Controlling Factors of Organic nanopore Development: A Case Study on Marine Shale in the Middle and Upper Regions, South China

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Abstract: Upper Ordovician Wufeng - Lower Silurian Longmaxi and the Lower Cambrian Qiongzhusi shales are the major targets for shale gas exploration and development in China. Although the two organic-rich shales share similar distribution ranges and thicknesses, they exhibit substantially different exploration and development results. Nanopore structures of the shale reservoirs were analyzes in the paper. Pore development of 51 shale samples collected from various formations and locations was compared using the petromineralogical, geochemical, structural geological and reservoir geological methods. The results indicate that the reservoir space in these shales is dominated by organic pores and the total pore volume of micropores, mesopores, macropores in different tectonic areas and formations show different trends with the increase of TOC. The study found that organic pores of shale can be well preserved in areas with simple structure and suitable preservation conditions, and the shale with smaller maximum ancient burial depth and later hydrocarbon-generation-end-time is also more conducive to pore preservation. Organic pore evolution models are established, and they are as follows: ① Organic matter pore development stage, ② Early stage of organic matter pore destruction, and ③ late stage of organic matter pore destruction. The areas conducive to pore development are favorable for shale gas development. Research results can effectively guide the optimization and evaluation of favorable areas of shale gas.

Keywords: Mid-upper Yangtze regions; marine shale; Organic matter pores; controlling factors; pore evolution

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1 Introduction

There are two sets of marine organic-rich shale in Southern China, the Upper Ordovician Wufeng Formation-Lower Silurian Longmaxi Formation and the shale of Lower Cambrian Qiongzhusi Formation or its equivalent (Niutitang/Shuijingtuo Formations) (Zou Caineng et al., 2010; Hu Lin et al., 2012; Huang Jinliang et al., 2012; Zou Caineng et al., 2014; Liang Xing et al., 2015; Zou Caineng et al., 2016). Industrial gas flow was obtained from the Wufeng Formation-Longmaxi Formation shale in the Sichuan Basin and its surrounding areas. There are differences in shale gas production in various regions, and commercial shale gas flow was only achieved in the Jiaoshiba, Changning and Weiyuan blocks (Guo Tonglou et al., 2014; Liang Feng et al., 2016; Zou Caineng et al., 2016). The Qiongzhusi organic-rich shale has a similar gas-bearing area, thickness and TOC as Wufeng–Longmaxi shale (Zhao Wenzhi et al., 2016), but the shale gas production is inferior to Wufeng-Longmaxi Formation shale. According to incomplete statistics, there are no less than 40 shale gas drillings whose target interval is Qiongzhusi Formation in the mid-upper Yangtze region. Only four wells in Weiyuan-Qianwei block in the Sichuan Basin and two wells (Yangye 1 and Yiye 1) in western Hubei have obtained industrial gas flow (Dong Dazhong et al., 2016; Zhao Wenzhi et al., 2016). It is not yet clear why shale gas production varies by areas or strata. This paper attempts to analyze those differences from the nanopore structure of the shale reservoir.

Previous studies have shown that the degree of pore development of shale varies with maturity (Jop Klaver et al., 2015; Maxwell Pommer and Kitty Milliken, 2015). In view of the highly mature marine shale in southern China, some research clarifies the developmental characteristics of the shale pores of the Qiongzhusi Formation and the Wufeng-Longmaxi Formation (Ran Bo et al., 2016, Yang Feng et al., 2016, Yang Feng et al., 2016, Chen Qian et al., 2016; Chen Lei et al., 2017; Hou Yuguang et al., 2017; Hu Haiyan et al., 2017; Tong Shaoqing et al., 2017; Wang Yang et al., 2017; Yang Rui et al., 2017; Zhang Yuying et al., 2018; Zhou Shangwen et al.; 2018), and preliminarily clarified that tectonic movement and compressive stress have a destructive effect on nanopores in shale (Yang Rui et al., 2016, Liang Mingliang et al., 2017; Cui Huiying et al., 2018; Zhu Hongjian et al., 2018). This paper screens the organic-rich shale samples from various locations and different strata (Wufeng Formation-Longmaxi Formation and Qiongzhusi Formation) in middle and upper Yangtze regions, and systematically analyzes the pore characteristics of the shale to explain the differences in productivity.

