Characteristics of black shale in the Upper Ordovician Wufeng and lower Silurian Longmaxi formations in the Sichuan Basin and its periphery, China


To link to this article: http://dx.doi.org/10.1080/08120099.2017.1321581

Published online: 16 May 2017.
Characteristics of black shale in the Upper Ordovician Wufeng and lower Silurian Longmaxi formations in the Sichuan Basin and its periphery, China


© 2017 Geological Society of Australia

ABSTRACT

Geochemical and mineralogical analyses, in addition to isothermal adsorption experiments on field samples, are used to characterise the sedimentary environments, reservoirs and adsorbed gas of the Upper Ordovician Wufeng-lower Silurian Longmaxi formations in the Sichuan Basin and its peripheral areas. The sedimentary environment of the Wufeng and the lower part of Longmaxi formations is a deep-water shelf with five different lithologies identified: siliceous shale, black shale, siltstone, biolithite limestone and bentonite. The black shale in the Wufeng and the lower part of Longmaxi formations is 50 m thick, with an average organic carbon content (TOC) of 3.81 wt% and a maturity (Ro) of 1.62%. Quartz comprises 54.94 vol% of the shale and positively correlates with the TOC. Micropores in the black shale include intergranular pores, intragranular pores, organic matter pores and microfractures. Among these pores, spaces between clay sheets and organic molecules represent a favourable storage space for the accumulation and preservation of oil and gas. The Langmuir volume parameter ranges between 1.52 and 3.01 cm$^3$/g, with an average value of 2.33 cm$^3$/g. The presence of organic matter pores and pores between clay sheets in the black shale is the main and controlling factor for accumulated gas.

ARTICLE HISTORY

Received 2 July 2016
Accepted 15 March 2017

KEYWORDS

Sichuan Basin; Wufeng Formation; Longmaxi Formation; black shale; sedimentary environments; organic geochemistry; reservoir characteristics; gas resource

Introduction

Despite several decades of research on black shales as hydrocarbon source rocks in the USA and China (Liu et al., 2006; Tenger et al., 2006; Wang, Yan, & Li, 2008; Zhai, 1989), the geological background and organic geochemistry of Chinese black shales are not well known. In recent years, many studies have focused on the black shale of the Upper Ordovician Wufeng-lower Silurian Longmaxi formations in the Sichuan Basin (Chen et al., 2015; Dong et al., 2010; Jiang, 2003; Liang et al., 2014; Liu et al., 2013; Tuo, Wu, & Zhang, 2016; Wang et al., 2016; Zhang et al., 2003; Zou et al., 2010; Zou, Tao, & Hou, 2013), as it seems to have an effectively similar thickness and organic matter abundance as the Barnett Shale in the Fort Worth Basin, USA. However, the former has a lower gas content, and its organic matter is chiefly Type I kerogen, which is of great maturity.

China has recently intensified its efforts to explore unconventional gas resources, including shale gas, and has achieved major progress in technological innovations such as horizontal hydraulic fracturing, resource calculations, the optimum identification of strata with optimum gas accumulations and the selection of gas-exploration areas. Gas exploration in the black shale of the Upper Ordovician Wufeng-lower Silurian Longmaxi formations in the Sichuan Basin and its periphery is currently at the forefront of Chinese shale-gas exploration and exploitation. Gas shows were found in several exploratory wells (such as the W-201, N-201, Wuke-1, Tai-13, Jiaoye-1, Dingshan-1 and Lin-1 wells), which penetrated the Lower Silurian black shale. The Changxin-1, Yuye-1, Wei-201, Ning-1 and Jinye-1 wells in the Upper Yangtze area were recently drilled, and gas shows in the shale were recorded in the Wei-201, Ning-201 and Jioaye-1 wells. For this reason, many researchers have focused their studies on the Silurian black shale located in the southeastern corner of the Sichuan Basin (Chen et al., 2011; Nie et al., 2012; Wan et al., 2012; Xiong et al., 2015; Yang, Ning, Wang, Zhang, & Krooss, 2016a, 2016b; Zhang et al., 2008, 2015, 2016). In 2010, the Wei-201 well in the southern Sichuan Basin produced $10 \times 10^3$ m$^3$/d of shale gas from the Silurian Longmaxi Formation, whereas in 2011, the Ning-201-H1 horizontal well produced $150 \times 10^3$ m$^3$/d of shale gas from the Longmaxi Formation. In November 2012, in the Jiaoshiba structure at the eastern edge of the Sichuan Basin, testing for high-yield industrial gas in the Jiaoye-1HF well produced $203 \times 10^3$ m$^3$/d of shale gas from the Wufeng–Longmaxi formations. Shale gas in the Wufeng–Longmaxi formations is of marine origin and comprises an estimated...
geological reserve of 106.75 billion m$^3$. Recently, two shale-gas fields, Fuling, with production of more than 270 $\times$ 10$^3$ m$^3$/d, and Changning–Weiyuan, with production of more than 10 $\times$ 10$^3$ m$^3$/d, have been discovered that include eight wells with production of more than 100 $\times$ 10$^3$ m$^3$/d (Guo & Zhang, 2014; Guo et al., 2014; Guo, Li, Liu, & Wang, 2014; Hu, Zhang, Ni, & Yu, 2014; Liu, 2016; Zhang et al., 2016) and confirm that extensive shale-gas resources are present in the southeastern edge of the Sichuan Basin.

Sedimentary and geochemical data, reservoir characteristics and major controlling factors for the presence of adsorbed gas in the Wufeng–Longmaxi formations are reported. Shale gas resource calculations provide important data for the future exploration and development of shale gas in the Sichuan Basin.

