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Differences on Geochemical Characteristics and Their Implicating Significances of Nitrogen in Coal-Derived Gas and Oil-typed Gas in China

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Natural gases in China are mainly coal-derived gas, with assistance from oil-typed gas. At present, many genetic identification methods, from hydrocarbon composition and isotope to light hydrocarbon and biomarker indexes, have been formed, but combined methods from non-hydrocarbon gases are lacking. Based on compositions and isotopes geochemical characteristics and the differences of non-hydrocarbon nitrogen gas in coal-derived gas and oil-typed gas, and combining the isotopic geochemical characteristics of non-hydrocarbon helium, the comprehensive identification methods of coal-derived gas and oil-typed gas for hydrocarbon gases according to the associated non-hydrocarbon gases of nitrogen and helium are established and the preliminary applications have been engaged. The main recognitions are as follows: 1) Coal-derived gas generally has relatively lower nitrogen abundance, mainly distributed from 0 to 31.2% with main frequency from 0 to 2%. Oil-typed gas, on the other hand, usually has relatively higher nitrogen abundance, mainly distributed from 1.1 to 57.1% with main frequency from 2 to 16%. 2) Coal-derived gas generally has relatively heavier nitrogen isotope values, mainly distributed from -8 to 19.3‰ with main frequency from -8 to 8‰. Oil-typed gas usually has relatively lower nitrogen isotope values, mainly distributed from -10.6 to 4.6‰ with main frequency from -8 to 4‰. 3) The geochemical characteristic differences of coal-derived gas and oil-typed gas are mainly due to the fact that the sapropel parent material is relatively rich in nitrogen element and rich in light $\delta^{14}\text{N}$, while the humic parent material is relatively poor in nitrogen element and rich in heavy $\delta^{15}\text{N}$. The differences on thermal maturity of source rocks, the redox conditions of source rock sedimentary environment, and the salinity of water body are also important effective factors. 4) Differences on nitrogen abundances and isotopes in coal-derived gas and oil-typed gas have great significance in genetic identification. The genetic identification chart of $\text{R/Ra}-\delta^{15}\text{N}$ for organic and inorganic nitrogen in natural gas and the comprehensive joint identification charts of $\text{R/Ra}-\delta^{15}\text{N}-\text{N}_2$ of nitrogen and helium for coal-derived gas and oil-typed gas have been

established, and are of great reference in investigating the origins and sources of natural gas and guiding natural gas exploration in China.

Keywords: comprehensive identification, oil-typed gas, coal-derived gas, helium, nitrogen, geochemical characteristics differences

INTRODUCTION

Natural gas is an environmentally friendly, low-carbon, effective, and clean energy. It occupies an important position in the world's energy structure and is one of three important sources and targets in future energy development (natural gas, unconventional oil and gas, and new energy). The present proportion of natural gas in China's energy structure (only about 8%) is lower than the world average (about 25%).

Natural gas is usually composed of more hydrocarbon gases such as CH₄ (methane), C₂H₆ (ethane), C₃H₈ (propane), and C₄H₁₀ (butane), with lower or trace amounts of non-hydrocarbon gases such as CO₂ (carbon dioxide), N₂ (nitrogen), He (helium), Ne (neon), Ar (argon), Kr (krypton), and Xe (xenon). Non-hydrocarbon gases are very important components of natural gases, and usually have a close relation to hydrocarbon gases. Nitrogen, as a very important and common non-hydrocarbon gas component in natural gas, has closer physical properties with hydrocarbon gases than other non-hydrocarbon gas components, and has similar reservoir forming conditions with hydrocarbon gas reservoir. Therefore, studying the geochemical characteristics and origin of nitrogen in natural gases is helpful to find out the origin of formation, preservation, and enrichment of hydrocarbon gases. Nitrogen has two stable isotopes, ¹⁴N and ¹⁵N, with atmospheric abundances of 99.633 and 0.366% respectively (Rosman and Taylor, 1998). The atmosphere is the largest nitrogen reservoir on the earth. The origins of nitrogen in gas reservoirs are diverse. The total variation range of δ¹⁵N is 100‰, from about -50‰ to +50‰, and most of them fall in the range of -10‰ to +20‰ (Hoefs, 1972; Heaton, 1986; Owens, 1987; Peterson and Fry, 1987; Kendall, 1998). As the nitrogen isotope value in natural gas is similar to or overlaps with the isotope value of many kinds of nitrogen-bearing materials in nature, it is difficult to identify the origin and source of nitrogen in natural gas only by using nitrogen isotope value and nitrogen content. The isotope value of associated helium is an important indirect indicator for assisted identification of the organic and inorganic origin of nitrogen in natural gas. There are also reports on the use of associated helium to determine the origin of mantle-derived magma nitrogen globally. So, a comprehensive judging method including nitrogen isotope of δ¹⁵N and other possible isotope indexes for effectively identifying organic and inorganic nitrogen needs to be established.

In China, natural gases are mainly coal-derived gas with assistance from oil-typed gas. Coal-derived gas contributes more to the gas reserves and production (Dai et al., 2014), and plays a pivotal role in promoting the development of China's natural gas industry. The identification of oil-typed gas and coal-derived gas is of great significance for clarifying the origin and source of natural gas, guiding the exploration of

natural gas, and promoting the rapid development of the natural gas industry. At present, three methods involving 28 comprehensive indicators and charts for identifying the origin of natural gas, especially for coal-derived gas and oil-typed gas, have been developed, such as carbon isotopes and compositions, light hydrocarbons, and biomarkers (Dai et al., 1988; Dai et al., 1992; Dai et al., 1993; Dai et al., 1994; Dai et al., 1995; Dai et al., 1996; Dai et al., 1999; Dai et al., 2005; Dai et al., 2008; Dai et al., 2009; Dai et al., 2014; Dai and Qi, 1989; Li Jian et al., 2001; Li Jian et al., 2005; Hu Guoyi et al., 2007). However, there are few comprehensive identification methods for coal-derived gas and oil-typed gas by jointly using the non-hydrocarbon gases. The compositions and isotopes of the non-hydrocarbon gases of helium and nitrogen contain rich geological information, which play an important tracing and indicative role in identifying the origin and source of hydrocarbon gases of natural gases. So it is necessary and meaningful to promote and advance the comprehensive identification index system for coal-derived gas and oil-typed gas from a non-hydrocarbon gas point of view. Based on geochemical characteristics of non-hydrocarbon nitrogen gas in coal-derived gas and oil-typed gas, and combining the isotope geochemical characteristics of non-hydrocarbon helium, the comprehensive identification methods of coal-derived gas and oil-typed gas according to the associated non-hydrocarbon gases of nitrogen and helium need to be established.

In this study, the geochemical characteristics of non-hydrocarbon nitrogen gas and their differences in coal-derived gas and oil-typed gas are clarified first. Then the genesis of nitrogen in natural gases is identified and the reasons for the different geochemical characteristics of nitrogen are discussed. Finally, based on the difference of nitrogen content and δ¹⁵N value in coal-formed gas and oil-typed gas, combined with the R/Ra value of helium isotope, the genetic identification chart of R/Ra-δ¹⁵N for organic and inorganic nitrogen in natural gas and the comprehensive joint identification charts of R/Ra-δ¹⁵N-N₂ of nitrogen and helium for identifying oil-typed gas and coal-derived gas jointly by nitrogen and helium are established and applied in the selected typical gas-bearing basins. The research results are of great significance for clarifying the origins and sources of natural gas and guiding natural gas exploration.

