Relationship between volcanic activity and chemical composition of volcanic gases — A case study on the Sakurajima Volcano

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Concentrations of chlorine and sulfur bearing species in volcanic gases from the Sakurajima Volcano have been continuously measured by a variety of collection techniques and analytical methods. The results of analyses on water-soluble components in volcanic ashes, gases absorbed into alkaline solutions, and gases diffused into the atmosphere revealed that HCl/SO₂ ratio increased prior to any surface activity such as frequency of explosions.

It is suggested that HCl/SO₂ ratio can be one of the useful precursor indicators for volcanic activity.

INTRODUCTION

Some reports have dealt with the relationship between volcanic activity and changes in components of volcanic gases, particularly in the ratio of HCl(Cl) to SO₂(S). NAUGHTON et al. (1975) have found large Cl/SO₄ value in the fume from the Halemaumau crater of Kilauea Volcano two months prior to its eruption, and after that it was reduced. The increase in S/Cl in volcanic gases just before the eruption has been pointed out by GIGGENBACH (1975), and MENYAILOV (1975), in the cases of White Island, New Zealand and Kamchatka-Kurie Islands, respectively. FAIVRE-PIERRET et al. (1980) also have described, in their study of volcanic gases at Etna Volcano, that SO₂/HCl could be one of the parameters for estimating volcanic activity.

This paper reports changes in the ratio of HCl to SO₂ with time, in relation to geophysical data on the activity obtained by the Sakurajima Volcanological Observatory, Kyoto University. A discussion is also made with respect to the estimation of change in volcanic activity at Sakurajima Volcano from the geochemical point of view.

ACTIVITY OF SAKURAJIMA VOLCANO

Sakurajima Volcano has continued its explosive activity at the summit crater since 1955.
The peak stages of eruptive activity where the annual number of recognizable explosions exceeded 400, were observed in 1960 and 1974, and more than 200 explosions happened from 1975 to 1980, except for 1979, as shown in Fig. 1. Volcanic earthquakes with deep focus (A-type) during the period from 1975 to 1978 occurred in a limited zone as shown in Fig. 2. The foci migrated up to shallow part and succeededly micro-earthquakes (B-type) swarm occurred just below the active crater before remarkable explosions (Kamo, 1979). During the period of these activities, volcanic ashes of more than $10^8$ tons were ejected from the summit crater (Kamada, 1975). By recent detailed observations, especially in 1978, the volume of ash heaped on the ground around the volcano was estimated to be $865 \times 10^8$ m$^3$ for seven months from June to December, 1978 (Kamo, 1979).

Kamada et al. (1980) have recently measured the amount of volcanic gases emanated from the summit crater using a correlation spectrometer. They concluded that the averaged amount of SO$_2$ gas from the crater was ca. 1,000-2,000 ton/day since 1975.

**WATER-SOLUBLE COMPONENTS OF VOLCANIC ASHES**

Asahina and Miyake (1935) have first studied water-soluble components of volcanic ashes. Thereafter, Miyake (1938), Noguchi (1938), Kiyota (1942), Kamada (1958) and others developed the scope of investigation. From these studies, it has been revealed that Cl$^-$ and SO$_4^{2-}$ are the two major water-soluble components adhered to volcanic ashes.

Recently, we have measured the ratios of water-soluble components of volcanic ashes from several volcanoes in Japan. On the basis of these ratios, we have discussed the variation of the activity of volcano or the difference of the type of eruption (Ozawa et al., 1975, Ossaka et al., 1975a, 1975b, 1977, 1978, 1980a, 1980b, 1980c, Matsuo et al., 1977).

First the chemical composition of volcanic gases emanated from the crater was measured in order to relate the composition with the change in activity of the Sakurajima Volcano, where the summit crater is the only one place to produce volcanic gases and explode. Since the access to the summit crater has been difficult, we have used a radio-controlled aerocraft to collect the plume gases from the summit crater. The results are shown in Table 1. As seen in Table 1, the collected sample (air-diluted volcanic gases) contained 3-37 ppm of HCl, 17-68 ppm of SO$_2$, and molar ratio ranged from 0.18 to 0.80, with an average value of 0.40. Analyses of water-soluble components of volcanic ashes collected at the same time gave the result, Cl$^-$

