Analysis on the difference of material composition and reservoir space of Mesoproterozoic dark marine shale in the Yanshan area

Boyang Wang\textsuperscript{1,2}, Qiusheng Zhang\textsuperscript{3}, Gang Wang\textsuperscript{4} and Miao Liu\textsuperscript{5}

Abstract
The dark marine shales which are thick in the Mesoproterozoic Hongshuizhuang formation and Xiamaling Formation in the Yanshan area are the subject of this study. The material compositions and pore characteristics were analyzed, and the reasons for the differences in the adsorption capacity of shale were emphatically discussed through geochemical analysis, X-ray diffraction, scanning electron microscope, low-temperature nitrogen adsorption, mercury injection experiment, isothermal adsorption, and other analysis methods. The results indicate that the samples are rich in high organic carbon content, and vitrinite reflectance suggests that the degree of thermal evolution is in the late-mature to high-mature stage; the mineral compositions mainly consist of quartz and clay minerals. The micropores are relatively developed, which mainly include intergranular pores, intragranular pores, microcracks, and many other pores. Results from the nitrogen adsorption analysis suggest that the pore structures can be divided into three types. Porosity has obvious fractal characteristics. The fractal dimensions of the adsorption pore are larger than those of the seepage hole. The difference of shale adsorption between the Hongshuizhuang Formation and Xiamaling Formation is mainly determined by the volume of micropores and transition pores and the different mineral compositions.

\textsuperscript{1}Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process of the Ministry of Education, China University of Mining and Technology, Xuzhou, China
\textsuperscript{2}School of Resources and Geosciences, China University of Mining and Technology, Xuzhou, China
\textsuperscript{3}Suzhou NanZee Sensing Technology Co., Ltd, Suzhou, China
\textsuperscript{4}Key Laboratory of Resource Survey and Research of Hebei Province, Hebei University of Engineering, Handan, China
\textsuperscript{5}Daqing Oilfield Production Engineering and Researching Institute, Daqing Oil Field Co, Daqing, China

Corresponding author:
Boyang Wang, School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, China. Email: 15162186837@163.com

Creative Commons CC BY: This article is distributed under the terms of the Creative Commons Attribution 4.0 License (http://www.creativecommons.org/licenses/by/4.0/) which permits any use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en-us/nam/open-access-at-sage).
Keywords
Mesoproterozoic, Yanshan area, marine shale, material composition, reservoir space

Introduction
Shale gas is characterized by favorable self-generation and self-accumulation, which is becoming more and more important in unconventional areas of oil and gas resources. It is estimated that the annual output of marine shale gas in 2020 is expected to reach $(200–300) \times 10^8 \text{ m}^3$, which reveals the good prospect of exploration and development in shale gas field in China (Zou et al., 2015). With the large-scale development of shale gas in the Fayetteville shale of the Arkema Basin and Marcellus shale of the Appalachian Basin, it is found that the adsorbed gas content can account for 20% to 85% of the total gas content of shale gas, which has an important impact on shale gas exploitation plan and its long-term and stable output (Chen et al., 2016; Huang et al., 2012).

The influencing factors of adsorption of organic-rich shale are very complicated, such as total organic carbon (TOC), kerogen type, clay minerals, maturity and so on. Previous scholars have attributed it to the effect of pores of different genesis and their structural evolution on the adsorption capacity of shale gas (Hao et al., 2013; Hou et al., 2014). Many scholars believe that organic components in shale are the important controlling factors for methane adsorption capacity because micropore volume is positively correlated with TOC and micropores are important components of the shale porous media with relatively large internal specific surface area and strong adsorption capacity (Chalmers and Bustin, 2007, 2008; Ross and Bustin, 2007). Ross and Bustin (2009) found that the adsorption control factors of shale with different maturity are different, the high maturity shale sorption capacity is governed by the characteristics of organic carbon, and clay minerals also have a significant impact on shale sorption in shale with low TOC. At present, different scholars hold different views on the adsorption of clay minerals and organic matter. Chalmers and Bustin (2007) considered that the hydrophilicity of clay minerals can reduce the gas adsorption capacity, but Schettler and Parmoly (1990) considered that the adsorption of clay minerals is stronger than that of kerogen. Therefore, the material composition and pore structure on the adsorption capacity of shale need to be further studied.

Previous studies have shown that the Hongshuizhuang Formation and Xiamaling Formation in the Yanshan area, as the high-quality marine source rocks, already have the material basis for the formation of shale gas, but those studies have concentrated more on the characteristics of the hydrocarbon source rocks in the Yanshan area of the Proterozoic shale, and little research has been reported on their reservoir properties (Wang, 1980; Wang and Han, 2011; Xie et al., 2013). In order to strengthen the understanding of the dark shale reservoir property, organic geochemistry and X-ray diffraction (XRD) were used to analyze the composition characteristics of shale, the pore structure parameters of shale were obtained by low-temperature nitrogen adsorption and mercury injection experiment, and the adsorption capacity of shale gas was obtained by isothermal adsorption experiments of high-pressure methane. The influence of different material composition and pore structure characteristics of shale on methane adsorption performance was discussed.
Geological background

Yanshan area lies west to Zhangjiakou, east to Beipiao and Fuxin in nearly an east–west distribution. On the tectonic division, the Yanshan area is located on the northern margin of the North China platform and is an active tectonic unit, which can be divided into two ancient uplifts and five ancient depressions (Figure 1) (Liu et al., 2011; Wang, 1980; Zhong, 2010). The middle and late Proterozoic crustal movement in the area is evolved from relatively active tectonic environment to relatively stable tectonic environment, and the two states alternately appear, and finally tend to be stable (Hao et al., 1990; Pan et al., 2013). The strata are formed in the epicontinental sea environment, characterized by clastic deposits in the early stage and characterized by alternating development between the confined marine carbonate and argillaceous rocks in the middle and late stages (Zhong, 2010).

During the deposition of the Hongshuizhuang Formation, the sea area contracted, and the vast shallow sea turned into an abnormally shallow bay environment with narrow occlusion and underwater detention reduction, which is dominated by black, gray-black shale, argillaceous dolomite, and gray green shale. The sedimentary center is located in Jixian-Xinglong and Kuancheng areas of Yanshan area with a thickness of 0 m–170 m. In the early stage of the deposition of the Xiamaling Formation, the sea water is shallow, and the seafloor is in the condition of weak oxidation to reduction, and the sediments are dominated by mottled sand shale. In the middle and later stages, the seawater is deepened and the reducibility is enhanced. Gray-black and black shale with larger thickness are deposited and interbedded with siliceous mudstone. The sedimentary center is located in Huailai and Xinglong regions with a thickness of 100 m–600 m.

