Association of hydrothermal plagioclase alteration with micropores in a granite: Petrographic indicators to evaluate the extent of hydrothermal alteration

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This study presents the use of petrographic plagioclase alteration indicators as a new method for quantitatively evaluating the extent of plagioclase alteration within granites, using the Toki granite, central Japan, as an example. The new petrological indicator enables us to discuss the similarities/differences in the extent of alteration within a rock body and between rock bodies. Alteration indicators and areal fractions of microvoids in the plagioclase grains were obtained through the analysis of backscattered electron images. The volume of the micropores in the altered plagioclase was estimated using the areal fraction of microvoids in the grains. The plagioclase alteration indicators were obtained as the ratio between the alteration product domain and the original plagioclase domain. We found positive correlations between the plagioclase alteration and biotite chloritization indicators presented in Yuguchi et al. (2021), indicating that each alteration indicator can be used independently as a representative value for the sample. The positive correlations between the areal fraction of microvoids in the altered plagioclase and the alteration indicator in the samples and petrographic observations indicated the following: 1) the altered plagioclase contains the incipient micropores and the alteration microvoids, 2) the incipient micropores, which were caused by the dissolution of plagioclase during the incipient stage of plagioclase alteration, acted as a pathway of hydrothermal fluid within the plagioclase, resulting in alteration progress, and 3) the hydrothermal alteration resulted in the production of new alteration microvoids. In the Toki granite, the progress of plagioclase alteration is essentially dominated by the progress of biotite chloritization. The progress of biotite chloritization essentially influenced the progress of plagioclase alteration.

Keywords: Alteration indicator, Plagioclase, Hydrothermal alteration, Micropore, Microvoid

INTRODUCTION

The hydrothermal alteration of granitic rock is constrained mainly by the dissolution–precipitation processes during the infiltration of hydrothermal fluid along the microcracks (microfractures) and microvoids (Nishimoto and Yoshida, 2010; Yuguchi et al., 2015). Given that plagioclase is the dominant mineral in various rock types in the crust, reaction–induced pore networks in plagioclase could be the dominant fluid pathway in the crust (Nurdiana et al., 2021). That is, plagioclase micropores and nanopores can provide more pervasive fluid infiltration within a rock body and the crust (e.g., Plümper and Putnis, 2009; Plümper et al., 2017). Yuguchi et al. (2019a) described the distribution of micropores within the plagioclase as a key factor of the alteration. The alteration is also influenced by the mass transfer of chemical components owing to rock–matrix diffusion and through the micropore network (Alexander et al., 2009; Neretnieks, 2017; Yuguchi et al., 2019a). Engvik et al. (2008) studied the metasomatic albitization of plagioclase in granitic rocks from the Bamble sector of southeastern Norway. They found micropores and nanopores in albite replacement products and argued that albitization was responsible for fluid infiltration and the mineral replacement process. In contrast, the plagioclase albitization is frequently associated with the formation of micropores during hydrothermal alteration (e.g., Hövelmann et al., 2010; Putnis, 2015; Yuguchi et al., 2019a,
Association of plagioclase alteration with micropores in a granite

The Toki granite is an ideal example for understanding the hydrothermal alteration processes. Previous studies have suggested that the hydrothermal alteration of the Toki granite occurred through the following serial processes: 1) biotite chloritization, 2) plagioclase alteration, and 3) carbonate mineral precipitation (Nishimoto et al., 2008; Nishimoto and Yoshida, 2010). Biotite chloritization alteration and plagioclase alteration occur at 180–350 °C within the rock body (Yuguchi et al., 2015, 2019a). While our previous study (Yuguchi et al., 2021) focused on the progress of biotite chloritization, we focused on plagioclase alteration in this study. The alteration indicators for biotite chloritization were defined as the ratio of the alteration product domain and the original mineral domain (Yuguchi et al., 2021). In the Mizunami Underground Research Laboratory (MURL), two 500-m long vertical shafts were excavated in the Toki granite, allowing the extraction of non-weathered samples. Twenty-four samples were analyzed to evaluate the relationships between the alteration indicators and areal microvoid fractions in the altered plagioclase. Based on these data, we discuss the relationships between alteration progress and microvoids and 2) biotite chloritization and plagioclase alteration, which reveal the factors constraining the alteration progress of plagioclase.

