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Compositions and flux of soil gas in Liu-Huang-Ku hydrothermal area, northern Taiwan

Tefang Faith Lan [a], Tsanyao Frank Yang [a,*], Hsiao-Fen Lee [a], Yue-Gau Chen [a], Cheng-Hong Chen [a], Sheng-Rong Song [a], Shuhjong Tsao [b]

[a] *Department of Geosciences, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 106, Taiwan, ROC*
[b] *Central Geological Survey, MOEA P.O. Box 968, Taipei 235, Taiwan, ROC*

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Abstract

Soil CO_2 flux has been considered a useful proxy to remotely monitor volcanic activity in a hydrothermal area within a safe distance. The Liu-Huang-Ku (LHK) area, which is close to the Taipei basin and many existing active fumaroles and hot springs, was chosen for the first systematic soil gas study in a hydrothermal area of Taiwan in 2004 and 2006. The soil CO_2 flux was measured by the closed-chamber method with a non-dispersive infrared detector. Soil CO_2 emission rate was estimated 19.8 ± 0.2 t day^{-1} and 582 t km^{-2} day^{-1} in 2004, and 22.4 ± 0.2 t day^{-1} and 659 t km^{-2} day^{-1} in 2006, respectively. These values are close to those reported for other active high CO_2 flux hydrothermal areas of the world. It implies that magmatic gases are actively degassing from subsurface in northern Taiwan. Helium and carbon isotopic data reveal that soil gas in LHK is mainly derived from the mantle and is mixed with a small amount of crustal and air components. The abundance of soil CO_2 shows a positive correlation with the $^3He/^4He$ ratios and total sulfur contents, which are considered as magmatic-sensitive indicators for the fumarolic samples. Therefore, soil CO_2 could be used as a good proxy for future monitoring of magmatic activity in this area.

Keywords: soil CO_2 flux; closed-chamber method; monitoring; magmatic activity; Taiwan

1. Introduction

Soil gas surveys have been widely applied in the geosciences for decades, e.g. oil and mineral exploration, hydrothermal investigations, earthquake and volcanic eruption precursory studies, environmental pollution, active fault location and so on (e.g. Lombardi and Reimer, 1990; Suchomel et al., 1990; Klusman, 1993; King et al., 1996; Chiodini et al., 1998; Baubron et al., 2002; Chyi et al., 2005; Fu et al., 2005; Walia et al., 2005a,b; Yang et al., 2005b, 2006b). Anomalous climatic changes in recent years has provoked questions to whether the huge amount of greenhouse gases emitted from active and mud volcanoes might significantly affect the global climate (Pales and Keeling, 1965; Etiope, 1999). Therefore, a precise estimation of the diffuse gas emission is important to define any relationship between degassing and global climate change.

Important for volcanic surveys and monitoring, a large volume of volcanic gas is often released to the atmosphere through craters and/or soil, regardless of whether the volcanoes are erupting or passively degassing. The variation of volcanic gas flux is considered as an important index of volcanic activity. CO_2 is the most abundant component after water, and is also one of the

* Corresponding author. Tel.: +886 2 3366 5874; fax: +886 2 2363 6095.
E-mail address: tyyang@ntu.edu.tw (T.F. Yang).

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earliest and less reactive gases departing from the ascending magma (e.g. Syomnds et al., 1994; Giggenbach, 1996). Therefore, CO_2 is easily detected and observed in early stages of magma uprising in one area. Several techniques have been developed to measure CO_2 flux, whereby the CO_2 concentration is measured with a portable airborne mounted IR spectrometer, or the flux of SO_2 is measured and the CO_2 flux calculated from the known ratio between the two gases. In volcanic areas, a high CO_2 concentration may appear not only in the region close to craters and fumaroles, but also in areas far from apparent gas conduits (Allard et al., 1991). Thus, people could monitor volcanoes by soil gases at a safe distance. Furthermore, a contour map of soil CO_2 flux can also provide information of the characteristics and structures of volcanoes.

Taiwan is located at the collisional boundary of Eurasia and Philippine Sea plate. Different tectonic models have been proposed to explain the magma activity in northern Taiwan (e.g. Teng et al., 1992; Teng, 1996; Wang et al., 1999). Integrated mineralogical and stratigraphical data shows that the latest eruption may have occurred around 20 ka in the Tatun volcanic area in northern Taiwan (Chen and Lin, 2002), where hydrothermal activity is still active. Recent seismic (Yeh and Chen, 1991; Lin et al., 2005a,b) and geochemical data (Yang et al., 1999, 2005a; Lee et al., 2005) infer that a magma chamber may exist under northern Taiwan, hence, support the idea that the Tatun Volcano Group (TVG) may be still active (Song et al., 2000b).

The objective of this paper is to assess the feasibility of using the soil gas method to monitor the potential volcanic activity in this region. The relationship between soil gas and fumarolic gas compositions in the studied area will be also discussed. Lin et al. (2005a,b) reported some volcanic–seismic signals which are believed to be related to local hydrothermal activity. Continuous monitoring result also showed that the temperature of fumarolic gas in TVG has been increasing from 2004 until recent (Lee et al., 2006). In addition to regular sampling and analysis of fumarolic gas, we try to utilize a different monitoring method that enables us to safely monitor volcanoes in case of more vigorous volcanic activity. Therefore, the Liu-Huang-Ku (LHK) hydrothermal area, which is one of the most fumarole- and hot spring-active areas in TVG and administratively in the populated Taipei City, was chosen as a testing location for the first soil gas study in a hydrothermal area of

