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Pore system characteristics of the Permian transitional shale reservoir in the Lower Yangtze Region, China*

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Abstract

The Permian shale, a set of transitional shale reservoir, is considered to be an important shale gas exploration target in the Lower Yangtze region. Due to little research conducted on the pore system characteristic and its controlling factors of the shale gas reservoir, SEM, FE-SEM, low-pressure N2 adsorption, and mercury intrusion tests were carried out on the Permian shales from the outcrop and HC well in the southern Anhui. The results show that the Permian shales mainly consist of organic matter, quartz, illite, calcite, and pyrite, of which pyrite occurs as framboids coexisting with organic matter and the organic matter is distributed in shales in stripped, interstitial, thin film and shell shapes. The basic pore types are inorganic mineral pore (intercrystalline pore, intergranular edge pore, intergranular pore, and interlayer pore in clay minerals) and the organic pore and microfracture, of which organic pore and microfracture are the dominating pore types. In shale, organic pores are not developed at all in some organic grains but are well developed in others, which may be related to the types of and maceral compositions of kerogen. Under tectonic stress, shale rocks could develop mylonitization phenomenon exhibiting organic grains well blend with clay minerals, and produce a mass of microfractures and nanopores between organic matter grains and clay minerals. Mercury intrusion tests show that the shale is mainly composed of micropore and transition pore with high porosity, good pore connectivity and high efficiency of mercury withdraw, while the shale that mainly dominated by mesopore and macropore has a low porosity, poor pore connectivity, and low efficiency of the mercury withdraw. The volume percentage of mesopore and macropore is increasing with the increase of quartz, and that of micropore and transition pore has a decreased tendency along with the increase of soluble organic matter (S1). Organic matter is the main contributor to the specific surface area. However, clay minerals could significantly inhibit the numbers of the microscopic pore and specific surface area due to the clay minerals being mainly dominated by illite and chlorite.

Keywords: Transitional facies; Pore system; Specific surface area; Permian; Lower Yangtze region

1. Introduction

Shale gas consists of free gas that's existing in the matrix minerals-related pores and fractures, adsorbed gas on the surface of micropores in organic matter and clay minerals, and dissolved gas in bitumen and water [1]. It has been made known that the organic pores are the most important reservoir space, and that the shale gas content is increasing with the increasing TOC [2,3]. In addition to organic pores, the
inorganic pores and microfractures also play an important role in the gas storage and migration. The shale gas reservoir dominated by inorganic pores is rare, such as Haynesville shale gas reservoir, and the dominated pore type is matrix mineral pore with a relatively high content of free gas, therefore, has a certain significance of shale gas exploitation.

The shale gas exploited in North America mostly exists in marine shale gas reservoirs. Only Lewis shale gas is produced in the transitional shale reservoir, and its total porosity and gas content are obviously lower than that of marine shale reservoir [4]. There are several sets of transitional organic-rich mudstones that developed in China. The Permian transitional shales, with great thickness, high TOC (generally greater than 2%), and moderate high maturity ($R_{0}$ is about 1.3%–3.0%) [5,6] are widely distributed in the Lower Yangtze region, and are considered to be good shale gas geological conditions. The researchers have used a variety of techniques, such as low-pressure N$_2$ adsorption, mercury intrusion, and nuclear magnetic resonance, to study the pore structure characteristics of the Permian transitional shales, and some knowledge has been obtained. TOC is the main contributor of micropores, and clay minerals have limited contribution to pore system [7,8], whereas fractures may also be an important provider to pore space for these Permian shales [9]. Wang et al. [10] and Yuan et al. [11] investigated the pore characteristics of transitional shales of the Upper Permian Longtan Formation in Guizhou province and the Upper Carboniferous Shaxi Formation, respectively, and found that the main pore types are intergranular pores between mineral grains and shear fractures in interlayered sandstones and organic pores are not well developed. Hence, it is very necessary to systematically study the characteristics and possible controlling factors of microscopic pore system of transitional shales.

In this paper, we conducted the scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), low-pressure N$_2$ adsorption, and mercury intrusion experiments to study the pore morphology of the Permian transitional shales in the Lower Yangtze region, and summarize the characteristics of pore system and discuss their controlling factors. This not only has important reference significance for investigating the shale gas potential of the Lower Permian, but it also provides a good reference for evaluating the transitional shales in other regions in China.