![Figure 1. Location of the study area and sampling points.](image-url)
Experimental

Experimental samples

Because few shale gas wells have been drilled in this area, it was thus difficult to obtain shale samples. In this paper, the samples were collected from eight different fresh outcrop profiles in Yanshan area, and the latitude and longitude of profiles are shown in Figure 1. Samples kcd, xld, cpd were collected from three Hongshuizhuang Formation outcrops (Kuanchengdapooshang, Xinglongdabian, Changpingpanlongtai) with the depth of 7 m, 6 m, 7 m, respectively. Samples kcj, xlb, myb, cpd, xmz were collected from five Xiamaling Formation outcrops (Kuanchengjiguanshan, Xinglongbeishuiquian, Miyunbaishiling, Changpingdelingcun, Huailaizhaoiashan) with the depth of 5 m, 5 m, 3 m, 3 m, 10 m, respectively. Samples are taken at a certain distance to ensure that the samples are representative. The organic geochemical parameters and mineral compositions of shale samples are shown in Table 1. The distribution of TOC ranged from 0% to 6.71%, with an average of 2.35%. The TOC content of Hongshuizhuang Formation was relatively high, ranging from 0.04% to 5.63% with an average of 2.73%. The TOC content of Xiamaling Formation was 0.00% to 6.71% with an average of 2.00%. The results of previous studies show that the sedimentary center of Hongshuizhuang Formation is located in Jixian-Xinglong and Kuancheng of Yanshan area, and the sedimentary center of Xiamaling Formation is located in Huailai, Xinglong, Miyun (Yang, 2013). For Hongshuizhuang Formation, the average TOC content of Kuancheng and Xinlong samples (3.17) is larger than that of other regions (0.05). For Xiamaling Formation, the average TOC content of Xinglong and Huailai is larger than that of other regions (1.27). Therefore, the distribution of sedimentary centers is consistent with the distribution of TOC high values.

According to the pyrolysis results, the organic matter types are of types I and II, which is the inevitable result of lower biogenic. The vitrinite reflectance ($R_o$) of Hongshuizhuang Formation is 1.4% to 1.96%, with an average of 1.51% and that of Xiamaling Formation is 1.14% to 2.03%, with an average of 1.58%. The organic matter of the sample has a high degree of evolution and is in the stage of massive gas production, indicating that they have good shale gas generation conditions.

The whole rock XRD analysis of 7 samples from Hongshuizhuang Formation and 10 samples from Xiamaling Formation shows that the mineral composition of the shale mainly consists of quartz and clay minerals (Table 2). Quartz content ranged from 51.9% to 88.3%, with an average of 62.6%; clay mineral content ranged from 10.5% to 41.4%, with an average of 30.8%; potash feldspar content ranged from 1.1% to 15%, with an average of 4.4% (Figure 2). The average contents of clay minerals in the two groups are not the same, which are 30.8% and 30.9%, respectively; the average content of quartz of Xiamaling Formation (64.3%) is higher than that of Hongshuizhuang Formation (60.3%), and the average content of potash feldspar in the Hongshuizhuang Formation is 8.6% and that of the Xiamaling Formation is only 1.5%. Samples of Hongshuizhuang Formation do not contain plagioclase, while samples of Xiamaling formation have plagioclase content of 1.6%–9.5% with an average of 3.4%. Shale reservoirs with commercial development conditions, the content of brittle minerals, such as quartz, are generally higher than 40%, and clay mineral content is less than 30%. The middle Proterozoic shale has high content of brittle minerals, which is beneficial to the formation of artificial fracture (Jarvie et al., 2007; Zou et al., 2010). The results of XRD analysis of clay minerals show that the clay minerals of the two groups are mainly dominated by illite/smectite and illite, kaolinite and chlorite are less (Figure 3).
The different rocks can be classified by mineralogy and TOC content of each lithofacies. It is generally considered that the lower limit of TOC content of marine shale with economic exploitation of shale gas is 2% (Jiao et al., 2016). Therefore, the content of TOC in organic-rich shale is higher than 2%, whereas the TOC content of organic-poor shale is less than 2%. Secondly, the content of clay minerals, calcite + dolomite, and quartz + feldspar is used as three terminal members to classify lithofacies. The mineral composition of each lithofacies is shown in Table 2 (Jiang et al., 2016; Wang et al., 2016). The classification for the different rocks is shown in Table 3 and 4.

### Experimental methods

Low-temperature liquid nitrogen adsorption test was carried out using V-Sorb 2800TP rock specific surface and pore size distribution instrument based on SY/T 6154-1995. The relative

| Sampling sites      | Formation             | Sample number | TOC (%) | T_{max} (°C) | S_1+S_2 (mg/g) | HI (mg/g) | D (%) | R_o (%) |
|---------------------|-----------------------|---------------|---------|--------------|----------------|------------|-------|---------|
| Kuanchengdaposhang  | Hongshuizhuang Formation | kcd-3         | 1.37    | –            | –              | –          | –     | –       |
|                     |                       | kcd-8         | 3.98    | 443.8        | 12.04          | 254.36     | 22.02 | 1.41    |
|                     |                       | kcd-12        | 1.05    | –            | –              | –          | –     | –       |
|                     |                       | kcd-14        | 2.23    | 444.2        | 4.93           | 233.17     | 19.97 | –       |
|                     |                       | kcd-21        | 5.27    | 444.2        | 12.75          | 272.73     | 23.09 | 1.96    |
|                     |                       | kcd-22        | 5.04    | –            | –              | –          | –     | –       |
|                     |                       | kcd-24        | 5.33    | 450          | 13.41          | 279.2      | 23.53 | –       |
|                     |                       | kcd-25        | 5.63    | 443.8        | 19.34          | 343.1      | 29.78 | 1.4     |
| Xinglongdabianzhang | Hongshuizhuang Formation | xld-1         | 0.6     | –            | –              | –          | –     | –       |
|                     |                       | xld-2         | 0.66    | –            | –              | –          | –     | –       |
|                     |                       | xld-4         | 2.25    | 444.2        | 3.52           | 170.53     | 14.98 | 1.29    |
|                     |                       | xld-10        | 4.68    | 444.2        | 10.14          | 252.72     | 21.49 | 1.5     |
| Changpingpanlongtai | Hongshuizhuang Formation | cpd-16        | 0.04    | –            | –              | –          | –     | –       |
|                     |                       | cpd-19        | 0.07    | –            | –              | –          | –     | –       |
| Kuanchengjiguanshan | Xiamaling Formation   | kcj-16        | 1.7     | 464.6        | 0.01           | 0.27       | 0.04  | 1.14    |
|                     |                       | kcj-19        | 1.21    | –            | 0              | 0.06       | 0.02  | 1.51    |
|                     |                       | kcj-21        | 0.86    | –            | –              | –          | –     | –       |
| Xinglongbeishuian   | Xiamaling Formation   | xlb-5         | 1.46    | –            | 0              | 4.2        | 1.26  | 1.64    |
|                     |                       | xlb-8         | 0.92    | –            | 0              | 0.88       | 0.12  | 2       |
| Miyunbaishiling     | Xiamaling Formation   | myb-3         | 3.51    | –            | 0              | 2.43       | 0.34  | 1.83    |
|                     |                       | myb-5         | 1.37    | –            | 0              | 5.35       | 0.66  | 1.4     |
|                     |                       | myb-6         | 1.55    | –            | 0              | 2.84       | 0.27  | –       |
| Changpingdelingcun  | Xiamaling Formation   | cpd-4         | 0       | –            | –              | –          | –     | –       |
|                     |                       | cpd-7         | 0.01    | –            | –              | –          | –     | –       |
| Huailaizhaojiashan  | Xiamaling Formation   | xmnz-8        | 5.04    | 444.2        | 17.73          | 527.69     | 44.5  | 1.23    |
|                     |                       | xmnz-11       | 6.71    | 440          | 24.52          | 470.61     | 39.4  | 2.03    |
|                     |                       | xmnz-12       | 3.19    | 442.5        | 8.48           | 385        | 32.3  | 1.46    |
|                     |                       | xmnz-17       | 2.07    | –            | –              | –          | –     | –       |
|                     |                       | xmnz-22       | 0.4     | –            | –              | –          | –     | –       |

