A Geochemical Study of Selenium in Volcanic Exhalation and Sulfur Deposits

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Several investigations have previously been made concerning the abundance and behavior of selenium in various terrestrial materials. Recently, Anderson[1)] summarized the geochemical work on this chemical element. Many studies reveal that selenium is usually enriched in pneumatolytic and high temperatured hydrothermal sulfide rather than in sulfide ores of low temperatured hydrothermal or sedimentary origin.[2,3)] It has also been reported that most of the selenium in sedimentary sulfide or rock is not accumulated in pyrite but in independent minerals such as ferroselite.[4)] As to the native sulfur, it is known that selenium is usually concentrated in sulfur deposits of volcanic origin. The variation of selenium content in Kilauean sulfur deposits was regarded as being due to a partial sublimation of selenium during deposition.[1,5)] It is also said that the low selenium content in the sulfur which is produced in Mexico, West Indies, and Iceland may represent a selenium-poor, residual fraction of sulfur.

It was found by the continuous observation of the chemical constituents of the condensed water from an exhalation collected at a fumarole of the Showashinzan volcano on Hokkaido Island, Japan (42°30′N, 140°53′E), that the behavior or sulfur in volcanic gases was different from that of the other constituents.[6)] According to Matsuo and Mizutani, the sulfur content showed less variation with time than do those of such other constituents as halogen and boron.

This study was undertaken to investigate the content and distribution of selenium in volcanic matter from fumarolic gases and associated sulfur sublimates at the Nasudake (36°07′N, 139°57′E) and Kuju (33°07′N, 131° 13′E) volcanoes, Japan.

Sampling Sites and Samples

Nasudake volcano is situated at 36°07′N 139°57′E on Honshu, Japan. The activity of the volcano is moderate at present, but a large amount of volcanic gases is emitted from fumaroles near the top of the dome. As is shown in Fig. 1, these fumaroles are divided into three groups, NA, NB, and NC and ND, according to their locations, which are roughly in the order of decreasing gas temperature, ranging from 420 to 120°C.*

Kuju volcano is situated at 33°07′N 131°13′E in the north-eastern part of Kyushu Island, Japan. The active, high-temperatured fumaroles are gathered in the area KA near the top of volcano. These fumaroles also are divided into three groups according to their locations

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[1)] M. S. Anderson, H. W. Lakin, K. C. Beeson, F. F. Smith and E. Thacker, Agriculture Handbook No. 200, U. S. Department of Agriculture, 3 (1961).

[2)] A. B. Edwards and G. C. Calos, *Australian Inst. Min. Metallurgy Proc.*, No. 172, 31 (1954).

[3)] R. G. Coleman and M. Delevaux, *Economic Geology*, **54**, 499 (1957).

[4)] E. Z. Bur'yanova, *Geochemistry* (English translation), No. 7, 669 (1961).

[5)] H. G. Byers, K. T. Williams and H. W. Lakin, *Ind. & Eng. Chem.*, **28**, 821 (1936).

[6)] S. Matsuo and Y. Mizutani, *Bull. Volcanol. Soc. Japan, 2nd Ser.*, **3**, 119 (1959).

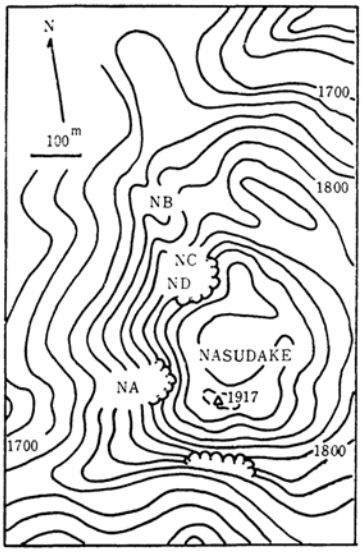

Fig. 1. Distribution of fumaroles at Nasudake.