THE TOKI GRANITE AND MURL

The Toki granite located in Tono District, central Japan, is one of the Late Cretaceous plutonic bodies of the Sanyo Belt in Southwest Japan (Fig. 1a; Ishihara and Chappell, 2007). The Toki granite is a zoned pluton consisting of three lithofacies: muscovite-biotite granite, hornblende-biotite granite, and biotite granite (Ishihara and Suzuki, 1969; Yuguchi et al., 2010). The Toki granite is a stock of approximately 14 × 12 km² (Ishihara and Suzuki, 1969) and is overlain unconformably by the Miocene Mizunami Group and the Mio-Pleistocene Tokai Group (Itoigawa, 1974; 1980; Todo Collaborative Research Group, 1999). The Toki granite has a whole–rock Rb-Sr isochron age of 72.3 ± 3.9 Ma (Shibata and Ishihara, 1979), a monazite chemical Th–U–total Pb isochron (CHIME) age of 68.3 ± 1.8 Ma (Suzuki and Adachi, 1998), and zircon U–Pb ages of 74.7 ± 4.2 to 70.4 ± 1.7 Ma (Yuguchi et al., 2016). A detailed description of its petrography and geochronology can be found in Yuguchi et al. (2011a, 2011b, 2019b, 2020). The MURL, which consists of two vertical shafts (a main shaft and a ventilation shaft) is located on the sedimentary Mizunami Group (Figs. 1b and 1c). The Mizunami Group unconformably overlies the Toki granite (Fig. 1c; Itoigawa, 1974, 1980). The main and ventilation shafts are 500 m deep with a ground level elevation of 201 meters above sea level (masl) (Fig. 1c).

ANALYTICAL PROCEDURES

Samples

Borehole 06MI03 was drilled to a depth of 191 m in the ventilation shaft before the shaft was excavated below 191 m (Fig. 1c). The borehole 06MI03 is 336 m long with a diameter of 123 mm. Twenty-four samples were collected from borehole 06MI03 for this study (Table 1); the same samples were analyzed by Yuguchi et al. (2021). The mineral assemblage of the samples consists of quartz, plagioclase, K-feldspar, biotite, hornblende, and muscovite, with accessory minerals including zircon, apatite, ilmenite, and magnetite and secondary minerals including chlorite, titanite, epidote, allanite, ililite, and calcite. Plagioclase occurs as subhedral to euhedral crystals 1–20 mm across. Subhedral–equigranular quartz with crystals 0.5–25 mm across and subhedral K-feldspar 1–15 mm across is observed in the rock samples. The biotite shows variable degrees of chloritization. Fractures (microracks) are distributed irregularly in the sample and are frequently filled with calcite. The feldspars include micropores and sub-solidus textures such as myrmekite and perthite. Sample Nos. 1 and 7 were employed as a control experiment. They were collected from the same depth range (307.7–312.7 m) to evaluate potential similarities or differences in the plagioclase alteration indicators and the areal fraction of microvoids.

Alteration indicators

Alteration indicators for plagioclase grains were obtained according to the following work sequence: 1) selection of the target plagioclase grains in the rock sample, 2) back-scattered electron (BSE) image acquirements, and 3) im-
ages analyses. Petrographic data, including BSE images, were obtained from thin sections that were carefully prepared to prevent mineral detachment. The target number of altered (unaltered) plagioclase grains for each thin section was 15. Fewer altered plagioclase grains were targeted than chloritized biotite grains (more than 20: Yuguchi et al., 2021) because the mode, grain size, and area of plagioclase are larger than those of biotite. The target plagioclase grains were selected using polarized microscopy. Two diagonal lines (the 1st and 2nd traverses) were established in a thin section. The width of the traverses was 0.2 mm (Fig. 2a). All plagioclase grains intersected by the first traverse were targeted. If less than 15 grains were identified in the first traverse, additional minerals were obtained from the second traverse until the target quantity was reached (Fig. 2a).

