

Methane adsorption effected by pore structure of overmature continental shale: Lower Cretaceous Shahezi Formation, Xujiaweizi Fault, Songliao Basin

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Abstract Overmature continental shale is commonly developed, but few studies have given insight into its pore structure and sorption capacity. Various techniques, including SEM, helium porosity and permeability, N₂/CO₂ adsorption, MICP, and NMR, were used to detect the pore structure of shale from the Shahezi Formation, Xujiaweizi Fault, Songliao Basin. The excess methane adsorption volumes were measured by the volumetric method and modeled by the Langmuir model. Based on the findings, the most developed pores are intraparticle pores in clay minerals, followed by the dissolution pores in feldspar, but organic pores are uncommon. The selected shales have low helium porosity (mean 1.66%) and ultralow permeability (mean $0.0498 \times 10^{-3} \mu\text{m}^2$). The pore throats are at the nanoscale, and the pore-throat size distributions are unimodal, with most less than 50 nm. The studied shales are characterized by the lower specific surface area (SSA) and pore volume (PV) but the larger average pore diameter. The total SSA is contributed by the micro- and mesopores, while the PV is dominated by meso- and macropores. The pore structures are more complex and controlled by multiple factors, such as mineral compositions and diagenesis, but organic matter is not critical. The maximum absolute adsorption methane volume (V_L) is 0.97–3.58 cm³/g (mean 1.90 cm³/g), correlating well with the total SSA, SSA, and pore volume of micropores, which indicates that methane is mainly adsorbed and stored in micropores, followed by mesopores.

Keywords continental shale, pore structure, methane

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adsorption, Shahezi Formation, Songliao Basin

1 Introduction

Recently, shale gas has developed rapidly in the USA (Zou et al., 2020). Following the shale gas revolution in the USA, more attention has been given to shale gas in China. The shale gas proved reserve is more than 2 trillion m³ in China, and the production was more than 20 billion m³ in 2020 (Zou et al., 2021). Different from conventional natural gas, shale gas shows different in two ways: shale is usually dominated by nanoscale pores and has a highly complex pore structure and mineral composition (Jarvie et al., 2007); shale gas occurrences in two primary states in reservoirs: adsorbed on the pore surface and free state within pores and fractures (Curtis, 2002). Thus, the complex pore structure and its controlling effect on gas storage capacity have drawn increasing attention (Jarvie, 2012; Tian et al., 2016; Wang et al., 2016a; Zhou et al., 2018; Hu and Mischo, 2020).

Various specialized methods have been employed to characterize the shale pore structure, including direct imaging and indirect methods. Shale pore structure (pore type, morphology, etc.) can be well described by these imaging technologies (such as FE/FIB/BIB-SEM, and X-ray CT) (Chen et al., 2016; Kelly et al., 2016; Klaver et al., 2016; Wang et al., 2016b; Li et al., 2017a; Zhang et al., 2020a; Zhao et al., 2021a). However, indirect methods, e.g., N₂/CO₂ adsorption-desorption, MICP, and NMR, are commonly employed to quantitatively measure the porosity, permeability, pore size distribution (PSD), pore volume (PV), and specific surface area (SSA), etc. (Zargari et al., 2015; Hu et al., 2017; Zhang et al., 2018;

2019; Xu et al., 2021; Zhao et al., 2021b; Bai et al., 2022; Zhang et al., 2022; Zhao et al., 2022). Recently, the pore structures of overmature marine shales have been reported in numerous literatures and have been well investigated (Chen et al., 2016; Tian et al., 2016; Wang et al., 2016b; Li et al., 2017a; Zhou et al., 2018; Feng et al., 2019; Hu and Mischo, 2020). The results showed that nanoscale pores with a larger SSA characterize overmature marine shale. Organic pores are the most developed and contribute to the primary storage space. Moreover, the organic matter (TOC) positively influences the PV and SSA, especially the micropore structure.

Gas adsorption content is a critical parameter for shale (Ambrose et al., 2012). Laboratory experiments, such as gravimetric, and volumetric methods, are commonly applied for measuring shale methane adsorption content (Gasparik et al., 2012; Rexer et al., 2013; Tian et al., 2016). The absolute adsorption isotherms and the absolute adsorption contents can be calculated based on the excess adsorption isotherms by Langmuir, supercritical Dubinin-Radushkevich (SDR), and simplified local density (SLD) models (Sakurovs et al., 2007; Luo et al., 2015; Wang et al., 2016c; Bi et al., 2017; Li et al., 2017b; Li et al., 2022). Previous overmature marine shale studies indicated that methane adsorption capacities positively correlate well with TOC content, total SSA, and micropore volume (Zhou et al., 2018; Hu and Mischo, 2020; Li et al., 2021). The methane adsorption is closely related to the microporosity associated with the organic matter.

Moreover, overmature continental shales are also widely distributed in the Ordos and Songliao Basins in China, which have production potential for shale gas (Zou et al., 2021). However, few data in the literature address the pore structures, methane sorption capacity, and their controlling factors of overmature continental shales. Due to the differences in sedimentary and diagenetic processes, the pore structures and methane sorption characteristics of overmature continental shales may differ significantly from overmature marine shales. Therefore, CO₂/N₂ adsorption, MICP, SEM, and NMR methods were employed to characterize the pore types, porosity, permeability, PSD, PV, and SSA of the shales collected from the Shahezi Formation. High-pressure methane isothermal adsorption tests were also performed. The controlling factors of pore structures and methane sorption capacity were analyzed and examined with the XRD and TOC results. This study attempts to give insight into the pore structure and methane sorption capacity of overmature continental shale.

2 Samples and methodology

2.1 Samples

Lower Cretaceous continental shales from the Shahezi Formation, Xujiaweizi Fault, Songliao Basin, north-

eastern China, were collected according to their variability in TOC contents and inorganic composition, which control the pore structures and gas storage capacity. The Xujiaweizi Fault is a dummy dustpan-like depression located in the northern Songliao Basin, with an exploration area of approximately 5350 km², including four structural stripes: the Anda-Xingcheng Uplift, Xuxi Sag, Xudong Sag, and Xudong Slope Belts (Fig. 1). The Shahezi Formation was deposited in fan delta, braided river delta, and lacustrine environments during fault depression (Lu et al., 2017; Zhang, 2017). The shales (including mudstones), developed in the lacustrine facies, are the primary source rocks and the exploration potential shale gas zone for the Xujiaweizi Fault, Songliao Basin (Wang et al., 2014).

This study sampled 18 shale layers, including 14 plugs and 4 pieces. TOC, XRD, CO₂/N₂ adsorption, and high-pressure methane isothermal adsorption were performed on all samples. Meanwhile, thin sections, SEM, NMR porosity, helium porosity and permeability, and MICP were only carried out on the 14 plugs.

2.1.1 Experiments

1) TOC and minerals

Shales were crushed to < 100 mesh (150 μm) to perform TOC and XRD measurements. After acid dissolution, the TOC content was measured on an Elab-TOC analytical instrument to eliminate carbonate minerals. XRD data of the mineral compositions of total shale were first detected using a Bruker diffractometer. Subsequently, the shales were crushed to less than 300 mesh to obtain the clay minerals. A Bruker diffractometer then determined the compositions of clay minerals.

2) Thin section and SEM imaging

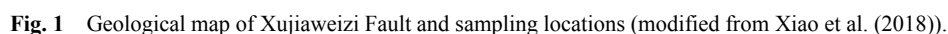
The thin section and SEM samples were cut from the plugs. Thin section images were collected using a polarizing microscope to observe the microstructures of the shales. An FFI Quanta 200F was employed to conduct SEM tests. The shale slices were first hand-polished on stubs and then polished by argon-ion milling to obtain a flat surface. The BSE and SE images magnified 500 to 15000 times were collected on the flat surface.

3) Porosity and permeability

The plugs were dried in a vacuum oven at 110°C for 24 h to eliminate residual pore water before the tests. A PorePDP-200 instrument tested the porosity and permeability under 200 psi and 1000 psi confining pressures, respectively. NMR porosity was conducted on a MesoMR23-060H-I spectrometer according to the procedure established by the authors, which includes two steps of dried and saturated shale tests (Zhang et al., 2019 and 2020b).

