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Research Article

Pore Structures of the Lower Permian Taiyuan Shale and Limestone in the Ordos Basin and the Significance to Unconventional Natural Gas Generation and Storage

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In the Ordos Basin, multiple sets of coal seams, organic-rich shale, and limestone are well developed in the Permian Taiyuan Formation, which are favorable targets for collaborative exploration of various types of unconventional natural gas resources, including coalbed methane, shale gas, and tight gas. In this study, core samples from the Permian Taiyuan Formation in the eastern margin of the Ordos Basin were used to carry out a series of testing and analysis, such as the organic matter characteristics, the mineral composition, and the pore development characteristics. In the shale of the Taiyuan Formation, the total organic carbon (TOC) content is relatively high, with an average of 5.38%. A thin layer of black shale is developed on the top of the Taiyuan Formation, which is relatively high in TOC content, with an average of 9.72%. The limestone in the Taiyuan Formation is also relatively high in organic matter abundance, with an average of 1.36%, reaching the lower limit of effective source rocks (>1%), being good source rocks. In the shale of the Taiyuan Formation, various types of pores are well developed, with relatively high overall pore volume and pore-specific surface area, averaging 0.028 ml/g and 13.28 m^2/g, respectively. The pore types are mainly mineral intergranular pores and clay mineral interlayer fractures, while organic matter-hosted pores are poorly developed. The limestone of the Taiyuan Formation is relatively tight, with lower pore volume and pore-specific surface area than those of shale, averaging 0.0106 ml/g and 2.72 m^2/g, respectively. There are mainly two types of pores, namely, organic matter-hosted pores and carbonate mineral dissolution pores, with a high surface pore rate. The organic matter in the limestone belongs to the oil-generation kerogen. During thermal evolution, the organic matter has gone through the oil-generation window, generating a large number of liquid hydrocarbons, which were cracked into a large number of gaseous hydrocarbons at the higher mature stage. As a result, a large number of organic matter-hosted pores were generated. The study results show that in the Ordos Basin, the shale and limestone of the Permian Taiyuan Formation have great potential in terms of unconventional natural gas resources, providing a good geological basis for the collaborative development of coal-bearing shale gas and tight limestone gas in the Taiyuan Formation.

1. Introduction

In recent years, with continuous breakthroughs in unconventional oil and gas exploration, unconventional resources such as shale gas, tight sandstone gas, coalbed methane, and shale oil have gradually become important replacement resources for energy supply in the world. In the Ordos Basin, multiple sets of strata of marine-continental transitional facies are well developed in the Upper Paleozoic Permian, with multiple sets of interbedded coal seams, organic-rich shale, and tight sandstones (e.g., [1, 2]). Therefore, the geological conditions are favorable for the accumulation of various types of unconventional natural gas resources in the Ordos Basin. At present, in the Ordos Basin, the Permian tight sandstone gas and coalbed methane resources have been commercially produced after years of exploration and development [3]. The Ordos Basin has huge oil and gas resources, being one of the basins with the greatest potential for increasing oil and gas reserves and production in the future. The geological resources of natural gas are $15.2 \times 10^{12}\,m^3$, and the recoverable resources are $8.93 \times 10^{12}\,m^3$. Meanwhile, unconventional oil and gas resources are also rich in the Ordos Basin, including coalbed methane, shale gas, and tight sandstone gas, and the geological resources are $9.86 \times 10^{12}\,m^3$, $(3.4\text{-}5.3) \times 10^{12}\,m^3$, and $(6-8) \times 10^{12}\,m^3$, respectively. The recoverable resources of coalbed methane and tight sandstone gas are $1.79 \times 10^{12}\,m^3$ and $(3, 4) \times 10^{12}\,m^3$, respectively [4, 5].

Despite large resources, the shale gas in coal measures is still at the initial stage of evaluation and exploration. In the northwestern part of the Ordos Basin, in Well Erye 1, which is a vertical well, an open flow capacity of $1.95 \times 10^4\,m^3/d$ was obtained from the Taiyuan Formation during the production test after fracturing. In three horizontal wells drilled in the shale interval of the Permian Shanxi Formation in the Yanchuan area in the southeast of the basin, a commercial gas flow after fracturing was obtained during the production test, with daily production of $2.0 \times 10^4\,m^3/d$ to $5.3 \times 10^4\,m^3/d$. These results demonstrate great exploration and development potential in the Permian marine-continental transitional shale gas in the Ordos Basin [6]. In general, in the Ordos Basin, the Upper Paleozoic Permian coal measures of the transitional facies are rich in shale gas, with great gas resource potential. However, the study on the accumulation characteristics of shale gas is still relatively weak, and the evaluation methods require further study, restricting the subsequent sustainable development of shale gas.

In the Ordos Basin, in the Permian Taiyuan Formation, besides the multiple sets of coal seams and organic-rich shales, there are multiple sets of bioclastic limestone with a large thickness formed in carbonate platform subfacies. Similar to mudstone or shale, limestone is also an important source rock type in petroliferous basins in the world, accounting for about 58% of all source rocks [7]. The marine carbonate rocks were developed during the depositional period of the transgressive system tract, and the sea level rose rapidly during that time. The depositional environment was generally under the dysoxic and anoxic environment with low deposition rate [5, 8]. The organic matters in Paleozoic limestone in the Ordos Basin are basically type I and type II, with the characteristics of sapropelic parent materials, which were mainly originated from bacteria, algae, and aquatic plankton [4]. They are better parent materials and have a much stronger oil-generation capacity than the type II_2 and type III kerogen in the marine-continental transitional coal-bearing shales. Under certain conditions of organic matter enrichment, the limestone can also be a good source rock, with self-generation and self-storage capability and thus can be a target for oil and gas exploration and development as unconventional reservoirs. In the Ordos Basin, in the Lower Paleozoic Ordovician Majiagou Formation carbonate rocks, many large-scale natural gas fields have been discovered, such as the Jingbian Gas Field. Previous studies on the natural gas source indicated that the limestone in the Majiagou Formation has great gas generation potential, with self-generation and self-storage capability [9, 10]. In the past, in the Ordos Basin, the exploration of unconventional resources in the Permian Shanxi Formation and Taiyuan Formation was mainly aimed at the exploration of coalbed methane, tight sandstone gas and shale gas, and so on, whereas the natural gas resource potential in the tight limestone of the Taiyuan Formation has not attracted enough attention.

In this study, with the shale and limestone of the Permian Taiyuan Formation in the eastern margin of the Ordos Basin as the study object, we have conducted a comparative study on the accumulation conditions of shale gas and tight limestone gas, such as the organic matter content, organic matter type, thermal evolution degree through observation and intensive sampling of cores in key wells, testing and analysis of geochemical and physical parameters, combined with thin section identification, low-temperature N_2 adsorption, scanning electron microscope analysis, X-ray diffraction analysis, and other methods. By comparing the pore types and difference in organic matter-hosted pores between shale and limestone, the pore formation mechanism of different reservoirs in the Taiyuan Formation is investigated. The results can provide a reference for the understanding of the accumulation conditions of shale gas and tight limestone gas in the Taiyuan Formation and can provide a theoretical basis for collaborative exploration of multiple types of unconventional natural gas in the Taiyuan Formation in the Ordos Basin.

2. Geological Setting

The Ordos Basin is one of the large-scale sedimentary basins in China, with an area of about $37 \times 10^4\,km^2$. It is bounded by Lvliang Mountain in the east, Qinling Mountain in the south, and Helan Mountain and Liupan Mountain in the west. According to the geological evolution and structural pattern, the regional structure of the basin can be divided into six structural units, namely, the western thrust structural belt, the Yimeng Uplift, the Tianhuan Depression, the Yishan Slope, the Weibei Uplift, and the western Shanxi Flexure Belt Fold area ([1, 11]; Figure 1).

