

Geochemical Characteristics of Natural Gas in the Upper Permian Reservoir of the Eastern Sichuan Basin, China: Implication of Multiple Sources Mixing

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ABSTRACT: For an improved understanding of gas enrichment mechanism in the eastern Sichuan Basin, South China, twelve natural gas samples were obtained from carbonate reservoirs of the Upper Permian strata to analyze the hydrocarbon and non-hydrocarbon gas compositions, stable carbon and hydrogen isotopes ratios of hydrocarbons, and noble gas isotope ratios. The gas samples in the Upper Permian reservoirs principally consist of alkane gas with a dryness ratio ranging from 127.9 to 1 564.4. The carbon isotope ratio of methane ($\delta^{13}\text{C}_1$) was almost constant at -34.1 to -31.3‰, but the carbon isotope ratio of ethane ($\delta^{13}\text{C}_2$) varied from -36.6‰ to -25.8‰. The hydrogen isotope ratio of methane ($\delta^2\text{H}\text{C}_1$) also displayed a wide range from -137‰ to -127‰. The large variations in the dryness ratio, $\delta^{13}\text{C}_2$, and $\delta^2\text{H}\text{C}_1$ with almost constant $\delta^{13}\text{C}_1$ suggest the mixing of sapropelic and humic origins for hydrocarbon gases in these reservoirs. A high concentration of hydrogen sulfide (H_2S) originated from the thermochemical sulfate reduction (TSR), which was positively correlated with $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) in individual gas fields. TSR altered $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) and resulted in the abnormal character of isotopic reversal in the individual samples. The $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) in most gas samples, independent of H_2S concentration, further displayed reversed carbon isotopes because of the mixture of thermogenic gases with various thermal maturity levels. The measured argon isotope ratio ($^{40}\text{Ar}/^{36}\text{Ar}$) varied from 310 to 1 225, which suggests that the oldest 320 Ma source rock age corresponds to Permian shales. The analysis of the gas origin and the identification of primary source rock have made a significant contribution to further understanding the resource potential and distribution of natural gas in the Upper Permian, and have great implications for gas exploration in the eastern Sichuan Basin.

KEY WORDS: gas origin, stable isotopes, thermochemical sulfate reduction, source rocks, gas accumulation, geochemistry.

0 INTRODUCTION

As one of the major petroliferous basins in China (or even globally), the Sichuan Basin yielded natural gas as early as 53 BC to 18 AD (Li, 2011). The reserve assessment of 2019 concluded a recoverable hydrocarbon resource of $136\,969 \times 10^8 \text{ m}^3$, and the statistical data for 2020 suggested a cumulative hydrocarbon production of $7\,134 \times 10^8 \text{ m}^3$ (dominated by natural gas production of $7\,052.8 \times 10^8 \text{ m}^3$) (Dai et al., 2021). Previous research summarized the hydrocarbon enrichment mechanism of

the Sichuan Basin as that the organic-rich shale and high-quality reservoir were the basis of gas accumulation, and the good preservation condition was the key to high production (Wu et al., 2023; Li A et al., 2021). Particularly, the multi-layers and multi-types of source rocks, which consist of at least nine organic-rich shale layers from the Ediacaran, Cambrian, Silurian, Permian, Triassic, and Jurassic periods, contributed to the massive hydrocarbon generation (Qiu et al., 2024; Dai et al., 2021; Hao et al., 2008; Ma et al., 2007). Most of these source rocks were high- or over-matured and generated hydrocarbons dominated by relatively few hydrocarbon compounds, including methane, ethane, and propane. The complicated source systems and low geochemical diversity made it a great challenge to reveal the geochemical origins and physicochemical processes associated with the accumulation and preservation of hydrocarbons after

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multiple tectonic deformations. In particular, the eastern Sichuan Basin was intensively deformed during the Yanshanian and Himalayan orogeny, resulting in a fold-thrust belt (Li C X et al., 2021; Liu S G et al., 2021; Liu R et al., 2019; Li J H et al., 2018; Yan et al., 2003). Furthermore, the natural gas found in the eastern Sichuan Basin contains various contents of non-hydrocarbon gases, including hydrogen sulfide (H_2S) and carbon dioxide (CO_2), which complicates the inorganic-organic interactions during hydrocarbon generation (Hao et al., 2015; Liu et al., 2013; Cai et al., 2010).

For an improved understanding of the gas enrichment mechanism in the eastern Sichuan Basin of South China, a series of advanced gas samples were obtained from the Upper Permian carbonate reservoirs to analyze the hydrocarbon and non-hydrocarbon gas compositions, stable carbon and hydrocarbon isotopes of hydrocarbons, and noble gas isotopes. By integrating our recent data with previously published data, the geochemical origins and physicochemical processes of the Upper Permian natural gas in the eastern Sichuan Basin were resolved.

1 GEOLOGICAL BACKGROUNDS

The Sichuan Basin, with a rhombus outline, is tectonically enclosed by fold-thrust belts, comprising the eastern boundary of the Qiyueshan fault, the northern boundary of the Qingling-Dabie fault, and the western boundary of the Longmenshan fault (Figure 1) (Hao et al., 2008). Sediments in the Sichuan Basin are 12 km thick and contain marine strata of Sinian to Middle Triassic and terrestrial deposits of Late Triassic to Cenozoic (Figure 2). Organic-rich marine shales deposited during intense transgressions, e.g., Lower Cambrian, Lower Silurian, and Upper Permian, were suggested to be major source rocks of numerous gas fields targeted in the Upper Permian and Lower Triassic carbonate platforms (Yang et al., 2023). The north-south stretching of the Sichuan Basin during the Late Permian generated the Kaijing-Liangping Ocean Through and the Wushen-Shizhu Depression, which were both characterized by the striking of north-west-southeast (Figure 1a) and prompted the development of carbonate platform during the Changxing period (Figure 2) (Liu S G et al., 2021). Reefs and bioclastic beaches were widely deposited along the margins of the Kaijing-Liangping Ocean Through and the Wushen-Shizhu Depression and were suggested to be high-quality reservoirs even after the mechanical and chemical diagenesis (Chen et al., 2022). Regional anhydrite beds from the Lower to Middle Triassic are the regional cap rocks of marine reservoirs. Organic-rich terrestrial shales with partly distributed coal beds were also deposited during the Late Permian to Triassic conversion during marine to continental deposition (Cai et al., 2003). Collisions along the Qinling-Dabie and Longmenshan fault zones during the Triassic resulted in the exhumation of the southern and northeastern areas of the Sichuan Basin (Liu S G et al., 2021). A flexural loaded foredeep ap-

peared in front of the Longmenshan fault, which was filled with a wedge-shaped aggregation of terrestrial clastic rocks during the Late Triassic (Richardson et al., 2008; Meng et al., 2005). Subsequently, a stepwise north-west progression of deformation generated a well-developed Mesozoic thrust system in the eastern Sichuan Basin from the Middle Jurassic to Late Cretaceous Period (Liu et al., 2021a, 2019; He et al., 2018; Dong et al., 2015; Yan et al., 2003). Numerous gas fields have been detected in the anticline structures of the eastern Sichuan Basin.

2 SAMPLES AND METHODS

2.1 Sampling

Twelve gas samples produced from the marine carbonate reservoir of the Upper Permian age were collected from 12 wells of the eastern Sichuan Basin (Table 1). All gas samples were directly collected from the wellhead employing an intake manifold to decrease the wellhead gas pressure prior to flowing into stainless-steel cylinders at 1–3 bar. To avoid air contamination, the sample collection system was flushed for at least 8 to 10 min prior to shutting off the valve connecting the gas cylinder and the wellhead.

2.2 Gas Components

The major gas composition was analyzed utilizing the gas chromatograph (GC) of Agilent 7890A connected with the flame ionization and thermal conductivity detectors. Alkanes were separated using an HP/ALS column. The oven temperature was initially set at 40 °C for approximately 10 min, and was subsequently elevated to 180 °C under the heating rate of 4 °C/min. The carrier gas of the system was helium.

2.3 Carbon, Hydrogen, Helium, and Argon Isotopes

The stable carbon isotope ratios of the gas were examined utilizing a mass spectrometer (MS) of Thermo MAT 253 with an HP 5890II GC. The hydrocarbon gas components were initially segmented using the GC, and further burned into CO_2 before being pumped into the MS. Initially, the GC oven temperature was elevated from 40 to 80 °C under the heating rate of 8 °C/min, subsequently to 250 °C (at 5 °C/min), and finally maintained for approximately 10 min. The measurement precision was within $\pm 0.5\%$ relative to the Vienna pee dee belemnite (VPDB) standard.

