ORIGINAL PAPER

Genetic types and geochemical characteristics of natural gases in the Jiyang Depression, China

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Received: 21 July 2014/Published online: 22 January 2015 © The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract Natural gases were widely distributed in the Jiyang Depression with complicated component composition, and it is difficult to identify their genesis. Based on investigation of gas composition, carbon isotope ratios, light hydrocarbon properties, as well as geological analysis, natural gases in the Jiyang Depression are classified into two types, one is organic gas and the other is abiogenic gas. Abiogenic gas is mainly magmatogenic or mantlederived CO₂. Organic gases are further divided into coaltype gas, oil-type gas, and biogas according to their kerogen types and formation mechanisms. The oil-type gases are divided into mature oil-type gas (oil-associated gas) and highly mature oil-type gas. The highly mature oil-type gases can be subdivided into oil-cracking gas and kerogen thermal degradation gas. Identification factors for each kind of hydrocarbon gas were summarized. Based on genesis analysis results, the genetic types of gases buried in different depths were discussed. Results showed that shallow gases (<1,500 m) are mainly mature oil-type gases, biogas, or secondary gases. Secondary gases are rich in methane because of chromatographic separation during migration and secondary biodegradation. Secondary biodegradation leads to richness of heavy carbon isotope ratios in methane and propane. Genesis of middle depth gases (1,500-3,500 m) is dominated by mature oil-type gases.

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Edited by Jie Hao

Deep gases (3,500–5,500 m) are mainly kerogen thermal degradation gas, oil-cracking gas, and coal-type gas.

Keywords Genetic types · Natural gases · Jiyang Depression · Light hydrocarbon properties · Carbon isotope ratios · Identification factors

1 Introduction

The Jiyang Depression is located in the north part of Shandong Province in China, on the fluvial plain and the delta where the Huanghe River runs into the Bohai Sea. Tectonically, the Jiyang Depression is located in the southeast part of the Bohai Bay Basin. It is a big terrestrial depression and ranks as one of the most prolific petroliferous area (Li et al. 2003). Since the discovery of the Shengli Oilfield in 1960, 50×10^8 t of OOIP and $2,500 \times 10^8$ m³ OGIP have been proved, at the same time, 10.7×10^8 tons of oil and 460×10^8 m³ gases have been produced.

Five sets of source rocks were developed in the Jiyang Depression, and they are distributed in the Carboniferous-Permian, the second member of the Kongdian Formation (Ek_2) , and the fourth, third, and first members of the Eogene Shahejie Formation $(Es_4, Es_3, and Es_1)$. The kerogen in those source rocks is mainly sapropelic type, and some of them are humic type. After a series of tectonic movements, these source rocks vary greatly in depth and evolution histories which influence gas generation and accumulation in many aspects, such as gas components, genesis, etc. (Zhang 1991). Thirteen commercial gas bearing layers have been discovered in the Neogene Minghuazhen and Guantao Formations, the Eogene Shahejie Formation, and the Paleozoic Carboniferous-Permian and Ordovician in the Jiyang Depression (Fig. 1). Gas reservoirs occurred widely at a depth from 192

to 4,750 m. In these reservoirs, gas compositions vary greatly from hydrocarbon gas to abiogenic gas. As for hydrocarbon gas, the paraffin hydrocarbon composition and carbon isotope ratios varied dramatically. There are several different genesis models such as oil-type gas, coal-type gas, biogas, and inorganic mantle source gas, etc. (Gao et al. 2011; Zhou 2004; Luo et al. 2008). Natural gases usually occur as normal gas reservoirs, tight sandstone gas reservoirs, shale gas reservoirs, and coal-bed methane.

To make a thorough investigation of the gas genesis in the Jiyang Depression, the authors collected abundant data from exploration wells with commercial gas flow including 472 sets of natural gas composition data, 293 sets of carbon isotope ratio data (both hydrocarbon gas and carbon dioxide), and 69 sets of light hydrocarbon properties data (Fig. 2). According to gas component contents, carbon isotope ratios and light

hydrocarbon properties, combined with geological analysis, natural gases in the Jiyang Depression are divided into two categories namely organic gas and abiogenic gas. Organic gas was further divided into coal-type gas, oil-type gas, and biogas according to kerogen type and formation mechanism. The oiltype gases were finally divided into mature oil-type gas (oilassociated gas) and highly mature oil-type gas (including oilcracking gas and kerogen thermal degradation gas) (Schoell 1980). The geochemical properties of each kind of natural gas were discussed, respectively.

2 Abiogenic gas

Abiogenic gas in the Jiyang Depression is mainly CO_2 , and its distribution is controlled by great deep faults (Tang



Fig. 1 Strata histogram and gas bearing layers in the Jiyang Depression

Fig. 2 Structural framework and typical gas producing wells in the Jiyang Depression



1-Shouguang Uplift; 2-Guangrao Uplift; 3-Chenjiazhuang Uplift; 4-Gudao Uplift; 5-Bonan Uplift; 6-Yihezhuang Uplift; 7-Qingyun Uplift; 8-Gaoqing Uplift;

et al. 2002). This type of gas is mainly found in Pingfangwang, Pingnan, and Huagou gas fields in the western part of the Dongying Sag and the Balipo gas field in the northern part of the Huimin Sag. Vertically, CO_2 is mainly distributed in the Shahejie Formation of Eogene (Es for short), Neogene, and Ordovician. The CO_2 content of such reservoirs ranges from 55.5 % sto 100 % and averages 82.4 %. Hydrocarbon gases were mixed into CO_2 reservoirs in varying degrees. The methane content in those reservoirs ranges from 0 % to 37.2 % with an average of 13.3 %, while the heavy hydrocarbon (C_{2+}) content was low with an average value of 1.4 % (Table 1).

There are usually three genetic types of natural CO₂, namely magma degassing, decomposition of carbon rich crustal rock, and decomposition of organic matter. Studies have confirmed that $\delta^{13}C_{CO2}$ can be used to identify its genesis. It is generally believed that $\delta^{13}C_{CO2} > -8 \%$ indicates inorganic genesis, and $\delta^{13}C_{CO2} < -10 \%$ indicates organic genesis (Zhang 1991; Dai 1993). In the Jiyang Depression, gas reservoirs with high CO₂ content (>60 %) usually have heavy carbon isotope ratios ranging from -9.8 ‰ to -3.4 ‰ (PDB). The $\delta^{13}C_{CO2}$ of most samples was higher than -7 ‰, and this can be classified as inorganic genesis. The CO₂ content in hydrocarbon gas reservoirs was usually lower than 10 % with $\delta^{13}C_{CO2}$ less than -8 ‰, and it can be deduced that the CO₂ came from decarboxylation of organic matter (Fig. 3).

