Geochemical and geological characterization of marine-continental transitional shale: A case study in the Ordos Basin, NW China

WEI Zhifu¹, WANG Yongli²*, WANG Gen¹, MA Xueyun¹,², ZHANG Ting¹,³, HE Wei¹,³, YU Xiaoli¹,³

¹ Key Laboratory of Petroleum Resources Research, Gansu Province, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, PR China
² Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences; CAS Center for Excellence in Life and Paleoenvironment, Beijing 100029, PR China
³ University of Chinese Academy of Sciences, Beijing 100049, PR China

Abstract: The organic-rich shale of the Shanxi and Taiyuan Formation of the Lower Permian deposited in a marine-continental transitional environment are well developed in the Ordos Basin, NW China, which is considered to contain a large amount of shale hydrocarbon resources. This study takes the Lower Permian Shanxi and Taiyuan shale collected from well SL¹ in the Ordos Basin, NW China as an example to characterize the transitional shale reservoir. Based on organic geochemistry data, X-ray diffraction (XRD) analysis, field-emission scanning electron microscopy (FE-SEM) observations, the desorbed gas contents of this transitional shale were systematically studied and the shale gas potential was investigated. The results indicate that the Lower Permian Shanxi and Taiyuan shale has a relatively high total organic carbon (TOC) (average TOC of 4.9%) and contains type III kerogen with a high mature to over mature status. XRD analyses show that an important characteristic of the shale is that clay and brittle minerals of detrital origin comprise the major mineral composition of the marine-continental transitional shale samples, while the percentages of carbonate minerals, pyrite and siderite are relatively small. FE-SEM observations reveal that the mineral matrix pores are the most abundant in the Lower Permian shale samples, while organic matter (OM) pores are rarely developed. Experimental analysis suggests that the mineral compositions mainly govern the macropore development in the marine-continental transitional shale, and mineral matrix pores and microfractures are considered to provide space for gas storage and migration. In addition, the desorption experiments demonstrated that the marine-continental transitional shale in the Ordos Basin has a significantly potential for shale gas exploration, ranging from 0.53 to 2.86m³/t with an average value of 1.25m³/t, which is in close proximity to those of terrestrial shale (1.29m³/t) and marine shale (1.28m³/t). In summary, these results demonstrated that the Lower Permian marine-continental transitional shale in the Ordos Basin has a significantly potential for shale gas exploration.

Key words: Marine-continental transitional shales; Desorbed gas; Pore structure; FE-SEM; Ordos Basin

E-mail: ylwang@mail.iggcas.ac.cn

1 Introduction
Shale gas, which is generated and stored in organic-rich shale, has become an important topic in modern oil and gas exploration (Curtis, 2002; Jarvie et al., 2007). The remarkable success of shale gas development in North America has aroused a shale gas exploration boom and encouraged investigation into the gas potential of shales worldwide (Curtis, 2002; Hill et al., 2004; Chalmers and Bustin, 2007; Jarvie et al., 2007; Tang et al., 2014). Most of the retrieved shale gas in the U.S. is produced from marine shales. However, in China, the potential of shale gas resources is also tremendous and black shales from three origins, including marine, marine-continental transitional and terrestrial origins (Bu et al., 2015; Tan et al., 2015). Widespread Cambrian and Silurian marine shales were found in southern China, while Carboniferous and Permian marine-continental transitional shales, as well as Triassic to Paleocene lacustrine shales, and were found in central and northern China, respectively (Zou et al., 2010). For marine shale, three demonstration plays like Weiyuan-Changning, Zhaotong, Fuling have been established and the production of marine shale gas from both CNPC (China National Petroleum Corporation) and SINOPEC (China Petro-Chemical Corporation) reached 45x10⁸ m³ in 2015. For terrestrial shale, Yanchang Petroleum has established demonstration play and multiple wells have been drilled, and some of the wells have achieved gas production. Compared with marine shale and terrestrial shale, the research and exploration of transitional shale are still at the initial stage and requires further improvement (Hao et al., 2011; Jiu et al., 2013; Tan et al., 2014; Wang et al., 2016).

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/1755-6724.13888.

This article is protected by copyright. All rights reserved.
In China, marine-continental transitional organic-rich shales are mainly distributed in the Benxi, Taiyuan, and Shanxi formations (Fms) of the Carboniferous and Permian age; in the Ordos, Qinshui, and southern North China basins; and the Longtang Fm of Permian age in the Yangtze plate (Zou et al., 2010). The Ordos Basin, which is located on the northwestern North China plate, is a prolific hydrocarbon-bearing basin that characterized by low-permeability reservoirs. The Ministry of Land and Resources of the People's Republic of China (MLR, 2012) have demonstrated that the marine-continental transitional shale in Ordos Basin has great potential as a shale-gas resource, the geological reserves of its shale gas reservoirs are estimated to be approximately 19.9 × 10^{12} m^3.

