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Research paper

Pore structure, wettability and tracer migration in four leading shale formations in the Middle Yangtze Platform, China

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ABSTRACT

Deposited in different sedimentary settings, four leading shale formations (Late Ordovician Wufeng, Early Silurian Longmaxi, Late Permian Dalong, and Early Jurassic Dongyuemiao Shales) are currently the most promising zones for shale gas development in the Middle Yangtze Platform of South China. Based on complementary tests [low pressure gas physisorption, mercury injection capillary pressure (MICP), contact angle measurement, fluid imbibition into initially dry shale, and tracer diffusion into initially fluid-saturated shale followed by tracer mapping with laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)], this work investigates their pore structure (both geometry and connectivity) and wettability characteristics, as well as the coupled effects of these characteristics on fluid flow and tracer migration.

Pores < 50 nm account for the majority of the pore volume in these organic shales. The shapes of hysteresis loop from gas physisorption show that the pores are mostly inkbottle-shaped in Wufeng, Longmaxi and Dongyuemiao Shales, while they are mostly narrow plate- or slit-like shaped pores in Dalong Shale. These four organic shales are strongly oil-wetting and moderately water-wetting. According to the imbibition behaviors toward aqueous (deionized water) and oleic (n-decane) phases, hydrophobic pores are better connected than hydrophilic pore networks, which is consistent with the measured contact angles. Diffusion of nano-sized nonsorbing (perrhenate [ReO_4^-]) and sorbing (cesium [Cs^+]) tracers into brine-saturated shales indicates a high spatial variability and limited pore connectivity in these organic shales. The effective diffusion coefficient values are on the order of 10^{-13} m^2/s with an associated geometric tortuosity ranging from 11.1 to 41.4. Due to the limited edge-connected pore spaces and low diffusion coefficients, the migration of hydrocarbons will be very slow from the shale matrix to hydraulically created fractures, with the initially high production of hydrocarbons from connected pore spaces near the sample edge (e.g., fracture face).

1. Introduction

Rapid advances in drilling-completion technologies (horizontal drilling and hydraulic fracturing) have promoted an increase of gas production from shale formations in the U.S. (EIA, 2016). The technically recoverable shale gas resource in China is estimated to be approximately 886.4 tcf, which is slightly larger than that in the United States (861.7 tcf) (EIA, 2016; Zhang et al., 2011). Encouraged by the commercial success in North America and urged by the central government to develop relatively clean fossil fuels, since 2008, the Chinese petroleum industry has been undertaking an ambitious shale gas development program (Zhang et al., 2011).

Shales are fine-grained sedimentary rocks and contain high volume fractions of organic matter (such as kerogen and bitumen) and clay minerals. As a heterogeneous porous medium, the composition and pore structure of shale can vary on multiple scales, and are often characterized by low porosity (< 10%) and extremely low permeability, on the order of nanodarcies (10^{-21} m^2) (Anovitz and Cole, 2015; Ghanizadeh et al., 2014; Monteiro et al., 2012; Pommer and Milliken, 2015). Compared to conventional hydrocarbon reservoirs (e.g., sandstone and carbonate) with pore sizes of tens to hundreds of microns, shale formations have much smaller pores with sizes at a scale

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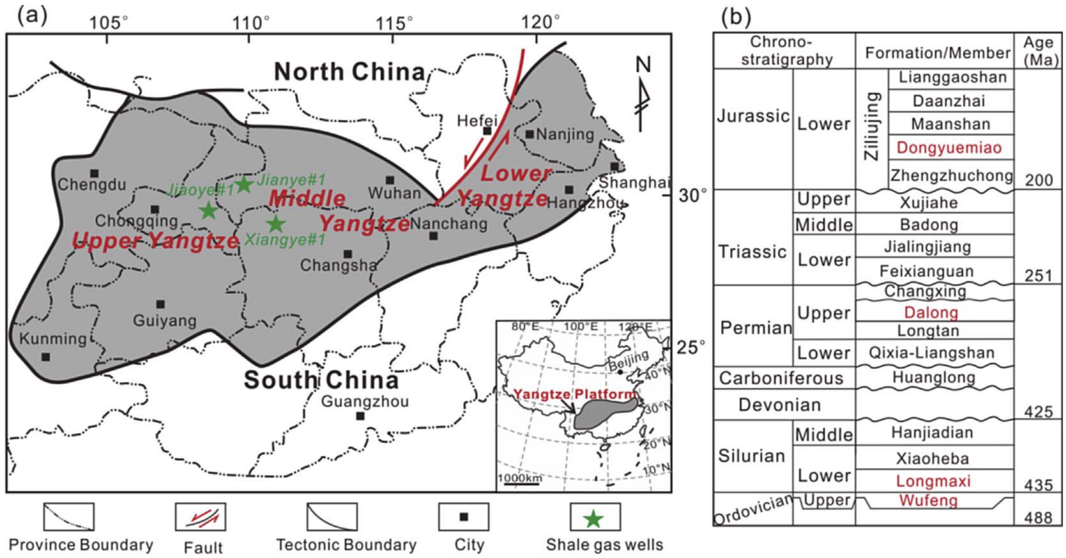

Fig. 1. (a) Locations of three shale-gas wells (in green) in the Middle Yangtze Platform, South China (modified from Tan et al., 2014); (1) Jiaoye No.1 well in Chongqing Province; (2) Jianye No.1 well in Hubei Province; (3) Xiangye No.1 well in Hunan Province. (b) Stratigraphic units in the Middle Yangtze Platform; wavy lines represent nonconformities. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of nanometers; therefore, conventional techniques are inadequate for characterizing those nanopores in shale (e.g., Milliken et al., 2013; Sun et al., 2017b; Yang et al., 2017b). These nanoscale pores are often irregular in their cross sections to exhibit elliptical, bubble-like and faveolated shapes (Yang et al., 2016b), further limiting pore connectivity.

