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Geochemical Characteristics of Radioactive Reservoir Rocks in the Niger Delta Basin: Implications for Source of Radioactivity and Environment of Deposition

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Abstract

The major, trace and rare-earth elements composition of core samples of shale and reservoir sandstone litho-units in a section of a sedimentary succession penetrated by Well (X) in the Niger Delta basin of Nigeria have been determined and compared with the gamma log of the section towards establishing the source(s) of the radioactivity in the sandstone units with anomalously high radiation signature referred to as 'hot sand'. The hot sand is characterized by high amount of Th, U, Ba, Hf, Zr and the heavy rare earth elements. This is attributed to higher amounts of heavy minerals in the hot sand. A very significant correlation of the radioactive elements with Zr and TiO₂ suggests that the radioactive elements are hosted mainly by zircon and rutile. Calculated gamma activities contributed by the radioactive elements indicate that the bulk of the radioactivity is due to Th and not U as once suggested by Weber (1971). Similarity in chondrite-normalized abundance patterns in the hot sand and the other sandstones implies common source rock for all the sandstone types. However, marked enrichment in the amounts of the heavy elements, including the radioactive elements U and Th as well as the heavy rare earth elements in the hot sand is indicative of different sedimentary processes in the transportation and deposition of the hot sands. Sedimentary process indicators such as Th/Sc and Zr/Sc suggest that hydraulic sorting was very important during the transportation and deposition of the hot sand. A possible impact of the high amount of Ba, probably from corresponding high amount of barite (barium sulphate) in the hot sand is the reaction of injection fluids with the barite (barium sulphate) in the reservoir rocks. This may cause a decrease in the permeability of the reservoir by precipitating salts in the pore spaces.

Keywords: geochemical composition; gamma log; Niger basin; hot sand; radioactive elements; hydraulic sorting.

1. Introduction

The occurrence of radioactive sandstones also known as **hot sands** within sedimentary sequences in the Niger Delta area of Nigeria has for some time been a major challenge to the

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Nigerian petroleum explorationist. This is because these potential reservoir rocks are indistinguishable from the source rocks (shale) on the gamma ray log. Intimately associated with these radioactive sands are non-radioactive sands. Texturally and mineralogically, except for different amount of heavy minerals in the sands, the radioactive and non-radioactive sands are similar and this makes it difficult to differentiate between radioactive and non-radioactive reservoir rocks petrographically. Furthermore, the occurrence of the radioactive sands is localized making it difficult to correlate them across oil fields.

In order to understand the nature of the radioactive reservoir rocks of the Niger Delta, a geochemical study was carried out on one occurrence of such rocks in one of the oil fields in the region. The use of geochemical data on sediments to understand their nature is now well accepted, principally due to the sensitiveness of some key elements in identifying subtle sedimentary features that are not easily recognized by petrographic methods. The intrinsic advantages that geochemical approaches to the study of sedimentary rocks have over the more traditional petrographic approaches have been discussed by McLennan *et al.* (1993).

2. Materials and Methods

The materials used for this study were selected from a section of a core recovered from **Well X** located in one of the oilfields of the Niger Delta. Petrophysical logs for the well were provided by Prof O. Omole of the Department of Petroleum Engineering, University of Ibadan. The investigated core interval was from 2082m to 2103m and occurred within the Agbada Formation. The lithologies of the investigated cores include dark grey to brown fissile shale, sandstone and siltstone. Observed sedimentary structures include lamination, cross stratification, ichnofossil and bioturbation.

Six lithologic units named *Unit L-I to Unit L-VI* recognised on the basis of hand specimen description of the investigated core are shown in Fig. 1 and successively described as follow:

Lithological Unit L-I (?-2103m). This is the base of the investigated section. It consists of laminated dark grey shale with some siltstone drapes at the top. It is moderately bioturbated. The observed biogenic structures include *Planolites*, *Terrebellina*, *Teichinicus* and *Paleophycis*.

Lithologic Unit L-II (2103m - 2098m). This unit is about 4 metres thick and consists of intercalation of fine grained sand, siltstone and shale. The shale content increases towards the

base of the unit while the siltstone component becomes thicker upwards and constitutes about 40% of the entire unit. Bioturbation is intense in this unit and it is associated with the presence of *Diplocritareon* and *Paleophycus*. For the purpose of this study the unit will be known as the **siltstone/shale Unit**.

Lithologic Unit L-III (2098m -2094m). This unit is composed predominantly of fine – grained and well sorted, very friable, creamy and thinly laminated sandstone. It is also characterized by cross – bedding and oil stain. Texturally this unit appears to be homogeneous. However, gamma-ray logs show that the upper part of the lithologic unit which is about 2.33m thick is characterized by abnormal gamma ray activity. This highly radioactive sandstone is referred to as the **Hot Sands**. The hot sands are the main focus of this study. The lower section of the unit will be referred to as the **Lower Sandstone**.

Lithologic Unit L- IV (2094m -2091m). This unit consists of about 3m thick dark brown fissile shale becoming sandy towards the base. The unit will be known as **the Lower Shale**.

Lithologic Unit L-V (2091m -2087m). This unit is composed of fine to coarse grained sandstone with angular to rounded grains. The sandstone is hard, oil impregnated and characterized by cylindrical shaped log structure with a coarsening up sequence, sharp base and sharp sand/shale boundary at the top. A thin coal layer lies on this unit. The unit will be referred to as the **Upper Sandstone**.

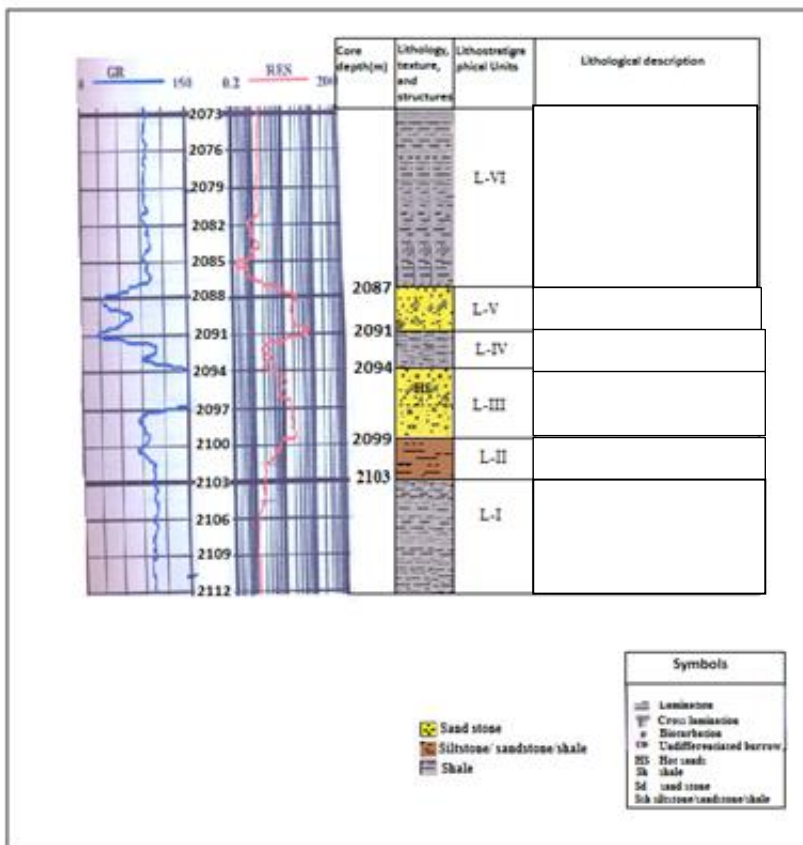


Figure1: Composite stratigraphic section of the investigated core.

Lithologic Unit L-VI (2087m-2084m –. This unit is at the top of the investigated section. It is predominantly dark grey and sideritic shale. It is moderately bioturbated. This unit is referred to as **Upper Shale**.

2.1 Sampling

The sampling scheme is shown in Table 1. Eighteen samples which covered five of the six sedimentary units of the investigated interval were taken for geochemical studies at sample interval of approximately 1.0m. Occasionally, however, this sample interval was adjusted for variations in lithology in each unit.

Table 1: Sampling scheme for this study

Sample No	Depth(m)	Lithology	Stratigraphic Unit/Subunit	Reference
XW-1	2084	Shale	L-VI	Upper Shale
XW-2	2086			
XW-3	2087			
XW-4	2088	sandstone	L-V	Upper Sandstone
XW-5	2090			
XW-6	2091			
XW-7	2092	Shale	L-IV	Lower Shale
XW-8	2093			
XW-9	2094			
XW-10	2095	Sandstone	L-III	Hot Sands
XW-11	2096			Lower Sandstone
XW-12	2097			
XW-13	2098			
XW-14	2099	siltstone/shale	L-II	Siltstone/shale
XW-15	2100			
XW-16	2101			
XW-17	2102			
XW-18	2103			
(not studied)		Shale	L-I	

2.2. Chemical Analysis

Samples to be analysed were first soaked in toluene and methanol to remove oil stains. In some cases where the oil stains could not be completely removed by the toluene- methanol wash, it was necessary to wash the samples again with a solution of detergent. The washed samples were then air-dried. About 100g of each of the air-dried samples was later ground to less than 75 μ in an agate mortar to minimize contamination. 30g of the ground samples were packed in a polythene sachet and shipped to ACME Laboratory Ltd, Vancouver, Canada where all analyses were carried out.

