[PS]A Combination of N_2 and CO_2 Adsorption to Characterize Nanopore Structure of Organic-rich Lower Silurian Shale in the Upper Yangtze Platform, South China: Implications for Shale Gas Sorption Capacity*

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Abstract

The pores in shales are mainly of nanometer-scale, and their pore size distribution is very important for the preservation and exploitation of shale gas. This study is focused on the organic-rich Lower Silurian black shale from four wells in the Upper Yangtze Platform. Their TOC, mineralogical composition, and pore characterization were investigated. Low pressure N_2 and CO_2 adsorption were conducted at 77.35 K and 273.15 K, respectively. The pore structures were characterized by modified Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (DR), t-plot, Barrett-Joyner-Halenda (BJH), and density functional theory (DFT) methods. The relationship between pore structure and shale gas sorption capacity is discussed. The results indicate that (1) The Lower Silurian shale have high TOC content in the range of 0.92-4.96%, high quartz content in the range of 30.6-69.5%, and high clays content in the range of 24.1-51.2%. The total specific surface area varies from 6.60 m^2/g to 24.35 m^2/g. Both the total specific surface area and quartz content are positively associated with the TOC content. (2) Shale samples with higher TOC content have more micropores, which results in more complex nanopore structure. Micropore volumes/surface areas and non-micropore surface areas all increase with increasing TOC content. (3) A combination of N_2 and CO_2 adsorption provides the most suitable detection range (~0.3-60 nm) and has high reliability and accuracy for nanopore structure characterization. (4) The TOC content is the key factor to control gas sorption capacity of the Lower Silurian shale in the Upper Yangtze Platform. Our studies are of great significance for the assessment and exploitation of natural gas in the shale reservoirs.

A combination of N_2 and CO_2 adsorption to characterize nanopore structure of organic-rich Lower Silurian shale in the Upper Yangtze Platform, South China: Implications for shale gas sorption capacity

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Geological setting

The Upper Yangtze Platform is located in the western part of the Yangtze Platform, South China (Fig. 1). The Lower Silurian shale, widely developed in the Upper Yangtze Platform, has recently been selected as the main target for shale gas exploration and development. Black shales are present in the Lower Silurian Longmaxi formation in the Upper Yangtze Platform with current burial depth of 1000-5000 m. The thickness generally ranges from 50 to 100 m with an EqRo of 2.5-3.0%, generating mainly dry gas and secondary gas.

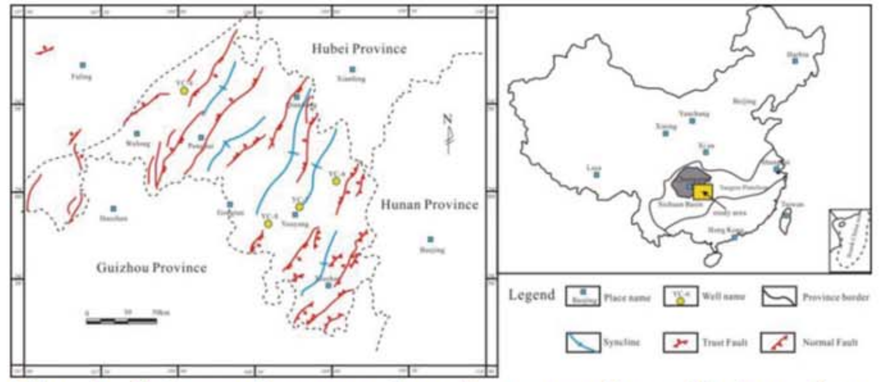

Fig. 1. Schematic map showing sample wells location.

Samples and methods

14 shale samples from the Lower Silurian Longmaxi shale were collected from four wells in the Upper Yangtze Platform, South China. The sampling well locations are shown in Fig. 1. A combination of gas adsorption, original and modified BET equation, DR equation, t-plot method, BJH and DFT methods were used to investigate the nanopore structure of organic-rich Lower Silurian shale.

