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作品名稱　Observation of volcanic gases with a simple alkaline filter paper method at Sakurajima Volcano in Kagoshima, Japan.

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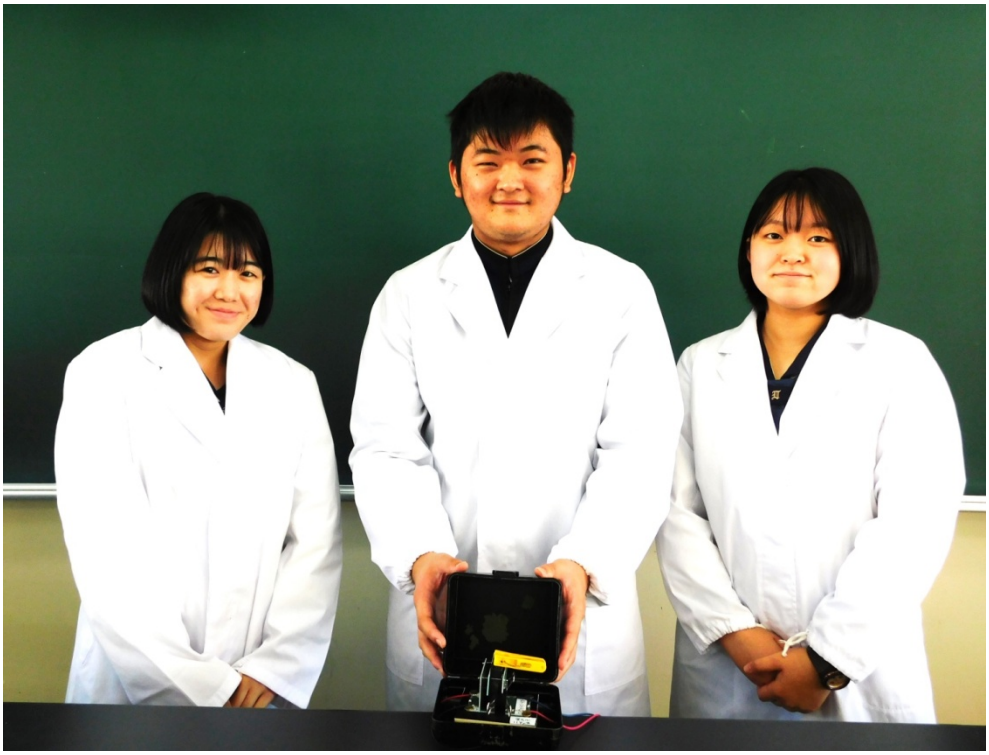

Observation of volcanic gases with a simple alkaline filter paper method at Sakurajima Volcano in Kagoshima, Japan.

簡易アルカリろ紙法を用いた桜島における火山ガス測定

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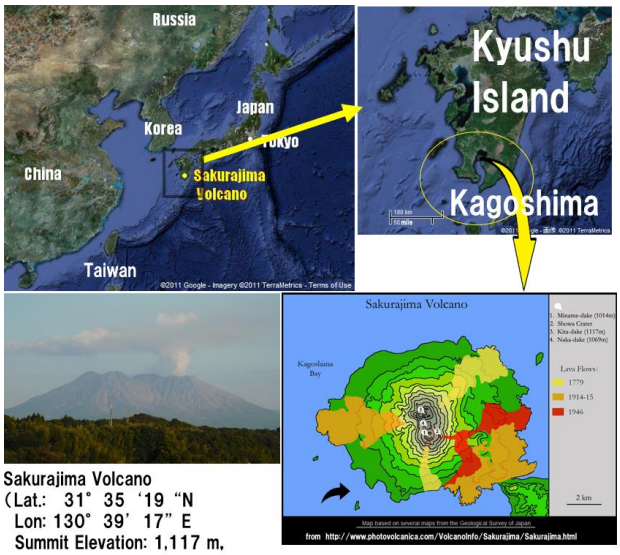
【Abstract】
我々が住む鹿児島県には桜島などの多くの活火山があり、火山防災は喫緊の課題といえる。また、東京工業大学の平林はHCl/SO_2が大きく，逆に少ない期間はHCl/SO2のモル比が，小さくなっていること，爆発が起こらない時期ではHCl/SO_2のモル比が大きくなってから１ヶ月後に爆発が増えることを報告している。そこで、火山活動を把握し、予知を目指すために桜島から放出されている火山ガス（二酸化硫黄、塩化水素、フッ化水素）の組成比変動を測定することにした。そこで、私たちは高校生でもできて多くの地点で測定ができるように、アルカリろ紙を用いた火山ガスの簡易捕集法と自作吸光度計による定量法を確立し、データから多角的な考察を行った。さらに、得られた桜島における火山ガスのCl^-/SO_2比変動は、噴火数変動とのよい相関が見られた。また、火山灰の量と噴火回数の比較から火山ガスの振る舞いに関するモデルを作成した。

