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Gas geochemistry and hydrochemical analysis of CBM origin and accumulation in the Tucheng syncline in western Guizhou Province

Lu Zhao¹, Tao Mingxin², Li Qingguang^{1,*}, Wu Pan¹, Gu Shangyi¹, Gao Wei³, Yan Zhihua³

¹ College of Resources and Environmental Engineering, Key Laboratory of Karst Georesources and Environment, Ministry of Education, Guizhou University, Guiyang 550025, China

² College of Resources Science and Technology/Key Laboratory of Environmental Change and Natural Disaster, Ministry of Education, Beijing Normal University, Beijing 100875, China

³ Guizhou Research Center of Shale Gas and CBM Engineering Technology, Guizhou Bureau of Coal Geology, Guiyang 550081, China

*Correspondence: leeqg12@163.com

Abstract: Coalbed water plays an important role in the process of coalbed methane (CBM) generation, storage (adsorption) and production. Because integrated analysis of hydrochemical characteristics and gas geochemical characteristics can offer fresh insights into CBM origin and accumulation, this paper presents an in-depth analysis of the gas geochemistry and hydrogeochemistry characteristics of CBM coproduced water to trace in-situ CBM accumulation in the Tucheng syncline. The main gaseous geochemical parameters ($C_1/\sum C_{1-5}$: 0.97~0.99; C_{HC} : 38.3~72.6; $CDMI$: 5.1~10.5%; $\delta^{13}C-CH_4$: -40.7~-43.2‰; $\delta D-CH_4$: -185.8~-169.2‰; $\delta^{13}C-CO_2$: -13.4~-9.3‰) indicate that thermal gas is the primary genetic type, and hydrogeochemical analysis reveals strong traces of microbial activity. Based on carbon isotope fractionation calculation of $DIC-CO_2-CH_4$ in CBM and coproduced water, we established a quantitative method for calculating biogenic methane production in CBM coproduced

water, finding that production can reach 0.002~0.104 m³/t. Accordingly, we identify a mixed pattern of thermogenic and secondary biogenic CH₄. Taking into account the region's tectonic evolution, we conclude that primary biogenic gas was generated from the Permian to the Early Triassic, thermogenic gas from the Middle Triassic to the Middle Cretaceous, and secondary biogenic gas from the Late Cretaceous to the Quaternary. Secondary biogenic methane's contribution to the gas pool is limited (20.8%~27.6%), whereas thermogenic methane accounts for 72.4%~79.2%.

Keywords: Origin and Accumulation of CBM; Hydrogeochemistry; Gas Geochemistry; Thermogenic Gas; Secondary Biogenic Gas

1. Introduction

Coalbed methane (CBM) is an unconventional and clean source of energy. Total of global resources (buried depth < 2,000 m) are about 268 trillion cubic meters (m³), with China ranking third globally at about 36.8 trillion m³, after Russia and the United States (Yun et al., 2012). Commercial development of CBM in China began in the 1990s, leading to significant progress in key CBM technologies such as those relating to drilling, reservoir modification, and drainage. Some crucial problems remain, however. For example, revealing the origin and accumulation processes of CBM would be an important step toward ensuring successful selection of well locations during CBM exploration and development (Dai, 2009; Tao et al., 2007).

1.1 Isotopic composition of CBM in relation to origin

Scholars classify CBM into biogenic gas and thermogenic gas, with the former classified as either primary or secondary (Rice, 1993; Scott et al., 1994; Tao et al., 2007). Biogenic gas is generated by microbial acetate fermentation, CO₂ reduction and microbial methyl-type fermentation (Rice, 1993; Yee et al., 1993; Strapoć et al., 2007; Mitterer, 2010). Rice (1993) reported $\delta^{13}\text{C-CH}_4$ values for CBM of -80.0‰ to -16.8‰ and $\delta\text{D-CH}_4$ values of -333‰ to -117‰, with $\delta^{13}\text{C-CO}_2$ values of -26.6‰ to +18.6‰, indicating the complexity of CBM's origin and accumulation. Some scholars treat $\delta^{13}\text{C-CH}_4 < -55\text{‰}$ and $\delta\text{D-CH}_4 < -250\text{‰}$ as discriminators of biogenic gas (Clayton, 1998; Scott et al., 1994; Tao, 2006) and R_o (vitrinite reflectance) = 0.5% as the boundary value between primary biogenic and thermogenic gas (Scott et al., 1994).

CH₄ may undergo oxidation during its migration, leading to enrichment of ¹³C and ²H values in the remaining methane in favor of heavier ones (Barker and Fritz, 1981; Whiticar and Faber, 1986). Thus biogenic methane can be also found even when CBM's $\delta^{13}\text{C-CH}_4$ distribution falls within the range of thermogenic methane ($\delta^{13}\text{C-CH}_4 > -55\text{‰}$; Humez et al., 2019). As a result, CBM's complex isotopic composition may create confusion about its source (Whiticar, 1999). For example, CBM's $\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$ values are -68.4‰ to -59.7‰ and -306‰ to -310‰ , respectively, in the Powder River Basin, USA, indicating biogenic methane characteristics, yet thermogenic gas still exists in the middle of the basin (Flores et al., 2008). Similarly, in the San Juan Basin, USA, mean $\delta^{13}\text{C-CH}_4$ value of CBM reached -44.13‰ , clearly above the biogenic methane boundary of -55‰ , but the biogenic gas production process has still been identified, a phenomenon attributed to the mixture of biogenic methane and thermogenic methane in different proportions (Zhou et al., 2005). Accordingly, reliance on isotope data models alone to identify CBM origin is unpersuasive, and more delicate work is needed.

1.2 Hydrogeochemical studies tracing CBM origin and accumulation

Studies have shown that hydrogeochemical characteristics can provide convictive indicators for CBM origin types, accumulation mechanisms, and enrichment (Zhang et al., 2009; Pashin et al., 2014; Zhang et al., 2018). Schlegel et al. (2011) pointed out that a reduced environment with Eh < 200mV, rich in organic matter and circumneutral pH value (pH=4~9), was conducive to generation of biogenic gas. In underground water, changes in dissolved inorganic carbon (DIC) can reveal the biogeochemical behavior of carbon, with positive $\delta^{13}\text{C-DIC}$ values usually associated with methanogenesis in organic matter-rich systems (Bao et al., 2019; Guo et al., 2012). As cases in point, the $\delta^{13}\text{C-DIC}$ values of coal-based water in the Huaibei coalfield, China; the Black Warrior Basin, USA; and the Powder River Basin, USA, are 21.1‰ ~ 26.0‰ , 2.8‰ ~ 13.1‰ , and 12.0‰ ~ 22.0‰ , respectively, and biogenic methane has been identified in all three (McIntosh et al., 2008; Sharma and Frost, 2008; Li et al., 2015a). Surface fresh water that seeps down cracks into coal seams can introduce microbes and nutrients that cause biogenic methane generation and accumulation (Golding et al., 2013; Tao et al., 2020).

In a reducing water environment, when the SO_4^{2-} concentration is consumed to less than several millimolars (mM) by sulfate-reducing bacteria, methanogens begin metabolizing organic matter or CO_2 to generate CH_4 (Brinck et al., 2008; Martini et al., 1998). Accordingly, integrated analysis of the geochemical characteristics of coalbed water and CBM is a prospective approach to evaluating CBM origin and accumulation.

1.3 Tectonic influences on CBM accumulation

Tectonics controls the burial and thermal evolutionary history of coal-bearing strata and influences the generation and accumulation process of CBM (Bao et al., 2016). At the beginning of coalification, organic matters was of low maturity in shallow burial conditions. During this stage, large amounts of primary biogenic gas were produced, but without a stable cap, these gases were not well preserved and were mostly released into the atmosphere. In the second stage, during continuous deposition and burial, coalification proceeded and large amounts of thermogenic gas were produced. However, due to later tectonic activity, most of the thermogenic gas was lost over long periods of geological history (Guo et al., 2020). Formation of secondary biogenic gas is often related to the uplift of coal bearing strata. With the infiltration of surface fresh water, methanogens and other microorganisms inoculated into the coal-bearing strata, allowing secondary biogenic gas generation (Brinck et al., 2008; Golding et al., 2013; Tao et al., 2007, 2020). However, the sealing effect of surface fresh water on structural fissures is also an important factor in CBM preservation. Clearly, comprehensive analysis of the tectonic evolution and hydrogeological processes of coal-bearing basins is needed to shed light on CBM enrichment and evolution.

