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Trace Element Geochemistry: Evaluation of Petroleum Prospectivity and Paleoenvironmental Interpretation of Upper Cretaceous Sediments of Bornu Basin, NE Nigeria

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Abstract
Detailed geochemical study of shale samples collected from NNPC exploratory wells (Mbeji-1, Murshe-1, Albarka- 1 and Kadaru-1) was carried out to determine their source generative potential. The studies revealed three potential horizons in some of the studied wells with relative increase in trace element concentrations, this virtually showed maturity. The horizons in the exploratory wells are; Mbeji-1 between 2290- 2295m, Albarka-1 between 1600- 1605m, and Kadaru-1 between 2200- 2205m respectively. A redox proxy was also carried out to deduce the ancient depositional environment of the sediments; it showed that the sediments were deposited in anoxic to euxinic paleo-environments which were interpreted from the values of V/Cr ratios.

Keywords: *Trace elements , Geochemistry, Palaeoenvironmental ,Upper Cretaceous and Bornu Basin*

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I. Introduction

In petroleum exploration, inorganic geochemistry is an indispensible tool for identifying source rocks and their classification. Trace elements data of crude oils have been reported to be equally effective in classifying and correlating crude oils and are relative to organic geochemical methods (Hitchon and Filby, 1984; Lewan, 1984; Curiale, 1987; Barwise, 1990, Udo et al., 1992; Oluwole et al., 1993; Akinlua et al., 2007).

The nature of occurrence of metals, their distribution patterns and concentrations in crude oils and extracts can give information on the origin, migration, environment of deposition and maturation of petroleum (Elirich et al., 1985; Barwise, 1990; Oluwole et al., 1993). Trace metals are incorporated into oils in form of porphyrin complexes (species) in petroleum source rocks and may involve direct incorporation from the biomass and formation during sedimentation. It may also involve diagenesis from organic molecules as well as metals derived from different biogenic and abiogenic sources (Akinlua et al., 2007). Lewan (1984) has shown that source rock, type of organic matter and depositional environment has profound effects on the concentration of trace elements in source rocks. However, metals of proven association with organic matter may be used as reliable correlation tools. Nickel, Vanadium and Cobalt are such examples.

The present study is therefore making an attempt to evaluate some raw shale obtained from NNPC drilled holes for their possible petroleum generation and to also determine the depositional environment of the sediments using the geochemical data obtained.