![Fig. 1. Annual number of summit explosions at Sakurajima Volcano (Maximum amplitude of explosion-quake is more than 10 $\mu$ and air shock more than 0.1 mb at Harutayama station ca. 2.7 km away from the active crater).](attachment:image.png)
(197 mg/kg) and SO$_4^{2-}$ (1,460 mg/kg), with the molar ratio, Cl/S, of 0.37, which was almost equal to the averaged HCl/SO$_2$ value described earlier for volcanic gases. These results show that Cl$^-$/SO$_4^{2-}$ ratio in water-soluble components can be replaced by HCl/SO$_2$ ratio in volcanic gases emanated from the crater. Therefore, we have collected, since 1974, freshest volcanic ashes just fallen at various points in Sakurajima such as Harutayama, Akamizu, Furusato, Arimura, Kurokami and so on (localities are shown in Fig. 3), and analyzed water-soluble Cl$^-$ and SO$_4^{2-}$. Concentrations of Cl$^-$ and SO$_4^{2-}$ ranged widely from 5.9 to 8730 mg/kg, and from 29.8 to 13,600 mg/kg, respectively. However, when we take the atomic ratio of Cl/S, it fluctuates in

**Fig. 2. Distribution of foci of volcanic earthquakes (A-type).**

**Table 1. Chemical compositions of volcanic gases collected by radio-controlled aerocraft**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Height* m</th>
<th>HCl ppm</th>
<th>SO$_2$ ppm</th>
<th>HCl/SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb. 14, 1975</td>
<td>Blank</td>
<td>0</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>9h28m</td>
<td>300</td>
<td>37</td>
<td>56</td>
</tr>
<tr>
<td>Feb. 15</td>
<td>13h20m</td>
<td>1100</td>
<td>8</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>20</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>16h05m</td>
<td>102</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>17h00m</td>
<td>450</td>
<td>24</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>27</td>
<td>68</td>
</tr>
<tr>
<td>Feb. 16</td>
<td>9h40m</td>
<td>5</td>
<td>20</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>12h14m</td>
<td>7</td>
<td>24</td>
<td>—</td>
</tr>
</tbody>
</table>

* Above sea level.
the range from 0.2 to 1.5, though higher ratios are found sporadically. Figure 4 shows the relationship between the Cl/S ratios averaged for a month, which are calculated excluding values higher than 1.5, and monthly frequencies of explosion. As shown in the figure, Cl/S was higher during the period with high frequencies of explosion, while the ratio was lower when frequencies are low. It can be said that a positive correlation has been found between the Cl/S ratio and the frequency of explosion, though a certain fractionation of HCl and SO₂ owing to their adsorption to the surface of volcanic ashes, and the contribution of wind-blowen salts to ashes should be taken into consideration. This suggests in turn that the Cl⁻/SO₄²⁻ molar ratio in water-soluble components adhered to volcanic ashes can be a good indicator of the change in the explosive activity of the Sakurajima Volcano.

**HCl and SO₂ Gases Absorbed into Alkaline Solutions**

The Cl/S ratio of water-soluble components of volcanic ashes can be useful information only when the volcanic ash is fresh, i.e., just fallen. In this respect, the ratio can be obtained only intermittently. In order to get continuous information on the change in the chemical composition of volcanic gases, containers with alkaline solution (6N KOH) to absorb ambient gases were set at five stations (Hikinohira, Harutayama, Furusato, Arimura and Gongenyama) around Minamidake (see Fig. 3) since January, 1976. Alkaline solutions were installed with covers to prevent contamination from rain. Alkaline solutions were exchanged every one or two months, and the total HCl and SO₂ (calculated from total S) contents of solutions were determined. The result of analyses gives the

![Fig. 3. Sakurajima Volcano and positions where volcanic gases were measured.](image_url)

- ○: Sampling station of volcanic ashes
- ●: Station where gases were absorbed into alkaline solution
- ▲: Station where HCl and SO₂ gas were measured by automatic recording instruments
- △: Station where volcanic gases were collected by radio-controlled aerocraft
amount of HCl and SO2 absorbed to be 0.009-1.3 mg/day and 0.011-1.55 mg/day, respectively; they were remarkably different for stations and periods observed. Results of measurements both at the west side of the crater, Haruyama, and the east side, Arimura, are shown in Fig. 5. Figure 5 shows that the amounts of HCl and SO2 absorbed were larger in summer and smaller in winter at Haruyama, whereas a reverse relationship was found at Arimura. This tendency is strongly dependent on the wind direction prevailing in a season, in other words, the wind blows generally from the east in summer, and from the northwest in winter, around the Sakurajima Volcano. On the other hand, the molar ratios of HCl to SO2 observed were not so different at both stations, as shown in Fig. 6, indicating that the ratios are independent of weather conditions such as the wind direction. Figure 6 also shows that frequencies of explosion averaged daily in each period when alkaline solutions were exposed. A positive correlation between the molar ratios of HCl to SO2 and frequencies of explosion, i.e. the surface activity, mentioned already is again confirmed in this case. The same trend is reproduced in Fig. 7, in which the averaged ratios of HCl/SO2 from all the stations were compared with frequencies of explosion. However, the molar ratio was significantly high, ca. 1.5, from May to August in 1979, although no explosion was observed. Besides most of the peaks of Cl/S ratio are "co-explosive", this exceptional feature may be regarded as a precursory incidence of the following activity.