### Regional geological background

The Sichuan Basin, which is one of the three major cratonic basins in China, contains oil and gas in strata from Sinian dolomites up to Cretaceous sandstone (Liu, Deng, Li, & Sun, 2012). The Sichuan Basin has experienced several tectonic events since the late Proterozoic. Tectonic movement beginning in the Late Triassic led to the formation of mountain chains surrounding the basins, with topography in the basin ranging from plains in the west to hills in the east (Guo, 1996; Liu et al., 2011; Tong, 1996). Silurian strata are missing between Longnvsi and the western Longmen Mountains in the central areas of the Caledonian (early Paleozoic) Leshan–Longnvsi paleo-uplift in the Sichuan Basin (Huang, 2009), but because of uplift and denudation, Silurian strata outcrop in the surrounding mountains. The Longmaxi Formation in the Sichuan Basin gradually thickens towards the south, east and north.

During the Late Ordovician (Katian and Hirnantian), the Sichuan Basin was compressed, and paleo-uplifts expanded in the centres of both the Guizhou and Sichuan basins. Confined by these paleo-uplifts, the Upper Yangtze marine basin became restricted. A major tectonic transformation that occurred in the Yangtze Craton during the lower Silurian represents the culmination of this paleo-uplift formation. The uplift in the central Sichuan and Guizhou basins continued to expand during this time, which resulted in the depositional environment of the basin being dominated by a restricted continental shelf surrounded by the paleo-uplift belt. Proximal to the uplifts, the depositional environment was mostly that of a tidal flat-lagoon, with the dominant sediments being silt and sandy shale (Figure 1; Li, Liu, Yin, & Lin, 1993; Liang, Guo, Chen, Bian, & Zhao, 2008, 2009; Liu, Xu, Feng, & Sun, 2010; Xu et al., 2009). The black shale present in the Wufeng Formation and the lower part of the Longmaxi Formation was deposited in a deep basin that formed on the continental shelf and had restricted bottom circulation. The upper part of the Longmaxi Formation is dominated by greenish siltstone, indicating its formation in a better oxygenated environment and a shallowing of the shelf. Horizontal differences in these lithofacies were mainly controlled by the Chuanzhong Uplift, the Qianzhong Uplift and a few minor uplifts (Li et al., 1993; Liang et al., 2008, 2009; Liu et al., 2010).

### Samples and methods

Field outcrop samples and core data from the Upper Ordovician Wufeng Formation and the lower Silurian Longmaxi Formation in the Sichuan Basin and its surrounding areas and core samples collected from the Changxin-1, Yuye-1, Dingshan-1, Lin-1 and Jiaoye-2 wells were collected. The properties of the black shale from the Wufeng and Longmaxi formations were determined using X-ray diffraction, bulk-rock mineral analysis, geochemical parameters such as TOC, organic matter maturity and type, thin-section microscopy, scanning electron microscopy (SEM) and analysis of specific surface areas, in addition to conducting isothermal adsorption experiments.

### Results

#### Sedimentary features

Sediment deposition in the Upper Ordovician Wufeng and the lower Silurian Longmaxi formations mainly occurred on a shallow continental shelf. Four major lithofacies deposited from the base to the top of the Wufeng–Longmaxi formations are summarised in Table 1. The black shale in the lower part of the Wufeng Formation was deposited in a deep continental shelf environment whereas the biolithite limestone in the Guanyinqiao section of the Wufeng Formation was deposited on a shallow continental shelf. The shale in the lower part of the Longmaxi Formation was deposited on a deep continental shelf and grades upwards into marine sandstone in the upper part of the Longmaxi Formation, which was deposited on a shallow continental shelf (Liu et al., 2013; Wang et al., 2012). The rock types present in this formation are summarised in Table 2.

Field outcrop profiles and well datasets for the Upper Ordovician Wufeng and lower Silurian Longmaxi formations from Qilong Village of Xishui, Guanyinqiao of Qijiang, Daijia Valley of Tongzhi, Rongxi of Xiushan, Guanyintang of Chengkou and wells Jiaoye-2 and Jiaoye-4 were synthesised to establish five major lithological types: black shale, siliceous shale, bentonite, sandstone and biolithite limestone (Figure 1a; Table 2). Graptolite fossils are common in the black shale of the Wufeng Formation and the lower part of the Longmaxi Formation (Figure 2a, c). Siltstone is common in the upper section of the Longmaxi Formation (Figure 2g); biolithite limestone is present in Guanyinqiao, in the upper part of the Wufeng Formation (Figure 2d); and bentonite (Figure 2e) and siliceous shale (Figure 2f) are mainly found at the northeastern border of the Sichuan Basin, in the Chengkou and Zhenba areas.

#### Wufeng Formation

Black shale, which primarily occurs in the lower part of the Wufeng Formation, contains rather high contents of carbon and calcium. Bentonite occurs on the northern edge of the Sichuan Basin (Figure 2e), indicating that volcanism occurred in this region during the deposition of the black shale. Graptolite fossils are frequently present and occur in samples with higher organic carbon contents (TOC $\sim$ 2wt%). The shale is laminated (Figure 3g), indicating a quiet bottom depositional...
Figure 1. (a) Upper Ordovician–lower Silurian paleogeographic map of the Sichuan Basin and its peripheral areas. (b) Upper Ordovician–lower Silurian regional distribution of the TOC and additional data in the Sichuan Basin and its peripheral areas. (Data presented are in part from Liang et al., 2008, 2009.)
environment with the occasional influence of turbidite plumes. Siliceous radiolarians microscopically observed in the shale (Figure 3c, d) suggest deposition on the continental shelf.

