Journal of Volcanology and Geothermal Research 178 (2008) 624–635

Contents lists available at ScienceDirect

Journal of Volcanology and Geothermal Research

journal homepage: www.elsevier.com/locate/jvolgeores

Temporal variations of gas compositions of fumaroles in the Tatun Volcano Group, northern Taiwan

Hsiao-Fen Lee [a], Tsanyao Frank Yang [a,*], Tefang Faith Lan [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
[b] Central Geological Survey, MOEA, P.O. Box 968, Taipei 235, Taiwan

ARTICLE INFO

Article history:
Received 15 October 2007
Accepted 10 June 2008
Available online 18 June 2008

Keywords:
Tatun Volcano Group
Taiwan
volcanic gases
^{3}He/^{4}He
geochemical monitoring

ABSTRACT

Hydrothermal activity is common in the Tatun Volcano Group of northern Taiwan. Helium isotopic compositions of fumarolic samples show that mantle component occupies more than 60% in the previous study. Along with recent seismic results, a magma reservoir is inferred to have existed beneath the area of Da-you-keng, where fumarolic venting is the most active in Tatun Volcano Group. Progressive increases of HCl concentrations and SO_2/H_2S ratio in fumaroles from Da-you-keng have been observed since August 2004. The HCl concentration changed from almost the detection limit to thousands of ppm, even up to 30,000 ppm. SO_2/H_2S ratios varied from almost 0 to 3; hence SO_2 became the dominated S species in this area. These variations were accompanied by rising temperature of fumaroles in the Tatun Volcano Group, especially in the area of Da-you-keng (from boiling point to 131 °C). Meanwhile, ^{3}He/^{4}He ratios showed a decreasing trend but returned to normal values shortly thereafter. We propose two possible processes, 1) new magma supply and 2) recent opening of fractures in local area, to explain these observations. Based on the change of ^{3}He/^{4}He ratio and lack of ground deformation, we consider the latter might be more plausible.

1. Introduction

The variation of volcanic gas composition is considered as an important index of volcanic activity (e.g. Ohnishi and Kamada, 1981; Sano et al., 1984; Menyailov et al., 1986; Chiodini et al., 1993; Giggenbach, 1996; Notsu et al., 2001). Compositions of volcanic gases can help to understand the sources and origin of magmas in one area (e.g. Symonds et al., 1994; Giggenbach, 1996; Capasso et al, 1997; Giammanco et al, 1998; Yang et al., 2003b, 2005; Chen et al., 2005; Pecoraino and Giammanco, 2005). Previous studies have shown that the compositions of volcanic gas and some reactive gas ratios change dramatically before eruption (e.g. Noguchi and Kamiya, 1963; Walker, 1974; Oskarsson, 1984; Hirabayashi et al., 1986; Fischer et al., 1996; Duffell et al., 2003; Carapezza et al., 2004; Aiuppa and Federico, 2004; Capasso et al., 2005). Integrated with other available data/investigations, observations of chemical and isotopic compositions of volcanic gases can monitor the volcanic activity and predict forthcoming eruptions (e.g. Aramaki, 1991; Aiuppa et al., 2007).

Taiwan is located on the boundary of the Philippine Sea Plate and the East Asian continent that makes the tectonic setting not merely a collision zone but also a transform region between Luzon and Ryukyu subduction systems (Fig. 1A) (e.g. Teng et al., 1992; Teng, 1996; Wang et al., 1999). Situated at the northern tip of Taiwan, the Tatun Volcano Group (hereafter called the TVG) is a part of the Northern Taiwan Volcanic Zone. It also belongs to the southwest part of the Okinawa Trough which might be related to post-collisional collapse rather than arc volcanism (Wang et al., 1999). The TVG includes more than 20 Quaternary volcanoes which are mainly composed of andesitic lavas and pyroclastic flows (Chen and Wu, 1971). The most important geological structure in the TVG is the Chinshan Fault, which strikes in the NE–SW direction. The major fumaroles and hot springs are distributed along this reverse fault indicating that volcanic activities of the TVG may be associated with the activities of Chinshan Fault (Yen et al., 1984).

The eruption history of the TVG can be divided into two major periods according to the results of K–Ar dating (Juang and Chen, 1989; Tsao, 1994) and fission track analysis (Wang and Chen, 1990). The first eruptive period began around 2.5–2.8 Ma, then ceased after about one million years. The second period started 1.5 Ma and continued until around 0.1–0.2 Ma (Song et al., 2000a). The TVG is considered dormant because of no previous historical eruptions, however, post-volcanic activities i.e., hot springs and gas fumaroles, are well developed now, suggesting that the TVG might not be extinct. Chen and Lin (2002) reported some volcanic ashes in sedimentary formations that are younger than about 20 ka along with grains of charcoals in the Taipei Basin deposits. In addition, helium isotopic results from fumarolic gas demonstrate that more than 60% of helium

---

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

0377-0273/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jvolgeores.2008.06.005

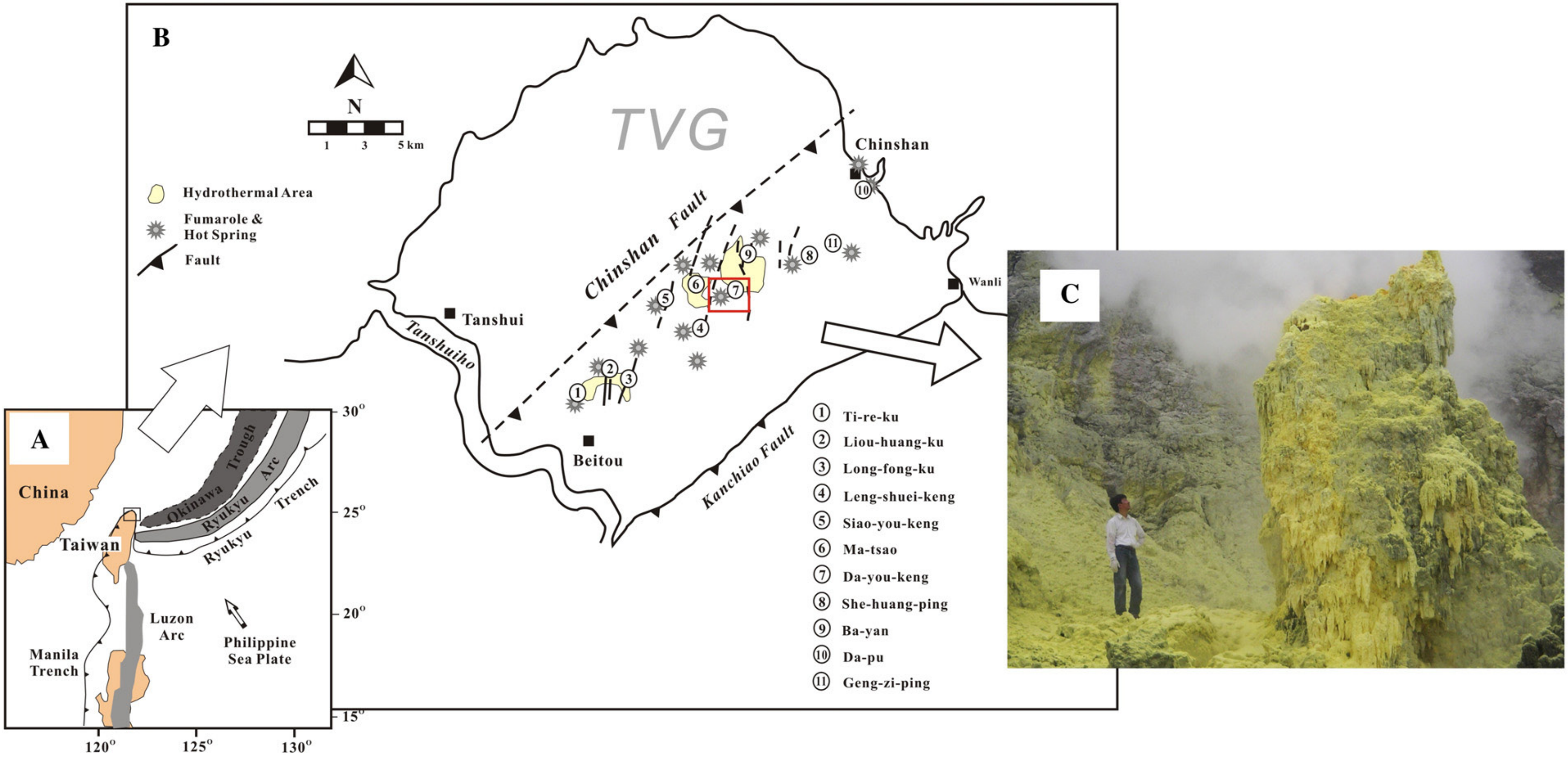

Fig. 1. (A) Sketch of the geologic setting of Taiwan. (B) Location of the Tatun Volcano Group (TVG) and sampling sites in this study. (C) Photograph of the biggest fumarole in Da-you-Keng (DYK). The cone has collapsed as of 2008.

from the majority of sample sites exhibit mantle-derived characteristics (Yang et al., 1999; Yang, 2000), indicating that a magma chamber might still exist beneath the TVG area. It is therefore concluded that the TVG could still be active (Song et al., 2000b). Recent seismic observations recorded some volcano-seismic signals, which are considered to be most probably associated with the direct or indirect interaction between hydrothermal or magmatic fluids and solid rock in the upper crust (Lin et al., 2005a, b; Konstantinou et al., 2007). Helium isotopic data and seismic results point towards existence of a magma chamber underneath Northern Taiwan, particularly in the area of Da-you-keng (DYK) (Yang et al., 2003b; Lin et al., 2005a, b).

The TVG is about 15 km north of metropolitan Taipei which has more than seven million inhabitants. Also there are two nuclear power plants located only a few kilometers northeast of the TVG. Thus, monitoring potential volcanic activity in the Tatun area is an urgent task.

