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A Geochemical Study of the Fumarolic Bismuthinite from Showashinzan

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In an active fumarole on the dome of the Showashinzan volcano, Hokkaido, Japan, a crystalline sublimate was found. It is lead grey, with a metallic luster, and forms loose clusters of aciculer crystals. X-Ray diffraction, spectrographic and micro-chemical analyses have been made of the sublimate. The results indicate that the sublimate consists of bismuthinite Bi_2S_3, with traces of lead, zinc, aluminum, copper, iron and titanium. A colorimetric determination has also been made of the bismuth in the fumarolic gases from Showashinzan. The variation in the bismuth content of the gases with the gas temperature suggests that, when the temperature falls to about 500°C, bismuth compounds lose their volatility in the gases and are precipitated to form a sublimate. On the assumption that the chemical equilibrium is established in the gases, the stability of bismuth minerals and a possible reaction for the formation of bismuthinite in the gases have been discussed, and it has been suggested that the bismuthinite is formed by the $2BiCl_3 + 3H_2S = Bi_2S_3 + 6HCl$ reaction in the gases.

Showashinzan, Hokkaido, Japan, is an active volcano formed during the period from 1943 to 1945. It is composed of a platform-shaped mountain with a dome on it. The dome consists of new lava, hyperthene dacite. Fumarolic activity still persists on and around the dome, with the emission of large amounts of high-temperature volcanic gases.

Recently, Mizutani[1] has made chemical and mineralogical investigations of volcanic sublimates from Showashinzan. His results show that many primary volcanic sublimates, such as crystobalite, hematite, thenardite, glaserite, sal ammoniac, and sassolite, are deposited in the fumaroles of

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[1] Y. Mizutani, *J. Earth Sciences, Nagoya Univ.*, **10**, 149 (1962).

Showashinzan.

In the present research, a volcanic sublimate from fumarole B-1b (Mizutani's notation2)) of Showashinzan was subjected to X-ray diffraction, spectrographic and micro-chemical analyses in order to clarify its mineralogical composition. An attempt was also made to explain the formation of the volcanic sublimate through a gas phase reaction.

Occurrence

The sublimate was found at fumarole B-1b (Fig. 1), about 10 cm. inside the opening of the fumarole. It had been developed on the inner wall of the fissure vent and had formed loose clusters of acicular crystals. The crystals are lead-grey

TABLE I. FUMAROLIC GASES FROM FUMAROLE B-1b

Date		1960	1961
Temp.	°C	260	227
H_2O,	l./1000 l.	986.2	991.7
CO_2,	l./1000 l.	12.2	7.06
H_2,	l./1000 l.	0.67	0.37
N_2,	l./1000 l.	0.70	0.64
HCl,	l./1000 l.	0.13	0.16
HF,	l./1000 l.	0.033	0.025
H_2S,	ml./1000 l.	100	74
SO_2,	ml./1000 l.	3	5
Ar,	ml./1000 l.	7.0	2.0
CH_4,	ml./1000 l.	16	11.2
CO,	ml./1000 l.	0.33	0.08
O_2,	ml./1000 l.	0.000	0.000

TABLE II. POWDER X-RAY DATA

Sample		Bismuthinite*1		Bismuthinite*2		Galenobismutite*3		Cannizzarite*4	
d, Å	I.	*d*, Å	I.	*d*, Å	I.	*d*, Å	I.	*d*, Å	I.
5.665	20	5.56	20	5.55	1.0	—	—	7.38	1
5.048	20	5.04	19	4.95	1.0	4.55	10	5.13	2
3.97	35	3.97	38	3.92	2.0	3.93	5	—	—
—	—	3.75	20	—	—	—	—	3.82	10
3.575	100	3.56	94	—	—	3.65	30	3.49	3
3.543	35	3.53	60	3.50	9.0	3.45	100	3.38	3
3.258	5	3.256	18	3.22	1.0	3.36	5	3.29	1
3.120	35	3.118	100	3.08	6.0	3.27	5	3.01	6
2.813	15	2.811	63	2.79	4.0	3.03	40	2.87	5
2.722	7	2.716	34	2.69	1.0	2.76	30	2.76	2
2.647	7	2.641	24	2.61	1.0	2.65	20	2.68	6
2.522	50	2.52	35	—	—	—	—	2.54	2
2.502	7	2.499	13	2.495	3.0	—	—	—	—
2.461	5	2.456	15	2.425	1.0	—	—	—	—
2.306	7	2.304	24	2.28	1.0	2.46	40	2.39	0.5
2.259	10	2.256	36	2.34	3.0	2.39	20	2.22	5
2.120	5	2.129	9	—	—	2.24	10	—	—
—	—	2.118	15	—	—	2.20	10	—	—
2.098	15	2.096	11	—	—	—	—	—	—
2.077	6	2.074	10	2.06	0.5	2.05	40	2.03	5
1.986	7	1.99	33	1.98	1.0	2.01	5	—	—
1.955	15	1.953	55	—	—	—	—	—	—
1.933	15	1.935	20	1.935	5.0	1.961	50	—	—
1.921	15	1.919	20	—	—	—	—	1.910	4
1.886	20	1.884	14	1.870	1.0	1.881	20	—	—
1.858	8	1.854	17	1.840	1.0	1.848	5	—	—
—	—	1.779	13	—	—	1.784	5	1.791	3
—	—	1.765	5	—	—	1.762	30	—	—
1.739	8	1.737	7	—	—	—	—	—	—
—	—	1.734	35	1.725	5.0	1.734	10	1.734	1
1.702	7	1.702	10	1.690	1.0	1.704	5	—	—

