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Diagenesis and Pore Formation Evolution of Continental Shale in the Da'anzhai Lower Jurassic Section in the Sichuan Basin

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Abstract: As an unconventional oil and gas reservoir, the diagenesis and evolution of continental shale controls the formation and occurrence of inorganic and organic pores. In order to quantitatively characterize the pore characteristics of a continental shale reservoir and their influence on the evolution of the diagenesis stage, the characteristics of organic and inorganic pore types of continental shale in the Da'anzhai section of the lower Jurassic Ziliujing Formation were identified by means of X-ray diffraction mineral composition analysis and argon ion polishing scanning electron microscope measurements and observations, and the influence control of the diagenesis stage on the pore development of the continental shale reservoir and its control were clarified. The results show the following: ① The organic matter pores in continental shale are developed in large quantities, including organic matter pores in the mineral asphalt matrix and organic matter pores in the kerogen; the pore types of inorganic minerals are very rich, the main pore types are linear pores between clay minerals, intergranular (intergranular) pores, and intragranular corrosion pores, and microcracks are also developed. ② When affected by compaction diagenesis, the inorganic pores of continental shale decrease with an increase in the burial depth and diagenesis degree. ③ The burial depth of continental shale is 2000–3000 m in the middle of diagenetic stage A, and a large number of organic matter pores and dissolved inorganic pores develop at this depth, meaning that the total porosity of shale increases significantly. The burial depth of continental shale is 3000–4000 m at diagenetic stage B, where kaolinite and other clay minerals are dehydrated and converted into illite, the brittleness of shale is increased, and the interior of the shale is subject to external stress, causing microcracks to form. In the late diagenetic stage, when the buried depth of the continental shale is more than 4000 m, the organic matter is subject to secondary cracking and hydrocarbon generation, the organic pores of shale increase in number again, and the inorganic pores decrease in number due to compaction. In conclusion, we found that the burial depth is the main control factor for the development of pores and microfractures in continental shale reservoirs; diagenesis caused by burial depth is the main factor affecting the development of pores and microfractures in continental shale reservoirs; and the shale burial depth in this case is more than 3500 m, which is in the middle of diagenetic stage B. Inorganic porosity in shale is reduced, and the number of microfractures is increased. When the shale is buried more than 4000 m deep in the late diagenetic stage, the thermal evolution of organic matter in shale is high, and methane gas is generated in large quantities, which is conducive to the formation and development of organic matter pores in continental shale.

Keywords: continental shale; diagenesis; organic–inorganic pores; pore evolution

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Citation: Fu, Q.; Hu, Z.; Qin, T.; Feng, D.; Yang, B.; Zhu, Z.; Xing, L. Diagenesis and Pore Formation Evolution of Continental Shale in the Da'anzhai Lower Jurassic Section in the Sichuan Basin. *Minerals* **2023**, *13*, 535. https://doi.org/10.3390/min13040535

Academic Editor: Georgia Pe-Piper

Received: 2 March 2023
Revised: 31 March 2023
Accepted: 5 April 2023
Published: 11 April 2023

1. Introduction

The exploration and development of shale gas are considered to be a revolution in the field of energy around the world, and they are the leading edge of and hot spots for international geoscience research. The difference between the pore types of shale reservoirs and conventional clastic reservoirs is that shale reservoirs develop both inorganic pores and abundant organic pores [1–3]. The formation and evolution of shale pores is a very complex geochemical process which is controlled by various geological and geochemical conditions such as sedimentary organic matter, sedimentary environment, burial and thermal evolution, and diagenetic environment [4–6]. The occurrence of shale pores and the type, shape, size, and connectivity of nanoscale pores play a key role in shale gas enrichment. Therefore, it is of great significance to determine the evolution mechanism and development model of shale pores during diagenesis in order to predict the formation of shale reservoir pores and the distribution of enrichment sweet spots.

Continental shale is an important hydrocarbon geological feature of China's hydrocarbon-bearing basins. With the discovery of shale hydrocarbons in Songliao Basin, Bohai Bay Basin, Ordos Basin, and other continental shales, especially the Da'anzhai shale of the Lower Jurassic Ziliujing Formation in the Fuling area of the Sichuan Basin, commercial hydrocarbon flow has been established [7,8]. Exploration has confirmed that continental shale in the Da'anzhai section of the Jurassic Ziliujing Formation has a large thickness, a wide distribution range, good preservation conditions, great resource potential, and good geological conditions for developing shale hydrocarbon reservoirs [9]. However, due to the strong heterogeneity of continental shale reservoirs and the uneven natural gas production in each well, the research demand for continental shale reservoirs is increasing.

In this study, we discuss the diagenesis evolution and pore evolution of the continental shale in the Da'anzhai section of the Lower Jurassic Ziliujing Formation in the Fuling area, Sichuan Basin. Core X-ray diffraction mineral composition analysis and argon ion polishing scanning electron microscope photo observations were utilized. The pore-type characterization of continental shale is solved, the formation and development evolution process of continental shale pores in different diagenesis stages are clarified, and the geological conditions and main controlling factors of continental shale pore formation are revealed.

2. Regional Geologic Setting

The Sichuan Basin has undergone several evolutionary stages, such as the early Paleozoic craton depression stage, the late Paleozoic craton rift stage, and the Mesozoic–Cenozoic foreland depression stage, forming a NE–SW-trending, diamond-shaped basin tectonic framework. It is surrounded by the western Longmen Mountain orogenic belt and the Songpan–Ganzi fold system, the northern Micang Mountain Daba Mountain fault-fold belt, the eastern Xiang'exi structural belt, and the southern Emei–Liangshan fault-fold belt (Figure 1). The Fuling area in south-eastern Sichuan is located in the southeast of the Sichuan Basin, bordering the Qiyao Mountain to the south-east and the Daba Mountain–Xuefeng Mountain tectonic composite zone to the north. The complex structural pattern has led to the influence of multiple orogenic belts in the Fuling area. The thickness of the strata is uneven, and there are also phenomena such as erosion and uplift [10].

The Jurassic layer in the Sichuan Basin is mainly a set of delta-inland lake facies freshwater deposits dominated by clastic rocks with shell limestone, and the residual thickness is generally 2000–3000 m. The sedimentary thickness of the lower Jurassic Ziliujing Formation is generally 300–500 m. According to lithology, it can be divided into four sections: the Zhenzhuchong Section, the Dongyuemiao Section, the Ma'anshan Section, and the Da'anzhai section, from bottom to top, respectively. The sedimentary environment of the Da'anzhai section involves a shore-shallow lake and a deep lake, mainly comprising dark gray and gray-black mudstone, shale and gray marlstone, siltstone, interbedded fine sandstone, and locally developing light gray shell limestone. The Da'anzhai section can be divided into three sub-sections from top to bottom, namely, the first sub-section, the second sub-section, and the third sub-section, respectively. The strata have three obvious parts and generally have the lithologic combination characteristics of "limestone + shale + limestone". The sedimentary period of the second sub-member of Da'anzhai is the lake flooding period. The sedimentary area in the middle of the lake basin is far away from the provenance and forms a large range of stable semi-deep lake to deep lake facies, a thin layer of clastic limestone, and a thick layer of organic-rich laminated black shale with a thickness of 37–76 m. The frequency and content of the upward thin layer of the clastic limestone interlayer also gradually decreases. The organic carbon content of continental shale in the Da'anzhai section is relatively high, with Corg representing between 0.5% and 4.27% of the carbon content, with an average of 1.28%. The organic matter type is mainly II1-II2, and the organic matter Ro% is mainly distributed between 0.8 and 1.5, which is in the mature–high mature stage. The burial depth span of continental shale in the Da'anzhai section is large (2200–5000 m), with many wells and abundant cores, which provide good geological conditions for conducting research on the pores and diagenetic evolution of continental shale.

