Study on pore evolution and diagenesis division of a Permian Longtan transitional shale in Southwest Guizhou, China

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Abstract
Organic-rich shales, deposited in marine-continental transitional environments, are widely distributed in southern China. The pore evolution of the Late Permian Longtan Formation shale (Guizhou Province) during its diagenesis and organic matter (OM) evolution was quantitatively and qualitatively investigated through thermal simulation, mercury intrusion capillary pressure, gas adsorption, fractal dimension, and field emission-scanning electron microscopy observation. Diagenesis and OM evolution stage were subdivided on the basis of X-ray diffraction, rock pyrolysis, and vitrinite reflectance test; moreover, the main controlling factors of pore structure during evolution were also discussed. Shales were heated to different temperatures with their vitrinite reflectance ranged between 1.23% and 3.12%, indicating that organic matter had evolved from a low- to a post-mature stage. According to the changes in clay mineral composition, hydrocarbon generation, and T_{max}, we subdivided diagenesis into four parts, each of which has a good correspondence with OM evolution. Pore volume (PV) varied between 0.012162 and 0.033482 cm³/g, while the specific surface area (SSA) varied between 13.3693 and 23.0094 m²/g. Mesopores were the main contributors to the total pore volume, while mesopores and micropores were the main contributors to the total specific surface area. In this study, the evolution of pore structure was not monotonous, but intermittent: The PV and SSA of shale samples first decreased and then increased. Maturity was the most important factor affecting the evolution of pore structure. The abundance of pores in OM, associated with hydrocarbon generation, resulted in large micro-PV and micro-SSA; moreover, the composition of clay minerals also influenced the pore structure evolution. The transformation of kaolinite into illite increased the content of illite and illite/smectite mixed layer, hence affecting the overall meso-PV and meso-SSA.

KEYWORDS
diagenesis, full-size pore distribution, hydrocarbon generation, Longtan shale, pore evolution, thermal simulation
1 | INTRODUCTION

With the increasing demand for energy, the continuous progress of experimental technology, and the improvement of development technique, shale gas, as a supply and alternative energy of conventional oil and gas, has attracted worldwide attention. Shale gas exploration began in the United States in the 19th century. In order to improve the energy structure and ensure energy security, in 2009, the Ministry of Land and Resources conducted an investigation and evaluation on the potential of shale gas resources in China. Located in the southeast margin of Yangtze plate, Guizhou Province received much attention of scholars in several years for the widely distributed organic-rich shale. The marine-continental transitional shale in this area has been proved to have certain exploration and development potential because of its large thickness, high organic matter content, and maturity associated with coal seam.

Shale gas is defined as free gas stored in natural fractures and intergranular pores, or adsorbed gas adsorbed on the surface of kerogen and clay mineral particles, or dissolved gas dissolved in kerogen and asphalt. Decades of research have shown that nanoscale pore plays an important role in shale and has a great influence on the adsorption capability and storage capacity of shale itself. On the basis of their diameter, pores are divided into micropore ($d < 2$ nm), mesopore ($d = 2-50$ nm), and macropore ($d > 50$ nm). Depending on their developmental position, pores can be divided into organic matter (OM) pore, inorganic pore, and microfracture. In order to investigate nanoscale pores, the transmission electron microscopy (TEM), the field emission-scanning electron microscopy (FE-SEM), and other visualization techniques are widely used to help us directly observe the characteristics of individual pore, such as pore size and shape. Mastalerz et al suggested that most of the OM pores related to hydrocarbon generation are elliptical and micro-sized to mesopore-sized. In addition, the heterogeneity of shale pores can be described by fractal theory, which has proved that fractal dimension ($D$) is an effective index to reflect the surface roughness or structural irregularity of shale pores. Li et al studied the pore structure and its fractal dimensions of transitional shale from east margin of the Ordos Basin, showing that the complex pore structure often has a larger $D$ value.

Pore structure is the most important part of shale reservoir research, which affects the mode of occurrence and migration of shale gas in the reservoir to a great extent, and reflects the reservoir capacity and development potential of shale. Pore structure research is mainly based on mercury intrusion capillary pressure (MICP) or gas adsorption ($N_2$ and $CO_2$) experiments to quantitatively calculate pore volume (PV), specific surface area (SSA), and to study pore size distribution (PSD) characteristics. Lu et al used MICP to analyze pores in OM in the Tuscaloosa Shale, while Chalmers et al used gas adsorption to study pore structure in the Barnett Shale. However, both of these two methods have their own limitations. Yang et al used the two methods to investigate Wufeng and Longmaxi shale and showed that pore structure obtained by MICP and $N_2$ adsorption are different due to different test conditions, sample sizes, and calculation models. In particular, the pore structure of micropores ($d < 2$ nm) cannot be measured accurately by MICP. Thus, a more accurate characterization of pore structure and full-size pore distribution in shale should combine image analyses and several quantitative experiments. However, review of previous studies on shale pore structure, such fine research is still rare.

Since the theory of diagenesis was put forward, a lot of studies have been carried out on sandstone and marine shale, and generally accepted results have been obtained. Li et al indicated that the linkage of diagenesis to diagenetic structure mainly includes: impacts of mechanical compaction during burial history, effects of depositional facies and stratigraphy, chemical process of mineralogical conversions, fluid chemistry, temperature, and stress experienced during evolution. Characteristics of pore type, pore structure, PSD, and clay mineral content have obvious changes during diagenesis. For example, macropores in montmorillonite decrease rapidly with increasing pressure, while micropores in OM gradually increase during the generation of hydrocarbon. In the past few years, pore evolution has been studied mainly by comparing shale samples with different maturities from different regions, and discussing their porosities, pore structure characteristics, and other uncertainties. After the temperature-time compensation effect of OM evolution had been proposed, many methods were developed to simulate the maturation and evolution of OM through rapid heating. Basically, the heating of low-maturity samples to different temperatures induces hydrocarbon generation, allowing the dynamic characterization of pore structure during different stages of thermal evolution. However, still little research has focused on the diagenetic stage division of transitional shales, especially the organic-rich shale widely distributed in Guizhou, and the characteristic of pore structure evolution during thermal maturation, moreover, the main factor controlling the PSD change during this process remains unclear.

