Geochemical characteristics of abiogenic alkane gases

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Abstract: Recently abiogenic alkanes have been found in various locations in the world and other celestial bodies. The chemical composition of abiogenic alkane gases varies widely. The content of methane is low and nearly no C_{2+} is found in the abiogenic alkane gases from fluid inclusions in volcanic rocks or hot springs in China. In the unsedimented submarine hydrothermal vent system C_1/C_{2+} ratios are much greater than those for the thermogenic gases, mostly >800 and in some cases up to 8,000. In the Songliao Basin, China, C_1/C_{2+} of some abiogenic gases are often less than 150. Abiogenic alkane gases which have been found in nature often have carbon isotopic reversal among C_1 - C_4 alkanes ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$), whereas both regular and reversed hydrogen isotope distribution pattern among C_1 - C_4 alkanes have been reported. The $\delta^{13}C$ of abiogenic methane is mainly greater than -30% though laboratory synthesized methane can have $\delta^{13}C$ as low as -57% , and its δD_1 values vary widely and overlap with biogenic gases. High $^3He/^4He$ ratios often indicate the addition of mantle-derived helium and are related to abiogenic gases. However, some biogenic gases can also have high $^3He/^4He$ ratios up to 8. The $CH_4/^3He$ end-member is often lower than 10^6 for abiogenic alkane gases while greater than 10^{13} for biogenic gases, and the values between these two end-members often reflect the mixing of biogenic and abiogenic gases.

Key words: Abiogenic origin, alkane gas, carbon isotopic reversal trend, geochemical characteristics

1 Introduction

In nature hydrocarbons are formed largely by the digestion of organic compounds by microorganisms (microbial origin) (Rice and Claypool, 1981; Schoell, 1988; Whiticar et al, 1986) and the thermal decomposition of organic matters (thermal origin) (Des Marais et al, 1981; Schoell, 1980; 1988; Dai et al, 1992). A number of recent studies demonstrated the existence of abiogenic alkane gases (Abrajano et al, 1988; Charlou et al, 1996a; Dai, 1988; Dai et al, 2000; 2008a; Galimov and Petersilie, 1967; Guo and Wang, 1994; Guo et al, 1997; Jeffrey and Kaplan, 1988; Jenden et al, 1993; Kelley, 1996; Potter and Konnerup-Madsen, 2003; Sherwood Lollar et al, 1993; 2002; Wang et al, 2009; Welhan, 1988; Ni et al, 2009), which might result from the mantle-degassing (Craig and Lupton, 1981; Gold, 1979; Gold and Soter, 1980) or chemical processes such as Fischer-Tropsch synthesis (Berndt et al, 1996; Charlou et al, 1998; Craig, 1953; Foustoukos and Seyfried, 2004; Fu et al, 2007; Giggenbach, 1980; Horita and Berndt, 1999; Hulston and McCabe, 1962a; 1962b; Kelley and Fröh-Green, 1999; Lancet and Anders, 1970; McCollom and Seewald, 2006; Sherwood Lollar et al, 2002).

Since natural gases are mainly dominated by methane, plus small amount of heavy hydrocarbons (C_{2+}) and non-hydrocarbons (CO_2 , N_2 , H_2S , etc.), the available geochemical

information is limited and studies of gas origin and gas-source correlation are largely dependent on their chemical composition and carbon, hydrogen and helium isotopes. To date, a series of studies have been focused on the discrimination of biogenic (referred to microbial origin and thermal origin in this text) and abiogenic gases. Jenden et al (1993) suggested three criteria for abiogenic gases: $\delta^{13}C_1 > -25\%$, $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$, and $R/R_a > 0.1$ (R_a =atmospheric ratio, 1.4×10^{-6}). According to previous studies, Dai et al (2008a) compiled the carbon and helium isotopes of biogenic and abiogenic gases in the world and provided four criteria for abiogenic gases: 1) $\delta^{13}C_1$ generally greater than -30% ; 2) $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$ and $\delta^{13}C_1$ generally greater than -30% ; 3) $R/R_a > 0.5$ and $\delta^{13}C_1 - \delta^{13}C_2 > 0$; and 4) $CH_4/^3He \leq 10^6$. However, due to insufficient knowledge of abiogenic gases, the discrimination of biogenic and abiogenic gases is a hot debate. Recent advances on abiogenic gases from the laboratory have deepened our knowledge of the geochemical characteristics of abiogenic gases. For example, the carbon isotope ratio of methane formed via Fischer-Tropsch synthesis under hydrothermal condition (200°C, 50 MPa) with Fe-Ni as catalyst can be as low as -57% , which is close to the value of biogenic gas (Horita and Berndt, 1999). Other experiments also found that products of the Fischer-Tropsch reactions also have regular distribution pattern of carbon isotopes between C_1 - C_4 n-alkanes, i.e., $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$, which is similar to that of the biogenic gases (Fu et al, 2007;

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McCollom and Seewald, 2006; Taran et al, 2007). Du et al (2003) found that pyrolysis of lignite under extremely high pressure and temperature (1-3 GPa, 500-700°C) can also lead to carbon isotopic reversal trend among C_1 - C_4 n-alkanes.