Results and discussion

TOC show a strong positive correlation with quartz content (Fig. 2A), which suggests that quartz is partially biogenic in origin. A negative correlation between TOC and total clays content is observed (Fig. 2B) and attributed this to decreasing total clays content with a increase of quartz content.

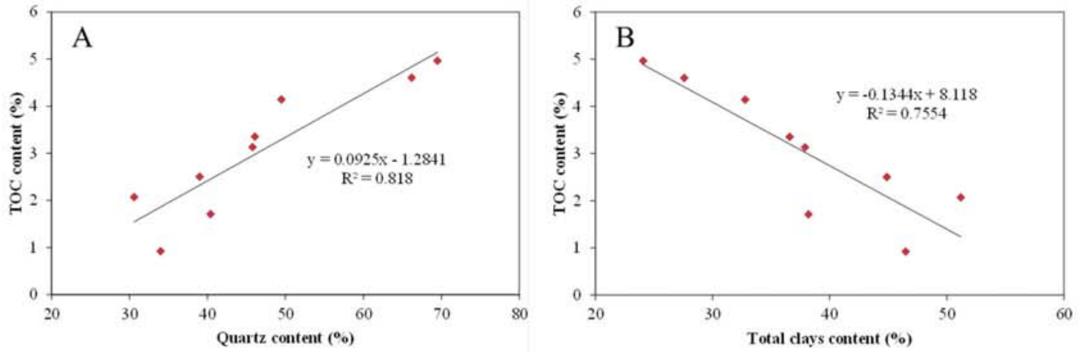

Fig. 2. Plots showing the relationships of TOC content with quartz content (A) and total clays content (B) of the shale samples.

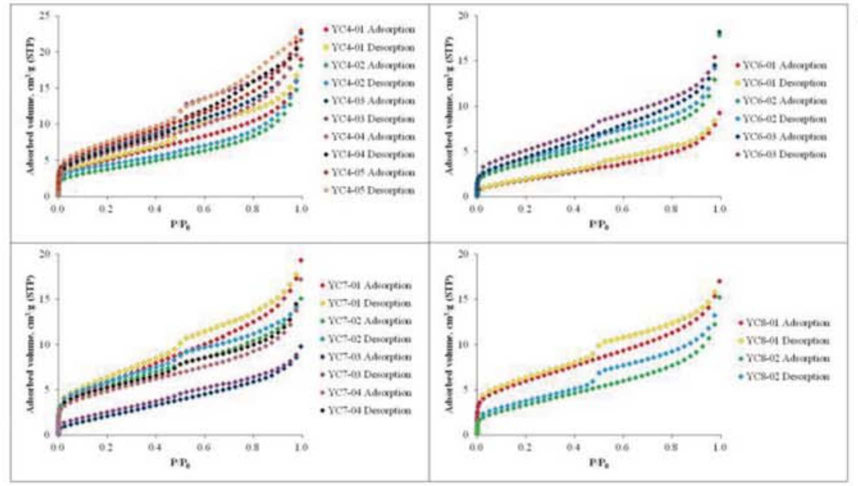

Fig. 3. N_2 adsorption and desorption isotherms of the shale samples.

The adsorption and desorption isotherms of N_2 are shown in Fig. 3, and similar to type II adsorption isotherm recommended by IUPAC, these isotherms showed hysteresis loops between type H3 and H4. The existence of hysteresis loops indicated that there are mesopores and macropores. 14 samples in the low pressure section ($P/P_0<0.05$) showed relatively large adsorption amounts, indicated by the dramatic surge of the adsorption isotherms, demonstrating the existence of a large amount of micropores.

