main sedimentary provenances: P1 = felsic igneous provenance; P2 = intermediate igneous provenance; P3 = Quartzose sedimentary provenance; P4 = mafic igneous provenance [11]. The discriminant plot indicates quartzose sedimentary provenance field (Fig 11).

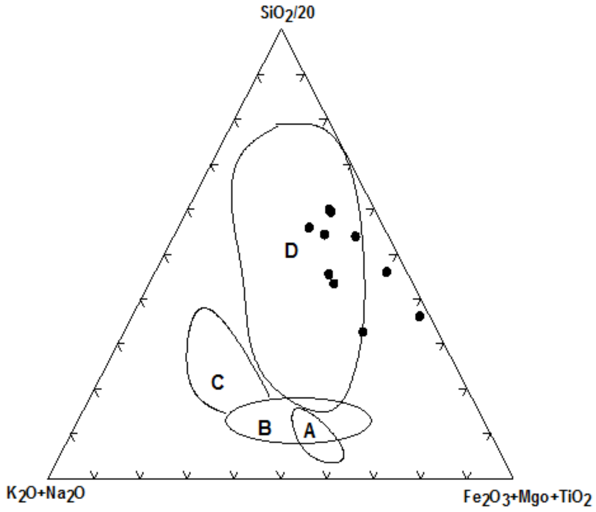

Fig 11: Plot of discriminant functions 1 and 2 for Agbabu sandstones [11] .

4. CONCLUSION

The provenance, tectonic setting, maturity status and source area weathering of Agbabu bitumen- rich soil were studied using the major elements. The results indicate that the SiO_2 content ranges from 68.23 to 88.74 wt % showing its enrichment.

Various plots of SiO_2 show strong negative correlation with Al_2O_3, Fe_2O_3, MgO and TiO_2 and positive correlation with CaO. The classification of [15,18], used for plotting showed that the soil samples plotted in different fields of quartz arenite few sublitharenite and arkose and these revealed mixed sources .The conglomerate of these sources tended towards increasing chemical maturity

having formed under semi-humid and semi-arid conditions. Semi-humid and semi-arid are conditions of moderate chemical weathering and moderate physical weathering respectively. The weathering indices indicated a high degree of weathering of the source materials. The weathered soil materials were deposited in the passive continental margins which are places known around the world as areas that house economic reservoirs of petroleum.

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