*1 ASTM X-ray powder card (6-0333)
*2 ibid. (11-138)
*3 Ref. 4
*4 Ref. 5

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2) Y. Mizutani, *J. Earth Sciences, Nagoya Univ.*, **10**, 135 (1962).

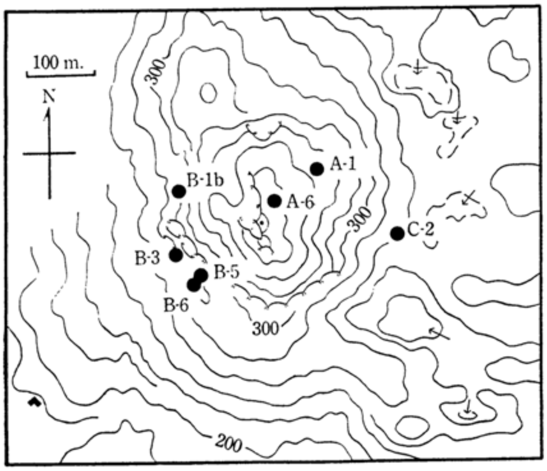

Fig. 1. Location of sampling.

with a metallic luster. Individual crystals reach a length of about 5 mm., but they are extremely thin. About 40 mg. of the sublimate was collected in 1960, and about 10 mg. in 1961, from the same place in the fumarole.

The vent of fumarole B-1b was 1—5 cm. wide and several meters long, running upwards on the slope of the dome. The surface of the inner wall of the fumarole was partly coated with a very thin film of a brown material, possibly hematite, but the inside of the wall rock, brecciated new lava, showed little evidence of having been attacked by fumarolic gases. From the fissure vent, gases with a temperature higher than 200°C were emitted at a rather low pressure, perhaps close to 1 atm. The temperature and chemical composition of the gases, determined at the same time as the sublimate was collected, are given in Table I.

Experimental

Identification.—A carefully-selected sample of the sublimate was subjected to qualitative spectrographic analysis and micro-chemical tests in order to get a provisional idea of its composition. The results showed that the sublimate consisted of bismuth sulfide, with trace amounts of lead, zinc, aluminum, copper, iron and titanium.

TABLE III. BISMUTH CONTENT OF FUMAROLIC GASES FROM SHOWASHINZAN

Sample*	Temp., °C	Bi, mg./kg. H_2O
A-1 (1960)	772	0.024
A-6 (1960)	695	0.026
C-2 (1960)	605	0.015
C-2 (1961)	560	0.046
B-5 (1960)	446	0.003
B-3 (1961)	375	0.003
B-6 (1960)	347	0.002
B-lb(1960)	260	0.002
B-1b (1961)	227	0.005
B-6 (1961)	211	0.003

*Sampling sites are shown in Fig. 1.

An X-ray powder pattern was prepared with a Norelco X-ray diffractometer using nickel-filtered copper radiation. The results obtained are given in Table II, together with the X-ray powder data of some bismuth minerals reported by ASTM,3) Harcourt4) and Graham et al.5) The X-ray powder pattern of the sample is very similar to that of bismuthinite given by ASTM. Although they are identical in *d*-value, however, they are different in the intensities of some lines. The X-ray pattern of the bismuthinite given by Harcourt is also similar to that of the sample, though they differ slightly in the intensities and *d*-values of some lines. On the other hand, the X-ray patterns of the galenobismutite and cannizzarite given by ASTM and Graham et al. respectively are distinctly different from that of the sample.

