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Helium and carbon isotope variations in Liaodong Peninsula, NE China

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ABSTRACT

Chemical and C–He isotopic compositions have been measured for N_2-rich hydrothermal gases from the Liaodong (abbreviation of East Liaoning Province) Peninsula from which the oldest crustal rocks in China with $\geqslant$3.8 Ga outcrop. With the exception of one sample containing tritogenic ^3He and atmospheric ^4He in Liaoyang, the observed $^3He/^4He$ ratios from 0.1 Ra to 0.7 Ra indicate 1–8% helium from mantle, 92–98% from crust and 0.1–0.8% from atmosphere. Despite the lack of Quaternary volcanism, such $^3He/^4He$ ratios suggest, together with geophysical evidences, the existence of intrusive magmas that contain mantle helium and heat within the Liaodong middle-lower crust. The $^3He/^4He$ ratios are high along the NE-trending Jinzhou faults and gradually decrease with the increase of distance from the faults. Such a spatial distribution suggests that the mantle helium exsolves from magmatic reservoir in the middle-lower crust, becomes focused into the root zones of Jinzhou faults, and subsequently traverses the crust via permeable fault zones. When transversely migrated by groundwater circulation in near surface, mantle helium with high $^3He/^4He$ ratio may have been further diluted to the observed values by addition of radiogenic helium produced in the crust. This pattern shows strong evidence that the major faults played an important role on mantle-derived components transport from mantle upwards.

1. Introduction

The isotopic composition of terrestrial helium varies by more than three orders of magnitude from a typical radiogenic value of ~0.02 Ra where Ra is atmospheric $^3He/^4He$ of 1.4×10^{-6}, produced through the decay of uranium and thorium series isotopes in crust, to 8 ± 1 Ra in mantle (e.g., Mamyrin and Tolstikhin, 1984). Therefore, $^3He/^4He$ is a powerful indicator to identify the source of volatile entering the crust and therefore sensitive to discern changes in the balance between crustal and mantle-derived volatiles contributing to the total volatile inventory. In continental environments, it has been established that the mantle-derived helium has a close relationship with recent magmatic activity (i.e., Sano et al., 1984) and can also present in areas of active extensional environment without recent surface volcanism (O'Nions and Oxburgh, 1988; Kennedy and van Soest, 2006). Recently, mantle-derived helium has been observed in tectonically compressional areas (Kennedy et al., 1997; Umeda et al., 2008). Since Kennedy et al. (1997) first reported high $^3He/^4He$ ratios along the San Andreas Fault, recent studies suggest that the mantle-derived helium can be transported from the mantle through fault fractures (Kulongoski et al., 2005; Kennedy and van Soest, 2006, 2007; Doğan et al., 2006; Doğan et al., 2009; Umeda et al., 2008; Umeda and Ninomiya, 2009; Klemperer et al., 2013).

$^3He/^4He$ ratios have been extensively investigated for natural gases and hydrothermal gases in the Chinese continent during last 20 years (i.e., Xu et al., 1995, 2004; Yokoyama et al., 1999; Dai et al., 2005; Du et al., 2006; Klemperer et al., 2013). However, detailed studies of mantle-derived components associated with the non-volcanic areas are sparse (Yokoyama et al., 1999; Du et al., 2006; Klemperer et al., 2013). Thus, this paper examines regional spatial distribution of $^3He/^4He$ ratios in hydrothermal fluids in Liaodong Peninsula, a non-volcanic area (Fig. 1). The general aim is to refine the relationships between $^3He/^4He$ ratios, tectonics and recent seismic activities.

2. Geological backgrounds

The Liaodong Peninsula is geologically located in the eastern margin of the North China Craton which is one of the world's oldest Archean cratons and preserves crustal remnants as old as $\geqslant$3.8 Ga in Anshan regions (Liu et al., 1992). In addition to the Archean and

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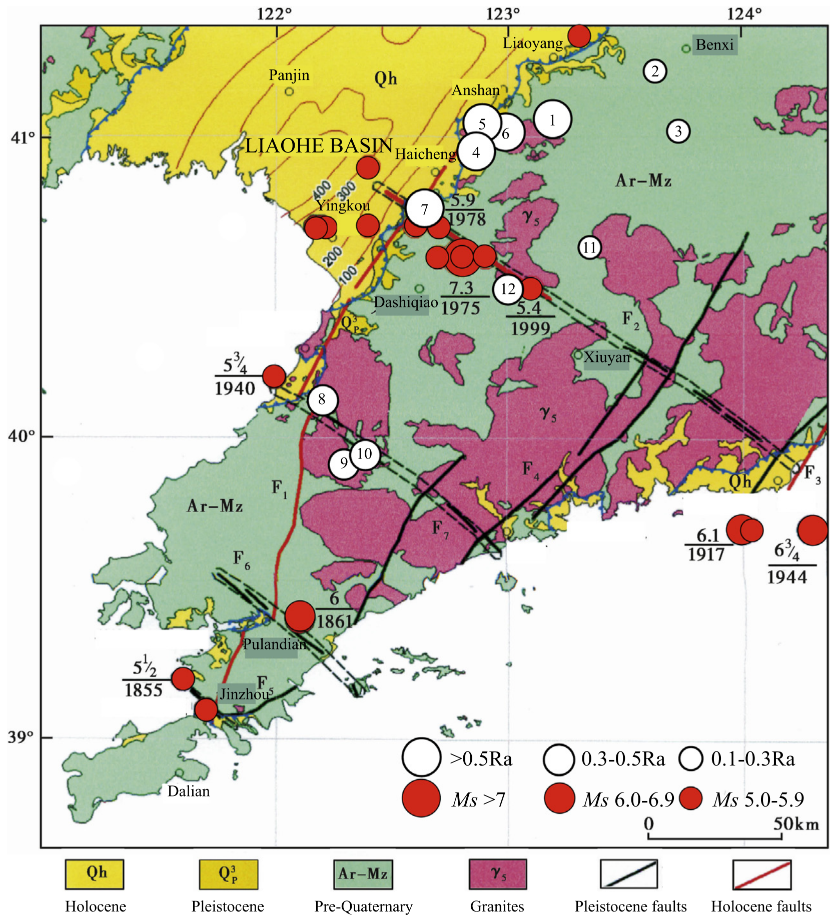

Fig. 1. Simplified geological map of Liaodong Peninsula (modified from Wan et al., 2013). Distributions of $^3He/^4He$ ratio (white circles) and historical earthquake (red circles) are shown. The regional major faults are labeled as F1–F7 (F1, Jinzhou; F2, Haichenghe; F3, Yalujiang; F4, Zhuanghe; F5, Daheshangshan; F6, Pulandian-changhai; F7, Xiongyue-zhuanghe). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Proterozoic metamorphic rocks, there are regional outcrops of Paleozoic and Mesozoic sedimentary rocks. These include Cambrian calcirudite, shale and dolomite, and Carboniferous sandstone, mudstone and conglomerate. Volcanic rocks include Archean granite, Permian diorite, Jurassic adamellite and Cretaceous granite. The most recent and extensive igneous activities are the Early Cretaceous granites with the age of 126 Ma, indicating Mesozoic extensional tectonic structures in Liaodong Peninsula (Wu et al., 2005; Yang et al., 2006; Liu et al., 2011).

