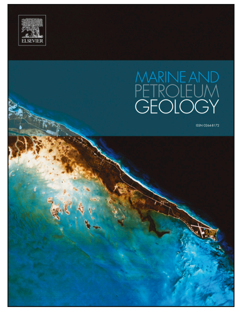

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Geochemical characteristics of water-dissolved gases and implications on gas origin of Sinian to Cambrian reservoirs of Anyue gas field in Sichuan Basin, China

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Abstract

The Anyue field is a supergiant gas field which was discovered recently in the Sichuan Basin, China where the Sinian Dengying Formation and the Cambrian Longwangmiao Formation are principal gas reservoirs. Gas in the Anyue field contains mainly methane (>98%) and a low content of heavy hydrocarbons, with minor H_2S component. Reservoirs commonly contain bitumen and produce formation water. It is currently suggested that natural gas in the Anyue field is derived from the secondary cracking of crude oil. However, carbon isotopic ratio of methane is significantly less negative than that of bitumen, which contradicts the isotopic signature oil cracking process would predict. Besides, this phenomenon also cannot be explained by the process of thermochemical sulphate reduction (TSR), because there is no remarkable correlation between the $\delta^{13}C_1$ values and H_2S contents as suggested in previous studies. Both free gas and water-dissolved gas from the Anyue gas field were analyzed in this study for their stable isotopes. Results show that the $\delta^{13}C_1$ of the gas derived from the formation water is much less negative than that of free gas. Therefore, it is inferred that the less negative $\delta^{13}C_1$ values in the free gas reservoir are attributable to addition of natural gas that is previously dissolved in formation water.

Geological setting of the gas reservoirs in Dengying and Longwangmiao formations of the Anyue gas field is favorable for the formation and preservation of water-dissolved gas. In addition, both formations had experienced significant structural uplifting before the gas reservoirs were formed. Reduced temperature and pressure in the formations by geological uplifting could cause super-saturation of methane in the formation water, and as a consequence, water-dissolved methane gas could exsolve from water phase into gas phase. Therefore, it is concluded that natural gas in the Anyue field is a mixture of free gas and gas exsolved from the formation water. As a result, the carbon isotope of methane gas in the Anyue field became less negative than that of a single free gas component would predict.

Key words: Sichuan Basin; Anyue gas field; Sinian-Cambrian gas reservoirs; Geochemical characteristics; Origin of gases

1. Introduction

Industrial gas flow was produced in 1964 from the Sinian Dengying Formation in the Weiyuan structure of Leshan-Longnüsi paleo-uplift in Sichuan Basin, China, thereby revealing the discovery of Weiyuan gas field (with a proved reserve of $408.61\times10^8 m^3$), which was the largest and oldest mono-block gas field in China at that time. Since then, exploration was carried out in the Sinian formation at the slope and axial area of the paleo-uplift, but no large-scale gas pools have been discovered until 2011. In July 2011, Well Gaoshi 1 (Fig. 1) was drilled in the Gaoshiti structure of the paleo-uplift, and achieved high-yield gas flow from the Sinian formation at a rate of 102.14×10^4 m^3/d. Anyue giant gas field was then discovered as a result of this exploration drilling. Later on, many wells produced industrial gas flow from the Sinian formation in the

Gaoshiti and Moxi structures of paleo-uplift, and thick gas reservoir was also found in the Lower Cambrian Longwangmiao Formation of the Moxi structure, representing the great achievement of gas exploration in the Sinian-Cambrian formations in the Leshan-Longnüsi paleo-uplift. So far, the reserves of the Sinian and Cambrian gas reservoirs in the Gaoshiti and Moxi structures have exceeded trillions of cubic meters (Wei et al., 2015a).

In the Anyue gas field, the gas reservoirs are mainly distributed in the Sinian Dengying Formation (Z_2dn) and Cambrian Longwangmiao Formation ($\in_1$l) (Fig.1). The natural gas is composed of predominantly hydrocarbon gases (mainly methane with small fraction of ethane). There are also small amount of non-hydrocarbon gases (e.g. CO_2, N_2 and H_2S), and trace amount of rare gases. Dry coefficient of the gas in the Anyue field is very high (C_1/C_{1+} close to 1). The natural gas is mainly generated by the highly over-mature argillaceous source rocks of Lower Cambrian Qiongzhusi Formation (Zheng et al., 2014，Wei et al., 2015b).

