Fumarolic Gas Composition of the Tatun Volcano Group, Northern Taiwan

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ABSTRACT

Giggenbach bottle technique is used to systematically analyze fumarolic gas composition of the Tatun Volcano Group, northern Taiwan. The area is quite active hydrothermally and is also considered volcanically active. The gas composition of fumarolic samples is predominantly steam water with CO_2 as the dominant component after de-watering. Minor components include sulfur species (mainly H_2S and SO_2), N_2 and CH_4. Interestingly, in the study area, H_2S concentration is always much higher than SO_2 for all measured fumarolic gases. This result resembles the typical composition of low temperature fumaroles, when comparisons are made on a worldwide basis.

Hsiao-you-keng and Liou-huang-ku were selected as testing sites to discuss factors pertaining to weather and sampling time as these may affect fumarolic gas composition. Test results show that the length of sampling time in this area mainly depends on the saturation of alkali solution. Furthermore, based on continuous data, gas composition of fumaroles seems not to be affected by weather factors. This implies that the de-gassing system in the Tatun volcanic area is quite steady and generated no significant variation in gas composition during the study period. These results indicate that current sampling and analytical procedures are suitable for volcanic gas study and further surveillance in the Tatun volcanic area.

(Key words: Tatun Volcano Group, Giggenbach bottle, Fumaroles, Gas composition)

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1. INTRODUCTION

The compositional variations of fumarolic gas and bubbling gas are closely related to volcanic activity (e.g., Ohnishi and Kamada 1981; Casadevall et al. 1983; Sano et al. 1984; Notsu et al. 2001). Detailed studies on the compositions of fumarolic gases can help to understand the sources and origin of magmas in an area (e.g., Rose et al. 1986; Allard et al. 1991; Symonds et al. 1994; Giggenbach 1996; Yang et al. 1999, 2005; Pecoraino and Giammanco 2005). A number of studies have pointed out that the composition of volcanic gas along with some reactive gas ratios changed dramatically before eruption (e.g., Noguchi and Kamiya 1963; Casadevall et al. 1983; Walker 1974; Oskarsson 1984). Integrated with other available data/investigations, the information can be used for further geohazard assessment and mitigation in susceptible areas (e.g., Aramaki 1991; Andal et al. 2005).

The Tatun Volcano Group (TVG), mainly composed of andesitic lavas and pyroclastic flows (Chen and Wu 1971), belongs to the Northern Taiwan Volcanic Zone and is the most southwesterly part of the Okinawa Trough (Wang et al. 1999). Previously, the group was considered dormant; however, Chen and Lin (2002) reported recording some very young eruption products (less than 20 ka) in the Taipei Basin. In addition, helium isotopic results demonstrate that more than 60% of helium from the majority of sample sites exhibits mantle-derived characteristics (Yang et al. 1999; Yang 2000), indicating an active degassing source underneath the region. Seismic observations also recorded some interesting volcanoseismic 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. 2005). Compiling results from geothermal and seismic research, Song et al. (2000) concluded that the TVG could be still active. Based on helium isotopic data, Yang et al. (2003) suggested that a magma chamber may exist underneath Northern Taiwan, particularly in the area of Da-you-keng (DYK) (Fig. 1).

As the TVG is located close to metropolitan Taipei, the group poses a serious geohazard to the residents of the city and as such requires urgent attention in terms of monitoring for potential future eruptions. Continuous measurement of helium isotopic composition of fumarolic gases would be one such effective monitoring method for volcanic activity (e.g., Sano et al. 1984; Sano and Wakita 1985; Yang et al. 2003). However, considering the high cost of helium isotopic analysis for long-term monitoring, it is necessary to establish more economic and efficient analytical methods, especially given the sensitive of the parameters being examined. Wang (1999) and Lin (2001) tried to analyze volcanic gases using alkali solution method. However, they could only measure the composition of dissolved gases in solution, these are unrepresentative of all the gases in a fumarolic sample. In this study, therefore, we refer to the method developed by Giggenbach (1975), which has been widely adapted by volcano-geochemists worldwide (e.g., Giggenbach and Matsuo 1991; Giggenbach et al. 2001). After a series of tests, we established suitable sampling and analytical procedures for fumarolic-gas measurements in the TVG; and have reported the preliminary results here for the purposes of comparison with measurements at other active volcanic sites. These, techniques can be applied in the future to survey the area.
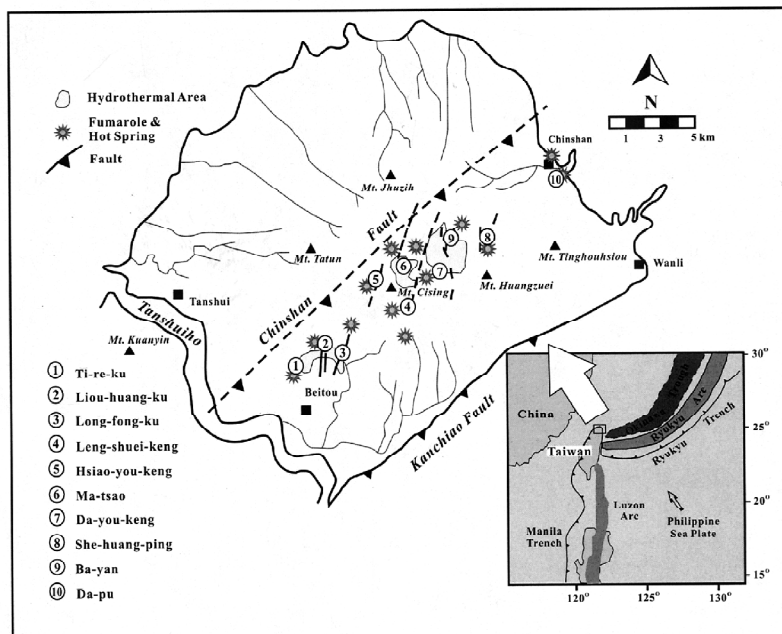
Fig. 1. Location of the Tatun Volcano Group and sampling sites in this study.

2. SAMPLE COLLECTION AND ANALYSIS

The TVG is located in northern Taiwan where fumaroles and hot springs distribute from Beitou to Chinshan (Fig. 1). In this study, fumarolic gas and bubbling gas samples were taken from the 10 representative sites shown in Fig. 1. Meanwhile, condensed water at these fumarolic gas sites was also collected for comparison with the composition of hot spring water in the same area.

Following the Giggenbach's method (Giggenbach 1975), evacuated Giggenbach bottles with 50 ml 4 N alkali hydroxide solution were used to collect the gas samples. A 1-m-long quartz or titanium tube was inserted into the fumaroles and a hand pump utilized to reduce air contamination (Fig. 2a). The water replacement method was then used to collect bubbles at the hot springs (Fig. 2b) (Piccardi 1982; Caprai 2005). When the tube is full of volcanic gas, the valve at the head of the Giggenbach bottle is opened to collect the gas. H_2O, CO_2, H_2S, SO_2, and HCl are dissolved in alkali hydroxide solution in the bottle with the remaining un-dissolvable gases such as CH_4, N_2, H_2, He, Ar, and CO collected in the headspace of the bottle.

