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Research paper

Pore structure of Cambrian shales from the Sichuan Basin in China and implications to gas storage

Feng Yang*, Zhengfu Ning, Qing Wang, Huiqing Liu

Ministry of Education Key Laboratory of Petroleum Engineering, China University of Petroleum (Beijing), #18, Fuxue Rd, Changping, Beijing 102249, PR China

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ABSTRACT

The microstructure of black siliceous shale from the lower Cambrian Niutitang Formation, Sichuan Basin in China was investigated by the combination of field emission scanning electron microscope (FE-SEM) and argon ion beam milling. The nanometer-to micrometer-scale pore systems of shales are an important control on gas storage and fluid migration. In this paper, the organic porosity in shale samples within oil and gas window has been investigated, and the formation mechanism and diagenetic evolution of nanopores have been researched.

FE-SEM reveals five pore types that are classified as follows: organic nanopores, pores in clay minerals, nanopores of framework minerals, intragranular pores in microfossils, and microfractures. Numerous organic nanopores are observed in shales in the gas window, whereas microfractures can be seen within the organic matter of shales in the oil window. Microfractures in oil window shales could be attributed to pressure buildup in the organic matter when incompressible liquid hydrocarbon are generated, and the orientation of microfractures is probably parallel to the bedding and strength anisotropy of the formation. 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 protect pores from collapse, and the increasing of silt content would lead to an increase in pressure shadows and improve porosity. Nanopores of rock framework are probably related to dissolution by acidic fluids from hydrocarbon generation, and the dissolution-related pores promote permeability of shales. Porosity in the low-TOC, low-thermal-maturity shales contrast greatly with those of high-TOC, high-thermal-maturity shales. While the high-TOC shales contain abundant organic microporosity, the inorganic pores can contribute a lot to the porosity of the low-TOC shales.

1. Introduction

Shale gas reservoirs, which have abundant gas stored in both free and adsorbed state, have recently received much interest. Shale gas is becoming a significant contributor to gas production all over the world. Shale gas comprises 34% of total U.S. dry natural gas production in 2011, and an assessment of shale gas resources has found that shale gas could increase the world's technically recoverable gas resources by 40% (E.I.A, 2013).

Despite increasingly commercial importance of shale gas, shale microstructures are still poorly understood compared to that of conventional reservoirs. Understanding the pore structure of these rocks has been hindered by our lack of tools to investigate their pore structure. Specialized methods have been developed for investigating pore systems in shales, such as gas adsorption (Bustin et al., 2008; Chalmers et al., 2012a; Yang et al., 2014), X-ray small angling scattering (Clarkson et al., 2012), and scanning transmission X-ray microscopy (Bernard et al., 2012a, 2012b). Recent development of argon ion beam milling provides cross-sections with exceptional high-quality (Reed and Loucks, 2007; Loucks et al., 2009, 2012), and minor topographic variations unrelated to different hardness in samples offer a new suitable alternative for high-resolution imaging. Innovation in electron microscopy has led to the development of high magnification FE-SEM. The combination of argon ion beam milling and FE-SEM has provided a visual tool for observation of nanopores in shales, and three-dimensional volumes of shales can be reconstructed from FE-SEM images (Curtis et al., 2010; Walls and Sinclair, 2011; Bai et al., 2013).

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* Corresponding author.
E-mail address: yangfeng227@163.com (F. Yang).

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Microstructures of shales exhibit a high degree of complexity and heterogeneity. Nanometer-to micrometer-scaled pore systems have been found in the organic matter and matrix of inorganic grains, which have significant influence on gas storage and fluid migration (Bustin et al., 2008; Chalmers et al., 2012a, 2012b, Chalmers and Bustin, 2013; Gasparik et al., 2012, 2013; Zhang et al., 2012). Recently, organic nanopores have recently been reported in numerous gas shale systems worldwide (Loucks et al., 2009, 2012; Passey et al., 2010; Slatt and O'Brien, 2011; Curtis et al., 2012a, 2012b; Chalmers et al., 2012a; Milliken et al., 2013), which have been interpreted as resulting from the exsolution of gaseous hydrocarbons during the secondary thermal cracking of retained oil (Loucks et al., 2009; Curtis et al., 2012a, 2012b). Despite their ubiquity, the chemical nature of these nanoporous organic compound remains puzzling. The nanoporous organic particles have been chemically identified as pyrobitumen using synchrotron techniques (Bernard et al., 2012a, 2012b). Organic porosity is deemed to increase with thermal maturation (Curtis et al., 2012a, 2012b; Bernard et al., 2012a; Loucks et al., 2012), but exceptions do exist (Fishman et al., 2012; Milliken et al., 2013). Organic matter porosity in shales in the oil window and the absence of porosity in shales in the gas window are observed (Curtis et al., 2012a, 2012b; Loucks et al., 2012; Klaver et al., 2012). Thermal maturity alone is insufficient to predict porosity development in organic shales. Other factors, such as organic matter composition, also complicate porosity development. The type of organic matter also plays a role in the organic porosity (Curtis et al., 2012a, 2012b). In addition, previous researches have been focusing on pores within gas window with high thermal maturity, few investigation of pore structure of shales in the oil window has been carried out (Curtis et al., 2012a, 2012b; Bernard et al., 2012a, 2012b).