A combination of N_2 and CO_2 adsorption to characterize nanopore structure of organic-rich Lower Silurian shale in the Upper Yangtze Platform, South China: Implications for shale gas sorption capacity

Results and discussion

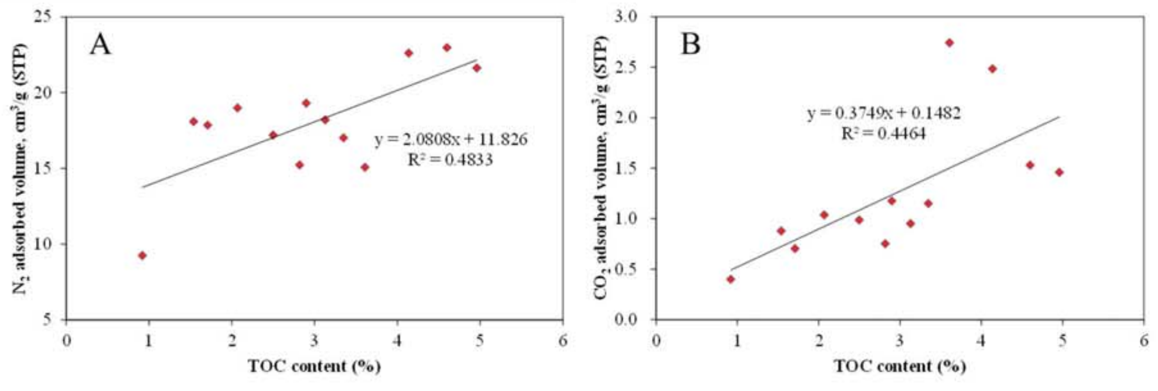

Fig. 4. Plots showing the relationships of TOC content with the maximum N_2 adsorption amount at $P/P_0=0.995$ (A) and the maximum CO_2 adsorption amount at $P/P_0=0.03$ (B) of the shale samples.

The maximum N_2 adsorption amount is significantly positive correlated with the TOC value (Fig. 4A), indicating that organic matters in the shale are important spaces for nanopores development.

The adsorption isotherms of CO_2 are shown in Fig. 5 and similar to type I adsorption isotherm, the existence of micropores is indicated.

There is a significantly positive correlation between the maximum adsorption amount and the TOC value (Fig. 4B), indicating that organic matters in the shales are important spaces for micropores development.

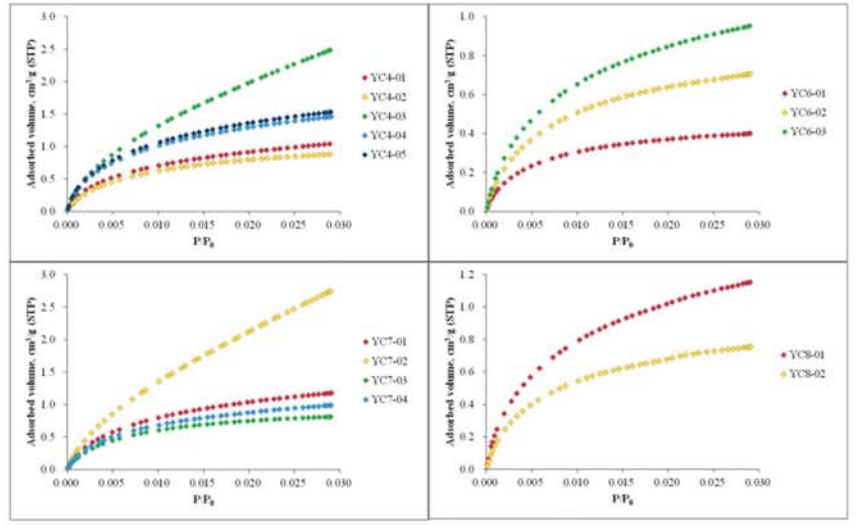

Fig. 5. CO_2 adsorption isotherms of the shale samples.