TOC: total organic carbon; T_{max}: Pyrolysis hydrocarbon peak temperature; S_1+S_2: Oil production potential; S_1: Soluble hydrocarbon content; S_2: Pyrolysis hydrocarbon content; D: Degradation potential; R_o: Vitrinite reflectance.

The different rocks can be classified by mineralogy and TOC content of each lithofacies. It is generally considered that the lower limit of TOC content of marine shale with economic exploitation of shale gas is 2% (Jiao et al., 2016). Therefore, the content of TOC in organic-rich shale is higher than 2%, whereas the TOC content of organic-poor shale is less than 2%. Secondly, the content of clay minerals, calcite + dolomite, and quartz + feldspar is used as three terminal members to classify lithofacies. The mineral composition of each lithofacies is shown in Table 2 (Jiang et al., 2016; Wang et al., 2016). The classification for the different rocks is shown in Table 3 and 4.
pressure varies from 0.01 to 0.99 with a measurable aperture range of 2 nm to 160 nm. Brunauer, Emmett and Teller (BET) method was used to calculate specific surface area, and pore volume was calculated by Barrett, Joyner and Halenda (BJH) method. The AutoPore IV9510 automatic mercury porosimeter was used for the test. The contact angle between metal mercury and coal surface is 140°, the mercury surface tension was 480 dyn/cm, and the measured pore diameter range was more than 3.0 nm. The shale surface was observed by

| Formation          | Sample number | Clay mineral (%) | Quartz (%) | Potash feldspar (%) | Plagioclase (%) | Pyrite (%) | Illite/smectite (%) | Illite (%) | Kaolinite (%) | Chlorite (%) |
|--------------------|---------------|------------------|------------|---------------------|-----------------|------------|---------------------|------------|---------------|--------------|
| Hongshuizhuang    | kcd-8         | 26.8             | 59.5       | 13.7                | 0               | 0          | 50                  | 48         | 0             | 2            |
|                    | kcd-21        | 32.1             | 58.9       | 9                   | 0               | 0          | 46                  | 53         | 0             | 1            |
|                    | kcd-25        | 28               | 64.2       | 4.9                 | 0               | 2.9        | 45                  | 54         | 0             | 1            |
|                    | xld-4         | 33.1             | 51.9       | 15                  | 0               | 0          | 41                  | 53         | 0             | 6            |
|                    | xld-10        | 35               | 58.9       | 6.1                 | 0               | 0          | 46                  | 54         | 0             | 0            |
|                    | kcd-14        | 31.4             | 62.4       | 6.2                 | 0               | 0          | –                   | –          | –             | –            |
|                    | kcd-24        | 28.9             | 66         | 5.1                 | 0               | 0          | –                   | –          | –             | –            |
| Xiamaling          | kcj-16        | 37.9             | 58.3       | 1.6                 | 2.2             | 0          | 58                  | 41         | 0             | 1            |
|                    | xlz-5         | 32.5             | 59.4       | 0                   | 8.1             | 0          | 30                  | 38         | 0             | 32           |
|                    | myb-3         | 33.3             | 53.7       | 3.5                 | 9.5             | 0          | 48                  | 46         | 0             | 6            |
|                    | xlmz-8        | 41.4             | 54.7       | 2                   | 1.9             | 0          | 71                  | 27         | 2             | 0            |
|                    | xlmz-11       | 31               | 64.3       | 2.1                 | 2.6             | 0          | 70                  | 30         | 0             | 0            |
|                    | kcj-19        | 34.4             | 61.8       | 1.6                 | 2.2             | 0          | –                   | –          | –             | –            |
|                    | xlz-8         | 37.3             | 57         | 0                   | 5.7             | 0          | –                   | –          | –             | –            |
|                    | myb-5         | 10.5             | 88.3       | 1.2                 | 0               | 0          | –                   | –          | –             | –            |
|                    | myb-6         | 11.1             | 87.3       | 1.6                 | 0               | 0          | –                   | –          | –             | –            |
|                    | xlmz-12       | 39.6             | 57.7       | 1.1                 | 1.6             | 0          | –                   | –          | –             | –            |

Figure 2. Mesoproterozoic shale mineral composition and content.
FEI Quanta450FEG high-resolution field emission scanning electron microscope (SEM). Adsorption test was carried out by the IS-300 isothermal adsorption instrument. The experimental data were processed according to the Langmuir monolayer adsorption principle. The overall temperature error is controlled within 0.2°C, the adsorption equilibrium time of each pressure point is more than 12 h, and the methane purity is 99.99%.

Results and discussion

SEM analysis

Intergranular pores, intragranular pores, and organic pores can be seen under an SEM (Loucks et al., 2012). Among them, abundant organic matter has been observed in the dark shale of the Hongshuizhuang Formation and Xiamaling Formation, and a large number of organic pores were formed.

Intergranular pores are commonly found between mineral particles, including intergranular pores formed by the irregular packing of mineral grains (Figure 4(a) and (f)), and the intergranular pores between aggregates of flocculent clay minerals (Figure 4(c)), including intercrystalline pores of mineral particles (Figure 4(e)). The morphology of intergranular
pores is irregular. The shape of intergranular pore is different, and it is irregular polygon, the size of which is between nanometer and micron, and the intergranular pores formed by flocculent clay minerals have good connectivity, while the mineral dissolution pores and intercrystalline pores are relatively isolated.

Intragranular pores are develop in the interior of the granule, which are mainly composed of interlayer pores formed during the transformation of clay minerals (Figure 4(b), (g), and (i)), and dissolution pores formed by dissolution of feldspar, calcite, and other mineral particles (Figure 4(h)), also includes fossil pore of Paleontological fossil remains (Figure 4(d)). The shape of intragranular pore varies with the cause of formation. The interlayer pores of clay minerals are generally parallel plates, extending several tens of microns and several microns in width. The dissolution pores are irregular, relatively isolated, and the pore size is mostly of a few microns. There are a small number of fossil holes in the shale, and the fossils are well preserved and well connected, most of which are nanoscale.