Previous studies have shown that helium of different genesis has different isotopic compositions, and the 3 He/ 4 He values of atmosphere, earth mantle, and crust are,

respectively, 1.4×10^{-6} , 1.1×10^{-5} , and 2×10^{-8} (Sun et al. 1996). As shown in Table 2, the ³He/⁴He value of CO₂ reservoirs in the Pingfangwang, Huagou, and Yangxin gas fields in the Jiyang Depression was high (3.55–4.49 × 10⁻⁶), and R/Ra was 2.5–3.2, indicating a mixed He origin of mantle genesis and crust genesis (Wang et al. 2013). The isotopic analysis of rare gases and CO₂ indicated that the highly concentrated CO₂ gas reservoir in the Jiyang Depression originated from magma–mantle degassing (Hunt et al. 2012).

3 Organic gases

Organic hydrocarbon gases are produced from sedimentary organic matter due to a series of biological-geochemical reactions. Organic matter of different types and in different thermal evolution stages will produce hydrocarbon gases with different component compositions and isotopic compositions. C_1/C_{1-5} and $\delta^{13}C_1$ of hydrocarbon gases in the Jiyang Depression changed regularly with depth, and could be divided into three categories according to the reservoir depth (Fig. 4):

(1) Buried less than 1,500 m: the C_1/C_{1-5} value is usually high and ranges from 0.8 % to 1.0, 90 % of the natural gases are dry gas ($C_1/C_{1-5} > 0.95$) with a methane content more than 95 %, while the values of $\delta^{13}C_1$ can be separated into two groups: the values of group one are between -40 ‰ and -50 ‰, and the values of group two are less than -55 ‰.

Area	Well	Formation	Depth, m	δ ¹³ C _{CO2} , ‰ (PDB)	$\delta^{13}C_1, \%$ (PDB)	CH ₄ , %	C ₂₊ , %	N ₂ , %	CO ₂ , %
Pingfangwang Gas Field	Bin1	Е	1890.0–1898.0	-6.1	-45.8	3.53	2.09	0	94.13
	Ping13-2	Е	1453.6-1483.2	-4.7	-52.7	26.43	2.79	1.07	68.85
	Ping13-4	Е	1450.8-1486.4	-4.4	-51.7	19.04	4.85	1.21	74.92
	Ping14-3	Е	1467.0-4684.6	-4.3	-51.8	18.17	3.30	0.61	77.93
	Ping4	Е	1459.4–1461.4	-5.4	-50.9	20.89	3.33	0.46	75.33
	Ping9-3	Е	1462.6-1489.2	-4.5	-51.6	22.46	3.40	0.25	73.87
	Pingq12	Е	1470.5-1472.5	-4.4	-51.9	21.63	3.39	0.63	74.2
	Pingq12-61	Е	1452.4–1487.6	-4.5	-51.8	17.13	3.19	0.38	79.17
	Pingq4	Е	1459.4–1474.5	-5.4	-51.7	20.89	3.32	0.46	75.33
Pingnan Gas Field	Bin11	Е	1980.2-2250.0	-5.9	-47.6	1.31	1.06	0	97.31
	Bing11	0	2301.0-2307.0	-6.3	-47.6	1.52	0.74	0.25	97.06
Binnan Oilfield	Bin4	Е	1510.0-1568.0	-9.8	-49.4	32.62	4.91	0	60.72
	Bin4-13-1	Е	1453.0-1455.0	-5.1	-52.4	22.71	3.76	0.85	72.68
	Bin4-6-6	Е	1469.7–1474.7	-4.6	-51.7	23.52	3.53	0.33	72.5
Huagou Gas Field	Gao10	Ν	824.3-838.9	-5.2		0	0	0	99.99
	Gao3	Ν	833.4-834.8	-4.4	-35	0.07	0	0	97.87
	Gao53	Ν	811.4-818.0	-6.8		0.04	0	0	99.96
	Hua17	Е	1965.1-1980.0	-3.4	-54.39	7.47	0.51	2.05	89.70
	Hua17	Е	2000.0-2009.6	-3.4	-54	10.99	0.35	9.03	79.56
Balipo Gas Field	Yang25	Е	2793.9-2805.0	-4.4	-42.51	0.52	0	3.83	95.64
-	Yang5	0	2380.4-2386.0			0.76	0	0	99.24

Table 1 Geochemical characteristics of CO₂ in the Jiyang Depression

E Eogene, N Neogene, O Ordovician



Fig. 3 Identifying inorganic and organic CO_2 with $\delta^{13}C_{CO2}\mbox{---}CO_2$ relationships (Dai 1993)

- (2) Buried between 1,500 and 3,500 m: the heavy hydrocarbon content is usually high, and C_1/C_{1-5} ranges from 0.4 to 0.9. Most gases are associated with oil, and their $\delta^{13}C_1$ ranges from -45 ‰ to -52 ‰.
- (3) Buried between 3,500 and 5,500 m: the value of C_1/C_{1-5} ranges from 0.6 to 1.0. Compared with the

natural gas buried between 1,500 and 3,500 m, the value of C_1/C_{1-5} is higher, and the $\delta^{13}C_1$ is also heavier with a value of -30 % to -50 %.

The carbon isotope composition can be used to determine the natural gas genesis as concluded below. Under conditions of similar maturity, hydrocarbon gases generated from sapropelic-type kerogen usually had heavier $\delta^{13}C_1$ than gases generated from humic kerogen; under the condition of similar kerogen type, the natural gases of high thermal evolution degree tend to have heavy $\delta^{13}C_1$. Due to multiple reasons such as various kerogen types, different thermal evolution degrees, and secondary changes, the distribution characteristics of $\delta^{13}C_1$ show that $\delta^{13}C_1$ values of natural gases at middle depth are much lower, but those at shallow and deep depths are higher (Fig. 4).

To identify the genesis of natural gases, the three categories of natural gases (shallow gas <1,500 m, middle gas 1,500–3,500 m, and deep gas >3,500 m) were put into the genesis identification template built by Dai (1993). As shown in Fig. 5, the genesis of shallow gas is complicated with biogas and oil-associated gas dominating, while there is still a small portion of shallow gas having a $\delta^{13}C_1$ value of -40 ‰ to -55 ‰ with high C_1/C_{1-5} and C_1/C_{2+3} values higher than 500, which indicate secondary changes.

