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Original research paper

Geochemical characteristics and genetic types of natural gas in the Changxing-Feixianguan Formations from the Yuanba Gas Field in the Sichuan Basin, China☆

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Abstract

The Yuanba Gas Field is a large gas field in the marine strata with the largest burial depth in China up to date. The studies performed on the mentioned gas field have achieved significant progress made possible by determining the characteristics of reef flat reservoirs in the marine strata and the main controlling factors of hydrocarbon accumulation. However, there is no consensus on the origin of natural gases stored in the reservoir in the Changxing-Feixianguan Formations in the Yuanba and its adjacent area. The study on geochemical characteristics indicates that natural gases in the reservoir in the Changxing-Feixianguan Formations in the Yuanba Gas Field are mainly composed of alkane gases which are dominated by methane with dryness coefficients generally higher than 0.995. The CO_2 and H_2S display an average content of 8.55% and 6.47%, respectively. The $\delta^{13}C_1$ and $\delta^{13}C_2$ values are from −31.2‰ to −27.9‰, and from −29.9‰ to −25.0‰, respectively, displaying the positive carbon isotopic series. The $\delta^{13}C_{CO2}$ values are generally higher than −8‰, and the δD_1 values are from −156‰ to −107‰. The identification of gas origin and gas−source correlation indicate that the natural gases reservoired in the Changxing-Feixianguan Formations in the Yuanba Gas Field have been altered by thermochemical sulfate reduction, and they are mainly composed of oil cracking gases derived from the secondary cracking of oil generated by the sapropelic-prone source rocks in the Permian Longtan Formation. The CO_2 in the gas pools are mainly inorganic and were derived from the interaction between the acidic fluid and carbonate reservoirs.

Keywords: Yuanba Gas Field; Changxing-Feixianguan Formations; Natural gas; Geochemical characteristics; Origin

1. Introduction

The natural gas exploration in the Sichuan Basin is notably one of the most important onshore gas producing areas in China. It has continuously achieved significant breakthroughs, and a series of giant gas fields such as the Puguang, Yuanba, and Anyue Gas Fields have been discovered in succession [1−5]. Of all the discovered gas fields, the Yuanba Gas Field is a large marine gas field with the largest burial depth in China to date, and the proven gas reserves reaches as much as 2195.82×10^8 m^3. Many fruitful studies have been conducted on the Yuanba Gas Field beforehand [6−8], and they are mainly concentrated on the marine reef flat reservoir characteristics, the main controlling factors of the accumulation, the reservoir characteristics [9], and the gas origin [10,11] of the terrigenous Xujiahe Formation, as well as the accumulation

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conditions of the shale gas in the Ziliujing Formation [12]. Nevertheless, only a few studies have been conducted on the geochemical characteristics and genetic types of natural gases contained in the reservoir within the Upper Permian Changxing Formation (P_2ch) and Lower Triassic Feixianguan Formation (T_1f) with no consensus. For example, several scholars considered that the P_2ch gas in the Yuanba Gas Field was mainly oil cracking gas [5,6,13], whereas some other scholars demonstrated that the P_2ch-T_1f gases in both the Yuanba Gas Field and the adjacent Longgang Gas Field were mainly coal-derived gases [14,15]. This divergence was caused by the different understandings about the organic types of the Permian source rocks or the geochemical characteristics of natural gases. Previous studies mainly concentrated on the chemical composition and carbon isotopes of the natural gas, but barely paying any attention to the hydrogen isotopes. Additionally, only a handful of comparative studies on the geochemical characteristics of natural gases from the different areas have been conducted. Therefore, the authors intend to identify the origin and source of P_2ch-T_1f gases in the Yuanba Gas Field based on the analyses of the chemical composition, stable carbon, and hydrogen isotopes, and compare the geochemical characteristics of gases from the Yuanba with those from the Longgang, Puguang, and Wolonghe Gas Fields. The authors also wish to further provide beneficial information for a deeper understanding of hydrocarbon generation and accumulation, as well as expansion of the subsequent exploration fields.

2. Geological setting

The Yuanba Gas Field is located in the northern Sichuan Basin and it goes across the structural units such as the Jiulongshan Anticline, Chixi Sag, Tongnanba Anticline, Tongjiang Sag, and Cangxi-Bazhong low and flat structural belt (Fig. 1) [7]. Blocked by the Jiulongshan Anticline, the Tongnanba Anticline, and the slope belt of the Chuanzhong Uplift to the south, the strata in the Yuanba Gas Field have a delicate occurrence with weak structural deformation and few faults. Meanwhile, the Sinian-Cretaceous strata are entirely developed in this area [6]. The marine gases in the Yuanba Gas Field are mainly stored in the reef flat carbonate rocks in the Upper Permian Changxing Formation assisted by the Lower Triassic Feixianguan Formation and the Middle Triassic Leikoupo Formation. The Late Permian sedimentary facies and the location of the reservoirs were controlled by the Dongwu Movement together with the formation of the oil and gas pools controlled by the Early-Middle Yanshan Movement, and the tectonic movements since the Late Yanshan Movement have established the present distribution of the oil and gas pools [6].

3. Geochemical characteristics of natural gases

Ten gas samples were collected from P_2ch and T_3x reservoirs in the Yuanba Gas Field, and the chemical composition and stable carbon and hydrogen isotopic compositions were measured in the Wuxi Research Institute of Petroleum Geology, Petroleum Exploration and Production Research Institute of Sinopec; the results are in Table 1. The geochemical characteristics of natural gases of the Yuanba Gas Field are comprehensively analyzed based on the measurements acquired in combination with the previously published data of marine gases from the Yuanba, Longgang, and Puguang Gas Fields.

3.1. Chemical compositions of natural gases

The P_2ch-T_1f natural gases in the Yuanba Gas Field are dominated by hydrocarbon gases, in which the methane content is in the range of 74.11%–92.57%. Meanwhile, the heavier hydrocarbons are in small amounts together with a bit of propane and butane. The gases are typically dry gas with the dryness coefficients being higher than 0.995 (Fig. 2a). The nonhydrocarbons are mainly composed of CO_2 and H_2S, in which CO_2 displays a content of 0.07%–32.51% with an average of 8.55%, and the H_2S displays a content of 0%–25.70% with an average of 6.47% (Fig. 2b). The data mentioned indicates that the gases were generally altered by

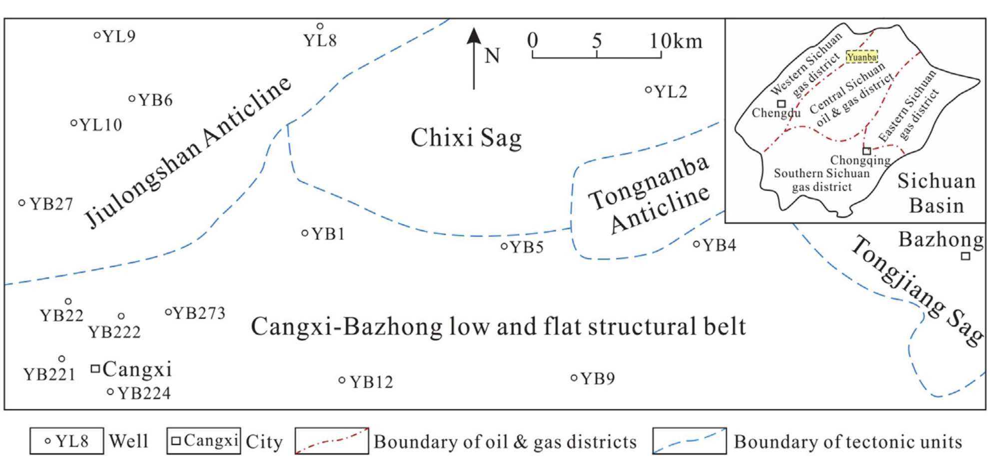

Fig. 1. The distribution of tectonic units and wells in the Yuanba Gas Field in the Sichuan Basin.

