Molecular Organic Geochemical Characteristics and Coal Gas Potential Evaluation of Mesozoic Coal Seams in the western Great Khingan Mountains

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Abstract: Coal-bearing strata are widespread in the western Great Khingan Mountains. Abundant coal resources have been found in the Jurassic Alatanheli Groups, the Cretaceous Bayanhua Groups, the Damoguaihe Formation and the Yimin Formation. The organic geochemical characteristics were analyzed in combination with hydrocarbon source rock evaluation and molecular organic geochemistry experiments, and the coal gas potential of coal seams was evaluated. The source rock evaluation results indicated that the Mesozoic coal samples have the characteristics of high organic matter abundance (TOC>30%), low maturity (Ro values of approximately 0.6%), and type III composition. The hydrocarbon generation potentials of the Alatanheli Groups and Bayanhua Groups are high, while the generation potentials of the Damoguaihe Formation and the Yimin Formation are low. The results of geochemistry show that the depositional environment of the coal seam was a lacustrine, oxidizing environment with a low salinity, and the source of the organic matter was mainly higher plants. Affected by weak degradation, the coal seams mainly formed low-maturity gas of thermal catalytic origin. The Cretaceous coal seams contain a large amount of phytoplankton groups deposited in a low-stability environment affected by a transgression event, and the potential range varied widely. For the Jurassic coal seams, the depositional environment was more stable, and the coal seams feature a higher coal-forming gas potential.

Key words: Western part of the Great Khingan Mountains; coal source rocks; molecular organic matter geochemical characteristics; low-maturity gas; coal gas

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I Introduction

Mesozoic coal seams are widely developed in the western part of the Greater Khingan Mountains. The main coal-bearing strata are distributed in the Alatanheli Group in the Erlian Basin and the Zhalainuoer Group in the Hailaer Basin, and these strata have the characteristics of high organic matter abundance, thick rock thickness and low degree of maturation (Liu, 1992; Liu et al., 2002; Guo et al., 2017). Based on these characteristics, coal seams can be treated as source rocks (Obaje, N.G., and Hamza, H., 2000; Wilkins, R.W.T., and George, S.C., 2002; Petersen, H.I. et al., 2008; Dong et al., 2015; Shan et al., 2018; Teng et al., 2019). The conventional source rock evaluation includes organic abundance, type and maturity, and a source rock evaluation standard can be established based on evaluation parameters (Chen et al., 1997; Xue, 2004; Saberi M. H. et al., 2015; Wu et al., 2015). However, conventional source rock evaluation is mainly aimed at continental and marine source rocks. For coal seam source rocks, analysis of the organic matter source of the coal source rock is necessary. Combined with the identification of organic matter and molecular organic geochemistry, the organic matter source can be determined (Chen et al., 1997; Xue, 2004; Cai et al., 2015).

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Based on the above methods, the source rock and coal gas potential evaluation of Mesozoic coal seams are analyzed in the western part of the Great Khingan Mountains.

2 Geological Settings

The western part of the Great Khingan Mountains is mainly composed of two large Mesozoic basins, Erlian and Hailar (Fig. 1). During the formation period of the Mesozoic strata in the Erlian Basin, a large number of small fault-related basins developed above the main tectonic units due to multistage fault depression and tectonic inversion events. The Alatanheli Group and the Bayanhua Group are the main coal seams formed in the Late Jurassic in the Erlian Basin. The upper part of the Alatanheli Group is covered by an unconformity with volcanic-sedimentary strata, and the thickness of the coal seam can reach a hundred meters. The main coal seam in the Bayanhua Group is the Saihantala Formation (Sun et al., 2017; Liu et al., 2000; Chen et al., 2007). In the Hailaer Basin, the Cretaceous Zhalainuoer Group is the main coal seam and has been subdivided into two sets of coal seams, the Damoguaihe Formation and the Yimin Formation (Liu et al., 2000; Chen et al., 2007).