Compared to the extensive investigations of marine shale reservoirs in North America (Loucks et al., 2009; Chalmers et al., 2012a; Clarkson et al., 2013) and South China (Tian et al., 2013, 2015; Cao et al., 2015a; Jiao et al., 2014) or the continental shale gas reservoirs in China (Yang et al., 2013; Tang et al., 2014; Liu et al., 2015; Jiang et al., 2016), studies on this marine-continental transitional shale gas reservoir have only occurred in recent years. The research includes gas generation capacity of source rocks (Yan et al., 2015), reservoir storage capacity (Zhao and Guo, 2015; Ding et al., 2013; Han et al., 2016; Yang et al., 2016), gas bearing characteristics (Yan et al., 2013), favorable area selection (Yan et al., 2013), shale gas resources (Lin, 2013) and geochemical characteristics (Dai et al., 2016).

Therefore, this study employs the X-ray diffraction (XRD) analysis, Field emission scanning electron microscopy (FE-SEM), low-pressure gas adsorption method and desorption experiments to provide a comprehensive characterization of desorbed gas and pore structure of Shanxi and Taiyuan marine-continental transitional shales collected from well SL# in Ordos Basin, China. It might produce valuable information for engineers to properly evaluate the storage capacity and transport capability of marine-continental transitional shales.

2 Geological backgrounds

The Ordos Basin, located on the northwestern North China plate, is a polycyclic superposition basin with geological reserves for shale gas reservoirs of approximately 19.9 × 10^{12} m^3 (MLR, 2012). Tectonically, the basin contains six major structural units (Xiao et al., 2005), including the Yimeng uplift zone in the north, the Weibei uplift zone in the south, the Jinxi flexural fold zone in the east, the Yishan slope in the midsection, the Xiyuan obduction zone, and the Tianhuan depression in the west (Fig. 1a). The study area is located in the Jinxi flexural fold zone (Fig. 1a) along the southeastern margin of the Ordos Basin.

![Fig. 1](image_url) (a) Location of the study area and the substructure zones of the Ordos Basin (modified from Duan et al., 2008). (b) Petrological characterization of the drilled section of SL# well that corresponds to the cored section samples in this study.
The evolution of the Ordos Basin experienced four major stages: (1) early Paleozoic marine platform, (2) late Paleozoic marine and terrestrial alternation, (3) Mesozoic foreland basin, and (4) Cenozoic basin-margin faulting and subsidence (Liu et al., 2007; Yao et al., 2013). The long-lived polycyclic Ordos Basin formed from the middle Proterozoic to the Tertiary; Paleozoic, Mesozoic, and Cenozoic sedimentary strata were developed and preserved in the basin (Yang et al., 2005, 2016). Influenced by the Caledonian movement, the Ordos Basin was in an uplift period from the middle Ordovician to the middle Carboniferous, which resulted in the denudation of strata from the late Ordovician to the early Carboniferous. During the late Carboniferous, tectonic subsidence began again in the Ordos Basin, which was accompanied by the transgression of seawater. Subsequently, regresses occurred from the last stage of the late Carboniferous to the beginning of the Permian (Zhang et al., 1997). During the Permian, fluvo-lacustrine depositional environments prevailed in the Ordos Basin. Overall, the upper Paleozoic strata of the Ordos Basin were deposited in a marine-continental transitional environment, and the Lower Permian Taiyuan and Shanxi Formation was deposited in the transition stage from marine-continental transitional environment to continental environment, and features delta front-coastal marsh sediments, thin-beded sandstone and coal seams, and two to four sets of black shale with a thickness of from 40 to 135 m (Ding et al., 2013). The Shanxi and Taiyuan shale in our study area is at a relatively shallower burial depth (1500-2500 m) today and has a consistent thickness ranging from 40 to 60 m.

3 Samples and experiments

Eighteen Shanxi and Taiyuan Formation core samples were taken from a depth of 1548.6 to 1596.7 m from well SL3 (Fig. 1a). The lithology of the core samples included gray thinly bedded fine sandstone, coal, and thick black shale (Fig. 1b). Freshly retrieved cores were immediately placed into a transparent sealed canister filled with saturated salt water and then immersed upside down in water for transportation. A relatively complete experimental program was conducted, including total organic carbon (TOC) analysis, X-ray diffraction (XRD) analysis, field-emission scanning electron microscope (FE-SEM) observations, and low-pressure N2 adsorption/desorption analysis and desorption experiments.

The total organic carbon (TOC) was measured using a LecoCS-344 analyzer. Firstly, hydrochloric acid was used to remove inorganic carbon in samples. After drying, the de-carbonated samples were heated to 1200 °C under oxygen flow to convert the organic carbon into carbon dioxide. The thermal pyrolysis of the shale samples was performed using a Rock-Eval VI instrument.

