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Characteristics of Micro–Nano-Pores in Shallow Shale Gas Reservoirs and Their Controlling Factors on Gas Content

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Abstract: This investigation ventures into the nuanced porosity traits of shallow shale gas reservoirs, pinpointing the critical determinants of their gas content with a nuanced touch. By harnessing sophisticated microscopy and analytical methods, we embarked on an exploration into the porosity architecture of shale, identifying the distinct pore spaces that harbor shale gas and applying gas adsorption techniques to evaluate its storage potential. Noteworthy is our utilization of diverse adsorption mechanisms and models to accurately fit methane adsorption data while carefully considering the influence of marine shallow shale's pore structure peculiarities, total organic carbon (TOC) content, and clay mineral content on its adsorption prowess. We introduce a refined model for appraising gas adsorption volumes, an innovative stride toward bolstering the precise estimation of reserves in marine dam shallow shale gas and shedding light on accurate gas adsorption volume calculations in analogous shallow shale gas scenarios. This manuscript offers profound insights into the sophisticated interplay between shale porosity and gas storage, enriching our understanding and enabling more accurate future resource estimations.

Keywords: shale gas; Wufeng–Longmaxi; methane adsorption; Langmuir pressure



Citation: Liu, Y.; Xian, C.; Huang, X. Characteristics of Micro–Nano-Pores in Shallow Shale Gas Reservoirs and Their Controlling Factors on Gas Content. *Energies* **2024**, *17*, 1682. <https://doi.org/10.3390/en17071682>

Academic Editor: Reza Rezaee

Received: 31 December 2023

Revised: 19 March 2024

Accepted: 29 March 2024

Published: 1 April 2024



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1. Progress in the Study of Pore Characteristics and Gas Content in Shale Gas Reservoirs

Shale gas, as a significant unconventional natural gas resource, has garnered widespread attention in the global energy sector [1,2]. The investigation of shallow shale porosity characteristics and the study of factors controlling gas content hold paramount importance in the realms of modern geology and energy development [3]. Firstly, as a clean and efficient unconventional natural gas resource, shale gas occupies an indispensable position within the global energy mix [4]. An in-depth exploration of the porosity traits of shallow shale can aid scientists and engineers in better understanding the gas storage mechanisms and flow properties of shale gas reservoirs. This understanding is crucial for evaluating the potential of shale gas resources, optimizing extraction methods, and enhancing gas recovery efficiency [5]. This manuscript not only elucidates the scientific significance of studying shallow shale porosity and gas content control factors but also emphasizes the role of shale gas in advancing a sustainable and efficient global energy landscape.

The primary storage spaces for shale gas are located within the micro- to nanoscale pores of shale, rendering in-depth analysis of its microscopic pore structure particularly crucial. The characterization techniques for shale porosity can be broadly categorized into two main types: those based on physical experimental measurements and those relying on high-resolution imaging observations [6]. In physical experimental measurement techniques, depending on the pore size, methods primarily include low-temperature nitrogen adsorption, low-temperature carbon dioxide adsorption, high-pressure mercury

intrusion, and nuclear magnetic resonance (NMR) technologies [7]. Each technique targets pores within different size ranges; for example, low-temperature gas adsorption is suitable for detecting mesopores and micropores [8], while high-pressure mercury intrusion is more apt for characterizing macropores [9]. Although these methods have their strengths, limitations exist, such as the potential for high-pressure mercury intrusion to damage samples [10], whereas low-temperature gas adsorption can avoid sample destruction, thereby increasing sample usability [11]. On the other hand, high-resolution imaging techniques employ various microscopic imaging technologies, such as optical microscopy and scanning electron microscopy (SEM), to directly observe the micro-features of shale pores [12–14]. These technologies provide intuitive images of pore structures but, due to the extremely small size of shale pores, require very high imaging resolutions [15,16]. Common experimental methods include isothermal adsorption experiments and high-pressure methane adsorption experiments. These experiments can determine the adsorption capacity of methane in shale under different conditions (such as varying temperatures and pressures) [17,18].

To predict and calculate the gas content of shale gas, researchers have developed experimental methods for determining gas content more accurately. These models and methods are designed to combine the pore characteristics of shale and the adsorption behavior of methane to provide more precise estimates of gas content. As early as 1915, Gibbs proposed the Gibbs adsorption equation based on classical thermodynamics, applicable to all interfaces [19]. In 1918, Langmuir introduced the classic monolayer adsorption model theory, which later became the Langmuir model [20]. In 1930, Mikhail I. Temkin proposed the original Temkin model [21], and in 1938, S. Brunauer, P.H. Emmett, and E. Teller derived the multilayer adsorption model equation based on monolayer adsorption, the BET (Brunauer–Emmett–Teller) model [22]. In the exploration of gas adsorption mechanisms, various theoretical models have been widely used to deepen the understanding of the adsorption process. These models include but are not limited to the Langmuir, Freundlich, and Temkin adsorption models, which provide a foundation for revealing the adsorption characteristics of gases such as methane on catalyst surfaces and within shale pores [23–25]. With the advancement of research, the phenomenon of adsorption under high-pressure conditions has prompted scholars to compare and revise traditional models, thereby proposing improved theories such as Toth–Langmuir and multicomponent adsorption [26]. Furthermore, in response to the complex behavior of methane adsorption, more advanced models such as Sips, Freundlich–Langmuir, and Redlich–Peterson have been developed to achieve the accurate fitting of adsorption data [27]. Recently, the proposal of micropore filling theory and the development of multiscale models based on the Sips model have provided new perspectives for the study of gas transport and adsorption mechanisms in microporous structures [28,29]. Especially considering the complexity of conditions such as multilayer adsorption, supercritical adsorption, and exceptionally high pressure in shale gas, the BET adsorption model has been modified to enhance its relevance and accuracy in practical applications [30,31]. The advancements in these theories have not only propelled a deeper understanding of adsorption science but also provided solid theoretical support for the exploitation and application of shale gas.

This study plans to first conduct mineral analysis; scanning electron microscopy; specific surface area and pore size analysis; low-temperature nitrogen adsorption; and methane isotherm adsorption experiments on samples collected from the research area. Following the analysis of empirical data to clarify the microstructural pore characteristics and properties of shallow marine shale gas, different adsorption mechanisms and models will be employed to fit the methane adsorption capacity. This will also consider the impact of marine shale pore structure features, total organic carbon (TOC) content, and clay mineral content on shale adsorption capacity. By establishing the correlation of these parameters with experimental parameters such as maximum adsorption capacity through nonlinear regression fitting, this study aims to refine the gas content calculation model, enhance the precision of model computations, and provide support for accurate reserve estimation.