In this study we present the variations of volcanic gases in chemical and isotopic composition in the TVG from 2003 to 2006 and explain possible reasons for the observed phenomena. Since August 2004, fumarolic gas composition of DYK had not only a progressive increase in HCl concentration but also in SO_2/H_2S ratio. Except for the fumaroles in the area of Leng-shuei-keng, the temperature of all measured fumaroles was higher than before, especially in DYK. Moreover, the total sulfur contents and CO_2 flux of soil gas in Liu-Huang-Ku hydrothermal area in 2006 were higher than in 2004 (Lan et al., 2007). Besides, the $^3He/^4He$ ratio was quite steady in last few years but showed a decreasing trend in this period

Table 1

The average outlet temperature and dry gas compositions of fumaroles from the Tatun Volcano Group

Sample	Year	T (°C)	Ar	N_2	CO	CH_4	C_2H_6	He	H_2	O_2	HCl	H_2S	SO_2	S_{total}	CO_2	H_2O	SO_2/H_2S
Da-you-keng (DYK): F	2004	–	23.1	2196	3.59	12.1	0.03	0.57	64.3	380	100	2196	69	2265	101,153	893,815	0.03
DYK: F	2005	106	57.1	5183	3.03	85.7	0.92	0.46	7.38	951	775	3091	209	3300	96,727	893,015	0.07
DYK: F	2006	115	66.9	6008	0.69	19.0	0.09	0.62	86.5	1215	795	2130	3539	5669	134,310	851,961	1.67
Liou-huang-ku (LHK-1): F	2004	–	6.15	1166	–	170	0.79	0.42	3.55	61.1	21.3	8037	18.9	8056	145,505	844,997	0.002
LHK-1:F	2005	99.7	6.37	953	2.31	901	3.30	0.48	3.83	46.6	7.28	4046	2.85	4049	97,104	896,923	0.001
LHK-1:F	2006	103.5	47.1	4324	0.23	163	0.37	0.21	0.03	55.6	6.04	6137	42.6	6180	69,790	919,435	0.007
Hsiao-you-keng (SYK): F	2004	–	63.4	5722	1.45	600	2.61	0.57	96.8	1227	10.6	3738	13.7	3752	135,075	853,450	0.004
SYK:F	2005	97.6	15.9	1745	2.72	696	4.02	0.64	35.1	90.5	6.28	3482	20.0	3502	91,324	902,579	0.006
SYK:F	2006	99.3	13.6	1671	0.35	431	1.82	0.25	11.2	51.9	10.5	3976	36.9	4013	77,311	916,496	0.009
Leng-shuei-keng (LFK): F	2004	–	12.7	1579	0.90	144	0.79	0.39	10.5	195	8.86	5321	14.6	5335	110,169	882,544	0.003
LFK:F	2005	99.5	72.0	7814	3.18	911	4.50	1.38	9.22	947	8.98	19,707	71.2	19,778	191,668	778,782	0.004
LFK:F	2006	105	63.1	6091	0.27	272	0.59	0.93	0.52	123	48.3	4764	1.86	4766	140,084	848,550	<0.001
Leng-shuei-keng (LSK): F	2004	–	28.7	4783	2.66	623	2.70	2.03	45.9	290	11.3	40,068	37.3	40,106	258,679	695,423	0.001
LSK:F	2005	66.2	203	23,492	15.0	2560	16.2	5.94	240	547	76.4	94,290	1227	95,517	572,751	304,590	0.013
LSK:F	2006	57.5	428	39,553	2.07	1762	5.16	4.00	71.0	787	52.8	49,786	559	50,345	601,057	305,953	0.011
Ma-tsao (MT-1):F	2004		6.96	832	1.90	443	6.38	0.45	7.81	61.8	11.3	2037	1.02	2038	123,043	873,549	0.001
MT-1: F	2005	98.9	25.1	2303	3.56	535	5.82	0.56	8.63	92.0	17.1	2505	15.0	2520	88,489	906,002	0.006
MT-1: F	2006	98.5	28.0	2463	0.10	1035	12.7	0.84	1.64	33.8	34.3	5054	140	5194	97,597	893,607	0.028
Ba-yan (BY): F	2004		276	3167	2.60	1487	6.80	1.45	3.16	411	7.99	3863	281	4144	144,498	846,001	0.073
BY: F	2005	99.1	27.3	3143	3.27	1116	10.5	1.23	4.36	324	14.7	896	590	1485	97,627	896,250	0.658
BY: F	2006	100	42.3	4385	0.09	1088	5.66	0.39	0.08	87.5	5.47	1657	645	2302	97,720	894,409	0.389
Geng-zi-ping (GZP): F	2005	99.1	14.3	1805	–	172	0.25	0.94	9.79	19.5	6.71	5308	9.41	5317	58,706	933,950	0.002
GZP:F	2006	108	20.3	2069	0.10	68.9	0.24	0.72	2.87	82.4	11.5	5694	2.33	5697	62,150	929,907	<0.001

Sample	Year	T (°C)	Ar	N_2	CO	CH_4	C_2H_6	He	H_2	O_2	HCl	H_2S	SO_2	S_{total}	CO_2	HCl/S_{total}
Da-you-keng (DYK): F	2004	–	92.4	10,337	34.0	166	0.28	5.02	705	906	1046	25,881	816	26,697	960,041	0.04
DYK: F	2005	106	283	27,367	31.2	1072	4.11	5.46	54.7	1186	9077	35,334	2390	37,724	923,407	0.24
DYK: F	2006	115	171	18,957	3.63	202	2.45	7.57	14.3	856	13,928	25,364	42137	67,500	898,495	0.21
Liou-huang-ku (LHK-1): F	2004	–	43.5	9126	–	1881	7.48	4.54	35.2	288	99.4	71,691	169	71,859	916,659	0.001
LHK-1:F	2005	99.7	70.9	9929	23.4	8445	31.7	4.46	32.1	461	65.3	41,056	29.0	410,85	939,859	0.002
LHK-1:F	2006	103.5	582	53,658	3.64	2019	4.61	3.38	0.41	828	70.2	68,963	478	69,442	873,394	0.001
Hsiao-you-keng (SYK): F	2004	–	361	33,434	13.6	4731	21.3	4.38	774	6769	78.4	29,457	108	29,565	924,254	0.003
SYK:F	2005	97.6	196	21,122	25.1	7733	45.1	7.40	394	1071	64.8	38,433	220	38,653	930,695	0.002
SYK:F	2006	99.3	183	21,009	3.06	5855	28.1	3.51	150	820	103	54,654	507	55,162	916,855	0.002
Leng-shuei-keng (LFK): F	2004	–	59.6	11,428	12.6	1935	5.40	5.46	159	441	69.0	68,648	189	68,837	917,057	0.001
LFK:F	2005	99.5	76.4	12,687	20.6	3550	13.7	6.21	56.1	902	52.8	59,203	214	59,417	923,224	0.001
LFK:F	2006	105	390	38,034	1.77	1909	4.10	6.97	3.85	797	290	32,594	12.7	32,606	925,961	0.009
Leng-shuei-keng (LSK): F	2004	–	140	18,830	18.0	1977	9.83	6.43	176	1578	45.5	123,525	115	123,640	853,574	<0.001
LSK:F	2005	66.2	269	31,518	20.8	3534	21.7	7.97	322	842	95.9	137,860	1794	139,654	823,732	0.001
LSK:F	2006	57.5	620	57,454	2.94	2423	6.54	6.29	120	1292	70.7	76,468	859	773,27	860,710	0.001
Ma-tsao (MT-1):F	2004	–	57.7	6874	18.4	3489	50.1	3.49	58.4	562	107	16,635	8.36	16,644	972,149	0.006
MT-1: F	2005	98.9	326	29,452	34.5	6085	74.3	6.53	91.1	1182	149	29,499	176.63	29,676	932,946	0.005
MT-1: F	2006	98.5	206	19875	0.89	8081	99.0	6.29	16.2	342	326	51,730	1428.6	53,158	917,964	0.006
Ba-yan (BY): F	2004	–	1460	20,751	16.8	10,165	43.4	10.1	18.2	2646	44.0	21,295	1552	22,847	942,028	0.002
BY: F	2005	99.1	303	34,255	33.5	10,817	101	12.5	46.7	3089	181	10,447	6877	17,324	933,907	0.010
BY: F	2006	100	372	39,283	0.87	10,416	55.8	4.90	0.83	506	51.4	16,692	6504	231,96	926,244	0.002
Geng-zi-ping (GZP): F	2005	99.1	239	29,278	–	2673	3.87	14.7	152	343	114	81,163	144	81,307	885,876	0.001
GZP:F	2006	108	271	28,509	1.19	920	4.12	11.4	23.8	1035	170	90,160	36.9	90,197	878,967	0.002

Note: Concentration is given in units of μmol/mol; F: fumaroles; $S_{total}=SO_2+H_2S$; –: not analyzed or not detected.

Table 2
The average temperature and dry compositions of the bubbling springs from the Tatun Volcano Group

Sample	Year	*T* (°C)	Ar	N_2	CO	CH_4	C_2H_6	He	H_2	O_2	HCl	H_2S	SO_2	S_{total}	CO_2	SO_2/H_2S
Dapu (DP): B	2004 –	–	354	53,674	17.0	28,190	44.5	35.5	14.8	4571	6346	1555	8.35	1563	905,197	0.005
DP: B	2005	50.4	268	45,877	29.4	29,191	119	21.8	41.7	2059	974	728	4.46	732	920,698	0.006
DP: B	2006	48.9	224	40,019	1.08	23,671	86.8	36.5	3.37	976	158	3084	100	3184	931,769	0.033
She-huang-ping (SHP): B	2004	–	55.4	6258	–	1253	6.69	2.78	17.3	309	95.8	17,617	12.9	17,630	974,373	0.001
SHP: B F	2005	99.4	100	11,583	20.9	4294	16.0	7.17	34.0	170	216	51,989	60.0	52,049	931,524	0.001
SHP: F	2006	101	229	22,938	1.10	1794	4.21	5.48	3.34	772	68.6	48,001	923	48,925	925,521	0.019
Liou-huang-ku (LHK-2): B	2004	–	253	24,593	9.86	3571	13.1	6.58	12.5	2857	82.4	31,355	151	31,506	937,096	0.005
LHK-2: B	2005	50.8	187	19,550	24.7	11,181	37.3	6.24	23.0	1990	72.0	22,398	29.0	22,427	944,511	0.001
LHK-2: B	2006	51.9	369	32,578	1.26	5943	13.3	8.59	2.61	1568	244	16,850	19.5	16,869	942,406	0.001
Ma-tsao (MT-2): B	2004	–	144	17,046	14.7	12,577	125	9.79	62.8	1498	77.6	40,432	53.6	40,486	927,966	0.001
MT: B	2005	64.5	143	12,727	25.2	9315	115	6.67	65.8	1457	73.9	18,331	80.7	18,412	957,670	0.004
MT: B	2006	63.8	220	18,222	0.48	9385	117	7.86	22.7	588	99.5	16,090	86.5	16,176	955,252	0.005
Ti-re-ku (TRK): B	2004	–	398	18,652	35.4	742	22.8	1.60	46.4	1975	10,696	8589	4.41	8593	95,8861	0.001
TRK: B	2005	84.1	351	18,001	30.8	2524	48.2	6.39	34.6	1862	1190	8349	4.62	8353	967,618	0.001
TRK: B	2006	87.2	618	38,319	2.98	1256	21.2	–	9.12	984	3629	10,431	90.5	10,522	944,841	0.009

Note: Concentration is given in units of μmol/mol; B: hot spring bubbles; F: fumaroles; $S_{total}=SO_2+H_2S$; –: not analyzed or not detected.

that lasted for approximately 6 months. These variations are probably correlated to local magma activity.

