The characteristics and developmental control factors of microscopic pore structure in shale gas reservoirs in the Lower Cambrian Qiongzhusi Formation

Wei Yang1*, Yuanyuan Qin1, Tingshan Zhang2
1 School of Resources and Environmental Engineering, Guizhou Institute of Technology, Guiyang, Guizhou Province, 550003, China
2 School of Geoscience and Technology, Southwest Petroleum University, Chengdu, Sichuan Province, 610500, China
*Corresponding author’s e-mail: rexswpu@163.com

Abstract. The Early Cambrian Qiongzhusi Formation on the southern margin of the Sichuan Basin (Southern China) has experienced a long geological process. High degree of thermal evolution of the organic matter shows a great impact on the organic evolution, reservoir microscopic pore types and structure characteristics in this formation. In this study, we investigate the major types and structural features of microscopic pores in shale gas reservoirs of the Qiongzhusi FM. Different types of matrix pores are found, over-mature shale gas reservoirs in the Qiongzhusi FM. mainly have well-developed micropores, but their average specific surface area (SSA) and pore volume are smaller than those in the Longmaxi Formation. The degree of thermal evolution poses the greatest impact on microscopic pore structure, which is significantly positively correlated with SSA and pore volume; however, when exceeding this range, SSA and pore volume both drastically decrease with increasing degree of thermal evolution. Compared with those in the Longmaxi FM., microscopic pores of shale gas reservoirs in the Qiongzhusi FM. feature pore- SSA and large surface porosity. The better the development of micropores, the larger the SSA and Vp of shales, which are more conducive to shale gas adsorption and accumulation.

1. Introduction
China has widely distributed organic-rich shales. Marine shales commonly present in South China, North China, and the Tarim Basin. These vast regions have excellent conditions for shale gas accumulation and show great resource potential.

In recent years, Chinese scholars have investigated shale gas occurrence, accumulation mechanisms and conditions, and reservoir formation[1-4]. However, few studies have investigated the microscopic characteristics and developmental mechanisms of shale gas reservoir spaces, or the control mechanism of microscopic reservoir spaces over shale gas occurrence.

Over the last decades, international studies have employed a variety of advanced techniques to study the microstructure of shales, achieving substantial innovative achievements and understanding. These techniques mainly include scanning electron microscopy (SEM), X-ray imaging, transmission electron microscopy, atomic force microscopy (AFM), confocal laser scanning electron microscope, nuclear magnetic resonance, argon ion polishing plus environmental SEM (ESEM), specific surface area (SSA) measurement, and backscattered electron imaging[5-6].
Different types of reservoir space and microstructures of reservoir formation contribute to shale gas reserves and production capacity to varying degrees. Therefore, research on microscopic reservoir space types, control mechanisms, gas accumulation mechanisms, and microstructure characteristics will help: (a) to innovate the geological theory of shale gas reservoirs, and to clarify the nature of Early Paleozoic marine shale gas reservoirs from the perspectives of mineral composition, diagenetic process, and microstructure characteristics; and (b) to provide theoretical support for the development of specialized engineering technologies required for shale gas exploration, such as staged fracturing of horizontal wells.

In this study, we focus on black shales from the Lower Cambrian Qiongzhusi FM. on the southern margin of the Sichuan Basin. Their microscopic reservoir characteristics and developmental control factors are investigated using a combination of electron microscopy and laboratory analysis.

2. Regional geological setting
The study site is located in an area of intersection among three provinces, i.e., Yunnan (Zhaotong), Guizhou (Bijie - Hezhang), and Sichuan (Yibin - Gulin). The geotectonic unit belongs to the North Yunnan-Guizhou Depression on the southwestern margin of the tectonic domain of Yangtze Block, while its main body lies in the central west of the Weixin Sag (Figure 1). In this region, Cambrian strata are basically comprised of a set of completely developed, continuously deposited marine sequences, except that the Maidiping FM. is missing in some areas. From bottom to top, the Lower Cambrian strata can be divided into Maidiping, Qiongzhusi, Mingxinsi, Jindingshan and Qingxutong FM.[7].