In this study, based on a thermal simulation experiment, we simulated the maturation and hydrocarbon generation evolution of OM in the Longtan Formation transitional shale from the Guizhou Province: the shale samples were rapidly heated, obtaining different grades of maturity. It can minimize the effect of initial conditions, such as sedimentary environment, lithofacies, OM content, etc, on the results. Based on X-ray diffraction (XRD) and Rock-Eval pyrolysis tests, we subdivided the diagenetic and pore evolution stages.
Combining MICP, gas adsorption, D, and FE-SEM analyses, we studied the characteristics of pore structure and full-size pore distribution at different evolution stages and discussed the controlling factors of PSD. This work links OM evolution, hydrocarbon generation, diagenesis, and dynamic characterization of pore structure, and the approaches and findings are also beneficial for other shale reservoirs.

2 | GEOLOGICAL SETTING

The Guizhou Province is situated on the southeastern margin of the Upper Yangtze Plate Figure 1A. On the basis of field geology and regional geology, the tectonic evolution of Western Guizhou can be divided into six stages: basement formation stage (Pt₂-Pt₃), passive continental margin stage (Z-S), intra-continental rifting stage (D-S), stable platform stage (T₁-T₂), intra-continental orogenic stage (T₃-K₁) and extrusion uplift stage (K₂-Q).43,44

The Upper Yangtze Coal-accumulating Basin is a huge coal-accumulating basin formed in a marine-continental transitional sedimentary environment of the Late Permian. The Kangdian Upland is its main provenance,45 and the sedimentary facies from land to sea includes delta, lagoon, and swamp Figure 2A.46 The Yanshanian and Himalayan movements decomposed the basin into many intermountain depression basins and fault basins in the north and south of Sichuan Basin. Coal seams are mainly preserved in S or anti-S shaped synclines,47 such as Panguan syncline, Gemudi syncline, Qingshan syncline, Bide syncline, and Santang syncline. Guo et al3 showed that Longtan Formation shales, which deposited in a typical transitional environment, are widely distributed in Southwestern Guizhou with large thickness and moderate burial depth. Associated with coal-bearing strata, TOC, and maturity of samples are relatively high, suggesting a good exploration potential.48 However, shales in transitional facies coal measures always have strong heterogeneity of organic matter, rock mineral composition, and pore structure.49 Studies on shale gas reservoirs in this area always on the basis of core observation, geochemistry test, reservoir physical property test, and well logging interpretation. Previous studies50,51 show that the lithological assemblages are diverse and form an interbedding of “sand-mud-coal” with obvious cyclicity characteristics. The transverse macroscopic heterogeneity may be affected by sedimentary environment, and the longitudinal microscopic heterogeneity may be controlled by diagenesis.52

We collected samples of Longtan Formation from well YV1 near Panxian County, which is restricted by the well-developed faults of the Panxian structural belt Figure 1B. The Longtan Formation here represents a transitional phase dominated by delta and tidal flat. The strata are mainly composed

![Figure 1](https://example.com/fig1.png)

**FIGURE 1** A, Location of the study area in Southwest Guizhou Province and distribution of maturity in the west of Guizhou Province; B, main structures in Panxian structural belt
of gray siltstone, gray-dark silty mudstone, dark mudstone, shale, and coal seam Figure 2B.

3. SAMPLES AND METHODS

Considering the shale heterogeneity, in the early stage of this study, we collected a series of samples with different depths and lithology from well YV-1, analyzed their geochemical and mineral characteristics, and finally selected one sample as a representative to study the evolution of pore structure. The analyzed rock material was massive, well preserved, without weathering or oxidation. The Longtan shale sample contains type-III kerogen, with TOC content of 2.56%, and an initial vitrinite reflectance ($R_o$) of 1.23% Table 1. The dominant mineral is clay, followed by quartz, additionally, clay minerals are represented by illite/smectite mixed layer (I/S) and kaolinite Table 2. The sample was split into 11 aliquots. Ten of these aliquots were used in thermal simulation experiments, while the remaining one was retained as a reference.

3.1. Thermal simulation experiment

A thermal simulation experiment was carried out using pyrolysis equipment from the SGE Company (Australia), following methods of Xie et al.53 The booster and heater in the semi-closed thermal simulation system could hold pressure and temperature variations < 1 MPa and < 1°C. Ten samples, each about 15 g, were powdered to 20 meshes and inserted in a gold tube. After air evacuation, samples were heated from room temperature to their respective preset temperatures (from 200 to 650°C, 50°C/step, 20°C/h) and then held isothermally for 2 hours. A more detailed description is discussed in previous work.54

3.2. Rock-Eval pyrolysis analyses

Hydrocarbons generated during thermal simulation were collected into a vacuum system, which was connected to a

| Table 1 | Initial geochemical characteristics of transitional shale sample |
|---------|---------------------------------------------------------------|
| Sample  | Depth (m) | $R_o$ (%) | TOC (wt.%) | $\delta^{13}$C (%) | Kerogen Type<sup>a</sup> |
| YV1-0   | 852.63    | 1.23      | 2.56       | −23.4             | III |

<sup>a</sup>Kerogen type: type-III with $\delta^{13}$C > −25‰.
modified gas chromatograph (GC-6890). The free gaseous, free liquid, and pyrolytic hydrocarbons discharged during pyrolysis were detected by a flame ionization detector (FID).

### 3.3 Organic petrography analyses

The $R_o$ test was carried out by a Leitz MPV-SP photometer microscope, following China National Standards (GB/T6948-1998), with temperature of 22°C and humidity of 30%. The TOC test was performed by using a Leco CS-200 carbon-sulfur analyzer, according to China National Standards (GB/T19145-2003) with temperature of 27°C. Samples should be put in 5% HCL for 2 hours to take off carbonates and impurities before use. The kerogen type was determined by a FM-252 gas isotope mass spectrometer, following Oil and Gas Industry Standards (SY/T5238-2008). Samples were leached in 5% HCL and HF for 12 hours in turn to remove carbonates and silicates. The kerogen type was distinguished by relative PDB value.

### 3.4 XRD mineral content analyses

According to Oil and Gas Industry Standards (SY/T5463-2010), the XRD mineral content was obtained by using a D8 Discover X-ray diffractometer (Bruker). Firstly, the shale samples were crushed to <300 meshes and mixed with ethanol, then, they were grinded in a mortar and smear-mounted on glass slides for XRD analysis. The polished samples were finally analyzed at a temperature of 24°C, using both reflected white light and fluorescence microscopy.

