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Characteristics and controlling factors of pore structure of the Permian shale in southern Anhui province, East China¹

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Abstract: The Permian shale reservoir in southern Anhui province, East China is regarded as a promising target for shale gas exploration. In order to investigate the characteristics of shale pore structures and their controlling factors, total organic carbon (TOC), Rock-eval, organic petrology, X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), nitrogen gas adsorption (N₂GA), mercury intrusion porosimetry (MIP) and helium pycnometry were conducted on the Permian shales collected from two shale gas parameter wells. The results indicate that the BET surface areas determined by N₂GA method vary between 1.05 and 49.25 m²/g. The porosities derived from MIP and helium pycnometry tests are in the range of 0.68%-8.9% and 1.15%-9.79%, respectively. FE-SEM reveals that organic matter (OM) pores and cracks are well developed in the Permian shales, though some OM grains contain few pores, which might be related to the maceral composition. At a high maturity stage, vitrinite do not develop secondary OM pores, and sapropelinite generally develop abundant OM

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pores. However, solid bitumen occupies interparticle space between minerals grains, and generally contains a small amount of pores documented in studied samples. The TOC contents have a positive relationship with the BET surface areas, suggesting OM is a primary factor in micropore and fine mesopore (<10 nm) development. TOC content has a positive relationship with porosity for samples with TOC<6.16%, but samples with TOC>6.16% usually have a low porosity probably due to compaction and/or different organic fractions. Residual bitumen (S_1) is weakly and negatively correlated with Hg-porosity, due to residual bitumen filling in OM and mineral pores and reducing the total porosity. In addition, BET surface area decreases with increasing clay mineral content and Hg-porosity decreases with increasing quartz content, illustrating that clay mineral is unfavorable to the development of micropores and fine mesopores and high content of quartz may reduce macropore space. Finally, the shales of the Gufeng and Dalong Formations display a higher TOC content and a better physical property than the Longtan Formation shales and appear to be superior prospective shale gas exploration potential.

Key words: Pore characteristics; N₂GA; MIP; FE-SEM; Permian shale; southern Anhui province

1. Introduction

The success of shale gas development across the North America has aroused great attention on shale gas exploration in many other countries, such as China, India, Australia and South Africa (Curtis, 2002; Jarvie et al., 2007; Chalmers and Bustin, 2007; Du et al., 2015; Yang et al., 2016). Currently, the exploration and development

of shale gas in China are mainly concerning on marine and lacustrine shales in the Upper Yangtze region and Ordos Basin (Sun et al., 2016; Tang et al., 2015; Li et al., 2015). However, compared to marine and lacustrine shales, the research and exploration on transitional shale are still weak, and few studies have been carried out to investigate the pore property and gas potential of the transitional shales which are widely distributed in China and are considered as a promising target for shale gas exploration (Pan et al., 2015; Dan et al., 2016).

Pore structure is very important in evaluating shale gas resource potential and contributes to a better understanding of shale gas storage and migration (Ross and Bustin, 2009; Kuila and Prasad, 2013). To accurately determine the complex pore system in shales, a series of multidisciplinary methods, both qualitatively and quantitatively, have been developed to characterize the pore structure of shales in recent years. The qualitative techniques, including field emission scanning electron microscopy (FE-SEM), focused ion beam scanning electron microscopy (FIB-SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM) and scanning transmission X-ray microscopy, could identify the type, shape, size and connectivity of the pore networks (Slatt and O'Brien, 2011; Bernard et al., 2012; Loucks et al., 2012; Jiao et al., 2014; Dong et al., 2015), and the quantitative characterization techniques including helium pycnometry, mercury intrusion porosimetry (MIP), low pressure CO₂/N₂ gas adsorption (CO₂/N₂GA) and small angle neutron scattering (SANS) are usually used to obtain porosity, pore volume, specific surface area and pore size distribution (Ross and Bustin, 2009; Clarkson et al., 2013;

Mastalerz et al., 2013). Researches in the last few years have identified the characteristics and controlling factors of pore structures in marine shales. For instance, Loucks et al. (2009, 2012) pointed out that OM pores are resulted from and controlled by thermal maturity. Milliken et al. (2013) and Jarvie et al. (2007) regarded that type I and II kerogen may be more prone to pore development than type III kerogen, because type I and II kerogen have a stronger ability to generate hydrocarbon than type III kerogen. Yang et al. (2014) stated that TOC controls the specific surface area and methane adsorption capacity of marine shale. In addition to TOC, mineral composition is also a significant factor of pore structure (Mastalerz et al., 2013). For instance, Curtis et al. (2010) found that the main pores are inorganic matrix porosity in Haynesville and Eagle Ford shales. Unlike the marine shales, transitional shales are usually interlayered with coal seams with their kerogens being mostly gas-prone (Liang et al., 2008; Xi et al., 2017), which would make the pore system, especially OM pore, more complicated. As illustrated by Jiang et al. (2017) and Zhang et al. (2017), the transitional shale has less micron-scale and nano-scale OM pores than the marine shale, and TOC contributes little to the development of micropores. While, Zhang et al. (2017) reported that transitional shale of the Upper Longtan Formation in southern Sichuan Basin is dominated by OM pores. OM pores are heterogeneously developed, which may be related to the maceral composition (Cao et al., 2016; Liu et al., 2017; Ardakani et al., 2018; Wood et al., 2018). Therefore, to clearly define the pore development characteristics in different organic maceral is a pressing need, because it can have a detrimental effect on shale gas reservoir quantity.

The Permian shale reservoir, containing the Gufeng (P_{2g}), Longtan (P_{3l}) and Dalong (P_{3d}) Formations, in the Lower Yangtze region is considered as a favorable target of shale gas exploration due to the large regional extent, shallow burial, large thickness (100-600m), abundant OM and moderate maturity (Du et al., 2015; Pan et al., 2015). However, only a few experimental researches have reported on this topic (Du et al., 2015; Pan et al., 2015). Two shale gas parameter drilling wells in the southern Anhui province provide an ideal condition to study physical properties of Permian shales. Therefore, in this study, 32 core samples of the Permian shale with a transitional environment collected from the two wells were conducted to investigate pore structure characteristics using FE-SEM, MIP, N₂GA and Helium pycnometry methods. To allow discussion the relationships between the compositions, especially TOC, organic maceral, residual bitumen and pore structure of the shale, TOC, Rock-eval, organic petrology and XRD measurements were carried out. Finally, comparison of physical property between Permian intervals with different deposition facies was conducted. The results of this study are meaningful for the cognition of pore development in different OM macerals. Meanwhile, it has implications for assessing gas exploration of the Permian shales and favorable intervals in Lower Yangtze region, as well as it is instructive for shale gas reservoirs of the Permian Longtan, Wujiaping and Dalong Formations in Upper and Middle Yangtze region, such as northeastern Sichuan Basin and central Hunan and Hubei provinces.