The weight difference of the before-and-after Giggenbach bottle is used to determine the total amount of sample collected. The un-dissolvable gas in the headspace is analyzed first as this helps prevent air contamination of the gases dissolved in solution. In this experiment, a gas chromatograph (GC, SRI 8610C), equipped with two thermal conductivity detectors (TCDs) and one flame ionic detector (FID), was used for routine gas analysis. The system utilized two
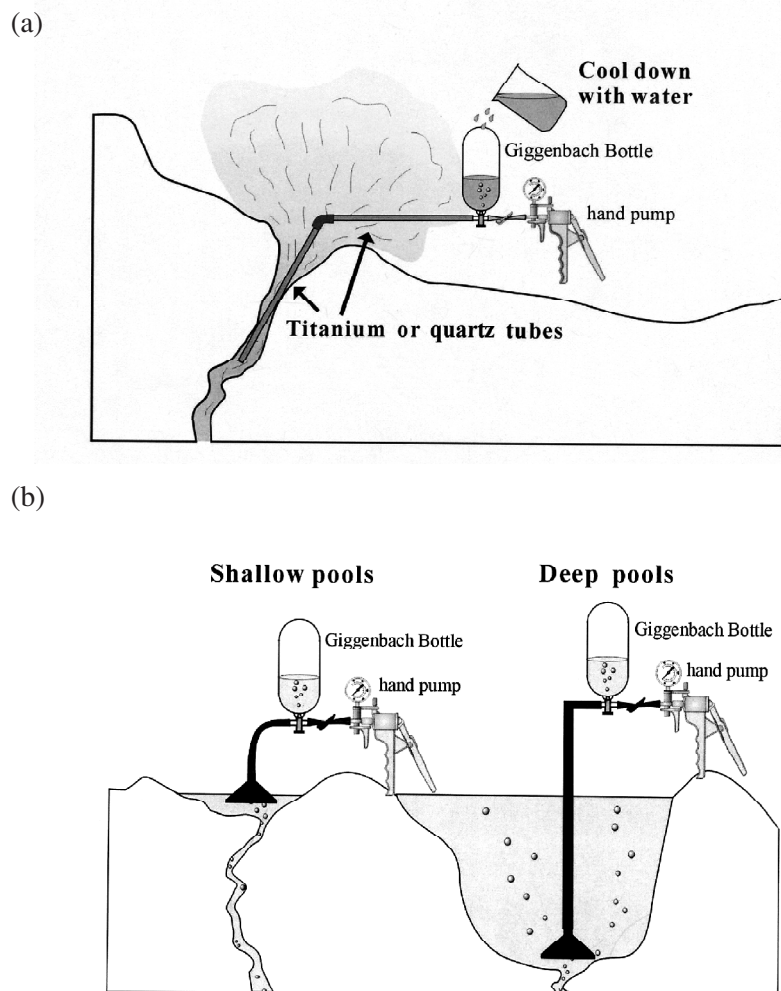
(a)

(b)

Fig. 2. (a) Sketch of sampling for fumarolic gases; (b) Sampling for bubbling gases from pools.

carrier gases, hydrogen and argon. Hydrogen was supplied by a hydrogen generator for use in the FID and in one TCD; whilst the other TCD utilized argon supplied by a cylinder tank. The loaded sample was introduced into three independent sample loops of fixed volume (1 cc) via two 10-port sampling valves (Fig. 3). Then, each loop sample passed through different columns for further analysis. As this is the first time publication of such a setting/configuration for this system has been made in an international journal, the system is described in more detailed in a latter section.

For the first 4 min, only EPC #1 (electronic pressure control) is open (Fig. 3), allowing sample from loops #1 and #2 to pass through the MS-13X (Molecular Sieve) column and Rh-
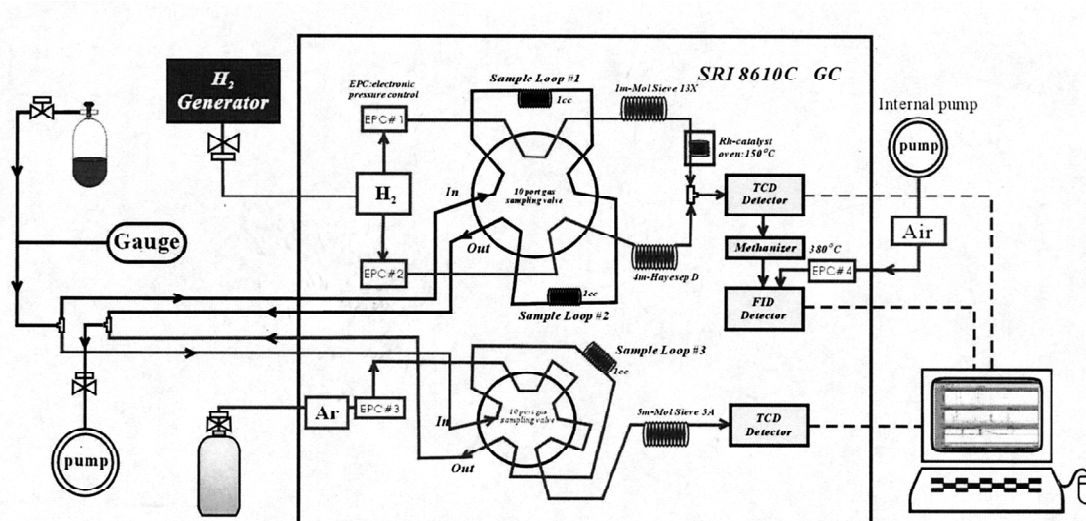
Fig. 3. Configuration of gas chromatography used in this study. The system can analyze most inorganic gas compositions under one single sample loading.

catalyst (Rh 1.5% in Al_2O_3) oven. Here the TCD can detect Ar, N_2 and CH_4 with a precision of ~5% and detection limit of several hundreds of ppm (Fig. 4a). Note that any oxygen in the sample combusts quickly with the hydrogen carrier gas given the help of the Rh-catalyst in the oven at 150°C. In which case oxygen is totally consumed before the gas sample reaches the TCD. This overcomes any problem of overlap and interference of oxygen and argon peaks in the molecular-sieve column at room temperature; thereby, allowing for the analysis of argon concentration precisely without additional treatment (see discussion by Jiang 2002). After, 4 - 5 min of retention time, EPC #2 is opened allowing sample from loops #1 and #2 to pass through Hayesep D column and methanizer (380°C). Here, CO, CH_4, CO_2, C_2H_6, can be detected by both the TCD and FID within 15 min (Figs. 4a, b). Although, the FID cannot detect other permanent gases, it exhibits much higher precision at ~1% and a lower detection limit (1 ppm level) than the TCD utilized for hydrocarbon gases. In addition, sample from loop #3 passes through the MS-5A column, with argon as a carrier gas, and the TCD can detect He and H_2 signals (Fig. 4c), which cannot be detected by the previous two settings, and also O_2, N_2, CH_4, and CO_2. Overall, the GC system can analyze most inorganic gas compositions, including CH_4, C_2H_6, CO, CO_2, Ar, N_2, H_2, He and O_2, simultaneously for a single sample loading. Detailed setup and discussion of the accuracy/precision and detection limits of this system were described by Lee (2004).

