Geochemical assessment and hydrocarbon potential of Oligocene–Pliocene source rocks from northeast onshore Nile Delta, Egypt

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Abstract

Recent exploration in the Nile Delta Basin has led to major oil and gas discoveries; however, source– reservoir relationships in the onshore part of the basin are still ambiguous. This work involves a comprehensive geochemical assessment of possible Oligocene–Pliocene source rocks, using TOC/Rock-Eval pyrolysis and gas chromatography–mass spectrometry. The aim is to investigate quantity, quality, thermal maturity, sources, and depositional paleoenvironment of the disseminated organic matter, and to correlate rock samples with hydrocarbons retrieved from the study area. Moreover, the chemical and isotopic compositions of gases were employed to examine origin, maturity, mixing and secondary alteration processes.

Results reveal fair to good organic richness (TOC \sim 1 wt.%) for the Oligocene–Pliocene rocks, with the highest TOC content from the Oligocene Tineh Formation. The kerogen is generally gas-prone Type-III and to a lesser extent Type-IV and Type-II/III. Molecular and biomarker results indicate mixed source facies with variable contributions from higher plants, algae, bacteria, and plankton, deposited under suboxic to anoxic nearshore marine or lacustrine depositional settings. Significant biomarkers include elevated C_{26}/C_{25} tricyclic terpane ratios (0.82–3.62), low C₃₁ homohopane (22R)/C₃₀ hopane ratios (0.17– 0.63), and low oleanane and gammacerane contents. Maturity-related biomarkers, Rock-Eval T_{max} and vitrinite reflectance values are consistent and suggest immature to early mature rock samples.

Molecular and isotopic compositions of mud gases indicate complex origins and mixing histories ranging from primary microbial to pure thermogenic, where thermogenic processes dominate the pre-Miocene intervals.

Chemometric analysis of 18 source-related biomarker ratios for rock extracts revealed four genetic families. Hierarchical cluster analysis (HCA) of biomarker data for rock extracts and condensate oils from the onshore Nile Delta indicates no correlation between Miocene–Pliocene rocks and condensates or oils in the area. Therefore, pre-Miocene source rocks are suggested to be the most probable candidates for hydrocarbons in the onshore Nile Delta.

Keywords: *Oligocene–Miocene source rocks, biomarkers, chemometrics, mud gas, onshore Nile Delta*

1. Introduction

The Nile Delta Basin is the growth engine for Egypt's large gas discoveries. Such giant discoveries and favorable export infrastructure make Egypt a regional hub for natural gas (EGAS, 2019; Dolson, 2020). Source rock samples from the onshore Nile Delta have been examined by several authors (e.g., Shaaban et al., 2006; El Nady, 2007; El Nady and Harb, 2010; Keshta et al., 2012; Ghassal et al., 2016; Leila and Moscariello, 2017). Total organic carbon (TOC) and Rock-Eval pyrolysis data suggested that Oligocene– Miocene intervals are the primary source rocks in the Nile Delta (EGPC, 1994). These layers are associated with transgressive depositional cycles and are generally rich in Type-III and Type-II/III kerogens (Schlumberger, 1995; Sharaf, 2003; El Nady, 2007; Lučić and Bosworth, 2019; El Diasty et al., 2022). The younger Upper Miocene–Pliocene formations also represent possible source rocks, especially in basinal areas where their thickness could compensate for poor source rock quality (EGPC, 1994). However, the Pliocene succession is mainly immature throughout the Nile Delta Basin (Abdel Aal et al., 2001; Sharaf, 2003; El Diasty et al., 2022).

Hydrocarbons derived from ultra-deep Jurassic–Cretaceous source rocks cannot be completely ruled out (Feinstein et al., 2002; Al-Balushi et al., 2016). Similar Jurassic and Cretaceous source layers occur in the adjacent prolific Western Desert, and equivalents of these layers were likely deposited across the Nile Delta (Shaaban et al., 2006; Vandré et al., 2007). Recent geochemical and petrographic assessment of both intervals in the northern Western Desert was reported (Mansour et al., 2020, 2023). The Cenomanian Bahariya Formation and the Middle Jurassic Khatatba Formation in the northern Western Desert are mainly enriched in Type-III kerogen, and the later reveals fair to excellent hydrocarbon generation potential (Mansour et al., 2020, 2023). Moreover, hydrocarbons produced from the Nile Delta and Western Desert basins show similar geochemical features and can be genetically related (El Diasty and Moldowan, 2013). Nevertheless, the contribution of these deep intervals to hydrocarbon generation in the Nile Delta is still ambiguous (Lučić and Bosworth, 2019). This is a consequence of limited available samples due to the thick Miocene cover and limited penetrations, which limit understanding of the generative potential of these plays.

Several source rock evaluation studies were conducted for the onshore Nile Delta (Shaaban et al., 2006; El Nady, 2007; El Nady and Harb, 2010; Ghassal et al., 2016; Leila and Moscariello, 2017). However, these studies focused mainly on routine assessment using TOC/Rock-Eval pyrolysis data, whereas detailed investigations of the biomarker, isotopic or molecular geochemical features of the disseminated organic matter are still lacking. Furthermore, no comprehensive oil–source correlation was developed. The limited availability of rock samples is an issue in the onshore Nile Delta. The petroleum-system bottom is still not identified, with only a few wells reaching pre-Miocene targets due to thick sedimentary cover. Thus, the hydrocarbon generation potential of deeper pre-Miocene intervals remains unclear (Shaaban et al., 2006; Vandré et al., 2007; Dolson et al., 2014; Dolson, 2020). Additional comprehensive source–reservoir correlation studies may unlock extra plays undiscovered to date (Dolson, 2020).

This study resulted in a geochemical dataset including fluid hydrocarbons (headspace gases and Isotubes) and rock samples recovered from the onshore Nile Delta (Fig. 1). The present work includes the following: (1) Oligocene–Pliocene possible source rock samples were geochemically assessed to determine organic richness, kerogen type, thermal maturity, and depositional paleoenvironment of organic matter; (2) extracted bitumen samples were classified by applying multivariate statistical analysis (chemometrics) and correlated with oils from the study area (Khairy et al., 2022), based on their biomarker distributions to better understand source–reservoir relationships; (3) chemical and isotopic compositions of mud gas (headspace and Isotube) samples were examined to understand their origin, maturity, mixing and alteration; and (4) comparison the results of the current study with previous published data from the offshore and onshore Nile Delta to clarify the similarities/differences within the same rock-facies and discovered hydrocarbons in the basin.

2. Geological framework

The tectonic history of the Nile Delta Basin involves long periods of subsidence and deposition (EGPC, 1994). The basin formed as consequence of the extension between the Eurasian and Afro-Arabian plates (Dolson et al., 2005).

3 The tectonic and stratigraphic evolution of the basin was significantly controlled by a prominent E–W trending faulted flexure zone referred to as the Hinge Line or Hinge Zone (Harms and Wray, 1990;

Sestini, 1995). This line divides the Nile Delta Basin into southern and northern blocks located on the unstable shelf and steeply faulted continental shelf, respectively (Meshref, 1990; Kamel et al., 1998). In the southern delta block, the basement is relatively shallow and block faulting is more common, whereas large normal faults are more abundant north of the Hinge Zone (Schlumberger, 1984, 1995). In the northern part of the Nile Delta Basin, significant and rapid thickening of Tertiary deposits resulted from continuous subsidence along the Hinge Zone (Sestini, 1995).

The Rosetta (NE–SW) and Temsah (NW–SE) are the two main fault trends in the northern Nile Delta (Sestini, 1995; Loncke et al., 2006). Since Late Cretaceous and Neogene time, the reactivation of both fault trends resulted in thickness and facies changes in the post-Oligocene succession, subdividing the northern Nile Delta into western, central, and eastern sub-basins (Meshref, 1990; EGPC, 1994).

