Characterization of typical 3D pore networks of Jiulaodong formation shale using nano-transmission X-ray microscopy

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**Abstract**

The microscopic pore structure is one of the most important factors to understand shale gas reservoirs. Recognized as a non-destructive method, nano-transmission X-ray microscopy (Nano-TXM) is sufficiently powerful to resolve nanometer pore structures and to quantify the effective network in shale. In this work, three dimensional (3D) pore networks of typical pore structures, such as organic matter pores (OM pores), interparticle pores (InterP pores), intraplatelet pores within clay aggregates (IntraP pores) and intercrystalline pores within pyrite (InterC pores), developing in Jiulaodong (JLD) formation shale in the Weiyuan 201 well (W201) in Sichuan Basin were reconstructed by Nano-TXM. Meanwhile, the pore morphology, pore size, porosity and interconnectivity were analyzed using Pore Network Modeling (PNM). The results indicated that the pore shape, pore size distribution, porosity and interconnectivity varied between the four pore types. Nanometer pores ranging from 150 nm to 1000 nm dominate the OM pores in the samples. However, pores with a sheet-like structure that are larger than 1000 nm are mainly found in InterP and IntraP pores. OM pores and InterP pores have larger porosities (35% and 23.7%, respectively) than the other two pore types. OM pores, InterP pores and InterC pores exhibit good and homogenous 3D connectivity, whereas IntraP pores have good extensity parallel to the clay mineral orientation but have no connectivity perpendicular to it. The 3D morphology and pore parameters suggest that the nano-pores in OM and InterC pores store absorbed gas and might be connected by micropores that existed in InterP and IntraP pores. The characterization of the pore structure in shale samples provides useful information for shale gas development.

1. Introduction

Shale gas has become one of the focuses of world attention after its rapid and successful commercial development in North America [6]. Shale gas explorations have been carried out and recently attained significant progress in Canada, England, China, Germany and other countries, especially in China [4,12,7,18]. The lower Paleozoic reservoirs of the Sichuan Basin in southwestern China...
are typical gas-rich horizons with several sets of shale, indicating a tremendous potential for shale gas development [31,32]. In 2011, an industrial gas flow was first obtained by China National Petroleum Corporation at the Weiyan 201 well (W201). As a typical tight gas reservoir, information regarding shale pore structure, which has a strong influence on the petrophysical properties of reservoir rocks, is necessary to understand storage and transport mechanisms [11,16]. The 2D-pore morphology, size and distribution are acquired by SEM and other methods [20,10,15]. Meanwhile, the shale pore size can reach the nanometer scale, which is much smaller than that quantified in sandstone and carbonate reservoirs [21,20,2]. Macropores, with a length larger than 50 nm, make great contributions to the total pore volume and porosity, as determined by nitrogen adsorption, high pressure mercury injection tests and FIB-SEM observations [9,29]. The microscopic structure is considered to be important for shale gas reservoirs; therefore, the two-dimensional (2D) pore structure characteristics of the JLD formation shale from W201 have been thoroughly researched [28]. From previous studies [20,9], there are four major types of pore structures in the JLD shale from W201 including organic matter pores (OM pore), interparticle pores (InterP pore), intraplatelet pores within clay aggregates (Intrap pore) and intercrystalline pores within pyrite (InterC pore). The InterP and Intrap pores are nanometer to sub-micrometer scale, are the most widespread forms in JLD shale, and are spaces for the storage of free gas. The OM pores, which consist of kerogen and hydrocarbons, are approximately 50 nm to ~1 µm and provide the main storage space for absorbed shale gas. The 2D pore structure characteristics of shale samples have been researched intensively but provide information on only the pore shape and size. However, its three-dimensional (3D) pore morphology and connectivity are still poorly understood and need further study.

