Material sources of escaped gases from Tianchi volcanic geothermal area, Changbai Mountains*

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Abstract On the basis of the chemical components and stable isotopic compositions of escaped gases from the Tianchi volcanic geothermal area, the material sources of these gases are discussed, presenting that they are mainly derived from the residual mantle-derived magma in the crust; Changbai geothermal area may be directly interlinked with the eruption canal in history; there is a stable reservoir of the geothermal water and the deep-seated gases under the Changbai geothermal area, with water temperature of the reservoir being about (166 ± 9)℃.

Keywords: Tianchi volcanic geothermal area, modern deep-seated gases, residual mantle-derived magma in the crust.

Tianchi volcano is located in the Sino-Korean border region, eastern Jilin Province. It is the largest modern volcano in China. The area of Tianchi caldera lake is about 9.82 km^2, and the largest depth is 373 m, with a storage capacity of more than 2×10^9 m^3. Tianchi volcano erupted violently about A. D. 1000[1]. Afterwards the small volcanic erupting activity occurred many times. The latest erupting activity took place in 1903[2]. Field investigation results show that relatively large-scale hydrothermal anomaly with the deep-seated gas discharge happens near the Tianchi volcanic lake at present.

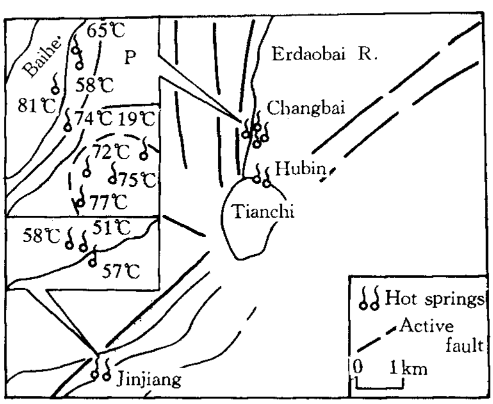

Fig. 1. A schetch map of the distribution of the sampling springs of escaped gas at the Tianchi volcanic area.

The escaped gas samples were collected by the drainage, and kept in the stainless steel vacuum bottles. The positions of the sampling springs are shown in fig. 1. The C, O, H, He isotopic compositions were determined on the mass spectrometers MAT-251 and VG-5400. The gas components were determined by means of chromatography, and the microcomponent He was corrected by the mass spectrographic analysis. Tables 1 and 2 show the escaped gas components and their isotopic compositions.

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Table 1 Escaped gas components from main springs at Tianchi volcanic geothermal area[a)]

Geothermal area	Water temperature /℃	Chemical components of main escaped gases (%)					
		CO_2	N_2	Ar	CH_4	H_2	He
Changbai	81.3—80.8	93.27—97.59	2.14—3.35	0.04—0.05	0	0.048 7—0.952 5	0.000 02
	77.3	94.52—95.19	5.14—3.25	0.05—0.10	0.47—0	0.036 5—0.721 0	0.000 1
	75.3	93.40	6.5	0.12	0.34	0.348 0	0.003 4
	72.3—71.5	89.80—73.55	7.9—5.2	0—0.06	0.22—0.34	2.000 0—1.369 0	0.000 6
	19.3—19.2	85.68—93.02	11.15—10.04	0.20—0.08	0	trace—0.297 6	0.006 0
Jinjiang	57.8	77.80—86.53	5.10—11.25	0—0.25	1.20—2.02	2.560 0—0.148 8	0.020 2
	57.4	84.28	3.86	0.09	1.25	0.020 3	0.031 2
	51.0	79.02	9.04	0.12	1.57	0.025 0	0.014 5

a) The change ranges of temperature and gas components are given for some springs.

Table 2 Isotopic compositions of escaped gases from main springs at Tianchi volcanic geothermal area[a)]

