パラゲネティック関係と物理化学条件によるイオノキタルの結晶化の研究

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<tr>
<th>著者</th>
<th>OBA Noboru, YAMAMOTO Masahiko, TOMITA Katsutoshi</th>
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<td>別言語タイトル</td>
<td>配位成分に基づく花崗岩黒雲母の共生関係と物理化学的生成条件</td>
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<th>佐野智郎, 山本雅彦, 木田耕俊</th>
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PARAGENETIC RELATIONS AND PHYSICOCHEMICAL CONDITIONS OF CRYSTALLIZATION OF BIOTITES FROM GRANITES ON THE BASIS OF OCTAHEDRAL COMPOSITIONS

By
Noboru OBA*, Masahiko YAMAMOTO* and Katsutoshi TOMITA*

(Received July 2, 1984)

Abstract

The result of the analysis of octahedral compositions in biotites from granitic rocks of the Southwestern Outer Zone-type, Japan, and circum-Pacific and other regions shows that biotites associated with pyroxene are high in both Mg- and Ti-contents and low in Al\textsuperscript{III}-content, but, on the contrary, those unaccompanied by other ferromagnesian mineral are low in both Mg- and Ti-contents and high in Al\textsuperscript{III}-content. Such a fact gives that the relative proportion of the octahedral compositions such as Ti, Al\textsuperscript{III} and Mg or Fe\textsuperscript{3+} in biotite formula is controlled by the paragenesis of biotite and physicochemical conditions during crystallization of biotite in magma: the higher Ti-content of biotite associated with pyroxene reflects the higher temperature involved in the crystallization of magma; the higher Al\textsuperscript{III}-content of biotite unaccompanied by other-ferromagnesian mineral indicates the chemical environment of the higher Al-activity; and the higher Fe\textsuperscript{3+}-content of biotite suggests the physical condition of higher oxygen fugacity during crystallization of magma.

Introduction

To understand the physicochemical conditions during crystallization of biotite in magma, detailed studies were made of octahedral compositions in biotites of granitic rocks of the Southwestern Outer Zone-type, Japan, those of which were reported by one of the present authors with respect to their petrographic provinces and geologic environments (OBA, 1974, 1977), and of circum-Pacific and other regions. This paper is a summary of papers presented by the authors at the Annual Meeting of Geological Society of Japan in 1964, and at the 1st, 7th and 9th Meetings of the IGCP Project No. 30, Circum-Pacific Plutonism Project, held in California, U.S.A, in 1972, in Japan and Korea in 1977, and in Khabarovsk, U.S.S.R., in 1979, and at the 3rd Regional Conference on Geology and Mineral Resources of Southeast Asia held in Bangkok, Thailand, in 1978 (OBA, 1964; OBA and others, 1977, 1978, 1979). Major attention will be given in this paper to the relative proportion of some octahedral compositions in biotite formulas; comparisons of octahedral compositions in biotites from different rock bodies; and the

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relationship between mineral associations and compositional variations of biotites.

Chemical relationships between biotites and host granitic rocks of the Southwestern Outer Zone-type and between biotites and its mineral associations

The definite relation between chemical composition of biotites and that of its host rocks has not yet well known, except for a few studies. This is originated from such a reason that there has been no definite work which was throughly investigated, from the geochemical viewpoint, with respect to both biotites and genetically related rocks of the biotites.

In 1947, Nockolds pointed out that chemical nature of biotite is predominantly controlled by chemical nature of its host rock. Granitic rocks of the Southwestern Outer Zone-type (Shibata, 1962) can be regarded that they belong to the same genetical system, i.e., the Southwestern Outer Zone Petrographic Province (Shibata, 1962) on the basis of the remarkable petrochemical characteristics in common throughout the whole of them, and that they would have been formed in almost the same physical condition from geologic and petrologic evidences (ŌBA, 1977; ŌBA and others, 1978). Thus, it will be worthwhile to examine whether chemical nature of biotites might have been controlled by chemical nature of its host rocks, and, by presence or not of coexisting ferromagnesian minerals in regard to a series of granitic rocks such as the Southwestern Outer Zone-type granitic rocks.