Table 1
Chemical, carbon, and hydrogen isotopic compositions of natural gas from the Changxing and Xujiahe Formations in the Yuanba-Tongnanba area in the Sichuan Basin.

Well	Strata	Depth/m	Chemical composition/%							$\delta^{13}C$/‰				δD_1/‰
			CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CO_2	H_2S	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}C_{CO2}$	
YB 221	P_2ch	6686–6720	61.98	0.04	0.00	0.00	15.06	22.90	0.00	−29.2	−28.6	−26.9	−0.4	−156
YB 222	P_2ch	7020–7030	99.15	0.47	0.02	0.00	0.28	0.07	0.00	−30.9	−29.7	−29	−8.1	−131
YB 224	P_2ch	6625–6636	88.46	0.06	0.00	0.00	0.00	4.68	6.85	−28.3	−25.9		1	−129
YB 273	P_2ch	6811–6880	92.57	0.05	0.00	0.00	0.84	6.04	0.45	−28.6	−25.4		0.5	−127
YL 10	T_3x^4	4069–4077	98.05	0.93	0.09	0.02	0.20	0.67	0.00	−32	−25.7	−27.3	−7.5	−162
YL 10	T_3x^3	4305–4327	96.93	0.31	0.03	0.00	2.64	0.08	0.00	−29.3	−25	−23.6	−1.5	−162
YL 8	T_3x^2	4065–4088	21.59	0.21	0.02	0.00	62.83	15.33	0.00	−30.4	−33.5	−33.5	−5.6	−160
YL 9	T_3x^2	4455–4479	89.71	0.72	0.06	0.02	1.29	8.13	0.00	−30	−33	−33.6	−0.5	−155
YL 10	T_3x^2	4533–4546	96.16	1.10	0.10	0.02	2.56	0.05	0.00	−31.5	−32.3	−32.7	−11.1	−157
YB 1	T_3x^2		96.60	2.390	0.35	0.08	0.58	0	0.00	−31.9	−28.5			

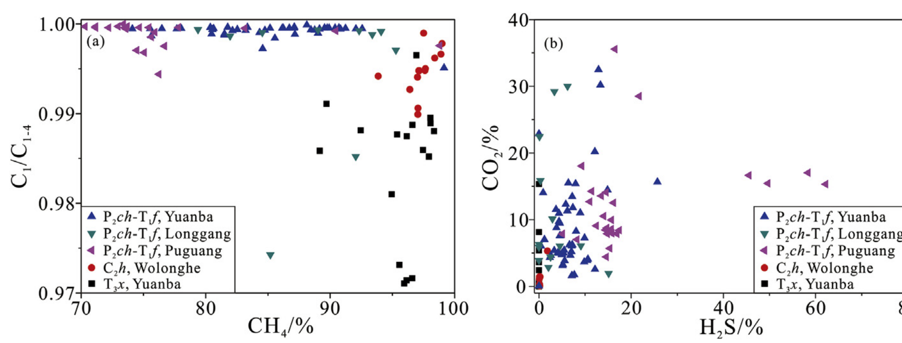

Fig. 2. Compositional characteristics of gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (data source: this study; Ref. [1,8,12,13,15–21]).

the thermochemical sulfate reduction (TSR). The N_2 content is generally lower than 3%.

The P_2ch-T_1f gases in the Longgang Gas Field display a similar dryness coefficient, CH_4, CO_2, and H_2S contents with those in the Yuanba Gas Field, whereas those in the Puguang Gas Field generally display a higher H_2S content and lower CH_4 content with similar dryness coefficient generally higher than 0.995. The natural gases in the Upper Carboniferous Huanglong Formation (C_2h) in the Wolonghe Gas Field have evidently higher CH_4 content and slightly lower dryness coefficient with only a trace amount of H_2S, and the gases in the terrigenous Upper Triassic Xujiahe Formation (T_3x) in the Yuanba Gas Field display the CH_4 content generally higher than 90% and dryness coefficient mainly in the range of 0.97–0.99 with no H_2S (Fig. 2a, b).

3.2. Carbon isotopes

The $\delta^{13}C_1$ values of P_2ch-T_1f gases in the Yuanba Gas Field are relatively concentrated with its values ranging from −31.2‰ to −27.9‰; these findings were consistent with those in the Longgang Gas Field, and they were mainly higher than those in the Puguang Gas Field. The values acquired are generally higher than the $\delta^{13}C_1$ values of T_3x gases in the Yuanba Gas Field, and C_2h gases in the Wolonghe Gas Field with only a few exceptions. The $\delta^{13}C_2$ values of P_2ch-T_1f gases in the Yuanba Gas Field are from −29.9‰ to −25.0‰, which are higher than those of C_2h gases in the Wolonghe Gas Field (Fig. 3). Since P_2ch-T_1f gases in the Yuanba Gas Field has insignificant propane content (often times no propane at all), the $\delta^{13}C_3$ value was only measured using only three gas samples. The three gas samples mentioned had a value ranging from −29.0‰ to −26.9‰. The P_2ch-T_1f gases from the Yuanba, Longgang, and Puguang Gas Fields display positive carbon isotopic sequences ($\delta^{13}C_1<\delta^{13}C_2$) in the correlation diagram between $\delta^{13}C_1$ and $\delta^{13}C_2$ values, with only a few

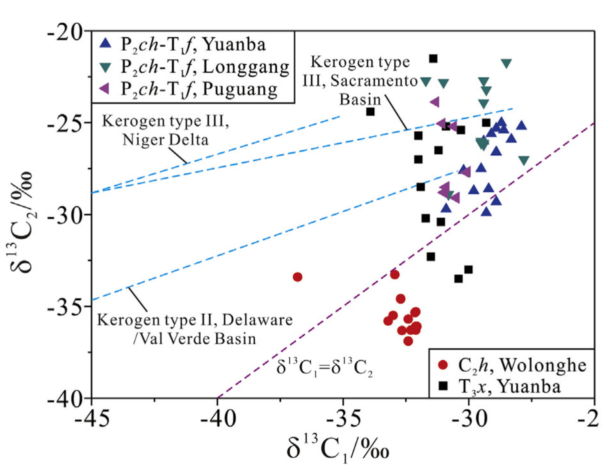

Fig. 3. Correlation diagram of carbon isotope ratios of methane and ethane in the Changxing-Feixianguan Formations in the Yuanba Gas Field (data source: this study; Ref. [1,8,12,13,15–21]; Sacramento Basin from Ref. [25], Niger delta and Delaware/Val Verde Basin from Ref. [26]).

samples displaying partial reversal ($\delta^{13}C_1 > \delta^{13}C_2$). The findings were obviously different from the C_2h gases in the Wolonghe Gas Field generally displaying partial carbon isotopic reversal.

