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Isotopic Characteristics and Origins of Coalbed Gas of Sijiazhuang Mine Field in Northern Qinshui Basin

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There are few studies on the origins of coalbed gas in the northern Qinshui Basin, therefore, the coalbed gas in the Taiyuan Formation of the Sijiazhuang mine field in the northern Qinshui Basin was extracted to test the chemical composition and isotope of effluent gas from six coalbed gas wells, and thus the origins of coalbed gas can be explored. The results show that the average volume fractions of CH4, C2H6, CO2 and N2 in the coal seam of the northern Qinshui Basin are 94.98 %, 0.11 %, 0.25 % and 4.8 %, respectively, with no hydrocarbons heavier than ethane detected. The carbon and hydrogen isotopic values of methane of coalbed gas are within the range of -42.5 ‰ ~ -36.7 ‰ and - 200.06 ‰ ~ -196.33 ‰, respectively; and δ13C (CO2) is between -17.1 ‰ and -15.1 ‰. The solution fractionation of groundwater is the main cause of the methane carbon isotope's becoming lighter with increasing depths. The chemical composition and isotope test data of the Sijiazhuang mine field indicate that the coalbed gas has been subjected to the secondary transformation effect, mainly from coal cracking thermo genesis and supplemented by secondary biogenesis of CH4.

1. Introduction

The chemical and isotopic compositions of coalbed gas are the main contents of coalbed gas geochemical investigation, and the carbon isotopic composition has become an effective index to determine the origins of the coalbed gas and to understand the distribution law. Some studies have shown that the carbon isotope value of methane of coalbed gas becomes heavier with the coal evolution (Song et al., 2012). Actually, the coalbed gas carbon isotopic composition varies greatly due to the influence of multiple factors including the desorption-diffusion-migration effect, thermal evolution degree, groundwater dynamic conditions and microbial effects. The structure geometry influences the distribution of coalbed gas (Hou et al., 2012). The isotopic differentiation effect of the coalbed gas formation under the thermodynamic mechanism leads to the heavier methane carbon isotope with the greater maximum reflectance of coal vitrinite and coal seam depth (Meng et al., 2014;). The experimental data confirm that the flowing water lightens the methane carbon isotope, so the coalfields with strong hydrodynamic force contain a small amount of coalbed gas, where the methane carbon isotope is relatively light.The carbon isotopes of microbial coalbed methane are generally lighter; the primary biogenic gases usually appear in the low-rank coals, and the secondary biogases occur in coal rocks with high thermal evolution and even in anthracite (Golding et al., 2013; Li et al., 2014). The microbiogenic gases can even constitute the main reason for the sustained and stable production of coalbed gas (Hamilton et al., 2014). Compared with the conventional natural gas, the coalbed gas composition and its carbon isotopic composition are differently affected by the secondary action with different influencing effects. The latter is determined in the geologic period with the highest evolutional level, which can reflect the thermal evolution process of coal seam. At present, few studies touch upon the relationship between origins of methane and carbon dioxide of coalbed gas in the northern Qinshui Basin, so it is necessary to study the origins of coalbed gas in this area.

Taking the effluent gas from the Sijiazhuang mine field in the northern Qinshui Basin as the research object (Figure 1a), this paper analyzes the chemical composition and carbon isotope of coalbed gas through