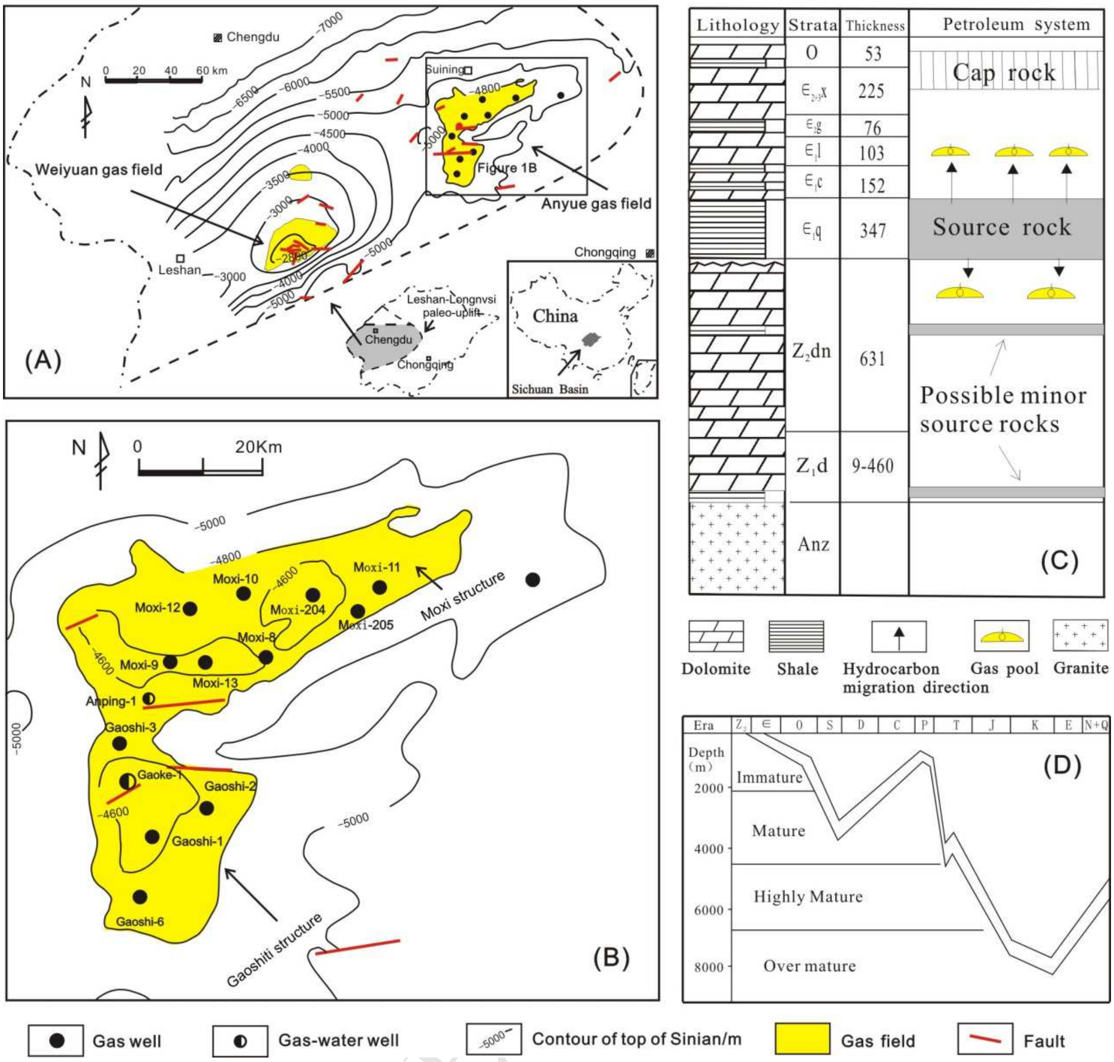

Fig. 1. Location of Anyue gas field and petroleum system of Cambrian-Sinian reservoirs

In the reservoirs, solid bitumen is widely present. It is a product generated from secondary cracking of crude oil, implying the possible existence of ancient oil reservoir or dispersed liquid hydrocarbon in the reservoirs in the early stage. The reflectivity of reservoir bitumen (BRo) is 2.5-3% (Tian et al., 2013), indicating that crude oil in the ancient oil reservoir was cracked sufficiently and the highly evolved reservoir bitumen was developed. Accordingly, it is suggested by many researchers that the natural gas in the Anyue field is originated from the secondary oil cracked gas (Cai et al.,2017; Liu et al., 2008; Wei et al., 2015a; Xiong et al., 2016; Yao et al., 2003; Zhou et al., 2015).

In the process of crude oil cracking, carbon isotopes in both gas phase and solid phase undergo fractional distillation. The carbon isotopic ratio in methane is much more negative than that of bitumen. However, our previous pilot study showed that the carbon isotope of methane in the gas reservoirs of Dengying and Longwangmiao formations was less negative than that of reservoir bitumen. This phenomenon has not been studied in detail. In this paper, the abnormally less negative methane carbon isotope of natural gases in the gas reservoirs of Dengying and Longwangmiao formations were studied from the aspects of characteristics of free gas, reservoir bitumen and water-dissolved gas, with consideration to the geological setting of Anyue gas field. The major aim is to understand the sources of gases in the Anyue field with the isotopic signatures persevered in the gas reservoirs.

