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# The effect of sample particle size on the determination of pore structure parameters in shales

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ABSTRACT

The combination of low-pressure $N_2$ and $CO_2$ adsorption could provide an effective approach for characterizing the pore structure of shales. Although gas adsorption methods generally do not destroy the pore structure during experimental process, sample particle sizes could significantly affect experimental results that can approach or deviate from the real value. Therefore, the determination of pore structure is closely related to the sample particle size. In the current study, 4 fresh core samples of different compositions and total organic carbon (TOC) ranges collected from the Sichuan Basin were analyzed to elucidate the effect of sample particle size on the determination of pore structure parameters. Samples were ground and then sieved into seven groups based on particle size ranges, i.e., <60, 60–80, 80–100, 100–120, 120–140, 140–200 and >200 mesh, for measurements of low-pressure $N_2$ and $CO_2$ adsorption, TOC contents, and X-ray diffraction (XRD) mineralogy.

TOC results show a slight enrichment whereas XRD minerals vary irregularly, with sample particle size decreases. Meanwhile, the TOC and mineral contents show insignificant statistical relation with pore structure parameters in all sample particle size ranges. Therefore, variations in organic matter content and mineral composition that result from sieving are unlikely to have a significant influence on the pore structure of shale. Rather, sample particle size may be the most important control on pore structure characteristics in the samples analyzed in this study.

The relative standard deviations (RSDs) for Brunauer–Emmett–Teller (BET) $N_2$ surface areas, Dubinin–Radushkevich (D–R) $CO_2$ micropore surface areas and non-local density functional theory (NLDFT) $N_2$ and $CO_2$ nanopore surface areas measurements are <5%, within analytical error. Therefore, in the studied grain size range (60–200 mesh), the sample particle size shows insignificant effects on surface area results. However, samples with smaller particle size have a greater effect on pore volume and pore size, especially for pore size distribution (PSD) of $N_2$ low-pressure adsorption. The RSDs of the Barrett–Joyner–Halenda (BJH) pore volumes and BET pore sizes of all samples in the 140–200 mesh range are obviously greater than the values of other mesh ranges. Moreover, in the dV/dlogw plots of PSD analysis, high $N_2$ peaks and new $N_2$ peaks appeared in the 10–100 nm pore-width range, particularly for samples in the >140 mesh range. The 60–140 mesh particle-size range is therefore recommended for $N_2$ low-pressure adsorption. Finally, the sample particle size has insignificant effect on the pore system parameters for grains in the 60–200 mesh range for $CO_2$ low-pressure adsorption. Overall, the results confirm that the 60–140 mesh particle-size range can be used for both $N_2$ and $CO_2$ low-pressure adsorption measurements.



## 1. Introduction

Natural gas may be stored in organic-rich shales as a combination of free gas, adsorbed gas and dissolved gas (Curtis, 2002; Ross and Bustin, 2009). Shales are generally characterized by low porosity and permeability, and shale gas production depends on the ability of pore systems to store and release hydrocarbon gas. Pore system characterization is therefore an important step in the evaluation of shale gas reservoirs. To improve our understanding of the relationship between a given pore system and gas storage capacity, various techniques (e.g., organic petrology, $CO_2$ and $N_2$ low-pressure adsorption, and high-pressure mercury intrusion) are used to quantify the surface area, pore volume, pore size, and pore size distribution of the shale.

Low-pressure gas adsorption is an important approach for characterizing the pore systems of shale samples, i.e., surface area and microporosity. Factors that may influence these measurements include pore size, particle size, and surface roughness (Jiang et al., 2014; Tsai, 2013). Although pore size is the most important factor, gas adsorption methods generally do not destroy the pore size during experimental process, while the surface area of shale may be closely related to particle size and surface roughness. Furthermore, surface roughness has little

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difference in the same sample preparation techniques. Therefore, the determination of pore structure is closely related to the sample particle size, and particle sizes could significantly affect experimental results that can approach or deviate from the real value. Despite the microstructural data of shale sample are growing (e.g., Ross and Bustin, 2007; Chalmers et al., 2012; Clarkson et al., 2013; Tan et al., 2014a, 2014b; Tian et al., 2015), a unified standard for sample particle size has not been adopted among the various low-pressure adsorption experimental methods. For example, in China, samples are generally ground to a maximum particle size of 100 mm, as outlined in the National Standards of the People's Republic of China (GB/T 21650.2-2008 and GB/T 21650.3-2011). Other studies report that samples were ground to grain sizes of 1–2 mm (Hou et al., 2014) or other millimeter-size particles (Clarkson et al., 2012). Tian et al. (2013, 2015) ground shale samples into grains of 60–80 mesh (250–180 μm) and 60–100 mesh (250–150 μm), and Zelenev et al. (2011) ground samples to 40 mesh (<380 μm). Many researchers ground samples so they pass through a 60 mesh sieve (<250 μm) (Chalmers and Bustin, 2007; Ross and Bustin, 2007, 2009; Chalmers et al., 2012; Clarkson et al., 2013; Labani et al., 2013; Lahann et al., 2013; Wang et al., 2014). However, in other studies samples have been ground to 70 mesh (<200 μm; Tan et al., 2014a, 2014b; Yang et al., 2014), 80 mesh (<180 μm; Guo et al., 2014), and 100 mesh (<150 μm; Wang et al., 2013; Cao et al., 2015). Furthermore, other studies did not explicitly state the sample particle size when conducting low-pressure adsorption measurements (Busch et al., 2008; Chareonsuppanimit et al., 2012; Ji et al., 2012; Han et al., 2013; Liu et al., 2013; Mastalerz et al., 2013; Chen and Xiao, 2014; Yuan et al., 2014; Li et al., 2015). It is therefore difficult to compare the pore structural data of different laboratories.