2. Sampling and measurements

Several fumaroles and hot springs are distributed from Beitou to Chinshan in the TVG area. Eleven sites were chosen for regular sampling (Fig. 1B). DYK is the most active and important geothermal area with one of biggest venting fumaroles (Fig. 1C) in the TVG because of its highest $^3He/^4He$ ratio (~6.8 R_A. Yang et al., 2003b). $^3He/^4He$ ratios decrease southwestward and northeastward from DYK along the strike of Chinshan Fault (Yang et al., 1999, 2003b). Based on the helium isotopic data, Yang et al. (2003b) suggested that a magma chamber may exist underneath DYK. DYK is at an elevation of 1400 m and contains a host of fumaroles, sulfur vents, and hot springs. The fumaroles and vents continuously discharge stream and gases. There are two major fumaroles in DYK and the distance between them is about 100 m. The bigger fumarole usually forms a high cone made of sulfur and ash, however, it collapses easily (Fig. 1C). For reasons of safety, the smaller fumarole which is located in a small platform is chosen as the regular sampling site. The gas compositions from DYK fumaroles, which are dominated by steam and CO_2, are similar to other geothermal areas in the TVG. The minor components are sulfur species (H_2S and SO_2), N_2 and CH_4. The H_2S concentrations are always much higher than SO_2 in all fumarolic gases in the TVG (Lee et al., 2005).

Giggenbach (1975) described a reliable method for sampling volcanic gases, and the method is by far the most widely used. Following the method, samples were collected using Giggenbach-bottles which were evacuated and filled with 50 ml 4N alkali hydroxide solution. By using such method, dissolvable species like H_2O, CO_2, H_2S, SO_2, and HCl are dissolved in the alkali hydroxide solution, whereas un-dissolvable species (H_2, N_2, Ar, O_2, He, CO, CH_4) remain in the headspace gas phase of the bottle. To collect gas samples, a 1-m-long titanium tube was inserted into the fumaroles. To reduce air contamination, a hand pump was used to evacuate the air in the titanium tube first.

After sampling gases using the Giggenbach-bottle, we used a pre-evacuated low permeability potassium-glass bottle with two vacuum stopcocks at both ends to collect volcanic gases for helium isotopic analyses. To separate H_2S and SO_2, iodine solution (20 ml 0.05 M) was prepared inside a bottle for fumarolic gas sampling in this study. H_2S

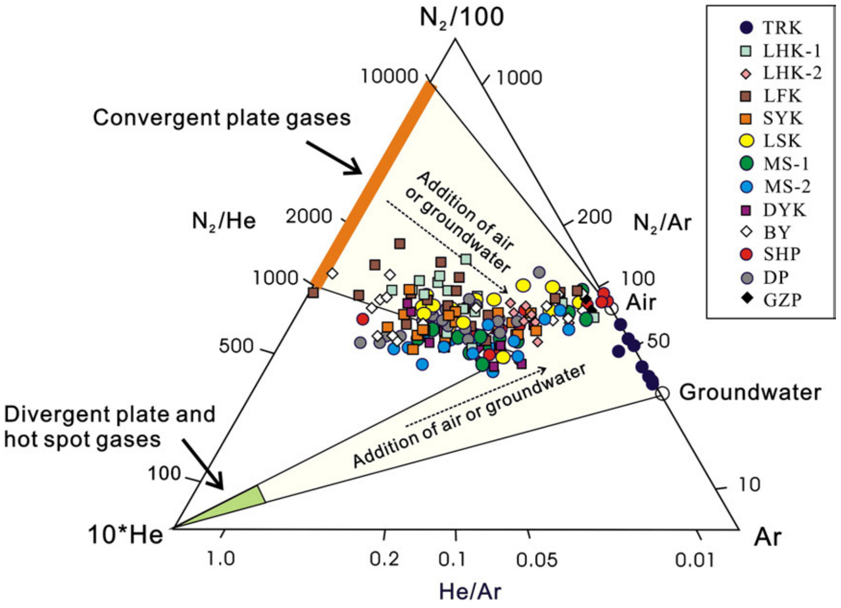

Fig. 2. N_2–He–Ar triangular plot for the Tatun Volcano Group gases. Most samples fall in the range of a mixing trend between convergent plate gases and air/groundwater. It suggests that the degassing sources for the TVG gases are closely related to the subducting process in NE Taiwan. Field boundary shown in the diagram is from Giggenbach (1992). Data from Lee et al. (2005) and this study.

in the fumarolic gases reacts with the iodine solution and the reaction generates solid elemental sulfur as precipitate. SO_2 reacts with iodine solution and turns into SO_4^{2-} which dissolves in the solution (Hirabayashi and Shinohara, 1989). The water replacement method was used to collect bubbles of hot springs.

The volcanic gas compositions of the headspace were analyzed by a gas chromatograph (GC, SRI 8610C) equipped with two thermal conductivity detectors (TCDs) and one flame ionic detector (FID) with methanizer. Hydrogen carrier gas is supplied to the FID and one TCD. Samples pass through a 1 m MS-13X (Molecular Sieve) column which is connected to a Rh-catalyst (Rh 1.5% in Al_2O_3) oven and can detect the composition of Ar, N_2, and CH_4 by TCD. Oxygen in the sample will become combustible by reaction with hydrogen carrier gas in the presence of the Rh-catalyst in the oven and at a temperature of 150 °C. We switch the EPC (electronic pressure control) valve so that samples can pass through 4 m Hayesep-D column and methanizer (380 °C), and then CO, CH_4, CO_2, C_2H_6 can be detected by both TCD and FID. Another TCD with 4 m Molecular Sieve and argon as a carrier gas is used to analyze the concentrations of He, H_2 O_2, N_2, CH_4, and CO_2. Overall, the GC system can analyze compositions of CH_4, C_2H_6, CO, CO_2, Ar, N_2, H_2, He and O_2, simultaneously in one single sample loading. The un-dissolvable gases in the headspace of Giggenbach-bottle had to be analyzed first in order to avoid air contamination which could easily happen while removing the alkali solution from the bottle. Afterward, the solution was extracted and analyzed with an ion chromatograph (IC, Metrohm 790 Personal) to determine the concentration of HCl and total sulfur in the sample. For measuring CO_2 concentration in gas sample, the titration method was applied (Metrohm 702 SM Titrion) by assuming that all of the CO_2 inside the sample had been dissolved as CO_3^{2-} in the alkali solution (Giggenbach, 1975). When the volcanic gases pass through iodine solution, H_2S will become precipitated sulfur and SO_2 will dissolve in the solution. Thus, we can separate SO_2 from precipitates using a filter paper. The filtrate can be used for IC analysis to determine the SO_2 concentration. Consequently, the precipitate part is heated in a vial, which is filled with alkali solution. After the precipitated sulfur is dissolved, H_2O_2 is added to convert SO_3^{2-} into SO_4^{2-}. Then, the solution can be analyzed to determine the concentration of H_2S. Detailed setups and discussions of accuracy/precision and detection limits of all gas compositions follow Lee (2004) and Lee et al. (2005).

Gas samples collected in the potassium-glass bottles were used for analyses of the concentrations and isotopic ratios of helium, neon and other noble gases. $^3He/^4He$ and $^4He/^{20}Ne$ ratios were analyzed by a high-precision noble gas mass spectrometer (Micromass 5400) with dual collectors in the Department of Geosciences, National Taiwan University. Observed $^3He/^4He$ ratios were calibrated against atmospheric standard gas and normalized to R_A (the $^3He/^4He$ ratio in air, 1.39×10^{-6}). Details of the measurements of helium isotopic ratios had been described by Yang (2000) and Yang et al. (2005, 2006).

3. Results and discussions

3.1. Spatial variations of gas compositions

The gas compositions of the TVG were found to be similar to those from all other low-temperature fumaroles in the world (Goff and McMurtry, 2000). The dominant species is H_2O, followed by CO_2, H_2S, N_2 and CH_4 (Tables 1 and 2). The outlet temperatures for these

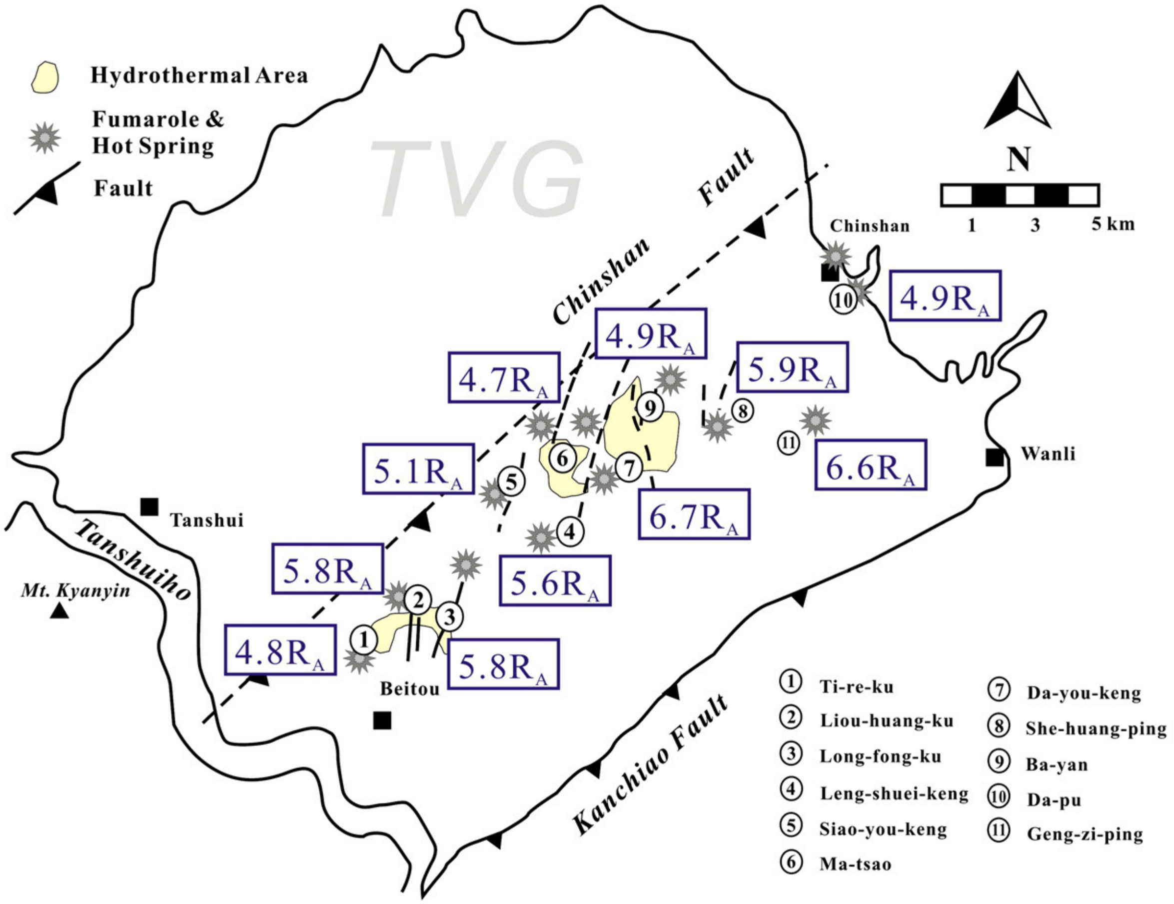

Fig. 3. Distribution of $^3He/^4He$ ratios of the TVG gas samples. $^3He/^4He$ ratios decrease southward and northward from DYK along the Chinshan Fault. The high $^3He/^4He$ ratios (higher than $^3He/^4He$ ratio in air) suggested that He is predominantly of upper mantle origin in the TVG area. The figure is modified from Yang et al. (2003b).