The Guanyinqiao section, in the upper part of the Wufeng Formation, is made up of limestone and/or dolomite, generally 30 cm thick but increasing up to 6 m thick in the Honghuayuan and Tongzi areas. The TOC is less than 2 wt% (Figure 2d). Fossils are dominated by brachiopods but also include some gastropods, bivalves and corals (Wang, 1989; Wang, Zeng, Zhou, Ni, Xiang, & Lai, 1986). Bivalves in the Guanyinqiao section of Qijiang, brachiopods and crinoids from the Qilongcun section of Xishui, and bryozoans from the Rongxi section of Xiushan (Figure 3b) are similar to those found at the Guanyinqiao section on the southern edge of Guizhou (Li, Matsrumoto, & Kershaw, 2005), and indicate deposition on a shallow to moderately deep shelf.

**Longmaxi Formation**

The Longmaxi Formation lithologies are chiefly black shale (Figure 2a) and black siltstone (Figure 2g) that are approximately 40 m thick. Graptolite fossils are plentiful, and the TOC is relatively high (TOC > 2 wt%). The shales are finely laminated (Figure 3g) with thin silty laminae common (Figure 3a), as are pyrite nodules, which indicate development within a dysoxic early diagenetic environment.

---

**Table 1.** Stratigraphic system and environmental characteristics of the Upper Ordovician–lower Silurian strata in the Sichuan Basin and its peripheral areas (after Chen et al., 2000; Chen, Melchin, Sheets, Mitchell, & Fan, 2005; Su et al., 2002; Wang et al., 2012).

<table>
<thead>
<tr>
<th>Time</th>
<th>Stratigraphic unit</th>
<th>Sea-level</th>
<th>Paleoclimate</th>
<th>Sedimentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Silurian</td>
<td>Shiniulan Formation</td>
<td>Medium</td>
<td>Glacial epoch-interglacial period</td>
<td>Shallow-water continental shelf</td>
</tr>
<tr>
<td></td>
<td>Longmaxi Formation</td>
<td></td>
<td></td>
<td>Deep-water continental shelf</td>
</tr>
<tr>
<td>Upper Ordovician</td>
<td>Wufeng Formation</td>
<td>Low</td>
<td>Glacial period</td>
<td>Shallow-water continental shelf</td>
</tr>
<tr>
<td></td>
<td>Guanyinqiao section</td>
<td></td>
<td></td>
<td>Deep-water continental shelf</td>
</tr>
<tr>
<td></td>
<td>Black shale section</td>
<td>High</td>
<td>Interglacial period</td>
<td>Deep-water continental shelf</td>
</tr>
<tr>
<td></td>
<td>Linxiang Formation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In some areas, such as the northern edge of Chengkou and Zhenba and the southern edge of Tongzi in the Sichuan Basin, more than 20 bentonite layers occur in the Wufeng and lower section of Longmaxi succession (Huang et al., 2011a; Su, He, Wang, Gong, & Zhou, 2002, 2007). In these outcrops, bentonite layers show horizontal bedding and enclose pyrite nodules (Figure 2e).

Siltstone and grey, thinly layered calcareous shale/mudstone are intermingled with some flaser lamination (Figure 2h). Graptolites dominate, and the organic carbon content is low, with a TOC of mostly less than 1 wt%. Clear calcite laminae (Figure 3e) and solution structures (Figure 3f) are also visible in the sandstone.

**Organic geochemistry**

**Organic matter abundance**

Various criteria are used for the classification of organic matter abundance in the black shale. TOC > 2.0 wt% is most frequently used by the petroleum industry to classify potentially productive source rocks, and it is therefore used here.

The statistical analysis of TOC values in the Wufeng–Longmaxi formations in the Sichuan Basin indicates that the TOC in the black shale in the lower section of the Wufeng Formation ranges from 3 to 6 wt%, with an average value of 3.48 wt%. The TOC in the non-black shale layers of the Wufeng Formation is less than 2 wt%. The black shale in the lower section of the Longmaxi Formation records variable TOC values ranging from 1 to 4 wt%, with an average value of 3.43 wt%. The grey shale in the upper section of the Longmaxi Formation records TOC ranging from 0.5 to 1 wt%, with an average value of 0.8 wt%. Stratigraphically, the black shales at the base of both the Wufeng and Longmaxi formations have high TOC contents, whereas the TOC content is lower in the grey shale at the top of the Longmaxi Formation.

To determine the regional distribution of TOC, additional data from four wells were used. The profiles compiled are: A–B: Moshigou, Leibo–Guanyinqiao, Qijiang; C–D: Sanquan, Nanxian–Rongxi, Xiushan; E–F: Liziya, Huaying–Maoba, Lichuan; and G–H: Shuanghui, Wangcang–Xitianba, Yiwu (Figure 1b).

