Research paper

Investigation of pore structure and fractal characteristics of organic-rich shale reservoirs: A case study of Lower Cambrian Qiongzhusi formation in Malong block of eastern Yunnan Province, South China

Ang Li a, b, c, Wenlong Ding a, b, c,*, Jianhua He a, b, c, Peng Dai a, Shuai Yin a, Fei Xie a

a School of Energy Resources, China University of Geosciences, Beijing 100083, China
b Key Laboratory for Marine Reservoir Evolution and Hydrocarbon Abundance Mechanism, Ministry of Education, China University of Geosciences, Beijing 100083, China
c Key Laboratory for Shale Gas Exploration and Assessment, Ministry of Land and Resources, China University of Geosciences, Beijing 100083, China

Abstract

In order to study pore structure and fractal characteristics of the organic-rich marine shale, fourteen shale samples from Lower Cambrian Qiongzhusi formation in Malong block of eastern Yunnan province were investigated by organic geochemical analysis (total organic carbon content analysis and thermal maturity analysis), X-ray diffraction (XRD) analysis, porosity and permeability tests, field emission scanning electron microscopy (FE-SEM), low-pressure nitrogen adsorption and methane adsorption experiments. Fractal dimensions D1 and D2 (at relative pressure of 0–0.5 and 0.5–1, respectively) were obtained from the nitrogen adsorption data using the fractal Frenkel–Halsey–Hill (FHH) method. Not only have the relationships among pore structure parameters of shale, the relationships between TOC content, mineral compositions, pore structure parameters and fractal dimensions been discussed, but also the significance of two fractal dimensions D1 and D2 and the impact of fractal dimensions on adsorption capacity have been investigated. The results showed that fourteen shale samples have TOC content ranging from 1.25% to 7.72%, two fractal dimensions both increase with the increasing TOC content, and gradually come to a standstill the curves present the shape of "parabola". The major mineralogical compositions of shales are quartz and clay minerals, the quartz contents are between 25.5% and 42.7%, the clay contents are between 26.6% and 44.2%. Fractal dimension D1 has a negative correlation with quartz contents and a positive correlation with clay minerals contents, but fractal dimension D2 has no apparent relationship with quartz and clay minerals contents. The specific surface area is in the range of 4.98 m²/g–19.66 m²/g, the total pore volume is between 0.00479 cm³/g and 0.01765 cm³/g, and the average pore diameter is between 3.37 nm and 6.02 nm. Two fractal dimensions increase with the increasing surface area and pore volume, and also increase with the decreasing average pore diameter because of the complicated pore surface and structure of small pores. Further investigation indicates that D1 represents fractal characteristics from the irregular pore surface, while D2 represents fractal characteristics related to the complicated pore structure, and shale samples with larger fractal dimensions have higher methane adsorption capacity. Therefore fractal analysis is helpful to have a better understanding of pore structure and adsorption capacity of marine shale.