There are many active volcanoes in Kagoshima Prefecture, including Sakurajima Volcano. So, the volcanic disaster prevention is an urgent issue. Also, Hirabayashi of Tokyo Institute of Technology reported that the molar ratio of HCl/SO_2 is large during periods of high HCl/SO_2 and conversely small during periods of low HCl/SO_2, and that explosions increase one month after the molar ratio of HCl/SO_2 increases during periods of no explosions. We decided to determine the composition ratio of volcanic gases (sulfur dioxide, hydrogen chloride, and hydrogen fluoride) emitted from Sakurajima crater in order to understand and predict volcanic activities. Thus, we established a simple collection method for volcanic gases using alkaline filter paper and a quantitative method using a self-made absorbance photometer so that even high school students could perform the measurement at many points, and we discussed the data from various perspectives. Furthermore, since last year, we have found a correlation between the variation of Cl^-/SO_2 ratio and the number of eruptions at Sakurajima volcano. Also, a model for the behavior of volcanic gases was developed based on a comparison of the amount of volcanic ash and the number of eruptions.

1. Motivation and purpose

Sakurajima volcano (Fig.1), located in Kagoshima City, where we live, resumed activity in 1955, and since then it has repeatedly erupted from Minamidake and Showa craters, emitting plumes and volcanic gases. The craters repeatedly erupt hot magma and emit volcanic gases such as water vapor, carbon dioxide, hydrogen halides (hydrogen fluoride and hydrogen chloride), and sulfur dioxide even when the volcano is not erupting.（Table1）

In order to determine changes in the composition of volcanic gases and the state of volcanic activity, Hirabayashi[1)] of the Tokyo Institute of Technology installed alkaline absorption solutions (KOH solution) at five locations at the foot of Sakurajima from January 1976 to June 1977, which were covered to prevent rainwater contamination. The acid volcanic gases naturally absorbed from the surface of the



Sakurajima Volcano
(Lat.: 31° 35 ‘19 “N
Lon: 130° 39’ 17” E
Summit Elevation: 1,117 m,
Around 50km) is located in Kagoshima Bay at the south end of Kyushu island, which is the most southern of the four main islands in Japan.

Fig. 1 Location of Sakurajima volcano

Table1 Volcanic gases emissions from Sakura jima Minamidake (estimate)

Gases	Release quantity			
H_2O	7500	-	15000	ton/day
CO_2	1100	-	2200	ton/day
SO_2	1000	-	2000	ton/day
HCl	180	-	360	ton/day
HF	1	-	2	ton/day
H_2	38	-	76	ton/day
N_2	200	-	400	ton/day
CO	2	-	4	ton/day
Total	10021	-	20042	ton/day

Hirabayashi estimated by using data of Surtsey Volcano (アイスランドの南にある火山島)
(HF/HCl≒0.01 HCl/SO_2≒0.4)

liquid were then chemically analyzed every one to two months. And, he reported that the molar ratio of HCl/SO_2 is large during periods when the average daily number of explosions is high, and conversely, the molar ratio of HCl/SO_2 is small during periods when the average daily number of explosions is low, and that explosions increase one month after the molar ratio of HCl/SO_2 increases during periods when no explosions occur. Also, a similar trend in concentration ratios was observed when automatic continuous gas sensor measurements were performed at Haruta in Sakurajima.

On the other hand, Japan Meteorological Agency's volcanic gas monitoring is conducted only for sulfur dioxide, and the Kagoshima Prefecture and Kagoshima City air monitoring stations observe sulfur dioxide as an air pollution gas but no other gases. In addition, atmospheric observation stations are unevenly distributed within Kagoshima Prefecture.

In order to understand Sakurajima's volcanic activity and changes in the composition of volcanic gases, last year we established a simple collection method for acid volcanic gases that can be easily observed by high school students and a simple analysis method for the collected gases. We collected atmospheric gases thought to contain volcanic gases at the homes of students and staff spread throughout the prefecture, chemically analyzed them, and determined their gas composition. This year, while continuing to collect and analyze volcanic gases, we compared volcanic activity and weather conditions based on gas composition data from the previous year. Ultimately, we hope to understand the behavior of volcanic gases in our living environment, and to detect chemical precursors to eruptions based on changes in volcanic gas composition, in order to predict eruptions.

As a collection method for acid volcanic gases, the static alkaline absorption method used by Hirabayashi is difficult for students to handle alkaline solutions of deleterious substances, so the alkaline filter paper method widely used in air pollution observation was used. The chemical analysis methods used were the turbidimetric method and the absorption method using a self-made absorbance photometer. Alkaline filter papers were set up at 15 locations in Kagoshima every month starting in April 2022. From these measurements.

We discussed the relationship between volcanic activity and volcanic gas composition

in 2022 and 2023, and aimed to elucidate the behavior of acid volcanic gases associated with eruptions.

