Geochemical Investigations of Volcanoes in Japan. LII. Vanadium Content of the Lava Flow in 1950—1951 from Volcano Ō-sima, Izu, Japan***

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Since the beginning of the twentieth century, the contents of various elements in volcanic rocks have been determined and these data have been compared with one another. A comparison of these data depends on the assumption that the contents of these elements in one volcanic body, such as one lava flow, are uniform[1]. An experimental approach to these uniformities has not yet been made systematically, but Grout[2] studied the method of selection and preparation of granite and other rock samples without consideration of the error in chemical analysis. Brown et al.[3] found the uniformity of Moune granite G-2 without regard to the selection and preparation of rock samples.

As a part of the geochemical study at our laboratory, an attempt has been made to show whether the contents of various elements in one lava flow are uniform or not, to determine the relation between the contents of these elements and the external appearance of rocks, and to examine the method of selection and preparation of rock samples from a large volcanic body for chemiacl analysis.

In the previous work, Volcano Ō-sima, one of the representative active volcanoes in Japan, was selected for the reasons described below. Volcano Ō-sima has been well studied in the fields of geophysics, geology and geochemistry and is covered with several lava flows, from one of which we can collect rock samples systematically. A systematic collection of the rock samples in the lava flow which erupted in 1950—1951 from Volcano Ō-sima was therefore carried out. From the results of chemical analysis, the major components such as iron[4], titanium[5], manganese[6], sodium[6] and potassium[6] were found to be very uniform in content in spite of the different appearances of the samples. On the other hand, the ratio of ferric

* Cf. Part LI of this series: I. Iwasaki et al., This Bulletin, 35, 448 (1962).

** Read before the Symposium on Geochemistry of the Chemical Society of Japan, Nagoya, 1960.

1) H. S. Washington, "The Chemical Analysis of Rocks" John Wiley & Sons, London (1930), p. 73.

2) F. F. Grout, *Am. J. Sci.*, **24**, 394 (1932).

3) P. E. Brown et al., *Geochim. et Cosmochim. Acta*, **18**, 193 (1960).

4) I. Iwasaki et al., *Bull. Volcanolog. Soc. Japan, Ser. 2*, **5**, 9 (1960).

5) I. Iwasaki et al.: Presented at the Symposium on Geochemistry of the Chemical Society of Japan, Fukuoka, 1959.

6) I. Iwasaki et al.: Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

oxide to ferrous oxide varied markedly with the degree of oxidation during cooling of the lava flow. This ratio is larger in the samples of red color, porus structure and scoria, or stalactitic structure than in normal compact samples. The vanadium contents of some of the volcanic rocks from Volcano Ō-sima had already been determined by Iwasaki et al.[7)]

In this paper, a minor component, vanadium, one of metallic elements, was selected for the determination. A discussion is made of its uniformity, and a comparison of its value with those of volcanic rocks erupted in other ages is made. The relation between the vanadium content and the contents of other elements is also discussed.

Experimental

Selection and Preparation of Rock Samples.— The lava flow, which erupted in 1950—1951, is about 6 m. thick, covers an area of 2.6 km^2, and totals 2×10^{10} kg. in weight. Figure 1 shows the original location of the rock samples collected.

The collection of the rock specimens was carried out as follows. Along the traverse line from Kakō-chaya to Gosinka-chaya, many parallel lines about 150 m. apart were set up. Along these lines, about 2 kg. of single hand specimen or aggregate sample were taken from each place at intervals of about 100 m. Furthermore, three samples were taken from the top, center and base at the particular place where the lave flow was about 13 m. thick. These collected samples were generally normal compact fragments and were often rock specimens of various appearances, such as red color, porus structure, scoria, etc. A total of 171 samples involving 9 samples of Anei lava erupted in 1778 and 3 samples of Meiji-Taisho volcanic rocks erupted in 1912 was collected; in all, 169 samples were analyzed.