3 Samples and Methods

A total of five fresh coal samples from four open pit coal mines were collected in this study (Table 1), and the organic carbon content, rock pyrolysis, kerogen composition, vitrinite reflectance and saturated hydrocarbon gas chromatography-mass spectrometry characteristics were measured in the coal samples. The evaluation of source rocks usually includes organic abundance, organic matter type and organic matter maturity. The hydrocarbon potential of source rocks can be quantitatively calculated by organic matter abundance evaluation, while the quality of source rocks can be analyzed by the evaluation of organic matter types and organic matter maturity (Zhang et al., 2012). The abundance of organic matter can be calculated by four methods: determination of the total organic carbon content (TOC), analysis of rock pyrolysis, analysis of soluble organic matter in rocks and analysis of components. The method of identification and type of kerogen via transmitted light and fluorescence was used to analyze the organic matter type. The organic matter maturity evaluation was performed following the methods of vitrinite reflectance measurement (Ro) and saturated hydrocarbon gas chromatography (Bertrand, 1990).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Age</th>
<th>Horizon</th>
<th>Lithology</th>
<th>Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY1</td>
<td>J1-2</td>
<td>Alatanheli Group</td>
<td>Coal</td>
<td>Erlian Basin</td>
</tr>
<tr>
<td>DG1</td>
<td>J1-2</td>
<td>Alatanheli Group</td>
<td>Coal</td>
<td>Erlian Basin</td>
</tr>
</tbody>
</table>

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The dry gravimetric method was used to determine the total organic carbon content. The inorganic carbon in the rock was removed by hydrochloric acid. Then, the organic matter was burned at a high temperature and fully oxidized to decompose it. Finally, the combustion product was measured and converted into TOC content. A rock pyrolysis analyzer (Rock-Eval) was used to analyze the abundance of organic matter in the rocks. The released hydrocarbons and carbon dioxide were quantitatively analyzed with a hydrogen flame ionization detector and a thermal conductivity detector in Rock-Eval (Espitalie et al., 1985; Chen et al., 2018). The Soxhlet extraction method was used to determine the content of soluble organic matter (chloroform asphalt “A”). The chloroform asphalt “A” from the samples was separated into four group components (saturated hydrocarbons, aromatic hydrocarbons, nonhydrocarbons and asphaltene) based on their dissolvability in organic solvents. A gas chromatography-mass spectrometry (GC-MS) instrument was used to analyze the components of the saturated hydrocarbons. In this study, m/z 191 and m/z 217 were selected to detect the distribution of the hopane, sterane and terpane molecular series (Lu and Zhang, 2008). The type index of the kerogen samples was calculated by mathematical statistics and classified based on the components identified by transmitted light and fluorescence microscopy. The vitrinite reflectance was measured under reflected light at a wavelength of 546 nm using a rock microscope. The maximum vitrinite reflectance (Ro) measured by oil immersion was used as the main identification index when determining the degree of evolution.

4 Results

4.1 Source Rock Evaluation

The total organic carbon content (TOC) of the coal samples ranges from 18.50% to 65.61% (Table 2). The limit value of the evaluation index of coal source rocks is higher than that of the evaluation of continental sandstone and shale. The TOC of the coal seam samples can reach up to more than 30% (Liu et al., 2002). The hydrocarbon generation potential (S1+S2) contents of the coal samples range from 0.88 mg/g to 152.77 mg/g, and the chloroform asphalt “A” contents of the coal samples range from 0.16% to 0.62% (Table 2). The Tmax value of the coal samples ranges from 426 °C to 444 °C, with an average of 434 °C, and the average content of the Ro is 0.66% (Table 2). The low values of Ro and Tmax indicate that the evolution stage of the coal seam is in the immature to low-maturity stage (Lu and Zhang, 2008). The organic matter types are all type III (Table 2).

Table 2 Evaluation table for the coal seam source rocks

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TOC/%</th>
<th>S1+S2/mg/g</th>
<th>Tmax/°C</th>
<th>“A”/%</th>
<th>Type</th>
<th>Ro/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY1</td>
<td>18.498</td>
<td>22.30</td>
<td>444</td>
<td>0.16</td>
<td>III</td>
<td>0.652</td>
</tr>
<tr>
<td>DG1</td>
<td>37.613</td>
<td>73.02</td>
<td>430</td>
<td>0.62</td>
<td>III</td>
<td>0.629</td>
</tr>
<tr>
<td>XW1</td>
<td>65.611</td>
<td>152.71</td>
<td>440</td>
<td>0.38</td>
<td>III</td>
<td>0.664</td>
</tr>
<tr>
<td>JL1</td>
<td>51.125</td>
<td>0.88</td>
<td>432</td>
<td>0.22</td>
<td>III</td>
<td>0.676</td>
</tr>
<tr>
<td>YM1</td>
<td>48.188</td>
<td>1.09</td>
<td>426</td>
<td>0.59</td>
<td>III</td>
<td>0.681</td>
</tr>
</tbody>
</table>

