Study on Pore Structure and Fractal Characterization during Thermal Evolution of Oil Shale Experiments

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ABSTRACT: In order to better study the characteristics of the pore structure and to explore the influence factors of its fractal dimensions during the thermal evolution of oil shale, the immature oil shale (T_{max} = 433 °C, TOC = 28.00%) of the Ordos Basin Extension Group was selected to simulate the whole thermal evolution process from immature to over mature in a semiopen system. Organic geochemical data show that the thermal simulation hydrocarbon generation threshold is between 300 and 400 °C. According to AIP-SEM observation, the pore types of the samples are different in different thermal simulation stages. The fractal dimensions are calculated by low-temperature N2 adsorption data using the fractal Frenkel–Halsey–Hill fractal model. The average surface fractal dimension (D1) is 2.26, indicating that the pore (<4 nm) surface is relatively smooth. The average pore structure fractal dimension (D2) is 2.49, indicating that the pore (>4 nm) structure is complex. Through the exploration of the relationship between fractal dimensions and organic geochemistry, whole rock X-ray diffraction, and N2 adsorption data, it is found that fractal dimensions have different degrees of correlation with thermal maturity, mineral composition, TOC content, and pore parameters. Through comprehensive research, it shows that hydrocarbon generation and expulsion, oil and gas cracking, and organic matter carbonization have important effects on the pore structure and fractal characteristics of oil shale.

1. INTRODUCTION

Oil shale is a kind of immature to low-maturity fine-grained sedimentary rock rich in organic matter, which can be obtained by low-temperature distillation. Due to the low maturity of organic matter in oil shale, it can be used as an important carrier for hydrocarbon generation simulation and the study of shale reservoir physical properties and reservoir spatial evolution.

After the principle of complementary temperature and time in oil and gas generation was proposed, many domestic and foreign scholars have performed relevant hydrocarbon generation simulation research. According to the closure of the system, the thermal simulation system is divided into an open system, a closed system, and a semiclosed system. In recent years, scholars have simulated the evolution of pores during the maturation of organic-rich shale in different thermal simulation conditions and have drawn some valuable experimental conclusions. Studies have shown that total organic carbon (TOC) content, kerogen type, clay minerals, and thermal maturity (R_o) are the main factors controlling the pore structure of shale, among which thermal maturity is the most important factor. The controlling factors of the pore structure are different in different thermal maturity stages of shale. During the evolution of organic matter, a large number of micropores, mesopores, and macropores will be formed.

The pores in shale reservoirs (nanometer scale) are one order of magnitude smaller than those in conventional carbonate and sandstone reservoirs (micron scale). Therefore, the characterization tools and techniques of traditional reservoir can not be used to characterize the pore structure of the shale reservoir. Some scholars use nano CT, SEM, FIB-SEM to qualitatively characterize the pores of the shale reservoir, while others use a gas adsorption, mercury injection, and nuclear magnetic resonance to quantitatively characterize the pores of the shale reservoir. The irregularity of shale reservoir space restricts the accurate quantitative evaluation of pore space. The fractal theory provides scientific theoretical support for describing the complexity and irregularity of shale micropore structure. Many scholars apply fractal theory to the description and quantitative evaluation of pore structure.
and explored the influencing factors of fractal dimensions.\textsuperscript{7,33–34} The fractal dimensions are usually between 2 and 3. The larger fractal dimensions represent more irregular surfaces and higher heterogeneity of pore structure. The smaller fractal dimensions represent smoother surfaces and the more uniform of hole structure.\textsuperscript{32,35} In other words, the closer the fractal dimensions approach single pore structure in porous media. When the fractal dimensions approach 3, it means that the structure is diverse. Further studies show that the fractal dimension $D_1$ is closely related to small pores (diameter <4 nm), and the fractal dimension $D_2$ is closely related to large pores (diameter >4 nm).\textsuperscript{36}

This paper takes the immature oil shale of member 73 of Yanchang formation as the research object and uses the thermal simulator to simulate the whole thermal evolution process of oil shale from immature to over mature in the semiopen system. The pores of thermal simulation samples were qualitatively observed by AIP-SEM, and low-temperature N$_2$ adsorption experiment, whole rock X-ray diffraction, and organic geochemical experiments were performed, which provided quantitative data for the study of pore structure parameters of oil shale. Combined with qualitative observation and quantitative analysis, the pore evolution of oil shale during thermal maturation is studied, and the influencing factors of fractal dimensions are discussed. Further improvement is made to the application of fractal theory in shale pore analysis from the perspective of experimental simulation data.

