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Mass transfer associated with chloritization in the hydrothermal alteration process of granitic pluton.

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ABSTRACT

This study, along with our previous studies (Yuguchi et al., 2015; 2019A), reveals the hydrothermal alteration processes in a pluton, with a focus on the mass transfer between minerals and hydrothermal fluid. It also depicts the sequential variations in fluid chemistry as alteration progresses. Hydrothermal alteration of the Toki granite in Tono, Japan—the study area of this research—progressed through the successive processes of chloritization, plagioclase alteration, and precipitation of a carbonate mineral [biotite chloritization described by Yuguchi et al. (2015) and plagioclase alteration by Yuguchi et al. (2019A)]. This paper describes the alteration process of hornblende chloritization, K-feldspar chloritization, and the formation of fracture-filling chlorite through petrography and mineral chemistry. A set of singular value decomposition analyses was conducted to obtain reaction equations for the chloritization processes, which facilitates the quantitative assessment of mass transfer between the reactant and product minerals, and the inflow and outflow of components through the hydrothermal fluid. Hornblende chloritization is accompanied by mass transfer with an inflow of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, and Mg$^{2+}$ and an outflow of Ca$^{2+}$, K$^+$, Na$^+$, and H$^+$. Mass transfer of K-feldspar chloritization is essentially characterized by an inflow of Al$^{3+}$, Fe$^{2+}$, and Mg$^{2+}$ and an outflow of H$_4$SiO$_4$, K$^+$, and H$^+$ into the hydrothermal fluid. Several types of chloritization reactions (including biotite chloritization) can be characterized by their reaction with the inflow of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, and Mg$^{2+}$ and the outflow of H$_4$SiO$_4$, Ca$^{2+}$, K$^+$, and F$^-$. The age and thermal conditions of hornblende chloritization (64–54 Ma and 330–190°C), K-feldspar chloritization (68–53 Ma and 350–210°C), and precipitation of fracture-filling
chlorite (66 and 63 Ma, 340 and 320°C) are overlapped with those of biotite chloritization
(68–51 Ma and 350–180°C). The reactions of chloritization (this study and Yuguchi et al.,
2015) and plagioclase alteration (Yuguchi et al., 2019A) represent the sequential variations
in fluid chemistry at temporal conditions from 68 Ma to 51 Ma as the temperature decreased
from 350°C to 180°C. As the alteration proceeds, the concentrations of aluminum, iron,
manganese, and magnesium ions in the hydrothermal fluid decrease gradually, and those of
calcium, hydrogen, and fluorine ions increase gradually.

Hornblende chloritization associates with formation of magnetite and ilmenite. The
thermal conditions of the hydrothermal fluid yielding the formation of magnetite and ilmenite
can be interpreted by the chemical characteristics of chlorite around their associated minerals.
The formation temperature of magnetite was higher than that of ilmenite, implying a decrease
in oxygen fugacity in the hydrothermal fluid with the decrease in temperature from 280–
310°C to 220–250°C.

Keywords: Hydrothermal alteration; chloritization; dissolution and precipitation; mass
transfer; singular value decomposition (SVD) analysis.
This study focuses on 1) the nature of the chloritization reaction and mass transfer due to hydrothermal alteration in a granitic pluton, based on petrography and mineral chemistry, 2) the physical conditions, including timing and temperature of alteration, and 3) the evolution of fluid chemistry as the alteration progresses, with the Toki granite in Tono district, central Japan, as an example. The degree and extent of hydrothermal alteration within a granitic body have a significant effect on the subsequent weathering of the granitic rock. It also influences the chemical characteristics of the palaeogroundwater and present-day groundwater due to water–rock interactions. Predicting geochemical behavior, evolution, and water–rock interaction is important to the safety assessment for long-term geological disposal of nuclear waste and underground storage of oil, natural gas, and hydrogen (e.g. Carpenter et al., 2017). For example, it allows us to predict whether oxidative fluid (groundwater) will cause the corrosion of artificial metal objects in the facilities (Yuguchi et al., 2019A).

The hydrothermal alteration of granitic rock is constrained mainly by the dissolution–precipitation processes during the penetration of hydrothermal fluid along the microcracks (Nishimoto and Yoshida, 2010; Yuguchi et al., 2015). The alteration is also influenced by the mass transfer of chemical components due to rock–matrix diffusion and through the micropore network (Alexander et al., 2009; Neretnieks, 2017; Yuguchi et al., 2019A).

The hydrothermal alteration of the Toki granite progresses through the following successive processes: 1) chloritization, 2) plagioclase alteration consisting of albitization, K-feldspathization, illitization, epidotization, smectitization, and formation of fluorite, and 3) precipitation of carbonate mineral (Nishimoto et al., 2008). Four processes occur during Toki
granite chloritization: biotite chloritization (Yuguchi et al., 2015), hornblende chloritization, K-feldspar chloritization, and fracture-filling chlorite formation (see petrography). Chlorites of hydrothermal origin in granitic rocks hold records of the hydrothermal fluid chemical characteristics (Yuguchi et al., 2015). This study describes the petrography and chemistry of the hornblende chloritization, K-feldspar chloritization, and fracture-filling chlorite precipitation, which enable us to further discuss the nature of alteration reactions and mass transfer due to hydrothermal fluid advection in granitic pluton, and the alteration temperatures leading to chloritization. Furthermore, a combination of this study and Yuguchi et al. (2015) provides a comprehensive characterization of the mass transfer of the overall chloritization and the sequential variation in fluid chemistry in the cooling pluton.

Plagioclase alteration is closely related to chloritization in the Toki granite (Yuguchi et al., 2019A). The mass transfer and physical conditions (age and temperature) of plagioclase alteration in the Toki granite have already been reported by Yuguchi et al. (2019A). Mass transfer through the overall chloritization process and the plagioclase alteration process provides significant clues regarding the nature of the sequential and long-term variations in fluid chemistry in a granitic pluton across a wide temperature range during sub-solidus cooling.

The Toki granite has two 500-m long vertical shafts (see Sampling and Analytical Procedures) that enables us to extract deep drill core samples from within the pluton. These samples have escaped weathering, and thus are suitable for the study of chloritization. The time–temperature (t–T) path of the sampling site, obtained by Yuguchi et al. (2019B), is also applicable to the study and can simultaneously yield both the age and temperature of the
secondary minerals (Yuguchi et al., 2019B). The chemical composition of the chlorite reveals the formation temperature through a chlorite geothermometer (e.g., empirical thermometer of Yoneda and Maeda, 2008), and subsequently, this formation temperature provides the corresponding age through examination of the $t$–$T$ path. Therefore, both the age and temperature of the chloritization can be determined, enabling us to discuss the sequential variations in the fluid chemistry.
In the inner zone (northern side of the Median Tectonic Line) of the Southwest Japan Arc, the late Cretaceous granitic rocks are widely distributed in parallel, east–west oriented Ryoke, Sanyo, and San-in Belts (Ishihara, 2003). The Toki granite in the Tono district of central Japan is one of the Late Cretaceous plutonic bodies of the Sanyo Belt (Fig. 1A: Ishihara and Chappell, 2007). The Toki granite is a stock of about $14 \times 12$ km$^2$ (Ishihara and Suzuki, 1969) that intrudes into the Jurassic sedimentary rocks of the Kamiaso unit in Mino Terrane (Sano et al., 1992), as well as the Late Cretaceous Nohi rhyolite (Sonehara and Harayama, 2007) (Fig. 1B). The Toki granite 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), zircon U–Pb ages of 74.7 ± 4.2 to 70.4 ± 1.7 Ma (Yuguchi et al., 2016), a hornblende K–Ar age of 74.3 ± 3.7 Ma (Yuguchi et al., 2011A), biotite K–Ar ages of 78.5 ± 3.9 to 59.7 ± 1.5 Ma (N = 33: Yuguchi et al., 2011A), zircon fission-track (ZFT) ages of 75.6 ± 3.3 to 52.8 ± 2.6 Ma (N = 44: Yuguchi et al., 2011A), and apatite fission-track (AFT) ages ranging from 52.1 ± 2.8 to 37.1 ± 3.6 Ma (N = 33: Yuguchi et al., 2017). Based on the phase relationships, Yamasaki and Umeda (2012) estimated that the emplacement depth of granitic magma was about 5–7 km below the surface.

A series of studies by the authors describes the formation history of the Toki granitic pluton from intrusion through emplacement to cooling (Yuguchi et al., 2010; 2011A; 2011B;
The Toki granite, a zoned pluton, has three rock facies grading from muscovite-biotite granite (MBG) at the margin through hornblende-biotite granite (HBG) to biotite granite (BG) in the interior (Fig. 1C). The geology and petrography of the Toki granite were described in detail in Yuguchi et al., (2010, 2011B; 2011C). A description of the hydrothermal alteration in the Toki granite was given in Nishimoto et al. (2008), Nishimoto and Yoshida (2010), Ishibashi et al. (2014), Yuguchi et al. (2015), Ishibashi et al. (2016), and Yuguchi et al. (2019A).
SAMPLING AND ANALYTICAL PROCEDURES

The Mizunami Underground Research Laboratory, which consists of two vertical shafts (the main and ventilation shafts), is located on the sedimentary Mizunami Group, which unconformably overlies the Toki granite (Fig. 1B, D, and E). The main and ventilation shafts are 500-m deep, ranging from an altitude of 201 masl (meters above sea level) (ground level) to an altitude of -299 masl (shaft bottom) (Fig. 1E). The unconformity between the Mizunami Group and the Toki granite is intersected by the shafts at a depth of about 170 m. This study employed borehole 06MI03 (vertical and 336-m long). The borehole 06MI03 was drilled from a depth of 191 m in the ventilation shaft before continuing the excavation below 191 m (Fig. 1E). Yuguchi et al. (2015) and Yuguchi et al. (2019A) describe the petrography and mineral chemistry of biotite chloritization and plagioclase alteration, respectively, in rock samples collected from the rock mass at a depth of approximately 500 m (-299 masl) in the ventilation shaft (Fig. 1E). This study employed the same samples originating from the deepest section of borehole 06MI03 in the depth range of -274 to -314 masl (9 samples spaced 5 m apart) (Fig. 1E). This restricted sampling interval provides rock samples of the same temperature and pressure history in the sub-solidus cooling process of the Toki granite.

