Research Article

Paleoenvironment, Geochemistry, and Pore Characteristics of the Postmature to Overmature Organic-Rich Devonian Shales in Guizhong Depression, Southwestern China

Yanqi Zhang^{1,2} , Li Liu,¹ Changxi Geng,^{1,2} Zhuang Cheng,³ and Xinxin Fang^{4,5}

¹School of Geosciences, Jilin University, Changchun 130061, China

²Daqing Drilling Engineering Company, Daqing Oilfield Co. Ltd., Daqing 163458, China

³Daqing Drilling & Geological Logging No. 1 Company, Daqing 163458, China

⁴Institute of Geomechanics, Chinese Academy of Geological Sciences, Beijing 100081, China

⁵Key Laboratory of Paleomagnetism and Tectonic Reconstruction, Ministry of Natural Resources, Beijing 100081, China

Correspondence should be addressed to Yanqi Zhang; 183268205@qq.com and Xinxin Fang; 8530324@qq.com

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Investigating shale pore characteristics has deepened our understanding of shale reservoir, while that of postmature-overmature shales is yet to be revealed, which is especially critical for shale gas evaluation in southern China. Ten Middle-Upper Devonian organic-rich shale samples were collected from well GY-1 in the Guizhong Depression, and the paleoenvironment, geochemistry, and pore system were analyzed with a series of experiments, including trace element analysis, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), low-pressure N₂ adsorption, and source rock geochemistry. Results show that the Middle-Upper Devonian shales in the Guizhong Depression are organic-rich mudstones with TOC ranging from 0.14% to 6.21%, which is highest in the Nabiao Formation (*D₂n*) and Lower Luofu Formation (*D₂l*) that were deposited in the anoxic and weak hydrodynamic deep-water shelf. They are thermally postmature to overmature with equivalent vitrinite reflectance (*EqVR_o*) of 3.40%~3.76% and type I kerogen. The lithofacies in *D₂n* and *D₂l* are primarily siliceous/argillaceous mixed shale as well as a few siliceous argillaceous shales and argillaceous siliceous shales as well. Organic matter- (OM-) hosted pores within bitumen are primary storage volume, rather than inorganic pores (interparticle and intraparticle) which are rare. The total helium porosity of samples varies between 1.20% and 4.49%, while total surface area and pore volume are 2.39-14.22 m²/g and 0.0036-0.0171 ml/g, respectively. Porosity, pore surface area, and pore volume are in accordance with increasing TOC, *R_o*, and siliceous mineral contents. Considerable OM-macropores are found in shales with *R_o* > 3.6% in our study which demonstrates that the porosity at postmature to overmature stage (*R_o* = 3.5–4.0%) does not change fundamentally. The high level of maturity is not considered the main controlling factor that affects shale gas content, and more attention should be paid to preservation conditions in this area.

1. Introduction

Shales have attracted significant attention in the past few years because of their emergence as unconventional hydrocarbon reservoirs [1–3]. Identifying and producing reserves from shales in south China have gained considerable exploration interest and activity, which have made significant progress [4, 5]. Unlike conventional sandstone and carbonate reservoirs with microscale pores, shales are typically domi-

nated by nanoscale pores [6]. The pore structure characterization using various techniques has gained a high research priority as they are essential in a potential shale reservoir evaluation. The direct imaging methods, e.g., CT scan, field emission scanning electron microscopy (FESEM), focused ion beam-scanning electron microscopy (FIB-SEM), and transmission electron microscopy (TEM) [7–11], provide information on pore size, pore morphology, and connectivity of the pore networks. The indirect methods, e.g., mercury

injection porosimetry (MIP), low-pressure gas adsorption (CO_2 and N_2), and small-angle and ultra-small-angle neutron scattering (SANS and USANS), can be employed to investigate porosity, specific surface area, and pore size distribution [10, 12, 13]. Organic matter-hosted pores have been identified as an important pore system in gas shales [9, 14–18]. Thermal maturity has been considered by previous studies as one of the critical controllers of organic pore growth [1, 13, 19–23]. Researchers have tried to restore the hydrocarbon generation process and associated organic pore growth through pyrolysis, which can cover the weakness of measurements mentioned above in pore system characterization and prediction [24–29]. However, pyrolysis differs remarkably with geological conditions in temperature, pressure, medium, heating model, etc. Many investigations reported that nanoscale pores were generated due to kerogen degradation with increasing thermal maturity, but commonly shrank as a result of high temperature and pressure and no available oil cracking into gas in deep basin [9, 13, 14, 30]. The conversation among micropore, mesopore, and macropore was found, and an evolution model of porosity with thermal maturity was established [13, 21, 31]. However, the pyrolysis results typically require the constraint from high- to over-high-mature natural shale samples. Therefore, characterizing the pore system of such high-mature Devonian shales in the Guizhong Depression can provide insight into the shale gas resource assessment in China.

