# Microbial Gas in the Mohe Permafrost, Northeast China and its Significance to Gas Hydrate Accumulation in Permafrost across China

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**Abstract: The Mohe permafrost in northeast China possesses favorable subsurface ambient temperature, salinity, Eh values and pH levels of groundwater for the formation of microbial gas, and the Mohe Basin contains rich organic matter in the Middle Jurassic dark mudstones. This work conducted gas chromatography and isotope mass spectrometry analyses of nearly 90 core gas samples from the Mk-2 well in the Mohe Basin. The results show that the dryness coefficient ($C_1/C_{1–5}$) of core hydrocarbon gas from approximately 900 m intervals below the surface is larger than 98%, over 70% of the $\delta^{13}C$ values of methane are smaller than −55‰, and almost all $\delta D$ values of methane are smaller than −250‰, indicative of a microbial origin of the gas from almost 900 m of the upper intervals in the Mohe permafrost. Moreover, the biomarker analyses of 72 mudstone samples from the Mohe area indicate that all of them contain 25-norhopane series compounds, thereby suggesting widely distributed microbial activities in the permafrost. This work has confirmed the prevailing existence of microbial gas in the Mohe area, which may be a potential gas source of gas hydrate formation in the Mohe permafrost. This result is of great significance to gas hydrate accumulation in the permafrost across China.**

**Key words: microbial gas, gas hydrate accumulation, permafrost, oil and gas, Mohe, northeast China**

## 1 Introduction

Gas hydrate, also known as flammable ice or methane hydrate, refers to ice-like crystalline compounds consisting of water and gas molecules, which are formed under low temperature, moderate pressure and proper methane concentration (Thakur et al., 2011; Merey et al., 2016). In nature, gas hydrate mainly exists on continental margins or in the permafrost of polar regions (Sloan, 1998; Majorowicz et al., 2000; Makogon et al., 2007; Makogon, 2010). Gas hydrate has attracted great interest from scientists in many disciplines, due to its great importance in energy resources, geohazards, and climate change (Kvenvolden, 1988a, 1988b; Macdonald, 1990; Milkov et al., 1990; Nisbet, 1990; Paull et al., 1991; Maslin et al., 1998; Bouriak et al., 2000; Kennedy et al., 2001; Collett, 2002; Collett et al., 2009).

In both continental margins and permafrost, hydrocarbon gas, in particular methane, is not only the main component of gas hydrate, which is the prime factor controlling the formation and stability of gas hydrate, and is also the goal of gas hydrate exploration and study. In terms of gas origin, the gas hydrates found on the Earth include microbial, thermogenic and mixed gases (Collect, 2002; Dallimore and Collect, 2002; Collect, 2008; Collect et al., 2011; Cheng et al., 2016; Jiang et al., 2016; Tan Furong et al., 2017). As for gas hydrate found in permafrost, the gas may be of a thermogenic origin, for example in the Qilian Mountains of China (Lu Zhenquan et al., 2010; Huang Xia et al., 2011; Lorenson et al., 2011), or of a mixed origin of microbial and thermogenic gases, such as on the North Slope of Alaska and the in Mackenzie Delta of Canada (Lorenson et al., 1999; Lorenson et al., 2005; Lorenson et al., 2011). That is to say, microbial gas has a significant contribution to gas hydrate formation in permafrost, and is likely to attract attention among researchers and explorers of gas hydrate.

According to previous reports, the Mohe permafrost of

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northeast China contains thermogenic gas required for gas hydrate accumulation (Zhao et al., 2012). Microbial gas, however, remains relatively scarce. Consequently, the topic of the present work aims to search for microbial gas, as well as its potential contribution to gas hydrate accumulation in the Mohe permafrost.

## 2 Requisites for Gas Hydrate Formation

### 2.1 Geological setting

The Mohe Basin is located north of 52°20′, is situated in the northernmost area of the Greater Khingan Mountains in China, across from Heilongjiang Province and Inner Mongolia Autonomous Region, extending northward to the Heilongjiang River and southward to Mohe and Tahe County Towns (Fig. 1). The basin covers around 21, 300 km$^2$ and has the highest latitude, with a lower elevation of about 400 to 600 m, and the lowest level of oil and gas exploration in China.

The Mohe Basin is a Mesozoic continental basin. Approximately 6000 m or more of strata fill the basin, consisting largely of clastic and volcanic rocks from the Middle Jurassic (with minor Cenozoic sediments), lying upon a Devonian basement. The Middle Jurassic includes the Xiufeng, Ershierzhan, Mohe and Kaikukang Formations, which consist mainly of fluvial and lacustrine clastic rocks. The Ershierzhan and Mohe Formations occur widely throughout the basin, and contain potential source and reservoir rocks for promising gas hydrate. The dark mudstones of the only Mohe Fm. average more than 200 m thick. The Xiufeng Fm. is also widely present in the Mohe Basin, and primarily includes reservoir rocks. The Kaikukang Fm. is restricted to the northeast part of the basin (Fig. 1). At present, four exploration wells were drilled at depths of around 500 to 2300 m. The Mk-2 well had the greatest depth, and drilled through approximately 2300 m of the Mohe Fm. (Fig. 2), but its base was not penetrated.

### 2.2 Requisites for gas hydrate formation in permafrost

Requisites for gas hydrate formation and stability in permafrost include thickness of permafrost, sufficient hydrocarbon gas, and underground water and its salinity. The thickness of permafrost creates the pressure-temperature regime required for gas hydrate formation and its existence in permafrost zone, which, combined with the salinity of the underground water, governs the gas hydrate formation and its stability. Hydrocarbon gas, special methane and water are major constituents of gas hydrate. Aside from sufficient hydrocarbon gas, the Mohe Basin has the following characteristics.

There is wide and continuous permafrost in the Mohe Basin (Zhou Youwu et al., 2000; Jin Huijun et al., 2009), which thickens to the northwest (Jin Huijun et al., 2009). According to the geophysical data collected in recent years, the thickness of permafrost is usually 60 to 80 m, with the greatest local thickness reaching up to 120 m (Fig. 3). The thicknesses are comparable to the gas hydrate -bearing Qilian mountains region in China (Zhu Youhai et al., 2009) and the Yamal Peninsula in Siberia, which show similar gas hydrate-speculated occurrences (Chuvilin, 1998; Yakushev, 2000).

Temperature is an important parameter in characterizing the pressure-temperature regime of gas hydrate formation. Here we include the surface temperature and geothermal gradient. The Mohe area has a surface temperature of about −0.5 to −3.0°C, and a geothermal gradient of 1.7 to 2.7°C/100 m. This is similar to the areas where gas hydrates are found, for example, −8 to −12°C (Romanovsky et al., 2007) and 1.0 to 3.0°C/100 m (Collett et al., 2008) in Messoyakha, Siberia; −4.6°C to −12.2°C (Kamath et al., 1987) and 1.5°C to 5.2°C/100 m (Collett et al., 2011) in Prudhoe Bay on the Alaskan North Slope; and −1.5°C to −2.4°C and 2.2°C/100 m (Zhu Youhai et al., 2009) in the Qilian Mountains of China.

The Mohe area has lower salinity of underground water. Analyses of three spring water samples from the Mohe region show groundwater salinity (Cl-ion concentration) of ~2.94 ppm to 17.6 ppm, which is higher than Prudhoe Bay on the North Slope of Alaska (＜1.0–19 ppb) (Collett et al., 2011), but lower than Messoyakha, Siberia (≤1.5wt%) (Makogon, 2010). Salinity throughout Mohe area thus has little effect on gas hydrate formation, and can be ignored.

For hydrocarbon gas, there is still lack of its occurrence evidence, due to the fact that no gas fields have been discovered in the Mohe Basin. However, below we show abundant evidence of existing microbial gas which can actually act as a potential gas source for gas hydrate formation in the Mohe permafrost.

