

METHANE ADSORPTION CAPACITY OF OVERMATURE LOWER CAMBRIAN SHALES UNDER HIGH TEMPERATURE AND HIGH PRESSURE CONDITIONS

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While the shale gas potential of Lower Silurian shales in China have been well documented, the Lower Cambrian shales, another important set of black shales in South China, are still poorly studied with respect to gas storage capacity, including both free gas and adsorbed gas. Compared to the Lower Silurian shales, the Lower Cambrian shales are more organic-rich with higher thermal maturity levels. Early studies have shown that the total porosity of Lower Cambrian shales is smaller than that of Lower Silurian shales with similar TOC contents because the former has been more severely compacted. However, it is still not clear whether the methane adsorption capacity is also correspondingly reduced due to severe compaction.

In this study, ten Lower Cambrian marine shale samples were collected in Guizhou province, a new shale gas prospect area in addition to the Sichuan Basin in China. These samples are buried in the depths of 2449–2539 m with TOC values ranging from 1.8 to 11.3 wt.% and have equivalent vitrinite reflectance values of approximately 4%. The macerals in organic matter are dominated by micrinite and pyrobitumen, suggesting a kerogen of type I and/or II, similar to the kerogen nature of Lower Silurian shales. Methane adsorption isotherms at 60 °C at pressures up to 35 MPa were measured for all ten samples using a magnetic suspension balance. To investigate the temperature-dependency of methane adsorption capacity, three samples (TOC=3.5, 7.3 and 11.3 wt.%) were selected for methane adsorption isotherms at various temperatures (40 °C, 60 °C, 80 °C, 100 °C and 120 °C) at pressures up to 35 MPa. Both Langmuir- and SDR (supercritical Dubinin–Radushkevich equation)-based models were used to fit the methane excess adsorption isotherms to investigate the adsorbed phase density of methane and its adsorption capacity. The methane adsorption capacity of the Lower Cambrian shales are also compared with those of the Lower Silurian shales with a lower thermal maturity level, which allows to investigate whether thermal maturity still affects the methane adsorption capacity of shales at very high thermal maturity stages (i.e., equivalent vitrinite reflectance values greater than 3.0%).

Our results show that the measured excess adsorption capacity of methane for the ten samples reaches a maximum at a pressure of approximately 9–11 MPa, then decreases gradually with increasing pressures. This is because that the density of methane in free phase is approaching to the density of adsorbed methane, and when they are equal, the excess adsorption is expected to be zero. Both the SDR- and Langmuir-based excess adsorption models can satisfactorily fit the measured excess adsorption isotherms within our experimental temperature and pressure ranges. When the decline trend is absent from the excess adsorption isotherms, the Langmuir-based model produces an adsorbed methane density that is remarkably larger than the liquid density of methane (424 kg/m³), whilst the SDR-based model still gives a reasonable value. This suggests that the SDR model might be more appropriate when the experimental pressure is not large enough to produce an excess methane adsorption isotherms with a remarkable decline trend.

Like other shales, methane adsorption capacity of the Lower Cambrian shales is also positively related to TOC and this relationship is valid in the TOC range of 1.8 to 11.3 wt.% (Fig. 1a). When these data are plotted together with those of Lower Silurian shales, a fairly good linearity still exists between TOC and methane adsorption capacity, suggesting this relationship is not or only trivially affected by thermal maturity when the equivalent vitrinite reflectance values are greater than 3.0% (Fig. 1a). The slope of regressed equation in Fig. 1a represents the contribution of 1% TOC to the methane adsorption capacity of the whole rock.

This value is similar to that reported by Gasparik et al. (2014) who performed adsorption experiments on whole rocks like the present study but is a bit larger than that reported by Zhang et al. (2012) who conducted adsorption experiments on kerogens. One reason for the smaller value in the case of kerogen is probably related to the destruction of pore structure of organic matter during the extraction of kerogen and some narrow pores that have higher methane adsorption potential are changed to be flat surfaces that have smaller methane adsorption potential (Mosher et al., 2013). Like other shales, both the maximum methane adsorption capacity and adsorbed phase density of methane decrease with increasing temperatures for the Lower Cambrian shales. The reduction rate of the maximum methane adsorption capacity ranges from the smallest value of $0.01 \text{ cm}^3/\text{g rock}/^\circ\text{C}$ for the sample with $\text{TOC}=3.5 \text{ wt.}\%$, through a medium value of $0.015 \text{ cm}^3/\text{g rock}/^\circ\text{C}$ for the sample with $\text{TOC}=7.3 \text{ wt.}\%$ to the largest value of $0.020 \text{ cm}^3/\text{g rock}/^\circ\text{C}$ for the sample with $\text{TOC}=11.3 \text{ wt.}\%$. The reduction rate of adsorbed phase density of methane varies only in a minor way, ranging from $0.85 \text{ kg}/\text{m}^3/^\circ\text{C}$ to $0.74 \text{ kg}/\text{m}^3/^\circ\text{C}$ for the three selected samples.

Under geological conditions, the presence of water will significantly reduce the methane adsorption capacity because the water may occupy the adsorption site or block the pore system (Gasparik et al., 2014). Therefore it is necessary to investigate the methane absolute adsorption capacity of organic matter that is water-phobic as compared to minerals, and the methane adsorption capacity by organic matter alone may represent the minimum methane adsorption capacity of a whole rock. The methane adsorption capacity of organic matter is expressed as the adsorbed methane per 1% TOC and is also temperature-dependent (Fig. 1b). The negative slope of the regressed equation in Fig. 1b means that the reduction of methane adsorption capacity by 1wt.% TOC alone is 0.001 cm^3 at every change of 1°C . In other words, if the rock has a $\text{TOC}=5 \text{ wt.}\%$ and the temperature increases from 50°C to 100°C , then the methane adsorption capacity by organic matter alone in the rock would be reduced from 2.0 cm^3 to 1.75 cm^3 , a change of 0.25 cm^3 ($0.001 \text{ cm}^3/1 \text{ wt.}\% \text{ TOC}/^\circ\text{C} \times 5 \text{ wt.}\% \text{ TOC} \times 50^\circ\text{C} = 0.25 \text{ cm}^3$). When combined with the temperature-adsorbed phase methane density equation, this equation can be used to estimate the specific methane adsorption amount by organic matter alone for a shale with any TOC content in the temperature range between 40°C and 120°C .

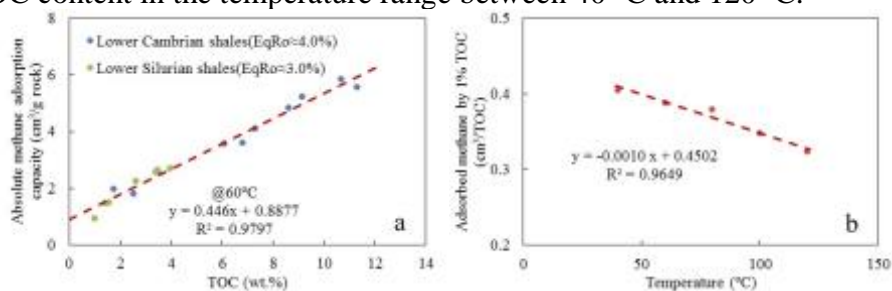


Figure 1 (a) A comparison of methane adsorption capacity at 60°C between the Lower Cambrian and the lower Silurian shales; (b) A plot showing the temperature-dependence of methane adsorption capacity by 1% TOC alone.

References

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