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Research paper

Pore structure characterization for the Longmaxi and Niutitang shales in the Upper Yangtze Platform, South China: Evidence from focused ion beam–He ion microscopy, nano-computerized tomography and gas adsorption analysis

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ABSTRACT

Pore structure is of great importance in the occurrence of shale gas. In this study, pores in shale samples from the Lower Silurian Longmaxi and Lower Cambrian Niutitang shales in Chongqing, in the Upper Yangtze Platform, South China, were examined using focused ion beam–He ion microscopy (FIB–HIM), nano-computerized tomography (nano-CT), and gas adsorption analysis. The results show that most pores in measured samples of the Niutitang shale are mineral matrix pores and have poor connectivity, including both intraparticle and interparticle pores. Organic matter pores in measured samples of the Niutitang shale are rare and have small diameters. In measured samples of the Longmaxi shale, OM pores—mostly macropores and large mesopores—are the most abundant. The nano-CT results revealed that the abundance of OM pores led to good pore connectivity in the Longmaxi shale samples, whereas the prevalence of mineral matrix pores resulted in poor connectivity in the Niutitang shale samples. N_2 and CO_2 adsorption analyses showed that the mean value of micropore–mesopore volumes in the Niutitang and Longmaxi shales samples are 0.0332 ml/g and 0.0261 ml/g, respectively. The mean values of micropores–mesopores surface area in the Niutitang and Longmaxi shales samples are 33.84 m^2/g and 32.46 m^2/g, respectively. Thus, there is little difference between measured samples of the Longmaxi and Niutitang shales in terms of volume and surface area of micropores–mesopores. The equal-vitrinite reflectance (equal-Ro) values of measured samples of the Longmaxi shale are lower than those of the Niutitang shale samples. Over-maturity (equal-Ro>3%) resulted in a reduction of the number of pores in organic matter, small pore size, and poor connectivity in measured samples of the Niutitang shale. Relatively low maturity (2%<equal-Ro<3%) resulted in better preservation of OM pores and good connectivity in measured samples of the Longmaxi shale. It is concluded that suitable thermal maturity is beneficial for pore development in shale, which is of great significance for shale gas exploration and development.

1. Introduction

Shale gas exploration and development in China is currently being vigorously conducted, especially in the Upper Yangtze Platform, South China. The Longmaxi shale in Southeast Chongqing and the Niutitang shale in Northeast Chongqing are the two main marine shale-gas-producing series in South China. Shale gas exploration and development have been actively conducted in both formations; however, development is unsatisfactory, especially for the Niutitang shale.

The Longmaxi shale in Southeast Chongqing in the Upper Yangtze Platform has produced industrial gas flow and has become a typical demonstration area for shale gas exploration and development in South China (Dai et al., 2014; Guo et al., 2014; Chen et al., 2015; Shi et al., 2015; Yan et al., 2015). However, exploration and development of the Niutitang shale in Chongqing are

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unsatisfactory; for example, Niutitang shale gas production is extremely low in Northeast Chongqing. Moreover, data from existing drilling wells demonstrate that the Niutitang shale has a low volume and short duration of gas production.

Shale gas production in the Niutitang shale in South China greatly varies with location. Wan et al. (2015) studied the diffusivity and porosity anisotropy of the Niutitang shale in Hunan Province and argued that there were different amounts of dead-end pores in the Niutitang shale. Chen et al. (2015) also studied swelling of the Niutitang shale in methane in Hunan Province and concluded that the adsorption capacity in Niutitang shale displayed strong anisotropy. However, some studies have indicated that the Niutitang shale has high exploration and development potential (Tan et al., 2014a; Wang et al., 2015b; Yang et al., 2016).

Tan et al. (2014a) stated that the methane sorption capacity of the Niutitang shale is controlled by TOC content, but can be influenced by clay minerals. Xing et al. (2011) argued that the Niutitang shale in the Weixian Sag of the Dianqianbei Depression contains a potential shale gas exploration series with very large quantity of shale gas resources based on the high total organic carbon (TOC) content (3%–15%), equal vitrinite reflectance (equal-Ro) values indicating moderate maturity (1.39%–2.24%), and large area. Yang et al. (2016) concluded that the Niutitang shale has high shale gas potential with a high TOC content and large thickness in the middle of the Mayang Basin in Hunan Province.

It has been found that the Niutitang shale displays exploration and development potential in several regions in southern China (Pan et al., 2015; Cao et al., 2015; Chen et al., 2015); however, the regions differ from one another, and analysis of specific regions is required. Previous studies have demonstrated that the pore structure of the Niutitang shale in Chongqing is not clear (Kříbek et al., 2007; Wang et al., 2012; Ma et al., 2015). The Niutitang shale reservoir is characterized by very high pore structure heterogeneity, which may influence gas production (Ross and Bustin, 2009). Furthermore, the distributions of pore type, pore volume, and pore surface area in the Longmaxi shale require research, and comparison of the Longmaxi and Niutitang shales should be performed.