## 3 Favorable Conditions of Microbial Gas Formation

### 3.1 Moderate environmental temperature

Environmental temperature is an important factor affecting microbial activity and biogenic gas formation. In general, around 30 to 50°C of background temperature is favorable for methanobacteria growth and microbial gas formation (Wilhelms et al., 2001; Kang Yan et al., 2004; Wei Shuijian et al., 2009). According to the data of temperature log of the Mohe Basin, the depth range corresponding to 30 to 50°C of temperature is approximately 1200 to 1900 m of the shallow subsurface

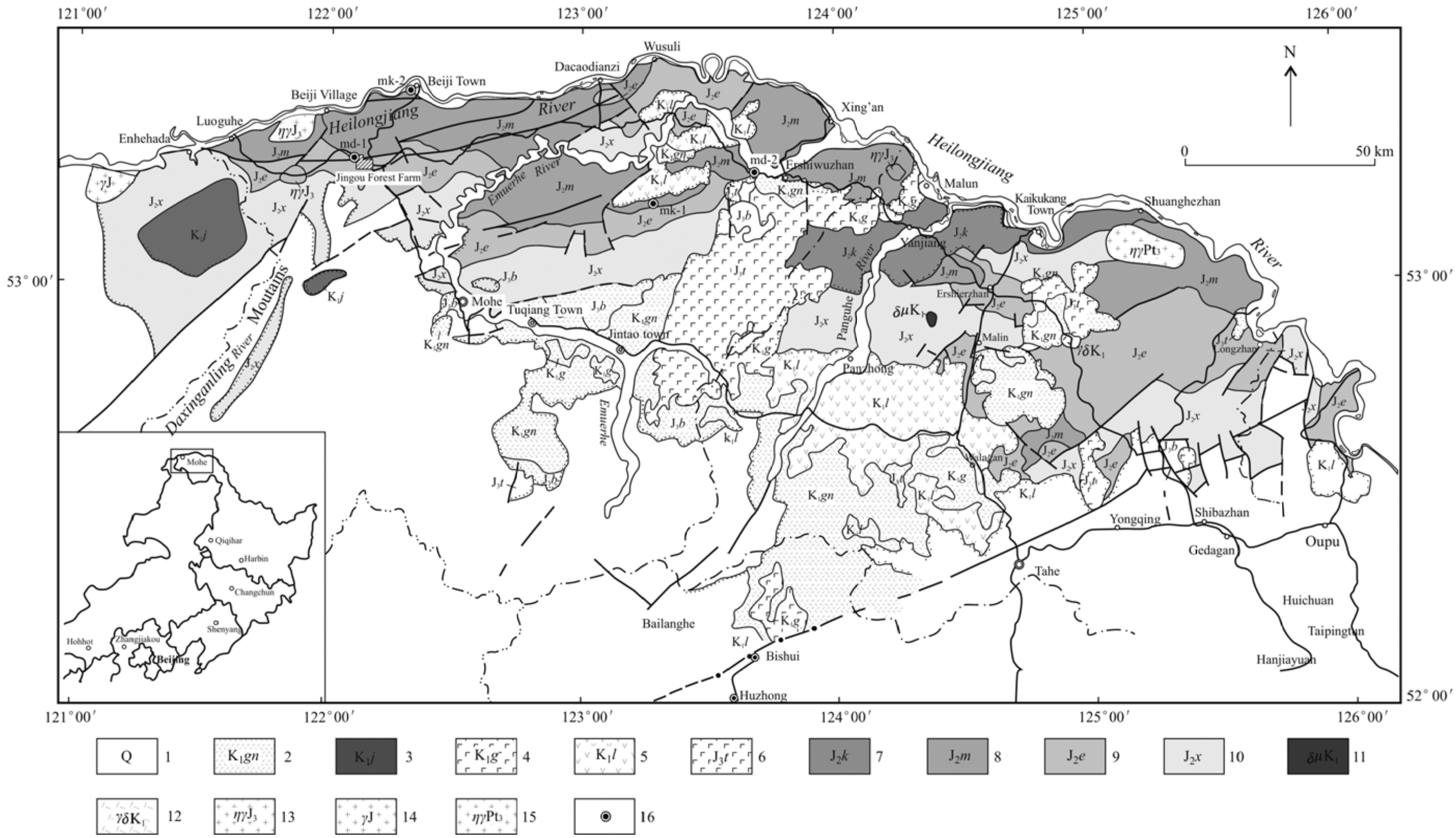


Fig. 1. Geological map of the Mohe Basin, northeast China.

1, Quaternary; 2, Ganhe Formation; 3, Jiufengshan Formation; 4, Guanghua Formation; 5, Longjiang Formation; 6, Tamulangou Formation; 7, Kaikukang Formation; 8, Mohe Formation; 9, Ershierzhan Formation; 10, Xiufeng Formation; 11, diorite-porphyrite of Early Cretaceous; 12, granodiorite of Early Creataceous; 13, monzonitic granite of Late Jurassic; 14, jurassic granite; 15, monzonitic granite of Archean; 16, drilling well.

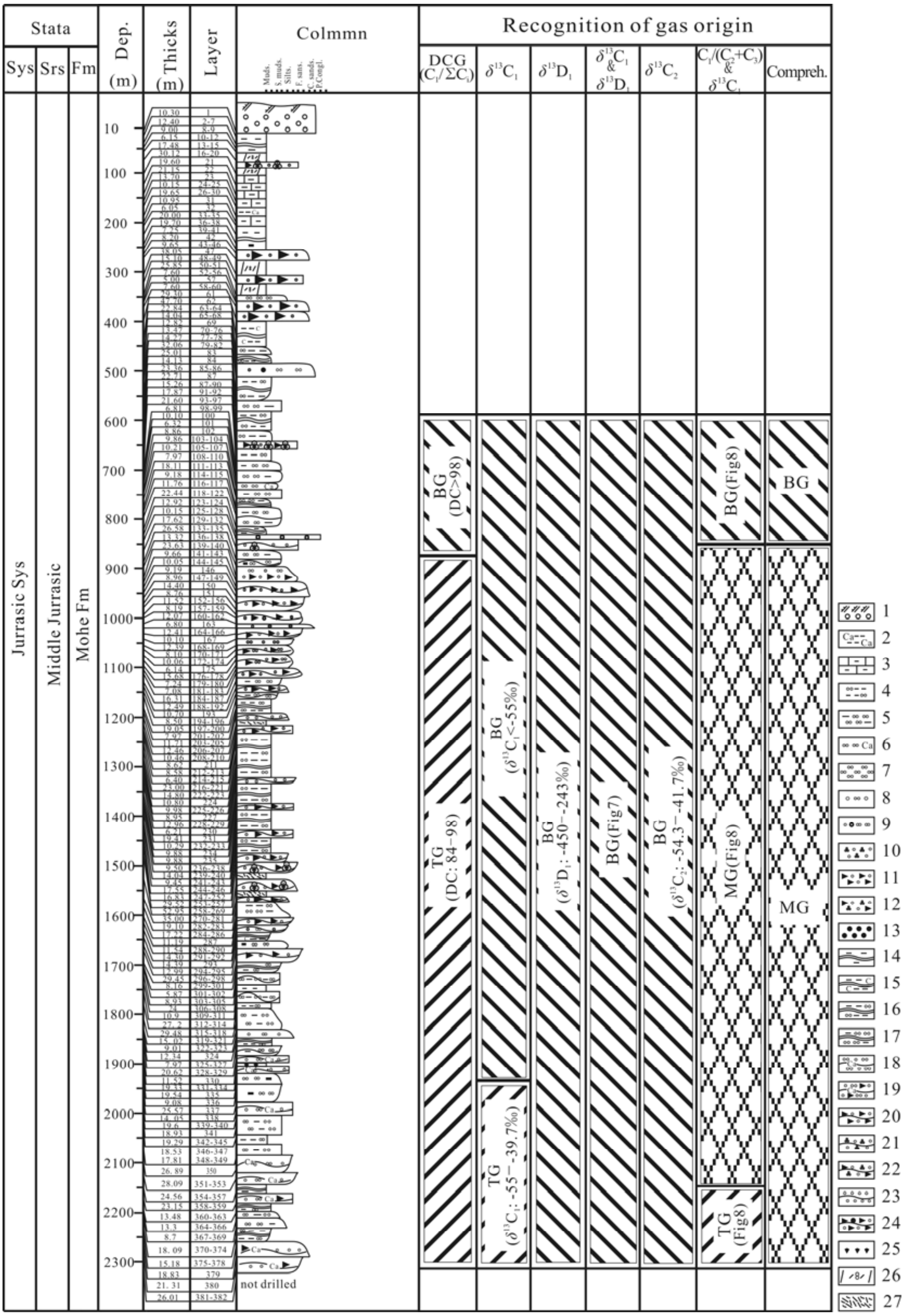

Fig. 2. Generalized geological section of Mk-2 well in the Mohe Basin, northeast China.