Recently hydrocarbons have been found on Mars, Enceladus, and Titan (Brown et al, 2008; Filacchione et al, 2007; Krasnopolsky et al, 2004; Niemann et al, 2005; Oze and Sharma, 2005) and discrimination of their origins will have great significance on life origin. In addition, the discrimination of abiogenic alkane gases and discovery of abiogenic alkane gas reservoirs open up a new research field and improve the oil-gas theory. This contribution is concentrated on the geochemical characteristics of abiogenic gases which have been reported in the world in order to provide some hints for the discrimination of abiogenic gases.

2 Chemical composition of abiogenic gases

The chemical compositions of abiogenic gases in nature vary widely. Dai et al (2000) made a detailed review of the abiogenic alkane gases from the inclusions of volcanic rocks and hot springs in China. They found these abiogenic gases are dominated by CO_2 and/or N_2 . A negative correlation was found between CO_2 and N_2 , and the gas could be dominated by either of them which could be up to 99%. The amount of alkane gases was low and characterized by methane and virtually no C_{2+} . However, abiogenic gases found in the Khibiny and Lovozero massif, Ilímaussaq complex, Canadian shield rocks are dominated by methane. The content of methane is more than 60% in general, and some can be up to 97%. Only a few of them are dominated by H_2 , with some amount of CO_2 and alkanes (Table 1, Fig. 1). The C_1/C_{2+} ratios are relatively low, normally lower than 100. As shown in Table 1, abiogenic gases from the Oman ophiolite are dominated by H_2 and N_2 , with small amount of methane and nearly no C_{2+} . The C_1/C_{2+} ratios of abiogenic gases from the mid-ocean ridges are much greater than those of thermogenic gases (Dai et al, 2005), and most of them are greater than 800, and some can be as high as 8,000 (Table 2, Fig. 1). The abiogenic gas fields in the Songliao Basin, China are characterized by methane and most of the methane accounts for more than 90%. Its C_1/C_{2+} ratios are normally lower than 150 (Table 3, Fig. 1).

Fig. 1 Histogram of C_1/C_{2+} ratios of abiogenic gases from volcanoes (a), oil and gas reservoirs (b) and hydrothermal fluids (c). Data from Table 1, Table 2, and Table 3 except the Oman and Philippines data

3 Isotopes of abiogenic alkane gases

3.1 Carbon and hydrogen isotopes of methane

Methane is a highly reducing state of carbon. It is also the dominant component of biogenic and abiogenic alkane gases. Its carbon and hydrogen isotopes can reflect its origin to some extent. For example, gas of microbial origin is normally formed at depth less than 1 km, and its carbon and hydrogen isotopes have a range of $-110\text{‰} < \delta^{13}C_1 < -55\text{‰}$, $-400\text{‰} < \delta D_1 < -150\text{‰}$, respectively; while the carbon and hydrogen isotopes of thermogenic gases vary between $-55\text{‰} < \delta^{13}C_1 \leq -20\text{‰}$ (some as high as -10‰), $-275\text{‰} < \delta D_1 < -100\text{‰}$, respectively (Dai et al, 2008b; Schoell, 1980; 1983; Whiticar, 1999; Dai et al, 1992). The carbon and hydrogen isotopes are -52‰ to -24‰ and -280‰ to -140‰ for coal-related gases, respectively and -58‰ to -30‰ and -300‰ to -130‰ for oil-associated gases, respectively in China (Wang, 1997). The carbon and hydrogen isotopic compositions are also characteristic for abiogenic methane. Table 4 and Fig. 2 demonstrate some carbon and

Table 1 Chemical composition of the abiogenic gas from various rocks

Location	Composition, vol%								C ₁ /C ₂₊	References
	CH ₄	C ₂₊	H ₂	CO ₂	CO	N ₂	He	O ₂ +Ar		
Khibiny	2.06-71.96	0-6.54	1.99-30.95	0-71	6.77-51.60	0-16.21			9-42	Petersilie et al, 1961
	93.42	1.37	0.91	0.00	2.30	2.20			68	Petersilie, 1962
	38.09-96.75	0-3.77	1.08-61.91	0-0.34	0-1.97		0-0.08		24-53	Petersilie and Sørensen, 1970
	89.70-90.00	2.15-2.53	1.77-3.45	0.19	1.32-4.13	0-4.59			35-42	Kogarko et al, 1987
	24.06-97.64	0.65-8.19	0-13.90	0-2.88		0-70.30	0-0.69		11-42	Voytov, 1992
	1.69-95.27	0-4.04	1.48-63.27	0-28.38		2.26-42.57	0-0.19		1-56	Potter, 2000
Lovozero	81.20	6.11	8.34	0.00	4.35	0.00			13	Petersilie, 1962
	79.47-91.36	4.30-8.48		0-1.50		0.12-0.41	0-0.04		10-21	Petersilie and Sørensen, 1970
	8.52-78.55	0.12-6.25	10.84-65.32	0.15-0.30	4.20-25.71				13-71	Kogarko et al, 1987
	15.70-76.10	0.50-5.80	4.80-39.20			3.00-37.50	0.02-1.90	0.80-11.30	11-31	Nivin et al, 1995
	62.68-89.43	1.92-6.91	0.04-27.76			2.69-6.48	0-0.05		9-47	Potter, 2000
	52.06-89.43	1.92-6.91	4.14-35.24			2.69-6.48	0-0.52		8-47	Potter et al, 2004
Ilimaussaq	5.30-83.72	0.06-12.07	5.04-93.11	0-0.06	0-6.93		0.16-3.66		7-88	Petersilie and Sørensen, 1970
	43.00-80.00	6.50-15.55	3.00-34.00	0.40-4.00		3.60-13.00			3-9	Konnerup-Madsen et al, 1979
	66.30-92.10	2.10-10.65	5.80-18.80	0-1.20		0-6.00	0-0.20		7-44	Konnerup-Madsen and Rose-Hansen, 1982
Canada	69.30-77.90	6.51-15.10	0.34-12.70			3.88-12.70	1.83-2.45		5-12	Sherwood Lollar et al, 2002; 2008
Oman	0.20-4.30	0-0.01	1.00-97.00			1.00-77.00		0-21.00	>80	Neal and Stanger, 1983
Philippines	13.00-55.30	0.04-0.22	8.40-42.60	<0.03	1.50-60.60 (CO+N ₂)		0-0.00069	0.1-17.23	251-343	Abrajano et al, 1988

