Investigation of pore structure and fractal characteristics of the Lower Silurian Longmaxi shales in western Hunan and Hubei Provinces in China

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A R T I C L E   I N F O

Article history:
Received 28 July 2015
Received in revised form 28 October 2015
Accepted 16 December 2015
Available online 22 December 2015

Keywords:
Longmaxi Formation shale
Pore structure
Mercury injection
N₂ adsorption
Fractal dimension

A B S T R A C T

The pore structure characteristics of the Lower Silurian Longmaxi Formation shales collected from western Hunan and Hubei were investigated using high-pressure mercury injection and low-temperature N₂ adsorption/desorption experiments. Total organic carbon values, thermal maturity values and mineralogical compositions were also obtained by relevant experimental methods. The TOC value varies from 0.71% to 4.75%, with a mean value of 2.58%, and their thermal maturities have reached the over-mature stage and dry gas generation window. Quartz and clay minerals are the major mineral compositions in the samples. In contrast to previous studies of other shales (Chalmers and Bustin, 2008; Han et al., 2013; Wang et al., 2013), there are no carbonates in the shale samples of this area. Due to their biogenic source, quartz content is positively correlated with TOC values. Pore size distributions obtained from mercury injection experiments were divided into three groups. Samples with higher TOC content always have smaller dominant pore sizes, and the pore sizes of samples with higher clay mineral content and lower TOC values may be larger, with a major peak between 30 nm and 1 μm. Through analyzing the N₂ adsorption and desorption isotherms, we found that the morphology of pores in the shales rich in organic matter is narrow neck and wide body, and that of those rich in clay minerals is flat-shaped. BJH and DFT models were used to derive pore size distributions using N₂ adsorption data, and both are representative. The differential distribution curves of pore volumes and surface areas show that all shale samples' dominant pore sizes are within the range of micropores and mesopores, and they are the major contributors to pore surface areas, while mesopores and macropores make more significant contributions to pore volumes. The specific surface area calculated by the BET method ranges from 6.12 to 28.42 m²/g, with an average value of 16.14 m²/g, and the total pore volume varies from 0.0105 to 0.0338 cm³/g, with a mean value of 0.0213 cm³/g. The correlational analysis between pore structure parameters and TOC value, quartz and clay mineral content indicates that organic matter and quartz are positively associated with the micropores and fine mesopores, though larger pores can also exist in organic matter, and clay minerals play an important role in mesopores and macropores generation. Due to the infeasibility of using mercury porosimetry data to obtain fractal dimensions, Dₙ calculated from N₂ adsorption data are used, its value ranges from 2.6353 to 2.7694, with an average value of 2.7284. As we know, the more micropores contained in the shale, the more complex the pore structure will be, and as a result, the fractal dimension will be larger. Therefore, organic matter and quartz positively influence fractal dimension, and there is a negative relationship between clay mineral content and fractal dimension.

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1. Introduction

Due to the shortage of fossil fuels and the need for energy security, exploration and development of unconventional oil and gas resources (including tight sands, coal bed methane, and shale oil and gas) have increasingly been the focus of global energy
geological scholars (Wang et al., 2009, 2013a, 2013b; Yun et al., 2012). Due to the combination of two technologies, horizontal drilling and hydraulic fracturing, the United States has successfully exploited shale gas over the past several decades (Hao et al., 2013; Ji et al., 2014). Shale gas production in the USA grew by an average of 48% per year from 2006 to 2010 (Conti et al., 2011) and reached 1800 × 10^8 m³ in 2011 (Pollastro et al., 2007). Although it was previously thought to be impossible or uneconomical to produce, shale gas has become one of the most important unconventional gas resources. The “shale gas revolution” in North America encouraged the Chinese government to investigate shale gas exploration and exploitation in China (Wang et al., 2015).

Shale gas refers to the gas system in fine-grained, clay- and organic-rich rock (shale) where the gas is thermogenic or biogenic in origin and stored as free gas in pores and fractures, adsorbed gas in organic matter or inorganic minerals, or dissolved gas in kerogen and bitumen (Curtis, 2002; Hill et al., 2007; Jarvie et al., 2007; Ross and Bustin, 2007). Shale, which is both a gas source and reservoir rock (Curtis, 2002), is a highly heterogeneous porous media whose pore structure characteristics are critical parameters for evaluating the resource potential and its effective exploitation (Ross and Bustin, 2008, 2009; Loucks et al., 2009; Ambrose et al., 2010; Clarkson et al., 2013; Gao et al., 2015). The pore sizes of shale typically range from a few nanometers to several micrometers in diameter (Chalmers et al., 2009; Loucks et al., 2009; Nelson, 2009; Chalmers et al., 2012a, 2012b; Miliken et al., 2013). Several classifications are used to define the size ranges of various pores. In this study, the following ranges of pore size as classified by the International Union of Pure and Applied Chemistry are used: micropores have widths less than 2 nm, mesopores have widths between 2 and 50 nm, and macropores have widths greater than 50 nm (Chalmers et al., 2009).