1. Chemical relationship between biotites and its host granitic rocks

Dmitriyev and others (1962) showed that a relation between chemical change of biotites with chemical change of its host alkalic rocks and the spatial position within a rock body is sharply expressed by using of the agpaitie parameter, i.e., the value of ratio of Na to (Al–K) in atomic percentage. In the meantime, the variation in chemical composition of biotites is expressed well by the value of ratio of alkalies to Mg in biotite formula against chemical change in the individual granitic rock bodies (ŌBA, 1964). Thus, the values of the (Na+K)/Mg ratios in structural formulas of biotites from the Southwestern Outer Zone-type granitic rocks were taken in ordinate, and the values of the Na/(Al–K) ratios in the granitic rocks of the analyzed biotites in abscissa (Fig.1).

The plots representing both biotites and its host rocks, as Fig. 1 shows, apparently fall within a different field following to the individual rock bodies. This fact shows that biotites from a single rock body have a similar structural formula. Such a fact can also be seen even within a single rock body, for example, Takakumayama granite composing of aplogranite called “Sarugajyo-type” and biotite granite called “Shinkōji-type.” Fig. 2 shows the locations of the plots representing both biotites and its host aplogranite and the plots representing biotites and its host biotite granite on the same diagram. They are sharply contrasted with each other in their locations. Therefore, it will be said that chemical nature of biotites is closely related with that of its host rock.
Paragenetic Relations and Physicochemical Conditions

Fig. 1. Relationship between the values of (Na+K)/Mg ratios in biotite formulas and those of Na/(Al-K) ratios in granitic rocks of the Southwestern Outer Zone-type of analyzed biotites. Symbols for rock bodies of analyzed biotites.—a, Ōkuyama; b, Ōsumi; c, Shibisan; d, Takakumayama; e, Yakujima; f, Obira; g, Uwajima; h, Ashizuri. d, e and f, rock bodies of analyzed biotites unaccompanied by other ferromagnesian mineral; a, b, c and h, rock bodies of analyzed biotites coexisting with amphibole; g, rock body of analyzed biotites associated with pyroxene. Rock types.—see Table 1 and Table 2. Analytical data from ŌBA and others (1982).

Fig. 2. Compositional variations within a single rock body of Takakumayama granite composed of aplogranite called “Sarugajō-type” and biotite granite called “Shinkoji-type” on the (Na+K)/Mg—Na/(Al—K) diagram. It is noted that the plots representing both biotites and its host aplogranites are sharply contrasted with the plots representing both biotites and its host biotite granites in their locations. Symbols.—a, biotite granite (Shinkōji-type); b, aplogranite (Sarugajō-type).
2. Relationship between chemical composition of biotites and mineral associations

Plotting of the analyzed biotites on Nockolds' (1947) triangular diagram MgO–total FeO–Al₂O₃ for biotites from calc-alkali igneous rocks (Fig. 3), most of the plots representing biotites associated with almandine from aplogranite (Sarugajyo-type) of Takakumayama rock body fall within the field I; the plots representing biotites unaccompanied by other ferromagnesian mineral from biotite granites of rock bodies of Yakujima, Takakumayama (Shinkoji-type) and Obira fall within the field II; and the plots representing biotites associated with amphibole, rarely with pyroxene in addition to amphibole, from granodiorites and adamellites of other rock bodies belonging to the Southwestern Outer Zone-type fall within the field III or nearby the boundary between both the fields II and III. Thus, it can be said that this fact, as Nockolds mentioned, shows that chemical composition of biotites is closely related with the presence or not of coexisting ferromagnesian minerals, that is, with mineral associations.

