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Geobiologists Solve 'Catch-22 Problem' Concerning the Rise of Atmospheric Oxygen

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Two and a half billion years ago, when our evolutionary ancestors were little more than a twinkle in a bacterium's plasma membrane, the process known as photosynthesis suddenly gained the ability to release molecular oxygen into Earth's atmosphere, causing one of the largest environmental changes in the history of our planet. The organisms assumed responsible were the cyanobacteria, which are known to have evolved the ability to turn water, carbon dioxide, and sunlight into oxygen and sugar, and are still around today as the blue-green algae and the chloroplasts in all green plants.

But researchers have long been puzzled as to how the cyanobacteria could make all that oxygen without poisoning themselves. To avoid their DNA getting wrecked by a hydroxyl radical that naturally occurs in the production of oxygen, the cyanobacteria would have had to evolve protective enzymes. But how could natural selection have led the cyanobacteria to evolve these enzymes if the need for them didn't even exist yet?

Now, two groups of researchers at the California Institute of Technology offer an explanation of how cyanobacteria could have avoided this seemingly hopeless contradiction. Reporting in the December 12 *Proceedings of the National Academy of Sciences* (PNAS) and available online this week, the groups demonstrate that ultraviolet light striking the surface of glacial ice can lead to the accumulation of frozen oxidants and the eventual release of molecular oxygen into the oceans and atmosphere. This trickle of poison could then drive the evolution of oxygen-protecting enzymes in a variety of microbes, including the cyanobacteria. According to Yuk Yung, a professor of planetary science, and Joe Kirschvink, the Van Wingen Professor of Geobiology, the UV-peroxide solution is "rather simple and elegant."

"Before oxygen appeared in the atmosphere, there was no ozone screen to block ultraviolet light from hitting the surface," Kirschvink explains. "When UV light hits water vapor, it converts some of this into hydrogen peroxide, like the stuff you buy at the supermarket for bleaching hair, plus a bit of hydrogen gas.

"Normally this peroxide would not last very long due to back-reactions, but during a glaciation, the hydrogen peroxide freezes out at one degree below the freezing point of water. If UV light were to have penetrated down to the surface of a glacier, small amounts of peroxide would have been trapped in the glacial ice." This process actually happens today in Antarctica when the ozone hole forms, allowing strong UV light to hit the ice.

Before there was any oxygen in Earth's atmosphere or any UV screen, the glacial ice would have flowed downhill to the ocean, melted, and released trace amounts of peroxide directly into the sea water, where another type of chemical reaction converted the peroxide back into water and oxygen. This happened far away from the UV light that would kill organisms, but the oxygen was at such low levels that the cyanobacteria would have avoided oxygen poisoning.

"The ocean was a beautiful place for oxygen-protecting enzymes to evolve," Kirschvink says. "And once those protective enzymes were in place, it paved the way for both oxygenic photosynthesis to evolve, and for aerobic respiration so that cells could actually breathe oxygen like we do."

The evidence for the theory comes from the calculations of lead author Danie Liang, a recent graduate in planetary science at Caltech who is now at the Research Center for Environmental Changes at the Academia Sinica in Taipei, Taiwan.

According to Liang, a serious freeze-over known as the Makganyene Snowball Earth occurred 2.3 billion years ago, at roughly the time cyanobacteria evolved their oxygen-producing capabilities. During the Snowball Earth episode, enough peroxide could have been stored to produce nearly as much oxygen as is in the atmosphere now.

As an additional piece of evidence, this estimated oxygen level is also sufficient to explain the deposition of the Kalahari manganese field in South Africa, which has 80 percent of the economic reserves of manganese in the entire world. This deposit lies immediately on top of the last geological trace of the Makganyene Snowball.

"We used to think it was a cyanobacterial bloom after this glaciation that dumped the manganese out of the seawater," says Liang. "But it may have simply been the oxygen from peroxide decomposition after the Snowball that did it."

In addition to Kirschvink, Yung, and Liang, the other authors are Hyman Hartman of the Center for Biomedical Engineering at MIT, and Robert Kopp, a graduate student in geobiology at Caltech. Hartman, along with Chris McKay of the NASA Ames Research Center, were early advocates for the role that hydrogen peroxide played in the origin and evolution of oxygenic photosynthesis, but they could not identify a good inorganic source for it in Earth's precambrian environment.

Source: Caltech