

The Behavior of Manganese, Titanium and Phosphorus in Fumarolic Gas at the Mihara Volcano, Japan

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As was described in a previous paper,¹⁾ the low volatile components present in rocks have really been transported in fumarolic gases, although in small amounts. Because magmatic gas cannot be collected directly, however, the behavior of the low volatile components there must be surmised from observations and analyses of minerals in ore deposits and of gases and sublimates evolved from lava and fumaroles, as well as from laboratory experiments at a high temperature and a high pressure.

From thermodynamic data, Krauskopf²⁾ showed that magmatic gas at 600°C is, with a few exceptions, capable of transporting the common heavy metals, such as volatile chlorides, to form an ore deposit. Morey^{3,4)} and Kennedy^{5,6)} demonstrated the strong solvent action of water vapor on the relatively low volatile components with a sufficient temperature and pressure. As has been suggested by Krauskopf, the low volatile components may be transported mechanically as solid particles in gas as well as vapor.

Matsuo⁷⁾ pointed out that many reactions in fumarolic gas are quenched to a certain extent at the orifices of fumaroles. The extent of their quenching, however, will depend on the kinds of reactions and on the temperature and pressure gradients in the fumarole.

Whatever factor plays the most important part in transporting the low volatile com-

ponents, it is certain that the results stated in the previous paper will correspond to the features of their behavior in the fumarolic gas.

In this paper the writer will describe the behavior in the fumarolic gas of manganese, titanium and phosphorus, which are less familiar but are yet widely distributed in rocks.

Experimental

The investigation of the behavior of manganese, titanium and phosphorus was made in the same way as that in the previous paper, i. e., by the collection and analysis of the condensed waters from a fumarole at the Mihara Volcano. The components in the condensed water were concentrated by evaporation or separated by coprecipitation, because their contents were too low to be determined directly.

Sample.—An equivolume mixture of three condensed waters collected in September, 1959, i. e., in the final period of the sample collection in that year, was used as the sample for 1959. Fifty condensed waters collected in 1961 were divided into five groups according to the iron concentrations. The numbers of the condensed waters included in each group are given in the first column of Table I. The samples in each group were then mixed in the same proportions by volume and used as the samples for 1961.

Analytical Method.—First 1000 or 1500 ml. of the combined sample was heated, gently to expel the hydrochloric acid and then strongly until no more sulfuric acid fumes were evolved. The evaporate was then dissolved in 3 ml. of concentrated sulfuric acid and made up to 50 ml. of the final volume by adding distilled water. An aliquot of 25 ml. was used for the determination of manganese, 20 ml., for titanium, and 1 ml., for iron and for aluminum. For the determination of phosphorus, 500 ml. of the raw combined sample was used.

Manganese.—Manganese was determined through the photometric measurement of the violet color

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1) H. Kamiya, *This Bulletin*, 37, 1477 (1964).

2) K. B. Krauskopf, *Econ. Geol.*, 52, 786 (1957).

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

4) G. W. Morey, *ibid.*, 52, 225 (1957).

5) G. C. Kennedy, *ibid.*, 45, 629 (1950).

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

7) S. Matsuo, *J. Earth Sci., Nagoya Univ.*, 9, 80 (1961).

developed by the periodate oxidation of manganese to permanganate, in the presence of orthophosphoric acid to eliminate interference.⁸⁾

Titanium.—The determination of titanium was made colorimetrically by comparing the yellow color formed with hydrogen peroxide in a 1:9 sulfuric acid solution with the standard color.⁹⁾

Phosphorus.—Phosphorus was separated by coprecipitation with aluminum hydroxide and determined by the molybdenum blue method.¹⁰⁾

Aluminum and Iron.—The determination of aluminum and iron was carried out by the method described in the previous paper.

Results and Discussion

The Concentrations of Iron, Aluminum Manganese, Titanium and Phosphorus in Condensed Water Collected in 1959 and 1961.—The average concentrations of iron, aluminum, manganese, titanium and phosphorus in the combined samples in both 1959 and 1961 are given in Table I. The 1959 sample was a mixture of only three condensed waters. The average concentrations in 1961 were calculated from the concentrations of the components in the five classified groups.