2. Geological setting

The tectonic evolution of the Lower Yangtze Platform experienced two stages: the continental margin of the Late Sinian to the Late Triassic, and the continental margin of the western Pacific after the Indosinian movement; they formed two large tectonic units, the Su-Wan structural belt and the Jiangnan uplift [12]. The study area is located in the southern Anhui in the Lower Yangtze region. This area covers the South Anhui-South Jiangsu depression with an area of about 12,000 km$^2$. The Paleozoic sedimentary-tectonic evolution of the Lower Yangtze Platform indicates that there are several sets of high-quality hydrocarbon source rocks in the Paleozoic strata in southern Anhui. A set of transitional facies organic-rich shale of the Permian is distributed in this region. The Permian is divided into the Xixia Formation (P$_1$x), Gufeng Formation (P$_3$g), Longtan Formation (P$_3$l), and Dalong Formation (P$_3$d) from bottom to top. The Permian shale has a moderate buried depth and is rich in organic matter, which is considered as a favorable shale gas exploration layer [5]. However, this region has undergone multi-phase strong tectonic reconstruction since the Indosinian period. The destruction of the Paleozoic strata in southern Anhui by the tectonic activity would affect the storage space and the gas storage of shale gas reservoirs, which may be a factor of controlling the gas-bearing capacity of shale [13]. The shale samples studied in this paper were collected from HC well in Wuhu area and Pingdingshan outcrop profile in Chaohu area (Fig. 1). These samples show that the thickness of the Permian strata is large and the organic matter is high. And hence the Permian shales in southern Anhui were selected as an object to study the pore system characteristics.

3. Samples and experiments

3.1. Samples

Fourteen core samples from the Longtan and Gufeng formations were taken from the HC well in the Wuhu area, with the sampling depth ranging from 109.9 m to 275.1 m (Table 1). Three outcrop samples from the Gufeng Formation were collected from the Pingdingshan profile in the Chaohu area (Table 1). The TOC value, Rock-eval, and mineral compositions were analyzed for all the samples. Several samples were selected to carry out SEM and FE-SEM analysis. The samples from the HC well were also measured by low-pressure N$_2$ adsorption and mercury intrusion techniques.

3.2. Experiments

The fresh section of shale was made perpendicularly to the shale bedding and was analyzed by S-4800 SEM instrument produced by Hitachi Company in Japan to observe the shale compositions and their occurrence states. Meanwhile, the shale samples were cut into slices of about 0.5 cm $\times$ 0.5 cm and then subjected to argon ion polishing. The treated samples were used to observe microscopic pore structure by Helios 650 FE-SEM manufactured by FEI Company. The maximum resolution of this instrument is 0.8 nm. In order to prevent electron beam damaging the surface of the sample, a lower acceleration voltage (2.0 kV) and the working distance of 3.0–3.6 mm were set in the experiment.

Porosity and pore size distribution were measured using Autopore 9510 porosimeter produced by Micromeritics Company. The pressure was continuously increased from 0.01 MPa to 413 MPa, and the corresponding pore diameter was varying from 120 $\mu$m to 3 nm. The pore size classification was adopted the decimal scheme [14], consisting micropore (<10 nm), transitional pore (10–100 nm), mesopore and macropore (>100 nm).
Low-pressure N\textsubscript{2} adsorption experiment was conducted on ASAP 2020 surface and pore size analyzer manufactured by Micromeritics Company. The test temperature is −196°C and the relative pressures are in the range of 0.001–0.995, and the specific surface area is calculated by BET method.

4. Shale composition and the occurrence states

The shales studied have TOC content in the range of 1.04%–18.8%, with an average value of 8.22%, suggesting a high TOC content. The free hydrocarbon obtained from Rock-
eval experiment is between 0.008 and 0.15 mg/g, suggesting that these shales have little potential for hydrocarbon generation. Liang et al. [15] found that the $\delta^{13}$C value of Gufeng Formation shales is ranging from $-28.7\%$ to $-26.5\%$, indicating type II kerogen, and that of Longtan Formation shales is varying from $-28.5\%$ to $-24.3\%$, suggesting a mixture of type II and III kerogen. The $R_O$ value of the Permian shales is between 2.3% and 2.7%, which suggests that the Permian shales have entered the high mature stage.