The stratigraphic sequence of the Nile Delta (Fig. 2) extends down to the Jurassic with a total thickness up to 10 km (EGPC, 1994; Abdel Aal et al., 2001). It is dominated by shale and sandstone and is generally subdivided into pre-Miocene, Miocene, and post-Miocene sequences (Dolson et al., 2001; Lučić and Bosworth, 2019). The Oligocene Tineh Formation represents the top of the pre-Miocene and comprises both sandstone (submarine fan facies) and shale (highstand prograding facies) (Lučić and Bosworth, 2019). The Miocene sequence includes Qantara, Sidi Salem, Qawasim and Abu Madi formations, with total thickness approaching 3000 m in the central part of the Nile Delta (Schlumberger, 1984; Dolson et al., 2001). The Kafr El Sheikh Formation represents the bottom of the post-Miocene sequence, and it is overlain by El Wastani and Mit Ghamr formations. A detailed description of the tectonic and stratigraphic evolution of the Nile Delta Basin is beyond the scope of this work but more details can be found in several other studies (e.g., Said, 1990; Abdel Aal et al., 2001; Loncke et al., 2006; Hanafy et al., 2016; Kellner et al., 2018).

3. Dataset and methodology

3.1. TOC, Rock-Eval pyrolysis, and vitrinite reflectance

A total of 335 cuttings samples collected from ten boreholes were available for this study (Supplementary data file). Only the Mocha-1 well reached the Oligocene intervals, whereas the maximum penetration of

other wells is the Miocene Sidi Salem Formation. Lithologically, the rock samples are primarily shale and any apparent contaminants were removed. To remove drilling-mud contaminants all rock samples were Soxhlet-extracted using 200 ml of dichloromethane (DCM)/methanol mixture (93:7 v/v) for 24–48 hours at 40 °C using \sim 4 g of each pulverized rock sample. The extracted bitumen was separated from the solvent mixture by rotary evaporation, and then transferred to a pre-weighted vial, whereas the rock residue was treated with HCl (37%) for 24 hours to remove carbonates. Once the reaction was complete, the samples were washed several times with distilled water until neutral pH and left to dry in a fume hood.

TOC contents were measured by a LECO CHN628 Elemental Analyzer using ~100 mg of the powdered rock. All TOC measurements were conducted in duplicate. Programmed pyrolysis was carried out using a Rock-Eval 6 instrument in standard mode applying Basic/Bulk-Rock method (Behar et al., 2001; Waters et al., 2020). Approximately 60 mg of crushed rock was pyrolyzed under flowing nitrogen at 300 °C for 3 min to release free volatile hydrocarbons (S_1) and then the oven temperature was increased from 300 to 650 °C (hold for 3 min) at 25 °C/min to crack organic matter from kerogen (S_2) . CO₂ released from the thermal cracking of kerogen is represented by S_3 peak. Following the pyrolysis stage, the residual carbon was heated from 300 \degree C to 850 \degree C in an oxidation oven at 20 \degree C/min. The released hydrocarbons from sample pyrolysis were measured by a Flame Ionization Detector (FID), whereas CO and $CO₂$ released during pyrolysis and combustion stages were detected by Infrared (IR) cells. Other parameters such as Hydrogen Index (HI = $S_2 \times 100/TOC$) and Oxygen Index (OI = $S_3 \times 100/TOC$) were also calculated (Supplementary data file). The analysis was conducted at StratoChem Laboratories (Cairo, Egypt) and the British Geological Survey (Nottingham, UK).

A total of 24 rock cuttings were subjected to kerogen isolation procedure by treatment of ~15 g of each sample with HCl (35%) and HF (45%) followed by sieving using a 15 μm nylon sieve (Traverse, 2007). Vitrinite reflectance measurements (%Ro) were carried out on polished epoxy plugs of unfloated kerogen concentrates at StratoChem Laboratories (Cairo, Egypt) using a Zeiss Axio microscope following the procedure of Taylor et al. (1998). Measurements were conducted under oil immersion in reflected white light, and the digital indicator was calibrated using a glass standard with reflectance of 1.02% in oil. Vitrinite reflectance measurements were based on the best quality vitrinite macerals, with unimodal histograms in most samples. The prepared samples were also examined utilizing fluorescence from blue light excitation via xenon or mercury lamp with an excitation filter at 495 nm coupled with a barrier filter of 520 nm.

3.2. Fractionation

Rock samples with high extracted bitumen yields were considered for further alumina/silica column chromatography. Fractionation was conducted on 31 extracted bitumen samples representing different stratigraphic intervals. Approximately 35 mg of the extracted bitumen was adsorbed on ~0.50 g of silica and then fractionated into aliphatic, aromatic, and polar fractions via silica-alumina column (6 g of silica and 2 g of alumina) by successive elution with hexane, hexane/DCM (60:40 v/v), and methanol/DCM (50:50 v/v), respectively. After evaporation of the solvent, the saturated and aromatic fractions were transferred to GC vials. For samples with low saturated or aromatic fractions (< 1.0 mg), GC insert vials were used.

3.3. Gas chromatography-mass spectrometry (GC–MS)

GC–MS analysis of 31 aliphatic fractions extracted from the studied rock samples was conducted using an Agilent GC–MS (7890B GC; 5977A MSD) fitted with an HP-5MS column (30 m \times 250 μ m \times 0.25 μ m film thickness). The instrument oven was heated from 50 \degree C (hold for 2 min) to 280 \degree C (hold for 25 min) at 4 °C/min. The GC injector was set in splitless mode, and the injection volume was 1 μL. Helium was used as a carrier gas with a constant flow rate of 1 mL/min (36.45 cm/sec average velocity), and the instrument operated in selected ion monitoring (SIM) mode. The selected ions comprised *m/z* 71 (*n*alkanes), *m/z* 191 (terpanes) and *m/z* 217 (steranes). A DCM blank and a standard sample (saturated fraction from the Oseberg oil, Norwegian North Sea) were run before GC–MS analysis and after every 10 samples, to make sure that the instrument was working properly. Identification of different peaks was achieved by comparison with those of the Oseberg standard and peaks reported in the literature (e.g., Peters et al., 2005). Different biomarker ratios were calculated based on integration of areas of the individual peaks. Additionally, GC results for five aliphatic fractions from the Oligocene Tineh Formation (Mocha-1 well) were kindly supplied by the Egyptian General Petroleum Corporation (EGPC).

3.4. Chemometric analysis

The chemometric analysis was achieved using Pirouette® 4.5 modeling software (InfoMetrix Inc). Pirouette includes two exploratory algorithms: hierarchical cluster analysis (HCA) and principal component analysis (PCA). HCA classifies rock extracts and oils into genetic families, typically by means of a dendrogram, according to the distance between samples in *n*-space where *n* stands for the measured independent variables. PCA reduces the effective dimensionality of the data to a few principal components that best describe the variation in the data, whereas noise or irrelevant information makes up the remaining variables. In this study, the HCA dendrogram was achieved using incremental linkage and Euclidean metric distance to show cluster distance between samples. Both HCA and PCA employed autoscale preprocessing of the independent variables to ensure that each variable has the same weight. For chemometric analysis, 18 source-related biomarker ratios were used (see Section 5.3). Maturity-related biomarkers such as C₃₀ moretane/hopane as well as hopane and sterane isomerization ratios were not employed in this approach.

3.5. Mud gas analysis

EGPC provided a dataset of chemical and isotopic data from 282 Isotubes and 218 canned headspace gas (HSG) samples collected from five wells (Supplementary data file). Stable carbon isotopic analysis of C_1 , C2, and C³ was carried out on 265, 239 and 221 samples, respectively, whereas hydrogen isotopic analysis of C_1 (δ^2 H-C₁) was conducted on 46 samples. Due to relatively low C₂ and C₃ concentrations in some samples, their δ^{13} C values were measured after purge and trap enrichment. Isotube samples were taken from the gas line to the logging unit (Böker et al., 2020). For HSG samples, cuttings from the shale shaker were transferred to clean cans and then submerged about one third of each can volume with water. A few drops of bactericide were added to preserve the sample before the cans were sealed. Light hydrocarbons (C_1-C_5) in the interstitial spaces of each sample diffuse into the can headspace volume, allowing their analysis for molecular and isotopic composition. These gases can provide useful information for source rock evaluation and reservoir geochemistry as they are similar to gases released from the pore space of the rock (Dembicki, 2017).

