

# Study of shale reservoir nanometer-sized pores in Member 1 of Shahejie Formation in JX area, Liao Zhong sag

Yong Cheng<sup>1</sup>, Yu Zhang<sup>2</sup> and Yiming Wen<sup>1,3</sup>

<sup>1</sup> Mining Engineering Faculty, Kunming Metallurgy College, 388 Xuefu Road, Wuhua District, Kunming 650033, Yunnan Province, PRC;

<sup>2</sup> Foreign Languages Faculty, Kunming Metallurgy College, 388 Xuefu Road, Wuhua District, Kunming 650033, Yunnan Province, PRC.

<sup>3</sup> yimingwen-kmmc@foxmail.com

**Abstract.** The microscopic pore structure is the key of the shale reservoir study; however, traditional Scanning Electron Microscopy (SEM) methods cannot identify the irregular morphology caused by mechanical polishing. In this work, Scanning Electron Microscopy combined argon ion polishing technology was taken to study the characteristics of shale reservoir pores of Member 1 of Shahejie Formation (E<sub>3</sub>s<sup>1</sup>) located in JX1-1 area of Liao Zhong Sag. The results show that pores between clay platelets, intraplatelet pores within clay aggregates and organic-matter pores are very rich in the area and with good pore connectivity, so these types of pores are of great significance for oil-gas exorption. Pores between clay platelets are formed by directional or semi-directional contact between edge and surface, edge and edge or surface and surface of laminated clay minerals, whose shapes are linear, mesh, and irregular with the size of 500 nm to 5  $\mu$ m. The intraplatelet pores within clay aggregates are formed in the process of the transformation and compaction of clay minerals, whose shapes are usually linear with the width of 30 to 500 nm and the length of 2 to 50  $\mu$ m. The organic-matter pores are from the process of the conversion from organic matters to the hydrocarbon under thermal evolution, whose shapes are gneissic, irregular, pitted and elliptical with the size of 100 nm to 2  $\mu$ m. This study is of certain guiding significance to selecting target zones, evaluating resource potential and exploring & developing of shale gas in this region.

## 1. Introduction

The increasing requirement for energy and the sustained consumption of conventional oil and gas has rendered the supply-demand problem ever critical. The objects of oil-gas exploration and development as a result, inevitably tend to be unconventional ones [1]. Shale gas is one of the unconventional hydrocarbon resources, which is clean and green. It owns great potential under the current technological conditions [2, 3]. In contrast to conventional reservoirs [4, 5], shale reservoirs has developed lots of nanometer-sized pores who are the reservoir spaces of shale gas and its flow channels. It is featured by the much smaller pore diameter and more complicated geometrical morphology, distribution, genetic mechanism and controlling factors [6]. Therefore, how to characterize the nanometer-sized pores has been one of the vital questions in shale reservoir studies [7].

At present, studies on shale reservoir pores generally focus on either quantitative analysis method or qualitative analysis method [8]. In the studies with quantitative investigation, technologies applied include Mercury Injection Capillary Pressure (MICP), nitrogen adsorption, carbon dioxide absorption, Porosity Measurement by helium, Nuclear Magnetic Resonance (NMR), Small Angle Scattering



(SAS), etc. These methods could be used to make quantitative analysis of shale pore porosity, pore size distribution and specific surface area; however, the openings can only be done indirectly, and the experiment results could be affected by sample grain sizes. On the other hand, technologies for the qualitative studies of shale reservoir pores are Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), Transmission Electron Microscope (TEM), Field Emission Scanning Electron Microscope (FE-SEM), Focused Ion Beam Scanning Electron Microscope (FIB-SEM) and other micro-region analysis techniques, in which the mineral composition and pores of shale could be observed directly. The uneven natural plane of fracture of shale and limitation from depth of focus however, may make it difficult to observe the original pore structure of shale. Thus, the experiment results could be also affected by mechanical polishing in the process of which a great deal of artificial fractures and pores may appear [9]. In this case, argon-ion polishing technique can be applied to bombard the sample surface with high-speed ion beam to polish the coarse surface and make it flat fairly enough [10]. Combined with Field Emission Scanning Electron Microscopy (FE-SEM) with higher magnification, the observation of nanometer-sized pores in shale reservoirs can be finally achieved [11].