In this paper, we document and illustrate pore structure of gas shales from China's Sichuan Basin by the combination of FE-SEM and argon ion beam milling. We also characterize their size, distribution, arrangements, and origins of the pores. Different shale samples with thermal maturation in both oil window and gas window have been studied to investigate relationship between organic porosity and thermal maturation, besides, diagenetic evolution and formation mechanism of inorganic pores have also been researched.

2. Materials and methods

Shale samples analyzed come from the Lower Cambrian Niutitang Formation in Sichuan Basin, Southwest China (Fig. 1). Sichuan Basin is a large sedimentary basin that contains thick, organic-rich shales with excellent potential for shale gas development. Geological reviews, petrographic analyses and organic geochemical evaluations of the hydrocarbon source rocks in Sichuan Basin have recently been published (Chen et al., 2011; Fu et al., 2011; Sun et al., 2012; Tan et al., 2011; Yang et al., 2014). The Cambrian stratigraphy of Sichuan Basin is shown in Fig. 2. The Niutitang Formation has been recognized as a promising source rock in the Sichuan Basin. The Niutitang Formation was deposited in a deep-water shelf environment and characterized by dysaerobic to anaerobic bottom conditions developed below storm-wave base. The upper part of Niutitang Formation consists of gray silty mudstone, siltstone and limestone. The fine silty laminations indicate that the sediment may have been deposited by turbidity currents. However, the lower part of Niutitang Formation is mainly black siliceous mudstones with interbedded carbonaceous mudstones. The Niutitang formation is also rich in pyrite which is present in several forms, including small framboids, euhedral crystals and annularity. There are mainly three sources of organic matter in these marine shales: pelagic algae, benthic organisms and bacteria (siliceous bacteria, sulfur bacteria) (Sun et al., 2012; Tan et al., 2011). The siliceous debris of these organisms deposited and formed the siliceous mudstones. The thickness of the Niutitang Formation ranges from 20 to 200 m across the Sichuan Basin. The lateral extent and thickness of this formation are stable in the southeast of the Sichuan Basin, and the average thickness is more than 100 m with a maximum of 200 m (Fig. 1). The analyses presented below are from the boreholes which were drilled in the southeast of the Sichuan Basin, and focused on the black siliceous mudstones in the Lower Cambrian Niutitang Formation.

Core samples for investigation come from three boreholes (XQ-1, M−64, and RN-1) and are in different thermal maturity (see below). Samples in well XQ-1 (depth range from 78.2 to 192.5 m) are all in the oil window, and samples in well M−64 (depth range from 54.6 to 103.75 m) have just passed gas window, but gas condensate could be produced, while samples in well RN-1 (depth range from 62.5 to 180.5 m) are at highly thermal maturity. All samples were carefully packed and then immediately sent to the laboratory for experiments. Helium porosity and pulse decay permeability were run on core plugs (2.5 cm in diameter and 3−5 cm in length). Then the core cuttings of all samples were used for X-ray diffraction (XRD) analysis, total organic carbon (TOC) content test, vitrinite reflectance test, FE-SEM imaging, and low-pressure nitrogen adsorption.

The core plug samples were first dried in a vacuum at 373 K for 24 h. Porosity measurements were carried out in ULTRAPORE-300 using helium expansion method while permeability measurements were conducted on pulse-decay permeameter (TEMCO PDP-200). Pulse-decay permeabilities were obtained respectively at the effective pressure of 5.5 MPa.

Shale samples were first ground into powder with average particle size of 100-mesh (0.15 mm), then XRD analysis was performed on Rigaku D/max-2500 PC with 0.001° 2θ step size and 1 min step time at indoor temperature of 293.15 K and relative humidity of 70%.

The TOC content was determined by LECO CS230 carbon/sulfur analyzer. Shale samples were crushed to powder finer than 100-mesh, then 1−2 g samples were pyrolyzed up to 540 °C.

Because the Cambrian marine shales lack vitrinite, thermal maturity was evaluated using vitrinite-like macerals mainly derived from macroalgae. Vitrinite-like material reflectance measurements were carried out on MPV-SP microscope equipped with oil-immersion objective lens and photometer. The vitrinite-like material reflectance was then converted to equivalent vitrinite reflectance using a conversion formula (Chen et al., 2011; Tan et al., 2011). What's more, RockEval pyrolysis analyses were performed on these samples using OGE Workstation. The maximum temperature required for volatilization of hydrocarbons (T_{max}) was also used to calculate the vitrinite reflectance using the formula provided by Jarvie et al. (2001).

FEI™ Quanta™ 200F scanning electron microscope was employed to observe the microstructure morphology. It could produce images of nanopore structure with high resolution of 1.2 nm and a magnification of × 25 k − 200 k. Shale samples were ground with fine grit sand paper, and argon ion beam milling was utilized to produce a much flatter surface, and coated with gold at a thickness of 4 nm to avoid charging.

Quantitative pore structure of these shales was investigated by low-pressure nitrogen adsorption experiment. The experiment was conducted on QUADRASORB™ SI Four Station Surface Area and Pore Size Analyzer, adopting standard static volumetric method to measure the amount of adsorbed gas. Before the experiment was performed, shale samples powder weighing 200−500 mg was outgassed at 423 K for 5 h under a vacuum of 10 μmHg. Then reagent grade nitrogen (99.999%) was used as adsorbent at 77 K, and