Stable isotope geochemistry of the nitrogen-rich gas from lower Cambrian shale in the Yangtze Gorges area, South China

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A B S T R A C T

The organic-rich marine shales from the lower Cambrian Niutitang formation in the Yangtze Gorges area are characterized by their high TOC values (0.54–5.13%), types I and II organic matter, and high Ro values (2.4%–2.6%). Geochemical parameters of 19 gas samples from the lower Cambrian shale formation from well ZD-1 were analyzed in this study. The gases are dominated by methane, with small amounts of ethane and no propane or butane. The δ13C(CH4) values range from −31.7% to −27.9‰, the δ13C(C2H6) values range from −35.2% to −33.4‰, and the δ2H(CH4) values range from −214‰ to −187‰. Furthermore, carbon isotopic compositions of the alkane gases from the lower Cambrian shale are characterized by δ13C1 > δ13C2; these results indicate that the gases are of thermogenic origin and are oil-derived. Moreover, methane with heavy carbon isotopic and light hydrogen isotopic values may be produced when water reacts with inorganic carbon. The isotopic reversal of alkane gases was probably due to destructive redox reactions at maximum burial resulting in Rayleigh-type fractionation and/or mixing by gases from the same source but at a different maturity. Nitrogen occurs in the analyzed gases at concentrations from 8.15 to 96.52%, and the δ15N(N2) values vary from 3.2 to 7.4‰. The δ15N(N2) values and high illite content suggest that nitrogen was mainly generated during thermal transformation of organic matter and/or from NH4-rich illites of the clayey facies of the lower Cambrian shale. Carbon dioxide concentrations vary from 1.13 to 4.96‰, and the δ13C(CO2) values range from −8.9 to −13.6‰. This suggests that carbon dioxide was mainly generated during thermogenic processes of transformation of organic matter. Moreover, the major reason for the change in nitrogen and methane contents in the studied well (ZD-1) is probably due to the development of micro cracks in core samples with high contents of nitrogen. A high nitrogen content may be caused by the strong adsorption capacity of nitrogen, which leads to the retention of nitrogen and the diffusion of methane in shale.

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1. Introduction

Natural gas storage in shale differs significantly from conventional gas reservoirs and may be composed of free gas within fractures and intergranular pores, absorbed gas within organic matter and on inorganic minerals, or as dissolved gas in oil and water (Curtis, 2002; Ross and Bustin, 2007; Gasparik et al., 2012, 2014; Zhang et al., 2012). Productive shale gas formations in North America are generally characterized by TOC > 2.0%, type II kerogen, and Ro (vitrinite reflectance) > 1.3% (Zumbehere et al., 2012). However, the formations of shale gas in China are characterized by old formation, deep burial, high thermal maturity, and a multi-stage structure (Dai et al., 2014b; Zou et al., 2015). Shale gas systems can be divided into two distinct types, namely, biogenic and thermogenic (Claypool, 1998), although there can also be mixtures of the two types of gas (Jarvie et al., 2007). Distinguishing between microbial and thermogenic CH4 is essential for natural gas exploration and production strategies and improved resource estimates (Osborn and McIntosh, 2010). Investigations into the origin and formation mechanism of highly mature and over-mature shale gas and the effect of intense tectonism on the deformation and alteration of shale gas reservoirs are more critical for Chinese shale gas exploration.

Stable carbon and hydrogen isotopic compositions of methane...
are key attributes that promote understanding of the origin of natural gases in surface ecosystems, clathrates in marine sediments, deep rocks or oil, and gas reservoirs (Schoell, 1980, 1988; Jenden et al., 1993; Whiticar, 1999; Etiope et al., 2009). In addition, the chemical composition and carbon isotopic composition of hydrocarbons have been widely applied to the geochemical study of conventional natural gases (Schoell, 1980, 1983, 1988; Xu, 1994; Berner and Faber, 1996; Tang et al., 2000). Numerous studies have indicated that the geochemical characteristics of shale gas have some special characteristics compared with that of conventional