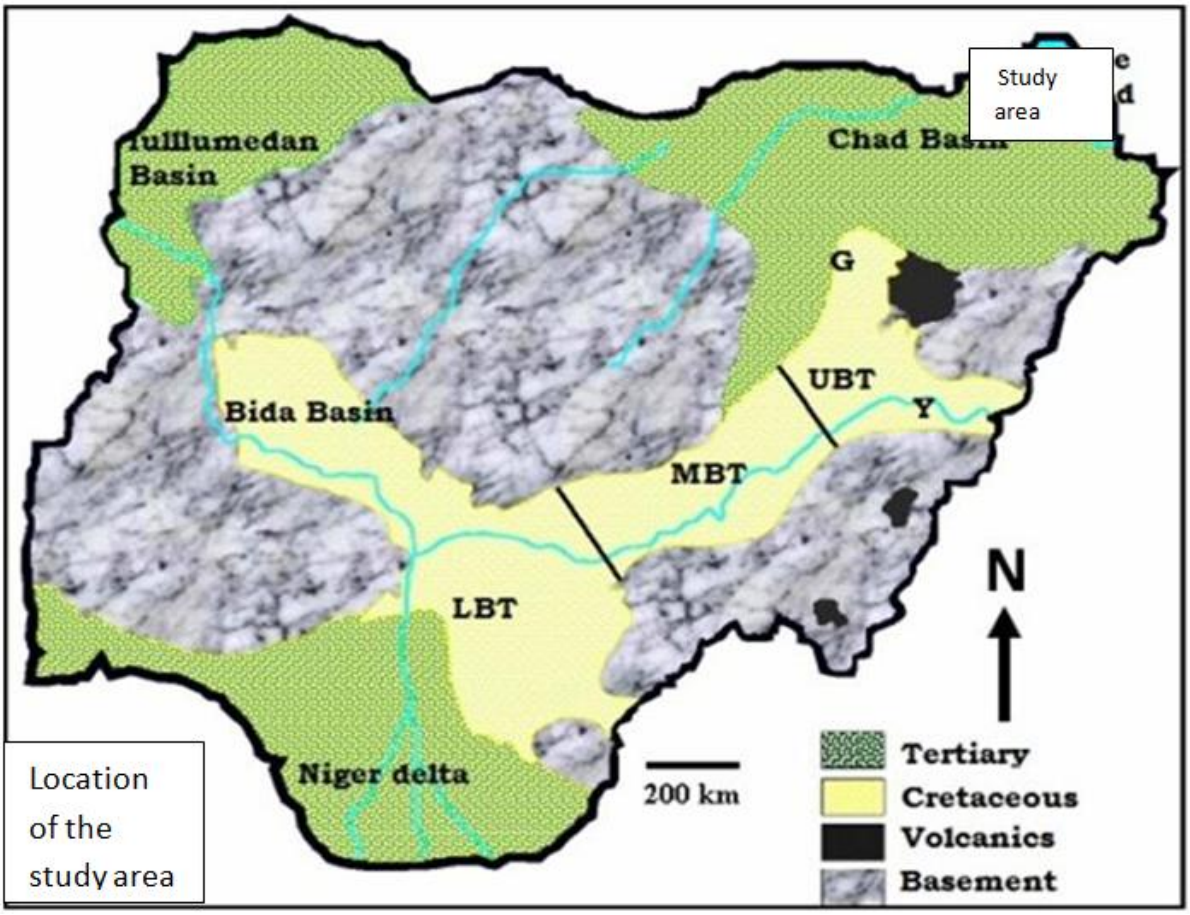

Fig. 1. Geological map of Nigeria showing the location of the study area (After Obaje et al., 1999)

Regional Geology of the Bornu Basin

The Bornu Basin is covered by a monotonous basin wide, Quarternary deposit, the Chad Formation. Sediments below this cover are nowhere exposed except at southern edge where the basin wedges with the neighbouring Benue Trough (Avbovbo et al., 1986; Olugbemiro et al., 1997) and Biu Plateau.

The Benue- Chad Trough is believed to be a third and "Failed Arm" of a triple-junction rift system that formed before the opening of the South Atlantic in the Early Cretaceous with the subsequent separation of the African and South American continents (Burke et al., 1970).

Sedimentation in the Bornu Basin began with a continental, sparsely fossiliferous, poorly sorted, medium to coarse- grained feldspathic sandstone known as the Bima Sandstone which consists of shales in some places. The Bima Sandstone is overlain by the Gongila Formation which is composed of calcareous shales and sandstones deposited in a shallow marine environment. The deposition of this lithological unit marked the onset of marine incursion into the basin. The marine transgression, which started in Albian, reached its peaked in Turonian, during which bluish- black, ammonite- rich, open marine Fika Shale was deposited, this deposition continued into the Senonian. The Turonian- Senonian transgression was succeeded by a regressive phase. In the Maastrichtian, an estuarine/deltaic environment prevailed in the NE Nigeria and the Gombe Sandstone, which contains siltsones, shales and ironstones, was deposited. During the Late Maastrichtian, a structural deformation occurred and reached up to the end of Cretaceous. Graben faults trending NE- SW with subsidiary faults trending NW- SE directions were reported by (Avbovbo et al., 1986 and Mohammed, 2021).

The remnant basin that succeeded this deformation formed the site for the deposition of the Tertiary Kerri- Kerri Formation, which unconformably rest on the Cretaceous sediments. In the Pliocene, the continental lacustrine deposits of the Chad Formation were laid down unconformably on top of the Kerri- Kerri Formation. In recent times, sand dunes have accumulated in the Bornu Basin (Olugbemiro et al., 1997) and the youngest deposits are river alluvium, deltaic and lagoonal clay flats which blankets wide areas to the south and SW of the Lake Chad.

Table1.Lithostratigraphic succession of the Bornu Basin(After Olugbemiro*etal.*,1997and Mohammed,2008).

