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The Solubility of Hydrogen Chloride in Volcanic Rock Melts at a Total Pressure of One Atmosphere and at Temperatures of 1200°C and 1290°C under Anhydrous Conditions

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The solubility of hydrogen chloride in volcanic rock melts was experimentally determined at temperatures of 1200°C and 1290°C with the variation in the partial pressure of hydrogen chloride mixed with nitrogen under one atmosphere. The solubility of hydrogen chloride decreases not only with a rise in the temperature, but also with an increase in the silica content of volcanic rock melts, while it increases with an increase in the partial pressure of hydrogen chloride. The equilibrated concentration of chlorine obtained by experiments was compared with those in natural basalts collected from Japan and Hawaii.

The volatile components in magma are believed to play important roles in magmatic differentiation, in ore deposition, and in other igneous phenomena. Of these volatile components, water is the most abundant. Many investigations have been made on the solubility of water in igneous rock melts and on the effect of water on the liquidus temperature of igneous rocks.¹⁾ These works showed that only a few weight per cent of dissolved water in silicate melts can significantly depress the liquidus temperature, and that about twenty weight per cent of water can be dissolved in pegmatite melts at 675°C and at 10 kb water pressure.²⁾ A few attempt have previously been made

to determine the effects of other volatile components, such as carbon dioxide, ammonia, hydrogen fluoride, sulfur dioxide, and hydrogen chloride, in the presence of water, on the solidus temperatures of albite and granite.³⁾ These studies have shown that hydrogen chloride in particular affects the rising of the solidus temperature of granite, while, on the contrary, it affects the lowering of the solidus temperature of albite in comparison with the solidus temperature in the presence of water vapor alone. On the other hand, all the other volatile components, except for hydrogen chloride, have the same effects in the case of either granite or albite. No attempt, however, has been made to study the

1) R. W. Goranson, *Am. J. Sci.*, **35**, 71 (1938).

2) C. W. Burnham and R. H. Johns, *ibid.*, **260**, 721 (1962).

3) P. J. Wyllie and O. F. Tuttle, *ibid.*, **258**, 498 (1960); **259**, 28 (1961); **262**, 930 (1964).

solubility of any of these volatile components except water.

The chlorine content of volcanic rocks has been determined by many authors; the results have ranged from 0.00n to 0.0n% Cl.⁴⁾ Iwasaki and Katsura⁵⁾ suggested that the chlorine in volcanic rocks is concentrated in the glassy parts, irrespective of their phenocrystic mineral assemblages. This seems to mean that the chlorine content in rocks is governed by the solubility of chlorine compounds in the liquid lava. If the equilibrium between the gas phase and the condensed phase represented by the liquid lava is maintained at the time of extrusion, the chlorine content of the liquid lava depends largely on the partial pressure of hydrogen chloride in the gas phase and on the temperature of the liquid lava. On the basis of the equilibrium constants of the reactions involving the chlorine compounds and water vapor in the gas phase, it may be said that hydrogen chloride is the most stable species of chlorine compounds at high temperature. In this paper, an attempt will be made to determine the solubility of hydrogen chloride in volcanic rock melts at a total pressure of one atmosphere and at temperatures of 1200°C and 1290°C under anhydrous conditions in order to make clear the reason why the chlorine contents of volcanic rocks show such large variations.

Experimental

Materials. Three fresh volcanic rocks with different chemical compositions were chosen; a basalt extruded in the 1950–1951 eruption from O-sima Volcano, off the Izu Peninsula; an andesite erupted in 1946 from Sakura-jima Volcano, Kagoshima Pref., and a liparite collected from Mt. Tenjyo-zan, Kozu-sima, in the Pacific Ocean south of Tokyo. The chemical compositions of these volcanic rocks are presented in Table 1, together with those reference articles which give petrographic descriptions of the specimens.

