Characteristics and Origins of the Natural Gas and Implications for Gas-Source Correlation in Deep Formations of the Songliao Basin, NE China

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Abstract: The Songliao Basin is the most productive petroliferous lacustrine basin in NE China, and numerous large gas fields with large proven reserves occur in its deep formations. However, considerable challenges remain: (1) the origins and genetic types of the natural gases are controversial; (2) the gas-source correlations are poorly studied; and (3) the migration distance is vague. In this study, these problems are addressed by the study of the gas compositions, light hydrocarbons, and stable hydrogen and carbon isotopes. The gases are predominantly of organic and thermogenic origins. The Huoshiling (J 3 h) and Shahezi (K 1 sh) gases are mainly mixtures of coal-derived and oil-associated gases and the mixed-sources of primary kerogen degradation and secondary oil cracking, while the Yingcheng (K 1 yc) gases are mainly coal-derived gases and predominantly derived from primary kerogen degradation. The gases in different sags are derived from the source rocks developed in the same sags where the gases accumulated, characterized by the proximal-source accumulation. Vertically, the gases in the J 3 h and K 1 sh are predominantly sourced by the proximal J 3 h and K 1 sh mudstones, while the gases in the K 1 yc are mainly derived from either the J 3 h or the K 1 sh source rocks, suggesting the gas migration with short distances.

Keywords: gas origin; gas-source correlation; stable carbon isotope; light hydrocarbon; deep formation; Songliao Basin

1. Introduction

Natural gases in sedimentary basins contain hydrocarbons (e.g., methane and its higher homologues), non-hydrocarbons (e.g., CO 2 , N 2 , H 2 , H 2 S, and Hg), and noble gases (e.g., He and Ar). Generally, hydrocarbon gases are proved to be the result of organic matter conversion by thermal
degradation, crude oil and wet gas cracking, and even bacterial action [1–10]. However, the hydrocarbon gas physical properties, compositions, and stable carbon isotopic distributions in gas reservoirs may change, as a result of the effects of microbial generation, thermal maturation, migration, mixing, leaking, biodegradation, and thermochemical sulfate reduction (TSR) [7,8,11–21]. Combined with stable hydrogen and carbon isotopes, the hydrocarbon gas compositions can be useful parameters to ascertain the gas origins and analyze gas-source correlations. Besides, the non-hydrocarbon gases can be significant markers to analyze the gas origins, genetic types, generation, and migration [4,22–35]. Accordingly, the geochemical characters of gas (hydrocarbon, non-hydrocarbon, and noble gas) compositions and their stable hydrogen and carbon isotopes are the basic parameters to analyze gas origins, mixtures of gases generated at different thermal-evolution stages or from different origins, and gas-source correlations [1,3,16,26,36–49].

In NE China rift basins which developed during the Late Jurassic to Early Cretaceous are widely distributed and have been studied extensively [50,51]. The Songliao Basin (SLB), the largest one, proves to be the most productive petroliferous lacustrine basin in China [52–57]. It is commonly accepted that the Upper Cretaceous petroleum systems are very important petroleum-bearing plays in the SLB [58–61], and numerous studies on these petroleum plays have been carried out [58–63]. Based on previous studies [64–66], large gas fields occur in the deep formations (the formations underlying the 3rd Member of the Lower Cretaceous Quantou Formation; [67]) with proven reserves of over 200×10⁹ m³ (706.3bcf). The deep gas reservoirs in the Dehui Depression (a sub-tectonic unit located in the uplift area of southeast SLB) possess proven reserves of over 20 × 10⁹ m³ (70.6bcf). The deep formations (mainly including the Jurassic Huoshiling Formation (J₃h) (156.0–145.0Ma), the Cretaceous Shahezi (K₁sh) (145.0–133.9Ma) and Yingcheng (K₁yc) (133.9–125.0Ma) Formations) are predicted to be the next main targets for hydrocarbon gases exploration in the Dehui Depression. However, considerable challenges remain. In the deep formations, (1) the gas origins and genetic types are confusing and debatable, (2) the gas-source correlations are poorly studied, and (3) the migration distance for hydrocarbon gas is controversial. During the last decades, some researchers have suggested that the gas origins in the deep formations of SLB are of inorganic and mantle-derived source [68–71]. However, some previous studies pointed out that the hydrocarbon gases in the deep formations of SLB are of organic origins, mainly derived from the K₁sh source rocks [72–75]. Nevertheless, some scholars held the view that the gases are mainly sourced by the J₃h source rocks [76,77]. These debates may constrain the exploration and exploitation of hydrocarbons in the deep formations of SLB, which can be addressed by using the geochemical characters of gas (hydrocarbon and non-hydrocarbon) compositions and their stable hydrogen and carbon isotopes [42,78–82].

In this study, the gases in the deep formations of the Dehui Depression are used for the systematic analyses of the gas density, chemical compositions, stable hydrogen and carbon isotopes, and light hydrocarbons characteristics. The gas origins, genetic types and gas-source correlations have been investigated, which can provide the needed theoretical support for natural gas exploration and target selection in the deep formations of the SLB, and the guidance for the gas exploration in the deep formations of similar geological settings around the world.

2. Geological Settings

2.1. Tectonics and Structure

The SLB, with an area of 260×10³ km², is an independent half-graben continental basin that was formed during the Late Jurassic-Neogene [56], and featured by a dual-structure of an earlier rift depression and a later thermal depression [56]. It is the most prolific petroliferous lacustrine basin in NE China [83]. The tectonic evolution of the basin was controlled by two active continental margins in the late Mesozoic: (1) the Sikhote-Alin Orogenic Belt to the east, and (2) the Mongol-Okhotsk Belt to the north and northwest [84], which can be divided into four stages: (1) mantle upwelling during the Middle–Late Jurassic, (2) synrift subsidence during the Late Jurassic-Early Cretaceous, (3)
As a result of synrift extension, the SLB in the synrift stage was characterized by “basin-and-range” fault blocks [56]. The Dehui Depression, located in the uplift zone of southeastern SLB, is NE trending and fault-controlled, with an area of 4053 km². The tectonic evolution stages of the Dehui Depression are approximately consistent with those of the SLB. Tectonic movements of multi-episodes have resulted in complex internal structures, and the Dehui Depression contains seven sags: the Nong’an sag, the Huajia sag, the Baojia sag, the Nong’annan sag, the Helong sag, the Longwang sag, and the Lanjia sag (Figure 1).

2.2. Stratigraphy and Lithology

As a consequence of mantel upwelling and doming, the Dehui Depression evolved into the Mesozoic rifting and subsidence, including the synrift subsidence and post-rift thermal subsidence. Highlands located in the west and south were the main sediment source areas [86].
The succession deposited during the synrift subsidence includes the Huoshiling (156–145 Ma), Shahezi (145–133.9 Ma), Yingcheng (133.9–125 Ma), and Denglouku (125–116 Ma) Formations [56,86] (Figure 2). The Huoshiling-Yingcheng Formations (H-YFs) include clastic floodplain, fluvial, delta, and lacustrine rocks intercalated with pyroclastic and volcanic rocks [56,86], consisting of volcanic, conglomerates, fine sandstones, mudstones, coals and tuff interlayers (Figure 2). The thickness of the H-YFs is generally <1000 m to max 3500 m, mainly 1500–2500 m. Large amounts of tight sandstone and volcanic gases have been discovered in the H-YFs, which are the main targets of unconventional hydrocarbon resources in the Dehui Depression [56,86].

![Figure 2. Integrated stratigraphic column in the Dehui Depression, SLB (modified after [56]).](image)

3. Samples and Methods

Firstly, the gases were flushed for 15–20 minutes to remove air contamination, then gas samples were collected directly from the wellheads. Stainless steel cylinders (Φ = 10.0 cm) equipped with two shut-off valves (P_{max} = 22.5 MPa) were utilized to contain the gas samples. The inside pressure of
the container should be maintained over 5.0 MPa. After the collection, the cylinders were subjected to leakage checks in water. Thirty-six samples from 11 wells in H-YFs were collected for molecular composition analysis. Twenty-seven samples from 11 wells in H-YFs were collected for stable carbon isotope analysis. Two samples from Well DS12 in the J3h and K1sh Formations were analyzed for stable hydrogen isotopes. Eleven mudstone samples from four wells and 23 gas samples from eight wells are collected out for light hydrocarbon analysis.