4. Results

4.1. Source-rock geochemistry

TOC and Rock-Eval results of 335 solvent-extracted cuttings from Oligocene–Pliocene intervals from the study area are presented in the Supplementary data file. As the analyzed samples were solvent-extracted before Rock-Eval analysis, S_1 and production index (PI= $S_1/(S_1+S_2)$) values were not used in the evaluation. Although extraction results in loss of S_1 (bitumen), many samples from EW-8, Marzouk-2, Luzi-1, and El Basant-2 wells show high PI and S_1 values (Supplementary data file), indicating that the drilling additives were not completely removed despite extraction for 24/48 hours using DCM-methanol mixtures. Therefore, these samples were excluded from discussion, and only 322 samples were considered for interpretation. Generally, the analyzed rock samples show varying ranges of TOC, S_2 , HI and OI values (Supplementary data file).

The Kafr El Sheikh Formation (82 samples) has TOC values ranging from 0.66–1.91 wt.% (0.96 average), while S_2 values vary from 0.11 to 2.12 mg HC/g rock (0.68 average). HI and OI values vary from 13 to 140 mg HC/g TOC (69 average) and 31 to 191 mg CO_2/g TOC (111 average), respectively. TOC contents of the Abu Madi Formation (17 samples) range from 0.42–1.10 wt.% (0.68 average), with S² values varying from 0.24 to 1.03 mg HC/g rock (0.45 average), while values of HI and OI are in range of 46 to 137 mg HC/g TOC (60 average) and 32 to 267 mg $CO₂/g$ TOC (149 average), respectively. The Qawasim Formation (35 samples) shows TOC contents ranging from 0.51–1.56 wt.% (0.80 average), while S_2 values range from 0.21 to 1.75 mg HC/g rock (0.83 average). HI values vary from 39 to 224 mg HC/g TOC (102 average), whereas values of OI are in the range of 26 to 460 mg $CO₂/g$ TOC (147 average).

TOC values of the Sidi Salem Formation (23 samples) range from 0.57 to 1.26 wt.% (0.93 average). S_2 values are in the range of 0.50 to 3.36 mg HC/g rock (1.69 average). On the other hand, HI values vary from 73 to 300 mg HC/g TOC (174 average), whereas values of OI are in the range of 104 to 356 mg $CO₂/g$ TOC (182 average). TOC and S₂ values of the Qantara Formation (5 samples) range from 0.71 to 87 wt.% (0.78 average) and 1.03 to 1.49 mg HC/g rock (1.21 average), respectively. HI values range from 134 to 170 mg HC/g TOC (154 average), whereas values of OI are in the range of 58 to 97 mg $CO₂/g$ TOC (74 average). The Oligocene Tineh Formation (160 samples) has TOC values ranging from 0.70 to

1.66 wt.% (0.98 average), while S_2 values are in the range of 0.25 to 1.97 mg HC/g rock (1.11 average). HI and OI values vary from 25 to 234 mg HC/g TOC (114 average) and 49 to 734 mg CO_2/g TOC (154 average), respectively (Supplementary data file).

4.2. Organic petrography

The Kafr El Sheikh Formation shows vitrinite reflectance values in the range of 0.32% to 0.66%, whereas Ro measurements for the Abu Madi Formation samples vary from 0.68% to 0.72%. The Oligocene Tineh Formation displays Ro values in the range of 0.61% to 0.96% (Supplementary data file). The investigated samples are generally dominated by liptinite group macerals, whereas vitrinite and inertinite groups occur in lower concentrations. Liptinite is mainly unstructured with massive, amorphous, or undifferentiated texture. Vitrinite reflectance measurements (Ro%), standard deviation, and number of measurements of the investigated samples are presented in Supplementary data file. Vitrinite reflectance measurements for two samples from the Tineh Formation, Mocha-1 well (5795–5800 m and 5835–5840 m, Supplementary data file) are questionable, as indicated by standard deviation as well as minimum and maximum measured vitrinite reflectance values (Table 8 in Supplementary data file).

4.3. Normal alkanes and isoprenoids

The analyzed extracts show variable GC patterns in the range of $n-C_{15}$ to $n-C_{35}$ (Fig. 3), maximizing mainly at *n*-C₁₈ and *n*-C₂₉ reflecting various organic materials and maturity levels. The Pr/Ph, Pr/*n*-C₁₇ and Ph/*n*-C₁₈ ratios range between 0.35–2.30, 0.22–2.74 and 0.13–1.82, respectively (Table 1). The highest Pr/Ph ratios are displayed by Sidi Salem and Tineh extracts (1.24–2.3 and 1.94–2.15, respectively). Additionally, the calculated carbon preference index (CPI) and the odd-to-even preference (OEP) ratios vary considerably (elevated values for Kafr El Sheikh samples and low for others; Table 1).

4.4. Biomarker distribution

Representative terpane (*m/z* 191) and sterane (*m/z* 217) mass chromatograms of the analyzed extracts from the onshore Nile Delta are shown in Figures 4 and 5. Characteristic biomarker ratios are listed in Table 2. All extracts are characterized by a predominance of pentacyclic terpanes and low concentrations of tricyclics. C_{30} hopane and C_{29} norhopane are the two most abundant hopanoid members. C_{23} and C_{26}

are the most common tricyclic compounds, while C_{19} counterpart is the least. Gammacerane is absent or detected in very low concentrations. C_{28} bisnorhopane and C_{30} diahopane are also present in very low concentrations (Fig. 4).

The analyzed extracts show low C_{19}/C_{23} and elevated C_{26}/C_{25} tricyclic terpane values (0.06–0.39 and 0.82–3.62, respectively), while ratios of C_{31} (22R)/C₃₀ hopane are low (0.17–0.63; Table 2). The C₃₅/C₃₄ homohopane and norhopane/hopane values vary from 0.37 to 1.39 and 0.57 to 0.94, respectively. Oleanane is present, but in mostly low concentrations (oleanane indices range from 0.02 to 0.17; Table 2). Steranes are dominated by C_{28} and C_{29} $\alpha \alpha \alpha$ (20R), while C_{27} diasteranes are low in abundance relative to regular steranes (Fig. 5). The studied extracts display C_{27} , C_{28} and C_{29} $\alpha \alpha \alpha$ 20R sterane ratios with considerable variations, varying between 11.78–33.58%, 20.79–60.92% and 26.47–53.10%, respectively (Table 2). Except for one sample, the C_{27} diasterane/regular sterane ratios are generally lower than unity (0.11–0.85; Table 2).

4.5. Gas geochemistry

Mud gas data are effective tools to identify the type and distribution of gases throughout sedimentary successions (Petersen and Smit, 2023). The molecular and isotopic compositions of the mud gas samples are listed in the Supplementary data file. Most HSG samples from Luzi-1 and Abu Monkar-3 wells show low headspace gas concentrations and were excluded from interpretation. This may be caused by the leakage and poor conditions of the sample cans. Carbon isotopic values for samples with $C_1 < 1000$ ppm or where C_2 , C_3 and C_4 were < 5 ppm were also disregarded (Böker et al., 2020). This quality control left 251, 226 and 210 of $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ results, respectively.

10 Mud gas analysis reveals high concentrations of total hydrocarbons (Supplementary data file). CH₄ is the dominant hydrocarbon component, while the heavier C_{2+} hydrocarbons occur in lower concentrations. Values of $\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$ and δ^2H-C_1 show considerable variations (Supplementary data file). The Oligocene Tineh Formation shows the heaviest stable isotopic signature with $\delta^{13}C_1$ ranging from -46.8‰ to -37.3‰, $\delta^{13}C_2$ from -33.9‰ to -29.2‰, and $\delta^{13}C_3$ from -30.2‰ to -26.9‰, respectively. Gases from Qantara and Tineh formations are wet gases with wetness indices $[100 \times C_{2+} / (\Sigma C_1 - C_5)]$ in the range of 7.04%–10.09% and 5.14%–26.32%, respectively, reflecting their thermogenic origin. In contrast, gases

recovered from Kafr El Sheikh, Abu Madi, Qawasim and Sidi Salem formations vary from dry to wet gases (Supplementary data file), supporting their various/mixed origin (e.g., Schoell, 1980).

