Gas storage and controlling factors in an over-mature marine shale: a case study of the Lower Cambrian Lujiaping shale in the Dabashan arc-like thrust–fold belt, southwestern China

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Abstract: Lower Cambrian units in the upper Yangtze area of China are important strata for shale gas exploration. The Lower Cambrian Lujiaping shale in the Dabashan arc-like thrust–fold belt of the upper Yangtze area is thermally over-mature and has been transformed to slate by epimetamorphism. The Lujiaping shale has also experienced strong structural deformation; its current stratigraphic dip is 35°–80°. Over-maturity and strong deformation are considered unfavorable conditions for gas storage. However, desorption tests using canisters indicate that gas contents in the Lujiaping shale range from 0.05 to 3.39 m³/t (average, 1.12 m³/t); this level of gas presents challenges for conventional theories of shale gas enrichment. To analyze the controls on gas enrichment, we performed petrological, geochemical, and petrophysical experiments on shale samples from the Lujiaping Formation. Results show that the TOC contents are between 1.17% and 6.91%. The porosities of the shales are very low, in the range of 0.68%–3.93%, possibly

related to over-maturity. The correlations between petrophysical parameters and the total organic carbon (TOC) content indicate that the organic fraction contribution to micropores and mesopores is highly significant. The Langmuir volumes for the studied shale samples are in the range of 1.07–5.87 m³/t. The gas content and methane adsorption capacity are strongly dependent on the TOC content. Because the studied shales have low porosities and are from shallow depths, their capacity for free gas storage is extremely limited, and the gas is stored mainly in an adsorbed state. The studied shales occur at temperatures of 20–37 °C. The maximum sorption methane capacity occurs at depths of 500–1500 m. Well-developed micropores, high surface area, and strong gas adsorption capacity are important controls on gas enrichment in the Lujiaping shales. The three controls may be related to the inter-particle pores between the organic matter and clay minerals.

Key words: The upper Yangtze area; Lower Cambrian; Lujiaping shale; over-mature; structural deformation; shale gas

1 Introduction

During the past decade, shale gas has provided substantive economic benefits in the United States (Curtis, 2002; Jarvie et al., 2007) and has inspired intensive research activity worldwide. Studies undertaken in the United States have identified total organic carbon (TOC) content, maturity, mineralogical composition, porosity, permeability, and thickness as key parameters in assessments of shale gas resources (Harris et al., 1978; Cluff and Dickerson, 1982; Pollastro et al., 2003; Montgomery et al., 2005). Moreover, the methods used to measure porosity and pore structure have received considerable attention, as these parameters are important in the evaluation of shale gas reserves (Ross and Bustin, 2008, 2009; Loucks et al., 2009, 2012). The

characteristics of gas-rich shales and the controls on these characteristics have been well documented (e.g., Loucks et al., 2009, 2012; Slatt et al., 2011; Kuila et al., 2012; Clarkson et al., 2013; Milliken et al., 2013). Micropore volume increased with increasing maturity due to the generation of pores hosted in organic matter (Ross and Bustin, 2009; Loucks et al., 2012). There exists a positive correlation between TOC content and porosity in the Longmaxi shales (Tian et al., 2013) and the Marcellus shales (Milliken et al., 2013). Kuila et al. (2012) suggested that small-scale pore volume in the Niobrara shales of Laramidia is controlled by the abundance of clay minerals. Pore gas in shales occurs in a compressed state, in an adsorbed state, and in solution (Curtis, 2002). The free gas content depends on the porosity and pressure of shales (Bustin et al., 2008). The adsorbed gas content increases with TOC content and pressure, and decreases with temperature (Ross and Bustin, 2009). The characteristics of reservoirs are key factors in the gas storage capacity (Clarkson et al., 2012). In the New Albany shale of the Illinois Basin, TOC content and micropore volume are the primary controls on gas content (Strapoć et al., 2010). The TOC content is the main control on the methane sorption capacity of shale (Chalmers and Bustin, 2008a; Ross and Bustin, 2009).

In China, as in North America, extensive investigations have been conducted in recent years on the pore characteristics and gas content of shales (e.g., Zou et al., 2010; Chen et al., 2011; Tian et al., 2013; Zhou et al., 2014). In China, marine shales in the upper Yangtze area (UYA) were deposited at three different times, in the Lower Cambrian, early Silurian, and upper Permian (Zou et al., 2010). Of these, the Lower

Cambrian shales and the shales of the lower Silurian Longmaxi Formation are the primary shale-gas development targets, because of high organic matter (OM) contents, favorable mineralogical compositions, and large thicknesses (Wang et al., 2009; Zou et al., 2010; Sun et al., 2012). Most published studies have been conducted on the Longmaxi shale (e.g., Chen et al., 2011; Tian et al., 2013), and gas from the Longmaxi shale has been produced commercially (Guo and Zhang, 2014).

