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Isotopic composition and content of coalbed methane production gases and waters in karstic collapse column area, Qinshui Coalfield, China

Zhanjie Xu [a], Qinfu Liu [a,*], Qiming Zheng [b], Hongfei Cheng [a], Yingke Wu [a]

[a] School of Geoscience and Surveying Engineering, China University of Mining and Technology, Beijing 100083, China
[b] School of Resources and Environment Engineering, Henan Institute of Engineering, Zhengzhou, Henan 451191, China

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ABSTRACT

The Qinshui Coalfield is one of the most important coalbed methane (CBM) coalfields in China with vast CBM resources, in which the Carboniferous Taiyuan Formation is one of the main coal-bearing sequences. Eleven CBM production gas samples and associated production waters were collected from the Taiyuan Fm. in the karstic collapse column (KCC) area of Sijiazhuang mining area, Qinshui Coalfield. The gas molecular and isotopic compositions and water quality, water carbon and hydrogen isotope compositions were analyzed. Results in this study reveal that CBM from Taiyuan Fm. of Sijiazhuang is dominated by CH_4 (95.9–99.4 mol%, air-free basis) with minor amounts of N_2 (average: 1.07%), CO_2 (average: 0.25%), and ethane (average: 0.02%). The carbon isotope ratios of the production CH_4 range from −40.8‰ to −33.2‰, with an average of −37.1‰, and the corresponding hydrogen isotope ratios of CH_4 −196‰ to −178‰, with an average of −186‰ ($n = 11$). Thermogenic methane is the primary source of CBM from the Taiyuan Fm. of Sijiazhuang, and its estimated proportion is calculated to range from 72% to 95%.

The type of CBM production water is Na–HCO_3, and the concentrations of total dissolved solids range from 1282 mg/mL to 1718 mg/mL, with an average of 1417 mg/mL. The δD values of the water samples range from −74.8‰ to −61.1‰, the $\delta^{18}O$ values from −9.6‰ to −8.0‰. The isotope compositions of water samples fall to the right of the GMWL, suggesting a combination of fluid–rock interaction under high temperature conditions and evaporation.

There is a good correlation between the distribution of KCCs and the isotopic compositions of CBM production gases and waters in the study area. KCCs in this area can be the free pathways going through the surface, the limestone beds and the 15# coal seam of Taiyuan Fm. KCC presence makes the CH_4 carbon isotopic composition become more enriched in ^{13}C in shallower areas, because of the stronger desorption–diffusion–migration isotope fraction effect of CBM in the north of Sijiazhuang mining area. In contrast, the $\delta^{13}C_1$ and $\delta^{13}C_{CO_2}$ values are lighter in deeper areas in the southwest of the study area. This could be due to the stronger groundwater stripping process in that area. The results can be used for CBM exploration and exploitation in KCC areas.

1. Introduction

The molecular and stable isotopic compositions of coalbed methane (CBM) and associated production waters, in combination with the type and maturity of organic matter, can be used to establish gas origins, such as thermal and microbial, and the microbial methane generation pathway (Berner and Faber, 1988; Chung et al., 1988; Golding et al., 2013; Schoell, 1980; Strąpoć et al., 2007, 2008; Whiticar et al., 1986). However, many factors can affect the isotopic compositions and content of coalbed methane (CBM), e.g. the hydrogeological conditions, tectonic evolution, type and maturity of organic matter, and microbial activity (Golding et al., 2013; Hamilton et al., 2014; Kinnon et al., 2010; Li et al., 2014a; Meng et al., 2014; Qin et al., 2006; Song et al., 2007; Tao et al., 2014; Ye et al., 2001; Zhang and Tao, 2000; Zhao and Zhang, 2004; Zhao et al., 2005). The flow of water can significantly impact the carbon isotopic fractionation of CBM because the ^{13}C of methane can be easily stripped away (Qin et al., 2006), and waters with lighter hydrogen and oxygen isotope compositions are associated with areas of low water production and high gas production (Kinnon et al., 2010). The gas content is lower and the methane carbon isotope lighter in meteoric recharge areas (Song et al., 2007). Tectonic evolution is another major factor that can impact CBM accumulation and enrichment (Hou et al., 2012; Song et al., 2007; Wu et al., 2011). The review by Golding et al. (2013) summarizes that carbon and hydrogen isotope compositions of CBM vary with source rock type and maturity in the case of thermogenic methane (Golding et al., 2013; Schoell, 1980). Microbial gases typically have methane carbon isotope compositions lighter than primary thermogenic gases (Golding et al., 2013; Strąpoć et al., 2007, 2008; Whiticar et al., 1986).

* Corresponding author.
E-mail address: lqf@cumtb.edu.cn (Q. Liu).

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In North China, karstic collapse column (KCC) is a kind of vertical structure, typically formed at Carboniferous–Permian coalfields, including the Qinshui Coalfield (Yin et al., 2004, 2005; Zhou et al., 2012). The bases of KCCs are developed in Ordovician limestone and the columns extend up through the coal seams, which may act as pathways between the limestone aquifers and the coal strata, but most KCCs in Yangquan or Taiyuan mining district, North China, are water barriers or media of aquifer uninfluenced (Yin et al., 2005). Yin et al. (2005) showed that the water-bearing properties of KCCs are controlled and influenced by several factors, such as tectonic movements, groundwater flow conditions, rock types, and cementation in the columns, as well as confining pressure.