AGE	FORMATION	LITHOLOGY	THICKNESS (M) *	THICKNESS FROM SEISMIC DATA (M) **	AVERAGE THICKNESS (M) ***	DEPOSITIOAL ENVIRONMENT
Pliocene, Pleistocene	Formation	Clay, Sand	Not investigated	800	400	Continental
Palaeocene	Kerri-Kerri Formation	Coarse sandstones, Claystones, Sandstones	Not investigated		130	Continental
Turonian-Santonian	Fika Shale	Blue-black Shale with volcanic	840-1453	0-900	430	Marine
Turonian	Gongila Formation	Sandstones, Shales	162-420	0-800	420	Marine, Estuarine
Cenomanian	Bima Formation	Sandstones	716-850	2000	3050	Continental

***************CRYSTALLINE BASEMENT**************************

*Carter*etal.*,(1963)**Avbovbo*etal*(1986)***Olugbemiro*etal*(1997)

II. Materials and Methods

About twenty (20) shale samples were collected from different wells drilled by the NNPC which were used for the geochemical analysis from Kadaru-1, Albarka-1, Murshe-1 and Mbeji-1 wells respectively.

Experimental Analysis

Sample Preparation

Twenty (20) shale samples were selected for the geochemical studies. The samples were used for the analysis to determine the concentrations of some trace elements with Microwave Plasma Atomic Emission Spectroscopy (MP-AES). Detail methodology of MP-AES agilent 4200 application is discussed below as described by (Laura et al., 2017). Rock samples used for the analysis were pulverized into fine powder of about 100-mesh size using pestle and mortar. They were grined, washed and dried to avoid contamination.

Sample Digestion

10mL of 1:1 HNO3 was added to 1.00g of shale sample in a 25x150mm glass digestion tube and the samples were heated to 95+/- 10oC for about 15 minutes. After cooling, 5mL of HNO3 was Milli-Q water and 3ml of 30% H2O2 was added and heated to 95+/- 5oC. After the digests were cooled, another 1mL of 30% of H2O2 was added. Heating continued until the sample volumes reduced to approximately 5mL. The digests were allowed to cool and then diluted to 50ml with Milli-Q water. Prior to analysis, the shale digests were diluted x10 with Mili-Q water to reduce the effect of background emission due the high sample matrix.

Microwave Plasma Atomic Emission Spectroscopy (MP- AES)

The agilent 4200- MP-AES generates a self-sustained atmospheric pressure microwave plasma (MP) using nitrogen gas and a modified inductively coupled plasma torch. Sample introduction to the MP is pneumatic using a concentric nebulizer and cycloric sprey chamber system, and emission line isolation and detection is sequential using a Czemy-Turner monochromator and charge-coupled device system. This analysis was carried out at the Centre for Dryland Agriculture, Bayero University, Kano (BUK).

III. Results and Discussions

Geochemical data of twenty selected raw shale samples which were analyzed for trace element concentrations is presented in Table 2 and Figures 2 and 3 respectively. Figures 2 and 3 are plots of trace element concentrations with three (3) peaks noticeable in Mbeji-1, Albarka-1 and Kadaru-1 wells respectively. No peak was observed within Murshe-1 well.

Trace Element Geochemistry

Transition metals have been found to be very useful in petroleum exploration, as well as crude oil characterization (Curiale, 1987; Barwise, 1990; Udo et al., 1992; Nwachukwu et al., 1995). In this study, special attention is given to the following metals: ZN, Cd, V, Fe, Cu, Ni, Co, Pb, Mo, Cr and Mn.

Table 1: Concentration of some trace elements of the Bornu Basin from (Albarka-1, Murshe-1, Mbeji-1 and Kadaru-1) exploratory wells.