The petrographical data in this study were obtained from two-dimensional thin sections. The thin sections were prepared carefully in order to prevent the detachment of minerals. Backscattered electron (BSE) images and chemical maps were generated using a JEOL IT100A scanning electron microscope with an energy-dispersive X-ray spectrometer (EDS), at Yamagata University, operating at an accelerating voltage of 15 kV and a beam current of 1.5 nA. Mineral compositions were analyzed using an electron microprobe analyzer (JEOL...
JXA-8900) with a wavelength-dispersive X-ray spectrometer (WDS), at Yamagata University. The analytical conditions required by the quantitative analysis were an acceleration voltage of 15 kV, a beam current of 20 nA, a beam diameter of 3 µm, and the ZAF data correction method. The area (pixel area) of the minerals and microvoids (and microcracks) were determined using Photoshop® image processing software. Details of the analysis procedure are described in Appendix A.
PETROGRAPHY

Hornblende chloritization

Hornblende chloritization represents chlorite partially replacing hornblende, as shown in Fig. 2. The distributions of hornblende and chlorite in the altered grain are shown by elemental silicon and calcium maps in Fig. S1. Hornblende exhibits composition from ferroedenite to ferropargasite (Table S1). Chloritization proceeds from the rim to the core in hornblende along its cleavage, and the micrometer-scale voids (hereinafter referred to as ‘microvoid’) occur between reactant hornblende and product chlorite (Fig. 2A-3 and A-4). Such microvoids and deformation texture of hornblende indicate the decrease in volume from the reactant to the product in the chloritization reaction. Biotite chloritization, however, does not exhibit microvoids between the reactant biotite and the product chlorite, in the sample with occurrences of hornblende chloritization and biotite chloritization (e.g., Fig. 6 of Yuguchi et al., 2015). In thin section, the difference in microvoid frequency between the hornblende and biotite chloritizations indicates that microvoid production is not attributed to mineral detachment during thin-section preparation. In the hornblende chloritization, the microvoids contain small isolated fragments of hornblende. The surfaces of small fragments are flat and smooth (refer to Fig. S2). If the fragment was caused by hornblende detachment due to polishing during preparation, the surfaces would not necessarily be flat and smooth. This is also an evidence that the hornblende fragments were not caused by the detachment during preparation. The chlorite composition ranges from 5.40–6.16 atoms per formula unit (apfu) in Si (mean: 5.64 apfu, N = 58), with an almost constant Fe / (Fe + Mg) of 0.71–0.79. Chlorite is associated with minerals such as titanite, epidote, albite, K-feldspar, ilmenite, magnetite,
quartz, fluorite, and calcite, which are all products of chloritization. Hornblende chloritization is further subdivided into the following five subtypes by the assemblage of product minerals (Table 1; Figs. 2, S2, S3, and S4):

Sample No. 3-2-9: chlorite, albite, K-feldspar, illite, and magnetite products (Fig. 2 and S1)
Sample No. 3-6: chlorite, titanite, epidote, quartz, and calcite products (Fig. S2)
Sample No. 7-8: chlorite, titanite, and albite products (Fig. 2)
Sample No. 10-1: chlorite, titanite, and quartz products (Fig. S3)
Sample No. 10-4: chlorite, titanite, epidote, fluorite, quartz, and calcite products (Fig. S4)

Titanite—identified by elemental titanium mapping—occurs as lenticular or bead-like grains, veinlets (>10 μm width: Fig. S2), and irregular grains (>5 μm across: Figs. S3 and S4) inside the chlorite. Similarly, epidote occurs as lenticular and bead-like grains (>5 μm wide: sample No. 3–6 of Fig. S2) and rounded grains (>100 μm across: sample No. 10–4 of Fig. S4). Albite occurs as rounded grains and K-feldspar occurs as lenticular, bead-like, and irregular grains (Fig. 2). Ilmenite (>25 μm wide) occurs as lenticular and bead-like grains in chlorite, and its elongations are oriented parallel to the hornblende cleavage (Fig. 2A-3). Rounded magnetite (sizes of up to 20 μm) occurs in chlorite (Fig. 2A-4). Magma-origin plagioclase has compositions ranging from Ab$_{70}$ to Ab$_{82}$ (Yuguchi et al., 2010). Hydrothermal albite in hornblende chloritization has a composition with > Ab$_{90}$ (Table S1), which is consistent with hydrothermal albite accompanying plagioclase alteration (> Ab$_{90}$: Yuguchi et al., 2019A). The chemical compositions are not substantially different between hydrothermal K-feldspar and ilmenite (Table S1) and magma-origin K-feldspar and ilmenite (Tables 3 and 4 of Yuguchi et al., 2010). Although the chemistries are the same, whether they have
hydrothermal or magmatic origin can be identified by their petrographical occurrences; hydrothermal albite, K-feldspar, and ilmenite occur at the boundary between hornblende and chlorite or occur as inclusions within chlorite. Hydrothermal magnetite contains more MnO and MgO components than magmatic magnetite (Table S1 and Table 4 of Yuguchi et al., 2010). Granular quartz, fluorite, and calcite with sizes of up to 20 μm are observed in the hornblende chloritization; quartz is identified by silicon maps of Figs. S2C, S3E, and S4D, and fluorite and calcite are identified by calcium maps of Figs. S2C and S4D. In sample No. 3-6, the calcite is included in chlorite (Fig. S2). Such an occurrence implies that calcite formation accompanies hornblende chloritization.

**K-feldspar chloritization**

K-feldspar chloritization represents the occurrence of chlorite partially replacing K-feldspar, as shown in Fig. 3A. The distributions of K-feldspar and chlorite are illustrated by elemental silicon, iron, magnesium, and potassium maps in Fig. S5. K-feldspar is often accompanied by perthitic textures (Fig. 3A-3). K-feldspar compositions range from Or$_{90}$ to Or$_{100}$ (Table S1). Chlorite fragments up to 20 μm across are distributed within the K-feldspar parts in contact with chlorite. Although the hornblende chloritization has microvoids between the reactant and the products, the K-feldspar chloritization does not. No deformation texture is observed within the chloritized grains (Fig. 3A), indicating solid volume conservation from reactant K-feldspar to chloritization products. Chlorite composition ranges from 5.33–6.06 apfu in silicon (mean: 5.64 apfu, N = 29), with an almost constant Fe / (Fe + Mg) of 0.73–0.82. Chlorite is essentially associated with titanite (sample No. 3-6: Table 1; Fig. 3A-4 and S5). The distribution of titanite, illustrated by elemental titanium maps (Fig. S5), shows that
it occurs as tiny grains (up to 5 μm) inside the chlorite.

**Fracture-filling chlorite**

Fracture-filling chlorite occurs in veinlets with a few micrometers wide, and there is an irregular boundary between the fracture-filling minerals and the original magmatic minerals. Fracture-filling chlorite frequently connects with the altered biotite along the microfracture network and grain boundary. Figure 3B shows fracture-filling chlorite with the largest thickness ranging from 30–100 μm (sample No. 8-1). The chemical composition of this chlorite was determined by electron probe microanalysis (EPMA). The compositions are 5.39 and 5.44 apfu in Si (N = 2), with an almost constant Fe / (Fe + Mg) of 0.75–0.78. Chlorite is essentially associated with titanite and K-feldspar (Table 1; Fig. 3B-3 and 3B-4). The distributions of chlorite, titanite, and K-feldspar are identified by the elemental maps of Fig. S6: chlorite (iron map), titanite (titanium and calcium maps), and K-feldspar (potassium map).
DISCUSSION

Volume changes from reactant to products

Chlorites have consistent composition ranges among the biotite chloritization, hornblende chloritization, K-feldspar chloritization, and fracture-filling processes: Mg# (Mg / (Fe + Mn + Mg) in apfu) ranging from 0.17–0.29 and Si in a range of 5.33–6.20 apfu (Fig. 4). However, the hornblende chloritization reaction shows a unique formation of microvoids and deformation texture, which imply a decrease in volume from the reactant to the products. The area (pixel area) of the reactant, products, and microvoids (and microcracks) in the chloritized hornblende were determined through image analysis of the samples No. 3-2-9, 3-6, 7-8, 10-1, and 10-4. The volume of the microvoids was estimated from their area, by simply assuming the area–volume equivalence (Yuguchi and Nishiyama 2008), that is, the area of the consumed (original) hornblende as a reactant equals the areal sum of products and microvoids. The image analyses showed a 6–12% decrease in volume from the reactant to the products (Table 1). No microvoids were observed in this biotite and K-feldspar chloritization process, indicating solid volume conservation between reactant and products (Table 1).

Chloritization reactions

The chloritization process consists of biotite chloritization, hornblende chloritization, K-feldspar chloritization, and fracture-filling chlorite formation. The biotite chloritization reactions—satisfying both the assemblage of product minerals and the volume relationship between the reactant and products—were previously studied based on the singular value decomposition (SVD) analysis (Yuguchi et al., 2015). This study presents the overall chemical reaction equations for hornblende and K-feldspar chloritization. From these
equations, the quantitative mass transfer between reactant and product minerals, and the inflow and outflow of components with chloritization are derived. The chemical reaction for producing the fracture-filling chlorite could not be established due to the lack of a reactant. **Hornblende chloritization reactions.** The overall reaction equations are constructed for each sample, from Nos. 3-2-9, 3-6, 7-8, 10-1, to 10-4, in hornblende chloritization. To determine alteration reactions in such an open system, we must specify some conservation conditions. We considered the process involving the decrease in volume from the reactants to the products as a conservation process: about 12% (sample No. 3-2-9), 11% (No. 3-6), 6% (No. 7-8), 12% (No. 10-1), and 11% (No. 10-4). We considered the additional condition of volume ratios of the product minerals in the alteration area, to derive the reaction equations (Table 1). Thus, the alteration reactions that satisfied both the volume relationship between the reactants and products and the volume ratios of the product minerals were developed.

