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Distribution and fractionation mechanism of stable carbon isotope of coalbed methane

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Abstract The stable carbon isotope values of coalbed methane range widely, and also are generally lighter than that of gases in normal coal-formed gas fields with similar coal rank. There exists strong carbon isotope fractionation in coalbed methane and it makes the carbon isotope value lighter. The correlation between the carbon isotope value and R_o in coalbed methane is less obvious. The coaly source rock maturity cannot be judged by coalbed methane carbon isotope value. The carbon isotopes of coalbed methane become lighter in much different degree due to the hydrodynamics. The stronger the hydrodynamics is, the lighter the CBM carbon isotopic value becomes. Many previous investigations indicated that the desorption-diffusion effects make the carbon isotope value of coalbed methane lighter. However, the explanation has encountered many problems. The authors of this article suggest that the flowing groundwater dissolution to free methane in coal seams and the free methane exchange with absorbed one is the carbon isotope fractionation mechanism in coalbed methane. The flowing groundwater in coal can easily take more $^{13}CH_4$ away from free gas and comparatively leave more $^{12}CH_4$. This will make $^{12}CH_4$ density in free gas comparatively higher than that in absorbed gas. The remaining $^{12}CH_4$ in free gas then exchanges with the adsorbed methane in coal matrix. Some absorbed $^{13}CH_4$ can be replaced and become free gas. Some free $^{12}CH_4$ can be absorbed again into coal matrix and become absorbed gas. Part of the newly replaced $^{13}CH_4$ in free gas will also be taken away by water, leaving preferentially more $^{12}CH_4$. The remaining $^{12}CH_4$ in free gas will exchange again with adsorbed methane in the coal matrix. These processes occur all the time. Through accumulative effect, the $^{12}CH_4$ will be greatly concentrated in coal. Thus, the stable carbon isotope of coalbed methane becomes dramatically lighter. Through simulation experiment on water-dissolved methane, it had been proved that the flowing water could fractionate the carbon isotope of methane, and easily take heavy carbon isotope away through dissolution.

Keywords: coalbed methane, methane stable carbon isotope, fractionation mechanism, accumulative effect.

1 Stable carbon isotopes of coalbed methane

Gas produced by coal or coal measure mudstone can be divided into two types: normal coal-formed gas and coalbed methane (CBM). Although both are mainly of methane, the carbon isotope value of coalbed methane is obviously lighter. This phenomenon has been realized by coal petrologists, coal geologists and coalbed gas geologists for long[1−5]. The following are the dispersal futures of the carbon isotope values of coalbed methane.

1.1 The carbon isotope value of coalbed methane is generally lighter

Compared with the methane carbon isotope values between the normal coal-formed gas from the main large-middle gas fields and coalbed methane from the basins in China (Fig. 1), it is clearly seen that the carbon isotope values of coalbed methane are quite different from normal coal-formed gas. Firstly, the carbon isotope values of coalbed methane are usually lighter than that of the normal coal-formed gas; secondly, the stable carbon isotope values of coalbed methane range from −35‰ to −90‰, while that of the normal coal-formed gas is only from −30‰ to −40‰. Obviously, the $^{12}CH_4$ are greatly concentrated in coal seam, showing evident carbon isotope accumulation.

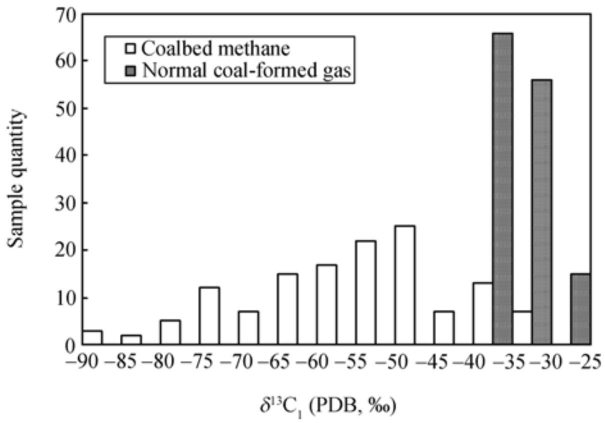

Fig. 1. Comparison on methane isotope values between normal coal-formed gas and coalbed methane.