The BSE images of the target plagioclase grains were obtained using a JEOL IT100A scanning electron microscope at Yamagata University, Japan. The operating conditions included an accelerating voltage of 15 kV and a beam current of 1.5 nA. The areas (pixels) of the individual plagioclase grains and corresponding alteration domains were determined using Adobe Photoshop® image processing software. Figure 3a shows the plagioclase (sample Nos. 1–14), involving non-altered plagioclase and the alteration products of albite, K-feldspar, ilmenite, calcite, and fluorite (Fig. 3a–1), which is defined as the original (magmatic) plagioclase domain. The image was binarized with white pixels corresponding to the albitionization domains (Fig. 3a–2) and black pixels for the remainder of the sample. The domains of the associated alteration products were also counted using the white pixels of a binarized image (Fig. 3a–3). The pixels were converted into areas using the image scale. The alteration indicators were obtained as the total area of the alteration products divided by the area of the original plagioclase (Fig. 3a).

The albitionization domain as alteration product has chemical compositions of >Ab85 (Yuguchi et al., 2019a). Magma-tic zoning in plagioclase has chemical compositions ranging from Ab60 at cores to Ab85 at rims (Yuguchi et al., 2010, 2019a). Thus, the alteration albite domains can be clearly distinguished from the Ab-rich domain in magmatic zoning. Myrmekite is an intergrowth texture consisting of vermicular quartz and Ab-rich plagioclase, occurring between plagioclase and K-feldspar (Phillips, 1974). The Ab-rich domain in myrmekite has chemical compositions of >Ab85 (Yuguchi et al., 2022) and is thus similar in

Figure 1. Map of Southwest Japan showing the location of Mizunami underground Research Laboratory (MURL) (a). Location of the shafts and boreholes in MURL (b) and schematic figure of the MURL shafts and borehole 06MI03 (c) based on Yuguchi et al. (2015).
composition to the alteration albite domain, that is, in the processing of BSE images, it is difficult to distinguish between them (Supplementary Fig. S1a; Fig. S1 is available online from https://doi.org/10.2465/jmps.220415). Therefore, prior to binarization in image processing, the domain of myrmekite was manually removed (Fig. S1b) and was binarized accordingly to black pixels (Fig. S1c). The alteration indicators were obtained as the total area of the alteration products (Fig. S1c and S1d) divided by the original plagioclase domain including the myrmekite domain. Plagioclase alteration indicators represent a range between 0 and 1, as the extent of hydrothermal alteration. A relatively weak alteration is defined by values closer to zero, and relatively strong alteration is defined by those closer to one. During the preparation of thin sections, the minerals are cut randomly, such that a cross-section that passes through the identical part (e.g., core part or rim part) of the minerals cannot be guaranteed, which may yield variations in the indicators of the altered plagioclase grains. Therefore, the indicator of a rock sample is represented by the mean value and standard deviation for the target plagioclase grains.

### Areal fraction of microvoids in minerals

Micropores and microcracks in plagioclase were observed in the BSE image. However, it is not possible to distinguish micropores from microcracks in image processing. Therefore, in this study, in order to determine the areal fraction, micropores and microcracks were together defined as microvoids. The areas (pixels) of the individual plagioclase grains and the areal fraction of microvoid domains were determined using BSE image analysis with Adobe Photoshop® software. Figure 3b–1 shows the altered plagioclase of sample Nos. 1–3, which displays the original plagioclase domain. The image was binarized.
with the white pixels corresponding to the mineral domain (plagioclase and alteration products such as albite, K-feldspar, illite, calcite, and fluorite in Fig. 3b–2) and the black pixels corresponding to the microvoid domains within the mineral and the area surrounding the mineral. The counted pixels were converted into areas based on the image scale, and the areal microvoid fractions were determined by dividing the total domain of the microvoids by the domain of the original plagioclase (Fig. 3b). The areal fraction of microvoids in altered plagioclase ranges between 0 and 1. In the areal fraction of microvoids, a relatively small area of the microvoid is represented by values closer to zero, and a relatively large area is defined by those closer to one. The areal fraction of microvoids in altered plagioclase grains of a rock sample is indicated by the mean value and standard deviation of the areal fractions of the target plagioclase grains.

