

Genesis of Natural Gas in the Bozhong Sag, Bohai Sea: Constraints from Pyrolysis Experiments

Kuo Li

CNOOC Energy Development Engineering Technology Branch,

Long Su

su1ong08@163.com

Northwest Institute of Eco-Environment and Resources

Tao Ye

CNOOC Tianjin Branch Company

Tongyao Zhang

CNOOC Energy Development Engineering Technology Branch,

Peng Hao

CNOOC Energy Development Engineering Technology Branch,

Ge Yan

CNOOC Tianjin Branch Company

Haidong Wang

Northwest Institute of Eco-Environment and Resources

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Abstract

To clarify the genesis of deep natural gas in the Bozhong Sag, closed-system gold-tube pyrolysis experiments coupled with online trace-gas analysis were conducted on Paleogene lacustrine source rocks, coal-measure source rocks, and representative crude oils at EasyRo values of 1.5%, 2.0%, and 2.5%. The geochemical characteristics of kerogen-cracking and oil-cracking gases were systematically compared. Kerogen-cracking gas generated from Bohai lacustrine source rocks has a markedly higher dryness coefficient and heavier carbon isotopic compositions than oil-cracking gas. With increasing thermal maturity, both $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-C}_2\text{H}_6$ become progressively enriched in ^{13}C . By contrast, oil-cracking gas is relatively wet and isotopically light; crude oils containing larger proportions of heavy components generate gases with higher methane contents. As oil cracking proceeds, $\delta^{13}\text{C-C}_2\text{H}_6$ becomes substantially heavier, whereas $\delta^{13}\text{C-CH}_4$ remains comparatively stable. Comparison of the experimental results with genetic discrimination diagrams shows that deep natural gas discovered in the Bozhong area has a substantially higher dryness coefficient than the experimental oil-cracking gas and closely resembles kerogen-cracking gas derived from lacustrine sapropelic organic matter. Kerogen cracking is therefore identified as the dominant gas-generating process. Coal-type gas can be distinguished from sapropelic kerogen-cracking gas by its heavier $\delta^{13}\text{C-CH}_4$ values. Consequently, the elevated $\delta^{13}\text{C-C}_2\text{H}_6$ values of natural gas in the Bozhong Sag do not necessarily indicate a humic or coal-derived origin; instead, they may reflect gas generated from highly to overmature lacustrine sapropelic kerogen, together with a contribution from the isotopically heavy source rocks of the third member of the Shahejie Formation (E_2s^3). These results provide experimental constraints on natural-gas genesis in continental lacustrine basins and a geological basis for deep-gas exploration in offshore areas.

0. Introduction

The Bohai Oilfield is located in the eastern offshore sector of the Bohai Bay Basin. Since the 1990s, numerous gas-bearing structures have been discovered, among which BZ19-6 is the world's largest metamorphic buried-hill condensate gas field. Its proven geological gas reserves exceed 200 billion m^3 , highlighting the considerable exploration potential of deep natural-gas resources¹. The Bohai Bay Basin is hydrocarbon-rich but contains abundant oil and comparatively limited gas, making it a typical continental oil-dominated basin. Most large gas fields worldwide are sourced from marine or marine–continental transitional strata and are dominated by coal-type, oil-cracking, or biogenic gas². In contrast, gas-generation mechanisms and resource potential in continental lacustrine basins remain poorly constrained and controversial. Wen³ concluded that natural gas in the central Bohai Sea is dominated by hydrocarbon gases. Gas in Paleogene and deeper reservoirs is generally wet, whereas that in Neogene reservoirs is mostly dry and has mixed oil-type, coal-type, and composite origins. Zhao⁴ investigated onshore gas fields in the Bohai Bay Basin and confirmed the coexistence of biogenic, oil-type, and coal-type gases, which were mainly derived from humic organic matter that had reached mature to highly mature stages. Hu⁵ proposed that natural gas in the BZ19-6 field was generated predominantly by the cracking of humic-rich kerogen. Wang⁶ suggested that deep natural gas in the Bozhong Sag is mainly kerogen-cracking gas derived from the advanced thermal evolution of oil-prone source rocks in the Shahejie and Dongying formations. As offshore exploration has progressed, the general characteristics of deep natural gas have become clearer. Nevertheless, major uncertainties remain regarding the distinctions among gases of different origins, the distribution of effective gas source rocks, the timing and efficiency of gas generation, and the formation mechanism of humic-affinity natural gas.

Gas composition and stable carbon isotopic composition are key indicators for determining natural-gas genesis^{7–10}. Empirical diagrams and genetic classification criteria developed from extensive analyses of alkane gases in major gas fields provide a basis for identifying gas origins^{11–13}. Laboratory simulation experiments offer a complementary forward approach for characterizing gases of different origins. Using geological samples from the Tarim Basin, Zhang¹⁴ and Huang¹⁵ investigated geochemical differences between oil-cracking and kerogen-cracking gases, whereas Tian¹⁶ systematically evaluated the gas-generation behavior of sapropelic source rocks in northwestern Sichuan. The geochemical characteristics of natural gas are jointly controlled by source-organic-matter properties, thermal maturity, and accumulation processes. On the basis of representative geological samples and the thermal history of the Bohai Sea region, this study uses pyrolysis

experiments to compare the geochemical characteristics and evolutionary trends of gases generated from different precursors. The results provide an experimental basis for clarifying the genesis of deep natural gas in the Bohai Sea.

1. Experimental Samples and Methods

To distinguish the characteristics of gases generated by sapropelic and humic kerogens, three low-maturity Paleogene lacustrine mudstones with high total organic carbon contents and two mature lacustrine source rocks from the third member of the Dongying Formation (Ed₃) in the Bozhong Sag were selected as sapropelic source materials. For comparison, a low-maturity coal from the Shahejie Formation in structure KL16A of the Laizhou Bay Sag and mature to highly mature Mesozoic coals from structure CFD23F were selected as humic source materials (Table 1). To further characterize gases generated by different oils, representative crude oils and extracts were subjected to closed-system gold-tube pyrolysis. These included light crude oil from the Mesozoic buried hill of structure BZ8CS, extra-heavy oil from the LD21B Oilfield, an oil-sand extract from the Kongdian Formation of structure BZ25AE whose chloroform bitumen “A” has a whole-oil $\delta^{13}\text{C}$ value of -23.3‰ , and an extract from a mature Ed₃ source rock in the Bozhong Sag representing in-source retained oil. Basic information on all oils and extracts used in the experiments is provided in Table 2.

Closed-system gold-tube pyrolysis was used to simulate thermogenic gas generation under elevated temperature and pressure. The method provides precise temperature control and effective containment of gaseous products. Coupling the apparatus with online product analysis enables accurate determination of gas composition, $\delta^{13}\text{C}$ values, and component yields¹⁷. The experimental procedure was as follows:

1. Solid source-rock or crude-oil samples were loaded into gold tubes, which were hermetically welded under argon to exclude oxygen.
2. The sealed tubes were placed in a heating furnace under a confining pressure of 50 MPa, heated from room temperature to the target temperature at 2°C h^{-1} , and then cooled and depressurized before recovery.
3. Each gold tube was punctured under vacuum to release the generated gas. Hydrocarbon-gas composition and carbon isotopic composition were measured online using an Agilent 8890 gas chromatograph coupled to an Elementar isoprime visION isotope-ratio mass spectrometer, after which gas yields were calculated.

Lacustrine oil-prone source rocks follow an “oil first, gas later” generation sequence during progressive thermal maturation¹⁸. They generate mainly oil at low maturity and progressively shift toward gas generation as maturity increases. The principal gas-generation interval begins at EasyRo $> 0.8\%$. The Bozhong Sag, the largest hydrocarbon-rich sag in the Bohai Sea region, contains source rocks buried to depths greater than 6000 m and spanning Ro values of approximately 0.5%–2.5%, thereby covering the principal gas-generation interval of Paleogene source rocks. To compare thermogenic gases derived from different source materials, experiments were conducted at EasyRo values of 1.5%, 2.0%, and 2.5%, corresponding to temperatures of 420, 450, and 480°C, respectively, at a constant heating rate of 2°C h^{-1} .