5. Discussion

5.1. Source rock assessment using Rock-Eval

5.1.1. Organic richness

The analyzed rock samples generally have TOC contents \sim 1 wt.% ranging from \sim 0.50 to \sim 1.9 wt.% (Supplementary data file), indicating fair to good source rock potential (Peters, 1986; Peters and Cassa, 1994). Rock samples from the Abu Madi and Qantara formations generally show fair organic enrichment with TOC values < 1.0 wt.%. Conversely, 51 rock samples (total samples $= 64$) from the deeper Tineh Formation (Rupelian) have TOC contents ≥ 1.0 wt.%, suggesting good source rock potential. Only 23 rock samples (total samples $= 96$) from the Tineh Formation (Chattian), 9 samples (total samples $= 35$) from the Qawasim Formation, 33 samples (total samples = 82) from the Kafr El Sheikh Formation and 9 samples (total samples = 23) from the Sidi Salem Formation have TOC contents ≥ 1 wt.%, reflecting the overall fair organic richness for these layers (Supplementary data file).

The prevalent low TOC content is attributed to clastic dilution of organic input associated with high sedimentation rates (Ibach, 1982). Such elevated rates of sedimentation are among the highest on the African margins. According to sink-source volume analysis, half of the clastic input was derived from Egyptian rift shoulders with an erosion rate assessed to be more than 80 m Ma⁻¹ (Macgregor, 2012). Microbial degradation also eliminates functional groups on organic molecules, reducing the TOC content of the source rock and its capacity to generate oil (Ibach, 1982; Tissot and Welte, 1984).

TOC does not distinguish between generative kerogen and dead carbon and indicates only quantity of organic matter, whereas S_2 values can indicate the source rock generative potential (quality) as these values represent the amount of hydrocarbons generated from kerogen during pyrolysis (Dembicki, 2009; Peters and Rodriguez, 2017). Only three samples from the Sidi Salem Formation show S_2 values > 2.5 mg HC/g rock, suggesting poor to fair hydrocarbon generation potential (Peters and Cassa, 1994; Carvajal-Ortiz and Gentzis, 2015). Even samples with TOC contents ≥ 1 wt.% have S₂ values < 2.5 mg HC/g rock (Supplementary data file). Maturity can affect both TOC and S_2 values of source rocks. With increasing maturity, more hydrocarbons are generated and expelled from the source rock, consuming the reactive kerogen, and lowering TOC and S_2 values (Dembicki, 2009). However, the investigated rock samples are mainly immature to early mature (see Section 5.1.3); therefore, original $S_2(S_2)$ of Jarvie et al. (2007) are presumed to be similar to the present-day S_2 values.

5.1.2. Kerogen type

The type of kerogen of the analyzed rock samples can be determined on the HI versus OI plot (modified van Krevelen diagram) as shown in Figure 6a. All Oligocene samples, except one sample, yield Type-III kerogen that can produce gas at optimum maturity. On the other hand, samples from other formations are rich in both Type-III (~71%) and Type-IV (~24%) kerogens. Type-IV kerogen is inert with no oil or gas potential, produced by severe alteration and/or oxidation of organic matter prior to deposition (Tissot and Welte, 1984). This kerogen type contributes to TOC with little contribution to the S_2 peak, resulting in low HI values and making the source rock appear as gas prone (Hunt, 1996). Only eight samples from the Sidi Salem Formation, one sample from the Qawasim Formation and one sample from the Tineh Formation contain Type-II/III kerogen (Fig. 6a; Supplementary data file).

TOC versus S_2 plot (Langford and Blanc-Valleron, 1990; Fig. 6b) is also used to interpret the initial type of kerogen where the slope of the plot is proportional to the hydrogen index (Cornford et al., 1998). This eliminates uncertainties regarding the oxygen index in the OI versus HI plot as elevated oxygen indices of carbonate-rich source rocks can occur (Peters, 1986). The distribution of the examined rock samples on Figure 6b is consistent with the previous conclusion where most samples plot in the organic lean field with mainly Type-III gas-prone kerogen. Elevated OI values for some samples from Tineh, Sidi Salem and Qawasim formations (Fig. 6a; Supplementary data file) reflect pervasive oxic depositional settings where oxidized and altered organic matter accumulated (Leila and Moscariello, 2017).

Previous studies reported that the Kafr El Sheikh Formation from the western and eastern offshore Nile Delta mainly contain Type-III and Type-IV kerogen of fluvial or deltaic origin, whereas more hydrogenrich oil-prone organic matter (Type-II/III) contribute to Abu Madi and Sidi Salem samples (Sharaf, 2003;

12 El Diasty et al., 2022). In the central onshore Nile Delta, the Sidi Salem Formation is also rich in TypeII/III kerogen derived mainly from marine organic matter, whereas the Abu Madi Formation contains Type-III terrigenous kerogen (El Nady, 2007; Keshta et al., 2012). More terrigenous-influenced facies of the Sidi Salem Formation occur in the eastern Nile Delta, compared to more marine facies in the western part, and the quality of organic matter increases with depth as terrigenous organic matter become less abundant (Ghassal et al., 2016). More marine input contributed to Rupelian source rocks in the offshore Nile Delta, compared to the shallower Chattian intervals rich in terrigenous organic matter (Villinski, 2013). However, Rock-Eval results (Supplementary data file) do not show any difference in kerogen type between Rupelian and Chattian samples.

5.1.3. Thermal maturity

Vitrinite reflectance (%Ro) and T_{max} are widely used to infer thermal maturity of source rocks. The latter is more favorable as it is faster to measure, more convenient, non-subjective, and can be determined for samples that lack vitrinite (Yang and Horsfield, 2020). However, two main issues of T_{max} as a maturity indicator include small S_2 peaks and sample contamination. T_{max} values are unreliable for small and poorly defined S² peaks (e.g., < 0.2 mg HC/g rock; Cornford et al., 1998; Peters and Rodriguez, 2017). Away from the Oligocene samples from the Mocha-1 well, \sim 33% of the analyzed samples have S₂ values < 0.5 mg HC/g rock, making interpretation of their T_{max} values problematic.

Contamination of cuttings samples by drilling additives or migrated oil can shift T_{max} to lower values due to the carry-over of heavy ends from S_1 into S_2 (e.g., Carvajal-Ortiz and Gentzis, 2015). Such samples may show bimodal S_2 patterns, and the software automatically assigns the temperature of the lower temperature peak as the T_{max} , which can be erroneous (Yang and Horsfield, 2020). Many analyzed samples showed S_2 peaks with bimodal distributions and unreliable T_{max} values. Therefore, T_{max} appears to be unreliable for thermal maturity assessment in the study area, except the Oligocene Tineh Formation samples from the Mocha-1 well. These samples display T_{max} values in the range of 362 to 445 °C (except one sample with T_{max} of 448 °C) and Ro from 0.61 to 0.74% (except two deep samples with Ro values of 0.92% and 0.96%), reflecting immature rock samples to the early oil window (Carvajal-Ortiz and Gentzis, 2015; Supplementary data file). Available Ro data from Luzi-1 and Abu Monkar-3 wells reveal that the Kafr El Sheikh Formation is mainly immature (0.32–0.58% Ro), except the deepest sample (0.66% Ro).

