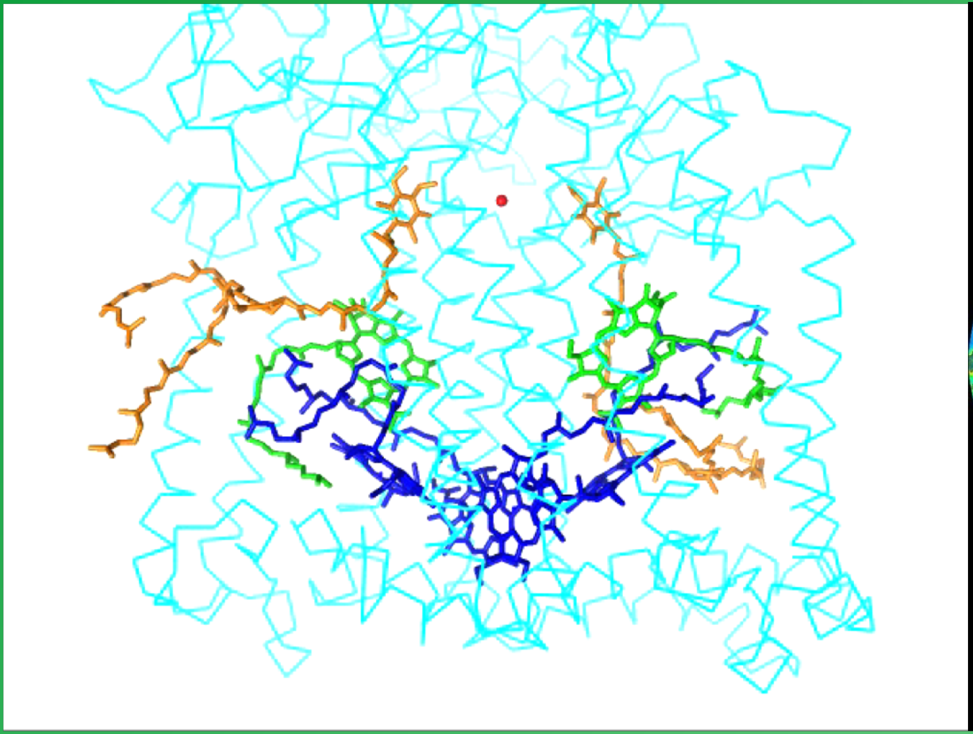
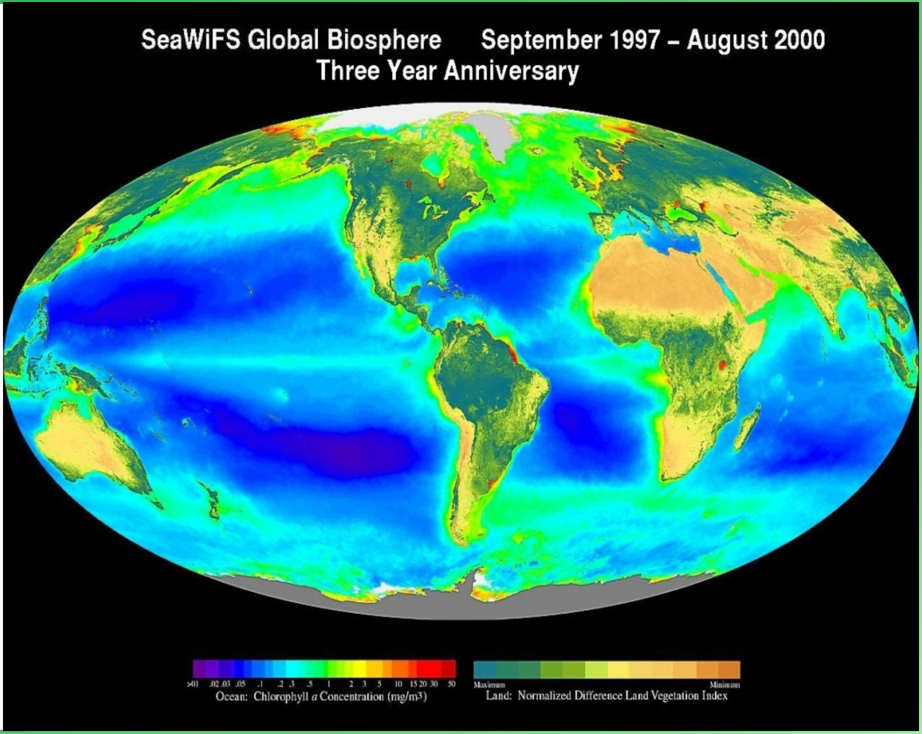
Photosynthesis

Molecular mechanisms



Michel, Deisenhofer, Huber – Nobel prize 1988

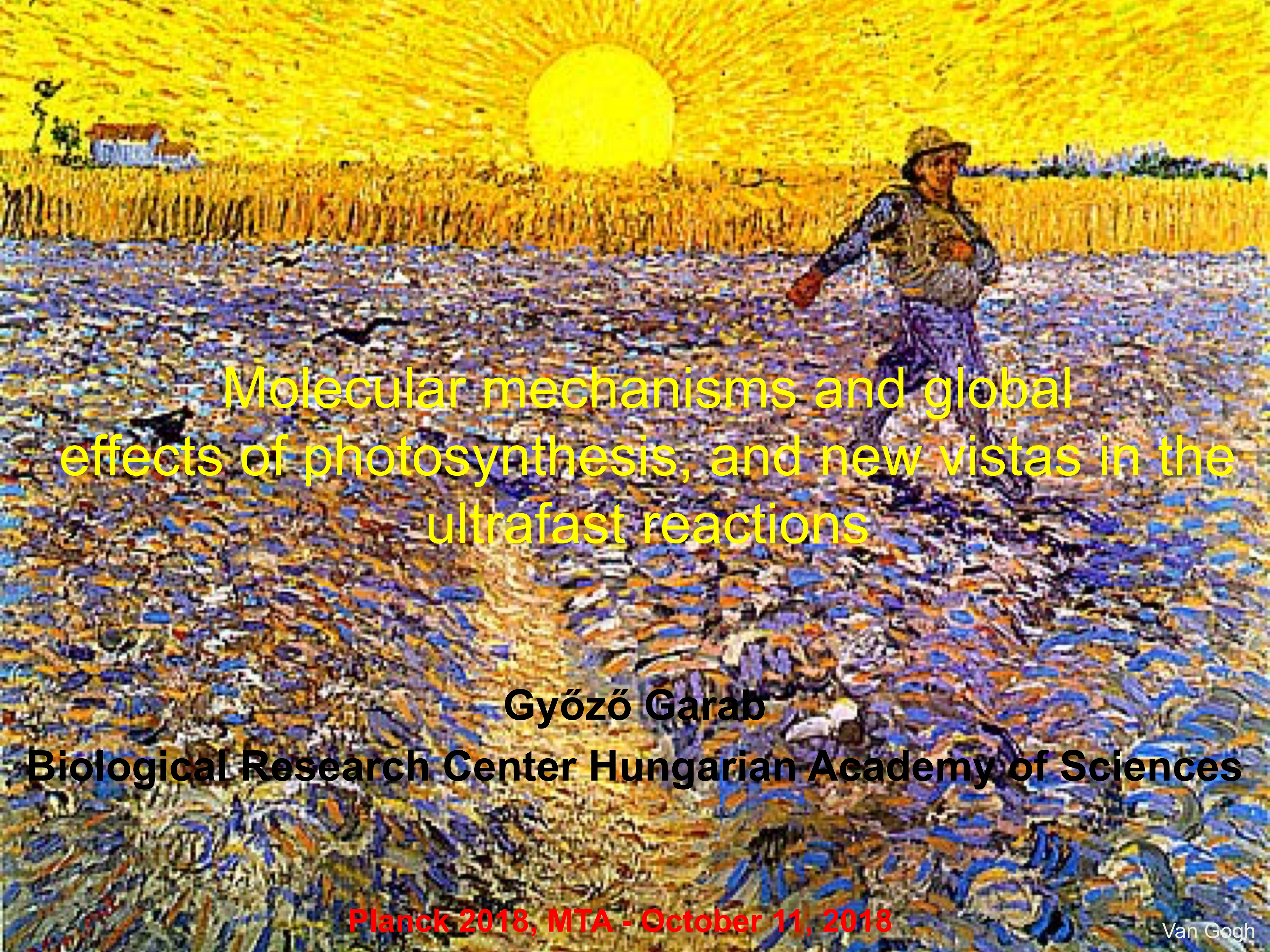
Global effects



$$6H_20 + 6CO_2 \xrightarrow{\text{photons}} C_6H_{12}O_6 + 6O_2$$

Oxygen-rich atmosphere (+ O_3-shield)

Energetic basis of virtually all life on Earth



Molecular mechanisms and global effects of photosynthesis, and new vistas in the ultrafast reactions

Győző Garab

Biological Research Center Hungarian Academy of Sciences

Planck 2018, MTA - October 11, 2018

Van Gogh

IN THIS TALK

Global Effects of Photosynthesis

Mechanisms of Photosynthesis

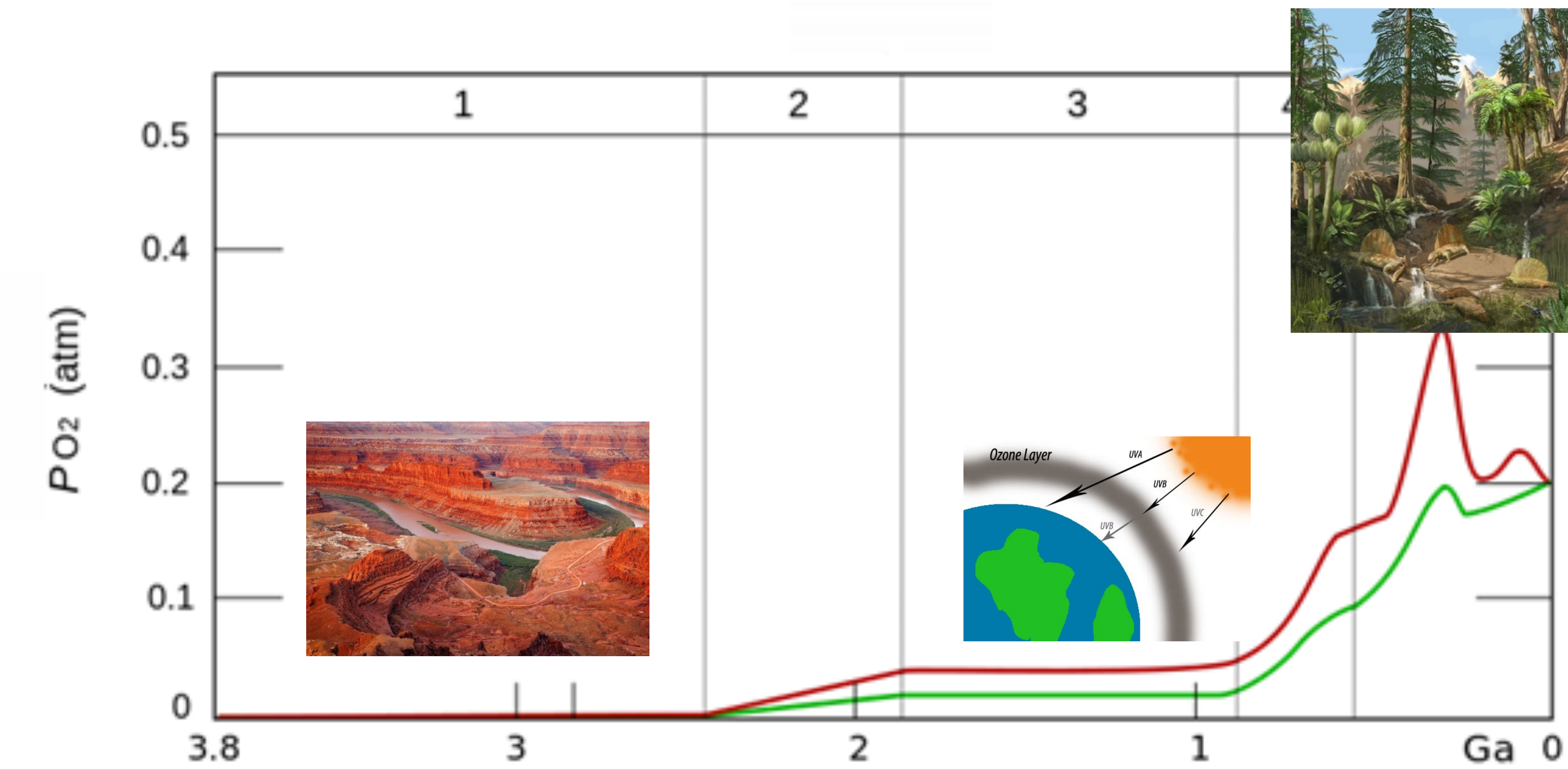
Ultrafast Processes - New Vistas at ELI-ALPS

Global Effects of Photosynthesis

Mechanisms of Photosynthesis

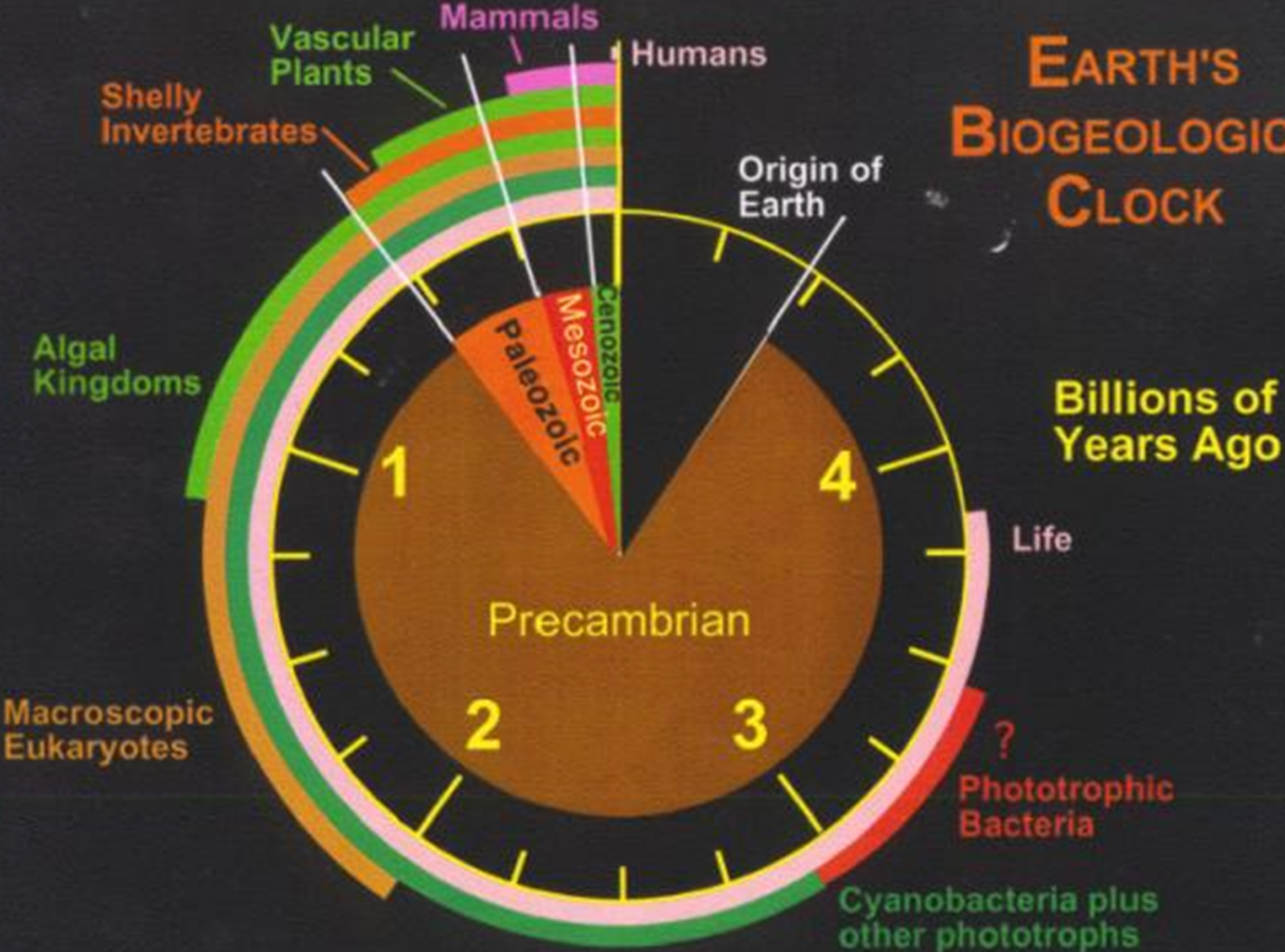
Ultrafast Processes - New Vistas at ELI-ALPS