Table 2 Characteristics of rare gas isotope in CO₂ gas reservoirs in the Jiyang Depression

Area	Well	Depth, m	3 He/ 4 He, 10 $^{-8}$	R/Ra	⁴⁰ Ar/ ³⁶ Ar	⁴ He/ ²⁰ Ne
Binnan Oilfield	Bin4-6-6	1469.7–1474.7	387	2.76	1,791	934
Huagou Gas Field	Hua17	1965.1-1980	445	3.18	770	
	Hua17	2000-2009.6	449	3.18	1,054	
Pingfangwang Gas Field	Ping13-2	1453.6-1483.2	359	2.56	1,220	493
	Ping13-4	1450.8-1486.4	355	2.54	1,722	
	Ping14-3	1467-1484.6	447	3.19	1,378	110
	Ping9-3	1462.6-1489.2	387	2.76	317	467
	Pingq12	1470.5-1472.5	385	2.75	1,051	
	Pingq12-61	1452.4-1487.6	361	2.58	1,478	495
	Pingq4	1459.4-1474.5	385	2.75	1,758	221
Yangxin Oilfield	Yang25	2793.9-2805	412	2.94		



Fig. 4 Variation of $\delta^{13}C_1$ and C_1/C_{1-5} of hydrocarbon gases with depth in the Jiyang Depression

The genesis of middle gas is comparatively simple and dominated by oil-associated gas. As for deep gas, there are several genesis options such as highly mature oil-cracking gas, associated gas with condensate oil, coal-type gas, and the mixture of two or more of them (Fig. 5).

Carbon isotope ratios of methane, ethane, and propane can also be used to identify the genesis of natural gases (Lin et al. 2011). As shown in Fig. 6, shallow buried hydrocarbon gases in the Jiyang Depression were located in the area of oil-associated gas, but the ethane and propane carbon isotope ratios of some samples were abnormally heavy, which might be caused by secondary changes such as biodegradation. The middle buried hydrocarbon gases are mainly oil-associated gas mixed with a small amount of coal-type gas. The deep natural gases were coal-type gas, oil-type gas, as well as a mixture of the both. In general, hydrocarbon gases in the Jiyang Depression include biogas, oil-associated gas, highly mature oil-type gas, coal-type gas, and their geochemical characteristics are separately discussed below.

3.1 Biogas

Biogas is defined as hydrocarbon gas or nonhydrocarbon gas that is produced due to biochemical reactions of fermentative bacteria and methanogens in the process of degradation of organic matter in source rocks or crude oil (Gao et al. 2010). Naturally existed biogas was formed due to two kinds of processes: one is methyl-type fermentation $(CH_3COOH \rightarrow CH_4 + CO_2)$ and the other is carbonate reduction (CO₂ + 4H₂ \rightarrow CH₄ + 2H₂O). Limited by the survival temperature of methanogens (0–75 °C) (Li et al. 2008), biogas was mainly developed in shallow-middle buried horizons. The present geothermal gradient in the Jiyang Depression is about 3 °C/100 m, and the surface temperature was about 17 °C, so biogas in the Jiyang Depression tends to occur above 2,000 m. Biogas reservoirs have already been discovered and they are scattered in the Huagou and Yangxin gas fields.

The composition of biogas is fairly simple and is mainly methane. Heavy hydrocarbon (C₂₊) contents are extremely low (usually less than 0.5 %), the value of C₁/C₁₋₅ is higher than 0.995, and there are also low levels of non-hydrocarbon components (mainly N₂, CO₂). δ^{13} C₁ ranged from -55 ‰ to -60.9 ‰ (Table 3) (Hu et al. 2010). Since very little ethane and propane exist in biogas, it is difficult to measure their corresponding carbon isotope ratios.

Biogas is mainly developed in the first member of the Eogene Shahejie Formation (Es₁ for short) in the Yangxin and Huagou gas fields. Source rocks in Es₁ were buried in less than 2,000 m, and were at an immature stage with an R_0 value of 0.3 %–0.6 %, the formation temperature was about 55–75 °C, which provided favorable conditions for





Fig. 6 Characteristics of $\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$ in the Jiyang Depression (Dai 1993)



 Table 3 Geochemical properties of biogas in the Jiyang Depression

Area	Formation	Well	Depth, m	CO ₂ , %	N2, %	CH4, %	$C_{2+}, \%$	$\delta^{13}C_1, \ \% \ (PDB)$
Yangxin Gas Field	Es ₁	Yang101	1504.2-1529.6	0.39	1.04	98.4	0.17	-60.6
	Es ₁	Yang16	1319.0-1325.0	2.98	2.17	94.66	0.19	-56.5
	Es ₁	Yang21	1412.0-1415.6	0.1	1.69	97.16	0.08	-60.9
Huagou Gas Field	Es ₁	Hua4	1276.0-1307.0	0.17	7.38	89.25	0.17	-55.4
	Es ₁	Hua171	1453.0	13.9	6.68	79.10	0.14	-55.0

survival of methanogens. Anaerobes and methanogens have already been detected in the formation water in this area, and this confirmed that natural gas occurring in this interval is biogas.

3.2 Mature oil-type gas (oil-associated gas)

Mature oil-type gas is generated by sapropelic-type source rocks in mature stage ($R_o = 0.6 \ \% - 1.3 \ \%$). Since sapropelic-type source rocks tended to generate more oil than gas during its mature stage, this kind of gas usually occurred as dissolved gas in oil reservoirs. Sometimes gas would exsolve from oil due to changes in temperature and pressure, and a gas cap would be formed.

Mature oil-type gas is the most important kind of natural gas in the Jiyang Depression. Most shallow gases and middle gases as well as part of deep gases are of this kind, and the reserves of this kind of gas resource account for 3/4 of all the proved gas reserves in place. Mature oil-type gas usually occurred in the third member and the fourth member of the Eogene Shahejie Formation (Es₃, Es₄), and sometimes in buried hills in the Paleozoic Carboniferous or Ordovician (e.g., Zhuangxi Oilfield). This kind of gas always occurred associated with oil reservoirs and gas was produced together with oil.