Table 1

Samples and Geochemical Characteristic Parameters of Source Rocks for Gas Generation Simulation Experiments

Sample Type	Sample ID	Structure	Stratigraphic unit	Depth (m)	Ro (%)	T _{max} (°C)	TOC (%)	S ₁ + S ₂ (mg g ⁻¹)	HI (mg HC g ⁻¹ TOC)	δ ¹³ C _{kerogen} (‰, VPDB)
Paleogene lacustrine mudstone	A	CFD18C	Dongying Fm., 3rd Mb.(E ₃ d ³)	3460–3470	0.47	441	3.01	18.37	564	-27.91
(low-mature)	B	PL25F	Shahejie Fm., 1st Mb.(E ₂ s ¹)	1595–1608	0.29	430	3.45	26.52	711	-27.50
	C	PL19C	Shahejie Fm., 3rd Mb.(E ₂ s ³)	1550–1565	0.40	439	2.81	13.82	472	-26.81
Paleogene coal (low-mature)	D	KL10F	Shahejie Fm(E ₂ s)	1670–1680	0.35	403	50	91.6	177	-23.22
Mesozoic coal (mature)	E	CFD23F	Mesozoic(Mz)	4160–4165	0.88	456	59.9	151.99	234	-22.68
	F	CFD23F		4170–4175	0.87 / 1.41	458	58.2	131.84	206	-22.16
	G	CFD23F		4200–4210	0.92 / 1.65	453	30.3	59.18	183	-22.57
Paleogene Lacustrine mudstone	H	BZ19F	Dongying Fm., 3rd Mb.(E ₃ d ³)	4420–4430	0.91	443	2.2	3.08	128	-28.86
(Mature)	I	BZ8C		4860–4870	1.11	449	1.8	1.87	102	-27.77

Table 2

Summary of Crude Oil Sample Information and Whole-Oil δ¹³C Values for Gas Generation Simulation Experiments

Sample Type	Sample ID	Structure	Stratigraphic unit	Depth (m)	δ ¹³ C (‰, VPDB)
Extractable bitumen	J	BZ19F	Paleogene	4420–4430	-29.72
	K	BZ8C	Dongying Fm., 3rd Mb. (E ₃ d ³)	4860–4870	-28.29
Light crude oil	L	BZ8C	Mesozoic(Mz)	4759–5182	-27.17
Heavy crude oil	M	LD21B	/	/	-28.50
Extractable bitumen	N	BZ25AE	Paleogene	3786	-23.27
Saturated hydrocarbon fraction	O		Kongdian Fm.		-25.46
Aromatic hydrocarbon fraction	P		(E ₁ k)		-22.26
NSO fraction	Q				-21.39
Asphaltene fraction	R				-20.92

2. Analysis of Gas Generation Experiment Results

2.1 Gas Generation by Cracking of Sapropelic Source-Rock Kerogen

Closed-system gold-tube pyrolysis experiments were performed on three low-maturity lacustrine source rocks (samples A–C) from the Bohai Sea region (Table 1) at a heating rate of 2°C h^{-1} . Nineteen temperature points were used, covering EasyRo values of 0.55%–2.52%. The hydrocarbon-yield curves (Fig. 1) show that the three sapropelic source rocks reached their oil-generation peaks at EasyRo values of 1.15%, 0.80%, and 0.94%, respectively. All three samples began effective gas generation in the mature stage at EasyRo > 0.8%.

Residual source rocks were recovered from the gold tubes after primary pyrolysis to EasyRo values of 0.80%–1.38%. Soluble organic matter was removed by repeated dichloromethane extraction and filtration. After drying, the residues were resealed in gold tubes and subjected to secondary pyrolysis to EasyRo values of 1.5% and 2.0%. Gas compositions from the two-stage experiments are listed in Table 3. Gas generated during primary pyrolysis of the low-maturity lacustrine source rocks generally has lighter $\delta^{13}\text{C}\text{-C}_2\text{H}_6$ values, higher proportions of $\text{C}_2\text{--C}_5$ hydrocarbons, and dryness coefficients below 60%. Under comparable maturity conditions, gas generated during secondary pyrolysis has heavier $\delta^{13}\text{C}\text{-C}_2\text{H}_6$ values and higher dryness coefficients. At EasyRo = 1.5%, for example, $\delta^{13}\text{C}\text{-C}_2\text{H}_6$ values of gases generated from the residual source rocks are more than 3‰ heavier than those generated during primary pyrolysis. Zhao et al.¹⁹ reported that, in closed-system experiments, gas generated from Type II₁ organic matter is derived mainly from high-temperature secondary cracking of previously generated liquid hydrocarbons and that its yield is four times that of kerogen pyrolysis gas under open-system conditions. Accordingly, gas from the primary experiments is more analogous to gas generated by cracking of source-derived oil, whereas gas from the secondary experiments represents kerogen-cracking gas. The latter is isotopically heavier and substantially drier.

Table 3

Carbon isotopic compositions and dryness coefficients of gases from the closed gold-tube pyrolysis experiments

Experiment group	Sample ID	Initial Ro/EasyRo (%)	Post-pyrolysis EasyRo (%)	$\delta^{13}\text{C}-\text{CH}_4$ (‰, VPDB)	$\delta^{13}\text{C}-\text{C}_2\text{H}_6$ (‰, VPDB)	$\delta^{13}\text{C}-\text{C}_3\text{H}_8$ (‰, VPDB)	Dryness coefficient (%)	$\Delta^{13}\text{C}-\text{C}_2\text{H}_6^*$ (‰, VPDB)
Primary pyrolysis of raw source rock	A	0.47	1.15	-40.51	-29.47	-27.37	48.58	/
	C	0.40	0.94	-38.88	-28.72	-28.33	48.77	
	B	0.29	0.80	-39.47	-34.84	-31.51	31.46	
	A	0.47	1.38	-37.85	-30.05	-29.46	50.03	
	C	0.40	1.26	-37.80	-28.35	-27.79	50.48	
	B	0.29	1.26	-40.04	-32.62	-30.63	41.84	
	A	0.47	1.52	-32.98	-29.71	-27.31	48.38	
	C	0.40	1.52	-35.99	-27.88	-27.29	49.98	
	B	0.29	1.52	-38.34	-31.82	-30.07	43.52	
	A	0.47	1.98	-39.18	-27.51	-25.14	53.74	
	C	0.40	1.98	-34.13	-26.86	-22.69	59.28	
	B	0.29	1.98	-35.95	-29.90	-25.94	52.68	
Secondary pyrolysis of residual source rock	A	1.15	1.52	-30.92	-26.59	-24.79	81.37	3.12
	C	0.94	1.52	-30.03	-24.49	-24.48	75.25	3.39
	B	0.80	1.52	-34.45	-28.52	-27.72	57.27	3.30
	A	1.38	1.98	-26.57	-21.30	/	93.03	6.21
	C	1.26	1.98	-24.50	-18.50	-17.32	91.76	8.36

* $\Delta^{13}\text{C}-\text{C}_2\text{H}_6$ denotes the difference in ethane carbon isotopic composition between the two pyrolysis experiments.

2.2 Gas Generation by Cracking of Crude Oil and Retained Oil

To characterize oil-cracking gas, the oil and extract samples listed in Table 2 were individually sealed in gold tubes and heated at 2°C h^{-1} to 420, 450, and 480°C , corresponding to EasyRo values of 1.5%, 2.0%, and 2.5%, respectively. The gaseous products were collected for compositional and carbon isotopic analyses. Coal samples (D–G) and lacustrine source rocks (H and I) from the Bohai Sea region (Table 1) were pyrolyzed under identical conditions for comparison, allowing the characteristics of coal-type and sapropelic kerogen-cracking gases to be evaluated.

Dryness coefficients of the simulated gases (Fig. 2a) show that sapropelic kerogen-cracking and coal-type gases are consistently drier than oil-cracking gas at all three temperatures. The dryness coefficients of all three gas types increase with thermal maturity. At 480°C (EasyRo = 2.5%), sapropelic kerogen-cracking and coal-type gases have dryness coefficients of 92.6% and 89.8%, respectively, compared with 40.7%–64.6% for oil-cracking gas. Figure 2b shows the dryness coefficients of gases generated from extractable bitumen sample N and its fractions (O–R) at 450°C (EasyRo = 2.0%). The order is asphaltenes > resins > aromatic hydrocarbons > chloroform bitumen “A” > saturated hydrocarbons. Thus, gases generated from heavy fractions are methane-rich, whereas those from light fractions contain larger proportions of C_2+ hydrocarbons. This pattern is also evident in Fig. 2a, where gas generated from extra-heavy oil (sample M) is distinctly drier than that generated from light oil (sample L).