4) CO₂/N₂ adsorption

Shales were crushed to 40–60 mesh (250–380 μm), and a split of 3–5 g crushed pieces was used for measurement. The crushed samples were first dried at



N₂ adsorption-desorption isotherms were collected at 77 K with P/P_0 between 0.01 and 0.993. The adsorption branch estimated the PV, SSA, and PSD. PV was the

5) MICP

The MICP experiments were conducted on the same plugs to helium porosity and permeability measurements by a Micromeritics AutoPore IV 9510 Porosimeter. The maximum mercury injection pressure is approximately 200 MPa, and as small as a pore throat of about 7 nm can be detected.

6) High-pressure methane isothermal adsorption

The 3H-2000PH690 high-pressure gas adsorption instrument was used to measure the Methane excess adsorption capacity. The 40–60 mesh (250–380 μm) shale particles were first dried at 110°C for 24 under a vacuum condition to obtain the dry state. Subsequently, the experiments were conducted according to the national standards of GB/T 35210.1-2017 (Determination methods of methane isothermal adsorption in shale—part 1: capacity method). For each shale, approximately 100 g crushed sample was used for measurement. Both the reference and sample cells were set at a consistent temperature of 40°C ($\pm 0.1^\circ\text{C}$). The shale's methane sorption capacities were measured up to a pressure of approximately 50 MPa. For the experimental conditions in this study, methane was in the supercritical state. Thus, the excess sorption capacity (V_{ex}) was the experimental sorption capacity. In this paper, the Langmuir-based extra adsorption model (Eq. (1)) was adopted to fit the V_{ex} and sorption pressure (P) to obtain the absolute sorption capacity (V_{ab}), which can be described as Eq. (2) (Li et al., 2020a):

$$V_{\text{ex}} = \frac{V_L P}{P_L + P} \left(1 - \frac{\rho_g}{\rho_a} \right), \quad (1)$$

$$V_{\text{ab}} = \frac{V_L P}{P_L + P}, \quad (2)$$

where V_{ex} represents the excess sorption capacity, cm^3/g ; V_L indicates the Langmuir volume, cm^3/g ; V_{ab} is the absolute sorption capacity, cm^3/g ; P is the equilibrium pressure, MPa; P_L denotes the Langmuir pressure (MPa), referring to the pressure at the methane adsorbed amount equaling half of the maximum methane sorption capacity (V_L); and ρ_a and ρ_g represent the densities of adsorbed and free methane, respectively, g/cm^3 .

3 Results

3.1 Petrological characteristics

The average TOC content is 2.06%, varying from 0.33% to 5.33%. Table 1 indicates that the selected shales mainly consist of clay minerals, quartz, and feldspar. The clay mineral content is 34.78%–62.12% (mean 47.48%). The quartz is between 23.39% and 41.89% (mean 34.91%), and the feldspar content is 5.48%–27.42% (mean 15.82%). In addition, the studied shales contain some amount of orthoclase and calcite, with means of 0.59% and 0.53%, respectively. The clay minerals mainly consisted of illite–smectite, illite, and chlorite, with average values of 52.66%, 37.15%, and 9.55%, respectively. Compared with shales from Wufeng and Longmaxi Formations (Li et al., 2019), the studied shales are characterized by higher clay minerals and feldspar contents, but lower contents of quartz and carbonate

Table 1 TOC contents and mineral compositions of the shale samples

Sample	TOC/%	Mineral composition/%					Clay mineral composition/%		
		Quartz	Orthoclase	Feldspar	Calcite	Clay mineral	Illite	Illite–Smectite	Chlorite
SS111-1	3.65	41.18	0.00	6.26	0.00	52.55	19.98	74.22	5.80
XS26-9	2.07	32.48	0.00	19.91	1.35	45.31	26.22	65.84	6.15
ZS6-12	1.91	41.56	0.00	6.87	0.00	50.11	57.24	28.11	12.33
ZS32-13	3.29	23.39	2.65	27.42	5.54	41.00	73.15	19.44	7.42
DS28-2	0.74	41.13	0.00	15.96	0.00	41.39	17.81	55.47	26.72
DS28-13	1.53	36.57	0.00	19.03	0.00	44.41	13.81	72.93	10.54
DS28-24	5.33	41.89	0.00	8.01	0.00	48.38	23.68	57.84	15.81
DS6-6	2.89	39.17	0.00	9.20	0.00	51.14	36.74	56.12	7.13
DS6-13	0.97	33.21	1.71	18.36	0.00	46.72	38.76	50.32	10.91
DS6-15	2.39	25.86	2.43	12.75	0.00	58.96	40.12	56.48	3.40
DS6-17	0.33	34.59	0.00	19.29	1.25	44.87	40.10	51.38	8.52
FS12-4	0.98	36.66	1.62	26.94	0.00	34.78	41.39	36.41	22.20
FS12-20	0.80	36.01	2.16	24.37	0.00	37.46	61.83	28.44	9.08
XS25-4	0.69	34.67	0.00	16.14	0.69	48.49	24.05	72.38	3.57
XS25-6	1.17	32.92	0.00	7.70	0.00	58.69	16.57	80.90	2.53
XS25-8	5.24	35.28	0.00	15.98	0.77	47.97	19.37	77.48	3.15
ZS14-4	1.73	32.97	0.00	25.10	0.00	40.32	61.44	28.16	9.05
ZS14-6	1.45	28.81	0.00	5.48	0.00	62.12	56.48	35.96	7.56

minerals (Fig. 2). Massive and laminated structures were identified from the thin section images, as shown in Fig. 3. Minerals are evenly distributed in the massive samples (Figs. 3(a)–3(d)). At the same time, two distinct layers were observed in the laminated shales, such as the clay mineral layer and detrital mineral (quartz and feldspar) layer (Figs. 3(e) and 3(f)).

3.2 Pore structure

3.2.1 Pore types

The shale matrix pores were mainly classified into

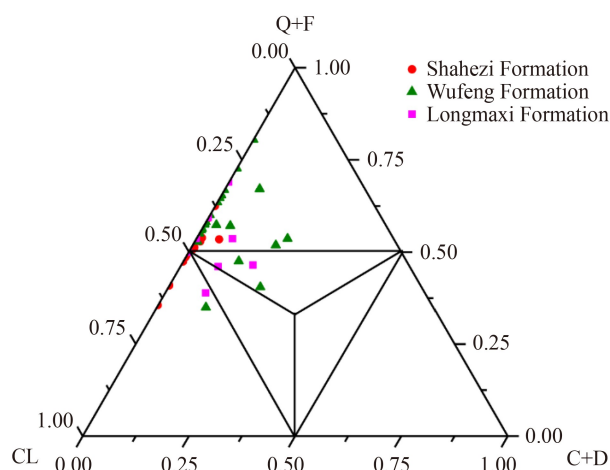


Fig. 2 Mineral compositions of Shahezi, Wufeng, and Longmaxi Formations (CL: clay mineral, Q + F: quartz and feldspar, C + D: calcite and dolomite).

intraparticle pores and microfractures (Loucks et al., 2012). The interparticle pores were almost invisible due to compaction by the overlying formation. Intraparticle pores are the most developed pores and are mainly intraplatelet pores within clay aggregates (Figs. 4(a) and 4(b)). Dissolution pores in feldspar are another common intraparticle pore in the studied shales (Figs. 4(c), 4(d), and 4(e)), providing shale gas spaces, especially for free gas. However, most dissolution pores were filled by illite–smectite (Fig. 4(d)).

Moreover, a small number of intercrystalline pores are identified in pyrite framboids, as shown in Fig. 4(f). However, organic pores are rare, and few organic pores can be observed in the organic matter, as shown in Figs. 4(b), 4(e), 4(f), and 4(g). Microfractures are essential avenues for shale gas transport and commonly occur between organic matter and inorganic minerals (Fig. 4(g)). In contrast, pores are well developed in organic matter in overmature marine shales, such as Wufeng Formation (Figs. 4(h) and 4(i)) (Wang et al., 2019). Thus, clay mineral intraparticle pores and feldspar dissolution pores are the main storage spaces in the continental shales in the Xujiaweizi Fault, rather than organic pores.