Geothermal area	Water temperature /℃	$^3He/^4He$ ($\times 10^{-6}$)	$^{40}Ar/^{36}Ar$	$^4He/^{20}Ne$	$^4He/^{40}Ar$ ($\times 10^{-3}$)	PDB (‰)			SMOW(‰)
						$\delta^{13}C_{CO_2(g)}$	$\delta^{13}C_{CH_4}$	$\delta^{13}C_{CO_2(L)}$	$\delta^{18}O_{CO_2}$
Changbai	19.2	7.89	291.6	40.62	43.9	-4.6		-5.5	27.8
	58.1	4.53	284.5	0.80	1.43	-5.6		-3.9	24.4
	71.5	7.92	310.1	7.28	7.89	-4.3	-35.65	-3.4	22.8
	75.3	7.99	295.7	14.44	16.0	-4.8	-36.36	-3.9	22.9
	77.3	7.77	313.0	9.01	1.99	-4.4		-4.2	22.8
	80.8	3.31	301.6	0.67	0.77	-4.2		-4.0	22.9
	81.3*	3.21	301.4	0.38	0.60	-6.6		-3.7	
Jinjiang	51.4*	7.70	347.2	65.67	37.5	-7.4	-30.40	-5.5	24.4
	57.8	7.51	303.4	73.12	60.2	-7.0	-30.44	-5.3	24.8
	51.0	8.24	301.5	99.00	79.3	-7.5	-26.15		25.7

a) The springs marked with * were determined in 1994, others in 1995.

1 Chemical components and isotopic compositions of main escaped gases

1.1 Carbon dioxide (CO_2)

The CO_2 is the principal component escaped from the Tianchi volcanic geothermal area, quite the same as other volcanic geothermal areas all over the world. The percentage contents are from 73.55% to 97.59%. The CO_2 content of escaped gases from the medium and deep-seated geothermal water shows an increasing trend with the rise of the water temperature.

The average $\delta^{13}C$ values of escaped CO_2 from Changbai and Jinjing geothermal areas are respectively −4.7‰ and −7.3‰. They all are in the range of the mantle-derived CO_2(−4.7‰—−8.0‰), derived from the basalt and its inclusion[3,4], but they are remarkably different. The $\delta^{13}C$ values of the CO_2 released from the Changbai geothermal area are always higher than that of Jinjiang, regardless of the dissolved and escaped CO_2. This indicates that their migrating and releasing mechanisms have a significant difference, although their source area could be the same.

1.2 Helium, argon, etc. rare gases

The $^3He/^4He$ ratio of the rare gas helium is the most reliable indicator of its material sources because the mantle, air and crust all have their fixed $^3He/^4He$ ratios. They are respectively

$(1.1—1.4)\times10^{-5}$, 1.4×10^{-6} and 2×10^{-8}[5]. At the Tianchi volcanic area, the $^3He/^4He$ ratios of Jijiang springs and the center springs of Changbai geothermal area (the round area in fig. 1) are remarkably the same, and average values are respectively 7.82×10^{-6} (5.59 Ra) and 7.89×10^{-6} (5.64 Ra). It is quite evident that most of the helium is derived from the mantle. The rare gas releasing features at that volcanic area indicate that these rare gases are mainly derived from the mantle and the air, the hybridism of the crust-derived gases is almost negligible[6]. Based on the bimodel mixed gases, we calculate that the average content of the mantle-derived He is about 67.29%, and the highest content is 71.25% in these eacaped gases. The $^3He/^4He$ ratios of the peripheral springs are relatively low in the Changbai geothermal area. The cause for this occurrence may be the outcropping positions of these springs to drift off the columnar field releasing area of mantle-derived He[6].

The relationships between the He contents and their $^3He/^4He$ ratios in natural fluids show that the gas samples of the Tianchi volcanic area have the lowest He content, with the highest $^3He/^4He$ ratio among three modern volcanic areas in China (figure 2).

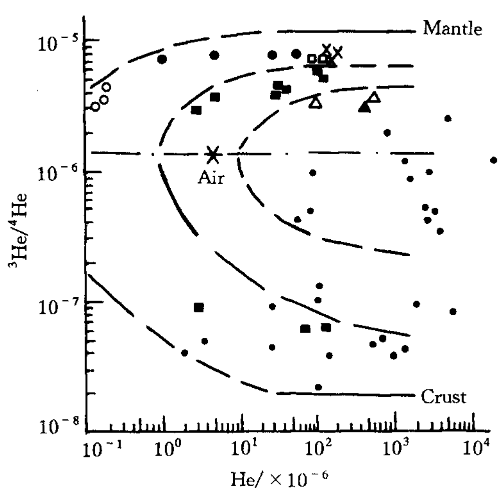

Fig. 2. Relationships between the He content of escaped gases from various springs and their $^3He/^4He$ ratios (the He data of the Tengchong and some active faults follow the reports of Wang, X., Dai, J. and Wang, W.[7—10]). ×, Jinjiang hot springs; ●, centric springs of Changbai hot springs; ○, peripheral springs of Changbai hot spring; □, Tengchong cold CO_2 springs; ■, Tengchong hot CO_2 springs; △, Wudalianchi cold CO_2 springs; ▲, surrounding cold CO_2 springs of Tianchi volcano; ·, hot and cold springs of various active faults.

