Methane Adsorption Measurements and Modeling for Organic-rich Marine Shale Samples

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ABSTRACT

Understanding methane sorption behavior in the gas-shale system is of great importance for evaluating reservoir production potential and reducing the exploration risk. The methane sorption capacity of total 12 organic-rich marine shale samples from southwest China was measured by volumetric method. The absolute sorption results were then modeled using Langmuir, BET, Dubinin–Radushkevich (D-R) and Dubinin-Astakhov (D-A) models. The accuracy of each model for quantifying shale gas sorption was analyzed and compared by using a residual error analysis technique. We also analyzed the impacts of the organic and inorganic constituents on the methane sorption capacity. The results indicate that the maximum methane absolute sorption of the collected marine shale samples is between 0.50 cm³/g and 3.41 cm³/g. The absolute sorption capacity of shale samples positively correlates with the total organic carbon (TOC) content. The TOC-normalized methane sorption capacity shows a positive correlation with the total clay mineral content and exhibits a

significant increase with increasing illite-montmorillonite mixed layers content. For gas sorption modeling, the D-A model superior to the Langmuir, D-R and BET models, because of the micro-heterogeneity. The most commonly used Langmuir model gives a reasonable fit for most of the samples, and D-R results are comparable to Langmuir results. The BET model performs poorly and thus it was not recommended for methane-shale sorption modeling exercise. The D-A model is recommended for describing methane adsorption on organic-rich shale samples.

Key words: Organic-rich shale; gas sorption capacity; sorption model; error analysis

1. Introduction

Shale gas is the fastest growing natural gas resource and has enormous resource potential in the United States and Canada [1-5]. Following the United States shale gas revolution and the continuous improvement of drilling and hydraulic fracturing techniques, shale gas has attracted interest from many other countries, such as China, Canada, India and Australia [6-7]. Gas is stored in shale source rocks in two principal ways: (1) as free gas within pores and natural fractures, (2) as adsorbed molecules on organic matter surfaces and on inorganic minerals [8]. With different petrophysical properties, the adsorbed gas varies from 20% to 85% of total gas capacity in shales [9]. In order to evaluate the economic potential of gas shale reservoirs as well as to reduce the subsequent exploration risk [3-4, 10-13], it is essential to obtain the reliable adsorption capacity in methane-shale system. The sorption isotherm plays an

important role in the reservoir evaluation and is routinely determined by direct experimental measurements. However, only limited investigations were reported for the methane sorption isotherms of shale in the literature. The gained knowledge from methane-coal sorption system lays the foundation for the sorption behavior characterization for methane-shale system [14-15]. In addition to the direct laboratory measurement, various adsorption models have been tested to define sorption capacity for coals. These models include Langmuir, extended Langmuir, Brunauer-Emmett-Teller (BET), Dubinin-Polanyi theory, Freundlich model and others [14-17]. Among these models, the Langmuir isotherm model is the most commonly used because of its simplicity.

Similar to coal, gas sorption isotherms in shale are conventionally modeled using Langmuir model [18-20]. However, the reported experimental data in the literature were not always well modeled by Langmuir model for methane-shale system [21-22]. Unfortunately, no effort has been made to test the validity of different sorption models for methane-shale adsorption behavior. Therefore, it is essential to evaluate the performance of different sorption models in methane-shale system.

Three marine shale units of Early Cambrian, Early Lower Silurian and Late Permian age are present within Upper Yangtze area (UPA) [23]. Among these three, the Cambrian and Silurian shale units are currently considered as the major development targets because of their great thickness, high TOC content, widespread occurrence, as well as favorable mineral composition [7, 23-24]. Nevertheless, the methane sorption capacity and adsorption behavior of these two shale intervals is still

poorly understood. In this study, both experimental investigation and modeling work were analyzed based on organic-rich marine shale samples. The goals of this study were: (1) to assess the maximum methane sorption capacity of marine shale samples from UPA of southwest China, (2) to test the validity of different sorption models for methane-shale system, and (3) to discuss the effect of organic matter and mineral constituent on shale sorption capacity. This work may have broad applications for reservoir assessment and evaluation, including gas-in-place (GIP) estimation[13], gas transport dynamics during depletion[25], reservoir geomechanical responses[26], carbon sequestration [27]and others.

2. Experimental methods

2.1 Sample collection and preparation.

Fresh shale blocks were collected from outcrops in the potential production regions located in UYA of southwest China (Fig. 1). The short-hole drillings were used to obtain the unweathered shale samples. In this study, 12 marine shale samples (7 samples from the Lower Silurian Longmaxi Formation and 5 samples from the Lower Cambrian Niutitang Formation) were prepared and investigated for gas sorption capacity estimation. Both formations were known to be organic-rich and the thickness of each formation is more than 80 meters as shown in Fig. 1 [28-29].