**PETROGRAPHY**

Plagioclase occurs ubiquitously throughout the samples and is characterized by alterations to variable extents (Fig. 2b). Furthermore, there are various distribution patterns of alterations in plagioclase grains as well; extensive alteration throughout the plagioclase grain (Fig. 2b–1), alteration of the cores of the grain (Fig. 2b–2), and alteration at the rims of the grain (Fig. 2b–3). The plagioclase alteration is characterized by albition; K-feldspathization; and formation of associated minerals such as ilmenite, calcite, and fluorite (Yuguchi et al., 2019a). Albite shows the largest distribution in the alteration products, and it occurs as a matrix that surrounds the associated minerals. K-feldspar and illite show a mosaic-like texture. K-feldspar occurs as acicular (<20 µm in width) or patchy (<200 µm in width) crystals. Illite (<80 µm in width) occurs as patchy aggregates with irregular boundaries. Calcite (<50 µm in the long axis) occurs as patchy, columnar, or granular crystals, and fluorite (<25 µm in the long axis) as granular crystals.

Figure 4 shows BSE and binary images of the microvoids in the alteration domain (Fig. 4b) and in the non-altered domain (Fig. 4c) of samples numbers 6–9, providing evidence of the microvoids and the distribution of their long axis direction. Both altered and non-altered domains include microvoids (Figs. 3 and 4). Microvoids occur as voids, their shapes are columnar and circular,
and less than 10 µm in size along their major axes. Linear microcracks are less than 5 µm in width and are interconnected. The altered plagioclase is typically accompanied by micropores rather than microcracks (Figs. 3 and 4). The altered domain contains more micropores than the non-altered domain; the areal fractions of micropores in the altered domain and the non-altered domain are 0.051 and 0.032, respectively (Fig. 4). Within the altered domains, albite and K-feldspar contained more micropores than illite, calcite, and fluorite. In particular, the albite domain contains more micropores in the alteration products. Larger-sized micropores were observed in the altered domain relative to the non-altered domain: major axes of <10 µm in the altered domain and that of <7 µm in the non-altered domain are observed (Figs. 4b and 4c). In the alteration domain, the long axis of the micropores is oriented toward the distributive direction of the associated minerals (such as K-feldspar in sample Nos. 6–9 in Figs. 4a and 4b). The difference in micropore frequency between the alteration domain and the neighboring non-altered domain indicates that the production of micropores cannot be attributed to the detachment of plagioclase and other minerals during the preparation of the thin section.

**RESULTS AND DISCUSSION**

**Alteration indicators and areal fraction of micropores in altered plagioclase**

The mean plagioclase indicator values ranged from 0.11 to 0.45 ($N = 24$; Table 1 and Supplementary Table S1; Table
A control experiment using sample Nos. 1 and 7 collected from the same depth range (307.7–312.7 m) was carried out to evaluate potential similarities or differences in the plagioclase alteration indicators and the areal fraction of microvoids. In the control experiment, the plagioclase indicator in sample No. 1 yielded a mean value of 0.18 and standard deviation of 0.07. Sample No. 7 yielded a mean value of 0.19 and standard deviation of 0.08 (Table 1). The standard deviation of sample No. 1 overlaps that of sample No. 7, indicating that two different samples collected from the same depth range show similar alteration indicators. This implies the relevance of the plagioclase alteration indicators and methodology in the evaluation of the extent of hydrothermal alteration of granitic plutons.

Figure 5a shows the relationship between the plagioclase alteration indicator and biotite chloritization indicator (Yuguchi et al., 2021) for the same samples, demonstrating a positive correlation ($R^2 = 0.71$). The regression lines are represented as $y = 0.47x + 0.09$, where $y$ denotes the plagioclase alteration indicator and $x$ stands for the biotite chloritization indicator. Therefore, each alteration indicator can be used independently as a representative value for the target sample. Such a positive correlation also implied that the plagioclase alteration is related to the biotite chloritization in the same sample.