2. SAMPLES AND METHODS

2.1. Samples. In this study, the black oil shale of the third submember of the seventh member of Yanchang Formation in Ordos Basin is selected as the research object. The organic matter type is II$_1$, and the oil content is 7.87%, which has strong hydrocarbon generation potential (Figure 1). The $T_{\text{max}}$ (${^\circ}$C) of the sample is between 430.5 and 439.5 ${^\circ}$C, which is in the immature to low-maturity stage. Through the thermal simulation experiment, the whole thermal simulation process of simulated samples from immature to over mature is studied to determine the evolution law of pore structure and to explore the controlling factors of fractal dimension.

2.2. Methods. First, the thermal simulation experiment is performed on the oil shale samples, and then the samples before and after thermal simulation are tested with an organic carbon test, a rock pyrolysis test, X-diffraction analysis, FIB-SEM observation, and low-temperature nitrogen adsorption experiment.

The thermal simulation experiment of oil shale is performed using a conventional high-temperature and high-pressure reactor at the Jilin Key Laboratory of oil shale and symbiotic energy and minerals. The experimental device belongs to a semiopen system. According to the research, the thermal simulation of the samples is performed in stages, which are as follows: I, 185 °C; II, 300 °C; III, 400 °C; IV, 475 °C; V, 520 °C, heating rate 5 °C/min, control pressure 10 MPa, constant temperature for 3 h after reaching the set temperature. In each
heating stage, 70–80 g block samples are placed in the reactor, and distilled water is injected into the reactor with a high-pressure constant-pressure pump to make the fluid pressure in the reactor increase to 10 MPa and then close. During the experiment, the hydrocarbon discharge is controlled by the pressure sensor. As the thermal simulation sample enters the mature stage, a large amount of organic matter is transformed into oil and gas, resulting in the increase of the pressure in the reactor. When the pressure in the reactor exceeds the critical pressure of the pressure sensor, the hydrocarbon discharge valve is opened, and the hydrocarbon and water are discharged from the reactor together to complete the hydrocarbon discharge process. The discharged oil, gas, and fluid enter the condensate tank for condensation storage, and the gas is collected with a collection device. As the oil and gas and fluid are discharged, the pressure in the reactor is reduced. The hydrocarbon expulsion valve is closed. The process of hydrocarbon generation and expulsion is repeated in the reactor until the end of the hydrocarbon generation (Figure 2).

After the experiment, the samples were naturally cooled to obtain thermal simulation samples of oil shale with different maturity levels, and then follow-up studies were performed.

3. RESULTS

3.1. Variation Characteristics of Rock Mineral Composition. The mineral characteristics of the thermal simulation sample are shown in Figure 3. X-ray diffraction analysis shows that the thermal simulation samples have various mineral components, mainly composed of pyrite, quartz, and clay, and the pyrite content is high. The content of quartz ranges from 13.4 to 30.8% (average 22.77%). The content of pyrite ranges from 4.1 to 49.8% (average 33.2%). The clay mineral content ranges from 25.0 to 40.9% (average 32.7%). The thermal simulation samples also contain a small amount of potassium feldspar, plagioclase, and magnetite minerals. With the increase of thermal simulation temperature, the contents of quartz and clay minerals increase as a whole, and the contents of feldspar minerals change little.
Table 1. Organic geochemical characteristics of thermal simulation samples