2. Sample and Experimental Methods

2.1. Sample Description

The research area of this study is located in the central part of the Zhaotong shale gas demonstration area in the Wumeng Mountain area, which transitions from the Yunnan–Guizhou Plateau to the Sichuan Basin. It is situated at the overlap of the western margin of the Yangtze Craton’s Sanjiang orogenic belt and the forefront of the southeastern margin’s Jiangnan–Xuefeng structural zone. The specific study range is within the pink rectangle, developing structural units from north to south in sequence, including the Taiyang anticline, the Xuyong syncline, the Haiba anticline, and the Hualang syncline (Figure 1). The samples for this study were collected from the Wufeng Formation of the Upper Ordovician (O3w) and the Longmaxi Formation of the Lower Silurian (S1L), with codes S1L111 to L114. The burial depth ranges from 2000 m to 500 m, and the lithology is predominantly black marine shale.

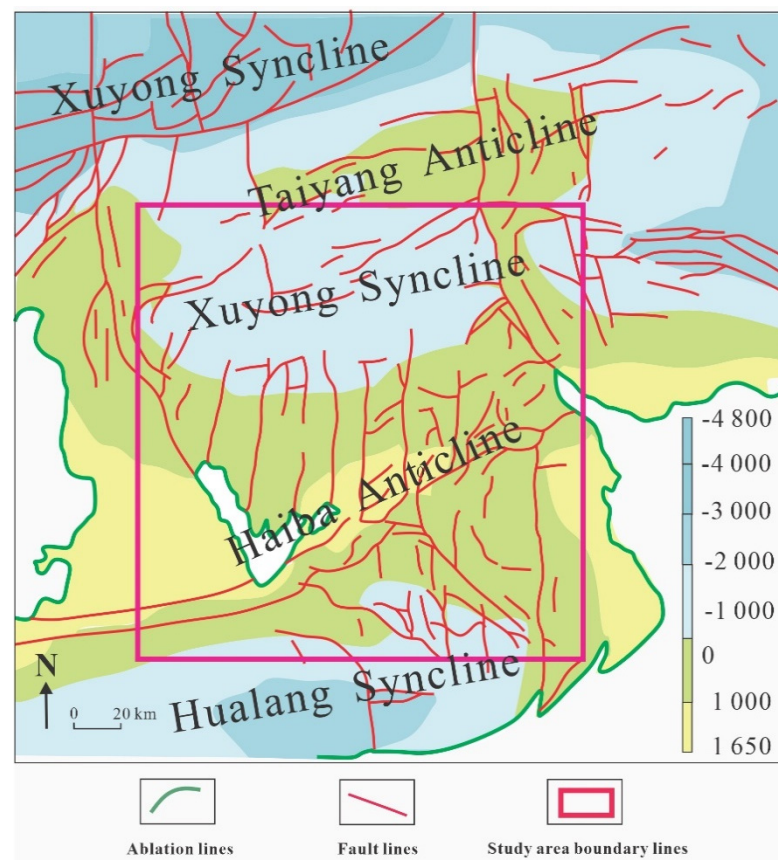


Figure 1. Research area location map. The green line indicates the extent of erosion of the target layer; the red line represents the fault line; the color scale denotes the elevation depth, ranging from −4800 m to 1650 m.

2.2. Experimental Methods and Procedures

2.2.1. Analysis of Microporosity Structure

Scanning electron microscopy (SEM) represents the most prevalent method for examining the microstructural characteristics of shale’s pore spaces, enabling the precise identification of microscopic pores and fracture types through high-resolution SEM imagery, thus determining the distribution features of shale pores [32,33]. In this SEM analysis, the equipment employed was the Quanta FEG 450 field emission scanning electron microscope from FEI Company (Hillsboro, OH, USA). The detailed experimental procedure commenced with the collected shale core samples first cut into small cubic pieces of approximately 0.8 cm in edge length. These pieces were then solidified with AB adhesive for over four hours, followed by polishing with a polishing wheel to achieve a smooth surface.

This was succeeded by extensive polishing with argon ions for four hours at a working voltage of 5 kV and a current of 2.2 mA. Finally, the samples were affixed to an SEM stub using carbon coating for scanning. The raw grayscale images obtained from scanning were converted into binary images, which were then subjected to image analysis using the Image J software (V1.8.0) to investigate the pore structure characteristics of the samples.

2.2.2. Analysis of Mineral Content

Prior to all experiments and analyses, the shale samples collected underwent necessary pre-treatment to ensure that they met the standards and requirements of the study. Total organic carbon (TOC) measurement was conducted using a YQ-VIIIA-type oil and gas show evaluation instrument. The samples were ground to a particle size of about 100 mesh to ensure uniformity. Inorganic carbon was removed from the samples through dilute hydrochloric acid treatment. The samples were then dried at specified temperatures to remove moisture. The treated samples were placed in a TOC analyzer. Under anoxic conditions, the samples were heated to a range of temperatures, typically from 300 °C to 1000 °C, to record the number of hydrocarbons released by pyrolysis, including parameters such as S0, S1, S2, S3, S4, Tmax, and RC, thereby evaluating the organic matter richness and hydrocarbon generation potential of the rock. Additionally, to determine the mineral composition of the samples, X-ray diffraction (XRD) technology was used. All samples were ground to a fine powder of about 100 mesh and then analyzed using a Panalytical X'Pert PRO MPD X-ray diffractometer (Almelo, Netherlands, utilizing Cu K α radiation, a working voltage of 40 kV, and a current of 40 mA) at angles ranging from 5° to 45°, with a scanning rate of 2°/min.

2.2.3. Low-Temperature Nitrogen Adsorption Experiment

This study initially involved the preliminary preparation of shale samples from different stratigraphic levels and burial depths, including sieving the samples to a specific granularity of 150 mesh and employing high-vacuum degassing at a temperature of 80 °C to remove physically adsorbed substances from the sample surfaces. Following this, the Micromeritics ASAP2420 surface area and porosity analyzer was used to conduct low-temperature nitrogen adsorption experiments at approximately 77 K. The total surface area and pore size distribution of the samples were calculated using the Brunauer–Emmett–Teller (BET) equation and the Barrett–Joyner–Halenda (BJH) algorithm, with a detailed analysis of the experimental data performed. The primary aim of this research was to analyze the trends in surface area, pore size distribution, and pore volume in shale samples from the Longmaxi to Wufeng Formations. Additionally, this study explored the correlation between these changes and the total organic carbon (TOC) content.

2.2.4. Methane Isotherm Adsorption Experiments and Adsorption Isotherm Curve Fitting

To measure the methane adsorption isotherms, approximately 100 g of crushed and sieved samples with diameters ranging from 0.84 mm to 2.36 mm (8 to 20 mesh) were used. Prior to analysis, all samples were dried at 110 °C and subjected to vacuum degassing for 7 h to fully eliminate impurity gases and moisture from the internal voids. All measurements were conducted at 40 °C using a high-pressure gas adsorption analyzer (3H-2000PH690, Micromeritics Instrument Corporation, Norcross, GA, USA), which operates within a temperature range of 20 °C to 70 °C and a pressure range of 0 to 30 MPa, employing the volumetric method.

