A Geochemical Study of Selenium in Volcanic Exhalation and Sulfur Deposits. II.* On the Behavior of Selenium and Sulfur in Volcanic Exhalation and Sulfur Deposits

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(Received April 1, 1965)

It has been reported by the present author that selenium is contained in the volcanic exhalations and sulfur deposits collected at the Nasudake and Kuju volcanoes. It has also been observed that the variations in the selenium content and in the sulfur/selenium ratio are closely related to the change in the temperature of fumarolic gases.[1] The main purpose of the previous study was to examine the content and the distribution of selenium in the matters emitted from volcanoes in Japan. From the results of the previous study, it is anticipated that the estimation of the conditions in natural vents from their inside to the outlets of the fumaroles may be possible by means of studying the change in the sulfur/selenium ratio with the temperature and with the concentration of selenium.

It has already been found, in the previous studies of the chemical equilibrium in volcanic gases, that some of the chemical constituents in volcanic gases are in equilibrium with respect to several chemical reactions associated with the volcanic activity.[2,3] It is also possible that a phase change such as vaporization plays an important role in the process of the occurrence of selenium and sulfur in volcanic gases because of the greater volatility of these substances. In the case of sulfur, as is well known, the hydrogen sulfide and sulfur dioxide which are in equilibrium with free sulfur are important in the transfer of sulfur in volcanic gases. As to the selenium, however, the chemical form of this element in volcanic gases is unknown. Therefore, it is necessary to estimate the chemical form of selenium by considering the chemical equilibria in the reactions with which selenium is possibly concerned. The effect of vapor pressure on the transfer of selenium into volcanic gases should also be studied.

Mizutani[4] found a linear relationship between the concentration of gaseous components and the temperature at the Showashinzan volcano; for this he gave the explanation that the low-temperature fumarolic gases are formed by the mixing of the original gases with water vapor. In this study, the author intends to examine whether or not similar processes are controlling the concentration of selenium in volcanic exhalations emitting from the Nasudake volcano.

From the above points of view, a thermodynamic consideration will be made in order to find the factors controlling the concentration of selenium and the sulfur/selenium ratio in volcanic matters. The cause and the mechanism producing the distribution of selenium and sulfur in the effusion process in the Nasudake volcano will also be discussed.

Theoretical Considerations

The Relation between the Temperature and the Equilibrium Constants.—By combining the chemical components whose presence may be expected in volcanic gases, we find four possible reactions for selenium:

$$3/2Se_2+2H_2O=2H_2Se+SeO_2 \qquad (1)$$

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[*] Part I of this series: This Bulletin, 37, 1200 (1964).

[1] T. Suzuoki, ibid., 37, 1200 (1964).

[2] K. B. Krauskoph, *Econ. Geol.*, 52, 786 (1957).

[3] S. Matsuo, *Bull. Volcanologique*, 24, 59 (1962).

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

$$1/2Se_2+2SO_3=SeO_2+2SO_2 \quad (2)$$

$$Se_2+2H_2=2H_2Se \quad (3)$$

$$3H_2+SeO_2=H_2Se+2H_2O \quad (4)$$

The equilibrium constants of the above reactions were calculated; the thermodynamical data were refferred chiefly to Kubaschewski et al.,⁵⁾ Latimer,⁶⁾ Palmer et al.,⁷⁾ and Altschuller.⁸⁾ The equations expressing the relation between the equilibrium constants and the temperature in these reactions are as follows:

$$\log K_1=\frac{1.25\times10^4}{T}-88.16-0.3314\log T$$
$$-0.2470\times10^{-3}T+0.5279\times10^{-7}T^2 \quad (5)$$
$$K_1=\frac{(SeO_2)\ (H_2Se)^2}{(Se_2)^{3/2}(H_2O)}$$

$$\log K_2=\frac{1.125\times10^4}{T}-81.45+7.432\log T$$
$$-10.36\times10^{-3}T+2.396\times10^{-7}T^2$$
$$-0.0038\times10^{-9}T^3 \quad (6)$$
$$K_2=\frac{(SeO_2)(SO_2)^2}{(Se_2)^{1/2}(SO_3)^3}$$

$$\log K_3=\frac{2.023\times10^3}{T}-22.94+1.220\log T$$
$$-0.7526\times10^{-3}T+1.105\times10^{-7}T^2 \quad (7)$$
$$K_3=\frac{(H_2Se)^2}{(Se_2)(H_2)^2}$$

$$\log K_4=\frac{8.855\times10^3}{T}-64.11-1.264\log T$$
$$+0.8798\times10^{-3}T-1.158\times10^{-7}T^2 \quad (8)$$
$$K_4=\frac{(H_2Se)(H_2O)^2}{(H_2)^3(SeO_2)}$$

