Geochemical characteristics and origin of natural gas in the Paleogene of northern Bohai Bay Basin, northeast China

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Abstract. As one of the most important prolific basins in the northeast of China, the proven ration for natural gases in the Bohai Bay Basin is low. In order to figure out the genetic types and origins of natural gases in the Paleogene, a study on their geochemical characteristics (such as C1+, C1/C1+, C1/C2+3, δ13C1, δ13C2) and kinetic behaviour of the lacustrine source rock have been carried out. The relationship between carbon isotopes and components of gases shows that oil-associated gas and coal-derived gas with low mature are the most important types in our research area. The gases were mainly generated from the lacustrine source rocks with type II2-III kerogen. The pyrolysis experiment on the kerogen indicates that the Paleogene source rock entered the main gas window at the late Miocene.

1. Introduction
The Bohai Bay Basin located on the northeastern part of China, which is considered as an important petroliferous basin for its abundant petroleum deposits [1]. It consists of several sub-basins, namely the Liaohe, Liaodong Bay, Bozhong, Jiyang, Huanghua, Jizhong and Linqing sub-basins (Figure 1, [2]). As a rift basin developed on the basement of the North China Platform [3,4], it attracted geologists’ attention as early as the nineteenth century and presents great prospect for oil and gas, especially oil. However, it is believed that there’s significant potential for gas exploration even though few obvious developments have been obtained in it up to now. Therefore, it is important to better understand these gases’ genetic types and origins, in addition to the hydrocarbon generation of the source rocks. In this study, the molecular and stable carbon isotopic compositions analysis of natural gases from the north part of Bohai Bay basin (i.e. Jizhong, Liaohe and Huanghua sub-basins) and series pyrolysis experiments on kerogens prepared by lacustrine source rocks in closed gold tube pyrolysis were conducted.

2. Geological setting
It is well known that the tectonic evolution of the Bohai Bay since Cenozoic consists two main stages, the syn-rift stage (65.0-24.6 Ma) and the post-rift stage (24.6-0 Ma) [5-7]. The first stage is particularly crucial for exploration and development of oil and gas because most reserves were found in these syn-rift sediments deposited in lacustrine environment, including the Shahejie (Es) and Dongying (Ed) Formations. The research area is located in the northeastern part of basin (Figure 1), and the natural gas accumulations were mainly discovered in the sandstone reservoirs in Es1, Es2, Es3 and Ed layers [8].
3. Samples and methods

3.1. Samples
Gas and source rock samples were collected from these three sub-basins in this study. The samples of natural gas samples were taken from the current development wells. The massive source rocks of Shahejie Formation are the main source of natural gases in the Paleogene of the northern Bohai Bay basin [9]. Therefore, a lacustrine shale sample was acquired from the Es₃ Formation in Huanghua subbasin to represent as a classic source rock. This shale contains type II kerogen, it has a relatively low maturity with a $T_{\text{max}}$ value of 443°C, and has a relatively low organic matter abundance with a TOC content of 1.54 wt%.

3.2. Methods
All gas samples were analyzed to acquire molecular and stable carbon isotopes. The experimental procedure was depicted by Qin (2018) [10]. The pyrolysis experiments on the kerogen were completed using sealed gold tubes. And the detailed information about this kind of experiment and determination of pyrolytic products had been described by Xiong et al. (2016) [11].

4. Results and discussion

4.1. Geochemical characteristics of natural gas
The composition of natural gas from Paleogene in research area is dominated by hydrocarbon gases, varying from 89.95% to 99.49% with an average of 96.08% (Table 1). As the hydrocarbon gases is concerned, it is characterized by medium to high abundance of methane, ranging between 76.31% and 96.16%, and relatively high concentration of heavy hydrocarbon gases (C₂₅), varying from 1.11% to
21.04%. And the dryness coefficient of natural gas (C1/C1i) lies in 0.789 to 0.989, with an average of 0.885, meaning that the natural gas from Paleogene in the northern Bohai Bay Basin is mainly wet gas.

Table 1. Geochemical characteristics of natural gases from North-eastern Bohai Bay Basin