1, Loose bed; 2, calcareous mudstone; 3, marl; 4, silty mudstone; 5, muddy siltstone; 6, calcareous sandstone; 7, siltstone; 8, fine-grained- to siltstone; 9, fine-grained- to siltstone with sporadic coarse gravel; 10, quartz sandstone; 11, lithic sandstone; 12, lithic quartz sandstone; 13, conglomerate; 14, muddy slate; 15, muddy slate with carbon; 16, muddy slate with silt; 17, meta-muddy siltstone; 18, meta-calcareous fined-grained sandstone; 19, meta-calcareous fine-grained- to silt lithic sandstone; 20, meta-lithic sandstone; 21, meta-quartz sandstone; 22, meta-lithic quartz sandstone; 23, meta-sandstone; 24, meta-lithic sandstone with sporadic gravel; 25, andesite; 26, mylonite; 27, fracture zone; BG, biogenic gas; DCG, dry cofficient of gas; MG, mixed gas; TG, thermogenic gas.

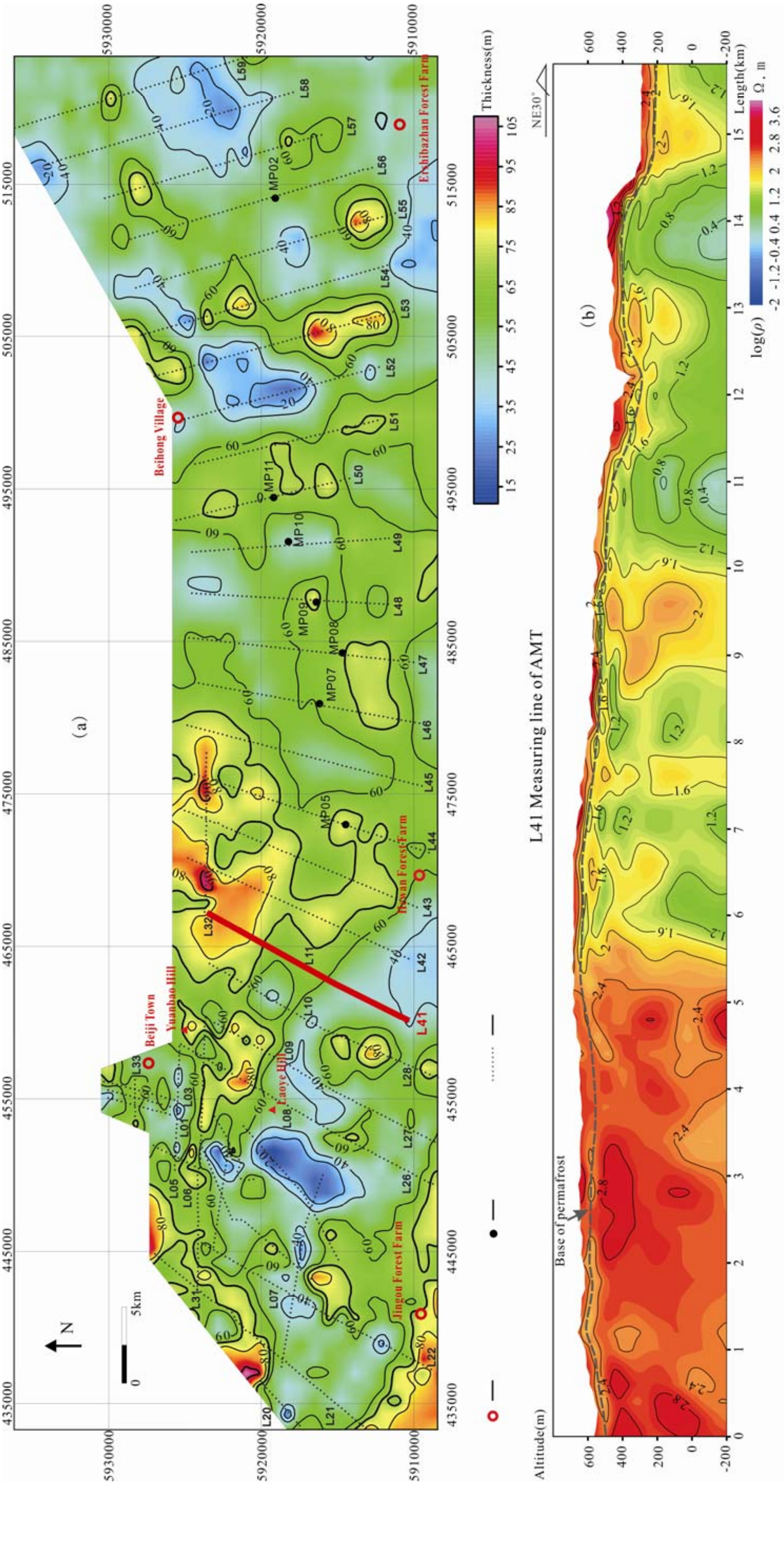


Fig. 3. Thickness of permafrost in northwest Mohe area, northeast China
(a), Thickness contour of permafros; (b), cross section of permafrost.

part below the Mohe permafrost, which is suitable for the growth and activities of methanogens and thus microbial gas formation.

### 3.2 Lower salinity of underground water

The impact of salinity on microbial gas formation is also enormous (Martini et al., 1998, 2003, 2008; Kang Yan et al., 2004; Strapoc et al., 2010; Schlegel et al., 2011; Su Xianbo et al., 2011). According to previous research, methanogens cannot survive in environments of which the salinity levels are higher than 4 mol/L (Martini et al., 1998). For example, the salinities of the underground water from the microbial shale gas plays of the Antrim shale and New Albany shale in the US are respectively lower than 4 mol/L (Martini et al., 2003) and 2 mol/L (Strapoc et al., 2010).

In the northern portion of Heilongjiang Province, i.e., the Mohe region, previous data show that the salinity of underground water is usually smaller than 0.05 mol/L (Wang Baolai et al., 1987). Our analysis shows that the Mohe area has salinity, i.e., concentration of chlorine ions, of around $0.05\times10^{-3}$ to $0.3\times10^{-3}$ mol/L, which is far less than the underground water from the microbial shale gas plays of the Antrim and New Albany shales in the US (Martini et al., 2003; Strapoc et al., 2010). Therefore, the salinity of underground water from the Mohe Basin is favorable for microbial gas formation.

### 3.3 Appropriate Eh and pH levels of underground water

The redox quality of underground water also has an important impact on microbial gas formation (Bryant et al., 1976; Wang Yuewen, 2005). In general, the exclusive microbes which form microbial gas can only survive in anoxic conditions, i.e., reduction environments of which the Eh level is lower than −300 to −340 mV (Bryant et al., 1976; Wang Yuewen, 2005). At present, no Eh data for the underground water from the Mohe Basin are available; however, based on the fact that a large number of authigenic minerals, such as pyrite, calcite, quartz etc., fill the rock fissures from the Mohe area (Figs. 4 and 5), it is speculated that the Eh level of the underground water in this basin is within the range of approximately −200 to −400 mV (Liu Baojun, 1980), which is conducive to the growth of methanogens and formation of microbial gas.

pH levels also have an importance to microbial gas formation. In general, it is believed that the neutral condition, pH levels of either 6.4 to 7.5 (Rudd and Taylor, 1980) or 6.8 to 7.8 (Zehnder and Wuhrmann, 1977), is conducive to the growth of methanogens. Although no pH data from the Mohe Basin are available, it is concluded that, due to the calcite and quartz veins alternately filling in the rock fissures from the Mohe area (Fig. 4), the pH level of the underground water in this region is roughly between 6.5 and 9.0 (Liu Baojun, 1980), paralleling the pH levels of around 6.1 to 9.34 from the surrounding areas (Wang Chunhe et al., 1996; Zhao Qin et al., 2001), and supports the growth and formation of microbial gas.

### 3.4 Rich parent matters for gas sources

Microbial gas is a hydrocarbon gas composed mainly of methane, which is generated by the microbial metabolism of both modern matter derived from sediments and ancient organic matter, i.e., kerogen, bitumen, oil, gas etc. (Brown, 2011) in anoxic circumstances. Hydrocarbons of thermal origin, such as oil, gas and bitumen, can produce microbial gas (James and Burns,1984; Jones et al., 2008; Lorenson et al., 2011), as can organic-rich rocks including ancient organic matter, such as coals and dark mudstones (Nobel and Henk Jr., 1998; Ahmed and Smith, 2001; Curtis, 2002; Tao Mingxin et al., 2005; Flores et al., 2008; Warwick, 2008; Liu Honglin et al., 2010; McIntosh et al., 2010;Park et al. ,2016). Within the Mohe Basin, only dark mudstones are present, and are rich as well, with the Mohe Formation alone having at least a 200 m thickness of dark mudstone, with no coal or petroleum having been discovered.

