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© 2025 Farouk, Ahmed Saada, Arafat, Al-Kahtany, Gentzis, Zaky and Jovane. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms. Thermal maturity and gas generation in Upper Cretaceous formations of the Beni Suef Basin, Egypt: insights from stable carbon isotopes and geochemical analysis of the Azhar-E1X well

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This study investigates the origin and thermal maturity of natural gases in Upper Cretaceous reservoirs within the Azhar-E1X well, Beni Suef Basin, Egypt, using stable carbon isotopic analyses of headspace gas samples. Gas shows within the Cretaceous succession, specifically the Bahariya Formation and the Abu Roash "F" Member (A/R "F" Member), were characterized. A total of 15 headspace gas samples and five mud gas samples were analyzed for molecular composition and stable carbon isotopic values ($\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$). Methane concentrations ranged from 69 to 1,446 ppm in headspace samples and 961–5,670 ppm in mud gases. Isotopic analysis suggests that gases from the A/R "E, F, and G" members are primarily derived from the primary cracking of kerogen. In contrast, gases from the underlying Bahariya Formation indicate a mixed origin, resulting from both primary cracking of coal-rich kerogen and secondary cracking of oil. The natural gases analyzed are predominantly thermogenic. A normal carbon isotope trend ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$) was observed in the headspace gas samples, where methane isotopic compositions are lower than those of ethane.

KEYWORDS

Beni Suef basin, Abu Roash Formation, Bahariya Formation, stable carbon isotopes, thermogenic gas, hydrocarbon maturation, biodegradation, Azhar-E1X well

1 Introduction

The Beni Suef Basin (BSB), located in north-central Egypt, is a structurally complex extensional rift basin that formed during the Cretaceous break-up

of Gondwana. The basin's evolution is characterized by significant tectonic subsidence, which has played a critical role in controlling the burial history, thermal maturation, and hydrocarbon generation within its stratigraphic units. Key intervals, such as the Abu Roash and Kharita Formations, serve as major source rocks, with their maturity levels closely tied to the basin's subsidence-driven burial history and associated heat flow (Tawfik et al., 2022; Farouk et al., 2024a; Farouk et al., 2024b).

Stable carbon (δ^{13} C) and hydrogen (δ D) isotope measurements are crucial in determining the thermal maturation and genetic origin of natural gas and correlating natural gas to its source rock (Schoell, 1988). Natural gas forms primarily through thermogenic and biogenic (microbial) processes. Microbial gas mainly results from microbial decomposition of organic matter at temperatures below 80°C (Schoell, 1988; Huang and Larter, 2014). Thermogenic gas, on the other hand, is produced by the thermal degradation of organic matter, involving both primary cracking of kerogen and secondary cracking of oil and gas (Dai et al., 1985).

By integrating isotopic data with genetic diagrams and maturity parameters, such as the iC_4/nC_4 ratio, this study provides enhanced insights into the hydrocarbon potential of the BSB. Unlike general descriptions of organic matter degradation into thermogenic gas, our work emphasizes the specific isotopic and geochemical processes within the basin. Furthermore, it critically examines the differences between headspace and mud gases to understand secondary alterations, including migration and fractionation, to present a more comprehensive understanding of the region's petroleum system. To date, no published studies have specifically examined the origin of natural gas in the Cretaceous reservoirs of the Beni Suef Basin (BSB) using high-resolution stable carbon isotopic data.

This study addresses this critical gap by integrating δ^{13} C analyses of headspace and mud gases from the Azhar-E1X well to evaluate the interplay between thermal maturity, subsidencedriven burial history, and secondary alteration processes. The main objectives are to (1) determine the origin and thermal evolution of reservoir gases through $\delta^{13}C_1 - \delta^{13}C_3$ signatures, (2) assess the impact of basin subsidence, hydrocarbon generation kinetics, and post-genetic processes (such as migration and isotopic fractionation) on gas composition, and (3) resolve discrepancies between headspace and mud gas isotopic signatures to refine models of secondary alteration effects in rift basin petroleum systems.

2 Geological setting

2.1 Structure and tectonic events

Beni Suef Basin (BSB) is an extensional rift basin that spans the West and East Nile provinces, in the Nile Valley and is a significant component of a NW-SE (northwest-southeast) network of Cretaceous basins (Figure 1). The study area covers approximately 57 km² in the western desert's northeastern region (Figure 1). The Azhar-E1X well in the Azhar oil field was used to evaluate the hydrocarbon potential in the Cretaceous sequence (Ali et al., 2024). It is located at latitude of 29° 08′45.25″N and longitude of 30°

56'50.07"E. Structures are mostly anticlinal with faults that result from the vertical movement of basement blocks (Schlumberger, 1984; Schlumberger Middle East, 1995). There are three major patterns displayed by faults in the Northwestern Desert: NE-SW (Northeast-Southwest), E-W (East-West), and NW-SE (Northwest-Southeast). Understanding the tectonic forces and processes that shaped the region's geological formation can be gained by studying fault trends. The shallower areas are characterized by several hanging faults. The initial conceptual model illustrates Africa's movement relative to Eurasia, indicating an eastward shift from the Lower Jurassic to the early Late Cretaceous, a subsequent westward movement from the later Late Cretaceous to the late Eocene, and a final northward shift from the latest Eocene to the present (Smith, 1971). Because of the collision of Africa and Asia, three tectonic events impacted northern Egypt. The oldest event resulted in NW or WNW trending structures. Another event that occurred during the Cretaceous resulted in the ENE trending Syrian Arc structures. Lastly, the third event occurred during the Late Eocene to the Early Oligocene and resulted in NW and NNE trending structures (Meshref, 1982). The BSB was controlled by the Aptian/Albian NE-SW extension movement. This movement resulted in deposition of the Albian Kharita Formation directly on the crystalline rocks of the Egyptian Basement Complex (Moustafa et al., 2008; Zahran et al., 2011; Abdel-Fattah, 2015; Salem and Sehim, 2017; Nabawy et al., 2022). These structural tectonics were caused by Africa's displacement with respect to Eurasia (Smith, 1971). Significant Miocene uplift that resulted from the pre-rift Red Sea thermal uplift was documented by Bosworth and Stockli (2016). Salem and Sehim (2017) evaluated the BSB's extensional rifting during Eocene time. With a few notable variations in the thickness and absence of certain rock layers, most wells that were drilled in the study area indicated the same geologic column as in the Northwest Desert of Egypt, where the Abu Roash Formation (A/R) "D" Member was absent due to faulting. The age of the rock units ranges from the Albian Kharita Formation to the Eocene - Oligocene Dabaa Formation (Figure 2).

