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Pore structure characteristics of lower Silurian shales in the southern Sichuan Basin, China: Insights to pore development and gas storage mechanism

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ABSTRACT

Silurian shale in Sichuan Basin is currently the most important target zone for shale gas exploration and development in China. Pore structure characteristics of Lower Silurian Longmaxi shales from southern Sichuan Basin were investigated. The combination of field emission scanning electron microscope (FE–SEM) and argon ion beam milling was utilized to describe the nanometer-to micrometer-scale (>1.2 nm) pore systems. The shales were characterized by organic geochemical and mineralogical analyses. Total porosity, pore size distribution (PSD), specific surface area, and gas content were determined. Controls of organic matter richness, thermal maturity, and mineralogy on porosity were examined. The contribution of individual mineral components to total porosity was analyzed quantitatively. Total gas contents of the shales determined from canister desorption data were compared with theoretical (sorptive and volumetric) gas storage capacities.

The total organic carbon (TOC) content of the shale samples ranges between 0.1 and 8.0 wt.% and helium porosity varies between 0.7 and 5.7%. Maturity in terms of equivalent vitrinite reflectance of bitumen (R_{eqv}) ranges from 1.8 to 3.2%. TOC content is a strong control for the pore system of these shales, and shows a positive correlation with porosity. Porosity increases with increasing thermal maturity when R_{eqv} is less than 2.5%, but decreases for higher thermal maturity samples. FE–SEM reveals four pore types related to the rock matrix that are classified as follows: organic matter (OM)–hosted pores, pores in clay minerals, pores of framework minerals, and intragranular pores in microfossils. Pores in clay minerals are always associated with the framework of clay flakes, and develop around rigid mineral grains because the pressure shadows of mineral grains prevent pores from collapsing. Pores of framework minerals are probably related to dissolution by acidic fluids, and the dissolution–related pores promote porosity of shales. A unimodal PSD exists in the micropore range of TOC–rich samples, while the PSD of carbonate–rich samples are bimodal. A PSD maximum in the micropore range is attributed by OM and another maximum in the range of mesopore–macropores is probably caused by the dissolution of carbonate minerals. Quantitative evaluation of the contribution of individual mineral components to porosity shows that the organic matter contributes approximately 62% to the total porosity. Framework minerals (quartz, feldspar, and carbonates, et al.) and clay minerals contribute 25% and 13%, respectively. The total gas content of these shales ranges from 0.4 to 6.2 m^3/t, and the total gas contents of selected samples determined from canister desorption tests agree with the theoretically estimated original gas-in-place (OGIP). OM-hosted pores are the main space for gas storage, and accounted for about 78% (55% adsorbed gas plus 23% free gas) of the OGIP, while pores in the inorganic matter accommodate 22% free gas of the OGIP.

1. Introduction

Shale gas reservoirs are classified as non–buoyancy driven accumulations, continuous hydrocarbon plays that are composed of fine-grained sedimentary rocks that include shales, mudstones, limestones and siltstones. Natural gas is stored in shale reservoirs as: (1) free gas in pores and fractures, (2) adsorbed gas in organic matter and inorganic minerals, and (3) dissolved gas in "in-situ" liquid hydrocarbons and formation water (Curtis, 2002). Microstructures of shales exhibit a high degree of complexity and heterogeneity. Nanometer-to micrometer-scale pore systems have been found in the organic matter and matrix of inorganic grains of shale reservoirs, which have significant influence on gas

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storage and fluid transportation. To elucidate the complex pore systems of shales, various methods have been developed for investigating the pore structure of shales. The fluid invasion methods, such as high-pressure mercury intrusion (MICP) methods, low-pressure gas adsorption, helium pycnometer, provide an estimation of petrophysical properties of shales, including porosity, specific surface area, and pore size distribution (Yang and Aplin, 2007; Bustin et al., 2008; Ross and Bustin, 2009; Chalmers et al., 2012a; Rexer et al., 2014; Yang et al., 2014; Ghanizadeh et al., 2014, 2015a,b). A combination of fluid invasion and radiation methods has also been used for the characterization of shales (Clarkson et al., 2012; Mastalerz et al., 2012; Ruppert et al., 2013). Direct imaging methods, including scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging methods, scanning transmission X–ray microscopy, provide information on pore size, pore morphology, and connectivity of the pore networks (Potter et al., 2005; Slatt and O'Brien, 2011; Bernard et al., 2012; Dong et al., 2015). Mechanically polished methods used in thin sections produce surface topographic irregularities, which greatly exceed the size of many pores in shales. Recent development of argon ion beam milling, which provides cross-sections with exceptional high-quality, offer a new suitable alternative for high-resolution imaging. The combination of argon ion beam milling and SEM has provided a visual tool for observation of pores in shales (Loucks et al., 2009, 2012; Passey et al., 2010; Schieber, 2010; Curtis et al., 2012a; Klaver et al., 2012, 2015a,b; Milliken et al., 2013), and three-dimensional structural models of shales can be reconstructed from SEM images (Walls and Sinclair, 2011; Curtis et al., 2012b).

