Multiple origins of the Paleogene natural gases and effects of secondary alteration in Liaohe Basin, northeast China: insights from the molecular and stable isotopic compositions

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Abstract: The molecular and isotopic (C and H) compositions of Paleogene [Shahejie Formation (E_{2-3s}) and Dongying Formation (E_{3d})] natural gases from 11 new gas samples as well as the data of 71 gases published from previous studies in the Liaohe Basin were analyzed, and the results were considered in combination with geochemical and distribution characteristics of the source rocks. The genetic type, gas–source correlation and secondary alteration of the natural gases were studied in detail, and the source rock maturities of the gases were estimated. The following conclusions were reached: (1) with the exception of dry gases in the major part of the third member of the Shahejie Fm. (E_{2s}³) reservoirs, the gases in other reservoirs are mainly wet; (2) variable carbon and hydrogen isotopes of the alkane gases are observed in different reservoirs of the basin with $\delta^{13}\text{C}_1$ values ranging from -60.7‰ to -34.2‰ , $\delta^{13}\text{C}_2$ from -47.3‰ to -22.3‰ , $\delta^2\text{H}_{\text{CH}_4}$ from -261‰ to -188‰ , and $\delta^2\text{H}_{\text{C}_2\text{H}_6}$ from -269‰ to -148‰ ; (3) the natural gases of the basin are of multiple origins, and mixing of thermogenic and microbial is observed — the mixing ratio in the first member of the Shahejie Fm. (E_{3s}¹) is the highest among all the reservoirs; (4) gases of different reservoirs suffered varying extents of biodegradation, which caused partial reversal of the carbon isotope series of methane and its homologues ($\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3 > \delta^{13}\text{C}_4$); the reversal of the gases in the shallow reservoirs (E_{3s}¹ and E_{3d}) is greater, while those in the deep reservoir (E_{2s}³) is less; (5) humic natural gases of the ED were mainly generated by source rocks at early maturity, while the sapropelic ones of the ED and WD were generated during the mature and high mature stages; (6) both the source rocks of E_{2s}³ and E_{2s}⁴ strata could contribute to the gas reservoirs of E_{2s}³ and E_{2s}¹ in the west depression. Sapropelic gases in east depression were generated by E_{2s}³ source rocks, while the other gases reservoired in the E_{2s}³, E_{3s}¹, and E_{3d} strata are probably sourced from the source rock strata of E_{2s}³ and E_{3s}¹⁻².

Keywords: Biodegradation; Origin; Gas-source correlation; Liaohe Basin; Mixing; Migration; Paleogene

Introduction

Natural gases have two genetic types: microbial or thermogenic. Microbial gas, which is mainly methane, is a product of biogeochemical processes associated with the remineralisation of labile organic matter at temperatures $<80\text{ }^{\circ}\text{C}$ by communities of microbes (Whiticar et al., 1986; Schoell, 1988; Whiticar, 1999; Huang et al., 2014). Microbial gas is characterized by a high dryness coefficient with $C_1/C_{1-5} > 0.95$ and is enriched in ^{12}C with $\delta^{13}\text{C}_1 < -55\text{ ‰}$, and it accounts for more than 20% of the world's gas (Rice and Claypool, 1981; Rice, 1993) and is considered to be one of the most important gas sources of gas hydrate (Collett, 2002). Thermogenic gas is generated by the degradation or cracking of organic matter (kerogen and oil) under high thermal stress (Stahl, 1977; Schoell, 1983; Dai et al., 1992). Thermogenic gas can be divided into two types: humic gas (generated by humic organic matter with kerogen type III) and sapropelic gas (generated by sapropelic organic matter with kerogen type I–II). The $\delta^{13}\text{C}_1$ value of thermogenic gas is often larger than -50 ‰ . When generated by a low maturity source rock, thermogenic gas is typically rich in heavy alkane gases (C_{2-5}); when generated by high-maturity source rocks, it has a high dryness coefficient. The carbon isotope values of the alkane gases of humic gas indicate enrichment in ^{13}C compared with those of sapropelic gases of similar maturity (Stahl, 1977; Dai et al., 1992; Galimov, 2006). The molecular and isotopic values of the gases can be affected by secondary alteration, including mixing, migration and biodegradation (Schoell, 1980, 1983; James, 1990; Dai et al., 1992; Whiticar, 1999; Martini et al., 2008; Hao et al., 2008; Osborn and McIntosh, 2010; Liu et al., 2013). Thus, isotopic values must be used to reliably identify the origins, sources and maturities of the gases.

Many previous works have studied the genetic types of the natural gases in the Liaohe Basin, and various genetic types (e.g. microbial gas, sapropelic gas, humic gas and mixed gas) have been identified (Xu et al., 1993; Liu et al., 1993; Zhang et al., 2002; Li et al., 2011; Huang et al., 2014; Li et al., 2015). Many of these previous studies focused on one oil and gas field or a local study area in the Liaohe Basin. However, the geochemical characteristics of the gases throughout the entire basin have not been deeply studied, and little has been reported on the effects of biodegradation, migration and mixing on the gases produced in different reservoirs of different

depressions. In this study, the molecular and stable isotopic compositions of the gases of the entire basin were studied comprehensively in combination with the Paleogene geological characteristics to determine the origins and sources of the gases in different reservoirs and depressions along with the effects of secondary alteration (e.g. biodegradation, migration and mixing). The findings of this work can significantly improve the understanding of the petroleum system and are beneficial to petroleum exploration in the Paleogene strata of the Liaohe Basin.

1 Geological setting

The geological setting of the petroleum systems of the Liaohe Basin has been summarized by numerous authors (e.g., Koopmans et al., 2002; Tuo et al., 2003; Fuhrmann et al., 2004; Huang et al., 2004; Hu et al., 2005; Li et al., 2013; Gu, 2016). The Liaohe Basin, located in northeast China, is one of the secondary tectonic elements of the Bohai Bay Basin groups (Fig. 1a). The Liaohe Basin is bounded by several structural elements: the Yanliao fold belt to the west, the Inner Mongolia axis to the north, the Liaodong anticline to the east, and the Liaodong Bay and Bohai Sea to the south (Fig. 1b). The basin is a Cenozoic rift basin developed after Mesozoic rifting and spans approximately 65 km in width and 470 km in length (Hu et al., 2005). The basin is subdivided into six structural units: the western uplift, central uplift, western depression (WD), eastern depression (ED), and the da'mintun depression. The WD and ED are separated by the central uplift (Fig. 1b). The three depressions were mostly isolated from each other during their development, and the tectonic and sedimentary differences among them caused the differences in their petroleum systems (Xu et al., 1993).

The thickness of the Cenozoic sedimentary layer is primarily 3000–4000 m, although some deep parts contain up to 6000 m of sediments. The Paleogene sediments mainly consist of clastic rocks with a few carbonates and volcanic horizons (Fig. 2). The Paleogene contains three formations, the Fangshenpao Fm. (E_1f), Shahejie Fm. (E_{2-3s}) and Dongying Fm. (E_3d) (Fig. 2, 3) and the oil and gas are mainly preserved in the Shahejie Fm. (Fig. 2) (Hu et al., 2005; Li et al., 2013). The Shahejie Fm. can be subdivided into four members; from oldest to youngest, they are the fourth member (E_{2s}^4), the third member (E_{2s}^3), the second member (E_{3s}^2) and the first member (E_{3s}^1). The ED was undergoing erosion during the E_{2s}^4 depositional period, and the E_{2s}^4 strata were only deposited in the WD. The sedimentary environment of the basin was deep-lake or semi-deep-lake during the E_{2s}^3 depositional period, and the E_{2s}^3 strata was distributed widely in

the basin (Zhang et al., 2002). Several source rocks developed in the basin (Fig. 2, Table 1); E_2s^4 and E_2s^3 are the major source units (Xu et al., 1993; Zhang et al., 2002; Hu et al., 2005; Li et al., 2013; Huang et al., 2014). The source rocks are mudstones and shales containing high contents of organic matter. Coal seams are also found in the E_2s^3 strata, and the vitrinite reflectance values (VR_o) of the ones in the WD are from 0.5% to 1.3%, while the ones in the ED are from 0.7%~1.3%. The E_2s^4 source rocks are sapropelic with mainly type II–I kerogen (oil prone) and their VR_o ranges from 0.5% to 2.0%. The E_2s^4 source rocks of WD began to generate hydrocarbon in the middle period during E_2s^3 deposition, and reach maturity (enter oil window) at the end of E_2s^3 period, and major part of the source rocks are mature to over mature stage at present. The kerogen types of the E_2s^3 source rock are different in the two depressions of the WD and ED. The former are mainly sapropelic with type I–II kerogen, whereas the latter are mainly humic with type III–IIkerogen (gas prone). The E_2s^3 source rocks of WD entered the oil window at the late period of the E_2s^3 , and most are mature to highly mature at present. (Xu et al., 1993; Zhang et al., 2002; Koopmans et al., 2002; Fuhrmann et al., 2004; Hu et al., 2005). In general, the evolution stages of the same source rock strata in the WD are earlier than the ones of ED, causing the present maturity values to be much greater than the latter. As a typical rifting basin, faults are very developed in the Liaohe basin (Fig.3), and hydrocarbons generated by the source rocks of different strata can migrate along the sands and the faults and accumulate in the reservoirs.

