INTRODUCTION

1.1 Shale gas exploration and development in China and Guizhou Province

It is known that China has abundant shale gas resources, with an estimated resource amount of 122 trillion cubic meters (m$^3$) above the depth of 4500 m, of which 22 trillion m$^3$ is expected to be technically recoverable.$^1$ The production of shale gas in China has maintained a fast-growing pace, which increased to about 9 billion m$^3$ in 2017 from 25 million m$^3$ in 2012; it is anticipated to reach 30 billion m$^3$ by 2020, and 80-100 billion m$^3$ by 2030.$^1$ However, current commercial shale gas productions in China are concentrated in the Sichuan Basin and the basin edge.$^2,3$ In order to reach the anticipated goal, it is necessary to speed up exploration and development activities in other potential regions.

Guizhou is a province located south of the Sichuan Basin in the southwest part of China (Figure 1). There are extensive and thick black shale formations in Guizhou, displaying a good potential for shale gas production. A general geological survey program named the “Shale Gas Survey and Evaluation...
Program” was performed from March 2012 to June 2013, the results of which indicated that recoverable shale gas resources in this province could be as high as 1.95 trillion m³, which is approximately 9% of the total in China. The survey also shows that the northern part of Guizhou, close to the Sichuan Basin, is the most promising region in terms of shale gas production. The Lower Cambrian Niutitang (NTT) formation and upper Ordovician Wufeng-lower Silurian Longmaxi (LMX) formation are considered to have the most potential because of their sufficient thickness, high organic content, high thermal evaluation, and high brittle mineral content. In recent years, some progresses in exploration and development activities drilled on these two formations have been made. However, fundamental research into, and detailed understanding of, shale gas storage mechanisms in these two formations are still needed to push production forward to commercialization in Guizhou.

1.2 | Effect of clay-organic complexes to adsorption

Gas is stored as adsorbed and free phases in reservoirs. Free gas is natural gas that is trapped in the pore spaces of the shale, and adsorption is the pressure-dependent attraction of gas molecules to the surface of a solid, resulting in a dense phase of gas at the surface. In the reservoir, the adsorbed gas is in equilibrium with the free-phase gas. Depending on the reservoir properties and conditions, adsorption may account for as much as between 20% and 85% of the gas in place in shales. However, the majority of this adsorbed gas may not be recovered as the sorption isotherms only indicate an obvious steepness at lower pressures. The two potential reservoirs of Guizhou also contain a high portion of adsorbed gas. Hence, to achieve further progress in shale production in this region, it is very important to investigate in depth the adsorption characteristics of NTT and LMX shales.

It is known, on the other hand, that the clay-organic complexes in the formation display a very different adsorption pattern when compared to clays or other lithologies. Because both clays and organic can carry electric charge, interlayer water, structure water, and colloid, they are commonly accreted together in water, clay sediments, and clay rocks. Most organics are integrated with clays, in a form which is called clay-organic complex. The organics might be physically adsorbed on the surface and in the pores of clay minerals, or exist in interlayers of clays. The clay-organic complexes are not a simple mixture of clay and organics, and do not possess all the characteristics of clays and organics. Instead, the abilities to exchange and resist microbiological destroy and thermal stability of clays in the complexes are significantly improved. The special characteristics of the clay-organic complexes have been researched by some scholars from the aspects of hydrocarbon maturation and petroleum generation. However, the adsorption characteristics of the clay-organic complexes, in comparison to other lithologies, and

FIGURE 1 Locations of unconventional resources in China and Guizhou Province. The study region is represented in red in the map. Modified from Refs 2 and 3
their effect to gas storage mechanism and resource estimation have yet to be examined. Such research is essential in order to more accurately evaluate the resource, reserve, and sweet spots in shale gas reservoirs.

