Pore Structure of Organic Matter in the Lacustrine Shale from High to Over Mature Stages: An Approach of Artificial Thermal Simulation

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ABSTRACT: The pore structure of organic matter (OM) is affected by the maturity and type of OM, and these exert an important control on the development of OM pores. However, it is often challenging to distinguish between autochthonous and secondary OM. In this study, different types of OM were distinguished by means of morphology and the form of its occurrence under scanning electron microscopy (SEM) observation. Pyrolyzed samples were used to obtain pore structures of autochthonous and secondary OM from a lacustrine shale from high to over mature stages. The SEM observations indicated that the secondary OM is porous, whereas the autochthonous OM is nonporous. Further, nitrogen adsorption data showed that nanopores in the autochthonous OM are blocked in non-extracted samples and reoccurred after extraction, whereas nanopores in the secondary OM remain open from high to over mature stages. Moreover, the pore structure, i.e., pore type and pore size, differed for autochthonous and secondary OM in the lacustrine shale. For instance, nanopores in the autochthonous OM were micropores (smaller than 1.5 nm); nanopores in the secondary OM were mesopores (ranging from 5 to 20 nm) and micropores. Nanopores in the autochthonous OM were formed at reflectance values (Ro) of 1.50%, but they were slightly destroyed at the over mature stage. Nanopores in the secondary OM were formed at 2.00% Ro and were preserved. Therefore, the development of OM nanopores in the lacustrine shale was synchronously affected by the type of OM and maturity. Furthermore, nanopores in the secondary OM were more developed than those in the autochthonous OM; thus, the OM nanopores at the high mature stage belonged to the autochthonous OM, and those at the over mature stage mainly belonged to the secondary OM. Besides, the nanopores in the autochthonous OM are easily blocked. Therefore, the secondary OM is important to the development of OM nanopores in the lacustrine shale at the over mature stage.

1. INTRODUCTION

The pore structure of organic matter (OM) is a crucial parameter in evaluating the potential and production of shale gas.1,2 OM pores have been extensively described as important components of shale pore systems.1−4 Understanding the complex OM pore networks and the influencing factors on the pore structure of OM has become a strategic subject and has attracted increasing attention during the past 2 decades.5−9 The main geological controlling factors on the pore structure of OM are mainly the OM content, type, and maturity.6,10 There are almost no secondary OM pores in immature shales.11 OM pores observed in the kerogen of immature shales12,13 are mostly considered to be primary.14,15 Secondary OM pores observed in shales are a result of hydrocarbon generation.12,14 Secondary OM pores are formed by gas release out of the OM space.14−18 Thermal maturity determines hydrocarbon production; therefore, maturity is an important factor in the development of OM pores.5,14,18−21 For instance, the dominant change in the Eagle Ford pore system from the early oil window (≈0.5% Ro) to the gas window (≈1.3% Ro) is an increase in the abundance of small secondary OM-hosted pores.13 However, OM pores are not observed in oil windows as the filling of bitumen overcomes the generation of OM pores.22,23 Kerogen swelling also leads to the destruction of OM pores but is usually weakened at higher maturity.15,21,24 Secondary OM pores can only be formed after the maximum kerogen swelling.15 Therefore, it is generally believed that secondary OM pores are well-developed from high to over mature stages,2,5,13,14,17,25 and these pores are mainly in the nanoscale.26 Secondary nanopores are progressively developed as the OM maturity gradually increases.1,14,27

OM from the high to over mature stage is referred to as bitumen and pyrobitumen in organic geochemistry and
includes oil, solid bitumen, and pyrobitumen in organic petrology terminology.26 Solid bitumen and pyrobitumen are the prevalent OM components in shales at the late oil window and dry gas window.28,29 Moreover, the secondary cracking of oil and formation of pyrobitumen are important reasons for the well-developed OM pores in the Barnett shale.16 Pyrobitumen, defined as the insoluble or slightly soluble product in CS2,30 is produced by the in situ cracking of oil or bitumen.13 Kerogen-rich parts in the La Luna shale are mainly macro/mesoporous with some microporosity development, while solid bitumen-rich parts are microporous.31 For shale samples with low oil-expulsion efficiency, the remaining bitumen could aid nanopore (<10 nm) generation at high mature stages.33 Small-scale spatial heterogeneity in OM-hosted porosity has been noted at the nanometer to micrometer scale in previous studies.2,17 Therefore, OM composition is likely an important control on predicting the OM pore development in addition to its maturity.

The most practical way to identify OM components is through SEM observation. Terms used for OM components include kerogen/solid bitumen16,17 and detrital/secondary/depositional/migrated OM in shales under SEM observation.2,17,28 Autochthonous detrital OM (kerogen) is used to be discriminated from secondary OM (diagenetic; solid bitumen and related diageneric products) in SEM images.12 Nevertheless, it remains difficult to accurately identify OM components in petrography-based definition under SEM observation, leading to recurrent inappropriate distinctions between kerogen and bitumen11 and limiting the understanding of whether the OM components are porous or nonporous.9 However, OM can be directly distinguished based on the morphology and the form of its occurrence under SEM observation.28 Our previous study found that the pore structure of one kind of OM is affected by solvent extraction, while the pore structure of another kind of OM is not affected by it.28 In this study, autochthonous and secondary types of OM were distinguished under SEM observation. Pyrolyzed samples were used to obtain the pore structures of autochthonous and secondary OM of a lacustrine shale from high to over mature stages. Moreover, this study determined the effect of maturity on the development of nanopores in the autochthonous and secondary OM.