Liaozhong sag is the second richest oil-gas area after Bozhong sag in the Bohai Bay Area, whose organic-rich shales mainly develop in Member 3 of Shahejie Formation ( $E_2s^3$ ), Member 1 of Shahejie Formation ( $E_3s^1$ ) and Member 1 of Dongying Formation ( $E_3d^1$ ). Studies on shale gas in Liaozhong sag, however, are still scarce in number so far. Therefore, the current study aimed to analyze the characteristics of shale reservoir pores of  $E_3s^1$  located in JX1-1 area of Liaozhong sag with argon ion polishing scanning electron microscopy. The type, geometrical shape, connectivity, size, generic mechanism and geological significance of the pores were analyzed systematically. This study may give insight to the selection of shale gas exploration, resource potential evaluation, exploration and development in this region.

## 2. Experimental method

The samples come from the shale in  $E_3s^1$  located in JX1-1 area of Jinxian County, Liaozhong sag. The sampling depth of JX1-1-1 well and JX1-1E-2 well are 2925.93m and 1778.34m respectively. The instruments used are GATAN PECS II 685 and Quanta 250 FEG FE-SEM. The microscopic examination of the rocks was taken to the relatively flat and smooth rocks polished with PECS II 685. When the sample loading and unloading were undertaken by an apparatus through a specially designed sampling tool in the vacuum chamber, the sample surface would not be exposed to the atmosphere, and then the sample to be polished could be processed. In the study, the sample surface was polished by two wide beam argon ion beams, and the high-quality samples were then obtained. At the same time, sputtering by the two ion guns to the target material could be used to deposit conductive metal film of samples to prevent the charge effect in the electron microscope. Then, the high quality samples were observed and analyzed with Quanta 250 FEG FE-SEM.

## 3. Results

This article has referred to the classification schemes of Loucks [6], Yu Bingsong [11] and Zhang Qin [7], and classified the shale pores in JX1-1 area of Liaozhong sag into three types as follows.

### 3.1. Interparticle pores

Interparticle pores are rich in young or shallow strata, and usually have good connectivity to form porous networks with better permeability. The pore size and effectiveness will decrease with the increase of overburden pressure, burial depth and diagenesis. At the time of sedimentation, interparticle pores were developed both in soft or plastic particles (clay flakes, mud shavings, dung pellets, organic matter, etc.) and hard or brittle particles (quartz, feldspar, autogenous pyrite, biological detritus, etc.). In the process of burial, the plastic particles can deform and close interparticle pore space, and even squeeze into the early interparticle pores, reducing the reservoir space and its permeability. Under the influence of compaction and cementation, the size and volume of interparticle

pores in older and deeper shale rocks were significantly reduced. Through scanning electron microscope, it was found that the types of interparticle pores in E<sub>3</sub>s<sup>1</sup> of Liao zhong sag are as follows.

**Pores between rigid grains:** These pores are formed by the mutual support of the rigid grains, and are actually the residual pore space between the grains after compaction and cementation. It is mainly developed between rigid grains such as quartz and feldspar (Figure 1, a). Particles of different shapes and mechanical strengths may result in different pore shapes, and among which most are of triangular, polygonal and slit-shaped, etc. The pore size is generally between 300nm to 4μm.

**Pores between granular clay minerals:** In the process of diagenesis, the clay minerals, due to their own mechanical instability, are easy to be broken and form some clay debris in the compaction process, and then stack together with pores among the clay debris (Figure 1, b). The shapes are generally irregular with narrow slits. This kind of pores varies greatly in the range, whose width is generally between 40nm to 4μm and the length is generally between 1μm to 10μm.

**Pores at the edge of rigid grains:** Because of the hardness difference between rigid mineral grains and clay minerals, rigid mineral grains can prevent the compaction of plastic particles around them as the compaction effect is strengthened. Being resisted by rigid grains, some pores are developed on the contact surface of the rigid grains surrounded by many plastic particles (Figure 1, c), which are linear, generally of 100nm to 1μm wide and 2μm to 8μm long.

