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## BIOTITES FROM THE TAKAKUMAYAMA GRANITE, KAGOSHIMA PREFECTURE AND THEIR HYDROTHERMAL EXPERIMENTS AT HIGHER OXYGEN FUGACITIES

by

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(with 3 tables and 4 text-figures)

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### *Abstract*

Compositional variation of biotites from the Takakumayama granite, located in the central part of the Ōsumi Peninsula, Kagoshima Prefecture, was observed. The biotites show compositionally a substitution of  $3\text{Mg} \rightarrow 2(\text{Al}^{\text{VI}} + \text{Fe}^{+3}) + \text{Vacancy}$  during the formation of the granite. Hydrothermal experiments on two analyzed biotites were carried out with the HM buffer at temperatures up to  $750^\circ\text{C}$  and 1 kb. An alkali feldspar phase was not formed by partial decomposition, but one or two of iron oxides. Comparison of physical and chemical properties between natural and experimentally treated biotites was examined. By the partial decomposition,  $\text{Al}^{+3}$  is hardly depleted from biotite, and  $\text{Fe}^{+3}$  and octahedral vacancies in biotite increase. The results indicate that the substitution will take place in an oxidizing condition during crystallization of a granitic magma.

### Introduction

The Takakumayama granite, composed of a granodiorite of the Shinkoji-type and an aplitic granite of the Sarugajo-type, is located in the central part of the Ōsumi Peninsula, Kagoshima Prefecture. Hydrothermal experiments on the granite recently studied by Yamamoto (1977) indicate that the biotite in the aplitic granite disappears in the presence of excess water at  $680^\circ\text{C}$  and 1 kb and has the lowest temperature range as compared to other coexisting constituent minerals. Similarly, crystallization of glasses made by fusion of granitic rocks reported by Yamamoto (1976) also indicates that in the presence of water at  $700^\circ\text{C}$  and 1 kb, biotite is synthesized from the glass of the aplitic granite not at  $f_{\text{O}_2}$  defined by the HM buffer, but at  $f_{\text{O}_2}$  below the NNO buffer. On the other hand, it is also synthesized from the glass of the granodiorite with all buffers.

A number of experimental studies have been made of biotite decomposition reactions (Eugster and Wones, 1962; Wones and Eugster, 1965; Ruther-

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ford, 1969, 1973). However, it is difficult that the experimental data are generally extrapolated to natural complex biotite. Hydrothermal experiments on natural biotite will provide useful informations for the crystallization in a granitic magma.

