FLUIDS IN THE CRUST

The mobility of Nb in rutile-saturated NaCl- and NaF-bearing aqueous fluids from 1–6.5 GPa and 300–800 °C†

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ABSTRACT

Rutile (TiO₂) is an important host phase for high field strength elements (HFSE) such as Nb in metamorphic and subduction zone environments. The observed depletion of Nb in arc rocks is often explained by the hypothesis that rutile sequesters HFSE in the subducted slab and overlying sediment, and is chemically inert with respect to aqueous fluids evolved during prograde metamorphism in the forearc to subarc environment. However, field observations of exhumed terranes, and experimental studies, indicate that HFSE may be soluble in complex aqueous fluids at high pressure (i.e., >0.5 GPa) and moderate to high temperature (i.e., >300 °C). In this study, we investigated experimentally the mobility of Nb in NaCl- and NaF-bearing aqueous fluids in equilibrium with Nb-bearing rutile at pressure-temperature conditions applicable to fluid evolution in arc environments. Niobium concentrations in aqueous fluid at rutile saturation were measured directly by using a hydrothermal diamond-anvil cell (HDAC) and synchrotron X-ray fluorescence (SXRF) at 2.1 to 6.5 GPa and 300–500 °C, and indirectly by performing mass loss experiments in a piston-cylinder (PC) apparatus at ~1 GPa and 700–800 °C. The concentration of Nb in a 10 wt% NaCl aqueous fluid increases from 6 to 11 μg/g as temperature increases from 300 to 500 °C, over a pressure range from 2.1 to 2.8 GPa, consistent with a positive temperature dependence. The concentration of Nb in a 20 wt% NaCl aqueous fluid varies from 55 to 150 μg/g at 300 to 500 °C, over a pressure range from 1.8 to 6.4 GPa; however, there is no discernible temperature or pressure dependence. The Nb concentration in a 4 wt% NaF-bearing aqueous fluid increases from 180 to 910 μg/g as temperature increases from 300 to 500 °C over the pressure range 2.1 to 6.5 GPa. The data for the F-bearing fluid indicate that the Nb content of the fluid exhibits a dependence on temperature between 300 and 500 °C at ≥2 GPa, but there is no observed dependence on pressure. Together, the data demonstrate that the hydrothermal mobility of Nb is strongly controlled by the composition of the fluid, consistent with published data for Ti. At all experimental conditions, however, the concentration of Nb in the fluid is always lower than coexisting rutile, consistent with a role for rutile in moderating the Nb budget of arc rocks.

Keywords: High field strength elements, niobium, synchrotron, hydrothermal diamond anvil cell, subduction, rutile, aqueous fluid

INTRODUCTION

Arc magmas bear a characteristic geochemical trace element signature consisting of a depletion of high field strength elements (HFSE) and enrichment in large ion lithophile elements (LILE) and light rare earth elements (LREE) relative to mid-ocean ridge basalts (Gill 1981; Hawkesworth et al. 1991). Three working hypotheses have been developed to explain the geochemical signature of arc magmas. The first hypothesis is that ascending aqueous fluids from the slab are enriched in LILE and LREE, relative to HFSE, and thus transfer this signature to partial melts produced in the mantle. This hypothesis suggests that mineral phases (e.g., clinopyroxene) in the mantle control the HFSE budget of mantle-derived silicate melt (Hawkesworth 1993; Hawkesworth et al. 1993; Kelemen et al. 1990; Foley et al. 2000; Audétat and Keppler 2005). The second hypothesis is that melt extraction from the mantle at a back-arc spreading center depletes the mantle in HFSE prior to its interaction with slab-derived fluid