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Chapter 2

Natural Gas Geochemistry in the Offshore Nile Delta, Egypt

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Abstract

The offshore Nile Delta basin is considered as one of the most promising province in Egypt which has an excellent potential gas and condensate reserves for future exploration. This study aimed to characterize the origin of natural gas and to determine whether it is biogenic, thermogenic or mixed processes which are considered the dominant generation pathways. Regional geochemical studies were conducted on 20 test gas samples produced from the Miocene and Plio-Pleistocene reservoirs of Abu Qir, N. Abu Qir, Temsah, Wakkar and Port Fouad fields representing the western and the eastern Nile Delta province. The geochemical analyses revealed that the main constituents of the natural gases are methane (96.2%–99.37%) with minor contribution from ethane and propane. Methane carbon isotopic composition ranges between -65.6‰ and -40.3‰ PDB displaying a strong indication for gas mixing of thermogenic and early microbial methane. The gas chromatography-mass spectrometry carried out on the produced natural gases exhibits high oleanane index that ranges between 19% and 42%, the medium concentration of moretane index between 11% and 16% and the absence of gammacerane index indicating that the natural gases were derived from siliciclastic source rocks containing type III kerogen of terrestrial origin and higher land plants input of Tertiary age. The calculated maturity parameters of the studied natural gas proportions based on various sterane isomerisation distributions, i.e. \( \frac{C_{\text{29} \alpha \beta \beta}}{C_{\text{29} \alpha \alpha \alpha}} \) and \( \frac{C_{\text{29} \alpha \alpha \alpha 20S}}{C_{\text{29} \alpha \alpha \alpha (S+R)}} \) reached 0.6 and 0.5 respectively indicating a medium stage of thermal maturation equivalent to the main peak of oil generation window (0.85 Ro%). The sterane isomerization ratios may reflect the rapid rate of subsidence and sedimentation in the Nile Delta and appear to have been generated during the early stage of source rock maturation.

Keywords: biogenic, thermogenic, Nile Delta, biomarkers, Egypt
1. Introduction

1.1. Location of the study area

The Nile Delta and the offshore Mediterranean Sea basin are hydrocarbon rich provinces that have generated natural gas and condensate from siliciclastic reservoirs ranging in age from Plio_Pleistocene to Miocene. Currently, these areas are the most active exploration and development province in Egypt. The proven huge reserves of the Pliocene gas discoveries made in the last decade firmly established the Pliocene sequence as a primary hydrocarbon potential target for the exploration activities in the Nile Delta and offshore Mediterranean region.

The study area lies in the offshore Mediterranean Sea to the north of Alexandria and Port Said cities within the northern eastern Nile Delta between longitudes 30° 10´- and 32° 54´-E and latitude 31° 25´- and 32° 00´- N. This area includes four giant natural gas fields namely; Abu Qir Field located to the north of Alexandria city and Temsah, Wakkar and Port Fouad fields located 65 kilometers to the north of Port Said in the offshore Mediterranean Sea, about 30 km from the Egyptian coast (Figure 1).

![Figure 1. Location map of the study gas fields, offshore Nile Delta, Egypt.](image)

1.2. Geologic setting and lithostratigraphy

The present Nile Delta lies on the north_external margin of the African plate. Its structural evolution is largely contemporaneous with the break–up of the African plate margin consequent to the opening of the Red Sea and the northward transition of the Arabian Peninsula [1, 2]. The northern part of the Nile Delta is characterized by a series of major tectonic features
with different orientations. Some of them are active during the deposition of Tertiary section while other flatten with depth, become horizontal and dies on top of the Rosetta Formation affecting only through the Kafr El-Sheikh Formation.

The Nile Delta is characterized by asymmetric fold, overthrust faults and diapirs. Its dates back to the Syrian Arc system having an arcuate trend from northeast to southwest through the northern part of the Nile Delta to the Western Desert of Egypt (Figure 2).

The regional subsurface stratigraphic succession of the Nile Delta has been represented in Figure 3. This succession is discussed by many authors [3-11].

The lithostratigraphy of the Nile Delta is represented by Miocene sediments:

Moghra, Sidi Salem and Abu Madi formations (from bottom to top). In addition, the Pliocene–Pleistocene sequences are represented mainly by shale or clay with sandstone interbeds. The Miocene sequence is summarized as follows:

1.2.1. Moghra formation (Early miocene)

Moghra Formation consists of marine to fluvio–marine deposits (shale and sandstone) of presumed deltaic origin, although it is associated with marine carbonate intervals. This formation is unconformably overlain by Sidi Salem Formation.