The hydrogen isotopic values were analyzed utilizing the Thermo MAT 253-Plus MS connected with the TRACE GC Ultra fitted with an HP-PLOTQ chromatographic column. The gas samples were purified and segmented into CO_2 and hydrogen (H_2). Later, H_2 was injected into the MS employing helium as the carrier gas under the flow velocity of 1.5 mL/min. The oven temperature was initially set to 40 °C (for approximately 10 min), subsequently increased to 80 °C (at the heating rate of 5 °C/min), later to 140 °C (following the heating rate of 8 °C/min), and finally to 260 °C (under the heating rate of 10

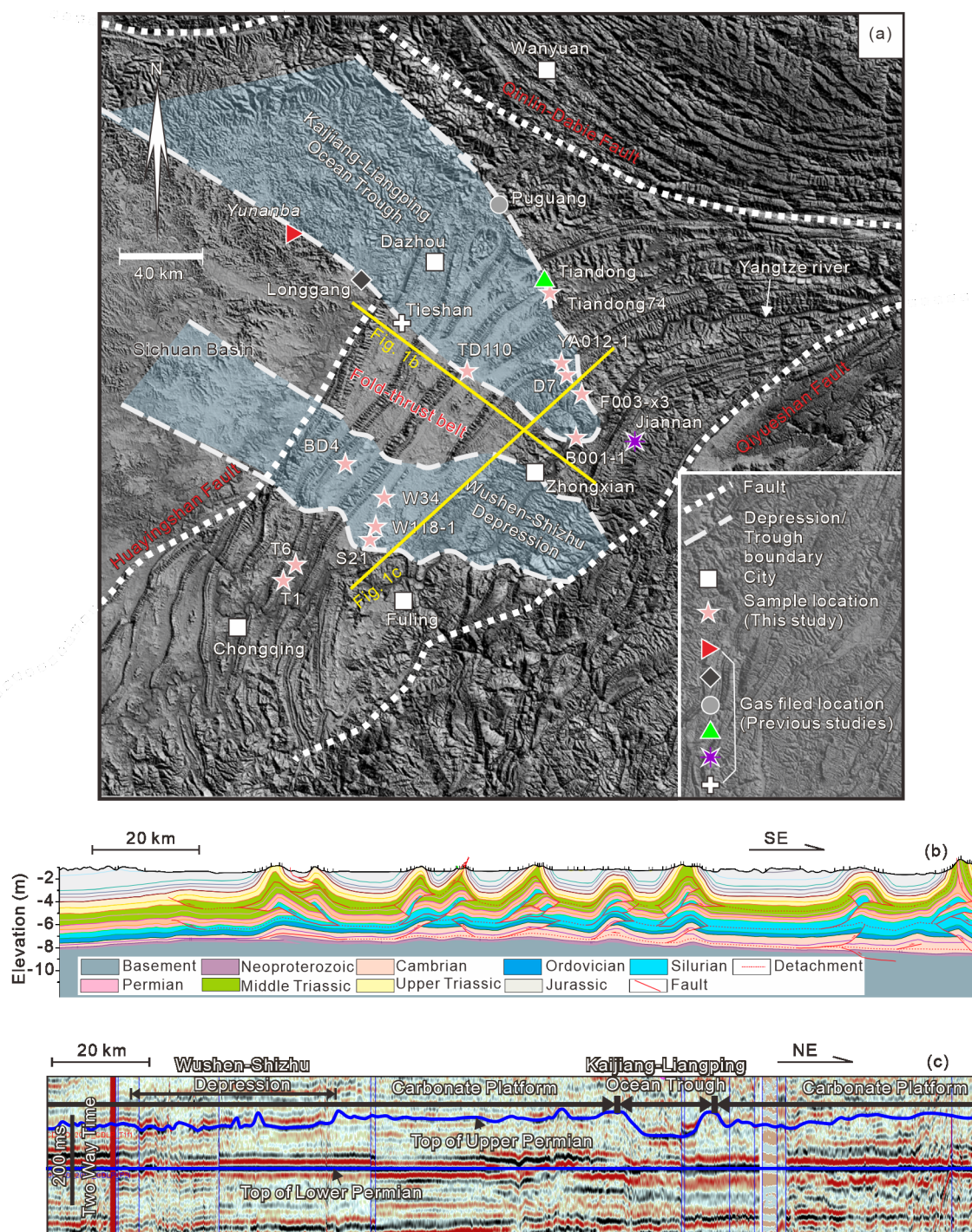


Figure 1. (a) Geological setting and topography of the eastern Sichuan Basin. Note the Kaijiang-Liangping Ocean Trough and the Wushen-Shizhu Depression were the under-compensated deposition area in the Late Permian marine setting. Sample locations from both this study and previous reports are also shown. (b) The geological profile across the eastern Sichuan Basin, adapted from Li A et al. (2021), shows the style of fold-thrust deformation. (c) The seismic profile across the eastern Sichuan Basin shows the deposition setting of the Late Permian.

°C/min). The measurement precision was within $\pm 0.3\%$ relative to the Vienna Standard Mean Ocean Water (VS-MOW) standard.

The helium and argon isotopes were determined using a VG5400 MS at the Langfang branch of RIPED. All gas samples were separated and purified before being pumped into the VG5400 apparatus. The $^3\text{He}/^4\text{He}$ ratios were reported relative to the atmospheric value (RA) of

$(1.384 \pm 0.006) \times 10^{-6} \text{ cm}^3 \text{ STP/cm}^3$ (STP = standard pressure and temperature, i.e., 0.101 MPa, 0 °C) (Ozima and Podosek, 2001; Clarke et al., 1976).

3 RESULTS

3.1 Composition of Natural Gas

The Upper Permian gas samples obtained from the eastern Sichuan Basin primarily consist of alkane gas, in-

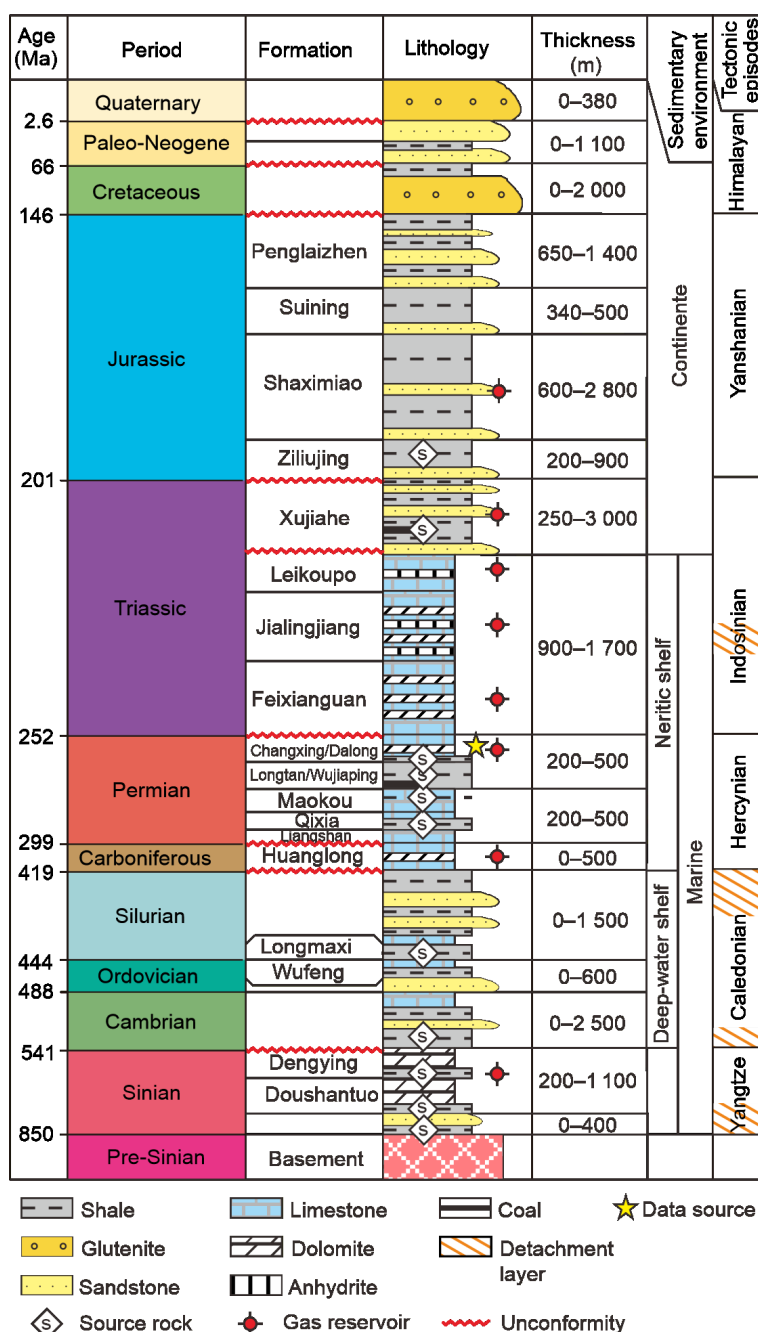


Figure 2. Stratigraphy, tectonic movements, and petroleum systems of the Sichuan Basin, adapted from Liu et al. (2020).

cluding the 78.22 mol%–98.83 mol% of methane (C_1), < 1 mol% of ethane (C_2), and < 0.2 mol% propane (C_3) (Table 1). The dryness ratio (that is, $C_1/(C_2 + C_3)$) of the alkane gas ranges from 127.9–1 564.4. Non-hydrocarbon gases are dominated by CO_2 and H_2S , which account for 0.23 mol%–11.83 mol% and 0.26 mol%–9.37 mol%, respectively. Our samples display the gas sourcing index defined by (Worden et al., 1995) (i.e., $GSI = H_2S/(H_2S + C_1 + C_2 + C_3)$) varying from 0.26% to 10.63%.

3.2 Stable Isotopic Ratios of Natural Gas

The carbon isotope ratios of methane ($\delta^{13}C_1$) and ethane ($\delta^{13}C_2$) ranged from -34.1‰ to -31.3‰ and -36.6‰ to -25.8‰, respectively (Table 2). Due to its low

concentration, the carbon isotope of propane ($\delta^{13}C_3$) was not measured successfully in all samples. Most of the samples exhibited $\delta^{13}C_3$ values ranging from -33.5‰ to -22.3‰. Cross plots of $\delta^{13}C_1$ with the dryness ratio and $\delta^{13}C_2$ indicated that alkanes in our samples belong to the highly matured thermogenic gas (Figure 3) (Milkov et al., 2020; Milkov and Etiope, 2018), which aligned with previous gas analyses of the Sichuan Basin (Li et al., 2020; Lin et al., 2020; Dai et al., 2018; Qin et al., 2016; Hao et al., 2015, 2008; Liu et al., 2014, 2013; Zhang et al., 2010; Yang et al., 2002). Although natural gas normally exhibits the enrichment of ^{13}C with carbon atoms in alkanes ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$) due to Rayleigh distillation (Rooney et al., 1995), several of our samples displayed

an abnormal isotopic reversal characteristic (i.e., $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$).