Dian-Qian-Gui Basin is an important petroliferous basin in south China with high petroleum exploration potential [32]. The Devonian marine deposits in the Guizhong Depression are characterized by good hydrocarbon accumulation conditions and considerable petroleum resource potential [33–36]. GY-1 well was drilled at the northwest of the Guizhong Depression to investigate the occurrence of the Devonian shale, understand its geochemical characteristics and storage capacity, and evaluate shale gas resource potential. It is the first well drilling all shales in the Devonian with a completion depth of 1205.5 m (Lower Devonian Lianhuashan Formation). Coring for the whole well section provides considerable evidence for us to analyze hydrocarbon generation potential and reservoir quality. In this study, we will (1) investigate geochemistry and pore system of Devonian shales in the Guizhong Depression that can be further compared with organic-rich shales from other basins in South China and other countries and (2) discuss the organic matter-hosted pores in postmature to overmature stage and the contributors to their development.

2. Geological Settings

The Dian-Qian-Gui Basin is situated in southwest China in the provinces of Yunnan (Dian), Guizhou (Qian), and Guangxi (Gui) (Figure 1). It lies in the northern Nanpanjiang orogenic fold zone along the southwest margin of the Yangtze (South China) Precambrian craton [37, 38] at the joint of the Tethyan Himalayan and Pacific Ocean tectonic plates [39, 40].

Guizhong Depression in the north-central Guangxi is a secondary structural unit in the northeastern Dian-Qian-

Gui Basin with an area of $4.6 \times 10^4 \text{ km}^2$. Structurally, it is located at the joint of the southwest margin of Yangtze block and South China Caledonian fold belt, which is sandwiched between the Pacific tectonism and the Tethys tectonism [41].

The Guizhong Depression is adjacent to the Xuefengshan Uplift in the north, Qiannan Depression in the northwest, Guilin Depression and Dayaoshan Uplift in the east, and Nanpanjiang Depression and Luodian Fault Depression in the west. It is bounded by the Longsheng-Yongfu Fault, the Nandan-Duan Fault in the west, and the Dayaoshan Fault in the east. The depression can be divided into several sags and salients (Figure 1).

Guizhong Depression was a large marine deposition center during Late Paleozoic due to the Caledonian movement, which is currently a residual basin filled by the Upper Paleozoic and Triassic [41]. During the Lianhuashan and Nagaoling period, terrigenous clastic sandstone with silty mudstone was deposited in the Guizhong Depression. The paleo-Tethyan extensional rift during the late Devonian resulted in regional tension with deposition as well as the growth of NW-trending and NNE-NE-trending faults. Meanwhile, the transgression extended from south to north, forming the platform-basin sedimentary framework, e.g., the basin facies mainly occurred at the western depression, depositing Yilan and Tangding siltstone, limestone, and black marl. The increasing rifting during the Middle Devonian gave rise to the growth of NW-trending and nearly NS-trending faults and high relative sea level, enlarging platform and basin and forming alternation of platform and basin. Consequently, Nabiao and Luofu black carbonaceous shale, siliceous shale, and marl were deposited in semideep water to deep water [41].

The Upper Devonian Liujiang Formation in the GY-1 well is mainly limestone and siliceous rocks in the upper section and calcareous mudstone interbedded with thin argillaceous limestone in the lower section. The Middle Devonian Luofuyang Formation is calcareous mudstone and thin gray marl, while the Nabiao Formation is characterized by calcareous mudstone with decreasing calcareous content from the top to the bottom with considerable tentaculites. The Tangding Formation is dominated by gray-light gray silty mudstone with marl lenses and framboidal pyrite at the top. The Lower Devonian is typically light gray fine sandstone and dark grey silty mudstone. The thickness of the Lower Liujiang Formation, Luofu Formation, Nabiao Formation, and the Upper Tangding Formation in the GY-1 well is over 600 m, which is dominated by carbonaceous shale and marl depositing in deep-water shelf and shallow-water shelf (Figure 2).