1.2 Poor relations between $\delta^{13}C_1$ of coalbed methane and VR_o

The $\delta^{13}C_1$ of normal coal-formed gas has good correlation with source rock maturity (R_o,%). So the source rock maturity can be judged by $\delta^{13}C_1$ value of normal coal-formed gas. Many researchers have established $\delta^{13}C_1$-Ro formula of coal-formed gas[6−10]. However, the $\delta^{13}C_1$ of CBM has a poor relationship with R_o. Qin (2000)[11] compared $\delta^{13}C_1$ values of coalbed methane of different coal ranks from various periods of coal. From long flame to lean coal, although Vitrinite reflectance (VR_o) increases much, the corresponding CBM $\delta^{13}C_1$ values have not become heavier obviously, just become heavier during meager coal and anthracite (Table 1). The CBM in meager coal and anthracite are from southern part of the Qinshui Basin, the best area for CBM exploration in China. The area has stagnant groundwater flow condition and is much favorable for CBM preservation[12−17], and thus has high gas content. The methane isotope values in this area are much heavier than that from other CBM basins (Table 2), but still lighter than the normal coal-formed gas of the same maturity.

1.3 The extent CBM becoming lighter influenced strongly by hydrodynamics

In North China, the carboniferous coal seam covers directly on the Ordovician limestone. The coal measure can easily connect with the strong groundwater runoff belt. It had been well accepted that the Carboniferous coal seams have stronger hydrodynamics than Permian. So, the hydrodynamics in upper dominant coal seam is weaker than in the lower dominant seam. In many places in North China, it is common that the CBM carbon isotopic value in lower dominant coal seam (Carboniferous) is lighter than the upper (Permian) dominant one. Take Well Shi A-2 and Well Shi A-3 for example. In the two wells, the CBM carbon isotopic value in Carboniferous lower dominant coal seams is obviously lighter than in the Permian upper dominant seam (Fig. 2).

To the desorbed CBM obtained from laboratory, there exists the same phenomenon. The desorbed CBM from lower coal seam with stronger hydrodynamics has lighter isotopic value than that from upper seam, in which the hydrodynamic condition is weaker. The methane samples are desorbed from coal seams 3 and 15 in Well HG2 and coal seams 3, 10, and 15. The desorption time is 4 hours. The methane isotopic value

Table 1 The CBM isotopic composition of different periods coal in China (Qin, 2000, the number in brackets is sample quantity)

Age	$\delta^{13}C_1$ (PDB, ‰)							
	lignite	long flame coal	gas coal	fat coal	coking coal	lean coal	meagre coal	anthracite
Eogene	–63.4(1)	–49.2(6)	–43.3(2)	–47(2)				
Jurrassic-Cretaceous		–57.3(1)	–59.1(4)	–56.2(2)				
Carboniferous-Permain			–58.4(30)	–56.2(27)	–55.0(7)	–55.3(2)	–41.8(4)	–36.7(7)

Table 2 The CBM carbon isotopic values in China's main coal bearing basins

Basin or coal field	Well (coal mine or area)	$\delta^{13}C_1$ (PDB, ‰)	Coal rank
Qinshui	Well Pan-1	–35.2	anthracite
	Well FZ002	–34.5	anthracite
	Well FZ003	–36.7	anthracite
	Well TL003	–34.0	anthracite
	Yangquan coal mine	–41.4	anthracite
	Sihe coal mine	–36.4	anthracite
Ordos	Wupu area	–38.3	meagre-lean coal
		–46.3	meagre-lean coal
	Liulin area	–61.0	meagre-lean coal
Kaiping Syncline	Majiagou coal mine	–59.1	fat-lean coal
	Zhaogezhuang coal mine	–68.6	fat-lean coal
	Tangshan coal mine	–60.2	fat-lean coal
Huainan coal field	Pan 1 coal mine	–72.3	gas-fat coal
	Pan 2 coal mine	–64.2	gas-fat coal
Huaibei coal field	Luling coal mine	–59.5	gas-fat coal
Fuxin coal field	Wangyingzi coal mine	–50.9	long flame coal
Nantong, Sichuan	Nantong coal mine	–40.7	lean coal