The alkaline solution method gave us continuous information on HCl/SO2 ratio. Contaminations due to direct ash fall and/or migration of ash deposit seem to be not serious so far as we deal with the ratio.

At the Izu-Oshima Volcano, NOGUCHI and KAMIYA (1963) found that the molar ratio of Cl/S increased to 0.5-0.7 one or two months prior to the eruption, and then decreased to ca. 0.2 just before the eruption. The precursory
Behavior of the Cl/S ratio was more remarkable in the Oshima Volcano probably because the interval of eruption is much longer at this volcano. This tendency, however, has not yet been found in the case of the Aso Volcano (Hirabayashi et al., 1979).

**Continuous Measurement of HCl and SO₂ Concentrations in Atmosphere by Using Automatic Recording Instruments**

The procedures described in the earlier sections are much useful to get information on the

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**Fig. 6.** HCl/SO₂ molar ratio of gases absorbed into alkaline solution at each station vs. averaged daily frequency of explosion (histogram) in a certain period of time.

**Fig. 7.** Averaged HCl/SO₂ molar ratio of gases absorbed into alkaline solution at five stations vs. averaged daily frequency of explosion.
change in the composition of volcanic gases for long period of time. In order to get information for shorter intervals, on the other hand, continuous measurements of volcanic gases should be carried out.

SO$_2$ gas concentration was measured continuously at Harutayama, Nojiri and Furusato using an automatic recording instrument (SO$_2$ in the atmosphere was introduced into the solution containing 0.006% H$_2$O$_2$ and 5 x $10^{-5}$N H$_2$SO$_4$, and the increase in electric conductivity of the solution caused by the increase in SO$_4^{2-}$ content was recorded automatically). Concentrations of SO$_2$ gas were averaged for a day on the basis of the data obtained for an hour-intervals. The pattern of time-variation is quite different from station to station (Fig. 8). This was apparently due to the change in geographical features, and the wind direction. The correlation between variations in the concentration of SO$_2$ gas and explosion-frequencies in the Sakurajima Volcano could not be obtained on

![Fig. 8. SO$_2$ gas concentration in the atmosphere measured by an automatic recording instrument and daily frequency of explosion at Sakurajima Volcano.](image)

![Fig. 9. Changes in HCl and SO$_2$ gas concentrations in the atmosphere measured by automatic recording instruments at Harutayama.](image)
the basis of the data from each station.

At Harutayama, the concentration of HCl gas, in addition to SO₂ gas, has been measured since November, 1978 (HCl in the atmosphere was introduced into a solution containing 0.02% mercury thiocyanate and 0.8% Fe (III) ammonium sulfate, and the change in absorbance at 460nm of the solution was recorded automatically). Figure 9 shows that concentrations have changed remarkably from 0.0008 to 0.98 ppm, and from 0.002 to 0.61 ppm for HCl and SO₂, respectively.

Figure 10 shows that molar ratios of HCl to SO₂, and some geophysical data on the activity of the Sakurajima Volcano; the top figure gives the variation of running average of HCl/ SO₂ for five days, and second to bottom figures show, in order, daily explosion-frequencies, frequencies of B-type earthquakes (running average for five days), which are considered to have occurred by movement or bubbling of magma at shallow part of the vent, kinetic energy of volcanic earthquakes and tremor, and frequencies of A-type earthquakes which are considered to be correlated to the movement of magma.