3. Samples and Methods

Ten core samples from the GY-1 well were collected to perform trace elements analysis, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), low-pressure N_2 adsorption, and source rock geochemistry (total organic carbon (TOC), kerogen microscopic examination, and bitumen reflectance).

3.1. Trace Element Analysis. Samples were cleaned in an ultrasound bath and then were oven-dried. After that, they

FIGURE 1: Location and structural units of the Guizhong Depression.

were disaggregated into grains (<200 meshes) by physical crushing with an agate mortar. The measurement was conducted using the acid dissolution method in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Dried powders were burned in the oven at 700°C for 3 hours to remove organic compounds. 0.37–0.45 mg of remaining was dissolved using HNO₃, HF, and HClO₄ in the PTFE sampling bottom. The analysis was performed using a PEELAN6000 ICP-MS.

3.2. X-Ray Diffraction (XRD) Analysis. The XRD experiment was performed using a ZJ207 Bruker D8 advance X-ray diffractometer following the oil and gas industry standards

(SY/T5463-2010). The shale samples were crushed smaller than 300 mesh sizing and hand-mixed with ethanol in a mortar and pestle and then smear-mounted on glass slides for XRD analysis. The X-ray diffractometer with Cu X-ray tube operated at 40 kV and 30 mA and scanned from 2° to 70° at a step of 0.02°, and the data was semiquantified using Jade® 6.0 software.

3.3. Geochemistry of Source Rocks. Kerogen microscopic examination, TOC, and bitumen reflectance measurements were carried out in the Experimental Research Center of Wuxi Research Institute of Petroleum Geology, SINOPEC. Kerogen maceral in the sediments was identified using

FIGURE 2: Stratigraphic column of the GY-1 well. The trace element data and the paleoenvironment are explained.

LEICA DMRX Polarization microscope DM4500P, while the kerogen type was determined using the percentage compositions of individual maceral and corresponding weighting coefficients following the Chinese National Standards SY/T 5125-2014. For TOC analysis, each sample (0.10 g) was prepared with 12.5% HCl to remove carbonates in a sterilized crucible and was washed in distilled water every half an hour for three days and then were oven-dried. TOC analysis was conducted in a LECO CS-230 carbon analyzer following the Chinese National Standards GB/T19145-2003. With no vitrinite in the samples, the optical feature and bitumen reflectance was determined through observing polished sur-

faces of samples using MSP 200 microphotometer following the Chinese National Standards SY/T5124-2012.

3.4. Field Emission Scanning Electron Microscopy (FESEM). The FESEM observation was carried out at China University of Petroleum, Beijing. Shale samples were cut into about one-centimeter square, which was polished to produce flat surfaces using dry emery paper. After that, they were milled by sputtering away shale material via momentum transfer with a focused 30 kV beam of argon ions in a focused ion beam (FIB) system. Representative samples were coated with carbon to produce a conductive surface, which was inspected

TABLE 1: Major element content and element ratios of Devonian shale of GY-1 well.

