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ГЕОХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ И ОБРАЗОВАНИЕ ГЛУБИННОГО МОРСКОГО КАРБОНАТНОГО ПРИРОДНОГО ГАЗА В КИТАЕ

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Нефть и газ больших и очень больших глубин были ведущим направлением развития международной разведки месторождений за последние годы, а глубинные нефтегазовые ресурсы распространены преимущественно в трех видах пород: карбонатных, обломочных и магматических, при этом залежи в карбонатных породах составляют около 40 % мировых запасов нефти и газа благодаря своим более высоким коллекторским свойствам. В последние годы ряд крупных нефтегазовых месторождений был открыт в глубокозалегающих морских карбонатных породах в Китае, в основном, в бассейнах Сычуань и Тарим, что создает большой потенциал для нефтегазовой разведки в глубинных морских карбонатных породах. В настоящей статье проведено систематическое исследование образования и источников глубинного природного газа в бассейнах Сычуань и Тарим. Результаты показывают, что источником природного газа в глубинных морских карбонатных коллекторах служат не только поздние глубоководные материнские породы. Крекинг сырой нефти и пиробитума в глубинных коллекторах при высоких температурах также может способствовать образованию в них крупных источников природного газа. Соответственно, при оценке ресурсов природного газа следует учитывать газ, образующийся при крекинге нефти.

Образование природного газа, морские карбонаты, осадочные бассейны Китая

GEOCHEMICAL CHARACTERISTICS AND GENESIS OF DEEP MARINE CARBONATE NATURAL GAS IN CHINA

Li Jian, Li Jin, Shi Jianglong, Li Zhisheng, Xie Zengye, Qi Xuening

Deep and ultradeep oil and gas have been the prominent direction of international exploration in recent years. The deep oil and gas resources are distributed predominantly in three domains of carbonate, clastic, and igneous rocks. The carbonate rock reservoirs contain about 40 % of global oil and gas reserves owing to their superior reservoir properties. In recent years, a number of large oil and gas fields have been discovered in deep marine carbonate rocks in China, especially in the Sichuan and Tarim basins, which shows a vast oil and gas exploration potential in these rocks. In this paper, the genesis and source of deep natural gas in the Tarim and Sichuan basins have been systematically studied. The results show that the natural gas in deep marine carbonate rock reservoirs is generated not only from the later deep-source rocks. The substantial cracking of crude oil and pyrobitumen in the reservoir under conditions of great burial depth and high geotemperature can also provide abundant natural gas sources for deep reservoir. Accordingly, the contribution of gas from oil cracking should be considered in the evaluation of deep natural gas resources.

Natural-gas; genesis; marine carbonate; Chinese sedimentary basins

INTRODUCTION

With the global increase in demand for oil and gas resources and the large-scale development of middle–shallow conventional oil and gas, the difficulty in petroleum discovering is on the increase. Thus, more and more attention is paid to the exploration and development of deep and ultradeep oil and gas (Dyman et al., 2002; Shi et al., 2005; Sun et al., 2010; Zhao et al., 2013; Pang et al., 2015). In the 1950s, the United States conducted the deep oil and gas exploration for the first time. In 1956, the deep petroleum reservoir in the Middle Ordovician Simpson Group, buried at a depth of 4663 m in the Carter-Knox gas field of the Anadarko basin, was discovered. So far, more than 100 countries have carried out deep oil and gas exploration. The results indicate that the deep oil and gas are predominantly in Central and South America, North America, Asia, Africa, the Middle East, and the former Soviet Union. Marine carbonate roks are a pivotal exploration domain which makes up roughly 40% of the world's total oil and gas reserves (Tang et al., 2006). The portion of newly increased global petroleum reserve in the deep and ultradeep layers represents a trend of apparent in-

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crease, and it has already become the alternative domain for future oil and gas exploration. The deep and ultradeep carbonate rocks also contain abundant natural gas resources in China. In recent years, great breakthroughs have been made in study of Sinian–Cambrian carbonate rocks in the central Sichuan Basin, the central area of the Tarim Basin, and other domains representing a vast exploration prospect. However, compared to the middle–shallow conventional oil and gas, the deep carbonate gas reservoirs in China have a large buried depth and complex geologic characteristics; thus, there is greater disagreement as to the source of natural gas. Therefore, the Cambrian–Ordovician natural gas in the Tarim Basin and the Sinian–Cambrian ultradeep natural gas in the Sichuan Basin were selected as the study samples in this paper. The geologic condition and geochemical characteristics of deep natural gas were analyzed to explore the sources of natural gas, providing a theoretical basis for deep natural gas exploration.

GEOLOGIC SETTING

The marine carbonate rocks of China are the oldest in the region and in stratigraphic chronology, and the exploration target layers are buried at a large depth. Especially after experiencing the superposition alteration of multiple tectonic movements, it made the regularity of hydrocarbon accumulation more complex (Zhao et al., 2007; Gu et al., 2012). According to the recent exploration results, the marine carbonate rocks in China have the conditions for the development of large–medium oil and gas fields, and large-scale oil and gas accumulation might take place under these conditions. Currently, the largest individual gas field, the Anyue bulk gas field, in marine carbonate rocks was found in the Sichuan Basin (Du et al., 2014). Also, the Cambrian dolomite primary petroleum reservoirs were found in the central Tarim Basin (Wang et al., 2014).

The Sichuan Basin in the central and western parts of China (Fig. 1), which covers an area of about 19×10^4 km^2, is the large natural gas-bearing superimposition basin in China. The carbonate rocks in the Sinian–Cambrian were in extensive distribution and developed multiple sets of high-quality source rocks and reservoir–seal assemblages, showing an excellent source–reservoir configuration relationship and abundant petroleum resources. The Anyue gas field is located in the central part of the gentle structural belt, the eastern axial part of the Leshan–Longnvsi paleouplift. The black shale in the Sinian Doushantuo Formation and the grayish black mudstone in the third member of the Dengying Formation and mud shale in the Cambrian Qiongzhusi Formation are two sets of major source rocks. The reservoirs of natural gas are the karst reservoir in the Sinian Deng 2 and Deng 4 Members and the fracture–pore reservoir in the Cambrian rocks, respectively (Xu et al., 2012, 2014; Wei et al., 2015a). By the end of 2013, the proved natural gas reservoir had been 4404×10^8 m^3 in the Cambrian Longwangmiao Formation in the Gaoshiti–Moxi area, which has been the huge bulk individual gas field with the largest gas reservoir so far in China.

