Research Article

The Influence of Reservoir Composition on the Pore Structure of Continental Shale: A Case Study from the Qingshankou Formation in the Sanzhaoy Sag of Northern Songliao Basin, NE China

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Determining the pore structure characteristics and influencing factors of continental shale reservoir in the oil generation stage is of great significance for evaluating the shale oil reservoir space and analyzing shale oil enrichment mechanism. In this paper, shale from the first member of the Upper Cretaceous Qingshankou Formation (K2qn1) in the Songliao Basin was selected. X-ray diffraction (XRD), Rock-Eval pyrolysis, total organic carbon content (TOC), scanning electron microscopy (SEM), nitrogen gas adsorption (N2GA), and high-pressure mercury injection (HPMI) were used to clarify the composition characteristics of inorganic minerals and organic matter and determine the influencing factors of pore development in the K2qn1 shale. The results show that intergranular pores related to clay minerals and quartz, intragranular dissolution pores related to feldspar, and other mineral intragranular pores are developed. The organic matter pore is less developed, mainly composed of intragranular pores and crack pores of organic matter. Mesopores related to clay minerals are widely developed, rigid quartz particles can protect and support mesopores and macropores, and carbonate cementation can inhibit pore development. Although the TOC contents of shale are commonly less than 2.5%, it has a good positive correlation with porosity; TOC is greater than 2.5%, and the increase of residual oil fills part of the pores, leading to a decrease in porosity with the increase of TOC. Three types (types I, II, and III) of the reservoir space were classified by the combined pore size distribution diagram of N2GA and HPMI. By comparing the characteristics of pore structure parameters, it is found that Type I reservoir space is favorable for shale oil enrichment. It provides scientific guidance for shale oil exploration in the Songliao Basin.

1. Introduction

With the massive consumption of conventional oil and gas resources, the contradiction between fossil energy supplies is increasing sharply; the exploration and development of traditional conventional oil and gas resources are gradually changing to unconventional ones ([1–3]). Oil and gas resources existing in shale have gradually become an important fossil energy supply in the world [4–6]. The United States and Canada are the main countries that realize the commercial development of shale oil and gas such as Bakken, Barnett, and Eagle Ford Marine shale formation in the United States and a proven unconventional shale oil and gas reservoir in the Western Canadian Sedimentary Basin (WCSB) ([7–10]. Compared with marine shale reservoirs, continental shale reservoirs display lower maturity, commonly ranging from oil window to wet gas window (Ro: 0.7–2.0; [2]). Furthermore, the continental shale is more sensitive to the variation of paleoclimate and tectonic settings because of the small scale of lacustrine basins [4, 11–13].
The type and structure of pores and its formation mechanism are very important for determining reservoir space and fluid enrichment [5, 8, 11, 14]. Therefore, understanding the reservoir characteristics of continental shale within the oil window and the influencing factors of its pore structure is one of the key scientific problems to the study of continental shale oil [15].

The pore structure of shale is complex and many types of pores are developed [16, 17]. The genesis of different pore types is different, understanding the genetic mechanism of pores is helpful to judge the contribution of different scale pores to the reservoir space [18]. With regard to the classification of shale reservoir pore types, reference [19] classified the pore types of shale into six types: porous fluidicules, organopores, fecal pellets, fossil fragments, intraparticle grain/pores, and microchannels [20] observed the pore characteristics from Devonian to Pliocene-Pleistocene shale under a microscope. According to the relationship between pores and mineral matrix particles, the shale reservoir space can be divided into three types: mineral matrix pores (including intergranular and intragranular pores), organic pores, and microfractures.
further subdivided according to the development location and component type. So far, Loucks’s classification of shale pore types is the most widely used [17, 21].

