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Nanoscale pore characteristics of the Lower Cambrian Niutitang Formation Shale: A case study from Well Yuke #1 in the Southeast of Chongqing, China

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ABSTRACT

The Lower Cambrian Niutitang Formation Shale is one of the most important shales being studied for unconventional development in China. In this work, we focused on 21 core samples of Niutitang Shale from Well Yuke #1 in the southeast of Chongqing, to better understand their vertical reservoir characteristics and pore evolution. Using complementary approaches of X-ray diffraction, N_2 and CO_2 adsorption, petrology microscope, and field emission-scanning electron microscopy, we conducted a series of analyses for pore volume, pore-size distribution, surface area, fractal characterization, organic geochemistry, petrology, and mineralogy. Results indicate that most micropores (<2 nm) are associated with grains of organic matter. Meanwhile, the meso-macropores (2–50 nm to >50 nm) are composed of organic pores and inorganic pores. Meso-macropore volume per unit of total organic carbon (TOC) content dramatically decreases with an increase of maturity and extent of diagenesis. Meanwhile, the TOC-normalized micropore volume also rapidly declines after maturity (R_o) values were higher than 3.13%. The surface fractal dimension D_1 for relative N_2 pressure $P/P_0 > 0.5$ with capillary condensation and surface fractal dimension D_2 for $P/P_0 < 0.5$ with mono- and multi-layer adsorption, derived from N_2 sorption isotherms, can be used to indicate the pore characteristics. D_1 is controlled by the percentages of micropore volume. D_2 seems to be affected by the clay mineral contents and thermal maturity.

1. Introduction

Since the commercial exploitation in 2000 in the U.S., shale gas has become an important unconventional gas resource. The commercial development of shale gas in the Fuling Gas Field in 2014 in China also indicates that Chinese shale gas exploration and development have entered a new era. A total of fifty prolific gas wells have been completed in November 2014, and the production capacity was 3.80×10^6 m^3/d; the annual gas production in China is expected to reach 3.2×10^9 m^3 in 2015 (Guo, 2015). The Lower Silurian Longmaxi Formation Shale is the exploited horizon of the Fuling Gas Field, and its successful development provides valuable information for the Lower Cambrian Niutitang Formation Shale in southern China.

Gas in the shales is generally stored in three ways (Curtis, 2002; Jarvie et al., 2007; Bustin et al., 2008): (1) in a free gas state in pores and fractures; (2) in an adsorbed state on the surface or inside organic matter and minerals; and (3) in a dissolved state in organic matter and water. Microscopic pore structure is the key factor influencing the occurrence of shale gas and gas storage capacity (Ross and Bustin, 2009; Chalmers et al., 2012; Kuila et al., 2012). Therefore, the studies of nanoscale pore characteristics and its evolution of shale can provide an effective way to explaining the shale gas occurrence, sorption capacity, and flow mechanism.

A range of multidisciplinary approaches, both qualitatively and quantitatively, has been applied to characterize the pore system of shale in recent years. Focused ion beam–scanning electron microscopy (FIB–SEM), field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) have been used to qualitatively and semi-quantitatively study the characteristics of pore system (Curtis et al., 2011a, 2011b; Loucks et al., 2012; Jiao et al., 2014). The quantitative characterization techniques include mercury injection capillary pressure (MICP), helium expansion and pulse-decay, low-pressure gas adsorption (N_2 and CO_2), small angle neutron scattering (SANS), and nano-computed tomography (Sinha et al., 2012; Mastalerz et al., 2013; Clarkson et al., 2013). Six types of pores are identified in Barnett and Woodford Shale; they are inter-particle pores produced by flocculation, organo-porosity

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produced during burial and maturation, intra-particle pores from organisms, intra-particle pores within mineral grains, micro-channels in the shale matrix, and microfractures (Slatt and O'Brien, 2011). Inter-particle pores, intra-particle pores, and organic matter pores are identified as predominant ones in Barnett Shale (Loucks et al., 2012).

Organic matter and inorganic minerals are the main components to evaluate the shale gas reservoir, and they constitute the complex pore-fracture system (Chalmers and Bustin, 2008a, 2008b; Ross and Bustin, 2009). The differences of organic matter in shales are mainly embodied in TOC contents, thermal maturity, and kerogen type. The organic matter of the northern America marine organic-rich shales is commonly dominated by sapropelic types I and II_1. However, there are large variations of TOC contents and thermal maturity (EIA, 2011) (Table 1). Lower Cambrian Niutitang Formation Shale in China contains marine type I kerogen with TOC contents from 0.43 to 9.25 wt.% and a maturity range from R_o 2.3% to 5.2% (Hao et al., 2013; Wang et al., 2014; Ma et al., 2015). It is clear that the maturities of marine shales in southern China are mostly higher than the northern America shales. Higher maturity means shale gas reservoirs have experienced a higher temperature, and at the same time underwent more complicated diagenesis, which can have a great influence on the pore characteristics of shale gas reservoirs (Bernard et al., 2012; Fishman et al., 2012).

