A Geochemical Study of Selenium in Volcanic Exhalation and Sulfur Deposits. III. On the Relation between Selenium and Certain Other Constituents, and on the Behavior of Volcanic Gases

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Regarding the relation beween selenium and other constituents in volcanic exhalations, it has been reported in previous papers[1,2] that the gas temperature at the outlets of fumaroles is one of the factors controlling the selenium content in volcanic gases and the amount of sulfur deposits. On the other hand, though the ratio of sulfur to selenium is correlated with the gas temperature at the outlets of fumaroles, the selenium content in the gases has little correlation with the contents of sulfur and chlorine. For instance, it was found that the sulfur content in gases of a certain area was several times higher than that in gases of other areas.

It has also been reported that difference in the behavior of sulfur and selenium in the transfer process of these chemical elements into volcanic gases is mainly caused by the difference in such of their characteristics as the chemical form and the vapor pressure. In addition, the variation of selenium and other constituents in volcanic gases is found to be due to the dilution process.

A continuous observation over a short period was undertaken in order to study the time variation in the contents of sulfur and selenium in volcanic gases from a fumarole at the Nasudake volcano. It was found that the time variation of the sulfur content in volcanic gases was small, while the selenium content showed a considerable variation.

It is necessary, therefore, to study the time variation of selenium in more detail, in connection with other components (sulfur, chlorine, fluorine and boron), by means of a continuous observation. It is also desirable to study the variation in the contents of these elements with the temperature in order to clarify the behavior of selenium and other elements in the effusion process of volcanic gases.

This study was carried out in order to examine the behavior of volcanic gases by observing the variation in the chemical nature of volcanic gases at the sub-surface of the Nasudake volcano.

Sampling Site and Samples

Samples were collected during the years from 1961 to 1964 at the Nasudake volcano (36°07'N, 139°57'E). The condition of the field has been previously described, and a part of the data for the selenium and sulfur contents, previously reported.[1)]

Two kinds of samples were collected; one was used to examine the variation in the constituents in fumarolic gases with the temperature and the other, to observed continuously the concentration of several components in the fumarolic gases.

The samples for the former purpose were collected from many fumaroles with different temperatures over a wide area of Nasudake. The samples for the latter purpose were collected at several fumaroles over a short period of time at intervals of 40 or 60 min. Simultaneous and continuous observation was made at two different fumaroles, representative ones in the NA and NB areas respectively.[1)] The distribution of fumaroles at Nasudake is shown in Fig. 1.

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1) T. Suzuoki, This Bulletin, **37**, 1200 (1964).
2) T. Suzuoki, ibid., **38**, 1940 (1965).

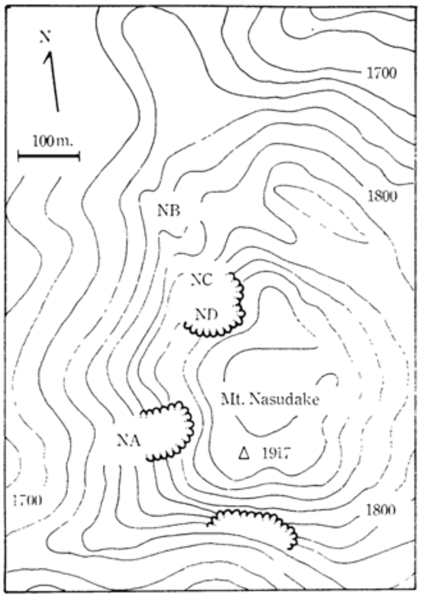

Fig. 1. Distribution of fumaroles at the Nasudake volcano.

Analytical Methods

The selenium, sulfur, chlorine, fluorine and boron in volcanic gases, which were collected as condensed water (alkaline solution), were determined by the following methods.

Selenium. — A colorimetric method using 3,3′-diaminobenzidine. A solution of 10—20 ml. containing 5—25 μg. of selenium is oxidized with hydrogen peroxide, followed by the reduction of the selenium in 6 M hydrochloric acid solution and neutralization with ammonia.[1]

Sulfur.—The total amount of sulfur is determined by the gravimetric method as barium sulfate. A solution of 2—5 ml. is oxidized by hydrogen peroxide and acidified with a dilute hydrochloric acid solution. The SO$_2$-sulfur is determined in the same way as the total sulfur after the sulfide has been removed as cadmium sulfide. The filtrate is oxidized by hydrogen peroxide. Sulfide-sulfur is obtained by the subtraction of the SO$_2$-sulfur from the total sulfur.