The mineral compositions of the Permian shales plotted in a triangular plot (Fig. 2) show that quartz, feldspar, pyrite, and clays are the main minerals. The quartz content is between 12% and 71.2%. Meanwhile, the feldspar content varies from 0 to 11.9%. Pyrite also has a high content, ranging from 0 to 10.4%, whereas the content of carbonates is relatively low, and the carbonate is absent in most of the Permian shales. The content of clay minerals is ranges from 24.5% to 72.7%, and it is mainly consisted of illite (24.5%–52.1%) and chlorite (0–32%). In addition, the gypsum has a high content in several samples studied.

The occurrence states of mineral and organic matter of the Permian shales are displayed in Fig. 3. Quartz is mainly formed by biological action and diagenesis effect, and minor quartz is a terrestrial input. The authigenic quartz usually has diameter larger than 5 μm. There are also some secondary-enlarged quartz particles in post-diagenetic process, with irregular boundaries, which mainly occur in the clay mineral layers (Fig. 3a). Calcite is shown as micrite and sparite grains in the Permian shales, and the grains are relatively loose (Fig. 3b). Clay minerals such as illite are present in the brittle mineral framework (Fig. 3c), and are patchy in distribution. Framboid pyrites, with diameter of 5–10 μm, usually co-exist with organic matter (Fig. 3d and e). The organic matter is distributed in shales in thin film, interstitial, and stripped, and shell shapes (Figs. 3f–5i). Thin film and interstitial organic matter with small particle size has no fixed form, which could be identified as sapropelinite [16]. The organic matter of stripped and shell shapes has the length of tens of microns and width of several microns and the occurrence state is debris-like, indicating this type organic matter may be mainly from algae and other biological debris [16]. Different forms of organic matter have great differences in their internal pores due to the differences in their compositions.

5. Pore system of the Permian shales

The pores in shale reservoir are not the only space for gas storage but also the channel for gas migration and production. The pores in different shale reservoirs have great differences. Hence, the pore classification schemes determined by scholars are quite different. Slatt et al. [17] divided shale pores into interstitial pores related to clay minerals, organic pores, pores in spheres, pores within fossil debris, interparticle pores, and microfractures, whereas Loucks et al. [18] classified the shale pores into interparticle pores, intraparticle pores, and organic pores. In this paper, we will investigate the pore development and morphology as well as analyze the characteristics of the Permian shale pores in combination with the researches of Slatt et al. [17] and Loucks et al. [18].

5.1. Organic pores

Organic pores with small size and hydrophobic property exhibit strong adsorption capacity, and are regarded as the most important pore type in mature shales. The previous studies have demonstrated that the pores within type I kerogen of the Lower Silurian in the Upper Yangtze region are well developed [19,20], but the pores in type III kerogen of the Permian mudrocks in the Ordos Basin and Guizhou province are poorly developed. Therefore, the development of organic pores is controlled not only by the abundance and maturity of organic matter but also by compaction, type, and maceral composition of organic matter.

SEM images display that many small organic matter grains are gathered together and the aggregate has the length of about 10 μm and width of about 5 μm (Fig. 4a), between which plenty of intergranular pores exist (Fig. 4b). These pores with several to tens of nanometers have good connectivity. Under SEM observation, the kerogen powder has a relatively rough surface and a certain amount of nanometer pores developed within the kerogen grains (Fig. 4c).

FE-SEM images show that the organic pores in different shales even in the same shale have different characteristics, which could be summarized as the following situations. (1) Some organic matter does not develop pores (Fig. 4d). This type of organic matter usually has a large volume and is with type III kerogen characteristics, indicating that the type of kerogen may influence the development of organic pores. Although some organic matter grains do not produce pores, they could be well mixed with clay minerals at the nanometer scale under geological tectonic stress, resulting in a larger number of nanoscale pores at the particle contact boundary (Fig. 4e) and a high specific surface area [21]. (2) In the same
shale, the two adjacent organic matter particles have different pore characteristics. One piece of organic matter almost contains no pores, but the other possesses a large amount of pores (Fig. 4f). Chalmers et al. [22] and Tian et al. [23] have also found similar cases, reflecting the development of organic pores is related not only to thermal maturity but also to kerogen type (or to the position of the slices). (3) Organic pores are well developed. The difference is that some organic matter grains have a small amount of pores but others have abundant pores (Fig. 4g-i). This type of organic matter is an important shale gas storage space which could store high content of adsorption gas and partial free gas. Therefore, SEM and FE-SEM images show that the differences of organic pores may be closely related to the type of kerogen. For example, type II kerogen has better pore development but type III kerogen contains less pores. Huang et al. [9], Wang et al. [10] and Yuan et al. [11] found that organic pores are poorly developed overall in transitional shales in different areas of China. Therefore, the development of pores is not common in the transitional shales, which indicates that the type II-III kerogen of the Permian shales in Lower Yangtze region would lead to the organic pores undeveloped in partial organic matter grains and then reduce the shale gas capacity to a certain extent.