Subsequently, we utilized three different models—Langmuir, spreading pressure-dependent real gas (SDR), and Ono–Kondo—to fit the methane adsorption data and compare the fitting precision of these three models to select the most suitable one for in-depth analysis. Through the Langmuir and SDR models, we calculated the maximum absolute adsorption capacity and adsorption phase density for each sample. Coupled with information on total organic carbon (TOC) content, specific surface area, and pore volume, we explored the factors influencing these parameters.

$$Nex = \frac{V_L P}{P_L + P} * \left(1 - \frac{\rho_{gas}}{\rho_{ads}}\right) \quad (1)$$

$$Vex(p) = TOC * \left(\frac{V_L p}{P_L + p}\right) * \left(1 - \frac{\rho_{free}}{\rho_{ads}}\right) \quad (2)$$

Many scholars have introduced an excess adsorption correction term based on the behavior that supercritical shale methane adsorption follows Gibbs's excess adsorption, resulting in the excess adsorption isotherm model (Equation (1)) [22,34–36]. Wenbin J, et al. [25] proposed the modified Langmuir equation (Equation (2)) on this basis, which includes three key parameters: V_L , P_L , and ρ_{ads} , primarily utilized to simulate the behavior of excess adsorption isotherms, $Vex(p)$. In this context, V_L signifies the maximum adsorption capacity (measured in g/mL), P_L refers to the Langmuir pressure (in MPa), and ρ_{ads} indicates the density of the adsorbed phase (in g/cm³). Additionally, ρ_{free} represents the density of free gas at a specific pressure, P (in MPa) (in g/cm³). This study opts to employ the revised Langmuir equation given its reduced parameter count and the clear physical significance of each parameter, thereby making the equation more straightforward to understand and interpret. However, it is crucial to emphasize that this mathematical formulation does not suggest that methane adsorption in shale strictly adheres to the monolayer adsorption mechanism proposed in the Langmuir model, particularly under actual reservoir conditions.

2.3. Analysis of Experimental Results

2.3.1. Electron Microscopy Analysis of Micropore Characteristics

As illustrated in Figure 2, through observations using scanning electron microscopy (SEM) and detailed statistical analysis of samples from the study area, we identified the primary pore types in the gas storage spaces to include organic matter pores, intergranular pores, intragranular pores, and microfractures. Among these pores, organic matter, predominantly of type III kerogen, exhibited a moderate development level, primarily characterized by elongated clay associations and in situ autogenic pores. Microfractures are commonly filled with organic matter.

The morphology and distribution of organic matter can be categorized into several types: regular-shaped organic matter, primarily distributed as isolated dots; dispersed amorphous organic matter, often concentrated between clay mineral particles and authigenic quartz grains, especially the organic matter between quartz grains, which tends to be net-like in distribution with organic matter of varying sizes interconnected; pore-filling organic matter, such as dissolution pores, clay pores, and pyrite-intergranular-filled organic matter—these types of organic matter are mostly flake-like in distribution among clay mineral particles, with some forming a network, although their connectivity is relatively poor; and organic matter associated with other minerals, commonly found in association with clay minerals.

Based on the origin of organic matter, it can be classified into two major categories: migrated organic matter and sedimentary organic matter. Migrated organic matter primarily resides within mineral pores and consists of asphalt or petroleum that has migrated from external locations. With increasing thermal maturity, it can transform into solid asphalt or pyrobitumen. Its typical characteristic is the development of authigenic minerals around the organic matter perimeter. Sedimentary organic matter, on the other hand, comprises the original organic material and its alteration products, which have not undergone migration. This category mainly includes kerogen and its evolution into solid asphalt or pyrobitumen, characterized by clear boundaries with inorganic minerals and the absence of surrounding authigenic minerals.

In SEM imaging analysis, types of organic pores include elongated-clay-associated organic pores, pyrite-associated organic pores, and in situ autogenic organic pores, among others. These organic pores exhibit a variety of shapes, including irregular, flattened, and circular forms, reflecting the complexity and diversity of the reservoir's microstructure.