RESEARCH SITUATIONS

Studies on nitrogen of natural gas overseas have been carried out as early as the 1950s. Hoering and Moore (1958) first studied the changes of nitrogen isotope during the migration of the gas in the Permian gas reservoirs in the Republic of Germany and

Groningen in the Netherlands. Jenden et al. (1988) summarized the data of 12,000 natural gas samples and found that the average content of N_2 in natural gas is 3%, of which 10% of the gas samples have $N_2 \geq 25\%$, 3.5% of gas samples have $N_2 \geq 50\%$, and 1% of gas samples have $N_2 \geq 90\%$. Studies on non-hydrocarbon gases of natural gas in China started in the 1980s. Zhang (1988) first analyzed the distribution and sources of nitrogen and the geochemical characteristics of nitrogen isotope in natural gas reservoirs in China and foreign countries, and concluded that nitrogen in gas reservoirs mainly came from the decomposition of organic matter, production of rock degassing, and atmospheric gas. Dai et al. (1992) calculated the analysis results of more than 1,000 gas samples in China and found that $N_2 \leq 4\%$ accounted for 76% and $N_2 \leq 8\%$ accounted for 86%. Since the 1990s, many domestic and foreign scholars have carried out a large number of studies on nitrogen composition, distribution, forming mechanism, origin and source, migration, accumulation, isotope analytical technique, nitrogen generation thermal simulation experiment, sedimentary environment, gas composition forecasting, and exploration risk reduction (Prisolov et al., 1991; Du, 1992; Zhu, 1994; Zhu and Shi, 1998; Krooss et al., 1995; Littke et al., 1995; Dai et al., 1995; Du et al., 1996; Zhu, 1999; He et al., 2001, 2011; Zeng, 2002; Shi et al., 2003; Chen et al., 2003; Chen, 2004; Liu et al., 2005; Liu et al., 2006; Qin et al., 2007; Zhang et al., 2008; Li et al., 2013; Xu et al., 2017; Chen et al., 2018), promoting rapid development of research into nitrogen in natural gases.

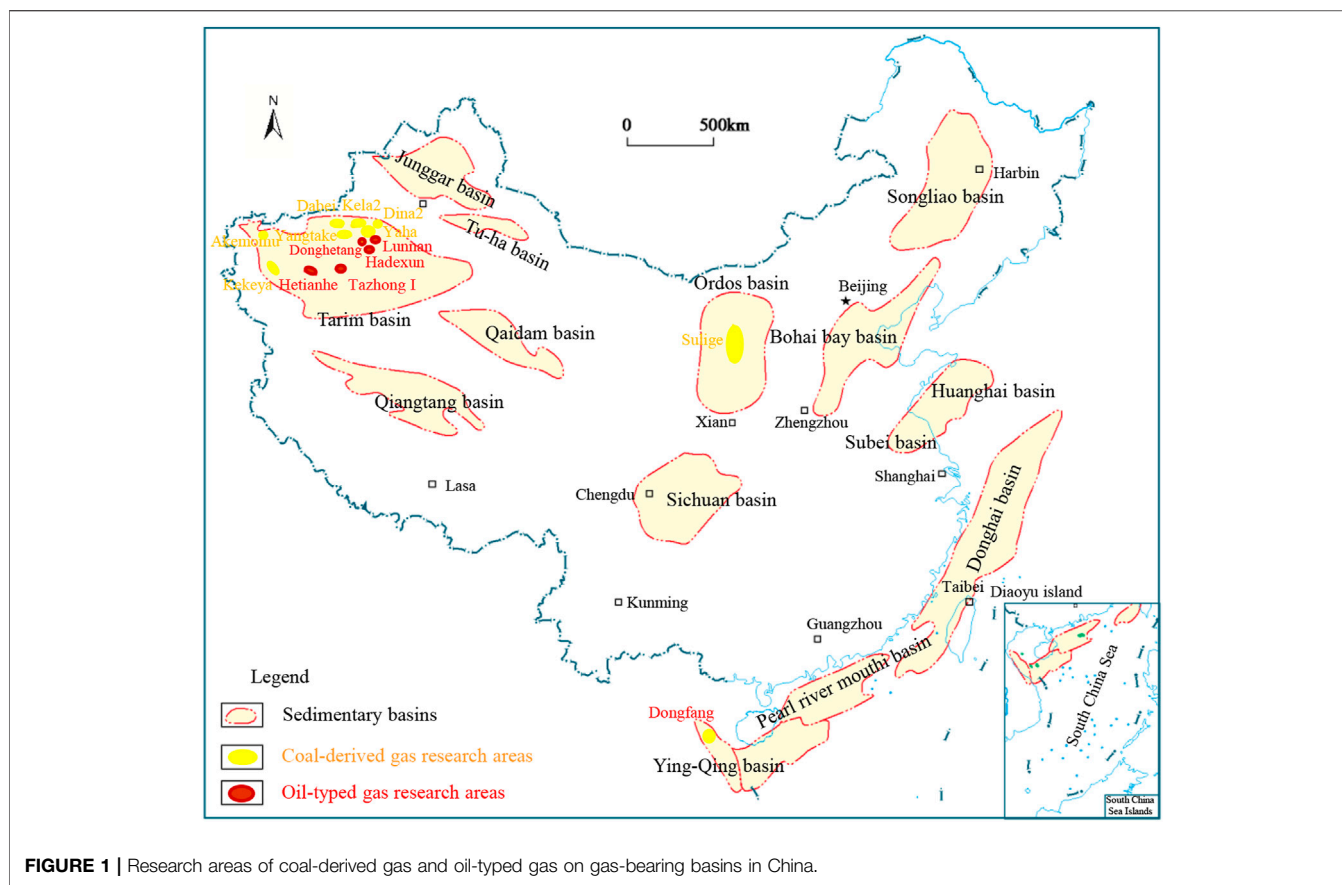
RESEARCH AREAS AND EXPERIMENTAL METHODS

China's natural gas is dominated by coal-derived gas, generally originating from coal-series source rocks, which are mainly distributed in the upper Paleozoic of the Ordos Basin, Upper Cretaceous in Kuche Depression of the Tarim Basin, and the Xujiahe formation of Upper Triassic in Sichuan Basin. Coal-derived gas plays a pivotal role in natural gas reserves and production increases and promotes the rapid development of China's natural gas industry. Oil-typed gas in China is mostly distributed in marine sediment strata in the three biggest marine basins: the Tarim, Sichuan, and Ordos Basin. Oil-typed gases also have an important position in China's natural gas development, having encouraged many great exploration discoveries in deep and ancient strata, especially in recent years. Non-hydrocarbon nitrogen and helium gases are important components of natural gases, and have rich geological information in indirectly tracing and identifying the origin and source of associated hydrocarbon gases in natural gases. For the purpose of conducting deep studies on geochemical characteristic differences and their significance in nitrogen in coal-derived gas and oil-typed gas in China, typical coal-derived gases from the Tarim and Ordos Basin and typical oil-typed gases from the Tarim Basin are especially selected. Considering the importance and representativeness of typical coal-derived gas and oil-typed gas basins and gas fields, as well as gas samples sampling accessibility, the research areas of typical coal-derived gas fields referred to are Kela 2, Dabei, Dina 2, Akemomu, Kekeya, and Yaha gas fields in the

Tarim Basin and the Sulige gas field in the Ordos Basin; the research areas of oil-typed gas fields referred to are Tazhong I, Hetianhe, Donghetang, Lunnan, and Hadexun oil and gas fields in the Tarim Basin. In order to make comprehensive and comparative studies, the nitrogen geochemical data from previous research on the Dongfang gas field in the YingQiong Basin are also selected (He et al., 2001, 2011).