5.2. Inorganic pores

Inorganic pores include intercrystalline pores, intergranular pores, intraparticle pores, interlayer pores related to clay minerals, dissolved pores, etc. [24]. Intercrystalline pores refer to the pores existing between various particles including clay, mud particle, quartz, feldspar, pyrite, and other detrital minerals. Intergranular pores refer to the pores occurring in the edge of the mineral particles due to inadequate compaction. Interlayer pores refer mainly to the pores existing in the layered sheet of clay minerals such as smectite, illite, chlorite, and other lamellar clay minerals. Intraparticle pores refer to the pores located within quartz, feldspar, apatite, and other mineral particles. The SEM images display that framboïd pyrites have the length of several microns and contain a large amount of dispersed pyrite microparticles (Fig. 5a). These pyrite particles experienced strong dissolution, and the surface...
of pyrites was collapsed, resulting in the microcrystalline particles more closely stacked. FE-SEM images also show that the pyrites have experienced more strong dissolution (Fig. 5b), in which intercrystalline pores and organic pores are developed. The organic pores co-existing with pyrite framboids are more developed than those in a single organic matter. The reason is probably that pyrite could reduce the activation energy of pyrolysis of organic matter and Fe\(^{2+}\) ions could affect the distribution of electron cloud of pyrolysis organic matter and thus promote the generation and decomposition of organic matter [25]. Cui et al. [26] also regarded that pyrite has a positive role in organic matter accumulation, hydrocarbon generation-expulsion and reserving property. Calcite grains fill in the matrix cracks, and some intergranular pores are developed between these calcite grains (Fig. 5c), which could lead to the closure of the migration channel, reduce of the permeability and enhance the autogenous sealing of shales. Influenced by the tectonic active, in the cleavage zone, the clay minerals particles are arranged in a directional arrangement and a large amount of organic matter grains are filled in the clay minerals and mixed sufficiently, forming a great deal of nanoscale grain contact boundaries (Fig. 5d). This means that a lot of nanometer intercrystalline pores are formed between the mixture of organic matter and clay minerals, forming a three-dimension pore-network with intergranular pores. Some intergranular edge pores developed around the hard mineral grains, which are formed from the primary pores not completely closed during the later compaction diagenesis (Fig. 5e and f). A small amount of intraparticle pores developed in the mineral grains. These pores are not well developed in these Permian shales and have poor connectivity. A certain amount of slit-shaped and irregular-shaped pores developed between illite and/or chlorite grains (Fig. 5h and i). However, they may have limited contribution to the porosity and specific surface area of the Permian shales due to these interlayered pores poorly developed caused by burial diagenesis.