The $\delta^2\text{HC}_1$ (hydrogen isotope ratio of methane) ranged from -137‰ to -127‰ (Table 2). A cross plot of $\delta^{13}\text{C}_1$ with $\delta^2\text{HC}_1$ confirms that alkanes in our samples were the result of the late mature thermogenic gas (Figure 4), aligned with the cross plots of $\delta^{13}\text{C}_1$ with the dryness ratio and $\delta^{13}\text{C}_2$. Although not all samples were analyzed successfully, the $\delta^2\text{HC}_2$ (hydrogen isotope of ethane) for most of the samples varied from -154‰ to -120‰ (Table 2).

The measured helium ratios ($^3\text{He}/^4\text{He}$) normalized to the air value ($R_A = (1.384 \pm 0.006) \times 10^{-6}$) (Ozima and Podosek, 2001; Clarke et al., 1976) ranged from 0.025 to 0.063 (Table 2). Most samples exhibited a significant contribution of crustal-derived He, which has a typical $^3\text{He}/^4\text{He}$ value of approximately 0.01–0.02 (Ballentine and Burnard, 2002). The measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios varied from 310 to 1 225 (Table 2), exceeding the atmospheric ratio of 298.56 (Mark et al., 2011).

4 DISCUSSION

4.1 Origin of Hydrocarbon Gas

4.1.1 Mixing of sapropelic and humic origins

The depositional setting of the eastern Sichuan Basin gradually transferred from marine to terrestrial ecosystems during the Late Permian to the Triassic, contributing to the potential mixing of hydrocarbons generated by sapropelic and humic organic matter in the marine and terrigenous shales, respectively. Nevertheless, the carbon and hydrogen isotopes of hydrocarbon gases can be applied to distinguish their origins (Milkov, 2021; Milkov et al., 2020; Prinzhofer et al., 2000; Prinzhofer and Huc, 1995).

Based on the statistics, the carbon isotope of thermogenic methane ($\delta^{13}\text{C}_1$) generally exceeds -50‰ and increases with elevated thermal maturity levels, resulting in a positive correlation between $\delta^{13}\text{C}_1$ and the dryness ratio (Milkov, 2021; Milkov and Etiope, 2018; Whiticar, 1994; Faber et al., 1988; Bernard et al., 1978). Even at a similar dryness ratio, methane generated from Type III kero-

Table 1 Compositions of the Upper Permian natural gas in the eastern Sichuan Basin

Wells	Reservoir	C ₁ (mol%)	C ₂ (mol%)	C ₃ (mol%)	C ₁ /(C ₂ + C ₃)	CO ₂ (mol%)	H ₂ S (mol%)	GSI (%)
T1	P ₂ c (MCR)	98.41	0.49	0.06	178.9	0.23	n.d.	n.d.
T6	P ₂ c (MCR)	98.83	0.36	0.02	260.1	0.28	n.d.	n.d.
S21	P ₂ c (MCR)	95.93	0.66	0.09	127.9	0.38	n.d.	n.d.
W34	P ₂ c (MCR)	97.70	0.32	0.03	279.1	1.11	0.26	0.26
W118-1	P ₂ c (MCR)	97.85	0.39	0.05	222.4	1.14	n.d.	n.d.
B001-1	P ₂ c (MCR)	87.74	0.11	n.d.	797.6	7.57	3.87	4.19
D7	P ₂ c (MCR)	98.34	0.47	0.03	196.7	0.50	n.d.	n.d.
TD74	P ₂ c (MCR)	90.59	0.16	n.d.	566.2	5.58	2.99	3.17
TD110	P ₂ c (MCR)	92.63	0.26	0.03	319.4	3.31	3.18	3.29
YA012-1	P ₂ c (MCR)	83.20	0.06	n.d.	1 386.7	8.54	7.33	8.01
BD4	P ₂ c (MCR)	97.30	0.50	0.13	154.4	1.32	n.d.	n.d.
F003-X3	P ₂ c (MCR)	78.22	0.05	n.d.	1 564.4	11.83	9.37	10.63

P₂c. Changxing Formation; MCR. marine carbonate reservoir; n.d.. no data.

Table 2 Isotope ratios of the Upper Permian natural gas in the eastern Sichuan Basin

Wells	Reservoir	$\delta^{13}\text{C}_1$ (‰)	$\delta^{13}\text{C}_2$ (‰)	$\delta^{13}\text{C}_3$ (‰)	$\delta^2\text{HC}_1$ (‰)	$\delta^2\text{HC}_2$ (‰)	$^3\text{He}/^4\text{He}$ (R/RA)	$^{40}\text{Ar}/^{36}\text{Ar}$	Source rock ages (Ma)
T1	P ₂ c (MCR)	-33.4	-33.6	-29.9	-134	-138	0.043	1 225	319
T6	P ₂ c (MCR)	-33.2	-36.6	-33.5	-130	-147	0.033	528	120
S21	P ₂ c (MCR)	-34.1	-37.1	-33.7	-137	-156	0.047	810	221
W34	P ₂ c (MCR)	-31.8	-31.7	-25.3	-128	-123	0.040	563	135
W118-1	P ₂ c (MCR)	-31.8	-28.1	-22.3	-133	-126	0.062	534	123
B001-1	P ₂ c (MCR)	-32.3	-36.6	n.d.	-129	-120	0.057	546	128
D7	P ₂ c (MCR)	-33.0	-35.0	-31.5	-132	-154	0.038	743	201
TD74	P ₂ c (MCR)	-32.2	-30.3	n.d.	-127	n.d.	0.025	331	10
TD110	P ₂ c (MCR)	-33.3	-25.8	n.d.	-127	n.d.	0.040	509	112
YA012-1	P ₂ c (MCR)	-31.3	-31.3	n.d.	-131	n.d.	0.063	426	69
BD4	P ₂ c (MCR)	-33.5	-30.7	-27.1	-134	-123	0.034	346	20
F003-X3	P ₂ c (MCR)	-31.7	-31.5	n.d.	-130	n.d.	0.043	310	0

The source rock ages are estimated by Eq. (2).

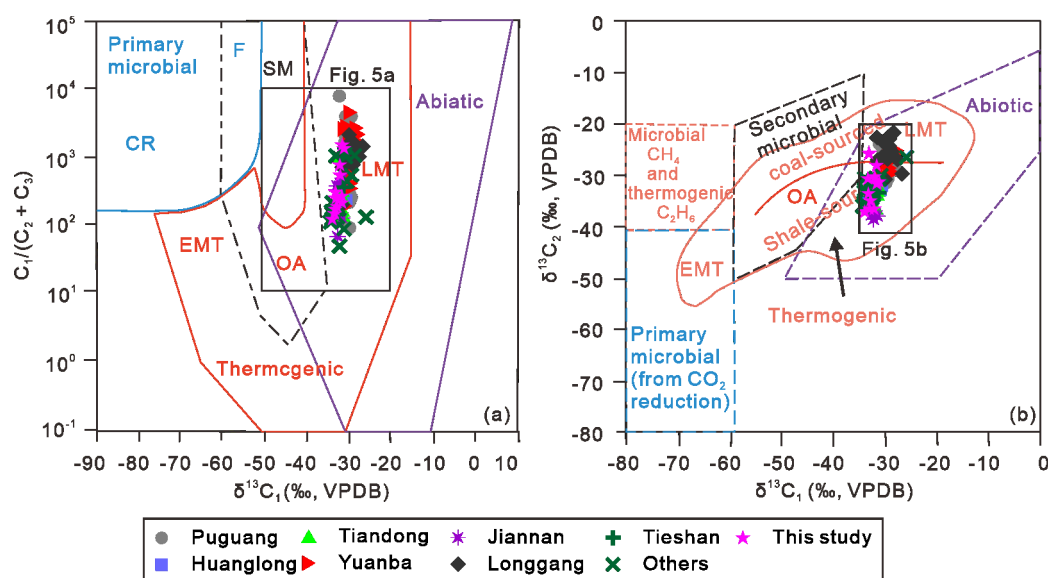


Figure 3. Molecular compositions and carbon isotopes of the Upper Permian gas samples along with previously reported data: PuGuang (Hao et al., 2015, 2008; Liu et al., 2014), Tiandong (Liu et al., 2014; Yang et al., 2002), Jiannan (Liu et al., 2013; Zhang et al., 2010), Tieshan (Liu et al., 2013; Yang et al., 2002), Huanglong (Liu et al., 2014), Yuanba (Dai et al., 2018), Longgang (Dai et al., 2018; Qin et al., 2016), others (Li et al., 2020; Lin et al., 2020). (a) The dryness ratio ($C_1/(C_2 + C_3)$) vs. methane carbon isotope ($\delta^{13}C_1$), and (b) ethane carbon isotope ($\delta^{13}C_2$) vs. $\delta^{13}C_1$ of all gas samples are aligned with thermogenic gas suggested by (Milkov et al., 2020; Milkov and Etiope, 2018). EMT, early mature thermogenic gas; SM, secondary microbial; OA, oil-associated (mid-mature) thermogenic gas; LMT, late mature thermogenic gas.

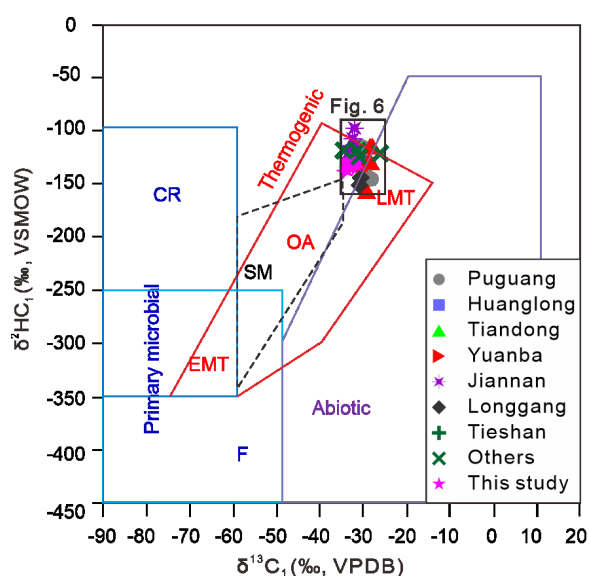


Figure 4. The methane hydrogen (δ^2HC_1) and carbon ($\delta^{13}C_1$) isotopes of gas samples in the Upper Permian reservoir are consistent with the thermogenic gas of Milkov et al. (2020) and Milkov and Etiope (2018). Please see Figure 3 for abbreviations and details of the previously reported data source.

gen (i.e., humic origin) has a relatively higher $\delta^{13}C_1$ value than that from Type II kerogen (Figure 5a). As shown in Figure 5a, our samples and previously reported data were plotted in the zone between typical areas of gases originating from the Type II and III kerogens, suggesting a mixing of sapropelic and humic origins for hydrocarbon gases in the Upper Permian reservoirs.