3.2.2 Pore structure characteristics

1) Porosity and permeability

The helium porosity of the selected shale is 0.64%–3.65%, with a mean of 1.66%, while the permeability is $0.0010\text{--}0.5299 \times 10^{-3} \mu\text{m}^2$ (mean $0.0498 \times 10^{-3} \mu\text{m}^2$) (Table 2). Most samples are less than $0.1 \times 10^{-3} \mu\text{m}^2$, indicating that the studied shales are typical tight

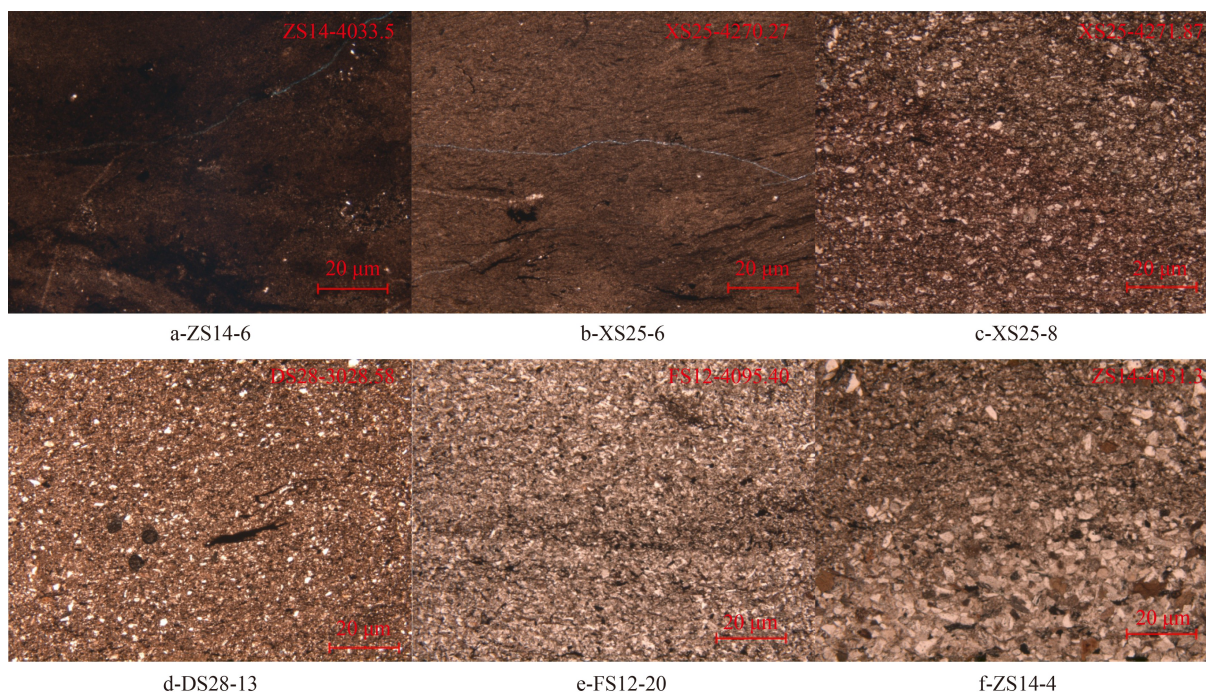


Fig. 3 Thin section images of studied shales.

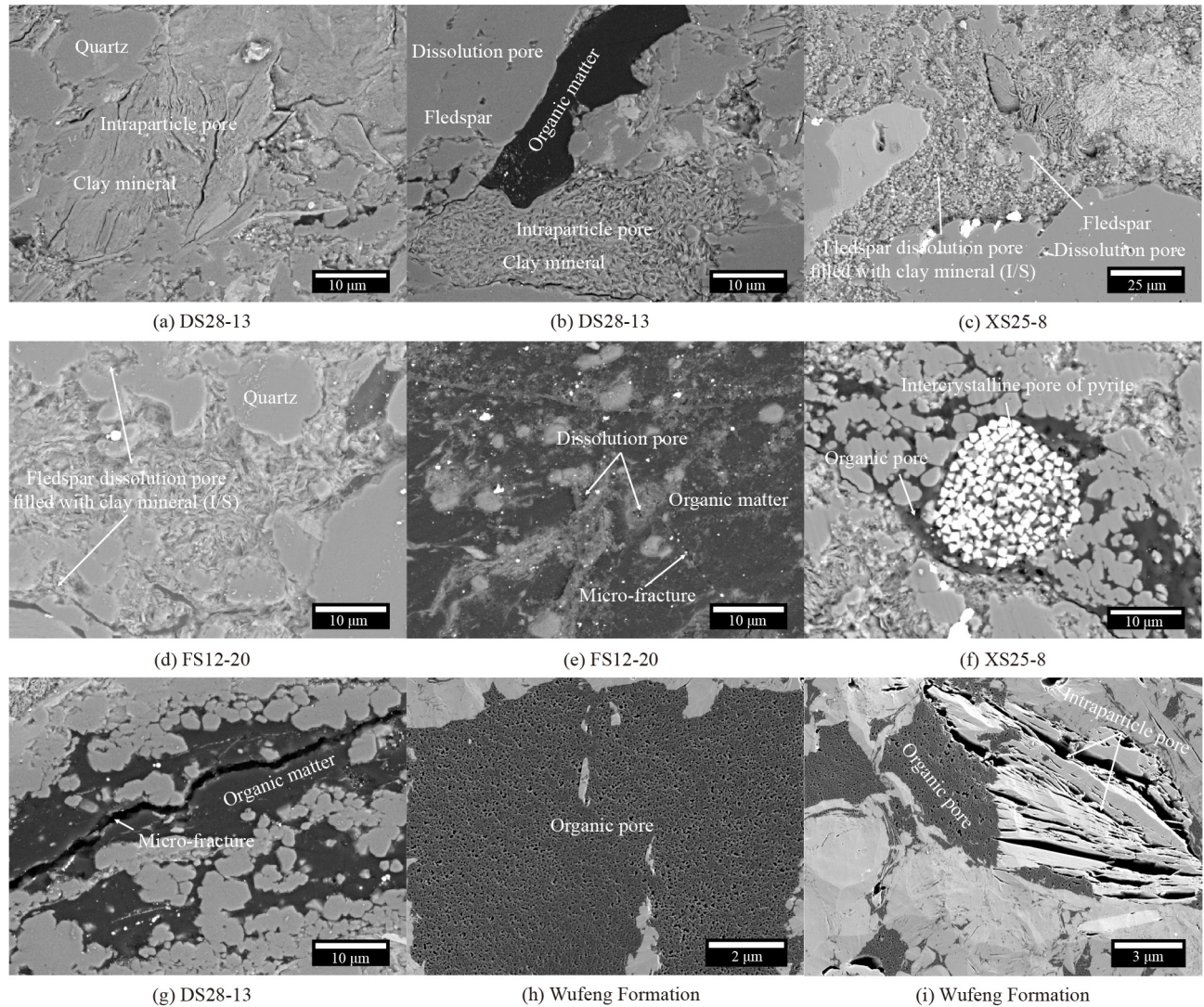


Fig. 4 SEM images of Shahezi and Wufeng Formations (Wang et al., 2019).

reservoirs. Moreover, NMR porosity is between 0.24% and 5.60%, with an average of 2.94%, generally larger than helium porosity. This may be because the shale sample was too tight to obtain accurate helium porosity by the expansion method (Kuila et al., 2014). Thus, NMR may be a more accurate method to detect shale porosity.

2) MICP

The studied samples' Mercury intrusion–extrusion curves are shown in Fig. 5. If the mercury intrusion pressure (P_c) was less than 10 MPa, little mercury intruded into the shale pore–fracture systems, while mercury began to invade shale rapidly when the P_c was higher than 10 MPa. The results suggest that most pore–throats in the shales are nanoscale. Moreover, the mercury withdrawal efficiency is low, with an average of 64.21%, ranging from 32.81% to 83.19%, indicating the complex shale pore structure. The pore–throat size distributions (PTSDs) are unimodal, and most pore–throats are less than 50 nm (Fig. 6). Thus, the PTSDs obtained from MICP mainly indicate the throats rather

than the pores. The pores in the studied shales are primarily connected by throats less than 50 nm, which results in an ultralow permeability of the shale.

3) CO₂ adsorption

CO₂ adsorption isotherms of 18 samples are all Type I adsorption isotherms, as shown in Fig. 7, suggesting that all studied shales are characterized by microporous features (Wang et al., 2016a). The average SSA value of the selected samples is 4.3222 m²/g (1.9871–9.2093 m²/g). The PV values are between 0.00085 and 0.00372 cm³/g (mean 0.00183 cm³/g), which corresponds to the maximum adsorption capacity of CO₂ (Fig. 7). The SSA is positively correlated with PV for the micropores (< 2 nm). As illustrated in Fig. 8, the micropore–size distributions vary from 0.45 nm to 0.9 nm and show a bimodal distribution characterized by two peaks at 0.5–0.6 nm and 0.75–0.85 nm.

