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Geochemical Appraisal of the Depositional Environment and Source Organic Matter of Crude Oils from Some Oil Fields in Bayelsa State, Nigeria

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Highlights

- Niger delta oil samples were assessed for depositional environment and organic matter source.
- Three samples were deposited in an oxic environment, while two were deposited in an anoxic environment.
- The organic source inputs showed type III kerogen (Terrestrial) and a mixture of types II and III (Marine).

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Abstract

The organic geochemical characterization of crude oil samples from the oil fields of the Niger delta was carried out using gas chromatography–mass spectrometry (GC–MS) to genetically characterize the oil samples in terms of their biomarker composition. Geochemical characteristics such as depositional environments, kerogen type, and source of organic matter were analyzed using aliphatic biomarkers as a supporting tool. Five samples were randomly collected from Tebidaba, Clough Creek and Azuzuama fields in Bayelsa State, Nigeria. The saturated hydrocarbons were analyzed using GC–MS. The n-alkanes, isoprenoids, biomarkers hopanes, and steranes fingerprints were extracted from chromatogram for m/z 57, 191, 217 values respectively. The results revealed that the five studied samples were characterized by C₂₉ sterane predominance and the presence of oleanane, depicting organic matter with vascular land plant material inputs and a deltaic contribution. Ternary plots showed that the oils were deposited in an estuarine environment. The pristane (Pr)/nC₁₇ versus phytane (Ph)/nC₁₈ showed that TEB 08 and WELL 2 are in the anoxic environment inferring kerogen II and a mixture of types I and II respectively. TEB 12, CCST, and AZU ST has kerogen type III deposited in an oxic environment.

Keywords: Biomarker, Depositional Environment, Kerogen, Organic Matter Source

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1. Introduction

The remains of plants and animals that lived and died on earth millions of years ago gave rise to origin

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of petroleum. These organisms died and their remains became buried under the earth. Bacterial decomposition, pressure, and heat converted these fossils into petroleum and other hydrocarbon compounds. The Niger delta is a region that is rich in crude oil and natural gas deposit; it also creates an enabling ground for crude oil studies because of the large deposits of crude oil in the region with a reserve of about 25 billion barrels of oil and 725 trillion cubic meters of natural gas (Adedosu and Sonibare, 2005).

The pristane/phytane (Pr/Ph) ratio is one of the most commonly used geochemical parameters and has been widely used as an indicator of the redox conditions in the depositional environment and source of organic matter (Powell and Mckirdy, 1973). Therefore, it is expected that oils originating predominantly from terrestrial plants contain high a Pr/Ph ratio (> 3.0) because of the availability of oxygen during the initial diagenesis of chlorophyll in comparison with oils and sediments containing marine organic matter (Powell and Mckirdy, 1973a; Brooks et al., 1969). However, it should be mentioned that multiple sources of these isoprenoids are possible. Recently, archaeobacteria have been proposed as another source of phytane (Risatti et al., 1984), and pristane may be derived from tocopherols (Ten Haven et al., 1987).

Biomarkers, as the compounds available in crude oil, store information concerning the oil. They are mainly from living organisms preserved through time. Petroleum biomarkers are complex compounds generated from formally living organisms (Mobarakabad et al., 2011). Due to biomarker origination from living organisms, they are termed geochemical fossils (Eglinton and Calvin, 1967).

The application of biomarker distribution and its successful use are in interpreting the environment of deposition and organic matter deposited in crude oil (Peters and Moldowan, 1993; Peters et al., 2005).

Geochemical correlation mainly depends on gas chromatography–mass spectrometry (GC–MS) of biomarker analysis and is useful for the development of organic geochemistry and oil and gas exploration activities (Killops and Killops, 1993). This work attempts to evaluate the organic geochemical characteristics of the crude oil obtained from three flow stations within Bayelsa state, Nigeria to characterize the oils and deduce their environment of deposition and source organic matter.

2. Materials and methods

2.1. Data collection

Well-heads at Azuzuama, Tebidaba and Clough Creek fields (Figure 1) represent locations where the crude oil samples were collected and are true representatives of the crude oil bulk. They were labelled AZU ST, WELL 2, TEB 08, TEB 12, and CCST. These samples were retained in glass vials and stored in a refrigerator for preservation before analysis.