The relations between the equilibrium constants and the temperature are illustrated in Fig. 1, in which the K-T relations for sulfur are also shown for the sake of comparison. The reactions for sulfur are:

$$3/2S_2+2H_2O=2H_2S+SO_2 \quad (9)$$

and:

$$3H_2+SO_2=2H_2O+H_2S \quad (10)$$

where the K-T relations are as follows:

$$\log K_9=-\frac{4.26\times10^4}{T^2}+\frac{0.2031\times10^4}{T}$$
$$+0.68-1.37\log T+4.77\times10^{-4}T \quad (11)$$

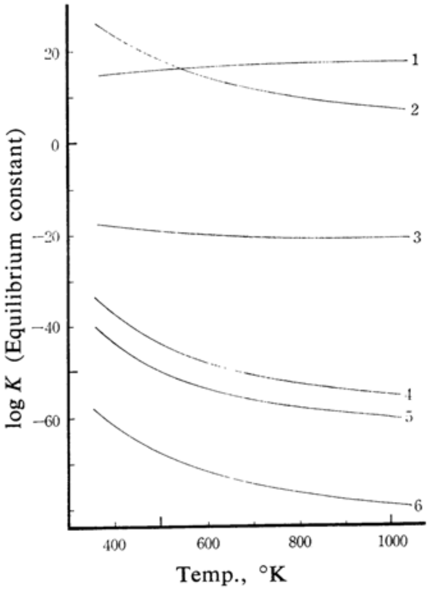

Fig. 1. Relation between temperature and equilibrium constant.

1, $\frac{[H_2Se]^2}{[Se_2][H_2]^2}$ 2, $\frac{[H_2S][H_2O]^2}{[H_2]^3[SO_2]}$

3, $\frac{[H_2S]^2[SO_2]}{[S_2]^{3/2}[H_2O]^2}$ 4, $\frac{[SeO_2][SO_2]}{[Se_2]^{1/2}[SO_3]^2}$

5, $\frac{[H_2Se][H_2O]^2}{[H_2]^3[SeO_2]}$ 6, $\frac{[H_2Se]^2[SeO_2]}{[Se]^{3/2}[H_2O]}$

$$K_9=\frac{(S_2)^{3/2}(H_2O)^2}{(H_2S)^2(SO_2)}$$

and

$$\log K_{10}=\frac{1.041\times10^4}{T}+5.45-2.82\log T$$
$$-5.24\times10^{-4}T+3.28\times10^{-7}T^2$$
$$-4.9\times10^{-11}T^3 \quad (12)$$
$$K_{10}=\frac{(H_2O)^2(H_2S)}{(H_2)^3(SO_2)}$$

The Relation between the Vapor Pressure of Selenium and the Temperature.—As to the data of the vapor pressure of selenium and sulfur, papers by Kubaschewski et al.,⁵⁾ West et al.,⁹⁾ and others¹⁰⁾ may be referred to. The empirical formulae for expressing the relation between the temperature and the vapor pressure of selenium and sulfur are given by the above authors as follows: For selenium:

$$\log P_{Se}=8.0886-4989.5/T \quad (13)$$

and for sulfur:

$(598°K>T>393°K)$

$$\log P_S=14.7-6.2238\times10^{-3}T-5405.1/T \quad (14)$$

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5) O. Kubaschewski and E. Evans, "Metallurgical Thermochemistry," Pergamon Press, London (1956).

6) W. M. Latimer, "The Oxidation States of the Elements and their Potential in Aqueous Solution," Prentice Hall, New York (1952).

7) K. J. Palmer and N. Elliott, *J. Am. Chem. Soc.*, **60**, 1309 (1938).

8) A. P. Altschuller, *J. Phys. Chem.*, **61**, 509 (1957).

9) W. A. West and A. W. Menzies, ibid., **33**, 1880 (1929).

10) "International Critical Tables of Numerical Data," McGraw-Hill, London, **3**, 201 (1933).

$(T > 598°\text{K})$

$$\log P_{\text{S}} = 7.4329 - 3268.2/T \tag{14'}$$

where P and T are, respectively, the vapor pressure in mmHg and the absolute temperature, °K.