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1. Introduction

Shale gas as a new unconventional energy relieves the pressure of global oil and gas resources shortage effectively. Especially the remarkable achievements of shale gas exploration and exploitation in North America have made the world strengthen the efforts to prospect this new energy. Shale gas existing in organic-rich shale is primarily in three states of free gas, adsorbed gas or a small amount of dissolved gas (Curtis, 2002). Pore size determines the state of shale gas: free gas is primarily stored in large pores or fractures, and adsorbed gas is primarily stored in small pores (Zhong, 2012). Previous studies have suggested that there are a
great mass of micro- and nano-scale pores and microcracks, and the mesopores with diameters between 2 and 50 nm play a dominant role in shale (Labani et al., 2013; Wu et al., 2013; Yang et al., 2013). TOC contents, organic matter maturity, the types and contents of clay minerals affect the development of shale pores: the development of organic matter pores is promoted by high TOC contents and appropriate organic matter maturity, whereas excessive maturity may reduce the number of organic matter pores (Nie et al., 2014; Tang et al., 2015; Guo et al., 2014; Curtis et al., 2012). Pores within organic matter are widely recognized as a significant component of gas storage and transport systems in shales (Ambrose et al., 2010; Loucks et al., 2009; Passey et al., 2010; Sonderegger et al., 2010). Clay minerals provide a certain specific surface area for shale, but different clay minerals contribute differently to the surface area in organic-rich shale (Ji et al., 2012; Cao et al., 2015). Shales with more porosity and higher surface area have higher CH₄ adsorption capacity. At present, field emission scanning electron microscopy (FE-SEM) and nano-CT imaging have proven to be effective methods to characterize the morphology and structure of shale pores qualitatively (Heath et al., 2011; Curtis et al., 2012; Tiwari et al., 2013; Kelly et al., 2015; Cui et al., 2012), low-pressure nitrogen adsorption, high-pressure mercury intrusion porosimetry, nuclear magnetic resonance, porosity and permeability tests are used for obtaining the quantitative surface area, pore-size distribution, pore volume, porosity and permeability (Ross and Bustin, 2007, 2009; Jiao et al., 2014; Clarkson et al., 2013; Chalmers and Bustin, 2007). Shale pores distribute in three-dimensional space, but not fill up it completely. It is too difficult to reflect the complexity and heterogeneity of shale microstructure directly by experiments. However, fractal concepts were introduced by Mandelbrot to reflect the real properties and states of porous materials which don't conform to Euclidean geometry in 1975 (Mandelbrot, 1975). The results are more accordant with the diversity and complexity of material structure, and the introduction of fractal theory provides a new way to evaluate quantitatively the complicated pore structure of oil and gas reservoir. Pfeifer and Avnir (1983) have proved that the porosity in reservoir rocks has fractal property by the method of adsorption. Shale as a porous material with complex microstructure and self-similarity satisfies the fractal conditions (Yang et al., 2014). In this paper, the fractal characteristics of pores in shales from the Lower Cambrian Qiongzhusi formation were investigated using low-pressure N₂ adsorption experiment data and the Frenkel–Halsey–Hill (FHH) method, which not only can describe the fractal characteristics of macropores, but also effectively evaluate that of mesopores and micropores. Fractal dimensions are used to represent the irregular degree of pore network of shale, higher fractal dimensions correlate to more complicated pore properties.

The mission of this paper is to investigate the pore structure of shales from the Lower Cambrian Qiongzhusi formation in Malong block of eastern Yunnan Province, located in the southwestern margin of the Yangtze plate (Fig. 1a). The Lower Cambrian Qiongzhusi formation was deposited in shallow-marine shelf, and the water depth gradually increased from northwest to southeast. The stratigraphy of the upper part of Qiongzhusi formation consists of gray-dark gray siltstone, mudstone, silty shale and pelitic siltstone, whereas the lower part of the formation is the main layer of hydrocarbon generation, the lithology of which is black carbonaceous shale, silty shale interbedded with pelitic siltstone and Dolomite (Fig. 1b).

A relatively complete experimental program was conducted, including TOC content analysis, thermal maturity analysis, XRD analysis, FE-SEM, porosity and permeability tests, nitrogen adsorption and methane adsorption. Organic geochemistry data (TOC, thermal maturity) was provided by the Geochemistry Laboratory of Yangtze University. A Leco CS–200 carbon–sulfur analyzer was used to measure the total organic carbon content (TOC) of fourteen samples following the Chinese standard GB/T19145-2003, “Determination of Total Organic Carbon in Sedimentary Rocks” (Xu et al., 2003), at a temperature of 25 °C and a relative humidity (RH) of 60%. The measurement of bitumen reflectance was performed using microscope photometer instruments according to the Chinese Standard SY/T5118-2005, “Determination of bitumen from rocks by chloroform extraction” (Wang et al., 2005), at a temperature of 20 °C and a relative humidity (RH) of 55%. The results were converted to equivalent vitrinite reflectance using the formula \( VR₀ = 0.618BR₀ + 0.4 \) (Jacob, 1985), where \( VR₀ \) is the equivalent vitrinite reflectance and \( BR₀ \) is the bitumen reflectance.

X-ray diffraction (XRD) was used to quantitatively analyze the mineral composition at the CNNC Beijing Research Institute of Uranium Geology. All samples were crushed into powder with a grain size of <80 µm and then analyzed with a “Panalytical X’PertPRO MPD” X-ray diffraction. The experimental standards and testing methods employed here are in accordance with SY/T6210-1996, the oil and natural gas industry standard of the People’s Republic of China entitled “Quantitative Analysis of Total Contents of Clay Minerals and Common Non-clay Minerals in Sedimentary Rocks by X-ray Diffraction” (Wang et al., 1996).