Mineral composition and organic matter characteristics are the main controlling factors for the physical properties and pore structure of shale. The mineral composition of organic rich shale is strongly heterogeneous, for example, Longmaxi Formation, Marcllus, Barnett, and Haynesville shale are mainly composed of clay minerals and quartz [22], while Shahejie Formation in Liaohe Sag, Green River shale, Eagle Ford shale, and Niobrara shale consist of carbonate with a small amount of quartz, feldspar, and clay minerals [8, 12, 17, 23, 24]. The mineral composition can reflect the sedimentary environment, and brittle minerals are of great significance to the development of fractures [25]. Quartz exists in the shale by the form of continental, biogenic, authigenic, secondary enlarged, and microcrystal-line types [23, 26]. In the process of hydrocarbon generation, the decarboxylation of organic matter generates CO₂, which combines with H₂S to form carbonic acid, phenolic acid, and so on [22]. It has certain dissolution effect on feldspar and calcite, which could increase the pore space and effectively improve porosity of shale [21]. Dissolution and recrystallization of calcite can exist simultaneously in shale [22]. Meanwhile, carbonate cementation will occupy the pore space and destroy the reservoir properties of shale [22]. The dehydration and transformation of clay minerals have a good corresponding relationship with the maturity and hydrocarbon generation of organic matter [27, 28]. The TOC content is a major controlling factor for the development of pores in shale, especially for the organic matter pores [20, 26, 29].

Characterization techniques of shale reservoir microstructure can be roughly divided into three categories: direct observation method mainly based on observation under...

Figure 2: Cross-plots of the bulk geochemical results. (a) Hydrogen index (HI) versus Tmax relationship for the shale samples from the K2qnp1 Formation. (b) Cross-plots of TOC versus S₂. (c) Cross-plots of TOC versus S₁ + S₂.
high-resolution microscope, indirect measurement method mainly based on fluid intervention method such as nitrogen adsorption, high-pressure mercury injection, nuclear magnetic resonance, and numerical simulation method [8, 14, 17, 30]. In this study, the pore type and morphology of shale samples were observed by SEM and Loucks’ classification of shale pore types was used, the pore structure parameters were measured by N2GA and HPMI, and geochemical parameters of mineral and organic matter composition were obtained by XRD, TOC, and Rock-Eval pyrolysis analyses. The main purposes of this study include (1) identifying the main pore types of shale in the K2qn1 of Songliao Basin, (2) determining the influence of mineral composition and TOC content on the pore structure of K2qn1 shale, and (3) classifying and evaluating the shale reservoir space of the K2qn1 shale based on the distribution characteristics of pore structure parameters.

### 1.1. Geological Setting

Songliao Basin is located in the northeast of China, stretched across Heilongjiang, Jilin, and Liaoning provinces. It is a diamond-shaped basin, which is bounded by the Nenjiang and Mudanjiang Fault in the east, and extends from NE to SW with a geographical location of 119°40′-128°24′ E, 42°25′-49°23′ N [31, 32]. Songliao Basin covers an area of approximately 26 × 10^4 km^2 and is divided into six first-order tectonic units according to the basement characteristics, including the northern dip area, the central depression area, the northeast uplift area, the southeast uplift area, the southwest uplift area, and the western slope area (Figure 1). The central depression is the main oil and gas enrichment area, which is further divided into six second-order tectonic units, including the Qi-jia-Gulong Sag, the Sanzhao Sag, the Chaoyanggou Terrace, the Changling Sag, the Fuyu Uplift, and the Daqing Placanticline (Figure 1).