The region is mainly controlled by the NE–SW and NW–SE trending active fault systems (Lei et al., 2008). The NE–SW trending Jinzhou fault is considered as one of the boundary faults to separate the Mesozoic-Cenozoic extensional Liaohe basin in west and the uplifted Liaodong Peninsula in east. Along the 220 km long Jinzhou fault, there are numerous hot springs and occurrence of historic earthquakes. Zhong and Xiao (1990) pointed out the fact that the hydrothermal fluids emerge in places where the NE–SW and NW–SE fracture systems intersect (Fig. 1). Moderate-strong earthquakes happened frequently in the Liaodong Peninsula. In addition to the well-known Haicheng $M7.3$ earthquake (40°42′N, 122°42′E), which occurred in 1975, there are 19 historical earthquakes of $M \geqslant 5$ recorded in this region since 1855 (Wan et al., 2013). Seismic and gravity evidences show that the crustal thickness under Liaodong today is approximately 32–36 km, significantly greater than the adjacent Liaohe basin (30–32 km). The regional terrestrial heat flow has been measured to 50–117 mW m^{-2} (Wang et al., 1987; Hu et al., 2000). Therefore, it is evident that recent seismic activity, hydrothermal activity and active faults are spatially coupling in the Liaodong Peninsula (Lu et al., 1990, 2002).

3. Sampling and experiments

Liaodong Peninsula is one of the strongest geothermal zones in China. There are more than 40 hot springs with temperature of over 20 °C and dominantly Na^+, SO_4^- and HCO_3^- types in water chemistry (Zhong and Xiao, 1990). The hydrothermal gases in this study were emanating from hot springs and geothermal wells with the temperatures from 13 °C to 80 °C. The bubbling gas samples were collected into a 50-mL volume glass container with vacuum valves in both sides using the water displacement method.

About 1 ml gases were introduced into a vacuum system to separate helium from other gas components. ^4He and ^{20}Ne concentrations were measured by a built-in quadrupole mass spectrometer. After helium being further separated from neon under temperature condition of 40 K, $^3He/^4He$ ratio was determined using a static mass spectrometer (VG5400, Micromass). Air was used as a standard for noble gas isotope analyses. Detailed description of the analysis procedure can be found elsewhere (Xu et al., 1995).

The $\delta^{13}C$ of CO_2 and CH_4 were measured by a conventional isotope ratio mass spectrometer (Delta S). The results are expressed as per mil derivations from the Pee Dee Belemnite (PDB) standard. The typical analytical precision is around ±0.3‰ on the δ scale.

4. Results and discussion

The analytic results of gas chemical and isotopic compositions are listed in Table 1. With the exception of sample No. 10 from Jiantang that contains 25% CO_2 and $\delta^{13}C$ value of −4.8‰, the other

Table 1
Chemical and isotopic compositions of hydrothermal gases from Liaodong Peninsula.

No.	Sample ID	Temperature (°C)	Location (N, E)	N_2 (%)	CH_4 (%)	CO_2 (%)	He (ppm)	$\delta^{13}C_{CO2}$ (‰)	$\delta^{13}C_{CH4}$ (‰)	$^3He/^4He$ (R/Ra)	$^4He/^{20}Ne$	$CO_2/^3He$ (10^6)	He_A[a] (%)	He_M[a] (%)	He_C[a] (%)
1	Tonghe, Liaoyang	13	41°07′, 123°22′	91.2		0.986	5.6	−22.6		1.57 ± 0.02	0.33	800	97	–	–
							5.7			1.58 ± 0.02	0.32		100	–	–
2	Wenquanci, Benxi	43	41°20′, 124°02′	92.6	0.004	0.566	1150	−19.5	–	0.225 ± 0.004	370	15.6	0.1	2.6	97.3
3	Caohezhang, Benxi	57	41°05′, 124°11′	97.3	0.173	0.152	720	−24.1	−48.3	0.129 ± 0.002	74	11.7	0.4	1.4	98.2
4	Tonggangzi, Anshan	69	41°00′, 122°54′	94.0	0.296	0.11	1320	−19.3	−28.5	0.623 ± 0.008	300	0.955	0.1	7.6	92.3
5	Tonggangzi, Anshan	59	41°00′, 122°54′	94.0	0.185	0.291	1220	−32.2	–	0.638 ± 0.008	280	2.67	0.1	7.7	92.1
6	Qianshan, Anshan	52	41°03′, 123°08′	90.0	–	0.639	1340	−23.9	–	0.531 ± 0.007	240	6.41	0.1	6.4	93.5
7	Donghuangdi, Haicheng	88	40°40′, 122°44′	94.3	0.287	0.312	1480	−12.9	−38.4	0.654 ± 0.008	340	2.30	0.1	7.9	92.0
8	Xiongyue, Gaixian	80	40°10′, 122°10′	94.4	0.68	2.16	1290	−14.5	−35.6	0.476 ± 0.006	230	25.1	0.1	5.7	94.1
9	Anbo, Pulandian	66	39°50′, 122°18′	94.3	0.558	0.177	1000	−20.1	−43.3	0.321 ± 0.005	110	3.94	0.3	3.8	95.9
10	Jiantang, Pulandian	54	39°55′, 122°25′	75.0	0.434	25.4	1150	−4.8	−25.7	0.327 ± 0.005	370	482	0.1	3.8	96.1
11	Chaoyang, Xiuyan	34	40°32′, 123°37′	97.4	0.055	0.051	530	−22.3	−44.0	0.205 ± 0.003	40	3.35	0.8	2.3	96.9
12	Hadabei, Xiuyan	47	40°23′, 123°10′	95.8	0.49	0.164	1220	−19.7	−37.0	0.340 ± 0.005	200	2.82	0.2	4.0	95.8
	Air						5.2			1	0.32				

[a] He_A, He_M and He_C denote percentage of helium from atompshere, mantle and crust, respectively.

gases from Liaodong area are N_2-dominant, and contain low CO_2 and CH_4 from 0.1% to 2% and from 0.004% to 0.7%, respectively. $\delta^{13}C$ values of CO_2 vary greatly from −13‰ to −32‰, indicating CO_2 enriched relatively in ^{12}C.

