Nanopores of the productive and non-productive sections within the Lower Silurian Longmaxi Shale Reservoir in the Southern Area of Sichuan Basin, China

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Abstract. This study focuses on nanopores of the productive and non-productive sections within the Lower Silurian Longmaxi shale reservoir in the southern area of Sichuan Basin. 4 rock samples from the productive section and 12 rock samples from the non-productive section were collected from a new exploration well in Changning Area. TOC, XRD and gas adsorption measurements were conducted on these samples. The productive section contains more organic matters, biogenic quartz, but less carbonates and feldspar and is much more porous relative to the non-productive section. Organic matters and clays have important impacts on the development of nanoporosity within the Lower Silurian Longmaxi shale reservoir in study area. Nanoporosity of the productive section is affected mainly by the organic matter contents, and hence implying the predominance of organic-matter pores within this section. Clay minerals have the primary controlling effects on the occurrence of nanopores within the non-productive section, and then indicating the predominance of mineral matrix pores in it. This study should be helpful for us to make a better understanding of in-situ shale gas resources and to optimize targets in this region.

1. Introduction
The Lower Silurian Longmaxi shale reservoir in Sichuan Basin has been one of the main targets in shale gas exploration and exploitation around the world [3]. Previous studies have been documented that the lower section of the Lower Silurian Longmaxi shale is usually productive with high gas flow rates relative to the upper section [3]. Nanopores are the main space for gas storage and transportation within this shale in the subsurface [3]. Hence better understanding of pore structures within the productive and non-productive sections is of importance for us to do the comprehensive evaluation of shale gas storage and in-situ gas resources. This study focuses on nanopores within the Longmaxi shale in the southern area of Sichuan Basin. 16 shale samples were collected from the lower Silurian Longmaxi formation of a new drilled exploration Well A with 4 samples from the lower section with high gas production and 12 samples from the upper non-productive section in Changning Area, Sichuan Basin (Figure.1). TOC, XRD and CO₂ and N₂ adsorption measurements were conducted on these samples. Nanopores and the relevant controlling elements of pore volumes were investigated comprehensively to better understand shale gas resources and the optimization of well targets.
2. Experimental

2.1. LECO TOC
The total organic carbon (TOC) was measured by LECO CS-200 analyzer on the samples with <200 mesh after treated with hydrochloric acid to remove the carbonates.

2.2. X-ray diffraction (XRD)
Shale powders with <200 mesh were used to do X-ray diffraction (XRD) analysis on a Bruker D8 Advance x-ray diffractometers at 40 kV and 30 mA with a Cu Kα radiation (λ = 1.5406 for CuKα1). Stepwise scanning analysis was performed at 4º/min within 3º - 85º (2θ). The relative minerals was evaluated by using the major peak areas of the specific minerals.

2.3. Gas adsorption
Gas adsorption measurements were performed on an Autosorb-iQ-MP instrument (Quantachrome Instruments) equipped with a vacuum pump capable of reaching 5E-7 Pa (7.25E-11 psi). Samples were crushed to 60-80 mesh size and then placed into 6-mm stem quartz sample cells and degassed for 12 h at 110°C under vacuum. Nitrogen at -196.15°C was used as the probe gas for all experiments. Specific surface areas were calculated using the best linear range between 0.05 and 0.3 pressure/initial pressure (P/Po) of N2 adsorption, with a minimum of five points used in the Brunauer-Emmett-Teller (BET) surface-area analysis. Pore volumes and pore size distributions were obtained using the Barrette Joyner Halenda method (BJH) and the BET method.

3. Results and Discussion

3.1. TOC and mineral compositions
The productive section contains more organic matter with TOC=2-5% relative to the upper non-productive section with TOC<1.0% (Figure.2). The mineral compositions of Well A are mainly quartz
and clay minerals, followed by feldspar and carbonates as well as a little bit pyrite with the average values of 41.56% for clays, 31.75% for quartz, 9.07% for feldspar and 16.19% for carbonates. In comparison with the upper section, the lower section contains more quartz, but less carbonates and feldspar (Figure.2). The good positive correlation between the contents of TOC and quartz indicates the predominance of biogenic quartz within the lower Silurian Longmaxi formation (Figure.3).