Coalbed methane production water (CMPW) is drained from the coal strata in order to release ground stress such that the CBM can be desorbed from the coal surface. Most pH values of CMPW are alkaline, and Na–HCO_3 and Na–HCO_3–Cl are the typical types of CMPW in China (Meng et al., 2014). The CBM gas content would be lower in this area, where the coal-bearing strata are connected to the strong runoff zones of its underlying Ordovician limestone karstic aquifer (Ye et al., 2001). Typically, CBM reservoirs contain higher volumes of water than conventional reservoirs, with large quantities of variably saline water being extracted during production, particularly in the primary production time (Kinnon et al., 2010) and the quantity and quality of CMPW both vary largely between coal basins and stratigraphic units in China (Meng et al., 2014). Usually, coal seams, as fractured aquifers, connect other recharge zones and thus meteoric recharge through drawdown can transport microbes from near-surface locations. However, this will not occur when the recharge zone is an Ordovician limestone aquifer. Furthermore, reservoirs with lower pressure can accumulate more CBM because of the meteoric recharge after coal seam forming of the coalfield (Kinnon et al., 2010).

This study used chemical and isotopic analyses to fingerprint the origins of the gases in Sijiazhuang CBM production field, northern Qinshui Coalfield, for further understanding the effect of KCCs on isotopic compositions, content and production of CBM and associated production water in a KCC reservoir.

2. Geological setting

The Qinshui Coalfield is one of the biggest coalfields in China, covering an area of about 30,000 km^2, and has a proven coal reserve of 300 Gt (Zheng et al., 2015a). The study area, Sijiazhuang, is located in the north of the Qinshui Coalfield (Fig. 1a).

The coal-bearing strata in the Qinshui Coalfield include the Benxi Fm., Taiyuan Fm. of the Upper Carboniferous, and Shanxi Fm. of the Lower Permian, with a total thickness of 184–272 m (Fig. 1b) (Ge et al., 1985; Liang et al., 2002; Shao et al., 2008). The Benxi Fm. is composed mainly of gray and dark-gray mudstone, sandy mudstone, fine–medium sandstone, and limestone with an average total thickness of 53.7 m. It unconformably overlies on the Middle Ordovician limestone and contains two to four thin mineable coal seams. The Taiyuan Fm. conformably overlies the Benxi Fm., whose thickness varies from 90 to 130 m (average: 99.5 m) with seven to nine coal seams, of which Nos. 8, 9, 12, and 15 are the principal mineable seams. Coal seam No. 8 includes 8_1 and 8_4 coal seams. The main coal seam is No. 15 and three limestone aquifers K_2, K_3, and K_4 lie above it. The coal of No. 15 belongs to anthracite class with a maximum vitrinite reflectance within 2.90%–3.42%, with an average of 3.11% (Yangquan Coal Industry (Group) Co. LTD, 2008). Above the Taiyuan Fm. lies the Shanxi Fm., whose thickness is 54–82 m (average: 69.5 m). The Shihezi Fm. comprises non-coal-bearing strata and lies conformably on the Shanxi Fm. Of all the coal seams in the Qinshui Coalfield, only No. 15 coal seam is mineable across the entire Qinshui Coalfield.

The Qinshui Coalfield has a NNE monoclinic pattern and a moderate degree of complexity of tectonic features. The strata dip toward the northwest at a gentle angle of 5°–10° with a local fold zone of 12°–20°. Outcrop ages are old to new from east to west. Ordovician strata are widely exposed in the east; however, outcrops of the Upper Carboniferous Benxi Fm. and Taiyuan Fm. and Permian Shanxi Fm. are sporadic only in eastern parts of the coalfield. Fold structures are mainly anticlinal and synclinal, and there is relatively little faulting. Yangquan Coal Industry (Group) Co. LTD (2008) reveals that KCCs have developed in the north of Sijiazhuang block in general (Fig. 2). The forms of the KCCs are generally nearly round or ovular with minimum diameters of 10 m (usually 20–50 m) and wall angles of 62–83° (generally 80°).

3. Materials and methods

3.1. Materials

The CBM production gases and associated production waters used in this study were obtained from 11 CBM wells in the Sijiazhuang mining area, northern Qinshui Coalfield, China. Fig. 2 shows the location of CBM wells where samples were collected. The CBM production gases mainly came from the Taiyuan Fm. Well No. 2 is near a KCC named Xs23, which is ellipse in shape (320 × 180 m) and is one of the largest KCCs in this area (Fig.2) (Yangquan Coal Industry (Group) Co. LTD, 2008). The associated production water samples were collected and stored in polyethylene plastic bottles in August 2015. The volume of each gas sample is 200 mL or 400 mL for the molecular and isotopic analyses, and the volume of each water sample is 1000 mL for stable isotope and quality tests.

3.2. Methods

The gas samples were analyzed at the Lanzhou Petroleum Resources Research Center, Institute of Geology and Geophysics, Chinese Academy of Sciences. The molecular compositions of the gas samples were analyzed using a MAT-271 trace gas mass spectrometer.

Carbon isotopes were determined using a MAT-253 GC-C-MS system, the values of which are relative to the PDB international standard with precision $\leq \pm 0.5‰$. Hydrogen isotopes were also determined using this system, the values of which are derived relative to the SMOW international standard with precision of $\leq \pm 10‰$. The stable isotope tests were conducted in the laboratory using precise and superior techniques (Li et al., 2007; 2012; 2014b).

The quality and stable isotope compositions of CMPW samples were tested at the Analytical Laboratory of Beijing Research Institute of Uranium Geology, according to Standards such as DZ/T 0184.19 (1997); DZ/T 0184.21 (1997); DZ/T 0064.9 (1993); DZ/T 0064.28 (1993); DZ/T 0064.49 (1993), and DZ/T 0064.51 (1993).