Depth	Sr × 10 ⁻⁶	Rb × 10 ⁻⁶	Th × 10 ⁻⁶	Pb × 10 ⁻⁶	As × 10 ⁻⁶	Zn × 10 ⁻⁶	Ni × 10 ⁻⁶	Mn × 10 ⁻⁶	Cr × 10 ⁻⁶	V × 10 ⁻⁶	Ti × 10 ⁻⁶	S × 10 ⁻⁶	Ba × 10 ⁻⁶	Nb × 10 ⁻⁶	Bi × 10 ⁻⁶	δU	V/V+Ni	V/Cr	Ni/Co	U/Th	Au × 10 ⁻⁶	Sr/Ba	
300.70 m	91.16	247.34	69.79	11.01	17.49	9.27	40.64	144.93	207.42	99.38	166.97	2735.54	22489.38	827.12	7.29	8.69	1.3	0.54	1.68	5.88	0.45	10.81	0.3
350.10 m	93.43	167.94	72.54	8.94	15.23	5.01	31.86	119.88	178.04	79.43	175.22	2730.23	10514.21	768.42	8.65	8.13	0.87	0.51	2.21	5.47	0.26	11.42	0.22
399.70 m	124.73	136.84	77.4	14.87	43.16	18.82	31.99	138.24	386.86	165.02	135.58	4063.01	21241.92	734.01	12.94	13.64	1.3	0.59	0.82	7.23	0.44	9.85	0.19
451.30 m	145.89	151.77	68.97	14.7	9.51	0.001	74.33	128.48	333.27	159.78	157.48	4373.91	6268.96	803.56	12.69	13.66	1.22	0.55	0.99	5.01	0.71	7.56	0.19
499.50 m	112.81	181	92.88	6.39	10.64	0.001	53.14	133.7	286.59	71.72	190.87	3464.37	3513.37	936.34	8.82	7.91	1.45	0.59	2.66	6.17	0.9	8.2	0.19
550.70 m	110.17	305.17	89.57	11.58	20.19	20.62	99.26	170.06	268.02	101.64	231.84	3718.66	19320.6	913.31	11.61	2.03	1.29	0.63	2.28	5.19	0.6	10.2	0.33
599.90 m	114.31	216.53	80.92	6.6	40.08	39.61	119.05	193.03	222.82	99.69	288.39	3620.85	24523.35	877.75	9.59	8.41	1.34	0.67	2.89	5.59	0.67	9.11	0.25
649.50 m	87.5	252.36	79.42	17.86	34.28	19.6	165.57	150.07	274.15	89.57	373.79	2523.86	7612.05	1211.87	9.12	18.34	1.42	0.71	4.17	6.93	1.3	7.63	0.28
700.30 m	31.04	294.81	21.94	5.45	13.58	8.7	81.84	97.68	348.11	0.001	132.09	531.95	2881.06	1341.49	6.01	9.44	1.43	0.87	5.67	7.12	0.84	6.32	0.43
750.20 m	86.64	96.75	81.85	9.54	59.83	25.87	255.47	173.8	216.88	134.4	381.8	2502.73	28648.95	1113.62	9.15	10.01	1.55	0.69	2.84	7.85	1.13	7.13	0.09
799.40 m	66.76	333.43	58.97	12.75	25.21	43.28	96.88	183.84	337.36	83.93	232.4	2182.99	15541.45	1428.57	8.75	10.64	1.04	0.68	2.77	8.32	0.47	9.89	0.33
848.30 m	33.21	454.22	26.63	6.04	13.29	7.77	93.99	128.95	3481.92	0.001	110.67	619	3735.33	807.5	6.23	9.01	0.92	0.46	1.75	6.26	0.55	11.49	0.56
901.80 m	151.6	36.03	84.64	14.5	48.94	8.29	48.16	101.39	148.73	120.8	178.74	5550.84	2847.54	511.3	16.74	10.66	0.89	0.42	1.48	4.93	0.64	8.73	0.03
951.20 m	95.12	49.52	125.06	22.98	6.54	8.72	19.58	76.69	249	120.38	217.8	4583.87	3012.26	762.31	14.06	20.54	1.16	0.51	1.81	5.76	0.46	10.03	0.04

TABLE 2: Kerogen microscopic composition and determined kerogen type index.

Depth (m)	Formation	Sapropelinite (%)		Exinite (%)	Vitrinite (%)	Inertinite (%)	TI	Type
		Amorphous solid	Alginite	Benthic algae				
231	D_3l	56	18	26	-	-	87	I
255	D_3l	58	17	25	-	-	87.5	I
475	D_2l	63	15	22	-	-	89	I
495	D_2l	64	18	18	-	-	91	I
579	D_2l	65	14	21	-	-	89.5	I
595	D_2l	62	14	24	-	-	88	I
639	D_2n	67	15	18	-	-	91	I
651	D_2n	62	13	25	-	-	87.5	I
739	D_2n	65	15	20	-	-	90	I
795	D_2n	70	14	16	-	-	92	I

Note: $TI = 100 \times a + 100 \times b1 + 50 \times b2 + 10 \times c1 + (-75) \times c2 + (-100) \times d$, where TI is the kerogen type index, a is the sapropelinite (%), $b1$ is the resinite (%), $b2$ is the cutinite, suberinite, sporinite, amorphous solid, and benthic algae (%), $c1$ is the perhydrous vitrinite (%), $c2$ is the normal vitrinite (%), and d is the fusinite (%).