HCl/SO₂ was high (1.0-2.0) from July to October, 1979, kept constant at ca. 0.5 from November, 1979 to March, 1980, and then decreased since June, 1980. On the other hand, no explosion (indicating surface activity) has been found for about 100 days, from May to August 19th, 1979, which was an extraordinarily calm stage at the Sakurajima Volcano. From September, explosion-frequency increased gradually, and then the volcano resumed high activities from October to December. In April and May, 1980, a number of explosions occurred, and then frequency decreased again since June. Considering these variations, we may conclude that the high ratio of HCl/SO₂ from July to October, 1979 is a precursory indication of the following surface activity started from September. The molar ratios of HCl/SO₂ can be concluded to increase one and a half months before the increases in the explosion-frequency.

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Fig. 10. HCl/SO₂ molar ratio at Harutayama vs. several geophysical data on the intensity of volcanic activity at Sakurajima Volcano.
The frequencies of B-type earthquakes also increased one month before (in the middle of August) the surface activity from September to December of 1979. When compared with B-type earthquakes, the molar ratios of HCl/SO$_2$ would give an approximately one month-earlier precursor. Since information on HCl/SO$_2$ ratios in the period from May to June, 1979 is poor, the relationship between the particular increase in the frequency of B-type earthquakes in July, 1979 and the ratios is not clear.

When an explosive activity starts and is maintained for a certain period of time, the variation in HCl/SO$_2$ ratios seems to be well correlated with the variations in the frequency of explosion, of B-type and A-type earthquakes, and the variations in the kinetic energy of volcanic earthquakes and tremors.

These results show that the variation in the molar ratio of HCl/SO$_2$ can be the best chemical parameter that describes the activity of the Sakurajima Volcano both at the surface and just below the crater. Further, it is to be noted that HCl/SO$_2$ ratio can even give a precursory indication of the rise in the activity after the calm stage for several months.

The purpose of this study is to pursue the possibility of predicting volcanic eruption through chemical means. Although the approach is phenomenological, we may conclude that HCl/SO$_2$ ratio changes prior to the change in volcanic activity. However, the plausible mechanism of the behavior of HCl and SO$_2$ when the magmatic conditions change has not yet been elucidated.

Basic information is as follows. KATSURA and NAGASHIMA (1974) and MYSEN and POPP (1980) measured the solubility of sulfur bearing species into silicate melts under various conditions, IWASAKI and KATSURA (1967) measured the solubility of HCl into various silicate melts under 1 atm. of total pressure. As for the partition of volatile materials between vapor phase and melt, KILINC and BURNHAM (1972), and HOLLAND (1972) found that chlorine is much enriched in the vapor phase. YOSHIDA (1962, 1975) pointed out that the behaviors of chlorine and sulfur are different in the process of degassing from volcanic rocks.

These pieces of information are all useful to understand the changes in HCl/SO$_2$ in volcanic gases in relation to the volcanic activity. It is still difficult, however, to reveal what is the major factor that controls the HCl/SO$_2$ ratio in volcanic gases. Full understanding of the mechanism is a fine future subject of chemical prediction of volcanic eruption.

**CONCLUSION**

Based on the chemical data obtained by a variety of method, we can draw following conclusions with respect to the relationship between chemical information and volcanic activity at the Sakurajima Volcano.

1. The atomic ratio of Cl/S in water-soluble components of volcanic ashes ranged from 0.2 to 1.5 since 1974, and its monthly variation was well correlated with the monthly variation of explosion-frequency.
2. The molar ratio of HCl to SO$_2$ in volcanic gases absorbed into alkaline solutions set at five stations exhibited a similar value regardless of stations, although absolute concentrations of each component were much dependent on the wind direction and the geographical features. The molar ratio was also well related with explosion-frequency. In some cases HCl/SO$_2$ ratios increased in the calm stage for several months prior to the re-active stage.
3. Continuous and automatic measurements of volcanic gas components in the atmosphere showed that their contents varied remarkably. When the volcano started its activity again after the calm stage for several months, the increase in HCl/SO$_2$ ratios was found to preced about one month the increase in the frequency of B-type earthquakes just below the crater, and one and a half month prior to the increase in the frequency of explosion, the surface activity. Furthermore, once activity increased, with continuous explosion, the variation of HCl/SO$_2$ was well related with those of activity observed by geophysical measurements.
Based on the results obtained in this study, we may conclude that the following temporal sequence is the characteristics of explosions of the Sakurajima Volcano, A) after the calm period; occurrence of A-type earthquakes → increase in HCl/SO2 in gases → increase in the frequency of B-type earthquakes → surface explosion, B) during the active period; the increase in HCl/SO2 ratio, increase in the frequency of B-type earthquakes, and surface explosions are all observed.

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