The abundance of organic matter in the Mohe Basin is able to support the formation of microbial gas. According to analyses of almost 300 mudstone samples from drilled cores, the Mohe Basin has a total organic carbon level of 0.06 to 9.46%, with an average of 1.46%, in the Ershierzhan Formation, and 0.19 to 17.73%, with an average of 1.55%, in the Mohe Formation (Table 1), which are slightly lower than the Antrim Shale level of 0.5 to 24% (Martini et al., 2008) and New Albany Shale level of 1.0% to 20% (Mastalerz et al., 2013). In general, a minimum of approximately 0.5% metabolizable organic carbon is required to support microbial methane production in marine sediments (Rice and Claypool, 1981). Based on this, almost 80% of the dark mudstone from the Ershierzhan Formation, and nearly 90% of the dark mudstone from the Mohe Formation, can act as source rock for microbial gas.

The type of organic matter from the Mohe Basin is able to sustain methanogens. Like the Quaternary system of the Qaidam Basin and many coals which produce microbial gas around the world (Table 1), the Mohe Basin possesses type-Ⅱ and type-III kerogens for microbial gas formation, being poorer than the Antrim Shale and New Albany Shale, producing a large of microbial gas, which are dominated by type-I and type-II kerogens. However, just like the Qaidam Basin, where a great amount of microbial gas was discovered, the kerogen types may be compensated by the great volume of gas source rock


Fig. 4. Minerals filled in fissures of Mk-2 well drilled cores of the Mohe Basin, northeast China.
(a), Calcite filled in approximately vertical crevices (38.65–40.15 m); (b), little quartz existing in vertical fissures (77.05 –95.75 m); (c), quartz with little calcite filled in approximately horizontal and vertical crevices (151.4–151.62 m); (d), calcite and quartz exiting in approximately horizontal and vertical fissures(151.62–151.85 m); (e), calcite with a little of quartz filled in vertical crevices (156.13–156.35m); (f), quartz with little calcite filled in approximately vertical fissures (229.2–229.4 m).

(Guan Zhiqiang et al., 2008).

Thermal maturity of organic matter is not the key to controlling the generation of microbial gas. The fact that immature or lower-mature source rocks with vitrinite reflectance lower than 0.4%, not higher than 0.7% at most (Shuai Yanhua et al., 2006; Hui Rongyue et al., 2009), are conducive to forming microbial gas, is widely accepted. However, it is important to note that some exploration and research results indicate that both mature and post-mature source rocks can generate microbial gas (Table 1). According to previous reports, in the circumstances of methanogen activities, medium- and high-rank coals (Johnson et al., 1994; Li Mingzhai et al., 2009) and the black mudstones of the metagenesis stage (Shi Zhanzheng et al., 2002) corresponding to vitrinite reflectance of 2.0% are able to form microbial gas. The analyses of 32 mudstone samples indicate that the vitrinite reflectance ($R_o$) of the Mohe Basin ranges from 0.8 to 3.54%, among which only approximately 20% of higher than 2.0% of the vitrinite reflectance is frequently distributed in the immediate vicinity of the fault zones. Based on the discussion in this paper, the organic matter from the Mohe area can completely support the generation of microbial gas.

### 3.5 Intense and wide microbe activities

Microbe activities resulting in the formation of microbial gas occur widely throughout the Mohe Basin, which is marked by extensive existence of 25-norhopane series compounds (Blanc and Connan, 1992; Bao Jianping, 1996; Du Hongyu et al., 2004; Bennett et al., 2006; Wang Zuodong et al., 2009). The biomarker analyses of 48 core and 24 outcrop mudstone samples in the Mohe Basin show that all of them contained 25-norhopane series compounds (Fig. 6), as first discovered

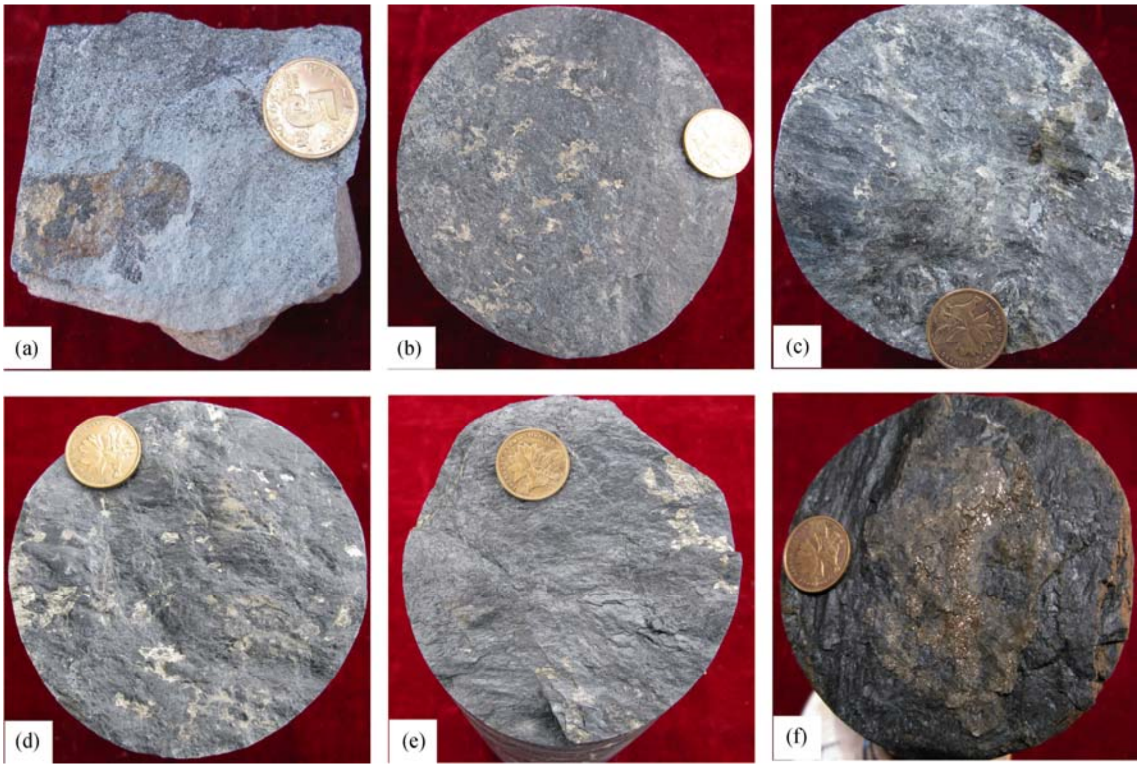


Fig. 5. Pyrite on fissured surfaces of Mk-2 well drilled cores of the Mohe Basin, northeast China.
(a), Film-shape pyrite on the crevice surface (36.5–38.65 m); (b), film-shape pyrite on the bedding surfaces (53.4–56.05 m); (c), film-shape pyrite on the fracture surface (62.6–67.53 m); (d), film-shape pyrite on the bedding surface (149.85–150.05 m); (e), film-shape pyrite on the bedding surface (151.2–151.4 m); (f), grain-shape pyrite on the fracture surface (229.5–241.45 m).

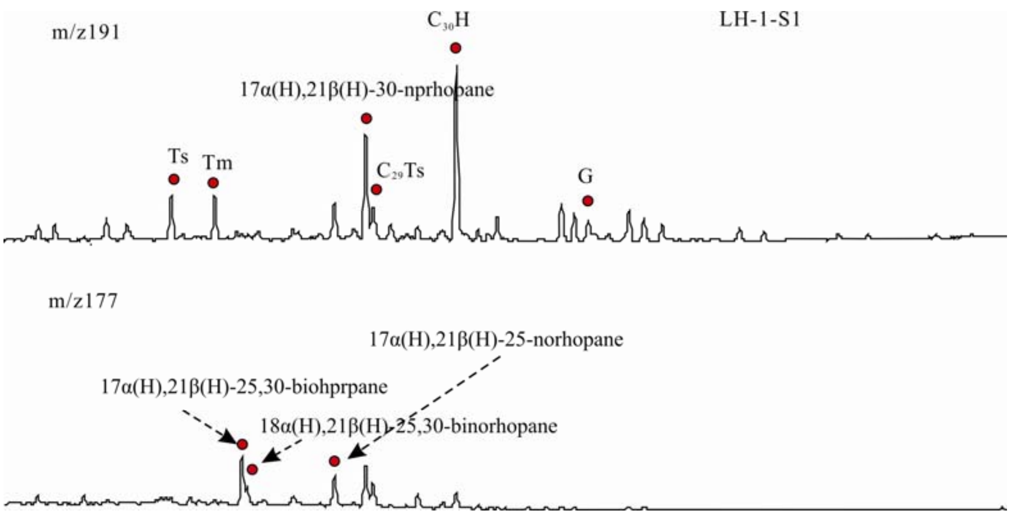


Fig. 6. Mass chromatogram maps (m/z191 and m/z191) of saturated fraction from dark mudstones in the Mohe Basin, northeast China (Well LH-1S1).