1.4 The research objectives of this paper

CBM resources in the Liupanshui coalfield total about 1.4 trillion m^3 . Uncertainty regarding the CBM enrichment mechanism has made selection of CBM wells unsuccessful, so that exploration and development of CBM have not been commercialized in this area. According to Tao et al. (2020), CBM is of thermogenic origin throughout the entire Panxian mine, but its $\delta^{13}\text{C}\text{-CH}_4$ values are very similar to those found in the San Juan Basin, where secondary biogenic methane has been found (-44.13‰ ; Zhou et al., 2005). Conversely, coal maturity is lowest in the research area

of this study, the Tucheng syncline, with $R_o=0.8\%\sim1.2\%$ (Li et al., 2015b). According to Ayers (2002), a R_o value around $0.3\%\sim1.5\%$ is favorable for secondary biogenic CH_4 generation. As a result, whether secondary biogenic CH_4 is generated in the Tucheng syncline remains unknown.

Based on the foregoing analysis, this study comprehensively researches water and gas samples from CBM experimental wells in the Tucheng syncline of Panxian mining area. Its aims are to (1) discover whether secondary biogenic CH_4 was generated in the study area, (2) identify the geochemical characteristics and origin of CBM in the Tucheng syncline, and (3) trace the accumulation and evolution of CBM of various origins.

2. Geological background

The Tucheng syncline is located in the northern part of the Panxian mining area in the Liupanshui coalfield, Guizhou Province, China ($104^{\circ}30'\sim105^{\circ}E$, $26.04^{\circ}N$, Fig. 1a). The main coal-bearing stratum is the Upper Permian Longtan Formation, which is 341 m thick and contains 47~66 coalbed layers (Wu et al., 2018). The total thickness of the coal seams is 37~47 m, and the coal-bearing index is about 12%. The Longtan Formation in the Tucheng syncline contains 18 layers of exploitable coalbeds, with Seams 1+3, 6, 9, 12, 15, 16, and 17 targeted for CBM exploration and development (Fig. 1b; Tang et al., 2017). The coal-bearing strata are buried at 560~960 m, and they consist mainly of coalbeds, sandstone, and mudstone, with a layer of bauxite at the bottom. The coal grade level is mainly coking coal ($R_o=0.8\%\sim1.2\%$; Li et al., 2015b), with a relatively simple coal body structure. At present, there are nine CBM development test wells in the study area, all cluster wells. The target coal-bearing strata are first fractured by stages, after which the CBM in these strata is drained. The average daily gas production is $302.88\sim668.40\text{ m}^3$, with accumulative water production of $1,410.8\sim3,229.8\text{ m}^3$ (Wu et al., 2018).

3. Samples and experiments

The nine gas samples were collected using the drainage method. Before sampling, a saturated NaCl solution was prepared in advance, with the solution acidified to a pH of <3 by using 6M HCl to remove CO_3^{2-} , HCO_3^- , and dissolved CO_2 from the saturated

NaCl solution, ensuring that the components and isotopic characteristics of CO₂ in CBM were not influenced. To ensure the stability of the gas sample properties, a saturated HgCl₂ solution was added to the saturated NaCl solution for sterilization (1:50), ensuring that the gas components did not change due to microbial degradation. The preassembled saturated solution was loaded into the glass vial and sealed with a rubber stopper, ensuring that no air bubbles remained during the sealing process. The gas sample was injected while an equal volume of solution was discharged. At least a third of the saturated solution was left in each glass vial to isolate the gas sample in contact with air. After gas collection, the glass vials were inverted and brought back to the laboratory for storage at room temperature pending experimental testing. The test items included gas components, $\delta^{13}\text{C-CO}_2$, $\delta^{13}\text{C-CH}_4$, $\delta\text{D-CH}_4$, $\delta^{13}\text{C-C}_2\text{H}_6$, $\delta\text{D-C}_2\text{H}_6$, and the like.

All the water samples were filtered through a 0.45 μm nylon membrane filter and stored at 4 °C in a refrigerator until analysis. The 50 mL centrifuge tubes containing the water samples had no air bubbles. For cation concentration tests, the samples were acidified to a pH of <3. For anion tests, the filtered water did not add any reagents. The alkalinity was titrated in situ by a Merck alkalinity titration box (production code: 1.11109.0001). Each sample was titrated three times with an error within 0.05mmol/L. For $\delta^{13}\text{C-DIC}$ analysis, the filtered samples were sterilized by a saturated HgCl₂ solution.

Gas components (CH₄, CO₂, N₂, H₂, C₂H₆, C₃H₈, iC₄H₁₀, nC₄H₁₀) were tested using a gas chromatograph (Agilent 78900A) with a hydrogen flame-ionization detector (FID) and a thermal-conductivity detector (TCD). Prior to sample testing, four standard gases with known components were tested in advance and corrected for errors. Anion concentrations such as Cl⁻, SO₄²⁻, and F⁻ were analyzed using an ion chromatograph (Dionex500). A PE-5100 atomic absorption spectrometer was used to analyze cation concentrations, such as K⁺, Na⁺, Ca²⁺, and Mg²⁺. Total dissolved solids (TDS) were equivalent to the total mass concentration of the major ions minus half the bicarbonate concentration.

Gas isotopes ($\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-CO}_2$, $\delta\text{D-CH}_4$, $\delta^{13}\text{C-C}_2\text{H}_6$, $\delta\text{D-C}_2\text{H}_6$) were tested through a MAT253 gas isotope mass spectrometer connected to a gas chromatograph

(GC/C/TC). Driven by a carrier (He) gas stream at a flow rate of 1.0 mL/s, the gas sample was segregated into a PoraplotQ column (25m×0.32mm×10um) at a temperature of 50 °C, followed by a reaction in an oxidation furnace at 940 °C (carbon isotope test) or in a combustion tube at 1,420 °C (hydrogen isotope test) and finally into MAT253 for testing. The $\delta^{13}\text{C}$ -DIC values of water were tested using a MAT253 gas isotope mass spectrometer equipped with a Gasbench. The test procedures were implemented in strict accordance with national norms and related analytical standards, with determination of carbon and hydrogen isotopes carried out using Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW) as the standard substances, respectively. The accuracy of the $\delta^{13}\text{C}$ test is $\pm 0.06\text{‰}$ and that of the δD test $\pm 1.0\text{‰}$. All analysis was carried out in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, China. To calibrate the isotopic test data, one international standard sample and two laboratory standard samples were used to analyze the carbon and hydrogen tests.

4. Result

4.1 CBM composition

From Table 1, the main components of the gas produced from the CBM wells in the Tucheng syncline are CH_4 , N_2 , CO_2 , and C_2H_6 . CH_4 content ranges from 79.6% to 86.7%, with a mean value of 83.6%. C_2H_6 content ranges from 1.1% to 2.0%, with a mean value of 1.5%. $\sum\text{C}_{2-\text{n}}$ content is less than 3.0%. CO_2 content ranges from 4.6% to 9.8%, with a mean value of 6.9%. N_2 content ranges from 3.0% to 12.8%, with a mean value of 8.3%. The content of other gases is below 1.0%. CDMI ($\text{CDMI} = \text{CO}_2 / (\text{CO}_2 + \text{CH}_4)$) values ranges from 5.1% to 10.5%, with a mean value of 7.7%. C_{HC} ($\text{C}_{\text{HC}} = \text{C}_1 / (\text{C}_2 + \text{C}_3)$) values are 38.3–72.6, with a mean value of 51.8. The $\text{C}_1 / \sum\text{C}_{1-5}$ ratio is 97.4% to 98.6%, with a mean value of 98.0%.

4.2 Isotopic composition of CBM

From Table 2, $\delta^{13}\text{C}$ - CH_4 values range from -40.7‰ to -43.2‰ , with a mean value of -41.4‰ . δD - CH_4 values range from -185.8‰ to -169.2‰ , with a mean value of -177.7‰ . $\delta^{13}\text{C}$ - CO_2 values range from -13.4‰ to -9.3‰ , with a mean value of -11.7‰ .