### 3.5 Pore structure analyses

Mercury intrusion data were obtained by an AutoPoreIV9500 instrument (Micromeritics Instrument Limited Company). The maximum pressure is 413 MPa, and its measuring range is 3 nm to 1000 μm. Macropore structure characteristics, including PV, SSA, and PSD, are calculated by the cumulative mercury volume, Young-Dupré equation, and Washburn equation. Before use, samples were cut into 1-cm-sized cubes, oven dried at 60°C for more than 48 hours to eliminate free and adsorptive water, and then cooled to room temperature in a desiccator with relative humidity <10%.

Nitrogen adsorption data were obtained by a Quadrasorb SI surface area and porosity analyzer (Quantachrome Company) at different relative pressure with temperature of 77.35 K and high purity nitrogen as medium. The relative pressure is 0.004-0.995, and its measuring range is 0.35-400 nm. Meso-SSA is calculated by the Brunauer-Emmett-Teller (BET) model, and meso-PV, meso-PSD are calculated using the Barrett-Joyner-Halenda (BJH) model. According to the type of hysteresis loop, the adsorption branch was selected to calculate pore size distribution. Before experiment, samples were ground to about 60 mesh and treated as MICP test.

Carbon dioxide gas adsorption data were obtained using a NOVA4200e surface area analyzer (Quantachrome Company) at 0°C, for CO2 in this temperature can enter pores with size of 0.36 nm. The measuring range is less than 0.36-2 nm. Micro-PV and micro-SSA are calculated by the Dubinin-Astakhov (D-A) model and Dubinin-Radushkevich (D-R) model. The Density Function Theory (DFT) model considers the interaction of adsorbent and adsorbate.

| Sample ID | Experimental temperature (°C) | $R_o$ (%) | Clays | Quartz | Plagioclase | Calcite | Pyrite | Other minerals | Clay mineral composition (wt.%) |
|-----------|-------------------------------|-----------|-------|--------|------------|---------|--------|---------------|-------------------------------|
| YV1-0     | 1.23                          | 70        | 20    | 2      | 1          | 1       | 6      | 38            | 12                            |
| YV1-1     | 200                           | 1.25      | 65    | 18     | 2          | 1       | 2      | 10            | 40                            |
| YV1-2     | 250                           | 1.30      | 66    | 17     | 2          | 3       | 2      | 10            | 38                            |
| YV1-3     | 300                           | 1.35      | 68    | 18     | 1          | 1       | 2      | 10            | 39                            |
| YV1-4     | 350                           | 1.45      | 64    | 19     | 1          | 1       | 4      | 11            | 42                            |
| YV1-5     | 400                           | 1.60      | 69    | 17     | 2          | 1       | 2      | 9             | 40                            |
| YV1-6     | 450                           | 1.70      | 66    | 18     | 1          | 4       | 2      | 9             | 39                            |
| YV1-7     | 500                           | 1.82      | 70    | 17     | 1          | 2       | 2      | 8             | 32                            |
| YV1-8     | 550                           | 2.10      | 71    | 18     | 1          | 1       | 1      | 8             | 20                            |
| YV1-9     | 600                           | 2.60      | 69    | 17     | 2          | 2       | 2      | 8             | 6                             |
| YV1-10    | 650                           | 3.12      | 70    | 17     | 2          | 1       | 2      | 8             | 2                             |

(a) Other minerals are siderite and anatase; (b) I/S means illite/smectite mixed layer.
adsorbate and fits for the calculation of micro-PSD.\textsuperscript{60,61}
Before use, samples were ground to about 100 mesh and treated as MICP test.\textsuperscript{62}

3.6 | FE-SEM image analysis

Pore type and pore geometry of shale samples were observed by a Quanta 200F scanning electron microscope (FEI Company) using back-scattering electron, with temperature of 24°C and humidity 35%. Thin slabs (1 cm × 1 cm × 2 mm tall) were prepared and polished by an argon-ion cross-section polisher, and impurities on the surface of thin sections were removed. Coated with a gold film, the conductivity was obviously enhanced, which is helpful for the observation and can provide a high-resolution image.\textsuperscript{44}

3.7 | Fractal dimension analysis

Fractal dimension \((D)\) can be calculated using the Frenkel-Halsey-Hill (FHH) model and equation: \(\ln(V) = C + (D - 3) \times \ln(\ln(P_0/P))^{19}\) if shale pore structure has fractal characteristic.\textsuperscript{56} In this equation, \(P \) (MPa) is equilibrium pressure, \(P_0 \) (MPa) is the gas saturation pressure, \(V \) (cm\(^3\)/g) is adsorbed N\(_2\) volume at \(P\), and \(C\) is a constant.

4 | RESULTS

4.1 | Organic petrography and mineral content analyses

Results of \(R_o\) and mineral content of the original sample and thermal simulated samples are presented in Table 2. The \(R_o\)

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**FIGURE 3** A, Mineral composition and B, clay mineral composition of transitional shale sample

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increased from 1.23% to 3.12% with the increasing experimental temperature, indicating that OM evolved from a low-mature stage to a post-mature stage. In particular, the OM in this study reached a high-mature stage at 450°C and a post-mature stage at 600°C.

Shale minerals are mainly composed of clay and quartz, and their content changes little in the whole thermal simulation process Figure 3A. Clay mineral was the dominant shale mineral, mainly represented by kaolinite, chlorite, illite, and I/S. With increasing diageneric and organic matter evolution, there was a clear decrease in kaolinite content and a significant increase in the illite and I/S content, while the chlorite content remained stable Figure 3B. As the result showed, the clay mineral evolution was mainly characterized by the notable transformation of kaolinite into illite during the development of transitional shale diagenesis.

### 4.2 Rock-Eval pyrolysis analyses

The Rock-Eval pyrolysis results of the ten thermal simulated samples are shown in Table 3 and Figure 4. With the increase of $T_{\text{max}}$ and maturity, the production of liquid and gaseous hydrocarbons changed greatly. The production of liquid hydrocarbon first increased and then decreased: when the rock maturity exceeded the 2.6%, the production tended to 0. Meanwhile, the production of gaseous hydrocarbon showed a general increase with maturity: once rock maturity reached values of 1.7%-2.6%, the production increased significantly Figure 4C.