Low-pressure N₂ adsorption experiments were conducted with a “Quantachrome-nova2000” Surface Area Analyzer and Pore Size Analyzer according to Chinese Oil and Gas Industry Standard SY/T 6154–1995 (Wu et al., 1995). Shale samples were sieved to obtain the same particle size of 2–4 mm and were dried at 378 K for 24 h in a vacuum oven. After drying, samples were crushed again to obtain the grain size of 0.28–0.45 mm. For all samples, N₂ adsorption isotherms at 77 K were measured for the relative pressure (P/P₀) range from 0.01 to 0.995. Moreover, we also obtained the pore surface area, pore volume and average pore diameter.

High-pressure methane sorption measurements were performed with a high pressure gas sorption & desorption instrument of HPVA Isotherm Measurement System. The experimental standards and testing methods that were employed referred to the China national standard GB/T 19560–2008, “Experimental method of high-pressure isothermal adsorption to coal” (Zhang and Zhang, 2008). High-pressure methane sorption isotherms were measured at moisture-equilibrated samples (120–150 g) that were crushed and sieved to less than 60 mesh particle size at a consistent temperature of 35 °C and up to a consistent pressure of 22 MPa. The analytical results include the Langmuir volume and Langmuir pressure.
The porosity and permeability of shale samples were measured following the Chinese Oil and Gas Industry Standard SY/T5336-1996 at the SGS Unconventional Petroleum Technical Testing (Beijing) Corporation Limited (Ren et al., 1996). Porosity measurements were carried out with an instrument of KXD-II porometer using a helium expansion method, and permeability measurements were conducted using a permeameter (QT-2) with dry nitrogen as the medium. The experiments were conducted under a temperature of 25°C and a pressure of 96.8 kPa.

The microstructure of shale samples was observed and analyzed at the China University of Petroleum (Beijing) through Quanta 200F field emission scanning electron microscopy (FE-SEM). These experiments utilized a temperature of 24°C and a humidity level of 35%.

3. Results

3.1. TOC content, thermal maturity and mineral constituents

Results pertaining to the TOC content, thermal maturity and mineral percentages of fourteen shale samples are presented in Table 1. The TOC content of shale samples ranges from 1.25% to 7.72% with an average of 3.16%. The values of equivalent vitrinite reflectance VR0 are between 2.26% and 5.36% with an average of 3.25%. The buried age of Qiongzhusi formation is so old that all samples are in stage of over-maturity. The dominant minerals in the over-maturity shale samples are quartz and clay minerals. Quartz content varies from 25.5% to 42.7%, with a mean value of 32.68%, whereas clay minerals content ranges from 26.6% to 44.2% with an average of 36.06%. Clay minerals mainly contain illite (average of 43.5%), illite/smectite mixed layer (average of 31.36%), chlorite (average of 19.21%) and also contain a small amount of kaolinite (average of 6.92%). Feldspars (Potash Feldspar and plagioclase) content ranges from 4.2% to 29.5% with a mean value of 15.84%. Carbonate mineral (calcite and dolomite) content averages 10.75% and is between 5% and 17.8%. Moreover, shale samples contain a small amount of pyrite with an average of 3.46%.

3.2. Porosity, permeability and methane adsorption results

The porosity of samples is between 1.28% and 4.89% with an average of 3.10% (Table 2). The permeability is in the range of 0.0022 mD to 0.0086 mD with a mean value of 0.0054 mD. Fig. 2 shows that there is a positive correlation between porosity and permeability, indicating that the connectivity among pores is appropriate, open pores take a high proportion in shales. The Langmuir volume obtained from methane adsorption ranges from 1.53 m³/t to 4.34 m³/t with an average of 2.61 m³/t, and the Langmuir pressure ranges from 1.68 MPa to 3.59 MPa.