2. Method

(1) Alkaline filter paper method

In the alkaline filter method, aqueous sodium carbonate solution (potassium carbonate is also used; 70 g/L aqueous sodium carbonate was used in this study) is soaked into filter paper, which is then dried and exposed to the open air to adsorb acidic gases (SO_2, HCl, etc.) through neutralization reactions, and is widely used for air pollution observation. It is widely used in air pollution monitoring.

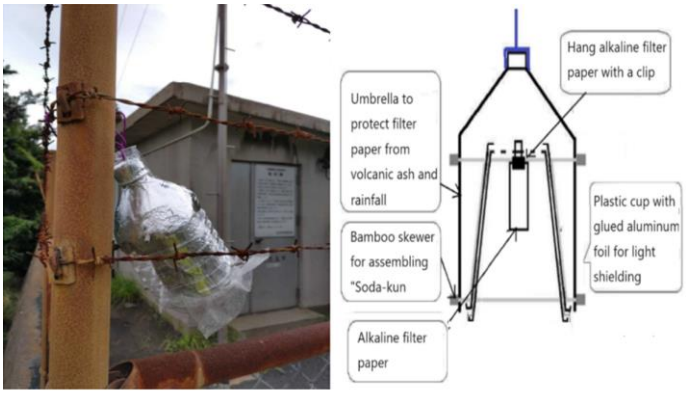


Fig. 2 Self-made simple exposure rack called "Soda-kun"

We decided to use the alkaline filter paper method for volcanic gas measurement. The usefulness of the alkaline filter paper method can be confirmed by the fact that it is already widely used to measure air pollutants (NOx, SOx), and that Furue at the Kagoshima Prefectural Agricultural Experiment Station have successfully measured HCl and HF using alkaline filter paper as a method to investigate damage to agricultural crops caused by volcanic gases.

Alkaline filter paper was prepared by washing the filter paper (10 × 2 cm) in Na_2CO_3 solution (70 g/L) by boiling it in distilled water and then drying it in a simple dessicator overnight. Also, volcanic ash contains volcanic gases, and if volcanic ash adheres to the filter paper, it will be difficult to measure volcanic gases of atmospheric origin. In addition, it is assumed that the carbonate in the filter paper is lost due to rain. To protect the filter paper from ash fall and rainfall, we made a simple exposure rack called "Soda-kun" (Fig. 2) using plastic bottles, bamboo sticks, and plastic cups. The filter paper was placed in the "Soda-kun" , and We place “Soda-Kun” about one month at 15 locations in Kagoshima prefecture, including the homes of students and teachers at our school.

(2) Self-built Absorbance Photometer "Hikaru-chan”

The filter paper exposed for one month was boiled in distilled water at 70℃ for 30 minutes to prepare a sample aqueous solution. Normally, quantitative analysis is performed using ion chromatography. However, since our school does not have ion chromatography equipment, so we measured in different way. And, to do our methods, we created an absorbance photometer "Hikaru-chan" (Fig. 3). A blue LED was used as the light source and a Si photodiode as the photodetector. A substrate was used as the base, and wire and solder were used for fixing. A thin black plastic was used to shade the light. "Hikaru-chan" was housed in a case with a lid, and when actually used, the box was closed to completely block out light.

HCl is adsorbed as Cl^-, so its concentration is measured by the silver chloride turbidimetric method. SO_2 is adsorbed as SO_3^{2-}, so it is oxidized with hydrogen

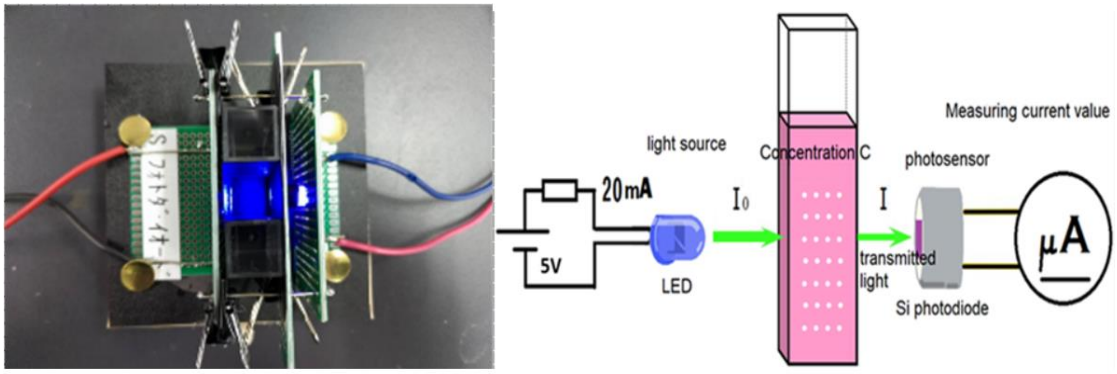


Fig.3 Self-builtSelf-built Absorbance photometer "Hikaru-chan".

peroxide to SO_4^{2-} and its concentration is measured by the barium sulfate turbidimetric method. The turbidimetric method is a method comparing the change in optical turbidity before and after a sample reacts with a reagent to form a precipitate, HF is adsorbed as F^-, so its concentration is measured using SPANDS reagent. The SPANDS method is a method for quantifying F^- from the change in absorbance. In each case, the photocurrent values before and after the reaction with the reagent were recorded, the absorbance was determined from the ratio of the photocurrents, and the concentration was determined based on a calibration curve (Fig. 4) prepared in advance.