According to Wang et al. on the basis of $T_{\text{max}}$, clay mineral content, and hydrocarbon production, the diageneric stage of shale can be subdivided into an early diageneric stage, a middle diageneric stage A, a middle diageneric stage B, and a late diageneric stage. In this study, (a) during the early diageneric stage, corresponding to the immaturity stage of OM ($R_o < 0.8\%$, $T_{\text{max}} < 400°C$), the argillaceous deposition has not fully consolidated into rock. Sedimentary OM is affected by the biological process and diageneric, converted to kerogen, and generates a small amount of biomethane. (b) During the middle diageneric stage A, which corresponds to the maturity stage of OM (0.8% < $R_o < 1.6\%$, 400°C < $T_{\text{max}}$ < 475°C), the OM reaches the “oil window,” kerogen is degraded under thermal catalysis, and the liquid hydrocarbon increases rapidly until it reaches the highest value. The content of kaolinite starts to decrease slowly. (c) During the middle diageneric stage B, which corresponds to the high-maturity stage of OM (1.6% < $R_o < 2.5\%$, 475°C < $T_{\text{max}}$ < 525°C), the OM reaches the “gas window,” and the liquid hydrocarbon starts to transformed into gaseous hydrocarbon by pyrolysis, leading to the rapid increase of gaseous hydrocarbon. At the same time, solid asphalt and remaining kerogen are pyrolyzed to produce.

### Table 3: Rock-Eval pyrolysis analyses results

| Sample ID | Experimental temperature (°C) | $R_o$ (%) | $S^1$ (mg/g) | $S^2$ (mg/g) | $S^3$ (mg/g) | $T_{\text{max}}$ (°C) | $C_1$ (mg/g) | $C_6$ (mg/g) | $C_{14}$ (mg/g) | $O_i$ (mg/g) | $G_i$ (mg/g) | $\text{Hydrocarbon}$ (mg/g) | $\text{OM maturity stage}$ |
|-----------|-------------------------------|----------|-------------|-------------|-------------|---------------------|-------------|-------------|-------------|-------------|-----------|----------------------|--------------------------|
| YV1-1     | 200                           | 1.25     | 0.0022      | 4.02        | 0.71        | 438                 | 0.00         | 1.39        | 0.51        | 0.00         | 1.90      | 1.90                 | Low-maturity              |
| YV1-2     | 250                           | 1.30     | 0.0235      | 3.61        | 0.36        | 439                 | 0.01         | 1.46        | 0.56        | 0.00         | 2.02      | 2.03                 | Maturity                 |
| YV1-3     | 300                           | 1.35     | 0.0414      | 3.50        | 0.22        | 444                 | 0.01         | 1.54        | 0.65        | 0.01         | 2.18      | 2.20                 | Maturity                 |
| YV1-4     | 350                           | 1.45     | 0.0339      | 3.11        | 0.46        | 443                 | 0.02         | 1.69        | 0.77        | 0.02         | 2.46      | 2.48                 | Maturity                 |
| YV1-5     | 400                           | 1.60     | 0.0359      | 2.63        | 0.42        | 462                 | 0.12         | 1.88        | 0.85        | 0.12         | 2.73      | 2.85                 | High-maturity             |
| YV1-6     | 450                           | 2.10     | 0.0018      | 1.32        | 0.45        | 523                 | 0.83         | 3.83        | 0.83        | 0.83         | 3.24      | 3.11                 | High-maturity             |
| YV1-7     | 500                           | 2.60     | 0.0013      | 0.26        | 1.32        | 502                 | 0.01         | 2.12        | 1.32        | 0.01         | 2.12      | 2.12                 | High-maturity             |
| YV1-8     | 650                           | 3.12     | 0.0013      | 0.18        | 0.01        | 538                 | 0.01         | 3.53        | 0.53        | 0.00         | 3.53      | 3.53                 | Post-maturity             |
| YV1-9     | 680                           | 3.12     | 0.0013      | 0.18        | 0.01        | 538                 | 0.01         | 3.53        | 0.53        | 0.00         | 3.53      | 3.53                 | Post-maturity             |
| YV1-10    | 680                           | 3.12     | 0.0013      | 0.18        | 0.01        | 538                 | 0.01         | 3.53        | 0.53        | 0.00         | 3.53      | 3.53                 | Post-maturity             |

(a) $S_1$ = the amount of free hydrocarbon; (b) $S_2$ = the amount of thermal cracking hydrocarbon; (c) $S_3$ = the amount of CO$_2$ produced during pyrolysis of kerogen; (d) $T_{\text{max}}$ = the temperature of maximum release of hydrocarbons; (e) Hydrocarbon $= G_i + O_i$. 

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**Note:** The table values are presented in a standardized format for clarity and readability. The content is structured to maintain coherence and flow, ensuring that each sentence and paragraph contributes to the overall understanding of the document. The table and text are integrated to provide a comprehensive view of the rock-eval pyrolysis analyses results.
a large amount of methane. In clay minerals, it is characterized by the notable transformation of kaolinite into illite and I/S. (d) During the late diagenetic stage, corresponding to the post-maturity stage ($R_o > 2.5\%$, $T_{\text{max}} > 525^\circ\text{C}$), the liquid hydrocarbon has disappeared. The remaining kerogen continues to pyrolyze, and the wet gas is cracked into methane. The content of illite and I/S reaches the highest value, and the smectite in I/S transforms rapidly to illite.

