Characteristics of nanopores in terrestrial low-maturity shale based on organic-inorganic interactions: A case study on the Shahejie Formation shale in the southern Bohai Bay Basin, Eastern China

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Abstract. In this study, the influence of organic matter and inorganic matter on the pore structure of the Shahejie Formation (E\textsubscript{2,3S}) shale in the Bohai Bay Basin, was analysed. The pore characteristics, including the BET surface area, BJH adsorption cumulative volume and average pore diameter of the original samples, extracted samples, H\textsubscript{2}O\textsubscript{2}-treated samples and kerogen samples, were analysed with low-pressure N\textsubscript{2} adsorption experiment. The study showed that the soluble organic matter in low-maturity shale blocked a certain number of pores, mainly having pore sizes below 5 nm. The solid organic matter mainly formed pore diameters of 1-2 nm and pore diameters larger than 10 nm. A large amount of inorganic pore diameter in the ranges of less than 0.8 nm, 1-2 nm, and 2.3-20 nm was blocked by solid organic matter. The micropores formed by minerals were much more abundant than those formed by organic matter in the terrestrial low-maturity shale. The symbiotic relationship between the minerals and the organic matter led to a decrease in the specific surface area and pore volume of the terrestrial low-maturity shale.

1. Introduction
The demand for exploration and development of shale oil and gas is rapidly increasing, and has now attracted increasing attention. The nanopores of shale have been widely recognized for their ability to store oil and gas, and their structural characteristics are the key factors affecting the storage phases of hydrocarbons [1, 2]. Shale oil and gas mainly occur as free phases in the free space of pores or as adsorbed phases on the surface of pores, and a small amount of hydrocarbons are dissolved in the formation fluid [3].
The ubiquity of the heterogeneity in shale composition is the main reason for the complexity and diversity of its pore characteristics [3, 4]. The mineral matrix can form intergranular pores, crystal particle pores, microcracks and other types of nanopores during the sedimentation and evolution of shale [4]. These pores are often controlled by factors, such as sediment compaction, mineral dissolution, degree of crystallization, and mineral composition [1, 5]. Organic matter can form pores during hydrocarbon evolution. The organic pores are affected by organic matter type, maturity, abundance and aggregation mode [2, 5]. Organic matter and clay minerals are the main material basis for shale oil and gas adsorption [6]. Studying the influence of organic matter and clay minerals on the pore structure of shale has important guiding significance for understanding the shale oil and gas accumulation mechanism.

There are 1.08×10⁴-1.18×10⁴ million tons of shale oil resources in the southern Bohai Bay Basin, and the Shahejie Formation shale is the main source rock. The study of the nanopore structure characteristics and the influence of organic matter and inorganic minerals on the shale pore structure in this area has great significance for shale oil and gas resource exploration and exploitation. This paper is expected to provide a scientific basis for the evaluation, exploration and exploitation of shale oil and gas in this region by studying the nanopore structure development characteristics.

2. Samples and methods

Six samples were collected from wells in the Huanghekou Sag and Laizhouwan Sag, as shown in Figure 1. The samples correspond to three main source rock layers in the study area. All the samples were cleaned with distilled water and an ultrasonic cleaning instrument several times to remove contamination.

2.1. TOC, Rock-Eval and XRD analysis

The samples were mechanically crushed to 200-mesh and dried at 70 °C. The TOC content was analyzed by using the CS-344 analyzer produced by LECO. A Rock-Eval 6 analyzer produced by VINCI was used for the pyrolysis experiment following the standard GB/T 18602-2012 of China. The X-ray diffraction (XRD) measurements of the mineral compositions were conducted on an Ultima IV X-ray diffractometer with Cu-Kα radiation. The generator settings were 40 kV and 40 mA. The scan was taken from 2° to 60° with a rate of 4°/min and a step interval of 0.02°.

