Article

Mercury Concentrations in Fumarolic Gas Condensates and Mercury Chemical Forms in Fumarolic Gases

—Case Study on Satsuma–Iwojima Volcano—

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The mercury concentrations in fumarolic gas condensates collected from volcanic areas in Hokkaido, Miyazaki, and Kagoshima Prefectures, Japan, were investigated. Mercury concentrations ranged from 0.12 to 135 μgl^{-1} in 44 collected samples. It was found that there was a positive correlation between mercury and chloride concentrations in fumarolic gas condensates collected from Satsuma–Iwojima Volcano, Kagoshima Prefecture. It was considered that the mercury in fumarolic gas was discharged in the form of mercury (I or II) chloride. However, the results from mercury chemical equilibrium calculations for the vapor in fumarolic gases indicated that mercury was discharged mainly in the form of metallic mercury vapor.

1. Introduction

Particular attention is devoted to the study of geothermal fluids, fumarolic gases and geothermal waters on conducting a geothermal survey. Mercury is a highly volatile element in its both elemental and compound forms and its presence in fumarolic gases can be directly linked to volcanic activity. Hence, mercury in volcanic gases can convey information about nature of magmatic gases. The estimates of volcanic mercury flux have previously been done by some investigators (Cadle, 1980; Unni *et al*., 1978; Phelan *et al*., 1982; Anderson, 1975) from Mount St. Helens, giving a range for mercury flux from 3 to 900 Mg/yr. Several studies have been carried out in Japanese volcanoes and geothermal areas in order to estimate the volcanogenic mercury contribution to the atmosphere.

Noda (1983) has previously reported concentrations of mercury in fumarolic gas condensates from volcanic areas in Japan. Fukuzaki *et al*. (1983) reported mercury emissions in fumaroles, Minami-jigokudani, Mt. Myoko. Nakagawa (1984; 1985) estimated the background levels of mercury in the atmosphere of the geothermal areas of Japan. The fumarolic gases analyzed by Noda (1983) and Nakagawa (1984; 1985) were of low temperature 100℃ or less. However, they have not reported on the mercury in high-temperature fumarolic gases.

The objective of the present study is to determine the mercury concentrations in fumarolic condensates from some Japanese volcanoes in which we collected the fumarolic gas by chance, and also to elucidate the chemical forms of the mercury in the fumarolic gas discharges. To this end, the concentrations of mercury and chloride in fumarolic gas condensates were determined. And the relationships between the volatile constituents in these condensates were investigated with particular attention on Satsuma–Iwojima Volcano. The overall fumarolic contribution of mercury to the atmosphere from all Japanese volcanoes will be reported in the future paper.

2. Sample Collection and Analytical Methods

Prior to the sampling, the gas collector and bottles used for sampling were immersed in 3 M nitric acid for two weeks and thoroughly washed with ultra-pure water in order to avoid mercury contamination from the sampling equipment. The sampling equipment used in the collection is shown schematically in Fig. 1. The fumarolic gas condensate samples were collected by inserting a quartz or teflon tube into fumarole. The fumarolic gas enters through the tube and condensed into an externally cooled ice water condenser attached to the tube. The tube tip was filled with quartz wool to prevent contamination of solid particles from fumarole. A mini suction pump was attached at the end of the condenser in order to suck non-condensable gases. In the case of fumarolic gas condensates collected from Satsuma–Iwojima

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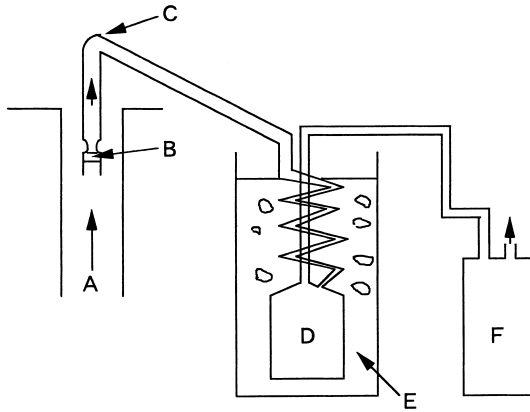Corresponding author: Hayao Sakamoto
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Fig. 1. Schematic diagram of collection equipment. A: Fumarole, B: Quartz wool, C: Quartz or teflon tube, D: Condenser, E: Cooling ice water, F: Suction pump

volcano, 78% to 88% of total mercury was collected by this sampling method. These condensates were preserved in polypropylene containers. Analyses were carried out in less than 2 weeks after the sampling.

