Preliminary Assessment of the Resource and Exploitation Potential of Lower Permian Marine-Continent Transitional Facies Shale Gas in the Huainan Basin, Eastern China, Based on a Comprehensive Understanding of Geological Conditions

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ABSTRACT: The Huainan Basin in eastern China contains abundant shale gas resources; the Lower Permian is an exploration horizon with a high potential for shale gas in marine-continent transitional facies. However, few detailed analyses have investigated shale gas in this area. In this paper, a comprehensive investigation of the geochemical characteristics, physical properties, and gas-bearing capacities of shale reservoirs was conducted, and the resource and exploitation potential were evaluated. The results show that the cumulative thicknesses of the Shanxi Formation (P1s) and lower Shihezi Formation (P2xs) are mostly greater than 35 and 65 m, respectively. The TOC contents of the P1s and P2xs shale vary from 0.11 to 8.87% and from 0.22 to 14.63%, respectively; the kerogens predominantly belong to type II with minor amounts of type I or type III kerogens; average R0 values range between 0.83 and 0.94% and between 0.82 and 1.02% in P1s and P2xs, respectively; the shale samples are primarily at a low maturity, while some shale samples have entered the high-maturity stage. The shale reservoirs have low permeability and porosity in P1s and P2xs, respectively. The pores of the P1s shale reservoir are characterized by well-developed micropores and transition pores and poorly developed mesopores, while the pores in the P2xs shale reservoir are all characterized by well-developed micropores and transition pores and some well-developed macropores; the different pore types in the shale reservoirs developed in the organic matter, clay minerals, and pyrite, while a few endogenous fractures developed in the organic matter and structural fractures developed in the minerals. The total shale gas contents in P1s and P2xs are 2.85 and 2.96 m3 t−1, respectively. The P2xs shale reservoir has a higher hydrocarbon generation potential than P1s and has a lower gas generation potential. The total shale gas amounts in P1s and P2xs are 3602.29−4083.04 × 108 and 2811.04−3450.77 × 108 m3, respectively. Further research on shale gas exploration and exploitation for these formations needs to be performed.

1. INTRODUCTION

Shale gas, which is an alternative to petroleum and coal as a hydrocarbon resource, has been intensively studied in recent years. Much work has emphasized the geochemical characteristics of shale1−6 and has evaluated the resource potential of shale gas,7,8 and some researchers have attempted to analyze the gas potential by quantifying hydrocarbon generation and expulsion.9,10 Others have investigated the microscopic characteristics of shale reservoirs.11−14 Furthermore, some researchers have analyzed the controlling factors for shale gas enrichment, favorable areas for shale gas, and shale gas exploration and development.8,15−17 These previous studies have strongly focused on marine shale gas, while only a few works have addressed marine-continent transitional shale gas18−20 and continental shale gas.21 In China, nonmarine organic shale contains two-thirds of all recoverable shale resources;22 organic shales deposited in nonmarine environments are usually interlayered with coalbeds, especially in marine-continental transitional environments, and the coal-bearing strata contain large quantities of shale gas resources in China and are very important for achieving success and breakthroughs in coal-bearing shale gas production.13 Therefore, multidisciplinary and comprehensive studies involving...
shale gas geology and an integrated understanding of marine-continent transitional shale gas in typical coal measure strata are desired.

The Huainan Basin, which is located in Anhui Province (Figure 1), contains abundant coal resources and coal-measure gas. The coal-bearing strata, with an average thickness of approximately 1000 m, were deposited in typical marine-continent transitional environments during the Permian and Carboniferous; the numerous shale gas wells that exist in the Huainan Basin provide an ideal study area to examine the shale properties and resource potential. However, previous investigations of shale gas in the Huainan Basin were focused only on the pore structures of the shales. Multidisciplinary and systematic studies of shale gas in the Huainan Basin are still needed. In this paper, the Lower Permian marine-continent transitional strata were chosen as the target formations, and we present a comprehensive study involving the geological conditions that include geochemical characteristics, physical properties, and gas-bearing capacities of the shale reservoirs to provide better estimations of the shale gas resource potential and exploitation potential in the Huainan Basin.

The Huainan Basin is located in the northern margin of the Qinling latitudinal structural belt. Its geology was mainly controlled by Indo-Yanshanian tectonic movements, development of the Fufeng nappe and Shangyaominglongshan nappe.
and the Huainan synclinorium formed in the studied area. Due to the effects of tectonic compression, a series of secondary folds and faults developed (Figure 1). Most of the strata have developed in the studied area, except during the Silurian and Devonian because of denudation, while the coal-bearing strata include the Taiyuan Formation of late Carboniferous (referred to as C3t), Shanxi Formation of early Permian (referred to as P1s), Lower Shihezi Formation of middle Permian (referred to as P2xs), Upper Shihezi Formation of late Permian (referred to as P3ss), and the Sunjiagou Formation of late Permian (referred to as P3sj) and were deposited in typical marine-continental transitional environ-