The P_2ch-T_1f gases in the Yuanba Gas Field mainly display high $\delta^{13}C_{CO2}$ values ranging from −10.9‰ to 3.3‰, and the statistical result indicates that 27 out of the 29 gas samples exhibited $\delta^{13}C_{CO2}$ values higher than −8‰. The P_2ch-T_1f gases in the Longgang and Puguang Gas Fields, as well as the T_3x gases in the Yuanba Gas Field display high $\delta^{13}C_{CO2}$ values (>−8‰), whereas most C_2h gases in the Wolonghe Gas Field display low $\delta^{13}C_{CO2}$ values (<−8‰).

3.3. Hydrogen isotopes

The P_2ch-T_1f gases in the Yuanba Gas Field display δD_1 values ranging from −156‰ to −107‰, with an average of −129‰; the $\delta^{13}C_1$ and δD_1 values are slightly correlated positively (Fig. 4). The δD_1 values of P_2ch-T_1f gases in the Puguang and Longgang Gas Fields are highly concentrated with values ranging from −124‰ to −114‰, and from −115‰ to −108‰, respectively. The δD_1 values of C_2h gases in the Wolonghe Gas Field are from −140‰ to −116‰, whereas those of T_3x gases in the Yuanba Gas Field are significantly lower; the determined values are from −162‰ to −155‰ (Fig. 4).

4. TSR alteration on the geochemical characteristics of natural gases

Gas souring index (GSI) has been widely used to characterize the TSR extent. The C_2h gases in the Wolonghe Gas Field have extremely low GSI, this suggests a low TSR content. Meanwhile, the P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang gas fields generally display high GSI, which indicates that the gases have experienced significant TSR alteration (Fig. 5). The TSR alteration is crucial to the marine gases in the northeastern Sichuan Basin, and it can not only

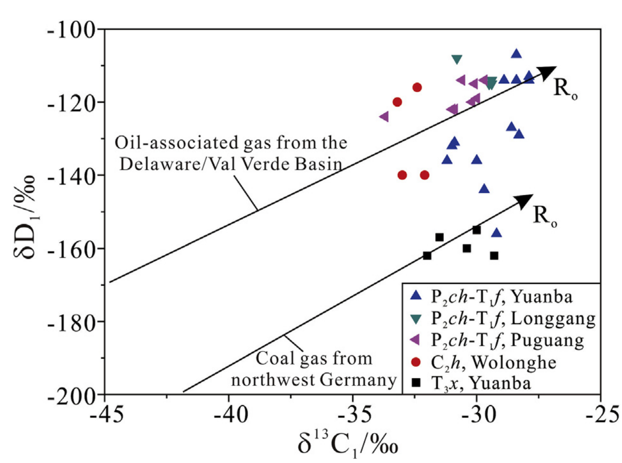

Fig. 4. Correlation diagram of δD_1-$\delta^{13}C_1$ of gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (based on Ref. [28]; data source: this study; Ref. [12,15,17−21,29]).

modify the deep carbonate reservoirs by dissolution, but also affect the geochemical characteristics of natural gases. TSR can be divided into heavy alkane-dominated TSR and methane-dominated TSR according to the TSR alteration extent [1,22−24].

The P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang Gas Fields display wide ranges of H_2S contents (Fig. 2b) with extremely high dryness coefficient (>0.995, Fig. 2a), this hardly reflects the influence of TSR alteration. However, these gases have concentrated $\delta^{13}C_1$ values with a wide range of C_1/C_{2+3} ratios in the modified Bernard diagram (Fig. 6). The said diagram indicates that the heavy alkanes were preferentially consumed during the TSR process. The generated H_2S and CO_2 increased with the TSR extent [23]; the relationship was verified by the certain positive correlation between H_2S% and CO_2% in Fig. 2b.

The gases from the Puguang, Tieshanpo, and Luojiazhai Gas Fields display certain positive correlations for the $\delta^{13}C_1$ value *versus* GSI and the $\delta^{13}C_2$ value *versus* GSI. These indicate that the gases experienced heavy alkane-dominated TSR. Several gas samples experienced a higher extent of alteration accomplished by means of methane-dominated TSR [1,21]. However, the P_2ch-T_1f gases from the Yuanba, Longgang, and Puguang Gas Fields displayed no obvious correlation for the $\delta^{13}C_1$ value *versus* GSI (Fig. 5a) or the $\delta^{13}C_2$ value *versus* GSI (Fig. 5b); these findings were consistent with the study on the Puguang and Maoba Gas Fields conducted by Hu et al. [27]. Considering the distribution areas of the gas fields, this might be related to the depositional environment and thermal maturity of source rocks in different gas fields.

The P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang Gas Fields mainly follow the maturity trend in the correlation diagram between $\delta^{13}C_1$-$\delta^{13}C_2$ and $\ln(C_1/C_2)$, whereas the T_3x gases in the Yuanba Gas Field follows a different maturity trend (Fig. 7). The P_2ch-T_1f gases in the Yuanba Gas Field displays the highest thermal maturity (Fig. 7), which is consistent with the generally high $\delta^{13}C_1$ values (Fig. 3). The C_2h gases in the Wolonghe Gas Field displayed low GSI and partial carbon isotopic reversal between methane and ethane, which was mainly caused by the addition of high-mature gas from the source and the mixing of oil-associated gases from different stages [16]. Nonetheless, the P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang Gas Fields display an evidently higher GSI and positive carbon isotopic sequence between methane and ethane (Figs. 5c and 7), this indicates that the TSR could unlikely cause the partial carbon isotopic reversal between methane and ethane, and it can cause the gas samples with partial carbon isotopic reversal between methane and ethane to be in positive sequence. This is consistent with the results of previous studies [1,29,30], and it may also attribute to the preferential TSR on the heavy alkanes. The aforementioned may cause the heavy alkane contents to decline and the $\delta^{13}C$ values of remaining heavy alkanes to increase; it may specifically cause the increase of $\ln(C_1/C_2)$ values and the decrease of $\delta^{13}C_1$-$\delta^{13}C_2$ values [1]. Therefore, caution is needed when the carbon isotopic compositions of heavy alkanes are used to identify the origin of natural gas.

