



The organic geochemistry of crude oil in the Saltpond Basin (Ghana): Organic source input, depositional environment, and thermal maturity

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Abstract The Saltpond Basin, situated within the South Atlantic margin of Ghana, is a significant area for petroleum exploration but has received relatively limited research attention. Previous studies have examined source rock composition, but data on crude oil organic chemistry are lacking, hindering understanding of the basin's petroleum system and evolution. To address this gap, we analyzed biomarkers and stable carbon-isotope ratios in Saltpond Basin crude oil using gas chromatography–mass spectrometry and gas chromatography–isotope ratio mass spectrometry to elucidate organic matter source, depositional environment, and thermal maturity. Findings were compared with oils from the West African segment of the South Atlantic margin, namely the Tano Basin and the Niger Delta Basin, to identify potential correlations and gain insights into regional variations. Molecular and isotopic results unveiled a significant prevalence of organic matter derived from lower marine organisms. Patterns of organic matter deposition and preservation in Saltpond oil samples suggested a suboxic marine transitional environment, contradicting conventional understanding of terrestrial dominance in such settings. Moreover, the potential for degradation processes to obscure

differentiation between terrestrial and marine organic matter origins underscores the complex nature of organic matter dynamics in transitional marine environments. Analysis of molecular thermal maturity indices suggested Saltpond oils were expelled from source rocks exhibiting thermal maturity at the early maturity stage. Correlation analysis unveiled genetic disparities among crude oils sourced from the Saltpond Basin and those from the Tano and Niger Delta Basin, primarily due to variations in source input and depositional environment conditions. Saltpond oil exhibits lower terrestrial organic input than Tano Basin's crude oils, which also have less terrestrial input than Niger Delta Basin crude oils. Additionally, its paleodepositional environment notably differs from oils in the Tano Basin (anoxic transitional marine-lacustrine settings) and the Niger Delta Basin (suboxic–oxic terrigenous deltaic or marine or lacustrine environments). Thermal maturity range of Saltpond oil is comparable to oils in the Tano Basin but lower than oils in the Niger Delta Basin. These findings provide valuable insights into petroleum generation history and unique organic geochemical characteristics within the Saltpond Basin, essential for exploration, production, and environmental management efforts in the region. Furthermore, correlation studies provide evidence that distinct biological, geological, and paleoenvironmental conditions shaped various oil types in the West African segment of the South Atlantic margin.

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1 Introduction

The South Atlantic margin is a significant area for petroleum exploration, harboring significant hydrocarbon reserves that

account for approximately 7% of the world's total reserves (Huc 2004). These reserves are predominantly located in sedimentary basins along the coastlines of West Africa and the eastern seaboard. The favorable geological configuration, which exhibits near symmetry on both sides of the ocean, has facilitated the development of petroleum systems with a shared history (Schiefelbein et al. 2000; Beglinger et al. 2012a, b). Recent advancements in drilling techniques have led to remarkable offshore discoveries in West Africa (Jianping et al. 2010) and the Brazilian coastal margins (Martins et al. 2000).

The Saltpond Basin, operational since the 1970s, remains a significant contributor to the regional hydrocarbon output. Presently, the Saltpond Oil Field produces approximately 550 barrels of oil per day, with estimated reserves of 1.2 million barrels of oil and $20,000 \times 10^9$ cubic feet of gas (PCG 2024). Situated in the Gulf of Guinea province of Ghana, the Saltpond Basin covers an area of approximately 12,294 km² (PCG 2024). With depths ranging from 800 to 4000 m, it is centrally located between the Tano-Cape Three Points and Accra-Keta Basins (Fig. 1a). The basin's sedimentary deposits, ranging from the Ordovician to Cretaceous ages, were laid down in non-marine to coastal marine environments (Atta Peters et al. 2015; PCG 2024). Characterized by multiple faults, the basin exhibits a complex system of horsts and grabens, serving as traps for hydrocarbon accumulation (Adda 2013). The Lower Paleozoic Petroleum System, the known and proven system in the Saltpond Basin, comprises Devonian source rocks and Devonian to Carboniferous reservoirs (PCG 2024). The main source rocks in the area are the Lower and Upper Takoradi Shales, known for their Type II and Type III kerogen and fair to good total organic carbon and hydrogen index values (Bansah et al. 2014; Atta-Peters et al. 2015). The reservoirs consist mostly of sandstones from the Takoradi Sandstone Formation (Fig. 1b; Adda 2013).

While existing literature extensively documents the biomarkers and isotopic composition of oils within the South Atlantic margin (e.g., Mello et al. 1988; Samuel et al. 2009; Ogbesejana et al. 2020; Amoako et al. 2024), a notable gap persists in data regarding the biomarker and isotope geochemistry of crude oils from the Saltpond Basin. This gap hinders our understanding of the petroleum generation history and system in the Saltpond Basin.

Advancements in mass spectrometry, particularly gas chromatography–mass spectrometry (GC–MS) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS) enable the identification and characterization of biomarkers and stable carbon isotope ratios in both rock extracts and crude oils (e.g., Reddy and Quinn 1999; Konan et al. 2022a, b; Amoako et al. 2023a, b). These techniques offer valuable insights into the origin, thermal maturity, and depositional environment of source rocks and crude oil, which are

essential for petroleum exploration. For example, biomarkers such as *n*-alkanes, steranes, and terpanes act as molecular fossils, providing insights into the organic matter sources, depositional environment, and the maturation history of crude oil (e.g., Brooks et al. 1969; Aquino 1983; Curiale et al. 1989). Similarly, stable carbon isotope ratios in crude oils aid in discerning the origin of organic matter and assessing the thermal maturity of crude oil (Craig 1953; Herz and Dean 1986; Konan et al. 2023; Amoako et al. 2023b). These analytical tools play a crucial role in hydrocarbon exploration and production, facilitating a deeper understanding of petroleum systems and the development of effective exploration strategies.

In this study, our objective was to analyze biomarkers and stable carbon isotopes in crude oil from the Saltpond Basin to infer their origin, depositional environment, and thermal maturity. Additionally, considering the shared geological conditions across basins along the South Atlantic margins (Beglinger et al. 2012a, b), we aimed to explore potential correlations with other types of crude oil in the region, focusing primarily on the Tano Basin and Niger Delta Basin.

2 Samples and experimental approach

2.1 Samples

Oil samples from the Saltpond oil field were collected from the Ghana National Petroleum Corporation's head office in Tema, Ghana, for biomarker and stable carbon isotope ratio analysis. To ensure accuracy, triplicate samples were taken and analyzed. An independent laboratory analysis revealed that the Saltpond oil samples exhibit a density at 15 °C of 848.6 kg/m³, a specific gravity of 0.8486, and an API gravity of 35.1 (Appenteng et al. 2013). Geochemical analysis of the Saltpond oil samples was conducted at the Petroleum Geochemistry Laboratory of the China University of Petroleum in Beijing. Moreover, biomarker characteristics and stable carbon isotope ratios in Saltpond crude oil, acquired from our study, were compared with published results of oil samples from the Tano Basin (Amoako et al. 2024) and Niger Delta Basin (Samuel et al. 2009; Ogbesejana et al. 2020), to investigate potential regional correlations.

2.2 Gas chromatography–mass spectrometry analysis

Biomarkers in the Saltpond oil samples were analyzed via gas chromatography–mass spectrometry (GC–MS). The saturated hydrocarbon fractions were analyzed using an Agilent 6890 gas chromatograph coupled with an Agilent 5975i mass selective detector. An HP-5 MS fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film coating) was employed with helium as the carrier gas. The initial

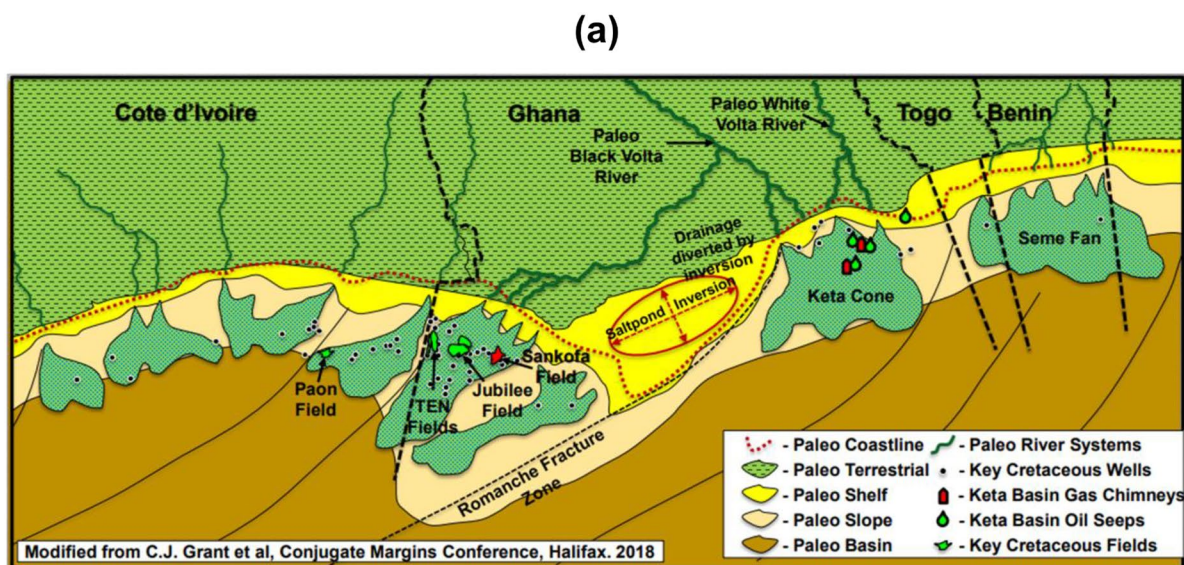


Fig. 1 **a** This geographic map illustrates the location of the Saltpond Basin, Ghana, positioned between the Sankofa field and the Accra-Keta/Eastern cone. **b** The stratigraphic sequence depicted here represents the Saltpond Basin. It's important to note that the crude oil examined in this study originated from the Early Devonian reservoir (Takoradi sandstone, indicated by red dotted lines) (after Atta-Peters et al. 2015) (Source: Retrieved from http://www.internationalpavilion.com/EnergyOps2023/geopartners_mexico2023.pdf)

gas chromatograph settings included an oven temperature of 50 °C and an injection temperature of 300 °C. Subsequently, the oven temperature increased at a rate of 20 °C per minute

until reaching 120 °C, followed by a further increase to a final temperature of 310 °C at a rate of 3 °C per minute.