2.2 Lithostratigraphy

The Cretaceous lithostratigraphic succession in the BSB commenced with deposition of fluvial siliciclastic sediments of the Kharita (Kh) Formation in the Early Cretaceous, followed by predominantly siliciclastic sediments from the Cenomanian Bahariya Formation.

The Cenomanian Bahariya Formation, as described by Said (1990), is situated above the fluviatile sediments of the Kh Formation and is conformably overlain by the marine A/R Formation. It consists of interbedded sandstone and siltstone, with occasional limestone and shale intercalations (Figure 2). The lower section of the formation is predominantly by sand-based units, exhibiting repeated patterns of blocky gamma-ray features (Figure 2). Conversely, the upper sections display a significant increase in gamma ray/neutron porosity readings, indicating higher mud content in the upward direction (Figure 2).

The Bahariya Formation was followed by clastic/carbonate units from the Upper Cenomanian-Santonian A/R Formation,



and eventually gives way to carbonates and chalk from the Campanian–Maastrichtian Khoman Formation (Zahran et al., 2011; Shehata et al., 2019; Shehata et al., 2020; Mansour et al., 2024).

The A/R Formation is thick in the BSB and has a thickness of more than 1,000 m (Hantar, 1990). Palynological dating of the A/R Formation in the Western Desert basins indicates Cenomanian to early Santonian age (Tahoun and Deaf, 2016). The A/R Formation, named by Norton (1967), are overlies the Bahariya Formation in the northwestern Desert and frequently underlies the Khoman Formation. The formation is mostly composed of limestone interbedded with shale and sandstone. In the north Western Desert, the A/R Formation is separated into seven conformable, well-defined, and clearly traceable clastic and carbonate members, known as from base to top: the "G", "F", "E", "D", "C", "B", and "A" members (Schlumberger Middle East, 1995) (Figure 2).

	Age		Stratigra	phy		Lithology			
	1150		Formation	Member	1	Zhilology			
	Oligo	ocene	Dala	_		Shale, medium to dark			
oic	sue	L	Daba	a		to sub-blocky, soft, steaky, non-calcareous.			
Cenoz	Paleo	E- M	Apollo	nia		Soft to moderately hard, brown to off-white, fine limestone, cherty			
			Khoma	an		Chalky limestone			
				A					
				В	COLUMN CLARKERS	Interbedded limestone and			
			oash	C		shale and sand			
		Late	bu R	D		Shale interbedded with			
			A A	E		limestone			
oic	ous			F		Argillaceous limestone			
SOZ	tace	tace	tace	tace			G		Shale interbedded with
Me	Cre					Upper		innestone and sandstone	
			Bahariya	Lower		Sandstone interbedded with shale and minor streaks of limestone			
		rly	Upper Kharita			Sandstone interbedded with shale			
		Ea	Lower			Fine to coarse sandstone Shale with streaks of sandstone			
Pre-C	ambria	mbrian Basement				White, light, pink, coarse, quartz, feldspars and mafic minerals.			

FIGURE 2 BSB stratigraphic column (after Edress et al., 2021).

2.3 Burial history

Subsidence in the BSB, driven by rifting and vertical movements of basement blocks, has led to significant burial depths and the progressive thermal maturation of organic matter. The Aptian-Albian extension initiated the deposition of the Kharita Formation directly on the crystalline basement. This was followed by the deposition of the Bahariya Formation and A/R Formation during successive transgressive and regressive cycles. The basin's subsidence history has resulted in varying burial depths and geothermal gradients, creating distinct thermal maturity zones across the stratigraphic column.

The geological assessment of subsidence in the basin reveals the interplay between tectonics, sedimentation, and organic matter maturation, which ultimately controls the hydrocarbon system. Geological subsidence in the BSB has resulted in the progressive burial and heating of organic-rich sediments, driving the thermal cracking of kerogen to generate hydrocarbons. For example, the lower Kharita Formation has reached peak maturity within the oil generation window, while the Abu Roash members range from immature to early mature stages. Elevated heat flow values (57–60 mW/m²) coupled with rapid subsidence during the Cretaceous have accelerated maturation rates, affecting gas composition and isotopic characteristics (Mansour et al., 2020; Mansour et al., 2023; Farouk et al., 2024a).

The Cretaceous succession, central to this study, includes Bahariya Formation and A/R "E, F, and G" members, which exhibit significant hydrocarbon potential. The Bahariya Formation, deposited in fluvial to shallow marine environments, represents deeper burial and higher thermal maturity than the overlying A/R Formation. Geochemical and isotopic data suggest the gases from the Bahariya Formation are thermogenically derived, with signatures indicating both primary kerogen cracking and secondary oil cracking. In contrast, the A/R "E, F, and G" members are associated with earlier stages of maturity, reflecting their relatively shallower burial.