| sample no. | heating temperature (°C) | TOC (wt %) | \( T_{\text{max}} \) (°C) | \( S_1 \) (mg/g) | \( S_2 \) (mg/g) | \( S_1 + S_2 \) (mg/g) | HI* |
|------------|--------------------------|------------|---------------------------|----------------|----------------|----------------------|-----|
| E0         | unheated                 | 28.00      | 433                       | 7.74           | 138.64         | 146.38               | 495.14 |
| E1         | 185 °C                   | 28.40      | 434                       | 7.95           | 127.96         | 135.91               | 450.56 |
| E2         | 300 °C                   | 28.30      | 433                       | 6.91           | 107.90         | 114.81               | 381.27 |
| E3         | 400 °C                   | 26.75      | 439                       | 30.31          | 71.48          | 101.79               | 267.21 |
| E4         | 475 °C                   | 24.70      | 599                       | 7.99           | 5.89           | 13.89                | 23.89 |
| E5         | 520 °C                   | 24.35      | 604                       | 4.47           | 1.57           | 4.04                 | 16.59 |

*HI = \((S_1 \times 100)/\text{TOC}\).

The pyrite content shows a downward trend as a whole. At the thermal simulation temperature of 475 °C, the pyrite content decreases rapidly and the pyrrhotite content increases rapidly.

3.2. Evolution Characteristics of Organic Geochemical Parameters. The geochemical characteristics of thermal simulation samples are shown in Table 1. The content of TOC ranges from 24.35 to 28.40 wt % (average 26.75 wt %). \( T_{\text{max}} \) is between 433 and 604 °C, indicating that the thermal simulation samples are in different stages of thermal evolution from immature to over mature. The content of free hydrocarbon \( (S_1) \) ranges from 2.47 to 30.31 mg/g (average 10.56 mg/g). The content of pyrolysis hydrocarbon \( (S_2) \) ranges from 1.57 to 138.64 mg/g (average 75.58 mg/g). The content of \( S_1 + S_2 \) ranges from 4.04 to 146.38 mg. With the increase of \( T_{\text{max}} \), TOC, \( S_1 + S_2 \), and HI begin to decrease rapidly in the temperature range of 300–400 °C, and the decrease range is the largest in the temperature range of 400–475 °C, while \( S_1 \) generally increases and then decreases, reaching the maximum in the temperature range of 300–400 °C. The content of TOC and \( S_1 + S_2 \) of the samples that are in different thermal evolution stages is measured in the process of thermal simulation, which represents the residual content in the samples.

\( T_{\text{max}} \) and HI of samples with different thermal simulation temperatures are projected, and the thermal simulation samples fall at the corresponding position of the plate (Figure 4). According to the position of the thermal simulation sample on the plate, the type of organic matter in the original sample is type II1, which has strong oil generation potential. The thermal simulation samples E0, E1, and E2 are located near the oil generation window, but do not fully enter the oil generation window, with a small amount of oil and gas generated. Thermal simulation sample E3 is completely located in the oil generation window, generating a large amount of gaseous hydrocarbons. The thermal simulation samples E4 and E5 are in the over mature stage, generating a large amount of gaseous hydrocarbons without liquid hydrocarbons.

3.3. Pore Characteristics. 3.3.1. Argon Ion Polishing SEM Analysis. The original sample E0 has a large number of hydrocarbon generation thermal simulation samples E0, and over mature thermal simulation samples E5 were studied by means of argon ion polishing scanning electron microscope, and the pore type and microstructure were clearly identified (Figure 5). Through SEM observation, the pore development types in the sample mainly include organic pores, inorganic pores, and microfractures. Organic matter pores are mainly developed in the organic matter of samples E4 and E5, which are mostly oval and irregular triangle shaped, and the pore size is between 10 to tens of nanometers (Figure 5d,f). Inorganic pores mainly include intergranular pores of quartz and feldspar particles, feldspar dissolution pore, pyrite intergranular pore, and clay mineral interlayer pore, among which feldspar dissolution pores and pyrite intergranular pores are relatively developed. Intergranular pores of pyrite are developed in samples E0, E5, and E6, with irregular shapes and pore sizes ranging from tens to hundreds of nanometers (Figure 5d,h). Dissolution pores of feldspar are relatively developed in samples E3 and E5, in dissolution and irregular shape, with pore sizes ranging from tens of nanometers to several microns (Figure 5e). Microcracks are mainly developed in sample E5, ranging from a few microns to more than ten microns (Figure 5g,h).