At the Ticanchi volcanic area, the Ar contents of escaped gases from the deep-seated geothermal water are very low, usually 0.05%—0.06%. Because these Ar migrate and release together with the microcomponent mantle-derived He, it is inconceivable that there is not the mantle-derived Ar of the similar proportion to the mantle-derived He. At present, it is difficult to be sure of the proportion of the mantle-derived Ar in these gases because the $^{40}Ar/^{36}Ar$ ratio of the mantle-derived Ar is not definite. We tried to select two typical hot springs which are releasing a lot of deep-seated gases (71.5℃ and 77.3℃) and supposed that there is the same proportion of mantle-derived Ar as the associated He, and calculated the $^{40}Ar/^{36}Ar$ ratios of the source area of these mantle-derived gases according to the bimodel mixed gases, and the results are respectively 312 and 322. It is noted that the similar calculated result (326) is obtained for the peripheral hot spring (80.8℃) which is obviously affected by the shallow gases. These results suggest that the $^{40}Ar/^{36}Ar$ ratio of the source area from which the modern mantle-derived gases are emitted is about 322, slightly higher than the air (the corresponding $^3He/^4He$ ratio is 1.1×10^{-5}).

At the Tianchi volcanic area, there is a good linear correlation between the $^4He/^{20}Ne$ and the $^4He/^{40}Ar$ of escaped gases. The correlation curves roughly coincide with the tie-line of the two points which represent separately the mantle and the air (fig. 3). Fig. 3 shows that the escaped gases from the peripheral springs of Changbai geothermal area are greatly affected by the air, but those from Jinjiang geothermal area are slightly affected by the air.

1.3 Methane (CH_4)

Tables 1 and 2 also show that the CH_4 contents and their $\delta^{13}C$ values of escaped gases could be divided into two groups at the Tianchi volcanic area. At the Jinjiang geothermal area, the CH_4 contents of escaped gases are from 1.2% to 2.0%. These CH_4 may be characterized by an inorganic origin CH_4 because of a range of $\delta^{13}C$ from −26.15‰ to −30.44‰. This range of variation is roughly consistent with that of the $\delta^{13}C$ value for the CH_4 erupted from the volcanic geothermal area in Italy and New Zealand[10]. But the CH_4 contents of 0.22%—0.47% and their $\delta^{13}C$ value of −35.65‰—36.36‰ of the escaped gases at the Changbai geothermal area are all lower than that of the Jinjiang hot spring. It is said that the $\delta^{13}C$ value of −30‰ is the limit between organic and inorganic CH_4, and the $\delta^{13}C$ value of a few inorganic CH_4 could be −39‰. Dai *et al*. suggest that these CH_4 are also the inorganic origin because of the surrounding geological conditions[8]. Our data show that at the Tianchi volcanic area, the stable isotopic compositions of the CH_4, CO_2 and Ar escaped from the shallow thermal water are all slightly lighter than that of gases escaped from the deep-seated thermal water (fig. 4). We consider that the cause for this occurrence may be the isotopic fractionations, including once more equilibrium and kinetic fractionations in the process of the deep-seated gases migration from deep to shallow.

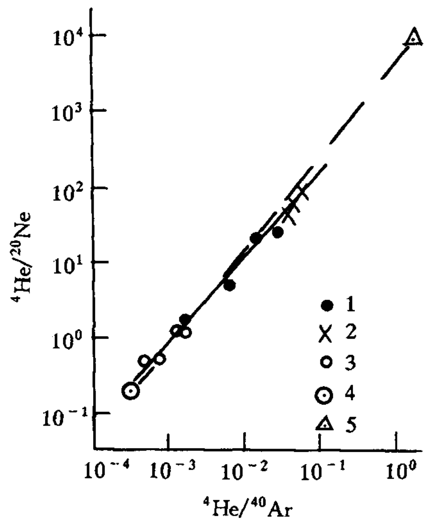

Fig. 3. Relationships between the $^4He/^{20}Ne$ and $^4He/^{40}Ar$ ratios of escaped gases from the Tianchi volcanic area. 1, Centric springs of Changbai hot springs; 2, Jinjiang hot spring; 3, peripheral springs of Changbai hot spring; 4, air; 5, mantle.