2.2 Petrophysical experiment

Before the sorption experiments, the total organic carbon (TOC) and mineral composition were characterized for all the collected samples. TOC was measured by LECO CS-230 carbon and sulfur analyzer. X-ray diffraction (XRD) instrument

(RIGAKU D/Max-3B diffractometer) was employed to characterize the mineral composition of each sample. During the XRD measurements, the intensity data were collected in the 2θ range of $5\text{--}80^\circ$ at steps of 0.02° (Cu $K\alpha$). Si was used as the internal standard. Both analyses were performed at the Experimental Research Center of East China Branch, SINOPEC. The shale petrographical properties were listed in Tables 1 and 2, including the total organic carbon content TOC and mineral composition for all 12 samples.

2.3 High-pressure sorption experiment

High pressure methane (up to $\sim 8.5\text{MPa}$) sorption isotherms at 30°C were measured using a volumetric apparatus (IS-300 isothermal adsorption/desorption analyzer) manufactured by Terra Tek, USA. The pulverized samples (<60 mesh) were prepared and used for the sorption capacity measurement. For each test, 100-150 g powder sample was used. In order to check the repeatability of the adsorption data, two of the shale samples were selected to carry out the repeatability tests and each sample was measured twice. The error for repeated measurements of sorption capacity is 1.2-2.5%.

2.4 Sorption isotherm models

2.4.1 Absolute adsorption estimation

The sorbed gas volume, as directly measured in the laboratory, is known as excess adsorption (or Gibbs adsorption). In fact, a certain volume in the pore space occupied by the adsorbed phase is no longer available to free gas, the excess adsorption capacity, however, ignores this adsorbed phase volume. Thus, the excess adsorption

will underestimate the total sorption capacity. Therefore, the absolute adsorption capacity was estimated by considering the adsorbed phase density. Mathematically, the absolute adsorption capacity can be calculated as follows:

$$V_{abs} = \frac{V_{Gibbs}}{\left(1 - \frac{\rho_{gas}}{\rho_{ads}}\right)} \quad (1)$$

where, V_{abs} and V_{Gibbs} are the absolute and Gibbs adsorption capacity; ρ_{gas} is the gas bulk density calculated by equation of state (EOS); ρ_{ads} is the gas adsorbed gas density and it was assumed to be liquid density of 0.421 g/ml [14].

2.4.2 Adsorption model

Langmuir model. The Langmuir model is based on the assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species [30]. The isotherm equation is commonly given as:

$$V = \frac{V_L b P}{1 + b P} \quad (2)$$

where, V is the volume of gas adsorbed, P is the equilibrium gas pressure, b is Langmuir constant, V_L is the Langmuir volume.

When the sorbed volume is half of the Langmuir volume (V_L), the pressure value is referred to as the Langmuir pressure, P_L . The above equation can be rewritten in terms of V_L and P_L , equation (1) can be transformed as follows:

$$\frac{V}{V_L} = \frac{P}{P + P_L} \quad (3)$$

BET model. The BET model extends Langmuir-type adsorption to multilayer

adsorption [31]. The common form of the BET isotherm equation is expressed as:

$$\frac{1}{V(P_0/P-1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0} \quad (4)$$

where, V_m is the monolayer volume, C is a constant, P_0 is the saturation vapor pressure. The larger the value of C , the earlier that the multilayer formation occurs.

To obtain the values of these constants, $1/(P_0/P-1)$ should be plotted versus relative pressure(P_0/P) and the plot should be shown as a straight line. Then, the V_m and the constant C can be calculated from the slope and intercept of the plot. With the assumption of multilayer adsorption, BET model has a broader application than the Langmuir model.

Dubinin-Astakhov (D-A) and Dubinin–Radushkevich (D-R) models. The D-A equation, was originally proposed by Polyanyi on the basis of adsorption potential theory. Dubinin applied this theory to describe adsorption on microporous solids and proposed a new theory, which is based on the theory of pore volume filling of micropore(TVFM) [32]. Two equations were developed by Dubinin and his coworkers, known as the D-A equation, it is expressed as

$$V = V_0 \exp \left\{ -D \left[\ln \left(\frac{P_0}{P} \right) \right]^n \right\} \quad (5)$$

Another one is D-R equation, which is expressed as:

$$V = V_0 \exp \left\{ -D \left[\ln \left(\frac{P_0}{P} \right) \right]^2 \right\} \quad (6)$$

where, V is the amount adsorbed; V_0 is the volume of micropores; n is a small number varying between 1 and 4, and is related to the structural heterogeneity; D is a constant

for a particular adsorbent-adsorbate system and is equal to $(RT/\beta E)^n$, where E is the characteristic energy and β is the adsorbate affinity coefficient. P_0 is the saturation vapor pressure of the adsorbate at temperature T, and P is the equilibrium vapor pressure. Dubinin and Radushkevich suggested that the value of $n = 2$ may be appropriate for some cases, and the equation (5) can be modified as equation (6). The above two equations (D-A and D-R equations) are also known as the Dubinin-Polanyi (D-P) equations.

