

Experimental constraints on Zr stable isotope fractionation during magmatic zircon crystallization

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Zirconium (Zr) belongs to a group of transition metals known as the High Field Strength Elements (HFSE), which due to their distinctive geochemical properties are used to trace magmatic differentiation and the co-evolution of Earth's mantle and crust [e.g., 1, 2]. Although mass-independent isotopic variations of Zr have been extensively studied [e.g., 3, 4], only recently have mass-dependent variations been explored [e.g., 5, 6, 7, 8]. These investigations have hypothesized that magmatic zircon crystallization can drive equilibrium stable isotope fractionation given that Zr⁴⁺ undergoes a shift in coordination state (from 6- to 8-fold) as zircon precipitates from a silicic melt. Although Zr isotope measurements from natural systems have confirmed significant $\delta \epsilon^{94/90}\text{Zr}$ variability, *ab initio* calculations predict negligible equilibrium fractionation between zircon and melt at magmatic temperatures, and therefore the exact mechanism(s) fractionating Zr stable isotopes remain unclear [9, 10]. To resolve this debate, we determined isotopic fractionation coefficients between zircon and silicic melt ($\alpha_{\text{zircon-melt}}$) as a function of temperature and melt composition using controlled zircon-growth experiments. We show that experimental values are in good agreement with *ab initio* predictions, and therefore the observed range of natural variability in most systems cannot be explained by equilibrium isotope fractionation during zircon crystallization.

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