Specific surface area analysis

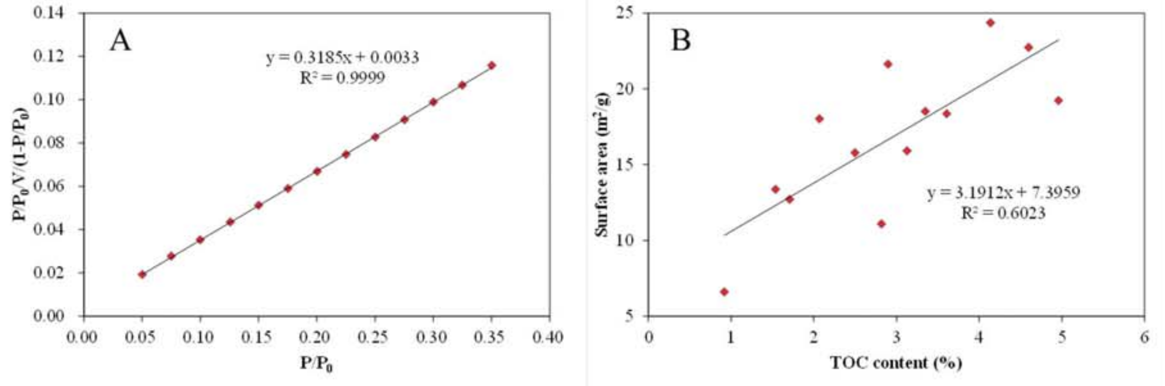

Fig. 6. Original BET equation (A) and the relationship between TOC content and total surface area calculated by original BET equation (B).

Fig. 6A shows an example of the result from the original BET equation. Fig. 6B shows the total surface area (S_{BET}) for 14 shale samples ranges from 7.56 m^2/g to 25.86 m^2/g, which has a strong positive correlation with the TOC content.

The non-micropore surface area (S_{ext}) determined by the modified BET equation ranging from 6.66 m^2/g to 17.41 m^2/g, S_{ext} determined by the t-plot method with the Harkins-Jura model are in the range of 5.84-14.70 m^2/g. Meanwhile, the micropore surface areas (S_{mic}) determined by the modified BET equation and t-plot method with the Harkins-Jura model are in the range of 0.15-8.45 m^2/g and 1.22-12.52 m^2/g, respectively.

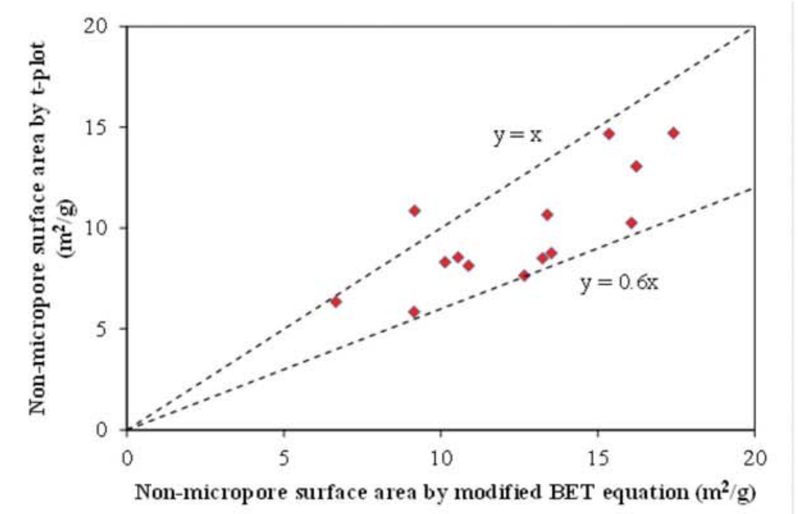

Fig. 7 shows a comparison between the S_{ext} values calculated by the modified BET equation and S_{ext} determined by the t-plot method. The result reveals that they are similar and linearly related. This implies that when a proper thickness model is used in t-plots, the BET equation and t-plot method are essentially identical.

Fig. 7. Plots showing the relationship of non-micropore surface areas calculated by the modified BET equation and t-plot method.

The micropore surface areas (S_{mic}) show positive correlations with the TOC content (Fig. 8A). As shown in Fig. 8B, the S_{ext} also show positive correlations with the TOC content. This suggests that organic matters provide not only micropores, but also mesopores and macropores in the Lower Silurian shale, which has also been reported in other shales.

