Evaluation of Nanoscale Accessible Pore Structures for Improved Prediction of Gas Production Potential in Chinese Marine Shales

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Supporting Information

ABSTRACT: The Lower Cambrian Niutitang and Lower Silurian Longmaxi shales in the Upper Yangtze Platform (UYP) are the most promising strata for shale gas exploration in China. Knowledge of the nanoscale pore structure may improve the prediction of the gas production potential in Chinese marine shales. A systematic investigation of the pore accessibility and its impact on methane adsorption capacity has been conducted on shale samples using various techniques including geochemical and mineralogical analyses, field emission scanning electron microscopy (FE-SEM), small-angle neutron scattering (SANS), helium porosimetry, and methane adsorption. The results show that organic matter (OM) pores with various shapes dominate the pore systems of these shales. OM tended to mix with clay minerals and converted to organoclay complexes, developing plentiful micro- and mesopores. A unified fit model with two pore structures, fractal pores and finite pores, was used to model the SANS data to characterize the pore structure of the shales. Both mass and surface fractals are identified for each pore structure. The total porosity estimated by the Porod invariant method ranges between 2.35 and 16.40%, of which the porosity for finite pores ranges between 0.35 and 6.36%, and the porosity for the fractal pores ranges between 2.07 and 8.51%. The fraction of open pores was evaluated by comparing the porosities estimated by He porosimetry and SANS. We find that the fraction of open pores is higher than 64% for most of these shales. Correlation analyses suggest that clay and total organic carbon (TOC) have opposite effects on pore structure and methane adsorption capacity. Samples with higher clay contents have higher pore accessibility and lower total porosity, surface area, and maximum methane adsorption, whereas samples with higher TOC content show the inverse relationships. The high percentage of open pores may reduce methane adsorption capacity in these shales, whereas low pore accessibility may reduce methane production at specific pressure differences. Thus, both TOC and pore accessibility may be essential controlling factors in methane production from shale gas reservoirs.

1. INTRODUCTION

In response to growing worldwide energy demands, shale gas is becoming an increasingly valuable energy resource. Following the shale gas revolution in North America and the development of the techniques of horizontal drilling and hydraulic fracturing, intensive efforts in shale gas explorations have been conducted in China. Unlike conventional gas reservoirs, “shale gas reservoirs” are self-contained source reservoir systems that are generally characterized by high total organic carbon (TOC) contents compared to conventional gas reservoirs, complex mineral compositions, low porosities, and low permeability matrices with extensive, heterogeneous, nanoscale pores. This nanoscale pore structure is one of the key factors influencing the occurrence, storage capacity, and flow behavior of gas in these reservoirs. Shale gases occur as both adsorbed and free gas and are thus directly affected by the nanoscale pore structure. Quantitative characterization of this nanoscale pore structure is, therefore, essential for evaluating gas production potential and providing clues to increasing gas extraction efficiency.

Due to the diversity, complexity, and heterogeneity of shale pore structures, it is difficult to characterize pore structures using a single technique. A variety of techniques have, therefore, been used to characterize the pore structures of shales, in particular their porosity, pore volume, and specific surface area. Direct imaging methods, including field emission-
scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and focused ion beam-scanning electron microscopy (FIB-SEM), have been successfully employed to observe the pore morphology and connectivity of pore networks. However, these direct imaging techniques assess only limited areas of a sample at a given time, and thus, their statistical reliability is limited. Indirect methods, including helium porosimetry, mercury intrusion porosimetry, and low-pressure N2/CO2 adsorption, are also commonly used to quantitatively characterize the pore size distribution, pore volume, and specific surface area of shales; however, these techniques typically interrogate larger sample volumes and can only characterize accessible pores and those with pore diameters larger than that of the probe molecule. Thus, adsorption techniques are unable to provide information about closed porosity. In contrast, small-angle neutron scattering (SANS), a nondestructive physical technique, can be used to characterize both accessible and closed pores, since it records the scattering intensity from all pores within the detectable size range. Closed pores may play an essential role in gas shale production because they may contain methane, and thus, the efficiency of gas recovery may depend on the extent to which they can be accessed. Given the apparent strengths and weaknesses of each of these approaches, therefore, a combination of different characterization techniques should lead to a more precise prediction of gas production potential.

The marine shales in the Upper Yangtze Platform (UYP), the Lower Silurian Longmaxi Formation, and the Lower Cambrian Niutitang Formation are the primary targets for shale gas exploration and development in China because of their widespread occurrence, large thicknesses, organic richness, and favorable mineral compositions. Compared to the Longmaxi shales, the Niutitang shales have been more deeply buried and have a higher thermal maturity. In addition, high initial gas production rates of \( (10^{−50}) \times 10^4 \) m\(^3\) per day have been reported for most pilot wells in the Jiaoshiba area of the Longmaxi shales. The breakthrough discovery of this shale gas field represents a significant milestone for shale gas exploration in China.

In order to provide a more thorough assessment of the pore structures and gas production potential of the UYP, a series of pore structure characterization techniques were applied to characterize pore morphologies, porosities, pore volumes, and specific surface areas of the marine shales from the Lower Cambrian Niutitang and Lower Silurian Longmaxi Formations. In this study, we have used a combination of FE-SEM, SANS, helium porosimetry, and high-pressure methane adsorption to investigate pore accessibility and its effect on methane adsorption. Uniquely, the correlations between pore accessibility and methane adsorption properties indicate that pore accessibility could be an indicator for methane production from shale gas reservoirs. The results will be broadly applicable to shale gas exploration and development including reservoir assessment and evaluation, gas-in-place estimation, carbon sequestration, and other characteristics of the UYP.