In order to check whether or not the equilibrium is established in respect to the solubility of hydrogen chloride at fixed condition, each volcanic rock was treated in the following order: Each original rock sample was crushed in a steel mortar and ground to fineness in an agate mortar. A fraction composed of these finely-powdered rock samples was used as the starting material: (1) the original powdered sample without treatment; (2) a sample which had been made glassy and which contained an adequate amount of chlorine added during the melting of the sample, and (3) a sample which had been made glassy and which contained a very small amount of chlorine. A rock-glass sample was prepared by melting the rock powder

TABLE 1. CHEMICAL COMPOSITION OF VOLCANIC ROCKS USED (Percentage in weight)

	1	2	2
SiO ₂	52.6	61.3	76.8
TiO ₂	1.19	0.74	0.07
Al ₂ O ₃	15.2	17.2	12.9
Fe ₂ O ₃	2.8	1.9	0.02
FeO	10.4	4.6	0.72
MnO	0.23	0.16	0.06
MgO	4.9	2.7	0.33
CaO	9.8	6.1	0.24
Na ₂ O	2.08	3.59	4.16
K ₂ O	0.45	1.60	3.18
H ₂ O(–)	0.1	0.2	0.00
H ₂ O(+)	0.3	0.3	0.95
P ₂ O ₅	0.12	0.04	0.07
Total	100.2	100.4	99.5

- 1) Augite-hypersthene-bytownite basalt, erupted in 1950–1951 from O-shima Volcano, Tokyo Metr.
- 2) Two pyroxene-labradorite andesite, erupted in 1946 from Sakura-jima Volcano, Kagoshima Pref.
- 3) Biotite plagioliparite, collected from Mt. Tenjyo-zan, Kozu-sima in the Pacific Ocean south of Tokyo. Analyst: H. Haramura.

in a platinum crucible by a Globar furnace in the air for 3 hr at 1400–1500°C, and then by dipping the melted sample into water as soon as possible. The rock-glass sample containing an adequate amount of chlorine was prepared as follows: The rock-glass powdered sample was thoroughly mixed with a certain amount of an aqueous sodium chloride solution in an agate mortar, dried at 110°C for 12 hr, then heated at 800°C for 12 hr, and after cooling, it was tapped into an 80%Pt-20%Rh tube welded at one end. The tube was sealed at the other end with an electric arc welder and then heated at 1200 to 1300°C for 30 min to 2 hr. After heating, it was quenched in water.

Furnace and Temperature Controls. A vertical-tube quench furnace with an 80%Pt-20%Rh winding was used for the equilibration runs. The furnace and its attachments are shown in Fig. 1. The furnace temperature was kept constant to approximately $\pm 5^\circ\text{C}$ by means of an electrical controller coupled with a Pt-87%Pt, 13%Rh thermocouple inserted close to the hot spot of the furnace. The other temperature-control system is similar to that adopted by Katsura and Kimura.⁶⁾

The Control of the Atmosphere. Atmospheres of the desired hydrogen chloride pressures were obtained by using pure hydrogen chloride and hydrogen chloride-nitrogen mixtures. The hydrogen chloride-nitrogen mixtures were prepared by proportioning the two gas components in the desired ratios in a gas mixer similar in principle to that described by Darken and Gurry.⁷⁾ The equilibrated partial pressure of hydrogen chloride

4) W. Behne, *Geochim. et Cosmochim. Acta*, **3**, 186 (1953); P. K. Kuroda and E. B. Sandell, *Bull. Geol. Soc. Am.*, **64**, 879 (1953); I. Iwasaki, T. Katsura, N. Sakato and M. Hirayama, *Nippon Kagaku Zasshi*, (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **73**, 164 (1957).

5) B. Iwasaki and T. Katsura, *This Bulletin*, **37**, 1827 (1964).

6) T. Katsura and S. Kimura, *ibid.*, **38**, 1664 (1965).

7) L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945).

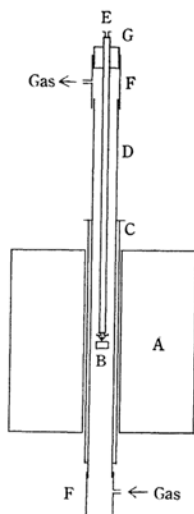


Fig. 1. Electric furnace and its attachments.