4) N₂ adsorption–desorption

As shown in Fig. 9, N₂ adsorption isotherms for the selected samples are Type II (Gregg and Sing, 1982).

Table 2 Helium porosity and permeability and NMR porosity of shales

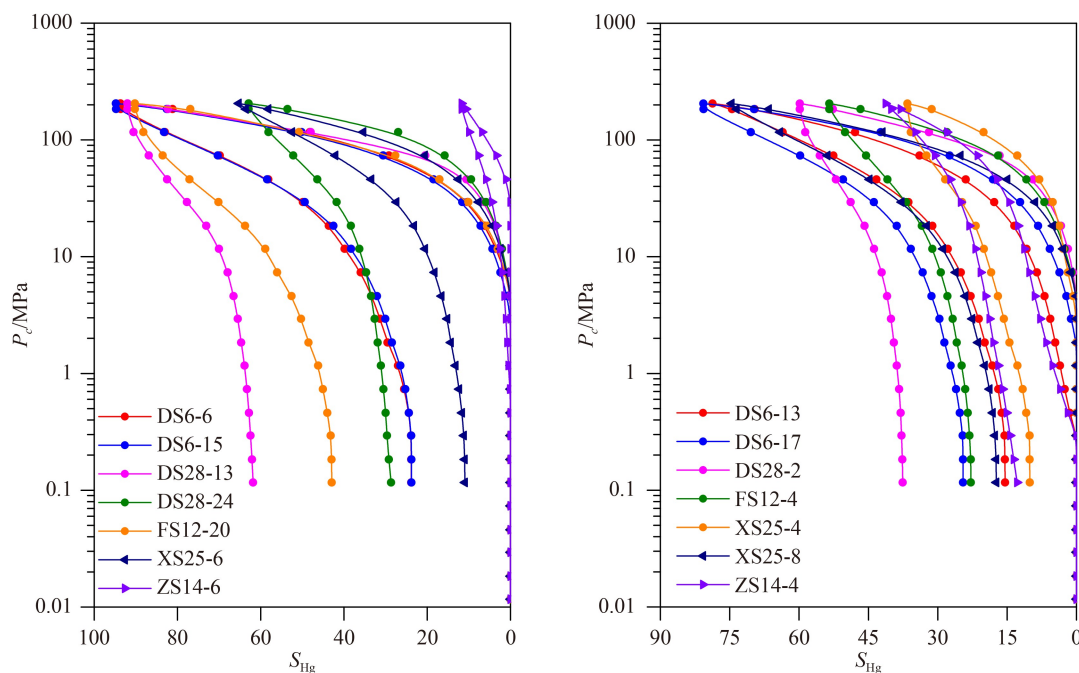
Sample	Helium method		
	NMR	Porosity/%	Permeability/mD
DS28-2	5.60	2.47	0.0100
DS28-13	5.49	2.93	0.0013
DS28-24	5.23	2.29	0.0163
DS6-6	2.75	0.75	0.0015
DS6-13	2.62	2.93	0.0026
DS6-15	3.45	0.83	0.0049
DS6-17	3.42	0.98	0.0044
FS12-4	2.43	1.16	0.0022
FS12-20	1.97	0.64	0.0012
XS25-4	0.24	0.69	0.5299
XS25-6	2.40	1.26	0.1171
XS25-8	2.87	0.89	0.0010
ZS14-4	1.39	1.74	0.0015
ZS14-6	1.31	3.65	0.0029

Type II adsorption isotherms are interpreted to be due to the monolayer coverage ($P/P_0 < 0.4$), multilayer coverage ($0.4 < P/P_0 < 0.8$), and capillary condensation ($P/P_0 > 0.8$), which suggests that meso- (2–50 nm) and macropores (> 50 nm) are developed. Moreover, hysteresis loops occur between the adsorption and desorption branches if P/P_0 is greater than 0.4, as shown in Fig. 9, belonging to Types H2 and H3. Type H2 is characterized by an apparent yielding point in the desorption branch at

$P/P_0 \approx 0.5$, indicating that the pores are mainly ink-bottle-shaped (Fig. 9(a)). Type H3 is characterized by nearly parallel adsorption-desorption branches with a narrow hysteresis loop suggesting silt-shaped pores (Fig. 9(b)). The pore-size distributions of Types H2 and H3 shales show bimodal distributions with peaks of 2–4 nm and 30–60 nm, respectively (Fig. 10). However, Type H3 shales have a more prominent right peak (30–60 nm) than Type H2 shales, suggesting that more mesopores and macropores are developed in Type H3 shales.

The BET nitrogen SSA values vary from 1.5803 to 9.0368 m²/g (mean 5.3247 m²/g), and the PV goes from 0.00606 to 0.001957 cm³/g (mean 0.001301 cm³/g) (Table 3). The average pore diameter (d_{Na}) is between 6.25 nm and 15.33 nm (mean 10.53 nm). Compared with the overmature marine shales (such as the Qiongzhusi, Longmaxi, and Niutitang Formations) (Wang et al., 2016a; Li et al., 2017b; Zhou et al., 2018), the continental shales are characterized by lower SSA and PV values but larger d_{Na} values, meaning that meso- and macropores are more developed in the studied shales.

To reveal the micropore structures of these samples, total SSA and total PV were calculated. The total SSA is the sum of the micro-, meso- and macropore SSAs. Micropore SSA is the BET SSA obtained from CO₂ adsorption, while meso- and macropore SSA are calculated from the BJH pore area. The same method received the total, micro-, meso- and macropore PVs. The average total SSA is 9.0452 m²/g, with a range of 3.5967–15.8252 m²/g. The micropore SSA is 1.9771–9.2093 m²/g (mean 4.3222 m²/g), and the mean mesopore SSA is 4.4393 m²/g (1.2182–6.8959 m²/g) (Table 3).

**Fig. 5** Mercury intrusion–extrusion curves of shales.

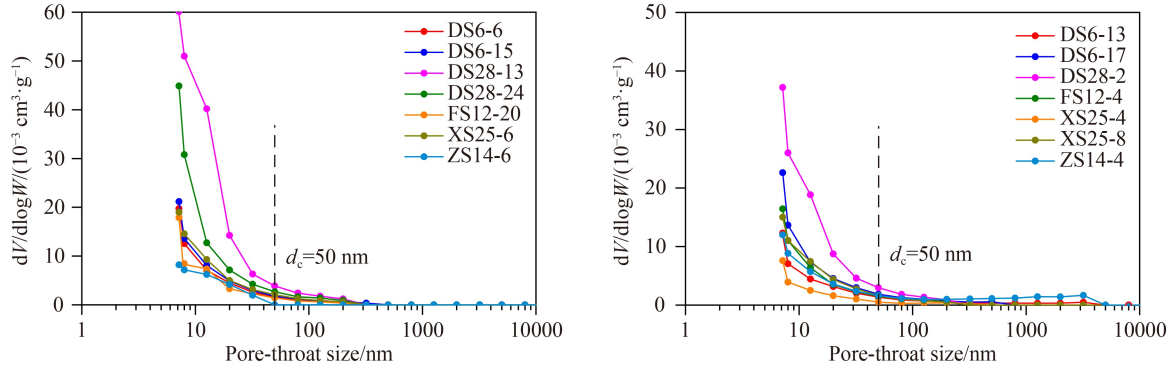


Fig. 6 Pore-throat size distributions of shales obtained from the MICP method.

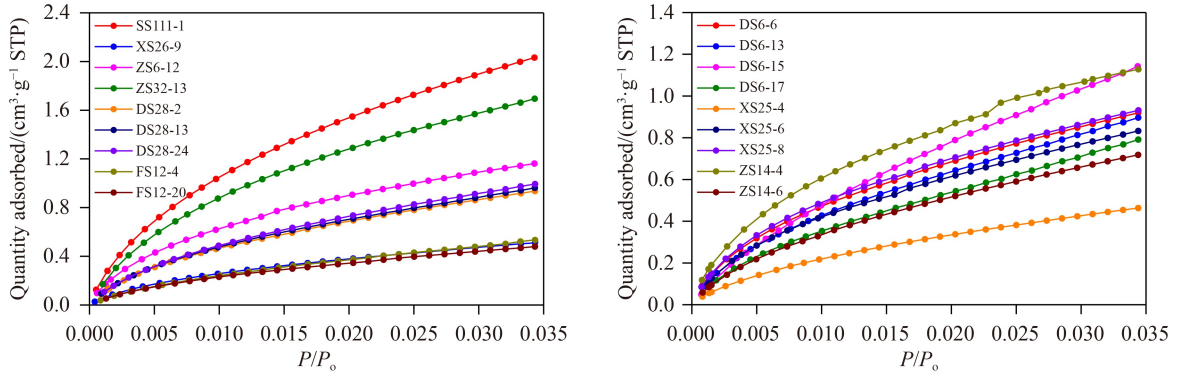


Fig. 7 CO₂ adsorption isotherms of shales.

