Photosynthesis: Molecular Mechanisms – Global Effects

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In this talk:

1. Why photosynthesis?
2. What is photosynthesis?
3. Some of own research
Why photosynthesis?

(i) global effects: evolution & bio-geo.chemical cycles

\[ 6\text{H}_2\text{O} + 6\text{CO}_2 \xrightarrow{\text{light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]
Earth's Biogeologic Clock

Billions of Years Ago

Precambrian

1. Origin of Earth
2. Algal Kingdoms
3. Cyanobacteria plus other phototrophs
4. Origin of Life

- Vascular Plants
- Shelly Invertebrates
- Mammals
- Humans

Macroscopic Eukaryotes

- Paleozoic
- Mesozoic
- Cenozoic

Science 289: 1703-1705.
Cyanobacteria, the first O$_2$-evolving PS organism.
Generalized scheme of bio-geo-chemical cycle

- Oxygen
- Carbon
Table 2: Annual gain and loss of atmospheric oxygen (Units of $10^{10}$ kg $O_2$ per year)

<table>
<thead>
<tr>
<th>Gains</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Photosynthesis (land)</td>
<td>16,500</td>
</tr>
<tr>
<td>Photosynthesis (ocean)</td>
<td>13,500</td>
</tr>
<tr>
<td>Photolysis of N2O</td>
<td>1.3</td>
</tr>
<tr>
<td>Photolysis of H2O</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>Total Gains</strong></td>
<td>~ 30,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Losses - Respiration and Decay</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Aerobic Respiration</td>
<td></td>
</tr>
<tr>
<td>Microbial Oxidation</td>
<td></td>
</tr>
<tr>
<td>Combustion of Fossil Fuel (anthropologic)</td>
<td></td>
</tr>
<tr>
<td>Photochemical Oxidation</td>
<td></td>
</tr>
<tr>
<td>Fixation of N2 by Lightning</td>
<td></td>
</tr>
<tr>
<td>Fixation of N2 by Industry (anthropologic)</td>
<td></td>
</tr>
<tr>
<td>Oxidation of Volcanic Gases</td>
<td></td>
</tr>
<tr>
<td><strong>Total Losses</strong></td>
<td>~ 30,000</td>
</tr>
</tbody>
</table>

2 $H_2O + 4$ hv → 4 $e^- + 4$ $H^+ + O_2$

Residence time in the atmosphere: 4 500 years

300 Gt $O_2$ per annum
Global carbon cycle and fixed C (Gt)
Calvin-Benison cycle of chloroplasts, mito-respiration

Global Flows of Carbon
(Petagrams of Carbon/Year)

ATMOSPHERE
750+

> 100*

PLANTS SOIL
2,000

OCEANS
800

COAL OIL GAS
10,000

1 Pg = 1 Gt

* Deforestation contributes between 1 - 2

6.5

Graphic by Michael Ernst & Ske Houghton
The Woods Hole Research Center
Mauna Loa CO$_2$ increases

CO$_2$ concentration in ppmv

IPCC 2000 Scenarios for 2100 AD

Vostok Ice Core
For photosynthesis, the present levels of CO2 and T are suboptimal—chance for some compensation.

Fig. 7.3 The greenhouse effect. Simplified version of Figure 7.2. Some incoming solar radiation is reflected back into space by clouds, some is absorbed by the atmosphere, and some (mostly visible light) reaches the Earth’s surface. In turn, the Earth radiates heat as infra-red. Some of this is again absorbed by the atmosphere which then radiates part of it back to Earth and part of it back into space. This raises the current global mean surface temperature from about -18°C (the estimated steady-state temperature at which heat input and heat lost would come into balance in the absence of an atmosphere) to 15°C.
**CO$_2$ concentration, temperature, and sea level continue to rise long after emissions are reduced**

<table>
<thead>
<tr>
<th>Magnitude of response</th>
<th>Time taken to reach equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ emissions peak</td>
<td>Sea-level rise due to ice melting: several millennia</td>
</tr>
<tr>
<td>0 to 100 years</td>
<td>Sea-level rise due to thermal expansion: centuries to millennia</td>
</tr>
<tr>
<td></td>
<td>Temperature stabilization: a few centuries</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ stabilization: 100 to 300 years</td>
</tr>
</tbody>
</table>

Figure SPM-5: After CO$_2$ emissions are reduced and atmospheric concentrations stabilize, surface air temperature continues to rise slowly for a century or more. Thermal expansion of the ocean continues long after CO$_2$ emissions have been reduced, and melting of ice sheets continues to contribute to sea-level rise for many centuries. This figure is a generic illustration for stabilization at any level between 450 and 1,000 ppm, and therefore has no units on the response axis. Responses to stabilization trajectories in this range show broadly similar time courses, but the impacts become progressively larger at higher concentrations of CO$_2$. 

Intergovernmental Panel on Climate Change
The annual oil consumption of an average American family in 1970 (by now, it has increased by about 40%).
Man’s footprint on the planet today.
Why photosynthesis?

(ii) energy conversion:
The energetic basis of (virtually) all life on Earth, also source of fossil fuels
Renewable, CO$_2$-free energy sources...