Mathematically, equation (5) can be re-arranged and written as:

$$\ln V = \ln V_0 - D \left(\ln \frac{P_0}{P} \right)^n \quad (7)$$

where, n is equal to 2 for the D-R equation, and is special case for the D-A equation. A plot of $\ln V$ versus $(\ln P_0/P)$ was obtained. The V_0 was then determined by taking the exponential of the Y-intercept, while the constant D can be estimated from the slope.

3. Results and discussion

3.1 Organic matter richness and mineralogy

Total Organic Carbon (TOC) is one of the most important factors for the shale reservoir evaluation since it strongly correlates with the gas sorption capacity. TOC contents of 12 marine samples ranged from 1.46% to 10.02% (Table 1). The mean TOC content is 3.91% (range 1.46%-7.68%) for Lower Silurian Longmaxi formation, and 5.81% (range 2.17%-10.02%) for Lower Cambrian Niutitang formation. Previous studies have shown that the Cambrian and Silurian shales from this study area are over-matured with type I to II organic matter [33-34].

The mineral compositions characterized by XRD were shown in Table 2. The

results indicate that marine organic-rich shales have an extremely complex mineral composition and that quartz and clay are the primary mineral constituents, with a mean content of 48.2% (35.2-62.1%) and 34.0% (20.1-48.7%), respectively. It was noted that the samples from Lower Silurian Longmaxi formation have high clay content and low quartz content compared to the Lower Cambrian Niutitang samples. The other mineral constituents are feldspar, carbonate, pyrite, dolomite and traces of unidentified amorphous substances. In all shale samples, the clay minerals are primarily illite with a mean content of 22.4% (14.1-30.1%) and illite-montmorillonite mixed layers, ranging from 2.4% to 12.4%, with a mean value of 8.3%.

3.2 Methane sorption isotherms of the marine shales

A series of CH₄ sorption isotherms for all studied shale samples were measured up to the final pressure of~ 8.5 MPa at 30°C. The difference between the excess and absolute adsorption capacity is presented in Table 3. It is obvious that the absolute adsorption capacity is higher than the excess adsorption capacity and the difference is not trivial. For examples, the maximum absolute adsorption capacity is 17% larger than the maximum excess adsorption capacity for sample LQ-1. The absolute adsorption capacities of all 12 samples were plotted in Fig. 2. For all shale samples, the methane sorption capacity increased with pressure increase. At low to moderate pressure (0 to 4 MPa), the sorption capacity increased rapidly. When methane pressure is greater than 4MPa, the rate of sorption increase slows down indicated by the decrease of the slope of isotherm at high pressures as shown in Fig. 2. In addition, within the measured pressure range, the maximum absolute methane sorption capacity

are ranging from $0.84 \text{ cm}^3/\text{g}$ to $3.41 \text{ cm}^3/\text{g}$ for the Lower Silurian formation samples and from $0.50 \text{ cm}^3/\text{g}$ to $2.28 \text{ cm}^3/\text{g}$ for the Lower Cambrian formation samples. For each formation, the methane sorption capacities varied greatly among samples. Generally, the sorption capacities of the Lower Silurian shale samples were higher than the Lower Cambrian ones as shown in Table 2 and Fig. 2. This suggests the Lower Silurian formation might possess higher shale gas potential than the Lower Cambrian formation.

3.3 Absolute shale adsorption modeling

Langmuir model. Due to its simplicity and providing reasonable fit results, the Langmuir model is widely used to model sorption isotherms. From statistical analyses of the P/V versus P plots, the fitted Langmuir parameters (Langmuir volume (V_L) and pressure (P_L)) for all 12 samples are listed in Table 4. The representative Langmuir modeled isotherms are shown in Fig. 3. It can be seen that the Langmuir modeled results agree reasonably well with the experimental results. Langmuir pressure is a measure of sorption isotherm shape. The isotherms of LQ-13, CX-18, HW-5 and HW-9 with relatively small Langmuir pressures have a steep slope at low pressure and then flattens out at relatively low pressure. In contrast, the isotherms of GS-6, CX-8 and CX-10 with high Langmuir pressure values reach the maximum plateau at much high pressure. It was also notable that the adsorption capacities of Longmaxi shale sample LQ-13 and Niutitang shale sample HW-9 have downward tails at high pressures as shown in Fig. 3. As a result, the Langmuir results did not agree well with the measured data for these samples. Similar results of methane adsorption isotherms

for many different shale samples have been reported by other authors [21,36]. This might be due to the inconclusive data on the adsorbed phase CH₄ density or experimental error [37].

BET Isotherm model. Based on the statistical analysis of the $1/V(P_0/P-1)$ versus P/P_0 plots, the BET parameters V_m and C for all 12 samples were computed and listed in Table 4. With the regressed BET constants, the modeled results versus the experimental data were plotted in Fig. 4. Compared to Langmuir model, the BET model has poor performance with one R^2 of 0.85. In addition, the BET plots for samples CX-18 and HW-5 of Lower Cambrian Niutitang Formation showed a negative Y -intercept. Therefore, these two samples sorption isotherms could not be modeled by using the BET approach. The BET model does not realistically describe the adsorption of CH₄ on shale, indicating that the assumption of this model is not suitable for the microporous organic-rich shale samples.