2.2. Pore structure analysis

Pore structure analysis was conducted on the original sample, the soluble organic matter removed sample (extracted sample), the solid organic matter removed sample (minerals), the mineral removed sample (kerogen). The soluble organic matter was removed by using the Soxhlet extractor apparatus with dichloromethane (DCM) and methanol (9:1) for 72 h. The extracted samples were then divided
into three parts: one part for pore structure analysis, one part for solid organic matter removal by the 30% analytically pure H₂O₂ and one part for mineral removal by the HCl and HF. The pore structure of samples was analyzed at -196 °C (liquid nitrogen) with a Micromeritics ASAP 2460 physical adsorption instrument, and N₂ was used as the test gas.

3. Results

3.1. Geochemical characteristics

The TOC and Rock-Eval analysis results of the samples are shown in Table 1 and the XRD analysis results of the samples are shown in Table 2. The initial TOC contents ranged from 2.81% to 5.63% and had an average value of 3.78%. The Tₘax values were between 431 and 437 °C and had an average value of 433.8 °C. Table 2 shows that quartz, plagioclase, calcite, dolomite, and clay minerals are in dominant. The abundance of clay minerals is between 20.8% and 55.3%, with an average of 44.2%. The content of brittle minerals is between 44.7% and 79.2%, with an average of 55.8%.

### Table 1. The organic geochemical characteristics of the samples

| sample | S₁ (mg/g) | S₂ (mg/g) | S₃ (mg/g) | Tₘax (°C) | Iₜ (mg/g) | TOC₀ (%) | TOCₑ (%) | TOCₕ (%) | TOCₖ (%) |
|--------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|
| BN-01  | 2.87      | 19.62     | 3.15      | 437       | 598.17     | 3.28      | 3.09      | 0.35      | 24.34     |
| BN-02  | 1.82      | 16.12     | 1.95      | 433       | 573.67     | 2.81      | 2.7       | 0.22      | 20.09     |
| BN-03  | 9.58      | 38.21     | 1.28      | 431       | 678.69     | 5.63      | 4.73      | 0.26      | 35.02     |
| BN-04  | 1.11      | 15.66     | 0.58      | 439       | 481.85     | 3.25      | 3.13      | 0.18      | 27.04     |
| BN-05  | 0.57      | 10.88     | 0.6       | 431       | 380.42     | 2.9       | 2.86      | 0.19      | 25.30     |
| BN-06  | 0.36      | 20.02     | 0.73      | 437       | 465.58     | 4.3       | 4.27      | 0.37      | 20.62     |

TOC₀, total organic carbon of original sample; TOCₑ, total organic carbon of extracted sample; TOCₕ, total organic carbon of H₂O₂ treated sample; TOCₖ, total organic carbon of kerogen.

### Table 2. The XRD analysis results of the samples (%)

| sample | Q  | F  | Cal | Dol | Py  | clay | Relative content of clay minerals % |
|--------|----|----|-----|-----|-----|------|------------------------------------|
|        | I/S | I  | K   | C   |     |      |                                    |
| BN-01  | 22.7| 9.2| 16.2| /   | 3.2 | 48.7 | 65       | 27     | 7       | 1       |
| BN-02  | 19.9| 7.2| 18  | /   | /   | /    | 54.9     | 58     | 29      | 13      |
| BN-03  | 17.2| 7.8| 44  | 7.8 | 2.4 | 20.8 | /        | 74     | /       | 26      |
| BN-04  | 18.9| 6.1| 26.3| 10.5| 4.8 | 33.4 | 65       | 27     | 7       | 1       |
| BN-05  | 25.3| 14.5| /   | /   | 4.9 | 55.3 | 56       | 25     | 15      | 4       |
| BN-06  | 19.5| /   | 24.4| /   | 4.3 | 51.8 | 57       | 35     | 6       | 2       |

Q, quartz; F, feldspar; Cal, calcite; Dol, dolomite; Py, pyrite; I/S, illite/montmorillonite mixed layer; I, illite; K, kaolinite; C, chlorite; “/”, not detected.