During Late Paleozoic, the Ordos Basin experienced a complex paleogeographic evolution process, including the epicontinental ocean basin dominated by marine sediments, the offshore lacustrine basin dominated by marine-continental transitional sediments, and the inland depressed lacustrine basin dominated by continental clastic sediments [11]. In the study area, the bottom of the Taiyuan Formation is in conformable contact with the underlying No. 8 coal seams of the Carboniferous Benxi Formation, and the top is in conformable contact with the overlying dark shale layer of the Permian Shanxi Formation (Figure 2). The Taiyuan Formation is generally 30-50 m in thickness, varying greatly in different areas of the basin. During the depositional

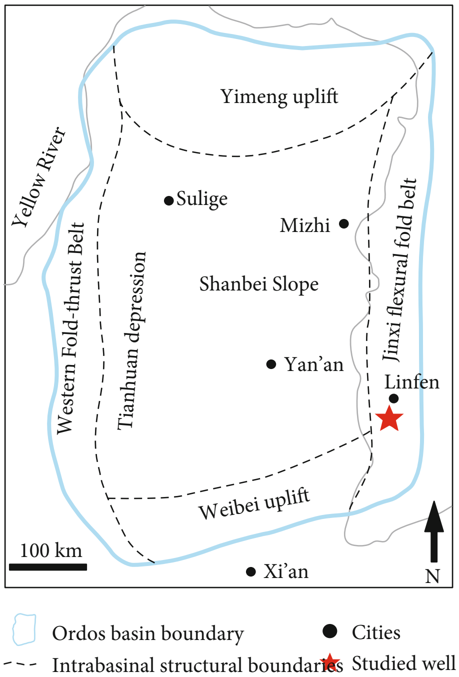


Figure 1: Tectonic map of the Ordos Basin and location of the study well.

period of the Taiyuan Formation, multiphase large-scale seawater transgression occurred in the Ordos Basin, and many sets of carbonate rocks were developed in the Taiyuan Formation in most areas of the basin [12]. Generally, the Taiyuan Formation was deposited under a shallow marine shelf and barrier island-coastal environment. The carbonate rocks were deposited on carbonate platforms, while the shales and coal seams were mainly deposited in tidal flat-swamp and lagoon environments.

3. Materials and Methods

A continuous cored well is located in Linfen City, Shanxi Province, south-eastern Ordos Basin, covering complex lithology of coals, sandstones, shales, and carbonates of the Carboniferous Benxi Formation to the Permian Shanxi Formation (Figure 1). Detailed geochemistry and sedimentary characteristics of the Shanxi Formation are discussed in another independent publication whereas this paper focuses on the Lower Permian Taiyuan Formation. 71 Taiyuan shale and limestone samples were collected at the depths from 2164.02 m to 2198.17 m in the studied well, with an average interval of 0.4 m. For the sake of clarity, all samples were named after their original depth. Total organic carbon content (TOC) and mineralogical composition were analysed for all 71 shale and limestone samples. A total of 36 shale and limestone samples were chosen for low-pressure nitrogen adsorption measurement and field emission-scanning electron microscopy. All analyses were performed at the National Energy Shale Gas Research and Development (Experiment) Centre, PetroChina Key Laboratory of Unconventional Oil and Gas.

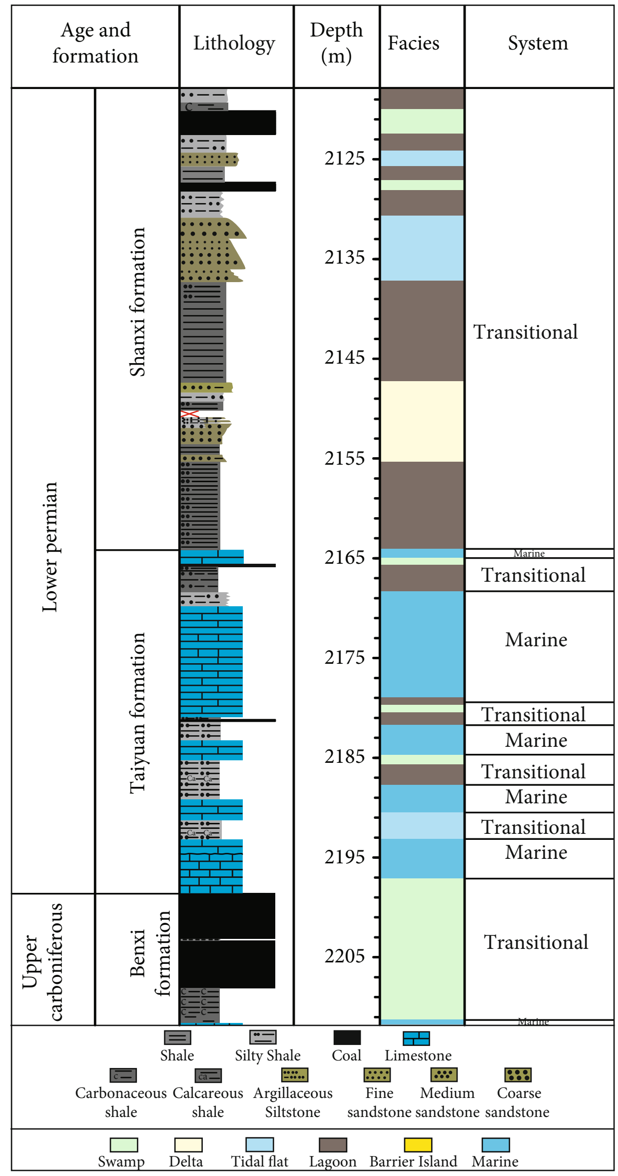


Figure 2: Stratigraphic column and sedimentary environment of the Carboniferous-Permian marine-nonmarine transitional strata (modified from [9]).

3.1. Sedimentological Characterization. Samples were collected from the continuously cored well, and lithofacies were determined. Shale and limestone samples are determined by core description based on the color, grain size, and texture. Then, sublithologies were determined by macroscopic observation. Thin sections were prepared for petrographic analysis, using Zeiss Axio Scope.A1, following the standard SY/T 5368-2016 [13].

3.2. Organic Geochemical Analysis. Total organic carbon (TOC) was measured by induction furnace combustion (LECO) with a CS230 analyser; the analytical precisions are ±0.5%. The samples were treated with 10% hydrochloric acid to remove carbonates. Then, each treated sample was washed with distilled water to neutral; then, the sample was dried in an oven at 60°C~80°C. Dried samples were added to the cosolvent and fully burned in the high-temperature oxygen flow. While ensuring the organic carbon can be completely converted into carbon dioxide, the content of total organic carbon was tested by an infrared detector.

3.3. Mineralogical Composition. Mineralogy and mineral compositions were determined and measured for the 71 selected samples with a Rigaku SmartLab9 rotating anode X-ray diffractometer using 40 kV and 100 mA with a Cu Kα radiation. It should be noted that these 71 samples do not correspond to the samples used for geochemical analyses. Stepwise scanning measurements were performed at a rate of 4°/min in the range of 3° to 85° (2θ). The analytical uncertainties of XRD mineralogy analysis are estimated to be 2%. The relative mineral percentages were estimated using the K-value method. K-value is the positive correlation between the content of a certain mineral and the intensity of its characteristic diffraction peak.

3.4. Low-Pressure Nitrogen Adsorption Measurement. Low-pressure nitrogen adsorption measurements were conducted on 36 selected shale and limestone samples. The shale and limestone samples were crushed into grains with approximately 40 mesh size and then automatically degassed at 110°C in a vacuum for 20 hours; adsorbed moisture and volatile matter are thus removed. Nitrogen adsorption volumes were measured over a relative equilibrium adsorption pressure (P/P_0) ranging from 0.001 to 0.998 (P = balance pressure; P_0 = saturation pressure). In order to investigate the hysteresis types for the low-pressure nitrogen adsorption, both adsorption and desorption isotherms were measured.

3.5. Field Emission-Scanning Electron Microscopy. The same selected 36 samples for low-pressure nitrogen adsorption measurements were also subjected to field emission-scanning electron microscopy (FE-SEM) imaging analyses. The FE-SEM imaging of nanopores and microfractures was performed on the surfaces prepared by Ar ion milling (IM4000, Hitachi High-Tech) using an accelerating voltage of 3 kV and a milling time of 3 hours.