There are various techniques or hybrid techniques to characterize the pore structure properties of shale (Bustin et al., 2009). Pore types, geometries and sizes can be qualitatively observed by advanced 2D/3D imaging techniques such as scanning electron microscopy (SEM) (Chalmers and Bustin, 2007; Loucks and Ruppel, 2007; Ambrose et al., 2012), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), focused ion beam scanning electron microscopy (FIB-SEM) (Bai et al., 2013; Jiao et al., 2014) and Nano CT-scan (Zou et al., 2011a, 2011b). Some scholars have analyzed the pore images quantitatively using image-processing software (Photoshop Pores and Cracks Analysis System) (Mao et al., 2004; Wang et al., 2013, 2013b). Low-temperature N2 and CO2 adsorption (N2-GA, CO2-GA), high-pressure mercury injection (HPMI), nuclear magnetic resonance (NMR) and small angle and ultra-small angle neutron scattering techniques (SANS/USANS) can be used to qualitatively investigate pore geometries and statistic characteristics of pore structure, including pore size distributions, pore volumes and specific surface areas (Ross and Bustin, 2007; Strapoc et al., 2010; Tian et al., 2013; Yang et al., 2014a, 2014b; Chen et al., 2015; Tian et al., 2015; Xiong et al., 2015). Among these, the HPMI and N2-GA are the most effective methods with which to characterize the pore structure. Because HPMI is incapable of measuring pores smaller than 3 nm (Bolton et al., 2000) and N2-GA has maximal accuracy when measuring pore sizes in the range of 1.7–100 nm (Kuila and Prasad, 2013), combining HPMI and N2-GA measurements may be an effective method with which to comprehensively characterize the pore structure (Wang et al., 2014a, 2014b, 2015). HPMI and N2-GA experiments data can also be used to calculate the fractal dimension of pores in coal, carbon and shale (Jiao et al., 2008a, 2008b; Cai et al., 2013; Yang et al., 2014a, 2014b; Liu et al., 2015).

According to previous studies, the Lower Cambrian (Niutitang Formation) and Lower Silurian (Longmaxi Formation) shales developing in the Upper and Middle Yangtze regions, which are both rich in organic matter and brittle minerals and have reached the dry gas generation window, show great potential for shale gas (Zhang et al., 2009; Zou et al., 2011a, 2011b; Han et al., 2013; Chen et al., 2014). In contrast to numerous studies of shale pore structure in Sichuan Province and a few studies of the Lower Cambrian shales in Hunan Province (Wang et al., 2013, 2013b, 2014; Wan et al., 2015), there are few studies of pore structure and fractal characteristics of the Lower Silurian shales in western Hunan and Hubei Provinces. Therefore, the aim of this article is to investigate the pore structure characteristics of 9 outcrops of the Lower Silurian shales collected in western Hunan and Hubei Provinces using high-pressure mercury injection and low-temperature N2 adsorption, and to use data from the HPMI and N2-GA experiments to calculate the fractal dimensions. The relationships between pore structure parameters (pore volume, specific surface area and fractal dimension) and the geochemistry and compositions of the shale will also be discussed.

2. Geological setting

The study area is located in the Western Hunan and Hubei Fold Belt, which is as part of the Middle and Upper Yangtze regions (Fig. 1) (Hu, 2002; Long, 2011; Wang et al., 2014a, 2014b). Geological studies indicate that the Longmaxi Formation in this area consists of a lower section of black/dark gray shales, silty shales and siliceous shales with abundant graptolite fossils. Its middle and upper sections are composed of gray/gray-green shales, yellow-green shales and siltstones, and the colors shift gradually upward, indicating the sedimentary environment varies from the deep shelf to the shallow shelf. The lower section of the Longmaxi Formation (rich in organic matter) is approximately 50–60 m thick and widely distributed over the study area. The TOC (total organic carbon) content in the black shale ranges from 1.0 to 4.0%. The kerogen types of the organic matter in the black shales are dominated by type I and type II, whereas the thermal maturity of the organic matter is higher than that in the North American shale and has equivalent vitrinite reflectance values in the range of 1.5–4% (Fan et al., 2014; Yang et al., 2014a, 2014b; Wan et al., 2015). Due to the similar geological conditions to the Lower Silurian shale in Sichuan, the Lower Silurian Longmaxi Formation shales in western Hunan and Hubei have been recognized as effective gas shales with enormous potential.

3. Samples and methods

3.1. Samples and experimental protocol

Few shale gas wells have been drilled in this area, and thus it is difficult to obtain cores with which to more accurately investigate the shale pore structure. Therefore, instead of cores, a total of 9 shale outcrop samples of Longmaxi Formation were collected in Western Hunan and Hubei; the location of the samples are shown in Fig. 1. In order to reduce the effect of weathering on outcrop samples (Petsch et al., 2000), all the samples were drilled from the fresh shale sections which is about half meter underground. A complete experimental project including measurement of TOC contents and thermal maturity (equivalent vitrinite reflectance), X-ray diffraction (XRD) analysis, high-pressure mercury injection and low-temperature N2 adsorption/desorption experiments were conducted.

