Light Hydrocarbon (C₅–C₇) Geochemistry in the Northern Margin of the Qaidam Basin, Northeastern Tibetan Plateau: Gas Mixing and Hydrocarbon Charge History

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ABSTRACT: Twenty natural gases from the northern margin of the Qaidam Basin were collected and examined for the composition and stable carbon isotopic characteristics of gas and light hydrocarbons (C₃–C₇). The results reveal that the carbon isotopes of isoalkanes and cyclo-alkanes in light hydrocarbons are mainly controlled by the bioprecursors, whereas the carbon isotopes of n-alkanes and aromatics in light hydrocarbons are primarily influenced by the bioprecursors and maturity. Based on the genetic types obtained from C₁–C₅ and C₅–C₇ fractions, three types of gases are identified: coal-type gas, oil-type gas, and mixed gas. Coal-type gas dominates the northern margin of the Qaidam Basin, oil-type gas is mostly distributed in the Lenghu no. 3 field, and mixed gas is mainly developed in the Dongping and Mabei fields. According to the maturity obtained from δ¹³C₁ and heptane and isoheptane ratios, the petroleum charge period is studied in combination with burial history and hydrocarbon generation history, and the result is roughly well matched with the research of homogeneous temperatures of petroleum inclusions. Furthermore, the generation temperature of the major reservoired hydrocarbons calculated from C₇ light hydrocarbon compositions ranges from 125.0 to 135.9 °C, suggesting that a major petroleum charge event may occur primarily during the Shangganchaigou period (N₁) in most fields. The deep paleo uplifts adjacent to the hydrocarbon-generating depressions at the margin of the basin and uplift zone in the inner basin are estimated as favorable areas for further exploration in the northern margin of the Qaidam Basin.

1. INTRODUCTION

Natural gas is a naturally gaseous mixture of hydrocarbon gases (such as methane, ethane, and propane) and nonhydrocarbon gases (such as carbon dioxide, nitrogen, and hydrogen sulfide) generated beneath the earth’s surface. Natural gas typically contains methane of 84.6–96.0 vol %, ethane of 2.0–6.4 vol %, propane of 0.6–5.3 vol %, and carbon dioxide and hydrogen sulfide are usually less than 5.0 vol %.¹ ² Natural gas is regarded as an environmentally friendly clean fuel compared with coal and crude oil, and it is found in oil fields, gas fields, and coal beds. In recent years, natural gas exploration has made breakthroughs in the northern margin of the Qaidam Basin. The successive discovery of Dongping, Niudong, and Jianbei gas fields in the piedmont zone of the Altun Mountains indicates a favorable prospect for natural gas exploration in this area.³–⁶ Most gas reservoirs in these structural belts are far from the hydrocarbon generation centers (Figure 1). Many studies have been conducted to investigate the source of gas here, but the origin of the gas remains controversial. The geochemical characteristics of natural gas indicate that the gas was mainly derived from the Jurassic coal measures,⁷ while the biomarker data in the Dongping field suggest that oil was probably derived from the Tertiary lacustrine mudstones.⁸

The hydrocarbon components of natural gas are primarily C₁–C₅ compounds with a little amount of C₆+ light hydrocarbon compounds. Natural gas is categorized into two types based on the composition of its hydrocarbons: wet gas and dry gas. The dry gas is mainly composed of methane, with little or no C₂+ components, and has dryness coefficients (C₁/ C₁₋₅) greater than 95%, whereas the wet gas generally contains C₂+ constituents greater than 10 vol % and has dryness coefficients less than 95%.⁹ Natural gases in the northern margin of the Qaidam Basin are mainly dry gases. C₁–C₄ hydrocarbons were mostly employed to investigate their origins.⁷ Besides, the composition of C₁–C₅ light hydrocarbons may also provide important information about the genetic type of natural gas, gas maturity, and gas–gas correlation.¹⁰–¹⁷ Furthermore, methylcyclopentane (MCC₅) and methylcyclohexane (MCC₆) are considered to inherit
kerogen geochemical characters, and the carbon isotopes of MCC₅ and MCC₆ are commonly used to distinguish the organic matter type of oil.¹⁸⁻²⁷ So far, carbon isotopes of C₅⁻C₇ light hydrocarbons have primarily been used to analyze mature oil, with little application to highly mature gas. Because of the low content of light hydrocarbons in dry gas, increasing injection volume of natural gas can meet the need for C₅⁻C₇ light hydrocarbon composition analysis. Examining the stable carbon isotopes of individual light hydrocarbons, on the other hand, is difficult. Previous research used direct injection and flush-trap injection to determine the carbon isotopic composition of individual light hydrocarbons in natural gas.²⁸⁻³⁰ However, the direct injection approach can only acquire data for high-content compounds, and the flush-trap injection method requires specialized equipment and is expensive. The solid-phase microextraction (SPME) method is an efficient, low-cost, simple-to-use sample preparation approach that is widely employed in enriching analytes of interest from a sample matrix. Because it is capable of enriching trace gas compositions while having little effect on isotopic fractionation, the SPME is a promising method in stable isotope analysis.³¹,³² The SPME coupled with gas chromatography–isotope ratio mass spectrometry can be an effective and reliable method for measuring the carbon isotopes of C₅⁻C₇ individual light hydrocarbons.

In this research, the molecular and stable carbon isotopic compositions of gas and light hydrocarbons (C₅⁻C₇), as well as the carbon isotopes of whole oil were analyzed in the northern margin of the Qaidam Basin. The aim is to investigate the source, mixing, and charge history of natural gas and to get a better understanding of the hydrocarbon generation and accumulation in the northern margin of the Qaidam Basin.