In the present study, physical and chemical properties of biotites from the

**Table 1** Chemical analyses, structural formulae and physical properties of biotites from the Takakumayama granite

| No.                            | TK21B | TK01B | TK04B | TK05B | TK07B | TK09B  |
|--------------------------------|-------|-------|-------|-------|-------|--------|
| SiO <sub>2</sub>               | 35.90 | 34.52 | 33.40 | 33.72 | 33.96 | 34.48  |
| TiO <sub>2</sub>               | 3.00  | 2.84  | 1.82  | 1.96  | 1.64  | 2.52   |
| Al <sub>2</sub> O <sub>3</sub> | 15.48 | 16.94 | 19.38 | 19.76 | 20.22 | 20.87  |
| Fe <sub>2</sub> O <sub>3</sub> | 3.56  | 4.19  | 4.84  | 4.48  | 6.79  | 4.85   |
| FeO                            | 18.82 | 18.52 | 20.72 | 19.76 | 18.76 | 19.88  |
| MnO                            | 0.27  | 0.41  | 0.82  | 0.68  | 0.84  | 0.52   |
| MgO                            | 9.60  | 9.12  | 5.20  | 5.43  | 3.28  | 3.03   |
| CaO                            | 1.24  | 0.60  | 0.74  | 0.45  | 0.67  | 0.69   |
| Na <sub>2</sub> O              | 0.30  | 0.40  | 0.48  | 0.26  | 0.28  | 0.24   |
| K <sub>2</sub> O               | 7.20  | 7.60  | 7.00  | 7.08  | 7.00  | 7.60   |
| H <sub>2</sub> O <sup>+</sup>  | 3.92  | 3.76  | 5.12  | 5.36  | 4.78  | 4.54   |
| H <sub>2</sub> O <sup>-</sup>  | 0.68  | 0.72  | 0.24  | 0.92  | 1.52  | 0.79   |
| P <sub>2</sub> O <sub>5</sub>  | 0.02  | 0.10  | 0.08  | 0.05  | 0.02  | 0.01   |
| Total                          | 99.99 | 99.72 | 99.84 | 99.91 | 99.76 | 100.02 |
| Si                             | 5.475 | 5.314 | 5.081 | 5.096 | 5.208 | 5.248  |
| Al <sup>IV</sup>               | 2.525 | 2.686 | 2.919 | 2.904 | 2.792 | 2.752  |
| Al <sup>VI</sup>               | 0.263 | 0.387 | 0.554 | 0.621 | 0.858 | 0.997  |
| Ti                             | 0.348 | 0.333 | 0.210 | 0.227 | 0.194 | 0.293  |
| Fe <sup>+3</sup>               | 0.404 | 0.481 | 0.548 | 0.509 | 0.793 | 0.549  |
| Fe <sup>+2</sup>               | 2.403 | 2.388 | 2.632 | 2.498 | 2.406 | 2.533  |
| Mn                             | 0.037 | 0.056 | 0.110 | 0.091 | 0.110 | 0.064  |
| Mg                             | 2.183 | 2.092 | 1.179 | 1.226 | 0.747 | 0.686  |
| Ca                             | 0.202 | 0.102 | 0.119 | 0.073 | 0.111 | 0.110  |
| Na                             | 0.092 | 0.111 | 0.146 | 0.073 | 0.074 | 0.073  |
| K                              | 1.394 | 1.500 | 1.353 | 1.363 | 1.364 | 1.481  |
| OH                             | 3.999 | 3.869 | 5.191 | 5.396 | 4.885 | 4.608  |
| α                              | 1.600 | 1.599 | 1.594 | 1.594 | 1.590 | 1.590  |
| β                              | 1.645 | 1.646 | 1.640 | 1.640 | 1.636 | 1.636  |
| γ                              | 1.651 | 1.650 | 1.646 | 1.645 | 1.642 | 1.642  |
| d <sub>005</sub> (Å)           | 2.013 | 2.012 | 2.008 | 2.006 | 2.006 | 2.006  |
| d <sub>060</sub> (Å)           | 1.543 | 1.543 | 1.540 | 1.540 | 1.539 | 1.538  |

TK21B and TK01B: Biotites from granodiorite of the Shinkoji-type.

TK04B and TK05B: Biotites from granite of the gradational zone.

TK07B and TK09B: Biotites from aplitic granite of the Sarugajo-type.

Takakumayama granite were determined, and hydrothermal experiments on two analyzed biotites were carried out with the HM buffer in the vicinity of the solidus temperature of the granite at 1 kb. Major attention will be given to comparison of physical and chemical properties between natural and experimentally treated biotites.

### Compositional Variation of Biotites

Six biotites from the Takakumayama granite were prepared for this study: two were separated from granodiorite of the Shinkoji-type; two from aplitic granite of the Sarugajo-type; and the other two from granite in the gradational zone of the two types. They were separated from the 60 – 100 mesh fraction of the crushed rock materials by a combination of magnetic separator and heavy liquid techniques.

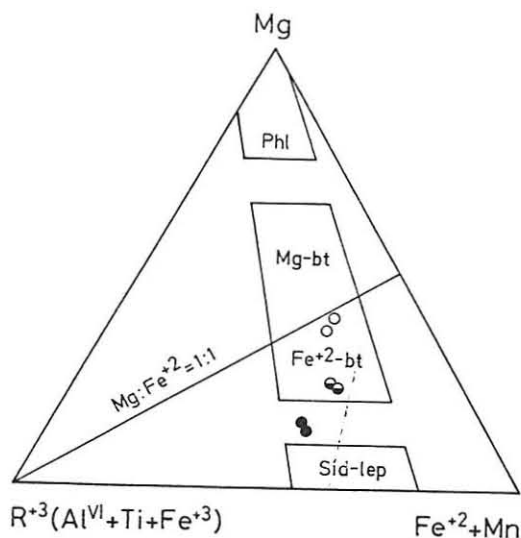


Fig. 1 Relation among Mg,  $R^{3+}(Al^{VI}+Ti+Fe^{+3})$  and  $(Fe^{+2}+Mn)$  of the octahedral group of biotites from the Takakumayama granite. Open circles: biotites from rocks of the Shinkoji-type. Half-solid circles: biotites from rocks of the gradational zone. Solid circles: biotites from rocks of the Sarugajo-type.