3.3.2. Low-Temperature Nitrogen Adsorption Analysis. There are obvious differences between isothermal curves of thermal simulation samples, but they generally present an anti-“S”-type and develop hysteresis loops. The adsorption capacity does not reach saturation when the relative pressure is close to 1.0 (Figure 6). The isotherm curve begins to appear with a hysteresis loop near \( P/P_0 = 0.2 \). There is an inflection point in the isothermal curve near \( P/P_0 = 0.6 \), which is the end of single-layer adsorption and the beginning of multilayer adsorption.39 The adsorption capacity is not saturated, and the hysteresis loop disappears near \( P/P_0 = 1.0 \). This stage corresponds to the capillary condensation stage, indicating that the thermal simulation sample contains a certain amount of medium and large holes.40 The \( N_2 \) adsorption capacity of thermal simulation samples ranged from 1.11 to 6.81 cm\(^3\)/g (average 2.76 cm\(^3\)/g).
3.4. Specific Surface Area, Pore Volume, and Average Pore Diameter. The results of N$_2$ isothermal adsorption analysis of thermal simulation samples are shown in Table 2. The specific surface area ranges from 0.48 to 2.69 m$^2$/g (average 1.06 m$^2$/g). The pore size ranges from 3.82 to 4.66 nm (average 4.12 nm). The pore volume ranges from 0.00162 to 0.00265 cm$^3$/g (average 0.00371 cm$^3$/g). The proportion of macropore volume ranges from 1.13 to 5.54% (average 2.99%). The specific surface area, average pore diameter, and macropore ratio all indicate that the pores of the thermal simulation sample are mainly small pores. The sample in this experiment was collected from the outcrop, and the long-term volatilization of soluble organic matter in the sample may be the main reason for the small specific surface area and pore volume of the original sample.41

3.5. Fractal Dimension of N$_2$ Adsorption Isotherm. According to the Frenkel–Halsey–Hill (FHH) fractal model, the equation for calculating the fractal dimensions of shale can be described as follows:

\[
\ln \left( \frac{V}{V_0} \right) = \text{constant} + A \left[ \ln \left( \frac{P}{P_0} \right) \right]
\]

where $V$ is the volume of adsorbed gas molecules at equilibrium pressure ($P$); $V_0$ is the volume covered by a single layer; $A$ is a power law index, which is related to fractal
The evolution characteristics of mesopores, macropores, and total pores were studied using a thermal simulation to achieve the purpose of pore evolution research. Some scholars choose shale in different thermal evolution stages to study pore evolution. In this study, shale in different thermal evolution stages was simulated by a high-temperature and high-pressure hydrocarbon generation simulator. The pore volume parameters of thermal simulation samples were obtained through a low-temperature N₂ adsorption test to study the evolution characteristics of pore volume during thermal simulation.

The evolution characteristics of mesopores, macropores, and total pores are basically the same, first decreasing and then increasing, then decreasing and increasing, and finally decreasing. However, the pore volumes of mesopores, macropores, and total pores generally increase first and then decrease. Pore volume evolution can be divided into five stages: E₀−E₁, E₁−E₂, E₂−E₃, E₃−E₄, and E₄−E₅.

In the E₀−E₁ stage, it is immature (Figure 4). Under the action of fluid pressure, the pore volume of mesopores, macropores, and total pores decreases. In the E₁−E₂ stage, it
Figure 7. Relationship characteristics between $\ln(V/V_0)$ and $\ln(\ln((P_0/P)))$ constructed from low-temperature N₂ adsorption data.

Table 3. Fractal Dimensions of Thermal Simulation Samples Obtained by the FHH Model