In the formation of the overall reaction of sample No. 3-2-9, the reactant is hornblende (analysis No. E3-2-3 in Table S1; the analysis number corresponds to the location shown in Fig. 2A) and the products are chlorite (No. C3-16), albite (No. E3-2-5), K-feldspar (No. E3-2-6), ilmenite (No. C3-12), and magnetite (No. C3-15). The molar volumes of the reactant and product minerals were derived from their chemical compositions (Table S1). The volume fractions of the product minerals are expressed as ratios, such as chlorite to albite to K-feldspar to ilmenite to magnetite = 1: 0.056: 0.056: 0.131: 0.002 (Table 1). Details of the image analysis procedure giving the mineral ratio are described in Appendix A. We considered the following reaction in an open system:

\[ \text{Hb} + \text{X} \rightarrow a \text{Chl} + b \text{Ab} + c \text{Kfs} + d \text{Il} + e \text{Mag} + Y \] (X and Y: open components), where X
denotes the influx of chemical components through an intergranular medium (hydrothermal fluid) and Y denotes the efflux from the system. Silicon species occur in the form of $H_4SiO_4$ in the reaction equation. The solution of a set of simultaneous equations was used to determine the stoichiometric coefficients, $a$, $b$, $c$, $d$, and $e$, and those of the open components involved in X and Y. The simultaneous equations consisted of conservations (1), (2), (3), (4), and (5):

\[
267.13 \times 0.88 = 212.08 \ a + 100.45 \ b + 108.74 \ c + 32.61 \ d + 41.74 \ e \text{ (volume decrease of 12\% from reactant to products)} \ldots \text{conservation (1)}
\]

\[
b = 0.1176 \ a \text{ (volume relation between chlorite and albite: 1:0.056 = 212.08} \ a: 100.45b) \ldots \text{conservation (2)}
\]

\[
c = 0.1087 \ a \text{ (volume relation between chlorite and K-feldspar: 1:0.056 = 212.08} \ a: 108.45c) \ldots \text{conservation (3)}
\]

\[
d = 0.8500 \ a \text{ (volume relation between chlorite and ilmenite: 1:0.131 = 212.08} \ a: 32.61d) \ldots \text{conservation (4)}
\]

\[
e = 0.0086 \ a \text{ (volume relation between chlorite and magnetite: 1:0.002 = 212.08} \ a: 41.74e) \ldots \text{conservation (5)}
\]

The numerical values in conservation Equation (1) denotes molar volumes in each mineral (see footnote of Table S1). Conservations (1)–(5) give the following equation:

\[
Hb + 0.495Ti^+ + 2.711Al^{3+} + 2.552Fe^{2+} + 0.265Mn^{2+} + 1.116Mg^{2+} + 0.200K^+ + 7.878H_2O \rightarrow 0.895Chl + 0.105Ab + 0.097Kfs + 0.761Il + 0.008Mag + 0.472H_4SiO_4 + 1.685Ca^{2+} + 0.500Na^+ + 0.131F^- + 0.016Cl^- + 13.870H^+ \ldots \text{reaction (A1) (Table 2)}
\]

The same procedures are applied to sample Nos. 3-6, 7-8, 10-1, and 10-4, to establish
the hornblende chloritization reaction equations, which are listed in Table 2 and described in Appendix B.

We also studied the reactions based on singular value decomposition (SVD) analysis (e.g. Fisher, 1989; 1993) to establish the hornblende chloritization reactions of sample Nos. 3-2-9, 3-6, 7-8, 10-1, and 10-4. The SVD analysis provides a simple yet powerful tool for determining univariant reactions in multicomponent mineral assemblages without considering T, P, fO₂, and pH constraints (Fisher, 1989; 1993). The SVD analysis is closely related to the least square method, which enables the determination of the precise mass balance relationships in multicomponent mineral assemblages based on mineral analyses with possible analytical errors (Fisher, 1989). The SVD analysis can also be used to analyze open-system changes (Shigeno et al., 2012). In our previous study, we applied the SVD analysis to model the possible reaction relationships satisfying both the assemblage of product minerals and the volume relationship between reactant and products (solid volume constant) in the biotite chloritization (Yuguchi et al., 2015). Thus, the SVD analysis can be applied to study hornblende and K-feldspar chloritization. To determine chloritization reactions in an open system, we also have to specify some conservation conditions for the SVD analysis. We defined the volume constraint as a conservation condition, and assumed one or more additional condition(s) of closure components among nine components (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K), for deriving the reaction relation. The matrices for SVD consist of arbitrary combinations of molar volume and closure component(s) in the reactant and products (Table S2). The composition matrix of the closure components is expressed in terms of atoms of element per formula unit for the mineral. The free software program
Scilab (Scilab Enterprises S.A.S) was employed to perform the SVD analysis. The most reasonable reaction among the possible reaction relationships was identified according to 1) the signs of stoichiometric coefficients of reactants (minus) and products (plus), and 2) the least difference from the volume fraction of product minerals in the observation (Table 1).

In the formation of the overall reaction of sample No. 3-2-9 in the SVD analysis, we consider a reaction in an open system as follows:

\[ a \text{Hb} + X = b \text{Chl} + c \text{Ab} + d \text{Kfs} + e \text{Il} + f \text{Mag} + Y \] (X and Y: open components)

The SVD analysis determines stoichiometric coefficients \(a, b, c, d, e,\) and \(f,\) and those of open components involved in X and Y. Some matrices consisting of arbitrary combinations of molar volume and closure components give several possible reactions. The SVD analysis consisting two matrices of molar volume and Ti component (Table S2) gives the most reasonable reaction among several possible reactions, as follows:

\[
0.714\text{Hb} + 2.252\text{Al}^{3+} + 1.982\text{Fe}^{2+} + 0.015\text{Mn}^{2+} + 0.825\text{Mg}^{2+} + 0.207\text{K}^+ + 0.022\text{F}^- + 5.432\text{H}_2\text{O} \rightarrow 0.678\text{Chl} + 0.058\text{Ab} + 0.127\text{Kfs} + 0.098\text{Il} + 0.049\text{Mag} + 0.240\text{H}_4\text{SiO}_4 + 1.169\text{Ca}^{2+} + 0.355\text{Na}^+ + 0.033\text{Cl}^- + 9.905\text{H}^+ \ldots \text{reaction (A2)} \] (Table 2)

The reaction gives the volume fraction (proportion) of the product minerals; chlorite: albite: K-feldspar: ilmenite: magnetite = 1: 0.040: 0.096: 0.022: 0.014 (Table 2). Table 2 shows the reasonable reaction equations in sample Nos. 3-2-9, 3-6, 7-8, 10-1, and 10-4 on the basis of each matrix (Table S2) for the SVD analysis, leading to hornblende chloritization.

Reactions (A1) and (A2) of sample No. 3-2-9 show the production of chlorite, albite, K-feldspar, ilmenite, and magnetite by consuming hornblende with an inflow of Ti\(^{3+}\), Al\(^{3+}\),...
Fe$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, K$^+$, F$^-$ (reaction A2), and H$_2$O from the hydrothermal fluid, accompanied by an outflow of H$_4$SiO$_4$, Ca$^{2+}$, Na$^+$, F$^-$ (reaction A1), Cl$^-$, and H$^+$ into the fluid (Table 2). The hornblende chloritization reactions in the SVD analyses, and the given characteristics of mass transfer among the reactant, products, and hydrothermal fluid for sample Nos. 3-6, 7-8, 10-1, and 10-4 are described in Appendix B.

**K-feldspar chloritization reactions.** The essential reaction equation was constructed for the K-feldspar chloritization as an example of sample No. 3-16. The chloritization has K-feldspar (No. E3-5) as the reactant, and chlorite (No. A042) and titanite (No. E3-9) as products (Table S1). To determine chloritization reactions in an open system, we must specify some conservation conditions. No microvoids or deformation structures were observed after K-feldspar chloritization, indicating the constant solid volume between the reactant and the products as a conservation condition (Table 1). Additional conservations include the volume ratios of product minerals; Chl:Ttn = 1:0.070 (Table 1). The reaction equation that satisfies both the volume relationship between the reactants and the products, and the volume ratios of the product minerals were constructed as follows:

\[
\begin{align*}
\text{Kfs} &+ 0.107\text{Ti}^+ + 1.644\text{Al}^{3+} + 3.255\text{Fe}^{2+} + 0.203\text{Mn}^{2+} + 0.818\text{Mg}^{2+} + 0.113\text{Ca}^{2+} + 0.016\text{F}^- + 0.009\text{Cl}^- + 7.150\text{H}_2\text{O} \rightarrow 0.478\text{Chl} + 0.125\text{Ttn} + 0.287\text{H}_4\text{SiO}_4 + 0.016\text{Na}^+ + 0.911\text{K}^+ + 13.152\text{H}^+ \ldots \text{reaction (B1) (Table 2).}
\end{align*}
\]

The SVD analysis of the matrix consisting of a conservation constraint of molar volume for the three phases (Table S2) gives the most reasonable reaction relation: 0.895Kfs + 0.051Ti$^+$ + 1.546Al$^{3+} + 3.010\text{Fe}^{2+} + 0.188\text{Mn}^{2+} + 0.756\text{Mg}^{2+} + 0.050\text{Ca}^{2+} + 0.007\text{F}^- + 0.009\text{Cl}^- + 6.456\text{H}_2\text{O} \rightarrow 0.443\text{Chl} + 0.055\text{Ttn} + 0.236\text{H}_4\text{SiO}_4 + 0.014\text{Na}^+ + 0.814\text{K}^+ +
The reaction equation gives the volume fraction of the product minerals; chlorite to titanite = 1: 0.033 (Table 2). Both reactions (B1) and (B2) represent the chloritization, and the production of titanite by the consumption of K-feldspar, with an inflow of Ti\(^{+}\), Al\(^{3+}\), Fe\(^{2+}\), Mn\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\), F\(^{-}\), Cl\(^{-}\), and H\(_{2}\)O from the hydrothermal fluid, accompanied by the outflow of H\(_{4}\)SiO\(_{4}\), Na\(^{+}\), K\(^{+}\), and H\(^{+}\) into the hydrothermal fluid (Table 2).