![Map showing the geology of the study area and the well location.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Strata</th>
<th>Depth (m)</th>
<th>TOC (%)</th>
<th>Ro (%)</th>
<th>Shale composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Quartz</td>
</tr>
<tr>
<td>ZD-01</td>
<td>1-1</td>
<td>263.4</td>
<td>0.95</td>
<td>2.4</td>
<td>32</td>
</tr>
<tr>
<td>ZD-02</td>
<td>1-1</td>
<td>265.9</td>
<td>0.83</td>
<td>2.5</td>
<td>35</td>
</tr>
<tr>
<td>ZD-03</td>
<td>1-1</td>
<td>268.6</td>
<td>1.07</td>
<td>2.5</td>
<td>42</td>
</tr>
<tr>
<td>ZD-08</td>
<td>1-1</td>
<td>282.2</td>
<td>0.54</td>
<td>2.5</td>
<td>40</td>
</tr>
<tr>
<td>ZD-10</td>
<td>1-1</td>
<td>288.6</td>
<td>1.64</td>
<td>2.6</td>
<td>46</td>
</tr>
<tr>
<td>ZD-13</td>
<td>1-1</td>
<td>306.4</td>
<td>2.07</td>
<td>2.6</td>
<td>51</td>
</tr>
<tr>
<td>ZD-18</td>
<td>1-1</td>
<td>334.7</td>
<td>4.43</td>
<td>2.5</td>
<td>54</td>
</tr>
<tr>
<td>ZD-20</td>
<td>1-1</td>
<td>351.4</td>
<td>5.13</td>
<td>2.6</td>
<td>56</td>
</tr>
</tbody>
</table>
natural gas. Variations in the gas isotopic composition in conventional gas reservoirs are mainly determined by the kerogen isotopic composition, maturity, and charging efficiency. However, for shale gas, residual oil in shale may convert to gas, and water may be involved in this conversion. Products from different chemical processes cause the isotopic composition to deviate from conventional models (Liu et al., 2016). Moreover, the δ13C of gaseous alkanes mostly shows a reversal in highly mature shale gases such as the Barnett, Haynesville, Fayetteville, Woodford, Marcellus, Horn River, Utica, and Longmaxi shales (Burruss and Laughrey, 2010; Tilley et al., 2011; Tilley and Muehlenbachs, 2013; Zumberge et al., 2012; Xia et al., 2013; Dai et al., 2014b).

Nitrogen is one of the most common non-hydrocarbons in natural gas, and many previous studies have focused on the composition and origin of nitrogen in natural gas using isotopic geochemical methods (Dai, 1992; Hoering and Moore, 1958; Littke et al., 1995; Stahl, 1977). Most conventional natural gases contain only a few percent nitrogen; however, high nitrogen contents in the natural gases from lower Cambrian shale have been observed in many areas in South China. Therefore, the increasing attention paid to non-hydrocarbons in shale gas will help to solve a series of problems in geological theories and reduce the investment risks encountered with high contents non-hydrocarbons in exploration and production.

The objective of this study is to determine the origin of hydrocarbon and non-hydrocarbon gases based on the molecular and stable carbon isotope compositions of gaseous hydrocarbons (CH4 and C2H6) and CO2, stable hydrogen isotope compositions of methane, stable nitrogen isotope compositions of gaseous nitrogen, and stable isotope compositions of noble gases in natural gases. By investigating the N2 content changes, the genetic types of nitrogen were classified, which are expected to provide geochemical evidence to explain nitrogen enrichment in natural gases from the lower Cambrian shale in the Yangtze Gorges area.

