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Research paper

Fractal characteristics of nano-pores in the Lower Silurian Longmaxi shales from the Upper Yangtze Platform, south China

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ABSTRACT

To better understand the fractal characteristics of nano-pore structure and their effects on methane adsorption in marine shales, we have conducted ultra-low pressure nitrogen adsorption, methane adsorption, X-ray diffraction (XRD), total organic carbon (TOC), and vitrinite reflectance for eleven shale samples of the Lower Silurian Longmaxi Formation from the Upper Yangtze Platform, south China. Two fractal dimensions D_1 and D_2 (at relative pressures of 0–0.5 and 0.5–1, respectively) were obtained using the fractal Frenkel–Halsey–Hill (FHH) method based on low-pressure nitrogen adsorption isotherms. The relationships among composition of the Longmaxi shale (TOC, clay minerals, brittle minerals), the pore structure parameters (i.e. average pore diameter, surface area, pore volume), and the fractal dimensions were investigated. The results show that the Longmaxi shale possesses fractal geometries with fractal dimension D_1 values ranging from 2.3542 to 2.4715 and fractal dimension D_2 values ranging from 2.5818 to 2.7497. The good positive correlation between fractal dimensions D_1 and the BET surface area and the strongly negative relationship between fractal dimensions D_2 and the average pore diameter indicate that D_1 can adequately characterize pore surface fractal dimension, while D_2 represents the pore structure fractal dimension. Organic matter has a positive influence on the BET surface area and the BJH pore volume and a negative effect on the average pore diameter. The BJH pore volume and the average pore diameter have a positive relationship trend with the clay minerals content, whereas a negative linear trend with the brittle minerals content. The mineralogical compositions and TOC of the Longmaxi shale have different impacts on the pore structures, which in turn exert different effects on the fractal dimensions D_1 and D_2. Both the fractal dimensions D_1 and D_2 have positive effects on the Langmuir volume of methane adsorption. However, the fractal dimensions D_1 and D_2 have opposite influence on the Langmuir pressures of methane adsorption. Thus the fractal dimensions can well be used to evaluate gas shale reservoir and shale gas accumulation in south China.

1. Introduction

Recent advances in horizontal drilling and hydraulic fracturing have made it technically and economically feasible to producing natural gas from shale formations (Rexer et al., 2013). Total dry natural gas production in the United States increased by 35% from 2005 to 2013, which resulted largely from the development of shale gas resources (EIA, 2015). Outside of North America, China also achieved great success in shale gas production which increases from 25 × 10^6 m^3 in 2012 to 200 × 10^6 m^3 in 2013 (Zhang et al., 2012a,b). Natural gas storage in shale differs significantly from conventional gas reservoirs and may be composed of free compressed gas, adsorption gas and dissolved gas (Curtis, 2002; Gasparik et al., 2014). Organic shale typically contains a complicated pore system with various pore types, multiple pore geometries and wide pore size distributions (Loucks et al., 2012; Clarkson et al., 2013). In addition, the pore size distribution of shale may lead to different gas accumulation mechanisms and gas transition

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mechanisms (Sondergeld et al., 2007; Wang et al., 2015a). Generally speaking, macropores would provide space for free gas, whereas mesopores or micropores could offer larger surface areas and higher adsorption energy for gas adsorption (Bu et al., 2015). Continuum and no slip flow are dominant in macropores and megapores but gas slippage and diffusion are dominant in micropores and mesopores (Sondergeld et al., 2007). Therefore, characterizing the pore structure is critical to understand shale gas storage and flow mechanisms.

Three groups of experimental techniques could be used to characterize shale pore structure (Wang et al., 2015a): microscopic observation (e.g., scanning electron microscopy, transmission electron microscopy) (Loucks et al., 2009, 2012; Chalmers et al., 2012; Klaver et al., 2012), radiation detection (e.g., small or ultra-small angle neutron scattering, nuclear magnetic resonance) (Clarkson et al., 2013; Bahadur et al., 2014; Sigal, 2015; Meng et al., 2015), and fluid invasion (e.g., gas physisorption, mercury intrusion, helium pycnometry) (Ross and Bustin, 2009; Chalmers et al., 2012; Clarkson et al., 2013; Tian et al., 2013; Yang et al., 2014). Among these, low-pressure nitrogen adsorption analysis has been proven to be an effective method in characterizing pore structures in shales (Clarkson et al., 2013; Labani et al., 2013; Tian et al., 2013), and N_2 adsorption data indicate that the porous materials have fractal geometries (Yao et al., 2008; Yang et al., 2014). However, there are relatively few case studies on the fractal characterization of marine shales and its effect on methane adsorption properties.

In this pater, we carried out fractal analyses on the Lower Silurian Longmaxi marine shale from the Upper Yangtze Platform in south China. Using the fractal Frenkel–Halsey–Hill (FHH) method and data measured from ultra-low pressure nitrogen adsorption isotherms, we obtained fractal dimension values of the pore structure and surface, respectively. Then the relationships between TOC, minerals content, pore structure parameters and fractal dimensions were documented. And the role of fractal dimensions in methane adsorption properties of marine shales was also discussed. The results could be helpful to understand the nano pore characterization in the Longmaxi marine shale and to evaluate the shale gas accumulation in south China.