2. GEOLOGICAL SETTINGS

The Qaidam Basin is located in the northeastern Tibetan Plateau (Figure 1a) and contains Mesozoic and Cenozoic lacustrine sediments with a maximum thickness of 17,280 m.³³,³⁴ The basin is surrounded by the Qilian Mountains to the northeast, the Altun Mountains to the northwest, and the Kunlun Mountains to the south. The basin can be structurally divided into three secondary tectonic units, namely, the northern fault-block belt, the western depression, and the eastern depression (Figure 1b). The northern margin of the Qaidam Basin is a major structure in the northern basin, consisting of several structural zones, such as east of Altun uplift, west of Qilian uplift, Maxian uplift, Eboliang structural belt, Lenghu structural belt, Pingxi Sag, Pingdong Sag, Kunyeyi Sag, Yibeil Sag, Saishenteng Sag, and Yuka Sag (Figure 1c).

Figure 1. Tectonic setting of the Qaidam Basin and the distribution of oil and gas fields in the study area. (a) Location of the Qaidam Basin in the Tibetan Plateau, red rectangle denotes the location of the Qaidam Basin, TB = Tarim Basin, QB = Qaidam Basin, OB = Ordos Basin, SB = Sichuan Basin, AFT = Altyn Tagh fault, EKF = East Kunlun fault, QL = Qilian Mountain; (b) location of three tectonic units in the Qaidam Basin and red rectangle indicates the study area; (c) tectonic zones and distribution of the oil and gas field in the northern margin of the Qaidam Basin (modified from Tian et al., 2018).⁷
in the northern margin of the Qaidam Basin (Figure 2). The source rocks consist of dark and gray-dark mudstones, carbonaceous mudstones, coal, and oil shale. The vitrinite reflectance ($R_o$) values are mainly higher than 1.4% with a maximum value of 4.0%. The kerogen type mainly includes type III and type II with carbon isotopes ranging from $-31.4$ to $-74.2$‰. The main reservoirs are conglomerates, sandstone, and siltstone in the Lulehe-Shangyoushashan formations, and magmatic rocks and metamorphic rocks in the basement rock. The caps are shale and calcareous rocks in clastic rocks (Figure 2).

3. RESULTS

3.1. Composition and Stable Carbon Isotope of Natural Gas. The composition of natural gas in the northern margin of the Qaidam Basin is mainly composed of hydrocarbons (Table 1). In the hydrocarbons, the methane content is 56.3–92.4%, with an average of 84.0%; ethane content is 2.0–13.1%, with an average of 4.7%; and propane content is 0.1–2.9%, with an average of 0.8%. The gas dryness coefficient ($C_1/C_{1-3}$) ranges from 0.78 to 0.99 (Table 1), with an average of 0.93, indicating that gases are mostly dry gases and some wet gases.

The $\delta^{13}C_{\text{methane}}$ values are from $-46.8$ to $-22.7$‰, with an average of $-29.9$‰; $\delta^{13}C_{\text{ethane}}$ values are from $-30.5$ to $-19.7$‰, with an average of $-23.1$‰; and $\delta^{13}C_{\text{propane}}$ values are from $-28.1$ to $-19.5$‰, with an average of $-22.8$‰ (Table 1). Most gases have a normal carbon isotopic distribution pattern among the $C_1$–$C_3$ alkanes, that is, $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$, implying primary gases (Table 1). While several gases in Jianbei, Dongping, and Mabei fields have partial carbon isotopic reversal between ethane and propane ($\delta^{13}C_2 > \delta^{13}C_3$), probably implying admixture of gases from multiple sources.

3.2. Molecular and Stable Carbon Isotopic Composition of Light Hydrocarbon. Table 2 shows the composition of light hydrocarbons and relevant parameters. Figure 3 displays the representative chromatograms of light hydrocarbons (i.e., samples DP1 and N1). Sample DP1 has higher contents of the $n$-alkanes of $C_5$–$C_7$ hydrocarbons, whereas sample N1 has higher contents of aromatics of $C_6$–$C_7$, implying that they were most likely generated from different types of kerogens. Table 3 lists the carbon isotopic ratios of the individual hydrocarbons of $C_5$–$C_7$ fractions with a large variation. The $\delta^{13}C$ of methylcyclopentane ranges from $-27.1$ to $-21.9$‰ and the $\delta^{13}C$ of methylcyclohexane ranges from $-25.6$ to $-22.4$‰.
3.3. Stable Carbon Isotope of Whole Oil. The stable carbon isotopic compositions of whole oil in the northern margin of the Qaidam Basin vary from −32.1 to −23.9‰ (Table 5), similar to the kerogen carbon isotopic variance. This result suggests that oil may be generated from different organic matters. The stable carbon isotopic values of oil derived from the sapropelic organic matter are generally between 32 and 30‰, while those derived from humic organic matter are commonly between 27 and 25‰. Thus, the oil and condensate in Dongping and Lenghu no. 3 fields were mainly generated from sapropelic organic matter (Figure 4), and those in Kunyetiebei and Pingtaei fields were primarily

Table 1. Component and Isotope Properties of Natural Gas in the Northern Margin of the Qaidam Basin

| field     | sample | depth (m) | strata | C1  | C2  | C3  | CO2 | N2  | dryness | C1/(C2 + C3) | δ13C (%) | Rr (%) |
|-----------|--------|-----------|--------|-----|-----|-----|-----|-----|---------|-------------|-----------|--------|
| Jianbei   | JH5    | 4500-6100 | bedrock| 81.8| 2.3 | 0.2 | 0.9 | 14.6| 0.97    | 32.9       | −23.1     | −21.6  |
| Dongping  | DP1    | 4778      | bedrock| 88.5| 2.0 | 0.1 | 0.2 | 7.6 | 0.97    | 41.2       | −25.0     | −20.8  |
| Niudong   | N105   | 2142-2149 | J     | 78.0| 6.8 | 0.7 | 0.8 | 7.0 | 0.90    | 10.4       | −35.5     | −23.0  |
| Kunyetiebei| K2    | 6875-6888 | bedrock| 90.7| 4.1 | 0.5 | 0.1 | 3.5 | 0.97    | 19.7       | −30.0     | −22.1  |

