Geochronology and trace element mobility in rutile from a Carboniferous syenite pegmatite and the role of halogens

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ABSTRACT

This study investigates Ti mobility in the presence of halogens, as shown by the hydrothermal alteration of magmatic rutile in syenite. The syenite pegmatite studied intrudes gabbro, is preserved as a tectonic block in a major strike-slip fault zone, and formed in a back-arc environment in which there was widespread A-type granite plutonism. Rutile was studied by SEM and Raman spectroscopy, trace elements were analyzed by LA-ICP-MS, and age was determined by in situ U-Pb analysis. Magmatic rutile in the syenite forms millimetric-scale crystals rimmed by magmatic titanite and magnetite and also occurs as smaller interstitial crystals. Hydrothermal alteration occurred preferentially along crystal margins and fractures by a layer-by-layer dissolution-reprecipitation process resulting in high Zr contents (~5000 ppm) in the rutile, together with enrichment in U and depletion in high field strength elements. The magmatic emplacement age of the syenite was ~360 Ma (dated rutile G) and no younger than 353.9 ± 5.7 Ma (mean Concordia age of interstitial rutile). The syenite was synchronous with the later phases of regional A-type granite plutonism. Most magmatic rutile has REE patterns either (1) with 1–50 times chondrite enrichment, LREE > HREE and a Eu anomaly, resulting from felsic melt inclusions, or (2) flat patterns with 0.1–10 times chondrite enrichment, present in ilmenite exsolution lamellae or inclusions. Later hydrothermal halogen-rich fluids, derived from dissolution of halite, produced widespread metasomatic scapolite in the syenite. These fluids also leached Ti and other HFSE, together with REE, from large fractured rutile crystals. Such fluids resulted in local dissolution-reprecipitation of Ti and Zr and resetting of the U-Pb system in the altered rutile, at 337.4 ± 3.5 Ma. Normalized REE abundances in the hydrothermal rutile show a U-shaped pattern, with the greatest depletion in the MREE. Variations in dissolution and transport of Zr and Ti by halogen-rich fluids affect the Zr in rutile geothermometer, which yields unrealistic temperatures when applied in this study. More generally, the complexities of rutile chemistry in this hydrothermal setting could be reproduced in deeper subduction settings as a result of variations in halogen content of fluids released by prograde metamorphism.

Keywords: Rutile, halogens, zirconium, hydrothermal, dissolution-reprecipitation

INTRODUCTION

Rutile is the most common, naturally occurring, polymorph of TiO2. It is a widely distributed accessory mineral in igneous and metamorphic rocks and in mantle xenoliths. It contains the minor elements Fe, Cr, and V, and is a major host for Nb, Ta, and other high field strength elements (HFSE). In amphibolites and eclogites, it can be the major repository of HFSE (Zack et al. 2002; Meinhold 2010), and it is generally accepted as playing a role in HFSE depletion of arc magmas (Ryerson and Watson 1987). Experimental data suggest that rutile favors incorporation of HFSE in the order Ta > Nb > Hf > Zr (Foley et al. 2000, 2002; Klemme et al. 2005).

Rutile is generally thought to be chemically inert with respect to aqueous fluids evolved during prograde metamorphism, and experimental data suggest that the solubility of rutile in pure water is very low (Tropper and Manning 2005; Audetat and Keppler 2005). However, there is a growing body of evidence from natural systems (e.g., John et al. 2011; Spandler et al. 2011), and experimental studies (e.g., Rapp et al. 2010; Hayden and Manning 2011; Tanis et al. 2015) that rutile is increasingly more soluble in halogen-bearing (e.g., F, Cl) aqueous fluids evolved during prograde metamorphism in subduction environments. Slab-derived fluids are not pure water, but instead contain significant amounts of dissolved alkalis (Na, K), halogens (F, Cl), and aluminosilicates (Si, Al) (Manning 2004).

This study investigates rutile hosted by a scapolite-rich syenite pegmatite (Owen and Greenough 1999) preserved as a megablock in a large-scale fault breccia that outcrops in cliffs and foreshore at Clarke Head, Nova Scotia (Donohoe and Wallace 1985, p. 50–53) (Fig. 1b). The fault breccia is part of the core zone of the Carboniferous Minas Fault Zone (MFZ; Murphy...