| sample no. | $P/P_0 = 0−0.5$ | $P/P_0 = 0.5−1$ |
|------------|------------------|------------------|
|            | $A_1$            | $D_1 = 3 + A$    | $D_1 = 3 + 3A$ | $R^2$ | $A_2$            | $D_2 = 3 + A$    | $D_2 = 3 + 3A$ | $R^2$ |
| $E_0$      | −0.793           | 2.207            | 0.622           | 0.982 | −0.562           | 2.438            | 1.315           | 0.996 |
| $E_1$      | −0.885           | 2.115            | 0.345           | 0.977 | −0.460           | 2.540            | 1.619           | 0.999 |
| $E_2$      | −0.777           | 2.223            | 0.669           | 0.982 | −0.525           | 2.476            | 1.4260          | 0.998 |
| $E_3$      | −0.836           | 2.164            | 0.492           | 0.964 | −0.514           | 2.486            | 1.459           | 0.999 |
| $E_4$      | −0.571           | 2.429            | 1.286           | 0.986 | −0.494           | 2.506            | 1.518           | 0.988 |
| $E_5$      | −0.588           | 2.412            | 1.235           | 0.986 | −0.501           | 2.499            | 1.498           | 0.975 |

Figure 8. Pore volume evolution characteristics of thermal simulation samples. (a) Variation characteristics of $T_{max}$ with thermal simulation temperature. (b) Variation characteristics of mesoporous volume with thermal simulation temperature. (c) Variation characteristics of macropore volume with thermal simulation temperature. (d) Variation characteristics of total pore volume with thermal simulation temperature.
has low maturity (Figure 4), and the mesoporous and total pore volume increase, but the macropore volume remains unchanged. The pyrolysis data show that the content of free hydrocarbon in sample E2 is lower than that in sample E1 (Table 1), indicating that the liquid hydrocarbon generated by pyrolysis gas will produce overpressure and form layered fractures along the foliation direction. The pyrite content in the samples in the study area is high, with an average content of 33.2%. When the thermal simulation temperature reaches 475 °C, the cracks on the surface of pyrite particles are developed (Figure 5h), and the cracks are formed during the decomposition of pyrite to form pyrrhotite. The development of interlayer pores of clay minerals and diagenetic contraction joints (Figure 5e) is formed by the dehydration and transformation of clay minerals and the change of mineral morphology and assemblage. The decomposition of pyrite and dehydration and transformation conversion of clay minerals increase the macropore volume, and the total pore volume reaches the maximum at this stage.

In the E4−E5 stage, it is over mature (Figure 4), and the mesoporous volume is significantly lower than that in the previous stage. The organic geochemical data show that the TOC content in sample E5 is high, whereas the contents of free hydrocarbon ($S_1$) and pyrolytic hydrocarbon ($S_2$) are low (Table 1), which may be caused by the carbonization and graphitization of organic matter caused by high temperatures.

Figure 9. Pore size distribution characteristics of thermal simulation samples.
At the same time, the pyrolysis data show that the content of free hydrocarbon in sample E5 is significantly lower than that in sample E4, and the content of sample E5 is very low (Table 1), indicating that a large amount of free hydrocarbon ($S_1$) produced by hydrocarbon generation in sample E5 is discharged, which connects the E5 macropores in the sample with each other to form microcracks (Figure 5e,f), resulting in the reduction of macropore volume. Therefore, in addition to diagenesis, hydrocarbon generation, and expulsion, oil and gas cracking and organic matter carbonization play an important role in the evolution of pore volume.

### 4.1.2. Pore Size Evolution

The pore size parameters of thermal simulation samples were obtained in the low-temperature N$_2$ adsorption test, and the pore size distribution diagram was made with the pore size as the abscissa and the volume increment as the ordinate (Figure 9).

