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Geochemical Investigation of Trace Metals in Crude Oils from Some Producing Oil Fields in Niger Delta, Nigeria

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Abstract

The geochemical investigation of trace metals in crude oils from some producing oil fields in the Niger Delta, Nigeria, was carried out to ascertain the petroleum source rocks and organic matter deposits. The concentrations of trace metals in crude oil samples obtained from eight producing fields from Niger Delta, Nigeria, were analyzed using a 700 model Perkin Elmer atomic absorption spectrophotometer. The results showed the following ranges for the trace metals: Cu (0.01–0.04 mg/kg), Fe (0.05–5.90 mg/kg), Ni (0.09–0.72 mg/kg); and V (0.008–1.05 mg/kg). Pb and Zn were lower than 0.01 mg/kg. Trace metal ratios such as V/Ni, V/Fe, and (V/V + Ni) were used to unravel the genetic correlation among the oils. All the crude samples except the sample from Nembe South-2 have a V/N ratio lower than 1.0, indicating that the organic materials produced the petroleum source rock. A cross plot of V/Ni revealed two genetic families for the crude oils, derived from a terrestrial and marine origin, which was confirmed by the ternary plot of V, Ni, and Fe, discriminating the crude oils from the producing fields into two distinct groups. The V/(Ni + V) of smaller than 0.5 showed that most crude oils were deposited in an oxic environment. A cross-plot of V/(Ni + V) and V/Fe showed a weak correlation, suggesting that it could not substitute for the V/Ni ratio in determining the origin and depositional environment of crude oil samples. Therefore, an in-depth knowledge of the concentration of trace metals, especially vanadium and nickel, within an environment during oil exploration is essential in developing new oil locations.

Keywords: Anoxic, Marine, Oxic, Organic material, Petroleum, Rock, Source, Terrestrial

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1. Introduction

Crude oil has been in very high demand over the past hundred years, so the environmental impact and degradation from oil exploration have also been on the rise. The origin of crude oil can be traced to ancient organisms beneath the earth's surface for several millions of years (Ahmad and Sarah, 2014). The remains of these ancient organisms that could convert energy from sunlight into organic compounds are subjected to microbial modification under anaerobic conditions to form organic layers that combine with benthic sedimentary rocks over a period to produce source rocks. Within this long period of geological processes, immature sedimentary source rocks begin to accommodate the formation of insoluble organic matter rich in carbon known as kerogens (Akinlua et al., 2007; Akinlua et al., 2015). The biochemical functional groups (carboxylic and amino acids) of kerogens are altered due to several chemical reactions leading to the final process of catagenesis, which involves cracking kerogens, thereby forming a hydrocarbon-rich liquid known as a hydrocarbon-rich liquid substance as petroleum (Peters et., 2005). Petroleum source rocks are coarse free sediments with enough organic matter capable of producing and releasing hydrocarbons which ultimately form oil or gas in commercial quantity (Ahmad and Sarah, 2014). One of the ways trace metals are introduced in the form of heterocyclic macrocyclic organic compounds in petroleum source rocks is by direct incorporation from biomass and sediment formation (Akinlua et al., 2007). Hackford (1922) was the first scientist to discover the presence of trace elements in petroleum and discovered the presence of lead, tin, silicon, vanadium, titanium, nickel, and gold in a Mexican crude oil from the Isthmus of Tehuantepec. After his discovery, other scientists have reported the presence of trace elements and even more in petroleum samples from many parts of the world (Mendelssohn et al., 2012). In 1954, Erikson et al. discovered 31 trace elements in the western half of the United States, covering half of the nation's land area. They also discovered that trace metals such as vanadium, nickel, copper, cobalt, lead, manganese, and arsenic were present in three grade types of bituminous materials, in addition to discovering several asphalts and petroliferous rocks (Mermet, 2005). Geologists are fascinated by the impact of trace metals in the genesis and accumulation of petroleum due to their presence in many sediments associated with bituminous rocks. The geochemical conditions responsible for the origin of petroleum source rocks are a function of the presence of trace elements in petroleum (Hill and Fisher, 2017). In-depth knowledge of the concentration of trace metals, especially vanadium and nickel, within an environment during oil exploration is essential for developing new oil locations (Galarraga et al., 2008). Vanadium (V) and nickel (Ni) were the first trace metals discovered in petroleum because they are usually found in the highest concentrations. However, many studies have been conducted to interpret the importance of the ratio of the concentration of V to Ni (V/Ni) in petroleum. Hodgson (1954) observed that the V/Ni decreased with geologic age for samples ranging from cretaceous to Devonian (Mendelssohn et al., 2012). Scott et al. (1954) presented something similar with respect to the V/Ni for lower cretaceous oils of Canada and concluded the possibility that these oils were from one source. There is a high tendency that these trace metals in petroleum may be lost during evaporation because they are incorporated in the heavier components of the crude (Hill and Fisher, 2017). In 1956, Bonham proposed that trace metals may be evacuated during oil migration because the concentrations of vanadium and nickel are near ancient shorelines and lowest in the Pennsylvanian oils from the Seminole area in Oklahoma (Mermet, 2005). Valuable information on the origin, migration, maturation, and deposition of organic matter from which the oils are generated could be obtained from the concentration, distribution, and nature of trace metals in the crude (Shazili et al., 2006). A trace metal can be defined as a metal with a relatively high density (> 7 g/cm^3) or atomic weight (> 20) and is often assumed to be toxic. Trace metals predominant in crude oil include aluminum (Al), cadmium (Cd), chromium (Cr^{3+} and Cr^{6+}), vanadium (V), copper (Cu), mercury (Hg), cobalt (Co), nickel (Ni), lead (Pb), zinc (Zn), and iron (Fe)