3.2. Description of the experimental analysis

The total organic carbon (TOC) content was measured on
powered samples using a Leco CS230 carbon/sulfur analyzer. A Leica MPV-SP microphotometer was used to measure vitrinite-like material reflectance which is also called marine vitrinite instead due to the lack of vitrinite in the Lower Paleozoic shales; the values of vitrinite-like material reflectance were converted to equivalent vitrinite reflectance values using the equation established by Zhong et al. (Chen et al., 2014).

X-ray diffraction (XRD) is a useful method for composition analysis, and the mineralogical compositions and the relative mineral percentages of the Lower Longmaxi Formation shales were estimated on a Bruker D8 Advance X-ray diffractometer after the samples were crushed into powders with a grain size ranging from 200 to 300 mesh.

A Micromeritics Autopore 9500 Porosimeter was used to measure the porosities and pore size distributions in sizes ranging from 3 to 12 μm (Bolton et al., 2000). The samples were weighed, and the bulk volume was measure by mercury immersion. The bulk density, which can be used to obtain the total porosity of the shale sample, was then calculated. The mercury injection pressure can range up to 60,000 psia (approximately 413 MPa), meaning that converting from the Washburn equation, mercury can be injected into a pore as small as 3 nm (Washburn, 1921).

A Micromeritics TriStar II 3020 surface area analyzer, which was primarily used to determine the pore size distributions in the range of 1.7–100 nm. N₂ adsorption–desorption isotherms were obtained from all samples under relative pressure ranging from 0.01 to 0.995 at 77.35 K, higher than the N₂ critical temperature (190.6 K). The N₂ adsorption–desorption isotherms can provide information on the total pore volume, specific surface area and pore size distribution. The BET surface area was calculated from the N₂ adsorption data under relative pressure ranging from 0.05 to 0.35 using the multilayer adsorption theory proposed by Brunauer–Emmett–Teller (Brunauer et al., 1938). The total pore volume was estimated to be the liquid molar volume of adsorbed nitrogen at relative pressure of 0.99. The t-plot method was used to calculate the external surface area (including the surface area from mesopores, macropores and other external surface area) and micropore volume from the N₂ adsorption data (Broekhoff and de Boer, 1968); micropore surface area can be estimated using the BET surface area excluding the external surface area. The pore size distributions, which were used to identify the range of the dominant pore sizes, were obtained from the N₂ adsorption–desorption data using the BJH (Barrett–Joyner–Halenda) (Barrett et al., 1951) and DFT (density function theory) models (Gregg and Sing, 1982; Dombrowski et al., 2000).

### 3.3. Fractal method

Fractal theory, which can be used to describe the geometric and structural properties of a solid surface, was first proposed by Pfeifer and Avnir in 1983 (Pfeifer and Avnir, 1983; Avnir and Jaroniec, 1989). Fractal dimension D is a quantitative index to characterize the roughness or complexity of the solid surface. The fractal dimension value varies from 2 to 3, and values closer to 3 indicate increasing roughness or complexity of the surface. Two calculation methods based on mercury porosimetry and low-temperature adsorption have been widely used to characterize the complexity of the pore structure in coalbed methane and shale gas resources.

Based on the Washburn equation (Washburn, 1921) and the Menger sponge fractal model, Friesen and Mikula obtained a fractal dimension calculation using mercury porosimetry data as follows (Friesen and Mikula, 1987; Friesen and Ogunsola, 1995; Yao et al., 2009):
\[
\log(\frac{dV_P}{dP}) = (D_m - 4)\log(P)
\]

(1)

where \(V_P\) is the cumulative injection volume at a given pressure, and \(D_m\) is the surface fractal dimension using mercury injection data. We can obtain \(D_m\) as follows: \(D_m = 4 + A_1\), where \(A_1\) is the slope of Eq. (1).

The fractal dimension can also be calculated by the Frenkel–Halsey–Hill equation (FHH model) based on the N\(_2\) adsorption data (Pfeifer and Avnir, 1983; Avnir and Jaroniec, 1989), and the FHH equation can be described as follows (Yao et al., 2008; Yang et al., 2014a, 2014b):

\[
\ln(V) = (D_n / C_0)\ln(\ln(p_0/p)) + \text{constant}
\]

(2)

where \(V\) is the volume of N\(_2\) adsorbed at each equilibrium pressure \(p\); \(p_0\) is the saturation pressure; and \(A_2\) is the slope of the plot of \(\ln(V)\) versus \(\ln(\ln(p_0/p))\). The fractal dimension \(D_n\) can be calculated from the following equation: \(D_n = 3 + A_2\).

Cai indicated that high-pressure mercury injection can damage the pore structure in coal (Cai et al., 2013) and the FHH equation was the only one to be used to calculate the fractal dimension value in studies of pore structure of shales in China (Yang et al., 2014a, 2014b; Liu et al., 2015). Thus as a feasibility study, \(D_m, D_n\) were both calculated.

4. Results and discussion

4.1. Geochemical and mineralogical characteristics

The total organic carbon (TOC) content of the 9 samples ranges from 0.71% to 4.75% (Table 1), with a mean value of 2.58%. The values of vitrinite-like material reflectance varies (equivalent vitrinite reflectance, after conversion with Zhong’s equation) from 2.03% to 3.87%, with an average value of 3.09% (Table 1), indicating over-mature thermal maturity of the organic matter in the samples (Jarvie et al., 2007); thus, the Longmaxi Formation shales have reached the dry gas generation window.

