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Integrated Assessment of Marine-Continental Transitional Facies Shale Gas of the Carboniferous Benxi Formation in the Eastern Ordos Basin

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Citation: Zhao, W.; Wen, Z.; Zhang, H.; Wu, C.; Liu, Y.; Song, H.; Zhang, L.; Xi, Y.; Sun, L. Integrated Assessment of Marine-Continental Transitional Facies Shale Gas of the Carboniferous Benxi Formation in the Eastern Ordos Basin. *Energies* **2021**, *14*, 8500. https://doi.org/10.3390/en14248500

Academic Editor: Xixin Wang

Received: 22 November 2021
Accepted: 15 December 2021
Published: 16 December 2021

Abstract: In the Benxi Formation of the Carboniferous system of the Upper Paleozoic in the Ordos Basin, there are many sets of coal measures dark organic-rich shale, being marine continental transitional facies, with significant unconventional natural gas potential. Previous studies are only limited to the evaluation of tight sandstone reservoir in this set of strata, with no sufficient study on gas bearing and geological characteristics of organic-rich shale, restricting the exploration and evaluation of shale gas resources. In this study, analysis has been conducted on the organic carbon content, the major elements, the trace elements, and the mineral composition of core samples from the Benxi Formation in key drilling sections. In addition, qualitative and quantitative pore observation and characterization of core samples have been conducted. The sedimentary environments and reservoir characteristics of the shale of the Benxi Formation have been analyzed. Combined with the gas content analyzing the results of the field coring samples, the shale gas resource potentials of the Benxi Formation have been studied, and the geological characteristics of the Benxi Formation shale gas in the eastern Ordos Basin have been made clear, to provide a theoretical basis for shale gas resource evaluation of the Benxi Formation in the Ordos Basin. The results show that (1) in the Hutian Member, Pangou Member, and Jinci Member of the Benxi Formation, organic-rich shale is well developed, with the characteristics of seawater input as a whole. There is a slight difference in sedimentary redox index, which shows that the reducibility increases gradually from bottom to top. (2) There is an evident difference in the mineral characteristics of shale in these three members. The Hutian Member is rich in clay minerals, while the Jinci Member is high in quartz minerals. (3) The pores are mainly inorganic mineral intergranular pores, clay interlayer fractures, and micro fractures, and organic matter pores are developed on the surface of local organic matter. (4) The mud shale in the Jinci Member has a large cumulative thickness, has relatively high gas-bearing property, and is rich in brittle minerals. The Jinci Member is a favorable section for shale gas exploration of the Benxi Formation.

Keywords: shale gas; marine-continental transitional facies; Benxi Formation; sedimentary environment; pore characteristics

1. Introduction

Petroleum and natural gas are a national strategic resource. Shale (mudrock) is a kind of traditional source rock, and a petroliferous system can be developed in shale by self-generation, self-storage, and self-sealing, with huge exploration potential. Three types of organic-rich shale are widely developed in China, including marine shale dominated by the Early Paleozoic, marine-continental transitional shale dominated by the

Carboniferous-Permian, and continental shale dominated by the Mesozoic and the Cenozoic [1,2]. Since the first shale gas survey well—Well Yuye 1 drilled in 2009, through more than ten years of exploration and development—a significant breakthrough has been made in the exploration of marine shale in Fuling, Changning, Weiyuan, Zhaotong, and other areas in the Sichuan Basin, and commercial developments have been realized. After many years of research, a mature understanding has formed about the sedimentary environment [3,4], reservoir performance [4], pore evolution mechanism [4,5], shale gas accumulation and enrichment conditions of marine shale [6–9], and other scientific issues. The marine-continental transitional facies shale in China covers a hugely large area, with a resource potential of about 19.8 $\times$ 10^{12} m^3, showing great prospects for exploration and development [1,10]. However, the exploration degree on the shale gas resources is low generally. Commercial gas flow has been obtained from the Permian Longtan Formation in the Eastern Sichuan Basin and the Permian Shanxi Formation in the Ordos Basin in the key horizontal well, showing the exploration and development potential of marine-continental transitional facies shale gas [10]. Because the geological conditions of marine-continental transitional shale gas accumulation not been made clear, and the geological theory of shale gas enrichment has not yet been established, the exploration and development of marine-continental transitional shale gas been restricted to a certain extent. Therefore, it is necessary to conduct further exploration research.

In the strata from Carboniferous to the Permian in Ordos Basin, three sets of marine-continental transitional shale facies are well developed, namely the Benxi Formation, Taiyuan Formation, and Shanxi Formation, which are favorable for shale gas exploration. At present, the research on the Carboniferous-Permian marine-continental transitional shale gas in the Ordos Basin is focused on the second member of the Shanxi Formation [10,11]; however, there have been fewer studies on the geological characteristics of shale gas accumulation in the Benxi Formation. Tight sandstone gas from the Benxi Formation has attracted more and more attention in the past few years, with 65 wells showing industrial gas from 165 tested wells, indicating good prospects for unconventional resources. Previous studies of the Benxi Formation were focused on the distribution of sand bodies, aiming at the resource potential of tight sandstone gas reservoirs [12,13], with few studies focusing on the shale section. Guo et al. [14] conducted a study on the geochemical characteristics, such as the abundance, type, and maturity, of shale organic matter and their plane distribution in the Benxi Formation in the Ordos Basin. In the Benxi Formation, there are three sets of organic-rich shale in the Hutian, Pangou, and Jinci Members. There is a lack of detailed characterization of the vertical heterogeneity distribution characteristics of organic matter, minerals, and reservoirs in the Benxi Formation through core samples of drilling profiles. In this study, with the drilling core samples from the eastern Ordos Basin as the research object, the sedimentary environment and shale gas geological characteristics of the organic-rich shale of the Benxi Formation in the eastern Ordos Basin have been studied, which can provide a theoretical basis for the evaluation of shale gas resources in the Benxi Formation of the Ordos Basin.

2. Geological Setting

The Ordos Basin is one of the large-scale sedimentary basins in China, generally covering about 37 $\times$ 10^4 km^2. It is bounded by Lvliang Mountain in the east, Qinling Mountain in the south, Helan Mountain and Liupan Mountain in the west, and the Yellow River Fault in the north. The Ordos Basin is a large multi-cycle craton basin, characterized by overall subsidence and depression migration. According to the geological evolution and structural pattern, the regional structure of the basin is divided into six primary units, including the northern Shaanxi slope in the middle, the flexure belt in the west of Shanxi in the east, the Tianhuan Depression in the west, and the thrust fault zone at the western edge, the Yimeng Uplift in the north, and the Weibei Uplift in the south (Figure 1).

