The influence of soluble organic matter on shale reservoir characterization

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Abstract

Shale with a maturity within the “oil window” contains a certain amount of residual soluble organic matter (SOM). This SOM have an important influence on characterization of shale reservoir. In this study, two shale samples were collected from the Upper Permian Dalong Formation in the northwestern boundary of Sichuan Basin. Their geochemistry, mineral composition, and pore structure (surface area and pore volume) were investigated before and after removing the SOM by means of extraction via dichloromethane or trichloromethane. The results show that the TOC, S1, S2, and IH of the extracted samples decrease significantly, but the mineral composition has no evident change as compared with their raw samples. Thus, we can infer that the original pore structure is thought to be unaffected from the extraction. The SOM occupies pore volume and hinders pores connectivity. The extraction greatly increases the surface area and pore volume of the samples. The residual SOM in the shale samples occur mainly in the micropores and smaller mesopores, and their occupied pore size range seems being constrained by the maturity. For the lower mature shale samples, the SOM is mainly hosted in organic pores that are less than 5 nm in size. For the middle mature shale samples, the micropores and some mesopores ranging between 2 and 20 nm in size are the main storage space for the SOM.

1. Introduction

Most of the North American shales are in the middle and high mature stage (1.2% < RO < 2.5%) [1–3]. Shales from various strata with various maturity levels are distributed extensively in China. The Lower Paleozoic shales in South China have relatively high maturity with EqRO (equivalent vitrinite reflectance) value ranging from 2.0% to 4.0% [4–9]. The Upper Paleozoic shales are mainly in the middle and high mature stage (1.5% < RO < 2.5%) [10–12], but some shales are still in relatively low mature stage (RO < 1.0%) [12,13]. The Lower Paleozoic shales in and around the Sichuan Basin were the focus of investigations and explorations in recent years [5–9], but the studies about reservoir properties in the Upper Paleozoic shales are comparatively few, especially shales with lower maturity. The studies about low mature coal have indicated that the SOM not only occupies a portion of porosity [14], but also has an important influence on methane adsorption [15]. The Soxhlet-extraction with dissimilar organic solvents have different product from shale [16], not to mention, the transformation of reservoir is also different [17]. The type and content of organic matter and the maturity of shale are the main factors in controlling pore structure [8,9,12,18–22]. The organic matter in shale is mainly composed of soluble organic matter and kerogen. For high mature shale, gas was generated and pyrobitumen formed by
cracking the heavy hydrocarbons and light hydrocarbons in the maturation process [18,19]. Shale with a maturity within “oil window” contains a certain amount of residual SOM. The amount of SOM for the type I-IIa shales can reach 20%—30% of total organic matter in the peak period of hydrocarbon generation. The SOM has apparent influence on the quantitative characterization of shale reservoir [12,18] that calls for further study. In this paper, shale samples were collected from the Upper Permian Dalong Formation in the northwestern margin of the Sichuan Basin. The pore structures were investigated before and after removing SOM by the extraction with dichloromethane or trichloromethane. The primary objective is to reveal the main storage sites of SOM and its influence on shale reservoir characterization.

2. Sampling and shale methodology

2.1. Samples and preparation

In this study, two gray shale samples from the Upper Permian Dalong Formation were collected from Changjianggou area in the northwestern margin of the Sichuan Basin. The fresh samples were dried at 48 °C for 24 h to remove moisture. After being crushed and sieved, a size fraction of 80 and 120 mesh (180 and 120 μm) was obtained and divided into three groups, namely, A, B, and C. 

H2O2 or NaClO treatments are commonly used methods in removing organic matter from shale. The methods not only remove the SOM and a part of kerogen, but it also changes the mineral components and destroys pores structure of the reservoir. The SOM can be effectively removed through Soxhlet-extraction preserving the pore structure of the reservoir. Therefore, the extraction with organic solvent is adopted to remove the SOM in this study. Approximately 40 g of each sample (Group B or C) was extracted for 72 h with dichloromethane and trichloromethane, respectively. The water bath temperature of dichloromethane extraction is 48 °C, and 80 °C for trichloromethane. The acquired filtrate was concentrated through rotary evaporation and was subsequently dried by nitrogen. The amount of SOM can be identified when its weight is constant in the drying box under room temperature. The extracted samples were dried at 90 °C in a vacuum for 24 h.

