# Characteristics of volcanic gas correlated to the eruption activity; Case study in the Merapi Volcano, periods of 1990-1994

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#### Abstract

Volcanic gases, collected from Gendol and Woro solfatara fields, the summit of Merapi Volcano during 1990-1994, show an increase in chemical composition of  $H_2$ , CO, CO<sub>2</sub>, SO<sub>2</sub>, and HCl prior to the volcanic events, on the contrary to the drastic decreasing water vapour. The carbon/sulfur ratio of the volcanic gases lies between 1.5 and 5.7 which means that they were derived from the fresh magma. The Apparent Equilibrium Temperature (AET) which is calculated from chemical compositions of volcanic gases using reaction of  $SO_2+3H_2 = H_2S+2H_2O$  showed an increasing value prior to the volcanic events. The Merapi activities lasted during August 1990 to November 1994 showed a significant increase in ratio  $SO_3/H_2S$  prior to the November 1994 pyroclastic flow.

The isotopic composition of volcanic gas condensates indicates that water vapour in Gendol is directly derived from the fresh magma. On the other hand, the contamination and cooling by the subsurface water occurred around the Woro field at a shallow part.

Keywords: volcanic gas, eruption, Merapi Volcano, 1990-1994

### Sari

Gas vulkanik yang diambil dari lapangan solfatara Gendol dan Woro, puncak Gunung Merapi pada periode tahun 1990-1994, menunjukkan peningkatan komposisi  $H_2$ , CO, CO<sub>2</sub>, SO<sub>2</sub>, dan HCI menjelang peningkatan aktivitas; sementara itu terjadi penurunan kadar uap air secara drastis. Rasio karbon/sulfur dalam gas vulkanik yang dianalisis dari Kawah Gendol dan Woro mempunyai nilai 1,5 dan 5,7. Hal ini menandakan bahwa gas vulkanik dari puncak Gunung Merapi berasal dari magma dalam. Temperatur hasil perhitungan berdasarkan kesetimbangan reaksi kimia  $SO_2+3H_2 = H_2S+2H_2O$ menunjukkan peningkatan menjelang letusan. Dari beberapa peristiwa aktivitas Merapi yang terjadi antara Agustus 1990 hingga November 1994 diindikasikan adanya peningkatan nilai rasio  $SO_2/H_2S$ yang signifikan menjelang terjadinya aliran piroklastika pada 22 November 1994.

Hasil analisis isotop gas kondensat menunjukkan bahwa gas di kawah Gendol berasal langsung dari magma, sedangkan gas di kawah Woro telah mengalami kontaminasi dan pendinginan oleh air permukaan pada zona dangkal.

Kata Kunci: gas vulkanik, letusan, Gunung Merapi, 1990-1994

### INTRODUCTION

### Background

Historically, a volcano monitoring was mainly based on geophysical and geological methods, but in the recent years a growing interest has been paid to chemical studies and monitoring of gas exhalation from volcanoes. A famous word from one of the Japanese geochemists, Matsuo (1975, 1979), "volcanic gas is a telegram from the earth's interior" with analogizing to a famous Japan saying "Snow is a letter from the sky" by Nakaya.

Volcanic gases may provide much information about the state and activity of a volcano from which some investigators have studied a possible relationship between a volcanic activity and the chemical composition of volcanic gases. Matsuo (1961), Mizutani (1962), Iwasaki *et al.* (1962, 1966), and Kusakabe (1969) reported that  $H_2S$  and  $CO_2$  were enriched with fumarolic gases at low temperature and that  $SO_2$  and  $H_2$  content increased with rising temperature. Casadevall *et al.* (1983) found that  $CO_2$  discharge rate from the summit of Mount St. Helens decreased before the eruptions on July and August 7, 1983.

Stoiber and Rose (1970) stated that CI/SO<sub>4</sub><sup>2-</sup> ratio in volcanic gas condensate decreased gradually, 1.3 years before the eruption of the Santiago Volcano. Besides, Menyailov *et al.*, (1975) reported that the ratio of S/Cl increased before the eruption of several volcanoes in Kamchatka. Osaka *et al.* (1980) successfully predicted the eruption of the Kusastsu-Shirane Volcano in 1976 on the basis of geochemical studies conducted for twenty years. They found the increasing of SO<sub>2</sub>/H<sub>2</sub>S in fumarolic gases around the summit was identified about one year before the 1976 eruption.