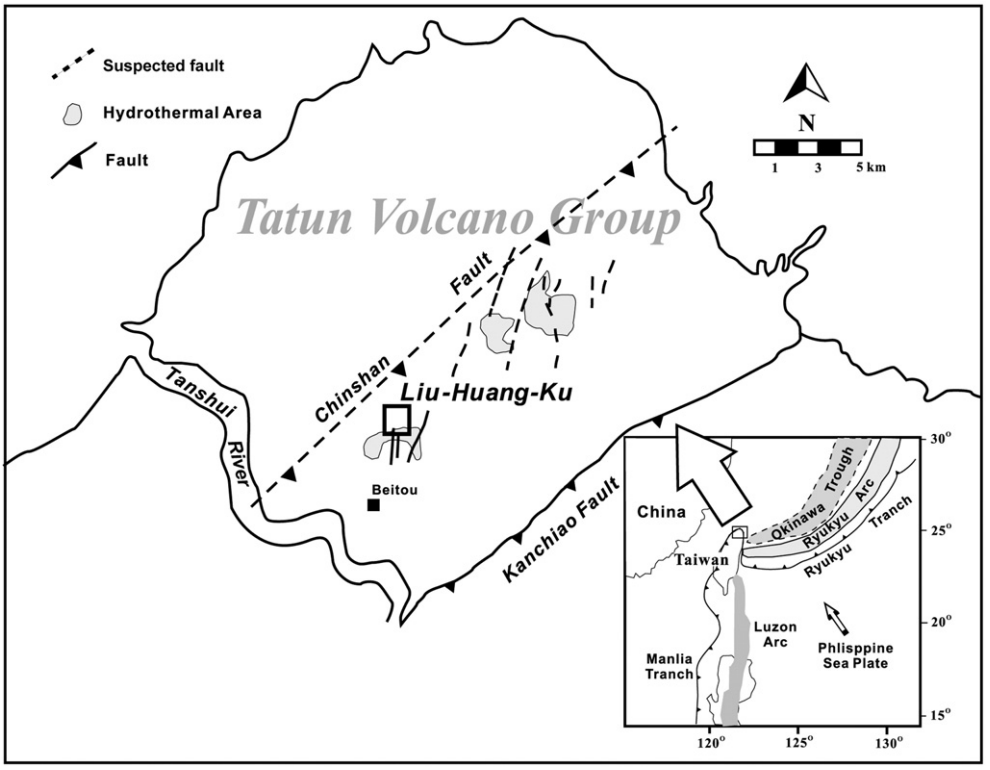

Fig. 1. Illustration of the principal tectonics of Taiwan and Tatun Volcano Group. Liu-Huang-Ku is located at the southwest part of Tatun Volcano Group.

Taiwan in 2004. The same work was duplicated in 2006 to compare the possible temporal variations of soil gas composition in the area.

2. Liu-Huang-Ku hydrothermal area

LHK hydrothermal area, formed ca. 0.8 to 0.6 million years ago (Song et al., 2000a), is a 1 km long, 150 m wide phreatic crater located on the hillside of southwest TVG with several steaming fumaroles and artificial hot springs utilized as resources of nearby hotels (Fig. 1). Fumarolic gas composition of TVG samples reflects a mixing signature between convergent plate gases and air/groundwater (Lee et al., 2005). This suggests that the magma source of the TVG gas is closely associated with the subduction system in NE Taiwan. The bed rocks are mostly hydrothermal-altered lower Miocene sedimentary rocks. The unaltered Wuchihshan Formation is composed of white sandstones and interbedded with thin layers of shale and coal, while the Mushan Formation contains quartzite sandstone, gray-to-black shale and coal (Ho, 1988).

3. Methods and procedures

3.1. Fieldwork in Liu-Huang-Ku

Chiodini et al. (1998) have described and compared some methods for soil flux measurement, including the indirect, direct, static and closed-chamber methods. These authors suggested that the closed-chamber method may be more suitable than others in the field. They further modified the method by using a hermetically sealed chamber on the soil from which the increase of CO_2 concentration in the chamber can be measured to derive flux. This method was successfully applied to agricultural sciences to measure the soil metabolism (Parkinson, 1981) and flux of other gas species (e.g. Kinzig and Socolow, 1994). This method has also been tested by Tonani and Miele (1991) as the

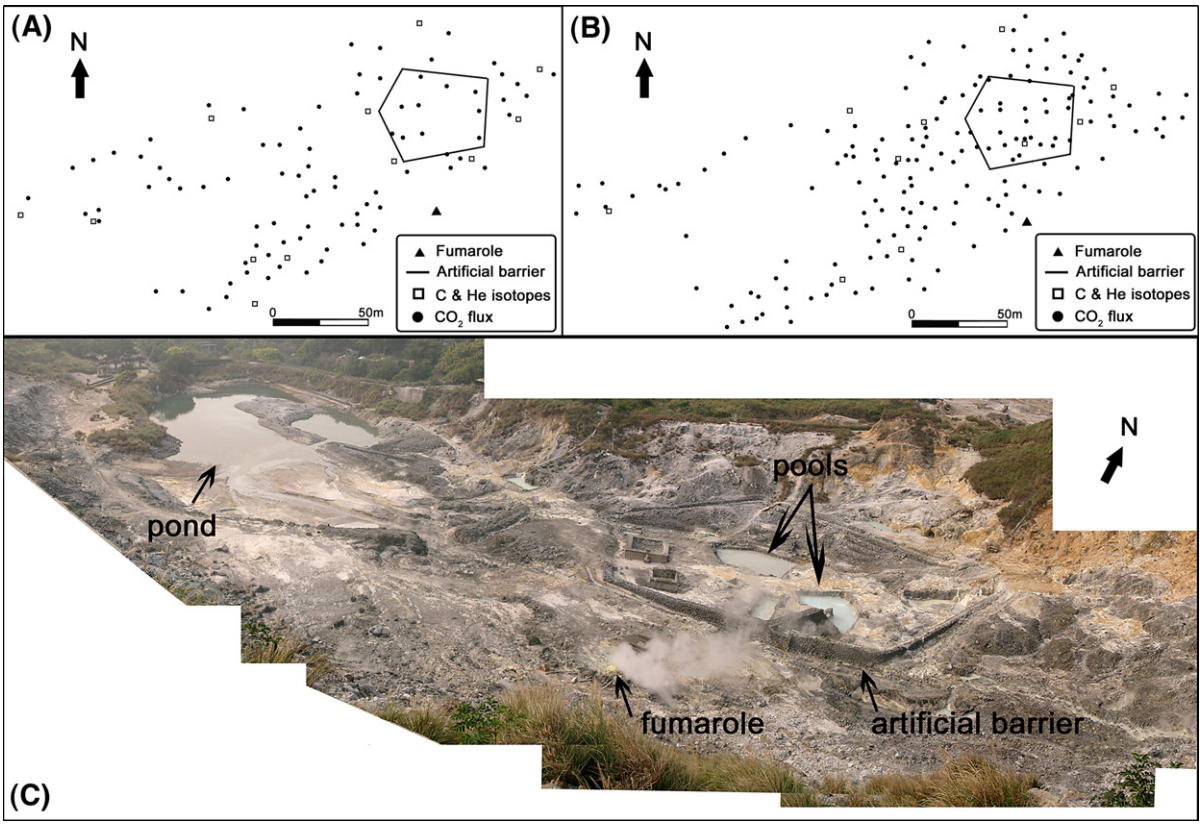

Fig. 2. Sampling sites at Liu-Huang-Ku in this study. (A) 94 CO_2 flux measurement points (solid circles) and 11 isotopic samples (squares) in 2004. (B) 163 CO_2 flux measurement points (solid circles) and 10 isotopic samples (squares) in 2006. The pentagon is the artificial barrier as shown in the photograph. (C) Photograph of LHK, which is a steam-eruptive crater with many fumaroles and spring pools.