Helium concentrations vary greatly from 6 ppm up to 1500 ppm in the hydrothermal gases. The observed $^3He/^4He$ and $^4He/^{20}Ne$ ratios also show wide variability from 0.1 Ra to 1.6 Ra and from 0.3 to 370, respectively. The sample No. 1 from Tanghe has air-like helium concentration and $^4He/^{20}Ne$ ratio, but the $^3He/^4He$ ratio is significantly higher than the atmospheric value. Duplicate analysis of this sample showed consistent results of helium concentration, $^3He/^4He$ and $^4He/^{20}Ne$ ratios, confirming high reproducibility of measurements. For the other samples, helium concentrations and $^4He/^{20}Ne$ ratios are two orders of magnitude higher than atmospheric value. However, $^3He/^4He$ ratios are significantly low from 0.1 Ra to 0.7 Ra.

With the exception of air-like sample (No. 1) and CO_2-rich sample (No. 10), the low $CO_2/^3He$ ratios are found in the other gases ranging from 10^6 to 10^7. Overall, no clear correlations can be found between temperature and gas concentrations, and isotopic compositions.

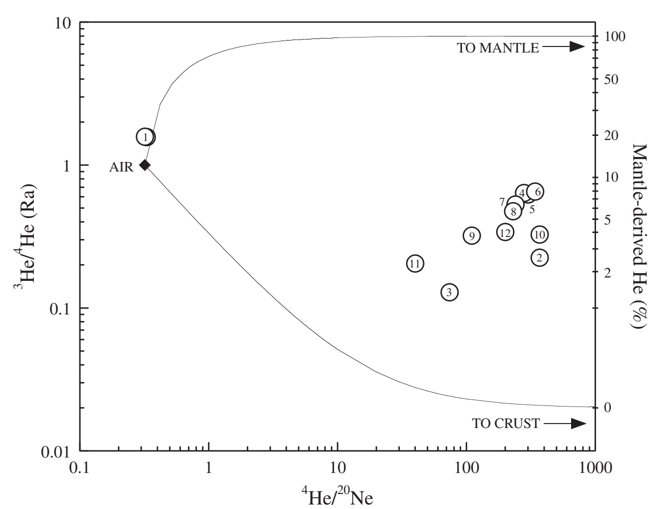

Fig. 2. Relationship of $^3He/^4He$ and $^4He/^{20}Ne$ ratios of hydrothermal gases in Liaodong Peninsula.

4.1. Helium origins in Liaodong Peninsula

In general, terrestrial helium has three major origins: atmospheric, crustal nucleogenic/radiogenic and mantle-derived origin, each of which has distinct $^3He/^4He$ and $^4He/^{20}Ne$ ratios (Fig. 2). However, anomalous excess of ^3He can be resulted from tritogenic ^3He produced by the decay of natural and anthropogenic tritium (^3H) in groundwater through reaction $^3H(\beta^-)^3He$. On the other hand, nucleogenic ^3He can also be anomalously produced by the nuclear reaction $^6Li(n,\alpha)^{three}H(\beta^-)^3He$ in lithium-rich surrounding rocks.

The Tanghe sample (No. 1) collected from a spring with low temperature of 13 °C displays air-like helium concentration and $^4He/^{20}Ne$ ratio. As neon is generally atmospheric in shallow fluids, the $^4He/^{20}Ne$ ratio is considered as an indicator of atmospheric component. Thus, the air-like $^4He/^{20}Ne$ ratio in this sample strongly indicates its atmospheric ^4He. However, the sample exhibits $^3He/^4He$ ratio significantly higher than the atmospheric value by ~60% (Table 1). Together with helium and neon chemical compositions, the elevated $^3He/^4He$ strongly suggests the presence of tritogenic ^3He, originating from the copious amounts of tritium released into the atmosphere as a result of global nuclear weapons testing from the 1960s (Happell et al., 2004). A similar observation has been found from some hydrothermal gases in Tibet (Yokoyama et al., 1999). Presence of tritogenic ^3He in the sample further indicates that the water emanating from this spring is very young (i.e., <50 years), suggesting a weak rock-water interaction by which radiogenic helium are generally released from surrounding rocks.

This observation clearly distinguishes this sample from the others that exhibit a low $^3He/^4He$ ratio range of 0.1–0.7 Ra and two orders of magnitude higher helium concentrations. Although we have no data of tritium concentration in local precipitations in 1960s, the very high helium concentrations in the samples exclude the possibility for their isotopic composition to have been affected by tritiogenic ^3He in the groundwater.

In nature, the nucleogenic ^3He is mainly produced by $^6Li(n,\alpha)^3H(\beta^-)^3He$ reaction described above and therefore subject to the lithium concentration, and neutron flux which is induced by radioactive elements such as uranium and thorium. On the other hand, the radiogenic ^4He is mostly formed by radioactive decay of natural uranium and thorium. Therefore, the ^3He and ^4He production rates can be calculated by equations (Castro, 2004).

$$P(^3He) = (6.035[U] + 1.434[Th]) \times [Li] \times 4.4516 \times 10^{-23}\ mol\ g^{-1}\ yr^{-1} \quad (1)$$

$$P(^4He) = 1.71 \times 10^{-25}[U] + 4.06 \times 10^{-26}[Th]\ mol\ g^{-1}\ s^{-1} \quad (2)$$

Gao et al. (1998) reported lithium contents in the upper, middle and lower Chinese continental crust ranging in 14–22 ppm, 14–18 ppm and 9–18 ppm, respectively. In the Liaodong crust, Teng et al. (2009) reported lithium concentrations from 10 ppm to 129 ppm with an average of 55 ± 50 ppm. These datasets seem to exclude the regional anomalous enrichment of lithium in Liaoodng crustal rocks. The uranium and thorium concentrations in the thirty granites are in range of 2–127 ppm (average 12 ± 25 ppm) and 9–31 ppm (average 16 ± 5 ppm), respectively (Yang et al., 2006). Taking into account of the average uranium, thorium and lithium concentrations in Liaodong crust, the theoretical calculation based on Eqs. (1) and (2) results in $^3He/^4He$ ratio $\sim 3 \times 10^{-8}$ (or ~0.02 Ra). This value is in good agreement with the typical crustal $^3He/^4He$ ratio. Thus, it is highly considerable that there is insignificant contribution of anomalous nucleogenic ^3He produced in the Liaodong crustal rocks.