Table 1. Experimental Parameters of Rock Pyrolysis Analysis

| sample no. | drilling no. | depth (m) | TOC (%) | \( T_{\text{max}} \) (°C) | \( S_0 \) (mg g\(^{-1}\)) | \( S_1 \) (mg g\(^{-1}\)) | \( S_2 \) (mg g\(^{-1}\)) |
|------------|-------------|----------|---------|----------------|----------------|----------------|----------------|
| WY-05\(^a\) | 11–1        | 1535.8   | 2.27    | 468            | 0.02           | 0.33           | 2.30           |
| WY-09\(^a\) | 10–1        | 1056.3   | 0.37    | 454            | 0.03           | 0.76           | 0.89           |
| WY-11\(^a\) | 10–1        | 1122.5   | 2.40    | 547            | 0.05           | 0.12           | 0.25           |
| WY-21\(^a\) | 20–2        | 1448.6   | 1.38    | 550            | 0.02           | 0.15           | 0.16           |
| WY-22\(^a\) | 20–2        | 1457.5   | 2.89    | 357            | 0.02           | 0.11           | 0.16           |
| WY-23\(^a\) | 20–2        | 1401.2   | 1.90    | 449            | 0.02           | 0.14           | 1.40           |
| WY-23\(^a\) | 20–2        | 1424.3   | 3.07    | 338            | 0.02           | 0.09           | 0.12           |
| WY-27\(^a\) | 12–2        | 1409.5   | 8.87    | 449            | 0.02           | 0.10           | 0.17           |
| WY-32\(^a\) | L4–1        | 1432.7   | 1.76    | 445            | 0.02           | 0.14           | 1.23           |
| WY-33\(^a\) | L4–1        | 1396.3   | 2.48    | 451            | 0.02           | 0.34           | 2.75           |
| WY-51\(^a\) | 10–2        | 1236.1   | 3.25    | 454            | 0.02           | 0.38           | 2.05           |
| WY-53\(^a\) | 10–2        | 1218.1   | 4.38    | 453            | 0.03           | 0.67           | 5.07           |
| WY-45\(^a\) | 10–2        | 1163.4   | 0.11    | 451            | 0.01           | 0.05           | 0.11           |
| WY-03\(^b\) | 11–1        | 1454.2   | 2.22    | 465            | 0.02           | 0.24           | 1.29           |
| WY-08\(^b\) | 10–1        | 1048.2   | 0.42    | 450            | 0.02           | 0.34           | 1.54           |
| WY-16\(^b\) | 20–2        | 1307.7   | 1.39    | 392            | 0.02           | 0.13           | 0.20           |
| WY-25\(^b\) | 20–2        | 1325.3   | 2.74    | 447            | 0.02           | 0.15           | 1.22           |
| WY-30\(^b\) | L4–1        | 1374.0   | 0.42    | 446            | 0.02           | 0.32           | 1.35           |
| WY-49\(^b\) | 10–2        | 1040.0   | 0.50    | 455            | 0.01           | 0.07           | 0.28           |
| WY-48\(^b\) | 10–2        | 1092.1   | 0.75    | 455            | 0.02           | 0.19           | 0.65           |
| A-50\(^b\)  | 17–1        | 969.0    | 14.63   | 436            | 0.71           | 0.70           | 38.83          |
| A-27\(^b\)  | 17–1        | 1107.0   | 0.77    | 446            | 0.82           | 0.05           | 0.70           |
| A-33\(^b\)  | 17–1        | 1070.0   | 0.22    | 435            | 0.21           | 0.02           | 0.13           |
| A-35\(^b\)  | 17–1        | 1059.0   | 0.42    | 444            | 0.09           | 0.02           | 0.25           |
| A-38\(^b\)  | 17–1        | 1041.0   | 11.91   | 439            | 0.61           | 0.73           | 32.64          |

The superscript “a” in the column sample no. means that the sample is from P1s, and the superscript “b” in the column sample no. means that the sample is from P2xs.
ments. In the studied strata, the coal seams are designated No. 1 to No. 9, and among them, the minable coal seams include the Nos. 8, 7, 6, 5, 4, and 1 coal; of the minable coal seams, the No. 8 and 7 coal seams distributed in P2xs are vertically stable. Additionally, several layers of mudstones or mudstone interbedding have developed in the coal-bearing strata (Figure 1); the thickness of P1s varies from 39 to 83 m with an average of 68 m; the thickness of P2xs varies from 105 to 165 m with an average of 132 m, and the average thicknesses of the shale in P1s and P2xs are 39 and 75 m, respectively.

2. RESULTS AND DISCUSSION

2.1. Geological Characteristics of Shale Gas Reservoirs. 2.1.1. Shale Thickness. As shown in Figure 1, some carbonates developed with certain thicknesses in P1s but mudstone and different types of sandstone mainly developed. Figures 2 and 3 show the cumulative shale thicknesses in P1s and P2xs. It can be seen that the cumulative shale thickness in P1s is unevenly distributed in the studied area and is thicker in the central-east portion than the other parts of P1s; the cumulative shale thickness in most of the studied area is greater than 35 m, while the maximum cumulative shale thickness is...
greater than 60 m (Figure 2). The cumulative shale thickness in P_{2xs} is generally greater than 65 m, and the cumulative shale thickness in some parts is greater than 100 m; also, the cumulative shale thickness in the central-east part of the studied area is higher than that in the west part of the studied area.

2.1.2. Geochemical Characteristics. Table 1 shows the main parameters from rock pyrolysis analysis of samples from P_{1s} and P_{2xs}. As shown in Table 1, the TOCs in the selected P_{1s} shale samples vary from 0.11 to 8.87% with an average of 2.70%, and the vast majority of TOCs are greater than 1.0%; the TOCs in the selected P_{2xs} shale samples vary from 0.22 to 14.63% with an average of 3.03%. If shale samples No. A-50 and No. A-38 are deleted, the average TOC in the remaining P_{2xs} shale samples is 0.99% according to Table 1, which indicates that the TOCs in the P_{2xs} shale samples are not stable and change significantly. T_{max} values of the selected P_{1s} shale samples vary from 338 to 550 °C (avg. 451.23 °C), and T_{max} values of the selected P_{2xs} shale samples vary from 392 to 465 °C (avg. 442 °C), and a comparison of T_{max} values of the shale samples from P_{1s} and P_{2xs} shows that the T_{max} of P_{1s} shale samples is slightly higher than those from P_{2xs}. The S_{0} values of the selected P_{1s} shale samples change slightly and vary from 0.01 to 0.05 mg g$^{-1}$ with an average value of 0.02; the S_{1} values of the selected P_{2xs} shale samples vary from 0.05 to 0.76 mg g$^{-1}$ with an average value of 0.26 mg g$^{-1}$; the S_{2} values of the selected P_{1s} shale samples vary from 0.11 to 5.07 mg g$^{-1}$ with an average value of 1.28 mg g$^{-1}$. The S_{0} values of the selected P_{2xs} shale samples change significantly and vary from 0.01 to 0.82 mg g$^{-1}$ with an average value of 0.21 mg g$^{-1}$; the S_{1} values of the selected P_{2xs} shale samples vary from 0.02 to 0.73 mg g$^{-1}$ with an average value of 0.25 mg g$^{-1}$; the S_{2} values of the selected P_{1s} shale samples vary from 0.20 to 32.64 mg g$^{-1}$ with an average value of 6.59 mg g$^{-1}$. As seen in the results shown in Table 1, the TOC, S_{0}, S_{1}, and S_{2} of shale samples Nos. A-50, A-27, A-33, and A-38 from P_{2xs} are higher than those of the other shale samples, which suggests that high-quality shale developed in some parts of P_{2xs}. A comparison of the results indicates that the P_{1s} shale is superior to the P_{2xs} shale.

Figures 4 and 5 show the distributions of TOCs in P_{1s} shale and P_{2xs} shale, respectively. It is clear that the TOCs in the P_{1s} shale decrease from the southwest to northeast parts of the studied area and there are distribution areas with high TOCs in the southeast part of the studied area in which the TOC is generally higher than 3.20%; however, there is a distribution area with low TOC in the northeastern part of the studied area in which the TOC is mostly lower than 1.10% (Figure 4). As seen in Figure 5, The TOCs in the P_{2xs} shale are distributed in a circular pattern in the east-west direction and there is a distribution area with high TOC in the central part of the studied area; a distribution area with low TOC only occupies a small zone in the eastern section of the studied area with a TOC below 1.30% (Figure 5).

