Redox-controlled dissolution of monazite in fluids and implications for phase stability in the lithosphere

DUSTIN TRAIL\textsuperscript{1,2,*}

\textsuperscript{1}Department of Earth & Environmental Sciences, University of Rochester, Rochester, New York 14627, U.S.A.
\textsuperscript{2}Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, California 90095, U.S.A.

ABSTRACT
Monazite is an important host of rare earth elements in the lithosphere including redox-sensitive Ce, which may occur as trivalent and tetravalent in terrestrial environments. Here, monazite solubility is explored as a function of oxygen fugacity through a series of dissolution experiments in alkali-rich and H\textsubscript{2}O fluids at 925 °C and 1.5 GPa. The oxygen fugacity was controlled with seven different solid-state buffers and ranged from about the iron-wüstite to the magnetite-hematite equilibrium reactions. The solubility of natural monazite increases monotonically at oxygen fugacities equal to or higher than the fayalite-magnetite-quartz equilibrium. Electron microscopy reveals incongruent dissolution at Ni-NiO and above, where Ce-oxide is observed with monazite as a stable phase. Solubility experiments were also conducted with synthetic crystals (CePO\textsubscript{4}, LaPO\textsubscript{4}, and Th+Si-doped monazite). End-member CePO\textsubscript{4} exhibits profound changes to the surface of the crystal under oxidized conditions, with erosion of the crystal surface to depths of \sim 100 \textmu m or greater, coupled with precipitation of Ce-oxide. In contrast, the solubility of LaPO\textsubscript{4} shows no sensitivity to the redox state of the experiment. The addition of Th (~3 wt\%) and Si (~0.3 wt\%) to monazite promotes crystal stability under oxidizing conditions, though small ThO\textsubscript{2}-CeO\textsubscript{2} (5–10 \textmu m) crystals are present on the surfaces of these crystals, whose abundance increases at higher oxygen fugacities. In aggregate, these experiments show that the stability and solubility of monazite is affected by oxygen fugacity, and that the redox state of a fluid may be partially responsible for redistribution of rare earth elements and phosphorus in the crust. Lithospheric fluids with oxygen fugacities at or above the fayalite-magnetite-quartz equilibrium may contribute to some of the complex textures, variable chemistry, and age relationships observed in natural monazite.

Keywords: Monazite, solubility, incongruent dissolution, oxygen fugacity

INTRODUCTION
Monazite is a major host of actinide and light rare earth elements (LREEs) in the crust, and it is of considerable interest in geochronology because it grows over a broad P-T range in metamorphic terrains (Spear and Pyle 2002; Harrison et al. 2002; Kohn and Malloy 2004; Catslo 2013). Thorium oxide (1–10\%) and \sim 1 wt\% UO\textsubscript{2} are common components due to high partition coefficients for actinide elements (Stepanov et al. 2012; Xing et al. 2013), though crystal chemistry can be highly variable even within a single grain (Catslo et al. 2002; Pyle and Spear 2003; Kohn et al. 2004). While monazite is amorphized due to displacive radiation effects, it recovers an ordered structure at relatively low temperatures, and it is therefore generally considered to be resistant to radiation damage (Meldrum et al. 1997, 2000). It is also extremely resistant to diffusive migration of U, Th, and Pb in the lattice, with closure temperatures for these elements approaching 900 °C or higher for 10 \textmu m grains and a cooling rate of 10 °C/Ma (Cherniak et al. 2004; Cherniak and Pyle 2008). These properties make monazite a potential host for nuclear waste disposal (e.g., Ewing and Wang 2002).

Monazite is also utilized as a geothermometer through application of mineral-mineral or mineral-fluid equilibrium reactions. For instance, Pyle et al. (2001) presented trace-element partitioning data for monazite, xenotime, and garnet in prograde pelitic rocks, and showed that Y partitioning between garnet and monazite is related to temperature. Plank et al. (2009) suggested that monazite (and allanite) solubility in hydrous silicic fluids can be used to estimate subduction slab temperatures. Principally, this involves a comparison of the temperature-dependent H\textsubscript{2}O/Ce ratio in fluids and melts in the presence of a LREE-buffering phases derived from 2.5–4.5 GPa experiments (Hermann and Rubatto 2009), with the H\textsubscript{2}O/Ce of mineral melt inclusions from arc magmas (Plank et al. 2009; Ruscitto et al. 2012; Cooper et al. 2012).

Key to the above applications is the P-T-X dependent stability and solubility of monazite. There are numerous studies that have investigated the alteration, stability, and solubility of monazite as a function of P, T, fluid, and/or silicate melt composition (e.g., Ayers and Watson 1991; Poitrasson et al. 1996; Spear and Pyle 2002; Hermann and Rubatto 2009; Klimm et al. 2008; Hetherington et al. 2010; Harlov et al. 2011; Budzyn et al. 2011; Skora and Blundy 2012). Yet, there is no experimental work that has explored the stability and solubility of monazite as a function of oxygen fugacity (f\textsubscript{O2}). The goal of this contribution is to help facilitate the interpretation of monazite geochronol-