Research during the last several years has identified a variety of pore types in unconventional reservoir rocks, such as pores associated with organic matter, interparticle mineral pores, intraparticle mineral pores, and microfractures (Loucks et al., 2009, 2012; Passey et al., 2010; Schieber, 2010; Slatt and O'Brien, 2011; Curtis et al., 2012a; Milliken et al., 2013). Porosity in shale reservoirs is a product of initial (depositional) porosity, compaction and chemical diagenesis (mineralogical transformation, cementation and dissolution). Differences in the origins and distribution of pore types have been shown to have different effects on gas storage and transportation (Passey et al., 2010; Milliken et al., 2013). Although considerable effort has been devoted to characterize the complex pore systems of shales, less attention has been paid to the controls on pore development. The relation of porosity to mineralogy and microstructures are still not well understood. Furthermore, gas in shale reservoirs is stored mainly as free gas and adsorbed gas. Evaluations about gas sorption capacity on shales have been carried out recently (Gasparik et al., 2012, 2014; Zhang et al., 2012; Rexer et al., 2013, 2014). However, sorption measurements on gas shales under "in-situ" conditions pose some technology challenges (Gasparik et al., 2014, 2015). The mechanism about gas adsorption and free gas storage needs further investigations.

This research focuses on the pore structure characteristics of marine shales from Lower Silurian Longmaxi Formation in southern Sichuan Basin, China. The Longmaxi shale in Sichuan Basin is currently the most important target zone for shale gas exploration and development in China, and commercial gas flow rates were obtained in this area since 2009 (Dai et al., 2014; Wang et al., 2014a,b). However, unlike the marine gas shales in the United States, the marine shales in southern Sichuan Basin have very high maturity (equivalent vitrinite reflectance between 2.0% and 4.5%, Zou et al., 2010; Dai et al., 2014), and experienced several episodes of intensive tectonic activity after the hydrocarbon generation. Investigating the controls on the pore structure, porosity, mineralogy, and gas content of the highly over-mature shales provides insights into the generation, migration, and storage of natural gas in these shales. In this paper, we document and illustrate pore structure (size, distribution, arrangements, and origins of the pores) of gas shales from the southern Sichuan Basin by the combination of FE–SEM and argon ion beam milling. The controls of organic matter richness, thermal maturity, and mineralogy on porosity were examined. Besides, based on the gas content results determined from canister desorption tests and theoretical estimation, the gas storage behavior of these shales has been discussed.

2. Samples and experiments

2.1. Geological setting

The Lower Silurian shale, deposited in a restricted marine basin environment, is widely developed in Sichuan Basin with a thickness of a few meters to 400 m (Zhou et al., 2014). The Silurian shales in this area have undergone a complicated tectonic evolution, which strongly affected the accumulation and preservation conditions of shale gas. The early Paleozoic strata experienced deep burial during the Early Mesozoic and an intense uplift from the Late Mesozoic to the Cenozoic (Zhou et al., 2014). At present, the burial depth of the Paleozoic shales is mostly within a range of 2000–7000 m in the Sichuan Basin. In some strongly uplifted areas, shales are buried at a shallow depth and even occur as outcrops (Wang et al., 2012). The lower section of the Lower Silurian Longmaxi Formation is mainly comprised of dark gray–black carbonaceous shale and arenaceous–silty mudstones interbedded with bioclastic limestone while the upper section mainly comprises of grayish–yellowish green shale and arenaceous mudstones. TOC of the Longmaxi Formation ranges from 0.4–18.4% with an average of 2.5% (Dai et al., 2014), and the high TOC sections mainly developed at the bottom of the Longmaxi Formation. The Longmaxi shale is highly over-mature with an equivalent vitrinite reflectance between 2.0% and 4.5% (Zou et al., 2010).

2.2. Samples

Since the first cored well for shale gas in China was drilled in the Southern Sichuan Basin in 2008, more than 47 shale gas wells have been completed in Sichuan Basin, and commercial gas flows were obtained from many wells (Wang et al., 2012; Dai et al., 2014). Maximum gas yield of a single well in Longmaxi Formation in the Southern Sichuan Basin ranges from 3×10^3 m^3/day to 430×10^3 m^3/day (Dai et al., 2014). From the recently drilled wells N203 and W201 designed for the evaluation of the Silurian Longmaxi Formation in the Southern Sichuan Basin, 18 shale samples were collected for detailed analyses. In addition, 6 outcrops of the same formation were also sampled. Information on stratigraphic units, thickness distribution, geochemical characteristic, and well identification of the Silurian Longmaxi Formation source rocks in southern Sichuan Basin has been published previously by Wang et al. (2012) and Dai et al. (2014).

2.3. Experiments

2.3.1. Mineralogy

XRD analysis was performed on powdered shale (~100 mesh) using a Rigaku D/max-2500PC diffractometer with 0.001° 2θ step size and 1 min step time at indoor temperature of 293.15 K and relative humidity (RH) of 70% (equipment maintenance). The relative mineral percentages were estimated semi-quantitatively using the area under the curve for the major peaks of each mineral.

2.3.2. Organic geochemistry

The TOC content was determined on a LECO CS230 carbon/sulfur analyzer. Shale powders were treated using hydrochloric acid to remove the inorganic carbon, and then pyrolyzed up to 540 °C.

Due to the absence of vitrinite in these Silurian shale samples, bitumen reflectance was measured using a microscope equipped with an oil-immersion objective lens and a photometer. The average bitumen reflectance was converted to equivalent vitrinite reflectance (R_{eqv}), according to the equation of Feng and Chen (1988).