2 | METHODOLOGY

2.1 | Geological background

The study region (Figures 1 and 2), north Guizhou Province, southwest China, is located in the upper Yangtze Plate and its main body is situated in the central Guizhou uplift area, which is an EW-trending uplift zone of the early Paleozoic. The multiperiod tectonic activity in north Guizhou was controlled by the temporal and spatial evolution of two tectonic systems: the Qinling orogenic belt and the Xuefeng tectonic belt. This is characterized by complex structures including fault sand folds that are common and generally have NE and NNE orientations, and most of these faults are reverse faults or strike-slip faults. The lower Cambrian NTT formation is mainly distributed in the north, central, and southeast parts of Guizhou Province. The sedimentary environments were mainly shallow sea shelf sedimentary facies and deep water shelf sedimentary facies. The transgression took place due to ice melting and rises in the sea level after the Sinian Nantuo Ice Age. Black shale series were widely deposited during the Upper Sinian and Lower Cambrian periods. The NTT shales are located in the lower part of the NTT formation and its dominant lithologies include a silty shale and a carbonaceous shale, intercalating by stone coal, silicolite, and phosphorite. Previous studies have shown that it contains kerogens of Type I and Type II with a relatively strong hydrocarbon generation potential.

The upper Ordovician-lower Silurian LMX formation is basically distributed in north part of Guizhou Province, close to the Sichuan Basin. In the early Silurian, the middle part of Guizhou gradually lifted up to form a continent due to Duyun movement, resulting in the continuous northward retrogradation of marine sediments in north Guizhou. LMX black shale deposits were developed in deep water shelf and stagnant basin only to the north part of Guizhou, and the formation becomes gradually thinner from the north to the south. The lithology of the LMX formation primarily consists of siliceous shale and gray to black shale. Kerogens of Type I and Type II in the shale dominate. The same formation in the nearby eastern Sichuan basin primarily formed the largest shale gas field outside of North America.

In this study, the NTT shales in Cengong and Fenggang Counties, and LMX shales in Zheng’an County are used as case studies (Figure 2). The Cengong region is a complicated structure transforming area, with reverse faults in NNE and NS directions as the major structure. The Fenggang region is also a structure transforming area, with folds and generated compression faults both in NS direction founded in this area. In the Zheng’an region, approximately NS directional spaced synclines made by gentle anticlines and tight synclines are the major structure, with some faults presented in this region.

The goal of this study is to investigate the effect of adsorption characteristics of clay-organic complexes on shale gas...
storage mechanism and estimation of resources. The authors used the NTT and LMX shales as an example, to research and compare the adsorption characteristics to methane (CH$_4$) of clay-organic complexes and regular shales. The clay-organic complexes were extracted from the core samples, and the original samples were considered as a representative of regular shales. Based on the test results and other reservoir properties, free gas content and adsorbed gas contents in the reservoirs were calculated, and the variation pattern of free gas and adsorption contents in clay-organic complexes and regular lithology were examined. The impact of reservoir depth and pressure to adsorbed and free gas contents were also examined.

### 2.2 Sampling, preparation, and testing

Core samples were obtained from three wells drilled in NTT and LMX shales in Guizhou Province: Well TM 1 (NTT formation) located in Cengong County, Well FC 1 (NTT formation) located in Fenggang County, and Well BZ 1 (LMX formation) located in Zheng’an County. Locations of these wells are displayed in Figure 2, and key information is listed in Table 1. These samples were prepared and tested following related standards. Basic physical properties, clay content, mineralogy, and isothermal adsorption were tested and measured.