![Fig. 3. Plots of biotites from the Southwestern Outer Zone-type granitic rocks on Nockolds' (1947) triangular diagram MgO–total FeO–Al₂O₃. I, Field of biotites associated with aluminous minerals; II, field of biotites unaccompanied by other ferromagnesian mineral; III, field of biotites associated with ferromagnesian minerals. Symbols are the same as those in Fig. 1.](image)

Physicochemical conditions during crystallization of magmas inferred from octahedral compositions of analyzed biotites from the Southwestern Outer Zone-type granitic rocks

Fe²⁺ and Mg in biotite formula are largely temperature-dependent, and Fe³⁺ and Fe²⁺ give an indication of the degree of oxidation. Thus, variation of these cations are important to consider the physical condition during crystallization of biotite in magma.

In Fig. 4, most of the analyzed biotites occupy an area between hematite-magnetite buffer curve and Ni–NiO buffer curve. If the experimental data by Wones and Eugster (1965) are applied and Al activity is neglected, it is suggested that composition of most
Paragenetic Relations and Physicochemical Conditions

Fig. 4. $\text{Fe}^{3+}$-$\text{Fe}^{2+}$-$\text{Mg}$ diagram for biotites of the Southwestern Outer Zone-type granitic rocks. Dashed lines represent compositions of "buffered" biotites in the ternary system $\text{KFe}_3^2+ \text{AlSi}_3\text{O}_{10}(\text{OH})_2-K\text{Fe}_3^2+ \text{AlSi}_3\text{O}_{10}(\text{OH})_2-\text{KMg}_3^2+ \text{AlSi}_3\text{O}_{10}(\text{OH})_2$ estimated by WONES and EUGSTER (1965). Symbols are the same as those in Fig. 1.

of the analyzed biotites is defined by oxygen fugacities ranging from hematite-magnetite buffer to Ni-NiO buffer.

The comparison of ratios of X-ray intensities for (001) reflection of biotites from run products from glasses of some granitic rocks, such as Ōsumi, Takakumayama and Shimo-koshikijima, belonging to the Southwestern Outer Zone-type on the hematite-magnetite, Ni-NiO and fayalite-silica-magnetite buffers at 700°C and 1 kbar with those calculated from the experimental data determined by WONES and EUGSTER (1965), suggests that the biotites would have crystallized at oxygen fugacity above the Ni-NiO buffer (YAMAMOTO, 1976). All studied biotites coexist with magnetite and potash feldspar in all studied host granitic rocks. Accordingly, it seems that the oxygen fugacity of granitic magmas of the studied rocks would have approximately been constant.

Meanwhile, some of biotites from Takakumayama granite fall within a distinctive area biased to the apex $\text{Fe}^{3+}$. Investigation for compositional variation on a substitution of Mg for the whole sum of Al$^6+$, Fe$^{3+}$ and octahedral vacancy and hydrothermal experiments with hematite-magnetite buffer at temperature up to 750°C and 1 Kbar for the same biotites indicated that Al$^6+$ is hardly depleted from the biotites, while Fe$^{3+}$ and octahedral vacancies in the biotites increase (YAMAMOTO, 1978). No depletion of Al$^6+$ and the increase of Fe$^{3+}$ and octahedral vacancies in the biotites will be explained by the increase of oxygen fugacity of a granitic magma which has a high activity of Al. Thus, it can be considered that such a substitution among these cations as seen in the biotites would have taken place in an oxidizing condition during crystallization of the magma.
Variations of Al\textsuperscript{IV}-content with change of Fe\textsuperscript{2+}-content, Mg-content with change of Al\textsuperscript{VI}-content and Ti\textsuperscript{VI}-content with change of Al\textsuperscript{IV}-content in biotite formulas

1. Variation of Al\textsuperscript{IV}-content with change of Fe\textsuperscript{2+}-content in biotite formulas

An increase in the ratio of Fe\textsuperscript{2+} to Mg, i.e., iron coefficient, of polymerized silicates diminishes electronegativity of non-bridging oxygen anions (Ramberg, 1952). As a result, the content of four-fold coordinated Al increases to balance the electronegativity.

Dmitriev and others (1962) recognized that four-fold coordinated Al increases with an increase of six-fold coordinated Fe\textsuperscript{2+} on the basis of analytical data of biotites reported by Nockolds (1947). Plotting of the analyzed biotites from the Southwestern Outer Zone-type granitic rocks on the Al\textsuperscript{VI}-Fe\textsuperscript{2+} diagram (Fig. 5), most of them fall within the distribution-range, representing by two dahsed lines, for Nockolds’ biotite data.