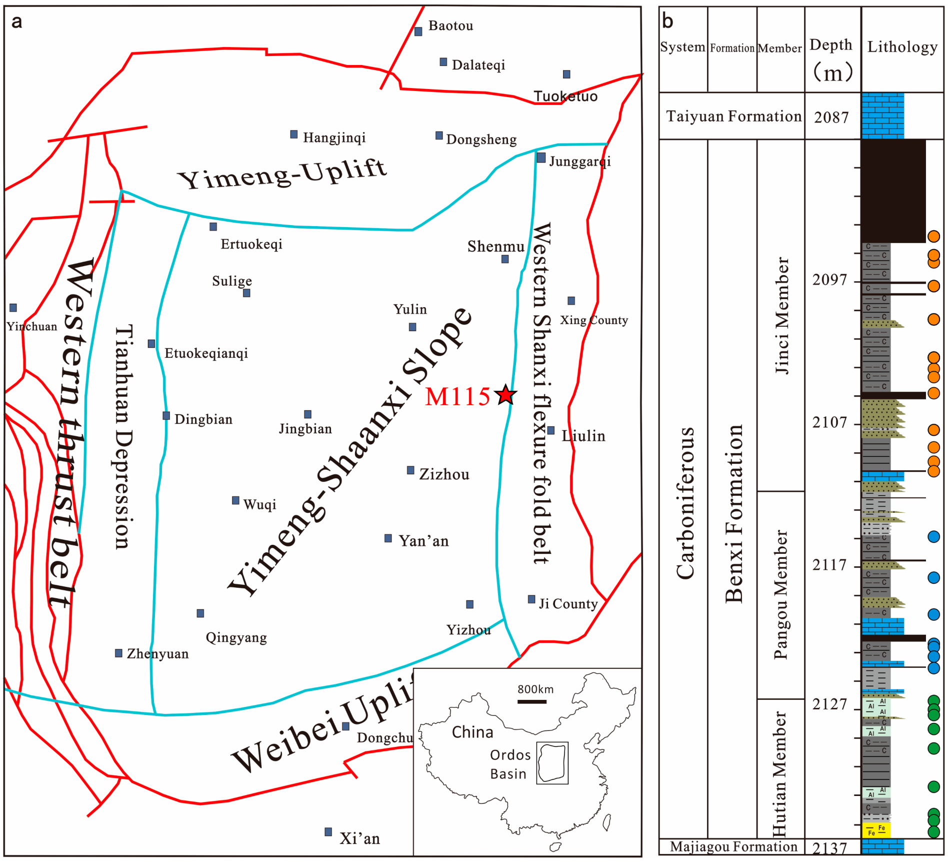

Figure 1. Structural diagram of the Ordos Basin (**a**) and histogram of the Benxi Formation (**b**). Green, blue, and orange circles represent samples from Hutian, Pangou, and Jinci members, respectively.

From the top denudation surface of the Middle Ordovician, the Carboniferous-Permian marine-continental transitional facies is extensively deposited in the Ordos Basin, including the Upper Carboniferous Benxi Formation, the Lower Permian Taiyuan Formation, and Shanxi Formation [10]. The Benxi Formation covers the unconformable Ordovician weathering crust, the top is separated from the Taiyuan Formation by a stable 8# coal seam, and the bottom consists of a widely distributed bauxitic rock layer. The middle is mainly characterized by the interbed of gray-black mudstone and sandstone. The thickness of the Benxi Formation ranges from 10 m to 110 m. The thickness distribution is evidently different from east to west, generally being thick in the east and thin in the west. The sedimentary cycles are mainly reverse cycles, with small positive rhythms inside the Benxi Formation. The changes in sedimentary cycles are the basis for stratigraphic division. The Benxi Formation can be divided into three members upwardly, including Hutian, Pangou, and Jinci. The Jinci Member mainly consists of oil sands, coal seams, and mudstones, forming multiple sedimentary cycles. The tidal channel sand bodies and lagoon mud flats are superimposed alternately, reflecting multiple transgressions and regressions. In more detail, it can be divided into an 8# coal seam, Zhaoxian shale, Ximing sandstone, Wujiayu limestone layer, and Jinci sandstone layer downwardly. The Pangou Member is mainly gray-black mudstone, gray siltstone, limestone, and coal seams. The Hutian Member is at the bottom, and it is lithologically dominated by bauxite and black mudstone (Figure 1).

3. Materials and Methods

By the drilling Well M-115 in the eastern Ordos Basin, it is revealed that the Benxi Formation is in unconformably overlain the Ordovician Majiagou Formation limestone. At the bottom of the section is the Hutian Member, with developed ferrous rocks and bauxite mudstones, intercalated with thin-layered black mudstone in the middle. The Pangou Member is the black mudstone, interbedded with silty sandstone and thin-layered sandstone, with a thickness of about 15 m. The Pangou Member and the Jinci Member are bounded by Jinci sandstone. In the Jinci Member, the black shale and carbonaceous mudstone are interbedded with thin-layered coal seam, with the cumulative thickness of mudstone being about 25 m. The 8# coal seam is developed at the top of Jinci Member, and it is overlaid by the Taiyuan Formation limestone, which can be identified in borehole lithology identification. In this study, the core samples from the Benxi Formation in Well M-115 are the research object. The collected samples include bauxite mudstone, black shale, silty mudstone, carbonaceous mudstone, and coal samples. The specific sampling information is shown in Figure 1b.

In this study, in order to study the paleo-sedimentary environment and reservoir characteristics of the Benxi Formation shale, analysis has been conducted on the organic carbon content, the major elements, the trace elements, and the mineral composition. In addition, qualitative and quantitative observation and characterization of porosity system for typical samples has been done. Combined with the analyzing results of gas content test on onsite core samples from Well M-115, the potential of shale gas resources in the Benxi Formation has been analyzed.

The organic carbon content (TOC) was measured by the CS-230 carbon and sulfur analyzer. The organic carbon detection was based on GB/T19145-2003 with an analytical accuracy of ±0.5%. The mean random *Ro* values of shale samples were measured using a Zeiss Photoscope III microscope more than 25 readings were taken on each sample. Vitrinite were distinguished based on the dispersed particle occurrence of vitrinite. According to the vertical heterogeneity distribution characteristics of organic matter abundance, representative samples are selected to carry out analysis and testing of mineral composition, major elements, trace elements, and pore characteristics. The mineral composition of the whole rock is quantitatively analyzed by the Rigaku D/max-rA12KW rotating anode X-ray diffractometer (according to SY/T 6210-1996). The major element was analyzed by using X-ray fluorescence spectrometer of Axios PW4400/40. The trace element content is obtained by testing and analyzing the digested shale sample in an inductively coupled plasma mass spectrometry (ICP-MS) instrument. The shale reservoir characteristics are quantitatively analyzed by the ASAP 2020 low-temperature gas adsorption instrument, and the shale samples after argon ion polishing are qualitatively observed by scanning electron microscope (SEM).

4. Results and Discussion

4.1. Characteristics of Organic Matter in the Benxi Formation Shale

The organic matter abundance is an important geochemical index to measure the quality of black organic-rich shale to generate gas [15–18]. As an important part of the organic-rich shale, organic matter abundance provides a necessary material basis for shale gas resources [19,20]. The exploration and development practice shows that the total gas content of shale is positively correlated with TOC, indicating that the abundance of organic matter has a significant control effect on the gas content of shale [3,5,21,22]. Due to the great variations in the lithologies of the Benxi Formation, the vertical variation of organic matter abundance was relatively great, showing serious heterogeneity (Figure 2). The aluminous mudstone in Hutian Member is low in organic matter abundance, and TOC ranges from 0.15% to 0.59%, with an average of 0.4%. The abundance of organic matter in the black mudstone which is interbedded with the aluminous mudstone and the mud shale in the Pangou Member ranges from 0.46% to 8.97%, with an average of 2.69%. For the black shale of the Jinci Member, the TOC ranges from 0.81% to 5.33% with an average of 2.16%. The organic-rich mud shale of the Jinci Member is continuous in development as a whole, with a cumulative thickness of about 15 m. There are multiple sets of carbonaceous mudstone and coal seams that are interbedded with the organic-rich shale of the Jinci Member. Therefore, the abundance of organic matter is relatively high generally. The organic matter of the Benxi Formation was mainly Type III and Type II_2, with the characteristics of gas-generating parent material. Vitrinite reflectance (*Ro*) ranges from 1.5% to 1.7%, which is in the mature to high-mature stage. Generally, the shale has the basic geological conditions for shale gas accumulation.