2 Material and methods

Eleven free gas samples were collected from the Liaohe Basin, and the molecular and stable isotopic compositions were calculated at the RIPED Key Laboratory of Petroleum Geochemistry (KLPG) of PetroChina. The previously published geochemical data for 71 wells of the basin were also used in this paper. The geochemical data are listed in Tables 2 and 3.

2.1 Analysis of molecular composition

An Agilent 6890N gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) was used to determine the molecular composition of gas samples. The hydrocarbon gas components were separated using a capillary column (PLOT Al_2O_3 , 30 m $\times$ 0.32 mm $\times$ 20 μ m). Helium was used as the carrier gas with a rate of 40 mL/min. The inlet temperature was set at 150 °C, and the TCD temperature was 200 °C. The initial oven temperature was maintained at

40 °C for 7.5 min isothermally and then rose from 40 °C to 90 °C at 15°C/min, finally from 90 °C to 180 °C at 6 °C/min. Peak areas were integrated, and the mole percent of the compositions is given. The precision of the analysis is 0.01%.

2.2 Stable carbon and hydrogen isotopic analysis

International standard gas samples NG1 (humic gas), NG2 (biogas), and NG3 (sapropelic gas) were co-developed by the Gas Accumulation and Development Laboratory, PetroChina Research Institute of Petroleum Exploration and Development (Langfang Branch) China, and foreign laboratories from USA and Germany (Dai et al., 2012), and were used for the carbon and hydrogen isotope ratio analysis here. The calibrated consensus values of NG1, NG2 and NG3 are:

NG1 (humic gas):

Methane: $\delta^{13}\text{C}_{\text{VPDB}} = -34.18 \text{ ‰} \pm 0.10 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -185.1 \text{ ‰} \pm 1.2 \text{ ‰}$

Ethane: $\delta^{13}\text{C}_{\text{VPDB}} = -24.66 \text{ ‰} \pm 0.11 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -156.3 \text{ ‰} \pm 1.8 \text{ ‰}$

Propane: $\delta^{13}\text{C}_{\text{VPDB}} = -22.21 \text{ ‰} \pm 0.11 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -143.6 \text{ ‰} \pm 3.3 \text{ ‰}$

i-Butane: $\delta^{13}\text{C}_{\text{VPDB}} = -21.62 \text{ ‰} \pm 0.12 \text{ ‰}$

n-Butane: $\delta^{13}\text{C}_{\text{VPDB}} = -21.74 \text{ ‰} \pm 0.13 \text{ ‰}$

CO₂: $\delta^{13}\text{C}_{\text{VPDB}} = -5.00 \text{ ‰} \pm 0.12 \text{ ‰}$

NG2 (biogas):

Methane: $\delta^{13}\text{C}_{\text{VPDB}} = -68.89 \text{ ‰} \pm 0.12 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -237.0 \text{ ‰} \pm 1.2 \text{ ‰}$

NG3 (sapropelic gas):

Methane: $\delta^{13}\text{C}_{\text{VPDB}} = -43.61 \text{ ‰} \pm 0.09 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -167.6 \text{ ‰} \pm 1.0 \text{ ‰}$

Ethane: $\delta^{13}\text{C}_{\text{VPDB}} = -40.24 \text{ ‰} \pm 0.10 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -164.1 \text{ ‰} \pm 2.4 \text{ ‰}$

Propane: $\delta^{13}\text{C}_{\text{VPDB}} = -33.79 \text{ ‰} \pm 0.09 \text{ ‰}$, $\delta^2\text{H}_{\text{VSMOW}} = -138.4 \text{ ‰} \pm 3.0 \text{ ‰}$

An on-line method was used to measure the carbon and hydrogen isotopic compositions of natural gas. The stable carbon and hydrogen isotopic values are reported in ‘ δ ’ notation in per mil (‰). The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values were measured and expressed relative to the Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW) scale, respectively. The measurement tolerances of the carbon and hydrogen isotopic values are $\pm 0.3 \text{ ‰}$ and $\pm 3 \text{ ‰}$, respectively. Specific procedures of the measurement are as follows.

Stable carbon isotope ratios were determined using a Finnigan MAT Delta S mass spectrometer interfaced with an HP 5890II chromatograph. The gas components were separated on the gas chromatograph in a stream of helium, converted into carbon dioxide in a combustion interface, and then introduced into the mass spectrometer. Alkane gases (C_1 – C_5) and carbon dioxide were initially separated using a fused silica capillary column (PLOT, 30 m $\times$ 0.32 mm). The helium was used as the stream gas with flow rate of 10 mL/min. The inlet temperature was 150 °C, the temperature of oxidation oven was 950 °C. The GC oven temperature was ramped from 35 °C to 80 °C at 8 °C/min and then to 260 °C at 5 °C/min; the oven maintained this final temperature for 10 min. Each gas sample was analyzed three times, and the average was calculated.

Hydrogen isotopic ratio was determined on a MAT253 isotopic mass spectrometer (Thermo Fisher Scientific) equipped with a Trace GC UltraTM using the gas chromatography pyrolysis interface and the water removal device. The helium was used as the stream gas, and an HP-PLOT Q column (30 m $\times$ 0.32 mm $\times$ 20 μ m) was used with flow rate of 1.4 mL/min. The inlet temperature was set at 180 °C. The gas was injected into the gas chromatograph in split injection model (split ratio = 1:7). The oven temperature was initially set at 40 °C, and maintained for 5 min, ramped to 40–80 °C at 5 °C/min, 80–140 °C at 10 °C/min, and 140–260 °C at 30 °C/min. The pyrolysis oven temperature was 1450 °C.

3 Results

3.1 Molecular composition of natural gas

The Paleogene natural gases are dominated by methane with various contents of heavy alkane gases (C_2 – C_5) (Tables 2 and 4, Fig.4). The average content of methane in the ED decreases from the E_2s^3 to the E_3s^1 reservoirs and then to the E_3d reservoirs (Table 4, Fig. 4a); the average content of heavy alkane gases shows the opposite trend (Table 4). In general, much more variable contents of the molecular compositions are found in the ED than the ones of WD, especially for the ones of methane and ethane (Fig.4)

The dryness coefficients (C_1/C_{1-5}) of the gases in the same reservoirs of the Liaohe basin decrease with increasing depth (Fig. 5a). According to Schoell (1980) a gas may be classified as dry if it exhibits a dryness coefficient greater than 0.95. The gases preserved in the E_3d Fm.

reservoir are mainly wet gases. The gases of the E_3s^1 reservoir in the WD are slightly dryer than those of E_3s^1 reservoir in the ED. The gases in the E_2s^3 reservoirs of the ED are mainly dry and the ones of WD are mainly wet (Table 4).

Carbon dioxide and nitrogen are the main non-hydrocarbon gases, and the content of each is generally lower than 5 % (Tables 2 and 4). In general, the content of nitrogen is higher than that of carbon dioxide. The contents of the non-hydrocarbons in the WD are higher than those in the ED.

3.2 Stable isotopic composition of natural gas

3.2.1 Carbon isotopes of the alkane gases and the carbon dioxide

No apparent correlations have been found between the carbon isotopic compositions of the alkane gases and the depth except for the ones of the $\delta^{13}C_2$ values of the ED (Fig.5). In the individual fields trends are more obvious. The $\delta^{13}C_1$ values of Dongying Fm. in the Niuju field show good positive correlation with depth. The $\delta^{13}C_2$ and $\delta^{13}C_3$ values of Dongying Fm. and E_3s^1 in the Rongxingtun field of ED also show positive correlations. Carbon isotopic compositions of the alkane gases reservoired in E_2s^3 in Lengjiapu oil field show no trend at all with depth but generally $\delta^{13}C_1$ is less scattered than in E_3s^1 of Lengjiapu oil field.

Significant variations are observed in the carbon isotopic compositions of the natural gases in the Liaohe Basin, particularly for the gases in the E_3s^1 reservoirs throughout the entire basin and for the gases in the E_2s^3 reservoirs in the ED (Tables 3 and 4; Fig. 5 and 6). The differences among the $\delta^{13}C$ values of methane in different gases are the most obvious. The $\delta^{13}C_{2-4}$ values of different gases also have a large range. The carbon isotope curves of the alkane gases in the E_3d reservoirs of the ED are also very similar, even though their $\delta^{13}C_1$ values differ by up to 10 ‰.

Carbon isotope reversals between propane and butane ($\delta^{13}C_3 > \delta^{13}C_4$) are common in the Paleogene gases of the Liaohe Basin. These reversals are only observed in the $\delta^{13}C$ values of the two alkane gases (Table 3, Fig. 6a, b, c and d). Because some of the alkane gas $\delta^{13}C$ values were not determined, only nine gases of the E_3d reservoirs in the ED have the carbon isotopic values from methane to butane ($\delta^{13}C_{1-4}$), and seven of them have the carbon isotope reversal exhibiting a reversal ratio of 77.8 % (reversal ratio=number of the gas samples with reversed isotopes/ total gas numbers of the same strata×100%). The reversal ratios of the E_3s^1 reservoirs in the ED and WD are 63.6 % and 57.1 %, respectively. The reservoirs with smaller burial depths have greater carbon isotope reversal ratios, whereas deeply buried reservoirs exhibit lower reversal ratios. For example,

the ratios of the E_2s^3 gases in the ED and WD are only 25 % and 44.4 %, respectively. The reversal ratios of the gases in E_3d and E_3s^1 in the ED are higher than those in the WD, while the reversal ratios of the gases in the E_2s^3 exhibit the opposite trend. The extent of reversal between the $\delta^{13}C_3$ and $\delta^{13}C_4$ values of the gases in the E_3s^1 and E_2s^3 reservoirs in the WD increases with decreasing depth (Fig. 6a and b); The extent of reversal between the $^{13}C_3$ and $^{13}C_4$ values of the gases in the Ed Fm. is larger than the ones in the E_3s^1 and E_2s^3 reservoirs in the ED (Fig. 6c, d and e).