2. Variation of Mg-content with change of Al\textsuperscript{VI}-content in biotite formulas

Table 1 gives octahedral compositions, arranged in order of decreasing Mg-content, in the half-cell structural formulas of the analyzed biotites from selected granitic rocks of Southwestern Outer Zone-type. For comparison, average compositions calculated by Foster (1960) are placed. Table 2 presents the Mg–Al\textsuperscript{VI} relation in octahedral layers of the analyzed biotites, which are arranged in order of decreasing Mg-content. It is clear that the decrease of the Mg-content is accompanied by the increase of the Al\textsuperscript{VI}-content.

Variations of the Mg-content with change of the Al\textsuperscript{VI}-content in biotites from granitic rocks of the Southwestern Outer Zone-type and of circum-Pacific and other regions are shown in Fig. 6 and Fig. 7. Fig. 8 compiled from the former two diagrams gives a relation between the Mg–Al\textsuperscript{VI} variation and mineral associations in the biotites. It is noted that the decreasing of the Mg-content increases the Al\textsuperscript{VI}-content, in other words, an
Table 1. Octahedral compositions (half-cell) of biotites from selected granitic rocks of the Southwestern Outer Zone-type in order of decreasing Mg-content

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<th>AL\textsuperscript{VI}x0.15</th>
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* FOSTER’S (1960) average octahedral compositions of biotites. Abbreviations for rock-types.—AG, aplogranite; BG, biotite granite; HBGD, hornblende-biotite granodiorite. Analytical date from ŌBA and others (1982).

increase of the iron coefficient increases the Al\textsuperscript{VI}-content to balance the electronegativity. It is also noted that biotites associated with pyroxene are very high in the Mg-content and very low in the Al\textsuperscript{VI}-content, but, on the contrary, most of biotites unaccompanied by other ferromagnesian mineral are low to moderate in the Mg-content and very high to high in the Al\textsuperscript{VI}-content. Such a fact shows that the Mg–Al\textsuperscript{VI} variation in biotite is controlled by mineral associations.

3. Variation of Ti\textsuperscript{IV}-content with change of Al\textsuperscript{VI}-content in biotite formulas

Variations of Ti\textsuperscript{IV}-content with change Al\textsuperscript{VI}-content in biotites from granitic rocks of the Southwestern Outer Zone-type and of circum-Pacific and other regions are shown in
Table 2. Comparison of Al\(^{VI}\)-content in biotites from the Southwestern Outer Zone-type granitic rocks in order of decreasing Mg\(^{II}\)-content in octahedral compositions (half-cell)

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* FOSTER’s averages. Abbreviations for rock bodies.—A, Ashizuri; OB, Obira; OK, Okueyama; OS, Osumi; S, Shibisan; T, Takakumayama; U, Uwajima; Y, Yakujima. Other abbreviations are the same as those in Table 1. Analytical data from OBA and others (1982).

Fig. 9 and Fig. 10. Fig. 11 compiled from the former two variation diagrams presents a relation between the Ti\(^{VI}\)-Al\(^{VI}\) variation and mineral associations in the biotites. It is clear that there is a trend of the increase of the Ti\(^{VI}\)-content accompanied by the decrease of the Al\(^{VI}\)-content on Fig. 11.
Paragenetic Relations and Physicochemical Conditions

Fig. 6. Variation of Mg-content with change of Al\textsuperscript{VI}-content in biotites of the Southwestern Outer Zone-type granitic rocks. Symbols are the same as those in Fig. 1.