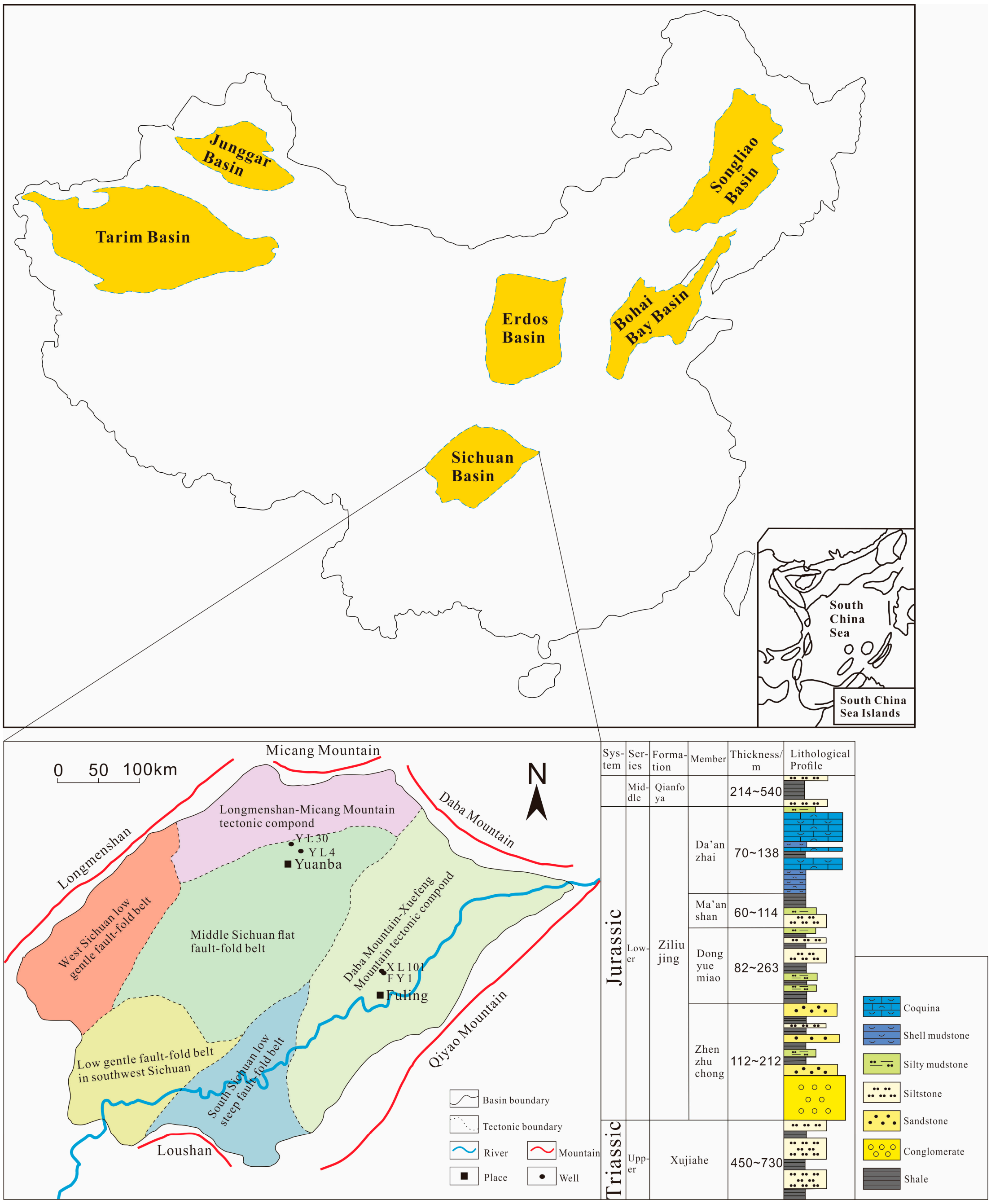

Figure 1. Regional structural map of the Sichuan Basin and a columnar section of the Jurassic Ziliujing Formation.

3. Characteristics of Mineral Assemblages for Continental Shale

The shale in the Da'anzhai section of the Lower Jurassic Ziliujing Formation in the Sichuan Basin mainly comprises gray silty clay rock and silty clay rock. The type and relative content of clay minerals were determined via the X-ray diffraction of clay minerals in cores (X'Pert Pro X-ray diffractometer produced by PANalytical Company). The data on quartz, feldspar, calcite, total clay, and pyrite were obtained by analyzing the composition of clay rocks (JXA-8230 electron probe from Japan). The transformation characteristics of authigenic clay minerals in shale at different diagenesis stages were studied. The changes in the mineral structure and chemical composition (Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Si^{2+}) during the transformation from montmorillonite or illite–montmorillonite mixed layers to chlorite (illite) were analyzed, and the diagenetic material basis was established by restoring the pore formation and the filling of continental shale that was conducive to pore formation and enrichment.

The mineral composition of the shale in the four wells that have encountered shale is basically the same. However, due to the large burial depth of the shale in Well YL4 and Well YL30, the illite content in the shale is higher than that in Well FY1 and Well XL101, while the change in chlorite content is just the opposite. Taking the analysis of the mineral composition of shale from Well FY1 as an example, this paper expounds the following.

The mineral composition of continental shale in the Da'anzhai section of well FY1 is complex. Inorganic minerals are mainly composed of clastic minerals and clay minerals. Detrital minerals are mainly composed of quartz, feldspar, carbonate minerals, and pyrite. According to the mineral composition data (Figure 2), the clay mineral content is the highest, ranging from 42.5% to 68.3%, with an average of 54.3%, followed by quartz, which had a content distribution range of 21.5%–40.3%, with an average of 29.7%. The calcite content was high, with an average content of 12.14%, and the plagioclase content was relatively low, with an average of 3.01%. Other minerals' contents comprised less than 1% of the total. However, the occurrence of a small amount of pyrite in continental shale indicates that the formation has experienced a certain period of hydrostatic anoxic reduction environment, which indicates that the sedimentary environment of continental shale in the Da'anzhai section is an anoxic reduction environment.

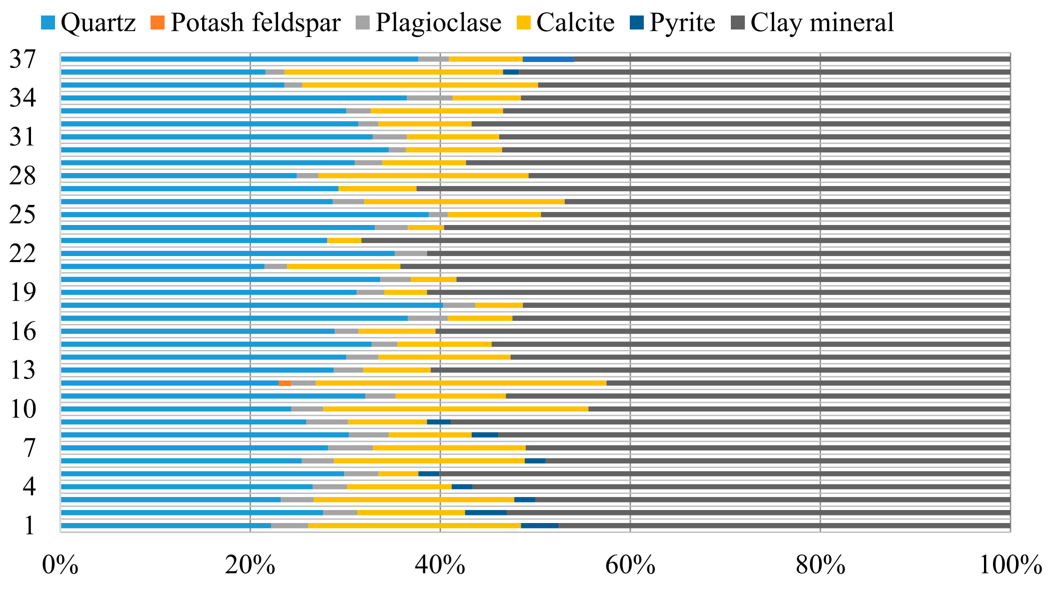

Figure 2. The distribution of shale mineral composition in the Da'anzhai section, FY1 Well.

The clay mineral composition usually reflects the diagenetic evolution stage and sedimentary environment of shale, which is of great significance to the study of shale adsorption capacity and gas content [11]. The statistical analysis of the clay mineral composition of the Da'anzhai section (Figure 3) showed that the clay minerals of the continental shale in the Da'anzhai section mainly comprised an illite–montmorillonite mixed layer, along with illite, chlorite, and kaolinite. The montmorillonite content was low. The illite–montmorillonite mixed layer comprised between 31% and 66% of the total, with the average being 52%; the relative content of illite was between 10% and 38%, with an average content of 22%. The average relative content of chlorite was 13%. The average relative content of kaolinite was 12%. The content of illite–montmorillonite mixed layer and illite in the clay minerals of Da'anzhai shale was dominant. The content of the illite–montmorillonite mixed layer was large, which provided more adsorption sites and was conducive to the occurrence of adsorbed gas. The high content of illite indicated that the Da'anzhai shale in the Fuling area had entered the late stage of intermediate diagenesis.

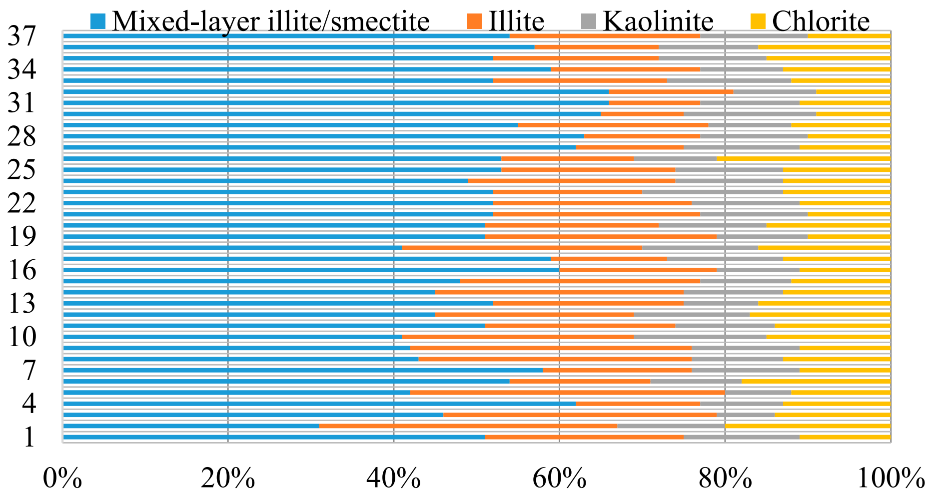

Figure 3. Histogram of the clay mineral composition of Da'anzhai shale, FY1 Well.

