
APPLICATION OF ORGANIC AND INORGANIC PETROLEUM GEOCHEMISTRY IN EXPLORATION AND EXPLOITATION OF A PROLIFIC BASIN: A GENERAL REVIEW

Y. B. Mohammed¹, H. Hamza² and U. A. Danbatta²

¹*Department of Geology, University of Maiduguri, Maiduguri, Nigeria*

²*Department of Geology, Ahmadu Bello University, Zaria, Nigeria*

ABSTRACT

This paper overviews organic and inorganic petroleum geochemical methods from some selected prolific basins for exploration and exploitation. The geochemical parameters includes: Carbon Preference Index (CPI) whose value is influenced by the type of organic matter and maturity. Biomarker indicator of oxicity and anoxia which basically determines the environmental conditions of deposition of a source rock and perhaps most especially the degree of oxygenation using these parameters such as: Pr/Ph ratio; trisnorneohopane versus (trisnorneohopane + trisnorhopane)TS/TS + TM) ratio; steranes as maturity indicator; C₂₇: C₂₈: C₂₉ regular steranes and saturated hydrocarbons (SHC), aromatic hydrocarbons (AHC) and Nitrogen, Sulphur and Oxygen (N,S,O) and Soluble Organic Matter (SOM). Trace elements geochemistry of transition metals is also very useful in crude oil characterization especially in oil- oil correlation. Ratios of transition metals, particularly V/Ni, V/Ni+V, Co/Ni and Fe/V are use for determination of maturity level of source rocks and source input of organic matter type.

Keywords: *Organic, inorganic, petroleum, exploration and exploitation.*

INTRODUCTION

In petroleum exploration, organic geochemistry has been found to be an indispensable tool both at the initial and advanced stage in identifying source rocks and classifying crude oils into families (Ekweozor *et al.*, 1979; Doust and Omotsola, 1990). Classification of crude oils into families helps locate hydrocarbons in explored areas at different stratigraphic units of a basin. It is now known that organic geochemistry is also very useful in petroleum production (Karlsen *et al.*, 1995; Larter and Aplin, 1995). Organic geochemical methods of crude oil include biomarker fingerprints, stable isotope ratios and hydrocarbon contents etc., which are fairly expensive (Akinlua *et al.*, 2007). Trace elements data of crude oils have been reported to be effective in classifying and correlating oil 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 and Abubakr *et al.*, 2010). The nature of occurrence of metals, their distribution patterns and concentrations in crude oils can give information on the origin, migration, environment of deposition and maturation of petroleum (Elirich *et al.*, 1985; Barwise, 1990; and Oluwole *et al.*, 1993). Trace metals are incorporated into oils in form of porphyrin complexes (species) in petroleum source rocks and may include direct incorporation from the biomass and formation during sedimentation (Akinlua *et al.*, 2007). It may also involve diagenesis from organic molecules as well as metals derived from biogenic (biomass) and abiogenic (weathering of minerals) sources. Lewan (1984) has shown that source rock, type of organic matter and depositional environment have profound effects on the concentration of trace elements in source rocks. There may be difficulty in correlating

oils and or/source rocks using trace elements contents. However, metals of proven association with organic matter may be used as reliable correlation tools. Nickel, Vanadium, and Cobalt (usually referred to as biophile elements) are such examples. Concentration of metals in crude oils can be used to classify oils into families. Low V/Ni ratio (<0.5) are expected for petroleum derived from marine organic matter, with high to moderate Sulphur content, while V/Ni ratios (1- 10) are expected for petroleum derived from lacustrine and terrestrial organic matter (Barwise, 1990). Oils from marine organic matter have high concentrations of metals (particularly Ni and V), this is expected since for marine source rocks, there is an abundant input of porphyrin- precursor chlorophylls to the organic matter derived from algae and bacteria (Barwise, 1990).