Both micropores and microcracks in plagioclase were
detected as microvoids in the image analysis. The mean values for the areal fraction of microvoids in the altered plagioclase grains show a range of 0.02–0.05 ($N = 24$: Table 1 and Supplementary Table S2; Table S2 is available online from https://doi.org/10.2465/jmps.220415). In samples Nos. 1 and 7, the mean areal fractions of microvoids in sample No. 1 show a mean value of 0.04 with a standard deviation of 0.01. Sample No. 7 shows a mean value of 0.03 with a standard deviation of 0.01 (Table 1). The standard deviation range of sample No. 1 overlaps with that of sample No. 7, which implies that they represent similar areal fractions of microvoids. Figure 5b shows the relationship in the areal fraction of microvoids between the altered plagioclase ($x$) and the chloritized biotite ($y$) in the analyzed rock samples, which demonstrates a positive correlation with $y = 0.30x + 0.02$ and $R^2 = 0.64$.

**Relationship between the alteration progress and microvoids**

Figure 6 shows the relationship between the areal fraction of microvoids in the altered plagioclase ($x$) and the alteration indicator ($y$) in the samples. Low areal fractions of microvoids correspond to small alteration indicators, and high areal fractions correspond to large indicators, demonstrating positive correlations, with $y = 8.77x - 0.06$ and $R^2 = 0.60$, where $x$ is the areal fraction and $y$ is the alteration indicator. The positive correlations in Figure 6 indicate that plagioclase alteration is related to the areal fraction of the microvoids.

The altered domain of plagioclase is characterized by the fact that the long axis of the micro pores is oriented toward the associated minerals (Fig. 4). The long axis direction represents the stretching direction of the micropore networks. Occurrences in which the alteration spreads from the rim of the plagioclase in contact with the chloritized biotite are often observed (Fig. 7). The stretching directions of the micro pores are not completely consistent, indicating that their directions do not follow with the cleavage of plagioclase.

The distributive directions of the associated minerals are perpendicular to the boundary between the target plagioclase and the neighboring chloritized biotite (Figs. 7a and 7b), i.e., the micropores act as a hydrothermal fluid.
pathway. Such petrographic observation is consistent with the sequential alteration processes from biotite chloritization to plagioclase alteration reported by Nishimoto et al. (2008) and Nishimoto and Yoshida (2010). In the serial mass transfer model from biotite chloritization to plagioclase alteration of the Toki granite (Fig. 8), biotite chloritization was accompanied by mass transfer with inflows of \( \text{Al}^{3+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ca}^{2+}, \text{H}^+ \) from the hydrothermal fluid and outflows of \( \text{Si}^{4+}, \text{K}^+, \text{F}^- \) into the plagioclase (Yuguchi et al., 2015). Plagioclase alteration was accompanied by mass transfer with inflows of \( \text{Si}^{4+}, \text{K}^+, \text{F}^- \) from the chloritized biotite and \( \text{Al}^{3+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+} \) from the hydrothermal fluid and outflows of \( \text{Ca}^{2+} \) and \( \text{H}^+ \) (Yuguchi et al., 2019a). The hydrogen ion is a component of the inflow of the biotite chloritization reactions (Yuguchi et al., 2015; Fig. 8); i.e., the chloritization provides a gradual decrease in the concentration of \( \text{H}^+ \) and a concomitant gradual increase in the potential of hydrogen (pH) of the hydrothermal fluid. The high pH condition of the fluid due to chloritization influences and advances the subsequent plagioclase alteration (Yuguchi et al., 2019a) because hydrothermal fluid with a high pH enhances the dissolution of plagioclase (Knauss and Wolery, 1986; Yasuhara et al., 2012). The dissolution of plagioclase leads to the formation of micro pores, which corresponds to the incipient stage of plagioclase alteration (Yuguchi et al., 2019a). Therefore, the micro pores during the incipient stage of plagioclase alteration are defined as ‘incipient micropores’. The incipient micropores contribute to the infiltration of the components released by biotite chloritization inward into the plagioclase via hydrothermal fluid, resulting in the alteration progress.

The areal fraction of micro pores was extracted from both altered and non-altered domains in 48 representative plagioclase grains (Table S3; available online from https://doi.org/10.2465/jmps.220415). For example, areal fraction of micro pores in the altered domain and non-altered domain of No. A3–P12 plagioclase were 0.057 and 0.042, respectively (Fig. 9a), 0.074 and 0.031 in No. A3–P14 grain (Fig. 9b), and 0.055 and 0.030 in No. A12–P13 grain (Fig. 9c). Areal fractions of micro pores in the altered do-

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**Figure 8.** Schematic figure displaying the mass transfer of chemical components through the hydrothermal fluids in serial alteration processes from biotite chloritization to plagioclase alteration (after Yuguchi et al., 2015, 2019a).