By excluding the possible existence of anomalous tritogenic and nucleogenic ^3He origins in samples other than sample No. 1 that enriches in tritogenic ^3He, we can conclude that helium in Liaodong exhibits a mixture of atmospheric, crustal radiogenic and mantle-derived components. The high $^4He/^{20}Ne$ ratios indicate that atmospheric helium can be neglected in Liaodong. For example, the lowest $^4He/^{20}Ne$ ratio of 40 is observed in sample No. 11. This value is two orders of magnitude higher than those for atmospheric or atmospheric dissolved water, suggesting only about 0.8% helium contribution from the atmospheric component. Thus, taking the mantle-derived and crustal radiogenic $^3He/^4He$ of 8 Ra and 0.02 Ra respectively, we estimate the mantle-derived helium in the Liaodong hydrothermal fluids ranging from 1% to 8% (Table 1 and Fig. 2).

The mantle-derived helium in Liaodong is significantly lower than those observed in the other hydrothermal systems in Chinese continent and adjacent sedimentary basins. For example, $^3He/^4He$ ratios up to 5 Ra have been found in Tengchong and Changbaishan (Xu et al., 2004; Hahm et al., 2008), both of which are characterized by high temperature hydrothermal activity associated with Quaternary volcanism. The highest $^3He/^4He$ in the adjacent Mesozoic-Cenozoic extensional Liaohe basin is 4 Ra (Xu et al., 1995). However, the low $^3He/^4He$ ratios in this study are comparable with those observed in non-volcanic area such as the thickened Tibetan crust (Yokoyama et al., 1999) and seismic active areas in Sichuan (Du et al., 2006). In these two studies, the mantle-derived helium was interpreted in items of existence of hidden magmatic reservoir and strong seismic activity, respectively.

Thus, our results are consistent with the previous findings that the mantle-derived mantle can occur in non-volcanic area (O'Nions and Oxburgh, 1988; Kennedy and van Soest, 2006). Then question arises of how the mantle-derived helium was transformed from the lithosphere mantle to the surface. It has been known that the most plausible means of scavenging and concentrating helium with very low concentrations in the mantle is partial melting and that the existence of mantle-derived components in near surface fluids may provide evidence of sub-surface magmatism when other indicators are lacking (O'Nions and Oxburgh, 1988). Such partial melting process most likely occurred at boundary between lithospheric mantle and crust. However, they can remain in situ at boundary between mantle and crust (Kennedy et al., 1997), but also can rise along fissures and pond in the crust (Yokoyama et al., 1999). In any case, fault is considered an important path way for the mantle-derived component to escape from the partial melting zone, as proposed in the San Andrew Fault in North America (Kennedy et al., 1997), the Median Tectonic Line in Japan (Doğan et al., 2006), the North Anatolian Fault in Turkey (Doğan et al., 2009), and Karakoram Fault in Tibet (Klemperer et al., 2013).

There are several geophysical data suggesting the intrusion of magma in the Liaodong crust. It has been discovered that there exists a train of key geophysical anomalies of low wave velocity, high conductance, low density, high heat flow, etc., all of which are spatially consistent with the Haicheng *M*7.3 earthquake hypocentral area (Lu et al., 1990, 2002). For example, the materials with P wave velocity of 6 km s^{-1} exist between 15 and 22 km beneath the Haicheng area, which is 0.2–0.4 km s^{-1} lower than the upper and lower crustal materials. Resistivity of crustal materials between 15 and 20 km are 4–6 Ωm while that of the surrounding rocks up to 10^3–10^4 Ωm. The density of crustal materials between 15 and 20 km differs from the other depths by 0.02–0.04 kg m^{-3}. In addition, the Haicheng and adjacent areas are located in high heat flow zone. The regional highest heat flow of 117 mW m^{-2} was obtained from the well where the sample No. 7 with the regional highest $^3He/^4He$ ratio was collected (Wang et al., 1987). This high heat flow value is comparable with those observed in high temperature hydrothermal systems at Tengchong and Tibet (Hu et al., 2000). Thus, these geophysical anomalies have been attributed in terms of molten or partially molten materials at 15–22 km beneath the Haicheng and adjacent area. Our elevated $^3He/^4He$ ratios are compatible with model that the molten or partially molten materials are most likely the intrusive magma which was initially produced at boundary between lithospheric mantle and crust around 32 km and subsequently rose into the crust and pond around 15–22 km along fissures in the studied area.

It should be pointed out that the partially melting materials at 15–22 km were proposed to probably originate from the surrounding Mesozoic granites (Li et al., 1997). Indeed geochemical and Sr–Nd–Hf isotopic evidence suggested about 20–25% subcontinental lithospheric mantle origin for the Qianshan A-type granites during the Early Cretaceous (Yang et al., 2006). However, signature of mantle-derived helium in the granitic reservoir, if exists, might be totally hided or diluted by radiogenic helium produced since the isolation from the lithospheric mantle. The $^3He/^4He$ ratio in the granitic reservoir is the sum of the initial $^3He/^4He$ value and radiogenic helium produced in situ from uranium and thorium since intrusion.

$$\left(\frac{^3He}{^4He}\right)_t = \frac{[^3He]_0 + [^3He]_t}{[^4He]_0 + [^4He]_t} \quad (3)$$

where subscript *0* stands for the initial mantle-derived ^3He and ^4He concentrations in the magmatic reservoir, whereas *t* the accumulated radiogenic ^3He and ^4He concentrations produced from Li, U and Th elements after a certain time period as expressed in Eqs. (1) and (2). In most circumstances, $[^3He]_t$ is much less than $[^3He]_0$

in continental crustal systems so that the Eq. (3) can be simplified as following.

$$\left(\frac{^3He}{^4He}\right)_t = \left(\frac{^3He}{^4He}\right)_0 \left(\frac{1}{1+[^4He]_t/[^4He]_0}\right) \quad (4)$$