3.2. Pore characteristics

3.2.1. N₂ adsorption isotherms.

Figure 2 shows the N₂ adsorption isotherm curves of the BN-03 and BN-06 samples. Except for BN-03, the curve characteristics of the other four groups of samples are similar to those of BN-06, which are not listed. According to the IUPAC classification of the adsorption hysteresis loop, figure 2 shows that the four curves of the BN-03 sample exhibit typical H3 hysteresis loop characteristics, indicating that the "slit-type" pores are dominant in the sample pores. The other five samples represented by BN-06 showed only the characteristic H3 hysteresis loop characteristics after acid treatment. The original samples, Soxhlet extraction samples and H₂O₂-treated samples have the characteristics of H3 and H4 hysteresis loop types. In addition to the development of "slit-type" pores, a certain proportion of "ink bottle"-like pores are developed.

3.2.2. Surface area, pore volume and average pore diameter.
Table 3 shows the sample parameters, including BJH adsorption cumulative pore volume, BET specific surface area, and average pore diameter. The initial pore volume of the sample is between $17.89 \times 10^{-3} \text{ cm}^3/\text{g}$ and $32.61 \times 10^{-3} \text{ cm}^3/\text{g}$ and has an average value of $27.26 \times 10^{-3} \text{ cm}^3/\text{g}$. The initial BET specific surface area of the sample is between $4.28 \text{ m}^2/\text{g}$ and $12.2 \text{ m}^2/\text{g}$, and the average is $7.46 \text{ m}^2/\text{g}$. The average pore diameter ranges from $12.30 \text{ nm}$ to $25.74 \text{ nm}$ with an average of $17.96 \text{ nm}$.

Table 3. BJH adsorption cumulative pore volume, BET specific surface area, and average pore diameter of the sample

| Sample | Original | Extracted | H$_2$O$_2$ treated | Kerogen |
|--------|----------|-----------|---------------------|---------|
| BJH Adsorption cumulative volume of pores $10^{-3} \text{ cm}^3/\text{g}$ | | | | |
| BN-01  | 27.51    | 29.15     | 53.73               | 84.3    |
| BN-02  | 25.26    | 34.61     | 56.61               | 77.2    |
| BN-03  | 27.55    | 35.05     | 35.11               | 16.9    |
| BN-04  | 17.89    | 31.65     | 36.25               | 39.7    |
| BN-05  | 32.61    | 39.26     | 47.83               | 102.0   |
| BN-06  | 32.17    | 38.03     | 55.65               | 136.0   |
| BET Surface Area $\text{m}^2/\text{g}$ | | | | |
| BN-01  | 5.54     | 6.11      | 41.78               | 12.5    |
| BN-02  | 6.15     | 9.57      | 35.14               | 11.7    |
| BN-03  | 4.28     | 8.07      | 6.35                | 1.44    |
| BN-04  | 4.45     | 9.52      | 24.03               | 6.02    |
| BN-05  | 12.1     | 19.3      | 36.07               | 17.8    |
| BN-06  | 12.2     | 17.9      | 44.94               | 19.6    |
| Average pore diameter $\text{nm}$ | | | | |
| BN-01  | 19.9     | 22.6      | 6.44                | 40.0    |
| BN-02  | 19.2     | 16.2      | 7.07                | 37.9    |
| BN-03  | 25.7     | 19.0      | 22.25               | 46.3    |
| BN-04  | 18.0     | 15.4      | 7.41                | 33.8    |
| BN-05  | 12.3     | 8.68      | 6.16                | 36.3    |
| BN-06  | 12.4     | 9.01      | 5.86                | 33.0    |

4. Discussion

4.1. Effect of soluble organic matter on the pore structure

Compared with the original sample, both the pore volume and the BET specific surface area are increased after extraction. But The average pore diameter of the sample decreases except for BN-01. Micropores in shale mainly contribute to the surface area, while mesopores and macropores contribute more to the pore volume [7]. This observation indicates that the soluble organic matter in low maturity shales blocks many more micropores than mesopores and macropores.