2. SAMPLES AND METHODS

2.1. Samples. Two large-diameter organic-rich (total organic carbon [TOC] ≥ 2%) shale samples were acquired from the Upper Triassic Yanchang Formation (Chang 7 members) in the Fuxian Lake in the southern part of the Yishan slope, Ordos Basin. The Yanchang lacustrine shale has been defined as a self-sourced and self-preserved petroleum system containing oil and gas in ultratight fine-grained rocks with high OM content, making it a key formation for shale gas exploration and development.6,24 The initial samples came from the FY2 and FY3 wells at 1425 and 1256 m depth, respectively. The locations of raw samples were described in our previous study.35 The quality used for the hydrous pyrolysis and OM abundance of the initial sample from the FY2 well (sample FY2) was higher than that of the initial sample from the FY3 well (sample FY3); consequently, sample FY3 was a supplement to sample FY2. The dominant macerals in the Yanchang Shale (in the Chang 7 members) are amorphous OM formed by the sapropilification products of alginite (lamlaginite and telalginite) and vitrinite.38 Therefore, the OM type of the FY2 and FY3 organic-rich shale sample was type II, as supported by the published literature.39

2.2. Methods. 2.2.1. Hydrous Pyrolysis. The structure of the instrument and experimental scheme (Table 1) of the hydrous pyrolysis with restricted conditions have been fully described in our previous study.35 Hydrous pyrolysis experiments were performed in a semiclosed simulation system where the fluid medium used was distilled water. The sample kettle was heated to a specified temperature at a fixed rate and kept steady for 72 h. When the hydrodynamic pressure of the sample kettle exceeded 5 MPa, the system discharged redundant hydrocarbon products into the liquid condensation collector to keep the hydrodynamic pressure consistent. When the temperature of the sample kettle was lower than 150 °C, the products were discharged to the collector system after the heating stopped. The set temperature was the steady temperature of the furnace and not the temperature of the sample surface or the sample kettle. The actual heating temperature of the sample was less than the set temperature. The maturity of the heated sample started to change only when the heating temperature was higher than 425 °C; therefore, the initial set temperature was 425 °C (Table 1).

Table 1. Summary of the Pyrolysis Experimental Conditions

| experiment no. | temperature (°C) | lithostatic pressure (MPa) | fluid pressure (MPa) |
|---------------|-----------------|---------------------------|---------------------|
| 1             | 425             | 88                        | 39                  |
| 2             | 450             | 94                        | 41                  |
| 3             | 475             | 99                        | 44                  |
| 4             | 500             | 110                       | 48                  |
| 5             | 525             | 118                       | 51                  |
| 6             | 550             | 140                       | 60                  |

2.2.2. OM Geochemistry and Mineralogy. The untreated and heated samples were crushed and then partially packed into the independent packets for the solvent extraction with 250 mL of dichloromethane/methanol (93:7 v/v) for 72 h. Thereafter, 5% HCl was added into the non-extracted and extracted samples (80 mesh) to remove carbonates at 80 °C, and then the samples were washed with distilled water for 3 days. The residual samples were measured through a Leco-CS230 carbon and sulfur analyzer to obtain the TOC content (wt %). The rock pyrolysis analyses were conducted through an OGE-IV oil and gas evaluation workstation following a standard procedure (GB/T 18602-2001).

The untreated and heated samples were cut into blocks and then polished on a Buehler automatic grinding and polishing machine (EcoMet 250 with AutoMet 250) to obtain smooth surfaces for microscopic examination. The vitrinite random reflectance (VRo) measurements under the nonpolarized light were conducted on a Leica DM4500P reflected light microscope equipped with a CRAIC microscope photometer. The microscope was linearly calibrated with standard materials before the measurements (sapphire 0.589% Ro, gadolinium–gallium–garnet 1.725% Ro, and cubic zirconia 3.08% Ro). Over 30 data points were measured on each sample. The mineral composition characteristics of the extracted untreated/heated shale samples were analyzed using X-ray diffraction. Samples with 200 mesh were tested on a Bruker D8 X-ray diffractometer at 40 kV and 40 mA.

2.2.3. The Pore Structure Analysis. Nitrogen adsorption and SEM observation were applied to obtain pore structures of
the samples. The low-pressure nitrogen adsorption/desorption analyses of the non-extracted and extracted pulverized samples (60 to 80 mesh) were performed on a Quadrasorb IQ Surface Area Analyzer and Pore Size Analyzer under relative pressures (P/P0) from 0.01 to 0.99. Samples of about 3 g were degassed at 150 °C for 8 h before the measurements.

Non-extracted samples of about 1 cm² were polished with an emery paper to create level surfaces and then milled with argon ions. Samples were fixed on the stub using a conducting resin without carbon coating to prevent pores from clogging and placed into a ZEISS Merlin field emission scanning electron microscope (FE-SEM) in secondary electron mode with an accelerating voltage of 1.5–3 kV and a current of 0.8 to 2.8 nA of I probe to obtain the morphological characteristics of OM. Dual Bruker Quantax energy-dispersive X-ray spectroscopy (EDS) detectors were installed into the Merlin FE-SEM for the chemical analysis with an accelerating voltage of 15 kV and a distance of 7.5 mm.

3. RESULTS

3.1. Organic Geochemistry and Mineralogy. The VRo values, extractable organic matter (EOM) content, and TOC content/rock pyrolysis parameters of the initial and artificial FY2 and FY3 shale samples are listed in Table 2. The TOC contents of initial samples FY2 and FY3 were 8.51 and 3.46%, respectively, which implied the abundant presence of OM. There were downward trends of the contents of TOC and residual hydrocarbon (S2) of the non-extracted and extracted samples along with increasing maturity due to the conversion of kerogen to hydrocarbons. The free hydrocarbon (S1) contents of the extracted samples were close to zero. The EOM contents decreased from mature to over mature stages (Figure 1). The EOM contents of FY2 and FY3 shale samples were similar, and both were rich in clay minerals (70–83 and 76–84%), the minor type of clay minerals in the FY2 and FY3 shale samples was illite. The content of other clay minerals was mostly less than 5%.