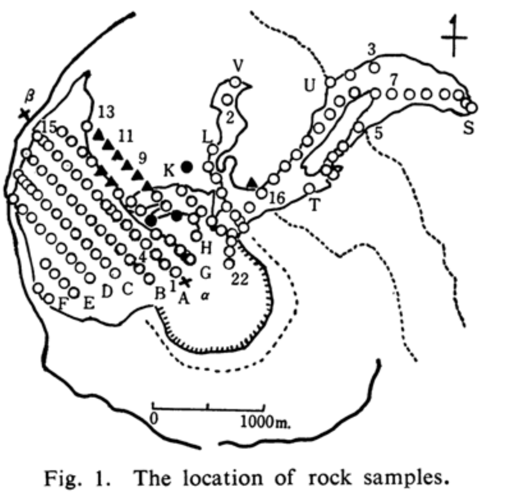

Fig. 1. The location of rock samples.
○ The lava in 1950—1951
● Meiji-Taisho volcanic rock
△ Anei lava
×α Kakō-chaya
×β Gosinka-chaya

About 4 g. of rock specimens, which was found in the previous paper[4)] to be sufficient for the determination of the total iron, was crushed in a steel mortar and ground to fineness with an agate mortar and a pestle.

The Colorimetric Method. — About 200 mg. of rock powder was fused with anhydrous sodium carbonate in a platinum crucible, and vanadium was completely extracted with hot water. The colorimetric determination of vanadium in the extract was made directly by the phosphotungstic acid method modified by Katsura[8)]. As a test of the reproducibility of this method, the determinations on the samples A-1 were repeated six times. These analyses were carried out on six separate fragments from a single had specimen. The results obtained are presented in Table I.

TABLE I. THE RESULTS OF REPEATED DETERMINATIONS

Sample (A-1)	V, %
1	0.046
2	0.046
3	0.047
4	0.047
5	0.048
6	0.046
Mean value	0.0467
Standard deviation	0.00055

By this method, it is possible to ascertain the vanadium contents of rocks with an precision of $\pm2\%$ when they fall in a range of 0.04 to 0.05%.

Results and Discussion

Vanadium Contents. — Table II shows the contents of vanadium, total iron and ferric iron of 169 rock specimens from Volcano Ō-sima.

The Vanadium contents of 159 rock specimens from the lava flow erupted in 1950—1951 range from 0.043 to 0.048% and average 0.0455% (standard deviation 0.0014%). Even in view of possible error in chemical analysis, these ranges clearly show the differences among them, although they are small.

As a result, the vanadium contents of the lava flow stated above are considered to show a high degree of uniformity.

Figure 2 shows the frequency curve drawn on normal probability paper to test whether this distribution is normal or not.

7) I. Iwasaki et al., *Memoirs Fac. Sci. Kyushu Univ., Sec. Chem.* No. 1, 76 (1950).

8) T. Katsura, "Experimental Chemistry", Vol. 15, Maruzen, Tokyo (1958), p. 142.

Table II. The contents of total iron, ferric iron and vanadium in volcanic rocks from Volcano Ō-sima

