Nanopore Structure and Origin of Lower Permian Transitional Shale, Eastern Ordos Basin, China
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ABSTRACT: Nanopores in the shale play a vital role in methane adsorption, and their structural characteristics and origins are of great significance for revealing the mechanism of methane adsorption, desorption, and diffusion. In this paper, through low-temperature ashing and low-pressure gas adsorption experiments, the nanopore structure of original shales and ashed shales was quantitatively characterized, and the nanopore origins in the transitional shale of lower Permian in eastern Ordos Basin were analyzed. The results show that the pore volume (PV) and specific surface area (SSA) of nanopores in transitional shale reservoirs are 0.0217–0.0449 cm$^3$/g and 13.91–51.20 m$^2$/g, respectively. The average contribution rates of micropores (<2 nm), mesopores (2–50 nm), and macropores (50–100 nm) to PV are 18.78, 72.26, and 8.96%, respectively, and the average contribution rates to SSA are 66.19, 33.10, and 0.71%, respectively. In addition, it is found that the average contribution rates of inorganic minerals and organic matter to the SSA of micropores are 55.9 and 44.1%, respectively, and the average contribution rates to SSA of mesopores are 92.3 and 7.7%, respectively. Combining the adsorption properties of the main clay minerals and kerogen in shale, it is concluded that organic pores control the adsorption of methane with an absolute advantage in transitional shales. It is of great significance to understand the mechanism of methane occurrence, desorption, and diffusion in shales by clarifying the origins of multiscale pores.

1. INTRODUCTION
In recent years, with the industrial development of marine shale gas in North America and southern China, researchers have been attracted to study the exploration potential of marine-continental transitional shale gas. China’s transitional shale gas resources amount to 19.8 trillion cubic meters, accounting for 25% of the total shale gas resources. The previous studies on the transitional shale mainly focused on resource potential evaluation and pore structure characterization, but the pore origin was rarely studied. The transitional shale reservoir which is located in Shanxi Formation, eastern Ordos Basin, is characterized by wide distribution, large cumulative thickness, and high organic matter (OM) content, showing good prospects for gas exploration and development. With the increasing understanding of shale gas resources, researchers have found that the proportion of adsorbed gas in the shale is 20–85%, and the smaller the pores, the higher the adsorption capacity of methane, due to their large specific surface area (SSA). Moreover, the adsorption capacity of organic pores and inorganic mineral pores in the shale matrix also shows a big difference. Therefore, it is of great significance to carry out the quantitative characterization of the nanopore structure and origin of the shale to reveal the occurrence mechanism of methane.

The research on the reservoir pore structure is generally based on experiments such as low-pressure CO$_2$/N$_2$ adsorption (LP-NGA), high-pressure mercury injection, nuclear magnetic resonance, nano-CT, and field emission scanning electron microscopy (FE-SEM). However, the understanding of multiscale pore origins in shales mostly comes from qualitative research on the correlation between pore structure parameters and the content of total organic carbon (TOC) or inorganic minerals, and there is no accurate quantitative research. In recent years, some scholars have used the means of separating kerogen to quantitatively study the effect of organic pores on methane adsorption capacity and pore structure. The authors of the work conducted high-pressure methane adsorption experiments on Posidonia shales and kerogens and inferred that approximately half of the gas was adsorbed in OM based on the isotherm adsorption mass balance. The authors of the work conducted methane isothermal adsorption experiments on the shales and kerogens of the Lower Cambrian–Lower Silurian in the Sichuan Basin. Supercritical Dubinin Radushkevich and Langmuir excess
adsorption models were applied to estimate that the contribution of kerogen to shale methane adsorption capacity was less than 50%. The authors of the work performed gas adsorption experiments on the lacustrine shale and separated the OM in the Chang 7 member of the Ordos Basin and estimated that the average contribution of OM to pore volume (PV) was approximately 30.83%. Remarkably, the purity of kerogen used in the abovementioned experiments was often low because only chemical reagents were used to remove carbonates and silicates, and it was difficult to successfully interfere with other common inorganic components, such as pyrite and anatase. In addition, it was unknown whether the pore structure of OM would be affected by chemical treatment. Therefore, the kerogen obtained by the chemical reagent may affect the results of adsorption experiment. In this study, we used the experiment of oxygen plasma low-temperature ashing (LTA) to remove the OM without affecting inorganic minerals, to achieve the purpose of quantitatively analyzing the origins of pores.