fumaroles were around boiling point (57.5–115 °C, the average temperature). Different tectonic environments of the gases were differentiated by plotting the gas compositions on the N_2–He–Ar diagram (Giggenbach, 1992). In this diagram the gas composition is described in terms of the three end members, meteoric (air and air-saturated water), mantle-derived, and arc type fluids. Based on the relative amounts of N_2, Ar, and He, most samples of the TVG gases exhibited the affinity of convergent plate gases (Fig. 2). It suggests that the degassing sources for the TVG gases were closely related to the subducting process in NE Taiwan.

Helium isotope ratio (^{3}He/^{4}He) of fumaroles and hot springs provides information on the activity and source of magma (Sano and Wakita, 1985; Marty et a1., 1989; Yang et al., 2003a). A postulated magma chamber may exist underneath DYK and the ^{3}He/^{4}He ratios decrease southwestward and northeastward from DYK along the Chinshan Fault (Fig. 3) (Yang et al., 2003b). However, there was a gap in this systematical trend. Ma-tsao (MT) hydrothermal area is very close to DYK hydrothermal area which has the highest ^{3}He/^{4}He ratio in the TVG. Nevertheless, the lowest ^{3}He/^{4}He ratio in the TVG was observed in MT (~4.7 R_A). Distribution of ^{3}He/^{4}He ratios did not fit the linear change described above. This result might be caused by geological structures. Still, ^{3}He/^{4}He ratios of samples from the TVG were much higher than ^{3}He/^{4}He ratio in air. It suggested that He is predominantly of upper mantle origin in the TVG area.

In general, the gas compositions of fumarolic samples from the studied area all exhibited much lower concentration of HCl than other volcanoes in the world (Goff and McMurtry, 2000; Fischer, 2008). SO_2/H_2S ratio is also an important proxy to determine the gas sources. The SO_2/H_2S ratios of the TVG area were found to be similar to those from other low-temperature volcanic gases in the world, i.e. SO_2/H_2S ratio <1 (Lee et al., 2005). For the purpose of using geothermal energy, a lot of geothermal explorations have been done in the TVG area (MRSO, 1969, 1970, 1971, 1973). Two geothermal wells, E208 and E204 which are 1250–1500 m and 1400 m deep, respectively, were drilled in Ma-tsao area. The geothermal wells tapped acid sulfate–chloride water caused by the dissolution of acidic volcanic gases, especially HCl and SO_2 in the water phase (Chen, 1970). The acidic–sulfate–chloride water could be associated with the variations of HCl concentration and SO_2/H_2S ratio.

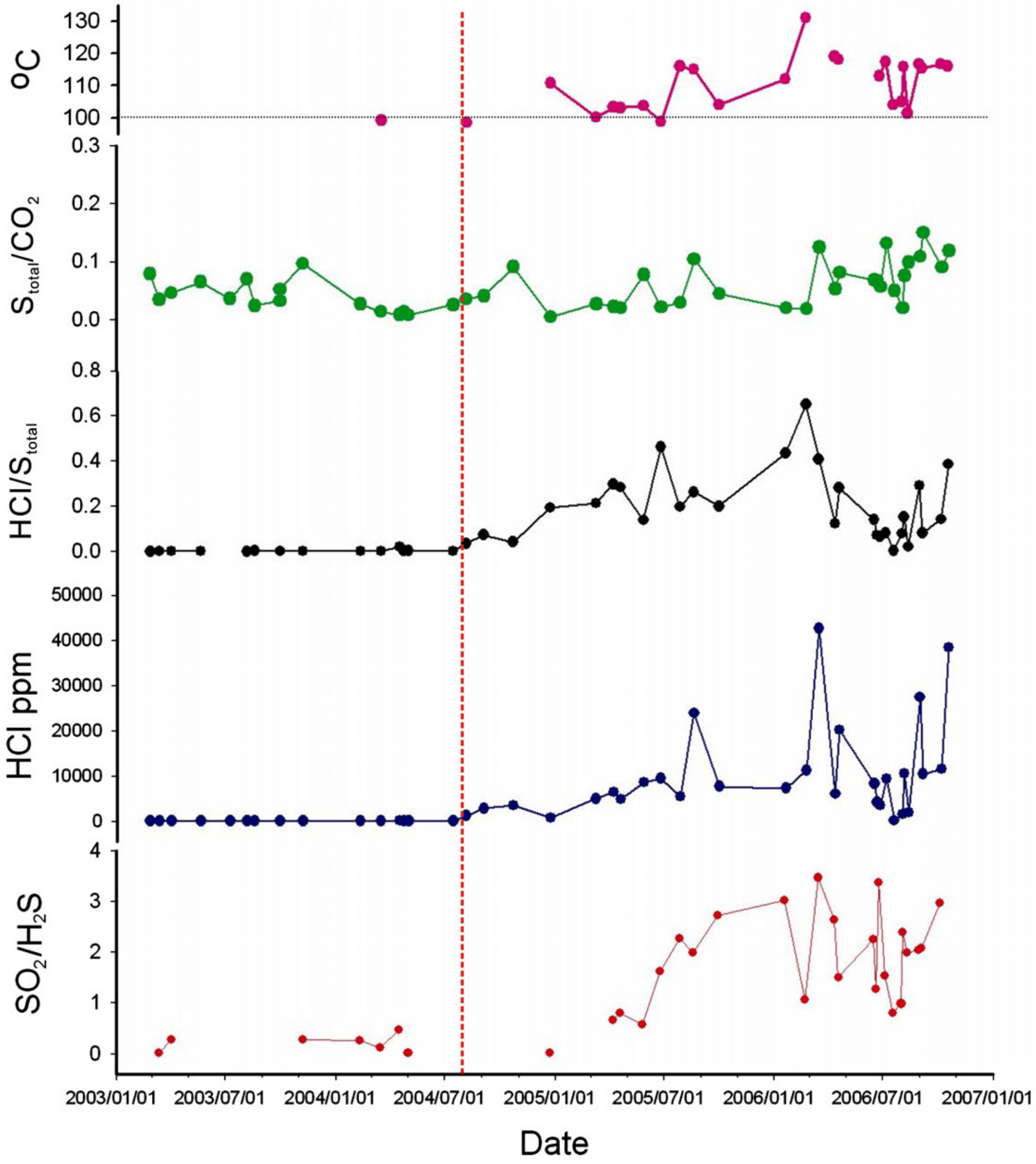

Fig. 4. Variations of gas compositions of fumaroles from DYK. The very low measured HCl concentration and low SO_2/H_2S (<1) ratio are the primary characteristics of the TVG area. The fumarolic gas compositions of DYK started to vary since August 2004 (vertically dashed line). An increase of outlet temperature of the fumaroles was observed at DYK. Progressive increases of HCl concentrations and SO_2/H_2S ratios in DYK fumarolic gases were also observed.

The springs in the TVG area are classified into volcanic and sedimentary types depend on their different aquifers. Spring waters of the volcanic type are mainly supplied by volcanic gases and andesitic rocks, while those of the sedimentary type are from volcanic gases, rhyolitic pebbles and brines in the Wuchihshan Formation (sandstone). Some hot springs located near the sea might be also affected by seawater (Liu et al., 1984; Chen et al., 2001). According to sulfur and hydrogen isotope, petrography and resistivity data, Liu et al. (1984) inferred that another shallow aquifer in depth of 300–600 m should exist at the volcanic rock formation. This aquifer might be divided into several individual segments because of the faults and fractures. The high concentration of CH_4 in gas compositions (Table 1) and temperatures which approach to boiling point both indicate that vapor separated from boiling water near the surface, probably separated from this aquifer(s).

3.2. Temporal variations of gas compositions

From 1999 to 2003, $^3He/^4He$ ratios and other gas components did not show significant variations, implying that the degassing system in the studied area was quite stable (Yang et al., 2003b). From 2003 on particularly since August 2004, fumarolic gases sampled from DYK present significant increases not only in HCl concentration but also in SO_2/H_2S ratio. The increase of SO_2/H_2S ratio is consistent with the result of recent in situ real time measurement at DYK (Witt et al., 2008-this issue). The outlet temperature of fumaroles in the TVG was

