Paleoclimatology

APT of Organic Matrices in Biogenic Carbonates

Biominerals, minerals formed by living organisms, are commonly composed of both mineral and organic phases, and their chemical signatures are essential for understanding their formation. Biominerals possess interesting physical properties that can evolve with their environment. For example, some biominerals are observed to change composition based on temperature or pH changes in the ocean, which is of great interest in geosciences for applications in paleoclimatology and paleoceanography.

Crystalline fraction is a prominent unknown factor in the chemistry of organic matrices. By using atom probe tomography (APT), investigators at the University of Alabama probed the nanoscale chemical composition of mineral-organic interfaces in calcite from mussel shells [1]. The biomineral formed by the mussel shells contains elements of its local environment, providing information about the changes to ocean salinity over time.

Three-dimensional APT data reconstructions of calcite specimens from Galicia, Spain, reveal the presence of organic matrix domains, indicated by the red arrows in the Figure 1A. In this reconstruction, the depletion of calcium cations was noted and an enrichment in oxygen and carbon was observed, with at least 1% atomic increase in ^{16}O relative to the surrounding mineral phase.

This is the first relative quantification of the chemical composition of the inter-crystalline organic matrix (IOM) for a carbonate biomineral, with implications for a better understanding of the formation of these biocarbonates. Atom probe tomography proves to be a powerful, promising tool for biomineral studies, providing quantitative insights into local compositional variation at the nanoscale.

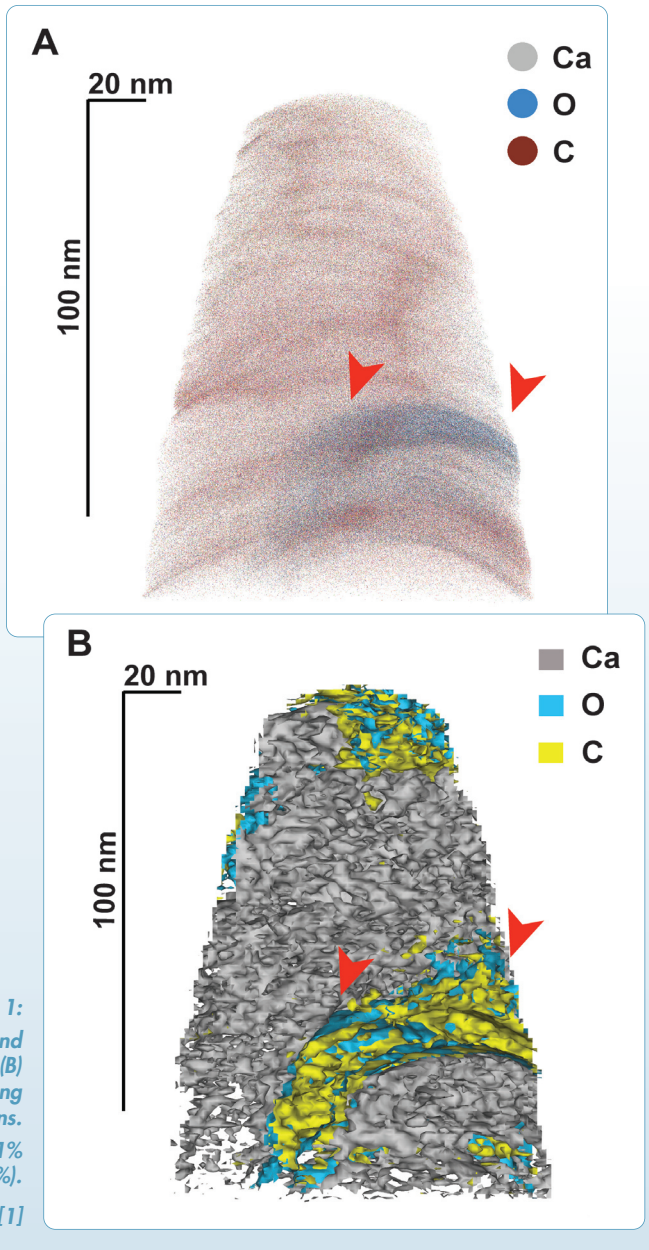


Figure 1:
Example of 3D atomic (A) and atomic isoconcentration surfaces (B) reconstructions for biogenic calcite showing enriched carbon and oxygen regions.
Note the mineral phases are identified with Ca >41% and the IOM with O+ (>43%) and C+ (>15%).
Data collected with the LEAP 5000 XS [1]