The present identification is incomplete in the absence of quantitative chemical data, but it is thought to be sufficiently significant to prove that the sublimate examined consists of bismuthinite (Bi_2S_3).

The Determination of the Bismuth Content of Fumarolic Gases.—In order to discuss the formation of fumarolic bismuthinite throuhg a gas phase reaction, the bismuth content of the gases of Showashinzan was determined as follows.

Fumarolic gases were drawn into a cold trap containing a small amount of concentrated nitric acid by using a syringe through a silica tube inserted into the fumarole. By this process, the water vapor in the gases was condensed in the trap and bismuth compounds in the gases were completely dissolved in the condensed water. The nitric acid prevents the precipitation of bismuth as sulfide. The condensed water was then subjected to the following chemical analysis.

Two hundred and fifty milliliters of the condensed water was placed in a dish and concentrated to about 20 ml. Bismuth was separated from the solution as bismuth dithizonate in chloroform by Sandell's dithizone extraction method.6) After the chloroform solution of bismuth dithizonate had been shaken with sulfuric acid (1 : 300), the aqueous phase was transferred to a small beaker and boiled gently until the odor of chloroform disappeared. Then the solution was subjected to Goto's colorimetric method.7) The results obtained are given in Table III, together with the observed temperatures of the gases.

Discussion

The Behavior of the Bismuth in the Fumarolic Gases.—As may be seen from Table III, there is a notable decrease in the bismuth content at a temperature of about 500°C. This implies that, when the temperature falls to about 500°C, bismuth compounds lose their volatility in the gases

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3) "X-Ray Powder Data File," American Society for Testing Materials.

4) G. A. Harcourt, *Am. Mineral*, **27**, 63 (1942).

5) A. R. Graham, R. M. Thompson and L. G. Berry, ibid., **38**, 536 (1953).

6) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers Inc., New York (1950).

7) H. Goto and S. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **74**, 142 (1953).

and are precipitated to form volcanic sublimate. Therefore, it is suggested that the occurrence of the bismuth mineral may be common in low-temperature fumaroles of Showashinzan. The difficulty of finding fumarolic bismuth minerals may be attributable to the fact that the rate of the accumulation of the minerals in a fumarole is very small, as may be expected from the observed bismuth contents of the gases.

Stable Bismuth Minerals under Fumarolic Conditions.—Three minerals are considered: the metal itself, the sulfide and the oxide. Stability relationships among these minerals may be expressed as a function of the temperature and the chemical compositon of the gaseous phase in equilibrium with the minerals.

The reactions considered are:

$$2/3\,\mathrm{Bi} + \mathrm{H_2O} = 1/3\,\mathrm{Bi_2O_3} + \mathrm{H_2} \qquad (1)$$

and

$$1/3\,\mathrm{Bi_2S_3} + \mathrm{H_2} = 2/3\,\mathrm{Bi} + \mathrm{H_2S} \qquad (2)$$

The values of the free energy change, ΔG, for these reactions were obtained from the thermodynamic data given by Kubaschewski and Evans[8] and by Rossini et al.,[9] and the equilibrium constant of the reaction, K, was calculated from the $\Delta G = -\boldsymbol{R}T\ln K$ relation, where $\boldsymbol{R}$ is the gas-law constant and T is the absolute temperature of the system. The equations of K thus obtained are: for Reaction 1,

($T<271$°C)

$$\log K_1 = -8.961 + 2.323\,\log T - 2.98\times10^{-4}\,T - 2320T^{-1} \qquad (3)$$

($T>271$°C)

$$\log K_1 = -7.950 + 1.650\,\log T + 0.963\times10^{-4}T - 1973T^{-1} \qquad (4)$$

$$K_1 = \frac{P_{\mathrm{H_2}}}{P_{\mathrm{H_2O}}}$$

and for Reaction 2:

($T<271$°C)

$$\log K = 8.36 - 2.02\,\log T - 1790\,T^{-1} \qquad (5)$$

($T>271$°C)

$$\log K_2 = 7.35 - 1.35\,\log T - 0.394\times10^{-3}T - 2120\,T^{-1} \qquad (6)$$

$$K_2 = \frac{P_{\mathrm{H_2S}}}{P_{\mathrm{H_2}}}$$

The stability relationships obtained from these equations are shown in Figs. 2 and 3. The observed values of $P_{\mathrm{H_2}}/P_{\mathrm{H_2O}}$ and $P_{\mathrm{H_2S}}/P_{\mathrm{H_2}}$ in fumarolic gases of Showashinzan[2,10] are also plotted in Figs. 2 and 3 respectively.