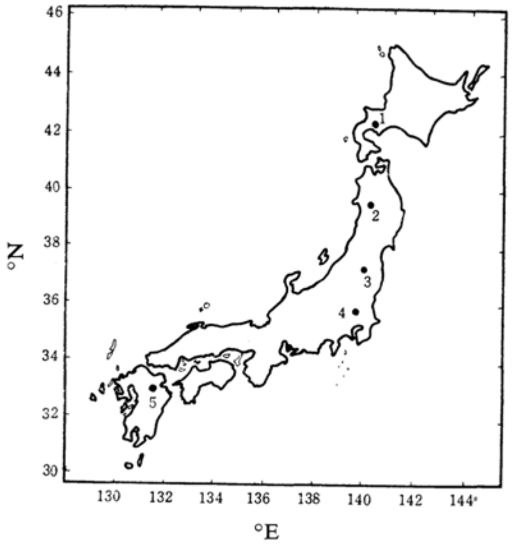

Fig. 2. Location of volcanoes where samples were collected.

1 Showashinzan
2 Tamagawa
3 Issaikyo
4 Nasudake
5 Kuju

KA, KB and KC, of which the temperature ranges from about 120 to 300°C.*

Sulfur is economically mined in both volcanoes. It is, however, usually difficult to collect gas sample directly from the natural outlet of a fumarole. Because, in order to collect a sulfur deposit efficiently, the gases emitted from the fumaroles are introduced into tunnels, as is shown schematically in Fig. 3. Therefore, most of samples were collected from leaks and from the outlets of tunnels.

Two kinds of sulfur deposits were collected, one obtained at leaks and the other, at the outlets of tunnels. The former (deposit I) is a sublimation deposit from gases, while the latter (deposit II) is the solidified sulfur from the out-flow of the liquid.

At Nasudake, three samples of condensed water and sulfur deposits from the NB area were collected from three different leaks of the same tunnel. At Kuju, two kinds of sulfur deposits, as has been mentioned above, were collected from the outlet of each tunnel.

The Method of Sampling and Analysis

Sampling Method.—Fumarolic gases are introduced into an ice-cooled water trap as is shown in Fig. 4. Water and other condensable substances are trapped in a cold trap containing sodium hydroxide. Selenium, sulfur and chlorine in condensed water are analyzed in laboratory.

Analytical Method. — 1) *Sulfur* is determined by the gravimetric method as barium sulfate after oxidation.

2) *Chlorine* is determined by the colorimetric method with mercuric thiocyanate and iron alum.7)

3) *Selenium* is determined by the colorimetric

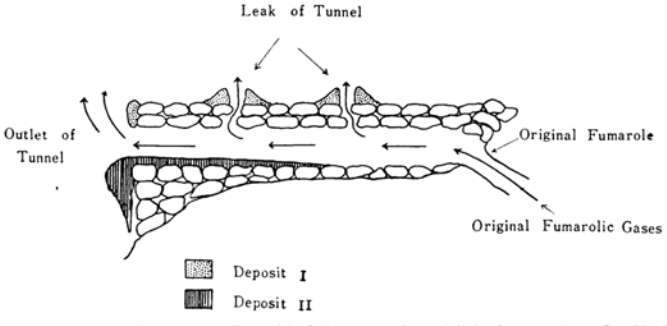

Fig. 3. Schematic diagram of artificial tunnel, which is made of piled stones.

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* There are fumaroles at Nasudake and Kuju, the gas temperature of which may be 500°C or higher. It is, however, diffcult to get a gas sample directly from those fumaroles.

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

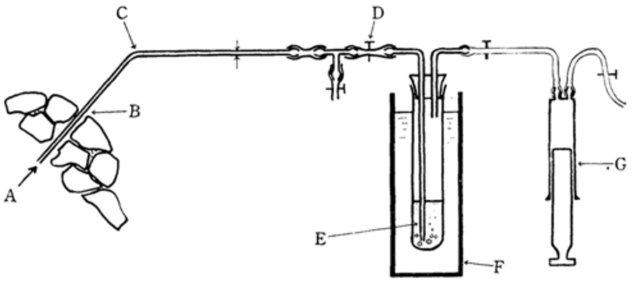

Fig. 4. Apparatus for collection of volcanic gases.

