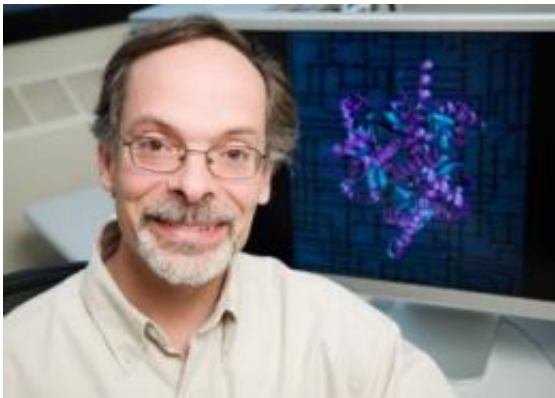


# Researchers identify molecular 'culprit' in rise of planetary oxygen

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University of Illinois crop sciences and Institute for Genomic Biology professor Gustavo Caetano-Anollés and his colleagues identified an oxygen-generating enzyme that likely was a key contributor to the rise of molecular oxygen on earth. Credit: L. Brian Stauffer

A turning point in the history of life occurred 2 to 3 billion years ago with the unprecedented appearance and dramatic rise of molecular oxygen. Now researchers report they have identified an enzyme that was the first – or among the first – to generate molecular oxygen on Earth.

The new findings, reported in the journal *Structure*, build on more than a dozen previous studies that aim to track the molecular evolution of life by looking for evidence of that history in present-day protein structures. These studies, led by University of Illinois crop sciences and Institute for Genomic Biology professor Gustavo Caetano-Anollés, focus on

structurally and functionally distinct regions of proteins – called folds – that are part of the universal toolkit of living cells.

Protein folds are much more stable than the sequences of amino acids that compose them, Caetano-Anollés said. Mutations or other changes in sequence often occur without disrupting fold structure or function. This makes folds much more reliable markers of long-term evolutionary patterns, he said.

In the new study, Caetano-Anollés, working with colleagues in China and Korea, tackled an ancient mystery: Why did some of the earliest organisms begin to generate [oxygen](#), and why?

"There is a consensus from earth scientists that about 2.4 billion years ago there was a big spike in oxygen on Earth," Caetano-Anollés said. They generally agree that this rise in oxygen, called the Great Oxygenation Event, was tied to the emergence of photosynthetic organisms.

"But the problem now comes with the following question," he said. "Oxygen is toxic, so why would a living organism generate oxygen? Something must have triggered this."

The researchers looked for answers in the "molecular fossils" that still reside in living cells. They analyzed protein folds in nearly a thousand organisms representing every domain of life to assemble a timeline of protein history. Their timeline for this study was limited to single-fold proteins (which the researchers believe are the most ancient), and was calibrated using microbial fossils that appeared in the geologic record at specific dates.

The analysis revealed that the most ancient reaction of aerobic metabolism involved synthesis of pyridoxal (the active form of vitamin

B6, which is essential to the activity of many protein enzymes) and occurred about 2.9 billion years ago. An oxygen-generating enzyme, manganese catalase, appeared at the same time.

Other recent studies also suggest that aerobic (oxygen-based) respiration began on Earth 300 to 400 million years before the Great Oxidation Event, Caetano-Anollés said. This would make sense, since oxygen production was probably going on for a while before the spike in oxygen occurred.

Catalases convert hydrogen peroxide to water and oxygen. The researchers hypothesize that primordial organisms "discovered" this enzyme when trying to cope with an abundance of hydrogen peroxide in the environment. Some geochemists believe that hydrogen peroxide was abundant at this time as a result of intensive solar radiation on glaciers that covered much of Earth.

"In the glacial melt waters you would have a high concentration of hydrogen peroxide and that would be gradually exposing a number of the primitive organisms (alive at that time)," Caetano-Anollés said. The appearance of manganese catalase, an enzyme that degrades [hydrogen peroxide](#) and generates oxygen as a byproduct, makes it a likely "molecular culprit for the rise of oxygen on the planet," he said.

**More information:** "Protein Domain Structure Uncovers the Origin of Aerobic Metabolism and the Rise of Planetary Oxygen," in journal *Structure*.

Provided by University of Illinois at Urbana-Champaign

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