The Lower Cambrian shales in the UYA are important strata for shale gas exploration (Hao et al., 2013). The shales are highly mature, with equivalent vitrinite reflectance (eqR_o) values of 2.5%–3.5% (based on measured pyrobitumen reflectance values; see Zhang and Zhu, 2006a; Zhu et al., 2006a; Ma, 2007). The Lower Cambrian strata were deeply buried during the early Mesozoic, and extensive uplift occurred in the late Mesozoic and Cenozoic (Zhu et al., 2006b; Ma et al., 2008). At the end of the Early Cretaceous, the thickness of Mesozoic strata were 5000–6000 m, and the depth of burial of Lower Cambrian shale had reached 7000–9000 m (CPGEC, 1989). During the Late Cretaceous, the UYA was uplifted and 3000–6000 m of strata was denuded (Zhu et al., 2006b; Ma et al., 2008).

Several studies have documented the basic characteristics of the Lower Cambrian shales in the UYA (Chen et al., 2012; Wei et al., 2012; Han et al., 2013a). Tan et al. (2014a, b) conducted a preliminary evaluation for the gas potential of the Lower Cambrian shales based on mineralogical, lithofacies, petrophysical, rock mechanical properties, and methane sorption capacity. The inter-particle pore space between OM and minerals in the Lower Cambrian Lujiaping shale has been well described by Ma

et al. (2015), who speculated that intergranular pore space is the dominant storage space for gas. However, previous studies have not examined the occurrence of shale gas or the controls on its distribution.

Over-maturity and strong deformation are considered to be unfavorable conditions for shale gas enrichment (Jarvie et al., 2007). However, the results of desorption tests using canisters have shown that the gas content of the Lower Cambrian Lujiaping shale at depths of <1000 m is in the range of 0.05–3.39 m³/t (average, 1.12 m³/t) (Han et al., 2013b). This finding challenges the conventional understanding of shale gas enrichment. However, Han et al. (2013b) did not explain the high gas content. Therefore, the mechanism of gas enrichment in the Lower Cambrian shales is still to be determined.

In this study, we examined the geochemical, mineralogical, and petrophysical properties of the Lower Cambrian Lujiaping shale in the Dabashan arc-like thrust–fold belt (DATB) in southwestern China, as well as the gas content and methane adsorption capacity of the shale. Based on these parameters, we analyzed the controls on gas storage. The results of the study have implications for gas exploration in the Lower Cambrian shales of the UYA and other shales that are highly over-mature.

2 Geological setting and sampling

The DATB is situated along the northern margin of the UYA (Fig. 1a) and is composed of two parts: the South Dabashan and North Dabashan belts (Fig. 1a). The basement of the UYA was formed after the Lüliang Orogeny (1700 Ma). Tillites were

deposited on the basement rocks in the early Sinian, across a parallel unconformity. Limestones were deposited unconformably on the tillites during the late Sinian, and marine siliciclastics were deposited on the tillites during the early Paleozoic (Fig. 2). The Lujiaping shale was formed in the South Qinling area in the Early Cambrian. A stronger uplift occurred in the Early Cambrian in the study area. At this time, the UYA started to move beneath the North China block, which initiated uplift that started in the late Silurian, and the development of a parallel unconformity on the Silurian strata (Fig. 2) (Meng and Zhang, 2000). The South Qinling collided with the UYA in the Late Triassic, at which time the Qinling orogenic belt was influenced by the formation of a thrust-fold system and the emplacement of extensive granitic intrusions (Zhang et al., 1996). The DATB took shape during this collisional orogenesis. The study area was rapidly uplifted in the Late Cretaceous and Cenozoic (Meng and Zhang, 2000).

Well C1, located in the study area, was drilled to evaluate the gas potential of the Lujiaping shale (Fig. 1). Thirty-six samples of shale for measurements of gas content were obtained for all depths from 0 to 854 m; the lengths of samples ranged from 22 to 29 cm. The thickness the shale normal to bedding (i.e., corrected for the angle of dip) was 563 m. The Lujiaping Formation, dominated by shale and silty shale, was deposited on a deep-water continental shelf margin (Fig. 3).

Figure 1. (a) Location and tectonic condition of the DATB (modified from Zhang et al., 2001) 1, middle–upper Proterozoic rocks; 2, DATB; 3, fault; 4, fold; F₁₂, Chengkou Fault; F₂₂, Lujiaping Fault; F₂₃, Zhenba Fault. (b) Simplified geological cross-section along the line A–A' in (a) (modified from Ma et al., 2015).

