

Research points to Earth's first breaths

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Two multinational teams of scientists, including four researchers from ASU, are reporting that traces of oxygen appeared in Earth's atmosphere earlier than previously thought.

The discovery places the traces at 50 million to 100 million years before the "Great Oxidation Event." This event happened between 2.3 billion and 2.4 billion years ago, when most geoscientists think atmospheric oxygen rose sharply from very low levels. The amount of oxygen before that time is uncertain – and controversial.



After analyzing layers of sedimentary rock in a core sample 1 kilometer long from the Hamersley Basin in Western Australia, the researchers report finding evidence that a small but significant amount of oxygen – a whiff – was present in the oceans (and possibly Earth's atmosphere) 2.5 billion years ago. The data also suggest that oxygen was nearly undetectable just before that time. Their findings appear in a pair of papers in the Sept. 28 issue of the scientific journal *Science*.

"We seem to have captured a piece of time before the Great Oxidation Event during which the amount of oxygen was actually changing – caught in the act, as it were," says Ariel Anbar, an associate professor in ASU's School of Earth and Space Exploration, and the Department of Chemistry and Biochemistry in the College of Liberal Arts and Sciences.

Anbar, a biogeochemist, led one of the teams of investigators and participated in another team led by Alan Jay Kaufman, an associate professor of geology at the University of Maryland-College Park. The collaborators analyzed a drill core for geochemical and biological tracers representing the time just before the rise of atmospheric oxygen.

The project brought researchers together from ASU and four other major research universities, including the University of Maryland, the University of Washington, the University of California-Riverside and the University of Alberta. It received financial support from the Astrobiology Drilling Program (ADP) of the NASA Astrobiology Institute (NAI) and the National Science Foundation (NSF), and logistical support from the Geological Survey of Western Australia.

Drilling deep into time

In the summer of 2004, as part of the Deep Time Drilling Project of the ADP, the scientists bored into the geologically famous Hamersley Basin in western Australia, extracting a core of sedimentary rock 908 meters (about 3,000 feet) long from underground. The drilling was led by research team member Roger Buick, a professor at the University of Washington, who developed the idea for the project with Anbar and others as part of the NAI's "Mission to Early Earth" focus group.

"The core provides a continuous record of environmental conditions, analogous to a tape recording," Anbar says.

Because it was recovered from deep underground, it contains materials untouched by the atmosphere for billions of years.

After retrieval, the scientists sliced the core longitudinally, leaving half archived at the Geological Survey of Western Australia. The other half – the working half – is housed in laboratories at ASU.

Anbar and his ASU research group – including doctoral student Yun Duan, and assistant research scientists Gail Arnold and Gwyneth Gordon – began an analysis of selected bands of the late Archean Mount McRae shale found in the upper 200 meters of the drill core. They were analyzing the amounts of the trace metals molybdenum, rhenium and uranium. The amounts of these metals in oceans and sediments depends on the amount of oxygen in the environment.

Using state-of-the-art facilities and instruments in ASU's W.M. Keck Foundation Laboratory for Environmental Biogeochemistry, Anbar's group took rock samples from the core and pummeled them to powders, dissolved the powders in acid and vaporized the acid solutions for analysis, using an inductively coupled plasma mass spectrometer.

Their goal was to characterize the nature of the environment and life in the oceans leading up to the Great Oxidation Event. But they were not expecting much from this particular stretch of core. "We expected these analyses to be boring," says Arnold, who also participated in the research led by the University of Maryland's Kaufman, studying the chemistry of sulfur from the same samples.

As Anbar explains: "The Maryland group started their analyses first, because they were eager to try out a new method they had just developed. They began seeing funny variations in the chemistry of sulfur along this stretch of the drill core. Yun sped up our research to see if we found variations in metal abundances in the same places – and we did."

"Instead of it being boring, we found this big change," Arnold says.

Finding evidence of oxygen some 50 to 100 million years earlier than what previously was known was unexpected, Anbar says.

‘Just’ before the Great Oxidation Event

For the first half of Earth’s 4.56-billion-year history, the environment held almost no oxygen, other than bound to hydrogen in water, or to silicon and other elements in rocks. “Then, some time between 2.3 and 2.4 billion years ago, oxygen rose sharply in the Earth’s atmosphere and oceans,” Anbar says. “We call this the ‘Great Oxidation Event.’ ”

The event was a big step in Earth’s history, but its cause remains unexplained. How did Earth’s atmosphere go from being oxygen-poor to oxygen-rich? Why did it change so quickly? And why did its oxygen content stabilize at the present 21 percent?

“Studying the dynamics that gave rise to the presence of oxygen in Earth’s atmosphere deepens our appreciation of the complex interaction between biology and geochemistry,” says Carl Pilcher, director of the NAI. “Their results support the idea that our planet and the life on it evolved together.”

One possibility for explaining the findings is that the ancient ancestors of today’s plants first began to produce oxygen by photosynthesis at this time. On the other hand, many geoscientists think that organisms began to produce oxygen much earlier, but that this oxygen was destroyed in reactions with volcanic gases and rocks.

“What we have now are two new lines of evidence for there being some oxygen in the environment 50 million to 100 million years before the big rise of oxygen,” Anbar says. This discovery strengthens the notion that organisms learned to produce oxygen long before the Great Oxidation Event, and that rise of oxygen in the atmosphere ultimately was controlled by geological processes.

“This knowledge is relevant to today’s global studies of environmental and climate issues, because it helps us understand the interactions between biology, geology and the composition of the atmosphere,” Anbar says. “It also has implications for the search for life on planets outside our solar system because, in the near future, the only way we can look for evidence of life in such far-off places is to look for the fingerprints of biology in the compositions of their atmospheres.”

Adds Anbar: “We are not far off from being able to detect Earth-like planets elsewhere in the galaxy, and eventually we will be able to use telescopes to measure the oxygen content of their atmospheres. If we find that none of them have undergone a Great Oxidation Event, what will that mean about life? Is it inevitable that the evolution of oxygen-producing organisms results in an oxygen-rich atmosphere? Our results indicate that the connection is not so simple.”

“These results are the culmination of a successful effort to recover suitable rock material, and to test hypotheses regarding the evolution of biogeochemical cycles in early Earth, which is largely unknown,” says Enriqueta Barrera, program director in the National Science Foundation (NSF)’s Division of Earth Sciences.

The findings from the Anbar-led team are reported in “A Whiff of Oxygen Before the Great

Oxidation Event?” Authors on the paper include Duan, Arnold, Gordon, Buick, Kaufman and Brian Kendall, a doctoral student at the University of Alberta who was a visiting graduate student at ASU in 2006. Other authors are Timothy Lyons of the University of California, Robert A. Creaser of the University of Alberta, Clinton Scott of the University of California-Riverside, and Jessica Garvin, University of Washington.

The findings from the Kaufman-led team are reported in “Late Archean Biospheric Oxygenation and Atmospheric Evolution.” Authors include Anbar, Arnold, Buick, Garvin and Lyons. Also, David Johnston, James Farquhar and Andrew Masterson, of the University of Maryland-College Park, and Steve Bates, University of California-Riverside.

Together, these papers provide “compelling new evidence” of early oxygen, Anbar says. The question he now asks is, “Can we find evidence that oxygen was produced even earlier?”