Major oxides (whole rock) determination was undertaken by fusing 0.200g of the ground sample with a 1:1 mixture of lithium borate and lithium tetraborate. This was followed by a dilute nitric acid digestion and analysis by inductively coupled plasma – emission spectrometry to obtain the abundances of the major element oxides. Loss on ignition (LOI) was obtained by weight difference after ignition at 1000°C. Total carbon and sulphur determination was by Leco. Trace element determinations for the precious and base metals was by digesting 0.5g sample in 3mL of a mixture of 2-2-2 HCl-HNO₃-H₂O at 95°C for one hour and diluting to 10mL by distilled water. The digestion was followed by analysis by inductively coupled plasma – mass spectrometry (ICP – MS). Refractory and rare earth elements were determined by ICP-MS following a lithium borate/lithium metaborate fusion and dilute nitric acid digestion of a 0.2g sample.

3. Results and Discussion

The geochemical data for all the analysed sandstones are presented in Tables 2, 4 and 5. The geochemical data for the shales can be found in Oshin (2005).

3.1 Major Elements Geochemistry

The major element oxides concentrations in the investigated sandstones are shown in Table 2 and Fig.2. A starting point in establishing the nature of the sandstones under study is their classification. Although it is difficult to find a simple relationship between the mineralogy of sandstones and their chemical composition (Rollinson, 1993), geochemical classification schemes of using the major element oxides, for example: Pettijohn *et al.* (1972) and Herron (1988) have shown that geochemical classification of sedimentary rocks is generally consistent with classification based on petrographic data. The plot of $\log (\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$ against $\log (\text{SiO}_2/\text{Al}_2\text{O}_3)$ (Fig.3) shows that the investigated sandstones belong to different classes. While the Upper sandstones fall in both the litharenite and sublitharenite fields, the hot sands fall only in the sublitharenite field and the Lower sandstone fall in the sublitharenite and subarkosic fields. However, the average composition of each of the sandstones falls in the sublitharenite field, indicating moderately mature sediments. Crook (1974) has also classified sandstones as quartz rich, quartz intermediate and quartz poor based on their K₂O and Na₂O contents. The plot of K₂O wt. % against Na₂O wt. % bivariate diagram (after Crook, 1974) indicates that all the sandstones in this study are quartz rich (Fig.4)

Table 2: Major element concentrations (wt. %) of the Well-X reservoir sediments.

Sample	Rock	Depth (m)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	LOI	SUM
	UCC		66.00	15.20		2.20	4.20	3.90	3.40	0.50				
XW-4	Upper sandstone	2088	79.96	7.01	2.81	0.34	0.21	0.61	1.67	1.53	0.07	0.03	6.7	99.97
XW-5	Upper sandstone	2090	84.12	4.82	2.18	0.14	0.16	0.51	1.63	0.83	0.09	0.04	5.4	99.92
XW-6	Upper sandstone	2091	84.77	4.88	2.75	0.13	0.17	0.32	1.44	0.88	0.04	0.03	4.7	100.11
XW-10	Hot Sand	2095	76.14	5.63	3.78	0.31	0.67	0.82	2.18	2.95	0.11	0.12	6.1	98.81
XW-11	Hot Sand	2096	75.63	5.47	3.95	0.33	0.65	0.76	2.03	2.83	0.09	0.11	5.6	97.45
XW-12	Lower sandstone	2097	81.41	6.48	2.57	0.29	0.51	0.96	2.64	0.65	0.03	0.04	4.1	99.68
XW-13	Lower sandstone	2098	81.05	5.89	2.94	0.32	0.51	0.91	2.52	0.81	0.04	0.05	4.4	99.44

UCC = Upper continental crust

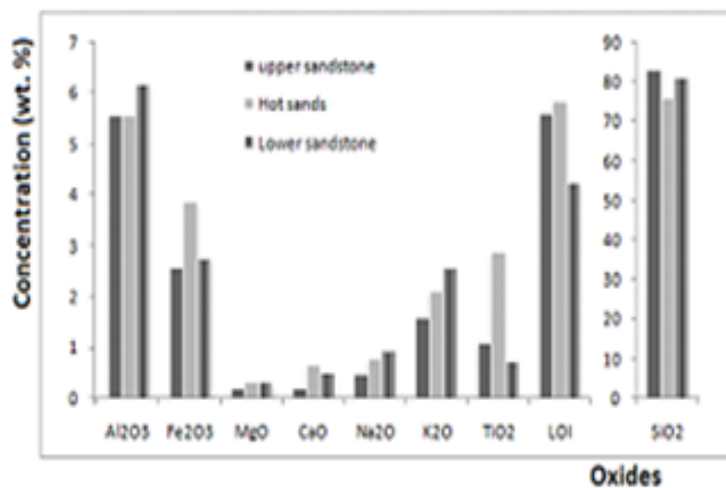
**Fig. 2:** Average oxides concentrations in the investigated sandstones



Fig.3: Geochemical classification of the investigated sandstones based on log (Fe₂O₃/K₂O) vs. log (SiO₂/Al₂O₃) diagram of Herron (1988).

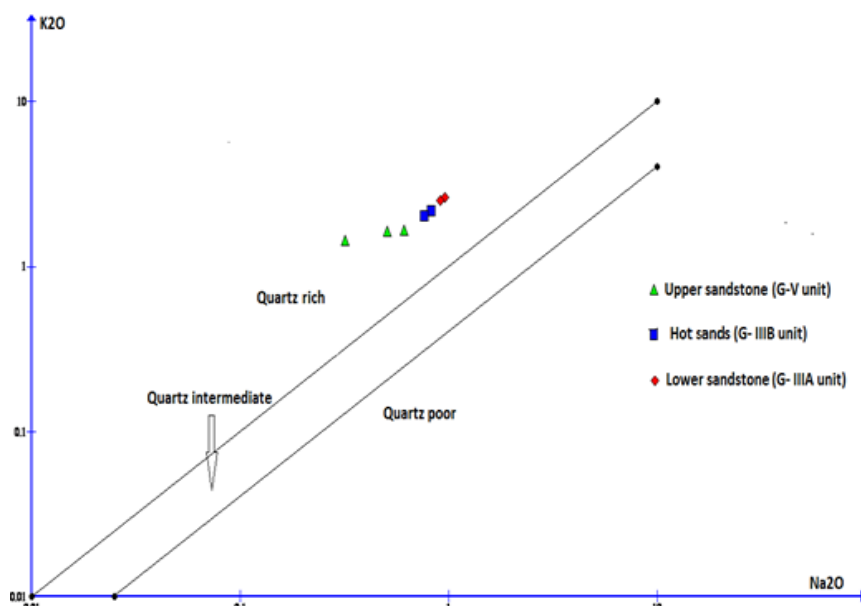


Fig.4: Geochemical classification of the investigated sandstones based on log K₂O vs. Na₂O (after Crook, 1974).

Comparison of the composition of the investigated sandstones shows some minor differences in their concentrations of many of the oxides. Al₂O₃, MgO, CaO contents in the Upper sandstone are lower than those of the hot sands and Lower sandstone but SiO₂ contents are higher in the Upper sandstone. The hot sands are higher in Fe₂O₃, CaO and TiO₂ but lower in SiO₂ than the Upper and Lower sandstones. Na₂O and K₂O show a progressive increase in concentration from the Upper sandstone through the hot sands to the Lower sandstone. Generally, K content in sediments is controlled by K-feldspar, the micas and clay while Na and Ca contents are controlled by the amount of plagioclase feldspars. Therefore, the K₂O/CaO ratios or

$K_2O/(Na_2O+CaO)$ in sandstones may be used as a measure of the proportion of K-feldspar relative to plagioclase in the sandstones. Both the K_2O/CaO and $K_2O/(Na_2O+CaO)$ ratios in the Upper sandstones are higher than those of the hot sands and Lower sandstones (Table 5) suggesting that the Upper sandstones contain more K-feldspar relative to plagioclase than the hot sands and the Lower sandstone. The lower K_2O/Al_2O_3 ratio in the Upper sandstone suggests that K resides more in the micas and clays than the K-feldspar in the rock.

