New technique unlocks secrets of ancient ocean

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ASU graduate student Greg Brennecka stands in the W.M. Keck Foundation Laboratory for Environmental Biogeochemistry at ASU in front of the powdered carbonate rock samples collected in Dawen, Southern China. These samples are prior to chemical processing to ready for measurement on the mass spectrometer. There were about 40 samples total for this study. Credit: P.S. Noonan

Earth's largest mass extinction event, the end-Permian mass extinction, occurred some 252 million years ago. An estimated 90 percent of Earth's marine life was eradicated. To better understand the cause of this "mother of all mass extinctions," researchers from Arizona State University and the University of Cincinnati used a new geochemical

technique. The team measured uranium isotopes in ancient carbonate rocks and found that a large, rapid shift in the chemistry of the world's ancient oceans occurred around the extinction event.

The mechanism of the end-Permian mass extinction has been much debated. One proposed cause for the extinction, the release of toxic hydrogen sulfide gas, is directly related to oceanic anoxia, which is a depletion of dissolved oxygen from the ocean.

Widespread evidence exists for oceanic anoxia before the extinction, but the timing and extent of anoxia remain unknown. Previous hypotheses posited that the deep ocean was depleted of oxygen for millions of years before the end-Permian extinction. The new research using measurements of uranium isotopes in ancient carbonate rocks indicates that the period of ocean-wide anoxia was much shorter.

"Our study shows that the ocean was anoxic for at most tens of thousands of years before the extinction event. That's much shorter than prior estimates," says Gregory Brennecka, the lead author of the study and a graduate student in ASU's School of Earth and Space Exploration in the College of Liberal Arts and Sciences.

Brennecka, working in Professor Ariel Anbar's research group, conducted the analysis of the samples. Anbar is a professor in ASU's School of Earth and Space Exploration and the Department of Chemistry and Biochemistry. Achim Herrmann, a senior lecturer at Barrett, the Honors College at ASU, and Thomas Algeo of the University of Cincinnati, who collected the samples in China, helped guide the selection of samples and interpretation of data.

The team studied samples of carbonate rock from Dawen in southern China for uranium isotope ratios (238U/235U) and thorium to uranium ratios (Th/U). The study presumes that carbonate rocks capture

238U/235U and Th/U of the seawater in which they were deposited. If so, they can be used to study changes in the chemistry of ancient oceans. In separate, related work, the team is testing the limits of this assumption.

In a section of rock spanning the time of the extinction, the team found a marked shift in 238U/235U in the carbonate rocks immediately prior to the mass extinction, which signals an increase in oceanic anoxia. The team also found higher Th/U ratios in the same interval, which indicate a decrease in the uranium content of seawater. Lower concentrations of uranium in seawater also serve as signals of oceanic anoxia.

These decreases in 238U/235U and increases in Th/U only occur at the section of rock that contains the end-Permian extinction horizon. This shows that a period of oceanic anoxia existed only briefly prior to the mass extinction, rather than the previously hypothesized much longer timeframe.

The team's findings represent an increase in knowledge about the ocean's chemistry at a critical period of the Earth's history. "This technique gives us a better understanding of how ocean chemistry can change over time, and how sensitive it is to certain environmental factors," says Brennecka.

The implications of the new geochemical tool the researchers developed are just as important as the study's findings.

Uranium isotope ratios have been utilized to study the ocean's chemistry before, but only in black shale, a different and less common type of rock. This study represents the first time uranium isotope ratios have been studied in carbonates for paleo-redox purposes, which is a promising new geochemical tool for future research.

"One of the important outcomes of this study is that we were able to

quantify the relative change in the amount of oceanic anoxia across the extinction event in the global ocean. Previous studies were only able to show whether anoxic conditions existed or not. We can now compare this event to other events in Earth history and develop a better understanding of how the amount of oxygen in the Earth's ocean has changed through time and how this might have affected marine diversity," says Herrmann.

Carbonates are much more widespread than black shales on Earth through space and time. "By focusing on carbonates we can study ancient anoxic events in many more places and times," says Anbar. "This was our major motivation in developing the uranium isotope technique."

It is only recently that researchers have developed the ability to precisely measure slight variations in uranium ratios, largely due to research completed at ASU. Most of the team's research in this study was conducted at ASU. The study samples were analyzed at ASU's W. M. Keck Foundation Laboratory for Environmental Biogeochemistry.

"Over the past decade, my research group has worked with many collaborators to develop new techniques to study changes in oxygen in the Earth's ocean through time," says Anbar. "We are especially interested in the connections between ocean oxygenation and biological evolution. The uranium isotope technique is the newest method. We expect it will be very useful. This study shows that it is yielding insights pretty quickly."

"It is exciting to be here, because most of the development work to measure uranium isotopes was done at ASU over the past five years. It is exciting to be at the forefront of these advancements," says Brennecka.

The team's results will be published in the *Proceedings of National Academy of Sciences* Oct. 10 in a paper titled, "Rapid expansion of

oceanic anoxia immediately before the end-Permian mass extinction."

Provided by Arizona State University

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