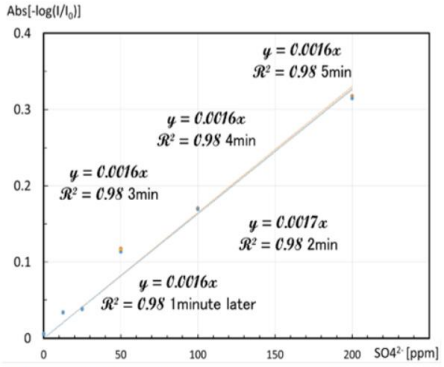


Fig.4 Calibration curve for sulfate ions

3. Preliminary experiments

(1) Alkaline filter paper preparation procedure manual preparation

Alkaline filter paper is prepared according to the previous literature. After examining several types of alkaline for the alkaline filter paper, we decided to use a 70g/L sodium carbonate solution. The filter paper is washed twice with distilled water in a water bath for 30 minutes by shaking and boiling in hot water. Drying was performed in a simple digicator for one day, and storage was also performed in a digicator.

(2) Sample preparation from alkaline filter paper

Samples are prepared from the alkaline filter paper that has been collected with reference to the literature. Place the filter paper in a test tube containing 20 ml of distilled water and boil it in 70°C water bath for 30 minutes.

(3) Analysis Procedure

The procedure for quantitative analysis of the

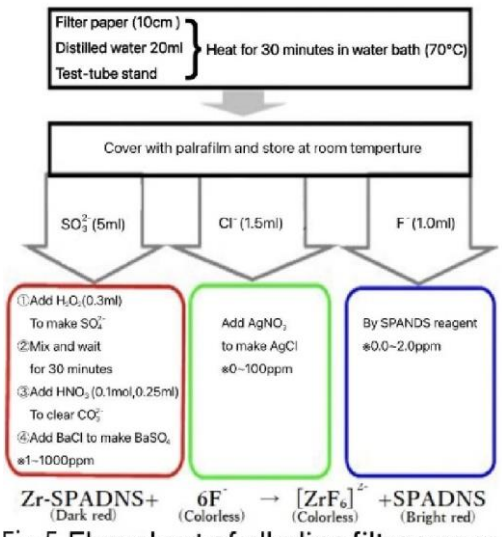


Fig.5 Flowchart of alkaline filter paper

aqueous sample solution prepared in (2) is shown in Fig.5. Sulfur dioxide, hydrogen chloride, and hydrogen fluoride, which are acidic volcanic gases absorbed by alkaline filter paper, are boiled in distilled water, and the sulfite, chloride, and fluoride ions in the sample aqueous solution dissolved in the distilled water are determined.

(4) Establishment of a method for determination of chloride ion

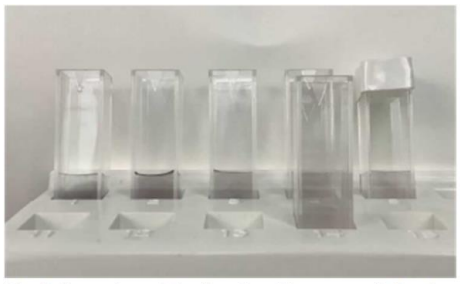


Fig.6 Sample with simple silver precipitation

Chloride ion is determined by precipitation with silver nitrate (see Fig. 5). For this purpose, five different sodium chloride standard solutions (0, 12.5, 25, 50, 100, and 180 ppm) and distilled water were prepared, and the stability of silver nitrate precipitation was examined by adding silver nitrate reagent. Since silver nitrate is photodegradable and silver particles precipitate as shown in Fig.6, the photocurrent tended to decrease gradually from the time when silver nitrate was added.

The calibration curve for each elapsed time is shown in Fig.7. From these results, we decided to use the calibration curve at 1 minute, when the R2 value is closest to 1 and the reaction of silver oxide is not so strong. The reagent used was DPR-Cl reagent manufactured by Kyoritsu Riken, and measurements were made with a self-made absorbance pectrophotometer "Hikaru-chan".