**Table 1 Comparison of main characteristics of gas source rocks from representative areas abroad and the Mohe Basin, northeast China**

| Area | strata | Lithology | TOC (%) | Type of kerogen | Maturity of organic matter ($R_o$, %) | Origin of gas | Isotopes of methane(‰) |
|---|---|---|---|---|---|---|---|
| Mohe Basin | Mohe Fm. | Mudstone | 0.19–17.73/ 1.55 (256)* | type-Ⅱ, Ⅲ | 0.8–3.54/ 2.05(32) | Biogenic gas, thermogenic gas | $\delta^{13}C_{C1}$: −82.9–−39.7; $\delta D_{C1}$: −450–−243 |
| Qaidam Basin (Wei Guoqi et al., 2005) | Quaternary | Muddy sediment | 0.15–0.46 | Majority of type-Ⅲ, a little of type-Ⅱ | 0.22–0.47 | Biogenic gas | $\delta^{13}C_{C1}$: −69.9–−65 |
| Tuha Basin (Zhang Jinchuan et al., 2009) | Lower Jurassic | Shale | 1.3–20 | Majority of type Ⅱ$_1$, Ⅱ$_2$ | 0.6–1.3(Chen Jianping et al.,1999) | Biogenic gas,thermogenic gas | $\delta^{13}C_{C1}$: −65–−45(Liu et al ,2010) |
| Michigan Basin (Martini et al., 2003) | Devonian | Antrim Shale | 0.5–24 | Majority of type- Ⅰ | 0.4–0.6<br>1.0 | Biogenic gas(northern margin)<br>thermogenic gas(central basin) | $\delta^{13}C_{C1}$: −55–−48.3; $\delta D_{C1}$: −258–−207(Martini et al.,1998) |
| Illinois Basin | Devonian | New Albany Shale | 1.2–20 (Martini et al., 2008, Mastalerz et al 2013) | Majority of type- Ⅱ (Johnson et al., 1994) | 0.4–0.6 (Mastalerz et al., 2013)<br>1.0 (Martini et al., 2008) | Biogenic gas(northern margin) (Zehnder et al.,1977)<br>thermogenic gas(southern margin) (Martini et al., 2008; Strapoc et al., 2010) | $\delta^{13}C_{C1}$: −56.3–−48.4; $\delta D_{C1}$: −156–−254(Martini et al.,2008; Strapoc et al ,2010) |
| Huainan, Anhui province | Permain | Coal | | Majority of type-Ⅲ (Zhang Hong et al., 2005) | 0.72–1.48 (Qin Guojian, 2010) | Biogenic gas, thermogenic gas (Tao Mingxin et al., 2005; Zhang Hong et al., 2005; Zhang Xiaojun et al., 2007) | $\delta^{13}C_{C1}$: −72.3–−49.2(Zhang et al ,2005);$\delta D_{C1}$: −243–−219( Tao et al.,2005) |
| Hongen, Yunnan Province (Tao Mingxin et al., 2005) | Permain | Coal | | type-Ⅲ | 1.24–1.43 | Biogenic gas, thermogenic gas | $\delta^{13}C_{C1}$: −54.5–−49.8; $\delta D_{C1}$: −206–−196 |
| East Australia (Ahmed et al., 2001) | Permain | Coal | | type-Ⅲ | 0.72–1.48 | Biogenic gas (Sydney Basin etc.) | $\delta^{13}C_{C1}$: −55±10; $\delta D_{C1}$: −217±17 |
| Mexico Gulf (Warwick et al., 2008) | Paleogene | Coal | | type-Ⅲ | 0.5–1.2 | Biogenic gas (north part) | $\delta^{13}C_{C1}$: −65.6–−56.8; $\delta D_{C1}$: −220.7–−181.6 |

Note: * minimum-maximum/mean value (sample number).

in the Mohe permafrost, thus confirming the microbial activities exiting broadly throughout the Mohe area.

## 4 Proof of Microbial Gas Occurrence

### 4.1 Gas components

Microbial gas is marked by methane-dominated gas, i.e., the ratio of $C_1$ to $C_{1–5}$ higher than 98% (Rice and Claypool, 1981). In the shallow section of the Mohe Basin there is a great quantity of methane-dominated gas. In effect, the Mohe Basin has highly variable hydrocarbon gas constituents. According to the gas chromatograph analyses of 88 core gas samples from the Mk-2 well in the Mohe Basin (Table 2), the methane content ranges from 84 to 100%, with the ratio of $C_1$ to $C_{1–5}$ being greater than 98% in the shallow subsurface of 870 m (Fig. 2), in the range of 91 to 98% from 870 to 1300 m, and from 84 to 97% deeper than 1300 m. It then displays characteristics of microbial gas at the shallower section of the Mohe Basin (Fig. 2).

### 4.2 Hydrocarbon gas isotopes

Compared with thermogenic gas, the methane of microbial origin is generally enriched with $C^{12}$ and $H^1$, i.e., characterized by very low isotopic ratios of $\delta^{13}C_{CH4}$ and $\delta D_{CH4}$, with the $\delta^{13}C_{CH4}$ being less than −55‰ and $\delta D_{CH4}$ less than −150‰ (Rice and Claypool, 1981; Rice, 1993). It was reported that the Mohe area has relatively lighter methane carbon isotopes (Zhao et al., 2012), which is confirmed in the present study. The mass spectrometric analyses of almost 90 core gas samples from the Mk-2 well drilled in the Mohe Basin indicate that the methane carbon isotope $\delta^{13}C_{CH4}$ values are in the range of −82.9‰ to −39.7‰ (Table 3), among which 71.6% of the $\delta^{13}C_{CH4}$ values are less than −55‰ (in the upper subsurface of 1940 m), 20.5% are between −55‰ and −50‰ (approximately 1940 to 2200 m below the surface), and 7.9% are more than −50‰ (below 2200 m). In addition, the methane hydrogen isotope $\delta D_{CH4}$ values of the core gas range from −450‰ to −243‰, which are all significantly lower than these of microbial gas from the modern Yangtze River estuary (Zhang et al, 2017), and almost all are lighter than −250‰ (Table 3). These isotope characteristics show a microbial gas occurrence in the upper subsurface of the Mohe permafrost.

In the interpretive diagram of the gas origin, through the combination of the $\delta^{13}C_{CH4}$ and $\delta D_{CH4}$ information, all of the 89 pairs of methane isotopic ratios of $\delta^{13}C_{CH4}$ and