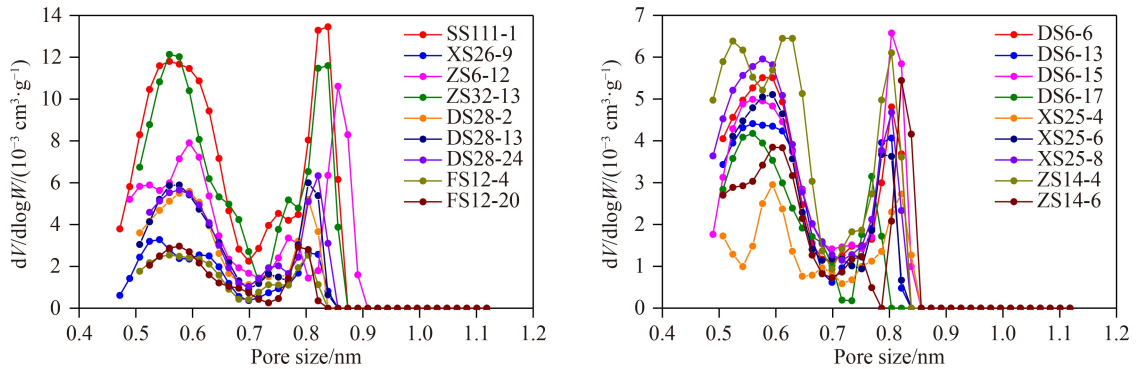


Fig. 8 Pore-size distributions of the shales determined by CO₂ adsorption.

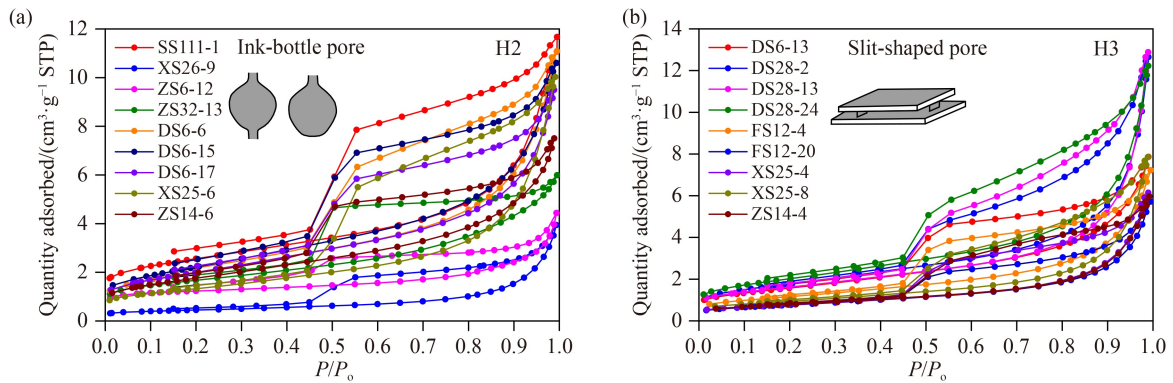


Fig. 9 N₂ adsorption-desorption isotherms of shales.

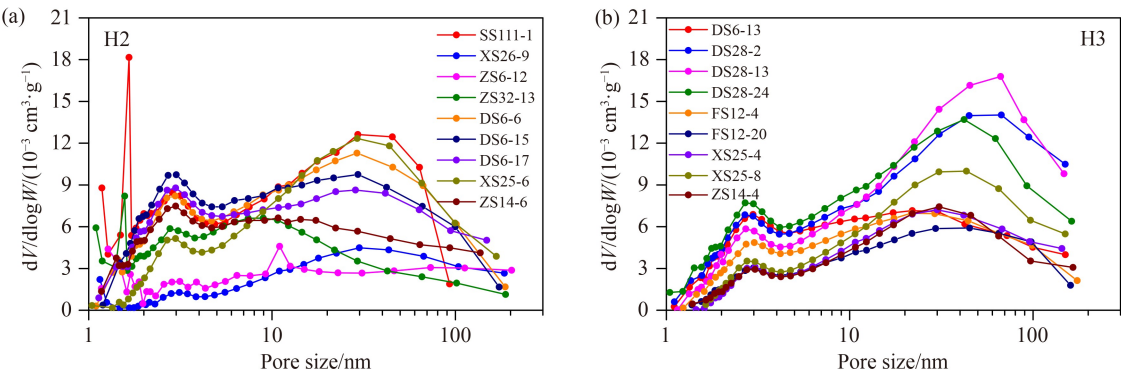


Fig. 10 Pore-size distributions of shales obtained from N₂ adsorption–desorption.

However, the macropore SSA goes from 0.1060 to 0.5366 m²/g (mean 0.2836 m²/g). The results show that micropores and mesopores occupy almost all total SSA. As illustrated in Fig. 11(a), both the micro- and mesopore SSAs show positive relationships with the total SSA, with similar *R*² of 0.6761 and 0.6717, respectively.

The average total PV is 0.001458 cm³/g (0.00699 to 0.02113 cm³/g) (Table 3). Mesopores occupy the largest proportion of the total PV, with an average of 0.008 cm³/g (0.00304–0.001154 cm³/g), characterized by a positive relationship between mesopore and total PVs

(*R*² = 0.9094) (Fig. 11(b)). Macropores range from 0.00192 to 0.00898 cm³/g (mean 0.00475 cm³/g), making the second-largest contribution to the total PV. A positive relationship is recognized between macropore PV and total PV (*R*² = 0.7) (Fig. 11(b)). The average micropore PV is 0.00183 cm³/g (0.00085–0.00372 cm³/g). There is no obvious correlation between micropore PV and total PV, with a low correlation coefficient of 0.1197. For the studied continental shales, micropores and mesopores make the largest contribution to the SSA, while mesopores and macropores occupy the largest proportion of PV.

Table 3 Pore-structure parameters of the shales

Sample	CO ₂ adsorption		N ₂ adsorption						Total SSA ^a / (m ² ·g ^{−1})	Total PV ^b / (10 ^{−3} cm ³ ·g ^{−1})	
	BET-SSA/ (m ² ·g ^{−1})	PV/ (10 ^{−3} cm ³ ·g ^{−1})	BET-SSA/(m ² ·g ^{−1})			PV/(10 ^{−3} cm ³ ·g ^{−1})					<i>d</i> _{Na} /nm
	Micro	Micro	Total	Meso-	Macro	Total	Meso-	Macro			
SS111-1	9.2093	3.72	9.0368	6.2995	0.3164	15.95	11.54	4.72	7.06	15.83	19.98
XS26-9	2.2153	0.94	1.5803	1.2182	0.1631	6.06	3.04	3.01	15.33	3.60	6.99
ZS6-12	4.8567	2.22	4.2141	1.6707	0.1217	6.73	3.14	2.65	6.38	6.65	8.01
ZS32-13	7.9241	3.10	5.8561	4.5421	0.1060	9.15	6.78	1.92	6.25	12.57	11.80
DS28-2	3.9235	1.71	6.4637	5.5374	0.5005	19.57	10.33	8.82	12.11	9.96	20.87
DS28-13	4.3258	1.76	6.2603	5.3346	0.5366	19.37	10.39	8.98	12.38	10.20	21.13
DS28-24	4.2468	2.10	7.3007	6.1958	0.4729	18.91	10.96	7.47	10.36	10.92	20.52
DS6-6	3.7288	1.69	7.2246	6.3857	0.3153	17.15	11.24	5.44	9.50	10.43	18.36
DS6-13	3.4569	1.64	5.7036	5.0664	0.2361	12.17	8.06	3.76	8.53	8.76	13.46
DS6-15	6.0962	2.09	8.0300	6.8959	0.3134	16.40	10.89	4.98	8.17	13.31	17.96
DS6-17	3.1823	1.45	7.1930	6.2813	0.2957	14.69	9.64	4.58	8.17	9.76	15.67
FS12-4	4.8753	2.27	4.1866	3.8111	0.2191	11.17	6.99	4.02	10.68	8.91	13.28
FS12-20	2.1441	0.88	2.7432	2.5359	0.2008	8.84	5.09	3.68	12.90	4.88	9.65
XS25-4	1.9871	0.85	2.7522	2.5655	0.2533	9.50	5.48	4.01	13.81	4.81	10.33
XS25-6	3.3478	1.52	4.7455	4.5400	0.3617	15.52	9.65	5.78	13.08	8.25	16.96
XS25-8	3.7973	1.71	3.3605	3.0811	0.3257	12.15	6.93	5.20	14.46	7.20	13.84
ZS14-4	5.4553	2.07	2.8322	2.5640	0.1926	9.24	5.76	3.40	13.05	8.21	11.23
ZS14-6	3.0275	1.31	6.3612	5.3826	0.1741	11.61	8.11	3.00	7.30	8.58	12.43