The titanium concentration increased and those of manganese and phosphorus decreased in 1961, as compared with their concentrations in 1959. While the increase in titanium and the decrease in phosphorus were in the same order of magnitude, the manganese concentration in 1961 was almost two orders of magnitude lower than that in 1959; i.e., the decrease in the manganese concentration in 1961 was quite remarkable.

In view of the fact that the average concentration of iron, 0.047 mmol./l., in 1959 given in the previous paper differs from that, 0.060 mmol./l., for the same year in Table I, despite the identity in aluminum concentration, it cannot be said that the fumarolic gas in 1959 described in the previous paper had the same quality as the gas from which the three condensed waters in this experiment were obtained.

The Correlation of Aluminum, Manganese, Titanium and Phosphorus with Iron.—In order to find the relationship between aluminum, manganese, titanium, phosphorus and iron, the fifty condensed waters collected in 1961 were classified into five groups. As may be seen in Fig. 1, when the concentrations of aluminum, manganese, titanium and phosphorus are plotted against that of iron in the five groups

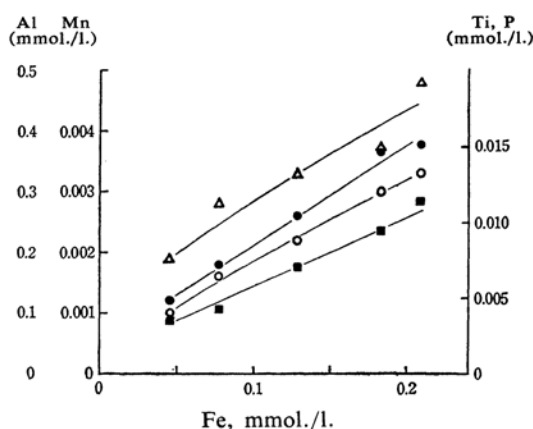


Fig. 1. Correlation of Al, Mn, Ti and P with Fe.

△ Al, ● Ti, ○ Mn, ■ P

of samples in 1961, they tend to increase simultaneously with the iron concentrations. Manganese and titanium show a nearly linear relation with iron, but the same kind of correlation between aluminum and iron is not clear. A linear increase in the concentration of phosphorus with an increasing concentration of iron is noticed.

The behavior of manganese, titanium, phosphorus, etc., in the fumarolic gas of 1959 may not be fully displayed, inasmuch as the concentrations in 1959 given in Table I are the average values from only three condensed waters. However, if the concentrations of aluminum, titanium and phosphorus are plotted against that of iron in 1959, the points fall not so far from the lines in Fig. 1 which represent the relations of aluminum, titanium and phosphorus to iron in 1961. In contrast to the above components, the unusually high concentration of manganese in the combined sample of 1959, when compared with that of iron, is quite noticeable.

The Transport of Manganese, Titanium and Phosphorus in Gas in Comparison with the Other Major Components.—The ratios between the mole percentages of the twelve components, including chlorine, sulfur, manganese, titanium and phosphorus, in the condensed water and those in the lava were calculated from the average concentrations of the components in the condensed waters in 1959 and in 1961 and from their contents in the lava (1951) reported by Tsuya et al.¹¹⁾ and Iwasaki et al.¹²⁾ Due to the lack of data on the analysis of sulfur in the lava of 1951, the sulfur content in the lava of

8) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., New York (1954), p. 392.

9) F. D. Snell and C. T. Snell, *ibid.*, p. 438.

10) D. F. Boltz (Editor), "Colorimetric Determination of Nonmetals," Interscience Publisher, New York (1958), p. 29.

11) H. Tsuya, R. Morimoto and J. Osaka, *Bull. Earthq. Res. Inst.*, **30**, 231 (1952).

12) I. Iwasaki, T. Katsura, N. Sakato and M. Hirayama, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **78**, 1641 (1951).