- A Electric furnace
- B Platinum envelope
- C Mullite tube
- D Silica tube
- E Platinum wire
- F Glass-made attachment
- G Mullite tube

at a desired temperature was virtually identical to the initial partial pressure, since the dissociation of hydrogen chloride to H_2 and Cl_2 is negligibly small for the present purposes.⁸⁾ The gases were passed through the furnace from bottom to top, the linear flow rate being kept at 14 mm per second.

Run Procedure. About 0.1 g of each sample, packed into a 0.22 cc Pt thin envelope, was suspended by a thin platinum wire in the center of the furnace. In the case of a powdered sample which had been made glassy with an adequate amount of chlorine, it was first suspended in the cool top of the furnace tube, and then pure hydrogen chloride or a gas mixture was conducted at a fixed linear flow rate through the tube into the furnace. In the latter case, after the tube had been flushed for a sufficient time, the charge was lowered until it was approximately centered in the furnace. After equilibrium was attained among gas and condensed phases, the sample was rapidly quenched into the glass-made jacket cooled by ice by burning away the thin platinum wire with an electric current.

The Identification of Phases and Chemical Analysis. The phases present in the quenched samples were identified by a polarized microscope. The total chlorine in the quenched samples was determined by the method of Iwasaki *et al.*⁹⁾ with some improvements, while the water-soluble chlorine in the quenched samples was determined by the thiocyanate method previously described.^{5,10)}

8) K. K. Kelley, *U. S. Bur. Mines*, No. 584, 1960.
 9) I. Iwasaki, T. Katsura and N. Sakato, *Nippon Kagaku Zasshi*, (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **76**, 1116 (1955).
 10) A. Tomonari, *ibid.*, **83**, 693 (1962).

Results

Table 2 gives the results of the equilibration runs, together with the maximum uncertainties in the measurements. All samples were of clear glasses after quenching from 1200°C, except for the case of liparite, and all the samples were completely in a glassy state at 1290°C. The experiments also showed that there was only a very small amount of water-soluble chlorine in some quenched samples; thus we can neglect the amount of water-soluble chlorine for the present purposes.

The Check of the Equilibration. To check the establishment of the equilibrium, the three kinds of materials, which had been treated differently as has already been described, were used as the starting materials for equilibration runs. In Fig. 2, the chlorine content dissolved in the

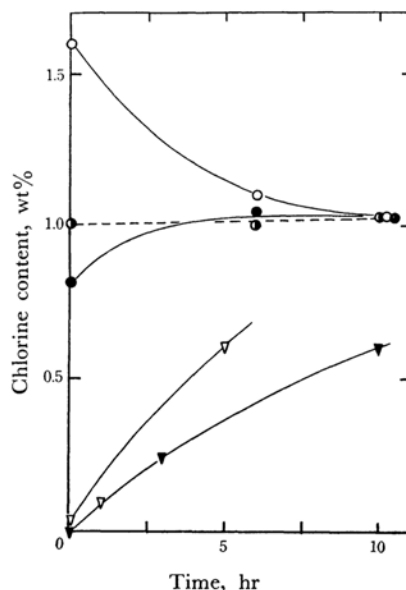


Fig. 2. Saturation time and chlorine content in basalt melt at 1290°C and 1 atm of HCl.