Table 2 Chemical composition of abiogenic gases from the submarine hydrothermal systems

Location	CH ₄	C ₂₊	H ₂	CO	CO ₂	N ₂	Ar	H ₂ S	C ₁ /C ₂₊	References
	mmol/kg	nmol/kg	mmol/kg	nmol/kg	mmol/kg	mmol/kg	umol/kg	mmol/kg		
30°N MAR Lost City	0.89-1.98	1023-1991	0-14.38						869-1122	Proskurowski et al, 2008
6°14'N MAR Rainbow	2.5	1145	16	5000	16	1.8		1.2	2183	Charlou et al, 2002
37°17'N MAR Lucky Strike	0.30-0.85	84-394	0-0.73		15.10-39.90	0.50-1.77	11.7-30.2	2.0-3.0	1500-7935	Charlou et al, 2000
37°50'N MAR Menez Gwen	1.35-2.15	285-826	0.02-0.05		20.10-22.60	0.37-1.82	11-38	1.3-1.8	2603-5263	
14°45'N MAR Logatchev	0		0	0.3	2.3	0.59	16	0		Charlou et al, 1998
23°N MAR Snakepit	0.06							2.7		Jean-Baptiste et al, 1991
26°N MAR TAG	0.15-0.16		0.18-0.23		3.31-3.56	0.8-0.95	21.6-24.3	3.2-3.8		Charlou et al, 1996a
29°N MAR Broken Spur	0.065-0.13		0.43-1.03		6.0-7.1			8.5-11.0		Lein et al, 2000
21°N EPR	0.07	108	1.7						648	Welhan and Lupton, 1987

Table 3 Chemical composition and helium isotopes of abiogenic gases from the Songliao Basin, China

Composition, vol%								C_1/C_{2+}	R/Ra	$CH_4/{}^3He$ $\times 10^9$	References
CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	N_2	He	H_2				
82.12-95.95	0.74-2.45	0.11-0.64	0.02-0.27	0.1-14.41	0.86-6.35	0.008-0.034	0-1.94	28-105	0.6-1.8	1.2-8.6	Dai et al, 2008a
81.59-96.85	0.55-2.37	0.02-1.06	0-0.16	0.09-13.35	1.21-9.05			28-126			Wang et al, 2009

hydrogen isotopes of abiogenic methane in the world. The carbon isotopes of abiogenic methane vary widely, -1% to -44.9% , however, except the abiogenic methane from the Canadian and Fennoscandian shield rocks, most methane has $\delta^{13}C > -30\%$. The hydrogen isotopic composition of methane also varies widely, -102% to -419% , overlapping with that of biogenic methane.

Fig. 2 Compilation of carbon and hydrogen isotope variation in abiogenic methane (data from Table 4)

Debates arise concerning the lower limit of carbon isotope of abiogenic methane, namely, $> -20\%$ (Shen et al, 1991; Xu et al, 1993; Zhang, 1991; Chen, 1989), $> -25\%$ (Jenden et al, 1993), and generally $> -30\%$ (Dai et al, 2008a; Fuex, 1977; Dai, 1992a; 1992b). At present all these lower limits of carbon isotopes are mainly a comprehensive generalization of the carbon isotopes of various reported occurrences of abiogenic methane in the world, but the field lacks exact methods. As discussed above, Horita and Berndt (1999) found that the carbon isotopes of abiogenic methane formed through Fischer-Tropsch synthesis in the laboratory can be as low as -57% , which is similar to the value of microbial gases.