2. MATERIALS AND METHODS

2.1. Sample Collection. The UYP is located in the western portion of the Yangtze Platform in southern China (Figure 1). It includes the Chongqing city, northern Guizhou and Yunnan, western Hubei and Hunan, and eastern Sichuan province. Geological studies indicate that the Niutitang Formation and the Longmaxi Formation formed on a neritic shelf with a stagnant marine sedimentary environment. These marine shales are currently the most prominent exploration and production targets for shale gas in China.
A total of six shale samples were analyzed in this study. Four fresh Longmaxi Formation shale core samples were collected from the WX1 well, located in northeast Chongqing near the edge of the Sichuan Basin. Two fresh Niutitang Formation shale core samples were collected from the QD1 well located in northeast Yunnan near the southwestern edge of the UYP. Both of these shales are widely distributed around the UYP. Although both are thermally immature, the thermal maturity of the Niutitang shales is much greater than that of the Longmaxi shales, which indicates that the Niutitang Formation experienced more severe compaction and underwent more complicated diagenesis than the Longmaxi Formation.

2.2. Geochemical and Mineralogical Tests. Geochemical parameters and mineral compositions were characterized for all of the shale samples measured in this study. Analysis of TOC content was performed using a LECO CS-230 carbon and sulfur analyzer. Due to the lack of vitrinite in the Lower Paleozoic shales, the reflectance of pyrobitumen was measured using a Leica MPV-SP microphotometer. The average pyrobitumen reflectance was then converted to an equivalent vitrinite reflectance (EqVR) using the equation of Schoenherr et al. (2007), i.e., EqVR = (BR + 0.2443)/1.0495, where BR is the pyrobitumen reflectance.22 The mineralogy of each sample was obtained using a RIGAKU D/Max-3B type X-ray diffractometer (XRD). Preparation, analysis, and interpretation procedures were conducted following the Chinese Oil and Gas Industry Standard SY/T 5163-2010. Multicomponent quantifications were achieved by Rietveld refinement using the TOPAS software package. All analyses were carried out at the Experimental Research Center of East China Branch, SINOPEC.

2.3. FE-SEM. FE-SEM observations were performed using a Quanta 200F instrument at the China University of Petroleum, Beijing Campus (CUP). The FE-SEM images provide a spatial resolution of 1.2 nm, which is sufficient to characterize the nanoscale pore morphology. Before the experiment, the samples were prepolished using an argon ion beam to create an artifact-free surface. Au was then coated onto the artifact-free surface to improve the image quality by enhancing the electrical conductivity. The experiment and subsequent analysis were carried out at a constant temperature of 24 °C and a constant humidity of 35%. High-resolution images were obtained at an accelerating voltage of 10−15 kV with a working distance of 4−5 mm.

2.4. SANS. Of the six samples analyzed by SANS in this study, the first two (WX2-8 and WX3-33) were analyzed as powders and the other four (QD1-L3, QD1-L4, WX2-49, and WX2-54) as disks. Analysis of the powdered shales was conducted using the general-purpose small-angle neutron scattering diffractometer (GP-SANS) at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL).23 The samples had a nonuniform particle size of <0.5 mm and an overall sample thickness of 1.6 mm. These samples were measured under ambient conditions with sample-to-detector distances of 1.1, 8.8, and 19.2 m. The neutron wavelength \( \lambda \) was set at 4.75 Å for the 1.1 and 8.8 m measurements and 12 Å for the 19.2 m measurements to extend the scattering vector Q range to values as small as possible (the largest sizes possible), where \( Q = 4\pi \sin \theta /\lambda \) and \( \theta \) is half of the neutron scattering angle. The overall Q range was between \( 1.5 \times 10^{-3} \) and \( 0.8 \times 10^{-2} \) Å\(^{-1}\), which corresponds to pore sizes between \( \sim 3 \) and \( \sim 1.6 \times 10^{-3} \) Å using the empirical relation \( R \approx 2.5 / Q \).16 The absolute scattering intensities were obtained using measured sample transmission and thickness values as well as a standard scattering intensity measured on porous silica.46 All of the 1D scattering curves were obtained using the NCNR Igor macros package.

In order to reduce multiple scattering, especially at low Q and long wavelengths,25,47 the remaining samples were analyzed as thin disks with an arbitrary orientation, using the method outlined by Anovitz et al. These analyses were performed using the NG-7 30m small-angle neutron scattering diffractometer (NG7-SANS) at the NIST Center for Neutron Research (NCNR) at the National Institute of Standards and Technology (NIST).24 Four thin disk shale samples were commercially polished to a thickness of 0.1 mm and mounted on 1 mm thick quartz glass slides.24,47 These samples were analyzed with the normal to the incident beam and under ambient conditions. Four SANS geometries were used: 1 and 4 m sample-to-detector distances and a 13 m distance with and without a set of biconvex MgF\(_2\) lenses. The neutron wavelength was set at 6 Å for SANS geometries of 1, 4, and 13 m and at 8.1 Å for the configuration with the lenses. These settings cover a scattering vector Q range between \( \sim 1 \times 10^{-3} \) and \( \sim 0.6 \times 10^{-2} \) Å\(^{-1}\), which corresponds to a pore size range between \( \sim 4 \) and \( \sim 2.5 \times 10^{-3} \) Å.

2.5. Porosity Using Helium Porosimetry. The total accessible porosity of the shale samples was determined at the Experimental Research Center of East China Branch, SINOPEC, using a technique based on Boyle’s law, by measuring the grain volume under ambient conditions and bulk volume by Archimedes’ principle with helium porosimetry.12 Samples were oven-dried at 115 °C to a constant mass (±1 mg). Porosity was calculated from the difference between bulk volume and grain volume.