4. Pore Characteristics, Diagenetic Evolution, and Pore Evolution of Continental Shale

In order to study the pore characteristics of continental shale, a Leica EM TIC020 triple ion beam milling machine was used to polish cross-sections of the small cylinders of the core collected from different wells at different depths, and a flat surface was obtained. A FEI Nova Nano-SEM 430 field emission scanning electron microscope was used to scan and image the various types of pores and the correlation between organic matter and inorganic mineral particles under an acceleration voltage of 10–15 keV and a working distance of 4–5 mm. Field emission scanning electron microscope imaging after argon ion polishing can characterize the pore characteristics of continental shale well and can also distinguish the irregular morphology caused by different surface hardnesses of continental shale during mechanical polishing and the false pores caused by sample fracture on fresh sections. The obtained images mainly observe the pores in the samples so as to obtain the pore shape, size and distribution, and particle distribution [12].

4.1. Pore Types and Characteristics of Shale in the Da'anzhai Section

4.1.1. Inorganic Mineral Pores

There are two main formation mechanisms of shale inorganic mineral pores: one is the residual pores after the compaction and cementation of early intergranular pores; the second is the secondary dissolution pores formed by later dissolution. In addition, some pores can also be produced during the process of mineral diagenesis and alteration [13–15]. An argon ion polishing–scanning electron microscope observation and analysis showed that the inorganic mineral pore types of shale in the Da'anzhai section were rich, and linear pores, intergranular pores, and dissolution pores between clay minerals had been developed. Among them, linear pores between clay minerals were the most developed, followed by intergranular pores, and local dissolution pores were developed.

① Linear pores between clay minerals

Argon ion polishing–scanning electron microscopy observation and analysis showed that a large number of linear micro-pores between clay minerals were widely developed in the shale of the Da'anzhai section of the Ziliujing Formation (Figure 4a), and they were mainly developed between clay mineral aggregates. The lengths and widths were different, and some were completely filled and partially filled with bitumen. This kind of pore was mainly formed by the early clay mineral pore shrinking linearly with an increase in burial depth under the action of strong compaction. Such linear clay inter-mineral pores were mainly developed between illite lamellae and between illite and mineral particles, and were partially filled with a small amount of asphalt. The pore length was hundreds of nanometers to 5 microns, and the width was several nanometers to hundreds of nanometers.

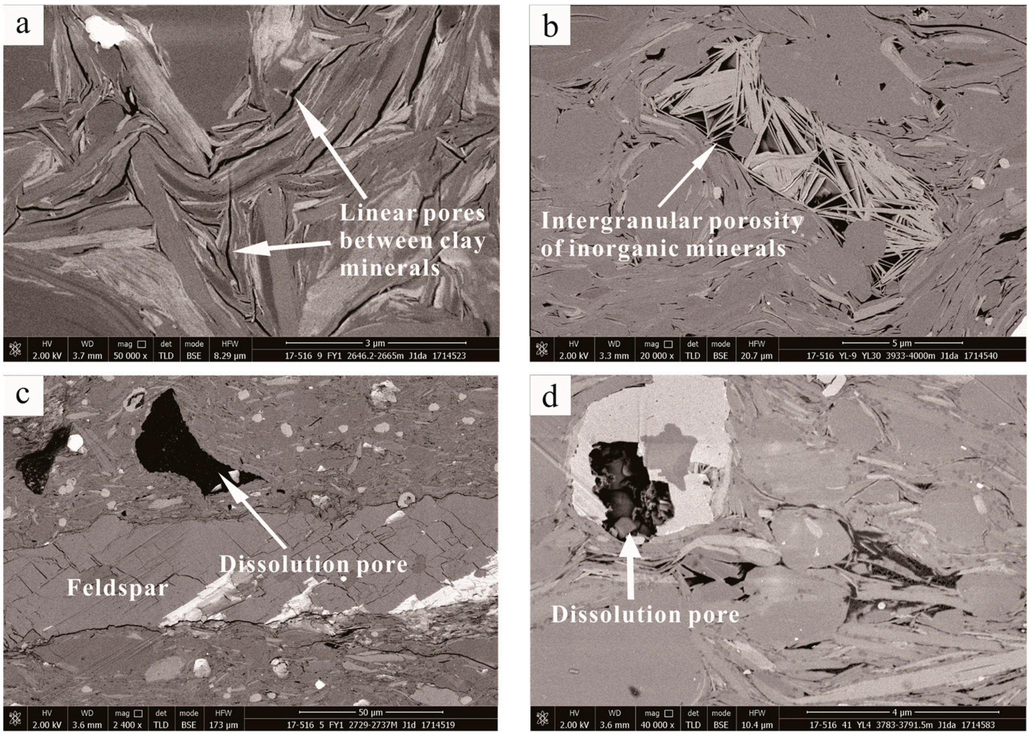

Figure 4. Microscopic characteristics of inorganic mineral pores in Da'anzhai shale by scanning electron microscopy. (**a**) Linear pores between clay minerals, Well FY1, 2646.2 m, Da'anzhai section. (**b**) Inorganic mineral intergranular pores, Well FY1, 3933 m, Da'anzhai section. (**c**) Nanoscale intragranular dissolution pores, Well FY1, 2737 m, Da'anzhai section. (**d**) Micron-scale intragranular dissolution pores, Well YL4, 3783 m, Da'anzhai section.

② Intergranular pores

The intergranular pores in the shale mainly refer to the pore space between the clastic particles such as quartz and feldspar in the shale and carbonate minerals, pyrite clusters, clay minerals (such as illite, chlorite, etc.). The diameter of these pores is usually several nanometers to several hundred microns. Residual primary pores between particles after diagenetic compaction are one of the main reservoir space types of a shale reservoir. Observation and analysis using argon ion polishing instrument–scanning electron microscopy showed that the intergranular pores in the shale of the Ziliujing Formation in the Fuling area of the Sichuan Basin had various shapes and a large pore size range, and the pore diameter ranged from several nanometers to hundreds of nanometers (Figure 4b). They were mainly developed between clay minerals and quartz particles or feldspar, between clay mineral wafers, and between local quartz particles with a certain level of pore connectivity. Most of these pores are filled with clay minerals or organic matter particles during the later burial diagenesis, and only some intergranular pores with relatively small pore sizes remain.

③ Intragranular dissolution pores

Dissolution pores are very common in Da'anzhai shale in the Fuling area of the Sichuan Basin. During the pyrolysis of organic matter, a large number of organic acids are generated. These organic acids can not only dissolve carbonate, but also dissolve aluminosilicate minerals, forming a large number of nano-scale intragranular dissolution pores in skeleton minerals such as quartz and feldspar (Figure 4c). A single mineral particle could also be seen under the microscope to be severely corroded, forming a single micron-sized intragranular dissolution pore (Figure 4d). These kinds of pores are involved in calcite grains or are formed via the dissolution of the shell calcite, which is irregular, polygonal, or needle-shaped, and the pore size is several nanometers to several hundred nanometers.

4.1.2. Organic Matter Pores

Organic pores are an important part of the shale pore system in the Da'anzhai section of the Fuling area, Sichuan Basin. The shape is mainly ellipsoidal and irregular, and the diameter varies greatly. According to the occurrence form of organic matter in shale, organic pores can be divided into three categories: organic pores in kerogen, organic pores in solid bitumen, and organic pores in a mineral bitumen matrix [16].

① Organic pores in kerogen

Argon ion polishing SEM observation results show that some humic kerogen is deformed due to compaction and enriched along the bedding direction. The organic pores in this type of kerogen were not developed, or only a small number of isolated organic pores were developed (Figure 5a), most of which showed strong heterogeneity, uneven distribution, and poor connectivity [17]. However, hydrogen-rich algal bacteria vitrinite has no fixed form and is the product of liquid oil transportation, filling, cracking and solidification [8]. A large number of organic matter pores were generally developed and remain in the interior. The pore morphology was mostly spongy or honeycomb (Figure 5b), round or compound oval with coexisting sizes, and had an irregular shape or slit shape (Figure 5c), and the pore size varied from 26 nm to 300 nm.

② Organic pores in a mineral bitumen matrix

A mineral bitumen matrix is only found in a few samples in the Fuling area of the Sichuan Basin. The observation and analysis showed that the shale mineral bitumen matrix in the Da'anzhai section was secondary organic matter, which was mainly the product of microbial degradation in the early diagenesis stage of sedimentation and the hydrocarbon immersion adsorbed and bound by minerals. As is shown in Figure 5d, shale organic matter was wrapped in kaolinite booklets, and a large number of nanoscale pores were developed inside. Most of the organic matter pores in solid asphalt were formed by liquid oil solidification, cracking, gas accumulation, or residual pores after gas escape. The organic matter carrier in the pore had no fixed shape, and the organic pores were oval and star-shaped, with pore diameters of between 4.5 nm and 350 nm.

4.1.3. Microcracks

Observation and analysis with an argon ion polishing–scanning electron microscope showed that there were nano-millimeter microcracks in the shale samples of the Ziliujing Formation in the Fuling area of the Sichuan Basin, which were mainly the result of mechanical genesis. Such microcracks are formed by tectonic stress or local stress during diagenesis [18]. They are mostly curved or elongated in shape. They are tensile microcracks with certain directionality formed under the action of tectonic fractures. The width of the fracture was 105 nm to 5 microns. The microcracks in some samples were filled with asphalt, kaolinite, and siderite (Figure 6a,b). The microcracks of Da'anzhai shale with large burial depths were more developed, which may be related to the increase in shale burial depth and the deepening of the diagenetic evolution of clay minerals. In addition to the above mechanical microcracks, it could also be observed in some electron microscope photos that there were organic matter shrinkage fractures at the edge of the organic matter in Da'anzhai shale (Figure 6c), as well as organic matter internal fractures (Figure 6d). The width of microcracks ranged from 100 nanometers to tens of microns.