After analysis of the un-dissolved gases, the solution is removed from the Giggenbach bottle and mixed with 5 ml of H_2O_2 and left overnight to allow all dissolved sulfur species to convert to SO_4^{2-}. The solution was then heated to 90°C to remove excess H_2O_2. Consequent analysis utilizing ion chromatography (IC, Metrohm 790 Personal) obtained the concentration
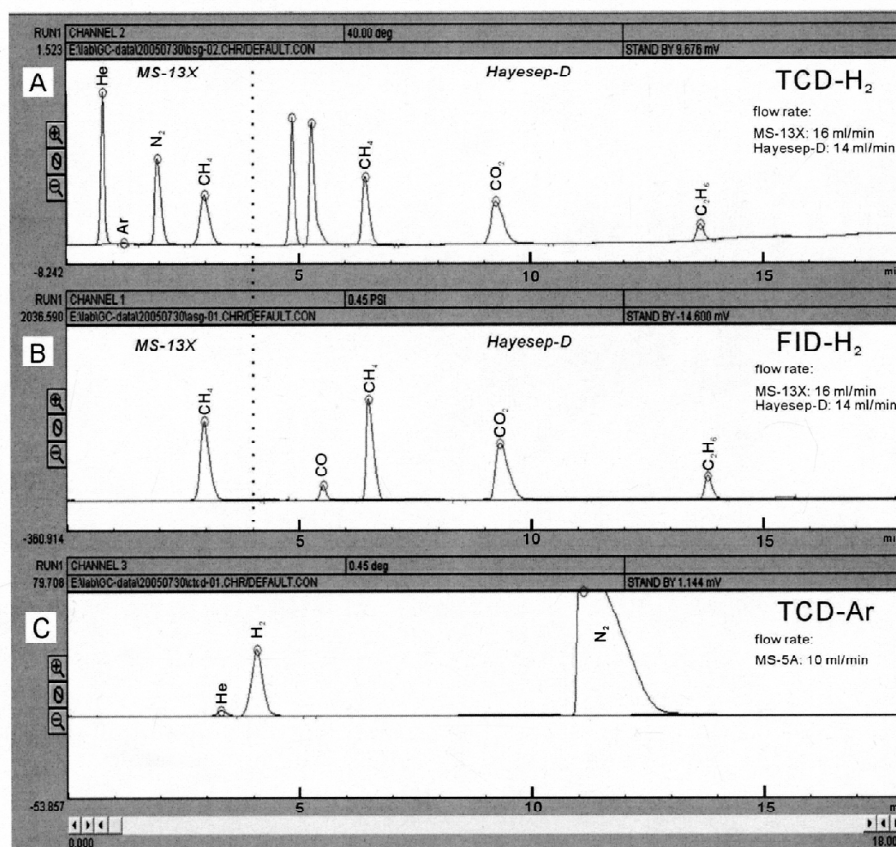
Fig. 4. Example spectra of artificial standard recorded by present GC system. (a) Spectrum of detector TCD with hydrogen as carrier gas. Note that small argon peak can be clearly observed after oxygen peak has been removed by Rh-catalyst. (b) Spectrum of detector FID with hydrogen as carrier gas. Hydrocarbon peaks, CO, CH_4, CO_2 and C_2H_6, will appear at the retention time of 5 - 15 minutes. Note that the vertical scale, output voltage (mV) of the peak signal, is different from that of Fig. 4a. The scale in Fig. 4b is three orders of magnitude higher than in Fig. 4a, although they share the same standard sample with the composition of 0.1% Ar; 1% CO and C_2H_6; 10% N_2, CH_4 and CO_2 balance in pure helium gas. This indicates the sensitivity of the FID is much higher than TCD. (c) Spectrum of detector TCD with argon as carrier gas. He and H_2 peaks, which cannot be detected by previous two settings, appear within 5 minutes. Oxygen peak, not shown in this gas standard sample, can also be easily detected with this setting. The standard gas, shown in this spectrum, consists of 1000 ppm He and 1% H_2 in pure N_2 gas.

of Cl^- and SO_4^{2-} which was used to determine the concentration of HCl and total sulfur in the samples.

The Metrohm 702 SM Titrion allows for CO_2 concentrations in gas samples to be determined by titration; this assumes all the CO_2 of the sample has been dissolved as CO_3^{2-} in the alkali solution.

Montegrossi et al. (2001) suggest using $Cd(OH)_2$ to collect sulfide species as the Giggenbach-bottle method cannot separate individual quantities of H_2S and SO_2. However, this method requires toxic $CdCO_3$ to prepare $Cd(OH)_2$. For the sake of safety, we replace $CdCO_3$ with iodine. This technique requires a longer processing time for sampling and analysis.

The iodine method was described by Ozawa (1968), and the following equations describe how iodine solution reacts with sulfide species:

$$SO_2 + I_2 + 2H_2O \Leftrightarrow SO_4^{2-} + 4H^+ + 2I^- \ , \tag{1}$$

$$H_2S + I_2 \Leftrightarrow S\downarrow + 2H^+ + 2I^- \ , \tag{2}$$

$$S + I_2 \Leftrightarrow no\ reaction \ \ .$$
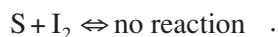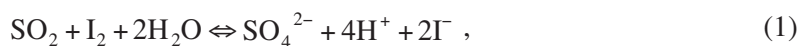
In this study, iodine solution (20 ml 0.05 M) was put into a bottle for fumarolic gas sampling H_2S in the fumarolic gases reacts with the iodine in solution to produce solid elemental sulfur which precipitates. SO_2, however, reacts with iodine to become SO_4^{2-} and remains in solution. The benefit here being that the volcanic sulfur gases can be separated (simply with filter paper) measured and analyzed in the laboratory. The complete analytical procedure of iodine solution to determine the concentration of SO_2 and H_2S in the samples is demonstrated in Fig. 5.

The composition of the dry fumarolic gas sample can be calculated from the summation result of GC, IC and titration described above (Tables 1 and 2). Water concentration in the sample is calculated from the weight difference between total weight of collected samples and dry gas composition. In general, all gas components, including H_2O, CO_2, H_2S, SO_2, HCl, He, H_2, O_2, Ar, N_2, CO, CH_4, C_2H_6, analyzed in this system have analytical errors less than 5% for most components with low detection and quantification limits. Detailed discussion about the precision and accuracy of the system is given by Lee (2004).

3. RESULTS AND DISCUSSION

3.1 Influence of Sampling Time

Although the Giggenbach method has been widely used for collecting fumarolic gases, sampling time may be a crucial issue as different sample sites exhibit different exhalation rates and composition of fumaroles. Therefore, we need to test for an appropriate sampling time before systematically collecting fumarolic samples in TVG area.
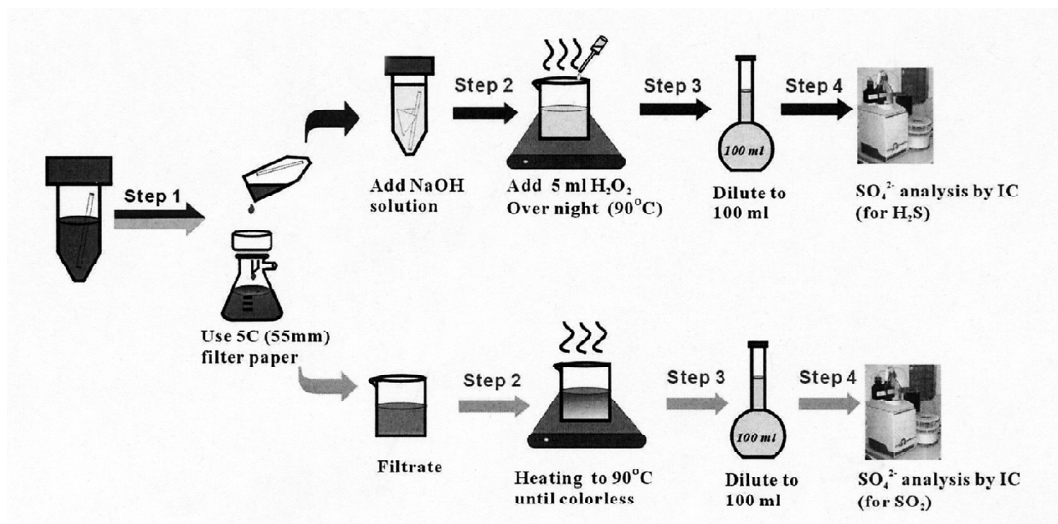
Fig. 5. Analytical procedure to determine SO_2 and H_2S concentrations in gas
samples by iodine solution method. First step is to separate the precipi-
tate and solution with filter paper. Then the filtrate can be used for IC
analysis directly after some treatments as shown in the figure to deter-
mine the SO_2 concentration in the sample. Nevertheless, the precipitate
part needs to be treated together with the filter paper and the sampling
glass tube in the plastic vial, because there may be some precipitate ad-
here to them. Next add some H_2O_2 to convert them into soluble sulfate,
which can be used for IC analysis to determine the concentration of H_2S
as shown in the figure.