2. Geological setting

Wuhu basin, covering an area of approximately 4839 km², is located in the Lower Yangtze Platform, which is bounded by the Tanlu Fault zone to the west, by the Sulu Belt to the north and by the Jiangnan Uplift to the south (Fig.1; Cai et al., 2013; Pan et al., 2015). The sedimentary evolution of Wuhu Basin had underwent three

main stages (Yuan et al., 2006), forming marine sediment deposition from Sinian to Middle Silurian, marine-lacustrine transitional sediment deposition from Late Devonian to Permian, and terrestrial sediment deposition after Middle Triassic (Chen et al., 2013). Sandwiched between the Sulu and Wuyi Foldbelts, the Lower Yangtze Platform had successively experienced several extrusion-stretch structures caused by the continuing effect of Indochina, Yanshan and Himalayan movements which led to an erosion of the Paleozoic strata (Ding et al., 2009). The Wuhu Basin is in the middle of the Lower Yangtze Platform, and the Paleozoic strata are relatively less affected by tectonic activities, most of which are covered by Quaternary sedimentary (Ding et al., 2009). This is also the main reason why the Wuhu area was selected as the target of shale gas exploration.

Fig.1. Regional geological background (according to Pan et al., 2015) and sampling sites of Permian shales in Lower Yangtze Platform.

The Permian strata in the Lower Yangtze region, including the Qixia (P_{1x}),

Gufeng (P_{2g}), Longtan (P_{3l}), and Dalong (P_{3d}) Formations (Fig.2), from older to younger, have a total thickness of about 500-1000m. The Qixia Formation consists mainly of limestone with nodular or layer-like black chert in a carbonate platform. The Gufeng Formation is mainly consisted of black shale, mudstone, siliceous mudstone, silicalite which commonly yield phosphate, radiolarians and sponge spicules in a slope-shelf-basin environment (Du et al., 2015). The Longtan Formation consists of sandstone, mudstone, coal and limestone in a deltaic environment (Du et al., 2015; Kametaka et al., 2005). The Dalong Formation is dominated by mudstone, siliceous mudstone and calcareous mudstone in deep-shelf basin environment. Ammonoids, conodonts, and radiolarians are also found in the Dalong Formation (Kametaka et al., 2005). The organic-rich shales generally with TOC value of 1-10% and occasionally reaching 18.8% are mainly distributed within the Middle and Upper Permian strata (Fig.2).

Fig.2. The columnar section showing lithology and TOC distribution of samples from

HC well (a) and CC well (b).

3. Samples and methods

3.1 Sample collection

A total of 32 core samples were selected, according to the change of TOC content, from the Lower (1 samples), Middle (15 samples) to Upper (16 samples) Permian of two shale gas parameter wells (HC and CC wells). The two wells were drilled at the high points of two different anticline structures in Wuwei county and Jingxian county, respectively. The current burial depth of Middle (P_{2g}) and Upper Permian (P_{3l} and P_{3d}) shales studied ranges from 20.1 to 275.1 m in HC well and from 123.4 to 341.8 m in CC well. Prior to analysis, the samples were preprocessed to meet experimental requirements. First, shale samples were placed in a ball mill pulverizer and crushed into a powder with particle sizes less than 0.15 mm, and then the powdered samples were used for TOC, Rock-eval, X-ray diffraction (XRD), N_2GA analyses. Bulk rock samples were used for MIP, organic petrology, SEM and FE-SEM tests.

3.2 Experimental methods

3.2.1 Organic geochemistry

TOC was determined using a Leco CS230 carbon/sulfur analyzer. Approximately 100 mg of powdered sample was treated with 5% HCl at 80 °C to remove any carbonate and then washed the samples several times using ultra-high purity water to eliminate the residual HCl. The treated samples were mixed with tungsten-tin and iron

power as additives, using N₂ as the carrier gas and O₂ as the combustion gas. The combustion temperature automatically increases to 3000 °C and the TOC is calculated according to the peak area of CO₂ generation from combustion of OM.

Rock-eval pyrolysis analysis was carried out on a Rock-eval 6 instrument. Parameters measured include residual bitumen (S₁), remaining generation hydrocarbon (S₂), and the temperature at the S₂ peak (T_{max}) which could be used to characterize the level of thermal maturity, and hydrogen index (HI) determined by the ratio of S₂ / TOC.

An aliquot of about 1 g crushed and sieved rock was mounted and polished to form pellets for maceral analyses with a DM 4500P08015 microscopy equipped with a microphotometer according to the Chinese Oil and Gas Industry Standard SY/T 6414-2014.

3.2.2 Mineralogy

Semi-quantitatively relative mineral percentage analysis was performed on the samples using a Bruker D 8 X-ray diffractometer (XRD) at 40 kV and 30 mA with Cu K α radiation (λ = 1.5046 for Cu K α). Stepped scanning measurements were performed at a rate of 4°/min in the range of 3-85° (2 θ).

3.2.3 Specific surface area, porosity and pore types

Specific surface area and pore size distribution of micropore and mesopore were investigated by N₂GA technique at a low temperature and pressure (-196 °C and <127 kPa) using a Micromeritics ASAP 2020 apparatus. About 3-5g powdered samples

were degassed under high vacuum for 12 hours at 110°C to remove moisture and residual volatile material. The specific surface area (BET surface area) was calculated using the Brunauer-Emmette-Teller (BET) method in the relative pressure of 0.05-0.25, and the pore volume was obtained using Barrette-Joynere-Halenda (BJH) method (Gregg and Sing, 1982). Pore size distribution was determined from the adsorption branch of the isotherm using the density functional theory (DFT) method (Guo et al., 2018).

Hg-porosity and pore size distribution of mesopore to macropore were determined by MIP technique using a Micrometrics Autopore 9510 analyzer. Between 3 and 5g rock sample was oven dried at 110 °C for 12 hours under vacuum. The pressure during the mercury intrusion was initially set 0.01 MPa and then was increased continuously to 413 MPa. The equivalent pore size was determined according to the mercury pressure using the Washburn equation (Washburn, 1921).

Massive shale samples were selected to carry out He-porosity test by a QK-98 porosimeter following GB/T 29172-2012 standard. Shale samples used in this study were cut into cylindrical shapes with 2.5 cm in diameter and a height of about 3.5 cm. He-porosity was calculated from the difference between bulk density and skeletal density with a helium expansion method, and the experimental setup was referred to Wang et al. (2017).