THE ACCUMMULATION OF OXYGEN IN THE ATMOSPHERE



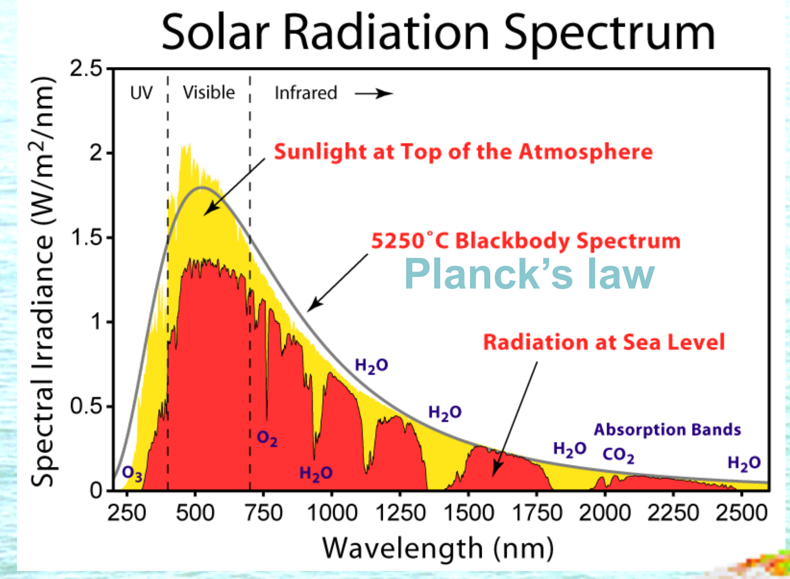
Based on Holland, H.D. (2006) *Phil. Trans. R. Soc. B*,

EARTH'S BIOGEOLOGIC CLOCK

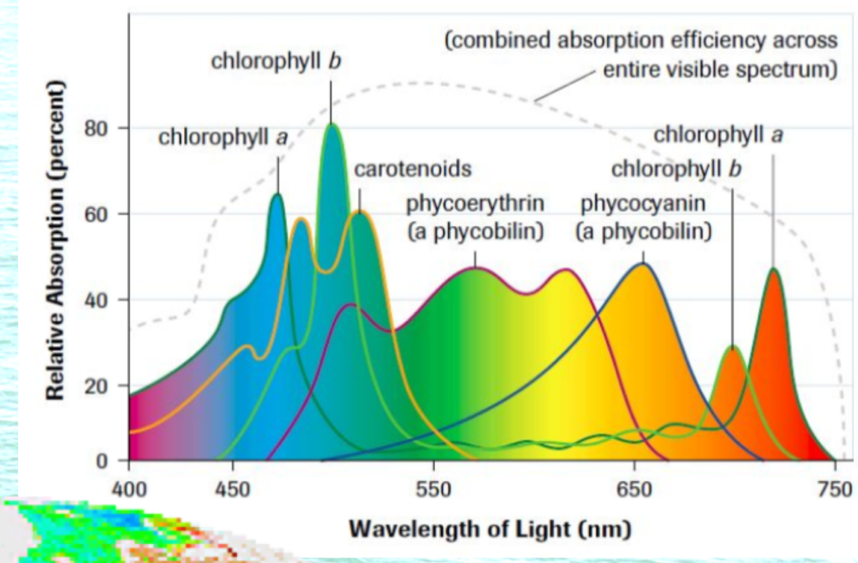


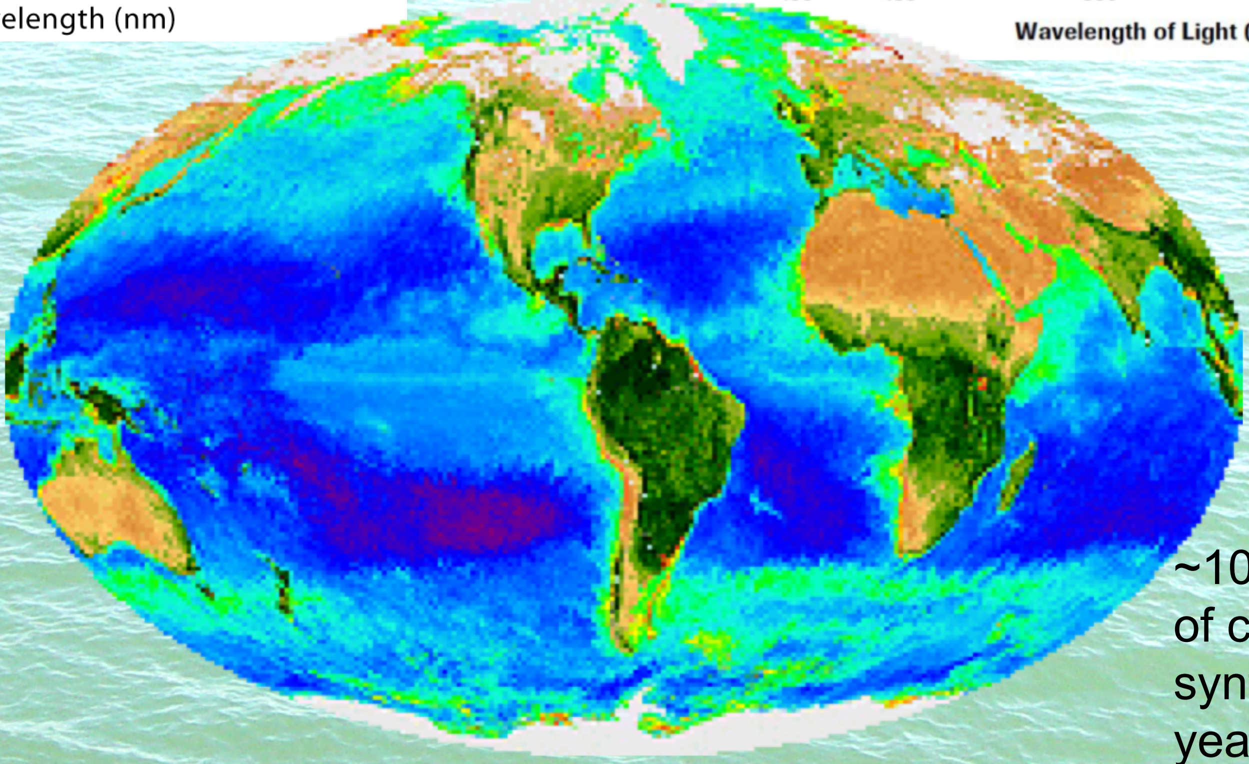
D. J. Des Marais (2000)
Science 289: 1703-1705.

Chlorophyll biosynthesis on a global scale

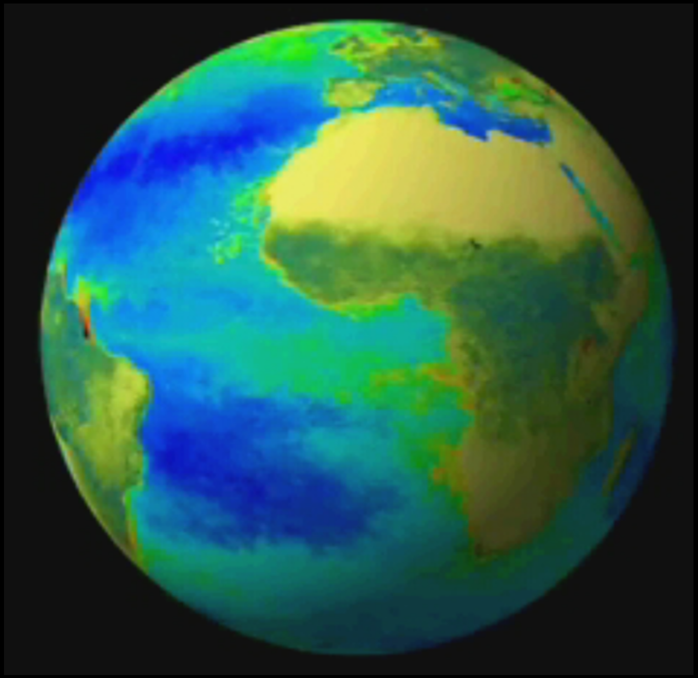


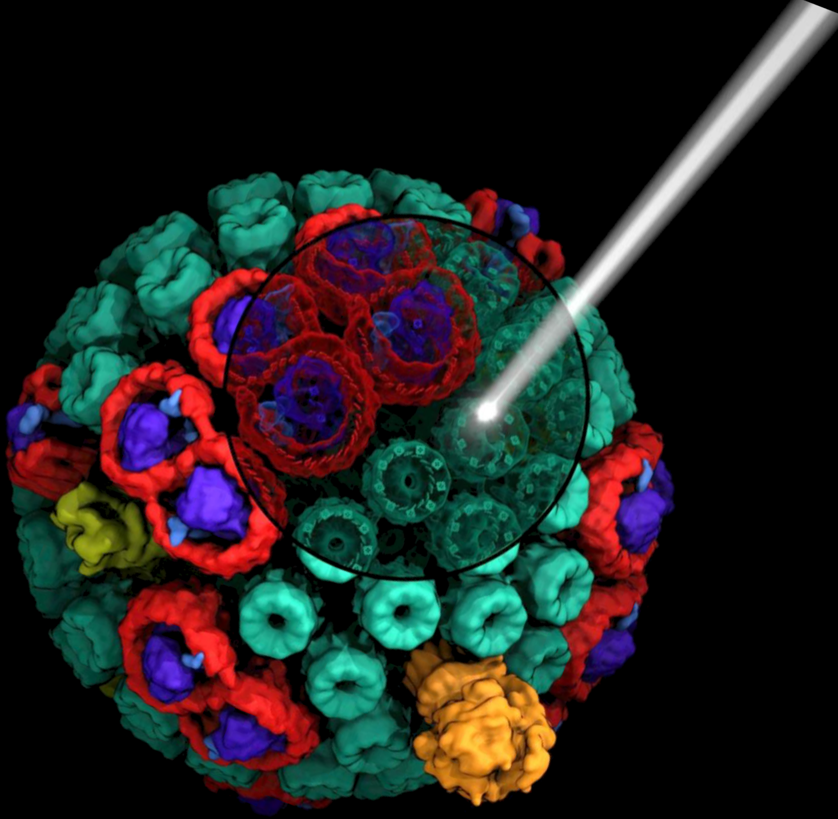
Solar Radiation Spectrum





~10^8-10^9 tonnes of chlorophyll synthesised per year.





$\longleftrightarrow$

1.3 x 10^{16} nm

$\longleftrightarrow$

60 nm

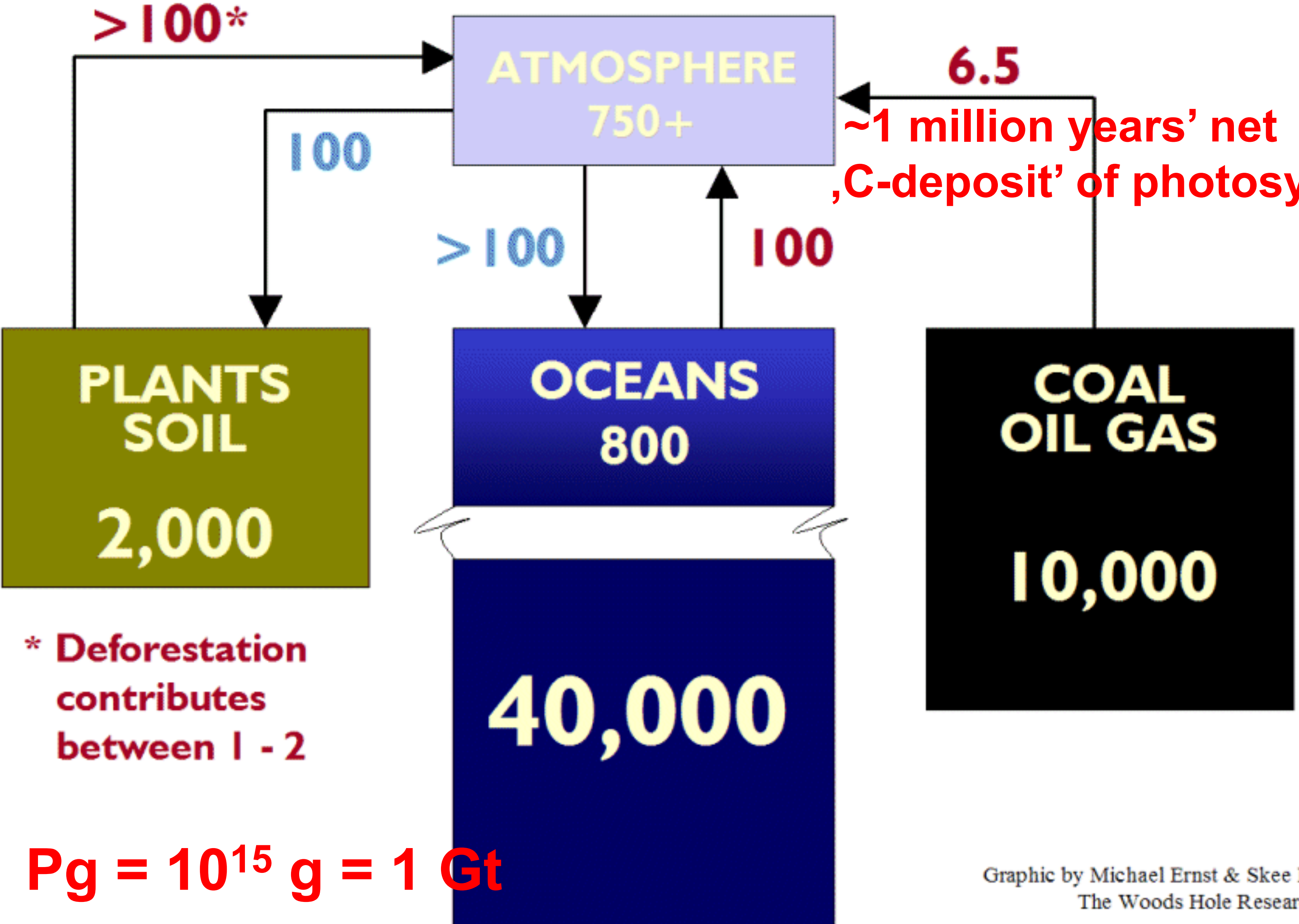
10^{32-34} chlorophylls on Earth

A single photosynthetic membrane representing ~4,000 chlorophylls

Global Flows of Carbon

(Petagrams of Carbon/Year)

The Woods Hole Research Center



>100*

ATMOSPHERE
750+

100

>100

100

6.5

~1 million years' net
,C-deposit' of photosynthesis

PLANTS
SOIL
2,000

OCEANS
800

40,000

COAL
OIL GAS
10,000

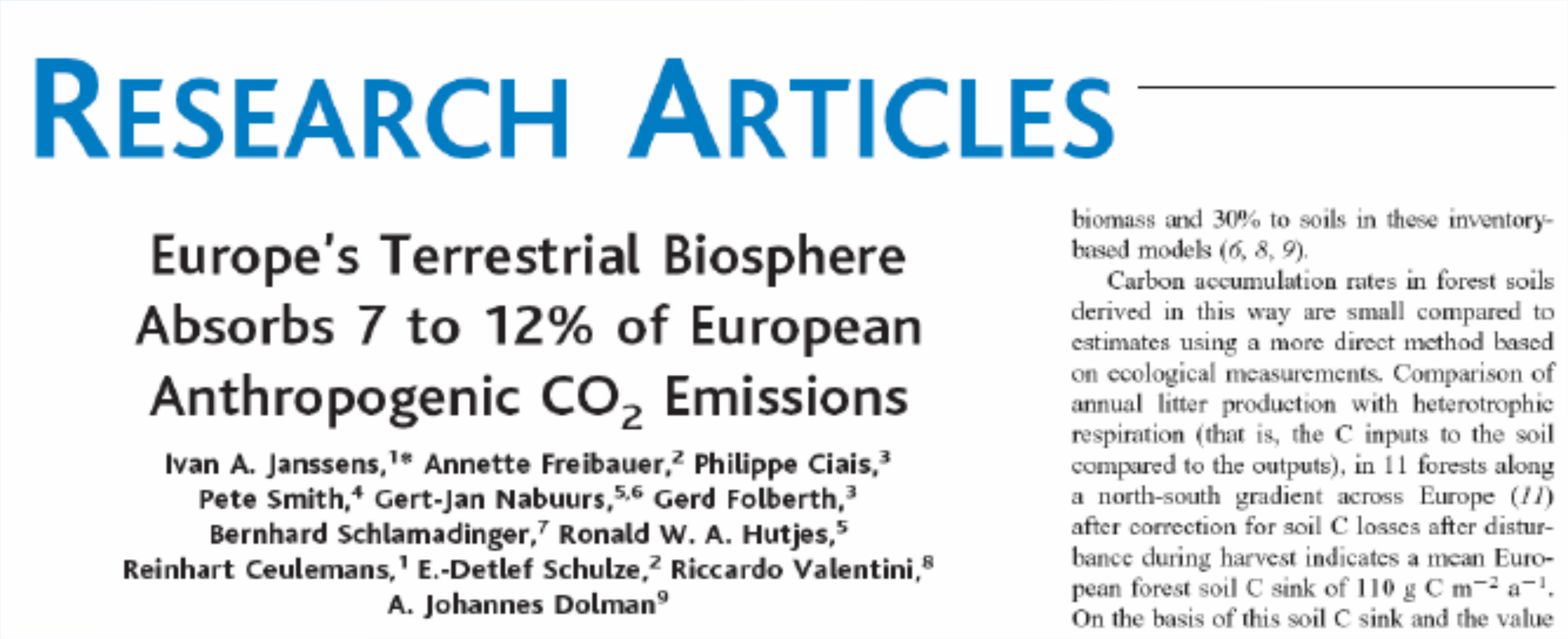
* Deforestation contributes between 1 - 2

1 Pg = 10^{15} g = 1 Gt

Graphic by Michael Ernst & Skee Houghton
The Woods Hole Research Center

In this 1970 picture, an average American family is surrounded by the barrels of oil they consume annually. Now this consumption is about 40% higher.

