Nanogeochronology by Atom Probe Tomography

Isotopic quantification of Pb-bearing nanocrystals (galena) in monazite

Accessory minerals such as zircon and monazite are widely used in Earth and Planetary Sciences to understand the timing and rate of geological processes. One of the most popular methods for dating ancient rocks is based on the radioactive decay of uranium (U) and thorium (Th) into different isotopes of lead (Pb) within monazite crystals ($CePO_4$). Unfortunately, minerals are affected by physical and chemical processes that promote decoupled mobility of parent (U, Th) and daughter (Pb) elements increasing the uncertainty of this dating method. The mechanisms of U, Th and Pb mobility within monazite may leave traces only detectable at the nanometer scale.

Precambrian rocks from the Napier Complex (Antarctica) have a geological history spanning multiple thermal events and are ideal for identifying the causes of U-Th-Pb disturbances in minerals. Napier Complex monazite crystals containing nanoinclusions of galena (PbS) were analyzed by atom probe tomography at Curtin University (Perth, Australia); the reconstructed data are shown in Figure 1. By using atom probe tomography, both the $^{207}Pb/^{206}Pb$ isotopic ratios in galena and the $^{208}Pb/^{232}Th$ ratio in the host monazite have been quantified separately. These analyses revealed that the isotopic composition of the two minerals is consistent with two events of Pb mobility with partial retention of radiogenic Pb within nanocrystals of the galena. These events are dated at 1 billion and 500 million years, and reflect large-scale geological events at these times [1]. Importantly, these nanoscale traces of isotopic disturbance are hidden at the microscale meaning previous studies produced erroneous dates.

These results have significant implications for the geoscience community by increasing our knowledge of element mobility in minerals used for dating geological events. Atom probe tomography provides a major advance in the understanding of such mechanisms and for the development of nano-geochronology.

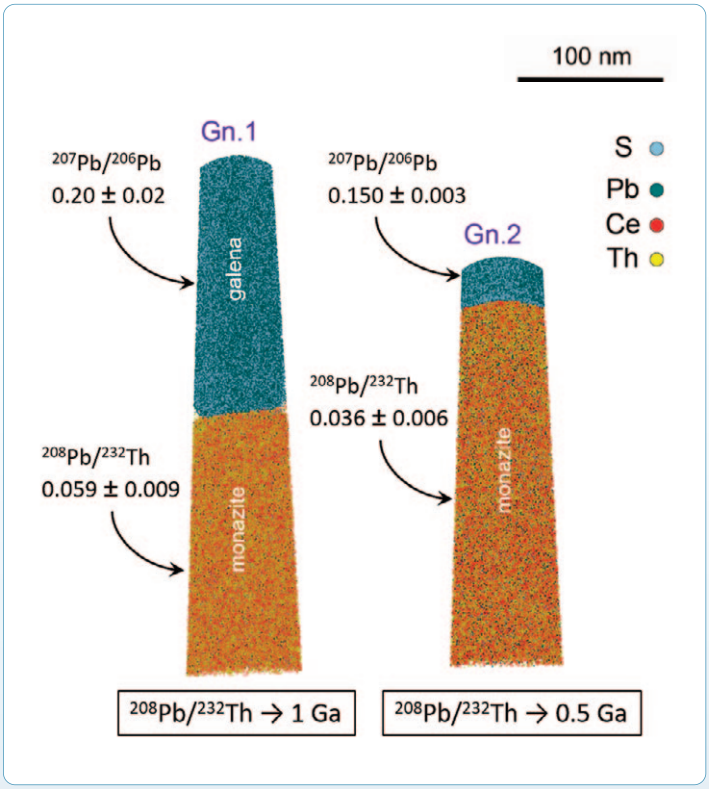


Figure 1:
Three-dimensional reconstructions of two specimens showing the distribution of S, Pb, Ce and Th atoms. The two specimens target galena nanocrystals (blue areas) in host monazite (orange areas).
Isotopic quantification of $^{207}Pb/^{206}Pb$ in galena and of $^{208}Pb/^{232}Th$ in monazite highlights two events of Pb mobility over time.
Data collected with a Local Electrode Atom Probe at Curtin University, Perth, Australia.