It may be seen from these figures that the equilibrium ratio, $P_{\mathrm{H_2}}/P_{\mathrm{H_2O}}$, is far below the ratios observed in the fumarolic gases, so the metal is more stable in the gases than is the oxide (Fig. 2), and similarly, that the sulfide is stable at temperatures below about 230°C with repect to the

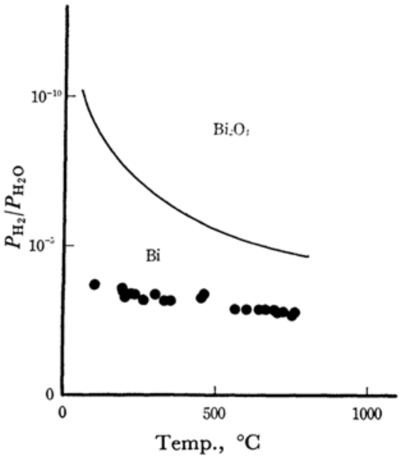

Fig. 2. Stability relationship between $\mathrm{Bi_2O_3}$ and Bi as a function of temperature and $P_{\mathrm{H_2}}/P_{\mathrm{H_2O}}$ ratio of the gas phase in equilibrium with the minerals.
—— : $\mathrm{Bi_2O_3}$-Bi boundary
● : observed $P_{\mathrm{H_2}}/P_{\mathrm{H_2O}}$ ratio of fumarolic gases of Showashinzan.

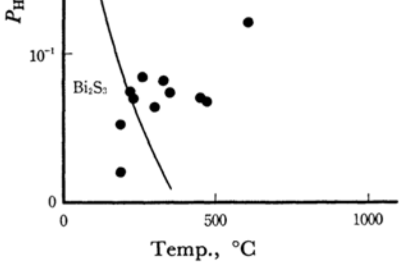

Fig. 3. Stability relationship between Bi and $\mathrm{Bi_2S_3}$ as a function of temperature and $P_{\mathrm{H_2S}}/P_{\mathrm{H_2}}$ ratio of the gas phase in equilibrium with the minerals.
—— : Bi - $\mathrm{Bi_2S_3}$ boundary
● : observed $P_{\mathrm{H_2S}}/P_{\mathrm{H_2}}$ ratio of fumarolic gases of Showashinzan

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[8] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," John Wiley, New York (1956).

[9] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards, Circ. 500 (1952).

[10] S. Oana and his co-workers, unpublished.

metal, but unstable at temperatures above 230°C (Fig. 3). Thus, in fumarolic gases of Showashinzan, bismuth, if present in an amount sufficient to form a solid, must exist as the sulfide or native metal.

A Possible Reaction to Form Bi_2S_3.—Theoretical evidence for the transportation of bismuth in magmatic vapor as chloride was adduced in Krauskopf's thermodynamic calculations[11] of the heavy metal content of magmatic vapor. His calculations suggest that high temperature magmatic vapor containing an appreciable amount of hydrogen chloride may transport bismuth in the form of bismuth chloride. On the basis of this theory, the following reaction may be offerred to account for the formation of bismuthinite under fumarolic conditions:

$$2\,BiCl_3 + 3\,H_2S = Bi_2S_3 + 6HCl \qquad (7)$$

This reaction may also be expressed as:

$$K_3 = \frac{X^6{}_{HCl} \cdot P}{X^2{}_{BiCl_3} \cdot X^3{}_{H_2S}} \qquad (8)$$

where K is the equilibrium constant, X is the molar fraction of the gaseous components in the system, and P is the total pressure on the system.