Mercury analyses were conducted by the dithizone extraction method using chloroform (Kamada and Sakamoto, 1979) and also by measuring mercury vaporized by reduction using tin (II) chloride at which the mercury was concentrated with a porous gold collector (Sakamoto and Kamada, 1981; Sakamoto et al., 1988) followed by atomic absorption spectrometry. The mercury vapor that evolved from the collector upon heating was analyzed by cold vapor atomic absorption spectrometry. The mercury was analyzed using a Nippon Instruments Co. Mercury System S-1 and a Shimadzu-MA Atomic-Absorption Spectrophotometer. The detection limit of mercury concentration (based on $S/N = 2$) of the atomic vapor produced by reduction was found to be approximately 0.4 ngl^{-1}. In order to confirm the reproducibility of the analysis, standard samples containing 15.0 ngl^{-1} of mercury were analyzed five times repeatedly. The average value and relative standard deviation were found to be 2.9_5 and $1.3_7\%$, respectively (Sakamoto et al., 1997).

The chloride analyses were done by the Vollhard method and by colorimetry using thiocyanic acid-mercury (Utsumi, 1952). Both methods were applied after the hydrosulfide ions and sulfite ions were oxidized to sulfate ions using hydrogen peroxide.

3. Results and Discussion
3-1 Sampling locations and analytical results

Sampling locations of fumarolic condensate samples are shown in Fig. 2. The location numbers,
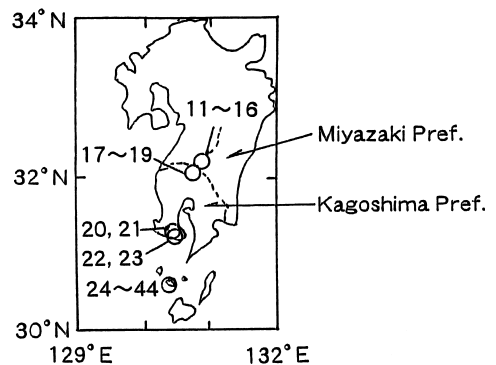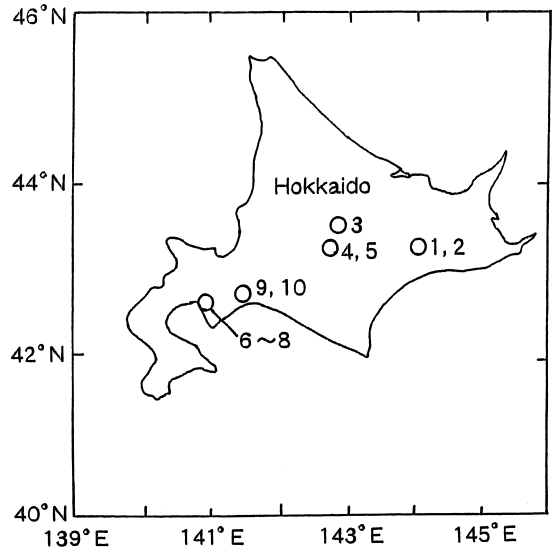
Fig. 2. Map of sampling locations of fumarolic gases condensates.
1, 2: Meakandake, 3: Asahidake, 4, 5: Tokachidake, 6~8: Usuzan, 9, 10: Tarumaesan, 11~16: Ebino, 17~19: Kirishima, 20~23: Yamagawa, 24~44: Satsuma-Iwojima

sampling localities and the results of mercury concentration analyses are shown in Table 1, together with fumarolic outlet temperature, pH, and chloride concentrations.