### Table 2: XRD results of the shale samples from the K2qn1 Formation.

| Sample number | Quartz (%) | K-feldspar | Plagioclase | Calcite | Ankerite | Siderite | Pyrite | Clay (%) | Illite (%) | Chlorite (%) | I/S |
|---------------|------------|------------|-------------|---------|----------|----------|--------|----------|------------|--------------|-----|
| 1             | 36.2       | 0          | 14.8        | 0       | 5.4      | 0        | 2.6    | 41.0     | 66.0       | 14.0         | 20.0 |
| 2             | 22.8       | 0          | 30.6        | 3.8     | 5.5      | 0        | 18.6   | 18.1     | 66.0       | 12.0         | 22.0 |
| 3             | 19.4       | 0          | 4.4         | 0       | 65.6     | 0        | 1.2    | 9.3      | 68.0       | 17.0         | 15.0 |
| 4             | 27.8       | 0.9        | 15.8        | 28.5    | 8.8      | 0        | 1.9    | 16.2     | 79.0       | 6.0          | 15.0 |
| 5             | 18.6       | 0          | 21.5        | 0       | 20.6     | 0.5      | 0      | 38.8     | 67.0       | 11.0         | 22.0 |
| 6             | 5.6        | 0          | 3.3         | 0       | 84       | 0        | 0      | 7.1      | 64.0       | 19.0         | 17.0 |
| 7             | 28.9       | 0          | 15.7        | 0.3     | 12.7     | 1        | 3.3    | 38.1     | 73.0       | 11.0         | 16.0 |
| 8             | 37         | 0          | 18.7        | 0       | 0        | 0        | 6.8    | 37.5     | 68.0       | 10.0         | 22.0 |
| 9             | 22.9       | 0          | 18          | 0       | 33.9     | 0        | 1.8    | 23.4     | 70.0       | 13.0         | 17.0 |
| 10            | 35.1       | 4.9        | 20.9        | 0       | 0        | 0        | 7.5    | 31.5     | 65.0       | 13.0         | 22.0 |
| 11            | 26.8       | 0          | 1.2         | 0       | 64.7     | 0        | 0      | 7.3      | 59.0       | 18.0         | 23.0 |
| 12            | 34.6       | 0          | 1           | 40.2    | 0        | 0        | 10.3   | 13.9     | 64.0       | 16.0         | 20.0 |
| 13            | 35         | 0          | 28.9        | 0.3     | 0        | 0        | 4.4    | 31.5     | 49.0       | 25.0         | 26.0 |
| 14            | 40.8       | 0          | 15.1        | 0       | 5.9      | 2.7      | 3.6    | 31.9     | 73.0       | 12.0         | 15.0 |

**Figure 3:** (a) Cross-plot of quartz versus clay minerals of the shale samples. (b) Cross-plot of the carbonate minerals versus quartz of the shale samples.
Sedimentary strata in Songliao Basin show different characteristics in different stages of tectonic evolution, which is presented as a sedimentary sequence of lower fault depression and upper depression in general. From bottom to top, the strata can be divided into the Huoshiling Formation (J2h), Shahezi Formation (K1sh), Yingcheng Formation (K1y), Denglouku Formation (K1d), Quantou Formation (K1q), Qingshankou Formation (K2qn), Yaojia Formation (K2y), Nenjiang Formation (K2n), Sifangtai Formation (K2s), and Mingshui Formation (K2m). K2qn is dominated by a lacustrine deposit under warm and humid paleoclimate with a semideep to deep lacustrine environment. At the same time, two times of slight uplift and subsidence also occurred, resulting in the delta advancing towards the basin in different levels forming a lithologic assemblage mainly composed of black thick mudstone with gray siltstone and fine sandstone. K2qn1 Formation is not only the main source of rock formation in the basin but also the main development section of shale oil ([11]; Figure 1).

2. Samples and Methods

For this study, 14 dark shales were selected from the K2qn1 of Sanzha Sag in the central depression, Songliao Basin. The buried depth of the selected samples ranges from 1985 m to 2060 m.