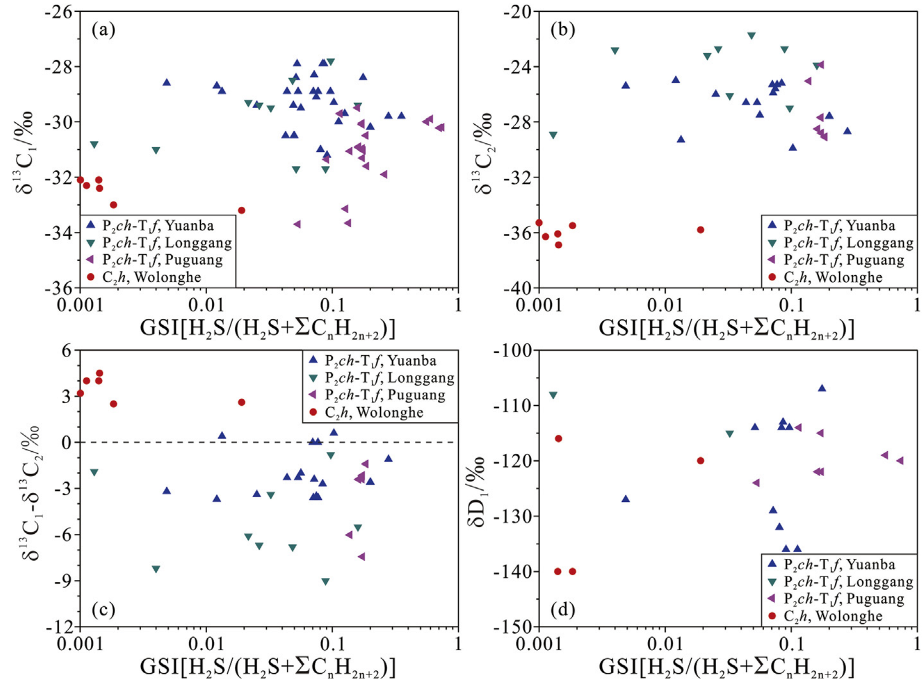

Fig. 5. Correlation diagram of carbon and hydrogen isotopic compositions *versus* the GSI of gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (data source: this study; Ref. [1,8,12,13,15–21]).

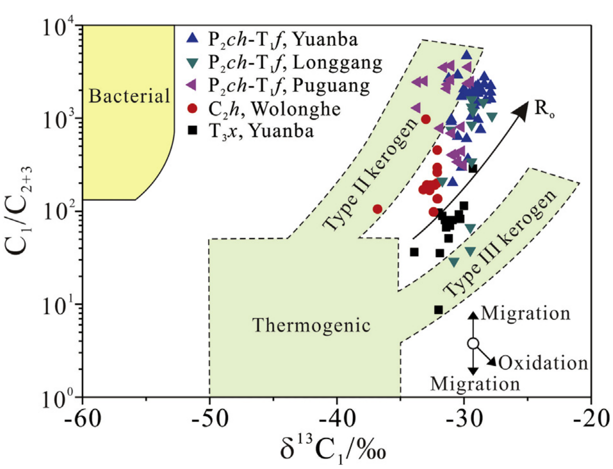

Fig. 6. Modified Bernard diagram of C_1/C_{2+3}-$\delta^{13}C_1$ of gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (based on reference [32]; data source: this study; Ref. [1,8,12,13,15–21]).

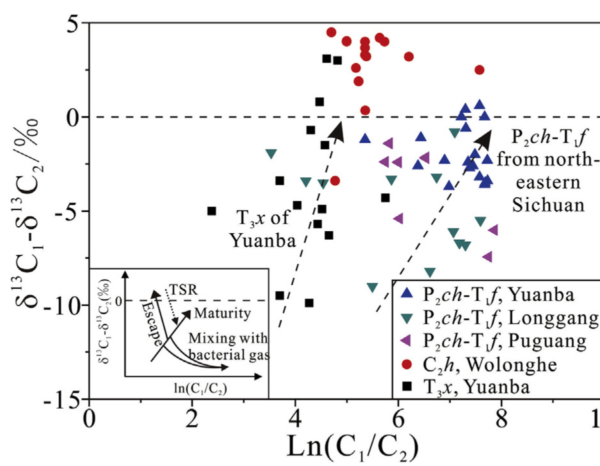

Fig. 7. Correlation diagram of ($\delta^{13}C_1$-$\delta^{13}C_2$)-ln(C_1/C_2) gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (based on Ref. [1,36]; data source: this study; Ref. [1,8,12,13,15–21]).

Moreover, as to the hydrogen isotopic compositions, Hu et al. [15] proposed that since the natural gases from the northeastern Sichuan Basin displayed a certain positive correlation between δD_1 values and GSI, the δD_1 values would increase as TSR proceeded. However, the statistical result indicates no obvious correlation between δD_1 values and GSI for the P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang Gas Fields (Fig. 5d), which are consistent with Liu et al.'s point [29]. Liu et al. claimed that the methane hydrogen isotopic composition may be unlikely affected by the TSR and could be further used to identify the gas origin. In addition, it also indicates that the conclusions based on limited data might be inadequate or even one-sided. Although both the δD_1-δD_2 and $\delta^{13}C_1$-$\delta^{13}C_2$ values of gases from the eastern Sichuan Basin decrease with the increase of TSR extent [29], the P_2ch-T_1f gases in the Yuanba Gas Field has extremely low contents of heavy alkanes (e.g. ethane) and the δD_2 values are hardly measured. Therefore, the effect of TSR on the hydrogen isotopic fractionation still needs further study.

5. Genetic types and source of natural gases

5.1. Genetic types of alkane gases

The P_2ch-T_1f gases in the Yuanba Gas Field mainly display positive carbon isotopic sequence between methane and ethane (Fig. 3), which is consistent with the organic alkane gas. The gases from different strata in the field display low helium isotopic values with R/Ra within the range of 0.0033−0.0181, indicating crust-derived helium [31]. They are distinct from biogenic gas due to the higher $\delta^{13}C_1$ values, and it displays the characteristics of thermogenic gas in the modified Bernard [32] diagram (Fig. 6). Thermogenic gas can be divided into oil-associated (sapropelic) and coal-derived (humic) gases according to different types of organic matters [33], which follow the different trends in the Bernard diagram [32]. The P_2*ch*-T_1*f* gases in the Yuanba Gas Field display the characteristics close to that of the gas from type II kerogen, and they are oil-associated gas with similar characteristics to the P_2*ch*-T_1*f* gases in the Puguang Gas Field, as well as the C_2*h* gases in the Wolonghe Gas Field. The T_3*x* gases in the Yuanba Gas Field are coal-derived gas with the characteristics close to the gas from type III kerogen, whereas the P_2*ch*-T_1*f* gases in the Longgang Gas Field covers a broad area in the diagram and display the characteristics of both coal-derived and oil-associated gases (Fig. 6).