(Pandey et al., 2005). Trace metals can be naturally introduced into petroleum source rocks in the form of heterocyclic macrocyclic organic molecules known as porphyrins (Bonetti et al., 2009).

Studies from previous researchers focused on identifying the presence of trace metals in petroleum, petroleum source rocks, and their roles in the generation and accumulation of petroleum. Other researchers further studied the presence of trace metals to envisage the actual location of the organic deposits from which the petroleum is produced. During the post-impact assessment of an environment, trace metals in crude oil also serve as indicators to ascertain the cleanliness of an oil spilled environment after cleanup and remediation. The ability to predict the source of petroleum accumulation in the absence of source rock data has always been a challenge in petroleum exploration.

This study aims to conduct a geochemical investigation of trace metals in crude oil to determine the source of organic matter depositional environment and correlate the oil to their source rocks from the different oil locations in Niger Delta, which is vital for discovering new oil locations around the Niger Delta basin.

2. Materials and methods

2.1. Description of the study area

The Niger Delta basin, the study area for this research, is a region characterized by an abundant quantity of petroleum resources and presently the only basin that houses commercial quantities of petroleum resources in Nigeria. Before developing the depobelt concept, the Niger Delta basin operated a single active petroleum system called the tertiary Niger Delta. The geology of the study area is representative of the Niger Delta basin, which is made up of three basic geologic formations, namely the Agbada, Akata, and Benin formations (Abrakasa et al., 2016). Figure 1 shows a geological map with the various depobelts in the Niger Delta basin. These depobelts form one of the largest regressive deltas in the world with an area, volume, and thickness of 300,000 km^2, 500,000 km^3, and 10 km, respectively. The sample locations as circled in the map are obtained within the various depobelts. From Figure 1, it can be deduced that the onshore areas of the Niger Delta basin are described by the geology of southern Nigeria and southwestern Cameroon, while the Cameroon volcanic line describes the offshore boundaries of the province to the east and the eastern boundary of the Dahomey basin (Reijers, 2011).