3.2 Carbon and hydrogen isotopic distribution pattern of methane and its homologues (C_1 - C_4)

Isotopic analyses found that thermogenic gases (C_1 - C_4) become more enriched in ^{13}C with increasing molecular mass ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$) due to kinetic isotopic effects. When one alkyl is separated from the original organic matter, the ^{12}C - ^{12}C bond is weaker than the ^{12}C - ^{13}C bond and breaks faster, causing the pyrolytic products to be more depleted in ^{13}C than the higher molecular weight organic precursor (Des Marais et al, 1981). A typical characteristic of abiogenic alkane gases is the carbon isotopic reversal trend, i.e., the carbon isotope of alkane gases become more depleted in ^{13}C with increasing molecular mass ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$) (Des Marais et al, 1981; Galimov and Petersilie, 1967; Lancet and Anders, 1970; Yuen et al, 1984). The reason is that during the control process of isotope kinetics distillation effect, synthesizing a high molecular homologue from a low molecular compound, the ^{12}C - ^{12}C bond is weaker and thus breaks faster than ^{12}C - ^{13}C , the $^{12}CH_4$ reacts faster than $^{13}CH_4$ to form hydrocarbon chains, that is, in the process of polymerization, ^{12}C is preferentially incorporated into the long chains formed during polymerization, thus obtaining a reverse carbon isotope trend (Des Marais et al, 1981; Yuen et al, 1984). In a similar fashion, due to the kinetic isotopic effects both thermogenic and abiogenic gases have a regular hydrogen isotopic distribution pattern whereby the C_1 - C_4 alkane gases become more enriched in 2H with increasing molecular mass, i.e., $\delta D_1 < \delta D_2 < \delta D_3 < \delta D_4$.

Bacterial oxidation of methane will lead to isotopic depletion of C_2 versus C_1 (Coleman and Risatti, 1981), conclusive evidence of isotopic depletion of higher hydrocarbons with respect to C_1 requires comparison to a larger range of higher hydrocarbons, particularly C_3 and C_4 (Sherwood Lollar et al, 2002). Dai (1990) and Dai et al (2004) proposed that the partial reversal of carbon and hydrogen isotopes might be due to secondary alteration (e.g., bacterial oxidation) or mixing of gases with different origins. At present, there are not too many reports about the carbon and hydrogen isotopic distribution patterns among the abiogenic C_1 - C_4 alkanes (Table 5, Fig. 3, and Fig. 4). Most of these reports are focused on the abiogenic gases from the mid-ocean ridges, shield rocks, and volcanic rocks, and the abiogenic alkane gas reservoirs are only reported in the Songliao Basin, China. Sherwood Lollar et al (1993; 2002) and Wang et al (2009) found that the carbon and hydrogen isotopes of abiogenic gases are negatively correlated while in contrast Proskurowski et al (2008) found that the carbon

Table 4 Carbon and hydrogen isotopes of abiogenic methane

Location	$\delta^{13}\text{C}_{\text{CH}_4}$, ‰	$\delta\text{D}_{\text{CH}_4}$, ‰	$\delta^{13}\text{C}_{\text{CO}_2}$, ‰	R/Ra	$\text{CH}_4/{}^3\text{He}$, $\times 10^6$	References
Zaohetang, Tengchong, China	-19.9	-130	-6.3 - -1.9	2.9		Dai, 1993
Tuoba, Ganzi, China	-26.6 - -23.8	-213 - -111	-4.8 - -2.4	0.4-0.5		
New Zealand	-29.5 - -24.4	-197 - -142	-9.1 - -3.2			Lyon and Hulston, 1984
New Zealand	-32 - -20.4	-170 - -144	-8.9 - -4.8	4.2-7.5		Giggenbach, 1995
Yellowstone, USA	-28.4 - -10.4	-239				Welhan et al, 1983
Milos	-17.8 - -9.4	-189 - -104	-1.1 - -0.6	1.0-1.3		Botz et al, 1996
Iceland	-39.3 - -22.0		-18.7 - -4.8	2.1-16.8		Sano et al, 1985
Mediterranean Sea	-32.3 - -16.4		-4.3 - 0.1	2.5-5.1		Fiebig et al, 2007
13°N EPR	-19.1 - -16.7		-4.4 - -4.1	7.0-7.5	3.1-3.9	Kim et al, 1984; Merlivat et al, 1987
21°N EPR	-17.6 - -15.0	-126 - -102	-7.0	7.8	3.5-6.5	Kim et al, 1984; Welhan and Craig, 1983
17°-19°S EPR	-23.9 - -22.0			6.2		Charlou et al, 1996b; Jean-Baptiste et al, 1997
14°45'N MAR Logatchev	-13.6		-4.1	7.2		Charlou et al, 1998; Jean-Baptiste et al, 2004
26°N MAR TAG	-9.5 - -8.0		-10.0 - -8.4	7.5-8.2	8.8-52	Charlou et al, 1996a; 2002
29°N MAR Broken Spur	-19.0 - -18.0		-9.0	8.9		Jean-Baptiste et al, 2004; Lein et al, 2000
30°N MAR Lost City	-13.6 - -9.4	-147 - -125				Proskurowski et al, 2008
36°14'N MAR Rainbow	-15.8		-3.15	5.7-7.8		Charlou et al, 2002; Jean-Baptiste et al, 2004
37°50'N MAR Menez Gwen	-19.6 - -18.8		-9.1 - -6.8	8.7		Charlou et al, 2000; Jean-Baptiste et al, 1998
37°17'N MAR Lucky Strike	-13.7 - -12.7		-10.6 - -7.2	8.1		
Southwest Indian Ridge T=450-500 °C	-33.8 - -9.1	-149 - -99	-28.5 - -8.7			Kelley and Früh-Green, 1999
Southwest Indian Ridge T>900°C	-30.1 - -18.8	-244 - -128	-23.9 - -1.9			
19°33'S Central Indian Ridge Roger Plateau	-17.5			1.1-1.6		Kawagucci et al, 2008
Zambales, Philippines	-7.5 - -6.1	-137 - -118	-32	3.98-4.07		Abrajano et al, 1988
	-12.8 - -3.2					Galimov, 1975
	-28.6 - -12.8					Potter, 2000
	-19.3 - -3.2		-8.5 - 10.6			Galimov and Petersilie, 1967
Khibiny	-11.2 - -3.2	-56 - 173				Voytov, 1992
	-6.5	-66 - 82				Yerokhin, 1978
	-14.0 - -7.7					Nivin et al, 2001
	-22.4 - -5.4		-16.8 - -13.6			Beeskow et al, 2006
	-13.3 - -7.6		-18.6 - -14.6			Potter and Longstaffe, 2007
	-15.7 - -7.1					Nivin et al, 2001
Lovozero	-11.8	-167 - -132				Nivin et al, 1995
Ilímaussaq	-7 - -1	-145 - -132				Konnerup-Madsen, 2001
Canada and Fennoscandia	-44.9 - -22.4	-372 - -133				Sherwood Lollar et al, 1993
	-40.7 - -33.0	-419 - -390				Sherwood Lollar et al, 2002
Songliao, China	-28.9 - -17.4	-203 - -196	-5.1 - 18.9	0.6-1.8	1.2-8.6	Dai et al, 2008a; Wang et al, 2009