3.2. OM Morphology. Both the morphology and the form of occurrence of OM are important optical properties to help in identifying the type of OM. Structureless OM mainly consisted of kerogen. The minor type of clay minerals in the FY2 and FY3 shale samples was illite. The content of other clay minerals was mostly less than 5%.

![Figure 1. EOM contents of the FY2 (circles) and FY3 (squares) shale samples from mature to over mature stages.](image.png)

| samples | FY2-550 | FY2-525 | FY2-475 | FY2-450 | FY2-425 | FY2 untreated |
|---------|---------|---------|---------|---------|---------|--------------|
| untreated | 0.94 | 1.43 | 1.70 | 2.41 | 2.68 | 1.22 |
| Ro (%) | 3.46 | 3.05 | 3.20 | 2.67 | 2.68 | 7.51 |
| illite (%) | 2.92 | 2.02 | 0.22 | 0.17 | 0.15 | 4.36 |
| illite–smectite (%) | 2.49 | 2.49 | 0.94 | 0.94 | 0.94 | 2.92 |
| total clays (%) | 0.48 | 0.48 | 0.48 | 0.48 | 0.48 | 0.48 |
| quartz (%) | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 |
| feldspar (%) | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 |

| samples | FY3-450 | FY3-425 | FY3-500 | FY3-525 |
|---------|---------|---------|---------|---------|
| untreated | 2.68 | 2.68 | 2.68 | 2.68 |
| Ro (%) | 0.83 | 0.83 | 0.83 | 0.83 |
| illite (%) | 0.83 | 0.83 | 0.83 | 0.83 |
| illite–smectite (%) | 0.83 | 0.83 | 0.83 | 0.83 |
| total clays (%) | 0.83 | 0.83 | 0.83 | 0.83 |
| quartz (%) | 0.83 | 0.83 | 0.83 | 0.83 |
| feldspar (%) | 0.83 | 0.83 | 0.83 | 0.83 |

Table 3. Mineral Compositions of Extracted FY2 and FY3 Organic-Rich Shale Samples

Table 2. Organic Geochemistry Characteristics of the Non-extracted and Extracted FY2 and FY3 Shale Samples

| samples | FY2 | FY3 |
|---------|-----|-----|
| VRo (%) | 1.22 | 0.94 |
| TOC (wt %) | 8.51 | 2.68 |
| S1 (mg/g) | 4.85 | 2.68 |
| S2 (mg/g) | 26.58 | 2.74 |
| EOM (wt %) | 0.17 | 0.02 | 0.05 | 0.03 |

Figure 1. EOM contents of the FY2 (circles) and FY3 (squares) shale samples from mature to over mature stages.
grains were blocky, and the boundaries between them and minerals were clear and regular. There were evident pores or fractures between some autochthonous OM grains, and they were surrounded by minerals (Figures 4A, 5D, and 7A). The bending of the autochthonous OM grains was small. Moreover, the surfaces of the autochthonous OM grains were clean, indicating that no mixing of mineral particles occurred. The sizes of these grains were within the micrometer scale.

The occurrences of pore-filling OM and fracture-filling OM conformed to the occupied space morphologically, which were the most notable difference from the autochthonous OM. The pore-filling OM usually occurs within intergranular spaces partially lined by euhedral crystals; meanwhile, autochthonous OM can be distinguished for the presence of sharp edges and distinctive internal fabric. The pore-filling OM grains are those filling interparticle pores of pyrite crystals (Figures 2B, 4B, and 7BC) and other inorganic pores (Figures 2A, 3B, 4C, 5B, and 7B,D). These grains tend to be dispersed in the mineral matrix and are surrounded by mineral particles because oil remains in the shale matrix and solidifies with thermal input and devolatilization. Conversely, the OM strips that occur as microfracture fillings or concentrations accumulate along bedding planes; these are referred to as fracture-filling OM (Figures 2A, 3C, and 6). The primary part of some fracture-filling OM strips was meandering or tortuous with many biforked OM strips (Figure 2A), while some had a distinct flowing structure (Figure 6A).

Some pore-filling OM grains and fracture-filling OM strips contained several mineral particles (Figures 4C,D, 6C, and 7D), a morphology that implied the migration of OM rather than its in situ occurrence. The sizes of these mineral particles were in the nanoscale. Mineral particles within the OM matrix were attributed to the mobilization and entrain-
The morphologies of pore-filling OM grains were limited by the arrangement of pyrite (Figures 2B, 4B, 5B, and 7B,C) or other mineral particles (Figures 4C, 6A, and 7D); therefore, the sizes of the pore-filling OM grains within the interparticle pores of pyrite frambooids decreased along with the increasing maturity or lithostatic pressure (Figures 2B, 4B, and 7C). The lengths of fracture-filling OM strips were up to tens of microns (Figures 2A and 6A). The edges of pore-filling OM grains and fracture-filling OM strips were irregular, but the boundaries between them and the mineral particles exhibited a perfect fit. Such grains and strips result from the conversion of oil filling the pores/fractures. The curved margins of the pore-filling OM may reflect an original oil–water interface.33