The Abu Madi Formation samples in the Luzi-1 well are in the early stage of oil window (0.68–0.72% Ro) (Carvajal-Ortiz and Gentzis, 2015). The sample at 2504–2513 m depth from the Abu Monkar-3 well shows high vitrinite reflectance (0.59% Ro) compared to deeper samples. However, this is based on very good quality vitrinite particles. In contrast, reflectance values of some deeper Sidi Salem samples (e.g., 2639–2648 m, 2792–2801 m and 2855–2864 m) are low (Supplementary data file), which may be related to the presence of low quality vitrinite or the low number of measured vitrinite particles (Supplementary data file). In the Nile Delta Basin, maturity increase northwards because of thin sedimentary cover and low heat flow southwards (Sharaf, 2003; Ghassal et al., 2016).

5.2. Biomarker analysis

5.2.1. Organic matter input and depositional environment

The relative abundance of certain *n*-alkanes from $n-C_{13}$ to $n-C_{35}$ in source-rock extracts can indicate terrigenous versus marine input (Bourbonniere and Meyers, 1996; Meyers, 1997). Abundant $n-C_{27}$, $n-C_{29}$, and *n*-C₃₁ in extracts and oils reflect high contribution from higher-plant waxes to the source rock facies, whereas dominance of $n-C_{15}$, $n-C_{17}$ and $n-C_{19}$ suggests aquatic algal contributions (Gelpi et al., 1970; Tissot and Welte, 1984).

GC chromatograms of the analyzed samples vary significantly (Fig. 3), with *n*-alkane distributions ranging mainly from $n-C_{15}$ to $n-C_{35}$. The Tineh extracts show GC patterns characterized by unimodal distributions and low abundance of long-chain *n*-alkanes. In contrast, the high abundance of $n-C_{27}$, $n-C_{29}$, and $n-C_{31}$ (mainly maximize at $n-C_{29}$) in most other samples, especially Kafr El Sheikh extracts, in addition to elevated CPI values in the range of C_{25} to C_{33} (Table 1) reflect significant input of higher-plant waxes and low thermal maturity (Bray and Evans, 1961; Eglinton and Hamilton, 1967; Tissot and Welte, 1984). This is in accordance with abundant C_{29} steranes in these samples. Some gas chromatograms from Qawasim and Sidi Salem extracts are highly enriched in mid-chain alkanes, reflecting organic input from mixed sources. Gas chromatograms with bimodal distributions maximizing at *n*-C₁₈-*n*-C₂₀ in addition to *n*-C₂₉ and *n*-C₂₇ (e.g., EW-7 1400 m and EW-7 1650 m) may have resulted from either contamination of these samples by organic-based drilling fluids (diesel range) or organic matter from mixed sources (Fig.

Isoprenoid distributions and isoprenoid/*n*-alkane ratios are widely used in source rock evaluation studies (e.g., Peters et al., 1999). Pr/Ph, Pr/*n*-C¹⁷ and Ph/*n*-C18 values of the analyzed extracts (Table 1) indicate mainly mixed organic matter (Type-II/III kerogen) deposited under transitional to reducing (suboxic to anoxic) depositional settings (Fig. 7). Good correlation between the M-1(3) condensate sample (Khairy et al., 2022) and extracts from the Tineh Formation can be inferred from Pr/*n*-C¹⁷ and Ph/*n*-C18 values. Condensates from Miocene reservoirs substantially differ from those reservoired in the Oligocene Tineh Formation. The latter were interpreted to have been derived from more mature source rocks rich in mixed Type-II/III kerogen, whereas the former were generated from more terrigenous Type-III sources (Khairy et al., 2022). The Pr/Ph values of Sidi Salem and Tineh extracts are relatively higher compared to other samples (1.24–2.3 and 1.94–2.15, respectively), reflecting more terrigenous input accumulated under more oxic depositional settings (Table 1). CPI and OEP values are very high for Kafr El Sheikh extracts (1.5–4.7 and 1.25–3.19, respectively), reflecting low maturity levels and elevated input from land plants (Bray and Evans, 1961; Scalan and Smith, 1970).

15 C_{27} , C_{28} , and C_{29} regular steranes can be used to infer depositional settings of source rocks (e.g., Huang and Meinschein, 1979) and the sources of their organic matter (Volkman, 1986; Volkman et al., 1998; Liu et al., 2022). C_{27} steranes originate from marine algae/marine photosynthetic organisms, while C_{29} steranes are related to higher plants and sometimes to marine green/brown algae (Moldowan et al., 1985; Czochanska et al., 1988). Interestingly, extracts from the Sidi Salem Formation in addition to two Kafr El Sheikh extracts from the EW-8 well can be easily differentiated from other samples by abundant C₂₈ regular steranes (up to 60.92%) and very low C₂₇ steranes (average 14.46%). This indicates a lacustrine or nearshore marine depositional environment (Fig. 8) and source rock with high input from diatoms, coccolithophores and dinoflagellates (Grantham and Wakefield, 1988), lacustrine algae (Waples and Machihara, 1991) or cyanobacteria (Liu et al., 2022). Based on isotopic evidence, abundant C_{28} steranes could result from algae blooming in the water column (Zhang et al., 2020). Abundant C₂₈ steranes for Sidi Salem extracts is first reported here for samples from the onshore Nile Delta Basin, which differs from extracts from the offshore part of the basin dominated by C_{29} or C_{27} steranes (El Diasty et al., 2022). Such differences in sterane distributions between the onshore and offshore parts of the basin may be attributed to different depositional conditions. Middle Miocene deposits are non-marine in the southern Nile Delta,

whereas the depositional facies range from paralic to shelf and slope northwards. Due to sea level fluctuations during that time followed by later uplift and erosion, such conclusions are very generalized and do not represent the true complexity (Harms and Wray, 1990). The Sidi Salem Formation in the onshore Nile Delta contains mixed terrigenous and marine organic matter with some algal and bacterial contribution deposited under anoxic to suboxic settings (El Nady and Harb, 2010).

On the other hand, all other extracts from the Kafr El Sheikh, Abu Madi and Qawasim formations have elevated abundance of C_{29} steranes (average 43%) with relatively sub-equal contributions from C_{28} (average 28%) and C_{27} (average 29%) steranes, suggesting mixed source facies dominated by higher plants and marine green algae in addition to bacteria and plankton (Moldowan et al., 1985; Grantham and Wakefield, 1988). This interpretation is commensurate with GC chromatograms of these samples with maxima at *n*-C₂₉, particularly for extracts from the Kafr El Sheikh Formation (Fig. 3). The mixed nature of organic matter in these samples can be attributed to the rapid influx of mixed organic matter precursors as well as high sedimentation rates (El Diasty et al., 2020b).

 C_{19} and C_{20} tricyclic terpanes dominate non-marine source rocks with high terrigenous input, whereas marine source rocks are dominated by C_{23} homologs (Peters and Moldowan, 1993). In most of the analyzed extracts, the C_{23} peak exceeds C_{19} tricyclic terpanes, signifying more marine organic matter input to the source rocks. However, three extracts from the Kafr El Sheikh Formation (Bals-1 2850 m, EW-8 1250 m and EW-8 2000 m) in addition to most extracts from the Sidi Salem Formation (except two samples) have low C_{23} peaks compared to other samples, where $(C_{19} + C_{20})$ tricyclics exceed the C_{23} peaks, suggesting more contribution from terrigenous organic matter. These samples also exhibit the lowest C_{27} sterane ratios (Fig. 9).

In contrast to marine source rocks, lacustrine and nearshore source (i.e., paralic/deltaic) facies are characterized by low C_{31} 22R homohopane/C₃₀ hopane and elevated C_{26}/C_{25} tricyclic terpane ratios (Zumberge, 1987; Peters et al., 2005). Strikingly, the analyzed extracts show very high C_{26}/C_{25} tricyclic terpane ratios (up to 3.62, average 2.35) coupled with low C_{31} 22R/C₃₀ hopane ratios (0.17–0.63; average 0.36; Table 2), suggesting lacustrine or nearshore marine deposition (Fig. 9a). Interestingly, there is a positive correlation between C_{26}/C_{25} tricyclic terpane and the predominance of C_{28} regular steranes in the

analyzed extracts (Fig 9b). For instance, Sidi Salem extracts show the highest C_{28} sterane content and the C_{26}/C_{25} tricyclic terpane ratios, suggesting more lacustrine input compared to the other samples. This is consistent with the high $(C_{19} + C_{20})/C_{23}$ tricyclic terpane and high Pr/Ph ratios of these samples.

