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Research paper

Nanoscale pore structure and fractal characteristics of a marine-continental transitional shale: A case study from the lower Permian Shanxi Shale in the southeastern Ordos Basin, China

Chao Yang [a, b], Jinchuan Zhang [a, b, *, 1], Xiangzeng Wang [c], Xuan Tang [a, b], Yongchang Chen [d], Lulu Jiang [e], Xue Gong [a, b]

[a] *School of Energy Resources, China University of Geosciences, Beijing, 100083, PR China*
[b] *Key Laboratory of Shale Gas Exploration and Evaluation, Ministry of Land and Resources, Beijing, 100083, PR China*
[c] *Shanxi Yanchang Petroleum (Group) Corp. Ltd., 100083, Xi'an, 710075, PR China*
[d] *Zhongyuan Oil Field 2nd Oil Factory of Sinopec, Puyang, 457532, PR China*
[e] *Shandong Provincial Geo-mineral Engineering Exploration Institute, Jinan, 250014, PR China*

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ABSTRACT

Shale samples collected from seven wells in the southeastern Ordos Basin were tested to investigate quantitatively the pore structure and fractal characteristics of the Lower Permian Shanxi Shale, which was deposited in a marine-continental transitional (hereinafter referred to as the transitional) environment. Low-pressure nitrogen adsorption data show that the Shanxi Shale exhibits considerably much lower surface area (SA) and pore volume (PV) in the range of 0.6–1.3 m^2/g and 0.25–0.9 ml/100 g, respectively. Type III kerogen abundant in the transitional Shanxi Shale were observed to be poorly developed in the organic pores in spite of being highly mature, which resulted in a small contribution of organic matter (OM) to the SA and PV. Instead, I/S (illite-smectite mixed clay) together with illite jointly contributed mostly to the SA and PV as a result of the large amount of inter-layer pores associated with them, which were evident in broad-ion-beam (BIB) imaging and statistical analysis. Additionally, the Shanxi Shale has fractal geometries of both pore surface and pore structure, with the pore surface fractal dimension (D1) ranging from 2.16 to 2.42 and the pore structure fractal dimension (D2) ranging from 2.49 to 2.68, respectively. The D1 values denote a pore surface irregularity increase with an increase in I/S and illite content attributed to their more irregular pore surface compared with other mineralogical compositions and OM. The fractal dimension D2 characterizing the pore structure complexity is closely related to the pore arrangement and connectivity, and I/S and illite decrease the D2 when their contents increase due to the incremental ordering degree and connectivity of I/S- or illite-hosted pores. Meanwhile, other shale constituents (including kaolinite, chlorite, and OM) that possess few pores can significantly increase the pore structure complexity by way of pore-blocking.

1. Introduction

Shale gas, as one type of unconventional hydrocarbon resource, is an important energy supply. Because shale is a complex and heterogeneous porous medium, its pore structure parameters, such as pore volume, surface area, size distribution, and fractal dimensions, are very important in understanding adsorption, desorption, diffusion and gas flow (Ross and Bustin, 2009; Chen et al., 2011; Ji et al., 2012; Zhang et al., 2012a; Hao et al., 2013; Hu et al., 2014). Furthermore, the producibility of shale gas mainly depends on pores and their connectivity for storing and releasing gas (Mastalerz et al., 2013); thus, the pore structure, as well as the fractal characteristics, are important issues to be studied for sustainable shale resource development.

Currently, qualitative visualization of nanoscale pores in shales

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[*] Corresponding author. School of Energy Resources, China University of Geosciences, Beijing, 100083, PR China.

E-mail address: zhangjc@cugb.edu.cn (J. Zhang).

[1] Jinchuan Zhang is a professor and the director of the Shale Gas Research Group at the School of Energy Resources, China University of Geosciences (Beijing). He has focused on the unconventional petroleum system valuation in China for more than fifteen years.

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can be established by advanced 2/3D imaging techniques, such as combined broad ion beam-milling and scanning electron microscopy (BIB-SEM), to characterize pore types and development (e.g. Loucks et al., 2009; Milliken and Reed, 2010; Slatt and O'Brien, 2011; Chalmers et al., 2012; Keller et al., 2013). Quantitative determination of the surface area, pore volume and pore-size distribution in shales is primarily performed using Nitrogen Gas Adsorption (N_2GA) and Mercury Injection Capillary Pressure (MICP) techniques (e.g. Clarkson et al., 2013; Kuila and Prasad, 2013; Cao et al., 2015a, b). Additionally, fractal geometries that were previously used to describe the porous structure and surface irregularities of a given solid such as activated carbon or coal (Fu et al., 2005; Mahamud and Novo, 2008; Yao et al., 2008; Cai et al., 2011; Zhang et al., 2014a) have also been applied in the characterization of organic-rich shales (Chen et al., 2011; Chalmers et al., 2012; Yang et al., 2014; Wang et al., 2015; Li et al., 2016; Yang et al., 2016a; Wang et al., 2016). Such methods for calculating fractal dimensions include the fractal Frenkel–Halsey–Hill (FHH) model and the thermodynamic method (Avnir and Jaroniec, 1989) on the basis of gas adsorption isotherms, of which the fractal FHH model has proven to be the most effective.

