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Inorganic Geochemical studies of Sediments penetrated in two Wells, Central Swamp, Niger Delta, Nigeria

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Abstract
The elemental composition of sedimentary rocks has proven to be useful in understanding sediment history and composition. This study is aimed at characterizing sediments penetrated in Wells X1 and X2, central swamp, Niger Delta so as to understand the composition of the sediments. The technique involved the use of atomic absorption and X-Ray fluorescence to acquire values for ten major oxides. The values obtained were plotted on binary and ternary plots and these plots were subsequently used to interpret the geochemical composition of the sediments, their tectonic history and provenance. The results showed that the sediments in both Wells were predominantly Lith arenites formed in a passive continental margin, the sands were non-marine and deltaic while the shales were rich in iron, the sediments were formed from felsic igneous materials.

Keywords: Inorganic Geochemistry, Major Oxides, Provenance, Tectonic Setting

Introduction
Inorganic geochemistry is a branch of earth sciences that deals with the use of chemical fingerprints in rocks to determine its composition and unravel geologic history, the elemental composition of rocks is mainly a reflection of it’s mode and origin and formation (Mallory-Greenough & Greenough 2004). The elemental composition of rocks are usually measured in relation to the major oxides, the minor oxides or the trace elements, most studies use the major oxides to study as geochemical tools for characterizing sediments and rock samples. For this study, the major oxides are used as excellent tools for determining the geochemical characteristics of the sediments.

Literature Review
Madukwe, *et al*., (2014) in their work titled provenance, tectonic setting and maturity of Ishara Sandstone, SouthWestern Nigeria: Insights from major element Geochemistry carried out major element geochemical study of the Ishara sandstone of the Ise Formation of the Dahomey basin, South Western Nigeria, the study was carried out to determine the provenance, tectonic setting and maturity of the sandstones. Based on

geochemical data, the sediments were classified as continental sands that are lithic Arenites, the tenary plot of Na_2O-K_2O-(Fe_2O_3+MgO) enabled the determination of the source rocks to be ferromagnesian potassic sandstones from acidic igneous rock and gneisses. There was negative correlation between silica (SiO_2) and other major oxides, this negative correlation suggest the relative abundance of quartz, it was determined from the bivariate plot of SiO_2 versus Al_2O_3+K_2O, Na_2O that the sandstones were formed in semi humid/humid conditions.

Methodology
Laboratory Procedure
About 100 g of the sample was pulverized with a motorized agate mortar to a fine powder with grains passing the 300-mesh screen (53 µm). Two main analytical techniques were employed for this study. They are the Energy Dispersive X-Ray Fluorescence (EDXRF) and Atomic Absorption Spectrometer (AAS). Loss on Ignition was determined by Gravimetry using Furnace method.

Sample preparation for Atomic Absorption Spectroscopy (AAS) analysis:
5 g of the powdered sample was weighed into a beaker and digested with 30 ml of concentrated hydrochloric acid and 10 ml of nitric acid on the thermostat regulated hot plate inside the fume cabinet. The digested sample was filtered using whatman filter paper into a 100ml plastic bottle and the volume made up to mark with distilled water. The sample solution was analyzed for the minor and trace elements by AAS. The elements standard solutions and their hollow cathode lamps were used for plotting calibration graphs after which the sample solution was aspirated into the Spectrometer. This technique was used to generate data for 10 key major elements.