3.1. Analysis of Molecular Composition

A Trace GC Ultra gas chromatograph (GC) (Thermo Fisher, USA) equipped with flame ionization and thermal conductivity detectors was utilized to ascertain the gas chemical components. The C1−C4 components were isolated utilizing a porous-layer open-tabular capillary column (PLOT, Al2O3 50 m×0.53 mm). The carrier gas was helium (He, flowrate=1 mL/min). At the beginning, the GC oven temperature was 30 °C and kept there for 10 minutes, then raised to 180 °C (rate of 10 °C/min) and held for 20–30 minutes [87–93].

3.2. Analysis of Stable Carbon and Hydrogen Isotope

A Finnigan Mat Delta S mass spectrometer (Thermo Fisher, USA) interfaced with a HP 5890II chromatograph (HP, USA) can be used to ascertain the stable carbon isotopes. A gas chromatograph (a fused silica capillary column (PLOT Q 30 m×0.32 mm)), with helium as the carrier gas (1 mL/min) was utilized to separate the gas components (C1−C4 and CO2). The gases were converted into CO2 in a combustion interface, then transferred into the mass spectrometer. The GC oven temperature was initially heated from 35 °C to 80 °C (8 °C/min), then heated up to 260 °C (5 °C/min) and held 10 minutes. Gas samples were analyzed in duplicate. The stable carbon isotope values are recorded in the customary “δ” notation in per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard. The value of ± 0.5‰ should be the reproducibility and analytical precision with respect to the VPDB standard [87–93]. A Finnigan MAT 253 mass spectrometer with the GC–TC–IRMS method was used to ascertain the stable hydrogen isotope. A chromatographic column (HP-PLOTQ column, 30 m × 0.32 mm × 20 mm) was used to separate the gas components. The accuracy should be ±3‰, and stable hydrogen isotope results are recorded relative to Vienna Standard Mean Ocean Water (VSMOW) [87–93].

3.3. Analysis of Light Hydrocarbons

A HP5890A gas chromatograph and a PONA capillary column (50 m × 0.25 mm × 0.5 µm) were utilized to analyze the light hydrocarbons. Helium was used as the carrier gas. A container with liquid nitrogen was used to trap the low content of light hydrocarbons. The liquid nitrogen container can be removed after a large volume of gas (15–20 mL) was injected after 20 minutes. Utilizing a FID at 320 °C, the eluted light hydrocarbons were analyzed. At the beginning, the temperature was held at 30 °C for 10 minutes, then heated up to 70 °C (1 °C/min), and then raised to 160 °C (3 °C/min), and finally heated up to 270 °C (5 °C/min) and maintained 20 minutes. An Agilent PONA gas chromatograph was utilized to analyze the light hydrocarbons qualitatively. 53 individual compounds (from isobutane to n-octane) were tested in the experiment. The peak areas of individual compounds on the gas chromatograph were utilized to quantify the light hydrocarbon compounds [87–93].

4. Results

4.1. Gas Chemical Composition

The gas chemical components in the H-YFs are shown in Table 1 and Figure 3. C1−C5 hydrocarbons are the main gases in the natural gas of the Dehui Depression, accounting for 93.23%–99.16% (Avg. = 96.60 %) in volume, while those average values in the J3h, K1sh and K1yc (H-YFs) are 96.49%, 96.84%, and 96.55%, respectively. The non-hydrocarbons (including N2, CO2, H2, and H2S) account for 0–6.75%, with a mean of 3.27%, and the noble gases (He and Ar) account for 0–4.45%, with a mean of 0.13%.
Table 1. Chemical components and density of the natural gas in the H-YFs of the Dehui Depression, SLB.

| Well Layer | Depth (m) | Density (kg/m³) | Dryness Coefficient | CH₄ | C₂H₆ | C₃H₈ | iC₄H₁₀ | nC₄H₁₀ | iC₅H₁₂ | nC₅H₁₂ | N₂ | CO₂ | H₂ | H₂S | He | Ar |
|------------|----------|-----------------|---------------------|-----|------|------|-------|--------|--------|------|-----|-----|-----|----|----|---|
| DS11 Huoshiling | 2551.50 | 0.88 | 83.9 0.93 1.22 0.49 1.36 0.95 6.69 | / | / | / | 4.45 | |
| DS11 Huoshiling | 2553.00 | 0.64 | 88.7 4.17 1.25 0.21 0.23 0.53 0.52 | 3.12 1.26 | |
| DS11 Huoshiling | 2556.00 | 0.62 | 90.5 4.78 1.15 0.20 0.19 | 0.09 0.06 | 1.69 1.31 |
| DS11 Huoshiling | 2560.00 | 0.62 | 90.7 4.52 1.03 0.18 | 0.18 0.09 | 0.07 1.99 1.29 |
| DS11 Huoshiling | 2562.00 | 0.63 | 89.7 4.19 1.11 0.23 | 0.25 0.17 | 0.26 | 2.86 1.28 |
| DS12 Huoshiling | 3067.00 | / | 91.7 4.06 1.06 0.19 | 0.22 0.11 | 0.41 0.81 1.39 0.01 | 0.02 |
| DS12 Huoshiling | 3328.50 | / | 92.1 3.76 0.98 0.18 | 0.20 | 0.11 | 0.35 0.85 | 1.41 0.01 | 0.02 |
| DS12 Huoshiling | 3328.90 | / | 95.9 0.70 0.05 | / | / | / | 0.02 | 1.30 | 2.04 | / | 0.02 |
| DS2 Huoshiling | 3030.55 | 0.67 | 92.8 1.75 0.27 | 0.02 | 0.02 | / | / | 0.37 | 4.77 | / | / |
| N101 Huoshiling | 2520.10 | 0.59 | 93.5 3.44 0.74 | / | / | / | 1.84 0.46 | / | / |
| N101 Huoshiling | 3044.00 | 0.61 | 90.2 4.40 1.45 | 0.15 | 0.20 | / | / | 2.80 | 0.77 | / | / |
| N103 Huoshiling | 2335.00 | 0.72 | 76.1 14.41 | 5.45 | 2.02 | / | / | / | / | 1.29 | 0.77 | / |
| N103 Huoshiling | 3011.00 | 0.69 | 86.7 8.29 | / | / | / | / | 3.20 | 1.86 | / | / |
| DS19 Huoshiling | 2295.50 | / | 85.6 6.64 | 2.28 0.33 | 0.47 | 0.15 | 0.51 | 2.34 1.66 | 0.01 | / | 0.04 |
| DS11 Shahezi | 2368.50 | / | 85.7 6.65 | 2.27 | 0.33 | 0.47 | 0.15 | 0.51 | 2.25 1.58 | 0.01 | / | 0.04 |
| DS11 Shahezi | 2368.50 | / | 92.5 3.45 | 0.69 0.20 | 0.13 | 0.08 | 0.21 | 2.49 | 0.14 | 0.08 | / | 0.03 |
| DS11 Shahezi | 2369.50 | / | 94.0 3.90 | 0.72 0.21 | 0.13 | 0.08 | 0.12 | 0.71 | / | 0.10 | / | 0.02 |
| DS11 Shahezi | 2370.50 | / | 85.6 6.64 | 2.28 0.33 | 0.47 | 0.15 | 0.51 | 2.34 | 1.66 | 0.01 | / | 0.04 |
| DS15 Shahezi | 2578.00 | / | 91.2 6.04 | 1.33 0.15 | 0.06 | / | / | 1.14 | 0.05 | 0.01 | / | 0.02 |
| DS15 Shahezi | 2578.00 | / | 91.2 6.04 | 1.32 0.14 | 0.06 | / | / | 1.13 | 0.05 | 0.01 | / | 0.02 |
| N101 Shahezi | 2354.40 | / | 87.2 3.39 | 0.68 0.20 | 0.13 | 0.09 | 1.54 | 6.47 | 0.20 | 0.08 | / | 0.03 |
| N101 Shahezi | 2354.50 | 0.62 | 90.7 3.33 | 1.30 0.32 | 0.28 | / | / | 1.61 | 2.44 | / | / |
| N101 Shahezi | 2354.90 | 0.60 | 91.9 3.26 | 1.08 | / | 0.16 | / | / | 2.37 | 1.20 | / | / |
| DS12 Yingcheng | 2662.38 | 0.71 | 79.0 9.58 | 4.49 | 0.82 | 0.92 | 0.27 | 0.32 | 3.77 | 0.81 | / | / |
| DS12 Yingcheng | 2664.75 | 0.70 | 80.1 9.75 | 4.28 | 0.75 | 0.89 | 0.24 | 0.27 | 3.23 | 0.52 | / | / |
| DS17 Yingcheng | 2249.00 | / | 87.2 3.39 | 0.68 | 0.20 | 0.13 | 0.09 | 1.54 | 6.47 | 0.20 | 0.08 | / | 0.03 |
| DS17 Yingcheng | 2249.00 | / | 92.5 3.45 | 0.69 | 0.20 | 0.13 | 0.08 | 0.21 | 2.49 | 0.14 | 0.08 | / | 0.03 |
| DS17 Yingcheng | 2273.50 | / | 94.2 3.69 | 0.72 | 0.21 | 0.13 | 0.08 | 0.12 | 0.71 | / | 0.10 | / | 0.02 |
| DS2 Yingcheng | 2368.50 | 0.71 | 85.3 6.07 | 1.98 | 0.44 | 0.55 | 0.19 | 0.30 | 0.67 | 4.46 | / | / |
| H12 Yingcheng | 2163.50 | 0.73 | 74.0 12.15 | 4.77 | 1.24 | 1.05 | 0.26 | 0.32 | 6.03 | 0.16 | / | / |
| H3 Yingcheng | 1971.50 | 0.71 | 80.7 5.55 | 4.39 | 1.23 | 1.04 | 0.41 | 0.52 | 2.19 | 2.01 | / | / |
| H3 Yingcheng | 1971.70 | 0.70 | 82.3 7.46 | 4.10 | 1.18 | 0.99 | 0.39 | 0.49 | 1.88 | 1.02 | / | / |
| H3 Yingcheng | 1971.70 | 0.69 | 83.6 7.67 | 4.15 | 1.19 | 1.00 | 0.39 | 0.48 | 0.92 | 0.62 | / | / |
| H5 Yingcheng | 1665.20 | 0.69 | 82.6 8.06 | 3.71 | 0.95 | 0.90 | 0.35 | 0.48 | 2.68 | 0.31 | / | / |
| H5 Yingcheng | 1665.20 | 0.67 | 84.4 8.09 | 3.39 | 0.82 | 0.86 | 0.32 | 0.44 | 1.57 | 0.09 | / | / |
| H5 Yingcheng | 1897.00 | 0.72 | 80.7 8.69 | 5.05 | 1.47 | 1.26 | 0.54 | 0.78 | 1.20 | 0.30 | / | / |
Figure 3. Relationships between the burial depth, the contents of chemical components and density of the natural gas in the deep formations of the Dehui Depression, SLB. (a) for CH$_4$; (b) for C$_2$; (c) for dryness coefficient; (d) for CO$_2$; (e) for N$_2$; (f) for density.