We performed testing with different sampling time intervals at Liou-huang-ku (LHK).
The results indicate that when alkali solution is under-saturated, i.e., sampling time less than
10 min, all the CO_2 in both fumaroles and hot spring bubbles samples is dissolved in the alkali
solution and, no CO_2 in the headspace of the Giggenbach bottle can be detected by GC (Table 3).
For sampling times greater than 10 min, CO_2 is detectable in the headspace; i.e., the alkali
solution is over-saturated withand not able to dissolve CO_2 any more. Excess CO_2 in the
headspace produces errors in final analysis. This means sampling time is dependent on the
alkali solution saturation time for CO_2. For the LHK site this time is ~10 min. Although
sampling time depends on gas composition and the gas to steam ratio at different venting sites,
the estimated length of sampling time in this test is applied to the other sampling sites in the
TVG area as typically no CO_2 was detected in the headspace of the Giggenbach bottles in this
study.

We also tested the iodine solution method for the measurement of H_2S/SO_2 ratio with
different sampling times at Hsiao-you-keng (SYK). The results indicate that more sampling
time increases the measured amounts of H_2S and SO_2. However, the H_2S/SO_2 ratios re-

Table 1-1. Gas compositions of fumaroles from the Tatun Volcano Group.

Site	Date	Ar	N_2	CO	CH_4	C_2H_6	He	H_2	O_2	HCl	H_2S	SO_2	CO_2	H_2O
DYK	2003/7/9	4.49	399	-	12.7	0.77	0.34	5.09	48.9	0.85	1402	152	44081	953893
DYK	2003/8/6	6.64	693	-	26.5	0.03	0.29	10.3	90.4	0.11	2145	497	45184	951347
SYK	2004/3/16	3.07	676	0.04	554	3.02	0.57	118	26.6	2.85	3102	17.9	80026	915471
SYK	2004/10/5	12.5	1316	2.26	751	3.37	0.57	37.4	179	1.12	3450	188	70074	923985
LHK-1	2004/4/16	6.94	1420	-	143	0.86	0.66	6.21	89.8	13.7	9815	20.7	122336	865983
LHK-1	2004/8/18	3.84	1096	-	330	3.15	0.48	1.53	5.98	20.3	7720	39.9	95972	894806
LFK	2004/4/16	4.69	1018	-	68.2	0.62	0.56	0.19	46.7	14.2	5100	7.41	121570	872125
LFK	2004/5/1	3.26	845	0.12	99.0	0.25	0.30	47.0	53.7	6.02	6346	26.7	143680	848892
LSK	2003/5/20	2.80	634	-	134	-	0.21	14.9	19.5	0.62	7662	140	42568	948824
LSK	2003/6/5	4.33	714	7.89	94.3	0.47	0.35	18.5	34.7	0.77	6632	86.3	47004	945402
BY	2003/8/5	4.46	886	-	912	3.72	0.71	2.71	30.2	0.36	664	152	51439	945905
BY	2003/10/21	5.78	1533	-	1772	4.24	1.71	13.2	43.0	0.91	828	319	86272	909208

DYK: Da-you-keng; SYK: Hsiao-you-keng; LHK: Liou-huang-ku; LFK: Long fong-ku; LSK: Leng-shuei-keng; BY: Ba-yan.

Note: Concentration is given in the unit of μmol/mol; -: not analyzed or not detected.

Table 1-2. Dry gas compositions of fumaroles from the Tatun Volcano Group.

Site	Date	Ar	N_2	CO	CH_4	C_2H_6	He	H_2	O_2	HCl	H_2S	SO_2	CO_2	Ar^*	N_2^*	CO_2^*
DYK	2003/7/9	97.4	8654	-	275	16.7	7.37	110	1061	18.4	30407	3297	956056	51.0	4725	960918
DYK	2003/8/6	136	14244	-	545	0.62	5.96	212	1858	2.26	44087	10215	928694	55.2	7384	937000
SYK	2004/3/16	36.6	7997	0.47	6554	35.7	6.74	1396	315	33.7	36697	212	946717	22.5	6835	948140
SYK	2004/10/5	164	17312	29.7	9880	44.3	7.50	492	2355	14.7	45386	2473	921842	61.5	8633	932316
LHK-1	2004/4/16	51.8	10609	-	1068	6.42	4.93	46.4	671	102	73327	155	913959	22.4	8134	916893
LHK-1	2004/8/18	36.5	10419	-	3137	29.9	4.56	14.5	56.8	193	73389	379	912341	34.0	10210	912588
LFK	2004/4/16	36.7	7964	-	534	4.85	4.38	1.49	365	111	39897	58.0	951024	20.7	6614	952685
LFK	2004/5/1	21.6	5592	0.79	655	1.65	1.99	311	355	39.8	41997	177	950847	5.95	4275	952462
LSK	2003/5/20	54.7	12389	-	2618	-	4.10	291	381	12.1	149719	2736	831796	38.0	10988	833310
LSK	2003/6/5	79.3	13077	145	1727	8.61	6.41	339	636	14.1	121471	1581	860917	51.5	10741	863535
BY	2003/8/5	82.4	16379	-	16859	68.8	13.1	50.1	558	6.65	12275	2810	950898	58.0	14336	953438
BY	2003/10/21	63.7	16885	-	19517	46.7	18.8	145	474	10.0	9120	3513	950207	42.9	15154	952359

DYK: Da-you-keng, SYK: Hsiao-you-keng, LHK: Liou-huang-ku, LSK: Leng-shuei-keng, BY: Ba-yan.

$N_2^* = N_2 - 3.727 \times O_2$; $Ar^* = Ar - 0.044 \times O_2$; $CO_2^* = CO_2 - 1.67 \times 10^{-3} \times O_2$. The corrected values will be re-normalized to 100% with rest gases in the sample.

Note: Concentration is given in units of μmol/mol; - : Not analyzed or not detected.

Table 2. Dry gas compositions of bubbling springs from the Tatun Volcano Group.