3.3. N₂ gas adsorption isotherms and pore structure

Pore structure is characterized using low-pressure N₂ adsorption isotherms illustrated in Fig. 3. According to the IUPAC classification, the isotherms of fourteen samples belong to Type IV (Gregg and Sing, 1982), indicating that shale possesses a continuous and complete pore system which develops from nano-scale pores to relatively infinite pores (Yang et al., 2013). At the low relative
pressure (P/P₀ = 0–0.4), the adsorption amount is low because of the interaction force between N₂ and pore surface, and adsorption isotherms rise gently. N₂ can be adsorbed on the surface of pores in the form of monolayer coverage at this stage. At the medium-high relative pressure (P/P₀ = 0.4–0.8), the adsorption amount of N₂ increases significantly and the adsorption branch and desorption branch of the isotherms do not overlap, resulting in a hysteresis loop. This process belongs to the stage of multilayer coverage. When the relative pressure P/P₀ ranges from 0.8 to 1.0, the adsorption amount of N₂ increases sharply, whereas adsorption saturation phenomenon doesn’t appear when P/P₀ approaches to saturated vapor pressure, which may be due to the capillary condensation occurred within the mesopores (Gregg and Sing, 1982). This phenomenon may reflect the strong heterogeneity of pore size of shale samples.

In reality, pores and fractures in shale are complicated as well as varied, so the shape of hysteresis loops just reflects the pore types which take a large proportion in number. Furthermore, in the pores closed at one end (e.g., cylindrical pores with a closed end and wedge-shaped pores), the relative pressure of capillary condensation equals that of capillary evaporation, which results in the overlap between adsorption branch and desorption branch, and hysteresis loop fails to appear. Therefore, hysteresis loops can’t be used to judge whether this type of pores exists (Wei et al., 2013). According to the hysteresis loop shape of N₂ adsorption–desorption isotherms, the shale samples can be divided into three types: Type H₂, Type H₃ and Type H₄ (Table 3). For Type H₂, adsorption branch exhibits an obvious yielding point at the medium relative pressure, which reflects the pores with narrow necks and wide bodies (referred as inkbottle-shaped pores). Micropores as the “bottleneck” are well developed in shale. Inkbottle-shaped pores are good for shale gas accumulation, but bad for seepage. For Type H₃, the adsorption/desorption branches are parallel at lower–medium P/P₀ ratios, and steeply increase when P/P₀ approaches to saturated vapor pressure and exhibit a narrow hysteresis loop, which associated with plate-like pores. The Type H₄ isotherms are characterized by narrow loops and flat adsorption/desorption branches from the beginning to the end of desorption, and represents the slit-shaped pores. Plate-like pores and slit-
Fig. 3. Nitrogen adsorption–desorption isotherms of shale samples.
Table 3
Pore types obtained from the adsorption isotherms using low-pressure N\textsubscript{2} adsorption.

<table>
<thead>
<tr>
<th>Loop type</th>
<th>Sample</th>
<th>Pore type</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>WX-3</td>
<td>Inkottle-shaped pore</td>
</tr>
<tr>
<td>H\textsubscript{3}</td>
<td>WX-1</td>
<td>WX-2 WX-11 WX-12 WX-13 Plate-like pore</td>
</tr>
<tr>
<td>H\textsubscript{4}</td>
<td>WX-4 WX-5 WX-8 WX-9 WX-14 Slit-shaped pore</td>
<td></td>
</tr>
</tbody>
</table>

shape pores are advantageous to the flow of hydrocarbons because of excellent openness, and these two types of pores have a high proportion among 14 samples, which is just in accordance with the positive correlation between porosity and permeability.

The pore structure parameters obtained from N\textsubscript{2} adsorption, i.e., specific surface area, pore volume and average pore diameter, are shown in Table 2. Specific surface area is between 4.98 m\textsuperscript{2}/g and 19.66 m\textsuperscript{2}/g, with a mean value of 12.07 m\textsuperscript{2}/g. Pore volume ranges from 0.00479 cm\textsuperscript{3}/g to 0.01765 cm\textsuperscript{3}/g, with an average value of 0.01083 cm\textsuperscript{3}/g. Average pore diameter generally is in the range of 3.37 nm–6.02 nm, with an average value of 4.47 nm, which is considered mesopore sized.