Chlorine.—Mohr's titration method, or the colorimetric method using iron alum and mercury thiocyanate.[3] A solution of 1—2 ml. is oxidized with hydrogen peroxide.

Fluorine.—The colorimetric method using alizarin sodium monosulfonate and thorium nitrate. A solution of 1—2 ml. is oxidized, and then 100—300 mg. of silver oxide is added to avoid the disturbance from chlorine: fluorine is then distilled as hydrofluorosilicic acid.[4,5] The distillation apparatus is a little modified in order to apply it to volcanic samples.

Boron. — The titration method using a 0.002 N sodium hydroxide solution and mannitol. A solution of 10—20 ml. is oxidized and acidified by a dilute hydrochloric acid solution in order to expel the carbon dioxide, bicarbonate and carbonate; then the pH of the solution is adjusted to 7.0 with a sodium hydroxide solution before titration.[6]

Results

A) The following results of analysis were obtained for condensed water from various fumarolic gases of the Nasudake volcano collected in 1964: The sulfur and selenium contents range from 2350 to 8730 p.p.m. and from 0.01 to 0.31 p.p.m. respectively. The chlorine,

TABLE I. THE CONTENTS OF SELENIUM, SULFUR, CHLORINE, FLUORINE AND BORON IN VOLCANIC GASES FROM THE NASUDAKE VOLCANO

Location No.	Temp. °C	Se	S	Cl p.p.m.	F	B
NA-1b	365	0.08	3050	295	10.9	81
NA-2	325	0.09	4900	1010	12.5	54
NA-3a	339	0.09	3800	570	11.7	59
NA-3b	264	0.06	4900	880	14.5	41
NB-2	170	0.07	5030	535	18.7	54
NB-3	300	0.24	4180	595	21.1	51
NB-4	130	0.08	6030	730	15.9	43
NC-1	115	0.01	4220	913	4.3	57
NC-2	119	0.01	2350	460	2.0	20
ND-1	110	0.01	5600	782	4.0	39
NE-1	120	0.01	8780	1350	7.2	34

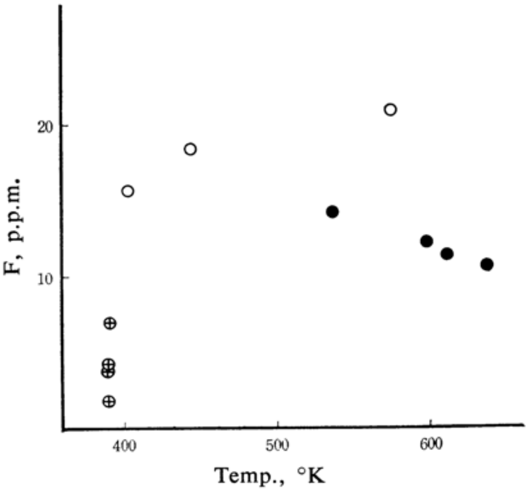

Fig. 2. Relation between fluorine content and gas temperature.

● Gases from the NA area
○ Gases from the NB area
⊕ Gases from the others

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[3] S. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 401 (1960).

[4] J. M. Icken and B. M. Blank, *Anal. Chem.*, **25**, 1741 (1953).

[5] J. Samachson, N. Slovik and A. E. Sobel, ibid., **29**, 1888 (1957).

[6] ASTM, "Standard on Glass and Glass Products," 346 (1950).

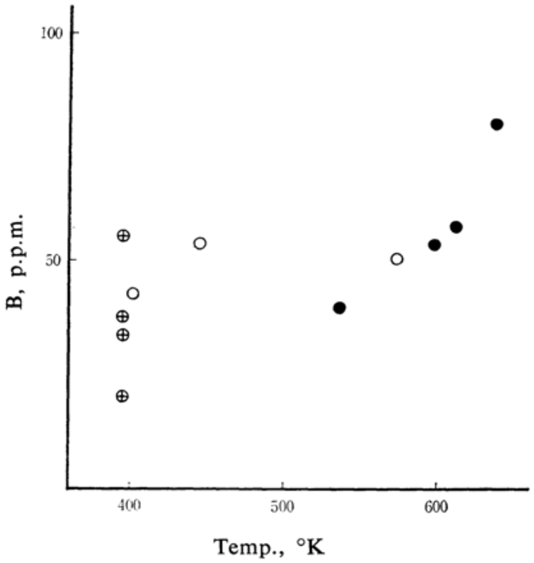

Fig. 3. Relation between boron content and gas temperature.