3.3. Pore Structure Parameters. The specific surface area and pore volume of micropores ($S_{\text{micro}}$ and $V_{\text{micro}}$), mesopores ($S_{\text{meso}}$ and $V_{\text{meso}}$), and macropores ($S_{\text{macro}}$ and $V_{\text{macro}}$) of the non-extracted and extracted FY2/FY3 shale samples from

| samples   | VRo (%) | $S_{\text{micro}}$ | $S_{\text{meso}}$ | $S_{\text{macro}}$ | $V_{\text{micro}}$ | $V_{\text{meso}}$ | $V_{\text{macro}}$ |
|-----------|---------|---------------------|-------------------|-------------------|-------------------|-----------------|-----------------|
| FY2       | 1.22    | 0.87                | 1.55              | 0.06              | 0.03              | 0.37            | 0.09            |
| FY2-425   | 1.51    | 0.13                | 4.70              | 0.10              | 0.00              | 1.11            | 0.17            | 13.99           | 7.09               | 0.10              | 0.44              | 1.32             | 0.15              |
| FY2-450   | 1.84    | 2.01                | 3.48              | 0.09              | 0.05              | 0.82            | 0.11            | 13.61           | 5.91               | 0.08              | 0.43              | 1.11             | 0.13              |
| FY2-475   | 2.08    | 14.33               | 4.23              | 0.11              | 0.35              | 1.00            | 0.18            | 24.23           | 5.95               | 0.11              | 0.63              | 1.22             | 0.17              |
| FY2-525   | 2.63    | 13.02               | 9.61              | 0.22              | 0.34              | 2.45            | 0.35            | 24.04           | 9.58               | 0.17              | 0.57              | 2.22             | 0.28              |
| FY2-550   | 2.82    | 9.20                | 6.05              | 0.16              | 0.23              | 1.62            | 0.26            | 13.22           | 5.66               | 0.15              | 0.32              | 1.46             | 0.23              |
| FY3       | 0.94    | 0.00                | 4.71              | 0.09              | 0.00              | 1.25            | 0.26            | 0.00            | 11.84              | 0.12              | 0.00              | 2.38             | 0.19              |
| FY3-425   | 1.43    | 0.00                | 2.11              | 0.12              | 0.00              | 0.77            | 0.19            | 0.51            | 3.59               | 0.13              | 0.02              | 1.01             | 0.21              |
| FY3-450   | 1.70    | 0.00                | 5.31              | 0.17              | 0.00              | 1.72            | 0.26            | 3.35            | 5.40               | 0.14              | 0.11              | 1.48             | 0.22              |
| FY3-500   | 2.41    | 0.64                | 6.76              | 0.35              | 0.02              | 2.48            | 0.56            | 2.72            | 7.32               | 0.36              | 0.08              | 2.34             | 0.55              |
| FY3-525   | 2.68    | 3.00                | 11.14             | 0.20              | 0.08              | 3.28            | 0.31            | 4.11            | 11.88              | 0.19              | 0.10              | 3.35             | 0.29              |

4. DISCUSSION

4.1. Pore Development of Autochthonous and Secondary OM. The pore development of both types of OM was related to the maturity. The surfaces of the pore-filling OM grains and fracture-filling OM strips were smooth in the FY2 shale samples at 1.22% Ro (Figure 2B), 1.51% Ro (Figure 3C), and 1.84% Ro (Figure 3D). There were some shrinkage fractures commonly occurring within the OM grains (Figures 2B and 3D) or between the OM strip and mineral particles (Figure 3C). Such shrinkage of OM pores/fractures appears to be related to postexperimental temperature/confining pressure decreases or the pressure release.26 However, the surfaces of the pore-filling OM grains and fracture-filling OM strips were porous in the FY2/FY3 shale samples at 2.08% Ro (Figures 4B,C,D), 2.63% Ro (Figure 5B), 2.68% Ro (Figure 6B), and 2.82% Ro (Figure 7B,C,D).

The pores of the pore-filling OM grains found within the intraparticle pores of pyrite frambooids were few in number and dispersed; these were limited by the distribution and sizes of...
OM grains (Figures 4B and 7B,C). The shale samples with high OM content are easily compacted, which are harmful for the preservation of OM pores. However, the supporting effects of mineral particles contribute to the preservation of OM pores when exposed to tectonic compression. Consequently, the close packing of pyrite particles was

**Figure 8.** Specific surface areas and pore volumes of micropores/mesopores of the non-extracted (filled squares) and extracted (empty squares) FY2 shale samples. (A) $S_{\text{micro}}$, the specific surface area of micropores; (B) $V_{\text{micro}}$, the pore volume of micropores; (C) $S_{\text{meso}}$, the specific surface area of mesopores; and (D) $V_{\text{meso}}$, the pore volume of mesopores.

**Figure 9.** Specific surface areas and pore volumes of micropores/mesopores of the non-extracted (filled squares) and extracted (empty squares) FY3 shale samples. (A) $S_{\text{micro}}$, the specific surface area of micropores; (B) $V_{\text{micro}}$, the pore volume of micropores; (C) $S_{\text{meso}}$, the specific surface area of mesopores; and (D) $V_{\text{meso}}$, the pore volume of mesopores.
beneficial to the preservation of OM pores. However, when the accumulation of pyrite particles becomes closer with increasing lithostatic pressure, the morphology of OM pores changes (Figures 4B and 7C). It was found that the quantity of pores in the pore-filling OM grains was small, with sizes up to hundreds of nanometers, and had irregular shapes (Figures 4C and 7D). Besides, few widely distributed pores at the contact points between the massive pyrite particles and the pore-filling OM grains were found (Figure 5B); on one side of these pores were pyrite particles, and on the other side were OM grains. The shapes of these pores were mostly subelliptical and not microfractures with sizes ranging from tens to hundreds of nanometers.

