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# Comparison of organic matter occurrence and organic nanopore structure within marine and terrestrial shale

Han Zhang [a, b], Yanming Zhu [a, b, *], Yang Wang [a, b], Wei Kang [a, b], Shangbin Chen [a, b]

[a] Key Laboratory of Coalbed Methane Resource and Reservoir Formation Course, Ministry of Education, China University of Mining and Technology, Xuzhou, Jiangsu 221006, China
[b] School of Resources and Geoscience, China University of Mining and Technology, Xuzhou, Jiangsu 221006, China

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ABSTRACT

Samples from Cambrian Qiongzhusi Formation (Fm.), the Silurian Lungmachi Fm. of the middle-upper Yangtze, and the Triassic Yanchang Fm. of the Ordos Basin were comprehensively investigated by high-resolution scanning electron microscopy (SEM) and image analysis, to further elucidate the influence of preservation parameters on organic matter (OM) and intraparticle pores (intraP) within OM. OM preserved in shale is divided into three types: organic residues, bitumen particles, and amorphous remains. Development of organic nanopores is controlled by factors such as preservation of OM, biological sources of organic residues, and thermal evolution. The original biological structure and hydrocarbon generation control the nanopore structure within organic residues. Thus, the intraP of organic residues have the highest facial porosity and fractal dimension among the pore types examined. Nanopores associated with bitumen particles vary greatly within different shales and provide considerable pore volume. Amorphous remains are mixed with inorganic matrix, indicating the presence of OM–mineral matrix compound, while nanopores are rarely seen within these remains. The development of organic nanopores in the Yanchang Fm. appears dominated by maturity, indicating that appropriate maturity is critical for the formation of effective pore spaces. With increasing maturity, there is less dissimilarity among bitumen intraP spaces. The Qiongzhusi Fm. possessed the highest facial porosity among organic residues, but the isolated fossils could not form an effective pore network. Among the shales investigated, the thoroughly interconnected pores of the carbonaceous graptolite and bitumen particles from the Lungmachi Fm. are most promising for gas accumulation.



## 1. Introduction

Shale is a tight gas reservoir that stores gas primarily in free and adsorbed states. The intricacy of reservoir pore structure, especially well-developed nanopores with complex thermodynamic state, is considered the main challenge for research into accumulation mechanism and exploitation. Organic nanopores have received increased attention due to the critical role of organic matter (OM) in shale gas reservoirs. As an origin of hydrocarbon and important composition materials, organic matter has a positive effect on the occurrence of gases in both adsorbed and free states. Finely Dispersed fine OM particles are preserved within the inorganic matrix, in which nano-intra pores and capillaries are well developed. A significant proportion of the gases in place is related to the interconnected organic nanopores (Ambrose et al., 2010). The high adsorption entropy and complex organic nanopore structure imply the importance and difficulty of revealing the organic nanopore structure (Curtis et al., 2012; Zhang et al., 2012). Total organic carbon (TOC) is one of the primary factors affecting nanopore structure characteristics (Wang et al., 2014).

Factors influencing pore development include the OM type, maturity and evolution rate, and amalgamation with mineral compositions. Recent research has shown that maturation led to the development of fine pores on the nanoscale, increasing both matrix porosity and gas storage capacity (Reed and Loucks, 2007; Jarvie et al., 2007; Hou et al., 2014; Cao et al., 2015). Organic nanopores are well developed in vitrinite- and intertinite-enriched shales. Nanopore volume was found to increase with maturity (Chalmers and Bustin, 2007, 2008a, 2008b).

* Corresponding author. Key Laboratory of Coalbed Methane Resource and Reservoir Formation Course, Ministry of Education, China University of Mining and Technology, Xuzhou, Jiangsu 221006, China.
*E-mail address:* yanmingzhu@sohu.com (Y. Zhu).

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Study samples were taken from the Cambrian Qiongzhusi Fm. and the corresponding isochronous Niutitang Fm., the Silurian Lungmachi Fm. of the marine facies in the middle-upper Yangtze, and the terrestrial Triassic Yanchang Fm. of the Ordos Basin (Fig. 1). The differences in OM occurrence and OM-related nanopores between the different shales were investigated to further describe the factors that control the formation of organic nanopores.

## 2. Samples and methodology

### 2.1. Geological background of the target shale

The Qiongzhusi and Lungmachi Fm. are both deep-sea sediments. The organic-rich shale of the Qiongzhusi Fm. and the corresponding Niutitang Fm. strata formed under the influence of the ascending current on the marine shelf (Ma et al., 2011; Yu et al., 2013), with an abundance of species including algae, sponges, and arthropods. Samples were collected from northwest Hunan (Niutitang Fm.) and northeast Yunnan (Qiongzhusi Fm.) (Fig. 1B). The lower member of Lungmachi Fm. sediment in the deep-water shelf environment and the uplifting palaeo-continents led to the formation of the entrapped basin (Su et al., 2007; Zhang et al., 2007). Prosperous graptolites formed the typical graptolithic facies shale (Wang et al., 2001; Fan et al., 2011). As the water became shallower, the hydrocarbon source-rock quality of the upper Lungmachi Fm. deteriorated. Thus, the samples were collected from the lower member of the Lungmachi Fm. in Qijiang, Chongqing and from Yongshan, Yunnan. The early Palaeozoic strata in the middle-upper Yangtze experienced complex structural and thermal evolution, leading to a high and over-matured thermal evolution stage in these two marine shale facies (Table 1).