According to the different organic matter types, the coal-derived gas displays higher $\delta^{13}C_2$ value under similar $\delta^{13}C_1$ value than oil-associated gas. In addition, they follow different trends in the correlation diagram between the $\delta^{13}C_1$ and $\delta^{13}C_2$ values [26]. Overall, the P_2*ch*-T_1*f* gases in the Yuanba, Longgang, and Puguang Gas Fields display no evident positive correlation between the $\delta^{13}C_1$ and $\delta^{13}C_2$ values (Fig. 3), this indicated the insignificant effect of thermal maturity. These gases have a wide $\delta^{13}C_2$ range with a narrow $\delta^{13}C_1$ range, and some gases are consistent with the gas from type II kerogen in the Delaware/Val Verde Basin, whereas some other gases are consistent with the gas from type III kerogen in the Sacramento Basin due to the high $\delta^{13}C_2$ values, which is different from the C_2*h* gases in the Wolonghe Gas Field displaying typically oil-associated gas with significantly low $\delta^{13}C_2$ values (Fig. 3).

Heavy alkanes, such as ethane, generally inherit the carbon isotopes of the organic matters; they are often used to discriminate between coal-derived and oil-associated gases. A great example is the boundary of the $\delta^{13}C_2$ value for coal-derived and oil-associated gases from the Sichuan Basin is approximately −29‰ [34]. The P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang Gas Fields seem to be coal-derived gas with the $\delta^{13}C_2$ values mainly higher than −29‰. However, on one hand, these gases have extremely high dryness coefficients and are dominated by methane, and the origin of methane could not be directly inferred simply based on the trace components such as ethane, propane, and even light hydrocarbons. On the other hand, the carbon isotopic compositions of heavy alkanes might be altered by post-genetic modification processes such as TSR and bacterial oxidation, which would affect the identification of gas origin. Therefore, one-sided conclusions might be achieved simply based on the carbon isotopic compositions of heavy alkanes.

The hydrogen isotopic composition of natural gas have a unique advantage in revealing the depositional environment of the source rocks [35], and it plays an increasingly important role in the identification of gas origin and gas−source correlation. The hydrogen isotopic compositions of alkane gases are controlled by the organic matter types, thermal maturity, and depositional environment [33]. The P_2*ch*-T_1*f* gases in the Yuanba Gas Field displays a unapparent correlation between $\delta^{13}C_1$ and δD_1 values without the simultaneous increase of the values (Fig. 4), indicating that thermal maturity was not the main controlling factor of carbon and hydrogen isotopic compositions of methane. These gases display characteristics between oil-associated gas from the Delaware/Val Verde Basin and coal gas from northwest Germany, both are prone to the former, which indicate that these gases are mixing gas prone to oil-associated gas and derived from the mixing types of sapropelic prone organic matters. As a comparison, the P_2*ch*-T_1*f* gases in the Longgang and Puguang Gas Fields and the T_3*x* gases in the Yuanba Gas Field display characteristics of oil-associated and coal-derived gas, respectively. Although the marine gases in the Puguang Gas Field are generally believed to be oil-associated gas [1,3,21], the P_2*ch*-T_1*f* gases in the Longgang Gas Field are mainly considered as coal-derived gas due to the high $\delta^{13}C_2$ values [14,15]. However, it is not supported by the limited hydrogen isotopic data of methane [15], indicating the characteristics of the oil-associated gas, which needs more hydrogen isotopic data to prove.

The statistical result indicates that the marine and terrigenous gases in the Sichuan Basin can be divided by the δD_1 value of −150‰ [20,37]. The δD_1 values of the P_2*ch*-T_1*f* gases in the Longgang and Puguang Gas Fields are obviously higher than −150‰, whereas those of the T_3*x* gases in the Yuanba Gas Field are significantly lower than −150‰, suggesting terrigenous gases, and the δD_1 values of the P_2*ch*-T_1*f* gases in the Yuanba Gas Field are mainly higher than −150‰ with several gas samples lower than −150‰, indicating that these gases are mainly marine gases assisted by terrigenous gases.

Oil-associated gas can be derived from kerogen cracking and secondary oil cracking (including accumulated oil and disperse dissoluble organic matter) according to the generation pathways [38]. During the kerogen cracking and oil cracking processes, the C_1/C_2 and C_2/C_3 ratios display different variation trends as the thermal evolution proceeds. Therefore, the correlation diagrams of $\ln(C_1/C_2)$ *versus* $\ln(C_2/C_3)$ and $\delta^{13}C_2$-$\delta^{13}C_3$ *versus* C_2/C_3 are often used to discriminate between kerogen cracking gas and oil cracking gas [36,39]. Since the P_2*ch*-T_1*f* gases in the Yuanba Gas Field contain little propane, the $\delta^{13}C_3$ values are hardly measured, and the correlation diagram of $\delta^{13}C_2$-$\delta^{13}C_3$ *versus* C_2/C_3 can't be used effectively. The P_2*ch*-T_1*f* gases in the Yuanba Gas Field displays a wide range of $\ln(C_2/C_3)$ value with consistent $\ln(C_1/C_2)$ value, suggesting the characteristics of oil cracking gas, which is similar to the gases in the Puguang Gas Field and different from the T_3*x* gases in the Yuanba Gas Field displaying the characteristics of kerogen cracking gas. The gases in the Longgang Gas Field are mainly oil cracking gas assisted by kerogen cracking gas (Fig. 8). Moreover, the observations on the core samples and under the microscope revealed the occurrence of plenty of bitumen in the P_2*ch* reservoirs in the Yuanba Gas Field, and a small quantity distribution of bitumen occurred in T_1f. The recovery of paleo-temperature indicates that the P_2ch-T_1f strata reached 160 °C and 200 °C in Late Jurassic and Early Cretaceous, respectively [40], which also indicated that the P_2ch-T_1f gases in the Yuanba Gas Field were mainly oil-cracking gases.

5.2. Source of alkane gases

Two sets of effective source rocks in the marine strata are developed in the northeastern Sichuan Basin in the Upper Permian Longtan Formation (P_2l), Wujiaping Formation (P_2w), and the Silurian strata. As an example, the C_2h gases in the Wolonghe Gas Field were considered to be derived from the mixing of oil-associated gases from different stages of the Silurian source rocks [16]. The P_2ch-T_1f gases in the Longgang and Puguang Gas Fields were believed to be from the P_2l argillaceous source rocks [1,3,14,15]. As indicated by the chemical compositions (Fig. 2) and the correlation diagrams of $\delta^{13}C_1$ *versus* $\delta^{13}C_2$ (Fig. 3) and $\delta^{13}C_1$ *versus* δD_1 (Fig. 4), the P_2ch-T_1f gases in the Yuanba Gas Field have a good affinity with those in the Puguang and Longgang Gas Fields, and are significantly different from the C_2h gases in the Wolonghe Gas Field.