Hirabayashi *et al.* (1986) observed the chemical study of volcanic gases at the Sakurajima Volcano, were connected with significant increasing ratio of originated HCl/SO<sub>2</sub> 1.5 two months before the volcano resumed its explosive activity, and H<sub>2</sub> concentration in gas from hot spring started to increase about two weeks before the beginning of drastic increase of explosive activity in mid-December 1982. Moreover, Hirabayashi *et al.*, (1990) also reported the (HF+HCl)-(SO<sub>2</sub>+H<sub>2</sub>S)-(CO<sub>2</sub>+CO) trigonal diagram of Mount Tokachi, Miyakejima, Izu Oshima with the result was that relative content



Figure 1. Location map of Merapi Volcano.

of  $CO_2$  increased coincidentally with the decrease of volcanic activity, and showed an increase either HCl or ( $SO_2$ +H<sub>2</sub>S) as well as the volcanic activity.  $CO_2$  becomes the major component of dry gases at the end of the activity.

To compare the study of volcanic gas from several volcanoes within Indonesia, Merapi Volcano is one of the most active volcanoes in Indonesia situated in Central Java (Figure 1), with elevation 2968 m above sea level which is a basaltic andesite strato volcano. During 4 years (1990-1994) there are 4 significant crisis events in Merapi which can be used to study gas characteristics of Merapi volcano. The events are seismic crisis on August 1990, pyroclastic flow on August 1992, rock fall on March 1994, and pyroclastic flows on November 1994. The biggest event is pyroclastic flow on 22 November 1994 which killed 66 people and a number of animals. It also damaged plantations.

The activity of Merapi is marked by the fast growth of the lava dome. The dome extrusion accompanied by its partial gravitational collapse, produced block, ash, and pyroclastic flows. The eruption is well-known as "Merapi Type" (Figure 2). At the summit, there are high temperatures fumarolic area named Gendol and Woro. The Centre of Volcanology and Geological Hazard Mitigation uses Merapi Volcano as a natural laboratory and a field experiment for many volcanologists. To develop the methods of investigation of volcano, several cooperative study have been carried out with foreign countries such as Italy, Japan, France, New Zealand, Netherlands, and Germany, and so on.

The main purpose of the study on volcanic gases is to study an empirical relationship between the composition of fumarolic gases and temperature, and to show that the changes in composition of volcanic gases can be indicators of volcanic activity and may possibly useful to predict a volcanic eruption.

#### METHODOLOGY

To monitor the activity of Merapi Volcano, the Centre of Volcanology and Geological Hazard Mitigation located the Volcanology and Technology Development Research Centre in Yogyakarta, at about 25 km from the centre of the volcano and



Figure 2. Photograph of "Merapi Type" eruption of Merapi Volcano.

five observation posts around the volcano. Various methods of monitoring had been carried out, such as gas geochemistry, seismometry, ground deformation, magnetism, gravity, Global Posisitioning System, and visual observation. The data from the field and observation post were transmitted to the Volcanology and Technology Development Research Centre in Yogyakarta and reported to Centre of Volcanology and Geological Hazard Mitigation in Bandung.

Volcanology and Technology Development Research Centre has already investigated the volcanic gas at the summit since 1985. The study was concerned with the correlation between the variation of chemical composition in the volcanic gas and its activity. Geochemistry is also one of the interesting studies of Merapi Volcano. The active fumaroles with high temperature (Woro 570° C and Gendol 820° C) were the main the suitable object of observation for many geochemists to study the characteristic of Merapi gas in relation to its activity. Geochemical observation at Merapi Volcano consisted of chemical analysis of volcanic gas, lava, condensated water, measurement of fumarolic temperature, and SO<sub>2</sub> gas emission rate by COSPEC.

# **Analytical Method**

A round-bottomed flask equipped with a stopcock was used for sampling of fumarolic gases, containing 50 ml of NaOH as absorbing solution. After evacuating, the flasks are weighed. In the field, the titanium tubes and silica pipe were joined in a suitable way and were deeply inserted into fumarolic vents. After flushing the tubes or taking a sufficient time to remove air then the sample flask was connected. The fumarolic gas is admitted by slowly opening the stopcock. The flow rate then slowed down due to warming up of the flask contents. By shaking and cooling the flask more considerably condensate can be collected at about 5 - 10 minutes. As entirely sampling was complete all stopcocks were securely close.