2.1. TOC and Rock-Eval Pyrolysis. The TOC content is determined by a C-744 Carbon Analyzer of the American Leica Company. Firstly, the samples were crushed, and then, the
Figure 5: Continued.
inorganic carbon was removed with dilute hydrochloric acid. The Rock-Eval 6 instrument was used to obtain the pyrolysis parameters, including $S_1$, $S_2$, Tmax, HI ($HI = S_2/TOC \times 100$). Before the analysis, the powder was pulverized to the following 100 mesh and dried for 24 h at 80°C in a vacuum. According to the TOC contents, the weighing sample of...
2.4. N$_2$ Gas Adsorption (N$_2$GA) and Mercury Injection Capillary Pressure (MICP). The nitrogen adsorption experiment was determined by the American ASAP 2460 automatic surface area and pore size analyzer. First, an appropriate amount of sample was crushed to 60–80 mesh and drying. Then, the adsorption and desorption curves were measured and the pore structure information according to the theoretical model was obtained. In this study, the BET model was used to get the surface area, the BJH model was used to get the average pore size and pore volume, and the DFT model was used to get the pore size distribution characteristics. The mercury injection experiment was performed on the PORE MASTER-60 automatic mercury injection apparatus of the Quantachrome. The pore throat distribution and porosity of the sample with a diameter of 1 cm–2 cm were measured. The range of the pore throat was 3 nm–1000 μm, and the pore volume distribution was calculated by the Washburn equation. At the same time, the skewness was used to judge the asymmetry of pore throat size distribution and the sorting coefficient was used to reflect the concentration degree of pore throat distribution. The better the sorting is, the more concentrated the distribution of pore throat is, the lower the gentle section is, the closer it is to the horizontal axis, and the coarser the skew. Otherwise, it is the fine skewness [33]. In this study, nitrogen adsorption and mercury injection were used to evaluate the pore size distribution of the selected shale samples. The pores with a pore size greater than 100 nm are defined as macro pores, the pores with a pore size between 10 nm and 100 nm are defined as mesopores, and the pores with a pore size less than 10 nm are defined as micropores.

3. Results

3.1. Bulk Geochemical Parameters. The TOC content of shale ranges from 0.52% to 6.81%, with an average of 2.87%. The content of free hydrocarbon $S_1$ ranges from 1.26 mg/g to 6.14 mg/g, with an average of 2.55 mg/g. The content of pyrolysis hydrocarbon $S_2$ ranges from 2.61 mg/g to 43.26 mg/g, averaging 16.69 mg/g. The hydrocarbon generation potential $(S_1 + S_2)$ ranges from 4.27 mg/g to 49.41 mg/g, averaging 19.52 mg/g. T$_{max}$ ranges from 452°C–445°C, with an average T$_{max}$ of 448°C (Table 1). HI ranges from 366.25 mg/g to 727.19 mg/g, with an average HI of 576.84 mg/g. According to the relationship between HI and T$_{max}$ and the relationship between TOC and $S_2$, most of the samples are type 1 kerogen (Figures 2(a) and 2(b)). $S_1$ + $S_2$ and TOC have a positive correlation (Figure 2(c)); the quality of the source rock is good.

3.2. Mineral Composition. The XRD results show that the shale samples are mainly composed of quartz and feldspar, followed by clay and carbonate minerals, accompanied by...
a small amount of pyrite. The content of quartz ranges from 5.6% to 40.8%, averaging 27.9%. The feldspar is mainly plagioclase; the content of plagioclase varies between 1.0% and 36%, averaging 15.4%. The content of K-feldspar is relatively low; the content of K-feldspar ranges from 0 to 4.9%, averaging 0.4%. Carbonates are mainly composed of calcite and ankerite; the content of calcite ranges from 0 to 40.2%, averaging 5.2%. The content of ankerite ranges from 0 to 84%, averaging 21.9%. Only three samples contain siderite (samples 5, 7, and 14). The content of clay ranges from 7.1% to 41%, averaging 24.6%. The content of pyrite ranges from 0 to 18.6%, averaging 4.4%. Clay minerals are mainly composed of illite and I/S, which account for more than 86% of the content of clay. The average content of illite (66.5%) is much higher than the average content of I/S (19.4%), followed by chlorite (6.0%–25.0%), with an average content of 14.1% (Table 2). Quartz has a positive correlation with clay minerals (Figure 3(a)); the content changes tend to be consistent and have a significant negative correlation with carbonate minerals (Figure 3(b)), which indicates that most of quartz and clay may have the same material source, which is different from carbonate minerals.

