Study on the Pore Structure and Fractal Characteristics of Different Lithofacies of Wufeng–Longmaxi Formation Shale in Southern Sichuan Basin, China

Chao Qian, Xizhe Li,* Weijun Shen,* Qing Zhang, Wei Guo, Yong Hu, Yue Cui, and Yuze Jia

ABSTRACT: Gas content and flow characteristics are closely related to shale lithofacies, and significant differences exist in the pore structure and fractal characteristics among lithofacies. In this study, X-ray diffractometer (XRD), field-emission scanning electron microscopy (FE-SEM), gas adsorption (N₂ and CO₂), and fractal theory were employed to systematically characterize the pore attributes of the marine Wufeng–Longmaxi formation shales. The information of various pores and microfractures among lithofacies was extracted and quantified via high-resolution FE-SEM image stitching technology. Shales were classified into four types based on mineral compositions, and siliceous shales possess the largest SEM-based surface porosity (2.84%) and the largest pore volume (PV) (average 0.0243 cm⁢³/g) as well as specific surface area (SSA) (average 28.06 m²/g). The effect of lithofacies variation on the PV of shale is minor. In contrast, the lithofacies variation has a significant impact on the SSA, and the SSA of siliceous shale is 39.11% higher than that of argillaceous shale. PV and SSA show strong positive correlation with the total organic carbon (TOC) content but negative correlation with clay minerals. Siliceous shales have the greatest fractal dimension D₁ (pore surface roughness) (average 2.6821), which is contributed by abundant organic matter pores with more complicated boundaries. The largest fractal dimension D₂ (pore structure complexity) (average 2.8263) is found in mixed shales, which is attributed to well-developed intraparticle (intrap) pores associated with carbonate mineral dissolution. This indicates that siliceous shales have the highest methane adsorption capacity and that shale gas desorption, diffusion, and seepage are more difficult in mixed shales.

1. INTRODUCTION

Shale gas, as a recognized clean energy source, is becoming increasingly crucial in satisfying the growing energy demand. According to the statistics, shale gas production in the United States accounts for more than half of its total natural gas production; meanwhile, shale gas production will reach 500 × 10⁸ m³ by 2030 in China.¹ Due to the extremely low permeability in shales, large-scale horizontal drilling and hydraulic fracturing, as well as multistage hydraulic stimulation technologies, were realized to improve the development of shale gas reservoirs in the past decades.³ As the reservoir space and migration channel of shale gas, the pore structure of shale affects not only the reservoir and adsorption capacity of shale gas but also the seepage characteristics of shale gas. Therefore, understanding the shale pore structure is greatly significant for the effective evaluation and exploration of shale gas reservoirs. Shale gas is mainly adsorbed on the surface of pores as adsorbed gas and exists in the pores and microfractures space as free gas.⁴ Shale gas reservoirs are characterized by low porosity (2–8%), which are dominated by a much more complex and heterogeneous nanoscale pore structure.⁵ Gas storage and seepage capacity of shale reservoirs are determined by the pore structure characteristics, and thus, accurate characterization of shale pore structure parameters [such as pore volume (PV), specific surface area (SSA), porosity, and pore diameter] is the primary task in shale gas evaluation.⁶–¹¹ Various advanced testing and analysis techniques are used to quantitatively characterize the shale nanopores.⁵,¹² The morphology and size of shale pores can directly be observed by (field emission or focused ion beam) scanning electron microscopy (FE-/FIB-SEM).¹³,¹⁴ Meanwhile, high-resolution imaging and image analysis aid the visual representation of the pore structure and its distribution.¹⁵,¹⁶ Furthermore, the information of various pores and microfractures among lithofacies can be extracted and counted via high-resolution imaging.
field-emission scanning electron microscopy (FE-SEM) image stitching technology. The 3D images reconstructed by micro/nano-CT and FIB-SEM are an effective method to characterize shale nanopore systems. The quantitative characterization methods, including gas adsorption, mercury intrusion capillary pressure, and low-field nuclear magnetic resonance, can reveal the pore size distribution and SSA characteristics ranging from nanometers to millimeters. However, these testing techniques have different advantageous measurement intervals of pore sizes, and thus, the combination of other techniques is a practical approach to characterize pore structure comprehensively. Gas adsorption data and SEM images indicate that the porous media, such as shale and coal, have fractal geometries. The fractal dimension value $D$ is usually used to evaluate the roughness and the complexity of pore surfaces and structures in shales. Meanwhile, the fractal dimension values range from 2 to 3, and the larger $D$ values indicate the stronger pore surface roughness and complexity as well as higher methane adsorption capacity. The fractal dimension of the shale pore is usually calculated by the Frenkel–Halsey–Hill (FHH) model based on $N_2$ adsorption isotherms.

The previous studies have investigated the main factors affecting the pore structure of shale, such as total organic carbon (TOC) content, lithofacies, sedimentary environment, and tectonic movement. Lithofacies is the sum of the lithological characteristics, including rock color, stratification, texture, particle size, mineral compositions, and so on. Different lithofacies were deposited in various environments and were composed of different mineral compositions, and the shale pores system varies significantly among different lithofacies. Some researchers have suggested that organic-rich siliceous shale lithofacies with higher $P_V$ and SSA are the most favorable lithofacies for gas content. Although there are significant differences in the pore structure and fractal characteristics of shales having different lithofacies, a detailed systematic relationship between lithofacies and pore structure and fractal dimension is still lacking. Consequently, there is a significant necessity to understand the pore structure and fractal characteristics of shales with different lithofacies.

In this study, marine Wufeng–Longmaxi formation shales were first classified into four lithofacies based on mineral compositions, and the pore parameters were characterized by FE-SEM images and gas adsorption measurements. The fractal dimension values were calculated by the FHH$^{33,34}$ and Wang–Li$^{35}$ (WL) models based on $N_2$ adsorption data. Furthermore, the relationship between lithofacies and pore structure characteristics was analyzed. Finally, the effects of TOC and mineral compositions on pore parameters, heterogeneity, and complexity were systematically discussed.