The results indicate that the highest TOC content occurs at the base of the formation and decreases towards the top. The
black shale with TOC > 2.0 wt% is approximately 20 m thick. The A–B section (Moshigou, Leibo–Changxin-1 well–YQ1 well–Heini, Xuyong–Qian 5 well–Qilongcun, Xishui–Dingshan-1 well–Guanyinqiao, Qijiang) is parallel to the Qianzhong Uplift, and the organic carbon enrichment indicates the presence of two depositional centres. One depositional centre, located in the southern part of the Sichuan Basin, is represented in the Changxin-1 well with black shale with TOC > 2 wt% up to 40 m thick. The second centre, located in the northern area of Guizhou, is represented by Qilongcun, black shale with TOC > 2 wt% is up to 50 m thick. The C–D (Sanquan, Nanchuan–Lujiao, Pengshui–Heishui, Quyang–Rongxi, Xiushan) profile shows that the black shale is approximately 20 m thick and was deposited in a similar sedimentary environment. The E–F (Liziya, Huaying–Sanxing 1 well–Qiniao, Shizhu–Maoba, Lichuan) section is oriented perpendicularly across the basin, demonstrating that the depositional area of west Hubei and east Chongqing became shallower from the sedimentary centre represented by Qiniao, Shizhu (where the black shale with TOC > 2 wt% is up to 110 m thick), to Liziya, Huaying in the central Sichuan uplift, where the depositional thickness of the black shale is only 15 m. In contrast, in Maoba, Lichuan (which is parallel to the central Guizhou uplift to the east), the thickness of the shale is 55 m. The difference in thickness from that in the Qiliao area might indicate the influence of the Yichang uplift in the east on the evolution of the basin. The G–H (Shuanghui, Wangcang–Qiaoting, Nanjiang–Guanyin, Zhenba–Shuanghe, Chengkou–Tianba, Wuxi) profile is roughly parallel to the frontal edge of the Daba Mountains. In general, the thickness of the black shale gradually increases from west to east. Therefore, the depositional basins in the Taoyuan, Chengkou and Tianba, Wuxi areas became deeper, consequently increasing the thickness of the black shale up to 70 m, with an average TOC value of almost 4.0 wt%. We therefore conclude that the black shale in the Taoyuan, Chengkou–Tianba, Wuxi belt at the front edge of the Daba Mountains was deposited in a relatively deep water environment.
Organic matter maturity and types

Previous studies (Huang et al., 2011a; Wan et al., 2012; Zou et al., 2013) of the Upper Ordovician Wufeng–lower Silurian Longmaxi formations demonstrate that the vitrinite reflectance ($R_o$) of organic matter is 2.4–4%, and is over mature. By comparing the $\delta^{13}C$ values of kerogen, four types of organic matter can be recognised in these samples (Table 3) (Dai et al., 2008; Feng & Chen, 1988; Liang et al., 2009; Wang et al., 2011).

Published data of 107 samples from the Upper Ordovician Wufeng–lower Silurian Longmaxi formations have $\delta^{13}C$ values in kerogen ranging from $-30.8$ to $-23.7\%_{\text{VPDB}}$ (Zhai, 2013) (Figure 4). Among these, 64 samples indicate the presence of sapropel ($\delta^{13}C \leq -28.0\%_{\text{VPDB}}$); 33 samples contain organic matter of the sapropelic–humic type ($-28.0 < \delta^{13}C \leq -26.5\%_{\text{VPDB}}$); nine samples contain organic matter of the sapropel–humic type ($-26.5 < \delta^{13}C \leq -24.0\%_{\text{VPDB}}$); and one sample contains organic matter of the humus type ($\delta^{13}C > -24\%_{\text{VPDB}}$). In mudstone samples with TOC $\geq 0.4$ wt%, kerogen isotopic values range from $-30.8$ to $-27.7\%_{\text{VPDB}}$.

Table 3. Classification of organic carbon based on carbon isotope kerogen analyses (Dai et al., 2008; Feng, 1988; Liang et al., 2009; Wang et al., 2011).

<table>
<thead>
<tr>
<th>Type of kerogen</th>
<th>Sapropel type (I)</th>
<th>Humic sapropelic type (IIa)</th>
<th>Sapropelic–humic type (IIb)</th>
<th>Humus type (III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}C$</td>
<td>$-28%_{\text{VPDB}}$</td>
<td>$-28 \sim -26.5%_{\text{VPDB}}$</td>
<td>$-26.5 \sim -25%_{\text{VPDB}}$</td>
<td>$&gt; -25%_{\text{VPDB}}$</td>
</tr>
</tbody>
</table>

Figure 3. Thin-section microphotographs of the Wufeng–Longmaxi formations in the Sichuan Basin and its peripheral areas. (a) Horizontal lamination in the Longmaxi Formation black shale at Rongxi, Xiushan; (b) silty limestone with bryozoan in the Guanyinqiao section at Rongxi, Xiushan; (c) radiolarite in the Wufeng Formation at Qilongcun, Xishui; (d) radiolarian microfossil in siliceous rock in the Wufeng Formation at Mingzhong, Chengkou; (e) sandstone laminae in shale of the Longmaxi Formation at Qilongcun, Xishui; (f) etching structure of Longmaxi Formation silt from the profile of Rongxi, Xiushan; and (g) bentonite laminae in shale of the Wufeng Formation at Mingzhong, Chengkou.

Figure 4. Distribution of kerogen carbon isotopes of the Wufeng–Longmaxi formations in the Sichuan Basin and its surrounding areas (Zhai, 2013).
Among the 37 samples with TOC ≥ 0.4 wt% (of which 18 are from the Wufeng Formation, and 19 are from the Longmaxi Formation), only four samples have δ¹³C values on kerogen higher than −28‰ VPDB, which indicates that most of the organic matter in the Wufeng–Longmaxi formations is of the sapropel type (I) and that few are the humic–sapropelic type (II).

**Reservoir characteristics**

**Mineralogy**

The lithologies of the lower part of the Upper Ordovician Wufeng Formation comprise greyish dark siliceous shale, sandy shale, carbon siliceous shale, carbonaceous clay shale and bentonite. The lithology of the upper Wufeng Formation is that of a thinly bedded limestone. In the lower Silurian Longmaxi Formation, the lithology comprises dark greyish-black mudstone, organic matter-rich shale and siliceous shale with the base dominated by black carbonaceous shale. A ternary diagram displaying the mineral components of the Wufeng–Longmaxi formations shows that quartz and feldspars are more common than clay, with carbonate present as a minor constituent (Figure 5). In the chert, quartz comprises over 70 vol% of the rock.