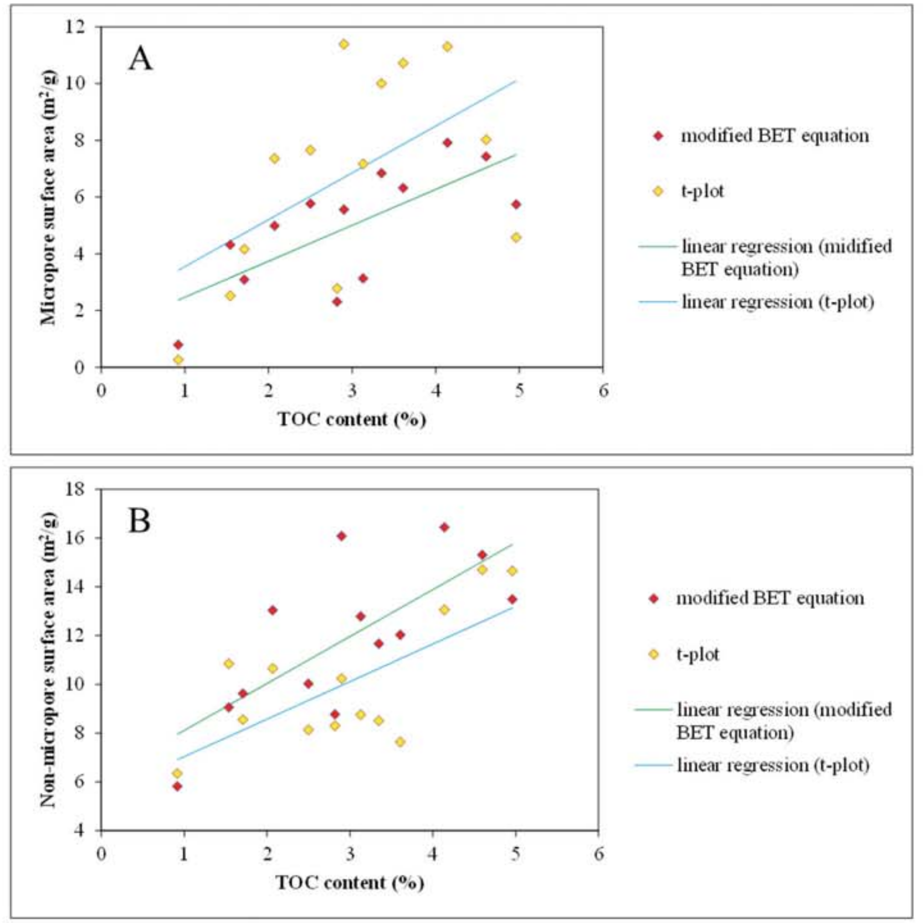

Fig. 8. Plots showing the relationships between TOC content and micropore surface areas (A) and non-micropore surface areas (B).

Micropore volume analysis

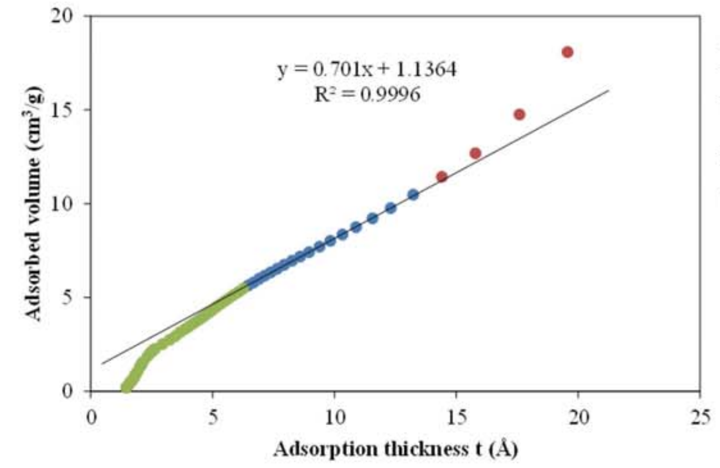

Fig. 9 shows an example of the micropore volume result from the t-plot method with the Harkins-Jura model.

Fig. 9. Plot showing the micropore volume determined by t-plot method with the Harkins-Jura model.