To further these aims, this paper used FE-SEM, LP-CO2/N2GA, X-ray diffraction (XRD) experiments, rock pyrolysis experiments, and LTA experiments to study the transitional shales in the Shanxi Formation in Ordos Basin. Specific objectives are to (1) present the nanopore structure of the transitional shale; (2) quantitatively characterize the origins of nanopores in the transitional shale; (3) discuss the controlling factors of inorganic mineral pores; and (4) introduce the geological significance of the nanopore structure.

2. RESULTS

2.1. Basic Composition of Shales. The composition of shale is complex and mainly composed of inorganic minerals such as quartz, kaolinite, illite, pyrite, siderite, calcite, dolomite, feldspar, anatase, and a small amount of OM. The mineral composition and TOC content of the analyzed samples are listed in Table 1. TOC contents show large variations, ranging from 0.05 to 7.78% (2.70% on average). The quartz content in shale ranges from 17.82 to 50.51, 31.47% on an average, which is lower than the average quartz content of marine shale (51.20% on an average) in Jiaoshiba area, southern China. The clay mineral content ranges from 17.82 to 50.51, 31.47% on an average, which is lower than that of the marine shale (26.10% on an average) in Jiaoshiba area, southern China.48

2.2. Pore Morphology. This paper used a classification scheme proposed by the International Union of Pure and Applied Chemistry (IUPAC) to classify the pore into micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Nanopores refer to the pores of less than 100 nm in this paper.

The SEM study shows that the freshly fractured surfaces of shales can fully visualize the texture and pores. The OM in shale reservoirs is usually randomly distributed around minerals. Previous studies have shown that pores with chemical macromolecular structures are common in OM of the marine shale, continental shale, coal, and even meteorites. Therefore, we believe that such pores also exist in the OM of the transitional shale. The width of these pores is generally less than 1 nm (Figure 1B), which can be observed under a high-resolution transmission electron microscope. By observing the organic pores under FE-SEM, we can see bubble pores (Figure 1C) and slit cracked pores (Figure 1D). Secondary bubble pores are largely related to the formation of hydrocarbons. The slit pores may be related to the shrinkage of OM, and some people believed that they are caused by OM hydraulic fracturing driven by volume changes during hydrocarbon generation.

Table 1. Mineral Composition and Organic Carbon Content of Shales

| sample   | TOC (%) | quartz | feldspar | calcite | dolomite | pyrite | siderite | anatase | kaolinite | illite |
|----------|---------|--------|----------|---------|----------|--------|----------|---------|-----------|-------|
| SY 1     | 2.43    | 25.66  | 0.38     | 0.33    | 0.61     | 0.80   | 6.37     | 1.61    | 15.32     | 48.92 |
| SY 2     | 5.26    | 20.17  | 1.09     | 0.20    | 0.57     | 0.68   | 8.72     | 2.26    | 34.74     | 31.56 |
| SY 3     | 2.94    | 17.82  | 1.68     | 0.68    | 1.12     | 1.25   | 0.91     | 2.50    | 30.43     | 43.62 |
| SY 4     | 0.1     | 31.17  | 0.41     | 0.27    | 0.37     | 0.97   | 0.29     | 1.57    | 25.97     | 38.98 |
| SY 5     | 0.05    | 50.51  | 5.77     | 0.49    | 2.17     | 1.35   | 9.57     | 1.39    | 5.18      | 23.57 |
| SY 6     | 1.61    | 30.51  | 0.50     | 0.30    | 2.32     | 8.06   | 9.17     | 1.06    | 5.05      | 43.03 |
| SY 7     | 2.11    | 30.91  | 0.95     | 0.53    | 4.55     | 11.91  | 3.77     | 1.18    | 5.56      | 40.64 |
| SY 8     | 1.93    | 42.04  | 0.23     | 0.18    | 9.56     | 8.08   | 2.67     | 0.73    | 1.86      | 34.66 |
| SY 9     | 7.87    | 34.47  | 0.60     | 0.32    | 6.78     | 22.16  | 0.56     | 0.92    | 9.96      | 24.22 |
| average  | 2.70    | 31.47  | 1.29     | 0.37    | 3.12     | 6.14   | 4.67     | 1.47    | 14.90     | 36.58 |
| Longmen formation | 3.06 | 51.20 | 6.90 | 7.50 | 5.70 | 2.60 | 0.00 | 26.10 |