The comprehensive mineralogy and clay analyses were performed by X-ray Diffraction (XRD) at the testing center of the Research Institute of Petroleum Exploration and Development, China National Petroleum Corporation. Currently there is no standard guide for preparation of clay-organic complex samples. The preparation procedures were referred to related steps stated in the “Analysis method for clay minerals and ordinary nonclay minerals in sedimentary rocks by the X-ray diffraction” (SY/T 5163-2010), a standard used by the petroleum industry in China (National Energy Administration of China). The samples were prepared according to the following steps:

- The collected samples were cleaned and dried in 80°C, and crushed below 200 mesh;
- The crushed sample was further grinded to −2 μm, and treated repeatedly by hydrochloric acid solution until no further reaction observed, this step removed calcite and dolomite in the sample;
- The treated sample was then neutralized by ammonia solution;
- The neutralized sample was washed by distilled water and then dispersed;

#### Table 1 List of well samples and well information

| Sample ID | Depth (m) | Well | Formation |
|-----------|-----------|------|-----------|
| TM-2      | 1430.61   | Well TM 1, Cengong County | NTT, lower Cambrian |
| TM-4      | 1447.67   | Well TM 1, Cengong County | NTT, lower Cambrian |
| TM-6      | 1466.65   | Well TM 1, Cengong County | NTT, lower Cambrian |
| FC-1      | 2447.18   | Well FC 1, Fenggang County | NTT, lower Cambrian |
| FC-2      | 2454.91   | Well FC 1, Fenggang County | NTT, lower Cambrian |
| FC-4      | 2496.15   | Well FC 1, Fenggang County | NTT, lower Cambrian |
| BZ-01     | 1097.35   | Well BZ 1, Zheng’an County | LMX, lower Silurian |
| BZ-02     | 1102.25   | Well BZ1, Zheng’an County | LMX, lower Silurian |
| BZ-03     | 1106.50   | Well BZ 1, Zheng’an County | LMX, lower Silurian |
| BZ-04     | 1111.30   | Well BZ 1, Zheng’an County | LMX, lower Silurian |
| BZ-05     | 1117.00   | Well BZ 1, Zheng’an County | LMX, lower Silurian |
| BZ-06     | 1120.10   | Well BZ 1, Zheng’an County | LMX, lower Silurian |

LMX, Longmaxi; NTT, Niutitang.
• The clay particles were separated by centrifugation of the suspension, and dried in an environment lower than 60°C, this step removed pyrite and quartz in the sample; and
• The dried clay particles were further ground in an agate mortar until they were free from particle roughness to the touch.

All the samples used in this study are black shale, in which the clays are associated with organics. Through the treatment procedures stated above, most nonclay minerals were removed from the sample. A small trace of pure clay left in the sample would impose little influence to the adsorption experiments. The original shale samples and clay-organic complexes were activated under the temperature of 250°C for 4 hours. The methane adsorption experiments were then conducted by a high-pressure gas isothermal adsorption system (GAI-100) manufactured by Core Lab. The experiment temperature was set at 30°C, and CH₄ and Helium (He) were used as the gas sources.

3 | EXPERIMENT RESULTS

3.1 | XRD

The XRD testing results are presented in Figures 3 and 4. The results show that, for the NTT shale in northern Guizhou region, quartz, feldspar, calcite, dolomite, pyrite, and clays are the major minerals. The clay minerals almost consist of illite, indicating that the NTT is already in the gas window. The tested samples have a high brittle mineral content, with 42.8% of quartz, 18.1% of feldspar, and 24.1% of clays.

For the LMX shale samples, quartz, feldspar, calcite, dolomite, pyrite, and clays are the major minerals. The clay minerals basically consist of illite, illite/smectite mixed layer and chlorite. The tested samples are also characterized by a high brittle mineral content (55.1%), mainly quartz and feldspar (K-feldspar and Na-feldspar), with 37.0% of quartz, 9.2% of...
feldspar, and 42.8% of clays, of which 72.5% is illite, 5.0% is illite/smectite mixed layer, and 22.5% is chlorite, indicating that the LMX is already in the gas window.