The mineral compositions of the samples are also presented in Table 1. The dominant minerals in the shale are quartz and clay minerals, with average values of 53.3% and 34.5%, respectively. The quartz contents are between 37.7% and 63%, whereas the clay mineral contents range from 25.5% to 50.7%. According to the theory proposed by Bustin et al., 2009, quartz may be positively (biogenic) or negatively (detrital) correlated with TOC, and Fig. 2 shows that the relationship between the quartz content and TOC content of the samples is positive except for the sample esd-1 due to the biogenic origins of quartz; as an outlier, the sample esd-1 may be affected by weathering, therefore its TOC content is very low. Clay minerals consist of illite (14.8%–30.5%) and illite-smectite mixed layer (0–19.8%) and chloride (0–4%); thus, illite is the primary clay mineral. The feldspar (potash feldspar and plagioclase) content range from 6.2% to 13% with an average value of 9.3%; pyrite is detected in 7 of the 9 samples, indicating a reducing environment (Wang et al., 2014a, 2014b). The biggest difference in minerals between the shale samples in this region and those from previous studies on North America shale and South China Basin shale is the absence of carbonates (Chalmers and Bustin, 2008; Wang et al., 2013, 2013b; Han et al., 2013).

4.2. High-pressure mercury injection (HPMI)

4.2.1. Porosity

The HPMI method has been widely used to evaluate the...
parameters of shale pore structure, whose measurement range is broader than that of nitrogen sorption measurement (measurement ranging from 3 nm to 12 μm) (Bolton et al., 2000). Table 2 lists the parameters of porosity, bulk density and skeletal density. The bulk densities and skeletal densities range from 1.96 to 2.55 g/cm³ and from 2.18 to 2.76 g/cm³, respectively. Their porosities are derived from density differences (skeletal density minus bulk density) and between 3.11% and 17.47%, with an average value of 9.93%.

The pores in the gas shales are grouped into the following three types (Loucks et al., 2012): interparticle pores that are found between mineral particles and crystals, intraparticle pores that are located within mineral particles and organic matter pores that are intraparticle pores located within organic matter. According to this pore classification, the organic matter and minerals are regarded as the two primary factors controlling the porosity of gas shale. In contrast to recent domestic studies (Tian et al., 2013; Cao et al., 2015), there is a negative correlation between the total porosities of the 9 samples and their TOC values (Fig. 3a), while the porosities are negatively correlated with quartz content (Fig. 3b). This seemingly strange phenomenon can be interpreted by the thought (Bustin et al., 2009) that if the shales in this area are rich in biogenic quartz, they have lower porosities than those rich in detrital quartz, and thus clay mineral content will be the major factor controlling the porosity; in fact, Fig. 3c shows a positive correlation between porosities and clay mineral content.

4.2.2. Pore size distribution

Due to the limitation of its measuring range, HPMI results were used to quantitatively analyze the pore structure of the mesopores and macropores. Fig. 4 shows incremental intrusion of the 9 samples versus pore size diameter plots, and according to the pattern, these plots were divided into the following three groups: semi-modal, unimodal and multimodal. Unimodal plots are those with the pore size distributions of samples esd-1, esd-2 and p3, which highly concentrate in the mesopores range, and there are very few mercury intrusions (<5%) in the macropore range. Multimodal plots are those of samples p3, stp-1 and stp-2, which are dominated by multimodal meso- and macropores; their primary pore size ranges are 50–200 nm, 50–500 nm and 200–2000 nm, respectively; however, their secondary pore size ranges are the same and range from 10 nm to 50 nm. Semi-modal plots are those with the dominant pore size range of samples esl3-1, esl3-2 and esl3-3; these are difficult to confirm because the mercury intrusion volume continues to increase, and there is no complete peak in the HPMI measurement range. It must be noted that except for samples stp-1 and stp-2, the incremental intrusion volumes are not 0 ml/g at the highest pressure, which is to say that, the shale samples have a certain number of pores that cannot be detected by the HPMI experiments.

Comparing samples p2 (TOC 1.14%; clay content 50.7%) and p3 (TOC 1.41%; clay content 34.7%), the former has greater pore volumes than the latter, both in the meso-macropores range (20 nm–50 nm) and in the macropores range (larger than 50 nm), but their pore volumes in the micro-mesopores range (3 nm–20 nm) are similar (Fig. 4c). It may be concluded that pores generated in the clay minerals are larger than those generated in organic matter, and they are the primary components of the pore structure of the shales in this study. The positive correlation between porosities and clay contents (Fig. 3c) and incremental pore volume plots of sample esd-1 (TOC 0.71%; clay content 29%) and sample esd-2 (TOC 3.84%; clay content 30.2%) also support this conclusion (Fig. 4a).