The methane content of mature oil-type gas varied greatly and ranged from 25.6 % to 99.6 %. The methane content of most oil-associated gas (81 %) was about 60 %–90 %, the heavy hydrocarbon content ranged from 0 % to 70.9 %, and C_1/C_{1-5} ranged from 0.6 to 0.99. $\delta^{13}C_1$ of mature oil-type gas in the Jiyang Depression ranged from -38 ‰ to -55 ‰, $\delta^{13}C_2$ ranged from -26.3 ‰ to -34.9 ‰, $\delta^{13}C_3$ ranged from -25.6 ‰ to -32.1 ‰, $\delta^{13}C_4$ ranged from -25.6 ‰ to -32.1 ‰, $\delta^{13}C_4$ ranged from the order of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$ (Table 4).

 $\delta^{13}C_1$ and $\delta^{13}C_2$ of mature oil-type gas in the Jiyang Depression correlated well with depth, so it is possible to calculate the maturity using gas carbon isotope ratios. Comparison between gas samples and source rock samples was carried out, and the relationship between $\delta^{13}C_1$ and R_0 was established:

$$\delta^{13}C_1 = 6.942 \ln R_0 - 45.254 (R_0 = 0.4 - 1.3), \tag{1}$$

where $\delta^{13}C_1$ is the methane carbon isotope ratios of mature oil-type gas, %; R_0 is vitrinite reflectance, %.

3.3 Highly mature oil-type gas

Highly mature oil-type gas was generated by sapropel-type source rock in highly mature stage ($R_o > 1.3 \%$) (Zhao et al. 2013). There are two options for the genesis of highly mature oil-type gas, one is kerogen thermal degradation gas

which means that sapropel-type kerogen degrades into natural gas at high temperature; and the other is oil-cracking gas which means that oil cracks into natural gas at high temperature (Lu et al. 2006).

Compared with mature oil-type gas, kerogen thermal degradation gas usually has a higher value of C_1/C_{1-5} , and heavier $\delta^{13}C_1$ and $\delta^{13}C_2$. Methane comprises 70.78 %-88.6 % of kerogen thermal degradation gas and heavy hydrocarbons about 5 %-29 %, usually in the range of 10 %–15 %. The value of C_1/C_{1-5} ranged from 0.7 to 0.9 and was a little higher than that of mature oil-type gas. $\delta^{13}C_1$ ranged from -43.9 ‰ to -33.9 ‰, $\delta^{13}C_2$ ranged from -27.6 ‰ to -28.7 ‰, $\delta^{13}C_3$ ranged from -23.3 % to -25.9 %, and $\delta^{13}C_4$ ranged from -25.0 % to -26.6 %. There was an apparent reversal of $\delta^{13}C_3$ and $\delta^{13}C_4$ (Table 5). There are multiple reasons for the isotope reversal such as mixture of gases from different kerogen types, mixture of gases from the same kerogen type but of different maturities, inorganic originated hydrocarbon gas, and biodegradation gas (Burruss and Laughrey 2010). Analysis of the reservoir forming processes indicated that the discovered highly mature oil-type gases originated from the same source rocks, i.e., the fourth member of the Eogene Shahejie Formation (Es₄), which was deeply buried with little chance of undergoing biodegradation. Therefore, it can be inferred that the reversal in $\delta^{13}C_3$ and $\delta^{13}C_4$ was caused by the mixing of gases of different maturities.

Only oil-cracking gas was discovered in the Minfeng area (Chen et al. 2014), where the fourth member of the Shahejie Formation (Es₄) was deeply buried, and the temperature might exceed 210 °C in its maximum depth. According to the experiment carried out by Luo et al. (2008), crude oil would crack into gases when the temperature exceeded 160 °C. Compared with kerogen thermal degradation gas with the similar maturity, $\delta^{13}C_1$ and $\delta^{13}C_2$ of oil-cracking gas were fairly light and, respectively, ranged from -48.4 % to -50.4 % and from -33 % to -34 % (Song et al. 2009; Tian et al. 2009).

Based on comparison of light hydrocarbon compounds in oil-cracking gas and kerogen thermal degradation gas, Hu et al. (2005) put forward that MCC_6/nC_7 and (2- $MC_6 + 3-MC_6$)/nC_6 of oil-cracking gas were higher than those of kerogen thermal degradation gases (MCC_6 means methylcyclohexane, 2-MC_6 means 2-methylhexane, 3-MC_6 means 3-methylhexane, nC_7 means *n*-heptane, nC_6 means *n*-hexane). Based on simulation experiments, Wang (2005) discovered that there were differences in MCC_6/ CC_6, MCC_6/nC_7, and (2-MC_6 + 3-MC_6)/nC_6 between these two kinds of highly mature oil-type gases (CC_6 means cyclohexane). The content of thermally stable compounds in kerogen thermal degradation gas was higher than that in oil-cracking gas. In the Jiyang Depression,

 Table 4 Geochemical characteristics of typical mature oil-type gases in the Jiyang Depression