The Tarim Basin, located in the northwest of China and sandwiched between the Tianshan and Kunlun Mountains tectonic belts, is a large-scale superimposition basin formed by the superposition from the Paleozoic basin to the Mesozoic–Cenozoic foreland basin (Zhai and He, 2004). The natural gas is mainly distributed in the foreland region and platform zone. The ultradeep carbonate rock natural gas is mainly distributed in the platform basin zone. The Cambrian–Lower Ordovician argillaceous limestone and the Middle–Upper Ordovician dark-colored mudstone are two sets of major marine source rocks. The widely distributed thick dolomite is the high-quality reservoir, which is a superior condition of source–reservoir–sealing and has extremely abundant natural gas resources. Currently, the Cambrian–Ordovician ultradeep carbonate rock natural gas is mainly discovered in the Tazhong and Tadong petroliferous zones. The Tazhong petroliferous zone, located in the central part of the Tarim Basin, is a chronically developed successive paleouplift. Upsection, the Cambrian dolomite is made up of the Yuertusi ($€_1$y), Xiaoerbulak ($€_1$x), Wusonggeer ($€_1$w), Avatage ($€_2$a), and Qiulitage ($€_3$ql) formations (Pang et al., 2011). By the end of 2014, industrial oil and gas flow had been obtained in the Zhongshen 1, Zhongshen 1C, and Zhongshen 5 wells, respectively. The primary petroleum reservoir in the Cambrian dolomite was discovered, laying a foundation for the petroleum exploration in the deep car-

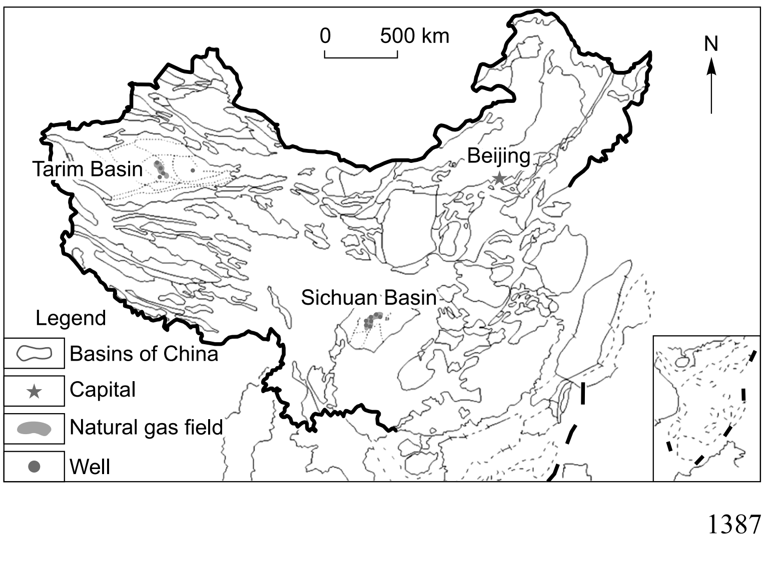

Fig. 1. Regional tectonic division of sedimentary basins and gas field location.

bonate rocks in the Tazhong uplift. The natural gas in the Ordovician carbonate rocks in the Tazhong petroliferous zone is mainly distributed in the Tazhong No. 1 structural belt, and the reservoirs of natural gas are the Upper Ordovician Lianglitage reef and shoal complex and partial karst weathering crust in the Lower Ordovician Yingshan Formation. The Tadong petroliferous zone, located in the eastern part of the Tarim Basin, includes the eastern part of the Manjiaer sag, Yingjisu sag, Luobupo sag, and Tadong low uplift. In the early Cambrian to Ordovician, this area was a continental passive margin of an undercompaction basin and developed thick high-quality source rocks. Currently, these source rocks are at their thermally mature stage and show a huge gas generation potential (Wang et al., 2011).

Study area and sample distribution

The natural gas samples were systematically collected in the Anyue gas field of the Gaoshiti–Moxi area in the Sichuan Basin and in the Tarim platform basin. In the Sichuan Basin, the collection contains 35 samples in the Sinian Dengying Formation of the Anyue gas field and 21 samples in the Cambrian Longwangmiao Formation. In the Tarim platform basin, it contains seven Cambrian samples and 11 Ordovician samples in the Tazhong oil and gas field (eight samples from the central–eastern part in the Tazhong No. 1 fault zone, three from the central–eastern part in the Tazhong No. 1 fault zone) as well as two Cambrian samples from the Tadong low uplift, a total of 86 samples.

RESULTS AND DISCUSSION

Geochemical characteristics of hydrocarbon source rocks

The Sinian–Cambrian hydrocarbon source rocks in the Sichuan Basin are kerogen type I; upsection, they are the Sinian Doushantuo Formation mudstone, Deng 3 Member mudstone, and lower Cambrian Qiongzhusi Formation mud shale (Zou et al., 2014). The Sinian Dengying Formation source rocks are mainly distributed in the northwest, northeast, and southeast parts of the Sichuan Basin (mostly in the southeast Sichuan Basin), and the maximum thickness reaches about 300 m. In the northeast and northwest Sichuan Basin, the thickness is 130 m and a general thickness of 20–40 m, respectively. The residual organic matter content ranges between 1.8 and 2.6%, with an average of 2.0%. The thermal maturity of organic matter (Ro, %) ranges between 1.9 and 6.1%, an average of 3.2%. The gas generation intensity is between 0 and 20×10^8 m^3/km^2. The thickness of the third member of the Sinian Dengying Formation mudstone is 0–40 m; it is mainly distributed in the middle–western, northern, and eastern parts of the basin. The residual organic matter content ranges between 0.1 and 2.2%, with an average of 0.6%. The Ro value ranges between 2.2 and 6.0%, an average of 3.2%. The gas generation intensity is between 0 and 13×10^8 m^3/km^2. The lower Cambrian Qiongzhusi Formation source rocks are mainly distributed in the northeast and middle parts of the Sichuan Basin. The residual organic matter content ranges between 0.1 and 6.6%, with an average of 1.5%. The Ro value ranges between 2.0 and 5.8%, an average of 2.7%. The gas generation intensity is between 0 and 160×10^8 m^3/km^2.