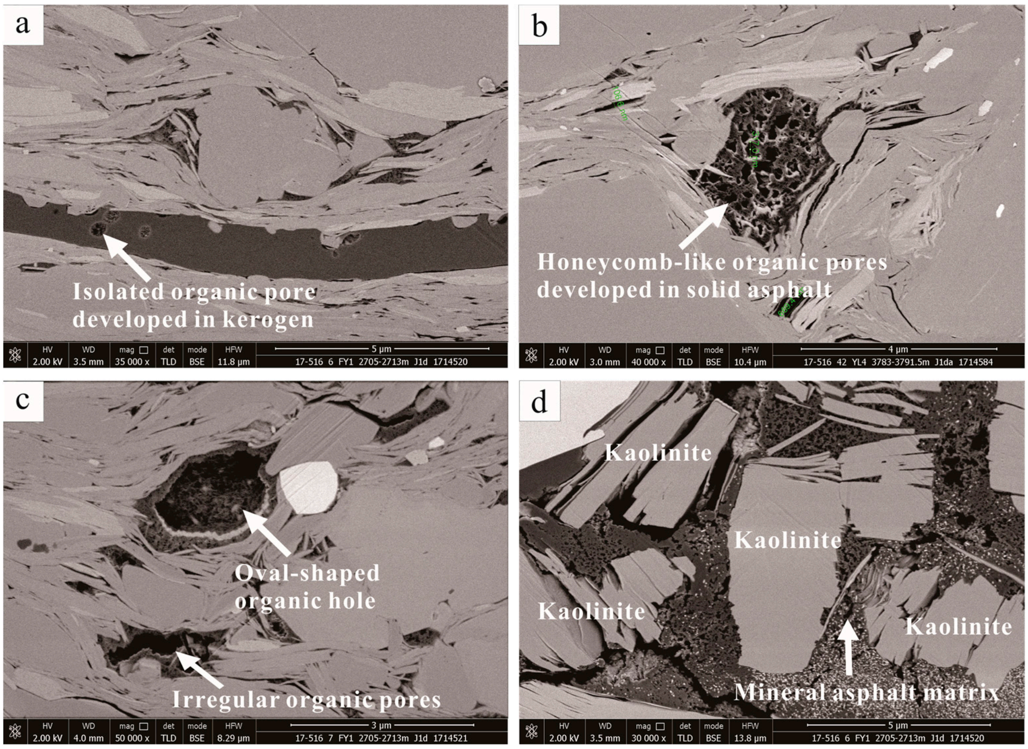

Figure 5. Scanning electron microscopic characteristics of organic pore development in Da'anzhai shale. (**a**) Organic pores in kerogen, Well FY1, 2705 m, Da'anzhai section. (**b**) Honeycomb organic pores in solid bitumen, Well YL4, 3783 m, Da'anzhai section. (**c**) Elliptical and irregular organic pores in solid bitumen, Well FY1, 2705 m, Da'anzhai section. (**d**) Organic pores in mineral bitumen matrix, Well FY1, 2705 m, Da'anzhai section.

4.2. Porosity and Permeability Characteristics of the Shale Reservoir

The porosity and permeability of shale directly determine the capacity for shale gas storage and the possibility of gas seepage, diffusion, and migration in shale pores, which is one of the key parameters of shale gas resource evaluation [19]. Based on the pore identification of the shale reservoir, we used ImageJ software to intelligently identify effective pores and microcracks and calculate the surface porosity of samples.

The continental shale in the Da'anzhai section of the Lower Jurassic Ziliujing Formation in Sichuan Basin was characterized by low porosity and permeability. According to the test results of 89 shale core samples from wells FY1, FY4, and XL101, the porosity of continental shale was 1.21%–8.37%, with an average of 4.13%. The permeability of continental shale was 0.006×10^{-3} μm^2–3.887×10^{-3} μm^2, with an average 0.2349×10^{-3} μm^2. According to the statistical results, the physical property change trends of Wells FY1, FY4, and XL101 in the Fuling area are shown in Figure 7. The average porosity was 1.91%, and the average permeability was 0.1233×10^{-3} μm^2 in the Da'anzhai section of Well FY1. The porosity and permeability were positively correlated. The average porosity of the Da 2 sub-member was 3.34%, and the physical properties were much better than the entire Da'anzhai section. The porosity and permeability of the Da'anzhai section of Well FY4 were positively correlated, and the porosity gradually decreased with depth, indicating that the compaction controlled the change of shale pores at this time. If the Da'anzhai shale was buried 3500 m or deeper, the porosity decreased first and then increased with an increase in depth. The former may be due to the influence of compaction, and the latter may have been caused by clay mineral transformation, organic matter hydrocarbon generation, and microcracks.

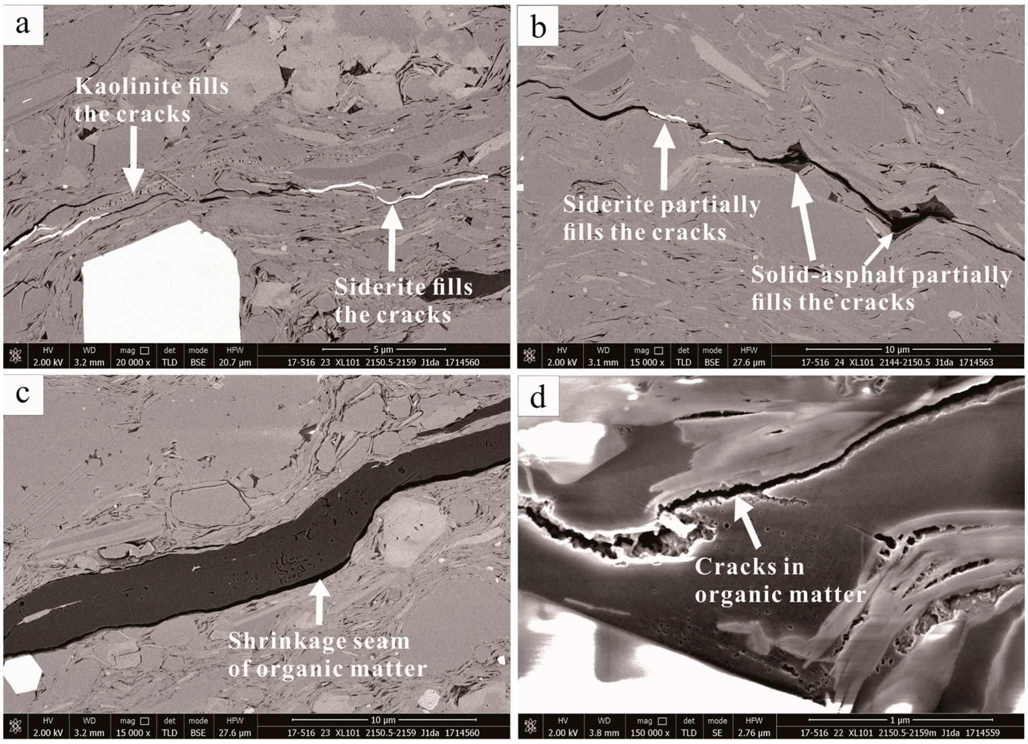

Figure 6. Scanning electron microscope microscopic characteristics of organic micro-fracture development in Da'anzhai shale. (**a**) Microcracks filled with kaolinite and siderite, Well XL101, 2150.5 m, Da'anzhai section. (**b**) Microcracks partially filled with siderite and solid bitumen, Well XL101, 2144 m, Da'anzhai section. (**c**) Organic matter shrinkage fractures, Well XL101, 2150.5 m, Da'anzhai section. (**d**) Organic matter internal fractures, Well XL101, 2150.5 m, Da'anzhai section.

4.3. Diagenesis Types of Shale

The diagenesis of shale mainly involves compaction, cementation, dissolution, recrystallization, replacement, the transformation of clay minerals, the thermal maturity of organic matter, and disruption [20]. These effects are related to each other. Among them, compaction and cementation reduce reservoir pores, organic matter thermal evolution, and dissolution; rupture increases reservoir pores; and replacement and clay mineral transformation have little effect on reservoir pore development.

4.3.1. Compaction

Compaction is the most important reason for the reduction in porosity in the early stage of shale deposition, which plays a destructive role in the preservation of pores and runs through the whole process of burial diagenesis to uplift table rock evolution [21]. Under the influence of compaction, the following changes took place in shale: the original fluid discharge and the original intergranular pore volume greatly reduced, and the physical properties deteriorated; under stress, the particles were oriented as shown in Figure 8a. Compaction elicits different responses from different particles. Plastic mineral particles were deformed by compaction, and primary pores basically disappeared. The rigid particles had a certain resistance to compaction and supported each other to form a framework so that the filled organic matter and pores were not affected by extrusion and retained a certain number of primary pores [22,23].