$\delta^{13}\text{C}-\text{C}_2\text{H}_6$ values range from -27.5‰ to -25.1‰ , with a mean value of -26.1‰ . $\delta\text{D}-\text{C}_2\text{H}_6$ values range from -102.8‰ to -90.6‰ , with a mean value of -96.2‰ .

4.3 Hydrochemical composition of CBM coproduced water

As Table 3 indicates, the test results show water samples that are neutral to weakly alkaline, with pH of 7.0~8.5. The concentration of Na^+ is 1,526.6~3,674.6 mg/L, and the concentration of Cl^- is 2,581.4~5,224.5 mg/L. The concentration of HCO_3^- is the second most anion, ranging from 79.3 to 954.0 mg/L, and the concentration of SO_4^{2-} is very low, with a mean value of 0.1 mg/L. Ca^{2+} and Mg^{2+} concentrations are low, at 24.0~108.1 mg/L and 7.0~26.1 mg/L, respectively, and the TDS concentration is 4,414.2~9,307.8 mg/L. $\delta^{13}\text{C}-\text{DIC}$ ranges from $+0.4\text{‰}$ to $+21.3\text{‰}$, with a mean value of $+8.7\text{‰}$.

5. Discussion

5.1 Origin of CBM in the Tucheng syncline

5.1.1 CBM gas component index

According to Table 1, the mean CO_2 content is 6.9% in the CBM of the Tucheng syncline, a figure similar to those seen in Huaibei coalfield, China, where CBM is of mixed source ($=7.0\%$; Li et al., 2015a). CDMI is commonly used to identify the source of CO_2 in CBM: If CO_2 composition exceeds 60%, the gas is inorganic, versus organic for compositions below 15% (Clayton, 1998). As Table 1 shows, CDMI values in CBM range from 5.1% to 10.5%—substantially lower than 60%, ruling out an inorganic origin of CO_2 . The $\delta^{13}\text{C}-\text{CO}_2$ values and CDMI values are used as the discriminatory basis for building the model, as Fig. 2a shows, and it can be found that the CO_2 in the Tucheng syncline has an organic thermal source. Golding et al. (2013) took $\delta^{13}\text{C}-\text{CO}_2=-10\text{‰}$ as the boundary between organic and inorganic sources of CO_2 (Fig. 2b), with CO_2 data points of Tucheng CBM distributed mainly inside the organic source area.

A hydrocarbon index ($\text{C}_{\text{HC}}=\text{C}_1/(\text{C}_2+\text{C}_3)$) below 100 might indicate that CH_4 is thermogenic, an index above 1,000 that biogenic gas is present, an index of 100–1,000 that the gas is from a mixture of sources, and an index above 1,000 that a classic biogenic gas is present (Faber and Stahl, 1984). Distribution of C_{HC} in Tucheng CBM ranges from 38.3 to 72.6, with a mean value of 58.1 (Table 1)—well below 100,

demonstrating the characteristics of thermogenic gas on the whole. The gas dryness index ($C_1/\sum C_{1-5}$) can indicate the source of CBM, and the distribution of $C_1/\sum C_{1-5}$ values in Tucheng CBM ranges from 97.4% to 98.6%, indicating that the gas is dry (dryness index > 95%; Moore, 2012; Tao et al., 2007). In general, only biogenic and pyrolysis gas have the characteristics of dry gas (Moore, 2012; Scott et al., 1994; Tao et al., 2007). The coal in the Tucheng syncline is merely coking coal, with R_o values of only 0.8%~1.2%—far from the stage of pyrolysis gas ($R_o > 2.0\%$; Scott et al., 1994)—so the $C_1/\sum C_{1-5}$ values also indicate the existence of biogenic gas. Additionally, the R_o value (>0.5%) indicates that if biogenic gas is present, it is likely secondary.

5.1.2 CBM isotope index

Many leading scholars took $\delta^{13}C-CH_4 = -55\text{‰}$ as the boundary between thermogenic and biogenic methane and concluded that $\delta^{13}C-CH_4 < -55\text{‰}$ pointed to biogenesis (Clayton, 1998; Rice, 1993; Scott et al., 1994), whereas Smith and Pallasser (1996) considered that the $\delta^{13}C-CH_4$ value of biogenic methane can reach -50‰ . The distribution of $\delta^{13}C-CH_4$ values in the Huaibei coalfield, China, ranges from -75.5‰ to -42.8‰ (Li et al., 2015a), which is lighter than in the Tucheng syncline overall. Combining $\delta^{13}C-CH_4$ and C_{HC} values, the CBM sources from these two mining areas were analyzed using the diagram in Fig. 3a (Whiticar, 1999). All Tucheng data points are located within the range of thermogenic gas, whereas the Huabei data points are more dispersed.

The $\delta D-CH_4$ values of acetate fermentation gas range from -400‰ to -250‰ and CO_2 reduction gas from -250‰ to -150‰ , with the $\delta D-CH_4$ values of thermogenic gas not less than -250‰ and pyrolysis gas even heavier than -200‰ in CBM (Table 4, Rice, 1993; Whiticar and Faber, 1986; Whiticar, 1999). Whiticar (1999) concluded that the $\delta^{13}C-CH_4$ and $\delta D-CH_4$ boundary values for microbial gas from CO_2 reduction versus methyl-type fermentation may be -60‰ and -250‰ , respectively. The $\delta D-CH_4$ values in the Tucheng syncline range from -185.8‰ to -169.2‰ , with a minimum value of -185.8‰ —greater than -250‰ , indicating a gas of thermal origin and excluding acetate fermentation gas, consistent with the results in Fig. 3b. The $\delta D-CH_4$ values of CBM in the Tucheng syncline all exceed -200‰ within the distribution range of pyrolysis gas,

but analysis of the previous section showed that the coal grade in this area does not reach the stage of generating pyrolysis gas, so this thermogenic gas should be thermal degradation gas. In addition, $\delta D-CH_4$ values range from -250‰ to -150‰ , so the possibility of CO_2 reduction cannot be ruled out.

Evaluation of the isotopic composition of CO_2 is a very efficient method of identifying CBM origin. Rice (1993) summarized the range of $\delta^{13}C-CO_2$ values for CBM as -26‰ to $+18.6\text{‰}$, but this can vary for gases of different origin. Whiticar and Faber (1986) reported that $\delta^{13}C-CO_2$ relevant to microbial methane ranged from -40‰ to $+20\text{‰}$, that thermal degradation gas ranged from -5‰ to -25‰ , and that mantle sources ranged from -5‰ to -9‰ (Fleet et al., 1998; Kotarba et al., 2001). From Table 2, the $\delta^{13}C-CO_2$ values in the Tucheng syncline range from -13.4‰ to -9.3‰ , within the range of thermal degradation gas—consistent with the results shown in the classical illustration of Fig. 3c, in which all Tucheng data points fall within the range of thermal genesis. What's more, the maximum $\delta^{13}C-CO_2$ value in Tucheng is -9.3‰ , lower than the minimum $\delta^{13}C-CO_2$ boundary value of mantle source CO_2 of -9‰ , which excludes it as a mantle source gas. Additionally, because the $\delta^{13}C-CO_2$ values fall in the range -40‰ to $+20\text{‰}$, their variance might be relevant to microbial methanogenesis.

CBM sources can be distinguished by exploiting fractionation between CO_2 and CH_4 (Flores et al., 2008; Strapoć et al., 2007). Flores (2008) revealed that the carbon isotope fractionation coefficients between CO_2 and CH_4 ($\alpha_{CO_2-CH_4}$) for microbial gas from methyl-type fermentation ranged from 1.03 to 1.06, versus 1.06 to 1.09 for CO_2 -reduction gas. To more precisely define of the origins of CBM, Li et al. (2015a) refined the $\alpha_{CO_2-CH_4}$ values (Fig. 3d), finding that $\alpha_{CO_2-CH_4}$ values ranged from 1.020 to 1.040 for thermogenic gas and from 1.060 to 1.080 for CO_2 -reduction gas, with $\alpha_{CO_2-CH_4}$ values between 1.040 and 1.060 indicating CBM of mixed sources. In Fig. 3d, the Tucheng data points are distributed in the thermogenic region only, indicating that CBM is the thermal origin under this model.

