# *Geochemical Investigations of the Volcanoes in Japan. LI*. Titanomagnetites in Volcanic Rocks of Nekodake, Aso Volcano***

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There have been many reports on the magnetochemical or mineralogical properties of titanomagnetites in volcanic rocks(1-4). Also, many investigations have been made of the titanomagnetites in relation to the chemical or petrological properties of their host rocks. Iwasaki and Katsura(5) have studied the relation between the chemical composition of titanomagnetites in various Japanese volcanic rocks and the stage of magmatic differentiation of their host rocks. Buddington, Fahey, and

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* Part L: M. Kamada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1346 (1961).

** Presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

1) S. Akimoto, *J. Geomag. Geoelect.*, **3**, 47 (1951).

2) S. Akimoto, ibid., **6**, 1 (1954).

3) S. Akimoto, *Japan. J. Geophys.*, **1**, No. 2, 1 (1955).

4) R. Chevallier, J. Bolfa and S. Mathieu, *Bull. Soc. Franc. Miner. Crist.*, **78**, 307 (1955).

5) I. Iwasaki and T. Katsura, *Kyûshû. Min. Assoc. J.* (*Kyûshû Kôzan Gakkai-shi*), **18**, 197, 256, 291 (1950).

Vlisidis6) have reported that the titanium content of magnetite is largely a function of the temperature of its formation. Vincent and Phillips7) investigated titanomagnetites from the Skaergaard gabbroic intrusion and discussed the variation in content of major and minor constituents in a suite of differentiated gabbros. Recently, Marmo8) has reported on the correlation of the titanium content of magnetite with certain geological facts. The problems discussed in these papers have, however, been mostly restricted to the variation in the titanium content of titanomagnetite, that is, the changes along the ulvöspinel-magnetite join in the $FeO-Fe_2O_3-TiO_2$ system.

Recent study by Akimoto and Katsura9) has shown that the chemical composition of titanomagnetite in volcanic rocks does not always accord with ulvöspinel-magnetite join, but in most cases deviates from this join towards the ilmenite-hematite join side. In other words, some natural titanomagnetites have a more oxidized composition than the solid solutions between ulvöspinel and magnetite. The existence of such an oxidized titanomagnetite is also supported by synthetic investigation10). The state of oxidation of that natural titanomagnetite which is represented by the deviation of its chemical composition from ulvöspinel-magnetite join in the $FeO-Fe_2O_3-TiO_2$ system should be intimately related to the physicochemical history of its host rock.

Vincent and Phillips7) concluded that the compositions of the magnetite are largely determined by the oxidation-reduction equilibria between ferrous and ferric oxides and oxygen in the crystalizing magma. However, the variation in the degree of oxidation of titanomagnetite dealt with in their report is rather small as compared with those of volcanic rocks. This paper is concerned chiefly with the relation between the state of oxidation of titanomagnetites (free from the ilmenite-hematite series minerals) in volcanic rocks and the chemical and petrological properties of their host rocks.

### Materials and Methods

The volcanic rocks of Nekodake, Aso Volcano, from which titanomagnetites were extracted came in through the courtesy of Mr. H. Matsumoto, Institute of Geology, Kumamoto University, who has made geological studies and chemical analyses of these rocks11). The localities where these rocks were collected are shown in Table I*. They all belong to andesite ($SiO_2$ content 52～57%). It is considered that the volcanic activity of Nekodake has been in three stages: that is, the first was an activity of the Old Nekodake, which was followed by the second one forming the chief part of it (Nekodake lava), and then a number of dykes were injected as the last phase of the volcanic activity11).