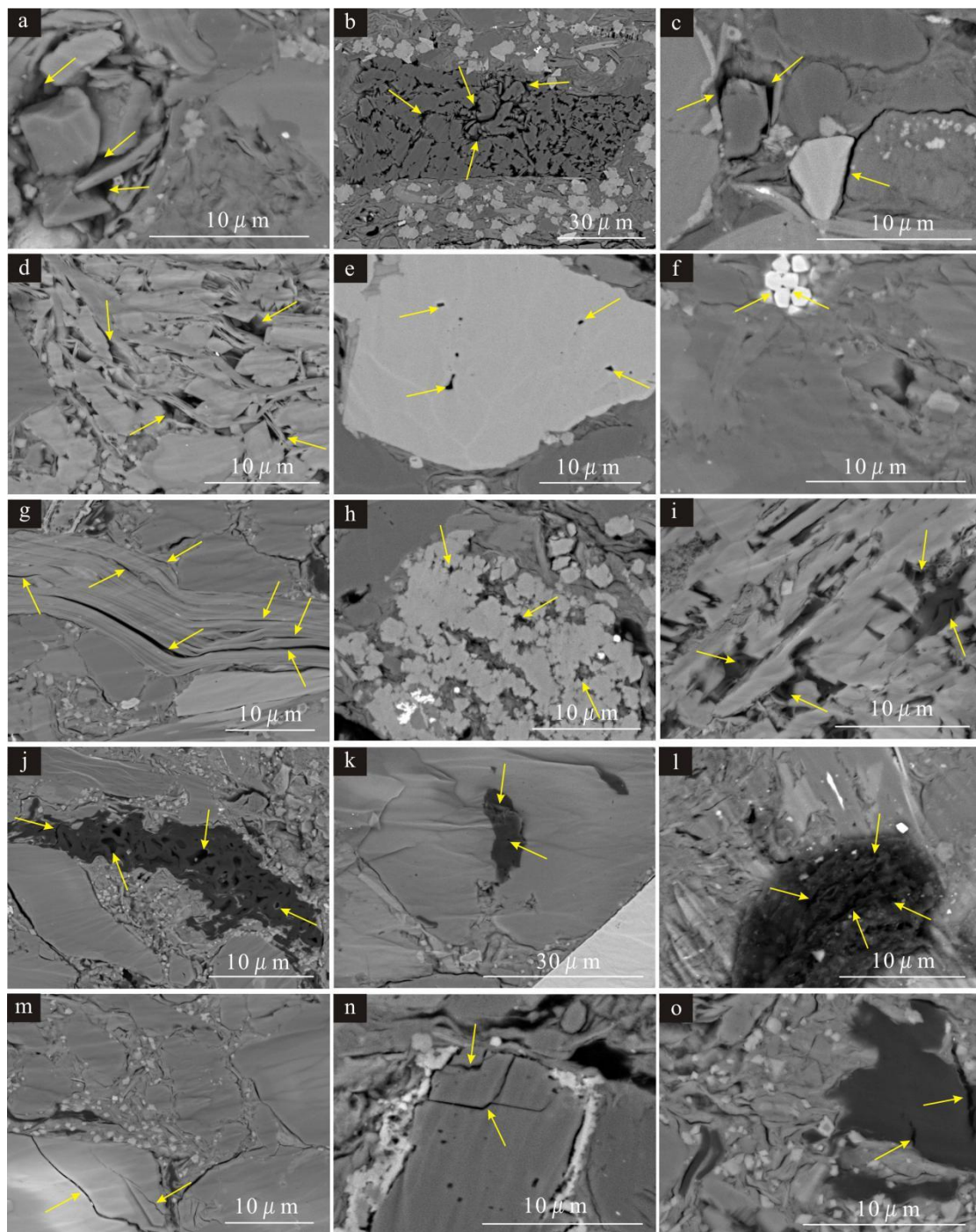
**Pores between clay platelets:** In shale, the clay minerals are mainly montmorillonite, illite and other silicate minerals, which are formed by the oxygen-silicon tetrahedron and can form relatively large clay platelets. The flaky clay minerals can form a so-called “paper house structure” through the directional or semi-directional contact between edge and surface, edge and edge, or surface and surface. This kind of pores are developed in the bedding layer, which is characterized by narrow linear pores, mesh pores and irregular pores, and the pore size distribution of which is of 500 nm to 5μm (Figure 1, d). This kind of pores is greatly developed and serves to be the main storage space of shale gas in this area.