1.2.2. Sidi Salem formation (Middle miocene)

The lower limit of this formation is not known in the central part of the Nile Delta where it overlies the Moghra Formation to the west and south. Sidi Salem Formation is composed mainly of mudstone with interbeds of marls, sandstones and siltstones. This formation...
corresponds to a lower neritic slope environment. Sidi Salem Formation is unconformably overlain by Abu Madi Formation.

1.2.3. Abu Madi formation (Late miocene)

Abu Madi Formation is composed of interbedded sandstones and mudstones. This formation was deposited as an incised valley fill at the end of the Late Miocene. The depositional environment of Abu Madi Formation changes from fluvial to lagoonal with marine influence increasing upward.

The Plio- Pleistocene sequences are represented by the following formations.

1.2.4. Kafr El Sheikh formation (Early–middle pliocene)

Kafr El Sheikh Formation consists of mudstone sequence with thin limestone and sandstone interbeds. This formation extends all over the Delta area. In the Nile Valley it is accumulated at outer neritic to upper bathyal water depths, following a major lower Pliocene transgression resulted in the flooding of the former Eonile canyon and transforming it into a long, narrow gulf far south Aswan [12]. Rizzini et al. [4] suggested that the Kafr El Sheikh Formation is accumulated as neritic mudstones on the present onshore delta and in a basinal setting offshore. They suggested that the sands incorporated into this formation are essentially storm sands. This formation is conformably overlain by El Wastani Formation.

Figure 3. Lithostratigraphic succession of Northern Nile Delta, Egypt modified from Kamel et al. [8].
1.2.5. El Wastani formation (Late pliocene)

El Wastani Formation consists of thick sand beds interbedded with thin clay beds which become thinner toward the top of the formation. This formation is transitional between the shelf facies of the underlying Kafr El Sheikh Formation and the coastal and continental sands of the overlying Mit Ghamr Formation. It shows large forests due to the progradation and could also contain deltaic deposits.

1.2.6. Mit Ghamr formation (Late pliocene)

Mit Ghamr Formation consists of thick layers of sand and pebbles which show clay interbeddings of limited thickness. The depositional environment of this formation is probably shallow marine to fluvial. It is a typical fill-up basin with coastal sands, coquina beds, clay and peat. It conformably underlies the Bilqas Formation.

1.2.7. Bilqas formation (Holocene)

Bilqas Formation is the top sedimentary cover of the Nile Delta province. It consists of sand interbedded with clay rich in pelecypod, gastropod and ostracod fragments. The clays contain many fragments of vegetal matter and peat deposits. The deposition occurred most likely in lagoons and brackish swamp, interrupted by beach sands.

During the last two decades, the Nile Delta and the offshore Mediterranean Sea have been intensively investigated by the petroleum industry. Till now over 36 TCF of gas have been discovered since drilling began in 1966 [13]. The geologic history of the Nile Delta created multiple source, reservoir and seal combinations. Main source rocks are believed to occur in Late Mesozoic and Oligocene to Miocene sedimentary succession.

2. Sampling and analytical techniques

A total of twenty gas samples were obtained through drill stem testing or modular dynamic testing from 20 wells located in the offshore area of the eastern and western Nile Delta fields namely, Abu Qir and North Abu Qir from the western Nile Delta while Temsah, Wakkar and Port Fouad representing the eastern Nile Delta province and the different reservoir stratigraphic ages namely Miocene and Plio-Pleistocene.

The isotopic composition of twenty gas samples was determined in BGR (Bundesanstalt für Geowissenschaften und Rohstoffe) lab in Hannover. Gas chromatograph (GC Varian CP-3800) was equipped with a Flame Ionization Detector and a Thermal Conductivity Detector for separation of gas components (C1–C5) using three capillary columns (First, Silica PLOT 30 m×0.32 mm, Second, CP-Sil 5CB 30 m x 0.32 mm). Permanent gases (atmospheric gas components) were separated using three packed columns (Molsieve-12× 1.5 m ×1/8 in., Hayesep Q 0.5 m ×1/8 in. nickel, and a Hayesep T 0.5 m ×1/8 in. nickel). All six columns are placed in one oven, heated to 50 °C at the start of the analysis. After 10 min, temperature was increased at 10 °C/ min up to 180 °C, which is held for another 10 min. Finally the oven temperature was reduced to become 50 °C.
Measurements of $\delta^{13}$C and $\delta$ D on the hydrocarbon gases were conducted with a Thermo Finnigan Delta plus XL mass spectrometer. Gas components were separated on a gas chromatograph and injected into the mass spectrometer. Isotope values are reported in the $\delta$ notation in per mil ($‰$) relative to the common PDB and SMOW standards.

Data of analysis including gas chromatography, gas chromatography-mass spectrometry were conducted through Stratochem and Corex Laboratories (New Maadi, Cairo).