2.3. Results of LTA. The weight of the shale and ashed sample is shown in Table 2. The correlation between the weight loss percentage of the samples in the ashing process and TOC.
contents of the shales is analyzed (Figure 2A), and the correlation coefficient is 0.9512, indicating that the ashing result was reliable.

2.4. Nanopore Structure Characteristics.

2.4.1. LP-CO$_2$/$N_2$ GA Isothermal Adsorption Curves. The experimental results of gas isothermal adsorption are shown in Figure 3. In the low relative pressure stage, when the pore width is close to the molecular diameter of CO$_2$, the adsorption potential overlaps, and the adsorption energy is very large, which makes the adsorption curve rise sharply. As the relative pressure ($P/P_0$) increases and the adsorption energy decreases, the adsorption capacity increases slowly. Concerning the classification scheme of the adsorption curve proposed by IUPAC, the LP CO$_2$ adsorption curve of shale conforms to Langmuir isothermal adsorption. The maximum adsorption capacity of the samples varies, indicating that the scale of micropore development is different (Figure 3A,C).

Figure 3B,D shows the $N_2$ isotherm adsorption and desorption curves of shale and ashed shale. According to the classification method reported by IUPAC, they are all type IV isotherm adsorption and desorption curves. In addition, they are $H_1$-type hysteresis loops, indicating that there are a large number of slit-shaped pores in the matrix.

2.4.2. Nanopore Structure Analysis. When analyzing the experimental data of LPGA, Langmuir monolayer adsorption, Brunauer–Emmett–Teller, Barret–Joyner–Halenda, density functional theory, Dubinin–Radushkevich, and Dubinin–Astakhov gas adsorption models can be considered. Different models are suitable for different types of adsorbates and adsorbents, and there are also differences in their effective pore size range. Through the analysis and comparison of theoretical models and SPSS reliability statistics, some scholars believed that the nonlocal DFT (NLDFT) model was suitable for 0.3–100 nm range pore analysis because of its smaller fitting error and higher accuracy. Therefore, the NLDFT model was used to analyze the experimental data of CO$_2$ and $N_2$ adsorption, and the pore structure parameters in the pore size range of 0.3–1.5 and 1.3–100 nm were obtained in this study. When $N_2$ adsorption experiment is used to characterize small micropores, the relative pressure needs to be lowered to $10^{-5}$–$10^{-7}$, and the diffusion rate and adsorption equilibrium are slow, which makes the measured adsorption data generally low. Therefore, it is more appropriate to use CO$_2$ adsorption data for the overlap range of 1.3–1.5 nm when characterizing all nanopores.