3 Methodology and sample collection

3.1 Differences between headspace gases and mud gases

The sampling methodology for this study follows established protocols (Ferworn et al., 2008), using headspace gas samples collected in isojars and mud gas samples collected in isotubes. While both methods provide insights into hydrocarbon composition, isotopic fractionation during degassing can skew $\delta^{13}C$ measurements, affecting interpretations of gas maturity and origin. Headspace gas samples, processed in controlled lab conditions, yield higher-resolution data, but discrepancies with mud gas highlight the need to evaluate fractionation effects.

An isotube is a stainless-steel device for collecting mud gas directly from the degasser tank during drilling. Isojars, airtight containers for cutting samples, prevent biodegradation with water and bactericide. Over 24 h, gases desorb into the jar's headspace, capturing formation gas with lighter isotopes (^{12}C) released first, while heavier isotopes (^{13}C) remain in the pores (Ferworn et al., 2008; Dominato et al., 2018; Chatellier et al., 2018).

Mud gas analysis provides real-time data for largescale surveys but may lack precision for specific maturity assessments (Tretner et al., 2008). In contrast, headspace gas samples from core cuttings enable detailed lab analysis of gas composition and isotopic signatures, ensuring accurate maturity evaluation.

3.2 Sampling

A total of fifteen headspace gas samples were collected in isojars and analyzed for molecular gas concentrations using gas chromatography (Table 1). Additionally, five mud gas samples were collected in isotubes and analyzed for molecular gas concentrations using gas chromatography (Table 2) from the Upper Cretaceous succession. This study primarily focused on headspace gas analyses due to their higher accuracy, whereby headspace gas sampling offers higher resolution and more direct measurements for assessing the maturity of specific rock intervals and source rocks (Kolb and Ettre, 2006). Six of the headspace gas samples were also subjected to methane stable carbon isotopic analysis, while 15 headspace gas samples were analyzed for ethane and propane stable carbon isotopic analyses (Table 1). In addition, five samples of mud gas were analyzed for methane, ethane, and propane stable carbon isotopic analyses (Table 2).

3.3 Gas composition by gas chromatography (GC) and isotopic analysis

To determine the molecular composition of gases, a fused silica capillary column with a diameter of 0.20 mm and a length of 25 mm was used in a Carlo Erba gas chromatograph. The thermal ionization detector was operated at 200°C, while the inlet temperature was maintained at 150°C. The oven temperature was initially held at 40°C for 8 min and then gradually increased to 180°C at a rate of 6°C per minute. The measurement of various hydrocarbon concentrations (methane, ethane, propane, iso-butane, and n-butane) involved comparing the integrated peak areas of the sample and a standard mixture. This chromatographic technique determines the concentrations of hydrocarbons in the sample. Gas chromatography was used to separate the various substances in the gas mixture, enabling the initial separation of gas components. Following this separation, the constituents underwent combustion and subsequent isotope ratio mass spectrometry, which determined the isotopic composition of elements in distinct molecules. The temperature program included a rise from 30°C at 8°C per minute up to 70°C, and then at 3°C per minute up to 270°C, with an inlet temperature of 200°C. The Vienna Pee Dee Belemnite (VPDB) Standard is a commonly used reference material for measuring carbon isotope ratios. The difference between a sample's stable carbon isotope ratio (13C/12C) and the VPDB standard is expressed using the δ^{13} C notation. This notation indicates the variation in parts per thousand from the VPDB standard, symbolized by per mil (‰).

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δ ¹³ C ₂ (Etha
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TABLE 1 He

C1/(C2+C3)	1.54	0.8	1.08	0.205	0.35	0.28	0.36	0.22	0.24	0.34	0.41	0.24	0.12	0.22	0.51
C2/C3	0.388	0.77	0.699	0.32	0.25	0.19	0.29	0.355	0.33	0.311	0.52	0.44	0.21	0.407	0.61
$\delta^{13}C_2$ - $\delta^{13}C_3$	1.9	1.2	-2.8	-1.4	-1.7	-2.1	-2.4	-1	-1.2	-1.2	-1.4	-0.9	-1	-0.1	-0.4
$\delta^{13}C_1$ - $\delta^{13}C_3$	N/A	N/A	-20.7	-10.1	-10.3	N/A	N/A	N/A	N/A	N/A	N/A	-7.7	N/A	-2.6	-6.2
δ ¹³ C ₁ - δ ¹³ C ₂	N/A	N/A	-17.9	-8.7	-10.3	N/A	N/A	N/A	N/A	N/A	N/A	-6.8	N/A	-2.5	-5.8
δ ¹³ C ₃ (‰)	-33.9	-27.6	-28.3	-30.5	-30.1	-28.5	-27.1	-27.2	-26.9	-27.4	-26.3	-26.5	-25.1	-25.5	-25.5
δ ¹³ C ₂ (‰)	-32	-26.4	-31.1	-31.9	-31.8	-30.6	-29.5	-28.2	-28.1	-28.6	-27.7	-27.4	-26.1	-25.6	-25.9
δ ¹³ C ₁ (‰)	N/A	N/A	-49	-40.6	-42.1	N/A	N/A	N/A	N/A	N/A	N/A	-34.2	N/A	-28.1	-31.7
C3 (ppm)	291	677	538	3,282	2,434	205	436	824	1,058	593	892	2,618	2,165	2,375	1749
C2 (ppm)	113	528	376	1,064	616	40	129	293	354	370	468	1,177	456	67	1,073
C1 (ppm)	625	964	966	891	1,089	69	208	250	351	328	562	920	324	763	1,446
TVD depth (ft)	4,550	5,450	5,700	6,250	6,350	6,600	7,150	7,561	7,640	7,850	7,886	7,965	8,000	8,060	8,120
Formation name	A/R "A"	A/R "C"	A/R "E"	A/R "F"	A/R "G"1	A/R "G"2	A/R "G"3	BAHARIYA1	BAHARIYA2	BAHARIYA3	BAHARIYA4	BAHARIYA5	BAHARIYA6	BAHARIYA7	BAHARIYA8