Therefore, $^3He/^4He$ ratio in the granitic magmatic reservoir depends on initial $^3He/^4He$ ratio and ^4He concentration, and accumulated radiogenic ^4He concentrations. Adopting the typical subcontinental lithospheric mantle value of 7 Ra (6.1 ± 0.9 Ra in Gautheron and Moreira, 2002), the initial $^3He/^4He$ ratio in the granite containing 20–25% mantle components is then estimated to be 1.8 Ra. Accumulation of radiogenic ^4He concentrations in the granites can be estimated from Eq. (2) with the uranium (12 ± 25 ppm) and thorium (16 ± 5 ppm) concentrations in intrusion rocks and time period of 126 Ma (Yang et al., 2006). Although there is no available ^4He data of local subcontinental lithospheric mantle, ^4He concentrations in mantle-derived xenoliths from adjacent Kuangdian, ~250 km northeast of Haicheng were reported in range of 0.2–1 × 10^{-8} cm^3 STP g^{-1} (Xu et al., 1998). Thus, assuming that the initial ^4He concentration is 10^{-8} cm^3 STP g^{-1}, the $^3He/^4He$ ratio in the granitic magmatic reservoir would be 0.001 Ra. It has been argued that the mantle xenolith might not be the ideal representative of lithospheric mantle component (Gautheron and Moreira, 2002). The measured ^4He concentration in the worldwide subcontinental lithospheric mantle varies within the range of 10^{-10}–10^{-6} cm^3 STP g^{-1} (Gautheron and Moreira, 2002 and references therein). Gautheron and Moreira (2002) suggested that the helium contents (10^{-7}–10^{-6} cm^3 STP g^{-1}) of the subcontinental lithospheric mantle are realistic compared to the measurements. Thus, taking the maximal ^4He of 10^{-6} cm^3 STP g^{-1} as an initial value, the $^3He/^4He$ ratio in the granitic reservoir would still be 0.007 Ra. It is possible that a lot more mantle He was involved in the melting event than estimated from the Sr–Nd–Hf system because the Sr–Nd–Hf system is highly decoupled from the very mobile He. If this is a case, given the most extreme case (100% subcontinental lithospheric mantle helium component in granite with $^3He/^4He$ = 7 Ra and ^4He = 10^{-6} cm^3 STP g^{-1}), the resulted $^3He/^4He$ in the 126 Ma-old granitic magma would be still less than 0.03 Ra after radiogenic ^4He accumulation during the isolation period from the subcontinental lithospheric mantle. It is clear that in any cases, the resulted $^3He/^4He$ ratios in the granitic melts are comparable with the typical crustal value. Therefore, it is highly considerable that the molten or partially molten materials at 15–22 km might not have been produced from the surrounding Mesozoic granites, but instead most likely originated from the boundary between lithospheric mantle and crust beneath the Liaodong Peninsula.

4.2. $^3He/^4He$ spatial distribution and upflow of mantle-derived helium

As illustrated in Fig. 1, the regional highest $^3He/^4He$ ratios (~0.7 Ra) are observed between Haicheng and Anshan along the Jinzhou fault. There appears to be a general trend in decreasing $^3He/^4He$ ratio from the Jinzhou fault eastwards (Fig. 3). Such a trend suggests that mantle-derived helium leakage through hydrothermal degassing in Liaodong is greater along the Jinzhou fault (~8% of total He) than east of the fault (1–3% of total He). The similar feature has been observed in other continental settings with extensional and compressional tectonics such as the San Andrew Fault in North America (Kennedy et al., 1997), the Median Tectonic Line in Japan (Doğan et al., 2006); the North Anatolian Fault in Turkey (Doğan et al., 2009), and Karakoram Fault in Tibet (Klemperer et al., 2013). In addition, in active earthquake area like Tottori area, SW Japan, the maximum $^3He/^4He$ ratio (~4 Ra) was observed from the epicenter of the main shock and decreased with distance away

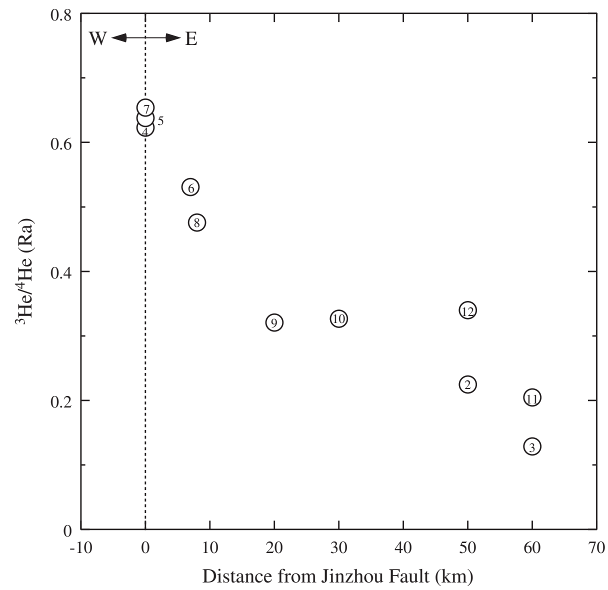

Fig. 3. Plot of $^3He/^4He$ ratios as a function of distance from the Jinzhou fault in Liaodong Peninsula.

from the main trace of the fault segments (Umeda and Ninomiya, 2009). These observations have been explained that mantle helium exsolves from partially-melted regions in the upper mantle, becomes focused into the root zones of major crustal faults, and subsequently traverses the crust via permeable fault zones. Under these circumstances, this idea has been postulated to account for the range in $^3He/^4He$ ratios, and seems appropriate in this study.

Obviously, due to mantle-derived helium released from magmatic reservoir in local shallow crust in Liaodong Peninsula, we consider that mantle-derived helium may have been vertically transformed from the reservoir along the Jinzhou faults. As fluids circulate through and equilibrate with the crust, the isotopic compositions of dissolved constituents will be modified by water–rock processes such as mineral dissolution, diffusive exchange, etc. It is expected that the isotopic composition of mantle helium (~8 Ra) would be diluted with radiogenic helium (0.02 Ra) during transfer through the crust. In this way, slow transport of mantle helium would result in relatively greater dilution with radiogenic helium, and mixing helium with relatively low $^3He/^4He$ ratio (i.e., the regional highest ratio ~0.7 Ra) would be expected at the surface. When this mixing helium was incorporated in the hydrothermal fluids near surface, further lateral contamination by radiogenic helium resulted in low and variable $^3He/^4He$ ratios depending on the distance from the Jinzhou faults.

4.3. Heat source of Liaodong hydrothermal system

Continental heat flow can be generally described as the sum of heat produced in the crust and the mantle heat flow. The heat in the crust is mainly generated form radioactive decay of long-lived nuclides such as uranium, thorium and potassium. In Chinese continent, there are mainly three types of geothermal systems, high-temperature, low-middle temperature, and low temperature geothermal systems. There is no doubt that the heat source of the high-temperature hydrothermal system associated with recent volcanism can be concluded from the upper mantle (i.e., Tengchong, Xu et al., 2004). However, heat sources for the low-middle and low temperature geothermal zones are generally considered to be resulted from the heat producing elements in crust. This is particularly considered to be true in areas like Southeastern China

Coast and Liaodong Peninsula where the Mesozoic granites extensively distribute. If this is the case, the $^3He/^4He$ ratios in these environments would be expected to be typical crust value. However, the existing mode cannot explain the observed high $^3He/^4He$ ratios of the geothermal gas in Liaodong Peninsula. Like the observation in Tibet (Yokoyama et al., 1999), our $^3He/^4He$ results require the injection of helium from the mantle and therefore suggest partially mantle-derived heat source. This finding is supported by the regional geophysical observations.

