Geological Applications of Atom Probe Tomography
LEAP® Analysis of a 4.4 Billion Year Old Zircon

Application Note #APT-05

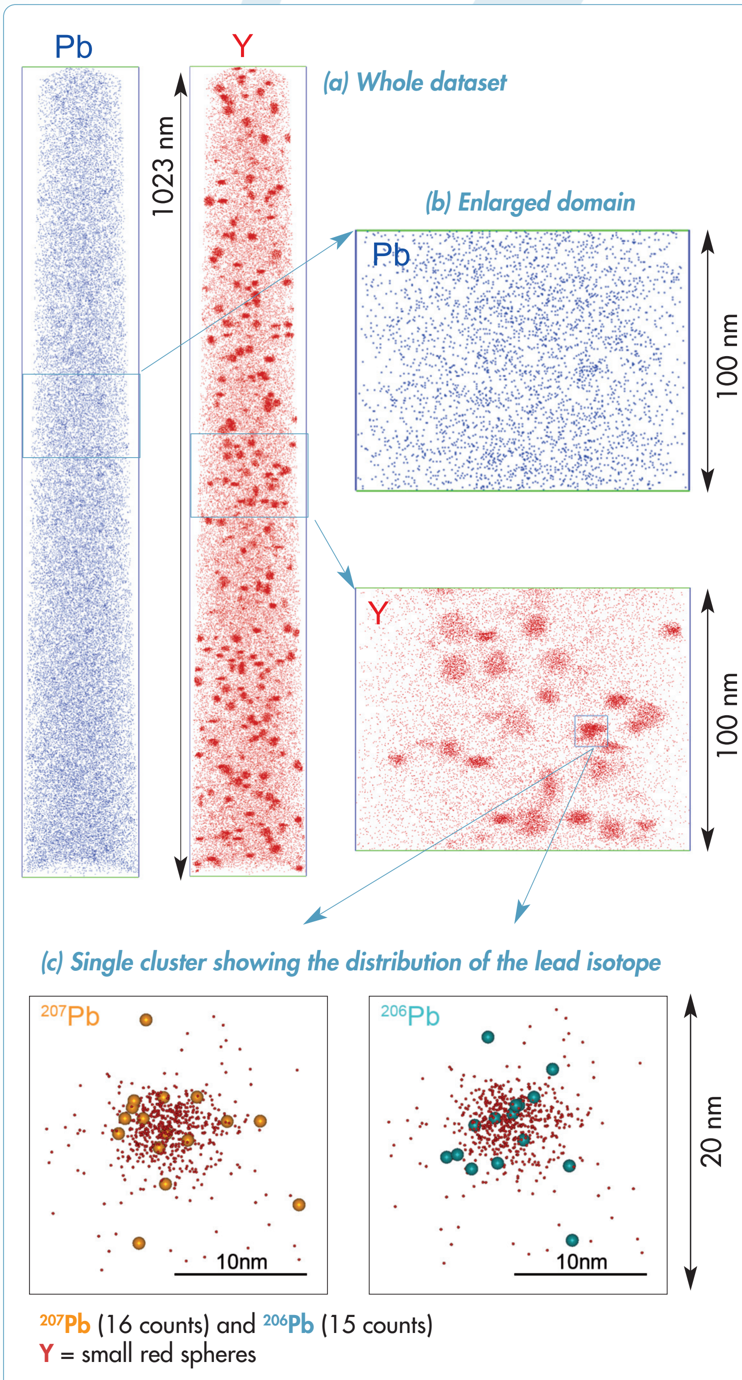
Atom Probe Tomography (APT) is a powerful and promising elemental and isotopic analysis technique for the nanoscale characterization of geological and extraterrestrial materials.

The only physical evidence from the earliest phases of Earth's evolution comes from zircons, ancient mineral grains that can be dated using the U–Th–Pb geochronometer. Unfortunately, the accuracy of the zircon ages can be biased by poorly understood processes of intracrystalline Pb mobility.

In a recent study by J. Valley et al., APT was used to identify and map individual atoms in the oldest known intact mineral grain from Earth, a 4.4-Gyr-old Hadean zircon with a high-temperature overgrowth that formed about 1Gyr after the mineral's core. The analysis showed for the first time that isolated nanoclusters, measuring about 10nm and spaced 10–50nm apart, are enriched in incompatible elements including radiogenic Pb with unusually high $^{207}Pb/^{206}Pb$ ratios.

The enrichment confirms that the length scales of these clusters make U–Pb age biasing impossible, and that they formed during the later reheating event. The APT data thereby confirm that any mixing event must have occurred before 4.4Gyr ago, consistent with a magma ocean formation by an early moon-forming impact about 4.5Gyr ago.

APT technology provided unique nanoscale lead isotopic ratio analysis. This groundbreaking work demonstrates how advanced microscopies like APT not only can provide understanding of the physical properties of materials but also contribute to the interpretation of historical events in unexpected ways. This nanoscale chemical length analysis has provided insight into gigascale geological events.



APT images of clusters in the 4.4-Gyr old zircon:

(a) co-localized Y and Pb clusters from the same 1,000 nm long segment.

(b) enlarged view of a 100nm region from the whole dataset. Upon initial inspection, the Pb appears uniform, but statistical methods show a strong correlation to the yttrium rich clusters.

(c) distribution of ^{89}Y and ^{206}Pb and ^{207}Pb atoms. The volume shown measures 20x20 nm in the plane of the image by 10 nm deep and demonstrates that strong correlation of the Pb isotopes to the yttrium clusters.