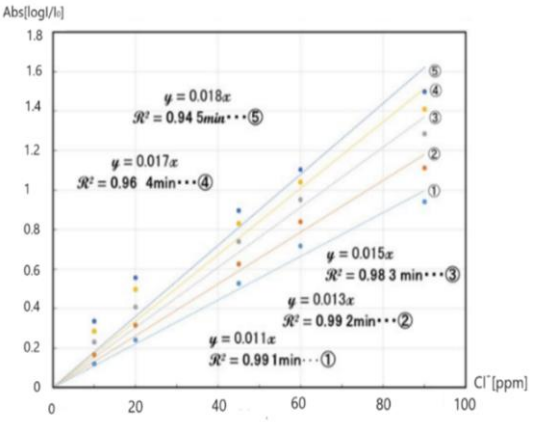


Fig.7 Calibration curve for chloride ion

(5) Establishment of a method for determination of sulfur dioxide

Since sulfur dioxide is adsorbed as sulfite ions, sulfite ions are oxidized to produce sulfate ions for determination by turbidimetric analysis using barium sulfate precipitation.

(a) Verification of the amount of hydrogen peroxide water that participates sulfurous acid ions to sulfate ions.

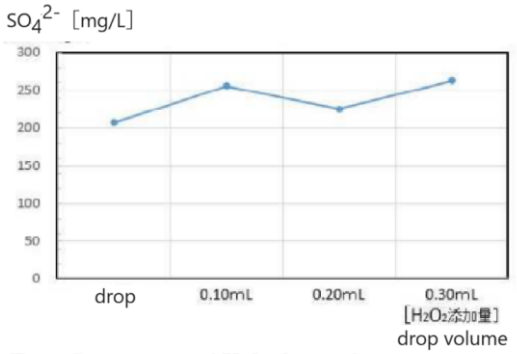


Fig.8 Comparison of H_2O_2 drop volume and SO_4^{2-} concentration

Sulfur dioxide is adsorbed on alkaline filter paper in the form of sulfite ions. Therefore, the amount of hydrogen peroxide necessary to oxidize sulfite ions with hydrogen peroxide water as an oxidant to create sulfate ions for turbidimetric analysis by barium sulfate precipitation was confirmed experimentally, referring to the method of Mitsunaga et al. To a standard solution of 250 mg/L (Class 1 reagent) of sodium hydrogen sulfite, 5.0 mL was placed in a test tube, and 1 drop (approximately 0.03 mL) of hydrogen peroxide water (special reagent 30%), 0.10, 0.20, and 0.30 mL was added with a micropipette, stirred, and left for 30 minutes for

oxidation, and then 1.0 mol/L of Add 0.25 mL of nitric acid and boil in hot water at 70°C for 15 minutes. The results of quantification by barium sulfate precipitation are shown in Fig. 8. This result shows that 0.30 mL is effective for sufficient oxidation.

(b) Calibration curves for the establishment of a method for the determination of sulfate ions

The DPR-SO4 reagent manufactured by Kyoritsu Riken was used to measure sulfate ions, and measurements were made with a self-made absorbance spectrophotometer "Hikaru-chan". In order to determine the analytical conditions, the absorbance was determined according to the time elapsed after the addition of the barium chloride reagent, and a calibration curve was obtained as shown in Fig.9. From this result, the absorbance after 3 minutes, when the R2 value is close to 1, is used.

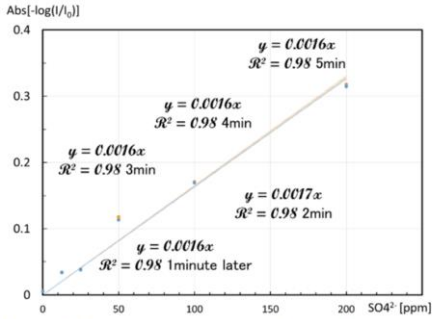


Fig.9 Calibration curve for sulfate ions

(6) Establishment of a method for the determination of fluoride ions

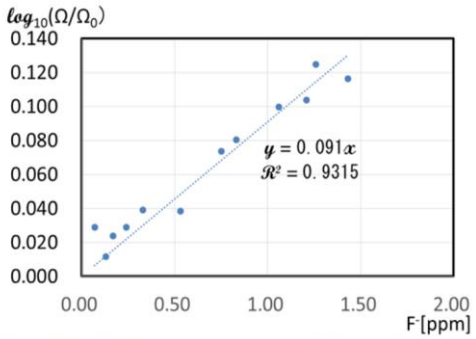


Fig.10 Calibration curve for sulfate ions

As mentioned above, fluoride ions are measured for concentration using the SPANDS method. The concentration of F^- is measured by the change in absorbance of green light. The chemical reaction equation is shown in Fig. 11.

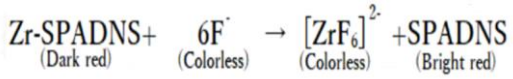


Fig.11 Chemical reaction formula of SPANDS reagent

Originally, the Digital Tester Low Concentration Fluoride HI 729 manufactured by Hanna Instruments was used for the SPANDS method, but since the amount of sample used was 8 ml out of 20 ml, we decided to consider a method of measuring F^- using a self-made absorbance spectrophotometer. A new absorbance spectrophotometer using a green L.E.D. and a CdS element was made, the CdS element was connected to the tester, and absorbance was obtained by taking the ordinary logarithm of the ratio of the resistance when measuring distilled water to that of the aqueous sample solution.