4. Results and Discussion

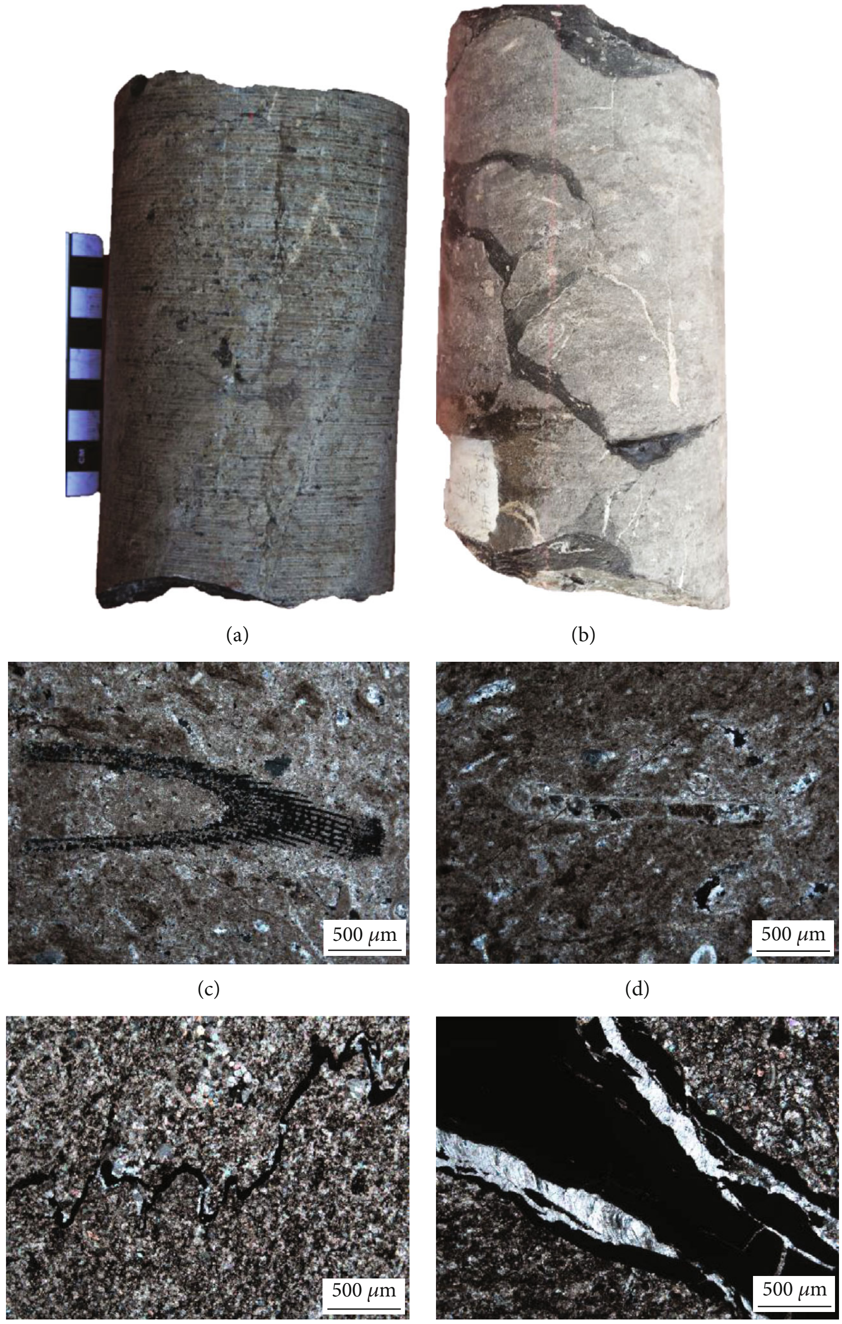
4.1. Sedimentological Characteristics. Carbonates in the Lower Permian Taiyuan Formation comprise mainly bioclastic limestones and micrites with abundant marine fauna and flora, such as Schwagerina, sea urchin (Figure 3(c)), Brachiopod, Foraminifera, sponge spicules, and Bryozoans (Figure 3(d)). Carbonates are characterized by grey to dark-grey color, mottled structure, and typical stylolite structures. Microfractures are developed, filled by pyrites and organic matter (Figure 3(f)). Carbonates are interpreted as deposited within shallow marine environment, perhaps on the shallow carbonate platform with occasional regression of seawater resulting in transitional environment. Two sets of thin coal seam at the depth ~2165 m and 2180 m suggest swamp-tidal flat transitional depositional environment.

Shales in the Lower Permian Taiyuan Formation comprise calcareous shale and silty shale. Shales are characterized by dark grey-black color and mostly massive structure. For silty shales, parallel to subparallel silty laminations are developed with frequent bioturbation (Figures 3(i) and 3(j)), suggesting relatively medium-high hydrodynamic conditions. Calcareous shales are characterized by black color, and massive structure with abundant pyrite grains and sometimes pyrite bands, suggesting rather quiet and oxygen-depleted environment. Compared to the Shanxi Formation shales [12], the Taiyuan Formation shales have rare horizontal beddings; fragments of marine fossils and bioturbations are more frequently occurred and interbedded with thick limestones, suggesting a high sedimentation rate yet stronger impact of seawater. The Taiyuan Formation shales are interpreted as being deposited within tidal-flat to lagoon environment.

4.2. Organic Geochemical and Mineralogical Characteristics. The TOC content is a key indicator for evaluating whether the shale and limestone rocks are effective source rocks, and it is also an important criterion for determining whether shale and limestone reservoirs can be effective unconventional reservoirs. For self-generation and self-storage oil and gas resources, the degree of organic matter enrichment determines the material basis. Studies on shale as unconventional oil and gas reservoirs are vast, and it is widely believed that TOC greater than 2.0% is a key indicator for determining whether shale can form commercial shale gas resources [14–16]. The organic matter abundance of the shale in the Taiyuan Formation is relatively high, ranging from 0.14% to 26.6%, with an average of 5.38%. Within the Taiyuan Formation, a thin-layer black shale at its uppermost part has the highest TOC content, ranging from 8.47% to 10.2%, with an average of 9.72% (Figure 4).

In terms of the question that whether marine limestone rocks are effective source rocks, predecessors have conducted a lot of studies and discussion on the lower cut-off limit of TOC, and the criteria and methods for evaluation of hydrocarbon generation potential. It is believed that the organic facies of high-quality carbonate source rocks have three characteristics. First, they usually lack continental organic matter and detritus but are rich in algae. Second, dark laminations are generally developed because they are deposited under an anoxic environment with high salinity. Third, the TOC is generally higher than 1.5%, and the lower limit of the organic matter abundance as a source rock is not less than 0.5% [17–21]. The limestone in the Taiyuan Formation has a relatively high TOC, ranging from 0.08% to 7.96%, with an average of 1.36% (Figure 4). It has reached the lower limit of the effective source rock, belonging to a good source rock.

Since the parent material of carbonate source rock is generally oil-generation kerogen, the conversion rate of organic matter is relatively higher during the conversion of organic matter to hydrocarbon. Therefore, the residual organic carbon content is generally much lower than the original organic carbon content. Generally, for a suite of high-quality limestone source rocks, TOC content ranges from 8% to 12% at the low-medium thermal evolution stage. However, when it comes to the high thermal evolution stage,



(a) (b) (c) (d) (e) (f)

Figure 3: Continued.