Table 3: Comparison of element oxide ratios in investigated sandstones

Sample	XW-4	XW-5	XW-6	XW-10	XW-11	XW-12	XW-13
Depth (m)	2088	2090	2091	2095	2096	2097	2098
Reference	upper sandstone			hot sands		lower sandstone	
K_2O/CaO	7.96	10.19	8.47	3.25	3.12	5.18	4.94
$K_2O/(Na_2O+CaO)$	1.99	2.43	2.94	1.46	1.44	1.80	1.78
$Al_2O_3/(CaO+Na_2O)$	8.55	7.19	9.96	3.78	3.88	4.41	4.15
K_2O/Al_2O_3	0.23	0.34	0.30	0.39	0.37	0.41	0.43
SiO_2/Al_2O_3	11.41	17.45	17.37	13.52	13.83	12.56	13.76
Fe_2O_3/MgO	8.26	15.57	21.15	12.19	11.97	8.86	9.19
Al_2O_3/TiO_2	4.58	5.81	5.55	1.91	1.93	9.97	7.27

SiO_2/Al_2O_3 ratio has been used by many workers (e.g. Bhatia, 1983) as a measure of the quartz: clay ratio in siliclastic sediments. SiO_2/Al_2O_3 ratios in the studied sandstones range from 11.41 to 17.45 with an average of 15.41 in the Upper sandstone, 13.68 in the hot sands and 13.16 in the Lower sandstone (Table 3). These ratios are relatively high, indicating enrichment in the quartz or paucity of clay contents in the sandstones, with the Upper sandstones having the most quartz enrichment relative to the hot sands and the Lower sandstones. It is also observed that SiO_2/Al_2O_3 ratios are similar in the hot sands and the Lower sandstone, indicating similar maturity in the two rock types. On account of higher SiO_2/Al_2O_3 ratios in the upper sandstones, it may be concluded that the Upper sandstones are texturally more mature than the hot sands and the Lower sandstones. A plot of SiO_2 against Al_2O_3 (Fig 5.) shows a strong negative correlation between SiO_2 and Al_2O_3 . However, the two hot sands samples plot away from the other sandstones. This may be explained in three ways : (i) The hot sands have a different source than the other sandstones in the study area. In that case, the hot sands may be regarded as a distinct unit not geochemically related to the Lower sandstone. (ii). The hot sands have suffered some loss of either SiO_2 or Al_2O_3 . However, both SiO_2 and Al_2O_3 are believed to be immobile during weathering and the loss of either oxide from the hot sands is highly unlikely. (iii) The apparent loss of either SiO_2 or/and Al_2O_3 is a reflection of high amounts of some trace elements

in the hot sands, particularly Ba (average 10288 ppm or 1.0288 wt. %) and Zr (average 7770ppm or 0.777 wt. %) which have in effect diluted the concentrations of the major elements.

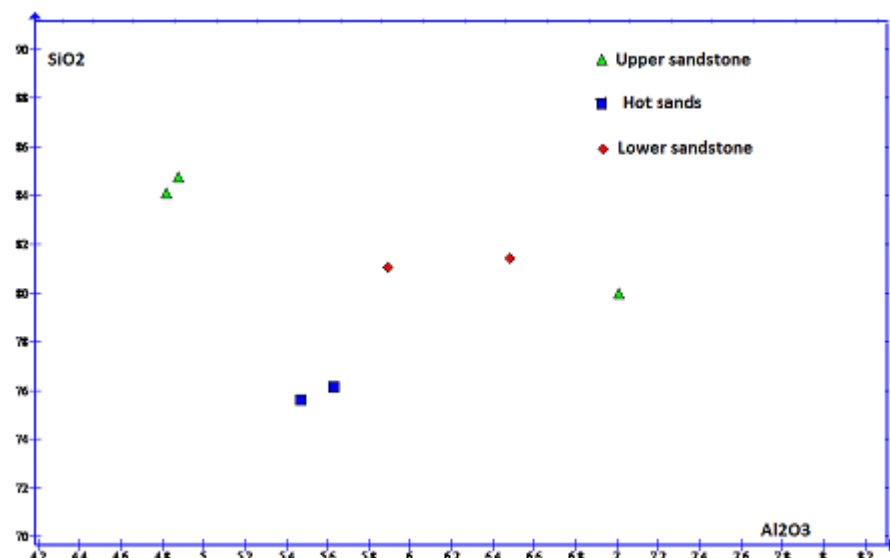


Fig. 5: Plot of SiO₂ wt. % against Al₂O₃ wt. %

Saito (1988) used the plot of K₂O/CaO ratio versus Na₂O/Fe₂O₃ ratio to discriminate between the different rock types of nonbiogenic sediments from East Greenland Continental Rise. The K₂O/CaO versus Na₂O/Fe₂O₃ plot of the studied sandstones (Fig. 6) clearly shows the Upper sandstones plotting in a different field from the hot sands and the Lower sandstones. All the samples from the hot sands and the Lower sandstones plot on a straight line, suggesting a geochemical relationship between the hot sands and the Lower sandstones.

Fe and Mg are major element constituents of ferro-magnesian minerals. Consequently, high Fe and Mg contents in sandstone are indicative of high proportion of ferro-magnesian minerals in the sandstone. Conversely, low concentrations of Fe and Mg reflect low abundances of ferro-magnesian minerals in the rock. Except for the hot sands, the studied sandstone samples have moderate concentrations of Fe (2.18-2.94 wt. % Fe₂O₃) and low concentrations of Mg (0.13-0.33 wt. % MgO). The low concentrations of Mg in the rocks indicate low abundances of ferro-magnesian minerals.

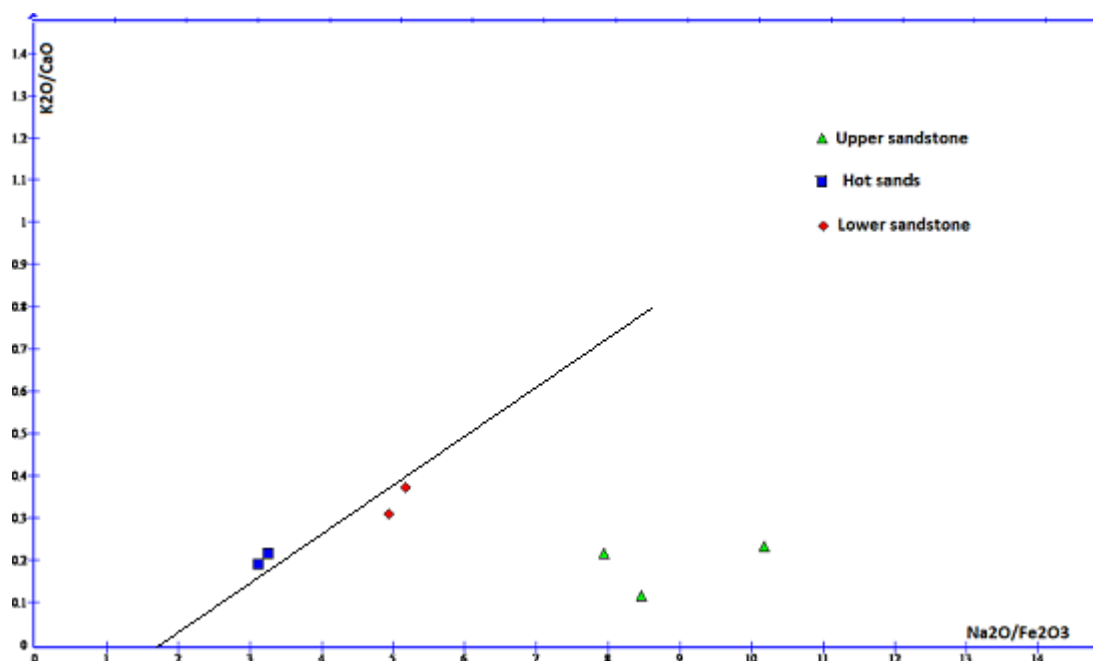


Fig.6: Plot of K_2O/CaO against Na_2O/Fe_2O_3 in the investigated sandstones.

The moderately high concentration of Fe in the rock is therefore interpreted as due to the occurrence of Fe-bearing minerals such as ilmenite and magnetite in the rocks. The hot sands, unlike the other sandstones in the study area have relatively high Fe contents (3.78-3.95 wt. % Fe_2O_3), low Mg contents (0.31-0.33 wt. % MgO) and relatively high concentrations of Ti (2.83-2.95 wt. % TiO_2). High concentrations of Fe_2O_3 and TiO_2 in the hot sands most probably reflect high abundances of Ti-bearing heavy minerals in the hot sands. This view is supported by the poor correlation of Al_2O_3 and TiO_2 in the sandstones. In igneous rocks Ti resides mostly in the mafic minerals which include olivine, pyroxene, hornblende and biotite as well as accessory minerals which include ilmenite and rutile. In texturally mature sediments as the investigated sandstones in this study only biotite apart from ilmenite and rutile may be expected to be present. If the Ti contents of the sandstones are mainly influenced by biotite, then there should be a strong positive correlation between Al_2O_3 and TiO_2 . A plot of Al_2O_3 against TiO_2 in the sandstones (Fig. 7) shows a poor correlation between the two oxides indicating an insignificant influence of biotite on the concentrations of Ti in the sandstones.