X-ray diffraction (XRD) analysis was carried out on shale powder less than 200 mesh using a Bruker D8 DISCOER diffractometer (Co Ka-radiation, 45 keV, 35 mA) following the two independent processes of the CPSC procedure. Scintillation was used to measure the diffracted beam with 0.02°20 step size and 20 s step time. Diffractograms were derived from 2° to 76° 20. The relative mineral percentages were estimated semi-quantitatively using the area under the curve for the major peaks of each mineral with correction for Lorentz Polarization (Chalmers and Bustin, 2008).

The FE-SEM imaging of nanopores was performed using the Hitachi S8010 systems on the surfaces prepared by Ar ion milling (IM4000, Hitachi High-Tech) with an accelerating voltage of 3 kV and a milling time of 4-8 h. Small cubes of shale (1-2 cm3) were polished and milled by a broad argon-ion beam (GATAN, PECS II model 685 cross-section polisher) to produce a flat surface allowing for higher resolution FE-SEM imaging, and the artefacts were not formed during the ion milling of the shale samples. The detailed identification method has been documented by Loucks et al. (2009).

The low pressure nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 HD88 apparatus, following the procedures described in detail by Li et al. (2016). About 0.3 g of 40-60 mesh pre-treatment and treated cylindrical shale samples were measured. The samples were degassed at 110 °C under vacuum for 20 h to remove adsorbed moisture and volatile matter. Degassed sample were exposed to nitrogen at the temperature of liquid nitrogen (-196 °C) along a series of precisely controlled gas pressures. Nitrogen adsorption volumes were measured over the relative equilibrium adsorption pressure (P/P0) range from 0.0001 to 0.995, where P represents the actual gas pressure, and P0 is the saturation pressure. The surface area was calculated from the sorption curve based on the adsorbed volume in a relative pressure (P/P0) range of 0.05-0.35 using the Brunauer-Emmet-Teller (BET) method (Brunauer et al., 1938). The pore volume and pore-size distribution were obtained from the sorption curves for a pore size range of 1.7-200 nm under a relative pressure (P/P0) range of 0.06-0.99 using the Barrett-Johnner-Halenda (BJH) method (Barrett et al., 1951).

The desorption experimental setup and gas collection method used in this study follows the procedure described in Wang et al. (2015). Gas samples were collected at temperatures of 20, 60, 80, 90, and 100 °C, and then the desorbed gas content was measured. The ambient temperature (20 °C) was used to measure the free gas quantity, and 60 °C was the estimated in situ reservoir temperature (assuming that the surface temperature was 20 °C and the geothermal gradient was 30 °C/km) used to...
measure the geochemical character of gases at reservoir conditions. The temperatures of 80, 90, and 100 °C were tested to ensure that the adsorbed gas was completely released. Each temperature test was finished when the released gas fell below 5ml within a 5 h window.

4. Result and discussion

4.1 Organic geochemistry and mineral compositions

The TOC content, desorbed gas content, δ¹³Corg, pyrolysis parameters and mineralogical composition of the Lower Permian marine-continental transitional shales from well SL³ in Ordos Basin, China are listed in Table 1.