● Gases from the NA area
○ Gases from the NB area
⊕ Gases from the others

fluorine and boron contents range from 295 to 1350 p.p.m., 2.0 to 26.0 p.p.m. and 20 to 81 p.p.m. respectively. The results are listed in Table I.

The fluorine content in the NB area is higher than that in other areas. The boron content is a little higher in the NA area than that in other areas. Regarding the variation in chlorine, little correlation was found with the gas temperature or with the location of the fumarole. The correlation with the temperature found in the case of selenium content was not observed for some of the other elements over a wider area of Nasudake. The

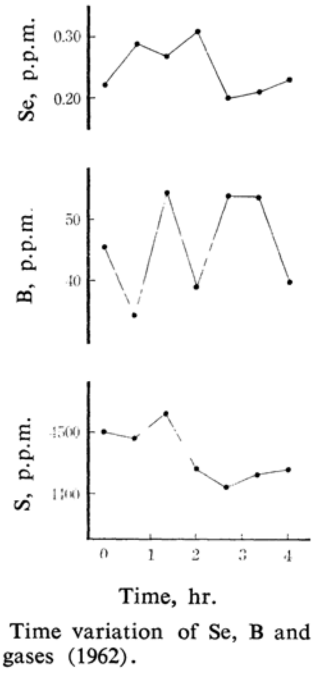

Fig. 4. Time variation of Se, B and S in volcanic gases (1962).

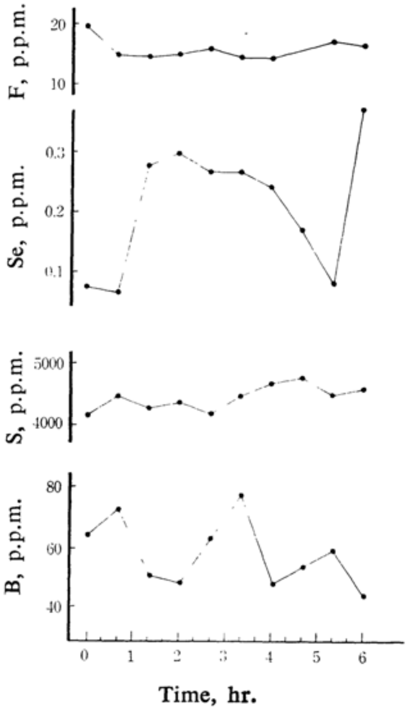

Fig. 5. Time variation of F, Se, S and B in volcanic gases (1963).

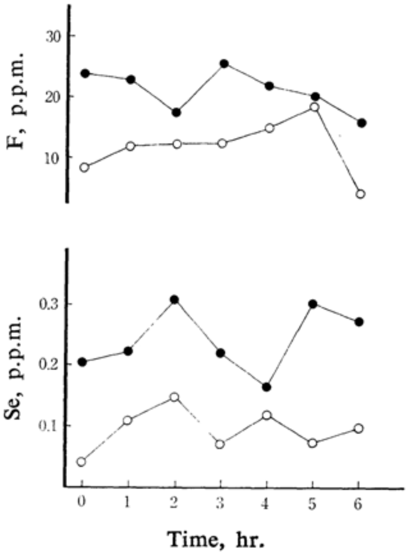

Fig. 6-a. Time variation of Se and F contents in volcanic gases (1964).

○ Collected at the NA area (612°K)
● Collected at the NB area (573°K)

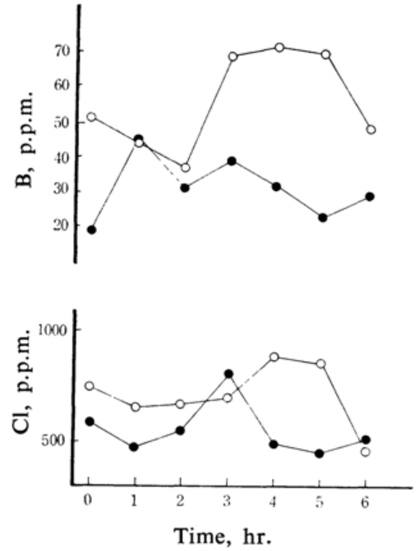

Fig. 6-b. Time variation of Cl and B contents in volcanic gases (1964).