2. GEOLOGICAL SETTING

Sichuan Basin is a multistage superimposed basin located at the southwest margin of the Upper Yangtze Platform in South China. It is a diamond-shaped basin composed of five tectonic zones, including the northwest district, the central district, the eastern district, the southwest district, and the southern district, with a total area of approximately $18 \times 10^4$ km$^2$, and surrounded by Longmen Mountain, Boxing Mountain, Daba Mountain, and Daliang Mountain, as illustrated in Figure 1a. The study area is situated in the southwest district and the southern district of Sichuan Basin. The stratigraphy is relatively well-developed in Sichuan Basin, but the Devonian to Carboniferous stratum is seriously eroded. Before the Permian, the basin was dominated by marine deposition, mainly developed shale and carbonate rocks, as shown in Figure 1b; the Wufeng–Longmaxi marine shales in this study area were deposited in a shelf plain to shallow water shelf with a low-energy, anoxic sedimentary environment; and the abundant organic matter (OM) was preserved well, with a thickness of more than 200 m. The equivalent vitrinite reflectance of the studied shale is greater than 2.0%, indicating that it has undergone the mass gas production phase.
3. SAMPLES AND METHODS

3.1. Samples. In this study, core samples were collected from wells W1 and L1 of Wufeng–Longmaxi formation shale in the Luzhou–Weiyan area (Figure 1). The depth, porosity, and TOC content of samples are listed in Table 1. The mineralogical compositions of samples were tested by the RINT–TTR3 X-ray diffractometer following the Chinese oil and gas industry standard (SY/T) 5163-2018. The most accurate melt sheet method and X-ray fluorescence spectrometry (XRF) were used for major element analysis. The experiment was conducted based on the reference materials GB/T 14506.28-2010 and GB/T14506.14-2010.

3.2. FE-SEM. The morphological and distribution characteristics of pores can be obtained via a combination of argon ion milling and FE-SEM. The sample observation was performed using a Crossbeam540 apparatus after the top surface of shale samples was meticulously polished, as well as ion milled and coated with gold to enhance conductivity.19,27 The SEM image stitching technology can effectively handle the contradiction between high resolution and large vision, for which an elaborated explanation can be found in Li et al.17 In this study, four visions (100 μm × 100 μm) were selected stochastically on the surface of one sample, and each vision was composed of 10 matrix images with 4 nm resolution. The pore and microfracture characteristics (type, size, and the number of pores and microfractures) were identified and extracted from each image using Image J and Avizo software.

3.3. Low-Pressure Gas Adsorption Measurements. The nanoscale pore characteristics of shale can be quantitatively characterized by the low-pressure gas adsorption experiment using N2 and CO2 as absorbates.20,40,41 Prior to the experiments, the shale samples were crushed into powder of 60–80 mesh and dried at 65 °C for 48 h to remove residual moisture. The degassed samples were loaded into the Quantachrome Autosorb-IQ fully automatic physisorption analyzer, and N2 adsorption isotherms were conducted at 77 K with relative pressure ranging from 0.001 to 0.03. The microscopic pore size distribution and SSA of shales can be obtained by combining adsorption isotherm data, density functional theory (DFT), and Brunauer–Emmett–Teller (BET) models.7,40,41

3.4. Fractal Theory. Wood42 systematically elaborated the fractal dimension calculation methods of the FHH, NM, and WL models. He also proposed that the fractal dimension values are uncertain for some sample isotherms. In such cases, it is preferable to quote the fractal dimension as a possible range that should typically include FHH D and WD D values rather than as a single value.

Recently, the fractal dimensions of the shale pore have been usually calculated by the FHH model based on N2 adsorption isotherms,33,35 which can be written as

\[ \ln V = C + K \ln \left[ -\ln \left( \frac{P}{P_0} \right) \right] \]  

(1)

\[ D = 3 + K \]  

(2)

where V is the adsorption volume, K is the slope of ln V versus ln \( -\ln \left( \frac{P}{P_0} \right) \), P is the equilibrium pressure corresponding to each pressure increment measured, \( P_0 \) is the saturation pressure of nitrogen, and D is the fractal dimension.

Wang and Li35 provided the WL model, and it assumed that the specified fractal surface is an inscribed equicurved surface with a variable mean curvature radius. D and r can be used to denote the surface area, which can be expressed as

\[ S(r) = k_0 r^D \]  

(3)

where \( k_0 \) is a constant and N is the volume. The Kelvin equation is used to calculated the pore radius r

\[ r = \frac{-2\sigma V_L}{RT \ln X} \]  

(4)

where X refers to the ratio P/P0, R is the universal gas constant, T is the absolute temperature, \( V_L \) is the molar volume of liquid

Table 1. Lithofacies, TOC, Porosity, and Mineralogical Compositions of Wufeng–Longmaxi Formation Shales in the Luzhou–Weiyan Area