4.3. Low-temperature N₂ adsorption/desorption

4.3.1. N₂ adsorption/desorption isotherms

The N₂ adsorption and desorption isotherms of the 9 shale samples are illustrated in Fig. 5. It shows that every sample's adsorption isotherm coincides with the desorption branch when the relative pressure is lower than 0.45. However, when the relative pressure exceeds 0.45, the adsorption branch of the isotherm will be inconsistent with the desorption branch, and the hysteresis loop occurs (Gregg and Sing, 1982; Mastalerz et al., 2013). According to the IUPAC classification (Sing, 1985), the isotherm shapes of all samples are Type IV, and they are then divided into two groups based on the shapes of hysteresis loops. The first group, whose shapes of hysteresis loops belong to Type H2, consists of sample esd-2, esl3-1, esl3-2 and esl3-3; Type H2 hysteresis loops reflects the morphology of the generated pores are narrow necks and wide bodies (often referred to as ‘ink bottle’ pores). It must be noted that all four samples in the first group have higher TOC content and lower clay mineral content than those in the second group, and the shapes of pores generated in organic matter may be inkbottle-shaped. The rest of samples belong to the second group, and their hysteresis loop shapes are Type H3, indicating that the pores generated in these samples are usually flat-shaped (Sing, 1985). In combination with their higher clay mineral content, we can conclude that pores generated from clay minerals are generally slit-shaped.

Fig. 3. The relationships between TOC content (a), quartz content (b), clay mineral content (c) and porosity.
4.3.2. Pore size distribution from \( N_2 \) adsorption and desorption

The pore size distribution can be presented by cumulative, incremental and differential pore volume or surface area versus pore size diameter curves, from which we can obtain significant information on pore structure, including pore size range, dominant pore size and contributions provided by different pore size ranges to the total pore volume (total surface area) (Meyer and Klobes, 1999; Clarkson et al., 2012a, 2012b; Chalmers et al., 2012a, 2012b; Mastalerz et al., 2012; Kuila and Prasad, 2013).

The differential curve, which includes a \( dV/dW \) (\( dS/dW \), V and S are pore volume and surface area, respectively) versus W (pore diameter) plot and a \( dV/d\log(W) \) (\( dS/d\log(W) \)) versus W plot, is widely used to display pore size distribution (Clarkson et al., 2012a, 2012b; Kuila and Prasad, 2013). The \( dV/dW \) (\( dS/dW \)) plot calculated from the cumulative pore volume curve is identical to the pore size distribution and reflects the concentration of pore sizes. Because the area under its curve can be used to calculate the actual pore volume (surface area) by integral operation, the \( dV/d\log(W) \) (\( dS/d\log(W) \)) plot, obtained by the equation \( dV/d\log(W) = \ln 10 \times dV/dW \times W \) (\( dS/d\log(W) = \ln 10 \times dS/dW \times W \)), is more suitable to compare the contributions provided by different pore size ranges to the total pore volume (total surface area) than the \( dV/dW \) (\( dS/dW \)) plot (Meyer and Klobes, 1999). Due to the presence of the tensile strength effect phenomenon (Groen et al., 2003), the pore size distribution calculated from \( N_2 \) desorption branch data using the BJH model, \( dV/dW \) (\( dS/dW \)) and \( dV/d\log(W) \) (\( dS/d\log(W) \)) curves as shown in Fig. 7a, b, c, d. For comparison, \( dV/d\log(W) \) (\( dS/d\log(W) \)) curves derived by the density functional theory (DFT model) (Dombrowski et al., 2000) are shown in Fig. 7e, f.

Except for sample p2, all \( dV/dW \) curves of the other samples continue to rise from larger pore sizes (50 nm) to smaller pore sizes (1.7 nm, the limitation of the BJH model) and show unimodal distributions, which means the pore sizes of the remaining samples are micro-mesopores or micropores, and their peak values vary from 0.00065 to 0.00005 cm\(^3\)/g Å (Fig. 7a). The \( dV/dW \) curve of sample p2 rises steadily until the pore size diameter approaches 2 nm, at which point it reaches a peak, declines slightly and finally flattens; in conclusion, sample p2 has a larger concentration value of pore size than the other samples (Fig. 7a). The \( dV/d\log(W) \) curves can be divided into the following four groups (Fig. 7c): group A, which contains samples esd-2, esl3-1, esl3-2 and esl3-3, shows curves continuing to rise until reaching a peak at the micropore range, though the plots are gentler than their \( dV/dW \) curves; group B, which contains sample esd-1, has a multistep curve demonstrating several dominant pore sizes and superimposed ranges of the dominant pore sizes; group C contains sample stp-2, which is similar to sample esd-1 in that it is also multimodal and has several dominant pore sizes, but its curve values in the pore size range of 2–10 nm are lower than those of the other pore sizes; finally, group D consists of p2, p3 and stp-1, whose plots are unimodal and continue to decline after they peak. As the area under the \( dV/d\log(W) \) curve is equal to the pore volume, we observe that among all of the samples, mesopores are the major contributors to pore

![Fig. 4. Incremental pore volume plots of the nine shale samples.](image-url)
volumes. Samples rich in TOC have less dominant pore sizes than those with high clay mineral contents, which is to say that, the diameters of pores developed in clay minerals are larger than those developed with hydrocarbon-generation, and this is consistent with the conclusion of Section 4.2.1.