Calibration curves (Fig.10) were obtained for about 20 times by drawing a scatter plot of the relationship between the concentration obtained with the HI 729 analyzer and the resistance value obtained with a self-made absorbance spectrophotometer, and then drawing an approximate straight line.

For each calibration curve, the error due to the calibration curve is considered to be less than 5% based on the results of calibration experiments, but the error is considered to be about 20% based on previous studies[6] because the adsorption of alkaline filter paper is affected by wind.

4. Results and discussion

(1)Verification of the relationship between volcanic activity and eruptions and HCl/SO_2 variations

First, we compared the Cl^-/SO_2 ratios obtained from volcanic gas collection at Akamizu and Arimura on Sakurajima with the number of eruptions during the period. Fig.12 shows the results of Hirabayashi's study, with the bar graph representing the

number of eruptions and the line graph the volcanic gas composition ratio. Hirabayashi reported that volcanic activity increased when the HCl/SO_2 ratio increased in the 1980s, when the volcano was more active than it is today. Hirabayashi also reported that the peak in 1979 was a precursor to an eruption.

During the period when Hirabayashi was observing Sakurajima, the number of explosions at Sakurajima was about 200 per year, as shown in Fig. 14, and from 2021 to 2023, the number was about 100 per year.

Fig.15,16 shows our determination of Cl^-/SO_2

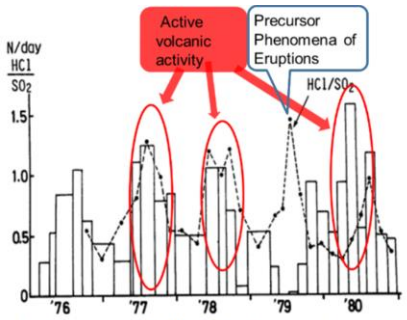


Fig.12 Average daily HCl/SO_2 and average daily eruption frequency by alkaline absorption method



Fig.13 Location of Akamizu and Arimura

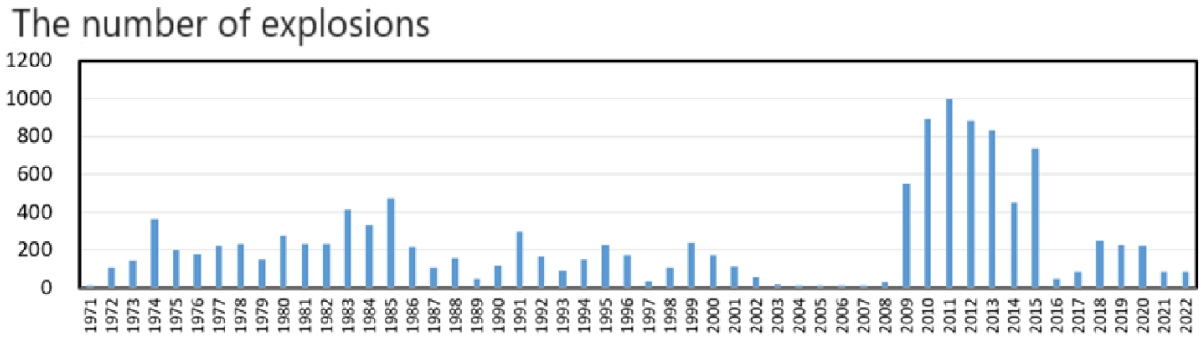


Fig.14 Number of explosions at Sakurajima volcano (1971-2022)
(Minamidake and Showa craters)

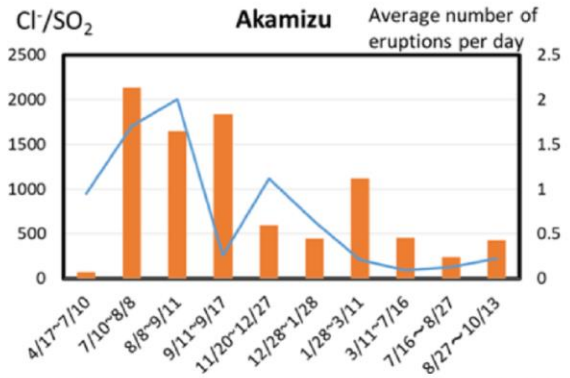


Fig.15 Comparison of HCl/SO_2 variability and daily average number of eruptions at Akamizu

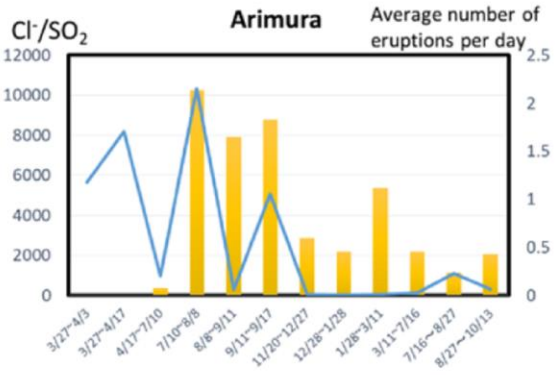


Fig.16 Comparison of HCl/SO_2 variability and daily average number of eruptions at Arimura

and the number of eruptions over a period of time. The bar graph shows the number of eruptions, the line graph shows the ratio, the vertical axis shows the ratio and the number of eruptions, and the horizontal axis shows the observation period. The number of eruptions was found to be larger when Cl^-/SO_2 values were large, consistent with observations at Hirabayashi during a period of high volcanic activity in the present relatively calm conditions.