3.4. Fractal dimensions from low-pressure N\textsubscript{2} adsorption isotherms

At present, several methods have been proposed to calculate the fractal dimension of porous material on the basis of gas adsorption isotherms, including fractal BET model, fractal FHH model and the thermodynamic method (Avnir and Jaroniec, 1989; Cai et al., 2011; Pyun and Rhee, 2004; Yao et al., 2008). Among these methods, the FHH model has been proven to be most effective and is widely used for many types of porous materials (Yao et al., 2008). The calculation of fractal dimensions using the FHH model on the results of nitrogen adsorption has been discussed in detail (Qi et al., 2002; Pyun and Rhee, 2004; Yao et al., 2008), and the FHH model can be described as follows:

\[
\ln \left( \frac{V}{V_0} \right) = A \left[ \ln \left( \frac{P_0}{P} \right) \right] + \text{constant} \tag{1}
\]

where \(V\) is the volume of adsorbed gas molecules at the equilibrium pressure \(P\); \(V_0\), the volume of monolayer coverage; \(A\), the power-law exponent that is dependent on \(D\) and the mechanism of adsorption; and \(P_0\), the saturation pressure of the gas. If the pores of shale sample are fractal, a plot of \(\ln(V)\) versus \(\ln(\ln(P_0/P))\) will show a linear relationship. \(A\) is the slope of the straight-line and fractal dimension \(D\) can be derived from the line slope \(A\)

\[
A = D - 3 \tag{2}
\]

or

\[
A = (D - 3)/3 \tag{3}
\]

Both interpretations have been frequently invoked (Qi et al., 2002; Pyun and Rhee, 2004; Rigby, 2005), but no consensus has been reached on which one is better. The FHH plots of samples WX-5 and WX-14 are shown in Fig. 4. There are two distinct linear segments at a relative pressure (\(P/P_0\)) of 0–0.5 and 0.5–1, indicating that the pore spaces in shale have fractal characteristics in these two regions. Based on the research of fractal characteristics of coal, Yao et al. (2008) discussed that fractal dimension \(D_1\) reflected the surface fractal dimension and fractal dimension \(D_2\) represented the pore structure fractal dimension.

The values of fractal dimension \(D_1\) calculated by Eq. (3) are in the range of 2.1750–2.5848, but the values of fractal dimension \(D_1\) calculated by Eq. (3) are from 1.5618 to 1.8834 (all of them are less than 2), which deviates from the definition of fractal dimension of pore surface and pore structure (Peifer and Avnir, 1983; Xie, 1996).

In general, the fractal dimension \(D\) can vary from 2 for a perfectly regular smooth pore system to 3 for a highly complex pore system. In contrast, the values of fractal dimensions \(D_1\) and \(D_2\) derived from expression Eq. (2) range from 2 to 3, which provides more realistic results. Therefore, Eq. (2) is used in this paper. The equations of fitting straight lines and fractal dimensions at the relative pressure (\(P/P_0\)) range of 0–0.5 and 0.5–1 are shown in Table 4, fractal dimension \(D_1\) varies from 2.5206 to 2.6278 with a mean of 2.5990, and fractal dimension \(D_2\) is between 2.7250 and 2.8616 with a mean of 2.8022. Fractal dimensions of all shale samples are far from 2 and closer to 3, indicating that the pore surface and pore structure of shales are heterogeneous.

4. Discussion

4.1. Pore structure parameters characteristics and their relationships with mineral compositions

The relationships among various pore structure parameters of shale samples are illustrated in Fig. 5, there are negative correlations between average pore size and specific surface area, total pore volume (\(R^2 = 0.6105\) in Fig. 5a and \(R^2 = 0.5744\) in Fig. 5b, respectively), which is in agreement with previous studies (Chalmers et al., 2012; Yang et al., 2014; Fu et al., 2015). Micro-pores and mesopores make a significant contribution to the specific surface area and pore volume in shale samples on the basis of pore diameter distribution. Shales with smaller average pore diameters would also have more micropores and mesopores, which could lead to relatively high specific space areas and total pore volumes. The specific surface area is positively correlated with the total pore volume (\(R^2 = 0.9165\) in Fig. 5c), which is consistent with the results of Zeng et al. (2014) and Wei et al. (2013). All samples show an increase in specific surface area with increasing total pore volume.