2 Geological Setting

Marine shale is widely distributed in the middle and upper Yangtze regions, which is located in the Sichuan basin and surrounding areas of Southwest China (Zhao Wenzhi et al., 2016; Zou Caineng et al., 2016; Liu Zhongbao et al., 2017; Ma Xinhua et al., 2018). The Wufeng Formation-Longmaxi Formation shale is a black organic-rich graptolite shale deposited in the deep-water continental shelf. The Wufeng Formation generally has a thickness of 3–5 m, generally not more than 10 m (Chen Xu et al., 2015) and, while the Longmaxi Formation shale (rich in gas content) ranges from 20–50 m (Zou Caineng et al., 2016). The Wufeng-Longmaxi Formation is considered to be one of the most favorable prospective shale gas plays in China. The shale of the Qiongzhusi Formation a thick widely distributed deep-water continental shelf deposit with an abundance of organic matter. It is one of the most important layers for Shale gas exploration and development in southern China (Liu Zhongbao et al., 2017). The middle and upper Yangtze regions have experienced Caledonian, Hercynian, Indosinian, Yanshanian and Himalayan tectonic cycles since the two shale deposits formed and resulted in the current tectonic pattern (Figure 1).

3 Samples and methods

3.1 Position and characteristic of the samples

The samples are mainly collected from core and outcrop profiles in different tectonic areas and formations in the middle and upper Yangtze regions. The basic properties of samples are shown in Table 1. The position of the
profiles and the drilling are shown in Fig. 1. Fifty-one samples were collected in this study, including 15 shale samples from the Qiongzhusi Formation, located within 30 m of the bottom of the Qiongzhusi Formation, and 36 shale samples from the Wufeng-Longmaxi Formation, located within 10 m of the bottom of the Wufeng Formation.

3.2 Analytical method

Fig. 1 Geological structure of the middle and upper Yangtze regions and the sample location map

Table 1 Basic characteristics of the sample

<table>
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<tr>
<th>NO.</th>
<th>Sample ID</th>
<th>Well or section</th>
<th>Formation</th>
<th>TOC (%)</th>
<th>Quartz (%)</th>
<th>K-Feldspar (%)</th>
<th>Plagioclase (%)</th>
<th>Calcite (%)</th>
<th>Dolomite (%)</th>
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In this paper, the pore characteristics of shale are analyzed by nitrogen adsorption-desorption and field emission scanning electron microscopy (FESEM). The nitrogen adsorption-desorption method enables an analysis of pore size distribution for pores less than 200 nm, which enables a macroscopic understanding of the distribution range of pore size for the whole sample and a preliminary understanding of the morphological characteristics of pores. The FESEM method provides an opportunity to determine the type of pores in different mineral and organic matter in shale through imaging. However, a relatively small portion of each samples can be imaged because of the limited field of vision.

**Nitrogen adsorption method:** A 2—3g was selected and dried at 110 °C for five hours to remove water and volatile impurities in the sample. The sample was placed in the instrument and vacuumed at 120 °C for three hours, and then the sample was backfilled with N₂. The corresponding pore size distribution is obtained by the adsorption and desorption isotherms obtained under various conditions. With data of P/P₀ < 0.3, the universal BET method is used to compute the specific surface area of samples. The Barrett-Joyner-Halenda (BJH) model is used to compute the adsorption isotherm for determining the distribution of pore size and pore volume of samples, and the Faas method provides a tool for correction.

**FIB-SEM:** FIB-SEM can directly observe the size, shape and distribution of nano pores of the shale. However, this method can only provide pore structure and characteristics for a limited field of view. Shale samples of about 1 cm² were polished to create a level surface using dry emery paper and then milled by argon-ion. After polishing, the samples should be coated with carbon to provide a conductive surface layer. Each sample was inserted into an FEI Helios NanoLab 650 DualBeam FIB-SEM for imaging. The SEM images the newly milled shale surface in situ with a resolution of 2.5 nm at 2 kV accelerating voltage and a working distance of 4 mm.