3.3. Pore Types. Three types of pores were identified by SEM analysis, including organic pore, intergranular pore, and intragranular pore (Figures 4 and 5).
Figure 8: Continued.
In the shale samples of the K2qn1 Formation in Sanzhao Sag, the organic pores are poorly developed. It exists in two forms: one is the intragranular pores of organic matter, which are rare, oval, or round in shape, with a maximum pore diameter of about 400 nm (Figures 4(c) and 4(f)). They are nanomicropores and mainly produced by hydrocarbon generation of organic matter. The other type of organic pore is the crack pores; it develops between the organic matter and mineral matrix and is mainly in the strip shape. The pore size can reach 2 μm in length and 1 μm in width (Figures 4(c) and 4(f)). Intergranular pores are well developed in the shale, which are partly independent and partly connected with each other, generally displaying an irregular shape. Smaller intergranular pores are widely found in clay particles, which are in the shape of cracks or triangles, and the pore sizes are generally between 50 nm and 100 nm (Figures 4(a), 4(b), 4(d), and 5(e)). The pores developed between the irregular mineral particles are larger, such as those between quartz particles, with pore sizes ranging from 50 nm to 0.5 μm (Figures 4(e), 5(c), and 5(e)). Pores at the edge of rigid grains develop at the contact point between quartz or feldspar and clay minerals, and the shape is related to the mineral grain edge morphology. Generally, it has the features of a more curved seam shape and smaller seam width (Figures 4(d), 4(e), and 5(c)). The shale samples of K2qn1 Formation mainly develop intragranular pores dominated by dissolution pores and a small amount of intercrystalline pores. The dissolution pores are mostly developed in feldspar particles and a small amount in calcite and other carbonate particles. The pores are distributed in groups, with small spacing, nearly circular or irregular shape, generally 100 nm (Figures 4(a), 4(b), 4(e), 4(f), 5(b), 5(c), and 5(d)). Intercrystalline pores are common in framboid pyrite, with pore sizes up to about 0.5 μm (Figures 5(a) and 5(b)). In addition, intergranular pores related to clay minerals and quartz are also developed (Figures 4(e) and 5(c)).

### 3.4. Nitrogen Adsorption Experiment

#### 3.4.1. Pore Volume and Surface Area.

For the K2qn1 shales, the BET surface area ranges from 0.44 m²/g to 13.58 m²/g, averaging 3.96 m²/g. The pore volume ranges from 0.00306 cm³/g to 0.027262 cm³/g, averaging 0.014332 cm³/g. Among them, the 0 nm–10 nm pore volume ranges from 0.000625 cm³/g to 0.026605 cm³/g, averaging 0.005999 cm³/g. The 10 nm–100 nm pore volume ranges from 0.001096 cm³/g to 0.010907 cm³/g, averaging 0.0006536 cm³/g (Table 2).

#### 3.4.2. Pore Size Distribution.

The average pore diameter measured by N₂GA analysis is between 7.85 nm and 36.59 nm. According to the pore size distribution characteristics, two types of pore structures were classified. Type A sample structures include samples 1, 2, 3, 4, 6, 7, 8, 9, 11, 12, 13, and 14, of which the mesopores within 35 nm are the most developed and the micropores at 10 nm are relatively developed. It has good connectivity and a large number of samples with pore size distribution characteristics of type A (Figure 6(a)). Type B samples include samples 5
Figure 9: Continued.
and 10, of which the micropores within 10 nm are the most developed, and the mesopores at 35 nm are relatively developed, showing relatively good connectivity (Figure 6(b)).

3.4.3. Adsorption Isotherms. The International Union of Pure and Applied Chemistry divided the adsorption and desorption isotherms into six types [34].

The adsorption isotherm of K$_2$qn$_1$ shale is type IV adsorption and desorption isotherm. The adsorption isotherm of type IV has a hysteretic loop phenomenon due to the effect of mesopore capillary condensation. Different types of hysteresis loops correspond to different pore development morphologies [35]. There are two types of pores in the shale in this study, which are ink bottle-shaped pores and slit-shaped pores (Figure 7). Samples with H2-type ink bottle-shaped pores correspond to type B pore size distribution. Samples with H3-type slit-shaped pores correspond to type A pore size distribution.