2.2. Experimental methods

The vitrinite reflectance (R0) was determined on polished core samples using a 3Y-Leica DMR XP microphotometer. The instrument was calibrated using the sapphire standard (R0 = 0.596%), and measurements were conducted in an oil medium using a 50×/0.85 oil lens with an optical fiber (d) of 0.6 mm. In each sample, 30–50 different vitrinite particles were randomly selected for measurements, and the average value represented the vitrinite reflectance [23].

The mineralogical composition analyses of the samples were carried out using a Bruker D8 Advance X-ray diffractometer at 40 kV and 30 mA. In a series of distinct stages, the scanning measurements were performed at a rate of 4°/min with a slit of 1 mm between 3° and 85° (2θ). The analogous mineral content was semi-quantitatively determined using peak area integration approach correlated for Lorentz Polarization [24].

The pore structure of the shale reservoir is dominated by nanometer-sized pores (i.e. micropores and mesopores). Organic matter is the main carrier of the pores, which provides the adsorption site and storage space altogether for the adsorption and free gas [18–21]. Nanometer-sized pores in low maturity shale are also the place where shale oil is stored [6]. Low-pressure N2 adsorption is considered a standard and preferable method for surface area and pore volume measurement of porous materials [9,25]. In the modern day, CO2 adsorption is one of the most operative methods to characterize the micropores [26,27]. Low-pressure gas adsorption has been widely used to characterize the pore structure of shale [16,18,19]. Prior the adsorption analysis, approximately 1–2 g dried samples (Groups A, B and C) were taken and degassed. Then the low-pressure N2 and CO2 adsorption experiments were carried out on an ASAP-2020 (Micromeritics Instruments). Supposedly the degassing treatment should not destroy the physical and chemical structure of shale [28], hence, for safety measures, a relatively low temperature (110 °C) under a vacuum condition and with longer degassing time (24 h) were adopted. Before moving the sample tube to the analysis station, the sample should be weighed again to determine the reduction. After the N2 adsorption analysis, a second degassing (4 h) in situ was requested before CO2 adsorption analysis.

N2 adsorption—desorption isotherms were obtained at 77.4 K with pressure (P/Po) ranging from 0.001 to 0.998. The adsorption branching was chosen for the calculation of surface area and pore volume [22,21]. The surface area was calculated using the BET equation [29,30]:

\[ \frac{P}{V(P - P_0)} = \frac{1}{V_mC_{BET}} + \frac{(C_{BET} - 1)}{V_mC_{BET}} \left( \frac{P}{P_0} \right) \]

where \( P \) is the equilibrium pressure, \( P_0 \) is the saturated vapor pressure, \( V \) is the adsorbed volume, \( V_m \) is the monolayer volume, and \( C_{BET} \) is the BET constant whose value is positive. The BET surface area (\( S_{BET} \)) was calculated using the following equation [31]:

\[ S_{BET} = \frac{V_m \times N \times A_N}{0.001 \times 22.4} \]

where \( V_m \) is the monolayer volume, \( N \) is the Avogadro' number, and \( A_N \) is the atomic surface area of N2 at 77.4 K (0.162 nm²). The BJH model was used to characterize pore volume distribution with an effective range of 2–100 nm.

N2 molecules are not completely entering the narrow micropores at low temperature (77.4 K) due to lack of sufficient energy [18,32]. Therefore, N2 was replaced by CO2 as an adsorbent for the micropores’ analysis. CO2 molecules with a cross-sectional area of 0.17 nm² have higher energy in ice water bath (273.1 K). The micropores’ surface and pore
volume were calculated using the Dubinin-Radushkevich (D-R) equation in the pressure \( (P/P_0) \) ranging 1 \( \times 10^{-5} \)–3.2 \( \times 10^{-2} \) [18,27,33].

\[
V_a = V_{micro}\exp \left[-\left(\frac{RT}{\beta E_0} \ln\left(\frac{P_0}{P}\right)\right)^2\right]
\]

where \( V_a \) is the volume of adsorbed gas at equilibrium pressure, \( V_{micro} \) is the total micropore volume, \( R \) is the gas constant, \( T \) is the Kelvins temperature, \( E_0 \) is the adsorption potential, and \( \beta \) is a constant. The micropore-sized distribution was determined by the density functional theory (DFT) method [17,19].