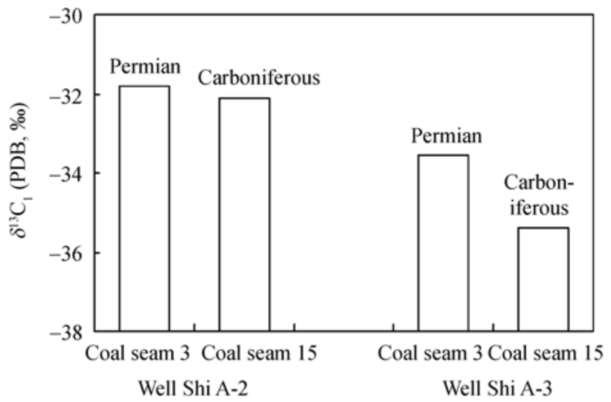

Fig. 2. Isotopic values of CBM in upper dominant coal seams vs. lower ones in Fanzhuang.

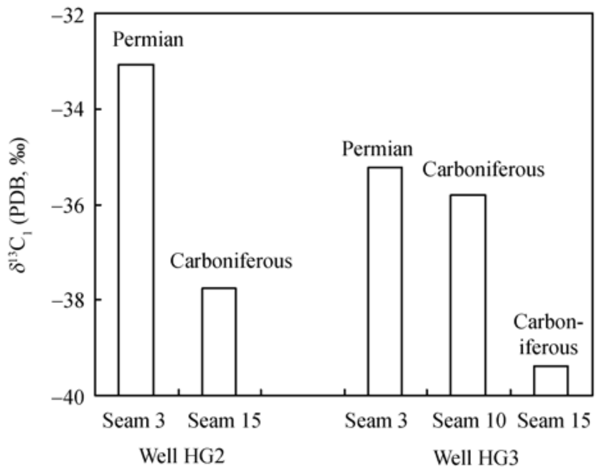

Fig. 3. Carbon isotopes of absorbed methane from the upper and lower coal seams in Qinshui Basin (Data cited from Zhang *et al.*).

becomes gradually lighter from lower seams to the upper ones (Fig. 3).

2 Teichmuller's CBM carbon isotope fractionation mechanism and existing issues

2.1 Teichmuller's CBM carbon isotope fractionation mechanism

The famous Coal Petrologist Teichmuller firstly put forward the mechanism of CBM carbon isotope fractionation. The coal seam was divided into desorbed and original gas belts, corresponding to the buried depth[1]. The tectonic movement makes coal seam shallow and the methane release from coal matrix and diffuses. This is called gas desorption belt. The desorption-diffusion occurs weakly in deep-buried coal seam, and this is called original belt. Teichmuller had studied the coalbed methane from desorbed and original gas belts in Ruhr and Saar coalfields, and found that the carbon isotopic values in desorbed belts were lighter, ranging from –40‰ to –70‰. The original gas belts ranged from –20‰ to –30‰. It was thought that carbon isotopic values in desorbed belts were lighter due to the CBM desorption-diffusion while coal seam uplifted. Actually, the desorbed belt Teichmuller mentioned is usually called coal seam weathering belt. The depth is usually 150 m—800 m. The fractionation mechanism put forward by Teichmuller that the desorption-diffusion actions causes the carbon isotopic values of CBM to become lighter has been referred by many researchers[2,11,19−21].