4. Results and discussion

4.1. Gas molecular compositions

Table 1 shows the molecular and isotopic composition data of the CBM production gases from the KCC area. The molecular compositions of CBM production gases are 95.9–99.4% CH_4 (mol%, air-free basis), with an average of 98.6%. Ethane content is very small (volume: 0.008–0.038%, average: 0.021%) and heavier hydrocarbons are not detected. The principal non-hydrocarbon gases are N_2 followed by CO_2.

The contents of CBM well production CH_4 are >98% except for wells (No. 2 and 11), and the depths of these CBM wells vary between 464 m and 819 m (Fig. 3a, Table 1). The N_2 concentrations of the study samples are mostly <1%, except for wells No. 2 and No. 11 (Fig. 3b, Table 1). However, the contents of CO_2 are dispersed at every depth (Fig. 3c, Table 1).

Two CBM wells (No. 2 and No. 11) have lower content of CH_4 and higher content of N_2 in the production gases than others (Fig. 4a–b, Table 1). Golding et al. (2013) discussed that the nitrogen content of gases often correlates with the thermal maturity of the source rocks, and the thermal decomposition of organic matter and high ammonium

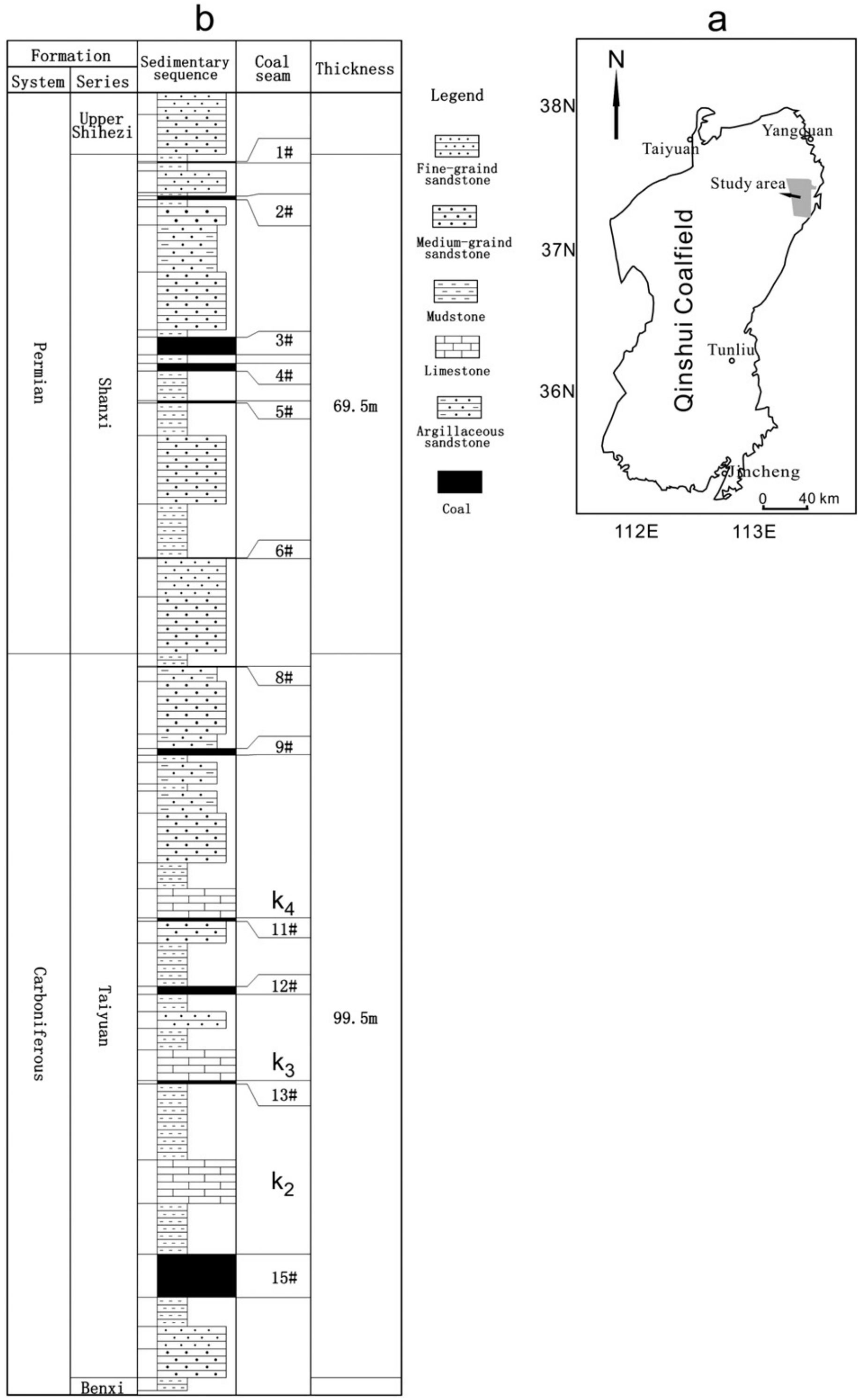

Fig. 1. (a) Location of the study area, Sijiazhuang mining area and (b) sedimentary sequences of Qinshui Coalfield, China. Cited from Zheng et al. (2015a).

clays can produce nitrogen. Previous studies show that ammonium illite and ammonium-illite smectite interlayers widely exist in the Taiyuan Fm., Qinshui Coalfield (Liu et al., 1996; Xu and Liu, 2013; Zheng et al., 2012). The mantle or igneous sources can also contribute to the high concentrations of nitrogen in gases of the coal seam (Boreham et al., 2001b; Liu et al., 2011). The high nitrogen concentration of the two gas samples (No. 2 & No. 11) may correlate with the enrichment of the ammonium illite and ammonium-illite smectite interlayers in the Taiyuan Fm. of Sijiazhuang mining area. Another possible reason is that air could perhaps enter the Taiyuan Fm. through faults or KCC with the recharge water because gas sample No. 11 is very close to a normal fault and No. 2 is near the KCC Xs23 (Fig. 2).

