

MAIN FACTORS INFLUENCING THE DEVELOPMENT OF NANOPORES IN OVER-MATURE ORGANIC-RICH SHALES

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China is the most promising country for shale growth outside North America that has so far dominated shale gas supply. At present, shale gas evaluation and exploration in China are focused on South China, especially in and around the Sichuan Basin (Zou et al., 2010; Tian et al., 2013). The first large-scale developed shale gas field in China, the Fuling shale gas field, was found by SINOPEC in the Longmaxi Formation of the eastern Sichuan Basin in 2014. Marine shales in China are characterized by high thermal maturity (R_o 2.0%–3.5%) and have experienced deep burial as well as multiple tectonic events. The pores in organic-rich shales are predominantly nanometer in scale. Therefore, an accurate depiction of the nanopore structure in over-mature organic-rich shales is critical for the quantification of producible resources and the evaluation of long-term production behavior for shale gas in China.

In this study, 87 black shale core samples were collected from what is considered to be the most favorable target for future shale gas exploration (i.e., the bottom of the lower Silurian Longmaxi Formation) and the current exploration zones (i.e., Fuling demonstration zone, Changning–Weiyuan demonstration zone, and Wuxi exploration block) of shale gas in China. The samples were investigated using organic, geochemical, and petrological analyses, low pressure nitrogen (N_2) and carbon dioxide (CO_2) adsorption, broad ion beam–field emission scanning electron microscopy (BIB-FESEM), statistical analysis, and contrastive analysis. We aim to: (1) quantitatively evaluate the main factors controlling nanopore generation and distribution in over-mature organic-rich shales; and (2) comprehensively analyze the characteristics and major influencing factors of organic matter-pore development in over-mature organic-rich shales. This study provides key insights into the evaluation of shale gas resources in China.

The results indicate that micro- and fine mesopores (<10 nm) are the major contributor to the total surface area comprising a significant portion (up to 99%) of total surface area measured. Mesopores are the major contributor to the total pore volume with a maximum proportion up to 77%. The amount of adsorbed gas in shale primarily depends on the micropore and fine mesopore surface area. The free gas content is determined by micropore and mesopore volume, especially the mesopore volume. Therefore, micropore and fine mesopore surface area and mesopore volume are the most important parameters related to nanopore structure development in the lower Silurian Longmaxi Formation shale. The studied samples have micropore and fine mesopore surface areas of 10.03–46.47 m^2/g (mean 22.65 m^2/g) and mesopore volumes of 6.28×10^{-3} to $38.35 \times 10^{-3} cm^3/g$ (mean $18.36 \times 10^{-3} cm^3/g$).

The strong linear correlation between TOC content and surface area ($D < 10$ nm) and organic-matter-hosted pore sizes observed in BIB-FESEM images indicate that organic matter is the major control on pore development for pores with diameters less than 10 nm. Factor analysis indicates that TOC, quartz, and illite contents are the main controlling factors on the formation of medium mesopores. Coarse mesopore volume and illite content obey a power law relationship, meaning that the generation and distribution of coarse mesopores is mainly controlled by the illite content. Based on the quantitative and qualitative analysis of BIB-

FESEM images, it is suggested that most of the macropores are mineral-associated (e.g., calcite- and albite-dissolved pores and combined effected pores) (Fig. 1).

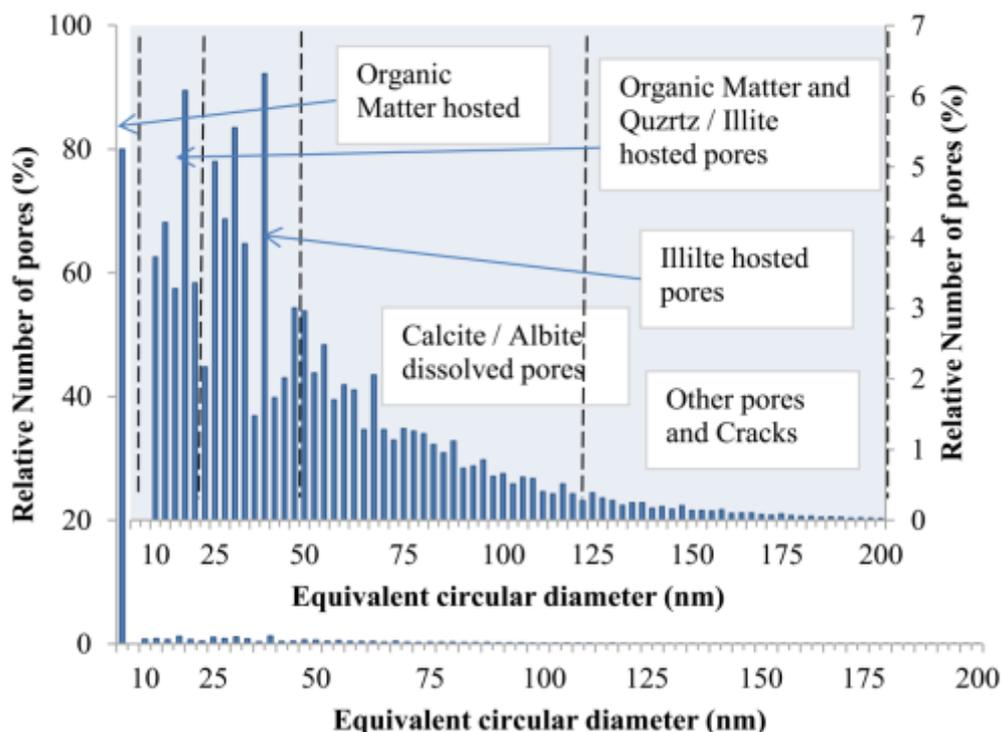


Figure 1 Key factors of nanopores generation and distribution in over mature organic-rich shales.

The increase of the micropore surface area per unit mass TOC in organic-rich shales during the early mature to mature stage is mainly attributed to the formation of a large number of nanopores within organic matter. However, the gas generative ability of residual organic matter at over-mature stages is weakened, and subsequent compaction caused by increased burial has a stronger control on the loss of primary porosity with the increase of maturity. A conversion, or decrease, in the micropore surface areas per unit mass TOC occurs during the over-mature stage.

References

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