D-R and D-A models. The D-R modeled results were shown in Fig. 5 and the D-A modeled results were plotted in Fig. 6. The D-R model constants (V_0 and D) and D-A model constants (V_0 , D , and n) were regressed for all samples and the data were listed in Table 4, too. Among all samples, the LQ-1 has the maximum micropore volume filling capacity of 4.00 ml/g calculated by the D-A model. Overall, the D-A modeled results agree better with experimental results than the D-R model does since all R^2 values for D-A model are greater than the R^2 values of D-R model for each sample. For example, the D-A model results fit well with the measured adsorption data for LQ-13 and HW-9. However, the D-R model performed relatedly poor with small R^2

values. The D-A plot R^2 values for samples LQ-13(0.9561) and HW-9(0.9725) are larger than D-R plot R^2 values for samples LQ-13(0.8149) and HW-9(0.8592). The reason why D-A model is superior lies in the value of the structure heterogeneity parameter, n , which related to the pore size distribution in the shale structure. This brings the micro-pore structure information into adsorption prediction and modeling.

3.4 Comparison of different isotherm models: error analysis.

All experimental results were fitted by different analytical models as previously described. Fig. 7 depicts the isotherms using Langmuir, BET, D-R and D-A models, for HW-9. For this particular sample, D-A model has shown best agreement with measured data. In order to conduct a quantitative comparison and to evaluate the accuracy of fitting for each model, residual analyses were performed for all models. Residuals, were calculated as:

$$\delta = \frac{(V_{exp} - V_{cal})}{V_{exp}} \times 100 \quad (8)$$

where, δ is the residual; and V_{exp} and V_{cal} are the experimental and modeled results, respectively. The average relative error (ARE), as defined below:

$$ARE = \frac{1}{N} \sum_{i=1}^N abs(\delta_i) \quad (9)$$

where, N is the number of experimental data points and $abs(\delta_i)$ is the absolute residues for each experimental point. This ARE analysis serves as a criterion for sorption model selection and it quantitatively defines the accuracy of each model for a given shale sample.

The model with the least ARE is considered to be the best model to describe

methane adsorption behavior. Table 5 listed the AREs for each measured sample and Fig. 8 is the plot of ARE for each sample. From Fig. 8, we can conclude that the D-A model gave the lowest ARE for all studied shale samples, which suggests D-A is the best model for all samples. The mean ARE for all samples is 2.59% for the D-A model. If we exclude D-A model, the Langmuir model gave the lowest ARE for four samples including LQ-6, LQ-9, GS-6, CX-10 and the D-R model performs better for the remaining eight samples. By comparing the Langmuir model and the D-R model, we can conclude that these two models have similar values of ARE, with means of 4.37% and 3.96% as indicated in Table 5.

It is obvious that the BET model has the highest ARE for each sample except for sample CX-8 (Fig. 8). These results indicate that the BET model is inferior for describing methane adsorption data on the collected shale samples. To summarize, it can be concluded that the D-A model is the best model for defining methane adsorption behavior for the selected shale samples. And the modeled results are comparable between D-R model and Langmuir model.

3.5 Effect of organic and inorganic constituents on methane sorption capacity

The literature have shown that the TOC content have been considered as one of the primary determining factors for methane sorption capacity, while organic matter type and maturity are less important [8, 10-11]. When we plot gas sorption capacity versus TOC for tested shale samples, it was found that gas sorption capacity somewhat positively correlates with TOC content as shown in Fig. 9. This positive relationship between sorption capacity and TOC has been observed on different shale samples by

many other scholars [38-41]. However, based on Tables 1 and 2 and Fig. 9, it was seen that the TOC is not the only controlling factor for the sorption capacity. For example, the sample GS-6 with 5.23% of TOC has methane sorption capacity of 1.80cm³/g, while the sample GS-7 with a lower TOC content of 4.82% has a higher sorption capacity of 2.18 cm³/g. This might be attributed to other factors such pore size distribution, maturity of the organic matter, high surface area of the mineral framework, as well as weak hydrolysis in expandable illite-montmorillonite mixed-layer clay [38].