**Characteristics of mass transfer leading to chloritization**

**Mass transfer leading to biotite chloritization.** Biotite chloritization occurs with high frequency among all chloritization processes. It involves two formation mechanisms: 1) solid volume replacement from the reactant biotite to the chloritization products, and 2) the dissolution of biotite and the precipitation of chloritization products (Ishii et al., 2017). Characteristics of mass transfer leading to biotite chloritization are described in Yuguchi et al. (2015) in detail. Biotite chloritization is characterized by essential mass transfer: inflow of Al\(^{3+}\), Fe\(^{2+}\), Mn\(^{2+}\) Ca\(^{2+}\), and H\(^{+}\) from the hydrothermal fluid and outflow of H\(_{4}\)SiO\(_{4}\) (Si\(^{4+}\)), K\(^{+}\) and F\(^{-}\) into the hydrothermal fluid (Fig. 5).

**Mass transfer leading to hornblende chloritization.** Hornblende chloritization was derived from the dissolution of hornblende and the precipitation of chlorite and associated minerals, which is characterized by the following features: inflow of Al\(^{3+}\), Fe\(^{2+}\), Mn\(^{2+}\), and Mg\(^{2+}\) and outflow of Ca\(^{2+}\), K\(^{+}\), Na\(^{+}\), and H\(^{+}\) (Table 2; Fig. 5). Titanium derived from hornblende and inflow of Ti\(^{+}\) from the hydrothermal fluid produce the formation of ilmenite or titanite, while hornblende-derived titanium is released into the hydrothermal fluid for small quantities of ilmenite or titanite (Table 2). Calcium derived from hornblende produces...
calcium-bearing minerals such as titanite, epidote, fluorite, and calcite, and the rest is released into the hydrothermal fluid (Table 2). The inflow of CO$_2$ from the hydrothermal fluid results in calcite production. Hydrogen ions are observed as a product (right-hand side) in the overall reactions (Table 2). Therefore, the H$^+$ concentration of the hydrothermal fluid gradually increases as the plagioclase alteration proceeds, indicating a gradual decrease in potential of hydrogen (pH) in the hydrothermal fluid.

**Mass transfer leading to K-feldspar chloritization.** K-feldspar chloritization is caused by the dissolution of K-feldspar and the precipitation of chlorite and titanite. K-feldspar chloritization is essentially characterized by the decomposition of K-feldspar with an inflow of Al$^{3+}$, Fe$^{2+}$, and Mg$^{2+}$ and an outflow of H$_4$SiO$_4$, K$^+$, and H$^+$ into the hydrothermal fluid (Table 2). Hydrogen ions are observed as products (right-hand side) in the chloritization reactions (Table 2), indicating a gradual increase in the H$^+$ concentration of the hydrothermal fluid as the plagioclase alteration proceeds, i.e. a gradual decrease in pH of the hydrothermal fluid.

**Mass transfer leading to the formation of fracture-filling chlorite.** The formation of fracture-filling chlorite is due to the precipitation of chlorite, titanite, and K-feldspar, which is characterized by the inflow of H$_4$SiO$_4$, Ti$^+$, Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Na$^+$, K$^+$, F$^-$, and Cl$^-$ from the hydrothermal fluid. All components constituting chlorite, titanite, and K-feldspar are supplied by the hydrothermal fluid.

**Thermal and temporal relationships among all chloritizations**

**Temperature conditions in all chloritizations.** Chlorite geothermometers have been proposed based on compositional variability (De Caritat et al., 1993) including: 1) an
empirical thermometer based on tetrahedral aluminum occupancy as a function of temperature (e.g., Cathelineau and Nieva, 1985; Cathelineau, 1988; Kranidiotis and MacLean, 1987; Jowett, 1991; Yoneda and Maeda, 2008) and 2) a thermodynamic thermometer based on equilibrium between chlorite and aqueous solution (solid solution model) (e.g. Walshe, 1988; Vidal et al., 2001; Inoue et al., 2009; 2010, 2018). Both empirical and thermodynamic studies indicate that tetrahedral aluminum in chlorite is a temperature-dependent parameter. The variation in not only in the tetrahedral aluminum but also that the Fe / (Fe + Mg) in chlorite should be considered in the determination of the formation temperature (Bourdelle et al., 2013).

In the Toki granite, chlorite compositions show that tetrahedral aluminum values range from 1.70–2.67 apfu (mean value of 2.31 apfu, N = 143) in biotite-origin chlorite (Yuguchi et al., 2015), from 1.84–2.60 apfu (mean value of 2.36 apfu, N = 57) in hornblende-origin chlorite, from 1.94–2.67 apfu (mean value of 2.38 apfu, N = 28) in K-feldspar-origin chlorite, and are 2.56 and 2.61 apfu (N = 2) in fracture-filling chlorite (Fig. 6A). The Fe / (Fe + Mg) range is from 0.82–0.92 (mean value of 0.86) in biotite-origin chlorite (Yuguchi et al., 2015), 0.80–0.91 (mean value of 0.85) in hornblende-origin chlorite, 0.85–0.92 (mean value of 0.89) in K-feldspar-origin chlorite, and are 0.84 and 0.87 in fracture-filling chlorite (Table S1). There is no correlation between tetrahedral aluminum and Fe / (Fe + Mg). The above chemical observation indicates that the tetrahedral aluminum in chlorites can be used to show at least the relative difference in chloritization temperature conditions among all chloritization processes.

A rough temperature index was estimated using the chlorite geothermometer by Yoneda
and Maeda (2008), on the assumption that the equilibrium among minerals and hydrothermal fluid is established (Fig. 6B). This geothermometer was employed for estimating the temperature for the biotite chloritization in the study of Yuguchi et al. (2015). All the chloritization processes have temperature intervals between about 350°C and 180°C. Such temperature intervals indicate the chloritization stage in the sub-solidus cooling process of the Toki granite (Fig. 6B). The biotite, hornblende, and K-feldspar chloritization processes have temperature conditions from 350–180°C (Yuguchi et al., 2015), from 330–190°C, and from 350–210°C, respectively. The precipitation of fracture-filling chlorite occurred at temperature conditions of 320°C and 340°C.

**Estimation of the temporal conditions of the chloritization processes.** The temperature conditions facilitating chloritization were found in the range of 180–350°C; however, the formation age could not be determined due to the absence of geochronometry applicable to chlorite. The temporal conditions of all the chloritization processes were determined from their temperatures, using the $t–T$ path of sample DH2 RA03 (-302.1 masl of borehole DH2) within the Toki granite (Fig. S7A). Sample DH2 RA03 was obtained from a location close to the sample location of this study (approximately 90 m away in horizontal distance: Fig. 1D). The $t–T$ path of sample DH2 RA03 was constructed from the thermochronological data, including the ages of zircon U–Pb, biotite K–Ar, ZFT, and AFT and the FT inverse calculation (Yuguchi et al., 2019B). Therefore, the weighted mean $t–T$ path derived from the FT inverse calculation was employed for this discussion. The intersection of the weighted mean $t–T$ path and the thermal condition of 350°C (blue horizontal line) give a formation age of about 68 Ma, and that of the $t–T$ path and the thermal condition of 180°C give an age of about 51 Ma.
This indicates that all the chloritization processes had occurred over a period of about 17 million years from 68 to 51 Ma (Fig. S7B). The same analysis shows that the biotite, hornblende, and K-feldspar chloritization processes had occurred over a period of about 17 million years from 68 to 51 Ma, over a period of about 10 million years from 64 to 54 Ma, and over a period of 15 million years from about 68 to 53 Ma, respectively. The precipitation of fracture-filling chlorite occurred at about 66 and 63 Ma.

**Temporal and thermal relationships of all chloritizations and plagioclase alteration.**

Having determined both the temporal and thermal conditions for all chloritization processes, we can now discuss the sequential relationship among these processes. The temporal and thermal conditions of biotite chloritization (68–51 Ma and 350–180°C) overlapped with that of hornblende chloritization (64–54 Ma and 330–190°C) and K-feldspar chloritization (68–53 Ma and 350–210°C), and the precipitation of fracture-filling chlorite (66 and 63 Ma, 340 and 320°C). In the same physical conditions of the alteration age and temperature, 1) the same products occurred as chlorite regardless of the different species of reactants, and 2) the precipitation of chlorite occurred within the fracture. Plagioclase alteration ages are identified by illite K–Ar age of 59.2 ± 1.4 Ma (Yuguchi et al., 2019A) and K-feldspar K–Ar age of 62.2 ± 1.4 Ma (Yuguchi et al., in press), and the corresponding temperatures also are 305–290°C and 307–325°C, respectively. The above temporal and thermal consistency indicate that the serial alteration processes from all the chloritization processes to plagioclase alteration process occurred within the rock body during 68–51 Ma in the temperature range of 350–180°C.
Sequential variations in the characteristics of the hydrothermal fluid