FABLE 2 Mud g ppm), and rem	jas samples fr ain molecular	om the Azha r ratios (ppm)	ır-E1X well, ta).	ogether with t	heir stable car	bon isotopic	composition	s (‰), incluc	ding $\delta^{13} C_1$	(Methane),	δ ¹³ C ₂ (Ethane	e) and ôC3 (Propan	e) and their n	nolecular con	centration
Formation	TVD depth (ft)	δ ¹³ C ₁ (‰)	δ ¹³ C ₂ (‰)	δ ¹³ C ₃ (%)	C1 (ppm)	C2 (ppm)	C3 (ppm)	C2/C3	i-C4	n-C4	iC4/nC4	C1/(C2+C3)	$\delta^{13}C_1^{-}$ $\delta^{13}C_2^{-}$	$\delta^{13}C_1 - \\ \delta^{13}C_3$	$\delta^{13}C_2^{-}$ $\delta^{13}C_3^{-}$
A/R "G"	6,350	-45.7	-32.6	-29.7	5,670	1,590	2,840	0.55	512	1,320	0.38	1.2	-13.1	-16	-2.9
BAHARIYA	7,561	-41.5	-30	-27.3	954	318	413	0.76	66	149	0.44	1.3	-11.5	-14.2	-2.7
BAHARIYA	7,886	-41.1	-29.6	-26.6	1,110	519	588	0.88	98	207	0.47	1	-11.5	-14.5	-3
BAHARIYA	7,965	-41.1	-29.5	-27	1,460	866	1,020	0.84	155	349	0.44	0.77	-11.6	-14.1	-2.5
BAHARIYA	8,032	-40.2	-29.6	-27.2	961	518	705	0.73	115	263	0.43	0.78	-10.6	-13	-2.4

4 Results

4.1 Concentration of headspace gases

Methane (C_1) is the dominant gas in the Azhar E–1X well, with concentrations ranging from 69 ppm to 1,446 ppm. The highest methane concentration (1,446 ppm) was found in the Bahariya Formation at 8,120 ft, indicating higher thermal maturity, while the lowest (69 ppm) was in the A/R "G" Member at 6,600 ft, suggesting lower maturity or biodegradation (Table 1). Ethane ($_{C2}$) and propane (C_3) concentrations vary significantly, with ethane ranging from 40 ppm to 1,177 ppm and propane from 205 ppm to 3,282 ppm. The highest propane concentration (3,282 ppm) was in the A/R "F" Member at 6,250 ft, indicating oil-derived gases. The iC4/nC4 ratio, a thermal maturity indicator, decreases with depth from 2.5 to 0.5, reflecting increasing maturity, as branched hydrocarbons (iC₄) are more stable than straight-chain hydrocarbons (nC₄) (Table 1).

4.2 Stable carbon isotope compositions

Stable isotopic analysis of headspace gases offers a powerful tool to understand the origins, pathways, and environmental implications of hydrocarbon fluids in geological systems (Philp and Monaco, 2012). Stable carbon isotope values ($\delta^{13}C_1$) for methane ($\delta^{13}C_1$), ethane ($\delta^{13}C_2$), and propane ($\delta^{13}C_3$) were measured. Methane $\delta^{13}C_1$ values range from -49.0‰ to -28.1‰, with the most negative value (-49.0‰) in the A/R "E" Member (5,700 ft), indicating lower maturity, and the least negative (-28.1‰) in the Bahariya Formation (8,060 ft), reflecting higher maturity. Ethane $\delta^{13}C_2$ values range from -32.0‰ to -25.9‰, and propane $\delta^{13}C_3$ values range from -33.9‰ to -25.1‰, both showing less negative values with depth, consistent with increasing thermal maturity (Table 1).

4.3 Isotopic trends and thermal maturity

The $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$ trend confirms a normal thermogenic gas origin. The differences in isotopic compositions ($\Delta^{13}C_{C1-C2}$ and $\Delta^{13}C_{C1-C3}$) provide insights into thermal maturity. $\Delta^{13}C_{C1-C2}$ ranges from -17.9% to -2.5%, with the most negative value in the A/R "E" Member (-17.9%), indicating lower maturity, and the least negative (-2.5%) in the Bahariya Formation (8,060 ft), reflecting higher maturity. Similarly, $\Delta^{13}C_{C1-C3}$ ranges from -20.7% to -2.6%, with the most negative value in the A/R "E" Member (-2.6%) in the Bahariya Formation.

4.4 Mud gas vs. headspace gas comparison

Mud gas samples show higher methane concentrations (961 ppm–5,670 ppm) compared to headspace gases (Table 2), likely due to continuous sampling during drilling. Ethane and propane concentrations in mud gases are also higher, averaging 762 ppm and 1,113 ppm, respectively. Mud gas δ^{13} C values are slightly less negative than headspace gases, with $\delta^{13}C_1$ ranging from -45.7‰ to -40.2‰, compared to -49.0‰ to -28.1‰

for headspace gases (Table 2). This difference is attributed to isotopic fractionation during gas desorption and diffusion, which preferentially releases lighter isotopes (e.g., ¹²C).

4.5 Statistical analysis

Statistical analysis reveals strong correlations between depth and thermal maturity indicators. $\delta^{13}C_1$ values increase (become less negative) with depth, from -49.0‰ at 5,700 ft to -28.1‰ at 8,060 ft. The C_2/C_3 ratio increases with depth, from 0.19 in the A/R "G" Member to 0.61 in the Bahariya Formation, reflecting increasing maturity. The i C_4/nC_4 ratio decreases with depth, from 2.5 in the A/R "E" Member to 0.5 in the Bahariya Formation, further supporting the trend of increasing thermal maturity.