The N_2 and CO_2 micropore volumes (V_{mic}) obtained by the DR equation are in the range of 0.16-0.76 cm^3/100 g and 0.12-0.85 cm^3/100 g, respectively. The V_{mic} values ranges from 0.11 cm^3/100 g to 0.63 cm^3/100 g according to the modified BET equation, and 0.09-0.86 cm^3/100 g by the t-plot method with the Harkins-Jura model.

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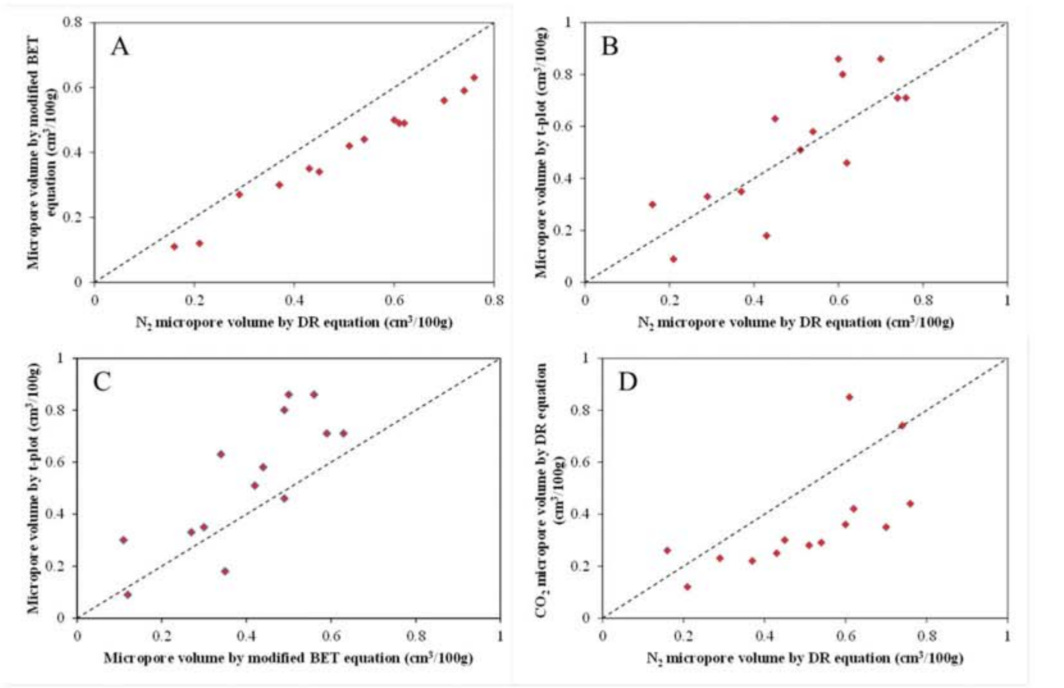

Fig. 10A-C shows the comparison of the micropore volumes calculated by the modified BET equation, DR equation (N_2) and t-plot method with the Harkins-Jura model and reveals that N_2 micropore volume determined by the DR equation predicts similar results as the modified BET equation. At the same time, the DR equation generally provide the larger value than the modified BET equation (Fig. 10A). The reason is that the DR equation is bestly applied to microporous materials and it could overestimate the micropore volume of a material containing mesopores and macropores. Fig. 10D shows that the micropore volumes calculated by the DR equation applied to N_2 adsorption are greater than those determined by the DR equation based on CO_2 adsorption.

Fig. 10. Plots showing the relationships of micropore volume calculated by the modified BET equation, DR equation and t-plot method.

The N_2 and CO_2 micropore volumes (V_{mic}) calculated with DR equation both show positive correlations with TOC content (Fig. 11A), and the micropore volumes calculated by modified BET equation and t-plot method also show positive correlations with TOC content (Fig. 11B), indicating that organic matters provide important spaces for micropores development.

Pore size distributions (PSDs)

The pore size distribution is commonly illustrated with a plot of dV/dD versus D (pore diameter) for N_2 and CO_2 adsorption. Pore size analysis from micropores to macropores to a size of ~60 nm can be carried with a combination of N_2 and CO_2 adsorption.