From the above equations, the ratios of the vapor pressure of sulfur to that of selenium are given by the following equations as functions of the temperature:

$(598°\text{K} > T > 393°\text{K})$

$$\text{los } P_{\text{S}}/P_{\text{Se}} = 6.6114 - 6.2238 \times 10^{-3}T - 415.6/T \tag{15}$$

$(T > 598°\text{K})$

$$\log P_{\text{S}}/P_{\text{Se}} = -0.6557 + 1.7213/T \tag{15'}$$

Discussion

The Chemical Form of Selenium and Sulfur in Volcanic Gases.—As is shown in Fig. 1 the calculated equilibrium constants in reactions 1, 2, 3 and 4 at temperature between 400 and 1000°K range from 10^{-60} to 10^{-56}, from 10^{-56} to 10^{-34}, from 10^{14} to 10^{18}, and from 10^{-60} to 10^{-40} respectively. The chemical equilibrium constants in reactions 1, 2 and 4 show that a gaseous form of selenium is most stable in the temperature range quoted above. On the contrary, the higher value of the equilibrium constants in reaction 3 shows that hydrogen selenide is more stable than gaseous selenium. However, it is known that hydrogen selenide tends to be unstable in the presence of much water. The volcanic gases usually contain an excess amount of water vapor (more than 99% of the total). Therefore, the hydrogen selenide would not remain stable in the volcanic gases. Thus, the most probable chemical form of selenium in volcanic gases near the outlet of a fumarole is gaseous, perhaps such elementary forms as Se_2 and Se_6. The value of the Se_2/Se_6 ratio depends on the equilibrium constants in the dissociation reaction, $\text{Se}_6 = 3\text{Se}_2$, which is given by the following equation as a function of the temperature: $\log K = -13000/T + 18.40$, where $K = (\text{Se}_2)^3/(\text{Se}_6)$.11) On the other hand, as is well known, most sulfur exists in the forms of sulfur dioxide and hydrogen sulfide in volcanic gases.

It should be noted that in volcanic gases the stable form of selenium is different from that of sulfur despite the similarity of these elements.

The Vapor Pressure of Selenium and Sulfur in Their Respective Chemical Forms.—It may be said that an abundance of selenium and sulfur in volcanic gases depends on the volatility of these chemical elements. Therefore, the effect of vapor pressure on the behavior of selenium and sulfur in volcanic gases must be examined.

The ratio of the vapor pressures of free sulfur and selenium is expressed by Eqs. 15 and 15′ as a function of the temperature. The relation between the temperature and the sulfur/selenium ratio is illustrated in Fig. 3 as a

TABLE I. THE S-Se ABUNDANCE RATIO FROM OBSERVATIONS AND DATA OF VAPOR PRESSURE

	S/Se ratio	
Temp., °K	Observed	Estimated
694	2.0×10^4	66.7
683	2.0	73.1
659	2.4	90.4
653.5	2.7	95.1
569	6.7	278
539	14	306
534	11	324
525	11	357
514	10	402
509	15	424
500	55	458
499	6.8	471
479	25	579
468	38	647
454	57	742
413	53	1100
393	310	1300
391	120	1310
391	200	1310

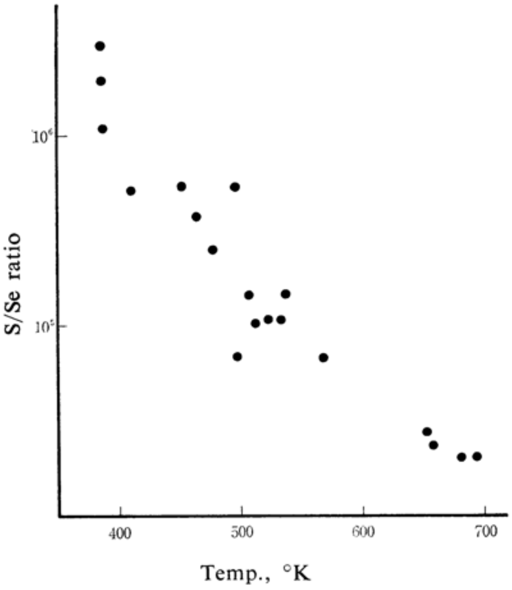

Fig. 2. Relation between S/Se ratio in fumarolic gases and gas temperature.