2.2. Sample preparation

Thirty milligrams of the oil sample was transferred to a 2 mL bottle with a Teflon-lined plastic cork and diluted with 1 mL of dichloromethane. The samples were fractionated and subjected to GC–MS analysis. The fractionation of the oil samples was performed using the procedures outlined elsewhere (Abrakasa, 2006).

2.3. Techniques

The fractions were subjected to GC analysis using HP3890GC serial II, and separation was performed on a fused silica capillary column (30 m \times 0.25 mm id.) coated with 0.25 μ m, 5% phenyl methyl silicone

(HP-5) supplied by HP, currently known as Agilent United Kingdom. Hydrogen gas was used as a carrier gas at a rate of 2 mL/min with a split/splitless injector; temperature was programmed at 50 °C for 2 min, then raised at a rate of 4 °C/min to 300 °C, and finally remained at this temperature for 20 min.

The GC-MS analysis was carried out using the conditions and procedures stated by El Nady et al. (2016) at Giolee Global Resources Limited, Port Harcourt.

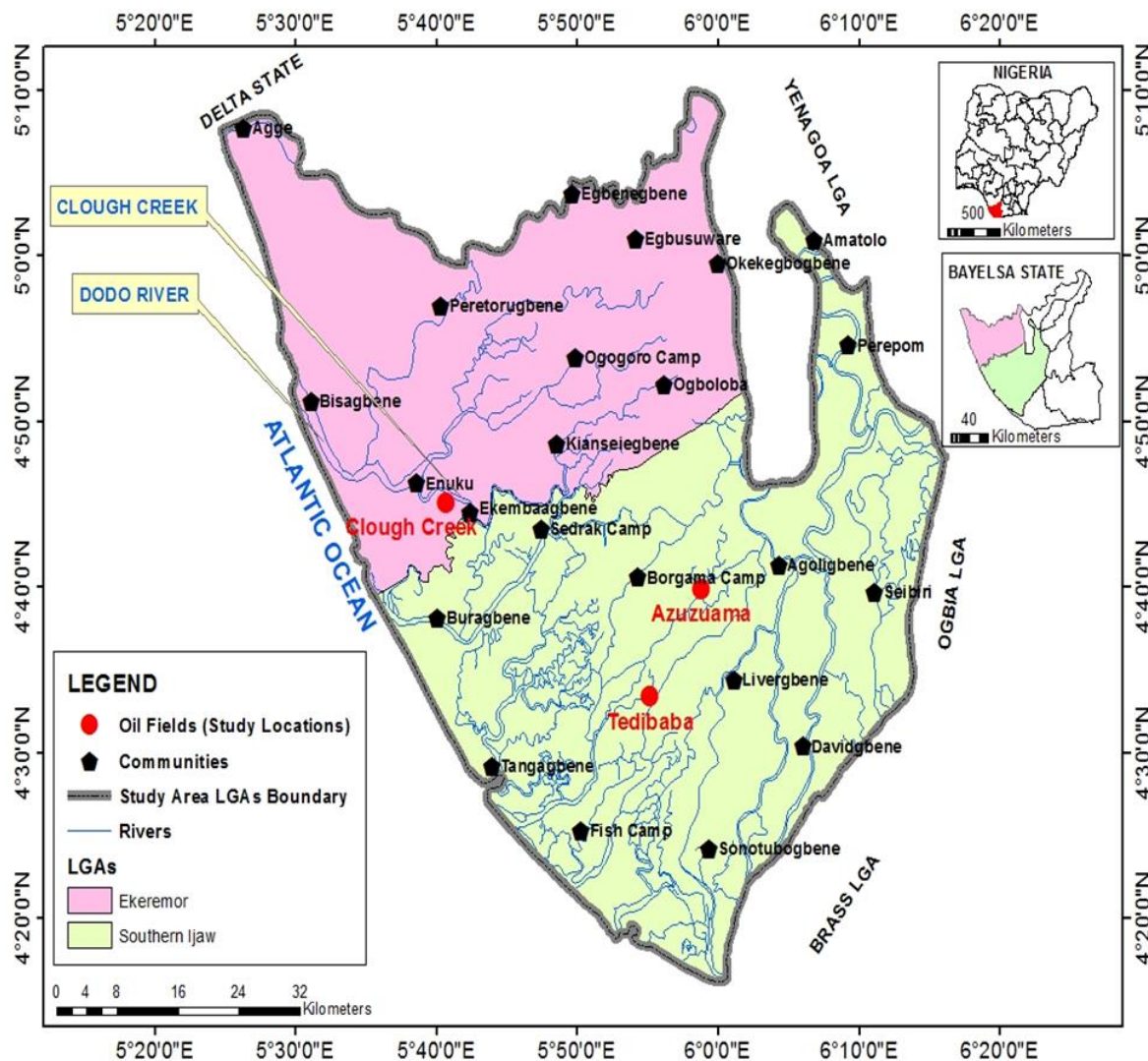


Figure 1

Map showing oil fields where the crude oil samples were obtained.

3. Results and discussions

Depositional environment plays an important role in determining the amount of the organic matter and the rate at which organic matter will accumulate in a basin (Demaison and Moore, 1980). Biomarker parameters identify the certain environment where oil is deposited, especially in an unexplored region. These unique biomarkers, in most cases, are connected to specific microorganisms that will grow in definite conditions peculiar to a particular environment such as lacustrine, reducing, oxic, hypersaline environments (Philip and Lewis, 1987). The cross plot of Pr/nC₁₇ versus Ph/nC₁₈ is an important parametric ratio used to characterize the environment, to preliminarily determine the kerogen type, and

