# *The Behavior of Silicon, Aluminum, Iron, Magnesium, Calcium, Sodium and Potassium in Fumarolic Gas at the Mihara Volcano, Japan*

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The studies by Day and Shepherd[1,2] of gases evolved from the lava lake at Kilauea and by Allen and Zies[3,4] from the fumaroles at Valley of Ten Thousand Smokes are well known among the many investigations of volcanic gases. Recently Ellis[5] and Matsuo[6-8] also discussed the chemical equilibria in highly volatile components.

Krauskopf[9] has reviewed the possibility of vapor transport in the course of ore deposition. Observation of materials deposited in fumaroles shows that low volatile elements have been deposited directly from gases. In volcanic gases, water is the most abundant component, although the water content is variable. Morey[10,11] believes that water vapor would be able to dissolve and transport many elements of a low volatility at a high temperature and a high pressure. In some cases the vapor transport of relatively low volatile components, either as dissolved or gaseous compounds, is considered to account for the compositional differences in minerals and rocks of volcanic origin.[12,13]

According to White,[14] the vapor transport plays an important part in feeding various kinds of chemical species into hot spring water which has brought a great amount of the elements to the earth's surface. It is evident that water in either a gas or a liquid state would be an efficient transporting agent of many elements.

The principal purpose of this paper is to investigate the behavior of low volatile components in fumarolic gas at relatively high temperatures.

## A Description of the Mihara Volcano

The Mihara Volcano on Izu-Oshima Island, situated 120 km. south of Tokyo, is one of the most active volcanoes in Japan. Geological, mineralogical and chemical studies on Mt. Mihara have been made in detail by Tsuboi,[15] Iwasaki,[16] Tsuya,[17] Kuno[18] and many other investigators.[19-21]

Since the eruption in 1957, however, the volcano has been dormant; recently only a small amount of ashes is sometimes ejected from the crater. There are many fumaroles along the cracks on the scoria cone in the southwestern part of the crater. The highest

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[1] A. L. Day and E. S. Shepherd, *Geol. Soc. Am. Bull.*, **24**, 573 (1913).

[2] E. S. Shepherd, *Am. J. Sci.*, **35A**, 311 (1938).

[3] E. T. Allen and E. G. Zies, *Nat. Geog. Soc., Contributed Tech. Papers, I, Katmai Ser.*, No. 2, 75 (1923).

[4] E. G. Zies, *Am. J. Sci.*, **35A**, 385 (1938).

[5] A. J. Ellis, ibid., **255**, 416 (1957).

[6] S. Matsuo, *J. Earth Sci., Nagoya Univ.*, **8**, 222 (1960).

[7] S. Matsuo, ibid., **9**, 80 (1961).

[8] S. Matsuo, ibid., **9**, 101 (1961).

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

[10] G. W. Morey and J. M. Hesselgesser, ibid., **46**, 821 (1951).

[11] G. W. Morey, ibid., **52**, 225 (1957).

[12] C. H. Smyth, *Am. J. Sci.*, **36**, 33 (1913).

[13] H. Kuno and S. Taneda, *J. Geol. Soc. Japan*, **47**, 62 (1940).

[14] D. E. White, *Geol. Soc. Am. Bull.*, **68**, 1637 (1957).

[15] S. Tsuboi, *J. Coll. Sci., Tokyo Imp. Univ.*, **43**, pt. 6,1 (1920).

[16] I. Iwasaki, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **56**, 1511 (1935).

[17] H. Tsuya, *Bull. Earthq. Res. Inst.*, **15**, 215 (1937).

[18] H. Kuno, *Tr. Am. Geoph. Union*, **34**, 267 (1953).

[19] H. Tsuya, R. Morimoto and J. Ossaka, *Bull. Earthq. Res. Inst.*, **32**, 35 (1954).

[20] H. Tsuya, R. Morimoto and J. Ossaka, ibid., **32**, 289 (1954).