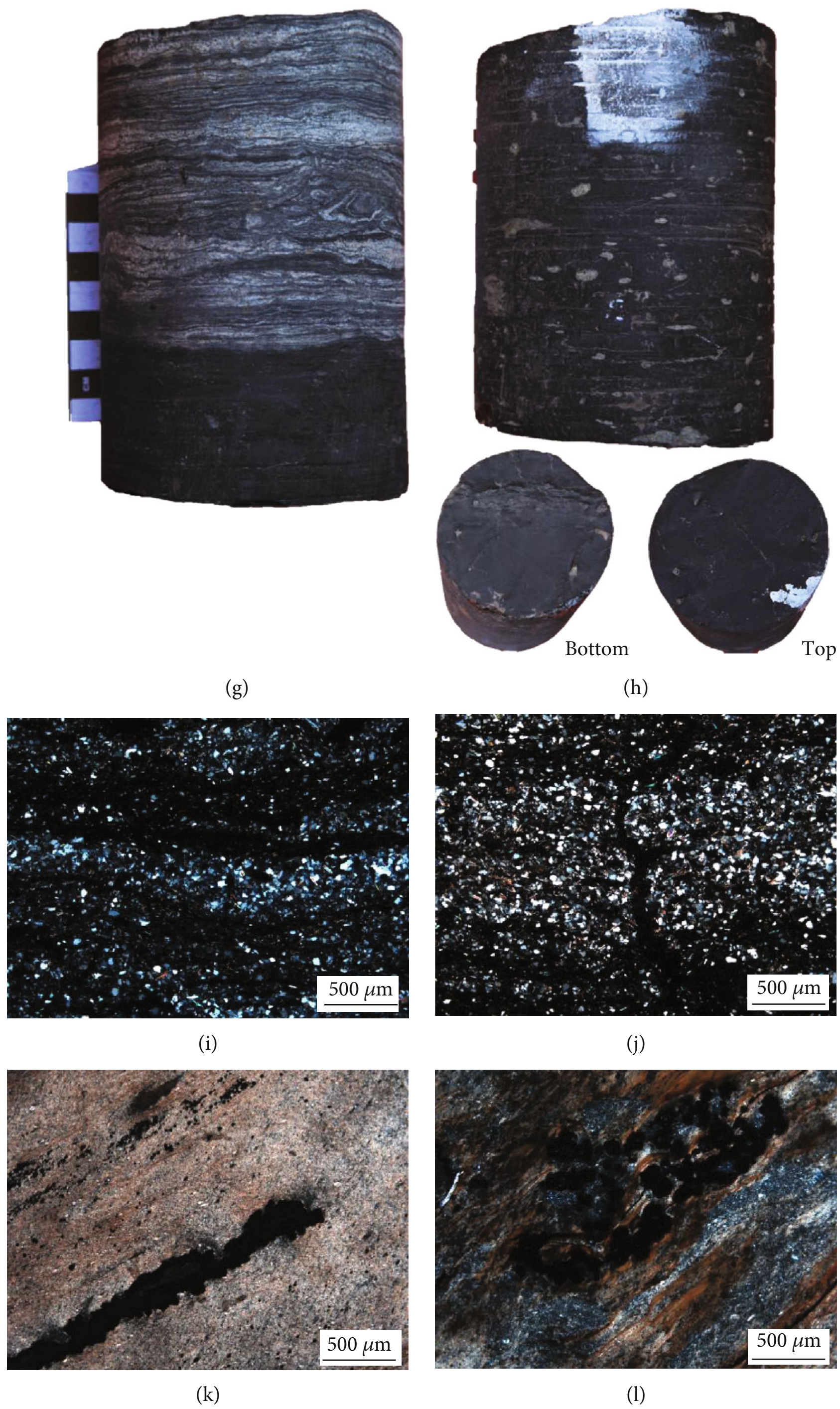


Figure 3: Examples of Taiyuan Formation limestones: (a) core of bioclastic limestone, 2172.1~2172.4 m; (b) core of limestone, 2195~2195.4 m; (c) micrograph of limestones with sea urchin fossil, 2172.2 m; (d) micrograph of limestone with bryozoan, 2172.3 m; (e) micrograph of limestone with typical stylolite structure, 2195.0 m; (f) micrograph of limestones with microfractures filled by pyrites and organic matter, 2195.1 m; and examples of Taiyuan Formation shales: (g) core of calcareous shale and calcareous siltstone, 2191.9~2192.2 m, with irregular calcareous-silty beddings with abundant bioturbations; (h) core of massive shale and its top and bottom surface, 2181.6~2181.8 m; (i) micrograph of shale with silty laminations consisting of quartz and feldspars, 2191.9 m; (j) photomicrograph of shale with silty laminations disturbed by bioturbations, 2192.0 m; (k) micrograph of shale with pyrites, 2169.2 m; (l) micrograph of shale with clustered pyrite grains.

the TOC content will drop rapidly to 1-4%. It is inferred that the source rocks with good parent material types have a more significant decline in TOC content during thermal evolution [10]. Jarvie [18] conducted a systematic analysis on the change of TOC content during the evolution process. The study results indicated that the TOC content of good

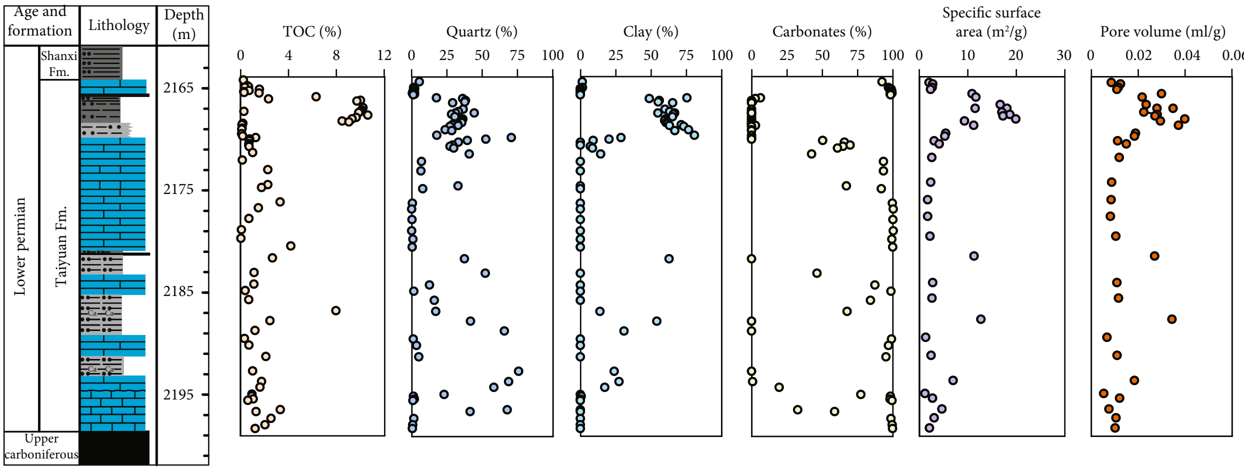


Figure 4: Vertical distribution of TOC content, mineral, and pore characteristics for Taiyuan shales and limestones.

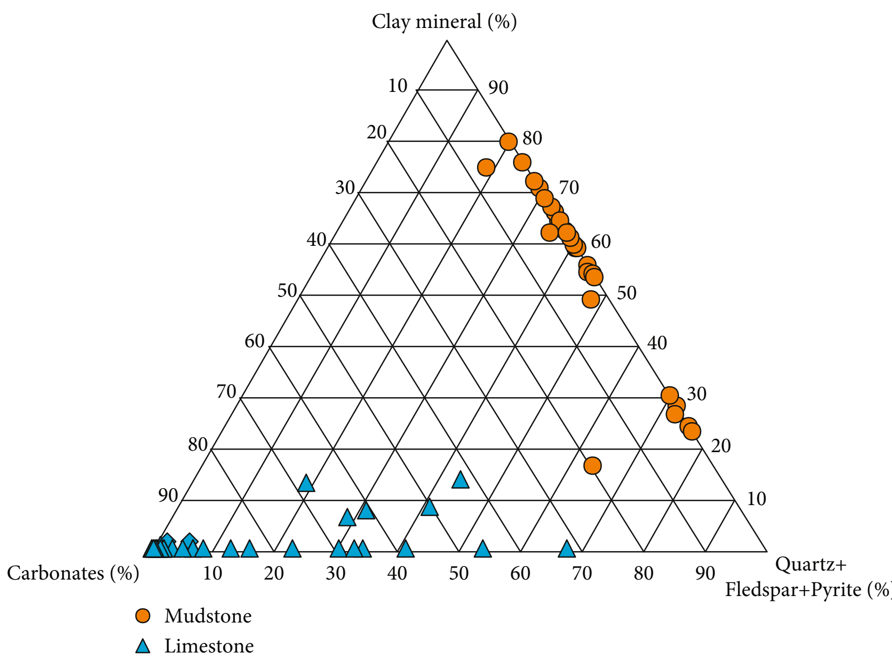


Figure 5: Ternary diagram of the mineralogical compositions of Taiyuan shales and limestones.

source rocks can be reduced by up to 80% at the high thermal evolution stage, while the TOC content of source rocks with poor organic matter types can be reduced only 20% at most. In the study area, the measured thermal evolution degree of organic matter in the Taiyuan Formation is generally higher than 2.0% (R_o), being at high to overmature thermal evolution stage. The original organic matter has gone through the entire hydrocarbon generation process. Therefore, the currently measured TOC content of the Taiyuan Formation is the residual organic carbon content, which is somewhat different from the original organic carbon content. Particularly for the oil-generation type limestone of the Taiyuan Formation, there is still a certain amount of residual organic matter, reflecting that the limestone in the Taiyuan Formation has a good hydrocarbon generation potential as a source rock.