The mass selective detector operated using electron impact ionization at 70 eV, scanning from 50 to 600 Da.

The Agilent 5975i gas chromatography–mass spectrometry (GC–MS) system was employed to analyze fractions of aromatic hydrocarbons. The system consists of an HP-5 MS fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) coated with 5% phenyl-methylpolysiloxane. The GC conditions comprised an initial temperature of 80 °C for 1 min, followed by a programmed ramp to 310 °C at a rate of 3 °C/min over 16 min, with the injector temperature maintained at 300 °C. Helium was utilized as the carrier gas, and the mass spectrometer operated in electron impact (EI) mode with a scan range spanning 50–600 Da and an ionization energy of 70 eV.

For sample identification, the retention times of their saturated and aromatic molecular markers were compared against those of a meticulously characterized reference sample utilized as the standard for this investigation.

2.3 Stable carbon isotope ratio analysis

Asphaltene isolates from the Saltpond oil sample were subjected to analysis using an elemental analyzer–isotope ratio mass spectrometer (EA–IRMS). Approximately 0.3 mg of each asphaltene sample and analytical standard was precisely measured and placed into small tin sample cups. These samples were introduced into a Dumas combustion EA through a zero-blank autosampler, combusting at 1030 °C under an oxygen atmosphere. The resulting combustion products were desiccated using an MgCl₂ trap and directed into a preparative gas chromatography (GC) column with helium as the carrier gas, effectively separating carbon dioxide (CO₂) during chromatography. The purified CO₂ was then passively introduced via an open split into the inlet of a Micromass Optima IRMS for subsequent carbon isotope analysis. Carbon isotope values were reported as the average of multiple replicate analyses, typically exceeding two ($n > 2$), with a standard deviation of less than 0.2 ‰. These values are presented relative to the internationally recognized standard, Vienna Pee Dee Belemnite (VPDB) carbonate.

3 Results

3.1 Aliphatic hydrocarbon distribution

The Saltpond oil displays a wide array of normal alkanes (n -C₁₂ to n -C₃₅) and acyclic isoprenoids (pristane and phytane) within the n -alkane and isoprenoid fraction (m/z 85, Fig. 2a). Notably, n -C₁₅ predominates in the n -alkane fraction. The absence of lighter n -alkanes ($\leq n$ -C₁₂) in the Saltpond crude oil may be attributed to evaporation during sample preparation. The oil samples exhibit a unimodal

distribution, with a significant prevalence of lower molecular weight (LMW) homologues ($\leq n$ -C₂₂) (Fig. 2a). The average ratio of $(n$ -C₂₁ + n -C₂₂)/(n -C₂₈ + n -C₂₉) in the Saltpond oil is 3.16 (Table 1). Compared to acyclic isoprenoids, the n -alkane series is notably more abundant in the Saltpond oil (Fig. 2a). The mean Pr/Ph ratio observed in Saltpond oil stands at 1.65, while the mean ratios of Pr/ n -C₁₇ and Ph/ n -C₁₈ are recorded as 0.25 and 0.16, respectively (Table 1). Additionally, carotene is absent in the Saltpond oil samples (Fig. 2b). In the m/z 191 fragmentogram (Fig. 2c), the Saltpond oil features tri-tetracyclic terpanes and pentacyclic terpanes, including Ts, Tm, C₃₀E, C₂₉ and C₃₀ hopane (h), and moretanes such as C₂₉Ts, C₃₀D, C₃₀ diahopane, gammacerane (g), and C₃₁–C₃₅ homohopanes (HH). The average ratio of Ts/(Ts + Tm) in the Saltpond oil is 0.62, while the ratio of C₂₉H/C₃₀H is 0.42 (Table 1). Additionally, the average ratio of gammacerane/C₃₀α hopane in the Saltpond oil is 0.15 (Table 1). A significant abundance of C₃₁ to C₃₅ homohopanes is observed in the Saltpond oil (Fig. 2c), with the average ratio of C₃₅HH/C₃₄HH being 0.51 (Table 1). The C₃₁22S/(22S + 22R) homohopane ratios average 0.59, and the average ratio of C₃₀D/C₂₉Ts in the Saltpond oil is 1.30 (Table 1). Moreover, the Saltpond oil exhibits a comprehensive distribution of tricyclic terpanes (TT) and C₂₄ tetracyclic terpene (TeT) ranging from C₁₉ to C₂₉, including the C₂₇TT peak, with C₂₃TT being the most predominant homologue (Fig. 2c). Longer chain tricyclic terpanes, C₃₀TT and C₃₁TT, are either absent or below the level of detection. Additionally, in the Saltpond oil, the 17α-hopane peak is higher than all the tricyclic and tetracyclic terpanes. In the sterane fraction (m/z 217), the Saltpond oil exhibits homopregnane, pregnane, C₂₇–C₂₉ regular sterane, and diasterane (Fig. 2d). The 4-methyl sterane peaks are either low or below the level of detection in the Saltpond oil (Fig. 2d). The distribution of C₂₇–C₂₉ regular sterane peaks in the oils generally follows the order C₂₇ > C₂₈ < C₂₉ (Table 1). The average ratio of C₂₇diasterane/C₂₇regular sterane in Saltpond oil is 0.93 (Table 1).

3.2 Aromatic hydrocarbon distribution

The aromatic fraction of Saltpond oil was initially scrutinized using total ion chromatography (TIC) mode (Fig. 3), revealing a diverse spectrum encompassing 2–3-ring aromatic hydrocarbons, notably featuring compounds such as naphthalene, phenanthrenes, triaromatic steroids, fluorenes (F), dibenzothiophenes (DBT), dibenzofuran (DBF), and their alkyl derivatives, each demonstrating distinct distributions and relative concentrations (Figs. 4, 5, 6, 7, 8, 9). The TIC mode analysis further unveiled a rich array of 2–3-ring polyaromatic hydrocarbons (PAHs), with naphthalene exhibiting conspicuous prominence.

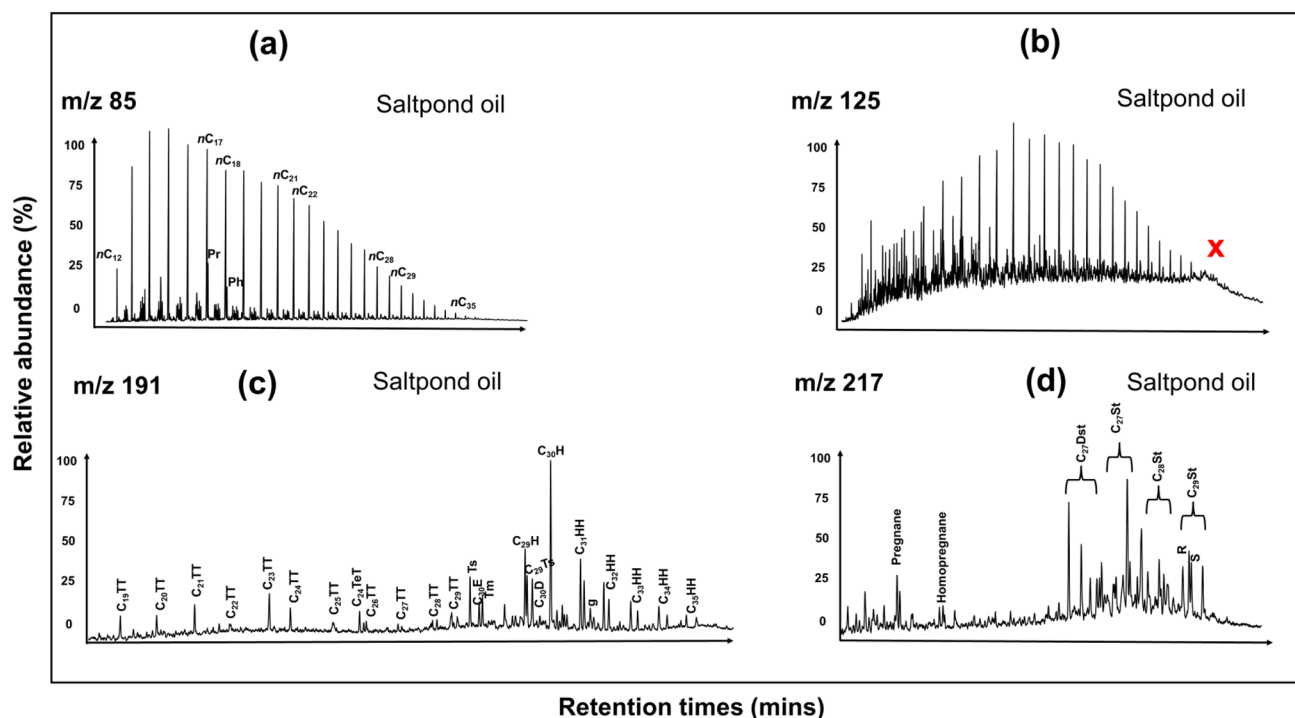


Fig. 2 Mass chromatogram illustrating the aliphatic hydrocarbons present in oil from the Saltpond Basin, Ghana. **a** Distribution of n -C₁₂ to n -C₃₅ alkanes and isoprenoids (m/z 85); **b** Fragmentogram at m/z 125, indicating the absence or undetectable levels of Carotenoids in the Saltpond Basin oil; **c** Distribution of Tri-tetracyclic terpanes and hopanoid series (m/z 191); **d** Distribution of pregnane, homopregnane, diasteranes, and C₂₇ to C₂₉ steranes (m/z 217)