The Triassic Yanchang Fm. recorded the complete evolution of the terrestrial lake basin. The Chang 7 member sedimented during the culmination of the sag evolution in the Yanchang Fm., with the largest lake basin area (Chen et al., 2007; Yang et al., 2008). It formed the horizontally stable oil/organic-rich shale at the bottom of Chang 7, which is the preferred target stratum in the Ordos Basin. Samples were collected from Tongchuan, Yichuan, and Yan'an (Fig. 1C). The samples display high TOC content and relatively low thermal evolution stage (Table 1).

### 2.2. Methodology

High-resolution scanning electron microscope (SEM) imaging is suitable for on-site analysis of pore structure and formation. In this study, field emission SEM and an energy-dispersive spectrometer (EDS) were utilized to acquire back-scattered SEM images and material information. Forty-eight items were investigated: 24 samples with two preparation states for each, comprising the origin state and finely polished state processed by focused ion beams. All samples were sprayed with gold to enhance conductivity. The EDS uses a semi-quantitative method, especially for elements with smaller atomic numbers (5–10), and metal element is another source of error, so that the carbon content reported for each OM state spans a relatively wide range.

The facial porosity and fractal dimensions of organic nanopores are indicative of the development of pores and the complexity of the pore structures; their quantitative evaluation allows each pore type to be thoroughly examined. Facial porosity is the ratio of the pore area across certain zones (i.e., pore area/the area of a certain OM particle). Fractal dimension represents the irregularity of complex features, with larger dimension indicating more complex pore structure.

The grayscale values of back-scattered SEM images are proportional to the atomic number, hence carbonaceous particles are shown darker than the inorganic matrix while the pores are represented by the maximum grayscale value. By selecting zones of preserved OM and analyzing the grayscale values of the SEM images, pore development can be identified and facial porosity further analyzed. Then, by recognizing the boundaries of the pores, the fractal dimensions of the pores in a particular particle can be calculated. The facial porosity analysis and fractal dimension

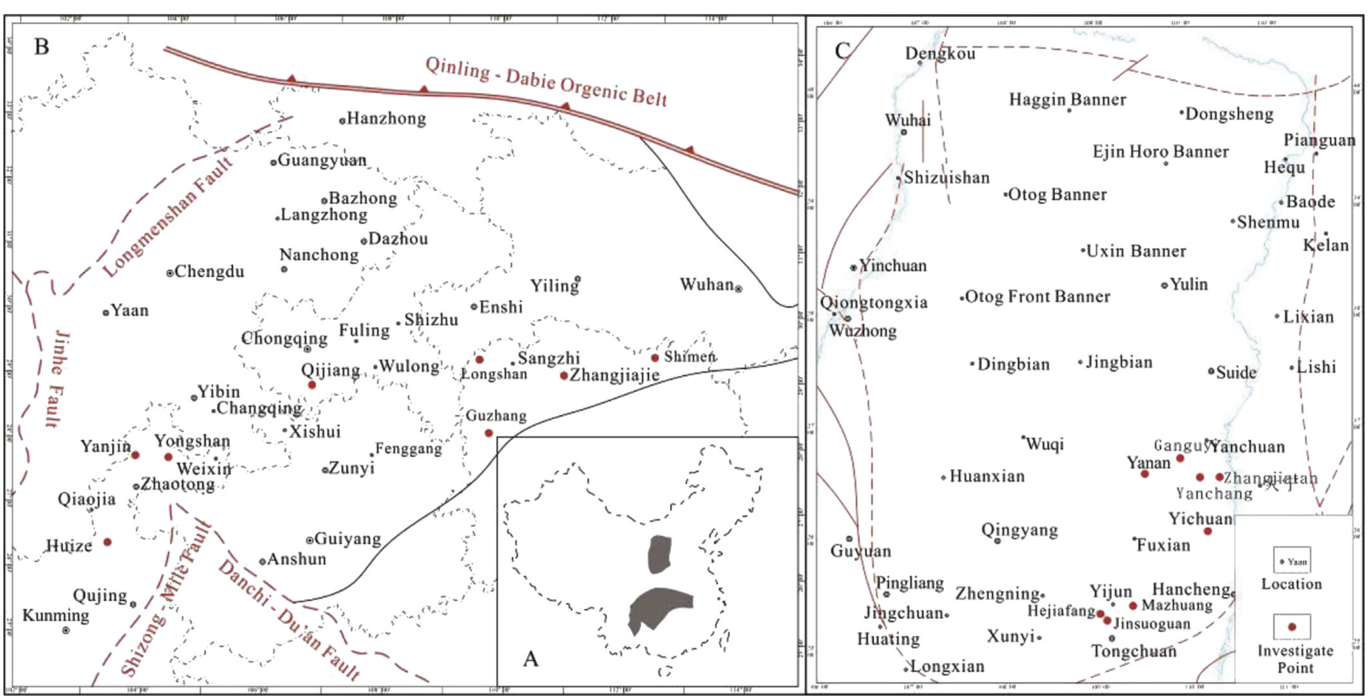


**Fig. 1.** Location of the research area and sample collection points. A) Location of the research area in China; B) Middle-upper Yangtze; C) Ordos Basin.