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Hf and Ti zoning in zircons: detailed records of magmatic processes

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As a consequence of its refractory nature and very low elemental diffusivity, zircon is well known as an extraordinarily robust geochronometer. These same characteristics present intriguing potential for use of elemental zoning in zircon as a record of evolving magmatic environments. Recent work has demonstrated that Ti concentration in zircon is temperature sensitive and can be used for quantitative thermometry (Watson & Harrison, 2005). We demonstrate that Ti and Hf zoning taken together yield a record of T and melt fractionation history: combining these data with sufficiently precise *in situ* geochronology promises to provide quantitative constraints on timing and rates of fractionation and of T fluctuations.

As zircon is the dominant reservoir for both Zr and Hf, crystallization of zircon controls Zr/Hf of the coexisting melt. As zircons crystallize, incorporating Zr preferentially over Hf, the Zr/Hf of the surrounding melt is reduced. If efficient fractional crystallization occurs and the zircon is removed from the melt, a low Zr/Hf is preserved in the remaining melt, in zircon that grows from that melt, and in rocks that form from that melt. Thus, high-silica rhyolites and aplites typically have Zr/Hf well below chondritic ratios of 35-40 (Lowery et al., in review). Zircon that grows from fractionating melt should be zoned toward higher Hf, whereas zircon that is transferred from one melt to another or that resides in melt that is heated may show reversals in the zoning pattern. Zoning visible in CL and BSE images corresponds to Hf content, and thus imaging provides a qualititative record of fractionation history.

As an example of the application of Ti-Hf zoning studies, we have used the USGS/Stanford SHRIMP to measure elemental concentrations in zircons from the Miocene Spirit Mountain batholith, Nevada. Whole-rock elemental chemistry of rocks ranging from felsic cumulates to leucogranites and aplites demonstrates fractionation,

and SHRIMP geochronology and field relations document repeated recharging and melt segregation events (Walker et al., in review). Ratios of Zr/Hf are ~30-40 for cumulates and 18-30 for high-SiO_2 granites. In zircons, Hf, U and Th show a tight inverse correlation with Ti,and concentrations indicate large fluctuations in melt composition and T_{TiZ} (>100^o C) for individual zircons. The preservation of robust variations in Ti zoning and the consistently negative correlation with Hf, U, and Th suggest that these elements, including Ti, are not diffusively exchanged within the zircon. Such variations support field relations and SHRIMP zircon geochronology that indicate a million years of repeated replenishment, fractionation, and extraction of melt from crystal mush.

Hf-Ti (and U, Th) zoning studies can provide a uniquely detailed record of complex histories of the magmas from which zircons grow. *In situ* analysis by SHRIMP can provide valuable constraints on timing and rates of these processes, but, due to limited resolution (10^5 yr), it probably cannot define the detailed history recorded by Hf-Ti zoning. *In situ* U-series dating, and Hf-Ti-U series analyses, however, has a potentially much higher resolution and may elucidate pre-eruptive events and true timescales of magmatic processes.