Quantitative calculations and petrographic observations have revealed that a finite number of pore types exist in spite of the considerable variability in composition, depositional setting, and compaction history of different shales. The different pore types in shales include those associated with organic matter (OM), clay minerals, and detritus minerals (e.g. Loucks et al., 2009, 2012; Slatt and O'Brien, 2011). With respect to the organic pores within the OM, it is generally believed to be generated as a result of expulsion of hydrocarbons during thermal degradation of the kerogen and solid bitumen. Additionally, recent studies also reveal that some OM have initial pore spaces even in immature shales (Löhr et al., 2015; Chalmers and Bustin, 2017). Overall, organic-associated pores are found more often in highly mature shales (Loucks et al., 2012; Bernard et al., 2012; Curtis et al., 2012; Milliken et al., 2013; Loucks and Reed, 2014), whereas they are relatively less seen in low maturity shales (Klaver et al., 2012; Yang et al., 2013; Tang et al., 2014; Reed and Loucks, 2015; Cao et al., 2015b). Clay-associated pores, are mostly intra-aggregate pores formed by the curling of clay aggregates and the interlayer pores of the crystalline clay confined by their laminated inner structure, with a size range of 30 nm to 2 μm (Milliken and Reed, 2010; Ji et al., 2012; Kuila et al., 2014; Yang et al., 2016b). Pores associated with detrital minerals are mainly mineral intercrystalline pores and intergranular pores, with a small amount of secondary dissolution pores within minerals prone to dissolution. However, these primary intergranular pores can be gradually lost due to strong compaction and diagenesis, particularly in the late diagenesis stage (Loucks et al., 2012; Kuila et al., 2014).

While marine shales with type I and II kerogens are hot targets for shale gas, transitional shales with type III kerogen are also becoming increasingly important in China and other places. The Lower Permian Shanxi Shale is such a typical shale that is widely distributed in the Ordos Basin and is considered an important gas source rock for many gas fields (Zhang et al., 2012b). According to the Ministry of Land and Resources of the People's Republic of China, the geological reserves of its shale gas reservoirs are estimated to be approximately 19.9×10^{12} m^3 in the Ordos Basin (MLR, 2012). Compared to the extensive investigations of marine shale reservoirs in North America (Loucks et al., 2009; Chalmers et al., 2012; Clarkson et al., 2013) and South China (e.g. Tian et al., 2013, 2015; Cao et al., 2015a,b; Jiao et al., 2014; Wang et al., 2014) or the continental shale gas reservoirs in China (Yang et al., 2013; Tang et al., 2014; Liu et al., 2015; Jiang et al., 2016), studies on this transitional shale gas reservoir have only occurred in recent years, and most of them have focused on the assessment of shale gas resource potential (Tang et al., 2012; Ding et al., 2013). The lack of understanding of the micro pore structures seriously hinders an effective evaluation of the shale gas play in this region.

In this paper, we attempted to characterize the pore structure, as well as the fractal characteristics, in the transitional Shanxi Shale using the nitrogen adsorption-desorption method integrated with BIB-SEM observations. Our results are significant for the exploration of transitional shale gas reservoirs in this field.

2. Geological setting

The Ordos Basin is in central China and is a large, asymmetric fold with a broad, gently dipping eastern limb and a narrow, steeply dipping western limb (Wang et al., 2011). Tectonically, the basin can be subdivided into six secondary tectonic units: the Weibei Uplift in the south, the Yimeng Uplift in the north, the Jinxi Fold Belt in the east, the Tianhuan Sag and the western edge thrust belt in the west and the Yishan Slope in the central part. Among these, the Yishan Slope, which covers a large area of the basin and dips 1–2°, is the main location of hydrocarbon exploitation in the Ordos Basin. The study area is along the southeastern Yishan Slope (Fig. 1a).

A simplified stratigraphic column of the upper Paleozoic transitional strata is shown in Fig. 2. From the middle Proterozoic to the early Paleozoic, carbonates thousands of meters thick were deposited in the Ordos Basin (Wang et al., 2011). Influenced by the Caledonian movement, the Ordos Basin was in an uplift period from the middle Ordovician to the middle Carboniferous, which resulted in the denudation of strata from the late Ordovician to the early Carboniferous. During the late Carboniferous, tectonic subsidence began again in the Ordos Basin, which was accompanied by the transgression of seawater. Subsequently, regressions occurred from the last stage of the late Carboniferous to the beginning of the Permian (Zhang et al., 1997). During the Permian, fluvio-lacustrine depositional environments prevailed in the Ordos Basin. Overall, the upper Paleozoic strata of the Ordos Basin were deposited in a marine-continental transitional environment, and the Lower Permian Shanxi Formation was deposited in the transition stage from transitional environment to continental environment, and features delta front-coastal marsh sediments, thin-bedded sandstone and coal seams, and two to four sets of black shale with a thickness of from 40 to 135 m (Ding et al., 2013). The Shanxi Shale in our study area is at a relatively shallower burial depth (2000–3500 m) today and has a consistent thickness ranging from 90 to 110 m.

3. Samples and experiments

Nine shale samples were collected from 7 wells (Fig. 1b) in the southeastern Ordos Basin and were tested for total organic carbon (TOC), mineralogical composition and pore structure. The sample numbers, core numbers, and depths are shown in Table 1. Most of the organic petrographic and geochemical analyses for the studied shale samples were carried out at the Energy Laboratory located in the School of Energy Resources, China University of Geosciences (Beijing).

Organic petrographic examinations were performed using a LEICA DM 6000M microscope photometry system, in which identification of the kerogen type was done using normal white light. The vitrinite reflectance (R_o) measurements of the lacustrine and transitional shales were carried out using an MPV-SP microscope equipped with an oil-immersion objective lens and a photometer obtained using the standard SY/T 5124 (2012). The TOC content was determined using a LECO CS230 carbon/sulfur analyzer. Samples were crushed to a powder less than 100-mesh in size, then 1–2 g