### 4.3 Full-size pore distribution analyses

In this research, N$_2$, CO$_2$ adsorption, and MICP methods were used to investigate pore structure. Affected by sample size, experimental instrument, theoretical model, and calculational model, each method has its own precision and dominant measuring range. For example, in order to avoid irreversible damage to shale pore structure caused by excessively high mercury injection pressure and reduce the measurement error, MICP is limited by the maximum mercury injection pressure, and mercury cannot enter micropores. At high relative pressure, the excess adsorption capacity of CO$_2$ gradually deviates from the absolute adsorption capacity, resulting in the adsorption of CO$_2$ can only reflect micropore characteristics. The DFT theory considers the interaction of adsorbent and adsorbate and fits for micropores, while the BJH method takes into consideration monolayer adsorption, multilayer adsorption, and capillary condensation phenomenon.
and fits for mesopores. 65 Yang and Guo 66 pointed out that CO2 adsorption has advantages for 0.3-1.0 nm pore characterization, and N2 adsorption has advantages for 2-50 nm, while MICP has advantages for 100-10 000 nm Figure 5. Based on the dominant measuring range and the division standard of pore type, we take 2 and 50 nm as the boundary, and combined results from CO2 adsorption, N2 adsorption, and MICP to obtain an accurate characterization of full-size pore distribution. The average pore diameter was calculated by equation: \((4V_p/A_s) \times 2\), where \(V_p\) = total PV of shale, and \(A_s\) = total SSA. 67 Incremental PV distribution curves were used to investigate the characteristics of PSD, and each peak in the PSD curve represents the development of a specific pore size. 56

The PV, SSA, and average pore diameter of each shale sample are shown in Table 4. The PV values varied between 0.012162 and 0.033482 cm3/g, the SSA between 13.3693 and 23.0094 m2/g, and the average pore diameter between 7.16 and 14.47 nm. The PV and SSA of the samples first decreased and then increased with increasing maturity Figure 6. The average micro-, meso-, and macro-PV values were 0.002912, 0.019986, and 0.003864 cm3/g, accounting for 11.24%, 73.97%, and 14.79% of the total PV, respectively. Mesopores were the most abundant pores (the main contributors to the total PV), followed by macropores and micropores. The PSD curve of the shale samples was multimodal: the highest peak is at 10-30 nm, corresponding to a maximum value of 0.0067 cm3/g. Other peaks were observed at 0.4-0.8 and 2-4 nm, with maximum values of 0.0021 cm3/g Figure 7A. The average micro-, meso-, and macro-SSA values were 8.9202, 9.1812, and 0.0600 m2/g, accounting for 49.29%, 50.38%, and 0.33% of the total SSA, respectively: Micropores and mesopores were the main contributors to the total SSA, while the contribution of macropores was negligible. The major peak of SSA was observed at 0.4-0.8 nm, corresponding to a maximum value of 8.4 m2/g. Other peaks were found at 2-4 and 10-30 nm, with maximum values of 3.9 m2/g and 2.1 m2/g, respectively Figure 7B.

4.3.1 | Micro pore

The micro-PV varied between 0.001626 and 0.004424 cm3/g, while the micro-SSA varied between 5.269 and 11.960 m2/g Table 4. According to the CO2 adsorption curve Figure 8A, the min and max adsorbed gas volumes were registered for samples YV1-2 and YV1-6, respectively. With increasing of maturity, it appears that the amount of adsorbed gas first increased, then decreased, and finally increased again. The micro-PV and micro-SSA followed the same trend. In fact, the PV and SSA tended to increase from the original sample YV1-0 (Ro = 1.23%) to the mature sample YV1-2 (Ro = 1.30%, T_max = 439°C). At a further temperature
increase, however, the PV and SSA began to decrease, reaching the min value in the high-mature sample YV1-6 ($R_o = 1.70\%$, $T_{max} = 502^\circ C$). Afterward, the PV and SSA increased again, reaching maximum values in the post-mature sample YV1-10 ($R_o = 3.12\%$, $T_{max} = 538^\circ C$). When $R_o$ was between 1.35% (in sample YV1-3, $T_{max} = 441^\circ C$) and 1.45% (in sample YV1-4, $T_{max} = 443^\circ C$), the proportion of micro-PV and SSA decreased significantly, increasing again afterward Figure 6C,D. As shown in Figure 7, the PV and SSA of samples having different maturity depended mainly on pores ranging between 0.4 and 0.8 nm. For the mature sample YV1-2 ($R_o = 1.30\%$, $T_{max} = 439^\circ C$), we identified an additional peak at 2 nm, this peak results in a larger micro-PV than in other samples.

4.3.2 | Mesopore

The meso-PV varied between 0.007965 and 0.025036 cm$^3$/g, while the meso-SSA varies between 5.7956 and 13.5514 m$^2$/g Table 4. From the N$_2$ adsorption-desorption isotherms Figure 8B, we found the amount of adsorbed gas first decreased and then increased, and the meso-PV and meso-SSA followed the same trend. The PV and SSA decreased from the original sample YV1-0 ($R_o = 1.23\%$, $T_{max} = 462^\circ C$) to the high-mature sample YV1-5 ($R_o = 1.60\%$, $T_{max} = 462^\circ C$). Afterward, the PV and SSA began to increase, reaching maximum values in the post-mature samples YV1-9 ($R_o = 2.60\%$, $T_{max} = 533^\circ C$) and YV1-10 ($R_o = 3.12\%$, $T_{max} = 538^\circ C$). During the evolution of OM from a low-mature to a mature stage (from sample YV1-0 ($R_o = 1.23\%$) to sample YV1-4 ($R_o = 1.45\%$, $T_{max} = 443^\circ C$), the proportion of meso-PV and meso-SSA increased, although the total PV and SSA were decreasing Figure 6C,D. When the $R_o$ reached values between 1.45% (YV1-4, $T_{max} = 443^\circ C$) and 1.60% (YV1-5, $T_{max} = 462^\circ C$), the proportion of meso-PV and meso-SSA decreased significantly, and then increased again. As shown in Figure 7, the PV and SSA of samples having different maturity levels were mainly influenced by the presence of pores with sizes between 10 and 30 nm. On the other hand, the low-mature samples YV1-0 ($R_o = 1.23\%$) and YV1-1 ($R_o = 1.25\%$, $T_{max} = 438^\circ C$) presented an additional peak at 3 nm, which resulted in a higher meso-PV than in other samples.
4.3.3 Macropore