The PV and SSA of micropores, mesopores, and macropores (50–100 nm) in shale reservoirs are presented in Table 3 and Figure 4. The PV distribution ranges of micropores, mesopores, and macropores are 0.0025–0.0125, 0.0159–0.029, and 0.0015–0.0056 cm$^3$/g, respectively. The average volume ratio of mesopore and micropore is 72.2 and 18.8%, respectively. The SSA distribution ranges of micropores, mesopores, and macropores are 7.64–41.07 m$^2$/g, 5.96–10.57 m$^2$/g, and 0.99–3.4 m$^2$/g, respectively. The average rate of micropores is 66.2% and that of mesopores is generally more than 50%, and the contribution of micropores and mesopores to SSA was generally more than 98%. The development of pore
structure (PV and SSA) is similar to that of commercially developed marine Jiaoshiba shale reservoirs in southern China. Multiscale PV and SSA of samples after ashing are listed in Table 4. We compared the experimental results of LTGA between shales and corresponding ashed samples (Tables 3 and 4). The change in total PV is small, with a range of $-0.0058$–$-0.0119$ cm$^3$/g. The total SSA varies from 10.76 to 44.04 m$^2$/g.

The PV and SSA of micropores decreased significantly in the ranges of $0.0020$–$0.1111$ cm$^3$/g and $6.21$–$37.36$ m$^2$/g, respectively. The PV and SSA of mesoporous also decreased to a certain extent in the ranges of $-0.0038$–$-0.0062$ cm$^3$/g and $4.20$–$6.58$ m$^2$/g, but the PV of samples SY-1 and SY-8 increased slightly after ashing. The PV of macropores generally increased, and the SSA slightly increased or decreased, with the range of variation being $-0.0087$–$-0.0009$ cm$^3$/g and $-0.22$–$0.20$ m$^2$/g, respectively.

2.4.3. Nanopore Size Distribution Characteristics. The pore size distribution (PSD) can usually be expressed by the relationship between the differential PV $[dV/(d)]$ and pore size, where $dV$ represents the PV of a certain pore interval, and $(d)$ represents the unit pore size interval. From the PSD of shales (blue curve, as shown in Figure 5), the number of pores on the micropore scale is the largest, especially the pores smaller than 1 nm, followed by mesopores of 3–10 nm, and the number of macropores is relatively small. From the peak, the differential PVs of SY-2, SY-3, and SY-9 are significantly larger than those of other shales, indicating that the three samples have a larger number of micropores (<1 nm).

Figure 2. (A) Correlation analysis between TOC and ashing weight percentage of shale. (B) XRD contrast pattern of SY-1 and ashed SY-1.

Figure 3. Isothermal adsorption curve of CO$_2$ and N$_2$ experiments at low pressure. (A,B) LP CO$_2$ and N$_2$ isothermal adsorption curves of shale samples and (C,D) LP CO$_2$ and N$_2$ isothermal adsorption curves of ashing samples, respectively. (B,D) Solid lines represent adsorption curves, and dotted lines represent desorption curves. $P =$ actual gas pressure and $P_0 =$ saturated vapor pressure of the adsorption gas.
From the PSD of ashed samples (red curve, as shown in Figure 5), it can be seen that the number of micropores smaller than 1 nm is significantly reduced, and the number of mesopores of 3−10 nm is slightly reduced, indicating that these pores may mainly develop in the OM.

### 3. DISCUSSION

#### 3.1. Origin of Nanopores in the Lower Permian Transitional Shale

**3.1.1. Contribution of the OM and Inorganic Minerals to the Nanopore**

Through the analysis and observation of previous research and the OM particles by SEM, it was found that the particle size of OM is widely distributed, mainly in the micron scale, and there may be a small amount in the nano-scale.56−58 Therefore, after the LTA experiments, the space occupied by OM particles itself evolved into new pores, which are generally micro-scale macropores, but mesopores and macropores less than 100 nm may also form. These new pores have a great influence on PV analysis, which is also the main reason for the increase in PV of some samples after the ashing experiment. Therefore, the PV of the sample after ashing cannot be directly identified as the PV of inorganic minerals in shale.