TABLE I. ROCKS OF NEKODAKE ASO VOLCANO FROM WHICH TITANOMAGNETITES HAVE BEEN SEPARATED11)

| No. | Rocks* | Locality |
|---|---|---|
| 1 | horn-two-pyr-andesite, D | Tengu-iwa |
| 2 | horn-aug-hy-andesite, D | Oshoji-iwa |
| 3 | two-pyr-andesite, O | southern part |
| 4 | ol-hy-aug-andesite, N | western part |
| 5 | ol-hy-aug-andesite, N | western part |
| 6 | horn-aug-hy-andesite, D | Jigoku-dani |
| 7 | two-pyr-andesite, N | between Tengu-iwa and Higashi-mine |
| 8 | hy-aug-andesite, O | northwestern part |
| 9 | aug-hy-andesite, N | southeastern part |
| 10 | ol-bearing-two-pyr-andesite, N | western part |
| 11 | horn-bearing-two-pyr-andesite, D | Tengu-iwa (chilled margine) |
| 12 | aug-hy-andesite, O | northern part |
| 13 | aug-hy-andesite, O (aggromeratic) | northwestern part |
| 14 | two-pyr-andesite, N | southern part |
| 15 | aug-hy-andesite, N | Yamaguchi-dani |
| 16 | aug-hy-andesite, O | southern part |
| 17 | two-pyr-andesite, N | southern part |
| 18 | ol-aug-hy-andesite, N | Wakudo-iwa |
| 19 | ol-bearing-aug-hy-basaltic andesite, O | southern part |

* horn = hornblende
pyr = pyroxene
aug = augite
hy = hypersthene
ol = olivine
D = dike rock
N = Nekodake lava
O = Old Nekodake lava

About 100～300 g. of volcanic rock was crushed by a gunmetal crusher, and the ferromagnetic fraction was separated from silicate minerals by a small permanent magnet. The fraction thus separated was then finely pulverized in an agate

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6) A. F. Buddington, J. Fahey and A. Vlisidis, *Am. J. Sci.*, 253, 497 (1955).

7) E. A. Vincent and R. Phillips, *Geochim. et Cosmochim. Acta*, 6, 1 (1954).

8) U. Marmo, *Am. J. Sci.*, 257, 144 (1959).

9) S. Akimoto and T. Katsura, *J. Geomag. Geoelect.*, 11, 69 (1959).

10) S. Akimoto, T. Katsura and M. Yoshida, ibid., 9, 165 (1957).

11) H. Matsumoto, Read at the Meeting of the Volcanological Society of Japan, October, (1957). (Abstract, *Bull. Volcanological Soc. Japan* (*Kazan*), 2nd Series, 2, 95 (1957)).

* The sample numbers used in this paper correspond to those used by H. Matsumoto as follows:
No. 1 : 56062111, No. 2 : 56062301, No. 3 : 56110301,
No. 4 : 56050302, No. 5 : 56050509, No. 6 : 56050605A,
No. 7 : 56050612, No. 8 : 56050703, No. 9 : 56062102,
No. 10 : 56071605, No. 11 : 57100501, No. 12 : 57100502,
No. 13 : 56071603, No. 14 : 56T062111, No. 15 : 56050410,
No. 16 : 56062010, No. 17 : 56062107, No. 18 : 56082004,
No. 19 : 56062108.