5 Discussion

5.1 Genetic characterization of natural gases

The types of methane production, the nature of organic sources, and the rate of thermal evolution significantly influence the stable isotopic composition and molecular structure of natural gas. Understanding these factors is essential for evaluating the geochemical characteristics of natural gas and the processes responsible for its formation (Tissot and Welte, 1984; Waples, 1985; Whiticar and Faber, 1986). In geochemistry and source rock analysis, the stable carbon isotopic compositions of ethane ($\delta^{13}C_2$) and propane ($\delta^{13}C_3$) are critical for distinguishing between gases derived from different organic sources. Specifically, natural gases with $\delta^{13}C_2$ values less than -29‰ and $\delta^{13}C_3$ values less than -27‰ are typically generated from oil-prone source rocks (Type II kerogen), reflecting the isotopic signature of hydrocarbons derived from marine or lacustrine organic matter rich in liptinite (Dai et al., 1985; Zou et al., 2007; Zumberge et al., 2012). In contrast, gases with $\delta^{13}C_2$ values greater than -27.5‰ and $\delta^{13}C_3$ values greater than -25.5‰ are generally associated with coal-bearing source rocks (Type III kerogen), indicating a terrestrial origin dominated by vitrinite and inertinite, which are more prone to gas generation (Saxby and Shibaoka, 1986; Dai et al., 2004; Gao et al., 2018). Additionally, gases with $\delta^{13}C_2$ values greater than -27.5% and $\delta^{13}C_3$ values less than -27‰ suggest a mixed origin, where contributions from both oil-prone and coal-prone source rocks are present, often due to the co-existence of different organic facies within the same basin or during migration and accumulation processes (Zou et al., 2007). The influence of oil-derived gas is reflected in the carbon isotopic composition of C2+ hydrocarbons in mixed gases, whereas the coal-derived gas composition mostly determines the $\delta^{13}C_{\rm C1}$ composition of the mixture. When describing the origins and contributions of different hydrocarbons in complex gas mixtures, this kind of isotope study is helpful (Zou et al., 2007). The methane isotopic composition in mixed gas is largely affected by the higher methane content in gas from coal.

In this study, and according to the values of $\delta^{13}C_2$ and $\delta^{13}C_3$, gas samples from the A/R "E, F and G" members are located in the oil-derived gas zone, whereas the underlying Bahariya Formation

samples range from mixed gas (7,561 ft–7,886 ft) to coal-derived gas (7,886 ft–8,120 ft) (Table 1; Figure 3).

A comparison between the $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ confirms that the headspace gas samples of the A/R "E, F and G" members are oil-derived and that the headspace gas samples of the Bahariya Formation are coal-derived (Figure 4).

To differentiate between the thermogenic and microbial origins of natural gases, the $\delta^{13}C_1$ valuesare widely used (Schoell, 1980; Schoell, 1983; Whiticar, 1994; Whiticar, 1999; Prinzhofer and Battani, 2003; Xia and Gao, 2017). $\delta^{13}C$ values for methane and ethane facilitate differentiation of gas samples while providing insights into gas origins and alteration histories (Cesar et al., 2021). The $\delta^{13}C_1$ values of the headspace gas samples range from -49.0 to -28.1‰, which confirms that they are they are predominantly thermogenic and were generated at relatively low thermal maturity (Figure 5), possibly in the early to middle stages of the oil window. The samples from the Bahariya Formation also plot along with the kerogen Type III trend whereas the A/R Formation samples plot in proximity to the mixed Type II/Type III and kerogen Type II trends (Figure 5).

Gas molecules form in geological formations through primary and secondary cracking of organic matter. While heavier hydrocarbons break down during secondary cracking, kerogen breaks down directly during primary cracking. The specific conditions of thermal maturation significantly impact the composition of the resulting natural gases (Tissot and Welte, 1984). Separating primary gas cracking from secondary gas cracking is crucial. In the early phases of the oil window and the wet gas window, kerogen cracking is the main process that produces hydrocarbons (Curtis, 2010).

Tian (2006) proposed a plot of $\delta^{13}C_2 - \delta^{13}C_3$ versus $\delta^{13}C_1$ to distinguish between oil and kerogen-derived gases. As thermal stress increases, the $\delta^{13}C_2 - \delta^{13}C_3$ gap between oil and kerogen-derived gases becomes significantly larger. The $\delta^{13}C_2 - \delta^{13}C_3$ versus $\ln(C_2/C_3)$ plot of Prinzhofer and Huc (1995) was used to indicate the origin of gases. The A/R "E, F, and G" members exhibit higher fractionation of $\delta^{13}C_2 - \delta^{13}C_3$ than $\ln(C_2/C_3)$, indicating primary cracking of kerogen (Type II). In contrast, the Bahariya Formation shows two distinct trends. In the first trend, the fractionation of $\delta^{13}C_2 - \delta^{13}C_3$ is lower than $\ln(C_2/C_3)$, indicating secondary cracking of oil (Type III). In the second trend, the fractionation of $\delta^{13}C_2 - \delta^{13}C_3$ is higher than $\ln(C_2/C_3)$, suggesting primary cracking of kerogen (Type II).

5.2 Fractionation of carbon isotopes and alteration processes

Changes to the isotopic and molecular compositions in natural gases can occur as a result of several factors, including high thermal maturity, migration, biodegradation, mixing of gases from various sources, and thermochemical sulphate reduction (TSR) (Schoell, 1983; Dai et al., 1985; Whiticar, 1994; Whiticar, 1999; Hao et al., 2008), The lack of detectable H_2S in the studied gases suggests that TSR has not influenced the natural gas at the well site.