Area	Formation	Well	Depth, m	δ ¹³ C ₁ , ‰(PDB)	δ ¹³ C ₂ , ‰ (PDB)	δ ¹³ C ₃ , ‰ (PDB)	δ ¹³ C ₄ , ‰ (PDB)	CH4, %	C ₂₊ , %	N ₂ , %	CO ₂ , %
Chengdao	Ν	Chengbs19	1308.2	-53.9	-36.2	-34.9	-32.1	98.03	1.2	0.37	0.2
Oilfield	Е	Chengb12	2144.5	-38.0	-28.3	-27.8	-27.1	60.63	38.79	0.62	0.63
	Pz	Chengb242	2936.6	-45.7	-31.2	-28.9	-28.1	70.97	26.37	0.29	2.26
Linpan Oilfield	Ν	Lin2-6	1582.8	-44.5	-32.5	-26.7	-27.7	96.6	2.728	0.594	0.177
Yanjia Gas Field	Е	Yan22	1573.0	-47.4	-33.5	-29.2	-27.7	70.77	25.39	0.39	3.45
Dongfenggang Oilfield	Е	Che57	4067.0	-44.2				81.8	11.86	0.06	6.28
Shengtuo	E	Ning3	1805.6	-45.8	-35.6	-29.4	-28.4	83.79	13.98	0	0.4
Oilfield	E	Tuo113	1948.6	-53.8				91.86	6.18	0	0.34
	E	Tuo165	3391.1	-50.3	-35.1	-30.5	-29.0	65.95	19.02	2.79	12.24
Gubei Oilfield	E	Gub1	2138.5	-47.1				75.36	17.03	0.77	6.84
Bonan Oilfield	Е	Xiny12	2454.9	-52.3	-33	-31.2	-29.8	74.78	20.5	0	4.3
	Е	Yi37	3220.3	-45.6	-31.7	-32.9	-28.3	66.2	22.45	0	9.55
	Е	Yi170	3817.6	-52.6	-31.2	-27.3	-27.2	84.44	12.4	0.14	2.72
	Е	Bos4	3911.5	-52.7	-30.8	-28.2	-28.1	83.38	14.59	1.53	1.4
Gudong Oilfield	Е	Gud9	2506.4	-48.7	-27.4	-27.3	-25.6	60.05	20.99	24	2.52
Guangli Oilfield	Е	Lai10	2665.1	-50.6				81.35	15.39	0	0.46
Liangjialou	Е	Liang60	2844.8	-52.3				73.12	20.23	0	3.61
Oilfield	Е	Ling35	3119.9	-50.8				89.84	5.93	0	1.28
Lijin Oilfield	Е	Li54	2904.3	-49.5				70.11	22.23	0	5.93
Xianhe Oilfield	Е	Niu23	3289.8	-52.1				73.2	20.13	0	4.05
	Е	Wang53	3389.0	-50.4				67.63	23.94	0	4.99
Dawangzhuang Oilfield	0	Dag23	1738.3	-44.4				90.18	7.23	0	2.04
Chengdong Oilfield	Р	Chengk1	2588.0	-51.5	-34.1	-31.7	-29.8	73.92	25.53	0.18	0.71
Yong'anzhen Oilfield	Е	Yong12-21		-47.6	-39.9	-31.3	-28.5	98.55	1.28	1.109	0.663
Zhuangxi	Е	Zhuang202	2644.5	-51.6	-34.9	-31.7	-29.4	86.22	7.49	0	1.13
Oilfield	Е	Zhuang50	3228.2	-49.7	-33.5	-30.1	-28.2	89.44	7.47	0	1.73
	Е	Zhuang74	3634.5	-47.6	-33.3	-28.9	-27.5	68.44	23.49	0	4.81
	0	Zhuangg10	3627.2	-44.1				63.74	28.75	0	3.56
	0	Zhuangg21	3929.1	-42.4	-27.9	-27.7	-26.4	67.15	25.73	0	3.13
	0	Zhuangg4	4013.5	-45.4				77.5	16.97	0	4.55
	∈-Anz	Zhuangg25	4277.6	-43.2	-29.7	-26.3	-27.7	71.34	25.48	0	1.36
	0	Zhuangg14	4318.5	-46.1	-32.0	-29.6		76.77	13.21	0	9.24
	0	Zhuangg13	4367.5	-42.2	-29.5	-28.1	-27.2	69.54	27.75	0	1.87
	0	Zhuangg18	4582.4	-44.4				71.18	24.65	0.59	3.08
	e	Zhuangg17	4886.2	-45.8	-31.9	-29.2	-28.5	85.99	10.25	0.58	3.09

 MCC_6/nC_7 of oil-cracking gas was higher than 1.0, (2- $MC_6 + 3-MC_6$)/ nC_6 of oil-cracking gas was higher than 0.4, which were higher than those of kerogen thermal degradation gas and mature oil-type gas, while MCC_6/nC_7 of oil-cracking gas was less than 0.8 which was lower than that of kerogen thermal degradation gas and mature oil-type gas (Fig. 7).

3.4 Coal-type gas

Coal-type gas is defined as natural gas generated by coal or humic kerogen due to biochemical and chemical action. Coal-type gas discovered in the Jiyang Depression was mainly developed in the Paleozoic Ordovician and Carboniferous—Permian in the Gubei buried hill belt, the

Table 5 Geochemi	cal properties	and genesis of	typical highly ma	ature oil-type	gas in the J	iyang Depres	SION						
Area	Formation	Well	Depth, m	δ ¹³ C ₁ , ‰ (PDB)	δ ¹³ C ₂ , ‰ (PDB)	δ ¹³ C ₃ , ‰ (PDB)	$ \begin{split} \delta^{13}C_4, \ \% \\ (PDB) \end{split} $	C_1/C_{1-5}	CH4, %	C ₂₊ , %	N ₂ , %	CO ₂ , %	Genetic type
Bonan Oilfield	0	Bo601	5007.0-5009.0	-43.8	-28.7	-25.8	-26.1	0.716	70.78	29.22			Kerogen thermal
	Е	Bos5	4491.9–4587.3	-38.0				0.859	79.55	13.07	0.43	7.03	degradation gas
	0	Bos6	4165.5-4246.0	-40.8	-27.6	-24.5		0.799	74.98	19.27	0.51	4.77	
Laohekou Oilfield	Pz	Chengb39	4173.0-4320.0	-41.3	-27.6	-25.9	-25.7	0.835	75.02	15.47	2.04	7.48	
Shengtuo Oilfield	Е	Tuo765	4354.1 - 4386.0	-43.9	-28.6	-24.9	-26.6	0.880	87.82	12.03	0	0.15	
Lijin Oilfield	Е	Xinlis1	4271.2-4371.0	-41.8				0.905	87.82	9.27	0.04	2.87	
Zhuangxi Oilfield	0	Zhuangg23	3897.0-3988.5	-38.3	-27.6	-23.3	-26.2	0.890	86.38	10.65	1.14	1.53	
Dongxin Oilfield	Е	Feng8		-49.0				0.798	62.92	16.61	1.25	19.16	Oil-cracking gas
	Е	Fengs1	4314.0–4316.0	-48.4	-33.0	-26.8	-25.0	0.862	46.73	8.12	0.39	44.76	
	Э	Fengs1	4316.0–4343.0	-50.4				0.876	81.01	11.59	1.6	5.74	
	Е	Fengs1	4400.0-4402.0	-48.0	-34.0	-27.3	-25.6	0.860	71.39	11.75	0.53	16.28	

fourth member of the Shahejie Formation in the Bonan deep sag, and the Shahejie Formation in the Qudi Oilfield in the Huimin Sag. Coal-type gas in the Gubei buried hill and Qudi Oilfield was generated by coal and humic kerogen in the Shanxi Formation and Taiyuan Formation in Carboniferous—Permian, while that in the Bonan Sag (Well Yi115 and Yi121) was generated by humic kerogen in the upper part of Es₄.