On the assumption that chemical equilibrium is attained in fumarolic gases of Showashinzan, the bismuth content of the gases may be estimated from the above relation if the equilibrium constant of the reaction, the chemical composition and pressure of the gases are given. The equilibrium constant for the reaction may be calculated in the way described above. The equation of the equilibrium constant thus obtained is:

$$\log K_3 = -\,17.23 + 5.34\,\log T + 1.18 \times 10^{-3}\,T + 5190\,T^{-1} \qquad (9)$$

With respect to the chemical composition of the gases, Mizutani[2] showed that the variation in the hydrogen chloride and hydrogen sulfide contants of the fumarolic gases of Showashinzan could be approximately expressed as a function of the temperature. Thus the following relations, which are obtained from the analytical data of the fumarolic gases[2,12] by using the method of least squares, may be used for the estimation of the equilibrium bismuth chloride content of the gases:

$$C_{HCl} = 0.77 \times 10^{-3}\,T - 0.25 \qquad (10)$$

$$C_{H_2S} = -0.19 \times 10^{-3}\,T + 0.21 \qquad (11)$$

where C is the content of the chemical components in fumarolic gases in l./1000 l. and T is the temperature of fumarolic gases in °K. For the pressure it is assumed that the static pressure of fumarolic gases near the outlet is 1 atm. The result obtained is illustrated graphically in Fig. 4, together with the observed bismuth contents of fumarolic gases.

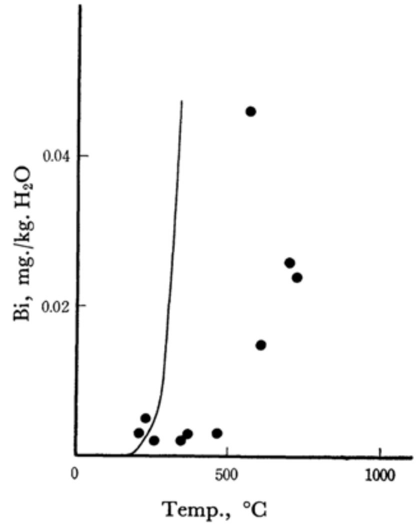

Fig. 4. Theoretical bismuth content in fumarolic gases of Showashinzan in equilibrium with Bi_2S_3 as a function of temperature at a total pressure of 1 atm., solid line.

● : observed bismuth content of fumarolic gases of Showashinzan

(0.01 mg. Bi/kg. $H_2O = 8.6 \times 10^{-4}$ ml. $BiCl_3$/1000 l. water vapor)

Figure 4 indicates that the fumarolic gases are capable of forming bismuth sulfide when the temperature falls to about 250°C. This temperature of the formation of bismuth sulfide is in good agreement with that obtained by the field observations. This agreement suggests that the major part of the bismuth that is volatilized out of Showashinzan magma is transported as bismuth chloride and that the bismuthinite is formed by Reaction 7 in the fumarolic gases as the temperature falls. A problem, however, arises about the decrease in the actual bismuth content observed at a temperature of about 500°C. As is shown in Fig. 4, the theoretical curve deviates significantly from the observed bismuth contents at temperatures above 250°. This discrepancy may be due to uncertainties in the thermodynamic estimation or to the formation of bismuth minerals other than bismuthinite which are more stable in the fumarolic gases with temperatures between 250 and 500°C than is bismuthinite. This problem, however, remains unsolved, because available data are not enough to make discussion significant. Thus, it is necessary to find other bismuth minerals in fumaroles with gas temperatures between 250 and 500°C and to have more thermodynamic data on various bismuth compounds in order to be able to extend the discussions concerning the formation of fumarolic bismuth minerals.

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[11] K. B. Krauskopf, *Econ. Geol.*, **52**, 786 (1957).

[12] S. Matsuo, *J. Earth Sciences, Nagoya Univ.*, **9**, 80 (1960).

Summary

A volcanic sublimate from fumarole B-1b of Showashinzan has been subjected to X-ray diffraction spectrographic and micro-chemical analyses. These analyses indicate that the sublimate consists of bismuthinite with trace amounts of lead, zinc, aluminum, copper and other substances. A possible reaction for the formation of bismuthinite in fumaroles of Showashinzan has been discussed by using the results of the analyses of fumarolic gases. It has been suggested that the bismuthinite is formed by the $2\ BiCl_3 + 3H_2S = Bi_2S_3 + 6HCl$ reaction in the fumarole.

The author wishes to express his deep appreciation to Professor Shinya Oana for his encouragement throuhgout this study. He is also indebted to Dr. Yoshiro Tsuzuki for his help in carrying out the preparation of the X-ray powder pattern, to Dr. Chuzo Iida for his spectrographic analysis, and to Mr. Tsutomu Sugiura for his help in the collection of samples.