[21] H. Tsuya, R. Morimoto and J. Ossaka, ibid., **33**, 79 (1955).

temperature of the fumaroles was over 400°C in 1959. The temperature of these fumaroles, however, gradually decreased, until in 1961 the highest fell to 350°C.

Unlike the fumarolic gases in many other volcanoes, the gases at this volcano are admixture, with a great amount of air.[22] Excluding the air, the major constituents of the gas are carbon dioxide, hydrogen halides and sulfur compounds, water being extremely dominant. The fact that sulfur dioxide and free sulfuric acid, but no hydrogen sulfide, are detected in those fumarolic gases would account for a lack of free sulfur deposits at the orifice of the fumaroles. Deposits from gases and such decomposition products of ash and scoria as anhydrite, opal and clay minerals have been found at the orifices.[23-25] A map of the crater is shown in Fig. 1.

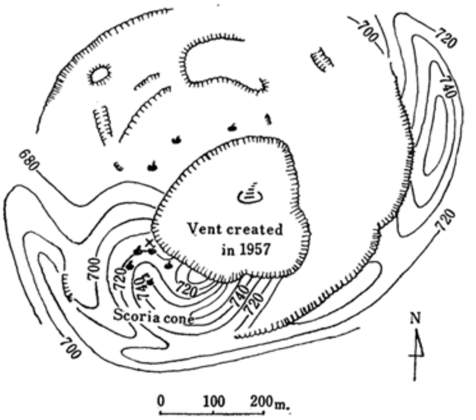

Fig. 1. Crater of Mihara Volcano.

Numerals in map represent meter above the sea-level.

× Position where condensed water was collected.

(≡) Fumarole

This was published by Oshima observatory of the Japan Meteorological Agency, on 20th in June, 1961.

## Experimental

**The Sampling of Condensed Water.**—One end of a hard glass tube 2.5 cm. in diameter, bent at a right angle, was inserted into a fumarole, and the other end was connected with a 5 m. glass tube to which a 5 m. polyvinyl-chloride tube was attached. A 1 l. polyethylene bottle was fitted with the end of the polyvinyl-chloride tube in order to collect any water condensed by air cooling (Fig. 2). By this means, the elements transported in gases for the most part come to dissolve in the condensed water.

From one of the many fumaroles, thirty-eight samples of condensed water were collected during the period from April to September, 1959, and fifty samples, from May to July, 1961.

The orifice temperature of the fumarole was measured by an alomel-chromel thermocouple and an electric-resistance thermometer with an attached recorder.

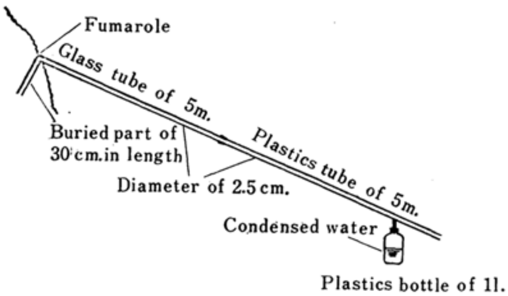

Fig. 2. Equipment for collecting condensed water from a fumarole.

**The Analytical Method.**—The condensed water was analyzed for acidity and for sulfate, chloride, silicon, aluminum, iron, calcium, magnesium, sodium and potassium.

*1) Acidity.*—The determination of acidity was carried out by titration with a sodium hydroxide solution using methyl orange as an indicator.

*2)* $SO_4^{2-}$.*—The sulfate was measured by means of the barium sulfate turbidity developed with a barium chloride gelatin solution.

*3)* $Cl^-$.—The chloride was determined by Mohr's method.

*4) Silicon.*—The silicon was determined colorimetrically by a molybdenum blue method.**

*5) Aluminum.*—The determination of aluminum was made by measuring the optical density of the red color of the complex formed with aluminon after extraction of iron with cupferron into chloroform.