The carbon isotope of ethane ($\delta^{13}C_2$) also increases

with increasing thermal maturity, but commonly exhibits relatively higher values in humic-origin gas than in sapropelic-origin gas (Milkov, 2021; Jenden et al., 1988; Rooney et al., 1995). Several researchers have also summarized that humic-origin gas commonly has $\delta^{13}C_2 > -28$ ‰, but sapropelic-origin gas has $\delta^{13}C_2 < -28$ ‰ (Dai et al., 2014). Both our samples and previous data demonstrated a large variation in $\delta^{13}C_2$ (-40‰ to -20‰), which implies both humic and sapropelic origins (Figure 5b).

Corresponding to the carbon isotope, the hydrogen isotope of hydrocarbon gas varies with thermal maturity levels and organic matter types (Wang et al., 2015; Schoell, 1980). ^2H was gradually enriched in methane with elevated maturity, which resulted in a linearly positive correlation between $\delta^{13}C_1$ and δ^2HC_1 . Nevertheless, the ambiguous correlation between the measured $\delta^{13}C_1$ and δ^2HC_1 of the Permian gas samples can exclude the dominant effect of thermal maturity on δ^2HC_1 (Figure 6). The δ^2H of hydrocarbon gas is primarily inherited from organic matter and the aqueous depositional medium. Aquatic organisms are more enriched in δ^2H than terrigenous organisms, and saline marine organisms are more enriched in δ^2H than freshwater lacustrine organisms (Wang et al., 2015; Schoell, 1980). The wide δ^2HC_1 range, which is practically independent of $\delta^{13}C_1$, also suggests the mixing of sapropelic and humic origins for hydrocarbon gases in the Upper Permian reservoirs (Figure 6).

4.1.2 Mixing of various thermal maturities

In addition to organic matter types and thermal maturity levels, $\delta^{13}C_1$ and $\delta^{13}C_2$ are controlled by post-genetic

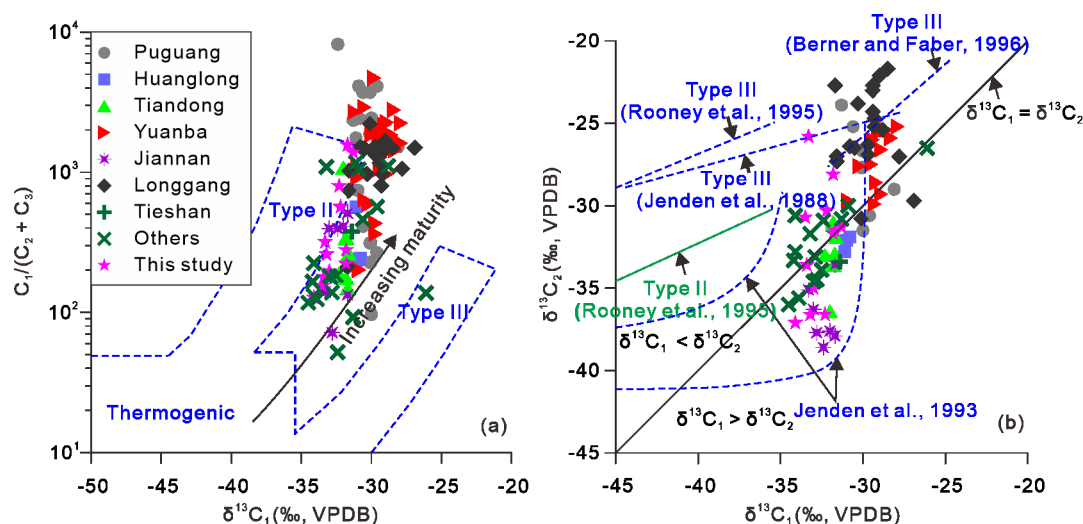


Figure 5. (a) Modified Bernard diagram; (b) $\delta^{13}\text{C}_2$ vs. $\delta^{13}\text{C}_1$ cross plot, zoomed-in views of Figures 3a and 3b respectively, showing the variation in gas origins in the Upper Permian reservoirs of the eastern Sichuan Basin.

alteration processes, including thermochemical sulfate reduction (TSR) (Torghabeh et al., 2021; Cai et al., 2019; Hao et al., 2015), migration fractionation (Tilley et al., 2011), mixing of gases of various origins (thermal maturity levels), and various source layers (Prinzhofer and Huc, 1995).

As shown in Table 1, various H_2S contents were detected in the Upper Permian reservoir, consistent with previously reported data (Li et al., 2016; Liu et al., 2013; Cai et al., 2010; Hao et al., 2008). Potential mechanisms that account for H_2S in hydrocarbons include the thermal decomposition of sulfur compounds in organic matter (TDS), bacterial sulfate reduction (BSR), and TSR (Loefering et al., 2022; Torghabeh et al., 2021). The low abundance of organic sulfur compounds in organic matter commonly limits the TDS-associated H_2S concentration to no more than 5%; BSR generally appears in recent sediments with a maximum temperature of approximately 80 °C and accounts for $\text{H}_2\text{S} < 5\%$; and high H_2S concentrations ($> 5\%$) are widely assumed to be related to TSR that occurs at temperatures > 110 °C (Torghabeh et al., 2021; Cai et al., 2019, 2010; Li et al., 2016; Liu et al., 2013; Hao et al., 2008; Worden et al., 1996). Regionally, the H_2S concentration in the Upper Permian reservoirs increases from south to north (Table 1; Figure 1a), which is consistent with the conclusion that the H_2S concentration was positively correlated with the thickness of anhydrite-bearing evaporitic rocks that supplied sulfur during the TSR and primarily appeared in the Triassic strata of northern Sichuan Basin (Zhu, 2005).

The plot of GSI, the proxy for TSR extent, against $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$), indicates that $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) in the Upper Permian reservoirs can be positively correlated with elevated GSI ($> 5\%$), for example, samples from the Puuguang field (Figures 7a, 7b). This positive correlation suggests that the TSR altered $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) in individual gas fields (e.g., Puuguang field) of the northern Sichuan Basin. The TSR favors the removal of ^{12}C , contributing to

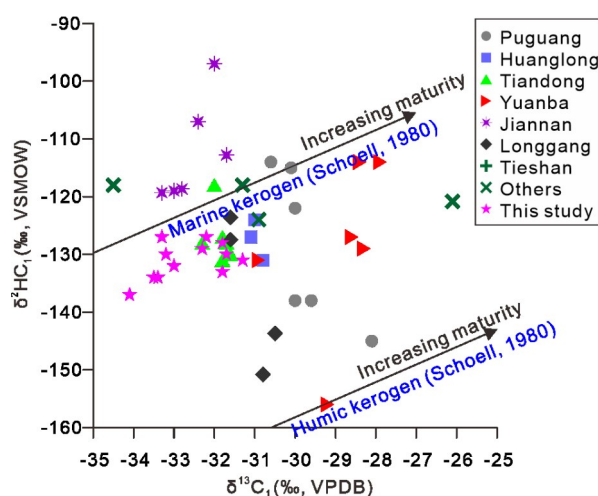


Figure 6. The $\delta^2\text{HC}_1$ vs. $\delta^{13}\text{C}_1$ plot, a zoomed-in view of Figure 4, shows the variation in gas origins in the Upper Permian reservoirs. The kerogen lines were adapted from Schoell (1980). The arrows indicate the pathway of increasing maturity in the source rocks.

the enrichment of ^{13}C in residual hydrocarbon gases (Cai et al., 2019; Hao et al., 2008; Rooney et al., 1995). Due to the difference in reactivity, heavy hydrocarbon gases (C_{2+}) are preferentially involved in TSR, which can account for the increase in $\delta^{13}\text{C}_2$ but no change in $\delta^{13}\text{C}_1$ with elevated GSI (Mankiewicz et al., 2009); thus, the difference between $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ (i.e., $\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2$) theoretically decreased with TSR progress (Figure 7c).

