Research on the Shale Porosity–TOC Maturity Relationship Based on an Improved Pore Space Characterization Method

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Abstract: Shale pore structure characterization is key to shale reservoir evaluation, sweet spot selection, and economic exploitation. It remains a challenge to accurately characterize shale micro-nano pores. Common experimental characterization methods for shale pore systems are listed, and advantages and weaknesses of each method are analyzed. An improved pore structure characterization method for shale is proposed by combining Helium and NMR. The new method does not affect shale samples and has a higher accuracy. The affecting factors for shale pore evolution for shale are also discussed, showing that organic matter content and maturity are key factors in total porosity development. Furthermore, a shale porosity–TOC maturity relationship chart is developed based on the experimental data of shale samples selected from six shale reservoirs. The application of this chart in Well X in the Gulong field of Songliao Basin proves its utility in evaluating shale reservoirs.

Keywords: shale; pore evolution; organic matter; pore structure; logging evaluation

1. Introduction

Shale has drawn increasing attention in recent years and has become an important successor field for oil and gas exploration and development [1]. Avalon Shale in the Delaware Basin, Chang 7; Shale in the Ordos Basin, Da’anzhai Shale in the Sichuan Basin, the Qingshankou Formation in the Songliao Basin, and the Fengcheng Formation in the Junggar Basin have entered exploration and development stages [2–5]. Shale reservoirs have complex mineral composition and diverse pore styles, and their porosity evolution is closely related to organic matter content and maturity. In addition, oil and gas usually exist in an adsorption state on the pore surfaces. Therefore, accurate pore structure characterization is crucial for predicting and developing shale oil and gas resources.

At present, the micro-nano pore structure characterization of shale samples mainly relies on experimental methods [6,7]. Due to differences in principles, operating procedures, and handling methods, the characterization accuracy of the pore structure varies so much, significantly depending on the selected measurement methods [8,9]. Table 1 shows the features and principles of different methods. Figure 1 shows the range of pore sizes for various experiment types. According to the size, shale pores are divided into micropores (pore size ≤ 2 nm), mesopores (pore size between 2 and 50 nm), and macropores (pore size > 50 nm).
Table 1. A list of physical experimental methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Principle</th>
<th>Feature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium expansion measurement (He)</td>
<td>Accessible pores of helium are connected.</td>
<td>Temperature changes and pressure fluctuations lead to reduced measurement accuracy. For crushed samples, the method for determining the mesh size to ensure that helium enters the isolated pores has no unified standard.</td>
<td>[10,11]</td>
</tr>
<tr>
<td>High pressure mercury injection (MIC)</td>
<td>Accessible pores of mercury are connected.</td>
<td>The maximum mercury injection pressure is 60,000 psi, and its corresponding throat size is 3.6 nm. The range of measured pore throats is wide, and rich information of the pore structure can be obtained. For shale samples, mercury is disabled to enter micro-nano pores; also, injecting mercury usually causes microcracks, and the damage of the pore structure leads to significant deviations between the tested and actual pore structure.</td>
<td>[12]</td>
</tr>
<tr>
<td>Fluids saturation</td>
<td>Saturate the evacuated core with salt water, oil, or alcohol under pressurized conditions; the pores saturated with fluids are tested.</td>
<td>The testing result is influenced by the fluid type, pore surface wettability, saturation method, pre-treatment of rock cores and the experimental environment.</td>
<td>[13]</td>
</tr>
<tr>
<td>Low pressure gas adsorption (LPGA)</td>
<td>Pore structure parameters can be calculated according to theoretical models from the measured gas adsorption content on the pore surface under low temperature conditions.</td>
<td>Certain gases selecting according to experimental conditions, and reasonable calculation models are the key to accurately obtaining test results.</td>
<td>[14]</td>
</tr>
<tr>
<td>Nuclear magnetic resonance (NMR) testing</td>
<td>Pore distribution is obtained from the relaxation time of hydrogen nuclei in pore fluids.</td>
<td>NMR testing is non-destructive, convenient, fast, and has rich measurement information. Influential factors of quantitative pore structure characterization from NMR T2 distribution include the content and maturity of organic matter, pore surface wettability, and measurement parameters.</td>
<td>[15,16]</td>
</tr>
<tr>
<td>Small angle scattering (SAS)</td>
<td>Pore structure is characterized through elastic coherent scattering using X-rays or neutrons as probes.</td>
<td>Micro-nano pore structure can be tested, but its application in oil and gas field is rare.</td>
<td>[17,18]</td>
</tr>
<tr>
<td>Scanning electron microscope (SEM)</td>
<td>Pore structure is scanned by focused high-energy electron rays.</td>
<td>The resolution of SEM can reach nm level, but its view field is too small to represent the whole rock.</td>
<td>[19]</td>
</tr>
<tr>
<td>Micro-CT</td>
<td>Micro-structure of rock samples is scanned by using microfocus X-ray, without damaging the samples.</td>
<td>Digital core can be built to simulate physics experiments, micrometer pores can be scanned, but its application in nanoscale shale is limited.</td>
<td>[20]</td>
</tr>
</tbody>
</table>