to suggest the depositional environment (Duan et al., 2006). The cross plot of Pr/nC₁₇ versus Ph/nC₁₈ (Figure 2) indicates that TEB 08 and WELL 2 are in the anoxic environment, implying that kerogen type II has generated the oil in TEB 08, while a mixture of kerogen types II and III has produced WELL 2; however, the CCST, AZU ST, and TEB 12 are in the oxic depositional environment and obtained from kerogen type III. Phytane series are compounds with a fewer number of carbon atoms (< C₂₀) and found in chlorophyll pigments. Under oxidizing conditions, phytane present in the pigment material causes the formation of pristane, which is accompanied by reducing conditions, to progress. Nevertheless, pristane to phytane ratio (Pr/Ph) can be used in assessing the depositional environment of crude oil and source rocks. Ten Haven (1996) reported that a high Pr/Ph ratio indicates a terrigenous input under oxic conditions and a low Pr/Ph ratio implies anoxic/hypersaline or carbonate environments. There is also a general acknowledgement that Pr/Ph ratios smaller than 0.5 indicate a strong anoxic sedimentary environment, and Pr/Ph ratios in the range of 0.5–1.0 and 1.0–2.0 point to an anoxic and weak reducing–weak oxidizing environment respectively, while a Pr/Ph ratio larger than 2.0 denotes a strong oxidizing environment (Ten Haven et al., 1987). According to the cross plot of Pr/Ph versus C₂₉/C₂₇ in Figure 4, TEB 12 has a high Pr/Ph ratio of 3.67 (see also Table 1) showing that it is the most terrigenous oil deposited in an oxic environment, while TEB 08 and WELL 2 with Pr/Ph ratios of 1.70 and 1.84 respectively (Table 1) are the least terrigenous oils deposited in an anoxic environment.