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**Figure 9.** Backscattered electron image (a–1) and (b–1) the corresponding binary images of the micro pores (a–2) and (b–2) of altered plagioclase grains in sample No. A3–P12 (a) and sample No. A3–P14 (b), representing the areal fractions of micro pores in the alteration domain and the non-altered domain. The increase rates in the areal fractions of micro pores from the non-altered domain to the altered domain are 1.35 (a) and 2.40 times (b).
main have a larger value than those in the non-altered domain. In these samples, the increase rate in areal fractions of microvoids from the non-altered domain to the altered domain ranged from 1.04 to 38.71 times (Table S3). The areal fraction of microvoids in the non-altered domain can be interpreted as the incipient micropores. Such large areal fractions of micropores in the altered domain can be assumed to be the result of alteration influences. The albitionization is frequently associated with formation of micropores during the hydrothermal alteration in plagioclase (Hövelmann et al., 2010; Putnis, 2015; Yuguchi et al., 2022). Putnis (2015) described that some silica in the hydrothermal fluid must not participate in the reaction, and both calcium and aluminum are released into the fluid to account for the micropores in plagioclase albitionization because the reactant plagioclase has a larger molar volume than albite. The following two points of petrographical evidence are consistent with the interpretations of Putnis (2015) on micropore formation associated with plagioclase albitionization: 1) areal fractions of microvoids in the altered domain are larger than those in the non-altered domain (incipient micropores), and 2) the plagioclase alteration is characterized by albitionization, and the albite domain contains more micropores among the alteration products. Therefore, the formation of micropores is attributed essentially to the removal of calcium and aluminum (anorthite (An) component) from plagioclase. Figures 7 and 9 show that micropore generation and alteration preferentially occur in the core of the plagioclase. Magmatic zoning in plagioclase has chemical compositions ranging from An40 at the core to An15 at the rim. The An-rich core of the plagioclase is accompanied by a relatively large amount of incipient micropores, resulting in the progress of alterations. The alteration therefore results in the production of micropores; the micropores resulting from the plagioclase alteration can be defined as ‘albition micropores.’

Figure 10 shows the relationship in the areal fraction of microvoids between the non-altered domain (incipient micropores) and the entire domain (incipient and altered micropores); $\gamma = 0.76x + 0.02$ and $R^2 = 0.57$. A high correlation cannot be obtained in the regression due to the wide range of increase rates in the areal fraction of microvoids from the non-altered domain to the altered domain. The increase rate ranges from 1.044 to 38.71 times (Table S3). However, the correlation in Figure 10 indicates that the incipient micropore domain is the predominant factor for the developmental extent of plagioclase alteration.

The above discussions conclude that 1) the altered plagioclase contains the incipient micropores and the alteration micropores, 2) the incipient micropores act as a hydrothermal fluid pathway within the plagioclase, resulting in alteration, and 3) the hydrothermal alteration results in the production of new alteration micropores.

**Relationship between the biotite chloritization and plagioclase alteration**

The relationship between the areal fractions of microvoids (x) and the alteration indicators (y) for chloritized biotite also demonstrate positive correlations: $y = 6.42x − 0.06$ and $R^2 = 0.74$ (Yuguchi et al., 2021). The progress of biotite chloritization appears to be related to the areal fraction of microvoids. Micropores including microcracks within biotite grains act as conduit pathways for hydrothermal fluid flow, resulting in the progress of chloritization due to the dissolution-precipitation processes (Yuguchi et al., 2021). In both cases of biotite chloritization and plagioclase alteration, the volume of the microvoid in the mineral considerably constrains the progress of hydrothermal alteration.