Delving into the molecular ratios of individual PAHs, specific mass chromatograms of aromatic hydrocarbons and their alkyl derivatives were scrutinized across various mass-to-charge ratios (Figs. 4, 5, 6, 7, 8, 9). Tetra-methyl naphthalene predominantly characterized the naphthalene fractions, while di-methyl phenanthrene exhibited prominence within the phenanthrene fractions (Table 2). Additionally, within the triaromatic steranes fragmentogram (m/z 245), peak predominance was observed for C₂₉ aromatic steroids (Fig. 4). The distribution of heterocyclic aromatic compounds (HTCs) and hydrocarbons, including dibenzothiophene (DBT), dibenzofuran (DBF), and fluorenes (Fs), alongside their alkyl derivatives, displayed non-uniform patterns within the Saltpond oil (Table 2). Relative abundance analysis ranked these HTCs as F > DBF > DBT (Table 2). Notably, both alkyl phenanthrenes and alkyl naphthalenes serve as reliable indicators of thermal maturity in crude oils and other organic matter (Table 2). Ratios of Alkyl naphthalene and alkyl phenanthrene in Saltpond oil are summarized in Table 2. Remarkably, the alkyl phenanthrene index suggests a thermal maturity range from marginally mature to peak mature for the organic matter in Saltpond oil, while the Alkyl naphthalene indices propose a range from peak mature to overly mature.

3.3 Stable carbon isotope ratios

The stable carbon isotope ratios of the Saltpond oil indicate a relatively lighter signature, as summarized in Table 3. The bulk oil presents an average $\delta^{13}\text{C}$ value of -29.44% . Additionally, the average $\delta^{13}\text{C}$ values for the saturated and aromatic fractions of the Saltpond oil are relatively heavier at -28.79% and -28.67% , respectively. Moreover, the average $\Delta\delta_{\text{Aro}} - \Delta\delta_{\text{Sat}}$ value, representing the isotopic difference between the saturated and aromatic fractions, is calculated to be 0.12 (Table 3).

4 Discussions

4.1 Origin of organic matter in crude oil

Here, the organic matter source in the Saltpond crude oil was elucidated within the framework of the source rock organic chemistry discussed in previous research (Bansah et al. 2014). Bansah et al. (2014) identified Type II and Type III as the predominant kerogen types in the potential source rocks of the Saltpond Basin. Type II kerogen originates from a complex mixture of zooplankton, phytoplankton, and bacterial remnants typically deposited in reducing environmental

Table 1 Key parameters of selected *n*-alkanes, tricyclic (TT) and tetracyclic terpanes (TeT), hopanes (H), homohopanes (HH), and steranes (St) and diasteranes (DSt) utilized for evaluating the sources, thermal maturity and depositional environment of organic matter in crude oil samples originating from the Saltpond Basin, Ghana

Geochemical Indices	Saltpond Basin crude oil			
	S1	S2	S3	Average
Pr/Ph	1.65	1.65	1.65	1.65
Pr/ <i>n</i> -C ₁₇	0.25	0.24	0.25	0.25
Ph/ <i>n</i> -C ₁₈	0.17	0.16	0.16	0.16
<i>n</i> -C ₂₁ + <i>n</i> -C ₂₂ / <i>n</i> -C ₂₈ + <i>n</i> -C ₂₉	3.16	3.15	3.15	3.16
Ts/(Ts + Tm)	0.62	0.62	0.62	0.62
C ₃₅ HH/C ₃₄ HH	0.52	0.51	0.51	0.51
C ₂₉ H/C ₃₀ H	0.42	0.42	0.42	0.42
C ₃₀ D/C ₂₉ Ts	1.30	1.29	1.30	1.30
Gammacerane/C ₃ OH	0.15	0.15	0.15	0.15
C ₃₁ HH22S/(22S + 22R)	0.59	0.59	0.59	0.59
C ₁₉ TT + C ₂₀ TT%	41.88	41.75	41.67	41.77
C ₂₁ TT%	25.47	25.40	25.35	25.41
C ₂₃ TT%	32.65	32.55	32.49	32.56
C ₁₉ TT/C ₂₃ TT	0.57	0.57	0.57	0.57
(C ₁₉ TT + C ₂₀ TT)/C ₂₃ TT	1.85	1.84	1.84	1.84
C ₂₃ TT/C ₂₁ TT	0.90	0.89	0.89	0.89
C ₂₄ TeT/C ₂₃ TT	0.96	0.96	0.96	0.96
C ₂₄ TeT/(C ₂₄ TeT + C ₂₃ TT)	0.49	0.49	0.49	0.49
C ₂₄ TeT/C ₂₆ TT	1.35	1.35	1.35	1.35
C ₂₄ TeT/(C ₂₄ TeT + C ₂₆ TT)	0.58	0.57	0.57	0.57
C ₂₈ TT/C ₃₀ H	0.12	0.12	0.12	0.12
C ₂₉ TT/C ₃₀ H	0.20	0.20	0.20	0.20
% C ₂₇ St	38.37	38.26	38.29	38.31
% C ₂₈ St	33.32	33.22	33.25	33.26
% C ₂₉ St	28.31	28.23	28.26	28.27
C ₂₇ St/C ₂₉ st	1.24	1.24	1.24	1.24
C ₂₇ DSt/C ₂₇ St	0.93	0.93	0.93	0.93
C ₂₉ 20S/(20S + 20R)	0.46	0.47	0.46	0.46

conditions (Durand and Espitalie' 1976). In contrast, Type III kerogen primarily arises from the decomposition of terrestrial plant matter (Durand and Espitalie 1976) or the oxidation of marine organic matter (Khorasani and Michelsen 1992).

In source rocks and crude oils, the distribution of *n*-alkanes provides insights into their origins, distinguishing between marine and terrestrial sources. The predominance of lower molecular weight (LMW) *n*-alkanes ($\geq n$ -C₂₂) over higher molecular weight (HMW) *n*-alkanes ($\leq n$ -C₂₈) (n -C₂₁ + n -C₂₂/ n -C₂₈ + n -C₂₉) in the Saltpond oil indicates a greater contribution of organic matter from lower aquatic organisms. Additionally, the composition of C₂₇–C₂₉ regular steranes is instrumental in identifying different sources of organic matter in petroleum and hydrocarbon source rocks. The abundance of C₂₉ steranes

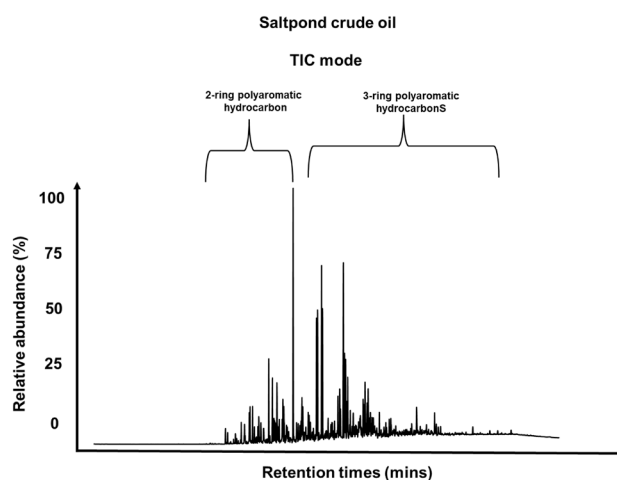


Fig. 3 Total ion current (TIC) chromatogram illustrating the combined intensity of 2-ring and 3-ring polyaromatic hydrocarbons identified in crude oil sourced from the Saltpond Basin, Ghana

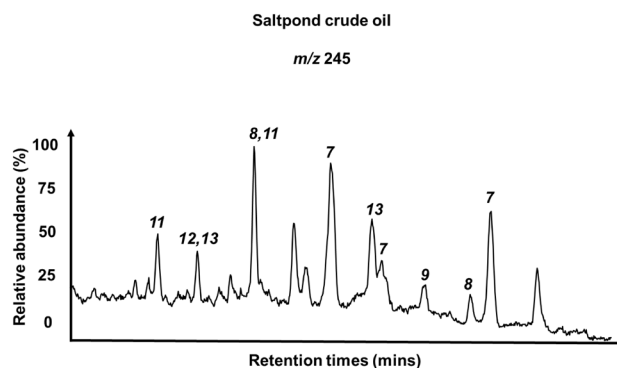


Fig. 4 Representative mass chromatograms (m/z 245) of the aromatic hydrocarbon fraction, depicting the distribution of methyl triaromatic steroids in crude oil derived from the Saltpond Basin, Ghana. Peak 7 corresponds to 4,23,24-trimethyltriaromatic steroids (C₂₉ triaromatic steroids), peak 8 represents 4-methyl-24-ethyltriaromatic steroids (C₂₉ triaromatic steroids), peak 9 indicates 3-methyl-24-ethyltriaromatic steroids (C₂₉ triaromatic steroids), peak 11 depicts 4-methyltriaromatic steroids (C₂₇ triaromatic steroids), peak 12 signifies 3-methyltriaromatic steroids (C₂₇ triaromatic steroids), and peak 13 denotes 3,24-dimethyltriaromatic steroids (C₂₈ triaromatic steroids)

typically signifies a higher input from higher plants or green algae, while the presence of C₂₇ steranes suggests the presence of eukaryotic algae and animal phyla (Volkman 2005; Summons and Douglas 2018). The ternary plot of C₂₇–C₂₉ regular steranes (Fig. 10a) indicates that the organic matter in the Saltpond crude oil is predominantly derived from lower aquatic organisms, mainly algae. The high peaks of C₂₉ aromatized steroids in the aromatic fraction (Fig. 4) signal terrestrial input or they may have