○ Collected at the NA area (612°K)

● Collected at the NB area (573°K)

fluorine and boron contents, however, are likely to show the linear relation with the temperature in the NA area shown in Figs. 2 and 3.

B) The following results of analysis were obtained by the continuous observation of fumarolic gases at the Nasudake volcano in 1962, 1963 and 1964:

Continuous Observation.—The contents of sulfur, selenium, chlorine, fluorine and boron in condensed water samples, which were collected at several fumaroles at time intervals of 40 and 60 min., were determined in order to examine the time variations in the contents of those elements. As is shown in Figs. 4, 5 and 6, the contents of selenium, chlorine, fluorine and boron in volcanic gases show comparatively wide variations, while the sulfur content shows a smaller variation, as in the previous observation at the Nasudake volcano.

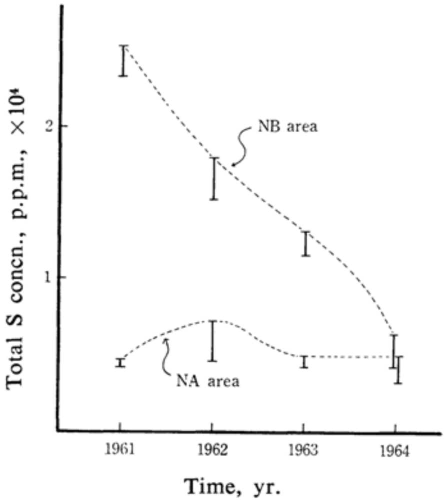

Fig. 7. Year to year variation of total sulfur content in fumarolic gases from Nasudake.

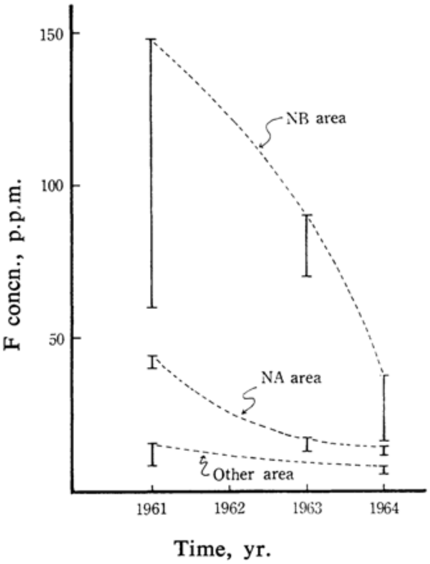

Fig. 8. Year to year variation of fluorine content in fumarolic gases from Nasudake.

Simultaneous and Continuous Observations.—A continuous observation for several hours was done simultaneously at two different fumarole areas (NA and NB) in order to examine the differences in several gaseous components with the location. As is shown in

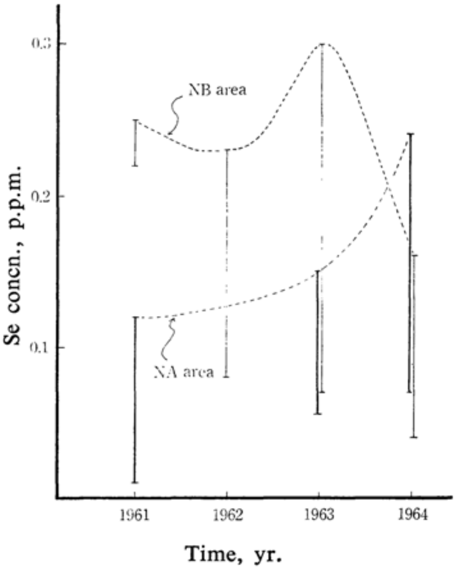

Fig. 9. Year to year variation of the selenium content in fumarolic gases from Nasudake.

Fig. 6, the mode of time variation in the contents of the constituents in gases were considerably different according to the fumarolic area of the volcano.

C) The following results were obtained concerning the year-to-year variations in the contents of sulfur, selenium and fluorine, and in the gas temperature.

As is shown in Figs. 7 and 8, it was found that the contents of sulfur and fluorine remarkably decrease with four years' lapse of time, except that the sulfur in the NA area and the fluorine in the NC and ND areas may be regarded as constant. On the other hand, the selenium content slightly decreased in the NA area and increased in the NB area, as is shown in Fig. 9. In 1964, it was found that the gas temperature in the NB area rose from 195°C to 300°C. It was also noted that the sulfur/selenium ratio in gases decreased slightly in the NA area and increased in the NB area, and that the local variation in the sulfur and fluorine contents in fumarolic gases through the wider areas became smaller during the four years' period.