Fig. 7. Variation of Mg-content with change of Al\textsuperscript{VI}-content in biotites of granitic rocks of circum-Pacific and other regions. Symbols for rock bodies of biotites—\(a\), Sierra Nevada batholith, Calif., U.S.A.; \(b\), Rosses complex, Ireland; \(c\), Palmer granite, Australia; \(d\), Sierra Navada batholith; \(e\), Aregos complex, Portugal; \(f\), Ben Nevis complex, Scotland; \(g\), Sierra Navada batholith; \(h\), Ben Nevis complex; \(i\), Hirota and Orikabe messes, Kitakami mountainlands, Japan. Mineral associations—\(a\), \(b\) and \(c\), biotites unaccompanied by other ferromagnesian mineral; \(d\), \(e\) and \(f\), biotites coexisting with amphibole; \(g\), \(h\) and \(i\), biotites associated with pyroxene. Analytical data from DODGE and others (1969), HALL (1969), WHITE (1966), DE ALBUQUERQUE (1973), HASLAM (1968), KANISAWA (1972) and KATO (1972).
Fig. 8. Variation of Mg-content with change of Al⁶⁺-content in biotites of granitic rocks of the Southwestern Outer Zone-type and of circum-Pacific and other regions. Compiled from Fig. 6 and Fig. 7 in regard to mineral associations. Symbols—open circles, biotites unaccompanied by other ferromagnesian mineral; open triangles, biotites coexisting with amphibole; solid circles, biotites associated with pyroxene.

Fig. 9. Variation of Ti⁶⁺-content with change of Al⁶⁺-content in biotites of the Southwestern Outer Zone-type granitic rocks. Symbols are the same as those in Fig. 1.

Fig. 10. Variation of Ti⁶⁺-content with change of Al⁶⁺-content in biotites of granitic rocks of circum-Pacific and other regions. Symbols are the same as those in Fig. 7.

Attention should also be given to the fact that biotites associated with pyroxene are clearly high in the Ti⁶⁺-content and low in the Al⁶⁺-content, but, on the contrary, biotites coexisting with no other ferromagnesian mineral are apparently high to very high in the Al⁶⁺-content and low in the Ti⁶⁺-content. Higher temperature is favourable for the en-
Fig. 11. Variation of Ti$^{IV}$-content with change of Al$^{VI}$-content in biotites of granitic rocks of the Southwestern Outer Zone-type and of circum-Pacific and other regions. Compiled from Fig. 9 and Fig. 10 in regard to mineral associations. Symbols are the same as those in Fig. 8.

trance of Ti into biotite during crystallization of magma. Accordingly, it can said that some octahedral compositions such as Ti and Al in biotite formulas will be useful indicators to give both temperature of crystallization and the paragenesis of biotite.

**Relationship between the relative proportions of octahedrally coordinated Ti, Al and Fe$^{3+}$ and mineral assemblages in biotites**

According to De Albuquerque (1973), who stated that the Ti–Al$^{VI}$–Fe$^{3+}$ diagram for biotite will reflect various conditions such as temperature, pressure and mineral assemblage during crystallization of magma, Ti-content of biotite depends on temperature of crystallization, Fe$^{3+}$-content depends on oxygen fugacity of magma and Al$^{VI}$-content depends on the paragenesis of biotite.

Fig. 12. Ti–Al$^{VI}$–Fe$^{3+}$ diagram for biotites from the Southwestern Outer Zone-type granitic rocks. Distribution-areas for rock bodies of analyzed biotites.—A, Takakumayama; B, Yakujima; F, Ōkueyama; G, Ōsumi; H, Shibisan. Cross and diagonal cross represent pelitic xenolith and basic xenolith of analyzed biotites, respectively (analytical data from Ōba and others, 1982). Other symbols are the same as those in Fig. 1.
Comparisons of distribution-areas for biotites from different batholiths or rock-bodies on the Ti–Al\textsuperscript{VI}–Fe\textsuperscript{3+} diagram were made for inference of physicochemical conditions during crystallization of biotite in magma. On Fig. 12 showing the distribution-areas for the analyzed biotites from the Southwestern Outer Zone-type granitic rocks, the distribution-areas A and B for biotites coexisting with no other ferromagnesian mineral from granitic rocks of Takakumayama and Yakujima occupy wider areas with low Ti and very high to moderate Al, but, in contrast, the distribution-area F for biotites coexisting with amphibole from granitic rocks of Ōkueyama is limited in a narrow and distinctive area with relatively high Ti and very low Al. On Fig. 13 showing the distribution-areas for biotites from granitic rocks of circum-Pacific and other regions, biotites unaccompanied by other ferromagnesian mineral from granitic rocks of Sierra Nevada, Palmer and Rosses (C, E and D in Fig. 13) occupy the areas with low Ti and very high to moderate Al, but, in contrast, biotites associated with pyroxene from granitic rocks of Hirota and Orikabe (Kitakami mountainlands), Sierra Navada and Ben Nevis (N, L and M in Fig. 13) occupy the areas with high to very high Ti or just on the Ti–Fe\textsuperscript{3+} join close to Ti-apex.