### 3.2. *Intraparticle pores*

Intraparticle pores are those developed in the interior of grains. Quite few are originally developed and the majorities are formed by diagenetic transformation. Through SEM observation, the types of intraparticle pores are as follows.

**Pores within rigid grains:** It refers to the pores inside the rigid grains such as quartz, feldspar and carbonate rock. In the diagenetic process, with the change of the temperature and pressure of the diagenetic environment, under the influence of demineralization of ground water, air and kerogen, mineral particles are dissolved and then form the pores from the surface to the interior of the grains. In the study area, the inner pores of rigid grains are less developed, whose shape are generally rhombic and square, and the ones with smaller pores are triangular, elliptical or suborbicular (Figure 1, e). The pores concentration is within hundreds of nm, and few can reach the size of 1~2μm. This is because the dissolution degree is low, the dissolved pores are basically isolated, and its connectivity is poor.

**Intercrystalline pores within pyrite framboids:** Usually shale is developed in the quiet and weak reducing environment of water body and this kind of pores are very common in the dark shale. In this case, the intercrystalline pore within pyrite framboids is one of the most common pore types in shale gas reservoirs. The pyrite crystals are often gathered into strawberry-like aggregates, and the single pyrite crystal in the aggregates is cubic, octahedron, pyritohedron, which develops in the clay-mineral grains, inside the clay aggregates, or within the organic matters (Figure 1, f). The quantity of the pore is common. The developmental situation of Intercrystalline pores within pyrite framboids is affected by the size, shape, structure and relationship of the micro-crystal grains and the existing state of the clay minerals or organic matter around the pyrite aggregate. Intercrystalline pores within pyrite framboids in clay minerals are usually triangular or rhombic in shape and develop between the skeletons of several tiny crystals. The pore size is 100nm to 1μm. The ones within the clay aggregate or organic-matter are relatively small with the size of 1 to 100nm.



**Figure 1.** Scanning electron microscopic images of shale reservoir pores.

a) Pores between rigid grains, JX1-1E-2 Well; b) Pores between granular clay minerals, JX1-1-1 Well; c) Pores at the edge of rigid grains, JX1-1-1 Well; d) Pores between clay platelets, JX1-1E-2 Well; e) Dissolved pores within quartz grains, JX1-1-1 Well; f) Intercrystalline pores within pyrite framboids, JX1-1E-2; g) Intraplatelet pores within clay aggregates, JX1-1E-2 Well; h) Intercrystalline pores within siderite framboids, JX1-1-1 Well; i) Organic-matter pores of pitted or slit-shaped, JX1-1E-2 Well; j) Gneissose organic-matter pores, JX1-1-1 Well; k) Suborbicular organic-matter pores, JX1-1E-2 Well; l) Irregular organic matter pores, JX1-1-1 Well; m) Biggish fracture pores within quartz grains, JX1-1E-2 Well; n) Fracture pores within quartz grains, JX1-1-1 Well; o) Fracture pores within organic-matter, JX1-1-1 Well.



**Intraplatelet pores within clay aggregates:** The clay mineral has low hardness and poor chemical stability. Affected by its own transformation and compaction, a large amount of intraplatelet pores within clay aggregates have been developed in the shales. For instance, in the process of dewatering and translating of illite smectite mixed layer into illite, the spacing of its own layered silicate skeleton increases and makes the pores more developed. In the case of strong compaction, the illite smectite mixed layer is characterized by a structure of slit, and it is not good for the development of pores. Then the pores appear to be linearly fractured pores. This kind of pores is widely distributed in the study region, whose width is generally from 30 nm to 500 nm, and the length from 2 $\mu$ m to 50 $\mu$ m. This type of pores is featured with good connectivity, and they are important permeating channels of shale gas (Figure 1, g).

**Intercrystalline pores within siderite framboids:** In JX1-1-1 well, it was found a large number of irregular granular siderite aggregates (Figure 1, h). At the stage of diagenesis,  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  under the reducing action of organic matters; Thus, siderite is generated through the chemical combination of  $\text{Fe}^{2+}$  with  $\text{CO}_2$  produced by organic matter decomposition. Shape of this kind of pore is irregular, whose general size is of 1 $\mu$ m to 10 $\mu$ m.