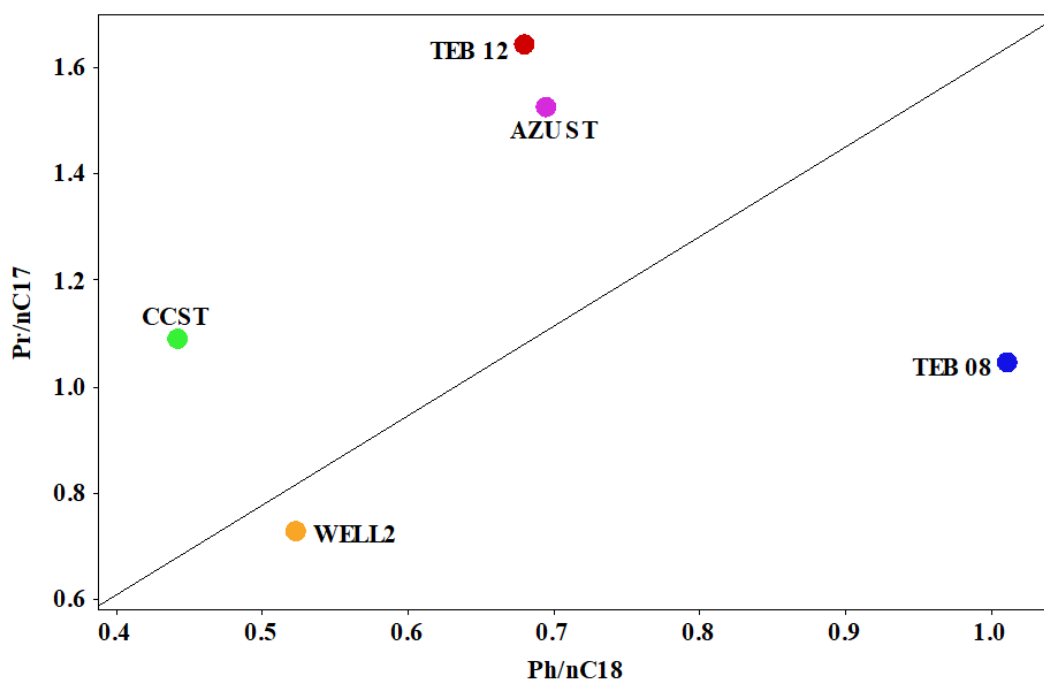


Figure 2

Cross plot of Pr/nC₁₇ versus Ph/nC₁₈ showing kerogen type and depositional environment.

The ternary plot of the C₂₇, C₂₈, and C₂₉ regular steranes (Figure 3) was used to delineate the depositional environment of the source rocks. The plot indicates that the similar organic inputs generating the oils were deposited in a similar environment characteristic of an estuary (open marine). This may indicate a combination of continental runoffs and marine algae in the distal environment (Mackenzie, 1984; Shanmugan, 1985).

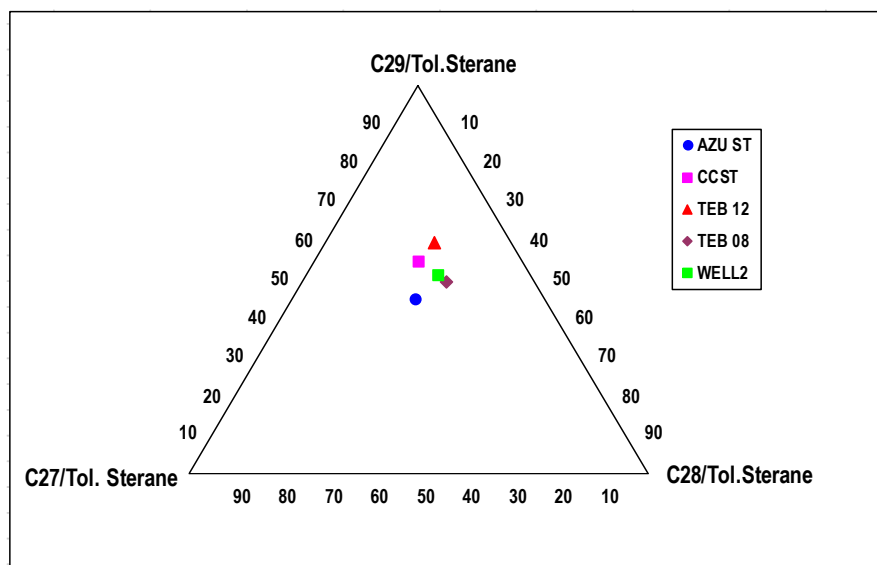


Figure 3

Ternary plots of sterane ratios in the studied samples.

Table 1

Ratios of isoprenoids in the studied crude oil samples.