Figure 1
Map showing fields used in this study

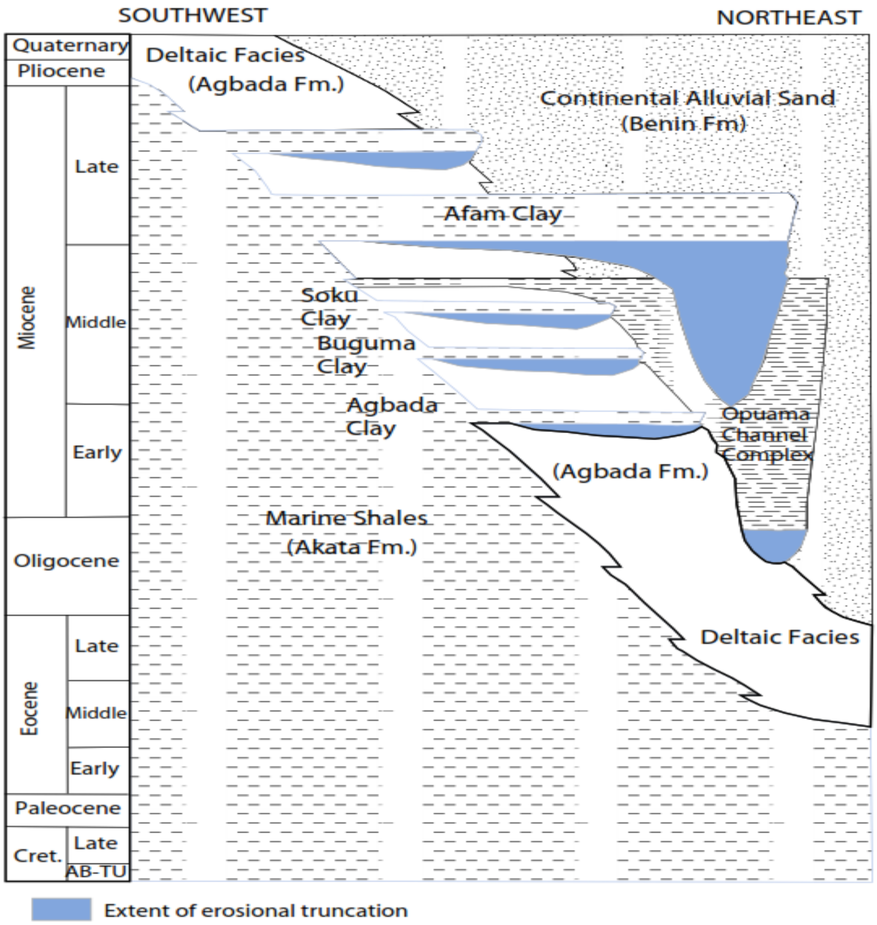

Figure 2
The stratigraphic column showing the three formations of the Niger Delta. Modified from Doust and Omatsola (1990).

a. Stratigraphic column of the Niger Delta

The Niger Delta consists of three broad formations, the hydrocarbon habitat: the Akata, Agbada, and Benin formations. The Akata formation is situated at the delta base and has a marine origin. Moreover, it begins in the Paleocene through the Recent, possesses high pressure, and underlies the delta. It comprises thick shale arrangements: potential source rocks, turbidite sand, potential reservoirs in deep water, and a small amount of clay and silt (Figure 2). The characteristics of Akata formation formed in low stands when terrestrial organic matter and clays were transported to deep water areas are characterized by low energy conditions and oxygen deficiency (Stacher, 1995). The estimated thickness of the formation, according to Doust and Omotsola (1990) is about 7,000 m. The second is the Agbada formation which consists of sand and shale and is the primary petroleum-bearing unit that began in the Eocene and continues into the Recent. The formation comprises paralic siliciclastic, which is more than 3700 m in thickness and signifies the actual deltaic area of the sequence. The clastics accumulate in delta-front, delta-topset, and fluviodeltaic environments. Shale and sandstone beds were deposited in equivalent magnitudes in the lower Agbada formation. Nevertheless, the upper portion is typically sand with minute shale interbeds. The third formation after Agbada formation is the Benin formation, a continental latest Eocene to Recent deposit of sedimentary and upper coastal plain sands up to 2000 m thick (Avbovbo, 1978). The upper Benin formations consist of freshwater bearing, continental sand,

and gravels stone. The formation is a continental latest Eocene to Recent deposit of sedimentary and upper littoral plain sands with a thickness of up to 2000 m (Avbovbo, 1978; Smith-Rouch et al., 1996).

2.2. Sample collection and analyses of trace metals

Crude oil samples were obtained from eight oil-producing locations in Niger Delta, Nigeria, labeled TEB WELL-12, NEMBE SOUTH-2, OKAKI FLOW ST, NEMBE STATION, OGBAN 8LS, KOLO CREEK, CC5T, and OGBAIN L2 based on their respective locations. A crude oil sample weighing 1 g was digested with 3 mL of 50% hydrogen peroxide and 2 mL of sulfuric acid. Standard solutions containing known concentrations of the trace elements to be determined were obtained from stock solutions through a dilution process using deionized water for calibration (Quinby-Hunt and Wilde, 1994). The concentration of the trace metals in the digested crude oil samples was determined using a 700 model Perkin Elmer atomic absorption spectrophotometer, and the analyses were performed on eight crude oil samples. Elemental quantification was based on the calibration curves of standard solutions of elements. The accuracy of the analytical method was evaluated by including blanks in each batch of analyses (Hill and Fisher, 2017).