| Sub-basin | Well | Strata | Main molecular composition (%) | δ13C (%)VPDB |
|-----------|------|--------|-------------------------------|--------------|
|           |      |        | C1 | C2 | C3 | N2 | CO2 | C1/C1i | C1 | C2 | C3 | iC4 |
| Liaohe    | D40  | Es     | 87.02 | 7.90 | 2.57 | 0.77 | 0.88 | -38.9 | -25.9 | -24.7 | -27.2 |
|           | H26  | Ed     | 91.96 | 2.02 | 0.22 | 5.25 | 0.97 | -42.5 | -24.9 | -23.2 | -26.4 |
|           | H12-6| Ed     | 82.70 | 8.39 | 3.90 | 2.69 | 0.85 | -40.3 | -26.8 | -25.7 | -27.1 |
|           | R121-22C | Ed3 | 86.99 | 5.76 | 2.16 | 2.08 | 0.89 | -42.2 | -27.7 | -26.2 | -29.0 |
|           | T5   | Ed     | 85.72 | 4.78 | 2.88 | 3.10 | 0.88 | -34.9 | -26.1 | -25.0 | -27.0 |
|           | O26  | Ed     | 95.89 | 0.80 | 0.17 | 3.00 | 0.99 | -54.9 | -35.7 | -26.3 | -25.8 |
|           | X139 | Ed     | 96.16 | 0.98 | 0.05 | 2.42 | 0.99 | -44.8 | -25.7 | -14.0 | -28.1 |
| Ji zhong  | A56  | Es4    | 83.51 | 6.72 | 3.78 | 0.16 | 1.24 | 0.86 | -41.5 | -26.8 | -25.2 | -25.7 |
|           | J39  | Es4    | 78.45 | 9.58 | 7.58 | 2.37 | 0.03 | 0.79 | -44.8 | -28.0 | -25.1 | -24.7 |
|           | Q63  | Es3    | 76.31 | 5.23 | 4.66 | 5.42 | 1.99 | 0.85 | -51.5 | -29.3 | -28.4 | -27.9 |
|           | AT1X | O      | 79.73 | 6.75 | 2.27 | 2.22 | 6.58 | 0.88 | -38.1 | -25.2 | -23.3 | -25.5 |
|           | AT3  | O      | 81.82 | 6.47 | 2.18 | 1.83 | 5.44 | 0.88 | -37.5 | -26.3 | -24.3 | -26.4 |
| Huanghua  | BH2  | Es3    | 87.24 | 5.82 | 1.48 | 2.35 | 1.32 | 0.91 | -35.1 | -24.8 | -21.9 | -22.8 |
|           | BH24 | Ed     | 86.72 | 5.98 | 3.04 | 1.01 | 0.19 | 0.88 | -36.8 | -26.7 | -25.0 | -27.1 |
|           | Q8SX1| Es3    | 80.88 | 6.23 | 2.24 | 0.33 | 6.82 | 0.87 | -34.6 | -26.2 | -22.3 | -25.9 |
|           | BG1  | Es3    | 83.46 | 7.25 | 4.12 | 0.32 | 0.88 | 0.84 | -39.0 | -26.8 | -25.1 | -26.6 |
|           | BH28 | Es1    | 86.47 | 6.94 | 3.03 | 0.10 | 1.92 | 0.88 | -37.6 | -27.6 | -26.1 | -27.6 |
|           | BS22 | Es2    | 83.42 | 6.79 | 3.27 | 0.06 | 3.17 | 0.86 | -41.6 | -26.9 | -23.7 | -26.9 |

As for the stable carbon isotopes, a big difference exits in the value of methane (δ13C1). It varies from -54.9‰ to -34.6‰ with an average of -40.8‰ (Table 1). This characteristic indicates that these gases have multiple types. The carbon isotopes composition of ethane ranges from -35.7‰ to -24.8‰, and most samples have a ratio between -27.6‰ to -25.2‰. Furthermore, most samples show partial reversals between isotopes of propane and butane (δ13C1 < δ13C2 < δ13C3 > δ13C4). According to previous research, this feature stands for secondary alterations, such as biodegradation, mixing, or TSR effects [12,13].

4.2. Genetic type of natural gas

A set of geochemical database has been established by collecting the published data in order to analyze the genetic types and origins of natural gas in northern Bohai Bay basin. According to the relationship of Δδ13C1 vs. C1i/C2+3, these gases have various genetic types. Most samples are located in the area of oil-associated gas and condensate gas/coal-derived gas with low mature (Figure 2). In addition, some
samples from Jizhong subbasin and Liaohe subbasin are situated in the area of biogenic gas. And few samples lie in the area of coal-derived gas.

The relationship between $\delta^{13}C_1$ and $\delta^{13}C_2$ values can be used to distinguish natural gases of different genetic types. The result shows that most gases can be identified as coal-derived gases which are generated form type III kerogen, because the evolution trend of these samples is as the same as samples in Niger Delta and Sacramento Basin (Figure 3). On the other hand, only a few samples were generated from type II kerogen as they have a similar evolution trend with these of Delaware/val Verde basin [15].

4.3. Kinetic characteristics of hydrocarbon generation

All pyrolysis products were collected and quantified during the pyrolysis experiment, including $C_1$-$C_5$ gases, $C_6$-$C_{12}$ Light hydrocarbons (LHs) and liquid hydrocarbons (Figure 4). The results indicate that four main stages could be classified during the thermal evolution process of organic matters, corresponding to oil generation, condensate generation, wet gas generation, and dry gas generation, respectively. And 1.0%, 1.5% and 2.2% Easy Ro can be acted as the dividing line.

**Figure 4.** Yield curves of $C_1$-$C_5$ gaseous hydrocarbons and $C_6$-$C_{12}$ (LHs) generated from the artificial maturation of kerogen.

According to the geological heating rate of the research area, the kinetic parameters of hydrocarbon generation from kerogen were calculated and extrapolated to the geological condition (Figure 5). It shows that oil generation began as early as the Late Oligocene, and wet gas was generated from the late Miocene. According to exploration practice, most gas fields are located near the center of gas generation. Hence, the exploration potential of natural gas mainly counts on the development of source rocks, the organic matter abundance and thermal maturity for example. And other geological conditions such as cap rock sealing property and reservoir physical property are also critical to the formation of gas fields.

**Figure 5.** Transformation ratio vs. geological time by extrapolation. The geological heating rate is 3.5 °C/Ma.

5. Conclusions

The natural gases from northern Bohai Bay basin are mainly wet gases with gas dryness coefficients ranging between 0.789 and 0.989 with an average of 0.885. The stable carbon isotopes of methane ($\delta^{13}C_1$) vary from -54.9‰ to -34.6‰ indicating that there are various genetic types of natural gas in which oil-associated gas and condensate gas/coal-derived gas with low mature are the main two types.
The characteristics of carbon isotopes of $\delta^{13}C_1$ and $\delta^{13}C_2$ shows that these are mainly originated from type II - III kerogen. Hydrocarbon generation kinetics study on kerogen shows that wet gas was generated from the late Miocene. The development of source rocks, such as organic matter abundance and thermal maturity, is the main factor controlling the formation of gas field.

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