



# Change in composition and pore structure of Longmaxi black shale during oxidative dissolution



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## ABSTRACT

Owing to the presence of chemically unstable compositions (e.g., clay minerals, carbonate, pyrite, and organic matter (OM)) which are closely related to shale structure failures or dissolution pores, the methods to increase gas well long-term productivity from tight shale matrix need to take into account the chemical interaction of shale with injected fluid. In this study, black shale samples obtained from Lower Silurian Longmaxi formation in Sichuan basin, China were treated with 15 wt% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for the comprehensive understanding of the change in shale composition and the associated dissolution structures. The measurements of mass loss, total organic carbon content, and mineralogical composition showed that carbonate, reductive inorganic minerals containing ferrous iron (e.g., pyrite and chlorite), and OM in samples exhibited strong dissolution; however, the other minerals behaved in a non-reactive manner at the experimental time scale. After the oxidative treatment for 240 h, a large amount of oxidation-induced fractures and dissolution pores were observed by field-emission scanning electron microscopy. The fractures mainly oriented parallel to lamination were attributed to the dissolution of OM and structural alteration of clay minerals. All the dissolution pores seemed to be strongly dependent on the loss of dolomite, pyrite, and OM. Results from high-pressure mercury intrusion and low-pressure nitrogen adsorption analysis showed that these dissolution pores ranging from 10 to 500 nm in diameter exhibited a significant increase in pore volume due to the removal of interconnected pore-filling OM, while the volume of pores > 1 μm in size exhibited a minor increase because the micrometer-size dissolved particles appeared to be discrete or unconnected. Thus the oxidative dissolution could lead to the higher porosity and better connectivity of nanometer-size pore networks in shale samples. The induced fractures reduced the size of diffusion dominant zones in shale matrix, and the dissolution pores increased the size of gas transport pathways into fractures. These results indicate that the injection of H<sub>2</sub>O<sub>2</sub> may play an important role in shale matrix stimulation by oxidative dissolution which is likely to improve matrix diffusivity.

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## 1. Introduction

The shale gas transport controlled by pore structure at different length scales is a combination of matrix diffusion (surface and Knudsen diffusion) (Javadpour, 2009; Kang et al., 2011; Fathi and Akkutlu, 2012; Yang et al., 2016a), slip flow, and Darcy flow (Cui et al., 2009; Wang et al., 2009; Darabi et al., 2012; Akkutlu and Fathi, 2012). Results from triple-porosity model simulations showed that the contribution of Darcy flow to total flux in fractures is far greater than matrix diffusion (Alharthy et al., 2012). Therefore, a rapid initial decline of shale gas well production followed by low productivity is attributed to the extremely low matrix diffusivity (Cipolla et al., 2009, 2010; Anderson et al., 2010; Wang, 2016). Enhancing the rate of methane out of shale matrix requires higher diffusivity of adsorbed and free gas. Hydraulic fracturing, a technique capable of significantly reducing the size of diffusion

dominant zones in shale matrix, is the most commonly used method for improving matrix diffusivity. However, post-fracture production rate declines rapidly in the first few months or years (Baihly et al., 2010; Wang, 2016), thus making the extraction of shale gas less economical and efficient compared to conventional reservoirs. Another way to improve matrix diffusivity involves the enlargement of the nanopore size by chemical interaction between the shale and injected water (fracturing fluid). Unfortunately, previous investigations (Bustin and Bustin, 2012; Barton and Quadros, 2014; Gomaa et al., 2014) have largely focused on mechanical problems for optimum shale gas stimulation design such that the impacts of shale-fluid interaction on pore structure have been neglected.