2.6. High-Pressure Methane Adsorption. High-pressure methane adsorption isotherms were measured at a constant temperature of 40 °C and pressure up to 9 MPa using a volumetric sorption apparatus (IS-300 isothermal adsorption/desorption analyzer) manufactured by Terratek, USA. Before the adsorption measurement, samples were crushed to a particle size of less than 250 \( \mu \)m (60 mesh) and dried for 24 h at 105 °C. The detailed methane adsorption measurement procedure is described by Ji et al.49 Methane sorption data were normalized to sample weight and parametrized using the Langmuir monolayer adsorption model.50

3. RESULTS AND DISCUSSION

3.1. Geochemical and Mineralogical Parameters. Detailed geochemical and mineralogical characteristics of the marine shale samples are listed in Table 1. Mass fraction is used for the chemical compositions. TOC contents range between 1.52 and 6.33 wt %. The marine shales in UYP have experienced strong thermal maturation and reached the postmature stage with EqVR values ranging from 2.06 to 3.03%.

XRD analysis demonstrates that both Cambrian Niutitang shales and Silurian Longmaxi shales have complex mineralogy (Table 1 and Figure 2). Quartz and clay are the major components with an average of 49.3 wt % (38.0−56.6 wt %) and 28.9 wt % (22.0−41.0 wt %), respectively. Figure 2a shows that these shales also contain pyrite, calcite, dolomite, K-feldspar, and plagioclase. Illite is the most abundant clay mineral ranging between 10.6 and 26.3 wt % with a mean value of 17.4 wt %. Figure 2b shows the other clay minerals including smectite, chlorite, and illite/smectite mixed layer clays.

3.2. Qualitative Pore Morphology Characteristics Using FE-SEM. Pore structure has an enormous impact on the occurrence of shale gas, the calculation of gas in place (GIP), and hydraulic fracturing. Qualitative analysis of pore morphology helps reveal the origin of nanoscale pores and the nature of microscopic pore structures. On the basis of detailed pore classifications proposed in previous studies,6,9,51,52 we have divided the pores observed in our marine shales into four categories: interparticle (interP) pores, intraparticle (intraP) pores, organic matter (OM) pores, and microfractures.

FE-SEM observations (Figure 3) suggest that OM pores dominate the pore system of the marine shales. Their diameters vary from several to hundreds of nanometers, and they display various shapes such as spherical to ellipsoidal, schistose-like, irregular polygons, and honeycombs (Figure 3a−c). OM pores are well-developed and often form pore networks with functional connectivity. Since these shales have reached the overmature stage, it is likely that OM pores were formed gradually during thermal evolution. Furthermore, OM does not, necessarily, exist in isolation. OM is commonly intergrown with pyrite framboids (Figure 3b and c), forming a large number of nanoscale pores (pore size in the nanometer range). OM also tends to partially mix with clay minerals (Figure 3a), becoming
Table 1. Chemical Composition of the Six Chinese Marine Shales

<table>
<thead>
<tr>
<th></th>
<th>Quartz (wt %)</th>
<th>K-feldspar (wt %)</th>
<th>Plagioclase (wt %)</th>
<th>Dolomite (wt %)</th>
<th>Calcite (wt %)</th>
<th>Pyrite (wt %)</th>
<th>Clay (wt %)</th>
<th>Illite/smectite mixed layer (wt %)</th>
<th>TOC (wt %)</th>
<th>EqVRr (wt %)</th>
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<tbody>
<tr>
<td>Niutitang (ϵ1)</td>
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<tr>
<td>QD1-L3</td>
<td>46.61</td>
<td>4.64</td>
<td>7.25</td>
<td>1.35</td>
<td>5.61</td>
<td>1.64</td>
<td>29.59</td>
<td>15.09</td>
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<tr>
<td>QD1-L4</td>
<td>54.15</td>
<td>1.44</td>
<td>3.64</td>
<td>6.98</td>
<td>2.39</td>
<td>27.08</td>
<td>19.61</td>
<td>1.15</td>
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<td>WX2-33</td>
<td>46.33</td>
<td>9.60</td>
<td>2.94</td>
<td>13.71</td>
<td>3.82</td>
<td>21.54</td>
<td>10.38</td>
<td>2.55</td>
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<td>Longmaxi (S1)</td>
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<td>WX2-49</td>
<td>49.41</td>
<td>1.15</td>
<td>5.27</td>
<td>3.26</td>
<td>9.10</td>
<td>27.58</td>
<td>16.09</td>
<td>1.53</td>
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<tr>
<td>WX2-54</td>
<td>50.77</td>
<td>3.09</td>
<td>8.43</td>
<td>5.27</td>
<td>11.5</td>
<td>8.32</td>
<td>6.90</td>
<td>3.35</td>
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</table>

In contrast to OM and intraP pores, interP pores are susceptible to mechanical compaction and difficult to preserve. InterP pores are usually developed at the points of contact between particles. They exist between the contact areas of OM and clay minerals and along the pyrite and quartz grains (Figure 3d and i). The distribution of interP pores observed in these samples was quite heterogeneous with low connectivity.

Various kinds of microfractures were observed in the tested shales. Some microfractures were observed within unstable minerals and appeared to be formed as a result of dissolution (Figure 3f). Microfractures within OM are usually related to hydrocarbon generation (Figure 3h). Some microfractures were also developed within clay minerals (Figure 3h). Typically, these are 20–100 nm wide and about 3 μm long. Note that the origin of the microfractures in clay minerals remains uncertain which is likely formed due to clay shrinkage, either during diagenesis or perhaps secondarily as a result of core sample recovery and processing. Meanwhile, nanoscale pores and microfractures are also influenced by mechanical compaction, since both Longmaxi and Niutitang Formations experienced multiphase tectonic movements. Figure 3i shows that microfractures connect micro pores (pore size <2 nm) and macropores (pore size >50 nm), which can improve the connectivity of the pore networks. Therefore, microfractures not only provide space for free and adsorbed gas to accumulate but may serve an important role in shale gas migration.