The $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-C}_2\text{H}_6$ values of gases generated in the experiments are shown in Fig. 3. Both values are substantially lighter for oil-cracking gas than for kerogen-cracking gas. The initial carbon isotopic compositions of the samples (Tables 1 and 2) follow the order coal > lacustrine mudstone > crude oil, and the generated alkane gases show the corresponding order coal-type gas > kerogen-cracking gas > oil-cracking gas. The $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-C}_2\text{H}_6$ values of oil-cracking gases are closely related to the isotopic compositions of their precursor oils. For conventional oils with whole-oil $\delta^{13}\text{C}$ values of -30‰ to -27‰ , the $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-C}_2\text{H}_6$ values of gases generated at 450°C (EasyRo = 2.0%) are no heavier than -40‰ and -30‰ , respectively. Under the same conditions (Fig. 4), an isotopically heavy oil with a whole-oil $\delta^{13}\text{C}$ value of -23.3‰ generates gas with $\delta^{13}\text{C-CH}_4 = -37.7\text{‰}$ and $\delta^{13}\text{C-C}_2\text{H}_6 = -26.8\text{‰}$. These results demonstrate that the carbon isotopic compositions of cracked alkane gases are strongly controlled by those of their precursors. Thermal maturity also affects isotopic fractionation. As temperature increases from 420 to 480°C , kerogen-cracking gas becomes progressively enriched in ^{13}C in both methane and ethane. For oil-cracking gas, $\delta^{13}\text{C-C}_2\text{H}_6$ increases markedly, whereas $\delta^{13}\text{C-CH}_4$ changes only slightly.

2.3 Gas Yields and Principal Gas-Generation Stages

Determining the generation windows of kerogen-cracking and oil-cracking gases is a central objective of this study. Gas yields measured during closed-system gold-tube pyrolysis (Fig. 1) are dominated by products of oil cracking and therefore do not directly represent gas generated from kerogen. To isolate the kerogen contribution, source-rock aliquots were recovered after each experiment, extracted with dichloromethane to remove chloroform bitumen “A,” and then subjected to Rock-Eval pyrolysis. The relationship between residual hydrocarbon-generating potential (S_2) and thermal maturity (EasyRo) was subsequently established (Fig. 5). The residual hydrocarbon-generation curves decline rapidly between EasyRo = 0.8% and 1.5%, identifying this interval as the principal stage of kerogen-derived gas generation.

Yields of oil-cracking gas are shown in Fig. 6a. In-source retained oil (sample J) generated 142, 390, and 412 mg g^{-1} of gas at EasyRo values of 1.5%, 2.0%, and 2.5%, respectively. Under the same conditions, extra-heavy oil (sample M) generated 155, 286, and 314 mg g^{-1} . Thus, retained oil and extra-heavy oil generate most of their gas between EasyRo = 1.5% and 2.0%, with only a minor yield increase from 2.0% to 2.5%. By contrast, light oil (sample L) generated 117, 379, and 744 mg g^{-1} at the same maturity levels, indicating a higher cracking threshold and a principal gas-generation interval of EasyRo = 1.5%–2.5%. Light oil therefore retains substantial gas-generating potential at EasyRo = 2.0%–2.5%.

At EasyRo = 2.5%, the oil-cracking gas yield of light oil (sample L) reaches 744 mg g^{-1} , considerably higher than the 314 mg g^{-1} obtained from extra-heavy oil (sample M; Fig. 6a). At 450°C (EasyRo = 2.0%), gas yields from the oil and its fractions decrease in the order saturated hydrocarbons (533 mg g^{-1}) > chloroform bitumen “A” (366 mg g^{-1}) > aromatic hydrocarbons (317 mg g^{-1}) > resins (261 mg g^{-1}) > asphaltenes (255 mg g^{-1}) (Fig. 6b). At EasyRo = 1.5%, saturated hydrocarbons and asphaltenes generate similar amounts of gas, whereas at EasyRo = 2.0%, the yield from saturated hydrocarbons is substantially higher (Fig. 6c). These results indicate that light oil fractions have higher cracking thresholds but greater maximum gas yields than heavy fractions. Low-maturity oils and heavy fractions contain abundant heteroatomic structures and oxygen-bearing functional groups with relatively weak C–C bonds and therefore crack at lower maturity²⁹. In contrast, light oils and fractions are dominated by alkyl structures and consequently have greater potential to generate low-molecular-weight alkanes at higher maturity.

2.4 Genetic Interpretation Using Geochemical Diagrams

The $\delta^{13}\text{C-CH}_4$ versus $\text{C}_1/(\text{C}_2+\text{C}_3)$ cross-plot is widely used to distinguish genetic types of natural gas¹². Wang et al.⁶ used this diagram to compare natural gas from the Bozhong area with coalbed methane from the Wenliu area of the Dongpu Sag and found that the latter has substantially heavier $\delta^{13}\text{C-CH}_4$ values. The simulated gases analyzed here are plotted in Fig. 7a. Coal-type gas has $\text{C}_1/(\text{C}_2+\text{C}_3)$ ratios similar to those of kerogen-cracking gas generated from lacustrine sapropelic source rocks but is characterized by heavier $\delta^{13}\text{C-CH}_4$ values. Oil-cracking gas has distinctly lower $\text{C}_1/(\text{C}_2+\text{C}_3)$ ratios than kerogen-cracking gas, coal-type gas, and natural gas from the Bozhong area. As EasyRo increases from 1.5% to 2.5%, $\delta^{13}\text{C-CH}_4$

becomes progressively heavier and $C_1/(C_2+C_3)$ increases, reflecting the coupled effects of thermal maturation on methane isotopic composition and gas dryness.

The $\ln(C_1/C_2)$ versus $\ln(C_2/C_3)$ cross-plot was first proposed by Bernard et al.²¹. Kerogen-cracking gas shows only minor variation in $\ln(C_2/C_3)$ despite large changes in $\ln(C_1/C_2)$, whereas oil-cracking gas exhibits pronounced variation in $\ln(C_2/C_3)$ but comparatively small changes in $\ln(C_1/C_2)$. These contrasting trends provide a basis for differentiating the two gas types. Huang¹⁵ showed that both oil and kerogen cracking increase C_2/C_3 and C_1/C_2 ; C_2/C_3 is controlled primarily by maturity, whereas C_1/C_2 is more closely related to gas genesis. At comparable C_2/C_3 ratios, oil-cracking gas has a lower C_1/C_2 ratio and dryness coefficient than kerogen-cracking gas. Xie²² found that both $\ln(C_1/C_2)$ and $\ln(C_2/C_3)$ increase with maturity during the evolution of sapropelic organic matter and that $\ln(C_2/C_3)$ in oil-cracking gas stabilizes only at the overmature stage. In Fig. 7b, data for lacustrine kerogen-cracking gas at EasyRo = 1.5%–2.5% overlap those for coal-type gas. Both $\ln(C_1/C_2)$ and $\ln(C_2/C_3)$ are higher for kerogen-cracking gas than for oil-cracking gas, and the kerogen-cracking gas data are consistent with those of natural gas from the Bozhong area. Both ratios increase progressively with thermal maturity for the oil- and kerogen-cracking gases.

Overall, at EasyRo = 1.5%–2.5%, oil-cracking gas differs markedly from natural gas in the Bozhong area because it contains a much larger proportion of C_2+ hydrocarbons. In contrast, kerogen-cracking gas generated from lacustrine source rocks closely resembles the discovered natural gas. The three simulated gas types also differ in $\delta^{13}C\text{-CH}_4$: coal-type gas is isotopically heaviest, followed by sapropelic kerogen-cracking gas, whereas natural gas from the Bozhong area is lightest. The relatively light methane in the discovered gas may reflect migration-related fractionation and mixing with biogenic gas.

3. Discussion

3.1 Gas-Generation Mechanisms and Geochemical Characteristics

Closed-system pyrolysis reveals systematic differences between kerogen-cracking and oil-cracking gases at EasyRo = 1.5%–2.5%. First, under comparable thermal conditions, kerogen-cracking gas has substantially heavier $\delta^{13}C_1$ and $\delta^{13}C_2$ values. Second, kerogen-cracking gas has a higher dryness coefficient at the same maturity. Third, gas from lacustrine sapropelic kerogen is generated mainly at moderate to high maturity (EasyRo < 1.5%), whereas retained hydrocarbons and reservoir oils undergo extensive cracking at high to overmaturity (EasyRo > 1.5%), indicating a higher maturity threshold for oil-cracking gas. Fourth, coal-type gas is compositionally similar to kerogen-cracking gas derived from highly to overmature lacustrine sapropelic source rocks, although coal-type gas has heavier methane carbon isotopic compositions at equivalent maturity.