and hydrogen isotopes of abiogenic gases from the 30°N MAR Lost City are positively correlated (Fig. 4). The exact situation is still unclear at the moment.

Fig. 3 Carbon isotopic distribution of abiogenic methane and its homologues (data from Table 5). Data from the Murchison meteorite are on right y axis and all other data are on left y axis.

Fig. 4 Hydrogen isotopic distribution pattern of abiogenic methane and its homologues (data from Table 5)

3.3 $^3\text{He}/^4\text{He}$ isotope (R/Ra)

Since the discovery of ^3He anomaly in the East Pacific Rise in the 1960's (Craig and Lupton, 1981), helium isotopes have been widely used as traces of mantle volatiles. Due to the different origin of the two stable isotopes of helium, ^3He and ^4He , helium can be divided into three different types:

atmospheric helium, $^3\text{He}/^4\text{He}=1.4\times 10^{-6}$, i.e., Ra; crustal helium, product of the radioactive decay of U and Th (yielding ^4He) and the (n, α) reaction of ^6Li (yielding ^3He), $^3\text{He}/^4\text{He}$ normally less than 0.04 Ra (Andrews, 1985; Mamyrin and Tolstikhin, 1984); mantle helium, a mixture of radiogenic and primordial helium which has $^3\text{He}/^4\text{He}$ of 100-300 Ra (Craig and Lupton, 1981; Mamyrin and Tolstikhin, 1984). Since the atmospheric helium in the commercial gas wells can be neglected, helium in the natural gas can be approximately regarded as a mixture of crustal and mantle helium. In general, mantle $^3\text{He}/^4\text{He}$ is far greater than the crustal $^3\text{He}/^4\text{He}$. For example, the $^3\text{He}/^4\text{He}$ value is 7-9 Ra for the depleted upper mantle, >30 Ra for the lower mantle and <0.1 Ra for the crust (Andrews, 1985; Craig and Lupton, 1981; Hiyagon and Kennedy, 1992; Welhan et al, 1983). Hence, the high $^3\text{He}/^4\text{He}$ values of natural gas mean addition of mantle volatiles. Jenden et al (1993) proposed that $^3\text{He}/^4\text{He}>0.1$ Ra in the natural gas was an indication of the existence of mantle helium. Dai et al (2008a) suggested that $^3\text{He}/^4\text{He}>0.5$ Ra indicates the addition of mantle helium.