Selected samples were cut to subsamples 0.3-0.5 cm thick, 0.5-1.0 cm wide and about 2 cm long. The subsamples were dried in an oven at 60 °C for 24 h to remove moisture. Analysis was conducted using a FEI Quanta 200 SEM instrument with 20

kV acceleration voltages to observe the OM morphology, mineral composition and location. Meanwhile, in order to observe the characteristics of pores and micro-cracks, several shale samples were selected to be polished by with gas argon to create a smooth surface using a Hitachi Ion Milling System IM 4000 with an acceleration of 3 kV and a milling time of 4-8 h. The samples were then imaged using a Helio 650 FE-SEM instrument. Lower accelerating voltages (<10.0kV) with a working distance of about 1.5-4.7 mm were set on the instrument to prevent electron beam damaging these samples.

4 Results

4.1 OM features

The TOC content and Rock-eval pyrolysis parameters of the studied samples are shown in Table 1. The TOC content ranges between 0.12% and 18.8% with an average value of 6.73% for the Permian shales. One limestone sample from the Lower Permian Qixia Formation is 0.03%. Organic-rich shales are mainly distributed within the Gufeng and Dalong Formations. $T_{\max}$ value of these shales is generally above 484 °C, except two samples, and the R_o value ranges between 2.3% and 2.7% (Pan et al., 2015), illustrating that they are at a high maturity stage. Residual bitumen (S_1) value ranges from 0.008 to 0.058 mg/g and 0.027 to 2.39 mg/g for the shales of the two wells, respectively. Pyrolysis hydrocarbon (S_2) and HI values are in the range of 0.022-0.15 mg/g and 0.047-1.70 mg/g for the samples from HC well, and range from 0.047-1.70 mg/g and 3.09-153.09 mg/g for the samples from CC well.

Table 1 TOC and Rock-eval pyrolysis parameters of the Permian shales from HC and CC wells.

Sample	Depth (m)	Unit	TOC (%)	T _{max} (°C)	S ₁ (mg/g)	S ₂ (mg/g)	HI (mg/g)
HC-32	109.9	P _{3l}	1.52	492	0.021	0.028	1.84
HC-36	122.8	P _{3l}	7.21	549	0.019	0.017	0.24
HC-38	124.5	P _{3l}	1.04	498	0.01	0.022	2.12
HC-43	140.1	P _{3l}	15.3	449	0.058	0.15	0.99
HC-45	140.7	P _{3l}	4.94	448	0.016	0.038	0.77
HC-69	220.5	P _{2g}	2.32	489	0.008	0.022	0.95
HC-77	247.2	P _{2g}	15.5	529	0.018	0.021	0.14
HC-79	252.2	P _{2g}	18.8	519	0.054	0.060	0.32
HC-80	254.4	P _{2g}	8.1	499	0.019	0.021	14.29
HC-81	257.8	P _{2g}	17.2	496	0.029	0.027	0.16
HC-83	264.2	P _{2g}	10.4	493	0.03	0.029	0.28
HC-86	273.8	P _{2g}	11.8	484	0.019	0.028	0.24
CC-7	90.7	P _{3d}	0.12	514	0.042	0.058	47.93
CC-12	121.7	P _{3d}	2.64	513	0.55	0.61	23.26
CC-13	123.4	P _{3d}	8.19	554	2.39	1.70	20.72
CC-14	128.1	P _{3d}	4.36	499	1.37	0.99	22.78
CC-15	131.2	P _{3d}	0.86	551	0.039	0.097	11.23
CC-16	132.9	P _{3d}	7.08	492	1.97	1.01	14.32
CC-20	145.9	P _{3d}	3.3	495	0.64	0.72	21.67
CC-21	152.7	P _{3d}	6.13	549	1.44	0.80	13.02
CC-29	187.4	P _{3l}	5.46	547	0.17	0.33	7.13
CC-36	208.9	P _{3l}	2.35	543	0.19	0.39	16.68
CC-48	239.6	P _{3l}	1.03	549	0.04	0.10	9.90
CC-76	305.9	P _{2g}	6.16	538	1.4	0.48	7.84
CC-77	308.5	P _{2g}	12.2	550	0.84	0.38	3.09
CC-78	312.4	P _{2g}	0.79	556	0.038	0.12	14.70
CC-79	314.7	P _{2g}	1.78	558	0.091	0.15	8.54
CC-80	317.5	P _{2g}	8.01	559	1.58	0.82	10.20
CC-82	321.5	P _{2g}	11.1	561	1.80	1.20	10.77
CC-85	330	P _{2g}	3.96	553	0.89	0.57	14.44
CC-90	341.8	P _{2g}	8.93	549	2.13	1.58	17.68
CC-93	355.1	P _{1x}	0.03	547	0.027	0.047	153.09

The organisms in the Permian shales are consisted of algae, amorphous bodies, higher plant, organic shelf, etc. (Table 2; Fig.3). The algae and amorphous bodies with smaller particles usually co-exist with pyrite framboids, while the higher plant and

organic shelf usually have a large volume and are independently distributed (Fig.3). The maceral composition determined from the whole rock shows that solid bitumen is the main composition, accounting for 25-100%, with some sapropelinite (0-75%), vitrinite (0-15%), inertinite (0-8%) and organic detritus (0-2%). In the Dalong and Gufeng Formations, the OMs are mainly constituted of sapropelinite and solid bitumen, while in the Longtan Formation, the shales have rare sapropelinite. These features suggest that the kerogen is attributed to be type II with minor type III, which had also been confirmed by Huang et al. (2015).

Fig.3. The morphology and characteristic of OM in the Permian shales.

Table 2 Relative content of maceral groups in the Permian shales from CC well.

Sample	Depth (m)	Unit	TOC (%)	Sapropelinite (%)	Vitrinite (%)	Inertinite (%)	Solid bitumen (%)	Organic detritus (%)
CC-13	123.4	P _{3d}	8.19	23.4			76.6	
CC-14	128.1	P _{3d}	4.36	33.5	8.2		56.3	2
CC-16	132.9	P _{3d}	7.08	28	3		67	2
CC-21	152.7	P _{3d}	6.13	16		8	76	
CC-31	193.1	P _{3l}	1.04				100	
CC-35	206.7	P _{3l}	1.21				100	
CC-40	217.6	P _{3l}	3.23		8		92	
CC-53	250.7	P _{3l}	1		15		85	
CC-76	305.9	P _{2g}	6.16				100	
CC-77	308.5	P _{2g}	12.2	75			25	
CC-81	320.2	P _{2g}	11.8	38			62	
CC-82	321.5	P _{2g}	11.1	38			62	
CC-83	324.2	P _{2g}	7.73	28.5			71.5	
CC-86	331.1	P _{2g}	10.7	41			59	
CC-89	339.1	P _{2g}	4.79	68			32	

4.2 Mineral compositions

The mineral compositions of the studied samples are tabulated in Table 3 and summarized in a ternary plot (Fig.4). The results show that the Permian shales are mainly composed of clay mineral, quartz, feldspar, calcite and pyrite. Quartz averages 33.84% (ranges from 8.9% to 71.2%), carbonate mineral (calcite and dolomite) content averages 7.66% (ranges from 0 to 63.7%), feldspar content averages 4.65% (ranges from 0 to 15.7%), and pyrite content ranges from 0 to 25.5%. Clay mineral content of most shale samples is between 24.5% and 81.5%, except one sample contains no clay mineral. The clay minerals are dominated by illite, in spite of some samples having high contents of chlorite and kaolinite. However, no smectite is detected in these Permian samples.