Moderate quantities of metals are found in oils derived from lacustrine source rocks while little nickel and vanadium are found in land- plant derived. The V/Ni ratios tends to increase with increasing Pr/Ph ratios and 18H- oleanane/ 17H, C₃₀- hopane ratios, suggesting high terrigenous source input (Udo *et al.*, 1992). Lewan (1984) reported that V/(V+Ni) ratio is negatively correlated with the even predominance of n-alkanes and the Pr/Ph ratio, but it is positively correlated with the Ph/nC₁₈ ratio, which infers marine organic matter input. Nickel, Cobalt, Strontium, Silver and Bismuth have been found to correlate positively with the absolute amount of heavy n-alkanes in the petroleum, as these elements are relatively more abundant in parafinic petroleum (Karlsen *et al.*, 1995). Enriched V and Ni concentrations greater than 100ppm are observed in bitumens that are associated with Type II and Type I kerogens. Bitumens associated with Type III kerogens contained V and Ni concentrations less than 100ppm (Lewan, 1984).

Lewan and Maynard (1982), Lewan (1984) reported that source rock type and depositional environment have a profound effect on the predicted levels of nickel and in the source rocks. Barwise (1990) also reported that there is a systematic variation in the nickel and vanadium content of crude oils which can be related to depositional environment and source rock types. This implies that the source depositional environment determines the proportion of vanadium to nickel in crude oil. It has been proved that high V/Ni ratio is associated with anoxic palaeoenvironment of deposition ((Lewan, 1984) whilst both V/Ni and Co/Ni ratios have been shown to be anoxic/oxic related parameters (Udo *et al.*, 1992). An inverse proportional relationship exists between American Petroleum Institute (API) gravity and the total transition metal contents. The API gravity is also inversely correlated with each of Cu, Ni, V, Se, Mn and Cr (Oluwole *et al.*, 1993). These infer that total transition metal content decreases with an increase in oil maturity. Many workers have used the V/Ni ratio as indicator of oil maturity (Barwise, 1990; Udo *et al.*, 1992). Udo *et al.* (1992) reported that V/Ni ratio decrease as Pr/nC₁₇ ratio decreases and as depth and API gravity of oils increase, thus suggesting that V/Ni decrease with increasing maturation. Barwise (1990) also reported that high concentrations of metals are only associated with oil of low to moderate API gravity. He further stressed that the highest concentrations of metals are found in matured oils.

Organic and Petroleum Geochemistry

Organic geochemistry is the application of chemical principles to the study of the origin, migration, accumulation and alteration (Hunt, 1979). Petroleum is generally considered oil and natural gases having various compounds composed primarily of hydrogen and carbon. They are usually generated from the decomposition and/or thermal maturation of organic matter. Organic matter originated from plants and algae. The organic matter is deposited after the death of plants and animals in sediments, where after considerable time, heat, and pressure, the compounds in the plants and animals are altered to kerogen, oil and gas. Kerogen can be thought of as the remaining solid material in the plant and animals. The sediment – usually clay and/or calcareous (time) ooze, hardens during this alteration process into rock i.e. shale or limestone. The distribution of n-alkanes in crude oils can be used to indicate the organic matter source (Han and Calvin, 1969; Volkman *et al.*, 1981; Duan, 2000; Duan and Ma, 2001; and Duan *et al.*, 2006). Generally, short and medium chain odd carbon numbered compounds of aliphatic hydrocarbons with carbon numbers between n-C₁₅ and n-C₂₅ are associated with aquatic sources, where shorter derivatives originate from lacustrine algae (Abubakr *et al.*, 2010), in contrast to mainly macrophytic plants as sources of the longer chain derivatives (Duan and Ma, 2001 and Ficken *et al.*, 2000). Compounds with carbon numbers between n-C₂₇ to n-C₃₃ mainly originate from cuticular waxes of higher land plants (Cranswell, 1973).