5.3. Microcracks

The development of microcracks is not controlled by individual matrix particles, but is mainly controlled by tectonic stress, hardness difference of minerals, diagenesis effect and abnormal pressure during organic matter evolution [27]. Yang et al. [28] divided the microcracks into interlayer crack, mineral-related crack and organic-related based on the relationship between microcrack locations and the surrounding matrix. Guo et al. [29] divided the crack into structural crack, diagenetic crack, stratigraphic slip crack, abnormal pressure crack caused by the evolution of organic matter.
The Permian shales in Lower Yangtze region have significant crumple structure in Fig. 6a. Fig. 6a also shows that microcracks are filled by calcite grains. The crumple structure would make the organic matter mix well with clay minerals, and the clay particles are arranged in an orderly manner. Ma et al. [21,30] regarded this feature to be a mylonitic structure. A large number of microcracks, generally with several nanometers in width and tens of nanometers in length, are developed at the contact boundaries between organic matter and clay minerals and the alignment of these microcracks is in coincident with the direct of the cleavage (Figs. 5d and 6b). Mylonitization makes the organic matter dispersed in the clay minerals, which greatly increases the specific surface area of organic matter and adsorption capacity of shales [21,31]. The scholars have also demonstrated that the coal with mylonitic structure has more nanometer pores and higher specific surface area than the raw coal [30]. Mylonitized coal has greater adsorption capacity than raw coal, and is more likely to desorb gas than raw coal [32,33]. Therefore, the mylonitization plays a positive role in increasing the specific surface area of organic matter and the development of microcracks. It can been seen from SEM images of Fig. 6c that microcrack system is well developed with an open-like staggered distribution, reflecting that the complex tectonism in the Lower Yangtze region could cause the abnormal development of microcracks in the Permian shales. Drilling in the Appalachian Basin shows that slippage and its associated extension and shrinkage cracks are prone to be developed in high TOC shales. Zeng et al. [34] also deemed that the number of microcracks increased with increasing TOC content. FE-SEM image in Fig. 6d shows that the tectonic microcracks are large in scale with lengths of up to 30 µm. In addition, a lot of small-scale microcracks are also developed in the Permian shales, mainly occurring within brittle minerals or at the contact boundaries of clay minerals and brittle minerals, with the length of a few nanometers and width of tens of nanometers. There are a few microcracks caused by hydrocarbon expulsion along the bedding plane, and some scattered pyrite grains are distributed around them. Fig. 6g shows that organic matter fills the microcracks, which not only reduces the porosity of shales but also hinders natural gas migration. Some microcracks are also existed at the contact boundaries of organic matter and minerals or within the organic matter grains (Fig. 6h and i). The microcracks at the edge of the organic matter may be caused by the dehydration and demethylation during the hydrocarbon generation process, and the microcracks in the organic matter are typical structural crack formed by tectonic extrusion which can effectively connect non-structural cracks and become the reservoir space for gas accumulation and channel of gas migration. The development degree of this type microcrack is related to organic matter type, content and distribution [35]. Huang et al. [9] found microcracks are an important reservoir space,
mainly interlayer crack, network crack, and high-angle crack, which are more developed than inorganic pores in the Permian shales.

Based on a large number of SEM and FE-SEM images, the characteristics of shale pores were qualitatively described, and the locations and the development regularities of the pores were summarized. We also discussed the dominant pore types and pore system characteristics of the Permian shales in Lower Yangtze region, and regarded that the basic pore types are inorganic pores (intercrystalline pores, intergranular pores, intraparticle pores and interlayer pores related to clay minerals), organic pores and microcracks (Table 2). The intercrystalline pores between pyrite, calcite, and clay minerals mixed with organic matter, organic pores and microcracks are the dominated pore types. Whereas, intergranular pores, intraparticle pores and interlayer pores associated clay minerals are poorly developed. Affected by kerogen type, the pores in different organic matter grains have great differences.

6. Pore structure characteristics and controlling factors

6.1. Pore size distribution

The mercury injection/ejection curves and pore size distribution characteristics of the Permian shales from HC well are shown in Fig. 7. There are three types of mercury injection/ejection curves, with mercury saturation ranging from 3% to 95% and corresponding porosity ranging from 0.68% to 21.08% (Table 1). The shapes of injection/ejection curves could be used to distinguish the pore morphology and size distribution. Fig. 7a shows that the mercury injection saturation slowly increases with increasing pressure below 10 MPa, and mercury saturation is increasing rapidly with increasing pressure when pressure is above 10 MPa. The shale samples with this injection curve have a great deal of microscopic pores, mainly smaller than 100 nm (Fig. 7d), and a high porosity. With the decrease of pressure, the mercury slowly withdraws from the pores, indicating better pore connectivity. Fig. 7b shows that the mercury increases rapidly at the initial pressure, but when the pressure is in the range of 0.1–100 MPa, the mercury saturation remains almost unchanged, reflecting that the Permian shales have few microscopic pores but has a small amount of macropores or microcracks (Fig. 7e). These shale samples have a low porosity with low efficiency of mercury withdraw and poor pore connectivity. In Fig. 7c, the mercury increases sharply in the pressure of 1–10 MPa, indicating the shale samples are dominated by the pores with diameter of 10-100nm (Fig. 7f) and have a high porosity. Meanwhile, these shales have high efficiency of mercury withdraw and good pore connectivity. Therefore, the high porosity of the Permian shales is mainly contributed by the nanometer pores, including microscopic pores and microcracks, but some shales has a low porosity when they are lacking nanometer pores.
The nitrogen adsorption/desorption curves of two different TOC shales are displayed in Fig. 8. It could be seen from the Fig. 8 that the adsorption curve is type IV on the whole, exhibiting that the front part of adsorption isotherm rising slowly and having slightly convex upward. Until the relative pressure of 0.995, the adsorption does not reach saturation state, suggesting the capillary condensation occurs during the adsorption process which indicates that the shales contain a certain amount of mesopores and macropores. The desorption and adsorption curves have a good coincidence for the shale with a low TOC content, indicating the low TOC shales are dominated by the pores in plate or cylinder shapes. However, desorption and adsorption curves do not coincide with each other, indicating that the shale has a certain amount of slit-type pores. In the low pressure ($p/p_0 < 0.01$), the adsorption capacity of low TOC shale is far lower than that of high TOC shales.