The mercury concentrations in fumarolic gas condensates, based on 44 samples collected during the period 1973~2000, range from 0.12 to 135 μgl^{-1}. The found values are at the level which are almost equal to the values by Nakagawa (1984; 1985) and Fukuzaki et al. (1983). The previous measurements of mercury in geothermal waters from several volcanic areas in Japan (Sakamoto et al., 1988) showed concentrations from 0.0026 to 0.0898 μgl^{-1}, suggesting that the concentration of mercury in fumarolic

Table 1.　Mercury concentrations, outlet temperature, pH and chloride ion concentrations in fumarolic gas condensates.

No.	Sampling location	Date	Temp. ℃	pH	Hg μgl^{-1}	Cl$^-$ mgl^{-1}
1	Meakandake 1st fumarole (Hokkaido)	Aug. 24. '88	163	0.60	47.8	6,240
2	Meakandake 1st fumarole (Hokkaido)	Aug. 27. '89	256	0.80	71.9	2,200
3	Asahidake (Hokkaido)	Aug. 22. '88	137	1.28	4.2	1,450
4	Tokachidake 62 fumarole (Hokkaido)	Aug. 23. '88	450	0.59	30.7	3,510
5	Tokachidake 62-1 fumarole (Hokkaido)	Aug. 25. '89	328	0.65	73.2	2,380
6	Usuzan 1 fumarole (Hokkaido)	Jun. 27. '85	648	1.40	19.5	3,000
7	Usuzan 1 fumarole (Hokkaido)	Aug. 18. '88	579	1.59	2.9	973
8	Usuzan 1 fumarole (Hokkaido)	Aug. 22. '89	557	1.62	13.8	744
9	Tarumaesan B fumarole (Hokkaido)	Nov. 13. '88	168	1.28	60.9	3,230
10	Tarumaesan B fumarole (Hokkaido)	Aug. 24. '89	210	1.24	57.0	3,300
11	Ebino Shiratoriiwoyama (Miyazaki Pref.)	Aug. 19. '73	245	3.00	0.90[a]	567
12	Ebino Shiratoriiwoyama (Miyazaki Pref.)	Nov. 19. '88	96	3.20	0.60	0.8
13	Ebino Shiratoriiwoyama (Miyazaki Pref.)	Feb. 15. '95	105	2.26	0.30	7.5
14	Ebino Shiratoriiwoyama (Miyazaki Pref.)	Oct. 19. '95	97.1	3.27	0.58	1.0
15	Ebino Shiratoriiwoyama (Miyazaki Pref.)	Nov. 19. '95	96.4	3.14	0.44	1.4
16	Ebino Shiratoriiwoyama (Miyazaki Pref.)	Oct. 07. '00	96.6	4.13	0.15	1.2
17	Kiirishima Iwodani (Kagoshima Pref.)	Oct. 19. '95	97.2	5.30	2.2_8	21.5
18	Kiirishima Iwodani (Kagoshima Pref.)	Nov. 19. '95	97.2	5.33	1.4_3	32.6
19	Kiirishima Iwodani (Kagoshima Pref.)	Oct. 07. '00	98.1	4.07	0.69	5.4