Using X-ray diffraction analysis, 78 rock samples from several profiles were analysed for mineral contents. Of these samples, 14 samples were black shale from the lower Wufeng Formation; nine samples were limestone from the Guanyinqiao section; 25 samples were black shale from the basal part of the Longmaxi Formation; and 30 samples were grey silty shale from the upper part of the Longmaxi Formation (Figure 6). These data show that, moving from the bottom to the top of the Wufeng–Longmaxi formations in the northern Guizhou area, the quartz content gradually decreases from 44.3 vol% in the lower Wufeng Formation to 27 vol% in the upper Longmaxi Formation. Clay mineral...
contents increase from 35 vol% in the lower Wufeng Formation, to 40.1 vol% in the black shale of the lower Longmaxi Formation, and to 53 vol% in the grey shale of the upper Longmaxi Formation.

The relationship between quartz and TOC contents in the Wufeng–Longmaxi formations is shown in Figure 7. In the black shale and siltstone, TOC content gradually increases as the quartz content increases with a correlation coefficient of $R^2 = 0.6264$ (Figure 7a). In contrast, in the siliceous shale, TOC decreases as the quartz content increases (correlation coefficient of $R^2 = 0.1233$; Figure 7b). Higher contents of brittle minerals, accompanied by a decrease in clay minerals, thus cause organic matter contents to decrease.

**Macroscopic porosity**

Clarkson et al. (2013), Curtis (2012), Loucks, Reed, Ruppel, & Hammes, 2012, Loucks, Reed, Ruppel, and Jarvie (2009), Roger and Neal (2011), Wang et al. (2011) and Ye et al. (2012) demonstrated that shale is not entirely without pores, as it contains a variety of micropores. Roger and Neal (2011) proposed the concept of shale micro-reservoirs, or nanoscale reservoirs, and that even though pores in shale are on the micro- and nano-scales, they are mostly interconnected. Connections by even tinier pore throats form a complicated pore structure, formed from various types of microscopic pores.

Porosity was tested in rocks from the field outcrop profiles of the Wufeng–Longmaxi formations in northern Guizhou (in Tuhechang, Qilongcun in Xishui, Houtan and Guanyinqiao in Qijiang) and in rock samples from the key Dingshan-1 and Lin-1 wells (representing a total of 214 samples) (Huang, 2011b) with most porosity values less than 2%; these rocks are classified as compact reservoir-type rocks (Huang, 2011b). In this study, 32 outcrop samples from Qilongcun in Xishui, Guanyinqiao in Qijiang and Dajiaogou in Tongzi in northern Guizhou were also tested for their porosity. For this porosity study, the Wufeng–Longmaxi formations were subdivided into two sections: the black shale at the base of the formation and the non-black shale at the top of the formation. The porosity in the lower black shale section, which ranges from 4 to 8% with an average value of 6.17%, is smaller than the porosity in the upper non-black-shale section, which ranges from 5 to 10%, with an average value of 6.63%. Generally, the porosity of the black shale is lower than that of the non-black shale (Figure 8). Porosity analysis of the Wufeng–Longmaxi formations demonstrates that the peak porosity ranges from approximately 4 to 8% (Figure 9), with the overall porosity being lower; therefore, these can be classified as compact reservoirs. The higher porosity of the field outcrop samples from northern Guizhou may be related to the large quantity of secondary pores in the mudstone.

**Specific surface area**

Nitrogen adsorption experiments of 30 shale samples from the Wufeng–Longmaxi formations indicate that the specific surface area BET (Brunauer-Emmet-Teller) is 10.75–30.101 m$^2$/g, with an average value of 20.459 m$^2$/g. There is a high statistical correlation between the specific surface area of the borehole samples and the TOC of the Wufeng–Longmaxi formations in Pengshui ($R^2 = 0.9753$; Figure 10, blue line; Tian et al., 2013). The correlation between the specific surface area of outcrop samples of the Wufeng–Longmaxi formations and
the TOC in the study area is much lower ($R^2 = 0.4725$; Figure 10, black line). Generally, the specific surface area of the rock is positively correlated with TOC, which indicates that the presence of organic matter contributes greatly to the specific surface area (Ambrose, Hartman, Diaz-Campos, Akkutlu, & Songdergarten, 2010, 2012; Qiu et al., 2015; Ross & Bustin, 2009). The measured specific surface area values of outcrop samples are larger than those of borehole samples, which may result from weathering of outcrop samples.

**Microscopic porosity**

The pore-size distributions in the Wufeng–Longmaxi formations were determined from SEM images. In the siliceous shale of the Wufeng Formation, pores <1 μm account for 78.3% of the 1328 measurements performed on two samples. In four samples of carbonaceous mudstone from the lower Longmaxi Formation, pores <1 μm account for 58.3% of 3950 pore measurements; in siltstone from the upper Longmaxi Formation, pores <1 μm account for 49.2% of 5610 pore size measurements obtained from two samples. These measurements show that the occurrence of pores <1 μm decreases stratigraphically upward, and the number of pores >1 μm increases upward. In black carbonaceous mudstone, pores that are 500 nm to 1 μm in diameter are most common (Figure 11). Therefore, in the Wufeng–Longmaxi formations, the abundance of small-diameter pores decreases stratigraphically upward, while that of large-diameter pores increases.
Nitrogen adsorption tests performed on samples from Qilong Village at Xishui section measured the volume of pores with diameters $<1 \mu m$ and the distribution of different pore sizes (Figure 12). For pores measuring 3–10 nm, the pore volume percentage ranges between 50 and 83%, with an average value of 71%; for pores $>10$ nm, the pore volume percentage ranges between 17 and 50%. Pore measurements demonstrate that pores 3–10 nm in size are the main type of pores with diameters of $<1 \mu m$ in the shale. The percentage of pore volume increases with increasing TOC content. The volume percentage of pores $<10$ nm also increases with increasing TOC content; conversely, the volume percentage of pores $>10$ nm decreases.

