

# New Evidence About the Rise of Oxygen

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Scientists believe that oxygen first showed up in the atmosphere about 2.7 billion years ago. They think it was put there by a one-celled organism called "cyanobacteria," which had recently become the first living thing on Earth to make oxygen from water and sunlight.

The rock record provides a good bit of evidence that this is so. But one of these rocks has just gotten a great deal more slippery, so to speak.

In an article appearing in the Geological Society of America's journal *Geology*, investigators from the California Institute of Technology, the University of Tübingen in Germany, and the University of Alberta describe their new findings about the origin of the mineral deposits known as banded-iron formations, or "BIFs." A rather attractive mineral that is often cut and polished for paperweights and other decorative items, a BIF typically has alternating bands of iron oxide and silica. How the iron got into the BIFs to begin with is thought to be a key to knowing when molecular oxygen first was produced on Earth.

The researchers show that purple bacteria--primitive organisms that have thrived on Earth without producing oxygen since before cyanobacteria first evolved--could also have laid down the iron oxide deposits that make up BIFs. Further, the research shows that the newer cyanobacteria, which suddenly evolved the ability to make oxygen through photosynthesis, could have even been floating around when the purple bacteria were making the iron oxides in the BIFs.

"The question is what made the BIFs," says Dianne Newman, who is

associate professor of geobiology and environmental science and engineering at Caltech and an investigator with the Howard Hughes Medical Institute. "BIFs are thought to record the history of the rise of oxygen on Earth, but this may not be true for all of them."

The classical view of how the BIFs were made is that cyanobacteria began putting oxygen in the atmosphere about 2.7 billion years ago. At the same time, hydrothermal sources beneath the ocean floors caused ferrous iron (that is, "nonrusted" iron) to rise in the water. This iron then reacted with the new oxygen in the atmosphere, which caused the iron to change into ferric iron. In other words, the iron literally "rusted" at the surface of the ocean waters, and then ultimately settled on the ocean floor as sediments of hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ).

The problem with this scenario was that scientists in Germany about 10 years ago discovered a way that the more ancient purple bacteria could oxidize iron without oxygen. Instead, these anaerobic bacteria could have used a photosynthetic process in which light and carbon dioxide are used to turn the ferrous iron into ferric iron, throwing the mechanism of BIF formation into question.

Newman's postdoctoral researcher Andreas Kappler (now an assistant professor at the University of Tübingen) expanded on this discovery by doing some lab experiments to measure the rate at which purple bacteria could form ferric iron under light conditions relevant for different depths within the ocean.

Kappler's results showed that iron could indeed have been oxidized by these bacteria, in amounts matching what would have been necessary to form one of the Precambrian iron deposits in Australia.

Another of the paper's Caltech authors, Claudia Pasquero, determined the thickness of the purple bacterial layer that would have been needed

for complete iron oxidation. Her results showed that the thickness of the bacterial layer could have been on the order of 17 meters, below wave base, which compares favorably to what is seen today in stratified water bodies such as the Black Sea.

Also, the results show that, in principle, the purple bacteria could have oxidized all the iron seen in the BIFs, even if the cyanobacteria had been present in overlying waters.

However, Newman says that the rock record contains various other kinds of evidence that oxygen was indeed absent in the atmosphere earlier than 2.7 billion years ago. Therefore, the goal of better understanding the history of the rise of oxygen could come down to finding out if there are subtle differences between BIFs that could have been produced by cyanobacteria and/or purple bacteria. And to do this, it's best to look at the biology of the organisms.

"The hope is that we'll be able to find out whether some organic compound is absolutely necessary for anaerobic anoxygenic photosynthesis to occur," Newman says. "If we can know how they work in detail, then maybe we'll be fortunate enough to find one molecule really necessary."

A good candidate is an organic molecule with high geological preservation potential that would have existed in the purple bacteria three billion years ago and still exists today. If the Newman team could find such a molecule that is definitely involved in the changing of iron to iron oxide, and is not present in cyanobacteria, then some of the enigmas of oxygen on the ancient earth would be solved.

"The goals are to get at the types of biomolecules essential for different types of photosynthesis—hopefully, one that is preservable," Newman says.

"I guess one interesting thing from our findings is that you can get rust without oxygen, but this is also about the history of metabolic evolution, and the ability to use ancient rock to investigate the history of life."

Better understanding microbial metabolism could also be of use in NASA's ambitious goal of looking for life on other worlds. The question of which organisms made the BIFs on Earth, therefore, could be useful for astrobiologists who may someday find evidence in rock records elsewhere.

Source: Caltech

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