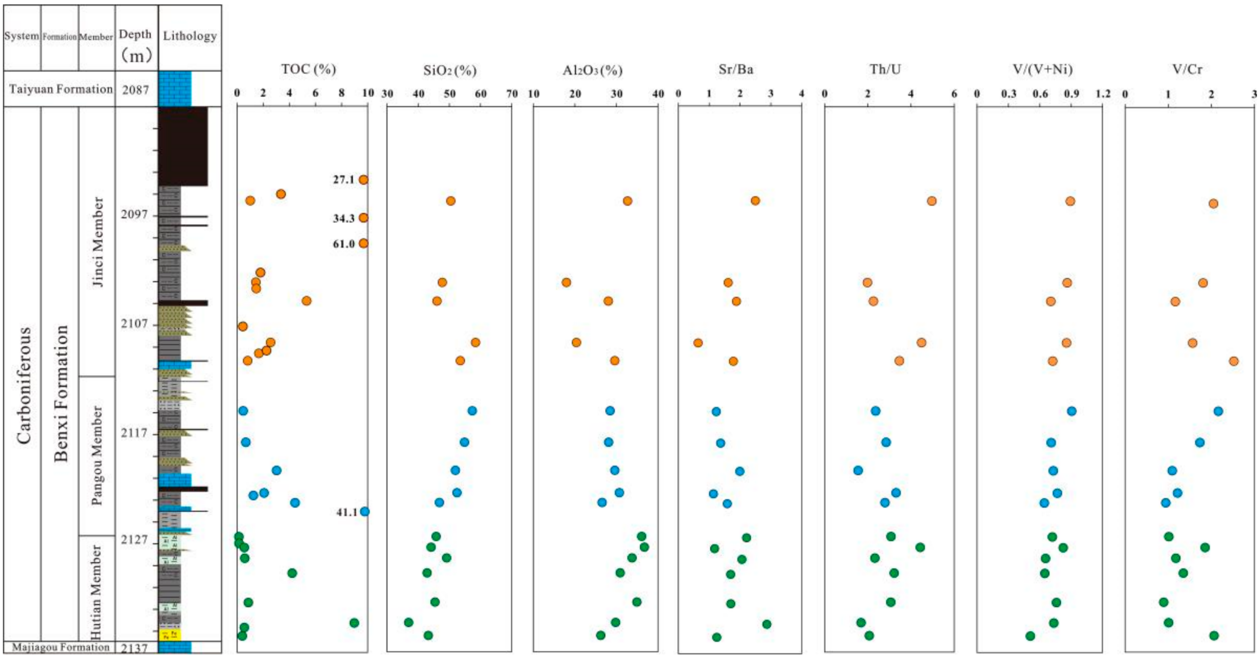

Figure 2. Vertical distribution characteristics of elemental geochemical parameters of the Benxi Formation shale.

4.2. Sedimentary Environment of the Benxi Formation Shale

Previous studies have shown that in the Benxi Formation in the eastern Ordos Basin, a barrier coastal sedimentary system is mainly developed, and shelf sedimentary system is developed locally [14,23]. The sedimentary system can be subdivided into several microfacies, including sand flat, mixed flat, mud flat, marl flat, barrier sand bars, lagoon mud, and mud continental shelf microfacies [16]. In the Hutian Member at the bottom of the Benxi Formation, iron-aluminum-bearing mudstone and shale is mainly developed, which are the initial deposits of the Late Paleozoic epeiric sea, and superimposed on the underlying Majiagou Formation, which has experienced 150 million years of exposure and denudation after the deposition of Majiagou Formation [23]. The sea water was low and shallow, and sometimes withdraws, resulting in the formation of ferrous layer, a product of multiple periods of deposition and denudation. The Pangou Member is composed of sandstone, limestone, shale, and thin-layered coal seams in marine-continental transitional facies, and it is the product of the tidal flat-shallow shelf environment after the formation of the basin by transgression. The sedimentary environment was sand bar-tidal flat deposition [14]. The biological composition includes fossils of marine and terrestrial animals and plants. There are abundant Fuzulinid fossils in the limestone. The Jinci Member is composed of Jinci sandstone and black shale at the bottom. It is composed of shale, carbonaceous mudstone, and coal. The black shale was mainly deposited in the depositional environment of lagoons and shallow continental shelf. Carbonaceous mudstone and the 8# coal seam at the top of the Jinci Member were deposited in coastal plain littoral swarm environment.

The organic-rich shale is usually rich in sulfur elements in various forms, including organic sulfur, sulfate, and pyrite. The occurrence and content of sulfur can indicate the depositional environment. The correlation between organic carbon and sulfur (sulfide or total sulfur) is an effective method for studying current and ancient sedimentary environments and diagenetic processes. Leventhal (1983) [24] explained the paleo-environment by studying the organic carbon-sulfur correlation of black shale in the Black Sea. According to the TOC/S ratios, the normal marine sedimentary environments with oxygen-bearing bottom water for benthic activities or biological disturbances can be distinguished, and the marine-continental environments such as swamps and offshore lacustrine basins, as well as non-marine sediments (low S content, high TOC/S ratio) can also be distinguished. The shale of the Benxi Formation generally is the marine sedimentary and transitional sedimentary environment, as shown in Figure 3a.

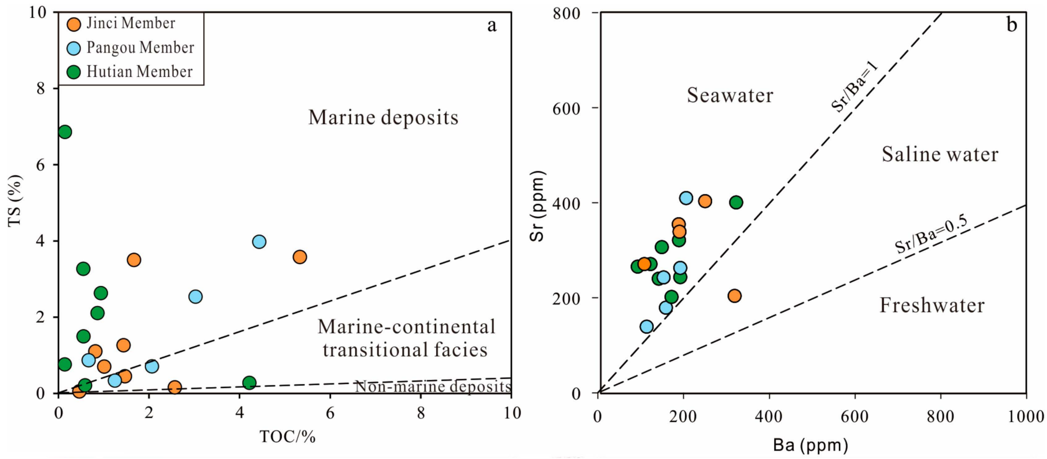

Figure 3. Identification of salinity of ancient water bodies for mud shale in the Benxi Formation. (**a**) Cross plot of total sulfur (TS) vs. total organic carbon (TOC), (**b**) Cross plot of Sr content vs. Ba content.

The preserved paleo-water salinity in sediments is also an important indicator reflecting the sedimentary environment in geological history. Previous studies have shown that the migration ability of Sr in natural waters is greater than that of Ba [25,26]. Because the solubility of Ba compounds is lower, with the increase in water salinity, Ba might precipitate in the form of insoluble $BaSO_4$. With the continuous increase in water salinity, Sr might continue to dissolve in the water until the salinity increased to a certain extent, and precipitation occurred. Ba was relatively enriched in nearshore sediments, and only a small amount entered into the open sea. While Sr was still enriched in pelagic sediments due to its high solubility and strong migration ability. Therefore, the Sr/Ba can be used as an indicator to distinguish paleo-salinity [25–28]. Deng et al. [25] proposed that when Sr/Ba > 1, 0.5–1.0, and <0.5, the salinity characteristics is sea water, saline water, and fresh water, respectively. The Sr/Ba of the shale samples of the Benxi Formation ranges from 0.64 to 2.87. The average Sr/Ba ratios of the Hutian, Pangou, and Jinci Members are 1.78, 1.46, and 1.68, respectively. The Sr/Ba of the Benxi Formation suggest marine water input during the depositional period of shales from the three members.