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Diagram</th>
<th>Size</th>
<th>Location</th>
<th>Development level</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic pores</td>
<td>Intercrystalline pores</td>
<td></td>
<td>Tens of nanometers to microns</td>
<td>Between the grains such as framboid pyrites, calcite, clay minerals and organic matter</td>
<td>Good</td>
<td>Diagenesis</td>
</tr>
<tr>
<td></td>
<td>Intergranular pores</td>
<td>Polygonal, slit, irregular</td>
<td>Hundreds of nanometers to microns</td>
<td>Along the edge of quartz, feldspar and clay minerals</td>
<td>Weak</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Intraparticle pores</td>
<td>Triangle, slit</td>
<td>Tens to hundreds of nanometers</td>
<td>Within quartz, feldspar, carbonate and apatite</td>
<td>Weak</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interlayer pores related to clay minerals</td>
<td>Slit, irregular, reticular</td>
<td>Hundreds of nanometers to microns</td>
<td>Clay minerals such as illite and chlorite</td>
<td>Weak</td>
<td></td>
</tr>
<tr>
<td>Organic pores</td>
<td>Irregular, nearly circular, elliptic</td>
<td>Several to hundreds of nanometers</td>
<td>Within organic matter</td>
<td>Some are weak; some are good</td>
<td>Thermal maturity; kerogen type</td>
<td></td>
</tr>
<tr>
<td>Microcracks</td>
<td>linear, serrated</td>
<td>Tens of nanometers to microns</td>
<td>Organic matter, the boundaries of brittle minerals and organic matter, clay minerals</td>
<td>Good</td>
<td>Tectonism; diagenesis; abnormal pressure</td>
<td></td>
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Table 2
Pore types and characteristics of the Permian shales in the Lower Yangtze region.

Fig. 7. Mercury injection/ejection curves (a–c) and pore size distributions (d–f) of the Permian shales in the Lower Yangtze region.
shale, but in the high pressure, the adsorption volume of low TOC shale is higher than that of high TOC shale, illustrating the high TOC shale possesses more microscopic pores but the number of mesopores and macropores do not increase with increasing TOC. This phenomenon is agreement with the result of Pan et al. [36], indicating that the presence of organic matter mainly provides micropores rather than mesopores and macropores.

The volume percentages of micropores, transitional pores, mesopores and macropores determined by mercury intrusion method are 0.45.88%, 0.45.32% and 22.92% (Fig. 9), illustrating the main pore space is contributed by mesopores and macropores, and the micropores and transitional pores are less developed. The shales with a high percentage of mesopores and macropores usually have a low porosity, which is consistent with the mercury injection/ejection curves in Fig. 7. The volume proportion of micropores and transitional pores is low, especially that in individual sample is approximately zero, which is not well consistent with the development of organic pores in SEM images. The possible reason is that the organic matter would take up a lot of shale volume and influence the connectivity of pore network, which could lead to the mercury cannot enter the organic pores or organic pores undeveloped in some shale samples (see Fig. 4).