Sample ID	Zn	Cd	V	Fe	Cu	Ni	Co	Pb	Mo	Cr	Mn
Mbeji-1765-1770m	46.00	9.34	127.77	369.33	4.70	23.85	8.01	1.47	0.23	0.83	404.62
1875-1880m	65.59	11.01	2.87	445.93	3.55	5.31	2.75	4.93	0.23	0.55	296.76
1995-2000m	57.21	10.62	7.22	369.54	4.41	2.56	3.11	3.48	0.34	0.11	206.99
2180-2185m	39.60	13.90	3.61	516.85	5.93	4.64	5.40	7.59	0.32	3.60	267.88
2235-2240m	42.68	11.57	6.12	418.77	8.00	5.05	4.05	2.97	0.25	9.83	246.97
2290-2295m	247.94	207.06	40.09	3040.10	71.19	43.83	31.18	240.21	2.88	55.61	1325.31
2385-2390m	20.89	14.00	5.46	422.15	4.29	8.38	2.77	3.90	0.40	6.60	46.96
Murshe-1320-1325m	42.53	12.60	5.27	454.04	7.31	2.92	3.15	2.19	0.32	0.03	184.78
1845-1850m	28.10	9.48	7.57	416.16	5.12	5.22	2.62	1.47	0.21	0.08	128.50
1940-1945m	31.13	15.21	2.57	571.48	5.66	11.96	5.78	10.51	0.44	4.55	95.33
2000-2005m	31.47	10.26	124.74	480.45	8.39	7.80	7.27	5.25	0.33	4.29	392.93
2545-2450m	24.82	24.82	6.07	576.00	5.77	4.81	3.49	5.73	0.40	17.49	177.34
3920-3925m	23.57	14.04	6.50	519.71	5.90	1.92	2.64	5.72	0.39	4.52	51.18
Albarka-1600-1605m	551	113.40	27.41	3430.64	89.28	43.52	24.34	2.83	3.13	1.86	1856.10
1605-1610m	21.11	18.84	4.66	723.59	10.20	1.77	2.51	8.76	0.41	6.71	97.89
1800-1805m	72.46	10.66	7.74	344.97	5.90	4.71	2.98	2.47	0.24	0.01	193.89
1985-1990m	46.12	12.67	68.78	442.20	6.28	4.14	4.25	5.72	0.34	0.43	101.77
Kadaru-2200-2205m	403.89	156.77	24.38	4001.51	76.68	34.05	14.77	5.76	4.43	2.86	1500.05
2800-2805m	21.79	21.79	4.32	574.59	6.79	2.93	3.54	2.20	0.40	1.24	214.74
3825-3830m	28.08	12.73	3.45	545.25	8.34	1.93	2.52	2.54	0.34	3.76	92.42
Total	1845.98	710.77	486.6	8,718.51	343.69	221.3	137.13	325.7	16.03	127.93	3,825.55
Average	92.29	35.53	24.33	435.92	17.18	11.06	6.85	16.28	0.80	6.39	191.27

Table3.RedoxoftraceelementconcentrationofV/Crratio

Sample ID	V/Cr
Mbeji-1765-1770m	0.622
1875-1880m	2.87
1995-2000m	230.90
2180-2185m	1.002
2235-2240m	65.63
2290-2295m	0.82
2385-2390m	0.72
Murshe-1320-1325m	29.07
1845-1850m	94.62
1940-1945m	175.66
2000-2005m	1.43
2545-2450m	0.56
3920-3925m	0.34
Albarka-1600-1605m	774
1605-1610m	159.95
1800-1805m	0.69
1985-1990m	14.73
Kadaru-2200-2205m	0.91
2800-2805m	3.48
3825-3830m	8.52
Total	1,566.44
Average	78.32

Zn range from 21.11 to 551ppm with an average of 92.29ppm, the values are higher than those obtained by Mohammed (2018) in the Bornu Basin and Onajake et al., (2011) from Umutu/Bomu Fields in SW Niger Delta. The result therefore shows some prospect in terms of maturity. Cd range from 9.34 to 207.06ppm with an average of 35.53ppm, the values are higher than those obtained by Mohammed (2018) and most of Niger delta crude oils, and this signifies prospectivity. The greater depth of burial has aided the maturation and high values especially in Kadaru-1 well at a depth between 2200- 2205m and Albarka-1 well at a depth between 1600- 1605m as well as Mbeji-1 well at a depth between 2290- 2295m. The values at these horizons are greater than those obtained by the former authors who worked in the basin, such that at every 1km there is an increased of approximately 10oC. Time temperature index (TTI) of maturity plays a vital role in aiding maturation of organic matter, the greater the depth, the more a sediment is expected to mature and the higher the temperature the faster the organic transforms into kerogen as well. Fe concentration range from 344.97 to 4001.51ppm with an average 435.92ppm, the values are higher than those reported by Mohammed (2018) and Niger Delta crude oils (Udo et al., 1992; Oluwole et al., 1995; Onajake et al., 2011) and New Zealand crude oils (Frankenberger, 1994).