Notes: Micro-, meso- and macro- are the micropore, mesopore, and macropore, respectively; SSA is the specific surface area; total SSA^a is the sum of micro-, meso- and macropore SSA; and total PV^b is the sum of the micro-, meso- and macropore PV.

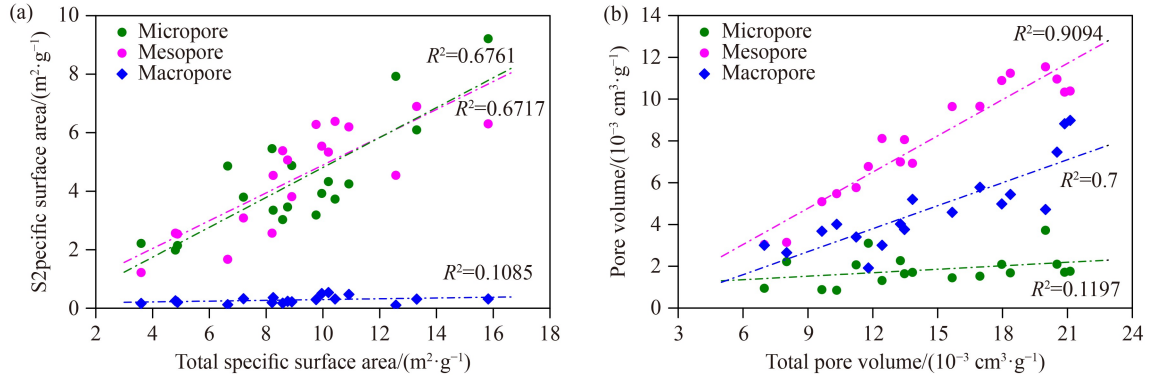


Fig. 11 Relationships between different pore sizes' SSA and BET SSA (a) and PV and total PV (b).

3.3 Shale methane adsorption capacity

The experimental results show that the excess sorption amount of methane (V_{ex}) increases rapidly with the pressure rising and then reaches a maximum amount when the pressure is approximately 10 MPa, as illustrated in Fig. 12. Subsequently, V_{ex} decreases with increasing pressure gradually. This phenomenon was commonly encountered in literatures (Tian et al., 2016; Zhou et al., 2018; Feng et al., 2020; Hu and Mischo, 2020; Li et al., 2021). This is because V_{ex} is calculated based on the assumption that the adsorbed methane volume is negligible (Zhou et al., 2018). According to Eq. (1), V_{ex} approaches zero if the free methane density approaches that of the adsorbed state at high methane pressure.

As shown in Fig. 12, the Langmuir-based excess sorption model (Eq. (1)) was employed to fit the experimental excess sorption isotherms. The excess sorption isotherms are fitted quite well by this model, with correlation coefficients larger than 0.98. The fitted parameter of the adsorbed methane density (ρ_{ads}) values are listed in Table 4, ranging from 0.29 to 0.38 g/cm³ (0.32 g/cm³). The fitted ρ_{ads} values are all less than the liquid methane density, suggesting that the Langmuir-based excess sorption model is reliable. According to Eq. (1), the absolute sorption isotherms were obtained, well-fitted by the Langmuir sorption model (Eq. (2)) (Fig. 13).

Meanwhile, the V_L and P_L were determined (Table 4).

P_L ranges from 1.66 to 4.26 MPa (mean 3.03 MPa). V_L is the maximum absolute adsorption methane volume, reflecting the maximum adsorption capacity. The V_L varies 0.97 from 3.58 cm³/g, with a mean of 1.90 cm³/g, which is lower than those of the lower Cambrian Qiongzhusi shale reported by Li et al. (2017b) and similar to those of the Longmaxi and Niutitang shale outcrops written by Wang et al. (2016a), indicating that the Shahezi Formation continental shale has the potential for shale gas. However, it should be noted that the methane adsorption measurements in this study were conducted on dry shale samples rather than the moisture-equilibrated sample. Thus, the absolute adsorption methane amounts cannot represent the adsorption methane amounts of the *in situ* shales.

4 Discussion

4.1 Pore structure influenced by TOC and minerals

Minerals and organic matter are essential factors for the shale pore structure. As shown in Fig. 14, the micropore SSA first increases, but decreases with TOC content increasing, while the mesopore and macropore SSAs do not correlate with TOC (Fig. 14(a)). This indicates that some micropores occur in organic matter, which cannot be observed from SEM images because their pore size is

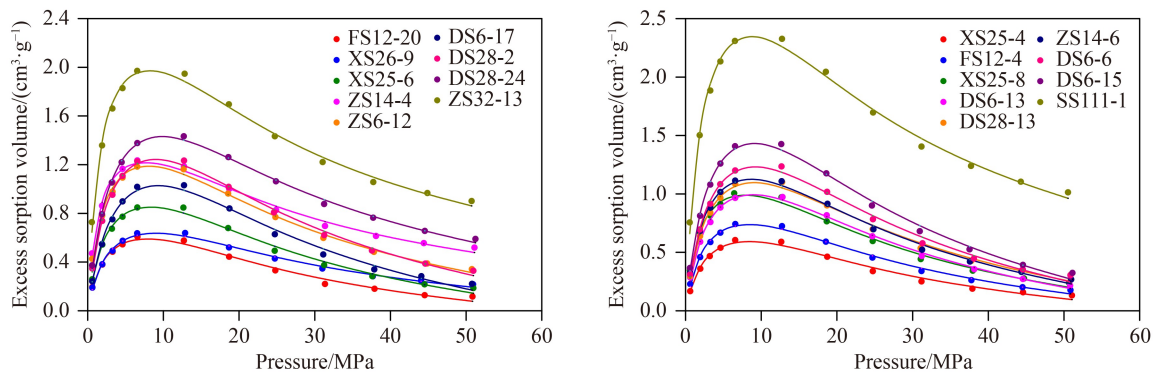


Fig. 12 Excess sorption isotherms of the shale samples.

Table 4 Fitting parameters of the Langmuir-based excess sorption model

Sample	$V_L/(\text{cm}^3 \cdot \text{g}^{-1})$	P_L/MPa	$\rho_{\text{ads}}/(\text{g} \cdot \text{cm}^{-3})$	R^2
SS111-1	3.58	2.40	0.36	0.9910
XS26-9	1.06	3.09	0.33	0.9892
ZS6-12	1.85	2.35	0.32	0.9912
ZS32-13	2.83	1.86	0.38	0.9897
DS28-2	2.14	3.39	0.31	0.9942
DS28-13	1.91	3.51	0.31	0.9893
DS28-24	2.43	3.63	0.35	0.9955
DS6-6	2.22	3.89	0.30	0.9915
DS6-13	1.75	3.55	0.30	0.9954
DS6-15	2.57	3.79	0.30	0.9933
DS6-17	1.92	4.26	0.29	0.9886
FS12-4	1.24	2.97	0.30	0.9917
FS12-20	0.97	2.64	0.29	0.9850
XS25-4	1.01	3.09	0.29	0.9842
XS25-6	1.43	2.92	0.29	0.9893
XS25-8	1.56	2.35	0.30	0.9890
ZS14-4	1.72	1.66	0.37	0.9898
ZS14-6	1.92	3.18	0.30	0.9932