# Volcanic Gas Condensates

The fumarolic gas was cooled in a glass condenser, by water or some organic solvent (e.g., acetone or alcohol), and collected in a flask. The collected water condensate had to be inserted into plastic bottle and closed tightly for storage.

# Meteoric Water

A bottle was rinsed and filled with the water sample, if the water pool or source was deep. The bottle was immersed below the surface and the bottle was capped tightly as soon as possible.

# Chemical Composition of Volcanic Gases

After finishing collecting gas samples in the field, the first step in analysing the chemical composition of volcanic gases was to weigh the flasks to determine the total amount of the condensate. The nonabsorbed gases, such as  $H_2$ , CO,  $O_2$ +Ar were analyzed by gas chromatography after separation on a 5 m long molecular sieve 5 A at room temperature with Helium as carrier gas.

As analysis of nonabsorbed gases was completed, the condensates solution was drawn from inverted sampling flask into a partly evacuated aspirator bottle. The alkaline samples together with blanks of 4 N NaOH absorbent were then diluted by 200 ml distilled water and analyzed for  $CO_2$ , total sulfur, HCI, and H<sub>2</sub>S.

# Isotope Ratio of Volcanic Gas Condensate

The D/H analysis of volcanic gas condensates and water samples used a method of hydrogen from the water by a conventional zinc reduction technique, followed by the isotope mass spectrometry. The <sup>18</sup>O<sup>/16</sup>O ratio of volcanic condensates and water samples were determined using the automated  $CO_2$ -H<sub>2</sub>O ratio equilibration techniques, followed by mass spectrometric measurements. The analytical error of isotopic measurement is  $\pm 1$  and 0.1 °/<sub>∞</sub> respectively. Analysis results for all hydrogen and oxygen isotopic ratios D/H and <sup>18</sup>0/<sup>16</sup>0 are represented by a common  $\delta$ notation, and called per mil deviation from those of Vienna Standard Mean Ocean Water (V-SMOW).

$$\delta = \frac{\text{R sample}}{\text{R standard}} - 1 \times 1000 \,(^{\circ}/_{_{00}}) \qquad (1)$$

### DISCUSSIONS

#### **Chemical Composition of Volcanic Gas**

The analytical results of volcanic gases at Gendol and Woro solfatara fields are represented in Table 1 and Table 2. Their general feature can be summarized as follow; Gendol: 1) Water Vapour contents: 83 to 93% mole, 2) Hydrogen chloride, sulfur dioxide, hydrogen sulfide, and carbon dioxide contents: 0.11 to 1.88% mole; 0.25 to 2.92% mole, 0.13 to 1.49% mole, 2.86 to 11.9% mole. Woro; 1) water Vapour contents 83 to 97%, 2) Hydrogen chloride, sulfur dioxide, hydrogen sulfide, and carbon dioxide contents: 0.02 to 6.27% mole; 0.1 to 3.25 % mole; 0.12 to 1.05% mole; 1.28 to 6.84% mole. R-gas contents both for Gendol and Woro were very small proportion which was composed of nitrogen, hydrogen, carbon monoxide, oxygen, and argon. Out let temperatures are almost constant about 800 to 820 °C at Gendol and 550 °C to 580 °C at Woro.

From the composition of  $H_2O-(CO_2+CO)-(SO_2+H_2S)$  triangle diagram (Allard, 1983), the ratio C/S = 0.2 means the volcanic gas came from later degassing magma, while C/S = 1.5 means the volcanic gas came from magma. Almost all data from Gendol and Woro (Table 3 and Table 4) are plotted between 1.5 and 5.7 of C/S ratio. It means the Merapi volcanic gas came from the fresh magma (Figure 3).

### **Isotopic Composition**

Isotopic ratio of volcanic gas condensate collected from Gendol and Woro since 1993 were