Methane is the main gas among the hydrocarbons, accounting for 74.0%–95.9% (Avg. = 87.4%), and the average methane contents in the J$_3$h, K$_1$sh, and K$_1$yc are 89.2%, 90.0%, and 83.6%, respectively. The contents of C$_2$ in the J$_3$h, K$_1$sh, and K$_1$yc are 0.8%–21.9% (Avg. = 7.3%), 4.5%–10.4% (Avg. = 6.8%), and 4.8%–19.8% (Avg. = 13.0%), respectively. The dryness coefficients (C$_1$/C$_1$-5) of gaseous hydrocarbons in the J$_3$h, K$_1$sh, and K$_1$yc are 0.78–0.99 (Avg. = 0.93), 0.89–0.95 (Avg. = 0.93), and 0.79–0.95 (Avg. = 0.87), respectively.

The contents of CO$_2$ in the J$_3$h, K$_1$sh, and K$_1$yc are 0–4.77% (Avg. = 1.56%), 0–2.44% (Avg. = 0.90%), and 0.09%–4.46% (Avg. = 0.89%), respectively, and the contents of N$_2$ in the J$_3$h, K$_1$sh, and K$_1$yc are 0–3.20% (Avg. = 1.88%), 0.71%–6.47% (Avg. = 2.28%), and 0.67%–6.47% (Avg. = 2.60%), respectively.

Helium is the predominant noble gas, accounting for 0–4.45% (Avg. = 0.91%), 0.02%–0.04% (Avg. = 0.03%), and 0.02%–0.04% (Avg. = 0.03%), respectively, in the J$_3$h, K$_1$sh, and K$_1$yc of the Dehui Depression.
4.2. Stable Hydrogen and Carbon Isotopes

The stable carbon isotope values for gases in the H-YFs of the Dehui Depression are shown in Figure 4 and Table 2. The δ^{13}C_1 values in the J_{3h}, K_{1sh}, and K_{1yc} are −42.5‰−34.3‰ (Avg. = −38.7‰), −37.0‰−30.2‰ (Avg. = −34.2‰), and −40.3‰−30.8‰ (Avg. = −33.7‰), respectively, and the δ^{13}C_2 values in the J_{3h}, K_{1sh}, and K_{1yc} are −33.9‰−27.3‰ (Avg. = −30.9‰), −33.7‰−25.0‰ (Avg. = −28.0‰), and −26.6‰−24.7‰ (Avg. = −25.2‰), respectively. The δ^{13}C_3 values in the J_{3h}, K_{1sh}, and K_{1yc} are −32.9‰−27.4‰ (Avg. = −29.1‰), −32.8‰−22.9‰ (Avg. = −26.4‰), and −24.6‰−22.8‰ (Avg. = −23.9‰), respectively. The values of stable carbon isotope for CO_2 range from −20.4‰ to −13.0‰, with a mean of −16.1‰.

Figure 4. Relationships between the burial depth and the stable carbon isotopes of the natural gas in the deep formations of the Dehui Depression, SLB. (a) for δ^{13}C_1; (b) for δ^{13}C_2; (c) for δ^{13}C_3.

The stable hydrogen isotope values of CH_4 in the J_{3h} and K_{1sh} are −211‰ and −216‰, respectively, and those of ethane in the two formations are −213‰ and −215‰, respectively (Table 3).

4.3. Light Hydrocarbons of Natural Gas

The chemical components of the light hydrocarbon fraction are shown in Table 4. C_5–C_7 compounds are the main components, including heptane (n-C_7), methylcyclohexane (MCH), and dimethylcyclopentane (DMCP)). For the C_7 compounds in the J_{3h}, the relative contents of ΣDMCP is the highest (16.6% to 59.1%, average of 39.3%), and that of n-C_7 and MCH is 20.9%–34.0% (Avg. = 28.3%) and 20.0%–55.1% (Avg. = 32.4%), respectively. For the C_7 compounds in the K_{1sh}, the relative contents of ΣDMCP is the highest (17.1% to 47.1%, average of 33.6%), and that of n-C_7 and MCH is 24.8%–38.6% (Avg. = 29.9%) and 24.9%–57.5% (Avg. = 36.5%), respectively. For the C_7 compounds in the K_{1yc}, the relative abundance of MCH is the highest (39.2% to 68.9%, average of 57.2%), and that of n-C_7 and ΣDMCP is 18.0%–44.0% (Avg. = 27.5%) and 13.1%–16.8% (Avg. = 15.4%), respectively.

