Radiation Damage, APT and Pb mobility in Zircon: The Good, the Bad, and the Ugly

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The mobility of radiogenic Pb in geochronology minerals such as zircon has been a concern in U-Th-Pb dating for over a century and potentially causes erroneous ages to be old or young. Many tests are applied that correlate to age fidelity to identify "good" zircon domains including: imaging by SEM (CL, BSE), TEM & SIMS; EBSD; XRD; calculated α-dose; Raman spectroscopy; birefringence; U-Pb concordance; trace elements; water content; $\delta^{18}O$; acid solubility; magnetism; density; microcracks; and, most recently, APT. Atom-Probe Tomography (APT) measures the X,Y,Z position and mass/charge of individual atoms in 100-nm-scale samples; the technique is capable of spatial precision ±0.3 nm, MRP ~1000, MDL ~10 ppm, and a useful ion yield of ~50%. No other technique measures atom-scale Pb mobility. Although molecular interferences make spectra complex and analysis of some elements is difficult, peaks for $^{207}Pb^{2+}$ and $^{206}Pb^{2+}$ appear clean in zircon and have yielded accurate model Pb ages from as few as 1400 atoms of Pb [1]. "Good" zircons that are well behaved at the micron scale are found by APT to either have homogeneously distributed Pb atoms or isolated nm-scale clusters of radiogenic Pb. These clusters are interpreted to result from migration of non-formula-unit elements into isolated (i.e. below the first percolation point) amorphous domains caused by α-recoil. Pb mobility at the nm-scale is homogenized and has no affect on compositions measured at µm-scale by SIMS, ICPMS or TIMS. In contrast, migration distances can be longer and retentivity should be questioned in zircons (or sub-grain domains) that experienced higher degrees of radiation damage, ductile deformation or UHT (>900 C) metamorphism; such grains may be badly altered and unfit for geochronology, trace elements or stable isotope analysis. The ability to track intracrystalline element and isotope mobility at single-atom scale provides a new tool for studying thermal and fluid history of good zircons, and can add confidence to macroscopic tests that correlate to geochemical fidelity. More generally, APT can provide fundamental new insight for many solids including bad and ugly zircons.

[1] Valley et al. (2015) *Am. Min.* **100**, 1355-1377.