In order to minimize the impact of air pollution and sampling process on the accuracy of data measurement, samples should be collected as follows: 1) Use a stainless steel cylinder with double valves to collect natural gas samples in the study area to be tested, and the stainless steel cylinder should be vacuumed by a mechanical or molecular pump for more than 15 min, or to be below 10^{-2} Pa before collecting the sample; 2) connect the stainless steel cylinder to the valve of the natural gas well through a relief valve, then collect the mid-stage gas flow until the gas pressure in the stainless steel cylinder is 3–6 MPa after using the wellhead high-pressure natural gas to repeatedly flush the cylinder more than 6 times and for more than 15 min; and 3) Gas sample analysis and testing must be carried out within 1 week after sample collection.

In this paper, the typical coal-derived gases were sampled from the Kela 2, Dabei, Dina 2, Akemomu, Kekeya, and Yaha gas fields in the Tarim Basin, and Sulige gas field in the Ordos Basin. The typical oil-typed gases were sampled from the Tazhong I, Hetianhe, Lunnan, and Hadexun oil and gas fields in the Tarim Basin (Figure 1). The analysis of nitrogen component and isotope in natural gas was completed in the Key Laboratory of Gas Reservoir Formation and Development of China National Petroleum Corporation. The nitrogen composition was analyzed on an Agilent 6890 N gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), using helium as the carrier gas. It was separated using a capillary column with $30 \text{ m} \times 0.32 \text{ mm} \times 20 \mu\text{m}$ PLOT Q. The gas chromatograph oven temperature was initially set at 30°C for 10 min, and programed at $10^\circ\text{C}/\text{min}$ to 180°C and then isothermal at 180°C for 10 min. The precision of the nitrogen composition is estimated to be $\pm 0.07\%$. The nitrogen isotopic compositions of natural gases were determined on the MAT 253 (GC/IRMS) isotopic mass spectrometer equipped with an Agilent 6890N Gas Chromatography with a $30 \times 0.32 \text{ mm} \times 20 \mu\text{m}$ capillary column of HP Plot molesieve 5 Å molecular sieves. Helium was used as the carrier gas. Compositions of CO , N_2 , O_2 , CH_4 , and C_2H_6 can be completely separated by the above capillary column and the separated nitrogen is directly detected by MAT 253 isotopic mass spectrometer. The temperature of the GC oven was initially set at 30°C and maintained at such for 8 min, and then raised to 280°C at $10^\circ\text{C}/\text{min}$. The atmospheric nitrogen was selected as the standard material for nitrogen isotopic analysis. The nitrogen isotopic values of samples are reported in conventional δ notation in per mil (‰) relative to atmospheric nitrogen as the standard. The international atmospheric nitrogen isotope value of $\delta^{15}\text{N}/^{14}\text{N} = 0.00361$ is defined as $\delta^{15}\text{N} = 0\text{‰}$. The nitrogen isotope of the gas sample was calculated based on atmospheric nitrogen as the standard according to the formula of $\delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000\text{‰}$. In order to check the reliability of the instrument in the long-term detection process, air standard and a natural gas sample are selected for nitrogen isotope repeatability test at a



relatively fixed time interval. The air standard was tested 5 times; the detected average nitrogen isotope value of $\delta^{15}\text{N}$ for atmospheric nitrogen was -0.0065‰ and the standard deviation was 0.047‰ . The gas sample was tested 7 times; the detected average nitrogen isotope of $\delta^{15}\text{N}$ for gas sample was 4.6‰ , and the standard deviation was 0.135‰ . The tested results indicated that the repeatability of the test system was good and the stability of the instrument was reliable. In order to systematically study nitrogen in coal-derived gas and oil-typed gas, some previous research was collected and referenced (Du et al., 1996; He et al., 2001, 2011; Chen et al., 2001; Chen and Zhu, 2003; Liu and Xia, 2005; Liu et al., 2007; Li et al., 2013). Based on the experimental analysis and previous researcher's data statistics, the geochemical characteristics of nitrogen component and isotope of coal-derived gas and oil-typed gas in China were systematically studied and discussed.

RESULTS AND DISCUSSIONS

Differences on Geochemical Characteristics of Nitrogen in Coal-Derived Gas and Oil-typed Gas in China

According to the comparative analysis of nitrogen components of 109 coal-derived gas samples and 47 oil-typed gas samples in the nitrogen content distribution histogram of coal-derived gas and

oil-typed gas in China (**table 1**), it can be seen that the content of nitrogen in coal-derived gas is mainly distributed from 0 to 31.2%, with main frequency from 0 to 2%; the content of nitrogen in oil-typed gas, meanwhile, is mainly distributed from 1.1 to 57.1%, and with main frequency from 2 to 16% (**Figure 2**). From **Figure 2**, it can also be seen that the nitrogen component content of coal-formed gas and oil-typed gas can be obviously divided by 2% in the dominant frequency distribution.

From the relationship between nitrogen content and ethane isotope $\delta^{13}\text{C}_2$ of coal-derived gas and oil-typed gas in China, it can be obviously seen that oil-typed gas has a relatively high nitrogen content with most ethane isotope $\delta^{13}\text{C}_2$ generally from -41.5‰ to -30‰ , while coal-derived gas has a relatively low nitrogen content with most ethane isotope $\delta^{13}\text{C}_2$, generally from -26.5‰ to -16‰ (**Figure 3**). From **Figure 3**, it can be seen that the nitrogen content of coal-derived gas and oil-typed gas is significantly different and distinct in total distributed range, and the overlapped areas of nitrogen content is mostly less than 10% in low-content areas.

From the histogram depicting nitrogen isotope distribution of coal-derived gas and oil-typed gas in China, it can be concluded that the value of the nitrogen isotope ($\delta^{15}\text{N}$) of 41 coal-derived gas samples is totally distributed from -8 to 19.3‰ with main frequency from -8 to 8‰ , while the value of the nitrogen isotopes of 40 oil-typed gas samples is generally distributed from -10.6 to 4.6‰ with main frequency from -8 to 4‰ (**Figure 4**). From **Figure 4**, it can be seen that the nitrogen isotopic composition

TABLE 1 | Composition and isotope data of non-hydrocarbon gases of nitrogen and helium in some typical coal-derived gas and oil-typed gas in China.

