Bicarbonate is not a physiological substrate of Photosystem II

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Photosystem II (PSII) produces essentially all the molecular oxygen (O_2) in the atmosphere. The photochemistry of this large transmembrane protein complex has radically changed the planet since its evolutionary origin over 2.5 billion years ago. PSII catalyses a light dependent charge separation to drive electron transfer from water to plastoquinone and, as a by product of the reaction, oxidizes water, which releases O_2. The oxidation chemistry proceeds *via* a catalytic component called the oxygen evolving complex (OEC). The OEC consists of a bio-inorganic core containing four manganese ions joined by oxo bridges, and a calcium ion ($Mn_4O_xCa_1$). Additionally, it is coordinated to a number of surrounding amino acids from the supporting protein matrix. The mechanism of oxygen formation is subject to considerable speculation.

During the last several decades there has been simmering debate over the precise nature of the immediate substrate of the OEC. It is widely accepted that water is the ultimate substrate based on labeling studies with $H_2{}^{18}O$. However bicarbonate has been considered as an alternative intermediate and this has never been fully discounted. The interest in HCO_3^- has recently been rekindled by the inclusion of a (bi)carbonate ligand in the OEC in a crystal structure of PSII at 3.5 Å resolution (Ferreira *et al*., 2004).

Using ^{18}O labeled bicarbonate in conjunction with membrane inlet mass spectroscopy the substrate flux into O_2 has been measured in three species of photosynthetic organisms, including a cyanobacterial species requiring high bicarbonate (400 mM) to grow. Evidence is presented that bicarbonate is not the physiological substrate of the OEC. Bicarbonate can only be oxidized by one in a few thousand PSII.

Ferreira, K.N., Iverson, T.M., Maghlaoui, K., Barber, J. & Iwata, S. (2004) *Science* **303**, 1831–1838.in 0