Variable $\delta^{13}C_{CO_2}$ values are found in the gases of different Paleogene reservoirs in the Liaohe Basin (Tables 3 and 4). Generally, the $\delta^{13}C_{CO_2}$ values of the gases in the ED are much more negative than those in the WD, and the variations in $\delta^{13}C_{CO_2}$ are less obvious in the ED than in the WD.

3.2.2 Hydrogen isotopes of the alkane gases

The differences of the δ^2H values of methane among the E_3s^1 and E_2s^3 reservoirs of the WD are not obvious, whereas the differences in the δ^2H values of ethane and propane of different gases reservoid in the E_3s^1 and E_2s^3 are much more apparent (Tables 3 and 4; Fig. 7a and b). The trends of the curves for the hydrogen isotope values of methane and its homologues in the E_3s^1 reservoirs are similar, whereas those of the E_2s^3 reservoirs display two obviously different styles (Fig. 7a and b).

The δ^2H values of the methane and ethane of the E_3d reservoirs in the ED are distributed in a narrow range excepting the gas in well R161-25 of Rongxingtun oil and gas field, whereas those of propane are distribute widely (Fig. 7c). The curve styles for the hydrogen isotope values of methane and its homologues in the E_3d reservoirs in the ED are similar (Fig. 7c), and the hydrogen isotope values of the alkane gases in the E_3s^1 and E_2s^3 reservoirs both exhibit wide distributions (Fig. 7d).

The δ^2H values of the alkane gases in the E_3s^1 and E_2s^3 reservoirs in the WD decrease with increasing depth (Figs. 8a, b and c). The $\delta^2H_{CH_4}$ values in the E_3s^1 and E_3d reservoirs in the ED increase with increasing depth, whereas those of methane in the E_2s^3 reservoirs show no clear correlation with depth (Fig. 8a). The $\delta^2H_{C_2H_6}$ values in the E_3d , E_3s^1 and E_2s^3 reservoirs of the ED all decrease with increasing depth, although a few values in the E_3s^1 do not follow this trend (Fig. 8b). No obvious correlation between the $\delta^2H_{C_3H_8}$ values with depth is observed in the ED (Fig.

8c).

4 Discussion

4.1 Genetic types of the natural gases

Chung et al. (1988) suggested that in an unaltered gas, co-generated components will exhibit linearity in the isotope type curve (Fig. 6). The isotope type curves of the gases in the E_3s^1 and E_2s^3 reservoirs in the WD and in the E_3d and E_3s^1 reservoirs in the ED do not display linearity, indicating that these gases are mixtures of gases of different genetic types or result from alteration within the reservoir. The Paleogene gases of the Liaohe Basin are all organic gases, and most are thermogenic (Figs. 9 and 10). A few of the gases in the E_3s^1 reservoirs are mixtures of microbial and thermogenic gases, as shown in Fig. 9. Fig.10 displays the genetic types of the gases of the basin, and the identification results of the gas types made by it are very similar to the ones made using Fig. 9, except that some gases in the E_2s^3 reservoirs in the WD experienced a little mixing with microbial gas. Gases reservoired in the E_2s^3 and E_3s^1 strata in WD with $\delta^{13}C_{CO_2} > +2\text{‰}$, and isotopically light methane ($\delta^{13}C_1 < -50\text{‰}$) (Fig. 10) indicate that the methanes are of secondary microbial methane which were generated from CO_2 reduction under anaerobic conditions.

The $\delta^{13}C$ value of ethane is commonly used to differentiate humic gas from sapropelic gas, with the empirical value of -28‰ usually being the distinguishing value ($\delta^{13}C_2 < -28\text{‰}$ indicates sapropelic gas, and $\delta^{13}C_2 > -28\text{‰}$ indicates humic gas) (Dai et al., 1992; Dai., 2011; Liang et al., 2002; Liu et al., 2008, 2011; Xu and Shen, 1996). The $\delta^{13}C$ values of ethane in the WD are generally less than -28‰ (Fig. 5c, Fig. 6a and b), indicating that the majority of these gases are sapropelic gases. The $\delta^{13}C$ values of ethane in the E_3d reservoirs of ED are mainly greater than -28‰ (Fig. 5c and Fig. 6c), suggesting that these are mainly humic gases. Some of $\delta^{13}C_2$ values of the gases in the E_3s^1 and E_2s^3 reservoirs of ED are less than -28‰ , while some are greater than -28‰ , indicating that both sapropelic and humic gases are present in these two reservoirs. The $\delta^{13}C_2$ value of the gases in the KH8 well of the E_3d reservoir in the offshore Kuihuadao oil field is -26.6‰ , indicating typical humic gases.

$\delta^{13}C_1$ versus $\delta^{13}C_2$ diagrams are often used to identify gas types of different origins (Fig. 11) (Jenden et al., 1988; Dai and Qi., 1989; Rooney et al., 1995; Berner and Faber., 1996; Tilley and Muehlenbachs, 2006). The gases in the E_3d reservoirs in the ED distribute along the trend of gases generated by type III kerogen, indicating that the gases are mainly humic gases. The gases of other

reservoirs are widely distributed; some of them distribute along the trend of type III kerogen, while others distribute along the trend of type II kerogen (Fig. 11), suggesting that both sapropelic and humic gases are present in these reservoirs. The $\delta^{13}\text{C}_2$ values in the WD are generally more negative than those in the ED, indicating that the gases of the two depressions have different sources; the gases of the WD were generated by source rocks with much more negative carbon isotope values, which is of type I-II probably.

The $\delta^{13}\text{C}_1$ versus $\text{C}_1/\text{C}_{2+3}$ diagram can also identify microbial gas and mixed gas (Fig. 12) (Whiticar, 1999). Fig. 12 indicates that the gases of the E_2s^3 and E_2s^4 reservoirs in the Lengjiapu oil field in the WD mainly distribute along the trend of type II kerogen, suggesting that the gases are mainly sapropelic ones. The gas in the X10 well of the E_2s^3 reservoir in the Yulou oil and gas field (ED) is mainly microbial gas with very negative $\delta^{13}\text{C}_1$ values. The gases in the E_3d reservoirs in the ED are mainly humic gases with a few sapropelic gases. Many of the gases in the E_3s^1 reservoirs of the entire basin and the E_2s^3 reservoirs of the ED are mixtures of thermogenic and microbial gases, and the mixing ratios of the gases in the E_3s^1 reservoirs are much greater than those of the E_2s^3 gases. The sapropelic gases of the E_3s^1 reservoirs in the ED are mainly distributed in the Rehetai and Qinglongtai oil and gas fields, whereas the humic gases of the E_2s^3 reservoirs (ED) are mainly distributed in the Dapingfang and Yushutai oil and gas fields; the gases of the E_2s^3 reservoirs of other fields in the ED are mainly sapropelic gases (Table 2, Table 3 and Fig. 12).

4.2 Mixing ratios of microbial and thermogenic gases

Microbial gases are characterised by depleted methane $\delta^{13}\text{C}$ values ($-60\text{‰} \sim -100\text{‰}$) (Schoell, 1980; Whitchar, 1999; Valentine et al., 2004). The methane $\delta^{13}\text{C}$ values of thermogenic gas in the Liaohe Basin are approximately -40‰ (Figs. 5a and 11); thus, -60‰ and -40‰ were chosen as the $\delta^{13}\text{C}$ values of microbial and thermogenic gases, respectively, to estimate the mixing ratio.

The methane $\delta^{13}\text{C}$ values of the gas in the E_3s^1 reservoirs range from -50.5‰ to -55.4‰ in the Lengjiapu oil field in the WD, and the microbial gas accounts for 50 % to 75 % of the whole gas. The contributions of microbial gas are all below 15% in the other gases in the E_3s^1 reservoirs of the field.

The methane $\delta^{13}\text{C}$ values of the E_3s^1 reservoir in the Qinglongtai oil and gas field (ED) range

from -52.0‰ to -55.5‰ , and the microbial gas ratios are 60 % to 75 %. The percentage contribution of microbial gas to total volume in the Y9 well from the E_3s^1 reservoir in the Yulou oil and gas field reaches 60 %. The methane $\delta^{13}C$ values of the L12 well in the E_3s^1 reservoir of the Oulituozi field is -60.1‰ , and the gas is typical microbial gas. Methane $\delta^{13}C$ values of the gas in the E_3s^1 reservoir of well RQ2 and R44, Rehetai field are -49.4‰ and -53.5‰ , and the contribution of the microbial gas are approximately 45 %, and 65 %, respectively. Except the above-mentioned gases, the contributions of microbial gas to the gases of other wells in the E_3s^1 reservoir in the ED are very low ($< 15\%$), and most of the gases are purely thermogenic.

A few gases in the E_2s^3 reservoirs of the ED have some microbial gas contribution, including gases in the R20–11 well in the Rehetai field, the L26–20 and L25–16 wells in the Qinglongtai field; the methane $\delta^{13}C$ values of these three wells are -49.6‰ , -47.9‰ , and -50.6‰ , respectively, and the corresponding contributions of microbial gas to these four gases are 50 %, 40 % and 55 %, respectively. The gas reservoired in the E_2s^3 of the X10 well in the Yulou field has a methane $\delta^{13}C$ value of -59.3‰ , and the contribution of the microbial gas is more than 95% (Fig.12).