Tao et al. (2020) noted that $\delta^{13}C-CH_4$ is positively correlated with coal rock maturity (R_o), using the thermal simulation regression equation ($\delta^{13}C-CH_4 = 22.42 \log R_o - 34.8$; Liu and Xu, 1999) to explore the $\delta^{13}C-CH_4$ characteristics of CBM

from adjacent synclines. Based on the previous, the R_o values of Tucheng coal are 0.8%~1.2%, with $\delta^{13}\text{C-CH}_4$ values of -35.0‰ ~ -33.0‰ produced by the foregoing equation. However, based on Table 2, the $\delta^{13}\text{C-CH}_4$ values measured in the laboratory ranges from -43.2‰ to -40.7‰ , for measured values clearly much lighter than theoretical ones. This divergence may reflect the action of microbial modification, hydraulic erosion, bitumen, or liquid hydrocarbon pyrolysis (Kinnon et al., 2010). Because hydrodynamic conditions in the Tucheng syncline are relatively weak, hydraulic erosion is less likely (Wu et al., 2018). What's more, because the maturity of the Tucheng coal (0.8%~1.2%) is far below the stage of pyrolysis ($R_o > 2.0\%$), microbial action is quite likely responsible for this phenomenon.

As the foregoing analysis indicates, microbial modification can cause divergence in the values of $\delta^{13}\text{C-CH}_4$, $\delta\text{D-CH}_4$, and $\delta^{13}\text{C-CO}_2$, which may obscure the origins of CBM. To avoid such an effect, more isotopic characteristics should be investigated. Rice (1993) stated that the $\delta^{13}\text{C-C}_2\text{H}_6$ of global CBM ranges from -32.9‰ to -22.8‰ and that coexistence of heavier isotopes of ethane (-28‰ to -24‰) and lighter isotopes of methane ($< -55\text{‰}$) may indicate a mixture of thermogenic ethane and biogenic methane. According to the classic diagram (Fig. 4; Kotarba et al., 2001; Tao et al., 2007), carbon isotopic compositions of methane and ethane in the Tucheng syncline are located to the left of the R_o split line, indicating that thermogenic CBM is subject to obvious bacterial reduction and generated biogenic methane. Accordingly, although the dominant source of Tucheng CBM is thermogenic gas, it does suffer from microbial modification.

5.2 Hydrochemical characteristics and water-rock interactions

5.2.1 Water quality type and solute sources

Van Voast (2003) pointed out that coal-based water in China is mainly Na-HCO_3 and $\text{Na-HCO}_3\text{-Cl}$, with $\text{Na-SO}_4\text{-Cl}$, Na-SO_4 , and Na-Cl types also distributed. Based on Table 3, the concentrations of both Cl^- and Na^+ are the largest among all ions in CBM coproduced water in the study area, and the sum of Cl^- and Na^+ concentrations accounts for about 93% of the TDS concentration. In the major ions distribution diagram (Fig. 5a), the concentrations of Cl^- and Na^+ are at two peaks, so the dominant water quality

is the Na-Cl type, as is well supported by its ionic distribution in the Piper diagram (Fig. 5b).

Analysis of end-member discrimination is an effective way to identify the source of solutes of formation water. The equivalent ratios of HCO_3^- , Mg^{2+} , and Ca^{2+} to Na^+ , respectively, can effectively classify the solute sources of formation water into three regions of evaporites, silicates, and carbonates (Fig. 6a, b), with ionic composition governed mainly by the nearest end-member group. According to Li et al. (2016), the CBM coproduced water in the Huabei coalfield is governed by evaporites and silicates. Analysis of CBM coproduced water in the Tucheng syncline shows that the data points distributed around the evaporites, revealing that the solute source is the dissolution of evaporites.

The variation of $(\text{Na}+\text{K})^*/\text{HCO}_3^-$ versus $(\text{Mg}+\text{Ca})^*/\text{HCO}_3^-$ in formation water can reveal the contributions of carbonate and silicate weathering. The end members of carbonates have a higher $(\text{Mg}^{2+}+\text{Ca}^{2+})^*/\text{HCO}_3^-$ ratio and lower $(\text{Na}^++\text{K}^+)/\text{HCO}_3^-$ ratio, whereas the end members of silicates have a higher $(\text{Na}^++\text{K}^+)/\text{HCO}_3^-$ ratio and lower $(\text{Mg}^{2+}+\text{Ca}^{2+})^*/\text{HCO}_3^-$ ratio (Fig. 6c, Gaillardet et al., 1999). The data points in the study area are distributed mainly around the silicates end member, indicating that CBM coproduced water is governed by silicate dissolution. Meanwhile, based on variations in $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$, the sources of hydrochemical compositions can be divided into three end-member groups (Fig. 6d), the limestone end member has a lower $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio (0.03) and $\text{Na}^+/\text{Ca}^{2+}$ ratio (0.005), and the dolomite end member has a higher $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio (1.00) and a lower $\text{Na}^+/\text{Ca}^{2+}$ ratio (0.01; Gaillardet et al., 1999). The relative ion ratios in the study area are distributed mainly in the silicate region in Fig. 6d, also indicating that the chemical compositions of the formation water are controlled by silicate dissolution. In summary, we believe that the coal-based water of the Tucheng syncline is a mixture of coalbed water controlled by evaporites and silicates. In addition, according to Wu et al. (2018), the hydrogen and oxygen isotopic compositions of CBM coproduced water in Tucheng are all above the LMWL, indicating that the formation's water was recharged by meteoric water.

5.2.2 Water–rock interactions

Ion ratio can offer insights into water–rock interactions. The mean value of the sodium chloride coefficient ($r\text{Na}^+/r\text{Cl}^-$) of the CBM coproduced water in Tucheng is about 1.09 (Table 5), indicating an excess of Na^+ . According to Magesh et al. (2020), $r\text{Na}^+/r\text{Cl}^-$ of formation water in excess of 1.00 indicates that the water column has undergone intense silicate weathering, with Na^+ coming mainly from silicate dissolution (feldspar) and evaporite dissolution. This conclusion is in accordance with end-member analysis in Section 5.2.1.

Excess of Na^+ also indirectly indicates ion exchange in the formation water (Zhang et al., 2018). Chlor-alkali index (CAI) can indicate the exchange process of Na^+ (Magesh et al., 2020). Positive CAI_1 (Eq. 1) and CAI_2 (Eq. 2) indicates a forward reaction consistent with Eq. 3, whereas negative values signify a reversible reaction. The average values of CAI_1 and CAI_2 in the CBM coproduced water within the study area were calculated to be -0.12 and -1.15 (Table 5), respectively, revealing exchange of Ca^{2+} and Mg^{2+} in formation water with Na^+ in the surrounding rocks:

$$\text{CAI}_1 = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / \text{Cl}^- \quad (1)$$

$$\text{CAI}_2 = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / (\text{HCO}_3^- + \text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{NO}_3^-) \quad (2)$$

$$(\text{Ca}^{2+} + \text{Mg}^{2+})(\text{rock}) + 2\text{Na}^+(\text{water}) = (\text{Ca}^{2+} + \text{Mg}^{2+})(\text{water}) + 2\text{Na}^+(\text{rock}) \quad (3)$$

The mean value of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ in our water samples is about 0.49 (Table 5), indicating excess DIC. The main sources of DIC are carbonate dissolution, atmospheric input, and organic matter degradation. According to Table 6, the saturation index (SI) of carbonates (aragonite, calcite, dolomite) generally exceeds zero, indicating supersaturated carbonates and almost no dissolution of limestone. Combined with analysis of end member discrimination, the possibility of HCO_3^- originating from carbonate dissolution can be ruled out. Considering the good confinement of the stratum in the study area, the infiltration of atmospheric precipitation could not be its dominant source. In addition, according to the analysis in Section 5.1, CO_2 is an organic source and the main origin of CBM is thermal degradation gas. CO_2 from thermal degradation of organic matter might thus be an important source of HCO_3^- in the formation water. What's more, microbial degradation releases CO_2 , often accompanied by sulfate reduction and methanogenesis.

According to the saturation index in Table 6, the dissolution of sulfate minerals is favorable in CBM coproduced water within the study area. However, the SO_4^{2-} concentration (0.001 mM) in formation water is very low, even lower than for Ca^{2+} , Mg^{2+} , Ba^{2+} (1.34 mM; 0.69 mM; 0.08 mM). When the desulfurization coefficient ($r\text{SO}_4^{2-}/r(\text{SO}_4^{2-}+\text{Cl}^-)$) of the water samples approaches zero (0.001% to 0.002%), SO_4^{2-} should be consumed in large quantities by sulfate reduction, generating appreciable amounts of HCO_3^- (Eq. 4; Brinck et al., 2008). When the sulfate reduction reaction nears completion, hydrochemical conditions are favorable for methanogenesis.