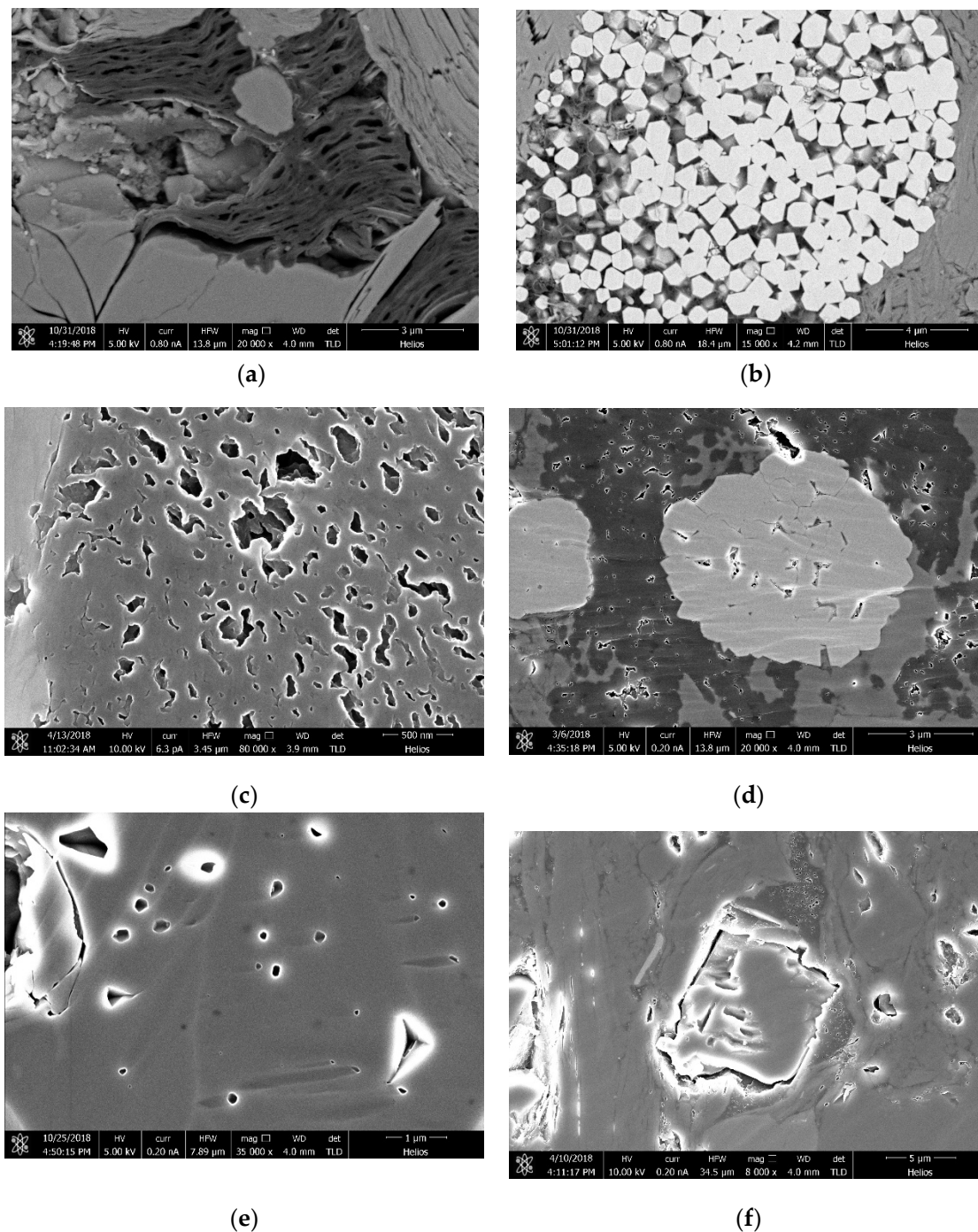


Figure 2. Examples of SEM images of shale micropores and microfractures: (a) organic pores accompanied by elongated clay; (b) organic pores accompanied by strawberry-shaped pyrite; (c) in situ authigenic bubble-like organic pores; (d) intercrystalline pores developed between straw-berried pyrite crystals exhibiting rhombus-like shapes; (e) slit-like intergranular pores; (f) microfractures.

2.3.2. Total Organic Carbon and Mineral Content

Figure 3 displays the distribution of total organic carbon (TOC), the content of clay minerals (TClays), and quartz mineral content measured via X-ray diffraction in 155 samples from the study area. The TOC values of the samples in the study area range from 0.16% to 7.4%, with an average value of 2.55% and a standard deviation of 1.53%. The TClay values range from 7.8% to 49.0%, with an average value of 29.63% and a standard

deviation of 8.29%. Meanwhile, the X-ray diffraction quartz mineral content ranges from 7.0% to 63.3%, with an average value of 32.98% and a standard deviation of 8.79%.

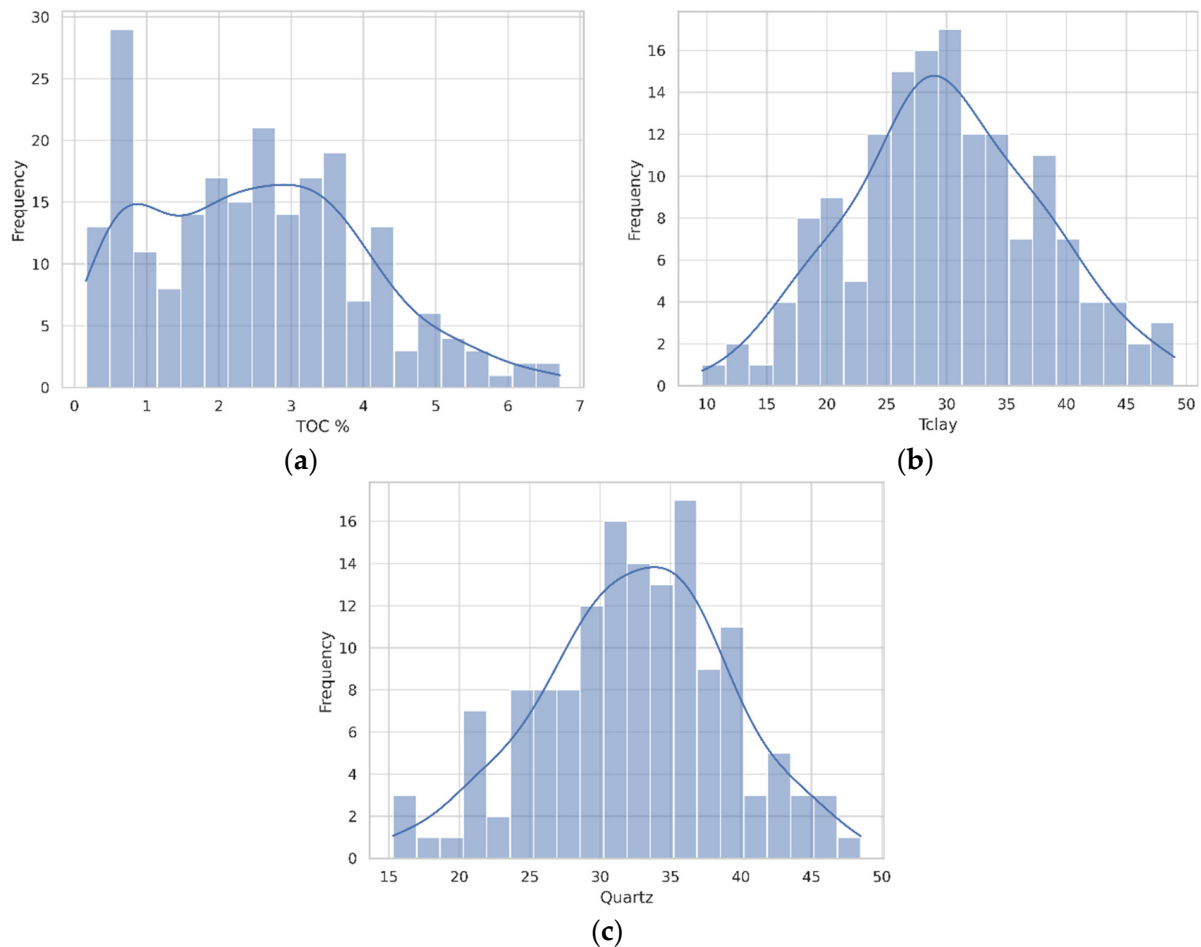


Figure 3. The histogram summarizes the experimental results for total organic carbon (TOC) measurements and part of the X-ray diffraction experimental outcomes for samples from the study area. Specifically, (a) represents the histogram for the statistical distribution of the TOC percentage content; (b) shows the histogram for the statistical distribution of TClay mineral content; and (c) illustrates the histogram for the statistical distribution of quartz mineral content. These histograms visually represent the variation and distribution of TOC, clay minerals (TClays), and quartz minerals within the samples, highlighting the range, average values, and variability of each parameter across the collected samples.

As shown in Figure 4, the analysis of whole-rock minerals and clay minerals from 155 samples across 31 wells in the target area reveals that the Haiba Wufeng–Longmaxi Formation is predominantly composed of quartz, with an average content of 34.42%, followed by carbonate minerals, with an average of 34.94%, and clay minerals, averaging 26.74%. Among the clay minerals, illite is the dominant type, averaging 55.8%, followed by mixed-layer illite/montmorillonite, averaging 29.32%. The content of brittle minerals is relatively high, accounting for 34.4%, indicating the rocks' moderate brittleness. Vertically, within a single well, as the burial depth increases, the content of illite in the Longmaxi Formation gradually decreases. Horizontally, the correlation between burial depth and mineral composition is not significant; high-quality reservoirs with high gas content tend to have lower illite content.