Compared to iso-alkanes and non-hydrocarbons, n-alkanes are more susceptible to biodegradation. Hydrocarbons exhibit various degrees of resistance to biodegradation (Peters et al., 2005). Alkanes







crack (thermally degrade) in the following order: C₃; nC₄; nC₅; iC₅; iC₄; neoC₅. Ethane is difficult to biodegrade (Chung et al., 1988; Head et al., 2003; Meng et al., 2017). Microbial degradation involves the consumption of propane and the production of methane. As a result, the amount of propane is reduced and the amount of methane, which has a more negative composition of hydrogen and carbon isotopes (δD and $\delta^{13}C$), increases. The iC₄/nC₄ ratio is a dependable indicator of gas biodegradation, and certain threshold values offer a qualitative evaluation of the degree of biodegradation. Non-biodegraded gas is indicated to have iC4/nC4 ratio of less than 0.8, whereas biodegraded gas has iC_4/nC_4 ratio more than 1.75 (Horstad and Larter, 1997). The hydrocarbons generated would have positive trends ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$) in their carbon isotopic values and the carbon number (n) and a linear connection with 1/n. As the molecular weight increases, there is a progressive increase in δ^{13} C values. This lends shows that isotope fractionation occurs during thermal maturation. The linear relationship with 1/n provides more evidence of a regular shift in isotopic composition as carbon number increases. The preferential fractionation of isotopes during thermal degradation could be the cause of this relationship. Although the linear relationship with 1/n and the indicated isotopic trend of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$ are theoretical expectations under specific circumstances, it is critical to recognize that natural gas origins are diverse, and that actual data frequently deviate from such idealized patterns. Natural gas isotopic compositions can be influenced by complex geological and geochemical processes.

In many situations, the linear relationship might not be obvious (Chung et al., 1988).

According to Milkov et al. (2020), inverted carbon isotope ratios $(\delta^{13}C_2 < \delta^{13}C_1)$ result from isotope fractionation via desorption brought on by uplift and depressurization in gases drawn from conventional and unconventional reservoirs. Ethane and propane isotope "rollover" (reversals or positive shift) can occur in high maturity shale gas wells (Hao and Zou, 2013). These wells appear to be among the most productive shale wells because *in situ* cracking produces smaller molecules, which increases fluid pressure and brittleness of the organic matter due to increased kerogen porosity and permeability (Jew et al., 2022). Such behavior is observed in well-known shales such as Fayetteville, Woodford, Haynesville, Utica, Marcellus in the US, portions of the US Rockies, and in the Vaca Muerta and Los Molles in South America. Wells without such anomalies or reversals are usually not good producers (Györe et al., 2021).

Thermal maturity is a key factor influencing the isotopic composition of natural gases. Reservoirs affected by significant uplift and depressurization tend to exhibit higher thermal maturity levels (>2% Ro), indicating overmature conditions. In such cases, isotopic reversals ($\delta^{13}C_1 > \delta^{13}C_2$) may occur due to advanced cracking of hydrocarbons or secondary migration pathways (Evans, 2019; Wang et al., 2021). Conversely, reservoirs subjected to less uplift and depressurization exhibit lower maturity levels (<2% Ro) and display normal isotope trends ($\delta^{13}C_1 < \delta^{13}C_2$), supporting the thermogenic



origin of the gases. This trend is consistent with gases generated through primary kerogen cracking and secondary oil cracking in rift basins (Tang et al., 2005; Dai et al., 2016). The absence of isotopic reversals ($\delta^{13}C_1 > \delta^{13}C_2$), which are typically observed in high-maturity shale gas systems (Li et al., 2022), further reinforces the thermogenic nature of the analyzed gases.

In addition to physical phenomena like desorption and diffusion, thermal maturity significantly impacts carbon isotope series in natural gases. The higher molecular mobility of isotopologues containing lighter carbon isotopes (¹²C) facilitates carbon isotope fractionation during gas migration or secondary alteration processes (Zhang and Krooss, 2001). This fractionation alters the δ^{13} C values of methane ($\delta^{13}C_1$), ethane ($\delta^{13}C_2$), and propane ($\delta^{13}C_3$), potentially masking original isotopic signatures. Such effects are particularly pronounced in overmature reservoirs where secondary processes dominate, leading to isotopic shifts or reversals (Tilley and Muehlenbachs, 2013; Xia and Gao, 2018).

The studied headspace gas samples show a normal carbon isotopic trend between $\delta^{13}C_1$ and $\delta^{13}C_2$ that follows the trend

 $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$. This indicates that the carbon-13 isotopic composition in methane is lower than that of ethane, and ethane has lower ¹³C than propane. The negative values of $\delta^{13}C_{C1-C2}$ and $\delta^{13}C_{C1-C3}$ indicate that isotopic fractionation is occurring between methane (C₁) and ethane (C₂), as well as between methane (C₁) and propane (C₃). This suggests that during the formation or transformation processes, the carbon isotopes are being preferentially partitioned in a way that results in lighter isotopes being more enriched in methane compared to ethane and propane. The samples exhibiting normal isotopic trends are further categorized into pre oil window, low mature, oil/wetgas, and wet-gas to dry gas windows according to their level of maturity (Figure 7).

Berner and Faber (1988), James (1990), and Dai et al. (2004) draw attention to the difficulties in interpreting carbon isotopic series in natural gases. The observed isotopic trends can be attributed to a variety of reasons. The fact that these effects are acknowledged emphasizes how crucial it is to understand carbon isotopic series in natural gases.



To properly understand the isotopic data, geochemists must consider source rock properties, maturation history, and geological environment. Although isotopic series analysis can offer useful insights into the origin, migration, and modification of natural gases, a thorough comprehension necessitates considering the different contributing variables. According to Chung et al. (1988), the origin of all natural gases in the A/R "E, F and G" members is oil-derived gas (except for one sample in A/R "E" that is coal-derived). The Bahariya Formation natural gas origin is coal-derived (Figure 8).

