

## Going small: nanoscale geochronology using atom probe tomography

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Abstract - Leaps forward in analytical technology often stimulate major discoveries in geochemistry. In some cases, the improvements are in sensitivity and precision. For example, recent measurements of minute variations in  $^{142}\text{Nd}$ ,  $^{182}\text{W}$  and U-series (to name a few) have revolutionized our understanding of terrestrial and planetary geochemical evolution. In other cases, the improvements are in the spatial scale of the analysis. Isotopic analysis of individual melt inclusions, single shell layers in mollusks and zoning layers in zircons, all have provided fundamental insights into geologic processes. Historically, whenever we look more closely at the composition of materials, we find unexpected features. These variations often are mystifying at first (see all of the above) and often somewhat unwelcome (too much information!). But it is precisely such new, headache-producing details that provide new insights into geological processes. On page ???, Valley and co-workers use a promising new analytical method called atom probe tomography (APT) to analyze one of the oldest materials on the planet (Jack Hills zircons; (Valley et al., 2014; Wilde et al., 2001)). APT has a unique combination of spatial and geochemical analytical capabilities, which Valley et al use to confirm the Hadean age of the zircons, and to gain new insights into their thermochronologic history. This is one of the first geochemical studies to use APT, and offers an early glimpse of future research paths.

What differentiates APT is its ability to quantify ppm-level concentrations of isotopes at the same time as it records the position of the atoms with sub-nm spatial resolution in three dimensions. It is the combination of trace element analytical capabilities with TEM-

like spatial resolution that makes APT unique. A number of excellent reviews on the method have been written in the materials science literature (Blavette et al., 2008; Kelly and Larson, 2012; Seidman, 2007).

Most micro-analytical methods strike the sample with a beam of some sort (electrons, photons, ions, protons...) and measure what is emitted (X-rays, electrons, sample ions, recoiled ions...). In APT, it is the sample that is turned into the beam. This is achieved by shaping the sample into an extremely fine needle, generally 1 micron tall and 100 nm in diameter (Thompson et al., 2007). Once the sample is inside the APT device, a combination of a high electric field and a femto-second laser is used to 'evaporate' atoms off the tip of the needle, ideally one-by-one. A large 2D detector records both where on the needle tip the atom came from and how long it took the ion to get from the tip to the detector (Blavette et al., 2008; Kelly and Larson, 2012; Seidman, 2007).

The spatial information is used to reconstruct the position of the atoms in three dimensions, typically to nm-scale spatial resolutions; sometimes better. The timing information is used to determine the mass/charge ratio of the ion (time-of-flight mass spectrometry). Around 60% of the evaporated atoms are detected. Detection limits are at the ppm concentration level. The end result is a three-dimensional image of the sample in which nearly two thirds of the atoms are located and identified. This comes close to being the 'ultimate analysis', in which the location and identity of every atom in a sample is known (Miller et al., 2012). In some ways, it is like the first part of a Star Trek transporter in which the sample is completely evaporated and transferred to a computer. All that is needed is an atomic-scale 3D printer and the sample could be reconstructed at another location! At this point, typical analytical volumes are 1000's of cubic nm. So don't cancel your frequent flier membership just yet.

APT has existed in some form for many years, but was limited to analysis of metals because the high electric fields destroyed non-conductors. The recent addition of a laser to the ablation process allows lower fields to be used, permitting semi-conductors and insulators to be analyzed (Blavette et al., 2008; Kelly and Larson, 2012; Seidman, 2007). The result is that most geologic materials can now be analyzed.

What is new in the Valley et al paper is not the great age of the zircons. That has been known from SIMS analysis for over a decade (Cavosie et al., 2005; Harrison, 2009; Wilde et al., 2001). Rather, it is what APT reveals about the subsequent history of the zircons that points to new ways of interrogating geomaterials. In some of the zircon crystals, Pb, Y and rare earth elements are found in clusters, typically 100 atoms or so. While in other samples, there are no such clusters. Why is this? What does this reveal about the history of the zircons? Can the SIMS 'bulk' analysis be trusted if they are analyzing such chemically and isotopically mottled material? This is what happens when you look closer at materials (some might say too close!). New questions, and hopefully answers, are created.

Valley and co-workers argue convincingly that the clustering is formed by incompatible trace elements diffusing into radiation damaged areas of the zircons. Such damage is removed by heating (annealing). This allows Valley et al to use their presence, and the age of the clusters calculated from U-Pb isotope ratios, to make thermochronologic reconstructions of nm-sized regions of their zircons! A remarkable result. To my knowledge, it is the smallest chemical object or feature to ever be radiometrically dated. The results confirm the ages determined by the SIMS analysis (Valley et al., 2014; Wilde et al., 2001).

The paper demonstrates how APT allows (forces!) one to merge geochemistry with mineralogy. Lattice features such as point defects, grain boundaries and dislocations are generally the preserve of rock mechanics and mineral physics, and are studied in relation to the physical properties of materials. However, such features will also fractionate elements and isotopes. This is well known in materials science, and has even been imaged in synthetic metals with early versions of APT (Blavette et al., 1999; Cadel et al., 2003). Much less work has been done in geoscience, in large part because no analytical method could see trace element variations at such small spatial scales (though see Ando et al (2001) for a study of major-element enrichment on dislocations in olivine). APT fills in this analytical gap and, if history is any guide, should stimulate a range of new discoveries.

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