A Volcanic gases B Outlet of fumarole C Quartz tubing D Stop cock
E Condensed water F Cold trap G Injector

method using 3,3′-diaminobenzidine.[8,9] As 3,3′-diaminobenzidine reacts only with quadrivalent selenium, it is necessary to convert all the selenium to a quadrivalent state. Selenium of various ionic forms is first oxidized with hydrogen peroxide to a sexivalent state, and then reduced, by using hydrochloric acid, to a quadrivalent state. Generally the oxidation proceeds smoothly, while the reduction is strongly affected by the concentration of hydrogen chloride and by the time of heating. As is shown in Figs. 5 and 6, a time for heating of longer than 90 min. and a concentration higher than 4 M for hydrochloric acid are required for complete reduction. The concentration of hydrochloric acid must be adjusted during the heating, because selenium forms volatile compound such as Se_2Cl_2 and $SeO_2 \cdot HCl$ when the concentration of acid rises. Sulfate ion interferes with the coloration when its concentration exceeds 16 g.-SO_4/l. in the final solution (ca. 50 ml.) for solvent extraction.[10] In addition, the S/Se ratio (by weight) should be kept below 5.6×10^4 in the final solution. The excess amount of sulfate is removed as barium sulfate after reducing the selenate to selenite in order to avoid the coprecipitation of selenium.

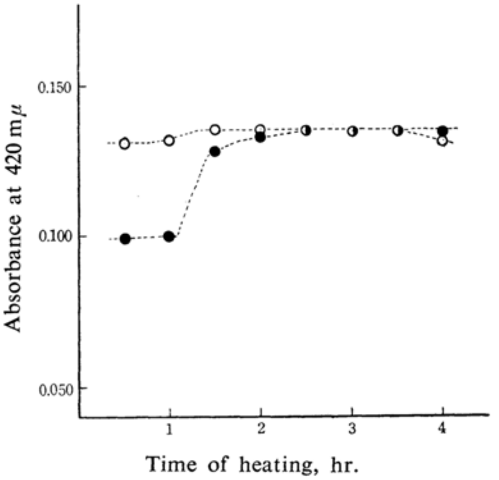

Fig. 5. Time of heating and reduction of selenium(VI) to selenium(IV).
●: 4 M HCl solution ○: 8 M HCl solution

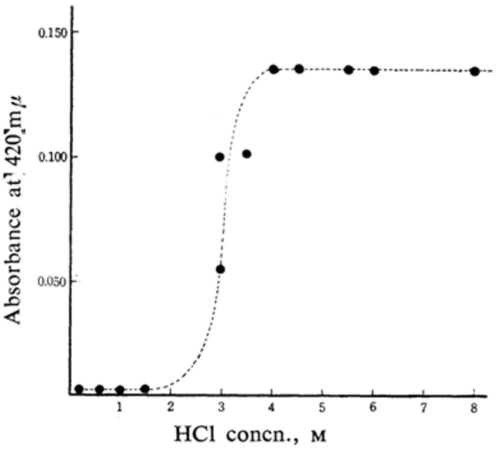

Fig. 6. HCl concentration and reduction of selenium(VI) to selenium(IV).

The Procedure of Sample Preparation for the Solvent Extraction of Selenium.—Native sulfur is pulverized and ground about finer than 100 mesh. One tenth to 0.3 g. of ground sulfur and 2 g. of sodium hydroxide are put into a test tube and heated on a water bath. Hydrogen peroxide is added to the tube until free sulfur disappears. An aliquot of this solution or condensed water is then transferred into a 100 or 200 ml. beaker with a few grams of sodium hydroxide. A small amount of hydrogen peroxide (30%) is added to the solution to assure complete oxidation. The solution is heated on a water bath to approximate dryness. After the residue is neutralized with a (1 : 1) hydrochloric acid solution, the volume of the solution is doubled with concentrated hydrochloric acid. The solution is then heated on a water bath for 180 min., after which the solution is neutralized again with dilute ammonium hydroxide (1 : 1). To remove the excess sulfur, a 20% barium chloride solution is added to the solution after it has been heated with hydrochloric acid. The barium sulfate precipitate is removed by centrifuge, and the filtrate is neutralized with ammonium hydroxide. After the solution is evaporated to a volume less than about 50 ml.