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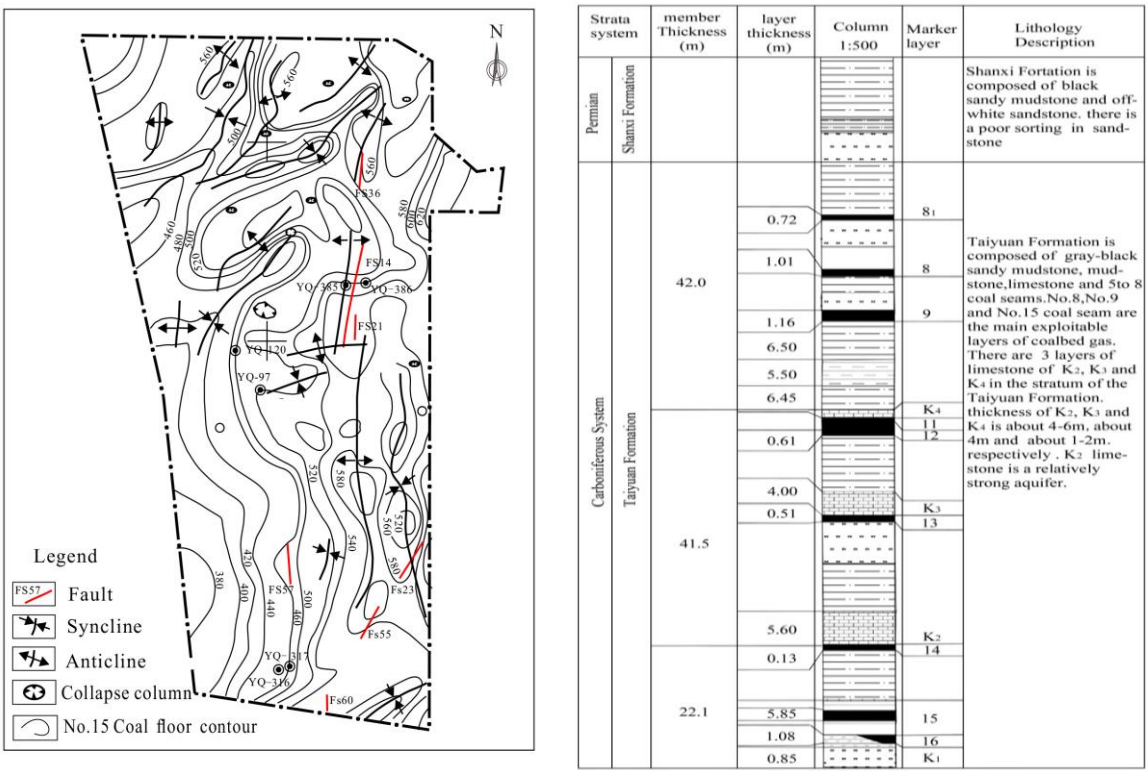
experiments. Also, the carbon isotopic characteristics and origins of methane and carbon dioxide are explored.



(a) (b)

Figure 1: (a) Location and Geological Structure of Sijiazhuang Mine Field; (b) Stratigraphic Column of Sijiazhuang Mine Field

2. Regional Geological Background

Located in the southeastern part of Shanxi Province, the Qinshui Basin as a craton fault basin with relatively weak tectonic activities is sandwiched between the Lvliang Mountains and the Taihang Mountains. It is a multiple-syncline structure with a main trend of NNE and average dip angles of respective 4.2 ° and 4 ° in the east and west sides. There are relatively few faults, whose fall is generally within 20 m. Since the Late Paleozoic era, the tectonic stress field has experienced three stages of evolution or two transitional periods. The Sijiazhuang mine field is located in the northwest edge of the Qinshui Basin and west to the Taihang uplift. Similar to the Qinshui Basin, its strata are also old in the east and new in the west. With a north-west direction, the strata are inclined southwest at a dip angle of generally 5 °~10 °, and the dip angle of some fold areas is 12 °~20 °. The main coal-bearing strata are located at the Carboniferous Taiyuan Formation and the Permian Shanxi Formation. The total thickness of the coal-bearing strata is 171 m, which contains 18 layers of coal, measuring 15m. No.8, No.9 and No.15 in the Taiyuan Formation are the exploitable layers of coalbed gas resources in the region, among which No.15 is the major one for mining (see the Stratigraphic of Figure 1 b).

The tectonic structure of Sijiazhuang mine field is very simple with the fold structure of alternating anticlines and synclines as the basic structural featureof this area. The tectonic directions are mainly near south-north and north-east. The group of south-north folds, mainly distributed in the middle and the east, is characterized by compact arrangements with a spacing of 1,000 m. The two flanks of the syncline are asymmetrical: the east flank is steep with a dip angle of 20 °, and the west flank is gentle with a dip angle of about 10 °. And the anticline axis is open and flat. The group of north-east folds is mainly distributed in the northwest and southeast of the exploration area, characterized by sparse arrangements with a spacing of 1,500 m. The two wings are mostly asymmetrical with the southeast steep and the northwest slow. The fault is a normal one with 33 collapse columns of 124 km^2, which are more developed in the north. The columns are mostly round and oval with a diameter generally between 20~50 m (the smallest one is 10 m) and a wall angle of 62 °~83 °

(generally 80°) (Figure 1 a). The geometric distribution of the structure leads to uneven distribution of coalbed gas.