The TOC in hydrocarbon source rocks is a key parameter for identifying high-quality hydrocarbon source rocks, and the consensus of scholars worldwide is that when the TOC in shale is higher than 0.5%, the shale is considered as a hydrocarbon source rock with resource potential; potential hydrocarbon source rocks with TOCs between 0.5 and 1% are identified as poor hydrocarbon source rocks, while hydrocarbon source rocks with TOCs between 1 and 2% are identified as fair source rocks; hydrocarbon source rocks with TOCs between 2 and 4% are identified as good source rocks, and hydrocarbon source rocks with TOC above 4% are identified as very good or excellent source rocks. When examining Table 1, Figure 4, and Figure 5, these results indicate that the probability of good and very good hydrocarbon source rocks is 61.54% and the probability of fair to very good hydrocarbon source rocks is 84.62%; in contrast, the probability of poor hydrocarbon source rocks is 58.33% (Table 2), and the probability of good to excellent hydrocarbon source rocks is only 33.33%. To summarize, the P_{1s} shale is mainly associated with fair to excellent hydrocarbon source rocks, while the P_{2xs} shale is mainly associated with very poor to poor hydrocarbon source rocks.

The results of the maceral kerogen compositions of the P_{1s} shale samples are shown in Figure 6. It can be observed that there are exinite- and vitrinite-dominated maceral compositions of kerogen in the P_{1s} shale samples. The observations of maceral kerogen compositions show that sapropelinite and exinite occur as large fragments. The maceral kerogen compositions indicate that the organic matter in the P_{1s} and P_{2xs} shale is typical marine-continent transitional organic matter, which is supported by the following results.

To confirm the organic type in the shale samples, the kerogen type index (abbreviated as KTI) and hydrogen index (abbreviated as HI, equal to S_{1} × 100/TOC, mg g$^{-1}$ TOC) were calculated, and the plots of KTI, HI versus T_{max} were generated to identify the kerogen types, combined with the carbon isotope of kerogen expressed as δ^{13}C). KTI was calculated according to eq 1:

$$
KTI = (S \times 100 + E \times 50 − V \times 75 − I \times 100) ÷ 100
$$

where S denotes the sapropelinite content in the maceral kerogen composition, %; E denotes the exinite content in the maceral composition of kerogen, %; V denotes the vitrinite content in the maceral kerogen composition, %; and I is the inerrinite content in the maceral kerogen composition, %. When KTI is greater than 80, the organic matter is type I kerogen (sapropel-type kerogen); when KTI is between 40 and 80, the organic matter is type II, kerogen (humic-sapropel-type kerogen); when KTI is between 0 and 40, the organic matter is type II, kerogen (sapropel-humic-type kerogen); when KTI is below 0, the organic matter is type III kerogen (humic-type kerogen). The combination of the KTI plot, the plot of HI versus T_{max} based on the genetic chart of kerogen, and the comprehensive chart are shown in Figure 7. As shown in Figure 7, the organic matter in the shale from P_{1s} and P_{2xs} mainly belongs to type II kerogen although there is a deviation from HI and KTI. Meanwhile, the organic matter type is classified according to the δ^{13}C of kerogen, and the δ^{13}Cs of the kerogen from P_{1s} are between −25.5 and −23‰ (Table

| TOC (%) | kerogen quality | P_{1s} sample number | probability (%) | P_{2xs} sample number | probability (%) |
|--------|----------------|----------------------|----------------|----------------------|----------------|
| <0.5   | very poor      | 2                    | 15.38          | 4                    | 33.33          |
| 0.5−1  | poor           | 0                    | 0              | 3                    | 25.00          |
| 1−2    | fair           | 3                    | 23.08          | 1                    | 8.33           |
| 2−4    | good           | 6                    | 46.16          | 2                    | 16.67          |
| 4−12   | very good      | 2                    | 15.38          | 1                    | 8.33           |
| >12    | excellent      | 0                    | 0              | 1                    | 8.33           |
the organic matter type belongs to a type II kerogen.\textsuperscript{34} Integrated with Table 1, Table 2, and Figure 7, HI is between 100 and 300 mg g\textsuperscript{-1} TOC and 84.62\% of the shale samples are from P\textsubscript{1s}, which indicate that the organic matter of the P\textsubscript{1s} shale mainly belongs to type II kerogen and indicates that the hydrocarbon source rock is a fair-very good hydrocarbon source rock that can generate both oil and gaseous hydrocarbons.\textsuperscript{35,36} However, HI varies from 0 to 450 mg g\textsuperscript{-1} TOC, the organic matter in the P\textsubscript{2xs} shale mainly belongs to type II kerogen, and the partial organic matter belongs to type I and type III kerogen, and the shale samples from P\textsubscript{2xs} are hydrocarbon source rocks that can generate oil, both oil and gas, and gaseous hydrocarbons.\textsuperscript{35,36}

$\text{R}_0$ and $T_{\text{max}}$ were combined to represent the maturity of organic matter in the shale. It can be seen that the minimum $R_0$ is between 0.73 and 0.85\%, the maximum $R_0$ is between 0.91 and 1.05\%, the average $R_0$ is 0.83–0.94\%, in P\textsubscript{1s} (Figure 8), and that the minimum $R_0$, maximum $R_0$, and average $R_0$ in P\textsubscript{2xs} vary from 0.71–0.96, 0.87–1.09, and 0.82–1.02\%, respectively (Figure 8). The $R_0$ values of the P\textsubscript{1s} shale decrease from south to north in the studied area, but in contrast, the $R_0$ values of the P\textsubscript{2xs} shale decrease from north to south in the studied area. Furthermore, the distributions of $R_0$ in the P\textsubscript{1s} shale indicate $R_0$ values over 0.7\% (Figures 9 and 10). When $R_0$ is greater than 0.70\%, the organic matter evolution enters a mature stage;\textsuperscript{30}

![Figure 6. Maceral composition of kerogen in shale from Huainan: (a) samples from P\textsubscript{1s}; (b) sample from P\textsubscript{2xs}.](image)

![Figure 7. Plots of hydrogen index versus $T_{\text{max}}$ (a) and KTI (b).](image)

Table 3. $\delta^{13}$C of Kerogen in Shale Samples in Huainan

| sample no. | drilling no. | depth (m) | formation | $\delta^{13}$C (‰) |
|------------|--------------|-----------|-----------|-------------------|
| WY-51      | 10–2         | 1163.4    | P\textsubscript{1s} | $-23.3$           |
| WY-45      | 10–2         | 1236.1    | P\textsubscript{2xs} | $-23.6$           |
| A-50       | 17–1         | 969       | P\textsubscript{2xs} | $-24.1$           |
| A-27       | 17–1         | 1107      | P\textsubscript{2xs} | $-24.9$           |
| A-33       | 17–1         | 1070      | P\textsubscript{2xs} | $-24.3$           |
| A-35       | 17–1         | 1059      | P\textsubscript{2xs} | $-24.0$           |
| A-38       | 17–1         | 1041      | P\textsubscript{2xs} | $-24.4$           |

[$R_0$](https://doi.org/10.1021/acsomega.1c00290)
The $R_o$ values of the shale samples from both P1s and P2xs are over 0.7%, which indicates that the organic matter in the shale in the studied area has entered the mature stage. As seen from Figures 810, the $R_o$ values of the shale samples are close to 1.0% but are lower than 1.3%, which suggests that the source rock is still in the active oil generation window and that its evolution is close to the first hydrocarbon generation peak.