EUROPE gives a substantial contribution to anthropogenic carbon imbalance



RESEARCH ARTICLES

Europe's Terrestrial Biosphere Absorbs 7 to 12% of European Anthropogenic CO_2 Emissions

Ivan A. Janssens,[1*] Annette Freibauer,[2] Philippe Ciais,[3]
Pete Smith,[4] Gert-Jan Nabuurs,[5,6] Gerd Folberth,[3]
Bernhard Schlamadinger,[7] Ronald W. A. Hutjes,[5]
Reinhart Ceulemans,[1] E.-Detlef Schulze,[2] Riccardo Valentini,[8]
A. Johannes Dolman[9]

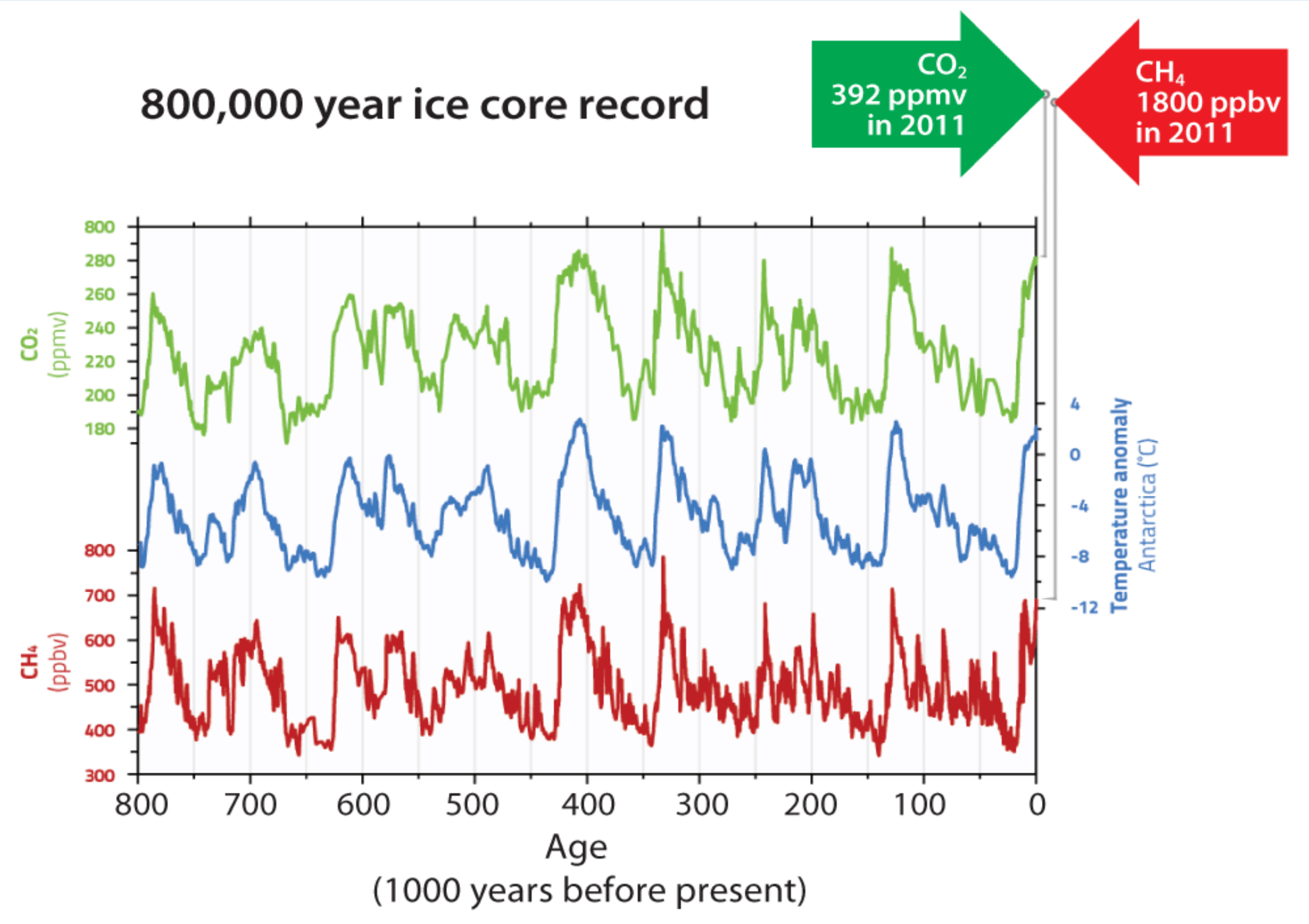
biomass and 30% to soils in these inventory-based models (*6*, *8*, *9*).

Carbon accumulation rates in forest soils derived in this way are small compared to estimates using a more direct method based on ecological measurements. Comparison of annual litter production with heterotrophic respiration (that is, the C inputs to the soil compared to the outputs), in 11 forests along a north-south gradient across Europe (*11*) after correction for soil C losses after disturbance during harvest indicates a mean European forest soil C sink of 110 g C m^{-2} a^{-1}. On the basis of this soil C sink and the value

Science **2003**, *300*, 1538

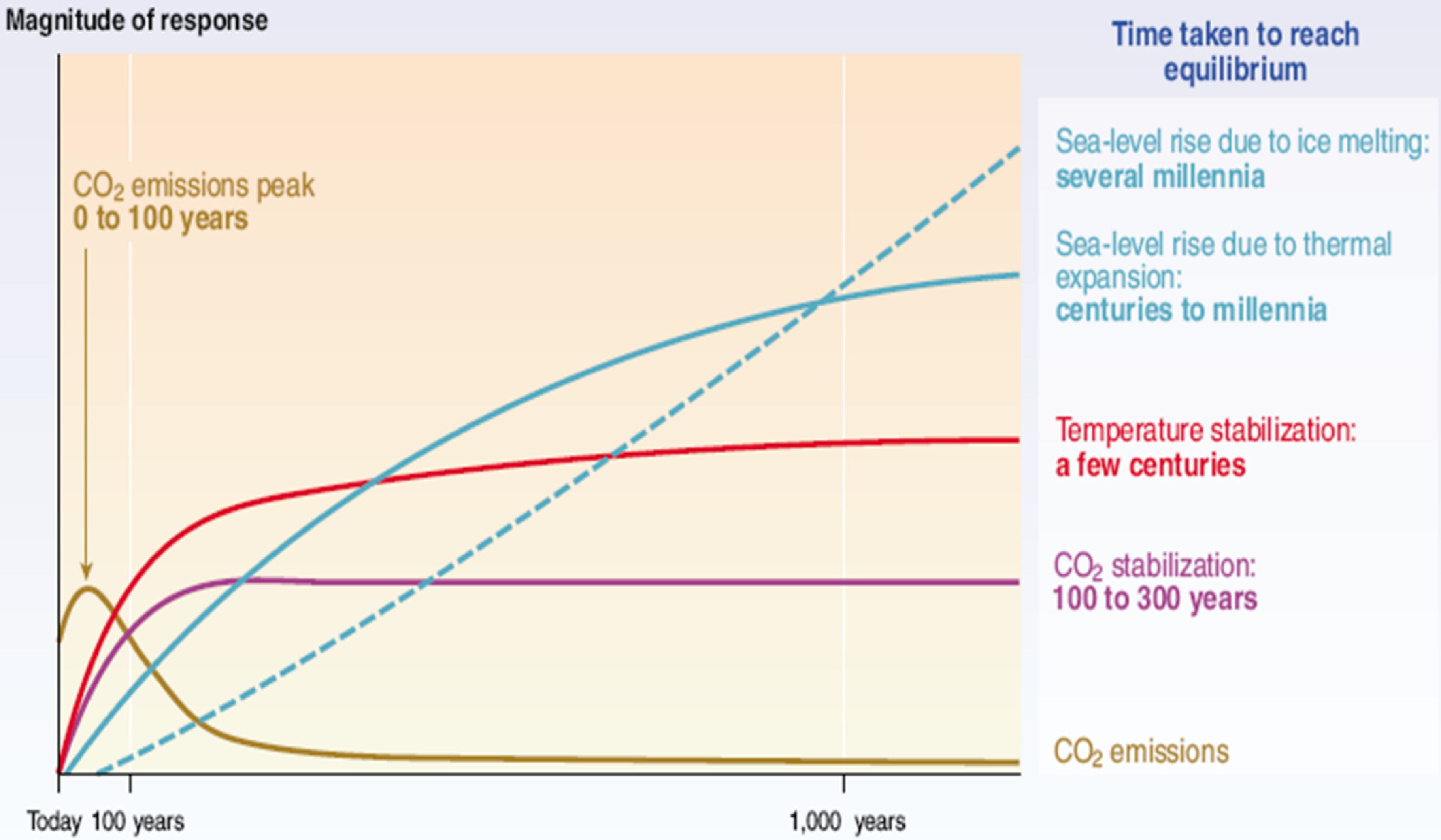
Correlation between the main greenhouse gases (CO_2 CH_4) and the temperature

www.co2.earth/daily-co2 - Oct 5, 2018: 405.44 ppm



http://anthropocenejournal.com/2012/02/21/is-civilization-at-risk-of-collapse/

CO_2 concentration, temperature, and sea level continue to rise long after emissions are reduced



Intergovernmental Panel on Climate Change

The Impacts of Climate Change on Growth and Development

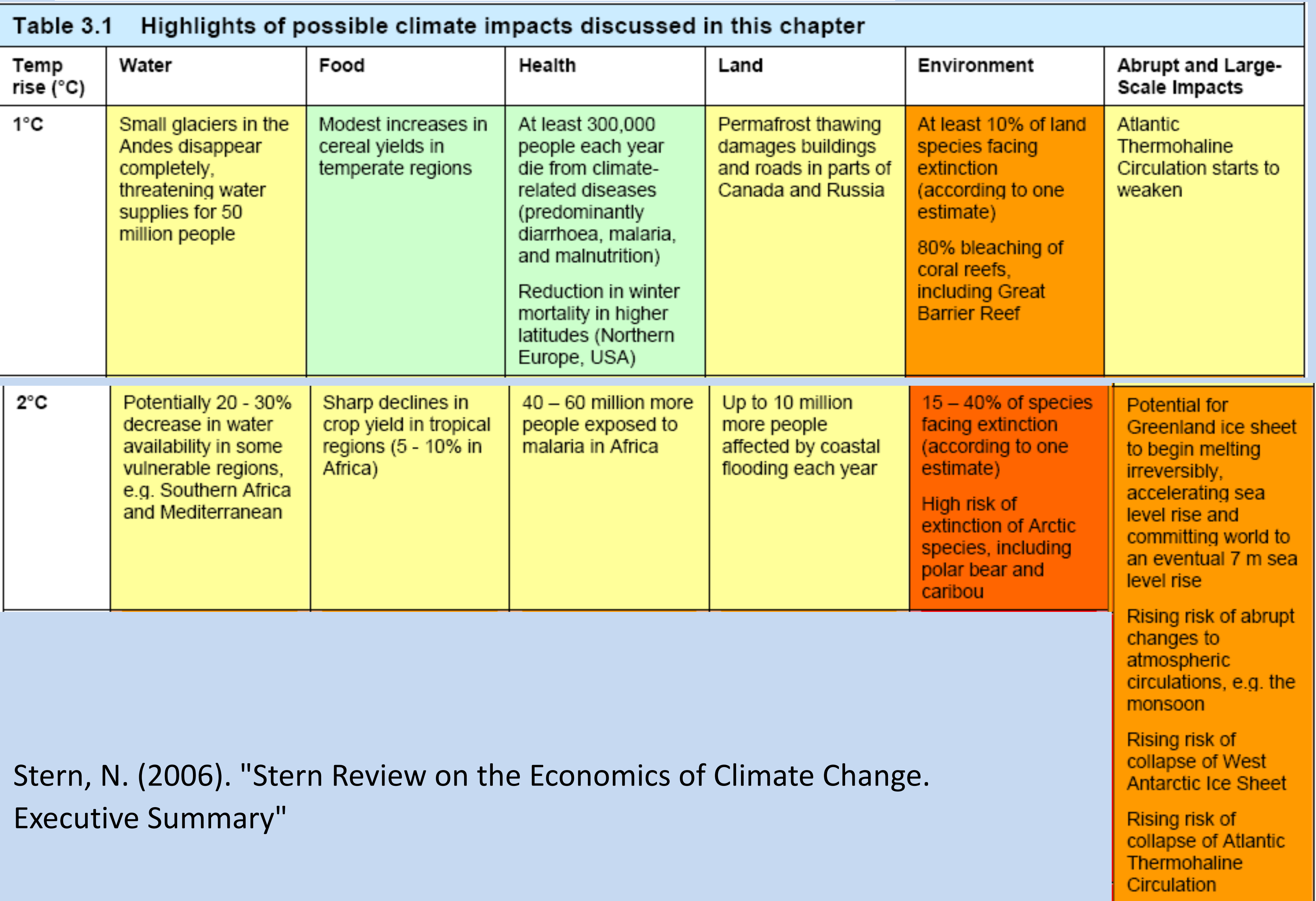
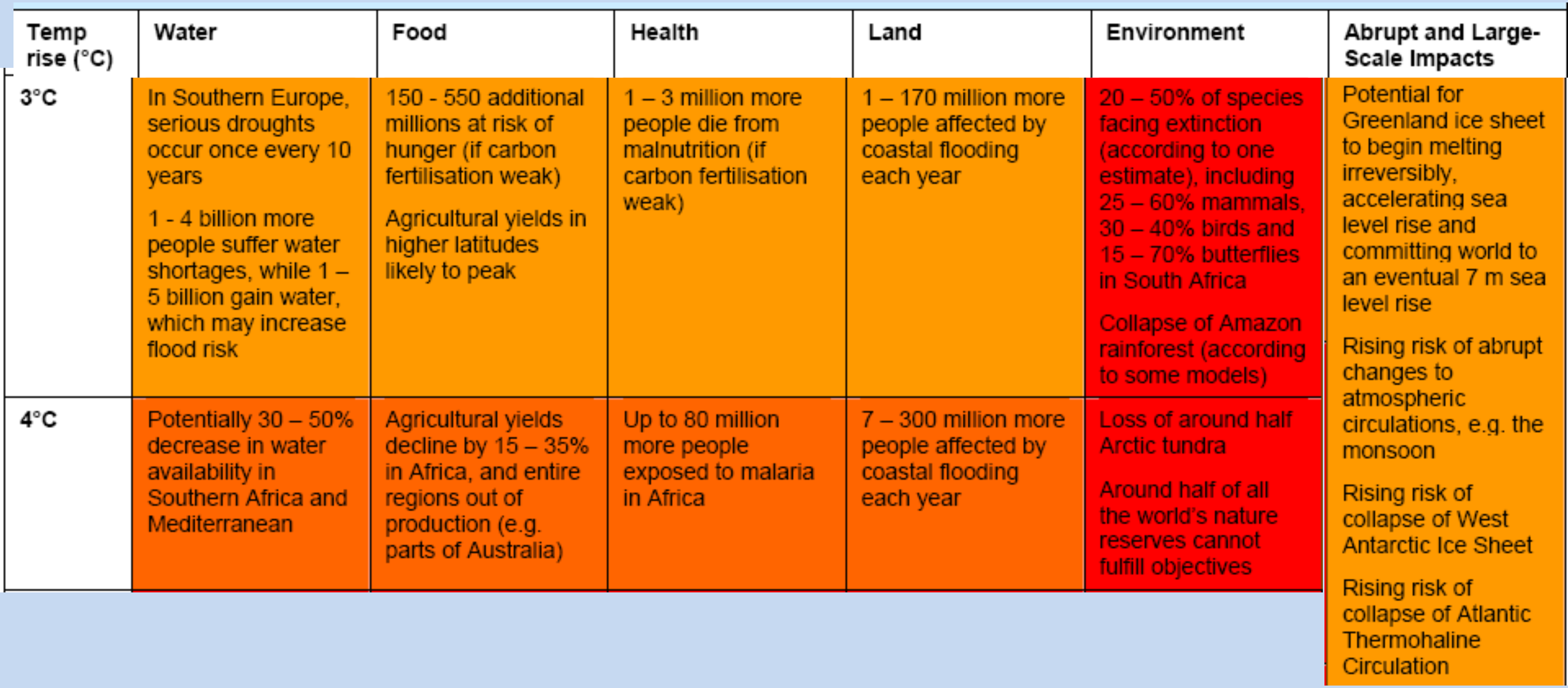