2.2 The issues that Teichmuller's mechanism encountered

Teichmuller's isotopic fractionation mechanism has to face some problems.

Firstly, if the lighter isotopic values in the desorbed belt were caused by CBM desorption-diffusion, the carbon isotope of remained CBM would become heavier, not lighter. For $^{12}CH_4$ will firstly be desorbed, prior to $^{13}CH_4$. The desorbed methane will dissipate through diffusion and $^{13}CH_4$ will remain in coal relatively. The remained CBM in coal seam will certainly has heavier isotopic values.

Secondly, if the CBM isotopic values in the desorbed belt become lighter like this: the $^{12}CH_4$ in the original belt desorbs from coal matrix and diffuses to the upper desorbed gas belt, and is adsorbed again by upper coal seam, then the carbon isotopic values of CBM from the original belt should become heavier than that of normal coal-formed gas with the same source rock maturity. In fact, there is no doubt that the stable carbon isotopes of coalbed methane are generally lighter than that of gas in normal coal-formed gas fields of similar source maturity. Moreover, in many places in North China the $\delta^{13}C_1$ in the lower coal seam, on the contrary, is lighter than that of upper coal seam (Figs. 2 and 3). It is also difficult to explain using the mechanism mentioned above. In addition, in Zhaogezhuang coalmine of North China, it also explains why in the depth of 1200 m, much beneath the weathering belt, the carbon isotopic value is about –65‰, much lighter to so much degree[22]. So, there is some limitation using the desorption-diffusion mechanism to explain the lighter isotopic value of CBM.

As for the mechanism of ^{12}C enrichment in methane, some researchers have put forth other possible mechanisms up to now: (1) the carbon isotope exchange between CH_4 and CO_2[3]; (2) secondary biogenic gas origin[23−27]. The two mechanisms also have their limitations. A new mechanism will be put forward here to explain the ^{12}C enrichment in coalbed methane.

3 The flowing groundwater causes carbon isotope to become lighter in CBM

Through the study about hydrogeology, gas content, geochemical characteristics of coalbed gas in the main CBM basins of China, it has been found, both in horizontal and vertical directions, that in the area with stronger hydrodynamics, not only the gas content is low, but the stable carbon isotope of CBM is much lighter compared with the normal gas in coal-formed gas pools. Moreover, in areas with weaker hydrodynamics, the coal usually has high gas content and the stable carbon isotope of coalbed methane is also light but to a lesser degree. The gas contents have a good correlation with $\delta^{13}C_1$ values. The lower the gas content is, the lighter the CBM carbon isotopic value is.

3.1 The flowing groundwater affects CBM content

Horizontally, the flowing groundwater has much influence on CBM content. In the area with a stronger hydrodynamics, the coalbed gas content is low; in the water stagnated area, the water flows slowly, and the coal has higher gas content. Take the southern part of Qinshui Basin for example, the CBM rich area[15−17], the hydrological condition in this area trends to be stagnant. Take Kaiping Syncline as another example. The groundwater hydrodynamics of northwest limb is weaker than southeast one. However, the southeast limb has lower CBM contents than the northwest one[17].

Vertically, the stronger hydrodynamics is, the less CBM content it will also have. In the Qinshui and Ordos basins, the gas contents in Carboniferous coal seams with stronger hydrodynamics are less than in the Permian coal with weaker hydrodynamics[17].

3.2 The flowing groundwater affects CBM carbon isotope

In North China, the groundwater in upper dominant coal seam is more active than in the lower one. And the phenomenon that the stable isotope of CBM in lower coal seam is lighter than in the upper coal seam has also easily been noticed. In the Wupu area of Ordos Basin, the carbon isotope of CBM from upper coal seam 3 is −38.25‰, and −46.26‰ from lower coal seam 10. The CBM carbon isotopic values in lower coal seam are also lighter than in the upper coal seams in Well Shi A-2 and Well ShiA-3 (Fig. 2).