## 2. Geological setting

The Yangtze platform is located between the Qin-Ling orogen to the North and the Cathaysia suture to the Southeast (Zhu et al., 2003; Jiang et al., 2011). The marine black shales are widely distributed on the Yangtze Platform, particularly in the Lower Paleozoic formations. The Niutitang shale from the Lower Cambrian and the Longmaxi shale from the Lower Silurian have been regarded as prolific shale gas formations (Tang et al., 2014). They are generally characterized by large distribution, large thickness, high TOC content, high over maturity, and high quartz content (e.g., Zhang et al., 2008a,b; Zou et al., 2010; Tian et al., 2013; Tan et al., 2013). Until recently, shale gas was produced from these formations in the Sichuan Basin.

The Yangtze Gorges area is located 25 km to the northwest of Yichang city in central Hubei province (Fig. 1). The study area contains nine formations: Liantuo, Nantuo, Doushantuo, Dengying,
Yanjiahe, Shuijingtuo, Shipai, Tianheban, and Shilongdong formations in ascending order (e.g., Zhang, 1981; Zhao et al., 1985; Chen, 1987; Zhou and Xu, 1987; Zhao et al., 1988; Ding et al., 1996). In several recent studies, the Yanjiahe and Shuijingtuo formations have collectively been referred to as the Niutitang Formation (Wang et al., 2008; Jiang et al., 2012). The lower Cambrian marine black shale in this area is considered a high-quality hydrocarbon source rock (Wang et al., 2008; Jiang et al., 2012) that was deposited in a period of extensive transgression in the early Cambrian (Goldberg et al., 2007; Li et al., 2015a, b; Wang et al., 2012).

In recent years, significant attention has been paid to the Niutitang organic-rich shale in the Sichuan basin and the peripheral area for the high shale gas potential (Zhang et al., 2008a, b; Zou et al., 2014; Wang et al., 2015). In early 2015, the vertical drill (well ZD-1) in the lower Cambrian shale found shale gas for the first time in the Yangtze Gorges area, which marked a major breakthrough in the exploration of shale gas in this area.

3. Samples and methods

In this study, 19 shale core samples were collected from shale gas well ZD-1 in the Yangtze Gorges area. The TOC values of these shale core samples range from 0.54% to 5.13%, and the vitrinite reflectance values (Ro) range from 2.4% to 2.6% (Table 1). These cores were placed as quickly as possible inside a hermetically sealed canister immersed in a water bath at the reservoir temperature, and the volumes of gas released inside the canister were periodically measured using a graduated cylinder at atmospheric pressure (Liu et al., 2016). The gas samples were collected from the gas released in the desorption process of the above-mentioned 19 core samples. The molecular composition of the gas was analyzed at the Key Laboratory of Marine Reservoir Evolution and Hydrocarbon Abundance Mechanism, China University of Geosciences, Beijing. Stable isotopes analyses were performed at the Nuclear Industry Beijing Geological Research Analysis and Test Research Centre.

The molecular compositions of natural gases (CH₄, C₂H₆, CO₂, and N₂) were determined using an Agilent 6890N gas chromatograph (GC) equipped with a flame ionization detector and a thermal conductivity detector. The GC oven temperature was initially set at 30 °C for 10 min and then increased to 180 °C at 10 °C/min and held at this temperature for 20–30 min. Analytical precision was estimated to be ±1%. For all of the gas compositions, oxygen-free corrections and the corresponding correction for nitrogen were performed (Ni et al., 2013). Nitrogen was corrected for the presence of traces of oxygen using the area ratio of nitrogen to oxygen peaks measured for air (Jenden et al., 2015).

Stable carbon, hydrogen, and nitrogen isotope analyses were performed using a Finnigan MAT-253 instrument. The stable carbon and hydrogen isotope data are presented in δ-notation relative to V-PDB and V-SMOW standards, respectively. The measurement precision was estimated to be ±0.5‰ and ±3‰, respectively (Ni et al., 2013; Dai et al., 2014a, 2014b). The results of stable nitrogen isotope analysis are presented in δ-notation (δ¹⁵N, ‰) relative to an air nitrogen standard. Analytical precision is estimated to be ±0.4‰. Gaseous nitrogen was separated chromatographically for stable nitrogen isotope analysis and was transmitted to a mass.