Generally, the R_o values of coal increase with the depth of coal seams in one study area. The pyrolysis experiment of different rank coals shows that nitrogen is mainly released in the forms of NH_3 and HCN in lower rank coal, but as NH_3 in higher rank coal (Liu et al., 2015). In addition, ammonium illite and ammonium-illite smectite interlayers are generated when K^+ is substituted by NH_4^+ transformed from organic

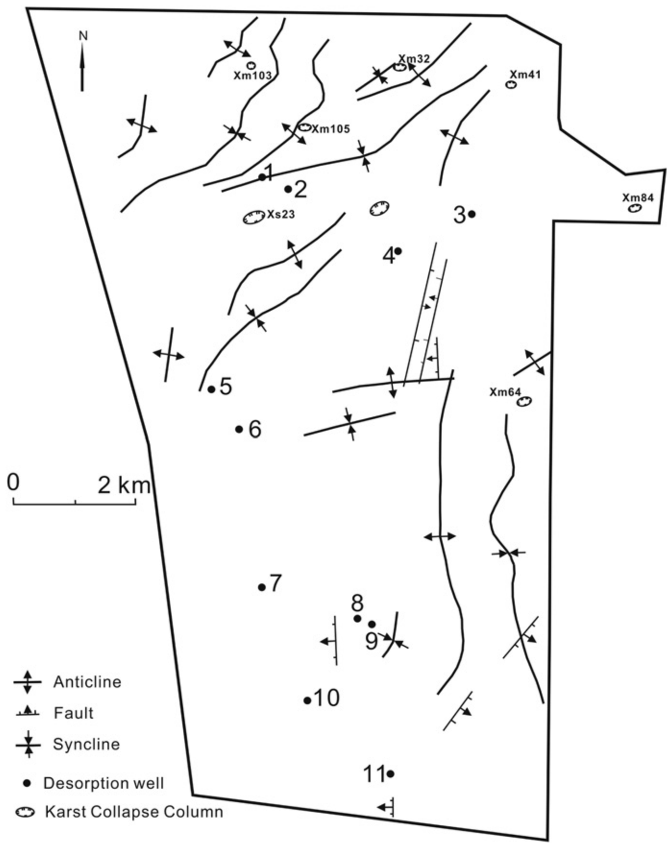

Fig. 2. Map showing the locations of CBM wells where samples were collected and the distribution of karstic collapse columns in Sijiazhuang mining area, Qinshui Coalfield. (The base map is cited from Yangquan Coal Industry (Group) Co. LTD (2008).)

nitrogen under relatively high maturity of coals (Xu and Liu, 2013; Zheng et al., 2012, 2016). Therefore, NH_4^+ concentration increases and more ammonium illite or ammonium-illite smectite interlayers or both form with increasing coals' R_o; in other words, with increasing depth of coal seams. Subsequently, the ammonium illite or ammonium-illite smectite interlayers or both release nitrogen and the amount of nitrogen increases with the depth of the coal seam such that the methane content in gas samples decreases with depth (Fig. 3a). This is why the nitrogen content in Carboniferous coals is lower than Permian ones in the Qinshui Coalfield (Zheng et al., 2015a).

Table 1
Molecular and isotopic compositions of CBM production gases from Taiyuan Formation of Sijiazhuang mining area, Qinshui Coalfield.

SN	Depth/m	Molecular composition[a]/%						Stable isotopic data/‰		
		CH_4	C_2H_6	N_2	CO_2	Ar	He	$\delta^{13}C_1$[a]	δD_{CH4}	$\delta^{13}C_{CO_2}$[a]
1	594	99.2	0.03	0.51	0.29	0.02	0	−33.2	−179	−9.8
2	464	95.9	0.02	3.75	0.27	0.06	0.015	−37.9	−182	−6.0
3	555	99.4	0.01	0.44	0.14	0.02	0	−36.6	−188	−7.5
4	590	99.0	0.02	0.76	0.25	0.02	0	−37.7	−189	−9.0
5	521	99.2	0.01	0.53	0.23	0.01	0.002	−36.2	−186	0.1
6	518	99.4	0.04	0.31	0.21	0.01	0.013	−33.4	−178	−6.8
7	617	99.0	0.01	0.72	0.21	0.02	0.006	−38.3	−188	−10.1
8	543	98.9	0.04	0.61	0.40	0.02	0	−34.8	−179	−4.4
9	579	98.4	0.02	1.22	0.35	0.03	0.006	−39.0	−196	−16.0
10	723	99.0	0.02	0.79	0.17	0.02	0.006	−40.0	−193	−9.2
11	819	97.5	0.03	2.18	0.23	0.03	0.009	−40.8	−186	−15.9

SN, sample No.; Depth, depth of No. 15 coal seam floor; C_1, methane.
[a] Data cited from Xu et al. (2016).