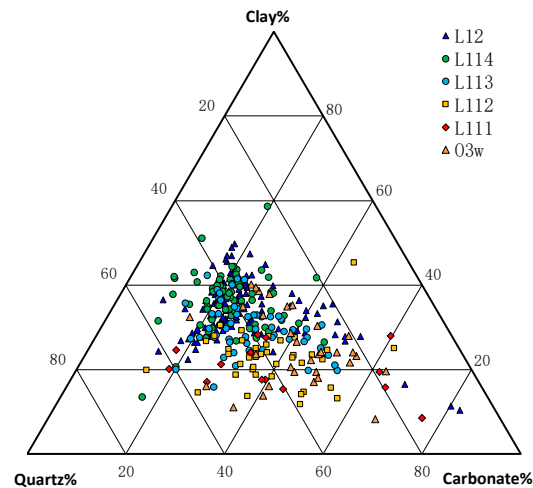


Figure 4. Rock component triangular composition diagram. The mineralogical characteristics of shale constituents in the stratigraphic units of the research area are illustrated through a ternary composition diagram. Within this diagram, from the L12 sub-unit to the O3w sub-unit, the burial depth of shale successively increases, whereas the content of clay and quartz minerals successively decreases, and the content of carbonate rocks successively increases.

2.3.3. Specific Surface Area Analysis

Figure 5 presents the isothermal adsorption–desorption curves from partial low-temperature nitrogen adsorption experiments. The curve shape is essentially a reverse S-type, akin to the type IV classification in the BDDT isothermal adsorption curve categories proposed by Brunauer et al. [20]. This suggests that the shale samples exhibit monolayer–multilayer adsorption at low pressure. Parameters such as the specific surface area of the experimental samples can be calculated using the BET equation based on experimental data obtained before capillary condensation occurs.

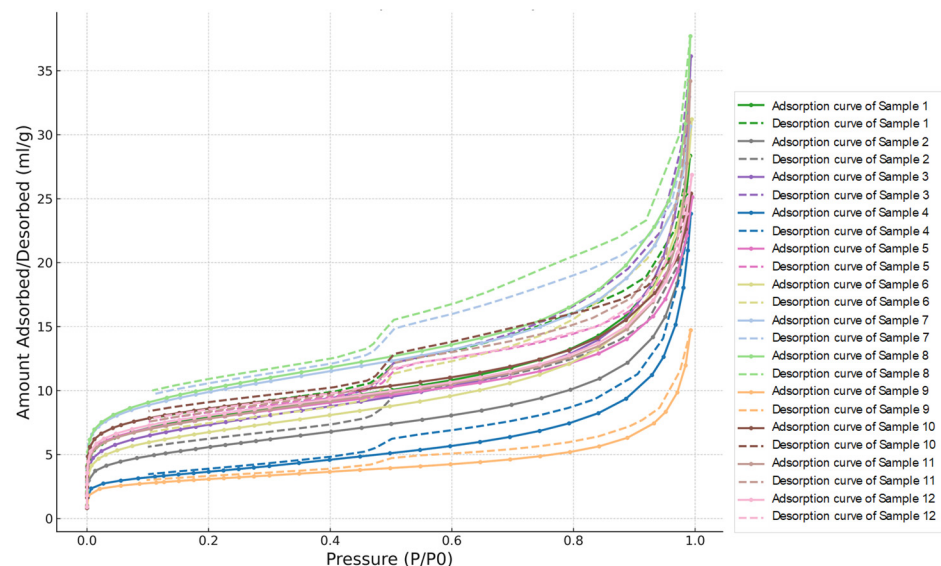


Figure 5. The isothermal adsorption–desorption curves for some experimental samples are presented. The X-axis represents the ratio of the gas pressure during adsorption to the saturated vapor pressure of the gas; the Y-axis denotes the amount of gas adsorbed, with solid lines indicating the calculated adsorption curve and dashed lines representing the calculated desorption curve.

Figure 6 presents the distribution of specific surface area, total pore volume, and average pore diameter for 85 samples from the study area. The specific surface area values of the samples range from 5.40 m²/g to 40.62 m²/g, with an average of 20.832 m²/g

and a variance of $6.732 \text{ m}^2/\text{g}$. The total pore volume values range from 0.0098 mL/g to 0.0467 mL/g , with an average of 0.0279 mL/g and a variance of 0.0077 mL/g . The average pore diameter distribution ranges from 7.03 nm to 11.05 nm , with an average of 9.17 nm and a variance of 0.93 nm .

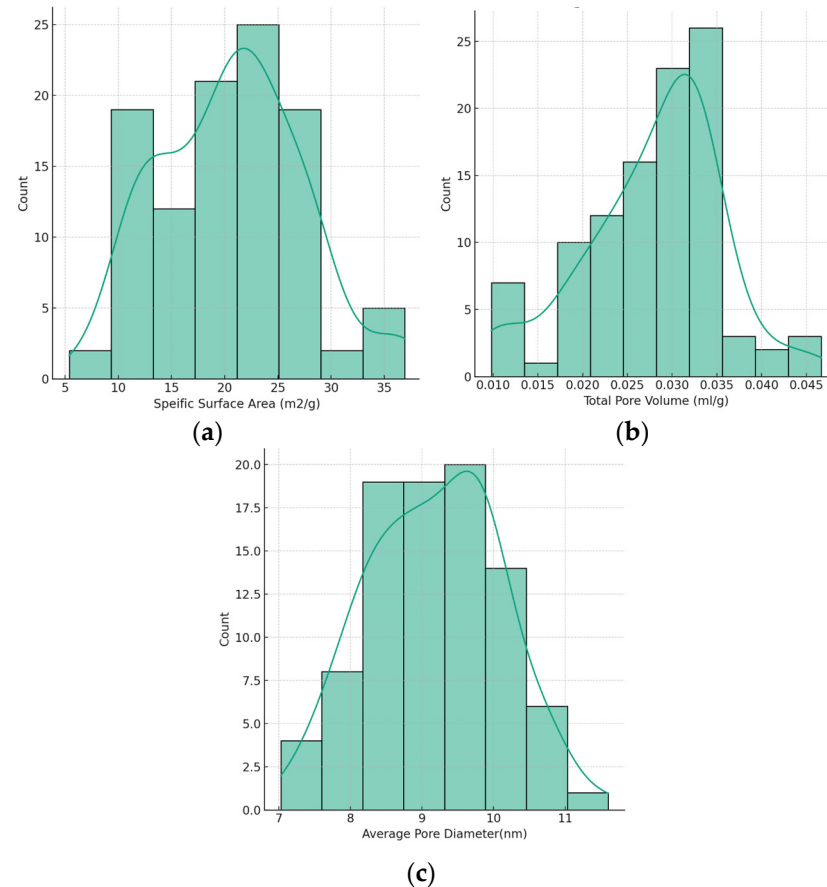


Figure 6. The distribution histograms for specific surface area (a), total pore volume (b), and average pore diameter are as follows (c).