### 4 Results

#### 4.1 Result of nitrogen adsorption-desorption test

The BET specific surface area (hereinafter referred to as "specific surface area") was between 4.86 and
29.3811 m²/g and the total pore volume of BJH (hereinafter referred to as "total pore volume") was between 0.0134 and 0.0360 ml/g. The average pore size is between 6.98 and 14.34 nm. The adsorption and desorption curves of shale have the characteristics of H2 and H3 hysteresis loop in the IUPAC standard classification (Rouquerol F et al., 1999; De Boer J H et al., 1958). The adsorption and desorption curve morphology of representative samples in different regions is shown in Fig. 2. The results show that most of the nanopores are well-connected parallel-plate pores with four sides open, and there are some ink bottle-like pores.

4.2 Pore development characteristics and controlling factors

Total pore volume and specific surface area of two sets of marine shale are positively correlated with TOC, and $R^2$ values are found to be 0.32 and 0.56, respectively (Fig. 3a, b), which are consistent with the previous result (Chen Lei et al., 2017). There are some differences in sedimentary and tectonic settings between different strata and areas, resulting in a low correlation coefficient. $R^2$ is higher in the same Formation and area, for example, the $R^2$ for total pore volume versus TOC, the specific surface area versus TOC of the Changde area are 0.835 and 0.996, respectively (Fig. 3c), indicating that organic matter provides the main total pore volume and specific surface area. The correlation and $R^2$ between the total volume and TOC, the specific surface area and TOC of different blocks are shown in Table 2. In general, the total pore volume and specific surface area are primarily controlled by TOC. So, a low correlation coefficient indicates that TOC has little influence on the total pore volume and specific surfaces area. However, it is worth noting that the Total Pore Volume of the shale samples in Chengkou decreased with the increase of TOC (Fig. 3d), which was significantly different from other areas.

Table 2 Correlations between TOC and total pore volume and specific surface area of various strata and blocks

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<tr>
<th>Block</th>
<th>Wuxi 2</th>
<th>Yanjin 1</th>
<th>Yanjin 1</th>
<th>Changde 1</th>
<th>Longshan 1</th>
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4.3 Characteristics of shale pore development in different tectonic areas

As there are some differences in the pore variation rules of different pore sizes, the pores are divided into three types, namely micropores (<10 nm), mesopores (10–20 nm) and macropores (>20 nm). Measurements indicate that the total pore volume and specific surface area of shale are mainly controlled by TOC. The following focuses on the systematic analysis of the relationship between the Total Pore Volume and TOC of different pore sizes in shale.

4.3.1 Longmaxi Formation

The total pore volume of micropores, mesopores and all pores is positively correlated with TOC and the pore development degree ranking from good to bad is Qianjiang, Changning, Yanjin and Wuxi (Fig. 4 a–c). The relationship between the total pore volume of macropores and TOC showed a different trend. The total pore volume of macropores in Qianjiang 1 well increased with the increase of TOC. The total pore volume of the macropores in Yanjin 1 well increased at low TOC and then decreased at high TOC. If two points with high TOC (>5%) were removed, then there was a positive correlation ($R^2=0.36$). The total pore volume of macropores in Wuxi 2 well slightly increased with the increase of TOC, and the trend of total pore volume increasing with TOC is inferior to wells of Qianjiang 1 and Yanjin 1 (Fig. 4d).
4.3.2 Qiongzhusi Formation

As the TOC increases, the total pore volume of different pore sizes of the Qiongzhusi shale samples show different trend. The pore development of the shale samples in Longshan 1 and Changde 1 wells is significantly better than that in Chengkou samples. There is a positive correlation between TOC and total pore volume of all pores in Longshan 1 samples, while there is negatively correlated with total pore volume of all pores in Chengkou samples (Fig. 5a). The total pore volume of macropores decreases in Changde 1 with the increase of TOC and the total pore volume of micropores and mesopores increases with the increase of TOC (Fig. 5b, c, d).
4.3.3 Summary