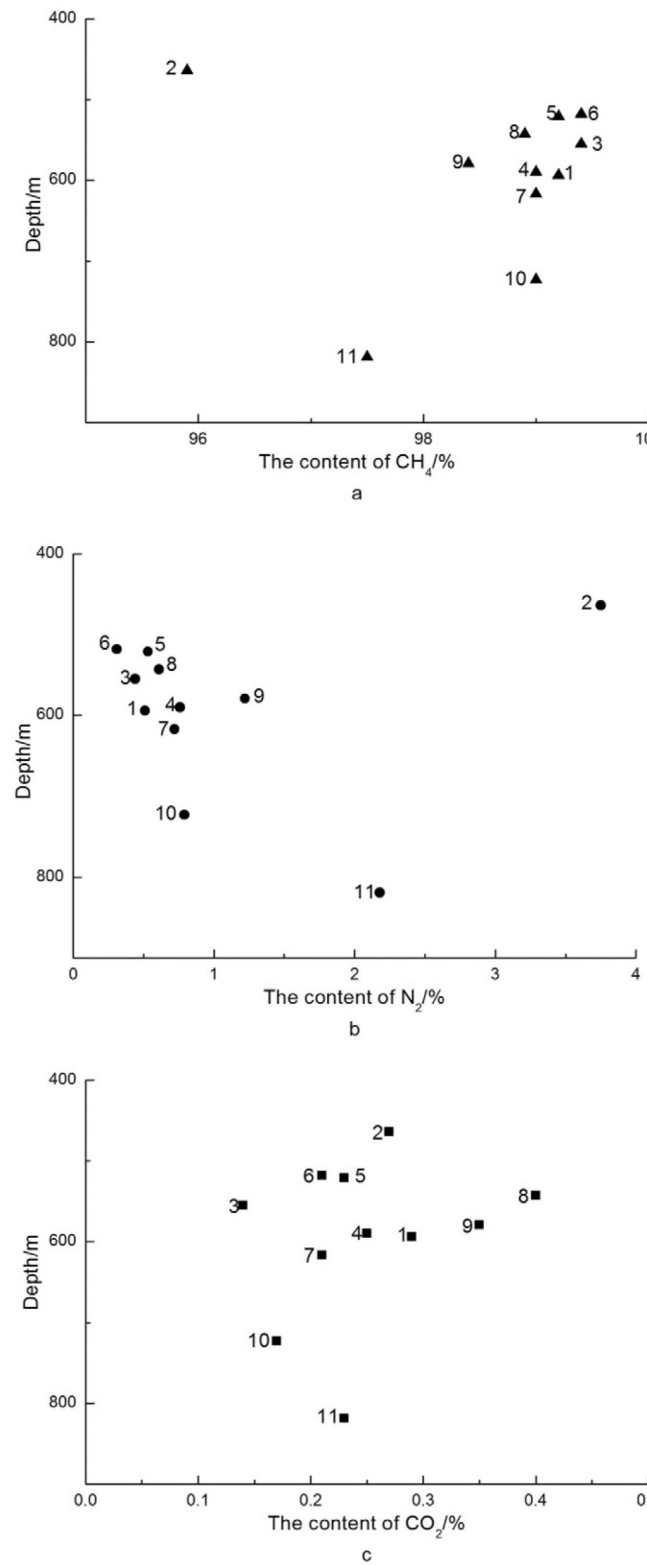

Fig. 3. Plots of coal seam depth vs molecular compositions of CBM production gases: (a) CH_4, (b) N_2, and (c) CO_2.

4.2. Gas isotopic compositions and CBM origin

Golding et al. (2013) discussed that the molecular and stable isotopic compositions of CBM can be used to establish gas origin, particularly regarding the relative roles of thermal and microbial processes and

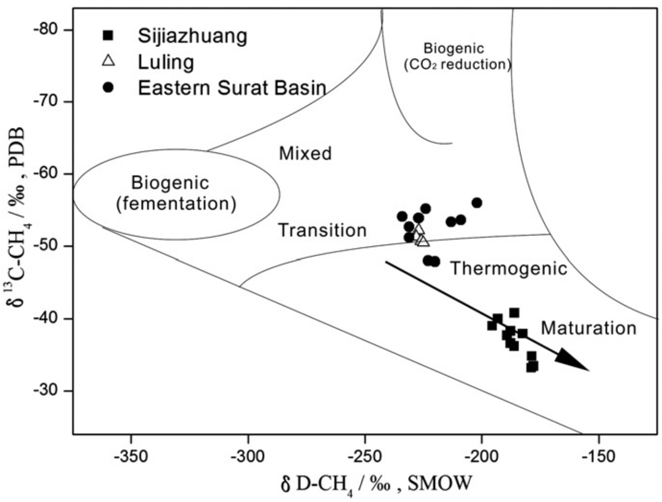

Fig. 4. δ^{13}C vs. δD plot of CH_4 stable isotope compositions for CBM well produced gas samples analyzed in this study. Results from other coal seams in Luling coalfield, China and Eastern Surat Basin, Australia are included for comparison. Luling coalfield CBM production gas data are from Bao et al. (2014). Eastern Surat Basin desorption gas data are from Hamilton et al. (2014).

the microbial methane generation pathway. Coal is almost pure carbon (Moore, 2012) and the bulk of the carbon element in CBM is mainly derived from coal. Variations in δ^{13}C values depend on the coal-forming environment, organic matter type, maturity of thermodynamics and physicochemical and biological actions. The methane carbon isotope compositions of primary thermogenic gases are greater than −50‰ and those of microbial gases are typically less than −50‰ (Golding et al., 2013; Schoell, 1980). Water stripping or cracking of bitumen and liquid hydrocarbons can make the methane carbon isotope lighter like by mixing between thermogenic and microbial gases between −50‰ and −60‰ methane carbon isotope compositions (Golding et al., 1999, 2013; Kinnon et al., 2010; Whiticar, 1996).

The methane carbon isotope values in study area are between −40.8‰ and −33.2‰ (average: −37.1‰) and the δD of CH_4 is −196‰ to −178‰ (Table 1). According to the methane classification of Whiticar et al. (1986), the gas samples in this study fall in the thermogenic gas area, and CBM production gas data from Luling Coalfield, China and eastern Surat Basin, Australia, which are considered for comparison (Bao et al., 2014; Hamilton et al., 2014) (Fig. 4). Considering Fig. 4 and the high maturity of the coal from Taiyuan Fm. Sijiazhuang mining area, it can be concluded that the CBM production gases are primarily of thermogenic origin.

