The Vertical Distribution of Chlorine in a Lava Flow from the O-sima Volcano in the Izu Islands

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The horizontal distribution of chlorine in a lava flow has been reported by Iwasaki and Ozawa.[1] They found that the chlorine content of approximately 120 rock samples was quite homogeneous irrespective of the appearance and locality of the samples.

The vertical distribution of chlorine in a lava flow has also been studied by Kuroda and Sandell,[2] and Yoshida et al.[3] The number of rock samples employed in their studies was too small to permit a detailed study to be made.

Recently, many core holes were drilled in the northwestern part of the O-sima caldera in the Izu Islands. The drill-hole samples were studied by Issiki et al.[4] from standpoints of geology, geophysics, and petrography. As one of the results of their studies, several thick basaltic lava flows were distinguished.

We have determined the chlorine content of two of those lava flows in order to study the vertical distribution of chlorine in such a volcanic body. In addition, the uniformity of major chemical components in the two lava flows is discussed on the basis of the total iron content.

Experimental

Selection and Preparation of Rock Samples.— The rock samples of the two lava flows used in this study originated from two core holes, termed

1) I. Iwasaki and T. Ozawa, read at the Meeting of the Volcanological Society of Japan, May, 1959.

2) P. K. Kuroda and E. B. Sandell, *Bull. Geol. Soc. Am.*, **64**, 879 (1953).

3) M. Yoshida, T. Ozawa and T. Katsura, read at the Meeting of the Volcanological Society of Japan, March, 1963.

4) N. Issiki, K. Nakamura, M. Hayakawa, K. Hirasawa, T. Yukutake, Y. Arai and B. Iwasaki, *Bull. Volcanological Soc. Japan, 2nd Series*, **8**, 61 (1963).

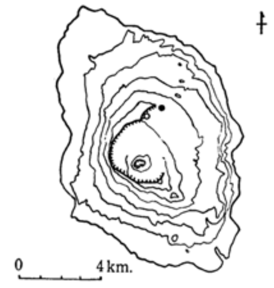

Fig. 1 The locations of the two core holes.
● OH 1 ○ OY 4

OH 1 and OY 4, respectively. The locations of those core holes are given in Fig. 1.

These drill-hole samples, weighing about 1 kg., were taken at about 2 m. intervals through the lava flow. A total of 65 samples, involving 38 samples in one lava flow (OH 1-2) and 27 samples in the other lava flow (OY 4-2), was collected. About 15 g. of each core-hole sample was selected for chemical analysis from the central part of the core to avoid cavities. Then, these rock samples were crushed in a steel mortar and ground to fineness in an agate mortar. In particular, precaution was taken throughout the whole procedure of selection and preparation of rock samples, to avoid any possibility of chlorine contamination.

Method of Analysis.—Two or more repeated determinations of the total chlorine content in each rock sample were made by the method of Iwasaki et al.[5] with some improvements, while the water-soluble chlorine in the rock was determined by the thiocyanate method,[6] according to the procedure previously described.[7] By these methods, it is possible to ascertain the chlorine content of the rock within a precision of $\pm 5\%$ for the whole range analyzed.

The total iron in the rock was determined colorimetrically by the α, α'-dipyridyl method,[8] within a precision of $\pm 1\%$ in a range of 10.0 to 15.0%.

Results and Discussion

The Uniformity of the Two Lava Flows.—According to the geological observations of Issiki et al.,[4] the two lava flows involved in this study are considered to be uniform, on accunt of the smallness and rareness of phenocrysts such as olivine and augite, and to have formed through ponding into a depression on the caldera floor.

The uniformity of a lava flow can also be determined by the method of Iwasaki et al.,[9] involving chemical analysis. Their results have shown that determination of one of the major chemical components, in a large number of samples from the lava flow, is useful in deciding whether a lava flow containing infrequent and small phenocrysts is uniform in major chemical composition. Accordingly, the total iron contents in each of 14 rock specimens were determined to ascertain the uniformity of the two lava flows. The results obtained are shown in Table I.