3.3. Quantitative Pore Structure Characteristics Using SANS. 3.3.1. Experimental Scattering Intensities. Figure 4 shows the background-subtracted 1D scattering profiles on logarithmic scales for the six Chinese marine shale samples tested. In each case, the log of the intensity decreases nearly linearly with increasing log(Q) over the entire measured Q range, although careful examination by plotting log(Q²f(Q)) as a function of log(Q) shows that this is not completely true, especially for samples WX2-8 and WX2-33. This scattering profile is typical for shales in this Q range.

The scattering intensities measured for the two Niutitang samples and one of the Longmaxi samples, QD1-L3, QD1-L4, and WX2-49 (all disk samples), were similar over the measured Q range, indicating that the total pore volumes and pore volume distributions in this size range (between ~0.4 and ~250 nm) among these samples are quite similar. The scattering intensity of WX2-54 is the highest among the tested samples over the entire Q range, and the slope of the scattering curve is shallower. This indicates that the total pore volume of WX2-54 is greater than the other five samples over this specific size range and that this difference is probably the largest at smaller pore sizes. At the opposite extreme, the scattering intensity of WX2-8 is smaller than that of the other five samples at Q > ~0.01 Å⁻¹, implying converted to organoclay complexes with a full range of micro/mesopores sizes (pore size <50 nm). IntraP pores are another major contributor to the porosity of these marine shales. This type of pore is mainly associated with pyrite framboids, clay aggregates, and dissolution of unstable minerals such as plagioclase and calcite (Figure 3f). Pyrite framboids were observed in these shales, and nanoscale pores were commonly observed between individual pyrite crystals. These were probably formed by incomplete cementation or dissolution of the pyrite grains (Figure 3d and g). Figure 3e shows an example of intraP pores within clay mineral aggregates displaying a “card house” structure. This provides interconnected pores which may serve as essential pathways enhancing gas permeability.
that this sample has a smaller total pore volume over this pore range compared to the others. A hump is present at low $Q$ for samples WX2-8 and WX2-33, and there is a broad hump in the data for WX2-54 around 0.03 Å$^{-1}$ ($\sim$8 nm). A small hump in the scattering profile was also observed for samples QD1-L4, WX2-8, and WX2-49 around 0.2 Å$^{-1}$. Similar results have been seen in both SANS and SAXS data for shales, coals, and sandstones. Interestingly, a hump that is typically observed in the SAXS profiles of coal samples is absent in the SANS profiles for the same samples. Thus, these may be caused by the interlayer spacing of clays in QD1-L4, WX2-8, WX2-49, and WX2-54.

### 3.3.2. Pore Structure Determination.

In order to quantitatively characterize the nanopore structure of the tested shales, we have applied an empirical SANS model that combines Guinier and power-law equations to fit the experimental SANS data. In this unified model, the scattering intensity $I(Q)$ is expressed as:

$$I(Q) = \sum_{i=1}^{n} G_i e^{-Q R_g^{\frac{2}{3}}/3} + B \left[ \frac{\text{erf} \left( \frac{Q R_g}{\sqrt{6}} \right)}{Q} \right]^{3/2} + \text{Bkg} \tag{1}$$

where $Q$ is the scattering vector; $G$ is the Guinier coefficient, which is equal to the scattering intensity at $Q = 0$; $R_g$ is the radius of gyration representing a domain size; $B$ is the power-law coefficient; $\alpha$ is the power-law exponent; $i$ is the number of the pore structure, as several independent pore structures can be fitted with this model; $n$ is the total number of pore structures considered; and Bkg is the scattering background. On the basis of the experimental scattering data shown in Figure 4, the presence of power-law scattering at low and medium $Q$ implies the existence of a fractal pore structure in the tested shales, with the exceptions of WX2-8 and WX2-33. Furthermore, both the deviation in the scattering intensity from power-law scattering at high $Q$ and the "humps" may reflect additional fractal pore structures with finite size ranges. Thus, a model with two pore structures based on eq 1 (with $n = 2$) has been used to fit the data for the shale samples.

The first reflects the power-law scattering for a fractal pore structure (fractal pores); the second is fitted with a combined Guinier and power-law model and reflects a fractal pore structure with a finite pore range (finite pores).

Fitting eq 1 to the scattering data for each shale sample was performed using the Irena software package. The results are shown in Figure S1 in the Supporting Information, and detailed model parameters are listed in the Supporting Information tables. Note that, because the thickness of the samples led to excess multiple scattering at low $Q$ for samples WX2-8 and WX2-33, the low $Q$ cutoff of model fitting was chosen at the linear range in the log($I(Q)$) vs log($Q$) plot. The modeled scattering intensity was then extrapolated to the experimental low $Q$ limit for each sample, as shown in Figure S1c and d. When the value of the fitted power-law exponent $\alpha$ is between 3 and 4, the data may

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**Figure 2.** Chemical composition of the six Chinese marine shales: (a) total mineral contents; (b) clay mineral contents.
be interpreted as a surface fractal with dimensionality $D_s$ given by $D_s = 6 - \alpha$, so that $D_s$ lies between 2 and 3. When the value of $\alpha$ was smaller than 3, the correlation $D_m = \alpha$ was used to estimate the mass fractal dimension $D_m$.47,65

The estimated fractal dimensions for these shale samples are shown in Table 2. For the finite pores, the model yields mass fractal dimensions between 1.94 and 2.68 except for sample QD1-L4, which suggests a surface fractal dimension of 2.85. For the fractal pores, samples QD1-L4, WX2-49, and WX2-54 have mass fractal dimensions $D_m$ between 2.84 and 2.93, whereas samples QD1-L3, WX2-8, and WX2-33 generate surface fractal dimensions $D_s$ ranging between 2.42 and 2.78. The sample preparation procedure could be the reason for the existence of both mass and surface fractals in the shales tested. The unified
model suggests that the pore structure of the finite pores has a maximum pore size ranging between ∼3.8 and ∼7.8 nm assuming spherical pore shape, where $R_g = \frac{3}{5} R$, as the radius of gyration $R_g$ ranges between ∼3.0 and ∼6.1 nm (Tables S2–S7 in the Supporting Information). This represents the maximum domain size of this structure, which is within the meso/micropore size range. The results also indicate that the shale pores have different fractal characteristics at different pore sizes.