Table 1
Estimated parameters of partitioned populations of soil CO_2 flux in Liu-Huang-Ku hydrothermal area

Population	Proportion (%)	Sample quantity	Mean CO_2 flux and 95% confidence interval (g m^{-2} day^{-1})	Total diffuse CO_2 output and 95% confidence interval (t day^{-1})
2004 survey				
A	38	37	25 (16–33.3)	0.32 (0.21–0.43)
B	56	52	521 (361–680)	9.92 (6.87–13.0)
C	6	5	4678 (3035–6321)	9.54 (6.19–12.9)
Total	100	94		19.8 (13.3–26.3)
2006 survey				
A	34	56	21 (16.5–25.8)	0.24 (0.19–0.30)
B	63	101	711 (552–870)	15.2 (11.8–18.6)
C	3	6	6866 (5652–8079)	7.00 (5.77–8.24)
Total	100	163		22.4 (17.8–27.1)

Area = 34,000 m^2.

preferable way to measure flux of volcanological and geothermal areas because it does not require any assumptions or corrections for soil characteristics, like grain size, porosity, permeability etc.

We adopted the closed-chamber method to determine the soil CO_2 flux by using a commercial portable flux meter (West System, Italy). The system is composed of three parts: (1) Non-dispersed Infrared (NDIR) Gas Sensors (LICOR LI820): for measuring CO_2 concentration. (2) Circular chamber: a hermetically sealed chamber with a volume of 6.2×10^{-3} m^3, and a height of 0.2 m. An inlet and an outlet make the system as a circular loop. A capillary is assembled to the top of the chamber for balancing pressure ins and outs. A fan is equipped in the chamber to well-mix air and soil gas. (3) Pocket PC: for equipment control and data storage. To prevent the contamination of water vapor, we use silica gel as the water trap. Before measuring flux, the rim of chamber was covered by soil and sealed well, or leakage of air might influence flux significantly especially in windy days. Furthermore, pressure in the chamber is maintained nearly equal to the air, or duration of measurement would last longer (Welles et al., 2001). Error of this method is ±10% evaluated by laboratory experiments with replicate measurements of known effluxes. In addition to the soil flux measured with the closed-chamber method, a stainless steel probe (1 m in length, 1 cm diameter) was inserted into soil to at least 50 cm depth, the gas then pumped into pre-evacuated low-permeability sample bottles for isotope analysis. Detailed procedures and method of soil gas sampling and analysis were described by Fu et al. (2005).

Soil CO_2 flux measurements were conducted in 2004 and 2006. In the first survey, 94 sites were measured in the study area (Fig. 2) from January to February of 2004, during the dry season in northern Taiwan. The second survey was conducted in February 2006, 163 sites were measured under similar meteorological condition to avoid the influence of weather factors. Soil temperature (measured at the depth of ca. 15 cm) and atmospheric pressure were recorded at the same time for calibration. In addition, representative soil gas samples were also collected for measurement of the carbon and helium isotopic compositions to distinguish their gas sources.

3.2. Analyses of soil gas compositions and isotopes

Soil gas compositions were analyzed by a gas chromatograph (GC, SRI 8610C), equipped with two thermal conductivity detectors (TCDs) and one flame ionic detector (FID). One Hayesep-D column uses hydrogen as a carrier gas, whereas a MS5A column uses argon as a carrier gas. Analyses of fumarolic gas composition were conducted using the same method described by Lee et al. (2005). Concentration and isotopic ratio of helium, neon and other noble gas were analyzed by a high-precision noble gas mass spectrometer (Micromass 5400) using potassium-glass bottles with vacuum stopcocks at both ends. Observed $^3He/^4He$ ratios were calibrated against atmospheric standard gas and normalized to the R_A, where R_A is the air $^3He/^4He$ ratio equal to 1.39×10^{-6}. The overall error of the ratio, including analytical error of the sample and working standard gas, and long-term variations of the standards, was less than 2.5% (Yang et al., 2005a, 2006a). After purification of soil gas samples by traps held at liquid N_2 and ethanol–dry ice temperatures, carbon isotopes of carbon dioxide were analyzed using a Finnigan MAT mass spectrometer. Measured $^{13}C/^{12}C$ ratios are expressed in the delta (δ) notation, as parts per thousand (‰) compared to the international standard, PDB. The experimental error on the carbon isotopic ratios was ~0.1‰ (Hsieh, 2000).

4. Results and discussion

4.1. Spatial distribution of CO_2 flux and soil temperature

A large quantity of literature has been published on the feasibility of using soil flux measurements to detect active structures such as fractures and faults in a volcanic area (e.g. Giammanco et al., 1998; Baubron et al., 2002; Finizola et al., 2003; Alparone et al., 2004; Giammanco et al., 2006). However, a spatial distribution of soil flux in a hydrothermal area not only indicates the structures and/or fractures, but also associates to the possible positions of heat sources.

The soil CO_2 flux in LHK area shows a wide range from 16 to 8079 g m^{-2} day^{-1} in this study (Table 1). The spatial distribution of the CO_2 flux is shown as Fig. 3 using Krigging method with interpolation based on a linear variogram model. Due to some severe strikes of typhoons in 2005; the landscape of LHK area changed somehow. Masses of sands and mud were carried into the valley-like area and buried two spring pools; some originally immeasurable hard-ground was covered by soil. Therefore the study area became larger and the number of CO_2 flux data was increased from 94 in 2004 to 163 in 2006. Due to the changes of ground surface, re-measurement at the exact same locations is difficult; however, from a large scale of geographical distribution, the resembling NE–SW distributed pattern can be observed (Fig. 3), which is probably associated with the structure in this area (Song, 1994). This observation