SOLAR: 178,000 TW

GEOTHERMAL: 92,000 TW

- TIDAL POWER: 0.1 TW
- WAVE: 2 TW
- OCEAN THERMAL: 10 TW
- Wind: 172 TW
- WORLD ENERGY DEMAND: 13 TW

Photosynthesis: ~120 TW

World energy demand: 13 TW
To get 20 TW, 0.16% of land covered with PV panels with 10% efficiency (Current 13 TW, 150,000 Km²)

Global need. This map shows the amount of land needed to generate 20 TW with 10% efficient solar cells.
Whie Book - E

Photosynthesis
Biomass
Biofuels

Semiconductor/
liquid junctions
Hybrid systems

Photovoltaic
⇒ electricity
⇒ chemical
EBSA Biophysics Course on Solar Energy - Biological and Biomimetic Solutions
August 27 – 31, 2011
BRC, Szeged

http://www.artificialphotosynthesis.eu/solarschool/
gyozo@brc.hu
What is photosynthesis?

Light energy converted into chemical energy

$6\text{H}_2\text{O} + 6\text{CO}_2 \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$
Solar spectral irradiance outside atmosphere

Curve for black body at 5900°K

Solar spectral irradiance at sea level for direct beam (air mass 1 clear conditions)
Figure 2.3 Absorption spectrum of chlorophyll-\(a\) (chl-\(a\)) and chlorophyll-\(b\) (chl-\(b\)) and of the xanthophyll lutein dissolved in acetone. The intensity of the sun’s radiation at different wavelengths is given as a comparison.
The graph shows the absorption spectra of various pigments:

- **Chlorophyll b**
- **Phycoerythrin**
- **Phycocyanin**
- **Chlorophyll a**
- **β-Carotene**

The colors represent the absorption efficiency across different wavelengths, ranging from 250 nm to 700 nm, with peaks indicating high absorption at specific wavelengths. The x-axis is labeled as **Wavelength (nm)**, and the y-axis is labeled as **Absorption**.
The fate of excitation in molecular assemblies

Energy transfer: $D^* + A \rightarrow D + A^*$
(usually) depends on the distance ($R^{-6}$) and the mutual orientation of the pigment dipoles (ordered arrays!)
Funnel concept of the ‘energy flow’ in the light harvesting antenna and the reaction center

Figure 5.3 The funnel concept in photosynthetic antennas. Sequential excitation transfers from higher-energy pigments (blue-absorbing) to lower-energy pigments (red-absorbing) deliver excitations to the proximity of the reaction center.
Fig. 3.7. Fluorescence spectra of *Porphyridium cruentum* taken at different delay times after the exciting light pulse. B-phycoerythrin was selectively excited at 540 nm (taken from Yamaizaki et al., 1984).
Scheme of the light harvesting antenna and the photochemical reaction center

- Primary acceptor
- Photon
- Reaction center
- Pigment molecules
Molecular order in the antenna
Light harvesting complexes and reaction center in purple bacterial membranes

Model
Cogdell’s structure

AFM image of the native membrane
Hunter and coworkers, Nature, 2004
Ordered array of transition dipoles in LH2
emerging quantum mechanical descriptions
Energy migration / heat dissipation dynamics in reconstituted bacterial LH1 antenna

Control LH1

LH1 with Ni-Bchl

Chlorosome – ordered arrays of Bchls
Anisotropy (FDLD) of ‘artificial chlorosomes’ (synthetic porphyrin nanorods)

Orientation of transition dipoles w respect to the rod axis:

- $Q_x \ 43^\circ \pm 8$
- $Q_y \ 37^\circ \pm 7$
- $B_x \ 39^\circ \pm 4$
Anisotropic organization and microscopic manipulation of self-assembling synthetic porphyrin micro-rods that mimic chlorosomes, bacterial light-harvesting organelles

Submitted to JACS
Reaction center complex of purple photosynthetic bacteria

Michel, Deisenhofer, Huber – Nobel prize 1988
Bacterial Reaction Center
LHCII monomer

Kühlbrandt, Nature, 1994
Photosystem I: ReCe& LH antennae

Nelson and coworkers, 2003, Nature

45 transmembrane helices
PSII reaction center and core complexes

Barber and coworkers, Science, 2004; Umena et al. 2011 Nature: 1.9 Å resolution
PSII reaction center complex
PSII particulum

Barber, 2000
\[ \Delta \mu_{H^+} \sim \Delta \text{pH} + \alpha \Delta \psi \]
### Block diagram (the hierarchy) of photosynthesis

<table>
<thead>
<tr>
<th>Photophysics</th>
<th>Photochemistry</th>
<th>Biochemistry</th>
<th>Physiology</th>
<th>Ontogeny</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light absorption energy migration</td>
<td>charge separation redox chain</td>
<td>CO₂ ‘fixation’, Signal transduction Short-term regulation</td>
<td>synthesis, self-assembly repair transport Regulation</td>
<td>Ecology</td>
</tr>
<tr>
<td>~ 10⁻¹⁵ – 10⁻⁹ s</td>
<td>~ 10⁻¹² – 10⁻² s</td>
<td>~ 10⁻³ – 10³ s</td>
<td>~ 10² – 10⁶ s</td>
<td>~ 10⁵ – 10¹⁷ s</td>
</tr>
</tbody>
</table>

- **Pigments, complexes**
- **Membrane vesicle**
- **chloroplast**
- **cell, plant, ecosystem, biosphere**