Both the total porosity and the porosities of each pore structure were estimated using the Porod invariant method. The Porod invariant $Q_{INV}$ can be expressed as

$$Q_{INV} = \int_{Q_{min}}^{Q_{max}} Q^2 I(Q) dQ = 2\pi^2 (\rho_s^* - \rho_p^*)^2 \phi (1 - \phi)$$

(2)

where $\rho_s^*$ and $\rho_p^*$ are the scattering length densities (SLDs) of the solid matrix and pores, respectively; $Q_{max}$ and $Q_{min}$ are the experimental maximum and minimum $Q$ values, respectively; and $\phi$ is the porosity. Here we assume that the SLD is the same for the fractal and finite pores for porosity estimation. Nonetheless, if one were primarily OM filled, or one contrasted with a different mineral than the other, the SLDs could be different, although probably not very different. The value of $\phi$ estimated for each pore structure and the total porosity for all samples are shown in Table 2. Note that the $Q$ range for porosity estimation was confined between $\sim 1.5 \times 10^{-3}$ and $\sim 0.5 \text{ Å}^{-1}$. $\phi$ total and each pore structure were estimated from the total scattering intensity and scattering intensity of each pore structure, respectively. The experimental scattering intensity is used to estimate $\phi$ total, while the modeled scattering intensity is used to estimate $\phi$ for each pore structure.

**Table 2. Fractal Dimension $D$ and Porosity $\phi$ for the Six Chinese Marine Shales**

<table>
<thead>
<tr>
<th>formation</th>
<th>sample ID</th>
<th>finite pores</th>
<th>fractal pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niutitang (ε1)</td>
<td>QD1-L3</td>
<td>2.64 ± 0.05</td>
<td>2.78 ± 0.01</td>
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<tr>
<td></td>
<td>QD1-L4</td>
<td>2.85 ± 0.31</td>
<td>2.89 ± 0.01</td>
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<tr>
<td>Longmaxi (S1)</td>
<td>WX2-8</td>
<td>2.68 ± 0.04</td>
<td>2.42 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>WX2-33</td>
<td>2.34 ± 0.01</td>
<td>2.55 ± 0.00</td>
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<tr>
<td></td>
<td>WX2-49</td>
<td>1.94 ± 0.06</td>
<td>2.93 ± 0.01</td>
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<tr>
<td></td>
<td>WX2-54</td>
<td>2.26 ± 0.06</td>
<td>2.84 ± 0.02</td>
</tr>
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</table>

"The $Q$ range for porosity estimation is between $\sim 1.5 \times 10^{-3}$ and $\sim 0.5 \text{ Å}^{-1}$. $\phi$ total and each pore structure were estimated from the total scattering intensity and scattering intensity of each pore structure, respectively. The experimental scattering intensity is used to estimate $\phi$ total, while the modeled scattering intensity is used to estimate $\phi$ for each pore structure."
estimate \( \phi \) total while the modeled scattering intensity is used to estimate \( \phi \) for each pore structure. Another reason could be the assumption of equal SLDs for the total, fractal, and finite pores, which may be different. With the exception of sample QD1-L3, the pore volume of the finite pores is generally smaller than that of the fractal pores.

3.3.3. Pore Structure Affected by Shale Properties. With the exception of sample WX5-49, there may be a U-shaped correlation between the fractal dimension and TOC for the finite pores (Figure 5b), while \( D \) increases and then becomes generally constant with increasing TOC for the fractal pores (Figure 5b). The maximum fractal dimension, including both mass and surface fractals, occurs at \( \sim 27\% \) clay content and \( \sim 4.2\% \) TOC, as shown in Figure 5a and b. This implies that the maximum complexity of shale fractal pore structure could require specific clay and carbon contents. In contrast, there is no obvious correlation between the fractal dimension of the finite pores and clay content and at best a weak decreasing or U-shaped one for the fractal pores (Figure 5a).

Parts c and d of Figure 5 show the total porosity and the porosities of the pore structures estimated by both SANS and helium porosimetry as a function of clay and TOC contents. Negligible correlations between the concentrations of other minerals and porosity were found; they do not seem to be controlling factors for methane adsorption in these shales.27 However, parts c and d of Figure 5 show that, in general, the SANS total porosity, the porosity of each pore structure, and the helium porosity increase with increasing TOC. There is no obvious or weak correlation for clay content. The results show a relatively strong correlation for TOC (\( R^2 > 0.77 \)) as a function of porosity, indicating that TOC is a controlling factor in shale porosity. The weak correlation between clay and porosity may reflect variations in the types of clay minerals present, as different clay minerals may contribute to porosity differently.

3.4. Methane Adsorption Characteristics. 3.4.1. Adsorption Capacity Determination. Figure 6 shows the results of the methane adsorption isotherm measurements. Methane adsorption exhibited a two-stage change with increasing pressure for all samples measured. At low to moderate pressures (0–4 MPa), the adsorption capacity rapidly increased with increasing pressure, as indicated by the slope of the adsorption profile. When the adsorption pressure exceeded 4 MPa, however, the rate of sorption gradually decreased. However, although the overall sorption patterns are similar, the methane adsorption capacity dramatically varies among the different samples. In general, as shown in Figure 7b, the maximum adsorption capacity for methane in these shales increased as a function of TOC content.