The shale of the Wufeng–Longmaxi formations was deeply buried and underwent a complex transformation. Porosity was studied by SEM in 20 samples of black shale from the Wufeng–Longmaxi formations. The micropores in these samples can be classified as nine types: intergranular lattice pores, inter-clay platelet micropores, grain boundary pores, hypergenetic dissolved pores, intra-framboid micropores, clay mineral intrapores, diagenetic dissolved pores, organic pores and microfissures. Of these pore types, intergranular lattice pores, inter-clay platelet micropores, grain boundary pores and hypergenetic dissolved pores can all be classified as intergranular pores, whereas intra-framboid micropores, clay intragranular pores and diagenetic dissolved pores can be classified as intragranular pores (Figure 13; Loucks et al., 2009; Wang et al., 2009).

Micropores mainly developed during the stages of deposition, diagenesis and hypergenesis. During deposition, micropores such as inter-clay platelet micropores, clay intragranular pores and intra-framboid micropores developed. In contrast, microfissures, organic pores, diagenetic dissolved pores, grain boundary pores and intergranular lattice pores chiefly developed during diagenesis. Owing to their grain-supported fabric, intergranular pores, which are up to several hundred nanometres in diameter, have a higher connectivity than other types of micropores.

In the shale of the Longmaxi Formation, large numbers of intergranular pores in clay minerals are present. The
connectivity of this pore type is good although not as good as that of other intergranular pores. Grain boundary pores are commonly several tens to hundreds of nanometres in diameter, but their connectivity is poor (Hu, Ewing, & Rowe, 2015; Loucks et al., 2009; Wang et al., 2009; Yang et al., 2016a). Clay intragranular pores are typically about several hundred nanometres in diameter but are relatively isolated and feature poor connectivity.

Diagenetically dissolved pores were formed by organic acid dissolution, but this type of pore features relatively poor connectivity. Intra-framboid micropores are only developed in some samples (Figure 14a–c) with the voids between pyrite crystals in the inner parts of single frambooids having favourable connectivity, like intragranular lattice pores. However, the connectivity is not good between frambooids or between this type of micropore. A siliceous cavity framework can clearly be observed in samples with frambooidal pyrite and can contribute to the micropore volume of the shale (Hu, Ewing, & Rowe, 2015; Loucks et al., 2009; Wang et al., 2009; Yang et al., 2016a). Clay intragranular pores are typically about several hundred nanometres in diameter but are relatively isolated and feature poor connectivity.

Organic pores were not developed before undergoing massive hydrocarbon generation; that is, these organic pores were not affected by compaction, and a large quantity of organic pores partially compensate for the porosity loss caused by compaction. As an important channel linking different pore systems, microfissures show favourable connectivity and play a significant role in facilitating artificial fracturing during exploration. To summarise, organic pores and intergranular pores represent the highest-value hydrocarbon storage sites (Figure 15).

**Gas-bearing properties**

**Analysis of isothermal adsorption data**

The gas content of shale refers to the total amount of gas remaining after the solution gas, adsorbed gas and free gas per ton of shale are converted to a standard atmospheric pressure at 25°C (Daniel, Ronald, & Tim, 2008). The present study of shale gas content focuses on the measurement of adsorbed gas, which can be determined by the gas absorption of isothermal methane. Narrow spaces, such as micropores and microfissures, provide spaces and passages for the migration of adsorbed gas; adsorbed gas is chiefly adsorbed onto clay mineral surfaces.

The gas content of the Longmaxi Formation shale in the Sichuan Basin and its peripheral area is 0.3–5.09 m³/t. The gas content in the Weiyuan area in the southern Sichuan Basin is 0.3–5.09 m³/t with an average value of 1.82 m³/t; in the Changning area, it is 0.3–3.5 m³/t with an average value of 1.93 m³/t (Zou et al., 2013); and in the Jiaoshina area of Chongqing, it is 1.13–3.4 m³/t with an average value of 2.05 m³/t. Adsorbed gas contents were studied in the Wufeng–Longmaxi formations in northern Guizhou, especially in the profile in Qilongcun, Xishui. The saturation adsorption of shale samples from northern Guizhou ranges between 1.52 and 2.77 m³/t, with an average value of 1.95 m³/t, at a pressure of approximately 12 MPa. The minimum Langmuir volume (VL) is 1.62 m³/t, with a maximum of 3.09 m³/t and an average of 2.13 m³/t.

Adsorbed gas contents were also measured in the Wufeng–Longmaxi black shale samples from southern Sichuan, western Hubei and eastern Chongqing, as well as the northern edge of the Sichuan Basin. The 10 black shale samples from the Changxin-1 well in southern Sichuan record VL values ranging from 0.42 to 1.13 m³/t, with an average value of 0.67 m³/t (Chen et al., 2011). Analysis of the Wufeng–Longmaxi black shale samples from the Yuye-1 well and the profile at Rongxi, Xiushan show that when the pressure reached 10.83 MPa, VL values increased to range between 0.81 and 2.88 m³/t, with an average value of 1.66 m³/t. The northern edge of the Sichuan Basin is represented by the profile of the Wufeng–Longmaxi formations in Mingzhong, Chengkou, which has a VL of 2.57 m³/t.