### 3.3. Organic-matter pores

Organic-Matter pores are the pores in the organic matters, which are formed in the process of the burial and maturation of organic matter. The study has found that when vitrinite reflectance ( $R_o$ ) was less than 0.6%, organic pores were not developed or very few in number. And only when  $R_o$  reached about 0.6% or more, organic pores began to develop, and this is precisely the beginning of the peak of oil generation. The organic-matter pores often appear solitary in two-dimensional plane, but they are connected with each other in three dimensional space. However, not all types of organic matters are easy to form organic pores. According to the current limited research data, type II kerogen is easier to form organic pores than type III kerogen. The study area is rich in organic-matter pores, with the shape of concave pits (Fig 1, i), gneiss (Figure 1, j), ellipse (Figure 1, k) and irregular (Figure 1, l). Usually the size of organic-matter pores is between 100nm ~2 $\mu$ m.










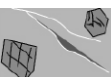

### 3.4. Fracture pores

Fractures are very important to the shale with low porosity and permeability. It not only provides the space to adsorption and storage of shale gas resource, but also is the most effective migration channel of hydrocarbon. Therefore, it plays a very important role in hydrocarbon production. The development of fractures then, often directly affects the quality of shale reservoir. Most of the fractures in shale reservoir are formed by the non-tectonic formation of clay minerals dehydration or hydrocarbon pressurization. High content of quartz, organic carbon and thin shale are favorable to the formation of the fractures. Fractures in the research area however, are not very well-developed with low extensibility. Fractures developed mainly in quartz and other rigid grains are mostly in nearly-parallel distribution. Some may cut through the rigid mineral grains, and some are only inside grains, with the length of 3 $\mu$ m to 20 $\mu$ m, and width of 100nm to 500nm (Figure 1, m, n). Fractures in organic-matters are the tiny fractures formed due to hydrocarbon expulsion and shrinkage effect of organic matters resulted from hydrocarbon generation and evolution of shales (Figure 1, o). The fracture sizes are different, and the width scale is generally of 100nm to 500nm, the length is generally 1 $\mu$ m to 10 $\mu$ m. But some can form large fractures with several  $\mu$ m wide, and dozens of  $\mu$ m long. The connectivity of fractures also varies a lot: while some cut through organic-matters and are connected with the surrounding pores, others only develop partially.

## 4. Discussion

Based on the observation above, the current study has analyzed the pore types, pore shapes, pore size ranges, their genesis mechanisms and development conditions (Table 1). The results have shown that pores between clay platelets, intraplatelet pores within clay aggregates and organic-matter pores are very rich in the research area. The genesis mechanisms are discussed as follows:

**Table 1.** Classification of pore types and characteristics of the containing shale.

		Pore type	Shape	Schematic	Size	Genetic Mechanism	Quantity
Mineral matrix pores	Interparticle pores	Pores between rigid grains	Triangular, polygonal, or slit-shaped		300nm~4μm	Residual pore space between grains after compaction and cementation	Common
		Pores between granular clay minerals	Irregular or slit-shaped		40nm~4μm wide, 1~10μm long	Pores between clay debris from fragments of clay minerals	Sparse
		Pores at the edge of rigid grains	Linear		100nm~1μm wide, 2~8μm long	Rigid mineral grains preventing the compaction of the surrounding plastic particles	Common
		Pores between clay platelets	Linear, mesh, or irregular		500nm~5μm	Formed by directional or semi-directional contact between edge and surface, edge and edge, or surface and surface of slit-shaped clay minerals.	Abundant
	Intraparticle pores	Pores within rigid grains	Rhombic, square, or suborbicular		200nm~2μm	Dissolution with the change of temperature, pressure and other factors in the diagenetic environment	Sparse
		Intercrystalline pores within pyrite framboids	Alveolate		100nm~1μm	Between skeletons of tiny crystals in autogenous pyrites	Common
		Intraplatelet pores within clay aggregates	Fissuriform, cambered		30~500nm wide, 2~50μm long	Transformation and compaction of clay minerals aggregates	Abundant
		Intercrystalline pores within siderite framboids	Irregular		1~10μm	Formed by chemical combination of Fe <sup>2+</sup> reduced from Fe <sup>3+</sup> with the CO <sub>2</sub> produced by organic matter decomposition	Common
	Organic-Matter pores		Gneissic, pitted, suborbicular, irregular		100nm~2μm	Organic pores formed in kerogen during burial and maturation of organic matters	Abundant
	Fracture pores	Fracture pores within rigid grains	Nearly-parallel		100~500nm wide, 3~20μm long	Dehydration of clay minerals or formation of hydrocarbon pressurization	Sparse
		Fracture pores within organic matter	Nearly-parallel		100~500nm wide, 1~10μm long	Hydrocarbon expulsion and shrinkage effect of organic matters after hydrocarbon generation and evolution	Common