Sample	V, %	Fe*, %	Fe**, %		Sample	V, %	Fe*, %	Fe**, %	
A-1	0.047	10.0	2.0	X	C-7	0.043	10.0	1.3	X
A-2-1	0.044	10.0	1.7	X	C-8-1	0.045	10.0	1.5	X
A-2-2	0.046	10.0	1.5	X	C-8-2	0.044	10·0	1.4	X
A-2-3	0.045	10.0	1.8	Z	C-8-3	0.044	10.0	2.0	X
A-3-1	0.046	10.0	1.7	X	C-9-1	0.044	10.1	2.0	X
A-3-2	0.046	10.1	1.7	Z	C-9-2	0.047	10.0	1.6	X
A-4	0.046	10.0	1.7	X	C-10	0.043	10.0	2.3	Y
A-4-1	0.045	10.0	2.1	Y	C-11	0.045	10.0	1.4	X
A-4-2	0.047	10.0	3.1	Y	C-12	0.043	10.0	1.7	X
A-4-3	0.047	10.1	2.5	Y	C-12.3-1	0.045	10.0	1.8	X, R
A-4-4	0.044	10.0	2.4	Y	C-12.3-2	0.043	10.0	0.9	X
A-4-5	0.046	10.0	2.3	Y	C-13	0.043	10.0	1.7	X
A-5-1	0.047	10.1	1.9	X	C-13.4	0.044	9.9	2.0	X
A-5-2	0.048	10.0	1.8	X	C-14-1	0.045	10.0	1.6	X
A-5-3	0.046	10.0	2.0	Z	C-14-2	0.044	10.0	1.7	X
A-6-1	0.047	10.0	1.8	X	D-13-2	0.045	10.0	1.5	X
A-6-2	0.045	10.0	2.8	Z	D-13-1	0.045	10.0	1.5	X
A-6-3	0.045	10.0	2.0	X	D-12	0.045	10.0	1.7	X
A-7	0.046	10.0	1.8	X	D-11-2	0.045	10.0	1.7	X
A-7-1	0.048	10.0	1.8	X	D-11-1	0.044	10.1	1.7	X
A-7-2	0.048	10.1	1.9	X	D-10	0.044	10.0	1.8	X
A-7.5	0.047	10.0	2.0	X	D-9-2	0.043	10.0	1.8	X
A-8	0.048	10.0	1.9	X	D-9-1	0.044	10.0	1.7	X
A-9-1	0.047	10.0	1.7	X	D-8-3	0.045	10.1	2.0	X
A-9-2	0.045	10.0	1.7	X	D-8-2	0.046	10.0	1.7	X
A-10-1	0.048	10.0	1.8	Z	D-8-1	0.045	10.0	2.0	X
A-10-2	0.048	10.0	2.2	Z	D-7	0.045	10.0	1.5	X
A-10-3	0.044	10.0	1.8	X	D-6	0.045	10.0	1.7	Y
A-10-4	0.047	10.0	2.0	X	D-5	0.045	10.1	2.2	X
A-11	0.046	10.0	2.2	X	E-8	0.044	10.1	1.8	Z
A-12-1	0.044	10.0	2.0	X	E-7-6	0.045	10.0	2.4	W
A-12-2	0.047	10.1	1.9	X	E-7-5	0.045	10.0	2.2	X
A-12-3	0.047	10.0	2.4	Y	E-7-4	0.046	9.9	2.7	Y
A-13	0.047	10.0	2.9	Y	E-7-3	0.047	10.0	3.1	Z
A-14	0.047	10.0	2.0	Z	E-7-2	0.046	10.0	2.7	W
A-14.5	0.045	10.0	1.7	X	E-7-1	0.045	10.0	2.4	W
A-15	0.045	10.0	1.7	X	E-6	0.045	10.0	2.6	Z
B-2	0.046	10.0	1.9	X	E-5	0.047	10.0	3.2	Y
B-3	0.047	10.0	1.7	X	F-7-2	0.044	10.0	2.4	Y
B-4	0.045	10.0	1.7	X	F-7-1	0.047	10.0	1.8	X
B-5	0.045	10.0	1.6	X	F-6	0.045	10.0	1.6	Z
B-6	0.044	10.0	1.7	X	G-14	0.046	10.0	1.5	X
B-7	0.045	9.9	2.1	X	G-13	0.046	9.9	1.4	X
B-8	0.046	10.1	1.7	X	G-12	0.046	10.0	2.0	X
B-9	0.043	10.0	1.5	X	G-11	0.047	9.9	1.3	Z
B-10	0.045	10.0	1.7	X	G-10	0.050	10.6	1.9	X
B-11	0.046	10.0	1.5	X	G-9	0.050	10.6	2.0	X
B-12	0.045	10.0	1.6	X	G-8	0.046	10.0	1.7	X
B-13	0.045	10.0	1.5	X	G-7	0.046	10.1	2.0	X
B-14	0.044	10.1	1.5	X	G-6	0.046	10.2	2.0	X
B-15	0.045	10.0	1.5	X	G-5	0.041	8.9	2.0	X
C-4	0.044	10.0	1.3	X	G-4	0.046	10.1	2.6	Z
C-5	0.045	10.0	1.4	X	G-3	0.046	10.0	2.4	Z
C-6-1	0.044	10.0	1.5	X	G-2	0.044	10.0	1.7	X
C-6-2	0.044	10.0	1.4	X	G-1.5	0.045	10.1	2.4	X

TABLE II. (Continued)