**Table 2 Main components of the core hydrocarbon gas from Mk-2 well of the Mohe Basin, northeast China**

| No. | Well depth (m) | $CH_4$ (μL/L) | $C_2H_6$ (μL/L) | $C_3H_8$ (μL/L) | $C_1/\sum C_i$ | No. | Well depth (m) | $CH_4$ (μL/L) | $C_2H_6$ (μL/L) | $C_3H_8$ (μL/L) | $C_1/\sum C_i$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 675 | 22301.17 | 0.00 | 81.41 | 1.00 | 45 | 1595 | 180669.22 | 7538.39 | 4857.43 | 0.93 |
| 2 | 735 | 223481.63 | 0.00 | 11.64 | 1.00 | 46 | 1608 | 134739.04 | 6486.93 | 4181.51 | 0.92 |
| 3 | 754 | 28709.34 | 115.37 | 54.82 | 0.99 | 47 | 1619 | 536681.07 | 46384.98 | 24515.14 | 0.88 |
| 4 | 804 | 4843.80 | 11.22 | 10.67 | 0.99 | 48 | 1646 | 438871.49 | 20076.10 | 10050.97 | 0.93 |
| 5 | 813 | 58927.12 | 63.82 | 43.63 | 1.00 | 49 | 1653 | 320134.29 | 6992.91 | 2080.57 | 0.97 |
| 6 | 833 | 167347.74 | 72.23 | 0.00 | 1.00 | 50 | 1666 | 99846.95 | 2333.69 | 961.10 | 0.96 |
| 7 | 842 | 275592.47 | 17.54 | 7.33 | 1.00 | 51 | 1674 | 176714.34 | 7524.91 | 4303.13 | 0.93 |
| 8 | 856 | 73776.22 | 0.00 | 9.04 | 1.00 | 52 | 1700 | 482594.54 | 10844.14 | 2273.60 | 0.97 |
| 9 | 877 | 107189.57 | 736.49 | 562.07 | 0.98 | 53 | 1732 | 10125.74 | 368.73 | 214.29 | 0.94 |
| 10 | 889 | 305871.42 | 7242.38 | 5218.86 | 0.95 | 54 | 1745 | 154549.05 | 5897.62 | 1833.56 | 0.95 |
| 11 | 899 | 69275.53 | 1671.03 | 242.61 | 0.97 | 55 | 1759 | 25684.32 | 1050.88 | 535.17 | 0.94 |
| 12 | 908 | 80518.56 | 1070.63 | 235.60 | 0.98 | 56 | 1798 | 249305.87 | 13545.57 | 2267.03 | 0.94 |
| 13 | 922 | 74283.78 | 1964.53 | 0.00 | 0.94 | 57 | 1810 | 371596.67 | 29267.74 | 9524.86 | 0.90 |
| 14 | 929 | 235035.20 | 5213.97 | 1213.48 | 0.97 | 58 | 1823 | 25778.35 | 785.18 | 239.21 | 0.96 |
| 15 | 945 | 156604.23 | 2946.42 | 938.23 | 0.97 | 59 | 1846 | 262181.73 | 17975.99 | 6995.79 | 0.91 |
| 16 | 981 | 196350.98 | 3659.22 | 2762.62 | 0.96 | 60 | 1863 | 494597.06 | 26836.44 | 8916.29 | 0.93 |
| 17 | 988 | 64611.15 | 1428.55 | 1447.89 | 0.93 | 61 | 1879 | 45217.77 | 1218.75 | 323.46 | 0.96 |
| 18 | 1054 | 57932.23 | 1259.04 | 1863.75 | 0.92 | 62 | 1897 | 255282.94 | 10035.27 | 4101.57 | 0.94 |
| 19 | 1067 | 193792.85 | 3139.73 | 1357.96 | 0.98 | 63 | 1908 | 22548.11 | 799.46 | 222.51 | 0.95 |
| 20 | 1081 | 104081.56 | 2469.86 | 977.38 | 0.96 | 64 | 1916 | 226556.59 | 11267.43 | 2207.41 | 0.94 |
| 21 | 1094 | 295853.35 | 15261.24 | 12667.97 | 0.90 | 65 | 1934 | 192515.76 | 10771.78 | 2550.83 | 0.93 |
| 22 | 1126 | 381178.24 | 0.00 | 2970.05 | 0.99 | 66 | 1941 | 262404.62 | 13135.50 | 1896.80 | 0.95 |
| 23 | 1134 | 426214.08 | 11516.53 | 2921.45 | 0.96 | 67 | 1975 | 493719.14 | 13574.37 | 2818.60 | 0.97 |
| 24 | 1142 | 319912.70 | 8487.01 | 2145.90 | 0.96 | 68 | 1995 | 362323.93 | 9855.23 | 2463.95 | 0.97 |
| 25 | 1149 | 415161.99 | 15225.93 | 6591.21 | 0.94 | 69 | 2004 | 308473.34 | 18627.51 | 4845.28 | 0.93 |
| 26 | 1156 | 520134.36 | 16093.71 | 3674.08 | 0.96 | 70 | 2014 | 446849.95 | 25107.68 | 8297.20 | 0.93 |
| 27 | 1163 | 344191.89 | 17970.26 | 8041.57 | 0.92 | 71 | 2025 | 309596.02 | 17311.22 | 4924.99 | 0.93 |
| 28 | 1173 | 252131.40 | 10468.79 | 4398.91 | 0.94 | 72 | 2037 | 375953.83 | 22535.83 | 6787.21 | 0.93 |
| 29 | 1182 | 126302.05 | 4259.11 | 1334.27 | 0.95 | 73 | 2045 | 3205.62 | 90.41 | 55.72 | 0.95 |
| 30 | 1194 | 514210.26 | 18952.43 | 10434.36 | 0.93 | 74 | 2054 | 528920.06 | 28505.85 | 4187.70 | 0.94 |
| 31 | 1204 | 417314.13 | 18541.73 | 12691.45 | 0.92 | 75 | 2075 | 191224.75 | 5605.01 | 4018.96 | 0.94 |
| 32 | 1213 | 303627.90 | 9558.78 | 4821.89 | 0.95 | 76 | 2121 | 106001.12 | 3396.51 | 1755.20 | 0.94 |
| 33 | 1217 | 521075.53 | 10185.59 | 3568.57 | 0.97 | 77 | 2135 | 254980.76 | 4934.36 | 826.50 | 0.98 |
| 34 | 1227 | 430863.86 | 10748.26 | 4640.66 | 0.96 | 78 | 2148 | 497658.97 | 23656.42 | 10112.91 | 0.93 |
| 35 | 1235 | 377362.54 | 6696.65 | 1655.03 | 0.98 | 79 | 2171 | 422868.98 | 36727.07 | 11387.63 | 0.90 |
| 36 | 1294 | 437919.49 | 15298.27 | 5577.10 | 0.95 | 80 | 2178 | 112232.02 | 4224.36 | 1748.44 | 0.94 |
| 37 | 1300 | 384542.07 | 11101.69 | 3375.96 | 0.96 | 81 | 2195 | 606032.38 | 50001.59 | 12023.68 | 0.91 |
| 38 | 1421 | 18194.04 | 1277.16 | 850.23 | 0.88 | 82 | 2212 | 207213.85 | 7850.24 | 1137.14 | 0.96 |
| 39 | 1444 | 487928.11 | 57934.22 | 27202.19 | 0.84 | 83 | 2235 | 571491.40 | 50801.41 | 6994.31 | 0.91 |
| 40 | 1478 | 414491.33 | 31582.20 | 10037.01 | 0.90 | 84 | 2241 | 22696.85 | 994.30 | 388.93 | 0.94 |
| 41 | 1494 | 427387.34 | 36565.75 | 9182.43 | 0.89 | 85 | 2259 | 106032.38 | 6834.26 | 4483.49 | 0.88 |
| 42 | 1500 | 503094.23 | 38232.11 | 12105.81 | 0.90 | 86 | 2272 | 115446.51 | 3192.65 | 1103.26 | 0.96 |
| 43 | 1511 | 156318.01 | 6469.55 | 1648.79 | 0.95 | 87 | 2281 | 352145.99 | 35481.06 | 20658.92 | 0.84 |
| 44 | 1575 | 417983.83 | 12129.10 | 6136.83 | 0.95 | 88 | 2302 | 228310.36 | 12195.01 | 2538.94 | 0.94 |

$\delta D_{CH4}$ of the core gas from the Mk-2 well in the Mohe Basin fall within the scope of the microbial origin gas (Fig. 7), displaying the presence of microbial gas in the Mohe permafrost.

The carbon isotope $\delta^{13}C_{C2H6}$ ratio of ethane also exhibits the characteristics of the microbial gas of the Mohe Basin. According to some scholars, the carbon isotopes of coalbed ethane of thermal origin $\delta^{13}C_{C2H6}$ are higher than −33‰ (Rice and Claypool, 1981). Through the mass spectrometric analyses of 74 core gas samples from the Mk-2 well, the carbon isotopes of the ethane are in the range of −54.3 to −41.7‰ (Table 3), suggesting the existence of microbial gas in the Mohe permafrost.

As shown above, the fact that the Mohe Basin has an occurrence of microbial gas is proven to be true and credible, and the microbial gas primarily exists in the shallower section of the Mohe permafrost (Fig. 2).

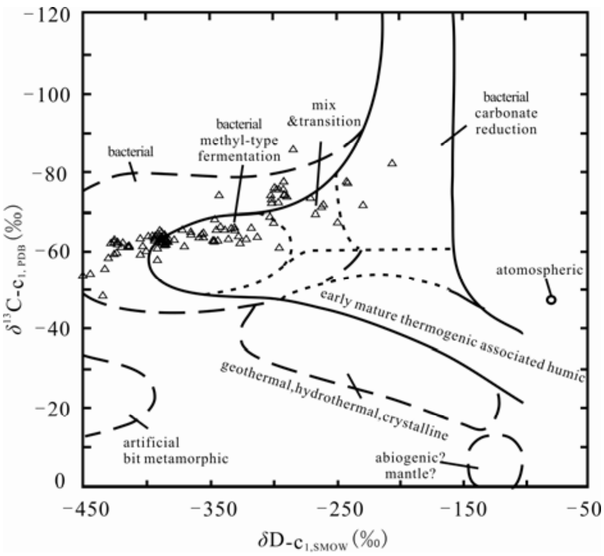


Fig. 7. Interpretive diagram of carbon and hydrogen isotopes of the core gas from the Mk-2 well of the Mohe Basin, northeast China (after Whiticar, 1999).