Black shales contain a large amount of chemically unstable compositions (e.g., clay minerals, carbonate, pyrite, and organic matter (OM)) which are closely related to shale structure failures or dissolution pores. The physical and chemical interactions between these compositions and fluids have been discussed extensively (Oort, 2003; Ewy et al., 2008; Hemphill et al., 2008; Gomaa et al., 2014; Wu and Sharma,

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2016). For example, during spontaneous imbibition in gas shales, microfractures caused by water adsorption on clay surface have been observed by Roychaudhuri et al. (2013) and Dehghanpour et al. (2013). Furthermore, Aderibigbe and Lane (2013) also indicated that the impacts of chemical interaction between surfactant solution and shales on fracture behavior should be considered to improve the generation of conductive microfractures. However, the creation of conductive water-induced microfractures in-situ stress cannot be confirmed because these fractures are greatly influenced by confining pressure. On the other hand, it is well known that shale composition and texture are unstable when exposed to oxic environments (Leythaeuser, 1973; Cerling et al., 1989; Pye and Miller, 1990; Peucker-Ehrenbrink and Hannigan, 2000). For example, OM is sensitive to oxidation reaction (Elie et al., 2000; Marynowski et al., 2011a,b; Tamamura et al., 2015), thus organic-rich shale and coal have high chemical reactivity compared to carbonate or siliceous rocks (Martínez and Escobar, 1995; Lo and Cardott, 1995; Faure et al., 1999). Jin et al. (2013) reported that black shale with high OM content weathers faster than gray shale which has less organic material. Moreover, pyrite ( $\text{FeS}_2$ ), an indicator of anoxic environments (Wilkin et al., 1996; Wilkin and Barnes, 1997; Bond and Wignall, 2010; Yang et al., 2016b), is a ubiquitous constituent of organic-rich shale, e.g., the average quantity of pyrite is 2.0 wt% in Longmaxi shales (Tan et al., 2014a,b), 1.6–10.4 wt% in Marcellus shale (Milliken et al., 2013), and 1.0–7.0 wt% in Haynesville shale (Woodruff, 2014). The reductive sulfur and iron (II) in pyrite being are stable only at very low oxidation states; therefore, pyrite can be rapidly oxidized in oxic environments (Huggins et al., 1987; Evangelou and Zhang, 1995; Hutcheon, 1998). Some researchers observed that the weathering or oxidation of rocks can be accelerated due to the presence of pyrite (Martínez and Escobar, 1995; Evangelou and Zhang, 1995; Jin et al., 2013). As a result, the oxidative weathering of OM and pyrite can increase the connectivity of pore networks to fractures, thus leading to higher porosity with more weathering (Jin et al., 2013).

Although the soil OM, shale, and coal compositional changes caused by oxidative reaction or weathering have been extensively investigated (Leythaeuser, 1973; Wu et al., 1988; Mastalerz et al., 2009), it is still not clear whether this dissolution and the corresponding pore structure alteration occur at the laboratory time-scale when shales are exposed to oxidative aqueous solutions. This study extended the previous investigations (Jin et al., 2013; Aderibigbe and Lane, 2013; Wu and Sharma, 2016) and focused on the characterization of multiscale pore structure in Longmaxi black shale samples after oxidative dissolution. Factors influencing shale oxidation were also discussed. Finally, we discussed the implication of oxidative dissolution for developing higher performance fracturing fluid to optimize well productivity and to enhance shale gas recovery.

## 2. Sampling and methods

### 2.1. Fluids

Oxidative reagents, such as sodium hypochlorite ( $\text{NaOCl}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and sodium peroxodisulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ), have been widely applied in the removal of OM from soil (Mikutta et al., 2005; Zimmermann et al., 2007). Undoubtedly,  $\text{H}_2\text{O}_2$  has become the most widely used oxidant for OM destruction (Mikutta et al., 2005; Helfrich et al., 2007) because of its high removal efficiency toward OM and relatively low price. Thus 15 wt%  $\text{H}_2\text{O}_2$  was used in this study to investigate the oxidative dissolution of organic-rich shale and its effect on pore structure.