The dark marlstone and black argillaceous rocks display the thickness of 40–80 m in the Yuanba Gas Field, and the P_2l kerogen of the Well YB 3 displays $\delta^{13}C$ values from −27.8‰ to −24.9‰, with an average of −26.8‰ [41]. The organic matters are of mixing type, and the TOC contents range 0.27%–7.20%, with an average of 2.90%. The measured vitrinite reflectance (R_O) values are generally in the range of 2%–3%; this suggests that it was in the over-mature stage. The gas generation intensity ranges (20–30) × 10^8 m^3/km^2, which has fulfilled the gas source conditions of the formation of a large gas field [6].

The P_2l source rocks display regional differences of source compositions of organic matters and depositional environment; additionally, they also transformed gradually from the gulf lagoon facies to the coastal lake basin-swamp facies. The

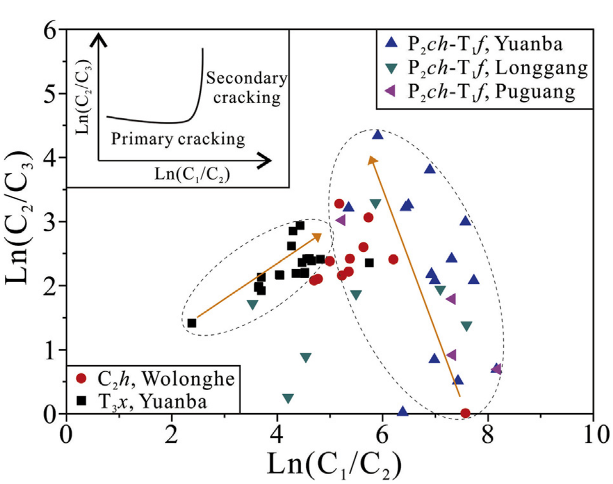

Fig. 8. Correlation diagram of $\ln(C_2/C_3)$—$\ln(C_1/C_2)$ of gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (based on Ref. [36]; data source: this study; Ref. [1,8,12,13,15–21]).

geochemical parameters such as the aromatic molecules indicators and the carbon isotopes of kerogen indicate the dominance of aquatic organism in the source composition of organic matters. The organic matter was deposited in the reducing or weak oxidizing environment; these were all done with mainly the kerogen type II and the undevelopment of coal seam [41]. The correlation between $\delta^{13}C_1$ and δD_1 values indicate that the P_2ch-T_1f gases in the Yuanba Gas Field are mainly mixing gas prone to an oil-associated gas (Fig. 4), this is consistent with the mixing of organic matters prone to a sapropelic type of the P_2l source rocks in the field. This is also the reason why the P_2ch-T_1f gases in the Longgang Gas Field display the characteristics of both coal-derived and oil-associated gases (Fig. 6), in which the coal-derived gas was generated from the humic-prone organic matters. Moreover, the carbon isotopes and the dibenzothiophene compositions of the P_2ch-T_1f reservoir bitumen and the source rocks of gases in the Yuanba Gas Field suggest the same source of bitumen in P_2ch and T_1f reservoirs, i.e., the Permian source rocks [42]. Therefore, the P_2ch-T_1f gases in the Yuanba Gas Field were mainly derived from the secondary cracking of oil generated from the P_2l source rocks.

5.3. Origin and source of CO_2

The P_2ch-T_1f gases in the Yuanba Gas Field mainly display heavy carbon isotopes of CO_2 with $\delta^{13}C_{CO2}$ values generally higher than −8‰, and the P_2ch-T_1f gases in the Longgang and Puguang Gas Fields, as well as the T_3x gases in the Yuanba Gas Field also display similar characteristics. Organic CO_2 generally has a $\delta^{13}C_{CO2}$ value lower than −10‰, whereas inorganic CO_2 commonly displays $\delta^{13}C_{CO2}$ value ranging from −8‰ to 3‰ [43]. Therefore, the CO_2 in these gases are mainly inorganic (Fig. 9).

The T_3x gases in the Yuanba Gas Field does not contain H_2S (Fig. 2b), and they display lower CO_2 contents in its P_2ch-T_1f gases (Fig. 9). Dai et al. [11] demonstrated that the inorganic CO_2 in the T_3x gases in the Yuanba Gas Field were generated from the dissolution of carbonate cement in the sandstone and clastic particles in the carbonate rocks by the organic acid. The high CO_2 content is generally accompanied by the H_2S in the P_2ch-T_1f gases (Fig. 2b), suggesting the TSR alteration. However, the CO_2 derived from TSR alteration is oxidized from the hydrocarbons, and it is of typically organic origin with low $\delta^{13}C_{CO2}$ value. The CO_2 in the natural gases in the northeastern Sichuan Basin has been widely studied, and although the formation mechanism of CO_2 is still controversial, it is generally believed that the CO_2 with low $\delta^{13}C_{CO2}$ value derived from TSR alteration preferentially reacts with the Ca^{2+} and generates calcite cement with low $\delta^{13}C_{CO2}$ value, whereas the CO_2 with high $\delta^{13}C_{CO2}$ value in the gas reservoirs is mainly derived from the interaction between acidic fluid and carbonate reservoirs [30,44–46]. It is supported by the $\delta^{13}C_{CO2}$ values of the P_2ch-T_1f gases in the Yuanba, Longgang, and Puguang Gas Fields increase with the CO_2 contents and gradually tend to be the $\delta^{13}C$ values of reservoir carbonate rocks (0.9‰–3.7‰) (Fig. 9).

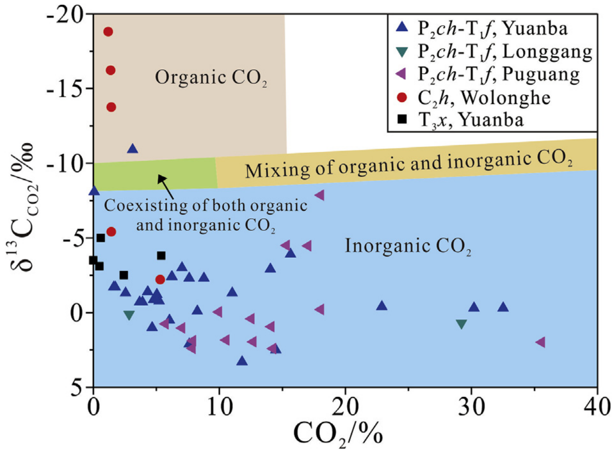

Fig. 9. Correlation diagram of $\delta^{13}C_{CO2}$–CO_2% of gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field (based on Ref. [43]; data source: this study; Ref. [1,8,13,15,16,18,19,21]).