The methane content of coal-type gas ranged from 75 % to 92 %, and the heavy hydrocarbon content varied greatly from 0.51 % to 19.5 %. C_1/C_{1-5} ranged from 0.8 to 0.99 and the value of most samples exceeded 0.9. C_1/C_{1-5} of coal-type gas is usually higher than that of oil-type gas with a similar maturity. $\delta^{13}C_1$ of coal-type gas in the Jiyang Depression ranged from -32.6 ‰ to -41.0 ‰, $\delta^{13}C_2$ ranged from -22.0 ‰ to -27.6 ‰ (Table 6). There was a slight reversal in $\delta^{13}C_3$ and $\delta^{13}C_4$ and this might be caused by mixing with oil-type gas. It is pointed out that $\delta^{13}C_2$ of coal-type gas in China is usually higher than -28 ‰ (Song et al. 2012; Dai et al. 2012; Wang et al. 2010), and in the Jiyang Depression, the carbon isotope ratios of coal-type gas are located in the "I" area of the "V" shaped $\delta^{13}C_1$ - $\delta^{13}C_2$ - $\delta^{13}C_3$ template (Fig. 6).

 C_7 light hydrocarbon information can also be used to distinguish coal-type gas from oil-type gas. The C_7 system is composed of three kinds of compounds: normal heptane (nC_7) , methylcyclohexane (MCC₆), and multi-structured dimethylcyclopentane ($\sum DMCC_5$). MCC₆ mainly came from higher plants and was a major component of C_7 system in coal-type gas, and $\sum DMCC_5$ mainly came from aquatic organisms and was a major component of C_7 system in oil-type gas (Song and Zhang 2004).

As shown in Fig. 8, coal-type gas differed significantly from oil-type gas. $MCC_6/\sum C_7$ of the coal-type gas exceeded 50 %, while $\sum DMCC_5/\sum C_7$ was less than 40 %; as for oil-type gas, $nC_7/\sum C_7$ exceeded 30 %, $MCC_6/\sum C_7$ ranged from 20 to 40 %.

4 Secondary changes of natural gas

Most shallow gas in the Jiyang Depression was originally dissolved gas that escaped from oil when temperature and pressure changed due to migration of oil along faults or sand bodies. This kind of natural gas was located in the "d" area (oil-associated gas) of " $\delta^{13}C_{CH4}-C_1/(C_2 + C_3)$ template" in Fig. 5, and in "II" area of "V" shaped " $\delta^{13}C_1-\delta^{13}C_2-\delta^{13}C_3$ template" in Fig. 6, and was typical mature oil-type gas.

There is a kind of shallow gas whose hydrocarbon carbon isotope ratios are similar to mature oil-type gas, but its heavy hydrocarbon content is extremely low, the methane content is very high (>95 %), C_1/C_{1-5} is higher than 0.95,

Area	Formation	Well	Depth, m	$\delta^{13}C_1, \%$ (PDB)	$\delta^{13}C_2, \%$ (PDB)	$\delta^{13}C_3, \%$ (PDB)	$\delta^{13}C_4, \%$ (PDB)	CH ₄ , %	$C_{2+}, \%$	N ₂ , %	CO ₂ , %
Gudao Oilfield	C–P	Bo93	3230.0-3249.4	-38.1	-22.7	-21.25	-21.8	88.99	7.81		2.29
	0	BoG4	4375.0-4460.0	-38.2	-24.9	-22.5	-23.6	85.32	10.02	0	4.66
	0	BoG403	3850.5-3889.3	-37.1	-24.2	-22.0	-23.5	85.16	8.68	0.83	5.31
	Es	BoS3	4450.1-4472.4	-39.1	-26.7	-23.4	-23.9	83.15	10.8	0.73	5.05
	Р	GBG1	4020.6-4139.5	-35.9	-23.1	-21.2	-21.2	88.44	6.48	0.55	4.54
	C–P	GBG1	4120.6-4139.0	-35.8	-22.9	-21.5	-20.8	82.52	10.09	0.74	6.66
	C–P	GBG2	3689.0-3731.0	-41.0	-25.8	-23.6	-23.6	75.87	19.52	0.96	3.65
	Mz	Yi132	3374.0-3387.0	-37.0	-25.3	-25.0	-25.5	87.01	7.9	1.98	2.18
	Р	Yi155	4696.3-4706.7	-32.7	-22.0	-21.5	-21.0	87.64	4.85		6.64
Bonan Oilfield	Es	Yi115	5110.4-5164.4	-35.9	-24.9	-21.8		80.18	0.51	0.05	19.27
	Es	Yi121	4426.1-4438.4	-38.0	-22.0	-19.3	-20.6	91.36	1.46	0	7.09
	0	BoS6	4165.5-4246.0	-40.8	-27.6	-24.5		74.98	19.27	0.51	4.77
Qudi Oilfield	Es	QuG1	1514.0-1520.0	-32.6	-23.9	-20.3	-20.2	77.25	9.53	11.99	0.93

Table 6 Geochemical properties of typical coal-type gas in the Jiyang Depression



Fig. 7 Light hydrocarbon property differences between oil cracking gas and kerogen thermal degradation gas

and is located above the "d" area of the " $\delta^{13}C_{CH4}-C_1/(C_2 + C_3)$ template" (Table 7; Fig. 5). Such characteristics are caused by composition changes during long distance migration of natural gas. Gas migration experiments in porous sandstone core samples indicated that, with increasing migration distance, the methane content tended to increase while the heavy hydrocarbon content (C_{2+}) decreased correspondingly. Furthermore, the carbon isotopes of hydrocarbon differentiated slightly and this means that carbon isotopes became lighter with an increase of migration distance (variation range usually less than -2 %). Therefore, it is believed that this kind of natural gas with a high content of methane was dissolved gas that escaped from oil after long-distance migration.