The pores in the OM grains/strips (the pore-filling OM grains and the fracture-filling OM strips), containing many small gray mineral particles, were well-developed (Figures 4D and 6B); these pores had rounded or subangular shapes and sizes up to tens of nanometers. The appearance of these OM nanopores was dense, and their distribution and quantity were scattered, like spongy OM nanopores and unlike modified mineral pores (with relic OM) or shrinkage OM pores.26 These OM nanopores were deep (Figure 4D), implying that they had a good connectivity.

The surfaces of the autochthonous OM grains were smooth in the FY2 shale samples at 2.08% Ro (Figure 4A), 2.63% Ro (Figures 5C,D), and 2.82% Ro (Figures 7A,C). There were also some shrinkage pores/fractures commonly occurring between the OM grains and the mineral particles (Figures 4A, 5C,D, and 7A) or within the OM grains (Figure 7C). For instance, the anticorrelation between OM content and the number of SEM-visible pores in the Marcellus shale used to be interpreted as a consequence of great OM connectivity and framework compaction.17 However, the anticorrelation may also be related to the different pore developments of the autochthonous OM and the secondary OM.

The observations of the nonporous autochthonous OM at the over mature stage were in contrast to the common view that OM pores usually develop at the over mature stage.2,14,18,20,21 The SEM observations of porous secondary OM grains/strips and autochthonous OM grains in the non-extracted FY2/FY3 shale samples were similar to the reports on the Woodford and Longmaxi shale.1,16,45,50 OM pores in the siliceous shales are heterogeneously distributed within OM, as some OM grains contain numerous pores and others not so much.51 Many scholars have noticed that it is more closely related to the OM composition. The nonporous OM is kerogen, but the porous OM is pyrobitumen.16 However, it is argued that some of the pores identified in gas-window-maturity samples are developed in OM that is unlikely to be pyrobitumen.52 Moreover, the nonporous OM in the Longmaxi shale in South China corresponds to relatively heavy conversion products (micrinite) of oil-prone kerogen macerals considering their thermal degradation process.48 In addition, the previous study observed that the surfaces of vitrinite are always nonporous.50

4.2. The Pore Structure of the Autochthonous OM and Secondary OM from High to Over Maturity. The OM composition experiences a continuous conversion process with increasing maturity,7,28,53 including (1) primary cracking of kerogen to pre-oil bitumen; (2) primary cracking of pre-oil bitumen to oil, post-oil bitumen, and gas; and (3) secondary cracking of oil and post-oil bitumen to pyrobitumen. In a previous study, Luo and Zhong35 have proposed that the nanopores in the pyrobitumen originating from post-oil bitumen are blocked in non-extracted samples and reoccur after extraction, but nanopores in the pyrobitumen originating from oil are always open from high to over mature stages. Therefore, the definitions of pyrobitumen that originates from post-oil bitumen/pyrobitumen and originating from oil28,53 as well as the SEM observations of the secondary and autochthonous OM allow one to infer that the pyrobitumen originating from oil is the secondary OM and the pyrobitumen originating from post-oil bitumen is the autochthonous OM. The changes in specific surface areas and pore volumes between extracted and non-extracted samples from high to over mature stages resulted from the OM nanopores of the autochthonous OM or inorganic nanopores rather than those of the secondary OM. These changes are listed in Table 5 for micro pores (ΔS_{micro} and ΔV_{micro}) and mesopores (ΔS_{meso} and ΔV_{meso}) of FY2 and FY3 Shale Samples

| samples | VRo (%) | EOM (%) | ΔS_{miero} (m²/g) | ΔS_{meso} (m²/g) | ΔV_{micro} (x10⁻⁹ cm³/g) | ΔV_{meso} (x10⁻³ cm³/g) |
|---------|---------|---------|-----------------|-----------------|-----------------|-----------------|
| FY2      | 1.22    | 0.598   | 9.93            | 7.55            | 0.31            | 0.53            |
| FY2-425  | 1.51    | 0.489   | 13.86           | 2.39            | 0.44            | 0.21            |
| FY2-450  | 1.84    | 0.262   | 11.60           | 2.43            | 0.38            | 0.29            |
| FY2-475  | 2.08    | 0.070   | 9.90            | 1.72            | 0.28            | 0.22            |
| FY2-500  | 2.63    | 0.061   | 11.02           | -0.03           | 0.23            | -0.23           |
| FY2-525  | 2.82    | 0.015   | 4.02            | -0.39           | 0.09            | -0.16           |
| FY3      | 0.94    | 0.792   | 0.00            | 7.13            | 0.00            | 1.13            |
| FY3-425  | 1.43    | 0.334   | 0.51            | 1.48            | 0.02            | 0.24            |
| FY3-450  | 1.70    | 0.203   | 3.35            | 0.09            | 0.11            | -0.24           |
| FY3-500  | 2.41    | 0.018   | 2.08            | 0.56            | 0.06            | -0.14           |
| FY3-525  | 2.68    | 0.030   | 1.11            | 0.74            | 0.02            | 0.07            |