Fig.4. Ternary plot of mineral compositions obtained by XRD method for the Permian shales.

Table 3 The mineral composition of the Permian shales from HC and CC wells.

Sample	Quartz (%)	Feldspar (%)	Illite (%)	Chlorite (%)	Calcite (%)	Pyrite (%)	Others (%)	Total clays (%)
HC-32	30.1	6.3	42	21.7				63.7
HC-36	22	4.9	52.1	19		2		71.1
HC-38	32.8	5.7	38.1	23.3				61.4
HC-43	48.3		29.6		16.4	5.7		29.6
HC-45	26.5	5.4	42.2	23.5		2.4		65.7
HC-69	24	3.3	40.5	32.2				72.7
HC-77	54.2		26.6		17.6	1.5		26.6
HC-79	49.8		35.7		11.5	3.1		35.7
HC-80	56		25		15.8	3.2		25
HC-81	60.2		32.2		4.8	2.8		32.2
HC-83	71.2		24.5			4.3		24.5
HC-86	30.8	11.9	31.9	25.4				57.3
CC-7	18.2	9.6	45.5	26.7				72.7
CC-12	27.3	12.6	41.7		10.7	2.6	Dolomite5.1	41.7
CC-13	35.3	13.3	45		2.2	1.9	Dolomite2.4	45
CC-14	21.9	6.7	56.1		10.5	4.8		56.1
CC-15	28.2	13.5	36.5	21.7				58.2
CC-16	26	10.3	59.2			4.5		59.2
CC-20	19.4	10.5	65.8		1.5	2.7		65.8
CC-21	39.2	15.7	36.1		4.7	4.3		36.1
CC-29	23.9		34.6				Kaolinite41.5	76.1
CC-36	18.5		60.7	10.4			Kaolinite10.4	81.5
CC-48	21.2	8.4	51.5	19				70.5
CC-76	10.7					25.5	Dolomite63.7	0
CC-77	39.4		56.5			4.1		56.5

CC-78	26.2	7.8	55.1	11			66.1
CC-79	27.6	6.1	45	18.4		Siderite2.9	63.4
CC-80	72.1		27.9				27.9
CC-82	50.3		44.7		5.1		44.7
CC-85	35.8		48	4.3	1.7	Kaolinite10.2	58.2
CC-90	19.3		47.9	17.3	8.1	Dolomite7.5	47.9
CC-93	8.9		30	61.1			30

Mineral composition in shales could reflect the deposition environment and diagenetic evolution during sedimentation and maturation. The linear positive correlation between TOC and quartz contents is due to the biogenic origins of quartz, such as silicified sponge spicules and diatoms (Jarive, et al., 2007; Tian et al., 2013; Sun et al., 2016). The biogenetic quartz is correlated with the siliceous biology grown in deep marine shelf (Yang et al., 2017). In this study, a scattered positive correlation is also observed between TOC and quartz contents in Fig.5a, suggesting quartz is at least partial of biogenic origin (Fig. 3). This would be attributed to the change of sedimentary facies (marine-terrestrial transition) of the studied samples. A negative relationship occurs between clay and TOC contents for the Permian shales in Fig.5b, which is consistent with the previous results of the Longmaxi Formation shales (Liu et al., 2011), implying that clay mineral did not produce the OM retention in the studied shales (Zhao et al., 2017a).

Fig.5. Relationship between TOC and (a) quartz content and (b) total clay content for the Permian shales.

4.3 Pore structure parameters

The parameters commonly used to characterize pore structures are specific surface area, porosity (Table 4) and pore size distribution. The BET surface area is ranging from 1.05 to 49.25 m²/g, averaged 15.70 m²/g. Hg-porosity of 32 shale samples is between 0.68% and 8.9% with most less than 4%, and He-porosity of 17 shale samples is varying from 1.15 to 9.79%. As illustrated in Fig.6, He-porosity is usually higher than Hg-porosity. This is because MIP could only measure the porosity of pores larger than 3 nm. While, He-porosity tested by helium expansion method represents the total porosity of shale. The higher porosities and BET surface areas mainly occur in the shales of the Dalong and Gufeng Formations.

Fig.6. Histogram of He-porosity and Hg-porosity of the Permian shales from HC and CC wells

Table 4 The BET surface area and porosity of the Permian shales from HC and CC wells.

Sample	Depth (m)	Unit	TOC (%)	Specific surface Area (m ² /g)	Hg-Porosity (%)	He-Porosity (%)
HC-32	109.9	P _{3l}	1.52	16.86	2.66	4.43
HC-36	122.8	P _{3l}	7.21	19.59	3.53	8.87
HC-38	124.5	P _{3l}	1.04	10.45	1.51	4.01
HC-43	140.1	P _{3l}	15.3	41.62	4.44	/
HC-45	140.7	P _{3l}	4.94	20.97	0.68	/
HC-69	220.5	P _{2g}	2.32	12.79	3.67	4.82
HC-77	247.2	P _{2g}	15.5	/	0.86	3.28
HC-79	252.2	P _{2g}	18.8	24	0.92	/
HC-80	254.4	P _{2g}	8.1	25.59	2.73	9.61
HC-81	257.8	P _{2g}	17.2	/	1.98	4.53
HC-83	264.2	P _{2g}	10.4	49.45	1.44	1.46
HC-86	273.8	P _{2g}	11.8	20.27	8.9	/
CC-7	90.7	P _{3d}	0.12	1.05	3.64	/
CC-12	121.7	P _{3d}	2.64	12.85	4.68	/
CC-13	123.4	P _{3d}	8.19	17.09	2.15	1.39
CC-14	128.1	P _{3d}	4.36	13.44	3.78	2.44
CC-15	131.2	P _{3d}	0.86	4.71	3.35	/
CC-16	132.9	P _{3d}	7.08	21.24	2.69	6.28
CC-20	145.9	P _{3d}	3.3	20.52	3.23	6.58
CC-21	152.7	P _{3d}	6.13	17.79	3.22	2.26
CC-29	187.4	P _{3l}	5.46	9.77	3.69	/
CC-36	208.9	P _{3l}	2.35	8.77	2.27	/
CC-48	239.6	P _{3l}	1.03	6.80	3.59	/
CC-76	305.9	P _{2g}	6.16	10.58	6.58	9.79
CC-77	308.5	P _{2g}	12.2	7.37	1.64	3.15
CC-78	312.4	P _{2g}	0.79	9.40	3.53	/
CC-79	314.7	P _{2g}	1.78	11.89	4.95	/
CC-80	317.5	P _{2g}	8.01	12.75	1.18	/
CC-82	321.5	P _{2g}	11.1	8.31	2.6	1.15
CC-85	330	P _{2g}	3.96	8.04	1.80	/
CC-90	341.8	P _{2g}	8.93	21.86	2.57	3.63
CC-93	355.1	P _{1x}	0.03	1.30	1.28	/