Abbreviations: Phl, phlogopite; Mg-bt, Mg-biotite;  $Fe^{+2}$ -bt,  $Fe^{+2}$ -biotite; Sid-lep, siderophyllite and lepidomelane.

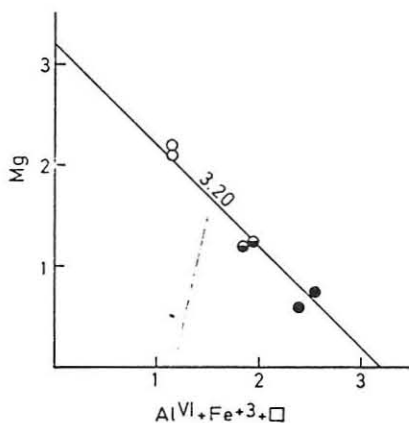


Fig. 2 Relation between Mg and the sum of  $Al^{VI}$ ,  $Fe^{+3}$  and octahedral vacancy of biotites from the Takakumayama granite. The symbols correspond to those in Fig. 1.

Chemical analyses and structural formulae of the biotites are presented in Table 1. The analyses were determined by a combination of 'standard' and 'ion exchange resin and chelate titration (Oki *et al.*, 1962)' methods, and the formulae were calculated on the basis of  $24(\text{O}, \text{OH})$  to the general formula of trioctahedral mica,  $\text{X}_2\text{Y}_6\text{Z}_8\text{O}_{20}(\text{OH})_4$ . The biotites are compositionally similar to those from other calc-alkaline plutonic rocks published by Heinrich (1946), Nockolds (1947), Foster (1960) and Deer *et al.* (1962a).

Figure 1 shows relation among  $\text{Mg}$ ,  $\text{R}^{+3}(\text{Al}^{\text{VI}} + \text{Ti} + \text{Fe}^{+3})$  and Solid lines represent the classification grid of trioctahedral micas after Foster (1960). Plots of biotites from rocks of the Shinkoji-type and the gradational zone fall within the  $\text{Fe}^{+2}$ -biotite field, and those of the Sarugajo-type within an area between the  $\text{Fe}^{+2}$ -biotite and siderophyllite-lepidomelane fields. As clearly seen in Fig. 1, chemical variation in the octahedral members is mainly controlled by the ratio between  $\text{Mg}$  and  $\text{R}^{+3}$ , and variation in  $(\text{Fe}^{+3} + \text{Mn})$  component is very small.

Figure 2 shows relation between  $\text{Mg}$  and the sum of  $\text{Al}^{\text{VI}}$ ,  $\text{Fe}^{+3}$  and octahedral vacancy of the analyzed biotites. Solid line represents 3.20 of a constant amount in total of  $\text{Mg}$ ,  $\text{Al}^{\text{VI}}$ ,  $\text{Fe}^{+3}$  and vacancy. The biotites are closely plotted along the line. This implies that the sum of  $\text{Al}^{\text{VI}}$ ,  $\text{Fe}^{+3}$  and vacancy makes up for the decrease of  $\text{Mg}$ . It is indicated, therefore, that principal compositional variation from biotite in the granodiorite to that in the aplitic granite is mainly caused by a substitution of  $3\text{Mg} \rightarrow 2(\text{Al}^{\text{VI}} + \text{Fe}^{+3}) + \text{Vacancy}$ .