From FE-SEM, it can be observed that some shrinkage interface cracks exist at the junction of inorganic minerals and OM (Figure 1A), and the SSA of inorganic pores at these positions remains unchanged after ashing. However, some joints may be tightly connected without interface cracks, which leads to the formation of new pores and an increase in SSA at these positions after ashing. However, the newly formed pores are generally large, and their influence on the entire SSA of the inorganic pore system is negligible. Therefore, it is believed that the SSA of ashed shales is the SSA of inorganic minerals in the shale.

#### 3.2. Correlation between TOC Content and SSA

Through the correlation analysis of the TOC content and the reduced SSA after ashing (Figure 6), it is found that ashing will still cause the reduction in the SSA of some micropores and mesopores when the content of TOC is 0. Since shale ashing does not affect the type and content of inorganic minerals (analyzed in 3.2 of this paper), it is speculated that ashing may cause slight changes in the combination of minerals.

### Table 3. Statistical Table of Multiscale PV and SSA of Shales

| sample | PV_{mic} (cm³/g) | SSA_{mic} (m²/g) | PV_{mes} (cm³/g) | SSA_{mes} (m²/g) | PV_{mac} (cm³/g) | SSA_{mac} (m²/g) | PV (cm³/g) | SSA (m²/g) |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------|-----------|
| SY-1   | 0.0054           | 17.08            | 0.0180           | 7.97             | 0.0015           | 0.09             | 0.0248     | 25.14     |
| SY-2   | 0.0081           | 26.94            | 0.0202           | 8.60             | 0.0020           | 0.12             | 0.0303     | 35.66     |
| SY-3   | 0.0052           | 17.36            | 0.0294           | 10.57            | 0.0004           | 0.02             | 0.0349     | 27.95     |
| SY-4   | 0.0032           | 10.36            | 0.0198           | 7.21             | 0.0024           | 0.15             | 0.0255     | 17.72     |
| SY-5   | 0.0025           | 7.64             | 0.0175           | 5.96             | 0.0049           | 0.31             | 0.0249     | 13.91     |
| SY-6   | 0.0052           | 16.89            | 0.0263           | 9.93             | 0.0047           | 0.29             | 0.0362     | 27.11     |
| SY-7   | 0.0059           | 19.28            | 0.0206           | 9.29             | 0.0016           | 0.10             | 0.0281     | 28.67     |
| SY-8   | 0.0043           | 14.26            | 0.0159           | 6.95             | 0.0015           | 0.09             | 0.0217     | 21.30     |
| SY-9   | 0.0125           | 41.07            | 0.0268           | 9.78             | 0.0056           | 0.34             | 0.0449     | 51.20     |
| average| 0.0058           | 18.99            | 0.0216           | 8.47             | 0.0027           | 0.17             | 0.0301     | 27.63     |
| Longmaxi formation   | 0.0055           | 17.54            | 0.0138           | 9.27             | 0.0044           | 0.57             | 0.0236     | 27.39     |
| Wufeng-Longmaxi formation | 0.0086           | 24.99            | 0.0114           | 6.95             | 0.0070           | 0.22             | 0.0270     | 32.16     |

### Table 4. Statistical Table of Multiscale PV and SSA of Low-Temperature Ashed Shales

| sample | PV_{mic} (cm³/g) | SSA_{mic} (m²/g) | PV_{mes} (cm³/g) | SSA_{mes} (m²/g) | PV_{mac} (cm³/g) | SSA_{mac} (m²/g) | PV (cm³/g) | SSA (m²/g) |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------|-----------|
| ashed SY-1 | 0.0010       | 2.85             | 0.0218           | 2.93             | 0.0078           | 0.22             | 0.0306     | 6.01      |
| ashed SY-2 | 0.0022       | 6.51             | 0.0194           | 2.81             | 0.0070           | 0.19             | 0.0286     | 9.51      |
| ashed SY-3 | 0.0018       | 5.30             | 0.0274           | 4.43             | 0.0091           | 0.24             | 0.0383     | 9.97      |
| ashed SY-4 | 0.0012       | 3.21             | 0.0150           | 2.25             | 0.0051           | 0.14             | 0.0213     | 5.60      |
| ashed SY-5 | 0.0006       | 1.43             | 0.0112           | 1.61             | 0.0041           | 0.11             | 0.0159     | 3.15      |
| ashed SY-6 | 0.0019       | 5.22             | 0.0234           | 3.93             | 0.0074           | 0.20             | 0.0328     | 9.34      |
| ashed SY-7 | 0.0020       | 5.78             | 0.0201           | 3.29             | 0.0063           | 0.17             | 0.0284     | 9.24      |
| ashed SY-8 | 0.0016       | 4.48             | 0.0161           | 2.75             | 0.0048           | 0.13             | 0.0225     | 7.36      |
| ashed SY-9 | 0.0014       | 3.71             | 0.0225           | 3.20             | 0.0091           | 0.24             | 0.0330     | 7.16      |