4.4. CO_2 and CH_4 in Liaodong hydrothermal gases

Terrestrial CO_2 may be released from three main sources each of which has different carbon isotope compositions: (1) mantle-derived CO_2 with $\delta^{13}C$ values in the range of −3‰ to −8‰ (i.e., Javoy et al., 1986); (2) dissolution of marine limestone and metamorphic CO_2 having CO_2 with $\delta^{13}C$ value around 0‰; (3) organic CO_2 with $\delta^{13}C$ values less than −20‰. Dai et al. (2005) compiled $\delta^{13}C_{CO2}$ values of more than 200 natural gases in China ranging from +7‰ to −39‰. Indeed, they proposed a $\delta^{13}C$ value range of organic CO_2 (−10‰ to −30‰) and an inorganic CO_2 (metamorphic or magmatic) range from −8‰ to +3‰. It can be somewhat distinguished that the $\delta^{13}C$ values of metamorphic CO_2 derived from carbonate thermal decomposition are close to the mean $\delta^{13}C$ values of carbonate rocks (0 ± 3‰), while the $\delta^{13}C$ values of magmatic or mantle derived CO_2 mainly cluster around −6 ± 2‰. However, the partially overlapping $\delta^{13}C$ values between magmatic and metamorphic CO_2 do not allow us to identify their source by certain. Thus, combinations of $^3He/^4He$, $\delta^{13}C$ and $CO_2/^3He$ are considerable to assess the CO_2 source.

It is well known that the escape of mantle-derived He and CO_2 is coupled (i.e., O'Nions and Oxburgh, 1988; Karlstrom et al., 2013). If mantle-derived fluids pass through the lithosphere without any significant fractionation, then the $CO_2/^3He$ ratio in near surface should reflect binary mixture between a mantle and a crustal source. There should be a negative correlation between $^3He/^4He$ and $CO_2/^3He$ ratios in the hydrothermal system, if two-component mixing is valid (O'Nions and Oxburgh, 1988). As a result, the mixed fluid would be expected to have a $CO_2/^3He$ ratio between typical mantle (2×10^9) and crustal value (>10^{10}). Compared with these end-members (Marty and Jambon, 1987), all hydrothermal gas samples in Liaodong have significantly low $CO_2/^3He$ from 1×10^6 to 8×10^8. In comparison with other studies of similar systems (i.e., Giggenbach et al., 1993; Xu et al., 2004; Gilfillan et al., 2008; Doğan et al., 2009), the Liaodong samples are characterized by extremely low $CO_2/^3He$ ratios by several orders of magnitude. Three processes are suggested to explain the very low ratios: (1) fractionation between carbon and helium, (2) preferential loss of CO_2 by precipitation of calcite and (3) addition of crustal radiogenic helium. It seems clear that process (3) cannot explain the very low ratios, since the He source associated with the crustal end-member carbon components (e.g., metamorphic and organic in Fig. 4) is radiogenic. In process (1), fractionation of C and He is most likely driven by solubility differences during phase separation. If this is the case, this process by itself cannot explain the very low $CO_2/^3He$ ratios, since He and CO_2 solubility in water is very similar and degassing would not have a large (several orders of magnitude) impact on the residual $CO_2/^3He$ ratio. However, CO_2 loss by phase separation near the surface will drive calcite precipitation. Therefore, a combination of both processes (1) and (2) would be the most possible explanation.

Combination of carbon and helium isotopes can provide further information of the carbon sources. Fig. 4 shows the analytical results of Liaodong hydrothermal gases. Two mixing lines (between mantle and crustal metamorphic component, and between mantle and crustal organic component) are plotted on the basis of $CO_2/^4He$ of each end members. Here the $CO_2/^3He$ ratios of mantle, crustal metamorphic and organic components are 2×10^9, 10^{11}, and 10^{11}, respectively. It is then clear that all Liaodong hydrothermal gases are plotted within the two mixing lines. This feature strongly suggests that CO_2 in Liaodong hydrothermal fluids are released from three different sources: mantle, crustal metamorphic and organic components. It is not simple to quantify each end members because of relatively large $\delta^{13}C$ range for each end members. The sample No. 10 contains 25% CO_2 with $\delta^{13}C$ value of −4.8‰, which is overlapping with that for the typical magmatic CO_2. Taking into account of the local occurrence of Paleozoic carbonates and relatively low $^3He/^4He$ ratio, the CO_2 can be attributed in terms of dominant metamorphic origin mixed with minor contributions from mantle-derived and organic CO_2. The other samples show $\delta^{13}C$ values of CO_2 from −32‰ to −13‰ that are significantly less than those for typical inorganic carbon (metamorphic or magmatic), but instead consistent with the range of typical $\delta^{13}C$ values for sedimentary organic carbon. This feature suggests the CO_2 origin in Liaodong might be mainly attributed to be organic carbon from the surrounding sedimentary rocks with minor addition of mantle-derived and metamorphic carbon enriched in ^{13}C. The organic CO_2 is further supported by the combination plot of $\delta^{13}C_{CO2}$ vs $\delta^{13}C_{CH4}$ in hydrothermal gas samples (Fig. 5). The lines represent varying values of fractionation factor α_C [$\alpha_C = (\delta^{13}C_{CO2} + 1000)/(\delta^{13}C_{CH4} + 1000)$]. Whiticar (1999) summarized carbon isotopic compositions during bacterial methane formation and consumption. The typical α_C values for CO_2 reduction, acetate fermentation and methane oxidation range in 1.055–1.090, 1.040–1.055 and 1.005–1.035, respectively. It is clear that apart from sample No. 10 Liaodong gas samples ranging α_C from 1.01 to 1.03 are plotted within the range of bacterial methane oxidation.