Fig. 14 compiled from the former two triangular diagrams Fig. 12 and Fig. 13 gives a relation between the Ti\textsuperscript{VI}–Al\textsuperscript{VI}–Fe\textsuperscript{3+} variation and mineral associations in biotites. As seen from this, the locations of solid circles representing biotites associated with pyroxene are sharply contrasted with those of open circles representing biotites coexisting with no other ferromagnesian mineral. That is, the biotites coexisting with no other ferromagnesian mineral are low in the Ti-content and high to moderate in the Al\textsuperscript{VI} content, but, on the contrary, those associated with pyroxene are high in the Ti-content.
Fig. 14. Relationship between mineral associations and the relative proportions in Ti-, Al$^{VI}$-, and Fe$^{3+}$-contents in octahedral compositions of biotites of granitic rocks. Compiled from Fig. 12 and Fig. 13. Symbols are the same as those in Fig. 8.

and low in the Al$^{VI}$-content. It is clear that there is a close relation between the paragenesis of biotite and octahedral compositions.

In conclusion, therefore, it will be possible to say that the higher Ti-content in biotite reflects higher crystallization temperature and mineral assemblage with association of pyroxene, while the higher Al$^{VI}$-content in biotite indicates the chemical environment of the higher Al-activity and the paragenesis with no other ferromagnesian mineral.

Summary

Biotites from a single rock body have a very similar octahedral composition. This fact means that chemical nature of biotite is characterized by octahedral composition, which reflects well both mineral association and physicochemical conditions as a consequence of chemical and physical factors at the time when biotite crystallized out in magma.

As a result of the analysis of octahedral compositions in biotites from granitic rocks of the Southwestern Outer Zone-type and of circum-Pacific and other regions, the following facts were recognized. The decrease of the Mg-content increases the Al$^{VI}$-content, and the increase of the Ti-content decreases the Al$^{VI}$-content. Biotites associated with pyroxene are clearly high in both the Mg- and Ti-contents and very low in the Al$^{VI}$-content, but, in contrast, biotites coexisting with no other ferromagnesian mineral are clearly low in both the Mg- and Ti-contents and high to very high in the Al$^{VI}$-content.

These facts give that the relative proportion of the octahedral compositions Ti, Al$^{VI}$ and Mg or Fe$^{3+}$ in biotite formulas is controlled by the paragenesis of biotite and the physicochemical conditions during crystallization of biotite in magma. That is, it can be considered that the higher Ti-content of biotite reflects the higher temperature involved
in the crystallization of magma; the higher Al\textsuperscript{IV} content of biotite indicates the chemical environment of the higher Al-activity; and the high to moderate Fe\textsuperscript{3+} content of biotite, as seen in some granitic rocks of the Southwestern Outer Zone-type, suggests the physical condition high to moderate in oxygen fugacity during crystallization in magma.

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Appendix

Ashizuri 足摺; Hirota 広田; Kitakami 北上; Obira 尾平; Oki 隠岐; Ökuayama 大崩山; Orikabe 折壁; Ösumi 大隅; Sarugajyo 猿ヶ城; Shibusan 紫尾山; Shimokoshikijima 下総島; Shinkōji 新光寺; Takakumayama 高隈山; Uwajima 宇和島; Yakujima 屋久島