Interplanar spacings for (005) and (060) reflections in the single layer monoclinic polytype determined with an X-ray powder diffractometer employing  $\text{CuK}\alpha$  radiation and indices of refraction determined by the immersion method are presented in Table 1, together with the chemical analyses. The spacings and the indices decrease considerably from biotites of the granodiorite into those of the aplitic granite. Although it is not clear that they are controlled by any single chemical constituent, it is evident that these decreases are mainly related to the increase of the  $\text{Al}^{\text{VI}}$ -content, as studies by Müller (1966a, b) and Dodge *et al.* (1969).

## Hydrothermal Experiments of Biotites

### Experimental Method

Hydrothermal experiments on two analyzed biotites Nos. TK01B of the granodiorite of the Shinkoji-type and TK09B of the aplitic granite of the Sarugajo-type, were carried out with the HM buffer at temperatures up to  $750^\circ\text{C}$  and 1 kb. The experiments were all performed in standard 'cold seal'

pressure vessels (Tuttle, 1949). The total pressure was maintained within  $\pm 20$  bars. The temperature was measured with chromel-alumel thermocouples and regulated to a precision of  $\pm 5^\circ\text{C}$ . The charge of biotite plus water was sealed into an Ag-Pd capsule. The capsule surrounded by the hematite-magnetite (HM) buffer was enclosed in an outer Au capsule. Quenching was all achieved by first removing pressure vessel from furnace, and the vessel was cooled down to room temperature. Run products were removed from charge containers, dried at  $60^\circ\text{C}$  in air, and subsequently examined by means of a petrographic microscope and an X-ray powder diffractometer employing  $\text{CuK}\alpha$  radiation.

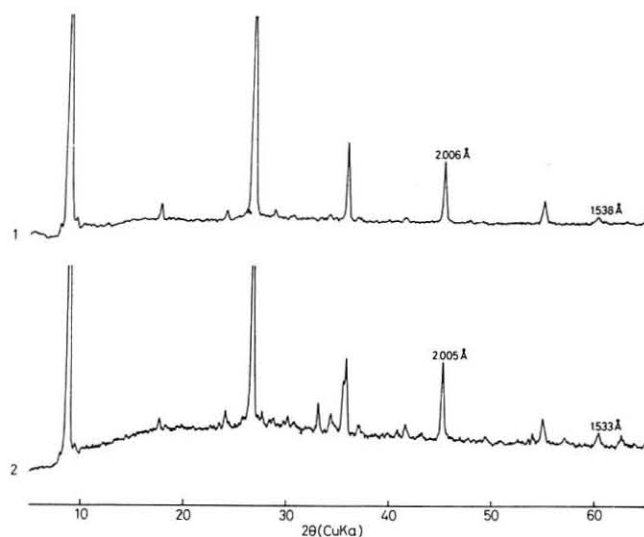


Fig. 3 X-ray powder diffraction patterns for the biotite No. TK09B and its run product with the HM buffer at  $750^\circ\text{C}$  and 1 kb. 1: Natural biotite. 2: Run product.

Table 2 Results of selected runs of hydrothermal experiments on biotites from the Takakumayama granite with the HM buffer at 1 kb

| No.   | Temp.               | Time   | Crystalline Phases |
|-------|---------------------|--------|--------------------|
| TK01B | $750^\circ\text{C}$ | 5 days | Bt + Hm            |
|       | 700                 | 5      | Bt + Hm            |
| TK09B | $750^\circ\text{C}$ | 5 days | Bt + Hm + Mt       |
|       | 710                 | 5      | Bt + Hm + Mt       |
|       | 670                 | 5      | Bt + Hm            |
|       | 620                 | 5      | Bt + Hm            |

Abbreviations: Bt, biotite; Hm, hematite; Mt, magnetite.

### *Experimental Results*

As an example, X-ray powder diffraction patterns for the biotite No. TK09B and its run product at 750°C are shown in Fig. 3, and the results of selected runs of the hydrothermal experiments are listed in Table 2. The biotites decomposed partially in all runs, and one or two of iron oxides such as hematite and magnetite were formed. However, no alkali feldspar phase was observed in the partial decomposition.