A large number of microcracks exist in the Mesoproterozoic samples in the study area, mostly clay mineral interlayer fractures, and the extension is good. The width is generally several microns, and the length is from tens of microns to hundreds of microns. It is generally open and interlinked with other types of pores to form an intricate three-dimensional seepage network that facilitates the seepage and migration of shale gas (Figure 5).

**Low-temperature nitrogen adsorption analysis**

As shown in Figure 6, the morphology of low-temperature nitrogen adsorption–desorption curves of five samples from Hongshuizhuang formation and nine samples from Xiamaling formation shows an overall anti-S pattern, which is similar to type II adsorption isotherm (Chen et al., 2012). In the section with higher relative pressure \( \frac{P}{P_0} > 0.4 \), the adsorption isotherms and desorption isotherms of the samples do not overlap, forming a hysteresis
loop, indicating that there is no adsorption saturation when the saturated vapor pressure is reached, and there are some mesopores and macropores in shale samples (Chen and Tang, 2001). According to the classification of International Union of Pure and Applied Chemistry (IUPAC), the hysteresis loop of the sample is close to that of the H2-type hysteresis loop and has the characteristic of the H3-type hysteresis loop.

Further analysis shows that the adsorption–desorption curves of 14 shale samples can be divided into three types (Figure 6).

Type A: Take kcd-21 and kcd-25 as the representatives. There is no obvious turning point in the desorption curve. When the relative pressure is less than 0.4, the adsorption–
desorption curve almost coincides, the adsorption volume is small, and the hysteresis loop is narrow. The pores of this kind of shale samples are mainly impermeable pore closed at one end, and also contain a small amount of open pores, which are beneficial to the migration of shale gas and unfavorable to the adsorption of gases.

Type B: Take xld-4 and xmz-11 as the representatives. This type includes kcd-8, xld-10, xmz-8, and xmz-12. When the relative pressure is about 0.5, the desorption curve shows an obvious inflection point. When the relative pressure is less than 0.4, the desorption curve and the adsorption curve do not coincide, indicating that there may be a certain number of micropores in the shale sample, capillary coalescence occurs, and less pressure is required to evaporate and desorption. The adsorption volume is medium and hysteresis loop increases. The pores of these shale samples are mainly cylindrical pores with two ends open, around the opening of a parallel plate pore; they also contain a number of inkwell pores.

Type C: Take xlb-5 and myb-3 as the representatives. This type includes kcj-16, kcj-19, xlb-8, and myb-5. The desorption curve shows an obvious turning point when the relative pressure is about 0.5, and the desorption curve drops faster. When the relative pressure is less than 0.4, the desorption curve and adsorption curve coincide. The adsorption volume and the hysteresis loop are larger. This kind of shale samples contain open pore and inkwell pore, and the number of ink bottle pore is higher than that of Type B.

**Pore specific surface area, pore volume, pore size distribution, and porosity**

The specific surface area of the 14 shale samples is 0.34 m$^2$/g to 14.57 m$^2$/g with an average of 6.89 m$^2$/g using the BET model. The average surface area of Hongshuizhuang Formation and Xiamaling Formation is 2.46 m$^2$/g and 9.35 m$^2$/g, respectively (Table 5). The pore volume of the samples is 0.004 mL/g to 0.029 mL/g with an average of 0.0128 mL/g. The average pore volume of Hongshuizhuang Formation and Xiamaling Formation is 0.0045 mL/g and 0.0173 mL/g, respectively (Table 5). The average pore size of the samples is 3.728 nm to 12.609 nm with an average of 5.635 nm. The average pore size of Hongshuizhuang Formation is larger than that of Xiamaling Formation.

Figure 7 shows the pore size distribution of six typical samples of Type A, Type B, and Type C. The pore size distribution of Type A is mainly between 2nm – 4nm and 18 nm. The
peak value of the pore size of Type B and Type C is between 2 nm and 4 nm. The specific surface area, pore volume, and average pore size of three types also have the obvious characteristics of classification. The average pore size of Type A is the largest, the specific surface area and pore volume are the smallest. The pore size of Type B is the smallest, the pore specific surface area and pore volume are moderate. The pore size of Type C is moderate, and the specific surface area and pore volume are generally larger (Table 5).

According to the test results of true density and apparent density, the porosity of 14 shale samples is between 0.807% and 10.267%, with an average of 4.221%. The average porosity of Hongshuizhuang Formation (2.419%) is lower than that of Xiamaling Formation (5.222%). Compared with the porosity of the shale reservoir in North America, the porosity

**Figure 6.** Adsorption–desorption curves of Mesoproterozoic shale samples in Yanshan area.
of the Hongshuizhuang Formation is low and the porosity of Xiamaling Formation is moderate.

Based on the IUPAC classification, the pore volume and pore specific surface area of each pore diameter section of 14 samples were calculated according to the range of <2 nm,
2–10 nm, 10–30 nm, 30–50 nm, >50 nm. The pore volume of the samples is mainly distributed in three aperture sections of 2–10 nm, 10–30 nm, and >50 nm with the ratios of 25.74%, 28.31%, and 35.94%, respectively. In the pore size range of 2 nm to 10 nm, the average pore volume of Hongshuizhuang and Xiamaling samples was 20.10% and 28.88%, respectively. In the pore size range of more than 50 nm, the average pore volume ratios of Hongshuizhuang and Xiamaling samples were 42.79% and 32.13%, respectively (Figure 8). Comparing the above pore volume distribution characteristics, the Xiamaling formation shale is more conducive to adsorption, and the Hongshuizhuang shale is more conducive to seepage. The specific surface area of the sample is mainly contributed by the pores of <2 nm, 2–10 nm, and 10–30 nm, with the average ratios of 10.65%, 62.46%, and 18.28% (Figure 8). More than half of the specific surface area of the two groups of samples comes from the pore size range of 2 nm to 10 nm, all of which have favorable pore conditions for adsorption.

**Pore fractal dimension characteristics**

Surface fractal dimension can quantitatively characterize the pore surface complexity, which deserves to be obtained by mercury intrusion method and low-temperature nitrogen adsorption method. As high-pressure mercury destroys the micropores and mesopores and causes errors, N₂ adsorption can avoid this error and provide information about pore structure information on micropore and mesopore from a few nanometers to hundreds of nanometers (Cai, 2015).