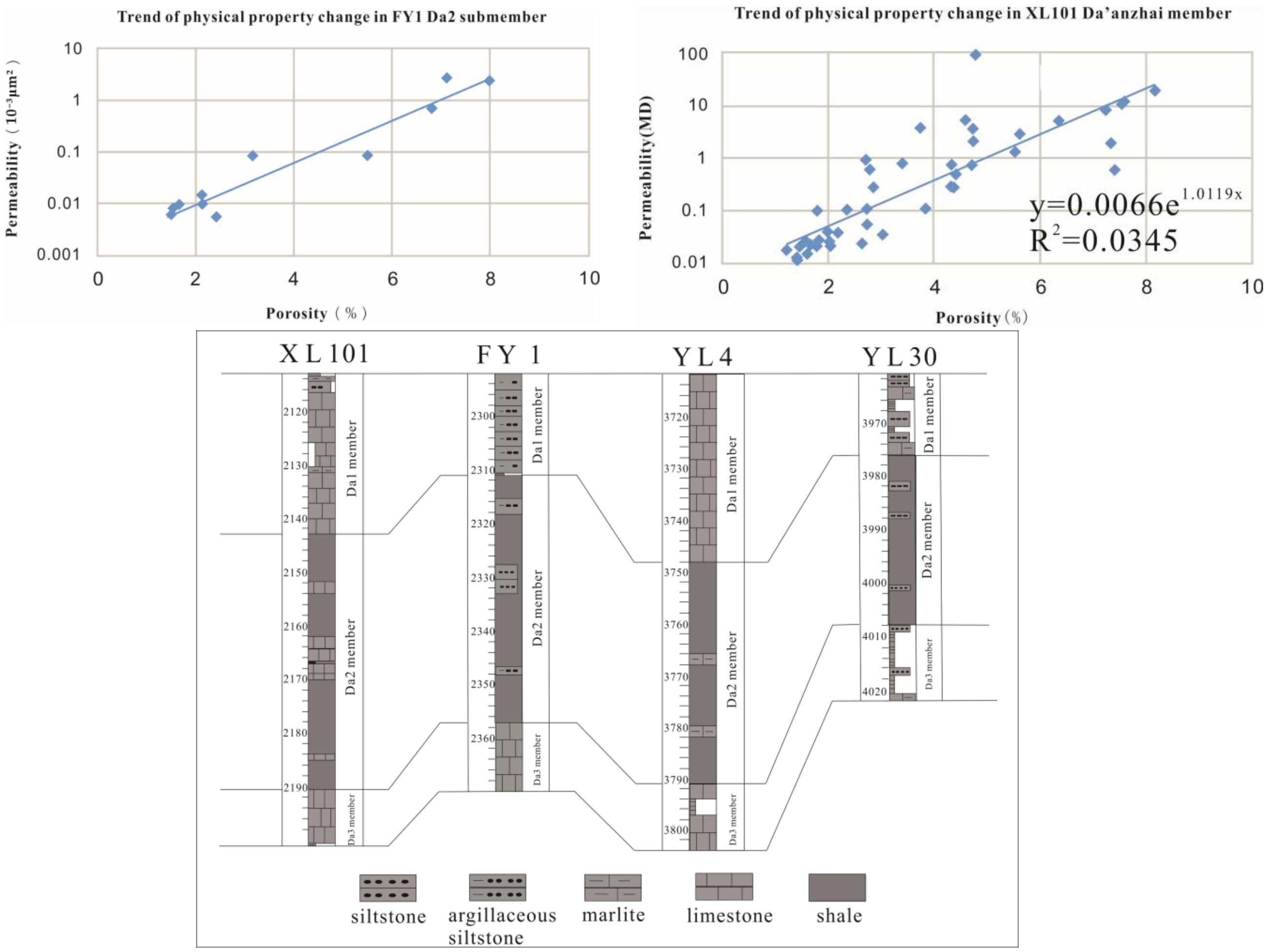

Figure 7. The cross section and trend of physical properties of Da'anzhai shale in the Fuling area.

4.3.2. Cementation

Cementation can fill the original pore space, causing rock densification and reservoir damage [24]. According to the type of cementation cement, the cementation of shale reservoirs in the Da'anzhai section can be divided into three categories: siliceous cementation, calcareous cementation, and iron cementation.

① Siliceous cementation

Siliceous cementation is mainly manifested as the authigenic enlargement of quartz and authigenic quartz particles. The authigenic enlargement of quartz particles is relatively rare in the Da'anzhai section, and authigenic quartz particles are common in shale. Quartz particles are derived from the diagenetic transformation of clay minerals. Previous studies have shown that siliceous minerals can be formed during the transformation of clay minerals in the late diagenesis stage in the form of microcrystalline quartz (Figure 8b).

② Calcareous cementation

Calcareous cement mainly includes calcite, dolomite, and ankerite. The sedimentary period of the Da'anzhai section is a freshwater carbonate lake environment, and calcite cement was developed in the shale of the Da'anzhai section. The microscopic existence of the calcite cement was mainly filled in the intergranular pores or microcracks (Figure 8c), and the particle shape was irregular.

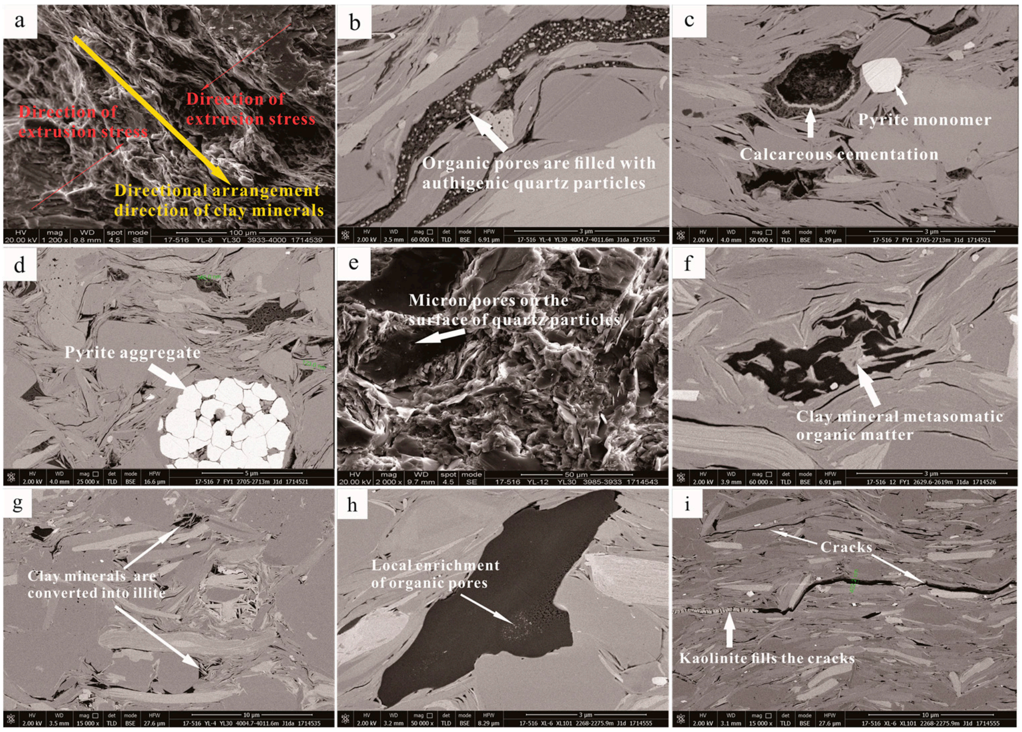

Figure 8. Scanning electron microscope microscopic characteristics of Da'anzhai shale diagenesis. (**a**) Compaction leads to a directional arrangement of clay minerals, Well YL30, 3933 m, Da'anzhai section. (**b**) Organic pores filled with authigenic quartz particles, We YL4, 4004.7 m, Da'anzhai section. (**c**) Calcareous cementation and pyrite monomer, Well FY1, 2705 m, Da'anzhai section. (**d**) Pyrite aggregate, Well FY1, 2705 m, Da'anzhai section. (**e**) Dissolution pores on the quartz particle surface, Well YL30, 3985 m, Da'anzhai section. (**f**) Clay minerals replace organic matter, Well FY1, 2619 m, Da'anzhai section. (**g**) Transformation of clay minerals into illite, Well YL30, 4004.7 m, Da'anzhai section. (**h**) Local enrichment of organic pores formed by hydrocarbon generation of organic matter, Well XL101, 2268 m, Da'anzhai section. (**i**) Microfractures partially filled by kaolinite, Well XL101, 2268 m, Da'anzhai section.

③ Iron cementation

The iron cement of the Da'anzhai shale in the Yuanba and Fuling areas of the Sichuan Basin is mainly pyrite. In the organic-rich shale of the Da'anzhai section, the pyrite cement appears as strawberry-like monomers (Figure 8c) and aggregates (Figure 8d). The existence of pyrite indicates that the shale is rich in organic matter and can be used to restore the sedimentary environment, indicating an anoxic reduction environment [25].

4.3.3. Dissolution

The dissolution is related to the acidic water or organic acids produced during the maturation of organic matter. With the maturation of organic matter, the thermal cracking of kerogen can produce a large amount of CO_2 and organic acids. These acidic fluids contact soluble components to form secondary dissolution pores (Figure 8e). The dissolution in shale reservoirs is generally not developed. Because the shale is relatively closed and the permeability is extremely low, the fluid exchange in the system is not smooth, and the H^+ in the fluid cannot be updated in time after the dissolution reaction, which hinders further dissolution [26,27].