Discussion

It may be said that, in addition to the study of the behavior of selenium and sulfur, the study of the behavior of other chemical constituents is important in order to elucidate the effusion process of volcanic gases. Both selenium and boron form volatile compounds with halogens, especially with fluorine. However, there is no indication that these compounds play an effective role in controlling the respective concentrations of these elements in volcanic exhalations. It has already been found that the chemical composition of fumarolic gases gives an average value which is fairly reproducible with the repeated collection of samples when a sample of more than about 200 ml. of condensed water is collected. The results of continuous observation, however, show that the chemical composition varies considerably over a short period of time (i.e., several hours) when a small fraction of gases (less than about 50 ml.) is collected as condensed water. It was also found that the patterns of the time variations of several components are different; this finding indicates that there are some causes of the different patterns of the time variation with each components, besides the common effect over the wider area of the Nasudake volcano. Thus, it is likely that the observed time variation is due to a local effect superposed on the general and common change. The following local effects are to be considered as factors producing the time variation in each constituent in fumarolic gases: i) an accidental addition of particulated matters from wall rocks constituting the vents to volcanic gases, ii) the intermittent addition of water, in which some components are dissolved, and iii) a change in the fumarolic activity.

It is, however, difficult to give a right answer to the question of the variation in the content of substances in the volcanic gases, because of the insufficient data obtained so far.

It was reported in a previous paper[2] that the dilution effect of mixing the primary gases with water vapor is important in the content variation of selenium in fumarolic gases. In this paper, "primary gas" means the source gas of the Nasudake volcano, not a magmatic gas. If the same is true for the variations of sulfur, fluorine, chlorine and boron, a relation similar to that in the case of selenium of each component and the mixing ratio with the temperature should be obtained. The total sulfur content, however, increases with the decreasing temperature, as is shown in Fig. 10. Regarding boron, fluorine and chlorine, no intimate relation was found with respect to the temperature. As has been mentioned above, only the boron and fluorine contents have a linear relation with the temperature, and they only in the NA area, not in the NB area. It is also found that sulfur, boron and fluorine contents, except for chlorine, show a tendency to increase in the NB area. In the effusion process, it is not reasonable to expect that these components will be enriched in the lower-temperature gases if the presence of a single source for each

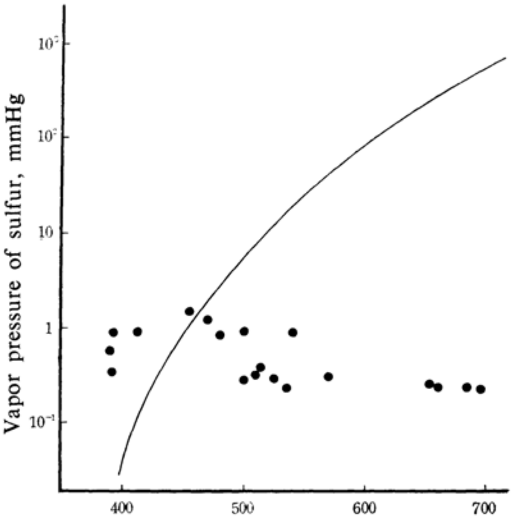

Fig. 10. Relation between vapor pressure ot sulfur and temperature.

● Obtained from observation

TABLE II. YEAR-TO-YEAR VARIATIONS OF TOTAL SULFUR, SELENIUM, FLUORINE AND GAS TEMPERATURE IN VOLCANIC GASES EMITTED AT THE NASUDAKE VOLCANO DURING THE FOUR YEARS' PERIOD (FROM 1961 TO 1964)

Year	Temp., °C		Sulfur, p.p.m.		Selenium, p.p.m.		Fluorine, p.p.m.	
	NA	NB	NA	NB	NA	NB	NA	NB
1961	410	200	4390	25400	0.25	0.12	44	148
			4430	23300	0.22	0.01	40	60
1962	421	—	7150	18100	0.23	0.12	—	—
			4500	15200	0.08	—	—	—
1963	396	266	4800	13100	0.30	0.15	17	90
			4200	11700	0.07	0.05	12	70
1964	360	300	4900	6030	0.15	0.22	14	36
			3050	3180	0.04	0.07	11	26

fumarolic gas is considered. Judging from the distribution and the year-to-year variation of these components, it may be expected that a part of the components is derived from the secondary source in the sub-surface, and also that the high-temperature gas from the NA area is closely related to the primary gas of Nasudake. In other words, it is likely that the source gas in the NB area is almost the same as that in the NA area, and that the sulfur, fluorine and boron in fumarolic gases of the NB area are concentrated in the sub-surface in this area when primary gas is encountered with the secondary source near the sub-surface. In the case of sulfur, the additional sulfur is derived from the distillation of the underlying sulfur deposits, which are the products of the past effusion process.