3. Results and discussions

3.1. Bulk geochemical characteristics of natural gas

The abundant composition of the natural gases is dominated by methane ranging between 92.72% and 99.96%. The natural gas wetness denoted by the formula $C_{2+}/\sum(C_{1-C5} \times 100$ and cumulative contents of the higher hydrocarbons from ethane up to pentane range from 0.05% to 6.76%. According to Schoell [14] the natural gas may be classified as wet if it exhibits a wetness index greater than 5%. The natural gas samples examined from the western Nile Delta can therefore be classified as wet gas, while the major number of gas samples from the eastern Nile Delta is classified as dry gas except the samples produced from the two wells PSE-1 and DEN-1. Wet gas is thermogenic in origin but associated with condensate in most cases while the dry gas may have either a microbial or late mature thermal origin [14] or may be related to that microbial alteration occurring within the reservoirs through the preferential removal of the C3+ components [15].

![Figure 4](image_url)

Figure 4. Relationship between isoprenoids $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ showing source and depositional environments of the natural gas samples from the two provinces of the Nile Delta from Shanmugam[17]. All the study gas samples are located within the terrestrial to peat coal source depositional environments.
The predominance of pristane over phytane (Pr/Ph) ratio was used as an indicator of source rock depositional environments [16]. The ratio of Pr/Ph was ranged between 2 and 3 for the natural gas produced from the eastern province indicating fluviomarine and coastal swamp environment. The same ratio was found to be in the range between 6.4 and 9.4 which indicates peat swamp depositional environment. Figure 4 summarizes the achieved results concerning the nature of the source rock depositional environments is strongly supported by the plot of the isoprenoid ratios Pr/\(n\)-C\(_{17}\) versus Ph/\(n\)-C\(_{18}\) [17]. It can be seen from this figure that both the natural gases produced from the eastern and western provinces of the offshore Nile Delta and Mediterranean Sea are located within the region of terrestrial to peat coal source depositional environments. The high odd even carbon preference index (CPI > 1) for the studied natural gas samples from the two provinces reflect the generation from source facies dominating terrigenous and wax-rich components [18].

3.2. Source and maturation dependent biomarker distributions

The results of organic geochemical analyses of twenty gas samples representing the western Nile Delta province namely, Abu Qir and North Abu Qir fields and the eastern Nile Delta province, namely Temsah, Wakkar and Port Fouad fields. The results of gas chromatogram mass fragmentogram of the study gas samples show a predominance of C\(_{29}\) stereoisomers > 50% over C\(_{27}\) regular steranes between 20% and 27% suggesting a significant input of terrestrial organic matter [19, 20]. Also, the achieved result is strongly supported by the relative abundance of diasterane index that ranges between 55% and 69% of the study gas samples.
All the study gas samples that exhibit higher oleanane index ranging from 19% and 42% strongly support the enrichment of angiosperm higher land plants input to the siliciclastic source kerogen which is thought to be derived from Late Cretaceous to Tertiary age [21, 22]. The medium concentration of moretane index in all the study samples ranges between 11% and 16% and the absence of gammacerane index strongly supports a terrestrial input [23, 24].

Biomarker maturity parameters, include the sterane isomerization ratios C29 ααα20S/(S+R), and C29 αββ/(αββ+ααα) which according to Seifert and Moldowan [25] are genetically related to the effect of thermal maturity processes. The average sterane isomerization ratios C29ααα20S/(S+R) and C29αββ/(αββ+ααα) of natural gas are 0.6 and 0.5 respectively indicating a medium stage of thermal maturation equivalent to the main peak of oil generation window (0.85 Ro%) [18]. The medium sterane isomerization ratios may reflect the rapid rates of subsidence and sedimentation in the Nile Delta and appear to have been generated during the early stage of source rock maturation from type III kerogen [26].

Figure 6. Carbon and Hydrogen isotope ratios of natural gases. Genetic fields according to Schoell[27, 31] and Whiticar et al. [32].

3.3. Relation between isotopic composition and origin of natural gas

The isotopic composition of natural gas depends on the type and maturity of source rock [27, 28]. Stable isotope geochemistry helps to differentiate the original gas derived from a single source rock. The methane carbon isotope compositions range between -65.6 ‰ and -41.1‰. Methane hydrogen isotope data ranges from -193 ‰ to -149‰. The isotopically lightest δ 13C sample was obtained from the SEM-1 well, while the heaviest δ 13C value was received from
Many of the δ^{13}C values have intermediate positions between these end members, which are consistent with what is commonly interpreted as mixed microbial and thermogenic gas [14, 28]. A general increase in the δ^{13}C values with depth from Miocene to Plio-Pleistocene reservoir is consistent with the increasing thermal maturity and the decreasing relative concentration of biogenic gas.