Currently, many methods are used to directly characterize the nano-scale pore structure in shale gas reservoirs, such as field-emission scanning electron microscopy (FE-SEM) coupled with argon-ion-milled technique, focused ion beam scanning electron microscopy (FIB-SEM) and X-ray computed tomography (X-CT). FIB-SEM, with a maximum resolution of several nanometers, is used to visualize the nano-scale pore–throat structure in 3D, but it does unrecoverable destruction to the shale sample, making it impossible for further study with other methods [9,1]. Therefore, nano-transmission X-ray microscopy (Nano-TXM, also called Nano-CT) has received much more attention since the discovery of nano-pore in unconventional oil reservoirs. Recognized as a non-destructive method, X-ray computed tomography has been used to study pore structure, mineral contents and their spatial distributions as a function of different X-ray absorption coefficients. Meanwhile, permeability and porosity can also be calculated using relative computing software [23,14]. Additionally, Nano-TXM has a higher efficiency than FIB-SEM, while for example, a cube with a 10 µm side takes the latter at least 10 min to mill. With a resolution ranging from several micrometers to tens of nanometers, TXM is sufficient to resolve pore–throat structures down to the nanometer scale and to quantify the effective network in shale. When combined with an advanced dual-beam FIB-SEM milling-imaging technique, a typical area can be obtained by gallium ion milling, allowing SEM imaging of a newly milled shale surface in situ. Thus, the different types of pores that develop in shale can be clearly identified and chosen for Nano-TXM experiments to independently obtain their 3D structural information.

In this paper, the 3D pore networks of typical pore structures including OM pore, InterP pore, Intrap pore and InterC pore from a JLD formation shale sample from W201, Sichuan Basin were determined by Nano-TXM. Three dimensional models were built to intuitively show the pore spatial distributions. Furthermore, the quantitative information of pore size distribution (PSD), porosity and interconnectivity that are significant for shale gas accumulation and exploration were also calculated.

2. Samples and methods

2.1. Samples

The W201 shale samples from JLD formation were provided by Institute of Geology and Geophysics, Chinese Academy of Sciences. They are from the well that first provided the industrial gas flow by the China National Petroleum Corporation in 2011. The W201 shale samples were from approximately 2756 m in depth and had formed in a marine sedimentary environment, the lithology of

![Fig. 1](image-url)
Fig. 2. SEM images of the typical pore types in the W201 shale samples: (A) OM pores, (B) InterP pores, (C) IntraP pores, and (D) InterC pores.

Fig. 3. Results of the TXM tomography of OM pores and the 3D pore network reconstruction. (A) Reconstructed 2D images in the XY-plane. (B) Segmentation of the TXM slice into pores (black) and non-pores (white). (C) Reconstructed 3D microstructures. (D) 3D pore network reconstruction. (E) 3D pore–throat skeletal structure.
which mainly consists of dark shale mixed with siltstone and fine sandstone [5].

2.2. 2D pore structure characterizations

The W201 shale samples for SEM observation were prepared using ion milling (LJB 1A, Shenyanghuaye, China). The 2D pore structure were imaged with a Zeiss Merlin Compact LE0 1530 VP scanning microscope equipped with Inca X-Max energy dispersive spectroscopy (manufactured by Oxford Instruments) at the Shanghai Institute of Applied Physics, Chinese Academy of Sciences. For imaging, an acceleration voltage of 5 kV with a working distance of 5–6 mm was used; an acceleration voltage of 15 kV with a working distance of approximately 8–10 mm was used for the quantitative and qualitative identifications of minerals by energy dispersive spectroscopy (EDS).

2.3. 3D pore-network characterizations

2.3.1. Samples preparation and experimental facility

The Nano-TXM samples were prepared by an FEI Helios NanoLab 600 DualBeam FIB-SEM (Fig. 1A). A typical pore structure area was selected and milled into cylindrical samples with the focused ion beam. Then, the cylindrical sample, typically ~9 μm diameter × 12 μm length, was attached to a tungsten pin with a micro manipulator and fastened by a Pt film around the interface (Fig. 1B).

Nano-TXM experiments were carried out at beamline BL01B (Fig. 1C), the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. They provided 2D micrograph and 3D tomography at spatial resolutions of 50 nm [26], with a first-order diffraction of a Fresnel zone plate at an X-ray energy of 8 keV; the image field of view was 15 × 15 μm² for the first-order diffraction of the zone plate. The exposure time is 60 s for a 2D image. Meanwhile, the phase term can be retrieved by the Zernike’s phase contrast method. The gold phase ring is positioned at the back focal plane of the objective zone-plate retards or advances the phase of the zeroth order diffraction by π/2 resulting a recording of the phase contrast images at the detector. After acquiring a series of 2D images were collected with the sample rotated stepwise azimuthally. Then, the 3D tomography data sets were reconstructed by applying a filtered back-projection algorithm based on 181 sequential image frames taken with the azimuth angle rotating from −90° to +90°.