In terms of mineral composition, the shale in the Taiyuan Formation is mainly composed of clay minerals and quartz (Figure 4). The content of clay minerals ranges from 17.2% to 80.6%, with an average value of 55.6%. The thin shale layer at the uppermost part with high TOC values is characterized by high proportion of clay minerals (Figure 4). The content of quartz ranges from 17.5% to 75.5%, with an average value of 38.9%. Some samples with low organic matter abundance are silty shale, and they have a relatively high content of quartz. The carbonate content of the limestone in the Taiyuan Formation ranges from 32.5% to 100%, with an average of 85.7%. Calcite is predominant in carbonate minerals, and its content ranges from 32.5% to 100%, with an average of 77.0%. Quartz, carbonate, pyrite, and feldspar are all brittle minerals, suggesting that the shale

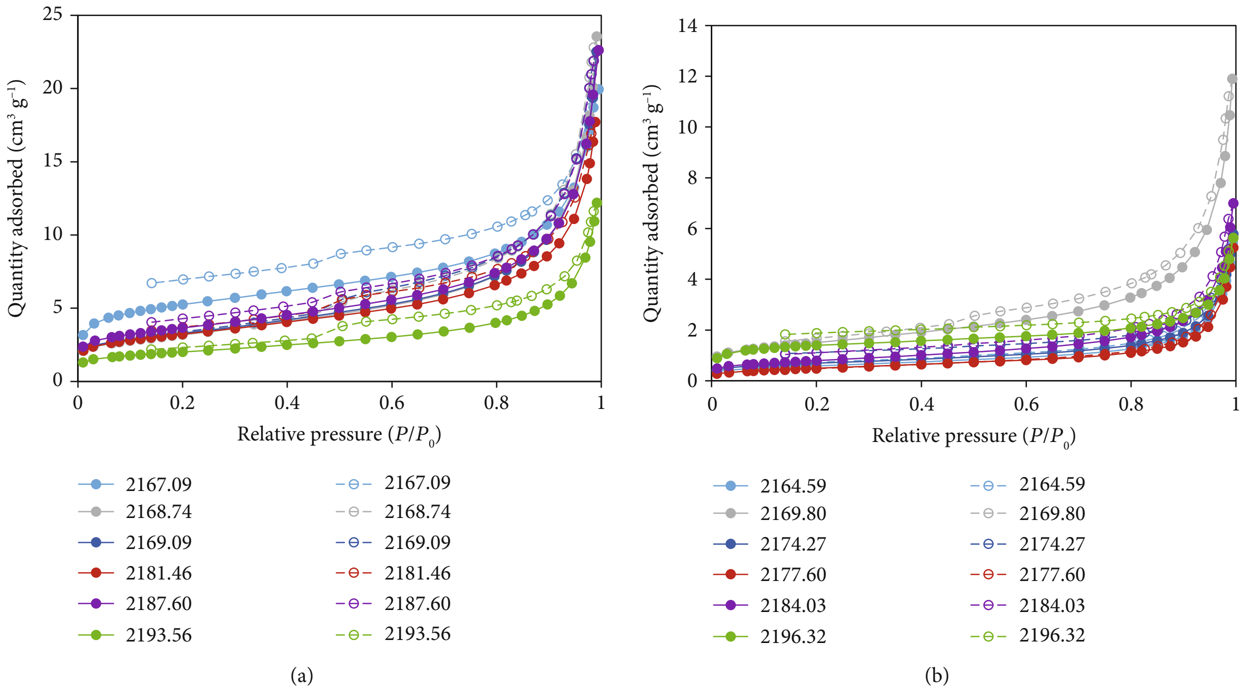


Figure 6: Isotherms of nitrogen adsorption and desorption for (a) shale and (b) limestone samples with different depths.

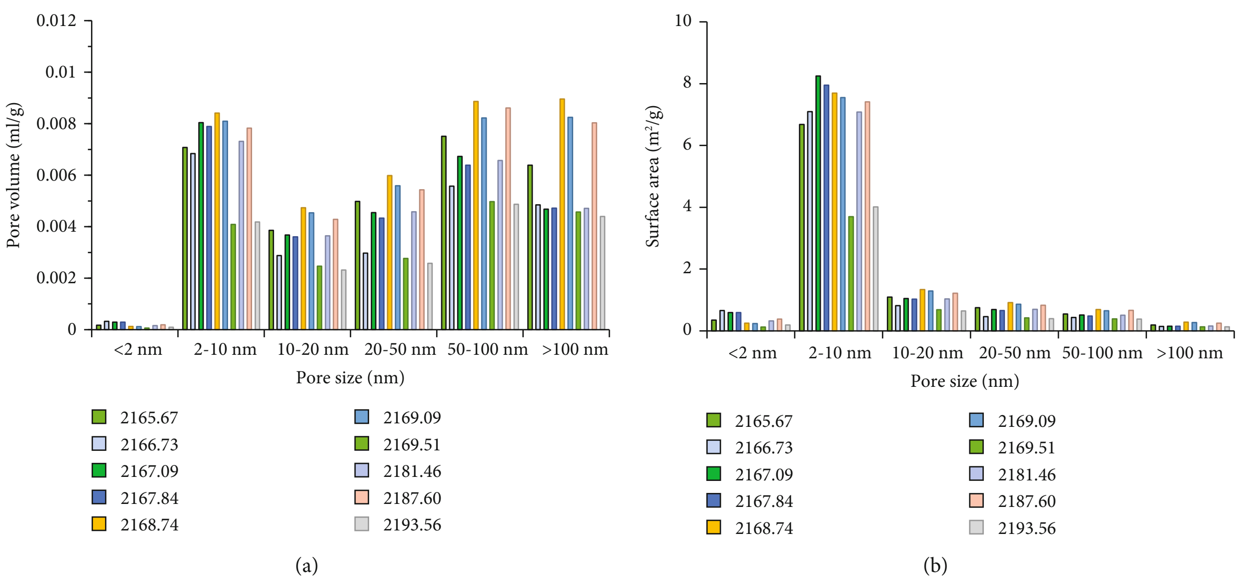


Figure 7: Cumulative pore volume (a) and pore surface area (b) of different pore diameter ranges for shale samples with different depths.

and limestone of the Taiyuan Formation contain a large number of brittle minerals (Figure 5).

4.3. Pore Structure of Lower Permian Taiyuan Shales and Limestone. The pores of tight reservoirs are generally in nanometer scale. Nanopores can provide good storage space for self-generation and self-storage oil and gas resources. Therefore, the study on nanopores is crucial for evaluation on self-generation and self-storage reservoirs. According to the applicability of different test methods on different scales of pores, CO_2 adsorption, N_2 adsorption, mercury intrusion, and other methods which can greatly improve the characterization range of micropores in tight reservoirs are generally accepted as a practical means for characterizing the size, shape, and distribution of pores in tight reservoirs [22–24]. According to the classification criteria for nanoporous reservoirs of IUPAC (International Union of Pure and Applied Chemistry), pores larger than 50 nm are defined as macropores, pores of 2-50 nm are mesopores, and pores smaller than 2 nm are micropores [25]. In a shale reservoir, the main

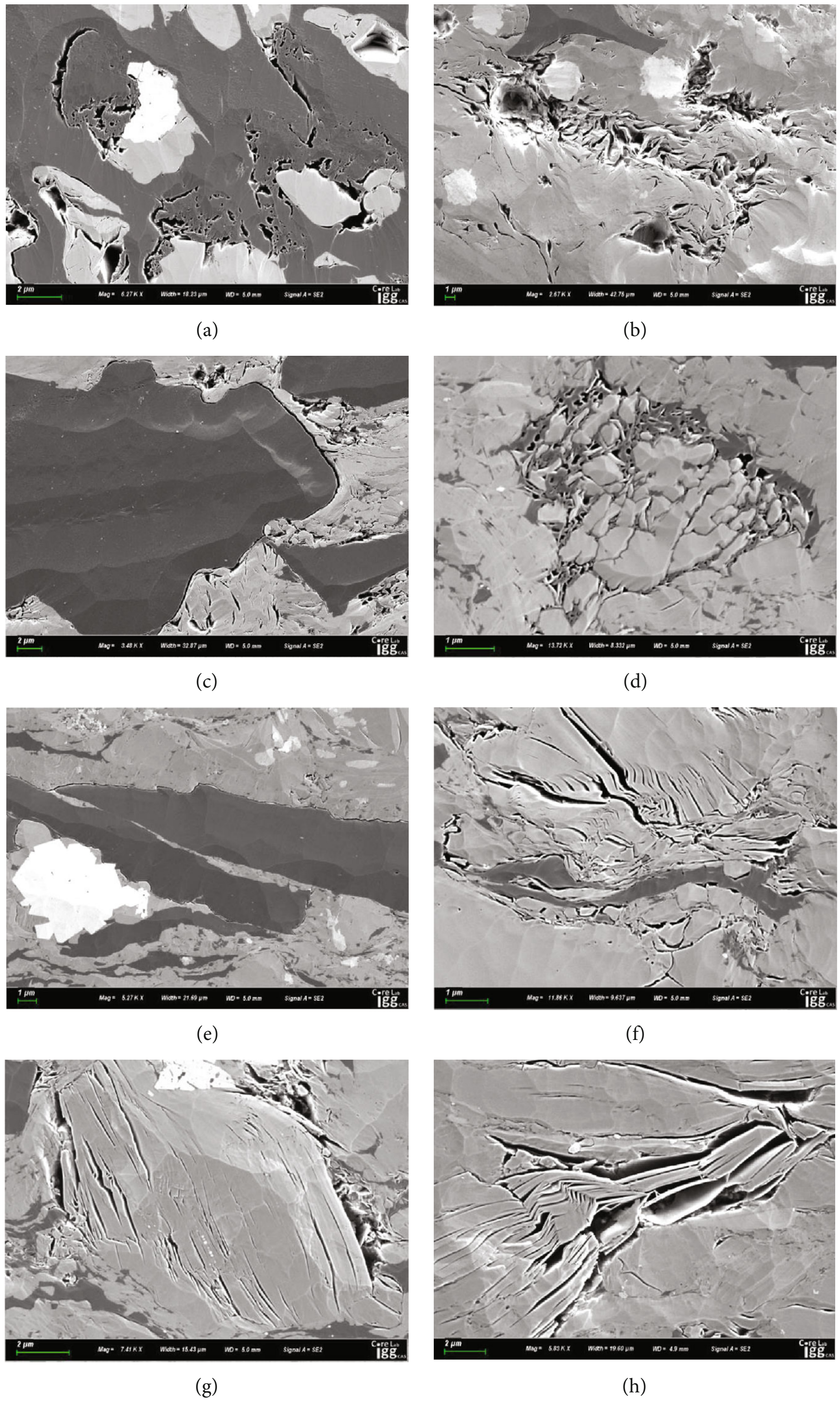
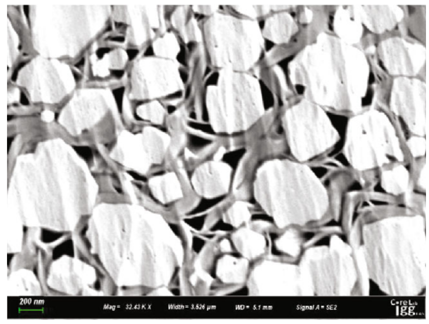