Fig. 2. A scatter plot between organic carbon content (TOC) and hydrocarbon generation potential (S1+S2). The parameters of TOC and S1+S2 measured from experiments represent residual organic matter abundance, which
indicates the residual source rock potential in the coal samples. The TOC of the coal samples in the Erlian Basin show a positive correlation with hydrocarbon generation potential, and the hydrocarbon potential is higher than 20 mg/g. However, the coal samples in the Hailaer Basin have different characteristics, with a high TOC and a low hydrocarbon generation potential (Table 2). The measured results of chloroform asphalt “A” indicate that the content of soluble organic matter in all coal samples is high (Table 2). The organic matter in the coal seams is highly enriched, and the adsorption capacity for soluble organic matter is stronger than that of mudstones and carbonate rocks (Chen et al., 2012). A high TOC content does not mean that the coal seams have a high hydrocarbon generation potential. Therefore, the conventional organic matter abundance evaluation of source rocks is unable to accurately evaluate the source rock potential of the Mesozoic coal seams in the western Great Khingan Mountains.

Based on the study of organic matter abundance, the organic matter sources of 5 coal samples in the western Great Khingan Mountains were analyzed. The results of the kerogen microcomponent experiment show different characteristics between Jurassic and Cretaceous samples. The percentage content of the inertinite group in Jurassic coal samples is dominant, accounting for 64% and 40%, followed by the sapropelinite group, accounting for 10% and 25%, with a small amount of the exinite group. However, the vitrinite content of coal samples in Cretaceous is dominant (accounting for more than 70% in all samples), and there is no exinite group content (Table 3).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Horizon</th>
<th>Sapropelinite/%</th>
<th>Exinite/%</th>
<th>Vitrinite/%</th>
<th>Inertinite/%</th>
<th>Type Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY1</td>
<td>J1-2</td>
<td>10</td>
<td>3</td>
<td>25</td>
<td>64</td>
<td>-72.25</td>
</tr>
<tr>
<td>DG1</td>
<td>J1-2</td>
<td>25</td>
<td>3</td>
<td>32</td>
<td>40</td>
<td>-37.5</td>
</tr>
<tr>
<td>XW1</td>
<td>K1</td>
<td>8</td>
<td>/</td>
<td>75</td>
<td>17</td>
<td>-65.25</td>
</tr>
<tr>
<td>JL1</td>
<td>K1</td>
<td>5</td>
<td>/</td>
<td>70</td>
<td>25</td>
<td>-72.5</td>
</tr>
<tr>
<td>YM1</td>
<td>K1</td>
<td>8</td>
<td>/</td>
<td>75</td>
<td>17</td>
<td>-65.25</td>
</tr>
</tbody>
</table>

The inertinite content of Jurassic samples high, and the sapropelinite groups are mostly hydrogen-poor amorphous components. These components have no fixed outline under fluorescence with a few brown vitrinite groups (Fig. 3a, Fig. 3b). The sapropelinite groups in the Cretaceous coal samples are also amorphous components under fluorescence and represent hydrocarbon-rich amorphous components. The dominant components of the Cretaceous coal samples are dark brown vitrinite groups with fixed outlines and are mostly translucent (Fig. 3c, Fig. 3d). Several transitional components are also found in the kerogen identification photomicrographs and are characterized as opaque, black and dark brown (Fig. 3). The results of 5 coal samples indicate that the organic matter sources are terrestrial higher plants with a small amount of aquatic lower organisms. There are more inertinite groups in the Jurassic samples, which have a strong degree of metamorphism, and the lignocellulosic components of higher plants are largely oxidized.

Fig. 3. Photographs of microscopic kerogen components
(a. BY1, under transmitted light; b. BY1, under fluorescence; c. YM1, under transmitted light; d. YM1, under fluorescence).
4.2 N-alkanes and isoprenoids