Gas type	Basin	Gas field or gas bearing structure	Well	Gas production strata	N ₂ (%)	δ ¹⁵ N(‰)	R/Ra	Reference	
Coal-derived gas	Tarim	Kela 2	kela 2-7	K _{1bs} ,E	0.69	-0.62	0.028	This paper	
			kela 2-10	K _{1bs} ,E	0.56	-1.03	0.061		
			kela 2-4	K _{1bs} ,E	0.36	-0.78	0.048		
		Dabei	DB201	K _{1bs} ,E	0.54	0.43	0.045		
			DB302	K _{1bs} ,E	0.58	0.39	0.062		
		Dina 2	DN2	E	1.41	11.57	0.025		
			DN2-24	E	1.58	11.89	0.024		
		Akemomou	AK1	K	8.40	-3.01	0.597		
			AK1-2	K	7.80	-2.89	0.592		
		Kekeya	K2	N ₁	3.91	-0.98	0.052		
			K241	N ₁	3.45	-0.70	0.051		
			K8002	N	1.97	-1.6	—		Li et al. (2013)
		Yaha	YH23-1-18	E + K	3.74	17.20	0.025		This paper
			YH3	E	3.87	16.60	0.023		
			YH1-6	E	3.85	19.3	—		Li et al. (2013)
	Ordos	Sulige	S47-44-37	P	6.72	-4.81	0.052	This paper	
			S11-18-36	P	0.92	-4.29	0.048		
			S54-24-65	P	1.45	-4.13	0.032		
	Yiong-Qiong	Dongfang	DF1-1-4	Ny1	27.55	-9.0	0.126	He et al. (2001), (2011)	
			DF1-1-8	Ny1	18.63	-1.0	0.081		
			DF29-1-2	Ny1	23.70	-3.0	0.132		
Oil-typed gas	Tarim	Tazhong 1	TZ117	S	12.89	-4.42	0.027	This paper	
			ZG162	OI	6.65	-8.39	0.025		
			TZ101-1	C _{III}	9.17	-6.52	0.029		
			TZ16	C _{III}	57.1	2.53	—		Chen and Mei. (2001)
			TZ30	O	55.3	3.51	—		
		Hetianhe	MA4-H1	C	12.31	-3.62	0.066	This paper	
			MA5-1	O	9.15	-3.48	0.074		
			MA401	O	14.0	1.51	—		Chen and Mei. (2001)
		donghetang	DH23	O	5.1	4.08	—		
			—	O, D,C	52.56-57.25	10-15	0.047-0.054	Chen and Zhu,(2003)	
		Lunnan	LG11	O	1.25	-2.07	0.022	This paper	
			LN2-2-3	T	5.26	4.53	0.042		
		Hadexun	HD10-3-3H	C	47.64	—	0.021		
		—	Sanshui	Sanshui	SS3	E	10.97	-1.6	4.11
SS12	E				15.26	6.8	4.86		

of coal-derived gas and oil-typed gas are obviously overlapped from -8 to 8‰ in their distribution range with the dominant frequency distributed from -8 to 4‰.

From the relationship between nitrogen isotope δ¹⁵N and ethane isotope δ¹³C₂ of coal-derived gas and oil-typed gas in China, it can be obviously seen that the distribution values of the nitrogen isotopes in coal-derived gas are relatively heavier than these of oil-typed gas. Oil-typed gas generally has relatively lighter nitrogen isotope from -11 to 5‰ with most ethane isotope δ¹³C₂ generally from -38 to -29‰, while coal-derived gas has relatively heavier nitrogen isotope from -4 to 20‰ with most ethane isotope δ¹³C₂ generally from -26 to -17.5‰ (Figure 5). From Figure 5, it can also be concluded that there is an overlap of nitrogen isotopic composition that exists in coal-derived gas and oil-typed gas, and the overlapped area is generally from -4 to 5‰ with limited data distribution points. The reason for this phenomenon will be discussed and given in the following section.

In general, from the relationship between nitrogen content and isotope of coal-derived gas and oil-typed gas in China, the content of nitrogen is relatively low and the δ¹⁵N is relatively heavy in the coal-derived gas, while the content of nitrogen is relatively high and the δ¹⁵N is relatively light in oil-typed gas (Figure 6).

Discussions on Nitrogen Genesis and Reasons for Geochemical Characteristics Differences in Coal-Derived Gas and Oil-typed Gas in China

Nitrogen, as a very important and common non-hydrocarbon gas component in natural gas, has closer physical properties with hydrocarbon gas than other non-hydrocarbon gas components and has similar reservoir forming conditions with hydrocarbon gas reservoir. Therefore, studying the geochemical characteristic and origin of nitrogen in natural gases is helpful to find out the

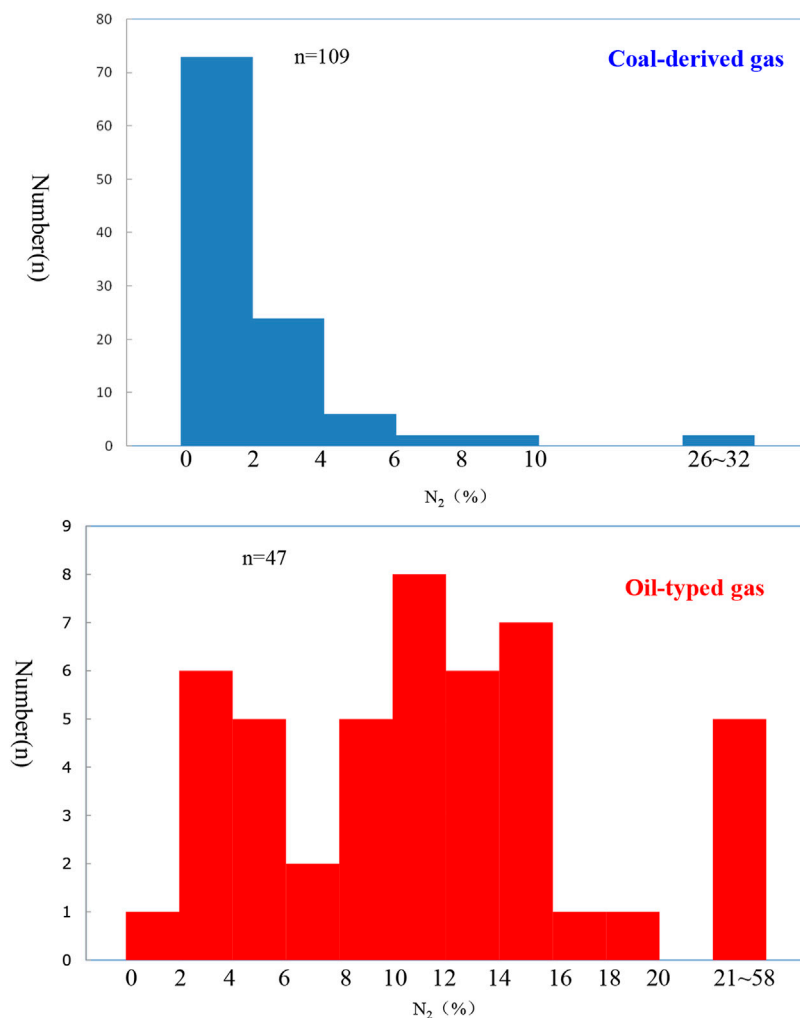


FIGURE 2 | Nitrogen content distributions in coal-derived gas and oil-typed gas in China.