The platform of the Tarim Basin includes two sets of source rocks: the Cambrian–Lower Ordovician argillaceous limestone and the Middle–Upper Ordovician dark-colored mudstone. The source rocks have a higher content of organic matter and the organic matter with kerogen type I–II. The Cambrian–Lower Ordovician argillaceous limestone, 10–80 m thick, is mainly distributed in the Manjiaer sag and platform facies located in the west of the basin. The residual organic matter content ranges between 1.2 and 6.5%, with the maximum reaching 14%. The Ro value ranges between 1.1 and 2.1% at the high–overmature stage, which is dominated by gas generation. The thickness of the Middle–Upper Ordovician dark-colored mudstone ranges between 30 and 180 m, and it is mainly distributed in the platform facies located in the Tadong area and between the Tazhong and Tabei areas. The residual organic carbon content ranges between 0.6 and 1.1%, averaging 0.9%. The Ro ranges between 0.6 and 1.1% at the mature stage, which is dominated by oil generation.

GEOCHEMICAL CHARACTERISTICS OF NATURAL GAS

Component characteristics of natural gas

The natural gas in the Anyue gas field of the Sichuan Basin is dominated by hydrocarbons with a drying coefficient (C_{CH4}/C_{CH4+}) of more than 0.99, belonging to typical dry gas. The content of CH_4 in the natural gas of the Sinian Dengying Formation is 82.65–93.70%, and C_2H_6 content is 0.03–0.07% (Fig. 2), with a trace of propane occasionally. The content of CH_4 in the natural gas of the Cambrian Longwangmiao Formation is 71.46–97.36%, and C_2H_6 content is 0.11–0.27%, with a trace of propane.

The gas components in natural gas from the Cambrian and Ordovician Tazhong and Cambrian Tadong petroliferous zones of the Tarim Basin are dominated by hydrocarbons; the drying coefficient is in a wide range, including dry and wet gas (Fig. 2). The CH_4 content of the natural gas in the Cambrian Avatage Formation of

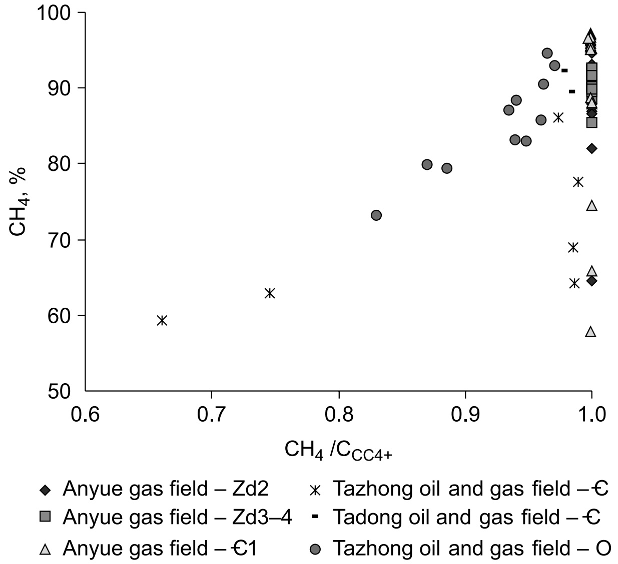

Fig. 2. Relationship of CH_4 and C_{CH4}/C_{CH4+} of deep gas in the Sichuan and Tarim Basins.

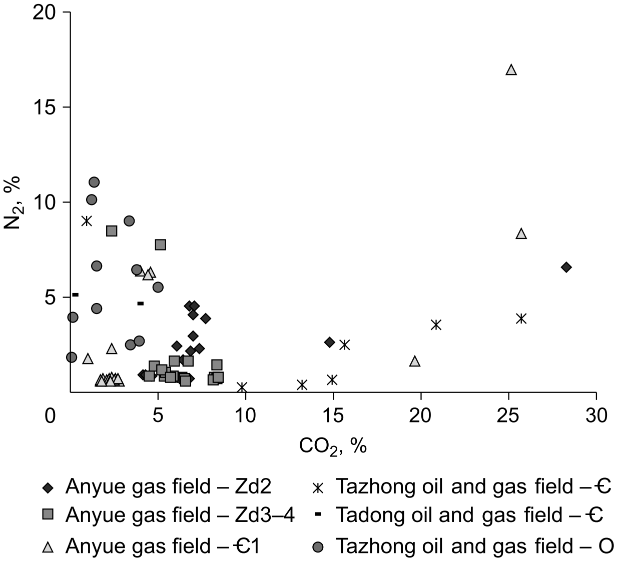

Fig. 3. Relationship of CO_2 and N_2 contents of deep gas in the Sichuan and Tarim Basins.

the Tazhong zone is 62.9–68.6%; C_2H_6 content, 7.4–11.6%; and propane content, 5.7–6.5%. The CH_4 content of the natural gas in the Cambrian Wusonggeer Formation of the Tazhong zone is 59.3–63.4%; C_2H_6 content, 9.5–14.2%; and propane content, 7.0–9.8%. The drying coefficient of the natural gas from these two formations ranges between 0.66 and 0.75, belonging to typical wet gas. The CH_4 content of the natural gas in the Cambrian Xiaorebulake Formation of the Tazhong zone is 62.7–77.7%; C_2H_6 content, 0.47–0.55%; and propane content, 0.14–0.18%. The drying coefficient of the natural gas in the Xiaorebulake Formation is greater than 0.98, which belongs to typical dry gas. The CH_4 content of the Ordovician natural gas in the Tazhong zone is 68.4–93.6%; C_2H_6 content, 0.68–8.46%; and propane content, 0.1–6.3%. The drying coefficient of the Ordovician natural gas in the Tazhong zone ranges between 0.73 and 0.99, averaging 0.93, and it is dominated by wet gas. In the Tadong petroliferous zone, the CH_4 content of the Cambrian natural gas is 89.6–96.3%; C_2H_6 content, 1.3–1.7%; and propane content, 0.23–0.4%. The drying coefficient is greater than 0.97, belonging to typical dry gas.

The natural gas in the Anyue gas field of the Sichuan Basin has a considerable content of nonhydrocarbons dominated by CO_2 and N_2 (Fig. 3), and H_2S is ubiquitously contained. The CO_2 content of the natural gas in the Sinian Dengying Formation is 2.4–27.7%, and N_2 and H_2S contents are 0.74–6.5 and 0.0–3.1%, respectively. The CO_2 content of the natural gas in the Cambrian Longwangmiao Formation is 0.99–19.7%, and N_2 and H_2S contents are 0.6–6.8% and 0.0–4.0%, respectively.