The C_{35}/C_{34} homohopane index is usually used to infer redox potential (Eh) during source rock deposition (Peters and Moldowan, 1991). Generally, high ratios reflect marine reducing (low Eh) depositional conditions, whereas low ratios indicate more oxic depositional settings (Peters and Moldowan, 1991; Dahl et al., 1994). The C_{35}/C_{34} of the analyzed extracts range from 0.37 to 1.39 (average 0.85), reflecting suboxic to anoxic depositional settings (medium to low Eh). This is consistent with relatively high norhopane/hopane ratios ranging from 0.57 to 0.94 (average 0.76) and low diahopane/hopane range of 0.0 to 0.08 (average 0.03). This is also in line with Pr/Ph values ranging from 0.35 to 2.3 (Table 1). For example, most extracts from the Sidi Salem Formation display high Pr/Ph and low C_{35}/C_{34} ratios compared to other samples (Figure 9d), suggesting more oxic conditions. The Sidi Salem Formation contain high contributions of allochthonous organic matter, deposited under high-energy conditions and oxic bottom water facilitating decay of labile, marine organic materials (Ghassal et al., 2016).

The general low abundance of oleanane in the analyzed rock-extracts (oleanane index ranges from 0.02 to 0.17, average 0.05) suggests low biomass of angiosperms/flowering plants during deposition, which is not anticipated for Miocene–Pliocene source rocks (Riva et al., 1988; Moldowan et al., 1994; El Diasty et al., 2022). Dabayaa-1 (2600 m), EW-8 (2695 m) and Marzouk (3510 m) extracts show the highest oleanane index (0.12, 0.14 and 0.17, respectively). The low concentration or absence of gammacerane suggests freshwater depositional conditions or absence of stratified water column (Sinninghe Damsté et al., 1995). This could be due to dilution of marine water in the Tethys by inflow of freshwater from the proto-Nile River in the south where more rainfall most likely occurred (El Diasty et al., 2022).

5.2.2. Maturity-related biomarkers

17 Ts/Tm and diasterane/regular sterane ratios of the examined extracts are generally low (0.12 to 0.85 and 0.11–1.23, respectively), while moretane/hopane ratios are > 0.15 (Table 2), indicating immature rock samples. In addition to maturity, these ratios are also affected by carbonate versus clay-rich depositional settings (Seifert and Moldowan, 1978; Rullkötter and Marzi, 1988; Waples and Machihara, 1991; Isaksen

and Bohacs, 1995). Thus, sterane and hopane stereoisomer ratios are more reliable maturity indicators (Peters, 1999; Peters et al., 2005).

Only three samples achieved the endpoint for C_{32} hopane %22S/(22S + 22R) isomerization ratio [(endpoint $\sim 0.57-0.62$); Table 2], while no extracts reached the endpoint for $\frac{\%20}{S/(20S + 20R)}$ and ββ/(αα+ββ) C²⁹ sterane (endpoint ~0.52–0.55 and ~0.67–0.71, respectively). This reflects immature to early mature rock samples (Seifert and Moldowan, 1986; Fig. 10). However, the rapid burial of sedimentary layers in the Nile Delta may have affected these ratios and resulted in short time insufficient to complete hopane and sterane isomerization (Sharaf, 2003; El Diasty et al., 2022). Based on T_{max} values, Kafr El Sheikh Formation is immature in the eastern offshore Nile Delta, whereas Sidi Salem and Qantara formations are in the oil window towards the north and immature in the southern parts (Sharaf, 2003). El Nady (2007) concluded that the Abu Madi Formation in the central onshore Nile Delta range from thermally immature to marginally mature, whereas the Sidi Salem Formation is mature.

Burial history modelling for the West Dikirnis-2 well, onshore Nile Delta, indicates that oil and gas windows occur in the Upper Cretaceous–Lower Tertiary and Jurassic layers, respectively, whereas younger formations are thermally immature (Leila and Moscariello, 2017). Nevertheless, basin modelling of the Abu Hammad-1 well, southeastern Nile Delta, revealed low maturity for the Jurassic Khatatba Formation because of low heat flow and thin sedimentary cover due to long periods of erosion and/or non-deposition (Ghassal et al., 2016). The thickness of the eroded section also increases southwards (Harms and Wray, 1990). Basin modelling results indicated that the Abu Madi and Sidi Salem formations in northern onshore Nile Delta entered the oil window in the Middle to Late Miocene and the Early Miocene, respectively (Keshta et al., 2012).

5.3. Chemometrics and oil-source correlation

18 Chemometrics or multivariate statistical analyses of biomarker data are effective oil-source correlation techniques. This multi-parameter approach allows more reliable interpretation of genetic relationships than traditional binary plots (Peters et al., 2008; 2016; 2019; El Diasty et al., 2020a). Based on 18 sourcerelated biomarker ratios (Table 2), the HCA cluster dendrogram for 31 rock extracts from the onshore Nile Delta identified four genetic families (Fig. 11a). This was confirmed by the PCA plots in different orientations (Fig. 11b), where PCA Factors 1, 2 and 3 account for 37.2%, 20.4% and 10.3% of the variance, respectively.

Family-1 includes 10 extracts: two Kafr El Sheikh extracts from EW-8 well (1250 and 2000 m) in addition to all Sidi Salem extracts from the Marzouk-2 well, except one sample (3510 m). This family shows the highest % C_{28} sterane (47.67–60.92%) and C_{26}/C_{25} tricyclic ratios (2.32–3.23). This family also has low C₃₁ 22R homohopane/C₃₀ hopane ratios (0.18–0.30), low C₂₂/C₂₁ tricyclic terpanes (0.11–0.24), elevated Pr/Ph and low C_{35}/C_{34} hopane ratios (0.44–1.31 and 0.78–2.3, respectively). In addition, samples from this family show high C₂₀ tricyclic terpane peaks, where $(C_{19} + C_{20})/C_{23}$ ratios are mostly > 1. Such features suggest more terrigenous or mixed organic matter deposited in lacustrine or nearshore marine environments under more oxic conditions compared to the other samples.

Marzouk-2 (3510 m) and EW-8 (2695 m) extracts from both Sidi Salem and Abu Madi formations form Family-2. The two samples are like Family-1 samples in having high C_{26}/C_{25} tricyclic ratios (3.09– 3.3.62), low C_{31} 22R homohopane/ C_{30} hopane ratios (0.17–0.18), and abundant C_{28} regular steranes (0.42.67–55.28). Extracts from this family can be distinguished by their high Ts/Tm (0.68–0.85), diasteranes/regular steranes (0.24–1.23), oleanane index (0.14–0.17) and C_{24} tetracyclic/ C_{23} tricyclic terpane ratios (0.13–0.35). This suggests more clay-rich source rock depositional settings with mixed organic matter input.

Family-3 is represented by 13 extract samples, including all Qawasim extracts, two Abu Madi extracts [Dabayaa-1 (2670 m) and Balsam-1 (2950 m)] and two extracts from the Kafr El Sheikh Formation [Dabayaa-1 (2450 m and 2600 m)]. This family is characterized by predominance of C_{29} steranes (37.36– 49.05%) with sub-equal C_{28} and C_{27} contributions (26.25–31.25% and 24.70–33.35%, respectively). C_{26}/C_{25} tricyclic ratios are lower than Family-1 and -2 (1.67–2.80), whereas C_{31} 22R/C₃₀ hopane values are higher (0.31–0.44). Ratios of $(C_{19} + C_{20})/C_{23}$ tricyclics are generally low (mostly < 0.70), whereas C_{35}/C_{34} ratios range from 0.37 to 1.21. These features indicate mixed organic input dominated by higher plants and/or marine green algae with some algal and bacterial contribution deposited under anoxic to suboxic depositional conditions.