Chemical characteristics of hydrothermal fluid. Sequential processes from the chloritizations to the plagioclase alteration occur ubiquitously in the Toki granitic rock body, which impacts the fluid chemistry through hydrothermal convection throughout the pluton. The ongoing reactions decrease the concentration of the inflow components and increase that of the outflow components in the hydrothermal fluid. Figure 5 shows a schematic of the exchange of components among the reactant, products, and hydrothermal fluid in all the chloritization processes and also in the plagioclase alteration process. Chloritization reactions are characterized by the following significant features: reaction with the inflow of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, and Mg$^{2+}$ and the outflow of H$_4$SiO$_4$ (Si$^{4+}$), Ca$^{2+}$, K$^+$, and F$^-$ (Fig. 5). Hydrogen ions are observed as the reactant in biotite chloritization, whereas they are observed as the product in hornblende and K-feldspar chloritizations. There is a gradual decrease in the H$^+$ concentration of the hydrothermal fluid as the biotite chloritization proceeds, indicating a gradual increase in the pH of the hydrothermal fluid. Contrary to the former case, the hornblende and K-feldspar chloritizations influence the gradual decrease in the pH of the fluid as the alteration proceeds. The pH of the fluid gradually increases as the biotite chloritization proceeds, which influenced and advanced the subsequent plagioclase alteration because hydrothermal fluid with a high pH enhances the dissolution of plagioclase (Yuguchi et al., 2019A). Yuguchi et al. (2019A) showed that the alteration reactions are characterized by the following significant features: the inflow of H$_4$SiO$_4$ (Si$^{4+}$), Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, K$^+$, and F$^-$ and the outflow of H$^+$ and Ca$^{2+}$. The inflow components of plagioclase alteration, H$_4$SiO$_4$ (Si$^{4+}$), K$^+$, and F$^-$ correspond to the outflow components of chloritization processes.
(Fig. 5). The consistency between the outflow components of chloritization and the inflow components of plagioclase alteration indicates that chloritization is the dominant source of mass transfer for the plagioclase alteration. That is, there is a sequence of mass transfer from chloritization to plagioclase alteration.

The reactions of chloritization and plagioclase alteration represent the sequential variations in the fluid chemistry at temporal conditions from 68 to 51 Ma as the temperature cooled from 350 to 180°C. Chloritization and plagioclase alteration require the consumption of aluminum, iron (ferrous), manganese, and magnesium ions (Fig. 5). Therefore, the concentrations of these ions in the fluid decrease gradually as the alteration proceeds (Fig. 5). The alterations are accompanied with the outflow of calcium, hydrogen, and fluorine ions. Thus, their concentrations in the hydrothermal fluid increase gradually as the alteration proceeds (Fig. 5). The liberated calcium ions are precipitated as carbonate minerals after the chloritization and plagioclase alteration (Nishimoto et al. 2008).

As the alteration processes progresses, a gradual increase in the concentration of hydrogen ions yields a gradual decrease in pH, resulting in the termination of mineral dissolution. That is, the hornblende chloritization, K-feldspar chloritization, and plagioclase alteration inhibit dissolution of reactant minerals in the hydrothermal alteration. Although biotite chloritization partially produces chlorite and entirely replaces the reactant, the chlorite in hornblende and K-feldspar chloritizations only partially replace the reactants, which are derived from the termination of mineral dissolution due to the gradual decrease in pH.

**Oxygen fugacity and chemistry of hydrothermal fluid.** The hornblende-origin chlorite
in sample No. 3-2-9 involves both magnetite and ilmenite, separated by a small distance of
about 400 μm apart (Fig. 7A-1 and B-1). The formation of magnetite and ilmenite are
associated with hornblende chloritization because their minerals are surrounded by chlorite.
However, the minerals were not simultaneously produced in the alteration process because
each mineral required a different oxygen fugacity: magnetite for high fO$_2$ condition and
ilmenite for low fO$_2$ condition under the same temperature. A grain of the mineral during the
chloritization exhibits sequential variation in its chlorite composition, representing the
progression of temperature conditions and chemical reactions (mass transfer) during
chloritization. By determining the chemical characteristics of chlorite around magnetite and
ilmenite, the thermal conditions of the hydrothermal fluid yielding magnetite and ilmenite
can be interpreted. Figure 7 shows the profiles of formation temperatures deduced from the
tetrahedral aluminum in the chlorite of sample No. 3-2-9: ‘A area (A-1)’ with scanning line
from 0 μm to 132 μm through ilmenite (80–115 μm) and ‘B area (B-1)’ with scanning line
from 0 μm to 84 μm through magnetite (50–65 μm). The change in chloritization temperature
along the scanning line in the grain indicates the extent (e.g., alteration direction) of
chloritization progress with temperature decrease. Area A shows a minimum temperature of
about 200°C, at about 50 μm in the scanning line, and the temperatures increase from there
to both the 0 and 132 μm sides (Fig. 7A-2). That is, the hydrothermal chloritization
progressed from both the sides (0 and 132 μm) and terminated at the 50-μm position in the
profile. Chloritization temperatures in contact with ilmenite are about 220°C (80 μm in
distance) and 250°C (110 μm), indicating that ilmenite was produced at temperatures
between 220°C and 250°C.
In area B, the chloritization temperature decreases from about 50 µm towards both sides (0 and 84 µm) in the scanning line, indicating that the chloritization started at the 50-µm position in the profile, and extended in both directions (Fig. 7B-2). Chloritization temperatures in contact with magnetite are about 310°C (55 µm) and about 280°C (70 µm), indicating that the formation temperatures of magnetite between 280 and 310°C. Therefore, the formation temperature of magnetite was higher than that of ilmenite, implying a decrease in oxygen fugacity in the hydrothermal fluid as temperature decreased from 280–310°C to 220–250°C.

By determining the chemical characteristics and formation temperatures of chlorite in sample No. 3-2-9, the sequential variations in the fluid chemistry can be interpreted. Figure 8 shows the chemical variations of Al₂O₃ (A), FeO (B), MnO (C), SiO₂ (D), and MgO (E) against temperature conditions of chlorite in sample No. 3-2-9. The decrease in chloritization temperature is accompanied by 1) the decrease in the mass of aluminum, iron, and manganese in chlorite, and 2) the increase in silicon and magnesium (Fig. 8).

Such profiles reflect the rates of decreasing and increasing concentrations of chemical components in the hydrothermal fluid with chloritization progress, because the chemical variation of chlorite corresponds to the requisite amounts of inflow and outflow components in the chloritization reaction. In the trend of reduction in metallic components (aluminum, iron, manganese, and magnesium ions) with the progress of hornblende chloritization (overall reaction of sample No. 3-2-9: Table 2), the rates of decreasing concentrations of aluminum, iron, and manganese in the hydrothermal fluid become progressively smaller, while that of magnesium becomes progressively larger. The rate of increasing concentration...
of silicon in the hydrothermal fluid becomes progressively smaller.
IMPLICATIONS

The methodology and interpretations for providing new insights into the mass transfer due to hydrothermal alteration are described in our serial works (Yuguchi et al., 2015, 2019A, and this study). They reveal the nature of the sequential, long-term variations in fluid chemistry in a granitic pluton across a wide temperature range during sub-solidus cooling. This study focuses on the petrography and mineral chemistry of hornblende chloritization, K-feldspar chloritization, and fracture-filling chlorite formation. A combination of this study and Yuguchi et al. (2015) dealing with biotite chloritization reveals the comprehensive characteristics of mass transfer in the overall chloritization process, which has been either overlooked or not fully appreciated in previous studies. For this study, rock samples were extracted from 500-m deep boreholes. The deep drill samples enabled us to observe the microvoids in hornblende chloritization. Such microstructures have not been observed clearly in samples taken from the surface outcrops or from boreholes near the surface due to weathering. This reveals the importance of studying deep drill samples to clarify the nature of hydrothermal alteration. The SVD analysis was used to determine the chloritization reaction equations, based on closure component and molar volume. This analysis can serve as an effective technique to reveal the mass transfer in hydrothermal alteration and metamorphic reactions with volume change. The overall reactions lead to the mass transfer between the reactant and the products, and the associated inflow and outflow of components with respect to the hydrothermal fluid. The time–temperature ($t–T$) path for the sampling site is an effective tool for determining unknown alteration age from the known thermal conditions of the target mineral. The sequential variations were made possible by determining
both the alteration age and the temperature. Determining the chemical characteristics of chlorite around magnetite and ilmenite reveals that the oxygen fugacity in the hydrothermal fluid during hornblende chloritization decreases as the temperature. This study, by exploring the sequential variations in mass transfer and fluid chemistry, provides important procedures and parameters for future forecasting the geochemical features of a granitic rock.
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belt, southwest Japan: constraints from CHIME monazite ages of gneisses and granitoids.