**Longitudinal variation of adsorptive capacity**

Comparisons of vertical VL and TOC values in profiles of the Wufeng–Longmaxi formations in Qilongcun, Xishui and the Jiaoye-2 well (Figure 16) show that the sedimentary environment controls the TOC. Black shale sections in the lower parts...
<table>
<thead>
<tr>
<th>Time period</th>
<th>Pore type</th>
<th>Control action</th>
<th>Schematic micropores</th>
<th>Micropores characteristics</th>
<th>Petroleum significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supergene stage</td>
<td>Solvopores</td>
<td>Near-surface phreatic water dissolution</td>
<td>Large pore diameter (tens of microns); generally hypergenesis minerals within pores.</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Diagenesis stage</td>
<td>Fracture pores</td>
<td>Hydrocarbon generation Tectonic Clay dehydration</td>
<td>Microcracks generally tens of nanometres wide and several hundred nanometres to micrometres long; generally do not cross brittle mineral particles</td>
<td>Good connectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organic-matter pores</td>
<td>Hydrocarbon generation</td>
<td>Small diameter pores; generally less than a few nanometres; organic particles commonly have hundreds of organic pores</td>
<td>Good connectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solvopores</td>
<td>Organic acids and other acidic fluid dissolution</td>
<td>Relatively smooth appearance; nanometre pore size; generally no authigenic minerals in pores</td>
<td>Poor connectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle-rim pores</td>
<td>Clay dehydration</td>
<td>Partly or completely surround brittle particles; particle-rim pores generally mimic brittle particle shape</td>
<td>Poor connectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Framework pores</td>
<td>Recrystallisation Metasomatism Deposition Compaction</td>
<td>Framework pore shape is triangular and similar to pores between coarse clastic particles</td>
<td>Good connectivity</td>
<td></td>
</tr>
<tr>
<td>Deposition stage</td>
<td>Pores between clay platelets</td>
<td>Mechanical deposition Chemical deposition Compaction Clay dehydration</td>
<td>Pore shape generally parallels clay mineral fabric; in places bent into crescent shape</td>
<td>Good connectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Intrapores within clay minerals</td>
<td>Mechanical deposition Chemical deposition Compaction Clay dehydration</td>
<td>Pore shape is relatively equant and commonly perpendicular to clay layers</td>
<td>Poor connectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Intergranular pore within framboidal pyrite</td>
<td>Chemical precipitation Recrystallisation</td>
<td>Pores are similar to framework pores; diameter depends on size of pyrite frambooids</td>
<td>Connectivity within pyrite frambooids good but between frambooids poor</td>
<td></td>
</tr>
</tbody>
</table>

Figure 13. Analysis of pore types and pore characteristics of the Wufeng–Longmaxi formations in the Sichuan Basin and its surrounding areas (Loucks et al., 2009; Wang et al., 2009).
of both the Wufeng and Longmaxi formations were deposited in a deep-water shelf environment with a TOC higher than in the non-black-shale section in the upper part of the Longmaxi Formation, which has been interpreted to reflect deposition on a shallow-water shelf. Within a deep-water shelf setting, the VL of black shale (which is normally higher than 2.5 m³/t) is higher than it is in the shallow-water shelf, and the VL measured in both outcrop samples and samples collected from wells decreases from the bottom to the top; VL also records a positive correlation with TOC.

Discussion

Previous studies (Liu et al., 2011; Ross & Bustin, 2006; Zou et al., 2013) have demonstrated that two requirements must be met for a black shale to be classified as a gas reserve: (1) its TOC should normally be higher than 2 wt%; and (2) it should contain a higher quantity of brittle minerals, such as quartz and feldspar. For example, the average content of brittle minerals (i.e. quartz) in the Barnett black shale in the USA is greater than 30 vol% (Ross & Bustin; 2006). Why must these requirements be satisfied? First, the adsorption capacity of black shale is positively correlated with TOC (Figure 17), as gas absorption is related to organic matter and clay minerals; second, the presence of brittle minerals, such as quartz, provides textural support for the preservation of space during compaction. At the same time, brittle minerals (i.e. quartz) can enhance the fracture-making capacity of shale (Liang et al., 2014; Liu et al., 2011; Loucks et al., 2009, 2012; Yang et al., 2016a; Zeng et al., 2016).

Relationship between adsorptive capacity and organic carbon content

Ross and Bustin (2006), who studied the Jurassic Gordondale Member in NE Canada, and Hickey and Henk (2007), who
studied the Barnett Shale in Texas, demonstrated that calcareous or siliceous shales with higher organic carbon contents have a stronger storage capacity for adsorbed gas. Lu, Li, and Watson (1995) and Hill, Lombardi, and Martin (2002) also concluded that a favourable positive linear correlation exists between organic carbon content and methane adsorption capacity. That is, the higher the organic carbon content, the stronger the adsorption capacity of the shale.
Extensive research has been carried out on the controlling role of organic carbon on gas-bearing content (i.e. adsorbing capacity). Ross and Bustin (2009) demonstrated that the methane-adsorbing capacity of shale is positively correlated to TOC, with $R^2 = 0.445$. Data from Shuanghe, Changning and Qilongcun, Xishui yield similarly positive correlations between methane adsorption capacity and TOC, with $R^2 = 0.3973$. Data from the Jiaoye-2 well record similar results, yielding an even higher correlation coefficient of $R^2 = 0.870$.

The methane adsorption capacity of shale from the Wufeng-Longmaxi formations in the study area also positively correlates with TOC, yielding a correlation coefficient of $R^2 = 0.5032$ (Figure 17), and demonstrates that organic carbon content is one of the major controlling factors affecting the adsorption capacity of the shale.

**Correlation between adsorptive capacity and pore structure**

The average content of free gas in shale production gas is 50%; within black shale, this gas is enclosed in micropores, including organic pores and microfractures (Ambrose, Hartman, Diaz-Campos, Akkutlu, & Songdergeld, 2012; Curtis, 2002; Jarvie, 2012; Zou et al., 2013). On average, the content of adsorptive-phase gas is 50%, which represents the gas adsorbed on the surfaces of mineral grains, kerogen and pores (Curtis, 2002; Ran et al., 2013). Therefore, to some degree, the micropore constitution of black shale controls the adsorptive capacity of shale gas.