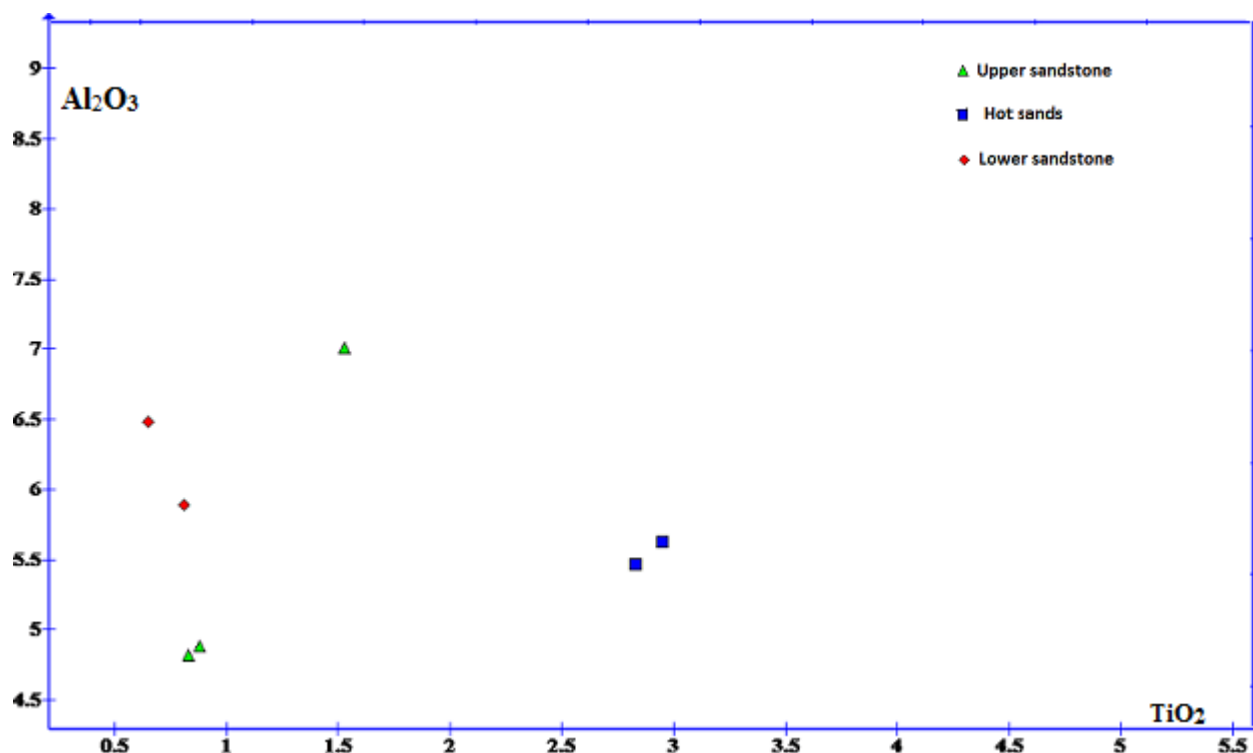


Fig.7: Plot of Al₂O₃ against TiO₂ in the investigated sandstones

3.2 Trace Elements Geochemistry

The trace element contents of the 7 investigated reservoir samples are presented in Table 4. Trace elements may be studied in groups, based on either their positions in the periodic table or their geochemical behaviour. In this study, the trace elements are grouped into (i) **transition elements** (elements in the d-block of the periodic table) which include Sc, V, Cr, Co, Ni, Cu and Zn (ii) the **low field strength elements (LFSE)** or **large ion lithophile elements (LILE)** and (iii) **the high field strength elements (HFSE)**. The low field strength elements are those that preferentially partition into the melt fraction during the partial melting of the mantle (incompatible elements) and have large ions and relatively small charges, and include Rb, Sr, Cs, Ba and Pb while the high field strength elements are incompatible elements with high charges and relatively small ions and include Y, Zr, Nb, Hf, Ta, Th and U.

Table 4: Trace element concentrations (ppm) in investigated reservoir rocks

Sample	Rock	Depth(m)	Ba	Co	Cu	Cr	Cs	Ga	Hf	Nb	Ni	Pb
UCC	UCC		700	10.0	25.0	35.0	3.5	17.0	5.8	25.0	20.0	25.0
XW-4	Upper sandstone	2088	698	11.7	9.2	34.2	1.9	11.5	47.9	28.2	11.2	8.1
XW-5	Upper sandstone	2090	1166	6.2	5.2	13.7	0.7	6.1	36.4	15.4	5.5	5.7
XW-6	Upper sandstone	2091	1551	6.5	6.8	13.5	0.8	6.2	14.1	10.3	6.7	5.5
XW-10	Hot Sand	2095	10309	8.4	6.5	47.3	0.7	7.6	204.6	44.8	7.6	18.5
XW-11	Hot Sand	2096	10268	7.9	7.1	48.7	0.7	7.2	207.8	46.3	7.3	19.2
XW-12	Lower sandstone	2097	2153	6.8	4.2	13.5	0.9	7.4	23.9	12.4	7.1	6.6.
XW-13	Lower sandstone	2098	2582	9.2	4.4	13.8	0.8	7.3	36.4	15.5	9.7	6.5

UCC = Upper crust

Table 4 (contd): Trace element concentrations (ppm) in investigated reservoir rocks

Sample	Rock	Depth(m)	Rb	Sc	Sr	Th	U	V	Y	Zn	Zr
UCC	UCC		112.0	10.0	350.0	10.7	2.8	60.0	22.0	71.0	190
XW-4	Upper sandstone	2088	49.8	10.2	103	21.1	6.6	55	60.1	40	1746
XW-5	Upper sandstone	2090	36.7	3.8	130	17.2	4.4	27	30.1	25	1305
XW-6	Upper sandstone	2091	26.3	3.4	86	8.7	1.7	25	12.3	26	554
XW-10	Hot Sand	2095	46.5	12.3	228	75.1	17.6	67	138.8	51	7729
XW-11	Hot Sand	2096	45.7	11.8	226	76.3	18.3	71	140.4	54	7812
XW-12	Lower sandstone	2097	60.4	4.2	189	11.2	2.8	35	26.9	42	878
XW-13	Lower sandstone	2098	57.4	4.8	191	17.7	3.7	38	34.5	41	1284

UCC = Upper crust

The average concentrations of elements in each of the geochemical group are summarized in Figs 8-10. The average abundances of the normalized values plotted in a spider diagram with elements arranged in order of selected trace elements were normalized to the average crustal abundances of the elements and increasing atomic number is shown in Fig.11. This is to determine the relative enrichment of the elements over their average values in the average upper crust of Taylor and McLennan (1981). In order to accommodate the long range in the

concentrations of some elements, the concentration values on the y-axis are recorded on a logarithmic scale.

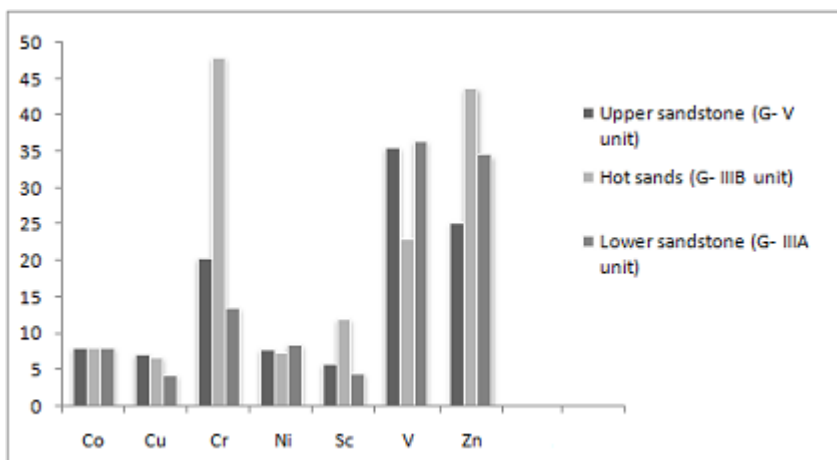


Fig. 8: Average concentration of transition elements in ppm for the investigated sandstones.

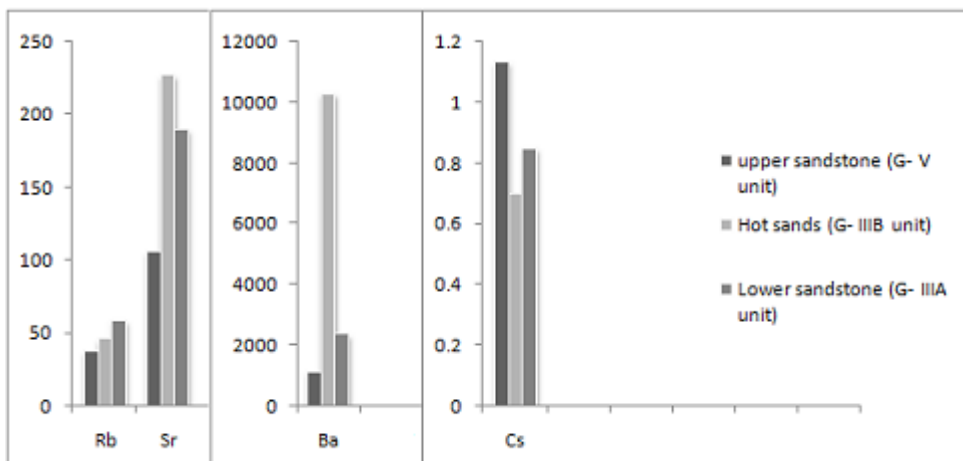


Fig. 9: Average concentrations of large ion lithophile elements (LILE) in ppm for the investigated sandstones.