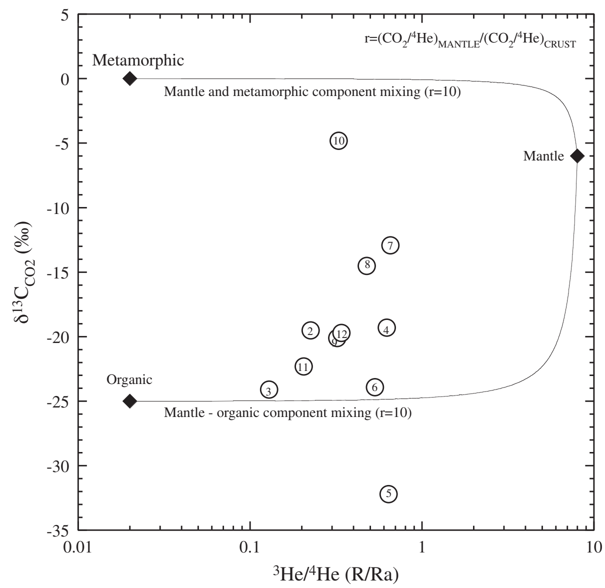

Fig. 4. Relationship of $^3He/^4He$ ratio and $\delta^{13}C$ values of hydrothermal gases in Liaodong Peninsula.

It should be pointed out that carbon isotope fractionation can occur during processes such as phase separation and calcite precipitation as discussed above. Such a carbon isotope fractionation is dependent on the hydrothermal reservoir temperature. Indeed, the resulted CO_2 in calcite precipitation would be enrich in ^{12}C with the temperature decreasing from 190 °C (Bottinga, 1969). However, because of the large $\delta^{13}C_{CO2}$ variation from −5‰ to −32‰ in this study and no available data of the reservoir temperatures, detailed

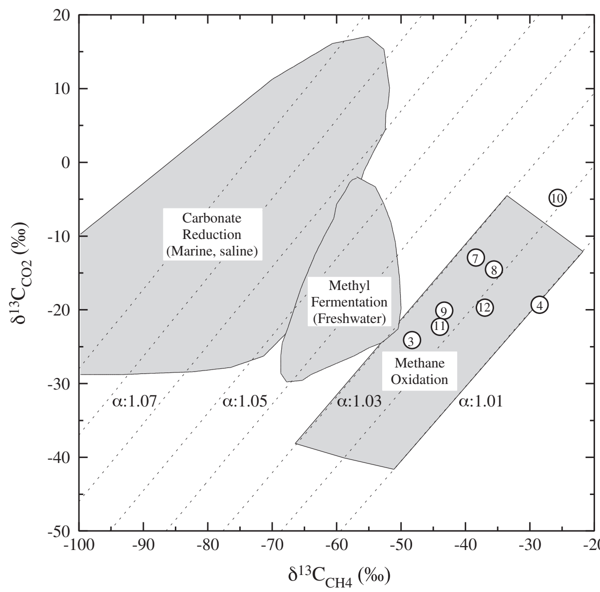

Fig. 5. Combination plot of $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ with carbon isotope fractionation lines.

assessment of carbon isotope fractionation would be beyond the present dataset.

5. Conclusions

The elevated $^3He/^4He$ ratios (0.1–0.7 Ra) relative to that expected for radiogenic production in the crust (0.02 Ra) indicate that as much as approximately 8% of the helium in the fluids from the Liaodong crust are mantle-derived. The regional high $^3He/^4He$ ratios (0.5–0.7 Ra) observed along the Jinzhou fault are considerably associated with injection of magmatic reservoir beneath the fault. Low $^3He/^4He$ ratios observed away from the fault can be explained by mantle-derived He gradually diluted by more radiogenic helium during the fluid circulations through the E–W and SW–NE orientated fault system. This study confirms previous findings that the active faults play an important role in transferring mantle-derived components to the surface in the nonvolcanic regions.