Table 1. Volcanic Gases Composition at Gendol Crater, Merapi Volcano

No	Date	T °C	H <sub>2</sub> O	HCI	SO <sub>2</sub>	$H_2S$	CO <sub>2</sub>	H <sub>2</sub>	0 <sub>2</sub> +Ar	N <sub>2</sub>	СО
1	08-89	792	83.02	0.37	1.20	1.49	11.23	0.65	0.08	1.24	0.04
2	10-89	793	85.50	0.46	1.42	0.34	10.30	0.29	0.13	1.52	0.02
3	11-89	791	91.87	0.44	1.11	0.39	4.74	0.79	0.01	0.61	0.05
4	01-90	806	86.11	0.47	2.92	0.48	6.50	0.44	0.02	3.04	0.04
5	02-90	814	83.62	0.29	1.89	0.55	9.10	1.05	0.80	3.38	0.05
6	04-90	816	83.46	0.31	1.89	0.51	10.90	0.94	0.05	1.87	0.06
7	08-90	830	87.79	0.38	2.70	0.54	7.97	0.31	0.80	0.19	0.04
8	05-92	802	93.31	0.11	0.79	0.44	4.57	0.63	0.02	0.11	0.03
9	06-92	818	86.76	0.29	1.57	1.35	4.48	1.19	0.05	0.27	0.04
10	07-92	820	83.29	0.42	1.77	1.10	11.17	1.33	0.09	0.27	0.06
11	09-92	816	92.26	0.17	0.71	0.32	4.46	1.03	0.04	0.27	0.05
12	10-92	807	92.57	0.32	1.99	0.83	2.90	1.13	0.03	0.19	0.04
13	12-92	824	90.66	0.51	1.06	1.29	5.13	1.00	0.01	0.28	0.07
14	09-93	809	92.02	0.00	1.52	0.33	4.73	0.74	0.02	0.60	0.04
15	09-93	798	94.70	0.13	0.84	0.15	3.32	0.40	0.01	0.43	0.03
16	11-93	808	88.82	0.17	0.76	0.14	6.36	0.81	0.03	2.57	0.07
17	04-94	715	93.10	0.23	2.21	0.68	2.86	0.53	0.03	0.32	0.04
18	06-94	714	92.55	0.38	0.25	0.84	3.50	0.67	0.05	1.64	0.08
19	07-94	803	92.70	0.37	0.70	0.13	3.62	0.45	0.01	1.95	0.02
20	10-94	798	92.90	0.40	0.95	0.28	4.27	0.60	0.01	0.51	0.04
21	11-94	799	86.72	0.32	2.32	0.34	6.63	1.17	0.03	2.41	0.07

No	Date	T °C	H <sub>2</sub> O	HCI	SO <sub>2</sub>	$H_2S$	CO <sub>2</sub>	H <sub>2</sub>	0 <sub>2</sub> +Ar	N <sub>2</sub>	СО
1	04-90	530	86.81	0.17	1.13	0.53	6.66	0.75	0.44	3.49	0.02
2	06-90	537	93.73	0.02	0.16	0.13	1.28	0.12	0.01	0.54	0.01
3	11-90	555	86.76	0.36	2.12	0.32	6.84	0.25	0.01	3.33	0.01
4	04-91	536	83.61	3.51	2.05	0.32	6.12	0.17	0.01	4.20	0.01
5	06-91	535	83.72	1.46	1.05	0.31	6.56	0.17	0.09	6.62	0.01
6	09-91	558	88.37	0.51	3.42	0.91	4.60	0.03	0.03	2.23	0.01
7	05-92	550	95.22	0.09	0.36	0.29	3.53	0.21	0.01	0.10	0.01
8	09-92	561	94.04	0.26	0.95	0.20	4.00	0.32	0.03	0.19	0.01
9	10-92	559	96.32	0.22	0.53	0.31	2.33	0.19	0.01	0.10	0.01
10	12-92	535	95.02	0.27	0.45	1.05	2.97	0.15	0.01	0.08	0.01
11	05-93	551	95.52	0.19	0.40	0.25	3.08	0.17	0.01	0.39	0.01
12	08-93	449	93.29	0.04	0.66	0.31	4.07	0.13	0.03	1.44	0.20
13	11-93	547	90.02	0.08	0.68	0.12	6.02	0.26	0.02	2.76	0.04
14	05-94	471	94.71	0.05	1.15	0.19	3.24	0.22	0.01	0.42	0.02
15	06-94	438	91.42	2.35	0.51	0.33	4.69	0.22	0.02	0.43	0.01
16	07-94	575	93.13	0.17	1.25	0.25	4.90	0.10	0.01	0.20	0.01
17	09-94	577	87.49	4.27	1.00	0.30	4.25	0.19	0.01	0.48	0.01
18	10-94	580	93.33	0.62	0.71	0.56	4.41	0.19	0.01	0.16	0.01