The $dS/dW$ and $dS/d\log(W)$ plots are similar, and both continue to rise from larger pore sizes to smaller pore sizes, meaning that the smaller the pore diameter, the larger the surface area (Fig. 7b, d).

Though sample p2 has fewer pores ranging from 2 nm to 3 nm than the other samples, except for samples p3 and stp-1, it has a larger surface area due to its higher proportion of pores whose diameters are larger than 3 nm. It must be noted that clay minerals, which generally develop larger pores, can also provide considerable surface areas. The $dV/d\log(W)$ and $dS/d\log(W)$ curves derived by the DFT model show similar results with those derived by the BJH model, though the absolute values are different (Fig. 7e, f). Similar to the PSD calculated by HPMI, which has a lower point at a pore size equal to 50 nm (Fig. 4), all PSD curves derived by the DFT model on the basis of N$_2$ adsorption have a relative lower point at a pore size equal to 2 nm (Fig. 7e, f). This strange phenomenon will be studied in future work.

### 4.3.3. Pore structure parameters

Table 3 shows the pore structure parameters calculated from low-temperature N$_2$ adsorption analysis. The specific surface area, which is calculated by the BET method (Brunauer et al., 1938), ranges from 6.12 to 28.42 m$^2$/g with an average value of 16.14 m$^2$/g. On the basis of the BJH method (Barrett et al., 1951), the total pore volume estimated from N$_2$ single point adsorption total pore volume at relative pressure 0.99 varies from 0.0105 to 0.0338 cm$^3$/g, with a mean value of 0.0213 cm$^3$/g. The average pore size ranges between 4.1 and 7.3 nm, with a mean value of 5.6 nm, which corresponds to mesopores. The surface area and space volume of macropore, mesopore and micropore is obtained by BET, BJH and t-plot method (Broekhoff and de Boer, 1968), and these results are also listed in Table 3.

Fig. 8 shows the relationships among average pore size, BET surface area and total pore volume. Similar to the results obtained...
from North America and South China shales (Chalmers et al., 2012a, 2012b; Yang et al., 2014a, 2014b), there is a positive relationship between total pore volume and BET surface area (Fig. 8c) and a weakly negative relationship between average pore size and BET surface area (Fig. 8a). No obvious relationship between average pore size and total pore volume can be found (Fig. 8b), which is very different from the results derived from studies of other shales (Chalmers et al., 2012a, 2012b; Yang et al., 2014a, 2014b; Liu et al.,

**Table 3**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average pore size/Å</th>
<th>S$_{mic}$/m$^2$/g</th>
<th>S$_{mes}$/m$^2$/g</th>
<th>S$_{max}$/m$^2$/g</th>
<th>V$_{BJH}$/cm$^3$/g</th>
<th>V$_{mic}$/cm$^3$/g</th>
<th>V$_{mes}$/cm$^3$/g</th>
<th>V$_{max}$/cm$^3$/g</th>
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<tbody>
<tr>
<td>esd-1</td>
<td>56.9</td>
<td>23.76</td>
<td>5.79</td>
<td>16.57</td>
<td>1.4</td>
<td>0.0338</td>
<td>0.0025</td>
<td>0.0252</td>
</tr>
<tr>
<td>esd-2</td>
<td>43.7</td>
<td>28.42</td>
<td>10.2</td>
<td>12.26</td>
<td>5.96</td>
<td>0.031</td>
<td>0.0046</td>
<td>0.0185</td>
</tr>
<tr>
<td>esl3-1</td>
<td>45.06</td>
<td>15.34</td>
<td>5.47</td>
<td>6.45</td>
<td>3.42</td>
<td>0.0173</td>
<td>0.0024</td>
<td>0.0099</td>
</tr>
<tr>
<td>esl3-2</td>
<td>41.9</td>
<td>18.06</td>
<td>5.93</td>
<td>7.81</td>
<td>4.32</td>
<td>0.0189</td>
<td>0.0026</td>
<td>0.0113</td>
</tr>
<tr>
<td>esl3-3</td>
<td>41</td>
<td>18.24</td>
<td>6.13</td>
<td>8.39</td>
<td>3.72</td>
<td>0.0187</td>
<td>0.0027</td>
<td>0.0118</td>
</tr>
<tr>
<td>p2</td>
<td>72</td>
<td>16.32</td>
<td>2.96</td>
<td>10.81</td>
<td>2.55</td>
<td>0.0294</td>
<td>0.0012</td>
<td>0.0195</td>
</tr>
<tr>
<td>p3</td>
<td>68.6</td>
<td>6.12</td>
<td>2.07</td>
<td>3.23</td>
<td>0.82</td>
<td>0.0105</td>
<td>0.0009</td>
<td>0.0064</td>
</tr>
<tr>
<td>stp-1</td>
<td>72.8</td>
<td>7.75</td>
<td>3.44</td>
<td>3.24</td>
<td>1.07</td>
<td>0.0141</td>
<td>0.0016</td>
<td>0.0072</td>
</tr>
<tr>
<td>stp-2</td>
<td>65.4</td>
<td>11.21</td>
<td>4.88</td>
<td>5.86</td>
<td>0.47</td>
<td>0.0183</td>
<td>0.0024</td>
<td>0.0108</td>
</tr>
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</table>
The percentages of micropores, mesopores and macropores in BET surface area and total pore volume are illustrated in Fig. 9. Whether in BET surface area or total pore volume, the mesopores always occupy the largest proportion. Due to their larger pore size, macropores make the second largest contribution to the total pore volume, while micropores offer moderate surface area for their smaller pore diameters. The fitting degrees of the relationships between different pore sizes’ surface areas and BET surface areas and pore volumes and total pore volumes have also proved this concept (Fig. 10).