| sample ID | well | depth (m) | lithofacies     | TOC (%) | porosity (%) | quartz (%) | feldspar (%) | calcite (%) | dolomite (%) | pyrite (%) | total clay (%) | relative content of clay minerals (%) |
|-----------|------|----------|----------------|---------|--------------|------------|--------------|-------------|--------------|-----------|----------------|--------------------------------------|
| S1        | W1   | 2747.60  | siliceous shale | 3.76    | 5.61         | 66.2       | 1.9          | 10.3        | 8.8          | 1.5       | 11.3           | 59 21 20 10 |
| S2        | L1   | 4309.87  |               | 4.14    | 6.01         | 55.8       | 5.1          | 4.9         | 6.5          | 5.9       | 21.8           | 72 7 25 23 |
| S3        | L1   | 4039.00  |               | 4.11    | 5.81         | 47.2       | 3.3          | 6.8         | 12.6         | 3.0       | 11.0           | 80 4 16 5  |
| S4        | L1   | 4041.45  |               | 3.62    | 4.09         | 59.8       | 10.6         | 18.7        | 10.2         | 2.3       | 14.5           | 73 4 23 5  |
| A51       | W1   | 2737.43  | argillaceous–siliceous shale | 2.28 | 5.48 | 54.1 | 5.5 | 1.9 | 3.4 | 4.0 | 31.1 | 49 9 42 15 |
| A52       | W1   | 2743.45  |               | 2.55    | 5.24         | 43.9       | 7.7          | 4.7         | 5.0          | 3.1       | 35.6           | 51 9 40 15 |
| A53       | L1   | 4303.75  |               | 2.53    | 4.26         | 44.7       | 9.8          | 4.6         | 9.5          | 1.5       | 29.9           | 58 14 28 10 |
| A54       | L1   | 4012.98  |               | 2.48    | 3.76         | 44.7       | 8.4          | 9.0         | 6.7          | 2.2       | 29.0           | 54 15 31 10 |
| A55       | L1   | 4029.08  |               | 3.56    | 5.38         | 49.3       | 4.6          | 3.8         | 5.0          | 3.2       | 34.1           | 64 9 27 10 |
| M1        | W1   | 2734.88  | mixed shale   | 2.53    | 5.24         | 34.8       | 5.2          | 10.8        | 14.3         | 4.7       | 30.2           | 44 10 46 10 |
| M2        | W1   | 2744.95  |               | 4.70    | 4.13         | 31.8       | 3.0          | 15.6        | 19.6         | 8.4       | 21.6           | 46 8 46 15 |
| M3        | L1   | 3991.00  |               | 4.37    | 5.29         | 33.0       | 5.1          | 12.4        | 11.3         | 3.6       | 34.6           | 64 12 24 10 |
| M4        | L1   | 4033.00  |               | 4.07    | 4.10         | 48.4       | 4.3          | 4.3         | 10.1         | 4.1       | 28.8           | 86 6 8 10 |
| A1        | W1   | 2716.90  | argillaceous shale | 0.46 | 4.53 | 40.6 | 4.8 | 0.9 | 1.2 | 1.4 | 5.1 | 51 52 27 21 |
| A2        | W1   | 2750.25  |               | 0.46    | 3.70         | 21.9       | 3.2          | 9.1         | 6.9          | 7.5       | 51.4           | 54 6 40 10 |
| A3        | L1   | 4005.25  |               | 2.38    | 4.21         | 27.0       | 4.8          | 5.2         | 4.0          | 4.4       | 54.6           | 61 8 31 10 |
| A4        | L1   | 4284.00  |               | 2.43    | 4.50         | 36.6       | 5.0          | 2.4         | 6.1          | 1.0       | 48.9           | 70 13 17 10 |
adsorbate (the molar volume of liquid nitrogen is \(3.46535 \times 10^{-5} \text{ m}^3/\text{mol}\)), and \(\sigma\) is the adsorbate’s surface tension (0.04624 N/m).

\(S\) can be calculated using the Kiselev relationship

\[
S(X) = \frac{RT}{\sigma} \int V_0 \ln X \, dV(X) \tag{5}
\]

where \(V_0\) is the amount of adsorbate adsorbed as \(P/P_0\) approaches 1.

Assuming that the adsorbate is incompressible and \(V\) becomes a function of \(N(X)\)

\[
N(X) = [V_0 - V(X)]V_0 \tag{6}
\]

Entering \(S(X)\) and \(N(X)\) values into eq 3 results in

\[
\int_{V(X)}^{V_0} \frac{\ln X \, dV(X)}{r^2(X)} = \frac{k_0 D Z^3}{p RT \left\{ \frac{[V_0 - V(X)]^{1/3}}{r(X)} \right\}^D} \tag{7}
\]

Wang and Li\(^{35}\) denoted the left side of eq 7 as \(A(X)\) and the right side as \(B(X)\)

\[
A(X) = -\int_{V(X)}^{V_0} \frac{\ln X \, dV(X)}{r^2(X)} \tag{8}
\]

\[
B(X) = \frac{[V_0 - V(X)]^{1/3}}{r(X)} \tag{9}
\]

Equation 7 can be simplified by using natural logarithms on \(A(X)\) and \(B(X)\)

\[
\ln A(X) = l + D \ln B(X) \tag{10}
\]

where \(D\) is the linear equation’s slope as well as the fractal dimension and \(l\) is a constant.

The relationship between the \(V\) and \(\ln X\) power curves is denoted by eq 11

\[
- \ln X = mt^b \tag{11}
\]

where \(m\) is the slope and \(b\) is the exponent.

An integral solution to eq 5 can be found by taking the \(m\) and \(b\) values from the “best” fit to the curve. For this purpose, the WL approach employs the same best-fit solution as with eq 11. For given \(V\) values, eq 12 expresses the integral solution to eq 8.

\[
A(X_N) = \frac{m (V_0^{b+1} - V^{b+1})}{(b + 1) r^2(X_N)} \tag{12}
\]

The slope of the \(\ln A\) versus \(\ln B\) trend would obviously provide an accurate value of \(D\) when the cross-plot of \(\ln A\) and \(\ln B\) trend approximates a straight line.