Numerous influential factors in shale pore evolution have been studied in recent years [21]. Gao et al. have found that inorganic and organic diagenesis jointly control shale pore evolution [22]. Liang et al. have analyzed the influence of geological stress on shale porosity [23]. Yu et al. have developed a function depicting the relationship between porosity and kerogen content [24,25]. Curtis et al. have graded the porosity development using the maturity of organic matter [26,27]. Tan et al. have calculated shale kerogen content based on the core NMR experiment [28]. Iqbal and Rezaee have estimated the porosity and water saturation of shale reservoirs based on a revised Archie model [29]. Chen et al. have developed a revised expulsion efficiency method for organic porosity estimation in shale reservoirs [30]. Lots of studies show that shale pore evolution is closely related to the content and maturity of organic matter. However, there is a shortage of research on quantitative evaluation methods for the relationship of porosity to TOC (total organic carbon, unit: %) maturity.
In this paper, we systematically analyze and summarize the main properties of various micro-nano shale pore characterization methods. These methods can be divided into visual methods and physical experimental methods. To improve the accuracy of shale pore structure evaluation while minimizing damage to shale samples, integrating the advantages of multiple methods is a promising research direction.

To achieve this goal, an improved pore structure characterization method for shale is proposed by combining helium and NMR pore structure characterization methods. Twenty-eight shale samples from the Fengcheng Formation in the Junggar Basin have demonstrated that the new method has higher accuracy. Influential factors of shale pore evolution are also discussed. With the increase in organic maturity, oil- and gas-generating pores develop. At the end of the hydrocarbon generation state, a high content of brittle minerals is beneficial for the preservation of organic pores. In addition, organic matter content and maturity are key factors for shale pore evolution. Furthermore, a quantitative evaluation method for the porosity–TOC maturity relationship is developed based on experimental data of shale samples in Montney shale of the Lower Triassic in Canada, the Longmaxi Formation and Qiongzhusi Formation in Sichuan Basin, the Ganchaigou Formation in Qaidam Basin, and the Qijia Gulong of Daqing. Finally, the new porosity–TOC maturity method is applied to Well X in Gulong field in the Songliao Basin, and the result shows consistency with geological laws, and the new method provides a new idea for studying the porosity–TOC–R0 relationship using logging data.

2. An Improved Pore Structure Characterization Method for Shale

To improve the pore structure characterization accuracy of shale samples, achieve wide ranges of pore distribution, and avoid time wasting and the effects of residual hydrocarbon, a combination of nuclear magnetic resonance and helium porosity is proposed. Figure 2 shows the measurement diagram. Pore space occupied by hydrocarbons (commonly oil and gas) can be obtained through NMR testing, and pores without hydrocarbons are measured by the helium expansion method; by combining NMR and helium porosity, the accuracy of shale pore structure characterization is improved. Experimental steps are as follows:

1. Put shale samples into an oven with a constant temperature of 60 °C until the cores’ weight changes little (generally, core weight variance is less than 5%). Then, place
dry samples into a sample warehouse. Vacuum the sample warehouse and control the warehouse to ensure that the residual gas in the pores of the shale sample is evacuated.

(2) Fill the control warehouse with helium to a certain pressure. Open the connecting valve between the sample warehouse and control warehouse to let shale samples become fully saturated with helium gas. When the pressure gauge stabilizes, the skeleton volume of shale samples (Vs) can be obtained according to Boyle’s law.