FIGURE 3: Mineral composition of the Upper-Middle Devonian samples of GY-1 well determined by XRD.

using an FEI Helios NanoLab™ 650 FESEM with a resolution of 2.5 nm under accelerating voltage of 2 kV and a working distance of 4 mm.

3.5. Ultra-Low-Pressure N_2 Adsorption. Ultra-low-pressure N_2 adsorption analyses were carried out at -196°C and relative pressure of 10^{-7} -0.995 using a Quantachrome® Autosorb-iQ2-MP apparatus at China University of Petroleum, Beijing. Detailed information can refer to [42]. Pri-

mary parameters in this measurement are surface area, pore volume, average pore diameter, etc. The surface area was calculated using the BET (Brunauer-Emmett-Teller) equation. The pore volume and pore size distribution were determined using the Barrett, Joyner, and Halenda (BJH) method with relative pressure of 0.06-0.99. The average pore diameters were calculated using the ratio of the total adsorbed nitrogen amount to the available surface area with the assumption of cylindrical pore geometry [43].

FIGURE 4: The amorphous and algal bodies of sapropelite from kerogen microscopic examination: (a) D_3l (231 m), (b) D_2l (579 m), (c) D_2n (639 m), and (d) D_2n (795 m).

FIGURE 5: TOC statistical results of the D_3l , D_2l , and D_2n source rocks.

4. Results

4.1. Paleoenvironment and Petrology. Basin paleo-environment generally determines its initial productivity and redox conditions, which can be recorded by sedimentary geochemistry [44, 45]. Main and trace elements of shale have been employed to rebuild the paleoenvironment [46], e.g., redox-sensitive elements including V, Co, Cr, Ni, Mo, and U, which can be used to infer redox conditions [46, 47], because these elements are typically insoluble in reducing

FIGURE 6: The bitumen reflectances and the determined equivalent vitrinite reflectance of GY-1 well.

environment and consequently accumulate in the anaerobic environment but loss in the oxygen-rich environment. Parameters, e.g., Ni/Co, V/Cr, and U/Th, are widely used to identify redox conditions [48]. The measurement shows

(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 7: Continued.

FIGURE 7: SEM images of microscopic pores from the siliceous shale (255 m of well GY-1, S-2 in Figure 3): (a, b) OM-pores, (c, d) OM-clay mineral complexes, (e, f) micropores in the quartz particles, (g) residual pores between pyrite crystals are filled with organic matter, and micropores are developed within it or/and at the edge, and (h) no OM-pores developed in some organic matter.

that the $V/(V+Ni)$ is in a range of 0.31–0.90 with a high value in the Upper-Middle Nabiao carbonaceous shale (636.00 m–771.7 m) and Lower Luofu Formation (536.20–592.83 m). Ni/Co generally ranges from 4.74 to 9.69 with a high value in the Middle-Lower Nabiao Formation (648.35 m–790.60 m). U/Th varies between 0.09 and 2.03, while the value is higher in the Nabiao Formation (684.10 m–807.50 m) and Lower Luofu Formation (523.74 m–598.20 m) and decrease toward the Upper Luofu Formation and Tangding Formation. Uranium isotope is relatively high in the Nabiao Formation and Lower Luofu Formation. Au ($\times 10^{-6}$) varies in a similar trend with other elements, which is high in the Nabiao carbonaceous shale (Figure 2 and Table 1). These trace elements suggest that the Nabiao Formation and the Lower Luofu Formation were deposited in an anaerobic and reducing environment, while Luofu Formation and Tangding Formation were in the high-energy and well-circled environments. Also, TOC and indicators of redox environment, e.g., V/Cr , Ni/Co , and U/Th , follow a similar trend (Figure 2). Furthermore, tentaculites were found in both Devonian outcrop and Luofu and Nabiao core samples. These thin-wall tentaculites are typically zooplankton in deep water, indicating a deep-water deposition environment. In addition, the occurrence of considerable framboidal pyrite is a good indicator of a reductive deep-water environment. Thus, the Tangding Formation was deposited in oxygen-poor and shallow water with low TOC. Nabiao black shale was developed in an anoxic and deep-water environment with weak hydrodynamic, which contributes to the development and preservation of abundant organic matter. Different from that, the Luofu Formation was deposited in a weakly toxic environment with low organic matter abundance.