20	Yamagawa Unagi (Kagoshima Pref.)	Aug. 17. '95	101	2.81	0.24	0.7
21	Yamagawa Unagi (Kagoshima Pref.)	Oct. 04. '00	99.0	3.91	0.21	0.2
22	Yamagawa Fushime (Kagoshima Pref.)	Jun. 21. '94	105	5.30	0.34	0.8
23	Yamagawa Fushime (Kagoshima Pref.)	Oct. 04. '00	99.7	6.59	0.33	0.1
24	Satsuma−Iwojima Kamanokuchi (Kagoshima Pref.)	Aug. 22. '73	235	0.70	0.80[a]	16,600
25	Satsuma−Iwojima Nakanoe (Kagoshima Pref.)	Aug. 24. '73	465	0.72	1.8[a]	12,200
26	Satsuma−Iwojima Nakanoeshita (Kagoshima Pref.)	Aug. 23. '73	109	0.62	135[a]	30,100
27	Satsuma−Iwojima Arayama (Kagoshima Pref.)	Aug. 23. '73	850	0.70	5.0[a]	12,800
28	Satsuma−Iwojima Arayama (Kagoshima Pref.)	Aug. 22. '88	189	0.76	46.2	20,200
29	Satsuma−Iwojima Arayama (Kagoshima Pref.)	Aug. 22. '88	783	0.84	3.2	14,100
30	Satsuma−Iwojima Kuromoe (Kagoshima Pref.)	Aug. 25. '73	710	0.69	0.62[a]	14,000
31	Satsuma−Iwojima Kuromoe (Kagoshima Pref.)	Aug. 25. '73	108	0.72	0.71[a]	13,900
32	Satsuma−Iwojima Kuromoe (Kagoshima Pref.)	Aug. 24. '88	105	0.55	96.8	19,800
33	Satsuma−Iwojima Kuromoe (Kagoshima Pref.)	Aug. 24. '88	705	0.85	4.8	18,400
34	Satsuma−Iwojima Kuromoeshita (Kagoshima Pref.)	Oct. 23. '90	216	0.66	1.0	16,500
35	Satsuma−Iwojima Kuromoe (Kagoshima Pref.)	Oct. 23. '90	702	0.73	1.0	14,400
36	Satsuma−Iwojima Kuromoechuudan (Kagoshima Pref.)	Oct. 24. '90	110	0.66	0.12	20,400
37	Satsuma−Iwojima Oukabeshita (Kagoshima Pref.)	Aug. 24. '73	224	0.68	0.62[a]	15,100
38	Satsuma−Iwojima Oukabeshita (Kagoshima Pref.)	Aug. 24. '73	138	0.65	0.53[a]	17,400
39	Satsuma−Iwojima Ouhati (Kagoshima Pref.)	Oct. 20. '90	876	0.53	1.2	13,300
40	Satsuma−Iwojima Ouhati (Kagoshima Pref.)	Oct. 22. '90	872	0.66	1.8	13,400
41	Satsuma−Iwojima (Kagoshima Pref.) No. 1	Oct. 19. '00	105	0.75	0.20	12,400
42	Satsuma−Iwojima (Kagoshima Pref.) No. 2	Oct. 19. '00	112	0.75	0.20	15,100
43	Satsuma−Iwojima (Kagoshima Pref.) No. 3	Oct. 21. '00	818	0.73	1.7_0	13,470
44	Satsuma−Iwojima (Kagoshima Pref.) No. 4	Oct. 21. '00	267	0.62	2.7_0	16,500