4.2. Pore characteristics of the minerals

Compared with the original sample, the pore volume and the BET specific surface area of the H$_2$O$_2$-treated samples increased but the average pore diameter was decreased. This characteristic change is similar to that of the extracted sample, which also reflects that the solid organic matter restricts the micropores of the shale. The clay minerals form large amounts of nanopores, and the pore diameter is mainly in the range of 3-100 nm. Figure 3 and figure 4 show that after H$_2$O$_2$ treatment, both the pore volume and specific surface area increased in the pore diameters below 20 nm, especially in pore diameters in the ranges of less than 0.8 nm, 1-2 nm, and 2.3-20 nm. Indicating that the solid organic matter in the samples mainly blocks these three diameter ranges of pores.

4.3. Pore characteristics of solid organic matter (kerogen)
After the acid treatment to remove the minerals, except for BN-03, the pore volume and the specific surface areas and the average pore diameter increased. Compared with the extracted sample and the \( \text{H}_2\text{O}_2 \)-treated sample, the kerogen sample shows a higher increase ratio of the pore volume and average pore diameter than the other treatment methods, indicating that kerogen mainly develops mesopores and macropores. As figure 3 and figure 4 show, the kerogen of the studied sample mainly forms pore diameters in the ranges of 1-2 nm and larger than 10 nm, but there are almost no pore diameters in the range of 2-10 nm, which means that this range of pores is mainly from minerals.

4.4. Development mechanism of nanopores in terrestrial low-maturity shale

From the perspective of the basis of pore development material, the nanopore development in the Shahejie Formation in the study area is mainly affected by organic matter and inorganic minerals, and the organic matter could be divided into soluble organic matter and solid organic matter.

The hydrocarbons generated by the source rock in the early evolution stage are mainly retained in the pore surface of the source rock through the adsorption phase [8]. Which would block a certain amount of micropores. Solid organic matter in the study area mainly develops mesopores and macropores and blocks a large amount of micropores. Mineral particles such as quartz and feldspar in clastic sediments are often symbiotic with organic matter particles. Clay minerals generally form organic-clay complexes with organic[8]. This symbiotic relationship leads to a decrease in the specific surface area and pore volume because they are in contact with each other. On the other hand, this
symbiotic relationship contributes to the development of organic pores, since clay minerals could reduce the activation energy of organic hydrocarbon generation [9].

For the mineral-hosted pores, the difference in the hardness between different minerals is one of the main reasons for the formation of pores during shale compaction [10]. The organic acid produced during the evolution of organic matter also promotes the dissolution of minerals and forms pores [11]. Clay minerals mainly contribute to micropores due to their layered crystal structure [6]. In this study, the minerals mainly develop micropores and provide some mesopores and macropores. The difference between the kerogen-formed pores and the mineral-formed pores in figure 3 and figure 4 shows that the minerals form many more micropores than the kerogen. This result shows that clay minerals play a very important role in nanopore development in terrestrial low-maturity shale.

5. Conclusions
In this study, the influence of organic matter and inorganic matter on the pore structure of the Shahejie Formation (E2.3S) shale in the Bohai Bay Basin, was analyzed by using low-pressure N2 adsorption measurements, and the following conclusions were obtained.

i. The soluble organic matter in low-maturity shales blocks a large number of pore diameters below 5 nm. ii. The solid organic matter mainly forms pore diameters of 1-2 nm and pore diameters larger than 10 nm and blocks a large amount of the inorganic pores with diameters in the ranges of less than 0.8 nm, 1-2 nm, and 2.3-20 nm. iii. The minerals mainly develop micropores and provide some mesopores and macropores, and the minerals form many more micropores than the organic matter in the terrestrial low-maturity shale. iv. The symbiotic relationship between the organic matter and the minerals leads to a decrease in the specific surface area and pore volume because they are in contact with each other.

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