TSR was suggested as a potential mechanism for inducing reversed carbon isotope ratios between methane and ethane (i.e., $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$), despite hydrocarbon gases originating from the same source layer and similar thermal maturity levels, theoretically showing the elevation of the carbon isotope ratio with carbon atom numbers in the gas molecule ($\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2$) (i.e., the normal carbon isotope ratios) (Feng et al., 2021; Milkov et al., 2020; Liu et al., 2013; Tilley and Muehlenbachs, 2013;

Hao et al., 2008). Hao et al. (2008) proposed that methane, as the only organic reactant, is involved in the TSR after the exhaustion of most of the heavy hydrocarbon

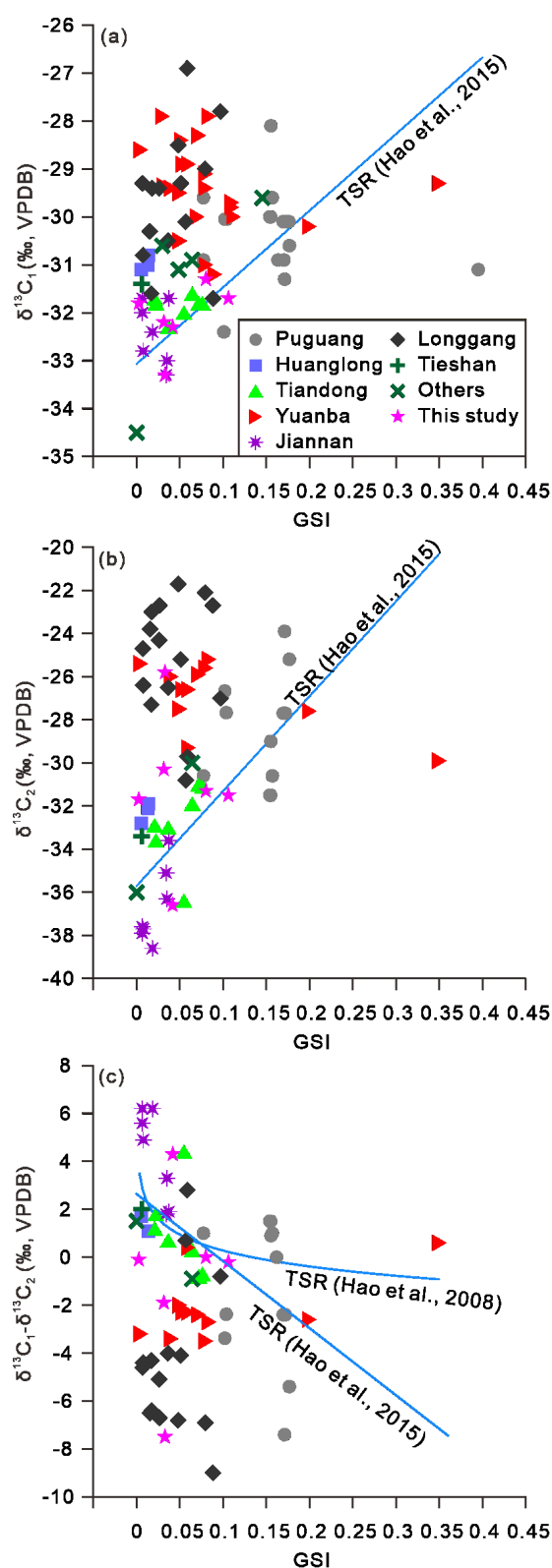


Figure 7. Change of (a) $\delta^{13}\text{C}_1$, (b) $\delta^{13}\text{C}_2$, and (c) $\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2$ with gas sourcing index (GSI) for gas samples in the Upper Permian reservoir. The effects of thermochemical sulfate reduction (TSR) were adapted from Hao et al. (2015).

gases (C_{2+}). Nevertheless, no direct correlation between the reversed carbon isotope ratios and the methane-involved TSR was identified in our data. Although methane was involved in TSR progress, $\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2$ may not be increased to > 0 (i.e., reversed carbon isotope ratios) (Figure 7c). As shown in Figures 7a and 7b, $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) of the Upper Permian gas samples were independent of low GSI values ($< 5\%$) (e.g., samples from the Longgang field), suggesting that TSR-independent samples also showed the reserved carbon isotopes. Prinzhofer and Huc (1995) pointed out that the fractional leakage of a gas reservoir can cause the preferential loss of lighter carbon isotopes (i.e., ^{12}C) and lighter molecular weight (i.e., methane), resulting in the enrichment of C_{2+} and heavier carbon isotopes (i.e., ^{13}C) in the residual gas. This partial diffusion model preferentially increases $\delta^{13}\text{C}_1$, which conflicts with the narrow change in $\delta^{13}\text{C}_1$ in the gas samples of the Upper Permian reservoir (Figure 5b). Jenden et al. (1993) suggested that a mixture of thermogenic gases with different thermal maturity levels can complicate the molecular and isotopic signatures of hydrocarbon gases. Because the highly matured gas contains significantly less C_{2+} than the low-maturity gas, the mixing of a minor amount of highly matured gas with the less matured gas can primarily elevate $\delta^{13}\text{C}_1$ without a significant change in $\delta^{13}\text{C}_2$. In contrast, adding a minor amount of low-maturity gas within the high-maturity gas can distinctly decrease $\delta^{13}\text{C}_2$. Abundant gas samples in the Upper Permian reservoir indicate a wide variation in $\delta^{13}\text{C}_2$ with almost constant $\delta^{13}\text{C}_1$, which aligns with the bivariate mixture model of Jenden et al. (1993) (Figure 8).

The artificial maturity of kerogen or oil in closed-system pyrolysis revealed the general tendency of molecular composition change (Prinzhofer and Huc, 1995). In the closed-system experiments, the C_1/C_2 ratio increased significantly during the primary cracking of kerogen but remained almost stable during the secondary cracking of

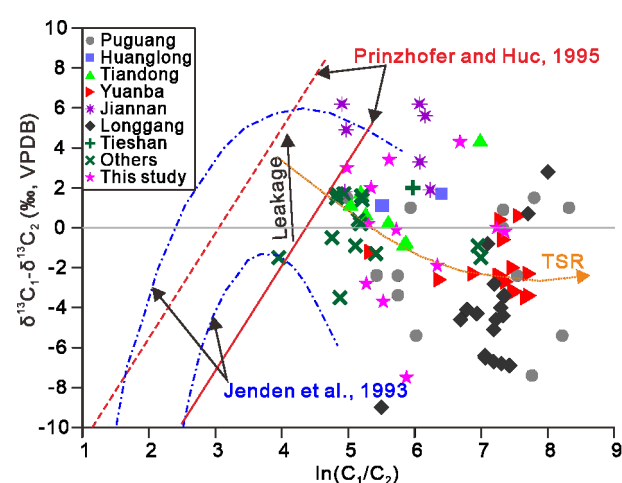


Figure 8. Correlation diagram of $\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2$ with $\ln(\text{C}_1/\text{C}_2)$ for gas samples in the Permian reservoir. The leakage model established by Prinzhofer and Huc (1995), the bivariate mixture model of Jenden et al. (1993), and the TSR effect identified by Hao et al. (2008) are also plotted.

oil. Conversely, the C_2/C_3 ratio remained stable during the primary cracking of kerogen but increased drastically during the secondary cracking of oil. As shown in Figure 9, the C_2/C_3 ratio varied more rapidly than the C_1/C_2 ratio in the Upper Permian gas samples, implying the dominance of secondary cracking. However, the Upper Permian samples deviated from the correlation between the C_1/C_2 and C_2/C_3 ratios in the Sichuan Basin, which was quantified by the oil cracking experiments of Hao et al. (2008). Notably, the system openness of the Upper Permian reservoir may be higher than that in the artificial pyrolysis experiment. Adding various amounts of the less matured gas primarily cracked from kerogen, within the highly mature gases cracked from the oil can induce a parallel shift in the correlation of Hao et al. (2008) to account for the measured C_1/C_2 and C_2/C_3 ratios of most gas samples in the Upper Permian reservoirs. Some samples involved in the TSR reaction showed increasing values of $\ln(C_1/C_2)$ and a relatively wider range of values with the TSR process.

4.2 Identification of Primary Source Rock

Noble gas isotopes have been suggested as powerful tools for source-rock identification (Zhang et al., 2005; Liu and Xu, 1993). ^{36}Ar in the crust is principally derived from the atmosphere and introduced through dissolution in groundwater; ^{40}Ar (in atoms/g) is primarily generated from the decay of ^{40}K following the equation.

$$^{40}\text{Ar} = X_K[K] \times 10^{-6} \left(\frac{N_A}{A_K} \right) \left(\frac{\lambda_e}{\lambda_k} \right) (e^{\lambda t} - 1) \quad (1)$$

where, $X_K = 1.167 \times 10^{-4}$ (the fractional natural abundance of ^{40}K), $[K]$ is the K concentration (in ppm), $N_A = 6.023 \times 10^{23}$ (Avogadro's number), $A_K = 39.964$ g (molar mass of K), $\lambda_e = 0.581 \times 10^{-10} \text{ yr}^{-1}$, $\lambda_k = (5.463 \pm 0.054) \times 10^{-10} \text{ yr}^{-1}$, and t = age (yr) (Ballentine and Burnard, 2002). The atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is almost constant at 298.56 (Mark et al., 2011). Assuming a closed system in-

volving source and reservoir rocks, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the hydrocarbon gas is controlled by the K concentration and age of the source rock. Based on the statistical analysis of Liu and Xu (1993), the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of hydrocarbon gas sourced from shale is positively correlated with the source rock age (T) in most Chinese basins (including the Sichuan Basin)

$$T(\text{Myr}) = 544.5 \log \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right) - 1362.3 \quad (2)$$

The measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of hydrocarbon gas in the Upper Permian reservoir ranged from 310 to 1225 (Table 2), which suggests a source rock age of 320–0 Ma, referring to the oldest source rock of the Permian age (Figure 2). Previous studies also suggested that gas in the Upper Permian reservoir of the Sichuan Basin mainly came from the Permian source rocks (Borjigen et al., 2014; Tang et al., 2011; Zhu et al., 2006). The Permian source rocks consist of shale interbedded with carbonates in the Lower Permian, and marine shale interbedded with terrestrial shale or coal (Figure 2). In particular, shales of the Dalong and Wujiaping formations (Upper Permian) with deposition centers around Dazhou City and Chongqing City (Figure 1) were suggested to have generated $3290 \times 10^8 \text{ t}$ of oil and $420 \times 10^{12} \text{ m}^3$ of gas; nevertheless, the gas reserves originating from the cracking of oil and kerogen reached $4.45 \times 10^{12} \text{ m}^3$ and $4.45 \times 10^{12} \text{ m}^3$, respectively (Yi et al., 2024; Chen et al., 2018).

The wide range of inferred source rock ages primarily accounts for the mixing of hydrocarbon gases generated from younger shales, for example, from the Triassic. Nevertheless, Zhang et al. (2005) suggested that the K concentration in special source rocks, such as coal and carbonate rocks, is an order of magnitude lower than that in shale, which may cause an underestimation of the source rock age from Eq. (2). The assumption of an ideal closed source-reservoir system may be too harsh; the mixing of atmosphere-saturated groundwater and the subsequent water-gas interaction (Liu et al., 2021b) may also decrease the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio to approach the atmospheric ratio (298.56) (Mark et al., 2011) and underestimate the source rock age.