Carbon Preference Index

The CPI value is influenced by the type of organic matter and by maturity (Tissot and Welte, 1984). High CPI values represent an odd carbon number preference, over even, and occur in response to the chemistry in higher plants of surface waxes (an important precursor components in sedimentary organic matter), Abubakr *et al.* (2010). Hydrocarbon thought to have been derived from coaly organic matter sources contain CPI value equal to or greater than one. Moldowan *et al.* (1985) reported that, an odd carbon preference is characteristics of oils derived from source rocks deposited in non-marine depositional environments. Similarly, the predominance of an even numbered n-alkane preference is commonly observed in bitumens and oils derived from carbonate or evaporite rocks (Fischer, 2004). If the total even and odd numbers of paraffins are equally abundant the value of the (CPI) will be equal to one, as is generally observed in high maturity samples (Tissot and Welte, 1984).

Biomarker Indicators of Oxicity and Anoxia

Determining the environmental conditions of deposition of a source rock and perhaps most especially the degree of oxygenation (which influences organic matter preservation) is of fundamental importance in source rock quality prediction within a basin. The following parameters are use for such exercise: i) Pr/Ph ratio; ii) Triesnorneohopane versus (triesnorneohopane + triesnorhopane) TS/(TS+TM) ratio; iii) Steranes as maturity indicators; iv) C₂₇: C₂₈: C₂₉ regular steranes: and v) Saturated Hydrocarbons (SHC), Aromatic Hydrocarbons (AHC) and Nitrogen, Sulphur and Oxygen (N,S,O) and Soluble Organic Matter (SOM).

Pr/Ph Ratio

The most widely used biomarker parameter for the assessment of redox conditions during sediments accumulation is the Pristane/Phytane ratio. The idea that the ratio of these two acyclic isoprenoid alkanes is influenced by the degree of oxygenation was first voiced by Brooks *et al.* (1969) and developed by Didyk *et al.* (1978). These authors proposed that Pr/Ph ratios of >1 indicated oxic conditions of sedimentation (at the sediment/water interface), whilst values of <1 reflected anoxic conditions and recommend the use with other parameters. Peters *et al.* (2005) recommend that Pr/Ph ratio should not be used in immature samples. Obaje *et al.* (2004) reported Pr/Ph ratios from 0.80 to 2.98 in the Chad Basin indicating fluctuating anoxic and oxic depositional environments and the predominance of Type III organic matter with dominantly marine (as confirmed by the high contents of C₂₇ steranes) which may be attributed to high oxic level (high Pr/Ph ratios) in the marine systems. Relatively higher trinis and trisnorneo- hopanes (Ts/Tm) and lower moretane/hopane level in some studied wells showed that the source rocks have entered the early and main phase of hydrocarbon generation. Table 1 below shows some biomarker parameters of selected wells from the Chad Basin in Nigeria.

Table 1. Biomarker parameters of some studied wells in the Nigerian sector of the Chad Basin (After Obaje *et al.*, 2004)

Samples ID	Formation	Pr/Pr	Ts/Tm	m/αβH	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)	C ₂₇ /C ₂₈
KM-1 1680	Fika	0.80	0.33	0.15	46.6	21.1	32.3	1.4
KM-1 1620	Gongila	1.66	0.85	0.10	41.7	18.9	39.4	1.1
MS-1 1005	Gongila	1.01	0.38	0.18	47.2	19.2	33.6	1.4
MS-1 1155	Gongila	0.72	0.88	0.13	17.8	18.8	63.4	0.3
TM-1 2605	Gongila	1.30	0.83	0.10	44.7	22.0	33.3	1.3
ZY-1 885	Fika	2.83	0.22	0.31	52.2	22.8	25.0	2.1
ZY-1 1210	Fika	2.85	1.25	0.11	46.8	18.8	34.4	1.4
Zy-1 1325	Gongila	2.97	0.97	0.10	49.1	20.8	30.2	1.6
ZY-1 1880	Gongila	2.98	0.92	0.10	46.2	18.5	35.3	1.3
ZY-1 2840	Gongila	0.98	0.94	0.09	48.6	18.9	32.4	1.5

Furthermore, moretanes are less stable than 17α (H)- hopanes (Waples and Machihara, 1990) and 0.8 was reported immature sediments to about 0.15- 0.05 in mature source rocks and oils (Mackenzie *et al.*, 1980; Seifert and Moldowan, 1981).