The Cambrian natural gas in the Tazhong and Tadong petroliferous zones of the Tarim Basin showed a greater variance in nonhydrocarbon components, which are dominated by CO_2 and N_2 (Fig. 3), and H_2S is partially contained. The content of CO_2 in the Cambrian natural gas of the Tazhong zone is 0.86–25.7%, and N_2 content is 0.3–9.1%. Among them, the natural gas in the Cambrian Xiaoerbulake and Wusonggeer Formation has a high content of H_2S, which is 0.3–10.1 and 0.1–20.2%, respectively. The content of CO_2 and N_2 in the Cambrian natural gas of the Tadong zone is 0.1–3.8 and 4.7–5.1%, respectively, and there is no H_2S. The Ordovician natural gas in the Tazhong zone has a CO_2 content of 0.01–5.2%; N_2 content is 2.3–11.8%, and there is no H_2S.

Geochemical characteristics of carbon isotope in natural gas components

The $\delta^{13}C_1$ values of the natural gas in the Sinian Dengying and Cambrian Longwangmiao formations are similar, with the former being –33.9 to –32.0‰ and the latter being –34.7 to –30.8‰. The heavier carbon isotope of methane showed a high maturity of natural gas; so, the natural gas of the Sinian Dengying and Cambrian Longwangmiao formations uniformly reached the overmature stage. However, it is worthy to note that the $\delta^{13}C_{C_2H_6}$ values in the Dengying and Longwangmiao formations are radically different. The natural gas of the Sinian Dengying Formation shows a higher $\delta^{13}C_{C_2H_6}$ value, –34.9 to –26.3‰, and the natural gas of the Longwangmiao Formation shows a lower $\delta^{13}C_{C_2H_6}$ value, –35.3 to –29.6‰ (Fig. 4). The variance in the $\delta^{13}C_{C_2H_6}$ value of natural gas from different formations in the Anyue gas field mainly reflects the differences in the type of source materials.

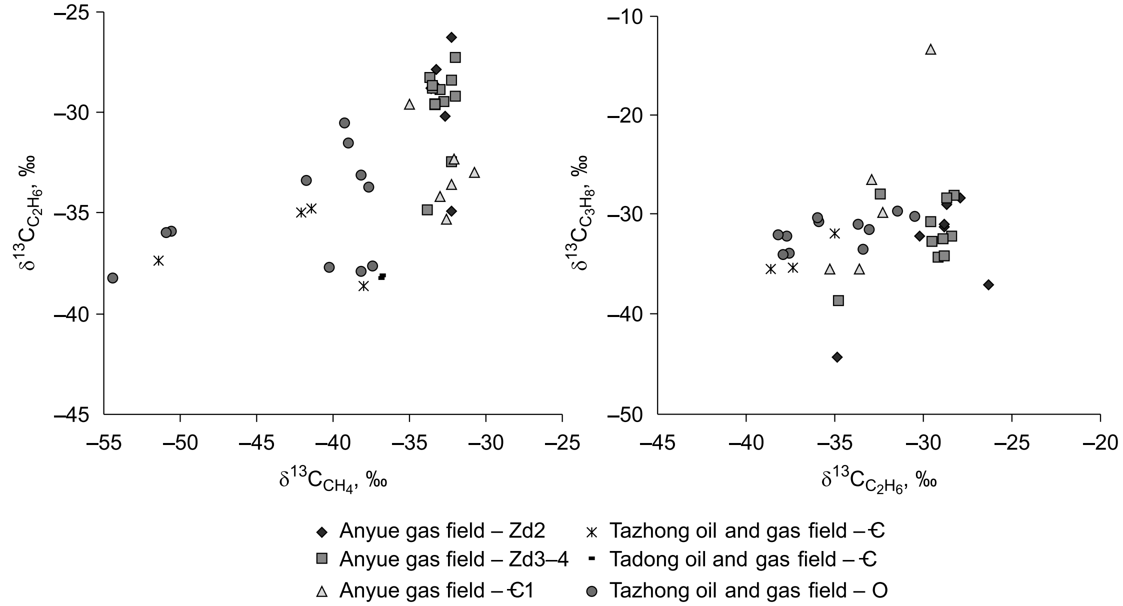

Fig. 4. Distribution of $\delta^{13}C_1$–$\delta^{13}C_2$–$\delta^{13}C_3$ of deep natural gas in the Sichuan and Tarim Basins.

The $\delta^{13}C_2$ value of the Cambrian and Ordovician natural gas in the Tarim Basin is uniformly less than –28.8‰, which belongs to typical oil-type gas (Li et al., 1999; Guo et al., 2007). Compared to that of the gas in the Anyue gas field in the Sichuan Basin, it has a wider range of carbon isotopes. The $\delta^{13}C_1$ value of the Ordovician natural gas in the Tazhong zone is mainly –54.4 to –37.4‰; the $\delta^{13}C_2$ value, –40.6 to –30.5‰; the $\delta^{13}C_3$ value, –38.2 to –30.3‰. The $\delta^{13}C_1$ value of the Cambrian natural gas in the Tazhong zone is –54.4 to –37.4‰; the $\delta^{13}C_2$ value, –38.6 to –34.8‰; the $\delta^{13}C_3$ value, –35.3 to –31.9‰. In the Tadong petroliferous zone, the $\delta^{13}C_1$ value of the Cambrian natural gas is –37.0‰; the $\delta^{13}C_2$ value, –38.1‰; the $\delta^{13}C_3$ value, –32.7‰ (Fig. 4). This lighter carbon isotope of the Ordovician and Cambrian gas reservoirs in the Tarim Basin may be affected by gas generated from cracking of crude oil.

With the increase of the carbon atom number, the natural gas carbon isotope composition becomes heavier, belonging to a normal carbon isotope sequence. The positive carbon isotope series in natural gas usually indicate a single source of natural gas (Chung et al., 1988). However, the reversal of the carbon isotope indicates secondary alteration or a mixed source of natural gas (Dai et al., 2003).

The carbon isotope series of the natural gas in the Cambrian Longwangmiao and Sinian Dengying formations in the Anyue gas field show obvious difference in the carbon isotope sequence. The carbon isotope series in the natural gas of the Sinian Dengying Formation mostly presents characteristics of $\delta^{13}C_1 < \delta^{13}C_2 > \delta^{13}C_3$ (Fig. 5*a*, *b*). At the same time, the $\delta^{13}C_2$ value of the natural gas of the Cambrian Longwangmiao Formation is lower than that of the gas from the Dengying Formation, presenting $\delta^{13}C_1 > \delta^{13}C_2$ (Fig. 5*c*). It is speculated that it resulted from thermal maturity and gas source materials.