The Bohai Bay Cenozoic Basin is generally considered as continental rift basins [12], and the sedimentary period of E<sub>3</sub>s<sup>1</sup> is in the thermal subsidence stage after the first rifting where the tectonic activity was weakened in relative prophase. The depositional system of braided river delta and fan delta were mainly developed in the lake basin by the influence of paleo-topography and paleo-

structure, which was widely extended from the both east and west sides to the inner basins. Jinxian County in Liaozhong sag is a depocenter with semi-deep and deep lake environment. Here has deposited a set of oil shale and dark mudstone stratum with a thickness exceeding 100m [13, 14]. Therefore, compared with the marine shale, the near-source continental shales have lower compositional maturity, high terrigenous detrital and clay minerals, and their pores related clay minerals are very developed.

Pores between clay platelets are the pores generated by the directional or semi-directional contact of laminated clay minerals' edge and surface, edge and edge or surface and surface. On the other hand, intraplatelet pores within clay aggregates are the pores and space resulted from the transformation and compaction of the clay minerals.

In the process of burial diagenesis and organic matter evolution, the solid kerogen transforms into hydrocarbon fluids, produces bubbles, reduces the volume of organic matter, and expands the volume of the gas, resulting in the formation of organic matter pores [15]. In the Jinxian County area of Liaozhong sag, the organic matter abundance of shale is high, the average degree of Total Organic Carbon (TOC) is 1.99%, the type of kerogen is mainly II<sub>A</sub> and II<sub>B</sub>, and the small amount is III. The Ro is more than 0.5%, and it reaches the level of oil-generating window, which is in the low mature to mature stage [13, 14]. Therefore, in the process of thermal evolution, large amounts of organic matter are transformed into hydrocarbons and the organic-matter pores are well-developed in this shale.

## 5. Conclusions

There are three types of pores, that is, mineral matrix pores, organic-matter pores and fracture pores in JX1-1 area of Liaozhong sag. The mineral matrix pores are subdivided into interparticle pores and intraparticle pores. Interparticle pores are comprised of pores between rigid grains, pores between granular clay minerals, pores at the edge of rigid grains and pores between clay platelets. Intraparticle pores are comprised of pores within rigid grains, intercrystalline pores within pyrite framboids, intraplatelet pores within clay aggregates, and intercrystalline pores within siderite framboids. Pores between clay platelets, intraplatelet pores within clay aggregates and organic-matter pores are very well-developed, with good connectivity and thus, of the greatest significance to study on oil and gas in study area.

The shale is a near-source deposition formed in the semi-deep or deep lake environment in the background of thermal subsidence after the rifting of Bohai Bay Basin. It has a large amount of clay minerals with high abundance of organic matter, and the kerogen types are II<sub>A</sub> and II<sub>B</sub> at a low mature to mature stage. Pores between clay platelets are formed by directional or semi-directional, contact between edge and surface, edge and edge or surface and surface of laminated clay minerals, whose shapes are linear, mesh, and irregular with the size of 500 nm to 5μm. The intraplatelet pores within clay aggregates are formed in the process of the transformation and compaction of clay minerals, whose shapes are usually linear with the width of 30 to 500 nm and the length of 2 to 50μm. The organic-matter pores are from the process of the conversion from organic matters to the hydrocarbon under thermal evolution, whose shapes are gneissic, irregular, pitted and elliptical with the size of 100 nm to 2μm.

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