The pore size distribution of the thermal simulation samples has multiple peaks, mainly concentrated in the range of 5−30 nm, indicating that the pore size distribution in the sample is not concentrated and relatively scattered. In the process of thermal simulation, the peak value generally moves to the direction of decreasing the aperture, then to the direction of increasing the large aperture, and finally to the direction of decreasing the aperture. Under the experimental condition with a thermal simulation pressure of 10 MPa, the average pore diameter of the thermal simulation sample E1 is slightly smaller than that of unheated sample E0. Thermal simulation sample E1 is immature, and organic matter has not yet begun to convert to hydrocarbons. Due to the action of fluid pressure, the pores are compressed, so that the peak value of pore diameter distribution first moves in the direction of pore diameter reduction. The thermal simulation sample E2 is in the low-maturity stage, and the hydrocarbon generation is weak. The average pore diameter of thermal simulation sample E2 is slightly larger than that of thermal simulation sample E1, which may be caused by the early release of liquid hydrogen.$^{15}$ The simulated sample E3 is located in the oil generation window and has strong hydrocarbon generation. The average pore size of the simulated sample E3 is similar to that of the thermal simulated samples E1 and E2. The pyrolysis data show that the content of free hydrocarbon in the sample is high (Table 1), indicating that most of the liquid hydrocarbon and asphalt generated by hydrocarbon generation are retained in the pores of the sample E3. The liquid hydrocarbon and asphalt in the pores effectively prevent further compaction of the pores, causing a large number of pores with large pore diameters to
be occupied. Therefore, the pore size of the thermal simulation samples \((E_0-E_5)\) generally moves in the direction of pore size reduction. The thermal simulation sample \(E_5\) is in the high mature over mature stage. The gaseous hydrocarbons produced by kerogen pyrolysis and liquid hydrocarbon pyrolysis can produce high pore pressure in the shale. The higher pore pressure can offset the effect of fluid pressure and prevent further compaction, which promotes the growth of mesopores and macropores and moves the peak value of pore size distribution in the direction of pore size increase.

The thermal simulation sample \(E_5\) is in the over mature stage; the organic matter is partially carbonized and graphitized, and the kerogen pyrolysis and liquid hydrocarbon pyrolysis are weakened. At the same time, the macropores are interconnected to form microcracks, resulting in the reduction of macro pore content and the movement of the peak value of pore size distribution in the direction of pore size reduction.

4.2. Influence Factors of Fractal Dimensions. 4.2.1. Relationship between Fractal Dimensions and Thermal Maturity. During the thermal simulation, the thermal maturity \((T_{\text{max}})\) of oil shale samples continued to increase and the hydrocarbon generation potential \((S_1 + S_2)\) continued to decrease (Figure 10). In order to explore the correlation between the fractal dimensions of thermal simulation samples and thermal maturity and hydrocarbon generation potential, a correlation diagram is made (Figure 11). There is a strong positive correlation between fractal dimension \(D_1\) and thermal maturity, and there is no correlation between fractal dimension \(D_2\) and thermal maturity (Figure 11a). There is a strong negative correlation between fractal dimension \(D_1\) and hydrocarbon generation potential, and there is no correlation between fractal dimension \(D_2\) and hydrocarbon generation potential (Figure 11b). The heating temperature is about 400 °C \((T_{\text{max}} = 439 °C)\), which is the critical temperature at which the asphaltene in the oil shale begins to decompose in large amounts. The internal structure and structure of the particles have undergone a series of changes, resulting in strong irregular characteristics of the pore structure. The volatilization of some oil and gas and the cross-linking between adjacent pores have resulted in complex three-dimensional spatial structure inside the particles. Therefore, the shape dimensions \(D_1\) and \(D_2\) change greatly within the temperature range of 400–475 °C. The experimental results show that the increase of thermal maturity and the decrease of hydrocarbon generation potential of thermal simulation samples increase the fractal dimension \(D_1\) of pore surface area but has no obvious relationship with the fractal dimension \(D_2\) of pore structure.

4.2.2. Relationship between Fractal Dimensions and Composition Parameters of Thermal Simulation Samples. Previous studies have shown that the fractal dimensions increase with the increase of TOC content,\(^{30,34,36,46}\) or the relationship between fractal dimensions and TOC content is a U-shaped curve.\(^{33,47}\) However, Tan et al. showed that the fractal dimensions of thermal simulation samples after extraction increased with the decrease of TOC content through thermal simulation experiments.\(^7\) In order to explore the effect of TOC content in thermal simulation samples on fractal characteristics, the correlation between fractal dimensions and TOC content in thermal simulation samples is shown in Figure 12.