The results of the observation of year-to-year variation of sulfur (Fig. 7) show that the sulfur content in the NA area may be regarded as constant compared with that in the NB area, and that the lowest sulfur/selenium ratio in the NA area is close to the sulfur/selenium ratio in the primary gas. The fluorine content also shows a year-to-year variation like sulfur, whereas a gradual decrease in the fluorine content in the NA area is observed, as Fig. 8 shows. These results may be taken to indicate that the amount of the underlying source of sulfur and fluorine decreased during the four years' lapse of time. The result for selenium, on the other hand, indicates that the selenium in the NB area increases during the four years, as is shown in Fig. 9, while the temperature of the gases in this area is found to rise from 200 to 300°C as is listed in the second column of Table II. The increase in the selenium content might not be regarded as being due to the secondary source, unlike the sulfur and fluorine, but rather to the increase in the temperature of gases in the NB area. This fact also indicates that the selenium concentration has a strong temperature dependency, which reflect the peculiar nature of selenium and which is followed by a change in the fumarolic activity. As one of the causes of the higher concentration of fluorine in lower-temperature gases, it may be expected that fluorine has accumulated in the sub-surface in the form, like calcium fluoride, through the past effusion process of volcanic gases and that it is derived to the fumarolic gases by a leaching of calcium fluoride with water vapor or volcanic gases according to the change in fumarolic activity, for it is known that the reaction rate of calcium fluoride with water vapor increases with a lowering of the temperature and an increase of the silica content in the gases.[7,8]

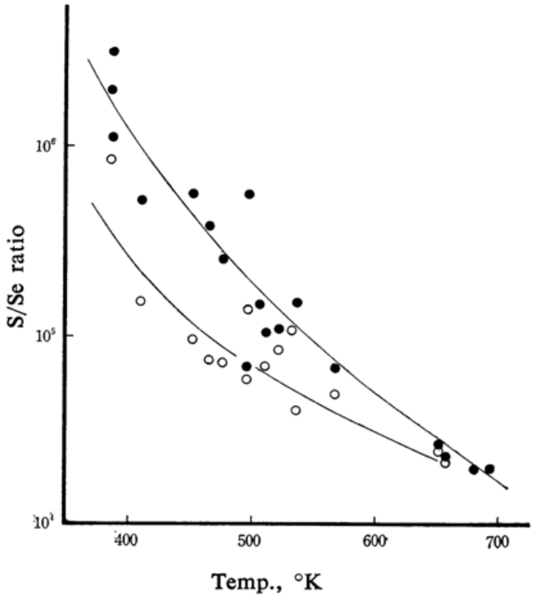

Fig. 11. Relation between S/Se ratio in fumarolic gases and gas temperature.

● Observed
○ Obtained by eliminating excess sulfur

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[7] H. S. Booth and R. M. Bidwell, *J. Am. Chem. Soc.*, **72**, 2570 (1950).

[8] A. J. Ellis and W. A. Mahon, *Geochim. Cosmochim. Acta*, **28**, 1323 (1964).

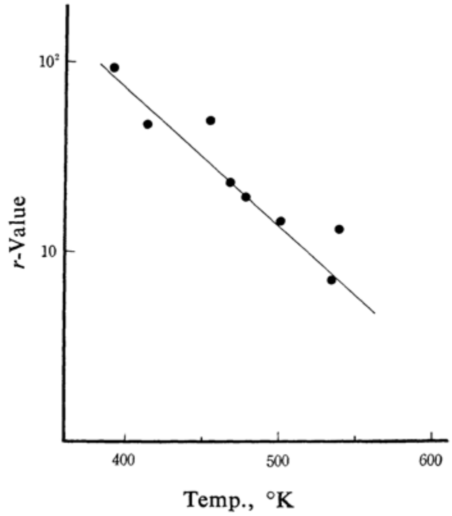

Fig. 12. Relation between gas temperature and S-Se fractionation factors (*r*).