### 2.2. Shale sample

#### 2.2.1. Geological overview

In this study, we investigated the oxidation of OM and minerals present in black shale from lower Silurian Longmaxi formation in

Southeast Chongqing, China. The Longmaxi shale formation occurs in a 15,000 km<sup>2</sup> area with a thickness of 20 to 200 m in Southeast Chongqing (Han et al., 2013). Liang et al. (2012) and Zou et al. (2015) reported that the lithofacies of lower Longmaxi formation, deposited in bathyal- to abyssal-sea and anoxic environment, are carbonaceous black shale and siliceous black shale. Owing to the sufficiently buried depth of Longmaxi shale to reach gas window thermal maturity (2.5 to 3.0%  $R_{\text{ob}}$ ) (Dai et al., 2014; Pan et al., 2016), there are substantial gas resources, making the Fuling and Pengshui county in Southeast Chongqing the hottest target zone for shale gas production. The geology of Longmaxi formation in Southeast Chongqing has been discussed in detail by Zou et al. (2015) and Yang et al. (2016c).

#### 2.2.2. Characteristics of shale samples

Shale samples used in this study were collected from a road outcrop of Longmaxi black shale. The location is alongside the Pengshui first middle school, Pengshui County, Southeast Chongqing, China. Before the sampling, the soil and disintegrated rocks covering the shale samples were removed to ensure that there were no visible signs of weathering. Subsequently, shale “outcropping” samples were taken from the unweathering zones by digging 2.5 m into fresh exposure of the Longmaxi formation.

There are two reasons for the use of outcrops rather than core samples from wells. The Southeast Chongqing belongs to high-steep tectonic belt, and the outcrops of Longmaxi black shale are widely distributed throughout this area. Thus sufficient shale samples can be obtained from the outcrops. Besides, numerous literature reports about the mineralogical composition (Liu et al., 2011; Liang et al., 2012; Tan et al., 2014a), methane sorption capacity (Tan et al., 2014b; Yang et al., 2016c), and pore structures (Chen et al., 2013; Yang et al., 2016c) of these outcrop samples are easily available. Results from Littke et al. (1991) revealed that pyrite is the most affected constituent in black shales during weathering, and it was strongly recommended that the microscopic appearance of pyrite crystals should be used to differentiate between unweathered and weathered black shales. Similarly, Wildman et al. (2004) and Jin et al. (2013) considered the depth profile of sulfur loss as an indicator of pyrite oxidation in the weathering study of the outcrop samples from New Albany shale and Marcellus black shale.

In order to determine the weathering extent of shale samples in this study, pyrite content and morphology of subsurface shale samples from PY1 and JY1 well were used for the comparison with that in our “outcropping” sample. The distance between these two shale gas wells and the location of sampling in this study is <75 km. For the same member of Longmaxi formation, the quantity of pyrite is 2.6 wt% in our “outcropping” sample and 1.5–3.8 wt% in samples below 2144 m from PY1 well (Tian et al., 2013). No significant differences exist between these two sets of shale samples. Moreover, there is no clear difference in the microscopic appearance of pyrite between our “outcropping” samples and subsurface samples from JY1 well (Yang et al., 2016b). Thus it seems that the shale samples used in this study are not affected by the oxidative weathering.

### 2.3. Experimental studies

Core holes were drilled parallel to bedding structure of the shale strata. Two cylindrical core samples with a core size of 2.5 cm diameter and 5.0 cm length were selected from the same hole. Furthermore, >200 g core fragments collected in the boreholes were crushed and sieved to provide the ground samples (380–830  $\mu\text{m}$ ). The ground shale samples were divided into eight groups, and the weight of sample in each group was 20.0 g. The first group was considered as the untreated sample, and the others were used for dissolution experiments, defined as the treated samples. Moreover, in order to investigate the oxidation reaction of the important forming-rock minerals in organic-rich shales, eight different pure minerals (e.g., pyrite, chlorite, illite, calcite, dolomite, k-feldspar, albite, and quartz) were used. The purity of

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