The influences of mineralogical compositions upon the pore structure parameters are obvious in Fig. 6, specific surface area and total pore volume have no apparent relationship with clay content. Clay minerals such as Montmorillonite and illite/smectite mixed layer have relatively high specific surface area because they possess not only external surface area but also more internal surface area provided by the interlayer structure, the specific surface area of these two minerals is 76.4 m\textsuperscript{2}/g and 30.8 m\textsuperscript{2}/g, respectively. However, the N\textsubscript{2} BET measurements yielded surface area of 15.3 m\textsuperscript{2}/g for kaolinite, 11.7 m\textsuperscript{2}/g for chlorite and 7.1 m\textsuperscript{2}/g for illite, the surface area of these three minerals is smaller than that of Montmorillonite and illite/smectite mixed layer (Ji et al., 2012). The high content (on average 62.71%) and small surface area of illite and chlorite in shale make clay minerals have no apparent contribution to the surface area of shale samples. Furthermore, because of compaction, we can observe that part of the plate-like pores and interparticle pores of clay minerals are filled or closed on the microscale (Fig. 7a and b). Therefore, the specific surface area and total pore volume of 14 shale samples irregularly vary with the increasing clay minerals content. As shown in Fig. 6c and d, the slightly negative relationships between quartz content and specific surface area, total pore volume (\(R^2 = 0.3148\) and \(R^2 = 0.3552\), respectively), suggested that quartz isn't the major contributor to specific surface area and total pore volume in shales. The SEM images also illustrate that there is less pores on the smooth surface of quartz and quartz provides less specific surface area and total pore volume (Fig. 7c and d).
4.2. Relationships between fractal dimensions and the TOC and composition content of shales

In order to understand the role of mineralogical compositions and TOC of shale investigated on fractal characteristics, all correlations between fractal dimensions and TOC content, mineralogical compositions are plotted in Fig. 8. The fractal dimensions $D_1$ and $D_2$ are positively correlated with TOC content, which is consistent with the gas shale data documented by Yang et al. (2014) and Liu et al. (2015). The results of Yang et al. (2014) and Liu et al. (2015) demonstrated that fractal dimension $D$ had a positive linear correlation with TOC content, and the correlation coefficients of two fitting straight lines are $0.84$ and $0.62$ respectively. However, the relationships between fractal dimensions (both $D_1$ and $D_2$) and TOC content are characterized by a parabola curve, with a yielding point at 4.5% TOC content in this study. When TOC content is less than 4.5% (4.5% is an approximation), fractal dimensions $D_1$ and $D_2$ increase rapidly with the increase of TOC content, because organic matter itself possesses the porous structure, coupled with a lot of nano-scaled pores develop during the thermal evolution of organic matter. More surface areas and adsorption space for gas molecules provided by the complicated three-dimensional pore network composed of the connection of external and internal pores make the pore structure and surface more irregular, thus increasing fractal dimensions $D_1$ and $D_2$. In more than 4.5% TOC content, fractal dimensions increase slowly with the increase of TOC content, and the fitting curve tends to be horizontal or declining eventually. This is because shale samples with a higher TOC content generally produce more micropores, mesopores and residual carbonaceous organic matter due to the hydrocarbon generation effect. An increase in the proportion of pores and residual carbonaceous organic matter would reduce the stability of shale internal structure, facilitating the compaction and filling of pores under the action of gravity of the overlying strata. Therefore, the reduction of pores results in surface area, pore volume and fractal dimensions (both $D_1$ and $D_2$) remaining stable or even declining. The SEM