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11) O. V. Al'tshuller, G. N. Zwinadadze and D. M. Chizhikow, *Zhur. Neorg. Khim.*, 2, 1581 (1957).

straight line extending from about 10^2 to 10^3. As is shown in Table I and Fig. 2, however, the abundance ratio of sulfur to selenium in volcanic gases is much higher than the sulfur/selenium ratio shown in Fig. 3. This discrepancy is doubtless due to the presence of much sulfur dioxide and hydrogen sulfide. Therefore, the amount of S_2 vapor was calculated by using Eq. 11, putting into it the observed values of hydrogen sulfide and sulfur dioxide; the ratio of the elementary sulfur to selenium was thus obtained. It was found that the ratio of S_2 sulfur to selenium is nearly equal to or little less than the theoretical value of the sulfur/selenium ratio, as is shown in Fig. 3.

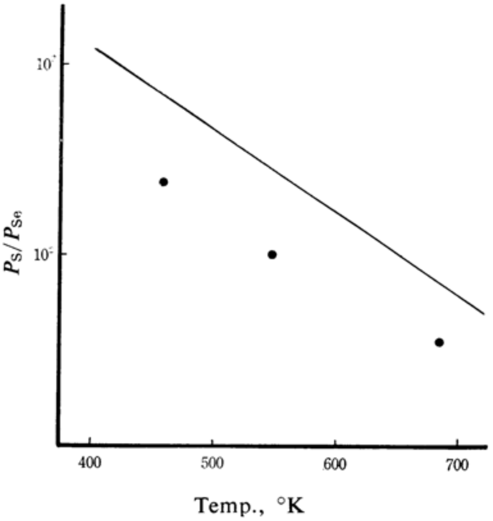

Fig. 3. Comparison of vapor pressure ratio $(P_S/P_{Se})_{saturation}$ with the ratio calculated from observations.
——: Vapor pres. of S/vapor pres. of Se
●: Calculated from observations

The above results suggest that the main part of the sulfur is present and is transferred in form other than that of free gaseous sulfur. Thus, it may be concluded that the behavior of selenium and sulfur in the transfer process is determined by the differences in their chemical forms and in the vapor pressure of each substance.

The Absolute Concentration and the Distribution of Sulfur and Selenium.—Regarding the vapor pressure of selenium and sulfur, the observed vapor pressure in volcanic gases have been compared with the saturated vapor pressure obtained by Eqs. 13, 14 and 14′ respectively. As Table II and Fig. 4 show, both selenium and sulfur in volcanic gases are present in quantities very much less than the saturation point. For instance, the degrees of saturation at 800°K for selenium and sulfur are as small as 10^{-6} and 10^{-4} respectively.

TABLE II. THE DEGREE OF SATURATION FOR SELENIUM AND SULFUR IN VOLCANIC GASES (SATURATION=1)

	Ratio to saturation	
Temp., °K	Sulfur	Selenium
694	0.00045	0.0000015
683	0.00056	0.0000021
659	0.00084	0.0000033
653.5	0.00095	0.0000033
569	0.0084	0.000035
539	0.045	0.000093
534	0.014	0.000041
525	0.023	0.000075
514	0.040	0.00016
509	0.041	0.00012
500	0.16	0.00013
499	0.051	0.00035
479	0.32	0.00074
468	0.76	0.0013
454	1.6	0.0021
413	8.3	0.0017
393	29	0.012
391	13	0.014
391	21	0.014

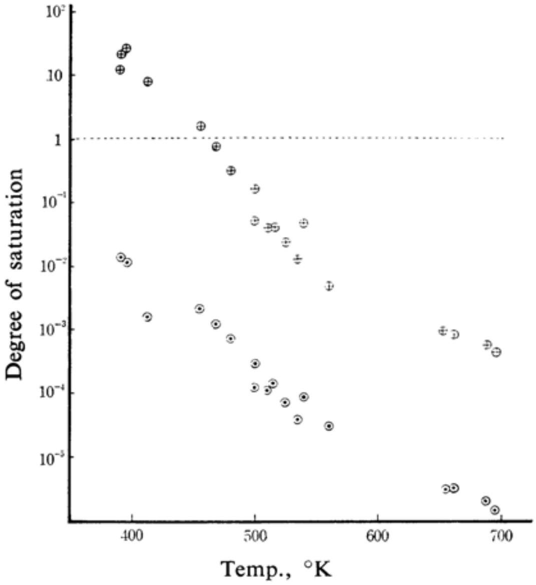

Fig. 4. The degree of saturation for selenium and sulfur in volcanic gases.
⊕: Sulfur
⊙: Selenium

