Emergence of the First Oxygenic Phototroph on Earth: Effect of Carbonate Equilibria on the Microbial Oxidation of Manganese

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The innovation of oxygenic photosynthesis is argued to have transformed the Earth's atmosphere and been the driving force that led to the evolution of O_2-based respiratory metabolisms. At the heart of this biological innovation is the photosystem II (PSII) enzyme complex with ability to

split water into O_2. This energy demanding chemical reaction is carried out in PSII by coupling the free energy of the already existing chlorophyll photochemistry (evolved from ancestral anoxygenic photosynthesis?) with an inorganic catalyst (Mn_4CaO_x) in the active site. Remarkably, little bio-diversity exists among PSIIs; all use the same inorganic core and nearly identical reaction center proteins. We have previously postulated that the first oxygenic PSII may have originated from anoxygenic phototrophs that bound and photooxidized Mn^{2+} as bicarbonate complexes. Here we use electrochemistry and electron paramagnetic resonance (EPR) to characterize the Mn^{2+} bicarbonate complexes that form in solution. The charge and structure of these complexes together with the greatly reduced oxidation potential to Mn^{3+} explains why bicarbonate stimulates the rate of photoassembly of the Mn_4CaO_x-cluster during biogenesis of PSII. To test the impact of carbonate equilibria on cyanobacteria, we carried out carbonate depletion/repletion studies on whole cells of *Arthrospira maxima*, a cyanobacteria isolated from alkaline soda lakes. Bicarbonate depletion lowers the electron donation rate and the O_2 yield at a site within the Mn_4CaO_x-cluster. This work supports the hypothesis that carbonate binding to this cluster is essential in some PSIIs and could have played a key role in the evolution of oxygenic photosynthesis in the CO_2-rich archean era.