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 (Online Material[1] Fig. OM8a). The binary image processing using the Photoshop was divided into white pixels, which includes hornblende and chloritization minerals (9726,377 pixels), and black pixels (Online Material[1] Fig. OM8b). These pixels corresponded to the microvoids, microcracks, and areas other than the target chloritization area (9934,423 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 (9374,431 pixels) (Online Material[1] Fig. OM8c). The chloritization products consist of chlorite (3473,645 pixels: Online Material[1] Fig. OM8d), titanite (689,597 pixels: Online Material[1] Fig. OM8e), epidote (131,809 pixels: Online Material[1] Fig. OM8f), quartz (207,341 pixels: Online Material[1] Fig. OM8g), and calcite (151,928 pixels: Online Material[1] Fig. OM8h).

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 Online Material[1] Table OM1) 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):

$Hb + 0.111Ti^{+} + 3.238Al^{3+} + 2.066Fe^{2+} + 1.284Mg^{2+} + 0.076F^{-} + 7.039H_2O + 0.212CO_2 \rightarrow 0.843Chl + 0.619Ttn + 0.102Ep + 0.473Qtz + 0.212Cal + 0.399H_4SiO_4 + 0.015Mn^{+} + 0.916Ca^{2+} + 0.629Na^{+} + 0.178\ K^{+} + 0.027Cl^{-} + 12.479H^{+}$ …reaction (3) (Table 2)

The SVD analysis of the matrices consisting of two conservation constraints of molar volume and manganese components for six phases (Online Material[1] Table OM2) gives the most reasonable reaction:

$0.681Hb + 0.148Ti^{+} + 2.601Al^{3+} + 1.543Fe^{2+} + 0.820Mg^{2+} + 0.107F^{-} + 6.352H_2O + 0.118CO_2 \rightarrow 0.582Chl + 0.382Ttn + 0.180Ep + 0.073Qtz + 0.118Cal + 0.440H_4SiO_4 + 0.431Ca^{2+} + 0.485Na^{+} + 0.133\ K^{+} + 10.945H^{+}$ …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_2O, and CO_2 from the hydrothermal fluid, followed by the outflow of H_4SiO_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 (Online Material[1] Table OM1). 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):

$Hb + 0.167H_4SiO_4 + 3.649Al^{3+} + 2.751Fe^{2+} + 0.056Mn^{2+} + 1.242Mg^{2+} + 6.525H_2O \rightarrow 0.933Chl + 0.253Ttn + 0.414Ab + 0.106Ti^{2+} + 1.427Ca^{2+} + 0.307Na^{+} + 0.172\ K^{+} + 0.147F^{-} + 0.030Cl^{-} + 13.719H^{+}$…reaction (5) (Table 2)

The SVD analysis of matrices consisting of two conservation constraints of molar volume and Ti components for four phases (Online Material[1] Table OM1) gives the most reasonable reaction relation:

$0.672Hb + 0.036H_4SiO_4 + 2.541Al^{3+} + 2.192Fe^{2+} + 0.056Mn^{2+} + 0.945Mg^{2+} + 5.099H_2O \rightarrow 0.677Chl + 0.279Ttn + 0.113Ab + 0.877Ca^{2+} + 0.335Na^{+} + 0.119\ K^{+} + 0.080F^{-} + 0.020Cl^{-} + 10.341H^{+}$…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 H_4SiO_4, Al^{3+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, and H_2O from the hydrothermal fluid, and are accompanied by the outflow of Ti^{2+}, Ca^{2+}, 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 (Online Material[1] Table OM1). 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):

$Hb + 3.262Al^{3+} + 2.790Fe^{2+} + 0.090Mn^{2+} + 1.203Mg^{2+} + 0.090F^{-} + 7.753H_2O \rightarrow 0.944Chl + 0.323Ttn + 0.680Qtz + 0.340H_4SiO_4 + 0.096Ti^{+} + 1.432Ca^{2+} + 0.381Na^{+} + 0.222\ K^{+} + 0.070Cl^{-} + 14.146H^{+}$…reaction (7) (Table 2)

The SVD analysis of the matrices consisting of two conservation constraints of molar volume and Ti components for four phases (Online Material[1] Table OM1) gives the most reasonable reaction relation:

$0.677Hb + 2.339Al^{3+} + 1.990Fe^{2+} + 0.066Mn^{2+} + 0.848Mg^{2+} + 0.091F^{-} + 6.288H_2O \rightarrow 0.653Chl + 0.339Ttn + 0.025Qtz + 0.453H_4SiO_4 + 0.843Ca^{2+} + 0.258Na^{+} + 0.150\ K^{+} + 0.047Cl^{-} + 10.765H^{+}$…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^{-}, H_2O and the production of chlorite, titanite, and quartz with an outflow of H_4SiO_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):

$Hb + 1.200H_4SiO_4 + 4.487Al^{3+} + 2.740Fe^{2+} + 0.069Mn^{2+} + 0.860Mg^{2+} + 0.486Ca^{2+} + 0.730F^{-} + 7.397H_2O + 0.226CO_2 \rightarrow 0.824Chl + 0.028Ttn + 0.858Ep + 0.337Fl + 0.723Qtz + 0.226Cal + 0.199Ti^{+} + 0.483Na^{+} + 0.207\ K^{+} + 0.069Cl^{-} + 19.592H^{+}$…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 (Online Material[1] Table OM1) gives the most reasonable reaction relation:

$0.649Hb + 0.351H_4SiO_4 + 2.984Al^{3+} + 2.078Fe^{2+} + 0.063Mn^{2+} + 0.714Mg^{2+} + 0.305F^- + 6.324H_2O + 0.102CO_2 \rightarrow 0.607Chl + 0.249Ttn + 0.359Ep + 0.092Fl + 0.017Qtz + 0.102Cal + 0.313Na^+ + 0.131\ K^+ + 0.046Cl^- + 14.052H^+$…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 H_4SiO_4, Al^{3+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}(reaction 9), F^-, H_2O, and CO_2 from the hydrothermal fluid, followed by an outflow of Ti^+, Na^+, K^+, Cl^-, and H^+ into the hydrothermal fluid.