Gas-generation kinetic experiments have shown that solid and soluble organic matter generate gas at different stages. Zhao et al.²³ proposed that Type I and Type II kerogens generate gas mainly during the mature stage at Ro < 1.6%, whereas cracking of crude oil and retained oil is affected by mineral assemblages and formation pressure and occurs primarily at Ro > 1.3%. Mature to highly mature lacustrine source rocks are widespread from the margins to the center of the Bozhong Sag. Seismic data indicate burial depths of 4–8 km and Ro values of 0.6%–3.0% across the secondary sags²⁴. On the basis of these constraints, the geochemical characteristics and approximate burial-depth ranges of the principal thermogenic gas types in the Bozhong area are summarized in Table 4.

Table 4

Comparison of geochemical characteristics between primary and secondary gas generation of lacustrine source rocks

Gas type	Parent material type	Dryness coefficient	$\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-C}_2\text{H}_6$ characteristics	Gas generation window
Kerogen-derived	Lacustrine source rock (Type II-I)	> 70%; wet gas dominant	Generally heavy in isotopic composition, yet lighter than coal-type gas at equivalent maturity. High-mature or carbon-rich lacustrine source rocks exhibit isotopic characteristics similar to coal-type gas.	Ro: 0.8–1.5%; Burial depth threshold: 3500–5000 m
	Coal measures (Type III)	> 90%; predominantly dry gas	Generally heavy in isotopic composition, with a distinct difference from oil-type gas at mature stages.	Ro: >0.8%; Burial depth threshold: >3500 m
Oil-derived	In-situ retained oil	< 70%; wet gas dominant	Generally light in isotopic composition; may become heavier during cracking of oils with high $\delta^{13}\text{C}$ values.	Ro: >1.3%; Burial depth threshold: >4500 m
	Reservoir oil	< 70%; wet gas dominant	$\delta^{13}\text{C-C}_2\text{H}_6$ becomes significantly heavier with increasing cracking degree, while $\delta^{13}\text{C-CH}_4$ shows little change.	Ro: >1.3%; Burial depth threshold: >4500 m

Natural-gas generation is governed by organic molecular structure and thermal maturity^{25–27}. Immature lacustrine sapropelic kerogen is dominated by long aliphatic chains, contains few branched moieties, and has a low degree of aromatic substitution. Within the oil window, nonpolar alkyl moieties are extensively degraded, aromatic structures become concentrated, and abundant long-chain alkanes and low-molecular-weight hydrocarbons are released²⁸. With further maturation, aliphatic structures are progressively depleted. At high temperatures, cleavage and hydrogen-transfer reactions involving short alkyl substituents, mainly methyl groups attached to aromatic structures, directly generate methane, ethane, and other low-molecular-weight alkanes, producing gas with a high dryness coefficient^{29–30}. Oil-cracking gas forms through stepwise secondary cracking of long-chain alkanes, cycloalkanes, and aromatic hydrocarbons into lighter components. Closed-system pyrolysis indicates that predominantly dry gas is generated only above EasyRo $\approx$ 2.2%; below this threshold, oil cracking produces appreciable C_2+ hydrocarbons and gas with a low dryness coefficient¹⁸.

The carbon isotopic composition of a hydrocarbon product inherits, in part, that of its precursor organic matter. Accordingly, gas generated from an isotopically heavy oil has relatively heavy methane and ethane $\delta^{13}\text{C}$ values (Fig. 3). In the Bohai Sea region, coal-measure kerogen has $\delta^{13}\text{C}$ values of -24‰ to -22‰ , substantially heavier than those of lacustrine kerogen at comparable maturity (-29‰ to -26‰). Coal-type gas therefore generally has heavier $\delta^{13}\text{C-CH}_4$ values and can be distinguished in the $\delta^{13}\text{C}_1$ versus $\text{C}_1/(\text{C}_2+\text{C}_3)$ cross-plot (Fig. 7a). At EasyRo = 1.5%–2.5%, methane and ethane generated by oil cracking are isotopically lighter than those generated by kerogen cracking. This difference reflects kinetic isotope fractionation: bonds containing ^{13}C have slightly higher bond energies than those containing ^{12}C , so $^{12}\text{C}-^{12}\text{C}$ bonds preferentially break during thermal decomposition. Generated hydrocarbons are therefore depleted in ^{13}C , whereas the residual material becomes progressively enriched. The $\delta^{13}\text{C}$ values of soluble bitumen generated in the gold-tube experiments increase during the oil-generation stage, consistent with kinetic fractionation, but decrease after the system enters the gas-generation stage. This reversal reflects disproportionation during secondary oil cracking: newly generated short-chain soluble hydrocarbons are depleted in ^{13}C , whereas carbon-rich pyrobitumen is enriched in ^{13}C . Meanwhile, residual kerogen becomes progressively heavier with maturity (Fig. 8b), and methane and ethane generated from its short alkyl chains also become enriched in ^{13}C . For a single source rock, the isotopic sequence is therefore mature-stage oil <

mature kerogen < highly mature kerogen. Under comparable maturity conditions, oil-cracking gas remains isotopically lighter than kerogen-cracking gas.

The compositions of gases generated from lacustrine sapropelic kerogen and coal are broadly similar (Fig. 7b). Coal contains predominantly Type II₂–III organic matter, which is hydrogen-poor, carbon-rich, and dominated by aromatic structures with limited aliphatic moieties, making it intrinsically gas-prone³¹. In Type I–II₁ kerogen, extensive cleavage of long aliphatic chains during oil generation and concurrent condensation reactions rapidly increase aromaticity²⁹. By the gas-generation stage, sapropelic kerogen is likewise hydrogen-poor and carbon-rich, and gas is generated mainly by cracking of short alkyl substituents attached to aromatic structures. This mechanism resembles gas generation from Type II₂–III organic matter and explains the similar geochemical characteristics of the resulting gases.

3.2 Genesis of Natural Gas in the Bozhong Area and Remaining Uncertainties

Natural gas discovered in the Bozhong area is methane-dominated, with dryness coefficients of 0.73–0.94 and generally normal carbon-isotope ordering, consistent with a thermogenic origin⁶. At the maturity levels prevailing locally, oil-cracking gas is expected to contain abundant C₂+ hydrocarbons and to have a dryness coefficient below 0.70. This compositional discrepancy indicates that reservoir-oil cracking is not the dominant source of natural gas in the Bozhong area. Since the Neogene, rapid subsidence has driven source rocks through rapid oil generation and into late gas generation. Secondary cracking of reservoir oil requires higher temperatures. Burial-history modeling for pseudo-wells in the central Bozhong Sag²⁴ places the onset and peak thresholds of oil cracking at approximately 4500 m (160°C) and 6000 m (210°C), respectively—conditions rarely attained by oil-bearing traps. The principal source rocks in the southwestern and southern Bozhong Sag currently have Ro values of 0.8%–2.0%, spanning the main generation interval of kerogen-cracking gas and part of the interval for retained-oil cracking. Retained-oil cracking may therefore contribute materially to offshore gas resources. Previous studies suggested a kerogen-cracking-gas to liquid-hydrocarbon-cracking-gas contribution ratio of approximately 1:2 for highly to overmature Type I and II source rocks¹⁹. This estimate is not directly applicable to the Bozhong Sag, however, because most source rocks are mature to highly mature rather than overmature. Retained hydrocarbons of different compositions vary substantially in cracking threshold and gas-generating capacity, while their abundance and composition are controlled by expulsion efficiency and secondary cracking²³. Contributions from retained-oil cracking therefore vary among source rocks with different organic-matter types and maturities.

Natural gas in the Bozhong Sag has relatively heavy $\delta^{13}\text{C}\text{-C}_2\text{H}_6$ values ($> -28\text{‰}$) and may therefore be misclassified as humic-type gas on conventional genetic diagrams⁵. The present experiments demonstrate that gas generated by cracking of sapropelic kerogen can also have heavy $\delta^{13}\text{C}\text{-C}_2\text{H}_6$ values (Table 3). Both the initial isotopic composition and thermal maturity of kerogen strongly influence the ethane isotopic composition of kerogen-cracking gas and must be considered when inferring source-organic-matter type. At comparable maturity, coal-type gas generally has heavier $\delta^{13}\text{C}\text{-CH}_4$ values and higher dryness coefficients. The natural gases discovered in the Bozhong area instead closely resemble kerogen-cracking gas from lacustrine sapropelic source rocks. Coal-bearing strata in the Bohai Sea region are limited in distribution and thickness³², whereas the principal source rocks contain predominantly lacustrine sapropelic organic matter²⁴. The close association of oil and gas in deep reservoirs further accords with the hydrocarbon-generation characteristics of sapropelic organic matter³³.