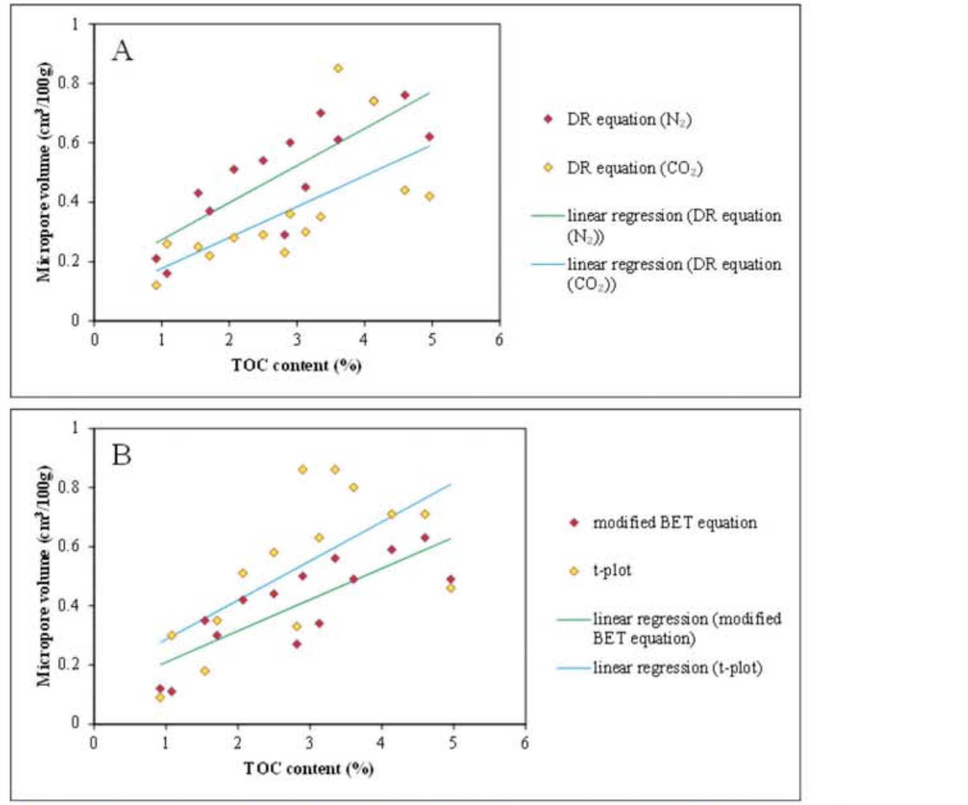

Fig. 11. Plots showing the relationships between TOC and micropore volumes calculated by modified BET, DR equation and t-plot method.

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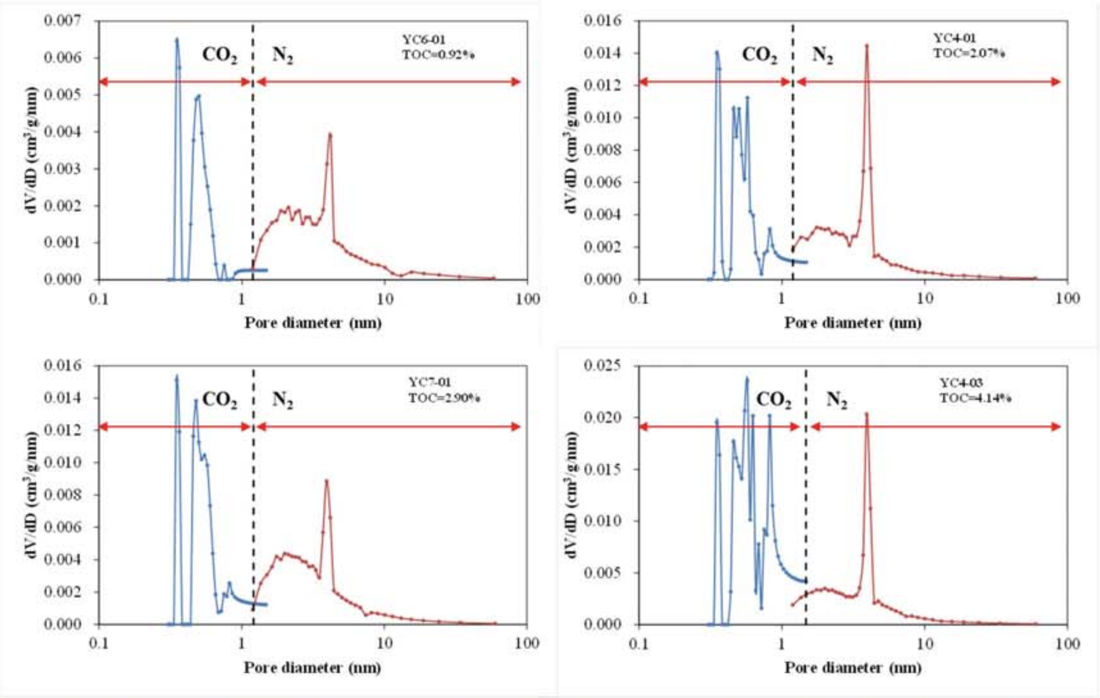