3.2 | TOC and Ro

The total organic carbon (TOC) and vitrinite reflection (Ro) were measured at the laboratory of the Coal Mine Exploration Bureau of Guizhou Province. The method of oxidation non-dispersive infrared adsorption was employed for the TOC test, and the Ro test was performed using the method of determining microscopically the reflectance of vitrinite in sedimentary according to the standard SY/T 5124-2012, a standard used by the petroleum industry in China.35 The TOC and Ro test results are displayed in Table 2. In general, the NTT samples show a higher TOC than the LMX samples, also higher than most commercially developed gas shales in North America. The TOC and Ro numbers indicate that both formations have a promising gas generation potential.

3.3 | Isothermal adsorption experiment

The experiment results were processed by the Langmuir isotherms.36,37 This theory assumes that the gas is adsorbed as a monolayer on the rock surface. It describes the relationship between the adsorption of pure gas molecules on a coal or shale surface and gas pressure at a constant temperature. The Langmuir Volume ($V_L$) and Langmuir Pressure ($P_L$) were obtained through the isothermal curves. The Langmuir Equation is expressed by Equation 1:

$$V = V_L \frac{P}{P + P_L}$$  \hspace{1cm} (1)

where $V$ is the adsorbed gas, m$^3$/t; $V_L$ is the Langmuir volume, or the maximum adsorbed gas content, m$^3$/t; $P_L$ is the Langmuir pressure, MPa; and $P$ is the reservoir pressure, MPa.

The derived Langmuir parameters are presented in Table 3.

The measured adsorption isotherms of both clay-organic complexes and original samples, are displayed in Figures 5-7, for the three wells respectively. The experiment results show that the original samples and clay-organic complexes samples both fit for the type I isothermal adsorption curve. It is clear that the clay-organic complexes have a stronger adsorbatbility than the original shale samples. For the samples collected from Well TM1, the adsorbatbility of the clay-organic complexes is 1.4 times of that of the original samples; for the samples collected from Well FC1, the adsorbatbility of the clay-organic complexes is 2.1 times of that of the original samples; and for the samples collected from Well BZ1, the adsorbatbility of the clay-organic complexes is 1.4 times of that of the original samples.

4 | CALCULATION OF ADSORBED GAS AND FREE GAS CONTENTS

Based on the experimental results presented in Section 3, and assuming different reservoir pressure conditions, namely normal pressure, over pressure (O.P.) = 1.2, and O.P. = 1.5, the free gas and adsorbed gas contents were calculated.

The free gas content, $X_F$ (m$^3$/t, cubic meters of gas at standard condition per ton of reservoir rock) can be calculated by Equation 2:38

$$X_F = \frac{V_P}{V_L}$$

| Sample                  | $V_L$  | $P_L$  | Coefficient of correlation, $R^2$ |
|-------------------------|--------|--------|----------------------------------|
| FC original             | 2.4114 | 0.5431 | 0.973                            |
| FC clay-organic complexes | 4.9917 | 0.1126 | 0.996                            |
| TM original             | 2.3785 | 1.1123 | 0.903                            |
| TM clay-organic complexes | 3.4244 | 0.8613 | 0.935                            |
| BZ original             | 2.3582 | 0.6694 | 0.831                            |
| BZ clay-organic complexes | 3.3339 | 1.6918 | 0.998                            |

TABLE 2 | Measured TOC and Ro results

| Sample | TOC (%) | Ro  |
|--------|---------|-----|
| TM-2   | 4.04    | 3.11|
| TM-4   | 6.85    | 3.14|
| TM-6   | 2.25    | 2.79|
| FC-1   | 2.52    | 2.84|
| FC-2   | 4.74    | 2.52|
| FC-4   | 6.55    | 2.57|
| BZ-01  | 0.47    | 2.41|
| BZ-02  | 0.68    | 2.36|
| BZ-03  | 0.88    | 2.33|
| BZ-04  | 0.85    | 2.26|
| BZ-05  | 4.47    | 2.28|
| BZ-06  | 1.82    | 2.23|

TABLE 3 | Measured Langmuir Parameters

LMX, Longmaxi; NTT, Niutitang.
where $V$ is the pore volume per ton of reservoir rock, $m^3/t$; $P$ is the reservoir pressure, MPa; $T$ is the reservoir temperature, K; and $\xi$ is the compressibility of methane.