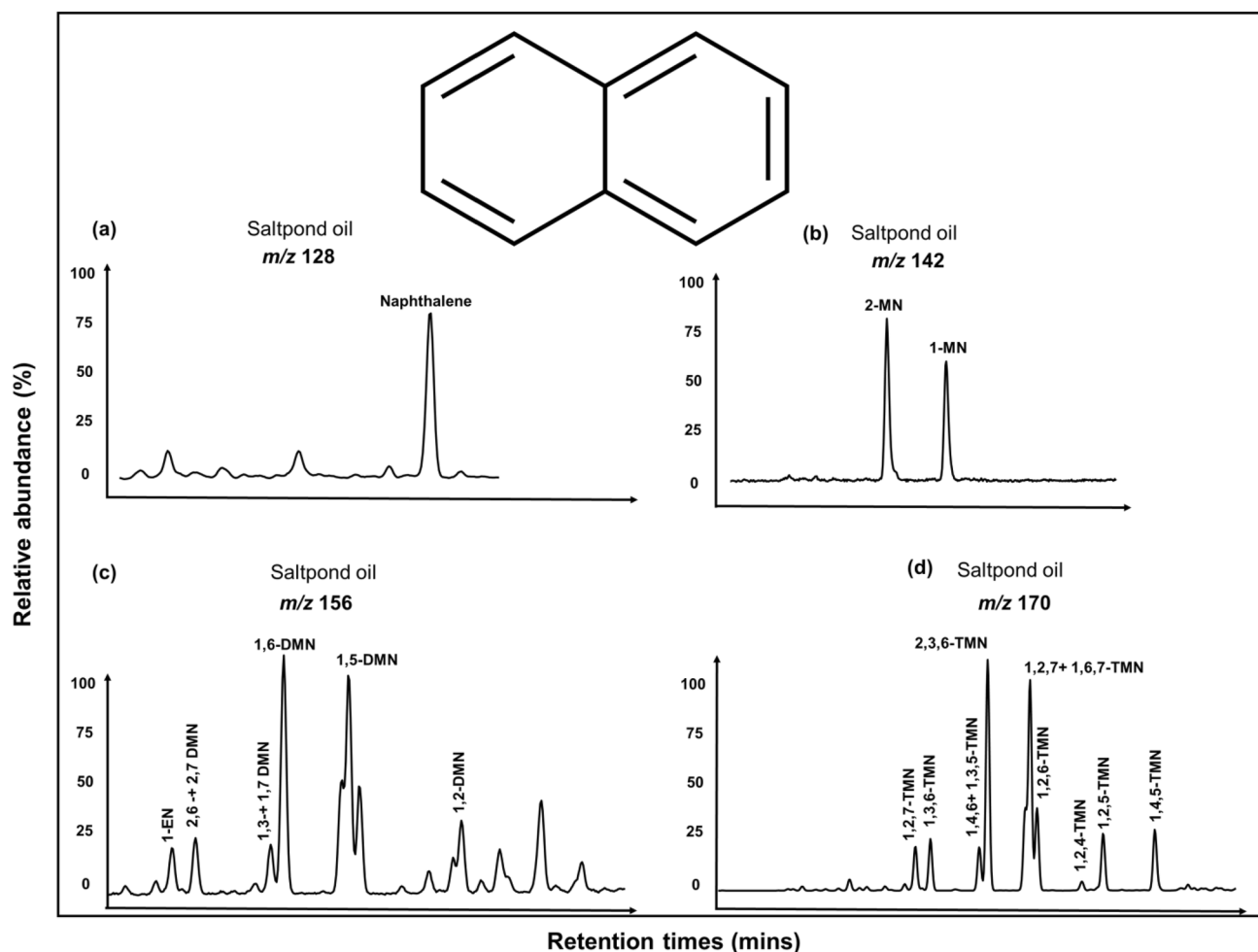


Fig. 5 Representative mass chromatograms of the aromatic hydrocarbon fraction illustrating various compounds: **a** naphthalene at m/z 128, **b** methyl naphthalene at m/z 142, **c** dimethyl naphthalene at m/z 156, and **d** trimethyl naphthalene at m/z 170, observed in crude oil sourced from the Saltpond Basin, Ghana

originated from algal precursors that have been subjected to high thermal conditions (Mackenzie and McKenzie 1983).

The isotopic ratios of ^{13}C – ^{12}C within kerogen and organic matter found in source rocks and crude oils are crucial for deciphering the origins and geological evolution of the organic material. $\delta^{13}\text{C}$ values serve as indicators of the dominant types of plants or algae present in the ancient environment during sediment deposition. Different photosynthetic pathways in plants lead to distinct isotopic signatures. Specifically, C3 plants typically exhibit lighter $\delta^{13}\text{C}$ values compared to C4 plants, with typical carbon isotope ratios of around -26.5% and -12.5% , respectively (Cerling et al. 1989). On the other hand, CAM plants demonstrate highly variable carbon isotope ratios, ranging from -28% to -12.5% , depending on the plant species and environmental factors (Messerschmid et al. 2021). Lighter carbon isotope

ratios typically characterize terrestrial organic matter, such as plants and soil, while heavier carbon isotope ratios are more common in marine organic matter, such as plankton and algae (Friedman and O’Neil 1977). This is due to the preferential absorption of the lighter isotope, carbon-12, by plants during photosynthesis, leaving a higher proportion of the heavier isotope, carbon-13, in the atmosphere and soil (Larsen et al. 2013). Conversely, the ocean contains a higher concentration of carbon-13 compared to the atmosphere, leading marine organisms to incorporate this isotope into their tissues (Oczkowski et al. 2018). Empirical evidence demonstrates very light carbon isotope ratios in microalgae and phytoplankton. Additionally, lighter isotopic signatures in source rocks and crude oils may suggest higher thermal maturation of organic matter, as lighter isotopes are preferentially released as hydrocarbons during this process (Wada 2009).

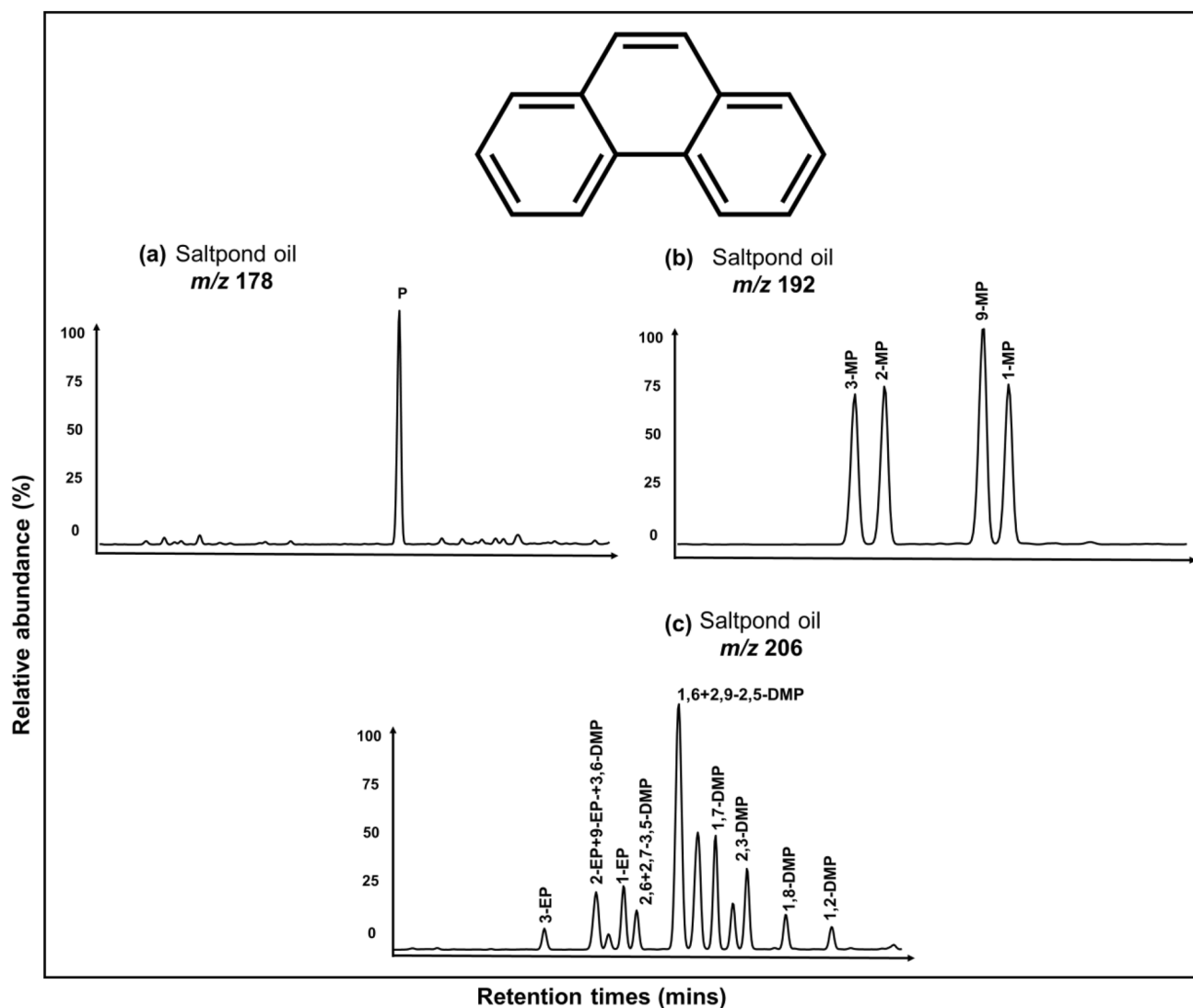


Fig. 6 Representative mass chromatograms of the aromatic hydrocarbon fraction depicting various compounds: **a** Phenanthrene at m/z 178, **b** methyl phenanthrene at m/z 192, and **c** dimethyl phenanthrene at m/z 206, identified in crude oil derived from the Saltpond Basin

Integrating isotope data with complementary biomarker information is essential for obtaining a comprehensive understanding of the origins and historical evolution of organic matter during the petroleum formation process. This approach enables the contextualization of the complex biological, environmental, and geological processes involved in converting organic matter into petroleum. Consistent with the C_{27} – C_{29} sterane triangular plot (Fig. 10a) and high C_{27}/C_{29} sterane ratios (>1 ; Table 1), the lighter $\delta^{13}C$ values observed in the whole, saturated, and aromatic fractions of the Saltpond oil suggest a greater contribution from lower aquatic organisms.