Regarding the scantiness of both chemical elements in volcanic gases, two interpretations are possible. One is based on the static process, and the other, on the dynamic process. In the former, it is supposed that the vapors of selenium and sulfur in primary gases are once in the equilibrium condition with their solid or liquid phases, that these are quenched in situ, and that the gases are then isolated from the source and transported. The unsaturation may result from the addition of water vapor to the primary gas mixtures. In the second interpretation, it is supposed that the gaseous selenium and sulfur have never been in equilibrium with other phases of the same elements because of the dynamic process of transfer. If the unsaturation results, as in the first interpretation, from only the dilution with water vapor with a temperature of 373°K, the mixing ratio of the latter to the primary gases will be about 10^5. The addition of such a large amount of water vapor will decrease the temperature very much below the observed value. Therefore, the interpretation based on the static process is inadequate to explain the selenium and sulfur deficiency. It may, therefore, be said that the dynamic process is more probable than the static one in bringing about a deficiency of these elements at a high temperature.

The Dilution of the Primary Gases with the Water Vapor near the Surface.—As has been mentioned above, the gas emitted from each fumarole is considered to derive from a common source. In addition, if selenium and sulfur enter into the gases through, for instance, distillation taking place at certain zones in natural vents, and if there is no change in the composition of volcanic gases near the surface, the partial pressure of each component may not vary despite the temperature lowering, provided that the concentration is far below the saturation point. It was found from observation that the concentrations of selenium and sulfur show, respectively, a gradual decrease and a gradual increase with the decrease in the temperature, as is shown in Figs. 5 and 6. The decrease in selenium may be the result of dilution with recyclic water vapor near the surface. Here, the fumarolic gas with the highest temperature is assumed to represent the primary gas.

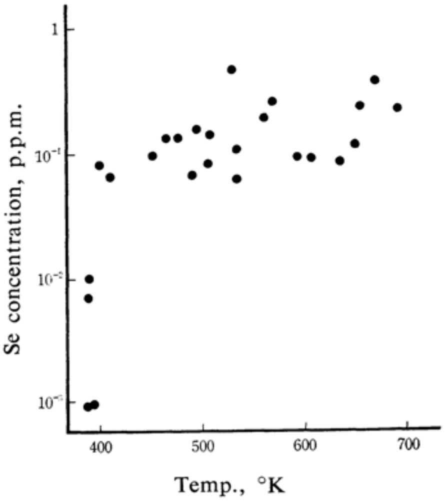

Fig. 5. Relation between temperature and selenium content in fumarolic gases from Nasudake.

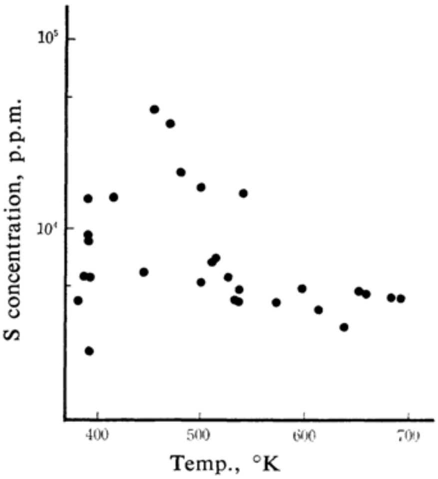

Fig. 6. Relation between temperature and sulfur content in fumarolic gases from Nasudake.

When the primary gases with a temperature of 873°K is diluted with a different amount of water vapor with a temperature of 373°K, the change in the fraction of the primary gases or in the concentration of selenium will be linear with respect to the temperature of the mixture as may be seen in Fig. 7. The calculation is made on the basis of the thermal balance in mixing the respective gases with different temperatures, as is represented in the following equation:

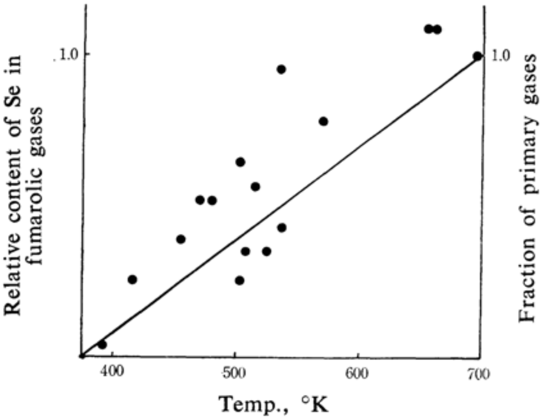

Fig. 7. Relation of selenium concentration and fraction of primary gases to gas temperature.