6.2. Controlling factors of pore structure

Fig. 10 shows the relationships of micropore, transitional, and mesopore and macropore volume percentage determined by mercury intrusion method with TOC, soluble organic matter ($S_1$), quartz and clay mineral contents. TOC has no apparent relationships with the volume fraction of micropores, and mesopores and macropores, suggesting that TOC is not the main factor controlling micropores, transitional pores and mesopores and macropores. No relationship between TOC and volume fraction of micropores may be related to that (1) organic pores unable to be totally detected by mercury method [7] or (2) pores poorly developed in partial organic matter grains. With the increase of $S_1$ content, the volume percentage of mesopores and macropores increases and the volume percentage of micropores and transitional pores decreases, because the free organic matter occupies the organic pores and throats of shales. As the $S_1$ content increases, the occupied pore volume increase, and therefore the volume percentage of micropores and transitional pores decreases [37]. There is a positive relationship between quartz and volume fraction of mesopores and macropores, the increase of quartz would increase the microfractures in shales and then increase the volume fraction of mesopores and macropores. However, the volume percentage of micropores and transitional pores decreases with increasing quartz content. There is no apparent relationship between clay content and the percentage of mesopores and macropores, micropores, and transitional pores reflecting that the clay minerals are not the main factors controlling the microscopic pore structure.

Though there is no obvious relationship between the volume fraction of micropores and transitional pores determined by mercury intrusion method and TOC, clay minerals contents, but FE-SEM images show that there are many nanometer pores in the Permian shales. Therefore, based on the results of this paper and previous studies, we analyzed the relationship of TOC and clay mineral contents with the specific surface area of the Permian shales, and found that the specific surface area has a good positive relationship with TOC content but a negative relationship with clay mineral content (Fig. 11), illustrating that TOC has an inhibition effect on porosity obtained from mercury intrusion experiment but a
positive effect on the specific surface area. This suggests that organic matter itself has more micropores or the organic matter after mylonitization could significantly increase the specific surface area of shales. Hence, some organic matter, despite the underdeveloped organic pores, dispersed within in clay minerals in the form of nano-particles, could greatly increase the specific surface area of organic matter, which is a reason why TOC has a positive relationship with TOC content. The experiments have demonstrated that the specific surface area increases from broken coal to fragmented coal to mylonitic coal, which is related to the rough surface of the organic particles. Ma et al. [21] have also found that the organic pores are poorly developed but organic matter has obvious mylonitic structure in the Lower Cambrian Lijiapin Formation shales in northeastern Sichuan Basin, which makes a good relationship between TOC content and shale gas content. Therefore, the mylonitic organic matter may be an important factor influencing the reservoir property and gas-bearing capacity, which should be of concern. The negative relationship between the specific surface area and clay mineral...
content may indicate the microscopic pores related to clay minerals are less. In the process of compaction, the clay mineral pores could be reduced to a great extent, and meanwhile, the clay minerals in these Permian shales are dominated by illite and chlorite which have much lower specific surface area than smectite and the mixed-layer of illite and smectite [38]. The higher content of illite and chlorite is, the smaller contribution of clay minerals is to the pore system of the Permian shales, and the clay mineral content may not be the main contributor to the microscopic pores of the Permian shales studied.

7. Conclusions

(1) The components of the Permian shales in the Lower Yangtze region are mainly organic matter, quartz, illite, calcite, and pyrite. The pyrite occurs as framboi d shape and co-exists with organic matter. Organic matter is distributed as stripped, interstitial, thin film, and shell shapes in shales, which is closely related to the sources of organic matter.

(2) The basic pore types of the Permian transitional shales in the Lower Yangtze region are intercrystalline pores, intergranular edge pores, interlayer pores related to clay minerals, intragranular pores, organic pores, and microcracks. Organic pores and microcracks are the chief pore types. Some organic matter grains have no developed pores, whereas some organic matter grains contain a great deal of pores, which may be related to the type and maceral composition of organic matter. In several shale samples, organic matter and clay mineral are fully mixed with each other to produce mylonitic phenomenon. Many microcracks would develop in or at the edge of the organic matter grains.

(3) The porosity of the Permian shales dominated by nanometer pores measured by mercury intrusion method is high, and the connectivity of pore structure is good and the efficiency of mercury withdraw is high. While, the shales dominated by mesopores and macropores have low porosities, poor pore connectivity and low efficiency of mercury withdrawal.

(4) The mesopores and macropores in the Permian shales are related to brittle minerals such as quartz, and the percentage of mesopore and macropore volume in total pore volume increases with increasing the quartz content. The soluble organic matter could reduce the volume of micropore, mesopore, and macropore by occupying the organic pores and throats related to minerals. The mylonitic organic matter is the main contributor to the specific surface area of the Permian shales, exhibiting that the specific surface area increases with increasing TOC content. The increase of clay minerals could inhibit the development of micropores and reduce the specific surface area of shales.

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**Conflict of interest**

The authors declare no conflict of interest.

**References**