In the process of thermal simulation, TOC content decreases and fractal dimension \(D_1\) increases with the increase of oil shale maturity (Figure 12). There is an obvious linear negative correlation between fractal dimension \(D_1\) and TOC content, and there is no obvious negative correlation between fractal dimension \(D_2\) and TOC content (Figure 12a). Further research shows that the relationship between fractal dimension \(D_2\) and TOC content is a U-shaped curve (Figure 12b). The results of this experiment are similar to the conclusions drawn by Tan but different from the previous research conclusions. Shale with high TOC content is easy to form micropores and mesopores in thermal evolution,\(^{35,49}\) and these pores can form a complex heterogeneous pore network.\(^{50,50}\) In the process of thermal simulation, with the increase of thermal simulation temperature, the thermal maturity continuously increases. The TOC is continuously consumed while forming organic matter pores. During the formation and evolution of organic matter pores, the heterogeneity of the pore surface increases, increasing the fractal dimension \(D_1\) (Figure 12). Especially in the high-maturity process maturity stage, the fractal dimension \(D_1\) increases rapidly, which may be due to the continuous cracking of asphaltene and residual oil in oil shale samples, resulting in the irregular enhancement of the pore surface. Therefore, the reflections of the two are essentially the same. This study shows that, in the thermal simulation process, the TOC content not only has a greater impact on the irregularity of the pore surface but also shows that the organic pores are an important part of the sample pores. Therefore, the reflections of the two are essentially the same. This study shows that, in the thermal simulation process, the TOC content not only has a greater impact on the irregularity of the pore surface but also shows that the organic pores are an important part of the sample pores.

4.2.3. Influence of Minerals on the Fractal Dimensions. Many scholars have discussed the relationship between fractal
dimensions and minerals\textsuperscript{34,36,51} and draw some different conclusions. The mineral content of the thermal simulation sample is quantitatively obtained by X-ray diffraction. The thermal simulation samples are mainly composed of quartz, pyrite, and clay minerals (Figure 3). Therefore, this study mainly explores the correlation between double fractal dimensions and the content of quartz, pyrite, and clay minerals in thermal simulation samples. The correlation between fractal dimensions and quartz content is poor (Figure 13a), which is due to the strong corrosion resistance of quartz and no micropores caused by corrosion. The correlation between fractal dimensions and clay mineral content is poor (Figure 13c), which may be due to the different types of clay mineral crystals arranged and stacked in different ways, which has different effects on the fractal dimensions.\textsuperscript{52} There is a weak linear negative correlation between fractal dimension $D_1$ and pyrite content, and the correlation between fractal dimension $D_2$ and pyrite content is very poor. With the increase of thermal simulation temperature, pyrite decomposes into pyrrhotite, while cracks will be formed on the particle surface, which enhances the heterogeneity of the pore surface, resulting in the fractal dimension $D_1$ increasing.

Further research shows that the relationship between fractal dimension ($D_2$) and the content of pyrite, clay minerals, and feldspar is a U-shaped curve (Figure 13d–f), indicating that pyrite, clay minerals, and feldspar are the main minerals constituting pores of the samples, and quartz is not the main mineral constituting pores of the samples. Pyrite intergranular pores, clay mineral interlayer pores, and feldspar dissolution pores constitute the main pores in the samples, which are consistent with the pore types observed by argon ion polishing scanning electron microscope (Figure 5).