![Diagram](image)

Figure 1. The geological structure position of study area

The Qiongzhusi FM. is also known as the Niutitang FM. in the northern Guizhou region. This formation mainly develops gray-black and dark shales. It can be divided into two segments along the direction of the hammer: the lower segment is mainly comprised of gray-black and black shales, with siliceous shales seen at the bottom; and the upper segment has a significantly lighter color with increased calcareous and silty contents, mainly comprised of gray and dark-gray shales. The Qiongzhusi FM. is generally in disconformity with the underlying Sinian Dengying FM. and in conformity with the overlying Mingxinsi FM.

3. Methodology
Outcrop and drill-core specimens were collected from the lower black shale segment of the Qiongzhusi and Longmaxi FM. in the study area. Because of their small average pore size at the nano-scale, the pore volume (Vp) and pore structure of shales cannot be fully described with ordinary
techniques. It seems that there is no effective method to directly observe and quantitatively measure the microscopic pore structure and porosity of shales. Practice in recent years has proved that SEM can be an effective tool for observation and measurement of the microstructure of shales[6][8-9].

In this study, polarized light microscopy was used to preliminarily examine more than 200 specimens of Early Paleozoic drill-cores and outcrops. For comprehensive analysis, 21 appropriate specimens were selected by consideration of lithological characteristics, rock structure, mineral type, and high TOC content (qualitative). First, the selected specimens were subjected to precision polishing and examined by ESEM analysis to identify various types of microscopic pores. Then, microscopic pores on ESEM and AFM images were quantitatively analyzed using the geographic information system (ArcGIS for data analysis and spatial statistical analysis). The surface porosity of microscopic pores in shales from the Qiongzhusi FM. was determined, and the quantity and size of pores were compared between different formations.

Additionally, SSA measurement is performed in a liquid nitrogen (N2) bath at cryogenic temperatures. The shale is injected with liquid N2 to saturation, followed by desorption at room temperature. Since the adsorption capacity is closely linked to pore development in the shale, the amount of N2 desorption can be used to measure SSA. This method can also be used to calculate Vp and pore size distribution, as well as to study pore structure[10].

The use of ESEM and AFM allows for direct observation of micron- and nano-scale pores, whereas SSA measurement quantitatively determines nano- and micronano-scale pores in the specimens. Combining the two complementary methods can directly reflect pore structure characteristics of shale gas reservoirs.

Combined with the above analysis, the developmental control factors of microscopic pores in shales of the Qiongzhusi FM. were identified on the basis of X-ray diffraction, TOC content, vitrinite reflectance, and kerogen type analysis of different shale formations.

4. Microscopic pore structure characteristics

4.1. Microscopic pore types

The shale can serve as a source rock as well as a reservoir. The internal structure of shales is riddled with a large number of different types of microscopic pores. These pores vary in shape and size, which play an important role in controlling oil and gas accumulation. According to the IUPAC classification scheme[11], microscopic pores in shales from the Qiongzhusi FM. in the study area can be divided into four size classes: micropore (<10 nm), pore (10~100 nm), and mesopore (100~1000 nm), and macropore (> 1000 nm). With respect to their genesis, the matrix pores can be divided into: mineral interlayer micropore, organic matter pore, intercrystalline pore, mineral mold pore, and secondary dissolution pore (Figure 2). These pores represent different pore structure of genetic types and sizes. Among these, micropores make the greatest contribution to the reservoir space of shale gas, whereas pores and macropores are probably the major spaces for capillary condensation - diffusion and seepage - laminar flows in shales, respectively.
4.2. SSA and Vp characteristics

In this study, we performed SSA and Vp measurements on shale specimens from the Qiongzhusi FM. (pore size test range 1.5~300 nm). Shale gas reservoirs in the Qiongzhusi FM. have the SSA of 1.915~7.691 m²/g, with an average area of 5.185 m²/g; Vp of 0.0051~0.0108 mL/g, with an average volume of 0.0080 mL/g; and average pore size of 5.38~10.85 nm. The shales have relatively large SSA and Vp, which are conducive to shale gas adsorption.