TABLE I. THE TOTAL IRON CONTENT IN THE TWO LAVA FLOWS

Sample	Fe_2O_3*, %
OH 1-2-1	14.1
OH 1-2-3	14.4
OH 1-2-9	14.3
OH 1-2-14	14.3
OH 1-2-17	14.4
OH 1-2-20	14.4
OH 1-2-23	14.4
OH 1-2-25	14.2
OH 1-2-31	14.1
OH 1-2-34	14.4
OH 1-2-38	14.3
OH 1-2[4]	14.4
Mean value	14.3_1
Standard deviation	0.11
OY 4-2-1	14.0
OY 4-2-12	14.0
OY 4-2-27	14.0
OY 4-2[4]	14.1
Mean value	14.0_3

Fe_2O_3*: Total iron content

In the case of OH 1-2, the total iron content (as Fe_2O_3) ranges from 14.1 to 14.4%, and in the case of OY 4-2, from 14.0 to 14.1%. Judging from the total iron content, the two lava flows are considered to be uniform in major chemical composition.

Chlorine Content.—The total chlorine content in the rock samples from the two lava flows are shown in Table II.

The rock samples analyzed are presented in order of increasing depth beneath the surface. The water-soluble chlorine in the rock was determined to see whether chlorine is present by contamination in the rock specimens. The results obtained are shown in Table III.

The water-soluble chlorine content in 9 rock samples ranges from 0.001 to 0.003%. As this amount of water-soluble chlorine is normally present in fresh rock specimens,[2,10] it may be said that the chlorine in these rock samples does not come from the cooling water applied

5) I. Iwasaki, T. Katsura and N. Sakato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 778 (1955).
6) A. Tomonari ibid., **83**, 693 (1962).
7) B. Iwasaki and T. Katsura, This Bulletin, in press.
8) M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941).
9) I. Iwasaki, T. Katsura, T. Ozawa, M. Yoshida, M. Mashima, H. Haramura and B. Iwasaki, *Bull. Volcanological Soc. Japan, 2nd Series*, **5**, 9 (1960), etc.
10) I. Iwasaki, T. Katsura, N. Sakato and M. Hirayama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1116 (1955).

TABLE II. THE TOTAL CHLORINE CONTENT IN THE TWO LAVA FLOWS

Sample	Depth, m. beneath the surface	T-Cl, %	Sample	Depth, m. beneath the surface	T-Cl, %
OH 1-2-1	37.1	0.009	OH 1-2-34	105.0	0.013
OH 1-2-2	39.0	0.011	OH 1-2-35	107.2	0.012
OH 1-2-3	41.0	0.017	OH 1-2-36	110.0	0.011
OH 1-2-4	42.8	0.016	OH 1-2-37	111.5	0.010
OH 1-2-5	46.0	0.016	OH 1-2-38	112.2	0.012
OH 1-2-6	48.0	0.017	OY 4-2-1	63.3	0.020
OH 1-2-7	50.0	0.016	OY 4-2-2	65.0	0.016
OH 1-2-8	52.0	0.015	OY 4-2-3	67.0	0.014
OH 1-2-9	54.0	0.015	OY 4-2-4	69.1	0.012
OH 1-2-10	56.7	0.016	OY 4-2-5	71.1	0.014
OH 1-2-11	58.7	0.017	OY 4-2-6	73.0	0.012
OH 1-2-12	60.0	0.015	OY 4-2-7	75.1	0.013
OH 1-2-13	62.0	0.016	OY 4-2-8	77.0	0.011
OH 1-2-14	64.6	0.019	OY 4-2-9	79.0	0.013
OH 1-2-15	67.5	0.016	OY 4-2-10	81.0	0.012
OH 1-2-16	69.2	0.019 S	OY 4-2-11	83.0	0.012
OH 1-2-17	71.0	0.020 S	OY 4-2-12	85.0	0.012
OH 1-2-18	73.0	0.019 S	OY 4-2-13	87.0	0.015
OH 1-2-19	75.0	0.016	OY 4-2-14	89.0	0.013
OH 1-2-20	77.0	0.014	OY 4-2-15	91.0	0.014
OH 1-2-21	79.0	0.017	OY 4-2-16	93.0	0.012
OH 1-2-22	81.0	0.019	OY 4-2-17	95.0	0.013
OH 1-2-23	83.0	0.020 S	OY 4-2-18	97.0	0.014
OH 1-2-24	85.0	0.016	OY 4-2-19	99.0	0.012
OH 1-2-25	87.0	0.014	OY 4-2-20	101.0	0.012
OH 1-2-26	89.1	0.014	OY 4-2-21	103.0	0.013
OH 1-2-27	91.0	0.014	OY 4-2-22	105.0	0.012
OH 1-2-28	93.0	0.013	OY 4-2-23	106.9	0.013
OH 1-2-29	95.0	0.012	OY 4-2-24	109.3	0.011
OH 1-2-30	97.0	0.011	OY 4-2-25	111.0	0.011
OH 1-2-31	99.0	0.010	OY 4-2-26	113.0	0.013
OH 1-2-32	101.0	0.012	OY 4-2-27	115.1	0.011
OH 1-2-33	103.0	0.011			