Table 1 TOC content, desorbed gas content, δ¹³Corg, pyrolysis parameters and mineralogical composition of the Lower Permian marine-continental transitional shales from well SL³ in Ordos Basin, China.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Depth (m)</th>
<th>Strata</th>
<th>TOC (%)</th>
<th>Gas yield (m³/t)</th>
<th>δ¹³Corg (‰)</th>
<th>Tmax (°C)</th>
<th>Qtar (%)</th>
<th>Feldspar (%)</th>
<th>Carbonate (%)</th>
<th>Pyrite (%)</th>
<th>Siderite (%)</th>
<th>Total Clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL-1 1548.6</td>
<td>Shanxi</td>
<td>5.0</td>
<td>-24.1</td>
<td>506</td>
<td>40.1</td>
<td>n.d.</td>
<td>2.0</td>
<td>2.7</td>
<td>n.d.</td>
<td>55.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-2 1549.9</td>
<td>Shanxi</td>
<td>7.5</td>
<td>-23.9</td>
<td>498</td>
<td>49.8</td>
<td>2.3</td>
<td>1.3</td>
<td>n.d.</td>
<td>1.0</td>
<td>45.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-3 1552.3</td>
<td>Shanxi</td>
<td>2.7</td>
<td>-23.1</td>
<td>495</td>
<td>49.7</td>
<td>2.3</td>
<td>3.3</td>
<td>1.2</td>
<td>n.d.</td>
<td>43.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-4 1560.2</td>
<td>Shanxi</td>
<td>2.6</td>
<td>-23.5</td>
<td>498</td>
<td>36.6</td>
<td>11.4</td>
<td>1.1</td>
<td>n.d.</td>
<td>1.8</td>
<td>49.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-5 1563.9</td>
<td>Shanxi</td>
<td>2.7</td>
<td>-23.4</td>
<td>488</td>
<td>45.0</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.8</td>
<td>n.d.</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-6 1572.0</td>
<td>Shanxi</td>
<td>2.5</td>
<td>-23.1</td>
<td>494</td>
<td>38.0</td>
<td>7.3</td>
<td>1.5</td>
<td>n.d.</td>
<td>2.7</td>
<td>50.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-7 1573.0</td>
<td>Shanxi</td>
<td>4.5</td>
<td>-24.1</td>
<td>502</td>
<td>49.0</td>
<td>4.5</td>
<td>1.9</td>
<td>5.0</td>
<td>n.d.</td>
<td>40.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-8 1581.8</td>
<td>Shanxi</td>
<td>10.4</td>
<td>-25.5</td>
<td>477</td>
<td>46.0</td>
<td>8.0</td>
<td>2.7</td>
<td>4.0</td>
<td>n.d.</td>
<td>38.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-9 1583.4</td>
<td>Shanxi</td>
<td>2.3</td>
<td>-23.9</td>
<td>493</td>
<td>41.5</td>
<td>4.8</td>
<td>2.0</td>
<td>1.5</td>
<td>n.d.</td>
<td>50.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-10 1585.5</td>
<td>Taiyuan</td>
<td>8.1</td>
<td>-24.3</td>
<td>493</td>
<td>42.7</td>
<td>5.6</td>
<td>3.9</td>
<td>5.3</td>
<td>7.9</td>
<td>34.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-11 1587.0</td>
<td>Taiyuan</td>
<td>2.6</td>
<td>-23.3</td>
<td>495</td>
<td>43.1</td>
<td>8.1</td>
<td>3.1</td>
<td>2.6</td>
<td>2.3</td>
<td>40.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-12 1588.1</td>
<td>Taiyuan</td>
<td>3.1</td>
<td>-23.6</td>
<td>508</td>
<td>41.1</td>
<td>6.8</td>
<td>4.3</td>
<td>1.8</td>
<td>3.7</td>
<td>42.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-13 1589.9</td>
<td>Taiyuan</td>
<td>2.9</td>
<td>-23.8</td>
<td>471</td>
<td>33.5</td>
<td>1.4</td>
<td>5.0</td>
<td>2.7</td>
<td>n.d.</td>
<td>58.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-14 1590.5</td>
<td>Taiyuan</td>
<td>3.3</td>
<td>-23.6</td>
<td>520</td>
<td>23.9</td>
<td>1.9</td>
<td>n.d.</td>
<td>n.d.</td>
<td>7.8</td>
<td>66.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-15 1592.4</td>
<td>Taiyuan</td>
<td>2.7</td>
<td>-23.7</td>
<td>506</td>
<td>36.4</td>
<td>7.9</td>
<td>n.d.</td>
<td>2.1</td>
<td>3.9</td>
<td>49.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-16 1594.2</td>
<td>Taiyuan</td>
<td>10.9</td>
<td>-25.3</td>
<td>517</td>
<td>25.3</td>
<td>12.0</td>
<td>4.7</td>
<td>5.6</td>
<td>n.d.</td>
<td>52.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-17 1595.4</td>
<td>Taiyuan</td>
<td>9.0</td>
<td>-24.6</td>
<td>519</td>
<td>37.6</td>
<td>3.6</td>
<td>n.d.</td>
<td>1.3</td>
<td>n.d.</td>
<td>57.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-18 1596.7</td>
<td>Taiyuan</td>
<td>5.1</td>
<td>-24.0</td>
<td>511</td>
<td>32.2</td>
<td>3.4</td>
<td>n.d.</td>
<td>1.0</td>
<td>n.d.</td>
<td>63.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d. = no detected.

TOC is one of the most important indicators for shale to evaluate the hydrocarbon generation potential. TOC can also have a decisive influence on the gas-sorption capacity of the shale (Ross and Bustin, 2009). Higher organic carbon content implies higher hydrocarbon generation potential and better adsorption capacity for shale gas. Currently, the lower limit of TOC for commercial exploitation of shale gas is generally 2.0%. However, a few scholars suggested that the lower limit of TOC of shale with a high-maturity stage can be reduced to 1% (Hunt, 1979; Curtis, 2002; Jarvie et al., 2007; Zou et al., 2010). As shown in Table 1, the Lower Permian marine-continental transitional shales have a relatively high TOC contents, ranging from 2.3 to 10.9% with an average value of 4.9%. It is suggested that the shales met shale reservoir criteria of high TOC. The thermal maturity is another important parameter for the evaluation of shale gas. It can affect not only gas generation potential, but also gas sorption capacity (Nie et al., 2009). With the increase of thermal maturity, the gas generation potential decreases, but the gas sorption capacity increases. According to the Rock-Eval data from 18 shale
samples, $T_{\text{max}}$ values of the shale samples are between 471 and 520 °C, indicating a high mature to over mature status. Furthermore, the results of Wang et al. (2011) in the Shilou area of Ordos Basin showed that the vitrinite reflectance (Ro) ranging from 2.0% to 2.4. The organic carbon isotopes are mainly controlled by the organic matter source and remain stable during the thermal evolution of the geologic history, generally used to evaluate the organic matter type of over-mature shales. The $\delta^{13}C_{\text{org}}$ values of the Lower Permian shales range between -25.5% and -23.1%, indicating that the organic matter in the Lower Permian shales is dominated by type III kerogen.