In the current research, we aim to evaluate the effect of sample particle size on the determination of specific surface area, pore volume, pore size and pore size distribution in shale samples, and to propose a suitable particle-size range for low-pressure $N_2$ and $CO_2$ adsorption measurements.

## 2. Samples and experimental methods

### 2.1. Sample preparation

Four fresh core samples of different compositions and TOC ranges from the large-scale development shale gas fields of China were collected and analyzed in this study. The measured samples are black shales deposited in marine environments from Sichuan Basin located in the northwest part of the Upper Yangtze Platform, South China (Fig. 1) (Tan et al., 2013, 2015). The organic rich lower Silurian Longmaxi shale formation is widely present in the basin, and the principal rock types are black carbonaceous and siliceous shale that is rich in organic matter, mudstone and siltstone (Fig. 2). This formation has been identified as an important target for shale gas exploration (Wang et al., 2013; Tan et al., 2014a, 2014b, 2015).

Prior to analysis, the samples were cut into fragments of ~10 mm, and then ground for ~30 s in a Mini Superfine Mill. The ground samples were sieved into seven particle-size ranges: <60, 60–80, 80–100, 100–120, 120–140, 140–200, and >200 mesh. The mass fraction of each particle-size range is listed in Table 1. The groups with a sample particle size larger than 200 or <60 mesh were not analyzed because of the mass range limitation.

### 2.2. Total organic carbon (TOC) content and X-ray diffraction (XRD) analysis

The behavior of shale as a reservoir rock for gas is influenced not only by storage mechanisms, which are controlled by mineral content (Bruant et al., 2002), but also, and more importantly, by the characteristics of organic matter that offers sorption sites on the organic surface area of mesopores or volume filling in micropores (Clarkson et al., 2013). Therefore, it is necessary to determine the TOC content and mineral composition for different particle sizes.

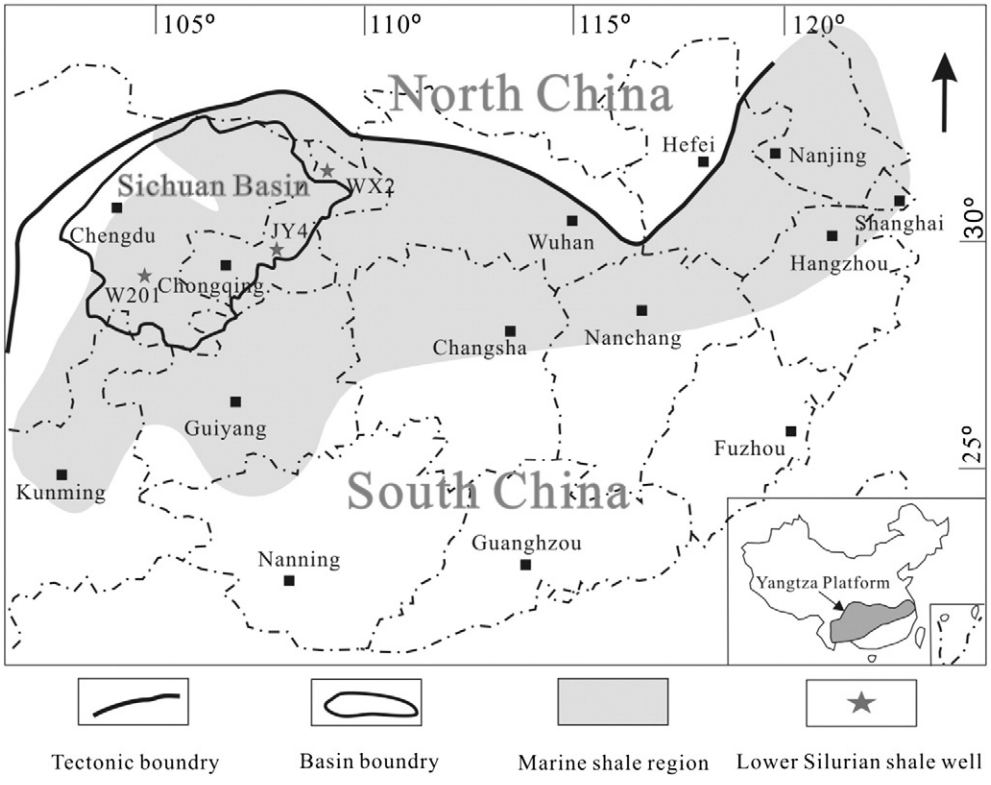


**Fig. 1.** Locations of the sampled wells in Sichuan Basin of the Upper Yangtze Platform, South China.