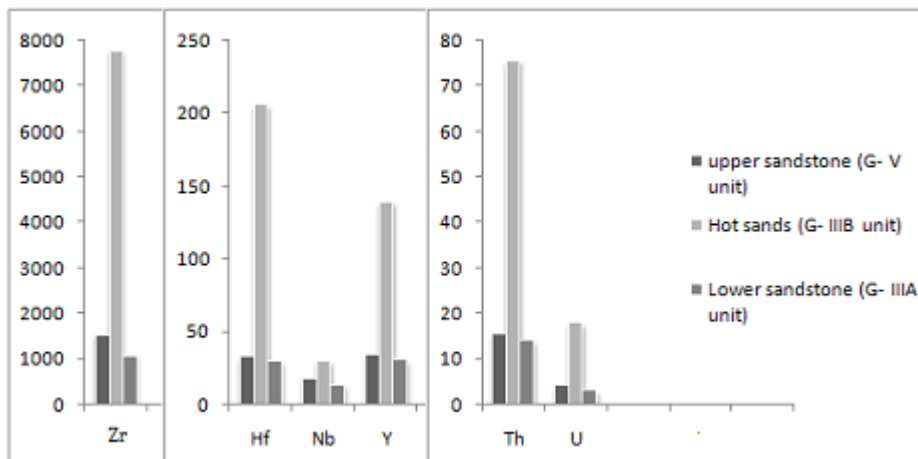


Fig. 10: Average concentrations of the high field strength elements (HSFE) in ppm for the investigated sandstones.

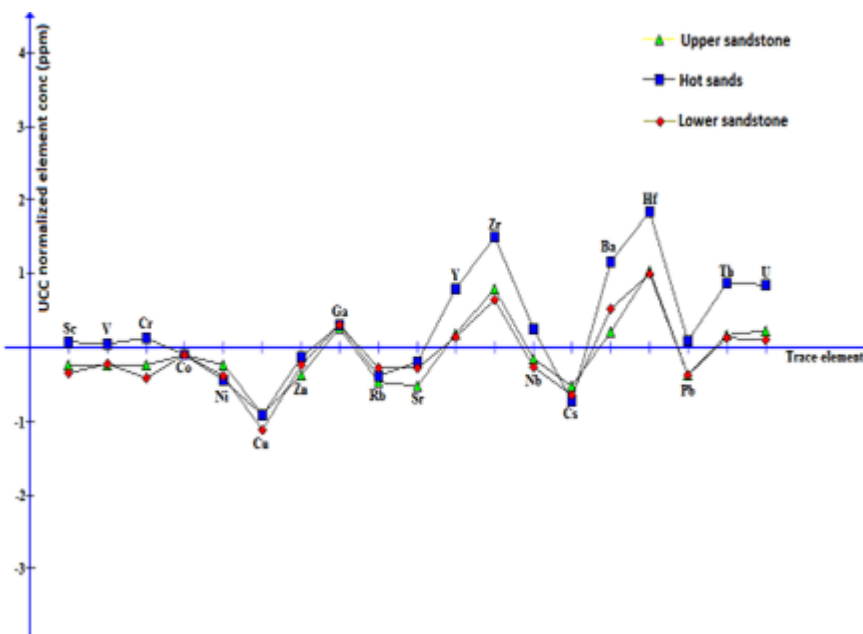


Fig. 11: Spider diagram of trace elements in the investigated sandstones.

The spider diagram indicates that except for Cr, Sc and V in the hot sands, the investigated sandstones are depleted in the transition elements relative to the upper crust. Transition elements normally reside in ferromagnesian minerals; therefore, their depletion in the investigated sandstones indicates an insignificant contribution of mafic rocks as source rocks for the sandstone. The high contents of Cr, Sc and V in the hot sands relative to the Upper and

Lower sandstone without simultaneous enrichment in other transition elements further supports insignificant contribution of mafic rocks to the source of the sandstone.

Similar to the transition elements, the investigated sandstones are depleted in most large ion lithophiles (LILE) including Cs, Rb, Pb and Sr relative to the upper crust. The hot sands however have similar Pb contents as the upper crust. A major departure from the general depletion of LILE in the sandstones is the strong enrichment of Ba in the sandstones. The only minerals that can accommodate Ba in their structures are the K-bearing minerals including K-feldspar, biotite and to some extent hornblende (Mason and Moore, 1982). A plot of Ba against K₂O in the sandstones (Fig.12.), however shows two trends – the upper sandstone trend and the hot sand-Lower sandstones trend. Both trends show that a strong negative correlation between BaO and K₂O suggesting that barium is not hosted by silicate minerals but by a barium mineral such as barite.

The high field strength elements (HFSE) display a distribution pattern different than those of the transition and large lithophile elements. In the hot sands, the high field strength elements are enriched in all the HSFES relative to upper crust. Enrichment (rock/upper crust) in the HFSE range from moderate (rock/upper crust =1.5 – 5) as in Nb to high (rock/upper crust >5) in Y, Th and U to extreme (rock/upper crust > 25) as in Hf and Zr. High Field Strength Elements are elements which on account of their large ionic valences (or high charges) have difficulty in entering cation sites of minerals. They therefore concentrate in the earliest melt phase of magma during magma generation by partial melting of the mantle or in highly evolved products of fractional crystallization of magma, such as pegmatites or granitic rocks. The enrichment of the HSFES in the hot sand may therefore be attributed to a significant contribution of pegmatites or granitic rocks as source materials for the hot sand. An extreme enrichment of Zr and Hf, a proxy of Zr, suggests a high abundance of zircon which is believed to have concentrated the other HFSEs in the hot sand (Wikipedia).

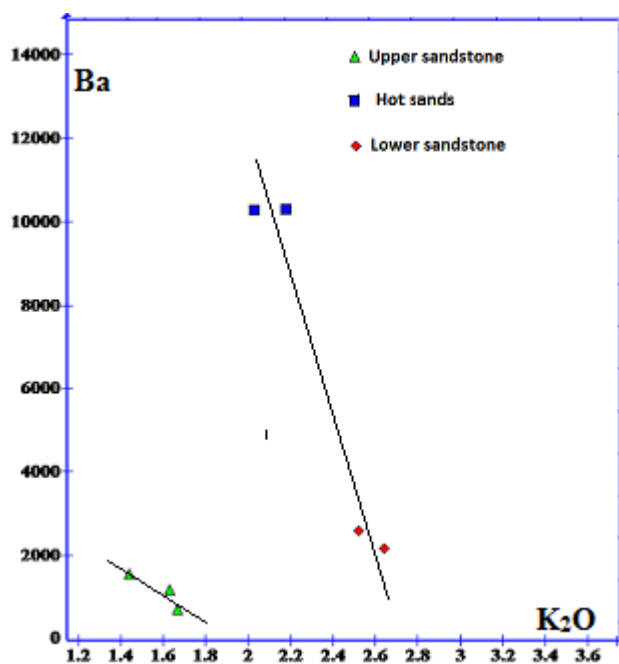


Fig. 12: Plot of Ba against K₂O in investigated sandstones.

3.3 Rare Earth Elements Geochemistry

The concentrations of the rare earth elements in the investigated sandstones are summarized in Table 5 and Figs 13 and 14.

Table. 5: Concentrations of REE (ppm) for the investigated sandstone

Sample	Rock	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	CH	0.367	0.957	0.137	0.711	0.231	0.087	0.306	0.058	0.381	0.085	0.249	0.036	0.248	0.038
XW-4	US	54.6	122.4	12.63	48.9	8.9	1.53	7.26	1.49	8.62	1.91	6.12	1.09	6.5	1.05
XW-5	US	42.4	97.7	9.93	38.9	6.8	0.86	5.66	0.91	5.17	1.01	2.93	0.49	3.1	0.48
XW-6	US	21.6	50.2	5.16	18.5	3.5	0.57	2.33	0.44	2.09	0.38	1.31	0.21	1.3	0.23
XW-10	HS	157.2	333.8	35.33	128.3	23.8	2.18	19.31	3.21	20.05	4.26	13.5	2.43	17.1	2.82
XW-11	HS	161.5	342.7	36.1	133.2	24.1	1.89	18.76	2.79	21.11	4.84	14.1	3.12	16.9	2.95
XW-12	LS	24.2	59.4	6.37	24.2	4.7	0.93	3.94	0.68	4.38	0.86	2.79	0.48	3.1	0.45
XW-13	LS	32.2	73.5	7.87	29.9	5.7	0.95	4.63	0.87	5.11	1.12	3.56	0.61	4.2	0.65

