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An Experimental Study of the Vaporization of Chlorine Compounds from Basaltic Lavas during the Cooling Process. I

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An attempt was made to make clear the manner of the vaporization of chlorine compounds from basaltic rocks at a series of temperatures ranging from 1000 to 1300°C, in atmospheres of air and of a mixed gas (CO_2-H_2), and on cooling from 1200 to 800°C in air, neglecting the effect of water vapor. The vaporization of chlorine compounds was found to take place from the surface of a melt and through the interstices of rock grains. When crystals began to separate from the melt, they suddently prevented the vaporization. From the results of cooling experiments on the basaltic melt, it was concluded that the chlorine compounds in the liquid basaltic lava extruded at approximately 1200°C are continously vaporized until the liquid lava is covered with thin films including crystals and glassy materials. The temperature at which the vaporization of chlorine compounds ceases is 1100°C at the highest.

It is of great importance to make clear the behavior of volatile components in lavas while they cool after extrusion, because the volatile components may change in content as lavas solidify in a sensitive reaction to the change in the enviromental conditions which is connected to the intensive properties of these volatiles. Indeed, several studies have been carried out on the vaporization from lavas during their cooling process,[1] and the vaporization of some components has also been studied by heating igneous rocks at desired temperatures.[2] However, there are few experimental studies on the vaporization of volatile components from lavas during their cooling process.

On the other hand, the chlorine content of volcanic rocks has been determined to range widely from 0.00*n* to 0.*n*% Cl.[3] The chlorine content of the liquid lava is considered to show the highest value immediately after the extrusion, and to decrease during cooling because of the vaporization of chlorine compounds. In a previous paper,[4] we have determined the solubility of hydrogen chloride in volcanic rock melts at a total pressure of 1 atm and 1200°C and 1290°C under anhydrous conditions; we did this in order to clarify the significance of the chlorine content of the liquid lava in equilibrium with magmatic gas at the time of extrusion. In this paper, an attempt will be made to make clear the manner of the vaporization of chlorine compounds from melted rocks at constant temperatures and on their cooling as a second step in determining the reason why the chlorine content of volcanic rocks varies over the wide range mentioned above. For the sake of experimental convenience, we chose the experimental conditions which will be shown later, neglecting the effect of water vapor.

Experimental

Material. A basaltic rock erupted in 1950—1951 from the O-sima Volcano, off the Izu Peninsula, was chosen because the horizontal distribution of chlorine in the lava flow had been studied.[5] Two kinds of materials, *e. g.*, the original rock sample and the rock-glass sample containing adequate amounts of chlorine compounds, were prepared according to a procedure previously described.[4]

Furnace and Temperature Control. The temperature control system was similar to that adopted by Katsura and Kimura.[6] The furnace temperatures were kept within ±5°C at a series of temperatures from 1000 to 1300°C. In the case of the temperature-descending experiments, the furnace temperatures were held to a desired temperature with a precision of approximately ±10°C.

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[1] A. L. Day and E. S. Shepherd, *Bull. Geol. Soc. Am.*, **24**, 573 (1913); E. S. Shepherd, *Am. J. Sci.*, **35A**, 311 (1938); T. A. Jaggar, *ibid.*, **238**, 313 (1940).

[2] R. T. Chamberlin, "The Gases in Rocks," Carnegie Inst., Wash., Rebl., Washington D. C. (1908); A. Brun, "Recherches sur l'Exhalation Volcanique," Libraire Kündig, Genéve (1911); E. S. Shepherd, *J. Geol.*, **33**, 289 (1925); I. Iwasaki, T. Katsura and N. Sakato, *Nippon Kagaku Zassi (J. Chem. Sec. Japan, Pure Chem. Sect.)*, **76**, 778 (1950); M. Yoshida, This Bulletin, **36**, 773 (1963); M. Yoshida, I. Makino, N. Yonehara and I. Iwasaki, *ibid.*, **38**, 1436 (1965).

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[4] B. Iwasaki and T. Katsura, This Bulletin, in press.

[5] I. Iwasaki and T. Ozawa, read at the Meeting of the Volcanological Society of Japan, May, 1959.

[6] T. Katsura and S. Kimura, This Bulletin, **38**, 1664 (1965).

