Experimental determination of stability relations between monazite, fluorapatite, allanite, and REE-epidote as a function of pressure, temperature, and fluid composition

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ABSTRACT

The experimental alteration of monazite to allanite, REE-epidote, fluorapatite, and/or fluorapatite-britholite was investigated at 450 to 610 MPa and 450 to 500 °C. Experiments involved monazite + albite ± K-feldspar + muscovite ± biotite + SiO₂ + CaF₂ and variety of fluids including H₂O, (KCl + H₂O), (NaCl + H₂O), (CaCl₂ + H₂O), (Na₂SiO₃ + H₂O), 1 M HCl, 2 M NaOH, 2 M KOH, 1 M Ca(OH)₂, 2 M Ca(OH)₂, and (CaCO₃ + H₂O). The reaction products, or lack thereof, clearly show that the stability relations between monazite, fluorapatite, and allanite or REE-epidote are more dependent on the fluid composition and the ratio of silicate minerals than on the P-T conditions. A high Ca content in the fluid promotes monazite dissolution and the formation of fluorapatite and allanite or REE-epidote. Lowering the Ca content and raising the Na content in the fluid decreases the solubility of monazite but promotes the formation of allanite. Replacing Na with K in the same fluid causes fluorapatite, with a britholite component, to form from the monazite. However, allanite and REE-epidote are not formed. Monazite is stable in the presence of NaCl brines. In KCl brine, monazite shows a very limited reaction to fluorapatite. When the fluid is (Na₂SiO₃ + H₂O), strong dissolution of monazite occurs resulting in the mobilization of REEs, and actinides to form fluorapatite-britholite and turkestanite. These experimental results are consistent with natural observations of the partial to total replacement of monazite by fluorapatite, REE-epidote, and allanite in fluid-aided reactions involving the anorthite component in plagioclase at mid- to high-grade metamorphic conditions. In contrast, an alkali-bearing environment with excess Na prevents the growth of allanite and eventually promotes the precipitation of secondary monazite. The results from this study provide implications for geochronology and for deducing fluid compositions in metamorphic rocks.

Keywords: Monazite, fluorapatite, allanite, REE-epidote, experimental petrology

INTRODUCTION

Monazite [(REE, Th)₂(U,PO₄)₃], allanite [(CaREE)(Al₁,F₃)Si₂O₆(OH)₂], and fluorapatite [(Ca₅PO₄)₃F] are relatively common accessory minerals in igneous and metamorphic rocks. They are also three of the principal hosts for the rare earth elements (Y+REE) in the Earth’s crust and lithospheric mantle. The geochemical behavior of these minerals depends on pressure, temperature, fluid composition, and bulk rock composition (Spear and Pyle 2002; Gieré and Sorensen 2004; Harlov 2011). Monazite can be replaced by allanite during progressive low-grade metamorphism, followed by a reversed transition to form monazite at higher P-T (Gieré and Sorensen 2004). Mineral-fluid interactions leading to the replacement of monazite by fluorapatite, allanite, and/or epidote [Ca₅(Al₁,F₃)Si₂O₆(OH)] have been recognized in a number of igneous and metamorphic rocks (e.g., Broska and Siman 1998; Finger et al. 1998; Claeson 2002; Wing et al. 2003; Broska et al. 2005; Janots et al. 2006, 2008, 2011; Majka and Budzyn 2006; Krenn and Finger 2007; Broska and Majka 2008; Harlov 2011). Recently, the formation of secondary monazite and secondary fluorapatite with thorianite inclusions, at the expense of primary monazite in clasts of metamorphosed granites from the Carpathian flysch, was proposed to have occurred during retrograde metamorphism at 400 to 550 °C (Budzyń et al. 2010). In general, allanite did not form, although rare secondary textures of fluorapatite intergrown with allanite were observed. Under mid-greenschist facies conditions (ca. 350–400 °C), monazite breakdown also does not lead to the formation of allanite/epidote but rather to the secondary low-Th monazite growth (Rasmussen and Muhling 2007, 2009).

Previous experimental studies on monazite have been focused on monazite-fluid interactions (e.g., Teufel and Heinrich 1997; Ayers et al. 1999; Seydoux-Guillaume et al. 2002a, 2002b; Harlov et al. 2007, 2011; Harlov and Hetherington 2010; Hetherington et al. 2010) or the fluid-induced alteration of fluorapatite to form monazite inclusions (e.g., Harlov and Förster 2002; Harlov et al. 2002, 2003, 2005). In contrast, experimental studies involving allanite are limited to a series of allanite-zoisite [Ca₅(Al₁,Si₂)(OH)] experiments at 700 °C and 2000 MPa (Hermann 2002) and there are no experimental studies investigating monazite reacting to form fluorapatite. None of the previous experimental investigations has considered the stability...