Sequential alteration processes from biotite chloritization to plagioclase alteration occurred. The biotite chloritization is constrained by the chemical components of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Ca$^{2+}$, and H$^+$ supplied from the hydrothermal fluid through microvoids (Yuguchi et al., 2015, 2021). In particular, the progress of biotite chloritization is dominantly constrained by the volume of the microvoid based on the positive correlation ($R^2 = 0.74$) (Yuguchi et al., 2021). Thus, the amounts of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Ca$^{2+}$, and H$^+$ supplied from hydrothermal fluid are not the controlling factors for the progress of chloritization, indicating that they occur sufficiently in the fluid. The factors contributing to plagioclase alteration include not only the occurrence of micro pores and the components of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, and Mg$^{2+}$ supplied by hydrothermal fluid, but also the components of Si$^{4+}$, K$^+$, and F$^-$ supplied by biotite chloritization. The formation of the incipient microvoids in plagioclase was also derived from...
the high pH condition of the hydrothermal fluid due to biotite chloritization. The progress of plagioclase alteration is essentially dominated by the progress of biotite chloritization, which yields the correlation in alteration indicators between plagioclase alteration and biotite chloritization (Fig. 5a), and thus, the areal fractions of microvoids between them (Fig. 5b). Plagioclase grains, which have a high increase rate in the areal fractions of microvoids from the non-altered to the altered domain (Table S3), occur in contact with the chloritized biotite: an increase rate of 28.15 times in sample No. A9-P19 (Fig. 7c) and 38.71 times in sample No. A11-P14 was observed (Fig. 7d). Biotite chloritization yielded a high pH condition of the hydrothermal fluid and effectively induced the formation of incipient micropores within the neighboring plagioclase. The large-volume incipient micropores influenced the effective alteration, resulting in the formation of many more alteration micropores. This observation supports the assertion that the plagioclase alteration is controlled by biotite chloritization.

The correlation coefficient between the alteration indicator and the areal fraction of microvoids in the altered plagioclase ($R^2 = 0.60$; Fig. 6) is lower than that in the chloritized biotite ($R^2 = 0.74$). If biotite chloritization results in micropore production in plagioclase and the components (e.g., $\text{Al}^{3+}, \text{Fe}^{2+}, \text{Mn}^{2+}$, and $\text{Mg}^{2+}$) are not supplied adequately from the hydrothermal fluid, sufficient progress of plagioclase alteration does not occur, which yields a low correlation coefficient between the alteration indicator and areal fraction of the microvoids. In addition, the formation of new alteration micropores also decreases the correlation coefficient.

CONCLUSIONS

This study proposes petrographic indicators of plagioclase alteration, using the Toki granite in central Japan as a worked example, which can be used as a new method to quantitatively evaluate the progress of hydrothermal alteration within granites. The following conclusions were obtained in this study.

1) Alteration indicators and areal fractions of microvoids in the plagioclase grains can be obtained via backscattered electron image analysis. The plagioclase alteration indicators were characterized as the ratio between the alteration product domain and the original plagioclase domain. The volume of microvoids in the altered plagioclase was obtained by quantitative determination of the areal fraction of microvoids in the minerals.

2) There is a positive correlation between the plagioclase alteration and biotite chloritization indicators in the rock samples, demonstrating that each alteration indicator can be used independently as a representative value for the sample. In cases of biotite chloritization and plagioclase alteration, the volume of the microcracks and micropores in the mineral considerably constrains the developmental extent of hydrothermal alteration.

3) In the Toki granite, the altered plagioclase contains the incipient micropores and the alteration micropores. In the formation of plagioclase alteration and micropores, biotite chloritization induces the formation of incipient micropores. The incipient micropores act as a pathway of hydrothermal fluid within the plagioclase, resulting in alteration progress, and the hydrothermal alteration results in the production of new alteration micropores. That is, biotite chloritization influences the production of incipient micropores within plagioclase, and the incipient micropores effectively influence the plagioclase alteration.

The proposed methodologies that characterize the relationship between the extent of alteration and areal fraction of microvoids is innovative for petrological studies focusing on hydrothermal alterations. In particular, the new indicator allows us to discuss the similarities and/or differences in the alteration extent within a rock body and between rock bodies. Our methodology and interpretations are novel in this field, and their validity and usefulness should be evaluated in future studies.

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SUPPLEMENTARY MATERIALS

Supplementary Tables S1–S3 and Figure S1 are available online from https://doi.org/10.2465/jmps.220415.

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