*6) Iron.*—The determination of iron was carried out by reducing with hydroxylamine all the iron to a ferrous state, and then by making a colorimetric measurement of the absorbance of the red color developed with $\alpha, \alpha'$-bipyridyl or *o*-phenanthroline.

*7) Calcium and Magnesium.*—The sum of calcium and magnesium was determined by titrating them with an EDTA solution in the presence of Eriochrome Black T at pH 10. The calcium was independently determined by titration with an EDTA solution in strong alkaline media using Dotite NN as an indicator. The amount of magnesium was

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[22] I. Iwasaki, T. Ozawa, M. Yoshida, T. Katsura, B. Iwasaki, M. Kamada and M. Hirayama, *Bull. Tokyo Inst. Tech.*, No. 47, 1 (1962).

[23] R. Morimoto and J. Ossaka, *J. Geog.*, **60**, 136 (1951).

[24] I. Iwasaki, ibid., **60**, 140 (1951).

[25] K. Noguchi, H. Kamiya and H. Kawase, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 121 (1963).

* In the condensed water samples which were transferred to the laboratory, neither sulfur dioxide nor hydrogen sulfide was detected.

** By this method only the dissolved or less coagulated silica can be determined. However, no difference was found between the results of the above direct determination and those of the total silica determination.

calculated by subtracting the amount of calcium from the sum.

*8) Sodium and Potassium.* — The sodium and potassium were determined by means of flame photometry.

## Results and Discussion

**The Variation in the Concentration of the Components in Condensed Water.** — Figure 3 shows the variations in the orifice temperature of the fumarole, the acidity of the condensed waters and the concentrations of the nine components (i. e., sulfate, chloride, silicon, aluminum, iron, calcium, magnesium, sodium and potassium), in the period from April to September, 1959, and from May to July, 1961.

In 1959 the measurement of the orifice temperature was discontinued because the thermometer was damaged. However, the continued gradual decrease in the temperature was assured by interpolation.

As may be seen in Fig. 3, the concentrations of the components in the condensed waters changed markedly, even in a short