Because the coal samples in this study are at the stage of low maturity, with slight kerogen cracking hydrocarbon generation and degradation, the n-alkanes and isoprenoids of the coal samples provide a relatively accurate indication of the source and depositional environment. The odd-even predominance (OEP) of 5 samples ranges from 1.18 to 2.14, and the ratio is greater than 1 with an obvious odd carbon advantage (Table 4). The OEP results indicate that the organic matter is in the immature stage, which is consistent with the $R_o$ results. The ratios of pristane to phytane ($P/r/P_h$) of the samples are all greater than 1, and the maximum ratio reaches 9 (Table 4). Thus, the Pr content is significantly greater than the $P_h$ content. Based on the results of the saturated hydrocarbon gas chromatography experiment, the carbon numbers of the main peak are all higher than $C_{23}$ (Fig. 4), indicating a source of terrestrial organic matter, which is consistent with the identification results of kerogen components (Lu and Zhang, 2008). The organic matter has undergone decarboxylation transformation under the conditions of an oxidation environment, leading to the enrichment in odd-carbon n-alkanes and pristane. Therefore, the high OEP and $P/r/P_h$ values indicate that the environment of the depositional process was a strongly oxidizing environment. The indicators of $P_r/nC_{17}$ and $P_h/nC_{18}$ also indicate the characteristics of an oxidizing environment and terrestrial organic matter (Fig. 5).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CPI</th>
<th>OEP</th>
<th>$P/r/P_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY1</td>
<td>1.82</td>
<td>1.55</td>
<td>7.48</td>
</tr>
<tr>
<td>DG1</td>
<td>2.18</td>
<td>1.47</td>
<td>9</td>
</tr>
<tr>
<td>XW1</td>
<td>1.56</td>
<td>1.18</td>
<td>5.95</td>
</tr>
<tr>
<td>JL1</td>
<td>0</td>
<td>1.21</td>
<td>1.6</td>
</tr>
<tr>
<td>YM1</td>
<td>1.18</td>
<td>2.14</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Fig. 4. Gas chromatographic results for saturated hydrocarbons.
(a. DG1 coal sample, Jurassic; b. YM1 coal sample, Cretaceous)
4.3 Terpane and Hopane series

The relative content of the pentacyclic triterpene (hopane) series is higher than that of tricyclic terpane and tetracyclic terpane (Fig. 6). The carbon number distribution of the hopane series ranges from C_{27} to C_{35}, and the main peak carbon of the coal samples is 17α(H),21β(H)-C_{30} hopane (C_{30}αβ). The hopane series in coal- and coal-based mudstones generally have high Tm C_{29} and C_{31} contents relative to C_{30} (Lu and Zhang, 2008). Therefore, a high C_{30} content indicates that terrigenous sediments mixed with the coal during sedimentation. The relative contents of the compounds gradually decrease from C_{30} to C_{35}, indicating an oxidative depositional environment (Peters and Moldowan, 1991). A relatively high content of C_{30}H_{52} (gammacerane) is not found in the m/z 191 spectrogram, indicating a low-salinity depositional environment with no bacterial organic sources in the coal samples. The ratio of Ts/Tm and the content of tetracyclic terpane can be used as indicators for analyzing the degree of biodegradation (Huang et al., 1987; Bao and Zhu, 2008). The Tm values of four samples are larger than the Ts value because of the low tetracyclic terpane contents, indicating that the Mesozoic coal seams have a low degree of biodegradation. The lower tricyclic terpane contents of the coal samples indicate the samples are characterized by a low salinity, a low maturity and a high plant source input (Gao et al., 2009).
4.4 Sterane series

The relative content of regular steranes in the Mesozoic coal samples is high. The $C_{29}$ sterane is generally derived from the sterols in higher plants, whereas the $C_{27}$ sterane comes from lower aquatic organisms and marine algae (Huang and Meinschein, 1979). The $C_{29}$ sterane is dominant in four of the five samples, indicating that higher plants are the main organic matter source in the Mesozoic coal samples (Wang et al., 2017) (Fig. 7). In contrast, sample JL1 is dominated by $C_{28}$ (Fig. 7). In the continental sedimentary coal seam of the Cretaceous Damoguaihe Formation, the high content of $C_{28}$ may be related to the addition of phytoplankton during a transgression (Grantham and Wakefield, 1988; Cao et al., 2016). Similarly, the large amount of $C_{30}$ steranes in sample YM1 may also be the result of various transgressions events during the Cretaceous period in the study area (Hou and Wang, 1995). The relative content of diasterane is low in the Mesozoic coal samples (Fig. 7). The formation of diasterane is related to clay minerals and thermal catalysis, and the thermal stability of diasterane is stronger than that of regular sterane (Peters et al., 1990). Therefore, the low content...
of diasterane in Mesozoic coal samples indicates that the coal seam is in an immature to low-maturity evolutionary stage. The relative contents of pregnane and progesterone (L pregnane) in the five coal samples are low, indicating that the coal seam was deposited in a low-salinity environment (Fig. 7). The ratio of \( \frac{C_{29} \beta \beta}{(\alpha \alpha + \beta \beta)} \) ranges from 0.21 to 0.44 (Fig. 7), indicating a low-maturity stage for the Mesozoic coal samples (Didyk B.M., 1978; Goodarzi et al., 1989).