5.2.3 Identification of microbial activity and microbial methane generation

5.2.3.1 Identification of methanogenesis based on hydrogeochemistry analysis

Previous researchers have reported that hydrogeochemical information such as pH, ion concentration, $\delta^{13}\text{C}$ -DIC values, hydrogen and oxygen isotopic composition, and hydrodynamic conditions are strongly linked to the genesis of biogenic methane (McIntosh et al. 2004; Brinck et al., 2008; Kinnon et al., 2010; Schlegel et al., 2011; Golding et al., 2013; Pashin et al., 2014). Methanogens are strictly anaerobic and thus prefer conditions of reduction for generation of methane. As Table 3 shows, Eh values are generally low, with a mean value of -40 (<200 mV); dissolved oxygen (DO) values are uniformly below 4; and pH values are 7.1~8.5, indicating that CBM coproduced water is in anaerobic, which facilitates generation of biogenic methane (Schlegel et al., 2011).

Ionic concentration can also provide important information about the origin of CBM. McIntosh et al. (2004) observed that microbial gas is generated when sulfate concentration falls below several millimolars, as well as that methanogenesis significantly alters hydrochemical composition, commonly in the form of very high HCO_3^- concentrations (10~70 mM), low Ca/Mg molar ratios (<1.5), and minimal dolomite precipitation. According to Table 3, HCO_3^- concentrations range from 0.8 to 9.8 mM, and the molar ratio distribution of Ca to Mg ranges from 1.07 to 3.40, with partly values below 1.5—slightly differing from the characteristic values proposed by McIntosh et al. (2004), perhaps owing to the scale of biogenic gas enrichment and the

degree of water–rock interaction. What is certain, however, is that these values reflect the characteristics of biogenic gas modification.

The quality type of CBM coproduced water and CBM origin seem clearly linked. In Table 7, we summarize the relationships between both in various coalfields from around the world, observing that the share of thermogenic gas exceeds that of biogenic gas in Na-Cl-type formation water, whereas biogenic gas share exceeds that of thermogenic gas in Na-HCO₃ and Na-HCO₃-Cl-type formation water—showing that higher concentrations of Na⁺ and Cl⁻ coalbed water tend to be related with thermogenic gas. The dominant origin of CBM in Tucheng is thermogenic gas, which verifies our conjecture.

According to Wu et al. (2018), D and ¹⁸O isotopic compositions both tend to be heavier in our study area. The causes of D drift include alteration of formation water by methanogenesis, in which methanogens preferentially deplete water-derived H and enrich residual groundwater with D (Eq. 5; Whiticar, 1999); water–rock interactions at low temperature, such as precipitation of carbonate and clay in the coal interlayers leading to depletion of ¹⁸O and enrichment of D in groundwater (Kloppmann et al., 2002); and hydrocarbon exchange reactions in reducing conditions, with the H isotope exchange reaction between formation water and hydrocarbon of coal enriching D in residual water (Eq. 6; Zhang et al., 2018). This study proposes that D drift is caused by a combination of the water–rock interactions and methanogenesis.

The most efficient evidence for biogenic gas generation is DIC. Positive $\delta^{13}\text{C}$ -DIC values occur commonly during methanogenesis in an organic matter–rich system (e.g., coal and shale), which generates methane by the microbial degradation of organic matter (Golding et al., 2013). Aravena et al. (2003) and Strapoc et al. (2007) pointed out that methanogenesis occurs in shallow groundwater when widespread distribution of $\delta^{13}\text{C}$ -DIC values in the water column ranges from –20‰ to +6.5‰. Additionally, according to Yang et al. (2020), $\delta^{13}\text{C}$ -DIC values of 0~+10‰ indicate potential influence by microbial reduction. Because the $\delta^{13}\text{C}$ -DIC values of CBM coproduced

water in Tucheng are +0.4‰~+21.3‰, with a mean value of +8.7‰, generation of biogenic gas is likely.

As already noted, dissolution of CO₂ from thermal degradation process is the leading source of DIC; thus analysis of the carbon isotope composition between CO₂ and DIC may reveal a basis for generation of biogenic gas. According to Martini et al. (1998), δ¹³C-CO₂ values are controlled by carbonates' dissolution equilibrium and fractionation through microbial respiration, with equilibrium of δ¹³C-CO₂ and δ¹³C-DIC (α_{DIC-CO2}) described by the following equation:

$$1000\ln\alpha_{\text{DIC-CO}_2}=\delta^{13}\text{C-DIC}-\delta^{13}\text{C-CO}_2=9.552\times1000/T-24.09 \quad (7)$$

Taking the δ¹³C-CO₂ values (−13.4‰ to −9.3‰; Table 2) and surface temperature (T=15+273, K) into Eq. 7. The theoretical results is approximately −4.9‰~−1.1‰ for δ¹³C-DIC. However, measured δ¹³C-DIC values range from +0.4‰ to +21.3‰, much heavier than those calculated by Eq. 7, which indicates that equilibrium between δ¹³C-CO₂ and δ¹³C-DIC has not yet been reached, likely owing to microbial behavior (Martini et al., 1998).

Cheung et al. (2010) took a classic diagram to partition CBM genesis (Fig. 7a), concluding that the C isotope fractionation coefficient between the DIC and CH₄ (α_{DIC-CH4}) of CO₂-reduction gas is below 0.935, whereas the α_{DIC-CH4} values of acetate-fermentation gas are above 0.950. Clearly, the data points in the Huabei coalfield are scattered within the CO₂ reduction region, whereas those in Tucheng are distributed above the acetate-fermentation line, indicating the presence of almost no acetate-fermentation gas in the Tucheng CBM. Conversely, two Tucheng data points fall within the CO₂ reduction region, indicating the presence of CO₂-reduction gas, consistent with the conclusion in Section 5.1.

Zhang et al. (2009) investigated the origin of CBM in the Uinta Basin, USA, using the equilibrium function of D isotopes between δD-CH₄ and δD-H₂O for microbial fractionation of methane (Fig. 7b) with a margin of error of ±10‰, as seen between the two dashed lines, indicating a source of CO₂-reduction gas. When inserting relative values of Tucheng into Fig. 7b, two data points fall in the CO₂ reduction region, consistent with the results shown in Fig. 7a, confirming generation of CO₂-reduction

gas. Yang et al. (2020) investigated the microbial structure in CBM coproduced water of Tucheng, using 16S rDNA amplification sequencing and found that its dominant methanogenic strain was Methanobacterium, which is hydrogenotrophic and can metabolize CO₂ and H₂ to CH₄ (Guo et al., 2012). This finding confirms that the generation pathway of secondary biogenic gas is the reduction of CO₂.

5.2.3.2 Estimation the production potential of biogenic methane in coalbed water

Furthermore, based on the carbon isotope conservation law (Eq.8) and the carbon isotope fractionation equation between DIC and CO₂ (Eq.7), we can crudely calculate the biogenic methane production efficiency of CBM in the Tucheng syncline.

$$A \times \delta^{13}\text{C-DIC}^a + \delta^{13}\text{C}_1 \times B = \delta^{13}\text{C-DIC}^b \quad (8)$$

$$A + B = 1 \quad (9)$$

$$T = t + 273 \quad (10)$$

$$A/B = [\text{DIC}]^a / [\text{CH}_4] \quad (11)$$

In these equations, A is the proportion of laboratory-measured DIC, B the proportion of DIC that becomes biogenic methane, and [CH₄] the molar concentration of biogenic methane in CBM coproduced water. [DIC]^a is the test data of DIC concentration. $\delta^{13}\text{C-DIC}^a$ signifies the laboratory-measured values of $\delta^{13}\text{C-DIC}$ (+0.4‰~+21.3‰, Table 3) and $\delta^{13}\text{C-DIC}^b$ the theoretical calculation values of $\delta^{13}\text{C-DIC}$ (-4.9‰~-1.1‰, Table 8; calculated by Eq.7). $\delta^{13}\text{C}_1$ represents the $\delta^{13}\text{C}$ value of biogenic methane, which equals -70‰.