- ▽ Rock sample
- ▼ Rock-glass sample
- } Rock-glass sample containing an adequate amount of chlorine compounds
- }

quenched samples of the basalt is shown against the treating time for saturation with hydrogen chloride of 1.00 atm at 1290°C. As may be seen in Fig. 2, an equilibrium state was not attained even after 10 hr whenever we used the original or a rock-glass sample in which the chlorine content is significantly small compared with the equilibrated chlorine content. This was the case with basalt and andesite, while in the case of liparite, the equilibrium was reached in only 6 hr at the same temperature. On the other hand, if we used a rock-glass sample containing an adequate amount

TABLE 2. SOLUBILITY OF HYDROGEN CHLORIDE IN BASALT, ANDESITE, AND LIPARITE MELTS

Material	Temp., °C	P_{HCl} , atm ^{*1}	C_{HCl} , molality ^{*2}
Basalt melt	1290±5	1.00	0.29±0.01
	1290±5	0.100±0.001	0.061±0.001
	1290±5	0.030±0.002	0.027±0.001
	1200±5	1.00	0.41±0.02
Andesite melt	1290±5	1.00	0.091±0.005
	1290±5	0.030±0.002	0.0073±0.0005
	1200±5	1.00	0.119±0.005
Liparite melt	1290±5	1.00	0.0119±0.0003
	1200±5 ^{*3}	1.00	0.0152±0.0005

*1 P_{HCl} means an equilibrium partial pressure of hydrogen chloride at each temperature.

*2 C_{HCl} means the solubility of hydrogen chloride in melts in terms of molality (number of moles per 1 kg of melt).

*3 This quenched sample contained small amounts of feldspar and silica minerals.

of chlorine, the equilibrium was, without exception in the present study, virtually reached in only 10 hr over a wide range of chlorine content.

It is also necessary to check the loss of the chemical components from the melts during equilibration runs, because a number of metal chlorides have appreciable vapor tensions at high temperatures, and also the solubility of hydrogen chloride changes with a change in the composition of a melt. Thus the apparent or partial equilibrium state may be recognized as a result of the competition between the rate of the diffusion of hydrogen chloride into the condensed phase and the rate of the escaping tendency of metal chlorides into the gas phase if we adopt the present technique. A total chemical analysis was made to determine the rate of loss of each component during runs for every 6 hr period; the results will be published elsewhere. The important results for the present study are that the amounts of chemical components lost from the melts increase with an increase in the treating time, and that considerable amounts of alkali compounds and moderate amounts of iron compounds are mainly lost during the first 6 hr of treatment. On the other hand, the saturation time necessary for an equilibrium state becomes shorter when the starting material contains chlorine nearer to the saturation value, which may be estimated by repeated preliminary experiments. Thus, after an approximate saturation value had been estimated, it was corrected by careful equilibration runs, as is shown in Fig. 2.

Discussion

Change in Solubility with the Partial Pressure of Hydrogen Chloride. Figure 3 is drawn on the log-log relation in order to find the relationship between the solubility of hydrogen chloride in volcanic rock melts and its partial pressure at 1290°C. Two straight lines of about the same

slope are observed and are expressed as logarithmic functions as follows:

$$\log C_{\text{HCl}} = 0.63 \log P_{\text{HCl}} - 0.538 \quad \text{for basalt}$$

$$\log C_{\text{HCl}} = 0.72 \log P_{\text{HCl}} - 1.041 \quad \text{for andesite}$$

where C_{HCl} is the solubility of hydrogen chloride in the melt expressed by molality, and P_{HCl} is the equilibrium partial pressure of hydrogen chloride at 1290°C in terms of atmosphere. Judging from the mean slope, 0.68, of these equations, the solubility of hydrogen chloride in the melt is considered to be proportional to two-thirds the power of its partial pressure. On the other hand, two laws on the solubility of gas in a liquid are known;

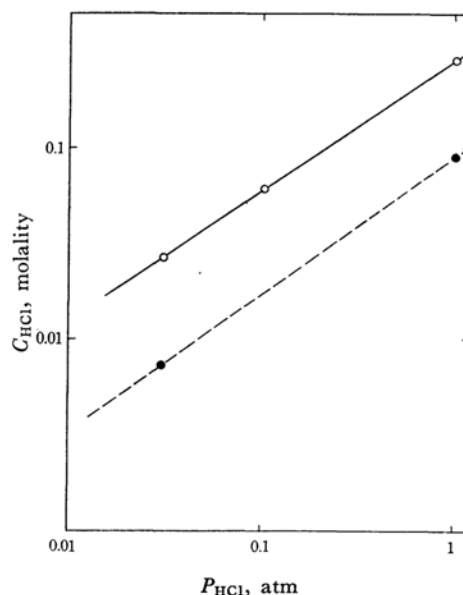


Fig. 3. Change of solubility with partial pressure of HCl at 1290°C.