Previous studies show that the methane carbon isotope values have a positive correlation with the maturity of organic matter (e.g. Bao et al., 2013, 2014; Berner and Faber, 1988; Dai et al., 1986). The $R_{o,max}$ values of No. 15 coal seam in Sijiazhuang are between 2.90% and 3.42%. Based on the equation of $\delta^{13}C_1 = 25.85\log R_{o,max} - 43.08$ ($R_{o,max} \geq 1.30\%$) constructed by Bao et al. (2014), the calculated $\delta^{13}C_1$ values of CBM production gases from the Taiyuan Fm., Sijiazhuang range from −31.1‰ to −29.3‰. However, the laboratory measured $\delta^{13}C_1$ values ranged from −40.8‰ and −33.2‰. This difference may be due to microbial processes, water stripping, or cracking of bitumen and liquid hydrocarbons (e.g. Golding et al., 1999; Hu et al., 2001; Kinnon et al., 2010; Whiticar, 1999). Primarily microbial origins of methane are usually found in low-maturity coals and the presence of secondary microbial methane can be found at shallow depths in many higher-maturity uplifted coals (Golding et al., 2013; Hu et al., 2001; Li et al., 2014a). There may be a contribution from secondary microbial methane in shallower parts of Sijiazhuang mining area. The majority microbial methane $\delta^{13}C_1$ values of the world average −70.0‰ (Tao et al., 2007). If we assume microbial process only impacts methane carbon fractionation, the estimated proportion of thermogenic methane from Taiyuan Fm. in Sijiazhuang mining area is calculated to range from 72% to 95%.

4.3. Impact of KCCs on isotopic distribution of CBM production gases

4.3.1. Distribution of KCCs in Sijiazhuang

In general, the Sijiazhuang mining area is located in the north of Qinshui Coalfield, lacks faults, and features a large number of folds and KCCs.

KCC is a type of vertical structure, typically formed in the Carboniferous–Permian coalfields of North China, widely distributed at 45 mines in 20 coalfields, including the Qinshui Coalfield (Yin et al., 2004, 2005). KCCs rapidly collapse under the force of gravity because of the pressure of overlying rocks, stress concentration, and the vacuum of the cave formed by strong groundwater conditions.

In the study area, there are 152 KCCs, 146 of which are found at the ground surface and 6 KCCs were discovered during underground drilling (Yangquan Coal Industry (Group) Co. LTD, 2008). KCCs usually occur in the north of Sijiazhuang mining area and are distributed near the axes of synclines (Fig. 2).

4.3.2. Chemistry and stable isotope compositions of coalbed methane production waters

Obviously, the main anion is HCO_3^- and main cation is Na^+, and therefore, the type of CMPW in Sijiazhuang is Na–HCO_3 (Table 2). Compared with CMPW from the Bowen Basin, the Sijiazhuang CMPW has higher F concentration (average: 5.1 mg/L) than those in the Bowen Basin (average: 1.8 mg/L) and seawater (average: 1.4 mg/L) (Kinnon et al., 2010; Table 2). The concentration of total dissolved solids in Sijiazhuang CMPW ranges from 1282 mg/mL to 1718 mg/mL, with an average of 1417 mg/mL, which is less than that in Liulin mining area of the eastern Ordos Basin (2300–6800 mg/mL) and similar to that in Jincheng mining area, southern Qinshui Basin (691–3409 mg/mL) (Meng et al., 2014). In the study area, coal from the Taiyuan Fm. Carboniferous System is anthracite (R_o, 2.90–3.42%) which is a higher coal rank than those from the Carboniferous System, Ordos Basin (R_o, 1.59–1.93%) (Meng et al., 2015). Between 110 Ma and 140 Ma, the late Mesozoic, a period of intense tectonic thermal activity occurred (Ren et al., 2005), because of which the Carboniferous coal of Qinshui Coalfield has a higher coal rank than that in the Ordos Basin.

The δD values of the water samples range from −74.8‰ to −61.1‰ and the δ^{18}O values range from −9.6‰ to −8.0‰. Table 2 contains statistical data of isotopic compositions. Fig. 5 is a plot of δD vs δ^{18}O of CMPW, which is categorized according to the KCC distribution in Sijiazhuang. The majority of water samples plot below and to the right of the global meteoric water line (GMWL). Mixing with seawater, evaporation, and fluid–rock interaction under high temperature conditions can shift the isotopic composition of meteoric water to the right of the GMWL, whereas open system CO_2 exsolution from CO_2-rich groundwater or spring water, microbial CO_2 reduction, eliminates carbonates and clays from the residual fluids (depleted in ^{18}O and enriched in D) in the coal seams (Cartwright et al., 2002; Kinnon et al., 2010; Schofield and Jankowski, 2004; Whiticar, 1999). It is likely that the CMPW samples in the current study, which fall to the right of the GMWL, were affected by a combination of fluid–rock interaction under high temperature conditions and evaporation. The presence of KCCs in the north of the study area may contribute to groundwater evaporation, which may also be a reason for the high F levels in groundwater samples.

4.3.3. The correlation between KCC and geochemistry of CBM production gases and waters

Fig. 6 shows contour maps of (a) the depth of 15# coal seam, (b) $\delta^{13}C_1$, (c) δD of methane, and (d) $\delta^{13}C_{CO_2}$, drawn based on the limited data from the study area using the Modified Shepard's Method. The CH_4 carbon isotopic composition becomes more enriched in ^{13}C in

Table 2
The stable isotope and quality statistics of coalbed methane production waters and data of CBM wells where the waters were sampled in Sijiazhuang mining area, Qinshui Coalfield.

