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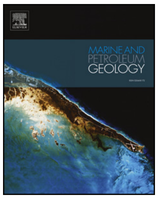

Research paper

# Investigating the spontaneous imbibition characteristics of continental Jurassic Ziliujing Formation shale from the northeastern Sichuan Basin and correlations to pore structure and composition

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ABSTRACT

Shale gas has been successfully explored in the Sichuan Basin of China, and the marine Silurian Longmaxi Formation shale is the main gas-bearing target layer. However, economic shale gas production from continental shale layers within the Sichuan Basin is still minimal, and its potential requires further investigation. This study focuses on the pore structure and spontaneous imbibition behaviors of continental Jurassic Ziliujing Formation shale samples from northeastern Sichuan Basin. Mercury intrusion porosimetry (MIP) was used to obtain the pore-throat size distribution information and field emission-scanning electronic microscope (FE-SEM) was conducted to observe the pore structure directly. The slopes of spontaneous imbibition curves were used to indicate the oil-wet or water-wet pore connectivity, and the wettability of our shale samples was investigated qualitatively by contact angle measurements and by comparing the directional spontaneous imbibition behaviors. The effects of shale composition and pore structure on spontaneous imbibition behaviors were also investigated in this study. Our results show that organic matter (OM) pores and OM-clay interparticle pores are quite developed in Ziliujing shale samples. The protection of pore spaces by rigid minerals is also observed for these samples. The oil-wet pore connectivity is generally better than water-wet pore connectivity, which could be indicated from the higher n-decane imbibition slopes compared with water imbibition slopes. The wettability of our shale samples can be classified into "weakly more oil-wet", "more oil-wet" and "more water-wet" according to the directional spontaneous imbibition results. The well-connected oil-wet pores could also be confirmed by the fast spreading of n-decane on the sample surfaces during contact angle measurements. In summary, the continental Jurassic Ziliujing Formation shale samples used in this study contain numerous OM pores and OM-clay interparticle pores, which provide both storage spaces and adsorption sites for shale gas and contribute to the better oil-wet pore connectivity.

## 1. Introduction

Different from North American marine shale gas, in China, continental shale gas contributes significantly to shale gas resources in addition to marine shale gas (Zou et al., 2010; Zhang et al., 2012). Many studies have been conducted to investigate the characteristics of marine shale gas from multiple aspects (Curtis, 2002; Loucks et al., 2009; Jiao et al., 2014; Pan et al., 2016; Chen et al., 2017). The premium gas-bearing marine shale layers usually contain high total organic carbon (TOC) content ($>2$ wt%), and high amounts of brittle minerals but low total clays (Dai et al., 2014; Guo and Zhang, 2014; Liang et al., 2014). Micrometer-to nanometer-sized organic matter (OM) intraparticle pores represent the dominant pore type within these marine shale layers; these OM pores provide large surface areas for adsorbed gas as well as pore spaces for free gas (Loucks et al., 2012; Mastalerz et al., 2013; Wang et al., 2016). However, the commercial exploration of shale gas in China has only been accomplished in marine shale layers, while continental shale gas exploration is still in its infancy (Zou et al., 2016). Compared with marine shale, continental shale has its own features; e.g., lower thermal maturity, higher clay content and rapid sedimentary facies changes, all of which complicate the exploration and exploitation of continental shale gas in China (Pu et al., 2015; Jiang et al., 2016).

Jurassic Ziliujing Formation shale from northeastern Sichuan Basin is one of the promising continental shale gas layers in China (Guo, 2016). The Da'anzhai Member shale of the Ziliujing Formation, which

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was mainly deposited in shallow lacustrine, moderately deep lacustrine, and deep lacustrine environments, is widely distributed in northeastern Sichuan Basin and contains generally greater than 1 wt% TOC, which consists mainly of the $II_1$-$II_2$ organic type with Ro ranges from 1.05% to 1.82% (Li et al., 2013). As to the pore structure of Ziliujing Formation shale, OM pores are less developed due to the lower thermal maturity compared with marine Longmaxi shale samples; furthermore, the abundant inorganic pores within clay minerals provide more specific surface areas for gas adsorption (Hou et al., 2014).

Spontaneous imbibition (SI) is a capillary force-controlled process during which a wetting fluid displaces a nonwetting fluid spontaneously by capillary force only, which is an important phenomenon during the exploitation process of shale gas using hydraulic fracturing (Bahrami et al., 2012; Cheng, 2012; Dehghanpour et al., 2013). As mentioned in the literature, the pore structure of shale matrix and the physical properties of fluids and their interactions control the SI process (Morrow and Mason, 2001; Cai et al., 2010, 2012; Shahri et al., 2012). Consequently, the SI process could be used to indicate the pore structure properties and predict the gas production behavior in the field (Mattax and Kyte, 1962; Zhang et al., 1996; Ma et al., 1997).

The following assumptions are proposed: (1) the water imbibes in a piston-like manner; (2) the pressure gradient in the gas phase ahead of the water front can be neglected; and (3) gravity is much less than capillary forces. Handy (1960) proposed equation (1) (Handy's equation) to describe the SI process in a water-air system during which water moves vertically upward:

$$\boldsymbol{Q_w^2 = \left(\frac{2P_c k_w \varnothing A^2 S_w}{\mu_w}\right) t} \tag{1}$$

where $\boldsymbol{Q_w}$ is the volume of water imbibed into the sample; $\boldsymbol{P_c}$ is the capillary pressure; $\boldsymbol{k_w}$ is the effective permeability to water; $\varnothing$ is fractional porosity; $\boldsymbol{A}$ is the cross-sectional area of the core; $\boldsymbol{S_w}$ is fractional water content of the pore spaces; $\boldsymbol{t}$ is the imbibition time (sec); and $\boldsymbol{\mu_w}$ is the viscosity of water.