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[8] J. Hoste and J. Gillis, *Anal. Chim. Acta*, **12**, 158 (1955).

[9] K. L. Cheng, *Anal. Chem.*, **28**, 1738 (1956).

[10] T. Danzuka and K. Ueno, ibid., **30**, 1370 (1958).

on a water bath, the selenium content is determined by the colorimetric method using 3,3′-diaminobenzidine.

TABLE I. SELENIUM, SULFUR AND CHLORINE CONTENTS, AND S/Se RATIO IN THE CONDENSED WATER FROM EXHALATION OF NASUDAKE FUMAROLES

Locality No.	Temp. °C	S p.p.m.	Se p.p.m.	S/Se 10^4	Cl p.p.m.
NA-2d	421	4390	0.23	1.9	
NA-2c	410	6270	0.25	1.8	554
NA-3a	386	4730	0.25	1.9	
NA-3b	380.5	4790	0.22	2.2	
NA-3c	291	6300	0.18	3.5	
NA-2a	261	4430	0.22	2.0	8340
NA-3d	252	5690	0.08	7.1	
NA-2e	241	7150	0.13	5.5	
NA-2f	236	6800	0.08	8.5	
NA-3e	226	5350	0.15	3.6	
NB-2	195	23300	0.12	19	960
NB-1	181	25400	0.09	28	1000
NB-3	118	14700	0.01	150	1300
NC-1	120	5590	0.01	560	390
ND-1	118	9490	0.01	950	5000

TABLE II. SELENIUM CONTENT AND S/Se RATIO IN SULFUR DEPOSITS OF NASUDAKE AND KUJU

Locality No.	Temp. °C	Se p.p.m.	S/Se 10^3	Type*
(Nasudake)				
NA-2a	261	368	2.72	I
NA-3	120	291	3.34	II
NB-2	195	124	8.05	I
NB-1	181	175	5.98	I
NB-3	118	49	21.6	I
NB-4	119	404	2.54	II
NC-1	120	20	50	II
ND-1	118	20	50	II
(Kuju)				
KA-a	297.5	213 741	3.20 1.35	I II
KA-b	118.5	15.5 22.3	64.5 44.8	I II
KA-c	228.5	201 369	4.97 2.71	I II
KA-d	278.5	335 555	2.99 1.80	I II
KA-d′	285.0	578	1.73	II
KA-f	126.5	77.8 490	12.9 2.09	I II
KB-1	205.0	36.9 98.1	27.1 10.1	I II
KB-2	128.0	14.8 15.2	67.6 65.9	I II
KC-1	133.0	17.4 49.7	57.6 20.1	I II
KC-2	155.0	18.3 89.8	54.6 11.1	I II

* Type I and II represent respectively deposit I and II which are described in page 1201.

Results

In Tables I and II, the selenium, sulfur, and chlorine contents in condensed water and two types of sulfur are given. The amount of selenium and sulfur in the tables represent the total amounts, regardless of their chemical forms.

A) The following results were obtained for condensed water and the sulfur deposits of the Nasudake volcano:

Condensed Water.—The sulfur content ranges from 4390 to 25400 p.p.m. In the NB area it was several times higher than in other areas. The NB area is thus characterized by a higher total concentration of sulfur. The chlorine content and selenium content range from 390 to 8340 p.p.m. and 0.01 to 0.35 p.p.m. respectively. The variation in the selenium content is greater than those of sulfur and chlorine.

Sulfur Deposits. — The selenium content in deposits I and II ranges from 49 to 368 p.p.m. and 20 to 404 p.p.m. respectively.