3. Samples and Test Methods

3.1 Sample Collection

The gas samples used in this experiment are collected by the drainage gas-collection method, and the sampling water is deionized saturated salt water sealed in glass bottles.
The sampling points of coalbed gas are distributed in the Sijiazhuang mine field of northern Qinshui Basin. YQ-385 and YQ-386 are located in east-central mine field, YQ-120 and YQ-97 in the west-central mine field, and YQ-317 and YQ-316 in the southern mine field. The YQ-317 hole and YQ-316 hole are only used to mine No.15 coal seam, and other holes are used for the mining of No.8+9+15 coal seam. Six groups of samples are collected from 6 coalbed gas wells, two samples in each group for contrast. 200~500 mL of each gas sample is collected for indoor tests of the chemical composition and isotopic composition.

3.2 Test Methods and Conditions

The chemical composition and isotope testing of coalbed gas are completed at the Key Laboratory of Lanzhou Oil and Gas Resources Research Center, Institute of Geology and Geophysics, Chinese Academy of Sciences. The chemical composition of coalbed gas is tested by the large-scale gas isotope mass spectrometer (type: MAT 271). The carbon isotope of methane and carbon dioxide and the hydrogen isotope of methane are tested and analyzed on the stable isotope analysis system, which is mainly composed of the gas chromatography (GC) and isotope ratio mass spectrometer, referred to as "GC-IRMS" analysis system. The chromatograph type is Agilent 6890, and the type of the stable isotope mass spectrometer is Deltaplus XP. The accuracy of the carbon and hydrogen isotope test is ± 0.2 ‰~± 1 ‰. The test results are shown in Table 1.

Table 1: Geochemical Composition of Coalbed Gas in Sijiazhuang Mine Field

Well No.	Composition / %					Dryness coefficient $c_1/(c_1+c_2)$	CDMI / %	δ-value of isotope /‰			coal seam	Depth of No. 15 coal seam/m
	CH_4	C_2H_6	CO_2	N_2	Ar			$\delta^{13}C$ (CH_4)	δD	$\delta^{13}C$ (CO_2)		
YQ-097	92.95	0.01	0.09	6.82	0.12	>0.99	0.097	-36.7	-186.33	-15.6	8+9+15	473.23
YQ-120	94.55	0.01	0.11	5.25	0.08	>0.99	0.116	-37.3	-191.88	-15.3	8+9+15	520.70
YQ-316	96.7	0.04	0.12	3.08	0.05	>0.99	0.124	-41.2	-199.58	-16.3	15	677.85
YQ-317	95.3	0.01	0.17	4.44	0.08	>0.99	0.178	-42.5	-200.06	-17.1	15	661.25
YQ-385	95.4	0.01	0.08	4.43	0.08	>0.99	0.084	-37.9	-186.79	-16.0	8+9+15	469.03
YQ-386	27.59	0	0.05	56.99	0.64	1	0.181	-37.6	-194.96	-15.1	8+9+15	509.16

