Oxygen-free early oceans likely delayed rise of life on planet

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Geologists at the University of California, Riverside have found chemical evidence in 2.6-billion-year-old rocks that indicates that Earth's ancient oceans were oxygen-free and, surprisingly, contained abundant hydrogen sulfide in some areas.

"We are the first to show that ample hydrogen sulfide in the ocean was possible this early in Earth's history," said Timothy Lyons, a professor of biogeochemistry and the senior investigator in the study, which appears in the February issue of *Geology*. "This surprising finding adds to growing evidence showing that ancient ocean chemistry was far more complex than previously imagined and likely influenced life's evolution on Earth in unexpected ways – such as, by delaying the appearance and proliferation of some key groups of organisms."

Ordinarily, hydrogen sulfide in the ocean is tied to the presence of oxygen in the atmosphere. Even small amounts of oxygen favor continental weathering of rocks, resulting in sulfate, which in turn gets transported to the ocean by rivers. Bacteria then convert this sulfate into hydrogen sulfide.

How then did the ancient oceans contain hydrogen sulfide in the near absence of oxygen, as the 2.6-million-year-old rocks indicate? The UC Riverside-led team explains that sulfate delivery in an oxygen-free environment can also occur in sufficient amounts via volcanic sources, with bacteria processing the sulfate into hydrogen sulfide.

Specifically, Lyons and colleagues examined rocks rich in pyrite – an iron sulfide mineral commonly known as fool's gold – that date back to the Archean eon of geologic history (3.9 to 2.5 billion years ago) and typify very low-oxygen environments. Found in Western Australia, these rocks have preserved chemical signatures that constitute some of the best records of the very early evolutionary history of life on the planet.

The rocks formed 200 million years before oxygen amounts spiked during the so-called "Great Oxidation Event" – an event 2.4 billion years ago that helped set the stage for life's proliferation on Earth.

"Our previous work showed evidence for hydrogen sulfide in the ocean more than 100 million years before the first appreciable accumulation of oxygen in the atmosphere at the Great Oxidation Event," Lyons said. "The data pointing to this 2.5 billion-year-old hydrogen sulfide are fingerprints of incipient atmospheric oxygenation. Now, in contrast, our evidence for abundant 2.6 billion-year-old hydrogen sulfide in the ocean – that is, another 100 million years earlier – shows that oxygen wasn't a prerequisite. The important implication is that hydrogen sulfide was potentially common for a billion or more years before the Great Oxidation Event, and that kind of ocean chemistry has key implications for the evolution of early life."

Clint Scott, the first author of the research paper and a former graduate student in Lyons's lab, said the team was also surprised to find that the Archean rocks recorded no enrichments of the trace element molybdenum, a key micronutrient for life that serves as a proxy for oceanic and atmospheric oxygen amounts.

The absence of molybdenum, Scott explained, indicates the absence of oxidative weathering of the continental rocks at this time (continents are the primary source of molybdenum in the oceans). Moreover, the development of early life, such as cyanobacteria, is determined by the amount of molybdenum in the ocean; without this life-affirming micronutrient, cyanobacteria could not become abundant enough to produce large quantities of oxygen.

"Molybdenum is enriched in our previously studied 2.5 billion-year-old Archean rocks, which ties to the earliest hints of atmospheric oxygenation as a harbinger of the Great Oxidation Event," Scott said. "The scarcity of molybdenum in rocks deposited 100 million years earlier, however, reflects its scarcity also in the overlying water column. Such metal deficiencies suggest that cyanobacteria were probably struggling to produce oxygen when these rocks formed.

"Our research has important implications for the evolutionary history of life on Earth," Scott added, "because biological evolution both initiated and responded to changes in ocean chemistry. We are trying to piece together the cause-and-effect relationships that resulted, billions of years later, in the evolution of animals and, ultimately, humans. This is really the story of how we got here."

The first animals do not appear in the fossil record until around 600 million years ago – almost two billion years after the rocks studied by Scott and his team formed. The steady build-up of oxygen, which began towards the end of the Archean, played a key role in the evolution of new life forms.

"Future research needs to focus on whether sulfidic and oxygen-free conditions were prevalent throughout the Archean, as our model predicts," Scott said.

Provided by University of California - Riverside

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