Table 2. Representative Light Hydrocarbon Geochemical Parameters of Natural Gas in the Northern Margin of the Qaidam Basin

| field     | sample | depth (m) | strata | C5  | C6  | C7  | MCC | isoheptane value | heptane value | T (°C) |
|-----------|--------|-----------|--------|-----|-----|-----|-----|------------------|---------------|--------|
| Jianbei   | JH5    | 4500-6100 | bedrock| 81.8| 2.3 | 0.2 | 0.9 | 14.6 | 0.97 | 32.9 | −23.1     | −21.6  |
| Dongping  | DP1    | 4778      | bedrock| 88.5| 2.0 | 0.1 | 0.2 | 7.6 | 0.97 | 41.2 | −25.0     | −20.8  |
| Niudong   | N105   | 2142-2149 | J     | 78.0| 6.8 | 0.7 | 0.8 | 7.0 | 0.90 | 10.4 | −35.5     | −23.0  |
| Kunyetiebei| K2    | 6875-6888 | bedrock| 90.7| 4.1 | 0.5 | 0.1 | 3.5 | 0.97 | 19.7 | −30.0     | −22.1  |

Appendix:

Dryness defined as C1/(C1 − C3); Rr % values of oil-type gases were calculated according to the δ13C1−Rr relationship suggested by Shen et al. (1991); δ13C1 = 40.49 × log Rr − 34; Rr % values of coal-type gases were calculated based on the δ13C1−Rr relationship suggested by Dai and Qi (1989); δ13C1 = 14.13 × log Rr − 34.39.

Isopentane value = (2-MC6 + 3-MC6)/(t1,2-DMCC5 + c1,3-DMCC5 + t1,3-DMCC5); heptane value = (100 × nC7)/Σcyclohexane through methylcyclohexane not include c1,2-DMCC5; generation temperature (T, °C) = 140 + 15 × ln (2,4-DMCC2/2,3-DMCC3).

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alkanes and toluene have little change with maturity. 20 Hydrocarbons become heavier as maturity increases, but that the carbon isotopes of the pyrolysis experiment of asphaltene, researchers proposed attributed to the source and maturity factors. Carbon isotopic variations are usually increasing maturity. As the increase of maturity, the 12C bond will be broken preferentially, resulting in the enrichment with increasing maturity. 39

δ13C numbers and the corresponding light hydrocarbons are listed in Table 4.

4. DISCUSSION

4.1. Carbon Isotopic Variability of C5−C7 Light Hydrocarbons. Carbon isotopic variations are usually attributed to the source and maturity effects. According to the pyrolysis experiment of asphaltene, researchers proposed that the carbon isotopes of n-alkanes and iso-alkanes in light hydrocarbons become heavier as maturity increases, but cyclo-alkanes and toluene have little change with maturity. 20 However, several natural oil studies suggested that the carbon isotopes of iso-alkanes in light hydrocarbons are mainly controlled by their sources. 21,22 In this study, the carbon isotopic variability of light hydrocarbons is investigated preliminarily via the relationships between 13C of C5−C7 light hydrocarbons and δ13C C2−δ13C C1. The 13C of C5−C7 light hydrocarbons are chosen because of a restriction from co-elution in some C7 light hydrocarbons, and δ13C C2−δ13C C1 is employed as a maturity-dependent parameter that decreases with increasing maturity. 39

Figure 5a exhibits that n-C5 becomes generally enriched in 13C with the decrease of δ13C C2−δ13C C1, indicating that n-alkanes in light hydrocarbons may become enriched in 13C with increasing maturity. As the increase of maturity, the 12C−13C bond will be broken preferentially, resulting in the enrichment of 13C in the remaining compounds, causing the carbon isotopes of n-alkanes to become heavier gradually. 59 In addition, the δ13C (nC) of samples from Dongping, Lenghu no. 3, and Mabei fields are lighter than those from other fields, which is attributed to the organic matter differences (will be discussed below). Thus, it is suggested that n-alkanes in light hydrocarbons are mainly controlled by source and maturity. Figure 5b shows no evident linear relationship between δ13C 2MC5 and δ13C 2−δ13C 1, implying maturity has little effect on the 13C of iso-alkanes in light hydrocarbons. The δ13C 2MC5 from Dongping, Lenghu no. 3, and Mabei fields are lighter than those from other fields. Therefore, the isotopic variation of iso-alkanes in light hydrocarbons is most likely due to the source differences. Figure 5c also displays no apparent linear relationship between δ13CM C5 and δ13C C2−δ13C 1, and δ13CM C1 values from Dongping, Lenghu no. 3, and Mabei fields are lighter than those from other fields, indicating that cyclo-alkanes in light hydrocarbons are probably controlled by the source. Figure 5d shows a general negative relationship between δ13C benzene and δ13C C2, and δ13C C2, and samples from Dongping, Lenghu no. 3, and Mabei field are depleted in 13C, indicating that δ13C benzene is probably influenced by the source and maturity. At the immature and mature stages, benzene is thought to stem from biological precursors and its carbon isotope is inherited from kerogen. 40 While at the higher maturity stage, the 12C−13C bond of toluene or other aromatic hydrocarbons breaks, 41 and the formed benzene will increasingly enrich 13C, resulting in the gradual heavier carbon isotope of benzene.