Note: CDMI=$\varphi(CO_2)/[\varphi(CO_2)+\varphi(CH_4)]$

4. Geochemical Characteristics of Coalbed Gas

4.1 Characteristics of Geochemical Components of Coalbed Gas

The coalbed gas of Sijiazhuang mine field mainly consists of methane (Table 1), whose volume fraction is 92.95 % ~ 96.7 % with an average content of 94.98 %. The ethane content is few with a volume fraction of 0.01 % ~ 0.04 % and an average content of 0.016 %. No hydrocarbons heavier than ethane are detected, and the non-hydrocarbon gases contained are mainly nitrogen, carbon dioxide and argon, whose volume contents are 3.08 %~6.82 %, 0.08 %~0.17 % and 0.05 % ~ 0.12 %, respectively, averaged 4.8 %, 0.11 % and 0.08 %. The dry coefficient values are greater than 0.99, which indicates that they are extremely dry gases judging from the chemical components with the CDMI of 0.084 %~ 0.178 %. In addition, the methane content of YQ-386 is obviously low at 27.59 %, the nitrogen content is significantly high at 56.99 %, the carbon dioxide content is relatively low at 0.05 %, and the argon content is relatively high at 0.64 %. The coalbed gases produced during the low-rank and high-rank stage are mostly dry gases (C_1/C_{2+}> 19), and those produced during the middle-rank stage are wet gases (C_1/C_{2+}≤ 19) (Clayton, 1998). The coal in Sijiazhuang mine field is high in metamorphic grade, and the maximum reflectance (R_o) of the vitrinite of No.15 in Sijiazhuang mine field is 2.9 %~3.1 %. The metamorphic stage is stage VI, indicating that it belongs to the anthracite No.3 (Report on Coal Resources/Reserves in Sijiazhuang, Qinshui Coalfield in Shanxi Province [R]. 2008). The high maturity is one of the reasons for the extremely dry gases in the coalbed gas. Both the biogenetic gas and the thermal cracking gas possess the characteristics of dry gas (Tao et al., 2007; Ahmed et al., 2001; Golding et al., 2013). Strong uplift and denudation has occurred in the Qinshui basin since the Cenozoic Himalayan period, leading to the exposure of the coal seam to air or surface water. Thus, the methanogens and other microorganisms may gain access to the coal seam and produce secondary biological gas, contributing to the possibility of dry coalbed gases.

The limestone of Taiyuan formation is exposed in a limited range in Sijiazhuang mine field, and the limestone of the underlying outcrop and the shallow layer of the Songxi River and other valleys play an important role in groundwater supply. Hence, it becomes the important aquifer of a certain area with the field being its runoff area. The average salinity of water from the Sijiazhuang coal field is relatively low at 1,433 mg/L, indicating relatively good mobility of groundwater. Previous studies have shown that origin difference of the organic and atmospheric nitrogen can be determined by the ratio of nitrogen to argon dissolved in groundwater (Marty et al., 1988).It can be seen from Table 1 that $\varphi(N_2)/\varphi(Ar)$ is between 55~66 with the average being 59 (between 40 and 84), which indicates that the organic and atmospheric nitrogen coexist in the coalbed gas. This further illustrates the good fluidity of groundwater in Sijiazhuang mine field. The N_2 content in the sample YQ386 is abnormally high, and it is possibly because of its location near the fault FS14, where the groundwater mobility is strong, leading to the access of N_2 in the atmosphere into the coal seam.

The CO_2 content in the coal seam is greatly increased in the early stage of coalification; and with the thermal evolution, the CH_4 content gradually increases and the CO_2 content decreases gradually (Ju et al., 2014). The CO_2 content of coalbed gas in Sijiazhuang coal mine is 0.08 % ~ 0.17 %, with an average of 0.11 %, which is at a low level. Therefore, it mainly comes from the organic macromolecules Decarboxylase reaction of coal and the bacterial decomposition of organic matter with little influence by the CO_2 from inorganic origin and carbonate mineral dissolution.

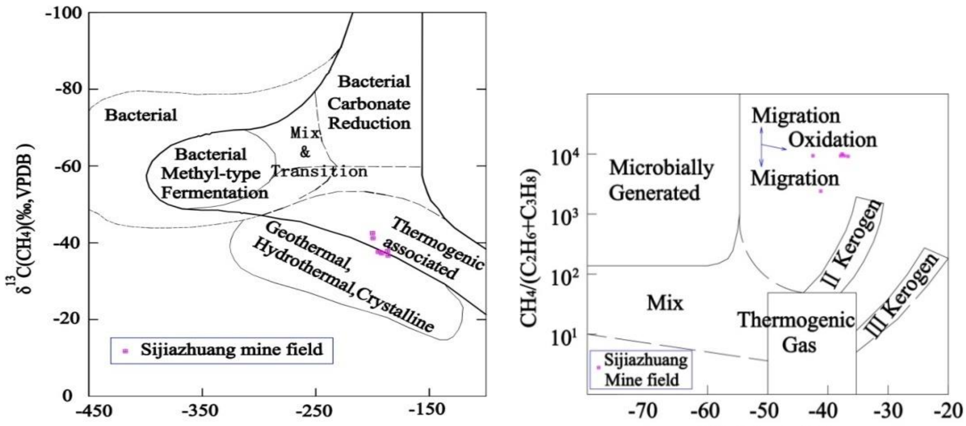
4.2 Carbon isotope Characteristics of Coalbed Gas