There exists a strong positive correlation between pore-SSA and Vp. That is, as the SSA increases, the Vp increases correspondingly (Figure 3a-b). In contrast, SSA and Vp are negatively correlated with average pore size. That is, SSA and Vp decrease with increasing pore size (Figure 3c-d). When pore size <10 nm, the Vp distribution curve appears very steep; and when pore size ≥10 nm, the curve gradually becomes flat. These results indicate that pores of the size 1–8 nm make the greatest contribution to the SSA and Vp of shales (Figure 3e). In other words, the better the development of pores, the larger the SSA and Vp of shales, which are more favorable for shale gas adsorption and accumulation.

In addition, shale specimens from the Qiongzhusi FM. exhibit similar characteristics in the cryogenic liquid N₂ adsorption and desorption curves. The major characteristics are: (1) The adsorption curve is below the desorption curve, both of which show a slowly rising trend with increasing relative pressure; (2) At a relative pressure close to 1, the adsorption and desorption curves rise in a higher speed; (3) The adsorption loop curve shows up at a relative pressure in the range of 0.4~1.0; and (4) At a relative pressure close to 0.5, there is a significant inflection point on the desorption curve, which causes a nearly steep decrease (Figure 3f).
4.3. Quantitative statistical analysis of microscopic pores
Cryogenic liquid N\textsubscript{2} adsorption test can be used for quantitative statistical analysis of selected microscopic pores (size 1.5~300 nm) in shales. However, quantification of microscopic pores larger than 300 nm requires the aid of other means, propose that the number, area, and surface porosity of microscopic pores can be calculated by combining ESEM and AFM with the aid of statistical tools in ArcGIS. In the present study, AFM and ESEM image processing and analysis were performed on representative polished shale specimens from the Qiongzhusi FM. Image data were loaded into the ArcGIS platform for raster reclassification. The white area is the distribution area of pores or fissures (Figure 4d-e). In this way, the number and surface porosity of microscopic pores in different specimens were obtained (Table 1).
Table 1. Results of Microscopic pore quantitative analysis

| sample No. | QZS 1 | QZS 2 | LMX 1 | LMX 2 | LMX 3 |
|------------|-------|-------|-------|-------|-------|
| Formation  | Qiongzhusi | Qiongzhusi | Longmaxi | Longmaxi | Longmaxi |
| total pore No. | 254 | 194 | 34 | 160 | 275 |
| avg. pore size (nm²) | 4016 | 5583 | 11692 | 19659 | 13380 |
| min. interstitial surface area (nm²) | 172 | 167 | 161 | 1024 | 1080 |
| max. interstitial surface area (nm²) | 122069 | 119620 | 151744 | 497888 | 368160 |
| total interstitial surface area (µm²) | 1.02 | 1.083 | 0.398 | 3.145 | 3.679 |
| area pore rate (%) | 4.575 | 4.582 | 1.824 | 2.257 | 2.641 |
| scan area (µm²) | 22.295 | 22.295 | 22.295 | 22.295 | 22.295 |

Compared with the Longmaxi FM., the Qiongzhusi FM. is characterized by large pore number, pore size and single-pore area, and high surface porosity. AFM cross-sectional profiles clearly show the presence of nanoscale pores between regularly arranged raster grids, which are characterized by a tightly arranged zigzag structure (Figure 4a-c). This regular, light/dark alternating, grid-like surface morphology is possibly resulted from the tight arrangement of kerogen macromolecules in the shale.

5. Development control factors of microscopic pores

The development and evolution of microscopic pores within shale are a complex process controlled by multi-factors rather than a single factor. TOC content, kerogen type, clay mineral type and content, and thermal evolution degree jointly control the development of microscopic pores in shale to varying levels. A comparative study of multiple analyses shows that the above factors are closely related to the
development and evolution of microscopic pores in shales from the Qiongzhusi FM. in the over-mature zone of northern Yunnan-Guizhou region.