Hematite was found in all runs. Peak of (104) reflection for the hematite was also detected in X-ray patterns. Two forms of the hematite are recognized under the microscope: one is a light brown- to brown-colored and hexagonal-shaped grain with several microns in size; and the other is an aggregate of very small grains in a partially decomposed biotite plate. Unit-cell dimensions of the hematite formed in the run of the biotite No. TK01B at 750°C are  $a = 5.307 \pm 0.002\text{\AA}$ ,  $c = 13.776 \pm 0.005\text{\AA}$  and  $V = 302.7 \pm 0.2\text{\AA}^3$  in hexagonal symmetry and greater than those of pure hematite published by Deer *et al.* (1962b).  $2\theta$  values of the reflection are fairly uniform in all hematites.

Magnetite was found in the run of the biotite No. TK09B. Peak of (311) reflection for the magnetite was also detected only in the run product at 750°C. Like hematite, two forms of the magnetite are recognized: one is a cube-shaped grain with several microns in size; and the other is an aggregate of very small grains in a partially decomposed biotite plate. Unit-cell dimension,  $a$ , of the magnetite formed in the run is  $8.384 \pm 0.001\text{\AA}$  and slightly smaller than that of pure magnetite determined by Turnock and Eugster. (1962).

### Comparison of Physical and Chemical Properties between Natural and Experimentally Treated Biotites

Physical and chemical properties were compared between natural biotites and partially decomposed ones at 750°C.

#### *Physical Properties*

Indices of refraction determined by the immersion method and unit-cell dimensions calculated on the basis of the single layer monoclinic polytype by a least squares refinement for the natural and the partially decomposed biotites are presented in Table 3. The indices and the dimensions of the partially decomposed biotites are obviously smaller than those of the natural ones.

#### *Electron Microprobe Analyses*

Line analyses of major elements in the octahedral group of the natural and the partially decomposed biotites were performed with an electron microprobe

analyzer (Fig. 4). Analyzed samples were in the form of biotite plate coated with a thin carbon film and traversed under the electron beam at a rate of  $25\mu/\text{cm}$  on chart. The biotite LP-6 of the U.S. Geological Survey was used as

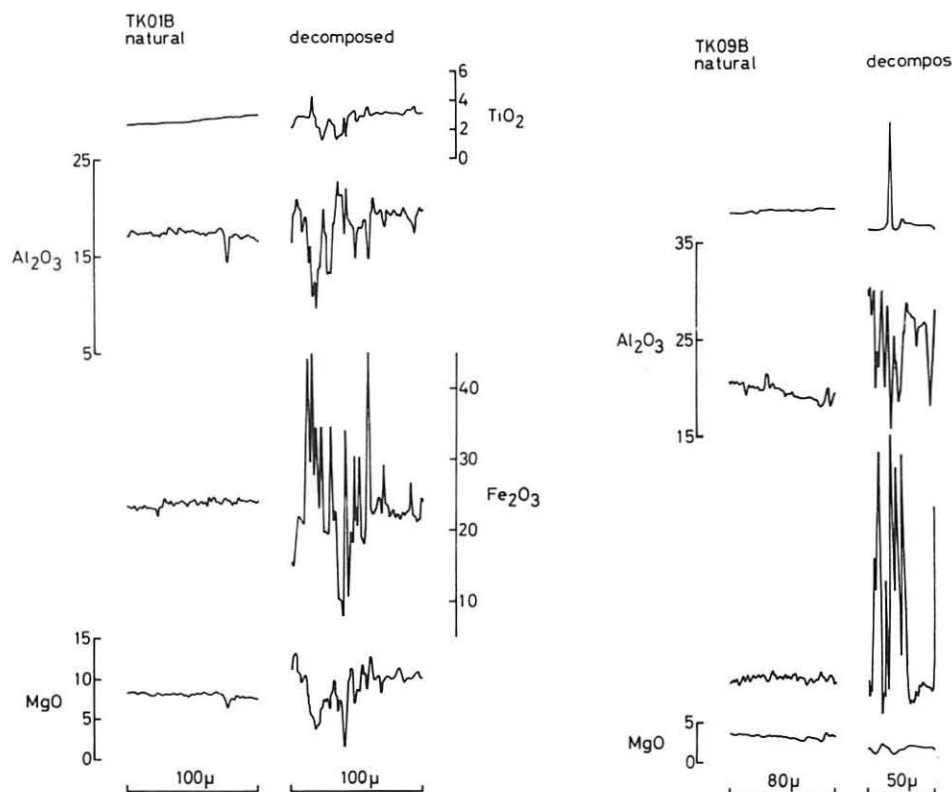


Fig. 4 Line analyses of natural biotites and partially decomposed ones with the HM buffer at  $750^{\circ}\text{C}$  and 1 kb