4.2. Genetic Types of Natural Gas. The plot of δ13C C1 versus C1/(C2 + C3) is widely used to determine the genetic types of the gas. 42−46 Figure 6 shows that most gases plot within and adjacent to the area of type-III kerogen, and only one gas sample from the Lenghu no. 3 field distributes in the area of thermogenic, indicating that gases in the northern margin of the Qaidam Basin were primarily generated from humic source rocks, whereas the gas in the Lenghu no. 3 field...
was produced from sapropelic source rocks. In addition, δ^{13}C_{2} is an important parameter in identifying different types of gas. Based on a comprehensive study of natural gas in China, Dai et al. (2005) proposed that generally coal-type gas is characterized by δ^{13}C_{2} > −27.5‰ and oil-type gas by δ^{13}C_{2} < −29.0‰. By using this criterion, it suggests that most gases in the northern margin of the Qaidam Basin are coal-type gases, except one in the Lenghu no. 3 field is an oil-type gas.

The composition of C_{5}−C_{7} light hydrocarbons may provide vital information about the genetic type of natural gas. Figure 7

### Table 3. Carbon Isotope Ratios (‰, VPDB) of Light Hydrocarbons in the Northern Margin of the Qaidam Basin

| number | chemical name | abbreviation |
|--------|---------------|--------------|
| 1 | i-C_{5} | i-C_{5} |
| 2 | n-C_{5} | n-C_{5} |
| 3 | 2,2-dimethylbutane | 2,2-DMC_{5} |
| 4 | cyclopentane | C_{5} |
| 5 | 2-methylpentane | 2-MC_{5} |
| 6 | 3-methylpentane | 3-MC_{5} |
| 7 | n-C_{6} | n-C_{6} |
| 8 | 2,2-dimethylpentane | 2,2-DMC_{5} |
| 9 | methylcyclopentane | MCC_{5} |
| 10 | 2,4-dimethylpentane | 2,4-DMC_{5} |
| 11 | 2,2,3-trimethylbutane | 2,2,3-TMC_{4} |
| 12 | benzene | Benz. |
| 13 | 3,3-dimethylpentane | 3,3-DMC_{5} |
| 14 | cyclohexane | C_{6} |
| 15 | 2-methylhexane | 2-MC_{6} |
| 16 | 2,3-dimethylpentane | 2,3-DMC_{5} |
| 17 | 1,1-dimethylcyclopentane | 1,1-DMC_{5} |
| 18 | 3-methylhexane | 3-MC_{6} |
| 19 | cis-1,3-dimethylcyclopentane | 1,3-DMC_{5} |
| 20 | trans-1,3-dimethylcyclopentane | 1,3-DMC_{5} |
| 21 | trans-1,2-dimethylcyclopentane | 1,2-DMC_{5} |
| 22 | n-C_{7} | n-C_{7} |
| 23 | methylcyclohexane | MCC_{6} |
| 24 | toluene | Tol. |

### Table 4. Number and the Corresponding Light Hydrocarbon

| number | chemical name | abbreviation |
|--------|---------------|--------------|
| 1 | i-C_{5} | i-C_{5} |
| 2 | n-C_{5} | n-C_{5} |
| 3 | 2,2-dimethylbutane | 2,2-DMC_{5} |
| 4 | cyclopentane | C_{5} |
| 5 | 2-methylpentane | 2-MC_{5} |
| 6 | 3-methylpentane | 3-MC_{5} |
| 7 | n-C_{6} | n-C_{6} |
| 8 | 2,2-dimethylpentane | 2,2-DMC_{5} |
| 9 | methylcyclopentane | MCC_{5} |
| 10 | 2,4-dimethylpentane | 2,4-DMC_{5} |
| 11 | 2,2,3-trimethylbutane | 2,2,3-TMC_{4} |
| 12 | benzene | Benz. |
| 13 | 3,3-dimethylpentane | 3,3-DMC_{5} |
| 14 | cyclohexane | C_{6} |
| 15 | 2-methylhexane | 2-MC_{6} |
| 16 | 2,3-dimethylpentane | 2,3-DMC_{5} |
| 17 | 1,1-dimethylcyclopentane | 1,1-DMC_{5} |
| 18 | 3-methylhexane | 3-MC_{6} |
| 19 | cis-1,3-dimethylcyclopentane | 1,3-DMC_{5} |
| 20 | trans-1,3-dimethylcyclopentane | 1,3-DMC_{5} |
| 21 | trans-1,2-dimethylcyclopentane | 1,2-DMC_{5} |
| 22 | n-C_{7} | n-C_{7} |
| 23 | methylcyclohexane | MCC_{6} |
| 24 | toluene | Tol. |