2. Geological setting

2.1. Structure

The Anyue gas field is located in the gentle tectonic region of central Sichuan Basin, China, the eastern end of the Leshan–Longnüsi paleo-uplift which is a NEE-trending and W-NE-plunging long-term inheriting giant paleo-uplift (Song, 1996). Due to the Tongwan Movement (570 Ma) and Caledonian Movement (439 Ma), the strata below the Permian structure in the paleo-uplift were eroded and even absent. Particularly, the Sinian Dengying Formation and the Cambrian Longwangmiao Formation were weathering-eroded, giving birth to two sets of modified reservoirs by dissolution which provides good reservoir conditions for the formation of the Anyue gas field. The core of this paleo-uplift is located at the south part of western Sichuan Basin, and its oldest stratum is denuded to the top of Sinian Dengying Formation. Outward from the core, the strata is denuded to Cambrian, Ordovician and Silurian in sequence (Fig.1). During the Late Hercynian–Early Yanshan, the paleo-uplift was constantly buried deeply. Since the Late Cretaceous, the areas inside the Sichuan Basin have been uplifted, making the structural high of Leshan–Longnüsi paleo-uplift shift to the current location of the Weiyuan gas field as a new structural high after uplifting by about 4000 m (Liu et al., 2008). Due to much less deformation in the eastern part of the paleo-uplift, the structures at the tops of Longwangmiao Formation in Gaoshiti and Moxi structures are gentle (Song, 1996; Xu et al., 2012) with uplifting amplitude of about 2500 m (Liu et al., 2008; Liu et al., 2015).

2.2. Stratigraphy

In the Anyue gas field, the strata include (from top to bottom) Jurassic, Triassic, Permian, Ordovician, Cambrian and Sinian. The principal gas layers are distributed in Cambrian and Sinian strata. The Cambrian stratum consists of Middle and Upper Cambrian Xixiangchi Formation ($\in_{2+3}x$), Middle Cambrian Gaotai Formation ($\in_2g$), and Lower Cambrian Longwangmiao Formation ($\in_1l$), Canglangpu Formation ($\in_1c$) and Qiongzhusi Formation ($\in_1q$). The Xixiangchi Formation is mainly composed of light gray, gray and yellowish gray dolomite, occasionally interbedded with oolitic dolomite, dolorudite and argillaceous dolomite. The Gaotai Formation is composed of purplish red and gray mudstone, argillaceous siltstone and yellowish gray linen gypseous dolomite. The Longwangmiao Formation is mainly composed of gray and dark gray dolomite, locally interbedded with thin dolomitic siltstone and dolomitic shale. The Canglangpu Formation is mainly composed of gray sandstone and siltstone with interbedded mudstone, argillaceous siltstone and dolomitic siltstone. The Qiongzhusi Formation is composed of black and dark gray shale, silty mudstone and argillaceous siltstone.

The Sinian system consists of Dengying Formation (Z_2dn) and Doushantuo Formation (Z_1d) from top to bottom. The Dengying Formation is mainly composed of algal dolomite, interbedded with thin dark mudstone at the upper middle parts. The Doushantuo Formation is mainly composed of dolomite interbedded with thin dark mudstone.

The principal source rocks in the Anyue field are black mudstone and shale of Lower Cambrian Qiongzhusi Formation, with thickness of over 40 meters. They remain at high over-mature stage with TOC averaging 1.95% (Wei et al., 2015b). The principal reservoirs in the Anyue gas field comprise the Lower Cambrian Longwangmiao Formation and the Sinian Dengying Formation. The Longwangmiao Formation reservoir is mainly composed of grain dolomite and crystalline dolomite, with its reservoir space formed by intergranular pores and intercrystal pores, as well as dissolution vugs (Jin et al., 2015). The Dengying Formation reservoir is mainly composed of algal dolomite, with its reservoir space formed by secondary dissolution pores and dissolution vugs (Wei et al., 2015b). The Longwangmiao and Dengying reservoirs are filled partially with bitumen. Gaotai Formation siltstone, gypseous dolomite and mudstone acted as the direct caprocks. Permian mudstone and the Lower Triassic thick gypsum salt rock are the most important regional caprocks.

2.3. Type of gas reservoirs

The Gaoshiti and Moxi structures in the Anyue field are relatively gentle. Longwangmiao Formation is developed into complete traps. The gas and water distribution is controlled by reservoirs and local structures, and gas-water contact is complex, suggesting a structural-lithologic gas reservoir. In the Dengying Formation, the upper part acted as a structural-stratigraphic gas reservoir and the lower part as a structural gas reservoir with water at the bottom (Wei et al., 2015b). The Longwangmiao Formation gas reservoir is of high temperature and ultrahigh pressure with reservoir temperature about 140℃ and pressure coefficient 1.5-1.7. The Dengying Formation gas reservoir is of high temperature and normal pressure with reservoir temperature about 160℃ and pressure coefficient 1.07-1.10.

3. Sample collection

The samples of natural gas and formation water were taken from the development wells in the Gaoshiti and the Moxi structures. These development wells produced gas and water simultaneously. Both gas sample and water sample of the same well were taken from the same formation. In order to avoid the impact of condensate water on formation water, the development wells with higher water production rate were selected. Besides, in order to eliminate the external interference, the sampled development wells were in normal operation for a long time without injecting any chemical additives in the wells that help to increase gas production recently (e.g. foam drainage agent).