3. Results and discussions

3.1. Organic geochemistry

The organic geochemical data of the two group samples are shown in Table 1, and the comparisons of TOC content are presented in Fig. 1. The \( R_o \) values of the two original rocks are 0.72% and 0.64%, respectively. The Hydrogen index is 251 mg\text{g}\text{/T OC} and 367 mg\text{g}\text{/T OC}, respectively. The SOM contents of extracted samples with dichloromethane are 0.24% and 0.21%, respectively. The SOM contents of extracted samples with trichloromethane are 0.30% and 0.34%, respectively. The percentages of dichloromethane extractions to total organic matter are 9.5% and 3.6%, respectively. Meanwhile, the percentages of trichloromethane extractions are 11.9% and 5.8%, correspondingly. The evident high extraction contents of Sample 1 are related to the higher maturity.

The TOC content of extracted samples afterwards decreases. The B group of Sample 1 decreases by 0.12% with a decline of 4.8%, while Sample 2 decreases by 0.17% with a decline of 2.9%. The C group of Sample 1 decreases by 0.28% with a decline of 11.1%, while Sample 2 decreases by 0.30% with a decline of 5.12%. Both the dichloromethane and trichloromethane can partially remove SOM in shale. More extractions obtained with trichloromethane because of its stronger polarity.

The soluble hydrocarbon content (\( S_1 \)) of extracted samples decrease noticeably. The pyrolysis hydrocarbon content (\( S_2 \)) and hydrogen index (\( I_H \)) also show a certain reduction. Due to the fact that the SOM content in Sample 1 is higher, the decrease of pyrolysis parameters became ever more apparent than that of Sample 2. The oxygen index of the extracted samples increases slightly. The peak temperature of pyrolysis hydrocarbon (\( T_{max} \)) is still the same, which implies that extraction does not change the significance of \( T_{max} \) as the maturity index.

3.2. Mineral composition

Accurate quantification of mineral components is still difficult. The X-ray diffraction used in this study can only be semi-quantitative [34]. The results show that the difference between mineral compositions of extracted samples with that of the original rock is insignificant and is limited within the analysis precision of X-ray diffraction (Table 2). Therefore, it can be considered that the extraction of SOM does not lead to changes in mineral compositions. The mineral compositions can be transformed into each other by oxidizing organic matter with H\(_2\)O\(_2\) or NaClO, which would lead to the transformation

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Grouping and fundamental geochemical parameters of the samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>Group</td>
</tr>
<tr>
<td>Sample 1</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Sample 2</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>C</td>
</tr>
</tbody>
</table>

\( R_o \): vitrinite reflectance; \( \theta \): the percentage of soluble organic matter from extraction.
of reservoir structure. The pore structure of shale reservoir has not changed throughout the extraction. Therefore, the difference in the analysis of the reservoir structure is vital.

3.3. Gas adsorption analysis

In comparison to the raw samples (Group A), the surface area and pore volume of the extracted samples (Groups B and C) increased in varying degree (Table 3). The SOM in shale reservoir occupies part of the pore volume. The solid state of SOM at 77.4 K reduces the pore volume occupied by the nitrogen molecules, thus, the pore volume of the extracted samples increased. The SOM presents liquid properties at 273.1 K. Although some of the carbon dioxide molecules can be dissolved in SOM, the content remains very low at relatively low-pressure and can be overlooked due to its insignificance [35]. There are two explanations for the increase of surface area. One is that SOM exists in a small throat channel and it blocks the passage of gas diffusion. The low-pressure gas molecules (\(N_2\) or \(CO_2\)) experience difficulties entering internal pores blocked by SOM. The other is that SOM is attached directly on the surface of the porous kerogen. The more irregular surface was exposed after removing SOM. Therefore, more micropores and small mesopores could be probed by gas molecules as the surface area increases.