Meanwhile, the $T_{max}$ values of most shale samples from P1s and P2xs vary from 435 to 455 °C with an average of 451.23 °C; the $T_{max}$ values of some shale samples are above 455 °C, which suggests that these samples are mainly of low maturity and that some shale samples have entered a high maturity stage.

2.1.3. Mineral Composition. The mineral compositions of the shale samples are the main factor that affects the storage, collection, seepage, transport, and mining effect of shale gas. The results from the XRD analysis of 10 shale samples from P1s and 23 shale samples from P2xs are shown in Figures 11 and 12. The quartz contents in the P1s vary from 29.2 to 46.3% with an average value of 33.9%, the albite content varies from 0 to 5.5% with an average value of 1.3%, the pyrite content varies from 0 to 4.9% with an average value of 1.5%, the siderite content varies from 0 to 11.3% with an average value of 3.7%, the dolomite content varies from 0 to 3.6% with an average value of 0.4%, and the total clay minerals content varies from 50.6 to 69.7% with an average value of 59.2%; in the P1s shale samples (Figure 11a), the mass fraction of kaolinite is slightly higher than that in the illite/smectite mixed layer and its average mass fraction is approximately 40% while the accumulated contents of kaolinite and illite/smectite in the mixed layer in the clay minerals are greater than 80% (Figure 11b). Similarly, the contents of quartz, albite, pyrite, siderite, dolomite, and clay minerals in the P2xs shale samples range from 18.6−46.9, 0−14.6, 0−2.1, 0−10.2, and 0 with averages of 32.7, 1.5, 0.1, 2.8, 0, and 62.8%, respectively (Figure 12a); the average contents of kaolinite and illite/smectite in the mixed layer are 55.7 and 31.3%, respectively (Figure 12b). A comparison of the mineral contents of the P1s shale samples shows that the quartz content of the P1s shale is slightly higher than that of the P2xs shale.

2.2. Physical Properties of Shale Reservoirs. 2.2.1. Shale Permeability and Porosity. The results from pulse decay permeability measurements of the shale samples show that the reservoir permeabilities in both P1s and P2xs are low; the pulse decay permeability values of the shale samples in P1s vary from 0.000254 to 0.000901 mD with an average of 0.000464 mD, and the pulse decay permeability values of the shale samples from P2xs vary from 0.000324 to 0.000418 mD.
with an average of 0.000317 mD (Table 4). The MIP results show that the porosities of the shale samples are poor to moderate (Table 4). The porosity ($\varphi_m$) values range from 1.28 to 4.29% with an average of 2.34% in the P1s shale samples, and the porosity values range from 0.87 to 2.20% with an average of 1.54% in the P2xs shale samples (Table 4). The results shown in Table 4 suggest that the shale reservoirs have poor reservoir properties, which are perhaps unfavorable for shale exploitation.

2.2.2. PSD and Fractures of Shale. The relationships of the cumulative pore volumes with intrusion pressures in the shale sample plot using mercury intrusion and mercury extrusion and the incremental pore volume plots versus pore diameters of the shale samples are shown in Figure 13 and show that the cumulative pore volumes in the shale samples increase to their maximum values when the pressures are close to 100 MPa (Figure 13a), and the incremental pore volumes in the shale samples increase greatly when the pore diameters are less than...
100 nm (Figure 13b). Wide hysteresis loops are evident between the mercury intrusion curve and mercury extrusion curve, which indicate that many poorly interconnected pores are present in the shale samples. A comparison of $P_{1s}$ and $P_{2ns}$ suggests that the cumulative pore volumes and incremental pore volumes of the shale samples from $P_{1s}$ are higher than those of $P_{2ns}$. The pore volumes and percentages of different pore types in the shale samples are shown in Table 5, and the surface areas of the pores are shown in Table 6. As indicated in Tables 5 and 6, the pore volumes of different pore types in the shale samples from $P_{1s}$ are mostly higher than those in $P_{2ns}$ and the pore volumes of the transition pores and micropores are higher than those of the macropores and mesopores in the shale samples from both $P_{1s}$ and $P_{2ns}$. The volume fractions of the transition pores are highest in the WY-14 and WY samples among the shale samples from $P_{1s}$, but the volume fraction of micropores is highest for the WY-46 sample. The results from the pore volumes of different pore types show that there is little difference among the pore volumes for different pore types, which further indicates that the pores in the shale samples developed poorly not only in $P_{1s}$ but also in $P_{2ns}$. The surface areas of the pores in the $P_{1s}$ and $P_{2ns}$ samples suggest that the surface areas, surface area fractions of the transition pores, and micropores are dominant in the PSD of the shale samples.

$N_{2}$ adsorption can be used to determine the volumes of the vast micropores relative to the partial transition pores. The adsorption curves and $N_{2}$ dV/dlog $r$ values for the shale samples are shown in Figure 14. As Figure 14a indicates, sample WY-05 has the highest adsorption quantity whereas samples WY-33 and WY-45 have moderate adsorption quantity, and samples WY-09, WY-19, WY-27, and WY-51 exhibit relatively poor adsorption quantity, which demonstrates that the transition pores and micropores in sample WY-05 developed the best, the transition pores and micropores in samples WY-33 and WY-45 developed relatively well, and the transition pores and micropores in samples WY-09, WY-19, WY-27, and WY-51 developed the least. Additionally, there is a wide hysteresis loop and an inflection point in the adsorption curve of sample WY-14, a relatively wide hysteresis loop and inflection point in the adsorption curves of samples WY-09, WY-33, and WY-45, and a narrow hysteresis loop and an inflection point in the adsorption curves of samples WY-05, WY-19, and WY-27, which indicate that open pores developed best in sample WY-14; however, they developed well in samples WY-09, WY-33, and WY-45, but there are narrow hysteresis loops or inflection points for samples WY-05, WY-19, and WY-27, which suggest that there is an abundance of closed pores. The dV/dlog $r$ plots suggest bimodality for all shale samples (i.e., peaks at ~2 and 18 nm) (Figure 14b), which reveals that there are obvious incremental pore volumes when the pore radii are near 2 and 18 nm. Table 7 shows the pore volumes and BET surface areas from the $N_{2}$ adsorption analysis. The results of Table 7 show that the pore volumes and BET surfaces from the pores with pore radii of 2 to 50 nm dominate the total pores, which is consistent with the analysis of $N_{2}$ dV/dlog $r$ values.

