How likely is it for oxygenic photosynthesis to evolve?

Robert E. Blankenship
Washington University in St. Louis
Departments of Biology and Chemistry
Photosynthesis - The Conversion of Light Energy into Chemical Energy

PS is the source of all our food and most of our energy resources on Earth

Michael Hagelberg
Types of Phototrophic Organisms

- Chlorophyll-based phototrophic organisms are found only in the Bacterial and Eukaryal domains.
- Phototrophs are either **oxygenic** (oxygen evolving) or **anoxygenic** (non-oxygen evolving).
- All phototrophic Eukaryotic chloroplasts were derived via **endosymbiosis** of cyanobacteria.
All PS organisms contain a light-gathering antenna system and an electron-transferring reaction center.
Extreme diversity of antenna systems strongly suggests multiple independent evolutionary origins - Adaptation to different photic environments.
Photosynthetic Reaction Centers

Structural conservation of RCs suggests a single evolutionary origin.
Photosynthetic Prokaryotes

- There are six seven known bacterial phyla with chlorophyll-based photosynthetic members.
- They have varied modules of antennas, reaction centers, cofactor biosynthesis, and carbon fixation pathways.
- Each module has a unique evolutionary history.

Homann-Marriott and Blankenship, *ARPB* (2011)
Oxygenic Photosynthetic Organisms

Electron transport proteins

- \( \text{bc}_{1} \) complex
- \( \text{b}_{6}f \) complex
- alternative complex
- cytochromes
- iron sulfur cluster
- auracyanin
- plastocyanin
- oxygen-evolving complex

Oxygenic phototrophs have two RCs working in tandem.
Chlorophyll is a highly colored molecule that is central to photosynthesis.

- Light must first be absorbed by chlorophyll or other pigments before it can be stored as chemical energy.
- Chlorophyll is usually associated with specific proteins.
Chlorophyll Photon Absorption

Electron transfer takes place from the lowest excited state.
Pigment Conjugation and Electronic Properties

- Pyrrole-ring reduction: Decreased size of $\pi$-$e^-$ system (porphyrin $\rightarrow$ chlorin $\rightarrow$ Bchlorin) gives bathochromic $Q_y$ shift.

- Substituent type and position: 3-formyl etc. add conjugation length and give bathochromic $Q_y$ shift; 7-formyl (chlorin) and 7-oxo (bacteriochlorin) do the opposite.

Slide courtesy of Dewey Holten and Jon Lindsey
Excited states can be both strong oxidizing and strong reducing agents—very chemically reactive.

- The primary energy storing step in chlorophyll-based photosynthesis is the excited state acting as a reductant.
These diagrams incorporate both kinetic and thermodynamic information, and also suggest evolutionary relationships among photosynthetic reaction centers.

Origin and Early Evolution of PS

To understand the origin and early evolution of photosynthesis, must consider mechanisms and evolution of many subsystems and processes:

- Reaction centers (including
- \( \text{O}_2 \) Evol Center)
- Pigments (Chls, carotenoids, bilins)
- Antenna complexes
- Electron transfer pathways
- Carbon fixation pathways
- Photoprotection mechanisms

Horizontal gene transfer has been widespread.
Mosaic Evolution of Photosynthesis

- All photosynthetic organisms are chimeric.
- Different parts of the photosynthetic machinery have distinct evolutionary histories.
- There is no simple path for “evolution of photosynthesis”.

Reaction Center

Pigments

Antenna

Photosynthetic Cell
Reaction Center Evolution

基因复制

Homodimeric zone

Oxygen evolving zone

 PSI

PSII

RCI - Type 1.5 RC ??

Root?

Earliest RCs

Type 2 RC

Type 1 RC

= Gene Duplication

The slight structural asymmetry of the reaction center L and M subunits gives rise to a strong functional asymmetry of electron transfer pathway and the $2 \, e^- \, Q_A/Q_B$ gate.
Reaction Center Evolution

Insertion-deletion (Indel) analysis

Khadka et al. Submitted
Transition to Oxygenic Photosynthesis

Extensive gene recruitment/HGT

Transitional forms

Gloeobacter

Cyanobacteria

Plastid Origin

Anoxygenic Photosynthesis

Time

Oxygenic Photosynthesis

Raymond and Blankenship *BBA* (2004)
Cyanobacterial Photosystem II

Umema et al. (2011)
Nature 473: 55-61
Photosystem II from cyanobacteria

Umena et al. (2011)
Nature 473: 55-61
Origin of Oxygen Evolution

Reaction: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

Changes between the anoxygenic RC and PS2 are:

- A redox potential $> 1$ V, which requires change from BChl (870 nm) to Chl (680 nm)
- A charge-accumulating system to interface $1$ e$^-$ photochemistry to $4$ e$^-$ oxygen chemistry - Mn cluster - Singular event!
- A much more complex protein complement
- Linked photosystems ??

Possible intermediate stages involve:

- Transitional electron donor, eg \( \text{H}_2\text{O}_2 \)
- Recruitment of Mn center, eg catalase or Mn mineral
- Switch of pigment to Chl from BChl

Too big of a change to occur in one step

Is oxygenic photosynthesis an inevitable evolutionary development?

- Oxygenic photosynthesis is mechanistically much more complex than anoxygenic PS.
- It is very unlikely to be an early form of PS on any world.
- Oxygenic PS uses a ubiquitous electron donor molecule, $\text{H}_2\text{O}$, and produces a high energy form of stored products.
- It is so efficient that it is likely to be the dominant form of PS, providing that the very high barrier to its evolution can be surmounted.

What is the long wavelength limit for oxygenic photosynthesis?

• The red limit for oxygenic PS using the familiar two photosystem architecture is not certain but is probably about 750 nm.
• Using a three or more photosystem architecture, it could be at significantly longer wavelengths.
• Anoxygenic PS works out to 1000 nm.
• Depending on the type of photopigments used, the red edge might be in the visible or near IR or there may be multiple red edges or a gradual one.
• It is difficult to see how photosynthesis could be driven using infrared light that only excites vibrational transitions.
Acknowledgements

Former Group Members

Jason Raymond  Wes Swingley  Martin Hohmann-Marriott  Sumedha Sadekar

Supported by NASA Exobiology and Astrobiology

Collaborators
Peter Gogarten-U Conn.
Hyman Hartman-MIT
Radhey Gupta-McMaster U
Nancy Kiang-NASA GISS
Niki Parenteau-NASA Ames