[a] Dithizone chloroform extraction

gas condensates was about 1,000 times higher than that in geothermal waters.　This is supported by the fact that mercury fractionates more readily into the vapor phase, and hence occurs in greater abundance in fumarolic gases.

3−2　Correlation between various constituents
Table 2a shows the correlation coefficients of fum-arolic outlet temperature, pH, and the concentrations of mercury and chloride ions among the completed data set of 23 samples from various fumaroles in Japan, excluding the data from Satsuma−Iwojima. Among those variables, significant positive correlation is found only between mercury and chloride ($r = +0.75$), whereas, negative correlation is found be-

Table 2.　Correlation coefficients between temperature, pH, mercury and chloride ion concentrations in fumaloric gas condensates.

a)　all fumaloric gas condensate samples excluding Satsuma–Iwojima.

	T	pH	Hg	Cl$^-$
T				
pH	−0.56			
Hg	0.23	−0.67		
Cl$^-$	0.38	−0.73	0.75	

(n=23)

b)　fumaloric gas condensate of Satsuma–Iwojima.

	T	pH	Hg	Cl$^-$
T				
pH	0.18			
Hg	−0.34	−0.38		
Cl$^-$	−0.48	−0.23	0.82	

(n=21)

tween pH and chloride (r=−0.73), and pH-mercury (r=−0.67). Table 2b shows the correlation coefficients of among the completed fumarolic data set of 21 samples obtained from Satsuma–Iwojima. A significantly high correlation (r=+0.82) is also found between mercury and chloride ions as shown in Fig. 3, however correlations for other variable pairs as between mercury and temperature are not significant.

　The positive correlation may be explained by the following assumptions; 1) The mercury in the fumarolic gas is discharged in the form of mercury chloride ($HgCl_2$ or Hg_2Cl_2) or 2) There is only one source of volatile components, and the dilution of mercury as well as other components is occurring on the way from the source to the vents of Satsuma–Iwojima. However, the former possibility from the chemical equilibrium calculation has been denied as described in section 3–4. Our data indicate that higher concentration of mercury was observed in the condensate of lower temperature fumarolic vents and in more acidic chloride-rich condensates. The fact suggests that the dissolution of metallic mercury occurs easily in acidic chloride-rich conditions.

　The mercury emission route is not simply one. However, mercury in the fumarole region may occur independently from chloride, in the form of metallic mercury vapor from fumarole (Braman and Johnson, 1974; Sakamoto et al., 1989).
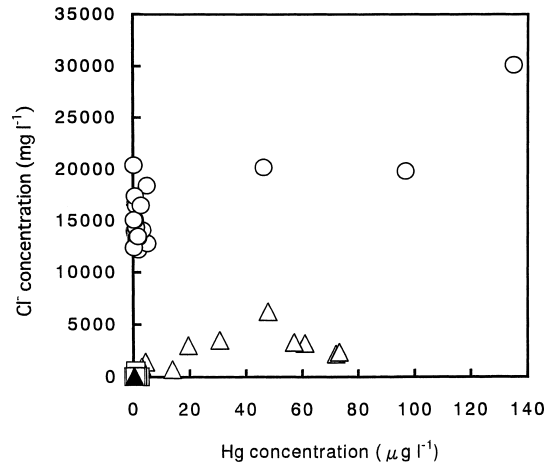

Fig. 3.　Relationship between mercury and chloride ion concentrations in fumarolic gas condensates.
　△: Hokkaido
　□: Ebino, Kirishima
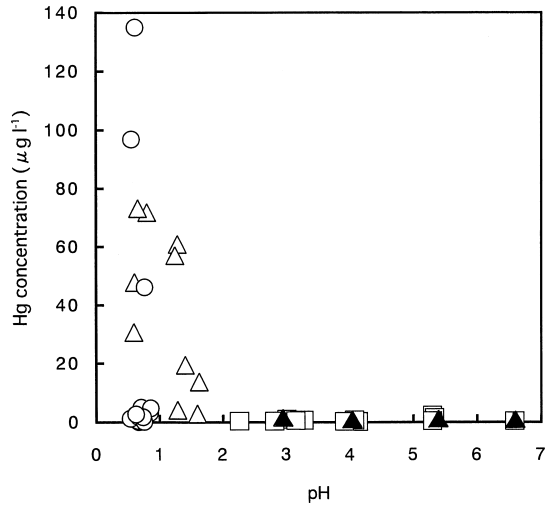　▲: Yamagawa
　○: Satsuma–Iwojima

Fig. 4.　Relationship between pH and mercury concentrations in fumarolic gas condensates.
　△: Hokkaido
　□: Ebino, Kirishima
　▲: Yamagawa
　○: Satsuma–Iwojima

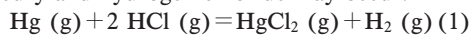## 3–3　Relationships between mercury, pH and temperature

　A negative relationship between mercury and pH in the fumarolic condensates is shown in Fig. 4. This observation indicates that mercury concentration was high in the samples with low pH, particularly in those excluding Satsuma–Iwojima.