4. RESULTS

4.1. Geochemical and Lithofacies Characteristics. The shales of the Wufeng–Longmaxi formation in the studied area are dominated by quartz and clay minerals, which are listed in Table 1. The higher values of the \(Al/(Al + Fe + Mn)\) ratio indicates that the siliceous minerals of the Wufeng–Longmaxi formation shale are primarily of biogenic origin, as shown in Figure 2a,\(^{17}\) and the TOC content shows a positive correlation with the quartz content in Figure 2b. However, the TOC decreases as the content of clay minerals increases, as illustrated in Figure 2c, and it suggests that biogenic origin quartz is favorable for the enrichment and preservation of OM.\(^{44,45}\) The typical classification scheme is based on mineral compositions of the siliceous minerals (quartz and feldspar), calcareous minerals (calcite and dolomite), and clay minerals.\(^{14,30}\) Thus, these shales are classified into four types: siliceous shale lithofacies (S), argillaceous–siliceous shale lithofacies (AS), mixed shale lithofacies (M), and argillaceous shale lithofacies (A), which is shown in Figure 3. Both the siliceous shale and argillaceous–siliceous shale are quartz-rich, with contents ranging from 47.2 to 66.2 and 44.7 to 54.1%, respectively. The mixed shales consist of moderate quartz content and clay mineral content, with an average of 37.0 and...
28.8%, respectively. The argillaceous shale is dominated by clay, which varies between 48.9 and 54.6%. Furthermore, there is obvious discrimination in different lithofacies; the siliceous shales and mixed shales possess a higher TOC content, which ranges from 3.62 to 4.14 and 2.53 to 4.7%, respectively. The argillaceous shales have moderate TOC content ranging from 2.28 to 3.56%, with an average of 2.68%. The TOC content of the argillaceous shale is the lowest among the four types, varying between 0.46 and 2.43%. In addition, the equivalent reflectance of vitrinite (EqRo) of Wufeng–Longmaxi formation shales is greater than 2.0% and the OM is in the overmature gas generation stage.46,47

4.2. Pore Characteristics from FE-SEM. 4.2.1. OM Pores. The OM pores are the primary gas storage space of shale reservoirs, and the degree of OM pore development has a direct impact on shale gas content and productivity.48 Figure 4 demonstrates that OM is widely dispersed in the voids between brittle mineral particles such as quartz and flexible particles such as clay minerals. The shape of the OM pores is elliptical or bubble-like, with irregular boundaries, as shown in Figure 4a–d. The cellular OM pores in siliceous shales and mixed shales are well developed and dominated by larger pores of hundreds of nanometers, as shown in Figure 4a,c, which are created mainly with large amounts of gas generation in the bitumen and with good pore connectivity. These findings indicate that OM pores have strong heterogeneity. The OM in argillaceous–siliceous shales and argillaceous shales is mixed with flaky clay minerals. Meanwhile, OM pores in argillaceous–siliceous shales and argillaceous shales are relatively poorly developed with angular and irregular shapes, dominated by small pores of tens of nanometers with poor connectivity, as shown in Figure 4b,d.

4.2.2. Inorganic Pores. The most dominant inorganic pores are interparticle (interP) pores and intraparticle (intraP) pores. The interP pores are commonly found on the edges of brittle mineral particles such as quartz, feldspar, carbonate, and pyrite. InterP pores are triangular or polygonal in form, with straight edges determined by mutual contact particles, as shown in Figure 4f,g,k. InterP pores, on the other hand, are associated with clay, with triangle or slit shapes forming within laminar clay cleavages, as shown in Figure 4d,f–h. Furthermore, brittle mineral particles have strong resistance to compaction, thus allowing for the formation and preservation of OM pores.45 The intraP pores are often associated with the dissolution of carbonate minerals and are isolated on the surface of the particles as triangles and ellipsoids with smooth edges (Figure 4e,g,i–l). The sedimentary environment of the study area was highly reductive and created a certain amount of pyrite (1.4–8.4%) as well as intraP pores in pyrite frambooids, as illustrated in Figure 4c,e, and the sizes of intraP pores are smaller than 300 nm.

4.2.3. Microfractures. Microfractures are helpful for increasing the storage space of shale reservoirs and allow the accumulation of gas. The microfracture network usually has excellent connectivity, which enhances the seepage capacity of shale reservoirs.49 Microfractures consist of OM microfractures (OM penetrated by microfractures), as shown in Figure 4i,k; interlayer fractures of clay minerals; and compression microfractures caused by compaction and fragmentation of brittle minerals, as shown in Figure 4e,h,j,l. Microfractures present in terms of isolated points, thin lines, or jagged curves in a relatively low proportion ranging from 3.89 to 10.53%. The width of microfractures varies between 20 nm and 1.6 μm, and is dominated by 20–120 nm, which accounts for 81.1% of the total amount, as shown in Figure 12.

4.3. Pore Characteristics from Gas Adsorption. 4.3.1. CO₂ Adsorption. The maximum CO₂ adsorption volume of all the shale samples varies between 0.94 and 2.36 cm³/g. The maximum adsorption volume of siliceous shales and mixed shales is higher, ranging from 1.70 to 2.36 and 1.65 to 2.32 cm³/g, respectively. The maximum adsorption volume of

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**Figure 4.** FE-SEM images of various pores in the Wufeng–Longmaxi formation shale. OM pores in siliceous shale (a), argillaceous–siliceous shale (b), mixed shale (c), and argillaceous shale (d); intraP pores and interP pores in siliceous shale (e), argillaceous–siliceous shale (f), mixed shale (g) and argillaceous shale (h); OM and inorganic microfractures in siliceous shale (i), argillaceous–siliceous shale (j), mixed shale (k), and argillaceous shale (l).
argillaceous shales is the lowest of the four types, ranging from 0.94 to 1.88 cm³/g (Figure 5a−d).

The DFT model is used to calculate the micropore size distributions within 1.4 nm from CO₂ adsorption isotherms. All shale samples have similar characteristics of pore size distributions, with three apparent peaks at 0.4, 0.5, and 0.85 nm, respectively, as shown in Figure 6a−d, indicating that these pores account for the majority of PV. Accumulative micropore volumes of siliceous shale and mixed shale are higher, averaging 0.00643 and 0.00651 cm³/g, respectively.

Figure 5. CO₂ and N₂ adsorption isotherms of shale samples from Wufeng−Longmaxi formation. CO₂ adsorption isotherms of siliceous shale (a), argillaceous−siliceous shale (b), mixed shale (c), and argillaceous shale (d); N₂ adsorption isotherms of siliceous shale (e), argillaceous−siliceous shale (f), mixed shale (g), and argillaceous shale (h).