(3) The total volume of shale samples (Vt) (unit: v/v) can be measured through the caliper measurement method and the Archimedes immersion method. The helium porosity can be calculated as \( \varphi_{He} = (Vt - Vs)/Vt \) (unit: v/v).

(4) \( \varphi_{NMR} \) is obtained by integrating the NMR T2 spectrum, the resonance frequency is 4.52 MHz, the waiting time is 3000 ms and echo spacing is 0.35 ms, and the number of scans was 128.

(5) Then, the total porosity of shale samples is \( \varphi = \varphi_{He} + \varphi_{NMR} \) (unit: v/v).

Figure 2. A measurement principal diagram of the improved shale pore structure characterization method. \( \varphi \) (v/v) is total porosity, \( \varphi_{He} \) (v/v) is helium porosity, \( \varphi_{NMR} \) (v/v) is NMR porosity, t (ms) is time, M(t) is echo string, \( \phi(t) \) (v/v) is T2 porosity of specific T2 time, \( t_2 \) (ms) is T2 time, \( V_k \) (mL) is gas volume of the control warehouse, \( P_k \) (psi) is the gas pressure of control warehouse, V(mL) is the gas volume of sample warehouse, and P (psi) is gas pressure of a sample warehouse.

3. Shale Porosity–TOC Maturity Relationship Based on the New Pore Structure Characterization Method

3.1. Effect Factors for Shale Pore Evolution

Shale pore evolution is a combined result of permeability, fluid pressure, formation temperature, thermal maturity, etc. It has a vital influence on geophysical response parameters, such as formation velocity, density, resistivity, and the NMR T2 spectrum [31,32]. Inorganic pores of shale are mainly controlled by diagenesis and fluid interaction [33,34], while organic pores are influenced by different factors during different stages. Figure 3 shows the evolution of organic pores.
At stage A, the pore structure of immature shale is mainly controlled by mechanical compaction, and organic porosity is low. As the organic matter maturity increases, oil- and gas-generating pores develop successively. From stage B to E, organic pores develop and porosity exhibits a positive correlation with organic matter content (TOC) [35–39]. From stage E to F, when the maturity of organic matter reaches its peak and enters the dry gas stage, organic matter gradually transforms from a liquid to solid state. At this time, the organic pore volume reaches its maximum. From stage F to G (G'), at the end of hydrocarbon generation, organic pores even disappear due to mechanical compaction [40], and the organic porosity reduction rate is correlated to mineral composition, and brittle minerals can resist the decrease in porosity. On the other hand, mineral composition is also controlled by organic maturity. With the increase in organic maturity, the conversion rate of the clay mineral component increases, which has significant effects on pore structure [41].

Figure 4 shows that pore evolution is influenced by the clay composition of rocks. It shows that from the early to late diagenetic stage, kerogen and organic pores increase, while primary pores gradually decrease. During the sedimentary period, before organic matter produces hydrocarbons, clay minerals converge slowly and organic pores are rare, corresponding to stages A to B in Figure 3. And as the diagenetic stage develops from early to late, with increasing hydrocarbons, secondary pores that are formed by clay mineral conversion appear and organic pores increase gradually, and the porosity in the high-maturity stage is positively correlated with the increase of illite [42,43], corresponding to stages B to E in Figure 3. At the end of the late diagenetic stage, the maturity of organic matter had reached its peak, with the cessation of hydrocarbon generation, and clay mineral conversion ended and organic pores tended to stabilize, corresponding to stages E to F in Figure 3 [44].
Figure 4. Pore evolution is influenced by the clay composition of rocks (modified according to Zhao et al. 2017 [43]).

3.2. The Shale Porosity–TOC Maturity Relationship

According to the analysis above, the content and maturity of organic matter are key parameters influencing pore evolution. In order to study the shale porosity–TOC maturity relationship, shale samples selected from Montney shale of the Lower Triassic in Canada, the Longmaxi Formation and Qiongzhusi Formation in the Sichuan Basin, the Ganchaigou Formation in the Qaidam Basin, and the Qijia Gulong of Daqing were taken to experiment to obtain the total porosity, TOC, and maturity. The total porosity was measured using the new method mentioned in Section 2. The vitrinite reflectance Ro is a common parameter reflecting organic maturity; it is the intensity percentage of the reflected light and vertical incident light of the vitrinite polishing surface at a wavelength of 546 nm, measured with a microscope photometer.