Observable hysteresis loops are present in the \(N_2\) adsorption—desorption isotherms of Sample 1 (Groups A, B, and C) whose area vary with different solvents (Fig. 2a–c). The areas of hysteresis in the increasing order: Group A < Group B < Group C. The hysteresis loops of Sample 2 are not noticeable, but the fine differences between adsorption and desorption curves could be seen (Fig. 3a–c). The \(N_2\) adsorption curves of Sample 1 show more obvious differences, while the curves of Samples 2 almost coincide only with a slight difference in the maximum adsorption (Figs. 2d and 3d). This phenomenon implies that mesopores structure of extracted Sample 1 change significantly, and the Sample 2 has not changed greatly after the extraction. The surface area data showed a similar pattern. The surface area of Sample 1 increased significantly after extraction. However, the surface

Table 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>Group</th>
<th>(N_2) BET surface area/(m²/g)</th>
<th>(N_2) total pore volume/(cm³/g)</th>
<th>(N_2) mean pore size/Å</th>
<th>(CO_2) micropore surface area/(m²/g)</th>
<th>(CO_2) micropore volume/(cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>A</td>
<td>2.61</td>
<td>0.0143</td>
<td>20.60</td>
<td>5.22</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3.54</td>
<td>0.0132</td>
<td>17.20</td>
<td>6.59</td>
<td>0.0027</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>4.24</td>
<td>0.0168</td>
<td>15.81</td>
<td>6.80</td>
<td>0.0027</td>
</tr>
<tr>
<td>Sample 2</td>
<td>A</td>
<td>2.84</td>
<td>0.0178</td>
<td>25.62</td>
<td>5.51</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>2.89</td>
<td>0.0182</td>
<td>25.21</td>
<td>6.32</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>3.13</td>
<td>0.0197</td>
<td>25.15</td>
<td>7.25</td>
<td>0.0029</td>
</tr>
</tbody>
</table>

Fig. 2. Low-pressure nitrogen adsorption—desorption isotherms of Sample 1 (77.4 K)
The area of Sample 2 increased minimally. The variation of the pore size is in the opposite trend with the surface area. The mean pore size of Sample 2 is larger than that of Sample 1 (Table 3).

The characteristics of mesopores are extended to the measure of micropores by CO₂ adsorption (Fig. 4). The micropores' surface area and volume of extracted samples increase in different degrees (Table 3). Compared to N₂ adsorption, CO₂ adsorption amounts of extracted Sample 2 increase greatly, which show that the extraction mainly affects micropores.

The distributions of pore volume for the studied samples are presented in Fig. 5. Comparing with the raw sample (Group A), the micropores and mesopores ranging between 2 and 20 nm in size of the extracted sample 1 (Group B and C) increase noticeable, whereas there was no significant change in larger mesopores and macropores. However, only the pores less than 5 nm in size had a varying outcome in Sample 2.

According to the results above, it can be considered that the residual SOM in shale samples occur mainly in micropores and small mesopores. This is similar to the study about SOM in coal reported by Yang et al. [15]. They concluded that the SOM in coal is mainly stored in pores between 1.7 and 5.0 nm in size. The difference between Sample 1 and Sample 2 is mainly related to maturity. Sample 1 has been in the middle level of maturity, and a large number of SOM was generated by means of cracking kerogen. Partly, SOM has been migrated and stored in the pores of organic matter and clay minerals. Whereas the maturity of Sample 2 is lower, the SOM content is less than half of the Sample 1 value. The SOM in Sample 2 is still mainly stored in smaller pores in organic matter.
4. Conclusions

(1) The SOM in low mature shale can be effectively removed by Soxhlet extraction. Trichloromethane possesses stronger polarity which makes it better than dichloromethane for extraction. The pyrolysis parameters (e.g. TOC content, $S_1$, $S_2$, $I_H$) of the extracted samples declined, but the mineral composition was not altered. Thus, the original pore structure is thought to be unaffected by the extraction.

(2) The residual SOM in low mature shale has an important influence on the measurement and characterization of pore structure. The SOM inhabits pore volume, and it hinders pore connectivity. The extraction increases the surface area and pore volume of the samples greatly.

(3) The SOM occurs mainly in the micropores and small mesopores, and their occupied pore size range is influenced by the maturity. For the shale samples with lower maturity, the SOM is mainly hosted in pores with a diameter less than 5 nm. For the shale samples with moderate maturity, micropores and mesopores ranging between 2 and 20 nm are the main storage space for SOM.

Foundation items

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Conflict of interest

The authors declare no conflict of interest.

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