This suggests that acidic gas components and metallic mercury were mutually dissolved in condensates depending on acidity. The negative correlation between mercury concentration and pH is especially supporting in the light of the work by Varekamp and Buseck (1986) who showed that mercury is very soluble as mercury chloride complexes in oxidizing chloride rich solutions. Hence, our data indicate that more mercury was detected in more acidic chloride-ions-rich condensates from lower temperature vents. Fig.5 shows the relationship between mercury concentration and outlet temperature. Mercury concentration decreases with increasing temperature as shown in Fig. 5. This fact may be due to the sampling procedure inadequacy that mercury might have been released as metallic mercury vapor in high temperature fumarolic gas. Hence, low mercury concentration was detected in the high temperature condensates.

3–4 Chemical forms of mercury in fumarolic gases

The mercury tends to be rich in fumarolic condensates with high chloride ion collected from Satsuma–Iwojima Volcano. Mercury may be discharged in fumarolic gases in the form of metallic mercury vapor, and partly of mercury(I or II) chloride. Krauskopf (1957) calculated the composition of volcanic gases and the vapor pressures of various materials at 600℃ in order to explain the concentration of metallic elements in mineral deposits. The author reported that the vapor pressures of metallic elements and its chlorides are high. The present authors examined the chemical form of mercury in volcanic gases by calculating the stability of various species of mercury and mercury compounds based on the typical conditions of fumarolic gas discharge.

It is suggested that the following reaction between mercury and hydrogen chloride may occur:

$$Hg\,(g) + 2\,HCl\,(g) = HgCl_2\,(g) + H_2\,(g)\;(1)$$

$$Hg\,(g) + HCl\,(g) = HgCl\,(g) + \frac{1}{2}\,H_2\,(g)\;(2)$$

The equilibrium constant of reaction (1) can be expressed with the partial pressure of each component in the reaction:

$$K_{P_1} = \frac{P_{HgCl_2}\,P_{H_2}}{P_{Hg}\,P_{[HCl]^2}}$$

where K_{P_1} is the pressure at equilibrium constant, and P_{HgCl_2}, P_{H_2}, P_{Hg} and $P_{[HCl]^2}$ are the partial pressures. K_{P_1} is also defined as:

$$\ln K_{P_1} = -\Delta G/RT$$

where ΔG is the change in Gibbs free energy, R is the gas constant, and T is the temperature of the fumarole.

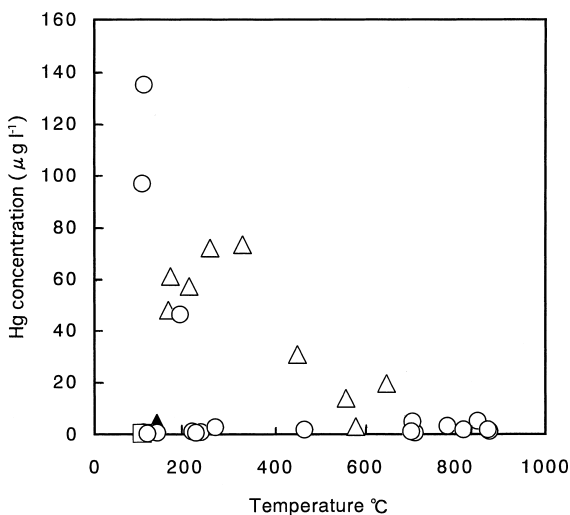It is considered for fumarolic gas to be in chemical

Fig. 5. Relationship between temperature and mercury concentrations in fumarolic gas condensates.
△: Hokkaido
□: Ebino, Kirishima
▲: Yamagawa
○: Satsuma–Iwojima

equilibrium when it was discharged from magma (Shinohara et al., 1993; Ohba, 1997).