The values of ΔS_{micro} and ΔV_{micro} of the FY2 shale samples at 1.51% Ro were distinctly higher than those at 1.22% Ro. However, the increased inorganic nanopores at 1.51% Ro were distinctly higher than those at 1.22% Ro. This indicates that the nanopores in the autochthonous OM are micropores. The values of ΔS_{micro} and ΔV_{micro} of the FY2 shale samples at 1.51% Ro were distinctly higher than those at 1.22% Ro. However, the increased inorganic nanopores at 1.51% Ro were distinctly higher than those at 1.22% Ro.
lower than those at 1.22% Ro based on the EOM contents (Table 5). Thus, the values of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ of the FY2 shale sample at 1.51% Ro were partly from the nanopores in the autochthonous OM. For the non-extracted and extracted
Therefore, the nonporous surfaces of the FY2 shale samples at 0.94% Ro, the zero values of \( S_{\text{micro}} \) and \( V_{\text{micro}} \) (Table 5 and Figure 9) indicated that the inorganic nanopores and autochthonous OM nanopores were not micropores. Thus, the values of \( \Delta S_{\text{micro}} \) and \( \Delta V_{\text{micro}} \) were entirely from the nanopores in the autochthonous OM. Besides, the values of \( \Delta S_{\text{micro}} \) and \( \Delta V_{\text{micro}} \) of the FY3 shale samples at 1.43% Ro were not zero (Table 5); therefore, nanopores in the autochthonous OM have formed at 1.51% Ro (1.43% Ro). The values of \( \Delta S_{\text{micro}} \) and \( \Delta V_{\text{micro}} \) of the FY2 shale samples from high to over mature stages were from nanopores in the autochthonous OM and inorganic nanopores. The results on the organic-lean shale samples show that the increased specific surface areas and pore volumes of inorganic nanopores after the extraction were linearly and positively correlated with the EOM content.\(^{35} \) The values of the increasing number of inorganic mesopores (\( \Delta S_{\text{meso}} \) and \( \Delta V_{\text{meso}} \)) of the FY2 shale samples from high to over mature were low, especially at 2.08 and 2.63% Ro (Table 5); consequently, the values of \( \Delta S_{\text{micro}} \) and \( \Delta V_{\text{micro}} \) were lower than those of inorganic nanopores and the autochthonous OM for the FY2 shale samples. The values of \( \Delta S_{\text{micro}} \) and \( \Delta V_{\text{micro}} \) of FY3 shale samples at 1.70 and 2.41% Ro belonged to the nanopores in the autochthonous OM. The micropores smaller than 1.5 nm increased after the extraction of the FY2 shale samples at 2.08 and 2.63% Ro (Figure 12) and the FY3 shale samples at 1.70 and 2.41% Ro (Figure 13). Therefore, the pore sizes of nanopores in the autochthonous OM were mainly smaller than 1.5 nm.

Nevertheless, these well-developed micropores in the autochthonous OM were easily blocked in the non-extracted samples because the values of \( S_{\text{micro}} \) and \( V_{\text{micro}} \) were much lower than those of the extracted shale samples from high to over mature stages (Figures 8A,B and 9A,B). Besides, the previous study on the coal samples indicated that the nanopores in the autochthonous OM were completely blocked in non-extracted samples.\(^{35} \) Therefore, the nonporous surfaces of the autochthonous OM grains under SEM observation were also caused by the blocking of autochthonous OM, except for the observation limitation of SEM resolution to micropores.

### 4.2.2. Secondary OM.
Inorganic nanopores in the non-extracted shale samples from high to over mature stages were derived from two sources: inorganic nanopores unaffected by residual bitumen and re-emerging inorganic nanopores. The re-emerging inorganic nanopores are first blocked by residual bitumen and then gradually exposed after the residual bitumen is transported.\(^{115} \) Limited by the flowability of residual bitumen and the destruction by the mechanical compaction and cementation, the number of re-emerging inorganic nanopores gradually decreases from high to over mature stages.

The values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) of the non-extracted FY2 shale samples slightly decreased from 1.51 to 1.84% Ro but sharply increased from 1.84 to 2.63% Ro (Figure 8C,D). The values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) of the non-extracted FY3 shale samples slightly increased from 1.70 to 2.41% Ro, while they sharply increased from 2.41 to 2.68% Ro (Figure 9C,D). Such sharp increases cannot come entirely from inorganic nanopores; this part of mesopores is partly due to nanopores in secondary OM.

The slight change in the values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) of the non-extracted FY2 shale samples from 1.51 to 2.08% Ro (Figure 8C,D) was mainly caused by pores ranging from 5 to 6 nm. However, the sharp increase of the values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) from 2.08 to 2.63% Ro was mainly caused by pores ranging from 5 to 20 nm (Figure 14). Besides, the values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) of the non-extracted FY3 shale samples from 1.51 to 2.63% Ro mainly correspond to inorganic nanopores with sizes ranging from 5 to 6 nm (Figure 15). Therefore, the mesopores in the secondary OM of FY2 shale samples (5 to 20 nm) formed at 2.08% Ro.

The distinct increase in the values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) of the non-extracted FY3 shale samples from 1.43 to 1.70% Ro was mainly caused by the pores ranging from 5 to 7 nm and the pores ranging from 8 to 40 nm; however, the slight increase of such values from 1.70 to 2.41% Ro was mainly caused by the pores ranging from 4.5 to 5 nm and the pores ranging from 15 to 40 nm (Figure 16). If the increase of the values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) from 1.43 to 1.70% Ro partially came from OM nanopores, the values of \( S_{\text{meso}} \) and \( V_{\text{meso}} \) must increase from 1.70 to 2.41% Ro. Besides, the values of \( \Delta S_{\text{meso}} \) and \( \Delta V_{\text{meso}} \) of the FY3 shale samples at 1.43% Ro correspond to inorganic nanopores ranging from 4 to 6 nm (Figure 17). Therefore, the mesopores of the non-extracted FY3 shale samples from 1.43 to 1.70% Ro are all re-emerging inorganic nanopores.