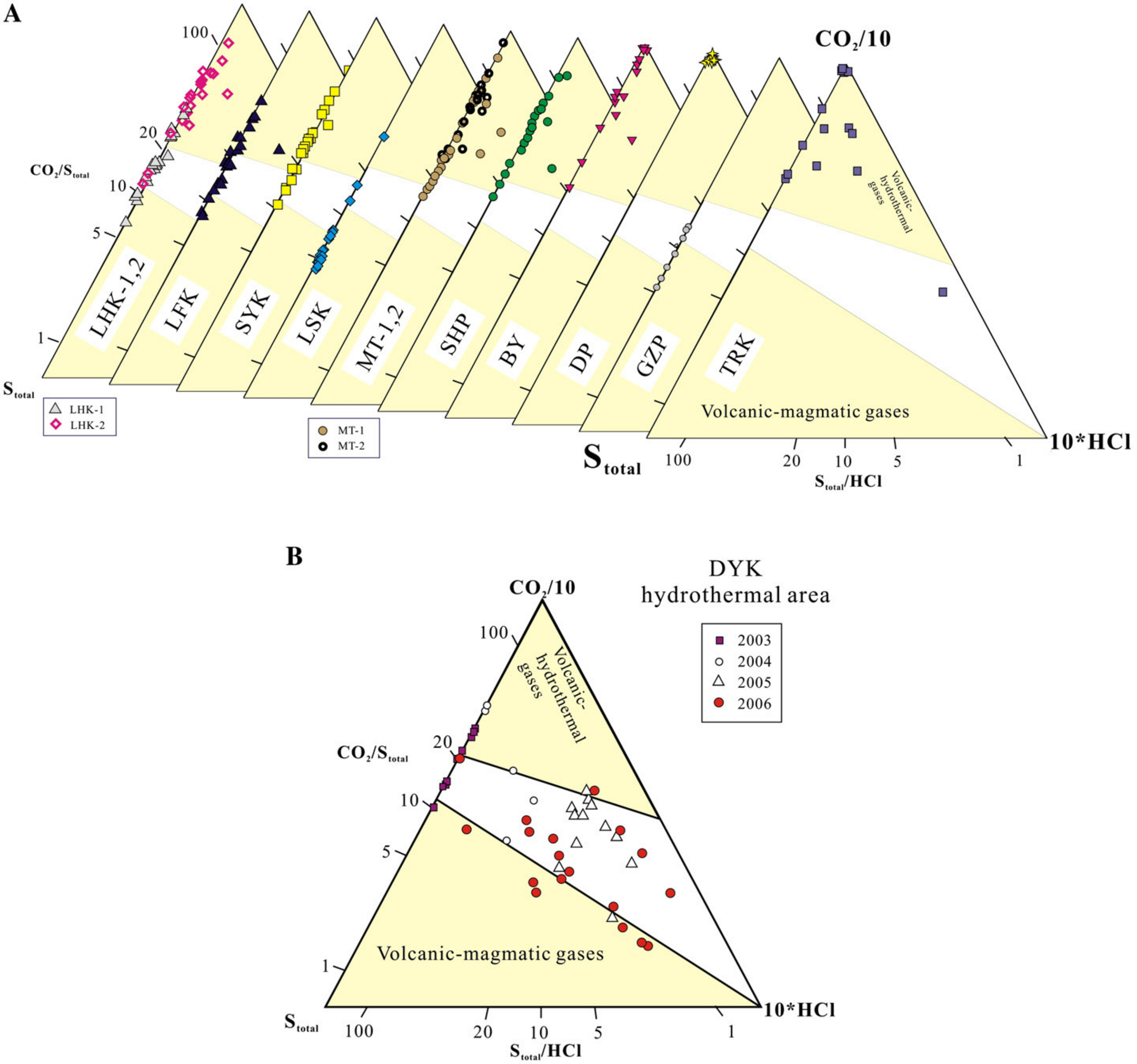

Fig. 5. CO_2–S_{total}–HCl triangular plot for the Tatun Volcano Group gases. (A) Except for LSK and GZP, most gases fall in the range of hydrothermal gases. Compared with the samples collected from fumaroles and hot springs in the same site (LHK-1, 2 and MT-1, 2), the samples collected from water have higher CO_2/S_{total} ratio. (B) CO_2–S_{total}–HCl triangular plot for DYK gases, exhibiting more a magmatic signature than before. Note: $S_{total} = H_2S + SO_2$; MT-1 and LHK-1 = samples collected from fumaroles; MT-2 and LHK-2 = samples collected from hot springs. LSK = Leng-shuei-keng fumaroles; GTP = Geng-zi-ping fumaroles; DYK = Da-you-keng fumaroles. Rest abbreviations are same as shown in Table 1. Field boundary shown in the figure is from Giggenbach (1992). Data from Lee at al. (2005) and this study.

also higher than before, especially in DYK (Fig. 4). The highest outlet temperature of fumaroles in DYK was recorded to be 131 °C in February 2006, and the temperature has been almost constant at 116 °C since then (Fig. 4). The outlet temperature of fumaroles located in other hydrothermal areas also increased slightly, in the range of 5 to 10 °C. For instance, the temperature of fumaroles located in LHK hydrothermal area changed from 97.6 to 106 °C. Besides, Lan et al. (2007) reported that soil temperature in LHK hydrothermal area was also higher in 2006 than in 2004.

HCl concentration is easily affected by water because of its high solubility. HCl may be lost or gained for the ascending gas due to a hydrothermal system. Although HCl concentration was variable, there was a quite obvious increase of HCl concentration in DYK (Fig. 4). The main Cl species in magmas are alkali chlorides, and HCl is released during shallow degassing. For low-temperature discharging (i.e. temperature <200 °C), HCl concentrations are generally low, except for some discharges affected by rapid heating (Giggenbach, 1996). Almost all boiling-point fumaroles in the world have low HCl because most they are derived from a boiling aquifer beneath a fumarolic field.

As we know that seawater contributes a little part to the spring water of Chinshan and Dapu near the sea, it may be considered that the increase of HCl concentration in DYK area was caused by sea-water intrusion. The probable intruded pathway of seawater could go along the Chinshan Fault. If HCl concentration increased by sea-water intrusion indeed, all hydrothermal areas near the fault/sea should be affected. Nevertheless, this anomaly of HCl was only observed in DYK area where is located in the middle part of the Chinshan Fault. On the other hand, sea-water intrusion cannot cause temperature rise. The outlet temperature of fumaroles in DYK had risen for 10–20° degrees in the past two years. The sea-water intrusion is not suitable to account for the HCl concentration increase.

HCl and SO_2 are easily dissolved in water. H_2S and SO_2 are the dominant S species in volcanic gases and usually magmatic in origin. The solubility and relative proportions of the SO_2 and H_2S are strong functions of the composition and redox state of the melt (Haughton et al., 1974; Wallace and Carmichael, 1992). At a given O_2 fugacity, sulfur occurs as SO_2 at high temperature and as H_2S at lower temperature. Giggenbach (1987) suggested that Eq. (1) is important for a degassing magma during its ascend towards the surface.

$$SO_2 + 3H_2 \leftrightarrow H_2S + 2H_2O \tag{1}$$

Thermodynamic modeling indicates that the reaction shifts to the right at high pressures (i.e. the magma degasses at great depths), thus H_2S is the dominant sulfur species in the gas. Conversely, hot gases escaping from a magma body emplaced at shallow levels in the crust will tend to be SO_2-dominated, as frequently observed in the field (Giggenbach, 1987). Therefore, the SO_2/H_2S ratio can be an important indicator of magma activity.

The appearance of HCl and SO_2 in fumarolic gases in DYK could be related to the boiling of acidic sulfate–chloride water from the geothermal wells in the MT area, close to DYK. This deep aquifer (1250–1500 m deep) is assumed as the primary hydrothermal system (PHS) for the main source of the acid sulfate–chloride hot springs. The low concentration of HCl and SO_2 in gas compositions of fumaroles indicates that fumarolic gases cannot be generated from this acid sulfate–chloride water directly. The fumarolic gases could be produced by mixing meteoric water, the shallow aquifer (secondary hydrothermal system, SHS), with vapor phases generated by evaporation of primary hydrothermal system. More volcanic gases were released in association with magma activity and caused the increase of HCl and SO_2/H_2S ratio in DYK.

Since CO_2 and sulfur species (including H_2S and SO_2) are the major components in fumarolic gases, CO_2/S_{total} ratio has been suggested as useful proxy to identify their sources (Giggenbach, 1992, 1996). More significant contributions of magmatic gases or limited influence of aquifers can produce higher concentration of sulfur species. Gases originated from magmatic source usually have higher total sulfur concentrations and hence, exhibit lower CO_2/S_{total} ratios (<10). In contrast, hydrothermal gases exhibit lower total sulfur concentrations and higher CO_2/S_{total} ratios. By plotting CO_2–S_{total}–HCl as a ternary diagram, the CO_2 corner can be considered as a low-temperature extreme, and sulfur species can be taken as the main indicator of a magmatic influence. Most of the TVG gases belong to the hydrothermal gases because of their high CO_2/S_{total} ratios (Fig. 5A) (Lee et al., 2005). Based on this ternary diagram, we can recognize that DYK gases exhibited a more magmatic signature than before (Fig. 5B).

As described above, more than 60% of the helium is mantle-derived for fumaroles in most of the sampling sites in the TVG, and the highest $^3He/^4He$ ratio was obtained from the fumarolic gas of DYK (Yang et al., 1999). The $^3He/^4He$ ratio had been kept at a constant level in DYK from 1999 to 2004. However, it changed during a few months after August 2004 with a decreasing trend, and returned to prior values after approximately 6 months (Table 3, Fig. 6).

The $^3He/^4He$ ratio may increase if new magmatic material is added to the source, or it is decreased when more crustal material is added during the ascent of the gases. The decrease of the $^3He/^4He$ ratio in

Table 3
The $^4He/^{20}Ne$ and $^3He/^4He$ data of DYK fumaroles from 2003 to 2006

Sample no.[a]	$^4He/^{20}Ne$	$^3He/^4He$ ($\times 10^{-6}$)	$[R/R_A]$[b]	$[R/R_A]_c$[c]	±1σ	Note
20030226-DYK-1	3.59	8.12	5.84	6.32	0.40	
20030313-DYK-1	25.1	9.34	6.72	6.79	0.10	
20030402-DYK-1	75.0	9.44	6.79	6.81	0.10	
20030521-DYK-1	133	9.18	6.60	6.62	0.11	
20030709-DYK-1	37.9	10.58	7.61	7.67	0.12	
	38.4	10.54	7.58	7.64	0.14	Duplicate
20030723-DYK-2	4.34	8.61	6.19	6.60	0.10	
20030930-DYK-1	2.12	7.95	5.72	6.56	0.10	
20031107-DYK-2	4.70	8.38	6.03	6.40	0.09	
20040211-DYK-1	6.47	9.62	6.92	7.23	0.10	
20040501-DYK-1	37.0	9.47	6.82	6.87	0.09	
20040527-DYK-1	6.67	8.59	6.18	6.44	0.16	
20040714-DYK-1	1.13	7.59	5.46	7.22	0.11	
20041022-DYK	47.9	9.34	6.72	6.76	0.11	
		9.41	6.77	6.79	0.11	Duplicate
20041107-DYK (G)	1.32	7.56	5.44	6.85	0.10	
20041215-DYK-1	18.9	7.55	5.43	5.51	0.08	
20041223-DYK	7.92	9.16	6.59	6.83	0.10	
20050307-DYK-1	7.36	8.57	6.17	6.40	0.09	
20050407-DYK	14.7	8.93	6.43	6.55	0.09	
20050419-DYK-1	8.25	7.99	5.75	5.94	0.09	
20050527-DYK-1	9.16	9.25	6.65	6.86	0.11	
20050625-DYK	8.06	8.14	5.86	6.06	0.09	
20050727-DYK	5.33	6.68	4.81	5.05	0.07	
20050930-DYK	3.34	6.48	4.66	5.05	0.11	
20051119-DYK	71.1	8.18	5.89	5.91	0.09	
20060214-DYK	8.03	9.26	6.66	6.89	0.12	
20060222-DYK-2	10.3	9.41	6.77	6.96	0.11	
20060315-DYK	36.6	9.72	6.99	7.04	0.11	
20060411-DYK	43.7	9.17	6.60	6.64	0.14	
20060418-DYK	35.9	9.01	6.48	6.53	0.15	
20060422-DYK	59.8	9.76	7.02	7.05	0.10	
20060509-DYK	61.9	9.54	6.87	6.90	0.10	
20060525-DYK	42.7	9.75	7.01	7.06	0.10	
20060615-DYK	53.3	9.59	6.90	6.93	0.10	
20060620-DYK	2.54	8.29	5.96	6.68	0.26	
20060705-DYK	9.20	9.47	6.82	7.02	0.10	
20060718-DYK	9.20	9.17	6.60	6.80	0.11	
20060801-DYK	39.4	9.54	6.86	6.91	0.10	
20060811-DYK	17.0	9.40	6.76	6.87	0.10	
20060904-DYK	6.62	9.33	6.72	7.00	0.10	
20061005-DYK	5.19	8.12	5.84	6.16	0.09	
Air	0.319	1.39	1.00			

[a] The affix of the sample name (20041022-) is the sampling date (2004/10/22).