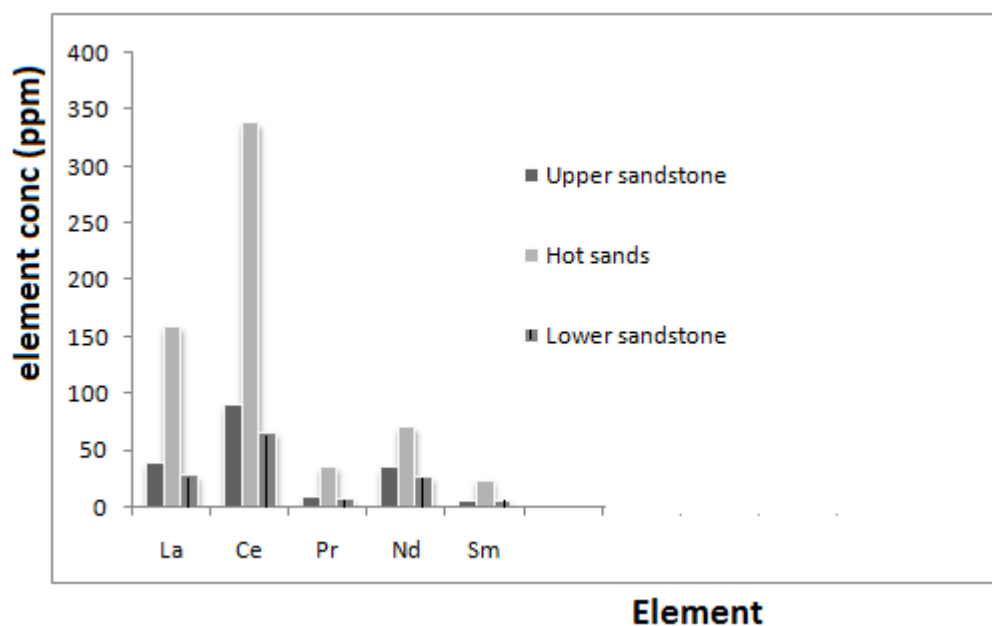
Rock: US = Upper sandstone; HS = Hot sands; LS = Lower sandstone; CH = Chondrite – data from Taylor and McLennan (1985)

Table 6: REE ratios in the investigated sandstones.

Rock type	Upper sandstone	Hot sand	Lower sandstone
Σ LREE (La-Sm)	180.7	688.0	134.0
Σ HREE (Gd-Lu)	20.61	83.64	18.74
Σ REE	202.28	771.64	153.68
Σ LREE/ Σ HREE	8.77	8.23	8.15
La _N /Sm _N	3.89	4.19	3.41
La _N /Yb _N	7.35	6.33	5.22
Gd _N /Yb _N	1.13	0.91	0.95
Eu/Eu*	0.53	0.24	0.61
Ce/Ce*	1.13	1.05	1.10

$$\text{Eu/Eu}^* = \text{Eu}_N / (\text{Sm}_N \times \text{Gd}_N)^{0.5}$$

$$\text{Ce/Ce}^* = \text{Ce}_N / (\text{La}_N \times \text{Pr}_N)^{0.5}$$

**Fig. 13:** Average concentration (ppm) of the light REE in the investigated sandstones.

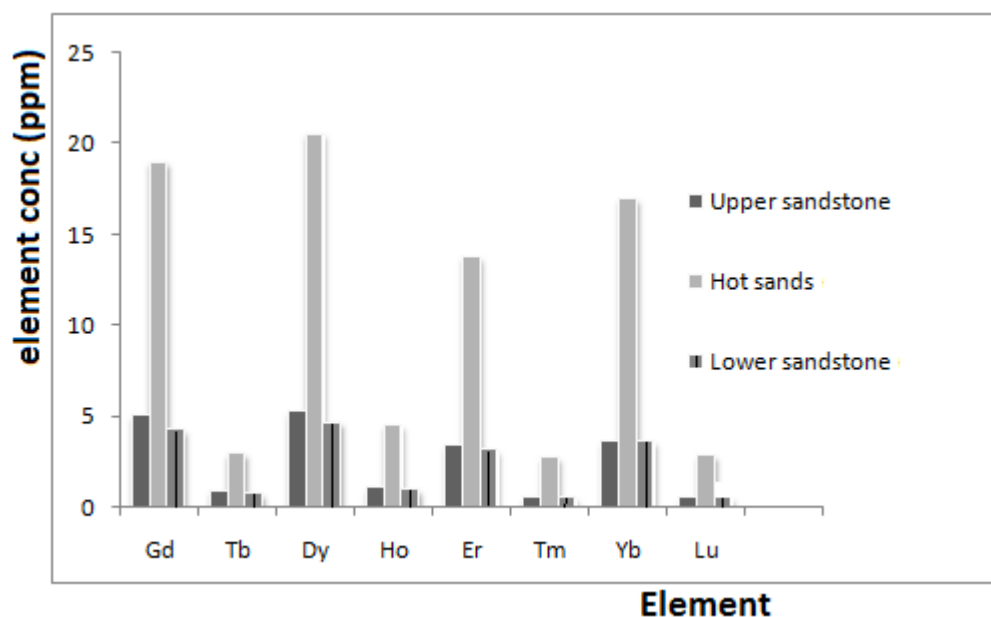


Fig. 14: Average concentration (ppm) of the middle and heavy REEs in the investigated sandstones.

Total rare earth elements content (Σ REE) in hot sands (771.64 ppm) is more than thrice the Σ REE in the Upper sandstones (202.28 ppm) and Σ REE in the Lower sandstone (153.68 ppm). All the different types of sandstones exhibit significant enrichment of the LREE relative to the HREE as shown in their high (8.15-8.77) LREE/HREE ratios as well as high La/Yb_N ratios ranging from 5.22 in the Lower sandstone to 6.33 in the hot sands to 7.35 in the Upper sandstone. Enrichment of the LREEs in the sandstones implies that terrigenous detritus may have been major sources supplying the REEs to the sandstones (Ferreira da Silva *et al.*, 2009).

Variations in Σ REE in sediments are commonly attributed to hydraulic sorting in which the REEs are preferentially concentrated in different grain-size fractions and mineral contents (Armstrong-Altrin *et al.*, 2004). Cullers *et al.* (1979) proposed that the REEs are preferentially partitioned in fine to very fine grain-size fractions of sediments than the medium grain-size fractions. The observed variations in the abundances of the REEs in the investigated sandstones may however not be related to variations in grain-size fractions. This view is supported by the fact that both the hot sand and the Lower sandstone are fine to very fine grained, but the average Σ REE in the hot sand is more than 3 times higher than those of the Lower sands. Besides the Upper sandstone which is medium grained has higher average Σ REE than the fine grained Lower sandstone.

Chondrite-normalized abundance patterns in the investigated sandstones are shown in Figure 15. A significant feature in the REE geochemistry of the sandstones is the striking similarity of chondrite-normalized abundance patterns of the sandstone types despite the wide variation

in their total REE concentrations. All the sandstones exhibit some degree of Eu anomaly. However, while the negative anomaly is moderate in both the Upper sandstone ($\text{Eu}/\text{Eu}^* = 0.53$) and Lower sandstone ($\text{Eu}/\text{Eu}^* = 0.61$) it is quite prominent in the hot sand ($\text{Eu}/\text{Eu}^* = 0.23$). The similarity in the abundance patterns of the sandstones strongly suggests common origin (provenance) for the sandstones.

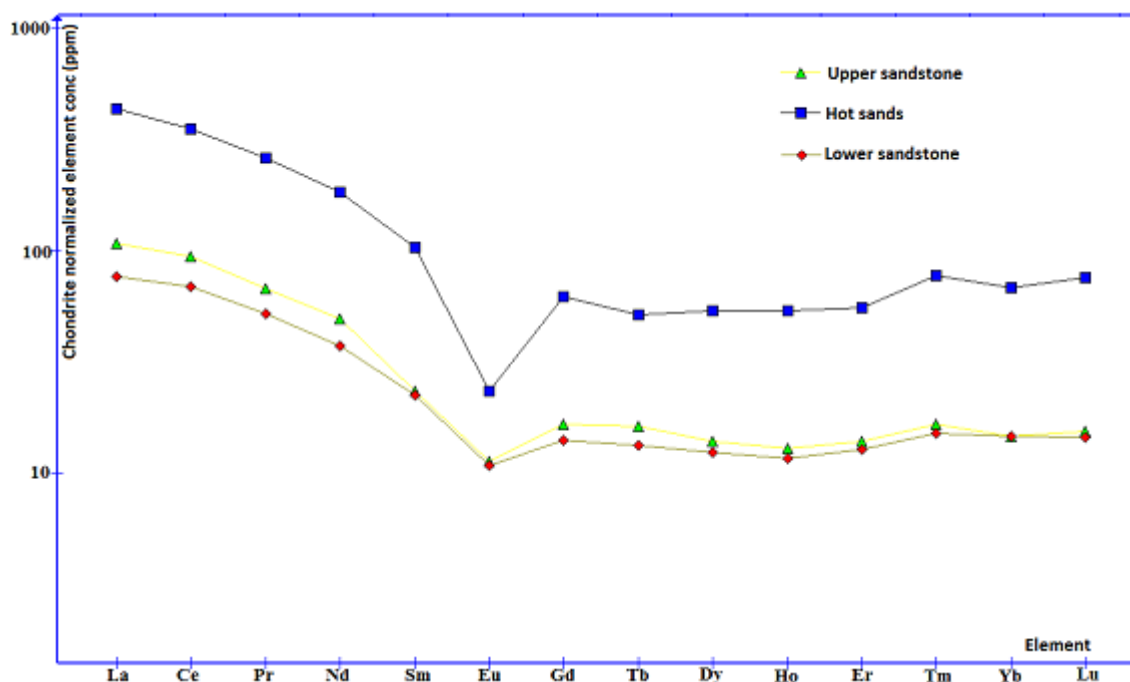


Fig.15: REE abundances in the investigated sandstone normalized to chondrite values from Taylor and McLennan (1985).