5.1. TOC content
The degree of microscopic pore development in shale is closely related to the TOC content. In organic-rich shales, SSA and Vp are relatively large, whereas the average pore size is generally smaller than that of inorganic clay[12]. For shale specimens from the Qiongzhusi FM. with similar properties (thermal evolution degree and clay mineral type and content), those with higher TOC content have larger SSA and Vp (Table 2); and SSA and Vp are strongly positively correlated with TOC content (Figure 5g-h). These results indicate that when the other factors are under similar conditions, TOC content is the primary factor affecting the SSA and Vp of shales.

Table 2. Trast table of microscopic pore development comprehensive factors Qiongzhusi and Longmaxi FM. shale

| Formation          | Sample No. | TOC (%) | RO (%) | Content of clay minerals (%) | Kerogen type | BET specific surface (m²/g) | BJH total pore volume (ml/g) | Avg. pore diameter (nm) |
|--------------------|------------|---------|--------|-----------------------------|--------------|-----------------------------|-----------------------------|-------------------------|
| Qiongzhusi Formation | QZS 1      | 0.81    | 3.89   | 19                          | I            | 2.548                       | 0.0064                      | 10.24                   |
|                    | QZS 2      | 0.82    | 4.12   | 20                          | I            | 1.915                       | 0.0051                      | 10.85                   |
|                    | QZS 3      | 1.86    | 4.03   | 26                          | I            | 5.225                       | 0.0086                      | 6.80                    |
|                    | QZS 4      | 1.13    | 4.06   | 30                          | I            | 4.414                       | 0.0073                      | 6.79                    |
|                    | QZS 5      | 1.66    | 4.14   | 30                          | I            | 6.929                       | 0.0098                      | 5.95                    |
|                    | QZS 6      | 1.72    | 4.06   | 27                          | I            | 7.691                       | 0.0081                      | 5.38                    |
|                    | QZS 7      | 2.13    | 4.22   | 32                          | I            | 7.571                       | 0.0108                      | 5.89                    |
| Longmaxi Formation | LMX 1      | 1.21    | 2.56   | 43                          | I            | 12.598                      | 0.0181                      | 5.87                    |
|                    | LMX 2      | 1.08    | 3.75   | 16                          | I            | 8.691                       | 0.0110                      | 5.41                    |
|                    | LMX 3      | 1.02    | 2.64   | 52                          | I            | 9.363                       | 0.0133                      | 5.97                    |
|                    | LMX 4      | 1.66    | 2.78   | 40                          | I            | 15.869                      | 0.0186                      | 5.07                    |
|                    | LMX 5      | 2.26    | 2.93   | 49                          | I            | 20.357                      | 0.0220                      | 4.62                    |
|                    | LMX 6      | 2.41    | 2.99   | 55                          | I            | 20.463                      | 0.0216                      | 4.60                    |
|                    | LMX 7      | 2.46    | 3.21   | 20                          | I            | 14.225                      | 0.0164                      | 5.06                    |

5.2. Clay mineral type and content
The SSA and Vp of shales are closely related to clay minerals. Different types of clay minerals have varying SSAs. For example, among the three kinds of clay minerals chlorite, illite, and montmorillonite, SSA is largest for montmorillonite (up to 800 ml/g) but significantly smaller for illite and chlorite (as low as 30 and 15 ml/g, respectively)[13]. Thus, there exist differences in the SSA and Vp of various types of clay mineral combinations.

Compared with the Longmaxi FM., the Qiongzhusi FM. is characterized by decreased contents of montmorillonite and illite (with larger SSA), but increased contents of kaolinite and chlorite (with smaller SSA). Thus, shale specimens from the Longmaxi FM. have significantly larger SSA and Vp than those from the Qiongzhusi FM. This result indicates that clay mineral type and content to some extent affect the SSA and Vp of shales.

5.3. Thermal evolution degree
The relationship between microscopic pore structure and thermal evolutionary degree of shale is more complex, which is not a simple positive or negative correlation. This is because thermal evolution will
not only cause pore structure changes in organic matter, but also induce transformation of clay minerals. These mechanisms lead to variations in SSA of interlayer micropores in clay minerals, thus changing the SSA and Vp of shales.

