

FLUIDS IN THE CRUST

Constraints on the mobilization of Zr in magmatic-hydrothermal processes in subduction zones from in situ fluid-melt partitioning experiments‡

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ABSTRACT

The partitioning of Zr between high P - T aqueous fluids and melts has been investigated in situ in the haplogranite-H₂O and haplogranite-(F)-H₂O systems to assess the mobilization of high field strength elements (HFSE) in magmatic-hydrothermal processes in subduction zones. The partition coefficients $D_{Zr}^{f/m}$ were determined from Zr concentrations measured in situ by synchrotron X-ray fluorescence (SXRF) in both aqueous fluids and F-free or F-bearing hydrous haplogranite melts equilibrated in diamond-anvil cells at 575 to 800 °C and 0.3 to 2.4 GPa. This experimental approach eliminates the need for internal or external calibrations of the SXRF signal and/or *post-mortem* analysis of the melt phase, hence decreasing the total uncertainties on $D_{Zr}^{f/m}$ below 16%. Above 0.6 GPa, Zr partitions favorably into the hydrous silicate melt in both F-free and F-bearing systems, with $D_{Zr}^{f/m}$ that range between 0.19 ± 0.02 and 0.38 ± 0.03 . However, the relatively high $D_{Zr}^{f/m}$ values indicate that alkali-silica rich aqueous fluids generated by metamorphic devolatilization may contribute significantly to the recycling of HFSE in subduction zones. The efficient uptake of Zr (and likely other HFSE) by subduction zone fluids, regardless of their nature (aqueous fluid, hydrous melt, or supercritical fluid), supports the idea that the typical HFSE depletion recorded in arc magmas does not result from their incompatibility in water-rich slab-derived fluids but most probably originates from complex fluid-melt-rock interactions occurring at the slab interface and within the mantle wedge. At shallow crustal pressure conditions (800 °C and 0.3 GPa), Zr partitions reversely into the aqueous fluid in the presence of fluorine ($D_{Zr}^{f/m} = 1.40 \pm 0.10$) as observed for Nb at similar conditions by Webster et al. (1989). The enrichment of the aqueous phase in HFSE (Zr, Nb) at shallow crustal conditions is likely related to the enhanced peralkalinity of low pressure, F-bearing aqueous fluid with temperature, that provides the favorable conditions for their mobilization via the formation of HFSE-O-Si/Na clusters. This mechanism may control the enrichment in HFSE (and plausibly other rare metals such as REE) in early magmatic fluids exsolved from granitic melts, leading to the formation of HFSE-enriched aggregates in shallow magmatic-hydrothermal environments (e.g., Strange Lake and Thor Lake Nechalacho deposit, Canada; Galineiro complex, Spain).

Keywords: Zirconium, HFSE, fluid-melt partition coefficients, SXRF, subduction zones, rare metal deposits