4.4 Nitrogen gas adsorption and desorption isotherms

Nitrogen gas adsorption/desorption isotherms measured at a low temperature and pressure (-196 °C and 127 kPa) could provide physisorption mechanism and pore characteristics of shales (Kuila and Prasad, 2013). The adsorption and desorption

isotherms of selected samples with different TOC contents are shown in Fig.7. In terms of IUPAC classification (Sing, et al., 1985), the isotherm shape of all samples is Type IV and their shapes of hysteresis belong to Type H3. Type H3 hysteresis loops usually reflects the pores of narrow slit-like shape. At a relative pressure (P/P_0) <0.01 , higher TOC samples exhibit much greater adsorbed volumes than the lower TOC samples, suggesting the number of micropores in a higher TOC shale is much more than that in a lower TOC shale (Kuila and Prasad, 2013). The lack of closure of the hysteresis loop below a relative pressure of 0.45 for high TOC shales was interpreted as being caused by swelling or N_2 gas incompletely desorption from micropores (Gregg and Sing, 1982). At the pressure of $P/P_0 = 0.995$, N_2 gas adsorbed volumes of the samples with a lower TOC content (HC-38) are greater than the samples with a higher TOC content (CC-90 and HC-79), which suggests that a low TOC shale may possess more mesopores and macropores than a high TOC shale. This phenomenon is quite different with the marine shales from the Longmaxi and Nititang Formations in Upper Yangtze region (Cao et al., 2015). An obvious “forced closure” of the desorption branch at $P/P_0 = 0.45$ is presented, which is attributed to the “tensile strength effect”, and is the result of the instability of the hemispherical meniscus during desorption in the pores with diameter of about 4 nm (Groen et al., 2003).

Fig.7. Isotherms of nitrogen gas adsorption and desorption for the Permian shales with different TOC content.

4.5 MIP analysis

The mercury intrusion/extrusion curves of three selected samples are shown in Fig.8. The levels of mercury saturation injected under high pressure are varied from 6% to 35%, and the corresponding Hg-porosities are between 1.51% and 8.9%. The mercury curves could be separated into two regions in terms of their shape. The mercury intrusion curves are approximately linear at the pressure of 0-1 MPa, and the volume of mercury intrusion increases with increasing pressure. This phenomenon reflects a slit-shaped pore structure consisting mainly of mineral matrix pores and/or fractures (Tang et al., 2015). When the pressure is greater than 1 MPa, the mercury intrusion curves show different increase slopes. For the sample HC-86, the mercury injection obviously increases, indicating that there are abundant nanopores with preferable connectivity and that the pores are mostly open, which is more

advantageous for shale gas flow and production (Cai et al., 2013; Tang et al., 2015). The straight linear increase of mercury intrusion for the sample CC-14 indicates that most pores are open, such as cylinders and parallel plates, and have good connectivity. Curve of sample HC-38 shows that little mercury injection and a low slope of mercury intrusion. This indicates that only few pores are developed in the shale and the pores are poorly connected, which is adverse for shale gas accumulation and diffusion (Zhang et al., 2015). In Fig. 8, obvious hysteresis is observed in MIP intrusion and extrusion curves in the studied samples. This suggests that a large amount of intruded mercury remains in the pores due to the high capillary pressure, implying some large pore space connected by narrow pore throat (or ink-bottle effect) and low ratio of throats to pores in these studied shales (Qu et al., 2016).

Fig.8. Curves of mercury intrusion and extrusion for the Permian shales with different TOC content.

4.6 Pore types from FE-SEM imaging

Many researchers have observed pore-appearance characteristics and determined pore types in a series of shales using TEM, FIB-SEM and FE-SEM (Slatt and O'Brien,

2011; Bernard et al., 2012; Loucks et al., 2012; Jiao et al., 2014). Three pore types proposed by Loucks et al. (2012) could be generally identified in gas shale reservoirs, namely OM pore, interparticle pore (interP pore) and intraparticle (intraP pore). Furthermore, microfractures with nanometers wide and micrometers long are also developed in shales. According to the pore network and the relationship with minerals, pore types in our selected shale samples can be summarized as follows.

4.6.1 OM pores

OM pores are an important component of pore system in the Permian shales. Fig.9a-f shows that a single OM particle with diameter of 1-5 μm could contain hundreds of pores. The majority of the OM pores in SEM images is mesopores and has oval, gneissic, linear and irregular shapes, but macropores are also present. It should be addressed that most of micropores could not be detected due to the resolution of FE-SEM instrument. Low-pressure N_2GA techniques can resolve much smaller pores, such as micropores and fine mesopores, in shales. Pores in OM are commonly more developed than those in matrix minerals (Fig.9b-f), which significantly contributes to specific surface area. Pyrite framboids are widespread in the studied shales, commonly co-existing with OM and developing a number of OM pores (Fig.9d-e). This phenomenon also present in the marine Nititang Formation and Longmxi Formation shales in Upper Yangtze region in China (Yang et al., 2016; Sun et al., 2016), suggesting that pyrite could promote hydrocarbon generation ability of OM (Ma et al., 2017) and increase the number of OM pores. Even though OM pores are widely distributed in the Permian shales, there are still many OM grains having few pores or no pores (Fig. 9f-i). Fig.9f shows that two OM grains in the same shale have heterogeneous pore characteristics. The OM grain on the right contains a large number of pores whereas the other OM grain on the left contains virtually no pores.

One possibility is that the OM grains are different organic fractions and kerogen types (Curtis et al., 2012). Similar phenomenon is also observed in the Woodford shale in America (Curtis et al., 2012), Wufeng-Longmaxi shale (Yang et al., 2016) and Nititang shale (Tian et al., 2015) in Sichuan Basin, China. This is often thought to be related to the differences of OM compositions (Curtis et al., 2012). Loucks et al. (2012) suggested that type II kerogen may be more prone to developing OM pores than type III kerogen. The OM in the Permian shales was interpreted as a mixture of Type II and III kerogen studied by Liang et al. (2008) and Pan et al. (2015), which complicates the development of OM pores. Some OM grains with rare pores usually fill in mineral pores, block pore connectivity and reduce the porosity of shale (Fig. 9g-i).