(1) Effects of thermal evolution degree on organic matter pore structure

The analysis of overmature shale specimens from the Qiongzhusi FM. shows that when TOC content occurs at similar levels within a certain range, SSA and Vp both increase with elevating the degree of thermal evolution (Ro) of organic matter (Figure 4). It is possible that the degree of thermal evolution has a decisive role in the development of organic matter pores. During organic matter pyrolysis and hydrocarbon generation, as the degree of thermal evolution increases, the structure of organic matter pores change while the numbers of pores and micropores increase, thereby increasing the SSA and Vp of organic matter pores[8]. Ultimately, the SSA and Vp of shale reservoirs are greatly increased.

(2) Effect of thermal evolutionary degree on interlayer micropores in clay minerals

The degree of thermal evolution not only affects the development of organic matter pores but also plays a significant role in the development of interlayer micropores in clay minerals. It mainly affects the type and content of clay minerals, further posing an effect on interlayer micropores in clay minerals. Generally, with increasing Ro, montmorillonite with larger SSA is decreased and successively transformed to interlayer minerals; the interlayer minerals are then gradually decreased, until eventually transformed to illite or chlorite. In this process, the SSA and Vp of interlayer pores in clay minerals are significantly reduced[9][13].

Figure 5 depicts the relationship between clay mineral content and Ro. When Ro <3.0%, with increasing Ro, the contents of illite and interstratified illite-montmorillonite with larger SSA increase, while those of chlorite and kaolinite with smaller SSA decrease; when Ro >3.0%, with increasing Ro, the contents of different clay minerals show opposite variation trends (Figure 4). The degree of thermal evolution in shale specimens from the Qiongzhusi FM. is above 3.0%, while that in the Longmaxi FM. is mostly below 3.0%. The SSA and Vp of interlayer micropores in clay minerals of the Qiongzhusi FM. are both significantly smaller than those of the Longmaxi FM., accounting for the smaller SSA and Vp of the shale specimens (Table 2). Therefore, the degree of thermal evolution controls the development of interlayer micropores in clay minerals through affecting the type and content of clay minerals.
TOC content, clay mineral type and content, kerogen type, and thermal evolution degree jointly control the development of microscopic pores in the shale to varying levels. In the study area, the development and evolution of microscopic pores in shale gas reservoirs are mostly affected by the over mature level of thermal evolution. The control of thermal evolution degree (as indicated by Ro) over the development of microscopic pore structure in shales lies in a “contradiction”. That is, with increasing Ro, the SSA and Vp of organic matter pores in the shale both increase, whereas those of interlayer micropores in clay minerals both decrease. These processes jointly control the development of microscopic pore structure in shales. Thus, there is a need to identify a critical point of Ro in order to maximize the space for shale gas adsorption by shale reservoirs.

When Ro <3.0%, the SSA and Vp of shale both increase with increasing degree of thermal evolution; and when Ro >3.0%, the two parameters first decrease drastically and then level off gradually with continuous increases in the degree of thermal evolution (Figure 6). Thus, the critical point of thermal evolution degree (Ro) is determined to be approximately 3% for the southern margin of the Sichuan Basin.

6. Conclusions
1. The Qiongzhusi FM. is characterized by a diversity of microscopic pores, which can be divided into four size classes: micropore (<10 nm), pore (10~100 nm), mesopore (100~1000 nm) and micropore
In terms of genesis, the matrix pores are divided into: mineral interlayer micropore, organic matter pore, intercrystalline pore, mineral mold pore, and secondary dissolution pore.

2. The SSA and Vp of shale specimens from the Qiongzhusi FM. were analyzed using liquid nitrogen adsorption experiments. Results show that shales from the Qiongzhusi FM. on the southern margin of the Sichuan Basin have relatively large SSA and Vp. These two parameters have a good positive correlation with each other. Micropores less than 10 nm in size are mainly developed, and pores of the size 1–8 nm made the greatest contribution to the SSA and Vp of shales in the study area.