The experimental total porosity and TOC were put into a porosity–TOC chart, and the result is shown in Figure 5; it can be seen that the total porosity had a positive correlation with TOC, with the increase in TOC; total porosity increased first and then stabilized. When the TOC was smaller than 2%, the porosity–TOC relationship tended towards linearity, but when TOC exceeded 2%, the relationship shifted to become logarithmic.

The follow formula can be used to fit the shale porosity–TOC relationship.

\[
\begin{align*}
\varphi &= a \cdot \ln(\text{TOC}) + b, \quad (\text{TOC} > 2\%) \\
\varphi &= a \cdot \text{TOC} + b, \quad (\text{TOC} \leq 2\%)
\end{align*}
\]

(1)
where $\varphi$ is the total porosity (%), $a$, $b$ are undetermined coefficients, and $b$ is the original porosity unaffected by organic matter. $a$ and $b$ are determined by the least square method with experimental TOC and porosity according to Equation (1).

Further, it can be seen that the slope value $a$ is in inverse proportion to $Ro$, which means that as organic maturity increases, the porosity increasing rate reduces. To qualitatively characterize the effects of organic maturity on the total porosity, parameter $k$ can be introduced as the pore increasing efficiency of organic matter. It is expressed as follows:

$$
k = \begin{cases} 
\frac{\varphi^*}{TOC} = f(Ro), & (TOC \leq 2\%) \\
\frac{\ln(\varphi^*)}{\ln(TOC)} = f(Ro), & (TOC > 2\%)
\end{cases}
$$

In Equation (2), $\varphi^*$ is the relative value of porosity (unit: $v/v$), and $\varphi^* = \varphi - b$ is the porosity eliminating the original porosity.

According to Equation (2), the shale porosity–TOC maturity relationship chart is developed, as shown in Figure 6. It helps to evaluate organic maturity with known TOC and total porosity $\varphi$. 
4. Application

The shale porosity–TOC maturity relationship chart is applied to Well X in Gulong field in the Songliao Basin. The total porosity and TOC are calculated from loggings using the empirical formula [45–47], as shown in Figure 7. The evaluation result of maturity through the shale porosity–TOC maturity relationship chart is shown in Figure 8 and listed in Table 2. It shows that the average pore-increasing efficiency of the organic matter $k$ is 4.34 and that the range of vitrinite reflectance $R_o$ is 1.2–2.0%. The maximum $k$ of Q4 is 6.04, and is relatively low compared with other sections, indicating that this section is in the hydrocarbon generation. The organic acid dissolution of unstable inorganic minerals will have positive effects on pore structure improvement. And for Section Q6, $R_o$ is relatively high, which means that Section Q6 is in the mature to over-mature stage, and both hydrocarbon generation and its effect on pore structure declines. The application result shows that the porosity–TOC maturity relationship chart can be used in the evaluation of shale reservoirs.
Table 2. The evaluation result of maturity through the shale porosity–TOC maturity relationship chart.

<table>
<thead>
<tr>
<th>Section</th>
<th>k (Min–Max)</th>
<th>Ro/ (%) (Min–Max)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td>Q4</td>
<td>4.7–7.3</td>
<td>1.2–1.6</td>
</tr>
<tr>
<td></td>
<td>6.04</td>
<td>1.56</td>
</tr>
<tr>
<td>Q5</td>
<td>0.3–6.4</td>
<td>1.5–1.8</td>
</tr>
<tr>
<td></td>
<td>3.95</td>
<td>1.77</td>
</tr>
<tr>
<td>Q6</td>
<td>0.8–4.7</td>
<td>1.6–2.8</td>
</tr>
<tr>
<td></td>
<td>3.37</td>
<td>1.84</td>
</tr>
<tr>
<td>Q7</td>
<td>0.2–4.9</td>
<td>1.2–1.9</td>
</tr>
<tr>
<td></td>
<td>4.06</td>
<td>1.81</td>
</tr>
<tr>
<td>Q8</td>
<td>1.1–5.2</td>
<td>1.2–1.9</td>
</tr>
<tr>
<td></td>
<td>4.08</td>
<td>1.85</td>
</tr>
<tr>
<td>Q9</td>
<td>0.2–5.9</td>
<td>1.2–2.0</td>
</tr>
<tr>
<td></td>
<td>4.55</td>
<td>1.87</td>
</tr>
</tbody>
</table>

Figure 7. Logging evaluation results of well X in Gulong, Daqing.