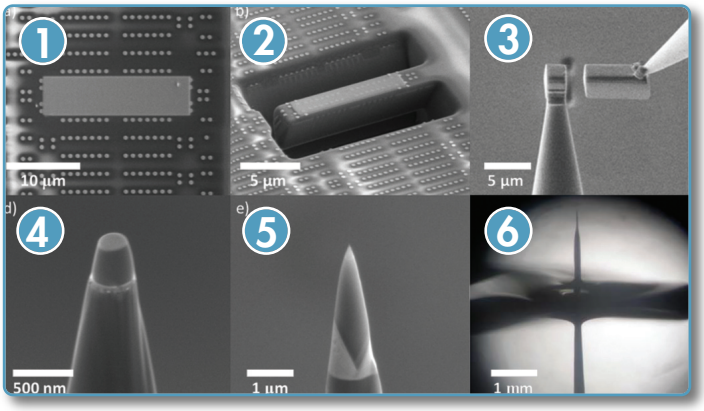
[1] *Pérez-Huerta, A. and Laiginhas, F., 2018. Preliminary Data on the Nanoscale Chemical Characterization of the Inter-Crystalline Organic Matrix of a Calcium Carbonate Biomineral. Minerals 8, 223; doi:10.3390/min8060223*

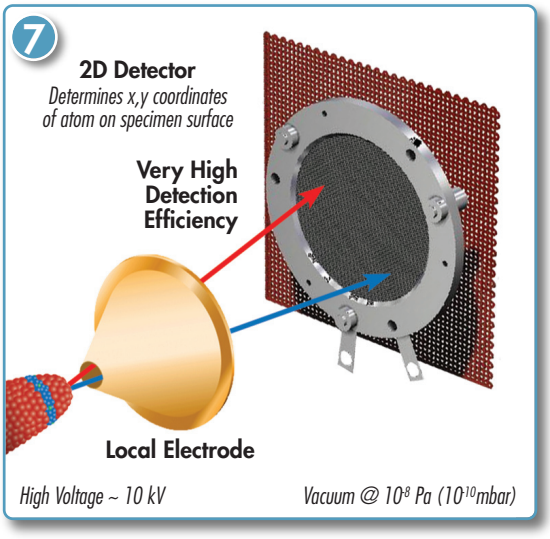
Three Steps to 3D Nanoscale Analysis

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.

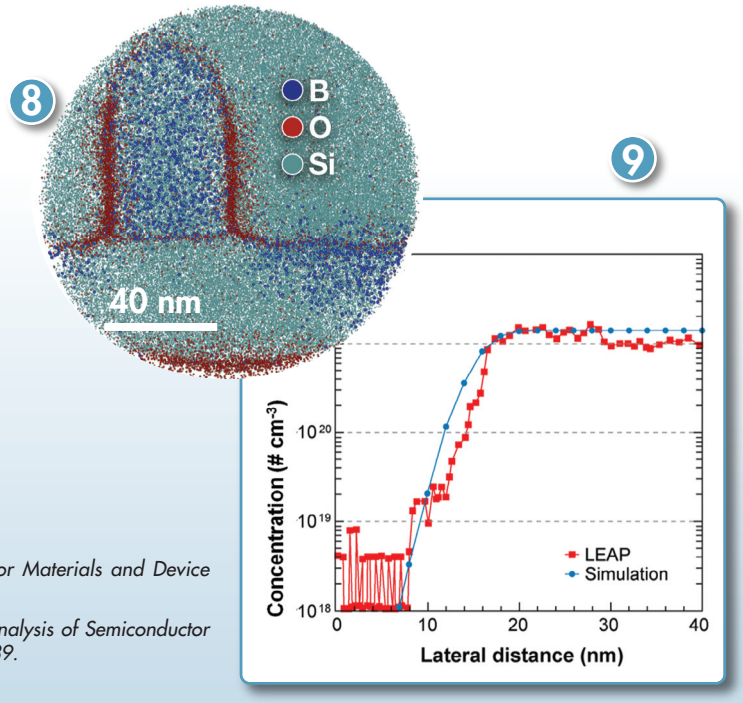
A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately 10^6.

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.*

CAMECA® SCIENCE & METROLOGY SOLUTIONS / AMETEK®

www.cameca.com • cameca.info@ametek.com