2.3.4. Methane Adsorption Characteristic Parameter Analysis

The three-parameter Langmuir equation, as illustrated in Equation (1), has been applied to fit various adsorption isotherms, and the fitting results have been consistently satisfactory. Through this fitting approach, the adjusted R^2 values obtained range from 0.98 to 1.0, with an average of 0.99. This indicates that the three-parameter Langmuir equation, encompassing V_L , P_L , and ρ_{ads} , effectively describes the trend of adsorption quantity as a function of pressure. Compared with using complete isotherms containing 10 to 12 data points, employing these three parameters for subsequent analysis and prediction is more convenient and efficient. This method not only enhances the efficiency of analysis but also maintains the accuracy and reliability of data processing.

As shown in Figure 7, the distribution ranges of the V_L and P_L values for all samples are summarized. The V_L values range from 0.68 mL/g to 8.57 mL/g , with an average of 2.7 mL/g . The P_L values vary from 0.18 MPa to 32.23 MPa , with an average of 3.25 MPa . Additionally, the ρ_{ads} values range from 0.169 g/cm^3 to 0.661 g/cm^3 , with an average of 0.367 g/cm^3 .

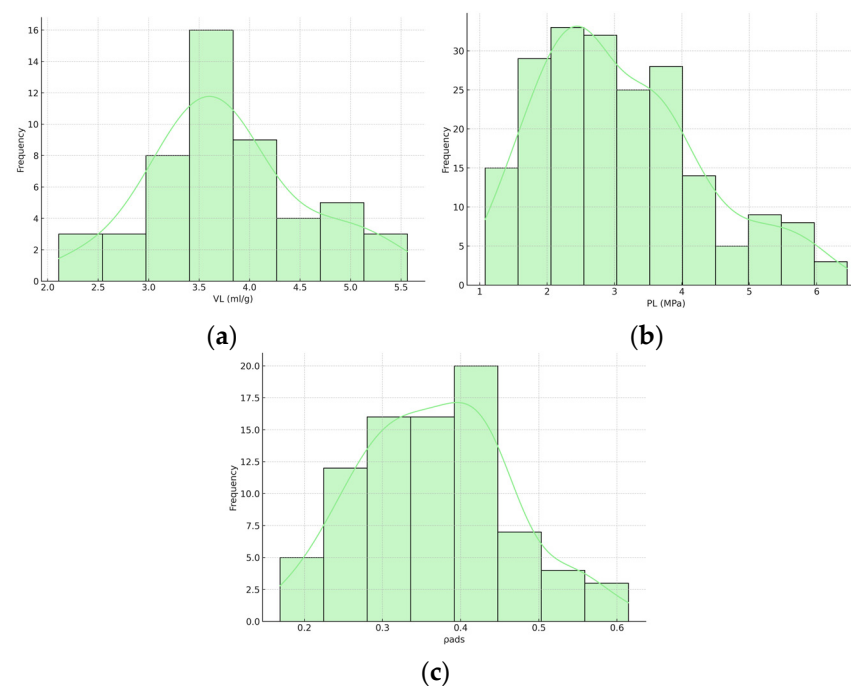


Figure 7. The distributions of the maximum adsorption capacity, V_L (a); Langmuir pressure, P_L (b); and ρ_{ads} (c).

3. Analysis of Factors Affecting Shale Gas Content

This study aims to analyze the factors influencing shale gas content by examining the correlations between various parameters, including the micropore characteristics (specific surface area (SSA) and total pore volumes (TPVs)) geochemistry (TOC), mineralogy (quartz and clay content as determined by XRD analysis), and methane adsorption (V_L , P_L , and ρ_{ads}) across different layers of shale within the study area. The objective is to identify the primary controlling factors of methane adsorption properties in shale and, consequently, unveil the determinants of shale gas content.

3.1. The Influence of Micropore Characteristics on Gas Content

As shown in Figure 8, an analysis of the correlation between specific surface area and total pore volume with Langmuir volume (V_L) in various layers of the Longmaxi and Wufeng Formations reveals a strong linear relationship. With increasing SSA and TPV values, V_L also demonstrates an increasing trend, suggesting a potential association between greater specific surface area and higher unit mass adsorption. Among these layers, as shown in Table 1, the layer with the strongest correlation between SSA and V_L is the Q3w layer, with a Pearson R value of 0.856 and an R-squared value of 0.732. For TPV and V_L , the layer with the strongest correlation is the L111 layer, with a Pearson R value of 0.850 and an R-squared value of 0.722.

As shown in Figure 9, an analysis of the correlation between specific surface area, total pore volume, and Langmuir pressure (P_L) in various layers of the Longmaxi and Wufeng Formations reveals interesting findings. It can be observed that the SSA and TPV values exhibit some degree of correlation with V_L in certain layers, but overall, they show a negative correlation. As indicated in Table 2, the layer with the strongest correlation between TPV and P_L is the L114 layer, with a Pearson R value of 0.841 and an R-squared (R^2) value of -0.707 . The layer with the strongest correlation between SSA and P_L is the L111 layer, with a Pearson R value of -0.605 and an R^2 value of 0.366. However, in most layers, the compatibility between SSA and TPV with V_L and P_L is relatively poor.

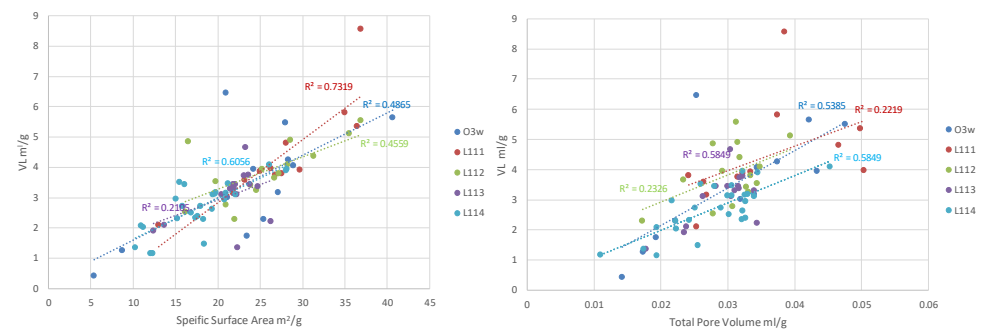


Figure 8. Correlations between V_L vs. SSA and V_L vs. TPV.

Table 1. The R-squared values (R^2) for the correlation between V_L , SSA, and TPV.