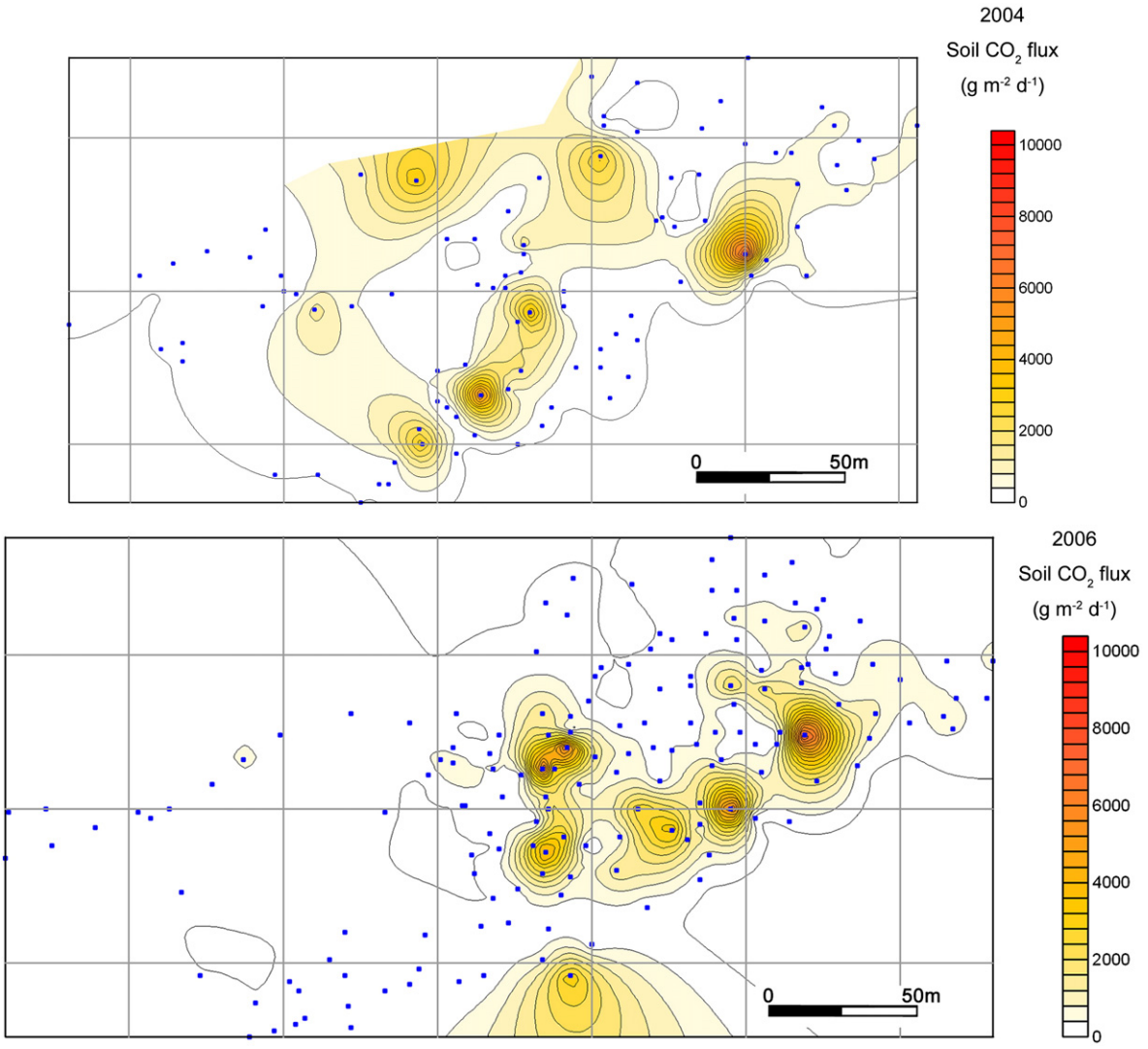

Fig. 3. Contour map of soil CO_2 flux of LHK with reference to sampling sites (dots) same as in Fig. 2A (upper) and Fig. 2B (lower).

could also help us to identify the displacement of heat sources or structures.

Comparing the CO_2 flux (Fig. 3) with the soil temperature (Fig. 4) in LHK, it can be found that they correlate each other sympathetically. This is best explained by a hot degassing source in this area. However, some measured points close to the pond in LHK show decoupling result of lower soil temperature with higher soil CO_2 flux. It might be due to the cooling effect of pond water while volcanic gases rising upward to the surface. Yet, higher soil temperature with lower CO_2 flux at some sites was found in the 2006 survey. It might be due to local changes of the permeability and porosity of the soil in the studied area during the typhoon season in 2005. A high temperature volcanic gas could diffuse through the soil easily and raise the soil temperature; however, if the soil permeability becomes low, gas can transport heat but may not be able to diffuse through the cover layer. This can cause the higher temperature for the soil with only low CO_2 flux.

4.2. Estimation of total CO_2 output

Due to high variability of flux value, a statistical method proposed by Sinclair (1974) was applied to find out how many normal distributions there are in the data sets. Three overlapped populations can be recognized in both the 2004 and 2006 data clusters and grouped in the probability graphs (Fig. 5) with the average flux of

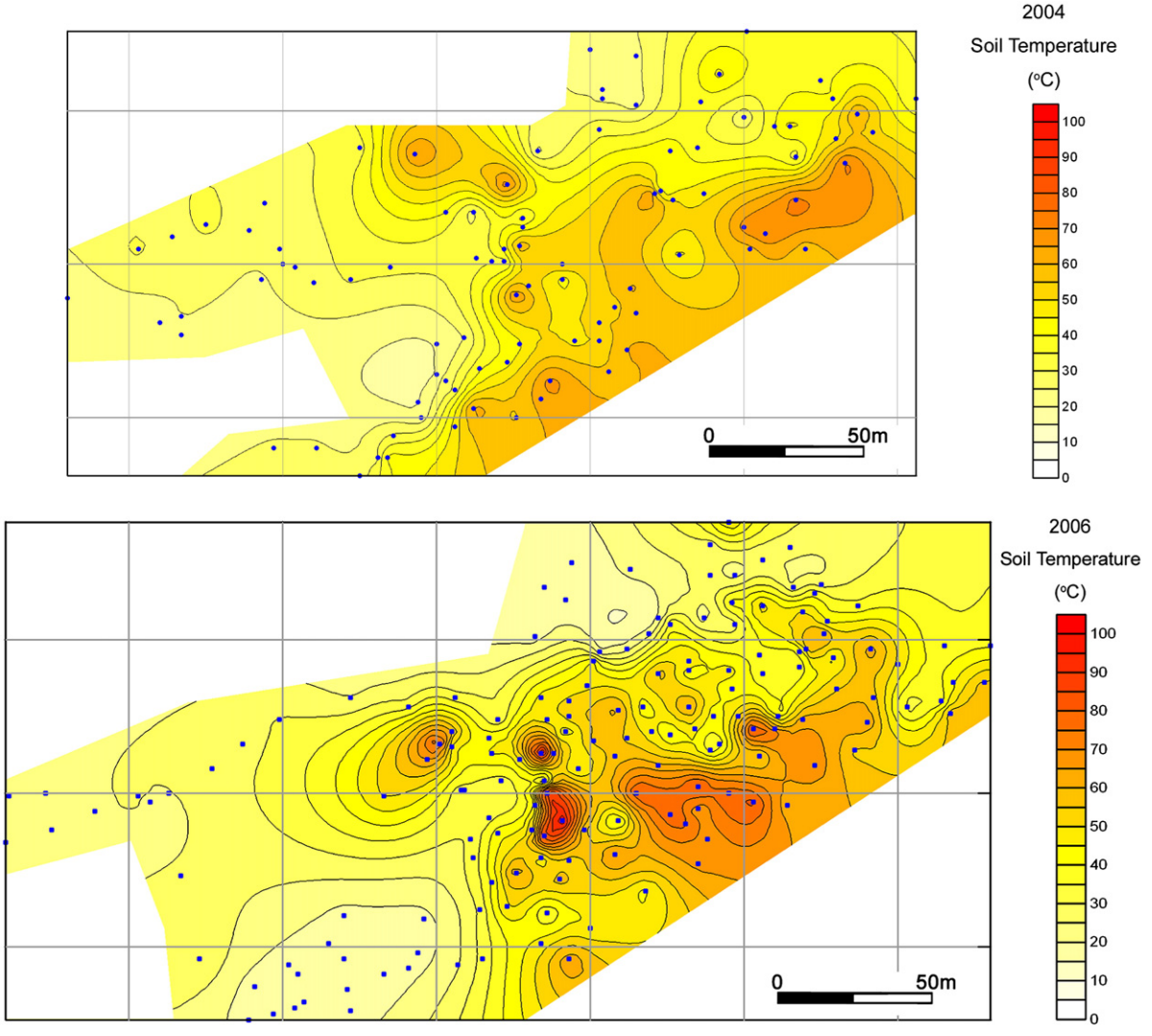

Fig. 4. Contour map of soil temperature of LHK with reference to sampling sites (dots) same as in Fig. 2A (upper) and Fig. 2B (lower).