Figure 4. Bar graph of PV (A) and SSA (B) distribution of multiscale pores in the shale (mic = micropore, mes = mesopore, and mac = macropore).

Figure 5. Bar graph of PV (A) and SSA (B) distribution of low-temperature ashed shales (mic = micropore, mes = mesopore, and mac = macropore).
Considering that slight changes are also due to the pores of inorganic minerals, the reduction in SSA when TOC = 0 (i.e., the intercept in y-axis) is added as a yardstick to the SSA of inorganic micropores or mesopores in shales. The macropore structure changes of the ashed sample are inconsistent, and the new pores formed by the ashing of OM are difficult to distinguish from the pores of shale inorganic minerals. Since these pores do not contribute substantially to the total SSA of shale, they are not discussed further in this paper.

Figure 5. Nanopore size distribution of the samples.

Figure 6. Correlation between TOC and the SSA of ash-reduced micropores (A) and mesopores (B).
By comparing the pore structure of the original shale and the ashed sample, the SSA from different origins was obtained (Figure 7). In shale, the contributions of inorganic minerals and OM to the SSA of micropores are 6.22–11.30 and 1.42–32.57 cm²/g, respectively, and the contributions to the mesopores are 5.96–9.27 and 0–1.74 cm²/g, respectively. It can be seen from Figure 7 that in SY-9, which has a high organic content, the contribution of the OM is large. In SY-4 and SY-5, which have lower organic content, the contribution of inorganic minerals is relatively large. In general, the contribution of the SSA of the OM increases with increasing TOC.

3.1.2. Control of the Inorganic Mineral Composition on Inorganic Pore SSA. Since the foregoing quantitatively demonstrates that inorganic mineral pores have a great effect on the SSA of shale reservoirs, it is particularly important to determine the origin of SSA for inorganic pores. Therefore, correlation analysis was conducted between the content of the main mineral components in the shale and the multiscale SSA of inorganic pores, and the minerals with good correlation can be considered as an important origin of the SSA of inorganic pores.

The results of Pearson correlation analysis are shown in Table 5. The table shows that only clay minerals have a weak positive correlation with the SSA of inorganic micropores and mesopores, indicating that clay minerals may have a small contribution to the inorganic SSA of the shale, but they are not the main contributors. The main reason may be that the transitional shale in the study area generally experienced a large burial depth and a high thermal evolution process. Clay minerals with a layered crystal structure and a large number of intergranular pores were illitized during the diagenesis process, which may form an overpressured pore system, resulting in a large reduction in mesopores and an increase in macropores. However, the increased macropores were not enough to compensate for the decreased mesopores. Therefore, the content of clay minerals has a certain positive correlation with the inorganic SSA, but the correlation is not very good (Figure 8). Other inorganic components in the shale, such as quartz, carbonate minerals, pyrite, and anatase, have no significant correlation with the multiscale inorganic SSA, indicating that the inorganic SSA is irregularly controlled by dispersed minerals in the shale matrix.