Tracks from left to right include Tracks 1–7, with Section No. (Formation), depth (meters), natural gamma-ray logging (GR: Gapi)/spontaneous potential logging (SP: mv)/Caliper logging (CAL: in), apparent resistivity logs (RLLD/RLLS: OHMM)/Microspherical focused logging (RMSL: OHMM), acoustic-wave slowness logs (DT24: us/ft)/bulk density...
(ZDEN: g/cm³)/neutron porosity (CNC: v/v), logging calculated porosity (POR: v/v)/experimental porosity (POR_CORE: v/v), and logging calculated TOC (TOC: kg/kg)/experimental TOC (TOC_CORE: kg/kg).

Figure 8. Shale porosity–TOC maturity relationship chart of Well X.

5. Discussion and Future Work

5.1. Discussion

Twenty-eight shale samples from the Fengcheng Formation in the Junggar Basin were tested using the improved pore structure characterization method mentioned in Section 1. The results are shown in Figure 9 and Table 3, and the porosity calculated using the new method had good consistency with the helium porosity tested after oil and salt washing; the goodness-of-fit was 0.98979 and the average relative error was 4.92%. Compared with the helium porosity method tested after oil and salt washing, the improved pore structure characterization method is more accurate, time-saving, and has no damage to rock samples.

Figure 9. Comparison between the new method for calculated porosity and the helium porosity tested after oil and salt washing.
### Table 3. Specific parameters of 28 rock samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Lith</th>
<th>Depth (m)</th>
<th>Length (mm)</th>
<th>Diameter (mm)</th>
<th>( \varphi_{\text{He}} ) (%)</th>
<th>( \varphi_{\text{NMR}} ) (%)</th>
<th>( \varphi_t ) (%)</th>
<th>No.</th>
<th>Lith</th>
<th>Depth (m)</th>
<th>Length (mm)</th>
<th>Diameter (mm)</th>
<th>( \varphi_{\text{He}} ) (%)</th>
<th>( \varphi_{\text{NMR}} ) (%)</th>
<th>( \varphi_t ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>4872.21</td>
<td>49.11</td>
<td>24.65</td>
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</tr>
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<td>11.97</td>
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</tbody>
</table>

Lith: lithology; Length: length of rock sample; Diameter: diameter of rock sample; \( \varphi_{\text{He}} \): porosity tested from Section 2 steps (3); \( \varphi_{\text{NMR}} \): porosity tested from Section 2 steps (4); \( \varphi_t \): helium porosity tested after oil and salt washing.
The calculation error of Figure 8 is mainly derived from I, and the actual porosity–TOC maturity relationship is far more complex than linear or logarithmic functions; II is the measurement errors of experimental parameters of shale.

5.2. Future Work
A The theoretical functions of the porosity–TOC maturity relationship need to be further improved to meet the accuracy of shale reservoir evaluation [48].
B The diagenetic evolution of a specific study area can be further analyzed using the porosity–TOC maturity relationship [49].
C Shale maturity can be predicted using the porosity–TOC maturity relationship, as TOC and porosity are calculated from logging data; this will improve the understanding of shale oil-rich mechanisms and sweet spot prediction [50].
D Kerogen type has a significant influence on physical properties, and the relationship between kerogen type and porosity–TOC maturity function has geochemical significance [51,52].
E Shale pore controlling factors and evolution vary significantly among regions, and the most suitable porosity measurements need to be tested for a specific region. The full-scale pore structure characterization method, combining multiple experimental methods, is a worthy study area for shale resource evaluation [53].

6. Conclusions
(1) Based on measurement advantages analysis, a new method combining helium and NMR is proposed: the new method does not need to wash oil and salt, it does no damage to shale core samples, and experimental data of 28 rock samples has verified that the new method has higher accuracy.
(2) Sorting out the pore evolution of organic and inorganic matter during geological periods, the organic matter content and maturity are key factors for total porosity development.
(3) The shale porosity–TOC maturity relationship chart is developed based on shale samples from six formations, and the application of the new chart in Well X in the Gulong field of the Songliao Basin demonstrates that the method can be used in the evaluation of shale reservoirs.

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