Experimental incorporation of Th into xenotime at middle to lower crustal $P$-$T$ utilizing alkali-bearing fluids

DANIEL E. HARLOV* AND RICHARD WIRTH

Section 3.3, GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam, Germany

ABSTRACT

In this study, a natural Th-absent xenotime \([(Y+HREE)PO_4]\), is enriched in specific areas with respect to Th + Si utilizing a series of alkali-bearing fluids that included $2N$ NaOH, $2N$ KOH, Na$_2$Si$_2$O$_5$ + H$_2$O, and NaF + H$_2$O, in addition to ThO$_2$ and SiO$_2$. Charge and fluid were sealed in Au capsules and placed in the piston-cylinder apparatus (CaF$_2$ assemblies) at 1000 MPa and 900 °C (8 to 25 days) or in cold-seal autoclaves on a hydrothermal line at 500 MPa and 600 °C (23 days). BSE imaging, EMP analysis, and TEM indicate that a fraction of the xenotime grains in the $2N$ KOH, Na$_2$Si$_2$O$_5$ + H$_2$O, and NaF + H$_2$O experiments have altered areas enriched in Th + Si. No reaction was observed in the $2N$ NaOH experiments. The altered areas occur as a series of curvilinear intergrowths with sharp compositional boundaries that extend from the edge of the xenotime grain into the interior. Formation of these Th + Si enriched areas is interpreted as a consequence of fluid-mediated coupled dissolution-reprecipitation.

Keywords: Xenotime, thorite, coupled dissolution-reprecipitation, alkali-bearing fluids

INTRODUCTION

After LREE-bearing monazite \([(Ce,LREE)(PO_4)]\) and fluorapatite \([(Ca,LREE,Na)\_2\_[(P, Si)O_5]_2(F, Cl, OH)]\), HREE-bearing xenotime \([(Y,HREE)(PO_4)]\) is one of the most common orthophosphate minerals in sedimentary, metamorphic, and igneous rocks. Experimental calibration of coexisting monazite and xenotime compositions as a function of temperature has been utilized as a geothermometer in metamorphic rocks (Heinrich et al. 1997; Gratzer and Heinrich 1997, 1998; Andrehs and Heinrich 1998). Concurrently, the Y content in garnet in the presence of coexisting xenotime has been calibrated as an empirical geothermometer for metamorphic rocks (Pyle and Spear 1999, 2000; Pyle et al. 2001).

In the same manner as monazite (Harlov and Hetherington 2010; Harlov et al. 2011), xenotime may incorporate Th and U utilizing the following coupled substitution reactions: $(Th^{4+} + U^{4+}) + Si^{4+} \rightarrow (Y + HREE)^{3+} + P^{5+}$ and $(Th^{4+} + U^{4+}) + Ca^{2+} \rightarrow 2(Y + HREE)^{3+}$. Of the two, the first is considerably predominant over the latter (cf. Förster 1998) indicating that Th and U are generally incorporated as the thorite (ThSiO$_4$) and coffinite (USiO$_4$) components, respectively. Analysis of most natural xenotime indicates that U is generally preferred over Th (cf. Van Emden et al. 1997; Förster 1998, 2006). In contrast, Th is naturally partitioned into monazite over xenotime (Seydoux-Guillaume et al. 2002), although there are some exceptions to this rule (e.g., Hetherington and Harlov 2008). Incorporation of Th and U allows for xenotime to be used as a geochronometer utilizing secondary ion mass spectrometry (SIMS) (McNaughton et al. 1999; Petersson et al. 2001; Vallini et al. 2006; Rasmussen et al. 2004, 2007a, 2007b, 2009), thermal ionization mass spectrometry (TIMS) (Viskupic and Hodges 2001; Tajcmanova et al. 2010), as well as the electron microprobe (Cocherie and Legendre 2007; Hetherington et al. 2008).

Distribution of Th, U, Si, and Ca within xenotime commonly takes the form of magmatic zoning (Hawkins and Bowring 1997; Broska et al. 2005; Schaltegger et al. 2005; Hetherington and Harlov 2008), crystallographic zoning (Kositcin et al. 2003), and/or in the form of complex compositional zoning due to successive overgrowths of xenotime (Petersson et al. 2001; Rasmussen 2005; Vallini et al. 2005). However, once incorporated, there is evidence from nature that xenotime can also be metasomatically altered with regard to its Th and U content resulting in either the addition or removal of Th and U. Removal of Th and U may be accompanied by the formation of thorianite, thorite, and/or coffinite inclusions in the altered areas (Kositcin et al. 2003; Hetherington and Harlov 2008; Crowley et al. 2009). Addition of Th and U normally occurs in variable amounts resulting in patchy, curvilinear intergrowths enriched in ThSiO$_4$ and USiO$_4$. These intergrowths have sharp compositional boundaries and extend from the rim of the xenotime grain rim into the interior (Hawkins and Bowring 1997; Cocherie and Legendre 2007).

To determine how and under what geochemical and $P$-$T$ conditions Th may be incorporated into xenotime, a series of experiments have been performed at amphibolite-facies grade (600 °C and 500 MPa) and granulite-facies grade (900 °C and 1000 MPa) $P$-$T$ utilizing natural, relatively homogeneous 50–300 μm sized grains of a gem quality, Th-poor natural xenotime + ThSiO$_4$ + ThO$_2$ + SiO$_2$ ± Al$_2$O$_3$ in conjunction with a series of alkali-bearing fluids, i.e., $2N$ NaOH, $2N$ KOH, Na$_2$Si$_2$O$_5$ + H$_2$O, and NaF + H$_2$O. Evaluation of the reacted xenotime grains was accomplished using backscattered electron (BSE) imaging,