4.2 Depositional environment

In this section, the paleoenvironmental conditions of the Saltpond oil are assessed based on selected biomarker ratios. Acyclic isoprenoid ratios, such as Pr/Ph, found in rock extracts and crude oils, serve as proxies for the redox conditions of the depositional environment (Ten Haven et al. 1987). The Pr/Ph ratio operates under the assumption that pristane is derived from phytol via an oxidative pathway, whereas phytane forms through multiple reductive pathways (Powell and McKirdy 1973). In general, a reducing redox environment is characterized by a Pr/Ph ratio below 1, while a sub-oxic environment typically falls between 1 and 2, and an oxidizing environment shows a Pr/Ph ratio exceeding 2 (Didyk et al. 1978; Ten Haven et al. 1987). The average Pr/Ph ratio of 1.65 (Table 1) observed in the Saltpond oil

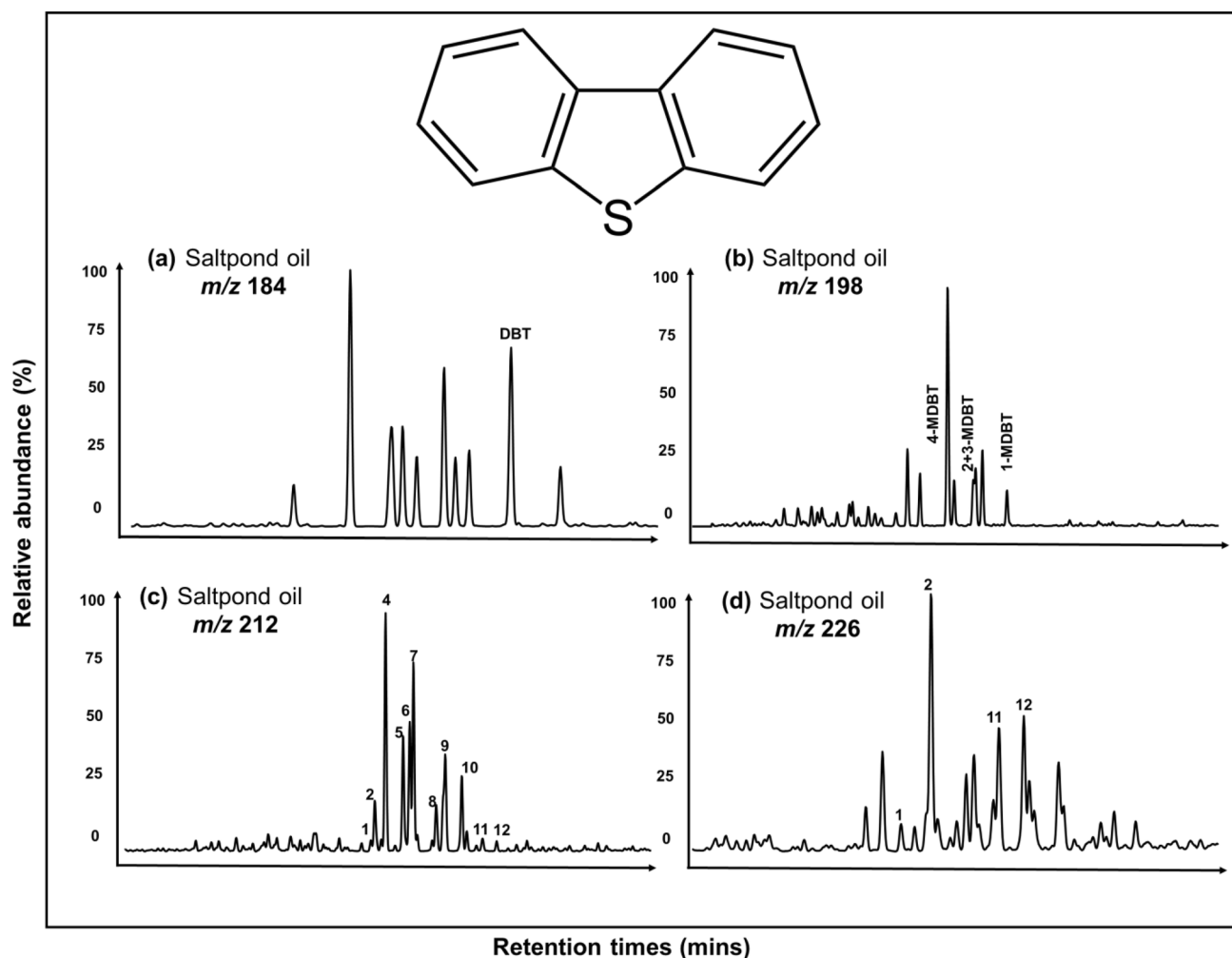


Fig. 7 **a** Representative mass chromatograms of the aromatic hydrocarbon fraction illustrating dibenzothiophene at m/z 184, **b** methyl dibenzothiophene at m/z 198, **c** dimethyl dibenzothiophene at m/z 212, and **d** trimethyl dibenzothiophene at m/z 226, identified in crude oil sourced from the Saltpond Basin

implies suboxic conditions prevailed during deposition. The $C_{35}HH/C_{34}HH$ parameter, representing homohopane (HH) ratios, is commonly utilized to assess redox conditions in marine source rocks (Peters and Moldowan 1991). Elevated $C_{35}HH/C_{34}HH$ ratios typically indicate the presence of marine carbonates or anoxic environments (Clark and Philip 1989). Conversely, lower $C_{35}HH/C_{34}HH$ ratios, accompanied by notable $C_{31}HH$ and $C_{32}HH$ signals, suggest a sub-oxic to oxic environment (Table 1). In line with the Pr/Ph ratio, an average $C_{35}HH/C_{34}HH$ ratio of approximately 0.5 lends support to the conclusion that the Saltpond oil was preserved under sub-oxic redox conditions (Table 1).

Gammacerane serves as a robust biomarker for assessing water column stratification (Hills et al. 1966; Moldowan et al. 1985; Damsté et al. 1995). While it is commonly identified in sediments formed under hypersaline conditions, its presence extends beyond such environments. Gammacerane

can also be detected in lacustrine deposits, particularly in lakes within temperate regions experiencing summer stratification (Damsté et al. 1995). Although the precise mechanisms underlying its formation remain uncertain, it is hypothesized that gammacerane originates from the reduction of tetrahymanol during diagenesis, as proposed by Venkatesan and Dahl (1989). Tetrahymanol, synthesized by various bacteria and a specific subset of ciliates and terrestrial eukaryotes, serves as its precursor (Banta et al. 2015). Due to their ability to delineate depositional conditions, the gammacerane index serves as a valuable parameter for distinguishing between saline and freshwater environments. Elevated ratios (>0.2) typically indicate saline conditions, whereas ratios below 0.2 suggest brackish to freshwater conditions (Moldowan et al. 1985). As depicted in Table 1, the gammacerane index of 0.15 observed in the Saltpond oil suggests deposition under brackish water conditions.