Redox change in the sedimentary environment is an important factor in controlling the development, burial, and preservation of paleo-productivity [29,30]. The trace elements, such as Ni, V, and U, are sensitive indicators of redox conditions of the paleo-sedimentary environment. Once the sedimentary environment changed, the abundance of these sensitive trace elements might also change accordingly. In an oxygen-depleted depositional environment, these trace elements might be abnormally enriched. The stronger the reduction of the depositional environment, the higher the enrichment of these elements. Some trace element abundance ratios, such as Th/U, V/Cr, V/(V + Ni), and Ni/Co [31,32], are often used to restore the redox conditions for paleo-sedimentary environment evaluation. It is theoretically based on the fact that one element is more enriched than the other in the reducing water environment. When Th/U < 2.0, it indicates an oxygen-deficient environment. When Th/U > 8, it indicates an oxidizing environment. When V/Cr < 2.0, it indicates an oxygen-rich environment. When V/Cr is in 2.0–4.25, it indicates an oxygen-deficient environment. When V/(V + Ni) > 0.84, it indicates a dynoxia environment with stratified water column. When V/(V + Ni) < 0.6, it indicates an oxygen-rich environment with weak stratification of water column. When the ratio is 0.6–0.84, it indicates an oxygen-deficient environment, with weak stratification of water column [31,32]. The sedimentary environment of the Benxi Formation shale is generally characterized by oxygen-deficient condition, as shown in Figure 4. Vertically, there is a slight difference in the redox index during the deposition of the Benxi Formation, with a trend of reducibility increasing in the profile upwardly.

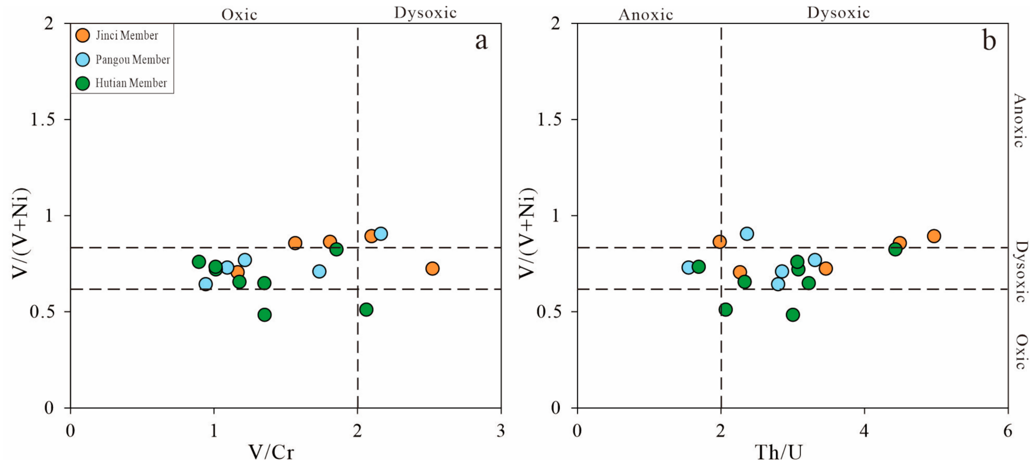

Figure 4. Redox environment of the Benxi Formation shale. (**a**) Cross plot of V/(V+Ni) vs. V/Cr, (**b**) Cross plot of V/(V+Ni) vs. Th/U.

4.3. Characteristics of Shale Reservoirs in the Benxi Formation

4.3.1. Distribution Characteristics of Brittle Minerals

There are evident differences in the mineral composition of different types of shale in the Benxi Formation. In general, the shale content of the Benxi Formation gradually increases in the downcore, while the clay minerals showed a gradual decrease (Figure 5). The iron-aluminum mudstone is developed in the Hutian Member, and the interbedded black shale is rich in clay minerals. The content of clay minerals ranges from 77.6% to 96.0%, with an average as high as 85.8%, while the content of quartz minerals was low, ranging from 2.3% to 17.2%, with an average of 7.1%. The content of clay minerals in the black shale developed in the Pangou Member ranges from 61.8% to 78.2%, with an average of 58.2%. The content of quartz minerals ranges from 21.8% to 37.1%, with an average of 27.6%. In the Jinci Member shale, the content of clay minerals ranges from 32.3% to 88.5%, and the content of quartz minerals ranges from 8.0% to 57.0%. The Jinci Member is very complex in lithological composition, and mainly contained black shale, carbonaceous mudstone, and coal seams. Compared with the carbonaceous mudstone, the black shale has a higher content of quartz minerals and a lower content of clay minerals. The vertical variation in the content of quartz and clay mineral in the Benxi Formation are consistent with that of Si and Al elements. In general, the Si content increases along the profile, while the content of Al, Ti, and other elements indicate decrease trend of mud input along the profile (Figure 2). It further confirms that the different types of mineral composition in the Benxi Formation shale have different distribution characteristics in the downcore.

The characteristics of mineral compositions in shale are important indicators to guide the exploration and development of shale gas. The higher the content of brittle minerals, such as quartz, feldspar, and pyrite, the more natural fractures with tree-like or network-like structures can be formed during later mining and fracturing. The seepage fractures are favorable for shale gas exploitation. The increase in clay mineral content made shale plasticity strengthen, which is not favorable for hydraulic fracturing [33]. The vertical variation of the brittle mineral content in the Benxi Formation is shown in Figure 5, which is basically consistent with the vertical variation of quartz minerals. The content of brittle minerals is lower in the bauxitic mudstone and black mudstone in the Hutian Member. The content of brittle minerals in shale is relatively high, and the content of brittle minerals in the carbonaceous mudstone of the Jinci Member is decreased. It can be seen from the triangle plot of brittle minerals (quartz + feldspar + pyrite)-clay minerals-carbonate minerals (Figure 6) that the Hutian Member is evidently rich in clay minerals, while the Jinci Member has a relatively high content of brittle minerals and black shales. The content of the brittle mineral of the rock samples is generally higher than 40%, which is comparable to the highly brittle shales from the Longmaxi Formation and Longtan Formation. A comprehensive comparison of the brittle mineral characteristics of the Benxi Formation shale indicates that the black shale in the Jinci Member has a higher content of brittle minerals and a higher brittleness index, which is favorable for fracturing and mining of shale gas.

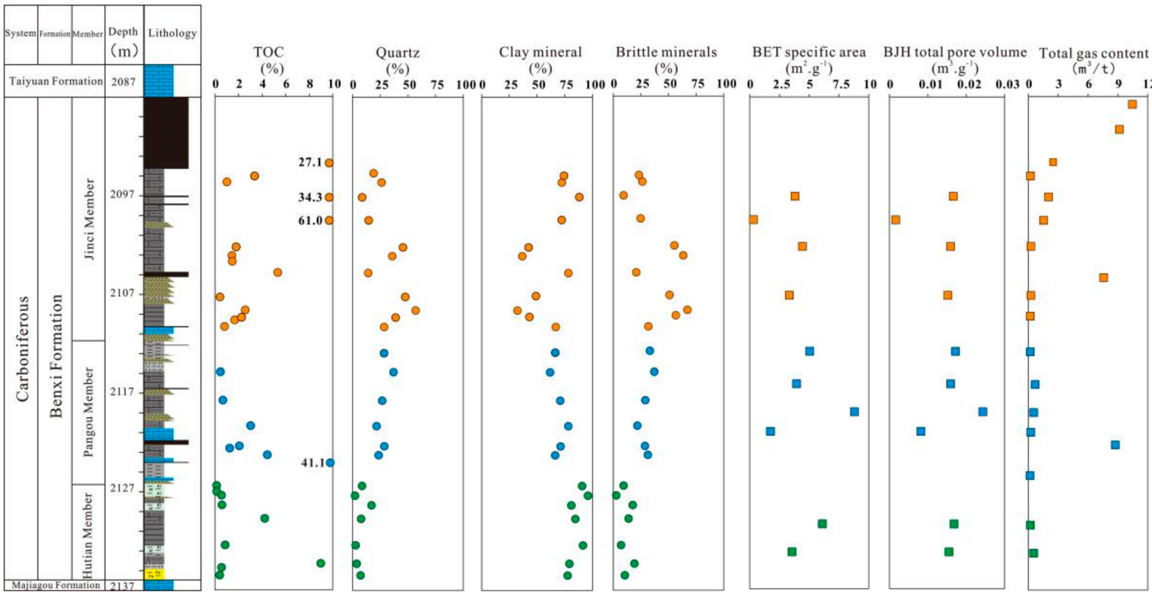

Figure 5. Vertical distribution characteristics of shale reservoirs and gas-bearing properties in the Benxi Formation.