TABLE II. CHEMICAL COMPOSITION AND CRYSTALLOGRAPHIC PROPERTIES OF TITANOMAGNETITES CONTAINED IN NEKODAKE VOLCANIC ROCKS

| No. | Purity* | Weight % | | | | | | Formula % | | | Atomic ratio | | Lattice parameter Å |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | FeO | $Fe_2O_3$ | $TiO_2$ | $V_2O_3$ | MnO | CoO | FeO | $Fe_2O_3$ | $TiO_2$ | 32× (Fe+Ti)/O | Fe/(Fe+Ti) | |
| 1 | 93.7 | 36.16 | 45.12 | 11.37 | 0.58 | 0.51 | n. d. | 54.23 | 30.44 | 15.33 | 23.69 | 0.883 | 8.422 |
| 2 | 92.9 | 33.44 | 46.72 | 11.70 | 0.48 | 0.53 | 0.027 | 51.46 | 32.35 | 16.19 | 23.41 | 0.878 | 8.400 |
| 3 | 89.4 | 22.33 | 53.89 | 11.91 | 0.91 | 0.37 | 0.037 | 38.98 | 42.32 | 18.70 | 22.40 | 0.869 | 8.387 |
| 4 | 90.7 | 32.49 | 45.16 | 11.90 | 0.73 | 0.46 | 0.034 | 51.16 | 31.99 | 16.85 | 23.36 | 0.872 | 8.417 |
| 5 | 91.6 | 36.54 | 40.37 | 13.40 | 0.76 | 0.51 | 0.039 | 54.74 | 27.21 | 18.05 | 23.60 | 0.858 | 8.442 |
| 6 | 91.6 | 35.08 | 47.40 | 7.97 | 0.70 | 0.42 | n. d. | 55.18 | 33.55 | 11.27 | 23.96 | 0.916 | 8.419 |
| 8 | 80.6 | 20.34 | 50.38 | 8.68 | 0.80 | 0.42 | n. d. | 40.03 | 44.61 | 15.36 | 22.62 | 0.894 | 8.391 |
| 9 | 73.1 | 21.95 | 43.80 | 6.93 | 0.44 | n. d. | n. d. | 45.84 | 41.15 | 13.01 | 23.13 | 0.908 | n. d. |
| 10 | 92.5 | 29.53 | 49.84 | 11.95 | 0.88 | 0.34 | 0.039 | 47.10 | 35.76 | 17.14 | 23.03 | 0.874 | 8.408 |
| 11 | 93.3 | 31.54 | 52.54 | 8.26 | 0.47 | 0.46 | 0.033 | 50.38 | 37.75 | 11.87 | 23.53 | 0.914 | 8.408 |
| 12 | 95.9 | 30.26 | 52.88 | 11.78 | 0.71 | 0.25 | 0.022 | 46.81 | 36.81 | 16.38 | 23.04 | 0.880 | 8.391 |
| 13 | 87.6 | 20.01 | 62.88 | 3.44 | 0.89 | 0.40 | n. d. | 38.93 | 55.04 | 6.03 | 22.96 | 0.961 | 8.397 |
| 14 | 95.0 | 33.21 | 46.82 | 14.02 | 0.52 | 0.46 | n. d. | 49.65 | 31.50 | 18.85 | 23.14 | 0.857 | 8.433 |
| 15 | 93.4 | 34.28 | 45.78 | 12.13 | 0.73 | 0.43 | n. d. | 52.11 | 31.31 | 16.58 | 23.45 | 0.874 | 8.421 |
| 16 | 92.8 | 26.97 | 52.93 | 11.66 | 0.73 | 0.49 | n. d. | 44.03 | 38.86 | 17.11 | 22.81 | 0.877 | 8.401 |
| 17 | 90.8 | 34.17 | 42.33 | 13.03 | 0.76 | 0.50 | n. d. | 52.62 | 29.33 | 18.05 | 23.42 | 0.860 | 8.436 |
| 18 | 91.0 | 28.64 | 50.87 | 10.27 | 0.74 | 0.47 | n. d. | 47.14 | 37.67 | 15.19 | 23.12 | 0.890 | 8.398 |
| 19 | 97.6 | 25.88 | 55.21 | 15.32 | 0.75 | 0.39 | n. d. | 40.13 | 38.51 | 21.36 | 22.34 | 0.846 | 8.388 |

* $FeO+Fe_2O_3+TiO_2+V_2O_3+MnO$ (in weight)

motor in the presence of water. The suspension thus prepared was poured into about 100 ml. of water, and the ferromagnetic fraction was attracted by a magnet, the suspension of silicate minerals being abandoned. These procedures were repeated until the purity could hardly be improved by the repetition of these procedures. Titanomagnetites in volcanic rocks are so finely grained that a small amount of silicate, such as olivine, pyroxene, etc., still remained as an impurity in spite of our efforts. As will be seen in Table II, the purity of these specimens mostly exceeds 90% and is sufficient for the present discussion.