Figure 6. Micropore structure parameters measured by CO₂ adsorption of shale samples. (a−d) Micropore size distribution of siliceous shale, argillaceous−siliceous shale, mixed shale, and argillaceous shale; (e−h) cumulative micropore volume of siliceous shale, argillaceous−siliceous shale, mixed shale, and argillaceous shale; (i−l) micropore SSA distribution of siliceous shale, argillaceous−siliceous shale, mixed shale, and argillaceous shale.
The micropore volumes of argillaceous shales are the lowest, ranging from 0.00336 to 0.00628 cm$^3$/g (average 0.00491 cm$^3$/g), as shown in Figure 6 e−h. Simultaneously, the characteristics of SSA are similar to the pore size distributions, revealing that these pores with sizes of 0.4, 0.5, and 0.85 nm have a relatively larger pore surface area, as shown in Figure 6i−l.

4.3.2. $N_2$ Adsorption. The nitrogen adsorption and desorption curves form a hysteresis loop, as shown in Figure 5e−h, because $N_2$ undergoes capillary condensation during the gas adsorption phase, and the shape of the hysteresis loop can reflect the geometry of shale pores. The hysteresis loops of $N_2$ adsorption and desorption curves are similar to the characteristics of both H2 and H3 types recommended by the International Union of Pure and Applied Chemistry.12 According to the geometry of the hysteresis loop, the pores in the shale samples are ink-bottle pores with narrow throats and large pore bodies, as well as parallel plate fracture pores.27 Naturally, this result agrees with the FE-SEM observations of pore characteristics shown in Figure 4.

The $N_2$ adsorption and DFT models provide pore size distributions and SSA characteristics in the range of 1.7−50 nm (Figure 7). The curves of all shale samples show bimodal distributions, with two primarily peaks at 1.6 and 4.0 nm,
Table 2. Fractal Dimension Derived from the N₂ Adsorption Isotherms by Using the WL and FHH Models

| sample ID | $P/P_0 < 0.45$ | $P/P_0 > 0.45$ |
|-----------|----------------|----------------|
|           | $m$ | $B$ | $D1$ | $R^2$ | $m$ | $b$ | $D2$ | $R^2$ |
| S1        | $2.300 \times 10^{-6}$ | $-2.6487$ | $2.5403$ | $0.9996$ | $8.676 \times 10^{-11}$ | $-3.7853$ | $2.5650$ | $0.9999$ |
| S2        | $1.698 \times 10^{-7}$ | $-3.2572$ | $2.5809$ | $0.9997$ | $2.351 \times 10^{-11}$ | $-5.1252$ | $2.6309$ | $0.9999$ |
| S3        | $3.612 \times 10^{-7}$ | $-2.9520$ | $2.5610$ | $0.9970$ | $2.792 \times 10^{-11}$ | $-4.3764$ | $2.6175$ | $0.9999$ |
| S4        | $2.007 \times 10^{-7}$ | $-3.1849$ | $2.5682$ | $0.9997$ | $1.895 \times 10^{-11}$ | $-6.0748$ | $2.6327$ | $0.9999$ |
| AS1       | $1.943 \times 10^{-6}$ | $-2.7061$ | $2.5564$ | $0.9998$ | $1.915 \times 10^{-10}$ | $-4.6267$ | $2.6001$ | $0.9999$ |
| AS2       | $8.302 \times 10^{-6}$ | $-2.2215$ | $2.5230$ | $0.9998$ | $4.821 \times 10^{-10}$ | $-6.3629$ | $2.5673$ | $0.9999$ |
| AS3       | $3.897 \times 10^{-7}$ | $-2.8209$ | $2.5782$ | $0.9999$ | $3.167 \times 10^{-10}$ | $-4.1947$ | $2.5785$ | $0.9999$ |
| AS4       | $4.004 \times 10^{-7}$ | $-2.8807$ | $2.5723$ | $0.9998$ | $3.245 \times 10^{-11}$ | $-4.7327$ | $2.5922$ | $0.9999$ |
| AS5       | $9.214 \times 10^{-7}$ | $-2.9105$ | $2.5801$ | $0.9999$ | $4.350 \times 10^{-10}$ | $-4.5332$ | $2.6101$ | $0.9999$ |
| M1        | $1.960 \times 10^{-6}$ | $-2.8015$ | $2.5671$ | $0.9998$ | $1.236 \times 10^{-10}$ | $-4.8961$ | $2.5926$ | $0.9998$ |
| M2        | $3.528 \times 10^{-6}$ | $-2.4653$ | $2.5293$ | $0.9997$ | $7.381 \times 10^{-11}$ | $-4.6004$ | $2.5811$ | $0.9998$ |
| M3        | $1.539 \times 10^{-6}$ | $-2.6901$ | $2.5592$ | $0.9998$ | $3.405 \times 10^{-11}$ | $-4.8665$ | $2.6511$ | $0.9989$ |
| M4        | $7.056 \times 10^{-6}$ | $-2.8789$ | $2.5662$ | $0.9998$ | $1.819 \times 10^{-10}$ | $-4.5818$ | $2.5771$ | $0.9998$ |
| A1        | $1.560 \times 10^{-6}$ | $-2.4485$ | $2.5671$ | $0.9997$ | $1.078 \times 10^{-10}$ | $-3.3387$ | $2.5701$ | $0.9999$ |
| A2        | $6.708 \times 10^{-6}$ | $-1.6881$ | $2.4892$ | $0.9999$ | $1.205 \times 10^{-7}$ | $-2.8467$ | $2.5197$ | $0.9997$ |
| A3        | $2.172 \times 10^{-6}$ | $-2.6640$ | $2.5603$ | $0.9999$ | $2.408 \times 10^{-10}$ | $-5.0162$ | $2.5851$ | $0.9999$ |
| A4        | $3.476 \times 10^{-6}$ | $-2.4637$ | $2.5439$ | $0.9998$ | $5.522 \times 10^{-11}$ | $-4.6618$ | $2.5805$ | $0.9998$ |

Figure 9. Relationship between WL D1 and FHH D1 (a); relationship between WL D2 and FHH D2 (b).