4.3.4. Replacement

The essence of replacement is that one mineral is replaced by another mineral, and this can involve the replacement of the edges of mineral particles or the complete replacement of mineral particles (Figure 8f).

Some scholars believe that deep clay minerals can be metasomatized with quartz and carbonate under high ground temperature and pressure and produce CO_2, which promotes a decrease in the pH value of pore water, resulting in the dissolution of minerals and the formation of new pores [28,29]. For example, the metasomatic reaction between kaolinite, dolomite, and quartz with the participation of water produces metasomatic chlorite and calcite, releasing CO_2. The reaction equation is as follows:

$$Al_2[Si_2O_5](OH)_4 + 2H_2O + 5CaMg(CO_3)_2 + SiO_2 \rightarrow Mg_5Al_2Si_3O_{10}(OH)_8 + 5CaCO_3 + 5CO_2$$

This mineral replacement phenomenon usually occurs in a geological environment with deep burial, high ground temperature, and high ground pressure, and is one of the typical late diagenetic characteristics.

4.3.5. Transformation of Clay Minerals

With an increase in burial depth, pressure, and ground temperature, a change in the physical and chemical environment, the release of interlayer water, and the removal of interlayer cations, the crystal structure and composition of clay minerals change. The transformation of clay minerals in the diagenetic evolution process of shale mainly involves the transformation of kaolinite and feldspar to illite and the transformation of montmorillonite to illite (Figure 8g).

4.3.6. Thermal Maturity of Organic Matter

In the oil generation window, kerogen is pyrolyzed to form and expel oil into adjacent intergranular pores or intragranular pores, and some organic pores are formed inside the kerogen. In the gas generation window, the bitumen migrating to the outside of the kerogen undergoes secondary cracking and is converted into a solid bitumen rich in pores [30,31]. In the process of hydrocarbon generation and evolution of kerogen, the generated hydrocarbon will form the phenomenon whereby organic pores are enriched on the edge of the kerogen side during the process of migration from inside to outside (Figure 8h).

4.3.7. Disruption

Rupture mainly occurs in the post-diagenesis stage, and fractures and microcracks are formed inside the shale reservoir under stress. The shale in the Da'anzhai section was reformed by large tectonic movement and local secondary tectonic movement, forming a large number of fractures and microcracks (Figure 8i), and the disruption was more developed.

5. Model of Diagenesis and Pore Evolution

The transformation of shale pores with burial diagenesis is a complex process affected by many variables and controlling factors [32]. The vitrinite reflectance Ro reflects the maximum paleogeo temperature of diagenesis and the hydrocarbon generation conditions of shale, and is the most suitable parameter to reflect diagenesis. At the same time, the mineral assemblage of the continental shale of the lower Jurassic in the Sichuan Basin is mainly illite, I/S, chlorite, and kaolinite, of which the I/S represents about 15%. The clay mineral assemblage characteristics and the large number of orderly I/S minerals indicate that the continental shale has entered the middle diagenetic stage. The main value of shale vitrinite reflectance (Ro) was between 1.0% and 1.8%, and the organic matter was in the mature to highly mature stage, i.e., indicating that it had entered the B stage of intermediate diagenesis. Therefore, based on previous studies on the factors affecting the evolution of various pores, the diagenesis and pore evolution of shale were divided into six stages according to the depth of continental shale encountered in actual drilling and the measured Ro value (Figure 9): these were the early diagenesis stage A ($Ro < 0.35\%$), the early diagenesis stage B ($0.35\% < Ro < 0.5\%$), the middle diagenesis stage A ($0.5\% < Ro < 1.3\%$), the middle diagenesis stage B ($1.3\% < Ro < 2.0\%$), the late diagenesis stage ($2.0\% < Ro < 2.7\%$), and the post-diagenesis stage ($Ro > 2.7\%$).

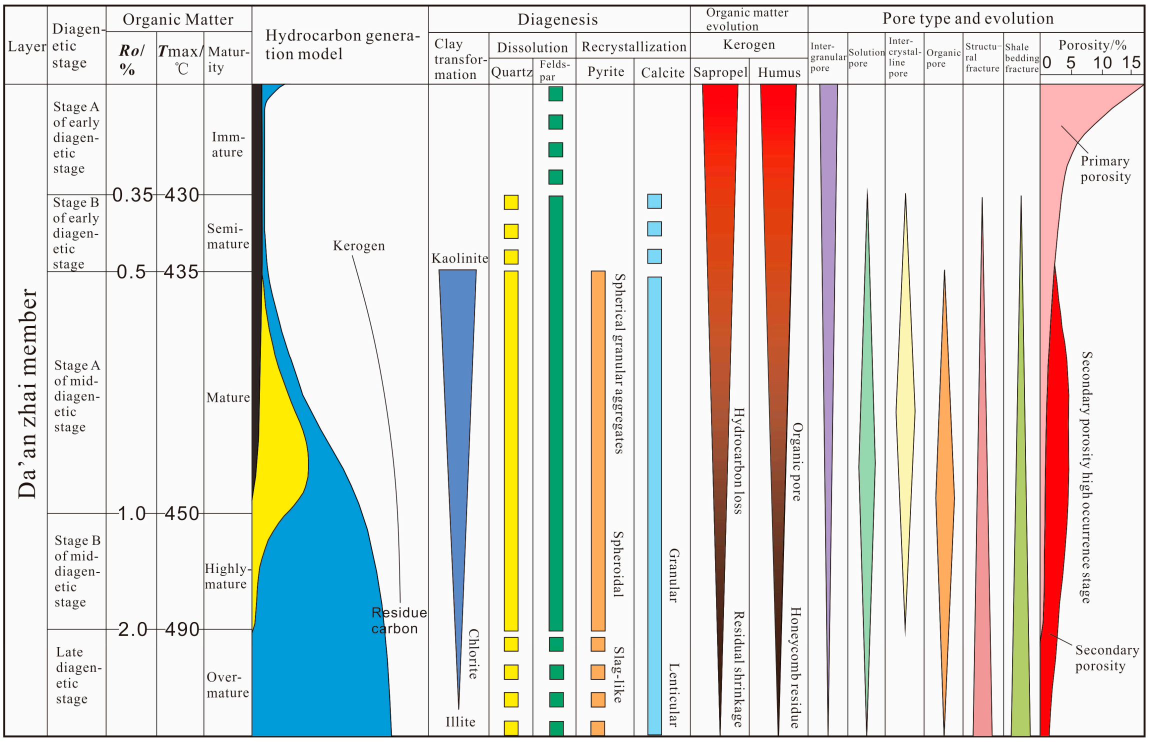

Figure 9. Diagenetic evolution and pore evolution model of Da'anzhai shale in the Sichuan Basin.

The analysis of shale clay minerals by X-ray diffraction showed that the clay minerals of continental shale in the Da'anzhai section had undergone an obvious transformation process between 2600 m and 3800 m in burial depth. Authigenic quartz is formed with the transformation of clay minerals, and silica is mainly released during the dissolution of feldspar and the transformation of clay minerals. Therefore, the diagenetic sequence of continental shale in the Da'anzhai section of the Lower Jurassic Ziliujing Formation in Sichuan Basin was as follows: pyrite was precipitated by authigenic quartz; authigenic quartz formation was accompanied by clay mineral transformation; the transformation of clay minerals occurred after deep burial and a significant increase in temperature and pressure; and compaction ran through the whole diagenetic process.

5.1. Early Diagenesis Stage

The early diagenetic stage corresponds to the biochemical gas generation stage of organic matter evolution. During this period, the strength of diagenesis was low, mainly compaction and pyrite precipitation; clay minerals were mainly montmorillonite; and pores were mainly primary intergranular pores.

5.1.1. Early Diagenesis Stage A

The shale buried depth was less than 1000 m, the vitrinite reflectance Ro of early diagenesis stage A was less than 0.35%, and the organic matter was in the immature stage. With an increase in burial depth, the compaction made the loose sediments compact into a weakly consolidated–semi-consolidated state. At this stage, pyrite precipitation and chlorite cementation also occurred, the primary intergranular pores were greatly reduced, and the original porosity was rapidly reduced.

5.1.2. Early Diagenesis Stage B

The burial depth of shale was between 1000 m and 2000 m, the compaction continued to increase, and the porosity of shale decreased to about 10%. The vitrinite reflectance Ro value of early diagenesis stage B was between 0.35% and 0.5%, and the organic matter was in a semi-mature state. With a further increase in the burial depth, the compaction strength increased, the rock was in a semi-consolidated–consolidated state, and the original porosity gradually approached about 5%. The organic matter initially entered hydrocarbon generation evolution, transformed into kerogen, and generated a small amount of biogenic methane and organic acids. The diagenetic environment gradually became acidic, with a small number of secondary pores, and organic pores were basically undeveloped. Ferrite calcite began to precipitate and fill pores and fractures, and montmorillonite minerals began to transform into illite montmorillonite mixed layers.

5.2. Middle Diagenesis Stage

The organic matter reached the threshold of hydrocarbon generation due to the temperature and the clay mineral catalyst, cracking hydrocarbon generation and producing a large number of organic acids, which further dissolved carbonate rocks, feldspar, and other soluble minerals. Clay minerals began to transform from montmorillonite into an illite–montmorillonite mixed layer and illite.