Table 3. Refractive indices and unit-cell dimensions of natural biotites and partially decomposed ones with the HM buffer at  $750^{\circ}\text{C}$  and 1 kb

| No.                             | 1          | 2          | 3           | 4          |
|---------------------------------|------------|------------|-------------|------------|
| $\frac{1}{2}(\beta + \gamma)^*$ | 1.648      | 1.629      | 1.639       | 1.629      |
| a, Å                            | 5.346 (2)  | 5.319 (2)  | 5.335 (4)   | 5.304 (3)  |
| b, Å                            | 9.259 (2)  | 9.215 (3)  | 9.234 (6)   | 9.193 (5)  |
| c, Å                            | 10.233 (3) | 10.194 (3) | 10.189 (6)  | 10.176 (5) |
| $\beta$                         | 100.04 (4) | 100.02 (2) | 100.02 (12) | 100.00 (9) |
| V, Å <sup>3</sup>               | 498.3 (2)  | 492.1 (2)  | 494.3 (5)   | 488.7 (4)  |

\*  $\pm 0.003$ .

1. Natural biotite No. TK01B. 2. Partially decomposed biotite TK01B.

3. Natural biotite No. TK09B. 4. Partially decomposed biotite TK09B.



standard, and correction was made for only background.

A natural biotite plate is compositionally homogeneous and compositional difference between biotite plates in the same rock is negligible. However, in the partially decomposed biotites, the data of the line analyses show irregular shapes, of which pattern for  $\text{Fe}_2\text{O}_3$  has the most irregularity. This implies that the irregularity is related to formation of iron oxides on a biotite surface not polished because of its small size. In the partially decomposed biotite No. TK01B, the patterns for  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  show similar shapes in each other, and they are reciprocal to those for  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , indicating that depletion of Fe and Ti easily takes place in oxidation states. On the other hand, in the partially decomposed biotite No. TK09B, the  $\text{TiO}_2$  and  $\text{MgO}$  contents decrease, as compared to the natural one, indicating that depletion of Mg also takes place, with Fe and Ti.

## Discussion

The isobaric univariant assemblage at  $f_{\text{O}_2}$  defined by the HM buffer in the phlogopite-annite join studied by Eugster and Wones (1962), Wones and Eugster (1965) and Rutherford (1969) is biotite+sanidine+hematite+magnetite. In this study, two phase assemblages obtained by the partial decomposition of natural biotites are biotite+hematite and biotite+hematite+magnetite, which will correspond to the isobaric divariant assemblage (biotite+sanidine+hematite) and the isobaric univariant one (biotite+sanidine+hematite+magnetite), respectively, in the join phlogopite-annite. It is thought, therefore, that by the partial decomposition of biotite at higher oxygen fugacities, hematite is generally formed at lower temperatures, whereas hematite+magnetite are at higher temperatures.

At 750°C and 1 kb, the magnetite was not found in the run of the biotite from the granodiorite of the Shinkoji-type, but of the biotite from the aplitic granite of the Sarugajo-type, indicating that a stability field of the former is located in a higher temperature range than that of the latter. This is consistent with hydrothermal experiments on the Takakumayama granite in the presence of excess water at 1 kb reported by Yamamoto (1977) that the biotite in the granodiorite remains up to 750°C, and the biotite in the aplitic granite disappears at 680°C. In this study, these biotites did not completely decompose at 750°C and 1 kb. It is suggested, therefore, that the stability field of biotite will generally decrease in the granite-water system, as studies by Rutherford (1969) that the stability field of the annite decreases in the presence of two feldspars.