T-Cl: Total chlorine content S: Spots

TABLE III. THE WATER SOLUBLE CHLORINE CONTENT IN THE TWO LAVA FLOWS

Sample	W-Cl, %
OH 1-2-1	0.0007
OH 1-2-9	0.0023
OH 1-2-14	0.0029
OH 1-2-17	0.0028
OH 1-2-20	0.0034
OH 1-2-23	0.0017
OH 1-2-31	0.0014
OH 1-2-38	0.0011
OY 4-2-15	0.0020

W-Cl: Water-soluble chlorine content

to drill holes, etc. Figures 2 and 3 show the relationship between the chlorine content of the rock samples and the depth of the drill core.

The chlorine content of the rock samples from one lava flow (OY 4-2) ranges from

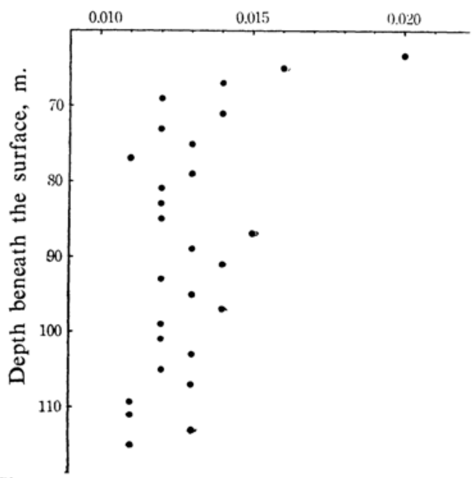

Fig. 2. Relation between the chlorine content of rock samples and the depth of drill core (OY 4-2).

0.011 to 0.020%, and averages 0.012%. It has been reported by Issiki et al.[4] that the base of this lava flow has been intruded by a dike. However, because of the low heat conductivity of rock, it is considered that the effect of this dike intrusion would have introduced no serious change in the vertical distribution of chlorine in the lava flow. Provided that the chlorine content of the basement rock is the same as that of the lower region of the lava flow. With the exception of two rock samples, all the samples would have a nearly uniform chlorine content. The two exceptional samples had been collected from the uppermost parts and are red

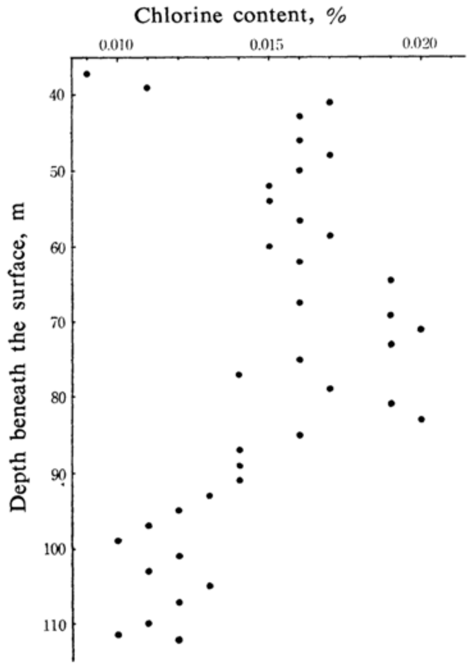

Fig. 3. Relation between the chlorine content of rock samples and the depth of drill core (OH 1-2).

in color. The presence of sublimates containing halogen compounds in these samples might explain the high amount of chlorine present.