**Figure 13.** Pore size distributions of the non-extracted (filled circles) and extracted (empty circles) FY3 shale samples at (A) 1.70% Ro and (B) 2.41% Ro.

**Figure 14.** Pore size distributions of the non-extracted FY2 shale samples from 1.51 to 2.63% Ro.
Thus, the values of $R_o$ implied the presence of undeveloped inorganic micropores extracted and extracted FY3 shale samples at 0.94 and 1.43% $R_o$ (Figure 16). It was certain that nanopores; however, the number of mesopores ranging from 5 1.70 to 2.41% $R_o$ (Figure 9C,D) partially corresponded to OM have formed at 2.41% $R_o$ with sizes ranging from 5 to 20 nm. The low to zero values of $S_{micro}$ and $V_{micro}$ of the non-extracted FY2 shale samples slightly increased from 1.51 to 1.84% $R_o$ (Figure 9C,D) and those of the non-extracted FY3 shale samples sharply increased from 1.84 to 2.63% $R_o$ (Figure 8A,B). It was uncertain whether the slight increase of the values of $S_{micro}$ and $V_{micro}$ for the non-extracted FY2 shale samples slightly increased from 1.51 to 1.84% $R_o$ but suddenly increased from 1.84 to 2.08% $R_o$ (Figure 8A,B), which indicated that the micropores in the secondary OM formed at 2.08% $R_o$. Thus, the pore sizes of micropores in the secondary OM were mainly smaller than 1.5 nm (Figures 14 and 16).

Generally, the pore structures (pore type and pore size) differ between autochthonous OM and secondary OM (Table 6). Nanopores in the autochthonous OM are micropores with sizes mainly smaller than 1.5 nm. Meanwhile, nanopores in the secondary OM are mesopores with sizes ranging from 5 to 20 nm and micropores with sizes smaller than 1.5 nm. The pore sizes of the mesopores in the secondary OM are larger than the pore sizes of the micropores in the autochthonous OM, which may be attributed to the fusion of multiple micropores at high maturity.2

4.3. Effect of Maturity on the Pore Structure of Autochthonous and Secondary OM. The formation of nanopores in the autochthonous and secondary OM occurred at different maturity stages (Table 6). Nanopores in the autochthonous OM formed at 1.51% Ro (1.43% Ro), whereas those in the secondary OM formed at 2.08% Ro (2.41% Ro). Based on the classic theory of gas generation,40,55 it was necessary to round the values of maturity (Table 6). The formation maturity of nanopores in the secondary OM was higher than that in the autochthonous OM because the second cracking of oil requires higher thermal inputs.40,55 Besides, a previous study has indicated that the pore sizes of OM nanopores increase along with increasing maturity.14

Similarly, the thermal evolutions of nanopores in the autochthonous and secondary OM differ (Table 6). The values of $\Delta S_{micro}$ and $\Delta V_{micro}$ of FY2 shale samples partly correspond to inorganic nanopores (Figure 11) and are positively correlated with the EOM contents, similar to the values of $\Delta S_{micro}$ and $\Delta V_{micro}$ (Figure 10). Thus, the values of $\Delta S_{micro}$ and $\Delta V_{micro}$ belonging to the OM nanopores in the autochthonous OM for the FY2 shale samples increased from 1.51 to 2.08% Ro and then slightly decreased from 2.08 to 2.63% Ro (except for the value of $\Delta S_{micro}$ at 2.63% Ro) (Figure 18). The values of $\Delta S_{micro}$ and $\Delta V_{micro}$ of FY3 shale samples increased from 1.43 to 1.70% Ro and slightly decreased from 1.70 to 2.68% Ro (Figure 11). Therefore, the nanopores in the autochthonous OM massively formed at high mature stages and were slightly destroyed at the over mature stage. The values of $S_{micro}$ and $V_{micro}$ for the non-extracted FY2 shale samples sharply increased from 1.84 to 2.63% Ro (Figure 8C,D), and those of the non-extracted FY3 shale samples increased from 2.41 to 2.68% Ro (Figure 9C,D). Thus, the
mesopores in the secondary OM mainly developed at the over mature stage. The values of $S_{\text{micro}}$ and $V_{\text{micro}}$ of the non-extracted FY2 shale samples sharply increased from 1.84 to 2.08% Ro but slightly decreased from 2.08 to 2.63% Ro. This may be ascribed to the fusion of multiple micropores into mesopores in the secondary OM at high maturity. In contrast, the values of $S_{\text{micro}}$ and $V_{\text{micro}}$ of the non-extracted FY3 shale samples slightly increased from 1.70 to 2.41% Ro but sharply increased from 2.41 to 2.68% Ro. Thus, the micropores in the secondary OM also developed at over mature stage. Therefore, the development of OM nanopores in the lacustrine shale was synchronously affected by both OM composition and maturity.

The values of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ of FY2 shale samples suddenly decreased from 2.63 to 2.82% Ro (Figure 18), as well as the values of $S_{\text{meso}}$ ($S_{\text{micro}}$) and $V_{\text{meso}}$ ($V_{\text{micro}}$) (Figure 8), because the development of nanoparticles in the autochthonous and secondary OM is related to the generation of the gas hydrocarbon. The death line of the gas hydrocarbon generation is 2.8–3.0% Ro. Thereafter, the internal OM nanopores of migrated bitumen barely develop if gas hydrocarbon generation does not occur again after bitumen migration. The formation of OM nanopores cannot offset the destruction of OM nanopores in the autochthonous and secondary OM from 2.63 to 2.82% Ro owing to strong lithostatic pressure. Conversely, OM-hosted nanopores increasingly developed until 3.5% Ro in an open simulation system without lithostatic pressure.

