

# The oxidation state of uranium in zircon from U M<sub>4</sub>-edge X-ray absorption spectroscopy

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Zircons are the oldest known terrestrial materials and one of the most important minerals for investigating Earth's history. Their physical and chemical resilience combined with the slow rates of volume diffusion for most elements allow them to retain their primary elemental and isotopic composition through weathering, diagenesis, and metamorphism on billion-year timescales. This durability has resulted in the zircon record being one of the most complete archives of Earth's evolution. Many methods for interrogating zircon exist, however it is prudent to develop new methods for extracting as much information as possible from these time capsules if Earth's history is to be fully explored.

We conducted X-ray absorption spectroscopy (XAS) at the U M<sub>4</sub>-edge on a set of well-characterized zircon samples, representing a range of magmatic conditions, to assess how U oxidation varies with key parameters such as magma composition, temperature, and oxygen fugacity. The position of the white line in an XAS spectrum is sensitive to the oxidation state of the element being interrogated, with higher oxidation states shifting the peak to higher energies. Results from our study show a range in white line position of ~1.5 eV indicating that U of variable valence can be incorporated into the zircon structure. This difference in energy is similar to that observed between U<sup>IV</sup> and U<sup>V</sup> in a recent study of U redox during magnetite precipitation [1]. Furthermore, we observe a ~1.25 eV difference between samples of known oxygen fugacity (FC-1:  $\Delta\text{FMQ} \sim 0$ , Fish Canyon tuff:  $\Delta\text{FMQ} \sim +2-3$ ), suggesting that a correlation exists between the energy where peak absorbance occurs (i.e. the relative proportion of U<sup>IV</sup> and U<sup>V</sup>) and the  $\text{A}^{\prime}\text{O}_2$  of the crystallizing magma. Beyond the potential for U oxidation state in zircon as a tracer of magma redox, these results have implications for the observed fractionation of U isotopes between coexisting zircon and other U-bearing igneous accessory phases (e.g titanite, apatite) [2; 3].

[1] Pan et al. (2022) *EST*; [2] Hiess et al. (2012), *Science*; [3] Tissot et al. (2019), *JAAS*