The high thermal maturity is the major factor resulting in the carbon isotope sequence of $\delta^{13}C_1 < \delta^{13}C_2 > \delta^{13}C_3$ in the natural gas from the Sinian Dengying Formation of the Anyue gas field. The main reasons are as follows: (1) The thermal maturity (Ro, %) of the Sinian Dengying Formation source rock is 1.97–3.46% at the overmature stage. The Ro of the Cambrian Qiongzhusi and Maidiping Formation source rock is 1.84–2.42%, which is slightly lower than that of the Dengying Formation source rock and corresponds to the high–overmature stage (Wei et al., 2015b); (2) through the thermal simulation experiments on different types of organic matter, the gas generated from organic matter (crude oil, shale, carbonaceous mudstone, etc.) with different sources uniformly presented characteristics of $\delta^{13}C_1 < \delta^{13}C_2 > \delta^{13}C_3$ (Li, 2012). Therefore, it is considered that the characteristic of $\delta^{13}C_1 < \delta^{13}C_2 > \delta^{13}C_3$ in the natural gas from the Sinian Dengying Formation results from the influence of thermal evolution maturity of source material at the overmature stage. Additionally, in light of the general occurrence of H_2S, the effect of thermochemical sulfate reduction (TSR) on the natural gas carbon isotope composition cannot be neglected. Typically, the TSR in the reservoir will preferentially consume heavy hydrocarbons, resulting in the low content of hydrocarbons, such as C_2H_6 and C_3H_8, and then the carbon isotope of residual hydrocarbon will become heavier. The natural gas from the Sinian Dengying Formation has a low content of C_2H_6 and a trace of C_3H_8, while the carbon isotope of C_2H_6 and C_3H_8 is heavier. The geochemical characteristics of natural gas are in accordance with the secondary effect of TSR, indicating that TSR affects the geochemical characteristics of the natural gas in the Sinian Dengying Formation to some extent.

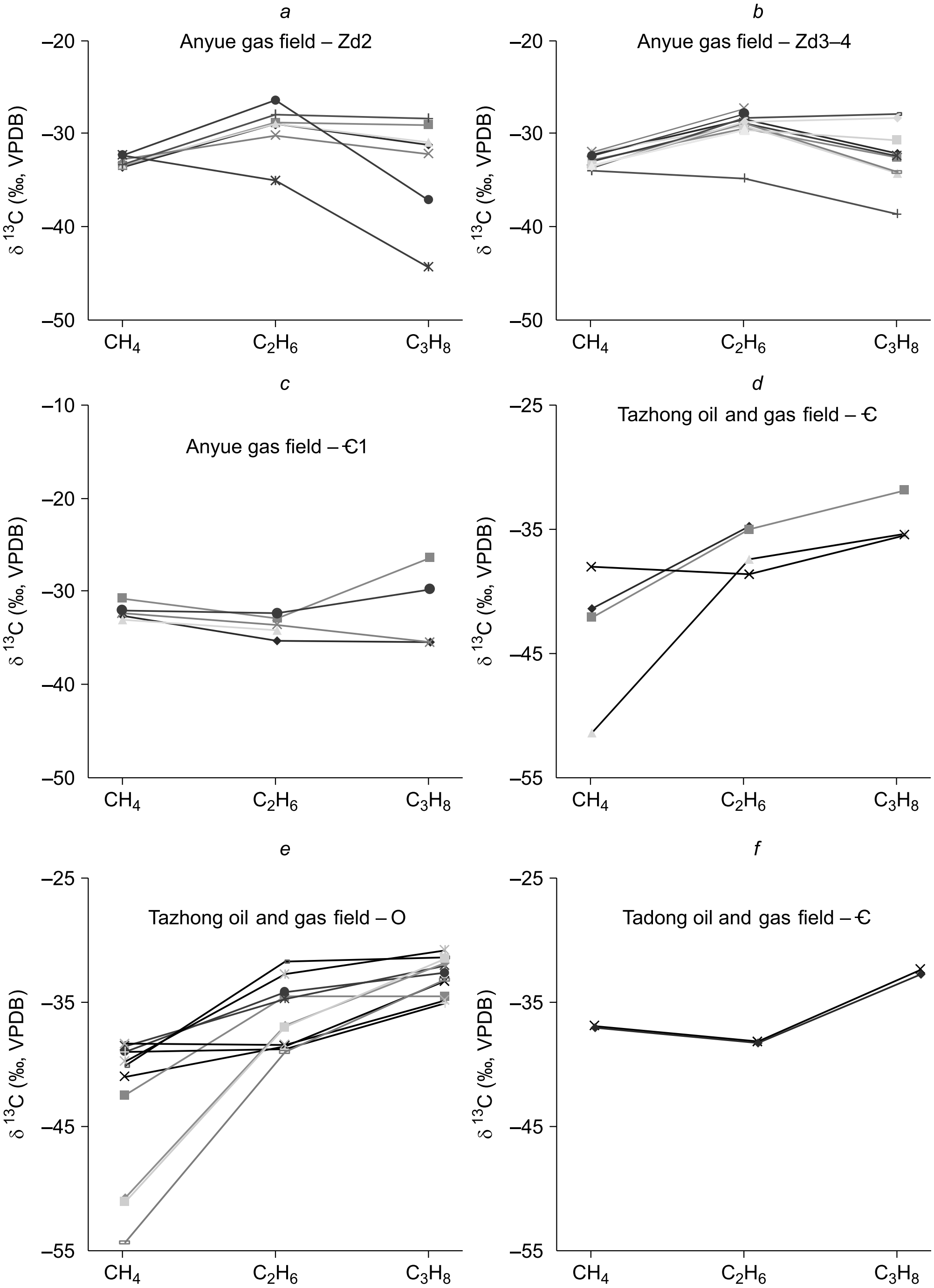

Fig. 5. Distribution diagram of the natural gas carbon isotope in the Sichuan and Tarim Basins.