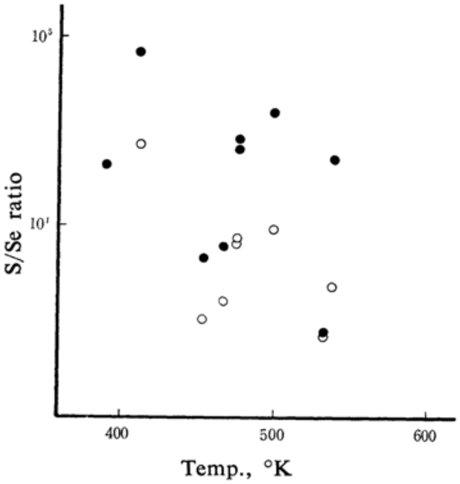

Fig. 13. Relation between S/Se ratio in sulfur deposits and gas temperature.

● Observed
○ Obtained by eliminating excess sulfur

On the basis of the above considerations, the observed sulfur/selenium ratio over the four-year period is corrected by eliminating the effect of the secondarily-added sulfur. The result gives the relation between the sulfur/selenium ratio and the gas temperature, as is shown in Fig. 11; this relation may represent the change in the ratio of sulfur/selenium with the temperature of primary gases. As Fig. 12 shows, it should be noted that a log-linear relation with the temperature is still maintained for the fractionation factors of selenium and sulfur between fumarolic gases and sulfur sublimates, regardless of the content variation of these elements in exhalations and in a dynamical process such as volcanic emission. The sulfur/selenium ratio in sulfur deposits from the primary gases is estimated to be as shown in Fig. 13 by using the above two relations. Accordingly, the proportion of the primary sulfur in the sulfur deposits can be estimated. The gas temperature and the sulfur/selenium ratio in gases co-existing at the time when the separation of sulfur deposits as free sulfur begins from the gaseous phase, can be estimated by means of sulfur/selenium ratio in the sulfur, solidified from the outflowing liquid, and by using the sulfur/selenium ratio in the curves, as is shown in Figs. 11, 12 and 13, which were obtained by the least-square method. Consequently, 1.0—1.7×10^4 were obtained for the sulfur/selenium ratio in the source gases from which the above-mentioned sulfur deposit was formed in the NA and NB areas. These data are consistent with the sulfur/selenium ratio (1.8×10^4) which is estimated from the data for fumarolic gases.1) This supports the supposition that the source gases in both areas are the same and suggests that the sulfur/selenium ratio in the original gases will be between 1—2×10^4. It might even be possible to guess the conditions of the formation of sulfur in the past effusion processes by means of the sulfur/selenium ratios in the deposits available at present.

The year-to-year variations in several components suggest that a certain mechanism through fractional distillation or occlusion process by the primary volcanic gases occurs in the sub-surface. It is thought that sulfur and selenium are derived by fractional distillation. In this case, it may be expected that the sulfur/selenium ratio will increase during the process, the stages of which may be divided into 4 steps as follows: I. The first step of distillation, in which only the sulfur content increases; II. The second step, in which the sulfur/selenium ratio remains nearly constant; III. The third step, in which the sulfur content decreases and the selenium content increases (decrease in the sulfur/selenium ratio); and IV. the last one, in which both sulfur and selenium contents decrease. It was mentioned above that there was the difference in sulfur and selenium content between the NA and NB area, and also that there has been a slight variation in the selenium content during the last four years. It may be said, on the basis of observation and the above considerations, that the process of fractional distillation certainly takes place in the sub-surface and the process in the NB area has proceeded from step II to III, and that in the NA area, from III to IV, during the last four years. In addition, it may also be said that the proportion of the secondary to the primary origin is much higher in the cases of sulfur and fluorine than in that of selenium.

Regarding the differences in the chemical nature of gases among fumarole areas, two interpretations may be given. One is that, as there is originally no secondary source in a certain area (i. e., the NA area), the entry of several components through distillation or occlusion process has not occured in the course of the effusion process. The other is that, after the secondary process has been carried out over a broader area at the same time, an apparent difference in the evolution stages among fumarole areas is brought about at the present time on account of the difference in each fumarolic activity, which corresponds to the temperature conditions of each fumarolic gas. Our consideration and our field observation of several gaseous constituents show that the latter interpretation is more probable.