### Table 5. Carbon Isotope Ratios (‰, VPDB) of Oil and Condensate in the Northern Margin of the Qaidam Basin

| field | sample | strata | δ^{13}C_{2} (%) |
|-------|--------|--------|----------------|
| Dongping | DP4 | E_{1+2} | −31.2 |
| | DP8 | E_{1} | −29.9 |
| | DP172 | bedrock | −31.8 |
| | DP173 | bedrock | −32.1 |
| | DP3 | E_{1} | −30.6 |
| Niudong | N102 | J | −28.1 |
| | N7 | E_{1+2} | −26.6 |
| | N108 | J | −28.5 |
| | N10 | E_{1+2} | −25.4 |
| | N105 | J | −27.5 |
| Kuntryibei | K2 | bedrock | −23.9 |
| Lenghu no.3 | LHZ14 | J | −30.6 |
| Lenghu no.4 | LQ9 | N_{1} | −27.7 |
| Pingtai | P3 | E_{1+2} | −26.9 |
| | P301 | E_{1+2} | −26.0 |
| Nanhuanxian | XZ1-1 | N_{2} | −28.6 |
| | XZ2-26 | N_{1} | −27.2 |
| Mabei | M7-5 | E_{1} | −28.1 |
| | MB2-9 | E_{1} | −28.4 |
presents the compositions of C₅−C₇ light hydrocarbons in ternary diagrams. Previous studies found that light hydrocarbons produced by sapropelic organic matter are abundant in n-alkanes, whereas those generated by humic organic matter are abundant in iso-alkanes and cyclo-alkanes. Figure 7a shows that gases in Jianbei, Niudong, Kunteyibei, Lenghu no. 4 and Nanbaxain fields have higher contents of iso-C₅−C₇ than n-C₅−C₇, indicating a greater contribution from humic organic matter, while gases in Dongping, Lenghu no. 3, Pingtai, and Mabei fields have higher contents of n-C₅−C₇ than iso-C₅−C₇, indicating more contributions from sapropelic organic matter. Moreover, the relative abundances of n-heptane (n-C₇), methylcyclohexane (MCC₆), and dimethylcyclopentane (DMCC₅) can be utilized to examine the organic matter.

Figure 4. ¹³C values of whole oil in the northern margin of the Qaidam Basin.

Figure 5. Cross-plots of δ¹³C₅/C₇, δ¹³C₅/C₂, δ¹³C₅/MCC₆, and δ¹³C₅/benzene versus δ¹³C₂−δ¹³C₁.

Figure 6. Diagram of C₁/(C₂ + C₃) versus δ¹³C₁ of gases in the northern margin of the Qaidam Basin.
isotopic value of MCC6 may be used to identify the organic matter type of the source rock. According to research, $\delta^{13}C_2$ is mostly derived from algae and bacteria, MCC6 is primarily generated from higher plants, and DMCC5 is mainly derived from aquatic organisms.\textsuperscript{49,51} Figure 7b displays that gases in Jianbei, Niudong, Kunteyibe, Lenghu no. 4, and Nanbaxian fields have higher MCC6 contents, indicating a greater contribution from humic organic matter, but those in Dongping, Lenghu no. 3, Pingtai, and Mabei fields have higher contents of $n$-$C_7$, indicating more contributions from sapropelic organic matter. According to the thermal simulation experiment, the carbon isotopic value of MCC6 may be used to identify the organic matter type of the gas.\textsuperscript{52} Previous research discovered that natural gas generated from sapropelic organic matter has $\delta^{13}C_{MCC6} < -25\%e$, while gas produced from humic organic matter has $\delta^{13}C_{MCC6} > -25\%e$.\textsuperscript{30} Figure 8 shows that gases in the Dongping and Lenghu no. 3 fields were mostly derived from sapropelic organic matter and other gases were primarily produced from humic organic matter. These findings are consistent with the composition study of $C_5$-$C_7$ light hydrocarbons. Different genetic types of gas, as determined by $C_1$-$C_3$ fractions and $C_5$-$C_7$ fractions, are mainly observed in Dongping and Mabei fields and several gases in Pingtai and Nanbaxian fields. Based on the maturity study of $\delta^{13}C_1$, heptane and isoheptane, both coal-type gas and oil-type gas were produced at the mature-over mature stage, with the coal-type gas having higher maturity (will be discussed below). Pyrolysis of source rocks reveals that the source rock in the northern Qaidam Basin is dominated by humic kerogens and some sapropelic kerogens.\textsuperscript{6,35} In contrast to sapropelic source rock at the maturity stage and the early stage of high maturity, humic source rock at the late stage of high maturity would generate more $C_1$-$C_3$ hydrocarbons and less $C_7$ hydrocarbons. Besides, previous research proposed that the oil/condensate in the Dongping and Mabei fields was mostly derived from sapropelic organic matters.\textsuperscript{8} As a result, it is assumed that the mixed gas was generated from the humic and sapropelic kerogens in the Jurassic formation. The Dongping and Lenghu no. 3 fields are characterized by $\delta^{13}C_{MCC6} < -25\%e$, whereas gases in other fields have $\delta^{13}C_{MCC6} > -25\%e$, indicating that gases in the Dongping and Lenghu no. 3 fields were most likely derived from sapropelic organic matter, and other gases were primarily produced from humic organic matter. These findings are consistent with the composition study of $C_5$-$C_7$ light hydrocarbons. Different genetic types of gas, as determined by $C_1$-$C_3$ fractions and $C_5$-$C_7$ fractions, are mainly observed in Dongping and Mabei fields and several gases in Pingtai and Nanbaxian fields. Based on the maturity study of $\delta^{13}C_1$, heptane and isoheptane, both coal-type gas and oil-type gas were produced at the mature-over mature stage, with the coal-type gas having higher maturity (will be discussed below). Pyrolysis of source rocks reveals that the source rock in the northern Qaidam Basin is dominated by humic kerogens and some sapropelic kerogens.\textsuperscript{6,35} In contrast to sapropelic source rock at the maturity stage and the early stage of high maturity, humic source rock at the late stage of high maturity would generate more $C_1$-$C_3$ hydrocarbons and less $C_7$ hydrocarbons. Besides, previous research proposed that the oil/condensate in the Dongping and Mabei fields was mostly derived from sapropelic organic matters.\textsuperscript{8} As a result, it is assumed that the mixed gas was generated from the humic and sapropelic kerogens in the Jurassic formation. Overall, based on the genetic type obtained from $C_1$-$C_3$ and $C_5$-$C_7$ hydrocarbons, three types of gases are identified: coal-type gas, characterized by the enriched $\delta^{13}C_1$ value and high MCC6 content; oil-type gas, characterized by the depleted $\delta^{13}C_1$ value and low MCC6 content; and mixed gas, characterized by the enriched $\delta^{13}C_1$ value and low MCC6 content (Figure 9). Coal-type gas dominates the northern margin of the Qaidam Basin; oil-type gas is primarily distributed in the Lenghu no. 3 field; and mixed gas is mostly developed in the Dongping and Mabei fields.