In this study, we also performed nitrogen adsorption experiments on samples collected from the profile in Qilongcun, Xishui. The distribution of pores of different sizes can be determined based on the proportion of pore volumes and specific surface areas of different pores (Figure 18), which demonstrates that: (1) for pores between 3 and 10 nm, their volume percentage ranges between 50 and 83% with an average value of 71%, and that of their specific surface area ranges between 86 and 97% with an average of 94%; and (2) for pores > 10 nm, their volume percentage ranges between 17 and 50%, and that of their specific surface area is far smaller than the values obtained from pores smaller than 10 nm. Moreover, these data also demonstrate that, with increasing TOC, the volume percentage of pores smaller than 10 nm increases, whereas that of pores larger than 10 nm decreases. The relationship between nanometre pore volume, specific surface area and pore distribution in shale indicates that pores smaller than 10 nm constitute the major pore volume and specific surface area in the shale.

TOC positively correlates with adsorptive capacity, and pores smaller than 10 nm comprise the major pore volume and specific surface area for shale (Figure 19). Additionally, the positive correlation between pore volume, the specific surface area of micropores (<10 nm), methane adsorptive capacity and TOC further confirms that the organic micropores in the Wufeng-Longmaxi shale, in the Sichuan Basin and its peripheral area, are the major factor affecting the gas-bearing content of this shale.

Whether organic matter or clay minerals contribute more to the pore volume or the specific surface area remains an open question. Ross and Bustin (2009) noted that clay contents in shale have high micropore volumes and specific surface areas and that TOC contributes a major space for gas storage. Other studies have also suggested that the small pores in shale are associated with both clays and kerogen (Lougcks et al., 2009). Both the basin evolution-controlled sedimentary facies and the sedimentary environment controlled the organic matter and mineralogic components of the shale. The thickening of the overlying sedimentary strata
created the original sedimentary conditions and caused the burial of organic matter. As temperature and pressure increased, the objective strata formation entered the diagenetic evolution stage (corresponding to the organic matter evolution stage), in which the buried organic matter generated hydrocarbons and transform clay minerals (i.e. montmorillonite was transformed into an illite/smectite mixed layer and illite, and kaolinite was transformed into chlorite and illite), which in turn controlled the porosity structure of the black shale (e.g. its organic pore volume, pores between clay minerals and specific surface area; Figure 15). Under the present-day conditions of formation pressure, shale gas is adsorbed onto pore surfaces and stored in the pore volume (Figure 20). Therefore, the basin evolution and sedimentary facies controlled the original conditions of this shale gas, whereas the diagenetic evolution stage controlled its pore volume and specific surface area.

Figure 18. Specific surface area with different pore diameter sizes in the Qilongcun profile.

Figure 19. Correlation diagram between (3–10 nm) pores and methane adsorption capacity (a) and TOC (b) of the Wufeng–Longmaxi formations in the Sichuan Basin and its surrounding areas.
Conclusions

1. The black shale present in the lower part of the Wufeng–Longmaxi formations was deposited on a deep continental shelf with restricted bottom circulation between paleo-uplifts in the centres of both Guizhou and Sichuan.

2. The organic matter in this shale is dominantly type I, with a small amount of type II. The abundance of organic matter is relatively high, and the TOC of the black shale is 2.0–8.0 wt%. The TOC in the lower section of the Wufeng Formation fluctuates from approximately 3 to 6 wt%, the TOC in the lower section of the Longmaxi Formation is 1–4 wt%, and the TOC in the upper section is 0.5–1 wt%. The black shales in the lower section of the Wufeng Formation and the lower section of Longmaxi Formation are the most favourable lithologies for shale-gas exploration. The southwestern Sichuan and northern Guizhou areas record high TOC contents.

3. The quartz content of the Wufeng–Longmaxi formations gradually decreases from the base to the top, while the content of clay minerals gradually increases. The carbon content of the Longmaxi Formation steadily increases through the succession. The TOC content

Figure 20. Black shale gas adsorption in the controlling factor model in the Yangtze Wufeng–Longmaxi formations. S, montmorillonite; I/S, illite/smectite mixed layer; I, illite; K, kaolinite; C, chlorite; Q, quartz; T, temperature; P, pressure; Sw, water saturation; 1, biogas; 2, asphalt, hydrocarbon and non-hydrocarbon compounds; 3, oil; 4, moisture/condensate gas; 5, gas.
appears to be positively correlated with quartz content and is negatively correlated with clay contents. This demonstrates that the quartz present is likely of biological origin.

4. The Wufeng–Longmaxi micropores can be categorised into four types: intergranular pores, intragranular pores, organic pores and microfractures. Organic matter is the main factor controlling the volume of these nanopores and their specific surface area.

5. The VL of black shale is 1.17–4.36 cm³/g, which is positively correlated with TOC. The positive correlation between pore volumes and the specific surface of micropores (<10 nm), methane adsorptive capacity and TOC further confirms that the organic micropores in the Wufeng–Longmaxi shale in the Sichuan Basin and its peripheral area are the major factors affecting the gas-bearing content in the shale.

6. The basin evolution and sedimentary facies controlled the organic matter and mineralogic components of this shale, while the diagenetic evolution stage controlled its organic matter, which generated hydrocarbons and caused the transformation of clay minerals. Therefore, basin evolution and sedimentary facies controlled the original conditions of shale gas, whereas the diagenetic evolution stage controlled its pore volume and specific surface area.

Acknowledgements

This research was supported by Science and Technology of the Sichuan Province support planning project (15ZC1390). We acknowledge the help of Luba Jansa in correcting the English in this manuscript. The authors appreciate the reviewers’ comments, which improved the quality of the paper.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

Science and Technology of Sichuan Province support planning project [grant number 15ZC1390].

References