3. Results

Table 1
Concentrations of trace metals in crude oil samples in Niger Delta, Nigeria.

Crude oil samples	Concentration of trace metals (ppm)								
Based on location	Cu	Pb	Fe	Ni	Zn	V	V/Ni	V/Fe	V/ (Ni+V)
TEB WELL-12	0.040	<0.010	5.900	0.170	<0.010	0.080	0.470	0.010	0.320
NEMBE SOUTH-2	0.030	<0.010	0.640	0.600	<0.010	1.050	1.750	1.640	0.640
OKAKI FLOW ST	0.010	<0.010	0.170	0.150	<0.010	0.060	0.400	0.350	0.290
NEMBE STATION	0.030	<0.010	0.008	0.360	<0.010	0.100	0.280	12.50	0.220
OGBAN 8LS	0.030	<0.010	0.006	0.640	<0.010	0.260	0.410	43.330	0.290
KOLO CREEK	0.010	<0.010	0.008	0.720	<0.010	0.300	0.420	37.500	0.290
CC5T	0.020	<0.010	0.005	0.250	<0.010	0.090	0.360	18.00	0.260
OGBAIN L2	0.030	<0.010	0.009	0.009	<0.010	0.008	0.889	0.890	0.470
Total Trace Element	0.200	<0.090	6.746	2.899	<0.090	1.948			

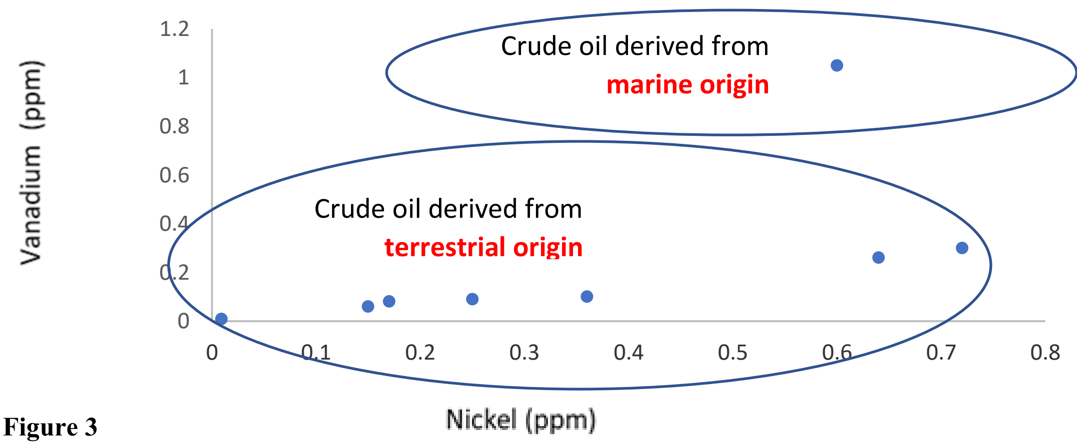

Figure 3
V/Ni plot showing the classification of crude oils based on two sources.

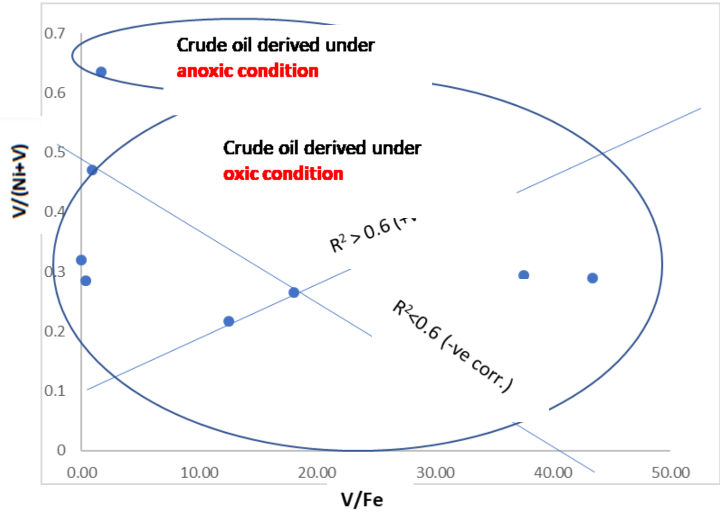

Figure 4

Plot showing relationship between V/(Ni+V) and V/Fe in crude oil.