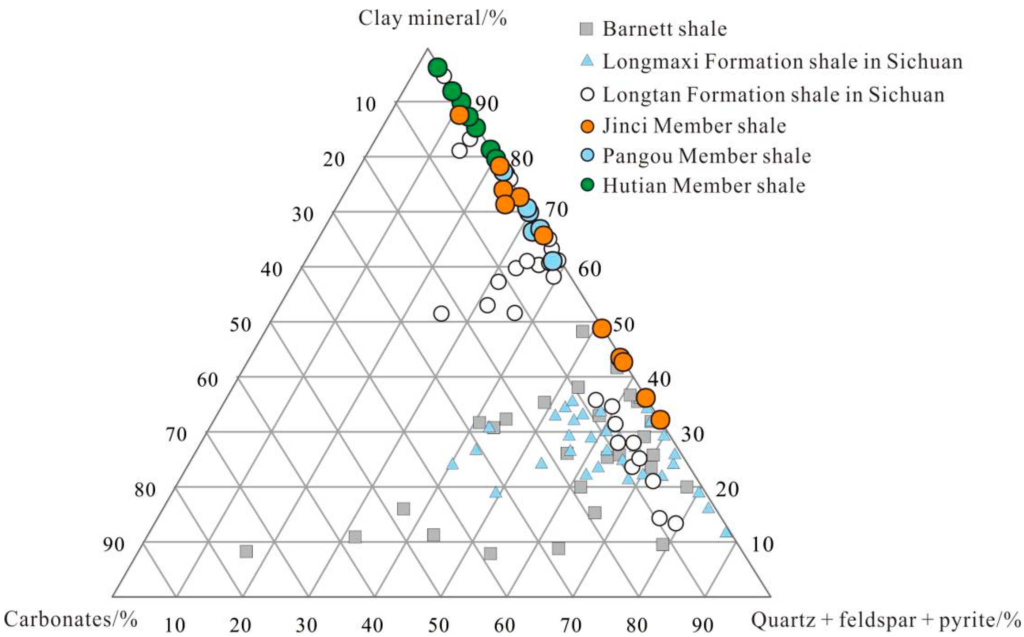

Figure 6. Triangular plot of the distribution of brittle minerals in the Benxi Formation shale.

4.3.2. Pore Development Characteristics

The reservoir characteristics of shale are important indicators for evaluating the potential of shale gas resources. Nano-scale pores are an important type of pores in shale reservoirs, which control the primary storage space of shale gas. The nano-scale pores of shale reservoirs are generally in the range of 5–100 nm, of which the micropores with a pore radius of about 10 nm carries substantial weight. Generally, pores smaller than 50 nm occupy most of the pores in shale [34,35]. The morphology of the "desorption loop" formed by the relative pressure changes 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 desorption loop. Nitrogen adsorption-desorption curves in different layers of the Benxi Formation are similar (Figure 7), reflecting similar pore types and maximum adsorption capacity of shale samples. Therefore, the pore development characteristics of shale are similar as well. The nitrogen adsorption-desorption curve of the Benxi Formation has similar characteristics to the H4 loop based on the IUPAC classification. The adsorption and desorption curves basically overlap in the low-pressure area. The adsorption curve showed no evident "inflection point" and was characterized by relatively flat and long extension, indicating that the pores of the Benxi Formation shale are dominated by slit pores.

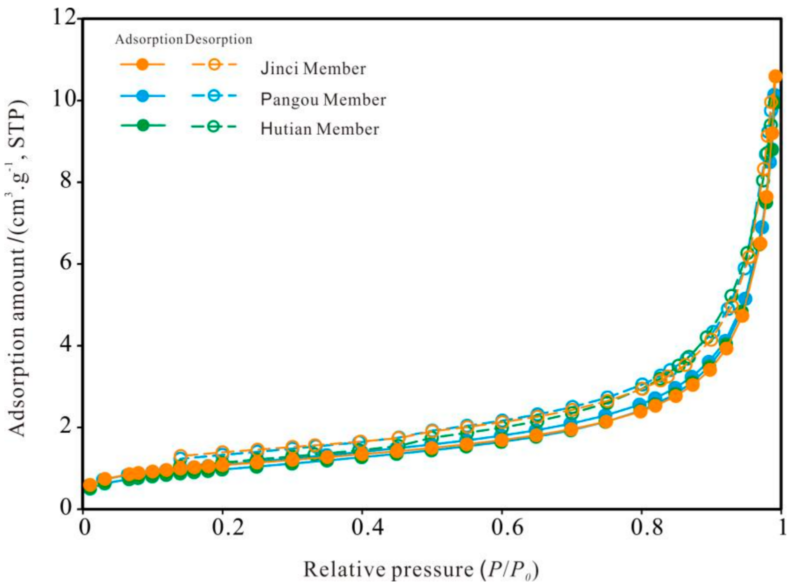

Figure 7. Nitrogen adsorption curve of the Benxi Formation shale.

The pore development characteristics of the shales in the three members of the Benxi Formation are relatively similar. The average pore volumes of the shale in the Hutian, Pangou, and Jinci members were 0.0162 m^3/g, 0.0191 m^3/g, and 0.0159 m^3/g, respectively; the pore-specific surface areas were, respectively, 4.83 m^2/g, 5.93 m^2/g, and 3.86 m^2/g (Figure 8). In terms of the contribution of pore volume, the contribution of pores of different types was relatively uniform, indicating similar contributions from varying pore types to free gas. The pores in 2–10 nm contribute the most to the specific surface area of pore, reflecting that the pores in the type provide more storage space for adsorbed gas (Figure 8).

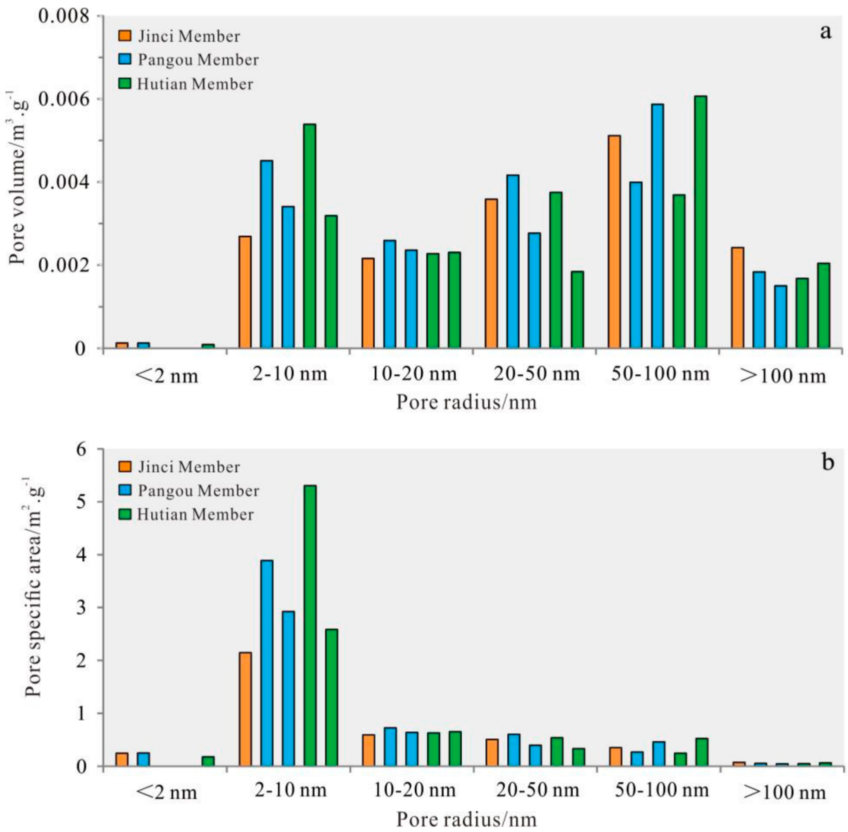

Figure 8. Distribution characteristics of pore volume (**a**) and pore specific surface areas (**b**) of the Benxi Formation shale.