In April at Arimura, Cl^-/SO_2 values were large even though there was no eruption, which is considered to be a precursor to an eruption.

(2) Evaluation of each volcanic gas as a precursor phenomenon

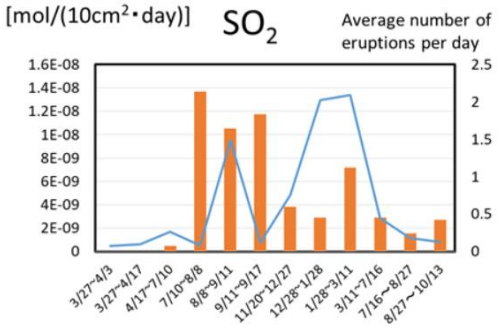


Fig.17 SO_2 deposition and daily average number of eruptions at Akamizu and Arimura

To evaluate the amount of volcanic gas deposition as a precursor to volcanic activity, we compared it to the average daily number of eruptions. Hirabayashi reported that HF, HCl, and SO_2 increase with increasing temperature at constant pressure and with increasing pressure at constant temperature, suggesting that the amount of volcanic gas deposition as well as composition ratio can be an important indicator for observing volcanic activity. At that time, it was thought that the period of low SO_2(4/17-7/10) might be a precursor to subsequent volcanic activity.

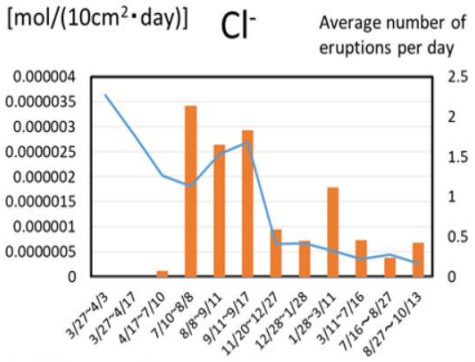


Fig.18 Cl^- deposition and daily average number of eruptions at Akamizu and Arimura

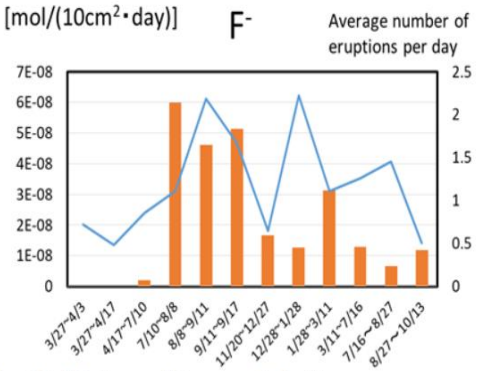


Fig.19 F^- deposition and daily average number of eruptions at Akamizu and Arimura

Fig. 18 and 19 shows that the variation in Cl^- and F^- deposition generally corresponds to the number of eruptions, but the amount of deposition in April 2022 may be a precursor to an eruption around August, and the variation in Cl^- and F^- deposition may serve as an indicator of volcanic activity.

(3) Comparison of each volcanic gases and ash fall and modeling of volcanic gas component emissions

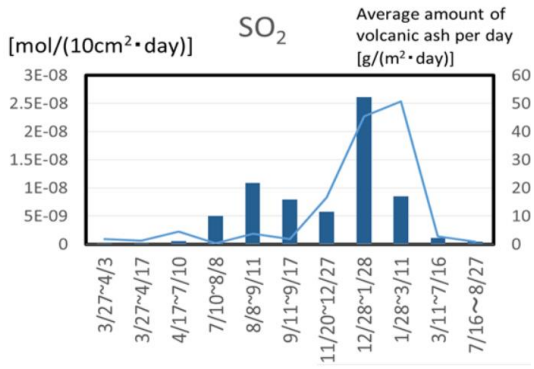


Fig.20 SO_2 deposition and average daily volcanic ash

To clarify the behavior of volcanic ash and volcanic gases during eruptions, we compared the average daily ash fall with volcanic gases. Fig.20 shows our comparison of daily average ash fall and SO_2, where the bar graph shows the daily average ash fall and the line graph shows the amount of SO_2 deposited as material per day. It can be seen that the period of large ashfall coincides with the period of large SO_2 amounts, which suggests that the behavior of SO_2 and volcanic ash is almost the same. However, Cl^- and F^- can be large even when the amount of volcanic ash is small, indicating that Cl^- and F^- may or may not behave together with volcanic ash（Fig.21, 22）.