○ Basalt melt

● Andesite melt

one is Henry's law, and the other is Sievert's law.¹¹⁾ In the latter case, the solubility is proportional to the square root of the partial pressure of the gas. Figure 4 shows the relationship between the curve experimentally obtained in the present study and the two lines which follow the two laws. As is shown in Fig. 4, the melt with more than 0.03 M of hydrogen chloride significantly deviates from the ideality of these laws.

Change in Solubility with the Chemical Composition of the Melt. Figure 5 shows the change in the solubility of hydrogen chloride with the silica content of the volcanic rock melts at 1 atm of hydrogen chloride and at 1200 and 1290°C. It is clear from Fig. 5 that both straight lines have about the same slope. These lines are expressed by the following equations:

$$\log C_{\text{HCl}} = 2.50 - 0.058 C_{\text{SiO}_2} \quad \text{at } 1290^\circ\text{C and}$$

$$\log C_{\text{HCl}} = 2.71 - 0.059 C_{\text{SiO}_2} \quad \text{at } 1200^\circ\text{C}$$

where C_{SiO_2} is the silica content of the melt in terms of weight per cent. These relationships indicate that the solubility of hydrogen chloride in the melt decreases with an increase in the silica content of the melts. In other words, the solu-

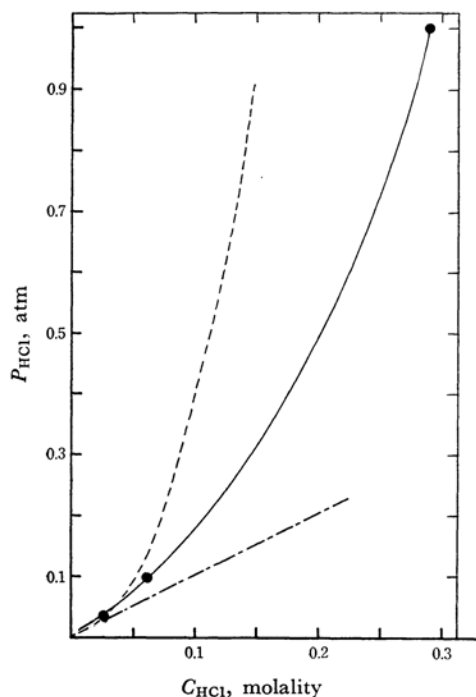


Fig. 4. Experimental solubility curve.

- Experimental curve in basaltic melt at 1290°C
- - - Curve derived from Henry's law
- - - Curve derived from Sievert's law

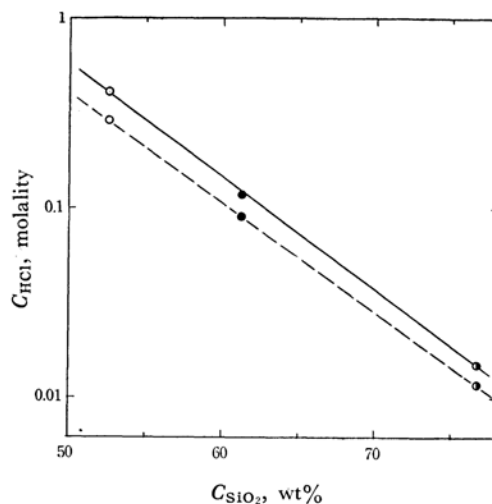


Fig. 5. Change of solubility with the silica content of melts.

- Basaltic melt
- Andesitic melt
- ◐ Liparitic melt
- Curve at 1200°C
- - - Curve at 1290°C

bility of hydrogen chloride in the melt seems to increase with an increase in the total cation content, except for the silicon of the melts.