Fig. 2. Natural gas interpretative “Bernard” diagram combining the molecular and isotopic compositional information shown that natural gases from the lower Cambrian shale in the study area are slightly outside the thermogenic gas outline, probably due to their relatively high gas dryness coefficient and heavy methane carbon isotopic values (After Bernard et al., 1978; Whiticar, 1999).

Fig. 3. Plot of δ¹³C₁₈ vs. δ²H of gases from the Lower Cambrian shale in the study area, implying a thermogenic origin (After Schoell, 1980; Whiticar, 1999).

Fig. 4. Plot of δ¹³C₂ vs. C₂H₆ of coal-derived and oil-derived gases shown that gases from the Lower Cambrian shale in the study area are oil-derived gases (modified after Dai et al., 2014a).
spectrometer via an on-line system (Kotbar and Nagao, 2008).

Noble gases (He, Ar) were isolated from other major components such as hydrocarbons, carbon dioxide, and nitrogen using two Ti-Zr getters heated at approximately 800 °C. The noble gas fraction was analyzed with a VG 5400 sector-type mass spectrometer (Fisons Instruments). Air standards were measured repeatedly between sample analyses to correct the mass discrimination of the mass spectrometer (Xu et al., 1995a, 1995b). Experimental uncertainties for the noble gas concentrations were estimated to be approximately 10%.

4. Results and discussion

4.1. Origin of alkane gases

Table 3 shows the compositional and stable carbon and hydrogen isotopic data for 19 gas samples from lower Cambrian shale in the Yangtze Gorges area. The content of methane and ethane varies from 0.99% to 89.23% and from 0.11% to 2.13%, respectively. The δ13CCH4 values range from −31.7‰ to −27.9‰ (average −29.8‰), while the δ13CC2H6 values range from −35.2‰ to −33.4‰ (average −34.3‰). The δ2HCH4 values range from −214‰ to −187‰ (average −198‰).

However, small amounts of ethane without propane and butane were detected in this study. The complete lack of propane or butane in this shale has a close relationship with the extremely high maturity of the lower Cambrian shale. This phenomenon is also reflected in the Rock-Eval pyrolysis data, which is illustrated in Table 2, samples have quite low values of S2 (the hydrocarbon yield by cracking of the remaining organic matter).

The natural gas composition and the stable isotopes have been widely used in the identification of natural gas origin (e.g., Whiticar et al., 1986; Berner and Faber, 1988; Chung et al., 1988; Schoell, 1980; Whiticar, 1999; Strapoń et al., 2007, 2008). Both molecular and isotopic compositions (Figs. 2 and 3) show that the analyzed gases are genetically related to thermogenic processes. Although natural gases from the lower Cambrian shale in the study area are slightly outside the thermogenic gas outline, this is probably due to their relatively high gas dryness coefficient and heavy methane carbon isotopic values caused by the extremely high maturity of the shale.

Thermogenic gas could be divided into coal-derived gas from terrestrial humic organic matter and oil-derived gases mainly from marine sapropelic organic matter (Ni et al., 2013). Multiple studies of the gases in Chinese basins suggest a cut-off point in the δ13C of ethane for differentiating the origin of thermogenic gases. Gang et al. (1997) indicated that δ13C(C2H6) > −29‰ for coal-derived gas and < −29‰ for oil-derived gas, according to hydrous pyrolysis of carbonates, mudstones, oil shales, and coals from different locations in the world. Dai et al. (2005) proposed a δ13C(C2H6) value > −27.5‰ for coal-derived gas and a δ13C(C2H6) value < −29‰ for oil-derived gas. However, based on a comprehensive study on the natural gases from 600 gas wells in China, Dai et al. (2014a) proposed a δ13C(C2H6) > −27.5‰ cutoff for coal-derived gas and a δ13C(C2H6) < −29‰ cutoff for oil-derived gas. As shown in Fig. 4, the gases from lower Cambrian shales in the study area are oil-derived gases.

