Morphological and chemical characterization of secondary carbonates in the Toki granite, central Japan, and the evolution of fluid chemistry

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ABSTRACT

This study describes: (1) morphological nature of the calcites in the Toki granite, central Japan; (2) the difference in chemical compositions in terms of morphological classification; and (3) the identification of the stages of calcite formation and the corresponding mass transfer between minerals and fluid owing to hydrothermal alterations and groundwater-rock interactions, which reveals the sequential variations in fluid chemistry during the sub-solidus stage. Calcites in the Toki granite were classified into four types: (1) lenticular calcite in the chloritized biotite; (2) granular calcite in the altered plagioclase; (3) intergranular calcite; and (4) fracture-filling calcite. The lenticular, granular, and intergranular calcites contain greater amounts of iron, manganese, and magnesium than fracture-filling calcites. The lenticular calcite in the chloritized biotite, granular calcite in the altered plagioclase, and intergranular calcite formed due to the precipitation of calcium, iron, manganese, and magnesium released from biotite and plagioclase owing to hydrothermal alterations. The fracture-filling calcites formed at a later stage than the lenticular, granular, and intergranular forms. In the hydrothermal fluid, the concentrations of aluminum, iron, manganese, and magnesium gradually decrease, and the concentration of calcium gradually increases as the alteration proceeds. The chemical characteristics of the fluid at the late stage of hydrothermal alteration and those of the subsequent groundwater are consistent with those of fracture-filling calcites, indicating that the fracture-filling calcites precipitated from the fluid at a late stage of hydrothermal alterations and then from the groundwater. Elements released from biotite and plagioclase owing to hydrothermal alterations were incorporated into and fastened to the calcite. Therefore, the calcites influenced the sequential variations in fluid chemistry during the sub-solidus stage.

Keywords: Carbonate mineral, calcite, hydrothermal alteration, precipitation, mass transfer, cathodoluminescence image

INTRODUCTION

Future forecasting of the geochemical characteristics of a granitic pluton is necessary for safety evaluations of the long-term geological disposal of nuclear waste and underground storage of oil, natural gas, and hydrogen (e.g., Carpenter et al. 2017). For example, whether oxidative fluid (groundwater) will cause the corrosion of artificial metal objects in the facilities can be predicted (Yuguchi et al. 2019). Understanding the long-term history of the chemical characteristics of the hydrothermal fluid and groundwater within a pluton contributes to such forecasts because the geochemical history of the granite influences the chemical characteristics of the present-day and future groundwater due to water-rock interactions.

Carbonate minerals in granitic rock have an important role in evaluating the sequential variations in fluid chemistry. Carbonates are some of the most prevalent secondary minerals in granitic rocks because they readily precipitate from fluids (Munemoto et al. 2015). Calcites of hydrothermal origin in granitic rocks have been recorded to have the chemical characteristics of the original hydrothermal fluid, and those of groundwater origin have been recorded to have the chemical characteristics of groundwater. Many studies have focused on the incorporation of metals and rare earth elements (REEs) in calcium carbonates (e.g., Tanaka et al. 2004; Zhou et al. 2012) because they reflect the precipitation conditions of the source solution (Munemoto et al. 2014). For example, Mizuno and Iwatsuki (2006) revealed the redox conditions of paleo-groundwater based on the uranium and iron contents of fracture-filling calcites. Négrel et al. (2000) demonstrated the similarity in REE patterns between precipitates and groundwater, which was of interest for the precipitation of calcites without ligand exchange of the carbonate aqueous complex between the precipitates and original water. Calcites in granite are known to occur either as a hydrothermal or groundwater origin (Nishimoto et al. 2008; Munemoto et al. 2015). However, there have been few studies relating the chemical composition of carbonates to petrological characteristics, such as morphology and occurrence, except for those on fracture-filling calcites.

This study conducted in the Toki granite in Tono district, central Japan focuses on: (1) the morphological nature of calcites; (2) the difference in chemical compositions in terms of morphological classifications; and (3) identification of the stages of calcite formation and the corresponding mass transfer between