Table 2. Volcanic Gas Composition at Woro Crater, Merapi Volcano

Table 3. Calculation of Total Water, Carbon, and Sulfur at Gendol Crater, Merapi

No	Date	H <sub>2</sub> O	SO <sub>2</sub>	$H_2S$	CO <sub>2</sub>	СО	$SO_2 + H_2S$	CO <sub>2</sub> + CO
1	08-89	83.02	1.20	1.49	11.23	0.04	2.69	11.27
2	10-89	85.50	1.42	0.34	10.30	0.02	1.76	10.32
3	11-89	91.87	1.11	0.39	4.74	0.05	1.50	4.79
4	01-90	86.11	2.92	0.48	6.50	0.04	3.40	6.54
5	02-90	83.62	1.89	0.55	9.10	0.05	2.44	9.15
6	04-90	83.46	1.89	0.51	10.90	0.06	2.40	10.96
7	08-90	87.79	2.70	0.54	7.97	0.04	3.24	8.01
8	05-92	93.31	0.79	0.44	4.57	0.03	1.23	4.60
9	06-92	86.76	1.57	1.35	4.48	0.04	2.92	4.52
10	07-92	83.29	1.77	1.10	11.17	0.06	2.87	11.23
11	09-92	92.26	0.71	0.32	4.46	0.05	1.03	4.51
12	10-92	92.57	1.99	0.83	2.90	0.04	2.82	2.94
13	12-92	90.66	1.06	1.29	5.13	0.07	2.35	5.20
14	09-93	92.02	1.52	0.33	4.73	0.04	1.85	4.77
15	09-93	94.70	0.84	0.15	3.32	0.03	0.99	3.35
16	11-93	88.82	0.76	0.14	6.36	0.07	0.90	6.43
17	04-94	93.10	2.21	0.68	2.86	0.04	2.89	2.90
18	06-94	92.55	0.25	0.84	3.50	0.08	1.09	3.58
19	07-94	92.70	0.70	0.13	3.62	0.02	0.83	3.64
20	10-94	92.90	0.95	0.28	4.27	0.04	1.23	4.31
21	11-94	86.72	2.32	0.34	6.63	0.07	2.66	6.70

No	Date	H <sub>2</sub> O	SO <sub>2</sub>	H <sub>2</sub> S	CO <sub>2</sub>	СО	$SO_2 + H_2S$	CO <sub>2</sub> + CO
1	04-90	86.81	1.13	0.53	6.66	0.02	1.66	6.68
2	06-90	93.73	0.16	0.13	1.28	0.01	0.29	1.29
3	11-90	86.76	2.12	0.32	6.84	0.01	2.44	6.85
4	04-91	83.61	2.05	0.32	6.12	0.01	2.37	6.13
5	06-91	83.72	1.05	0.31	6.56	0.01	1.36	6.57
6	09-91	88.37	3.42	0.91	4.60	0.01	4.33	4.61
7	05-92	95.22	0.36	0.29	3.53	0.01	0.65	3.54
8	09-92	94.04	0.95	0.20	4.00	0.01	1.15	4.01
9	10-92	96.32	0.53	0.31	2.33	0.01	0.84	2.34
10	12-92	95.02	0.45	1.05	2.97	0.01	1.50	2.98
11	05-93	95.52	0.40	0.25	3.08	0.01	0.65	3.09
12	08-93	93.29	0.66	0.31	4.07	0.20	0.97	4.27
13	11-93	90.02	0.68	0.12	6.02	0.04	0.80	6.06
14	05-94	94.71	1.15	0.19	3.24	0.02	1.34	3.26
15	06-94	91.42	0.51	0.33	4.69	0.01	0.84	4.70
16	07-94	93.13	1.25	0.25	4.90	0.01	1.50	4.91
17	09-94	87.49	1.00	0.30	4.25	0.01	1.30	4.26
18	10-94	93.33	0.71	0.56	4.41	0.01	1.27	4.42

Table 4. Calculation of Total Water, Carbon, and Sulfur at Woro Crater, Merapi



Figure 3. The  $H_2O - (CO_2 + CO) - (SO_2 + H_2S)$  Ternary Diagram of Merapi Volcano.

analyzed using mass spectrometer, and the results are shown in Table 5. The equation for meteoric water line sampled from Jrakah north of Merapi Volcano, Slamet Volcano, Baturaden flank of Slamet Volcano, and Lamongan Volcano were determined graphically,

$$\delta D = 8.\delta^{18}O + 12$$
 (2)

This equation was derived differently from equation for meteoric water line by Craig, (1961), that is well-known Craig's equation,

$$\delta \mathbf{D} = 8.\delta^{18}\mathbf{O} + 10 \tag{3}$$

This famous equation was derived from isotopic analysis of the worldwide fresh water river, lake, rain, and snow, covering wide ranges from -320 to + 40 (°/<sub>oo</sub>) for  $\delta$ D and -40 to + 6 for  $\delta$ <sup>18</sup>O, covering 130 water samples.