5.3 Carbon isotopic composition as a thermal maturity indicator

Plots from Cesar et al. (2020) are used to evaluate the thermal maturity of headspace gas samples and offer important insights into the potential for hydrocarbon generation. The plots show the difference in δ^{13} C values between CH₄ and C₂H₆ ($\Delta^{13}C_{C1-C2} = \delta^{13}C_{C1} - \delta^{13}C_{C2}$), and between CH₄ and C₃H₈ ($\Delta^{13}C_{C1-C3} = \delta^{13}C_{C1} - \delta^{13}C_{C3}$).

The differences in the carbon isotopic composition of propane (C₃), ethane (C₂), and methane (C₁) are represented by $\delta^{13}C_{C1-C2}$ and $\delta^{13}C_{C1-C3}$, respectively. The isotopic composition of the

hydrocarbons contained in the natural gas samples are evaluated using the values of $\delta^{13}C_{C1\text{-}C2}$ and $\delta^{13}C_{C1\text{-}C3}.$ Samples of natural gas with $\delta^{13}C_{C1\text{-}C2}$ values between –15 and –6‰ correspond to a range linked to the onset of wet gas generation. This range indicates a transitional phase from the oil window toward the wet gas zone, which is often characterized by a significant amount of heavier hydrocarbons (e.g., ethane, propane). The isotopic range associated with the onset of wet gas generation is also indicated by natural gas samples with $\delta^{13}C_{C1\text{-}C3}$ values between -20 and -12‰ (Cesar et al., 2020). According to Cesar et al. (2020), the $\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$ values of natural gases tend to increase with depth, reflecting the progressive thermal maturation of organic matter as burial depth increases. Figure 9a illustrates this trend in the Azhar-E1X well, where the δ^{13} C values for methane (δ^{13} C₁), ethane ($\delta^{13}C_2$), and propane ($\delta^{13}C_3$) all show an increase with depth across the 5,600-8,100 ft interval. However, the rate of increase for $\delta^{13}C_1$ (methane) is notably steeper compared to $\delta^{13}C_2$ (ethane) and $\delta^{13}C_3$ (propane). This steeper gradient in $\delta^{13}C_1$ is consistent with the higher sensitivity of methane to thermal maturation processes, as lighter hydrocarbons like methane are more susceptible to isotopic fractionation during gas generation and migration. The observed trends in δ^{13} C values with depth provide valuable insights into the thermal maturity and hydrocarbon generation history of the studied





formations, with the Bahariya Formation exhibiting higher maturity compared to the shallower Abu Roash (A/R) members.

The iC₄/nC₄ ratio is a well-established indicator of thermal maturity in natural gases (Zumberge et al., 2012; Chatellier et al., 2013). Typically, an increase in the $C_1/(C_2 + C_3)$ ratio corresponds to an increase in the iC_4/nC_4 ratio, reflecting higher production of iC₄ (isobutane) from the cracking of kerogen or oil (Hao and Zou, 2013). In this study, the iC4/nC4 ratio decreased with increasing depth and maturity, declining from approximately 2.5 to 0.5 (Figure 9b). As $C_1/(C_2 + C_3)$ increased, the iC₄/nC₄ ratio actually increased, which is consistent with the findings of Hao and Zou (2013) and Cesar et al. (2020). This pattern results from thermal decomposition processes, whereby larger hydrocarbon molecules crack into smaller ones. Branched hydrocarbons (iC₄) are more thermally stable than straight-chain hydrocarbons (nC₄) due to their compact structure, which reduces carbon skeleton

strain and enhances resistance to breakdown (Tissot and Welte, 1984). As thermal maturation progresses, selective cracking and migration cause a relative reduction in iC_4 concentrations, lowering the iC_4/nC_4 ratio. This process is also influenced by factors like volatility, molecular rearrangement, and hydrocarbon migration (Peters et al., 2005; Kang et al., 2021).

Furthermore, the thermal maturity was studied based on the $\delta^{13}C_{C1-C2 Vs} \delta^{13}C_{C1-C3}$ plot. The values of $\delta^{13}C_{C1-C2}$ (>–18‰) and $\delta^{13}C_{C1-C3}$ (>–21‰) became less negative and showed a linear increase from the A/R "E" Member to the Bahariya Formation (Figure 9c). More specifically, the values of $\delta^{13}C_{C1-C2}$ ranged from –17.9‰ to –2.5‰ and the values of $\delta^{13}C_{C1-C3}$ ranged from –20.7‰ to –2.6‰. These values indicate that the headspace gas samples from the A/R "E" Member are in the low mature stage, where Ro is less than 0.6% (Figure 9c). On the other hand, the gases from the A/R "F" and A/R "G members plot within the



(Continued). (a) Headspace Gas Carbon Isotope Composition Logs for well Azhar-E1X. (b) C_1/C_2+C_3 ratio vs. iC_4/nC_4 ratio for gases Azhar-E1X (modified after Cesar et al., 2022). (c) Thermal maturity plot of headspace gas stable carbon isotopic samples from Azhar-E1X well through the relationship between $\Delta^{13}C_{C1-C2}$ and $\Delta^{13}C_{C1-C3}$ (modified after Cesar et al., 2020).



oil window region and the Bahariya Formation gases plot in the region spanning the upper oil-window/wet gas transition to dry gas, where the Ro is >1.50% (Rokosh et al., 2012). Also, the differences between the isotope values of methane in mud gas samples and headspace gas samples were used as permeability and fracturing indicators. According to Ferworn et al. (2008), the Bahariya and A/R "G" reservoir $\delta^{13}C_{C1}$ of headspace gas samples is more positive than the $\delta^{13}C_{C1}$ of mud gas samples indicating low permeability (Table 1 and 2).