The fingerprints of light hydrocarbons (C_5–C_7) of the mudstone and natural gas samples, including 11 mudstone samples and six gas samples, have been listed in Table 5, and 15 fingerprint parameters are selected in this study.
Table 2. Stable carbon isotopes of the natural gas in the H-YFs of the Dehui Depression, SLB.

| Sample no. | Well   | Layer      | Depth (m) | δ\(^{13}\)CO\(_2\) (‰) | δ\(^{13}\)CH\(_4\) (‰) | δ\(^{13}\)C\(_2\)H\(_6\) (‰) | δ\(^{13}\)C\(_3\)H\(_8\) (‰) | δ\(^{13}\)iC\(_4\)H\(_10\) (‰) | δ\(^{13}\)nC\(_4\)H\(_10\) (‰) |
|------------|--------|------------|-----------|--------------------------|--------------------------|------------------------------|-------------------------------|---------------------------------|---------------------------------|
| 1          | DS11   | Huoshiling | 2553.00   | /                        | /                        | -34.3                        | -27.3                         | -28.3                           | /                               |
| 2          | DS12   | Huoshiling | 3328.90   | /                        | /                        | -37.3                        | -34.8                         | -33.0                           | /                               |
| 3          | DS12   | Huoshiling | 3328.50   | /                        | /                        | -35.3                        | -34.9                         | -32.9                           | /                               |
| 4          | N103   | Huoshiling | 2336.00   | /                        | /                        | -38.0                        | -29.9                         | -28.4                           | /                               |
| 5          | N103   | Huoshiling | 2337.20   | /                        | /                        | -42.4                        | -30.1                         | -28.2                           | -26.9                           |
| 6          | N103   | Huoshiling | 2335.50   | /                        | /                        | -42.5                        | -30.2                         | -28.1                           | /                               |
| 7          | N103   | Huoshiling | 2335.00   | /                        | /                        | -40.4                        | -30.5                         | -27.9                           | /                               |
| 8          | N103   | Huoshiling | 2335.20   | /                        | /                        | -40.3                        | -30.3                         | -27.9                           | -26.8                           |
| 9          | N103   | Huoshiling | 2336.20   | /                        | /                        | -37.8                        | -29.8                         | -27.4                           | -26.3                           |
| 10         | DS15   | Shahezi    | 2578.50   | /                        | /                        | -32.5                        | -25.4                         | -23.5                           | /                               |
| 11         | DS15   | Shahezi    | 2578.00   | /                        | /                        | -32.5                        | -25.3                         | -23.5                           | /                               |
| 12         | DS39-3 | Shahezi    | 2232.40   | /                        | /                        | -35.9                        | -25.0                         | -22.9                           | /                               |
| 13         | DS39-3 | Shahezi    | 2232.00   | /                        | /                        | -35.9                        | -25.2                         | -22.9                           | /                               |
| 14         | N101   | Shahezi    | 2354.90   | /                        | /                        | -37.0                        | /                             | /                               | /                               |
| 15         | N101   | Shahezi    | 2354.50   | /                        | /                        | -35.9                        | -33.7                         | -32.8                           | /                               |
| 16         | N101   | Shahezi    | 2354.40   | /                        | /                        | -36.9                        | -33.7                         | -32.8                           | -31.7                           |
| 17         | N101   | Shahezi    | 2022.46   | /                        | /                        | -33.7                        | /                             | /                               | /                               |
| 18         | N101   | Shahezi    | 2021.46   | /                        | /                        | -30.2                        | /                             | /                               | /                               |
| 19         | N104   | Shahezi    | 1935.50   | /                        | /                        | -31.4                        | /                             | /                               | /                               |
| 20         | DS21   | Yingcheng | 1756.50   | /                        | /                        | -30.8                        | -24.7                         | -24.6                           | /                               |
| 21         | DS21   | Yingcheng | 1756.00   | /                        | /                        | -30.9                        | -24.8                         | -24.6                           | /                               |
| 22         | DS35   | Yingcheng | 1400.00   | -13.0                    | -36.4                    | -26.6                         | -23.9                         | /                               |
| 23         | H3     | Yingcheng | 1971.50   | /                        | /                        | -34.5                        | -25.3                         | -22.8                           | /                               |
| 24         | H3     | Yingcheng | 1971.70   | -20.4                    | -34.6                    | -25.3                         | -22.8                         | -23.1                           | /                               |
| 25         | H4     | Yingcheng | 1508.70   | -14.9                    | -31.1                    | -24.8                         | -24.2                         | /                               | /                               |
| 26         | H4     | Yingcheng | 1508.50   | /                        | -31.0                    | -24.9                         | -24.1                         | /                               | /                               |
| 27         | N102   | Yingcheng | 1785.00   | /                        | -40.3                    | /                             | /                             | /                               | /                               |
Table 3. Stable hydrogen isotopes of the natural gas in the H-YFs of the Dehui Depression, SLB.

| Well  | Layer    | Depth (m) | $\delta^D$ % (VSMOW) |
|-------|----------|-----------|----------------------|
|       |          |           | $C_1$  | $C_2$  | $C_3$  | $iC_4$ | $nC_4$ |
| DS12  | Shahezi  | 3067.00   | −211   | −213   | −219   | /      | /      |
| DS12  | Huoshiling | 3328.90 | −216   | −215   | −192   | /      | /      |

Table 4. Relative contents of light hydrocarbons ($C_{5-7}$) in the natural gases of the deep formations in the Dehui Depression, SLB.

| Well  | Layer    | Depth (m) | Relative Contents of Light Hydrocarbons ($C_{5-7}$) (%) |
|-------|----------|-----------|------------------------------------------------------|
|       |          |           | $n-C_7$ | $\Sigma DMCP$ | MCH       |
| DS16  | Huoshiling | 2290.00 | 20.9   | 59.1  | 20.0  |
| DS16  | Huoshiling | 2291.00 | 24.1   | 55.0  | 20.8  |
| DS16  | Huoshiling | 3060.00 | 32.0   | 47.1  | 20.8  |
| DS16  | Huoshiling | 3080.00 | 28.3   | 48.0  | 23.7  |
| DS16  | Huoshiling | 3065.00 | 27.0   | 49.3  | 23.7  |
| DS12  | Huoshiling | 3335.00 | 30.2   | 44.9  | 24.9  |
| DS12  | Huoshiling | 3340.00 | 30.2   | 43.1  | 26.7  |
| DS12  | Huoshiling | 3328.90 | 34.0   | 34.1  | 25.0  |
| DS19  | Huoshiling | 2295.50 | 25.5   | 29.1  | 45.4  |
| DS11  | Huoshiling | 2556.00 | 31.7   | 16.6  | 51.7  |
| DS11  | Huoshiling | 2553.00 | 29.7   | 18.6  | 51.7  |
| DS11  | Huoshiling | 2562.00 | 27.6   | 17.3  | 35.1  |
| DS2   | Shahezi   | 2844.50  | 28.0   | 47.1  | 24.9  |
| DS2   | Shahezi   | 2845.50  | 29.0   | 44.1  | 27.0  |
| DS12  | Shahezi   | 2393.00  | 29.8   | 42.6  | 27.6  |
| DS12  | Shahezi   | 2396.00  | 33.7   | 36.7  | 29.6  |
| DS12  | Shahezi   | 2400.00  | 38.6   | 28.8  | 32.6  |
| DS15  | Shahezi   | 2578.00  | 24.8   | 19.1  | 56.1  |
| DS15  | Shahezi   | 2578.00  | 25.5   | 17.1  | 57.4  |
| DS17  | Yingcheng | 2273.50  | 44.0   | 16.8  | 39.2  |
| DS13  | Yingcheng | 1656.50  | 20.4   | 16.1  | 63.5  |
| DS13  | Yingcheng | 1658.50  | 18.0   | 13.1  | 68.9  |
Table 5. Fingerprint parameters of light hydrocarbons (C$_5$-C$_7$) in the natural gases of the deep formations in the Dehui Depression, SLB.