The Langmuir adsorption model was used to fit the experimental methane adsorption isotherms.67 The Langmuir equation is usually recommended for describing methane adsorption in shale samples due to its practical advantages and simplicity, as it only contains two important adjustable parameters \( V_L \) and \( P_L \). The usual form of the Langmuir model is

\[
V = \frac{V_L P}{P_L + P}
\]

where \( P \) is the experimental pressure, \( V \) is the experimental adsorption capacity at each pressure, \( V_L \) is the Langmuir volume showing the theoretical maximum adsorption capacity, and \( P_L \) is the Langmuir pressure representing the pressure at which half of the theoretical maximum adsorption for a given sample occurs. As can be seen in Figure 6, this model fits the measured data (Table 3) quite well. The Langmuir volume, \( V_L \), varies from 0.47 to 3.62 cm\(^3\)/g, and the Langmuir pressure, \( P_L \), ranges from 0.76 to 3.30 MPa.

3.4.2. Adsorption Capacity Affected by Shale Properties and Pore Structure. Figure 7 shows the correlations between the Langmuir constants and the clay and TOC contents of the shales. While there is some scatter, the Langmuir volume generally decreases with increasing clay content and increases with increasing TOC (Figure 7a and b). This implies that clay minerals have a smaller methane adsorption capacity than organic matter. The Langmuir pressure \( P_L \), however, decreases with both increasing clay content and TOC (Figure 7c and d). Note that sample WX5-8 is an outlier in Figure 7d, possibly because this sample has the lowest TOC content (1.52%), the highest plagioclase (>14%) and clay mineral contents (>40%), and the lowest total porosity (2.35%) of the shale samples. \( P_L \) is the pressure at which half of the maximum adsorption volume is achieved, describing the affinity of the adsorbed gas for the adsorbent.50,68 Thus, the results indicate that the affinities of methane for clay and organic matter in shale may be similar, although the correlations for clay are much poorer than those for TOC. Again, this could be due to variations in adsorption capability among different clay minerals. Regardless, the strong correlations between the Langmuir constants and TOC (\( R^2 > 0.83 \)) suggest TOC may be a controlling factor for methane adsorption in shales.

In order to quantify the effects of pore structure on methane storage in shales, the correlations between the Langmuir constants and the pore structure parameters derived from the SANS data need to be investigated. Parts a and c of Figure 8 show that the correlations between fractal dimension and the Langmuir constants for the pore structure of the finite pores are negligible. However, there may be U-shaped correlations between the fractal dimension and the Langmuir constants for the pore structure of the fractal pores when the Langmuir constants are treated as the independent variables, with maximum values of about 2.5 mL/g for \( V_L \) and 2 MPa for \( P_L \). The correlations between the Langmuir parameters and porosity are, however, somewhat better. The Langmuir volume, \( V_L \), the maximum adsorption capacity, increases with increasing porosity (Figure 8b). This is reasonable because both porosity
(Figure 5d) and $V_L$ (Figure 7b) increase with increasing TOC. However, the Langmuir pressure, $P_L$, the affinity of methane molecules for the shale, decreases with increasing porosities, with WX2-8 again being an outlier (Figure 8d). This result also seems reasonable, as porosities (Figure 5d) and $P_L$ (Figure 7d) increase with increasing TOC. The results indicate that shale porosity has the opposite effect on the $V_L$ and $P_L$ values for methane; higher porosity yields higher $V_L$ but lower $P_L$ for shale.

### 3.5. Shale Pore Accessibility

The combination of helium porosimetry with the SANS data described above was used to investigate pore accessibility quantitatively. Table 4 shows the estimated fraction of accessible pores, $\phi$, for each of the shale samples. The $\phi$ should be an approximate value, since the pore range for SANS is approximate between 0.5 and 167 nm, while the pore size range of open pores measured by He porosimetry is larger than 0.2 nm. In most cases, the measured $\phi$ value is greater than 64%. This indicates that the matrix pores of the tested shales are highly accessible. The exception is sample WX2-33, which has the lowest total pore accessibility ($\phi = 40.26\%$) and helium accessible porosity ($1.22\%$) as well as the second lowest total porosity ($3.12\%$). This may be caused by the mineralogy of this sample. WX2-33 has the highest calcite content ($13.71\%$) of all of the samples investigated. Late calcite precipitation may have filled or sealed off many of the pores. For the other samples, however, the pore accessibility results indicate that the transport pathways for methane production and CO$_2$ sequestration are, in fact, relatively open. This suggests that, to the extent that these samples are representative of the two formations, after drilling and hydraulic fracturing are completed, a significant amount of natural gas should be extractable from the Longmaxi and Niutitang Formations, possibly making them essential Chinese shale gas resources.

Figure 9 shows the correlations between the accessible pore fraction and the clay/TOC contents. In contrast to the porosity correlations shown in Figure 5, the fraction of accessible pores, $\phi$, increases with increasing clay content (Figure 9a) and decreases with increasing TOC (Figure 9b). As noted above, however, sample WX2-33 is an outlier with a $\phi$ value smaller than 41%. These correlations indicate that the fraction of accessible porosity in clay minerals is greater than that in organic matter. Since the percentage of TOC (<6.4% for the tested shales) is small compared to the mineral content, $\phi$ remains greater than 64% for all of these shale samples except for WX2-33. Again, the high calcite content of that sample (13.71%) could be the cause of the low accessible porosity ($1.22\%$) and pore accessibility ($40.26\%$) for this sample.

Figure 10 shows the correlations between pore accessibility, $\phi$, and the fractal dimensions and total, fractal, and finite porosities. There are negligible correlations between the fractal dimensions and the pore accessibility. However, $\phi$ seems to be anticorrelated with each of the porosities (again with WX2-33 as an outlier). This may be because most of the inaccessible pores are in the organic matter, so that samples with high TOC yield low $\phi$ (Figure 9b) as well as high $\phi$ (Figure 5d). These results suggest TOC has a more complex structure than the mineral matrix and that the gas transport pathways are in the minerals.