TABLE III. SELENIUM IN VOLCANIC SULFUR

Location	Se p.p.m.	Reference
Colorado, U.S.A.	8350	Byers11)
Kilauea, Hawaii	1400 2200	Byers et al.5)
	1600 1600 900 4	Lakin et al.1)
Mexico	0.6 0.5 10 0	Williams et al.12)
West Indies	5	Byers et al.13)
Alaska	1200	Zies14)
Iceland	18.9	Friend et al.15)
Showashinzan, Japan (42°31′N, 140°53′E)	129 92.9	Suzuoki
Tamagawa, Japan (39°56′N, 140°44′E)	89.9 45.3	
Issaikyo, Japan (37°45′N, 140°15′E)	214	
Nasudake, Japan (36°07′N, 131°13′E)	20 404	
Kuju, Japan (33°07′N, 131°13′E)	15.5 741	

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11) H. G. Byers, *U. S. Department of Agriculture Tech. Bull.*, **482**, 47 (1935).

12) K. T. Williams, H. G. Byers and H. W. Lakin, ibid., **702**, 59 (1940).

13) H. G. Byers, J. T. Miller, K. T. Williams and H. W. Lakin, ibid., **601**, 74 (1938).

14) E. G. Zies, *Natl, Geog. Soc. Contrib. Papers, Katomai Ser.*, **1**, No. 4, 79 (1929).

15) J. N. Friend and J. P. Allchin, *Mineralogist Mag.*, **26**, 9 (1941).

B) The following results were obtained regarding the sulfur deposits of the Kuju volcano:

Sulfur Deposits. — The selenium content in deposits I annd II ranges from 14.8 to 355 p.p.m. and 15.2 to 741 p.p.m. respectively.

Selenium is richer in deposit II than in deposit I. The selenium content in the sulfur deposits of Kuju is a little higher than that of Nasudake. It may be said that volcanic gases and sulfur from the two volcanoes contain various amounts of seleninum according to the location of the fumaroles. A comparison of the selenium contents in various volcanic sulfurs is given in Table III. It should be noted that the selenium content in sulfur from Mt. Kilauea, Hawaii, is about ten times higher than that of several volcanoes, the selenium contents of which have been determined by the present author.

C) The Continuous Observation of Fumarolic Gas at Nasudake.—A continuous observation over a short period was made in order to study the time variation of the sulfur and selenium contents in volcanic gases from a certain fumarole at the Nasudake volcano. The sulfur and selenium contents of seven samples which were collected from a fumarole (NA-3a) at intervals of 40 min. were determined (cf. Table IV). As Table IV shows, the time variation of the sulfur content in condensed water is small, whereas a considerable variation, ranging from 0.20 to 0.31 p.p.m., was found in the selenium content.

TABLE IV. THE TIME VARIATION OF SELENIUM AND SULFUR CONTENT IN THE CONDENSED WATER FROM NA-3a FUMAROLE OF NASUDAKE (30 AUGUST 1962)

Sample	Time hr. min.	S p.p.m.	Se p.p.m.	S/Se $\times 10^4$
1	9 40	4500	0.22	2.04
2	10 20	4490	0.29	1.55
3	11 00	4530	0.27	1.68
4	11 40	4440	0.31	1.43
5	12 20	4410	0.20	2.21
6	13 00	4430	0.21	2.11
7	13 40	4440	0.23	1.93

Discussion

As it is known that selenium forms certain volatile compounds with chlorine, the relationship between selenium and chlorine was studied. The results showed that there is no correlation between the two elements in condensed water. This suggests that selenium is not exclusively transferred by fumarolic gases in the form of a compound with chlorine. It was also found that selenium and sulfur in condensed water have no correlation with each other.

The relation between the temperature of gases at the outlet of the fumarole and the selenium content in condensed water and sulfur deposits was also considered. As is shown in Fig. 7, the higher the temperature, the higher the selenium concentration. A sharp correlation between the S/Se ratio (by weight) and the outlet temperature was also observed, as may be seen in Figs. 8, 9 and 10. The

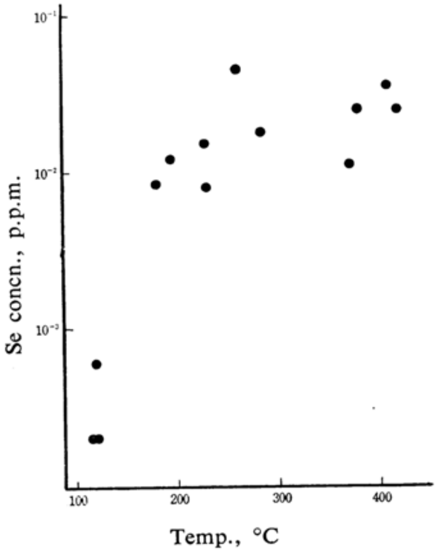

Fig. 7. Relationship between gas temperature and selenium content in condensed water.