Shale gas primarily exists in shale pores as adsorbed gas, free gas, or a small amount of dissolved gas, and pore structure is of great importance for the storage and permeability capacity of shale gas. The pore structure, which controls the transport mechanisms and occurrence states of shale gas, can be described in terms of type, size, volume, surface area, and spatial distribution, all of which have important effects on shale gas enrichment (Curtis, 2002; Loucks and Ruppel, 2007; Loucks et al., 2009, 2012; Slatt and O'Brien, 2011). Therefore, shale pore structure and storage capacity are of great importance for shale gas occurrence and may directly affect shale gas exploration (Scherdel et al., 2010; Schmitt et al., 2013; Yang et al., 2014). Previous studies have shown that the storage capacity of a shale reservoir plays vital roles in the storage and migration of hydrocarbon gas. Determinants of shale gas storage capacity include pore type, volume, surface area, and spatial distribution of pore connectivity, all of which have important effects on enrichment of shale gas.

Loucks and Ruppel (2007) and Loucks et al. (2012) first used scanning electron microscopy (SEM) with Ar-ion polishing to observe the pore types in shale. Pore types include both mineral matrix pores and organic matter pores (OM pores) with extremely complex network structures (Loucks et al., 2009, 2012; Clarkson et al., 2013; Chen and Xiao, 2014). OM pores are intraparticle pores developed inside organic matter during the process of hydrocarbon generation from kerogens. Mineral matrix pores are pores developed between or within mineral particles, including interparticle pores (interP pores) and intraparticle pores (intraP pores). Interparticle pores, forming during the process of diagenetic alteration and compaction, are found between particles and crystals such as siliceous minerals (quartz and feldspar), clay and carbonate minerals (calcite or dolomite). Intraparticle pores are found inside particles such as clay, pyrite and carbonate minerals (calcite or dolomite), as a result of diagenesis and dissolution (Loucks et al., 2012; Milliken et al., 2013). OM pores contain effective interconnections that are favorable for gas adsorption (Chalmers et al., 2012; Romero-Sarmiento et al., 2014; Jiao et al., 2014; Klaver et al., 2015). SEM has increasingly been adopted to study shale samples from different regions. For example, Slatt and O'Brien (2011) studied pore types in the Barnett and Woodford shales in the America, concluding that microfractures and OM pores provide storage spaces and permeability pathways for migration of natural gas molecules. Milliken et al. (2013) were the first to study OM pore systems in shale quantitatively and determined the influence of TOC content on the development of organic matter and pores. Klaver et al. (2012) used SEM technology to study the pore space morphology of the low-maturity Posidonia shale from Hils, Germany. Tian et al. (2013) studied the OM pore characteristics in the Lower Silurian Longmaxi shale in the Chuandong Thrust Fold Belt, southwest China using on field emission scanning electron microscope (FE-SEM) digital images. Jiao et al. (2014) and Wang et al. (2016a) obtained quantitative analysis of Lower Silurian Longmaxi shale pores using focused ion beam–scanning electron microscope (FIB-SEM) image processing and multifractal geometry.

Pores can be divided into three types based on their diameters according to the definition provided by the International Union of Pure and Applied Chemistry (IUPAC; Sing et al., 1985). Several previous studies have used indirect testing methods for quantitative characterization of pores (Clarkson et al., 2013; Tian et al., 2013), including high-pressure Hg analysis for macropores (diameter > 50.0 nm), N_2 adsorption analysis for mesopores (2.0 nm < diameter < 50.0 nm), and CO_2 adsorption analysis for micropores (diameter < 2.0 nm). Pathways that allow natural gas permeation primarily occur in macropores, whereas adsorption and diffusion occur in micropores and mesopores. Thus, pore structure controls the transport mechanism and occurrence state of shale gas (Slatt and O'Brien, 2011; Milliken et al., 2013; Clarkson et al., 2013).

Ross and Bustin (2009), Clarkson et al. (2013), and Schmitt et al. (2013) argued that N_2 adsorption and Hg-injection capillary pressure techniques could provide a database and system parameters for the shale pore structure and storage capacity. Subsequently, Hu et al. (2015) and Chen et al. (2015) measured the distributions of mesopores and micropores in shale and analyzed the gas storage capacity for methane adsorption based on N_2 and CO_2 adsorption data. Pan et al. (2015) analyzed the pore structure and porosity of the Permian shale in the Lower Yangtze region, Eastern China, based on N_2 and CO_2 adsorption data, and concluded that the TOC content was the key factor controlling the shale gas storage capacity.

To identify the reason for the large differences in shale gas production between the Longmaxi and Niutitang shales, the pore structure and storage capacity of both shales samples were studied. In this work, we used technologies such as focused ion beam–He ion microscopy (FIB-HIM), nano-computerized tomography (nano-CT), and gas adsorption and analyzed the pore structures in the Longmaxi and Niutitang shales samples. We used whole-aperture analysis to obtain the pore storage capacities of both shales samples and performed a comparison. Thermal maturity is the main reason for the differences between the pore structures in measured samples of the two shales. The results demonstrate that studying the pore structures and storage capacities of the two main sets of shale reservoirs is of crucial significance for shale gas exploration and development.