Figure 8: Continued.



(i)

Figure 8: Field emission scanning electron microscope (FE-SEM) images of shale samples. (a, b) Sample 2165.67, TOC = 6.32%, organic matter-hosted pores are developed in small part of organic matter; (c) sample 2166.73, TOC = 10.02%, organic matter-hosted pores are undeveloped, and organic matter shrinkage fractures can be found locally; (d, e) sample 2167.09, TOC = 10.0%, organic matter-hosted pores are rich (d) and undeveloped in different organic matter (e); (f) sample 2167.69, TOC = 9.64%; (g) sample 2168.13, TOC = 9.03%; (h) sample 2181.46, TOC = 2.70%; (i) sample 2193.56, TOC = 1.79%. (f)–(i) show various kinds of inorganic pores, including clay mineral interlayer fractures (f–h) and pyrite intergranular pores (i).

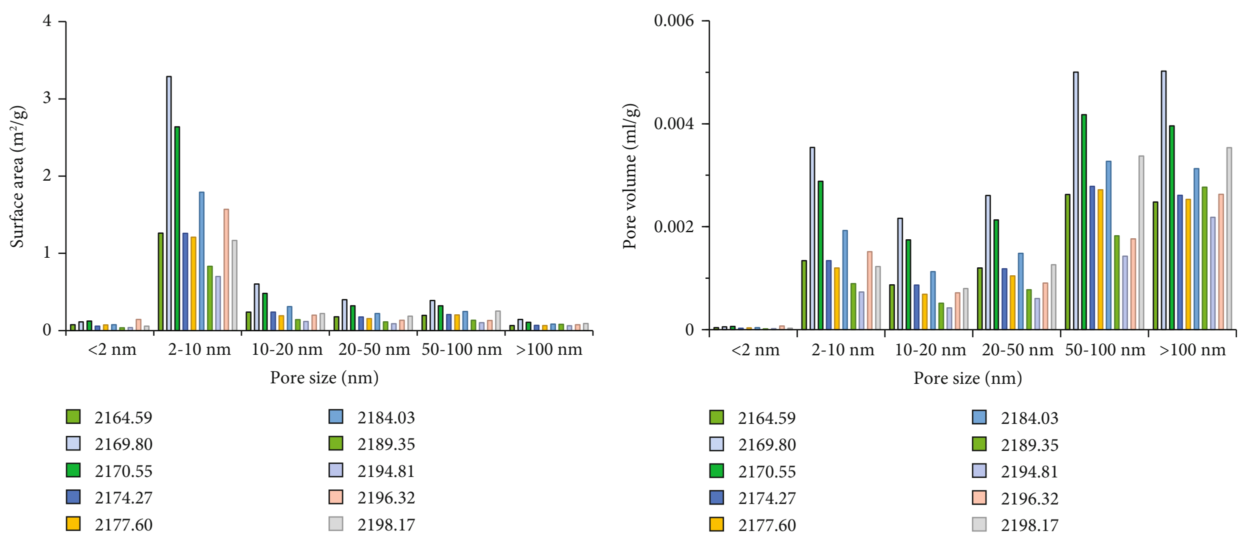
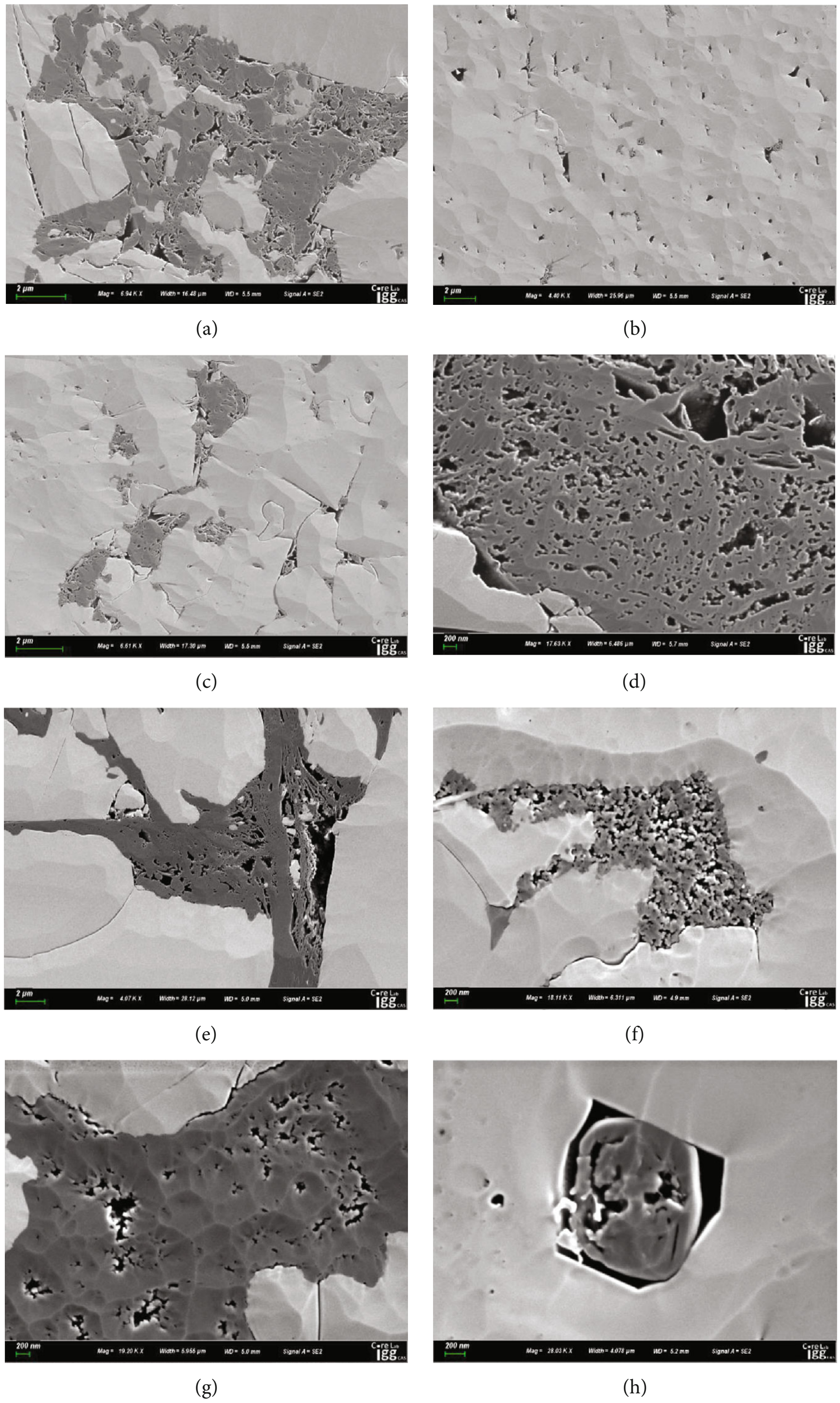


Figure 9: (a) Cumulative pore volume and (b) pore surface area of different pore diameter ranges for limestone samples with different depths.

range of pore size is between 5 and 100 nm, and pores of about 10 nm are the most abundant. Generally, pores smaller than 50 nm are dominated in shales [26, 27].