Additionally, the southern part of Qinshui Basin acts as the most successful place for CBM exploration. Owing to the stagnant hydrogeological condition in coal measure, not only it has higher gas content, but also the methane carbon isotopic values are comparatively heavier (Table 2), showing that the heavier carbon isotopic values are connected with stagnant groundwater[28].

4 The mechanisms of CBM isotope fractionation

4.1 Theoretic model

Coalbed methane is mainly composed of adsorbed gas and a small amount of free gas. The adsorbed gas exists in coal matrix and the free gas occurs in any kinds of fractures in coal. The water is weak polar solvent. The polarity of $^{13}CH_4$ is relatively stronger than that of $^{12}CH_4$. Therefore, the dissolving capacity of $^{13}CH_4$ in water is a little greater than that of $^{12}CH_4$. So, the movement of water in coal seams can easily take more $^{13}CH_4$ away from free gas and comparatively leave more $^{12}CH_4$. The remaining $^{12}CH_4$ in free gas then exchanges with the adsorbed methane in coal matrix. Some absorbed $^{13}CH_4$ can be replaced and become free gas. Some free $^{12}CH_4$ can be absorbed again into coal matrix and become absorbed one. Part of the newly replaced $^{13}CH_4$ in free gas will also be taken away by water, leaving preferentially more $^{12}CH_4$. These processes occur all the time. Through accumulative effect, the $^{12}CH_4$ will be greatly concentrated in coal. Thus, the stable carbon isotope of CBM becomes dramatically lighter (Fig. 4).

4.2 Carbon isotopic values of water-soluble methane are heavier

In oil or gas field, the isotope of water-dissolved methane is usually heavier than the gaseous one.

Zhang *et al.*[29] studied the water-soluble gas in Taibei Depression of Turpan-Hami Basin using the method of degassing in thermal vacuum. Compared with the normal gas from the same area, the methane carbon isotopes of water-soluble gases are heavier than the normal gas. The carbon isotopic value of water-soluble methane is −35.7‰—−28.7‰, averagely −33.8‰ by 5 samples. The free natural gas is −44.8‰—−36.8‰, averagely −33.8‰ by 39 samples.

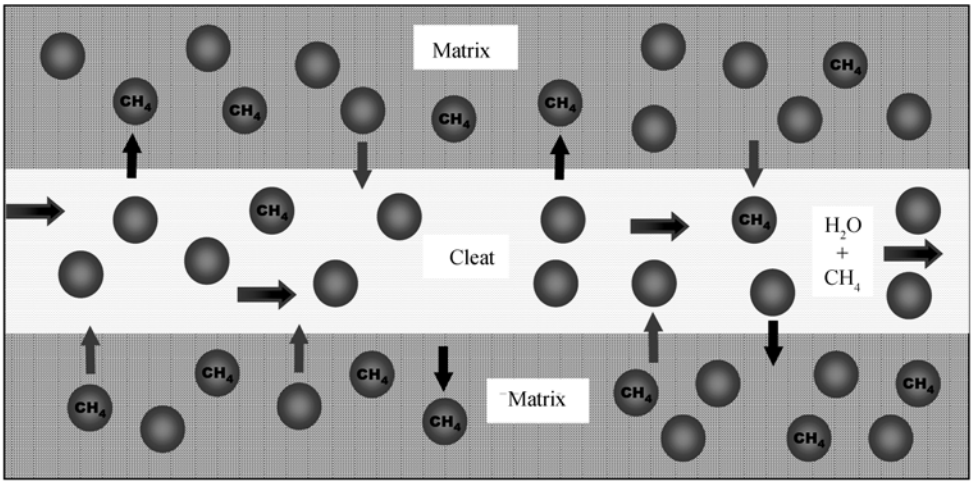

Fig. 4. The carbon isotope fractionation mechanism in CBM.

Though the studies on the water-dissolved methane and the gaseous one from the same wells, Ordos Basin, the carbon isotope of free gas is usually lighter than the methane from water in the same well (Fig. 5). These show that the water trends to dissolve $^{13}CH_4$ and take it away from water.