Jenden et al (1993) compiled the numerous studies of the helium isotopic distribution of different commercial oil and gas fields in the world and proposed that fields overlying ancient cratonic crust and in foreland basins formed by thrust-plate loading had $^3\text{He}/^4\text{He}$ ratios close to radiogenic values, while fields located near active plate margins in forearc, backarc, and rift basins might have $^3\text{He}/^4\text{He}$ ratios approaching mantle values. Xu et al (1998) made a statistical analysis of the distribution of helium isotopes in natural gases in China (Fig. 5) and found that about 30% natural gases were characterized by $^3\text{He}/^4\text{He}$ ratios greater than the atmospheric values ($R/Ra>1$), indicating the addition of mantle helium. The distribution of the helium isotope ratio (R/Ra) in the hot springs and hydrothermal systems in China are mainly in the range of 0.5-8 (Fig. 6, Table 6), indicating the addition of mantle helium as well. However, due to the helium loss through reservoirs or helium addition from radiogenic sources, $^3\text{He}/^4\text{He}$ ratios may decrease with time, leading to the low $^3\text{He}/^4\text{He}$ ratios in some natural gases of mantle origin (Kamenskiy et al, 1971). On the other hand, biogenic methane can also be associated with high $^3\text{He}/^4\text{He}$ ratios. For example, $^3\text{He}/^4\text{He}$ ratios in the oil and gas fields of the Green Tuff region in Japan are as high as 7.5 Ra ($\delta^{13}\text{C}_1$: -62‰ to -33‰) (Sakata, 1991); $^3\text{He}/^4\text{He}$ ratios in the geothermal vents along the East Pacific Rise in the Guaymas Basin, Gulf of California also approach 8.0 Ra ($\delta^{13}\text{C}_1$: -51‰ to -43‰) (Welhan and Lupton, 1987). In the Wudalianchi and Changbaishan areas in China, the high $^3\text{He}/^4\text{He}$ ratios are associated with relatively low $\delta^{13}\text{C}$ values of methane (Shangguan and Wu, 2008). According to the recent study on the geochemistry of natural gases from the inactive volcanoes in China by Shangguan and Wu (2008), $\delta^{13}\text{C}_1$ value of methane in the volcanic residual gas in Changbaishan was as low as -48.0 while the associated helium has $^3\text{He}/^4\text{He}$ ratios of 5.5 Ra (Table 6). The authors suggested an origin in the mantle for the hydrocarbons, however, debates exist concerning the mantle contribution to the hydrocarbons and further studies are required.

Table 5 Carbon and hydrogen isotopes of abiogenic methane and its homologues

Location	Sample	$\delta^{13}\text{C}$, ‰				δD , ‰				References
		C ₁	C ₂	C ₃	C ₄	C ₁	C ₂	C ₃	C ₄	
Khibiny	Inclusion	-3.2	-9.1	-16.2						Zorikin et al, 1984
	Inclusion	-12.8	-24.5	-26.0						Galimov, 1975; Voytov, 1992
	Inclusion	-3.2	-9.1	-25.7						
	Rischorrite	-14.4	-17.1	-17.3	-17.5					Beeskow et al, 2006
	Trachytoid foyaite	-8.0	-17.5	-19.6						
	Massive foyaite	-5.4	-14.3	-13.0	-13.2					
	Urtite	-8.1	-20.6	-19.7						
	Urtite					-88	-154			Potter and Longstaffe, 2007
	Urtite	-12.4	-23.2	-21.3	-17.4					
	Urtite					-52	-120			
Yellowstone, USA		-21.5	-26.5							Des Marais et al, 1981
Meteorite	Murchison	9.2	3.7	1.2						Yuen et al, 1984
Fennoscandian	CCS4000	-35	-25.1			-325				Sherwood Lollar et al, 1993
	Juuka 116-254 m	-28.6	-25.9			-281				
Sudbury Ontario	CCS846-2	-35.1	-33.3	-31.2		-237	-215	-185		Sherwood Lollar et al, 1988
	CCS844-2	-29.7	-28.0	-27.7		-335	-238			
Kidd Creek	7792	-38.3	-38.2	-37.6	-37.9	-390	-299	-256	-224	Sherwood Lollar et al, 2002
	8558	-32.7	-36.8	-35.3	-35.7	-419	-321	-264	-245	
	8282	-35.0	-38.3	-35.9	-36.3	-409	-316	-269	-252	
Lost City	H04-IGT8	-9.5	-15.2	-15.0		-119	-127	-140		Proskurowski et al, 2008
	H05-IGT7	-11.8	-13.7	-13.4		-147	-166	-160		
Songliao, China	Fs1	-18.6	-23.2							Dai, 1992a
	Fs1	-18.7	-22.4	-24.1	-28.2					Guo et al, 1997
	Fs7	-28.8	-30.4	-32.5	-32.6					
	Fs9	-27.1	-30.1	-30.5	-33.0					Wang et al, 2004
	Xs1	-29.7	-32.9	-34.3	-35.0					Dai et al, 2008a
	Xs6-2	-25.9	-32.4	-33.1	-33.7					
	Fs2	-17.4	-22.2	-30.5	-31.4					
	FS-2	-17.7	-22.0	-30.3		-200	-184	-138		Wang et al, 2009
	S-2-1	-22.7	-28.0	-32.1	-35.2	-202	-166	-120		
	S-502	-29.3	-30.3	-30.9		-197	-189	-188

Fig. 5 Histogram of the R/Ra values of the natural gases in China (Xu et al, 1998)

Fig. 6 Histogram of R/Ra values of natural gases from the hydrothermal systems and hot springs in China

Table 6 Chemical composition and isotopes of natural gases from the hydrothermal systems and hot springs in China