Triesnorneohopane Versus Triesnorneohopane + Triesnorhopane TS/(TS+TM) Ratio

This is applied in petroleum geochemistry as maturity parameter (Farrimond *et al.*, 1999). Therefore, the ratio increases with increasing organic matter maturity (Peters and Moldowan, 1991; Seifert and Moldowan, 1978). The ratio is particularly useful in oil windows, where it responds sensitively to maturity increments before approaching unity in zones of higher maturity (Murray and Boreham, 1992).

Steranes as Maturity Indicator

20S/(20S+20R) Ratio: With increasing thermal maturity, the concentrations of (20R) and C₂₇, C₂₈, C₂₉ regular steranes decrease relative to that of the corresponding 20S epimer (Mackenzie *et al.*, 1980, 1982), which has been used to assess the thermal maturity for both sedimentary organic matter and crude oils (Peters and Moldowan, 1991; Waples and Machihara, 1991; Mackenzie *et al.*, 1980; and Seifert and Moldowan, 1980). The ratio of 20S/(20S+20R) rises from 0 with increasing maturity until an equilibrium is reached at 0.52-0.55 (Seifert and Moldowan, 1981) or 0.5 (Gallegos and Moldowan, 1992). Abubakr *et al.* (2010) reported that some analyzed samples from Western Desert, in Egypt as in the table 2 below indicate mature oil, but have not reached the equilibrium stage.

Table 2. Steranes and Regular Steranes Distribution in Crude Oils (Modified from Abubakr *et al.*, 2010)

Sample NO.	C ₂₉ R/C ₂₇ R	C ₂₈ R/C ₂₉ R	20S/(20S+20R) ratio	Age
Elfaras-1	0.8681	1.00	0.295	Late
Elfaras-3	0.6063	1.08	0.256	Jurassic-
Raml-1	0.6235	0.96	0.298	Cretaceous

C₂₇: C₂₈: C₂₉ regular steranes: The relative abundance of C₂₇, C₂₈, C₂₉ steranes have been reported to be sensitive to organic matter type (Gurgey, 1999; Huang and Meinschein, 1979). It has been indicated that, C₂₇ steranes are derived essentially from marine phytoplankton, whereas abundant C₂₉ steranes indicate a strong contribution from higher plant organic matter. Consequently, the predominance of C₂₉ /C₂₇ steranes (>1) has been reported in terrestrial plant- rich sediments Czochanska *et al.*(1988), and the reverse has been obtained in rocks containing marine algae; abundance of C₂₈ compounds may indicate a contribution by lacustrine algae (Waples and Machihara, 1991).

Saturated Hydrocarbons (SHC), Aromatic Hydrocarbons (AHC) and Nitrogen, Sulphur and Oxygen (N, S, O) and Soluble Organic Matter (SOM)

These hydrocarbon and heteroatomic compounds have been reported from various wells and sections in the Nigerian sector of the Chad Basin by several researchers (e.g. Petters and Ekweozor, 1982; Idowu and Ekweozor, 1989, 1993; and Mohammed, 2010, Mohammed *et al.*, 2011) and their investigations mostly reveal gas- prone. This is due to possibility that the hydrocarbons generated have entered the gas phase and exceeded the oil generative window, but have not yet reached the dry gas preservation deadline. Tables 3&4 below shows analyzed samples from the Chad Basin of some selected wells and figures 1- 4 show maturity levels of the hydrocarbon (SHC&AHC) compounds in Herwa-1 well whereas in Kadaru-1 well the heteroatomic (N,S,O) compounds predominates. The data obtained for soluble organic matter also corresponds with that of the hydrocarbon compounds which relatively show increasing maturity in the same dimension.