Through the analysis above, the total pore volume of micropores, mesopores, macropores and all pores of the shale in various regions and formation show different trends with the increase of TOC which are summarized as follows:

① Total Pore Volume of micropore, mesopores, macropores and all pores increased with the increase of TOC (Qianjiang 1 well);
② Total pore volume of micropores, mesopores and all pores increased with the increase of TOC, and the macropore volume increased first and then decreased with the increase of TOC (Yanjin 1 well).
③ Total pore volume of micropores, mesopores and all pores increased with the increase of TOC, and the Total Pore Volume of macropores decreased with the increase of TOC (Changde 1 well);
④ The total pore volume of micropores, mesopores, macropores and all pores decreased with the increase of TOC (Chengkou section).

According to the pore development of the shale from good to bad, the order is as follows: ① > ② > ③ > ④.

5 Discussion

The study on the evolution of organic pores in shale shows that after the shale reaches maturity and over-mature evolution stage (Ro>1.2%), the pores in organic matter in the shale show an increasing trend with the increase of maturity (Jop Klaver et al., 2015; Tang Xuan et al., 2015). Two sets of marine shale in the middle and upper Yangtze region of China are currently in a mature to over-mature stage, and Ro is generally greater than 2.0% (Li Yuxi et al., 2009; Hu Lin et al., 2012; Liang Feng et al., 2015). The total pore volume in the organic matter of shale should increase with the increase of TOC. However, as the TOC increases, the total pore volume of various pore sizes in the marine sample differ depending on formation and tectonic background.

5.1 Pore size and organic matter content

The larger the pores in the shale, the easier it is to be destroyed by external forces (Yang Yongming et al., 2009). Because of the deterioration of organic pores in shale, the total pore volume of macropores in shale is inversely related to TOC, indicating that the larger the pore size in shale, the more unfavorable for pore preservation. In addition, when the organic matter content in the rock exceeds a certain value, the rock mineral skeleton is more likely to be destroyed by formation pressure or structural stress, which is not conducive to the preservation of organic pores (Jop Klaver et al., 2015; Rudnicki M, 2013; Wang Feiyu et al., 2013). For example, the Weight percentage of organic matter in the high TOC shale samples of Yanjin 1 well is 8% and 8.9%, and its volume percentages are 16.9% and 17.4% (organic density is estimated at 1.2 g/cm³ and rock skeleton density is estimated at 2.8 g/cm³). Excessive volume of organic matter (low compressive strength) reduces the support...
capacity of the mineral skeleton in the shale, causing the high TOC shale skeleton structure to be compressed or damaged first under the same confining pressure conditions (Changde 1 well and Chengkou section). The larger the pore size in organic matter, the higher the organic matter content of the shale, the more unfavorable the preservation of the pores.

5.2 Maximum ancient buried depth

The maximum ancient burial depth of the Qiongzhusi Formation in the Chengkou area of the South Daba Mountain fold belt is more than 11,000 m, and the maximum ancient burial depth of the Wufeng-Longmaxi Formation in the Wuxi area is over 9,000 m. The maximum ancient burial depths of the Qiongzhusi Formation and the Wufeng-Longmaxi Formation in the southern Sichuan area are relatively small (8000 and 6000m) (Fig. 6) (Liu Shugen et al., 2014), and the shale pore development in southern Sichuan is significantly better than that in the southern Daba Mountains in northeastern Sichuan (Figs. 4 and 5). The ancient burial depth is too large resulting in excessive overburden pressure of the reservoir, which is not conducive to the preservation of pores in shale.