In recent years, some researchers have conducted a lot of research on the main controlling factors of pore characteristics of shale. This work uses the pore-size definition of IUPAC (1994): micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). The study of New Albany Shale suggests that micropore volume has a positive relationship with TOC, which indicates that micropores mainly exist in organic matters (Strąpoć et al., 2010). When R_o is higher than 1.15%, the same study suggests that organic matter, together with clay minerals (dominantly illite), jointly contributes to the micropore volume. At this maturation level, shale will generate more micropores and mesopores (normally less than 25 nm) which is caused by secondary cracking of oil and bitumen to gas. Meanwhile, there are a number of pores that are in macropore region, which are conducive to methane adsorption (Mastalerz et al., 2013). It has also been suggested that the illite content in shale increases with maturity due to illitization (both kaolinite and montmorillonite change into illite), and a concomitant mesopore volume increase (Potter et al., 2005; Chalmers and Bustin, 2008a). The study of Ji et al. (2014) showed that the pores in clay minerals are normally at 3–100 nm diameter sizes, where illite and chlorite are mainly of meso-macropores.

On the basis of the above understanding, the purpose of this work is to provide the nanoscale pore characteristics of the Lower Cambrian Niutitang Formation Shale in Southeast of Chongqing. For this study, we selected Well Yuke #1 in this area and collected the whole core samples of the Lower Cambrian Niutitang Formation Shale. By continuous coring of Well Yuke #1, Niutitang Formation Shale can be analyzed as an independent unit to provide valuable findings about pore characteristics of over-mature shale in the world. In this study, the pore system was qualitatively characterized by FE-SEM images. Meanwhile, N_2 and CO_2 gas adsorption experiments were used to determine the pore

Table 1
TOC contents and thermal maturity of main northern America marine shales.

Shales	Woodford	Marcellus	Horn River	Barnett	Haynesville	Eagle Ford
Age	Devonian	Devonian	Devonian	Mississippian	Jurassic	Cretaceous
TOC/wt.%	1–14	3–12	3.5–5	4–8	0.5–4.0	4–8
R_o/%	1.1–3.0	1.5–3.0	1.6–2.7	1.0–2.2	2.2–3.2	0.5–2.0

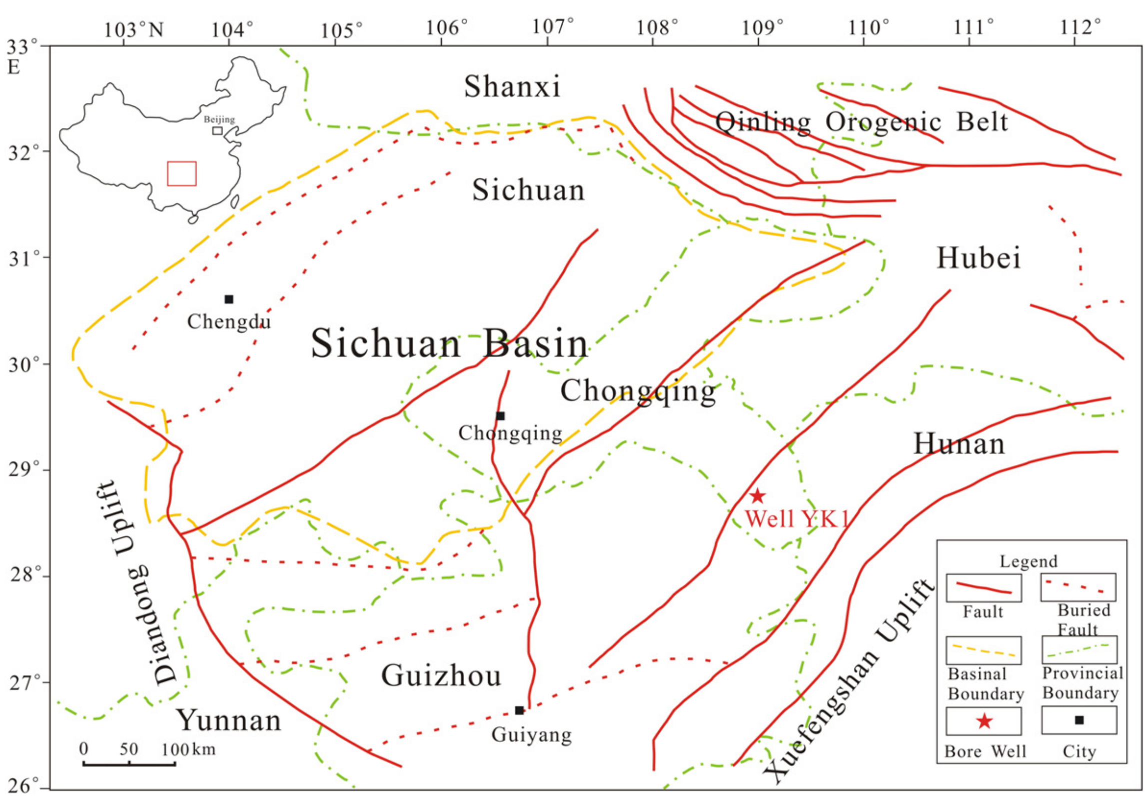

Fig. 1. Map showing the location of the Well Yuke 1 in Southeast of Chongqing.