**Table 3 Distribution of carbon and hydrogen isotopes f hydrocarbon gas from Mk-2 well in the Mohe Basin**

| No. | Depth (m) | $\delta^{13}C_1$-PDB (‰) | $\delta^{13}C_2$-PDB (‰) | $\delta Dc_1$-SMOW (‰) | No. | Depth (m) | $\delta^{13}C_1$-PDB (‰) | $\delta^{13}C_2$-PDB (‰) | $\delta Dc_1$-SMOW (‰) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 594 | −82.9 | n.d. | n.d. | 46 | 1595 | −63.4 | −51.2 | −322 |
| 2 | 675 | −79.0 | n.d. | n.d. | 47 | 1608 | −51.5 | n.d. | n.d. |
| 3 | 735 | −78.4 | n.d. | −293 | 48 | 1619 | −62.7 | −52.5 | −422 |
| 4 | 754 | −77.8 | n.d. | −243 | 49 | 1646 | −62.2 | −50.6 | −428 |
| 5 | 804 | −74.3 | n.d. | −344 | 50 | 1653 | −59.6 | −48.2 | −415 |
| 6 | 813 | −73.2 | n.d. | −301 | 51 | 1666 | −63.4 | −47.3 | −423 |
| 7 | 833 | −75.9 | n.d. | −298 | 52 | 1674 | −65.1 | −50.0 | −389 |
| 8 | 842 | −73.8 | n.d. | −272 | 53 | 1700 | −62.3 | −50.3 | −418 |
| 9 | 856 | −72.3 | n.d. | −297 | 54 | 1732 | −60.1 | n.d. | −383.1 |
| 10 | 877 | −67.7 | n.d. | −300 | 55 | 1745 | −59.7 | −47.3 | −416.5 |
| 11 | 889 | −66.2 | −50.5 | −334 | 56 | 1759 | −59.6 | −49.8 | −390.4 |
| 12 | 899 | −65.2 | −48.3 | −346 | 57 | 1798 | −59.5 | −46.4 | −413.5 |
| 13 | 908 | −64.7 | −54.1 | −356 | 58 | 1810 | −58.7 | −48.4 | −394.3 |
| 14 | 922 | −64.5 | −49.3 | −366 | 59 | 1823 | −60.1 | n.d. | n.d. |
| 15 | 929 | −64.4 | −50.5 | −358 | 60 | 1846 | −58.9 | −47.5 | −398.8 |
| 16 | 945 | −65.5 | −47.6 | −339 | 61 | 1863 | −57.8 | −47.5 | −402.5 |
| 17 | 981 | −66.3 | −54.3 | −318 | 62 | 1879 | −58.7 | n.d. | −401.6 |
| 18 | 988 | −66.7 | n.d. | −251 | 63 | 1897 | −58.3 | −46.5 | −408.7 |
| 19 | 1054 | −70.9 | −52.6 | −263 | 64 | 1908 | −55.7 | −46.8 | −418.7 |
| 20 | 1067 | −69.1 | −45.8 | −303 | 65 | 1916 | −53.4 | −51.2 | −428.0 |
| 21 | 1081 | −64.7 | −49.0 | −366 | 66 | 1934 | −55.4 | −43.6 | −437.7 |
| 22 | 1094 | −66.5 | −50.2 | −343 | 67 | 1941 | −55.4 | −43.1 | −446.5 |
| 23 | 1126 | −63.1 | −50.1 | −378 | 68 | 1975 | −54.0 | −43.7 | −445.4 |
| 24 | 1134 | −62.7 | −49.6 | −383 | 69 | 1995 | −53.9 | −42.8 | −427.5 |
| 25 | 1142 | −63.0 | −43.1 | −388 | 70 | 2004 | −54.5 | −44.0 | −432.0 |
| 26 | 1149 | −62.9 | −47.6 | −390 | 71 | 2014 | −53.8 | −43.4 | −426.4 |
| 27 | 1156 | −62.3 | −48.0 | n.d. | 72 | 2025 | −54.3 | −44.0 | −431.7 |
| 28 | 1163 | −63.9 | −50.6 | n.d. | 73 | 2037 | −53.3 | −43.4 | −428.9 |
| 29 | 1173 | −63.9 | −49.5 | −399 | 74 | 2045 | −52.8 | −45.5 | −371.9 |
| 30 | 1182 | −61.5 | −48.3 | −403 | 75 | 2054 | −51.6 | −42.3 | −435.4 |
| 31 | 1194 | −63.2 | −49.5 | −388 | 76 | 2075 | −52.0 | −44.3 | −419.0 |
| 32 | 1204 | −63.2 | −51.6 | −388 | 77 | 2121 | −53.3 | −46.1 | −339.3 |
| 33 | 1213 | −63.1 | −47.9 | −390 | 78 | 2135 | −53.3 | −43.6 | −359.8 |
| 34 | 1217 | −64.2 | −51.2 | −385 | 79 | 2148 | −52.5 | −44.8 | −363.6 |
| 35 | 1227 | −57.8 | −48.4 | −392 | 80 | 2171 | −49.7 | −41.7 | −428.0 |
| 36 | 1235 | −53.5 | −44.6 | −450 | 81 | 2178 | −50.5 | −44.3 | −429.7 |
| 37 | 1294 | −61.5 | −48.3 | −414 | 82 | 2195 | −51.4 | −43.8 | −438.3 |
| 38 | 1300 | −61.2 | −45.0 | −414 | 83 | 2212 | −45.9 | −43.0 | −432.5 |
| 39 | 1421 | −61.4 | n.d. | −415 | 84 | 2235 | −47.8 | −43.6 | −437.5 |
| 40 | 1444 | −59.1 | −51.4 | −405 | 85 | 2241 | −48.5 | −45.9 | −377.2 |
| 41 | 1478 | −48.6 | −44.5 | −434 | 86 | 2259 | −49.2 | −45.6 | −363.0 |
| 42 | 1494 | −53.8 | −50.8 | −444 | 87 | 2272 | −39.7 | −45.8 | −307.5 |
| 43 | 1500 | −55.5 | −49.7 | −432 | 88 | 2281 | −56.7 | −53.1 | −396.3 |
| 44 | 1511 | −65.5 | −50.0 | n.d. | 89 | 2302 | −58.8 | −49.1 | −385.6 |
| 45 | 1575 | −62.4 | −50.5 | −391 | | | | | |

### 4.3 Gas composition and isotopes

The origin of hydrocarbon gas in the Mohe Basin is also discussed from the perspective of the Bernard plot relating the $C_1/(C_2+ C_3)$ ratio (Bernard et al., 1978) to the carbon isotopic $\delta^{13}C_{CH4}$ value of methane. The study of the testing data of 84 core gas samples reveals that 67 gas samples fall within the scope of mixed gas of microbial and thermogenic origin, 11 samples of microbial gas, and only six samples of thermal origin (Fig. 8), suggesting that microbial gas exists in the Mohe permafrost.

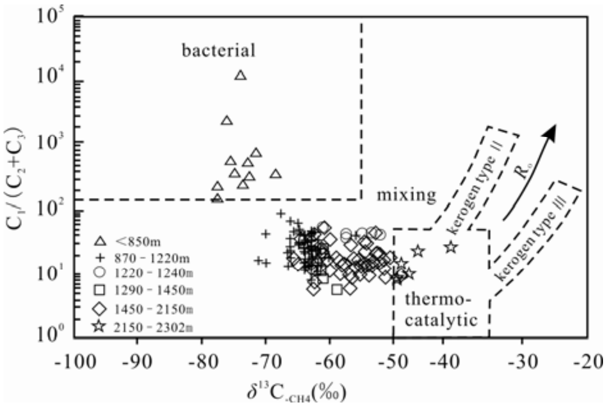


Fig. 8. Interpretive diagram of components and carbon isotopes of the core gas from Mk-2 well of the Mohe Basin, northeast China (modified from Whiticar, 1999).