X-Ray analysis was carried out for all specimens by means of a wide range X-ray spectrometer "Norelco" with Fe-K radiation. In all these specimens (with only the one exception of No. 13), the amount of the minerals which belonged to the ilmenite-hematite series was less than five percent. The lattice constant of each sample was also measured. In most cases, titanomagnetite lines in the X-ray diffraction diagram showed considerable broadening. This broadening can be attributed to the specimens being not strictly of a single phase which has a definite composition, but rather mixtures of phases with a spinel structure whose chemical composition differ continuously (probably along the oxidation-reduction lines in the $FeO$-$Fe_2O_3$-$TiO_2$ system⁹⁾). Therefore, the chemical and physical properties of these titanomagnetites obtained by several methods will show the average values of such phases and so will involve some ambiguity.

Chemical analyses of titanomagnetite ($FeO$, $Fe_2O_3$, $TiO_2$, $V_2O_3$ and $MnO$) have been made by the method devised by Iwasaki et al.¹²⁾ The cobalt contents of several specimens were determined by colorimetric methods, using nitroso-R salt¹³⁾.

## Results and Discussion

The results of the chemical analysis, together with the formular proportions of three oxides ($FeO$, $Fe_2O_3$, $TiO_2$), are given in Table II and are represented in the diagram of the $FeO$–$Fe_2O_3$–$TiO_2$ ternary system (Fig. 1).

The quantity of specimen No. 7 was insufficient for chemical analysis. The atomic ratio $Fe/(Fe+Ti)$ and the atomic proportions of the metals to oxygen calculated on the basis of 32 oxygen atoms $32\times(Fe+Ti)/O$ are also given in Table II. They are used in the report by Akimoto and Katsura⁹⁾ in the form of a parameter where the former shows the change along the ulvöspinel-magnetite join, while the latter shows the change along the oxidation-reduction lines in the $FeO$–$Fe_2O_3$–$TiO_2$ system.

As will be seen in Fig. 1, the chemical composition of these titanomagnetites generally does not accord with the $Fe_2TiO_4$–$Fe_3O_4$ solid solution line, but deviates considerably from this join towards the $FeTiO_3$–$Fe_2O_3$ join side. The $TiO_2$ contents of these titanomagnetites are confined to a relatively narrow range ($Fe/(Fe+Ti)=0.83\sim0.91$), except for No. 13, which contains a fairly large amount of hematite, as has already been mentioned. According to the previous studies⁵,⁹⁾, the titanium content of the titanomagnetite increases (or, $Fe/(Fe+Ti)$ decreases) gradually in the order of the decreasing $SiO_2$ content of the host rock: rhyolite, dacite, andesite, basalt. The host rocks in this study belong to andesite, and the result agrees satisfactorily with previous reports. It is very convenient for a discussion of the relation between the degree of oxidation of titanomagnetites and other properties that the variation in the $TiO_2$ contents of these titanomagnetites is small.

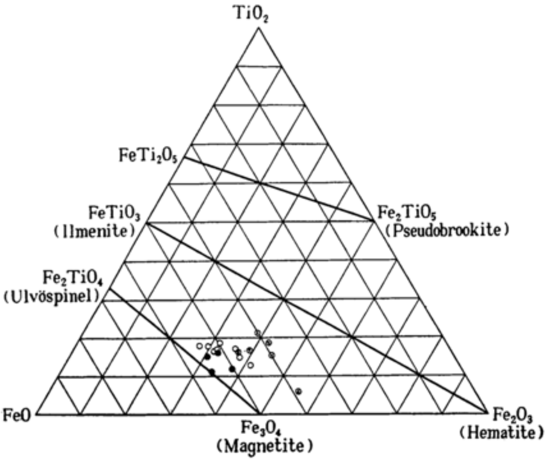

Fig. 1. Chemical composition of analysed titanomagnetites represented on a $FeO$–$Fe_2O_3$–$TiO_2$ system. (Formula %)
● dike rock ○ Nekodake lava
⊙ Old-Nekodake lava

