# Atom-by-atom growth chart for shells helps decode past climate

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Foraminifera are marine organisms whose shells, buried in marine sediments, provide a record of past climate stretching back 200 million years. A new study by UC Davis, University of Washington and Pacific Northwest National Lab applies material science techniques to understand how foraminifera build their shells, and may help improve our understanding of this climate record. Image shows the foraminiferan *Orbulina universa*. Credit: Howard Spero, UC Davis.

For the first time scientists can see how the shells of tiny marine organisms grow atom-by-atom, a new study reports. The advance provides new insights into the mechanisms of biomineralization and will improve our understanding of environmental change in Earth's past.

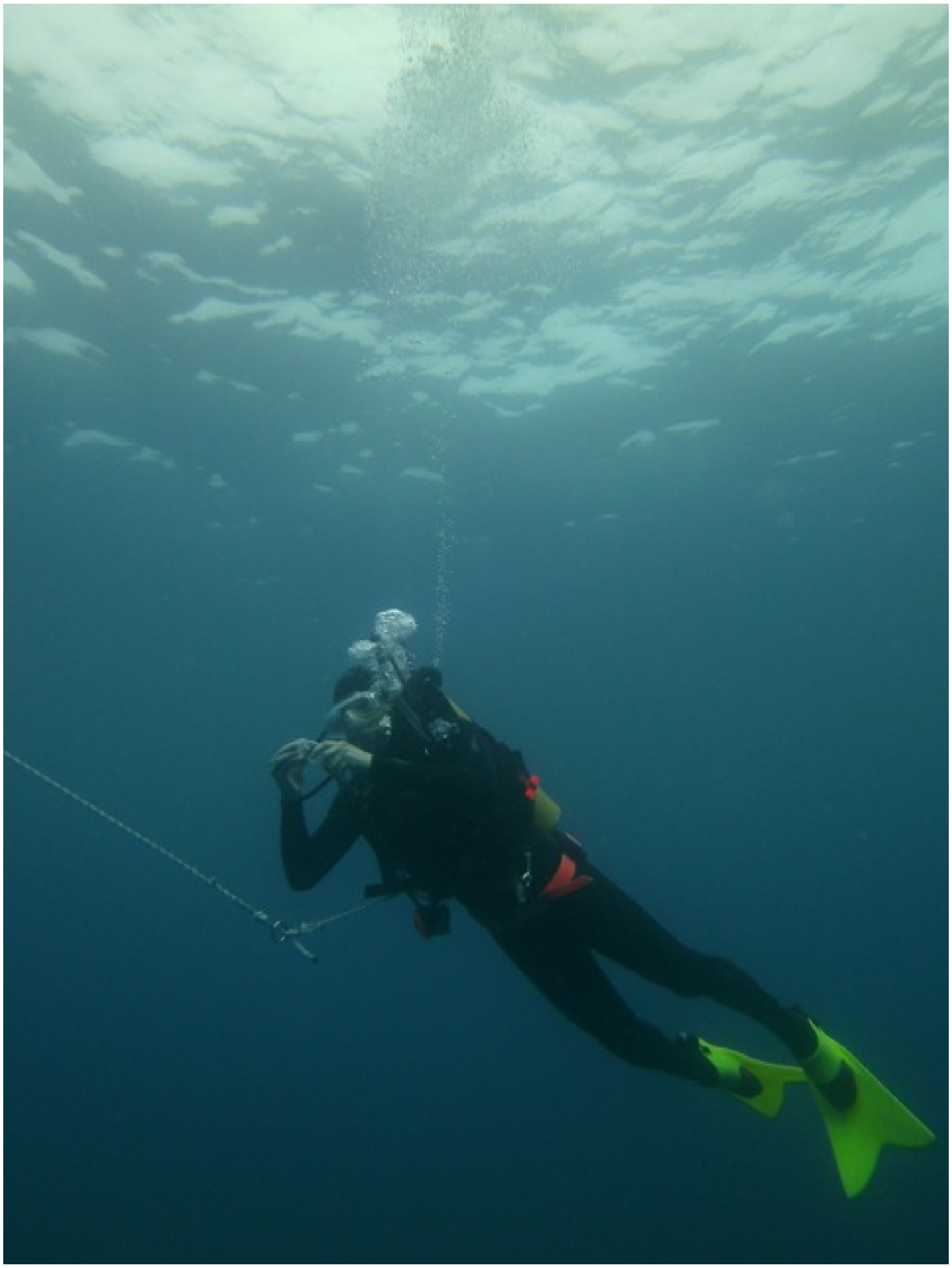
Led by researchers from the University of California, Davis and the University of Washington, with key support from the U.S. Department of Energy's Pacific Northwest National Laboratory, the team examined an organic-mineral interface where the first calcium carbonate crystals start to appear in the shells of foraminifera, a type of plankton.