19 Six extracts from the Kafr El Sheikh Formation comprise Family-4, including EW-8 (2600 m), EW-7 (1400, 1550, 1650 and 2100 m) and El Basant-2 (2250 m). These samples show the lowest C_{26}/C_{25} tricyclics (0.82–2.10), highest C₃₁ 22R homohopane/C₃₀ hopane (0.39–0.63), highest C₃₅/C₃₄ ratios (> 1.3, except one sample), highest C_{29} steranes (up to 53.10%) and the lowest C_{28} steranes (20.79–26.37%), high C_{22}/C_{21} (0.28–0.45) and low C_{24}/C_{23} (0.47–0.55) compared to the other samples, suggesting mixed organic matter deposited under more reducing conditions.

HCA of the biomarker data for the examined rock extracts and condensate oils discovered in the study area (Khairy et al., 2022) is shown in Figure 12. HCA clearly shows that the oil samples (Family-3) group together and substantially differ from the analyzed rock extracts (Family-1 and 2). Accordingly, these fluids from the onshore Nile Delta were likely generated from deeper pre-Miocene plays. Based on biomarker ratios for six oil samples from the onshore Nile Delta, Leila and Moscariello (2017) concluded that these oils originated from Upper Cretaceous–Lower Tertiary sources. However, these authors correlated their oil samples with only two extracts from the Qawasim Formation using only GC parameters. They did not correlate the discovered oils with deeper Lower Miocene and Oligocene intervals because of lack of data. In the western offshore part of the basin, El Diasty et al. (2020b) concluded that there is a good correlation between Sidi Salem extracts and condensates from the Rosetta and Abu Qir oilfields.

5.4. Origin, mixing and maturity of natural gas

Thermogenic and microbial gases are commonly identified based on $\delta^{13}C_1$ values ranging from -50‰ to [−]20‰ and < −55‰, respectively (Schoell, 1980; Whiticar, 1994; Milkov and Etiope, 2018). Thermogenic gases are enriched in C_{2+} components, whereas microbial gases are mainly pure methane. Mixing of these two end members commonly alters such diagnostic signatures (Whiticar, 1994). Plotting gas data on binary genetic diagrams is a common way to classify natural gases and identify their origin and alteration history (Bernard et al., 1977; Schoell, 1983; Whiticar et al., 1986). For more details on the evolution of these diagrams, the reader is referred to Milkov and Etiope (2018) who provided an updated version of these plots based on a global dataset.

20 Most of the analyzed gases have Bernard ratios $[C_1/(C_2 + C_3)]$ and $\delta^{13}C_1$ values ranging from 50 to 1000

and [−]65‰ to −40‰, respectively (Fig. 13a; Supplementary data file). Such values likely reflect complex origins and mixing histories (Milkov and Etiope, 2018). These gases range from primary microbial to pure thermogenic and scatter on the left-side of the U-shaped trend (Figs. 13b, c). The upper part of Kafr El Sheikh Formation contains microbial gas, whereas the lower part contains mixed microbial and thermogenic gases, and the thermogenic contribution increases with depth. Only a few deeper samples from this formation show isotopic signatures of pure thermogenic gas [e.g., Luzi-1 2393–2402 m ($\delta^{13}C_1$ = -42.3%), EW-6 2690–2699 m (δ¹³C₁ = −43.0‰)]. This is also supported by δ²H-C₁ values (Fig.13d). Most gases from the Miocene Abu Madi, Qawasim and Sidi Salem formations are thermogenic associated with oil, whereas Qanatra and Tineh formations contain only thermogenic gas. Figure 13b also suggests that biodegradation and mixing are the main pathways for microbial gases in Kafr El Sheikh Formation.

To estimate the microbial contribution in mixed gases, the investigated gas samples were plotted on the isotopic mixing diagram (Strąpoć et al., 2011; Fig. 14a). The microbial components in gases from the Pliocene Kafr El Sheikh Formation range from 40–80% and 80–100% in deeper and shallower samples, respectively. Mixed gases from the western offshore Nile Delta have microbial gas contributions of ~50% (Böker et al., 2020), up to ~95% (Vandré et al., 2007) and ~70% (El Diasty et al., 2020b). In contrast, microbial gas contributions in deeper Miocene Abu Madi, Qawasim and Sidi Salem samples range from 0% to \sim 40% and do not exceed 20% for most samples (Fig. 14a). Methanogenic input contributes \sim 20% to Miocene gases in the western offshore Nile Delta, although conditions such as high temperatures (> 80 °C) are not favorable for microbial life. During burial beyond 70–80 °C, paleo-microbial gas held in pore volumes of Miocene layers dilutes thermogenic gases generated from the Oligocene intervals (Böker et al., 2020).

Gas samples from the Oligocene Tineh Formation can be easily differentiated from other samples on Figure 14b. These gases were derived from Type-II kerogen at maturity $\sim 0.9\%$ to $\sim 1.3\%$ Ro, while other gases were mainly generated from Type-III or mixed Type-II/III kerogen in the range ~0.8% to ~1.6% Ro (Berner and Faber, 1996; Fig. 14b). Such maturity levels are in line with calculated thermal maturities (0.8%–1.4% Ro) by Vandré et al. (2007) for the thermogenic gas portions, reflecting pre-Miocene source. This agrees with the work of Khairy et al. (2022) who concluded that condensates and associated gases

from the Oligocene Tineh reservoir in the onshore Nile Delta show different geochemical features than other samples from Miocene pay zones, indicating derivation from different source rocks with variable thermal maturity or the presence of multiple charge systems from a common source.

6. Conclusions

Source–reservoir relationships in the onshore Nile Delta remain unclear, despite recent exploration campaigns. A comprehensive geochemical evaluation of Oligocene–Pliocene possible source rocks was conducted to determine their organic richness, kerogen type, thermal maturity and depositional paleoenvironment. TOC and Rock-Eval results indicate fair to good organic richness (TOC ~1 wt.%) and mainly gas-prone Type-III kerogen. S_2 values suggest poor to fair hydrocarbon generation potential. Molecular and biomarker results suggest mixed and variable contributions from planktonic, bacterial, algal and terrigenous sources. Characteristic biomarker ratios are elevated C_{26}/C_{25} tricyclic terpane (0.82– 3.62), low C_{31} homohopane (22R)/ C_{30} hopane ratios (0.17–0.63), and low oleanane and gammacerane contents, reflecting lacustrine or nearshore marine depositional settings. C35/C³⁴ homohopane index and Pr/Ph ratios suggest that these layers were deposited under suboxic to anoxic depositional settings. Sidi Salem extracts in addition to two extracts from the Kafr El Sheikh Formation show high relative abundance of C_{28} regular steranes (up to 60.92%). Sterane and hopane isomerization ratios suggest immature to early oil window maturity, supported by Ts/Tm, diasteranes/regular sterane and moretane/hopane ratios. This is consistent with T_{max} and vitrinite reflectance (% Ro) values. Molecular and isotopic compositions of mud gases reflect gases with complex origins and mixing histories ranging from primary microbial to pure thermogenic, where the pre-Miocene sequence is predominated by thermogenic gases. Four genetic families of rock extracts were identified by chemometric analysis using 18 source-related biomarker ratios. HCA of biomarker data for rock extracts and condensate oils from the onshore Nile Delta yields no definitive correlation between Miocene–Pliocene rocks and discovered oils in the study area. Therefore, hydrocarbons in the onshore Nile Delta are inferred to originate from deeply buried pre-Miocene source rocks.