Akimoto and Katsura⁹⁾ have referred to the titanomagnetite that lies almost precisely on the line of the $Fe_3O_4$–$Fe_2TiO_4$ join as "the normal titanomagnetite", to that which lies in the $Fe_3O_4$–$Fe_2TiO_4$–$FeTiO_3$ compositional field as "the abnormal titanomagnetite", and to that which lies in the $Fe_3O_4$–$FeTiO_3$–$Fe_2O_3$ field as "the very abnormal titanomagnetite". In accordance with this classification, only one specimen (No. 6) of titanomagnetite, can be referred to normal titanomagnetite, eight specimens (including No. 14) to abnormal titanomagnetite, and nine specimens to very abnormal titanomagnetite. As compared with the chemical composition of the already reported titanomagnetites in volcanic rocks⁵,⁹⁾, titanomagnetites in Nekodake volcanic rocks

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12) I. Iwasaki, T. Katsura, M. Yoshida and T. Tarutani, *Japan Analyst* (*Bunseki Kagaku*), 6, 211 (1957).

13) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd. Ed., Interscience Publishers, New York, London (1959), pp. 415, 429.

have a very oxidized composition (especially those in Old Nekodake lavas). It is also seen in Fig. 1 that titanomagnetites in Old Nekodake lava have the most oxidized composition and that those in dike rocks have the least oxidized composition. The chemical composition of titanomagnetite in Nekodake volcanic rock varies with the periods of volcanic activity.

In order to see the relation between the state of oxidation of titanomagnetite and that of the host rock, the $FeO/Fe_2O_3$ (by weight) of the titanomagnetites is plotted against the $FeO/Fe_2O_3$ of their host rocks (Fig. 2). A clear correlation is seen in this figure. It is also seen from the figure that the points which represent the Old Nekodake lavas take positions nearer to the axis of abscissa than do the others. This implies that titanomagnetite in Old Nekodake lava has a more oxidized composition than others in relation to the host rock. No difference seen is between Nekodake lava and dike rock. When the $32\times(Fe+Ti)/O$ value of titanomagnetite is taken in place of the $FeO/Fe_2O_3$ of titanomagnetite, the result is almost the same as the results obtained by Fig. 2. Some investigators[7,14] have emphasized the importance of the role of the volatile constituent (mainly water) on the state of the oxidation of iron in the rock. The $H_2O(+)$ content of the host rock is plotted against the $FeO/Fe_2O_3$ ratio of titanomagnetite in Fig. 3. As will be seen in the figure, Old Nekodake lava behaves in a different manner from others.

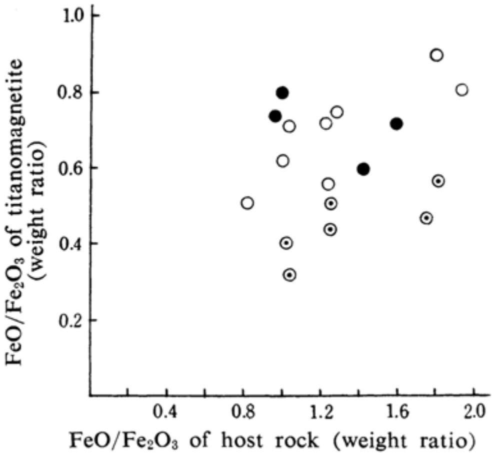

Fig. 2. Relation between $FeO/Fe_2O_3$ of the titanomagnetite and that of the host rock.
● dike rock ○ Nekodake lava
⊙ Old Nekodake

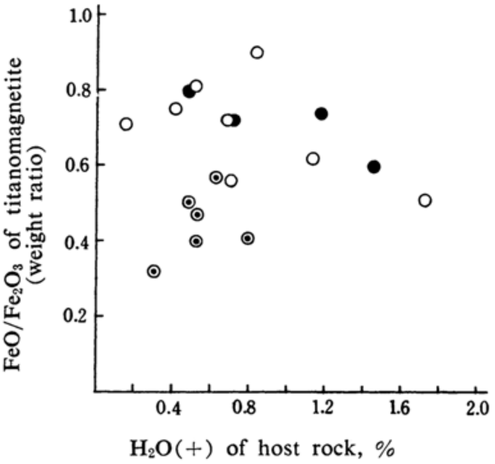

Fig. 3. Relation between $FeO/Fe_2O_3$ of the titanomagnetite and $H_2O(+)$ of the host rock.
● dike rock ○ Nekodake lava
⊙ Old Nekodake lava