Cu concentration range from 3.55 to 89.28ppm with an average of 17.18ppm, the highest was obtained at a depth of 1600- 1605m; this particular horizon is considered a prospective zone for petroleum generative window. Ni concentration range from 1.92 to 43.83ppm with an average of 11.06ppm, the values are relatively higher than those reported by Mohammed (2018) and most of Niger Delta crude oils reported by several authors. The high concentration value of Ni can be related to greater depth of burial, which is below the proximal zone drawn by Whiteman (1992) as an interdigitation between marine and non- marine sediments which have a good prospect for petroleum generation. Ni as a biophile element is very important tool used in the interpretation of petroleum generation and organic matter assessment for their kerogen type. Co concentration range from 2.51 to 31.18ppm with an average of 6.85ppm, these values are higher than the ones reported by Mohammed (2018) and most of Niger Delta crude oils, the average value signify maturity in terms of petroleum generation this is so because whenever biophile elements tends to have high concentration of elemental value than crude oils, it clearly shows promising oil window within such horizons. Pb concentration range from 1.47 to 240 ppm with an average value of 16.28ppm, the values are also higher those of Mohammed (2018) and Niger delta crude oils. Mo concentration range from 0.21 to 3.13ppm with an average of 0.80ppm, the values signify prospect with relative concentration of organic matter within matured zone, and further explains considerable input of trace elements. Cr concentration range from 0.03 to 55.6ppm with an average of 6.39ppm, the values are higher than those reported by Mohammed (2018) and most of Niger Delta crude oils. Cr is not mostly detectable, where it is detected, it can be used for oil- oil correlation (Barwise, 1990). Mn concentration range from 46.96 to 1856ppm with an average of 191.27ppm, this is the second most abundant trace elements analyzed and has concentration values higher than those reported from the fringes of the Bornu Basin and Niger Delta crude oils. Frankenberger (1994) reported that raw shales and extracts are relatively higher in terms of concentration than crude oils when they mature, therefore, the results obtained from the study area conform with the above statement and can be concluded that the three prospective horizon with high concentration of these trace elements are petroleum maturation zones.

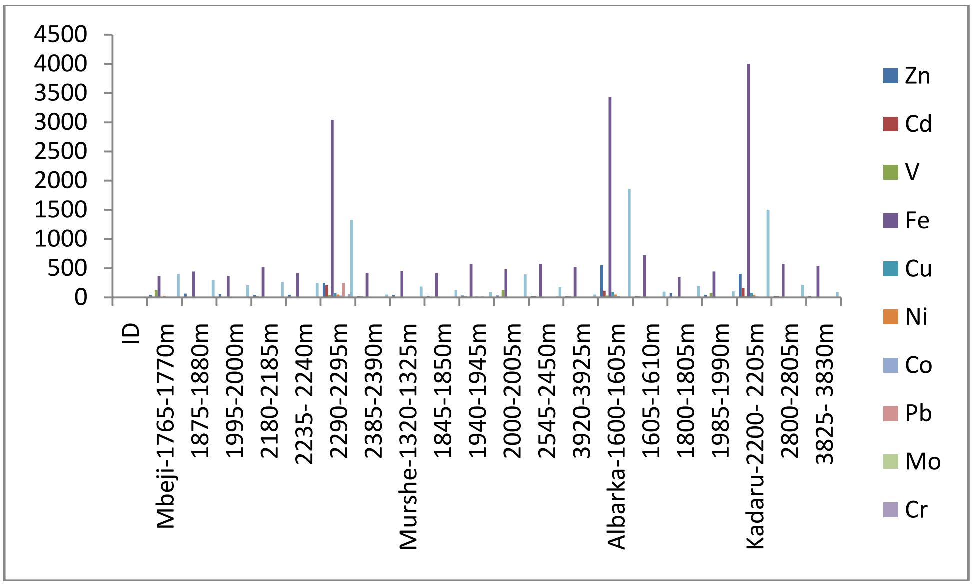

Fig.2.Plot of concentration of trace elements against burial depth represented in columns