Figure 2. Detailed explanation of the history of sedimentation, basin development, and tectonic evolution in the DATB (modified from Meng and Zhang, 2000).

Figure 3. Generalized section of lithological variations in the Lujiaping Formation of the UYA (modified after Ma et al., 2015). It is assumed that the surface temperature is 20 °C, the geothermal gradient is 20 °C/km (Han and Wu, 1993), and the hydrostatic pressure gradient is 9.8 MPa/km. According to these assumptions, the reservoir temperature and pressure were calculated.

3 Experiments

3.1 Gas content

As described by Ma et al. (2015), the gas content was determined using the canister desorption method after samples had been collected from the core barrel. The tested

core was placed in the canister, and the canister was filled with saturated salt water to reduce the solubility of gas. Then, the canister was placed in water and maintained at reservoir temperature; the released gas was collected and quantified using a measuring cylinder (Figure 4). The amount of gas got at the reservoir temperature was limited. Therefore, the shale was subjected to a higher temperature (90 °C) to expedite the gas release. The end content of the gas was determined when the gas release rate over a 2-hour period was <2 ml. Then, the released volume of gas was corrected to the gas volume at 0 °C and 101.325 kPa (Mavor and Nelson, 1997). After completion of the canister desorption test, a portion of each sample was tested for residual gas content. However, the residual gas contents were very small (<0.15 m³/t). Therefore, the residual gas was neglected in this study.

Figure 4. Equipment required for the canister desorption method (modified after Han et al., 2013b).

3.2 TOC content and reflectance

A CS-230 elemental analyzer (Leco Corporation, USA) was used to determine TOC contents. First, the shale samples were crushed to 100 mesh (<150 µm). Next, to

remove carbonate, the powdered samples were treated using 5% HCL at 80 °C. Third, the treated samples were washed more than 20 times with deionized water. Last, the TOC contents of the treated samples were determined using the elemental analyzer, according to the standard methods.

Due to the lack of vitrinite in the lower Paleozoic hydrocarbon source rocks, vitrinite-like macerals such as bitumen and marine vitrinite were used as maturity indicators (Jacob, 1989; Zhong and Qin, 1995). The reflectances of the vitrinite-like macerals were measured using a MPV-III microphotometer.

3.3 Mineral composition

Mineral compositions were measured using a D/MAX 2500 X-ray diffractometer. Prior to measurements, the rock samples were crushed to assure uniformity of crystallite sizes. Corundum (20 wt.%) was added as an internal standard.

3.4 Porosity and permeability

Bulk densities (ρ_{bulk}) were determined from the geometric dimensions of cylindrical plug samples. Grain densities (ρ_{grain}) were measured using a helium pycnometer. All bulk and grain density values were determined on the basis of dry sample weight (drying at 110 °C under a vacuum), and from these, total gas-filled porosities ($\emptyset$) were calculated according to: $\emptyset = 1 - \rho_{\text{bulk}}/\rho_{\text{grain}}$.

Prior to measurements, the plug samples were dried at 80 °C. The permeability was tested using a PDP-200 permeameter (Core Lab, USA); the resulting permeability value was calculated by the software supplied with the instrument. The method for calculating permeability was described in detail by Jones (1997).

3.5 Mercury injection capillary pressure (MICP)

A Micromeritics Autopore IVTM porosimeter was used to measure the pore size

distribution. During the experiments, a known amount of mercury was injected into the samples. The Washburn equation was then used to describe the variations in pore radius and pressure (Washburn, 1921):

$$r_T = \frac{2\gamma \cos \theta}{P} \quad (1)$$

where r_T is the pore radius, γ is the interfacial tension of Hg, θ is the contact angle of Hg, and P is the pressure used in the experiments. The pore radius was obtained using the values of $\theta = 140^\circ$ and $\gamma = 480$ dyne/cm. For the procedure, 5–10 g of each sample was oven dried at 115°C for at least 2 hours. The highest pressure achieved was 414 MPa. We were able to test pores with radii larger than 1.8 nm. The repeatability of the analyses was $\pm 9\%$.

3.6 Low-pressure gas adsorption

Low-pressure N_2 and CO_2 adsorption experiments were performed using a Micromeritics® ASAP 2020 surface area analyzer. The N_2 and CO_2 isotherms were measured at -196.15°C and 0°C , respectively. Equivalent surface areas were obtained using the BET method (Brunauer et al., 1938) according to the N_2 isotherms and at a relative pressure of 0.06–0.2:

$$1/W(P_0/P) - 1 = 1/W_m C + C - 1/W_m C(P/P_0) \quad (2)$$

where W is the weight of the sorbed N_2 in the relative pressure P/P_0 , W_m is the weight of the monolayer adsorbent (N_2), and C is the BET constant. The pore size distribution (PSD) was calculated by the Barrett–Joyner–Halenda (BJH) method (Barrett et al., 1951). The surface area was calculated using multilayer adsorption theory (Unsworth et al., 1989). The CO_2 adsorption isotherms were measured at 0°C , and the data were interpreted using density functional theory (DFT) (Do and Do, 2003).

