2994
doi:10.1017/S1431927620023454
Microsc. Microanal. 26 (Suppl 2), 2020

Application of SIMS and APT to Understand Scale Dependent U-Pb Isotope Behavior in Zircon

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For several decades, secondary ion mass spectrometry (SIMS) has provided the highest resolution for *in situ* measurement of isotope ratios and trace elements in minerals. One of the most common applications continues to be the analysis of zircon grains [1]; zircon is a common accessory mineral, and U-Th-Pb isotope ratios have long been considered one of the most accurate and precise methods for determining zircon crystallization ages, and by extension, constraining the timing of geologic events and processes. The proliferation of zircon age data has also reinforced the complexities encountered in understanding and interpreting U-Th-Pb ratios and their temporal (age) significance. Comparison of $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ isotope ratios (representative of the two independent decay chains) offer independent checks on the presence/absence of open-system behavior at the grain-scale (i.e. concordance and discordance) for zircon age determinations. While zircon is capable of preserving primary chemical information over billions of years, discordance and Pb loss, which alter the inferred age, are relatively common features, often associated with radiation damage accumulation from the U and Th α-decay chains [2]. Despite a long history of research, the nanoscale controls on Pb mobility and Pb loss remain poorly defined.

Recently, atom probe tomography (APT) has enabled analysis of trace elements and isotope ratios with sub-nanometer spatial resolution and detection limits of ~10 ppma [3]. This approach has documented the presence of nanoscale domains enriched in trace components, including radiogenic Pb [4,5]. The use of both SIMS and APT enables measurement of isotope ratios across nine orders of magnitude (by volume), and in doing so, provides a unique means to correlate age and composition between micron-scale growth textures and compositional zoning, and diffusion, radiation damage and annealing processes at the nanoscale. The workflow associated with correlative SIMS and APT, includes careful pre-analysis imaging and structural characterization, including SE, BSE & CL imaging, EBSD, and confocal Raman spectroscopy to identify internal growth domains, as well as evidence of alteration and deformation microstructures. This workflow enables careful placement of SIMS U-Pb, as well as site-specific sampling of relevant domains and/or microstructural features for APT analysis.

The observation of nanoscale clusters of Pb + REEs, and measurement of isotope ratios within them, has determined that (1) the formation of trace element rich clusters is a secondary process requiring the migration of Pb into structural sinks (such as amorphous domains caused by α-recoil), and (2) the $^{207}Pb/^{206}Pb$ ratios within these clusters have been preserved since cluster formation. Notable examples of this behavior include: (1) a 4.4 Ga zircon from the Jack Hills, Australia, where clustering is linked to re-entrainment of the grain in a magma at 3.4 Ga [4]; (2) a 3.8 Ga zircon from the Beartooth Mountains, having Pb-rich clusters formed during regional magmatism at ~2.8 Ga [5]; (3) a 4.4 Ga lunar zircon collected during Apollo 17, having Pb-rich clusters associated with the Serenitatis basin forming impact [6]. The observation that clusters form during secondary episodes, do not intrinsically disturb micron scale U-Pb concordance, and are subsequently preserved over billions of years, is of particular interest to the geochronology community. The immobilization of radiogenic Pb within nanoclusters requires more complex models in order to predict isotopic shifts during post-clustering Pb loss. The new MDEM (multi-

domain element (Pb) mobility) model predicts Pb-loss trajectories on concordia diagrams with systematic offsets for discordia as a function of the zircon crystallization age, the timing of cluster formation, and the timing of Pb mobility. These results explain formerly enigmatic discordia. The combination of SIMS and APT represent the most accurate and precise means to study trace element and isotope systematics between the micro and nanoscale and has unique applications in understanding cryptic records preserved in ancient mineral grains.

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https://doi.org/10.1017/S1431927620023454 Published online by Cambridge University Press