4.2. Isotopic rollovers and reversals

Reversed stable carbon trends have been found in conventional reservoirs in the U.S. (Jenden and Drazan, 1993; Burruss and Laughrey, 2010), China (Xia et al., 1999; Dai et al., 2004), and Canada (Tilley et al., 2011; Tilley and Muehlenbachs, 2013). They have also been identified in shale gas fields in Utica Shale of the Appalachian basin (Burruss and Laughrey, 2010), Barnett Shale of the Fort Worth basin (Zumberge et al., 2012; Xia et al., 2013), Fayetteville Shale of the Arkoma basin (Zumberge et al., 2012), Longmaxi shale of the southern Sichuan Basin (Dai et al., 2014b), and lower Permian shale of the southern North China basin (Liu et al., 2016).

A complete and partial reversed trend in the carbon isotopes of n-alkanes could be due to (1) mixing between biogenic and abiotic gases, (2) mixing between different types of gases, (3) mixing between gases from the same type of source rocks with different maturities, (4) mixing of gases from the same rock interval of varying maturities, and (5) the influence of secondary cracking or thermochemical sulfur reduction in carbonates (e.g., Xia et al., 1999; Dai et al., 2004; Burruss and Laughrey, 2010; Tilley et al., 2011; Zumberge et al., 2012).

The complete reversed trend of shale gas can be also caused by the Rayleigh fractionation of ethane and propane involved in redox reactions with transition metals and water at late stages of

![Fig. 5](image-url)
catagenesis at temperatures of 250–300 °C. Furthermore, the reversal in the δ2H composition of methane can be explained by mixing with a late stage, super-mature methane that has isotopically exchanged with formation water at these temperatures (Burruss and Laughrey, 2010).

As shown in Fig. 5a, all data points fall in the zone of mixed gases with negative carbon isotopic series. In addition, as shown in Fig. 5b, the trend line “S” is δ13C1 and δ13C2 values based on the data from typical marine shales in China, Canada, and the United States (Rodriguez and Philp, 2010; Zumberge et al., 2012; Tilley and Muehlenbachs, 2013; Dai et al., 2014b). The first turning point was considered to be the beginning of secondary cracking, and mixing of primary and secondary cracking gases may cause an isotope reversal (Rodriguez and Philp, 2010; Hao and Zou, 2013; Xia et al., 2013; Tilley et al., 2011; Tilley and Muehlenbachs, 2013). The second turning point may indicate a “post-reversal” stage of extremely high maturity (Dai et al., 2014b). In this study, all data points fall near the end of the trend line “S” after the second turning point in the zone of δ13C1 > δ13C2. This indicated that δ13C1 > δ13C2 in the study area is closely related to the extremely high maturity (Ro = 2.4%–2.6%) of the lower Cambrian shale.

The maximum burial depth reached approximately 10 km of lower Cambrian strata in the study area (Wo et al., 2007). Moreover, numerous studies have shown that the uplifting time of the Huangling granite developed from the Late Jurassic to Early Cretaceous (Wang et al., 2003; Liu et al., 2009; Shen et al., 2009; Xu et al., 2010; Li and Shan, 2011; Hu et al., 2012). Due to the influence of magmatic and hydrothermal activities, the lower Cambrian source rocks have obtained a maximum temperature of 250–450 °C (Ji et al., 2014).

As indicated above, the isotopic reversal of alkane gases from the lower Cambrian shale in the study area was probably due to destructive redox reactions at maximum burial, resulting in Rayleigh type fractionation and/or being mixed by gases from the same source but at different maturity. Moreover, compared with the gases from Longmaxi shale in the southern Sichuan Basin (Dai et al., 2014b), the methane with heavy carbon isotopic and light hydrogen isotopic values in the study area (Fig. 3) may be produced through the formation of water reacting with inorganic carbon.