### 4.3. Maturity

#### 4.3.1. Stable Carbon Isotope of Methane

Because natural gas and source rocks usually have a close maturity relationship with each other, the maturity estimated by the empirical relationships between $\delta^{13}C_1$ and $R_o$ can reflect the maturity of source rock.\textsuperscript{52,53} For the different types of natural gas in the northern margin of the Qaidam Basin, the maturity of gas was calculated by the $\delta^{13}C_1$-$R_o$% relationships: eq 1 for the coal-type gas (Dai and Qi, 1989)\textsuperscript{52} and eq 2 for oil-type gas (Shen et al., 1991).\textsuperscript{53}

\begin{align}
\delta^{13}C_1 &= 14.13 \log(R_o - 34.39) \\
\delta^{13}C_1 &= 40.49 \log(R_o - 34.00)
\end{align}

The calculated thermal maturity of gas is exhibited in Table 1. The oil-type gas in the Lenghu no. 4 field has a $R_o$ value of 0.7%, indicating that it is moderately mature. The $R_o$ values of the coal-type gas are from 0.7 to 2.3%, with an average of 1.5%, implying that coal-type gases were generated at the mature-highly mature stage, and mainly at the early stages of high maturity, which matched well with the real thermal maturity of the Jurassic source rocks.
of the Qaidam Basin are in the range of mature-over mature. Gases in the Jianbei, Kunteyibei, Lenghu no. 3, Lenghu no. 4, and Pingtai fields are mature; gases in the Niudong and Mabei fields’ plot are mature and highly mature; and gases in the Dongping field are highly mature and over mature.

The composition of \( C_7 \) light hydrocarbon can be applied to calculate the expulsion temperature of the oil and gas.\(^{14,55−57} \) The ratio of 2,4-dimethylpentane to 2,3-dimethylpentane (2,4-DMC\(_2\)/2,3-DMC\(_3\)) was found to be related to temperature, and it was calibrated to expulsion temperature.\(^{11} \) Dieckmann et al. (2002)\(^{55} \) proposed that the expulsion temperature calculated from \( C_7 \) light hydrocarbons can reflect the average temperature of hydrocarbon expulsion. Chen et al. (2020)\(^{58} \) proposed that the expulsion temperature could be regarded as the generation temperature of the major reservoired hydrocarbons (GTMRH). The GTMRH has a close relationship with homogeneous temperatures of petroleum inclusions and can reflect the major hydrocarbon charge in the western Qaidam Basin. The following empirically derived formula eq 3 was published to calculate the GTMRH using \( C_7 \) light hydrocarbons (Mango, 1997).\(^{14} \)

\[
T(°C) = 140 + 15 \ln \left( \frac{2,4-DMC_2}{2,3-DMC_3} \right)
\]

Based on the relationship, the GTMRH in the northern margin of the Qaidam Basin were calculated and exhibited in Table 2, and the GTMRH ranges from 125.0 to 135.0 °C, indicating high maturity.

4.3.3. Petroleum Charge History. Because the \( C_1 \) and \( C_7 \) fractions in natural gas may be dominated by different origins, the maturity results obtained from these fractions may be helpful to recognize the petroleum charge history.\(^{59} \) If maturity results obtained from \( C_1 \) and \( C_7 \) hydrocarbons are consistent, the reservoir most likely underwent one episode of petroleum charge; if maturity results are inconsistent, the reservoir most likely experienced at least two episodes of petroleum charge. In the Jianbei gas field, for example, the \( R_o \) value of the gas obtained from \( \delta^{13}C_1 \) is 2.2%, suggesting over maturity, whereas the heptane and isoheptane values of light hydrocarbons are 13.6% and 1.3, implying moderate maturity (Figure 10). The different maturity results indicate that reservoirs in the Jianbei field may experience at least two periods of hydrocarbon charge. Also, it advises that the reservoirs in Lenghu no. 3, Lenghu no. 4, and Pingtai fields may have one hydrocarbon charge, while that in Dongping, Niudong, Kunteyibei, and Mabei fields may have at least two periods of hydrocarbon charges and that in the Nanbaxian field may have at least three periods of hydrocarbon charge.

The maturity difference reflecting multiple periods of hydrocarbon charge is also found in other basins. In the Tabei Uplift of the Tarim Basin, NW China, the \( R_o \) value of gas is 0.7−2.2%,\(^{59} \) indicating mature to over mature, whereas the isoheptane values of light hydrocarbons range from 1.1 to 4.8,\(^{28,59} \) revealing mature to highly mature. The maturity difference suggests at least three periods of hydrocarbon charge in this area, basically consistent with three charge episodes evaluated from homogeneous temperatures of petroleum inclusions, which are always utilized to reconstruct petroleum charge history.\(^{60} \) In the Qibei sag, Bohai Bay Basin of China, homogeneous temperatures of petroleum inclusions reveal three periods of petroleum charge.\(^{61} \) The \( R_o \) value of gas is from 1.0 to 1.3%, mainly at the mature stage, and the heptane and isoheptane values reveal mature and highly mature,\(^{62} \) suggesting at least two periods of petroleum charge in this area.