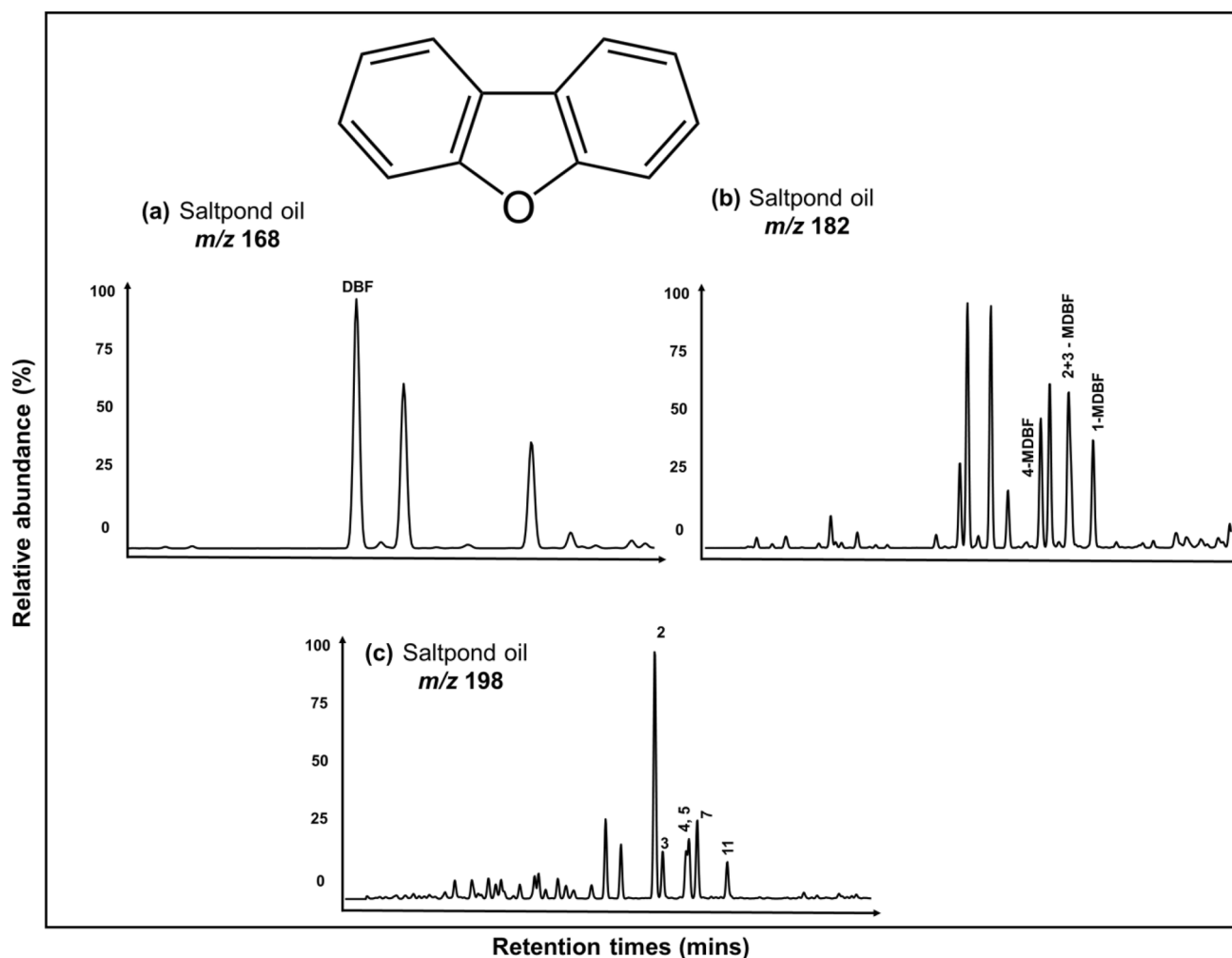


Fig. 8 a Representative mass chromatograms of the aromatic hydrocarbon fraction illustrating dibenzofuran (DBF) at m/z 168, b methyl dibenzofuran (MDBF) at m/z 182, and c dimethyl dibenzofuran at m/z 212, identified in a crude oil sample sourced from the Saltpond Basin, Ghana

Tricyclic and tetracyclic terpane ratios serve as valuable indicators for characterizing the depositional environments of source rocks and crude oils. The prevalence of C_{23} TT relative to other C_{19} TT– C_{23} TT homologs is frequently observed in marine or saline lacustrine source rocks and their associated oils (Neto 1983; Amoako et al. 2023a, b). In contrast, coal samples typically display a higher abundance of C_{19} TT (Zhu 1997; Fu et al. 2019). Recently, Xiao et al. (2019) introduced a ternary diagram capable of distinguishing between source rock depositional environments and associated oils by analyzing C_{19} TT– C_{23} TTs from a comprehensive dataset comprising 104 source rocks and 113 oils across multiple basins. Generally, swamp source rocks characterized by significant terrigenous organic matter input exhibit elevated concentrations of C_{19} TT and C_{20} TT, while sediments deposited in freshwater lacustrine environments are characterized by a predominance of C_{21} TT. The ternary

plot of C_{19} TT + C_{20} TT, C_{21} TT, and C_{23} TT (Fig. 10b) suggests that the Saltpond oil aligns with zone 4, indicating a fluvial or deltaic environment.

Li et al. (2013) employed a ternary plot comprising fluorene (Fl), dibenzofuran (DBF), and dibenzothiophene (DBT) to distinguish between various depositional facies, including marine carbonate, fluvial/deltaic/fresh lacustrine shale, and swamp, in 165 crude oil samples. Their analysis revealed that oils originating from marine shale display similar FL and DBF proportions, positioning them between the zones associated with fluvial/deltaic/fresh lacustrine shale and swamp, albeit with slightly higher DBT abundance. Oils sourced from brackish/saline lacustrine environments exhibited intermediate DBT concentrations with a wide range, partially overlapping with those from marine shale. Subsequently, a ternary plot (Fig. 10c) was generated based on Li et al.'s (2013) methodology to elucidate the depositional

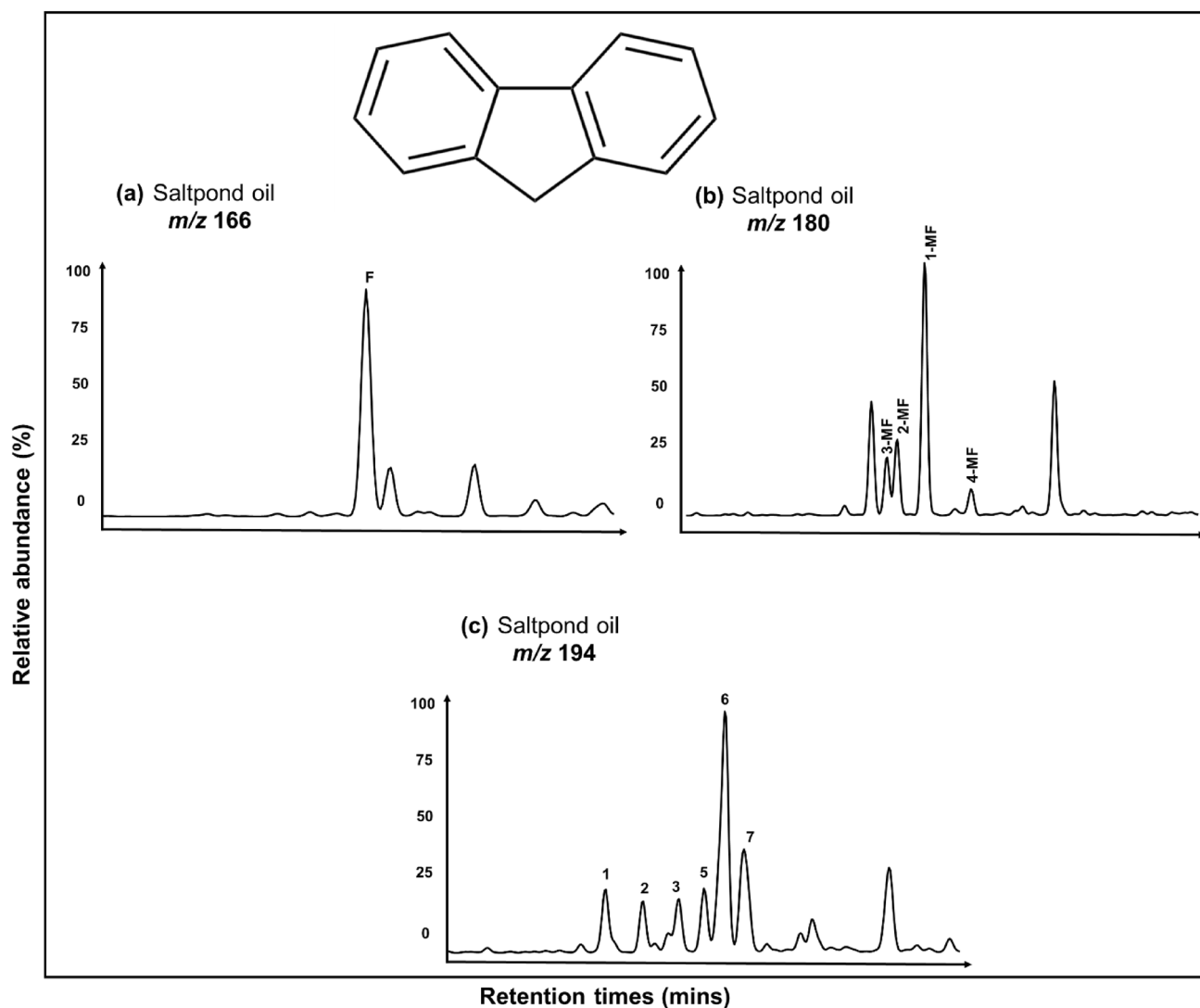


Fig. 9 a Representative mass chromatograms of the aromatic hydrocarbon fraction illustrating fluorene at m/z 166, b methyl fluorene at m/z 180, and c dimethyl fluorene at m/z 194, detected in a crude oil sample sourced from the Saltpond Basin, Ghana

environment of the Saltpond oil. The results indicate that oils within the Saltpond basin are affiliated with marine shales, suggesting a notable marine influence.

The presence of higher marine organic precursors compared to terrestrial organic precursors, as shown by the steranes ternary plot (Fig. 10a), along with the elevated ratios of $n\text{-C}_{21} + n\text{C}_{22}/n\text{-C}_{28} + n\text{-C}_{29}$ (3.16; Table 1) in the Saltpond oil, leads to the conclusion that the oils in the Saltpond Basin were deposited in a marine transitional environment. This conclusion is further supported by independent palynomorph studies on potential source rocks in the Saltpond Basin conducted by Atta Peters et al. (2015).

In marine transitional environments, the prevailing understanding has been that source rocks and crude oils contain a higher proportion of terrestrial organic matter, as highlighted by Zhang et al. (2018). However, our current molecular and

isotopic data present a contrasting view. Specifically, the crude oil from the Saltpond Basin indicates a dominance of marine-sourced organic matter over terrestrial sources in the crude oil samples, as depicted in Fig. 10a. Notably, studies by Hedges et al. (1997) and Kumar et al. (2016) have demonstrated that terrestrial organic matter is capable of undergoing degradation processes that can alter its composition to closely resemble marine organic matter signatures, adding a layer of complexity to the interpretation of organic matter sources in such environments.