### 4.3. Origin of nitrogen

As shown in Table 3, the 3He/4He and R/Ra values are 1.86 × 10−8–3.36 × 10−8 and 0.01–0.02, respectively. Nitrogen occurs in the analyzed gases in concentrations from 8.15 to 96.52%, and the δ15N(N2) values vary from 3.2 to 7.4‰. Usually, the R/Ra of crustal helium ranges from 0.01 to 0.1 (Wang, 1989), while that of mantle derived helium is often > 0.1 (Jenden et al., 1993). Low 3He/4He and R/Ra ratios indicate that the gases from the lower Cambrian shale in the study area are essentially of crustal origin.

Nitrogen present in most of the natural gases has variable concentrations, and its origin can be determined on the basis of stable isotope analysis (e.g., Stahl, 1977; Gerling et al., 1997). The origin of nitrogen in natural gases can be organic or inorganic processes in crust and upper mantle. Nitrogen can be part of the atmosphere or trapped in rock during sedimentation, or it may infiltrate the rock complex with surface water. It may also derive from ammonium in clay minerals (Mingram et al., 2005) or from N2-bearing fluid inclusions (Lüders et al., 2005, 2012). Furthermore, molecular nitrogen is produced in great quantities during the thermogenic transformation of organic matter and/or from NH4-rich illites of the clayey facies of the lower Cambrian shale (modified after Zhu et al., 2000a,b).

In this study, the content of clay minerals in the lower Cambrian shale is 11–43% (26% average) and is dominated by illite (10–27%). The δ15N(N2) values and high illite content suggest that nitrogen was mainly generated during thermal transformation of organic pyrolysis (Kotarba and Lewan, 2013) experiments.

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matter and/or from NH₄-rich illites of the clayey facies of the lower Cambrian shale (Fig. 6).

4.4. Origin of carbon dioxide

The carbon dioxide concentration in the analyzed gases from the lower Cambrian shale in the study area varies from 1.13 to 4.96%, and the δ¹³C values of the carbon dioxide range from −8.9‰ to −13.6‰ (Table 3). Various studies have been carried out to identify biogenic and abiogenic CO₂ (Moore et al., 1977). The δ¹³C(CO₂) values ranged from −4.5‰ to −6.0‰ in basalt inclusions from the Pacific Mid-Ocean Ridge (Moore et al., 1977); Gould et al. (1981) found that the magmatic CO₂ had a δ¹³C values of −7‰ ± 2‰ despite its variety; the δ¹³C values of the crustal abiogenic CO₂ commonly ranged from +1‰ to −3‰ (Shangguan and Gao, 1990).

Comprehensive study of more than 1000 gas samples from 16 gas fields in China as well as international data indicated that the δ¹³C values of biogenic CO₂ mainly ranging from −10‰ to −30‰, while those of abiogenic CO₂ are more than −8‰, mainly ranging from −8‰ to 3‰ (Dai, 2000; Dai et al., 2014b). The abiogenic CO₂ derived from the decomposition of carbonate sediments usually has a δ¹³C value of 0‰ ± 3‰. (Dai et al., 2014b).

A plot of δ¹³C(CO₂) versus δ¹³C(CH₄) (Fig. 7) and a plot of δ¹³C(CO₂) versus R/Ra (Fig. 8) suggest that the analyzed carbon dioxide was mainly generated during thermogenic processes of transformation of organic matter. This is distinctly different from carbon dioxide that occurs in natural gas from the Longmaxi shale in southern Sichuan Basin (Dai et al., 2014b), which is identified as abiogenic derived from the decomposition of carbonate sediments (Figs. 7 and 8).

4.5. Geological implications

High nitrogen contents in the natural gas from lower Cambrian shale have been observed in many areas in southern China. A few studies (Chen, 2005; Nie et al., 2012) suggest that the nitrogen derived from the atmosphere and migrated by infiltration of surface water into the strata. However, as discussed in the previous section, nitrogen occurring in the natural gases from the lower Cambrian shale in the study area was mainly generated during thermal transformation of organic matter and/or from NH₄-rich illites of the clayey facies of the lower Cambrian shale.