Fig. 12. Plot of dV/dD versus D for the pore size distribution of four typical shale samples, obtained by the BJH and DFT methods based on N_2 and CO_2 adsorption isotherms, respectively.

Fig. 12 shows the pore size distributions of four typical shale samples based on the N_2 and CO_2 adsorption data using the BJH and DFT methods, respectively. The N_2 and CO_2 curves begin and end, respectively, at approximately 1.2 nm in a near seamless transition in dV/dD vs. pore diameter plots (Fig. 12).

From Fig. 12, it can be concluded that shales with higher TOC content show better developed micropores. This indicates that, in general, smaller pores dominate the samples with elevated TOC content. Our study also shows that the samples with low TOC content (<2%) have total specific surface area <14 m^2/g, indicating lower gas sorption capacity. Samples with TOC content between 2% and 4% have total specific surface area of 11-22 m^2/g, and the gas sorption capacity increases with increasing TOC content. Samples with high TOC content (>4%) have total specific surface area of 19-25 m^2/g, which implies higher gas sorption capacity.

Shale gas sorption capacity

Adsorbed gas is located mainly within micropores and at the surface of mesopores and macropores, while free gas is mainly stored in macropores and larger mesopores (Fig. 13).

As discussed previously, it is clear that the organic matter mainly controls the nanopore structure of the Lower Silurian shale, thus influencing gas sorption capacity.

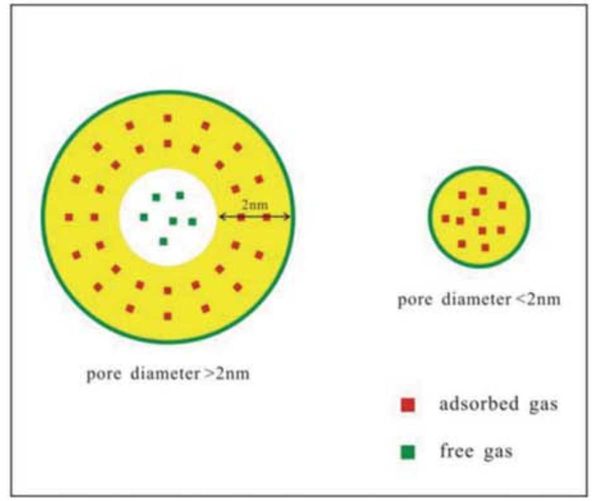

Fig. 13. Occurrence state of shale gas in pores of different size.

Conclusions

(1) Both the total specific surface area and quartz content are positively associated with TOC content.

(2) Shale samples with higher TOC content have more micropores, which results in more complex nanopore structure. Micropore volumes/surface areas and non-micropore surface areas all increase with increasing TOC content.

(3) A combination of N_2 and CO_2 adsorption provides the most suitable detection range (~0.3-60 nm) and has high reliability and accuracy for nanopore structure characterization.

(4) The TOC content is the key factor to control gas sorption capacity of the Lower Silurian shale in the Upper Yangtze Platform.

Thank you
for comments and suggestions!

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