Carbon is one of the most important elements of coalbed gas, and almost all the carbon in coalbed gas comes from coal. The carbon isotope ($\delta^{13}C(CH_4)$) of coalbed methane in Taiyuan formation of Sijiazhuang mine field is within the range of -42.5 ‰~-36.7 ‰, averaging -38.9 ‰; and the carbon isotope value $\delta^{13}C$ (CO_2) of carbon dioxide is -17.1 ‰ ~ -15.1 ‰, averaging -15.9 ‰.

The isotope content of $\delta^{13}C_1$ of Sijiazhuang mine field is close to that of the freshwater plants. The reason may be that the coal of Sijiazhuang mine field has a high degree of metamorphism, reaching the level of anthracite III. The carbon isotope value of $\delta^{13}C$ (CO_2) is smaller than that of conventional natural gas and biogas and equivalent to the upper limit of coal gas, averaging -15.9 ‰ and showing the carbon isotopic characteristics of coal gas-mixed methane.

5. Discussion

5.1 Origins of Methane in the Coalbed Gas



(a) (b)

Figure 2: (a) Identification of Origins of Carbon and Hydrogen Isotope in Coalbed Gas of Sijiazhuang Coalfield (The Base Map is Cited from Literature Whiticar,1999); (b) Bernard Discriminant Map of Coalbed Gas in Shijiazhuang Mine Field (Cited from Literature Kotarba, 2001)

The thermogenic and biogenic methane can be identified by carbon isotopic composition. The primary biogenic methane is mainly formed in the initial stage of peat and low-rank coal thermal evolution, and the secondary biogenic methane can be formed in the high-rank coal. The value of $\delta^{13}C(CH_4)$ generated under the microbial action is generally less than -50 ‰. The value of $\delta^{13}C(CH_4)$ produced by the reduction of carbon dioxide is in the range of -110 ‰~-60 ‰, and the value of $\delta^{13}C(CH_4)$ produced by acetate fermentation is in the range of -65 ‰~-50 ‰ (Whiticar et al. 1986). The carbon isotope of thermogenic methane is relatively heavy and generally heavier than -50 ‰.

In the early stage of coalification (R_0 value is within 0.50 %~0.80 %), the chemical components of the early thermogenic coalbed gas produced from high-volatile bituminous coal contain much moisture such as ethane and propane except methane. In the stage of moisture generation (R_0 value is between 0.60 %and 0.80 %), the drying coefficient of the coalbed gas is less than 0.8, and the ethane content may exceed 11 %. When the R_0 value is between 0.80 % and 1.00 %, the coal will produce a large amount of thermogenic methane; when the R_0 value is about 1.20 %, the coal seam is in the peak of gas generation (Scott et al. 1994). The R_0 value of No.15 in Sijiazhuang mine field is 2.9 %~3.1 %, greater than the peak value of gas generation. Theoretically, the coalbed gas may contain thermogenic gases. The average the value of $\delta^{13}C(CH_4)$ is actually measured at -38.9 ‰, larger than the upper limit (-50‰) of secondary biogas and smaller than the lower limit (-35 ‰) of the pyrolysis gas in Qinshui basin (Li et al., 2017). The degree of coal metamorphism is very high, reaching the level of anthracite Ⅲ. The model of relationship between methane hydrogen isotope and carbon isotope by Whiticar (1999) is employed to analyze the origins of coalbed gas in Sijiazhuang mine field (Figure 2 a). The test data of coalbed gases from Sijiazhuang mine field are within the range of thermogenic gas, mainly thermal cracking gas. Through the Bernard discriminant map (Figure 2 b), it is shown that the coalbed gas is not purely thermogenic gas but the products of secondary transformation after its formation.

5.2 Origins of Carbon Dioxide in the Coalbed Gas

Carbon dioxide in coalbed gas varies in contents and is soluble in water. When the carbon dioxide content is less than 15 %, it is considered to be organ ogenic; and when the concentration is more than 60 %, it is inorganic genetic (Dai et al., 2001). The average carbon dioxide content in the coalbed gas of Sijiazhuang coal mine is 0.11 %, indicating organic genesis. Since the coal in this area is anthracite III with a high degree of metamorphism, the carbon dioxide may derive from the decaboylation of organic matters in coal.