Table 3: Organic geochemical analysis of some sampled sections from Kadaru-1 well (After Mohammed, 2010)

Depth (m)	SOM (ppm)	SHC (ppm)	AHC (ppm)	NSO (ppm)
1645	200	41	37	163
1950	100	7	90	2
2200	100	2	1	71
2590	100	1	30	58
2800	100	30	21	48
3270	200	27	115	70
3445	200	110	7	93
3825	100	8	1	90
4300	100	1	74	2
5000	100	1	7	81

Table 4: Organic geochemical analysis of some sampled sections Herwa-1 well (After Mohammed, 2010)

Depth (m)	SOM (ppm)	SHC (ppm)	AHC (ppm)	NSO (ppm)
1745	200	1	31	125
1995	300	10	221	43
2250	500	10	70	383
2450	800	200	131	423
2875	200	2	5	171
3250	100	3	21	112
3500	200	3	8	172
3750	200	101	7	81
4355	200	4	108	52
4650	100	1	51	172

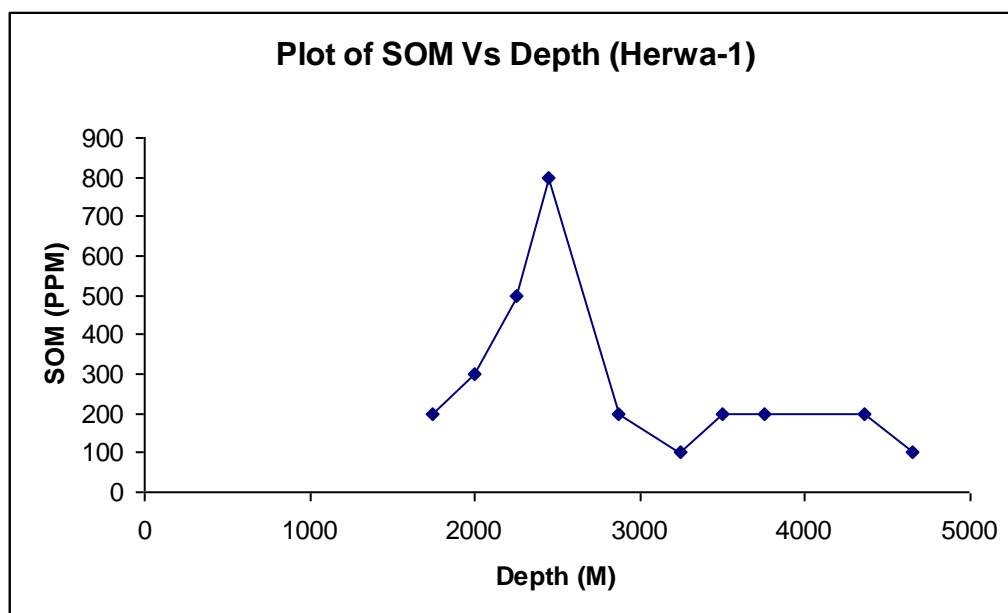


Fig. 1. Plot of soluble organic matter against depth for Herwa-1 well (After Mohammed, 2010)