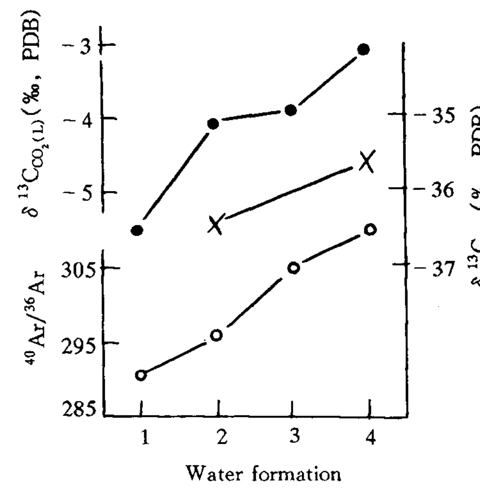

Fig. 4. Variation of the stable isotopic compositions of escaped gases from the various water formations at the Changbai geothermal area. ●, CO_2 (L); ×, CH_4; ○, Ar. 1, Cold spring; 2, shallow thermal water; 3, median thermal water; 4, deep-seated thermal water.

1.4 Hydrogen (H_2)

At the Tianchi volcanic area, the H_2 contents of escaped gases from geothermal water are from several hundred ppm to 2.56%, and the H_2 contents of escaped gases from the deep-seated thermal water are higher than that of shallow thermal water (fig. 5(a)). This fact shows that (i) these microhydrogens are derived from the deep inflow; (ii) the H_2 contents decrease gradually from the deep-seated to shallow thermal water. Fig. 5(b) shows that the H_2 contents of escaped gases at the Changbai geothermal area are negatively correlated with the δD values of the thermal water. Because the δD values of escaped H_2 from the geothermal area are very low with a range of δD from −310‰ to −826‰[10], it turns out that the δD reduction of the geothermal water appears to be related with the addition of the deep-seated H_2.

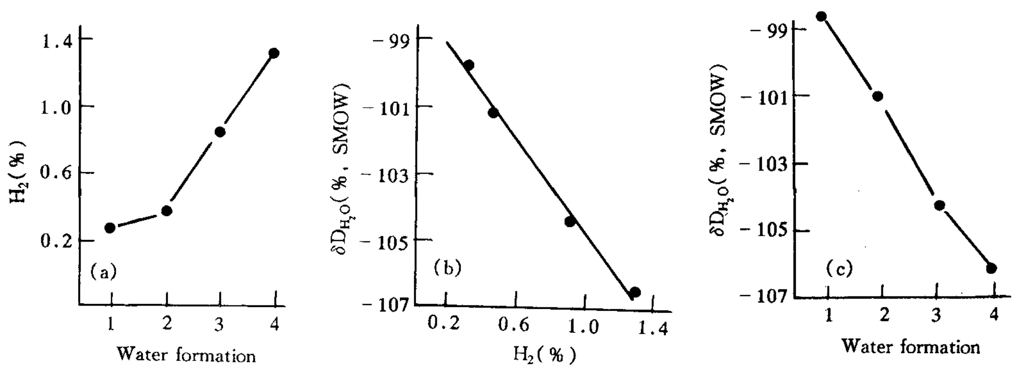

Fig. 5. H_2 contents of escaped gases from various water formations (a), δD values of the thermal water (c), and their relationship (b).

2 Material sources of main escaped gases from Tianchi volcanic geothermal area

The stable isotope features of the escaped He, CO_2, CH_4 from the Tianchi volcanic geothermal area suggest that these gases could be mostly derived from the emanation of the mantle-derived magma. But they are actually derived from the modern upper mantle or residual magma in the crust. Field investigation results indicate that in the area, the hydrothermal anomaly and deep-seated gas discharge which correlate with modern volcanic activity are all relatively low, the highest thermal water temperature is about 81℃, and there is not hot gas spring. The δD and $\delta^{18}O$ of these thermal water indicate that they are derived from the meteoric water[11]. Based on the lower δD and $\delta^{18}O$ values of deep-seated thermal water compared with the shallow thermal water, there is not significant addition of magmatic water derived from the upper mantle. Moreover, the average $^3He/^4He$ ratio (5.61 Ra) of the deep generated He which is not affected by the shallow gases is lower than the $^3He/^4He$ ratios (6—8 Ra) of the mantle-derived magma at the Western Pacific consuming zone. All the evidence suggests that the hydrothermal anomaly and the deep-seated gas discharges in that area are not caused by the magmatic intrusion of the modern upper mantle.