Sample	V, %	Fe*, %	Fe**, %		Sample	V, %	Fe*, %	Fe**, %	
G-1	0.045	10.0	4.0	X	S-5	0.048	9.9	2.0	X
H-2	0.046	10.1	1.5	X	S-6	0.046	9.9	1.8	X
H-3	0.047	10.0	1.9	X	S-7	0.045	9.9	2.2	Z
H-4	0.039	8.9	2.0	X	S-8	0.046	10.0	2.6	Z
H-5	0.045	10.0	4.0	Y	S-9	0.046	9.9	1.8	X
H-6	0.046	10.0	2.4	Y	S-10	0.046	10.0	2.1	Z
H-7	0.050	10.8	2.2	X	S-11	0.046	10.0	2.3	Y
H-8	0.050	10.8	2.1	X	S-12	0.047	10.0	2.1	X
H-9	0.051	10.6	2.2	X	T-4	0.045	10.0	2.0	X
H-10	0.052	10.8	2.3	X	S-13	0.045	10.0	2.0	Z
H-11	0.050	10.6	2.1	X	S-14	0.044	10.0	2.0	X
H-12	0.052	10.8	2.2	X	S-15	0.044	10.0	2.0	X
H-13	0.047	10.0	1.7	Z	S-16	0.046	10.0	3.0	Z
K-0	0.047	10.1	2.2	Y	S-17	0.047	10.0	3.1	Z
K-1-1	0.046	10.0	2.2	X	S-18	0.045	10.0	2.4	X
K-1-2	0.045	10.0	2.3	X	S-19	0.044	10.0	2.2	X
K-3	0.047	10.1	1.9	X	S-20	0.045	10.0	2.9	Z
K-4	0.043	10.1	2.0	X	S-21	0.047	10.0	2.4	X
K-5	0.048	10.1	1.9	X	S-22	0.045	10.0	2.2	X
L-6	0.048	10.1	2.4	X	T-1	0.046	10.0	2.9	Z
L-5	0.047	10.1	1.7	X	T-2-1	0.047	10.0	2.3	X
L-4	0.048	10.1	2.2	X	T-2-2	0.044	10.0	2.4	X
L-3	0.047	10.1	1.5	X	T-3	0.045	9.9	2.2	X
L-2	0.047	10.1	2.1	X	T-5	0.045	10.0	2.8	Z
L-1	0.046	10.0	1.9	X	U-1	0.045	9.9	2.2	X
L-0	0.046	10.0	1.5	X	U-2	0.045	10.0	3.1	Y
S-1	0.046	9.9	3.0	Z	U-3	0.044	9.9	2.2	Z
S-2	0.046	10.0	2.9	Y	V-1	0.044	9.9	2.0	X
S-3	0.046	10.0	3.1	Z	V-2	0.044	9.9	2.4	X
S-4	0.045	10.0	2.1	X					

Fe*: Total iron content; Fe**: Ferric iron content
Anei lava: G-10, G-9, H-7, H-8, H-9, H-10, H-11, H-12
Meiji-Taisho volcanic rock: G-5, H-4
Base: A-12-1, D-9-1, Center: A-12-2; Top: A-12-3, D-9-2
X: Normal compact sample; Y: Scoria-like sample
Z: Sample of porus structure; W: Sample of stalactitic structure
R: Sample of red color

This shows almost a normal distribution, although Ahrens[9] has reported that the concentration of a minor element is lognormally distributed in any specific igneous rock.

The vanadium contents of 8 specimens from Anei lava range from 0.050 to 0.052% and average 0.051% (standard deviation 0.0009%), while those of 2 specimens from Meiji-Taisho volcanic rocks average at 0.040%. Consequently, the distinction between the vanadium contents of Anei lava and of Meiji-Taisho volcanic rock is comparatively easy, but it is difficult to distinguish the lava in 1950—1951 from the volcanic rocks of the other ages on the basis of their vanadium contents.

When the vanadium content of Anei lava, the highest value of the three, is compared with those of volcanic rocks in Japan and in the world respectively, it was found to be the highest value of volcanic rocks in Japan, higher than the values (0.015~0.030%) found in gabbroic and basaltic rocks by Goldschmidt[10] which had already been observed by Katsura[11].