As Dongping and Niudong gas fields are favorable for natural gas exploration in the northern margin of the Qaidam Basin, their hydrocarbon charge histories are further discussed. Combining with the burial history and hydrocarbon generation history of the Pingdong-Kunteyibei sag (Figure 11), maturity results obtained from the gas and light hydrocarbons indicate that hydrocarbon charge in the Dongping field mainly occurred during the Shanggangchaigou period (\( N_3 \)), and the Xiayoushashan to the Shangyoushashan period (\( N_2^1−N_2^3 \)); hydrocarbon charge in the Niudong field primarily occurred during the Xiaganchaigou period (\( E_3 \)) and the Shanggangchaigou period (\( N_1 \)). This is roughly matched well with the petroleum charge period from homogeneous temperatures of petroleum...
inclusions. The homogeneous temperatures of petroleum inclusions suggest that there are primarily three petroleum charge episodes in the Dongping field, including the late Shangganchaigou period (N1), Shangyouyushan to the Shizigou period (N2), and Quanyagou to the present (Q1-present); there are two petroleum charge episodes in the Niudong field, including the late Xiaganchaigou period (E3) and the late Shangganchaigou period (N1). Thus, it seems that the maturity obtained from C1 and C2 hydrocarbons helps understand the hydrocarbon charge history. Numerous studies suggest primarily two and three petroleum charge events in the northern margin of the Qaidam Basin.4,7,62 Because each hydrocarbon charge event contributes differently to the reservoir oil, it is critical to identify the major charge event. The calculated GTMRH in the northern margin of the Qaidam Basin ranges from 125.0 to 135.9 °C, with an average value of 132.3 °C. Combining with burial history and hydrocarbon generation history, the corresponding major charge event occurred during the Shangganchaigou period (N1) (Figure 11). This is consistent with the basin modeling from Guo et al. (2020),59 who proposed that during the Shangganchaigou period (N1), the Jurassic source rocks produced the most abundant hydrocarbons, probably resulting in a huge amount of hydrocarbon charging.

The GTMRH calculated from C7 light hydrocarbons is greater than 120 °C, indicating that petroleum was predominantly generated at the highly mature stage from the Jurassic source rocks, which is similar to the δ13C study. Condensate is extensively distributed in the oil and gas fields in the northern margin of the Qaidam Basin. Because light hydrocarbons are most abundant in the condensate, the GTMRH calculated from C7 light hydrocarbons may suggest that petroleum in the northern margin of the Qaidam Basin was mainly accumulated in the reservoirs during the Shangganchaigou period (N1).

4.4. Implication for Hydrocarbon Exploration. The study above reveals that there are deep hydrocarbon fluid sources in Jianbei, Dongping, Kuntyeyi, Nanbaxian, and Mabei fields. The major hydrocarbon accumulation mainly occurred during the Shangganchaigou period (N1), simultaneous with the main hydrocarbon generation stage. The continuously developing paleo uplift is the most favorable zone for petroleum accumulation in the northern margin of the Qaidam Basin. Thus, abundant petroleum accumulated in the mid-shallow layers of paleo uplifts has been explored, and it is most likely that the earlier developed paleo uplifts in deep formations at the margin of the Qaidam Basin have high exploration potential. Besides, the later developed uplift zone in the inner basin also has high exploration potential. In addition, in the northern margin of the Qaidam Basin, oil and gas were mainly derived from humic source rocks of the Jurassic deposition, and also some contributions of the oil-type gas from the Jurassic source rocks. In summary, deep paleo uplifts adjacent to the hydrocarbon-generating depressions at the basin’s margin and uplift zone in the inner basin are estimated as favorable areas for further exploration in the northern margin of the Qaidam Basin.

5. CONCLUSIONS

The composition and stable carbon isotopes of natural gas and light hydrocarbons were analyzed in the northern margin of the Qaidam Basin. Three types of the gases are identified: coal-type gas, oil-type gas, and mixed gas. Coal-type gas is the predominant type of gas in the northern margin of the Qaidam Basin, oil-type gas is mainly distributed in the Lenghu no. 3 field, and mixed gas is mainly in the Dongping and Mabei fields. Maturity determined from C1 and C2 fractions reveals that reservoirs in Lenghu no. 3, Lenghu no. 4, and Pingtai fields may have one hydrocarbon charge, while reservoirs in Jianbei, Dongping, Niudong, Kuntyeyi, and Mabei fields may have at least two periods of hydrocarbon charge, and reservoirs in the Nanbaxian field may have at least three periods of hydrocarbon charge. Furthermore, the GTMRH calculated from C2 hydrocarbons is greater than 120 °C, indicating that petroleum was predominantly generated at the highly mature stage from the Jurassic source rocks and probably accumulated in the reservoirs during the Shangganchaigou period (N1). The deep paleo uplifts adjacent to the hydrocarbon-generating depressions at the margin of the basin and uplift zone in the inner basin are estimated as favorable areas for further exploration in the northern margin of the Qaidam Basin.