populations A, B and C listed in Table 1. The consequences in 2006, in contrast with data in 2004, present an obvious increase in the average value of population C, and in the meantime population B rose to 711 g m^{-2} d^{-1}; yet, population A remains with relatively the same extent as in 2004. It is noteworthy that the variation of soil gas flux is likely related to the sample size, but enlarging the sample size could increase the precision of the statistical estimation. Therefore, the possible reasons for the increase in soil gas flux could be: (1) more vigorous degassing from the magmatic source; (2) diffusive paths of soil gas in the overall area were more widened than those in 2004. The increase of average soil temperature and the isotopic variation (discussed in later session) support the two assumptions. Hence, it is worthwhile to monitor future possible fluctuation of soil CO_2 flux in LHK.

Consequently, emission rates of soil CO_2 were estimated by summing the contribution of each population (details described in Chiodini et al., 1998). The results are 19.8±0.2 t day^{-1} and 22.4±0.2 t day^{-1} for the survey in 2004 and 2006, respectively. The total CO_2 output of LHK is smaller than those of high-flux hydrothermal locations of the world (Table 2) due to

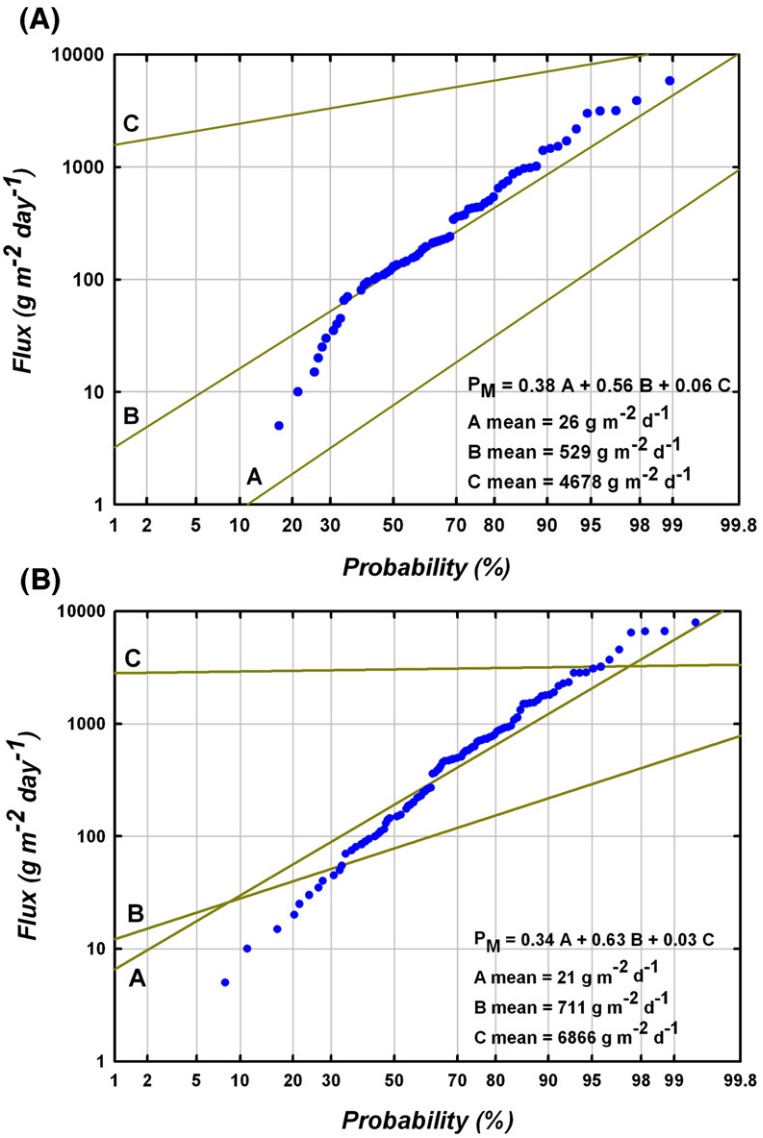

Fig. 5. Cumulative frequency plot of soil CO_2 flux of Liu-Huang-Ku in (A) 2004 and (B) 2006. Grey lines represent the partition components of population A, B and C. See text for detail discussion.

Table 2
Soil CO_2 emission rates observed in Liu-Huang-Ku and other volcanic areas of the world

Location (year)	Area (km^2)	CO_2 flux (t day^{-1})	CO_2 flux (t km^{-2} day^{-1})	Reference
Liu-Huang-Ku, Taiwan (2004)	0.034	19.8	582	This study
Liu-Huang-Ku, Taiwan (2006)	0.034	22.4	659	This study
Miyakejima, Japan (1998)	0.62	146	235	[1]
Hakkoda, Japan, September (1999)	0.58	74	120	[2]
Yanbajain, China (1996)	3.2	138	43.1	[3]
Vulcano, Italy (1995)	0.65	269	414	[4]
Solfatara of Pozzuoli, Italy (1994)	0.09	133	1478	[4]
Etna, Italy (1981)	n.d.	55,000	n.d.	[5]
Summit Teide, Spain (1996)	0.53	380	717	[6]
Mammoth Mountain, USA (1995)	0.145	350	2414	[7]
Mammoth Mountain, USA (1997)	0.145	130	897	[7]

[1] Hernández et al. (2001); [2] Hernández Perez et al. (2003); [3] Chiodini et al. (1998); [4] Chiodini et al. (1996); [5] Allard et al. (1987, 1991); [6] Hernández et al. (1998); [7] Gerlach et al. (1998); n.d. = no data.

relative smaller surveyed area in this study. However, the results of the emission rates with per unit area (Table 2) reveal that soil CO_2 output from LHK corresponds to that of other high soil CO_2 flux areas in the world with 582 t km^{-2} day^{-1} in 2004 and 659 t km^{-2} day^{-1} in 2006.

4.3. Compositions and sources of soil gas

The composition of soil gas in LHK resembles that of fumarolic gas, defined as having the typical composition of a low temperature fumarolic gas (i.e. high CO_2 concentration and the ratio of $H_2S/SO_2 > 1$). The major component is water (>85%) followed by N_2, CO_2, O_2 and Ar as shown in Table 3. Lee et al. (2005) proposed that the compositions of most TVG gas (including LHK) exhibit affinity with convergent plate gases based on the plot of N_2–He–Ar (Fig. 6). This suggests that the degassing sources for TVG gases are closely related to the subduction process in NE Taiwan.