### 4.2.4. Relationship between Fractal Dimensions and Pore Structure Characteristics

There is an obvious linear positive correlation between the fractal dimension $D_1$ and the specific surface area, and there is no obvious correlation between the fractal dimension $D_2$ and the specific surface area (Figure 14a). However, different scholars have different opinions on the relationship between fractal dimension and specific surface area.\textsuperscript{7,33,36} Generally speaking, the larger the surface roughness of the sample, the larger the specific surface area,\textsuperscript{73} therefore, the fractal dimension $D_1$ has a good correlation with the specific surface area. There is an obvious linear positive correlation between fractal dimension $D_1$ and N$_2$ adsorption capacity, and there is no obvious correlation between fractal dimension $D_2$ and nitrogen adsorption capacity (Figure 14b). The more irregular the pore surface is, the larger its specific surface area is, and the stronger its N$_2$ adsorption capacity is, which is reflected in the larger fractal dimension $D_1$. There is no obvious correlation between fractal dimension $D_1$ and the average BHJ aperture, and there is a weak negative correlation between fractal dimension $D_2$ and the average BHJ aperture (Figure 14c). Although there is no strong correlation between fractal dimension and BHJ average pore, it has a negative correlation trend as a whole, which is basically consistent with the conclusion that fractal dimension is negatively correlated...
with pore size. There is an obvious linear positive correlation between the fractal dimension $D_1$ and the total pore volume of the thermal simulation sample, and there is no obvious correlation between the fractal dimension $D_2$ and the total pore volume (Figure 14d). However, some scholars believe that the total pore volume can reflect neither the irregularity of pore surface nor the pore structure controlled by composition. In the process of thermal simulation, the proportion of micropores in the sample decreases due to thermal evolution, but the total volume and number of micropores increase. The increase of micropores enhances the irregularity of the pore surface, resulting in the increase of fractal dimension $D_1$. There is a positive correlation between the fractal dimension $D_1$ and the porosity of the thermal simulation sample, but there is no obvious correlation with the fractal dimension $D_2$ (Figure 14e), which is inconsistent with previous studies. This is because the pressure set in the thermal simulation experiment is fluid pressure and not the overlying pressure, and the fluid pressure has little effect on the compaction of the sample. At the same time, a large number of micropores, mesopores, and macropores will be formed in the process of thermal simulation, which will increase the total volume of pores. The formation of mesopores and macropores improves the porosity of thermal simulation samples, while the generation of a large number of micropores increases the fractal dimension. Therefore, it indirectly leads to a positive correlation between porosity and fractal dimension $D_1$. There is a positive correlation between the fractal dimension $D_1$ and the density functional theory (DFT) average pore diameter of the thermal simulation sample, and there is no obvious correlation with the fractal dimension $D_2$ (Figure 14f). The explanation of the correlation between the two is consistent with the correlation between the porosity and the fractal dimension.

5. CONCLUSION

From $E_0$ (unheated) to $E_5$ (520 °C), the pore types in the oil shale samples changed regularly: the unheated samples were dense, and the pores were not developed; when the thermal simulation temperature increased to 400 °C, the organic matter pores, dissolution pores, and pyrite intergranular pores were developed; when the thermal simulation temperature was 520 °C, the microcracks on the surface of pyrite and the edge fractures of elastic particles were further developed. During thermal simulation, when the heating temperature is 300−400 °C, a large number of hydrocarbons are generated but not discharged, existing in the sample in the form of residual oil. When the heating temperature is 400−475 °C, a large amount of residual oil in the sample is cracked and discharged.

There are different controlling factors for pore evolution in different thermal simulation stages: immature stage (unheated
to 185 °C), fluid pressure plays a leading role in the process of pore evolution. In the low-maturity stage (185–300 °C), early hydrocarbon generation and fluid pressure play a common role in the process of pore evolution, and fluid pressure plays a leading role. In the mature stage (300–400 °C), hydrocarbon generation and fluid pressure work together in the process of pore evolution, and hydrocarbon generation plays a leading role. In the high-maturity stage (400–470 °C), oil and gas cracking, pyrite decomposition, clay mineral transformation, and fluid pressure work together in the process of pore evolution, and oil and gas cracking plays a leading role. In the over mature stage (475–520 °C), the carbonation of organic matter and fluid pressure play a common role in the process of pore evolution.

In the process of thermal simulation, fractal dimension has different degrees of correlation with thermal maturity, TOC content, specific surface area, N₂ adsorption capacity, total pore volume, and porosity: thermal maturity is positively correlated with fractal dimension D₁ and has no obvious correlation with fractal dimension D₂, indicating that the irregularity of the pore surface is enhanced and the pore structure changes little in the process of thermal simulation. There is an obvious linear negative correlation between fractal dimension D₁ and TOC content, and there is a U-shaped curve between fractal dimension D₁ and TOC, pyrite, clay minerals, and feldspar. The fractal dimension D₁ has an obvious linear positive correlation with specific surface area, N₂ adsorption capacity, and total pore volume, while the fractal dimension D₂ has no obvious correlation with specific surface area, N₂ adsorption capacity, and total pore volume. There is no obvious correlation between the fractal dimension D₁ and the average pore diameter of BHJ, and there is a weak negative correlation between the fractal dimension BHJ average pore diameter.

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Notes

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