The macro-PV varied between 0.0018 and 0.0066 cm$^3$/g, while the macro-SSA varied between 0.016 and 0.131 m$^2$/g. The mercury intrusion-regression curve is illustrated in Figure 8C. The minimum and maximum injected mercury volumes were registered in samples YV1-0 and YV1-10, respectively. However, with increasing maturity, the macro-PV and macro-SSA did not change regularly, and the samples showed different PSD characteristics. During the evolution of OM from its low-mature to post-mature stage, the proportion of macro-PV increased and decreased intermittently, while the proportion of macro-SSA continued to decrease Figure 6C,D. When $R_o$ reached values between 1.45% ($YV1-4$, $T_{\text{max}} = 443^\circ \text{C}$) and 1.60% ($YV1-5$, $T_{\text{max}} = 462^\circ \text{C}$), the proportion of macro-PV and macro-SSA decreased significantly, and then increased again. As shown in Figure 7, the PV of the low-mature sample YV1-1 ($R_o = 1.25\%$, $T_{\text{max}} = 438^\circ \text{C}$) and of the high-mature sample YV1-8 ($R_o = 2.10\%$, $T_{\text{max}} = 523^\circ \text{C}$) mainly depended on the presence of pores with size of 5000 nm. Meanwhile, the PV of the high-mature sample YV1-8 ($R_o = 2.10\%$, $T_{\text{max}} = 523^\circ \text{C}$) and of the
FIGURE 8  Low-pressure CO\(_2\) adsorption isotherm (A), low-pressure N\(_2\) adsorption-desorption isotherm (B), and high-pressure mercury intrusion-regression curve (C) of transitional shale sample. \(P\) = actual gas pressure, \(P_o\) = vapor pressure of the adsorbing gas.
 ↑ post-mature sample YV1-10 ($R_o = 3.12\%$, $T_{\text{max}} = 538^\circ$C) mainly depended on the presence of pores with size of 500-50 000 nm.

### 4.4 Fractal dimension analyses

Fractal dimension can describe pore surface roughness and structure complexity of shale. The D value ranges between 2 and 3, with higher values indicating rougher surfaces or inhomogeneous pore structures. According to the N$_2$ adsorption data and the fractal FHH model, $D$ of Longtan shale samples are calculated according to slopes of ln($V$) vs ln(ln($P_0/P$)) Figure 9A. Fractal dimension of samples ranges between 2.555 and 2.813 Table 5. With increasing maturity, this value first decreased and then increased, similarly to the variation regular of PV and SSA Figure 9B, indicating that samples in the mature and post-mature stage tended to have rougher pore surfaces and more complicated pore structures. The $D$ values were positively correlated with the SSA, especially with the meso-SSA Figure 9C, indicating this is an important factor affecting the complexity of pore structure in shale.

### 4.5 Pore type and evolution characteristic analyses

The N$_2$ adsorption-desorption isotherms of samples with different maturity are shown in Figure 8B. All the adsorption isotherms have an anti-S shaped and can be classified as type IV curve, indicating an abundance of small pores (micropores and mesopores) according to IUPAC classification. The type of hysteresis loops contains information about pore shape and pore size distribution. In our study, all samples presented a type $H_2$ hysteresis loop, indicating an abundance of ink-bottle pore.

| Sample ID | Experimental temperature (°C) | $R_o$ (%) | Fitting equation | Fitting coefficient ($R^2$) | Fractal dimension |
|-----------|-------------------------------|-----------|------------------|---------------------------|------------------|
| YV1-0     | 1.23                          | $y = -0.187x + 1.514$ | 0.873            | 2.813                     |
| YV1-1     | 200                           | $y = -0.349 + 1.680$  | 0.973            | 2.651                     |
| YV1-2     | 250                           | $y = -0.372x + 1.543$ | 0.976            | 2.628                     |
| YV1-3     | 300                           | $y = -0.369x + 1.515$ | 0.969            | 2.631                     |
| YV1-4     | 350                           | $y = -0.387x + 1.493$ | 0.973            | 2.613                     |
| YV1-5     | 400                           | $y = -0.429x + 1.288$ | 0.978            | 2.571                     |
| YV1-6     | 450                           | $y = -0.445x + 1.150$ | 0.975            | 2.555                     |
| YV1-7     | 500                           | $y = -0.439x + 1.165$ | 0.981            | 2.561                     |
| YV1-8     | 550                           | $y = -0.420x + 1.390$ | 0.990            | 2.580                     |
| YV1-9     | 600                           | $y = -0.400x + 1.582$ | 0.989            | 2.600                     |
| YV1-10    | 650                           | $y = -0.380x + 1.630$ | 0.992            | 2.620                     |
which was considered as OM-hosted pore in many researches.\textsuperscript{71} In addition, compared with type H\textsubscript{1} hysteresis loop, which indicates cylindrical pores and a simple pore structure, the type H\textsubscript{2} hysteresis loop indicates a more complex pore structure and the existence of mixing effect (delayed condensation and network penetration), resulting in the PSD can only be calculated by adsorption branch rather than desorption branch.\textsuperscript{59}

The SEM observation Figure 10 and 11 showed that OM pores, inorganic pores, and microfractures developed differently in shale samples having different maturities. In this study, we observed two kinds of OM pores, one is primary organic pore,\textsuperscript{72} the other is pore in nanoporous bitumen, as the result of the secondary cracking of bitumen compounds.\textsuperscript{73} In the low-mature samples (from YV1-0 to YV1-2, $R_o = 1.23\% - 1.30\%, T_{max} = 438-439°C$), most OM surfaces were smooth and flat, with almost no organic pores. Only a few OM pores were observed sporadically in OM and they were irregularly distributed Figure 10A,B. Because temperature did not reach the “oil window,” the observed OM pores could have been original. In the mature samples (from YV1-3 to YV1-5, $R_o = 1.35\% - 1.60\%, T_{max} = 441-462°C$), the number of OM pores gradually increased. Here, the OM pores were mainly related to the generation of liquid hydrocarbon, and they presented angular or elliptical shapes Figure 10C,D. In the high-mature samples (from YV1-6 to YV1-8, $R_o = 1.70\% - 2.10\%, T_{max} = 465-523°C$), pores were observed both inside the OM and at the edge of OM and minerals Figure 10E. Bubble-shaped OM pores Figure 10F, associated with the generation of gaseous hydrocarbons, were observed in kerogen, moreover, we observed needle-like OM pores Figure 10G and some neighboring interconnected or merged sponge-like OM pores Figure 10H in asphaltene. Shrinkage cracks occurred at the edge of OM and minerals Figure 10I, they can be interpreted as the result of the expulsion of volatile matter and of the contraction of solid OM during hydrocarbon generation.\textsuperscript{11} In the post-mature samples (from YV1-9 to YV1-10, $R_o = 2.60\% - 3.12\%, T_{max} = 533-538°C$), a large number of tightly arranged OM pores, resulting from secondary cracking, was observed in asphaltene Figure 10J,K. Large pores or collapses resulting from the mass consumption of OM could also be observed in the OM itself Figure 10L.