Table 3.1 Highlights of possible climate impacts discussed in this chapter

Temp rise (°C)	Water	Food	Health	Land	Environment	Abrupt and Large-Scale Impacts
1°C	Small glaciers in the Andes disappear completely, threatening water supplies for 50 million people	Modest increases in cereal yields in temperate regions	At least 300,000 people each year die from climate-related diseases (predominantly diarrhoea, malaria, and malnutrition) Reduction in winter mortality in higher latitudes (Northern Europe, USA)	Permafrost thawing damages buildings and roads in parts of Canada and Russia	At least 10% of land species facing extinction (according to one estimate) 80% bleaching of coral reefs, including Great Barrier Reef	Atlantic Thermohaline Circulation starts to weaken
2°C	Potentially 20 - 30% decrease in water availability in some vulnerable regions, e.g. Southern Africa and Mediterranean	Sharp declines in crop yield in tropical regions (5 - 10% in Africa)	40 – 60 million more people exposed to malaria in Africa	Up to 10 million more people affected by coastal flooding each year	15 – 40% of species facing extinction (according to one estimate) High risk of extinction of Arctic species, including polar bear and caribou	Potential for Greenland ice sheet to begin melting irreversibly, accelerating sea level rise and committing world to an eventual 7 m sea level rise Rising risk of abrupt changes to atmospheric circulations, e.g. the monsoon Rising risk of collapse of West Antarctic Ice Sheet Rising risk of collapse of Atlantic Thermohaline Circulation

Stern, N. (2006). "Stern Review on the Economics of Climate Change. Executive Summary"

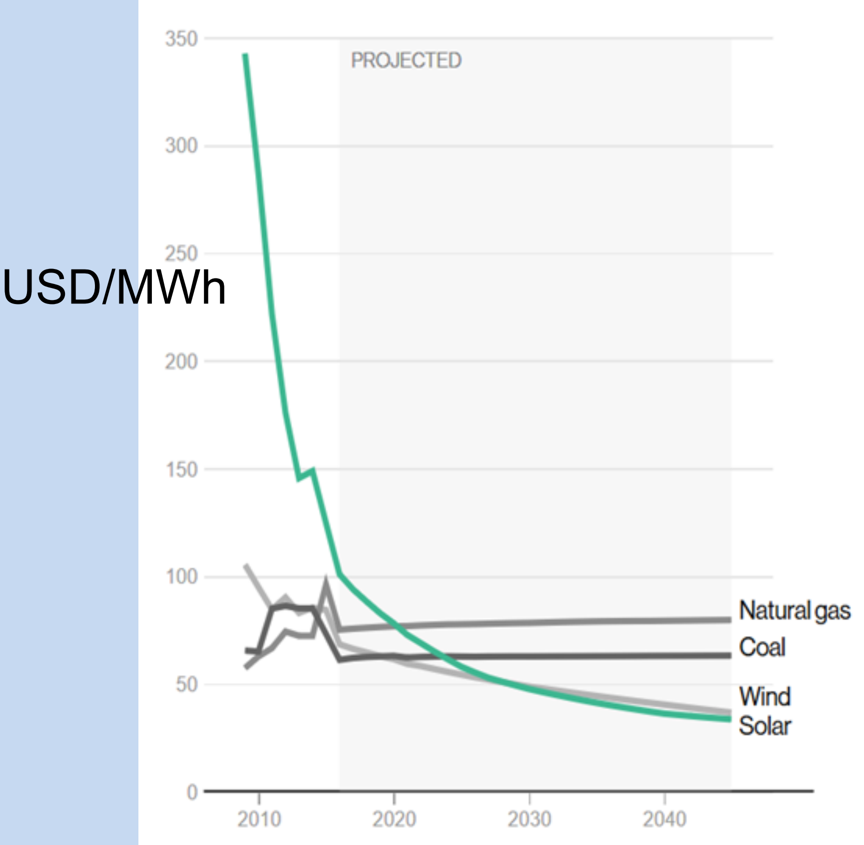


Temp rise (°C)	Water	Food	Health	Land	Environment	Abrupt and Large-Scale Impacts
3°C	In Southern Europe, serious droughts occur once every 10 years 1 - 4 billion more people suffer water shortages, while 1 – 5 billion gain water, which may increase flood risk	150 - 550 additional millions at risk of hunger (if carbon fertilisation weak) Agricultural yields in higher latitudes likely to peak	1 – 3 million more people die from malnutrition (if carbon fertilisation weak)	1 – 170 million more people affected by coastal flooding each year	20 – 50% of species facing extinction (according to one estimate), including 25 – 60% mammals, 30 – 40% birds and 15 – 70% butterflies in South Africa Collapse of Amazon rainforest (according to some models)	Potential for Greenland ice sheet to begin melting irreversibly, accelerating sea level rise and committing world to an eventual 7 m sea level rise Rising risk of abrupt changes to atmospheric circulations, e.g. the monsoon Rising risk of collapse of West Antarctic Ice Sheet Rising risk of collapse of Atlantic Thermohaline Circulation
4°C	Potentially 30 – 50% decrease in water availability in Southern Africa and Mediterranean	Agricultural yields decline by 15 – 35% in Africa, and entire regions out of production (e.g. parts of Australia)	Up to 80 million more people exposed to malaria in Africa	7 – 300 million more people affected by coastal flooding each year	Loss of around half Arctic tundra Around half of all the world's nature reserves cannot fulfill objectives	

„The Stone Age Did Not End Because the World Ran Out of Stones, and the Oil Age Will Not End Because We Run Out of Oil”

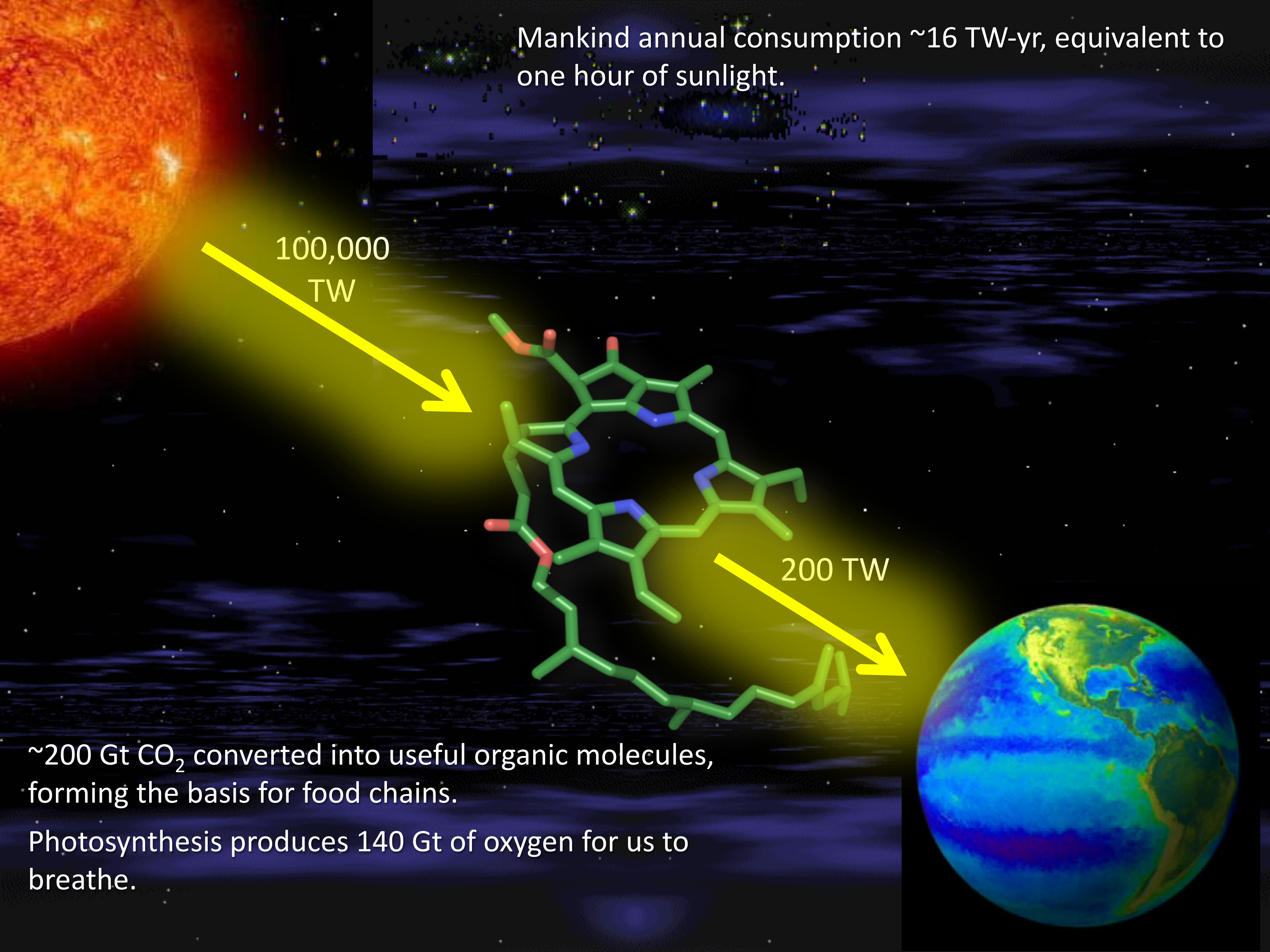
Don Huberts, Head of Shell Hydrogen Div., also attributed to (or just qouted by?) Ahmed Zaki Yamani, oil sheikh

„The Stone Age did not end because of a lack of stone. It ended because bronze tools became cheaper.”



National Geographic, 2017

Mankind annual consumption ~16 TW-yr, equivalent to one hour of sunlight.



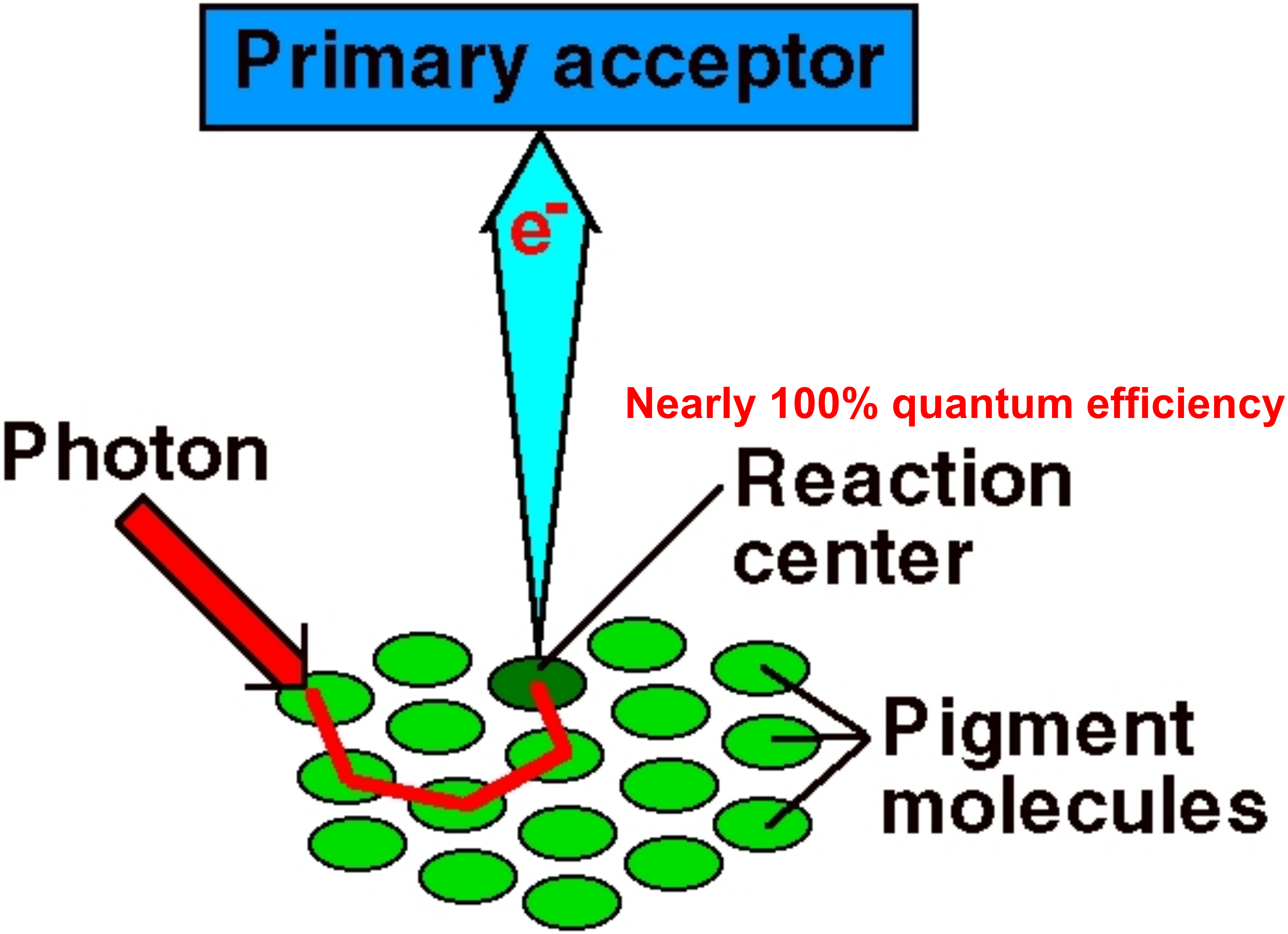
~200 Gt CO_2 converted into useful organic molecules, forming the basis for food chains.

Photosynthesis produces 140 Gt of oxygen for us to breathe.