Table 1. The volatility of chlorine compounds from basaltic rocks on heating

Sample	Atmosphere	Temperature °C	Heating time, hr	Residual Cl %	Volatilized Cl %	Volatility %
OR,* 0.032%Cl	air	1000	6 (min)	0.018	0.014	44
OR,* 0.032%Cl	air	1000	1	0.013	0.019	59
OR,* 0.032%Cl	air	1000	3	0.014	0.018	56
OR,* 0.032%Cl	air	1000	5	0.011	0.021	66
OR,* 0.032%Cl	air	1000	11.7	0.009	0.023	72
RG,** 0.47%Cl	air	1000	5 (min)	0.37	0.10	21
RG,** 0.47%Cl	air	1000	1.3	0.27	0.20	42
RG,** 0.47%Cl	air	1000	5.1	0.26	0.21	45
RG,** 0.47%Cl	air	1000	10.5	0.17	0.30	64
RG,** 0.47%Cl	air	1000	20.3	0.12	0.35	74
OR,* 0.032%Cl	air	1100	5 (min)	0.015	0.017	53
OR,* 0.032%Cl	air	1100	1	0.005	0.027	84
OR,* 0.032%Cl	air	1100	5	0.007	0.025	78
OR,* 0.032%Cl	air	1100	10	0.002	0.030	94
RG,** 0.47%Cl	air	1100	5 (min)	0.35	0.12	26
RG,** 0.47%Cl	air	1100	10	0.16	0.31	66
RG,** 0.47%Cl	air	1100	21.1	0.10	0.37	79
OR,* 0.032%Cl	air	1200	5 (min)	0.024	0.008	25
OR,* 0.032%Cl	air	1200	10.1	0.016	0.016	50
OR,* 0.032%Cl	air	1200	22.6	0.016	0.016	50
RG,** 0.47%Cl	air	1200	6 (min)	0.43	0.04	9
RG,** 0.47%Cl	air	1200	10.4	0.37	0.10	21
RG,** 0.47%Cl	air	1200	20.2	0.36	0.11	23
RG,** 0.54%Cl	air	1300	6 (min)	0.50	0.04	7
RG,** 0.54%Cl	air	1300	5.3	0.33	0.21	39
RG,** 0.54%Cl	air	1300	10.8	0.23	0.31	57
RG,** 0.47%Cl	mixed gas	1200	6 (min)	0.40	0.07	15
RG,** 0.47%Cl	mixed gas	1200	10.4	0.24	0.23	49
RG,** 0.47%Cl	mixed gas	1200	21.2	0.20	0.27	57

* OR means the original rock
** RG means the rock-glass sample

The Control of Atmosphere.—It was pointed out by Shibata and Katsura[7] that the rock sample used in this study contains hematite and plagioclase when it is in equilibrium with air at 1200°C, whereas the rock sample in equilibrium with a mixed gas of $CO_2/H_2=100$ melts completely at 1200°C. Therefore, two kinds of atmosphere, air and a mixed gas of $CO_2/H_2=100$, were used in order to examine whether or not the vaporization of chlorine compounds is influenced by the presence of crystals in melted rocks. The mixed gas, prepared by a procedure previously described,[6] was passed through the furnace from bottom to top at a linear flow rate of 8mm per second.

Run Procedure. About 0.1g of each sample, packed into a small 80% Pt 20% Rh-envelope 0.2 cc in volume, was suspended by a thin Pt wire in the center of the furnace. Then, the gas mixture was allowed to flow at a fixed linear flow rate through the tube into the furnace. When the experiments were carried out in air, the sample was simply suspended in air. After various periods of heating, the thin Pt wire was burned away with an electric current in order to quench the sample. The total chlorine in the quenched samples was then determined by the method proposed by Iwasaki *et al.*,[8] with some improvements.

Results

Table 1 shows the volatility of chlorine compounds from the basaltic rocks at a series of temperatures from 1000 to 1300°C in air and at 1200°C in the mixed gas. The term "Volatility" in Table 1 means the percentage ratio of the volatilized chlorine content to the original chlorine content. Table 2 shows the volatility of chlorine compounds from the basaltic rock melts as they cool from 1200 to 800°C in air.