4.3 Effects of biodegradation

The effects of biodegradation on the carbon isotopic compositions of gases have been comprehensively studied. The preferential removal of isotopically light components is known to result in somewhat higher $\delta^{13}C$ values in the residual gas (Fuex, 1977; Coleman and Risatti., 1981; Rice and Claypool, 1981; Katz et al., 2002; Dai et al., 2004). Among the wet gases, ethane is more resistive to biodegradation compared to other gases, and propane is typically the first gas to undergo biodegradation, likely because propane is the first and most water-soluble *n*-alkane to have a secondary carbon, which is the position that is primarily attacked in anaerobic alkane activation during biodegradation (Fuex, 1977; James and Burns, 1984; Xu et al., 1997; Head et al., 2003; Dai et al., 2004; Larter et al., 2005). The $\delta^{13}C_3$ values are greater than the $\delta^{13}C_4$ values for some of the gases in the E_3s^1 and E_2s^3 reservoirs of the Lengjiapu oil field in the WD (Fig. 6a, 6b and 13) and in the E_3d and E_3s^1 reservoirs in the ED (Figs. 6c, 6d and 13), indicating that these gases underwent biodegradation. The extent of the reversal of carbon isotopes in the gases of the E_2s^3 reservoir (ED) is lower than that of the E_3d gases (Fig. 6e), suggesting that the E_2s^3 gases experienced less biodegradation than the E_2d gases. Normal alkanes are more susceptible to

biodegradation than the corresponding *iso*-alkanes, and the iC_4/nC_4 ratio, which is a good indicator of gas biodegradation, increases significantly with increasing extent of biodegradation (James and Burns, 1984; Horstad and Larter, 1997; Pallasser, 2000; Larter and di Primio, 2005). The iC_4/nC_4 ratio for non-degraded gas samples is typically < 0.8 , while the ratio for biodegraded samples can be up to 1.75; furthermore, a positive correlation between the C_2/C_3 and iC_4/nC_4 ratios can indicate biodegradation (Huang et al., 2004). The gases in the E_{3d} reservoirs in the ED experienced intense biodegradation ($0.75 < iC_4/nC_4 < 2.75$, $C_2/C_3 > 1.0$), while the gases of the E_{3s}^1 reservoirs in the WD experienced weaker biodegradation ($0.55 < iC_4/nC_4 < 1.67$, $0.26 < C_2/C_3 < 2.33$). The extent of biodegradation was lowest for the gases in the E_{3s}^1 and E_{2s}^3 reservoirs in the ED (Fig. 14). The iC_4/nC_4 values should increase with increasing thermal maturity (Durand and Espitalié, 1972; Hunt, 1984). Because the gases in the E_{3s}^1 and E_{2s}^3 reservoirs are buried much deeper than the ones of the E_{3d} , and consequently the iC_4/nC_4 values of the E_{3s}^1 and E_{2s}^3 reservoirs would be much greater than the ones of E_{3d} in usual. However, the fact is that the iC_4/nC_4 values of the E_{3s}^1 and E_{2s}^3 are much less than the ones in the E_{3d} , indicating the gases in the latter reservoirs of the ED experienced intense biodegradation.

The reversal of carbon isotope values in alkane gases may be caused by (1) mixing of biogenic and abiogenic gas; (2) mixing of a humic gas with a sapropelic gas; (3) mixing of gases of the same type from different sources, or gases from the same source generated in different episodes (Berner and Faber, 1988; James, 1990; Dai et al., 2004); (4) biodegradation of certain gas components (James and Burns, 1984; Dai et al., 2004). The reversal of the carbon isotopic trends of the alkane gases ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 > \delta^{13}C_4$) in the Liaohe Basin is mainly caused by the biodegradation of propane. Since multiple gas types are found in the basin, the mixing of different kinds of thermogenic gases causing the reversion of carbon isotopic composition cannot be excluded.

4.4 Thermal maturity

The $\delta^{13}C$ values of alkane gas increase with increasing thermal maturity (vitrinite reflectance, VR_o), and many relationships have been proposed in past reports (Stahl and Carey, 1975; Stahl, 1977; Schoell, 1983; Berner and Faber, 1988; Dai and Qi, 1989). The mixing of the microbial and thermogenic gases would cause the methane $\delta^{13}C$ value to be much more negative; consequently, the value of R_o estimated using the $\delta^{13}C$ - VR_o relationship would be unrealistic (Katz et al., 2002;

Martini et al., 2008; Faber et al., 2015). Faber et al (2015) proposed using the bulk carbon isotopic compositions of the methane, ethane, and propane with different kerogen types to estimate the maturity at time of formation of the gas, and this method is used in this work (Fig. 15).

As discussed above, gases produced from the E_3s^1 reservoir in some wells of Qinglongtai field (well LQ4, LQ5, L9, L14-21, and L 20-21), Yulou Field (well Y9), Oulituozi field (well L12), Huangjindai field (H34), and Rehetai field (well R44 and RQ2), and the gases of E_2s^3 reservoir in Rehetai field (well R22-11), and Qinglongtai field (well L25-16 and L26-20) in ED are mixtures of microbial gas and thermogenic gas. Thus, these gases have to be excluded from the maturity evaluation.

Gases in the E_2s^3 reservoirs of well O6, O13 of Oulituozi field and well H202 of Huangjindai field of ED are oil associated gases, and the VR_o values of them are about 1.3 %~1.5 % (Fig. 15), indicating they were generated by the mature to highly mature sapropelic source rocks. The gas in the E_3s^1 of well Y4-2 of Yulou field of ED is oil associated, with a VR_o value of 1.2 %. Excepting the gases produced from the previous four wells, the ones reservoir in the E_3d , E_3s^1 and E_2s^3 reservoirs of ED are mainly of humic gas type, most of whose VR_o values are less than 1.0 % (Fig. 15), indicating they were generated in the early mature to mature stage by humic source rocks.

Gases reservoir in the E_3s^1 and E_2s^3 formations of Lengjiapu oil field of WD are mainly oil associated gases except for a few that are mixed with microbial gas in E_3s^1 . The VR_o values of the sapropelic gases in the E_3s^1 reservoir of Lengjiapu oil field are from 1.3 % to 1.7 % (Fig. 15), while the ones in the E_2s^3 reservoir are from 0.7 % to 1.2 % (VR_o ; Fig. 15). The gas produced from the E_2s^4 reservoir of the well Q4 in Qijia field of WD has a VR_o value of about 1.3 %.

4.5 Gas-source correlation

Since the Liaohe basin is a rift basin with well-developed faults vertically connecting different source rock strata (Fig. 3), hydrocarbons generated by different source rocks could mixed together in the same reservoir (Zhang et al., 1995; Chen et al., 1998; Koopmans et al., 2002). In this work, only molecular and isotopic compositions of the gases combined with thermal history of the potential source rocks are used to identify the gas-source correlations. Much additional work is needed to evaluate correlation possibilities in full.

As discussed above, the thermogenic gases in the E_3s^1 and E_2s^4 of WD were generated by highly mature source rocks. Most of the source rocks of E_2s^4 of WD are highly mature to over

mature at present (Zhang et al., 2002; Hu et al., 2005) and the gases in the E_3s^1 and E_2s^4 of WD would probably be derived from the E_2s^4 sapropelic source rocks. Because part of the E_2s^3 source rocks of WD are highly mature at present, its contribution to the gas accumulation of the E_3s^1 reservoir cannot be excluded. Thermogenic gases reservoired in E_2s^3 of WD were generated by mature source rocks. This is consistent with the thermal maturity of the E_2s^3 source rocks ($0.5 \% < VR_o < 1.3 \%$, Table 1), so the gases were probably generated by the E_2s^3 source rocks.

The sapropelic gases reservoired in the E_2s^3 and E_3s^1 strata of ED were derived in the highly mature stage, which is coincident with the thermal maturity of the E_2s^3 source rocks ($0.7 \% < VR_o < 1.3 \%$, Table 1), and the gases were probably generated by the E_2s^3 source rock strata. The origins of the remaining thermogenic gases of ED are not easy to determine because the E_2s^3 and E_3s^{1-2} source rocks could both generate early mature gases, and the gases generated by the two source rocks could migrated along the faults and accumulate together in the same reservoir, so both of these two source rocks strata could contribute to the gas reservoirs.

Gases with $\delta^{13}C_{CO_2} > +2 \text{ ‰}$ and isotopically light methane ($\delta^{13}C_1 < -50 \text{ ‰}$) were generated from CO_2 reduction under anaerobic conditions (Huang et al., 2014), while the ones with negative $\delta^{13}C_{CO_2}$ isotopes and isotopically light methane ($\delta^{13}C_1 < -50 \text{ ‰}$) were probably generated by acetate-type fermentation. Most of the reservoir depths of the gases with microbial gas mixed are less than 1800m (Table 2), and these reservoir temperatures are less than 80 °C. Under such condition, the microbial methane would be formed when the organic matter experienced acetate fermentation (Whiticar, 1999). The source rocks might be very close to the reservoirs making the microbial gas migrate and accumulate easily.