Well	Pr/Ph	(Pr+Ph)/(nC ₁₇ +nC ₁₈)	Pr/nC ₁₇	Ph/nC ₁₈
AZUST	2.66	1.15	1.52	0.69
CCST	3.19	0.81	1.09	0.44
TEB 12	3.67	1.26	1.64	0.68
TEB 08	1.70	1.03	1.04	1.01
WELL2	1.84	0.64	0.73	0.52

The cross plot of Pr/nC₁₇ versus Ph/nC₁₈ (see Figure 2) shows that TEB 12, AZU ST, and CCST plotted in the standard source rock evaluation plot of Shanmugan and Moiola (1984) have type III kerogen known for terrestrial input assigned to the organic matter, which is deduced to be land plant materials that can also generate both condensate and gas; nonetheless, oils from WELL 2 and TEB 8 are composed of mixed organic matter consisting of marine algae and marine zooplankton with kerogen type II.

Oleananes are molecular markers formed in sediments through changes in catagenesis and diagenesis of 3 β -functionalized angiosperm triterpenoids (Rullkotter et al., 1994). The presence of oleanane in crude oil serves as an indicator of terrestrial organic contribution into the oil-prone source rocks deposited in a deltaic environment (Ekweozor et al., 1979; Wang et al., 2011; Whitehead et al., 1974). This is because oleanane is a vascular land plant biomarker generated from the angiosperms (flowering plants) which resides in younger cretaceous sediments (Whitehead, 1973). Therefore, the presence of this molecular marker in oil sets an age constraint for petroleum systems, and they are one of the important molecular markers in petroleum geochemistry (Peters and Moldowan, 1993). Oleanane is present in crude oils from the Niger delta at relatively high concentrations (Dahlmann, 2003). Figure 5 depicts the presence of oleanane biomarker in one of the studied samples.

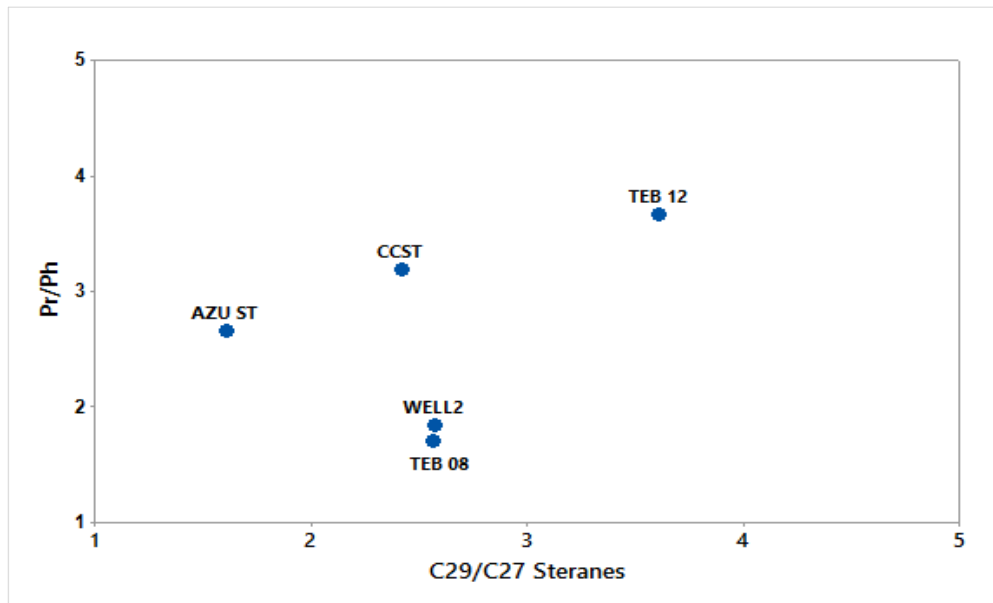


Figure 4

Cross plot of Pr/Ph versus C₂₉/C₂₇ sterane.