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Appendix A

Hornblende image analysis revealing the volume (areal) ratios of the alteration minerals obtained using image processing software, with sample No. 3-6 as an example

The hornblende chloritization of sample No. 3-6 is accompanied with chlorite, titanite, epidote, quartz, and calcite with microvoids and microcracks. The alteration hornblende was clipped from the BSE image using the Photoshop® image processing software (Fig. S8A). The binary image processing using the Photoshop® was divided into white pixels, which includes hornblende and chloritization minerals (9,726,377 pixels), and black pixels (Fig. S8B). These pixels corresponded to the microvoids, microcracks, and areas other than the target chloritization area (9,934,423 pixels). White pixels include hornblende, chloritization minerals, microvoids, and microcracks (10,286,369 pixels), while black pixels correspond to areas other than the target chloritization area (9,374,431 pixels) (Fig. S8C). The chloritization products consist of chlorite (3,473,645 pixels: Fig. S8D), titanite (689,597 pixels: Fig. S8E), epidote (131,809 pixels: Fig. S8F), quartz (207,341 pixels: Fig. S8G), and calcite (151,928 pixels: Fig. S8H).
Appendix B

Hornblende chloritization reactions of the sample No. 3-6, 7-8, 10-1 and 10-4

Sample No. 3-6: Overall reaction (Hb → Chl + Ttn + Ep + Qtz + Cal). Hornblende (chemical composition analysis No. C3-5 in Table S1) is the reactant and chlorite (No. C3-9), titanite (No. C3-1), epidote (No. C3-3), quartz (No. C3-4), and calcite (ideal CaCO$_3$ is assumed) are the products. The following reaction was established by conservation involving 1) about 11% decrease in volume from reactant to products, and 2) volume fractions of the product minerals (Chl: Ttn: Ep: Qtz: Cal = 1: 0.199: 0.038: 0.060: 0.044): Hb + 0.111Ti$^+$ + 3.238Al$^{3+}$ + 2.066Fe$^{2+}$ + 1.284Mg$^{2+}$ + 0.076F$^-$ + 7.039H$_2$O + 0.212CO$_2$ → 0.843Chl + 0.619Ttn + 0.102Ep + 0.473Qtz + 0.212Cal + 0.399H$_4$SiO$_4$ + 0.015Mn$^+$ + 0.916Ca$^{2+}$ + 0.629Na$^+$ + 0.178K$^+$ + 0.027Cl$^-$ + 12.479H$^+$ …reaction (3) (Table 2)

The SVD analysis of the matrices consisting of two conservation constraints of molar volume and manganese components for six phases (Table S2) gives the most reasonable reaction: 0.681Hb + 0.148Ti$^+$ + 2.601Al$^{3+}$ + 1.543Fe$^{2+}$ + 0.820Mg$^{2+}$ + 0.107F$^-$ + 6.352H$_2$O + 0.118CO$_2$ → 0.582Chl + 0.382Ttn + 0.180Ep + 0.073Qtz + 0.118Cal + 0.440H$_4$SiO$_4$ + 0.431Ca$^{2+}$ + 0.485Na$^+$ + 0.133K$^+$ + 10.945H$^+$ …reaction (4) (Table 2)

The reaction gives the volume fraction of the product minerals; Chl : Ttn : Ep : Qtz : Cal = 1 : 0.235 : 0.157 : 0.002 : 0.049 (Table 2). Reaction equations (3) and (4) represent the chloritization and production of titanite, epidote, quartz, and calcite by the consumption of hornblende, with an inflow of Ti$^+$, Al$^{3+}$, Fe$^{2+}$, Mg$^{2+}$, F$^-$, H$_2$O, and CO$_2$ from the hydrothermal fluid, followed by the outflow of H$_4$SiO$_4$, Mn$^+$ (reaction (3)), Ca$^{2+}$, Na$^+$, K$^+$, Cl$^-$, and H$^+$ into the hydrothermal fluid.
Sample No. 7-8: Overall reaction (Hb → Chl + Ttn + Ab). Hornblende (No. 73) is the reactant and chlorite (No. 80), titanite (No. 89), and albite (D7-1) are the products (Table S1). The following reaction equation was established by conservation involving 1) about 6% decrease in volume from reactant to products, and 2) volume fractions of the product minerals (Chl : Ttn : Ab = 1 : 0.071 : 0.211): Hb + 0.167H₄SiO₄ + 3.649Al³⁺ + 2.751Fe²⁺ + 0.056Mn²⁺ + 1.242Mg²⁺ + 6.525H₂O → 0.933Chl + 0.253Ttn + 0.414Ab + 0.106Ti²⁺ + 1.427Ca²⁺ + 0.307Na⁺ + 0.172K⁺ + 0.147F⁻ + 0.030Cl⁻ + 13.719H⁺…reaction (5) (Table 2)

The SVD analysis of matrices consisting of two conservation constraints of molar volume and Ti components for four phases (Table S2) gives the most reasonable reaction relation:

0.672Hb + 0.036H₄SiO₄ + 2.541Al³⁺ + 2.192Fe²⁺ + 0.056Mn²⁺ + 0.945Mg²⁺ + 5.099H₂O → 0.677Chl + 0.279Ttn + 0.113Ab + 0.877Ca²⁺ + 0.335Na⁺ + 0.119K⁺ + 0.080F⁻ + 0.020Cl⁻ + 10.341H⁺…reaction (6) (Table 2)

The reaction gives the volume fraction of the product minerals; Chl: Ttn: Ab = 1: 0.108: 0.079 (Table 2). Reactions (5) and (6) indicate that the chloritization, titanite, and albite are produced by the consumption of hornblende with an inflow of H₄SiO₄, Al³⁺, Fe²⁺, Mn²⁺, Mg²⁺, and H₂O from the hydrothermal fluid, and are accompanied by the outflow of Ti²⁺, Ca²⁺, Na⁺, K⁺, F⁻, Cl⁻, and H⁺ into the hydrothermal fluid.

Sample No. 10-1: Overall reaction (Hb → Chl + Ttn + Qtz). The reaction involves hornblende (No. C10-5) as the reactant and chlorite (No. A096), titanite (No. E10-1), and quartz (No. C10-6) as the products (Table S1). The following reaction equation was established by conservations involving 1) about 12% decrease in volume from reactant to products, and 2) volume fractions of the product minerals (Chl: Ttn: Qtz = 1: 0.091: 0.078):
Hb + 3.262Al$^{3+}$ + 2.790Fe$^{2+}$ + 0.090Mn$^{2+}$ + 1.203Mg$^{2+}$ + 0.090F$^-$ + 7.753H$_2$O → 0.944Chl +
0.323Ttn + 0.680Qtz + 0.340H$_4$SiO$_4$ + 0.096Ti$^+$ + 1.432Ca$^{2+}$ + 0.381Na$^+$ + 0.222K$^+$ +
0.070Cl$^-$ + 14.146H$^+$…reaction (7) (Table 2)

The SVD analysis of the matrices consisting of two conservation constraints of molar volume and Ti components for four phases (Table S2) gives the most reasonable reaction relation: 0.677Hb + 2.339Al$^{3+}$ + 1.990Fe$^{2+}$ + 0.066Mn$^{2+}$ + 0.848Mg$^{2+}$ + 0.091F$^-$ + 6.288H$_2$O → 0.653Chl + 0.339Ttn + 0.025Qtz + 0.453H$_4$SiO$_4$ + 0.843Ca$^{2+}$ + 0.258Na$^+$ + 0.150K$^+$ +
0.047Cl$^-$ + 10.765H$^+$…reaction (8) (Table 2)

The reaction gives the volume fraction of the product minerals; Chl : Ttn : Qtz = 1 : 0.138 : 0.004 (Table 2). The overall reactions are characterized by the consumption of hornblende with an inflow of Al$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, F$, \text{H}_2\text{O}$ and the production of chlorite, titanite, and quartz with an outflow of H$_4$SiO$_4$, Ca$^{2+}$, Na$^+$, K$^+$, Cl$^-$, and H$^+$ into the hydrothermal fluid.

Sample No. 10-4: Overall reaction (Hb → Chl + Ttn + Ep + Fl + Cal + Qtz). The reactant is hornblende (No. A110), and the product minerals consist of chlorite (No. A108), titanite (No. C10-3), epidote (No. C10-1), fluorite (ideal CaF$_2$), calcite (ideal CaCO$_3$), and quartz (No. E10-3). The following reaction equation was established by conservations involving 1) about 11% decrease in volume from reactant to products, and 2) volume fractions of the product minerals (Chl: Ttn: Ep: Fl: Cal: Qtz = 1: 0.330: 0.047: 0.094: 0.048):

Hb + 1.200H$_4$SiO$_4$ + 4.487Al$^{3+}$ + 2.740Fe$^{2+}$ + 0.069Mn$^{2+}$ + 0.860Mg$^{2+}$ + 0.486Ca$^{2+}$ + 0.730F$^-$ + 7.397H$_2$O + 0.226CO$_2$ → 0.824Chl + 0.028Ttn + 0.858Ep + 0.337Fl + 0.723Qtz +
0.226Cal + 0.199Ti$^+$ + 0.483Na$^+$ + 0.207K$^+$ + 0.069Cl$^-$ + 19.592H$^+$…reaction (9) (Table 2)
The SVD analysis of the matrices consisting of two conservation constraints of molar volume and Ti and Ca components for seven phases (Table S2) gives the most reasonable reaction relation:

\[ 0.649\text{Hb} + 0.351\text{H}_4\text{SiO}_4 + 2.984\text{Al}^{3+} + 2.078\text{Fe}^{2+} + 0.063\text{Mn}^{2+} + 0.714\text{Mg}^{2+} + 0.305\text{F}^- + 6.324\text{H}_2\text{O} + 0.102\text{CO}_2 \rightarrow 0.607\text{Chl} + 0.249\text{Ttn} + 0.359\text{Ep} + 0.092\text{Fl} + 0.017\text{Qtz} + 0.102\text{Cal} + 0.313\text{Na}^+ + 0.131\text{K}^+ + 0.046\text{Cl}^- + 14.052\text{H}^+ \ldots \text{reaction (10)} \] (Table 2)

The reaction gives the volume fraction of the product minerals; Chl : Ttn : Ep : Fl : Cal : Qtz = 1 : 0.110 : 0.187 : 0.018 : 0.003 : 0.029 (Table 2). Reactions (9) and (10) indicate that chlorite, titanite, epidote, fluorite, quartz, and calcite formed through the consumption of hornblende with an inflow of \( \text{H}_4\text{SiO}_4, \text{Al}^{3+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+} \) (reaction (9)), \( \text{F}^-, \text{H}_2\text{O}, \) and \( \text{CO}_2 \) from the hydrothermal fluid, followed by an outflow of \( \text{Ti}^+, \text{Na}^+, \text{K}^+, \text{Cl}^-, \) and \( \text{H}^+ \) into the hydrothermal fluid.
Figure captions

Figure 1. The Toki granitic pluton and Mizunami Underground Research Laboratory. (A) Map of Southwest Japan showing the location of the Toki granite (Tono district – TKG; square symbol) in central Japan, together with the distribution of the San-in, Sanyo, and Ryoke Belts in the inner zone of Southwest Japan, after Ishihara and Chappell (2007). (B) Geologic map of the Toki granite after Itoigawa (1980), the Mizunami Underground Research Laboratory and the borehole sites. The topographic contours inside the Tono district are based on Geographical Survey Institute 1:25,000 topographic maps, titled “Mitake,” “Takenami,” “Toki,” and “Mizunami.” Borehole investigations at the Toki granite were performed by the Japan Atomic Energy Agency (Japan Nuclear Cycle Development Institute 2000; 2002). (C) Rock facies cross-section of the Toki granite along the line from X to X’ on the geologic map (Fig. 1B). MBG: muscovite–biotite granite, HBG: hornblende–biotite granite, and BG: biotite granite (Yuguchi et al. 2010). (D) Location of the shafts and boreholes in the Mizunami Underground Research Laboratory. (E) Schematic overview of the shafts in the Mizunami Underground Research Laboratory, and the sample locations used in this study. The samples were collected from borehole 06MI03, at altitudes ranging from -274 masl (meters above sea level) to -314 masl in the HBG of the Toki granite.