There is another kind of shallow gas whose methane carbon isotope ratios are heavier than those of mature oil-type gas, and $\delta^{13}C_2$ and $\delta^{13}C_3$ are extremely heavy. $\delta^{13}C_3$ of



Fig. 8 Triangular template of C_7 light hydrocarbon in different kinds of natural gases in the Jiyang Depression

Table 7 Geochemical p	roperties and ge	enesis of shallo	w gas (part) in the	Jiyang Dep	ression							
Area	Well	Formation	Depth, m	$\delta^{13}C_1, \%_0$ (PDB)	$\delta^{13}C_2, \ \%_0$ (PDB)	δ ¹³ C ₃ , ‰ (PDB)	$\delta^{13}C_4, \ \%_0$ (PDB)	CH4, , %	N ₂ , %	Genesis		
Caoqiao Oilfield	Cao104	Es	1258-1265.6	-46.4	-35.7	-23	-22.12	97.87	0.4	1.23	0.42	High methane
Huagou Gas Field	Hua16	Z	828.1-831.1	-46.6	-30.4	-22.64	-26.1	98.99	0.31	0.71	0	secondary
	Hua6-4	Z	790-830	-44.7	-25.2			96.5	0.43	/	1.93	gases
Gudong Oilfield	Gud22-3	Z	1214.8–1219.6	-43.7	-30.6	-23.3	-22.4	97.17	2.41	0.26	0.13	
	Gud29-416	Z	1246-1270.4	-45.9	-29.1	-23	-21.1	94.99	1.6	1.52	1.83	
	Gud3-015	Z	1203.7-1207.4	-45.4	-30.7	-26.1	-23.3	95.19	3.92	0.33	0.54	
	Gud31-15	Z	1196.2-1238.2	-45.6	-30.3	-25.6	-23.6	93.51	5.01	0.83	0.51	
	Gud3-517	Z	1303.4–1315.4	-49.9	-31.4	-28.8	-29.2	96.79	0.37	2.26	0.49	
	Gud13-N11	Z	1252.8-1263.6	-41.9	-32.1	-27.7	-24.8	93.57	5.2	0.45	0.71	Biodegradation
	Gud13- P513	Z	1380.5–1562	-42.2	-31.9	-27.5	-25	88.25	10.59	0.5	0.56	secondary gases
	Gud2-2	Z	1191-1204	-41.9	-31.1	-27.8	-25.5	90.42	8.1	0	1.27	
	Gud22-N3	Z	1261.6–1294	-42.3	-31.3	-26	-23.9	83.12	5.42	0.28	1.15	
	Gud2-5	Z	1175.2-1204.2	-41.8	-31.4	-27.7	-25.2	73.28	12.42	12.41	1.63	
Chenjiazhuang Oilfield	Chenq11	Z	935–942	-52.9	-33.11	-20.08	-18.49	95.02	0.152	4.706	0.122	
	Chenq8	Z	945–948	-53.87	-25.7	-27.14	-29.03	88.436	0.315	10.49	0.752	
Shanjiasi Oilfield	Shan66	Anz	1076-1100	-46.79	-29.89	-18.92	-24.11	95.85	0.41	0	1.61	
Huagou Gas Field	Gao41-5	Mz	1965.1–1984	-41.8	-25.14	-8.52	-22.13	97.384	3.592		0.82	
	Gao42	Es	945–952	-42.95	-32.03	-16.49	-23.09	89.138	5.328	3.096	5.1	
	Hua6	Z	818-819.6	-44.28	-25.24	-20.33	-27.3	99.26	0.44	0.28	0.02	
	Hua6-2	Z	743.8-783.4	-44.35	-24.91	-20.11	-24.85	96.7	0.43		1.92	
Linpan Oilfield	Lin2-4	Z	1398.8–1426	-47.57	-29.27	-16.18	-20.81	96.624	0.719	2.496	0.16	
Yuhuangmiao Oilfield	Xia8	Ed	1457.7–1464	-46.95	-32.48	-22.03	-22.76	98	0.9	0	0	

normal mature oil-type gas ranged from -26 % to -34 %, while $\delta^{13}C_3$ of this kind of natural gas might as heavy as -8.5 %. $\delta^{13}C_3$ of most natural gas ranged from -8 % to -22 %, and carbon isotope ratios of light hydrocarbons arranged in the order of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 > \delta^{13}C_4$. $\delta^{13}C_1$ of some samples was about 2 % -7 % heavier than that of mature oil-type gas. Take the Gudong Oilfield as an example, $\delta^{13}C_1$ of mature oil-type gas (Well Gud3-517) was about -49.9 %, $\delta^{13}C_2$ was about -31.4 %, but $\delta^{13}C_1$ and $\delta^{13}C_2$ of the sample from the same horizon and similar depth (Gud2-2) were, respectively, -41.9 % and -31.1 %, that is to say $\delta^{13}C_1$ was about 8 % heavier than that in Well Gud3-517.

Analysis indicated that the main reason that caused abnormal carbon isotope ratios was biodegradation. James and Burns (1984) analyzed the carbon isotope ratios of light hydrocarbons of biodegradation natural gases in Australia and Canada, and discovered that $\delta^{13}C_3$ was abnormally heavy. They deduced that since propane is soluble in water, it is readily biodegradable. Secondary biodegradation shallow gas in the Jiyang Depression exhibited the similar characteristics.

Stahl (1980) carried out bacterial degradation experiments, and pointed out that long-chained paraffin hydrocarbon is more easily degradable than short-chained ones, and normal paraffin hydrocarbon is more easily degradable than isomeric ones. As shown in Fig. 8, $nC_7/\sum C_7$ of biodegradation shallow gas was less than 20 %, and was obviously less than that of mature oil-type gas.

Levthaeuser et al. (1979) studied biodegradation of oil using light hydrocarbon data, and summarized typical characteristics: the content of normal paraffin hydrocarbon was low, while the contents of isomeric ones (such as 3,3-DMC₅; 2,3,3-TMC₄; 2,2-DMC₅; 2,4-DMC₅ and 2,2- DMC_4) were high (DMC_5 means dimethylpentane, TMC_4 means triptane, DMC₄ means dimethylbutane). Based on analysis of light hydrocarbons in shallow gas in the Jiyang Depression, Zhang (1991) pointed out that the relationship between 2,4-DMC₅/ nC_6 and the heptane index can be used to distinguish biodegradation oil-type gas from other oil-type gases. As shown in Fig. 9, the value of 2,4- DMC_5/nC_6 for biodegradation gas was usually higher than 0.5, and the heptane index was usually less than 5; in contrast, the heptane index usually ranged from 20 to 50, and 2,4-DMC₅/ nC_6 for other oil-type gases was less than 0.1.