Thermal maturity is commonly estimated from gas genesis and $\delta^{13}\text{C}\text{-CH}_4$ values^{34–35}, but existing empirical equations are not fully applicable to the Bohai Sea region. Gas accumulations in several structures contain a biogenic component, producing large isotopic differences between methane and ethane; mixing with biogenic gas substantially lowers $\delta^{13}\text{C}\text{-CH}_4$. Moreover, the three Paleogene lacustrine source-rock intervals differ markedly in kerogen carbon isotopic composition. High-quality source rocks in the third member of the Shahejie Formation have relatively heavy kerogen $\delta^{13}\text{C}$ values³⁶ and consequently generate gas with heavier $\delta^{13}\text{C}\text{-CH}_4$. Maturity estimates may therefore be biased unless the gas source is independently constrained.

4. Conclusions

1. Closed-system pyrolysis experiments at EasyRo = 1.5%–2.5% demonstrate that kerogen-cracking gas generated from lacustrine source rocks and coal-type gas generally have high dryness coefficients and relatively heavy alkane-gas $\delta^{13}\text{C}$ values. Under the same maturity conditions, oil-cracking and retained-oil-cracking gases have lower dryness coefficients and lighter alkane carbon isotopic compositions. Comparison with natural gas discovered in the Bozhong area shows that lacustrine kerogen-cracking gas provides the closest geochemical match. Coal-type gas has heavier $\delta^{13}\text{C}\text{-CH}_4$ values than sapropelic kerogen-cracking gas, allowing the two to be distinguished using a $\delta^{13}\text{C}\text{-CH}_4$ versus $\text{C}_1/(\text{C}_2+\text{C}_3)$ cross-plot. Oil-cracking and retained-oil-cracking gases also plot separately from the discovered gas in $\ln(\text{C}_1/\text{C}_2)$ – $\ln(\text{C}_2/\text{C}_3)$ space and have markedly lower dryness coefficients.
2. Kerogen-cracking gas from lacustrine sapropelic source rocks is generated mainly at moderate to high maturity (EasyRo < 1.5%). In contrast, in-source retained hydrocarbons and reservoir oils undergo extensive cracking and gas generation at high to overmaturity (EasyRo > 1.5%) and therefore have higher generation thresholds. Light oil fractions have higher cracking thresholds but greater maximum gas yields than heavy fractions. Because the abundance and composition of retained hydrocarbons are governed by expulsion efficiency and secondary cracking, the contribution of retained-oil-cracking gas varies with source-rock organic-matter type and thermal maturity.
3. Heavy $\delta^{13}\text{C}\text{-C}_2\text{H}_6$ values are not unique to humic gas; gas generated by cracking of sapropelic kerogen can display similar signatures. The dryness coefficient of thermogenic gas is controlled jointly by gas-generating process and thermal maturity, whereas alkane-gas carbon isotopic compositions reflect precursor $\delta^{13}\text{C}$ values, generation mechanisms, and maturity. A refined model of late-stage gas generation from lacustrine source rocks is therefore required to improve genetic interpretation and resource assessment in the offshore Bohai Sea region.

Declarations

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Author Contribution

Kuo Li: Conceptualization, Investigation, Formal analysis, Writing – original draft;Long Su: Conceptualization, Supervision, Writing – review & editing;Tao Ye: Resources, Data curation;Tongyao Zhang: Investigation;Peng Hao: Investigation;Ge Yan: Resources, Data curation;Haidong Wang: Visualization.All authors have read and approved the final manuscript.

Data Availability

The datasets generated and analysed during the current study are available from the corresponding author on reasonable request.

References

1. Xu, C. Progress, future direction, and challenges of natural gas exploration in the Bohai Bay Basin. *Nat. Gas Ind.* **44**, 72–85 (2024).
2. Dai, J. et al. Formation conditions and main controlling factors of large gas fields in China. *Nat. Gas Geosci.* **18**, 473–484 (2007).
3. Wen, Z. & Tang, Y. Composition and origin of natural gases in central Bohai Sea area, China. *Pet. Explor. Dev.* **32**, 111 (2005).

4. Zhao, C. et al. Genetic types and exploration potential of natural gas in Bohai Bay Basin. *Nat. Gas Geosci.* **30**, 783–789 (2019).
5. Hu, A., Wang, D., Yu, H., Jiang, T. & Sun, Z. Genesis of natural gas and genetic relationship between the gas and associated condensate in Bozhong 19 – 6 gas condensate field, Bohai Bay Basin. *Oil Gas Geol.* **41**, 903–912 (2020).
6. Wang, F., Tang, G., Zhao, Z., Chen, R. & Yan, G. Geochemistry and the genesis of natural gases in the deep reservoirs of the Bozhong Depression, Bohai Bay Basin, China. *Nat. Gas Ind. B.* **11**, 645–660 (2024).
7. Galimov, E. M. Isotope organic geochemistry. *Org. Geochem.* **37**, 1200–1262 (2006).
8. Furmann, A., Schimmelmann, A., Brassell, S. C., Mastalerz, M. & Picardal, F. Chemical compound classes supporting microbial methanogenesis in coal. *Chem. Geol.* **339**, 226–241 (2013).
9. Dai, J. Major developments of coal-formed gas exploration in the last 30 years in China. *Pet. Explor. Dev.* **36**, 264–279 (2009).
10. Dai, J. Significance of the study on carbon isotopes of alkane gases. *Nat Gas Ind* **31**, (2011).
11. Dai, J., Ni, Y., Gong, D., Liu, Q. & Hu, F. Characteristics of carbon isotopic composition of alkane gas in large gas fields in China. *Pet. Explor. Dev.* **51**, 251–261 (2024).
12. Dai, J. Identification of various genetic natural gases. *China Offshore Oil Gas (Geol).* **6**, 11–19 (1992).
13. Prinzhofer, A. A. & Huc, A. Y. Genetic and post-genetic molecular and isotopic fractionations in natural gases. *Chem. Geol.* **126**, 281–290 (1995).
14. Zhang, M. et al. Geochemical study on oil cracked gases and kerogen-cracked gases (Ⅷ): experimental simulation and products analysis. *Sci. China Ser. D.* **52**, 1–9 (2009).
15. Huang, G., Zhang, M., Hu, G. & Xiao, Z. Geochemical study on oil cracked gases and kerogen-cracked gases (Ⅷ): discrimination method between oil-cracked gas and kerogen-cracked gas. *Sci. China Ser. D.* **51**, 9–16 (2008).
16. Tian, H., Wu, Z., Gai, H. & Wang, X. Experimental study on late gas generation characteristics of the Middle Devonian sapropelic source rocks in Northwestern Sichuan Basin. *Oil Gas Geol.* **44**, 46–54 (2023).
17. Mi, J., Zhang, S. & Wang, X. Comparison of different hydrocarbon generation simulation approaches and key technique. *Exp. Pet. Geol.* **31**, 409–414 (2009).
18. Li, K. et al. Experiment on hydrocarbon generation characteristics of lacustrine mudstone in third member of Dongying Formation, Bohai Oilfield, Bohai Bay Basin. *Nat. Gas Geosci.* **34**, 2210–2221 (2023).
19. Zhao, W. et al. Proposal of organic matter relay gas generation model and its significance in exploration. *Pet. Explor. Dev.* **32**, 1–7 (2005).
20. Feng, X. et al. Molecular dynamics simulation of pyrolysis characteristics and microscopic mechanism of different types of kerogen. *J. Chengdu Univ. Technol. (Sci Technol).* **53**, 463–476 (2026).
21. Behar, F., Kressmann, S., Rudkiewicz, J. L. & Vandenbroucke, M. Experimental simulation in a confined system and kinetic modelling of kerogen and oil cracking. *Org. Geochem.* **19**, 173–189 (1992).
22. Xie, Z. et al. Experimental research on the potential of sapropelic kerogen degradation gas and discrimination of oil cracking gas. *J. Nat. Gas Geosci.* **27**, 471–479 (2016).
23. Zhao, W. et al. Further discussion on the connotation and significance of the natural gas relaying generation model from organic matter. *Pet. Explor. Dev.* **38**, 129–135 (2011).
24. Zhang, Y., Liu, Z., Chen, S., Jia, W. & Lei, H. Main controlling factors for formation and evolution of source rocks in Bozhong Sag, Bohai Bay Basin. *J. Chengdu Univ. Technol. (Sci Technol).* **51**, 953–965 (2024).
25. Miknis, F. P., Netzel, D. A., Smith, J. W., Mast, M. A. & Maciel, G. E. ^{13}C NMR measurements of the genetic potentials of oil shales. *Geochim. Cosmochim. Acta.* **46**, 977–984 (1982).
26. Qin, K., Chen, D. & Li, Z. A new method to estimate the oil and gas potentials of coals and kerogens by solid state ^{13}C NMR spectroscopy. *Org. Geochem.* **17**, 865–872 (1991).

