

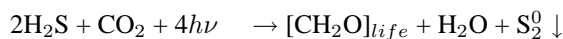


The theoretical case for the onset of oxygenic photosynthesis in the Hadean

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The process of anoxygenic photosynthesis was mastered at least by early Archaeal times (Westall et al., 2001, Precamb. Res. 106, 93). Why then should we assume that it took another billion years or so for life to figure out how to use water, energized by photons, as a reductant for biosynthesis? Imagine a tidal plane at 4 Ga where anoxygenic phototrophic bacteria are being supplied with organic and hydrothermal nutrient (e.g. $C_6H_{12}O_6$, H_2 and H_2S) and trace metals (Ca, Fe, Mg, Mn, Ni, Co) from subaerial hot springs. Using a reaction centre (RCI, precursor to photosystem I of cyanobacteria), they converted CO_2 into biomolecules, for example:

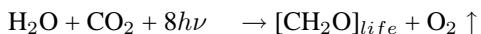


where $h\nu$ is the energy of a photon. These photosynthesizers were protected from harsh UV by chemical and detrital clays and photolytic manganates such as ranciéite [$CaMn_4O_9 \cdot 3H_2O$]. Manganese, as Mn^{III} and Mn^{II} , reduced from Mn^{IV} in ambient minerals by organic molecules and sequestered into the membrane (Parker et al. 2004, GCA, 68, 4809), would have adventitiously lent protection against hard photons. And it would have detoxified side-products of this radiation, i.e., various reactive oxygen species, through Mn-dependent superoxide dismutase as it does in the cyanobacterium *Chroococidiopsis* (Daly et al. 2004, Science 306, 1025). Manganese could protect cells from hard UV injury because of its proneness to short-wavelength photo-oxidation and its variable valence states.

Once adsorbed at carboxyl and hydroxyl sites in a prototype reaction centre on the surface of an anoxygenic photosynthesizer, four manganese ions were likely to have organized themselves, as they would in the mineral hollandite, in one of two possible

3Mn open cubane structures ligated to a fourth, 'dangling' Mn (Sauer and Yachandra, 2004, BBA, 1655, 140, fig. 3). The open cubane was closed with Ca. Fortuitously, the Ca^{2+} and the distal Mn^{2+} were hydrated, as they can be in ranciéite. Photons gathered from antennae drove the initially hydrated ($\text{Mn}_3\text{O}_4\text{Ca}\cdot\text{H}_2\text{O}\cdot\text{Mn}\cdot\text{H}_2\text{O}$) complex to higher redox states in 5 stages. Two oxygen atoms from water were retained while 2 protons and 2 electrons and 2 activated hydrogen atoms were released to the cell for biosynthesis. The oxygen was then released as O_2 waste, hence the name - the oxygen-evolving centre (OEC) (Messenger 2004, PCCP, 2004, 6, 4764).

The OEC is still housed at the outward-facing domain of photosystem (PSII) employed by all cyanobacteria and plants. Allen (2005, FEBS lett. 579, 963) argues that the emergence of oxygen-evolving photosynthesis was facilitated by gene doubling (a common form of genetic 'twinning') of an ancestral reaction centre (RCI) to give two differing reaction centres (RCI and RCII) of which only one was expressed at any one time, controlled by a redox switch. Then, a *simple* mutation disabled the redox switch so that both photosystems were expressed at the same time. This, like other entropy-driven evolutionary changes, must have happened quickly. Shared electron carriers then connected the two, newly co-existing photosystems, viz. PSI and PSII, with its newly acquired OEC, giving an electrochemical potential high enough to oxidize water:



Invagination of the cell membrane containing PSI and PSII led to the emergence of the cyanobacteria, organisms that were eventually to change the face of the planet to its present blue-green cast. Given such simple gene doubling, mutations and the fact that a minimum of genetic control was required for a hydrated $[\text{Mn}_3\text{CaO}_4]\text{-Mn}$ complex to take up a shape within the membrane that would facilitate the oxidation of water, the innovation surely would have followed soon after the onset of anoxygenic photosynthesis.

The common factor in the emergence of both chemosynthesis and oxygenic photosynthesis is the role minerals and mineral clusters took in providing a reactive and catalytic infrastructure as well as intrinsic vital function. Reaction with biogenic methane, the use of oxygen as an electron acceptor and the oxidation of ferrous iron, kept oxygen concentrations vanishingly low until the early Proterozoic

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