The samples of formation gas were taken at the wellheads by using a steel cylinder, and sampling was performed at Christmas tree gauge. In the process of sampling, the gauge was removed, and the steel cylinder was connected to the sampling pipeline. Before sampling, it was necessary to flush the air out of the steel cylinder completely by using the wellhead natural gas, and then filled it with the wellhead natural gas to the wellhead pressure. The formation water samples of gas field were taken by using 500 ml glass bottles at gas-water separators of the well sites. After sampling, the bottle was sealed with a rubber plug to ensure that the organic components of formation water were not leaked during the process of transportation.

The samples of reservoir bitumen were taken from the drilling cores of Gaoshiti and Moxi structures. The reservoir samples which were filled with bitumen were selected for analysis.

4. Analytical methods

4.1. Degasification workflow of formation water

In order to study the geochemical characteristics of water-dissolved gas, water heating vacuum system was used to extract the gas in formation water that had been taken from the developing wells. The degasification experiments of water-dissolved gas were carried out in a system as shown in Fig. 2. The extraction procedure for water-dissolved gas was as follows: (1) Piston 7 is opened to fill a solution saturated with NaOH into a U-shaped tube. This drove the liquid into a gas collection tube through the U shaped tube. When the liquid level reached position A and was slightly lower than the cross point C between the U-shaped tube and the coiled tube, then piston 7 was closed. (2) The degasification system is evacuated by a vacuum pump that kept the system in a vacuum less than 0.0999 MPa. (3) Through a separating funnel, 200 ml of water sample was added into a flat bottom flask, and heated in a hot water tank to 60 °C for 20 minutes in order to release the natural gas dissolved in water. (4) Piston 7 was re-opened and the system was filled with saturated NaOH solution till the flask was filled up, and the released gas was driven through a coiled tube into the gas collection tube. Then, a syringe was inserted into the rubber plug to extract the gas for the analysis of the carbon isotopic composition.

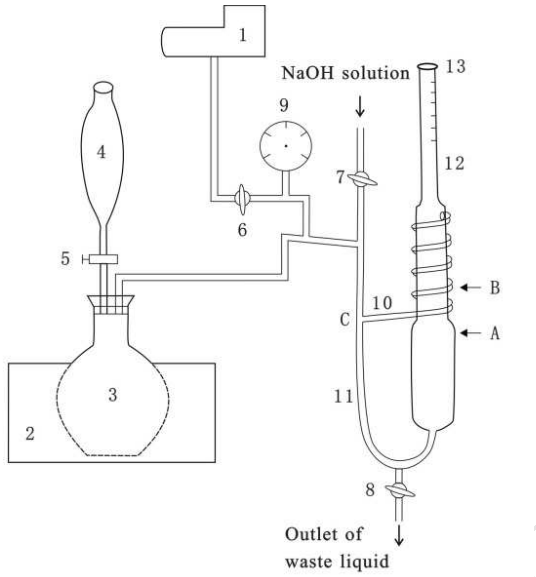

Fig. 2. Schematic diagram of degasification process for water-dissolved gas

4.2. Analysis of natural gas composition and carbon isotopic composition

The samples were analyzed in the Key Laboratory of the Research Institute of Petroleum Exploration and Development of PetroChina.

Natural gas compositions were determined using an Agilent 6890N Gas Chromatograph (GC) with He and N_2 as the carrier gases. Double thermal conductivity detectors (TCD) and a 30m × 0.25mm × 0.25μm quartz capillary column were used. The inlet temperature was 150 °C, and the TCD temperature was 200 °C. The initial oven temperature was maintained at 40°C for 7.5min isothermally, then rose from 40°C to 90°C at 15°C/min increment, and finally rose from 90°C to 180°C at 6 °C/min increment.

The off-line analysis was conducted for the measurement of carbon isotopic compositions with a MAT 253 gas isotopic mass spectrometer. Natural gas samples were separated to methane, ethane, propane, butane and CO_2 through the chromatography column of an SRI 8610C gas chromatograph, which were then transferred into combustion furnace by carrier gas (He) and oxidized into CO_2 by CuO at 850°C. All of the converted species were transferred by carrier gas (He) into MS to measure the isotopic compositions. Dual inlet analysis was performed with international measurement standard of NBS-19 CO_2 ($\delta^{13}C_{VPDB}$=1.95±0.04‰, International Atomic Energy Agency, 1995) and the stable carbon isotopic values were reported in the δ notation in per mil (‰) relative to the Peedee belemnite standard (VPDB). Reproducibility and accuracy were estimated to be ±0.2‰ with respect to VPDB standard.

4.3. Analysis of carbon isotopic composition for reservoir bitumen

Firstly, pure solid bitumen was obtained from bitumen-containing reservoir core samples using the method of kerogen preparation. Then the bitumen was burned into CO_2 in the combustion furnace. Finally the carbon isotopic ratios were measured with MAT 253 isotope mass spectrometer.