3.7 Field emission (FE) SEM observations

Prior to observations, samples were cut to ~1 cm in size. The cut samples were then polished using emery paper without water, and the polished samples were milled using Ar ion milling. The accelerating voltage was 4 kV and the polishing time was 10 hr. Then, the milled samples were Au-plated to obtain a conductive surface. Finally, the observations were performed using an FEI Quanta200F field emission SEM (FE–SEM) microscope at an accelerating voltage of 20 kV. All samples were examined using both secondary electron (SE) and backscattered electron (BSE) imaging.

3.8 Methane adsorption

The isothermal adsorption experiments were conducted using an ISO-300 instrument (Terra Tek Corporation, USA). The calibration gas was He, and N₂ was used as the valve carrier gas. The sample cells were maintained at 30 °C (± 0.2 °C), and the laboratory air temperature was maintained at ~25 °C. A total of 50–80 g of powdered sample was used for the analysis. The error of the results was 1.2%–6.8%. The amount of absorbed methane was recorded in units of m³/t, at 0 °C and 101.325 KPa.

4 Results

4.1 Geochemical characteristics and mineralogical compositions

Table 1 lists the compositions of the eight shale samples analyzed in this study. The TOC contents are 1.17%–6.91% (average, 3.04%) and the eq R_o values are 2.4%–3.0% (Table 1). Mineralogical compositions are listed in Table 1 and summarized on the ternary diagram in Fig. 5. The most abundant phase is carbonate (16.9%–83.8%), followed by quartz (3.0%–50.3%), clay (2.7%–31.7%), and feldspar (0%–14.5%) (Table 1; Fig. 3). Given the high maturity to over-maturity of the shale, illite is the only clay component. The shale has high TOC and carbonate contents. The TOC

content increases with the increasing clay mineral content (Fig. 6).

Table 1. Geochemical parameters and mineralogical compositions of the studied shale samples

Sample	Depth (m)	TOC (wt. %)	eqR _o [*] (%)	Relative percent (wt. %)				
				Quartz	Feldspar	Carbonate	Clays	Pyrite
C1-2	224.67	1.17	nd ^{**}	50.3	0	35.1	4.5	0
C1-3	244.06	3.57	nd	32.2	14.5	16.9	31.7	4.7
C1-4	266.47	1.17	2.4	15.3	2.5	75.8	2.7	0
C1-13	463.85	3.43	nd	47.9	10.9	20.2	17.6	3.4
C1-15	518.07	1.97	nd	3.0	1.6	83.8	5.3	5.6
C1-17	576.18	4.68	3.0	41.4	2.2	34.3	18.8	3.3
C1-18	589.41	1.41	nd	33.5	10.9	25.5	20.6	8
C1-29	721.85	6.91	2.9	49.5	9.1	19.6	20.5	1.3

^{*}, eqR_o is calculated according to the equation established by Jacob (1989); ^{**}, no data.

Figure 5. Ternary diagram of the mineralogical compositions of the studied shale samples.

Figure 6. TOC versus clay content for the studied shale samples.

4.2 Pore characteristics

4.2.1 Porosity and permeability

Total porosities of the Lujiaping shales are in the range of 0.17%–3.93% (Table 2) and permeabilities are in the range of 0.00021–0.00081 mD (average, 0.00147 mD) (Table 2). The samples show a positive correlation between porosity and permeability, except for sample C1-29 (Figure 7).

Table 2. Porosity and permeability values of the studied shale samples.

Sample	Porosity (%)	Permeability (mD)
C1-2	3.93	0.00057
C1-3	0.90	0.00040
C1-4	0.17	0.00021
C1-13	1.93	0.00039
C1-15	2.27	0.00083
C1-17	1.75	0.00088
C1-18	2.29	0.00037
C1-29	1.30	0.00810

Figure 7. Porosity versus permeability for the studied shale samples. a. Data for all eight samples.

b. Excluding sample C1-29.