Site	Date	Ar	N₂	CO	CH₄	C₂H₆	He	H₂	O2	HCl	H₂S	SO₂	CO₂	Ar*	N₂*	CO₂*
DP	2003/8/19	180	31518	-	23980	58.1	19.5	648	803	66.5	974	4.66	941725	145	28636	945369
DP	2004/3/7	332	51911	-	12671	5.49	24.2	6.17	3669	48.1	745	4.00	930584	174	38918	947164
TRK	2004/8/18	448	21687	-	1397	40.4	-	6.80	3162	1071	711	0.43	971478	314	10054	986356
TRK	2004/9/13	377	16773	-	418	22.3	-	17.3	1291	2306	1273	2.57	977519	322	12036	983578
SHP	2003/6/6	97.8	9627	61.3	1929	5.03	5.23	7.01	717	8.79	40973	544	946023	66.5	6979	949330
SHP	2003/8/6	132	13021	83.0	2610	6.80	7.07	9.48	970	12.1	51695	834	930619	89.7	9450	935024
MT	2003/7/8	83.6	9884	-	10017	129	13.0	28.9	904	14.8	35720	16.0	943189	44.0	6543	947275
MT	2003/10/2	104	14786	-	13290	-	10.5	58.1	1558	4.77	37898	39.8	932251	35.7	9047	939232
LHK-2	2003/5/20	149	16889	-	4232	-	3.77	1.69	1567	11.0	36788	290	940069	80.8	11132	947149
LHK-2	2004/7/14	149	14276	-	3116	9.56	8.33	11.0	522	17.6	37944	183	943764	126	12361	946120

DP: Da-pu; TRK: Ti-re-ku; SHP: She-haung-ping; MT: Ma-tsao; LHK: Liou-huang-ku.

$N_2^* = N_2 - 3.727 \times O_2$; $Ar^* = Ar - 0.044 \times O_2$; $CO_2^* = CO_2 - 1.67 \times 10^{-3} \times O_2$. The corrected values will be re-normalized to 100% with rest gases in the sample.

Note: Concentration is given in units of μmol/mol; - : Not analyzed or not detected.

Table 3. Testing result of dry gas compositions with different sampling time at Liou-huang-ku.

Sample No.	Sample type*	Sampling time (min)	Ar	N₂	CO	CH₄	CO₂*1	C₂H₆	He	H₂	O₂	HCl	Sₜ	H₂S	SO₂	CO₂*2
LHK-1-1	F	5	65.5	15441	-	3455	-	-	5.51	0.27	29.6	11.7	129320	128987	333	851671
LHK-1-2	F	10	77.3	16520	-	4070	-	4.61	6.37	0.33	854	5.33	140174	139936	237	838287
LHK-1-3	F	15	110	19444	-	4830	342	6.03	9.70	0.53	1266	5.39	152354	152119	235	821632
LHK-1-4	F	20	123	20628	-	5017	496	6.65	7.19	0.41	1250	1.08	151497	151279	218	820974
LHK-1-5	F	30	140	20038	-	4651	435	-	7.57	0.40	2169	99.1	16861	16855	6.54	955599
LHK-2-1	B	5	258	25781	-	5578	-	11.56	9.66	0.48	2561	254	60854	60811	42.6	904693
LHK-2-2	B	10	306	27734	-	5301	-	5.41	6.82	0.37	4178	23.2	47315	47229	86.8	915130
LHK-2-3	B	15	102	17547	-	4350	312	5.44	8.41	0.39	1136	296	67524	67397	127	908720
LHK-2-4	B	20	412	35971	-	7148	588	12.37	11.5	0.47	6894	303	56400	56221	179	892260
LHK-2-5	B	30	451	36849	-	6904	625	11.74	10.9	0.44	7566	5.55	62344	61970	374	885232

* F: fumarole sample, B: hot spring bubbles.

*1: Non-dissolved gases detected by GC; *2: Dissolved gases detected in alkali solution by titrations.

Note: Concentration is given in unit of μmol/mol; - : Not analyzed or not detected.;

$S_t = SO_2 + H_2S$.

Table 4. The ratio of H_2S/SO_2 analyzed with different sampling time from Hsiao-you-keng.

Sample No.	Volume of iodine solution (ml)	sampling time (min)	H_2S ppm	SO_2 ppm	H_2S/SO_2
20ml_30sec-1	20	0.5	299	2.41	124
20ml_30sec-2	20	0.5	305	2.53	120
20ml_30sec-3	20	0.5	292	2.25	129
20ml_30sec-4	20	0.5	330	2.11	157
average			306	2.32	132
20ml_1min-1	20	1	420	2.60	162
20ml_1min-2	20	1	411	2.67	154
20ml_1min-3	20	1	319	2.27	140
20ml_1min-4	20	1	362	2.71	134
average			378	2.56	148
20ml_2min-1	20	2	422	2.64	160
20ml_2min-2	20	2	389	2.91	134
20ml_2min-3	20	2	428	3.48	123
20ml_2min-4	20	2	468	2.82	166
average			427	2.96	144
20ml_3min-1	20	3	398	2.55	156
20ml_3min-2	20	3	443	3.10	143
20ml_3min-3	20	3	505	3.02	167
20ml_3min-4	20	3	475	3.62	131
average			455	3.07	148

mained within the same range with different sampling times (Table 4). Note H_2S/SO_2 ratios were highly variable even over short time periods at the same site due to the small amount of SO_2 in the area (see later discussion and Table 5). These test results suggest sampling time is not a major factor in affecting H_2S/SO_2 ratios.

3.2 Variations over Short Periods and under Different Weather Conditions

SYK was selected as the testing site for variations in gas composition over short periods and under different weather conditions as it is easily accessible and has steady gas exhalation. Fumarolic samples were collected several times with short breaks between subsequent samples

Table 5. Gas compositions of fumaroles from Hsiao-you-keng under different weather conditions.

No.	Collection time (min)	Sample weight (g)	Sampling rate (g/min)	Ar	N_2	CO	CH_4	C_2H_6	He	H_2	O_2	HCl	H_2S	SO_2	CO_2	H_2O
June 23, 2003 (sunny)																
S-1	10	53.2	5.3	2.63	398	0.02	447	2.01	0.32	106	N/A	0.20	2674	397	27485	968488
S-2	10	54.0	5.4	2.77	378	0.09	393	1.74	0.23	95.9	25.8	0.22	2519	129	29262	967193
S-3	10	38.2	3.8	3.49	481	0.11	462	2.16	0.27	115	32.2	0.45	2358	343	32058	964144
S-4	10	46.8	4.7	2.23	379	0.07	435	2.01	0.25	104	30.3	0.32	2545	113	30776	965613
S-5	10	48.2	4.8	2.62	398	0.07	448	2.07	0.26	107	27.2	0.16	2509	178	30438	965890
S-6	10	49.3	4.9	2.56	355	0.07	405	1.88	0.21	96.9	29.5	0.39	2302	282	27118	969406
S-7	10	49.2	4.9	2.06	347	0.06	390	1.82	0.30	94.1	24.7	0.26	2302	334	30027	966476
S-8	10	47.8	4.8	2.12	358	0.05	403	1.94	0.22	100	24.5	0.29	2242	183	28268	968417
S-9	10	42.9	4.3	2.85	442	0.16	457	2.13	0.25	112	22.8	0.37	2555	272	31926	964206
Mean				2.59	393	0.08	427	1.97	0.26	103	27.1	0.30	2445	248	29706	966648
SD				0.44	43.9	0.04	28.8	0.14	0.04	7.29	3.27	0.09	147	101	1808	1882
November 13, 2003 (rainy)																
S2-1	10	42.75	4.3	4.00	652	N/A	613	3.12	0.38	145	80.3	0.59	3497	20.1	38151	956833
S2-2	10	49.42	4.9	3.81	546	N/A	520	2.62	0.31	123	61.3	0.13	2998	10.2	32654	963081
S2-3	5	31.30	3.1	2.96	630	N/A	582	3.20	0.36	136	45.1	0.50	3044	14.4	36522	959019
S2-4	5	29.43	2.9	5.90	856	N/A	588	3.29	0.43	139	110	0.42	3137	30.9	38450	956679
S2-5	5	29.55	3.0	4.75	688	N/A	571	3.22	0.36	136	71.7	0.66	3085	19.0	37703	957717
Mean				4.28	674	N/A	575	3.09	0.37	136	73.7	0.46	3152	18.9	36696	958666
SD				1.11	114	N/A	34.3	0.27	0.04	8.04	24.2	0.21	199	7.78	2376	2637