Presentation of Result
Table 1: Major Oxides distribution for Well X1

Depth	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	SO_2	CaO	MgO	Na_2O	K_2O	MnO
6160	56.38	0.98	14.2	3.51	10.21	0.24	0.03	0.68	0.42	0.001
6280	58.22	2.25	15.44	5.23	0	3.28	0.46	0.77	0.43	0.07
6480	58.98	2.14	15.7	5.38	4.4	1.84	0.37	0.06	0.04	0.04
6800	55.5	2.18	14.2	3.36	6.4	2.44	0.45	0.83	0.37	0.08
7120	42	1.62	13.1	3.92	5.6	10.8	2.65	0.69	0.41	0.16
7280	53.99	1.64	16.06	2.41	2.2	1.68	0.31	0.06	0.02	0.09
7400	59.68	1.7	18.03	2.57	0	2.09	0.25	0.04	0.01	0.11
7480	48.18	1.75	14.04	3.74	4.2	2.85	0.32	0.04	0.03	0.04
7760	47.45	1.91	15.8	3.44	4.8	3.4	0.24	0.04	0.02	0.04
8040	51.18	2.17	15.48	4.79	2.9	0.82	0.47	0.06	0.02	0.04
8180	51.6	1.6	23.41	3.99	0	0.57	0.04	0.51	0.29	0.05
8560	50.22	2.27	14.3	5.84	2.7	0.97	0.48	0.04	0.02	0.03
9400	49.51	2.28	15.73	6.1	6.4	1.43	0.39	0.06	0.03	0.1
9800	49.97	2.15	15.83	4.58	3.1	2.95	0.3	0.05	0.02	0.09
10000	51.98	2.04	15.78	3.57	4.04	1.34	0.36	1.08	0.72	0.05
10200	43.09	1.83	15.7	4.51	6.7	1.3	0.37	0.05	0.03	0.03

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10400	51.87	2.26	15.3	4.39	3.5	0.98	0.46	0.05	0.04	0.09
10440	48.64	2.45	16.07	5.14	4	1.23	0.4	0.04	0.01	0.08
10600	45.9	1.97	15.33	5.4	6.3	1.13	0.33	0.04	0.03	0.001
10,900	47.5	2.49	15.83	5.32	3.04	1.24	0.38	0.05	0.02	0.1
11,160	42.9	2.32	15.81	4.92	5.05	0.87	0.36	0.05	0.03	0.02

Table 2: Major Oxides distribution for Well X2

Depth	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	S	CaO	MgO	Na_2O	K_2O	MnO
5820	44.19	1.99	13.52	4.16	11.8	3.16	0.53	0.82	0.48	0.05
5880	50.1	2.06	15.44	4.94	7.79	3.58	0.3	0.05	0.03	0.02
5910	50.28	2.32	15.34	4.12	5.85	4.38	0.31	0.67	0.43	0.01
6000	53.82	2.47	14.89	4.26	3.69	3.81	0.33	0.95	0.65	0.07
6300	53.36	2.08	15.5	5.69	8.55	3.59	0.32	0.91	0.49	0.07
6510	58.06	1.18	14.76	3.62	5.08	1.34	0.35	0.05	0.02	0.04
6660	52.4	1.83	15.07	3.8	7.54	3.67	0.04	0.66	0.54	0.07
6990	53.75	2.66	15.48	4.7	3.68	1.26	0.4	0.03	0.02	0.09
7440	50.09	2.66	15.47	4.59	7.3	1.4	0.39	0.97	0.53	0.14
7650	53.06	2.69	15.4	3.93	6.1	1.69	0.33	0.81	0.59	0.08
7800	50.68	2.57	15.2	4.34	4.9	2.98	0.36	0.83	0.67	0.12
8010	52.52	1.69	19.04	3.35	5.4	1.03	0.21	0.63	0.36	0.07
8070	51.79	2.24	15.45	3.93	6.67	2.12	0.37	0.94	0.76	0.14
8310	48.11	1.93	14.87	5.52	5.18	7.18	2.37	0.88	0.62	0.1
8670	51.28	1.92	16.3	3.19	7.14	2.36	0.34	0.51	0.38	0.1
9240	53.89	2.23	15.49	4.09	4.29	2.59	0.38	0.94	0.76	0.14
9390	54.76	2.13	18.02	3.29	3.27	1.2	0.31	0.06	0.01	0.12

Geochemical Classification of the sediments

Geochemical composition of sediments are readily classified on the scattergram of $\log(SiO_2/Al_2O_3)$ vs $\log(Na_2O/K_2O)$ (Fig. 1), which quartz arenite represents silica enrichment of $\log(SiO_2/Al_2O_3) \geq 1$ indicating that SiO_2 is at least 30X more abundant than Al_2O_3 while $\log(Na_2O/K_2O)$ varies. In this study, the sediments plotted on the litharenite field (Fig 1). This shows that the sediments are characterized by fairly high $\log(SiO_2/Al2O_3)$ values of ≤ 1.5 indicating a mature sandstone. The ratio Na_2O/K_2O reflects the relative abundance of potassic feldspar and plagioclase but is also affected by the compositions of the feldspars present.