2. Materials and experimental methods

The Upper Yangtze Platform is located in the western portion of the Yangtze Platform, south China (Fig. 1A). The Lower Silurian shale, widely developed in the Upper Yangtze Platform has recently been selected as the main target for shale gas exploration and development (Dong et al., 2012; Guo and Zhang, 2014; Dai et al., 2014; Luo et al., 2016). A total of 11 samples from the Lower Silurian Longmaxi marine shale were collected from four wells (YC4, YC6, YC7 and YC8) in the Upper Yangtze Platform on the southeastern edge of Sichuan Basin, south China (Fig. 1B). The Longmaxi Formation is composed mainly of marine shales and mudstones, which can be subdivided into two sections based on the lithology. The lower section of the Longmaxi Formation is composed mainly of arenaceous shale, carbonaceous shale and graptolitic shale interbedded with bioclastic limestone. The upper section is comprised mainly of shale and arenaceous shale interbedded with siltstone and marlstone (Dai et al., 2014). High TOC sections mainly developed in the bottom part of the Longmaxi Formation. The Longmaxi shale is currently highly over-matured, generating mainly dry gas and secondary oil cracked gas (Tan et al., 2015). More detailed information on the geological and geochemical characteristics of the shale gas in the Longmaxi Formation can be obtained from Dai et al., (2014).

The shale samples were crushed and sieved into grains of 80–100 mesh size for ultra-low pressure nitrogen adsorption, X-ray diffraction (XRD) and total organic carbon (TOC) measurement. The TOC content was determined by a Leco CS230 carbon/sulfur analyzer. Samples were crushed to a powder with grain size less than 100 mesh, and then 1 g of the shale samples, in a porous crucible, were treated using hydrochloric acid to remove carbonates. After 2 h the samples were washed out using distilled water. After the water had drained from the crucible, the crucible and sample were dried overnight at 70 °C. The total organic carbon content was then measured. Because no vitrinite occurs in rocks earlier than Devonian due to the absent of higher land plants, we measured the reflection of solid bitumen reflection (R_b). Then we converted the reflection of solid bitumen reflection (R_b) to equivalent vitrinite reflectance (R_o*) based on the following linear regression: $R_o^* = 0.618R_b+4$ (Jacob, 1985).

Bulk mineralogical compositions were determined from the X-ray diffraction patterns measured on a Bruker D8 DISCOVER diffractometer using Co Kα-radiation produced at 45 kV and 35 mA. Crushed samples were mixed with ethanol, hand ground and then smear mounted on glass slides for X-ray diffraction analysis. During

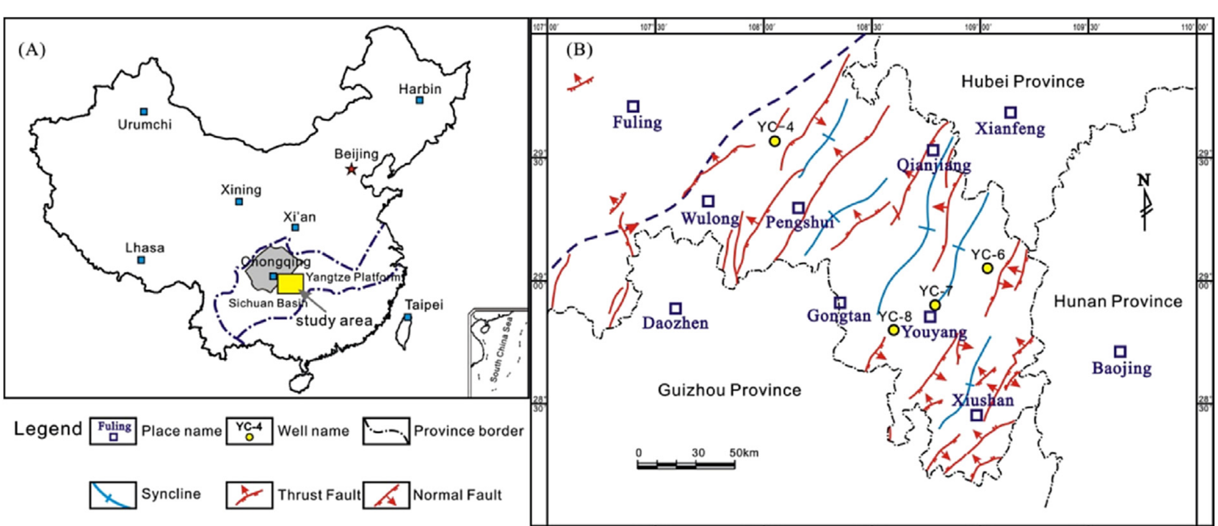

Fig. 1. Map showing the location of the sample wells (B) on the edge of the southeastern Sichuan Basin in the Upper Yangtze Platform, south China (A).