As already stated in connection with the total iron content, the vanadium contents of the lava in 1950—1951 are also independent of their appearances as rock specimens.

The Relation between the Vanadium and Ferric Iron Content of the Lava Flow in 1950—1951. —As stated above, the quantities of various elements, such as total iron, titanium, etc., in the lava in 1950—1951 are very uniform. They, therefore, can not be considered to show

9) L. H. Ahrens, *Nature*, **172**, 1148 (1953); *Geochim. et Cosmochim. Acta*, **5**, 49 (1954); **6**, 121 (1954); **11**, 205 (1957).

10) V. M. Goldschmidt, "Geochemistry", Oxford Univ. Press, London (1954), p. 489.

11) T. Katsura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 358, 1076, 1196 (1956).

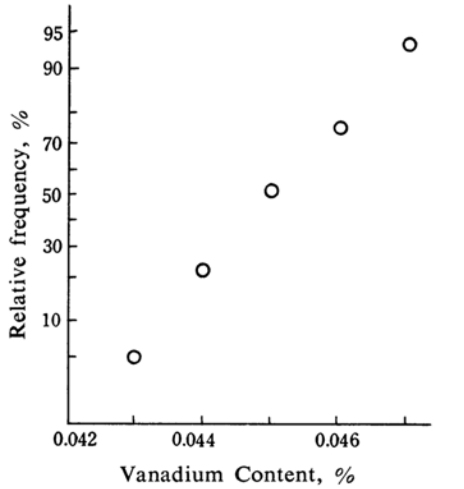

Fig. 2. The frequency curve on normal probability paper.

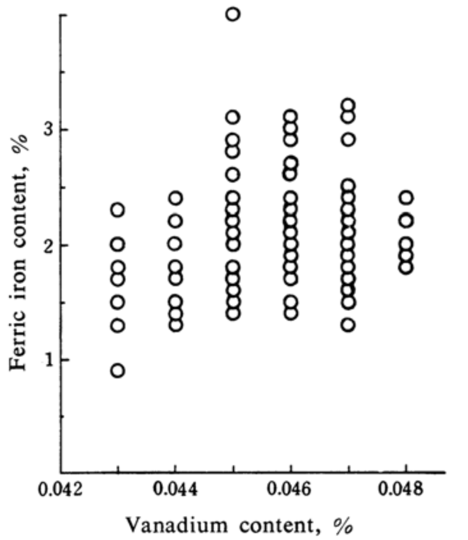

Fig. 3. The relation between vanadium and ferric iron content.

the relationship to the vanadium contents clearly. However, the ferrous iron and ferric iron contents vary markedly. As vanadium is believed to replace ferric iron, the relation between vanadium and ferric iron contents is shown in Fig. 3.

As shown in Fig. 3, there is no distinct, regular relation, although the contents of vanadium appear to become higher with increasing ferric iron contents. This seems to be attributable to the fact that vanadium had no time to replace the ferric iron, which increased rapidly by the oxidation of air and water vapor during the cooling of the lava flow at atmospheric temperature and pressure. In other words, it seems that the distribution of vanadium remains unchanged, but that ferric iron contents vary during the course of solidification and cooling. This consideration also agrees with that of the previous paper[4].

The Relation between the Contents of Vanadium and Other Elements in Volcanic Rocks in Different Ages.—The quantities of various elements[7,12] such as total iron, aluminum, titanium, magnesium and vanadium in volcanic rocks erupted in different ages are shown in Table III.

The number of rock specimens is too small to show the general relation definitely, but the relation may be discussed qualitatively. The positive correlation between the total iron and the vanadium content is shown in Fig. 4.