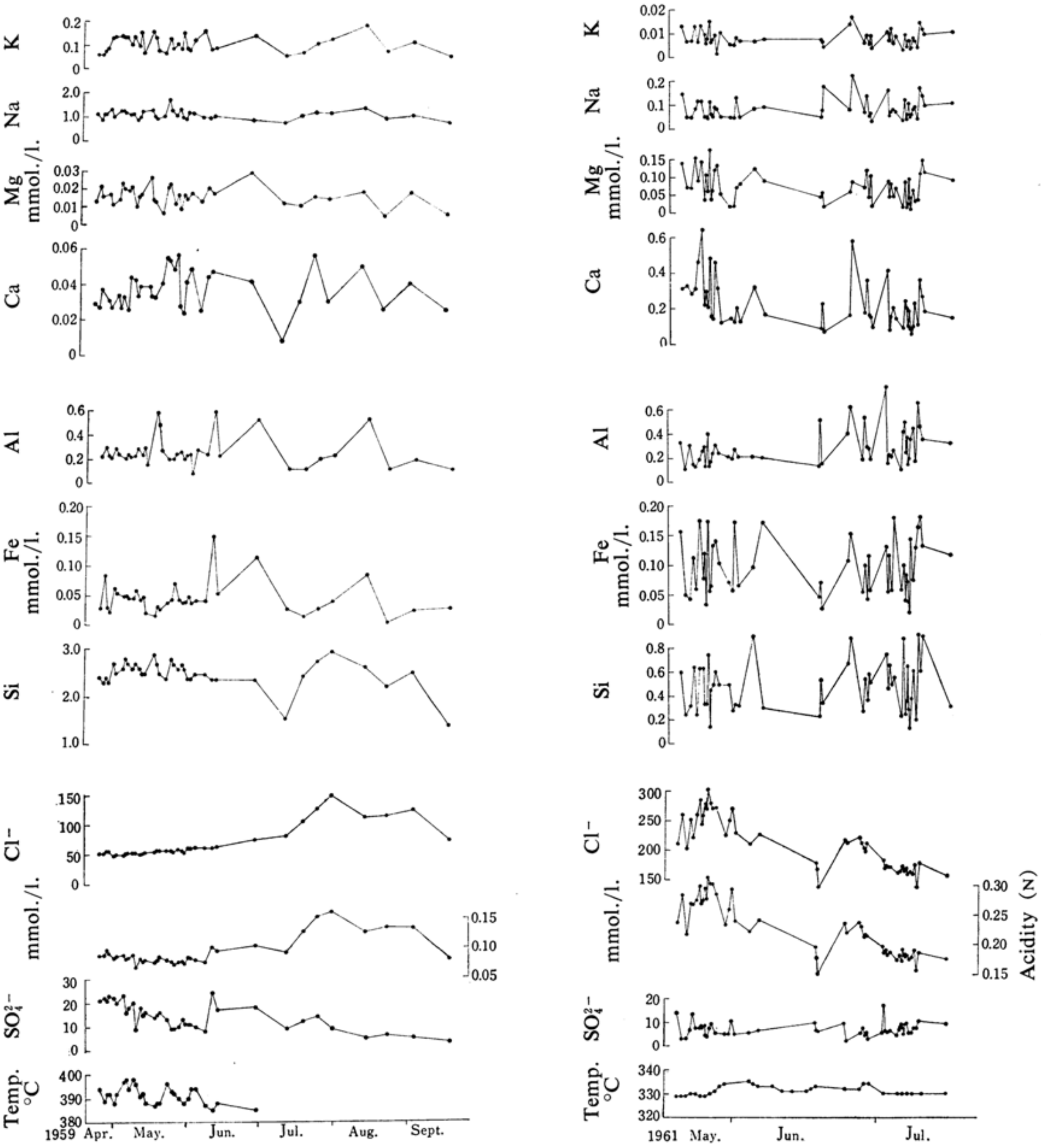

Fig. 3. Variation of orifice temperature of fumarole, acidity of condensed water and concentrations of components in condensed water in 1959 and 1961.

TABLE I. AVERAGE CONCENTRATION, ITS STANDARD DEVIATION AND VARIATION COEFFICIENT OF NINE COMPONENTS IN CONDENSED WATER, AND RATIO OF AVERAGE CONCENTRATION IN 1961 TO THAT IN 1959

| | In 1959 | | | In 1961 | | | |
|---|---|---|---|---|---|---|---|
| | Average concn. mmol./l. | Standard deviation | Std. Dev./Av. Concn. (ratio) | Average concn. mmol./l. | Standard deviation | Std. Dev./Av. Concn. (ratio) | Av. Concn. ('61)/Av. Concn. ('59) (ratio) |
| Si | 2.5 | 0.29 | 0.12 | 0.47 | 0.21 | 0.45 | 0.19 |
| Al | 0.27 | 0.12 | 0.46 | 0.28 | 0.15 | 0.53 | 1.0 |
| Fe | 0.047 | 0.027 | 0.57 | 0.094 | 0.047 | 0.50 | 2.0 |
| Mg | 0.016 | 0.005 | 0.32 | 0.072 | 0.042 | 0.59 | 4.5 |
| Ca | 0.037 | 0.011 | 0.29 | 0.22 | 0.14 | 0.62 | 5.9 |
| Na | 1.1 | 0.20 | 0.18 | 0.081 | 0.042 | 0.51 | 0.074 |
| K | 0.11 | 0.03 | 0.31 | 0.008 | 0.003 | 0.44 | 0.07 |
| $SO_4$ | 14 | 5.7 | 0.41 | 7.0 | 2.8 | 0.40 | 0.5 |
| Cl | 67 | 25 | 0.38 | 208 | 44.7 | 0.21 | 3.1 |
| Temp. | about 390°C | | | about 330°C | | | |

interval. Mizutani and Matsuo[26] have observed similar variations in calcium and magnesium concentrations in condensed waters drawn from a fumarole at the Showa-shinzan Volcano.