[b] R: $^3He/^4He$ ratio of measured samples; R_A: ratio of air ($=1.39\times10^{-6}$).

[c] $[R/R_A]_c$: air corrected helium isotopic ratio, assuming all the Ne derived from the air (Poreda and Craig, 1989).

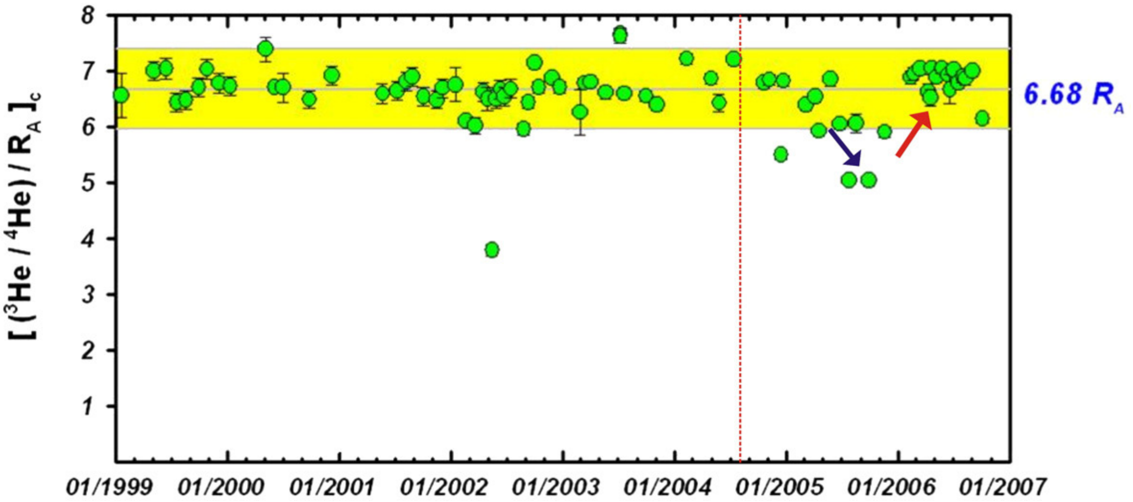

Fig. 6. Temporal changes of $^3He/^4He$ ratios in DYK. Most data fall in the range of two sigma standard deviation (the shaded area). However, the ratio showed a decreasing trend during a few months after August 2004 (vertically dashed line) and returned to the previous values after approximately 6 months. Data from Yang (2000), Yang et al. (2003b) and Table 3.

DYK was considered to be affected by crustal contamination when gases ascended to the surface. Consequently, the value returned to normal after the event stopped. However, the decreasing trend could also be caused by kinetic fractionation, which is generally significant in light molecules, during magma ascent as was recently suggested by Rizzo et al. (2006) for variations observed at Mt. Etna. In isotope mass fractionation, the light mass (^3He) diffuses very fast into the gas phase and is depleted in the residual melt. This process can be modeled by Rayleigh's distillation:

$$F^{(k-1)} = \frac{R}{R_0} \tag{2}$$

where R is the $^3He/^4He$ ratio in melt, F is the residual fraction of helium after a degassing event, the subscript "0" refers to initial conditions ($^3He/^4He$ in melt before the degassing event) and k is the kinetic fractionation factor. Eq. (2) predicts that degassing causes a decrease of the $^3He/^4He$ ratio in the melt, and the "depleted" melt generates a declining trend of the $^3He/^4He$ ratio in the released gases. As helium isotopes can be directly related to a magma source and are very sensitive to kinetic fractionation, the decrease of the $^3He/^4He$ ratios can be interpreted as geochemical signals of magma ascent (Nuccio and Valenza, 1998; Caracausi et al., 2003; Capasso et al., 2005; Rizzo et al., 2006). The $^3He/^4He$ ratio returned back to normal values soon after the decrease. It could be generated either by the release of kinetically-enriched ^3He gas-bubbles during magma vesiculation (Nuccio and Valenza, 1998), or by the outgassing of new volatile-rich magma ascending from depth.

3.3. Seismic data of the TVG area

In addition to geological and geochemical evidence, volcanic seismicity also suggests that volcanic activity might not have yet become completely extinct. A seismic array consisting of five seismic stations installed in the TVG area since 2003 indicates that a large number of micro-earthquakes are clustering beneath the Chihsingshan volcano and DYK area (Yu and Tsai, 1980; Chen and Yeh, 1991; Lin et al., 2005a, b; Konstantinou et al., 2007). Most of those were volcano-tectonic earthquakes which were caused by brittle failure of rock and interpreted as related to fluid–rock interaction (Lin et al., 2005a, b; Konstantinou et al., 2007). In addition to those volcano-tectonic earthquakes, volcano-seismic signals (tornillos, monochromatic events and high-frequency spasmodic bursts) were also detected among these micro-earthquakes. They have often been observed on active volcanoes worldwide, and some were detected before eruption (Chouet, 1996; McNutt, 1996; Kumagai, 2002). These signals are most probably associated with the direct/indirect interaction between hydrothermal or magmatic fluids and solid rock in the upper crust. Most of the spasmodic bursts events were detected in the DYK area. Taking all this evidence (active micro-earthquakes, special volcano-seismic signals and high $^3He/^4He$ ratio) into consideration, it is possible that the magmatic plumbing system beneath the TVG is still active.

3.4. Models for the variations of fumarolic gas composition and temperature

After a period of steady state for more than four years, fumarolic gas compositions of DYK began to change since August 2004, including a progressive increase of HCl concentrations and SO_2/H_2S ratios. The outlet temperature of fumaroles was also higher than before. Moreover, the $^3He/^4He$ ratios decreased and soon returned to normal a few months after August 2004, and most of the spasmodic bursts events most probably associated with volcanic activity were largely concentrated in the DYK area (Lin et al., 2005a, b; Konstantinou et al., 2007). All these phenomena suggest that the magma chamber beneath DYK became more active during this period.

As described above, there could be two aquifers existing beneath the TVG area (Fig. 7A). The deeper one is closer to the magma source and can be considered as the primary hydrothermal system (PHS); nevertheless, the shallower one could be the secondary hydrothermal system (SHS) since the source origin of meteoric water. When volcanic gases migrate upward and pass through the deep aquifer, HCl and SO_2 are dissolved easily because of their high solubility and, generate the acidic sulfate–chloride water. The low concentration of HCl and SO_2 in gas compositions could be the result of mixing between meteoric water (i.e. the SHS) with the vapor phases generated by evaporation of PHS.

Two possible processes are considered here to explain these observations. One is that more magmatic fluids were released from the ascending magma in DYK (Fig. 7B). The other is that more magmatic fluids were released from the fractures opened recently (Fig. 7C) (Martini, 1996). Under the first process, the ascending magma could provide more magmatic fluids and heat to the system. As a result, both HCl concentration and SO_2/H_2S ratio fluctuate with temperature (Giggenbach, 1996). HCl concentration and SO_2/H_2S ratio increased as temperature increased in DYK area. The decrease

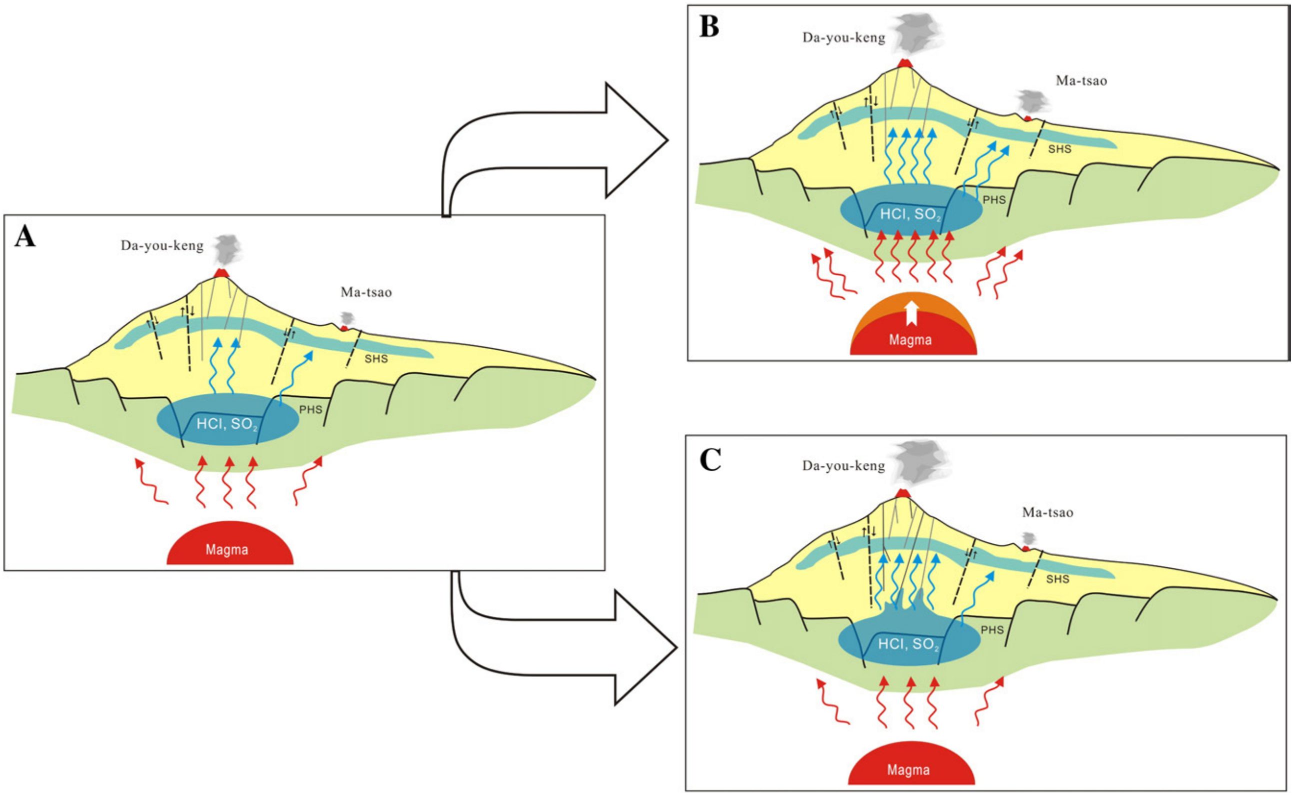

Fig. 7. (A) Sketch of the original state of the hydrothermal systems in the TVG area. PHS: the primary hydrothermal system; SHS: secondary hydrothermal system. See text for the details. Two possible processes are proposed to explain the observations of gas compositions in DYK. (B) First process is more magmatic fluids are released from ascending magma. Accompanied ground deformation caused by magma ascending would be observed and all fumaroles/hot springs should be affected. (C) Another process is the fluid and heat released through the recently opened fractures. These fractures may provide the pathway for both gases from a crustal component and heat.