## 5 Discussions

Microbial activities spreading throughout the Mohe permafrost provide agents for the formation of microbial gas in the region. As discussed above, almost all mudstones from the outcrop and downhole in the Mohe Basin bear variable amounts of 25-norhopane series compounds, which are considered to be indicators for, or products of, the microbial alteration of organic matter (Blanc and Connan, 1992; Bao Jianping, 1996; Du

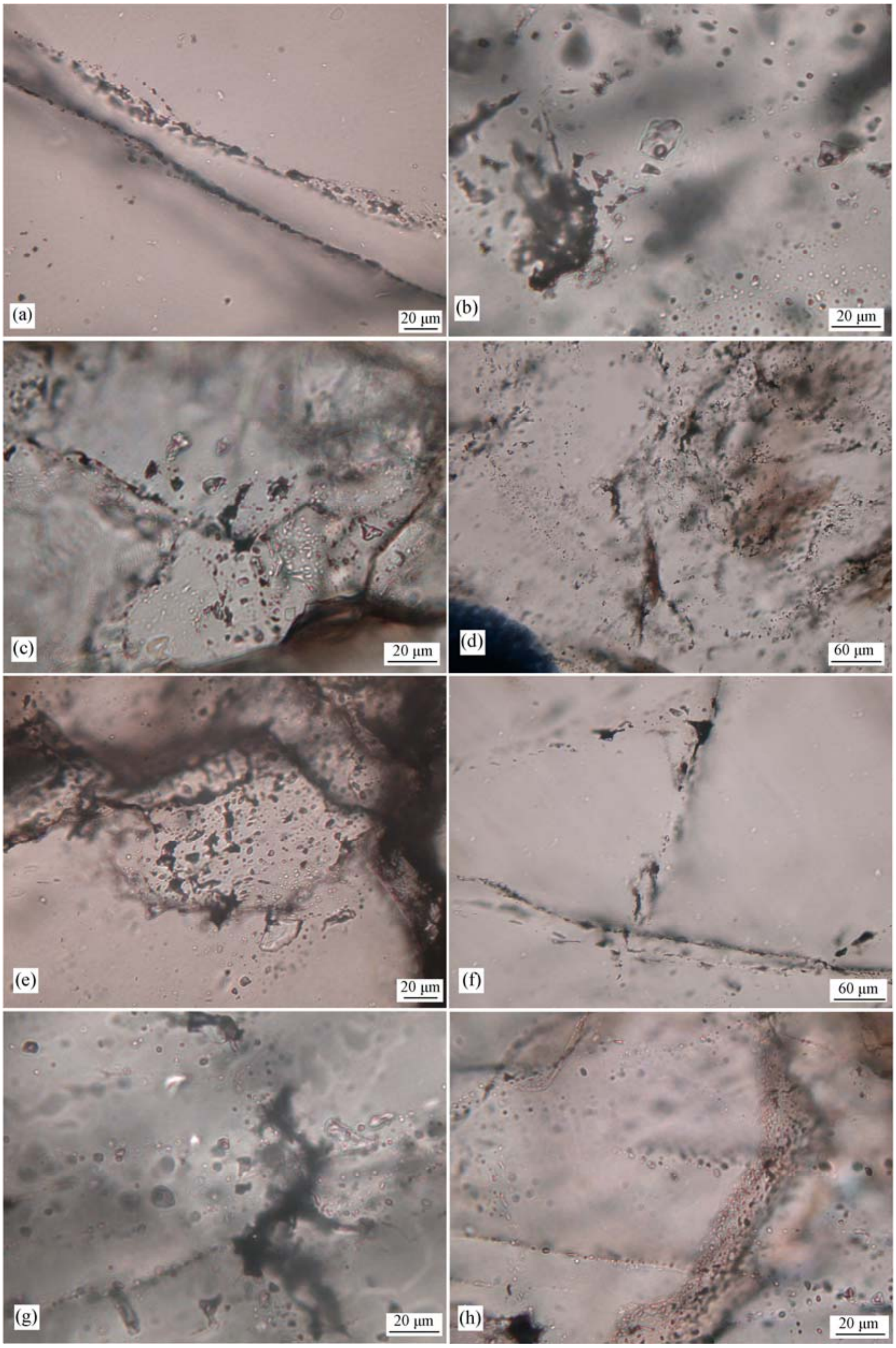


Fig. 9. All kinds of hydrocarbon inclusions in the Mohe Basin.

(a), dark brown bitumen-rich oil inclusions in the fissures of quartz veins (mk-2, 513.82–514.07 m, polarized light); (b), dark brown bitumen-rich oil and brownish to grey gaseous hydrocarbon-salt water inclusions in the fissures in quartz veins (mk-2, 576.2–576.4 m, polarized light); (c), dark brown bitumen-rich oil and brownish to grey gaseous hydrocarbon inclusions in the fissures in quartz veins (mk-2,738.00-738.20m,polarized light); (d), dark brown bitumen-rich oil and grey gaseous hydrocarbon-salt water inclusions in the fissures in quartz veins(mk-2, 763.57–763.67m, polarized light); (e), dark brown bitumen-rich oil inclusions in quartz cements in the coarse grained sandstones(mk-2,973.84–773.98m,polarized light); (f), dark brown bitumen-rich oil and brownish gaseous hydrocarbon inclusions in quartz cements in the fine grained sandstones(mk-2, 1012.15–1012.14m, polarized light); (g), dark brown bitumen-rich oil and brownish gaseous hydrocarbon-bearing salt water inclusions in quartz veins in the fine grained sandstones (mk-2, 1620.30–1620.40m, polarized light).

Hongyu et al., 2004; Bennett et al., 2006; Wang Zuodong et al., 2009), showing the active microbial activities throughout the Mohe permafrost that drive the formation of microbial gas in this region.

The Mohe permafrost displays a marked microbial origin of hydrocarbon gas. First, the Mohe Basin has relatively lighter hydrocarbon gas components in the shallower section, with a $C_1$ to $C_{1-5}$ ratio of greater than 98% (shallower than 870 m, Fig. 2). Second, there are relatively lighter carbon and hydrogen isotopic ratios for methane ($\delta^{13}C_{CH4}$, $\delta D_{CH4}$) in the upper section of the Mohe Basin, i.e., $\delta^{13}C_{CH4}$ of lighter than −55‰ in the shallower part (shallower than 1940 m, Fig. 2) and almost all the $\delta D_{CH4}$ values are lower than −250‰. Third, the low carbon isotope values of ethane from the Mohe Basin are lighter than −40‰. All of these factors confirm a microbial gas occurrence in the upper section of the Mohe permafrost (Fig. 2).

It was demonstrated that the microbial gas in the Mohe Basin were of secondary origin (Schoell, 1980; Tao Mingxin et al., 2005). First, the formation in the basin is of the Mesozoic age, and the primary microbial gas generated in the stage of diagenesis was possibly disappeared. The majority of the present microbial gas should be produced by the dark mudstones with matured organic matter which had 0.8% to 3.54% of the vitrinite reflectance ($R_o$). Second, it was also discovered that the gaseous, liquid and solid hydrocarbons of thermogenic origin were widely distributed throughout the basin (Fig. 9), which were probably the precursor to the secondary microbial gas, the latter two of which could greatly increase gas production in the Mohe Basin.

The existence of microbial gas, confirmed for the first time in the Mohe permafrost, and even among all the permafrost throughout China, largely extends the gas source of gas hydrate accumulation in the Mohe area, northeast China, due to microbial gas in addition to thermogenic gas (Zhao et al., 2012), thus likely contributing to gas hydrate formation, which enhances the accumulation and exploration potential for gas or gas hydrate in the area.

## 6 Conclusions

The Mohe permafrost in northeast China possesses several advantageous conditions for microbial gas formation. In the Mohe permafrost, all of the requisites for microbial gas formation, such as the abundance of total organic carbon, type of kerogen, subsurface temperature, salinity, pH levels and redox of the underground water, and the presence of microbial activities exist, thereby favoring the formation of microbial gas.

The presence of microbial gas in the shallower section of the Mohe permafrost (shallower than 870 m) is affirmative, and confirmed not only by the gas composition, methane carbon and hydrogen and ethane carbon isotopes, etc., but also by the microbial activity widely occurring in the Mohe area.

The existence of the microbial gas affirmed in the Mohe area is the first case in the permafrost across China, and has guiding implications for the accumulation of gas hydrate in permafrost across China. The microbial gas in the Mohe permafrost, together with the thermogenic gas, greatly enhance the accumulation and exploration potentials of gas hydrate in the permafrost of Mohe and even all of China, thereby improving the accumulation model of gas hydrate and guiding the exploration thereof in the permafrost of China.

## Acknowledgements

This study was entirely supported by Prospecting and Testing Production Project of Gas Hydrate resources, Ministry of Land and Resources of China (grants No. GZHL20110317, GZHL20110320, GZHL20110322). The authors thank Guo Wei and Ji Shengli for their assistance in the field, as well as Chen Liu (gas chromatograph) and Wang Guang (mass spectrometry) for their analytical expertise.

Manuscript received Apr. 11, 2018
accepted Jul. 27, 2018
edited by Hao Qingqing

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