The calculation results show that the proportion of A is 75.5%~95.1% and the proportion of B 4.9%~24.5% (Table 8). From Eq. 11, the distribution of molar concentration of biogenic methane ([CH₄]) in CBM coproduced water is 0.07~4.39 mM/L, so that the biogenic methane production per cubic meter of coproduced water is 0.002~0.104 m³, with a mean value of 0.039 m³ (C, Table 8). These formulations provide a rewarding approach to estimating secondary biogenic gas resources. For example, based on the similar calculation, the production of biogenic methane of coproduced water in the Huaibei Coalfield can reach 0.30~0.35m³/L. To highlight the shallow secondary biogenic gas formation process, we profiled the evolution of shallow groundwater in the Tucheng syncline (Fig. 8).

5.3 Tectonic evolution and CBM accumulation in the Tucheng syncline

Based on the tectonic evolution of the Panxian mining area and the results of Tang et al.'s (2016) simulation of sedimentary burial history and thermal evolution of coalbeds in Panxian, we diagrammed the relationship between tectonic evolution and CBM origin and accumulation in the Tucheng syncline (Fig. 9). As Fig. 9 shows, coal-bearing strata in Tucheng have undergone two periods of sedimentary burial, the Permian to the Late Triassic ($P\sim T_3$) and the Early Jurassic to the Early Cretaceous ($J_1\sim K_1$); two periods of tectonic uplift, the Middle Triassic to the Late Triassic ($T_2\sim T_3$) and the Early Cretaceous to the Early Paleogene ($K_1\sim E_1$); and three periods of hydrocarbon generation, the Permian to the Early Triassic ($P\sim T_1$), the Middle Triassic to the Middle Cretaceous ($T_2\sim K_2$), and the Late Cretaceous to the Quaternary ($K_3\sim Q$).

Tang et al. (2016) used the Lawrence Livermore National Laboratories (LLNL) dynamics model for the Panxian area, with R_o values of 0.72%~1.27%. According to the equivalent line diagram of R_o (Fig. 1), the R_o of the Tucheng coal is approximately distributed in the range 0.8%~1.2%. It is thus reasonable for this paper to use a value of 1.2% for R_o during the late stage of coalification (after K_1 , when coalbeds were lifted to a shallow depth <1,000 m).

The simulation shows that coalbeds in the Tucheng syncline mainly went through five stages of tectonic evolution. The Permian to Middle Triassic stage ($P\sim T_1$), when the coal grade level was low ($R_o<0.5\%$), was marked by a great deal of primary biogenic gas generation and accumulation. However, primary biogenic gas is difficult to preserve owing to the lack of a cap. In the Middle Triassic to Early Jurassic stage ($T_2\sim J_1$), the temperature rose, the coal grade level enhanced, and early thermogenic gas was generated; when the temperature exceeded 80 °C, the coal grade level reached the gas–coal stage, at which point the primary biogenic gas nearly disappeared and pure thermogenic gas began accumulating. Within coalbeds sunk below 3,000 m, which experienced a slight lift, geothermal temperature reached nearly 120 °C and the coal grade level reached the fat–coal stage, with the R_o value of coal rock reaching nearly 1.0%, at which point thermogenic gas accumulation peaked. During the Middle Yanshanian ($J_2\sim K_2$), plutonic metamorphism and magmatic thermal metamorphism

caused a steep upgrade in the geothermal gradient, reaching 5.5 °C/100 m (Tang et al., 2016). In response, the paleogeothermal temperature rose sharply to 140 °C and the coal grade level reached the coking-coal stage, with the R_o value reaching 1.2%, the point at which the largest quantities of thermal degradation gas were generated. In the Late Cretaceous to Quaternary stage (K_3 -Q), after the coalbeds were lifted to the shallow surface (<1,000 m), some thermogenic CBM escaped through the tectonic cracks during its aggregation owing to a lack of natural cover. However, bacteria infiltrated the shallower coalbeds with surface water across tectonic cracks, allowing generation of secondary biogenic gas. What's more, atmospheric precipitation sealed some open fractures, helping preserve coalbed methane reservoirs.

6. Proportions of different-origin CBM in the Tucheng syncline

Previous sections of this paper suggest that the origin of CBM in Tucheng is a mix of thermogenic and biogenic methane, with thermogenic predominating. We can further quantify the ratio between the two using the thermal simulation regression equation (Eq. 12) and the law of conservation of $\delta^{13}\text{C-CH}_4$ (Eq. 13):

$$\delta^{13}\text{C}_1 = 22.42 \log R_o - 34.8 \quad (12)$$

$$a * \delta^{13}\text{C}_{1-T} + b * \delta^{13}\text{C}_{1-B} = (a+b) * \delta^{13}\text{C}_{1-M} \quad (13)$$

$$a+b=1 \quad (14)$$

In the preceding equations, a is the proportion of thermogenic methane, b the proportion of biogenic methane, $\delta^{13}\text{C}_{1-T}$ the carbon isotope composition of thermogenic methane, $\delta^{13}\text{C}_{1-B}$ the carbon isotope composition of biogenic methane, and $\delta^{13}\text{C}_{1-M}$ the carbon isotope composition of gas samples analyzed in this study.

From Fig. 9, when secondary biogenic methane is generated, its R_o value is 1.2%. Using $R_o=1.2\%$ in Eq. 12 produces a solution of $\delta^{13}\text{C}_{1-T} = -33.0\text{‰}$. Tao et al. (2007) statistically summarized 576 $\delta^{13}\text{C-CH}_4$ values of conventional biogenic gas worldwide and identified -70.0‰ as the middle and plural value of biogenic methane. Accordingly, $\delta^{13}\text{C}_{1-B}$ takes a value of -70.0‰ in this study. In addition, $\delta^{13}\text{C}_{1-M}$ takes the values in Table 2. The calculated results are described in Table 9, with thermogenic methane accounting for about 72.4%~79.2% of the whole CBM in Tucheng and the rest (about 20.8%~27.6%) being biogenic methane. The proportion of secondary biogenic methane

is smaller than that of thermogenic methane.

7. Conclusion

Based on integrated analysis of the geochemical characteristics of CBM in the Tucheng syncline, we conclude that CBM in the study area originated as a mixture of thermal degradation gas and secondary biogenic gas, in the proportions 72.4%~79.2% and 20.8%~27.6%, respectively. The generation pathway of secondary biogenic gas is CO₂ reduction.

The water quality type of CBM coproduced water is Na-Cl, with water solutes governed mainly by dissolution of evaporites and silicates. CBM coproduced water originates from a mixture of coalbed water and meteoric precipitation.

Special hydrogeochemical features, including sulfate reduction, positive $\delta^{13}\text{C}$ -DIC values, D drift, and C isotope fractionation between DIC and CO₂ confirmed the presence of secondary biogenic gas. The percentage of DIC converted to CH₄ is 4.9%~24.5%, and the yield of biogenic CH₄ in coproduced water can reach 0.002~0.104 m³/t, with a mean value of 0.039 m³/t.

CBM origin and accumulation in situ differs among the stages of tectonic evolution (P~T₁; T₂~K₂; K₃~Q). The P-T₁ stage features substantial primary biogenic gas generation with a lower coal grade level ($R_o < 0.5\%$). The T₂~K₂ stage features the disappearance of primary biogenic gas and the generation of thermogenic gas: When the coal grade level reached the fat-coal stage, thermogenic gas accumulation peaked. During the K₃-Q stage, thermogenic gas underwent secondary microbial modification.