3.2. Significance of the Pore Structure to Adsorption, Desorption, and Migration of Methane. The adsorption properties of the shale are closely related to the pore SSA.18,19,21,61 The SSA of the OM in the transitional shale in the study area ranges from 1.42 to 34.31 m²/g, and the SSA of inorganic minerals ranges from 12.18 to 19.36 m²/g. Scholars studied the adsorption properties of kerogen and clay minerals by methane isothermal adsorption experiments (60 °C) and found that there is a little difference in the maximum adsorption capacity of kaolinite and illite, while the adsorption capacity of methane in type III kerogen is approximately 10 times that of both (Table 6).18 After normalizing the SSA, the normalized adsorption capacity of type III kerogen is approximately 50 times that of clay minerals (Table 6). In addition, the normalized adsorption capacity of type II kerogen obtained from the marine shale in southern China is 1.3 times that of type III kerogen (Table 6), indicating that type II kerogen has a stronger adsorption capacity for methane.

Combining the contribution of the OM and inorganic minerals to the SSA of shale reservoirs in this study, it is postulated that the methane adsorption capacity of organic pores in transitional shale reservoirs in the study area is 6 to 104 times that of inorganic pores. Therefore, organic pores control the adsorption of methane with an advantage of 2 orders of magnitude in shale reservoirs with high OM content, while organic pores play a major role in methane adsorption with an adsorption capacity several times that of inorganic pores, and inorganic pores play a secondary role in shale reservoirs with a low organic content.

Previous studies have documented the transport mechanism of the multiscale pore structure in shale reservoirs through methane diffusion experiments and modeling experiments.62–71 It is generally believed that in the early stage of shale gas production, free gas rapidly flows from the intercrystalline pores of berry-shaped pyrite (Figure 1F), carbonate dissolution pores (Figure 1G), and the intercrystalline pores of clay minerals (Figure 1H), through free molecular diffusion and Knudsen diffusion mechanism after fracturing damage of reservoir (corresponding to Figure 9 stage I). As the pressure decreases, the adsorbed gas in the pores (mainly refers to the micropores and small mesopores with a width of less than 10 nm) is desorbed by surface diffusion and mixed with free gas to into the large pores or cracks of the matrix and be produced (corresponding to Figure 9 stage II). With the massive consumption of free gas, the adsorbed gas desorbed from nanopores, especially organic micropores, becomes the main gas

| Table 5. Pearson Correlation Coefficient between the Content of Minerals and SSA of Inorganic Pores |
|---------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                                | quartz  | feldspar| calcite | dolomite| pyrite  | siderite| anatase | kaolinite| illite   | clay    |
| SSAmic                         | −0.654  | −0.519  | −0.036  | 0.051   | 0.120   | −0.034  | 0.271   | 0.326    | 0.279    | 0.396   |
| SSAmes                         | −0.771  | −0.517  | 0.354   | −0.144  | 0.211   | −0.0239 | 0.312   | 0.275    | 0.563    | 0.509   |
| SSAmic+mes                     | −0.764  | −0.567  | 0.123   | −0.025  | 0.169   | −0.123  | 0.314   | 0.336    | 0.424    | 0.481   |
source in the later stage of production (corresponding to Figure 9 stage III). Unfortunately, the widely developed type III kerogen in the transitional facies has low maturity and weak gas production capacity, which fails to produce many pores like the kerogen in the marine shale (Figure 1C,E). Instead, it exists in an isolated state, resulting in poor organic pore connectivity, which is an important factor, leading to low permeability of transition facies shale. In addition, compared with the marine shale, the content of brittle minerals in the transitional shale is lower, resulting in weak compressive resistance of the shale, which will also make pore connectivity worse. These are not conducive to effective diffusion and desorption of adsorbed gas.