5 Identification factors

Based on discussion above, the identification factors for different kinds of natural gases are summarized in Table 8,



Fig. 9 2,4-DMC₅/ nC_6 -heptane index template of natural gases in the Jiyang Depression (Zhang 1991)

Heptane index = $100 \times nC_7/(CC_6 + 2-MC_6 + 2,3-DMC_5 + 1,1-DMC_5 + 3-MC_6 + 1,C,3-DMCC_5 + nC_7 + MCC_6)$

and with the help of gas compositions, carbon isotope ratios of paraffin hydrocarbon and CO_2 , and light hydrocarbon index, it is feasible to identify the genesis of natural gases in the Jiyang Depression.

Take mature oil-type gas as reference, biogas has a high methane content, and $\delta^{13}C_1$ was less than -55 ‰; highly mature oil-type gases are divided into kerogen thermal degradation gas and oil-cracking gas. They both have a high value of C_1/C_{1-5} and heavy methane carbon isotope ratios, and they can be distinguished by the $(2-MC_6 + 3-MC_6)/nC_6-MCC_6/nC_7$ template. Ethane carbon isotope ratios of coal-type gas in the Jiyang Depression are usually higher than -28 ‰ and the compositions of C_7 can be used to effectively distinguish coal-type gas from oil-type gas.

Heavy hydrocarbons usually reduce in the process of gas migration. The C_1/C_{2+3} value of methane rich secondary gas might exceed 280, and its carbon isotope compositions and light hydrocarbon compositions are similar to those of mature oil-type gas. Secondary biodegradation gas is featured by heavy carbon isotope ratios of $\delta^{13}C_1$ or $\delta^{13}C_3$, and light hydrocarbon isotope ratios arrange in the order of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 > \delta^{13}C_4$. Influenced by biodegradation, the normal paraffin hydrocarbon content is low. The triangular template of C_7 and 2,4-DMC₅/nC₆—heptane index template can be used to distinguish the secondary biodegradation gas from other natural gases.

Genetic types		Gas con	nposition		Isotope c	ompositic	uc			Light hydrocarbon characteristics
		CO ₂ , %	C_1/C_{1-5}	$C_{1^{\prime}}$ C_{2+3}	δ ¹³ C ₁ , ‰	δ ¹³ C ₂ , ‰	δ ¹³ C ₃ , ‰	$\delta^{13}C_4,$ %0	Isotope series	
CO ₂ gas		>50 %	/	/	/	/	/	/	1	
Hydrocarbon	Biogas	<10 %	>0.995		<-55	/	/	/	/	
gases	Biodegradation secondary gas		0.95-1	17–207	-38 to -48	-20 to -34	-13 to -24	-14 to -25	$\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 > \delta^{13}C_4$	$nC_7/\sum C_7 < 0.2$; 2,4-DMC ₅ / $nC_6 < 0.5$; heptane index <5;
	High methane secondary gas		>0.95	>280	-42 to -55	-29 to -38	-26 to -34	-25 to -32	$\delta^{13}C_1<\delta^{13}C_2<\delta^{13}C_3<\delta^{13}C_4$	$nC_7 \sum C_7 = 30-60$; $MCC_6 \sum C_7 = 20-40$; 2,4- DMC $_5 nC_6 < 0.1$; heptane index = $30-40$;
	Oil-associated gas		0.6-0-90	2–39	-42 to -55	-29 to -38	-26 to -34	-25 to -32	$\delta^{13}C_1<\delta^{13}C_2<\delta^{13}C_3<\delta^{13}C_4$	$nC_7 \sum C_7 = 30-60$; $MCC_6 \sum C_7 = 20-40$; 2,4- DMC $_5 nC_6 < 0.1$; heptane index = 30–40;
	Kerogen thermal degradation		0.7-0.95	5-46	-33 to -44	-27 to -33	-23 to -26	-26 to -28	$\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$	$\begin{split} MCC_6/nC_7 < 1.0; \ (2-MC_6 + 3-MC_6)/nC_6 < 0.4; \\ MCC_6/CC_6 > 0.8; \end{split}$
	gas									$DMCC_{5}/\sum C_{7} = 40-60;$
	Oil-cracking gas		0.7–0.9	2–55	44 to 52	-28 to -34	-24 to -28	-24 to -26	$\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$	$MCC_6/nC_7 > 1.0; (2-MC_6 + 3-MC_6)/nC_6 > 0.4;$ $MCC_6/CC_6 < 0.8; DMCC_5/\sum C_7 = 30-40;$
	Coal-type gas		0.8-0.99	10–190	-29 to -41	-17 to -25	19 to 24	-20 to -25	$\delta^{13}C_1<\delta^{13}C_2<\delta^{13}C_3<\delta^{13}C_4$	$MCC_6/\sum C_7 > 50 \ \%; \ \sum DMCC_5/\sum C_7 < 40 \ \%;$ 2,4-DMC ₅ /nC ₆ = 0.03-0.1; heptane index = 30-50

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6 Conclusions

- Based on analysis of gases compositions, carbon isotope ratios, light hydrocarbon properties, combined with geological analysis, natural gases in the Jiyang Depression were classified into two categories namely hydrocarbon gas and abiogenic gas. The abiogenic gas was mainly magmatogenic or mantle derived CO₂. Hydrocarbon gases were further divided into coal-type gas, oil-type gas, and biogas according to the kerogen types and formation mechanisms. The oil-type gases were divided into mature oil-type gas. Highly mature oil-type gases were subdivided into oil-cracking gas and kerogen thermal degradation gas.
- 2) Analysis results showed that shallow gases (buried less than 1,500 m) are mainly mature oil-type gases, secondary gas is rich in methane after chromatographic separation during migration and secondary mature oil-type gas after biodegradation is featured by rich in ¹³C in methane and ethane. Meanwhile, biogas is another kind of shallow gas. The genesis of middle gases buried in the depth of 1,500–3,500 m was simple and was dominated by mature oil-type gases. Deep gases buried in the depth of 3,500–5,500 m were usually kerogen thermal degradation gas, oil-cracking gas, and coal-type gas.
- 3) Due to chromatographic effects, the methane content increases and heavy hydrocarbons decrease during the progress of migration. Secondary biodegradation gas was featured by heavy carbon isotope ratios of $\delta^{13}C_1$ or $\delta^{13}C_3$, and light hydrocarbon isotope ratios arranged in the order of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 > \delta^{13}C_4$. Influenced by biodegradation, the normal paraffin hydrocarbon content was low. Triangular template of C_7 and 2,4-DMC₅/nC₆—heptane index template can be used to distinguish secondary biodegradation gas from other natural gases.

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