5. Results

The composition and carbon isotope of free gas in the gas reservoirs of Dengying and Longwangmiao formations are in agreement with previous studies (Wei et al., 2014; 2015b). The free gas of both gas reservoirs is dry gas with methane content of 98.73-99.32% (Table 1). As for heavy hydrocarbon gas, only trace ethane is detected, and its content is 0.03-0.16%. There is a small amount of CO_2 and N_2 in the gas. In this project, H_2S content is not measured. The carbon isotope of methane in free gas ranges between -34.2‰ and -32.5‰, averaging -33.3‰ (Table 1). The carbon isotope of methane in water-dissolved gas taken from formation water is much less negative than that of free gas (Table 1, Fig.3), indicating the apparent distillation effect of formation water on carbon isotope in methane. Based on previous research on water-dissolved gas from coal gas reservoirs in the Sichuan Basin, the carbon isotope in methane from the gas derived from water is much less negative than that of free gas which was taken from the same well at the same time (Qin, 2012).

The carbon isotope in reservoir bitumen has also been analysed. It is shown that the carbon isotope in reservoir bitumen from the gas reservoirs of Dengying and Longwangmiao formations is much more negative than that of free methane in the gas reservoirs. The carbon isotope in reservoir bitumen ranges between -36.1‰ and -34.7‰, averaging -35.3‰ (Table 2), which is ~2‰ less negative than that of free methane shown in Table 1.

Table 1

Composition of free gas and $\delta^{13}C_1$ values of free gas and water-dissolved gas from the Dengying-Longwangmiao reservoirs in Anyue gas field.

Well	Strata	Main component (%)				δ^{13}C(‰)VPDB (Free Gases)		δ^{13}C(‰)VPDB (Water-dissolved Gas)
		CH_4	C_2H_6	CO_2	N_2	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_1$
GaoShi 1	Z_2dn	99.21	0.03	0.37	0.38	-32.5	-30.1	-30.2
GaoShi 2	$\in_1$l	98.92	0.04	0.38	0.66	-34.2	-30.5	-30.5
Moxi 8	$\in_1$l	99.05	0.14	0.21	0.60	-33.6	-32.5	-29.8
Moxi 008-7-H1	$\in_1$l	99.20	0.13	0.25	0.41	-34.0	-32.1	-24.4
Moxi 008-H1	$\in_1$l	99.32	0.13	0.22	0.33	-32.6	-32.2	-28.9
Moxi 11	$\in_1$l	98.73	0.12	0.20	0.95	-33.5	-31.5	-31.4
Moxi 16C1	$\in_1$l	99.18	0.13	0.13	0.56	-33.2	-31.5	-28.4
Moxi 205	$\in_1$l	99.16	0.16	0.13	0.55	-33.7	-32.8	-30.1
Moxi 204	$\in_1$l	99.87	0.13	0.07	0.66	-32.8	-31.5	-26.4
Moxi 10	$\in_1$l	98.90	0.11	0.14	0.84	-33.3	-31.3	-31.6
Moxi 12	$\in_1$l	98.96	0.11	0.35	0.58	-33.2	-31.9	-30.6
Moxi 009-3-X1	$\in_1$l	99.14	0.12	0.16	0.57	-33.5	-30.8	-23.9
Moxi 9	$\in_1$l	99.14	0.09	0.05	0.73	-33.1	-31.6	-30.4
Moxi 13	$\in_1$l	99.09	0.11	0.15	0.65	-33.2	-31.5	-28.4

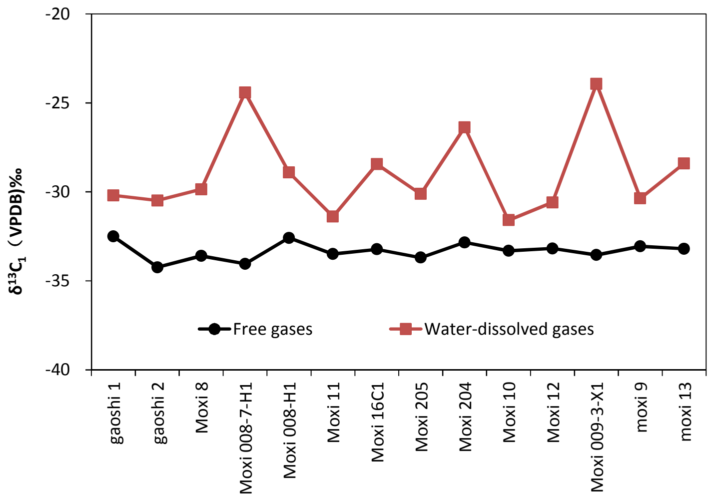

Fig. 3. Comparison of $\delta^{13}C$ values between free and water-dissolved methane in Dengying and Longwangmiao reservoirs in the Anyue gas field.