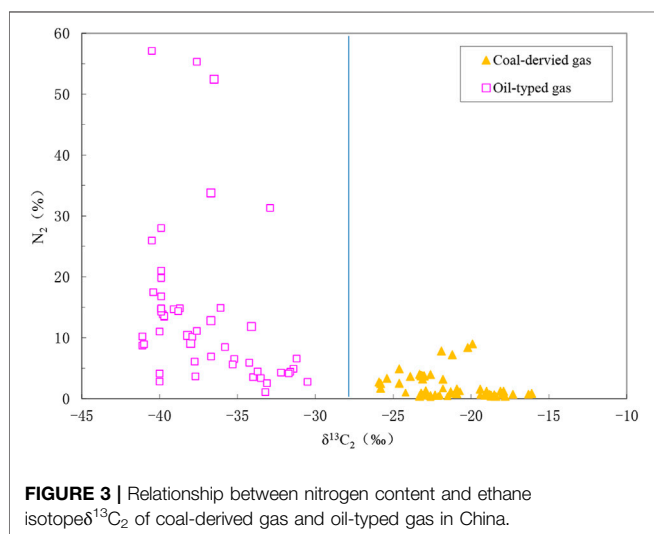
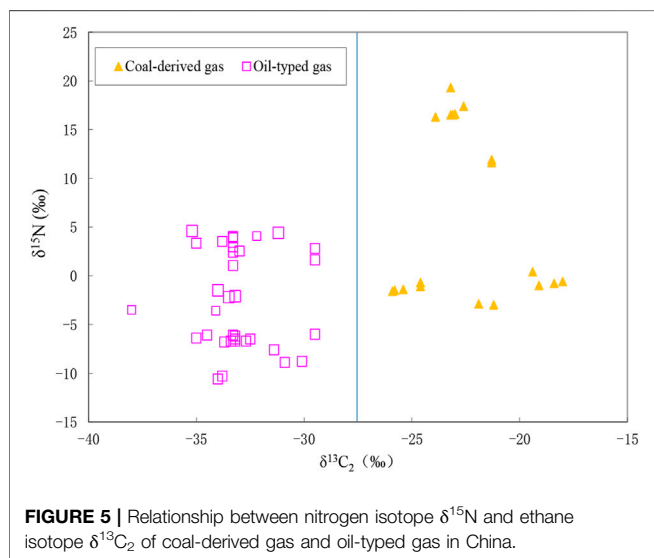
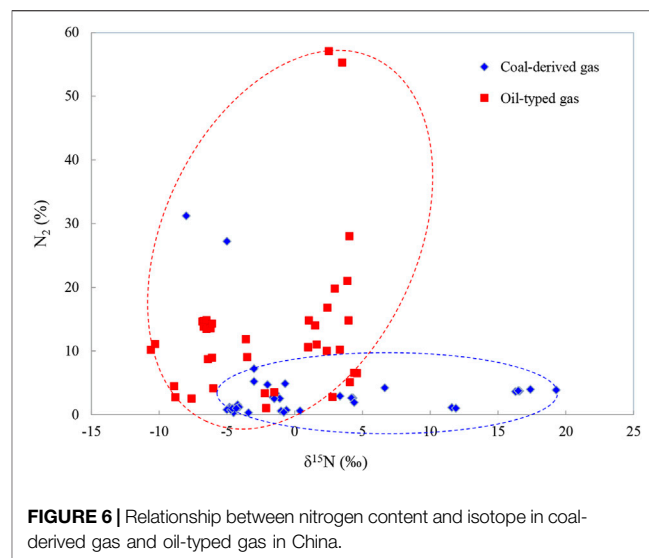
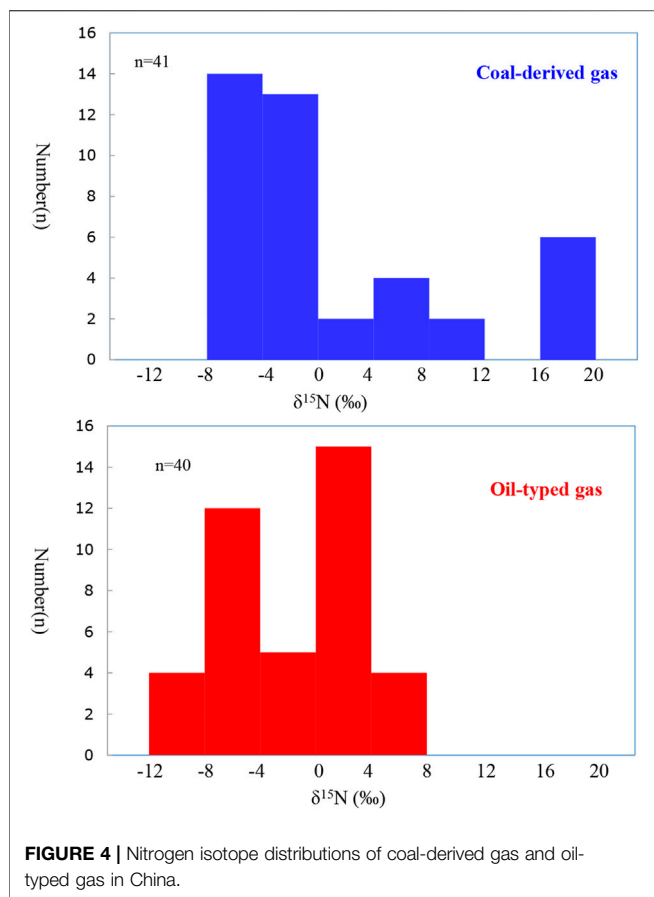


FIGURE 3 | Relationship between nitrogen content and ethane isotope $\delta^{13}\text{C}_2$ of coal-derived gas and oil-typed gas in China.

origin of formation, preservation, and enrichment of hydrocarbon gases. By exploring the geochemical characteristics and source of nitrogen in natural gases, great value will be added to the study of hydrocarbon generation, migration, and accumulation in the basin, forecasting favorable gas exploration areas.