Therefore, this paper studies the shale nanoscale pore through the low-temperature nitrogen adsorption method and uses the Frenkel-Halsey-Hill (FHH) model to calculate the fractal dimension of the pore. The calculation of pore fractal dimension by FHH model has been discussed in detail in the literature (Xie et al., 2014; Zhao et al., 2014). The calculation method of fractal dimension is as follows

\[
\ln\left(\frac{V}{V_0}\right) = \lambda \ln(\ln(p_0/p)) + K
\]  

where \( p \) is the equilibrium pressure (MPa), \( p_0 \) is the gas adsorption to reach saturated vapor pressure (MPa), \( V \) is the gas adsorption capacity at equilibrium pressure \( p \) (cm³/g), \( V_0 \) is the
When the relative pressure is greater than 0.45, different samples show different degree of hysteresis loops, capillary condensation occurs on the nitrogen adsorption. Therefore, the pore fractal dimension is calculated by the experimental data of adsorption process at relative pressure larger than 0.45. The fitting curves of \( \ln V \) and \( \ln(\ln(p/p_0)) \) are made, and the fractal dimension \( D \) can be calculated by the slope (\( \lambda \)) and the formula as follows

\[
D = 3 + \lambda
\] (2)

The shales in the study area all have significant fractal characteristics \( (R^2 \) is greater than 0.98), and the fractal dimension is between 2.503 and 2.765 (Table 6), indicating that the pore space of samples is very small, and the pore structure is extremely complicated with strong heterogeneity. Previous studies have shown that for samples with good correlation, the curve can be divided into two parts with the mean free path of methane molecules (the corresponding \( p/p_0 \) is between 0.85 and 0.9 when \( r \) is 7.5 nm). The \( r \) of seepage pores is larger than 7.5 nm and adsorption pores is opposite, and the corresponding fractal dimensions are obtained. The results show that the fractal dimension of the adsorption pore is greater than that of the seepage pore, indicating that the pore structure of the overall adsorption pores of shale in the study area is more complex than that of the seepage pore. The roughness and the irregular shape of the pore surface are higher, the pore connectivity is worse, and the heterogeneity is stronger (Table 7) (Zhao et al., 2014).

### Influence factors of pore fractal dimension

The fractal dimension of pore of Xiamaling Formation has a positive correlation with the increase of organic carbon content (Figure 9(a)), this is mainly related to the development of a large number of micropores in the organic matter of shale. The higher the content of organic matter in shale, the more the micropores are developed (Figure 10), and the more

| Sample number | Fractal dimensions | Fitting equation | \( R^2 \) |
|---------------|-------------------|------------------|---------|
| kcd-8         | 2.733             | \( y = -0.267x + 0.370 \) | 0.991   |
| kcd-21        | 2.507             | \( y = -0.493x - 2.129 \) | 0.997   |
| kcd-25        | 2.503             | \( y = -0.497x - 2.224 \) | 0.994   |
| xld-4         | 2.73              | \( y = -0.270x + 0.573 \) | 0.997   |
| xld-10        | 2.687             | \( y = -0.313x - 0.345 \) | 0.981   |
| kcj-16        | 2.684             | \( y = -0.316x + 1.492 \) | 0.991   |
| xlb-5         | 2.716             | \( y = -0.284x + 1.510 \) | 0.987   |
| myb-3         | 2.765             | \( y = -0.235x + 1.624 \) | 0.997   |
| xmxz-8        | 2.759             | \( y = -0.241x + 1.354 \) | 0.977   |
| xmxz-11       | 2.738             | \( y = -0.262x + 0.469 \) | 0.990   |
| kcj-19        | 2.618             | \( y = -0.382x + 1.309 \) | 0.996   |
| xlb-8         | 2.755             | \( y = -0.245x + 1.212 \) | 0.992   |
| myb-5         | 2.617             | \( y = -0.383x + 0.412 \) | 0.99    |
| xmxz-12       | 2.694             | \( y = -0.306x + 0.843 \) | 0.989   |

volume of monolayer adsorbed gas \( (\text{cm}^3/\text{g}) \). \( K \) is a constant, \( \lambda \) is a linear correlation coefficient.
complex the pore structure is, the larger the fractal dimension of shale is (Chalmers and Bustin, 2008). The pore fractal dimension of Hongshuizhuang Formation is negatively correlated with organic carbon content (Figure 9(a)), this is mainly related to the development of a large number of macropore in the organic matter of shale. With the increase of organic matter content, the development of macropore is more obvious (Figure 10), and the pore structure of micropores tends to be simple, and hence the fractal dimension decreases.

The pore fractal dimension of Xiamaling Formation is positively correlated with the increase of clay content, while the pore fractal dimension of Hongshuizhuang Formation is weakly related or not (Figure 9(b)). SEM observation shows that the clay mineral pore of Xiamaling Formation is mainly composed of small pores such as intragranular pores and intercrystalline pores. However, clay mineral pore of Hongshuizhuang Formation is mainly composed of large pores such as interlaminar pores and intergranular pores. Compared with Hongshuizhuang Formation, the Xiamaling Formation experienced a longer evolution of diagenesis and was more strongly compacted, the larger pores of clay minerals were closed or filled under the stress, and only pores developed within the particle contribute more to reservoir porosity. The existence of clay minerals in the pores will cause the increase of pore roughness, the more complex pore structure, and the larger fractal dimension of shale (Yang et al., 2014).

The pore fractal dimension of Xiamaling Formation has a negative correlation with the quartz content (Figure 9(c)). It is indicated that the increase of quartz content can effectively improve the pore structure of shale. This is related to quartz as brittle minerals. Under the same compaction conditions, coal with high quartz content can protect against overlying pressure, and macropores and mesopores can be saved. Otherwise, macropores and mesopores are compressed into micropores, which makes the micropore structure complex and the fractal dimension increases.

### Table 7. Fractal dimension of seepage and adsorption pore of Mesoproterozoic shale samples in Yanshan area.

| Sample number | $D_1$ | Fitting equation | $R^2$ | Sample number | $D_2$ | Fitting equation | $R^2$ |
|---------------|-------|------------------|-------|---------------|-------|------------------|-------|
| kcd-8         | 2.774 | $y = -0.226x + 0.503$ | 0.989 | kcd-8         | 2.702 | $y = -0.298x + 0.335$ | 0.999 |
| kcd-21        | 2.529 | $y = -0.471x - 2.053$ | 0.991 | kcd-21        | 2.523 | $y = -0.477x - 2.118$ | 0.998 |
| kcd-25        | 2.547 | $y = -0.453x - 2.064$ | 0.983 | kcd-25        | 2.514 | $y = -0.486x - 2.225$ | 0.997 |
| xld-4         | 2.751 | $y = -0.249x + 0.640$ | 0.990 | xld-4         | 2.725 | $y = -0.275x + 0.566$ | 0.999 |
| xld-10        | 2.748 | $y = -0.252x - 0.192$ | 0.992 | xld-10        | 2.647 | $y = -0.353x - 0.342$ | 0.978 |
| kcj-16        | 2.741 | $y = -0.259x + 1.671$ | 0.987 | kcj-16        | 2.647 | $y = -0.353x + 1.451$ | 0.999 |
| xlb-5         | 2.776 | $y = -0.224x + 1.699$ | 0.985 | xlb-5         | 2.672 | $y = -0.328x + 1.463$ | 0.999 |
| myb-3         | 2.786 | $y = -0.214x + 1.690$ | 0.998 | myb-3         | 2.745 | $y = -0.255x + 1.603$ | 0.999 |
| xmbz-8        | 2.823 | $y = -0.177x + 1.558$ | 0.979 | xmbz-8        | 2.702 | $y = -0.298x + 1.293$ | 0.997 |
| xmbz-11       | 2.779 | $y = -0.221x + 0.603$ | 0.989 | xmbz-11       | 2.703 | $y = -0.297x + 0.430$ | 0.998 |
| kcj-19        | 2.665 | $y = -0.335x + 1.459$ | 0.993 | kcj-19        | 2.592 | $y = -0.408x + 1.279$ | 1 |
| xlb-8         | 2.796 | $y = -0.204x + 1.340$ | 0.995 | xlb-8         | 2.723 | $y = -0.277x + 1.178$ | 0.999 |
| myb-5         | 2.692 | $y = -0.308x + 0.649$ | 0.992 | myb-5         | 2.561 | $y = -0.439x + 0.352$ | 0.999 |
| xmbz-12       | 2.749 | $y = -0.251x + 1.021$ | 0.982 | xmbz-12       | 2.659 | $y = -0.341x + 0.802$ | 0.999 |