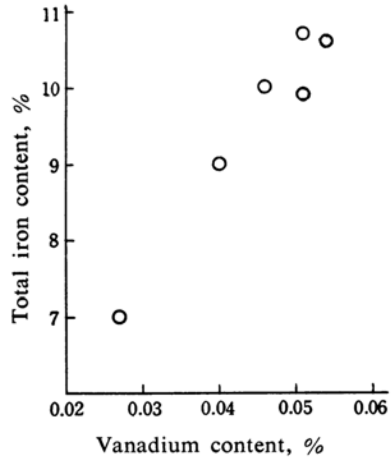

Fig. 4. The relation between vanadium and total iron content.
Regress coefficient, $\gamma=0.86$

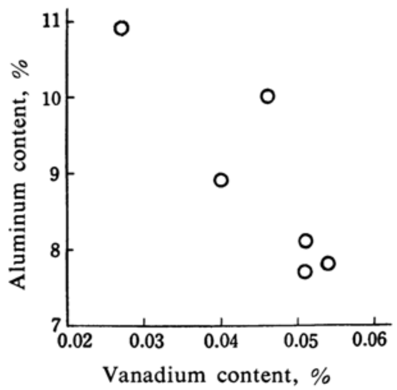

Fig. 5. The relation between vanadium and aluminum content.
Regress coefficient, $\gamma=-0.89$

12) I. Iwasaki, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **56**, 1518 (1935).

Table III. The contents of various elements in volcanic rocks from Volcano Ō-sima

Sample	Fe*, %	Al, %	Mg, %	Ti, %	V, %
Okata volcanic rock	7.0	10.9	3.5	0.47	0.027
Okata volcanic rock	10.6	7.8	3.3	0.49	0.054
Outer Somma lava	9.9	8.1	2.9	0.50	0.051
Anei lava	10.7	7.7	3.0	0.77	0.051
Meiji-Taisho volcanic rock	9.0	8.9	2.7	0.61	0.040
The lava in 1950—1951	10.0	8.0	3.0	0.70	0.046

Fe*: Total iron content.

Vanadium is found to be most concentrated in magnetite among the common rock-forming minerals[7]. Anei lava is 6% magnetite (according to a microscopic analysis by Kuno[13]), with about 0.7% vanadium[14]. This magnetite is not pure magnetite, but involves the glassy ground mass and pyroxene. Thus, the vanadium content in the magnetite corresponds to about 80% ($6\times0.007\times100/0.051$) in rock. If the amounts of magnetite are proportional to the total iron content, the relation under consideration may be understood completely[7].

The negative correlation to aluminum content is presented in Fig. 5.

The main rock-forming mineral involving aluminum in Anei lava is plagioclase (contained in 50% of rock), which generally contains little vanadium. If the amounts of plagioclase decrease along with an increase in the amount of magnetite, this seems to explain this relation.

The contents of vanadium are independent of the titanium and magnesium contents, but the correlation to the contents of total iron plus titanium is shown in Fig. 6.

The magnetite in Anei lava contains 38% total iron plus titanium[14]. If the titanium plus total iron contents are proportional to the amounts of magnetite, this relation seems to be explained well. This relation has also been shown in ultrabasic potassic rocks by Higazy[15].

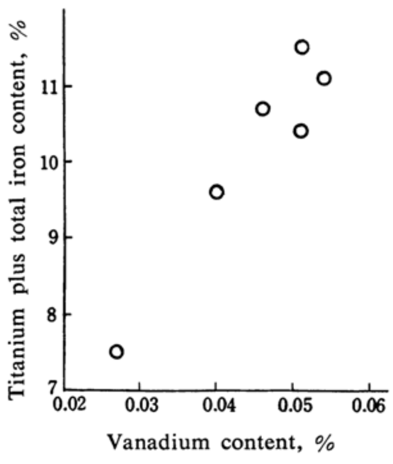

Fig. 6. The relation between vanadium and titanium plus total iron content.
Regress coefficient, $\gamma=0.90$

13) I. Iwasaki, *Bull. Volcanolog. Soc. Japan, Ser. 2*, **3**, 70 (1958).
14) I. Iwasaki et al., *J. Min. Inst. Kyushu*, **18**, 197, 256, 291 (1950).

Conclusion

1) The vanadium contents of the lava flow erupted in 1950—1951 show a high degree of uniformity.

2) The frequency diagram shows an almost normal distribution.

3) It is difficult to distinguish between the lava of 1950—1951 and the volcanic rocks of the other ages in the basis of their vanadium contents.

4) A relation between the vanadium and ferric iron contents of the lava flow in 1950—1951 could not be found.

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15) R. A. Higazy, *Bull. Geol. Soc. Am.*, **65**, 39 (1954).