5.2.1. Middle Diagenesis Stage A

The burial depth of shale was 2000–3000 m, the compaction basically stopped, the porosity was very low, and a large amount of authigenic quartz precipitated and filled the pores. The vitrinite reflectance Ro value of middle diagenesis stage A was between 0.5% and 1.3%, and the maturity of organic matter reached the hydrocarbon generation threshold and entered the stage of thermal catalytic hydrocarbon generation. The main diagenesis of middle diagenesis stage A was the hydrocarbon generation evolution of organic matter and the mutual transformation between clay minerals. Hydrocarbon generation by organic matter cracking led to the formation of a large number of organic pores dominated by micropores. In addition, a large number of organic acids were produced, which corroded feldspar, quartz, and other minerals to form secondary dissolution pores. The transformation of clay minerals caused montmorillonite to begin to transform into an illite–montmorillonite mixed layer, and the content of brittle minerals in rock increased, which led to structural fractures. Dehydration and recrystallization during the conversion of clay minerals also produced some pore fractures, which were developed in large quantities with medium pore sizes. At this stage, the pores of organic matter and inorganic minerals were developed in large quantities, and the total porosity of shale increased rapidly.

5.2.2. Middle Diagenesis Stage B

The burial depth of shale was 3000–4000 m. The Ro value of vitrinite reflectance in middle diagenesis stage B was between 1.3% and 2.0%, and the organic matter was in the highly mature stage and began to form condensed oil and moisture. The intensity of diagenesis reached its peak at this stage, and a large number of recrystallized minerals such as iron calcite and barite began to appear, and the illite–montmorillonite mixed layer and illite appeared in large numbers. The decrease in organic acid content, the increase in the pH value, and the decrease in acidity led to the weakening of dissolution and the enhancement of cementation. The organic pores were filled with bitumen, and the inorganic mineral pores were affected by cementation and compaction. As a whole, the shale pores were in the stage of closure and reduction. Due to the increase in burial depth, the reservoir gradually became denser and the tectonic fracture was obviously enhanced, forming a large number of microcracks.

5.3. Late Diagenesis Stage

The late diagenetic stage corresponds to the deep high-temperature gas generation stage of organic matter evolution, and shale burial depth exceeds 4000 m, and the vitrinite reflectance Ro value is between 2.0% and 2.7%. At this stage, the residual kerogen underwent aromatization under high temperature and produced methane gas. The organic pores increased in number again due to the secondary cracking of organic matter and the shrinkage of organic matter. The organic acid produced dissolved the originally filled bitumen and released the closed organic pores. The dissolution was limited by poor reservoir properties and poor fluid exchange, and the compaction led to a reduction in the number of inorganic pores. On the whole, the shale pores in this stage were slowly compacted, the organic pores and inorganic mineral pores were slowly reduced in number, and the pores were mainly micropores. On the whole, the pore composition was relatively stable and the total porosity of shale was about 2%–3%. The total porosity of the shale was lower than that at middle diagenesis stage B.

6. Discussion

The formation and existence of continental shale pores have a very contradictory and complex relationship with the type and composition of shale minerals, diagenesis, hydrocarbon generation, and the evolution of organic matter. In particular, the state of deep or ultra-deep continental shale pores needs to be further explored. The author puts forward the following three aspects for discussion.

(1) Whether the burial depth determines the existence of inorganic and organic pores in continental shale. Compaction will reduce the porosity of continental shale and continue to increase the burial depth of shale. However, the organic matter in shale generates hydrocarbons, which cause the dissolution of pores made up of soluble minerals (such as feldspar and carbonates), kerogen organic pores, and shale microfractures, which can also promote the formation of continental shale pores. What determines the number of shale pores? This study suggests that, in the middle diagenetic stage A, organic matter is in the oil generation window, and inorganic and organic pores are abundant. In this period, the burial depth of continental shale is 2000–3000 m, and the sub-ion polishing scanning electron microscope photos of individual well cores show that the buried depth can extend to 3500 m. Beyond this depth, the development degree of continental shale pores decreases sharply. The burial depth is more than 4000 m, and the shale is in the late diagenetic stage. Although the laboratory simulation of shale hydrocarbon generation showed that the organic pores in the organic matter were developed again at this stage [32], the actual drilling shale core showed that the organic–inorganic pores in the shale are rarely developed beyond this depth [24].

(2) Do linear pores between clay minerals really exist? Argon ion polishing–scanning electron microscope photos showed that the continental shale appears in the continental shale of the middle diagenetic stage A with a burial depth of 2000–3000 m and appears between compressed mudstone blocks. There is evidence that the pores of the continental shale with a burial depth of more than 4000 m disappear. The reasonable explanation is that this is the result of diagenetic compaction. Some scholars suspect that the reason is the separation and formation of clay blocks caused by the dehydration of clay blocks or the formation of clay minerals after the loss of crystal lattice water during the conversion process [33], but the true cause has not yet been determined.

(3) The carrier types of organic pores in continental shale and the changes in organic pores in the process of thermal evolution and hydrocarbon generation are still unclear. Organic matter derived from hydrocarbon-forming organisms often shows different forms due to its strong plasticity and tendency to be squeezed by compaction. At present, scholars do not have an exact unified standard for the identification and classification of carrier types of organic pores. In addition, research shows that organic pores are generated in continental shale when Ro is greater than 0.9%, while in marine shale a large number of organic pores are generated only when Ro reaches 1.2%. This phenomenon is related to the organic matter carrier parent material of organic pores or the diagenetic thermal evolution and hydrocarbon generation of buried depth, but this issue requires further research.

7. Conclusions

(1) Continental shale pores are divided into inorganic mineral pores, organic pores, and microcracks. There are many types of inorganic mineral pores in Da'anzhai shale. Linear pores, intergranular (intercrystalline) pores, and intragranular dissolution pores are

developed here among clay minerals. Among them, linear pores are the most developed, followed by intergranular pores, and intragranular dissolution pores are developed locally. Organic pores are divided into two types: organic pores in kerogen and organic pores in mineral bitumen matrix. The microcracks in the shale of the Da'anzhai section are mainly mechanically formed, and there are also organic shrinkage fractures. The organic pores are well developed in Da'anzhai section shale in the Fuling area. If the buried depth of shale is more than 3500 m, shale porosity decreases, but microfractures are relatively developed.

(2) The diagenesis of shale mainly includes compaction, cementation, dissolution, replacement, the transformation of clay minerals, and the thermal maturity of organic matter, which are related to and influenced by each other. According to the reflectance Ro of the organic vitrinite of continental shale, the diagenetic evolution of Da'anzhai shale experienced early diagenetic stage A and B and middle diagenetic stage A and B. The mixed layer of illite and montmorillonite in continental shale has undergone a process from disorder to order, involving the occurrence and transformation of kaolinite, the occurrence of inorganic acid and organic acid successively, a change in porosity from primary to secondary, and a change in the sediment from loose to consolidated to dense. At present, the Da'anzhai shale is in the middle diagenetic B stage, and the organic matter is in the high maturity stage.

(3) In the process of diagenesis evolution, shale pores also evolve. In early diagenesis stage A, compaction is the most important diagenesis, and shale porosity is greatly reduced. In early diagenetic stage B, compaction is still the main factor for shale porosity reduction, but at the same time the organic acids generated during the hydrocarbon generation process of sedimentary organic matter in shale cause secondary dissolution pores in shale minerals such as feldspar, carbonate minerals, and even clay minerals. In middle diagenesis stage A, a large number of organic acids are generated and a large number of organic pores and dissolution pores develop. Compaction still exists, but its effect is weak and the overall porosity of shale increases. In middle diagenetic stage B, the massive transformation of clay minerals leads to an increase in rock brittleness, which leads to ruptures and microfracture formation. The original organic pores are filled with bitumen produced by hydrocarbon generation. In the late diagenesis stage, the secondary cracking of organic matter generates hydrocarbons, and the organic acid produced dissolves the bitumen that originally filled the organic pores, meaning that the number of organic pores increases. The dissolution is limited by poor reservoir physical properties and poor fluid exchange.

(4) Diagenesis controlled by burial depth is the main factor affecting the development of pores and microfractures in continental shale reservoirs. When the shale burial depth is more than 3500 m (i.e., at middle diagenetic stage B), the inorganic porosity in shale is reduced and the number of microfractures is increased. When the shale is buried more than 4000 m deep in the late diagenetic stage, the thermal evolution of organic matter in the shale is high and methane gas is generated in large quantities, which is conducive to the formation and development of organic matter pores in continental shale.

Author Contributions: Conceptualization, Q.F. and Z.H.; methodology, D.F.; software and validation, Z.Z.; formal analysis and data curation, L.X.; writing—original draft preparation, T.Q.; writing—review and editing, B.Y.; project administration, Z.H.; funding acquisition, Q.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded on the task of Sinopec Key Laboratory of Shale Oil/Gas Exploration and Production Technology for the open found, Open Fund Project Name: Shale Diagenesis Evolution and Reservoir Pore Formation Mechanism of Ziliujing Formation in Sichuan Basin; grant number [22ZC06130006].

Data Availability Statement: The data has been disclosed in the manuscript figures. If you need the most original data, you can contact us via email: fqzldw@163.com.