X-ray diffraction measurement indicates that such shale gas reservoir is mineralogically composed of quartz, calcite, clay minerals, dolomite, plagioclase, siderite, and pyrite (Table 2). Liujiang Formation is characterized by the highest quartz content with a value over 90%, which is primarily siliceous rock with siliceous shale, mud-rich siliceous shale, and

silicon-/mud-rich shale of secondary importance. D_2n and D_2l are primarily siliceous/argillaceous mixed shale as well as a small proportion of siliceous argillaceous shale and argillaceous siliceous shale (Figure 3). Researchers have reported that the storage space of shales varies with lithofacies, which have a significant impact on organic matter enrichment, gas adsorption, and storage capacity [31, 49–51].

4.2. Geochemical Analysis

4.2.1. Kerogen Types. Kerogen's microscopic examination suggests that the Upper-Middle Devonian in the GY-1 well is dominated by the sapropelic group, with a small amount of exinite, but no vitrinite and inertinite. The sapropelic group consists mainly of amorphous bodies and algae bodies (Figure 4), while the exinite is mainly amorphous benthic algae. The determined kerogen type index indicates that the Upper-Middle Devonian is dominated by type I kerogen (Table 2).

4.2.2. TOC. TOC is highest in the D_2n shales, ranging from 0.53% to 6.0% with an average value of 2.65% (Figure 5), and is lower in the D_3l shales, ranging from 0.14% to 3.94% with an average value of 2.23%. The TOC of the D_2l shales are relatively low (0.43%–3.96%, averaging 1.52%). However, the lower D_2l have relatively high TOC values (Figure 2). In general, measured TOC values indicate high hydrocarbon generation potential in these shales, and the D_2n and the lower D_2l are high quality that were deposited in the anoxic and weak hydrodynamic deep-water shelf.

4.2.3. Thermal Maturity. As mentioned above, the kerogen of the Devonian source rocks in the GY-1 well is dominated by amorphous solid with no vitrinite. Thus, bitumen reflectances (R_b) were measured using organic maceral analysis. The equivalent vitrinite reflectance was determined using an empirical formula from [52]: $EqVR_o = (R_b + 0.2443)/1.0495$. The results show that samples are thermally

FIGURE 8: Continued.

FIGURE 8: SEM images of microscopic pores from the siliceous lime shale (231 m of well GY-1, C-1 in Figure 3): (a) OM-pores, (b) differentially developed OM-pores, (c, e) shrunk microfractures between organic matter and minerals, (d) OM-pores and clay minerals, (f) microfractures along with minerals, (g) residual pores between pyrite crystals and a little organic matter, and (h) shrunk microfractures.

postmature to overmature with equivalent vitrinite reflectance ($EqVR_o$) of 3.40–3.76% (Figure 6).

4.3. Pore Types. Significant effort has been devoted to identifying and describing the complex pore systems within fine-grained reservoirs [6–8, 16, 20, 31, 42]. Pores in shale can be classified as (a) organic-matter-hosted pores, (b) interparticle pores (pores between grains and crystals), (c) intraparticle pores (pores within grains, crystals, and clay aggregates), and microfractures [7, 31]. FESEM analysis was carried out on samples from GY-1 well to observe pore types. Various types of pores with different sizes were observed in these samples, including residual primary pores in the broken particles with infill of organic matter, isolated dissolution pores in particles, interlayer pores of clay mineral supported by rigid particles, micropores within biological residues (pores in preserved tentaculite fragments), microfractures between mineral grains, intercrystalline pore of pyrite, and organic matter-hosted pores (Figures 7–9). Organic matter-hosted pores are the most common and abundant pores with various shapes and sizes, while inorganic pores are uncommon in these samples, which may be attributed to the intensive compaction and high thermal maturity. Specifically, organic pores are generally bubble-like, honeycomb-like, and crescent-like as well as an ellipse in shape; they are generally connected by tubular throats, forming a micropore system in the organic matter. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, organic pores here are primarily mesopores with a pore diameter of 2–50 nm and macropores with pore diameter higher than 50 nm. The occurrences of organic pores are heterogeneous, since they cannot be found in some organic matters, but are abundant in migrated organic matters, namely, solid bitumen.