To determine the PSDs of the shale samples, the pore types and mineral compositions in samples WY-4 and WY-14 were analyzed and are shown in Figure 15. It can be seen that there are different pore types such as organic matter pores (gas pores), intergranular pores, intragranular pores, and dissolved pores in the organic matter, in the clay minerals, and the pyrite. Additionally, there are a few fractures such as endogenous fractures in organic matter and structural fractures in minerals. The FIM-SEM observations suggest that the pores and fractures have developed poorly in the shale, that the pores are mainly distorted pores, and that the pores and fractures are usually filled with minerals.

2.3. Gas-Bearing Capacity. Gas content is an important parameter used to evaluate unconventional gas reservoirs. The results of the CH$_4$ adsorption isotherms are shown in Figure 16. As seen from Figure 16, the adsorption capacities of the shale samples are over 1 m$^3$ t$^{-1}$ when the pressures are close to equilibrium. The adsorption volume is simulated according to the Langmuir model. Based on the simulated results, the adsorption capacity of sample WY-47 from $P_{1s}$ is 2.33 m$^3$ t$^{-1}$ and the adsorption capacities of the shale samples

| Table 4. Pulse Permeability, Porosity of Shale in Huainan |
|---------------------------------------------|
| sample no. | drilling no. | depth (m) | formation | $k$ (mD) | $\varphi_{M}$ (%) | bulk density (g cm$^{-3}$) |
| WY-04  | 11−1   | 1513.8  | $P_{1s}$ | 0.000901 | 4.29 | 2.1127  |
| WY-10  | 10−1   | 1056.3  | $P_{1s}$ | 0.000468 | 2.39 | 2.1648  |
| WY-20  | 20−2   | 1448.6  | $P_{1s}$ | 0.000254 | 1.38 | 2.1592  |
| WY-52  | 20−2   | 1236.1  | $P_{1s}$ | 0.000312 | 1.28 | 2.1586  |
| WY-14  | 20−2   | 1362.9  | $P_{2ns}$ | 0.000418 | 0.87 | 2.1672  |
| WY-46  | 10−2   | 1162.2  | $P_{2ns}$ | 0.000324 | 2.20 | 2.1238  |

Figure 13. Cumulative (a) and incremental (b) Hg pore volume in shale samples.

https://doi.org/10.1021/acsomega.1c00290
ACS Omega 2021, 6, 8502–8516
from the lower part of P2xs range from 1.83 to 2.85 m³ t⁻¹ with an average of 2.45 m³ t⁻¹.

The gas content of free gas is defined as $Q_f$ and is determined by the oil and gas saturation, shale volume, and shale porosity and can be expressed as

$$Q_f = V \times \Phi_g \times S_g$$  \hspace{1cm} (2)$$

where $S$ denotes the gas content of free gas, m³ t⁻¹, and $V$ denotes the shale volume, m³, and can be calculated based on the shale density, while the average shale density can be calculated from the results shown in Table 4; the average shale densities in P1s and P2xs are 2.1488 and 2.1455 g cm⁻³, respectively; $\Phi_g$ denotes the effective shale porosity, %, and is determined by MIP, the average values are 2.34 and 1.54%, respectively, in the P1s and P2xs shale; $S_g$ denotes the oil and gas saturation, %. $S_g$ is determined by neutron logging measurements, and the values are 48 and 35.5%, respectively, in P1s and P2xs. Therefore, the calculated gas content of the free gas in P1s

| Table 5. Pore Volume and Its Percent in Different Coal Samples by MIP* |
|-------------------------|-------------------------|-------------------------|-------------------------|
| sample no.              | $V_1$                   | $V_2$                   | $V_1$                   |
| WY-04                   | 0.001                   | 0.001                   | 0.001                   |
| WY-10                   | 0.002                   | 0.001                   | 0.004                   |
| WY-20                   | 0.001                   | 0.001                   | 0.002                   |
| WY-52                   | 0.002                   | 0.000                   | 0.002                   |
| WY-14                   | 0.002                   | 0.000                   | 0.001                   |
| WY-46                   | 0.001                   | 0.000                   | 0.003                   |

* $V_1-V_4$ the pore volumes of the macropore (pore diameter ≥ 1000 nm), mesopore (1000 > pore diameter > 100 nm), transition pore (100 > pore diameter > 10 nm), and micropore (10 > pore diameter), respectively; $V_t$ total pore volume; $V_i/V_j$, $V_i/V_t$ means the percentages from the macropore, mesopore, transition pore, and micropore in the total pore volume, respectively.

| Table 6. Surface Area of Pore and Its Percent in Different Coal Samples by MIP* |
|-------------------------|-------------------------|-------------------------|-------------------------|
| sample no.              | $S_1$                   | $S_2$                   | $S_3$                   |
| WY-04                   | 0.001                   | 0.019                   | 2.262                   |
| WY-10                   | 0.002                   | 0.025                   | 0.776                   |
| WY-20                   | 0.001                   | 0.009                   | 0.432                   |
| WY-52                   | 0.001                   | 0.004                   | 0.318                   |
| WY-14                   | 0.001                   | 0.004                   | 0.187                   |
| WY-46                   | 0.000                   | 0.008                   | 0.352                   |

* $S_1-S_4$ means the surface areas of the macropore (pore diameter ≥ 1000 nm), mesopore (1000 > pore diameter > 100 nm), transition pore (100 > pore diameter > 10 nm), and micropore (10 > pore diameter), respectively; $S_t$ total pore volume; $S_i/S_t-S_4/S_t$ means the percentages of surface areas from the macropore, mesopore, transition pore, and micropore in total surface area, respectively.

Figure 14. N₂ adsorption quantity (a) and dV/dlog $r$ (b) of shale samples.