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

1) Quartz arenite: log (SiO2/Al2O3) ≥ 1.5
2) Graywacke: log (SiO2/Al2O3) < 1 and log (K2O/Na2O) < 0
3) Arkose (includes subarkose): log (SiO2/Al2O3) <1.5 and log (K2O/Na2O≥ 0

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and log((Fe2O3+MgO)/(K2O+Na2O)) < 0
4) Lithic arenite (subgraywacke, includes protoquartzite): log (SiO2/Al2O3) < 1.5 and either log (K2O/Na20) < 0 or log ((Fe2O3+MgO)/(K2O+Na2O)) > 0.
Based on these sets, the value of log (SiO2/Al2O3) < 1.5 and Log Na2O/k2O < 0 for sediments of Well X1 and X2 and therefore under the litharenite category.

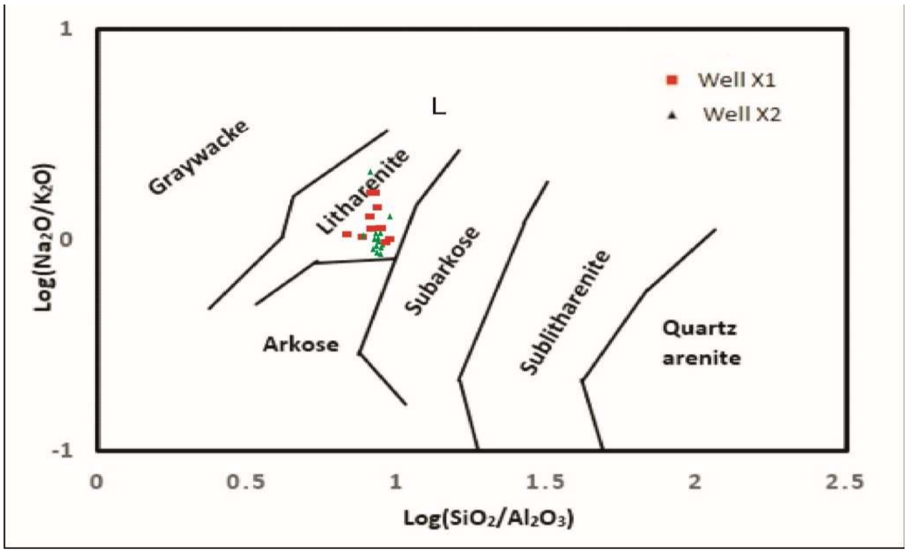

Figure 1: The classification of terrigenous sandstones of the study Wells using log (Na_2O/K_2O) vs log(SiO_2/Al_2O_3) from Pettijohn et al. (1972) with boundaries redrawn by Herron (1988).

The plot of log ratios of Fe_2O_3/K_2O against SiO_2/Al_2O_3 shows that the study area sediments fall within the iron shale field (Fig 2) which clearly distinguished the various classes of sandstone as well as shale and other iron-rich clastic sediments.