Table 2

The $\delta^{13}C$ values of bitumen and methane in Dengying and Longwangmiao formations of Anyue gas field

well	Strata	Depth(m)	Reservoir Lithology	$\delta^{13}C$(‰)VPDB (Bitumen)	$\delta^{13}C_1$(‰)VPDB (Free gas)	$\Delta(\delta^{13}C_1-\delta^{13}C_{bitumen})$ (‰)VPDB
Gaoshi 1	Z_2dn	4958	Dolomite	-34.7	-32.5	2.2
Gaoshi 1	Z_2dn	4982.98-4983.07	Dolomite	-34.7		
Gaoke 1	Z_2dn	5175-5175.12	Dolomite	-35.0	-32.4*	2.6
Gaoshi 2	Z_2dn	5395.87-5395.95	Dolomite	-35.7	-33.1**	2.6
Moxi 8	Z_2dn	5114.54-5114.64	Dolomite	-35.5	-32.3**	2.2
Moxi 13	Z_2dn	5101	Dolomite	-35.6	-32.9***	2.7
Moxi 17	Z_2dn	5066	Dolomite	-35.3	-33.5***	1.8
Moxi 21	Z_2dn	5054.5	Dolomite	-35.7		
Moxi 21	Z_2dn	5084	Dolomite	-35.5		
Gaoshi 6	Z_2dn	5035.68-5035.73	Dolomite	-36.1	-32.9**	3.2
Gaoshi 6	Z_2dn	5035.76-5035.84	Dolomite	-35.7	-32.8**	2.9
Moxi 12	$\in_1l$	4620.8	Dolomite	-34.7	-33.2	1.5
Moxi 16	$\in_1l$	4777	Dolomite	-35.3	-32.5***	2.8
Moxi 17	$\in_1l$	4140.38	Dolomite	-35.0	-32.7***	2.3
Moxi 17	$\in_1l$	4626.46	Dolomite	-34.9		
Moxi 202	$\in_1l$	4666	Dolomite	-35.3	-34.7***	0.6
Moxi 204	$\in_1l$	4672	Dolomite	-34.9	-32.8***	2.1

* Data cited from Hu et al, 2003; ** Data cited from Wei et al, 2014; *** Data cited from Wei et al, 2015a

6. Discussion

6.1. It is difficult to explain why the carbon isotope of methane is less negative than that of bitumen

The gas reservoirs in Dengying and Longwangmiao formations in the Anyue gas field are associated with a large amount of highly evolved solid bitumen. It is usually deemed that the natural gas and reservoir bitumen are the products of secondary oil cracking and the natural gas is mainly derived from the secondary cracking of crude oil. However, the carbon isotope of methane in the Anyue field is much less negative than that of reservoir bitumen (Table 2), which cannot be explained from the aspect of oil cracked gas. In the process of crude oil cracking, low-molecular-weight hydrocarbons are cracked into methane continuously and solid bitumen is finally generated from high-molecular substances with aromatic nucleus due to the condensation polymerization. During the formation of bitumen and alkane gas, carbon isotopes undergo fractional distillation, and their ratios follow the order of $\delta^{13}C_{bitumen} > \delta^{13}C_{crude\ oil} > \delta^{13}C_{alkane\ gas}$ (Dai et al., 1992). The crude oil in the reservoirs in the Anyue field had been completely cracked and the bitumen and methane were generated. It was expected that the carbon isotope of methane was much more negative than that of bitumen. However, the results showed opposite direction. Therefore, it is difficult to explain why the carbon isotope of methane is less negative than that of bitumen from the viewpoint of oil cracking as the origin of gas.

6.2. TSR cannot explain less negative carbon isotope values in methane

Since H_2S is common in Dengying and Longwangmiao reservoirs, some researchers argue that it is the TSR that makes the methane carbon isotope less negative during the H_2S generation (Cai et al., 2013; Cross et al., 2004; Liu et al., 2013). Simulation results show that TSR can increase

H_2S content while making methane carbon isotope less negative (Yao et al., 2003). Clearly, the stronger the TSR is, the more H_2S is produced and the less negative the methane carbon isotope is. This trend that methane carbon isotope becomes less negative with the increase of H_2S content, however, cannot be identified in the gas reservoirs in the Dengying and Longwangmiao formations (Fig.4). Therefore, TSR may not be the cause for less negative $\delta^{13}C_1$ values.

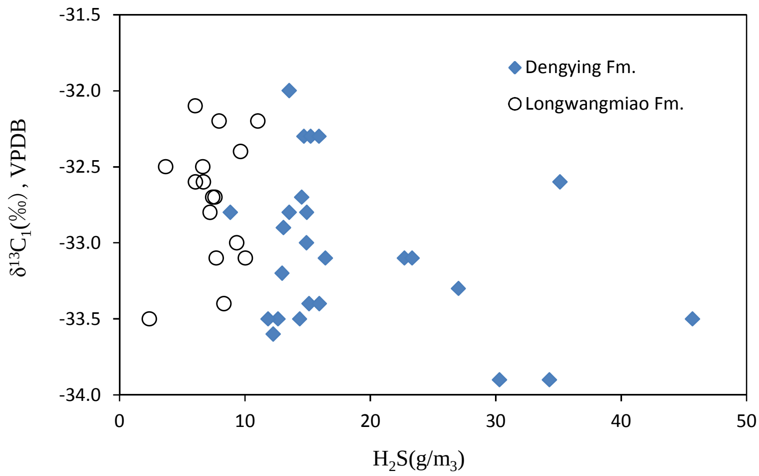

Fig. 4. The $\delta^{13}C_1$ variation with H_2S content for natural gases from the Dengying and Longwangmiao reservoirs of Anyue gas field (The data are from Wei et al., 2014; 2015b; Zou et al., 2014)