$D_1$: fractal dimension of adsorbed pore, $D_2$: fractal dimension of seepage pore.
The pore fractal dimension of Xiamaling Formation and Hongshuizhuang Formation has a positive correlation with the BET specific surface area (Figure 9(d)). Among them, the fractal dimension of Hongshuizhuang Formation is more obvious. It is indicated that the increase of specific surface area caused by small pores with organic matter or intergranular pore will lead to the complicating pore structure of micropores.

Figure 9. The relationship between pore fractal dimension and its influencing factors. TOC: clay mineral content, quartz content; BET: specific surface area, average pore size; and BJH: pore volume.
The pore fractal dimension of Xiamaling Formation and Hongshuizhuang Formation has a negative correlation with the average pore size (Figure 9(e)), which shows that the smaller the average pore size of the shale, the larger the fractal dimension. The smaller the average pore size is, the more micropores are contained in the shale. The more complicated the pore structure is, the rougher the pore surface is.

There is a positive correlation between the pore fractal dimension of Hongshuizhuang Formation and the pore volume of BJH (Figure 9(f)). According to the above analysis, the specific surface area and pore volume of the micropores of Hongshuizhuang Formation are increased with the increase of the fractal dimension, indicating that the fractal dimension of shale in Hongshuizhuang Formation is related to the development of micropores, which are the main contributors to pore specific surface area and pore volume. The fractal dimension can be used to describe the micropore development. The pore fractal dimension of Xiamaling Formation has only weak correlation with BET specific surface area and BJH pore volume. There is a positive correlation between the BET specific surface area and the

**Figure 10.** The relationship between TOC content and pore volume.

**Figure 11.** The relationship between BET specific surface area and BJH pore volume.
 BJH pore volume of Hongshuizhuang Formation and Xiamaling Formation. However, the correlation between fractal dimension and BET surface area, BET specific surface area and BJH pore volume of Xiamaling Formation is not significant than that of Hongshuizhuang Formation (Figure 11). The reason is that the micropores of Hongshuizhuang Formation are dominated by organic pores, while the pores of the Xiamaling formation are not only organic pores but also clay mineral intergranular pores. If the pore size of clay mineral intergranular pores is less than that of the organic pores, which will result in a smaller pore volume but the greater the specific surface area, and the greater the difference, the greater the pore contribution rate of clay minerals in the micropores, which will lead to the enhancement of pore heterogeneity.

Analysis of shale reservoir performance and its influencing factors

Evaluation of reservoir performance. Shale reservoir adsorption is an important indicator to evaluate the potential of shale gas resources. The gas content of the commercial shale in North America is 0.44 m$^3$/t to 9.91 m$^3$/t, and the adsorbed gas content accounts for 20% to 85% of the total gas content (Curtis, 2002; Sondergeld et al., 2010). The methane isothermal adsorption experiment of natural dry shale samples was carried out at 30°C, the Langmuir volume of four samples was 1.57 cm$^3$/g to 4.36 cm$^3$/g (Table 8). Under the adsorption pressure of 9.97 MPa (approximately 1000 m depth), the average adsorption capacity of samples in Hongshuizhuang Formation was 1.38 cm$^3$/g and that of Xiamaling Formation was 3.13 cm$^3$/g. The methane isothermal adsorption experiment results under the conditions of 30°C and humidity of 0.78% to 1.45% show that the adsorption capacity of dark shale of Xiamaling Formation is 1.07 m$^3$/t to 3.33 m$^3$/t with an average of 2.02 m$^3$/t (Liu et al., 2014). Therefore, the potential gas-bearing properties of the middle Proterozoic shale reservoirs in Yanshan area are comparable with those of commercially exploited shale gas reservoirs in North America. The adsorption gas content is high and the potential for resources is high.

Analysis of influence factors of reservoir performance

Previous studies have shown that shale adsorption capacity is related to the influence factors such as pore structure, organic carbon content, mineral composition, water content, and pressure (Bi et al., 2014; Zhao et al., 2016). The above research shows that there is little difference in material composition of Hongshuizhuang Formation and Xiamaling Formation, such as TOC, vitrinite reflectance, and clay mineral content. However, the difference in the adsorption capacity of the two layers is great, and the main controlling factors of its adsorption properties still need to be explored.

Table 8. Methane adsorption capacity of Mesoproterozoic shale in north China.

| Sample number | Formation | $P_L$ (MPa) | $V_L$ (cm$^3$·g$^{-1}$) | Adsorption capacity at 9.97 MPa (cm$^3$·g$^{-1}$) | Sample number | Formation | $P_L$ (MPa) | $V_L$ (cm$^3$·g$^{-1}$) | Adsorption capacity at 9.97 MPa (cm$^3$·g$^{-1}$) |
|---------------|-----------|-------------|--------------------------|---------------------------------|---------------|-----------|-------------|--------------------------|---------------------------------|
| kcd-25       | Jxh       | 1.78        | 1.57                     | 1.38                            | xmx-8         | Qnx       | 3.63        | 4.36                     | 3.20                            |
| xld-4        |           | 2.37        | 2.11                     | 1.80                            | xmx-11        |           | 2.24        | 3.74                     | 3.07                            |
Table 9. Mercury pressure data of Mesoproterozoic shale samples in Yanshan area.