Intraparticle pores, interparticle pores, and microfractures are important parts of the shale pore system.\textsuperscript{38} The intraparticle pores observed in this study mainly included dissolution pores and pores within mineral particles. The dissolution pores

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**FIGURE 10** Scanning electron microscope (SEM) images showing changes of organic matter pores in hydrocarbon generation and evolution of organic matter. A and B, Sporadically distributed irregularly organic matter (OM) pores within smooth organic matter surface; C and D, angular-shaped or elliptical-shaped OM pores within kerogen, as the result of liquid hydrocarbon generation; E, OM pores at the edge of the OM and minerals; F, bubble-shaped OM pores within kerogen, as the result of gaseous hydrocarbon generation; G, needle-like OM pores formed in asphaltene; H, interconnected OM pores, which form an effective pore network and enhance the heterogeneity of pore structure; I, shrinkage cracks at the edge of the OM and minerals; J and K, a large number of OM pores in asphaltene with compact arrangement; and L, large pores or collapses resulting from mass consumption of organic matter.
were characterized by irregular shapes and large sizes and occurred mainly in feldspar Figure 11A. Influenced by the particle deformation during sediment compaction, the intraparticle pores within mineral particles (e.g., illite) were relatively small Figure 11B. The interparticle pores were abundant in the shale samples and had a good connectivity. These pores usually occurred between minerals and were characterized by disordered shapes and large sizes Figure 11C, while interparticle pores between clay minerals were lamellar-shaped, slit-shaped, or wedge-shaped Figure 11D. Intergranular pores within pyrite framboids were angular-shaped, and some of these same pores were filled with OM Figure 11E. Microfractures, with length between several to tens of μm and a width of several μm, were abundant in the shale samples. In the clay, some fractures were oriented following a certain direction due to compaction Figure 11F.

5.1 | Relationship between maturity and pore structure

The relationship between maturity and pore structure parameters is illustrated in Figure 12. With increasing maturity, the meso-PV and total PV first decreased and then increased (Ro = 1.23%-1.60%). Meanwhile, the micro-PV first increased (Ro = 1.23%-1.30%), then decreased (from Ro = 1.30%-1.70%), and finally increased. The macro-PV increased and decreases intermittently during the whole process, while it increases clearly for Ro = 1.80%-2.10% Figure 12A. On the other hand, the SSA first decreased, and then (from Ro = 1.60%) increased Figure 12B.

During hydrocarbon generation and the evolution of OM, changes in shale pore structure were mainly related to the formation of OM pores.17 With increasing maturity, the number of OM pores in kerogen and asphaltene increased continuously, due to the generation of liquid and gaseous hydrocarbons Figure 10F,H,J,K. During the low-mature stage, the decrease in PV could have been related to asphalt filling, which perhaps blocked part of the pore space. During the high-mature stage, the observed significant increase in PV could have been related to the secondary cracking of asphalt, which was released from
early formed pores. Additionally, the increase in meso-PV and macro-PV could have been related to the interconnection of neighboring pores and collapses in the OM.\textsuperscript{11}

\subsection*{5.2 Relationship between clay mineral composition and pore structure}

Intraparticle and interparticle pores in minerals are affected by diagenesis. During the early diagenetic stage and the middle diagenetic stage A, compaction had a great influence on shale porosity: the PV showed a downward trend, since compaction can easily deform or close pores in minerals Figure 12A. After the middle diagenetic stage B, the effect of compaction on porosity was not so obvious anymore, and the effect of mineral composition on pore structure was gradually revealed Figure 12B.

As shown in Table 2, although the shale samples had different maturities, they presented overall similar mineral compositions, excluding clay minerals, which varied greatly. Harris et al (2011)\textsuperscript{75} suggested that silica-dominated rocks are more brittle and more prone to natural fracture, while clay-dominated rocks are more ductile. Based on the lithofacies classification scheme for organic mudstones proposed by, Gamer-Diaz et al.\textsuperscript{76} samples in this study deposited in the tidal flat and belong to silica-rich argillaceous mudstone, which has a certain resistance to compaction. Samples YV1-5 to YV1-10, rather than YV1-0 to YV1-4, were selected for this study, because they had already entered the middle diagenetic stage B, and the effect of compaction on pore structure was weakened. Moreover, the transformation of the clay minerals was significantly accelerated in this period, and the difference of mineral composition has become an important factor affecting pore structure Figure 4B. The relationship between clay mineral composition and pore structure parameters is shown in Figure 13. The R square values are mainly distributed between 0.6 and 0.8 (less than 0.9), however the relationship between a particular clay mineral and pore structure (no matter micro-, meso-, or macropore) is consistent: positive correlations were observed between I/S, illite and PV Figure 13A,C,E, SSA Figure 13B,D,F; negative correlations were instead observed between kaolinite and PV, SSA; no correlation was found.
between chlorite and pore structure. The weak correlation in this research may be related to sedimentary environment and lithofacies, because frequent changes in sedimentary environment may affect the material source of shale and lead to a complex mineral composition. As mentioned above, SSA and D were positively correlated Figure 9C, indicating that the
samples with larger SSA tended to have rougher pore surfaces and more complex pore structures. Compared with other minerals, illite and I/S were layered or flocculent and had rougher surfaces Figure 11B, resulting in larger SSAs and stronger adsorption capacities. The microfractures on the surface of illite and pores separated by needle-shaped clay minerals may have positively influence on the macro-PV. Hence, the transformation of kaolinite into illite and the increase in I/S content were important factors determining the increase in SSA.

5.3 Characteristics of pore structure during rock evolution

Our results show that thermal maturity is the most important factor affecting shale pore structure, although clay mineral composition also seems to have some influence. During evolution, the PV and SSA of the shale samples did not change monotonously, but intermittently. The main observed patterns are described below Figure 14.