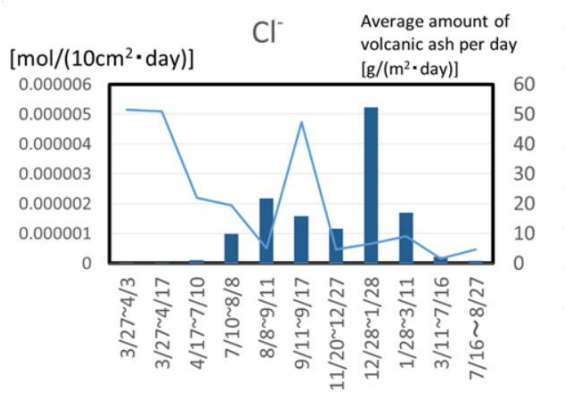


Fig.21 Cl^- deposition and average daily volcanic ash

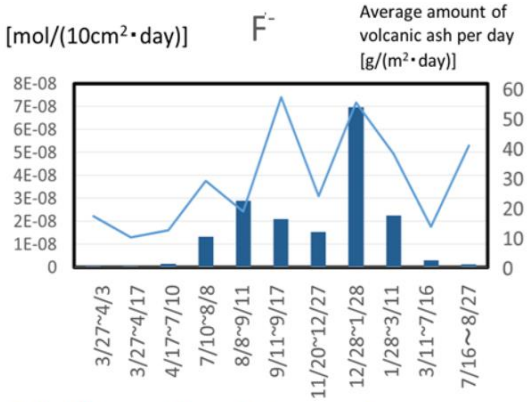


Fig.22 F^- deposition and average daily volcanic ash

We considered the relationship between the behavior of volcanic gases and the amount of volcanic ash, as well as the mechanism of the Sakurajima eruption, and developed a volcanic gas emission model as shown in Fig. 23.

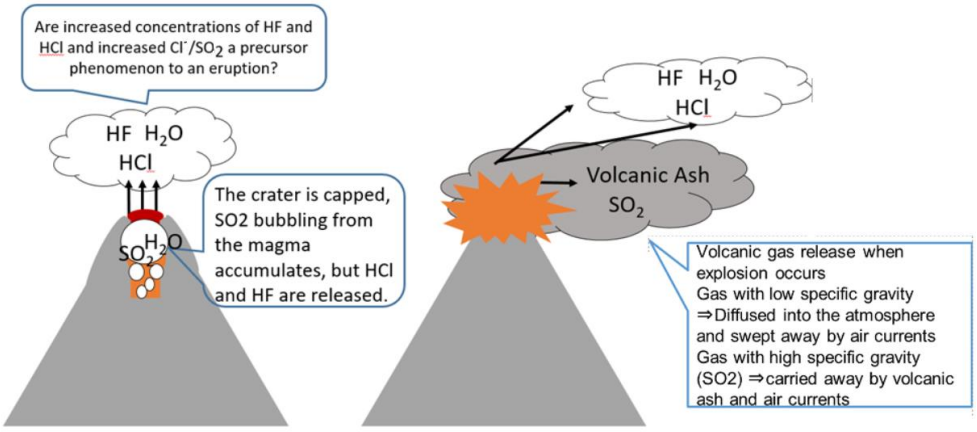


Fig.23 Model of volcanic gas emission before and after eruption

Before an eruption, the crater is covered with a lid, and volcanic gases such as water vapor, SO_2, and HCl that have foamed from the magma accumulate in the crater. However, we consider that a large amount of HF and HCl, which have relatively small molecular weights, and some of the water vapor escape from the lid that seals the crater. Before an eruption, the crater is covered with a lid, and volcanic gases such as water vapor, SO_2, and HCl that have foamed from the magma accumulate in the crater. However, we consider that a large amount of HF and HCl, which have relatively small molecular weights, and some of the water vapor escape from the lid that seals the crater.

When an eruption occurs, the crater cap is blown off and SO_2-rich volcanic gases are ejected together with volcanic ash. Relatively light gases such as HCl and HF are more diffused into the atmosphere than volcanic ash because their behavior is larger than that of volcanic ash, and they are more carried away and diffused by air currents than volcanic ash, but they are sometimes advected with volcanic ash.Volcanic gases with high specific gravity, such as SO_2, are often transported by air currents together with volcanic ash.

5. Future Plan

Future tasks include increasing the number of observation sites closer to the crater,

directly collecting and chemically analyzing volcanic gases and ash, and making continuous measurements using sensors. By doing these things, we hope to make progress in chemical eruption prediction.

6. Reference

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【評語】030031

Geographic-based research is important for local society. In this research, the students focused on the local volcanic activities and tried to build a quick analyzer for the gad composition and build the relationship between volcano eruption and the released-gas components. The research efforts are excellent even though the results do not show high relevancy.