| Sample number | Total pore volume (mL·g⁻¹) | Pore volume distribution (%) | Total surface area (m²·g⁻¹) | Specific surface area distribution (%) |
|---------------|----------------------------|-----------------------------|-----------------------------|---------------------------------------|
|               |                            | V_1 | V_2 | V_3 | V_4 | S_1 | S_2 | S_3 | S_4 |
| xld-4         | 0.0079                     | 31.34 | 28.36 | 0.00 | 40.30 | 2.287 | 82.49 | 17.24 | 0.26 | 0.00 |
| xld-10        | 0.0071                     | 28.57 | 22.86 | 12.86 | 35.71 | 2.099 | 87.01 | 12.37 | 0.62 | 0.00 |
| kcd-8         | 0.0059                     | 36.17 | 27.66 | 2.13 | 34.04 | 1.814 | 85.52 | 13.52 | 0.96 | 0.00 |
| kcd-21        | 0.0031                     | 47.37 | 10.53 | 15.79 | 32.62 | 0.73 | 85.52 | 13.52 | 0.96 | 0.00 |
| kcd-25        | 0.0047                     | 32.56 | 30.23 | 4.65 | 32.56 | 1.118 | 83.78 | 15.59 | 0.63 | 0.00 |
| kcj-16        | 0.0442                     | 38.95 | 48.06 | 8.66 | 3.33 | 16.555 | 76.75 | 22.74 | 0.51 | 0.00 |
| kcj-19        | 0.061                      | 8.62 | 73.80 | 13.43 | 4.15 | 8.638 | 42.49 | 54.83 | 2.69 | 0.00 |
| myb-3         | 0.0961                     | 6.24 | 29.55 | 58.90 | 5.31 | 8.414 | 51.28 | 35.50 | 13.14 | 0.08 |
| myb-5         | 0.0117                     | 36.96 | 33.33 | 0.00 | 2.70 | 6.222 | 87.58 | 12.37 | 0.05 | 0.00 |
| xlb-5         | 0.0318                     | 36.36 | 51.72 | 5.02 | 6.90 | 11.593 | 73.59 | 26.23 | 0.18 | 0.00 |
| xlb-8         | 0.0108                     | 38.39 | 35.71 | 11.61 | 14.29 | 3.866 | 81.19 | 18.32 | 0.49 | 0.00 |
| xmxz-8        | 0.0143                     | 54.55 | 28.79 | 4.55 | 12.12 | 6.731 | 87.93 | 11.91 | 0.16 | 0.00 |
| xmxz-11       | 0.0156                     | 59.60 | 23.84 | 6.62 | 9.93 | 8.234 | 89.88 | 9.98 | 0.15 | 0.00 |
| xmxz-12       | 0.0124                     | 57.66 | 28.83 | 6.31 | 7.21 | 5.993 | 87.43 | 12.39 | 0.18 | 0.00 |

Note: V_1, V_2, V_3, V_4 are the volume of micropore, transition pore, mesopore, and macropore, respectively; S_1, S_2, S_3, S_4 are the specific surface area of micropore, transition pore, mesopore, and macropore, respectively.

Figure 12. The relationship between BET, clay minerals, and TOC.
BET: specific surface area; TOC: clay mineral content, illite content; I/S: mixed layer mineral content.
As the most direct factor affecting the adsorption capacity of shale, pore specific surface area is mainly affected by micropores and transition pores. Irrespective of Hongshuizhuang Formation or Xiamaling Formation, the contribution rate of micropore and transitional pores to the specific surface area of pores was over 99% (Table 9). In terms of pore distribution, the average volume of micropore and transition pore in Hongshuizhuang formation (59.13%) is much lower than that of Xiamaling formation (79.18%), which is also one of the important reasons for the difference in adsorption between the two layers.

The BET surface area of Hongshuizhuang Formation is mainly influenced by the content of organic matter, and there is no correlation with clay minerals (Figure 12(a)), indicating that the distribution of pore structure (especially micropore and transition pore) in the organic matter is the main factor controlling the adsorption, and the inorganic pore formed by the mineral has a weak influence on it. Although the linear relationship between BET surface area and clay minerals of Xiamaling Formation is relatively low, it presents a certain positive correlation using the envelope method (Figure 12(b)). There is no correlation between the BET specific surface area and TOC (Figure 12(b)). The above phenomena show that the small pores (such as intergranular pores of clay minerals) have a certain contribution to pore specific surface area. The BET surface area of Xiamaling Formation has a positive correlation with the content of I/S mixed layer mineral, but has a negative correlation with the content of illite (Figure 12(c)). The reason is that the average pore size of illite is larger than that of I/S mixed layer mineral (Ji et al., 2014). During the process of diagenesis, the pores are continuously compacted, which may result in the pores of illite being more easily compacted or filled, indicating that the adsorption capacity of Xiamaling Formation mainly depends on the content of the I/S mixed layer mineral.

**Conclusion**

The organic carbon content of the marine shale is relatively high in the Hongshuizhuang Formation and Xiamaling Formation of the Yanshan area, and is in the main stage of gas generation with late maturity to the highest maturity. The mineral composition of shale is dominated by quartz and clay minerals, of which, the clay minerals of Hongshuizhuang Formation are mainly illite, while the Xiamaling Formation is dominated by the I/S mixed layer mineral.

The pores and microfractures of shale are well developed. The pores are dominated by a cylindrical pore with two ends open, around the opening of parallel plate pore also contain a number of inkwell pore. The pore volume ratio of the shales in Xiamaling Formation is larger than that of Hongshuizhuang Formation within the aperture range of 2 nm to 10 nm, which shows that the Xiamaling Formation is more beneficial to the seepage. In the aperture range of larger than 50 nm, the average pore volume ratio of the Hongshuizhuang Formation is significantly higher than that of the Xiamaling Formation, which shows that the Hongshuizhuang Formation is more favorable to the seepage. More than half of the specific surface area of the two formations came from the pore size range of 2 nm to 10 nm, all of which had favorable pore conditions for adsorption.

The shale pore in the study area has significant fractal characteristics. The fractal dimension of adsorption pores is larger than that of seepage pores, which indicates that the adsorption pores have poorer connectivity and stronger heterogeneity. The pore fractal dimension of Xiamaling formation is affected by organic carbon content, clay mineral content, quartz minerals, and average pore size, while that of Hongshuizhuang...
Formation is affected by organic carbon content, quartz mineral, average pore size, BET specific surface area, and BJH pore volume. The study shows that the pores of the Hongshuizhuang Formation mainly consist of organic pores, while the pores of the Xiamaling Formation are not only organic pores but also smaller pores in clay minerals.

The middle Proterozoic shale reservoirs in Yanshan area have higher adsorbed gas content and larger resource potential. The adsorption capacity of Hongshuizhuang Formation mainly depends on the volume of organic pores in its micropores and transition pores. In addition, the adsorption capacity of Xiamaling Formation also is affected by I/S mixed layer mineral content in addition to the above factors.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The project was financially supported by the Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process of the Ministry of Education (China University of Mining and Technology) (No. 2018-005), the Fundamental Research Funds for the Central Universities (2015XKZD07), and National Science and Technology Major Project (2016ZX05041-001).

