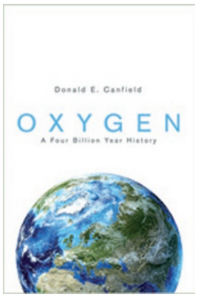
Earth's oxygen unravelled



Oxygen: A Four Billion Year History

by Donald E. Canfield

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Oxygen comprises 21% of the air we breathe. Before 2.5 billion years ago, the atmosphere was oxygen-free. In *Oxygen: A Four Billion Year History*, Donald Canfield, a gregarious scientist and lead researcher in the evolution of atmospheric oxygen, explains why. While exploring the history of Earth's oxygenation, he introduces a cast of characters — most of whom are his current or former collaborators — whose work has contributed to the field. In so doing, Canfield explores both what we know about the geologic history of oxygen, and how that understanding has been built from the scant bits of evidence that have survived the ravages of billions of years of exposure to damaging conditions.

The story begins with an exploration of modern environments that serve as analogues for ancient settings where life thrived in the absence of oxygen. Canfield takes the reader on an imaginary trip into the gut of a cow, and on a real expedition to the deep sea floor of the Guaymas Basin in *Alvin*, the deep-sea submersible that carries researchers to the depths of the ocean. In both of these locations, methanogens (anaerobic organisms that combine hydrogen gas and carbon dioxide to form methane) eke out an autotrophic lifestyle. He also shares the excitement of family vacations to Yellowstone National Park, where the odours of hydrogen sulfide, a compound that fuels non-oxygen-producing photosynthesis by green and purple sulphur bacteria, permeate the air.

By the third chapter, the focus is squarely on oxygen and its source — oxygenic photosynthesis, that is, the metabolic conversion of carbon dioxide and water into sugars and oxygen. When this key metabolism evolved, and from what ancestral organism, are some of the topics covered. Canfield presents the biochemistry and evolutionary biology of the photosynthetic reaction centres, the "business end of the process" of photosynthesis, demonstrating his ability to traverse the scientific disciplines with ease. Canfield explains how the coupling of two common reaction centres, photosystem I and photosystem II, was the remarkable achievement of oxygenic photosynthesis. This coupling allowed the abundant and ubiquitous compound water — as opposed to less-abundant reduced substances such as hydrogen gas, hydrogen sulphide or reduced iron — to fuel the process. The first organisms that manufactured and made use of this apparatus, the cyanobacteria, are the focus of chapter four. Long unrecognized and underappreciated because of their microscopic size, cyanobacteria are now known to be important primary producers not only in environments analogous to ancient Earth, such as microbial mats in intertidal zones, but in the open ocean as well. They also play a key role in nutrient cycles, converting inert dinitrogen gas to biologically available nitrogen through the process of nitrogen fixation.

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In the remainder of the book, Canfield marches through the 2.5-billion-year history of Earth's oxygenation. At each step of the way, Canfield presents the prevailing theories, and the evidence both for and against them. It transpires that seemingly compelling isotopic and fossil evidence from the 1980s that cyanobacteria evolved around 3.5 billion years ago has faced serious reinterpretation in the past decade. It turns out that the fossils may not be cyanobacteria, or even fossils at all, and the isotopic patterns can be generated by other means.

The debate surrounding the timing of atmospheric oxygenation — which seems to have followed the emergence of oxygenic photosynthesis by hundreds of millions of years — is also explored in some depth. This lag period can be explained by an initially overwhelming flux of reduced substances from Earth's interior into the atmosphere. This flux diminished gradually with time as the planet aged, making way for the accumulation of oxygen in the atmosphere. The disappearance of distinct sulphur isotope signatures that characterized rocks older than 2.5 billion years is taken as firm evidence for the appearance of atmospheric oxygen at the time; only in an oxygen-free atmosphere can these isotopic signatures be produced and preserved. Interestingly, it seems that the oceans remained anoxic until approximately 600 million years ago; this interval of time has come to be known as the 'Canfield Ocean' in recognition of Canfield's seminal 1998 paper on the topic. In that paper, Canfield reinterprets existing geologic evidence in terms of an anoxic and hydrogen-sulphide-rich deep ocean, and provides a quantitative model that explains how oceanic and atmospheric evolution could have been decoupled. It is only appropriate that Canfield himself presents a status update on the accumulating geologic evidence that the 'Canfield' deep ocean was rich in ferrous iron rather than hydrogen sulphide. Other uncertainties, such as whether a second rise in atmospheric oxygen levels approximately 550 million years ago triggered the advent and rise to dominance of animals, are also explored.

For someone who hasn't kept up with the fast-paced literature on the subject, Canfield's *Oxygen* — an authoritative account of the evolution of atmospheric and oceanic oxygen — is the perfect way to catch up. For those more familiar with the latest developments, the book reads like a warm-hearted family history of the scientists involved in the exploration of Earth's oxygenic history. The book also serves as a reminder for the research community of the outstanding debates: after nearly a century of investigation, much remains to be learnt about the trajectory of the oxygenation of the atmosphere and oceans, and the evolutionary history of the organisms that produce and consume this most important atmospheric gas. ❐

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