Figure 10. Relationship between lithofacies and fractal dimension D1 (a); relationship between lithofacies and fractal dimension D2 (b).

respectively, shown in Figure 7a–d,i–l, which indicates that these pores are essential in terms of PV and surface area. The accumulative PVs of siliceous shales and mixed shales are higher, ranging from 0.0202 to 0.0261 and 0.0185 to 0.0263 cm³/g, respectively. The argillaceous–siliceous shales and argillaceous shales possess a lower PV, ranging from 0.0170 to 0.0242 and 0.0148 to 0.0213 cm³/g, respectively, as shown in Figure 7e–h.

4.4. Fractal Dimension from Nitrogen Adsorption Isotherms. The calculation and fitting process of WL and FHH models are displayed in Figure 8, and the fractal dimension results are listed in Table 2. The data are divided into two parts based on the starting point of capillary condensation ($P/P_0 = 0.45$) in Figure 5e–h, and the fractal dimension D1 and D2 values are calculated, respectively.
Fractal dimension $D_1 (P/P_0 < 0.45)$ is introduced to characterize the pore surface roughness of shales, which reflects the effect of van der Waals force. The larger the $D_1$ value is, the rougher the pore surface is and the more adsorption sites would be on the pore surface, resulting in an increase in shale adsorption capacity. Fractal dimension $D_2 (P/P_0 > 0.45)$ reveals the heterogeneity and complexity of the pore structure, reflecting the capillary condensation effect. The larger the $D_2$ value, the more complex the pore structure, which makes it more difficult for desorption, diffusion, and seepage of shale gas.

Meanwhile, the correlation coefficients of two segments for two models are both greater than 0.99 in Figure 8, and the plots of WL $D_1$ versus FHH $D_1$ and WL $D_2$ versus FHH $D_2$ have a strong positive correlation in Figure 9, which suggests great applicability and reliability. The values of the fractal dimensions $D_1$ and $D_2$ calculated by the WL model are too close to each other, with a difference of less than 0.1. However, the difference of the fractal dimensions $D_1$ and $D_2$ calculated by the FHH model is larger and more stable than that of the WL model; thereby, the FHH fractal dimensions are selected for further investigation.

There is an obvious downward trend of fractal dimension $D_1$ in Figure 10a, indicating that the pore surface of the siliceous shales is the roughest. The fractal dimension $D_1$ values are the largest in the siliceous shale, ranging from 2.6437 to 2.7043, with an average of 2.6821. The argillaceous–siliceous shale and mixed shale possess moderate $D_1$ values, ranging from 2.5666 to 2.6668 and 2.6188 to 2.6648, averaging 2.6400 and 2.6457, respectively. The $D_1$ values of argillaceous shales are distributed widely, varying between 2.4146 and 2.6413.

The fractal dimension $D_2$ values of mixed shales are the highest, varying between 2.8165 and 2.8445 (Figure 10b). The reason is that intraP pores associated with carbonate mineral (calcite and dolomite) dissolution are relatively well developed in the mixed shales, as illustrated in Figure 4g,k. This indicates that it is more difficult for gas desorption, diffusion, and seepage in mixed shales. The $D_2$ values of siliceous and argillaceous shales vary greatly, ranging from 2.7565 to 2.8445 and 2.7350 to 2.8396, respectively, as listed in Table 2.

5. DISCUSSION

5.1. Correlation between Pore Structural Characteristics and Lithofacies. Based on the FE-SEM images, pore and microfracture characteristics (type and size) were identified and extracted via the ImageJ software. The pore size distribution and surface porosity of various pores and microfractures were quantitatively analyzed via the Avizo software. The data in Figure 11 are based on the classification of OM pores, inorganic pores, OM microfractures, and inorganic microfractures.

Figure 11. Pore and microfracture identification and extraction from FE-SEM image. (a) FE-SEM image grayscale map, (b) OM pores (red color), (c) inorganic pores (green color), (d) OM microfractures (yellow color), and (e) inorganic microfractures (blue color).

Figure 12. Pore size distribution of various pores calculated by FE-SEM: siliceous shale (a), argillaceous–siliceous shale (b), mixed shale (c), and argillaceous shale (d).
The number of pores is the greatest in siliceous shales (77,591), and the pore size distribution is small, with two peaks in the range of 10−40 nm, shown in Figure 12a. The OM pores and inorganic pores account for 45.70 and 50.41% of total statistics, respectively, while OM microfractures and inorganic microfractures are rare, sharing 2.77 and 1.12%, respectively. Furthermore, siliceous shales possess the maximum SEM-based surface porosity of 2.84%, primarily provided by pores with radii ranging from 20 to 100 nm, shown in Figure 13a. The SEM-based surface porosity is mainly contributed by inorganic and OM pores, accounting for 63.75 and 23.59%, respectively, followed by inorganic microfractures and OM microfractures, representing 9.51 and 3.15%, respectively.

OM and inorganic pores account for more than 90% of the pores in argillaceous−siliceous shales, sharing 21 and 73.4%, respectively, and the OM microfractures and inorganic microfractures are rare, as shown in Figure 12b. The SEM-based surface porosity of argillaceous−siliceous shales is mainly provided by pores with radii ranging from 20 to 70 nm. The inorganic pores provide the most surface porosity of 56.81%; inorganic microfractures come a close second, accounting for 29.96%; followed by OM pores, representing 12.06%; and OM microfractures are rare, as shown in Figure 13b.

Mixed shales have a pore size distribution characteristic similar to that of siliceous shales (Figure 12c). More than 90% of the pores in mixed shales are OM pores and inorganic pores, accounting for 47.01 and 46.95%, respectively. In the four types of shales, mixed shales possess the largest proportion of OM microfractures, sharing 5.09%, while inorganic microfractures are rare. Meanwhile, mixed shales have a relatively greater surface porosity of 2.35%, provided by pores with radii ranging from 20 to 120 nm (Figure 13c). More than half of the surface porosity is provided by inorganic pores, followed by OM pores and inorganic microfractures, accounting for 25.11 and 16.17%, respectively.