By using $CO_2/^3He$–$\delta^{13}C_{CO_2}$ mixing model proposed by Sano and Marty (1995), we can estimate the

Table 3
Chemical compositions and helium isotopic data of soil gas in Liu-Huang-Ku hydrothermal area

Sample	N_2 (%)	O_2 (%)	Ar (%)	H_2S (%)	SO_2 (%)	CO_2 (%)	$^4He/^{20}Ne$	$^3He/^4He$	R_A	Error	He (ppm)
Soil gas sampled in 2004											
2004LHK-S1	81.90	13.90	0.94	0.06	0.01	3.19	0.32	1.372×10^{-6}	0.99	0.04	5.48
2004LHK-S2	77.48	17.62	0.91	0.09	0.02	3.88	0.38	1.676×10^{-6}	1.21	0.04	6.47
2004LHK-S3	14.25	2.73	0.13	8.05	0.05	74.78	11.19	8.808×10^{-6}	6.34	0.10	8.37
2004LHK-S4	72.91	14.54	0.80	0.11	0.03	11.61	0.32	1.459×10^{-6}	1.05	0.03	4.70
2004LHK-S5	6.20	0.81	0.04	6.79	0.02	86.13	14.90	8.292×10^{-6}	5.97	0.10	5.10
2004LHK-S9-1	51.31	11.41	0.54	0.97	0.04	35.73	0.95	5.806×10^{-6}	4.18	0.06	7.04
2004LHK-S9-2	43.36	9.83	0.46	2.39	0.02	43.95	0.80	6.122×10^{-6}	4.40	0.08	6.93
2004LHK-S12	29.27	6.11	0.30	4.25	0.07	60.00	1.29	6.522×10^{-6}	4.69	0.08	5.54
Soil gas sampled in 2006											
2006LHK-S1	75.88	16.45	0.88	0.06	0.00	6.72	0.36	1.57×10^{-6}	1.13	0.03	5.53
2006LHK-S2	12.88	2.46	0.09	9.14	0.03	75.40	6.93	8.00×10^{-6}	5.76	0.09	7.92
2006LHK-S4	11.77	2.20	0.08	11.46	0.04	74.46	15.14	8.22×10^{-6}	5.91	0.10	7.48
2006LHK-S5	7.81	0.44	0.02	5.68	0.08	85.97	16.33	8.33×10^{-6}	5.99	0.09	7.87
2006LHK-S6	13.58	2.33	0.10	6.81	0.04	77.14	6.48	8.05×10^{-6}	5.79	0.10	7.41
2006LHK-S7	10.28	1.98	0.06	7.60	0.03	80.07	8.22	8.01×10^{-6}	5.76	0.09	7.32
2006LHK-S8	4.81	0.63	0.02	12.71	0.03	81.80	4.19	7.62×10^{-6}	5.48	0.09	6.79
2006LHK-S9	8.29	1.24	0.04	7.57	0.04	82.82	4.61	7.98×10^{-6}	5.74	0.09	7.47
2006LHK-S10	81.90	14.41	0.90	0.06	0.00	2.74	0.33	1.63×10^{-6}	1.17	0.03	5.55

proportion of each component for carbon source in a fumarolic gas sample. The calculation formulas are defined as follows:

$$({}^{13}C/{}^{12}C)_{Obs} = M({}^{13}C/{}^{12}C)_M + L({}^{13}C/{}^{12}C)_L + S({}^{13}C/{}^{12}C)_S \quad (1)$$

$$1/({}^{12}C/{}^{3}He)_{Obs} = M/({}^{12}C/{}^{3}He)_M + L/({}^{12}C/{}^{3}He)_L + S/({}^{12}C/{}^{3}He)_S \quad (2)$$

$$M + L + S = 1 \quad (3)$$

in which M: magmatic source, L: marine limestone, S: sediments; and Obs: observed data of the sample.

Table 4 shows the calculated percentages of soil gas from magmatic source, sediments and limestone. The range of componential percentage of LHK soil gas is: M=7–19%, L=63–85%, S=2–28% which is similar to that of TVG fumarolic gas (Table 4, Yang et al., 2003) and that from subduction zones in the world: M=7–17%, L=63–75%, S=17–28% (Sano and Marty, 1995). Data on the plot of $\delta^{13}C_{CO_2}$ versus $CO_2/{}^3He$ (Fig. 7A) indicate the source of soil gas from LHK bears a resemblance to volcanic gas from other island-arc areas (Sano and Marty, 1995). The high proportion of carbonate component commonly found in a subducting environment (Table 4, Sano and Marty, 1995; Shaw et al., 2003) are considered to be attributed to the subducted calcareous sediments and/or limestone interbedded in the basement rocks of upper crust.

The mixing characteristics of soil gas and fumarolic gas in LHK are shown in Fig. 8 in terms of three end members: air, crust and mantle. It is seen that the helium isotopic composition of fumarolic gas is about 5 to 6 R_A with a very small amount of air contamination. The features of soil gas dominant with high $^3He/^4He$ ratios are taken for representatives of fumarolic gas, they are in contrast with those which are as low as air compositions. Furthermore, a well-mixing relationship between air and the magmatic source of LHK is also illustrated. This implies that the migration channels of some soil gas measuring sites might be totally replaced by fumaroles, otherwise a more crustal signature should be observed. High total sulfur content and $^3He/^4He$ ratio are two most important features of volcanic gas. In Fig. 9A, it can be seen that there is a positive correlation between total sulfur content and soil CO_2 concentration; a similar relation is also found between CO_2 and $^3He/^4He$ ratios (Fig. 9B). Therefore, the concentration of soil CO_2 in LHK indicates the abundance of magmatic gas. Conclusively, we suggest that CO_2 is a good proxy for future monitoring in this area because it is not only an efficient parameter but also inexpensive for measuring.

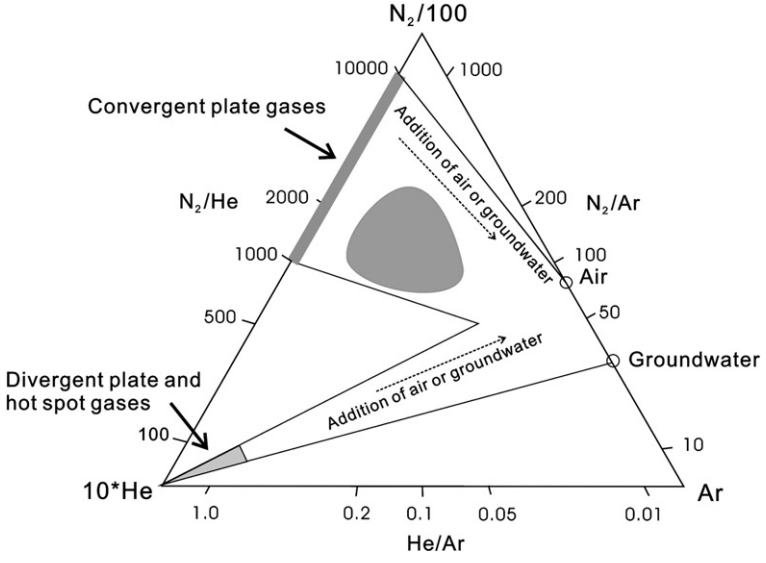

Fig. 6. N_2–He–Ar triangular plot of fumarolic gas from LHK. The shadowed area is the average composition of fumarolic gas from LHK which falls within the range of convergent plate gases mixing with air/groundwater. Data from Lee et al. (2005).