27. Tong, J. et al. Evaluation of the macromolecular structure of Huadian oil shale kerogen using molecular modeling. *Fuel* **181**, 330–339 (2016).
28. Ma, G. et al. Molecular structure and hydrocarbon generation characteristics of kerogen in low-maturity shales: a case of the Paleocene Shahejie Formation in Shuguang area, Liaohe Depression, Bohai Bay Basin. *Oil Gas Geol.* **46**, 427–442 (2025).
29. Zhang, D. Thermal evolution of molecular structure of oil-generating precursors of lacustrine source rocks in Songliao Basin. Doctoral thesis, Lanzhou University (2023).
30. Cao, X. et al. Chemical structure changes in kerogen from bituminous coal in response to dike intrusions as investigated by advanced solid-state ^{13}C NMR spectroscopy. *Int. J. Coal Geol.* **108**, 53–64 (2013).
31. Guo, J. et al. Evolution characteristics of kerogen molecular structure in low-maturity stage: evidence from infrared spectroscopy analysis. *Geochimica* **43**, 529–537 (2014).
32. Zhang, G. et al. Genetic theory of coal-type oil and gas in China offshore areas. *Oil Gas Geol.* **43**, 553 (2022).
33. Xue, Y., Wang, D., Wang, F. & Tang, G. Formation conditions and exploration potential of condensate and light oil reservoirs in Bohai Sea waters. *Acta Pet. Sin.* **42**, 1581–1591 (2021).
34. Dai, J., Qi, H. & Song, Y. Preliminary discussion on several indicators for distinguishing coal-derived gas and oil-type gas. *Acta Pet. Sin.* **6**, 31–38 (1985).
35. Shen, P. et al. *Studies on geochemical characteristics of gas source rock and natural gas and mechanism of genesis of gas* (Gansu Science and Technology, 1991).
36. Wang, Q., Hao, F. & Zou, H. Y. Some considerations on the origins and exploration prospects of deep gas in oil-rich basins: a case study of the Bozhong area of Bohai Sea. *J. Yangtze Univ. (Nat Sci. Ed.)*. **20**, 47–54 (2023).

Figures

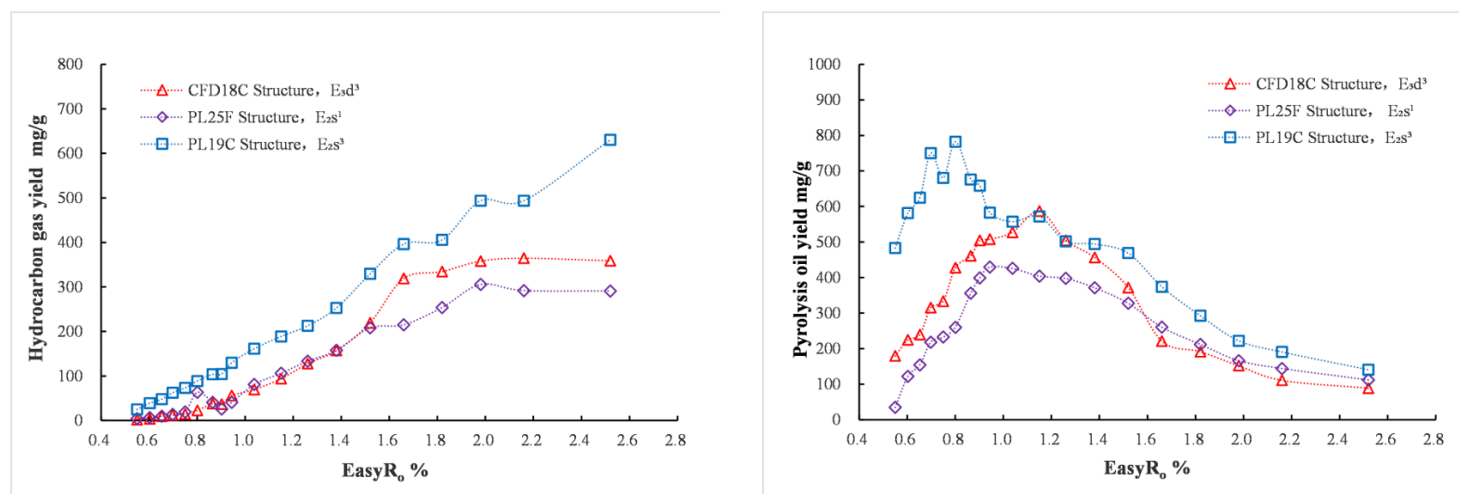


Figure 1

Oil and gas yield curves of lacustrine source rocks in the Bohai Sea from gold-tube pyrolysis experiments

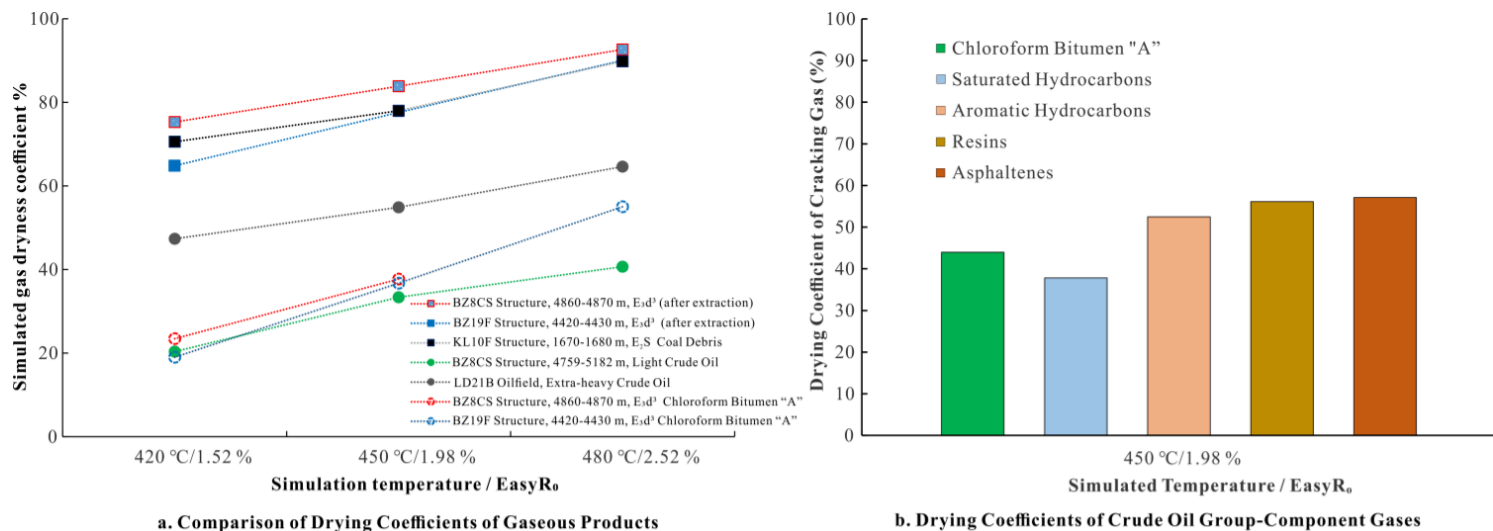


Figure 2

Dryness coefficients of gases derived from pyrolysis of different crude oils and their group components