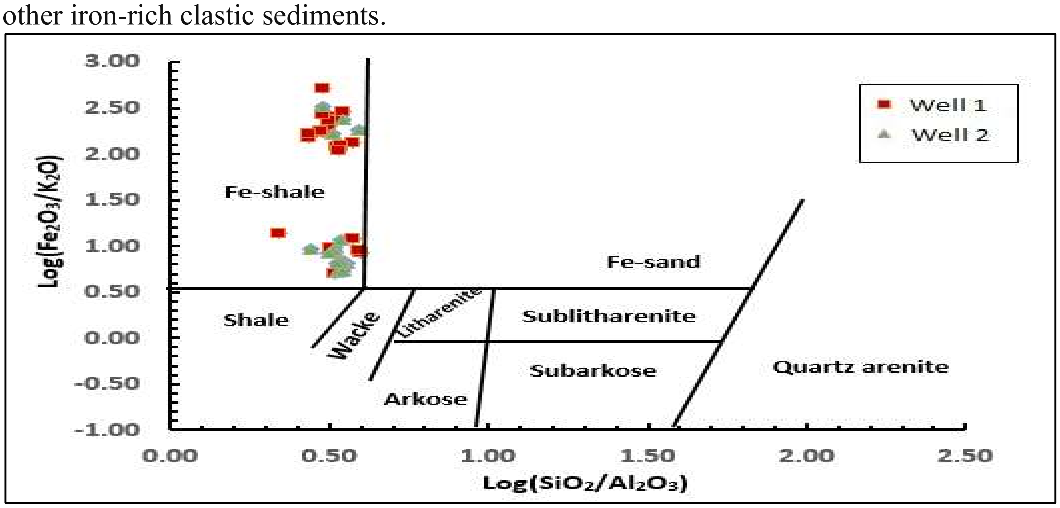

Figure 2. Chemical classification of the sediments based on log (SiO2/Al2O3) vs. log (Fe2O3/K2O) diagram of Herron (1988).

The sediments of the study Wells plotted mainly in ferromagnesian sodic sandstones field (Fig 3). Authors have suggested that the average greywacke are normally plotted in the ferromagnesian Potassic sandstones field, whereas average lithic arenites would plot in the sodic sandstone field while average arkose would appear in the potassic sandstones field.

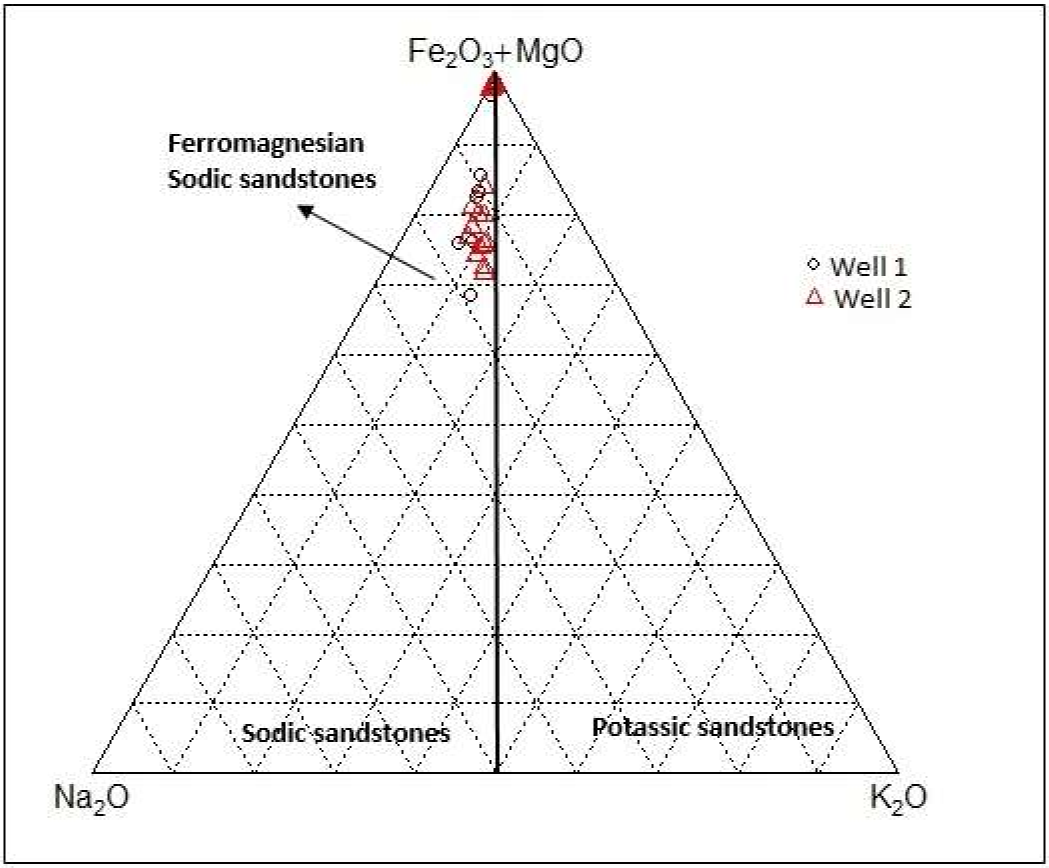

Figure 3. Ternary diagram of Fe_2O_3+MgO-Na_2O-K_2O of sediments in the study area from Blatt et al. 1972

Tectonic settings of the sediments

A knowledge of the tectonic setting of a basin is important for the exploration of petroleum and other resources as well as for paleogeography (Bhatia and Crook, 1983). This is as a result of the fact that processes of plate tectonics input a distinctive geochemical signature to sediments in dual ways. Firstly, tectonic environments have distinctive provenance characteristics and secondly they are characterized by distinctive sedimentary process.