Are these mantle-derived gases derived from the cold volcanic rocks? The answer is in the negative. The relationship between the He contents and their $^3He/^4He$ ratios in the hot spring gases indicates that only the surrounding cold CO_2 spring in that area appears to be related with the cold volcanic rocks (fig.2). At the Tianchi volcanic geothermal area, the escaped gas itself is the hot gas, and its very low level of He release, the very high value of $^3He/^4He$ ratios and the highest level of H_2 release in all hot springs in China all indicate that the source area of these mantle-derived gases may be still in the high thermal state. We consider that they may be derived from the residual magma chamber which was left in history.

3 Gaseous geochemical characteristics of source area of deep-seated gases at present

It is of practical significance to study the gaseous geochemical characteristics of the residual magma chamber for estimating the activity of this volcano. Our data suggest that the chemical components and the isotopic compositions of the escaped gases from the deep-seated geothermal water may be very similar to that of the source area of the mantle-derived gases in the studied area, but the temperature of the source area must be much higher. In the source area, the CO_2 and H_2 contents may be even higher, the percentage content of He and the $^4He/^{20}Ne$, $^4He/^{40}Ar$ ratios must be much lower because they all become lower with the increase of the water temperature (fig. 6). These facts suggest that the main body of the source area had undergone the strong degasification before. And that just is the proper features of the residual magma chamber.

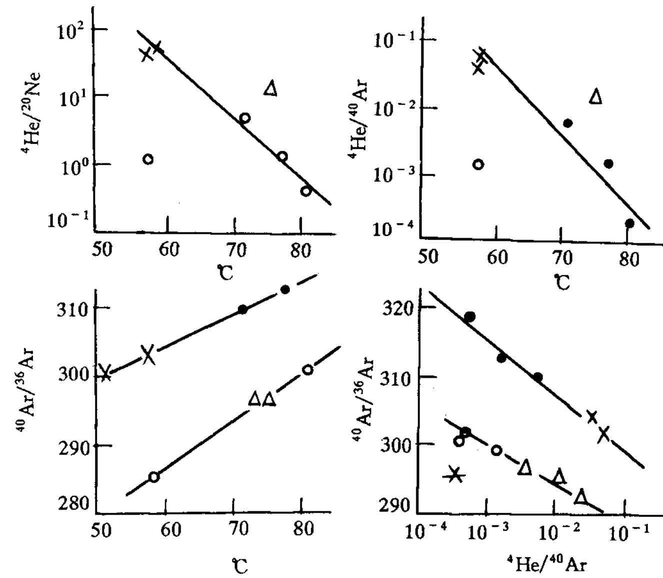

Fig. 6. Relationships between the temperature and the isotopic compositions of escaped rare gases from the Tianchi volcanic area. ×, Jinjiang hot spring; ●, deep-seated thermal water in the centric springs of Changbai hot springs; △, shallow thermal water in the centric springs of Changbai hot springs; ○, peripheral springs of Changbai hot springs; *, air.

Figure 6 also shows that the relationships between the temperature and the $^{40}Ar/^{36}Ar$ ratios of the escaped gases from the hot springs at the Tianchi volcanic area could be distinctly divided into two groups. And they all become higher with the increase of the water temperature. This indicates that the $^{40}Ar/^{36}Ar$ ratio of the source area of the deep-seated gases may be higher than that of escaped gases. In terms of the negative correlatogram between the $^{40}Ar/^{36}Ar$ and the $^4He/^{40}Ar$ ratios of escaped gases from those hot springs which are almost independent of the shallow gases (fig. 6), the $^4He/^{40}Ar$ ratio of the source area is about 10^{-4}, lower than that of the air. In general, the $^4He/^{40}Ar$ ratio of the upper mantle is 2 at least, or 4—5[5]. Hence it seems that the residual magma chamber may not be directly correlated with the upper mantle now. That is an isolated magma chamber.

At the Jinjiang geothermal area, besides the $^3He/^4He$ ratio, the contents of escaped CH_4, He, Ar from the hot springs and the $^4He/^{20}Ne$, $^4He/^{40}Ar$ ratios are much higher than those of Changbai hot springs, but the contents of escaped H_2 and CO_2 are relatively low. Their $\delta^{13}C_{CO_2}$, $\delta^{13}C_{CH_4}$, $^4He/^{20}Ne$, $^4He/^{40}Ar$, etc. are closer to the typical features of the mantle-derived gases. We consider that these deep-seated gases could reach quickly the surface by way of the active deep faults.