Argillaceous shales have the fewest pores (45,273) and pore size distributions similar to those of argillaceous−siliceous shale, shown in Figure 12d. Inorganic pores share 80.78% of the total amount, followed by inorganic microfractures, accounting for 10.28%, while OM pores account for the most minor proportion of the four types of shale (8.69%). The surface porosity of argillaceous shale is the lowest, mainly supplied by pores with radii ranging from 10 to 50 nm and dominated by inorganic pores, sharing 63.26%, followed by inorganic microfractures and OM pores, which account for 29.3 and 6.98%, respectively, and the OM microfractures are less than 1%, as illustrated in Figure 13d.

The porosity contributed by the various pores and microfractures varies among lithofacies, and the inorganic pores provide more than a half the porosity, as shown in Figure 14. The quartz-rich siliceous and argillaceous−siliceous shale possess higher OM pores because biogenic origin quartz particles have stronger resistance to compaction and allow for the preservation and accumulation of OM pores.27 However, the argillaceous−siliceous and argillaceous shales are clay-rich, and pores associated with clay minerals are susceptible to
compaction during diagenesis, which is not conducive to the migration of OM and the generation of OM pores in shale.\(^{27}\)

The parameters of micropores and mesopores are quantitatively characterized based on the gas adsorption experiments (CO\(_2\) and N\(_2\)), which is listed in Table 3 and illustrated in Figure 15. Siliceous shales possess the largest PV and SSA, ranging from 0.02162 to 0.02634 cm\(^3\)/g and 25.74 to 32.42 m\(^2\)/g, with an average of 0.0243 cm\(^3\)/g and 28.05 m\(^2\)/g, respectively. The PV and SSA of mixed shales differ slightly from that of the siliceous shales, with averages of 0.0241 cm\(^3\)/g and 27.03 m\(^2\)/g, respectively. The PV and SSA of argillaceous–siliceous shales considerably decrease, with an average of 0.0218 cm\(^3\)/g and 24.01 m\(^2\)/g, respectively. In contrast, the PV and SSA of argillaceous shale are the lowest, averaging 0.0194 cm\(^3\)/g and 19.43 m\(^2\)/g, respectively. The PV of argillaceous shales is 19.91\% lower than that of siliceous shale, which suggests that the effect of lithofacies variation on the PV of shale is minor. In contrast, the SSA of siliceous shales is 39.11\% higher than that of argillaceous shale, which indicates that the lithofacies variation has a significant effect on the SSA.\(^{27}\)

### 5.2. Controlling Factors of Pore Structural Characteristics

The shales of the Wufeng–Longmaxi formation in the studied area are dominated by quartz and clay minerals, and the pore structure characteristics are closely correlated with OM. The PV and SSA of pores are strongly positively correlated with the TOC content as illustrated in Figure 16a,d, which is consistent with Xu et al.\(^{27,32}\) and it implies that the micropores and mesopores mainly consist of OM pores and OM provides more PV and SSA. Meanwhile, the mesopore volume has a moderate positive correlation with quartz, while the micropores are not nearly related to it (Figure 16b,e). These findings indicate that the inorganic pores associated with quartz are larger. Besides, biogenic origin quartz particles formed a rigid framework, thus allowing for the formation and preservation of OM pores.\(^{45}\) Furthermore, point-to-point authigenic siliceous minerals are conducive to the migration of OM in shale.\(^{27,32,51}\) However, the PV and SSA of micropores and mesopores have a moderate–strong negative correlation with clay content (Figure 16c,f), because shales with a high clay content are susceptible to a great reduction in pore due to compaction. Although clay minerals can provide more PV and SSA, the TOC content decreases as the clay mineral content increases, as illustrated in Figure 2c, and it suggests that the volume and SSA increases in pores associated with clay minerals are lower than the volume decreases in micropores and mesopores associated with OM,\(^{27,32,51}\) as illustrated in Figure 16.

### 5.3. Controlling Factors of Fractal Dimension Characteristics

The correlation between fractal dimensions and pore structural characteristics is illustrated in Figure 16g,h, which is consistent with Xu et al.\(^{27,32}\) and it implies that the micropores and mesopores mainly consist of OM pores and OM provides more PV and SSA. Meanwhile, the mesopore volume has a moderate positive correlation with quartz, while the micropores are not nearly related to it (Figure 16i,j). These findings indicate that the inorganic pores associated with quartz are larger. Besides, biogenic origin quartz particles formed a rigid framework, thus allowing for the formation and preservation of OM pores.\(^{45}\) Furthermore, point-to-point authigenic siliceous minerals are conducive to the migration of OM in shale.\(^{27,32,51}\) However, the PV and SSA of micropores and mesopores have a moderate–strong negative correlation with clay content (Figure 16k,l), because shales with a high clay content are susceptible to a great reduction in pore due to compaction. Although clay minerals can provide more PV and SSA, the TOC content decreases as the clay mineral content increases, as illustrated in Figure 2c, and it suggests that the volume and SSA increases in pores associated with clay minerals are lower than the volume decreases in micropores and mesopores associated with OM,\(^{27,32,51}\) as illustrated in Figure 16.

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**Table 3. Pore Characteristic Parameters of Shale Samples Measured by CO\(_2\) and N\(_2\) Adsorption**