![Fig. 6 Maximum ancient buried depth map of the bottom of the Longmaxi Formation and the Qiongzhusi Formation](image)

The total pore volume of the Longmaxi Formation shale in the Well Qianjiang 1 well located in the west of the Hunan-Hubei trough-like structural belt is substantially higher than that in Qiongzhusi Formation Shale of Longshan 1 Well (Fig. 7a). The total pore volume of the Longmaxi shale sample in the Wuxi 2 well in the South Daba Mountain fault belt is significantly higher than that in the Qiongzhusi shale sample in Chengkou Section (Fig. 7b). Scanning Electron Microscopy observations also show that the pores in the organic matter in the Longmaxi Formation shale of Wells Qianjiang 1 and Wuxi 2 are more suitable for gas development than the pores of Longshan 1 and Chengkou (Fig. 8). Excessively large buried depth is not conducive to the preservation of shale pores, which is one of the reasons why shale pores are less developed in the Qiongzhusi Formation than that in the Wufeng-Longmaxi Formation.
a. Correlation between Total Pore Volume and TOC of well Longshan1 and Qianjiang 1

b. Correlation between Total Pore Volume and TOC of Wuxi 2 well and Chengkou section

Fig. 7 Relationship between total pore volume and TOC of different strata shale under similar structural background conditions

a. SEM photograph of Qianjing 1 well (SE, 50000×) (Longamxi Formation)

b. SEM photograph of Wuxi 2 well (SE, 25000×) (Longamxi Formation)
5.3 Tectonic conditions

Shale samples from the same formation have different pore development in different tectonic areas. Pore development in a simple structure is better than that in a complex structure. For example, the size and number of organic pores in the shale of Wells Qianjiang 1 and N201 in the simple structure (Fig. 9a) are better than those in the Wuxi 2 well (Fig. 9b) in the complex structure (Fig. 10a,b,c). The pore development (Fig. 10d and e) of the shale samples in the Longshan 1 well and the Changde 1 well in simple structure is better than that in the Chengkou county located in the strongly structural compression zone (Fig. 10f). The section and drilling location is shown in Figure 9b, c, d. Pore development of N201 well located in a simple structural area is substantially better than that of Yanjin 1 well in the fault development area (Fig. 9a, 4a). The results of the nitrogen adsorption desorption experiment also support the above conclusions.
The results of this study indicate that, the degree of pore development in the shale in a simple structural area is better than that in the structurally complex area even with similar degrees thermal evolution and ancient burial depth. The main reasons are as follows: ① Strong structural compression produces large compressive stress on the shale reservoir, causing the pores to be compressed or destroyed; ② Reduced internal pressure of the pore caused by poor preservation conditions in complex structure area makes shale pores more susceptible to compression or destruction.
5.4 Pore evolution model

The pore evolution of marine shale in the Middle and Upper Yangtze region can be divided into three stages, 

① Organic matter pore development stage (Fig. 11a), during which the total pore volume of all sizes of the pores are positively correlated with TOC. The shale mineral skeleton has not been destroyed, and the pore development is good. For example, the shale in Changning and Qianjiang areas is at this stage. 

② Early stage of organic matter pore destruction (Fig. 11b). Large pores, especially large pores in shale with higher organic carbon content, are first compressed or destroyed. Shale samples of Changde 1 and Yanjin 1 well are at this stage. 

③ Late stage of organic matter pore destruction (Fig. 11c). The Total pore volume of all sizes of the shale are negatively correlated with TOC. At this stage, the skeleton of the shale has been seriously damaged, like the shale samples of Chengkou section. Smaller pores will be further compressed and destroyed until the pores are completely destroyed. So it is inferred that external stress results in a decrease in gas pressure for the shale pores.
6 Conclusions

The nanopores of marine shale in middle and upper Yangtze regions are mostly well-connected parallel-plate pores with four sides open. The total pore volume and specific surface area are mainly controlled by TOC, and the organic pores provide the main storage space for free gas and adsorbed gas.

The total pore volume of micropores, mesopores, macropores and all pores in different tectonic areas and formations showed different trends with the increase of TOC. Quality of pore development, suitability for gas storage, from good to bad is N201, Qianjing 1, Yanjin 1, Wuxi 2, Longshan 1, Changde 1 and Chengkou.

The controlling factors of the organic pore development are clarified, and the organic pore evolution model of marine shale in middle and upper Yangtze region is established. The organic pore size, organic matter content, maximum ancient burial depth of the shale, regional tectonic conditions, and hydrocarbon generation end time will affect the shale pore development. The areas with simple structure, smaller maximum ancient buried depth, and later hydrocarbon generation end time are conducive to the preservation of organic pores and are a favorable area for pore development.

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