2.3.2. 3D tomography data analysis

Avizo Fire software 8.0 was used for the 3D tomography data analysis of the samples. Firstly, sub-volumes were extracted and smoothed with a Non-local Means filter. The sub-volumes of the OM pores sample, InterP pores sample, IntraP pores sample and InterC pores sample were 4.75 μm × 5.5 μm × 5.5 μm, 6.7 μm × 11.0 μm × 11.0 μm, 16.5 μm × 10.25 μm × 9.4 μm and 7.5 μm × 7.5 μm × 10 μm, respectively. Gray histograms related the different X-ray absorption coefficients of different materials were used to segment the pores, OM and the mineral matrix. Local thresholding schemes based on the indicator kriging method [22] were adopted for image segmentation. A lower T₀ for pores and an upper T₁ for the solid phase were visually selected from the gray scale image histograms by comparing the segmented image with original scanning slice. The remaining voxel values between T₀ and T₁ were then identified as pores or solids utilizing the local covariance determination in a second step. With the above segmentations, the 3D structural information of the W201 samples were reconstructed and visualized.

Furthermore, the Avizo Pore Network Model (PNM) was used to collect the petrophysic parameters of the microscopic pore structures. The 3D visualization of the medial axis (named skeleton, a network model of interconnected one-dimensional paths that reflect a strict geometrical relationship with the mineral surface) of the pore morphology was extracted from the segmented images.

Fig. 4. Results of the TXM tomography of InterP pores and the 3D pore network reconstruction. (A) Reconstructed 2D images in the XY-plane. (B) Segmentation of the TXM slice into pores (black) and non-pores (white). (C) Reconstructed 3D microstructures. (D) The 3D pore network reconstruction. (E) The 3D pore–throats model skeletal structure.
using morphological erosion based on the LKC algorithm [17]. Meanwhile, medial axis trimming was performed to remove disconnected and isolated voxel clusters that probably stemmed from unphysical origins. Next, the pore throats representing the cross-sectional area of each channel were determined using Dijkstra shortest paths algorithm [19]. The pores were displayed using spheres, and the throats were displayed using cylinders. Each of the shapes might be colored and scaled according to their attribution. Subsequently, the PNM data type was designed to store data that could be represented as linear lines in 3D space and that might be organized in networks of multiple lines. The extracted PNM parameters contained the pore size distribution, surface area and tortuosity et al. As the resolution of Nano-TXM was on the order of three pixels, pores and throats smaller than 50 nm were not included in the results.

3. Results and discussions

3.1. 2D pore structures

After observing dozens of W201 samples from JLD formation shale, it was concluded that the main pore types in the samples were OM pore, InterP pore, IntraP pore and InterC pore. This finding was also consistent with previous works [30,27,28]. SEM images of the typical pore structures of the samples are shown in Fig. 2. The ellipsoidal OM pores ranged from dozens of nanometers to hundreds of nanometers and were probably due to the conversion of kerogen to hydrocarbon, as shown in Fig. 2A. The InterP pores were exhibited in irregular, as shown in Fig. 2B, and were developing around or between brittle and clay clasts, which were the main materials in shale. However, the IntraP pores were seen as sheet and elongated pores, as shown in Fig. 2C, which were developing in laminar clay mineral. The InterC pores filled with little organic matter were triangular- or rectangular-shaped, as shown in Fig. 2D. With the SEM results, it could also be determined that most of InterP pores and IntraP pores are on the micro-meter level, but most of the OM pores are nano-scaled. The InterP pores and IntraP pores in W201 appear to possess a relatively good connectivity, and these pores are beneficial to the free gas storage. The nano-scale OM pores and InterC pores are good for the adsorbed gas storage. However, the OM pores and InterC pores in the samples seemed to be isolated in 2D-space. As is well known, SEM images exhibit only 2D microscopic structures of a surface and are incapable of providing 3D distribution and interconnectivity analyses.

3.2. 3D reconstructed structures

To obtain more information about the four typical pore structures of the W201 samples, Nano-TXM was used to investigate the 3D-space pore structure. The four typical pore structures, which were selected by FIB milling, were extracted from the...