The X-ray diffraction analyses of 18 shale samples indicate that clay minerals and brittle minerals (quartz, feldspar, and pyrite) are the major components of the Shanxi and Taiyuan Formation shale (Table 1). All the samples are clay rich with an average 49.4% (ranging from 34.6% to 66.5%). Quartz content averages 39.5% (ranging from 23.9% to 49.7%), feldspar content averages 5.1% (ranging from 0% to 12.0%), and carbonate minerals (calcite and dolomite) content averages 2.3% (ranging from 0% to 5.0%). Pyrite and siderite are present in most of the samples and is up to 5.3% and 7.9%, respectively. The ternary diagram plotting mineralogy clearly shows that, compared to marine shales, the Lower Permian marine-continental transitional shales is not similar to these marine shales in terms of mineral composition, which is poor in carbonate minerals and is relatively rich in clay minerals, while these marine shales contain a high abundance of brittle minerals (Fig. 2). Previous studies have shown that clay content has a positive relationship with gas sorption capacity (Ross and Bustin, 2009; Guo et al., 2014). Clay minerals have larger surface area values compared to quartz and carbonates (Passey et al., 2010), which can enhance gas sorption capacity. Clay-rich shale, however, tends to be ductile and to deform instead of shattering. When hydraulic pressure and energy are injected into shales, fracture can hardly be successfully stimulated. However, the brittle mineral content can greatly affect matrix porosity and micro-fracture development, gas content, and fracturing stimulation pattern (Li et al., 2007; Zou et al., 2010; Sondergeld et al., 2010). Shale with higher brittle mineral content usually has a stronger ability to induce fractures, which are favorable for shale gas development. Sondergeld et al. (2010) suggested that shales with brittle mineral content greater than 40% and clay content less than 30% have commercial development potential.

Fig. 2 Ternary diagram showing a comparison of the mineralogical constituents of the Lower Permian marine-continental transitional shales examined in this study with those of the Lower Silurian Longmaxi shales from Jiaoshiba shale gas field (Chen et al., 2017) and Barnett shales from the Fort Worth Basin (Loucks and Ruppel, 2007).

4.2 FE-SEM observation and pore types
Field emission scanning electron microscope (FE-SEM) was utilized to examine pore type in the Lower Permian shale samples. Overall, FE-SEM images (Fig. 3) show that various types of pores are developed with pore size between several nanometers and several hundred nanometers in the Lower Permian shale samples. Among these pores, both mineral matrix pores and microfractures are mainly developed in the Lower Permian shales with various pore shapes and pore sizes (e.g. Fig. 3a-h). The mineral matrix pores are mainly developed between and within brittle minerals (Fig. 3c, e). Microfractures are developed mainly in OM or brittle minerals (Fig. 3g, h), and they are elongated and range in size from several to tens of microns in length and range from 2 to 5 um in width. However, the OM pores are not well developed in the Lower Permian shale samples, which can occur within pyrite frambooids and between clastic minerals. The rarity of OM pores should be due to the organic type (type-III kerogen). This is because little liquid hydrocarbons can be generated by vitrinite and inertinite. Therefore, very few organic pores can be formed during thermal maturation. In addition, according to their occurrences, pores in shales can be grouped into inter-particle (interP) and intra-particle (intraP) pores (Chalmers et al., 2012a, b; Loucks et al., 2012). The interP pores in our samples are observed between grains that range from soft and ductile (e.g. clays) to hard and rigid (e.g. quartz) and have various shapes with pore size between tens to hundreds nanometers (Fig. 3). Especially, the interP pores are commonly observed between the organic matters and clay minerals (Fig. 3e) and this is probably related to the shrinking of clay minerals and/or decompression effect after the retrieval from subsurface (Chalmers et al., 2012a). The intraP pores are mainly identified within organic matters and clay minerals. In clay aggregates, both IntraP and InterP pores can be developed together (Fig. 3d), which form a complex pore structure. From plenty of FE-SEM observations, we can conclude that the mineral matrix pores are the most abundant in the Lower Permian shale samples with certain amount of clay hosted pores and the other pore types are relatively seldom.
Fig. 3 Field emission scanning electron microscope (FE-SEM) images of shale pore from the Shanxi and Taiyuan Formation in this study.