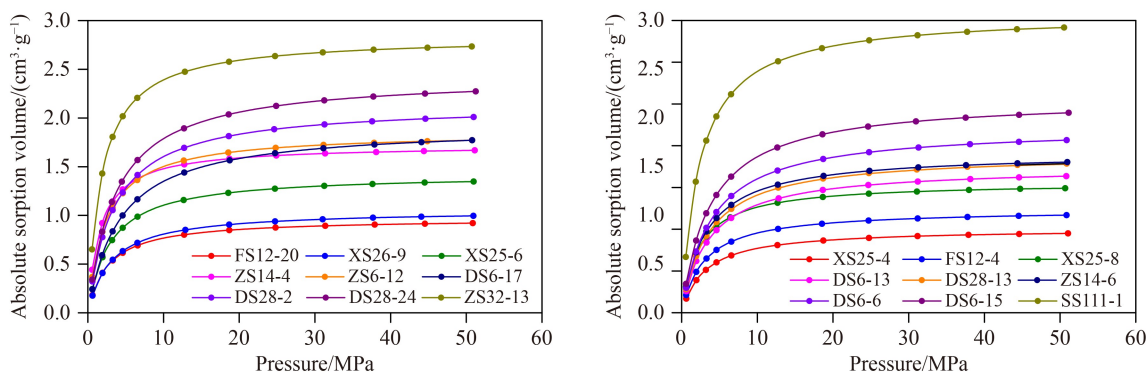
less than the resolution. A similar phenomenon can be observed between pore volume and TOC. It can be concluded that organic matter is not the critical factor for the studied continental shales, especially for the mesopore and macropores, which is significantly different from the results of North America and south China overmature marine shales (Wufeng-Longmaxi Formations) (Wang et al., 2016a; Zhou et al., 2018). Quartz in the studied shales was mainly derived from terrigenous clastic, which is considered a rigid mineral that resists compaction. Thus, the SSA and PV of macropores increase modestly with the quartz content increasing, while no correlations between the quartz content and the SSA and PV of micropores and mesopores are observed (Figs. 14(c) and 14(d)). Since illite usually fills the pores, the SSA and PV

of macropores decrease with increasing illite content (Figs. 14(e) and 14(f)). Different from illite, illite–smectite commonly fills dissolution pores of feldspar, and the content of illite–smectite may be an indicator of the development of dissolution pores. Hence, as illite–smectite content increases, residual dissolution pores increase, resulting in the SSA and PV of macropores increasing, as shown in Figs. 14(g) and 14(h). The results show that compared with the south China overmature marine shales, the studied continental shale pore structures are more complex, controlled by multiple factors, and organic matter is not the critical factor.

4.2 Methane sorption capacity influence factors

The relationships between the V_L and pore-structure parameters are illustrated in Figs. 15–16. The Langmuir volume is positively correlated with the total SSA ($R^2 = 0.8644$) (Fig. 15(a)), suggesting that shale with a larger surface area can adsorb more methane. Specifically, Langmuir volume is correlated well with the SSA of micropores ($R^2 = 0.7044$), while a weaker positive relationship is observed between the Langmuir volume and the SSA of mesopores ($R^2 = 0.474$) (Fig. 15(b)). Moreover, Langmuir volume shows no apparent connection with the SSA of macropores (Fig. 15(b)). Figure 11(a) can explain the results. Namely, the SSA of the studied shale is primarily contributed by micropores, followed by mesopores, while macropores make little contribution.

A weak positive relationship is recognized between the Langmuir volume and the total PV ($R^2 = 0.3472$) (Fig. 15(c)). The Langmuir volume increases linearly with the PV of micropores ($R^2 = 0.6927$). Still, it has slightly positive correlations with the PV of meso- and macropores, as shown in Fig. 15(d). This is because micropores provide larger unit specific surface and higher adsorption potential than that of meso- and macropores (Mosher et al., 2013; Feng et al., 2019); therefore, the higher the micropore volume is, the larger the adsorption space for methane. However, meso- and macropore adsorption is monolayer adsorption for supercritical

**Fig. 13** Absolute sorption isotherms of the shale samples.

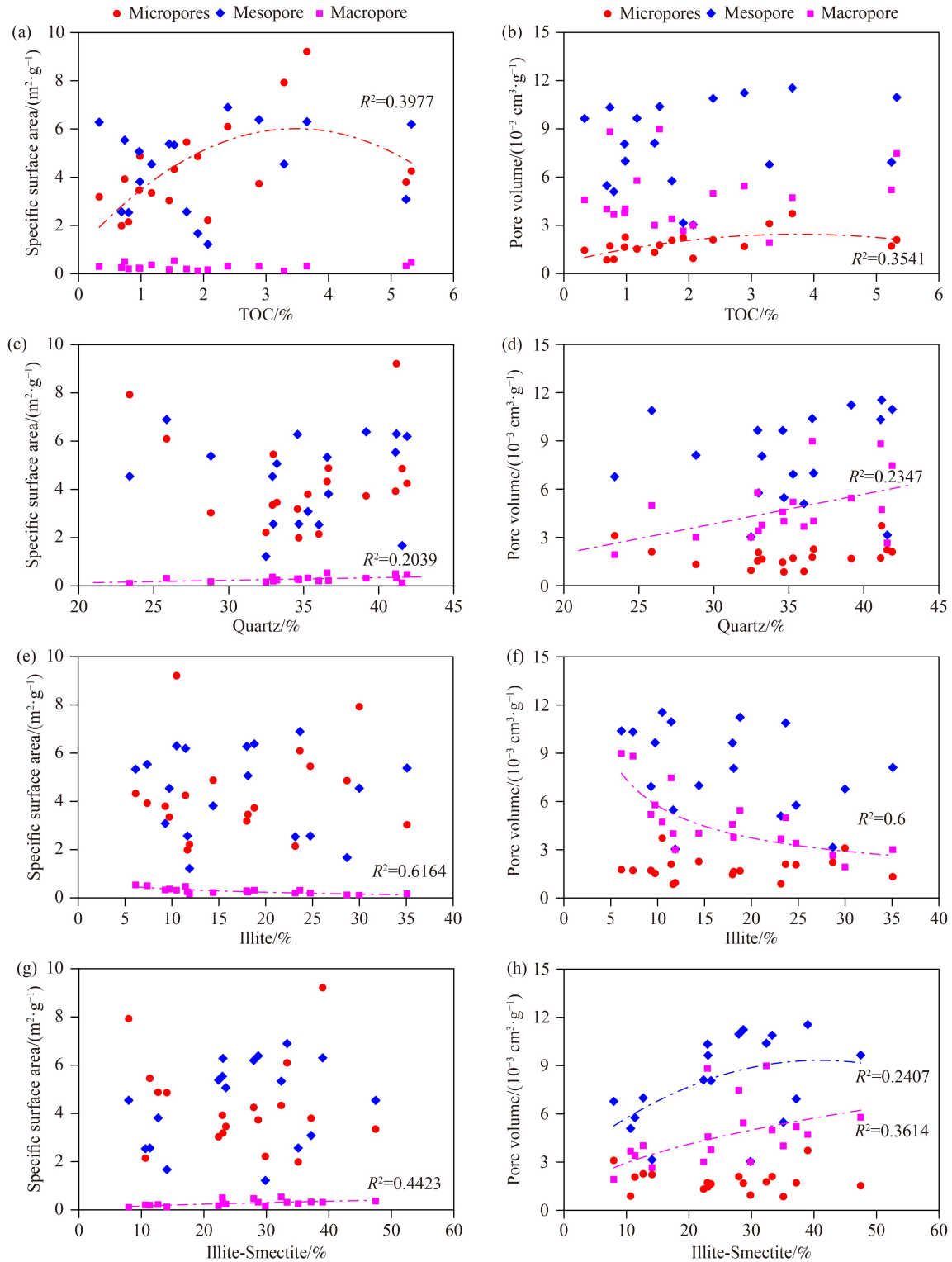


Fig. 14 Influences of organic matter and minerals on pore-structures.

methane under experimental conditions. Therefore, the SSA rather than PV is the determining factor of methane adsorbed in meso- and macropores. Thus, it can be concluded that methane is mainly adsorbed in micropores, followed by mesopores, while macropores make no significant contribution to methane adsorption.