Change in Solubility with the Temperature.

As is shown in Fig. 6, a lower solubility with an increase in the temperature was consistently found in three kinds of melts with different chemical compositions.

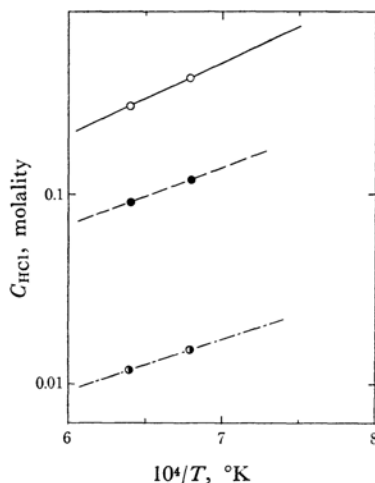


Fig. 6. Change of solubility with temperature.

- Basaltic melt
- Andesitic melt
- ◐ Liparitic melt

Since the experiments were carried out at only two different temperatures, it was impossible to justify the thermodynamic relationship between the

11) L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals," McGraw-Hill, New York (1953), p. 132.

TABLE 3. SOLUBILITY OF GASES IN SILICATE MELTS UNDER 1 ATM

Gas species	Material	Temp., °C	Molality in melt	$\bar{L}^{1)}$	Remark
He* ¹	Alkali silicate	1200—1480	0.00007—0.00011	—	K, Na, Li
H ₂ O* ²	Alkali and alkali earth silicate	1250—1700	0.026—0.15	±	K, Na, Li, Ba
HCl	Volcanic rocks	1200—1290	0.0119—0.41	+	basalt, andesite, liparite
CO ₂ * ³	Sodium silica	900—1300	0.0002—1.09	+	

1) $\bar{L} = \bar{H} + H^0$ means the relative partial molal enthalpy of solution.

*¹ H. O. Mulfinger and H. Scholze, *Glastech. Ber.*, **35**, 466 (1962).

*² H. Franz and H. Scholze, *ibid.*, **36**, 347 (1963) and C. R. Kurkjian and L. E. Russell, *J. Soc. Glass Technology*, **42**, 130 (1958).

*³ M. L. Pearce, *J. Am. Ceram. Soc.*, **47**, 342 (1964).

solubility and the temperature. Assuming, however, that the solubility is inversely proportional to the temperature,¹²⁾ the following empirical equations may be obtained:

$$\log C_{\text{HCl}} = 3.8 \times 10^3/T - 3.00 \quad \text{for basalt}$$

$$\log C_{\text{HCl}} = 3.0 \times 10^3/T - 2.95 \quad \text{for andesite}$$

and

$$\log C_{\text{HCl}} = 2.7 \times 10^3/T - 3.66 \quad \text{for liparite,}$$

where T is the absolute temperature.

Judging from the slope of the equations, it is clear that the relative partial molal enthalpies of a solution have positive values if the following equation holds in the present study:

$$R \ln a = \bar{L}/T + \text{constant},$$

where $\bar{L} = \bar{H} - H^0$, as defined by Lewis and Randall,¹³⁾ where $a = C_{\text{HCl}} \times \gamma_{\text{HCl}}$ is the activity of hydrogen chloride in the melt; γ_{HCl} is the activity coefficient of hydrogen chloride, and where R is the gas constant.

A Comparison with the Solubility of Some Other Gas Species in Silicate Melts. Many studies of the solubility of gas species in silicate melts have been carried out because of its importance in glass-refining and metallurgy. Table 3 compares the observed solubility of hydrogen chloride with those of some other gas species in silicate melts with respect to the magnitude of their values, their temperature effects, and their variation with the chemical composition.