5 Conclusions

Using the analysis of the molecular and isotopic (C and H) compositions of the Paleogene natural gases as well as the source rock characteristics of the Liaohe Basin, the genetic origins, maturities, secondary alteration and gas-source correlations of the gases were studied. The main conclusions are listed below.

a. The natural gases of the Liaohe Basin are mainly wet gases, with the exceptions of the dry ones in the E_2s^3 reservoirs of the ED. Methane is the dominant alkane component. Nitrogen and carbon dioxide are the two main non-hydrocarbons, and the contents of both are generally less than 5%.

b. The carbon and hydrogen isotopic values of the alkane gases have wide distributions, and except for the ones of the $\delta^{13}\text{C}_2$ values of the ED, the isotopic values of other alkane components do not display clear correlations with depth due to the influences of maturity, migration and mixing.

c. Multiple genetic gas types are found in the basin, including thermogenic gas (sapropelic gas, humic gas), microbial gas and mixed gas. The gases in the E_2s^3 and E_2s^4 reservoirs in the Lengjiapu oil field are mainly sapropelic gases, whereas the gas in the L12 well (E_3s^1 reservoir) of Oulituozi field and the well X10 (E_2s^3 reservoir) of the Yulou field in the ED are microbial. The gases in the E_3s^1 reservoir in the WD and the E_2s^3 reservoirs in the ED are of multiple genetic types, and a mixture of thermogenic and microbial is observed. Microbial gas accounts for 50 % to 75 % of the mixed gases in the E_3s^1 reservoirs in the WD, while it accounts for 40 % to 75 % of the mixed gases in the E_3s^1 reservoirs in the ED.

d. The natural gases in the E_3d reservoirs of the ED experienced substantial biodegradation, much more extensive than in the E_3s^1 reservoirs of the WD and in the E_3s^1 and E_2s^3 reservoirs in the ED. A reversal of the carbon isotopic trends ($\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3 > \delta^{13}\text{C}_4$) can be found in different reservoirs of the basin and is mainly caused by the biodegradation of propane. The reversed trends in the shallow reservoirs (E_3d and E_3s^1) are greater than in the deep ones (E_2s^3).

e. The humic natural gases of the ED were mainly generated by source rocks at the early mature stage, while the sapropelic ones of the ED and WD were generated during the mature to highly mature stages.

f. Both E_2s^3 and E_2s^4 source rocks could contribute to the gas reservoirs of E_2s^3 and E_3s^1 in the WD; sapropelic gases in ED were generated by E_2s^3 source rocks, while the other gases reservoired in the E_2s^3 , E_3s^1 , and E_3d strata of ED are probably sourced from E_2s^3 and E_3s^{1-2} .

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Table 1. Geochemical characteristics of the Paleogene source rocks in the Liaohe Basin (Zhang et al., 2002; Hu et al., 2005; Gu, 2016)

Items	Western Depression				Eastern Depression		
	Main source rocks		Secondary source rocks		Main source rocks	Secondary source rocks	
Strata	E ₂ s ⁴	E ₂ s ³	E ₃ s ¹⁻²	E ₃ d	E ₂ s ³	E ₃ s ¹⁻²	E ₃ d
Area of source rock (km ²)	2399.1	2310.8	2119.9	1742	2596.8	3002.9	3290
Thickness (m)	255	522	252	438	238	238	387
TOC range /average (%)	0.5-6.0/ 2.83	0.5-5.0/ 1.99	0.5-3.0/ 1.85	0.5-3.2/ 1.07	0.5-3.0/ 1.94	0.5-2.0/1.09	0.3-0.5/ 0.38
Kerogen type	dominate in II-I	dominate in I-II	I, II, III	dominate in II -III	dominate in II-III	dominate in III-II	III-II
Maturity (R _o , %)	0.5-2.0	0.5-1.3	0.5-0.8	0.5-0.6	0.7-1.3	0.5-0.7	<0.5

Table 2. Molecular composition of the Paleogene natural gases in the Liaohe Basin

Depression	Oil+gas field	Well	Reser- voir	Depth (m)	Main component (%)						Dryness	Data source	
					CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> C ₄ H ₁₀	<i>n</i> C ₄ H ₁₀	CO ₂	N ₂		C ₁ /C ₁₋₅
Eastern	Huang Jindai	H23	E ₃ d	1644.4-1786.0	94.99	4.30	0.31	0.17	0.06	n.d.	0.02	0.951	This paper
		H23	E ₃ d	1700-1786	93.93	4.93	0.14	0.04	0.05	0.07	0.78	0.948	Li et al., 2015
		H26	E ₃ d	1578.2-1702.0	95.59	3.43	0.35	0.10	0.06	n.d.	0.41	0.960	This paper
		H26	E ₃ d	1678.0-1770.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
		H105	E ₃ d	1335.0-1354.0	99.84	0.11 (C ₂ -C ₄)				0.00	0.05	0.999	
		H11-10	E ₃ d	2064	91.33	2.94	2.39	2.57 (<i>i</i> C ₄ - <i>n</i> C ₄)		n.d.	1.24	0.920	Chen et al., 1998
	Niuju	N13	E ₃ d	1793.4-1827.8	96.83	1.67 (C ₂ -C ₄)				0.00	1.46	0.983	Zhang et al., 1995
		N21-020	E ₃ d	1688.4-1978.1	96.38	2.33	0.61	0.25	0.16	0.07	0.03	0.966	This paper

Eastern		N22-020	E ₃ d	1688.0-2023.6	94.48	3.32	0.94	0.29	0.19	0.10	0.55	0.952	Li et al., 2015
		N22-320	E ₃ d	1706.6-1773.0	98.53	1.01	0.20	0.08	0.05		0.08	0.987	
		N22-022	E ₃ d	1894-1908	87.74	8.26	1.28	0.14	0.44	0.19	1.62	0.897	
		N23-22	E ₃ d	1935-2076	63.24	12.76	12.94	2.78	3.65	0.11	0.86	0.663	
	Rong Xingtun	R6	E ₃ d	1537-1539	96.67	1.99	0.26	0.25	0.10	0.07	0.59	0.974	Zhang et al., 1995
		R64	E ₃ d	1292.25-1295.25	97.91	1.98	0.05	0.02	0.01	0.00	0.04	0.979	
		R80	E ₃ d	2154.5-2146.0	70.49			28.61 (C ₂ -C ₄)		0.21	0.00	0.711	
		R161-25	E ₃ d	1905.6-1921.1	92.88	4.46	1.57	0.30	0.40	0.06	0.04	0.932	
		R201-19c	E ₃ d	1710.4-1726.5	97.18	2.62	0.07	0.05	0.00	0.06	0.01	0.972	
	Taoyuan	T7	E ₃ d	1270.1-1273.0	99.64			0.20 (C ₂ -C ₄)		0.00	0.16	0.998	Zhang et al., 1995
	Dapingfang	D11-16	E ₃ d	1887.4-1907.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
	Hongxing	H8-12	E ₃ d	1737-1761	68.67	17.23	7.93	1.22	1.85	n.d.	1.10	0.709	Li et al., 2015
		H5	E ₃ d	2365-2370	72.94	12.09	7.26	1.45	2.30	n.d.	1.53	0.759	
	Kuihuaao	KH8	E ₃ d	2417.0-2426.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		Zhang et al., 1995
	Huangjiandai	H34	E ₃ s ¹	2527	73.21	6.09	11.83	7.72 (iC ₄ -nC ₄)		0.54	n.d.	0.741	Chen et al., 1998
		H81	E ₃ s ¹	3065.0-3130.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		Zhang et al., 1995
		H105	E ₃ s ¹	1380-1384	99.51	n.d.	n.d.	n.d.	n.d.	0.02	0.38	1.000	
		H24	E ₃ s ¹	2287-2502	98.26	0.48	0.03	0.01	0.01	0.09	0.67	0.995	
		H9-15	E ₃ s ¹	2616.5-2836.7	88.43	6.97	2.97	0.56	0.63	0.13	0.05	0.888	This paper
	Rehetai	R11	E ₃ s ¹	1416-1487	98.70	0.93	0.05	0.02	n.d.	0.01	0.28	0.990	Li et al., 2015
		RQ2	E ₃ s ¹	1594-1661	98.63	0.80	0.05	n.d.	n.d.	0.04	0.46	0.991	
		R19-6	E ₃ s ¹	1616.5-1656.9	98.34	1.00	0.17	0.01	0.04	0.20	0.03	0.988	This paper
		R44	E ₃ s ¹	1662.1-1714.5	91.96	3.10	3.00	0.66	0.77	n.d.	0.02	0.924	
		R44	E ₃ s ¹	1662-1715	88.42	6.72	1.87	0.26	0.68	0.35	0.35	0.903	Li et al., 2015
	Niuju	N23-22	E ₃ s ¹	2276	90.34	1.43	3.35	2.14 (iC ₄ -nC ₄)		n.d.	2.75	0.929	Chen et al., 1998
		N23-23	E ₃ s ¹	2257-2276	90.34	1.43	3.35	0.71	0.91	0	2.75	0.934	Li et al., 2015
	Rongxingtun	R56	E ₃ s ¹	2476-2483	84.56	8.23	4.75	0.83	0.74	0.49	0	0.853	
		R66	E ₃ s ¹	2687-2891	96.59	0.91	1.26	0.21	0.45	0.01	0.27	0.972	