The wet gas (C2+) components also display a significant variability in their isotopic compositions. The δ^{13}C of ethane (δ^{13}C_2) ranges from -37.5‰ to -27.9‰ but that of propane (δ^{13}C_3) ranges from -32.2‰ to -11.1‰.

Natural gases become isotopically heavier and contain relatively more methane with increasing thermal maturity. Thermogenic methane is generally enriched in δ^{13}C compared with microbial methane [27].

Figure 5 represents the Bernard plot in which the molecular ratio C1/ (C2 + C3) is plotted versus methane’s stable carbon isotope ratio according to Bernard et al.[29] and Faber and Stahl [30]. The relationship between these two parameters allows distinguishing microbially generated methane from thermogenic hydrocarbon gases. The figure provides a strong indication for gas mixing of thermogenic and early microbial methane.

The δ^{13}C methane versus δ D methane plot (Figure 6) represents a scheme for the carbon and hydrogen isotope ratios of methane and their genetic implications. Although this diagnostic plot was initially established for determining the thermogenic origin of methane [31] it is useful for the discrimination of microbial methanogenesis, i.e. carbon dioxide (CO_2) reduction versus acetate fermentation [32]. The δ^{13}C values between -65.6 ‰ to -41.1 ‰ and δ D values between -193 ‰ and -149‰ obtained for the methane of the samples from this study classify methane as mixtures between thermogenic and biogenic origin. Figure 7 gives a good matching with the published regional gas data. The relatively heavy hydrogen isotopic compositions (Figure 7) suggest that the microbial gas proportions are probably generated through CO_2 reduction [31, 32].

In the offshore Nile Delta and Mediterranean Sea, the Oligocene to Early Miocene sedimentary sequence is considered as the primary source of natural gas and condensate characterized as mixed type II/III kerogen [8, 26].

The isotopic composition of the individual gas components is a function of thermal maturity of the generated source rock kerogen. Stahl [33] proposed an empirical relationship between methane carbon isotopic composition and vitrinite reflectance. Berner et al. [34] and Berner and Faber [35] illustrated a model between the carbon isotopic compositions of methane, ethane, and propane and source rock maturities represented by vitrinite reflectance measurements. In this study we used the isotope maturity models developed by Berner and Faber [35] to estimate the type and maturity of the precursor (source) material (Figures 7and 8). The geochemical characteristics of natural gas from the Nile Delta indicating a derivation from source rocks rich in terrestrial precursors [8, 36, 37]. Consequently, the admixture of light microbial methane to the thermogenic hydrocarbon gas takes place during secondary processes, such as migration, microbial oxidation, or mixing. These processes usually affect the gas properties within the reservoir [28, 40].
Figure 7. Isotopic composition of methane and ethane in natural gases of the western and eastern Nile Delta. The maturity line is according to Berner and Faber [35]. The terrestrial organic matters indicate the maturity of the source rock in vitrinite reflectance measurements.

Figure 8. Isotopic composition of ethane and propane in natural gases of the western and eastern Nile Delta. The maturity line is according to Berner and Faber [35].

Isotopic compositions of ethane and propane from the west and east Nile Delta samples proved their mixing origin and derivation from terrestrial organic matter with a source rock maturity between 0.1% and 2.0% Vitrinite Reflectance measurements.
4. Summary and conclusions

The molecular and isotopic composition of twenty natural test gas samples produced from the Miocene and Plio-Pleistocene reservoirs of Abu Qir, N. Abu Qir, Temsah, Wakkar and Port Fouad fields representing the western and the eastern Nile Delta province were used to examine the generation and alteration of natural gas and condensate accumulations. The geochemical analyses revealed that the main constituents of the natural gases are methane (96.2–99.37%) with minor contribution from ethane and propane. Methane carbon isotopic composition ranges from -65.6‰ to -40.3‰ PDB displaying a strong indication for gas mixing of thermogenic and early microbial methane. The gas chromatography_mass spectrometry carried out to the produced natural gases exhibit high oleanane index that ranges between (19% and 42%), a medium concentration of moretane index between 11% and 16% and the absence of gammacerane index and predominance of C29 stereo isomers > 50% over C27 regular steranes (between 20% and 27%) and a high diasterane index that ranges between 55% and 69%. The above mentioned results pointed out that the natural gases were derived from siliciclastic source rocks containing type-III kerogen of terrestrial origin and higher land plants input from Late Cretaceous to Tertiary age. The calculated maturity parameters based on various sterane isomerisation ratios, i.e., C29αßß/(αßß+ααα) and C29ααα20S/(S+R) reached to 0.6 and 0.5 respectively indicating a medium stage of thermal maturation equivalent to the main peak of oil generation window (0.85 Ro%). The medium sterane isomerization ratios may reflect the rapid rates of subsidence and sedimentation in the Nile Delta and appears to have been generated during the early stage of source rock maturation.

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