The $\delta^{13}C_1$ of the natural gas from the Longwangmiao Formation in the Anyue gas field is similar to that of gas from the Sinian Dengying Formation, while the $\delta^{13}C_1$ value of the Longwangmiao Formation is relatively lower. It is speculated that it was affected not only by the thermal evolution but also by the natural gas source material. The effect of TSR is minor. The evidence is as follows: (1) The $\delta^{13}C_2$ of the natural gas from the Longwangmiao Formation is –35.3 to –29.6‰, which is between the values typical of the natural gas from the Sinian Dengying Formation (–34.9 to –26.3‰) and the overlying Permian Qixia–Maokou Formation (mainly –37.0 to –31.1‰). With the shallow burial depth, the $\delta^{13}C_2$ value gradually becomes lower. It might result from the gas resource material in different strata; (2) the H_2S content of the Cambrian Longwangmiao Formation gas reservoir ranges between 0.0 and 4.0%, which is similar to that of gas from the Sinian Dengying Formation (0.0–3.1%). The presence of H_2S is a sign of TSR. The TSR will lead to higher values of $\delta^{13}C_2$ and

$\delta^{13}C_3$. However, the $\delta^{13}C_2$ value in the natural gas from the Longwangmiao Formation does not become higher. Conversely, it becomes lower than that of the gas from the Dengying Formation, which indicates that TSR has no obvious influence on the natural gas from the Longwangmiao Formation.

The carbon isotope sequence of the Cambrian–Ordovician natural gas in the Tazhong oil and gas field of the Tarim Basin is almost $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$, showing characteristics of a positive carbon isotope series (Fig. 5*d*, *e*). Only the individuals show local reversal, indicating that the Cambrian and Ordovician natural gas in the Tazhong zone is relatively single and the secondary factors have a minor effect. The current Ro of Cambrian strata in the Tadong zone is 2.8–3.2%, and the gas reservoir is at the overmature stage (Cheng et al., 2013). In this gas field, the natural gas carbon isotope series presents features of $\delta^{13}C_1 > \delta^{13}C_2 < \delta^{13}C_3$ (Fig. 5*f*), which is similar to the carbon isotope series of the natural gas from the Cambrian Longwangmiao Formation in the Anyue gas field of the Sichuan Basin. It is speculated that the natural gas is both affected by the thermal evolution degree and the source of parental material.

Characteristics of noble gas in natural gas

In the Tarim Basin, the noble gas $^3He/^4He$ ratio in the Tazhong oil and gas field is 3.06×10^{-8}–7.79×10^{-8}, and the $^{40}Ar/^{36}Ar$ ratio is 558–763, showing a typical characteristic of a sediment source. In the Anyue gas field of the Sichuan Basin, the $^3He/^4He$ ratio in the Sinian Dengying Formation is 8.6×10^{-8}–1.2×10^{-7}, and the $^{40}Ar/^{36}Ar$ ratio is 800–1544. The $^3He/^4He$ ratio in the Cambrian Longwangmiao Formation is 5.2×10^{-8}–6.7×10^{-7}; the $^{40}Ar/^{36}Ar$ ratio, 900–1254, also showing a typical characteristic of a sediment source.

Characteristics of nitrogen isotope in natural gas

In the Sinian–Cambrian strata of the Anyue gas field in the Sichuan Basin and the Cambrian–Ordovician strata in the Tazhong and Tadong oil and gas fields in the Tarim Basin, all the natural gas contains a certain amount of N_2, belonging to a middle–low nitrogen-bearing reservoir. The $\delta^{15}N$ of the natural gas from the Cambrian Longwangmiao Formation in the Anyue gas field ranges between –8.7 and –1.8‰; the value in the natural gas in the Sinian Deng 3–Deng 4 Members of the Anyue gas field ranges between –4.6 and –0.8‰ (Fig. 6). The $^3He/^4He$ ratio in the Tazhong oil and gas field is 5.2×10^{-8}–6.7×10^{-8}, and the $^{40}Ar/^{36}Ar$ ratio is 800–1544; therefore, the contribution of mantle-derived gases can be excluded. The genesis study of nitrogen gas indicates that the nitrogen gas in the Sinian–Cambrian natural gas was generated by thermal ammonification of sedimentary organic matter at the high–overmature stage. Additionally, the $\delta^{15}N$ value in the natural gas in the Anyue gas field shows a trend of becoming higher with the increasing age of strata. This indicates that $\delta^{15}N$ in the natural gas shows a close relationship with the thermal maturity of natural gas; therefore, N_2 and natural gas have similar sources.

The $\delta^{15}N$ value of the Ordovician natural gas in the Tazhong zone is relatively low, between 10.6 and –6.0‰ (Fig. 6); the $^3He/^4He$ ratio is 3.06×10^{-8}–7.79×10^{-8}; the $^{40}Ar/^{36}Ar$ ratio is 558–763, showing characteristics of a typical sediment source. It is indicated that nitrogen is generated by the ammonification of sedimentary organic matter at the mature to high mature stages.

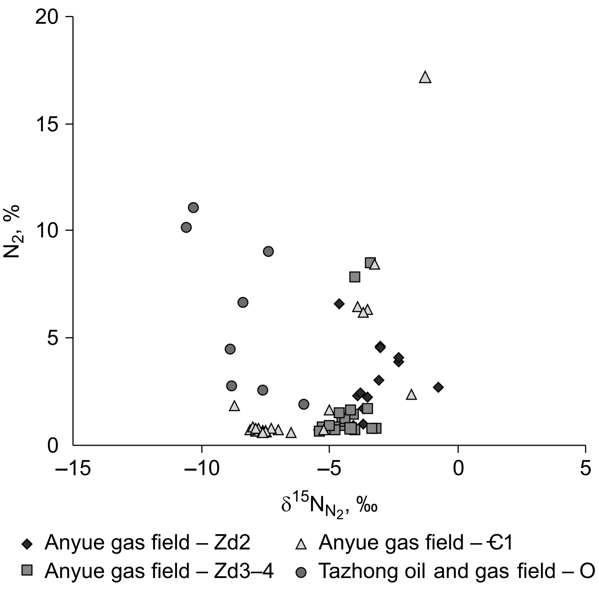

Fig. 6. Relationship of N_2 content and $\delta^{15}N$ of natural gas in the Sichuan and Tarim Basins.

DISCUSSION OF NATURAL GAS SOURCE

Discussion of the Sinian–Cambrian natural gas source in the Sichuan Basin

(1) The natural gas in the Sinian Dengying Formation in the Anyue gas field simultaneously contains the contribution of the Qiongzhusi Formation source rocks, Deng 3 Member dark-colored mudstone, and the crack of bitumen in pores and fractures.

