

Are Hadean & Archean Zircon $\delta^{18}\text{O}$ Values Altered?

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Crystalline zircon provides a robust record of $\delta^{18}\text{O}$ in parent magmas that have important implications for evolution of Hadean and younger crust. However, radiation damage causes amorphous domains and, depending on alpha-dose and annealing, facilitates alteration. If unannealed, amorphous domains accumulate, leading to various chemical and physical changes, including hydration, volume increase and faster rates of exchange/alteration. The $\delta^{18}\text{O}$ of altered zircon can be either higher or lower than primary magmatic values depending on temperature of alteration and $\delta^{18}\text{O}$ of ambient fluids. *In situ* analyses coupled with careful imaging make it possible to identify and avoid altered domains. Oxygen isotope studies should explicitly describe steps taken to avoid altered domains in zircon.

This study expands on existing data (Cavosie et al. 2006 GCA; Cameron et al. 2017 GSA Abst), and presents the first comprehensive evaluation of spatially correlated $\delta^{18}\text{O}$, CL, U-Pb, OH/O and radiation-damage state within the Jack Hills zircons. In situ laser-Raman data (900 spots on 128 Hadean and 60 Archean zircons) show limited 1008 cm^{-1} band shift or broadening, and thus document low levels of radiation damage and significant annealing; the present-day effective doses ($D(\text{eff})$) are uniformly less than the first percolation point and most zircons have $D(\text{eff}) < 1 \times 10^{15}$ alpha-decays/mg. There is no correlation in this suite of Hadean zircons between $\delta^{18}\text{O}$ and OH/O, $D(\text{eff})$, age, or U-Pb age-concordance (>85% concordant). Most zircons have <0.1wt% H_2O . Selected subsets of these Hadean zircons have been studied in detail for nm-scale Pb+REE clusters by Atom Probe (Valley et al. 2015 Am. Min.) and crystallinity. Fifteen Hadean zircons mapped by EBSD are dominantly highly crystalline as measured by EBSD pattern quality (band contrast). Local areas of diminished band contrast are typically correlated to discrete actinide-rich growth zones that are avoided during in situ analysis.

These well documented Hadean-age zircons preserve mildly elevated $\delta^{18}\text{O}$ values that are a primary-magmatic supracrustal signature. These results strengthen previous conclusions (Valley et al. 2002 Geology) that mildly elevated- $\delta^{18}\text{O}$ magmas existed during the Hadean, supporting the hypothesis that oceans, hydrous crust and a habitable Earth existed before 4300 Ma.