Figure 2. Polarization microscope (POM) and backscattered electron (BSE) images of the hornblende chloritization (A: sample No. 3-2-9, B: sample No. 7-8). The hornblende-origin chlorite of sample No. 3-2-9 includes ilmenite (A-3) and magnetite (A-4). Hb: hornblende, Chl: chlorite, Ab: albite, Kfs: K-feldspar, Mag: magnetite, and Il: ilmenite.
Figure 3. POM and BSE images of K-feldspar chloritization (A: sample No. 3-16) and fracture-filling chlorite formation (B: sample No. 8-1). The K-feldspar-origin chlorite of sample No. 3-16 includes titanite and chlorite fragments and are distributed within the K-feldspar grain in contact with chlorite (A-4). The fracture-filling chlorite formation is accompanied by titanite and K-feldspar as the associated minerals (B-3 and B-4). Bt: biotite, Chl: chlorite, Ttn: titanite, Ab: albite, and Kfs: K-feldspar.

Figure 4. Relationship between Si (atoms per formula unit (apfu)) and Mg# (Mg / (Fe + Mn + Mg) in apfu) in the overall chloritization (A), biotite chloritization (B: N = 143), hornblende chloritization (C: N = 57), K-feldspar chloritization (D: N = 28), and fracture-filling chlorite formation (E: N = 2). Original data of chlorite compositions in the biotite chloritization were taken from Yuguchi et al. (2015).

Figure 5. Schematic figure showing the mass transfer of chemical components through hydrothermal fluids in overall chloritization and plagioclase alteration processes. Bt: biotite, Hb: hornblende, Chl: chlorite, Ttn: titanite, Ep: epidote, Fl: fluorite, Cal: calcite, Ab: albite, Kfs: K-feldspar, Qtz: quartz, Mag: magnetite, and Il: ilmenite.

Figure 6. Plots of tetrahedral aluminum (AlIV) in apfu (A), and formation temperature deduced from Yoneda and Maeda (2008)’s geothermometer (B) among biotite chloritization (N = 143), hornblende chloritization (N = 57), K-feldspar chloritization (N = 28), and fracture-filling (N = 2). Original data of chlorite compositions in the biotite chloritization were taken from Yuguchi et al. (2015).

Figure 7. Continuous thermal variation of chemical components of the hydrothermal fluid associated with the formation of ilmenite (A) and magnetite (B) through the progress of...
hornblende chloritization (sample No. 3-2-9). BSE images of the hornblende chloritization
associated with the formation of ilmenite (A-1) and magnetite (B-1). The profiles of
chloritization temperature deduced from Yoneda and Maeda (2008)’s geothermometer
along the scanning line: arrows in the BSE images: 0–132 μm range (A-2) and 0–84 μm
range (B-2). Hb: hornblende, Chl: chlorite, Ab: albite, Kfs: K-feldspar, Mag: magnetite,
and Il: ilmenite.

**Figure 8.** Variations in chemical compositions during hornblende chloritization (sample No.
3-2-9) with decrease in temperature: Al$_2$O$_3$ (A), FeO (B), MnO (C), SiO$_2$ (D), and MgO
(E).

**Supplementary figure S1.** Chemical maps showing elemental Si, Ti, Al, Fe, Mn, Mg, Ca,
Na, and K concentrations in hornblende chloritization of sample No. 3-2-9 (BSE image
area of Fig. 2A-2). Hb: hornblende, and Qtz: quartz.

**Supplementary figure S2.** POM and BSE images, and chemical maps showing elemental
Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K concentrations in hornblende chloritization of sample
No. 3-6. Hb: hornblende, Chl: chlorite, Ttn: titanite, Ep: epidote, Cal: calcite, and Qtz:
quartz.

**Supplementary figure S3.** POM and BSE images, and chemical maps showing elemental
Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K concentrations in hornblende chloritization of sample
No. 10-1. Hb: hornblende, Chl: chlorite, and Qtz: quartz.

**Supplementary figure S4.** POM and BSE images, and chemical maps showing elemental
Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K concentrations in hornblende chloritization of sample
and Qtz: quartz.

**Supplementary figure S5.** Chemical maps showing elemental Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K concentrations in K-feldspar chloritization of sample No. 3-6.

**Supplementary figure S6.** Chemical maps showing elemental Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K concentrations for fracture-filling chlorite of sample No. 8-1.

**Supplementary figure S7.** The $t$–$T$ path determining both the temporal and thermal conditions of the secondary minerals. (A) The $t$–$T$ path of sample DH2 RA03 is constructed from thermochronological data including zircon U–Pb ages, biotite K–Ar age, ZFT age, AFT age, and the FT inverse calculation. The FT inverse calculation was derived from a dataset, including the AFT age, AFT lengths, ZFT age, and ZFT lengths, and provided the acceptable-fit paths, good-fit paths, best-fit path, and the weighted mean path below 400°C. The details of the FT inverse calculation are described Yuguchi et al. (2019B). The envelope of good-fit paths include the biotite K–Ar, ZFT, and AFT ages, resulting in a reasonable reproduction of the $t$–$T$ path from the biotite K–Ar closure temperature (350–400°C) through the ZFT partial annealing zone (PAZ) (190–390°C) to the AFT PAZ (60–120°C). (B) The temporal condition for overall chloritization, whose thermal condition is already known (Yuguchi et al., 2015 and this study), is obtained through the weighted mean $t$–$T$ path. In biotite chloritization, the intersection of the weighted mean $t$–$T$ path and the thermal condition of 350°C (blue horizontal line) gives a formation age of about 68 Ma, and that of the $t$–$T$ path and a thermal condition of 180°C gives an age of about 51 Ma. This indicates that the biotite chloritization occurred over about 17 million years, from about 68–51 Ma. The hornblende chloritization occurred at temperature conditions in the
range of 230–325°C and over about 10 million years from about 64–54 Ma. The K-feldspar chloritization occurred at temperatures in the range of 210–350°C and over about 15 million years of about 68 to 53 Ma. The formation conditions of fracture-filling chlorite are 320°C and 340°C (thermal condition) and about 63 Ma and 66 Ma in age, respectively.

**Supplementary figure S8.** Image analysis revealing the volume (areal) ratios of the alteration minerals obtained using image processing software, with sample No. 3-6 as an example.
Yuguchi et al. Fig. 3

A-1 K-feldspar chloritization
Biotite chloritization

A-2 K-feldspar chloritization
Biotite chloritization

A-3 A-4
Chl Bt
Chl
Ab

A-4
Chl B021
Ttn
E3-9
E3-5

B-1 Fracture-filling chlorite

B-2 B-3 B-4
A072 A074 A075
Chl
Kfs

B-3
Chl Kfs

B-4
Chl Kfs

3-16 POM image 500µm
3-16 POM image 500µm
3-16 POM image 500µm
8-1 BSE image 20µm
8-1 BSE image 500µm
8-1 BSE image 20µm
8-1 BSE image 10µm

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Yuguchi et al. Fig. 3
Yuguchi et al. Fig. 4

A

Bt chloritization

Hb chloritization

Kfs chloritization

Fracture-filling chlorite

B

(N=143: Yuguchi et al., 2015)

C

Hb chloritization

(N=57)

D

Kfs chloritization

(N=28)

E

Fracture-filling chlorite

(N=2)
Inflow

\[ \text{H}_4\text{SiO}_4 (\text{Si}^{4+}), \text{Al}^{3+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+} \]

Outflow

\[ \text{H}_4\text{SiO}_4 (\text{Si}^{4+}), \text{K}^+, \text{F}^- \]

**Biotite chloritization**

\[ + \text{Ttn}, \text{Il}, \text{Fl} \text{and Kfs} \]

**Hornblende chloritization**

\[ + \text{Ttn}, \text{Ep}, \text{Il}, \text{Mag}, \text{Fl}, \text{Cal} \]

**K-feldspar chloritization**

\[ + \text{Ttn} \text{and Kfs} \]

**Fracture-filling chlorite**

\[ + \text{Ttn} \text{and Kfs} \]

**Biotite chloritization**

\[ + \text{Ttn}, \text{Il}, \text{Fl} \text{and Kfs} \]

**Bt chloritization**

\[ + \text{Ttn}, \text{Il}, \text{Fl} \text{and Kfs} \]

**Plagioclase alteration**

\[ \text{Ab, Kfs, Ill, Ep, Cal, Fl} \]

**Plagioclase alteration**

\[ \text{Ab, Kfs, Ill, Ep, Cal, Fl} \]

**Connection of micropore network**

**Precipitation of fracture filling carbonate minerals**

**Gradual increase of pH**

**Gradual decrease of pH**

**Increase of H^+**

**Decrease of H^+**

**Increase of H^+**

**Precipitation of fracture filling carbonate minerals**

**Consequential chemistry of hydrothermal fluid through chloritization and plagioclase alteration**

**Gradual decrease: Al^{3+}, Fe^{2+}, Mn^{2+}, Mg^{2+}**

**Gradual increase: Ca^{2+}, K^+, H^+, F^-**

Yuguchi et al. (2015)

