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# Isotopic composition and content of coalbed methane production gases and waters in karstic collapse column area, Qinshui Coalfield, 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 $\delta D$ 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).

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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