Location	N ₂ , %	CO ₂ , %	CH ₄ , %	He, %	δ ¹³ C ₁ , ‰	δ ¹³ C _{CO₂} , ‰	R/Ra	CH ₄ /³He, ×10 ⁶	Reference
Tuoba, Ganzi, Sichuan	0-2.72	93.00-98.60	1.07-3.64	0-0.008	-26.6 - -24.8	-4.2 - -2.5	0.36-0.50	791.58	
Fushoushan, Pingjiang, Hunan	0.17	99.70		0.0038		-5.5	0.29		
Rucheng and Ningxiang, Hunan	96.88-97.55	0.75-2.92	0-0.38	0-0.24		-25.4	0.07-0.47	16.72	
Fengshun, Guangdong	95.71	3.19		0.07		-11.2	0.83		
Xunwu, Jiangxi	99.96	0.04				-27.7	1.36		
Chongren, Jiangxi	54.53	29.69		0.0056		-7.3	0.57		
Taishun, Zhejiang	98.86	0.40	0.15	0.44		-10.1	0.24	1.01	Dai et al, 2000
Keshiketeng, Inner-Mongolia	97.84	0.19	0.26	0.66	-22.7	-16.1	0.06	4.73	
Fujian	84.32-96.31	2.23-13.66	0-0.19	0.049-0.13			0.28-0.48	2.16	
Wudalianchi	0.24-2.34	97.41-99.45	0-0.02	0.057-0.067		-5.4 - -4.0	2.98-3.16	0-0.08	
Chuxiong, Yunnan	23.00	76.53	1.00	0.006		-6.0	0.82	146.20	
Tengchong, Yunnan	0-3.20	96.66-99.92	0.13-1.35	0.005-0.042	-32.7 - -16.2	-5.8 - -1.2	2.86-4.49	0.1-7.6	
Other places in Yunnan	86.03-94.83	3.04-11.99	0-6.54	0-0.19	-50.3 - -28.4	-16.3 - -8.9	0.01-0.40	144.76	
Hengjing, Jiangxi	0-2.01	96.47-99.84	0.04-1.86	0.002-0.014	-59.3 - -27.7	-5.5 - -4.4	1.36-2.11	1.9-424	Sun et al, 2004
Tengchong	14.52-71.23	10.33-80.13	0-1.03	0.0003-0.02			0.48-5.13	0.2-32.6	Wang et al, 1993
Changbai Mountain	2.14-10.04	73.55-97.59	0-0.47	0.00002-0.006		-6.6 - -4.2	2.29-5.71	12.5-604.9	Shangguan et al, 1997
Jinjiang	3.86-11.25	79.02-86.53	1.25-2.02	0.01-0.03	-30.4 - -26.2	-7.5 - -7.0	5.36-5.89	5.2-13.3	
Tengchong	0.80-32.75	57.49-96.64	0.01-2.73	0.00006-0.04		-5.8 - -0.5	1.01-4.81	0.2-133.4	Shangguan et al, 2000
Wudalianchi							3.09-3.51		
Tengchong							4.85		Shangguan et al, 2006
Changbai Mountain							5.62-5.95		
Tengchong	2.22-4.42	92.46-94.95	0.01-0.98	<0.000122	-27.3 - -18.8	-6.5 - -3.6	1.62-5.39		
Changbai Mountain	2.55-9.76	83.45-96.06	0.28-4.15	<0.000207	-48.0 - -26.2	-6.9 - -4.0	4.79-5.51		Shangguan and Wu, 2008
Wudalianchi	4.90-7.64	90.20-93.41	0.02-0.03	<0.000248	-47.2 - -44.4	-6.6 - -4.5	3.01-3.03		