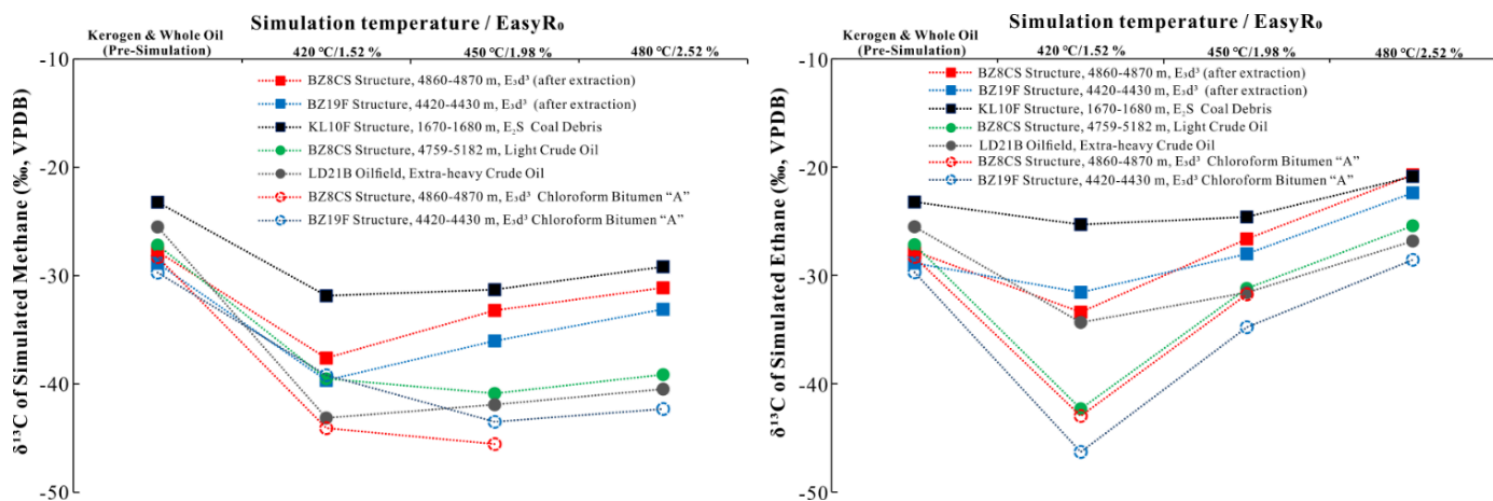


Figure 3

Comparative characteristics of $\delta^{13}\text{C}-\text{CH}_4$ and $\delta^{13}\text{C}-\text{C}_2\text{H}_6$ among different thermogenic simulated gases

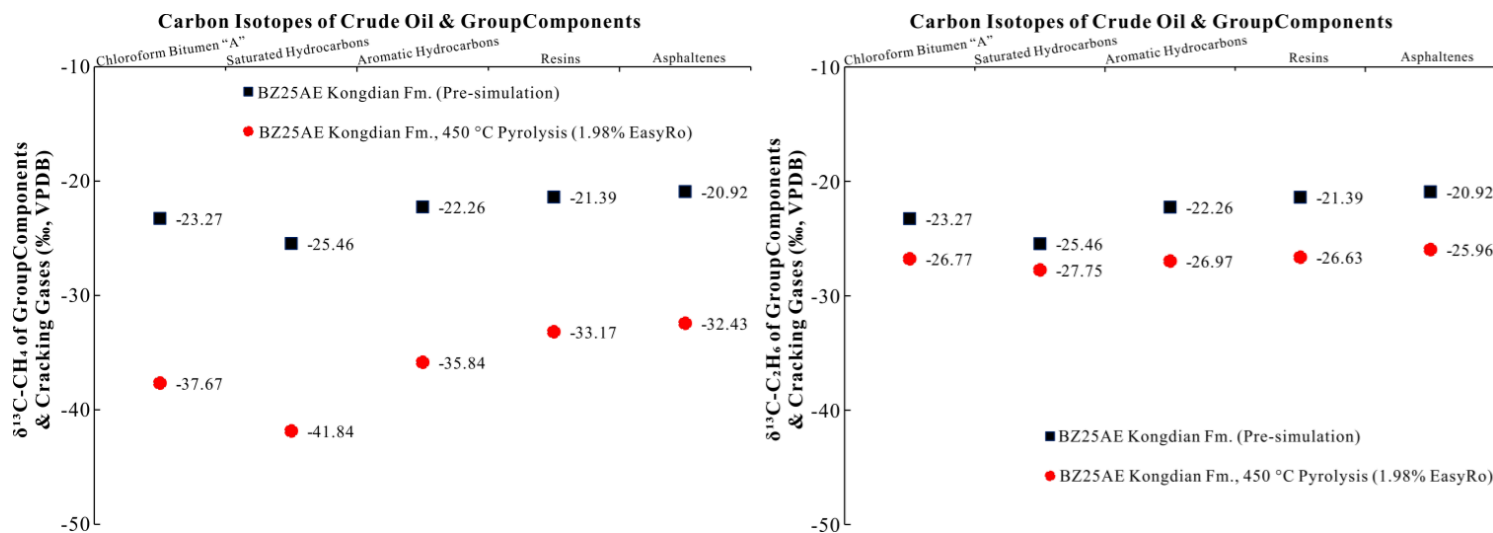


Figure 4

Correlation between carbon isotopes of oil group components and $\delta^{13}\text{C}$ signatures of oil-cracked gas

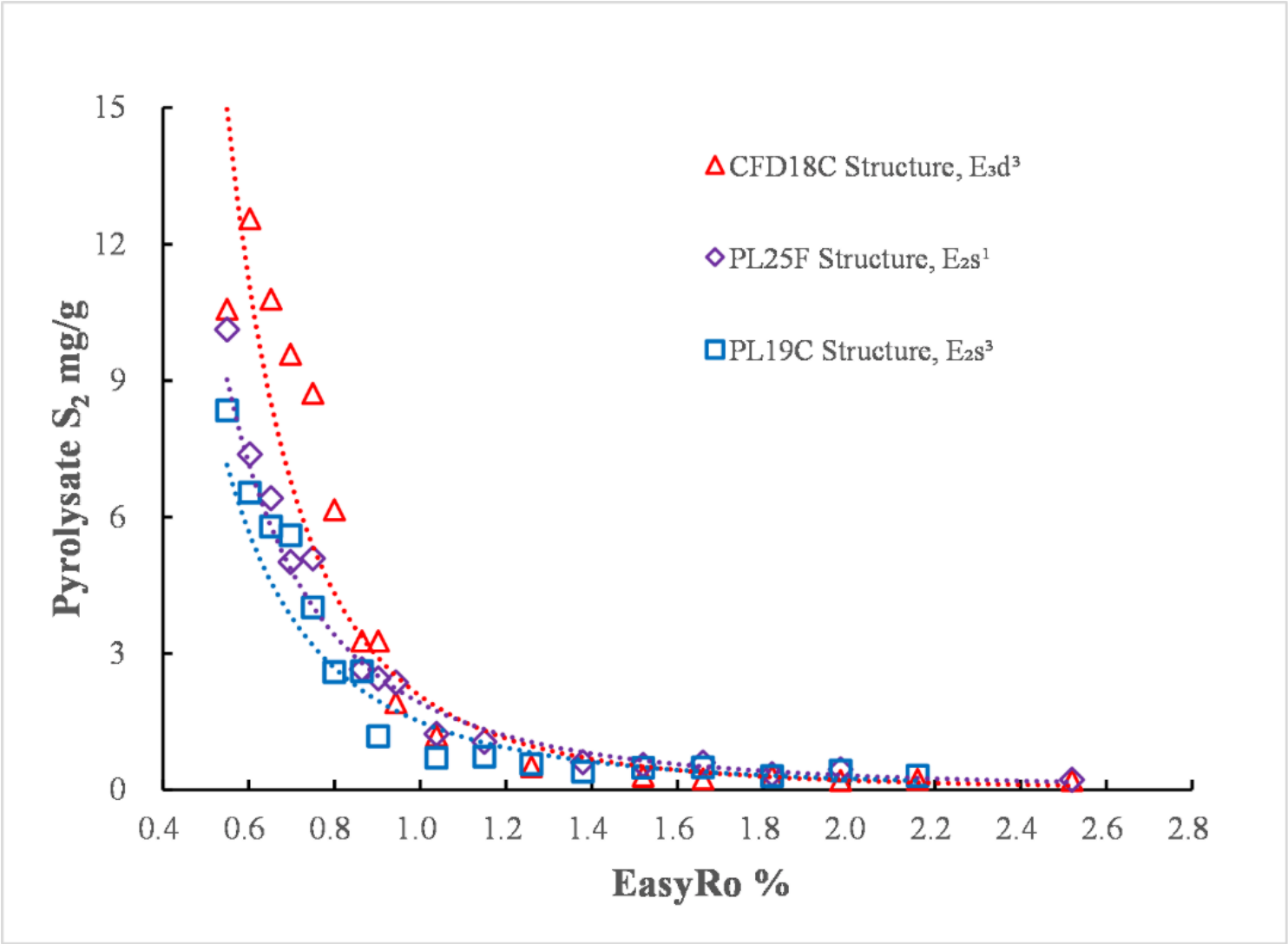


Figure 5

Residual hydrocarbon generation curves of source rocks with different maturities in gold-tube pyrolysis experiments