5 Discussion

Coal gas is natural gas produced by organic matter in coal seams (Tissot, B.P. and Welte, D. H., 1980). Considering the coalification stage, mode and formation mechanism of methane, coal gas can be divided into two types: biogenic origin and thermogenic origin. According to the coalification stage, biogenetic gas is further divided into protosomatic...
and secondary; thermogenic gas is further divided into early thermogenic gas and (narrowly defined) thermogenic gas. Thermogenic gas is the main source of coal gas. The gas source of low-degree coal gas reservoirs mainly comes from early thermogenic gas. Secondary biogenic gas is an important component of gas sources, and protosomatic biogenic gas is difficult to store (Lu and Zhang, 2008; Liu D. et al., 2016; Vandenbroucke M. and Largeau C., 2006).

The evaluation results of hydrocarbon source rock and molecular organic geochemistry show that the Mesozoic coal samples from the western Great Khingan Mountains have the characteristics of high organic matter abundance and low maturity. The coals were deposited in a low-salinity and strongly oxidizing terrestrial sedimentary environment. Higher plants and several algae were the main organic matter sources for the coal samples. The high content of higher plants produced a high degree of aromaticity in the organic macromolecules in the coal samples, forming a type of hydrogen-depleted organic matter. Therefore, gas is usually generated by coal, whereas oil is rarely generated by coal (Diechemann et al., 2006; Sun Yongge et al., 2013). Based on the evaluation criteria of the coal hydrocarbon generation potential, the TOC contents of the Mesozoic coal seams in the western Great Khingan Mountains are generally indicative of good source rocks (greater than 3%), and the hydrocarbon generation potential varies widely. The contents of chloroform asphalt “A” reach the coal source rock standard (Chen et al., 1997).

The natural gas generated by the Mesozoic coal seams is low-maturity gas. The low content of aquatic organisms and the weak biodegradation indicate that the low-maturity gas generated from the Mesozoic coal samples is mainly thermogenic gas. The high contents of organic carbon (TOC values generally greater than 18%) and the high contents of higher plants provided a hydrocarbon-generating basis for the formation of thermogenic gas. During the Cretaceous period, the sedimentary environment changed frequently due to the impact of transgressions. As a result, the coal seams affected by the transgressions have low hydrocarbon potential. Therefore, the TOC content of the Cretaceous coal seam samples are generally high (48%-66%), and the hydrocarbon generation potential varies greatly (1.09-152.71 mg/g). The organic matter type of the coal seam samples is type III, and the source is mainly higher plants. The peat swamp environments were relatively more stable in the Jurassic than in the Cretaceous. The organic matter from higher plants deposited in large quantities formed organic-rich coal seams with high TOC contents. The high TOC content and low hydrocarbon potential results indicate that the coal seams have generated large amounts of hydrocarbons. Thus, the Mesozoic coal seams in the western Great Khingan Mountains have a strong coal gas potential.

6 Conclusions

(1) The Mesozoic coal samples in the western Great Khingan Mountains are characterized by high organic matter abundances, with TOC contents greater than 30%. The organic matter type is mainly type III, and the Alatanheli Group and the Bayanhua Group have high hydrocarbon generation potential, while the Damoguahie Formation and Yimin Formation have low hydrocarbon generation potential. The maturity stage of the organic matter is at low.

(2) The vitrinite contents of the Cretaceous coal samples are greater than 70% and therefore dominate the composition of microscopic components, and the samples have no exinite content. The inertinite contents are higher in Jurassic coal samples, and its saprolite groups form a humus-type hydrocarbon-poor amorphous component. A large amount of oxidized wood fibers from higher plants constitute hydrocarbon-poor organic matter components in the coal samples.

(3) The results of the assessment of the molecular geochemical characteristics indicate that the coal seam samples were deposited in a continental, terrestrially sourced, oxidizing environment with a low salinity, and the samples exhibit a low maturity. The sources of the organic matter were mainly higher plants. The coal seams of the Damoguahie Formation and Yimin Formation in Cretaceous were sourced from a mixture of higher plants and phytoplankton because of transgressions.

(4) The natural gas generated from the Mesozoic coal samples in the western Great Khingan Mountains is mainly low-maturity gas with a thermal catalytic origin. The organic matter abundance and source of the coal seams play an active role in the formation of coal gas. The stability of the sedimentary environment is also a factor that determines the generation potential of coal gas.

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