The pore volume per ton of reservoir rock, $V$, can be calculated by Equation 3:

$$V = \frac{\rho P \xi}{T_0}$$

where $\rho$ is the density of reservoir rock, $t/m^3$; and $\Theta$ is the porosity of the reservoir rock.

The adsorbed gas content, $X_A (m^3/t)$, is calculated by Equation 4:

$$X_A = \frac{V_L bP}{1 + bP} e^{n(T_e - T)}$$

where $T_e$ is the experimental temperature during isothermal adsorption test, K; $b$ is the Langmuir constant, indicating the adsorbability of the surface of a medium to gas, and can be calculated by Equation 5:

$$b = \frac{1}{P_L}$$

and $n$ is a constant which can be calculated by Equation 6:

$$n = \frac{0.02}{0.993 + 0.07P}$$

Figure 5 ((A) for normal reservoir pressure, (B) for O.P. = 1.2, (C) for O.P. = 1.5) shows the calculated free gas and adsorbed gas contents of the TM well in NTT shales, Figure 9 ((A) for normal reservoir pressure, (B) for O.P. = 1.2, (C) for O.P. = 1.5) for the FC well in NTT shales, and Figure 10 ((A) for normal reservoir pressure, (B) for O.P. = 1.2, (C) for O.P. = 1.5) for the BZ well in LMX shales. The adsorbed gas contents were calculated based on adsorbabilities of clay-organic complexes and original samples respectively.

Adsorbed gas content in both clay-organic complexes and original samples mildly decreases with the reservoir depth and pressure. When compared, the effect of reservoir depth and pressure to free gas content is more obvious. Because the different of adsorbabilities of clay-organic complexes and original samples, the total gas contents calculated based on the two are also different. For samples collected from the Well TM1, the total gas content using adsorbability of clay-organic complexes was 40% higher than that using adsorbability of original samples; for the samples collected from Well FC1, the total gas content using adsorbability of clay-organic complexes was 70% higher than that using adsorbability of original samples; for
the samples collected from Well BZ1, the total gas content using adsorbability of clay-organic complexes was 30% higher than that using adsorbability of original samples. In general, the clay-organic complexes are expected to have a higher gas content than other regular shales in the reservoir formations.

The adsorbed gas ratios in total gas contents are also calculated. As the results shown in Figures 11-13, the adsorbed gas ratios calculated based on clay-organic complex isotherms are obviously higher than that based on original samples.

**FIGURE 8** Calculated free gas and adsorbed gas contents of TM well, Niutitang shale

**FIGURE 9** Calculated free gas and adsorbed gas contents of FC well, Niutitang shale
5.1 | Potential of the NTT and LMX shales

The NTT shale in the northern Guizhou region has a high organic content, and its high brittle mineral content would benefit the reservoir fracking and production. The clay in this formation is almost illite, which means it is already in the late diagenetic stage, and in the window of organic over mature and dry gas generation. The organic rich NTT shale in the north Guizhou region can be as thick as 80 m.

The organic content in the upper and middle portions of the LMX shale is not as high as the NTT, but still higher than the baseline of gas generation, which is 0.5%. Its average brittle mineral content is 48.0%. Its clay content is basically illite and chlorite with some illite/smectite mixed layers. The fraction of illite/smectite mixed layers in clay is 5%, at the late stage of its formation. This also means the stage of beneficial enrichment of shale gas at the same time. The thickness of LMX shale in the study region reaches to 50 m.

The analysis described above displays that both the LMX and NTT shales in the study region have a promising potential for gas development and production. This is in fact supported by the sufficient gas flow observed in several survey drilling wells in the study area. The total gas content is increased when the calculation is based on the data of organic-complex rather than that of original sample, and this further enhances the potential of these reservoirs. However, as presented in Section 4, the adsorbed gas shares a high portion in total gas content, which means that improvement of gas recovery in these reservoirs might be challenging using current technologies.

