Ancient ocean chemistry: Effects of biological oxygen production 100 million years before it accumulated in atmosphere

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UC Riverside's Chris Reinhard studies a sample of pulverized black shale in solution. Credit: UCR Strategic Communications.

(PhysOrg.com) -- 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.

Now a research team led by geoscientists at the University of California, Riverside corroborates recent evidence that oxygen production began in Earth's oceans at least 100 million years before the GOE, and goes a step further in demonstrating that even very low concentrations of oxygen can have profound effects on ocean chemistry.

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.

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 Ph.D. graduate student in the Department of Earth Sciences and one of the research team members. "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."

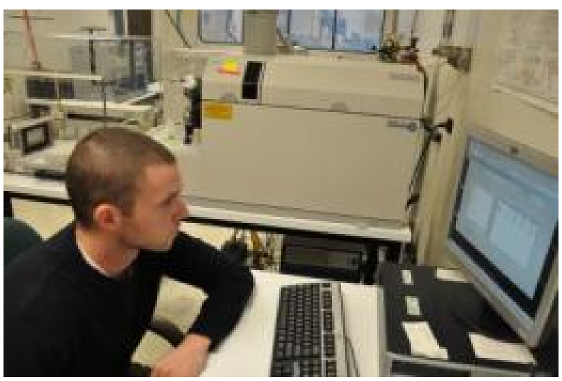
Reinhard explained that at even very low oxygen levels in the atmosphere, the mineral pyrite can weather on the continents, resulting in the delivery of sulfate to the ocean by rivers. Sulfate is the key ingredient in hydrogen sulfide formation in the ocean.

Timothy Lyons, a professor of biogeochemistry, 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."

Study results appear in the Oct. 30 issue of *Science*.

"Our data point to oxygen-producing photosynthesis long before concentrations of oxygen in the atmosphere were even a tiny fraction of what they are today, suggesting that oxygen-consuming chemical reactions were offsetting much of the production," said Reinhard, the lead author of the research paper.



UC Riverside's Chris Reinhard analyzes metal content in 2.5 billion-year-old black shale using a mass spectrometer seen to his left. Credit: UCR Strategic Communications.

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."

To analyze the shales, Reinhard first pulverized them into a fine powder in Lyons's laboratory. Next, the powder was treated with a series of chemicals to extract different minerals. The extracts were then run on a mass-spectrometer at UC Riverside.

"One exciting thing about our discovery of sulfidic conditions occurring before the GOE is that it might shed light on ocean chemistry during other periods in the geologic record, such as a poorly understood 400 million-year interval between the GOE and around 1.8 billion years ago, a point in time when the deep oceans stopped showing signs of high iron concentrations," Reinhard said. "Now perhaps we have an explanation. If sulfidic conditions could occur with very small amounts of oxygen around, then they might have been even more common and widespread after the GOE."

Said Lyons, "This is important because oxygen-poor and sulfidic conditions almost certainly impacted the availability of nutrients essential to life, such as nitrogen and trace metals. The evolution of the ocean and atmosphere were in a cause-and-effect balance with the evolution of life."

Source: University of California - Riverside (news : web)