

Sub-nanometer resolution of zirconium isotopes in zircon and baddeleyite by Atom Probe Tomography

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The mechanisms behind zirconium isotope fractionation in igneous systems at the atomic scale are actively debated. At magmatic temperatures, the equilibrium fractionation of Zr between zircon and melt determined by *ab initio* calculations and zircon growth experimental studies is small ($\Delta^{94/90}\text{Zr}$ zircon-melt ~ 0.05 ‰ [1, 2]). However, several studies have documented significant mass-dependent variability in natural systems, which would require much larger fractionation factors with $\Delta^{94/90}\text{Zr}$ zircon-melt values up to +1.0 ‰ [3]. Recent theoretical calculations [4] as well as zircon-growth experimental studies have suggested that these large fractionations must be driven by kinetic processes occurring at the liquid-solid interface [2]. To evaluate these nanoscale processes, we employ Atom Probe Tomography (APT) that utilizes point-projection Time-of-Flight (TOF) mass spectrometry to provide isotopic compositions of mineral samples with volumes on the order of $<0.02 \mu\text{m}^3$. In this study, we analyzed 12 samples by APT, including zircon samples from the Mud Tank carbonatite (MTUR1 crystal; [5]), as well as baddeleyite samples from the Duluth Gabbro (FC-1) and the Kovdor carbonatite. The bulk Zr isotope composition of the Mud Tank zircon has been well established [2,5], and as part of this study we provide new reference $^{94/90}\text{Zr}$ values for baddeleyite crystals studied by APT. The foremost challenge for determining Zr isotope compositions from APT is assigning a background correction model to the TOF spectra. To evaluate the best method for reproducibly determining isotopic ratios via APT, we employ multiple background correction models and use different Zr±O species identified from the TOF spectra. The ability to quantify isotope ratios using APT is significant for our ability to identify mechanisms driving isotopic variations and mineral-melt isotope partitioning at the atomic scale.

[1] Méheut et al., 2021. *Geochimica et Cosmochimica Acta* 292, 217-234.

[2] Tompkins et al., 2023. *Geochemical Perspective Letters* 25.

[3] Ibañez-Mejía and Tissot, 2019. *Science Advances* 5, 1-14.

[4] Bindeman and Melnik, 2022. *Geochemical Perspective Letters* 24.

[5] Tompkins et al., 2020. *J. Anal. At. Spectrom.* 35.