Note: Concentration is given in unit of μmol/mol; N/A: Not analyzed; SD: standard deviation.

on June 23, 2003 (a sunny day) and November 13, 2003 (a raining day), respectively, at the SYK site. The purpose being to see if the composition of volcanic gas in the selected area changes over short time periods and whether differing weather conditions affect gas composition. The results indicate that, in general, gas composition from SYK does not show significant variation over short periods, i.e., within one day (Table 5). The gas composition mainly contains steam water (95.7~96.9%) with CO_2 as the dominant dry gas and there was no significant variation in this composition over the few hours tested. For major components such as H_2O, CO_2, H_2S etc., variations were less than 10% (one standard deviation). However, for trace (< 1ppm) components much larger variations were evident with some species showing up to 50% variation (e.g., CO, HCl). Although the amount of total sulfur ($H_2S + SO_2$) did not show significant variation (~6%), it is interesting to note that SO_2, which was several tens to hundreds of ppm, but was not as low as CO and HCl, also showed large variation over short time periods (up to 40% variation). Such large variations may reflect internal variations in gas samples due to sudden changes in exhalation rates during testing and, also the general difficulty in measuring fumarolic gases (Giggenbach and Matsuo 1991; Giggenbach et al. 2001).

Comparing results of the two tests at the same site in June 2003 and November 2003, H_2O concentration did not show significant difference (0.8% difference only) between sunny

and rainy days, indicating rainfall is not a major factor in controlling H_2O concentration at fumaroles. However, the air component (O_2 + N_2 + Ar) of the samples was higher on rainy day than sunny day. Lin (2001) suggests rain drops take some air into the fumaroles. Therefore, air contamination may become more significant on rainy days, especially at sites with low exhalation flux of fumaroles. In addition, it is typically more inconvenient and dangerous to collect fumarolic samples close to vents on rainy days hence increasing the likelihood of air contamination during gas sample collection. This means, correction for air contamination is important when significant air contamination is present. Here, assuming all measured oxygen is from air contamination during sampling and/or transportation before analysis, the major components of air (N_2, Ar and CO_2) in the measured sample can be subtracted proportionally for correction (Tables 1-2 and 2). Except for SO_2, most major components, after air correction, did not exhibit significant differences between sunny and rainy days. SO_2 variation may be the result of frequent variation within vents and/or the influence of rainfall. Note that oxygen reacts with H_2S under high temperature meaning the above mentioned correction may be equivocal for high temperature fumarolic gases, however, this is not the case at the sites examined in this study.

Over all, the test results show that major gas composition of fumaroles at SYK was not affected significantly by environmental factors and the de-gassing system was quite steady over a short period (within a few hours). Saito et al. (2002) deployed similar testing in Japan and obtained similar results. Hence, the collection and analytical techniques used for fumarolic gases in this study are suitable for application in the TVG hydrothermal area.

3.3 Geochemical Characteristics of Gas Compositions of the TVG

The results indicate that most fumarolic gas samples from the TVG are predominantly steam water (85 - 95%) (Table 1-1). The occurrence of O_2 is generally considered to be from air contamination. Thus, O_2 is a good indicator to determine valid sampling. After dewatering, CO_2 is the dominant dry gas (83 - 96%), followed by significantly smaller amounts of hydrogen sulfide (1 - 15%), nitrogen and methane (Table 1-2). As for the bubbling gases, dry gas composition is also dominated by CO_2 (93 - 98%) (Table 2).

H_2O concentration in the gas sample is easily affected by condensation processes in the sampling train. The temperature of the fumaroles in the Tatun volcanic area ranges from 80 to 110°C. Water condenses easily and may cause an error in final measured results. Some species, such as H_2S, SO_2 and HCl, are very sensitive and would be easily dissolved in water. Therefore, it is important to make sure all water is collected to avoid loosing some components in the samples.

Carbon dioxide is generally the predominant component after water. According to the carbon isotopic data of CO_2, the $\delta^{13}C$ ratios range from -3.0 to -7.3‰ and are similar to those from some active volcanoes in the world. Hsieh (2000) and Yang et al. (2003) suggest they are magmatic in origin.

Sulfur species, H_2S and SO_2, are important components in fumarolic gases and usually magmatic in origin. Delmelle and Stix (2000) suggest equation (3) is important for degassing magma as gasses ascend toward the surface.

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

Thermodynamic modeling indicates that the reaction shifts to the right at higher pressure (i.e., magma degasses at greater depth), making H_2S the dominant sulfur species in such gas. Conversely, hot gases escaping from a magma body emplaced at shallow levels in the crust will tend to be SO_2-dominated, as frequent field observations confirm (Delmelle and Stix 2000).

However, sulfur species are easily affected by secondary processes, such as the formation of sulfides and elemental sulfur, and hydrolysis process of sulfur gases. Ho (2001) and Yang et al. (2003) suggest the following reactions dominate in hydrothermal areas and may control the formation of sulfur gas in the studied area of this paper.

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O \ . \tag{4}$$

$$2H_2S + 3O_2 \leftrightarrow 2SO_2 + 2H_2O \ . \tag{5}$$

$$2SO_2 + 2H_2O + O_2 \leftrightarrow 4H^+ + 2SO_4^{2-} \ . \tag{6}$$

Reaction (4) may be one of the processes producing elemental sulfur in this area. Here, hydrogen sulfide is oxidized to sulfur dioxide which is easily dissolved in water (equations 5 and 6) resulting in an acidic solution. H_2O plays an important role in the above equations where sulfur gases are easily affected by water. Another component, HCl, is also readily affected by water. As it is highly soluble in water, HCl in fumarolic gases may vary significantly even at the same sampling site (e.g., Giggenbach et al. 2001). Our data also show similar results for HCl concentrations (Tables 1 and 2).

Table 6 shows the chloride and sulfate compositions in the condensed water of fumarolic gases. It is interesting to note that a comparison of the composition of these components in the hot springs of the same area (Chen 2002) reveals much higher concentrations of chloride and especially sulfur in the hot springs than in the condensed waters of the fumaroles. This indicates that sulfur gases do not dissolve in the condensed water right after sampling. However, they will dissolve and oxidize as sulfate in water producing very acidic spring water with pH values as low as 2.2 (Chen 2002), through equations (5) and (6). Low concentrations in condensed water, however, indicate that hydrolysis is not the major process affecting the composition of fumarolic gases. This suggests that the very low measured HCl concentration, as shown in Tables 1 and 2, is a primary characteristic of TVG gases.

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 used as a useful proxy in identifying their sources (Delmelle and Stix 2000). Gases originating from a magmatic source usually have higher total sulfur concentrations and hence, exhibit lower CO_2/S_{total} ratios. Except for the Solfatara sample (Italy), all gas samples from other active volcanoes fall in the range of magmatic gases as shown in Fig. 6. By contrast, hydrothermal gases exhibit lower total sulfur concentrations and

Table 6. Chloride and sulfate concentrations in condensed water of fumaroles from representative venting sites.