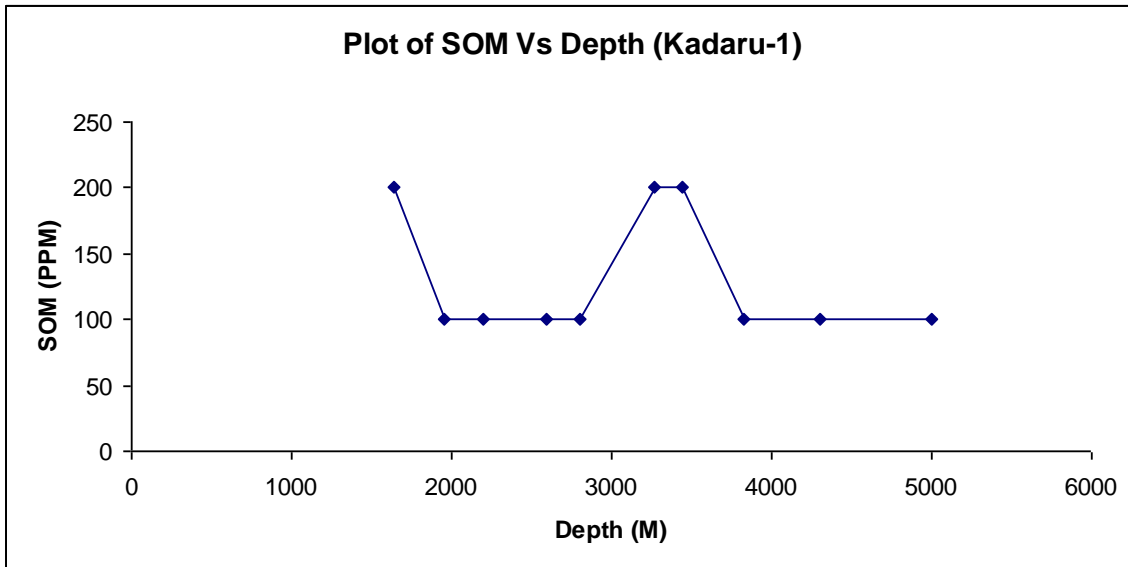


Fig. 2. Plot of soluble organic matter against depth for Kadaru-1 well (After Mohammed, 2010)

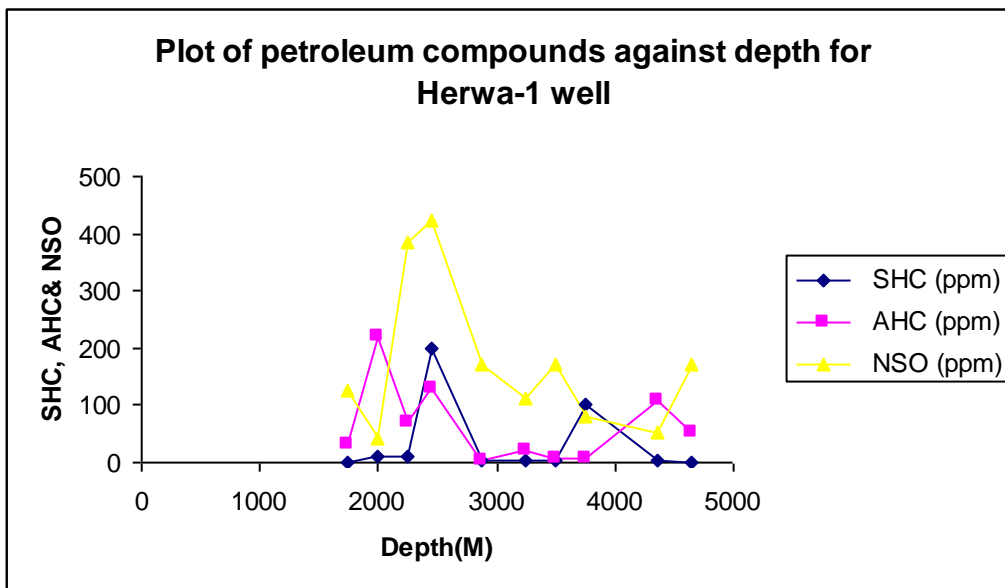


Fig. 3. Plot of petroleum compounds against depth for Herwa-1 well (After Mohammed, 2010)