A tectonic discrimination diagram using K_2O/Na_2O ratio versus SiO_2 (Fig. 5) was applied 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 Oceanic Island Arc tectonic settings.

The plot of logSiO_2/Al_2O_3 against logK_2O/ Na_2O in Fig 5 supports that the sediments in the studied area were deposited in the Oceanic Island Arc which was transitioned into the passive 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. Active continental margin which are likely to evolve into passive margins with time contains 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. Fig 6 shows that sediments of the two Wells fall within the passive margins.

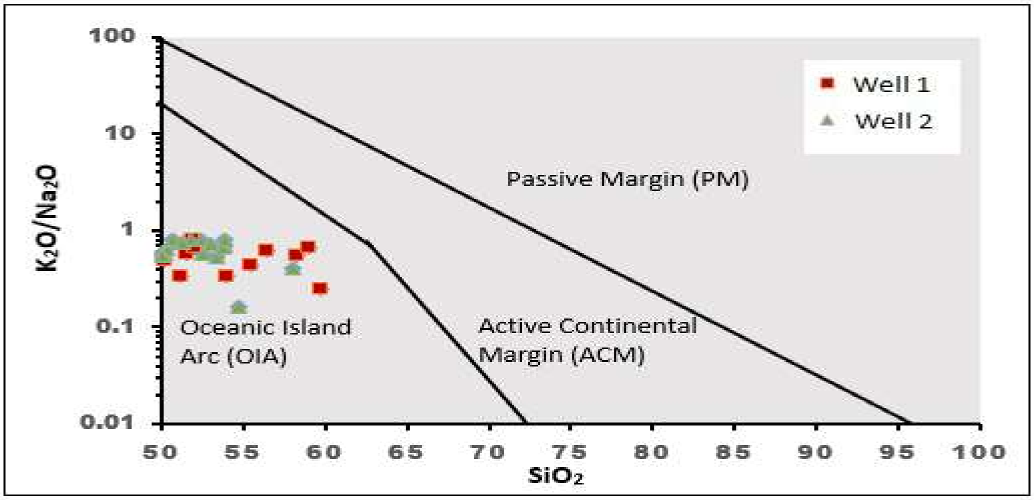

Figure 5. Tectonic discrimination plot for the sediments of the study area (After Roser and Korsch, 1986).