Eastern		R66	E ₃ S ¹	2813.1-2828.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		Zhang et al., 1995	
	Yushutai	T601	E ₃ S ¹	2196.3-2258.4	92.78	3.58	1.93	0.41	0.57	0.12	0.06	0.935	This paper
	Taoyuan	T17	E ₃ S ¹	2346.0-2353.0	87.08			11.90 (C ₂ -C ₄)		0.31	0.55	0.880	Zhang et al., 1995
	Dapingfang	D32	E ₃ S ¹	3011.3-3019.0	88.14			9.87 (C ₂ -C ₄)		0.46	1.38	0.899	
	Oulituozi	O6	E ₃ S ¹	2227.5-2267.0	93.61			4.24 (C ₂ -C ₄)		0.34	1.66	0.957	
		L12	E ₃ S ¹	1579.3-1591.2	92.22			5.80 (C ₂ -C ₄)		0.00	1.98	0.941	
	Yulou	Y4-3	E ₃ S ¹	1831.0-2192.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		Li et al., 2015
		Y9	E ₃ S ¹	1768-1782	96.49	2.06	0.60	0.07	0.12	0.00	0.62	0.971	
	Qinglongtai	L9	E ₃ S ¹	1376	97.85	0.68	0.41	0.01 (<i>i</i> C ₄ - <i>n</i> C ₄)		0.06	0.94	0.989	Chen et al., 1998
		LQ5	E ₃ S ¹	1504	97.96	0.83	0.21	0.01 (<i>i</i> C ₄ - <i>n</i> C ₄)		0.26	0.88	0.989	
		LQ4	E ₃ S ¹	1706	98.36	0.56	0.1	0.01 (<i>i</i> C ₄ - <i>n</i> C ₄)		0.01	0.91	0.993	Zhang et al., 1995
		L14-21	E ₃ S ¹	1401.0-1431.0	93.66		5.49 (C ₂ -C ₄)		0.00	0.85	0.945		
		L20-21	E ₃ S ¹	1435.8-1556.0	98.93		0.00 (C ₂ -C ₄)		0.00	1.08			
	Rehetai	R20-11	E ₂ S ³	2286.0-2291.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
	Yushutai	T28-26	E ₂ S ³	2388.7-2392.3	93.61	3.56	1.79	0.35	0.54	0.16	0.03	0.937	This paper
	Yulou	X10	E ₂ S ³	1526	98.37	0.39	0.13	0.01 (<i>i</i> C ₄ - <i>n</i> C ₄)		0.08	0.95	0.995	Chen et al., 1998
	Qinglongtai	L25-16	E ₂ S ³	1567.0-1580.6	98.21		0.15 (C ₂ -C ₄)		0.00	1.64	0.998	Zhang et al., 1995	
		L26-20	E ₂ S ³	1700-1734	96.79	1.03	0.28	0.16	0.17	n.d.	1.44	0.983	Li et al., 2015
	Oulituozi	O6	E ₂ S ³	2228-2267	93.60	1.55	1.62	0.45	0.40	0.34	1.66	0.959	
		O13	E ₂ S ³	2291-2302	95.50	1.19	0.79	0.26	0.25	0.06	1.76	0.975	
	Huangjiindai	H202	E ₂ S ³	2768-3152	89.05	8.80	0.27	0.00	0.02	0.85	0.83	0.907	
	Dapingfang	D32	E ₂ S ³	3011-3019	88.14	6.73	2.51	0.39	0.24	0.46	0.00	0.899	
		D40	E ₂ S ³	2079-2095	89.40	7.76	0.94	0.12	0.31	0.05	1.22	0.907	
Western	Lengjiapu	6	E ₃ S ¹	1387-1495	93.70	0.70	0.40	n.d.	n.d.	3.0	1.90	0.988	Huang et al., 2014
		7	E ₃ S ¹	1407-1437	97.20	0.60	0.20	n.d.	n.d.	1.40	0.10	0.992	
		8	E ₃ S ¹	1613.6-1650	97.10	0.80	0.30	n.d.	n.d.	1.20	n.d.	0.989	
		9	E ₃ S ¹	1485-1532	96.10	0.70	0.30	n.d.	n.d.	1.30	1.50	0.990	
		10	E ₃ S ¹	1555-1590	93.80	0.70	1.10	0.60	1.10	2.40	n.d.	0.964	

	11	E ₃ S ¹	1590-1620	48.90	5.40	21.0	8.10	9.10	6.60	n.d.	0.529	
	12	E ₃ S ¹	1334.9-1396.4	94.70	2.50	0.40	0	n.d.	1.70	n.d.	0.970	
	15	E ₃ S ¹	1374-1405	89.60	1.70	0.30	n.d.	n.d.	1.30	5.40	0.978	
	17	E ₃ S ¹	1373-1407.8	97.60	1.50	0.10	n.d.	n.d.	0.80	n.d.	0.984	
	19	E ₃ S ¹	1344.3-1401.5	98.40	1.20	0	n.d.	n.d.	0.30	n.d.	0.988	
	20	E ₃ S ¹	1351.2-1487	94.10	3.10	1.40	0.50	0.30	0.50	n.d.	0.947	
	21	E ₃ S ¹	1338-1382	95.90	2.10	0.90	0.30	0.20	0	n.d.	0.965	
	22	E ₃ S ¹	1451.8-1541.9	94.00	3.00	1.70	0.30	0.40	0.20	n.d.	0.946	
Shuangtaizi	S9	E ₃ S ²	2821	86.96	6.20	3.75	2.57 (<i>i</i> C ₄ - <i>n</i> C ₄)		0.03	0.51	0.874	Chen et al., 1998
	1	E ₂ S ³	2844.7-2885.6	90.40	2.10	4.70	0.80	1.30	0.60	n.d.	0.910	
	2	E ₂ S ³	2688.7-2690.4	91.80	2.50	3.60	0.40	1.00	0.60	n.d.	0.924	
	3	E ₂ S ³	2758.1-2937.2	87.00	3.30	6.50	1.0	1.30	0.70	n.d.	0.878	
	4	E ₂ S ³	1880-1895	90.30	1.90	4.70	0.80	1.40	0.60	n.d.	0.911	
Lengjiapu	5	E ₂ S ³	1781.2-1838.6	97.90	1.50	0	n.d.	n.d.	0.50	n.d.	0.985	Huang et al., 2014
	13	E ₂ S ³	1740-1802	96.20	2.00	0.70	0.30	n.d.	0.40	n.d.	0.970	
	14	E ₂ S ³	1745-1844	92.40	3.10	1.60	0.30	0.30	0.10	1.90	0.946	
	16	E ₂ S ³	1619-1746	90.20	4.80	3.20	0.50	0.50	0.40	n.d.	0.909	
	18	E ₂ S ³	1611.4-1755	83.40	3.80	2.20	0.20	0.30	2.00	6.90	0.928	
Qijia	Q4	E ₂ S ⁴	2590	70.96	13.74	8.99	5.87 (<i>i</i> C ₄ - <i>n</i> C ₄)		0.86	n.d.	0.713	Chen et al., 1998

Note: n.d.—not determined

Table 3. Stable carbon and hydrogen isotopic compositions of the Paleogene natural gases in the Liaohe Basin

Depression	Oil+gas field	Well	Reservoir	Depth (m)	$\delta^{13}\text{C}$ (‰, VPDB)						$\delta^2\text{H}$ (‰, VSMOW)				Data source
					CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	<i>i</i> C ₄ H ₁₀	<i>n</i> C ₄ H ₁₀	$\delta^{13}\text{C}_{\text{CO}_2}$	CH ₄	C ₂ H ₆	C ₃ H ₈	
Eastern	Huang Jindai	H23	E ₃ d	1644.4-1786.0	-43.2	-26.2	-18.7	-24.3	-25.3	-21.5	-11.6	-247	-189	n.d.	This paper
		H23	E ₃ d	1700-1786	-41.5	-26.5	-25.8	n.d.	n.d.	n.d.	-0.5	-235	-163	n.d.	Li et al., 2015
		H26	E ₃ d	1578.2-1702.0	-40.9	-26.2	-24.5	n.d.	n.d.	n.d.	-12.0	-243	-190	-137	This paper