Adapted from J. Valley et al. Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. Nature Geoscience 219 (2014).

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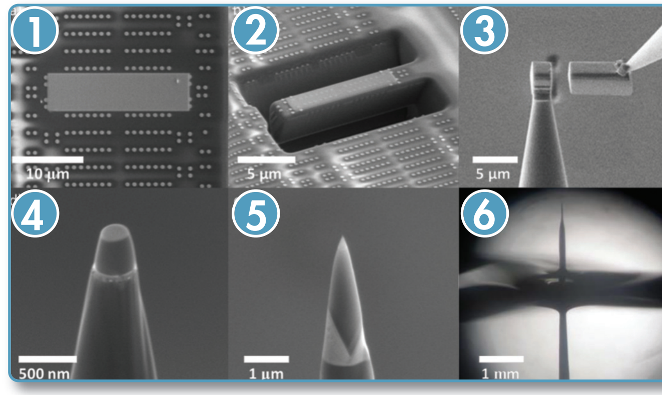
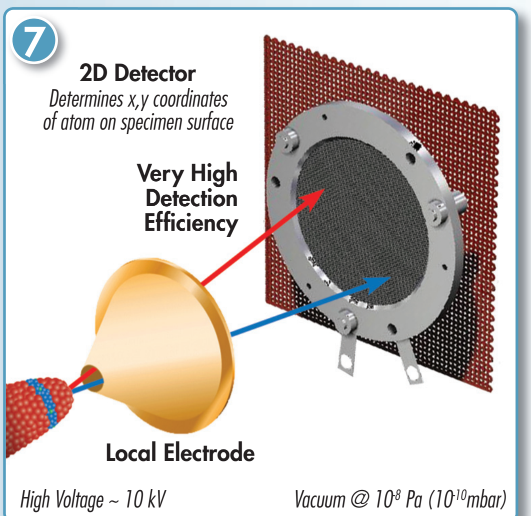
AMETEK® MATERIALS ANALYSIS DIVISION

Three Steps to 3D Nanoscale Analysis
An Introduction to Atom Probe Tomography

Step 1: Specimen Preparation

An atom probe specimen usually has a nanoscale region of interest (ROI) requiring both 3D compositional imaging and analysis. The sample is formed into a needle shape containing the ROI. Common APT specimen preparation methods using electropolishing or a Focused Ion Beam system (FIB) are very similar to TEM methods except instead of forming a thin sheet, a needle shaped sample is desired. At the right, standard FIB liftout and mounting of a specimen (figures 1 through 3) and then sharpening the sample with the ROI left at the very apex (4 and 5). In 6, a wire geometry sample is being electropolished.





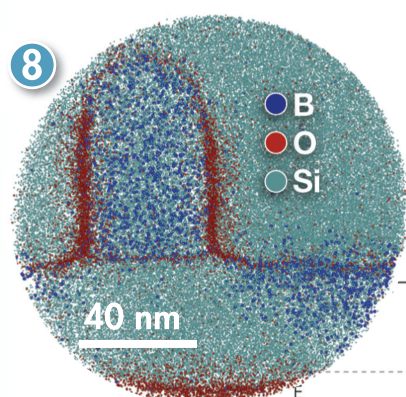
Step 2: Data Collection

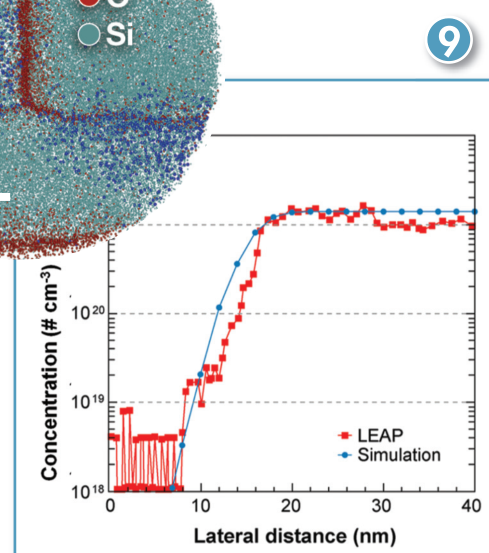
An atom probe produces images by field evaporating atoms from a needle-shaped specimen and projecting the resultant ions onto a detector 7.

A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately 10^6.

An atom probe identifies atoms by their mass-to-charge-state ratio *(m/n)* using time-of-flight mass spectrometry. Charge state, *n*, is typically 1 to 3.

The specimen is held at approximately 50K to reduce surface diffusion during the experiment. The high electric field results in 100% ionization and the high speed detector is capable of measuring up to 80% of the collected ions, independent of ion mass.





Step 3: Data Visualization and Analysis

Examples of data output are illustrated by a slice of a 3D atom map of a transistor† 8, and a dopant composition profile‡ 9. The image shows the positions of individual atoms (oxygen is red and boron is blue) in the transistor with subnanometer resolution. From the reconstructed data set many types of useful analyses are possible. These include 3D visualization, 2D atom mapping 8, 1D depth profiling and line scanning 9, as well as mass spectra and compositional analysis from user-selected volumes.

† *Lauhon, L. J. et al, MRS Bulletin "Atom Probe Tomography of Semiconductor Materials and Device Structures" 34(10) (2009) 738.*

‡ *Moore, J. S.; Jones, K. S.; Kennel, H.; Corcoran, S., Ultramicroscopy "3-D Analysis of Semiconductor Dopant Distributions in a Patterned Structure using LEAP" (2008), 108, 536–539.*