Table 4
Helium and carbon isotopes, $CO_2/^3He$ ratios and estimated sources of carbon in gas and fluids from LHK and subduction zones

No. name	R_A	$\delta^{13}C_{CO2}$ (‰)	$CO_2/^3He$	Carbon sources			References
				Magmatic (%)	Sediment (%)	Limestone (%)	
Soil gas of LHK							
2004-LHK-S3	0.99	−6.07	4.24×10^9	14.8	17.0	68.2	This study
2004-LHK-S4	1.21	−9.02	3.58×10^9	8.79	28.2	63.1	This study
2004-LHK-S5	6.34	−5.90	1.01×10^{10}	7.03	18.1	74.6	This study
2004-LHK-S9-1	1.05	−7.20	1.69×10^{10}	17.1	20.0	62.6	This study
2004-LHK-S9-2	5.97	−6.91	2.04×10^{10}	14.3	19.9	65.7	This study
Average	*3.11*	*−7.02*	*1.10×10^{10}*	*12.4*	*20.6*	*66.8*	
2006-LHK-S1	1.13	−2.17	7.74×10^9	19.3	3.05	77.7	This study
2006-LHK-S2	5.76	−1.45	1.19×10^{10}	12.5	2.12	85.4	This study
2006-LHK-S4	5.91	−2.51	1.21×10^{10}	12.3	5.71	82.0	This study
2006-LHK-S5	5.99	−3.63	1.31×10^{10}	11.4	9.65	79.0	This study
2006-LHK-S6	5.79	−4.17	1.29×10^{10}	11.5	11.4	77.1	This study
2006-LHK-S7	5.76	−3.93	1.37×10^{10}	10.9	10.7	78.4	This study
2006-LHK-S8	5.48	−5.32	1.58×10^{10}	9.43	15.7	74.9	This study
Average	*5.12*	*−3.31*	*1.25×10^{10}*	*12.5*	*8.3*	*79.2*	
Fumarolic gas of TVG							
LHK	*5.62*	*−3.15*	*1.22×10^{10}*	*12.2*	*7.9*	*79.9*	[1]
SYK	4.88	−3.40	1.28×10^{10}	11.6	8.8	79.5	[1]
DYK	6.79	−6.34	7.01×10^{10}	2.1	20.7	77.2	[1]
MS	4.55	−5.56	1.33×10^{10}	11.2	16.1	72.7	[1]
CSL	5.92	−3.04	1.32×10^{10}	11.3	7.7	81.0	[1]
TYK	4.49	−3.73	3.97×10^{10}	3.7	11.6	84.6	[1]
SHP	3.78	−3.28	7.61×10^{10}	1.9	10.5	87.5	[1]
Gas and fluids from subduction zones (Medium and low-temperature fumarole within caldera)							
Shinmoe, Japan	5.98	−4.9	2.79×10^{10}	5	15	80	[2], [3]
Vulcano, Italy	4.96	−2.0	7.40×10^9	20	2	78	[4], [5]
Purace, Colombia	6.19	−8.5	6.58×10^9	23	23	54	[6]
Oshima, Japan	5.08	−1.3	2.40×10^{10}	6	3	91	[7]
Ebino, Japan	5.87	−3.9	1.75×10^{10}	9	11	80	[3]

[1] Yang et al. (2003); [2] Sano and Wakita (1985); [3] Urabe (1985); [4] Marty et al. (1989); [5] Shinohara and Matsuo (1986); [6] Sturchio et al. (1992); [7] Sano et al. (1994). The shaded italic data highlight the average compositions of soil and fumarole samples in LHK for comparison.

4.4. Temporal variation of carbon isotopes

It is interesting to note the difference between data obtained in 2004 and 2006. The average percentages of the three sources of carbon shown in Table 4 reveal a variation in the sediment and limestone components, whereas the magmatic source is about constant. Moreover, the average values of the carbon isotopic ratio and calculated proportions of each component from the 2006 data are very close to results obtained for fumarolic gas (Yang et al., 1999, 2003). The helium isotopic composition was also similar to that measured in fumarolic gas. In fact, results of 2004 and 2006 can be grouped into two distinct data sets with an apparent shift toward a heavier carbon isotopic composition in 2006 (Fig. 7B). Moreover, the total sulfur contents in 2006 were also higher than in 2004, increasing from 8.1% in 2004 to 12.7% in 2006, a value closer to that measured in fumarolic gas. However, difference between the data sets of $^3He/^4He$ ratios plotted on the air–crust–mantle diagram (Fig. 8) cannot be identified.

There are two possible explanations for these phenomena as mentioned: (1) a change in the gas sources, (2) a modification within the path of gas uprising. The former is unlikely due to a steady helium isotopic composition, i.e. the variation is within a range of two standard deviations in the past few years, in this area (Lee et al., 2006). The monitoring results of the fumarolic gas composition and temperature showed some

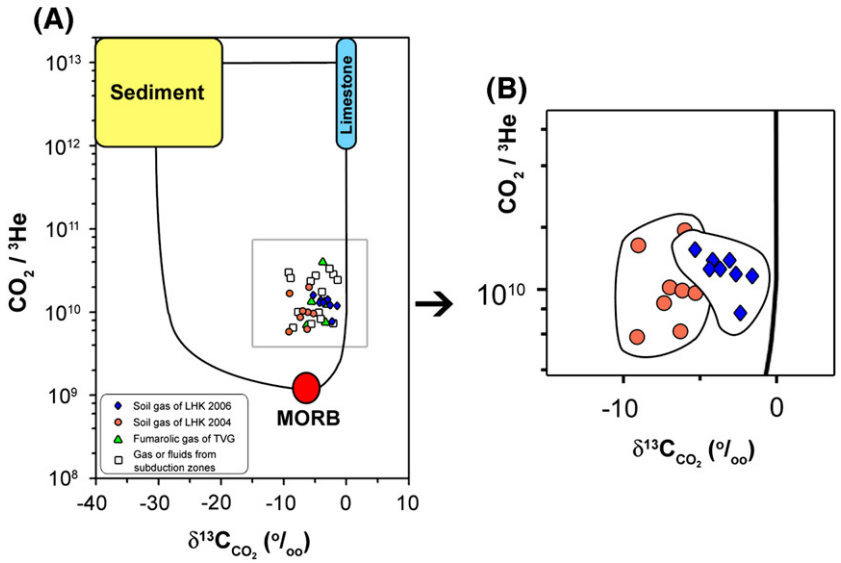

Fig. 7. Correlation between $CO_2/^3He$ and $\delta^{13}C$. (A) Soil gas of Liu-Huang-Ku is mainly derived from a mantle component and has a typical composition for its location in an island-arc area. (B) Two distinct data sets can be identified from samples in 2004 and 2006.