Apart from the results obtained by the study of titanomagnetites, the properties of Old Nekodake lava are almost same as those of Nekodake lava. The former can be distinguished from the latter only by the information of the geological field survey[11]. On the other hand, dike rocks are readily distinguished from others by the fact that dike rocks alone bear hornblende as a constituent. Differences between Old Nekodake lava and Nekodake lava in the degree of the oxidation of titanomagnetite might be explained in two ways. First, the Old Nekodake lava may have originally been different from the Nekodake lava in its volatile constituent and the difference may have had an effect on the state of the oxidation of iron ore minerals. Second, the Old Nekodake lava may have been almost the same as the Nekodake lava, but the Old

TABLE III.

| No. | Mn % in titanomagnetite | Mn % in host rock | Ratio |
|---|---|---|---|
| 1 | 0.40 | 0.12 | 3.3 |
| 2 | 0.41 | 0.11 | 3.7 |
| 3 | 0.29 | 0.12 | 2.4 |
| 4 | 0.36 | 0.14 | 2.6 |
| 5 | 0.40 | $0.08_5$ | 4.7 |
| 6 | 0.33 | 0.12 | 2.7 |
| 8 | 0.33 | 0.13 | 2.5 |
| 10 | 0.26 | 0.12 | 2.2 |
| 11 | 0.36 | 0.12 | 3.0 |
| 12 | 0.19 | 0.10 | 1.9 |
| 13 | 0.31 | 0.12 | 2.6 |
| 14 | 0.36 | 0.12 | 3.0 |
| 15 | 0.33 | 0.12 | 2.7 |
| 16 | 0.38 | 0.12 | 3.2 |
| 17 | 0.39 | 0.12 | 3.2 |
| 18 | 0.36 | $0.08_5$ | 4.2 |

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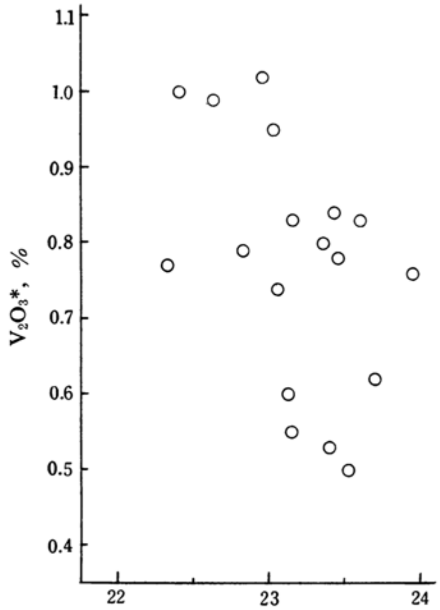
14) G. C. Kennedy, *Am. J. Sci.*, **246**, 529 (1948).

Nekodake lava may have suffered strong oxidative actions for some reason (for example, because of secondary heating in the atmospheric conditions). Most of the rocks which contain very abnormal titanomagnetite bear hematite. This fact seems to support the second of these possibilities.

The MnO contents of these titanomagnetites are 0.25～0.53%, and there is no correlation with the oxidation parameter 32×(Fe+Ti)/O. Manganese is somewhat concentrated in titanomagnetite. (Mn in titanomagnetite)/(Mn in host rock) are between 1.9 and 4.7 (Table III). The $V_2O_3$ contents of titanomagnetites are plotted against the oxidation parameter 32×(Fe+Ti)/O in Fig. 4. Generally speaking, the vanadium content increases as the oxidation parameter decreases. Vanadium is considerably concentrated in titanomagnetite, as is shown in Table IV, and this result agrees well with those of previous investigators[5,9,15].

Cobalt is also fairly concentrated in titanomagnetite (Table V). These results agree well with the results of Wager and Mitchell[15].