4.3 Hydrocarbon Accumulation Model

As shown in Figure 10, the Upper Permian reservoir mainly experienced two episodes of hydrocarbon evolution processes: (1) charging of oil and gas from five sets of the Permian source rocks (Figure 2), including deep marine mudstone of the Dalong and the Wujiaping formations dominated by Type II kerogen with the average equivalent reflectance of 1.75% and 2.32% (Wu et al., 2019), lagoon-facies mudstone of the Maokou and the Qixia formations (Zhu et al., 2006) which mainly contained Type II kerogen with the average equivalent reflectance greater than 2%, and humic mudstone with interbedded coal seams in the transitional facies of the Longtan Formation which consisted mainly of Type III organic compounds with an average equivalent reflectance of

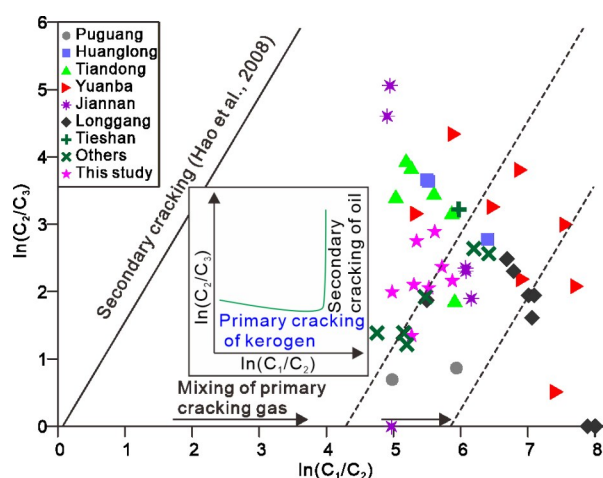


Figure 9. The C_2/C_3 versus C_1/C_2 ratios for gas samples collected from the Permian reservoir. The artificial oil-cracking line was adapted from the experiments of Hao et al. (2008), and the classical tendency established by Prinzhofer and Huc (1995) was illustrated.

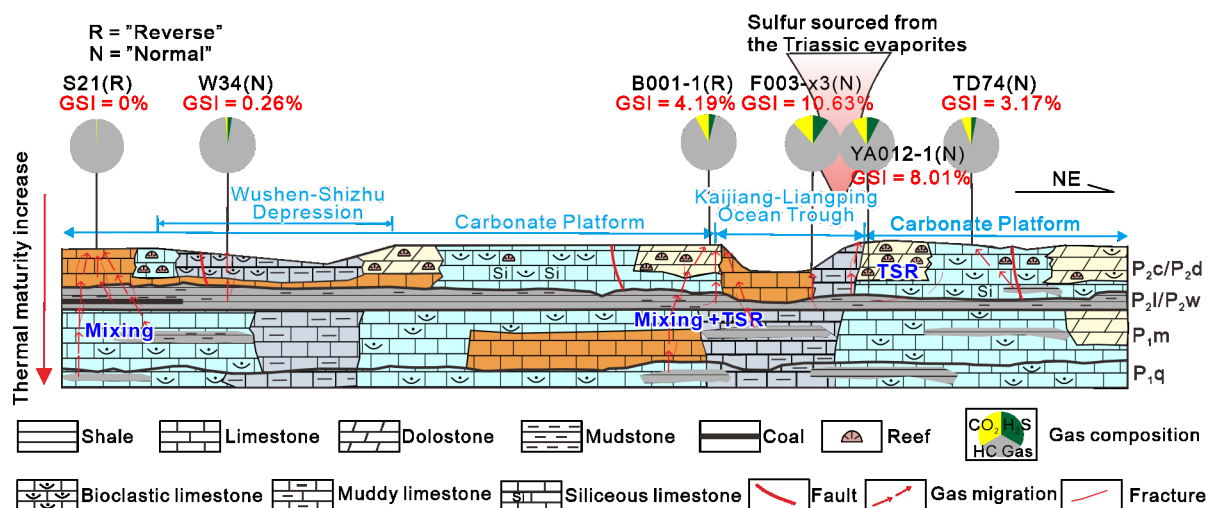


Figure 10. Gas enrichment model of the Upper Permian reservoirs.

2.13% (Chen et al., 2018; Zhu et al., 2006); and (2) hydrocarbon thermal alteration, e.g., oil-cracking gas and TSR. The mixing of various origins for hydrocarbon gas and thermal alteration processes varied spatially, and then complicated the molecular and isotopic compositions in the eastern Sichuan Basin. The sulfur-rich brine sourced from the Triassic evaporites was mainly distributed around the Kaijing-Liangping Ocean Through, which promoted the TSR reaction in that region and resulted in high GSI values. These TSR processes mainly consumed ethane and thus didn't successfully cause the reversed carbon isotope ratios. Gas originated from multiple sources (e.g., a mixing of Sapropelic and humic origins or a mixing of various maturity levels) which led to the reversed carbon isotope ratios and a relatively wider $\delta^{13}\text{C}_1$ range in the reservoirs around the Wushen-Shizhu Depression; whereas individual reservoirs that were not affected by mixing still show. In the transition zone between the Wushen-Shizhu Depression and the Kaijing-Liangping Ocean Through, the chemical processes were more complicated, which involved the superposition of mixing and TSR processes and resulted in greater carbon isotopic reversal (e.g., Well B001-1).

5 CONCLUSIONS

In this study, the origin of natural gases in the Upper Permian reservoir has been comprehensively analyzed, which is significant to further understand the resource potential and distribution of natural gas in the Upper Permian. Meanwhile, the source rocks' ages have been measured by the noble gas isotopes model, which suggests that the younger source rock from the Triassic might contribute to gases in the Upper Permian reservoir and reveals the gas enrichment mechanism in the eastern Sichuan Basin of South China.

The gas in the Upper Permian reservoir was altered by two important chemical processes: the mixing of various source rocks and hydrocarbon thermal alteration. Non-hydrocarbon gas dominated by CO₂ and H₂S spatially increased the concentration northward. A high concen-

tration of H₂S was primarily generated by TSR. For gases with GSI values (> 5%), TSR altered $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$). However, because of the mixing of thermogenic gases with various levels of thermal maturity, the majority of the $\delta^{13}\text{C}_1$ (or $\delta^{13}\text{C}_2$) values, independent of low GSI values (< 5%), demonstrated reversed carbon isotopes.

The measured helium isotope ratio (i.e., $^3\text{He}/^4\text{He}$) ranged from 0.025–0.063 ($R_A = (1.384 \pm 0.006) \times 10^{-6}$), indicating the dominance of crustal fluids without mantle fluid disturbance. The measured argon isotope ratio (i.e., $^{40}\text{Ar}/^{36}\text{Ar}$) varies from 310 to 1 225, which suggests that the source rock age is up to 320 Ma, corresponding to Permian shales.

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Conflict of Interest

The authors declare that they have no conflict of interest.

REFERENCES CITED

- Ballentine, C. J., Burnard, P. G., 2002. Production, Release and Transport of Noble Gases in the Continental Crust. *Reviews in Mineralogy and Geochemistry*, 47(1): 481–538. <https://doi.org/10.2138/rmg.2002.47.12>
- Bernard, B. B., Brooks, J. M., Sackett, W. M., 1978. Light Hydrocarbons in Recent Texas Continental Shelf and Slope Sediments. *Journal of Geophysical Research: Oceans*, 83(C8): 4053–4061. <https://doi.org/10.1029/JC083iC08p04053>
- Borjigen, T., Qin, J. Z., Fu, X. D., et al., 2014. Marine Hydrocarbon Source Rocks of the Upper Permian Longtan Formation and Their Contribution to Gas Accumulation in the Northeastern Sichuan Basin, Southwest China. *Marine and Petroleum Geology*, 57: 160 – 172. <https://doi.org/10.1016/j.mrg.2014.05.016>