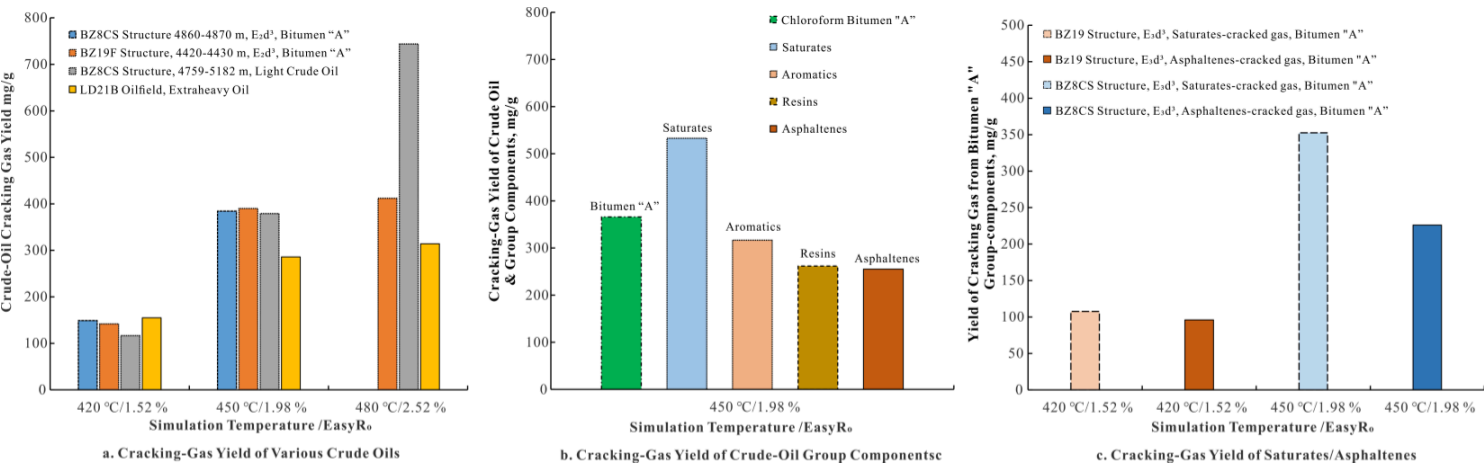


Figure 6

Comparison of oil-cracking gas yields for crude oil and group-type components generated in gold-tube pyrolysis experiments

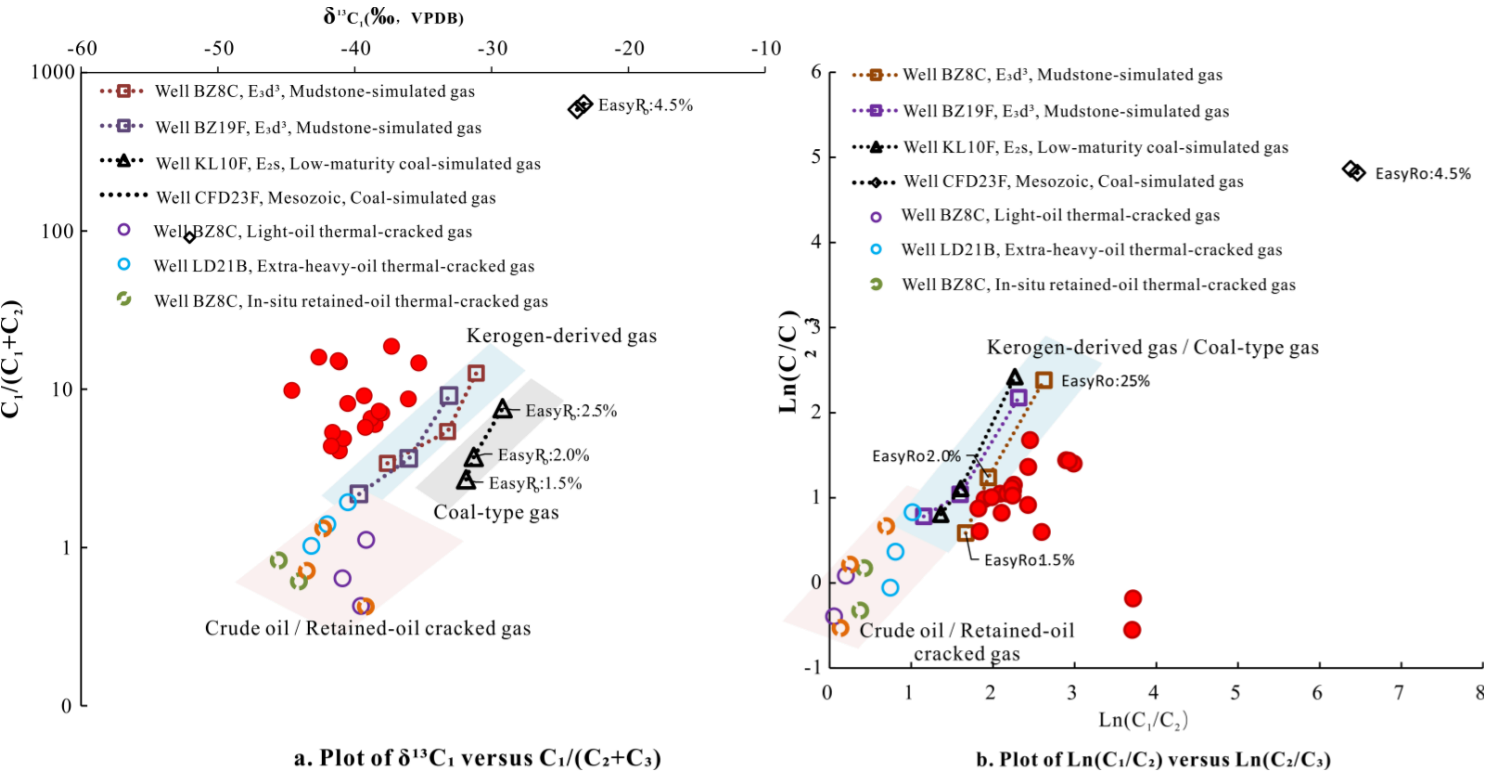


Figure 7

Differences in geochemical signatures between simulated gas generated in gold-tube pyrolysis experiments and indigenous natural gas in the Bozhong area

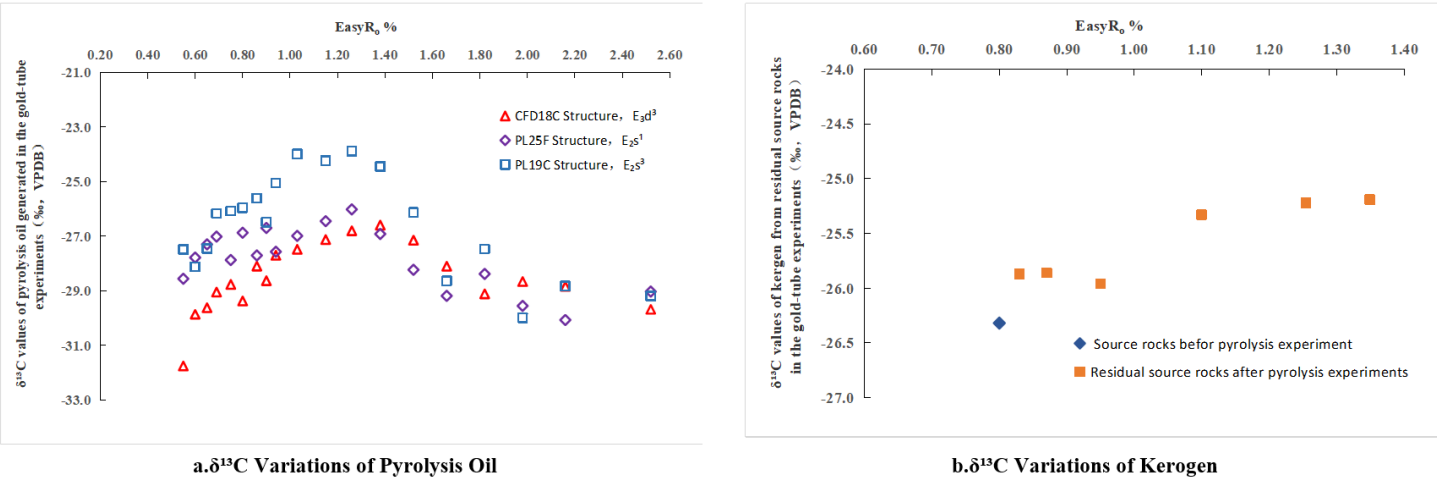


Figure 8

$\delta^{13}C$ Variations of Kerogen and Pyrolysis Oil with Increasing Thermal Maturity