3. Quantitative analysis of microscopic pores in shales from the Qiongzhusi FM. was performed by combining SSA and Vp measurements, SEM, and AFM analysis, with the aid of statistical tools in ArcGIS. The micropores in shales from the Qiongzhusi FM. are characterized by large number, high surface porosity, and large pore-SSA.

4. In the study area, development of microscopic pores in shale gas reservoirs is mainly controlled by TOC content, kerogen type, clay mineral type and content, and thermal evolution degree. Of these, thermal evolution degree poses the greatest effect. When thermal evolution degree reaches a certain critical point, the SSA and Vp of microscopic pores both reach the highest levels. Conversely, when thermal evolutionary degree exceeds the critical point, both SSA and Vp drastically decrease. The optimal degree of thermal evolution (Ro) for shale gas reservoirs in the study area is determined to be approximately 3.0%.

Acknowledgements

The work was supported by the Innovation-Seeking Program [Qiankehe (2017)5789-16], the Teaching Reform Program (2017JGYJ14) and Scientific and Technological Talent Growth Program [Qianjiaohe KY Zi (2016)232]. We would like to thank Qisen Gong for the assistance in field work.

References

[1] Cheng, K.M., Wang, S.Q., Dong, D. Z. (2009). Accumulation condition of shale gas reservoir in the Lower Cambrian Qiongzhusi formation, the Upper Yangtze region, Natural Gas Industry. 29(5):40-44.
[2] Fan, C.Y., Wang, Z.L. (2010). Geological Factors and process in enrichment and high production of shale gas, Petroleum Geology & Experiment. 32(5):465-469.
[3] Dong, D.Z., Cheng, K.M., Wang, Y.M. (2010). Forming conditions and characteristics of shale gas in the Lower Paleozoic of the Upper Yangtze region, China, Oil & Gas Geology. 31(3):288-299.
[4] Guo, L., Jiang, Z.X., Jiang, W.L. (2011). Formation condition of gas-bearing shale reservoir and its geological research target, Geological Bulletin of China. 30(2-3):385-392.
[5] Javadpour, F. (2009). Nanopores and Apparent Permeability of Gas Flow in Mudrocks (Shales and Siltstone), Journal of Canadian Petroleum Technology. 48(8): 16-21.
[6] Sondergeld, C.H., Newsham, K.E., Comisky, J.T., Rice, M.C., Rai, C.S. (2010). Petrophysical Considerations in Evaluating Producing Shale Gas Resources. Proceedings of the SPE Unconventional Gas Conference. 34. 10.2118/131768-MS.
[7] Hu, L., Zhu, Y.M. (2012). Resource potential analysis of shale gas in Lower Cambrian Qiongzhusi Formation in Middle & Upper Yangtze region, Journal of China Coal Society. 37(11):1871-1877.
[8] Jarvie, D.M., Hill, R.J. and Ruble, T.E. (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.
[9] Ross, D.J.K., Bustin, R.M. (2008). Characterizing the shale gas resource potential of Devonian Mississippian strata in the Western Canada sedimentary Basin: application of an integrated formation evolution, AAPG Bulletin. 92(1):87-125.
[10] Chen, S.B., Zhu, Y.M., Wang, H.Y., Liu, H.L., Wei, W., Fang, J.H. (2012). Structure characteristics and accumulation significance of nanopores in Longmaxi shale gas reservoir
in the southern Sichuan Basin, Journal of China Coal Society. 37(3):438-444.

[11] Sing, K.S.W., Everett, D.H., Haul, R.A.W. (1985). Reporting physisorption data for gas/solid systems with special reference to determination of surface area and porosity, Pure and Applied Chem. 57(4): 603-611.

[12] Kang, S.M., Fathi, E. and Ambrose, R.J. (2011). Carbon dioxide storage capacity of organic-rich shales, SPE Journal-134583-Paper: 1-17.

[13] Lu, Q., Lei, X. Y., Liu, H.F. (1993). Study of the stacking sequences of a kind of irregular mixed-layer illite-smectite (I/S) clay mineral-with a discussion of the existence of minerals with two-dimensional lattice and one-dimensional quasi-lattice, Acta Geologica Sinica. 67(2):123-130