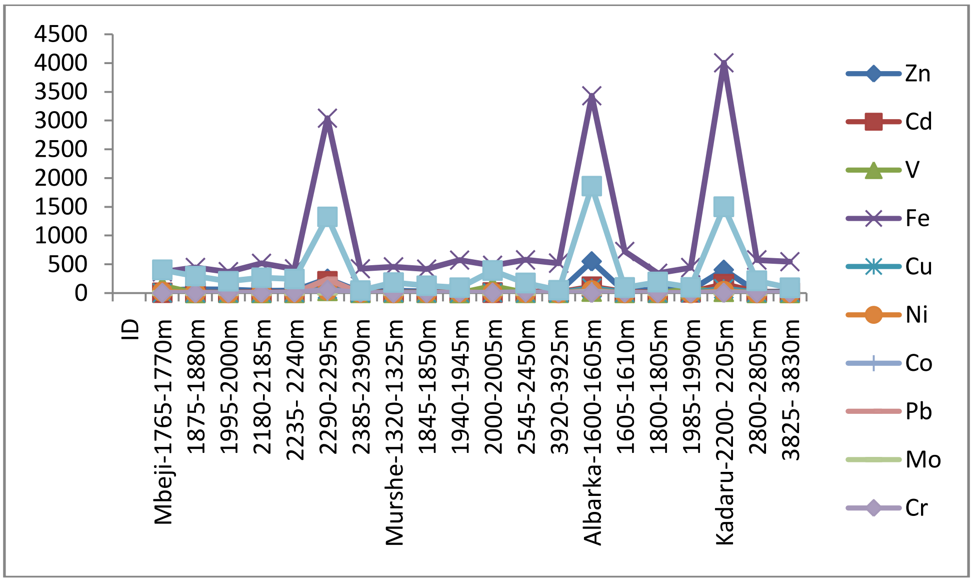

Fig. 3. Plot of concentration of trace elements against burial depth represented in line graph.

Distribution Pattern and Maturation of Source Rocks

Distribution pattern in terms of decreasing concentrations

Fe>Mn>Zn>Cd>V>Cu>Pb>Ni>Co>Cr>Mo

Three peaks can be observed in figures 3 and 4 which clearly demonstrate the horizons that are prolific with regards to petroleum generative potential. Mbeji-1, Albarka-1 and Kadaru-1 wells are the prospective wells.

The high concentration of Fe as reported by Mohammed (2018) in Bornu Basin may be due to substitution reaction which might have replaced other metals from original biological matter or could have been incorporated from solid or aqueous phases. The overall results can be said to be good for petroleum generation, such that the biophile elements tends to have considerable high concentrations than most Nigerian crude oils and shales at the fringes of Bornu Basin. The trace elements might have entered into the gas generative window as reported by several authors who have worked on different wells explored by NNPC (e.g. Olugbemiro et al., 1997; Obaje et al., 2004, 2006; Alalade and Tyson, 2010; Mijnyawa et al., 2012; Mohammed, 2010, 2018). The study area has been reported to have intra- sedimentary intrusives which might have aided the increase in temperature form oil generated to gas preservation deadline.

Redox Trace Element Concentrations

Redox trace element concentrations have been used as an indicator of paleo-redox conditions in the study source rocks (Vine and Tourtelot, 1970; Calvert and Pederson, 1993; Esmart and Mohammed, 2015; Nzekwe and Okoro, 2016). High enrichment of trace element in black shales are related to anoxic and euxinic environments (Vine and Tourtelot, 1970; Algeo and Maynard, 2004). The results of the redox- sensitive composition of Gongila Formation and Fika Shales is shown on Table 3.

Redox Proxies

Trace elements indices V/Cr have been used to evaluate paleo-redox conditions (Hatch and Levanthal, 1992; Jones and Manning, 1994;; Nzekwe and Okoro, 2016). According to Jones and Manning (1994), V/Cr ratios above 2 indicate anoxic condition, while values above 4 indicate euxinic condition. Values below 2 suggest more oxidizing condition. From the results obtained, it can therefore be interpreted that the Shales of the two formations (Gongila and Fika) are majorly deposited in essentially anoxic-euxinic paleo-environmental conditions whose value range between 0.34 to 230.90ppm with an average of 78.32ppm respectively.

IV. Conclusion

Geochemical investigation revealed source generative potential of Mbeji-1, Albarka-1 and Kadaru-1 wells of Gongila Formation and Fika Shales in the Bornu Basin. Results obtained showed the prospectivity of trace element concentrations at different horizons with uniform increased metals. Fe has the highest concentration with Mo having the less with low detection limits. Redox proxies indicates that V/Cr ratio supported anoxic and euxinic paleo-environment of deposition.

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