Table 7. Pore Volumes and BET Surface Areas of the Shale Samples by N₂ Adsorption

| sample no. | <2 nm | 2–50 nm | >50 nm | total | surface area (m² g⁻¹) | <2 nm | 2–50 nm | >50 nm | total |
|------------|-------|---------|--------|-------|----------------------|-------|---------|--------|-------|
| WY-05      | 4.92 × 10⁻⁴ | 0.019955 | 0.013099 | 0.33546 | 1.080235 | 9.484655 | 0.735128 | 11.3 |
| WY-09      | 2.58 × 10⁻⁴ | 0.014854 | 0.008793 | 0.023905 | 0.563981 | 7.063622 | 0.4963 | 8.123904 |
| WY-19      | 2.24 × 10⁻⁴ | 0.013642 | 0.007935 | 0.021801 | 0.491301 | 6.107043 | 0.427479 | 7.025823 |
| WY-27      | 9.07 × 10⁻⁵ | 0.01324 | 0.010478 | 0.023809 | 0.197907 | 4.922125 | 0.570962 | 5.690993 |
| WY-33      | 3.13 × 10⁻⁴ | 0.018177 | 0.012266 | 0.030756 | 0.684309 | 8.515186 | 0.685537 | 9.885032 |
| WY-45      | 4.9 × 10⁻⁴  | 0.01947 | 0.01074 | 0.03071 | 1.08412 | 9.64351 | 0.60343 | 11.33106 |
| WY-14      | 4.67 × 10⁻⁴ | 0.015013 | 0.007554 | 0.023034 | 1.027371 | 7.9867 | 0.428341 | 9.442413 |
is 0.52 m$^3$ t$^{-1}$, and the calculated gas content of the free gas in P2xs is 0.51 m$^3$ t$^{-1}$. The total gas content of shale is the sum of the gas contents of the adsorption gas and free gas; the total gas contents of the shale from P1s and P2xs are 2.85 and 2.96 m$^3$ t$^{-1}$, respectively, which are well above 1 m$^3$ t$^{-1}$, which is the limit for industrial shale gas exploration.

2.4. Resource and Exploitation Potential. 2.4.1. Resource Potential of the Shale Reservoir. As mentioned above, the Rock-Eval parameters $S_0$, $S_1$, $S_2$, TOC, and HI have been discussed. However, to analyze the hydrocarbon potential of the shale reservoirs in the studied area, the related calculated parameters including the hydrocarbon generation potential (defined as PG, PG = ($S_0 + S_1 + S_2$)), hydrocarbon index (abbreviated as HCl, equal to ($S_0 + S_1$)/TOC × 100), hydrocarbon generation potential index (defined as GPI, equal to ($S_1 + S_2$)/TOC × 100), production index (defined as PI, equal to $S_1/(S_1 + S_2)$), and degradation ratio (defined as D, equal to PG/TOC × 100) were calculated, and the ranges and averages of the results are shown in Table 8. The results from Table 8 show that the P1s and P2xs shales have a good hydrocarbon generation potential and also reveal that the P2xs shale reservoir has a higher hydrocarbon generation potential than P1s and has a lower gas generation potential than P1s.

However, the calculated parameters can only be used to evaluate the theoretical hydrocarbon generation ability and are based on the residual organic matter in the shale and are not used to evaluate the existing gas amounts in the shale reservoirs. Therefore, the resource potentials of the shale reservoirs in the studied area must be estimated based on the existing gas content of the shale gas. The volumetric method is adopted to evaluate the resource potential of unconventional gas. During the estimations, the following boundary conditions were assumed: the effective thicknesses of shale whose TOCs are greater than 1% are defined, the effective area of the shale distribution region is determined where the area is larger than 50 km², TOC is over 1.0%, $R_o$ is greater than 0.7%, and the burial depth of the shale is deeper than 500 m. Based on these conditions, the units of the estimated formation were divided, and the results from Figures 2, 3, 4, 5, 9, and 10 were combined; the parameters of the units are shown in Table 9. Table 10 shows the estimated results for shale gas resources and shale gas abundances; the total shale gas amounts in the P1s shale reservoir at burial depths of 500–800, 800–1200, and 1200–1600 m are 640.64 × 10$^8$ to 877.25 × 10$^8$, 1840.77 × 10$^8$ to 2036.01 × 10$^8$, and 1120.84 × 10$^8$ to 1169.78 × 10$^8$ m$^3$, respectively; the total shale gas amounts in the P2xs shale reservoir at burial depths of 500–800, 800–1200, and 1200–1600 m are 1674.79 × 10$^8$ to 2463.2 × 10$^8$, 3577.34 × 10$^8$ to 4096.88 × 10$^8$, and 2383.19 × 10$^8$ to 2348.19 × 10$^8$ m$^3$.

Figure 15. Pore types and mineral compositions in shale samples by FE-SEM: (a–c) the WY-4 sample of P1s; (d–f) the WY-14 sample of P2xs.

Figure 16. CH$_4$ adsorption capacities in shale samples (WY-47 sample from P1s, other samples from P2xs).

Table 8. Ranges and Averages of Calculated Parameters Based on Rock-Eval Parameters

| formation | PG (mg g$^{-1}$) | HCl (mg g$^{-1}$ TOC) | GPI (mg g$^{-1}$ TOC) | PI (%) | D (%) |
|-----------|-----------------|-----------------------|----------------------|--------|-------|
| P1s       | 0.17–5.77       | 1.35–213.51           | 48.48–89.74          | 9.09–48.39 | 37.33 |
| P2xs      | 0.35–40.24      | 6.20–112.50           | 35.97–96.49          | 1.77–2.09 | 37.55 |
|           | 7.05             | 42.04                 | 73.73                | 14.77   | 15.22 |

Table 10 shows the estimated results for shale gas resources and shale gas abundances; the total shale gas amounts in the P1s shale reservoir at burial depths of 500–800, 800–1200, and 1200–1600 m are 640.64 × 10$^8$ to 877.25 × 10$^8$, 1840.77 × 10$^8$ to 2036.01 × 10$^8$, and 1120.84 × 10$^8$ to 1169.78 × 10$^8$ m$^3$, respectively; the total shale gas amounts in the P2xs shale reservoir at burial depths of 500–800, 800–1200, and 1200–1600 m are 1674.79 × 10$^8$ to 2463.2 × 10$^8$, 3577.34 × 10$^8$ to 4096.88 × 10$^8$, and 2383.19 × 10$^8$ to 2348.19 × 10$^8$ m$^3$. 

https://doi.org/10.1021/acsomega.1c00290
The BI values can be calculated as follows:

\[
\text{BI} = \frac{C_{\text{quartz}}}{C_{\text{quartz}} + C_{\text{clay}} + C_{\text{carbonate}}} \times 100
\]

where \(C_{\text{quartz}}\) denotes the quartz content, \(C_{\text{clay}}\) denotes the content of clay minerals, and \(C_{\text{carbonate}}\) denotes the carbonate content. Integrating with the results from Table 1, Table 4, and Figures 2, 3, 4, 5, and 8, the basic conditions of the shale reservoirs in the studied area are shown in Table 11. It can be seen that \(R_o\) shale thickness, average TOC, average shale porosity (defined as \(\phi_{\text{shale}}\)), and average BI can meet the requirements for shale gas exploration and exploitation, which indicates that there is relatively good potential for shale gas exploration and exploitation in the studied area (Table 11).