4.3 N$_2$ adsorption-desorption isotherm
Pore structure basically refers to the specific surface area, total pore volume, pore size distribution, and average pore diameter. These parameters obtained from ultra-low pressure nitrogen physisorption experiment are presented in Table 2. Table 2 showed that the Lower Permian shale samples have a relative low BET surface area, ranging from 5.23 to 9.88 m²/g, with an average of 7.62 m²/g. Their BJH pore volumes are in the range of 0.85-1.72 cm³/100 g, with an average of 1.25 cm³/100 g. The average pore diameter of the Lower Permian shale is 5.44-7.69 nm with an average of 6.59 nm.

Table 2 BET surface area, pore volume and average pore diameter of the Lower Permian marine-continental transitional shale samples obtained from N₂ adsorption-desorption isotherms.

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>Strata Fm.</th>
<th>S BET (m²/g)</th>
<th>V BJH (cm³/100 g)</th>
<th>APD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL-2</td>
<td>Shanxi</td>
<td>6.94</td>
<td>1.09</td>
<td>7.03</td>
</tr>
<tr>
<td>SL-3</td>
<td>Shanxi</td>
<td>8.39</td>
<td>1.35</td>
<td>5.50</td>
</tr>
<tr>
<td>SL-5</td>
<td>Shanxi</td>
<td>8.67</td>
<td>1.56</td>
<td>5.44</td>
</tr>
<tr>
<td>SL-7</td>
<td>Shanxi</td>
<td>6.86</td>
<td>1.17</td>
<td>6.58</td>
</tr>
<tr>
<td>SL-8</td>
<td>Shanxi</td>
<td>5.23</td>
<td>0.85</td>
<td>7.69</td>
</tr>
<tr>
<td>SL-10</td>
<td>Taiyuan</td>
<td>5.83</td>
<td>0.88</td>
<td>7.52</td>
</tr>
<tr>
<td>SL-12</td>
<td>Taiyuan</td>
<td>8.07</td>
<td>1.25</td>
<td>6.04</td>
</tr>
<tr>
<td>SL-14</td>
<td>Taiyuan</td>
<td>9.88</td>
<td>1.72</td>
<td>5.82</td>
</tr>
<tr>
<td>SL-17</td>
<td>Taiyuan</td>
<td>7.69</td>
<td>1.21</td>
<td>7.59</td>
</tr>
<tr>
<td>SL-18</td>
<td>Taiyuan</td>
<td>8.62</td>
<td>1.43</td>
<td>6.67</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>7.62</td>
<td>1.25</td>
<td>6.59</td>
</tr>
</tbody>
</table>

Previous studies (Loucks et al., 2009; Curtis et al., 2012; Milliken et al., 2013) on gas shales have concluded that organic marine shale matter contains large amounts of nanopores. Thus, it is expected that organic matter should contribute significantly to surface area in the marine-continental transitional Shanxi and Taiyuan shales. However, neither the surface area (Fig. 4a) and pore volume (Fig. 4c) of the shales investigated exhibit any obvious correlation with the TOC content and more likely decrease slightly as TOC content increases, suggesting that the organic matter in the Lower Permian shales are poor developers of organic pores and more likely act as the padding materials in the shale matrix. The presence of nearly nonporous type III kerogen in the Shanxi and Taiyuan shales can be illustrated by the FE-SEM images in Fig. 3, which clearly showed that there are some pores associated with inorganic components but very few nanopores within the organics. At this point, it seems that type III kerogen does not easily develop organic pores, which is in agreement with previous work that organic nanopores are poorly developed in terrestrial shales (Ross and Bustin, 2009; Fishman et al., 2012) and transitional shales (Xiong et al., 2017) dominated by type III and II kerogens. The positive linear correlations between total clay content, surface areas (Fig. 4c), and pore volume (Fig. 4d) suggested that the clay-hosted pores were dominated in the marine-continental transitional Shanxi and Taiyuan shales. This can be well verified by FE-SEM observation (e.g. Fig. 3).
Fig. 4 Relationship of TOC content and total clay with surface areas (a, c), pore volume (b, d).