| sample ID | lithofacies                     | micropore PV (cm\(^3\)/g) | mesopore PV (cm\(^3\)/g) | total PV (cm\(^3\)/g) | micropore SSA (m\(^2\)/g) | mesopore SSA (m\(^2\)/g) | total SSA (m\(^2\)/g) | average pore diameter (nm) |
|-----------|---------------------------------|----------------------------|--------------------------|------------------------|---------------------------|--------------------------|-------------------------|---------------------------|
| S1        | siliceous shale                 | 0.00798                    | 0.01720                  | 0.02518                | 19.578                    | 6.163                    | 25.741                  | 5.1654                    |
| S2        |                                  | 0.00849                    | 0.01785                  | 0.02634                | 24.972                    | 7.449                    | 32.421                  | 4.2171                    |
| S3        |                                  | 0.00652                    | 0.01510                  | 0.02162                | 19.875                    | 7.364                    | 27.239                  | 3.7394                    |
| S4        |                                  | 0.00855                    | 0.01536                  | 0.02391                | 20.235                    | 6.582                    | 26.817                  | 4.4890                    |
| AS1       | argillaceous–siliceous shale    | 0.00754                    | 0.01631                  | 0.02385                | 19.217                    | 5.858                    | 24.081                  | 4.4193                    |
| AS2       |                                  | 0.00770                    | 0.01402                  | 0.02172                | 20.792                    | 5.486                    | 26.278                  | 5.5001                    |
| AS3       |                                  | 0.00602                    | 0.01371                  | 0.01973                | 16.531                    | 5.637                    | 22.168                  | 4.7177                    |
| AS4       |                                  | 0.00584                    | 0.01348                  | 0.01932                | 14.845                    | 5.784                    | 20.629                  | 4.2894                    |
| AS5       |                                  | 0.00711                    | 0.01729                  | 0.02440                | 19.428                    | 6.745                    | 26.173                  | 4.2198                    |
| M1        | mixed shale                     | 0.00800                    | 0.01646                  | 0.02446                | 20.930                    | 6.338                    | 27.268                  | 4.1050                    |
| M2        |                                  | 0.01000                    | 0.01574                  | 0.02574                | 24.540                    | 6.335                    | 30.875                  | 4.4460                    |
| M3        |                                  | 0.00702                    | 0.01589                  | 0.02291                | 19.455                    | 5.883                    | 25.338                  | 4.2319                    |
| M4        |                                  | 0.00659                    | 0.01660                  | 0.02319                | 18.078                    | 6.542                    | 24.620                  | 4.2319                    |
| A1        | argillaceous shale              | 0.00371                    | 0.01446                  | 0.01817                | 10.143                    | 5.233                    | 15.376                  | 6.1550                    |
| A2        |                                  | 0.00532                    | 0.01294                  | 0.01826                | 12.588                    | 5.485                    | 18.073                  | 6.8710                    |
| A3        |                                  | 0.00787                    | 0.01421                  | 0.02208                | 17.887                    | 6.172                    | 24.059                  | 3.9963                    |
| A4        |                                  | 0.00607                    | 0.01321                  | 0.01928                | 14.760                    | 5.436                    | 20.196                  | 4.4461                    |

**Figure 15.** Relationship between lithofacies and PV (a); relationship between lithofacies and SSA (b).
The fractal dimension ($D_1$ and $D_2$) is strongly positively correlated with the TOC content (Figure 16a), and the effect on $D_1$ is slightly higher than that on $D_2$. Meanwhile, quartz has a strong positive correlation with $D_1$, while there is no correlation with $D_2$ (Figure 17b). This result is consistent with the fractal dimension characteristics of shale lithofacies (Figure 10). The reason is that OM pores well developed in organic-rich siliceous shales provided more PV and SSA (Figures 4a, 12a, and 13a), and the pore form factors of organic-rich siliceous shales are generally greater than those of argillaceous shales, which suggests the more complicated pore boundary of organic-rich shale, as illustrated in Figure 4a,c. This implies that siliceous shales have the most methane...
adsorption site, that is, the highest adsorption capacity. However, the clay mineral content has a strong negative correlation with fractal dimension D1 and a weak–moderate negative correlation with fractal dimension D2 (Figure 17c), due to the more concentrated surface height distribution of clay-rich argillaceous shales.52 The reason is that triangle or slit-shaped pores between the clay minerals are susceptible to compaction in clay-rich shales. Furthermore, there is an extremely strong negative correlation between the fractal dimensions and average pore diameter, which indicates that clay-rich argillaceous shales contain larger pores with simple boundaries (Figure 17d).

6. CONCLUSIONS

In this study, the pore structure characteristics of shales with different lithofacies were investigated in the marine Wufeng–Longmaxi formation of the southern Sichuan Basin, China. The fractal dimensions were calculated by the WL and FHH models; then, the relationship between pore structure characteristics and lithofacies was analyzed. Furthermore, the controlling factors of shale pore structures characteristics, such as TOC content and quartz as well as clay minerals, were discussed. According to the above results, the main conclusions from this study are summarized as follows:

1. The marine Wufeng–Longmaxi formation shales are classified into four types based on mineral composition: siliceous shale, argillaceous–siliceous shale, mixed shale, and argillaceous shale. Siliceous shales possess the largest SEM-based surface porosity of 2.84% and the largest PV as well as SSA, with an average of 24.26 × 10−3 cm3/g and 28.06 m2/g, respectively. In contrast, the PV and SSA of argillaceous shale are the lowest, averaging 19.45 × 10−3 cm3/g and 19.43 m2/g, respectively.

2. The effect of lithofacies variation on the PV of shale is minor, while the SSA of siliceous shales is 39.11 % higher than that of argillaceous shale. PV and SSA are strongly positively correlated with the TOC content but negatively correlated with clay minerals. Moreover, TOC content has a great impact on the SSA. The PV and SSA increases in micropores and mesopores associated with clay minerals are lower than the PV and SSA decreases in micropores and mesopores associated with OM.

3. Siliceous shales have the largest fractal dimension D1 (pore surface roughness), with an average of 2.6821, which is contributed by abundant OM pores with more complicated boundaries. The largest fractal dimension D2 (pore structure complexity) (average 2.8263) is found in mixed shales, which is attributed to well-developed intraP pores associated with carbonate mineral dissolution. This indicates that siliceous shales have the highest methane adsorption capacity, and it is more difficult for gas desorption, diffusion, and seepage in mixed shale.

AUTHOR INFORMATION

Corresponding Authors
Xizhe Li — Research Institute of Petroleum Exploration and Development, PetroChina, Beijing 100083, China; Email: lixiz69@petrochina.com.cn
Weijun Shen — Key Laboratory for Mechanics in Fluid Solid Coupling Systems, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China; School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China; Email: wjshen763@imech.ac.cn

Notes
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