The morphology of the "adsorption curve" formed by the relative pressure change during the low-temperature nitrogen adsorption and desorption process of shale is mainly affected by the size and morphology of the micro-nano pores. Therefore, the pore structure characteristics of shale can be identified based on the morphological characteristics of the desorption curve. Figure 6 shows the nitrogen adsorption-desorption curves of shale and limestone of the Taiyuan Formation. In the low-pressure section ($P/P_0 < 0.2$), the adsorption curves of shale and limestone both increased slowly, indicating that nitrogen is adsorbed in a monolayer on the surface of the pores of the reservoir. In the middle pressure section ($0.2 < P/P_0 < 0.8$), the adsorption capacity of shale samples increased slowly with the increase of relative pressure, and the adsorption curve is approximately linear, indicating that nitrogen is adsorbed in multimolecular layers on the surface of the pores of the reservoir. At this stage, the adsorption curve of limestone rocks is relatively gentle. In the high-pressure section ($0.8 < P/P_0 < 1$), the adsorption curves of shale and limestone samples showed a rapid rise. The slope of the adsorption curve of most samples increases along with the equilibrium pressure approaching saturation, but the samples do not appear to be in adsorption saturation, indicating that the macropores in the samples are larger than 50 nm. The nitrogen adsorption capacity of shale samples is significantly higher than that of limestone samples, suggesting that shales have more pores than limestone, and limestone samples are relatively tighter.

According to the characteristics of pore development parameters, such as pore volume, pore specific surface area, and nanopore microscopic characteristics, it is found that



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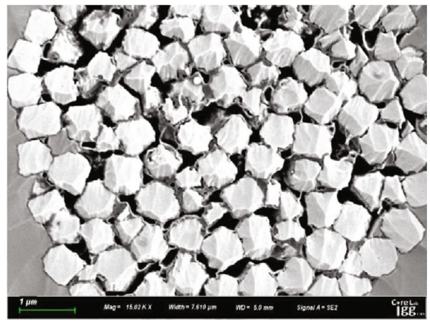

(i)

FIGURE 10: Field emission scanning electron microscope (FE-SEM) images of limestone samples. The type of pores is relatively simple for limestone samples, with mainly (a–h) organic matter-hosted pores, (b, c, h) carbonate dissolution pores, and (i) pyrite intergranular pores. (a, b) Sample 2164.59; (c) sample 2164.73; (d, e) sample 2165.06; (f) sample 2185.55; (g) sample 2189.35; (h) sample 2195.28; (i) sample 2198.17.

the pore volume of shale samples is mainly distributed in 0.0184-0.0398 ml/g, with an average of 0.028 ml/g, and it mainly comes from pores of 2-10 nm and pore larger than 50 nm (Figure 7), which provides good primary storage space for free gas. The specific surface area of the Taiyuan shales is mainly distributed in 5.5-19.93 m^2/g, with an average of 13.28 m^2/g, and nanopores with the size of 2-10 nm contribute most to the specific surface area. Figure 8 shows the FE-SEM observation results on microscopic pores in the Taiyuan shales. Organic matter-hosted pores are generally undeveloped (Figures 8(a)–8(e)), and only can be found in local areas (Figures 8(a) and 8(d)). The shape of organic matter-hosted pores is round or irregular ellipse, and the surface porosity is low. The type of pores in shales is various and mainly includes mineral intergranular pores (Figures 8(b) and 8(f)), clay mineral interlayer fractures (Figures 8(f)–8(h)), and pyrite intergranular pores (Figure 8(i)). In addition, organic matter shrinkage fractures can be found locally (Figure 8(c)).

The pore volume and pore-specific surface area of limestone samples of the Taiyuan Formation are lower than those of the Taiyuan shales. The pore volume is mainly distributed in 0.0054-0.0184 ml/g, with an average of 0.0106 ml/g, and the pore-specific surface area is mainly distributed in 1.22-5.33 m^2/g, g, with an average of 2.72 m^2/g. The contribution of different sizes of pores to pore volume and the specific area is similar to those of the Taiyuan shales, but the actual value of pore volume and specific surface area under different pore sizes is significantly lower than those of shale samples (Figure 9). SEM observation results indicated that the limestone of the Taiyuan Formation is very tight, with relatively poor developed pores. Compared with shale samples, the type of pores is relatively simple (Figure 10), with mainly organic matter-hosted pores (Figures 10(a)–10(h)) and carbonate dissolution pores (Figures 10(b), 10(c), and 10(h)). In addition, intergranular pores between pyrite particles can be found locally (Figure 10(i)). Unlike the shale samples, the limestone samples of the Taiyuan Formation have very well-developed organic matter-hosted pores and very high organic matter porosity. Porosity develops in both massive organic matter and organic matter filled in dissolved pores (Figure 10(h)) or intergranular pyrite (Figure 10(i)).

The correlation diagrams of pore parameters with the component content of shale (Figure 11) indicate that the pore volume and pore-specific surface area of Taiyuan shales are mainly related to the content of clay minerals (Figures 11(b) and 11(c)), and there is no obvious correlation between TOC and quartz mineral content. These statistic results are consistent with the qualitative observation results of the SEM, further indicating that the pore types of the Taiyuan shales are dominated by intergranular pores of clay minerals. In terms of the limestone, there is no significant relationship when the pore volume and specific surface area are correlated with the abundance of organic matter and mineral content. Only the SEM observation results suggest that organic matter-hosted pores are dominated in limestone. Therefore, it is concluded that the enrichment and development of nanopores are largely affected by the characteristics of organic matter.

4.4. Formation Mechanism for Pores and Significance for Gas Potential. According to the formation mechanism for pores, the organic matter-hosted pores can be classified into two types. One is the pores inherited from the parent source organic matter. This type of pores refers to the pores that the residual biological pore structure of the original organic matter formed during sedimentation and preserved from burial and diagenetic compaction, and it has no indicative significance for hydrocarbon generation of organic matter [28, 29]. The other is the pores produced by the conversion of organic matter into oil and gas during the hydrocarbon generation and evolution process. The formation of this type of pore generally occurs along with the increase of organic matter maturity, and pyrolysis, cracking of kerogen or liquid hydrocarbon [29–33]. Hydrocarbon-generation organic matter-hosted pores are widely developed in many sets of organic-rich shales such as Barnett, Woodford, and Longmaxi formations [23, 28, 29, 34–36], but they are rarely found in immature or low-mature samples. The organic matter-hosted pores of hydrocarbon generation are not only controlled by the degree of thermal evolution but also affected by organic matter type, that is, microscopic kerogen components (saprolite, exinite, vitrinite, and inertinite). At the hydrocarbon generation stage, humic kerogen is