R^2	SSA vs. V_L	TPV vs. V_L
Q3w	0.732	0.524
L111	0.486	0.855
L112	0.606	0.624
L113	0.263	0.233
L114	0.454	0.722

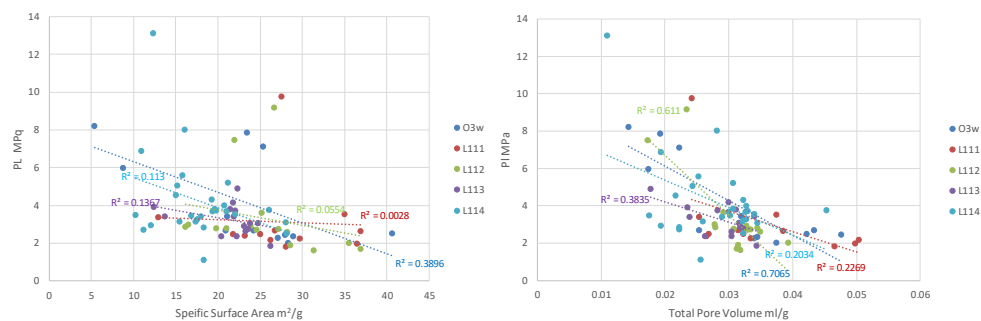


Figure 9. Correlations between P_L vs. SSA and P_L vs. TPV.

Table 2. The R^2 values for the correlation between P_L , SSA, and TPV.

R^2	SSA vs. P_L	TPV vs. P_L
Q3w	0.174	0.562
L111	0.366	0.337
L112	0.054	0.202
L113	0.003	0.027
L114	0.339	0.707

3.2. The Impact of Mineral Composition on Gas Content

As shown in Figure 10, an analysis of the correlation between total organic carbon (TOC) and Langmuir volume (V_L), as well as Langmuir pressure (P_L), in various layers of the Longmaxi and Wufeng Formations reveals significant insights. It can be observed that the TOC values exhibit a certain degree of linear correlation with V_L in all layers, and as TOC values increase, there is a corresponding increase in V_L . As indicated in Table 3, the average R-squared (R^2) value for the correlation between TOC and V_L across all layers is around 0.4.

However, the correlation between the TOC values and the P_L values in all layers is notably weak, with most layers having an R^2 value of less than 0.03.

As shown in Figures 11 and 12 and Tables 4 and 5, the analysis of the correlation between quartz mineral content, clay mineral content, and Langmuir volume (V_L), as well as Langmuir pressure (P_L), in various layers of the Longmaxi and Wufeng Formations

revealed that there is no significant correlation between mineral content and V_L or P_L in most layers.

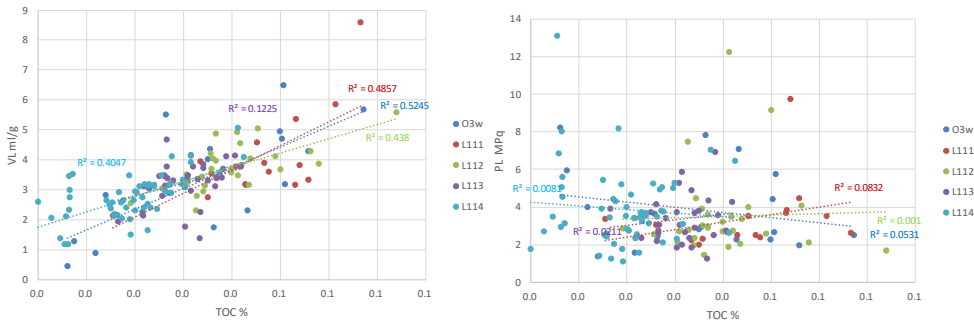


Figure 10. Correlations between TOC and V_L and P_L .

Table 3. R^2 values for the correlation between TOC and V_L and P_L .

R^2	TOC vs. V_L	TOC vs. P_L
Q3w	0.486	0.008
L111	0.123	0.030
L112	0.405	0.001
L113	0.525	0.003
L114	0.438	0.053

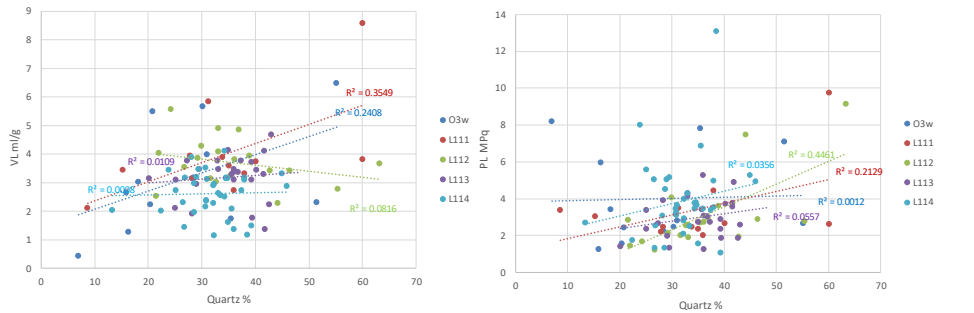


Figure 11. Correlations between quartz and V_L and P_L .

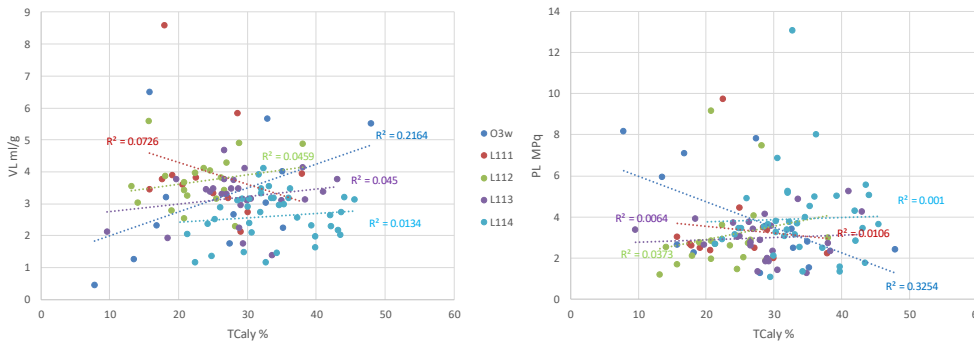


Figure 12. Correlations between TCaly and V_L and P_L .

Table 4. R^2 values for the correlation between quartz and V_L and P_L .

R^2	Quartz vs. V_L	Quartz vs. P_L
Q3w	0.011	0.446
L111	0.241	0.036
L112	0.011	0.001
L113	0.031	0.006
L114	0.355	0.122

Table 5. R² values for the correlation between TClay and V_L and P_L.