As has been mentioned already, the temperature effect on the solubility is expressed by the relative partial molal enthalpy of a solution as defined by Lewis and Randall;¹³⁾ it changes from a negative to a positive value in harmony with the increasing magnitude of the solubility. In other words, the solubility of helium increases with an increase

in the temperature, while the solubility of carbon dioxide and hydrogen chloride decreases with an increase in the temperature, as may be seen in Table 3.

The solubility of these gas species in the silicate melts depends on the chemical composition at a fixed temperature; it decreases in the order of going from left to right in the last column of Table 3. For instance, the solubility of helium in a potassium silicate is the highest, sodium silicate is next, and the lowest is in lithium silicate so far as these three are concerned. It has been reported¹⁴⁾ that the solubilities increase with an increase in the alkali or alkali earth content except for helium, and that water vapor and carbon dioxide dissolve as hydroxide and carbonate ions in the silicate melts respectively.¹⁵⁾ Thus, it may be assumed that such gases as water vapor and carbon dioxide are more soluble in a silicate melt containing larger amounts of the ionic compounds, such as alkali oxides, because of the ionic character of both the solvent and the solute. On the basis of this same assumption, the solubility of hydrogen chloride may be explained as increasing with an increase in the total cation content, except for the silicon content.

An Estimation of the Chlorine Content of Liquid Lava by Means of the Magmatic Gas Composition. As has already been described, the chlorine content of a liquid lava immediately after extrusion may be estimated on the basis of the solubility of hydrogen chloride in the volcanic rock melt, provided that the hydrogen chloride content of the gas phase in contact with the liquid lava, the temperature, and the total pressure of the gas phase can be observed. This estimation has, however, two main problems, concerning the liquid-gas equilibria in a magmatic state and the method of collecting the magmatic gas without

14) H. Franz and H. Scholze, *Glastech. Ber.*, **35**, 466 (1962); M. L. Pearce, *J. Am. Ceram. Soc.*, **47**, 342 (1964).

15) J. W. Tomlinson, *J. Soc. Glass Tech.*, **40**, 25 (1956); H. Franz and H. Scholze, *Glastech. Ber.*, **36**, 347 (1963); M. L. Pearce, *J. Am. Ceram. Soc.*, **47**, 342 (1964).

12) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York (1961), p. 227.

13) Cf. Ref. 12, p. 393.

TABLE 4. THE CHLORINE CONTENT OF MAGMATIC GASES AND THE ESTIMATED CHLORINE CONTENT OF THE LIQUID LAVAS IN HAWAII AND O-SHIMA VOLCANOES

Sample (date)	P_{HCl} , atm.	Cl wt% of lava
Kilauea* ¹		
S—7 (1917)	0.0050 (obs.)	0.053 (calcd.)
J—8 (1918)	0.0008 (obs.)	0.014 (calcd.)
J—18 (1919)	0.0026 (obs.)	0.035 (calcd.)
rock (1919)* ²	0.0014 (calcd.)	0.02 (obs.)
O-Sima		
condensed water	0.034 (obs.)	0.21 (calcd.)
rock (1950—1951)* ⁴	0.0019—0.0026 (calcd.)	0.029—0.036 (obs.)

*¹ Halemaumau lava lake in 1917—1919, Kilauea at 1200°C, 1 atm.

*² SiO₂ content is 50.19 wt%.

*³ Chlorine content is 67.6 g Cl/l, and temperature of the lava is 1150°C at 1 atm.

*⁴ SiO₂ content is 52.6 wt%.