The maximum values of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ of FY3 shale samples are 3.35 m$^2$/g and 0.11 $\times$ 10$^{-2}$ cm$^3$/g at 1.70% Ro (Table 6). After subtracting the value of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ belonging to inorganic pores in proportion of the EOM content (about 4.35 m$^2$/g and 0.14 $\times$ 10$^{-2}$ cm$^3$/g), the maximum values of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ belonging to the nanopores in the autochthonous OM are about 7.25 m$^2$/g and 0.24 $\times$ 10$^{-2}$ cm$^3$/g at 1.84% Ro. The increased values of $S_{\text{meso}}$ ($S_{\text{micro}}$) and $V_{\text{meso}}$ ($V_{\text{micro}}$) of the non-extracted FY2 shale samples from 1.84 to 2.63% Ro are 6.13 (11.01) m$^2$/g and 1.63 (0.28) $\times$ 10$^{-2}$ cm$^3$/g (Table 5). The increased values of $S_{\text{meso}}$ ($S_{\text{micro}}$) and $V_{\text{meso}}$ ($V_{\text{micro}}$) of the non-extracted FY3 shale samples from 1.70 to 2.68% Ro are 5.83 (3.00) m$^2$/g and 1.56 (5.83) $\times$ 10$^{-2}$ cm$^3$/g (Table 5). Then the nanopore developments of the autochthonous OM and secondary OM are listed in Table 6.

The maximum values of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ of FY3 shale samples were 3.35 m$^2$/g and 0.11 $\times$ 10$^{-2}$ cm$^3$/g at 1.70% Ro (Table 5). After subtracting the value of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ belonging to inorganic pores in proportion of the EOM content (about 4.35 m$^2$/g and 0.14 $\times$ 10$^{-2}$ cm$^3$/g), the maximum values of $\Delta S_{\text{micro}}$ and $\Delta V_{\text{micro}}$ belonging to the nanopores in the autochthonous OM were about 7.25 m$^2$/g and 0.24 $\times$ 10$^{-2}$ cm$^3$/g at 1.84% Ro. The increased values of $S_{\text{meso}}$ ($S_{\text{micro}}$) and $V_{\text{meso}}$ ($V_{\text{micro}}$) of the non-extracted FY2 shale samples from 1.84 to 2.63% Ro were 6.13 (11.01) m$^2$/g and 1.63 (0.28) $\times$ 10$^{-2}$ cm$^3$/g (Table 4). The increased values of $S_{\text{meso}}$ ($S_{\text{micro}}$) and $V_{\text{meso}}$ ($V_{\text{micro}}$) of the non-extracted FY3 shale samples from 1.70 to 2.68% Ro were 5.83 (3.00) m$^2$/g and 1.56 (5.83) $\times$ 10$^{-2}$ cm$^3$/g (Table 4). A comparison of the nanopore developments of the autochthonous OM and secondary OM is listed in Table 7.

Based on the values of the specific surface area and the pore volume of nanoparticles in the autochthonous and secondary OM for the FY2/FY3 shale samples (Table 6), the contributions of secondary OM to the total specific surface area of OM were found to be more than 70% for both, while the contributions of secondary OM to the total pore volume of OM were approximately 90%. The nanopores in the secondary OM were more developed than those in the autochthonous OM. Therefore, the OM nanopores at the high mature stage were from the autochthonous OM, whereas the OM nanopores at the over mature stage were mainly from the secondary OM.

The SEM observations of the autochthonous OM and the nitrogen adsorption data of non-extracted shale samples indicated that the nanoparticles in the autochthonous OM were easily blocked. Besides, the nanoparticles in the autochthonous

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**Table 7. Comparisons of Nanopore Developments of the Autochthonous OM (AOM) and Secondary OM (SOM)**

| OM component          | FY2                  | FY3                  |
|-----------------------|----------------------|----------------------|
|                      | AOM                  | SOM                  |
|                      | from 1.84 to 2.63% Ro| from 1.70 to 2.68% Ro|
| maturity (Ro)         | 1.84%                | 1.70%                |
| pore type             | micro-               | micro-               |
| specific surface area (m$^2$/g) | 7.25               | 11.01               |
| pore volume ($\times$10$^{-2}$ cm$^3$/g) | 0.24               | 0.28                |
| the contribution to the total specific surface area of OM | 30%                 | 70%                 |
| the contribution to the total pore volume of OM | 11%                 | 89%                 |
OM formed at the high mature stage and were slightly destroyed at the over mature stage. Therefore, the secondary OM is important to the development of OM nanopores in the lacustrine shale at the over mature stage.

5. CONCLUSIONS

Based on the OM morphology and the form of its occurrence under the SEM observation, the autochthonous and secondary types of OM were distinguished in lacustrine shale samples. The pores of autochthonous and secondary OM differ in pore size and thermal evolution. Nanopores in the autochthonous OM were micropores (<1.5 nm) that began to form at 1.50% Ro and were slightly destroyed at the over mature stage. Alternatively, nanopores in the secondary OM were mesopores (5–20 nm) and micropores (<1.5 nm) that began to form at 2.00% Ro. The development of such pores in the lacustrine shale was synchronously affected by both composition and maturity. The OM nanopores at the high mature stage belonged to the autochthonous OM, whereas those at the over mature stage belonged to the secondary OM. Finally, the secondary OM was found to be significant for the development of OM nanopores in the lacustrine shale at the over mature stage; the nanopores of the secondary OM were more developed than those of the autochthonous OM, which were slightly destroyed and became easily blocked.

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Notes
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