In connection with the behavior of the several constituents mentioned above, the movement of volcanic gases and the possible process occurring in the sub-surface are illustrated schematically in Fig. 14, which is based on the results obtained thus far.

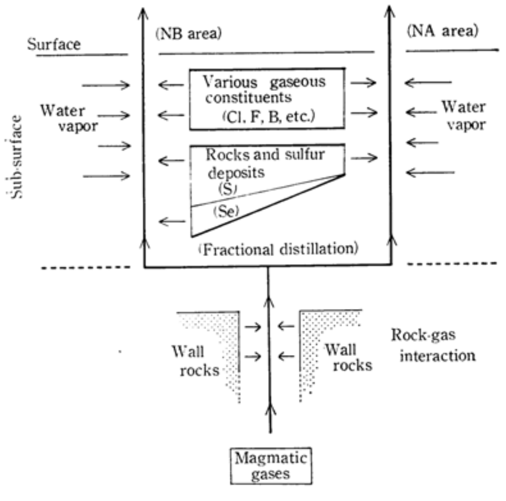

Fig. 14. Schematic diagram of behavior of volcanic gases at the sub-surface of volcano.

Conclusion

Unlike the case of the Showashinzan volcano,[9] the gaseous components at the Nasudake volcano show no linear relation with the gas temperature with the exception of selenium.

It is to be expected that, at an old solfataric volcano like Nasudake, certain constituents will have been accumulated in the sub-surface during the past effusion processes. It may also be possible that the constituents thus accumulated are leached by the volcanic gases with the change in volcanic activity, and that the observed variations in sulfur, chlorine, fluorine and boron with temperature and time are brought about through such effects. On the other hand, the variation in the selenium content as a result of local effects is much smaller than those of other components; it can be regarded as characteristic in the primary gases. In the cases of a volcano with secondary effects of a considerable extent on the content variations, it may be concluded that the behavior of selenium and the fractionation of selenium and sulfur are applicable to the study of the behavior of volcanic gases according to the stages of the effusion processes and the changes in the chemical nature of volcanic gases in the sub-surface.

The variation in the content of some gaseous constituents with time is an interesting problem to study before we can study in detail the behavior of fumarolic gases near the surface in relation to the change in volcanic activity, the accidental addition of fine particles from wall rocks, and the intermittent addition of water vapor. The problem, however, is still unsolved because not enough data are available for us to make a detailed discussion. Thus, it is necessary to obtain more data with sampling method device suitable to this purpose, one which would make possible the successive collection of fumarolic gases.

As has been mentioned in a previous paper,[2] it may be concluded, from the results of geochemical work on selenium and sulfur, that the entry and transfer of selenium and sulfur into the primary volcanic gases are controlled by certain dynamic factors, such as the rate of vaporization, the rate of gas flow, the ratio of the amounts of gases and rocks, and the reaction time in the rock-gas interactions. It is likely that these processes contribute to the common and general change in the contents of several constituents in volcanic gases. On the other hand, it has also been concluded, from the present study, that the several constituents accumulated in the sub-surface are occluded by primary gases after volcanic gases have branched into smaller vents on the way to the surface. It is likely that the local change in the contents of several constituents is caused by these processes. It may be expected that the above two processes will superpose on each other in the volcanic processes and that, consequently, the distributions of several components at the outlet of fumaroles are as has now been observed.

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[9] Y. Mizutani, *J. Earth Sci., Nagoya Univ.*, **10**, 135 (1962).

Summary

Continuous observations of fumarolic gases have been made in order to study the chemical nature of volcanic gases. A very wide variation in the content of some gaseous constituents has been observed in continuous observation over several hours, and over four years.

Judging from the field observation and the mode of the content variation of several components with the time and the temperature, it is likely that process of the alteration of volcanic gases occurring in the sub-surface plays an important role in producing the difference in the chemical nature of fumarolic gases among the fumarole areas. In addition, the year-to-year variation of the contents of some constituents might provide an indication of the stage of some processes, such as distillation and occlusion, which have occurred in the sub-surface.

It has been found that components like selenium are useful in an examination of the behavior of volcanic gases at an old solfataric volcano like Nasudake, because it is expected that most of the constituents except for selenium have been accumulated in the sub-surface by the past effusion processes and that the accumulated constituents have been occluded in the primary volcanic gases with the change in volcanic activity.

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