| Sample number | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | a   | b   | c   | d   | e   | f   |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Sample type   | Rock| Rock| Rock| Rock| Rock| Rock| Rock| Rock| Rock| Rock| Rock| Gas | Gas | Gas | Gas | Gas | Gas |
| Well          | DS12| DS2 | DS2 | DS2 | DS12| DS12| DS12| DS12| DS12| DS12| DS16| DS11| DS12| DS12| DS16| DS11| DS12|
| Location      | Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia| Huajia|
| Layer         | K$_1$yc| K$_1$yc| K$_1$sh| K$_1$sh| K$_1$sh| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h| J$_3$h|
| Depth (m)     | 1972.00| 2453.70| 2459.05| 2329.38| 2337.00| 2640.50| 2867.50| 3264.50| 3381.00| 2593.00| 2664.00| 2553.00| 3328.90| 3067.00| 2578.00| 2273.50| 2295.50|
| iC$_5$/nC$_5$ | 2.11| 1.10| 1.22| 0.68| 0.70| 1.28| 1.14| 1.06| 1.24| 1.57| 1.18| 1.54| 1.12| 1.12| 1.12| 1.12| 1.12|
| MCH/nC$_7$    | 2.62| 1.24| 1.90| 1.53| 1.60| 1.94| 1.93| 1.05| 2.05| 2.27| 1.83| 1.61| 1.96| 0.87| 3.10| 2.22| 1.76|
| 2,2-DMB/2-MP  | 0.13| 0.14| 0.20| 0.06| 0.06| 0.09| 0.11| 0.14| 0.12| 1.30| 0.13| 0.14| 0.25| 0.40| 0.54| 1.67| 0.25|
| 2,2-DMB/3-MP  | 0.23| 0.25| 0.32| 0.11| 0.10| 0.14| 0.19| 0.22| 0.20| 0.53| 0.20| 0.18| 0.39| 0.64| 0.85| 2.49| 0.43|
| 2-MP/3-MP     | 1.76| 1.72| 1.65| 1.71| 1.68| 1.62| 1.71| 1.59| 1.65| 0.41| 1.60| 1.34| 1.58| 1.61| 1.59| 1.49| 1.75|
| 2-MP/nC$_6$   | 0.77| 0.66| 0.77| 0.41| 0.41| 0.49| 0.58| 0.32| 0.64| 0.24| 0.54| 0.49| 0.68| 1.03| 1.50| 1.92| 0.89|
| 2-MP/3-MH     | 2.00| 1.38| 1.66| 1.94| 1.76| 1.82| 1.87| 1.04| 1.50| 0.27| 1.08| 1.67| 1.94| 2.74| 2.83| 3.20| 3.18|
| nC$_6$/CH     | 0.62| 1.89| 1.32| 2.19| 1.96| 1.05| 1.45| 2.02| 1.20| 0.99| 1.35| 1.40| 1.06| 3.79| 1.14| 2.22| 2.28|
| MCP/MCH       | 0.20| 0.28| 0.30| 0.29| 0.26| 0.29| 0.30| 0.23| 0.23| 0.14| 0.19| 0.54| 0.52| 0.66| 0.32| 0.11| 0.51|
| 1,3-DMCP/1,2-DMCP | 0.55| 0.67| 0.67| 0.67| 0.74| 0.67| 0.68| 0.62| 0.64| 0.42| 0.47| 0.66| 0.75| 0.62| 0.42| 0.33| 3.30|
| MCH Index     | 0.63| 0.49| 0.57| 0.53| 0.54| 0.58| 0.57| 0.46| 0.58| 0.59| 0.56| 0.52| 0.55| 0.39| 0.64| 0.57| 0.45|
| nC$_6$/((MCP+2,2-DMC) | 1.14| 2.11| 1.67| 2.83| 2.68| 1.45| 2.79| 1.62| 1.23| 1.73| 1.62| 1.39| 2.62| 1.13| 1.82| 1.91| 3.68|
| 3-MH/(L,1-DMCP+1,3-DMCP) | 1.30| 3.95| 3.06| 2.09| 1.86| 1.49| 1.90| 2.64| 1.89| 2.12| 2.26| 2.23| 2.17| 4.87| 4.27| 4.95| 0.72|
| 2,3-DMM/2-MHn | 0.33| 0.15| 0.00| 0.12| 0.14| 0.17| 0.22| 0.09| 0.20| 0.38| 0.30| 0.31| 0.27| 0.32| 0.40| 0.76| 0.34|
| (4-MHp+3,4-DMM)/3-MHp | 0.66| 0.43| 0.38| 0.21| 0.20| 0.31| 0.40| 0.44| 0.39| 0.62| 0.65| 0.39| 0.70| 0.32| 0.40| 1.00| 0.49|
5. Discussion

5.1. Gas Origins

The gas origins and the deposition environments of its parent material can be favorably identified utilizing gas chemical compositions and stable hydrogen and carbon isotopes [1,42,78–82,94]. Generally, a gas can be identified as organic or inorganic type. Dai et al. [41] proposed that: a) for the organic origin, the CO₂ content is less than 15% and δ¹³C₀₂ value is < −10‰; b) for the inorganic origin, the CO₂ content is over 60% and δ¹³C₀₂ value is > −8‰. Moreover, the thermogenic gas is predominantly characterized by δ¹³C₁<δ¹³C₂<δ¹³C₃<δ¹³C₄ (called normal carbon isotopic distribution pattern), while the negative carbon isotopic distribution pattern (δ¹³C₁>δ¹³C₂>δ¹³C₃>δ¹³C₄) generally indicates the inorganic type of natural gas [3,46,95,96]. In the Dehui Depression, the CO₂ contents and δ¹³C₀₂ values of the deep natural gas are mainly less than 5% and lower than −10‰, respectively, and the carbon isotopic distribution patterns of the gas hydrocarbons predominantly show the normal patterns, indicating that the origins of the deep natural gas are predominantly organic sources. However, as shown in Table 1 and Figure 5, parts with reversed δ¹³C series, including δ¹³C₁<δ¹³C₂<δ¹³C₃<δ¹³C₄, δ¹³C₁<δ¹³C₃<δ¹³C₂ and δ¹³C₂<δ¹³C₁<δ¹³C₃, exist in the study area, suggesting that secondary processes may have happened to the gas.

![Figure 5](image-url)
According to the gas parent materials, the oil-associated gas and coal-derived gas should be the two types. The $\delta^{13}C_2$ and $\delta^{13}C_3$ mainly reflect the inheritance of parent material, which can be utilized to differentiate between coal-derived gas and oil-associated gas [1,97–99]. It is favorably effective to use this method for gas derived from a single source, however, it is more complicated to identify the mixed sources of gas [42,94,100,101]. According to a number of analyses in China, Dai et al. [42] pointed out that gases derived from humic and sapropelic kerogens are characterized by the $\delta^{13}C_2 > -27.5\%$ and $\delta^{13}C_2 < -29.0\%$, respectively, while the gases of mixed origins are featured by $\delta^{13}C_2$ values between $-27.5\%$ and $-29.0\%$. The cross-plots of $\delta^{13}C_1$-$\delta^{13}C_2$ show that the $J_3h$ gases are mainly oil-associated gas derived from sapropelic kerogens, with a bit of coal-derived gas, and the $K_3sh$ gases are mixed-sources of coal-derived and oil-associated gases, while the $K_1yc$ gases are predominantly coal-derived gas derived from the humic kerogens (Figure 6). Moreover, according to the $\delta^{13}C_1$-$\delta^{13}C_2$-$\delta^{13}C_3$ cross-plots for the discrimination of coal-derived and oil-associated gases proposed by Dai [3], the results are similar that the gases in the $J_3h$ and $K_3sh$ are mainly the mixed-sources of coal-derived and oil-associated gases, while the $K_1yc$ gases are predominant coal-derived gases (Figure 7).

**Figure 6.** $\delta^{13}C_1$-$\delta^{13}C_2$ cross-plots for the determination of gas origins in the deep formations of the Dehui Depression, SLB.

**Figure 7.** Cross-plots of $\delta^{13}C_1$-$\delta^{13}C_2$-$\delta^{13}C_3$ indicating the gases origins in the deep formations of the Dehui Depression, SLB.
Besides, the $\delta^2\text{D}_{\text{CH}_4}$ value can be an indicator to determine the deposition environment ($\delta^2\text{D}_{\text{CH}_4} < -190\%$ for marine and lacustrine brackish environments and $\delta^2\text{D}_{\text{CH}_4} > -170\%$ for terrigenous fresh water environments [82,102]), while the $\delta^2\text{D}_{\text{C}_2\text{H}_6}$ value can be used to ascertain the parent material types [81,103,104]. The hydrogen isotope distribution of the J$_3$sh gas shows a normal pattern, while that of the K$_1$sh gas shows a negative pattern, indicating that the gases in the K$_1$sh may be affected by bacterial action or be mixed-sources of coal-derived and oil-associated gases. Moreover, the gases in the deep formations of Dehui Depression are produced by both terrigenous and lacustrine organic matters.