Acknowledgments: This work was funded by the Sinopec Shale Oil and Gas Exploration and Development Key Laboratory. We thank Peng Li and Tianyi Zhao of the Sinopec Exploration and Development Research Institute (Beijing) for providing us with analysis data, and Xiaoying Jiang and Lingdi Chen of the State Key Laboratory of Marine Geology of Tongji University for helping us complete the experiment.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Aringhieri, R. Nanoporosity Characteristics of Some Natural Clay Minerals and Soils. *Clays Clay Miner.* **2004**, *52*, 700–704. [CrossRef]
2. Borjigin, T.; Lu, L.; Yu, L.; Zhang, W.; Anyang Pan, A.; Shen, B.; Wang, Y.; Yang, Y.; Gao, Z. Formation, preservation and connectivity control of organic pores in shale. *Pet. Explor. Dev.* **2021**, *48*, 798–812. [CrossRef]
3. Clarkson, C.R.; Solano, N.; Bustin, R.M.; Chalmers, G.; He, L.; Melnichenko, Y.B.; Radlinski, A.P.; Blach, T.P. Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion. *Fuel* **2013**, *103*, 606–616. [CrossRef]
4. Chalmers, G.R.L.; Bustin, R.M. Geological evaluation of Halfway-Doig-Montney hybrid gas shale-tight gas reservoir, northeastern British Columbia. *Mar. Pet. Geol.* **2012**, *38*, 53–72. [CrossRef]
5. Curtis, M.E.; Ambrose, R.J.; Sondergeld, C.H.; Rai, C.S. Structural characterization of gas shales on the micro- and nano-scales. In Proceedings of the Canadian Unconventional Resources and International Petroleum Conference, Calgary, AB, Canada, 19–21 October 2010. SPE 137693-15.
6. Curtis, M.E.; Cardott, B.J.; Sondergeld, C.H.; Rai, C.S. Development of organic porosity in the Woodford Shale with increasing thermal maturity. *Int. J. Coal Geol.* **2012**, *103*, 26–31. [CrossRef]
7. Zhu, T.; Hu, Z.; Liu, Z.; Feng, D. Types and evaluation of the source-reservoir configuration of lacustrine shale gas in the Sichuan Basin. *Oil Gas Geol.* **2018**, *39*, 1146–1153.
8. Jiu, K.; Ding, W.; Wang, Z.; Huang, Y.; Zhu, B.; Zhang, Z.; Zeng, W.; Wang, R. Reservoir space and evolution process of Longmaxi shale in the Fenggang area of northern Guizhou. *Earth Sci. Front.* **2016**, *23*, 195–205.
9. Liu, Z.; Hu, Z.; Liu, G.; Liu, H.; Hao, J.; Wang, P.; Li, P. Pore characteristics and controlling factors of continental shale reservoirs in the Lower Jurassic Ziliujing Formation, northeastern Sichuan Basin. *Oil Gas Geol.* **2021**, *42*, 136–145.
10. Liu, W.; Zhang, C.; Gao, G.; Luo, C.; Wu, W.; Shi, X.; Zhang, J.; Li, W.; Deng, X.; Hu, X. Controlling factors and evolution laws of shale porosity in Longmaxi Formation, Sichuan Basin. *Acta Pet. Sin.* **2017**, *38*, 175–184.
11. Loucks, R.G.; Reed, R.M.; Ruppel, S.C.; Hammes, U. Spectrum of pore types and networks in mudrocks and a descriptive classification for matrix-related mudrock pores. *AAPG Bull.* **2012**, *96*, 1071–1098. [CrossRef]
12. Hackley, P.C.; Valentine, B.J.; Voortman, L.M.; Van Oosten, S.D.; Hatcherian, J. Utilization of integrated correlative light and electron microscopy (ICLEM) for imaging sedimentary organic matter. *J. Microsc.* **2017**, *267*, 371–383. [CrossRef] [PubMed]
13. Mastalerz, M.; Schimmelmann, A.; Drobniak, A.; Chen, Y. Porosity of Devonian and Mississippian new albany shale across a maturation gradient: Insights from organic petrology, gas adsorption, and mercury intrusion. *AAPG Bull.* **2013**, *97*, 1621–1643. [CrossRef]
14. Ross, D.J.K.; Bustin, R.M. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Mar. Pet. Geol.* **2009**, *26*, 916–927. [CrossRef]
15. Slatt, R.M.; O'brien, N.R. Pore types in the Barnett and Woodford gas shales: Contribution to understanding gas storage and migration pathways in fine-grained rocks. *AAPG Bull.* **2011**, *95*, 2017–2030. [CrossRef]
16. Katz, B.J.; Arango, I. Organic porosity: A geochemist's view of the current state of understanding. *Org. Geochem.* **2018**, *123*, 1–16. [CrossRef]
17. Reed, R.M.; Loucks, R.; Milliken, K.L. Heterogeneity of shape and microscale spatial distribution in organic-matterhosted pores of gas shales. In Proceedings of the AAPG Annual Convention and Exhibition, Abstract, Long Beach, CA, USA, 22–25 April 2012; pp. 22–24.
18. Jia, B.; Xian, C.G. Permeability measurement of the fracture-matrix system with 3D embedded discrete fracture model. *Pet. Sci.* **2022**, *19*, 1757–1765. [CrossRef]
19. Zanoni, G.; Segvic, B.; Moscariello, A. Clay mineral diagenesis in Cretaceous clastic reservoirs from West African passive margins (the South Gabon Basin) and its impact on regional geology and basinevolution history. *Appl. Clay Sci.* **2016**, *134*, 186–209. [CrossRef]
20. Chen, Q.; Yan, X.; Liu, C.; Wei, X.; Cheng, Z.; Qin, W.; Hong, T. Controlling effect of compaction upon organic matter pore development in shale: A case study on the Lower Paleozoic in southeastern Sichuan Basin and its periphery. *Oil Gas Geol.* **2021**, *42*, 76–85.
21. Yu, Z.; Chen, S.; Zhang, S.; Liu, X.; Tang, D.; Yan, J. Influence of diagenesis on reservoir performance of shale: A case study of the upper sub-member of Member 4 of Paleogene Shahejie Formation in Dongying sag. *J. Palaeogeogr. Chin. Ed.* **2022**, *24*, 771–784.
22. Shao, H.; Gao, B.; Pan, H.; Chen, G.; Li, L. Diagenesis-pore evolution for Gulong shale in Songliao Basin. *Pet. Geol. Oilfield Dev. Daqing* **2021**, *40*, 56–67.

23. Zhang, S.; Liu, H.; Wang, M.; Fu, A.; Bao, Y.; Wang, W.; Teng, J.; Fang, Z. Pore evolution of shale oil reservoirs in Dongying sag. *Acta Pet. Sin.* **2018**, *39*, 754–766.
24. Hu, W.; Yao, S.; Lu, X.; Wu, H.G.; Sun, F.N.; Jin, J. Effects of organic matter evolution on oil reservoir property during diagenesis of typical continental shale sequences. *Oil Gas Geol.* **2019**, *40*, 947–956+1047.
25. Liu, J.; Li, S.; Li, Z.; Liu, Q.; Guo, W.; Zhou, X.; Ma, X. Characteristics and geological significance of pyrite in Chang 73 sub-member in the Ordos Basin. *Nat. Gas Geosci.* **2021**, *32*, 1830–1838.
26. Kong, L.; Wan, M.; Yan, Y.; Zou, C.; Liu, W.; Tian, C.; Yi, L.; Zhang, J. Reservoir Diagenesis Research of Silurian Longmaxi Formation in Sichuan Basin. *Nat. Gas Geosci.* **2015**, *26*, 1547–1555. [CrossRef]
27. Lu, L.; Liu, W.; Wei, Z.; Pan, A.; Zhang, Q.; Teng, G. Diagenesis of the Silurian Shale, Sichuan Basin: Focus on pore development and preservation. *Acta Sedimentol. Sin.* **2022**, *40*, 73–87.
28. Zhao, D.; Guo, Y.; Yang, Y.; Wang, S.; Mao, X.; Li, M. Shale reservoir diagenesis and its impacts on pores of the Lower Silurian Longmaxi Formation in southeastern Chongqing. *J. Palaeogeogr. (Chin. Ed.)* **2016**, *18*, 843–856.
29. Wang, X.; Mu, C.; Wang, Q.; Ge, X.; Chen, X.; Zhou, K.; Liang, W. Diagenesis of black shale in Longmaxi Formation, southern Sichuan Basin and its periphery. *Acta Pet. Sin.* **2015**, *36*, 1035–1047.
30. Löhr, S.C.; Baruch, E.T.; Hall, P.A.; Kennedy, M.J. Is organic pore development in gas shales influenced by the primary porosity and structure of thermally immature organic matter? *Org. Geochem.* **2015**, *87*, 119–132. [CrossRef]
31. Ko, L.T.; Loucks, R.G.; Zhang, T.; Ruppel, S.C.; Shao, D. Pore and pore network evolution of Upper Cretaceous Boquillas (Eagle Ford–equivalent) mudrocks: Results from gold tube pyrolysis experiments. *AAPG Bull.* **2016**, *100*, 1693–1722. [CrossRef]
32. Dong, C.; Ma, C.; Luan, G.; Lin, C.Y.; Zhang, X.G.; Ren, L.H. Pyrolysis Simulation Experiment and Diagenesis Evolution Pattern of Shale. *Acta Sedimentol. Sin.* **2015**, *33*, 1053–1061.
33. Liang, J.; Sun, B. Research on Clayminerals during diagenesis of argillaceous rock. *Contrib. Geol. Miner. Resour. Res.* **2016**, *4*, 543–549.