The study results of scanning electron microscopy have shown that the pores of the shale in the Benxi Formation are dominated by inorganic mineral intergranular pores, intragranular pores, and micro-fractures (Figure 9), and organic pores are only developed in local organic matter. Organic matter pores are divided into two types: primary biogenic structural pores and organic-hosted pores generated during hydrocarbon generation. The morphology and development mechanism of the two types of organic matter pores are evidently different. These two types of organic pores can be observed on the surface of organic matter of the Benxi Formation shale. The primary organic-hosted pores, which are randomly distributed on the surface of organic matter, are characterized by varying shapes and sizes, such as round or slit shapes. The type of pore is related to the structure of inherited primitive organisms, as shown in Figure 9a,b. The organic matter pores produced during the hydrocarbon generation process, whether the hydrocarbon-generating materials in Type I/II or Type III, a large amount of gas will be generated due to the thermal maturation of organic matter, resulting in the generation of a large number of organic-hosted pores due to the rapid expansion of void pore space within organic matter. Therefore, most of them are regionally densely distributed on the surface of organic matter. The difference is that the pore size and porosity formed by different types of kerogens are evidently different. The organic matter pores of the Benxi Formation shale are visible on the surface of local organic matter, as shown in Figure 9c. The intergranular pores of inorganic minerals are dominated by elongated interlayer pores and dissolution pores of clay minerals (Figure 9e,f). The shrinkage fractures and micro-fractures of organic matter are mainly due to non-structural factors such as the expansion and contraction of rock volume, vertical gravity, or diagenesis [36]. The reason for the underdevelopment of organic pores in the Benxi Formation shale may be that the hydrocarbon generation process of Type III kerogen is carried out by the process of defunctionalization, which differs in the process of depolymerization and defunctionalization of Type I and II kerogens. The macromolecular structure of kerogen will not be damaged; therefore, the capacity to form organic pores is limited. Yang et al. [37] used the methane adsorption method to show that there are a large number of pores in the organic matter unidentifiable from the observation by SEM. By using the gas adsorption method, the pore size distribution was 0.3–0.4 nm, accounting for 87% and 13% of the total specific area and the total pore volume. At the same time, it was found by using the X-ray diffraction technique that the type of pore is mainly formed by the stacking of aromatic rings with average pore radius of 0.34 nm, which is consistent with that from the results from pore structure characterization by the nitrogen method.

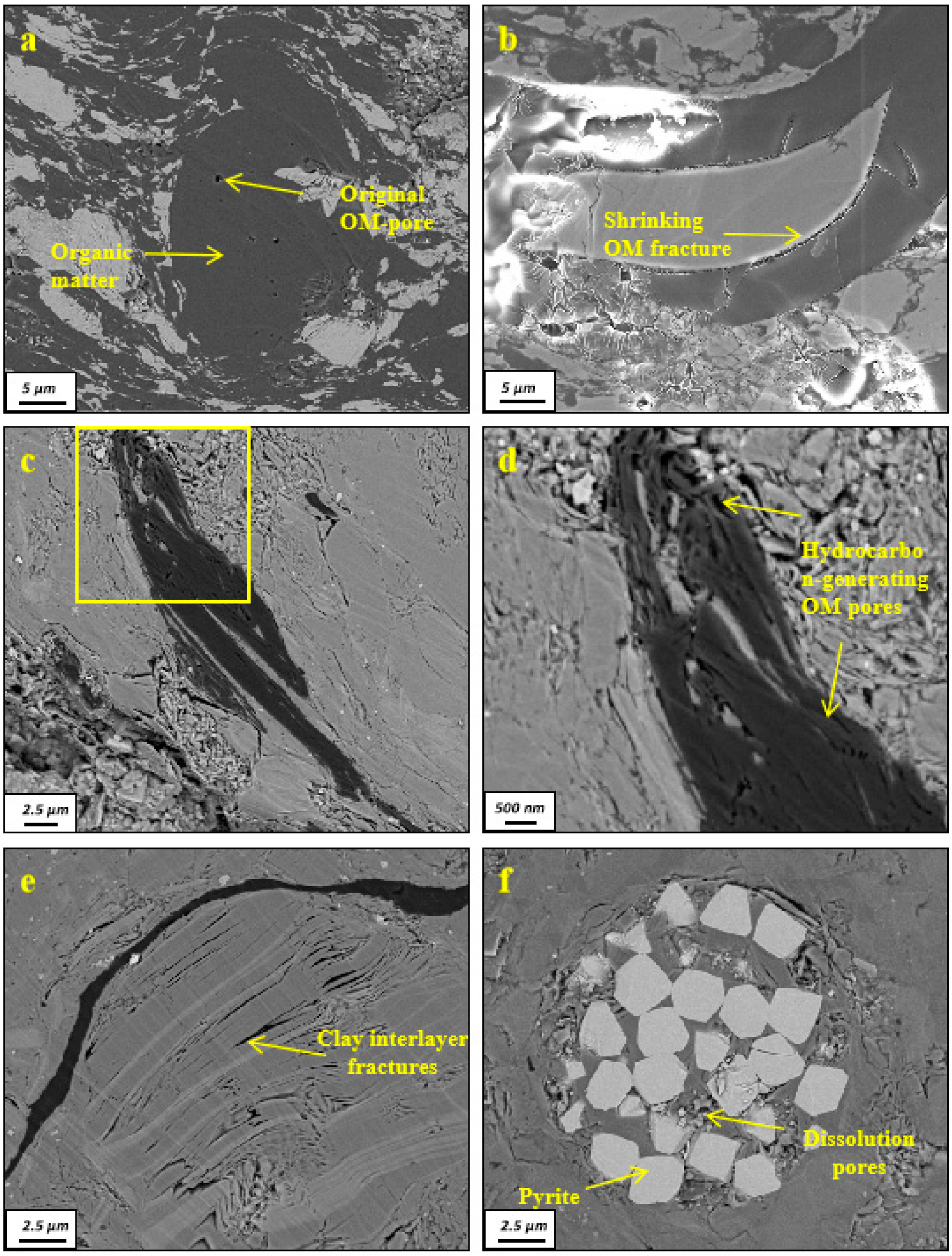

Figure 9. Scanning electron microscope microscopic characteristics of typical shale samples of the Benxi Formation. (**a**) Pores related to the structure of inherited primitive organisms; (**b**) shrinkage fractures and micro-fractures of organic matter; (**c**,**d**) Hydrocarbon generating organic matter pores; (**e**) clay interlayer fractures; (**f**) pyrite framboids and dissolution pores.

4.3.3. Discussion on the Shale Gas Potential of the Benxi Formation

Gas content is the most important parameter to evaluate the shale gas potential. The onsite desorption gas measurement results of typical samples from Well M-115 show that the shale gas content of Jinci Member is relatively high, ranging from 0.13 m^3/t to 2.48 m^3/t, with an average of 0.84 m^3/t. The Jinci Member contained multiple sets of coal seams, and the gas content of coal samples is as high as 7.61 m^3/t–10.45 m^3/t. The measured gas content of the mud shale in the Pangou and Hutian Members is lower than that of the Jinci Member, ranging from 0.16 m^3/t to 0.68 m^3/t, with an average of 0.39 m^3/t. In general, the shale gas content of the Jinci Member is evidently better than that of the Pangou and Hutian Members. The effect of shale gas development is controlled by gas-bearing properties, physical property conditions, mechanical properties, pressure and the fracturability, and the likes of shale reservoirs. The cumulative thickness of shale in the Jinci Member is relatively large and relatively high. The Jinci Member is a favorable interval for shale gas exploration in the Benxi Formation.