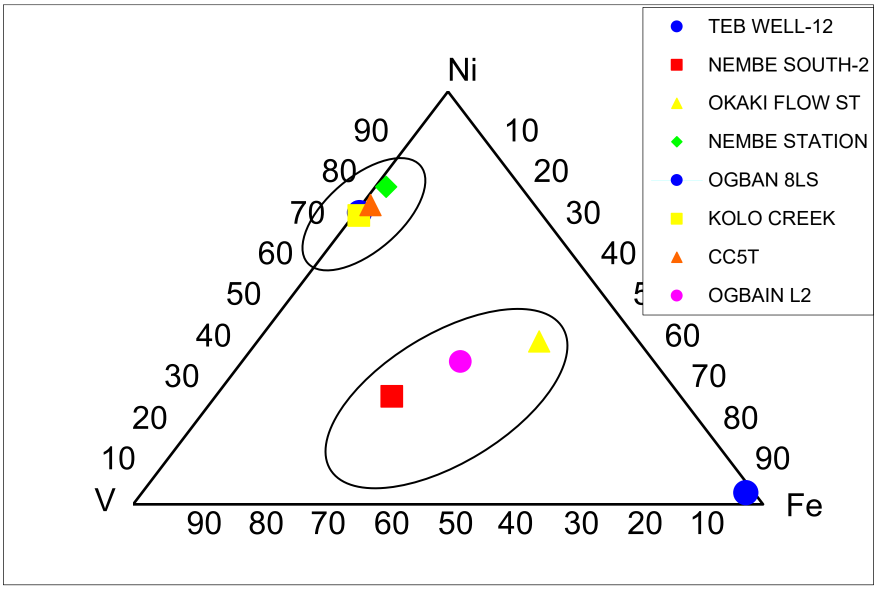

Figure 5

Ternary plot of crude producing fields showing two groups of oils.

4. Discussion

The presence of trace metals in crude oil provides much helpful information about the crude; however, several physicochemical processes such as temperature variation, selective separation of residues within the petroleum source rock, natural breakdown of materials by microorganisms or water washing, and migration could change the concentration of these elements in crude oil (Galarraga et al., 2008; Quesada et al., 1997). Table 1 lists the concentrations of trace metals in crude oil samples obtained from eight locations in the Niger Delta, Nigeria. From the Table, it can be deduced that iron (Fe) is the most abundant trace element in terms of crude oil samples TEB WELL-12, NEMBE SOUTH-2, and OKAKI FLOW ST, as well as the total trace element of the crude oil samples from all the locations. However, the iron (Fe) content of crude oil samples NEMBE STATION, OGBAN 8LS, KOLO CREEK, CC5T, and OGBAIN L2 is less than their nickel (Ni) and vanadium contents, indicating that they were obtained from petroleum source rocks very rich in carbonates. Carbonate rocks are often related to a high salinity environment associated with an aquatic system with minimal terrestrial inputs and low dissolved oxygen. Low pristane/phytane ratios also characterize carbonate source rocks and high-concentration D-type organic facies characterized by high organic matter such as burnt wood and recycled terrestrial materials (Mendelssohn et al., 2012; Quesada and Robles, 1995). The predominance of iron (Fe) in the crude oil samples indicates that the origin of the crude was dominated by silicate minerals, especially quartz, feldspar, and clays. The next in abundance is nickel (Ni) and then vanadium (V) (Akinlua and Torto, 2006; Labastidas, 1997). Zinc (Zn) and lead (Pb) were the least detected trace metals in the crude oil samples. Nickel (Ni) and vanadium (V) are trace metals with a proven relationship with organic materials. Table 1 demonstrates that the concentration of nickel (Ni) is more than vanadium (V), which depicts that the organic matter that produced the source rocks from which the crude oil samples were derived originated from an oxygenated environment (oxic sedimentary condition). It is important to note that the concentration of vanadium (V) usually predominates that of nickel (Ni) for crude oil samples whose origins are traceable to anaerobic sources devoid of oxygen (anoxic conditions) (Galarraga et al., 2008). This research has confirmed the predominance of Ni over V in the Niger Delta oils, as stated by researchers such as Akinlua and Torto (Akinlua and Torto, 2006). The classification of crude oils based on two sources is represented from the V/Ni cross plot of V/Ni, as shown in Figure 3. Crude oil samples with V/Ni values less than one are derived mainly from higher plant organic materials with the terrestrial origin, as is the case with all crude samples used in this study, except for sample NEMBE SOUTH-2 with a $V/Ni > 1.0$, indicating that it is derived from a marine origin (Lopez et al., 1991). Crude oils obtained from marine organic matter usually have a high concentration of trace elements due to the enormous contributions from aquatic organisms such as algae and bacteria, which release porphyrin-precursor chlorophylls to the organic matter (Peters et al., 2005; Galarraga et al., 2008). Several physicochemical processes can alter the concentration of trace elements in crude oil. However, the V/Ni remains unchanged due to the similarities in structure among organometallic compounds that contain vanadium and nickel (Galarraga et al., 2008; Merten, 2006).