On the basis of thermodynamic calculations, Ellis[5] and Matsuo[6-8] have shown that the chemical composition of volcanic gases should change in accordance with the temperature, the pressure and the type of magma. Some volcanologists even anticipate that eruptions can be predicted by measuring such a compositional change of gases.[26-29]

Table I gives the average concentrations, the standard deviations of the concentrations and the ratios of the standard deviations to the average concentrations denoting the variation coefficient, in both 1959 and 1961.

As given by the variation coefficients in Table I, the low volatile components differ considerably in their modes of variation in 1959; for example, the variation of silicon is the smallest, and that of iron the largest. In 1961, however, no marked differences exist among variation coefficients, which are generally larger than those in 1959. As for the highly volatile components, the variation of sulfate was much the same in both 1959 and 1961, while that of chloride in 1961 was much smaller than in 1959.

**A Comparison between the Average Concentrations in 1959 and 1961.**—The ratios of the average concentrations in 1961 to those in 1959 are shown in the final column of Table I.

The decrease in the orifice temperature, 390°C in 1959 to 330°C in 1961, resulted in the threefold increase in the chloride concentration; on the other hand, it also reduced the sulfate concentration by half.

The titrated acidity almost corresponds to the total gram-equivalent of the determined chloride and sulfate ions, as may be seen in Fig. 4. This means that chloride and sulfate ions are present in condensed water for the most part as free acid; in other words, the condensed water is practically a mixture of hydrochloric and sulfuric acids because of the small contribution of cations other than hydrogen ions (Table I).

The much stronger acidity in 1961 than in 1959 may be attributed to the increase in chloride (Fig. 4).

As for the low volatile components, in 1961 the average concentrations of sodium, potassium and silicon became lower; on the other hand, those of calcium, magnesium and iron became higher, while that of aluminum remained constant, as compared with those in 1959. This cannot be explained as a results of a simple vaporization of such a compound as metal chloride with a relatively high vapor pressure. As has been pointed out by Krauskopf,[9] coexistent water vapor and sulfur compounds should also be taken into consideration.

It will be evident that the amount of heat supplied by gas determines the orifice temperature of a fumarole.[30] Unfortunately, since neither the flow rate of the fumarolic gas nor the condensation rate of the water vapor was measured, it is uncertain whether the decrease

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

[27] J. H. Payne and S. S. Ballard, *Science*, **92**, 218 (1940).

[28] K. Noguchi, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **56**, 1495 (1935).

[29] K. Noguchi and H. Kamiya, *Bull. Volcanol.*, **26**, 368 (1963).

[30] K. Takahashi and S. Oana, *Repts. Geol. Survey Japan*, No. 170, 115 (1957).

TABLE II. MOLE PERCENTAGE OF SEVEN COMPONENTS IN LAVA AND CONDENSED WATER AND RATIO OF MOLE PERCENTAGE IN CONDENSED WATER TO THAT IN LAVA

| Component | Lava (*R*) | In 1959 |  | In 1961 |  |
|---|---|---|---|---|---|
|  |  | Condensed water (*G*) | *G*/*R* | Condensed water (*G'*) | *G'*/*R* |
|  | % | % | (ratio) | % | (ratio) |
| Si | 51.1 | 61 | 1.2 | 38 | 0.75 |
| Al | 17.7 | 6.5 | 0.37 | 23 | 1.3 |
| Fe | 10.5 | 1.1 | 0.10 | 7.7 | 0.73 |
| Mg | 6.8 | 0.4 | 0.06 | 5.9 | 0.87 |
| Ca | 10.2 | 0.9 | 0.09 | 18 | 1.8 |
| Na | 3.2 | 28 | 8.8 | 6.6 | 2.1 |
| K | 0.4 | 2.7 | 6.8 | 0.63 | 1.6 |