**Table 4**

Fractal dimensions derived from the FHH model.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fractal dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Po = 0–0.5</td>
<td>R²</td>
</tr>
<tr>
<td>WX-1</td>
<td>y = $-0.3949x + 1.6535$</td>
</tr>
<tr>
<td>WX-2</td>
<td>y = $-0.3775x + 1.3702$</td>
</tr>
<tr>
<td>WX-3</td>
<td>y = $-0.3746x + 1.9286$</td>
</tr>
<tr>
<td>WX-4</td>
<td>y = $-0.3722x + 2.0062$</td>
</tr>
<tr>
<td>WX-5</td>
<td>y = $-0.4274x + 1.0131$</td>
</tr>
<tr>
<td>WX-6</td>
<td>y = $-0.4095x + 1.2604$</td>
</tr>
<tr>
<td>WX-7</td>
<td>y = $-0.3989x + 0.9367$</td>
</tr>
<tr>
<td>WX-8</td>
<td>y = $-0.4794x + 0.3254$</td>
</tr>
<tr>
<td>WX-9</td>
<td>y = $-0.4150x + 0.8913$</td>
</tr>
<tr>
<td>WX-10</td>
<td>y = $-0.4264x + 1.0152$</td>
</tr>
<tr>
<td>WX-11</td>
<td>y = $-0.3960x + 1.6839$</td>
</tr>
<tr>
<td>WX-12</td>
<td>y = $-0.3740x + 1.8475$</td>
</tr>
<tr>
<td>WX-13</td>
<td>y = $-0.3844x + 1.5991$</td>
</tr>
<tr>
<td>WX-14</td>
<td>y = $-0.3804x + 1.6079$</td>
</tr>
</tbody>
</table>

**Fig. 4.** Fractal calculation results from In(V) vs. ln(ln(Po/P)) of N₂ adsorption for samples WX-5 (left) and WX-14 (right).

**Fig. 5.** Relationships between average pore diameter and specific surface area (a), total pore volume (b), and relationship between specific surface area and total pore volume (c).
Fig. 6. Relationships between pore structure parameters and shale composition. a and b: Clay content versus surface area (a), total pore volume (b); c and d: Quartz content versus surface area (c), total pore volume (d); and e and f: TOC versus surface area (e), total pore volume (f).

Fig. 7. FE-SEM images of Qiongzhusi shale in study area. (a) and (b): Compacted and closed clay minerals reduce the surface area and pore volume of shale samples; (c) and (d): Quartz produces less pores and reduces the heterogeneity and irregular of shale microstructure; (e) and (f): Thermal evolution of organic matter produces a mass of organic matter pores and residual carbon skeleton; (g) and (h): The compaction of organic matter pores and residual carbon skeleton reduces the fractal dimensions of shale samples.
images of residual carbonaceous organic matter and squashed organic matter pores are shown in Fig. 7e–h. In addition, the changing curves between TOC content and specific surface area, total pore volume also have the same trend (Fig. 6e and f). It just proves that thermal evolution of organic matter affects the complexity and heterogeneity of pore surface and structure, changing the fractal dimensions.

Fractal dimension D₁ shows a positive correlation with clay content ($R^2 = 0.732$ in Fig. 8c) but has a negative correlation with quartz content ($R^2 = 0.293$ in Fig. 8e). The layer structure and flocculent structure of clay minerals increase the specific surface area of pores, thus enhancing the complexity of pore surface. Hence, the higher the clay content is, the greater the fractal dimension D₁ is. As shown in Fig. 7c–d, the smooth surface of quartz suggests that quartz in shale weakens the development of pores and reduces the heterogeneity and irregular of shale microstructure. Thus fractal dimension D₂ decreases with the increase of quartz content. However, fractal dimension D₂ has no apparent relationship with the clay and quartz content, indicating that the mineral composition isn’t the major factor influencing fractal dimension D₂. In a word, the heterogeneity of pore surface has a great influence on the fractal dimension D₁.

4.3. Relationships between fractal dimensions and pore structure parameters

Fig. 9 shows relationships between the fractal dimensions (both D₁ and D₂) and pore structure parameters. The fractal dimensions both D₁ and D₂ have positive linear correlations with surface area and pore volume but show a negative linear correlation with average pore diameter, namely, shales with a greater surface area and pore volume as well as a smaller pore diameter have higher fractal dimensions and a more irregular pore surface or complicated pore structure. This phenomenon is consistent with the gas shale data documented by Yang et al. (2014), because shales with smaller average pore diameters would also have more micropores which generate more complicated pore structure and rougher pore surface, so the surface area and fractal dimensions of shales also increase. In addition, larger pore volume provides more adsorption space and adsorption sites for gas, and also increases the fractal dimensions.