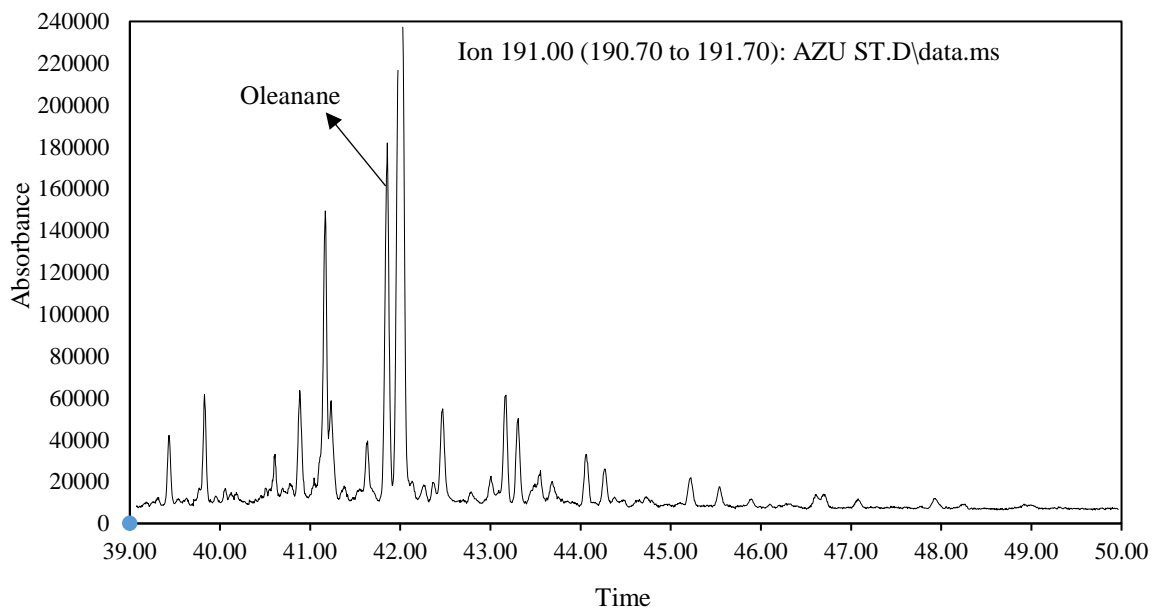


Figure 5

Mass chromatogram showing the presence of oleanane.

Sterane genetic fingerprint is represented by m/z 217, and the steranes originate mainly from algae and land plants and are common in ancient sediments. The precursors of the steranes are sterols and stanols which are converted to sterenes and then steranes via dehydrolysis. The C₂₇, C₂₈, and C₂₉ regular steranes serve as an indicator of a type of organic matter. Normal alkane distributions throw more light on the genetic origin of crude oil with respect to the organic matter source. Organic matter identified with the peak concentrations of C₁₅–C₂₅ is a reflection of marine origin. Consequently, the peak concentration of C₂₅–C₂₉ reflects vascular land plant materials which are of a terrestrial origin (El Nady et al., 2016). Table 2 and Figure 6 also present a predominance of C₂₉ steranes, which indicates sourcing organic matter with major inputs from vascular land plants (Huang and Meischein, 1979). In the studied

samples, the regular steranes have the highest amount of C₂₉ steranes (0.45–0.59) compared with C₂₇ steranes (0.17–0.28) and C₂₈ steranes (0.23–0.32).