(a) During the early diagenetic stage, corresponding to the immature stage of OM evolution \( (R_o < 0.8\%, \ T_{\text{max}} < 400^\circ\text{C}) \), the OM was not in the “oil window” and only a small amount of biogenic methane was produced through biological action. At this time, the sediment was still muddy (not completely consolidated)\(^3\) and the shale pore system was mainly composed of mesopores and macropores. With the development of diagenesis, compaction inhibited pore development, reducing PV and SSA. (b) During the middle diagenetic stage \( A_1 \), corresponding to the low-mature stage of OM evolution \( (R_o = 0.8\%-1.3\%, \ 400^\circ\text{C} < T_{\text{max}} < 450^\circ\text{C}) \), kerogen began to produce liquid hydrocarbons. Meanwhile, the number of OM pores increased, resulting in a micro-PV increase. During the middle diagenetic stage \( A_2 \), corresponding to the mature stage of OM evolution \( (R_o = 1.3\%-1.6\%, \ 450^\circ\text{C} < T_{\text{max}} < 475^\circ\text{C}) \), OM pores increased due to the degradation of kerogen and to the generation of liquid hydrocarbons. However, because of asphalt filling, the micro-PV decreased. Jarvie et al\(^28\) and Mastalerz et al\(^17\) also found this phenomenon, and they interpreted the observed decline in porosity during this time as the result of prior pore filling by oil, bitumen or asphaltenes that reduced the available open pore space and restricted gas flow. However, it is hard to observe this process directly by SEM. To test if the pore volume decrease is caused by pore filling by bitumen, Mastalerz et al\(^17\) extracted the most mature sample with dichloromethane and reanalyzed for micro-PV and meso-PV. The micro-PV of shale sample significantly increased, while the meso-PV remained comparable to that before extraction. These observations show that bitumen filled in small pores contributes to the decrease of pore volume at mature stage. With the development of diagenesis, kaolinite slowly began to transform into illite. Microfractures on the surface of illite increased the meso- and macro-PV. However, under the influence of compaction, there was an overall decrease in PV. (c) During the middle diagenetic stage \( A_3 \), corresponding to the high-mature stage of OM evolution \( (R_o = 1.6\%-2.5\%, \ 475^\circ\text{C} < T_{\text{max}} < 525^\circ\text{C}) \), solid asphalt and residual kerogen produced a lot of methane by cracking. The
production of liquid hydrocarbons decreased rapidly, while the production of gaseous hydrocarbon increased significantly. Moreover, bubble-shaped pores appeared in the OM and needle-like pores appeared in asphaltenes, resulting in an increase in micro-PV. Meanwhile, some neighboring sponge-like OM pores interconnected or merged with each other, increasing the meso-PV. Shrinkage cracks occurred at the edge of the OM and minerals. Additionally, a large amount of the kaolinite contained in clay transformed into illite and the content of illite and I/S increased significantly, resulting in an increase in meso-PV and macro-PV. The illite and I/S presented layered or flocculent surfaces, hence, an abundance of these minerals led to high SSA. Overall, these processes caused rapid PV and SSA increases in the shale samples. (d) During the late diagenetic stage, corresponding to the post-mature stage of OM evolution \((R_o > 2.5\%\), \(T_{\text{max}} > 525^\circ\text{C}\)), liquid hydrocarbons disappeared, while gaseous hydrocarbons slowly increased. A large number of tightly arranged OM pores appeared in asphaltenes due to secondary cracking. As mentioned above, pores filled by bitumen are released and increase the pore volume and porosity. Moreover, several collapses occurred due to the mass consumption of OM. As a result of the high pressure and temperature conditions, the width of the shrinkage cracks increased, while the composition of the clay minerals remained stable. Overall, the PV and SSA of the shale samples slowly increased during this stage.

However, this study presents some inadequacies. Firstly, there are few samples to choose from and the results may be affected by shale heterogeneity. Comparative experiments of samples selected form adjacent wells can provide more credibility to the conclusion. Secondly, the influence of sedimentary facies and rock type on pore structure needs further discussion. Thirdly, it did not involve the study of pore structure characteristics in extremely high-mature shales \((R_o > 3.5\%\), \(T_{\text{max}} > 550^\circ\text{C}\)). In this period pore structure may change greatly because of the extremely high temperature and pressure. Fourthly, it was not verified whether the OM content can play an important role in PSD in shales having similar maturity levels.

**6 | CONCLUSION**

In this work, shale samples represent transitional facies dominated by tidal flat and lagoon and have high content of OM and clay minerals. The pore system is dominated by nanoscale pores. Pores are mainly ink-bottle shape and have a type H2 hysteresis loop. Most of OM-hosted pores are bubble-shaped with small pore size, while mineral-hosted pores are mainly wedge-shaped or irregular with large pore size. Thermal simulation experiment can minimize the interference of other uncertainties and help the OM evolved from a low-mature stage to a post-mature stage.

1. In this work, shale samples represent transitional facies dominated by tidal flat and lagoon and have high content of OM and clay minerals. The pore system is dominated by nanoscale pores. Pores are mainly ink-bottle shape and have a type H2 hysteresis loop. Most of OM-hosted pores are bubble-shaped with small pore size, while mineral-hosted pores are mainly wedge-shaped or irregular with large pore size. Thermal simulation experiment can minimize the interference of other uncertainties and help the OM evolved from a low-mature stage to a post-mature stage.

2. The diagenesis stage is subdivided into four parts, and each of them has a good correspondence with OM evolution and hydrocarbon generation. The evolution of clay minerals was mainly characterized by the transformation of kaolinite into illite during the middle diagenetic stage B. The OM evolution was accompanied by the formation of liquid hydrocarbon and gaseous hydrocarbon. Both of them have important influence on pore structure evolution.

3. In the process of thermal evolution, the PV and SSA of shale samples varied between 0.012162-0.033482 cm³/g and 13.3693-23.0094 m²/g. Affected by compaction, clay mineral transformation, and hydrocarbon generation, pore structure did not change monotonously, but intermittently. The PV and SSA first decreased and then increased. However, mesopores contributed most to total PV, while micro- and mesopores together contributed most to total SSA. The plugging and cracking of asphalt are important reasons for the variation of pore volume and porosity during mature stage and over-mature stage.

4. Maturity was the most important factor controlling PSD. The abundance of pores in OM, associated with hydrocarbon generation, resulted in large micro-PV and micro-SSA. Moreover, the composition of clay minerals also influenced the pore structure evolution. The transformation of kaolinite increased the content of illite and I/S mixed layer, hence affecting the overall meso-PV and meso-SSA. Sedimentary facies and lithology also have some influence on pore structure.

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