Discussion

The Rate of the Vaporization of Chlorine Compounds from the Basaltic Rocks on

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7) K. Shibata and T. Katsura, read at the Meeting of the Volcanological Socicty of Japan, October, 1964. See also K. Shibata, This Bulletin, in press.

8) I. Iwasaki, T. Katsura and N. Sakato, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **76**, 1116 (1955).

Table 2. The volatility oe chlorine compounds from basaltic rocks during the cooling process in air

Sample	Quenched temperature, °C	Heating** time, hr	Residual Cl %	Volatilized Cl %	Volatility %
RG,* 0.50%Cl	1200	5 (min)	0.48	0.02	4
RG,* 0.50%Cl	1200	5.1	0.42	0.08	16
RG,* 0.50%Cl	1200	7.2	0.44	0.06	12
RG,* 0.50%Cl	1200	10	0.42	0.08	16
RG,* 0.50%Cl	1200	22.3	0.44	0.06	12
RG,* 0.50%Cl	1100	20.9	0.43	0.07	14
RG,* 0.50%Cl	1100	34.5	0.43	0.07	14
RG,* 0.50%Cl	1100	42.8	0.44	0.06	12
RG,* 0.50%Cl	1000	30	0.37	0.13	26
RG,* 0.50%Cl	1000	40.1	0.36	0.14	28
RG,* 0.50%Cl	900	40	0.39	0.11	22
RG,* 0.50%Cl	800	53	0.42	0.08	16

* RG means the rock-glass sample.

** Before quenching, the sample was heated at intervals of 100°C for each 10 hr from 1200°C to desired temperature, then the sample was heated at each quenched temperature.

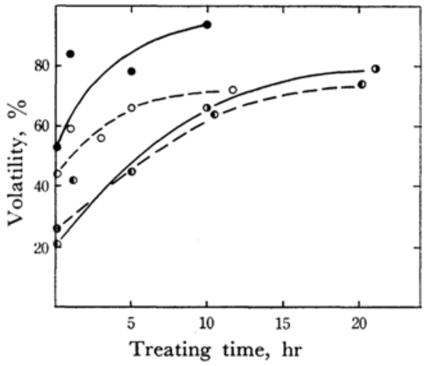

Fig. 1. Change of volatility of chlorine compounds of the sample with treating time at 1000°C and 1100°C in air.

○ The original sample at 1000°C
● The original sample at 1100°C
◐ The rock-glass sample at 1000°C
◑ The rock-glass sample at 1100°C

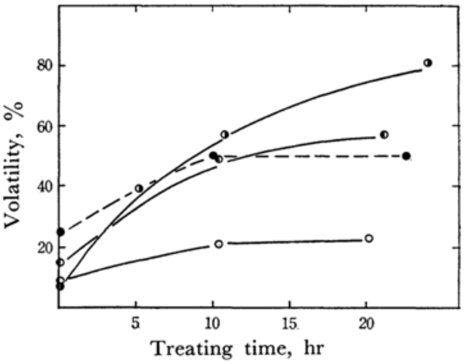

Fig. 2. Change of valatility of chlorine compounds of the sample with treating time 1200°C and 1300°C in air and 1200°C in CO_2-H_2 mixture.

● The original sample at 1200°C in air
○ The rock-glass sample at 1200°C in air
◐ The rock-glass sample at 1200°C in CO_2-H_2 mixture
◑ The rock-glass sample at 1300°C in air