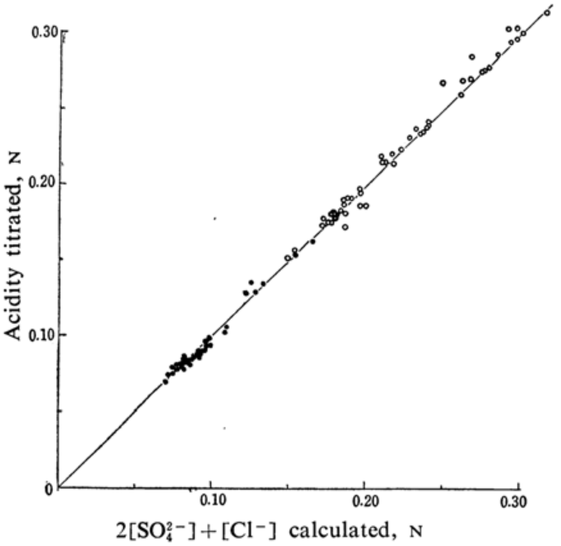

Fig. 4. Comparison between acidity titrated and acidity calculated by regarding all of the sulfate and chloride ions as free acids. A straight line, which meets with the axes at angles of 45 degree, represents the identity of both acidities.
• Sample in 1959 ○ Sample in 1961

in the orifice temperature can be attributed to the decrease in the gas temperature itself or to the decrease in the flow rate.

Assuming that the water vapor content in the fumarolic gas changes according to the environmental conditions, it seems likely that the variation in the ratio of the content of a certain component to that of water vapor in gas, i. e., the variation in the concentration of a chemical component in condensed water, differs by chance. Therefore, a simple comparison of two average concentrations of a component for the two periods (1959 and 1961) would not decisively indicate the increase or decrease in the content of a chemical component in gas.

**The Transport of the Low Volatile Components in the Fumarolic Gas.**—While the gas is ascending from magma to the earth's surface through conduits with a decreasing temperature and a decreasing pressure gradient, the low volatile components in the gas might be partly deposited and so removed from the gas in the course of its ascending. The chemical composition of the condensed water should, therefore, be considered to be the result of various reactions during the ascending process.

Table II gives the mole percentages of the seven components, i. e., silicon, aluminum, iron, magnesium, calcium, sodium and potassium, in the lava of this volcano[19] and in the condensed water, and the ratio of the mole percentage of each component in the condensed water to that in the lava. The ratio may be considered to be a measure of the ease with which a chemical component is transported in gas. The ratio for the seven components may be concluded to be in the following order:

Na>K>Si>Al>Fe and Ca>Mg in 1959

and

Na>Ca>K>Al>Mg, Si and Fe in 1961.

Sodium was the most mobile component in both 1959 and 1961. Silicon was relatively mobile in 1959, but it turned out to be one of the least mobile components in 1961. On the contrary, calcium was one of the least mobile components in 1959, but the most mobile one after sodium in 1961.

The great mobility of sodium, potassium and silicon in 1959 corresponds to the conclusions by Kennedy,[31,32] Moery[10] and White.[14] According to them, many alkali chlorides and silica are transported in water at sufficiently high temperatures and pressures.

As may be noticed in Table II, the mole percentages of the seven components in condensed waters, i. e., in gases, are considerably different from those in lava. If such gases

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[31] S. Sourirajan and G. C. Kennedy, *Am. J. Sci.*, **260**, 115 (1962).

[32] G. C. Kennedy, *Econ. Geol.*, **45**, 629 (1950).

are formed and separated out of a magma, compositional changes in the residual magma may be expected.

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