The volcanic gas condensates from Gendol and Woro were plotted on a  $\delta D$  vs.  $\delta^{18}O$  diagram (Figure 4). Volcanic gas condensates from Gendol plotted close to volcanic water area with narrow range both

 Table 5. Isotopic Data of Volcanic Gas Condensate and

 Meteoric Water at Merapi and some Areas in Java

No	Date	Locality	δ <sup>18</sup> Ο	δD
1	09-93	Gendol	6.7	-29
2	07-94	Gendol	7.2	-26
3	10-94	Gendol	6.7	-29
4	11-94	Gendol	6.8	-28
5	04-95	Gendol	6.8	-27
6	05-95	Gendol	6.9	-28
7	07-95	Gendol	6.4	-31
8	07-95	Gendol	6.6	-29
9	09-95	Gendol	6.8	-33
10	07-95	Woro	6.1	-26
11	04-95	Woro	5.3	-32
12	08-95	Woro	0.3	-36
13	09-95	Woro	3.8	-37
14	10-94	Lamongan	-5.1	-30
15	10-94	Slamet	-0.9	2
16	10-94	Baturaden	-5.5	-30
17	11-94	Jrakah	-8.4	-52
18	07-95	Guntur	-8.2	-51



Figure 4. Isotopic composition of volcanic gas condensate at Merapi Volcano.



Figure 5. H<sub>2</sub>O Content, Gendol Merapi Volcano.

for  $\delta D$  and  $\delta^{18}O$ , while volcanic gas condensates from Woro plotted on the mixing line of magmatic water and meteoric. The isotopic composition of water vapour can be affected by several proccess; between magmatic water and meteoric water (Kusakabe and Matsubaya 1986) and an open system degassing of magma. The shift in  $\delta^{18}O$  values of the waters was caused by the oxygen isotopic exchange with the hot wall rock.

The narrow range of  $\delta^{18}$ O from Gendol is indicated that water Vapour at Gendol is almostly magmatic water, which stable equilibrium with magma or high temperature. On the other hand, Woro gas condensates are plotted on the mixing line of magmatic water and meteoric water which was collected at Jrakah. This result and outlet temperature indicate that contamination and cooling with meteoric water have occurred around the vent of Woro gas at shallow part. This different source of magma will lead us to mainly discuss on the variation of volcanic gas from Gendol.

### Variation of Volcanic Gas Component

The water vapour content decreased prior to the increase of activity (Figure 5), on the contrary the R-gas such as hydrogen, carbon monoxide increased prior to the increase of the volcanic activity, (Figure 6 - Figure 10). These variations are explained by the increase of the volcanic gas component such as HCI,  $SO_2$ ,  $CO_2$ , CO,  $H_2$  from fresh magma in an active decrease of water vapour in fumarolic gas after the

1977-1978 eruption of Usu Hokkaido which were caused by the decrease of contamination with subsurface water (Hirabayashi *et al.*, 1984, Kusakabe *et al.*, 1988). Accordingly, the hydrogen has been a geochemical parameter for monitoring volcanic activity (*e.g.* Hirabayashi *et al.*, 1986; Kazahaya *et al.*, 1988).

Generally, the ratio of  $SO_2/H_2S$  in volcanic gases increased prior to the volcanic activity (Hirabayashi *et al.*, 1980). In the case of Merapi, several events were noted, but the  $SO_2/H_2S$  showed an increase clearly prior the biggest event on November 1994 (Figure 10). The increase of  $SO_2/H_2S$  ratio corresponds to the increase of which was calculated using  $SO_2 + 3H_2 = H_2S + 2H_2O$  reaction, where equilibrium reaction will move to the left as well as the increase temperature. In addition, the  $H_2/H_2S$  ratios increased prior to the rock fall on March 1994 and pyroclastic flow on November 1994 (Figure 12).