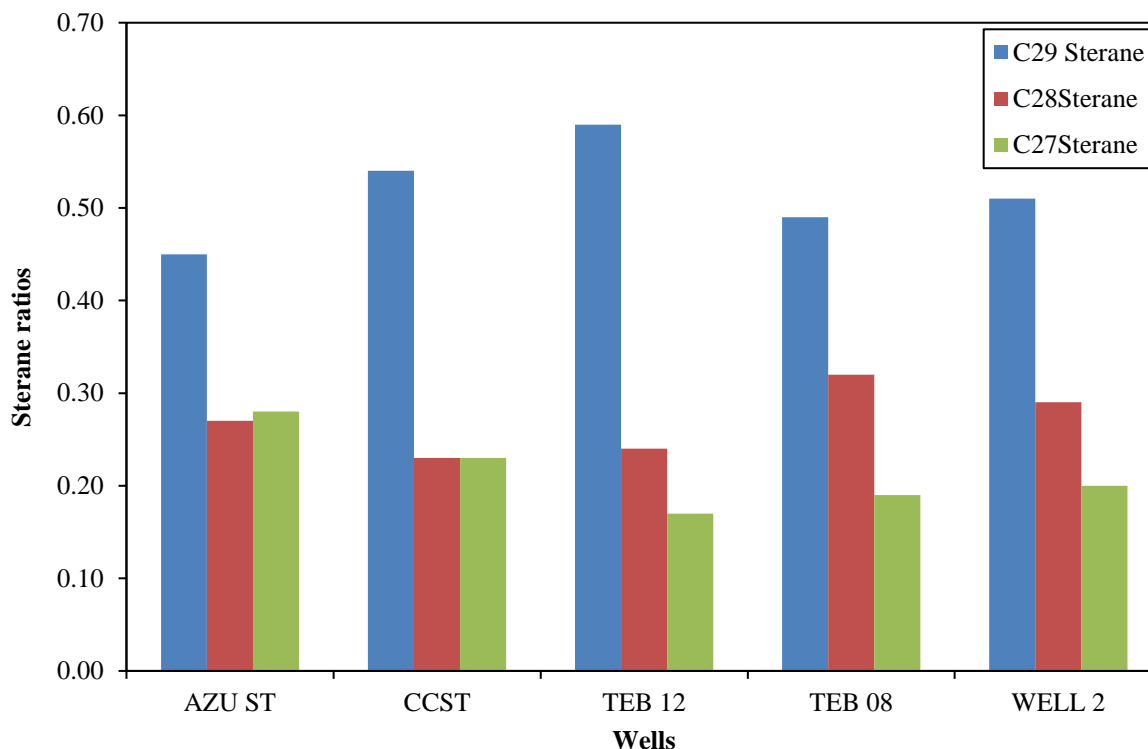


Figure 6

The relative fraction of C₂₇, C₂₈, and C₂₉ steranes in the studied crude oil samples.

Table 2

Ratios of steranes in the studied crude oil samples.

Well	C ₂₉ /Total sterane	C ₂₈ /Total sterane	C ₂₇ /Total sterane	Oleanane/Sterane
AZU ST	0.45	0.27	0.28	2.59
CCST	0.54	0.23	0.23	4.85
TEB 12	0.59	0.24	0.17	2.90
TEB 08	0.49	0.32	0.19	2.56
WELL 2	0.51	0.29	0.20	2.97

The Pr/Ph ratios of the studied oil samples listed in Table 1 suggests a gradual change in the depositional conditions of the source rocks; its relationship with C₂₉/Total sterane ratio is given in Figure 5 and Table 2. TEB 12 is characterized by a high Pr/Ph ratio of 3.67 (59%) and C₂₉ sterane value of 0.59 (see Table 2) indicating a high organic matter, which can be attributed to the land plant materials deposited under oxidizing conditions.

4. Conclusions

Biomarker parameters are described in detail for the studied oil samples, and their potential use as indicators of organic source inputs and depositional environments of petroleum source rocks is examined. The results of bulk property and the saturated biomarker analysis of the studied crude oils leads to the following key points:

The variation of Pr/Ph with C_{29}/C_{27} sterane indicates that the organic matter generating the oils in AZU ST, TEB 12, and CCST is deposited in an oxic environment which has sufficient oxygen and corresponds to a deltaic environment. These features are considered to be typical of the oil generated from clay-rich terrigenous source rocks that received higher plant inputs and from kerogen type III sources deposited under oxidizing conditions. TEB 8 and WELL 2 have the closest affinity with the biomarker signatures of kerogen type II sources that contain primarily marine algal organic matter. TEB 8 and WELL 2 with a low pristane/phytane ratio are pointing toward marine origin, and the source of these oils is marine algae/phytoplankton deposited in an anoxic environment. The ternary plots indicate that the studied samples were deposited in a similar estuarine environment. TEB 12 has the highest Pr/Ph ratio and C_{29} sterane indicating a high organic matter which is supposed to be vascular land plant materials. The presence of a diagnostic marker derived from angiosperms (flowering plants) termed oleanane was also noted.

Nomenclature

AZU ST	Azuzuama Well 5 Tubing
CCST	Clough Creek Well 5 Tubing
Mins	Minutes
Ph	Phytane
Pr	Pristane
TEB 08	Tebidaba Well 8
TEB 12	Tebidaba Well 12
WELL 2	Tebidaba Well GSS

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