The relationship between $V/(Ni + V)$ and V/Fe in the crude oils under study are shown in the cross-plot represented in Figure 3 and corroborated in Table 1. It can be shown that all the studied crude oils, except for sample NEMBE SOUTH-2, have $V/(Ni + V)$ values lower than 0.5. Crude oils with $V/(Ni + V)$ values lower than 0.5 are obtained from source rocks generated under an oxic sedimentary condition. In other words, the condition of the organic matter origin of the crude oils was oxygenated, which corresponds to the terrestrial environment. Sample NEMBE SOUTH-2 has a $V/(Ni + V)$ of greater than 0.5, indicating that the crude was obtained from source rocks generated under anoxic condition (absence of oxygen), which corresponds to the marine environment (Momodu and Anyakora, 2010). Figure 4 shows a cross-plot of $V/(V + Ni)$ and V/Fe with a weak positive and negative correlation between the crude oil samples, implying that V/Fe values cannot be used as an indicator to ascertain the origin and depositional environment of the crude oil samples under study (Galarraga et al., 2008). The environmental conditions in which petroleum source rocks are deposited are highly dependent on the rate at which vanadium is proportional to nickel in crude oils. Factors such as reservoir alterations, thermal migration, and maturation may alter the concentrations of vanadium and nickel by subtracting or adding adjustable portions of crude oil. However, the strong bond between them and high molecular weight organics such as polymeric materials indicates that their proportionality to one another remains constant (Hill and Fisher, 2017; Wilde et al., 2004).

The ternary plot of V, Ni, and Fe was used to discriminate the crude oils from the producing fields into two, as shown in Figure 5, substantiating the effect of source facies difference in the organic matter that formed the source rock (Oluwabamise et al., 2017).

5. Conclusions

The concentration of trace metals in crude oil samples plays a vital role in determining the origin of the organic material that produced the petroleum source rock from which the crude oil was derived. Iron (Fe) was the most abundant trace metal in samples TEB WELL-12, NEMBE SOUTH-2, and OKAKI FLOW ST, indicating that silicate minerals dominated the origins of these samples. In contrast, the concentrations of iron (Fe) were lower than that of the nickel (Ni) and vanadium (V) for samples NEMBE STATION, OGBAN 8LS, KOLO CREEK, CC5T, and OGBAN L2, which explains that the petroleum source rocks from which these samples originated were rich in carbonates. The V/N is very critical in affirming these assertions as crude oil samples with V/N lower than 1.0 are derived from organic matter with terrestrial origin characterized by the presence of oxygen (oxic environment). In contrast, those with V/N higher than 1.0 are derived from organic matter with marine origin characterized by the absence of oxygen (anoxic environment). The V/N of the crude samples used in this study will be critical for the identification of new oil locations within the Niger Delta basin, which will be of immense economic value to the region, using data obtained from the V/N. In fact, V/N is essential for the identification of the petroleum source rocks and organic deposits from which the respective crude oils are derived. The fact that the ratio of vanadium to iron did not correlate significantly with the V/(V + Ni) implied that the correlation between the two ratios could not be used as a substitute to ascertain the origin and depositional environment of the crude oils under study. In other words, the origin of petroleum source rocks rich in silicate materials with a preponderance of Fe cannot be determined using the same trend of V/Ni as those rich in carbonates with high concentrations of nickel and vanadium.

Nomenclature

Al	Aluminum
Cd	Cadmium
Cr	Chromium
Cu	Copper
Co	Cobalt
Fe	Iron
Hg	Mercury
Ni	Nickel
Pb	Lead
V	Vanadium
Zn	Zinc

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