4.3 Thermal maturity

To assess the thermal maturity of organic matter in the Saltpond crude oil samples, various aliphatic and aromatic thermal maturity parameters were utilized. To avoid

Table 2 Ratios and relative abundances of naphthalenes (N), phenanthrenes (P), dibenzothiophene (DBT), dibenzofuran (DBF), fluorene (F), and their alkyl derivatives (di, tri, tetra), employed to elucidate the depositional environment and thermal maturity of organic matter in crude oil sourced from the Saltpond Basin, Ghana

Parameters	Saltpond Basin crude oil			
	S1	S2	S3	Average
%N	0.07	0.02	0.07	0.06
% methyl	0.24	0.10	0.24	0.20
% di	1.07	1.73	1.07	1.29
% tri	18.61	55.68	18.58	30.96
% tetra	79.99	42.44	79.84	67.43
MNR	1.26	1.30	1.26	1.28
DNR-1	2.54	6.93	2.54	4.00
TNR-1	5.33	2.61	5.32	4.42
TMNr	0.44	0.52	0.44	0.47
TrMN	0.37	0.43	0.38	0.40
% P	19.02	19.49	18.99	19.17
%methyl P	40.43	40.55	40.35	40.45
% ethyl P	6.53	6.49	6.52	6.51
% di P	34.01	33.47	33.94	33.81
MPI-1	0.64	0.64	0.64	0.64
MPI-2	0.70	0.70	0.71	0.71
Rc-MPI-1	0.79	0.79	0.79	0.79
MPR	0.96	0.96	0.96	0.96
MDR	6.14	6.02	6.13	6.10
%Fluorene	39.72	37.93	39.64	39.10
%DBT	30.15	27.67	30.09	29.31
%DBF	30.12	34.40	30.06	31.53

Definition of parameters: MNR (Methyl Naphthalene ratio): (2-methylnaphthalene)/(1-methylnaphthalene); DNR-1 = [2,6 dimethyl naphthalene + 2,7 dimethyl naphthalene]/[1,5 dimethyl naphthalene]; TNR 1 (Trimethylnaphthalene ratio): (2,3,6-trimethylnaphthalene)/[1,4,6-trimethylnaphthalene + 1,3,5-trimethylnaphthalene]; TMNR = [1,3,7]/[1,3,7 TMN + 1,2,5 TMN]; TrMN (trimethylnaphthalene) ratio: (1,3,6-TrMN + 1,3,7-TrMN + 2,3,6-TrMN)/STrMN; MPI-1 = 1.5[2MP + 3MP]/[P + 1MP + 9MP], MPI-2: [3*(2-methylphenanthrene)]/[phenanthrene + (1-methylphenanthrene) + (9-methylphenanthrene)]; Rc-MPI-1 = 0.6[MPI-1] + 0.37; MPR (methylphenanthrene ratio): (2-methylphenanthrene)/(1-methylphenanthrene); MDR = 4MDBT/1MDBT

Rc: calculated vitrinite reflectances

After Radke et al. (1986)

Table 3 Carbon-13 to Carbon-12 isotopic ratios (relative to PDB) in crude oil derived from the Saltpond Basin, Ghana

Sample ID	Whole Oil fraction $\delta^{13}\text{C}_{\text{PDB}}$ (‰)	Fraction $\delta^{13}\text{C}_{\text{PDB}}$ (‰)	
		Saturated fraction	Aromatic fraction
S1	-29.61	-28.84	-28.88
S2	-29.40	-28.81	-28.60
S3	-29.31	-28.72	-28.51
Average	-29.44	-28.79	-28.67

underestimating or overestimating the thermal maturity of the oils based on molecular parameters (Alexander et al. 1986; Amoako et al. 2023a), the thermal maturity of potential source rocks (low to poor) in the Saltpond Basin determined in previous studies (Bansah et al. 2014) served as a control. Within the aliphatic fraction, the following parameters were used: Ts/(Ts + Tm) (Table 1; Seifert and Moldowan 1979), $\text{C}_{31}\text{HH}22\text{S}/(22\text{S} + 22\text{R})$, and $\text{C}_{29}20\text{S}/(20\text{S} + 20\text{R})$ (Table 1; Mackenzie et al. 1980; Seifert and Moldowan 1980). Within the phenanthrene fragmentogram of the aromatic fraction (Fig. 6), the following maturity parameters were used: MPI-1; MPI-2; Rc-MPI-1; MPR; MDR (Radke 1988). Within the naphthalene fraction of the aromatic fraction (Fig. 5), the following thermal maturity parameters were analyzed: MNR; DNR-1; TNR-1; TMNr; and TrMN (Table 2; Radke 1988). Amoako et al. (2024) recently noted that Ts/(Ts + Tm) greater than 0.4 in some Ghanaian offshore sediments is indicative of higher thermal maturity, although this parameter is sensitive to lithofacies (Seifert and Moldowan 1979). Ratios of $\text{C}_{31}\text{HH}22\text{S}/(22\text{S} + 22\text{R})$ petroleum samples between 0.50 and 0.54 suggest an early oil generation stage and from 0.57 to 0.62 during the main oil generation stage (Seifert and Moldowan 1986). Once isomerization equilibrium is reached, the 22S/(22 S + 22 R) ratio remains constant, providing no further insight into maturity (Seifert and Moldowan 1986). Similarly, $\text{C}_{29}20\text{S}/(20\text{S} + 20\text{R})$ ratio greater than 0.3 is indicative of higher thermal maturity (Peters et al. 2005; Xiao et al. 2018; Amoako et al. 2024). As indicated in Table 1, the higher Ts/(Ts + Tm) (0.62), $\text{C}_{31}\text{HH}22\text{S}/(22\text{S} + 22\text{R})$ (0.59), and $\text{C}_{29}20\text{S}/(20\text{S} + 20\text{R})$ (0.46) suggest the oils have reached at least the early oil generation phase. Given the greater stability, wider maturity range, and higher sensitivity of aromatic molecular parameters to maturity changes, these factors make aromatic parameters valuable tools for assessing the thermal maturity and evolutionary history of crude oil. Within the naphthalene fraction, the aforementioned parameters indicate a thermal maturity range from peak maturity to overmature, whereas the phenanthrene thermal maturity parameters suggest a thermal maturity range between early-peak mature. Consistent with the thermal maturity of the potential source rocks within the Saltpond Basin, it appears the phenanthrene maturity indices are more sensitive to the thermal maturity range of oil in the Saltpond Basin than the naphthalene maturity indices. Amoako et al. (2023a, b) also found that phenanthrene maturity indices are more sensitive to the thermal maturity of Cretaceous sediments in offshore wells in the Gulf of Guinea, indicating their reliability as maturity indicators in the region.