4 Temperature of the geothermal reservoir and its depth in the crust

It is considered that there are normal isotopic fractionations of the gas components among the deep-seated fluid while they migrate together. Based on the isotope chemistry principle, the stable isotopic fractionation between two gases varies with temperature, and has nothing to do with gas pressure. The fractionation between the CO_2 and CH_4 can be expressed as follows: $\Delta^{13}C_{CO_2\text{-}CH_4} = \delta^{13}C_{CO_2} - \delta^{13}C_{CH_4}$. In the studied area, the $\Delta^{13}C$ values between CO_2 and CH_4, dissolved and escaped CO_2, their carbon isotope geothermometer and the Na/K geothermometer of geothermal water are all shown in table 3. In general, the temperature which is got according to Craig's curve is relatively reasonable, and the temperature obtained from Bottinga's curve is much higher[16]. Table 3 shows that at the Changbai geothermal area the temperature of the carbon isotope and Na/K geothermometer apart from the temperature based on Bottinga's curve are both very similar, averaging (166 ± 9)℃. This fact indicates that there is a stable reservoir of the thermal water and the deep-seated gases. Our data suggest that this reservoir may be just located upon the residual magma chamber, and also accepts the remaining thermal energy and emanation derived from the magma chamber in a steady stream by way of the eruption canal in history. Based on the normal geothermal gradient (30℃/km), this reservoir could stably exist at a depth of 5.5 km in the crust, but its actual depth may be far shallower due to much higher geothermal gradient in general at the volcanic geothermal area.

Table 3 The stable carbon isotope of escaped gases and Na/K geothermometers at the Tianchi volcanic geothermal area

Geothermal area	Water temperature/℃	$\Delta^{13}C$(‰, PDB)		Na/K	Carbon isotope geothermometer/℃			Chemical geothermometer/℃ d)
		(CO_2-CH_4)	CO_2(L)-CO_2(g)		(CO_2-CH_4) a)	(CO_2-CH_4) b)	CO_2(L)-CO_2(g) c)	
Jinjiang	57.8	23.44	1.71	14.68	255	317	146	186
	57.4	23.00	1.88	14.93	260	323	141	185
Changbai	51.0	19.65			353	397		
	75.5	31.56	0.93	19.77	158	228	175	165
	71.5	31.35	0.92	20.28	161	230	175	163

a)—d) respectively follow the curves or equation of Craig[12], Bottinga[13], Deines *et al*.[14] and Fournier[15].

It is noted that three geothermometers are remarkably different according to the same method for the Jinjiang hot springs (table 3), suggesting that in that area the deep-seated gases could mainly migrate by way of the active deep faults. During the moving process from the deep-seated to shallow, the carbon isotope equilibrium between CO_2 and CH_4 may be frozen at first, but the equilibrium between the dissolved CO_2 and the gas-phase CO_2 may be frozen later. Our data show that the $\Delta^{13}C_{CO_2\text{-}CH_4}$ of the deep-seated gases in that area is correlated with their $^3He/^4He$ ratios (fig. 7). While the value of $\Delta^{13}C_{CO_2\text{-}CH_4}$ is smaller (corresponding to a higher temperature or a larger depth), the $^3He/^4He$ ratio of the deep-seated gas is much higher. And this phenomenon does not exist at the Changbai geothermal area. We consider that this phenomenon may be characterized by the migration of the deep-seated gases by way of the active deep faults at the volcanic area.

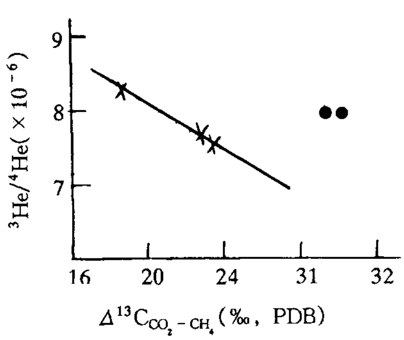

Fig. 7. Relationship between $\Delta^{13}C_{CO_2\text{-}CH_4}$ and their $^3He/^4He$ ratios of escaped gases from the Tianchi volcanic geothermal area. ×, Jinjiang geothermal area; ●, Changbai geothermal area.

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