Heating. Figure 1 shows the change in the volatility of chlorine compounds from the basaltic rocks with the heating time at 1000 and at 1100°C in air. Figure 2 shows the change in the volatility of chlorine compounds from the basaltic rocks with the heating time at 1200 and at 1300°C in air and at 1200°C in a mixed gas. From the results shown in Figs. 1 and 2, the following four points are clear: (1) The chlorine compounds volatilize more easily at 1100°C in air than at 1200°C in air. According to Shibata and Katsura,7) the sample is completely in the solid state at 1100°C, whereas at 1200°C the sample is in the melted state. In the latter case, therefore, the chlorine compounds may volatilize only from the surface of the melt. In the former case, however, the chlorine compounds will volatilize predominantly through the interstices of the solid rock-grains. In the case of the solid rock-powder, the chlorine compounds dissolved in the glassy parts seem to be forced to loose from them as soon as the glassy parts of the sample begin to crystallize, because the chloride ions could hardly replace the lattice points of the ordinary rock-forming minerals found in basalts. (2) In the case of heating at 1200°C in air, the chlorine compounds in the orginal sample volatilize more easily than in the rock-glass sample. The original sample contains about 0.03% of Cl, together with about 1.0% of H_2O, whereas the rock-glass sample contains 0.5% Cl and 0.0% H_2O. According to an experimental finding, which is not listed in Table 1, the volatility of chlorine compounds from the glassy sample containing 0.20% Cl is about 20% after 10 hr. Thus, the volatility of chlorine compounds from the glassy samples seems to be independent of the orginal chlorine content. On the other hand, it may be presumed that the water vapor serves as a carrier gas which will take the chlorine compounds off from the melts in the course of vaporization. This may be largely responsible for the high volatility when a sample contains a significant amount of water, as in the case of the orginal sample. (3) In the case of the mixed gas, the chlorine compounds are continuously volatilized for a fairly long period of heating at 1200°C compared with the case of heating at 1200°C in air. As has already been mentioned above, the sample completely melts in the mixed gas, while in air and at 1200°C crystals of hematite and plagioclase remain in the melted sample. Such crystals are favorably accumulated on the surface of the melt, and we actually observed that the surface of the melt at 1200°C was covered by these crystals after 10 hr. This accumulation on the surface may be an important clue to solving the problem of why the vaporization of chlorine compounds greatly decreases 10 hr after heating at 1200°C in air, as is shown in Table 1. (4) The chlorine compounds volatilize more easily at 1300°C in air than at 1200°C in the mixed gas. This may be due to the difference in temperature, because both samples melt completely.

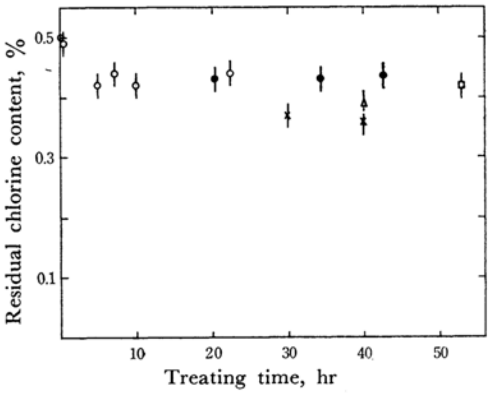

Fig. 3. Change of residual chlorine content of the melt with heating time during the cooling process from 1200°C to 800°C in air.

○ 1200°C ● 1100°C × 1000°C
△ 900°C □ 800°C

The Rate of the Vaporization of Chlorine Compounds from the Basaltic Rock Melt during the Cooling Process. Figure 3 shows the change in the residual chlorine content of the melt with time during the cooling process from 1200 to 800°C in air, marked at intervals of 100°C for each of 10 hr. The width of the lines in Fig. 3 shows the analytical errors in this study. Considering all the experimental errors except the analytical errors, the values of volatility obtained at 1200°C after 10 hr may be said to be almost the same as the other ones at temperatures from 1100 to 800°C. This result may be explained on the grounds already described. According to Shibata and Katsura,9) most of the basaltic rock samples in equilibrium with air and the mixed gas at 1100°C were almost entirely composed of crystals. It may, therefore, be safely said that when the temperature of the liquid basaltic lava falls to 1100°C, the chlorine compounds substantially cease to vaporize from the surface of the lava.

In comparison with natural volcanic phenomena, this seems to be one explanation of the fact that the lava erupted in 1950—1951 from O-sima Volcano shows only a small variation in chlorine content, ranging from 0.029 to 0.036% Cl.5)

Conclusions

The chlorine compounds in the liquid basaltic lava extruded at approximately 1200°C continue to vaporize until the liquid lava is covered with crystals or glassy materials, but after that the chlorine compounds substantially cease to vaporize (about 1100°C being the highest); indeed, the chlorine content may remain constant during the subsequent decrease in temperature.

The authors wish to express their hearty thanks to Professor Iwaji Iwasaki, Tokyo Institute of Technology, who encouraged them throughout the study.

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9) K. Shibata and T. Katsura, read at the Meeting of the Volcanological Society of Japan, November, 1966.