Fig.9. FIB-SEM images of OM pores within the Permian shales.

4.6.2 InterP and intraP pores

In contrast to OM pores, interP and intraP pores are less often observed in the

studied shales (Fig.10). InterP pores are generally observed between rigid mineral grains or at the margin of large particles, and are elongated or polygonal in shape (Fig.10a-c). These interP pores are nanometers wide and micrometers long. OM grains mixed up with clay minerals develop many nanometer-sized contact boundaries and form lots of interP pores (Fig.10d). This type of pores are usually long, narrow and arranged with the clay mineral grains, which may be a crumple structure caused by ductile deformation of clay minerals and OM particles under tectonic stress (Ma et al., 2015). The interP pores are always well connected, forming an effective pore networks (Loucks et al., 2012). IntraP pores developed within brittle minerals are generally linear, angular and irregular in shape, with pore sizes between tens and a few hundred nanometers (Fig.10e-f). These intraP pores may be caused by crystallography defects or dissolution according to their morphology and location. IntraP pores between pyrite crystals are commonly within pyrite framboids (Fig.10g-h). The sizes of such pores are normally in the range 100-500 nm. In addition, pyrite framboids commonly co-exist with OM and contain a significant number of OM pores. The intraP pores located along cleavage planes of clay minerals show little preferential orientation (Fig. 10i). These pores are linear in shape, which are defined by the lattice of randomly oriented clay mineral platelets. However, these clay mineral pores are in a small amount with their sizes commonly less than 100 nm, which may not play a major role in shale gas storage.

Fig.10. FIB-SEM images showing InterP and IntraP pores within the Permian shales.

4.6.3 Microfractures

Microfractures, serving as linkages between pores and artificial fractures, could improve the permeability of shale gas reservoir and also have an important influence on free gas accumulation. Under FE-SEM observation, microfractures are mostly found at the edge of minerals and OM grains or within OM particles (Fig.11). The sizes of microfractures are nanometers wide and micrometers long and they are usually in zigzag shape with great extensibility. The microfractures developed around minerals and OM grains are thought to be formed due to the volume reduction of clay minerals (Wang et al., 2015a) or OM at high maturity stage. However, other microfractures unrelated to matrix component in these shales may be formed due to late tectonic activities.

Fig.11. FIB-SEM images showing fractures within the Permian shales.

5 Discussions

Thermal maturity has been demonstrated as a key factor of OM pore development in shales due to the conversion of OM to hydrocarbon carbon (Loucks et al., 2009; Curtis et al., 2012; Mastalerz et al., 2013). The R_o value of the Permian shales varies in a very narrow range of 2.3-2.7% (Pan et al., 2015), which indicates that Permian shales have already entered a high maturity stage and have a close thermal maturation value. Hence, thermal maturation level on pore structure in these Permian shales might be excluded, and the pore structure would be influenced by TOC, organic fraction, mineral composition and other factors.

5.1 Effect of TOC content on pore structure

OM pores contribute significantly to the specific surface area and porosity of the marine shales (Tian et al., 2015; Zhang et al., 2015). For instance, Chalmers and Bustin (2007) found that there is a positive linear relationship between TOC content and specific surface area for the Cretaceous marine shale in northeastern British

Canada, suggesting that TOC is the main factor governing the nanopore structure. However, Zhu et al. (2014) and Xiong et al. (2016) observed negative relationships between specific surface areas and TOC contents for lacustrine shales in Dongying Sag and Ordos Basin, due to low thermal maturation level. In this study, the specific surface area is largely controlled by OM, as the TOC content has a positive relationship with specific surface area except for those samples with TOC>10% (Fig.12a). Nanometer pores are frequently observed in the FE-SEM images of the Permian shales shown in Fig 9a-f, which implies that OM contributes mainly to nanopores pore structure. For the shale sample with TOC>10%, the specific surface area does not increase with increasing TOC any more, which may be interpreted as other factors governing the development of OM pores. This pattern is also seen in the Lower Cambrian shales in northern Guizhou (Xia et al., 2017). BET surface area displays a general positive correlation with TOC for the Lower Cambrian shales with TOC<5%. However, when the TOC content is greater than 5%, BET surface area turns to decrease and exhibits no relationship with TOC (Xia et al., 2017). One reason of this phenomenon may be related to the increasing plasticity of shales with higher and increasing TOC, because higher TOC shales are more readily compressed and reduce OM pore space (Milliken et al., 2013; Xia et al., 2017). In addition, the studied shales contain plenty of solid bitumen and vitrinite, which are not favorable for developing OM nanopores, and these nonoporous OM fill nanopores and decrease the specific surface area.

As seen in Fig.12b, both Hg-porosity and He-porosity do not follow monotonous

trends with increasing TOC. There is a weak positive relationship between porosity and TOC content for the samples with $\text{TOC} < 6.16\%$. However, when the TOC content is greater than 6.16%, the porosity evidently drops and shows no correction with increasing TOC content. This result is similar but not totally consistent with Pan et al. (2015) who regarded that TOC shows a positive relationship with porosity when $\text{TOC} < 12\%$ and a negative relationship when $\text{TOC} > 12\%$ for the Permian shales in the Lower Yangtze region. Milliken et al. (2013) also noticed that the relationship between porosity and TOC is reverse for the Marcellus shale with a high TOC ($> 5.5\%$). This may be attributed to pore collapse and OM connectivity, because framework compaction or OM with low initial hydrocarbon index that is less prone to development of pores (Milliken et al., 2013). As revealed by Ardakani et al. (2018), TOC consists of different macerals or petrographic fractions, which contribute differently in total porosity. Hence, the amount of porosity with a single OM particle could range from 0 to 40% (Loucks et al., 2009). For instance, the OM particle in Fig.9g-i has the porosity approximate zero, while the porosity of the single OM particle in Fig.9a-b is relatively high. These characteristics of OM pores lead to the differences in porosity in different OM grains. Therefore, according to the previous studies and our data in this study, these shales with $\text{TOC} > 6.16$ usually have low porosities, because (1) the shales with higher TOC content are more readily compressed and consequently reduce pore number and size in shales, (2) high content of OM usually contains abundant less porous solid bitumen and vitrinite (Fig.9g-i) which could fill the pores associated with minerals and therefore subtract pore space

in a high TOC samples.

Fig.12. Relationship between TOC and (a) BET surface area and (b) porosity for the Permian shales.