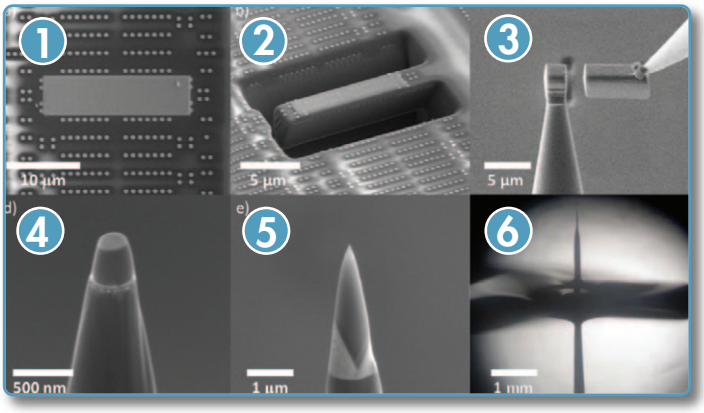
[1] Turuani M.J., Laurent A.T., Seydoux-Guillaume A.-M., Fougerouse D., Saxey D., Reddy S.M., Harley S.L., Reynaud S., Rickard W.D.A. *Partial retention of radiogenic Pb in galena nanocrystals explains discordance in monazite from Napier Complex (Antarctica) . Earth and Planetary Science Letters Volume 588 (2022) 117567. https://doi.org/10.1016/j.epsl.2022.117567.*

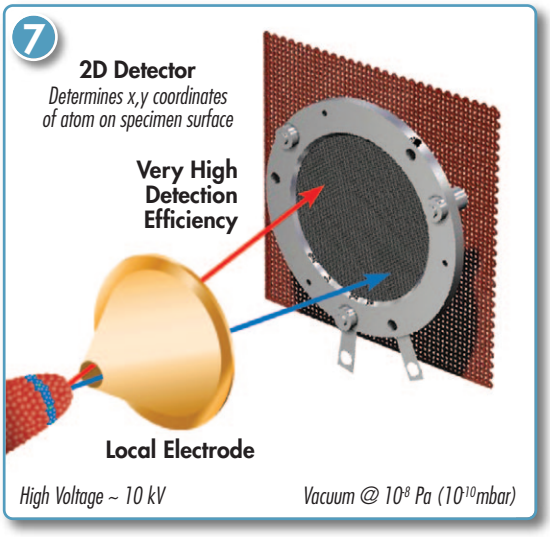
Three Steps to 3D Nanoscale Analysis

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.

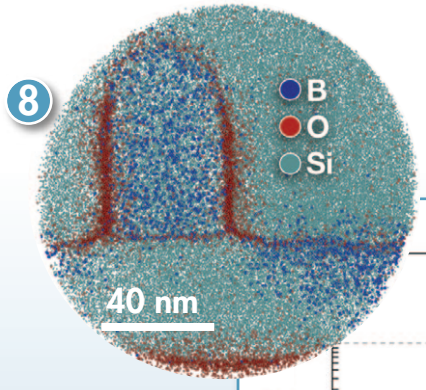
A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately 10^6.

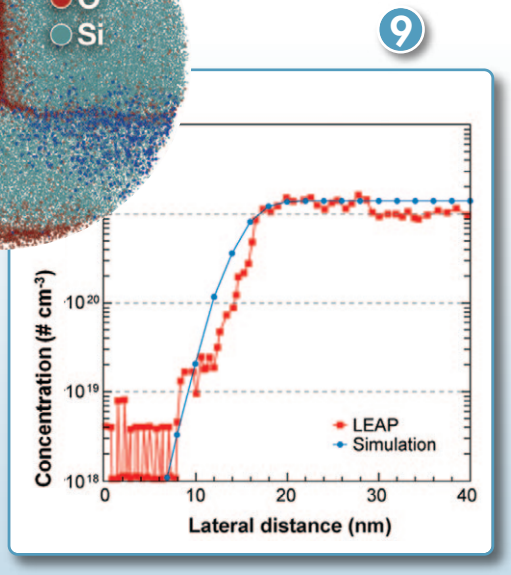
An atom probe identifies atoms by their mass-to-charge-state ratio *(m/n)* using time-of-flight mass spectrometry. Charge state, *n*, is typically 1 to 3.

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.*

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