3.2. Gas adsorption-desorption curves
The CO$_2$ adsorption curves are considered to be the type I curve [5] in accordance with the IUPAC standards, in which the gas adsorption volume increases with the relative pressure (P/P$_0$) increasing until approaching the saturation. Micropore volumes are higher for the lower part relative to that of the upper part as indicated by the adsorption volumes at P/P$_0$ of about 0.03. The N$_2$ adsorption curves are assumed to be the type IV curve, the hysteresis loops are the H3 type [5]. The gas adsorption volumes of samples from the lower part of Longmaxi Fm is obviously higher than that of the upper as shown by the adsorption-desorption curves of CO$_2$ and N$_2$ (Figure.4). This also suggests their higher nanopore volumes, which is partly responsible for the high gas production.

3.3. Pore size distribution
Nanopores in the collected shale samples are mainly the pores with the diameters of <10 nm as shown in Figure.5. Micropores are dominated by nanopores with the diameters of around 0.3-0.4 nm, 0.5-0.6 nm and 0.8-0.9 nm as indicated by CO$_2$ adsorption results (Figure.5A and B) as well as 1.0-2.0 nm nanopores as indicated by N$_2$ adsorption results (Figure.5C). The abundance of mesopores generally
decreases with their diameters increasing. Macropores are dominated by the 80-200 nm nanopores. In comparison with the non-productive section, the productive section is relatively enriched in various micropores and mesopores, but depleted in 100-200 nm macropores (Figure.5C and D).

**Figure 5.** Pore size distribution curves of shale samples from Longmaxi Fm

3.4. Pore types and pore volumes

Samples from the productive section are more porous than samples from the non-productive section as indicated by their higher pore volumes (Figure.6). For example, the average volumes of micropore, mesopore and macropore are 0.0085 cm$^3$/g, 0.0159 cm$^3$/g and 0.0082 cm$^3$/g for samples from the lower section and 0.0048 cm$^3$/g, 0.0085 cm$^3$/g and 0.0054 cm$^3$/g for samples from the upper. Except for NO.10, samples from the upper are relatively rich in macropores as suggested by the high relative percentages of macropore volumes with the average value of 29%. This is consistent with the results of pore size distribution (Figure.5D).

Organic matters and clays have important impacts on the development of nanoporosity within the Silurian Longmaxi shale reservoir. Nanoporosity of the productive section is affected mainly by the organic matter contents as indicated by the strong positive correlations between TOC and pore volumes (Figure.7). This also indicates the predominance of organic-matter pores within this section. The positive correlations between TOC and micropore volumes from the non-productive section are indicative of that organic matters are the preferred locations for the occurrence of micropores as well. However, the opposite situation is observed on mesopores and macropores. This is partially responsible for the low pore volumes and low gas production.

The other preferential habitation for nanopores within the non-productive section is assumed to be the clay minerals as indicated by the positive correlations on the plots of clays versus pore volumes. This further suggests that these pores are probably dominated by interparticle and intraparticle pores within or between clay particles. However, clay minerals are not the suitable accommodation for nanopores within the productive section as suggested by the negative correlations between nanopore volumes and clays. Weak negative correlations on the plots of feldspar and carbonate versus pore volumes, suggesting these minerals are not suitable for the occurrence of nanopores within both tow sections.
Figure 6. Pore volumes of shale samples in study area

Figure 7. Plots showing the correlations between pore volumes versus TOC and mineral contents in study area
4. conclusions
(1) The productive section is comparatively rich in TOC and biogenic quartz and depleted in clays, carbonates and feldspar relative to the non-productive section;
(2) Nanopores are mainly the pores with the diameters of <10 nm, pore volumes of the productive section are higher relative to that of the non-productive section; In comparison with the non-productive section, the productive section is relatively enriched in micropores and mesopores, but depleted in 100–200 nm macropores.
(3) TOC exerts the key impact on the nanopore formation within the productive section. The occurrence of nanopores within the non-productive section is affected mainly by the contents of clays. Hence the productive section is rich in organic-matter pores and depleted in mineral matrix pores relative to that of the non-productive section.

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