Generally, the relative contents of heptane ($n$-$\text{C}_7$), MCH, and $\sum$DMCP are useful parameters to analyze the gas origins [88,105–107]. Heptane ($n$-$\text{C}_7$) from algae and bacteria is sensitive to thermal maturation. As a result of a high thermodynamic stability, methylcyclohexane (MCH), mainly derived from components of terrestrial higher plants, is a good gas origin indicator, suggesting that a gas with a high MCH content should be the typical humic-type [106]. On the contrary, a gas with a high abundance of dimethylcyclopentane (DMCP), mainly sourced by aquatic microorganisms, is mainly considered to be of sapropelic-type [108]. In China, the ternary chart of $n$-$\text{C}_7$, MCH and $\sum$DMCP has been broadly utilized to differentiate the coal-derived and oil-associated gases [106,108]. The J$_3$sh and K$_1$sh gases are mainly mixed sources of coal-derived and oil-associated gases, while the K$_1$yc gases are predominantly coal-derived, as shown in Figure 8.

![Figure 8. Ternary diagram showing C$_7$ light hydrocarbons in natural gas in the deep formations of the Dehui Depression, SLB (modified after [108]).](image)

Consequently, natural gases in the deep formations of Dehui Depression are predominantly of organic origin. The J$_3$sh and K$_1$sh gases are predominantly mixed-sources of coal-derived and oil-associated gases and the proportion of oil-associated gas in the J$_3$sh is larger, while the K$_1$yc gases are predominantly coal-derived.

### 5.2. Genetic Types of Gas Hydrocarbons

Hydrocarbon gases are predominantly viewed to be from organic matter conversion by kerogen thermal-degradation, oil and gas cracking, and even bacterial action [1–10]. Generally, the $\delta^{13}\text{C}_1$ values and dryness coefficients, mainly affected by thermal maturity, can be as the effective indexes of gas thermal maturity [42,94,109]. Bernard et al. [110] proposed using the cross-plots of $C_1/(C_2 + C_3)$-$\delta^{13}\text{C}_1$ to distinguish the gas origins of both kerogen type and thermal maturity. As shown in Figure 9a,b,
the majority of the gases in the H-YFs belong to the thermogenic gas, and the parent materials of the J$_3$h and K$_1$sh gases are the mixed-sources of kerogen type II (sapropelic-humic) and type III (humic), while those of the K$_1$yc gas are mainly kerogen III (humic).

As the extensively studied before, the stable carbon isotopes of hydrocarbon gases have favorable correlations with the thermal maturity of their source rocks [1,40,78,112]. According to the geological observations and numerous statistics in the lacustrine basins of China, Dai [81] has proposed a semi-logarithmic equation between $\delta^{13}C_1$ value and vitrinite reflectance ($%Ro$):

$$\delta^{13}C_1 = 15.80 \log Ro - 42.20$$ (1)

$$\delta^{13}C_1 = 14.12 \log Ro - 34.39$$ (2)

Equation (1) is for oil-associated gas and Equation (2) is for coal-derived gas. According to these two equations, the source rock maturity can be estimated (Table 6). The thermal maturities of the J$_3$h gas range from 0.96 %Ro to 2.73 %Ro with a mean of 1.57 %Ro, and those of the K$_1$sh gas are 0.78–2.49 %Ro with a mean of 1.49 %Ro, while those of the K$_1$yc gas are 0.73–1.77 %Ro with an average of 1.37 %Ro. These indicate that these gases were mainly the products of the mature to over-mature source rocks, predominantly generated by thermal degradation and cracking.

James [113] and Jenden et al. [114] proposed that the values of $\delta^{13}C_3$-$\delta^{13}C_2$ and $\delta^{13}C_2$-$\delta^{13}C_1$ reduce with the increasing thermal maturity of gas. As shown in Figure 10a, the gases in the H-YFs predominantly belong to the mature gas class (Figure 10a). As shown in Figure 10b, the J$_3$h gas is mainly located on the trend line of kerogen type II with 0.6–1.2 %Ro, and the K$_1$sh gas is mainly located on the trend lines of kerogen type II and type III with 0.7 %Ro and 0.8 %Ro, respectively, while the K$_1$yc gas is mainly located in the trend line of kerogen type III with 0.7–0.9 %Ro, indicating that all the deep gas hydrocarbons are thermogenic and mature gases.
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Table 6. Thermal-maturity of the natural gas calculated by the formula $\delta^{13}C_1$-Ro in the Dehui Depression, SLB.

| Sample no. | Well   | Layer | Depth (m) | $\delta^{13}CH_4$ (%) | $\delta^{13}C_2H_6$ (%) | $\delta^{13}C_3H_8$ (%) | Gas Type          | Ro (%) |
|------------|--------|-------|-----------|------------------------|-------------------------|------------------------|-------------------|--------|
| 1          | DS11   | Huoshiling | 2553.00  | −34.3                  | −27.3                   | −28.3                  | Coal-derived     | 1.01   |
| 2          | DS12   | Huoshiling | 2328.90  | −37.3                  | −34.8                   | −33.0                  | Oil-associated   | 2.04   |
| 3          | DS12   | Huoshiling | 3328.50  | −35.3                  | −34.9                   | −32.9                  | Oil-associated   | 2.73   |
| 4          | N103   | Huoshiling | 2336.00  | −38.0                  | −29.9                   | −28.4                  | Oil-associated   | 1.85   |
| 5          | N103   | Huoshiling | 2337.20  | −42.4                  | −30.1                   | −28.2                  | Oil-associated   | 0.97   |
| 6          | N103   | Huoshiling | 2335.50  | −42.5                  | −30.2                   | −28.1                  | Oil-associated   | 0.96   |
| 7          | N103   | Huoshiling | 2335.00  | −40.4                  | −30.5                   | −27.9                  | Oil-associated   | 1.30   |
| 8          | N103   | Huoshiling | 2335.20  | −40.3                  | −30.3                   | −27.9                  | Oil-associated   | 1.32   |
| 9          | N103   | Huoshiling | 2336.20  | −37.8                  | −29.8                   | −27.4                  | Oil-associated   | 1.90   |
| 10         | DS15   | Shahezi   | 2578.00  | −32.5                  | −25.4                   | −23.5                  | Coal-derived     | 1.35   |
| 11         | DS15   | Shahezi   | 2578.00  | −32.5                  | −25.3                   | −23.5                  | Coal-derived     | 1.35   |
| 12         | DS39-3 | Shahezi   | 2232.40  | −35.9                  | −25.0                   | −22.9                  | Coal-derived     | 0.78   |
| 13         | DS39-3 | Shahezi   | 2232.00  | −35.9                  | −25.2                   | −22.9                  | Coal-derived     | 0.78   |
| 14         | N101   | Shahezi   | 2354.50  | −35.9                  | −33.7                   | −32.8                  | Oil-associated   | 2.49   |
| 15         | N101   | Shahezi   | 2354.40  | −36.9                  | −33.7                   | −32.8                  | Oil-associated   | 2.17   |
| 20         | DS21   | Yingcheng | 1756.00  | −30.8                  | −24.7                   | −24.6                  | Coal-derived     | 1.77   |
| 21         | DS21   | Yingcheng | 1756.00  | −30.9                  | −24.8                   | −24.6                  | Coal-derived     | 1.74   |
| 22         | DS35   | Yingcheng | 1450.00  | −36.4                  | −26.6                   | −23.9                  | Coal-derived     | 0.73   |
| 23         | H3     | Yingcheng | 1971.50  | −34.5                  | −25.3                   | −22.8                  | Coal-derived     | 0.98   |
| 24         | H3     | Yingcheng | 1971.70  | −34.6                  | −25.3                   | −22.8                  | Coal-derived     | 0.97   |
| 25         | H4     | Yingcheng | 1508.70  | −31.1                  | −24.8                   | −24.2                  | Coal-derived     | 1.20   |
| 26         | H4     | Yingcheng | 1508.50  | −31.0                  | −24.9                   | −24.1                  | Coal-derived     | 1.71   |