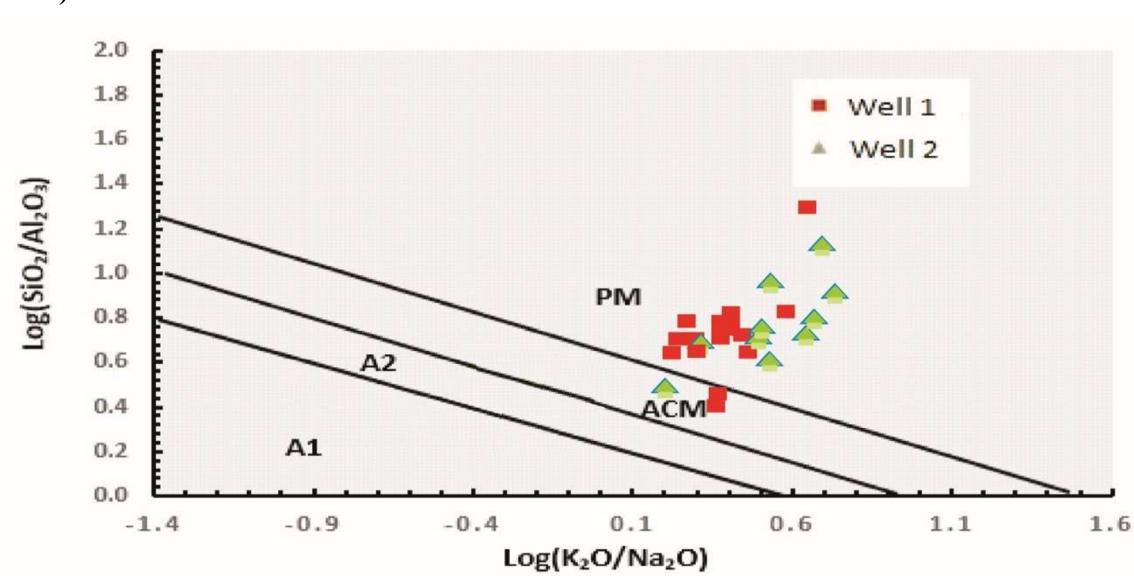

Figure 6. Plot of Log(SiO_2/Al_2O_3 versus Log(K_2O/Na_2O) for sediments of the study area (after Maynard et al.1982).

Provenance of the sediments

Provenance studies include the interpretation of the lithological source of sediment and/or sedimentary rock. Fine-grained sediments are mostly the final result of pre-existing clastic sediments, as these particles are stable weathering products and can be recycled through many episodes of burial, uplifting and erosion, depending on the region's tectonic processes. The origin of sediment and/or sedimentary rocks may be reconstructed on the basis of their geochemical and mineralological compositions. The analysis of the sources of siliciclastic sediment is a method to study the evolution of ancient sedimentary basins. Significant and trace element geochemistry of siliciclastic sediments provides details on the nature of source rock, the hydraulic sorting and the degree of recycling in the tectonic production of sedimentary basins (Nesbitt and Young, 1982).

Authors have related sandstone geochemistry to specific tectonic environment. Roser and Korsch (1988) used the discriminant function plot of (Fig. 7) to define four (4) main provenances: mafic igneous provenance; intermediate igneous provenance; felsic igneous provenance; and quartzose sedimentary provenance. The sediments of the study area plot converged in the felsic igneous provenance field suggesting that the felsic igneous source might have been the source area that provided the sediments that were deposited in the oceanic island arc.

The plots using the raw oxides (Fig. 7) revealed that the sediments in the well were sourced from felsic igneous provenance. The problem of biogenic CaO in $CaCO_3$ and also biogenic SiO_2 is circumvented by using ratio plots in which the discriminant functions are based upon the ratios of TiO_2, Fe $_2$O, MgO, Na_2O, and K_2O all to Al_2O. Felsic igneous rocks are rich in Feldspars, quartz and silicate minerals, they could be formed in areas which once experienced mild plate tectonic activities. The formula for the raw oxides used in Figure 7 is given as discriminant function1: −1.773TiO2 + 0.607Al2O3 + 0.76Fe2O3(total) − 1.5MgO+ 0.616CaO+ 0.509Na2O− 1.224K2O − 9.09; discriminant function 2: 0.445TiO2 + 0.7Al2O3 − 0.25Fe2O3(total) − 1.142MgO + 0.438CaO + 1.475Na2O + 1.426K2O − 6.861.

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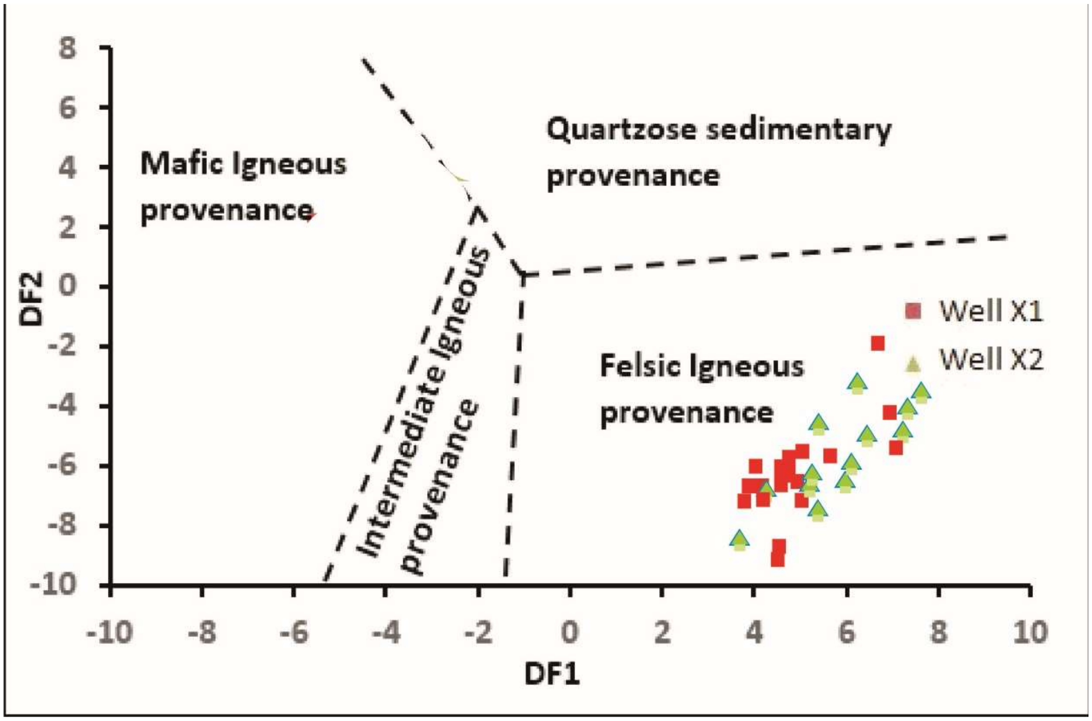