According to previous studies (Tian et al., 2013; Wang et al., 2014a, 2014b; Yang et al., 2014a, 2014b; Liu et al., 2015; Xiong et al., 2015), organic matter, clay minerals and quartz are the most important factors for shale pore structure. The influences of organic matter, clay minerals and quartz on the average pore sizes, surface areas and pore volumes are illustrated in Fig. 11. There is a strong negative relationship between TOC values and average pore sizes (Fig. 11a). As TOC content increases, the surface area and pore volume of micropores increase modestly (Fig. 11b, c), which is consistent with the results obtained from studies of North America and South China shales (Chalmers et al., 2012a, 2012b; Wang et al., 2014a, 2014b; Xiong et al., 2015). It must be noted that the
macropores surface areas also increase with increasing TOC content, and the fitting degree is higher than that of micropores (Fig. 11b), which may be caused by the macropores generated in organic matters. Due to its biogenic source, the influences of quartz are similar to that of organic matter (Fig. 11d, e, f), and this is in contrast to previous research (Tian et al., 2013; Liu et al., 2015; Xiong et al., 2015). A negative relationship can be observed between quartz content and average pore size, and there are positive relationships between quartz content and BET surface areas and total pore volumes. As the quartz content increases, the pore diameters of macropores decrease and their surface area increase. The quartz content increasing also enlarge the diameters of micropores, and thus their pore volumes also increase (Fig. 11f). The fitting degree of total pore volumes is lower than that of micropores volumes due to the decrease in mesopores and macropores diameters and their negative influences on total pore volumes. The relationship between clay mineral content and average pore sizes is positive, and BET and micropores surface areas decrease with increasing clay mineral content (Fig. 11g, h), which is consistent with the conclusion obtained from the previous section that the diameters of pores generated with clay minerals are larger than those generated in organic matter. With increasing clay mineral content, the TOC content decreases, and the pore volumes of

![Fig. 11. The influences of TOC, clay minerals and quartz on the average pore size, surface area and pore volume.](image)

![Fig. 12. The relationship between TOC content and clay mineral content.](image)
micropores that are mostly generated in organic matters also decrease. In general the total pore volumes should increase with increasing clay mineral content, though Fig. 11i shows that the relationship is slightly negative, which is probably because the larger pores in organic matter are replaced by smaller pores in clay minerals. However, this also proves that hydrocarbon-generation can also develop larger pores (Fig. 12).

4.4. Fractal dimension

4.4.1. Calculation

Mercury porosimetry and N₂ adsorption data can both be used to obtain fractal dimension (Pfeifer and Avnir, 1983; Friesen and Mikula, 1987). In previous studies, the most widely used method to calculate fractal dimension used the FHH model from the N₂ adsorption experiment to characterize the pore structure of shales in China (Yang et al., 2014a, 2014b; Liu et al., 2015). Fractal dimension of the shale samples calculated using this method Dₙ are listed in Table 4. Dₙ ranges from 2.6353 to 2.7694, with an average value of 2.7284, indicating that the pore structure in shale samples is very complex, and all FHH plots have very high degrees of fit. Fig. 13 shows three typical FHH plots of the shale samples. As a feasibility study, another widely used method based on mercury porosimetry data was also used to calculate fractal dimension (Fig. 14). As the first two typical plots shown (Fig. 14a, b), most samples lack data at the pressure P between 0.1 and 10 MPa (corresponding to pore size between 120 nm and 12 μm), and as there is no linear relationship when the pressure is higher than 10 MPa, this phenomenon may be related to the absence of pores in this range generated in the shale samples. Though linear relationships are observed with pressure below 0.1 MPa with a high goodness of fit, it cannot represent the characteristics of pore structure of the shale samples. The plot of sample stp-1 shows significant linear correlation in a high-pressure section, with a fit coefficient of 0.9916 and fractal dimension Dₙ as calculated by equation (1) as 2.377 (Fig. 14c); this can be interpreted as macropores being the dominant pores in sample stp-1. Due to the infeasibility of mercury porosimetry, Dₙ as calculated by the FHH model using N₂ adsorption data will be used to characterize the pore structure of shale samples in this article.

4.4.2. Factors that influence fractal dimensions

There is a positive relationship between fractal dimensions and TOC content as shown in Fig. 15a, with the exception of sample p2; this is because the higher the TOC content, the more micropores are generated in organic matter, which can lead to more complex pore structure and resulting larger fractal dimensions. The relationship between fractal dimensions and quartz contents is also positive due to biogenic quartz (Fig. 15b). In previous section, we found that the diameters of pores generated with clay minerals are larger than those of pores generated in organic matter, and therefore, the higher the clay minerals content, the smaller fractal dimensions, which is shown by the negative relationship in Fig. 15c. The special sample, p2, which has a medium TOC content and the highest clay mineral content, has the smallest fractal dimension, which is likely because the pores generated in organic matter can be as large as those generated in clay minerals, and this is consistent with the conclusion in Section 4.3.3.