"We've gotten the first glimpse of the biological event horizon," said Howard Spero, a study co-author and UC Davis geochemistry professor. The findings were published Monday, Oct. 24, in the *Proceedings of the National Academy of Sciences*.

## Foraminifera's Final Frontier

The researchers zoomed into shells at the atomic level to better understand how growth processes may influence the levels of trace impurities in shells. The team looked at a key stage—the interaction between the biological 'template' and the initiation of shell growth. The scientists produced an atom-scale map of the chemistry at this crucial interface in the foraminifera Orbulina universa. This is the first-ever measurement of the chemistry of a calcium carbonate biomineralization template, Spero said.

Among the new findings are elevated levels of sodium and magnesium in the organic layer. This is surprising because the two elements are not considered important architects in building shells, said lead study author Oscar Branson, a former postdoctoral researcher at UC Davis who is now at the Australian National University in Canberra. Also, the greater concentrations of magnesium and sodium in the organic template may need to be considered when investigating past climate with foraminifera shells.



Foraminifera are marine organisms whose shells provide a valuable record of past climate change. A new study used techniques from materials science to analyze how foraminifera build their shells. In this image, Alex Gagnon of the University of Washington collects floating foraminifera (less than one centimeter in size) for the study. Credit: Barbel Hönisch, Columbia University

**Calibrating Earth's Climate**

Most of what we know about past climate (beyond ice core records) comes from chemical analyses of shells made by the tiny, one-celled creatures called foraminifera, or "forams." When forams die, their shells sink and are preserved in seafloor mud. The chemistry preserved in ancient shells chronicles climate change on Earth, an archive that stretches back nearly 200 million years.

The calcium carbonate shells incorporate elements from seawater—such as calcium, magnesium and sodium—as the shells grow. The amount of trace impurities in a shell depends on both the surrounding environmental conditions and how the shells are made. For example, the more magnesium a shell has, the warmer the ocean was where that shell grew.

"Finding out how much magnesium there is in a shell can allow us to find out the temperature of seawater going back up to 150 million years," Branson said.

But magnesium levels also vary within a shell, because of nanometer-scale growth bands. Each band is one day's growth (similar to the seasonal variations in tree rings). Branson said considerable gaps persist in understanding what exactly causes the daily bands in the shells.

"We know that shell formation processes are important for shell chemistry, but we don't know much about these processes or how they might have changed through time," he said. "This adds considerable uncertainty to climate reconstructions."

## Atomic Maps

The researchers used two cutting-edge techniques: Time-of-Flight

Secondary Ionization Mass Spectrometry (ToF-SIMS) and Laser-Assisted Atom Probe Tomography (APT). ToF-SIMS is a two-dimensional chemical mapping technique which shows the elemental composition of the surface of a polished sample. The technique was developed for the elemental analysis of complex polymer materials, and is just starting to be applied to natural samples like shells.

APT is an atomic-scale three-dimensional mapping technique, developed for looking at internal structures in advanced alloys, silicon chips and superconductors. The APT imaging was performed at the Environmental Molecular Sciences Laboratory, a U.S. Department of Energy Office of Science User Facility at the Pacific Northwest National Laboratory.

**More information:** Nanometer-Scale Chemistry of a Calcite Biomineralization Template: Implications for Skeletal Composition and Nucleation, *Proceedings of the National Academy of Sciences*, www.pnas.org/cgi/doi/10.1073/pnas.1522864113

Provided by UC Davis

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