The carbon isotopic composition of carbon dioxide from different sources may be different. The value of $\delta^{13}C$ (CO_2) of organic genesis is less than -10‰; the inorganic genetic $\delta^{13}C$ (CO_2) is greater than -8 ‰ (Dai et al., 2001); the $\delta^{13}C(CO_2)$ relative to the secondary biogas is in the range of -40 ‰~+20 ‰ (Whiticar, 1986); and the carbon isotope value of carbon dioxide from thermal cracking of coal do not exceed 0.15 ‰ (Song, et al., 2012). The value of $\delta^{13}C$ (CO_2) in coalbed gas of Sijiazhuang mine field is within the range of -17.1 ‰ ~ -15.1 ‰, averaging -15.9 ‰. Therefore, Carbon dioxide of the coalbed gas in the Sijiazhuang mine field should be the secondary biogas and thermal cracking gas. The test results of carbon dioxide carbon isotope show that the values of $\delta^{13}C$ (CO_2) vary slightly with the $\delta^{13}C$ (CO_2) value of only YQ-317 and YQ-316 being slightly smaller, which is possibly because only coalbed gas from No.15 is extracted through them.

5.3 Relation between Origins of Methane and Dioxide Carbon in the Coalbed Gas

The genetic analysis can also be conducted according to the carbon isotope values of methane and dioxide carbon for origin identification of coalbed gas (Golding et al., 2013). The carbon isotopic values of methane and dioxide carbon in the coalbed gas of Sijiazhuang coal field are within the scope of thermogenic gas, and there is a certain positive correlation between the values. According to the results of the existing studies (Golding et al., 2013; Hamilton et al., 2014), the carbon isotopic values of methane and dioxide carbon are positively correlated. And the surface coalbed gas contains secondary biogenic gas, indicating the occurrence of secondary biogenic gas the coalbed gas of Sijiazhuang mine field.

The value of $\delta^{13}C$ (CO_2) reflects the percentage of methane produced by reduction of dioxide carbon. When the percentage is about 50 %, the $\delta^{13}C$ (CO_2) of dioxide carbon is about +2 ‰; when the percentage is about 30 %, the $\delta^{13}C$ (CO_2) of dioxide carbon is -15 ‰ (Jones, 2008). According to the average value (-15.9 ‰) of the $\delta^{13}C$ (CO_2) of six dioxide carbons samples from Sijiazhuang mine field, it can be estimated that the secondary biogas from bacterial degradation accounts for about 30 %.

The methane carbon isotope of Sijiazhuang mine field becomes lighter with the increase of depth. The coal seam of Sijiazhuang mine field leans to the southwest, meaning that the depth of coal seam increases in the southwest direction. The K_2 limestone in the Upper Carboniferous Taiyuan formation is about 51m below the No.8 and No.9 coal seam, covering the coal seam No.15 (Figure 1 b). Since $^{13}CH_4$ is soluble in groundwater (Qin et al., 2012), the limestone water is directly involved in the fractionation of No.15 coalbed gas, and No.8 and No.9 are less influenced. Therefore, with the depth increasing from northeast to southwest, the methane carbon isotope of No.15 becomes lighter, leading to the significantly lighter methane carbon isotope in the southwest (YQ-317 and YQ-316). YQ-385, YQ-386, YQ-120 and YQ-97 are used to mine the No. 8+9+15 coal seam, which explains the relatively heavy isotope. Therefore, the groundwater solution fractionation is one of the main origins for methane carbon isotope becoming lighter with increasing depths.

6. Conclusion

this paper analyzes the chemical composition and carbon isotope of coalbed gas through experiments. Also, the carbon isotopic characteristics and origins of methane and carbon dioxide are explored The groundwater solution fractionation is the main origins for methane carbon isotope becoming lighter with increasing depths.The coalbed gas in Sijiazhuang mine field has been influenced by secondary transformation effects, mainly from coal cracking thermogenesis and supplemented by secondary biogenesis of methane.

Acknowledgments

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