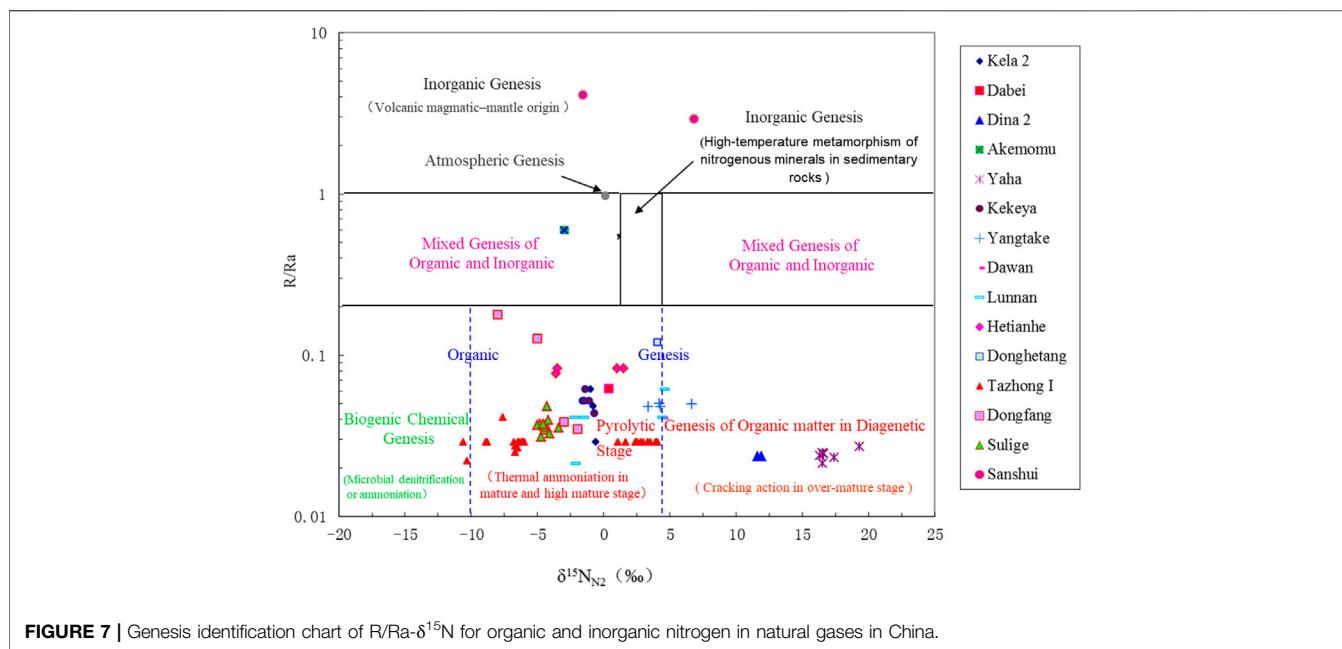
The atmosphere is the largest nitrogen reservoir on the earth. About 99% of the nitrogen in the near surface environment exists in the atmosphere or is dissolved in seawater in the form of nitrogen. There is little nitrogen in the biosphere, but it is one of the most indispensable elements in the process of life. The origins and sources of nitrogen in gas reservoirs are diverse, and many scholars have carried out a lot of research on nitrogen in natural gases. The total variation range of $\delta^{15}\text{N}$ is 100‰, from about -50 to +50‰, and most of them fall in the range of -10 to +20‰. Nitrogen from igneous rocks ranges from -16 to +31‰; nitrogen in the hydrosphere is represented by that in the ocean water, ranging from -8‰ to +10‰; nitrogen in plants ranges from -10 to +22‰; oil and coal fall within the range of modern biology,



ranging from 0 to +15‰; $\delta^{15}\text{N}$ of natural gas varies greatly ranging from -45 to +45‰; $\delta^{15}\text{N}$ of extraterrestrial matter varies the most, ranging from -40 to +100‰, while the value of Martian atmosphere is as high as 700‰ (Hoefs, 1972; Heaton, 1986; Owens, 1987; Peterson and Fry, 1987; Kendall, 1998). According

to the origins and sources, nitrogen in natural gas may be from a number of sources: the atmosphere, microbial ammoniation or denitrification, thermal ammoniation and thermal pyrolysis of organic matters in source rocks, high temperature metamorphism of nitrogenous minerals in sedimentary rocks, or the deep crust and upper mantle. There are certain differences in geochemical characteristics of nitrogen from different sources. Because of the overlapping distribution of $\delta^{15}\text{N}$ in different types of nitrogen (nitrogen isotope value in natural gas is similar to or overlaps with the isotope value of many kinds of nitrogen-bearing materials in nature), it is difficult to identify the origin and source of nitrogen in natural gas only by using nitrogen isotope value and nitrogen content. To solve this problem, it is necessary to combine geological information with other gas geochemical data for comprehensive identification. The isotope value of associated helium is an important indirect indicator for assisted identification of the organic and inorganic origin of nitrogen in natural gas. There are also reports on the use of associated helium to determine the origin of mantle-derived magma nitrogen globally. For example, the nitrogen in some high nitrogen natural gas in the Grand Canyon of California in the United States belongs to magma source (Jenden et al., 1988), the nitrogen in some hot spring gas in China is derived from magma (Dai et al., 1988), and the gas in Sanshui Basin of Guangdong also has magma-sourced nitrogen (Du et al., 1996).

Based on the above studies, R/R_a - $\delta^{15}\text{N}$ indexes and charts to identify organic and inorganic nitrogen have been established by using R/R_a (R and R_a denote $^3\text{He}/^4\text{He}$ of helium in natural gas and air respectively) and nitrogen isotope of $\delta^{15}\text{N}$ (Figure 7): ① When $R/R_a \leq 0.2$, the nitrogen in natural gas is generally organic in genesis and probably originated from biogenic chemical affection (such as microbial ammoniation or denitrification) or thermal pyrolysis of organic matters in source rocks during diagenetic stage (such as thermal ammoniation in mature and high mature stage or cracking action in over-mature stage); ② When $R/R_a \geq 1$ and nitrogen isotope of $\delta^{15}\text{N}$ range from -16 to 31‰, the nitrogen is usually inorganic in genesis from volcano-



mantle origin; ③ When $0.2 < R/R_a < 1$ and $1\% < \delta^{15}N < 4\%$, the nitrogen in natural gas is probably inorganic in genesis and originated from high-temperature metamorphism of nitrogenous minerals in sedimentary rocks; ④ When $0.2 < R/R_a < 1$ and $\delta^{15}N \geq 4\%$ or $\leq 1\%$, the nitrogen is usually of mixed genesis of organic and inorganic; and ⑤ When $R/R_a \approx 1$ and $\delta^{15}N \approx 0$, the nitrogen in natural gas is of atmospheric genesis.

The genesis identification chart of R/R_a - $\delta^{15}N$ for organic and inorganic nitrogen has been used to identify the genesis of nitrogen in natural gases from these selected gas fields in the Tarim, Ordos, and Ying-Qiong basin. The $^3He/^4He$ value of helium on natural gases in the gas fields of Kela 2, Dabei, Dina 2, Kekeya, Yaha, Sulige, Tazhong I, Hetianhe, Donghetang, Lunnan, and Hadexun are basically at the order of 10^{-8} , and $R/R_a < 0.1$; the helium is typically from the crust. So, according to the R/R_a - $\delta^{15}N$ chart (Figure 7), the nitrogen in natural gases of these gas fields are identified from crustal organic origin.

In coal-derived gas, the content of nitrogen is relatively low and the $\delta^{15}N$ is relatively heavy, while in oil-typed gas the content of nitrogen is relatively high and the $\delta^{15}N$ is relatively light. The geochemical characteristic differences of coal-derived gas and oil-typed gas are mainly due to the fact that the sapropel parent material is relatively rich in nitrogen element and rich in light $\delta^{14}N$, while the humic parent material is relatively poor in nitrogen element and rich in heavy $\delta^{15}N$. Sapropel organic matter is mainly originated from aquatic organisms (having an average protein content of 10.3%) and contains a large amount of protein and nucleic acid which provides a sufficient source for the production of N_2 ; humic organic matter is mainly originated from terrestrial plants (having an average protein content of 2.0%) and is poor in protein and acid and rich in carbon with a limited source of N_2 (Chen et al., 2001; Zhu and Shi, 1998). Therefore, the nitrogen content of sapropelic natural gas is much higher than that of humic natural gas. The nitrogen isotope values of source rocks in a marine