Shale gas usually consists of methane, small amounts of heavy hydrocarbons (C₂-C₆), and nonhydrocarbon gases (CO₂, N₂). In this study, the contents of nitrogen and methane vary greatly among the gas samples (Table 3), and there is an obvious negative correlation between N₂ and CH₄ concentrations (Fig. 9a). Furthermore, the negative correlation between N₂ concentration and the measured gas content was also shown in this study (Fig. 9b). As shown in Table 4, the porosity and permeability of core samples with a high content of nitrogen are from 1.8% to 3.2% and from 0.0958 × 10⁻¹³ m² to 0.2367 × 10⁻¹³ m², respectively, which were significantly higher than those of samples with a low nitrogen content (the porosity and permeability are from 0.8% to 2.2% and from 0.0056 × 10⁻¹³ m² to 0.0087 × 10⁻¹³ m², respectively). Li et al. (2015a,b) indicated that the shale adsorption capacity is higher for N₂ than for CH₄, and CH₄ has the lowest capacity. Liu et al. (2016) observed that CH₄ had a higher diffusion ability than N₂ according to the shale desorption experiments. Therefore, the major reason for the change in nitrogen and methane contents in the studied well (ZD-1) is probably the development of micro cracks in core samples with high nitrogen contents. The high nitrogen content may be caused by the strong adsorption capacity of

![Fig. 8. δ¹³C(CO₂) versus R/Ra for analysed natural gases (modified after Zhang et al., 2008a,b).](image url)

![Fig. 9. N₂ versus CH₄ concentrations (a) and measured gas content (b) of natural gases from the Lower Cambrian shale in the study area.](image url)
nitrogen, which leads to the retention of nitrogen and the diffusion of methane in shale.

Previous studies suggested that the study area underwent several stages of uplift and subsidence throughout the Neoproterozoic to Cretaceous times (Zhang, 1986; Dai, 1996; Jiang et al., 2002; Xu et al., 2004; Ge et al., 2010). Complex tectonic movements and faults accelerate the diffusion of methane in shale gas. In addition, the aquifers near the lower Cambrian strata in the study area have been observed by many studies (Wei et al., 2010; Liu et al., 2011). The water circulation in the aquifers and unconformity provide other paths for the diffusion of methane in shale gas.

5. Conclusions

(1) Stable isotopic data of carbon and hydrogen of gases from the lower Cambrian shale in the Yangtze Gorges area show that the gases are thermogenic in origin and oil-derived gases. Moreover, methane with heavy carbon isotopic and light hydrogen isotopic values may be produced through formation water reacting with inorganic carbon.

(2) The carbon isotopic compositions of all of the alkane gases from the lower Cambrian shale in the Yangtze Gorges area are characterized by \(^{13}\text{C}_2 > ^{13}\text{C}_2\), which was probably due to destructive redox reactions at maximum burial resulting in Rayleigh-type fractionation and/or being mixed by gases from the same source but at a different maturity.

(3) \(^{15}\text{N}(\text{N}_2)\) and \(\text{N}_2\) concentration suggests that nitrogen was mainly generated during thermal transformation of organic matter and/or from \(\text{NH}_4\)-rich illites of the clayey facies of the lower Cambrian shale. Carbon dioxide was mainly generated during thermogenic processes of transformation of organic matter. This is distinctly different from carbon dioxide occurring in the natural gas from the Longmaxi shale in the southern Sichuan Basin, which is identified as abiogenic derived from the decomposition of carbonate sediments.

(4) The high nitrogen content may be caused by the strong adsorption capacity of nitrogen, which leads to the retention of nitrogen and the diffusion of methane in shale. A complex faulting system and water circulation in the aquifers or unconformity provide paths for the diffusion of methane in shale gas.

Acknowledgments

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Table 4

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<th>Effective permeability (( \times 10^{-3} ) ( \mu \text{m}^2 ))</th>
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References