It is undeniable that the partial TOC is lower than 2.0%, the porosities of the partial shale in P2xs are lower than 1%, the shale formation ratios in the partial zone are lower than 0.5, and the partial BI is lower than 35%, which suggest that there are unfavorable zones in terms of TOC, shale formation ratios, shale porosities, and BIs for shale gas exploration and exploitation. Furthermore, the related pyrolysis parameters such as \(S_0\), \(S_1\), \(S_2\), HI PG, GPI, PI, relatively poor permeabilities and PSDs of the shale reservoirs, and relatively low free gas content all show that there are unfavorable conditions from the aspect of the hydrocarbon source rock, gas-bearing capacity, and physical properties. The above analysis shows that the studied shale reservoirs must be subjected to fracturing if the shale gas project is to be realized, and a BI evaluation for fracturing should be pre-performed because BI is a key factor that directly affects fracturing. Therefore, further work that includes source rock investigations, determinations of favorable zones for shale gas exploration and exploitation, and fracturing evaluations is necessary; in particular, investigation of the shale gas content will be the direction of further investigations.

3. CONCLUSIONS

In this study, a comprehensive investigation of the geological properties of shale gas, which included geochemical characteristics, physical properties, and gas-bearing capacity of the studied shale reservoirs, was conducted; the resource and exploitation potential was evaluated for Lower Permian marine-continent transitional facies shale gas in the Huainan Basin, China. The conclusions can be summarized as follows.

1. There is great potential for shale gas production in the shale of the Huainan Basin where the cumulative thicknesses are generally greater than 35 and 65 m, respectively, for P1s, and P2xs. The TOCs in the shale vary from 0.11 to 8.87% and from 0.22 to 14.63% for P1s, and P2xs respectively; the kerogen type predominantly belongs to type II with minor amounts of type I or type III kerogen; the average mineral contents in the shale samples range from 0.83 to 0.94% and from 0.82 to 1.02% for P1s, and P2xs respectively; the \(T_{\text{max}}\) values of most shale samples from P1s and P2xs vary from 435 to 455 °C with an average of 451.23 °C; the \(T_{\text{max}}\) values of the partial shale samples are greater than 455 °C; the shale samples are mainly of low maturity, and the partial shale has entered the high-mature stage. The quartz contents in shale vary from 29.2 to 46.3% and from 18.6 to 46.9% for P1s, and P2xs respectively. These conditions and geochemical characteristics indicate that the shale in the studied area presents relatively favorable conditions for shale gas generation and exploitation.

### Table 9. Parameters for Estimation Units

| formation | parameter | burial depth(m) |
|-----------|-----------|----------------|
|           |           | 500–800 | 800–1200 | 1200–1600 |
| P1s       | area (km²) | 852.6   | 1084.6  | 489.37   |
|           | thickness (m) | 4.5–55   | 15–50   | 9.3–67.4 |
|           | volume of shale reservoir (km³) | 25.58   | 48.81  | 24.47   |
| P2xs      | area (km²) | 990.12  | 962.1   | 400     |
|           | thickness (m) | 25–110  | 50–105  | 22.6–137 |
|           | volume of the shale reservoir (km³) | 64.36  | 86.59  | 44     |

respectively. The shale gas abundances in the P1s shale reservoir at burial depths of 500–800, 800–1200, and 1200–1600 m are 0.75 × 10³ to 1.03 × 10³, 1.7 × 10³ to 1.88 × 10³, and 2.29 × 10³ to 2.39 × 10³ m³ km⁻², respectively; the shale gas abundances in the P2xs shale reservoir at burial depths of 500–800, 800–1200, and 1200–1600 m are 1.69 × 10³ to 2.49 × 10³, 3.72 × 10³ to 4.26 × 10³, and 5.6 × 10³ to 5.87 × 10³ m³ km⁻², respectively. The amounts of adsorption gas, free gas, and the sum of the shale gas in P1s are 1232.78–1541.69, 151.27, and 3602.29 to 4083.04 m³, respectively. It can be seen that shale gas mainly occurs in the shales with burial depths exceeding 800 m and that the shale gas amounts from the adsorption gas and free gas in the shale reservoirs at burial depths of 800–1200 m are higher than the amounts at other burial depths and shale abundances increase with deeper burial depths.

2.4.2. Shale Gas Exploration and Exploitation Potential.

Shale reservoirs that would be favorable for shale exploration and exploitation must fulfill the requirements as follows: the shale formation ratio (i.e., the ratio between shale thickness and formation thickness) > 0.5; TOC > 2%; 0.5% < \(R_o\) > 2%; shale thickness > 6 m; 5% ≥ shale porosity \((\phi)\) ≥ 1%; 4000 m > burial depth; and brittleness index (abbreviated as BI) ≥ 35%. The BI values can be calculated as follows:

\[
\text{BI} = \frac{C_{\text{quartz}}}{C_{\text{quartz}} + C_{\text{clay}} + C_{\text{carbonate}}} \times 100
\]

where \(C_{\text{quartz}}\) denotes the quartz content, \(C_{\text{clay}}\) denotes the content of clay minerals, and \(C_{\text{carbonate}}\) denotes the carbonate content. Integrating with the results from Table 1, Table 4, and Figures 2, 3, 4, 5, and 8, the basic conditions of the shale reservoirs in the studied area are shown in Table 11. It can be seen that \(R_o\) shale thickness, average TOC, average shale porosity (defined as \(\phi_{\text{shale}}\)), and average BI can meet the requirements for shale gas exploration and exploitation, which
from unit-mass source rocks (decomposed shale samples, peak temperatures of pyrolysis (expressed as total organic carbon content (abbreviated as TOC) in the distributed on both sides of the Panji anticline in the Huainan 4. EXPERIMENTAL SECTION

| formation | TOC (%) | R <sub>0</sub> (%) | thickness of shale | average shale formation ratio | Φ <sub>4</sub> (%) | burial depth (m) | BI (%) |
|-----------|---------|---------------------|--------------------|-------------------------------|----------------|-----------------|--------|
| P<sub>1s</sub> | 0.11−8.87 | 0.83−0.94 | >15 | 0.574 | 1.28−4.29 | <1600 | 30.3−40.46 |
| | 2.70 | 0.91 | | 2.34 | 36.23 | |
| P<sub>2xs</sub> | 0.22−14.63 | 0.82−1.02 | >25 | 0.568 | 0.87−2.20 | <1600 | 18.6−55.96 |
| | 3.03 | 0.86 | | 1.54 | 34.50 | |

(2) The P<sub>1s</sub> and P<sub>2xs</sub> reservoirs have low permeability values of 0.000254−0.000901 and 0.000324−0.000418 mD and porosities from 1.28 to 4.29% and from 0.87 to 2.20%, respectively. The pores in the P<sub>1s</sub> shale reservoir are characterized by well-developed micropores and transition pores and poorly developed mesopores, while the pores in the P<sub>2xs</sub> shale reservoir are all characterized by well-developed micropores and transition pores, and partially well-developed macropores. The different pore types in the shale reservoirs have developed in organic matter, clay minerals, and pyrite, while a few endogenous fractures have developed in organic matter, and structural fractures have developed in minerals in which the pores are mainly distorted pores and the pores and fractures are usually filled with minerals.