- marpetgeo.2014.05.005
- Cai, C. F., Li, K. K., Zhu, Y. M., et al., 2010. TSR Origin of Sulfur in Permian and Triassic Reservoir Bitumen, East Sichuan Basin, China. *Organic Geochemistry*, 41(9): 871–878. <https://doi.org/10.1016/j.orggeochem.2010.03.009>
- Cai, C. F., Tang, Y. J., Li, K. K., et al., 2019. Relative Reactivity of Saturated Hydrocarbons during Thermochemical Sulfate Reduction. *Fuel*, 253: 106–113. <https://doi.org/10.1016/j.fuel.2019.04.148>
- Cai, C. F., Worden, R. H., Bottrell, S. H., et al., 2003. Thermochemical Sulphate Reduction and the Generation of Hydrogen Sulphide and Thiols (Mercaptans) in Triassic Carbonate Reservoirs from the Sichuan Basin, China. *Chemical Geology*, 202(1/2): 39–57. [https://doi.org/10.1016/S0009-2541\(03\)00209-2](https://doi.org/10.1016/S0009-2541(03)00209-2)
- Chen, J. P., Li, W., Ni, Y. Y., et al., 2018. The Permian Source Rocks in the Sichuan Basin and Its Natural Gas Exploration Potential (Part 1): Spatial Distribution of Source Rocks. *Natural Gas Industry*, 38(5): 33–45. <https://doi.org/10.3787/j.issn.1000-0976.2018.05.001> (in Chinese with English Abstract)
- Chen, X., Hu, M. Y., Xu, C. H., et al., 2022. Sedimentary Architectures of Reef-Shoal Facies at the Platform Margin during Changxing Times of the Late Permian around Kaijiang-Liangping Trough in the Sichuan Basin and Their Differences. *Oil & Gas Geology*, 43(4): 833–844. <https://doi.org/10.11743/ogg20220408> (in Chinese with English Abstract)
- Clarke, W. B., Jenkins, W. J., Top, Z., 1976. Determination of Tritium by Mass Spectrometric Measurement of ^3He . *The International Journal of Applied Radiation and Isotopes*, 27(9): 515–522. [https://doi.org/10.1016/0020-708X\(76\)90082-X](https://doi.org/10.1016/0020-708X(76)90082-X)
- Dai, J. X., Ni, Y. Y., Liu, Q. Y., et al., 2021. Sichuan Super Gas Basin in Southwest China. *Petroleum Exploration and Development*, 48(6): 1251–1259. [https://doi.org/10.1016/S1876-3804\(21\)60284-7](https://doi.org/10.1016/S1876-3804(21)60284-7)
- Dai, J. X., Ni, Y. Y., Qin, S. F., et al., 2018. Geochemical Characteristics of Ultra-Deep Natural Gas in the Sichuan Basin, SW China. *Petroleum Exploration and Development*, 45(4): 619–628. [https://doi.org/10.1016/S1876-3804\(18\)30067-3](https://doi.org/10.1016/S1876-3804(18)30067-3)
- Dai, J. X., Zou, C. N., Liao, S. M., et al., 2014. Geochemistry of the Extremely High Thermal Maturity Longmaxi Shale Gas, Southern Sichuan Basin. *Organic Geochemistry*, 74: 3–12. <https://doi.org/10.1016/j.orggeochem.2014.01.018>
- Dong, S. W., Zhang, Y. Q., Gao, R., et al., 2015. A Possible Buried Paleoproterozoic Collisional Orogen Beneath Central South China: Evidence from Seismic-Reflection Profiling. *Precambrian Research*, 264: 1–10. <https://doi.org/10.1016/j.precamres.2015.04.003>
- Faber, E., Gerling, P., Dumke, I., 1988. Gaseous Hydrocarbons of Unknown Origin Found While Drilling. *Organic Geochemistry*, 13 (4/5/6): 875–879. [https://doi.org/10.1016/0146-6380\(88\)90240-9](https://doi.org/10.1016/0146-6380(88)90240-9)
- Feng, Z. Q., Dong, D. Z., Tian, J. Q., et al., 2021. Geochemical Characteristics of the Paleozoic Natural Gas in the Yichuan-Huanglong Area, Southeastern Margin of the Ordos Basin: Based on Late Gas Generation Mechanisms. *Marine and Petroleum Geology*, 124: 104867. <https://doi.org/10.1016/j.marpetgeo.2020.104867>
- Hao, F., Guo, T. L., Zhu, Y. M., et al., 2008. Evidence for Multiple Stages of Oil Cracking and Thermochemical Sulfate Reduction in the Puguang Gas Field, Sichuan Basin, China. *AAPG Bulletin*, 92(5): 611–637. <https://doi.org/10.1306/01210807090>
- Hao, F., Zhang, X. F., Wang, C. W., et al., 2015. The Fate of CO_2 Derived from Thermochemical Sulfate Reduction (TSR) and Effect of TSR on Carbonate Porosity and Permeability, Sichuan Basin, China. *Earth-Science Reviews*, 141: 154–177. <https://doi.org/10.1016/j.earscirev.2014.12.001>
- He, W. G., Zhou, J. X., Yuan, K., 2018. Deformation Evolution of Eastern Sichuan-Xuefeng Fold-Thrust Belt in South China: Insights from Analogue Modelling. *Journal of Structural Geology*, 109: 74–85. <https://doi.org/10.1016/j.jsg.2018.01.002>
- Jenden, P. D., Drazan, D. J., Kaplan, I. R., 1993. Mixing of Thermogenic Natural Gases in Northern Appalachian Basin. *AAPG Bulletin*, 77(6): 980–998. <https://doi.org/10.1306/BDF8DBC-1718-11D7-8645000102C1865D>
- Jenden, P. D., Kaplan, I. R., Poreda, R., et al., 1988. Origin of Nitrogen-Rich Natural Gases in the California Great Valley: Evidence from Helium, Carbon and Nitrogen Isotope Ratios. *Geochimica et Cosmochimica Acta*, 52(4): 851–861. [https://doi.org/10.1016/0016-7037\(88\)90356-0](https://doi.org/10.1016/0016-7037(88)90356-0)
- Li, A., Shan, X. L., Luo, K. P., et al., 2021. A New Type of Unconventional Gas Reservoir from the Nodular Limestones of the Middle Permian Maokou Formation in the South-Eastern Sichuan Basin, South-West China. *Geological Journal*, 56(11): 5426–5439. <https://doi.org/10.1002/gj.4250>
- Li, C. X., He, D. F., Lu, G., et al., 2021. Multiple Thrust Detachments and Their Implications for Hydrocarbon Accumulation in the Northeastern Sichuan Basin, Southwestern China. *AAPG Bulletin*, 105(2): 357–390. <https://doi.org/10.1306/07272019064>
- Li, J. H., Dong, S. W., Cawood, P. A., et al., 2018. An Andean-Type Retro-Arc Foreland System beneath Northwest South China Revealed by SINOPROBE Profiling. *Earth and Planetary Science Letters*, 490: 170–179. <https://doi.org/10.1016/j.epsl.2018.03.008>
- Li, L. G., 2011. Technical Progress and Developing Orientation in Natural Gas Exploration and Development in the Sichuan Basin. *Natural Gas Industry*, 31(1): 1–6, 107. <https://doi.org/10.3787/j.issn.1000-0976.2011.01.001> (in Chinese with English Abstract)
- Li, P. P., Hao, F., Guo, X. S., et al., 2016. Origin and Distribution of Hydrogen Sulfide in the Yuanba Gas Field, Sichuan Basin, Southwest China. *Marine and Petroleum Geology*, 75: 220–239. <https://doi.org/10.1016/j.marpetgeo.2016.04.021>
- Li, Y. J., Xia, J. W., Li, M. L., et al., 2020. Spatial-Temporal Modelling of Oil and Gas Accumulation in Changxing Formation in the Shunan Area, Sichuan Basin. *Petroleum Geology & Experiment*, 42(6): 877–885. <https://doi.org/10.11781/sysydz202006877> (in Chinese with English Abstract)
- Lin, X. M., Wei, Q. C., Zheng, J., et al., 2020. Analysis on Natural Gas Source of Permian Changxing Formation in Fuling Area, Sichuan Basin, China. *Journal of Chengdu University of Technology (Science & Technology Edition)*, 47(1): 28–34. <https://doi.org/10.3969/j.issn.1671-9727.2020.01.03> (in Chinese with English Abstract)
- Liu, Q. Y., Worden, R. H., Jin, Z. J., et al., 2013. TSR versus Non-TSR Processes and Their Impact on Gas Geochemistry and Carbon Stable Isotopes in Carboniferous, Permian and Lower Triassic Marine Carbonate Gas Reservoirs in the Eastern Sichuan Basin, China. *Geochimica et Cosmochimica Acta*, 100:

- 96–115. <https://doi.org/10.1016/j.gca.2012.09.039>
- Liu, Q. Y., Worden, R. H., Jin, Z. J., et al., 2014. Thermochemical Sulphate Reduction (TSR) versus Maturation and Their Effects on Hydrogen Stable Isotopes of Very Dry Alkane Gases. *Geochimica et Cosmochimica Acta*, 137: 208–220. <https://doi.org/10.1016/j.gca.2014.03.013>
- Liu, R., Hao, F., Engelder, T., et al., 2019. Stress Memory Extracted from Shale in the Vicinity of a Fault Zone: Implications for Shale-Gas Retention. *Marine and Petroleum Geology*, 102: 340–349. <https://doi.org/10.1016/j.marpetgeo.2018.12.047>
- Liu, R., Hao, F., Engelder, T., et al., 2020. Influence of Tectonic Exhumation on Porosity of Wufeng-Longmaxi Shale in the Fuling Gas Field of the Eastern Sichuan Basin, China. *AAPG Bulletin*, 104(4): 939–959. <https://doi.org/10.1306/08161918071>
- Liu, R., Jiang, D. C., Zheng, J., et al., 2021a. Stress Heterogeneity in the Changning Shale-Gas Field, Southern Sichuan Basin: Implications for a Hydraulic Fracturing Strategy. *Marine and Petroleum Geology*, 132: 105218. <https://doi.org/10.1016/j.marpetgeo.2021.105218>
- Liu, R., Wen, T., Amalberti, J., et al., 2021b. The Dichotomy in Noble Gas Signatures Linked to Tectonic Deformation in Wufeng-Longmaxi Shale, Sichuan Basin. *Chemical Geology*, 581: 120412. <https://doi.org/10.1016/j.chemgeo.2021.120412>
- Liu, S. G., Yang, Y., Deng, B., et al., 2021. Tectonic Evolution of the Sichuan Basin, Southwest China. *Earth-Science Reviews*, 213: 103470. <https://doi.org/10.1016/j.earscirev.2020.103470>
- Liu, W. H., Xu, Y. C., 1993. Geochemistry on Mantle-Derived Volatiles in Natural Gases from Eastern China Oil/Gas Provinces (I) —Helium, Argon and Hydrocarbons in Mantle Volatiles. *Chinese Science Bulletin*, 38(9): 818–821 (in Chinese with English Abstract)
- Loefering, M., Kaminski, P., Hutchinson, I., et al., 2022. H₂S Origin, Generation, and Distribution in the Etame Marine Permit, Offshore Gabon: A Three-Dimensional Migration Modeling Prediction Using Field Data. *AAPG Bulletin*, 106(1): 145–178. <https://doi.org/10.1306/07202119094>
- Ma, Y. S., Guo, X. S., Guo, T. L., et al., 2007. The Puguang Gas Field: New Giant Discovery in the Mature Sichuan Basin, Southwest China. *AAPG Bulletin*, 91(5): 627–643. <https://doi.org/10.1306/110306060602>
- Mankiewicz, P. J., Pottorf, R. J., Kozar, M. G., et al., 2009. Gas Geochemistry of the Mobile Bay Jurassic Norphlet Formation: Thermal Controls and Implications for Reservoir Connectivity. *AAPG Bulletin*, 93(10): 1319–1346. <https://doi.org/10.1306/05220908171>
- Mark, D. F., Stuart, F. M., de Podesta, M., 2011. New High-Precision Measurements of the Isotopic Composition of Atmospheric Argon. *Geochimica et Cosmochimica Acta*, 75(23): 7494–7501. <https://doi.org/10.1016/j.gca.2011.09.042>
- Meng, Q. R., Wang, E., Hu, J. M., 2005. Mesozoic Sedimentary Evolution of the Northwest Sichuan Basin: Implication for Continued Clockwise Rotation of the South China Block. *GSA Bulletin*, 117(3–4): 396–410. <https://doi.org/10.1130/B25407.1>
- Milkov, A. V., 2021. New Approaches to Distinguish Shale-Sourced and Coal-Sourced Gases in Petroleum Systems. *Organic Geochemistry*, 158: 104271. <https://doi.org/10.1016/j.orggeochem.2021.104271>
- Milkov, A. V., Etiope, G., 2018. Revised Genetic Diagrams for Natural Gases Based on a Global Dataset of >20 000 Samples. *Organic Geochemistry*, 125: 109–120. <https://doi.org/10.1016/j.orggeochem.2018.09.002>
- Milkov, A. V., Faiz, M., Etiope, G., 2020. Geochemistry of Shale Gases from around the World: Composition, Origins, Isotope Reversals and Rollovers, and Implications for the Exploration of Shale Plays. *Organic Geochemistry*, 143: 103997. <https://doi.org/10.1016/j.orggeochem.2020.103997>
- Ozima, M., Podosek, F. A., 2001. Noble Gas Geochemistry. Cambridge University Press, Cambridge. 300
- Prinzhofer, A. A., Huc, A. Y., 1995. Genetic and Post-Genetic Molecular and Isotopic Fractionations in Natural Gases. *Chemical Geology*, 126(3/4): 281–290. [https://doi.org/10.1016/0009-2541\(95\)00123-9](https://doi.org/10.1016/0009-2541(95)00123-9)
- Prinzhofer, A., Rocha Mello, M., Takaki, T., 2000. Geochemical Characterization of Natural Gas: A Physical Multivariable Approach and Its Applications in Maturity and Migration Estimates. *AAPG Bulletin*, 84(8): 1152–1172. <https://doi.org/10.1306/A9673C66-1738-11D7-8645000102C1865D>
- Qin, S. F., Yang, Y., Lyu, F., et al., 2016. The Gas Origin in Changxing-Feixianguan Gas Pools of Longgang Gasfield in Sichuan Basin. *Natural Gas Geoscience*, 27(1): 41–49 (in Chinese with English Abstract)
- Qiu, Z., Dou, L. R., Wu, J. F., et al., 2024. Lithofacies Palaeogeographic Evolution of the Middle Permian Sequence Stratigraphy and Its Implications for Shale Gas Exploration in the Northern Sichuan and Western Hubei Provinces. *Earth Science*, 49(2): 712–748 (in Chinese with English Abstract)
- Richardson, N. J., Densmore, A. L., Seward, D., et al., 2008. Extraordinary Denudation in the Sichuan Basin: Insights from Low-Temperature Thermochronology Adjacent to the Eastern Margin of the Tibetan Plateau. *Journal of Geophysical Research: Solid Earth*, 113(B4): B04409. <https://doi.org/10.1029/2006JB004739>
- Rooney, M. A., Claypool, G. E., Chung, H. M., 1995. Modeling Thermogenic Gas Generation Using Carbon Isotope Ratios of Natural Gas Hydrocarbons. *Chemical Geology*, 126(3/4): 219–232. [https://doi.org/10.1016/0009-2541\(95\)00119-0](https://doi.org/10.1016/0009-2541(95)00119-0)
- Schoell, M., 1980. The Hydrogen and Carbon Isotopic Composition of Methane from Natural Gases of Various Origins. *Geochimica et Cosmochimica Acta*, 44(5): 649–661. [https://doi.org/10.1016/0016-7037\(80\)90155-6](https://doi.org/10.1016/0016-7037(80)90155-6)
- Tang, D., Zhang, Q., Wan, M. X., et al., 2011. Source Rock and Resource Potential of Upper Permian in Sichuan Basin. *Natural Gas Exploration and Development*, 34(3): 1–3, 7, 85. <https://doi.org/10.3969/j.issn.1673-3177.2011.03.001> (in Chinese with English Abstract)
- Tilley, B., McLellan, S., Hiebert, S., et al., 2011. Gas Isotope Reversals in Fractured Gas Reservoirs of the Western Canadian Foothills: Mature Shale Gases in Disguise. *AAPG Bulletin*, 95(8): 1399–1422. <https://doi.org/10.1306/01031110103>
- Tilley, B., Muehlenbachs, K., 2013. Isotope Reversals and Universal Stages and Trends of Gas Maturation in Sealed, Self-Contained Petroleum Systems. *Chemical Geology*, 339: 194–204. <https://doi.org/10.1016/j.chemgeo.2012.08.002>
- Torghabeh, A. K., Kalantariasl, A., Kamali, M., et al., 2021. Reservoir Gas Isotope Fingerprinting and Mechanism for Increased H₂S: An Example from Middle East Shanul Gas Field. *Journal of*

- Petroleum Science and Engineering*, 199: 108325. <https://doi.org/10.1016/j.petrol.2020.108325>
- Wang, X. F., Liu, W. H., Shi, B. G., et al., 2015. Hydrogen Isotope Characteristics of Thermogenic Methane in Chinese Sedimentary Basins. *Organic Geochemistry*, 83: 178–189. <https://doi.org/10.1016/j.orggeochem.2015.03.010>
- Whiticar, M. J., 1994. Correlation of Natural Gases with Their Sources. In: Magoon, L. B., Dow, W. G., eds., *The Petroleum System—From Source to Trap*. American Association of Petroleum Geologists. 261 – 284. <https://doi.org/10.1306/m60585c16>
- Worden, R. H., Smalley, P. C., Oxtoby, N. H., 1995. Gas Souring by Thermochemical Sulfate Reduction at 140 °C. *AAPG Bulletin*, 79 (6): 854 – 863. <https://doi.org/10.1306/8D2B1BCE-171E-11D7-8645000102C1865D>
- Worden, R. H., Smalley, P. C., Oxtoby, N. H., 1996. The Effects of Thermochemical Sulfate Reduction Upon Formation Water Salinity and Oxygen Isotopes in Carbonate Gas Reservoirs. *Geochimica et Cosmochimica Acta*, 60(20): 3925–3931. [https://doi.org/10.1016/0016-7037\(96\)00216-5](https://doi.org/10.1016/0016-7037(96)00216-5)
- Wu, W., Cheng, P., Liu, S. Y., et al., 2023. Gas-in-Place (GIP) Variation and Main Controlling Factors for the Deep Wufeng-Longmaxi Shales in the Luzhou Area of the Southern Sichuan Basin, China. *Journal of Earth Science*, 34(4): 1002–1011. <https://doi.org/10.1007/s12583-021-1593-x>
- Wu, X. Q., Liu, Q. Y., Liu, G. X., et al., 2019. Genetic Types of Natural Gas and Gas-Source Correlation in Different Strata of the Yuanba Gas Field, Sichuan Basin, SW China. *Journal of Asian Earth Sciences*, 181: 103906. <https://doi.org/10.1016/j.jseaes.2019.103906>
- Yan, D. P., Zhou, M. F., Song, H. L., et al., 2003. Origin and Tectonic Significance of a Mesozoic Multi-Layer Over-Thrust System within the Yangtze Block (South China). *Tectonophysics*, 361(3/4): 239–254. [https://doi.org/10.1016/S0040-1951\(02\)00646-7](https://doi.org/10.1016/S0040-1951(02)00646-7)
- Yang, J. J., Wang, Y. G., Wang, L. S., et al., 2002. The Origin of Natural Gases and Geochemistry Characters of Changxing Reef and Feixianguan Oolitic Beach Gas Reservoirs in Eastern Sichuan Basin. *Acta Sedimentologica Sinica*, 20(2): 349–352 (in Chinese with English Abstract)
- Yang, M. H., Zuo, Y. H., Duan, X. G., et al., 2023. Hydrocarbon Kitchen Evolution of the Lower Cambrian Qiongzhusi Formation in the Sichuan Basin and Its Enlightenment to Hydrocarbon Accumulation. *Earth Science*, 48(2): 582–595 (in Chinese with English Abstract)
- Yi, Y. H., Zhu, H. T., Lu, Y. Q., et al., 2024. Sedimentary Facies Evolution and Oncoidal Development Conditions of Wujiaping Formation of Upper Permian in Hongxing Area, East Sichuan. *Earth Science*, 49(12): 4546 – 4563 (in Chinese with English Abstract)
- Zhang, D. W., Liu, W. H., Zheng, J. J., et al., 2005. Helium and Argon Isotopic Compositions of Natural Gases in the Tazhong Area, Tarim Basin. *Petroleum Exploration and Development*, 32 (6): 38–41 (in Chinese with English Abstract)
- Zhang, J. Y., Liu, W. H., Teng, G. E., et al., 2010. Characteristics of Natural Gas in P₂ch–T₁f Layers in Jiannan Gas Field and Gas Source Correlation. *Natural Gas Geoscience*, 21(6): 1004–1013 (in Chinese with English Abstract)
- Zhu, G. Z., 2005. Relationship between Palaeoenvironment and the Distribution of H₂S in Feixianguan Formation, NE Sichuan Province. *Petroleum Exploration and Development*, 32(4): 65–69 (in Chinese with English Abstract)
- Zhu, Y. G., Zhang, S. C., Liang, Y. B., et al., 2006. The Characteristics of Natural Gas in the Sichuan Basin and Its Sources. *Earth Science Frontiers*, 13(2): 234–248 (in Chinese with English Abstract)