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References

Bottinga, Y., 1969. Calculated fractionation factors for carbon and hydrogen isotopes exchange in the system calcite–carbon dioxide–graphite–methane–hydrogen–water vapor. Geochim. Cosmochim. Acta 33, 49–64.
Castro, M.C., 2004. Helium sources in passive margin aquifers – new evidence for a significant mantle ^3He source in aquifers with unexpectedly low in situ $^3He/^4He$ production. Earth Planet. Sci. Lett. 222, 897–913.
Dai, J.X., Yang, S.F., Chen, H.L., Shen, X.H., 2005. Geochemistry and occurrence of inorganic gas accumulations in Chinese sedimentary basins. Org. Geochem. 36, 1664–1688.
Doğan, T., Sumino, H., Nagao, K., Notsu, K., 2006. Release of mantle helium from the forearc region of the Philippine Sea plate subduction. Chem. Geol. 233, 235–248.
Doğan, T., Sumino, H., Nagao, K., Notsu, K., Tuncer, M.K., Çelik, C., 2009. Adjacent releases of mantle helium and soil CO_2 from active faults: observations from the Marmara region of the North Anatolian Fault zone, Turkey. Geochem. Geophys. Geosyst. 10, Q11009.
Du, J., Cheng, W., Zhang, Y., Jie, C., Guan, Z., Liu, W., Bai, L., 2006. Helium and carbon isotopic compositions of thermal springs in the earthquake zone of Sichuan, South-western China. J. Asian Earth Sci. 26, 533–539.
Gao, S., Luo, T.C., Zhang, B.Z., Zhang, H.F., Han, Y.W., Zhao, Z.D., Hu, Y.K., 1998. Chemical composition of the continental crust as revealed by studies in East China. Geochim. Cosmochim. Acta 62, 1959–1975.
Gautheron, C., Moreira, M., 2002. Helium signature of the subcontinental lithospheric mantle. Earth Planet. Sci. Lett. 199, 39–47.
Giggenbach, W.F., Sano, Y., Wakita, H., 1993. Isotopic composition of He, and CO_2 and CH_4 contents in gases produced along the New Zealand part of a convergent plate boundary. Geochim. Cosmochim. Acta 57, 3427–3455.
Gilfillan, S.M.V., Ballentine, C.J., Holland, G., Sherwood Lollar, B., Stevens, S., Schoell, M., Cassidy, M., 2008. The noble gas geochemistry of natural CO_2 gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA. Geochim. Cosmochim. Acta 72, 1174–1198.
Hahm, D., Hilton, D.R., Cho, M., Wei, H., Kim, K.-R., 2008. Geothermal He and CO_2 variations at Changbaishan intraplate volcano (NE China) and the nature of the sub-continental lithospheric mantle. Geophys. Res. Lett. 35, L22304.
Happell, J.D., ÖStlund, G., Mason, A.S., 2004. A history of atmospheric tritium gas (HT) 1950–2002. Tellus B 56, 183–193.
Hu, S.B., He, L.J., Wang, J.Y., 2000. Heat flow in the continental area of China: a new data set. Earth Planet. Sci. Lett. 179, 407–419.
Karlstrom, K.E., Crossey, L.J., Hilton, D.R., Barry, P.H., 2013. Mantle ^3He and CO_2 degassing in carbonic and geothermal springs of Colorado and implications for neotectonics of the Rocky Mountains. Geology 41, 495–498.
Kennedy, B.M., van Soest, M.C., 2006. A helium isotope perspective on the Dixie Valley, Nevada, hydrothermal system. Geothermics 35, 26–43.
Kennedy, B.M., van Soest, M.C., 2007. Flow of mantle fluids through the ductile lower crust: helium isotope trends. Science 318, 1433–1436.
Kennedy, B.M., Kharaka, Y.K., Evans, W.C., Ellwood, A., DePaolo, D.J., Thordsen, J., Ambats, G., Mariner, R.H., 1997. Mantle fluids in the San Andreas fault system, California. Science 278, 1278–1281.
Klemperer, S.L., Kennedy, B.M., Sastry, S.R., Makovsky, Y., Harinarayana, T., Leech, M.L., 2013. Mantle fluids in the Karakoram fault: helium isotope evidence. Earth Planet. Sci. Lett. 366, 59–70.
Javoy, M., Pineau, F., Delorme, H., 1986. Carbon and nitrogen isotopes in the mantle. Chem. Geol. 57, 41–62.
Kulongoski, J.T., Hilton, D.R., Izbicki, J.A., 2005. Source and movement of helium in the eastern Morongo groundwater Basin: the influence of regional tectonics on crustal and mantle helium fluxes. Geochim. Cosmochim. Acta 69, 3857–3872.
Lei, Q.Q., Xu, L., Dong, X.Y., Yang, S.H., 2008. Main active faults and their seismic activities in Liaoning province. Technol. Earthquake Disaster Prevent. 3, 112–125 (in Chinese and English abstract).
Li, R., Xu, P., Jiao, M., Wang, X., 1997. Features of the three-dimensional crustal structure of the Haicheng seismic area. Seismol. Geol. 19, 9–13 (in Chinese with English abstract).
Liu, D.Y., Nutman, A.P., Compston, W., Wu, J.S., Shen, Q.H., 1992. Remnants of ⩾3800 Ma crust in the Chinese part of the Sino-Korean craton. Geology 20, 339–342.
Liu, J.L., Ji, M., Shen, L., Guan, H.M., Davis, G.A., 2011. Early Cretaceous extensional structures in the Liaodong Peninsula: structural associations, geochronological constraints and regional tectonic implications. Sci. China (Earth Sci.) 54, 823–842.
Lu, Z.X., Jiang, X.Q., Pan, K., Bai, Y., Jiang, D.L., Xiao, L.P., Liu, J.H., Liu, F.T., Chen, H., He, J.K., 2002. Seimic tomography in the northeast margin area of Sino-Korean platform. Chin. J. Geophys. 45, 338–351 (in Chinese and English abstract).
Lu, Z.X., Liu, G.D., Wei, M.H., Meng, P.Z., Zhao, J.M., 1990. Lateral inhomogeneity of crust and upper mantle in south Liaoning, China and its relationship with the M7.3 Haicheng earthquake. Acta Seismol. Sin. 12, 367–378 (in Chinese with English abstract).
Mamyrin, B.A., Tolstikhin, I.N., 1984. Helium Isotope in Nature. Elsevier, 273p.
Marty, B., Jambon, A., 1987. C/^3He in volatile fluxes from the solid Earth: implication for carbon geodynamics. Earth Planet. Sci. Lett. 83, 16–26.
O'Nions, R.K., Oxburgh, E.R., 1988. Helium, volatile fluxes and the development of continental crust. Earth Planet. Sci. Lett. 90, 331–347.
Sano, Y., Nakamura, Y., Wakita, H., Urabe, A., Tominaga, T., 1984. ^3He emission related to volcanic activity. Science 224, 150–151.
Teng, F.Z., Rudnick, R.L., McDonough, W.F., Wu, F.-Y., 2009. Lithium isotopic systematics of A-type granites and their mafic enclaves: further constraints on the Li isotopic composition of the continental crust. Chem. Geol. 262, 370–379.
Umeda, K., Ninomiya, A., McCrank, G.F., 2008. High ^3He emanations from the source regions of recent large earthquakes, central Japan. Geochem. Geophys. Geosyst. 9, Q12003.
Umeda, K., Ninomiya, A., 2009. Helium isotopes as a tool for detecting concealed active faults. Geochem. Geophys. Geosyst. 10, Q08010.
Wan, B., Jia, L.H., Dai, Y.L., Suo, R., 2013. Moderate-strong earthquakes and their tectonic 501 implications in the Liaoning Peninsula. Seismol. Geol. 35, 301–314 (in Chinese 502 and English abstract).
Wang, A.D., Ren, Y.H., Sun, W.F., Yu, L.W., Liang, J.M., Cao, T.Q., Gu, H.D., 1987. Geothermal observation in East Liaoning and the Haicheng seismic area. Acta Seismol. Sin. 9, 392–405 (in Chinese with English abstract).
Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem. Geol. 161, 291–314.
Wu, F.-Y., Lin, J.Q., Wilde, S.A., Zhang, X.O., Yang, J.-H., 2005. Nature and significance of the early cretaceous giant igneous event in eastern China. Earth Planet. Sci. Lett. 233, 103–119.

Xu, S., Nagao, K., Uto, K., Wakita, H., Nakai, S., Liu, C., 1998. He, Sr and Nd isotopes of mantle-derived xenoliths in volcanic rocks of NE China. J. Asian Earth Sci. 16, 547–556.
Xu, S., Nakai, S., Wakita, H., Xu, Y.C., Wang, X.B., 1995. Helium isotope compositions in sedimentary basins in China. Appl. Geochem. 10, 643–656.
Xu, S., Nakai, S., Wakita, H., Wang, X.B., 2004. Carbon and noble gas isotopes in the Tengchong volcanic geothermal area, Yunnan, Southwestern China. Acta Geol. Sinica 78, 1122–1135.
Yang, J.-H., Wu, F.-Y., Chung, S.-L., Wilde, S.A., Chu, M.-F., 2006. A hybrid origin for the Qianshan A-type granite, northeast China: geochemical and Sr–Nd–Hf isotopic evidence. Lithos 89, 89–106.
Yokoyama, T., Nakai, S., Wakita, H., 1999. Helium and carbon isotopic compositions of hot spring gases in the Tibetan Plateau. J. Volcanol. Geoth. Res. 88, 99–107.
Zhong, Y.Z., Xiao, X.Q., 1990. Study on spatial relationship between earthquakes and hot springs in Liaodong Peninsula. Seismol. Geol. 12, 344–350 (In Chinese with English abstract).