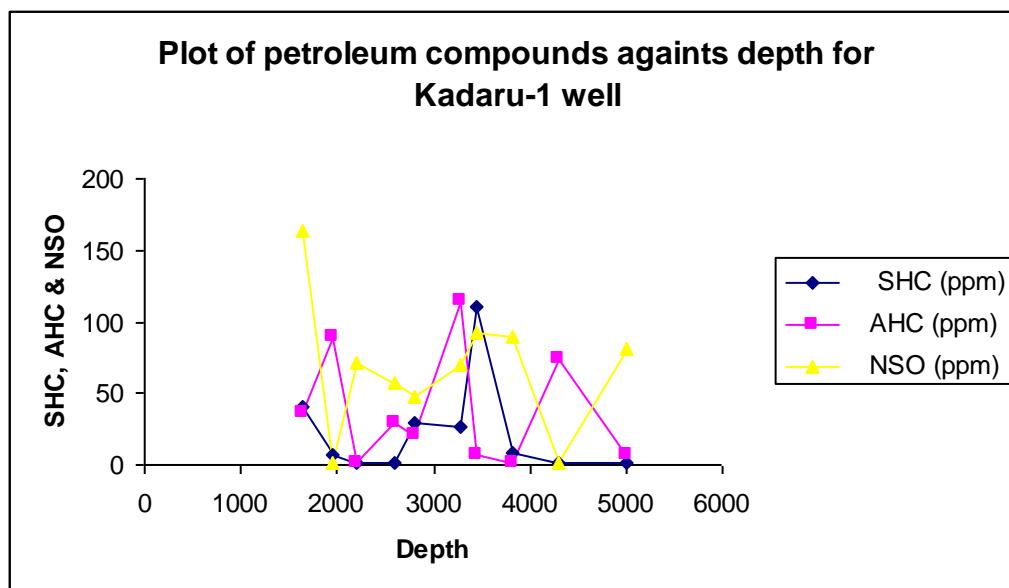


Fig. 4. Plot of petroleum compounds against depth for Kadaru-1 well (After Mohammed, 2010)

Trace Elements Geochemistry

The transition metals have been found to be very useful in crude oil characterization, especially in oil-oil correlation studies (Curiale, 1987; Barwise, 1990; Udo *et al.*, 1992; Oluwole *et al.*, 1993 and Nwachuckwu *et al.*, 1995). Special attention has been given to the following transition metals: Co, Cr, Cu, Fe, Ni and V. Table 5 shows data from analyzed samples in Niger Delta and Western Desert, Egypt.

Table 5: Average concentrations of transition metals and ratios in some studied wells (Modified by Mohammed, 2012)

Authors	Co (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Ni (mg/L)	V (mg/L)
Abubakr <i>et al.</i> (2010)	0.473- 0.708	0.023- 0.11	0.0- 0.008	1.6- 18.83	7.36- 10.925	12.4- 21.2
Akinlua <i>et al.</i> (2007)	0.89-32.44	6.2- 23.7	3.31- 19.4	11.4- 1241	26.3- 144.1	11.2- 29.2
Nwachukwu <i>et al.</i> (1995)	0.003- 1.174	0.021- 0.219	0.54- 42.308	0.006- 25.074	0.351- 11.282	0.009- 1.832
Oluwole <i>et al.</i> (1993)	0.008- 0.993	0.31- 0.129	1.86- 18.9	3.40- 9.54	0.54- 5.03	0.54- 1.195
Udo <i>et al.</i> (1992)	0.46- 3.54	0.3- 0.7	0.03- 0.07	0.06- 0.36	4.4- 6.9	3.70- 40.0
Ndiokwere. (1983)	1.42- 1.57	-	-	-	2.2- 5.6	0.1- 0.642