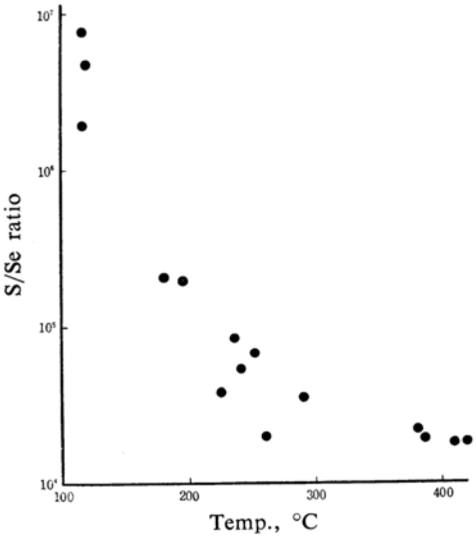

Fig. 8. Relationship between S/Se ratio and gas temperature in condensed water from Nasudake.

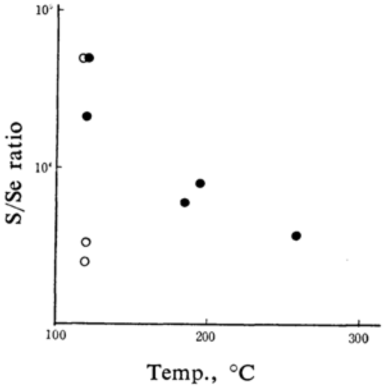

Fig. 9. Relationship between S/Se ratio and gas temperature in sulfur deposit from Nasudake.

●: Deposit-I ○: Deposit-II

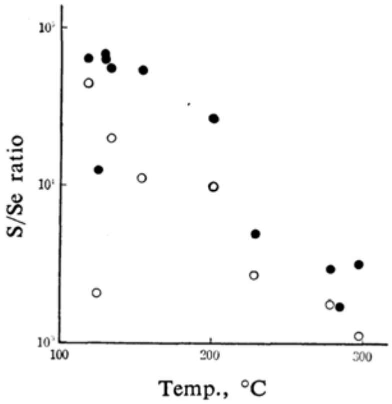

Fig. 10. Relationship between S/Se ratio and gas temperature in sulfur deposit from Kuju.

●: Deposit-I ○: Deposit-II

S/Se ratio in both condensed water and sulfur deposits has an inverse correlation with the gas temperature. This fact implies that the fractionation between selenium and surfur depends on the temperature of the fumarolic gases. The values of the $r=\{(\mathrm{S/Se})$ condensed water/ $(\mathrm{S/Se})$ volcanic sulfur$\}$ ratio for condensed water and sulfur deposits from the same outlet of fumaroles are listed in Table V. These values which extend from 7.5 to an extremely high number, may be said to reflect the degree of the fractionation of selenium and sulfur between volcanic gases and sulfur deposits. In addition, this factor is controlled by other factors related to the mechanism of the transportation of chemical elements in volcanic gases. The relationship between the ratio r and the outlet temperature is given in Fig. 11, which shows the temperature dependency of the ratio r.

TABLE V. VALUE OF (S/Se) CONDENSED WATER/ (S/Se) VOLCANIC SULFUR RATIO (r)

Locality, No.	Temp., °C	r
Na-2a	261	7.3
NB-2	195	23.6
NB-1	181	50.0
NB-3	118	93.0

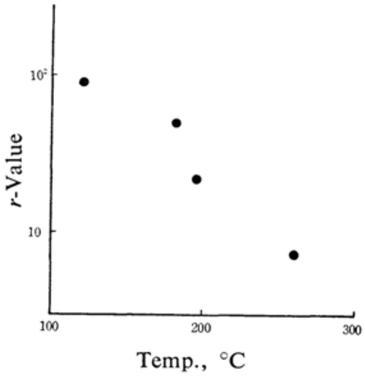

Fig. 11. Relationship between gas temperature and (S/Se) condensed water/(S/Se) volcanic sufur (=r).