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Figure captions

- Fig. 1. Location map of the study area and wells from which rock samples were taken.
- Fig. 2. Generalized lithostratigraphic column of the Nile Delta Basin. Brown, red, and pink boxes indicate pre-Miocene, Miocene, and post-Miocene sequences, respectively. Pre-Jurassic intervals have not been penetrated in the basin, but they are inferred from regional geology (modified after Schlumberger, 1984).
- Fig. 3. Representative gas chromatograms (GC) for aliphatic fractions from extracted bitumens from Kafr El Sheikh, Abu Madi, Qawasim, Sidi Salem and Tineh formations, onshore Nile Delta. Some samples (e.g., EW-7 1400 m, EW-7 1650 m, EW-8 2000 m and EW-8 2600 m) show possible contamination by diesel (narrow distillation cut) in the range $\sim n-C_{14}-n-C_{21}$.
- Fig. 4. Selected terpane (*m/z* 191) GC-MS chromatograms of the aliphatic fractions for extracted bitumen samples from Kafr El Sheikh, Abu Madi, Qawasim and Sidi Salem formations, onshore Nile Delta.
- Fig. 5. Representative sterane (*m/z* 217) distributions in the aliphatic fractions for extracted bitumen samples from Kafr El Sheikh, Abu Madi, Qawasim and Sidi Salem formations, onshore Nile Delta.
- Fig. 6. (a) Relationship between HI (mg HC/g TOC) and OI (mg $CO₂/g$ TOC) showing the kerogen type in rock samples from the onshore Nile Delta. (b) Plot of TOC (wt.%) versus S_2 (mg HC/g rock). The gradient of sloping lines equals hydrogen indices that distinguish different kerogen types (fields after Langford and Blanc-Valleron, 1990).
- Fig. 7. Pr/*n*-C¹⁷ versus Ph/*n*-C¹⁸ ratios for extracted bitumen samples from Kafr El Sheikh, Abu Madi, Qawasim, Sidi Salem and Tineh formations, onshore Nile Delta, showing sources of organic matter and their depositional environment (genetic fields after Peters et al., 1999). Comparison with previous published data is also included. Although the analyzed extracts plot mainly in the field of mixed Type-II/III organic matter, oils and condensates from the study area were generated from more mature source rocks rich in terrigenous Type-III kerogen deposited under more oxic conditions. Good correlation between M-1(3) condensate sample (Khairy et al., 2022) and extracts from the Tineh Formation can also be inferred.
- Fig. 8. $C_{27}-C_{28}-C_{29}$ sterane ternary diagram of rock extracts from the onshore Nile Delta to a) differentiate biogenic source of the accumulated organic matter and b) to infer depositional environments for the studied formations (fields after Huang and Meinschein, 1979; Hunt, 1996).
- Fig. 9. Plots of various biomarker ratios showing differences/similarities among the analyzed samples in terms of organic matter input and depositional settings.
- Fig. 10. Relationship between %C₂₉20S and %C₂₉ $\beta\beta$ sterane isomerization ratios to infer thermal maturity of extracted bitumen samples from the onshore Nile Delta. Inset shows qualitative hydrocarbon yield relative to the oil generation and vitrinite reflectance (%R₀, after Peters et al., 2005). GC–MS (m/z) 217) chromatograms of samples A, B and C are on the right to show changes in C_{29} isomerization ratios with increasing maturity.
- Fig. 11. (a) Hierarchical cluster analysis (HCA) dendrogram based on 18 source-related biomarker ratios suggests four genetic families for extracts from Kafr El Sheikh, Abu Madi, Qawasim and Sidi Salem formations, onshore Nile Delta. (b) Principal components analysis (PCA) plots in different orientation (PC1, PC2, PC3).
- Fig. 12. HCA dendrogram to correlate the examined rock extracts with discovered condensate oils from the study area (Khairy et al., 2022). There is no definitive correlation between the Miocene-Pliocene extracts (Family-1 and 2) and oils (Family-3; marked with solid black circles), suggesting that the oils originated from deeper more mature pre-Miocene source rocks.
- Fig. 13. (a) Genetic diagram of $\delta^{13}C_1$ versus Bernard ratio $[C_1/(C_2+C_3)]$ (after Bernard et al., 1977; Whiticar, 1999). (b) Revised genetic fields of this diagram (after Milkov and Etiope, 2018). (c) Plot of $\delta^{13}C_1$ versus δ^2 H-C₁ (after Schoell, 1983). (d) Revised genetic fields of this diagram (after Milkov and Etiope, 2018); $CR = CO_2$ reduction; $F =$ methyl-type fermentation; $SM =$ secondary microbial; $EMT =$ early mature thermogenic gas; $OA =$ oil-associated thermogenic gas; $LMT -$ late mature thermogenic gas; TSR = thermochemical sulphate reduction.
- Fig. 14. (a) Gas mixing diagram based on $C_1/(C_2+C_3)$ versus $\delta^{13}C_1$ to infer the origin of gases and the contribution of microbial versus thermogenic components in mixed gases. Fractions of microbial gas in mixed gases are represented by dashed lines (genetic fields after Strapoć et al., 2011). (b) $\delta^{13}C_2$ versus $\delta^{13}C_3$ plot for gases from the onshore Nile Delta showing the kerogen type and maturity for their source rocks (genetic fields after Berner and Faber, 1996). Black and green circles indicate natural gas samples in the study area from Oligocene and Miocene reservoirs, respectively (Khairy et al., 2022).

Table captions

Table 1: Isoprenoids and *n*-alkanes ratios for 36 aliphatic fractions from the Kafr El Sheikh, Abu Madi, Qawasim, Sidi Salem and Tineh formations, onshore Nile Delta Basin. TOC and Rock-Eval pyrolysis parameters for these samples are also included.

Table 2: Calculated biomarker ratios for the analyzed extracts from the onshore Nile Delta, Egypt.

- Acquisition time -

33

El Basant-2 well 2870 m Qawasim extract . Mulu /'WM

Balsam-1 well 3070 m Qawasim extract

Phytane/n- C_{18}

Table 1

Pr/Ph = Pristane/phytane ratio; Pr/n-C₁₇ = Pristane/n-C₁₇ ratio; Ph/n-C₁₈ = Phytane/n-C₁₈ ratio; CPI (Carbon preference index) = 1/2[(C25+C27+C29+C31+C33)/(C24+C26+C28+C30+C32) + (C25+C27+C29+C31+C33)/(C26+C28+C30+C32+C34)]; **OEP =** Odd-even predominance = $(C_{25} + 6C_{27} + C_{29})/(4C_{26} + 4C_{28})$; **ND**: No data or no analysis.

Table 2

A = C₁₉ /C₂₃ tricyclic terpanes **; B** = C₁₉+C₂₀/C₂₃ tricyclic terpanes; **C** = C₂₂/C₂₁ tricyclic terpanes; **D** = C₂₄/C₂₃ tricyclic terpanes; **E** = C₂₆/C₂₅ tricyclic terpanes; **F** = C₂₄ tetracyclic terpanes/C₂₆ tricyclic terpanese; **G** = C₂₄ tetracyclic terpanes/C₂₃ tricyclic terpanese; **H**: Ts/Tm = 18α(H)-22,29,30 trisnorneohopane (Ts) /17α(H)-22,29,30 trisnorhopane (Tm); **I** = C²⁸ bisnorhopane/C³⁰ hopane; **J** = C²⁹ norhopane/C³⁰ hopane; **K =** C³⁰ Diahopane/C³⁰ hopane; **L:** Oleanane index = 18α(H)-oleanane/C³⁰ hopane; **M:** Gammacerane Index = Gammacerane/C³⁰ Hopane**; N** = **C31** Homohopane (22R)/C³⁰ hopane **O:** Homohopane index = C35 Extended hopane/C34 extended hopane (22S + R); **P =** C30 Moretane/C³⁰ Hopane**; Q** = %C32αβ22S/(22S + 22R) C³² hopane ratio; **R:** %C27αααR =100*C27R/(C27R + C28R + C29R); **S:** %C²⁸ αααR **=** 100*C28R/(C27R + C28R + C29R); **T:** %C²⁹ αααR = 100*C29R/(C27R + C28R + C29R); **U =** C²⁷ diasteranes (S + R)/ C27 ααα regular sterane (S + R); **V:** % C29 20S sterane ratio = C²⁹ 20S/(C29 20S + C29 20R); **W:** % C29 ββ sterane ratio = $(C_{29}\beta\beta S + C_{29}\beta\beta R)/(C_{29}S + C_{29}\beta\beta R + C_{29}\beta\beta S + C_{29}R)$; *: parameters used for chemometrics.