### Table 3. Langmuir Volume and Pressure for the Six Chinese Marine Shales

<table>
<thead>
<tr>
<th>formation</th>
<th>sample ID</th>
<th>$V_L$ (cm$^3$/g)</th>
<th>$P_L$ (MPa)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niutitang ($\epsilon_1$)</td>
<td>QD1-L3</td>
<td>1.55</td>
<td>2.62</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>QD1-L4</td>
<td>1.86</td>
<td>2.39</td>
<td>0.969</td>
</tr>
<tr>
<td></td>
<td>WX2-8</td>
<td>0.47</td>
<td>0.76</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>WX2-33</td>
<td>1.15</td>
<td>3.30</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>WX2-49</td>
<td>3.18</td>
<td>1.72</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>WX2-54</td>
<td>3.62</td>
<td>1.54</td>
<td>0.990</td>
</tr>
<tr>
<td>Longmaxi ($S_1$)</td>
<td>WX2-8</td>
<td>0.76</td>
<td>3.30</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>WX2-33</td>
<td>3.18</td>
<td>1.72</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>WX2-49</td>
<td>3.62</td>
<td>1.54</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>WX2-54</td>
<td>4.18</td>
<td>1.34</td>
<td>0.990</td>
</tr>
</tbody>
</table>

Figure 7. Correlation between Langmuir constants and chemical compositions for the six Chinese marine shales: Langmuir volume vs (a) clay and (b) TOC contents; Langmuir pressure vs (c) clay and (d) TOC contents (note: WX2-8 was treated as an outlier in part d).
rather than in the organic matter, which is where the methane formed.

3.6. Possible Microstructural Reasons for Different Gas Prospectivity. The nanoscale accessible pore structure of marine shales is strongly influenced by regional geological conditions. Slight changes in geochemical and mineralogical parameters may greatly influence their nanoscale pore system. In this study, the Lower Silurian Longmaxi Formation and Lower Cambrian Niutitang Formation are lower Paleozoic, organic-rich shales that were deposited in a similar sedimentary environment with similar complex mineral compositions. Both formations have experienced a complex tectonic history involving significant burial, uplift, and erosion, and both are primary targets for shale gas development in China.1

There are, however, large differences in shale gas production between these two formations.3,7,70 Significant commercial gas

Figure 9. Correlation between the fraction of accessible pores and chemical compositions for the six Chinese marine shales: fraction of accessible pores vs (a) clay and (b) TOC contents (note: WX2-33 was treated as an outlier).
production has been developed from the Longmaxi shales, but no commercial gas has yet been obtained from the Niutitang shales. The main difference between the Niutitang and Longmaxi shales is paleo-burial depth. The Longmaxi shale was buried to between 3000 and 7000 m in the study area, whereas the Niutitang shale was buried to greater than 6000 m. The thermal maturity of both shales reached the overmature stage, but that of the Niutitang shale was significantly higher than that of the Longmaxi shale. At this thermal maturity, some of the organic matter in the Niutitang shale has been carbonized.

Figure 10. Correlation between pore accessibility and pore structure for the six Chinese marine shales: pore accessibility vs (a) fractal dimensions and (b) porosities (note: WX_33 was treated as an outlier in part b).

Figure 11. Images of diverse graptolites in Longmaxi shales: (a) abundant graptolites observed in core samples (sample WX_54); (b) flattened carbonaceous graptolite fossil observed by SEM (sample WX_54); (c) interconnected pore system within graptolite-derived OM (sample WX_54).

Figure 12. Correlation between Langmuir constants and pore accessibility for the six Chinese marine shales: (a) Langmuir volume and (b) Langmuir pressure vs pore accessibility; (c) schematic of an adsorption isotherm affected by the percentage of pore accessibility for shale (note: WX_33 was treated as an outlier in part a).
During carbonization, a subset of the OM pores may have been destroyed or collapsed, resulting in a decrease of pore accessibility. In addition, because it was buried deeper, the Niutitang Formation experienced more severe compaction, which may have resulted in a decrease in pore size and a change in pore morphology. These differences may partially explain why both $D_o$ and $D_r$ for the Niutitang shales are relatively larger than those of Longmaxi shales (Table 2).

In addition, whereas all six samples examined in this study can be described as black carbonateous shales, abundant and diverse graptolite fauna are observed in Longmaxi shales but not in Niutitang shales (Figure 11a and b). Numerous nanoscale pores are well developed within the graptolite-derived organic matter, which could comprise a complex pore system that may improve the pore accessibility of the Longmaxi shales (Figure 11c). Despite all of these observed and field-related differences, however, the results of this study (Table 4) show no obvious difference in pore accessibility between Longmaxi and Niutitang shales. This may simply be a factor of the limited data set in this study, but it may also suggest that other factors, such as having reached a minimum maturity level, are controlling and that the observed differences in recovery are related to large-scale structures. Thus, a more comprehensive comparison study of the pore structure of the two shale formations and a correlation of the results with regional patterns of gas production should be considered.