The mineral constituents, in particular the clay minerals, have also been widely considered as a potentially influencing factor on shale sorption capacity [11, 42-43]. In this study, we plotted sorption capacity versus total clay mineral content as shown in Fig. 10. The data seem to be randomly scattered and no definite correlations. However, this random scattering might be resulted from the cross-interaction effect between TOC and mineral composition. In order to remove the effect of TOC on the sorption capacity, we here proposed to normalize the sorption capacity to unit TOC basis by (sorption capacity)/(TOC content). Once the data are normalized to the unit weight of TOC, the influence of mineral composition on sorption capacity was evaluated. Normalized data were reported on a per unit TOC basis with the assumption of constant kerogen density. From Fig. 11a, we can observe that the sorption capacity generally increases with increase of total clay mineral although the correlation was not perfect. Additionally, in order to investigate the influence of different types of clay minerals on sorption capacity, TOC-normalized sorption

capacities were also plotted against the different clay mineral contents including illite and illite-montmorillonite contents. The results indicate that positive trend exists between TOC-normalized sorption capacity and illite content as shown in Fig. 11b. Interestingly, it shows a bilinear-model relationship between TOC normalized sorption capacity and illite-montmorillonite mixed layers content as shown in Fig. 11c. When the illite-montmorillonite content is less than 9%, the sorption capacity slowly increase with increase of illite-montmorillonite mixed layers content. However, the sorption capacity increase significantly with increase of illite-montmorillonite mixed layers content when the mixed layer content is greater than 9%. The reason why this bilinear model exhibits between sorption capacity and illite-montmorillonite mixed layers content is not clear and future work will be required for separate mineral sorption characterization.

3.6 Discussion of application of D-A and Langmuir models

Based on the aforementioned results, the BET model performs worst among all the models. The D-R and D-A isotherms fitted the data well in most cases. Since the D-R equation (equation 5) is a specific case of the D-A equation for $n=2$, the application of D-R equation was not examined separately. The Langmuir isotherm model fitted the data well for some samples, but in other samples the modeled results do not agree well with measured data, for example, LQ-13 and HW-9. As a matter of fact, the Langmuir model is simplest and most commonly used for describing the adsorption behavior of shales. Based on our analysis, it is adequate for most practical reservoir assessment since it gave quite similar results with the best D-A model. However, D-A

model is superior to Langmuir model at most of the cases. Further analysis was performed to analyze how the total TOC content influences the applicability of D-A and Langmuir models. We plotted ARE versus TOC as shown in Fig.12. Generally, the ARE decrease with an increase of TOC for both models. The results indicate that the accuracy of two models increase with TOC content. Interestingly, for the shale samples with TOC less than 5%, the D-A model gave much smaller error for the sorption capacity prediction than the Langmuir model did. When TOC is more than 5%, both D-A and Langmuir models show a satisfactory fit. Considering the practical advantages and its simplicity, Langmuir model is recommended for describing methane adsorption behavior when TOC is greater than 5%.

In addition, the correlation between ARE of two models and clay mineral content show a similar trend. Except for sample LQ-13, the Langmuir model fitted the sorption data well for the samples with the clay mineral content more than 30%. Sample LQ-13 has a clay mineral content of up to 48.7%, but its TOC value is only 1.46%, indicating that the TOC value may have a major influence on ARE.

4. Conclusion

In this study, the excess adsorption capacities were directly measured in the lab and the absolute adsorption capacities were estimated for all 12 marine shale samples. In order to analytically define the sorption behavior of shale, four well-established models including Langmuir, BET, D-R and D-A models were tested against our experimental data. Based on the results, the following conclusions have been made:

- Both Lower Cambrian and Lower Silurian shales with high TOC contents have an

extremely complex mineral composition and that quartz and clay are the primary mineral constituents. The absolute methane sorption capacity of the Lower Cambrian shale is between 0.50 cm³/g to 2.28 cm³/g and that of the Lower Silurian shale is between 0.84 cm³/g to 3.41 cm³/g.

- Among all four adsorption isotherm models, the D-A equation is the most accurate model to define the sorption behavior of gas-shale system. The BET sorption model performed worst compared to other three tested models, namely, Langmuir, D-A and D-R models.
- The Langmuir model is capable of accurately fitting the methane sorption data when the TOC of shale samples is greater than 5%.
- Generally, the sorption capacity positively correlates with TOC content, but TOC is not the only controlling factor for shale sorption capacity. The TOC-normalized sorption capacity shows a positive correlation with total clay mineral content and exhibits a significant increase with increasing illite-montmorillonite mixed layers content greater than 9%.

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Reference:

- [1] Montgomery S L, Jarvie D M, Bowker K A, et al. Mississippian Barnett Shale, Fort Worth basin, north-central Texas: Gas-shale play with multi-trillion cubic foot potential. *AAPG Bull* 2005; 89(2): 155-175.
- [2] Jarvie D M, Hill R J, Ruble T E, et al. Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. *AAPG Bull* 2007; 91(4): 475-499.
- [3] Chalmers G R L, Bustin R M. Lower Cretaceous gas shales in northeastern British Columbia, Part II: evaluation of regional potential gas resources. *BullCan PetrolGeol* 2008b; 56(1): 22-61.
- [4] Ross D J K, Bustin R M. Characterizing the shale gas resource potential of Devonian-Mississippian strata in the Western Canada sedimentary basin: Application of an integrated formation evaluation. *AAPG Bull* 2008; 92(1): 87-125.
- [5] Loucks R G, Reed R M, Ruppel S C, et al. Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale. *J Sediment Res* 2009; 79(12): 848-861.
- [6] Gasparik M, Ghanizadeh A, Bertier P, et al. High-pressure methane sorption isotherms of black shales from the Netherlands. *Energy Fuels* 2012; 26(8): 4995-5004.
- [7] Tian H, Pan L, Xiao X, et al. A preliminary study on the pore characterization of Lower Silurian black shales in the Chuandong Thrust Fold Belt, southwestern China using low pressure N₂ adsorption and FE-SEM methods. *Mar Petrol Geol* 2013; 48: 8-19.
- [8] Chalmers G R L, Bustin R M. The organic matter distribution and methane capacity of the Lower Cretaceous strata of Northeastern British Columbia, Canada. *IntJCoalGeol* 2007; 70(1): 223-239.
- [9] Curtis, JB. Fractured shale-gas systems. *AAPG Bull* 2002; 86(11), 1921-1938.
- [10] Chalmers GRL, Bustin, RM. Lower cretaceous gas shales in northeasternBritishColumbia, part I: geological controls on methane sorption capacity.*BullCan Petrol Geol* 2008a; 56, 1-21.
- [11] Ross D J K, Bustin R M. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Mar PetrolGeol*2009; 26(6): 916-927.
- [12] Zhang T, Ellis GS, Ruppel SC, et al. Effect of organic-matter type and thermal maturity on methane adsorption in shale-gas systems. *OrgGeochem*2012; 47, 120-131.
- [13] Hao F, Zou H, Lu Y. Mechanisms of shale gas storage: Implications for shale gas exploration in China. *AAPG Bull* 2013; 97(8): 1325-1346.
- [14] Harpalani S, Prusty B K, Dutta P. Methane/CO₂ sorption modeling for coalbed methane production and CO₂ sequestration. *Energy Fuels* 2006; 20(4): 1591-1599.
- [15] Dutta P, Harpalani S, Prusty B. Modeling of CO₂ sorption on coal. *Fuel* 2008; 87(10): 2023-2036.
- [16] De Silva P N K, Ranjith P G, Choi S K. A study of methodologies for CO₂ storage capacity

435 estimation of coal. *Fuel* 2012; 91(1): 1-15.

436 [17] Sakurovs R, Day S, Weir S, et al. Application of a modified Dubinin-Radushkevich equation to
 437 adsorption of gases by coals under supercritical conditions. *Energy Fuels* 2007; 21(2):
 438 992-997.

439 [18] Lu XC, Li FC, Watson A T. Adsorption measurements in Devonian shales. *Fuel* 1995; 74(4):
 440 599-603.

441 [19] Weniger P, Kalkreuth W, Busch A, et al. High-pressure methane and carbon dioxide sorption on
 442 coal and shale samples from the Paraná Basin, Brazil. *Int J Coal Geol* 2010; 84(3): 190-205.

443 [20] Chareonsuppanimit, P, Mohammad SA, Robinson RL, et al. High-pressure adsorption of gases
 444 on shales: measurements and modeling. *IntJ Coal Geol* 2012; 95, 34–46.

445 [21] Ross DJK, Bustin RM. Impact of mass balance calculations on adsorption capacities in
 446 microporous shale gas reservoirs. *Fuel* 2007; 86(17): 2696-2706.

447 [22] Rani S, Prusty B K, Pal S K. Methane adsorption and pore characterization of Indian shale
 448 samples. *J Unconv Oil Gas Resour* 2015; 11: 1-10.

449 [23] Zou C, Dong D, Wang S, et al. Geological characteristics and resource potential of shale gas in
 450 China. *Pet ExplorDev* 2010; 37, 641-653.

451 [24] Huang J, Zou C, Li J, et al. Shale gas generation and potential of the Lower Cambrian
 452 Qiongzhusi Formation in the Southern Sichuan Basin, China. *Pet ExplorDev* 2012; 39, 75-81.

453 [25] Cui X, Bustin A M M, Bustin R M. Measurements of gas permeability and diffusivity of tight
 454 reservoir rocks: different approaches and their applications. *Geofluids* 2009; 9(3): 208-223.

455 [26] Liu S, Harpalani S. Evaluation of in situ stress changes with gas depletion of coalbed methane
 456 reservoirs. *J Geophys Res: Solid Earth* 2014; 119(8): 6263-6276.

457 [27] Tao Z, Clarens A. Estimating the carbon sequestration capacity of shale formations using
 458 methane production rates. *EnvironSciTechnol* 2013; 47(19): 11318-11325.

459 [28] Zou, C.; Dong, D.; Yang, H.; Wang, Y.; Huang, J.; Wang, S.; Fu, C. Conditions of shale gas
 460 accumulation and exploration practices in China. *Nat. Gas Ind.* 2011, 31 (12), 26–39.

461 [29] Liang, D.; Guo, T.; Chen, J.; Bian, L.; Zhao, Z. Some progresses on studies of hydrocarbon
 462 generation and accumulation in marine sedimentary region, Southern China (Part 1):
 463 Distribution of four suites of regional marine source rocks. *Mar Origin Pet Geol* 2008, 13 (3),
 464 1–16.