	H26	E ₃ d	1678.0-1770.0	-41.5	-27.6	-22.4	-24.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
	H105	E ₃ d	1335.0-1354.0	-44.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	H11-10	E ₃ d	2064	-46.4	-28.7	-26.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al., 1998
Niuju	N13	E ₃ d	1793.4-1827.8	-43.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
	N21-020	E ₃ d	1688.4-1978.1	-44.2	-24.8	-21.1	-23.6	-24.6	-21.9	5.5	-244	-180	-169	This paper
	N22-020	E ₃ d	1688.0-2023.6	-42.8	-25.1	-23.1	-25.2	-26.2	-23.7	n.d.	-257	-190	-188	
	N22-320	E ₃ d	1706.6-1773.0	-44.1	-23.4	-21.8	-22.4	-22.4	-22.4	2.1	-244	-170	n.d.	
	N22-022	E ₃ d	1894-1908	-42.1	-26.4	-24.9	n.d.	n.d.	n.d.	-1.3	-240	-186	-163	Li et al., 2015
	N23-22	E ₃ d	1935-2076	-40.7	-27.3	n.d.	n.d.	n.d.	n.d.	n.d.	-217	n.d.	n.d.	
Rong Xingtun	R6	E ₃ d	1537-1539	-38.4	-25.6	n.d.	n.d.	n.d.	n.d.	n.d.	-220	n.d.	n.d.	Zhang et al., 1995
	R64	E ₃ d	1292.25-1295.25	-41.9	-24.7	-24.7	-22.5	n.d.	n.d.	n.d.	-219	n.d.	n.d.	
	R80	E ₃ d	2154.5-2146.0	-44.5	-28.9	-26.3	-28.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	R161-25	E ₃ d	1905.6-1921.1	-36.2	-26.5	-24.7	-24.9	-25.7	-24.3	n.d.	-205	-186	-198	This paper
	R201-19c	E ₃ d	1710.4-1726.5	-40.9	-24.4	n.d.	n.d.	n.d.	n.d.	n.d.	-233	-167	n.d.	
Taoyuan	T7	E ₃ d	1270.1-1273.0	-40.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
Dapingfang	D11-16	E ₃ d	1887.4-1907.0	-38.2	-26.8	-24.7	-25.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Hongxing	H8-12	E ₃ d	1737-1761	-37.0	-27.5	-26.9	n.d.	n.d.	n.d.	n.d.	-202	n.d.	n.d.	Li et al., 2015
	H5	E ₃ d	2365-2370	-39.2	-28.8	-26.0	n.d.	n.d.	n.d.	n.d.	-192	n.d.	n.d.	
Kuihuaao	KH8	E ₃ d	2417.0-2426.0	-35.8	-26.6	-24.5	-25.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
Huangjiandai	H34	E ₃ s ¹	2527	-49.9	-30.6	-27.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al., 1998
	H81	E ₃ s ¹	3065.0-3130.0	-34.2	-27.5	-24.8	-25.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
	H105	E ₃ s ¹	1380-1384	-44.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	H24	E ₃ s ¹	2287-2502	-41.1	-26.0	-27.5	n.d.	n.d.	n.d.	-4.3	-224	n.d.	n.d.	
	H9-15	E ₃ s ¹	2616.5-2836.7	-37.9	-25.9	-24.1	-24.5	-25.9	-23.2	-3.2	-214	-196	-191	This paper
Rehetai	R11	E ₃ s ¹	1416-1487	-45.7	-26.6	-27.5	n.d.	n.d.	n.d.	n.d.	-231	-157	n.d.	Li et al., 2015
	RQ2	E ₃ s ¹	1594-1661	-49.4	-38.7	-27.2	n.d.	n.d.	n.d.	n.d.	-234	-193	n.d.	
	R19-6	E ₃ s ¹	1616.5-1656.9	-44.3	-22.3	-21.1	-23.5	-21.5	-23.9	n.d.	-256	-174	-155	This paper
	R44	E ₃ s ¹	1662.1-1714.5	-53.5	-30.4	-27.0	-27.2	-28.9	-25.7	n.d.	-261	-246	-203	

	R44	E ₃ s ¹	1662-1715	-49.3	-38.7	-27.2	n.d.	n.d.	n.d.	n.d.	-234	-193	n.d.	Li et al., 2015
Niuju	N23-22	E ₃ s ¹	2276	-40.8	-27.3	-24.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al., 1998
	N23-23	E ₃ s ¹	2257-2276	-42.1	-26.4	-24.9	n.d.	n.d.	n.d.	-1.3	-240	-186	-163	
Rongxingtun	R56	E ₃ s ¹	2476-2483	-38.4	-28.6	-25.9	-26.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Li et al., 2015
	R66	E ₃ s ¹	2687-2891	-38.3	-28.6	-25.4	-24.4	n.d.	n.d.	-5.3	-213	-188	-155	
	R66	E ₃ s ¹	2813.1-2828.4	-34.8	-27.7	-25.1	-25.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
Yushutai	T601	E ₃ s ¹	2196.3-2258.4	-40.3	-26.0	-23.9	-24.1	-25.7	-22.9	0.1	-211	-189	-183	This paper
Taoyuan	T17	E ₃ s ¹	2346.0-2353.0	-40.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Dapingfang	D32	E ₃ s ¹	3011.3-3019.0	-41.8	-26.8	-24.5	-25.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Oulituozi	O6	E ₃ s ¹	2227.5-2267.0	-40.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
	L12	E ₃ s ¹	1579.3-1591.2	-60.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Yulou	Y4-3	E ₃ s ¹	1831.0-2192.0	-44.7	-30.9	-26.8	-26.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	Y9	E ₃ s ¹	1768-1782	-52.2	-33.6	-27.4	-25.4	n.d.	n.d.	n.d.	-248	-227	-173	Li et al., 2015
Qinglongtai	L9	E ₃ s ¹	1376	-52.6	-35.5	-24.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	LQ5	E ₃ s ¹	1504	-55.5	-47.3	-40.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al., 1998
	LQ4	E ₃ s ¹	1706	-52.2	-39.9	-38.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	L14-21	E ₃ s ¹	1401.0-1431.0	-52.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	L20-21	E ₃ s ¹	1435.8-1556.0	-50.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
Rehetai	R20-11	E ₂ s ³	2286.0-2291.0	-49.6	-31.0	-27.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Yushutai	T28-26	E ₂ s ³	2388.7-2392.3	-34.5	-26.6	-24.1	-24.4	-25.9	-23.4	-0.7	-188	-187	-179	This paper
Yulou	X10	E ₂ s ³	1526	-59.3	-39.8	-30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al., 1998
Qinglongtai	L25-16	E ₂ s ³	1567.0-1580.6	-50.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Zhang et al., 1995
	L26-20	E ₂ s ³	1700-1734	-47.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-224	n.d.	n.d.	
Oulituozi	O6	E ₂ s ³	2228-2267	-40.4	-28.8	-27.0	-26.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	O13	E ₂ s ³	2291-2302	-41.0	-29.7	-27.8	-27.3	n.d.	n.d.	n.d.	-215	n.d.	n.d.	Li et al., 2015
Huangjindai	H202	E ₂ s ³	2768-3152	-44.6	-29.5	-23.5	n.d.	n.d.	n.d.	-4.9	-250	-209	-106	
Dapingfang	D32	E ₂ s ³	3011-3019	-41.8	-26.8	-24.5	-25.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	D40	E ₂ s ³	2079-2095	-36.2	-26.1	-23.4	-22.3	n.d.	n.d.	n.d.	-191	-154	-131	

Western	6	E ₃ s ¹	1387-1495	-53.6	-38.3	-28.2	n.d.	n.d.	n.d.	9.0	-232	n.d.	n.d.	Huang et al., 2014
	7	E ₃ s ¹	1407-1437	-50.9	-39.0	-29.9	n.d.	n.d.	n.d.	7.3	-231	n.d.	n.d.	
	8	E ₃ s ¹	1613.6-1650	-50.5	-37.9	-28.7	n.d.	n.d.	n.d.	1.8	-234	n.d.	n.d.	
	9	E ₃ s ¹	1485-1532	-55.4	-39.4	-29.4	-23.3	-25.1	-21.4	1.1	-233	n.d.	n.d.	
	10	E ₃ s ¹	1555-1590	-54.8	-38.3	-27.6	-26.7	-28.3	-25.9	7.7	-222	-186	-182	
	11	E ₃ s ¹	1590-1620	-53.9	-31.2	-26.8	-26.2	-27.9	-24.7	10.2	-234	-202	-185	
	12	E ₃ s ¹	1334.9-1396.4	-38.0	-28.6	n.d.	n.d.	n.d.	n.d.	10.4	-224	n.d.	n.d.	
	15	E ₃ s ¹	1374-1405	-36.8	-29.5	n.d.	n.d.	n.d.	n.d.	6.9	-221	n.d.	n.d.	
	17	E ₃ s ¹	1373-1407.8	-43.4	-29.8	-16.4	n.d.	n.d.	n.d.	14.5	-221	n.d.	n.d.	
	19	E ₃ s ¹	1344.3-1401.5	-43.9	-29.3	-16.8	-25.7	-28.1	-23.3	-12.0	-209	-148	n.d.	
	20	E ₃ s ¹	1351.2-1487	-43.2	-29.4	-22.8	-26.8	-29.0	-23.0	8.4	-219	-173	-130	
	21	E ₃ s ¹	1338-1382	-44.0	-29.4	-20.7	-25.6	-29.1	-20.4	-7.8	-216	-162	-123	
	22	E ₃ s ¹	1451.8-1541.9	-43.3	-28.5	-23.6	-26.2	-29.7	-23.5	8.4	-225	-178	-144	
	Shuangtaizi		S9	E ₃ s ²	2821	-40.5	-28.1	-26.9	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al.,1998
	Lengjiapu	1	E ₂ s ³	2844.7-2885.6	-49.8	-33.0	-28.4	-27.3	-31.1	-24.9	-2.5	-248	-264	-228
		2	E ₂ s ³	2688.7-2690.4	-49.1	-32.4	-28.5	-32.5	-32.5	n.d.	-0.4	-256	n.d.	n.d.
		3	E ₂ s ³	2758.1-2937.2	-47.9	-31.1	-27.4	-26.0	-28.1	-24.3	0.9	-225	-257	-212
		4	E ₂ s ³	1880-1895	-47.2	-33.6	-29.3	-27.6	-29.3	-26.6	-2.2	-249	-269	-232
		5	E ₂ s ³	1781.2-1838.6	-49.4	-35.2	-26.7	-26.6	-29.7	-23.5	4.3	-231	-199	n.d.
		13	E ₂ s ³	1740-1802	-43.9	-32.2	-26.3	-27.4	-27.4	-24.1	10.7	-241	n.d.	n.d.
		14	E ₂ s ³	1745-1844	-44.4	-31.9	-26.1	-24.9	-28.7	-21.1	13.6	-241	n.d.	n.d.
		16	E ₂ s ³	1619-1746	-44.8	-30.2	-24.5	-28.0	-30.3	-25.7	8.7	-235	-189	-158
		18	E ₂ s ³	1611.4-1755	-45.0	-30.5	-25.1	-26.7	-30.9	-23.9	-10.4	-234	-187	-159
	Qijia		Q4	E ₂ s ⁴	2590	-47.2	-29.7	-25.1	n.d.	n.d.	n.d.	n.d.	n.d.	Chen et al., 1998