The fumarolic gases of Satsuma–Iwojima can also be assumed to be in chemical equilibrium at 1,000 K (Matsuo et al., 1974). Then, $\ln K_{P_1}$ can be estimated to be -12.79 ($K_{P_1} = 2.8 \times 10^{-6}$) based on data from JANAF Thermochemical Tables by Stull and Prophet (1971). Using this value of K_{P_1} and the concentration of H_2 and HCl gas (H_2: 0.12%, HCl: 0.71%) of the volcanic gases of Satsuma–Iwojima reported by Matsuo et al. (1974), the fumarolic temperature is reasonably estimated as 932 K (659℃). Therefore, the analytical data of Matsuo is assumed there being in the equilibrium state based on reaction (1), and so relative ratio of P_{HgCl_2}/P_{Hg} has been calculated to be 1.2×10^{-4}. This result suggests that under this condition the relative amount of elemental Hg is very high compared to that of $HgCl_2$. The ratio of P_{HgCl}/P_{Hg} for reaction (2) has been calculated in a similar manner, found to be 2.8×10^{-2} in fumarole of Satsuma–Iwojima, which also indicates that the vapor pressure of Hg is higher than that of HgCl ($P_{Hg} \gg P_{HgCl}$). The equilibrium constant of reaction 1) and 2) decreases with low temperature. Therefore, it can be seen that mercury does not exist as mercury (I, II) chloride, but rather occurs in the form of metallic mercury vapor in the volcanic gases of Satsuma–Iwojima.

The volcanic gases have local features on the

chemical composition. Therefore, there is a difference at the mercury concentration because the acidity of the fumaloric gas condensate is different.

The discharge of hydrogen sulfide and steam occurs in addition to the discharge of hydrogen chloride in fumarolic gases. These gases react with mercury, and the most probable chemical form is thought to be mercury (II) sulfide or mercury (II) oxide. Then, $[HgS]/[Hg]$ and $[HgO]/[Hg]$ has been calculated to be 6.2×10^{-5} and 1.4×10^{-8}, respectively in fumarole [$T = 1,000$K, $H_2O = 983$ (l/m^3, $H_2 = 0.9$ (l/m^3), $H_2S = 1.4$ (l/m^3)] of Satsuma–Iwojima, based on K^T values at arbitrary temperature by Symonds and Reed (1993), where K^T is the equilibrium constant, at the temperature, T, and $[Hg]$, $[HgS]$ and $[HgO]$ are concentration of gas species.

Mercury is transported as the elemental gas, which is at least five orders of magnitude more abundant than the main subordinate species, including HgS, HgCl$_2$, HgO, HgCl, HgBr$_2$, and HgH (Symonds and Reed, 1993). We previously reported that inorganic (HgO, HgS, HgCl$_2$, HgI$_2$) and organic mercury (CH$_3$HgCl, C$_2$H$_5$HgCl) compounds could be completely vaporized by heating and mercury only exist as metallic mercury vapor at temperatures over 550℃ (Sakamoto *et al.*, 1991). Hence, metallic mercury vapor is the main species of mercury in the fumarolic gases of Satsuma–Iwojima.

4. Conclusions

The concentrations of mercury in fumarolic condensates collected from Hokkaido, Miyazaki, and Kagoshima Prefectures in Japan were investigated. The results can be summarized as follows:

1) The concentrations of mercury in fumarolic condensates ranged from 0.12 to 135 μgl^{-1} in 44 samples.

2) A positive correlation was found between mercury and chloride concentrations in fumarolic gas condensates.

3) A negative correlation was observed between pH and mercury concentrations in condensates, suggesting that acidic gas components and metallic mercury were both dissolved in more acidic chloride-rich condensates.

4) The possibility that mercury (I or II) chloride exists in volcanic gases from Satsuma–Iwojima volcano was rejected.

5) Chemical equilibrium calculations for Satsuma–Iwojima suggested that mercury in fumarolic gases was discharged as metallic mercury vapor into the atmosphere from fumaroles.

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(Editorial handling Jun-ichiro Ishibashi)

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