Prinzhofe and Huc [43] established the cross-plots of $\ln(C_2/C_3)$ vs. $\ln(C_1/C_2)$ to distinguish gases generated from both primary degradation (also called primary cracking) and secondary cracking. The $C_1/C_2$ ratios rise gradually in the primary degradation and mainly keep constant in the secondary cracking, while the $C_2/C_3$ ratios mainly keep constant in the primary degradation and rise dramatically in the secondary cracking. The gases in the $J_{sh}$ are mainly sourced from kerogen type II and type III and generated by the primary kerogen degradation and secondary oil cracking, and the gases in the $K_{sh}$ are mainly sourced by kerogen type III and generated by primary kerogen degradation, while the $K_{yc}$ gases are mainly sourced by kerogen type II and type III and generated by primary kerogen degradation (Figure 11).
Lorant et al. [111] established the cross-plots of $C_2/C_3$ vs. $\delta^{13}C_2-\delta^{13}C_3$ to distinguish gases generated by primary degradation and secondary cracking. The gases in the J$_{3sh}$ and K$_{1sh}$ mainly plot in the secondary oil cracking area, with a bit in the primary degradation area, while the gases in the K$_{1yc}$ are located in the primary degradation area. Consequently, the gases in the deep formations of Dehui Depression are predominantly thermogenic types. The gases in the J$_{3sh}$ and K$_{1sh}$ are mainly generated by primary kerogen degradation and secondary oil cracking, while the gases in the K$_{1yc}$ are mainly produced by primary kerogen degradation.

5.3. Gas-Source Correlation

Although many features of the Cretaceous petroleum system of the SLB are known, the gas-source correlation in the deep formations are not fully understood. Huang et al. [9], Zhang et al. [72], Chen [77] and Shen and Liang [83] have proposed that the mudstones in J$_{3sh}$, K$_{1sh}$, and K$_{1yc}$, with high organic abundance (TOC = ~2.5 wt.%), high thermal maturity (Ro = ~1.5–2.0%) and type II-III kerogens, are the main source rocks for gas in the deep formations of the SLB. The main deficiency in the understanding of the multi-source, multi-reservoir gas system in the deep formations is gas-source correlation. Considering the huge lateral extension of the basin and sets of vertically-developed source rocks and reservoir rocks, the gas-source correlation is challenging. A recent attempt, which tried to determine possible source rocks for the J$_{3sh}$ gases using their chemical components and stable carbon isotopes [77], showed that the J$_{3sh}$ gas was mainly sourced by the J$_{3sh}$ mudstones. However, the sources of the gases in the K$_{1sh}$ and K$_{1yc}$ are still unknown.

Generally, the gas chemical components and stable carbon isotopes are influenced by the parent materials, thermogenic actions, migration, and bacterial actions. As shown in Figures 3 and 4, the $C_1$ contents and dryness coefficients rise with the increasing burial depth, while the $C_2$ contents reduce with the increasing burial depth, indicating that the gases in the deep formations were predominantly generated by thermogenic actions and accumulated in/approaching the source rocks. Besides, corresponding to the results, the density of gases in the deep formations decrease with the increasing burial depth. The results suggest that the gases in the deep formations should be mainly sourced by the J$_{3sh}$ and K$_{1sh}$ mudstones, or just the J$_{3sh}$ mudstones.

The relative contents of light hydrocarbon components with similar boiling points can be the fingerprints to ascertain the gas genetic type and access gas-source correlation. The fingerprint trends of the light hydrocarbons in the mudstones of the J$_{3sh}$ and K$_{1sh}$ do not display any obvious differences, while those in the K$_{1yc}$ show some differences (Figure 12). In Figure 12a,b, the fingerprint trends of the gases in the middle J$_{3sh}$ of Well DS11 and the lower J$_{3sh}$ of Well DS12 show high coherence with
those of the mudstone samples in the J3h of the Huajia Sag, indicating that the gases accumulated in
the low-middle J3h are predominantly sourced by the J3h source rocks, corresponding to the results
proposed by Shen and Liang (2015) [77]. In Figure 12c–d, about 70% of the total fingerprint parameters
of the gases in the upper J3h of Well DS12 and the K1sh of Well DS15 show similar trends with those
of the mudstones in the J3h and K1sh, suggesting that the gases in the K1sh and the upper J3h are
mainly produced by the mudstones both in the J3h and K1sh. In Figure 12e,f, less than 50% of the
total fingerprint parameters of the gases in the J3h of Well DS19 and the K1yc of Well DS17 show
similar trends with those of the mudstones in the deep formations of the Huajia Sag, indicating that
the gases in the Baojia and Nong’annan sags are not sourced by the mudstones of the deep formations
in the Huajia Sag. Combined with the geological conditions in Dehui Depression and the gas chemical
components and density, the gases in the K1yc may be derived from the three sets of source rocks (J3h,
K1sh, and K1yc), or one or two of them through the vertical faults shown in Figure 1.

**Figure 12.** The fingerprints trends of the gas and source rocks in the deep formations of the Dehui
Depression, SLB, indicating the gas-source correlation. (a) for Well DS11, 2553.00m, gas sample; (b) for
Well DS12, 3328.90m, gas sample; (c) for Well DS12, 3067.00m, gas sample; (d) for Well DS15, 2578.00m,
gas sample; (e) for Well DS17, 2273.50m, gas sample; (f) for Well DS19, 2295.50m, gas sample.
Rooney et al. [44] proposed that if the alkane gas comes from a single source, a linear correlation of carbon number (1/n) vs. $\delta^{13}C_n$ exists. The slope changes of regression line can ascertain the gas-mixing between different types at different thermal-maturity stages, and also indicate the bio-genetic gas and methane seepage [44]. In Figure 5d, the trends of 1/n vs. $\delta^{13}C_n$ of the $J_3h$ alkane gases in the Huajia sag mainly show linear relationships with bits of nonlinear relationships and can be divided into three groups (Groups A, B, and C), indicating the $J_3h$ gases may have two types (coal-derived and oil-associated gases) with two sources (maybe both the $J_3h$ and the $K_1sh$ mudstones). According to the Figure 5e, the trends of 1/n vs. $\delta^{13}C_n$ of the alkane gases in the $K_1sh$ of the Huajia (Well DS15 and Well N101) and Lanjia (Well DS39-3) sags mainly indicate predominant linear relationships and can be divided into three groups (Groups D, E, and F), and the slopes of the samples in each sag are similar. The Group D is similar with the Group B, and the Group E is similar with the Group A, and the Group F is similar with the Group C. Combined with the gas origins and genic types studied above (Sections 5.1 and 5.2), these three groups (Group D, E, and F) suggest that the two types gases (coal-derived and oil-associated gases) derived from two sources (two sags) may be mixed. Additionally, in Figure 5f, the trends of 1/n vs. $\delta^{13}C_n$ of the alkane gases in the $K_1yc$ of the Huajia (Well DS21) and Lanjia (Well DS35, Well H3, and Well H4) sags mainly indicate predominant linear relationships and can be divided into two groups (Group G and H). The Group G is similar with the Group A, and the Group H is similar with the Group C, suggesting that: 1) the two types (oil-associated and coal-derived) of gases may be mixed in the $K_1yc$; 2) the gases were derived from two sources (two sags) with one-type gas; and 3) the gases of two stages (mature or charging) were mixed. According to the study above (Section 5.1), the gases in the $K_1yc$ are mainly the coal-derived gases and came from the Baojia sag, so the two-group samples (Group F and G) suggest that the gas samples are mainly controlled by the mixed-sources of two mature or charging stages.