4.2.2 Pore type

This study uses the classification scheme for pores in shales reported by Loucks et al. (2012). According to this scheme, the pores are inter-particle, intra-particle, and organic-matter pores. Inter-particle pores are generally much more abundant in young than in old sediments (Loucks et al., 2012). However, our observations show that

inter-particle pores do exist in the old shales of the Lujiaping Formation; they are elongate and develop between clay platelets (Fig. 8a) or along the edges of quartz particles (Fig. 8b). The long dimensions of inter-particle pores are in the range of 55 nm to 10 μm , which are similar to the dimensions reported by Milliken and Reed (2010) and Loucks et al. (2012). Intra-particle pores are found in framboidal pyrite particles. The shapes of the intra-particle pores range from triangular to quadrangular, and their sizes are in the range of 200 nm to 4 μm (Figs 8c and 8d). Dissolution pores are present in calcite grains. Some of the dissolution pores are filled with clay (Fig. 8e). Fractures are also observed in the SEM images (Fig. 8f). The long dimensions of the fractures are >40 μm , and the width dimensions are ~65 nm. Pores in OM are rare in the Lower Cambrian Lujiaping shale (Fig. 8g). The particular pore system in the shale was described in detail by Ma et al. (2015). Cleavage is developed in some samples (Fig. 8h). A large number of nanometer-sized inter-granular pores (1–4 nm, with a peak value of 1.3 nm) occur in the cleavage zones, along the contact borders between OM particles and clay mineral (CM) particles (Ma et al., 2015).

Figure 8. SEM images of the studied shale using a backscattered electron (BSE) detector. a. Inter-particle pores between clay platelets (sample C1-2). b. Inter-particle pores between quartz grains (sample C1-29). c. Intra-particle pores in pyrite framboids (sample C1-4). d. Intra-particle

pores in crystalline pyrite (sample C1-29). e. Dissolution pores in crystalline calcite filled with clay (sample C1-29). f. Fracture (sample C1-17). g. Pores in OM (sample C1-17). h. Cleavage domain (sample C1-17).

4.2.3 Pore volume, surface area, and pore size distribution

Low-pressure CO₂ adsorption isotherms are of the Type I variety (Brunauer et al., 1940), indicative of microporous solids (Fig. 9). Maximum uptakes of the samples are in the range of 0.28–1.92 cm³/g. Low-pressure N₂ adsorption isotherms are of the Type II variety (Brunauer et al., 1940) (Fig. 10), which indicates multi-layer adsorption exists, and the isotherms can be analyzed using BET theory (Gregg and Sing, 1982). All the studied samples have Type H₄ hysteresis. Therefore, according to De Boer (1958), the pores were of the slit-type variety. The hysteresis loop shown by sample C1-29 is not closed (Fig. 10h), which can be attributed to swelling or the adsorption of nitrogen in micropores (Gregg and Sing, 1982).

Figure 9. Low-pressure CO₂ adsorption isotherms for the shale samples.

Table 3 summarizes the data of low-pressure CO₂ and N₂ adsorption, and the Hg intrusion analysis. Micropore volumes and surface areas determined from the CO₂ adsorption analysis are in the range 0.0007–0.0065 cm³/g and 2.71–20.14 m²/g,

respectively. Pore volumes and BET surface areas obtained from the N₂ adsorption analysis exhibit a wide range of values, of 0.0212–0.0578 cm³/g and 8.15–34.91 m²/g, respectively. Pore volumes and surface areas from the Hg intrusion analysis are in the range of 0.0047–0.0115 cm³/g and 0.0005–0.4666 m²/g, respectively. The dV/dD plots suggest a bimodal pore-size distribution in the studied samples, with peaks near 2 and 7 nm (Fig. 11); these results suggest that mesopores account for most of the pore volume in the shale samples.

Figure 10. Low-pressure N₂ gas adsorption isotherms for the shale samples: (a) sample C1-2; (b) sample C1-3; (c) sample C1-4; (d) sample C1-13; (e) sample C1-15; (f) sample C1-17; (g) sample C1-18; and (h) sample C1-29.

Table 3. Pore volume and surface area from low-pressure N₂ and CO₂ adsorption analyses and Hg intrusion analysis.

Sample	Pore volume (cm ³ /g)			Surface area (m ² /g)		
	CO ₂	N ₂	Hg	CO ₂ equivalent	N ₂ BET	Hg
C1-2	nd	0.0212	nd	nd	8.15	nd
C1-3	0.0016	0.0282	0.0047	4.84	14.70	0.0005
C1-4	nd	0.0322	nd	nd	9.53	nd
C1-13	nd	0.0295	nd	nd	17.20	nd
C1-15	0.0007	0.0320	0.0075	2.71	15.10	0.0006
C1-17	0.0036	0.0578	0.0115	12.47	24.26	0.4666
C1-18	nd	0.0370	nd	nd	18.92	nd
C1-29	0.0065	0.0218	0.0106	20.14	34.91	0.0009

Figure 11. Pore size distribution from low-pressure CO₂ and N₂ gas adsorption analyses and Hg intrusion analysis: (a) sample C1-2; (b) sample C1-3; (c) sample C1-4; (d) sample C1-13; (e) sample C1-15; (f) sample C1-17; (g) sample C1-18; and (h) sample C1-29.