5.2 | Impact to shale gas exploration and development in north Guizhou

A low value of Langmuir pressure ($P_L$) means a stronger adsorbability of the rock surface, and hence harder to liberate the methane. As can be seen in the test result, $P_L$ values of both LMX and NTT samples are very low, indicating a strong adsorbability to methane, and a high adsorbed gas content is anticipated. Therefore, it is of importance to understand where the adsorbed gas is relatively accumulated.

At the same time, the unique adsorption characteristics of the clay-organic complexes is different from regular shales matters. The isothermal adsorption experiments presented in this study show that adsorbability of the clay-organic complexes can be as high as 1.5-2 times of that of the original samples, or regular shales. From the calculated free gas content and adsorbed gas content, when it is the normal pressure, the adsorbed gas fraction based on TM NTT original sample ranges from 58% to 63%, and the adsorbed gas fraction based on TM NTT clay-organic complexes ranges from 69% to 73%. Similarly, the adsorbed gas fraction based on FC NTT original sample ranges from 56% to 58%, and the adsorbed gas fraction based on FC NTT clay-organic complexes ranges from 73% to 76%. The adsorbed gas fraction...
Based on BZ LMX original sample ranges from 73% to 79%, and the adsorbed gas fraction based on BZ LMX clay-organic complexes ranges from 79% to 84%. With the increase in the over pressure coefficient, the adsorbed gas fraction drops. Furthermore, increase in the reservoir depth results in the decrease in adsorbed gas fraction, although the effect is not very significant.
obvious. In general, adsorbed gas shares the major portion in both LMX and NTT shales. Especially in LMX shale, more than 70% of total exist in adsorption phase.

The clay-organic complexes exist in geological formations in separated forms, and can accumulate in certain areas. Therefore, it can be predicted that adsorbed gas content in certain areas where clay-organic complexes are accumulated would be much higher than other areas, and more attentions should be paid to the clay-organic complexes accumulated areas in the formation, as these areas could be the “sweet spots” for shale gas development. It is suggested that accumulation of clay-organic complexes could be considered as one of the factors in defining “sweet spots”, together with other factors such as maturation and brittleness. Besides, enhanced gas recovery technologies including gas displacement and increasing reservoir temperature that specially target at liberating the adsorbed gas in clay-organic complexes should be one of the focuses in future research works.

6 | CONCLUSIONS

In this study, core samples obtained from the LMX and NTT shales, the two potential gas reservoirs in northern Guizhou, China, were used to investigate the adsorption characteristics of the clay-organic complexes. The clay-organic complexes were extracted from the core samples, and their adsorption isotherms were compared to those of the original samples, a representative of regular shales. The experimental results were then used to estimate the free and adsorbed gas contents in the reservoirs.

1. The isothermal adsorption experiment result shows that the clay-organic complexes have a very different adsorption pattern to gas compared to regular shales in the reservoir. In general, the clay-organic complexes have an obviously stronger adsorbability than the regular shales by 1.5-2.0 times.

2. The stronger adsorbability of the clay-organic complexes results in a higher gas content in adsorbed phase in the reservoir. The gas content calculated based on the adsorbability of clay-organic complexes are higher by 30%-70% than that based on the original samples (regular shales) for the case study formations in this paper.

3. The clay-organic complexes exist in geological formations in separated forms and can accumulate in certain areas, so it is anticipated that clay-organic accumulations in the reservoir can form sweet spots, which are worthy to exploration and development.

4. Combined with other measured petrophysical properties presented in this study, including brittle mineral content, TOC, thermal maturity, and clay composition, the NTT and LMX shales in northern Guizhou have the potential for further exploration and development, and new production and reservoir treatment technologies specially targeting at the adsorbed gas should be developed.

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