The Apparent Equilibrium Temperature (AET) is calculated from chemical composition of volcanic gases using reaction of  $SO_2+3H_2 = H_2S+2H_2O$ , and several dynamic data (Table 6) (Ohba *et al.*, 1994). Almost all AET's are higher than the outlet temperature (Figure 13). We noted that during the 4 last years of Merapi activity a seismic crisis was present on August 1990; pyroclastic flow on August 1992, rock fall on March 1994, and pyroclastic flow on November 1994. The main attention to the biggest event was pyroclastic flow on November 1994. With variation in time, AET increased prior to these

Characteristics of volcanic gas correlated to the eruption activity; Case study in the Merapi Volcano, periods of 1994-1994 (Priatna and E. Kadarsetia)







Figure 7. CO, Gendol Merapi Volcano.



Figure 8. HCl, Gendol Merapi Volcano



Figure 9. SO<sub>2</sub>, Gendol Merapi Volcano.



Figure 10. CO<sub>2</sub>, Gendol Merapi Volcano.



Figure 11. SO<sub>2</sub>/H<sub>2</sub>S, Gendol Merapi Volcano.



Figure 12. H<sub>2</sub>/H<sub>2</sub>S, Gendol Merapi Volcano.

 Table 6. Apparent Equilibrium Temperature (AET) Gendol

 Crater Merapi

No	Date	SO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub> O	T°C	AET
1	08-89	1.20	0.65	1.49	83.02	792	773
2	10-89	1.42	0.29	0.34	85.50	793	740
3	11-89	1.11	0.79	0.39	91.87	791	843
4	01-90	2.02	0.44	0.48	86.11	806	805
5	02-90	1.89	1.05	0.55	83.62	814	903
6	04-90	1.89	0.94	0.51	83.46	816	890
7	08-90	2.70	0.31	0.54	87.79	830	752
8	05-92	0.79	0.63	0.44	93.31	802	792
9	06-92	1.57	1.19	1.35	86.76	818	864
10	07-92	1.77	1.33	1.10	83.29	820	901
11	09-92	0.71	1.03	0.32	92.26	816	869
12	10-92	1.99	1.13	0.83	92.57	807	886
13	12-92	1.06	1.00	1.29	90.66	824	821
14	09-93	1.52	0.74	0.33	92.02	809	857
15	09-93	0.84	0.40	0.15	94.70	798	782
16	11-93	0.76	0.81	0.14	88.82	808	881
17	04-94	2.21	0.53	0.68	93.10	715	795
18	06-94	0.25	0.67	0.84	92.55	714	733
19	07-94	0.70	0.45	0.13	92.70	803	796
20	10-94	0.95	0.60	0.28	92.90	798	813
21	11-94	2.32	1.17	0.34	86.72	799	952

activities. This fact indicates that the temperature changed at degassing process. The increase of AET indicates the ascend of magma from the deeper source to the shallow magma reservoir, where degassing occurred.



Figure 13. AET  $(SO_2 + 3H_2 = H_2S + 2H_2O)$  Gendol Merapi Volcano.

Supported by The Apparent Equilibrium Temperature (AET) and another datum as described above, the  $SO_2/H_2S$  ratio can be a key parameter to explain the pyroclastic flow on November 1994 in Merapi Volcano.

#### CONCLUSIONS

The results of the chemical study on volcanic gases at Merapi Volcano in the periods 1990 - 1994 as appear to show the following features, the volcanic gases at the summit of Merapi were derived from the magma. The concentration of HCl, SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, and CO increased prior to the events, just the opposite decrease of the water vapour content.

Isotopic compositions of volcanic gas condensate from Gendol imply that the water vapour was almost supplied from magma. On the other hand, the contamination and cooling with subsurface water occurred around the vent of Woro gas.  $SO_2/H_2S$  ratio of volcanic gas at Gendol can be a key parameter to monitor the activity of Merapi. This fact supported by the calculation of The Apparent Equilibrium Temperature (AET) is calculated by the chemical composition of volcanic gases using reaction of  $SO_2+3H_2 = H_2S+2H_2O$ .

Periodically, the observation of volcanic gases at Gendol will provide us with the characteristic of the volcanic gas and the precursory anomaly of Merapi activity. The development and introducing of new techniques for continuous monitoring of volcanic gases are very important for geochemical study at Merapi Volcano, and comparison with geophysical data will be a successful condition to predict the volcanic activity.

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