of $^3He/^4He$ ratio could be caused by kinetic fractionation. However, if more magmatic fluids injected into the PHS, not only DYK but all other areas should be influenced.

The other process involves release of deeper fluid and heat through newly developed fractures (Fig. 7C). This is consistent with the tectonics of northern Taiwan which is under a sustained extension due to the opening of the Okinawa Trough (Teng, 1996; Wang et al., 1999). Such a process could explain the variations in HCl concentration and SO_2/H_2S ratio, and the trend in $^3He/^4He$ ratio as well. According to seismic data, most of the spasmodic bursts events, often associated with the interaction between hydrothermal or magmatic fluids and solid rock in the upper crust, were located in the DYK area. Therefore, more magmatic fluid ascended along these fractures only in the DYK area and caused the increase of HCl concentration and SO_2/H_2S ratio. A short-term negative anomaly of $^3He/^4He$ ratios of the gas samples indicates that the crustal component affected the DYK degassing system instantaneously. The fracturing process can explain why we did not observe ground deformation here, and seems to be more suitable to account for all observations in DYK. However, one problem arises: all our observations should happen synchronously; however, $^3He/^4He$ ratios varied in a few months later than other parameters (HCl concentration, SO_2/H_2S ratio, and temperature). One possible explanation is that less crustal components were added at the beginning; therefore, variation in $^3He/^4He$ ratio was not observable. On the other hand, variations in HCl concentration, SO_2/H_2S ratio and temperature were more sensitive so that they were observed earlier.

4. Concluding remark

Fumarolic gas compositions of DYK varied since August 2004. Progressive increases were observed not only in HCl concentration but also in SO_2/H_2S ratio. The outlet temperature of fumaroles was also higher than before. Moreover, $^3He/^4He$ ratio changed in a few months after August 2004. $^3He/^4He$ ratios showed a decreasing trend which returned to normal after approximately 6 months. These anomalies were only observed in the DYK area. Combining the helium isotopic ratios and volcano-seismic data, we suggest that a magma chamber might still exist beneath the TVG area, particularly in the area of DYK.

A short-term decreasing trend of $^3He/^4He$ ratios of the gas samples indicates that the proportion of crustal component was increasing for only a pulse of its gas sources. Alternatively kinetic fractionation of helium isotopes due to degassing of ascending magma may explain the observed trend. Because there is no ground deformation and no abnormality in gas compositions in any other area, we consider these variations might be caused by recent opening of fractures in a local area. More magmatic or primary hydrothermal fluid ascended along these fractures and likely caused the increase of HCl concentration and SO_2/H_2S ratio.

Acknowledgements

We thank Mr. K. W. Wu and B. W. Lin for their assistance in collecting samples and helium isotopic analysis. Drs. A. Caprai, China Chen, T. Fischer, T. Ohba, Y. Sano, Y. Taran, O. Vaselli and G. Zellmer gave constructive comments/suggestions in different stages of this work. Drs. Y. Taran and S. Inguaggiato reviewed the paper and gave critical comments to improve the manuscript. Dr. T. Fischer carefully edited the revised manuscript and gave useful comments. National Science Council (TFY/NSC96-2628-M-002-026), Yangmingshan National Park and Central Geological Survey (TFY/5226902000-05-93-01) of Taiwan financially support this study.

References

Aiuppa, A., Federico, C., 2004. Anomalous magmatic degassing prior to the 5th April 2003 paroxysm on Stromboli. Geophysical Research Letters 31, L14607. doi:10.1029/2004GL020458.

Aiuppa, A., Moretti, R., Federico, C., Giudice, G., Gurrieri, S., Liuzzo, M., Papale, P., Shinohara, H., Valenza, M., 2007. Forecasting Etna eruptions by real-time observation of volcanic gas composition. Geology 35, 1115–1118.

Aramaki, S., 1991. Hazardous volcanic eruptions in Japan. Episode 14, 264–268.

Capasso, G., Favara, R., Inguaggiato, S., 1997. Chemical features and isotopic composition of gaseous manifestations on Vulcano Island (Aeolian Islands, Italy): an interpretative model of fluid circulation. Geochimica et Cosmochimica Acta 61, 3425–3440.

Capasso, G., Carapezza, M.L., Federico, C., Inguaggiato, S., Rizzo, A., 2005. Geochemical monitoring of the 2002–2003 eruption at Stromboli volcano (Italy): precursory changes in the carbon and helium isotopic composition of fumarole gases and thermal waters. Bulletin of Volcanology 68, 118–134. doi:10.1007/s00445-005-0427-5.

Caracausi, A., Favara, R., Giammanco, S., Italiano, F., Paonita, A., Pecoraino, G., Rizzo, A., Nuccio, P.M., 2003. Mount Etna: geochemical signals of magma ascent and unusually extensive plumbing system. Geophysical Research Letters 30 (2), 1057. doi:10.1029/2002GL015463.

Carapezza, M.L., Inguaggiato, S., Brusca, L., Longo, M., 2004. Geochemical precursors of the activity of an open-conduit volcano: the Stromboli 2002–2003 eruptive events. Geophysical Research Letters 31, L07620. doi:10.1029/2004GL019614.

Chen, C.-H., Lin, S.B., 2002. Eruptions younger than 20 ka of the Tatun Volcano Group as viewed from the sediments of the Sungshan Formation in Taipei Basin. Western Pacific Earth Sciences 2, 191–204.

Chen, C.H., 1970. Geology and geothermal power potential of the Tatun volcanic region. UN Symposium on the Development and Utilization of Geothermal Resources 2, 1134–1143.

Chen, C.H., Wu, Y.J., 1971. Volcanic geology of the Tatun geothermal area, northern Taiwan. Proceedings of the Geological Society of China 14, 5–20.

Chen, C.T.A., Zeng, Z., Kuo, F.W., Yang, T.F., Wang, B.J., Tu, Y.Y., 2005. Tide-influenced acidic hydrothermal system offshore NE Taiwan. Chemical Geology 224, 69–81.

Chen, K.J., Yeh, Y.H., 1991. Gravity and microearthquake studies in the Chinshan–Tamshui area, northern Taiwan. Terrestrial, Atmospheric and Oceanic Sciences 2, 35–50.

Chen, Y.L., Lo, H.J., Song, S.R., Fang, J.N., Huang, S.C., Chen, H.F., 2001. Chemical compositions of hot spring waters at Direku and Chingshan in the Tatun volcanic area, northern Taiwan. Western Pacific Earth Sciences 1, 187–198.

Chiodini, G., Cioni, R., Marini, L., 1993. Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance. Applied Geochemistry 8, 357–371.

Chouet, B.J., 1996. Long-period volcano seismicity: its source and use in eruption forecasting. Nature 380, 309–316.

Duffell, H.J., McGonigle, A.J.S., Burton, M.R., Oppenheimer, C., Pyle, D.M., Galle, B., 2003. Changes in gas composition prior to a minor explosive eruption at Masaya volcano, Nicaragua. Journal of Volcanology and Geothermal Research 126, 327–339.

Fischer, T.P., 2008. Fluxes of volatiles (H_2O, CO_2, N_2, Cl, F) from arc volcanoes. Geochemical Journal 42 (1), 21–38.

Fischer, T.P., Arehart, G.B., Sturchio, N.C., Williams, S.N., 1996. The relationship between fumarole gas composition and eruptive activity at Galeras volcano, Colombia. Geology 24, 531–534.

Giammanco, S., Inguaggiato, S., Valenza, M., 1998. Soil and fumarole gases of Mount Etna: geochemistry and relations with volcanic activity. Journal of Volcanology and Geothermal Research 81, 297–310.

Giggenbach, W.F., 1975. A simple method for the collection and analysis of volcanic gas samples. Bulletin of Volcanology 36, 132–145.

Giggenbach, W.F., 1987. Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand. Applied Geochemistry 2, 143–161.

Giggenbach, W.F., 1992. The composition of gases in geothermal and volcanic systems as a function of tectonic setting. Proc. Int'l Symp. Water–Rock Interaction 8, 873–878.

Giggenbach, W.F., 1996. Chemical composition of volcanic gases. In: Scarpa, R., Tillinh, R.I. (Eds.), Monitoring and Mitigation of Volcanic Hazards. Springer, Berlin, pp. 221–256.

Goff, F., McMurtry, G.M., 2000. Tritium and stable isotopes of magmatic waters. Journal of Volcanology and Geothermal Research 97, 347–396.

Haughton, D.R., Roeder, P.L., Skinner, B.J., 1974. Solubility of sulfur in mafic magmas. Economic Geology 69, 451–463.

Hirabayashi, J., Ossaka, J., Ozawa, T., 1986. Geochemical study on volcanic gases at Sakurajima volcano, Japan. Journal of Geophysical Research 91 (B12), 2167–2176.

Hirabayashi, J., Shinohara, H., 1989. Sampling and analytical methods of volcanic gases. Textbook for the Group Training Course in Volcanology and Volcanic Engineering, vol. II. Japan International Cooperation Agency (JICA).

Juang, W.S., Chen, J.C., 1989. Geochronology and geochemistry of volcanic rocks in northern Taiwan. Bulletin of Central Geological Survey 5, 31–66.