ORCID iD

Boyang Wang http://orcid.org/0000-0002-1487-8557

References

Bi H, Jiang ZX, Li P, et al. (2014) Adsorption characteristic and influence factors of Longmaxi shale in Southeastern Chongqing. Natural Gas Geoscience 25(2): 302–310 (in Chinese).
Cai YD (2015) Dynamic Evolution of Petrophysics of Coalbed Methane (CBM) Reservoir and its Impact on CBM Production. Beijing: China University of Geosciences (in Chinese).
Chalmers GRL and Bustin RM (2007) The organic matter distribution and methane capacity of the Lower Cretaceous strata of Northeastern British Columbia, Canada. International Journal of Coal Geology 70(1–3): 223–239.
Chalmers GRL and Bustin RM (2008) Lower Cretaceous gas shales in northeastern British Columbia, part II: Evaluation of regional potential gas resources. Bulletin of Canadian Petroleum Geology 56(1): 22–61.
Chen L, Jiang ZX, Ji WM, et al. (2016) Characteristics and significance of mineral compositions of the fifth member of Upper Triassic Xujiahe formation continental shale gas reservoir in Western Sichuan Depression. Bulletin of Mineralogy Petrology and Geochemistry 35(4): 750–755.
Chen P and Tang XY (2001) The research on the adsorption of nitrogen in low temperature and micro-pore properties in coal. Journal of China Coal Society 26(5): 552–556.
Chen SB, Zhu YM, Wang G, et al. (2012) Structure characteristics and accumulation significance of nanoporesin Longmaxi shale gas reservoir in the southern Sichuan Basin. Journal of China Coal Society 37(3): 438–444.
Curtis JB (2002) Fractured shale-gas systems. AAPG Bulletin 86(11): 1921–1938.
Hao F, Zou H and Lu YC (2013) Mechanisms of shale gas storage: Implications for shale gas exploration in China. AAPG Bulletin 97(8): 1325–1346.
Hao S, Gao YB, Zhang YC, et al. (1990) Petroleum Geology in Mesoproterozoic North China. Qingdao: Petroleum University Publishing House (in Chinese).

Hou YG, Sheng HE, Yi JZ, et al. (2014) Effect of pore structure on methane sorption capacity of shales. *Petroleum Exploration and Development* 41(2): 248–256.

Huang JL, Zou CN, Li JZ, et al. (2012) Shale gas generation and potential of the Lower Cambrian Qiongzhusi Formation in Southern Sichuan Basin, China. *Petroleum Exploration and Development* 39(1): 69–75.

Jarvie DM, Hill RJ, Ruble TE, et al. (2007) Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. *AAPG Bulletin* 91(4): 475–499.

Ji LM, Ma XX, Xia YQ, et al. (2014) Relationship between methane adsorption capacity of clay minerals and micropore volume. *Natural Gas Geoscience* 25(2): 141–152 (in Chinese).

Jiang Y, Song Y, Lin QI, et al. (2016) Fine lithofacies of China’s marine shale and its logging prediction: A case study of the Lower Silurian Longmaxi marine shale in Weiyuan area, southern Sichuan Basin, China. *Earth Science Frontiers* 23(1): 107–118.

Liu QJ, Ke BL, Lin HL, et al. (2014) Forming conditions and characteristics of the shale gas within the Mesoproterozoic Xiamaling Formation, Beijing Area. *Geological Science and Technology Information* 33(2): 92–97 (in Chinese).

Liu Y, Zhong NN, Tian YJ, et al. (2011) The oldest oil accumulation in China: Meso-proterozoic Xiamaling Formation bituminous sandstone reservoirs. *Petroleum Exploration and Development* 38(4): 503–512.

Loucks RG, Reed RM, Ruppel SC, et al. (2012) Spectrum of pore types and networks in mudrocks and a descriptive classification for matrix related mudrock pores. *AAPG Bulletin* 96(6): 1071–1098.

Pan J, Qu Y, Ma R, et al. (2013) Sedimentary and tectonic evolution of the Meso-Neoproterozoic strata in the northern margin of the North China Block. *Geological Journal of China Universities* 19(1): 109–122.

Ross DJK and Bustin RM (2007) Shale gas potential of the Lower Jurassic Gordondale Member, northeastern British Columbia, Canada. *Bulletin of Canadian Petroleum Geology* 55(1): 51–75.

Ross DJK and Bustin RM (2009) The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Marine and Petroleum Geology* 26(6): 916–927.

Sondergeld CH, Newsham KE, Comisky JT, et al. (2010) Petrophysical considerations in evaluating and producing shale gas resources. In: *SPE unconventional gas conference*, Pittsburgh, Pennsylvania, 23–25 February.

Schettler PD and Parmoly CR (1990) The measurement of gas desorption isotherms for Devonian shale. *GRI Devonian Gas Shale Technology Review* 7(1): 4–9.

Wang TG (1980) The primary property of Sinian Suberathem oil seepages and its petroleum geological significance in Yanshan Area. *Petroleum Exploration and Development* 7(2): 34–52 (in Chinese).

Wang TG and Han KY (2011) On Meso-Neoproterozoic primary petroleum resources. *Acta Petroleii Sinica* 32(1): 1–7 (in Chinese).

Wang YM, Wang SF, Dong DZ, et al. (2016) Lithofacies characterization of Longmaxi formation of the Lower Silurian, southern Sichuan. *Earth Science Frontiers* 23(1): 119–133.

Xie DL, Guo YH and Zhao DF (2014) Fractal characteristics of adsorption pore of shale based on low temperature nitrogen experiment. *Journal of China Coal Society* 39(12): 2466–2472.

Xie LJ, Sun YG, Yang ZW, et al. (2013) Evaluation of hydrocarbon generation of the Xiamaling Formation shale in Zhangjiakou and its significance to the petroleum geology in North China. *Science China Earth Sciences* 56(3): 444–452.

Yang F, Ning ZF, Wang Q, et al. (2014) Fractal characteristics of Nanopore in shales. *Natural Gas Geoscience* 25(4): 618–623 (in Chinese).
Yang Y (2013) Paleoceanographic Environment of the Mesoproterozoic Xiamaling Formation in the North China Platform: Evidence from Sedimentary Geochemistry. Beijing: China University of Geosciences.
Zhao DF, Guo YH, Xie DL, et al. (2014) Fractal characteristics of shale reservoir mu based on air adsorption. *Journal of Northeast Petroleum University* 38(6): 100–108 (in Chinese).
Zhao JZ, Wang R, Chuang ER, et al. (2016). Adsorption characteristics of Chang 7 shale from the Triassic Yanchang Formation in Ordos Basin, and its controlling factor. *Earth Science Frontiers* 25(2): 302–310 (in Chinese).
Zhong NN (2010) *Neo-Mesoproterozoic Thermal Evolution and Accumulation History of Hydrocarbon in Yanshan Area*. Beijing: Sinopec (in Chinese).
Zou CN, Dong DZ, Wang SJ, et al. (2010) Geological characteristics, formation mechanism and resource potential of shale gas in China. *Petroleum Exploration and Development* 37(6): 641–653.
Zou CN, Dong DZ, Wang YM, et al. (2015) Shale gas in China: Characteristics, challenges and prospects (II). *Petroleum Exploration and Development* 43(6): 753–767.