(3) The adsorption capacity of the sample from P<sub>1s</sub> is 2.33 m<sup>3</sup> t<sup>−1</sup>, the adsorption capacities of the samples from P<sub>2xs</sub> range from 1.83 to 2.85 m<sup>3</sup> t<sup>−1</sup>, the calculated gas contents of the free gas are 0.52 and 0.51 m<sup>3</sup> t<sup>−1</sup> in P<sub>1s</sub> and P<sub>2xs</sub> respectively. The total gas contents of the shale in P<sub>1s</sub> and P<sub>2xs</sub> are 2.85 and 2.96 m<sup>3</sup> t<sup>−1</sup>, respectively.

(4) The P<sub>1s</sub> and P<sub>2xs</sub> shales have a good hydrocarbon generation potential; the P<sub>2xs</sub> shale reservoir has a higher hydrocarbon generation potential than P<sub>1s</sub> and has a lower gas generation potential than P<sub>1s</sub>. The amounts of adsorption gas, free gas, and the sum of the shale gas in P<sub>1s</sub> are 1232.78−1541.69, 151.27, and 3602.29 to 4083.04 × 10<sup>3</sup> m<sup>3</sup> respectively, and the amounts of adsorption gas, free gas, and the sum of the shale gas in P<sub>2xs</sub> are 2513.4−3153.13, 297.64, and 2811.04 to 3450.77 × 10<sup>3</sup> m<sup>3</sup> respectively.

(5) The studied area has relatively good potential for shale gas exploration and exploitation, but there are unfavorable zones when considering TOC, shale formation ratios, shale porosities, and BIs for shale gas exploration and exploitation, and further work for shale gas exploration and exploitation in the studied area needs to be performed.

4. EXPERIMENTAL SECTION

4.1. Shale Samples. A total of 33 fresh mudstone samples were collected from eight sampling drillings and were distributed on both sides of the Panji anticline in the Huainan coalfield (Figure 1); all shale samples were from coal-bearing formations in the Lower Permian. The burial depths of all shale samples range from 900 to 1600 m.

4.2. Experimental Methods and Procedures. A total of 25 selected shale samples were selected for rock pyrolysis analysis according to GB/T 18602−2012<sup>46</sup> to measure the total organic carbon content (abbreviated as TOC) in the shale samples, peak temperatures of pyrolysis (expressed as T<sub>max</sub>), amounts of gaseous hydrocarbon in unit-mass source rocks (defined as S<sub>0</sub>), amounts of liquid hydrocarbon in unit-mass source rocks (defined as S<sub>1</sub>), amounts of kerogen cracked from unit-mass source rocks (defined as S<sub>2</sub>), which were measured at temperatures of 90, 300, and 300−650 °C, respectively, using a ROCK-EVAL6 rock pyrolysis analyzer (Vinci-Technologies Corporation Ltd., France). When the S<sub>0</sub> values were determined, a constant temperature of 90 °C should last for 2 min; when the S<sub>1</sub> values are determined, a constant temperature of 300 °C should last for 3 min. When TOC values are determined, a constant temperature of 300 °C should last for 2 min, and then the initial temperature was increased with a rate of 20 °C/min until it reached 850 °C.

A total of 26 selected samples were used for vitrinite reflectance measurements of kerogen (expressed as R<sub>0</sub>), which were performed under an MPV-SP microphotometer (Leica Corporation Ltd., Germany). A total of 25 selected samples were used for determining maceral kerogen compositions, and this work was performed under an Axioscope advanced biological transmittance-fluorescence microscope (Zeiss, Germany). Four selected samples were used to determine carbon isotopes, and these measurements were performed under an MAT-252 stable isotope mass spectrometer (Finnigan Corporation Ltd., USA). A total of 33 selected samples were used for mineral content analyses by X-ray diffraction (abbreviated as XRD), which was performed using a D/max-2500 X-ray diffractometer (Rigaku Corporation Ltd., Japan). Vitrinite reflectance measurements, maceral kerogen compositions, carbon isotope determinations, and mineral content analyses were conducted according to SY/T 5124−2009, SY/T 5238−2008, and SY/T 5163−2018, respectively.<sup>47−50</sup>

A total of six selected samples were used to determine pore size distribution (abbreviated as PSD), and porosities were determined by mercury intrusion porosimetry (referred to as MIP) and were performed with an Autopore IV 9500 instrument (Micromeritics Instruments, USA) at pressures of up to 60,000 psi (413.7 MPa) and followed ISO 15901-1-2008, SY/T 5238−2008, and SY/T 5163−2018, respectively.<sup>51</sup> Pulverized samples with 45−60 mesh particle sizes were used as the experimental samples in LTNA, and nitrogen was applied as the adsorbate with an analysis bath temperature of ~195.85 °C. The N<sub>2</sub> data that were collected from the crushed samples were interpreted using multipoint BET analysis for the surface area and BJH analysis for the PSD.<sup>11,53</sup> Six selected samples were used to determine pulse permeabilities with the pulse attenuation method under a PDP200 pulse permeability analyzer (Core Lab, USA) according to SY/T 5336−2006.<sup>54</sup> Additionally, the observations and quantitative analyses of pores and minerals in all coal samples were conducted on a Sigma FE-SEM (ZEISS, German) operating at 20 kV and equipped with an energy-dispersive spectrometer for analyses of mineral compositions based on SY/T 5162−2014.<sup>55</sup> The small coal pillars used for FE-SEM were polished using a cross section polisher to remove the oxide layers (approximately 1−
2 μm thick) on the coal pillars and were not splattered with a gold coating or other materials. The CH₄ adsorption isotherms of the four selected samples were determined at an experimental temperature of 30 °C using the volumetric method. The recommended procedure of the Chinese National Standard GB/T 19560−2008 was used and was performed under an IS-300 isothermal adsorption instrument (Terratek Corporation Ltd., USA).

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The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This study was supported by the University Natural Science Research Project of Anhui Province (KJ2019A0100), the Anhui Provincial National Natural Science Foundation (2008085MD121), the National Natural Science Foundation of China (Grant Nos. 41727801, 41302129), and the Anhui Postdoctoral Research Project (2017B171).

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