The Carboniferous Benxi Formation is not only an important horizon for gas sources in the Ordos Basin, but also has two large-scale sand bodies in the Pangou Member and Jinci Member. Previous exploration results have shown that the sandstones of the Jinci Member of the Benxi Formation generally contain gas, and the exploration potential of tight sandstone gas is great [12,14]. Commercial gas flow has been obtained in many wells, with the maximum open flow of 150×10^4 m^3/d, showing the good prospects for exploration of tight sandstone gas in the Benxi Formation in this area [38–40]. The tight sandstone gas source of the Benxi Formation mainly comes from the dark-colored coaly mudstone and coal seams [12,14,23]. The great breakthrough in oil and gas exploration of tight sandstone gas has also confirmed the great potential of dark-colored coaly mudstone in the Benxi Formation. The Benxi Formation shale in the Ordos Basin is characterized by high organic matter abundance and moderate maturity. In addition, the mudstone is interbedded with sandstone, which is favorable for the operation of shale fracturing. Therefore, the Benxi Formation is an important target for the exploration of shale gas in the marine-transitional facies in the Ordos Basin.

The marine-continental transitional facies shale gas is different from the marine facies in terms of reservoir distribution, mineral composition, organic matter type, burial depth, and pressure system. Therefore, the exploration evaluation and development methods of favorable shale gas intervals is also not the same. Different from the continuous development of marine organic-rich shale, the marine-continental transitional facies strata are evidently characterized by great variation in lithologies (the development of organic-rich shale, carbonaceous mudstone, coal, thin sandstone, and the likes in the shale interval) and thin single layer and great cumulative thickness of shale interval. Due to the small thickness of continuous distribution, the stability of regional distribution, relatively low content of brittle minerals, and high content of clay minerals generally contained in marine-continental transitional shale, the exploration potential of marine-continental transitional shale gas is not as good as that of marine shale gas. In the marine-continental transitional facies formation, there are multiple sets of interbeds of coal seams, carbonaceous mudstone, and organic-rich mudstone. The gas content of coal and carbonaceous mudstone is relatively high, which is equivalent to the highest-quality interval of marine shale gas. This diversity of lithology provides the material basis for the collaborative exploration and development of multiple gas types (shale gas, coalbed methane, and tight sandstone gas) in the future studies. At the same time, it also has considerable resource reserves of unconventional natural gas, which is an important target for future exploration and development of marine-continental transitional facies in Ordos Basin.

5. Conclusions

(1) In the Hutian, Pangou, and Jinci Members of the Benxi Formation, the organic-rich shale is well-developed, with an average organic matter abundance of more than 2.0%. Among them, the organic-rich shale of the Jinci Member is continuous in development, with

a cumulative thickness of about 15 m. There are many sets of carbonaceous mudstone and coal seams interbedded with organic-rich mud shale in the Jinci Member, and the organic matter abundance is relatively high generally. In terms of sedimentary environment, the sedimentary paleo-water bodies of the Benxi Formation are characterized by the input of seawater, and there is a slight difference in sedimentary redox index, with a trend of increasing reduction in the profile upwardly.

(2) In the Benxi Formation, the shale content increases gradually upward in the downcore, while the content of clay minerals decreases gradually. The black shale of the Jinci Member has a higher content of brittle minerals. The pore development characteristics of the three members of the Benxi Formation are similar, with small differences in pore volumes and pore-specific surface areas vertically. The pores are dominated by inorganic mineral intergranular pores, clay mineral interlayer fractures, and micro-fractures. The development of organic pores can be seen on the surface of organic matter.

(3) In the Jinci Member, the gas content of shale is higher than that of the Hutian Member and the Pangou Member, ranging from 0.13 m^3/t to 2.48 m^3/t. There are many sets of coal seams in the Jinci Member, with high gas content. In general, the shale of the Jinci Member has a large cumulative thickness, relatively high gas-bearing property, and is rich in brittle minerals. The Jinci Member is a favorable interval for shale gas exploration in the Benxi Formation. The collaborative exploration and development of various types of gas (shale gas, coalbed methane, and tight sandstone gas) in the marine-continental transitional facies is an important direction for unconventional natural gas development practice in the future.

Author Contributions: Conceptualization, W.Z., Z.W. and C.W.; methodology, W.Z.; software, H.Z.; validation, W.Z. and H.Z.; formal analysis, Y.L., L.Z., Y.X. and L.S.; investigation, C.W. and H.S.; resources, W.Z.; data curation, W.Z., Z.W., C.W., Y.L. and H.Z.; writing—original draft preparation, W.Z. and C.W.; writing—review and editing, Z.W.; supervision, Z.W.; project administration, W.Z.; funding acquisition, W.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Research Institute of Exploration and Development, PetroChina Changqing Oilfield, grant number 2020-151.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

References

1. Dong, D.Z.; Wang, Y.M.; Huang, X.N.; Zhang, C.C.; Guan, Q.Z.; Huang, J.L.; Wang, S.F.; Li, X.J. Discussion about geological characteristics resource evaluation methods and its key parameters of shale gas in China. *Nat. Gas Geosci.* **2016**, *27*, 1583–1601.
2. Zou, C.N.; Dong, D.Z.; Wang, Y.M.; Li, X.J.; Huang, J.L.; Wang, S.F.; Guan, Q.Z.; Zhang, C.C.; Wang, H.Y.; Liu, H.L.; et al. Shale gas in China: Characteristics, challenges and prospects (II). *Pet. Explor. Dev.* **2016**, *43*, 166–178. [CrossRef]
3. Jiang, Z.X.; Song, Y.; Tang, X.L.; Li, Z.; Wang, X.M.; Wang, G.Z.; Xue, Z.X.; Li, X.; Zhang, K.; Chang, J.Q.; et al. Controlling factors of marine shale gas differential enrichment in southern China. *Pet. Explor. Dev.* **2020**, *47*, 617–628. [CrossRef]
4. Jin, Z.J.; Bai, Z.R.; Gao, B.; Li, M.W. Has China ushered in the shale oil and gas revolution? *Oil Gas Geol.* **2019**, *40*, 451–458.
5. Qiu, Z.; Zou, C.N. Unconventional petroleum sedimentology: Connotation and prospect. *Acta Sedimentol. Sin.* **2020**, *38*, 1–29.
6. Wang, Z.G. Breakthrough of Fuling shale gas exploration and development and its inspiration. *Oil Gas Geol.* **2015**, *36*, 1–6.
7. Zhang, T.W.; Zhang, Y.J.; Jia, M.; Shao, D.Y.; Yan, J.P. Key science issues on controlling the variation of gas contents of Cambrian marine shales in southern China. Bulletin of Mineralogy. *Pet. Reochem.* **2018**, *37*, 572–579.
8. Zhao, W.Z.; Jia, A.L.; Wei, Y.S.; Wang, J.L.; Zhu, H.Q. Progress in shale gas exploration in China and Prospects for future development. *China Pet. Explor.* **2020**, *25*, 31–44.
9. Zou, C.N.; Zhao, Q.; Cong, L.Z.; Wang, H.Y.; Shi, Z.S.; Wu, J.; Pan, S.Q. Development progress, potential and prosprcts of shale gas in China. *Nat. Gas Ind.* **2021**, *41*, 1–14.