4.3 Gas content and adsorption capacity

The curves for the desorption volume are shown in Fig. 12a. Canister desorption times are in the range of 1500–5000 min (1–4 days). Figure 12b shows that desorption

volumes at low temperatures ($0.5\text{--}1040\text{ cm}^3$) are much smaller than volumes at high temperatures ($152\text{--}5610\text{ cm}^3$). The gas contents obtained from canister desorption are $0.06\text{--}3.39\text{ m}^3/\text{t}$ (average, $1.10\text{ m}^3/\text{t}$) (Table 4).

The isotherms of the studied samples are presented in Fig. 13. The sorption isotherms exhibit similar shapes among the samples, whereas the sorption amounts show marked differences. The shapes of the sorption curves indicate that the isotherms are of a type I variety. The Langmuir volumes of the studied samples are in the range of $1.07\text{--}5.87\text{ m}^3/\text{t}$ (average, $2.64\text{ m}^3/\text{t}$), and the Langmuir pressures are in the range of $1.27\text{--}2.23\text{ MPa}$ (average, 1.73 MPa) (Table 4).

Figure 12. (a) Canister desorption volumes vs. time for the shale samples. (b) Relative concentrations of desorbed gas under low-temperature (reservoir temperature) and high-temperature (90 °C). LT, low temperature; HT, high temperature.

Figure 13. Methane sorption isotherms for the shale samples.

Table 4. Canister desorption and Langmuir fitting results for the shale samples.

Sample	Canister Desorption			Langmuir volume (m³/t)	Langmuir pressure (MPa)
	Desorption volume at LT (cm³)	Desorption volume at HT (cm³)	Gas content (m³/t)		
C1-2	55	1122	0.55	1.87	1.45
C1-3	0.5	350	0.12	1.48	2.10
C1-4	3	152	0.06	1.07	1.27
C1-13	49	2968	0.87	2.30	1.57
C1-15	1040	920	0.68	1.72	2.21
C1-17	19	5610	1.87	3.82	1.46
C1-18	10	3972	1.26	2.97	1.52
C1-29	nd	3300	3.39	5.87	2.23

5 Discussion

5.1 Controls on porosity and pore structure

As shown in Table 2, the porosities and permeabilities of the studied samples are lower than those of shales with lower maturities, such as the Longmaxi shales (Tian et al., 2013), Barnett shales, Woodford shales, Eagle Ford shales, Haynesville shales,

Marcellus shales, and New Albany shales (Clarkson et al., 2013; Mastalerz et al., 2013). During the compaction process, a large number of inter-particle and intra-particle pores are destroyed, and thus porosity decreases with increasing maturity (Fig. 14). Consequently, the number of pores of the two varieties (inter-particle and intra-particle) observed in the studied shales (Fig. 8) is less than that observed in many other shales (e.g., Pliocene–Pleistocene mudstone from the Ursa Basin, Lower Cretaceous Pearsall Formation, Eagle Ford shales, Bossier shales, New Albany shales, Pennsylvanian Atoka interval shales, Posidonian shales (Germany), and Barnett shales) (see Loucks et al., 2012). In addition, not only maturity, but also the compositions of organic and inorganic components have important implications for the numbers and characteristics of pores (Kuila et al., 2012).

Figure 14. Porosity vs. vitrinite reflectance (R_0) values for shales. Data sources: Longmaxi shales (Tian et al., 2013); New Albany shales (Mastalerz et al., 2013); WCSB (D-M) and WCSB (J) (Ross and Bustin, 2009); and WCSB (K) (Chalmers et al., 2008b).

A positive correlation is observed between porosity and quartz content in the

studied shales, except for sample C1-15 (Fig. 15); the departure of sample C1-15 from the expected trend is due to its low quartz content and high carbonate content (Table 1). This correlation suggests that porosity is controlled by the amount of quartz and carbonate. However, positive variations between TOC and porosity have been reported in the Marcellus shales (Milliken et al., 2013), the Longmaxi shales (Tian et al., 2013), and other shales (Passey et al., 2010). Due to the relatively low grain density of OM, the impacts of pores in OM are amplified, which explains why a relatively small amount of TOC can impact a relatively large volume of rock (Passey et al., 2010). The TOC contents of the studied shales are similar to those of the Longmaxi shales (Tian et al., 2013), but no positive relationship was observed between TOC content and porosity in the studied shale samples (Figure 16). This absence of a relationship may indicate that relatively few pores are developed in the OM in the studied shales. In fact, the results of SEM observations support this speculation (Fig. 8g), which can be attributed to differences in the types and maturities of OM.