Global Effects of Photosynthesis

Mechanisms of Photosynthesis

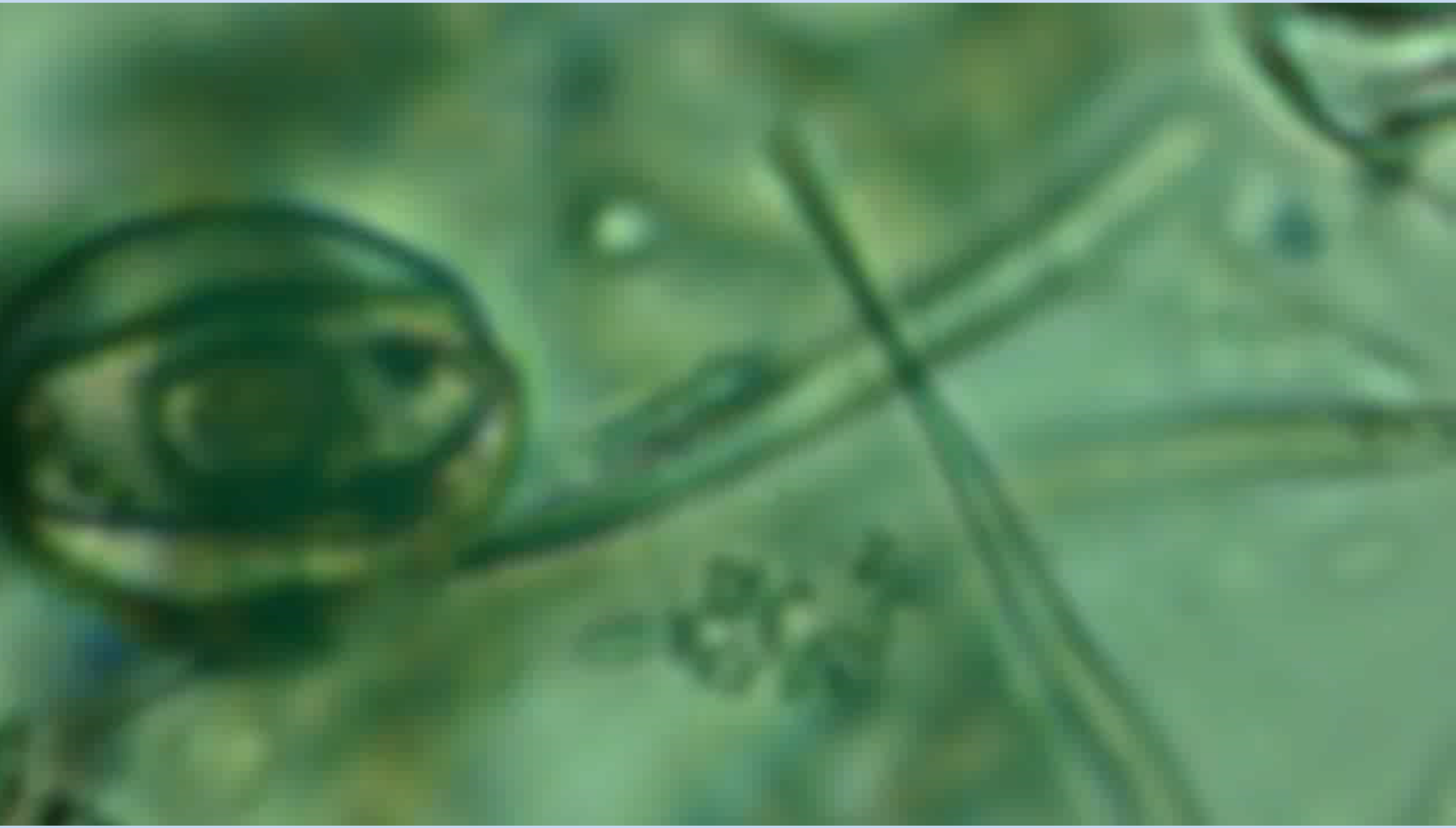
Ultrafast Processes - New Vistas at ELI-ALPS

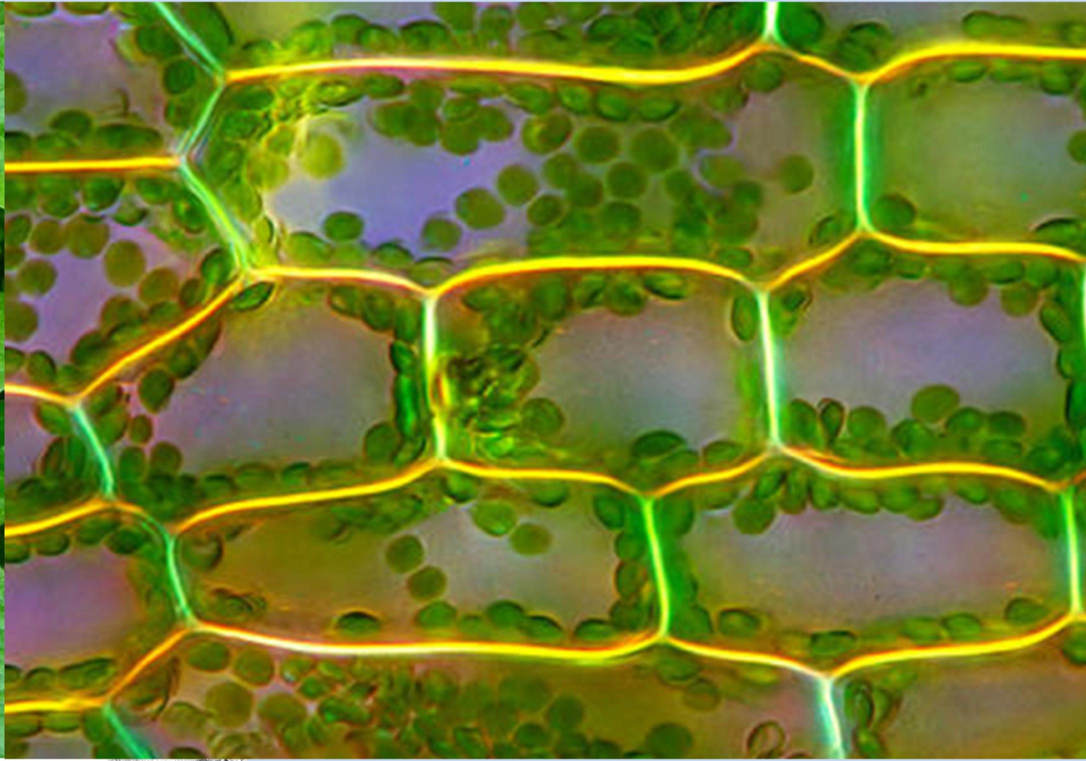


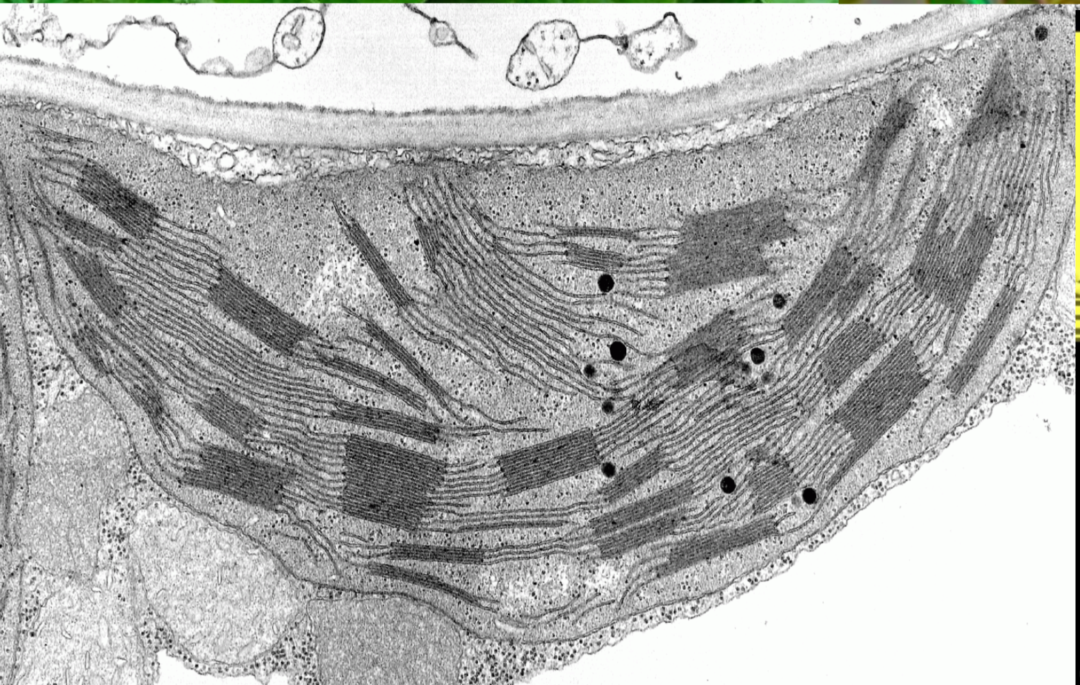
Nearly 100% quantum efficiency

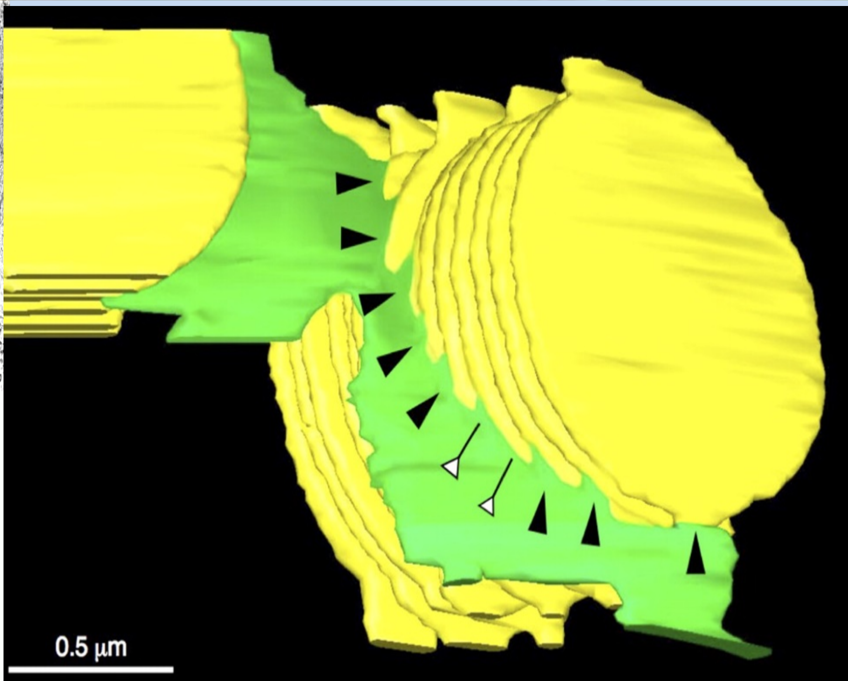
But: it can be downregulated

MOVIE ON THE STRUCTURE AND FUNCTION OF PURPLE BACTERIAL PHOTOSYNTHESTIC UNIT. BY NEIL HUNTER AND AND KLAUS SCHULTEN

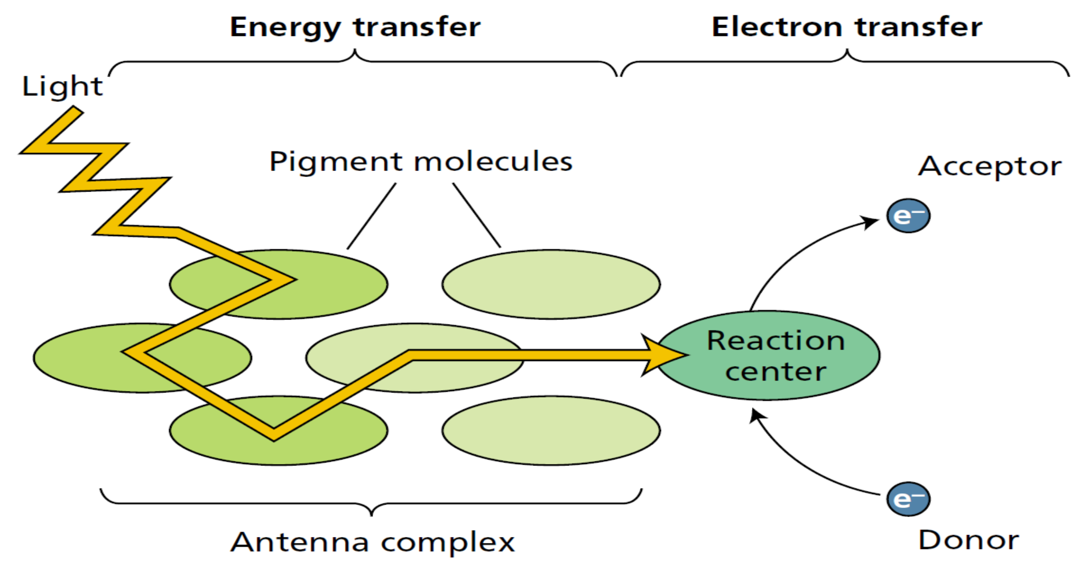


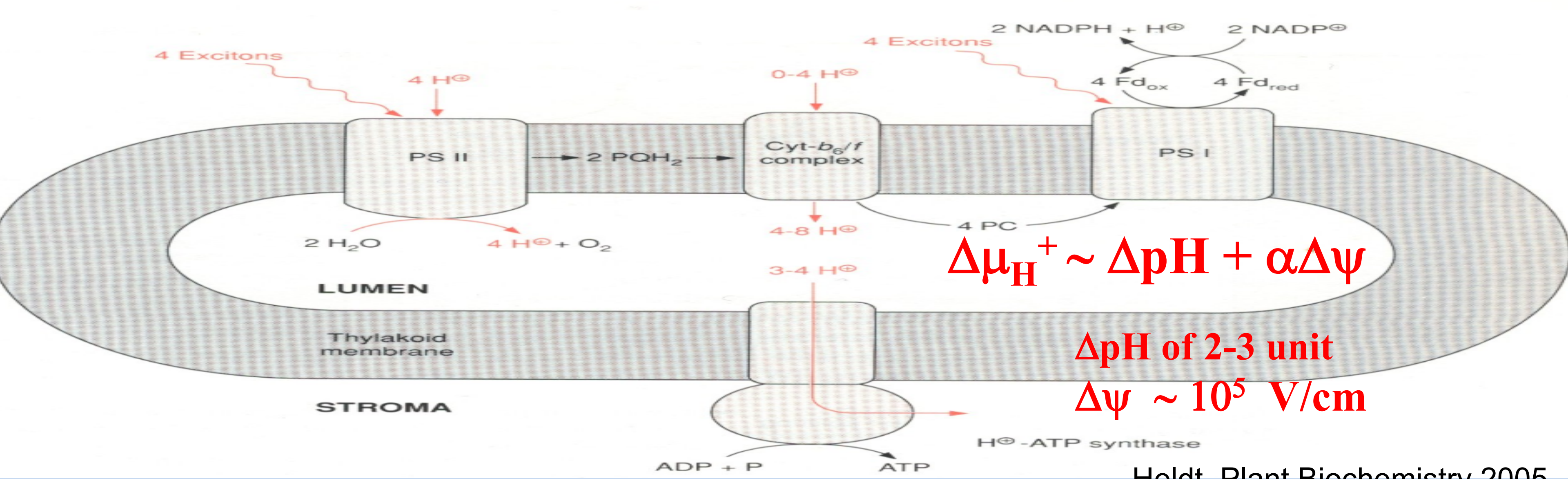





0.5 µm

SCHEME OF THE LIGHT REACTIONS OF OXYGENIC PHOTOSYNTHETIC ENERGY CONVERSION





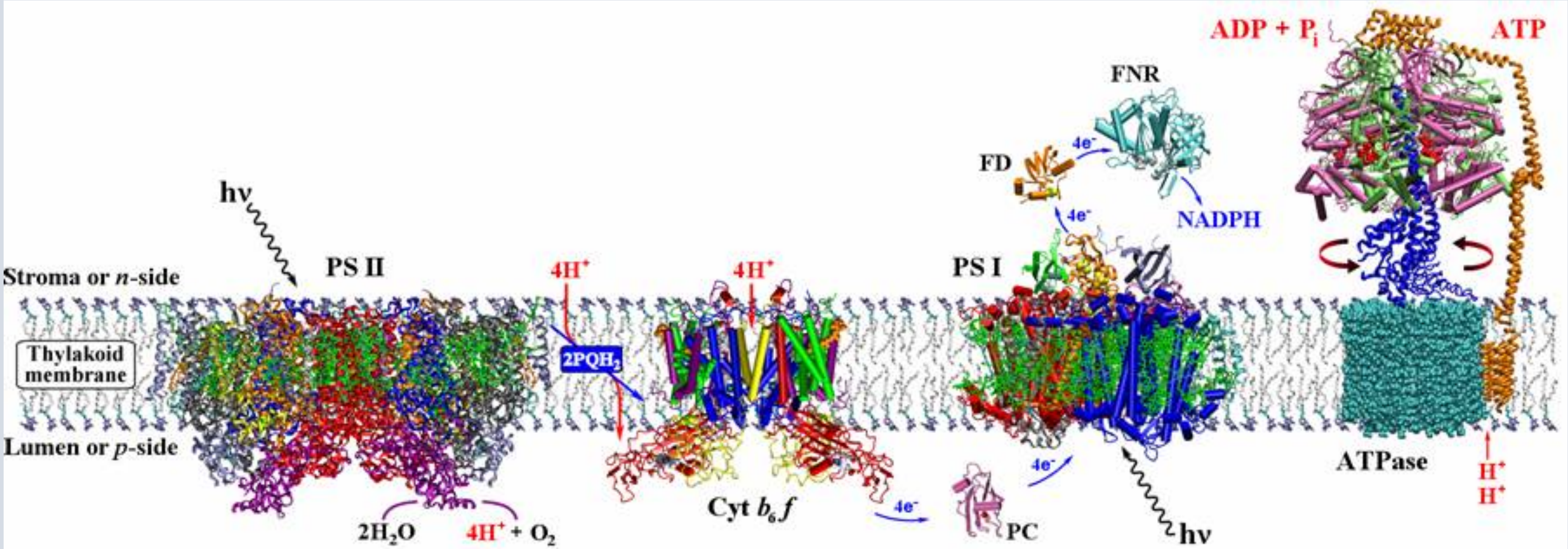
$$\Delta\mu_{H^+} \sim \Delta pH + \alpha\Delta\psi$$