R ²	TClay vs. V _L	TClay vs. P _L
Q3w	0.216	0.006
L111	0.045	0.133
L112	0.030	0.000
L113	0.049	0.011
L114	0.034	0.325

3.3. The Gas Content Prediction Model

Previous studies have attempted to augment the parameters V_L and P_L with related parameters such as kerogen and clay content, comparing them to the sha and le isotherms [37–39]. Previous studies have attempted to augment the parameters V_L, P_L, and ρ_{ads} with related parameters such as kerogen and clay content, comparing them to the shale isotherms [40]. Additionally, there are doubts about whether clay minerals, kerogen, and other substances extracted from specific samples truly represent the inorganic or organic components of shale.

In this study, we conducted a data analysis of shale micropore characteristics (SSA and TPV), geochemistry (TOC), mineralogy (XRD analysis of quartz and clay content), and methane adsorption (V_L; P_L) data from 218 samples collected from 31 wells in the study area. This analysis aimed to elucidate the complex relationship between shale gas content and various attribute parameters. Through the correlation analysis of these parameters at different layers, we found that the three parameters V_L, P_L, and ρ_{ads} of the Langmuir equation (Equation (2)) exhibited the highest correlation with TOC content, SSA, and TPV values. Consequently, we proposed a component-based model that involves weighting the equivalent unit content of organic matter (TOC) and pore size distribution (SSA and TPV) to estimate excess adsorption isotherm content (Equation (3)).

$$V_{ex} = TOC \left(\frac{V_{Lorg} p}{P_{Lorg} + p} \right) \left(1 - \frac{\rho_{free}}{\rho_{adsorg}} \right) + TPV \left(\frac{V_{LTPV} p}{P_{LTPV} + p} \right) \left(1 - \frac{\rho_{free}}{\rho_{adsTPV}} \right) + SSA \left(\frac{V_{LSSA} p}{P_{LSSA} + p} \right) \left(1 - \frac{\rho_{free}}{\rho_{adsSSA}} \right). \quad (3)$$

In this model, V_{Lorg}, P_{Lorg}, and ρ_{adsorg} are the three characteristic parameters of the adsorption isotherm for unit organic matter methane (1% TOC), while V_{LTPV}, P_{LTPV}, and ρ_{adsTPV} are the corresponding parameters for unit pore volume (mL/g), and V_{LSSA}, P_{LSSA}, and ρ_{adsSSA} are the corresponding parameters for unit specific surface area (m²/g).

During the measurement of adsorption isotherms, each sample typically includes 10 to 14 data points (pressure, *p*, and excess adsorption, *V_{ex}*). In this study, there are a total of 53 shale samples with complete data, resulting in a total of 720 data points. These nine unknown parameters can be determined through the nonlinear fitting of the 720 *p*-*V_{ex}* data points. The initial values for each parameter are set within the experimentally obtained minimum and maximum ranges.

Table 6 presents the optimal fitting results, with R² ranging up to 0.98. Using Equation (2) and the best-fit parameters, predictions were made for the 720 data points. The predicted values exhibit a strong linear correlation with the experimental results, with an R² of 0.968. The average error and standard deviation of the error are 0.0017 and 0.0048 mL/g, respectively (as shown in Figure 13a). The error is distributed within a range of −0.12 mL/g to 0.15 mL/g for 95% of the data (as seen in Figure 13b). Therefore, this model based on shale composition and pore structure characteristics is fully suitable for engineering applications and meets production requirements.

Table 6. Best-fitting parameters for each layer.

Parameter	V _{Lorg}	P _{Lorg}	ρ _{adsorg}	V _{LTPV}	P _{LTPV}	ρ _{adsTPV}	V _{LSSA}	P _{LSSA}	ρ _{adsSSA}	R ²
Value	16.547	0.371	0.087	0.008	4.733	0.08	0.141	5.114	20.1	0.98

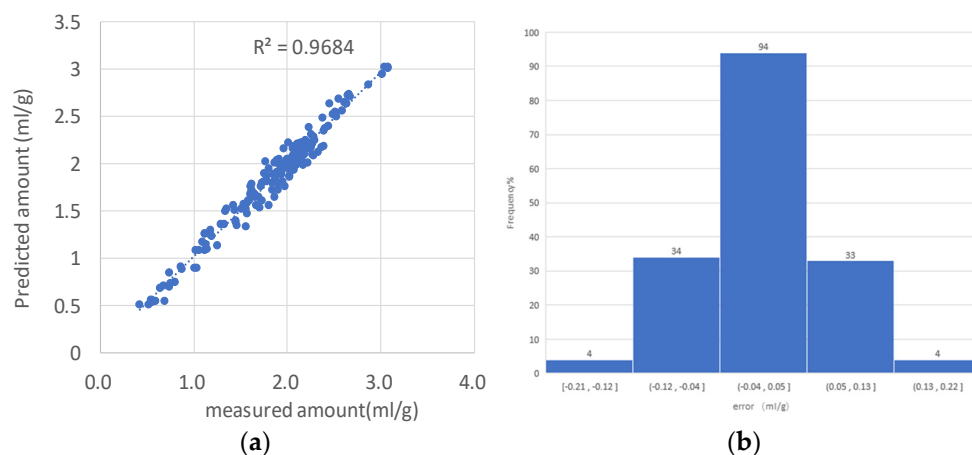


Figure 13. Correlations between predicted and measured amount (a) and error distribution (b).

4. Conclusions

- (1) This research employed methods such as scanning electron microscopy imaging, analysis of shale rock mineral components, and methane adsorption experiments to study 106 shale samples from the Wufeng–Longmaxi Formations in the Sichuan Basin. The findings revealed the potential impact of shale’s mineralogy and its microporous structures on methane adsorption characteristics.
- (2) This study analyzed the correlation between experimental data—like microporous structures (specific surface area and total pore volume), geochemical properties (e.g., total organic carbon TOC content), and mineral composition (e.g., clay and quartz content)—and the volume of adsorbed methane. A gas content model, developed based on nonlinear regression analysis, enhanced prediction accuracy, thereby providing a reliable computational tool for reserve estimation.
- (3) This research further elaborated on the variability in contributions to methane adsorption, offering new insights into the evaluation and development of shale gas reservoirs. The proposed component-based adsorption model successfully described shale’s excess adsorption isotherms, reflecting the weighted average effect of organic matter and clay composition in adsorption.
- (4) The outcomes not only improved the accuracy of shale gas reserve estimates under limited core sampling conditions but also advanced our understanding of methane adsorption mechanisms within shale. These findings have substantial implications for guiding exploration and production activities in the Sichuan Basin and other shale gas regions globally, providing a scientific basis and technical support for the effective development of future shale gas resources.

Author Contributions: Conceptualization, Y.L., C.X. and X.H.; Formal analysis, X.H.; Investigation, C.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key R&D Program of China (2020YFA0710604).

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: Author Xiaoqing Huang was employed by PetroChina Zhejiang Oilfield Company. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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