TABLE I. CONCENTRATION OF Fe, Al, Mn, Ti AND P

	Number of condensed waters combined	Fe	Al	Mn (mmol./l.)	Ti	P
In 1959	3	0.060	0.28	0.082	0.0063	0.0066
In 1961	18	0.045	0.19	0.0010	0.0048	0.0035
	14	0.077	0.28	0.0016	0.0072	0.0043
	10	0.128	0.33	0.0022	0.0104	0.0070
	4	0.183	0.37	0.0030	0.0147	0.0095
	4	0.209	0.48	0.0033	0.0151	0.0114
	Average	0.095	0.28	0.0018	0.0082	0.0055

TABLE II. MOLE PERCENTAGE OF 12 COMPONENTS IN LAVA AND CONDENSED WATER, AND RATIO

	In 1959			In 1961	
	Lava R, mol. %	Condensed water G ₁ , mol. %	G ₁ /R ratio	Condensed water G ₂ , mol. %	G ₂ /R ratio
Si	50.4	2.9	0.058	0.22	0.0043
Al	17.5	0.32	0.018	0.13	0.0074
Fe	10.4	0.055	0.0053	0.043	0.0042
Mg	6.7	0.019	0.0028	0.033	0.0050
Ca	10.0	0.043	0.0043	0.10	0.010
Na	3.1	1.3	0.42	0.037	0.012
K	0.41	0.13	0.32	0.0036	0.0088
Ti	1.1	0.0074	0.0070	0.0038	0.0036
P	0.098	0.0077	0.080	0.0025	0.026
Mn	0.081	0.096	1.2	0.00083	0.010
S	0.22	16.4	76	3.24	15
Cl	0.047	78.7	170	96.2	2040

TABLE III. ORDER OF RATIO FOR 12 COMPONENTS

In 1959	Cl > S > Mn > Na > K > P > Si > Al > (Ti, Fe) > Ca > Mg
In 1961	Cl > S > P > Na > (Ca, Mn) > K > Al > Mg > (Si, Fe) > Ti

the central cone as measured by Iwasaki¹³⁾ was employed. The results are given in Table II. Moreover, the order of the ratio for the components is shown in Table III. As was stated in the previous paper, it may be considered that the ratio denotes the measure of ease with which the components are transported in gas or the degree of concentration in gas relative to that in lava.

The low volatile components abundant in rocks probably originate from magma and/or wall rock. On the other hand, chlorine may originate from another source, as has been suggested by Matsuo.⁷⁾ Wherever they may originate, however, the general tendency of the transport of the components in gas is illustrated by the ratios.

Chlorine and sulfur, excluding the most dominant water vapor in gas, are the largest mobile elements, unless there is the possibility of the secondary addition of these components into gases. In other words, they are concentrated into gas, as they cannot enter the crystal lattice of common rock-forming minerals; in

general, chlorine is incorporated in the glassy part rather than in minerals,¹²⁾ and the minor sulfur content is due to the sulfur compounds in rocks. As may be seen in Table II, chlorine and sulfur made up over 95% of the whole in 1959 and 99% in 1961.

Manganese was much more mobile than alkali metals, and the component with the largest ratio, except for such highly volatile components as chlorine and sulfur, in 1959. As has been stated previously, although the concentration of manganese became much lower in 1961 than in 1959, still it belongs to the metallic components with a relatively large ratio. Titanium had a ratio comparable to iron in the fumarolic gas of a higher temperature in 1959, but it became less mobile at a lower temperature in 1961. Phosphorus had a smaller ratio than alkali metals in 1959, and it became more mobile than any metals, with a decrease in the ratio of metallic components, in 1961.

As has been stated above, there is a marked difference in the nature of the fumarolic gases between those of 1959 and those of 1961, based

13) I. Iwasaki, *ibid.*, 56, 1518 (1935).

on the chemical analysis of condensed waters. We are led, then, to inquire what factors govern the transport of these components, what kinds of compounds of these components are really transpired and, especially, why the fumarolic gas in 1959 had a particular ability to transport manganese. In order to answer these questions, further experiments at high temperatures and high pressures are needed.

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