	1	2	3	4	5	6	7	8	9	10	11	Seawater*
D (‰)	−66.0	−67.8	−74.8	−69.5	−64.3	/	−64.2	/	−65.9	−64.7	−61.1	
O (‰)	−9.0	−9.2	−8.9	−9.6	−8.7	/	−8.0	/	−9.1	−8.9	−9.1	
TDS (mg/L)	1718	1418	1469	1516	1482	/	1452	/	1409	1520	1282	35,000
Cl (mg/L)	37.7	42.3	52.3	42.9	36.7	/	33.7	/	36.0	39.9	41.0	19,700
Ca (mg/L)	7.7	7.88	6.17	7.06	8.12	/	5.81	/	6.40	5.60	7.61	410
Mg (mg/L)	2.36	2.50	1.96	2.75	2.94	/	2.05	/	2.50	1.80	2.47	1310
Na (mg/L)	475	390	409	429	411	/	404	/	399	423	359	1900
K (mg/L)	1.26	1.79	1.09	1.04	8.22	/	1.08	/	2.18	1.00	4.75	390
HCO_3 (mg/L)	1143	938	959	978	953	/	968	/	904	1009	801	
SO_4 (mg/L)	4.95	0.86	1.68	2.73	0.70	/	8.82	/	0.33	2.07	14.1	
F (mg/L)	4.27	3.96	5.76	5.28	4.45	/	5.12	/	5.55	5.31	6.23	1.4
WP (m^3/d)	0.5	3.6	24	1.2	0.1	0.1	0.6	0.1	0.6	0	0.1	
CCP ($\times 10^5$ m^3)**	/	2.5	/	15.8	1.6	29.1	14.5	/	1.9	12.7	1.8	
Drainage time (m)	44	44	40	44	49	46	65	49	49	49	49	
CC (m^3/t)	12	4	8	8	9	12	12	10	11	12	13	

WP, water production; CCP, cumulative CBM production (10^5 m^3); CC, CBM content of No. 15 coal seam, Taiyuan Fm. (m^3/t); m, month; *, seawater data cited from Kinnon et al. (2010); **, CCP data cited fromZheng et al. (2015b);/ no data.

shallower areas, where more KCCs have been identified in the north of Sijiazhuang mining area than in the south (Fig. 6a–b). One possible reason for the heavier $\delta^{13}C_1$ values in the north of the study area is the desorption–diffusion–migration isotope fraction effect of CBM. In contrast, the $\delta^{13}C_1$ and $\delta^{13}C_{CO_2}$ values are lighter in deeper areas such as in the southwest of the study area (Fig. 6d). This could be due to the stronger groundwater stripping process in that area.

Generally, the water in the coal-bearing strata decreases with ongoing drainage because it has limited volume. However, if Ordovician water seeps into the coal strata via the pathway of a KCC, the conservation and distribution of CBM may be affected. Most coal seams in the Taiyuan Fm. are above the Ordovician groundwater level, but in the west, the deepest depth of coal seam No. 15 is 340 m, which is below the Ordovician groundwater level (Yangquan Coal Industry (Group) Co. LTD, 2008). Furthermore, there are three main limestone aquifers K_2, K_3, and K_4 in the Taiyuan Fm. of Sijiazhuang mining area, and K_2 overlies the coal seam No. 15 (Fig. 1b). The outcrops of K_2, K_3, and K_4 are exposed by north–south distribution in the east. Karsts are developed as dissolved fissures, and sometimes as pores or caves in the limestone aquifers. When the caves collapse, KCC is generated and fractured rocks can obtain more groundwater. CBM well No. 3 may feature this situation because its water production is up to 24 m^3/d (Table 2), far more than others in Sijiazhuang mining area.

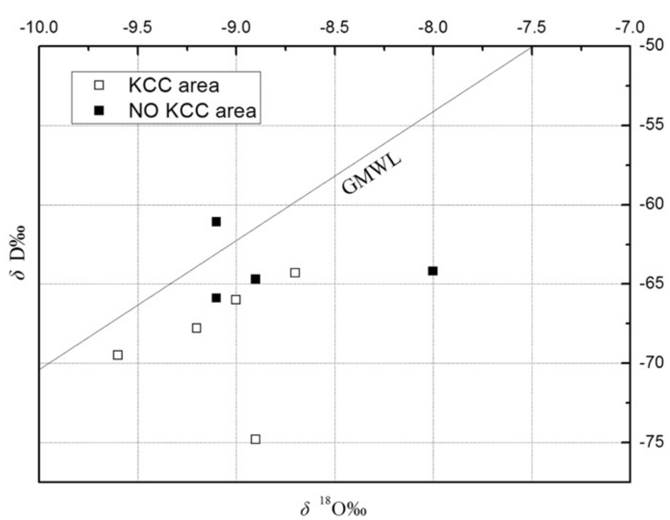

Fig. 5. Plot of δD vs $\delta^{18}O$ of Taiyuan Fm. coalbed methane production waters categorized according to the KCC distribution in Sijiazhuang mining area.