Locality	Sample No.	Sample site	Cl⁻ ppm	SO₄²⁻ ppm	note
Da-you-keng	0501 DYK-1	A	8.7	166.3	
	0501 DYK-2	A	35.2	150.3	
	0421 DYK-1	B	3059	59.0	close to major
	0421 DYK-2	B	3083	46.3	venting site
Hsiao-you-keng	0317 SYK-1	A	35.1	24.5	
	0317 SYK-2	A	34.7	19.3	
	0407 SYK-1	A	35.0	21.2	
	0407 SYK-2	A	35.8	21.9	
	0421 SYK7m-1	B	35.1	19.1	close to major
	0421 SYK7m-2	B	35.7	23.1	venting site
	0317 SYK-w	B	46.2	47.8	spring water
	SYK*	-	462	1015	hot spring
Liou-huang-ku	0317 LHK-1	A	35.7	32.2	
	0407 LHK-1	A	38.3	29.4	
	0407 LHK-2	A	34.9	17.3	
	LHK*	-	29.2	1011	hot spring
She-huang-ping	0317 SHP-1	A	34.9	21.7	
	0317 SHP-2	A	34.8	19.7	
	0407 SHP-1	A	35.3	25.4	
	0407 SHP-2	A	36.1	21.9	
	SHP*	-	10.2	184	hot spring
Ma-tsao	0317 MT-1	A	35.8	25.8	
	0317 MT-2	A	35.0	20.8	
	MS*	-	35.5	346	hot spring
Leng-shuei-keng	0317 LSK-2	A	35.3	33.6	
	0421 LSK-1	A	43.1	49.8	
	0421 LSK-2	A	37.4	39.4	
	LSK*	-	14.5	157	hot spring
Long-fong-ku	0317 LFK-2	A	35.2	28.9	
	0407 LFK-1	A	36.1	31.9	
	0407 LFK-2	A	36.5	22.4	
	LFK*	-	32.6	427	hot spring
Ba-yan	0317 BY-1	A	34.9	31.4	
	0317 BY-2	A	34.7	35.2	
	0407 BY-1	A	45.3	46.8	
	0407 BY-2	A	35.6	42.0	
	BY*	-	46.5	2040	hot spring

A: the same site as sampling site for fumaroles shown in Table 1 and bubbles in Table 2.

B: different sites from the regular sampling site for fumarole and bubbling gas samples.

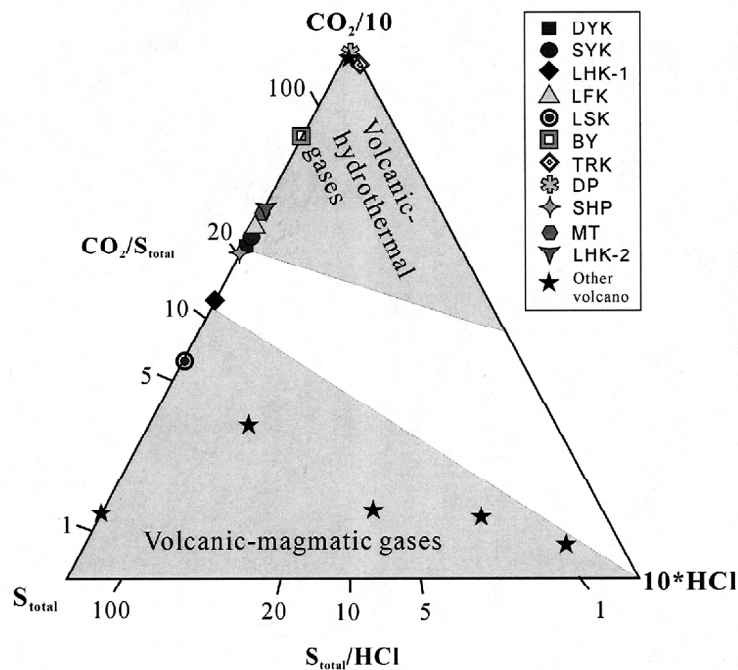*: compositions of hot spring waters; data from Chen (2002).

Fig. 6. CO_2-S_{total}-HCl triangular plot for the Tatun Volcano Group gases. Except for LSK and LHK-1 samples, most gases fall in the range of hydrothermal gases. Gas samples from other volcanoes are also shown for comparison. Note: S_{total} = H_2S + SO_2; LSK = Leng-shuei-keng fumaroles; LHK-1 = Liou-huang-ku fumaroles; LHK-2 = Liou-huang-ku hot spring bubbles; the rest of the abbreviations are same as shown in Tables 1 and 2. Field boundary shown in the figure is from Delmelle and Stix (2000); data of other volcanic gases taken from Table 7-1.

higher CO_2/S_{total} ratio. From the CO_2-S_{total}-HCl plot, we can see that TVG gases exhibit much lower concentrations of HCl compared with gases from other volcanoes in the world (Table 7-1). Except for the fumaroles from Leng-shuei-keng (LSK) and LHK (LHK-1), which exhibit higher total sulfur concentrations (Table 7-2) and fall in the range of magmatic gas, most of the TVG gases appear to be hydrothermal gases owing to their high CO_2/S_{total} ratios (Fig. 6).

Furthermore, we ought be able to differentiate the tectonic environments of the gases by plotting gas compositions on a N_2-He-Ar diagram (Delmelle and Stix 2000). Like gases from White Island (New Zealand) and Merapi (Indonesia), most TVG gases belong to convergent plate gases as opposed to divergent plate gases (Fig. 7), suggesting that the magma source for the TVG gases is closely related to the subduction process in NE Taiwan.
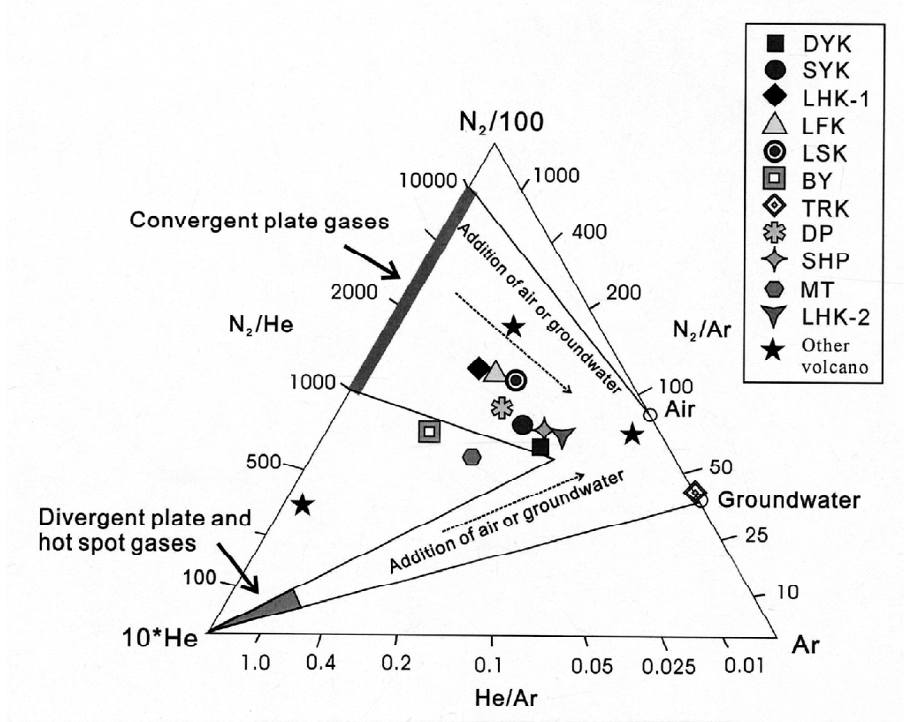
Fig. 7. N$_2$-He-Ar triangular plot for the Tatun Volcano Group gases. Most samples fall in the range of a mixed trend between convergent plate gases and air/groundwater. Gas samples from other volcanoes are also shown for comparison. Symbols are same as in Fig. 6. Field boundary shown in the figure is from Delmelle and Stix (2000); data of other volcanic gases taken from Table 7-1.