465 [30] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum.
 466 *J Am Chem Soc* 1918; 40(9): 1361-1403.

467 [31] Brunauer S, Emmett P H, Teller E. Adsorption of gases in multimolecular layers.
 468 *J Am Chem Soc* 1938; 60(2): 309-319.

469 [32] Dubinin M M. Adsorption in micropores. *J Colloid Interf Sci* 1967; 23(4): 487-499.

470 [33] Tan J, Weniger P, Krooss B, et al. Shale gas potential of the major marine shale formations in
 471 the Upper Yangtze Platform, South China, Part II: Methane sorption capacity. *Fuel* 2014; 129:
 472 204-218.

- [34] Wang S, Song Z, Cao T, et al. The methane sorption capacity of Paleozoic shales from the Sichuan Basin, China. *Mar Petrol Geol* 2013; 44: 112-119.
- [35] Wang Y, Zhu Y, Chen S, et al. Characteristics of the nanoscale pore structure in Northwestern Hunan shale gas reservoirs using field emission scanning electron microscopy, high-pressure mercury intrusion, and gas adsorption. *Energy Fuels* 2014; 28(2): 945-955.
- [36] Li T, Wu C. Research on the abnormal isothermal adsorption of shale. *Energy Fuels* 2015; 29(2): 634-640.
- [37] Sudibandriyo M, Pan Z, Fitzgerald J E, et al. Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa. *Langmuir* 2003; 19(13): 5323-5331.
- [38] Pashin J C, Kopaska-Merkel D C, Arnold A C, et al. Gigantic, gaseous mudwads in Cambrian shale: Conasauga Formation, southern Appalachians, USA. *Int J Coal Geol* 2012, 103: 70-91.
- [39] Gasparik M, Bertier P, Gensterblum Y, et al. Geological controls on the methane storage capacity in organic-rich shales. *IntJ Coal Geol* 2014; 123: 34-51.
- [40] Ji W, Song Y, Jiang Z, et al. Geological controls and estimation algorithms of lacustrine shale gas adsorption capacity: A case study of the Triassic strata in the southeastern Ordos Basin, China. *Int J Coal Geol* 2014; 134: 61-73.
- [41] Ma Y, Zhong N, Li D, et al. Organic matter/clay mineral intergranular pores in the Lower Cambrian Lujiaping Shale in the north-eastern part of the upper Yangtze area, China: A possible microscopic mechanism for gas preservation. *Int J Coal Geol* 2015; 137: 38-54.
- [42] Pashin J C, Grace RLB, Kopaska-Merkel DC. Devonian shale plays in the Black Warrior basin and Appalachian thrust belt of Alabama. *Univ Alabama, 2010 Int. Coalbed & Shale Gas Symposium Proc.* 2010b: 1016 (20 pp.).
- [43] Ji L, Zhang T, Milliken K L, et al. Experimental investigation of main controls to methane adsorption in clay-rich rocks. *Appl Geochem* 2012; 27(12): 2533-2545.

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Table1 Shale sample TOC contents

Formation	Sample ID	Location	TOC (wt%)	Mean(wt%)
Longmaxi (S ₁)	LQ-1	Chongqing	7.68	3.91
	LQ-6	Chongqing	4.24	
	LQ-9	Chongqing	2.18	
	LQ-13	Chongqing	1.46	
	GS-6	Sichuan	5.23	
	GS-7	Sichuan	4.82	
	GS-15	Sichuan	1.76	
Niutitang (C ₁)	CX-8	Chongqing	8.54	5.81
	CX-10	Chongqing	10.02	
	CX-18	Chongqing	2.17	
	HW-5	Hunan	4.40	
	HW-9	Hunan	3.90	

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Note: geological age:S₁-Lower Silurian; C₁-Lower Cambrian

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Table 2 Mineralogical composition of the shale samples based on XRD analysis

Sample ID	Relative percent (%)								
	Quartz	Feldspar	Carbonate	Pyrite	Total clay ^a	Illite	Montmorillonite	Chlorite	Montmorillonite-illite mixed layer
LQ-1	46.0	10.2	6.0	-	35.4	23.0	-	2.2	10.2
LQ-6	39.8	13.4	0.5	6.3	34.8	23.1	-	2.44	9.26
LQ-9	40.3	3.1	12.3	5	37.8	23.9	-	3.61	10.3
LQ-13	35.2	7.8	2.7	3.2	48.7	30.1	1.1	5.1	12.4
GS-6	53.7	6.5	3.8	-	34.1	22.2	-	-	11.9
GS-7	51.0	5.5	1.8	-	38.5	26.1	-	2.3	10.1
GS-15	50.1	7.9	2.1	2.3	36.1	20.4	-	4.4	11.3
CX-8	41.6	9.1	9.8	7.7	29.3	22.2			7.1
CX-10	51.5	7.9	1.7		37.4	26.1	1.3	4.4	5.6
CX-18	56.2	9.4	3.2	2.3	27.2	22.1		1.2	3.9
HW-5 ^b	62.1	10.2	4.1	2.1	20.1	15.3	1.6	0.8	2.4
HW-9 ^b	51.3	12.8	2.2	2.8	28.7	14.1	2.6	6.3	5.7
Mean	48.2	8.7	4.2	4.0	34.0	22.4	1.65	3.3	8.3