4. CONCLUSIONS

To explore the nanopore structure characteristics and origins of lower Permian transitional shale in the eastern margin of the Ordos Basin, based on LP-N$_2$/CO$_2$GA and LTA, the following conclusions are drawn:

1. The PV of micropores, mesopores, and macropores in the lower Permian transitional shale are 0.0025−0.012, 0.0159−0.0294, and 0.0015−0.0056 cm$^3$/g, respectively, and the corresponding SSA is 7.64−41.07, 5.96−10.57, and 0.09−0.34 m$^2$/g, which is similar to that of commercially developed marine shale reservoirs in southern China.

2. The average contribution rates of inorganic minerals and OM to the SSA of micropores are 55.9 and 44.1% respectively, and the average contribution rates to the SSA of mesopores are 92.3 and 7.7%, respectively. Through correlation analysis, it is found that clay minerals make a small contribution to the SSA of inorganic minerals, and more contributions may randomly come from minerals in the shale matrix.

3. Comparing the pore adsorption properties of different origins, it is found that the organic pores in the transitional shale in the study area play a dominant role in controlling the adsorption of shale. However, the migration pathway provided by the OM and inorganic minerals is limited, resulting in poor pore connectivity in the shale, which restricts the long-term effective exploitation of transitional shale gas wells.

5. SAMPLES AND EXPERIMENTS

5.1. Samples. The Ordos Basin, located in the west of the North China plate (Figure 10A), is rich in unconventional natural gas resources. In order to meet the research requirements, nine shale samples were systematically collected from the fresh core of well A in Shilou-Yonghe area, eastern Ordos Basin (Figure 10B,C). The lithology of the strata in the study area is mainly mudstone, sandstone, and coal, and it is delta facies. It is characterized by a large number of layers and a large cumulative thickness (43−190 m). In this study, a part of the massive shale was reserved for FE-SEM observation. The rest of the fresh shale was completely ground to 0.074 mm and placed in an oven at 80 °C for 24 h and then airtightly refrigerated. XRD, FE-SEM, rock pyrolysis, LP-CO$_2$/N$_2$GA, and LTA experiments were performed on all samples. In addition, XRD and LP-CO$_2$/N$_2$GA experiments were performed again on the low-temperature ashed shale.
5.2. FE-SEM, XRD, and Rock Pyrolysis Experiments. To visually observe the structure and distribution of macropores, the size and distribution of OM in the shale matrix, and the morphology and combination of inorganic minerals in shale, the experiment used a Quanta FEG 250 SEM produced by FEI Company in the United States. The maximum magnification can reach 300,000 times, and the resolution can reach 2.5 nm under a high vacuum. To obtain better observation results, the surface of the sample was polished by a Gatan697 argon ion polishing instrument.

A German Bruker AXS D8 Advance X-ray diffractometer was used for shale mineral composition analysis. The internal standard corundum and the samples were thoroughly mixed at a ratio of 1:4 and then scanned on the machine with a voltage of 40 kV, a scanning step of 0.02°, the scanning range of 5–65°, and a scanning speed of 1°/min. The original XRD spectra were analyzed using the Xpert Highscore Plus system, and minerals were quantitatively analyzed with Rockjock11 based on the XRD of whole samples.

A Y3000A rock pyrolysis analyzer was used for TOC determination. The shales were heated by programming in a high vacuum. To obtain better observation results, the surface of the sample was polished by a Gatan697 argon ion polishing instrument.

5.3. LTA Experiments. To quantitatively analyze the influence of OM and inorganic minerals on shale reservoirs, nine shale samples were ashed at a temperature lower than 120°C by a Nano plasma ashing instrument made in Diener Company, Germany. The samples were weighed and stirred every 3 h until the sample weight was no longer changed, and the total ashing time was not less than 24 h.

5.4. LP-CO₂/N₂GA Experiments. LPGA was conducted using the Autosorb-IQ-MP SSA and PSD analyzer of the American Quanta chrome company. Before the experiment, the samples were degassed under vacuum to remove the water vapor in the pores. The adsorption experiments of CO₂ and N₂ were carried out at 77 and 273 K, and the relative equilibrium pressure (P/P₀) varied from 0 to 0.03 and 0 to 1, respectively.

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