The ethane carbon isotope in natural gas mainly reflects the information on the types of gas source. By comparing the carbon isotope of kerogen in source rock and that of ethane, the gas source can be effectively identified. The lower Cambrian Qiongzhusi Formation shale, the Sinian Deng 3 Member mudstone, and the Sinian Doushantuo Formation mudstone and the Dengying Formation argillaceous carbonate source rocks were developed in the Sichuan Basin. The kerogen of the lower Cambrian (Qiongzhusi and Maidiping formations) shale in the Anyue gas field shows relatively low carbon isotope values, –36.4 to –29.9‰, with an average of –32.8‰. The kerogen carbon isotope value of the Sinian Dengying Formation mudstone samples is –34.5 to –29.0‰, averaging –31.9‰. The kerogen carbon isotope value of the Sinian Doushantuo mudstone samples is –33.7 to about –23.8‰, with the average of –27.8‰. In the Anyue gas field, the natural gas of the Sinian Dengying Formation has a higher $\delta^{13}C_2$ value, –34.9 to –26.3‰. Based on carbon isotope fractionation in oil and gas generation and combined with the accumulation condition of gas reservoirs, it is considered that a certain percentage of the natural gas in the Dengying Formation was generated from the source rocks with a higher kerogen carbon isotope value, while it cannot exclude the source rocks with a lower kerogen carbon isotope value. Thus, it is considered that the natural gas in the Dengying Formation comes from the Sinian and Cambrian source rocks.

The reservoir bitumen is the residue after cracking of crude oil. Therefore, the source rock of the paleoreservoir can be analyzed by making a correlation between the reservoir bitumen and biomarkers in source rocks, thereby indirectly conducting gas–source correlation. The distribution of alkyl dibenzothiophene changes dramatically under thermal conditions, and the relative abundance ratio (4-MDBT/1-MDBT) of isomers in high stability and low stability shows an increasing trend with the increase in the thermal evolution degree. In this paper, relative analysis with the source rock and reservoir bitumen was conducted in the Anyue gas field of the Sichuan Basin. This indicates that the 4-MDBT/1-MDBT ratio in abundant alkyl dibenzothiophene compounds was detected in the extracts from the source rocks of the Sinian Deng 4 and Deng 2 Members, the Cambrian Qiongzhusi Formation mudstone, and the Dengying Formation mudstone. Among them, the Cambrian Qiongzhusi Formation source rock has a 4-MDBT/1-MDBT ratio of 3.57–3.87; for the Sinian Dengying Formation mudstone, it is 3.73–5.65. However, the reservoir bitumen in the Sinian Dengying Formation has a 4-MDBT/1-MDBT ratio of 3.23–4.57, which lies between those of the Cambrian Qiongzhusi Formation source rock and the Sinian Dengying Formation mudstone. It verifies that the Sinian natural gas originated from the Sinian and Cambrian source rocks again.

As described before, the natural gas from the Sinian Dengying Formation in the Anyue gas field shows high thermal maturity, and the corresponding Ro is mostly above 3.0%, which corresponds to the overmature stage. According to the natural gas exploration in the Anyue gas field, there is a considerable quantity of reservoir bitumen in the Sinian Dengying Formation (Cui et al., 2008). The occurrence is dominated by filling in dissolved pores, fractures, and intercrystalline space. The reservoir bitumen indicates the presence of a paleoreservoir, and the cracking of reservoir bitumen and crude oil at a high evolution stage can provide an abundant natural gas source for the Dengying Formation. Zheng et al. (2014) carried out the thermal simulation experiments on the Dengying Formation bitumen filling the reservoir. The results indicated that both the $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{C_2H_6}$ values in the kerogen cracking product were higher, varying from –30.77 to 33.08‰ and from –19.85 to 23.29‰, respectively. The carbon isotope of natural gas generated from bitumen cracking is similar to that of the natural gas in the Dengying Formation of the Anyue gas field, showing a certain affinity between them. Since the mixing of ethane generated from bitumen cracking, it causes great changes in the $\delta^{13}C_{C_2H_6}$ value of the natural gas of the Dengying Formation in the current Gaoshiti–Moxi area and shows obviously higher values. These results indicate that the natural gas in the Dengying Formation is a mixture of gas generated from crude oil and bitumen cracking;

(2) The natural gas of the Cambrian Longwangmiao Formation in the Anyue gas field mainly originates from the Cambrian Qiongzhusi source rock, and the contribution of source rock in the overlying strata cannot be excluded.

The ethane carbon isotope of the natural gas from the Longwangmiao Formation is lighter, mainly owing to the kerogen type of source material. According to the correlation between the carbon isotope in the natural gas from the Cambrian Longwangmiao Formation and the kerogen of Cambrian–Sinian source rocks in the Sichuan Basin, based on the carbon isotope fractionation law in the petroleum generation, it is considered that the natural gas of the Longwangmiao Formation in the Anyue gas field mainly originates from the Cambrian Qiongzhusi Formation source rock.

The $\delta^{13}C_2$ value of the natural gas from the Cambrian Longwangmiao Formation in the Anyue gas field is –35.3 to –29.6‰, ranging between those of the natural gas from the Sinian Dengying Formation (–34.9 to –26.3‰) and the overlying Permian Qixia–Maokou Formation (mainly –37.0 to –31.1‰). The value of $\delta^{13}C_2$ becomes lower as the burial depth becomes shallower. It indicates that the natural gas of the Longwangmiao Formation is generated from the Cambrian Qiongzhusi Formation and the overlying Qixia–Maokou Formation source rocks.

In addition, the 4-MDBT/1-MDBT ratio of the Cambrian Qiongzhusi source rock is 3.57–3.87, and the ratio in reservoir bitumen of the Cambrian Longwangmiao Formation is 2.94–3.40, which is lower than that of the Cambrian Qiongzhusi source rock. To some extent, it also illustrates that the natural gas of the Cambrian Longwangmiao Formation is generated from the Cambrian Qiongzhusi Formation source rocks and some others.

natural gas genesis in the Tarim Basin

(1) The Ordovician natural gas in the middle–east part of No. 1 fault zone in the Tazhong oil and gas field originates from the Middle–Upper Ordovician source rock.