5. Discussion

5.1. Contributors to Pore Development. Researchers have concluded that the pore structure of organic-rich shale is

generally governed by diagenesis, organic matter, mineral components, thermal maturity, kerogen type, etc., depending on specific geological conditions [14, 23, 53–57]. Shale lithofacies have important controls on porosity and pore structure due to different sedimentary environments and mineralogical variations [19, 51, 58–61]. The same scenario can also be observed in our study. In the organic-rich siliceous shale, there are many micropores in the quartz grains, and the microcracks at the edges of the grains are well developed. The pores between mineral grains are generally filled with organic matter, and the OM pores are very developed. In siliceous lime shale, there are a few microcracks in the calcite grains. The pores between mineral grains are generally filled with organic matter and the OM pores are well developed. Siliceous dolomitic shale has a small number of microcracks developed along the edges of the grains. The pores between the clay mineral grains are filled with a small amount of finely dispersed organic matter with few pores developed. In carbonaceous shale, a small amount of organic matter is filled in the pores between mineral particles, and the organic matter is small and dispersed. The internal micropores of the organic matter are well developed, and the internal micropores of a small amount of massive organic matter are not developed.

In the FESEM images (Figures 7–9), considerable pores are concentrated in organic matter. Furthermore, the positive correlations between the porosity, the SSA, and the TPV and TOC confirm that organic matter contributes significantly to pore development (Figure 10, Table 3). Previous studies suggested that organic pores are not well developed in all organic matter [18, 62]. The FESEM images show that some organic matter does not develop pores (Figure 9(c)), and/or pore development is significantly different among adjacent organic matters (Figure 8(b)). Identifying OM types and deciphering their controls on OM pore developments is one of our next priorities.

Quartz of the Devonian shales in the Guizhong Depression is primarily biogenic in origin, as inferred from the positive correlation between the quartz content and TOC

FIGURE 9: Continued.

FIGURE 9: SEM images of microscopic pores from the siliceous carbonaceous shale (475 m of well GY-1, M-2 in Figure 3): (a, b, d, f, and h) OM-pores, (c) no OM-pores developed in the organic matter, (e) residual pores between pyrite crystals are filled with organic matter, and micropores are developed within it, and (g) different types of organic matter.

FIGURE 10: Variation of pore structure parameters (porosity, specific surface areas (SSA), and total pore volumes (TPV)) with R_o , TOC, and mineral content.

TABLE 3: TOC, R_o , mineral composition, and pore structure parameters of the studied samples from GY-1 well.

Formation	Depth (m)	TOC (%)	R_o (%)	Porosity (%)	Clay (%)	Quartz (%)	Potash feldspar (%)	Total rock XRD					Pyrite (%)	BET surface area(m ² /g)	BJH pore volume(ml/g)
								Plagioclase (%)	Calcite (%)	Dolomite (%)	Siderite (%)	Anhydrite (%)			
D_3l	231	2.07	3.62	3.29	8	35			55				2	7.245	0.009
D_3l	255	5.37	3.55	4.4	14	65			16	3			2	13.640	0.017
D_2l	475	1.49	3.4	2.59	40	36	1	3	2	11	2	2	3	4.376	0.0066
D_2l	495	0.7	3.48	1.2	35	27		2	2	30	2	1	1	2.385	0.0036
D_2l	579	1.72	3.5	1.81	48	23		2	4	18	2	1	2	4.949	0.0078
D_2l	595	3.85	3.58	1.52	40	31		2	17	5	2	1	2	14.215	0.0168
D_2n	639	2.67	3.67	1.41	45	37	1	3	1	7	2	1	3	8.880	0.01129
D_2n	651	3.07	3.68	2.59	41	40		2	8	5	1	1	2	7.615	0.011
D_2n	739	3.05	3.7	4.49	39	39		2	3	12		1	4	7.580	0.0096
D_2n	795	2.78	3.76	2.88	43	38	1	2	9	1	1	1	4	10.030	0.0124

FIGURE 11: The positive correlation between the quartz content and TOC.