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 783 (<https://doi.org/10.1016/j.gca.2005.06.027>)

784 Table 1 Composition of gas samples collected in the Tucheng syncline

Sample	H ₂	N ₂	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	iC ₄ H ₁₀	nC ₄ H ₁₀	C ₁ /∑C ₁₋₅	C _{HC}	CDMI
code	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)		(%)
SH1	0.07	6.8	7.1	85.3	2.0	0.23	0.017	0.021	97.4	38.3	7.7
SH2	0.00	9.2	8.6	81.3	1.4	0.14	0.011	0.011	98.1	52.8	9.6
SH3	0.00	10.9	6.5	81.0	1.3	0.09	0.007	0.006	98.3	58.3	7.4
SH4	0.00	9.0	9.3	79.6	1.3	0.09	0.006	0.005	98.3	57.3	10.5
SH5	0.00	12.8	5.2	81.0	1.3	0.12	0.010	0.010	98.3	57.0	6.0
SH6	0.00	3.0	9.8	86.4	1.9	0.20	0.016	0.018	97.6	41.1	10.2
SH7	0.00	7.9	5.5	85.7	1.1	0.08	0.006	0.006	98.6	72.6	6.0
SH8	0.00	6.7	5.9	86.7	1.8	0.17	0.013	0.014	97.7	44.0	6.4
SH9	0.00	8.8	4.6	85.0	1.7	0.19	0.016	0.019	97.8	45.0	5.1
Mean	-	8.3	6.9	83.6	1.5	-	-	-	98.0	51.8	7.7

785 Note: $C_1/\sum C_{1-5}=C_1/(C_1+C_2+C_3+C_4+C_5)$; $C_{HC}=C_1/(C_2+C_3)$; $CDMI=CO_2/(CO_2+CH_4)$

786

787 Table 2 Gas isotopic composition of CBM in the Tucheng syncline

Sample	$\delta^{13}\text{C-CH}_4$	$\delta^{13}\text{C-CO}_2$	$\delta^{13}\text{C-C}_2\text{H}_6$	$\delta\text{D-CH}_4$	$\delta\text{D-C}_2\text{H}_6$
code	(‰, VPDB)	(‰, VPDB)	(‰, VPDB)	(‰, VSMOW)	(‰, VSMOW)
SH1	-41.1	-11.7	-27.0	-175.9	-102.8
SH2	-41.3	-12.0	-26.1	-176.9	-102.5
SH3	-41.7	-12.0	-25.8	-185.1	-100.1
SH4	-41.4	-9.3	-25.7	-183.6	-90.7
SH5	-43.2	-10.3	-27.5	-185.8	-90.8
SH6	-41.3	-12.2	-26.0	-174.1	-97.9
SH7	-40.7	-13.3	-25.1	-175.2	-90.6
SH8	-41.0	-10.9	-25.5	-169.2	-97.9
SH9	-40.8	-13.4	-26.4	-173.8	-92.5
Mean	-41.4	-11.7	-26.1	-177.7	-96.2

788

789 Table 3 Ions and isotopic compositions of CBM coproduced water in the Tucheng syncline

Sample code	pH	Eh (mV)	DO (mg/L)	T (°C)	K ⁺ (mg/L)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	SiO ₂ (mg/L)	Sr ²⁺ (mg/L)	Ba ²⁺ (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Br ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	CO ₃ ²⁻ (mg/L)	δ ¹³ C- DIC (‰, VPDB)	TDS (mg/L)
SH1	7.1	-85	3.0	18.7	111.2	1,526.6	108.1	19.1	5.6	13.6	9.1	1.3	2,581.4	0.1	4.2	79.3	-	0.4	4,414.2
SH2	7.7	-133	3.8	13.0	77.8	1,963.9	28.6	16.1	9.5	8.5	6.3	0.5	2,884.9	0.1	6.1	585.0	22.2	7.0	5,285.0
SH3	7.7	-127	2.8	11.7	119.2	2,503.4	26.8	10.7	12.1	9.2	9.1	0.6	3,427.4	0.2	5.1	954.0	31.2	6.2	6,588.3
SH4	7.9	68	1.3	22.5	75.9	2,310.7	24.0	7.0	13.2	7.2	6.6	1.4	2,937.7	0.2	5.1	825.3	28.2	21.3	5,788.2
SH5	8.3	33	2.5	16.4	127.1	2,529.4	45.9	15.5	8.5	12.5	9.3	0.8	3,717.0	0.1	4.3	564.3	-	14.7	6,743.8
SH6	8.2	16	1.0	25.5	107.0	3,344.7	92.7	26.1	14.5	17.2	13.7	0.6	4,663.6	0.1	5.8	472.8	-	14.4	8,507.9
SH7	8.2	39	1.3	20.7	249.4	3,674.6	47.3	17.0	8.4	14.3	14.8	0.9	4,987.2	0.1	6.1	352.0	10.8	6.7	9,187.6
SH8	8.3	-76	2.8	12.8	163.2	3,515.0	78.0	22.0	15.1	16.5	16.2	0.6	5,224.5	0.1	7.0	529.5	-	2.2	9,307.8
SH9	8.5	-99	3.1	11.7	74.2	3,270.5	32.5	15.2	9.4	10.9	10.5	0.7	4,287.8	0.1	5.6	539.9	33.0	5.6	7,977.7
mean	8.0	-40	2.4	17.0	122.8	2,737.6	53.8	16.5	10.7	12.2	10.6	0.8	3,856.8	0.1	5.5	544.7	-	8.7	7,088.9

790

791 Table 4 $\delta\text{D-CH}_4$ distributions of gases from different geneses

Genetic types	δD (‰, VSMOW)	Reference
Biogenic gas		
acetate fermentation gas	-400~-250	Rice, 1993; Whiticar et al., 1986;
CO ₂ reduction gas	-250~-150	
Thermogenic gas		
thermal degradation gas	>-250	Whiticar, 1999
pyrolysis gas	>-200	
mantle origin	-350~-150	

792

793 Table 5 Parameters of equivalent ratio between ions according to Table 3

Sample code	$(\text{Na}^++\text{K}^+)/\text{HCO}_3^-$ (meq ratio)	$(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ (meq ratio)	$r\text{Na}^+/r\text{Cl}^-$ (meq ratio)	$\text{Ca}^{2+}+\text{Mg}^{2+}/\text{HCO}_3^-$ (meq ratio)	$r\text{SO}_4^{2-}/r(\text{SO}_4^{2-}+\text{Cl}^-)$ (meq ratio)	CAI ₁	CAI ₂
SH1	-2.68	2.64	0.91	2.69	0.001%	0.05	2.56
SH2	0.64	0.13	1.05	0.14	0.001%	-0.08	-0.61
SH3	0.98	0.06	1.13	0.07	0.002%	-0.16	-0.94
SH4	1.45	0.05	1.21	0.07	0.002%	-0.24	-1.39
SH5	0.92	0.18	1.05	0.19	0.001%	-0.08	-0.91
SH6	2.17	0.43	1.11	0.44	0.001%	-0.13	-2.15
SH7	4.45	0.31	1.14	0.33	0.001%	-0.18	-4.26
SH8	1.13	0.32	1.04	0.33	0.001%	-0.07	-1.12
SH9	2.63	0.16	1.18	0.16	0.001%	-0.19	-2.46
Mean	1.30	0.48	1.09	0.49	0.001%	-0.12	-1.15

794 Note: $(\text{Na}^++\text{K}^+)*=(\text{Na}^++\text{K}^+)-\text{Cl}^-$; $(\text{Ca}^{2+}+\text{Mg}^{2+})*= (\text{Ca}^{2+}+\text{Mg}^{2+})-\text{SO}_4^{2-}$; $\text{CAI}_1=\text{Cl}^--(\text{Na}^++\text{K}^+)/\text{Cl}^-$;

795 $\text{CAI}_2=\text{Cl}^--(\text{Na}^++\text{K}^+)/(\text{HCO}_3^-+\text{SO}_4^{2-}+\text{CO}_3^{2-}+\text{NO}_3^-)$

796 Table 6 Mineral saturation indexes

Sample code	SI (Anhydrite)	SI (Gypsum)	SI (Aragonite)	SI (Barite)	SI (Witherite)	SI (Calcite)	SI (Dolo mite)	SI (Fluorite)	SI (Goethite)	SI (Halite)	SI (Hema tite)	SI (Pyrite)	SI (Siderite)
SH1	-5.3	-5.1	-0.9	-1.2	-2.2	-0.8	-2.0	-0.9	2.8	-4.1	7.6	-23.7	-0.1
SH2	-5.7	-5.4	-0.1	-1.0	-1.0	0.0	0.0	-2.3	1.5	-3.9	4.9	-20.2	-0.6
SH3	-5.6	-5.3	0.0	-0.7	-0.7	0.1	0.0	-2.2	1.4	-3.8	4.8	-20.8	-0.5
SH4	-5.6	-5.3	0.2	-1.0	-0.6	0.4	0.5	-1.6	6.0	-3.9	14.0	-75.0	-0.2
SH5	-5.5	-5.3	0.6	-0.9	-0.4	0.7	1.2	-1.7	6.4	-3.7	14.8	-71.0	0.1
SH6	-5.5	-5.3	0.8	-1.3	-0.3	1.0	1.8	-1.8	7.3	-3.5	16.6	-68.8	0.9
SH7	-5.8	-5.5	0.4	-1.1	-0.4	0.5	0.9	-1.7	6.8	-3.5	15.5	-73.2	0.1
SH8	-5.4	-5.1	0.7	-0.7	-0.2	0.8	1.3	-1.7	4.3	-3.4	10.5	-42.7	0.0
SH9	-6.0	-5.7	0.6	-1.1	-0.1	0.7	1.3	-2.0	4.3	-3.6	10.6	-40.9	0.2