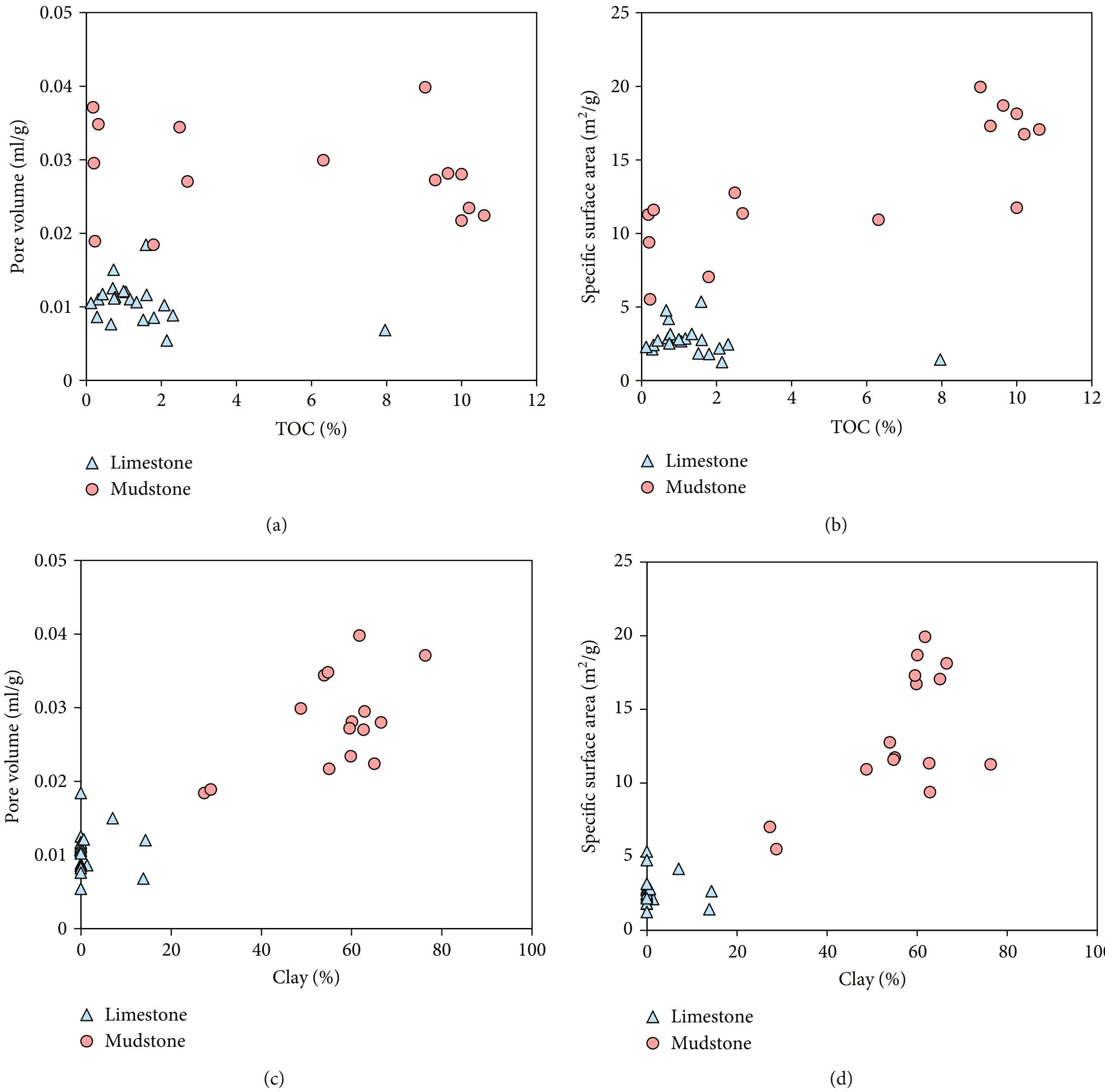

Figure 11: Continued.

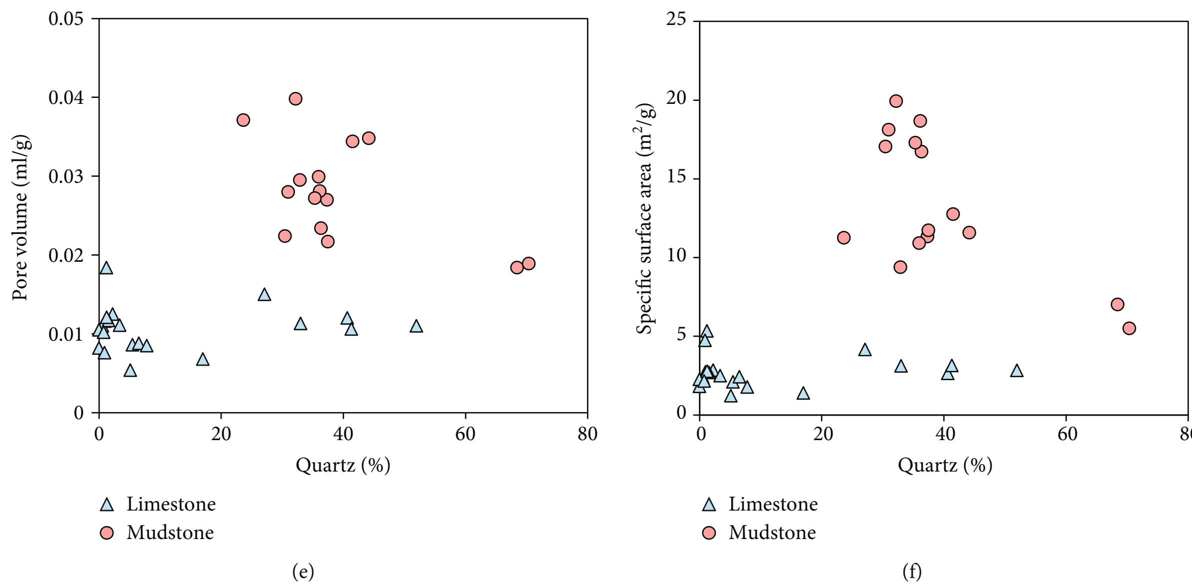

Figure 11: The correlation between organic matter abundance, mineral composition, and pore parameters.

dominated by kerogen demethylation to generate methane gas, and almost no organic matter-hosted pores form during the thermal evolution process [37]. The sapropel-type kerogen is more prone to generate oil, with a good oil-generation capacity. During the oil generation window period, a large number of liquid hydrocarbons were generated and preserved in situ and then being cracked and converted into gaseous hydrocarbons at the gas window stage, leading to a large number of organic matter-hosted pores in this process [38]. Therefore, for type I and type II kerogen, the development of organic matter-hosted pores is an important indicator for hydrocarbon generation and conversion, as well as the storage and preservation space.

The shales in the Taiyuan Formation were mainly deposited in tidal flat-marsh and lagoon environments and generally interbedded with coal. As a result, the organic matter is more likely to be gas-generation kerogen. It has been proved that the Permian Taiyuan Formation and the Shanxi Formation coal-measure strata are the gas source rocks of multiple conventional gas reservoirs in the Paleozoic in the Ordos Basin. The gaseous hydrocarbons are mainly generated by direct cracking of kerogen. Therefore, organic matter-hosted pores are not developed in large quantities. The shale in the Taiyuan Formation has high TOC, with various types of pores, such as intergranular pores and interlayer fractures of clay minerals. Therefore, they had good storage capacity and provided good space for gas preservation. The Taiyuan limestone has obviously more developed organic matter-hosted pores, which are similar to the Barnett and Longmaxi shale. The surface porosity of organic matter in the Taiyuan Formation is generally high. According to SEM, the organic matter-hosted pores are round or elliptical, which is a typical characteristic of hydrocarbon-generation organic matter-hosted pores, indicating that the organic matter has gone through the oil-generation window, producing a large number of liquid hydrocarbons, which were then cracked into a large number of gaseous hydrocarbon products at a higher maturity stage. The Taiyuan limestone has relatively high organic matter abundance and well-developed organic matter-hosted pores. Although it has a relatively tight matrix and poorly developed pores, the carbonate minerals are brittle and susceptible to dissolution by acidic fluids, thus forming an ideal pore network during the fracturing process. In summary, a collaborative development of coal-bearing shale gas and tight limestone gas in the Taiyuan Formation can have good resource prospect.

5. Conclusions

In this study, the organic matter characteristics, mineral composition, and pore development characteristics of the shale and limestone in the Taiyuan Formation have been studied to explore the hydrocarbon generation potential of the target strata. In addition, the pore types and development degree of organic matter-hosted pores in the shale and limestone were compared, and the pore formation mechanisms in different lithological reservoirs of the Taiyuan Formation were also studied. The conclusions are as follows:

(1) Interbedded shale and limestone are well developed in the Taiyuan Formation. The organic matter abundance of shale in the Taiyuan Formation is relatively high, ranging from 0.14% to 26.6%, with an average of 5.38%. The organic matter abundance of the limestone ranges from 0.08% to 7.96%, with an average of 1.36%. Overall, the Taiyuan Formation has reached the high to overmature thermal evolution stage. For the oil-generation limestone in the Taiyuan Formation in particular, the residual organic carbon content is still high, reflecting the relatively high hydrocarbon generation potential of the limestone in the Taiyuan Formation as a source rock

(2) The shale in the Taiyuan Formation has well-developed pores, with relatively high pore volume and specific surface area. There are various pore types, mainly mineral intergranular pores and clay mineral interlayer fractures. The pore development degree is affected by the abundance of clay minerals to a certain extent, and organic matter-hosted pores are poorly developed. The Taiyuan limestone is relatively tight, with lower pore volume, specific surface area, and higher organic matter surface porosity than those of shale. Organic matter-hosted pores and dissolution pores of carbonate minerals are the main pore types in the limestone

(3) In the Taiyuan Formation, the shale and limestone are different in the development of the organic pores. The organic matter in the shale is gas-prone kerogen. The gaseous hydrocarbon was mainly generated by direct cracking of kerogen in shale. Therefore, the organic matter-hosted pores were not developed in large quantities. In Taiyuan limestone, the kerogen is an oil-generation type. The organic matter has gone through the oil generation window. Therefore, a large number of liquid hydrocarbons were produced and were cracked into a large number of gaseous hydrocarbons at the higher thermal evolution stage. During this process, organic matter-hosted pores were produced in large quantities

Data Availability

We can also make data available on request through the authors ourselves. Please contact the first author to request the data (zhangleifu@petrochina.com.cn).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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