Cobalt concentration are within similar limits as reported by Abubakr *et al.* (2010), Udo *et al.* (1992), Oluwole *et al.* (1993), Nwachukwu *et al.* (1995) while Akinlua *et al.* (2007) and Ndiokwere *et al.* (1983) reported lower values as in Table 5. Chromium concentrations are low as reported by Ekweozor *et al.* (1979) and have higher values within similar ranges as reported Udo *et al.* (1992), Nwachukwu *et al.* (1995), Akinlua *et al.* (2007) and Abubakr *et al.* (2010), and these ranges of values further confirm Hitchon and Filby (1984) assertion that, most oils show no detectable chromium and where is detectable, it is useful in classifying crude oils. Copper concentrations are much higher as studied by Ekweozor *et al.*

(1979), Oluwole *et al.* (1993) and Nwachukwu *et al.* (1995) and relatively much lower as reported by Abubakr *et al.* (2010) and Udo *et al.* (1992). Iron concentration are high as reported by Abubakr *et al.* (2010) and Ekweozor *et al.* (1979) while Udo *et al.* (1992), Oluwole *et al.* (1993), Nwachukwu *et al.* (1995) reported values within similar ranges as in table 5. Abubakr *et al.* (2010) stated that with increasing Vanadium content, the concentrations of iron also increases in the same sample. Nickel concentrations have been reported with relatively higher values by Akinlua *et al.* (2007), Ndiokwere (1983) and Abubakr *et al.* (2010), while Udo *et al.* (1992), Oluwole *et al.* (1993), Nwachukwu *et al.* (1995) reported of values close ranges and lower than the former. Vanadium concentrations have within similar ranges for Udo *et al.*, (1992) and Abubakr *et al.*, (2010) table 5.

Ratios of Transition Metals

The ratios of transition metals in crude oils are useful in the determination of source rocks depositional environment and maturation, because they remain unchanged irrespective of diagenetic and in- reservoir alteration effect (Barwise *et al.*, 1990; Lewan, 1984; and Udo *et al.*, 1992).

Table 6 below shows the ratios of transition metals in Western Desert, Egypt as studied by (Abubakr *et al.*, 2010). Table 6. Ratios of transition metals from Western Desert, Egypt (Modified from Abubakr *et al.*, 2010)

Sample NO.	V/Ni	V/Ni+V	Co/Ni	Fe/V
Hamrah-1	2.486	0.713	0.064	0.0874
Farashah-1	1.941	0.660	0.048	0.5642
Rahmah-1	1.465	0.594	0.084	1.5185
Average	1.964	0.656	0.065	0.723

The V/Ni are within the values of 0.60- 6.60 reported by Udo *et al.*, (1992) and higher than the average values of 0.15 and 0.16 reported by Nwachuckwu *et al.*, (1995). The study carried out by Abubakr *et al.*, (2010) reveals that the crude oils are matured, because maturity increases with decreasing V/Ni ratio (Barwise, 1990 and Udo *et al.*, 1992). The V/Ni ratio tends to increase with increasing Pr/Ph, suggesting high terrigenous source input of organic as similarly reported by (Udo *et al.*, 1992). V/(V+Ni) ratios as in table 6 ranged from 0.0594- 0.0713 with an average of 0.656, which are generally present within the range of values reported by Nwachuckwu *et al.*, (1995) and is indicative of oils derived from terrestrial organic matter. Petters *et al.*, (2005), Hatch and Leventhal (1992) and Killops and Killops (2005) used V/(V+Ni) ratio to detect the oxidation- reduction environments of a sedimentary water body at which organic matter is deposited and preserved. The study carried out by Abubakr *et al.*, (2010) reflects weak water stratification to sub- intense water stratification and an anaerobic environment. Cobalt and Nickel ratios studied by Abubakr *et al.*, (2010) are (<0.1). Based on similar studies carried out by Udo *et al.*, (1992), interpreted Co/Ni values (>0.1) indicative of oil source rocks with more marine organic input. Therefore, these values corresponds with V/(V+Ni) which are not of marine input.

CONCLUSION

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