6.3. The less negative $\delta^{13}C_1$ values may be due to the release of water-dissolved gas

Most of the oil/gas-bearing basins in China have been influenced by the Himalayan orogenic movement. Tectonic movement leads to the uplifting of strata and the decompression exsolution of water-dissolved gas. The released methane flows into free gas reservoirs and supplies gas for traps as a supplementary source. Based on analytical results of water-dissolved gas, the carbon isotope of methane in gas released from the formation water is much less negative than that of free gas. If the gas released from the water migrated into free gas reservoir, the methane carbon isotope in free gas would become less negative.

Under certain favorable geological conditions, the exsolution of water-dissolved gas can make great contribution to gas accumulations. For example, previous studies in other gas fields in the Sichuan Basin suggested that water-dissolved gas might migrate and accumulate in gas reservoirs (Wang et al., 1997; Xu et al., 2004). A similar study of the natural gas in Hetianhe giant gas field in Tarim Basin, China supports the water-dissolved gas as the main source of the gas in the field (Wang et al., 1997; Xu et al., 2004). It was also deemed that the water-dissolved gas was contributing to the natural gas of Kela 2 giant gas field in China (Li et al., 2003; Qin et al., 2007; Wang et al., 2004). Furthermore, the natural gas of Ya 13-1 gas field, the largest offshore gas field in China, was derived from water-dissolved gas too (Chen et al., 1997). In addition, the natural gas in reservoirs in northern Siberia was related to the release of water-dissolved gas (Cramer et al., 1999; Littke et al., 1999). There is abundant formation water below the gas reservoirs of Dengying and Longwangmiao formations in the Anyue gas field. This geologically satisfies the requirements for the formation and release of water-dissolved gas after deep burial and uplifting afterwards.

6.4. Geological setting of Anyue gas field is favorable for the formation, preservation and release of water-dissolved gas

6.4.1. Favorable conditions for the formation of water-dissolved gas

Sufficient gas and abundant formation water are the prerequisites for the formation of water-dissolved gas. The black shale of Lower Cambrian Qiongzhusi Formation is distributed extensively in the Anyue gas field and the source rock is at over-mature stage with large thickness and high TOC. The distribution of reservoir bitumen shows that ancient oil reservoir and dispersed liquid hydrocarbon were once distributed in a large portion in the reservoirs, and their cracking may provide abundant gas source. Besides, the oil-cracked gas could well be in contact with formation water, and as a consequence, water-dissolved gas is formed.

Abundant formation water is another key factor for the formation of water-dissolved gas. In the Anyue gas field, gas is dominant in the gentle part (4200-4500 m) of the Longwangmiao Formation gas reservoir, and water is dominant in the monocline zones (below 4500 m). In some parts, however, water is produced from the interval of 4400-4300m, and in other areas, water is produced below 4385 m (Luo et al., 2015; Wei et al., 2015a). Water is common in the lower part of Dengying Formation. The Gaoshiti and Moxi structures have their own gas-water contacts and they are located at 5159.2m and 5167.5m respectively. Therefore, the formation of water-dissolved gas in Dengying and Longwangmiao formations is possible since they have abundant edge water and bottom water.

6.4.2. Favorable conditions for the preservation of water-dissolved gas

The Anyue gas field is located at the eastern part of the Leshan–Longnüsi paleo-uplift. In the Indosinian–Early Yanshan period, a large ancient oil reservoir was formed at the high part of the paleo-uplift. At the late stage of Yanshan period, the crude oil in the ancient oil reservoir underwent in-situ cracking at high temperature. When the structure was finally formed in the Himalayan period, the current structure was superimposed with the high point of palaeostructure (Wei et al., 2015a). Thus, the ancient oil reservoir, the oil cracked gas reservoir and the current gas reservoir containing water-dissolved gas are basically accordant, which make the natural gas in the Moxi and Gaoshiti structures not easy to migrate to other areas or escape while water-dissolved gas is formed, exsolved and accumulated. In this way, it provides favorable structural conditions for the preservation of water-dissolved gas.

The overpressured mudstone of Upper Permian Changxing and Longtan formations and the gypsum salt rock of Middle-Lower Triassic Leikoupo and Jialingjiang formations are widely developed in the Sichuan Basin and they are 200m and 300m thick respectively. They are good regional cap rocks with the overpressured sealing capacity (Chen et al., 2003; Zhang et al., 2015). Therefore, the reservoir fluid loss is reduced significantly and water-dissolved gas can be well preserved.