Equation (1) Could be rewritten simply as

$$\boldsymbol{H = at^{0.5}} \tag{2}$$

where $\boldsymbol{H}$ is the cumulative imbibition height which equals $\boldsymbol{Q_w/A}$; $\boldsymbol{a}$ is a constant.

It can be seen that a slope of 0.5 could be obtained theoretically if cumulative imbibition height is plotted vs. imbibition time on log-log coordinates. However, the classic imbibition time exponent of 0.5 in equation (2) is not always valid for natural rocks, as Cai and Yu (2011) investigated the effect of tortuosity on the imbibition time exponent. According to the percolation theory, the lower exponent ($< 0.5$) in equation (2) obtained in the SI of tight rocks may indicate their low pore connectivity (Sahimi, 1994; Stauffer and Aharony, 1994; Hu et al., 2012; Hunt et al., 2014). Different from conventional reservoir rocks, shale contains organic matter and inorganic minerals and exhibits strong heterogeneity, giving it a dual-wet pore system and showing different pore connectivity to various wetting fluids (Xu and Dehghanpour, 2014; Hu et al., 2015, 2017). Wettability, defined as the tendency of solid surfaces to be preferentially wet by one fluid, is an important parameter affecting the selection of fracturing fluids in shale gas recovery. However, the evaluation of shale wettability is a challenging task due to the strong heterogeneity and ultrasmall pore sizes within shale. Recently, the wettability of shale has been characterized tentatively by contact angle measurements and SI experiments as well as by nuclear magnetic resonance (NMR) methods. The fractional wettability (or "Dalmatian wettability") of shale has been verified by various recent studies (Sulucarnain et al., 2012; Gao and Hu, 2016a; b; Yassin et al., 2017).

In this study, we will evaluate the wettability properties of Ziliujing Formation shale samples from northeastern Sichuan Basin by contact angle measurements and directional SI experiments as proposed by Gao and Hu (2016a). Field emission-scanning electronic microscopy (FE-SEM) is used to observe the pore structure of shale samples directly, whereby mercury intrusion porosimetry (MIP) is applied to obtain the pore-throat size distribution. In addition, we will analyze the correlations between SI characteristics and shale pore structure as well as shale composition.

## 2. Samples and analytical methods

We selected 4 continental Da'anzhai Member shale samples of the Jurassic Ziliujing Formation at different depths from X Well located in northeastern Sichuan Basin. The mineralogy of these samples was analyzed using an X-ray diffractometer (PANalytical X'pert PRO MRD, Holland), and the TOC content was obtained by a CS-230 carbon and sulfur analyzer (Leco Corporation, St. Joseph, Michigan, USA).

An MIP instrument (Quantachrome PoreMasterGT 60) was used to obtain porosity and pore-throat size distribution of our shale samples. In addition, FE-SEM tests were conducted on Ar-ion-beam milling processed samples in order to observe the pore structure characteristics more clearly.

As for the SI experiments, 1 cm-cubed samples had all sides (except top and bottom) coated with quick-cure transparent epoxy to generate cocurrent imbibition in the vertical direction; these samples were prepared for imbibition tests with the experimental procedure previously described in detail by Hu et al. (2001). All the shale samples were oven-dried at 60 °C for at least 48 h before the SI experiments in order to maintain constant initial water saturation without causing serious damage to the pore structure. Water or oil phase (n-decane) was applied as the wetting fluid to displace the nonwetting air during the SI process; the physical properties of these fluids are listed in Table 1. SI experiments were conducted in two directions with respect to the shale bedding planes as presented in Fig. 1 of Gao and Hu (2016a): parallel (P) or transverse (T) to the bedding planes, which were also defined as directional SI experiments. As a result, at least 4 samples were taken from each depth to ensure the completion of water and oil imbibition experiments for both P and T directions; detailed information on all the samples used in SI experiments is listed in Table 1.

Contact angle measurements using water/n-decane were also conducted to evaluate the wettability of the shale samples. During the contact angle measurement, one cubic shale sample was used with the top surface was manually polished using sand paper. We then tapped one drop of n-decane or water on the top surface while photos with measured contact angles were captured continuously as soon as the fluid contacted the sample surface. To minimize the influence of bedding planes, the contact angle measurements were only conducted on the surface parallel to the bedding planes.

## 3. Results and discussion

### 3.1. TOC and mineralogy

The TOC and mineralogy of 4 Ziliujing formation shale samples are presented in Table 2. The TOC content ranges from 0.97 wt% to 1.72 wt% with an average value of 1.41 wt%, which is not very high according to the lower limit of TOC for marine shale gas reservoirs ($> 2$ wt%). However, the applicability of the TOC evaluation standard proposed for marine shale is debatable in the evaluation of continental shales; a TOC standard of $> 1$ wt% for continental shales to form a shale gas reservoir has been suggested in the literature (Li et al., 2013).

Regarding the mineralogy of our shale samples, one of the characteristics is the high total clay content (from 41.3 wt% to 54.0 wt% with an average value of 46.4 wt%). The clay minerals of our shale samples are mainly composed of mixed-layer (illite/smectite), illite and chlorite. The composition of clay minerals within Ziliujing Formation shale falls between Yanchang shale with dominant mixed-layer clay and Longmaxi shale with dominant illite, which is consistent with their