The shape of the adsorption isotherms and the hysteresis patterns provide useful information regarding the mechanism of the physisorption process and hence can be used to qualitatively predict the shapes and types of pores in a tight shale reservoir. The nitrogen adsorption/desorption isotherms and their hysteresis patterns may provide useful information regarding the physical adsorption mechanism and the pore structures of the shales (Kuila et al., 2012). The International Union of Pure and Applied Chemistry (IUPAC) has classified the sorption isotherms into six types, designated I to VI. A detailed description of the isotherm classification suggested by IUPAC was presented in Rouquerol et al. (1994). For this work, most of the shale samples investigated was similar to the Type IV isotherm with a hysteresis loop (Fig. 5), which is a result of capillary condensation taking place in the mesopores at the relative pressure range of 0.45-0.9 P/Po (Gregg and Sing, 1992). Therefore, the existing hysteresis loops suggest that the Lower Permian shale samples possessed a significant amount of mesopores (diameter, 2 < d < 50 nm). On the other hand, it is well known that micropore filling and mono-multi gas coverage by van der Waals occurs at a lower relative pressure (P/Po < 0.3), and macropore filling at a higher relative pressure (P/Po = 0.9-1.0). Therefore, the extremely low adsorption amount at P/Po < 0.3 and the large quantity absorbed at 0.9-1.0 P/Po indicates that the Lower Permian shale samples also contain a certain amount of macropores (d > 50 nm) but lack micropores (d < 2 nm). The IUPAC classified four hysteresis loop types and the desorption isotherms (namely hysteresis patterns) into four types, designated H1 to H4 (Sing, 1985). Accordingly, hysteresis loops of the Lower Permian shale samples can be identified as either Type H3, corresponding to a structure with many slit-shaped pores surrounded by clay platelets (Sing, 1985; Tian et al., 2013). The type H3 loop also indicates that the marine-continental transitional shale samples contain well developed mesopores (2-50 nm). These types of adsorption and desorption isotherms often indicate the presence of fracture pores in shales. Not surprisingly, FE-SEM observations demonstrate that bubble-, triangular-, and other irregularly-shaped pores were also found in this study, consistent with results for other shales in North American and China (Loucks et al., 2012; Löhr et al., 2015; Tian et al., 2015).
Fig. 5 Nitrogen gas adsorption and desorption isotherms for the Lower Permian marine-continental transitional shales.

4.4 Pore size distribution (PSD)

The pore size distribution (PSD) can be displayed as cumulative, incremental, or differential distribution curves with respect to pore volume or surface area (Clarkson et al., 2013; Tian et al., 2013; Cao et al., 2015). In this study, the BJH method was used to characterize the PSD. The pore size distributions of shale samples calculated according to the BJH method are illustrated in Fig. 6, the modal peak in the PSD curve represents the most probable pore size. As shown in Fig. 6, the different PSD curves of all samples are well comparable displaying similar variation trend. The plots of dV/d(D) of shales showed a distinct peak with pore size of 2 nm (Fig. 6a). However, the plots of dV/dlog(D) displayed multi-bimodal patterns with pore peaks around 3 nm, 11 nm and 90 nm, respectively (Fig. 6b). These pore size distribution patterns suggest that macropores and mesopores contribute significantly to the total pore volume and surface area (Fig. 7a, b), respectively. This is because a large pore can provide pore space volume equal to many small pores (Tian et al., 2013). There exist multi-prominent peaks in the curves of dV/dlog(D) maybe due to the effect of mineral compositions within shale samples on the pore development.
Fig. 6 The PSDs of pore volume of the Lower Permian marine-continental transitional shale samples from the N2 adsorption isotherms by the BJH method.

Fig. 7 The pore volume and specific surface area percentages based on IUPAC classification for the Lower Permian marine-continental transitional shale samples in the Ordos Basin, NW China.

4.5 The content of desorbed gas

The evaluation of shale gas content is very important for resource potential evaluation and productivity prediction (Strapoc et al., 2010). The desorbed gas content of samples at different temperatures is shown in Fig. 8. At ambient temperature (20 °C) the amount of gas released was relatively low; however, the amount of gas released at the reservoir temperature (60 °C) was significantly greater. At high desorption temperatures (80, 90, 100 °C), the amount of released gas was in equilibrium. The desorbed gas contents of shale samples varied from 0.53 to 2.86 m³/t with an average value of 1.25 m³/t. The amount of desorbed gas shows a positive correlation with TOC (Fig. 8b). Strong correlations between total gas and TOC ($R^2$ of approximately 0.9) were also found from canister desorption of fresh cores from the Devonian-Mississippian New Albany Shale in the Illinois Basin, United States (Strapoc et al., 2010), indicating that the organic matter content is primarily responsible for total gas content in these shale samples. Based on the experiments of high-pressure methane adsorption of the Longmaxi shale samples, Pan et al. (2016) found that the adsorbed gas capacity of the samples positively correlated to TOC. The quantity of organic matter in shales not only determines hydrocarbon generation potential but also creates abundant organic nanopores, which provide more internal surface area and promote shale gas adsorption (Sun et al., 2015; Li et al., 2018).
Fig. 8 (a) Plot of desorbed gas content of the Lower Permian marine-continental transitional shale samples at different desorption temperatures. (b) Relationship of desorbed gas content with TOC.

Following previous studies of the Longmaxi Formation marine shale in the Jiaoshiba area (Pu et al., 2010) and Chang 7 lacustrine shale in the Xiasiwan area (Fan et al., 2017), the desorbed gas content of shales from various depositional environments was compared (Fig. 9). As shown in Fig. 9, the mean desorbed gas content of the marine-continental transitional shale (1.25m$^3$/t) is in close proximity to those of terrestrial shale (1.29m$^3$/t) and marine shale (1.28m$^3$/t), and is more than that of the minimum standard for commercial shale gas development in China (1.0m$^3$/t) (Zhang et al., 2012a). This indicated that the Lower Permian marine-continental transitional shale in the Ordos Basin has a significant potential for shale gas exploration.