Methane is typically present in very small amounts in volcanic gases (Table 7-1) and considered a product of secondary processes, e.g., hydrothermal and/or organic processes (Giggenbach 1989; Goff and Janik 2000). Most CH$_4$ is oxidized quickly under high temperatures and hence, only trace amounts of CH$_4$ gas are detected in high temperature volcanic gases (Giggenbach 1996). It is interesting to note that some TVG gases, e.g., SYK, BY, DP, MT, have pretty high CH$_4$ concentrations compared with other volcanic gases in the world (Table 7-1), indicating that hydrothermal and/or organic processes exist in the area.

The H$_2$S/SO$_2$ ratio is also an important proxy for characterizing gas sources, although it may vary significantly in one single venting site as discussed in the previous section. High temperature volcanic gases usually have very low H$_2$S/SO$_2$ ratios following as per equation (3) (Giggenbach 1989; Delmelle and Stix 2000); in contrast, low temperature ones, including the TVG gases, have tens to hundreds of times higher H$_2$S/SO$_2$ ratios than those in high temperature gases (Table 7-2). These results indicate that the TVG gases exhibit similar characteristics to low temperature volcanic gases from other active volcanoes in the world.

Table 7-1. Temperature and the average compositions of dry fumarolic gases from the Tatun Volcano Group compared with those from other volcanoes in the world.

Site: sample type	T (°C)	CO_2	S_t	HCl	He	H_2	Ar	O_2	N_2	CH_4	C_2H_6	CO
Da-you-keng (DYK): fumarole	102	942	44.0	0.01	0.007	0.16	0.12	1.46	11.4	0.40	0.01	-
Hsiao-you-keng (SYK): fumarole	102	934	42.4	0.02	0.007	0.94	0.10	1.33	12.7	8.22	0.04	0.02
Leng-shuei-keng (LSK): fumarole	98	846	138	0.01	0.005	0.31	0.07	0.51	12.7	2.17	-	0.07
Liou-huang-ku (LHK-1): fumarole	102	913	73.6	0.15	0.005	0.03	0.04	0.36	10.5	2.10	0.02	-
Long-fong-ku (LFK): fumarole	98	951	41.1	0.08	0.003	0.16	0.03	0.36	6.78	0.59	-	-
Ba-yan (BY): fumarole	97	951	13.9	0.01	0.016	0.10	0.07	0.52	16.6	18.2	0.06	-
Da-pu (DP): hot spring bubbles	50.1	936	0.86	0.06	0.022	0.33	0.26	2.24	41.7	18.3	0.03	-
Ti-re-ku (TRK): hot spring bubbles	75	974	1.69	0.99	-	0.01	0.41	2.23	19.2	0.91	0.03	-
She-huang-ping (SHP): hot spring bubbles	99.5	938	47.0	0.01	0.006	0.01	0.11	0.84	11.3	2.27	0.01	0.07
Mu-tsao (MT): hot spring bubbles	88	938	36.8	0.01	0.012	0.04	0.09	1.23	12.3	11.7	0.13	-
Liou-huang-ku (LHK-2): hot spring bubbles	97	942	37.6	0.01	0.010	0.01	0.15	1.04	15.6	3.67	-	-
Solfatara, Italy *[1]	97	992	2.99	-	0.010	0.78	0.004	-	3.65	0.14	-	<0.001
Tangkuban Parahu, Indonesia *[2]	94	550	411	1.75	0.004	4.81	-	-	7.6	0.03	-	-
White Island, New Zealand *[3]	111	808	172	3.6	0.002	0.2	0.03	-	9.8	8.9	-	-
Papandayan, Lower Vent, Indonesia *[2]	282	691	234	28	0.005	2.94	-	0.67	10.4	0.01	-	0.002
Mt. Usu-2, Japan *[3]	690	575	75	68	-	294	-	-	16	0.9	-	0.08
Merapi, Gendol, Indonesia *[2]	803	489	108	53.8	0.004	44.3	4.29	1.59	319	-	-	1.08

Note: Concentration is given in the unit of mmol/mol; $S_t = SO_2 + H_2S$.
* Data from: (1) Chiodini et al. 2001; (2) Giggenbach et al. 2001; (3) Giggenbach and Matsuo 1991.

Table 7-2. Temperature and the average compositions of fumarolic gases with water and other major components from the Tatun Volcano Group compared with those from other volcanoes in the world.

Site	T (°C)	H_2O	CO_2	SO_2	H_2S	S_t	H_2S/SO_2
DYK	102	953	44.6	0.32	1.77	2.09	5.53
SYK	102	920	75.1	0.10	3.28	3.38	32.8
LSK	98	947	44.8	0.11	7.15	7.26	65.0
LHK-1	102	880	109	0.03	8.77	8.80	292
LFK	98	861	133	0.02	7.15	7.17	358
BY	97	906	68.9	0.24	0.75	0.99	3.13
Solfatara, Italy *[1]	97	846	153	-	0.46	0.46	-
Tangkuban Parahu, Indonesia *[2]	94	993	4.3	0.19	2.78	3.08	14.6
White Island, New Zealand *[3]	111	986	10.6	0.06	2.25	2.28	37.5
Papandayan, Lower Vent, Indonesia *[2]	282	965	24.9	1.49	7.01	90.3	4.7
Mt. Usu-2, Japan *[3]	690	993	3.6	0.32	0.18	0.46	0.56
Merapi, Gendol, Indonesia *[2]	803	887	55.6	9.8	1.34	11.1	0.14

Note: Concentration is given in the unit of mmol/mol; $S_t = SO_2 + H_2S$.
* Data from: (1) Chiodini et al. 2001; (2) Giggenbach et al. 2001; (3) Giggenbach and Matsuo 1991.

4. CONCLUDING REMARKS

(1) Utilizing the Giggenbach-bottle techniques, we successfully setup sampling and analytical procedures for volcanic gas studies in the Tatun volcanic area. The system is able to analyze the complete composition of fumarolic gases, including H_2O, CO_2, H_2S, SO_2, HCl, He, H_2, O_2, Ar, N_2, CO, CH_4, C_2H_6, etc.

(2) Test results indicate that the best sampling time for fumarolic gases in the TVG is around 10 minutes and, the composition of gases did not vary significantly over short-time periodic testing (a few hours) and was not affected by weather factors. This implies the degassing system is quite steady, or at least it was during the test period.

(3) Similar to other volcanic gases in the world, the TVG gases are dominated by H_2O (> 85%). After H_2O, CO_2 is the dominant dry gas followed by small amounts of sulfur species and nitrogen.

(4) Compared with other volcanic gases in the world, the TVG gases show the typical composition of low temperature volcanic gases, which exhibit high methane concentrations and H_2S/SO_2 ratios.

(5) Based on the ratios of CO_2/S_{total}, fumarolic gases in LSK and LHK belong to the magmatic gases. However, most TVG gases fall in the range of hydrothermal gases in the CO_2-S_{total}-HCl plot due to their low amount of S_{total} and high CO_2/S_{total} ratio.

(6) Most TVG gases exhibit affinity with convergent plate gases based on the plot of N_2-He-Ar, suggesting that the degassing sources for TVG gases are closely related to the subduction process in NE Taiwan.

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