sedimentary environment are generally lighter than those source rocks in a continental sedimentary environment. The nitrogen isotope analysis results of some hydrocarbons and kerogen in different sedimentary environments in China show that (Chen and Mei, 2001) the $\delta^{15}N$ of hydrocarbons in a freshwater environment is about 3–6‰. The nitrogen isotope of sedimentary organic matter formed in saline and brackish water environment is the heaviest, and the $\delta^{15}N$ is generally more than 10‰. The $\delta^{15}N$ of organic matter in Paleozoic marine carbonate rocks and generated hydrocarbons is close to 0 or less than 0. In addition, the release of nitrogen is closely related to the thermal evolution of source rocks. In the immature stage, the protein of deposited organic matter will be hydrolyzed to produce amino acids. Amino acids will produce NH_3 through microbial ammoniation, and NH_3 will be further decomposed into N_2 . After entering the mature stage, some nitrogen-containing compounds begin to ammoniate under thermal catalysis to produce ammonia until nitrogen is formed. Since the heat received by the organic matter in the mature stage has not yet reached the activation energy required for the pyrolysis and denitrification of nitrogen-containing organic compounds, a considerable amount of nitrogen still exists in the deposited organic matter. In the over mature stage of $R_o > 2.0\%$, especially when $R_o > 3.0\%$, the thermal energy received by the deposited organic matter begins to fully reach the activation energy required for the pyrolysis and denitrification of nitrogen-containing organic matter, and then produces a large number of nitrogen. Littke et al. (1995) and Kroos et al. (1995) considered that nitrogen formed by the pyrolysis of sedimentary organic matter in high to over mature stage is the main source of high nitrogen gas in petroliferous basins. Therefore, the thermal maturity of source rock has great influences on nitrogen content in natural gas. In addition, the redox conditions of source rock sedimentary environment and the salinity of water

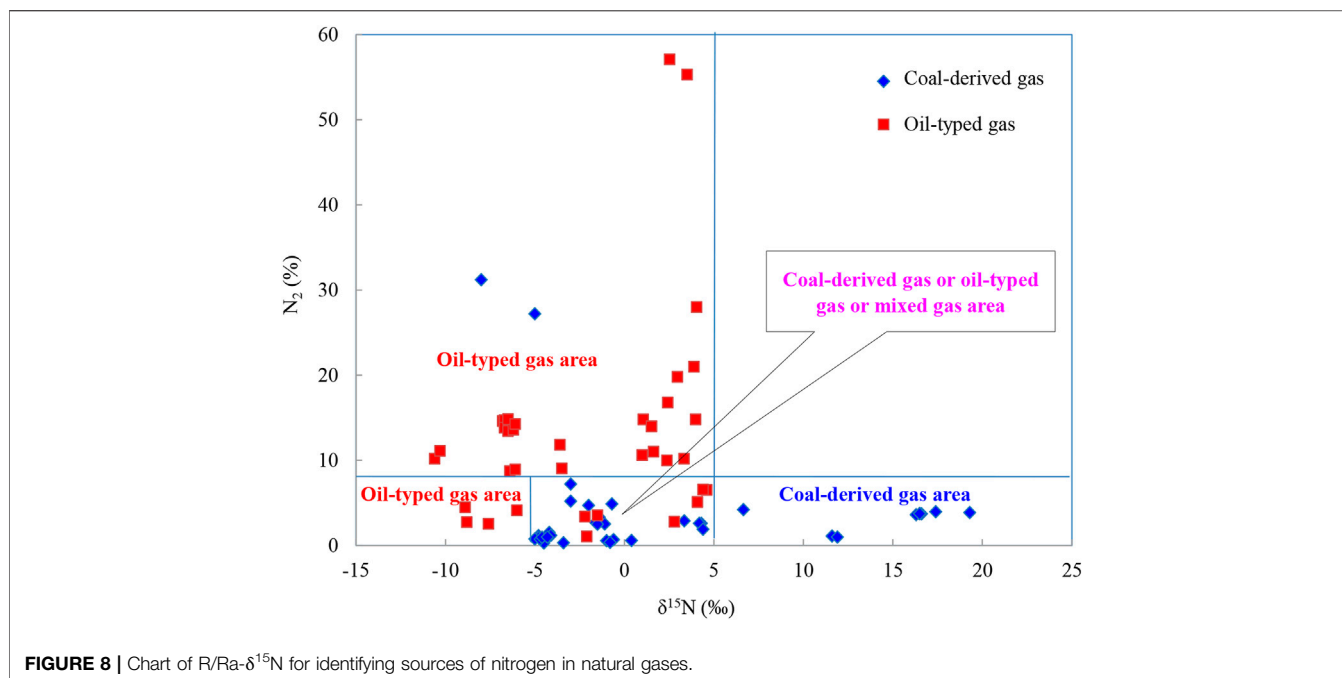


FIGURE 8 | Chart of R/Ra- $\delta^{15}\text{N}$ for identifying sources of nitrogen in natural gases.

body have different heterogeneity and are also important effective factors (Chen et al., 2015).

Discussions on the Tracing Implication of Geochemical Characteristics Differences of Nitrogen in Coal-Derived Gas and Oil-typed Gas

China's natural gas is mainly coal-derived gas, supplemented by oil-typed gas. Coal-derived gas is the main body of China's natural gas reserves and production growth, and plays an important role in promoting the development of China's natural gas industry. At present, about 28 comprehensive identification indexes and charts have been formed for the identification of coal-derived gas and oil-typed gas in three categories: carbon isotope and component of natural gas, light hydrocarbon, and biomarker. Non-hydrocarbon gas nitrogen and helium are important components of natural gas and are closely related to hydrocarbon gas. The components and isotopes of non-hydrocarbon gas contain very rich geological information, so they are important tracers and indicators for identifying the origins and sources of natural gas. However, there are few reports on genetic identification charts and methods on coal-derived gas and oil-typed gas by using nitrogen and helium jointly. This study has clarified the differences in the geochemical characteristics of nitrogen in coal-derived gas and oil-typed gas and considered the R/Ra ratio of helium isotope from crust and mantle sources. Finally, this paper established the comprehensive charts of R/Ra- $\delta^{15}\text{N}$ - N_2 for identifying coal-derived gas and oil-typed gas. Geological applications have achieved good results and are of great significance for deepening the research on the origins and sources of natural gas and guiding natural gas exploration. It is of great significance to optimize the related indexes of nitrogen and

helium to identify coal-derived gas and oil-typed gas, which is helpful to enrich the existing identification index system of coal-derived gas and oil-typed gas.