3.4 Source of Radioactivity in the Hot Sand

The natural gamma-emitting constituents in rocks are potassium-40 and the daughter isotopes of uranium and thorium decay series. Adams and Weaver (1958) estimated the relative contribution of gamma activity from each of the gamma ray producing elements in a rock to be in the ratio 1:1300: 3600 per unit concentration of K, Th and U respectively in the rock. These ratios have been used to calculate the relative gamma activity due to each of K, Th and U (Table 7) and the contributions of each radioactive element to the total radioactivity in the different investigated sandstones (Table 8).

Table 7: Estimated gamma activity of K, Th in average sandstone and the investigated sandstones.

	Elemental concentration			Estimated relative gamma activity (units of gamma radiation)			
	K(ppm)	Th(ppm)	U (ppm)	K	Th	U	Total
Average sandstone (Mason, 1982)	10700	1.7	0.45	10700	2210	1620	14,530
This Study							
Upper Sandstone	13114	15.7	4.2	13114	20410	15120	48,644
Hot Sands	17472	75.7	18.0	17472	98410	64800	180,682
Lower Sandstone	21414	14.5	3.3	21414	18850	11880	52,144

Table 8: Percentage contribution of K, Th and U to total gamma ray activity in the average sandstone and the investigated rocks.

	Contribution by K (%)	Contribution by Th (%)	Contribution by U (%)
Average sandstone	74	15	11
This study			
Upper sandstone	27	42	31
Hot sands	10	54	36
Lower sandstone	41	36	23

Table 8 shows that K contributes the bulk of the gamma activity (74%) in average sandstone. In the investigated rocks however, a different scenario is observed. In the investigated rocks Th is a principal contributor of gamma activity to the total radioactivity in the rocks. In all cases, activity from U is subordinate to that of Th. In both the Upper sandstone and the hot sand, Th contributes the most with K contributing the least gamma activity. It is only in the Lower sandstone that the order of contribution of gamma activity from K, Th and U observed is similar to that in the average sandstone. The observation that Th is the main contributor of gamma activity in the radioactive sandstone of Niger delta area is contrary to the view of Weber (1971) that the high gamma activity in the radioactive sandstones in the Niger delta comes principally from U.

3.5 Source of Thorium and Uranium in the Hot Sand.

Thorium and uranium commonly occur in sedimentary rocks in two ways. Uranium, and to a lesser extent thorium, are soluble in groundwater under oxidizing conditions. A solution

carrying uranium and thorium may migrate through the pores or fractures in a rock, and under a reducing condition the elements may precipitate out as uranium and thorium minerals either in pores or fractures or on grain boundaries in the rock. The elements may also be adsorbed on clay, organic matter or Fe-Mn oxides within the rock by ion-exchange process. There is no mineralogical evidence that uranium or thorium minerals are deposited in the pores or grain boundaries of the investigated rocks. The possibility that the radioactive elements are adsorbed on clays or organic matter or on Fe-Mn oxides can be evaluated by examining the relationship between the radioelements and the elemental constituents of clay, organic matter and Fe-Mn oxides. If the radioactive elements are adsorbed on clays, organic matter or Fe-Mn oxides by ionic-exchange the amount of radioelement adsorbed will vary as the amount of available sites for adsorption which is directly proportional to the major constituents of the materials.

Aluminium is a major constituent of clay. Fe and Mn are the major constituents of Fe-Mn oxides and organic carbon is the principal constituent of organic matter. There is no data on organic carbon for the investigated rocks. However, Leckie et al (1990) showed that elevated concentration of vanadium are associated with organic rich sediments, hence the abundance of V can be used to estimate the abundance of organic carbon.

The correlation coefficients between U, Th and Al_2O_3 , V, Fe and Mn as shown in Table 9 indicate poor correlation between U, Th and the elements of clay, organic matter and Fe-Mn oxides, suggesting that none of these materials is significant in the concentration of the radioactive elements in the investigated rocks.

Table 9: Summary of correlation coefficients between U, Th and heavy elements.

	Al_2O_3	Fe_2O_3	MnO	V	Th	U	Zr	Ce	La	TiO_2	P_2O_5	Y	Nb
U	-0.24	-0.11	0.17	-0.05	0.98	1.00	0.96	0.84	0.82	0.85	0.10	0.97	0.46
Th	-0.13	0.02	0.37	0.05	1.00	0.98	0.95	0.89	0.89	0.88	0.20	0.97	0.53

Alternatively, the radioactive elements may be concentrated by ionic substitution in some heavy minerals which may occur as detrital constituents of the sedimentary rocks. The heavy minerals that can host Th and U include, zircon ($ZrSiO_4$), monazite (Ce, La, Y, Th) PO_4 , apatite ($Ca_5(PO_4)_3(F, Cl, OH)$), sphene ($CaTiSiO_5$), xenotime (YPO_4), pyrochlore (Na, Ca, Nb_2O_6F) and rutile (TiO_2). The correlation coefficients between Th and U and the various elements of the heavy minerals which include Zr for zircon, Ce and La for monazite, Y for xenotime and monazite, Ti for sphene and rutile, Nb for pyrochlore and P_2O_5 for apatite, monazite and xenotime are

given in Table 9. A strong positive correlation between Th and U indicates that both elements are to a large extent carried by the same mineral phase(s).

It can be observed from Table 9 that significant correlation exists between Th and Zr, Th and La, Th and Y, Th and TiO₂ as well as between U and Zr, U and Ce, U and La, U and Y, U and TiO₂. The radioactive elements also weakly correlate with Nb. These correlations imply that the radioactive elements of U and Th are carried by the heavy minerals containing Zr, Ce, La, Y and TiO₂, that is, zircon (ZrSiO₄), monazite (Ce, La, Y, Th)PO₄, xenotime (YPO₄), rutile (TiO₂), apatite Ca₅(PO₄)₃(F, Cl, OH) and sphene CaTiSiO₅ and pyrochlore (Na, Ca, Nb₂O₆F). Lack of correlation between Th and U with P, a major constituent of monazite and xenotime suggests that the role of monazite and xenotime in hosting the radioactive elements is not significant.

The Th/U ratio in the investigated rocks may give a further insight into the possible role of monazite in hosting Th and U. The Th/U ratio in the rocks is relatively uniform, ranging between 4.07 and 4.30. These ratios are similar to the ratios found in zircon (Th/U \approx 0.2 – 5.0) and rutile (Th/U \approx 2) and substantially different from the Th/U ratio of more than 15 found in monazite (see Rogers and Adams, 1969). It is also possible that the correlation of U and Th with Nb is not related to pyrochlore but to the presence of Nb in rutile. According to Blatt et al (1980), rutile sometimes contains some appreciable amount of Nb, Ta and Fe.

The conclusion that can be drawn from above is that zircon and rutile are the main concentrators of U and Th in the investigated rocks including the hot sands with a Ce, La and Y bearing mineral, possibly monazite, playing a minor role. The amount of gamma ray activity given by any of the investigated rock type, therefore, depends mainly on the amount of zircon and rutile in the rock. Thus, the high gamma – ray activity in the hot sand, is coming from the very abundant zircon as shown by high amount of Zr (7729 Zr) and rutile as shown by high Ti (2.83% TiO₂) in the sediment.

3.6. Environment of Deposition of the Hot Sand

The most significant textural feature of the hot sand is the heavy mineral laminae observed in the rock (Fig. 16). Heavy mineral concentration in sedimentary rocks is often regarded as a product of sedimentary sorting and is a characteristic feature of deposits along the foreshore sub –environment (beach) of a shoreline Elliot (1980), Tucker (2001). It is suggested therefore that the hot sand was deposited in the beach environment.

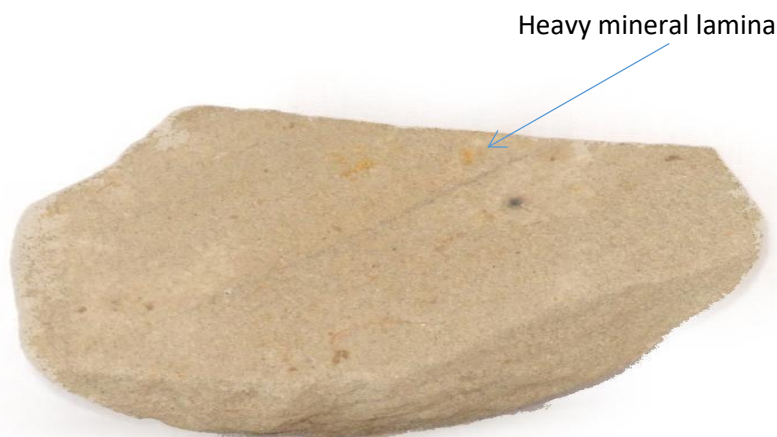


Fig. 16: Photograph of hand specimen of hot sand sample showing laminae of heavy mineral concentration.