The lattice constants of these titanomagnetites are plotted against the oxidation parameter. An almost linear relation, in which the lattice constant becomes smaller according as the oxidation proceeds, will be clearly found in Fig. 5. This result is in good accordance with the results obtained by the synthetic experiments[10] and the study on the natural titanomagnetites[9].



32×(Fe+Ti)/O (atomic ratio)

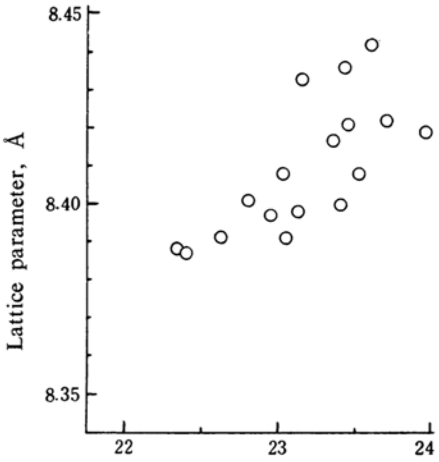
Fig. 4. Relation between $V_2O_3$ content and oxidation parameter of titanomagnetite
$V_2O_3^* = V_2O_3 \times 100/\text{purity}$
purity = $FeO + Fe_2O_3 + TiO_2 + V_2O_3 + MnO$ (weight %)

TABLE IV

| No. | V % in titanomagnetite | V % in host rock | Ratio |
|---|---|---|---|
| 1 | 0.40 | 0.023 | 17 |
| 2 | 0.33 | 0.008 | 41 |
| 9 | 0.30 | 0.009 | 33 |
| 14 | 0.35 | 0.022 | 17 |
| 18 | 0.51 | 0.026 | 20 |

TABLE V

| No. | Co % in titanomagnetite | Co % in host rock | Ratio |
|---|---|---|---|
| 5 | 0.031 | 0.0030 | 10 |
| 11 | 0.026 | 0.0027 | 9.7 |
| 12 | 0.017 | 0.0033 | 5.2 |



32×(Fe+Ti)/O (atomic ratio)

Fig. 5. Relation between lattice parameter and oxidation parameter of titanomagnetite.

## Conclusion

The study of the titanomagnetite in volcanic rocks of Nekodake, Aso Volcano, has given the following results:

1. The natural occurrence of titanomagnetite the chemical composition of which lies in the $Fe_3O_4$–$Fe_2O_3$–$FeTiO_3$ compositional field, far beyond the $Fe_2TiO_4$–$Fe_3O_4$ and $FeTiO_3$–$Fe_3O_4$ line in the $FeO$–$Fe_2O_3$–$TiO_2$ diagram (" very abnormal titanomagnetite "), is confirmed in these volcanic rocks. About a half of the specimens in this paper are " very abnormal titanomagnetite ", and it may be supposed that " very abnormal titanomagnetite " exists rather commonly in volcanic rocks.

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[15] L. R. Wager and R. L. Mitchell, *Geochim. et Cosmochim. Acta*, 1, 129 (1951).

2. The state of the oxidation of titanomagnetite must have an important relation to the physico-chemical history of the host rock.

From the study of the correlation between the state of the oxidation of titanomagnetites and some chemical properties of their host rocks, it becomes possible to distinguish the rock belonging to Old Nekodake lava from that belonging to Nekodake lava or dike rock. However, for the present, the method must be considered valid only for the rocks of Nekodake.

3. Vanadium and cobalt in volcanic rock are considerably concentrated in titanomagnetite, and the vanadium content in titanomagnetite has a correlation to the oxidation parameter $32\times(\mathrm{Fe}+\mathrm{Ti})/\mathrm{O}$ which represents the state of the oxidation of titanomagnetite.

The authors are much obliged to Mr. Hatao Matsumoto, the Institute of Geology, Kumamoto University, for kindly supplying the specimens of Nekodake volcanic rocks and for many valuable suggestions and discussions from the petrological point of view. They also wish to express their hearty thanks to Dr. Syun-iti Akimoto, Geophysical Institute, the University of Tokyo, both for his great help and valuable advice in X-ray study and for his fruitful discussions throughout the study.

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