The $\delta^{13}C_2$ values of the Ordovician natural gas in the middle–east part of No. 1 fault zone are mostly –42 to –35‰, according to the linear regression equation between $\delta^{13}C_1$ and Ro (Stahl and Carey, 1975). The Ro of natural gas is mainly 1.5–1.9%, which corresponds to the mature–high mature stage. The N_2 content of natural gas is between 1.89 and 11.1%, and the $\delta^{15}N$ is mainly –10.6 to –6.0‰. According to the nitrogen genesis discrimination standard proposed by Zhu (1999), it belongs to the nitrogen gas from organic matter at the mature–high mature stage (Li et al., 2013). The thermal maturity of the Ordovician natural gas in this area matches the thermal maturity of the Middle–Upper Ordovician source rock;

(2) The Ordovician natural gas in the west part of No. 1 fault zone in the Tazhong oil and gas field originates from the Cambrian–Lower Ordovician source rock. The natural gas is mixed with crude oil cracking gas.

The Ordovician natural gas in the west part of No. 1 fault zone shows a lower drying coefficient compared to the middle–east area; the heavy hydrocarbon content (C_{2+}) is usually greater than 10%, and the natural gas shows normal characteristics of oil-associated gas. The $\delta^{13}C_1$ value of the natural gas is low, from –54.4 to –50.6‰, and the $\delta^{13}C_2$ is –38.2 to –35.9‰. According to the linear regression equation between $\delta^{13}C_1$ and Ro (Stahl and Carey, 1975), the Ro of the natural gas in this area is merely 0.4–0.6%, being divided into low mature natural gas, which does not match with the exploration facts. However, the N_2 content of the natural gas in this area is between 6.5 and 10%. According to the relationship between N_2 content and Ro for oil-type gas established by Li et al. (2013), it is speculated that the corresponding Ro value ranges between 1.2 and 1.5%, which corresponds to the mature–high mature stage. Additionally, the $\delta^{15}N$ of natural gas is between –8.4 and –7.4‰. According to the nitrogen genesis discrimination standard proposed by Zhu (1999), it corresponds to the nitrogen gas from organic matter at the mature–high mature stage. It indicates that the Ordovician natural gas in the west part of No. 1 fault zone in the Tazhong oil and gas field is at the mature–high mature stage, which matches with the thermal maturity of the Middle–Upper Ordovician source rock. Since a series of deeply incised strike-slip faults and No. 1 fault zone in the Tazhong petroliferous zone were well developed, they formed the main pathway for oil migration. The petroleum generated from the Middle–Upper Ordovician source rock mainly migrated along No. 1 fault zone, especially the intersection part of the strike-slip fault and No. 1 fault which is for the longitudinal entering of petroleum into the reservoir. According to this, it is considered that the Ordovician natural gas in the west part of No. 1 fault zone is similarly generated from the Middle–Upper Ordovician source rock.

It is worthy to note that the $\delta^{13}C_1$ value in the Ordovician natural gas is extremely low. Therefore, it is speculated that there exists a mixture of crude oil cracking gas in the Cambrian–Lower Ordovician gas reservoir. It is mentioned above that the Ro of the natural gas in this region is 1.2–1.5%, at an evolution stage which is exactly for crude oil cracking (Hu et al., 2004). When the Ro is less than 1.5%, namely, 1.3–1.5%, the crude oil starts to crack. According to the carbon isotope kinetic theory in natural gas generation, the $\delta^{13}C_1$ of the oil cracking gas at the initial stage of cracking shows extremely low values. Therefore, it is the mixture of initial oil cracking gas that leads to the lower $\delta^{13}C_1$ value in the Ordovician gas reservoir of this area.

In summary, the Ordovician natural gas in the west part of No. 1 fault zone in the Tazhong oil and gas field is mainly generated from the Lower–Upper Ordovician source rock and mixed with the Cambrian–Lower Ordovician crude oil cracking gas;

(3) The Cambrian natural gas in the Tazhong petroliferous zone is crude oil cracking gas which originates mainly from the Middle–Upper Ordovician source rock.

The drying coefficient of the natural gas of the Cambrian Xiaoerbulake Formation in the Tazhong petroliferous zone is higher than 0.98, belonging to typical dry gas. The $\delta^{13}C_1$ of natural gas is mainly –42.2 to –41.8‰, and the corresponding Ro of natural gas is 1.1%, reaching the mature stage, which matches with the Middle–Upper Ordovician source rocks. Therefore, it is speculated that the gas is mainly generated from Lower–Upper Ordovician source rock.

The drying coefficient of the natural gas of the Cambrian Avatage and Wusonggeer formations in the Tazhong petroliferous zone is 0.74–0.78, belonging to typical wet gas. The $\delta^{13}C_1$ of natural gas is mainly –51.4 to –44.7‰. It matches with the Ordovician natural gas in the west part of the Tazhong No. 1 fault, which is speculated to have similar source rock with a mixture of oil cracking gas;

(4) The Cambrian natural gas in the Tazhong petroliferous zone is generated from the Cambrian–Lower Ordovician source rock, belonging to crude oil cracking gas.

The Cambrian natural gas in the Tadong area belongs to typical dry gas, and the $\delta^{13}C_1$ is –37.0‰ with a corresponding Ro of 2.1%. It matches with the thermal maturity of the Cambrian–Lower Ordovician source rock. At the same time, there is a considerable quantity of bitumen in the Cambrian reservoir in the Tadong petroliferous zone, which is filled mainly with dissolved, intercrystalline, and intergranular pores (Cheng et al., 2013). The temperature of the Cambrian gas reservoir reaches 190 °C (Lan et al., 2009), suggesting that the gas reservoir is at the gas generation stage of crude oil cracking. Also, it is speculated that the natural gas is crude oil cracking gas which originates from the Cambrian–Lower Ordovician source rock.

CONCLUSIONS

The natural gas of the Sinian Dengying Formation in the Anyue gas field of the Sichuan Basin originated from the Qiongzhusi source rock, Deng 3 black mudstone, and the cracking gas of bitumen in the Deng 4 pores and fractures. The natural gas of the Cambrian Longwangmiao Formation is mainly generated from the Cambrian source rock, not excluding the contribution of source rock in the overlying strata.

The Cambrian–Ordovician natural gas in the Tazhong area of the Tarim Basin is simultaneously generated from the Cambrian–Lower Ordovician and Middle–Upper Ordovician source rock, and the natural gas is mixed with oil cracking gas from the Cambrian–Ordovician source rock. The Cambrian natural gas in the Tadong oil and gas field is the typical oil cracking gas generated from the Cambrian–Ordovician source rock.

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