Note: n.d.—not determined

Table 4. The maximum, minimum and average values of the components, isotopes and dryness of the Paleogene natural gases in the Liaohe Basin

Depression	Strata	Value type	Natural gas component (%)							$\delta^{13}\text{C}$ (‰, VPDB)							$\delta^2\text{H}$ (‰, VSMOW)			Dryness
			CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> C ₄ H ₁₀	<i>n</i> C ₄ H ₁₀	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	<i>i</i> C ₄ H ₁₀	<i>n</i> C ₄ H ₁₀	$\delta^{13}\text{C}_{\text{CO2}}$	CH ₄	C ₂ H ₆	C ₃ H ₈	
Eastern	E ₃ d	Maximum	99.84	17.23	12.94	2.78	3.65	0.19	1.62	-35.8	-23.4	-18.7	-22.4	-22.4	-21.5	5.5	-192	-163	-137	0.999
		Minimum	63.24	1.01	0.05	0.02	0.00	0.00	0.01	-46.4	-28.9	-26.9	-28.5	-26.2	-24.3	-12.0	-257	-190	-198	0.663
		Average	89.96	5.58	2.42	0.65	0.67	0.08	0.59	-41.3	-26.4	-24.2	-24.7	-24.8	-22.8	-3.0	-228	-180	-171	0.909
	E ₃ s ¹	Maximum	99.51	11.90	11.83	7.72	0.91	0.54	2.75	-34.2	-22.3	-21.1	-23.5	-21.5	-22.9	0.1	-211	-157	-155	0.995
		Minimum	73.21	0.00	0.03	0.01	0.01	0.00	0.00	-60.7	-47.3	-40.3	-27.2	-28.9	-25.7	-5.3	-261	-246	-203	0.741
		Average	93.10	3.61	2.11	0.85	0.49	0.16	0.82	-45.4	-30.7	-26.9	-25.3	-25.5	-23.9	-2.8	-233	-195	-175	0.937
	E ₂ s ³	Maximum	98.37	8.80	2.51	0.45	0.54	0.85	1.76	-34.5	-26.1	-23.4	-22.3	-25.9	-23.4	-0.7	-188	-154	-106	0.998
		Minimum	88.14	0.15	0.13	0.00	0.02	0.00	0.00	-59.3	-39.8	-30.0	-27.9	-25.9	-23.4	-4.9	-250	-209	-179	0.899
		Average	93.63	3.46	1.04	0.22	0.28	0.25	1.06	-44.6	-29.8	-26.0	-25.6	-25.9	-23.4	-2.8	-214	-183	-139	0.951
Western	E ₃ s ¹	Maximum	98.40	5.40	21.00	8.10	9.10	6.60	5.40	-36.8	-28.5	-16.4	-23.3	-25.1	-20.4	14.5	-209	-148	-123	0.992
		Minimum	48.90	0.60	0.00	0.00	0.20	0.00	0.10	-55.4	-39.4	-29.9	-26.8	-29.7	-25.9	-12.0	-234	-202	-185	0.529
		Average	91.62	1.85	2.16	1.63	2.22	1.59	2.23	-47.1	-33.0	-24.6	-25.8	-28.2	-23.2	5.1	-225	-175	-153	0.941
	E ₂ s ³	Maximum	97.90	4.80	6.50	1.00	1.40	2.00	6.90	-43.9	-30.2	-24.5	-24.9	-27.4	-21.1	13.6	-225	-187	-158	0.985
		Minimum	83.40	1.50	0.00	0.20	0.30	0.10	1.90	-49.8	-35.2	-29.3	-32.5	-32.5	-26.6	-10.4	-256	-269	-232	0.878
		Average	91.07	2.78	3.02	0.54	0.87	0.66	4.40	-46.8	-32.2	-26.9	-27.4	-29.8	-24.3	2.5	-240	-228	-198	0.929

Figures

Fig. 1. Location map (a), structural subdivision and the oil-gas field distribution (b) of the Liaohe Basin (after Zhai, 1991)

Fig. 2. Cross-section (A-A') showing the different structural of the Liaohe Basin (After Zhang et al., 1995, revised)

Fig. 3. Content vs. depth of the methane and it homologues of the analyzed natural gases in the Liaohe Basin (a. CH₄ of the eastern depression (ED); b. CH₄ of the western depression (WD); c. C₂H₆ of the ED; d. C₂H₆ of the WD; e. C₃H₈ of the ED; f. C₃H₈ of the WD; g. i-C₄H₁₀ of the ED; h. i-C₄H₁₀ of the WD; i. n-C₄H₁₀ of the ED j. n-C₄H₁₀ of the WD) (Data sourced from Zhang et al., 1995; Cheng et al., 1998; Huang et al., 2014; Li et al., 2015; This paper).

Fig. 4. Dryness and Carbon isotope values vs. depth of the methane and it homologues of the Paleogene natural gases in the Liaohe Basin (a. dryness (C_1/C_{1-5}); b. $\delta^{13}C_1$; c. $\delta^{13}C_2$; d. $\delta^{13}C_3$; e. $\delta^{13}C_4$; f. $\delta^{13}C_3 - \delta^{13}C_4$) (Data sources as same as in Fig.3).

Fig. 5. Carbon isotope line of the methane and it homologues of the Paleogene natural gases in the Liaohe Basin (a. E_{3d} and E_{3s}¹ reservoirs in the WD; b. E_{2s}³ and E_{2s}⁴ reservoirs in the WD; c. E_{3d} reservoirs of the ED and offshore; d. E_{3s}¹ reservoirs in the ED; e. E_{2s}³ reservoirs in the ED) (diagram after Chuang et al., 1988) (Data sources as same as in Fig.3).

Fig. 6. Hydrogen isotope line of the methane and it homologues of the analyzed natural gases in the Liaohe Basin (a. E₃s¹ reservoirs in the WD; b. E₂s³ reservoirs in the WD; c. E₃d reservoirs of the ED; d. E₃s¹ and E₂s³ reservoirs in the ED) (Data sources as same as in Fig.3).

Fig. 7. Hydrogen isotope values vs. depth of the methane and it homologues of the analyzed natural gases in the Liaohe Basin (a. $\delta^2\text{H}_1$; b. $\delta^2\text{H}_2$; c. $\delta^2\text{H}_3$) (Data sources as same as in Fig.3).

Fig. 8. Genetic characterization of analyzed natural gases using $\delta^2\text{H}_1$ versus $\delta^{13}\text{C}_1$. (Diagram after Whiticar, 1999) (Data sources as same as in Fig.3).

Fig. 9. Genetic characterization of analyzed natural gases using $\delta^{13}C_{CO_2}$ versus $\delta^{13}C_1$. (Diagram after Gutsalo and Plotnikov (1981) and Kotarba (2001, 2014)) (Data sources as same as in Fig.3).

Fig. 10. $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ cross-plot of analyzed natural gases from the Liaohé Basin. Also shown are published maturity trends of type II kerogen (Berner and Faber, 1996; Rooney et al., 1995; Tilley and Muehlenbachs, 2006) and type III kerogen (Berner and Faber, 1996; Dai and Qi, 1989; Jenden et al., 1988; Rooney et al., 1995). All the samples were plot in the top area above the line of $\delta^{13}\text{C}_{\text{C}_2\text{H}_6} = -28\text{‰}$, which coincides with the gas maturity trend of the type III kerogen, indicating a coal-formed origin (Data sources as same as in Fig.3).

Fig. 11. Genetic characterization of analyzed natural gases using C_1/C_{2+3} versus $\delta^{13}C_1$. (Diagram after Whiticar, 1999) (Data sources as same as in Fig.3).

Fig. 12. $\delta^{13}\text{C}_3 - \delta^{13}\text{C}_4$ versus $\text{C}_3\text{H}_8/\text{C}_4\text{H}_{10}$ cross-plot of analyzed natural gases from the Liaohe Basin (Data sources as same as in Fig.3).

Fig. 13. $\delta^{13}\text{C}_3 - \delta^{13}\text{C}_4$ versus $\text{C}_3/\text{C}_{1-5}$ cross-plot of analyzed natural gases from the Liaohe Basin (Data sources as same as in Fig.3).

Fig. 14. C_2/C_3 versus iC_4/nC_4 cross-plot of analyzed natural gases from the Liaohe Basin (Data sources as same as in Fig.3).

Fig. 15. C_2/C_1 versus $\delta^{13}C_1$ cross-plot of analyzed natural gases from the Liaohe Basin (a. Ed reservoir in the ED; b. E_3s^1 reservoirs in the ED and WD; c. E_2s^3 reservoirs in the ED and WD) (Data sources as same as in Fig.3).

Fig. 16. Observed correlation between the estimated thermal maturity values for ethane and methane carbon isotopes using the relationships of Berner and Faber (1988), and Dai and Qi (1989). Dashed line represents a 1-1 correlation (Data sources as same as in Fig.3).