Decreases of refractive indices and unit-cell dimensions from the natural

biotites into the partially decomposed ones were large. The annite has the highest refractive indices and the largest unit-cell dimensions in the trioctahedral mica group. Wones (1963) has determined the variations of refractive indices and unit-cell dimensions in the join phlogopite-annite. According to the variation in interplanar spacing for (060) reflection, it is estimated that the decreases correspond to that Fe of about 2.5 atoms is depleted from the natural biotites. Judging from the electron microprobe analyses, this estimation will be too large. Rutherford (1973) has also determined the variation of interplanar spacing for the (060) reflection on the join aluminous-iron biotite-annite. According to the variation, it is estimated that the above-mentioned decreases correspond to that Fe of about 1 atom is depleted. This estimation will be in relatively good accordance with the electron microprobe analyses. It is suggested, therefore, that changes of refractive indices and unit-cell dimensions will be affected by a substitution of trivalent cations for divalent ones. A decrease of divalent cations will be mainly due to a depletion of  $\text{Fe}^{+2}$ , and an increase of trivalent ones by an oxidation of  $\text{Fe}^{+2}$ .

In the run which only hematite was formed, the electron microprobe analyses indicate that the depletion of Fe and Ti takes place by the partial decomposition. The unit-cell dimensions of the hematite was greater than those of pure hematite. These facts suggest that the hematite formed by the partial decomposition will contain an ilmenite molecule. On the other hand, in the run which both hematite and magnetite were formed, the depletion of Mg also takes place, with Fe and Ti. The unit-cell dimension of the magnetite is slightly smaller than that of pure magnetite. These facts also suggest that the magnetite formed by the partial decomposition will contain a magnesioferrite molecule. However, the electron microprobe analyses show that  $\text{Al}^{+3}$  is hardly depleted from the biotites. Judging from the above-mentioned results, in oxidizing conditions, Fe, Ti and Mg ions will be easily depleted from biotite, and composition of the biotite will be generally affected by associating Fe-Ti-Mg oxides. If a granitic magma had a higher activity of alumina under which aluminous mineral such as garnet or muscovite was crystallized, the biotite will compositionally become aluminous.

Wones and Eugster (1965) have stated that a higher oxygen fugacity will tend to produce a higher  $\text{Fe}^{+3}/(\text{Fe}^{+2}+\text{Fe}^{+3})$  ratio in biotite with charge balance being maintained through the creation of octahedral vacancies or by solid solution toward the dehydrogenated oxy-biotite end member. In this study, iron oxides were formed by the partial decomposition. If an oxy-biotite molecule was formed, alkali feldspar should appear. However, the fact that no alkali feldspar phase is found, will mean that the octahedral vacancies are produced in the partially decomposed biotites.

As mentioned above, by the partial decomposition in oxidizing conditions, it is indicated that  $\text{Al}^{+3}$  is hardly depleted from biotite, and  $\text{Fe}^{+3}$  and octahedral vacancies in biotite increase. These compositional changes are similar to the compositional variation of the natural biotites from the Takakumayama granite, although  $\text{Fe}^{+2}$  decreases in the former and  $\text{Mg}^{+2}$  in the latter, indicating difference between partial decomposition and crystallization. It is estimated, therefore, that oxygen fugacities of the Takakumayama granitic magma have increased during the emplacement. This is consistent with that the MnO content increases from ilmenite in the granodiorite of the Shinkoji-type into that in the aplitic granite of the Sarugajo-type as reported by Tsusue (1973), and that garnet and muscovite are found within the aplitic granite.

### Conclusion

The present study gave the compositional variation of biotites from the Takakumayama granite and their hydrothermal experiments. It has been known that  $\text{Mg}^{+2}$  in biotites increases with increasing oxygen fugacities of granitic magmas (*e.g.*, Murakami, 1960; Czamanske and Wones, 1973). In the present study, it was indicated that the increases  $\text{Al}^{+3}$ ,  $\text{Fe}^{+3}$  and octahedral vacancies in biotite will be also explained by the increase of oxygen fugacity of a granitic magma, which has a higher activity of alumina.

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