6. SAMPLES AND METHODS

6.1. Samples. 20 natural gas samples were collected at major fields in the northern margin of the Qaidam Basin, including Jianbei, Dongping, Niudong, Kuntyeyi, Lenghu no. 3, Lenghu no. 4, Pingtai, Mabei, and Nanbaxian oil and gas fields. These gas samples were probably generated from various hydrocarbon generation sags and accumulated in different structural belts, depths, and periods. Hydrocarbon generation sags, including Pingxi, Pingdong, Kuntyeyi, Yibe, Saishenteng, and Yuxia sags, all contribute to natural gas accumulation (Figure 1). The majority of gas fields are found on the paleo uplift or slopes of the basin margin, far away from the source rocks, whereas the K2 well is located near the source rocks. Gas samples were taken from reservoirs ranging in depth from 467 to 6888 m, including basement rocks, the Jurassic, and Paleogene-Neogene strata (Table 1). Based on previous studies, these gases were accumulated during the Xiaganchaigou period (E3), Shangganchaigou period (N1), and Shiyoushan to Shizigou period (N2). Therefore, the gathered gas samples could better reflect the geochemical characteristics of natural gas in the northern margin of the Qaidam Basin.
The reservoir temperature is estimated by an average temperature gradient of 30 °C/km and a surface temperature of 10 °C. The reservoir pressure is evaluated by an average gradient of 10 MPa/km and a pressure coefficient of 1.1–1.2. The strata temperature and pressure of the sample location in the Jianbei field are approximately 148 °C and 51 MPa and that in the Dongping field are about 106–154 °C and 35–56 MPa, in the Nuidong field are about 73–76 °C and 23–24 MPa, in the Kuntyeyi field are about 214 °C and 83 MPa, in the Lenghu no. 3 field are about 28 °C and 6.6 MPa, in the Lenghu no. 4 field are about 31 °C and 8 MPa, in the Pingtailai field are about 55 °C and 17 MPa, in the Nanbaxian field are about 73–76 °C and 13–32 MPa, and in the Mabei field are about 40–43 °C and 11–12 MPa.

Gas samples were gathered at wellheads using aluminum alloy cylinders with double valves. Before sampling, cylinders were flushed three times at the wellhead to remove air. Besides, oil and condensate in the same wells or fields were also collected. All geochemical analyses were conducted at the Key Laboratory of Petroleum Resources Research, Chinese Academy of Sciences.

6.2. Methods. 6.2.1. Gas Composition and Stable Carbon Isotopic Analysis. Gas compositions were analyzed on a GC-9160 gas chromatograph (GC). The GC was equipped with two flame ionization detectors, a thermal conductivity detector, and a capillary column (PLOT Al2O3 50 m × 0.53 mm i.d. × 0.32 μm film thickness). The GC oven temperature was initially set at 35 °C for 5 min, then increased to 200 °C at a rate of 10 °C/min, and held at this temperature for 10 min. The C1 to C5 hydrocarbons were determined by using GC. The non-hydrocarbons (N2, CO2, and H2S) were examined on a high-resolution mass spectrometer (MS) equipped with an electric impact ion source, using a selected ion monitoring method to determine molar percentages, which were converted to molar concentrations using the ideal gas function. The emission current was 40 μA, and the ionization energy of the ion source was 86 eV. The experimental error for each component was ±2%.

Stable carbon isotope ratios were determined using a Finnigan Mat Delta Plus mass spectrometer interfaced with a gas chromatograph. Gas components were separated on a gas chromatograph with helium as the carrier gas, converted into CO2 in a combustion interface, and then injected into a mass spectrometer. Individual hydrocarbon gas components (C1–C3) and CO2 were initially separated using a CP-CarboBOND column (50 m × 0.53 mm i.d. × 15 μm film thickness). The temperature of a GC oven was raised from 60 to 200 °C at a rate of 15 °C/min (held 20 min). High purity methane (−28.5 ± 0.5‰, VPDB) is used as an internal standard for each sample test to test the instrument’s stability. The precision was ± 0.5‰. Stable carbon isotopic compositions were presented as δ13C values relative to the VPDB scale.

6.2.2. Molecular and Stable Carbon Isotopic Composition of Light Hydrocarbon. The light hydrocarbon composition was analyzed on an Agilent 6890N gas chromatograph with a 5973N MS. The GC was equipped with a split/splitless injector, a fused silica column (100 m × 0.25 mm i.d. × 0.35 μm film thickness), and a flame ionization detector. The injected sample volume was 1 mL (split ratio set at 20:1) and the injector temperature was 150 °C. The oven temperature program was set to run from 40 °C (15 min) to 120 °C (held 20 min) at a rate of 2 °C/min, and then to 290 °C (held 20 min) at 12 °C/min. The carrier gas was helium (flow rate 1.0 mL/min). The MS conditions were as follows: electron ionization at 70 eV with and ion source temperature of 230 °C. Compounds were recognized by matching mass spectra with the NIST library of standard compounds (Figure 3 and Table 4). The light hydrocarbon data were obtained from the integrated peak areas on the gas chromatograms.

Stable carbon isotope of C1–C7 light hydrocarbons was measured on a gas chromatography–isotope ratio mass spectrometry (GC-IRMS) system with a GC (Ultra Trace GC) coupled to a stable isotope ratio mass spectrometer (MAT 253) via a pyrolysis furnace reactor. Before GC-IRMS analysis, solid-phase microextraction was employed for C1–C7 light hydrocarbon enrichment (CAR/DVB/PDMS fiber, 20 min, room temperature about 25 °C). The GC was equipped with a fused silica capillary column (HP-1, 100 m × 0.25 mm i.d. × 0.5 μm film thickness) with helium as the carrier gas at a constant flow rate of 1.0 mL/min. The oven temperature program setting was the same as that in analyzing the composition of light hydrocarbons. The precision was ±0.3‰ for each component.

6.2.3. Whole Oil Stable Carbon Isotope Composition. Stable carbon isotope of the oil/condensate was analyzed on a ThermoFisher MAT 253-FLASH 2000 instrument. The result is reported in per mil (‰) relative to VPDB (Vienna Pee Dee Belemnite) with an analytical precision of ± 0.3‰. The certified reference material was IAEA-600 caffeine with a δ13C value of −27.77‰ (Coplen et al., 2006).

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Notes

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