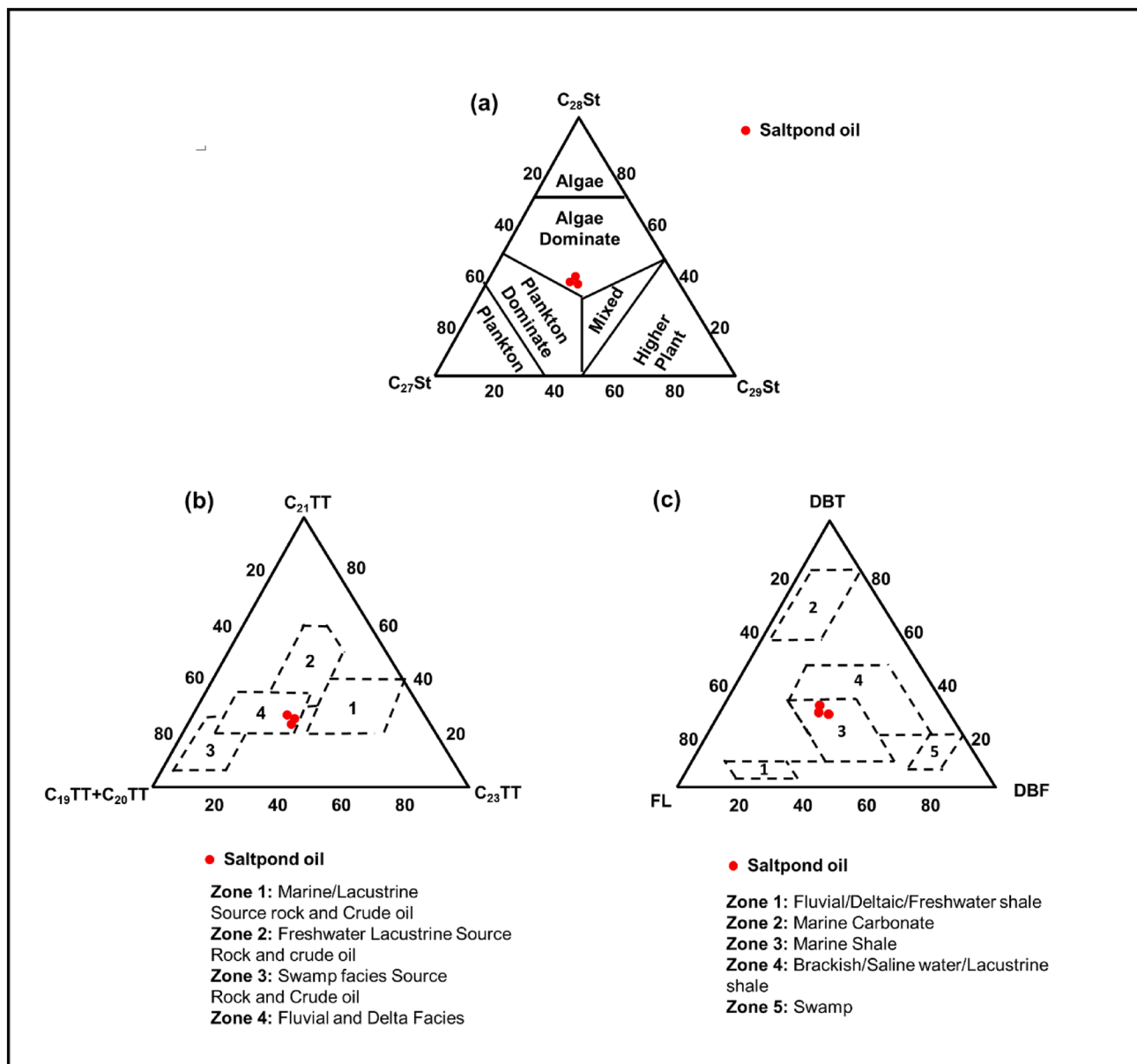


Fig. 10 **a** Ternary plot illustrating the distribution of C_{27} – C_{29} steranes to elucidate the sources of organic matter in crude oil sourced from the Saltpond Basin, Ghana (adapted from Amoako et al. 2024). **b** Ternary plot delineating the depositional environment of crude oil from the Saltpond Basin based on the distribution of C_{19} – C_{23} tricyclic terpanes (adapted from Xiao et al. 2018). **c** Ternary plot illustrating the depositional environment of crude oil in the Saltpond Basin through the distribution of fluorene (FL), dibenzofuran (DBF), and dibenzothiophene (DBT) (adapted from Li et al. 2013). Note: the marine transitional depositional environment of the Saltpond Basin crude oil contradicts the conventional understanding of terrestrial dominance in such settings. However, the potential for degradation processes could obscure the differentiation between terrestrial and marine organic matter origins in such a dynamic environment (Hedges et al. 1997; Kumar et al. 2016)

4.4 Regional correlation with crude oils in the South Atlantic margin

The correlation of crude oil types holds significant importance across various domains of the petroleum industry, including exploration, production, refining, and environmental management (Peters et al. 2005; Wang et al. 2002).

In this section, a comparative examination of the organic geochemistry of crude oil sourced from the Saltpond Basin with various crude oil types found in the West African portion of the South Atlantic margin was undertaken. The goal was to discern any similarities or differences in the geochemical composition between Saltpond Basin crude oil and oils in that region. Specifically, comparisons were made between

the Saltpond Basin crude oil and oils from the Cretaceous-aged Tano Basin and the Cretaceous-Tertiary-aged Niger Delta Basin. These basins were selected for correlation due to their integration within the broader tectonic framework of the South Atlantic rift basin, which originated during the Early Cretaceous period through the separation of Africa and South America (Schiefelbein et al. 2000; Brownfield and Charpentier 2006; Beglinger et al. 2012a, b). Previous molecular and isotopic studies on the Tano Basin (Amoako et al. 2024), and the Niger Delta Basin (Ogbesejana et al. 2020; Samuel et al. 2009), provided essential data for the correlation studies. The analysis was conducted within the context of three main factors: source input, depositional environment, and thermal maturity.

Geochemical findings and independent analyses using molecular and isotopic parameters indicate a ranking of terrestrial sourced organic matter signatures in the oils as follows: Niger Delta Basin > Tano Basin > Saltpond Basin (Fig. 11; Amoako et al. 2024; Samuel et al. 2009). This suggests the presence of distinct source input factors influencing hydrocarbon generation potential and petroleum characteristics in oils from the West African segment of the South Atlantic margin.

Regarding the depositional environment, molecular ratio analysis suggests that Saltpond Basin oil originated from a marine transitional environment. Independent analyses using molecular and isotopic parameters revealed that oils from the Tano Basin originated from anoxic transitional marine-lacustrine settings (Fig. 11; Amoako et al. 2024). In the Niger Delta Basin, they fall within suboxic–oxic terrigenous deltaic or marine or lacustrine environments (Fig. 11; Samuel et al. 2009). This diversity underscores the varied depositional settings that preserved oils from the West African portion of the South Atlantic margin. Additionally, distinct redox conditions influenced organic matter preservation in oils from these basins, with the Tano Basin oil preserved under anoxic conditions and the Niger Delta oils mainly preserved under suboxic to

oxic conditions (Fig. 11; Samuel et al. 2009; Amoako et al. 2024). These findings highlight the dynamic and varied redox conditions that prevailed over time during the petroleum formation process in the West African segment of the South Atlantic margin.

In terms of thermal maturity, Amoako et al. (2024) showed that the oils in the Tano Basin were generated during the early mature phase (Fig. 11), while oils from the Niger Delta Basin were expelled during the early-peak mature stages (Fig. 11; Samuel et al. 2009). This shows that the oils in the Saltpond Basin have comparable maturity levels with those in the Tano Basin but differ from oils in the Niger Delta Basin in terms of thermal maturity (Fig. 11).

In summary, correlation studies suggest that Saltpond Basin oil is genetically different from oils found in the Tano Basin and Niger Delta Basin. This distinction is mainly influenced by the sources of organic matter in the oils as well as the depositional environment conditions that preserved them. This closely aligns with the findings of Jian-Ping et al. (2008).

5 Conclusion

Gas Chromatography–Mass Spectrometry and Gas Chromatography–Isotope Ratio Mass Spectrometry were used for comprehensive analyses of the molecular and isotopic composition of crude oil from the Saltpond Basin. The primary objectives were to determine the origin of organic matter, characterize the depositional environment, and evaluate thermal maturity levels. Correlation analyses were performed on the Saltpond oil samples alongside existing data from crude oils in the Tano Basin and Niger Delta Basin to uncover potential regional correlations.

From our comprehensive analyses, the following conclusions were drawn:

Fig. 11 Regional correlation diagram delineating the distinct origins of crude oil from the Saltpond Basin in comparison to those from the Tano and Niger Delta Basins. Note: oil data from the Tano Basin includes the Jubilee and TEN fields, as originally reported by Amoako et al. (2024); oil data from the Niger Delta Basin covers the Eastern, deepwater, West, and Central regions of Nigeria's offshore, as originally reported by Samuel et al. (2009)

Petroleum Basin/classification	Source input	Depositional environment	Redox condition	Thermal maturity
Classification	Higher plants Mixed Lower organisms	Marine Marine Transitional Lacustrine Marine- Lacustrine Terrestrial	Anoxic Suboxic Oxic	Immature Early mature Peak mature
Saltpond Crude oil	■ ■ ⊗	■ ⊗ ■ ■ ■	■ ⊗ ■	■ ⊗ ■
Tano Basin oil	■ ⊗ ■	■ ■ ■ ⊗ ■	⊗ ■ ■	■ ⊗ ■
Niger Delta oil	⊗ ■ ■	⊗ ■ ■ ⊗ ■	■ ⊗ ■ ⊗	■ ⊗ ■ ⊗

Specific biomarker ratios, such as $n\text{-C}_{21} + n\text{-C}_{22}/n\text{-C}_{28} + n\text{-C}_{29}$ (3.16) and a high $\text{C}_{27}/\text{C}_{29}$ sterane ratio (1.24), in addition to light $\delta^{13}\text{C}$ values (approximately -29‰) of the bulk oil, suggest that the oils from the Saltpond basin originated from multiple sources, predominantly lower marine aquatic organisms.

Elevated pristane/phytane ratios (1.65), absence of carotenoids, ternary plot of $\text{C}_{19}\text{--}\text{C}_{23}$ tricyclic terpane series, along with dibenzofuran-dibenzothiophene-fluorene ternary plot, collectively indicate that the crude oil from the Saltpond Basin was deposited in a suboxic marine transitional environment. The prevalence of organic matter sourced from lower marine organisms in the Saltpond Basin crude oil challenges the established paradigm of terrestrial predominance in marine transitional environments. Furthermore, the capacity of degradation processes to conceal the distinction between terrestrial and marine organic matter sources highlights the complex organic matter dynamics inherent in marine transitional environments.

Molecular maturity indices, particularly $\text{C}_{31}\text{HH22S}/(\text{22S} + \text{22R})$, $\text{C}_{29}\text{20S}/(\text{20S} + \text{20R})$, and methyl phenanthrene indices, suggest that the Saltpond Basin crude oil was expelled from source rocks exhibiting thermal maturity at the early maturity stage.

Correlation analysis unveiled the genetic uniqueness of Saltpond crude oil in contrast to oils from the Tano and Niger Delta Basin. Notably, the Niger Delta Basin displays the highest terrigenous organic matter input, followed by the Tano Basin and then the Saltpond Basin. Additionally, differences in depositional environments were noted between Saltpond oil and those from the Tano Basin (anoxic transitional marine-lacustrine settings) and Niger Delta Basin which were either deposited in terrigenous deltaic or marine or lacustrine environments. Additionally, the thermal maturity of the Saltpond oil is comparable to oils found in the Tano Basin but lower than those found in the Niger Delta Basin.

Although this study offers valuable insights, it is essential to recognize specific limitations that could impact the generalization of the results. Specifically, the study is constrained by the limited availability of oil samples from the Saltpond Basin and the absence of source rock samples for oil–source correlation analysis. To enhance the reliability and extend the applicability of the findings presented herein, future research efforts should strive to include a larger number of both oil and source rock samples to facilitate comprehensive oil–oil and oil–source correlations.

In summary, our findings highlight the distinct organic geochemical traits of crude oil in the Saltpond Basin compared to those in the Niger Delta and Tano Basins. They also underscore the diverse biological, geological, and paleoenvironmental factors influencing different types of crude oil within the West African segment of the South Atlantic

margin. This information is crucial for regional exploration efforts, production, and environmental management initiatives in the area.

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Data availability Not applicable.

Declarations

Conflicts of interest The authors declare no conflict of interest.

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