Trace Element Mobility in Metamict and Altered Zircon from Late-stage Granophyres in the Stillwater Complex

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Zircon ($ZrSiO_4$) can be used to precisely date igneous events by U-Th-Pb geochronology and to simultaneously investigate the petrologic (Ti-in-zircon thermometry), geochemical (trace elements), and isotopic (O, Hf, Nd, Li) evolution of igneous rocks spanning a wide range of composition. In this study, the consequences of elemental redistribution during hydrothermal alteration of metamict zircon from granophyres in the Stillwater Complex have been investigated using laser ablation-ICP-MS. The 2.7 Ga Stillwater Complex, an 8 km-thick mafic-ultramafic layered intrusion in southwestern Montana that is host to a world-class platinum group element deposit (J-M Reef), contains a suite of discordant granophyres that represent late-stage magmatic differentiates. U-Th-Pb geochronology of accessory minerals (zircon, titanite, rutile) from the granophyres yield similar ages to the mafic cumulates (ca. 2709-2712 Ma) only for low-U minerals that have remained closed since crystallization. A 2709 Ma granitic pegmatite core from the Lower Banded Series, ~400 m beneath the J-M Reef, contains pristine igneous low-U zircon (37-154 ppm; Th/U = 0.75) with simple oscillatory zoning, low Hf (average 8519 ppm), a limited range of Ti (6-17 ppm), low HFSE (<1 ppm Ta, <2 ppm Nb), variable Li (0.5-23 ppm), and no measurable Ca. The granophyre contains coexisting zircon, rutile, and quartz with Ti-in-zircon thermometry results ranging from 701 to 799°C (average = 752°C). In contrast, samples from the Middle Banded Series and Upper Banded Series, bracketing the hydrothermal Picket Pin PGE deposit, contain high-U zircon (358-12,440 ppm; Th/U = 0.01 to 1) that is partially to completely metamict recording open-system U-Pb systematics during subsequent hydrothermal activity. Non-stoichiometric Ca (up to 37,800 ppm) characterizes the metamict zones or grains, which also show significant gains in Ti (up to 268 ppm), Nb (up to 93 ppm), light rare earth elements, and nearly complete loss of Li in the most altered zircon with a strong negative correlation between added Ca and lost Li. Abundant micrometer-scale pores are present in zircon from the most altered granophyres. Changes in elemental concentrations in zircon from the Stillwater granophyres during interaction with hydrothermal fluids appear to require a combination of processes, including (1) diffusion-reaction where elements such as U, Ca, Li, Zr, Th, and REE are exchanged at grain boundaries in contact with aqueous fluids following extensive metamictization, and (2) dissolution-reprecipitation producing the micro-porous structure.