Fig. 16 shows the relationships between fractal dimensions and pore structure parameters. With decreasing average pore sizes, the complexities of pore structure increase, which leads to larger fractal dimensions. Thus, as shown in Fig. 16a, the relationship between fractal dimensions and average pore sizes is negative. Only the positive relationships between fractal dimensions and the surface area and volume of micropore were observed in this study (Fig. 16b, c), and this is in agreement with Yang’s research on shales collected from Sichuan, China (Yang et al., 2014a, 2014b). Above all, TOC, quartz and clay mineral content are the primary influential factors for pore structure parameters, and fractal dimensions, which can be regarded as a comprehensive parameter with which to characterize the pore structure of shales, are important to analyze quantitatively in the future.

5. Conclusions

In this article, the pore structure characteristics of Lower Silurian Longmaxi Formation shales collected from western Hunan and

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fractal fitting equation</th>
<th>Dₙ</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>esd-1</td>
<td>y = 2.4737 – 0.3x</td>
<td>2.7</td>
<td>0.9936</td>
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<tr>
<td>esd-2</td>
<td>y = 2.6359 – 0.2324x</td>
<td>2.7676</td>
<td>0.9868</td>
</tr>
<tr>
<td>esd-3</td>
<td>y = 2.0149 – 0.2342x</td>
<td>2.7658</td>
<td>0.9875</td>
</tr>
<tr>
<td>esd-4</td>
<td>y = 2.1811 – 0.2353x</td>
<td>2.7647</td>
<td>0.9809</td>
</tr>
<tr>
<td>p2</td>
<td>y = 2.1418 – 0.3647x</td>
<td>2.6353</td>
<td>0.9945</td>
</tr>
<tr>
<td>p3</td>
<td>y = 1.1293 – 0.31x</td>
<td>2.69</td>
<td>0.9995</td>
</tr>
<tr>
<td>stp-1</td>
<td>y = 1.3536 – 0.2768x</td>
<td>2.7232</td>
<td>0.996</td>
</tr>
<tr>
<td>stp-2</td>
<td>y = 1.7442 – 0.2690x</td>
<td>2.7391</td>
<td>0.9981</td>
</tr>
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</table>

Fig. 13. Three typical FHH plots of the shale samples.
Hubei were investigated using high-pressure mercury injection and low-temperature N2 adsorption/desorption experiments. Fractal properties from N2 adsorption data obtained using the FHH model were also discussed. The following conclusions were reached.

1. The TOC content varies from 0.71% to 4.75%, with a mean value of 2.58%, and their thermal maturities have reached the over-mature stage and dry gas generation window. Quartz and clay minerals were the major mineral compositions in the samples, and this differs from previous studies of other shales (Chalmers and Bustin, 2008; Han et al., 2013; Wang et al., 2013, 2013b), as no carbonates were found in the shale samples of this area. Due to its biogenic source, quartz contents positively correlated with TOC values.

2. Pore size distributions obtained from mercury injection analysis were divided into three groups. Samples with higher TOC content always had smaller dominant pore sizes, and samples with higher clay mineral contents and lower TOC content may have larger pore sizes, with a major peak between 30 nm and 1 μm. The morphology of pores in shales
rich in organic matter are narrow necks and wide bodies, and those rich in clay minerals are flat-shaped. The BJH and DFT models were used to derive pore size distributions using N₂ adsorption data, and both are representative. The differential distribution curves of pore volumes and surface areas show the dominant pore sizes among all shale samples are within the range of micropores and mesopores, and they are the major contributors to pore surface area, while mesopores and macropores make more significant contributions to pore volume.

(3) The specific surface areas ranged from 6.12 to 28.42 m²/g, with an average value of 16.14 m²/g, and the total pore volume varies from 0.0105 to 0.0338 cm³/g, with a mean value of 0.0213 cm³/g. The correlation analysis between pore structure parameters and TOC values and quartz and clay minerals content indicates that TOC values and quartz content have positive influences on micropores and fine mesopores though larger pores can also exist in organic matter, and clay minerals play an important role for the generation of mesopores and macropores.

(4) Due to the infeasibility of mercury porosimetry, fractal dimension D₂ were calculated with the FHH model using N₂ adsorption data; it ranged from 2.6353 to 2.7694, with an average value of 2.7284. As we know, the more micropores within shales, the more complex the pore structure will be, and thus the fractal dimension will be larger. Therefore, organic matter and quartz positively influence fractal dimensions, and there is a negative relationship between clay mineral content and fractal dimensions.

Acknowledgments
This work was financially supported by the National Natural Science Foundation of China (grant no. 41272176/D0208) and the Fundamental Research Funds for the Central Universities of China grant no. 2-9-2015-134. The first author also acknowledges the Chinese Scholarship Council for providing a scholarship.

References