Yuguchi et al. (2019a)
Yuguchi et al. Fig. 6

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Yuguchi et al. Fig. 8
TABLE 1. Mineral assemblage and the volume (areal) ratio of alteration minerals in the hornblende chloritization, K-feldspar chloritization, and fracture-filling chloritite.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample No.</th>
<th>Mineral assemblage</th>
<th>Volume decrease (%)</th>
<th>Volume (areal) ratio of product minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hb chl</td>
<td>3-2-9</td>
<td>Hb Chl, Ab, Kfs, Il, Mag</td>
<td>88.39</td>
<td>Chl : Ab : Kfs : Il : Mag = 1 : 0.056 : 0.056 : 0.131 : 0.002</td>
</tr>
<tr>
<td>Hb chl</td>
<td>3-6</td>
<td>Hb Chl, Ttn, Ep, Qtz, Cal</td>
<td>89.26</td>
<td>Chl : Ttn : Ep : Qtz : Cal = 1 : 0.199 : 0.038 : 0.060 : 0.044</td>
</tr>
<tr>
<td>Hb chl</td>
<td>7-8</td>
<td>Hb Chl, Ttn, Ab</td>
<td>94.27</td>
<td>Chl : Ttn : Ab = 1 : 0.071 : 0.211</td>
</tr>
<tr>
<td>Hb chl</td>
<td>10-1</td>
<td>Hb Chl, Ttn, Qtz</td>
<td>87.52</td>
<td>Chl : Ttn : Qtz = 1 : 0.091 : 0.078</td>
</tr>
<tr>
<td>Hb chl</td>
<td>10-4</td>
<td>Hb Chl, Ttn, Ep, Fl, Cal, Qtz</td>
<td>89.12</td>
<td>Chl : Ttn : Ep : Fl : Qtz : Cal = 1 : 0.330 : 0.047 : 0.094 : 0.048</td>
</tr>
<tr>
<td>Kfs chl</td>
<td>3-6</td>
<td>Kfs Chl, Ttn</td>
<td>100.00 c</td>
<td>Chl : Ttn = 1 : 0.070</td>
</tr>
<tr>
<td>Fracture chl</td>
<td>8-1</td>
<td>- Chl, Ttn, Kfs</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

b Volume decrease from reactant to products (volume percent).  
c Constant volume from reactant to products (No decrease).  
d The volume fraction of product minerals in the plagioclase alteration was estimated from the areal fraction of them by simply assuming the equivalence of areal and volume fractions. The area of product minerals are identified by BSE images, and the areal ratio was calculated by image processing software of Photoshop®.
### TABLE 2. Overall reactions leading to chloritization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Overall reaction</th>
</tr>
</thead>
</table>
| Hb chl Grain No. 3-9 | [Volume decrease of 89.39% and volume ratio of product minerals]  
Hb + 0.495Ti⁺ + 2.711Al³⁺ + 2.552Fe²⁺ + 0.265Mn²⁺ + 1.116Mg²⁺ + 0.200K⁺ + 7.878H₂O → 0.895Chl + 0.105Ab +  
0.097Kfs + 0.761II + 0.008Mag + 0.472H₂SiO₄ + 1.685Ca²⁺ + 0.50Na⁺ + 0.131F⁻ + 0.016Cl⁻ + 13.870H⁻  

[SV: Volume decrease of 89.39% and closure component of Ti]  
0.714Hb + 2.252Al³⁺ + 1.982Fe²⁺ + 0.015Mn²⁺ + 0.825Mg²⁺ + 0.207K⁺ + 0.022F⁻ + 5.432H₂O → 0.678Chl + 0.058Ab +  
0.127Kfs + 0.09II + 0.049Mag + 0.240H₂SiO₄ + 1.169Ca²⁺ + 0.355Na⁺ + 0.033Cl⁻ + 9.905H⁻  

Volume ratio ¹ Chl : Ab : Kfs : II : Mag = 1 : 0.400 : 0.096 : 0.022 : 0.014 |
| Hb chl Grain No. 3-6 | [Volume decrease of 89.26% and volume ratio of product minerals]  
Hb + 0.111TI⁺ + 3.328Al³⁺ + 2.066Fe²⁺ + 1.284Mg²⁺ + 0.076F⁻ + 7.039H₂O + 0.212CO₂ → 0.843Chl + 0.619Ttn +  
0.102Ep + 0.473Qtz + 0.212Ca²⁺ + 0.431Na⁺ + 0.485K⁺ + 12.479H⁺  

[SV: Volume of 89.26% and closure component of Mn]  
0.681Hb + 0.148Ti⁺ + 2.601Al³⁺ + 1.543Fe²⁺ + 0.820Mg²⁺ + 0.107F⁻ + 6.352H₂O + 0.118CO₂ → 0.582Chl + 0.382Ttn +  
0.180Ep + 0.073Qtz + 0.073Cal + 0.440H₂SiO₄ + 0.485Ca²⁺ + 0.485Na⁺ + 0.133K⁺ + 10.945H⁺  

Volume ratio ¹ Chl : Ttn = 1 : 0.033 |
| Hb chl Grain No. 7-8 | [Volume decrease of 94.27% and volume ratio of product minerals]  
Hb + 0.167H₄SiO₄ + 3.262Al³⁺ + 2.790Fe²⁺ + 0.090Mn²⁺ + 1.242Mg²⁺ + 6.525H₂O → 0.933Chl + 0.253Ttn +  
0.414Ab + 0.106Ti²⁺ + 1.427Ca²⁺ + 0.307Na⁺ + 0.172K⁺ + 0.147F⁻ + 13.719H⁺  

[SV: Volume of 94.27% and closure component of Ti]  
0.672Hb + 0.036H₄SiO₄ + 2.339Al³⁺ + 1.990Fe²⁺ + 0.066Mn²⁺ + 0.945Mg²⁺ + 5.099H₂O → 0.677Chl + 0.279Ttn +  
0.113Ab + 0.877Ca²⁺ + 0.335Na⁺ + 0.119K⁺ + 0.080F⁻ + 0.020Cl⁻ + 10.341H⁺  

Volume ratio ¹ Chl : Ttn : Ab = 1 : 0.108 : 0.079 |
| Hb chl Grain No. 10-1 | [Volume decrease of 87.52% and volume ratio of product minerals]  
Hb + 0.120H₄SiO₄ + 4.487Al³⁺ + 2.740Fe²⁺ + 0.069Mn²⁺ + 0.860Mg²⁺ + 0.486Ca²⁺ + 0.730F⁻ + 7.397H₂O +  
0.226CO₂ → 0.824Chl + 0.028Ttn + 0.858Ep + 0.337F⁻ + 0.723Qtz + 0.226Ca + 0.197Tm + 0.483Na⁺ + 0.207K⁺ +  
0.069Cl⁻ + 19.592H⁻  

[SV: Volume of 87.52% and closure component of Ti]  
0.677Hb + 2.339Al³⁺ + 1.990Fe²⁺ + 0.066Mn²⁺ + 0.848Mg²⁺ + 0.091F⁻ + 6.288H₂O → 0.653Chl + 0.339Ttn + 0.025Qtz +  
0.453H₂SiO₄ + 0.843Ca²⁺ + 0.258Na⁺ + 0.150K⁺ + 0.047Cl⁻ + 10.765H⁻  

Volume ratio ¹ Chl : Ttn : Qtz = 1 : 0.138 : 0.004 |
| Hb chl Grain No. 10-4 | [Volume decrease of 89.12% and volume ratio of product minerals]  
Hb + 1.200H₄SiO₄ + 4.487Al³⁺ + 2.740Fe²⁺ + 0.069Mn²⁺ + 0.860Mg²⁺ + 0.486Ca²⁺ + 0.730F⁻ + 7.397H₂O +  
0.226CO₂ → 0.824Chl + 0.028Ttn + 0.858Ep + 0.337F⁻ + 0.723Qtz + 0.226Ca + 0.197Tm + 0.483Na⁺ + 0.207K⁺ +  
0.069Cl⁻ + 19.592H⁻  

[SV: Volume of 89.12% and closure components of Ti and Ca]  
0.649Hb + 0.351H₂SiO₄ + 2.984Al³⁺ + 2.078Fe²⁺ + 0.063Mn²⁺ + 0.714Mg²⁺ + 0.305F⁻ + 6.324H₂O + 0.102CO₂  
→ 0.607Chl + 0.249Ttn + 0.359Ep + 0.092F⁻ + 0.017Qtz + 0.102Cal + 0.313Na⁺ + 0.131K⁺ + 0.046Cl⁻ + 14.052H⁺  

Volume ratio ¹ Chl : Ttn : Ep : Fl : Qtz : Cal = 1 : 0.110 : 0.187 : 0.018 : 0.003 : 0.029 |
| Kfs chl Grain No. 3-16 | [Volume constant and volume ratio of product minerals]  
Kfs + 0.107Ti⁺ + 1.644Al³⁺ + 3.255Fe²⁺ + 0.203Mn²⁺ + 0.813Mg²⁺ + 0.016F⁻ + 0.009Cl⁻ + 7.150H₂O →  
0.478Chl + 0.478Ttn + 0.383Ab + 0.50Ca²⁺ + 0.207K⁺ + 0.069Cl⁻ + 19.592H⁺  

[SV: Volume constant]  
0.714Kfs + 0.051Tt + 1.546Al³⁺ + 3.010Fe²⁺ + 0.188Mn²⁺ + 0.756Mg²⁺ + 0.050Ca²⁺ + 0.007F⁻ + 0.009Cl⁻ +  
6.456H₂O → 0.443Chl + 0.055Ttn + 0.236H₂SiO₄ + 0.014Na⁺ + 0.814K⁺ + 11.968H⁻  

Volume ratio ¹ Chl : Ttn = 1 : 0.033 |

¹ Volume ratio of product minerals deduced from the overall reaction

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