On the other hand, the chlorine content of the rock samples from the other lava flow (OH 1-2) ranges from 0.009 to 0.020% and averages 0.014%. As seen from Fig. 3, the variation of chlorine is as follows: the chlorine content increases from the lower part to the middle part, and then, slightly decreases towards the uppermost part, where the chlorine content shows much lower values. The chlorine content in the rock samples from the uppermost parts shows a striking contrast to that found in similar regions of OY 4-2. Some of the rock specimens from the middle parts of the lava flow (OH 1-2) possess many cavities (showing the presence of volatile components) and many spots, which consist of glasses about 0.5 mm. in diameter, according to the microscopic observations of Issiki.* Furthermore, most of the rock specimens possessing these spots show higher amounts of chlorine, as seen in Table II, while the rock samples without the spots show lower amounts of chlorine. Since the former samples are not particularly enriched with apatites, it is considered that a relationship exists between the extent of occurrence of these spots and the chlorine content of the rock samples. Thus, the enriched chlorine content of the middle part is considered to be due to the fixation of chlorine in the glass, rather than the contribution of apatite as a chlorine carrier. A possible explanation for the vertical variation of chlorine content in the lava flow might be as follows: at high temperatures, the lava flow builds up to a thickness of about 76 m. during a short time, and then, begins to cool rapidly from the outside, i. e., the upper part and the lower part. This is supported by the fact that the crystals in the ground masses are very small and phenocrysts have not accumulated at the base. During such a cooling process, chlorine compounds may vaporize and be lost from the surface of the lava to the air; this would encourage diffusion of the chlorine compounds from the lower part to the upper part, and a concentration gradient of chlorine compounds would result in the lower and middle parts of the lava. As the chlorine compounds in the melt are prevented from escaping by the solidified lava surface, they would tend to diffuse downwards to be distributed uniformly in the melt. However, the diffusion rate in the lower part would be decreased by solidification of the lava in this region. Accordingly, the concentration gradient of chlorine compounds in the lower part may remain unchanged during solidificantion of the melt, whereas chlorine compounds in the melt at the upper and middle parts may be distributed uniformly. On the other hand, as the solidifying uppermost lava is heated by the underlying melt, chlorine compounds may be vaporized from the surface of the lava to the air. In this way, the solidification of the lava proceeds. At the final stage of the cooling process, those portions of the lava melt containing a high amount of chlorine compounds solidify as glasses, because chlorine compounds do not enter the rockforming minerals except apatite in this case.

Frequency Distribution of Chlorine Content.— Figure 4 shows two cumulative distributions of the chlorine content in the two lava flows

* Personal communications.

(OH 1-2, OY 4-2) and also shows that for the 1950—1951 lava in O-sima for comparison.

They show approximately normal distributions. In other words, a frequency distribution of the chlorine content in a lava flow seems to show a normality. This contrasts exceedingly with the frequency distributions found for the chlorine content in many lava flows in other regions, for example, Hawaiian and Japanese lava flows[7,10] show a lognormality. Perhaps, the difference is due to the much larger variation of the chlorine content in the latter than in the former. As seen from the slope of the lines in Fig. 4, OH 1-2 shows the largest variation, while OY 4-2 shows a variation close to that of the 1950—1951 lava. Judging from the latter fact, the formation of OY 4-2 may have been by a repeated accumulation of thin layers, as in the 1950—1951 lava, rather than by the generation of a lava lake.

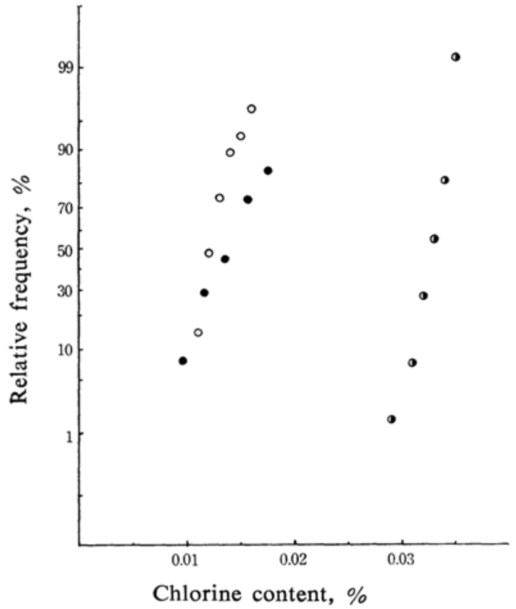

Fig. 4. The frequency curves on normal probability paper.
○ OY 4-2 ● OH 1-2
◑ the 1950—1951 lava

Conclusion

1) The chlorine content of the first lava flow (OY 4—2) is uniform with some exceptions.

2) The chlorine content of the second lava flow (OH 1—2) shows a vertical variation, increasing from the lower part to the middle part and decreasing towards the uppermost part.

3) The enrichment of chlorine in the middle part of the second lava flow is con sidered to be due to the fixation of chlorine in the glass.

4) The frequency diagrams of the chlorine content in the two lava flows show approximately normal distributions.

5) The two lava flows are uniform on the basis of total iron content.

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