6. Conclusions

The natural gases in the reservoir of the Changxing-Feixianguan Formations within the Yuanba Gas Field are mainly composed of alkane gases which are dominated by methane, and they have dryness coefficients generally higher than 0.995. The nonhydrocarbon gases present are mainly CO_2 and H_2S, which display the contents in the ranges of 0.07%–32.51% with an average content of 8.55%, and 0%–25.70% with an average content of 6.47%, respectively. The $\delta^{13}C_1$ and $\delta^{13}C_2$ values are in the ranges −31.2‰ to −27.9‰ and from −29.9‰ to −25.0‰, respectively; they generally displayed a positive carbon isotopic series. The $\delta^{13}C_{CO2}$ values are from −10.9‰ to 3.3‰, and the δD_1 values are from −156‰ to −107‰. The geochemical characteristics of natural gases such as the C_1/C_{2+3} ratios, the CO_2, and H_2S contents as well as the $\delta^{13}C_1$-$\delta^{13}C_2$ values indicate that the gases have been generally altered by thermochemical sulfate reduction. The identification of gas origin indicates that the natural gases in the Changxing-Feixianguan Formations in the Yuanba Gas Field are mainly composed of oil cracking gases derived from the secondary cracking of oil generated by the source rocks in the Permian Longtan Formation. The carbon and hydrogen isotopic compositions of natural gases display the characteristics of both oil-associated and coal-derived gases, and it leans more to the former, which are involved with the kerogen type II of the source rocks in the Permian Longtan Formation. The CO_2 gases in the gas pools are mainly inorganic and are different from the CO_2 derived from the TSR alteration; they were mainly derived from the interaction between acidic fluids and carbonate reservoirs.

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Conflict of interest

The author declares no conflict of interest.

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References

[1] Fang Hao, Tonglou Guo, Yangming Zhu, Xunyu Cai, Huayao Zou, Pingping Li, Evidence for multiple stages of oil cracking and thermochemical sulfate reduction in the Puguang gas field, Sichuan Basin, China, AAPG Bull. 92 (5) (2008) 611–637.
[2] Yongsheng Ma, Shuichang Zhang, Tonglou Guo, Guangyou Zhu, Xunyu Cai, Maowen Li, Petroleum geology of the Puguang sour gas field in the Sichuan Basin, SW China, Mar. Pet. Geol. 25 (4–5) (2008) 357–370.
[3] Yongsheng Ma, Geochemical characteristics and origin of natural gases from Puguang gas field on eastern Sichuan Basin, Nat. Gas. Geosci. 19 (1) (2008) 1–7.
[4] Keyou Han, Wei Sun, Conditions for the formation of large marine gas fields and gas field clusters in Sichuan Basin, Oil Gas. Geol. 35 (1) (2014) 10–18.
[5] Xusheng Guo, Renchun Huang, Xiaoyue Fu, Jinbao Duan, Gas accumulation and exploration direction of the Permian and Triassic reservoirs of reef-bank facies in Sichuan Basin, Oil Gas. Geol. 35 (3) (2014) 295–302.
[6] Tonglou Guo, Basic characteristics of deep reef-bank reservoirs and major controlling factors of gas pools in the Yuanba Gas Field, Nat. Gas. Ind. 31 (10) (2011) 1–5.
[7] Tonglou Guo, Reservoir characteristics and its controlling factors of the Changxing Formation reservoir in the Yuanba gas field, Sichuan Basin, China, Acta Petrol. Sin. 27 (8) (2011) 2381–2391.
[8] Xusheng Guo, Tonglou Guo, Exploration Theory and its Application in Puguang and Yuanba Gas Fields Located at the Carbonate Platform Margin, Science Press, Beijing, 2012, pp. 1–413.
[9] Xiafei Zhao, Dongfeng Hu, Wenlin Zhang, Yinde Zhang, Bo Tang, Hangjie Lin, Tide-dominated estuarine and deltaic deposition of the upper-Triassic Xujiahe Formation in the Yuanba area, Sichuan Basin, Acta Geol. Sin. 87 (11) (2013) 1748–1762.
[10] Feng Yin, Ruobing Liu, Wei Wang, Yaozu Zhang, Lei Pan, Geochemical characters of the tight sandstone gas from Xujiahe Formation in Yuanba gas field and its gas source, Nat. Gas. Geosci. 24 (3) (2013) 621–627.
[11] Jinxing Dai, Fengrong Liao, Yunyan Ni, Discussions on the gas source of the Triassic Xujiahe Formation tight sandstone gas reservoirs in Yuanba and Tongnanba, Sichuan Basin: an answer to Yinfeng et al. Pet. Explor. Dev. 40 (2) (2013) 250–256.
[12] Tonglou Guo, Yuping Li, Zhihong Wei, Reservoir forming conditions of shale gas in Ziliujing Formation of Yuanba area in Sichuan Basin, Nat. Gas. Geosci. 22 (1) (2011) 1–7.
[13] Pingping Li, Fang Hao, Xusheng Guo, Huayao Zou, Xinya Yu, Guangwei Wang, Processes involved in the origin and accumulation of hydrocarbon gases in the Yuanba gas field, Sichuan Basin, southwest China, Mar. Pet. Geol. 59 (2015) 150–165.
[14] Wenzhi Zhao, Chunchun Xu, Tongshan Wang, Hongjun Wang, Zecheng Wang, Congsheng Bian, Xia Li, Comparative study of gas accumulations in the Permian Changxing reefs and Triassic Feixianguan

oolitic reservoirs between Longgang and Luojiazhai-Puguang in the Sichuan Basin, Chin. Sci. Bull. 56 (31) (2011) 3310–3320.

[15] Guoyi Hu, Cong Yu, Deyu Gong, Xingwang Tian, Wei Wu, The origin of natural gas and influence on hydrogen isotope of methane by TSR in the upper Permian Changxing and the lower Triassic Feixianguan formations in northern Sichuan Basin, SW China, Energy Explor. Exploit. 32 (1) (2014) 139–158.

[16] Anping Hu, Hanlin Chen, Shufeng Yang, Quanyou Liu, Origin of natural gas and main controlling factors of reservoirs in Wolonghe gas field, Acta Pet. Sin. 29 (5) (2008) 643–649.

[17] Chunfang Cai, R.H. Worden, S.H. Bottrell, Lansheng Wang, Chanchun Yang, Thermochemical sulphate reduction and the generation of hydrogen sulphide and thiols (mercaptans) in Triassic carbonate reservoirs from the Sichuan Basin, China, Chem. Geol. 202 (1–2) (2003) 39–57.

[18] Quanyou Liu, Zhijun Jin, Jian Li, Anping Hu, Changchun Bi, Origin of marine sour natural gas and gas-filling model for the Wolonghe Gas Field, Sichuan Basin, China, J. Asian Earth Sci. 58 (2012) 24–37.

[19] Wanchun Wang, Xiaobao Zhang, Ruobing Liu, Houyong Luo, Guocang Wang, Origin of natural gas in terrestrial reservoirs in Yuanba and Heba regions in northeastern Sichuan Basin, China, Acta Pet. Sin. 35 (1) (2014) 26–36.

[20] Ruobing Liu, Tonglou Guo, Mingli Shao, Sources and genetic types of gas in the middle-shallow strata of the Yuanba area, northeastern Sichuan Basin, Nat. Gas. Ind. 31 (6) (2011) 34–38.