797 Note: SI=Saturation index, when SI>0, it means oversaturated, when SI<0, it means undersaturated.

798 Table 7 Water types vs. origins of CBM from different basins

Countries	Basins	Areas	Water types	Origins of CBM	References
USA	Powder River	Fort Union	Na-HCO ₃	B/T>1	Flores et al., 2008; Meng et al., 2014
USA	Uinta	-	Na-Cl	B/T<1	Zhang et al., 2009
Canada	Alberta	Mannville	Na-Cl	B/T<1	Cheung et al., 2010
Australia	Bowen	-	Na-HCO ₃ -Cl	B/T>1	Kinnon et al., 2010
China	Huaibei	Suzhou	Na-HCO ₃ , Na- HCO ₃ -Cl	B/T>1	Li et al., 2015, 2016
China	Qinshui	Jincheng	Na-HCO ₃	B/T<1	Meng et al., 2014
China	Ordos	Danling-Jixian	Na-SO ₄ -Cl	B/T<1	Li et al., 2014; Meng et al., 2014

799 Note: B=biogenic; T=thermogenic

800

801 Table 8 Estimation of CBM biogenic gas production in the Tucheng syncline

Sample code	t (°C)	$\delta^{13}\text{C-CO}_2$ (‰, VPDB)	DIC ^a (mmol/ L)	$\delta^{13}\text{C-}$ DIC ^a (‰)	$\delta^{13}\text{C-}$ DIC ^b (‰)	A (%)	B (%)	[CH ₄] (mmol/ L)	C (m ³ /t)
SH1	18. 7	-11.7	1.30	0.4	-3.0	95. 1	4.9	0.07	0.00 2
SH2	13. 0	-12.0	9.59	7.0	-2.7	87. 4	12. 6	1.38	0.03 2
SH3	11. 7	-12.0	15.64	6.2	-2.5	88. 5	11. 5	2.03	0.04 7
SH4	22. 5	-9.3	13.53	21.3	-1.1	75. 5	24. 5	4.39	0.10 4
SH5	16. 4	-10.3	9.25	14.7	-1.4	81. 0	19. 0	2.17	0.05 1
SH6	25. 5	-12.2	7.75	14.4	-4.3	77. 9	22. 1	2.20	0.05 3
SH7	20. 7	-13.3	5.77	6.7	-4.9	84. 9	15. 1	1.02	0.02 4
SH8	12. 8	-10.9	8.68	2.2	-1.6	94. 8	5.2	0.48	0.01 1
SH9	11. 7	-13.4	8.85	5.6	-3.9	87. 4	12. 6	1.28	0.02 9
Mean	17. 0	-11.7	8.93	8.7	-2.8	85. 8	14. 2	1.67	0.03 9

802 Note: *a*: the laboratory-measured values of DIC; *b*: the theoretical calculation values of $\delta^{13}\text{C-DIC}$;
803 A: the percentage of laboratory measured of DIC; B: the percentage of DIC that becomes CH₄; [CH₄]:
804 the molar concentration of biogenic methane in CBM coproduced water; C: biogenic
805 methane production per cubic meter of coproduced water.

807 Table 9 Percentage of CBM of different origins in the Tucheng syncline

Sample	$\delta^{13}\text{C-CH}_4$	<i>a</i>	<i>b</i>
code	(‰, VPDB)	(%)	(%)
SH1	−41.1	78.1	21.9
SH2	−41.3	77.6	22.4
SH3	−41.7	76.5	23.5
SH4	−41.4	77.3	22.7
SH5	−43.2	72.4	27.6
SH6	−41.3	77.6	22.4
SH7	−40.7	79.2	20.8
SH8	−41.0	78.4	21.6
SH9	−40.8	78.9	21.1
Mean	−41.4	77.3	22.7

Note: *a* is the percentage of themogenic origin gas, while
b is the percentage of biogenic gas.

Fig. 1. (a) Location of the Tucheng syncline (according to Li et al., 2015b). (b) Upper Permian Longtan Formation Stratum column diagram of the Tucheng syncline (modified from Tang et al., 2017).

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816

817 Fig. 2. (a) $\delta^{13}\text{C-CO}_2$ vs. CDMI of CBM in the Tucheng syncline and Huaibei coalfield

818 (according to Lan et al., 2013; Li et al., 2015a). (b) $\delta^{13}\text{C-CO}_2$ vs. CO₂ content of CBM

819 in the Tucheng syncline and Huaibei coalfield (according to Golding et al., 2013).

820

Fig. 3. (a) Genetic characterization of CBM from the Tucheng syncline and Huaibei coalfield using $\delta^{13}C-CH_4$ vs. C_1/C_2+C_3 (according to Whiticar, 1999). (b) Genetic characterization of CBM from the Tucheng syncline and Huaibei coalfield using $\delta^{13}C-CO_2$ vs. $\delta^{13}C-CH_4$ (according to Whiticar, 1999). (c) Genetic characterization of CBM from the Tucheng syncline and Huaibei coalfield using $\delta D-CH_4$ vs. $\delta^{13}C-CH_4$ (according to Li et al., 2015a; Flores et al., 2008). (d) Genetic characterization of CBM from the Tucheng syncline and Huaibei coalfield using carbon isotope fractionation between CO_2 and CH_4 (according to Li et al., 2015a).

833

834

835 Fig. 4. $\delta^{13}\text{C}-\text{CH}_4$ vs. $\delta^{13}\text{C}-\text{C}_2\text{H}_6$ diagram for classification of bacterial and thermogenic
836 gas in the Tucheng CBM (according to Kotarba et al., 2001; Tao et al., 2007).

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838

839

840 Fig. 5. (a) Main ionic concentrations of CBM coproduced water in the Tucheng syncline.

841 (b) Piper diagram of ions for CBM coproduced water in the Tucheng syncline.

Fig. 6. Diagrams for determining end-member compositions by (a) $\text{Ca}^{2+}/\text{Na}^+$ vs. $\text{Mg}^{2+}/\text{Na}^+$ and (b) $\text{Ca}^{2+}/\text{Na}^+$ vs. $[\text{HCO}_3^-]/\text{Na}^+$ equivalent ratios (according to Gaillardet et al., 1999; Xu and Liu, 2010); (c) $(\text{Mg}^{2+}+\text{Ca}^{2+})*[\text{HCO}_3^-]$ vs. $(\text{Na}^++\text{K}^+)*[\text{HCO}_3^-]$ equivalent ratios and (d) $\text{Mg}^{2+}/\text{Na}^+$ vs. $\text{Na}^+/\text{Ca}^{2+}$ equivalent ratios (according to Gaillardet et al., 1999).

Fig. 7. (a) Genetic characterization of CBM from the Tucheng syncline and Huaibei coalfield according to fractionation between $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-DIC}$ (according to Cheung et al., 2010). (b) Fractionation between $\delta\text{D-CH}_4$ and $\delta\text{D-H}_2\text{O}$ by CO_2 reduction (according to Zhang et al., 2009).

Fig. 8. Evolution of shallow groundwater in the Tucheng syncline (modified from Elizabeth et al., 2008). Note: E: Cambrian; C: Carboniferous; P: Permian; T: Triassic; J: Jurassic; Q: Quaternary.

Fig. 9. Burial history and thermal evolution of coalbeds in the Tucheng syncline (modified from Bao et al., 2020; Tang et al., 2016). Note: (a) represents the stage of primary biogenic gas generation and accumulation, (b) the stage of gradual generation of thermogenic gas, (c) the stage of large-scale generation and accumulation of thermogenic gas, (d) the stage of secondary biogenic gas recharge. P: Permian; T: Triassic; J: Jurassic; K: Cretaceous; E: Palaeocene; N: Neogene; Q: Quaternary.