Long-term productions of shale gas/oil resources from tight shale reservoirs in the U.S. suggest that the sustainable 'shale revolution' is strongly related to shale geology (Bowker, 2007; Jacops et al., 2017; Javadpour, 2009; Patzek et al., 2013), and the producibility is constrained by the complex pore systems, as well as their connectivity, for gas storage and production. Until now, economical flow rates of natural gas and light liquid hydrocarbons from shale formations, which are mainly controlled by the pore network (both geometrical and topological characteristics), wettability, pore fluid pressure and effective stress, are still technically difficult to sustain (Gao and Hu, 2016; Hu et al., 2015a; Jacops et al., 2017).

With the application of Ar ion beam milling and field emission-scanning electron microscopy (SEM), Loucks et al. (2009) first directly observed the dominant nanopores in Mississippian-age Barnett Shale from the Fort Worth Basin, one of the most leading and successful gas-producing shale reservoirs in the U.S. Since then, similar direct imaging methods, such as focused ion beam-SEM, broad-ion-beam SEM, transmission electron microscopy, helium ion microscopy, and computed tomography, have been reported in the literature for observing and characterizing the pore space in various shale reservoirs (Anovitz and Cole, 2015; Chalmers et al., 2012; Chalmers and Bustin, 2017; Curtis et al., 2012b; Houben et al., 2013; Klaver et al., 2015; Milliken et al., 2013; Sun et al., 2017b; Yang et al., 2016b). In addition, some indirect methods, such as low pressure carbon dioxide (CO_2)/nitrogen (N_2) physisorption, mercury injection capillary pressure (MICP), nuclear magnetic resonance, small-angle neutron/X-ray scattering, ultra-small-angle neutron scattering, helium porosimetry, and water immersion porosimetry, are often applied to obtain various pore structure parameters (Bahadur et al., 2015a; Barré, 2016; Chen et al., 2017; Clarkson et al., 2012; Daigle and Johnson, 2016; Mastalerz et al., 2013; Peng et al., 2017; Sun et al., 2017b; Yang et al., 2017b).

Each of above methods has its own advantages and disadvantages with respect to, for example, measurement principles, data interpretation, and sample sizes employed. However, many studies have mainly focused on the geometrical characteristics (e.g., shape, pore size distribution, pore volume and porosity), with less attention paid to the importance of pore connectivity. Assessing the pore connectivity of a 3-D space for a large (e.g., > mm^3) geological sample is still a problematic issue, and currently, there is no technique available that can effectively determine this important topological characteristic. According to the manifestation of some underlying microscale phenomena, such as the slope of a spontaneous imbibition curve and hysteresis from both gas physisorption and MICP, some researchers assessed the connectivity of porous solids (Armatas et al., 2003; Hu et al., 2012, 2015a; King et al., 2015; Liu et al., 1992; Seaton, 1991). Recent network modeling and direct observation of multiphase fluid flow in shale show that fluid migration and mass transport are closely related to the geometrical and topological characteristics, which can in turn affect the exploration and production of hydrocarbons from shale reservoirs (Hu et al., 2015a; Peng and Xiao, 2017; Sun et al., 2017a). Therefore, characteristics of pore structure (including geometry and connectivity), wettability and fluid migration in shale are important to understand gas storage and transport mechanisms in shale reservoirs.

Organic-rich shales, deposited in different sedimentary settings (by area: marine shale 26%, transitional marine shale 56%, and lacustrine shale 18%), are widely distributed in South China (Hao et al., 2013; Jiang et al., 2016; Tan et al., 2014). Based on successful applications of horizontal drilling and multi-stage hydraulic fracturing technologies in 2012, commercial success of shale gas extraction and production from marine Wufeng and Longmaxi Shales was achieved in 2014 in the Fuling District of Chongqing City, which is the first commercial shale gas field in China (Guo and Zhang, 2014; Guo et al., 2016). Since then, these two units of organic shales have been regarded as the main target zones for shale gas exploration and development in China. With the ongoing active shale program, the petroleum industry in China starts to realize that transitional marine and lacustrine organic shales also exhibit great resource potential, though they have been considered to be less promising in the past. Few comparative studies have been carried out to investigate the pore structure and wettability characteristics of marine, transitional marine and lacustrine shales, as well as their impacts on fluid flow and tracer migration.

In this work, four leading organic shales from Late Ordovician Wufeng (marine), Early Silurian Longmaxi (marine), Late Permian Dalong (transitional marine) and Early Jurassic Dongyuemiao (lacustrine) Shales were selected in the Middle Yangtze Platform (Fig. 1 and Table 1). These four leading shales have different geological characteristics, such as porosity, total organic carbon (TOC), thermal