Figure 15. Porosity versus quartz content in the studied shale samples.

Figure 16. Porosity versus TOC content in the studied shale samples.

Micropore volumes are positively correlated with TOC contents in the studied shales (Fig. 17), indicating a significant contribution of the organic fraction to micropores. A similar positive correlation between micropore volume and TOC content has been found in other shales, such as in the Muskwa and Besa River shales from northern British Columbia, western Canada (Ross and Bustin, 2009) and in the Lower Cretaceous Buckingham shales (Chalmers and Bustin, 2008a). Pore volumes in the size range of 0.1–1 nm are strongly controlled by TOC content. Sample C1-29 shows the highest TOC content (Table 1) of the studied shale samples, and accordingly, this sample has the largest pore volume (in the 0.1–1 nm size range) (Fig. 11h). Although samples C1-2 and C1-18 exhibit similar TOC contents, sample C1-18 has a higher CM content (Table 1). The pore volume in the 1–10 nm pore-size range observed in sample C1-18 is larger than that of sample C1-2 (Figs 11a and 11g). Samples C1-17, C1-18, and C1-29 show similar CM contents but different TOC contents (Table 1). Pore volumes in the size range of 1–10 nm for the three samples increase with increasing TOC content (Figs 11f–11h). The conditions above suggest

that pores in the size range of 1–10 nm are related mainly to the TOC content.

In contrast, pore volume in the ~3-nm pore size increases with clay content (Kuila et al., 2012). Several investigators have argued that the presence of a 3-nm pore-size distribution peak is a characteristic signature of clay microstructures (Neaman et al., 2003; Kuila and Prasad, 2011). The differences in the controls on pore volume can be attributed to lower maturities and different compositions of CMs between the studied shale samples and those in the studies mentioned above. As compared with the studied shale samples, the maturities (oil window) of the samples in other studies are much lower, and their CMs consist mainly of illite–smectite group clays. The surface area of smectite is 800 m²/g, which is much higher than that of illite (30 m²/g) (Passey et al., 2010). In general, a positive relationship exists between pore volume and surface area (Ross and Bustin, 2009). Therefore, differences in the factors that control pore volume may be caused by different CM compositions.

Micropore surface areas obtained from low-pressure CO₂ adsorption experiments are positively correlated with TOC content (Fig. 17b), and surface areas obtained from low-pressure N₂ adsorption experiments also increase with TOC content (Fig. 18a). The CM content in the studied shale samples is negatively correlated with the N₂ BET surface area normalized to TOC (Fig. 18b). The relationships between these parameters indicate that pores related to OM contribute significantly to micropore surface area, which agrees well with the positive relationship between TOC content and micropore volume (Fig. 17a). The contribution of pores related to OM to surface area in the studied shales is similar to that observed in many other shales, such as in

the Lower Cretaceous shales from northeastern British Columbia, Canada (Chalmers and Bustin, 2008a), Upper Triassic Yanchang shales in the Ordos Basin, China (Ji et al., 2014), and Longmaxi shales in the upper Yangtze area, China (Tian et al., 2013).

Figure 17. TOC versus (a) micropore volume and (b) micropore surface area for the studied shales.

Micropores are pores of < 2 nm in size (Rouquerol et al., 1994). Micropore volume was calculated from low-pressure CO₂ adsorption isotherms using density functional theory (DFT) (Do and Do, 2003).

Figure 18. N₂ BET surface area versus (a) TOC and (b) clay content for the studied shales.

5.2 Controls on gas content and adsorption capacity

The gas content is positively correlated with TOC content in the studied shales (Fig. 19a); a similar correlation has also been observed in the New Albany shales by Martini et al. (2008) and Strapoć et al. (2010). This pattern indicates that the abundance of OM is the primary control on amounts of gas in the studied shales. Shale gas is stored as a sorbed gas, a free gas, and a dissolved gas (Curtis, 2002). No correlation was observed between gas content and porosity in the studied shales (Fig. 19b), but a strong correlation existed between gas content and the Langmuir volume (Fig. 19c); these results suggest that the gas in the studied shales is stored mainly as sorbed hydrocarbons.