3.5. High-Pressure Mercury Injection Experiment. The results of HPMI show that the median pore diameter of the selected shale samples ranges from 10.01 nm to 5366.62 nm. The porosity ranges from 1.23% to 5.94%, averaging 3.20%.

Macropore volume ranges from 0.0002 cm$^3$/g-0.0168 cm$^3$/g, averaging 0.007007 cm$^3$/g (Table 3, Table 4). According to pore size distribution and capillary pressure curve, three pore types are classified: type A mainly developed macro pores greater than 1000 nm, and a few micropores less than 10 nm, with good sorting, rough skewness, and good connectivity. Samples 4, 7, 8, 12, and 14 correspond to this type (Figures 8(a), 8(b), 8(d), and 8(e)). Type B mainly developed micropores with a pore size less than 10 nm and a small number of macropores with a pore size greater than 1000 nm. It has good sorting, slightly coarse skewness, and good connectivity. Samples 1, 2, 3, 6, 10, 11, and 13 correspond to this type (Figures 8(c), 8(f), 8(g), and 8(j)). Type C mainly developed 10 nm–100 nm pores, having poor sorting, fineness, skewness, and connectivity. Samples 5 and 9 correspond to this type (Figures 8(h), 8(i), 8(k), and 8(l)).

4. Discussion

4.1. Effect of Mineral Composition on Pore Development. The correlation between different mineral composition and the pore structure is complex. In this study, a threshold value of $R^2 > 0.2$ was set to characterize the strength of the correlation. The $N_2$GA mainly characterized the pore structure in the range of the nanoscale pore size, and the MICP mainly characterized the pore structure of the micron pore size [23]. Therefore, the nitrogen adsorption experiment results were used for the pore volume analyzed with a pore diameter less than 100 nm, and the high-pressure mercury injection experiment results were used for the pore volume analyzed with pore diameter larger than 100 nm in this study.
Quartz is a typical rigid mineral with stable properties, high hardness, and compaction resistance, so the existence of quartz can protect the rock skeleton [23]. There is a positive correlation coefficient of 0.417 between quartz content and porosity. There is no obvious correlation between the quartz content and the micropore and mesopore volume, while there is a positive correlation between the quartz content and the macropore volume (Figures 9(a)–9(d)). The correlation indicates that quartz has little protective effect on the micropore and mesopore volume and mainly protects the framework structure of macropores, which is consistent with the previous research on shale in Western Canada.

Figure 10: Correlation of rock mineral (quartz, clay, and carbonate) with porosity, volumes of micropores, mesopores, and macropores for shale samples.
The correlation between clay and porosity is not obvious, which may be affected by other minerals and the correlation is masked. However, it can be observed that intergranular and intragranular pores related to clay are widely developed under the microscope (Figures 4(a), 4(b), and 4(d)) and the clay content is positively correlated with the mesopore volume, which indicates that the pores related to clay minerals are mostly mesopores (Figures 9(e)–9(h)). Some of the pores related to clay minerals are primary pores, which are preserved by mechanical compaction due to the protection of rigid quartz particles. In the process of transformation from smectite to illite, the dehydration process is also a process of shrinkage of mineral particles and relative increase of pores. Meanwhile, the conversion of smectite to illite releases silica, which increases the hardness of the rock [37]. There is negative correlation ($R^2 = 0.312$) between mesopore volume and carbonate and no correlation between micropore volume, macropore volume, and carbonate (Figures 9(i)–9(l)). The correlation between carbonate and porosity is also not obvious. The pore water of the original sediment contains $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$, which is beneficial to the formation of carbonate cements and resulting in a blocking effect on the pores [22]. During the thermal evolution process of organic matter, organic acids generated during the hydrocarbon generation will corrode calcite and generate dissolution pores but the dissolution is highly heterogeneous. Therefore, the pore throat is mainly filled with cementation of carbonate, which inhibits the development of shale pores to a certain extent.