The isotope compositions of CBM production gases (e.g. CH_4, CO_2) and groundwater type or hydrochemistry are influenced by many factors, like faults and KCCs. KCC Xs23, is generated at the Shanxi period of the Permian, shown on Figs. 3 and 6b–d; the CO_2 and methane carbon isotopes become heavier near the Xs23. Golding et al. (2013) discussed that the lighter $\delta^{13}C_1$ and $\delta^{13}C_{CO_2}$ values of deeper samples resulted from progressive depletion of the carbon reservoir, most likely related to the residence time of groundwater; otherwise, the overmature dry gas or abiogenic methane mixed with thermogenic gas results in ^{13}C enrichment in methane. According to the water type and TDS data, the residence time of groundwater in Sijiazhuang maintains a stable condition for a long geological time leading to the enrichment of overmature gas and thermogenic gas with more ^{13}C. The carbon isotope compositions of shallower gas samples are heavier because stronger desorption–diffusion–migration effects exist in the north of the study area, where more KCCs occurred. There is a normal fault and a syncline near CBM wells No. 8 and 9 in the south of the study area (Fig. 6d). The same reason can explain the heavy $\delta^{13}C_1$ values on the normal fault side and lighter $\delta^{13}C_1$ values on the syncline side; that is, there is a stronger desorption–diffusion–migration effect on the normal fault than that on the syncline side.

5. Conclusions

Molecular and isotopic analyses of the gases from eleven CBM production wells suggest that thermogenic methane is the primary source of the CBM from the Taiyuan Fm., with minority microbial methane in shallower parts in the Sijiazhuang mining area. The isotopic compositions of the CBM production gases and waters have good correlations with the distribution of karstic collapse columns in the north of the Qinshui Coalfield. A greater volume of CBM production water with lighter carbon and hydrogen isotopes, smaller gas content and heavier carbon isotopes of CH_4 and CO_2 is found in the north of the study area, where there are more KCCs. This could be related to the KCC or the limestone formation of the Taiyuan Fm. causing a stronger desorption–diffusion–migration effect. The results of this study can be used for CBM exploration and exploitation in KCC areas.

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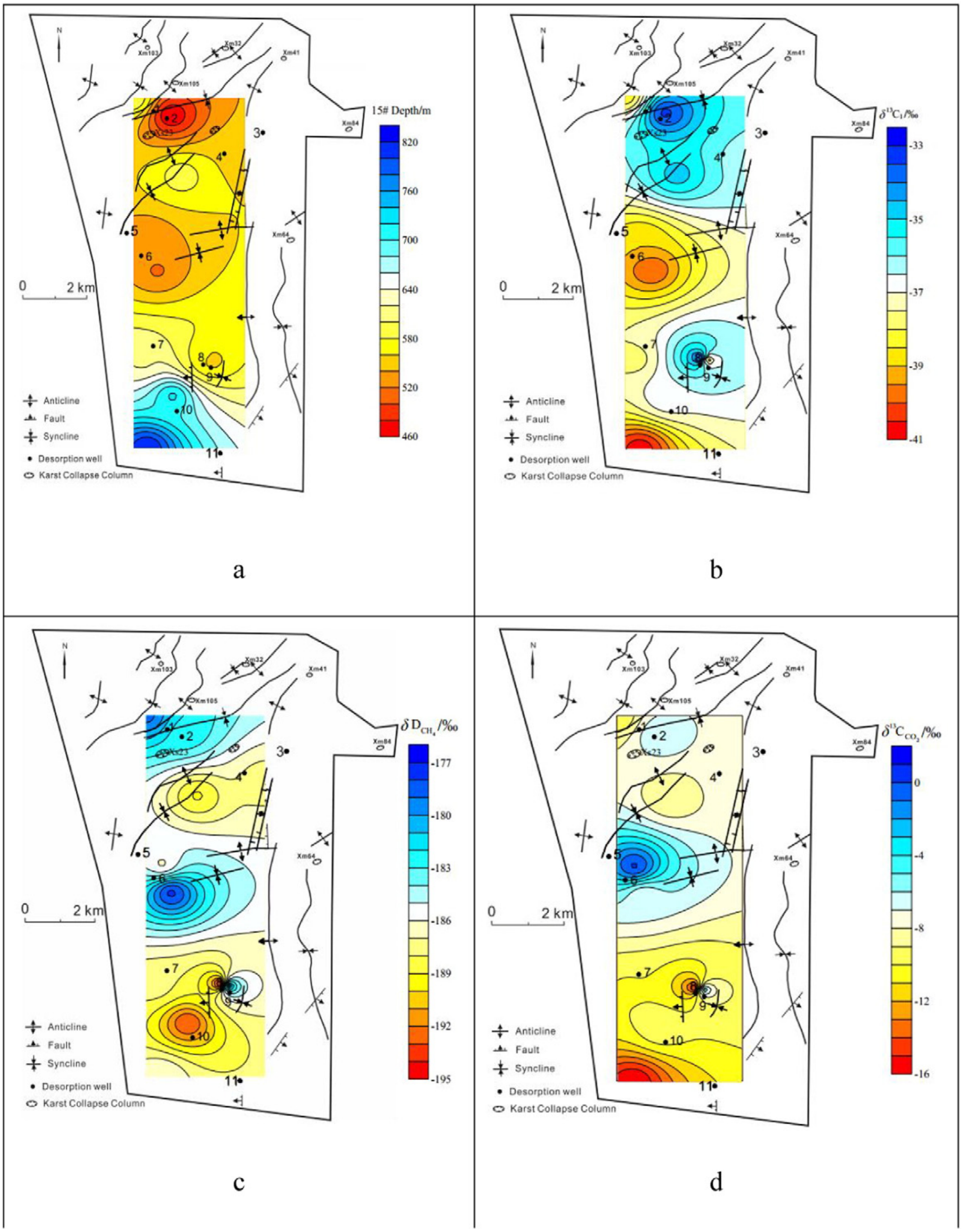

Fig. 6. Contour maps of (a) the depth of the No. 15 coal seam, (b) $\delta^{13}C_1$, (c) δD_{CH4} and (d) $\delta^{13}C_{CO_2}$, drawn based on limited data from Sijiazhuang mining area and using the Modified Shepard's Method.

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