As shown in Fig. 16(a), since some micropores occur in organic matter, a similar relationship is identified between V_L and TOC content. However, there is no apparent correlation between V_L and clay minerals (Fig. 16(b)). In addition, V_L increases with NMR porosity as a power function but has no apparent relationship with

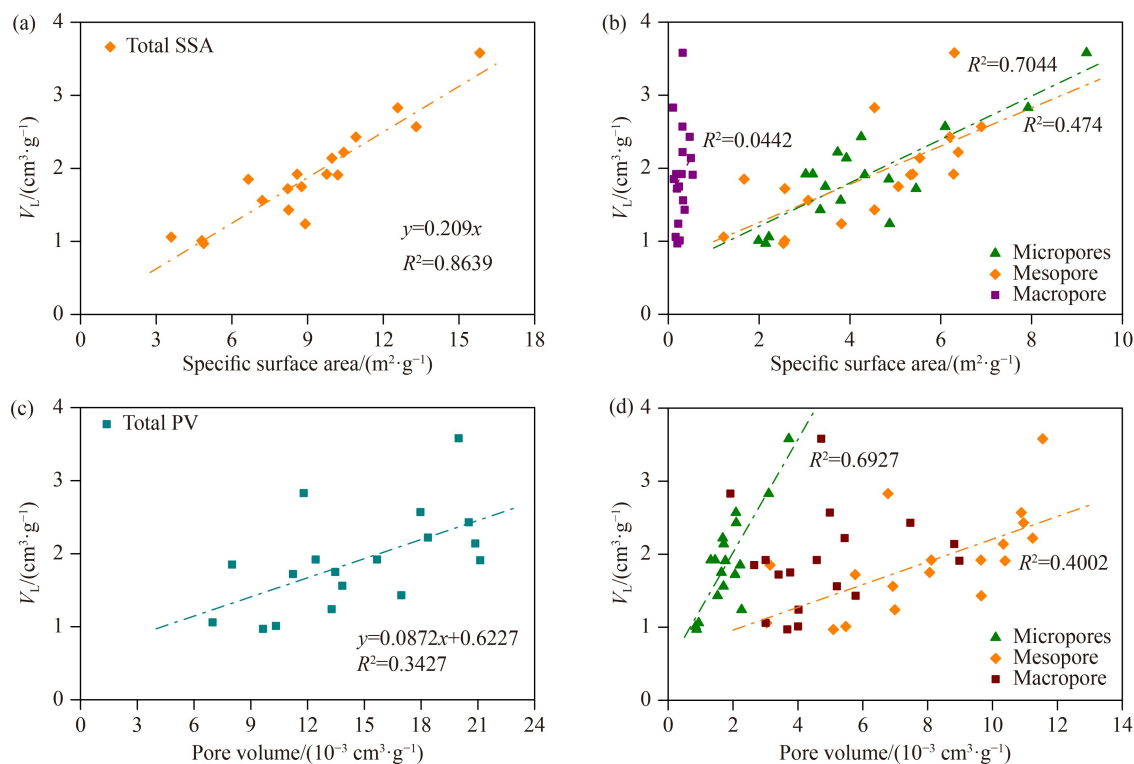


Fig. 15 Relationships between Langmuir volume (V_L) and pore-structures.

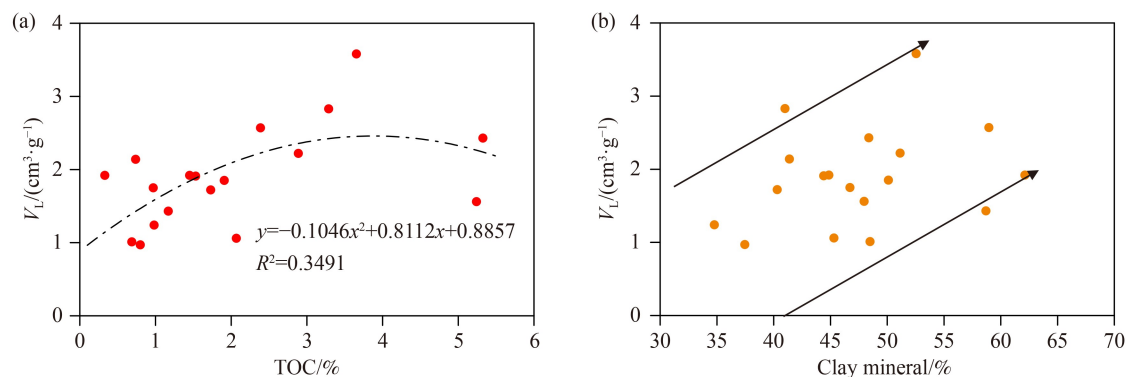


Fig. 16 Influences of TOC and clay minerals on Langmuir volume (V_L).

helium porosity, as shown in Fig. 17. This is because both total SSA and total PV have linear correlations with NMR porosity, which suggests that the NMR method seems to be more reliable for measuring the porosity of tight shale.

The results show that the pore structures of selected continental shales in the Xujiaweizi Fault are more complex and are characterized by many inorganic pores rather than organic pores. In contrast, organic pores commonly occur in the overmature marine shales in South China. Although the studied shales have high specific surface areas and methane adsorption capacities, they are all obtained in the dry state. The methane adsorption of the studied continental shale may be seriously influenced by matrix pore water because inorganic pores absorb more water than organic pores. In

addition, more macropores are more developed than the overmature marine shale. This indicates that free gas may contribute to the total gas content in the study area. Pore structure and methane adsorption characteristics under moist conditions are the subsequent critical investigation of continental shale gas.

5 Conclusions

The studied shales mainly consisted of clay minerals, quartz, and feldspar. The SEM images provided information about the pore types, indicating that the pores can be classified into intraparticle pores and microfractures. Intraparticle pores in clay minerals are the most typical, followed by dissolution pores in feldspar, which

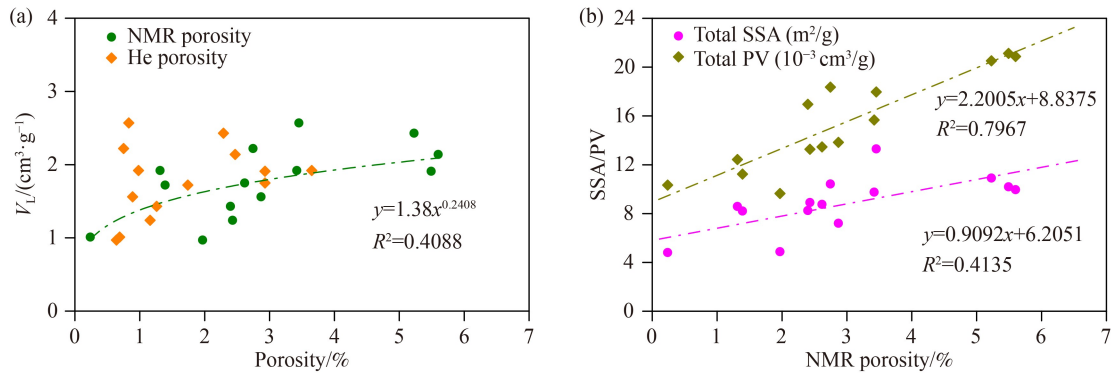


Fig. 17 Influences of helium and NMR porosity on Langmuir volume (V_L) and relationships between NMR porosity and total SSA and PV (b).

are generally filled by illite–smectite. However, organic pores are not developed in the studied shales.

The average helium porosity is 1.66% (0.64%–3.65%), which is commonly lower than the NMR porosity, and the permeability varies from 0.0010 to $0.5299 \times 10^{-3} \mu\text{m}^2$ (mean $0.0498 \times 10^{-3} \mu\text{m}^2$), implying that the selected shales are typical tight reservoirs. The pore throats are at the nanoscale according to the MIPC, the PTSDs are unimodal, and most pore throats are $< 50 \text{ nm}$.

Gas adsorption-desorption measurements revealed the size range of shale pores. Lower SSA and PV values characterize the studied samples but larger average pore diameters than the overmature marine shales. The micro- and mesopores are the significant contributors to SSA, while the PV is mainly occupied by meso- and macropores.

The continental shale pore structures are more complex and controlled by multiple factors, such as mineral compositions and diagenesis, while organic matter is not regarded as a critical factor. The maximum absolute adsorption methane volume (V_L) is 0.97–3.58 cm^3/g (mean 1.90 cm^3/g), correlating well with the total SSA, SSA, and pore volume of micropores. This indicates that micropores are the crucial factor controlling the methane adsorption capacity and storage, followed by mesopores, but macropores contribute not vitally to methane adsorption.

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