3.4 Methane concentration and ^3He abundance

^3He has proven to be of mantle origin, hence, except the $^3\text{He}/^4\text{He}$ ratios, the correlation between ^3He and the concentration of other gas composition such as CH_4 can provide some hints for the origin of natural hydrocarbon gases. Fluids from the East Pacific Rise and Mid-Atlantic Ridges have $\text{CH}_4/^3\text{He}$ ratios of 10^6 ($1.4\text{--}7.0\times 10^6$ for EPR and 2.4×10^6 for MAR), which have been considered as mantle origin (Jean-Baptiste et al, 1991; Welhan et al, 1983). According to the $\text{CH}_4/^3\text{He}$ ratios of 100 gas wells from the Bohai Bay, North Jiangsu, Songliao, Ordos, Sichuan, Tarim and Turpan-Harim basins in China and the comparison with those from New Zealand, Iceland, and Thailand, etc., Dai et al (2008a) proposed that abiogenic gas had $\text{CH}_4/^3\text{He}\leq 10^6$ and biogenic gas had $\text{CH}_4/^3\text{He}\geq 10^{11}$. Fig. 7 shows the correlation between ^3He abundance and the methane concentration of gases from the hot springs, hydrothermal vents and gas fields in China. The $\text{CH}_4/^3\text{He}$ ratios of biogenic alkane gases vary widely, $10^8\text{--}10^{13}$, overlapped with the $\text{CH}_4/^3\text{He}$ ratios for the abiogenic gases from the Songliao Basin. In general, $\text{CH}_4/^3\text{He}$ ratios from the gas fields are greater than those from the hot springs and hydrothermal vents, indicating that gases in the gas fields are characterized by biogenic gas while gases in the springs and hydrothermal systems are dominated by mantle volatiles. However, if reducing CH_4 -enriched fluids are degassed from mantle (Gold and Soter, 1980; 1982), the mantle $\text{CH}_4/^3\text{He}$ ratios can be expected to be as high as 3×10^9 . The CH_4 -enriched gases from the pyroclastic rock reservoirs of the gas fields in the Green Tuff region, Japan have $\text{CH}_4/^3\text{He}$ ratios of around 2×10^9 , regarded as mantle origin (Wakita et al, 1990). Whereas, the $\text{CH}_4/^3\text{He}$ ratios of biogenic gases can also be very high, even as high as 10^8 . For example, gases from the Well 843-2 of the Dagang Oil Field in the Bohai Bay Basin, China have $\text{CH}_4/^3\text{He}$ ratios of 5.3×10^8 and R/Ra ratios of 8.6, while the carbon isotopes of methane, ethane, and propane are -58.1‰ , -42.3‰ , and -30.7‰ , respectively; Gases from the Well Qi18 in the Songliao Basin also have $\text{CH}_4/^3\text{He}$ ratios of 5.3×10^8 and R/Ra ratios of 2.6, while carbon isotopes of methane, ethane, and propane are -54.7‰ , -31.9‰ , and -24.2‰ , respectively (Dai et al, 2008a). Similarly, the hydrothermal fluid from the Guaymas Basin, Gulf of California has $\text{CH}_4/^3\text{He}$ ratios of 3.1×10^9 , but its R/Ra ratios (8.0) are close to those of the 21°N East Pacific Rise. The carbon isotope of methane is -15.0‰ to -17.6‰ for 21°N East Pacific Rise while -43‰ to -51‰ for the Guaymas Basin. The $\text{C}_1/(\text{C}_2+\text{C}_3)$ ratios of gases from the Guaymas Basin fall in the range of biogenic alkane gases, so the $\text{CH}_4/^3\text{He}$ ratios in the Guaymas Basin indicate biogenic origin of the hydrocarbons, which is a result of the circulation flow of the hydrothermal fluid in the overlying organic sediments (Simoneit et al, 1988; Welhan and Craig, 1983; Welhan and Lupton, 1987). In fact, the high $\text{CH}_4/^3\text{He}$ ratios in many locations are explained as a mixture of mantle and crustal helium. For example, the high $\text{CH}_4/^3\text{He}$ ratios ($>10^{13}$) of the gases from volcanic rocks in Japan were interpreted that a large contribution of the methane was from crustal or subducted sediments (Marty et al, 1989). The variation of $\text{CH}_4/^3\text{He}$ ratios in the Sacramento Basin was taken as an

indicative of mixing (Poreda et al, 1986). Similarly, natural gas from the mud volcano in the Copper River Basin in Alaska was also explained as mixing origin (Motyka et al, 1989).

Fig. 7 Plot of $\text{CH}_4/^3\text{He}$ versus R/Ra of various natural gases. Data of hydrothermal systems and hot springs are from Table 6, the biogenic alkane gas data are from Dai et al (2008b), data of the 21°N East Pacific Rise are from Welhan and Lupton (1987), and the abiogenic data in the Songliao Basin are from Table 3

4 Conclusions

This contribution made a comprehensive study of the geochemical characteristics of abiogenic alkane gases. The chemical composition of abiogenic alkane gases vary widely. The various volcanic fluid inclusions and hydrothermal systems in China have very low amount of methane and nearly no C_{2+} . The C_1/C_{2+} ratios in the unsedimented submarine hydrothermal systems are far greater than those of biogenic alkane gases, mostly greater than 800 and some up to 8,000. The C_1/C_{2+} ratios of the abiogenic alkane gases in the Songliao Basin, China are generally less than 150. The reported abiogenic alkane gases in nature normally have a reversed distribution pattern of carbon isotope ratios among $\text{C}_1\text{--C}_4$ alkanes, while both reversed and regular distribution patterns of hydrogen isotope ratios have been reported. Abiogenic methane generally has $\delta^{13}\text{C}>-30\text{‰}$ and a wide distribution range of δD , -102‰ to -419‰ which overlaps with the hydrogen isotope ratios of biogenic gases. However, $\delta^{13}\text{C}$ of methane synthesized in the laboratory can be as low as -57‰ . The $^3\text{He}/^4\text{He}$ ratios of mantle helium are far greater than those of crustal helium, so the high $^3\text{He}/^4\text{He}$ ratios in the natural gases often indicate addition of mantle helium. Hence, $^3\text{He}/^4\text{He}$ ratios are often regarded as an auxiliary indicator of abiogenic gases. However, biogenic alkane gases can also have very high $^3\text{He}/^4\text{He}$ ratios, even up to 8 Ra. The $\text{CH}_4/^3\text{He}$ ratios can reflect the gas origin to some extent due to the proven mantle origin of ^3He . The $\text{CH}_4/^3\text{He}$ ratios are lower than 10^6 for abiogenic end-members while greater than 10^{13} for the biogenic end-member. It often reflects a mixing of biogenic and abiogenic alkane gases.

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