Fig. 9 Comparison of desorbed gas content of shales in different depositional environments.

4.6 Shale gas potential

Shale gas exists in three forms: free gas in pores and fractures, adsorbed gas on surface area of organic matter and clay minerals, and dissolved gas in oil and water (Clarkson and Bustin, 1996; Curtis, 2002; Zhang et al., 2012b; Hao and Zou, 2013). In shales with very high maturity, free and adsorbed gases are dominant with very low contents of dissolved gas (Curtis, 2002). While free gas occurs mainly in macropores and larger mesopores, adsorbed gas is located mainly within micropores as well as at surface of mesopores and macropores (Montgomery et al., 2005; Hill et al., 2007; Ross and Bustin, 2008; Chalmers et al., 2012a; Mosher et al., 2013).
In the Lower Permian marine-continental transitional shale samples, clay and brittle minerals (quartz and feldspar) of detrital origin comprise the major mineral composition; The Lower Permian shales contain a relatively high abundance of clay minerals, while the Lower Silurian Longmaxi shales contain a high abundance of brittle minerals. It appears that the clay mostly controls nanopore structure, thus influencing storage capacity and occurrence of the gas. The study shows that the samples have a relatively high TOC with an average value of 4.9% and a high mature to over mature status. In addition, the desorbed gas content of the Lower Permian Shanxi and Taiyuan shale is in close proximity to those of terrestrial shale (1.29m³/t) and marine shale (1.28m³/t), and is more than that of the minimum standard for commercial shale gas development in China (1.0m³/t). These results indicate that the Lower Permian marine-continental transitional shale in the Ordos Basin has a significantly potential for shale gas exploration.

5 Conclusions
A comprehensive study on geochanical and geological characterization and desorbed gas content of a marine-continental transitional shale core samples collected from the Lower Permian Shanxi and Taiyuan Formation in Ordos Basin, China were investigated using the X-ray diffraction (XRD) analysis, Field emission scanning electron microscopy (FE-SEM) observations, low-pressure gas adsorption method and desorption experimental setup and gas collection method, with the following preliminary conclusions:

(1) The Lower Permian marine-continental transitional shales are predominantly characterized by kerogen type III, with a relatively high TOC content (2.3-10.9%) and a high mature to over mature status (Tmax, 471 to 520 °C). High remaining TOC and high to over maturity indicate that the Shanxi and Taiyuan shale has generated significant amounts of gas and can be a good shale gas reservoir.

(2) The XRD results show that the Lower Permian marine-continental transitional shales are in rich clay mineral, brittle minerals are of low content, and carbonates are rare or absent.

(3) FE-SEM observations reveal that the mineral matrix pores are the most abundant in the Lower Permian shale samples, but OM pores are rarely developed. The mineral compositions mainly govern the macropore development in the marine-continental transitional shale, and mineral matrix pores and microfractures are considered to provide space for gas storage and migration.

(4) The desorbed gas content of the Lower Permian Shanxi and Taiyuan shale samples varies from 0.53 to 2.86m³/t with an average value of 1.25m³/t, which is in close proximity to those of terrestrial shale (1.29m³/t) and marine shale (1.28m³/t), and is more than that of the minimum standard for commercial shale gas development in China (1.0m³/t), indicating that the Lower Permian marine-continental transitional shales in the Ordos Basin has a significantly potential for shale gas exploration.

Acknowledgements
This work was financially supported by the Chinese Academy of Sciences Key Project (Grant No.XDB10030404), the National key R&D Program of China (Grant No.2017YFA0604803), the National Natural Science Foundation of China (Grant Nos. 41831176, 41572350 and 41503049) and the Key Laboratory Project of Gansu (Grant No.1309RTSA041).

References


This article is protected by copyright. All rights reserved.


About the first author
WEI Zhifu Male; born in 1985 in Baiyin City, Gansu Province; Ph.D.; Associate professor of Lanzhou Center for oil and Gas Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences; He is now interested in the study on oil and gas geochemical processes, including hydrocarbon generation kinetics, stable isotope of Fischer-Tropsch synthesis gases, C-H isotope of oil-cracking gases and the crude oil group-type analysis. E-mail: weizf@lzb.ac.cn; phone: 0931-4960903, 17361660860.

About the corresponding author
WANG Yongli, female, born in 1969 in Lanzhou City, Gansu Province; Ph.D; graduated from Lanzhou university; Professor of Institute of Geology and Geophysics, Chinese Academy of Geological Sciences. She is now interested in the study on the source and environmental specific biomarkers (or molecular markers) in lacustrine sediments to reconstruct the paleovegetation and paleoclimate. Email: ylwang@mail.iggcas.ac.cn; phone: 010-82998426, 15201057968.