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^a Total clay=illite+ montmorillonitechlorite+montmorillonite-illite mixed layer. ^b The mineralogical compositionfor

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HW-5 and HW-9 from Wang et al.[35]

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Table 3 Experimental methane adsorption data for shale samples.

Formation	Sample ID	Max pressure (Mpa)	Max Gibbs Adsorption (ml/g)	Max absolute adsorption (ml/g)
Longmaxi (S ₁)	LQ-1	8.48	2.91	3.41
	LQ-6	8.44	2.40	2.81
	LQ-9	8.33	1.45	1.70
	LQ-13	8.38	1.25	1.36
	GS-6	8.51	1.16	1.36
	GS-7	8.36	1.67	1.91
	GS-15	8.44	0.72	0.84
Niutitang (€ ₁)	CX-8	8.50	1.76	2.06
	CX-10	8.48	1.95	2.28
	CX-18	8.34	0.46	0.50
	HW-5	8.57	0.85	0.95
	HW-9	8.55	0.72	0.79

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Table 4 The parameters for different sorption models

Sample ID	Langmuir model		BET model		D-R model		D-A model		
	V _L (ml/g)	P _L (MPa)	V _m (ml/g)	C	V ₀ (ml/g)	D	V ₀ (ml/g)	D	n
LQ-1	4.33	2.33	3.04	32.90	4.21	0.086	4.00	0.064	2.20
LQ-6	3.58	2.39	2.51	30.69	3.49	0.089	3.21	0.051	2.37
LQ-9	2.19	2.61	1.52	27.33	2.12	0.093	1.95	0.058	2.32
LQ-13	1.71	1.98	1.25	31.88	2.01	0.110	1.46	0.006	4.0
GS-6	2.12	4.75	1.34	14.88	1.77	0.117	1.80	0.126	1.95
GS-7	2.70	3.14	1.84	22.63	2.61	0.107	2.18	0.036	2.74
GS-15	1.21	3.50	0.81	19.97	1.13	0.109	0.97	0.049	2.54
CX-8	3.07	4.36	1.99	15.69	2.58	0.109	3.12	0.215	1.57
CX-10	3.33	3.80	2.20	18.95	2.98	0.109	2.87	0.091	2.12
CX-18	0.52	0.71	-	-	0.58	0.055	0.51	0.010	3.15
HW-5	0.97	0.70	-	-	1.13	0.063	1.02	0.020	2.80
HW-9	0.93	1.45	0.69	52.00	1.11	0.096	0.84	0.005	4.0

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Table 5 The Parameters of different models for Sorption

Sample ID	The average relative error (%)			
	Langmuir model	BET model	D-R model	D-A model
LQ-1	1.24	3.84	1.21	0.77
LQ-6	1.39	3.99	1.68	1.38
LQ-9	1.96	3.52	2.18	1.85
LQ-13	11.66	14.70	10.82	5.89
GS-6	0.61	2.55	0.76	0.58
GS-7	3.25	6.18	2.87	1.79
GS-15	2.75	5.44	2.41	1.68
CX-8	1.36	0.90	2.31	0.28
CX-10	0.66	3.56	0.79	0.69
CX-18	6.46	-	5.29	5.03
HW-5	8.93	-	6.31	4.51
HW-9	11.09	15.44	10.84	6.48
Average	4.37	6.01	3.96	2.58

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Figure 1. Geographical map of upper Yangtze area and sampling location

Figure 2. Typical methane sorption isotherms of marine shales (Note: (a) Lower Silurian Longmaxi shale; (b) Lower Cambrian Niutitang Shale)

Figure 3. Representative Langmuir isotherms for methane sorption of shale samples with R^2 values

Figure 4. Representative BET isotherms for methane sorption of shale samples with R^2 values

Figure 5. Representative D-R isotherms for methane sorption of shale samples with R^2 values

Figure 6. Representative D-A isotherms for methane sorption of shale samples with R^2 values

Figure 7. Comparison of experimentally measured adsorption isotherms for HW-9

Figure 8. Average error analysis for adsorption with different isotherm models

Figure 9. Relationship between the TOC content and the sorption capacity in the marine shales.

Figure 10. Relationship between the clay mineral content and the sorption capacity of shales.

Figure 11. Relationship between sorption capacity normalized to TOC with the total clay content (a), illite content (b), and illite-montmorillonite content (c).

Figure 12. Correlation between ARE and TOC for different models

Figure 13. Correlation between ARE and clay mineral content for different models