The dissolution pores associated with feldspar can be seen under SEM (Figures 4(a), 4(b), and 4(e)). There is no obvious correlation between the feldspar content and porosity. The content of feldspar has a good correlation with the volume of mesopores and no obvious correlation with micropores and macropores, indicating that the dissolution pores related to feldspar are mostly mesopores (Figures 10(a)–10(d)). Therefore, in the $K_2qn_1$ shales, there are two reasons for the formation of dissolution pores, one is the dissolution of minerals by organic acids; the other is the consumption of $K^+$ in the process of transformation from smectite to illite, which promotes the dissolution of K-feldspar. There is a positive correlation between pyrite and porosity, and intergranular pores of pyrite can be seen in SEM (Figure 10(e)).

4.2. Effect of the TOC Content on Pore Development. TOC is one of the main factors affecting organic pores in shale. For $K_2qn_1$ shales, only a few organic pores are developed. Two kinds of organic pore were observed by SEM. There are two reasons for the development of crack organic pores: (1) organic matter dissolves the minerals that cover the organic matter, creating a crack between the organic matter and the mineral matrix (Figure 4(f)), and (2) the volume of organic matter will shrink to a certain extent after the
Figure 12: Combined pore size distribution of N$_2$GA and HPMI.
Figure 13: Continued.
hydrocarbon fluid is generated and released during the evolution process, thus forming crack pores between the organic matter and the surrounding mineral matrix (Figure 4(c)). The intragranular pores of organic matter are formed in the early stage of maturity, which were formed after the organic matter released hydrocarbon fluid (Figures 4(c) and 5(e)). Generally speaking, within a certain range, porosity increases with the TOC content. The average organic carbon content of the K2qn1 shales is moderate to high, with a TOC content of 2.5% as the boundary. When the TOC content is less than 2.5%, the porosity, surface area, and total pore volume content of shale increase with the increasing TOC content. When TOC is more than 2.5%, porosity decreases with TOC content increasing and the surface area and total pore volume are negatively correlated with the TOC content. The correlation between the TOC content and pore structure parameters can show that with the progress of hydrocarbon generation, nanopores are produced in organic matter, resulting in the increase of porosity (Figures 11(a)–11(c)). At the same time, Si is positively correlated with TOC (Figure 11(d)), with the increase of the TOC content, the generated residual oil is mainly adsorbed on the surface of kerogen or filled in the mineral pores, blocking the pore space of shale, and the residual oil occupies the surface area of shale, making the pore space and total pore volume decreased. Therefore, the TOC content has a strong control on the development of organic matter pores [23, 38].

4.3. Classification and Evaluation of the Reservoir Space. According to the pore size distribution, surface area, and total pore volume, the samples of K2qn1 can be divided into three types of the pore structure (Figure 12).

4.3.1. Type I: A-a (Samples 4, 7, 8, 10, 12, and 14). Mesopores and macropores are the most developed, and the micropores are relatively developed (Figure 12(a)). The large surface area, total pore volume, median pore diameter, and good connectivity are shown in Figures 13(a)–13(d). Clastic minerals and clay are the main minerals in type I samples, with average contents of 49.5% and 28.2%, respectively. The average content of carbonate is 16.6% and pyrite is 5.5%. The content of organic matter is between 2.51% and 3.57%, mainly developed clay mineral intergranular pores, dissolution pores, a small amount of pyrite intergranular pores, and organic pores. Organic pores are more numerous than other types. Taking sample 10 as an example, the mineral composition is dominated by quartz (35.1%), feldspar (25.8%), and clay minerals (31.5%), accompanied by a small amount of pyrite (7.5%) without carbonate minerals. The TOC content
is 2.01%, the surface area is 9.16 m$^2$/g, the total pore volume is 0.021077 cm$^3$/g, the average pore diameter is 9.11 nm, the median pore diameter is 26.91 nm, and the porosity is 3.82%. A large number of intergranular pores of clay minerals were observed under scanning electron microscopy, followed by dissolution pores (Figures 4(a) and 4(b)).