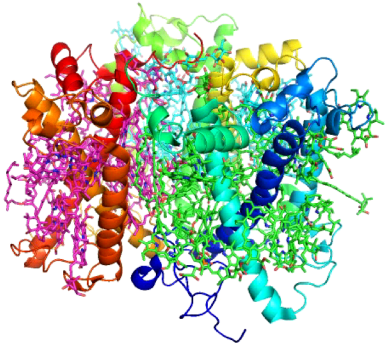
ΔpH of 2-3 unit

$\Delta\psi \sim 10^5$ V/cm

Heldt, Plant Biochemistry 2005

Components of Photosynthetic machinery

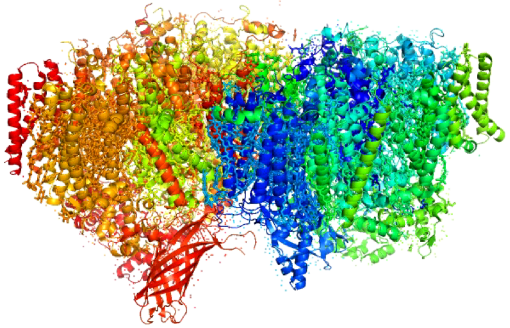




LHCII

Light-harvesting complex

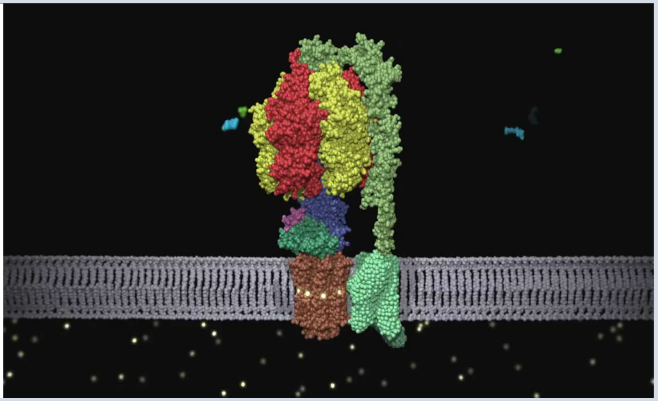
Liu et al 2005 Nature



Suga 2016 Nature

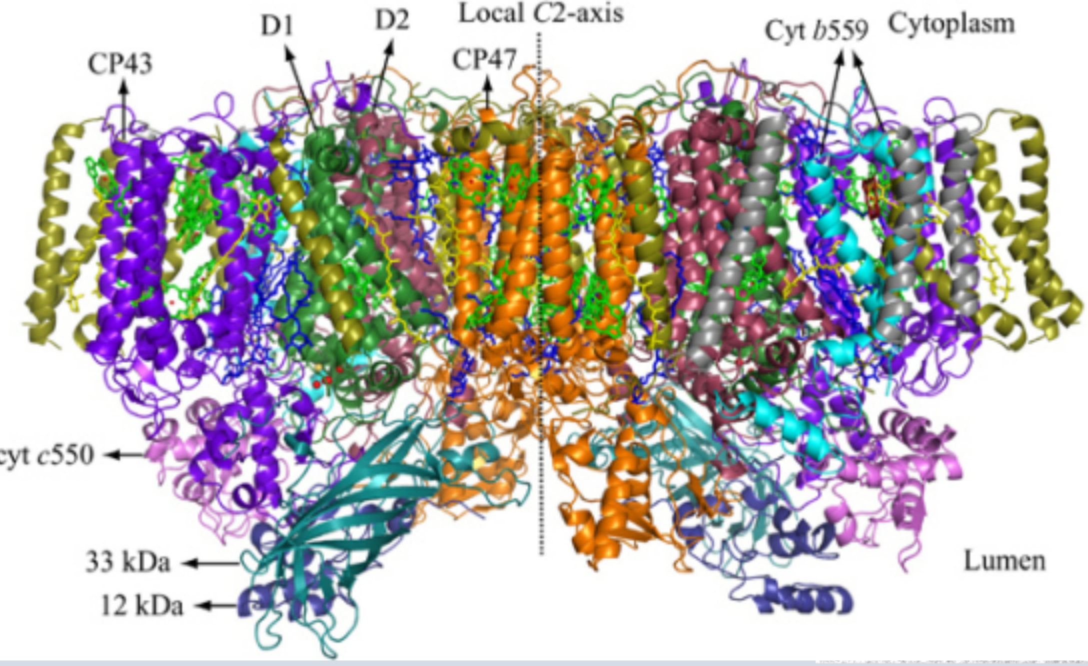
PSII

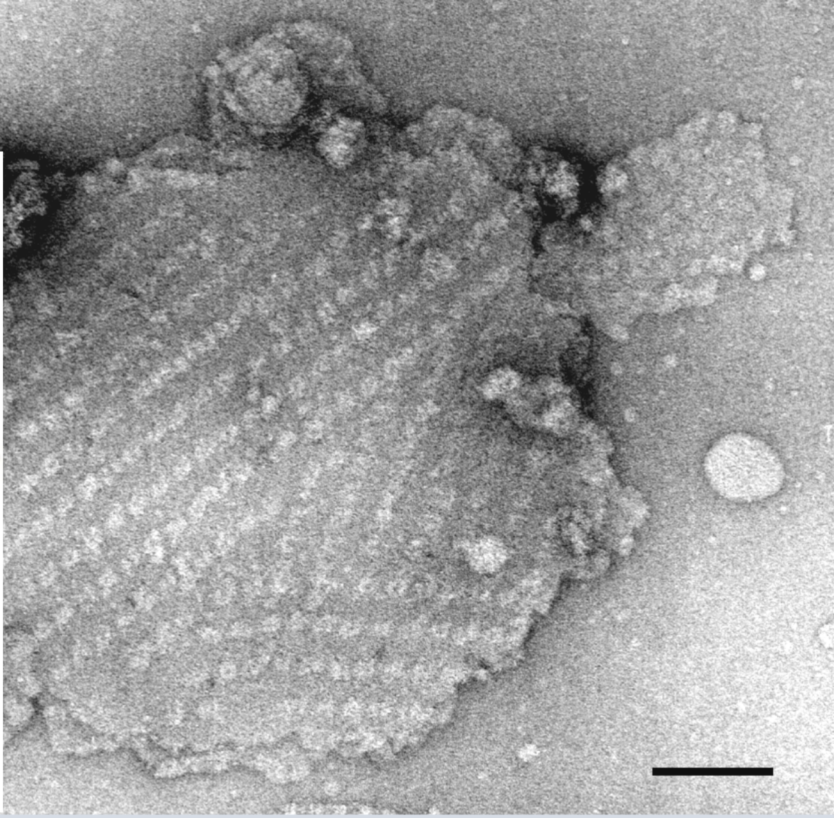
Driving the oxygen evolution

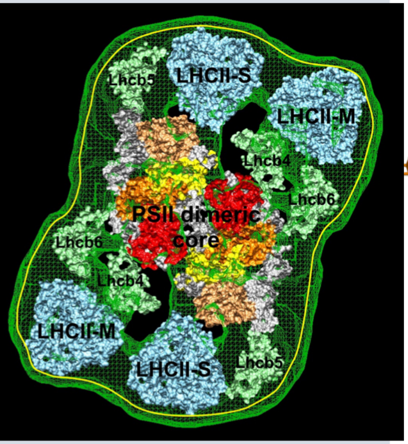


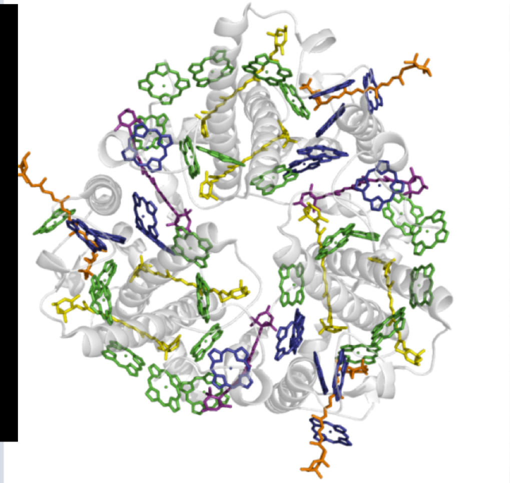
ATP synthase

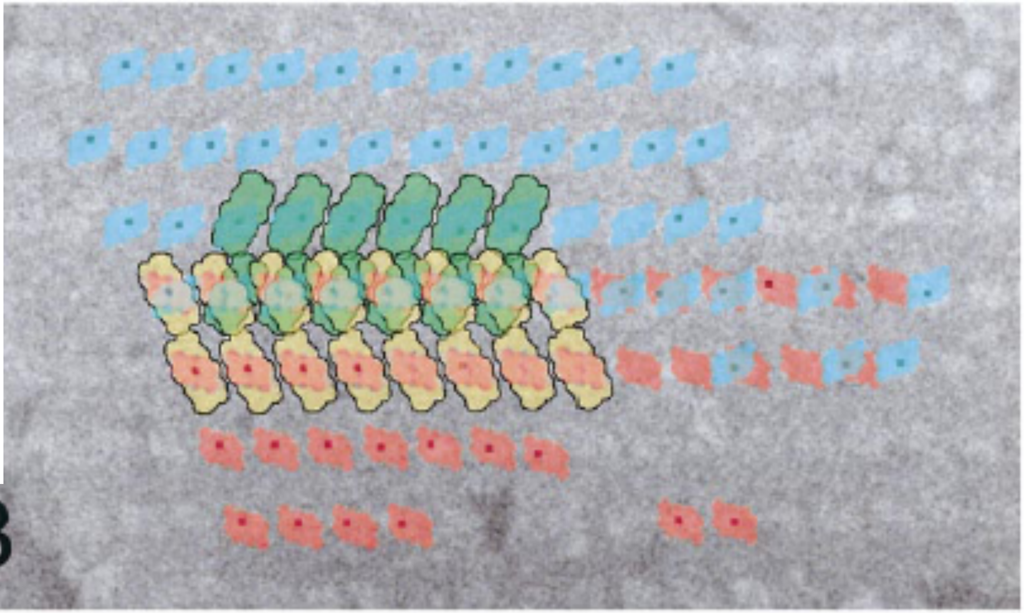
Skou, Walter, Boyer – Nobel prize 1997.









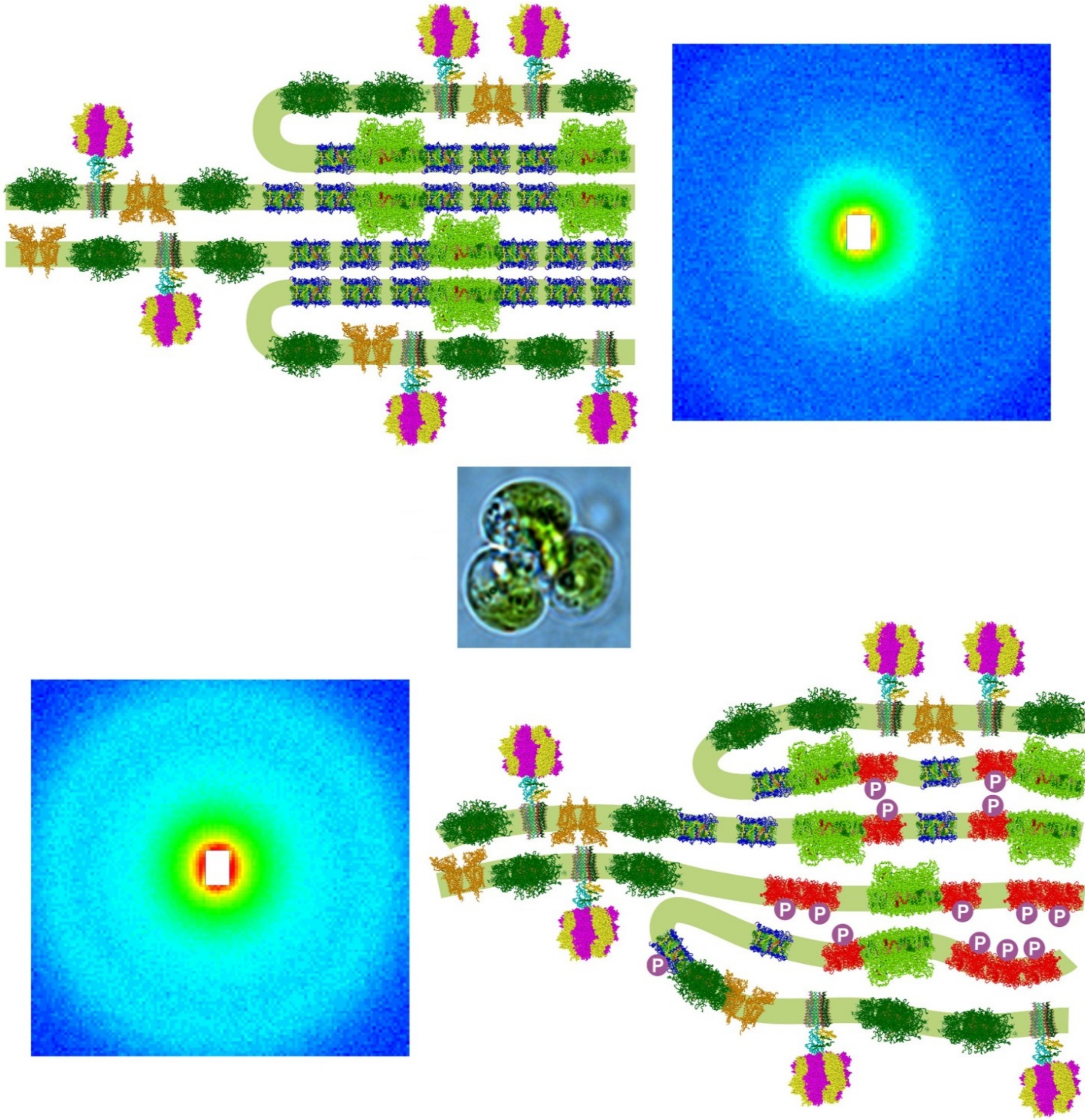


Shen and coworkers; Boekema&Dekker,
Chang and coworkers

Molecular organization and reorganization of thylakoid membranes in vivo

– feedback and regulation by not well understood physical mechanisms

Nagy et al. 2014, PNAS



Nagy et al. PNAS 2014

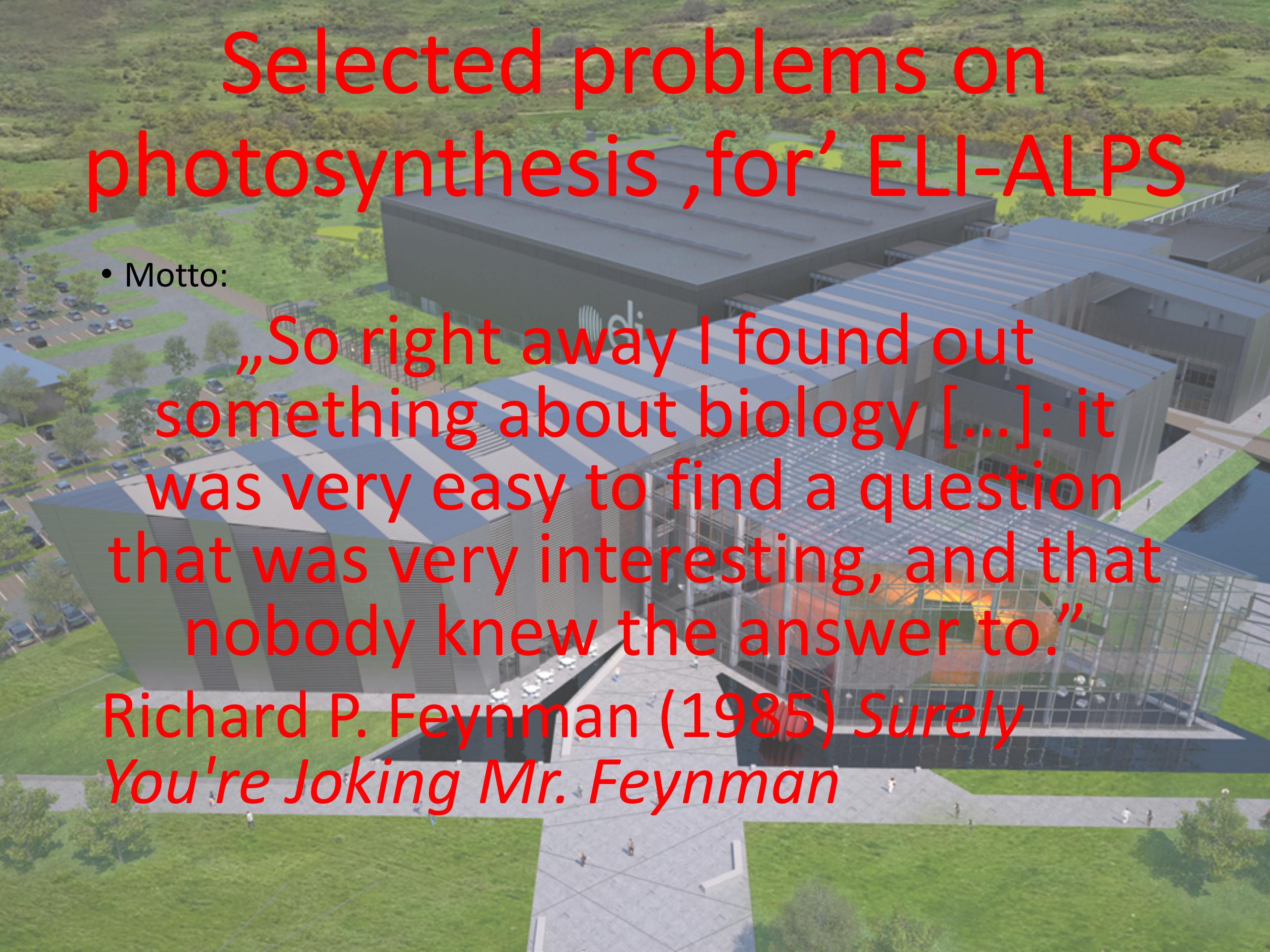
Block diagram of photosynthesis

Photophysics Light absorption energy migration	Photochemistry charge separation redox chain NADPH, ATP, O_2	Biochemistry CO_2 ‘fixation’, Signal transduction Short-term regulation	Physiology synthesis, self-assembly repair transport Regulation	Ontogeny Ecology Evolution
~ $10^{-15} – 10^{-9}$ s	~ $10^{-12} – 10^{-2}$ s	~ $10^{-3} – 10^{3}$ s	~ $10^{2} – 10^{6}$ s	~ $10^{5} – 10^{17}$ s
complexes	membrane	chloroplast	cell, plant, ecosystem, biosphere	