The same correlation of the selenium content with the temperature was also observed in deposit I, as is shown in Figs. 9 and 10. On contrary, some of deposit II is high in selenium content and low in S/Se ratio, unlike deposit I. The variation of the S/Se ratio in deposit II independently of the outlet temperature may be explained as follows. From field observation, it is known that deposit II is formed through the movement of separated sulfur in a liquid form toward the outlet of tunnel and that then the sulfur is deposited at the outlet of the tunnel. Judging from the outlet temperature of the tunnel, most of the sulfur and selenium would be completely trapped inside the tunnel during the effusion processes. From the above considerations, the lack of relationship between the temperature and the selenium content (and the S/Se ratio) in deposit II might be due to the difference in the mode of deposition rather than to that in temperature between the two types of deposits. In addition, the S/Se ratio in deposit II might depend mainly on the temperature at the original outlet on the fumaroles. Accordingly, the S/Se ratio in deposit II will be taken to serve to estimate the physical and chemical conditions at original outlet such as the S/Se ratio, the temperature, and the structure of the tunnel. From the observed data, it was found that the same separation process due to temperature gradient as in the tunnel occurs also inside the natural conduit of volcanic gases, and that the source gas at some fumarole areas (NC and ND) has an essentially lower selenium concentration than that in other areas.

The NA area is regarded as the most active area in Nasudake, as has been mentioned before. If fumarolic gages in this field have the same origin, it may be said that the S/Se ratio in the original volcanic gases of Nasudake is close to that found in NA fumarolic gases of the highest temperature (1.8×10^4).

Conclusion

On the basis of our observations, it may be concluded that the temperature at the fumarole outlet is one of the main factors controlling selenium concentration in volcanic gases and sulfur deposits. In the case of sulfur deposits collected at the outlet of tunnels, deposit II, the temperature of the source gases and the structure of the tunnel seem to play an important role in governing the selenium content. The variation in selenium content in the volcanic sulfur suggests the fractional distillation of selenium and sulfur through either natural or artificial conduits of volcanic exhalation. On the basis of findings that the S/Se ratio in sulfur deposits and gases increases with the decrease in the temperature at the sampling sites, it may also be concluded that the S/Se ratio gives an indication of the condition which governs the effussion process of volcanic gases.

There remain, however, a number of problems to be solved concerning selenium in volcanic matter, such as the mechanism of the fractionation of selenium and sulfur, and the reason for the variation in selenium content with respect to each fumarole and its general area.

Summary

Regarding selenium in volcanic materials collected at fumaroles of the Nasudake (36°07′N, 139°57′E) and the Kuju (33°07′N, 131°13′E) volcanoes, Japan, the following results have been obtained.

1) The selenium content in condensed water has no relation to that of sulfur and chlorine. The selenium content in certain sulfur deposits is strongly affected by the mode of occurrence, such as sublimation and solidification, as well as by the outlet temperature of the fumarole. The ratio of selenium to sulfur in both condensed water and sulfur deposit is related with gas temperature at the outlet of fumarole. The higher the gas temperature, the lower the degree of fractionation between selenium and sulfur.

2) The S/Se ratio in the original volcanic gases at Nasudake is close to 1.8×10^4, found in fumarolic gases with the highest temperature. The S/Se ratio in sulfur deposit is at least one-seventh that in condensed water.

3) Continuous observation over a short period (3 hr.) showed that the selenium content in condensed water varies considerably with time, while the sulfur content remains constant.

This study was made under the guidance of Professor Shinya Oana, Institute of Earth Sciences, Faculty of Science, Nagoya University, to whom the present author wishes to express his hearty thanks. Thanks are also due to Dr. Yoshihiko Mizutani and Mr. Tsutomu Sugiura for their help in the collection of samples.

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