Fig. 7: Discriminant function diagram for the provenance signatures of sediments of the study area using major elements (after Roser and Korsh, 1988)

Figures 8 confirm that the sediments of the study area are continental sands since the sediments plotted in the non-marine & deltaic sandstone fields of the binary diagram of Ratcliffe et al. (2007).

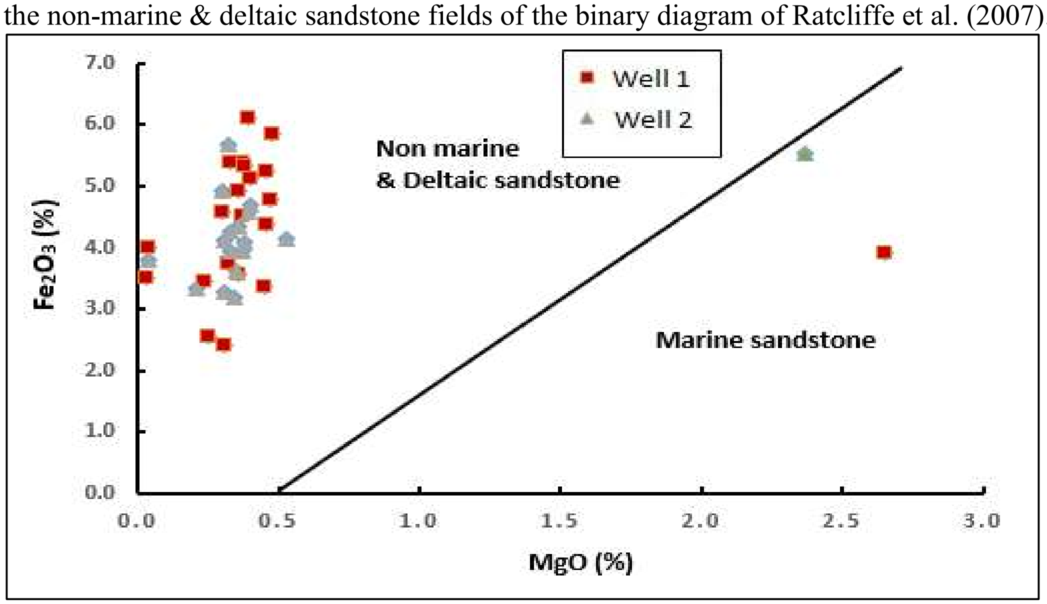

Figure 8. Binary diagrams showing characterization and differentiation of marine from nonmarine sediments in the study area (after Ratcliffe et al. 2007).

Conclusion

The sediments of Wells X1 and X2 plotted in the passive continental margin and few in the active continental margin, this suggest a syn rift faulting system of a transform margin, consistent with the known actively opening of a failed arm of the triple junction, this in line with findings of Madukwe et al (2014) in their study of Ishara sandstones, where the tectonic setting for deposition of the sandstone was ascribed to be from mixed tectonic setting of passive continental and active continental tectonic setting.

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