Based on the differences in nitrogen content and $\delta^{15}\text{N}$ value in coal-formed gas and oil-typed gas, combined with the R/Ra value of helium isotope, the R/Ra- $\delta^{15}\text{N}$ - N_2 identification indexes and charts of coal-formed gas and oil-typed gas jointly identified by nitrogen and helium are established (Figure 7, Figure 8). For the methods process, the R/Ra- $\delta^{15}\text{N}$ chart was used to identify the organic and inorganic origin of nitrogen in natural gas (Figure 7). When the nitrogen in natural gas was identified as an organic origin, then the $\delta^{15}\text{N}$ - N_2 chart and indexes of nitrogen was used to judge the associated hydrocarbon gas to be coal-derived gas or oil-typed gas subsequently (Figure 8). The specific identification index values of this method are as follows (Figure 8). When the R/Ra value of helium isotope in natural gas is less than 0.2 or $^3\text{He}/^4\text{He}$ value is less than 2.8×10^{-7} (to ensure that the hydrocarbon gas associated with helium and nitrogen in natural gas is crustal organic origin): ① Because the humic parent material from higher plants is poor in nitrogen and relatively heavy in $\delta^{15}\text{N}$, when the content of nitrogen is less than or equal to 9% and the $\delta^{15}\text{N}$ value is greater than or equal to 5%, it is generally coal-derived gas; ② Because the Sapropel parent material from lower zooplankton is rich in nitrogen and relatively light in $\delta^{15}\text{N}$, when the content of nitrogen is greater than or equal to 9% and the value of $\delta^{15}\text{N}$ is less than or equal to 5‰, or the content of nitrogen is less than 9% and the value of $\delta^{15}\text{N}$ is less than or equal to -5‰, it is usually oil-typed gas; ③ When the content of nitrogen is less than or equal to 9%, and $\delta^{15}\text{N}$ is from -5 to 5‰, it may be coal-formed gas or oil-typed gas or a mixture of the two, which can be further distinguished according to alkane value of $\delta^{13}\text{C}$.

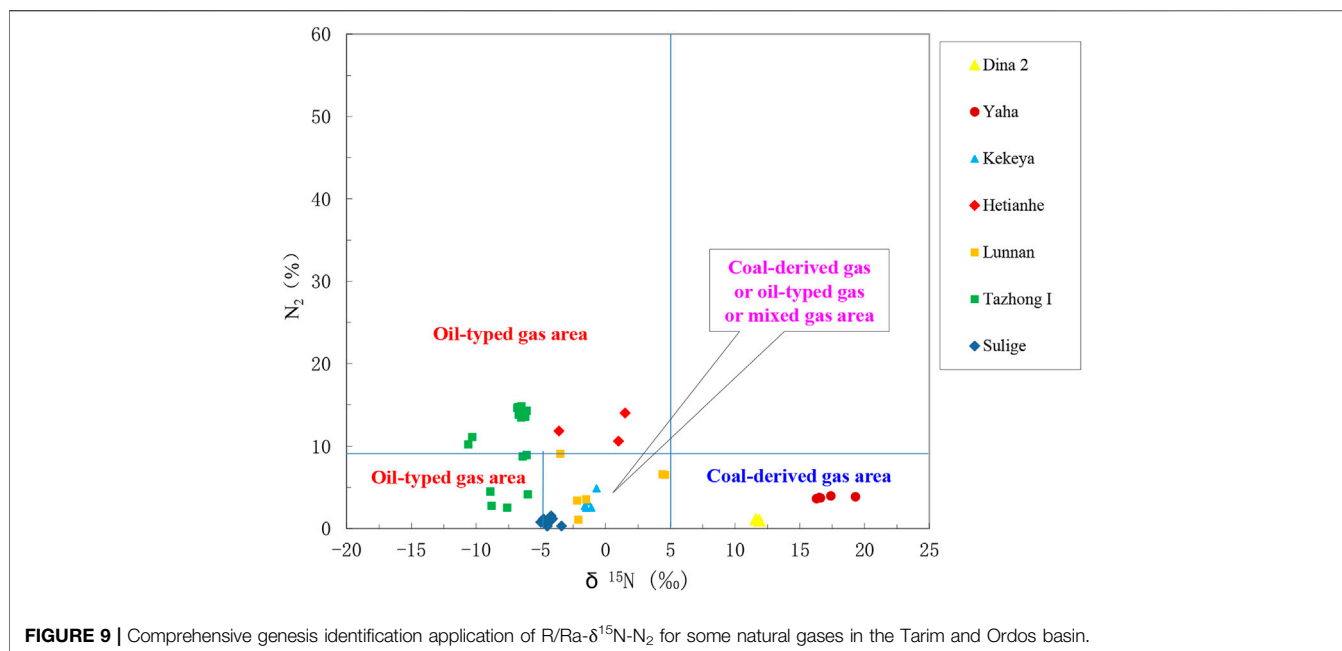


FIGURE 9 | Comprehensive genesis identification application of $R/Ra-\delta^{15}N-N_2$ for some natural gases in the Tarim and Ordos basin.

The comprehensive charts and indicators of $R/Ra-\delta^{15}N-N_2$ have been used to identify coal-derived gas and oil-typed gas from some gas fields in the Tarim and Ordos Basins. The $^3He/^4He$ value of helium on natural gases in the Tarim and Ordos Basin is basically at the order of 10^{-8} , and $R/Ra < 0.1$; the helium is typically from the crust. So, according to the $R/Ra-\delta^{15}N$ chart (Figure 7), the nitrogen of selected natural gases can be identified as originating from organic materials in the crust. Then, the established $\delta^{15}N-N_2$ chart (Figure 8) can be used for coal-derived gas and oil-typed gas identification according to geochemical indexes of accompanied nitrogen, and the final genetic identification is shown in Figure 9 and the detailed results are as follows: ① the Tazhong I and the Hetianhe gas fields fall onto the oil-typed gas zone, so the natural gases are oil-typed gases; ② Dina 2 and Yaha gas fields completely fall onto the coal-derived gas zone, so the natural gases are coal-derived gases; ③ Sulige gas field, Kekeya gas field, and Lunnan oil and gas field fall onto the mixture zone, and the oil-typed gas of Lunnan oil and gas field was distinguished from the coal-derived gas of Sulige and Kekeya gas fields by the alkane carbon isotope (Figure 9). The results obtained by this method are consistent with those obtained by the carbon isotope of conventional hydrocarbon gas.

CONCLUSIONS

- 1) Coal-derived gas generally has relatively lower nitrogen abundances, mainly distributed from 0 to 31.2% with main frequency from 0 to 2%. Oil-typed gas usually has relatively higher nitrogen abundances, mainly distributed from 1.1 to 57.1% with main frequency from 2 to 16%.
- 2) Coal-derived gas generally has relatively heavier nitrogen isotope values mainly distributed from -8 to 19.3‰ with

main frequency from -8 to 8‰ . Oil-typed gas, meanwhile, usually has relatively lower nitrogen isotope values, mainly distributed from -10.6 to 4.6‰ with main frequency from -8 to 4‰ .

- 3) Coal-derived gas has a relatively low nitrogen content and heavy $\delta^{15}N$ value, while oil-typed gas has a relatively high nitrogen content and light $\delta^{15}N$ value. The geochemical characteristic differences of coal-derived gas and oil-typed gas are mainly due to the fact that the sapropel parent material is relatively rich in nitrogen element and rich in light $\delta^{14}N$, while the humic parent material is relatively poor in nitrogen element and rich in heavy $\delta^{15}N$, as well as the differences on thermal maturity of the source rocks. In addition, the redox conditions of source rock sedimentary environment and the salinity of water body are also important effective factors.
- 4) The differences in the geochemical characteristics of nitrogen abundances and isotopes in coal-derived gas and oil-typed gas are of great significance for genetic identification. The genetic identification chart of $R/Ra-\delta^{15}N$ for organic and inorganic nitrogen in natural gas and the comprehensive joint identification charts of $R/Ra-\delta^{15}N-N_2$ of nitrogen and helium for coal-derived gas and oil-typed gas have been established, and are of great importance in investigating the origins and sources of natural gas and guiding natural gas exploration in China.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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