10. Kuang, L.C.; Dong, D.Z.; He, W.Y.; Wen, S.M.; Sun, S.S.; Li, S.X.; Qiu, Z.; Liao, X.W.; Li, Y.; Wu, J.; et al. Geological characteristics and development potential of transitional shale gas in the east margin of the Ordos Basin, NW China. *Pet. Explor. Dev.* **2020**, *47*, 435–446. [CrossRef]
11. Qiu, Z.; Song, D.; Zhang, L.F.; Zhang, Q.; Zhao, Q.; Wang, Y.; Liu, H.; Liu, D.; Li, S.; Li, X. The geochemical and pore characteristics of a typical marine-continental transitional gas shale: A case study of the Permian Shanxi Formation on the eastern margin of the Ordos Basin. *Energy Rep.* **2021**, *7*, 3726–3736. [CrossRef]
12. Li, J.; Zhang, C.L.; Jiang, F.J.; Pei, Y.; Wang, J.Y.; Wang, X.R.; Zhang, J.Q. Main factors controlling the enrichment of Upper Caiboniferous Benxi Formation tight gas in the Ordos Basin. *Nat. Gas Ind.* **2021**, *41*, 30–40.
13. Yu, X.H.; Wang, X.Z.; Wang, N.X.; Shan, X.; Zhou, J.S.; Han, X.Q.; Li, Y.L.; Du, Y.H.; Zhao, C.F. Sequence stratigraphic framework and sedimentary evolution characteristics of gas-bearing sandbody in the Upper Paleozoic in southeastern The Ordos Basin. *J. Palaeogeogr.* **2017**, *19*, 935–954.
14. Guo, S.B.; Wang, Y.G. Shale gas accumulation conditions and exploration potential of Carboniferous Benxi Formation in The Ordos Basin. *Acta Pet. Sin.* **2013**, *34*, 445–452.
15. Kontakiotis, G.; Karakitsios, V.; Cornée, J.; Moissette, P.; Zarkogiannis, S.D.; Pasadakis, N.; Koskeridou, E.; Manoutsoglou, E.; Drinia, H.; Antonarakou, A. Preliminary results based on geochemical sedimentary constraints on the hydrocarbon potential and depositional environment of a Messinian sub-salt mixed siliciclastic-carbonate succession onshore Crete (Plouti section, eastern Mediterranean). *Mediterr. Geosci. Rev.* **2020**, *2*, 247–265. [CrossRef]
16. Kontakiotis, G.; Karakitsios, V.; Maravelis, A.G.; Zarkogiannis, S.D.; Agiadi, K.; Antonarakou, A.; Pasadakis, N.; Zelilidis, A. Integrated isotopic and organic geochemical constraints on the depositional controls and source rock quality of the Neogene Kalamaki sedimentary successions (Zakynthos Island, Ionian Sea). *Mediterr. Geosci. Rev.* **2021**, *3*, 193–217. [CrossRef]
17. Vasiliev, I.; Karakitsios, V.; Bouloubassi, I.; Agiadi, K.; Kontakiotis, G.; Antonarakou, A.; Triantaphyllou, M.; Gogou, A.; Kafousia, N.; de Rafélis, M.; et al. Large sea surface temperature, salinity, and productivity—Preservation changes preceding the onset of the Messinian Salinity Crisis in the Eastern Mediterranean Sea. *Paleoceanogr. Paleoclimatol.* **2019**, *34*, 182–202. [CrossRef]
18. Peters, K.E.; Walters, C.C.; Moldowan, J.M. The biomarker guide. In *Biomarkers and Isotopes in Petroleum Exploration and Earth History*, 2nd ed.; Cambridge University Press: Cambridge, UK, 2005.
19. Neruchev, S.G.; Wassoevich, N.B.; Lopatin, N.V. On the scale of catagenesis in connection with oil and gas formation. In Proceedings of the XV Session of the International Geological Congress, Reports of Soviet Geologists, Greifswald, Germany, 15–27 October 1983; pp. 47–62.
20. Jarvie, D.M. Shale resource systems for oil and gas: Part 2—Shale-oil resource systems. In *Shale Reservoirs—Giant Resources for the 21st Century: AAPG Memoir 97*; Breyer, J.A., Ed.; AAPG: Tulsa, OK, USA, 2012; pp. 89–119.
21. Guo, X.S.; Hu, D.F.; Wen, Z.D.; Liu, R.B. Major factor controlling the accumulation and high productivity in matine shale gas in the Lower Paleozoic of Sichuan Basin and its periphery: A case study of the Wufeng-Longmaxi Formation of Jiaoshiba area. *Geol. China* **2014**, *41*, 893–901.
22. Tissot, B.; Velte, D. The fate of organic matter in sedimentary basins: Generation of oil and gas. In *Formation and Distribution of Oil*; Mir, M., Ed.; Springer: Berlin/Heidelberg, Germany; New York, NY, USA, 1981; p. 501.
23. Li, Y.; Zhang, J.W.; Li, J.; He, J.; Sun, G.M.; Qiao, Y.L. A study on sedimentary microfacies of Benxi Formation and its Controlling Effect on gas enrichment in Yanchang district of The Ordos Basin. *Northwestern Geol.* **2014**, *47*, 216–222.
24. Leventhal, J.S. An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. *Geochim. Cosmochim.* **1983**, *47*, 133–137. [CrossRef]
25. Deng, H.W.; Qian, K. *Sedimentary Geochemistry and Environmental Analysis*; Gansu Science and Technology Press: Lanzhou, China, 1993; pp. 30–50.
26. Zheng, R.C.; Liu, M.Q. Study on Palaeosalinity of Chang-6 oil reservoir set in The Ordos Basin. *Oil Gas Geol.* **1999**, *20*, 20–25.
27. Zhang, L.F.; Dong, D.Z.; Qiu, Z.; Wu, C.J.; Zhang, Q.; Wang, Y.M.; Liu, D.X.; Deng, Z.; Zhou, S.W.; Pan, S.Q. Sedimentology and geochemistry of Carboniferous-Permian marine-continental transitional shales in the eastern The Ordos Basin, North China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2021**, *571*, 110389. [CrossRef]
28. Zhang, L.F.; Zhao, Q.; Peng, S.Z.; Qiu, Z.; Feng, C.J.; Zhang, Q.; Wang, Y.M.; Dong, D.Z.; Zhou, S.W. Paleoenvironment and Organic Matter Accumulation Mechanism of Marine–Continental Transitional Shales: Outcrop Characterizations of the Carboniferous–Permian Strata, Ordos Basin, North China. *Energies* **2021**, *14*, 7445. [CrossRef]
29. Algeo, T.J.; Kuwahara, K.; Sano, H.; Bates, S.; Lyons, T.; Elswick, E.; Hinnov, L.; Ellwood, B.; Moser, J.; Maynard, J.B. Spatial variation in sediment fluxes, redox conditions, and productivity in the Permian-Triassic Panthalassic Ocean. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2011**, *308*, 65–83. [CrossRef]
30. Algeo, T.J.; Liu, J.S. A re-assessment of elemental proxies for paleoredox analysis. *Chem. Geol.* **2020**, *540*, 119549. [CrossRef]
31. Hatch, J.R.; Leventhal, J.S. Relationship between inferred red-ox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, USA. *Chem. Geol.* **1992**, *99*, 65–82. [CrossRef]
32. Jones, B.J.; Manning, A.C. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancientmudstones. *Chem. Geol.* **1994**, *111*, 111–129. [CrossRef]
33. 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]

34. 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]
35. Loucks, R.G.; Reed, R.M.; Ruppel, S.C.; Jarvie, D.M. Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale. *J. Sediment. Res.* **2009**, *79*, 848–861. [CrossRef]
36. Wang, R.Y.; Ding, W.L.; Gong, D.J.; Zeng, W.T.; Wang, X.H.; Zhou, X.H.; Li, A.; Xiao, Z.K. Devolopment characteristics and major controlling factors of shale fractures in the Lower Cambrian Niutitang Formation, southeastern Chongqing-northern Guizhou area. *Acta Pet. Sin.* **2016**, *37*, 832–845.
37. Yang, C.; Xiong, Y.Q.; Zhang, J.C.; Liu, Y.K.; Chen, C. Comprehensive Understanding of OM-Hosted Pores in Transitional Shale: A Case Study of Permian Longtan Shale in South China Based on Organic Petrographic Analysis, Gas Adsorption, and X-ray Diffraction Measurements. *Energy Fuels* **2019**, *33*, 8055–8064. [CrossRef]
38. Fu, J.H.; Duan, X.W.; Xi, S.L. Characteristics of Upper Paleozoic gas reservoirs in The Ordos Basin. *Nat. Gas Ind.* **2000**, *20*, 16–19.
39. Yang, H.; Xi, S.L.; Wei, X.S.; Li, Z.H. Evolution and natural gas enrichment of multicycle superimposed basin in The Ordos Basin. *Pet. Geol.* **2005**, *17*, 18–24.
40. Zhou, J.S.; Zhao, Q.; Yin, X. Sedimentary charicteristics if Carboniferous Benxi Formation, southeastern The Ordos Basin. *Nat. Gas Explor. Dev.* **2012**, *36*, 12–16.