The beach sequences along a shore line may be deposited under either regressive (prograding) or transgressive conditions. Pettijohn (1984) and Elliot (1985) described transgressive beach sequences as being characterized by facies dominated by a gradational fining upwards while regressive beach facies are dominated by a gradational coarsening – upward sequences. The investigated sands are characterized by increase in grain size from the bottom to the top sandy units. Busch and Link (1985) after extensive review of various examples of beach sequences concluded that the principal difference in distinguishing a transgressive from a regressive beach sequence is the type of the strata associated with the sands. According to these authors, in transgressive sequences, the sands are overlain by marine shale while in regressive sequences the sands are overlain by brackish (lagoonal) shales. It is instructive to note that a thin layer of coal normally associated with swamps lies between the Upper shale and the Upper sandstone. Pyrite, a mineral commonly found in estuarine and tidal – flat sediments has also been observed in the Lower shale. The pyrite together with coal is indicative of a lagoonal environment for the deposition of the shales of the investigated sequence.

The use of geochemistry in determining the environment of deposition of sediments is not yet widespread. However, some workers have successfully used trace elements concentrations to differentiate between argillaceous sediments of different origin. Degens *et al.* (1957) differentiated between freshwater and marine shales on the basis of the Ga, Rb and B contents. Adams and Weaver (1958) also used the Th and U contents in sedimentary rocks to

differentiate their environments. However, it is trace element ratios that are of more significance. The work of these authors is summarized below Table 10.

Table 10: Elemental ratios in shales associated with the investigated sandstones.

Criterion	Freshwater shale	Brackish water shale	Marine shale	Lower shale (this study)	Upper shale (this study)
*Rb/Ga	8.2	13.3	35.1	2.62	1.71
**Th/ U	>7	2-7	<2	4.62	5.50

* From Degens et al (1957) **From Adams and Weaver (1958)

It can be observed that the shales associated with the investigated sandstones have a considerable lower Rb/Ga ratio than those of marine origin and its Th/U ratios are similar to those found in brackish water shale. The investigated shales may therefore be considered as non – marine. From the discussion above, it can be concluded that the hot sand and the other investigated core samples were deposited during a regressive phase.

3.6.1 Sedimentary Processes of Deposition of the Hot Sand

Whole rock geochemistry, as well as rare earth geochemistry of the investigated sandstones indicates that all the sandstone types are derived from the same source. However the enrichment in high field strength elements (HFSE) – Y, Zr, Nb, Hf, Th and U, and the heavy REE in the hot sand suggest that the sedimentary processes involved in the transportation and deposition of the hot sands were different from those of the other investigated sandstones, particularly the Lower sandstone which is texturally similar to the hot sand. Enrichment of heavy elements in sedimentary rocks is a geochemical “signal” pointing to heavy mineral concentration resulting from hydraulic sorting during sediment transport (McLennan *et al.*, 1993).

Hydraulic sorting can be evaluated from Zr/Sc ratios, Zr is strongly enriched in zircon, whereas Sc is not enriched, thereby making Zr/Sc ratio a useful index of zircon (heavy mineral) enrichment. Rocks associated with heavy mineral concentration are therefore characterized by high Zr/Sc ratios. The hot sand is characterized by extremely high Zr/Sc ratio (average Zr/Sc ratio = 664.9) compared to the Zr/Sc ratio in the Upper sandstone (average Zr/Sc = 219.7) and in the Lower sandstone (average Zr/Sc = 238). McLennan *et al.* (1993) recognized Th/Sc as a good overall indicator of igneous chemical differentiation and used the plot of Th/Sc against Zr/Sc to establish zircon enrichment in modern deep-sea turbidites. A similar Th/Sc against Zr/Sc plot for the investigated sandstones is presented in Fig. 17. It can be observed in the plot

that samples from the Upper and Lower sandstones fall on the same straight line indicating that both Th/Sc and Zr/Sc vary sympathetically. This is attributed to compositional variation in the Upper and Lower sandstones consistent with igneous differentiation being the primary control of variation in the concentration of Th, Sc and Zr in source rocks of the sandstones. However, the hot sand plots a different trend of Th/Sc ratio increasing far less than increase in Zr/Sc ratio, consistent with zircon enrichment.

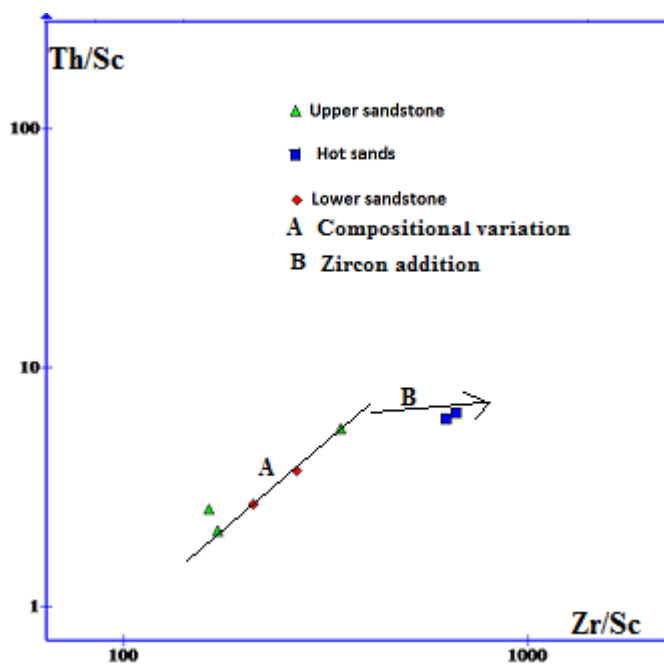


Fig. 17: Th/Sc against Zr/Sc plot for the investigated sandstones showing the enrichment of zircon (high Zr/Sc in the hot sand resulting from sedimentary sorting (after McLennan *et al.*, 1993).

It has earlier been suggested the hot sand was deposited in the beach environment. Deposition of sediments in the beach environment is greatly influenced by the amount of sediments carried by the depositing flow of water. A possible mechanism of deposition of the hot sand and the concentration of its heavy mineral laminae is similar to that described by Imman and Filloux (1960) and Clifton (1969). When concentration of sediment in the transporting medium is normal, the sediments are deposited as the energy of the flow decreases down the beach face. When the concentration of sediments within the bed flow is unusually high, the flow is mechanically placed in a region where the effects of grain inertia dominate. As the bed flow moves along the beach face, hydraulic sorting within the moving layer of densely concentrated sediments occurs. Sediments tend to segregate by settling as one layer of sediments move over another. For any particular density, the flow process tends to segregate the coarser grains towards the top and the finer grains of the same density towards the base of the flow. For

grains of equal size, however, those with greater densities will work their way down through the layer of relatively lighter grains.

Unusually high amount of sediment is only transported during storms. Thus, heavy mineral concentration and by extension hot sand, can only be deposited during storms. The limiting factor in the occurrence of hot sand is therefore the probability of occurrence of storms. The size of the hot sand formed will also depend on the size of the wave which forms it.

Units of mineral concentration formed by the mechanism just described are noted to take the form of irregular ellipses of limited size (Clifton, 1969). This irregular shape and limited size is due to the sporadic occurrence of storms when large amounts of sediments required for the bed flow can be supplied. This probably explains why the hot sands in the Niger delta are of limited thickness and lateral extent

3.7 Impact of the Geochemistry of the Hot Sand on Reservoir Quality

There is very little difference in the whole rock geochemistry of the investigated reservoir sands except for higher TiO_2 in the hot sand probably due to higher amount of titanium minerals like rutile. However, the trace element geochemistry of the hot sand significantly differs from those of the top and bottom reservoir sands. The hot sand is characterized by high amount of Ba, Hf, Zr and the heavy rare earth elements. This is attributed to the higher amount of heavy minerals in the hot sand. The abnormal amount of Ba is attributed to the presence of a barium compound such as barite. The impact of geochemistry on petroleum production capability of the reservoir rocks is the possible reaction of injection fluids with compound such as barite (barium sulphate) in the reservoir rocks. This may cause a decrease in the permeability of the reservoir by precipitating salts in the pore spaces.

4. Conclusion

In conclusion, the high radioactivity observed in the hot sands of the Niger delta is due to gamma activities generated by elevated abundance of Th and to a lesser extent U from concentration of heavy minerals, particularly zircon and to some extent, minor amounts of rutile within the sediments which are deposited in the foreshore environment. The heavy mineral concentration is occasioned by the sedimentary processes at the environment of

deposition. This heavy mineral concentration may constitute a flow barrier within the host reservoir rock.

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