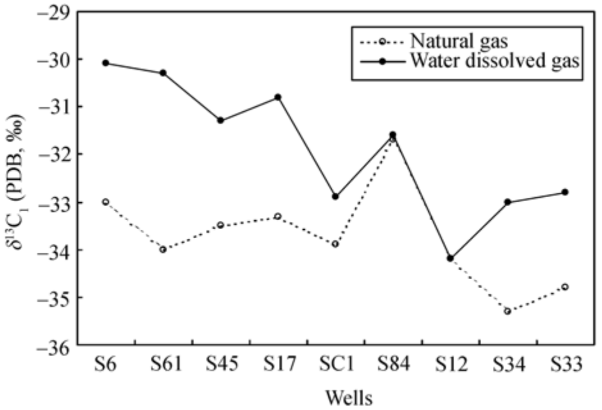

Fig. 5. Carbon isotopes of water-soluble vs. gaseous methane in Ordos Basin (Data provided by Li Jian, personal corresponding, 2000).

In coal seams, the flowing groundwater can also take more $^{13}CH_4$ away from free gas through dissolution and leaves more $^{12}CH_4$ portion.

4.3 Simulation experiment showing that water-dissolved action can take $^{13}CH_4$ away more easily

Using distilled water to pour gas for a long time under normal temperature and pressure, the result shows that the carbon isotope of eluvial gas has become lighter. As the eluvial time increases, the methane carbon isotopic value of the remaining free gas becomes lighter to more extent (Fig. 6). The experiment indicates that the water-dissolved action can fractionate carbon isotope, and take $^{13}CH_4$ away more easily.

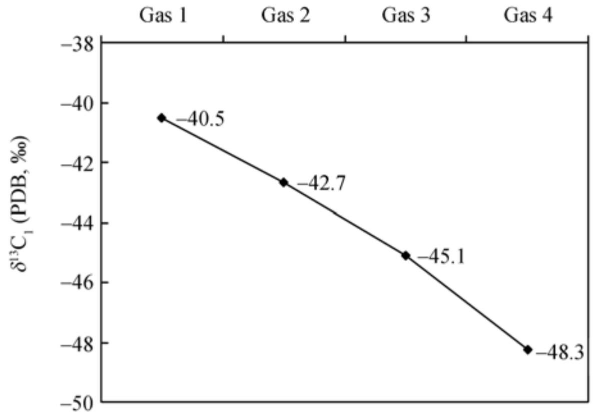

Fig. 6 Influence on methane carbon isotope during water eluviation (The experiment carried out by Wang Hongyan according to the first author's intention). Gas 1, Original gas; gas 2, eluviated for 4 h; gas 3 eluviated for 24 h, gas 4, eluviated for 72 h.

5 Conclusions

The CBM has the special storage mechanism, much different from that of normal gases. Under the influence of flowing water, the mechanism that the CBM enriches ^{12}C is water-dissolved and the exchange between absorbed and free gas. The flowing water in coal measures can easily take $^{13}CH_4$ away from free gas and leave comparatively more $^{12}CH_4$. The remaining $^{12}CH_4$ in free gas then exchanges with the adsorbed methane in coal matrix. Some absorbed $^{13}CH_4$ can be replaced and become free gas, which will also be taken away by water, leaving more $^{12}CH_4$. Thus, the $^{12}CH_4$ will be greatly concentrated in coal.

In the areas with strong hydrodynamics, the carbon isotope of CBM becomes lighter to a large extent because the water takes $^{13}CH_4$ away more frequently. This makes $^{12}CH_4$ accumulate more quickly, and then the carbon isotope of CBM becomes lighter to larger extent. On the contrary, in weak hydrodynamics areas, less gas has been taken away by water, and the water takes $^{13}CH_4$ away less frequently. Thus the $^{12}CH_4$ accumulative effect is less obvious.

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