At the boundary between OM and CM the cleavage (Fig. 8h) contains many

nanometer-sized (1–4 nm) intergranular pores, with a peak pore size of 1.3 nm (Ma et al., 2015). OM and CM provide the two walls of the inter-particle pores. Therefore, the OM and CM can provide sites for gas sorption. A positive correlation exists between the Langmuir volume and the TOC content of the studied shales (Fig. 20a). Similar positive correlations have also been observed in many other shales, such as the Lower Cretaceous Buckinghorse shales (Chalmers and Bustin, 2008a), Muskwa and Besa River shales (Ross and Bustin, 2009), and Woodford, and Green River shales (Zhang et al., 2012). This correlation indicates that OM provides storage sites for adsorbed gas. A positive relationship between clay content and Langmuir volume suggests that clay minerals made a minor contribution to the gas adsorption capacity (Figure 20b). Positive correlations between the Langmuir volume and the micropore volume and N₂ BET surface area were also observed in the studied shales (Figs 20c and 20d). As discussed above, micropore volume and N₂ BET surface area are correlated with the TOC content (Figs 17a and 18a). CMs in the studied shales consist of illite, and the CH₄ adsorption capacity of illite is much lower than that of montmorillonite, mixed illite/smectite, kaolinite, or chlorite (Ji et al., 2012; Liu et al., 2013). The contribution of CMs to the CH₄ adsorption capacity is extremely limited in the studied shales. Therefore, we conclude that the micropores which developed between OM and CM provide most of the adsorption sites for the gas, whereas the pores between CM particles made only a minor contribution.

Figure 19. Gas content versus (a) TOC, (b) porosity, and (c) Langmuir volume.

Figure 20. Langmuir volume versus (a) TOC, (b) clay content, (c) micropore volume, and (d) N₂ BET surface area.

Previous studies have indicated that the adsorption capacity of shales is inversely correlated with temperature (Sircar, 1992; Hildenbrand et al., 2006; Ross and Bustin,

2008). However, pressure also influences the gas sorption capacity of shales (Fig. 13). An empirical model describing the influence of OM, temperature, and pressure on gas adsorption was constructed by Guo (2015), based on experimental simulations and on experimental data from the Lujiaping shales. Although the desorbed gas was mainly CH₄ (95.38–98.80 vol.%), C₂H₆ (0.43–1.28 vol.%), CO₂ (0.25–0.79 vol.%), and N₂ (0–3.49 vol.%) (Han et al., 2013b), 100 vol.% CH₄ is assumed in this model to simplify the calculation. This model can therefore be used to predict adsorbed gas amounts under the conditions of the geological shale gas reservoir in this study. It is assumed that surface temperature is 20 °C, geothermal gradient equals 20 °C/km (Han and Wu, 1993), and hydrostatic pressure gradient is 9.8 MPa/km, and applying these parameters to the expression established by Guo (2015) (equation (3)), and assuming constant TOC content, the variation in the methane sorption capacity varies with depth, as follows:

$$V = ((0.744 \times \text{TOC} - 0.013 \times T + 1.15) \times P) / (P + e^{(0.007 \times T - 0.106)}) \quad (3)$$

where V is the volume of adsorbed gas (m³/t), T is temperature (°C), and P is pressure (MPa).

As shown in Fig. 21, the methane sorption capacity obtained from the empirical model of Guo (2015) initially increases with depth, reaches a maximum at depths of 500–1500 m (for shales with varied TOC contents), and then decreases at depths of >1500 m. The depth with a maximum gas sorption amount increases with increasing TOC content, a pattern that is analogous to that observed in published results (e.g., Hildenbrand et al., 2006; Ji et al., 2014). The gas content of the studied

shales shows a marked increase at depths of >460 m (Fig. 3), which supports the conclusions drawn above, that gas is stored as sorbed hydrocarbons. A greater proportion of free gas is adsorbed at depths of >1500 m.

Figure 21. Methane sorption capacity of the studied shales with varied depth and TOC contents calculated from the empirical model of Guo (2012).

6 Conclusions

Although the Lower Cambrian Lujiaping shales in the DATB of southwestern China are over-mature and have experienced strong deformation, they have high gas contents. To analyze the controls on gas enrichment in the shales, we characterized their mineralogical composition, pore structure, and adsorption capacity.

(1) Due to strong deformation and over-maturity, the porosity of the shales is low, but micropores and mesopores are well developed between OM particles and CM

particles.

(2) Gas in the studied shales is stored mainly as sorbed hydrocarbons. The adsorption capacity depends strongly on the TOC content. Methane sorption capacity reaches maximums at depths of 500–1500 m.

(3) Well-developed micropores, high surface area, and strong gas adsorption capacity are significant controls on gas enrichment in the Lujiaping shales. The three controls above may be related to the inter-particle pores between OM and CMs. Therefore, there still exists a strong positive relationship between gas content and TOC content.

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