4.4. Discrepancies of D₁ and D₂ and their contributions to CH₄ adsorption capacity

In general, there are two conventional definitions in describing the fractality of the porous material—the pore structure fractal dimension and the surface fractal dimension (Pyun and Rhee, 2004). Surface fractal dimension represents the pore surface irregularity: the greater the value of the surface fractal dimension is, the more irregular and rougher the pore surface is. Pore structure fractal dimension characterizes the complexity of pore distribution and connectivity in space: the larger the value of the pore structure fractal dimension is, the more complicated the pore structure is. In
In this study, fractal dimensions both $D_1$ and $D_2$ are used to characterize different surface behaviors occurred at the gas/solid interface. During the early stage of adsorption, we select the first linear segment in the range between the monolayer coverage and the multiple layer coverage just before the smoothing effect appears to calculate the fractal dimension $D_1$ (Pyun and Rhee, 2004). At this moment, the gas/solid interface is controlled by Van der Waals forces between gas and solid. Fractal dimensions $D_1$ reflects the state of pore surface indirectly by reflecting the behavior of Van der Waals forces, so $D_1$ represents the pore surface fractal dimension. However, the increase of adsorption capacity results in more adsorbed layers which make the interface smoother and weaken the control of Van der Waals forces between gas and solid. Fractal dimension $D_1$ would no longer characterize the gas/solid interface and fractal dimension $D_2$ is used to characterize the capillary condensation of gas clumps occurred in the shale pores. Because pore structure (e.g., pore shape, pore diameter) can affect the capillary condensation of gas clumps occurred in the shale pores. Therefore, a smaller pore diameter reflects stronger adsorption potential energy and leads to greater adsorption interaction between pore surface and gas molecules. Therefore, whether pore surface fractal dimension or pore structure fractal dimension would promote the adsorption capacity of shale and benefit gas accumulation.

5. Conclusion

In this paper, the pore structure and fractal characteristics of 14 shale samples from the Lower Cambrian Qiongzhusi formation in Malong block of eastern Yunnan Province, South China are investigated using various experiments and FHH theory with low pressure N$_2$ adsorption data. In addition, based on the physical significance of fractal dimensions, the impact of fractal dimensions on the adsorption capacity of shales has also been discussed. The following conclusions can be made:

Fig. 9. Relationships between pore structure parameters and fractal dimensions. a and b: Average pore diameter versus fractal dimension $D_1$ (a), fractal dimension $D_2$ (b); c and d: Surface area versus fractal dimension $D_1$ (c), fractal dimension $D_2$ (d); e and f: Total pore volume versus fractal dimension $D_1$ (e), fractal dimension $D_2$ (f).
Shale samples have different adsorption characteristics and fractal geometries at relative pressures of 0–0.5 and 0.5–1. Two fractal dimensions D1 and D2 can be obtained by using the fractal FHH method, with D1 ranging from 2.5206 to 2.6278, and D2 ranges from 2.7250 to 2.8616. D2 is greater than D1, indicating that the pore structure is more complex than pore surface in shales.

Pore types in shale samples mainly consist of plate-like pores, slit-shaped pores and inkbottle-shaped pores. There are negative correlations between average pore size and specific surface area, total pore volume, and a significant positive relationship between total pore volume and specific surface area. Surface area and total pore volume have no apparent relationship with clay content and slightly negative relationships with quartz content.

The relationships between fractal dimensions (both D1 and D2) and TOC content are characterized by a parabolic curve, with a yielding point at 4.5% TOC content in this study. Fractal dimension D1 increases with increasing clay content and decreasing quartz content, but fractal dimension D2 has no apparent relationship with the clay and quartz content. The fractal dimensions both D1 and D2 have positive linear correlations with the surface area and pore volume but show a negative linear correlation with the average pore diameter.

Fractal dimension D1 reflects the state of pore surface indirectly by reflecting the behavior of Van der Waals forces, so D1 represents the pore surface fractal dimension. Fractal dimension D2 is used to characterize the capillary condensation of gas clumps occurred in the shale pores. Because pore structure can affect the capillary condensation, D2 represents the pore structure fractal dimension. Furthermore, shale samples with greater fractal dimensions (both D1 and D2) have higher adsorption capacity.

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V. Li et al. / Marine and Petroleum Geology 70 (2016) 46–57

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