### 3.7. The Implication of Pore Accessibility on Methane Production in Shale

Parts a and b of Figure 12 show that both the Langmuir volume and pressure decrease with increasing accessible pore fraction (with WX2-33 again an outlier). The higher the pore accessibility, the lower the maximum methane adsorption capacity (Figure 12a). As noted above, $V_L$ increases with increasing TOC (Figure 7b) and the fraction of accessible pores decreases with increasing TOC and increases with increasing clay content (Figure 9). Thus, pore accessibility could be an indicator to methane transport in shale. It means that a shale sample with higher pore accessibility will have a lower TOC, higher clay content and lower methane sorption capacity, vice versa. Since methane adsorption capacity is controlled by micropores, the results indirectly confirm the conclusion that most of the micropores are in the organic matter, which tends to be disconnected in shales. In contrast, higher pore accessibility correlates with lower maximum methane adsorption pressure (Figure 12b). Shales with a higher affinity for methane will have a lower pressure at half of the maximum adsorption capacity. Thus, pore accessibility could be an indicator to methane transport in shale. Shale samples with a higher pore accessibility tend to have lower $P_L$ (higher methane affinity)—easier pathways for methane adsorption, vice versa, although our sampling size is limited. As $P_L$ decreases with increasing TOC and clay content (Figure 7c and d), the affinity of methane for organic matter combined with the pore accessibility could dominate the degree of difficulty for methane recovery from the shale nanopores.

While it may be surprising to find a relationship between the percentage of accessible pores and methane adsorption capacity in shale and this relationship needs further testing, if verified, it may be useful as a guide to methane production in shale gas reservoirs. Figure 12c schematically shows the effect of shale pore accessibility on methane adsorption isotherms given the relationships between pore accessibility and $V_L$, $P_L$, and $P_L$ described above. The inverse correlation between the pore accessibility and maximum adsorption capacity suggests that, when pore accessibility is low, decreasing transport pathways, maximum methane adsorption $V_L$ increases due to a simultaneous increase in adsorption sites. However, the data also suggest that under these conditions the affinity of methane gas for the available sites in shale pores decreases. That is, the pressure at half of the maximum adsorption capacity $P_L$ increases, so the amount of gas that can be desorbed at a given pressure decreases.

The methane adsorption capacity therefore increases gradually with increasing adsorption pressure (gray line in Figure 12c). This has a negative effect on shale gas production even with the high total methane adsorption capacity, because relatively little gas is desorbed, and therefore releasable, at a given pressure.

Samples with high pore accessibility have a relatively small maximum adsorption, i.e., low values of $V_L$ and $P_L$, but with steep adsorption profiles at low pressure and a plateau at high pressure, i.e., low values of $P_L, P_L$ (red line in Figure 12c). That is, relatively more gas can be released at lower pressures, but the maximum amount of gas storable is lower. Therefore, there may be an optimum value for shale pore accessibility that will maximize production of methane in shale reservoirs, and analysis of these values for target shales may help to direct drilling programs. In the short term, our data suggest that drilling in shale reservoirs with relatively high pore accessibility will allow a significant amount of gas to be quickly produced at relatively low threshold pressures. In the longer term, however, gradual production of larger total amounts of methane with decreasing borehole pressures could be achieved for low pore accessibility shales. Thus, the hydraulic fracturing plan may be tailored to control the percentage of accessible pores in shale for the production time and amount during shale gas recovery.

### 4. CONCLUSIONS

In this study, we have combined FE-SEM, SANS, He porosimetry, and volumetric high-pressure adsorption techniques to characterize the geochemical and mineralogical compositions, pore structure, and methane adsorption of six samples from two Chinese marine shale formations. On the basis of these results, the following conclusions have been drawn:

1. FE-SEM images show that OM pores are the most important pore type, dominating the pore systems of these shales. Intraparticle pores, interparticle pores, and microfractures resulting from sedimentary diagenesis occur between or within mineral grains. Meanwhile, nanoscale pores and microfractures are also influenced by mechanical compaction, since both Longmaxi and Niutitang Formations experienced multiphase tectonic movements.

2. Application of the unified fit model with two pore structures (finite pores and fractal pores) to the SANS data shows that both surface and mass fractals are present. Mass fractals with dimensions ranging between 1.94 and 2.68 are identified for finite pores except for sample QD1-L4 which has a surface fractal dimension of 2.85. For fractal pores, samples QD1-L4, WX2-49, and WX2-54 have mass fractal dimensions ranging between 2.84 and 2.93, while samples QD1-L3, WX2-8, and WX2-33 have a surface fractal dimension ranging between 2.42 and 2.78. Total porosity, estimated by the Porod invariant method, ranges between 2.35 and 16.40%, while the porosity of finite pores ranges between 0.35 and 6.36% and the porosity of fractal pores ranges between 2.07% and 8.51%.
(3) Pore accessibility estimated on the basis of combined helium porosimetry and SANS shows that the fraction of accessible pores is greater than 64% for most of the samples, except for sample WX2-33 which has only 40.26% accessible pores, possibly as a result of carbonate precipitation during diagenesis.

(4) Clay and TOC have opposite effects on the pore structure. Samples with higher clay contents have higher pore accessibilities and lower porosities and total methane adsorption capacities. Increasing TOC has the opposite effect. This suggests that, in shales, gas is stored in the organic matter, but the transport conduits are through the inorganic matrix, especially through the clay. Thus, the organic matter is the controlling factor for methane storage in shale gas reservoirs, but the inorganic matrix controls gas release.

(5) In comparing the two shale formations, both the mass and surface fractal dimensions for Niutitang shales are relatively greater than those of the Longmaxi shales. This may be a result of the relative depths to which the Niutitang shales were recovered are greater than those of Longmaxi shales).

(6) Both Langmuir adsorption capacity and Langmuir pressure decrease with increasing shale pore accessibility. This suggests that, in shales, high pore accessibility may reduce methane adsorption capacity, while low pore accessibility may reduce methane desorption. Pore accessibility could, therefore, become an essential factor in understanding and controlling methane production in shale gas reservoirs.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b03437.

Figure showing experimental and modeled scattering intensities for the six Chinese marine shales and tables showing SLD for the six Chinese marine shales and model parameters for the QD1-L3, QD1-L4, WX2-8, WX2-33, WX3-49, and WX3-54 samples (PDF)

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■ REFERENCES


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Notes
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