Global Effects of Photosynthesis

Mechanisms of Photosynthesis

Ultrafast Processes - New Vistas at ELI-ALPS



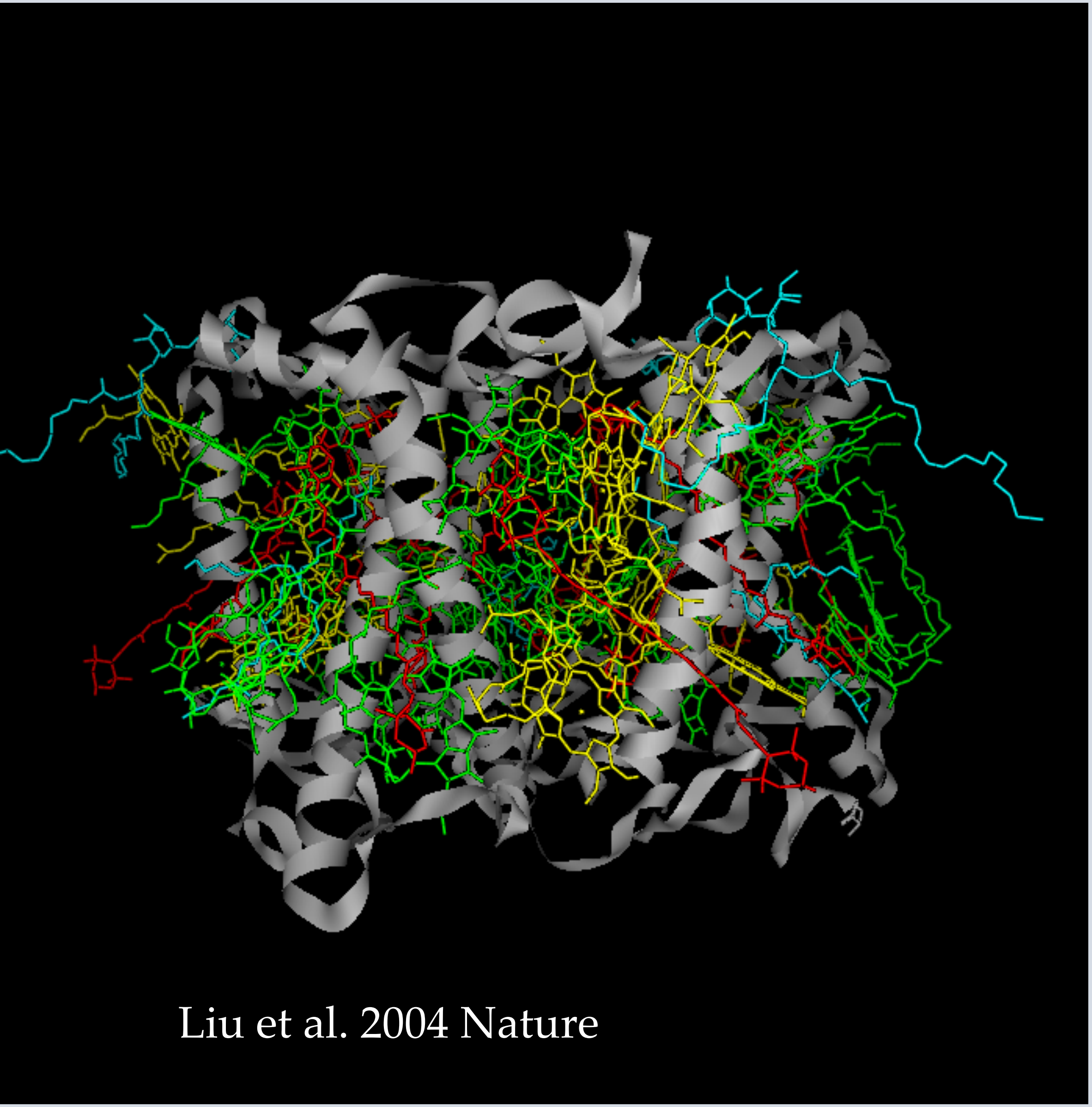
Selected problems on photosynthesis ‚for’ ELI-ALPS

- Motto:

„So right away I found out something about biology […]: it was very easy to find a question that was very interesting, and that nobody knew the answer to.”

Richard P. Feynman (1985) *Surely You're Joking Mr. Feynman*

LHCII – the most abundant membrane protein in the Biosphere



Liu et al. 2004 Nature

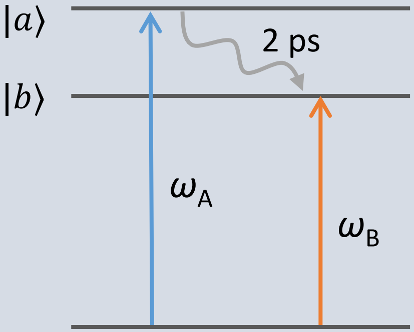
Finely-tuned pigment arrangement:

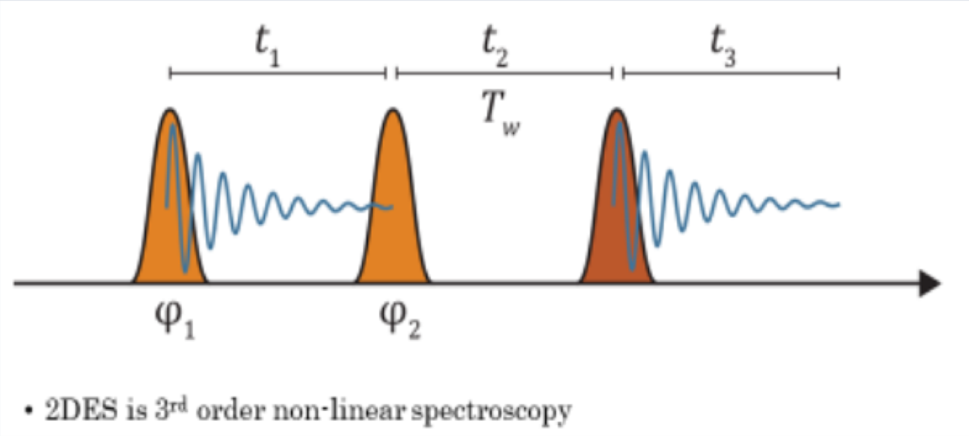
- Dipole-dipole (excitonic) interactions between pigments
- Enables ultrafast energy transfer via hopping mechanism and/or delocalized excitons
- Prevents quenching
- Dynamic switch between energy harvesting and dissipation – NPQ: **nearly 100% quantum efficiency light harvesting function vs ~80% dissipation**

The light-harvesting function is regulated

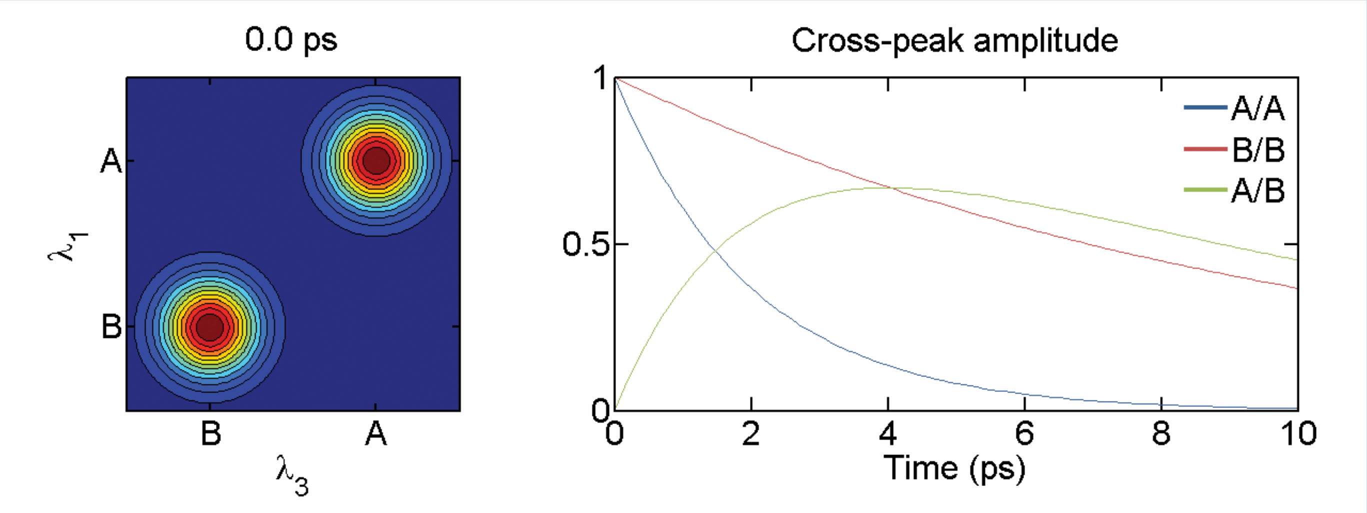
- ΔpH, PsbS protein, Zeaxanthin
- Phosphorylation
- Conformational changes?

Q1: energy migration pathways in LHCII Answer(s) from multidimensional transient fs absorption spectroscopy

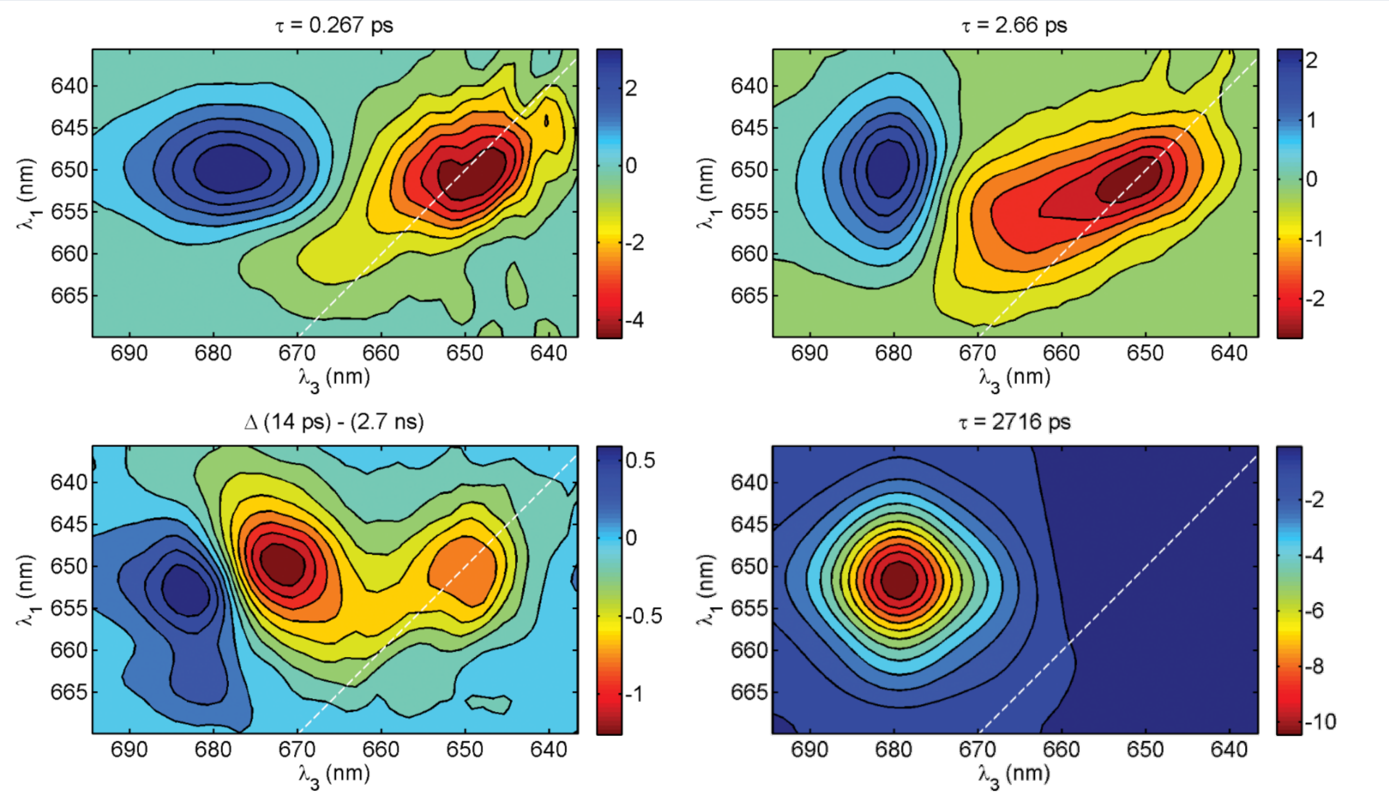




- 2DES is 3rd order non-linear spectroscopy

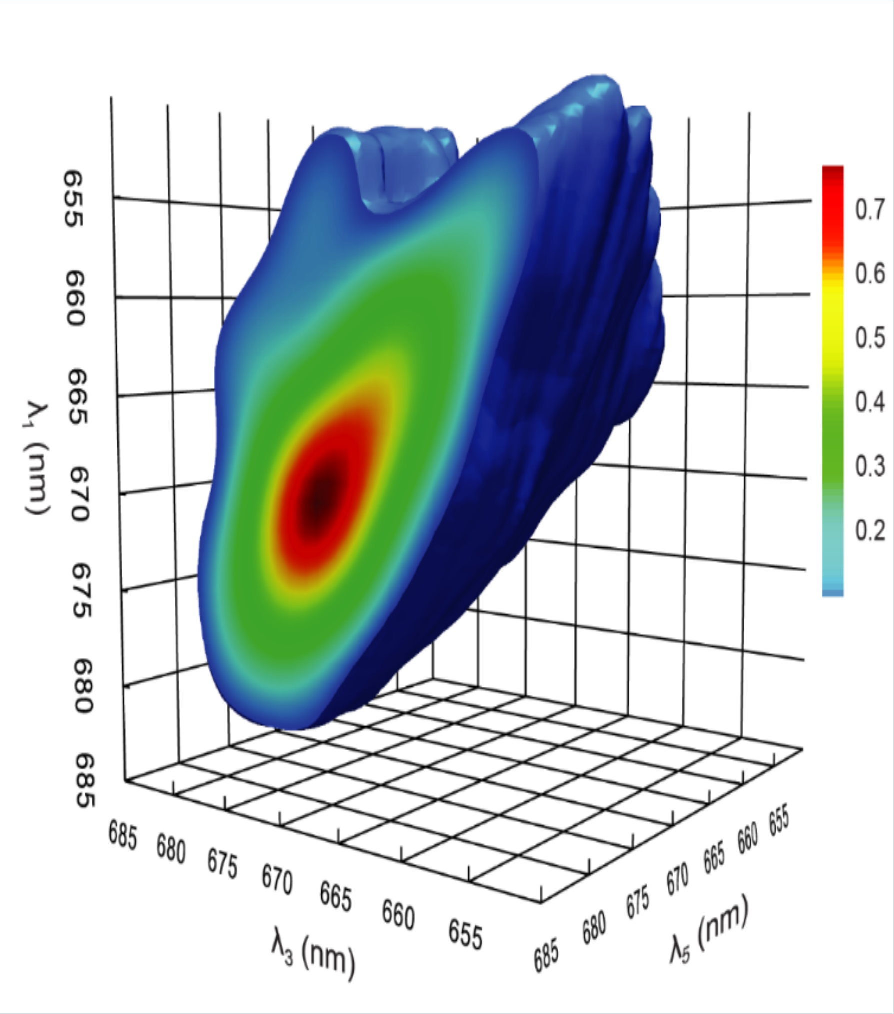


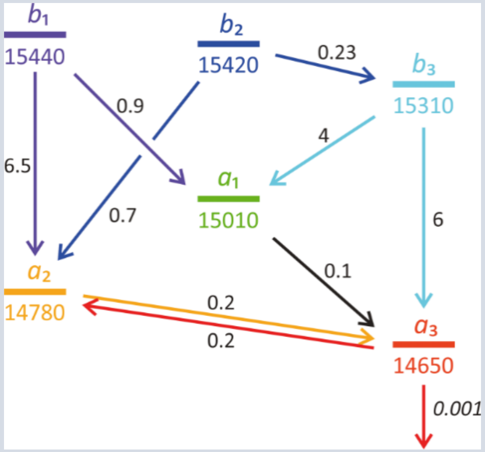
2D DAS of LHCII trimers (Chl *b* excitation)