According to the geological and geochemical analyses, as shown in Figures 13 and 14, the gas reservoirs in Well DS17 are mainly distributed in the upper $K_1yc$, and the lithology of the $K_1yc$ is predominantly igneous rocks (dacite) in the location of Well DS17. The gas reservoirs in Well DS11 are mainly distributed in the middle of $J_3h$ and $K_1sh$, and the reservoir beds are mainly igneous rocks in the $K_1sh$ and sandstones in the $J_3h$. The source rocks of both Wells DS17 and DS11 are mainly located in the $J_3h$–$K_1sh$, and the geochemical characters mainly suggest the good to excellent source rock potentials (Figure 13). The gas reservoirs in the $J_3h$ of Well DS11 are mainly sourced by the underlying $J_3h$ source rocks through the faults, and the gas reservoirs in the $K_1sh$ of Well DS11 may be sourced by both underlying $J_3h$ and overlying $K_1sh$ source rocks through faults and carrier beds, and the gas reservoirs are mainly sourced by the source rocks in the Huajia sag (Figure 14a). The gas reservoirs in the $K_1yc$ of Well DS17 are mainly sourced by the underlying $J_3h$ and $K_1sh$ source rocks through faults and carrier beds, and the gas reservoirs are mainly sourced by the source rocks in the Baojia sags (Figure 14b).

Consequently, the gases in the lower-middle $J_3h$ are predominantly derived from the $J_3h$ mudstones, and the gases in the $K_1sh$ and the upper $J_3h$ are mainly the mixed-sources of both the $J_3h$ and the $K_1sh$ mudstones, while the gases in the $K_1yc$ are mainly derived from either the $J_3h$ mudstones or the $K_1sh$ mudstones, or both the two sets of mudstones. Moreover, the gas accumulations in different sags are mainly controlled by the $J_3h$ and $K_1sh$ mudstones developed in the sags where the gases accumulated, indicating that the gas migration with a short distance was the main migration type in the deep formations of SLB.
the Group F is similar with the Group C. Combined with the gas origins and genetic types studied above (Section 5.1 and 5.2), these three groups (Group D, E, and F) suggest that the two types gases (coal-derived and oil-associated gases) derived from two sources (two sags) may be mixed. Additionally, in Figure 5f, the trends of 1/n vs. δ^{13}C of the alkane gases in the K_{1yc} of the Huajia (Well DS21) and Lanjia (Well DS35, Well H3, and Well H4) sags mainly indicate predominant linear relationships and can be divided into two groups (Group G and H). The Group G is similar with the Group A, and the Group H is similar with the Group C, suggesting that: 1) the two types (oil-associated and coal-derived) of gases may be mixed in the K_{1yc}; 2) the gases were derived from two sources (two sags) with one type gas; and 3) the gases of two stages (mature or charging) were mixed.

According to the study above (Section 5.1), the gases in the K_{1yc} are mainly the coal-derived gases and came from the Baojia sag, so the two-group samples (Group F and G) suggest that the gas samples are mainly controlled by the mixed sources of two mature or charging stages.

According to the geological and geochemical analyses, as shown in Figure 13 and Figure 14, the gas reservoirs in Well DS17 are mainly distributed in the upper K_{1yc}, and the lithology of the K_{1yc} is predominantly igneous rocks (dacite) in the location of Well DS17. The gas reservoirs in Well DS11 are mainly distributed in the middle of J_{3h} and K_{1sh}, and the reservoir beds are mainly igneous rocks in the K_{1sh} and sandstones in the J_{3h}. The source rocks of both Wells DS17 and DS11 are mainly located in the J_{3h}–K_{1sh}, and the geochemical characters mainly suggest the good to excellent source rock potentials (Figure 13). The gas reservoirs in the J_{3h} of Well DS11 are mainly sourced by the underlying J_{3h} source rocks through the faults, and the gas reservoirs in the K_{1sh} of Well DS11 may be sourced by both underlying J_{3h} and overlying K_{1sh} source rocks through faults and carrier beds, and the gas reservoirs are mainly sourced by the source rocks in the Huajia sag (Figure 14a). The gas reservoirs in the K_{1yc} of Well DS17 are mainly sourced by the underlying J_{3h} and K_{1sh} source rocks through faults and carrier beds, and the gas reservoirs are mainly sourced by the source rocks in the Baojia sags (Figure 14b).

Figure 13. Comprehensive geochemical columns of the deep formations in the Dehui Depression, SLB. ((a) is for Well DS 17 and (b) is for Well DS 11.) (The data in the columns are provided by the Research Institute of Petroleum Exploration and Development, Jilin Oilfield Branch, CNPC, which are unpublished.).
Figure 13. Comprehensive geochemical columns of the deep formations in the Dehui Depression, SLB. ((a) is for Well DS 17 and (b) is for Well DS 11.) (The data in the columns are provided by the Research Institute of Petroleum Exploration and Development, Jilin Oilfield Branch, CNPC, which are unpublished.).

Figure 14. Sketch profiles for the gas source and migration in the deep formations of the Dehui Depression, SLB. ((a) is for the profile crossing Well DS 11 and (b) is for the profile crossing Well DS 17.) (The seismic profiles are provided by the Research Institute of Petroleum Exploration and Development, Jilin Oilfield Branch, CNPC, which are unpublished.).

6. Conclusions

Integrated geochemical study suggests the methane contents and stable carbon isotopes and gas dryness coefficients increase with the increasing burial depth in the Dehui Depression, lacustrine SLB. The $\delta^{13}$C series mainly show normal carbon isotopic distribution pattern, with parts of reversal. The gases in the deep formations (generally the H-YFs (156–125 Ma)) of the Dehui Depression are predominantly organic and thermogenic. According to the determination charts utilizing gas components and stable carbon isotopes and the gas thermal maturity calculated by equation of $\delta^{13}$C$_{1}$-Ro%, the gases in the J$_{3}$h (156–145 Ma) and K$_{1}$sh (145–133.9 Ma) are mixed-sources of kerogen thermal degradation and oil secondary cracking, while the gases in the K$_{1}$yc (133.9–125 Ma) are predominantly derived from kerogen thermal degradation.
According to the stable carbon isotopes and fingerprints of light hydrocarbons (C$_{5-7}$), the gases in the lower-middle J$_3$h are sourced by the J$_3$h mudstones, and the gases in the K$_1$sh and the upper J$_3$h are mainly sourced by the J$_3$h and K$_1$sh mudstones, while those in the K$_1$yc are mainly sourced by either the J$_3$h or the K$_1$sh mudstones. In addition, the gas reservoirs in different sags are mainly sourced by the J$_3$h and K$_1$sh source rocks developed in the sags where the gas reservoirs were found, indicating the proximal-source accumulation. These indicate that the gas migration with a short distance was the main migration type in the deep formations of SLB.

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**Abbreviations**

The compounds and abbreviations of the light hydrocarbons are as follows:

| Compound                | Abbreviation |
|-------------------------|--------------|
| Isopentane              | iC$_5$       |
| n-Pentane               | nC$_5$       |
| n-Hexane                | nC$_6$       |
| n-Heptane               | nC$_7$       |
| Methylcyclohexane       | MCH          |
| 2,2-Dimethylbutane      | 2,2-DMB      |
| 2-Methylpentane         | 2-MP         |
| 3-Methylpentane         | 3-MP         |
| 2,2-Dimethylpentane     | 2,2-DMP      |
| 3-Methylhexane          | 3-MH         |
| Cyclohexane             | CH           |
| Methylcyclopentane      | MCP          |
| 1,1-Dimethylcyclopentane| 1,1-DMCP     |
| 1,trans3-Dimethylcyclopentane| 1,t3-DMCP |
| 1,trans2-Dimethylcyclopentane| 1,t2-DMCP |
| 1,cis3-Dimethylcyclopentane| 1,c3-DMCP |
| MCH/(n-Heptane+MCH+$\Sigma$DMCP) | MCH Index |
| 2,3-Dimethylhexane      | 2,3-DMH      |
| 3,4-Dimethylhexane      | 3,4-DMH      |
| 2-Methylheptane         | 2-MHp        |
| 3-Methylheptane         | 3-MHp        |
| 4-Methylheptane         | 4-MHp        |

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