increasing trend since August, 2004 (Lee et al., 2006). However, the helium isotopic composition remained stable, indicating that there was no new magmatic signature involved in this event but probably the opening of gas paths. Nevertheless the significant increase towards a heavier carbon isotopic signal is clear. It is reasonable to speculate the opening of gas paths in this area since northern Taiwan is now under extension tectonic settings. With regard to the second speculation, the recent isotopic components and total sulfur contents of soil gas resemble analyses of fumarolic gas, in contrast to those in 2004, implying a common source. If the gas source were remained unchanged, the paths for gas emission through the soil in LHK would have been similar to that of the fumaroles. This also reinforces the feasibility of adopting soil gas as a replacement of fumarolic gas as a suitable monitoring parameter in LHK. However, this

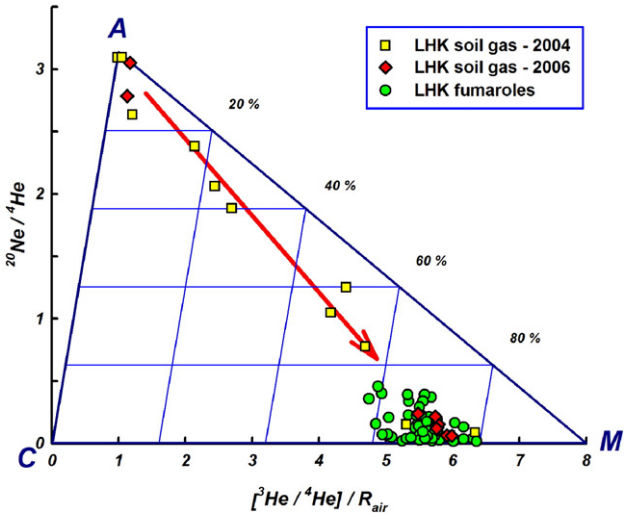

Fig. 8. Correlation between $^{20}Ne/^4He$ and $[^3He/^4He]/R_{air}$. Gas of fumaroles (circle) is mainly derived from mantle and mixes with small amount of crust. A distinct trend of air–mantle mixing is seen for the compositions of soil gas sampled in 2004 (square) and 2006 (diamond).

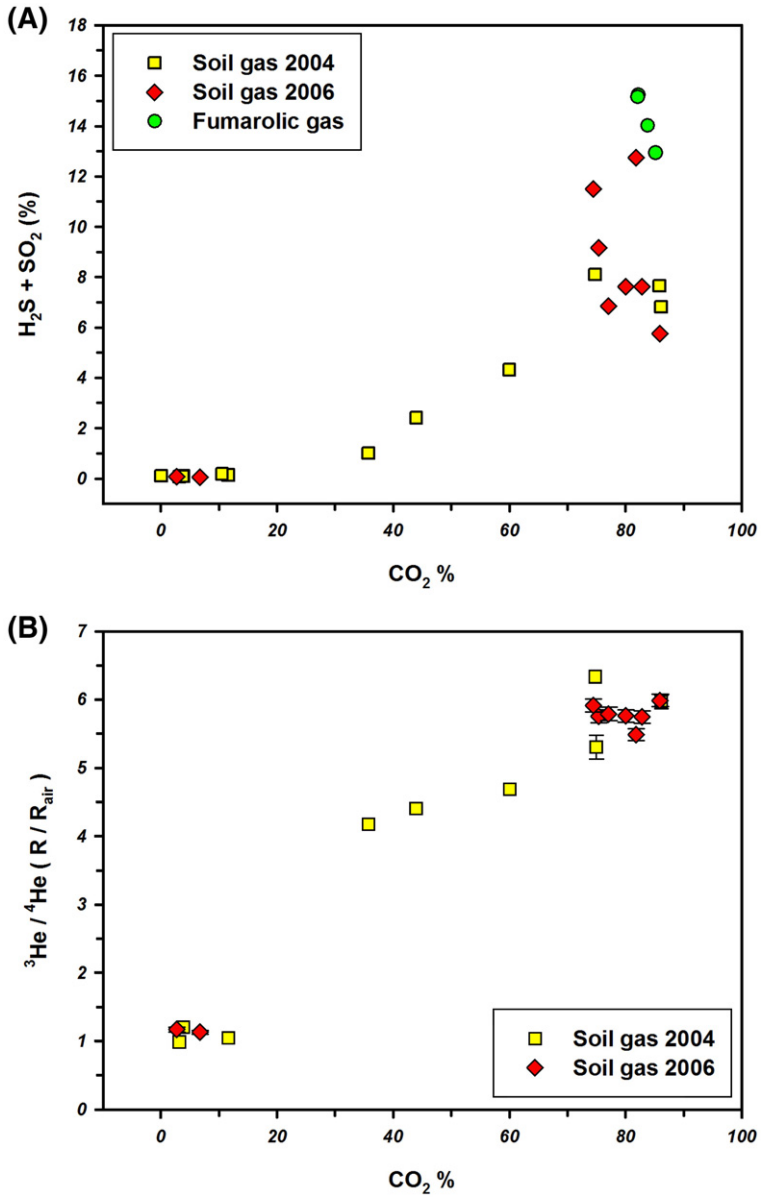

Fig. 9. Variation diagrams of (A) total sulfur vs. soil CO_2 concentration; (B) He isotopic ratio vs. soil CO_2 concentration. Samples with high CO_2 abundance also have high total sulfur contents and R_A values. Abundance of soil CO_2 therefore represents the abundance of magmatic gas composition, which could be a good proxy of future monitoring in the area.

needs to be confirmed through further monitoring in the future.

5. Concluding remarks

The study has confirmed the feasibility of using the closed-chamber method to measure the soil CO_2 flux in the Tatun Volcano Group. The calculated soil CO_2 emission rates from Liu-Huang-Ku in 2004 and 2006 are 19.8±0.2 and 22.4±0.2 t day^{-1} respectively. Furthermore, the soil CO_2 output per unit area was 582 and 659 t km^{-2} day^{-1} respectively, which is similar to other areas in the world with high soil CO_2 flux. The spatial distribution of soil CO_2 flux indicates the locations of possible heat sources and/or fractures in Liu-Huang-Ku. Helium and carbon isotopic data reveal that the principle magmatic source of soil gas is the mantle. The results of the isotopic composition of soil gas and its temporal variation support the conclusion that soil CO_2 can be a potential parameter for future monitoring in this area.

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