5.2 Effect of maceral composition on pore structure

Previous studies raised a question about the nature and type of OM on the evolution of OM pores, and noticed that small-scale spatial heterogeneity of pores developed in OM at the nanometer to micrometer scale (Loucks et al., 2009). Loucks et al. (2012) considered that the development of OM pores may also be controlled by kerogen types, some of which are not prone to pore generation at the mature stage. Type II kerogen is likely being more prone to generating pores than type III kerogen, which may be related to the chemical composition of kerogen. Liu et al. (2017) and Ardakani et al. (2018) regarded that porosity development is quite different within different organic macerals, which make different contributions to total porosity.

OM pores developed in the Permian shales show significant heterogeneities among different kerogen particles, which could be subdivided into three categories on the basis of their morphology and interpreted origins. The OM particle displaying as convoluted and curvature shapes in Fig.13a-b and wood fragment in Fig.13c, on basis of their appearances and cellular structures, could be observed and identified as

kerogen of terrestrial origin (type III kerogen) (Loucks et al., 2009, 2012; Milliken et al., 2013). It shows no OM pores, despite of entering a high-maturity stage, illustrating that vitrinite is not favorable for generating pores (Yang et al., 2016; 2017). Liu et al. (2017) also examined that OM pores developed in specific organic macerals in the New Albany shales, and regarded that vitrinite and inertinite derived from terrestrial woody materials distribute as discrete particles and do not developed secondary pores during thermal maturation. Some OM grains filling in the intergranular space of matrix minerals are possibly bitumen (Fig.13d-f). Solid bitumen does not have a certain shapes, depending on the shape of intergranular space between matrix particles (Dong et al., 2015; Cai et al., 2016). From the images of Fig.13d-e, there are a small number of pores with triangle, spherical and oval shapes developed within these solid bitumen grains, because liquid hydrocarbon will convert to solid bitumen and shrink to a bulk matter when cracking into gas. Whereas solid bitumen could reduce the total porosity due to filling in mineral-related pores. As revealed by Wood et al. (2018), solid bitumen in siltstones of the Montney Formation in western Canada was filled in void and fracture, and few pores were observed. However, as studied by Liu et al. (2017), though solid bitumen filling interP pores and cavity space, well-developed secondary nanopores are mainly located in solid bitumen and play a significant role in hydrocarbon storage and migration, which has significant deviations with our study. The third form of OM is sapropelinite, which usually distributes in dispersed microparticle with diameter in micrometer range (Fig.13g-i). Sapropelinite has great hydrocarbon generation potential and can generate

a large number of pores with small scale in the process of transforming to pre-oil bitumen (Liu et al., 2017). Whether in the Woodford shale of North America, the Longmaxi shale in southeastern Sichuan of China or the Permian shale in this study, there are abundant OM pores developed within sapropelinite grains, which fully illustrates that sapropelinite is the most favorable organic fraction for the development of OM pores.

Fig.13. Series of images showing maceral composition, including vitrinite, solid bitumen and sapropelinite, and its influence on pore development for the Permian shales.

5.3 Effect of residual bitumen on pore structure

For the low mature or mature shales, the residual bitumen (S_1) could fill the pores and pore-throats, and then dramatically decrease the BET surface area, porosity and methane sorption capacity (Jarvie et al., 2007; Guo et al., 2014). The Permian

shales are at a high maturity stage (Pan et al., 2015), and they contain a low content of residual bitumen. Fig.14a-b display positive relationships between S_1 and TOC contents for the Permian shales, indicating that the residual bitumen is closely related to OM (Kelemen et al., 2006). In this study, a positive relationship occurs between the BET surface area and S_1 content for the samples from the two wells in Fig.14c-d, but this phenomenon could not illustrate specific surface area increases with increasing S_1 content. Because the space occupied by solid bitumen cannot adsorb nitrogen gas in the process of N_2 GA test and could not provide surface area (Liu et al., 2016). Moreover, both the BET surface area and S_1 increase with increasing TOC, and therefore the effect of residual bitumen on specific surface area could be probably attributed to the function of TOC. That is because the kerogen, other than residual bitumen, is closely bonded with nanopores. Therefore, we regarded that residual bitumen would reduce OM pores other than increase the specific surface area. As reported in literatures, residual bitumen occupying the surface of solid kerogen would result in the swelling of solid kerogen and appear to like organic macromolecules, which are an important factor in reducing OM pore space within a connected OM framework (Guo et al., 2018). SEM images have shown that OM pores are invisible in un-extracted samples reappear after extraction (Löhr et al., 2015).

The Permian shales generally contain more residual bitumen within higher TOC content (Fig.14a-b), and therefore the effect of residual bitumen on porosity is more intense in high TOC shales (Liu et al., 2016). Hg-porosity of the Permian shales shows a weak negative correlation with S_1 content in Fig.14e-f, probably as a result of

OM pores and mineral pores filled by residual bitumen that reduces the available open pore space and restricts Hg intrusion. Wang et al. (2015b) regarded that residual bitumen is more likely to retain in low mature shale pores with larger diameters greater than 30nm. Xiong et al. (2016) regarded that the pore volume of the Triassic Yanchang shale samples in southern Ordos Basin after the extraction of residual bitumen significantly increases, which was closely related with pores of >30 nm and <10 nm. In the mature shales, some pores and pore-throats are still blocked by residual bitumen, as indicated by increased mesopore and micropore volumes after removing the residual bitumen (Wei et al., 2014).

Fig.14. Relationship between S_1 and (a-b) TOC, (c-d) BET surface area and (e-f) Hg-porosity for the Permian shales.

5.4 Effect of mineral compositions on pore structure

According to previous studies, clay minerals usually have pores with diameter larger than OM, ranging from mesopores and macropores (Chalmers and Bustin, 2008). In the Permian shales, the specific surface area shows a negative trend with clay content (Fig.15a), and the Hg-porosity has no relationship with clay content (Fig.15b), indicating that clay mineral is not conducive to shale porosity development and may inhibit the development of porosity in shales (Zhao et al., 2017b). Ye et al. (2017) pointed that clay content has a relatively negative effect on pore structure in Niutitang Formation shales in the Southern Yangtze region, China, especially showing better negative correlation with micropores and mesopores than macropores, illustrating that clay is especially unfavorable to the development of micropores and fine mesopores. XRD results show that illite and chlorite are the dominant clay minerals in the studied samples, which have a much lower specific surface area than smectite and illite-smectite mixed-layer and mature kerogen (Ji et al., 2012; Cao et al., 2015). Hence, the clay mineral has a negative effect on specific surface area. Chalmers and Bustin (2008) thought the pores in clay minerals range between mesopores and macropores, and therefore contribute limited to specific surface area. In addition, during burial process, ductile grains could be distorted, and thus shale pores and pore throats are closed or plugged which could result in a very low porosity in shale.