Konstantinou, K.I., Lin, C.H., Liang, W.T., 2007. Seismicity characteristics of a potentially active Quaternary volcano: the Tatun Volcano Group, northern Taiwan. Journal of Volcanology and Geothermal Research 160, 300–318.

Kumagai, H., 2002. Temporal evolution of a hydrothermal system in Kusatsu-Shirane Volcano, Japan, inferred from the complex frequency of long-period events. Journal of Geophysical Research 107 (B10), 2236. doi:10.1029/2001JB000653.

Lan, T.F., Yang, T.F., Lee, H.F., Chen, Y.G., Chen, C.-H., Song, S.R., Tsao, S., 2007. Compositions and flux of soil gases in hydrothermal area, Northern Taiwan. Journal of Volcanology and Geothermal Research 65, 32–45.

Lee, H.F., 2004. Compositions of fumarolic gases and the H–O isotopic ratios of the condensed water in Tatun Volcanic area, North Taiwan. MS Thesis, Institute of Geosciences, National Taiwan University, 83 pp. (in Chinese).

Lee, H.F., Yang, T.F., Lan, T.F., Song, S.R., Tsao, S., 2005. Fumarolic gas composition of the Tatun Volcano Group, northern Taiwan. Terrestrial, Atmospheric and Oceanic Sciences 16, 843–864.

Lin, C.H., Konstantinou, K.I., Liang, W.T., Pu, H.C., Lin, Y.M., You, S.H., Huang, Y.P., 2005a. Preliminary analysis of volcanoseismic signals recorded at the Tatun Volcano Group, northern Taiwan. Geophysical Research Letters 32, L10313. doi:10.1029/2005GL022861.

Lin, C.H., Konstantinou, K.I., Pu, H.C., Hsu, C.C., Lin, Y.M., You, S.H., Huang, Y.P., 2005b. Preliminary results of seismic monitoring at Tatun volcanic area of northern Taiwan. Terrestrial, Atmospheric and Oceanic Sciences 16, 563–577.

Liu, K.K., Chen, C.C., Shieh, Y.N., Chiang, S.C., 1984. Carbon, oxygen and hydrogen isotope studies of Tatun geothermal area in Taipei. Report of Institute of Earth Sciences. Academia Sinica: ASIES-CR 8401 39 pp. (in Chinese).

Martini, M., 1996. Chemical characters of the gaseous phase in different stages of volcanism: precursors and volcanic activity. In: Scarpa, R., Tillinh, R.I. (Eds.), Monitoring and Mitigation of Volcanic Hazards. Springer, Berlin, pp. 199–219.

Marty, B., Jambon, A., Sano, Y., 1989. Helium isotopes and CO_2 in volcanic gases in Japan. Chemical Geology 76, 25–40.

McNutt, S.R., 1996. Seismic monitoring and eruption forecasting of volcanoes: a review of the state-of-the-art and case histories. In: Scarpa, R., Tillinh, R.I. (Eds.), Monitoring and Mitigation of Volcanic Hazards. Springer, Berlin, pp. 100–146.

Menyailov, I.A., Nikitina, L.P., Shapar, V.N., Pilipenko, V.P., 1986. Temperature increase and chemical-change of fumarolic gases at Momotombo Volcano, Nicaragua, in 1982–1985 — are these indicators of a possible eruption? Journal of Geophysical Research 91 (B12), 2199–2214.

MRSO, 1969. The geothermal exploration of the Tatun Volcano Group (I). MRSO Report, 90. 63 pp. (in Chinese).

MRSO, 1970. The geothermal exploration of the Tatun Volcano Group (II). MRSO Report, 102. 86 pp. (in Chinese).

MRSO, 1971. The geothermal exploration of the Tatun Volcano Group (III). MRSO Report, 111. 48 pp. (in Chinese).

MRSO, 1973. The geothermal exploration of the Tatun Volcano Group (IV). MRSO Report, 126. 78 pp., (in Chinese).

Noguchi, K., Kamiya, H., 1963. Prediction of volcanic eruption by measuring the chemical composition and amounts of gases. Bulletin of Volcanology 26, 367–378.

Notsu, K., Nakai, S., Igarashi, G., Ishibashi, J., Mori, T., Suzuki, M., Wakita, H., 2001. Spatial distribution and temporal variation of $^3He/^4He$ in hot spring gas released from Unzen volcanic area, Japan. Journal of Volcanology and Geothermal Research 111, 89–98.

Nuccio, P.M., Valenza, V., 1998. Magma degassing and geochemical detection of its ascent. In: Arehart, G.B., Hulston, J.R. (Eds.), Water–Rock Interaction. Balkema, pp. 475–478.

Ohnishi, T., Kamada, M., 1981. Correlation between minor constituents of volcanic gas at Mochiki and volcanic activity of Sakurajima Volcano. Paper Presented at 1981 IAVCEI Symposium.

Oskarsson, N., 1984. Monitoring of fumarole discharge during the 1975–1982 rifting in Krafla volcanic center, North Iceland. Journal of Volcanology and Geothermal Research 22, 97–121.

Pecoraino, G., Giammanco, S., 2005. Geochemical characterization and temporal changes in parietal gas emissions at Mt. Etna (Italy) during the period July 2000–July 2003. Terrestrial, Atmospheric and Oceanic Sciences 16, 805–841.

Poreda, R., Craig, H., 1989. Helium isotope ratios in circum-Pacific volcanic arcs. Nature 338, 473–478.

Rizzo, A., Caracausi, A., Favara, R., Martelli, M., Nuccio, P.M., Paonita, A., Rosciglione, A., Paternoster, M., 2006. New insights into magma dynamics during last two eruptions of Mount Etna as inferred by geochemical monitoring from 2002 to 2005. Geochemistry Geophysics Geosystems 7, Q06008. doi:10.1029/2005GC001175.

Sano, Y., Wakita, H., 1985. Geographical distribution of $^3He/^4He$ ratios in Japan: implications for arc tectonics and incipient magmatism. Journal of Geophysical Research 90, 8729–8741.

Sano, Y., Nakamura, Y., Wakita, H., 1984. Helium-3 emission related to volcanic activity. Science 224, 150–151.

Song, S.R., Tsao, S.J., Lo, H.J., 2000a. Characteristics of the Tatun volcanic eruptions, north Taiwan: implications for a cauldron formation and volcanic evolution. Journal of the Geological Society of China 43, 361–378.

Song, R.S., Yang, T.F., Yeh, Y.H., Tsao, S., Lo, H.J., 2000b. The Tatun volcano group is active or extinct? Journal of the Geological Society of China 43, 521–534.

Symonds, R.B., Rose, W.I., Bluth, G.S.J., Gerlach, T.M., 1994. Volcanic gas studies: methods, results, and applications. In: Carrol, M.R., Holloway, J.R. (Eds.), Volatiles in Magma. Review of Mineralogical Society of America, Washington DC, pp. 1–64.

Teng, L.S., 1996. Extensional collapse of the northern Taiwan mountain belt. Geology 24, 949–952.

Teng, L.S., Chen, C.-H., Wang, W.S., Liu, T.K., Juang, W.S., Chen, J.C., 1992. Plate kinematic model for late Cenozoic arc magmatism in northern Taiwan. Journal of the Geological Society of China 35, 1–18.

Tsao, S.J., 1994. Potassium–argon age determination of volcanic rocks from the Tatun Volcano Group. Bulletin of Central Geological Survey 9, 137–154.

Walker, G.P.L., 1974. Volcanic hazards and the prediction of volcanic eruptions. In: Funnell B.M. (ed.), Prediction of geological hazards. Geological Society of London, Miscellaneous Paper, 3, 23–41.

Wallace, P., Carmichael, I.S.E., 1992. Sulfur in basaltic magmas. Geochimica et Cosmochimica Acta 56, 1863–1874.

Wang, K.L., Chung, S.L., Chen, C.H., Shinjo, R., Yang, T.F., Chen, C.-H., 1999. Post-collisional magmatism around northern Taiwan and its relation with opening of the Okinawa Trough. Tectonophysics 308, 363–376.

Wang, W.H., Chen, C.-H., 1990. The volcanology and fission track age dating of pyroclastic deposits in Tatun Volcano Group. Acta Geologica Taiwanica 28, 1–30.

Witt, M.L.I., Fischer, T.P., Pyle, D.M., Yang, T.F., Zellmer, G.F., 2008. Fumarole compositions and mercury emissions from the Tatun Volcanic Field, Taiwan: results from multi component gas analyser, portable mercury spectrometer and direct sampling techniques. Journal of Volcanology and Geothermal Research 178, 638–645 (this issue).

Yang, T.F., 2000. ^{3}He/^{4}He ratios of fumaroles and bubbling gases of hot springs in Tatun Volcano Group, North Taiwan. Journal of National Park 10 (1), 73–94 (in Chinese).

Yang, T.F., Sano, Y., Song, S.R., 1999. ^{3}He/^{4}He ratios of fumaroles and bubbling gases of hot springs in Tatun Volcano Group, North Taiwan. Nuovo Cimento Della Societa Italiana Di Fisica C22 (3–4), 281–286.

Yang, T.F., Chen, C.-H., Tien, R.L., Song, S.R., Liu, T.K., 2003a. Remnant magmatic activity in the Coastal Range of East Taiwan after arc–continent collision: fission-track date and ^{3}He/^{4}He ratio evidence. Radiation Measurements 36, 343–349.

Yang, T.F., Ho, H.H., Hsieh, P.S., Liu, N.J., Chen, Y.G., Chen, C.-H., 2003b. Sources of fumarolic gases from Tatun Volcano Group, North Taiwan. Journal of National Park 13, 127–156 (in Chinese).

Yang, T.F., Lan, T.F., Lee, H.F., Fu, C.C., Chuang, P.C., Lo, C.H., Chen, C.-H., Chen, C.T.A., Lee, C.S., 2005. Gas compositions and helium isotopic ratios of fluid samples around Kueishantao, NE offshore Taiwan and its tectonic implications. Geochemical Journal 39, 469–480.

Yang, T.F., Chuang, P.C., Lin, S., Chen, J.C., Wang, Y., Chung, S.H., 2006. Methane venting in gas hydrate potential area offshore of SW Taiwan: evidence of gas analysis of water column samples. Terrestrial, Atmospheric and Oceanic Sciences 17, 933–950.

Yen, T.P., Tzou, Y.H., Lin, W.H., 1984. Subsurface geology of the region of the Tatun Volcano Group. Petroleum Geology of Taiwan 20, 143–154.

Yu, S.B., Tsai, Y.B., 1980. Micro-earthquakes and seismic tremors in the Tatun volcanic area. Open-File Rept., Inst. Earth Sci., Academia Sinica, 68 pp.