4.3.2. Type II: A-b (Samples 1, 2, 3, 6, 11, and 13). Mesopores are the most developed, and the micropores and macropores are relatively developed (Figure 12(b)). The larger surface area, total pore volume, average pore size and median pore diameter, and better connectivity are shown in (Figures 13(e)–13(h)). In type II samples, clastic and carbonate are the main minerals, averaging 38.1% and 38.8%; next are clay minerals, averaging 19.0%, and a small amount of pyrite, averaging 4.6%. The content of organic matter is between 1.46% and 3.72%. The main pore type is a feldspar dissolution pore followed by a clay intergranular pore. Organic pore is less developed and carbonate cementation is obvious. Taking sample 2 as an example, the mineral composition of the rock is quartz (22.8%) and feldspar (30.6%), followed by clay (18.1%), pyrite (18.6%), and carbonate minerals (9.3%). The TOC content is 3.2%, the surface area is 1.49 m$^2$/g, the total pore volume is 0.011658 cm$^3$/g, the average pore diameter is 31.38 nm, the median pore diameter is 30.34 nm, and the porosity is 4%.

4.3.3. Type III: A-c (Samples 5 and 9). Mesopores are the most developed, and the micropores are relatively developed, with smaller total pore volume and average pore size and poor connectivity. In type III samples, clastic and carbonate are dominant, with average contents of 40.5% and 27.5%. The second is clay minerals with an average content of 31.1% and a small amount of pyrite with an average content of 0.9%. The content of organic matter ranged from 2.83% to 4.52% and mainly developed dissolution pores and intergranular pores of clay minerals, and carbonate cementation was obvious. Taking sample 5 as an example, the mineral composition of the rock is quartz (18.6%), feldspar (21.5%), and carbonate (21.1%), followed by clay (38.8%). The TOC content is 2.83%, the surface area is 13.58 m$^2$/g, the total pore volume is 0.027262 cm$^3$/g, the average pore radius is 7.85 nm, the median pore diameter is 14.73 nm, and the porosity is 2.22%. Scanning electron microscopy (SEM) shows that a large number of dissolution pores are developed in feldspar, followed by intergranular pores in clay minerals (Figures 5(b) and 5(c)).

5. Conclusion

(1) The mineral composition and TOC content will affect shale pore development characteristics. The selected K$_2$qn$_1$ shale samples are mainly composed of quartz and feldspar, followed by clay and carbonate, with a small amount of pyrite. Among them, quartz, feldspar, and clay promote the development of the pore space and carbonate inhibits the development of the pore space. The TOC content in the K$_2$qn$_1$ Formation is limited by 2.5%. When the TOC% is greater than 2.5%, the residual oil will increase, which will plug the pores and cause the porosity to decrease.

(2) Intergranular pores and intragranular pores are mainly developed in the shale of K$_2$qn$_1$ Formation, while organic pores are less developed. Intergranular pores include intergranular pores of minerals and pores at the edge of rigid grains. Intragranular pores include dissolution pores, pyrite pores, and clay mineral pores. Organic pores are mainly composed of internal pores and crack-type pores.

(3) Mesopores related to clay are widely developed in the shale of the K$_2$qn$_1$ Formation. Quartz has a protective effect on mesopores and macropores. Most of the pores related to carbonate are dissolution pores. Meanwhile, carbonate cementation has the effect of plugging and reducing pores, which mostly fills mesopores and macropores. The pores related to feldspar are mostly dissolution pores.

(4) Combined with nitrogen adsorption and high-pressure mercury injection experiments, the shale samples of K$_2$qn$_1$ Formation are divided into three types by using the joint pore size distribution figure. The type I micropores are relatively developed, the mesopores and macropores are the most developed, the connectivity is good, and the surface area, the total pore volume, and the median pore size are large. Type II micropores and macropores are relatively developed; mesopores are the most developed, with good connectivity, larger surface area, total pore volume, and larger average pore size and median pore size. Type III does not develop macropores, mesopores are the most developed, micropores are more developed, connectivity is poor, and the total pore volume and average pore size are small.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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