Fig. 5. Results of the TXM tomography of IntraP pores and the 3D pore network reconstruction. (A) Reconstructed 2D images in the YZ-plane. (B) Segmentation of the TXM slice into pores (black) and non-pores (white). (C) Reconstructed 3D microstructures. (D) The 3D pore network reconstruction. (E) The 3D pore–throat model skeletal structure.
W201 samples. The tomography and 3D pore network of the four typical pore structures in the W201 samples are shown in Figs. 3–5. With different X-ray absorption efficiencies for organic matter, the mineral matrix and the pores, the composition of the material in each sample could be determined from 2D slices. The TXM tomography and 3D network reconstruction of OM pores in the W201 samples are shown in Fig. 3. The sub-volume of the OM pore samples was 4.75 mm³/5.5 mm³/5.5 mm³. Combined with SEM observations, the sample containing OM pores was segmented into pores (black) and non-pores (white) for each TXM slice, and the 3D structures were reconstructed, as shown in Fig. 3 A–C. Then, the pore structures were independently extracted, as shown in Fig. 3D. Furthermore, the skeletal structure of the pore–throat obtained by the Avizo PNM is also shown with a rainbow color scale in Fig. 3E. The large pores are presented in red, and the small pores are in violet. With the above results, the OM pores in the W201 samples exhibited good connectivity. The diameters of the OM pores were similar in scale, and few nodal pores were found in the samples. This was significantly different from the SEM results.

The TXM tomography and 3D network reconstruction of InterP pores in the W201 samples are shown in Fig. 4. The sub-volume of the InterP pores sample was 6.7 mm³/11.0 mm³/11.0 mm³. From the different gray histograms, more than three components were found in this sample, as shown in Fig. 4C. The area with the lowest X-ray absorption was defined as the pore structure (black), and the others represented the non-pore structure (white), for each TXM slice shown in Fig. 4 A and B. The pore structure and its skeletal structure are also shown in Fig. 4 D and E. With the results, a few micro cracks with good extensity were found in the pore structure in Fig. 4 D. Meanwhile, there are many nodal pores in samples, as shown in Fig. 4 E. This means that the connectivity could be poor. However, the connectivity for micro cracks is very good. All of this information could not be given by 2D structural characterizations.

The TXM tomography and 3D network reconstruction of IntraP pores in the W201 samples are shown in Fig. 5. The sub-volume of the IntraP pores sample was 16.5 mm³/10.25 mm³/9.4 mm³. Two components, pore (black) and non-pore (white), were defined by means of the different gray histograms, as shown in Fig. 5B. The 3D reconstruction structures, pore structure and skeletal structure are shown in Fig. 5C–E. The micro cracks presented as a layered structure were clearly seen in Fig. 5D, which was

### Table 1

<table>
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<tr>
<th>Pore types</th>
<th>OM pores</th>
<th>InterP pores</th>
<th>IntraP pores</th>
<th>InterC pores</th>
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<tr>
<td>Volume fraction (%)</td>
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<td>6.0</td>
<td>14.8</td>
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<tr>
<td>Total no. of pores</td>
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<td>1614</td>
<td>624</td>
<td>440</td>
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<td>Maximum pore size (nm)</td>
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<td>760</td>
<td>835</td>
<td>1943</td>
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<td>Minimum pore size (nm)</td>
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<td>76</td>
<td>77</td>
<td>153</td>
</tr>
<tr>
<td>Average pore size (nm)</td>
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<td>266</td>
<td>279</td>
<td>577</td>
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<tr>
<td>Total no. of throats</td>
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<td>3996</td>
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<td>2708</td>
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<tr>
<td>Mean area of throats (µm²)</td>
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<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Average length of throats (nm)</td>
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<td>749</td>
<td>924</td>
<td>755</td>
</tr>
<tr>
<td>Average coordination number</td>
<td>5.6</td>
<td>5.0</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>2.4</td>
<td>3.2</td>
<td>9.8</td>
<td>2.7</td>
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</table>

**Fig. 6.** Results of the TXM tomography of InterC pores and the 3D pore network reconstruction. (A) Reconstructed 2D images in the XY-plane. (B) Segmentation of the TXM slice into pores (black) and non-pores (white). (C) Reconstructed 3D microstructures. (D) The 3D pore network reconstruction. (E) The 3D pore–throat skeletal structure.
consistent with the SEM images. Meanwhile, it was determined that the clay minerals were almost the same density, and only a few nodal pores were found inside of them, as shown in Fig. 5D. This means that the IntraP pores exhibit good connectivity along the clay orientation (the XY plane in our 3D reconstructed structure) but display almost no connectivity along the Z direction.

