Researchers discover new wrinkle in ancient ocean chemistry

Beneath the red-weathered and spinifex covered hills of Western Australia, drill core collected of 2.5 billion-year-old shales revealed evidence for early sulfidic conditions in the ocean and photosynthetic oxygen in the atmosphere. Photo: Ariel Anbar Download image

Scientists widely accept that around 2.4 billion years ago, the Earth's atmosphere underwent a dramatic change when oxygen levels rose sharply. Called the "Great Oxidation Event" (GOE), the oxygen spike marks an important milestone in Earth's history, the transformation from an oxygen-poor atmosphere to an oxygen-rich one, paving the way for complex life to develop on the planet.

Two questions that remain unresolved in studies of the early Earth are when oxygen production via photosynthesis got started and when it began to alter the chemistry of Earth's ocean and atmosphere.

ASU scientists, working with collaborators at other institutions, have been pursuing these questions in a series of studies of ancient rocks from Western Australia. The latest of these studies appears in the Oct. 30 issue of the journal Science.

The new findings corroborate previous results that oxygen production began in Earth's oceans at least 100 million years before the GOE, but also go a step further in demonstrating that even very low concentrations of oxygen can have profound effects on ocean chemistry. This research was led by geoscientists at the University of California, Riverside, working with Ariel Anbar, an astrobiologist and biogeochemist. Anbar, a co-author on the research, is a professor in the department of chemistry and biochemistry and the School of Earth and Space Exploration in ASU's College of Liberal Arts and Sciences.

To arrive at their results, the researchers analyzed 2.5 billion-year-old black shales from Western Australia. Essentially representing fossilized pieces of the ancient seafloor, the fine layers within the rocks allowed the researchers to page through ocean chemistry's evolving history. These rocks were obtained under the leadership of Anbar, with support from the NASA Astrobiology Institute of which ASU is a member.

Specifically, the shales revealed that episodes of hydrogen sulfide accumulation in the oxygen-free deep ocean occurred nearly 100 million years before the GOE and up to 700 million years earlier than such conditions were predicted by past models for the early ocean. Scientists have long believed that the early ocean, for more than half of Earth's 4.6 billion-year history, was characterized instead by high amounts of dissolved iron under conditions of essentially no oxygen.

"The conventional wisdom has been that appreciable atmospheric oxygen is needed for sulfidic conditions to develop in the ocean," said Chris Reinhard, a doctoral student at UCR and lead author of the research paper. "We found, however, that sulfidic conditions in the ocean are possible even when there is very little oxygen around, below about 1/100,000th of the oxygen in the modern atmosphere."

Reinhard explained that at even very low oxygen levels in the atmosphere, the mineral pyrite can weather on the continents, resulting in the delivery of sulfate to the ocean by rivers. Sulfate is the key ingredient in hydrogen sulfide formation in the ocean.

Timothy Lyons, a professor of biogeochemistry at UCR, whose laboratory led the research, explained that the hydrogen sulfide in the ocean is a fingerprint of photosynthetic production of oxygen 2.5 billion years ago.

"A pre-GOE emergence for oxygenic photosynthesis is a matter of intense debate, and its resolution lies at the heart of understanding the evolution of diverse forms of life," he said. "We have found an important piece of that puzzle."

"These data don't make much sense unless there were at least small amounts of oxygen in the environment. The simplest explanation is oxygen-producing photosynthesis long before concentrations of oxygen in the atmosphere were even a tiny fraction of what they are today," said Anbar. "The results are beautifully consistent with our previous results. The story just gets stronger and stronger the more we look at these ancient sediments."

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The researchers argue that the presence of small amounts of oxygen may have stimulated the early evolution of eukaryotes - organisms whose cells bear nuclei - millions of years prior to the GOE.

"This initial oxygen production set the stage for the development of animals almost two billion years later," Lyons said. "The evolution of eukaryotes had to take place first."

The findings also have implications for the search for life on extrasolar planets.

"Our findings add to growing evidence suggesting that biological production of oxygen is a necessary but not sufficient condition for the evolution of complex life," Reinhard said. "A planetary atmosphere with abundant oxygen would provide a very promising biosignature. But one of the lessons here is that just because spectroscopic measurements don't detect oxygen in the atmosphere of another planet doesn't necessarily mean that no biological oxygen production is taking place."

Anbar, Reinhard and Lyons were joined in the research by Clint Scott of UCR and Rob Raiswell of the University of Leeds, United Kingdom.

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