[21] Quanyou Liu, R.H. Worden, Zhijun Jin, Wenhui Liu, Jian Li, Bo Gao, Dianwei Zhang, Anping Hu, Chun Yang, 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, Geochim. Cosmochim. Acta 100 (2013) 96–115.

[22] Guangyou Zhu, Shuichang Zhang, Yingbo Liang, Yongsheng Ma, Jinxing Dai, Guoyuan Zhou, Dissolution and alteration of the deep carbonate reservoirs by TSR: an important type of deep-buried high-quality carbonate reservoirs in Sichuan basin, Acta Petrol. Sin. 22 (8) (2006) 2182–2194.

[23] Guangyou Zhu, Shuichang Zhang, Yingbo Liang, Jinxing Dai, Jian Li, Isotopic evidence of TSR origin for natural gas bearing high H_2S contents within the Feixianguan Formation of the northeastern Sichuan Basin, southwestern China, Sci. China Ser. D-Earth Sci. 48 (11) (2005) 1960–1971.

[24] Chunfang Cai, Chunming Zhang, Hong He, Youjun Tang, Carbon isotope fractionation during methane-dominated TSR in East Sichuan Basin gasfields, China: a review, Mar. Pet. Geol. 48 (2013) 100–110.

[25] P.D. Jenden, I.R. Kaplan, Origin of natural gas in Sacramento Basin, California, AAPG Bull. 73 (4) (1989) 431–453.

[26] M.A. Rooney, G.E. Claypool, H. Moses Chung, Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons, Chem. Geol. 126 (3–4) (1995) 219–232.

[27] Anping Hu, Maowen Li, Chun Yang, Jinxing Dai, Yongsheng Ma, Tonglou Guo, Characteristics of reservoir bitumen in Puguang and Maoba gas fields with high H_2S content in north-eastern Sichuan Basin, Acta Pet. Sin. 31 (2) (2010) 231–236.

[28] M. Schoell, The hydrogen and carbon isotopic composition of methane from natural gases of various origins, Geochim. Cosmochim. Acta 44 (5) (1980) 649–661.

[29] Quanyou Liu, R.H. Worden, Zhijun Jin, Wenhui Liu, Jian Li, Bo Gao, Dianwei Zhang, Anping Hu, Chun Yang, Thermochemical sulphate reduction (TSR) versus maturation and their effects on hydrogen stable isotopes of very dry alkane gases, Geochim. Cosmochim. Acta 137 (2014) 208–220.

[30] Xiaoqi Wu, Jinxing Dai, Fengrong Liao, Shipeng Huang, Origin and source of CO_2 in natural gas from the eastern Sichuan Basin, Sci. China Earth Sci. 56 (8) (2013) 1308–1317.

[31] Wanchun Wang, Xiaobao Zhang, Houyong Luo, Liwu Li, Carbon Isotopic characteristics of hydrocarbons and CO_2 of H_2S-rich natural gases and their origin in northeastern Sichuan Basin, Nat. Gas. Geosci. 22 (1) (2011) 136–143.

[32] B.B. Bernard, J.M. Brooks, W.M. Sackett, Natural gas seepage in the Gulf of Mexico, Earth Planet. Sci. Lett. 31 (1) (1976) 48–54.

[33] Jinxing Dai, Xigu Pei, Houfa Qi, Natural Gas Geology in China, vol. 1, Petroleum Industry Press, Beijing, 1992, pp. 1–149.

[34] Shiqian Wang, Geochemical characteristics of Jurassic-Sinian gas in Sichuan Basin, Nat. Gas. Ind. 14 (6) (1994) 1–5.

[35] Quanyou Liu, Jinxing Dai, Jian Li, Qinghua Zhou, Hydrogen isotope composition of natural gases from the Tarim Basin and its indication of depositional environments of the source rocks, Sci. China Ser. D. Earth Sci. 51 (2) (2008) 300–311.

[36] A.A. Prinzhofer, A.Y. Huc, Genetic and post-genetic molecular and isotopic fractionations in natural gases, Chem. Geol. 126 (3–4) (1995) 281–290.

[37] Fengrong Liao, Cong Yu, Wei Wu, Dan Liu, Stable carbon and hydrogen isotopes of natural gas from the Zhongba gasfield in the Sichuan basin and implication for gas-source correlation, Nat. Gas. Geosci. 25 (1) (2014) 79–86.

[38] Wenhui Liu, Research progress on manifold hydrocarbon source and its trace system in marine strata, Nat. Gas. Geosci. 20 (1) (2009) 1–7.

[39] F. Lorant, A. Prinzhofer, F. Behar, A.Y. Huc, Carbon isotopic and molecular constraints on the formation and the expulsion of thermogenic hydrocarbon gases, Chem. Geol. 147 (3–4) (1998) 249–264.

[40] Jingdong Liu, Guangxiang Liu, Liangshu Wang, Xiaoqi Wu, Geochemical characteristics and origin of Permian and Triassic natural gas in Yuanba-Tongnanba area, northeastern Sichuan Basin, Acta Pet. Sin. 35 (3) (2014) 417–428.

[41] Yangming Zhu, Shengxiao Gu, Ying Li, Fang Hao, Huayao Zou, Tonglou Guo, Biological organic source and depositional environment of over-mature source rocks of Longtan Formation in Sichuan basin, Geochimica 41 (1) (2012) 35–44.

[42] Yangming Zhu, Ying Li, Fang Hao, Tonglou Guo, Compositional characteristics and origin of marine and terrestrial solid reservoir bitumen in the northeast Sichuan basin, Acta Petrol. Sin. 28 (3) (2012) 870–878.

[43] Jinxing Dai, Yan Song, Chunsen Dai, Darui Wang, Geochemistry and accumulation of carbon dioxide gases in China, AAPG Bull. 80 (10) (1996) 1615–1626.

[44] Sijing Huang, Keke Huang, Hongpeng Tong, Lihong Liu, Wei Sun, Qianqian Zhong, Origin of CO_2 in natural gas from the Triassic Feixianguan formation of northeast Sichuan Basin, Sci. China Earth Sci. 53 (5) (2010) 642–648.

[45] Fang Hao, Xuefeng Zhang, Cunwu Wang, Pingping Li, Tonglou Guo, Huayao Zou, Yangming Zhu, Jianzhang Liu, Zhongxian Cai, The fate of CO_2 derived from thermochemical sulfate reduction (TSR) and effect of TSR on carbonate porosity and permeability, Sichuan Basin, China, Earth-Sci. Rev. 141 (2015) 154–177.

[46] Quanyou Liu, Zhijun Jin, Xiaoqi Wu, Wenhui Liu, Bo Gao, Dianwei Zhang, Jian Li, Anping Hu, Origin and carbon isotope fractionation of CO_2 in marine sour gas reservoirs in the Eastern Sichuan Basin, Org. Geochem 74 (2014) 22–32.