The relationships of BET surface area, porosity with quartz content are shown in

Fig.15c-d. The BET surface area is positively correlated with quartz content, which is similar to previous study on Devonian shales (Chalmers et al., 2012). Although quartz contains some intraP pores, it is unlikely to be a reason for the increased specific surface. Because the quartz content is positively correlated with TOC content, the quartz content are naturally shown the positive relationship with specific surface area (Pan et al., 2015). In addition, the pore system of the studied samples is mainly associated with nanopores. The macropores are mainly controlled by diagenesis and compaction. Although rigid quartz grains could shield the nanopores from compaction, the overly abundant quartz may have reduced the macropores due to precipitation within pore spaces (Xi et al., 2018), and therefore the porosity of the studied samples displays a roughly decrease with increasing quartz content (Fig. 15d).

Fig.15. Relationship between (a) total clay content and BET surface area, (b) total clay content and Hg-porosity, (c) quartz content and BET surface area and (d) quartz content and Hg-porosity for the Permian shales.

5.5 Combined pore size distribution from N₂GA and MIP

A combination of MIP data and N₂GA analyses could provide a more compressive understanding of a wide range of pore size distributions (Lei et al., 2015; Zhang et al., 2017). In this paper, the adsorption isotherm from N₂GA data could provide pore size distribution of 1.2-36 nm whereas MIP experiments give pore size between 3 nm-45 μ m. However, MIP is not accurate to measure nanometer pores due to pore deviation under high pressure (Li et al., 2017). In contrast, N₂GA is more suitable to measure micropores and fine mesopores (Fang et al., 2016). In this study, comparing pore size distribution of the two methods, we could found that the MIP data is well consistent with the N₂GA data at about 10 nm for the studied Permian shales with different TOC contents (Fig.16). As shown in Fig. 16, pores with a diameter smaller than 10 nm have the highest pore volume, indicating that micropores and fine mesopores contribute the most of the pore system. Pores ranging in size less than 10 nm are mainly OM pores, because the peaks of micropores and fine mesopores are obviously controlled by TOC, except for the sample CC-82, suggesting the main control factor for development smaller pores are the development of OM pores (Fang et al., 2016). However, pores greater than 10 nm show low amplitudes and no obvious peaks, suggesting that mesopores and macropores with size larger than 10 nm are not developed and contribute little to the pore system. In addition, pores ranging from 1 to 45 μ m are probably mainly fracture, which is similar to those documented using FE-SEM images (Fig. 11) and may provide some pore space for the Permian shale gas reservoir.

Fig.16. Pore volume distribution with respect to pore size derived from the adsorption branches of N₂GA with DFT mode and mercury intrusion branches of MIP for the Permian shales.

5.6 Comparison of physical property between Permian intervals

Natural gas primarily stores as adsorbed gas on surface area of OM and clay mineral and/or free gas in pores and fractures (Curtis, 2002; Zhang et al., 2012). Hence, free gas is closely related to the porosity, whereas adsorbed gas is controlled and could be characterized by specific surface area (Montgomery et al., 2005; Ross and Bustin, 2007; Mosher et al., 2013). For the Permian shales studied, they have a high specific surface area of 1.05-49.25 m²/g, with an average of 15.70 m²/g, which is

greater than that of marine Lower Cambrian shale in northern Guizhou region (Li et al., 2017; Wu et al., 2017) and approximate to the Longmaxi Formation shale in the Middle Yangtze region, central China (Wang et al., 2018). Hg-porosities of 32 shale samples, ranging between 0.68% and 8.9% with most less than 4%, are higher than the Lower Cambrian shale in north Guizhou (Wu et al., 2017; Xia et al., 2017) and Lower Silurian shale in Middle Yangtze region and Sichuan Basin (Wang et al., 2018; Zhao et al., 2017b). Therefore, the Permian shales have a good physical property compared with marine shale reservoirs in China.

In the Permian sedimentary system, the Gufeng and Longtan Formations belong to shelf basin facies, and the Longtan Formation is defined as deltaic facies. The Gufeng and Longtan Formations usually have much higher TOC contents than the Longtan Formation, as well as brittle mineral contents (Fig.17), suggesting that the shales of the Gufeng and Longtan Formations have a better gas generation condition and are more easily to be fractured. The shales of the Gufeng and Dalong Formations also have higher specific surface areas and Hg-porosities than the Longtan Formation shale (Fig.17), so they could be regarded as favorable zones when evaluating shale gas resource of the Permian shales in southern Anhui province.

(a) HC well

(b) CC well

Fig.17. Profiles of TOC, brittle mineral content, specific surface area and Hg-porosity of the Permian shales in HC and CC wells.

6. Conclusion

Organic geochemistry, mineral composition and pore characteristics of 32 Permian shales from two shale gas parameter wells in the southern Anhui province were investigated, and the controlling factors of pore structures were also identified in this study. Some preliminary conclusions are as follows.

(1) OM is dominated by a mixture of type II-III kerogen with TOC contents ranging from 0.12 to 18.8% for the Permian shales and $T_{\max}$ values is generally higher than 484 °C, indicating that the shales are at a high mature stage. The maceral of OM is dominated by sapropelinite and solid bitumen, followed by vitrinite. Based on XRD analysis, the mineral is dominated by quartz and illite, followed by feldspar, calcite, chlorite and pyrite.

(2) FE-SEM images show that four pore types exist in the Permian shales studied, namely, OM pores, interP, intraP pores and fractures, of which OM pores and fractures are the dominated types. OM pores are usually developed within sapropelinite grains other than solid bitumen and vitrinite. The specific surface area ranges from 1.05 to 49.45m²/g with an average value of 15.7 m²/g, and the Hg-porosity and He-porosity are varying from 0.68% to 8.9% and from 1.15% to 9.79%, respectively.

(3) Samples with TOC<10% have a positive correlation between TOC content and specific surface area, while the specific surface area does not show a positive covariation with TOC content for samples with TOC>10%. Samples with TOC<6.16 has a weak positive correlation between TOC content and porosity, however, samples

with TOC>6.16% usually have a low porosity. This may imply that in samples with high TOC content, primary pores were mostly filled by nonporous OM or closed by compaction. Residual bitumen plays a negative role in pore structures due to filling in mineral pores and/or OM pores. Clay mineral is not conducive to the development of shale pores and is particularly inhibitive to nanopores development, while quartz has a negative effect on porosity of the Permian shales.

(4) Compared with marine Niutitang and Longmaxi formation shales, the Permian shale has a good physical property condition. As revealed in vertical profile, the Gufeng and Dalong Formations shales have a higher TOC content, specific surface area and porosity than the Longtan Formation shale, and may be the favorable shale gas intervals in southern Anhui province.

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