For the mud gas samples, the values of $\delta^{13}C_{C1-C2}$ vary from -13.1% to -10.6% and the values of $\delta^{13}C_{C1-C3}$ vary from -16% to -13.4% (Table 1). For the headspace gas samples, the values of $\Delta \delta^{13}C_{C1-C2}$ vary from -17.9% to -2.5% and the values of $\delta^{13}C_{C1-C3}$ vary from -20.7% to -2.6% (Table 1). Headspace gas samples show an obvious offset over the trend line because of the significant variance in the values of $\delta^{13}C_{C1+C3}$ and to a lesser extent in those of $\delta^{13}C_{C2+C3}$ and $\delta^{13}C_{C3+R}$. This offset occurred due to carbon isotope fractionation (Cesar et al., 2022) (Figure 9c).

The headspace gas samples of the Bahariya Formation are more mature than those of the A/R "E, F and G" members because of the greater depth of burial and higher maturity attained by the Bahariya Formation.

While the C_2/C_3 ratio remains constant during bitumen or kerogen cracking, it increases during secondary cracking of the hydrocarbons (Cesar et al., 2022). According to the present study, the C_2/C_3 ratio increased with thermal maturity (Figure 10). Cesar et al. (2020) observed that at Ro = 1.5%, the C_2/C_3 ratio started to increase as thermal cracking of the wet-gas constituents became more pronounced and that a difference of 6‰ was reached between the $\delta^{13}C_{C1}$, $\delta^{13}C_{C2}$, and $\delta^{13}C_{C3}$ values (the so-called even isotopic distribution or EID).

In the headspace gas samples of this study, the EID ($\delta^{13}C_1 - \delta^{13}C_2 < -6\%$) was reached by samples from the Bahariya Formation at a depth of 8,060 ft. This indicates that samples below this depth are in the wet-gas stage of maturity and lie to the left of the EID (Tilley and Muehlenbachs, 2013; Cesar et al., 2022) (Figure 10). In



contrast, the headspace gas samples from the A/R "E, F, and G" members, which are in the oil window stage, have not reached the EID. When analyzing headspace gas samples, particular emphasis is placed on the distribution of carbon isotopes. The analysis shows that there is a fractionation of carbon isotopes that mainly affects C_1 (methane) and C_2 (ethane) to a lesser amount. It is known that isotopic fractionation process affects the isotopic ratios of carbon and hydrogen within hydrocarbons, such as propane (C_3) and ethane (C_2).

The $\delta^{13}C_{C2}$ - $\delta^{13}C_{C3}$ vs. C_2/C_3 plot is used to study gas generation from crude oil cracking at various stages of maturation. The total amount of gas generated from kerogen-cracking increases as thermal maturity progresses, as does the ratio of C_2/C_3 in gas derived from oil-cracking. To identify the gas that originates from oil cracking, Liu et al. (2018) suggested using the plot of $\delta^{13}C_{C2}$ - $\delta^{13}C_{C3}$ vs. C_2/C_3 that was initially introduced by Prinzhofer and Battani (2003).

The isotopic fractionation that occurs in headspace gases is due to desorption and diffusion effects. The anomalies in the carbon isotope ratios in headspace gas samples, which depend on nanopore throat size and overpressure, are due to diffusion effects (Wu et al., 2020). Hydrocarbon reservoirs that have low permeability do not show the effects of carbon isotopic fractionation caused by diffusion and desorption (Cesar et al., 2022). Most gases in the Bahariya Formation plot near the Type III kerogen trend (Figure 11). So, it can be expected that gas generation in the Bahariya Formation came from source rocks rich in vitrinite (Saxby and Shibaoka, 1986; Ogbesejana et al., 2021). The source rock is potentially the Lower Kharita Formation, which is a gas-prone, late-mature source rock. The gases generated from the A/R "E, F, and G" members plot close to the kerogen Type II trend, so these gases came from source rocks that were comparatively more liptinite-rich (Goodarzi et al., 1994). These source rocks is potentially A/R "E, F, and G" members, which are oil/mixed prone source rocks (low mature to marginally mature source rocks). The Bahariya Formation gases are more mature than gases from the A/R "E, F, and G" members (Figure 11).

6 Conclusion

The following conclusions can be made based on the carbon stable isotopic composition of headspace natural gases from the Upper Cretaceous successions in the Azhar field, BSB.

- The hydrocarbon gases from the A/R "E, F and G" members likely originated from mostly liptinitic (Type II kerogen) source rocks, whereas the Bahariya Formation gases originated from source rocks that were comparatively more enriched in vitrinite (Type III kerogen).
- The gaeous hydrocarbons in the A/R "E, F and G" members are oil-derived, whereas those in the Bahariya Formation range from mixed to coal-derived. Most gases were generated thermogenically by primary kerogen cracking in the A/R "E, F and G" members in the Bahariya Formation; the gases were generated by two processes, namely, secondary cracking of oil and primary cracking of kerogen.
- The plot of $\delta^{13}C_{C1-C2 V s} \delta^{13}C_{C1-C3}$ indicates that gases from the A/R "E" Member are low mature to oil window stage) and those from the A/R "F and G" members are mature

(in the oil window) The Bahariya Formation gases are mature to overmature (upper oil window to wet gas).

- The C2/C3 ratio increased as thermal maturity increased. The gas samples from the A/R "E, F and G" members did not reach the EID threshold, whereas the gas samples of the Bahariya Formation reached the EID threshold because the Bahariya gases are more mature than those from the A/R members.
- All studied gas samples showed normal carbon isotopic trend $(\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4)$ with weak biodegradation, which is reflected in the low iC_4/nC_4 ratio.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

Author contributions

SF: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, Writing - review and editing. SA: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - original draft, Writing - review and editing. MA: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - original draft, Writing review and editing. KA-K: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Software, Validation, Visualization, Writing - original draft, Writing - review and editing. TG: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, Writing - review and editing. AZ: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - original draft, Writing - review and editing. LJ: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - original draft, Writing - review and editing.

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