The chemical characteristics of formation water can also reflect the quality of conditions for oil and gas preservation. Following Sulin's classification (Sulin, 1946), the formation water of Dengying and Longwangmiao formations is of $CaCl_2$ type (Table 3), indicating that the study area is in the regional hydrodynamic detention environment isolated from the surface. Salinity of formation water is high, mainly in the range of 1752-5845mmol/L, indicating good sealing capacity. Overall, the formation water of Dengying and Longwangmiao formations is ancient primary water, and favorable for the preservation of natural gas.

Table 3

The ions and water types of Dengying and Longwangmiao reservoirs in Anyue gas field (The data was supplied by the laboratory of Southwest Oil and Gas Branch Company of PetroChina)

Well	Depth（m）	Strata	Main ions (mmol/L)								Water type	Salinity (mmol/L)
			K^+	Na^+	Ca^{2+}	Mg^{2+}	Ba^{2+}	Cl^-	SO_4^{2-}	HCO_3^-		
Moxi 11	4684-4734	$∈_1l$	61	1433	49	18	11	1824	1	12	$CaCl_2$	3426
Moxi 16C1	5055-5530	$∈_1l$	56	1324	40	17	9	1662	1	8	$CaCl_2$	3134
Moxi 18	4608-4659	$∈_1l$	35	733	40	28	6	894	1	7	$CaCl_2$	1752
Moxi 26	4915-4925	$∈_1l$	87	1542	183	105	14	2374	0	0	$CaCl_2$	4326
Moxi 27	4763-4777	$∈_1l$	92	1295	137	110	5	1948	0	0	$CaCl_2$	3599
Moxi 203	4725-4742	$∈_1l$	86	1304	197	94	15	2007	0	0	$CaCl_2$	3717
Moxi 203	4765-4782	$∈_1l$	180	1527	56	35	2	1805	0	0	$CaCl_2$	3608
Moxi 204	4700-4710	$∈_1l$	102	1942	60	9	19	2265	0	0	$CaCl_2$	4427
Moxi 205	4588-4654	$∈_1l$	50	1141	41	13	9	1423	1	13	$CaCl_2$	2705
Gaoshi 10	4613-4640	$∈_1l$	140	1862	170	65	12	2509	0	7	$CaCl_2$	4791
Gaoshi 1	4956-5399	Z_2dn	20	303	367	304	9	1815	0	0	$CaCl_2$	2989
Gaoshi 6	5334-5345	Z_2dn	66	678	478	265	2	2267	0	4	$CaCl_2$	3763

Moxi 8	5102-5172	Z_2dn	144	939	419	260	4	2071	0	0	$CaCl_2$	3837
Moxi 10	5449-5470	Z_2dn	59	973	385	289	6	2957	0	0	$CaCl_2$	4676
Moxi 17	5062.5-5073	Z_2dn	108	1695	259	190	10	3572	0	0	$CaCl_2$	5845

6.4.3. Structural uplift facilitates the exsolution and accumulation of water-dissolved gas

The solubility of methane in formation water is affected by the salinity, temperature and pressure (Duan et al., 2002). The Anyue gas field has been structurally uplifted since the Late Cretaceous (Fig.1). In the process of structural uplifting, the natural gas which was dissolved in the formation water at high temperature and pressure in the Yanshan period was released with the decrease of temperature and pressure of Dengying and Longwangmiao reservoirs. The released water-dissolved gas mixed with the oil cracked gas in free phase. As a result, the carbon isotope of methane in the natural gas from Dengying and Longwangmiao formations became less negative.

7. Conclusions

The carbon isotope of methane in the gas released from formation water is less negative than that of the reservoir bitumen. The carbon isotope composition of natural gas in the gas reservoir would be influenced, if significant amount of natural gas is released from the formation water and mixed with free gas in the gas accumulation process. The less negative carbon isotope of methane in the gas reservoirs of Sinian Dengying Formation and Cambrian Longwangmiao Formation from the Anyue gas field may be explained by the release of water-dissolved gas in gas reservoirs. There is abundant formation water below the gas reservoirs in Dengying and Longwangmiao formations, and the ancient formation water is well preserved. These provide suitable conditions to preserve the natural gas dissolved in the formation water. The Sinian-Cambrian reservoirs in the Anyue gas field are geologically favorable for the formation of water-dissolved gas. In the Himalayan period, the gas field was finally formed after uplifting at large amplitude. The methane which was dissolved in the formation water at high temperature and pressure exsolved into the water due to the uplifting of strata, it was then incorporated into the gas reservoirs in the form of free gas. As a result, the methane carbon isotope in free gas from the gas reservoirs became less negative than that in reservoir bitumen.

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Highlights

1. The $\delta^{13}C_1$ in Dengying and Longwangmiao gas reservoirs is abnormally less negative than that in reservoir bitumen.
2. TSR may not be responsible for less negative $\delta^{13}C_1$ values.
3. The less negative $\delta^{13}C_1$ values may be explained by the release of water-dissolved gas.
4. Geological setting of Anyue gas field is favorable for the formation, preservation and release of water-dissolved gas.