any contamination. In fact, there are very few available data for estimating the partial pressure of hydrogen chloride in magmatic gases. In Table 4, the estimated chlorine content of liquid lava is given in the cases of Kilauea, Hawaii, and O-sima Volcano, Japan, based on the observed chlorine content of the magmatic gases. For Kilauea, there are many data on the magmatic gases collected by Shepherd¹⁶⁾ and Jagger¹⁷⁾ during 1917—1919 from the Halemaumau lava lake. Some of these data have been considered to be excellent.¹⁷⁾ The maximum of these excellent values at each of three different periods was employed for the estimation of the chlorine content of the liquid lava, as is shown in Table 4. The volume per cent of chlorine in the original paper is recalculated as the partial pressure of hydrogen chloride, P_{HCl} (obs.), in Table 4. The calculated chlorine content of liquid lava in Table 4 was based on the hydrogen chloride content of magmatic gas, the following assumption being made: (1) the equilibrium was maintained between the gas phase and the liquid lava, (2) the slope of the equation of the partial pressure effect on the solubility is 0.68, independent of the temperature and the presence of water vapor, and (3) all the equations for solubility obtained previously can be applied, even though there were small amounts of minerals in the silicate melts. Table 4 also gives the calculated partial pressure of hydrogen chloride in the magmatic gas, P_{HCl} (calc.), based on the observed chlorine content of the volcanic rock in the same eruption. In the case of the O-sima Volcano, there is only one datum, that of condensed water collected by Iwasaki *et al.*¹⁸⁾ in the 1951 eruption. The temperature of the lava flow has, however, been recorded to be 1050—1200°C by other investiga-

tors.¹⁹⁾ Thus the calculated hydrogen chloride content of the magmatic gas was estimated at 1150°C and at a total pressure of 1 atm. The chlorine content of the volcanic rocks in the 1950—1951 eruption has been reported by Iwasaki and Ozawa²⁰⁾ to range from 0.029 to 0.036% Cl.

In Kilauea, the calculated chlorine content of the 1919 lava is 0.035% Cl, based on the observed partial pressure of hydrogen chloride, while the analytically observed chlorine content of the 1919 lava was 0.020% Cl.¹⁶⁾ In a previous paper,⁵⁾ we pointed out that the distribution of chlorine in one flow unit of a lava is surprisingly homogeneous, and that the value of 0.020% Cl in rocks of the 1919 eruption is highly significant and never rises as high as 0.035% Cl, the calculated chlorine content of the 1919 lava. Alternatively, if we calculate the partial pressure of hydrogen chloride in magmatic gas based on the observed chlorine content of the 1919 lava, we obtain the value of 0.0014 as P_{HCl} (calc.) in Table 4. This calculated value agrees well with the datum¹⁷⁾ of J-16 in the 1919 eruption, 0.0014 as P_{HCl} (obs.), which is not listed in Table 4. From these equilibrium calculations, we may say that, during the cooling process of the liquid lava after extrusion, the equilibrated chlorine content of the 1919 liquid lava, 0.035% Cl, was reduced to 0.02% Cl, and that about 40% of the original chlorine content was lost, as some volatile chlorine compounds, from the solidifying lava into the air. In the case of the O-sima Volcano, if the same assumption is applied, it may be said that about 80% of the original chlorine content was lost during the cooling process of the liquid lava.

Conclusion

From the preceeding discussion, we may conclude that:

- 16) E. S. Shepherd, *Am. J. Sci.*, **35A**, 311 (1938).
- 17) T. A. Jagger, *ibid.*, **238**, 313 (1940).
- 18) I. Iwasaki, T. Katsura, H. Shimojima, T. Ozawa, T. Tarutani and K. Sato, *Bull. Volcanol. Soc. Japan, Ser. II*, **3**, 70 (1958).

- 19) T. Minakami, *Bull. Earthq. Res. Inst.*, **29**, 487 (1951).

- 20) I. Iwasaki and T. Ozawa, read at the Meeting of the Volc. Soc. Japan, May, 1959.

1) the solubility of hydrogen chloride in volcanic rock melts increases linearly with an increase in the partial pressure of hydrogen chloride on the log-log scale;

2) the logarithms of the solubility of hydrogen chloride in volcanic rock melts decrease linearly with an increase in the silica content of melts;

3) the solubility of hydrogen chloride in volcanic rock melts decreases with an increase in the temperature, and;

4) the chlorine content of liquid lava can be

estimated on the basis of the solubility relationships, provided that the temperature, the total pressure, and the hydrogen chloride content of magmatic gas in equilibrium with liquid lava are known.

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