(Figure 11). The quartz-rich samples generally have higher porosities, SSAs, and TPVs. In addition, the brittle quartz cements provide a rigid framework that prevents pores from collapsing. Furthermore, the dissolution of quartz particles was observed (Figure 7(f)). Although pores associated with the framework of clay flakes and dissolution of carbonates can be observed, the porosity, SSA, and TPV have no clear relationship with clay or carbonate content (Figure 10). The pore volume of the shale matrix is made up of the volume provided by organic matter, clay minerals, and framework minerals [56]. Thus, this may mean that these two types of pores contribute little to the total pores of shale, compared to the pores provided by organic matter.

5.2. Organic Matter-Hosted Pores in a Postmature to Overmature Stage. Thermal maturation has been considered an important contributor to pore growth in shales due to the kerogen degradation into liquid hydrocarbon and gas [1, 13]. However, increasing burial depth and temperature enables kerogen in the shales to generate volatile hydrocarbon with increasing hydrogen and decreasing molecular mass, chemically converting the kerogen into residual carbon with low hydrogen, which is defined as carbonization of organic matter [31, 63]. During carbonization, OM-hosted pores are destroyed, merged, and collapsed [14, 64]. Specifically, previous studies show that the degradation of kerogen and dissoluble bitumen as well as methanation generally ceased with a minor increase in micropore and macropore volume at $R_o > 2.6\%$ [65]. Organic carbonification in shale commonly occurs at R_o of 3.2% when organic pore volume begins to decrease due to the compaction and mineral infill [65]. Organic pores in marine shale are typically poor at $R_o > 3.0\%$, with most of the pore diameter < 100 nm [66]. However, organic pores in this study are well grown at R_o of 3.5%, and surface areas and pore volume of nano-scale pores typically increase with thermal maturity despite a similar thermal maturity range (R_o 3.40%–3.76%) (Figure 9). Considerable macropores were found in samples with $R_o > 3.6\%$. Supplementally, Cheng and Xiao [67] found that both the specific surface area and nanopore volume of organic-rich shales increased with maturity, which allowed them to keep certain porosities even in very high maturities (R_o 3.5%–4.0). Thus, we are more confident than some scholars about the shale pore volume in postmature to over-

mature stage [13, 28, 70] and consolidate, to a certain extent, the pore evolution diagram with increasing thermal maturity proposed by [31].

We do agree with some studies in suggesting that the macroporous in the shales are transformed into mesopores and micropores, and the organic nanopores decrease, causing nanopore volume to be displayed a decreasing trend under the condition of extremely high thermal maturity [21, 22, 55]. Of course, it cannot be denied that the evolution of organic porosity with increasing maturity is influenced by several factors [30]. Our study, however, demonstrates also that porosity at postmature to overmature stage ($R_o = 3.5 - 4.0\%$) does not change fundamentally. In other words, the porosity under the high level of maturity is satisfying for shale gas storage. Consequently, the level of maturity may not be the main controlling factor that affects shale gas content, and more attention should be paid to preservation conditions.

6. Conclusion

- (1) Nabiao shale (D_2n) and Lower Luofu shale (D_2l) were deposited in anoxic and weak hydrodynamic deep-water shelf, which contributes to the development and preservation of organic matter. The Upper Luofu Formation (D_2l) and Liujiang Formation (D_3l) were deposited in an oxygen-poor shallow-water shelf. X-ray diffraction indicates that the lithofacies in D_2n and D_2l are primarily siliceous/argillaceous mixed shales as well as minor siliceous argillaceous shales and argillaceous siliceous shales
- (2) The Middle-Upper Devonian shales in Guizhong Depression are organic-rich with TOCs of 0.14–6.21%. TOC is highest in the Nabiao Formation (D_2n) and Lower Luofu Formation (D_2l), which are thermally postmature to overmature with $EqVR_o$ ranging from 3.40% to 3.76% and type I kerogen
- (3) OM-pores are dominant pore types. Porosity, surface areas, and pore volumes exhibit positive correlations with TOC, R_o , and siliceous mineral contents. Considerable macropores were found in shales with $R_o > 3.6\%$ in our study which demonstrates that porosity at postmature to overmature stage ($R_o = 3.5 - 4.0\%$) does not change fundamentally

Data Availability

All data included in this study are available upon request by contact with the corresponding authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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