InterC pores were also determined by TXM and reconstructed, as shown in Fig. 6. The sub-volume of the InterC pores sample was 7.5 μm × 7.5 μm × 10 μm. For the sample with the highest X-ray absorption, the pyrite framboids, it was hard to distinguish the pore structure from the organic matter in this sample. Therefore, the pyrite framboids were defined as the non-porous structure (white) and the others were the porous structure (black), as shown in Fig. 6B. The 3D pore reconstruction and the skeletal structure are also shown in Fig. 6D and E. With the results, the InterC pores were developing between the pyrite framboid micro-crystallites, which were almost similar in size. If the black areas have only the porous structure, then there was good connectivity. If not, then the real structure could not be determined by TXM, but it could be determined by FIB-SEM.

3.3. Pore morphology, porosity and interconnectivity

The petrophysical parameters of the four typical pore structures in the W201 samples are listed in Table 1; they were calculated with the Avizo PNM. The volume fraction of the pores in the samples, which means the porosity of the samples, was approximately 35.0%, 23.7%, 6.0% and 14.8% for OM pores, InterP pores, IntraP pores and InterC pores, respectively. The results indicate that the porosity of OM pore and InterP pore samples is much higher than those with OM pores and InterP pores have a higher coordination number (5.6 and 5.0) and a lower tortuosity (2.4 and 3.2) than IntraP pores. This means that these two types of pores provide good connectivity throughout the samples, and this property is of significant benefit for gas migration. The sample with IntraP pores has a lower coordination number (3.0) but a higher tortuosity (9.8). Combined with 3D tomography results, the IntraP pore structure exhibits good connectivity along the clay orientation (the XY plane in our 3D reconstructed structure) but no connectivity along the Z direction. This is why the tortuosity is so much higher in the sample. InterC pores have an average coordination number of 3.2 and an average tortuosity of 2.7, indicating good connectivity within a single framboid. Meanwhile, these results should be confirmed by FIB-SEM, which could distinguish the organic matter from the pores in such samples.

3.4. Shale gas transportation and storage

The pore size, total porosity and interconnectivity are very important factors for shale gas accumulation and transportation [25,29]. Pore size is one of the key factors that control the content of adsorbed gas and free gas in shale [13]. Free gas tends to concentrate in larger micrometer pores or fractures, but adsorbed gas tends to concentrate in smaller nanometer pores [8,24]. The nanometer pores with a large specific surface area could store
more adsorbed gas than other pores. The OM and InterC pores with larger numbers of nano-scale pores in the W201 samples could store an abundance of adsorbed gas, which is the likely potential resource. However, the micrometer cracks in InterP pores and IntraP pores, which possessed a sheet-like structure according to the TXM results, and the free gas might be enriched in this type of pore structure. Furthermore, this indicates that these types of pores are the main pore structures in the W201 samples, which means that the micrometer cracks are most likely determining the transport properties of the shale gas. In a previous work [3], it had been considered that micrometer cracks can be the channel connecting macropores with nanopores, ranging between 1 and 100 nm, especially during shale gas hydraulic fracturing. Therefore, the OM and InterC pores that were rich in nano-scale pores were connected by macropores, which mostly consists of InterP pores and IntraP pores. The characterization of pore structure in shale samples is beneficial for shale gas development.

4. Conclusions

Four typical pore structures in the W201 shale sample are characterized by nano-transmission X-ray microscopy. The nano-pores ranging from 150 nm to 1000 nm are dominated by the OM pore-type. However, the pores with a sheet-like structure that is larger than 1000 nm are mainly InterP pores and IntraP pores. OM and InterP pores have a larger porosity (35% and 23.7%, respectively) than the other two types of pores. The results indicate that nanopores are inclined to be more frequent, whereas micrometer micropores dominate porosity. Furthermore, OM pores, InterP pores and InterC pores exhibit good and homogenous 3D connectivity, whereas IntraP pores have a good extensity parallel to the clay mineral orientation but do not have connectivity perpendicular to it. The 3D morphology and pore parameters suggest that the OM and InterC pores store absorbed gas and might be connected by macropores that exist in InterP and IntraP pores. The characterization of the pore structure in shale samples is useful information for shale gas development.

Acknowledgements

This project was funded by Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB10002010), Major Program for the Fundamental Research of Shanghai Committee of Science and Technology (Grant No. 12JC1410400), National Natural Science Foundation of China (Grant No. 11275256 and 11179024) and Program of International S&T Cooperation (2014DFG60230). We thank working staff at beamline 01B1 of National Synchrotron Radiation Research Center (NSRRC) in Taiwan for their guidance.

References

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