$$F(T)=\frac{\int_{T}^{873} Cp_{H_2O}\mathrm{d}T}{\int_{373}^{T} Cp_{H_2O}\mathrm{d}T+\int_{T}^{873} Cp_{H_2O}\mathrm{d}T}$$

where $F(T)$ and Cp_{H_2O} are a fraction of the primary gas in the observed mixture at the temperature T°K and the heat capacity of water respectively. The selenium contents are also plotted in Fig. 7 in a relative scale. As Fig. 7 shows, the agreement between the calculated and the observed changes in the fraction of selenium suggests that the decrease in the selenium concentration with the decrease in the temperature is mainly due to dilution by water vapor supplied near the earth surface (in the respective vents). As for sulfur, the increase with the decrease in the temperature may result from the addition of sulfur near the surface. This problem will be discussed in the following paper.

The addition or removal of the components in the primary gas may take place in the process of mixing it with water vapor. It may be possible to obtain useful information on the mixing problem by examining the variation in the concentrations of some constituents with the temperature. It may be said that selenium is one of the most promising constituents or indicators for this purpose.

Mizutani explained the origin of low-temperature fumarolic gases of the showashinzan volcano on the basis of the linear relation between the concentration of some gaseous components and the temperature.[4)] The linear relation as found at the Showashinzan volcano was not observed at the Nasudake volcano for such components as chlorine, fluorine and boron. It is, therefore, necessary to determine the one component among others, in the primary and secondary gases which is applicable to the study of the mixing processes.

Conclusion

Regarding the presence of selenium and sulfur in volcanic exhalations and sulfur deposits, it may be concluded that the different behavior of selenium and of sulfur is mainly due to the differences in the vapor pressures and in the chemical forms of these elements in volcanic gases. From thermodynamic considerations, it may also be concluded that the most probable chemical form of selenium in volcanic gases is free selenium.

It may be said that the amount of selenium and sulfur in fumarolic gases is controlled not only by the above factors but also by other factors, judging from the fact that these elements are seldom saturated in volcanic gases, especially at high temperature. It is thought that the undersaturation may occur in the course of the transfer of both elements through fractional distillation, which is controlled by the rates of flow and vaporization. Such dynamic processes may be important as controlling factors in the introduction of selenium and sulfur into volcanic gases in natural vents.

Unlike the Showashinzan volcano, the Nasudake volcano exhibits no linear relation between the temperature and the concentration of most of the gaseous components, except for selenium. The dilution process through mixing with water vapor of a ground-water origin seems to be the cause of the apparent variation in selenium content with the temperature at or near the surface.

Generally, the variation in the concentrations of the chemical components in volcanic gases gives valuable information for a study of the alteration of volcanic exhalation through the mixing of the other components and so on. However, in such a study, careful consideration is required in selecting components which are as practical indicators of the above processes.

It is found in the study of the Nasudake volcano that the selenium and sulfur in volcanic gases are useful indicators for the study of the mixing processes in the course of the alteration of volcanic gases. In this connection, the selenium content and the variation in its concentration in volcanic gases may be regarded as an interesting problem in the study of volcanoes in other areas.

Summary

With regard to the temperature dependency of the sulfur/selenium ratio in volcanic gases, the factors which control the behavior of selenium and sulfur have been considered from the viewpoints of the chemical equilibrium, the vapor pressure and the thermal balance.

It has been found, from the examination of the equilibrium constants, that, unlike the case with sulfur, the most probable form of selenium in volcanic gases is free selenium. The effect of the vapor pressuse is significant in controlling the transfer of selenium and sulfur into volcanic gases. The results of the calculation of the thermal balance show that the observed wide variation in selenium concentration is due to the addition of water vapor.

On the other hand, it has been found that selenium and sulfur are extremely unsaturated at higher temperatures. This lack of saturation is caused by the dynamical processes of the introduction of these gases into volcanic gases.

The author wishes to thank Professor Yasuo Miyake and Dr. Sadao Matsuo, Department of chemistry, Faculty of Science, Tokyo Kyoiku University, who gave him valuable advice on many points throughout this study.

Thanks are also due to Dr. Yoshihiko Mizutani, the Institute of Earth Sciences, Faculty of Science, Nagoya University, and Mr. Eitaro Wada and Mr. Osamu Matsubaya, Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, for their help in the collection of samples.

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