

SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

## Hydrothermal mineral replacement reactions for an apatite-monazite assemblage in alkali-rich fluids at 300–600 °C and 100 MPa

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### ABSTRACT

Mineral replacement reactions are common in the various environments where rocks have undergone re-equilibration with geologic fluids. Replacement reactions commonly take the form of fluid-aided, coupled dissolution-precipitation and often result in pseudomorph formation. One class of environment that frequently shows significant examples of mineral replacements is hydrothermal ore deposit systems. The goal of this study was to test the simultaneous reactivity of fluorapatite and monazite in Na- and Si-rich hydrothermal fluids, which partially mimic the mineralogy and fluid chemistry of the Llallagua tin deposit in Bolivia. A series of experiments were performed at 300 to 600 °C and 100 MPa, utilizing various combinations of monazite, fluorapatite, and H<sub>2</sub>O + Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. Reaction products were evaluated using scanning electron microscopy, electron microprobe analysis, and single-crystal X-ray diffraction. The results of this experimental study show that fluorapatite and monazite are differentially reactive under the conditions studied. The reaction products, pathways, and kinetics have a large temperature dependence. The 300 and 400 °C experiments show variable amounts of monazite replacement and only minor, if any, dissolution or reactivity of fluorapatite. The high-temperature 500 and 600 °C experiments are characterized by massive replacement of monazite by vitusite and britholite. Exclusively at 600 °C, monazite alteration takes the form of symplectite development at the reaction front as vermicular intergrowths of vitusite and britholite. The higher-temperature experiments also show substantially more reactivity by fluorapatite, which is partially pseudomorphically altered into britholite. This is an example of regenerative mineral replacement where both fluorapatite and britholite share the same atomic structure and are crystallographically coherent after the partial replacement. The britholite replacement is characterized by the presence of oriented nanochannels, which facilitate fluid-based mass transfer between the bulk solution and the reaction front. The fluorapatite replacement is enhanced by monazite alteration through a self-perpetuating, positive feedback mechanism between these two reactions, which enhance the REE mobility in alkali-bearing fluids and further drives bulk re-equilibration. These results have potential geochronologic implications and may be significant in the evaluation of monazite and fluorapatite as potential solid nuclear waste forms. They also give us deeper insights into the mechanism of mineral replacement reactions and porosity development.

**Keywords:** Selective mineral replacement, dissolution-precipitation, fluorapatite, monazite, britholite, pseudomorphism, multi-phase reaction