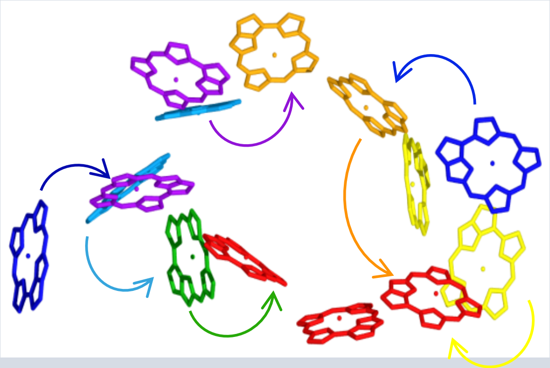
Wells KL, Lambrev PH, Zhengyang Z , Garab G, Tan H-S (2014) *Phys Chem Chem Phys* 16:11640-11645

3D optical spectroscopy of LHCII



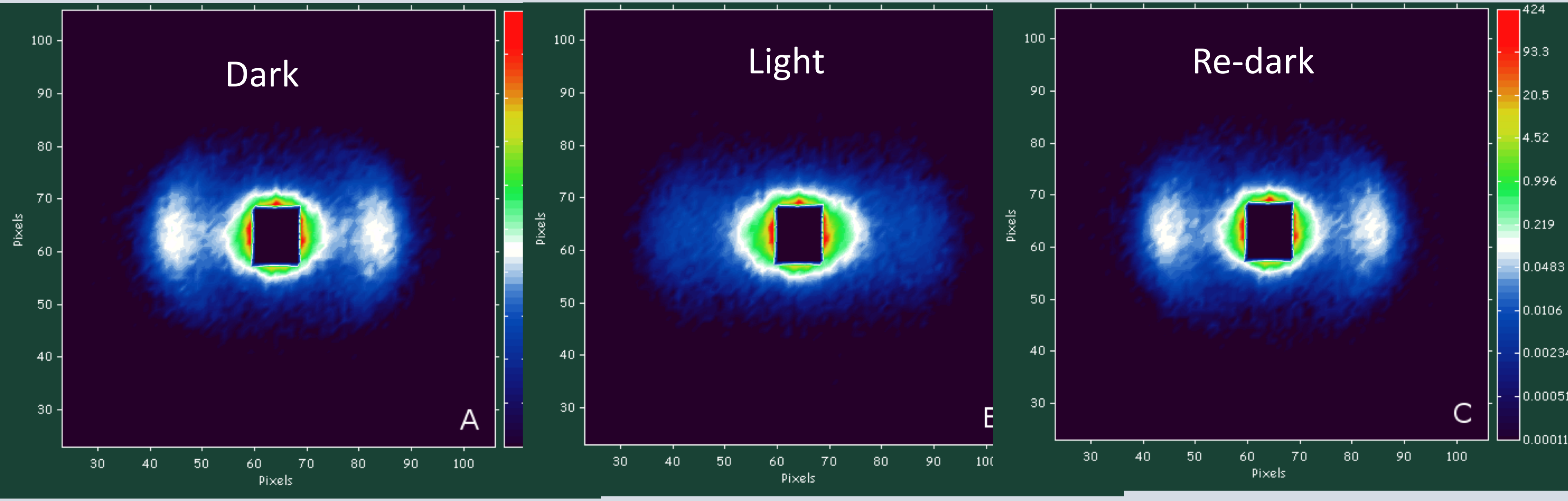


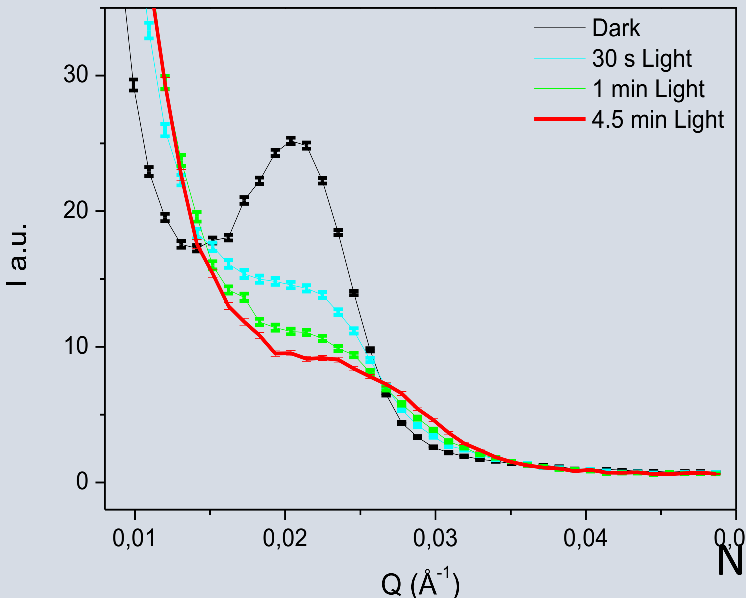
Pigment clusters in LHCII

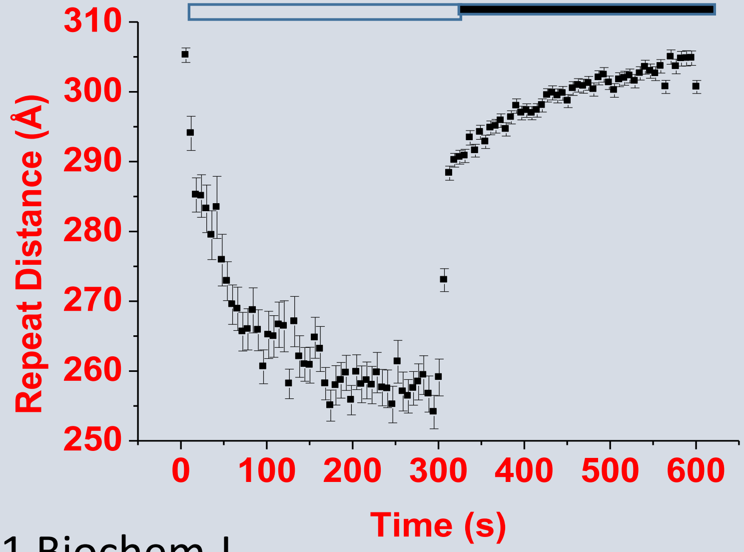


Zhang Z, Lambrev PH, Wells KL, Garab G, Tan H-S – 2015 Nature Communication

Q2: The fate of unused (absorbed and dissipated) excitation energy?
Light-induced reversible reorganizations (SANS) of isolated thylakoid membranes

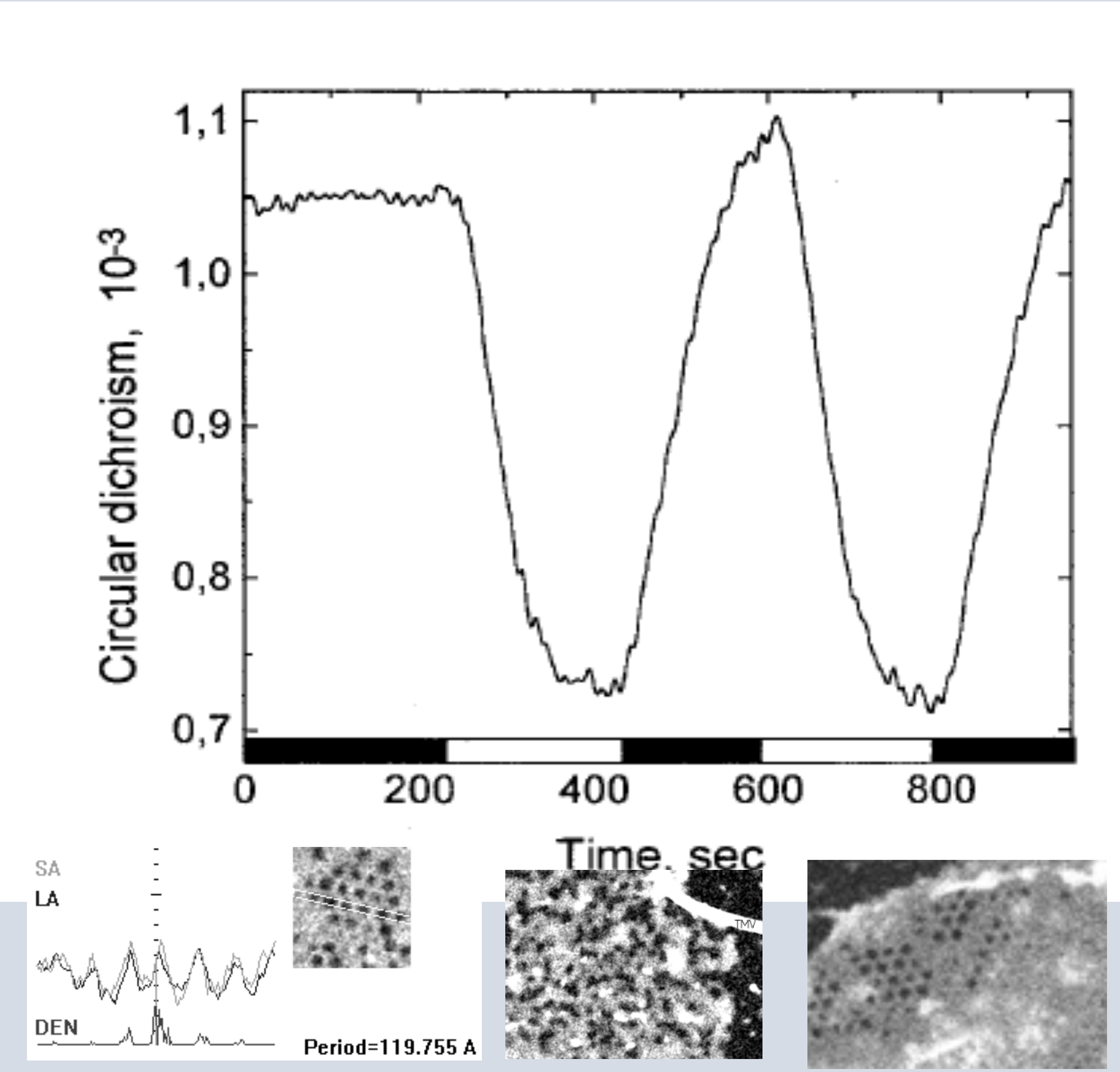






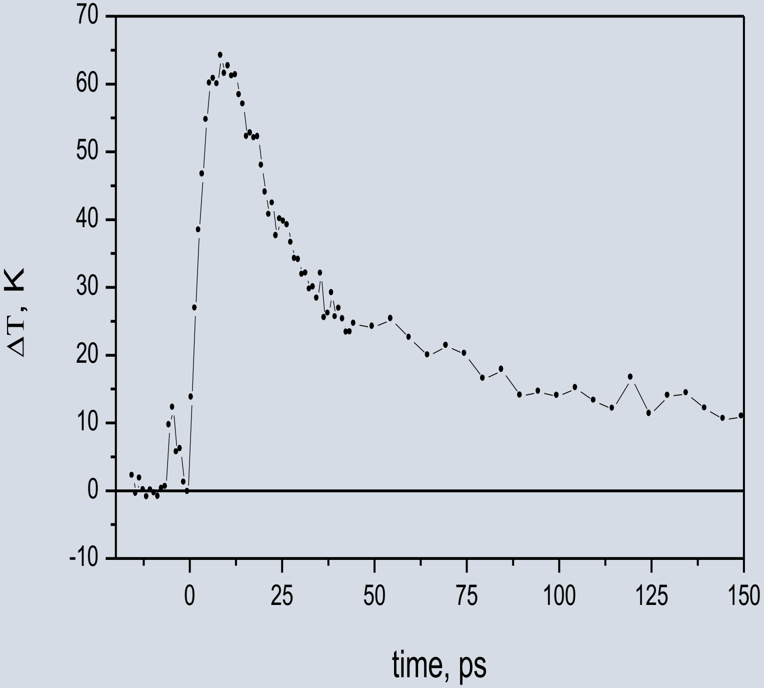
Nagy et al. 2011 Biochem J.

Thermo-optically driven (dissipation-assisted light-induced) reversible changes in lipid:LHCII membrane crystals



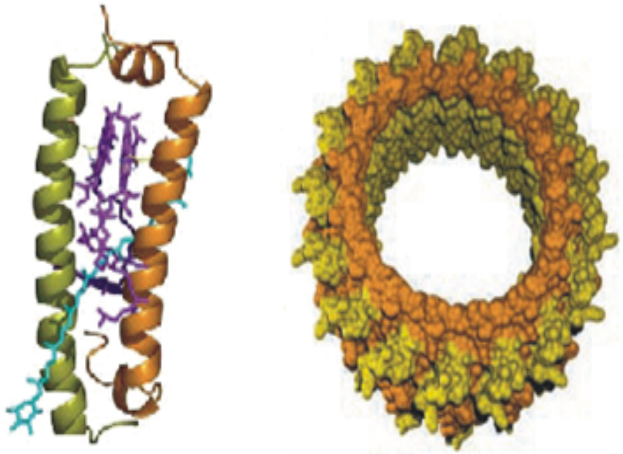
Hind et al. 2014 Plant and Cell Physiology

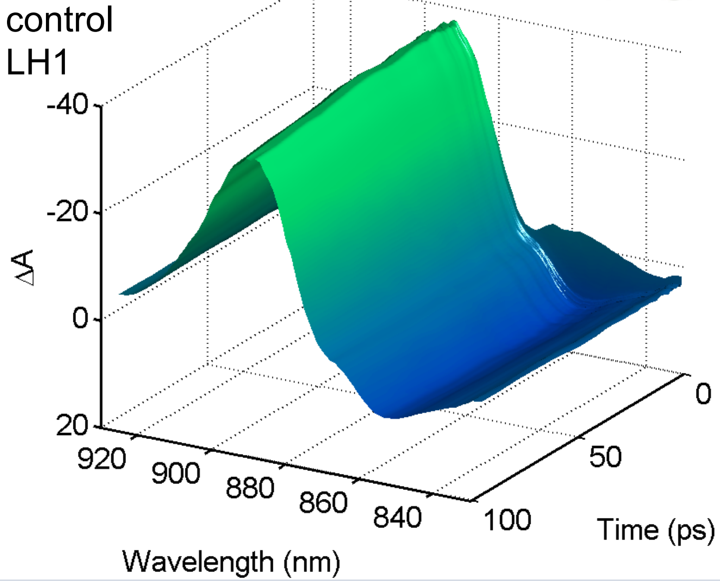
T-jump – transient: 1.8 eV dissipated in ~1 nm^3 (ultrafast local T-transient)

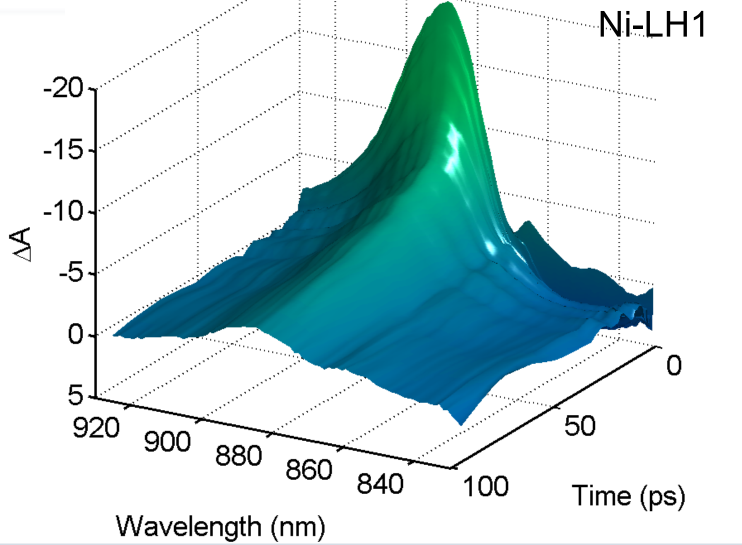


Gulbinas et al. 2006 Biochemistry

A: Ni-Bchl reconstituted bacterial light-harvesting complex LH1)



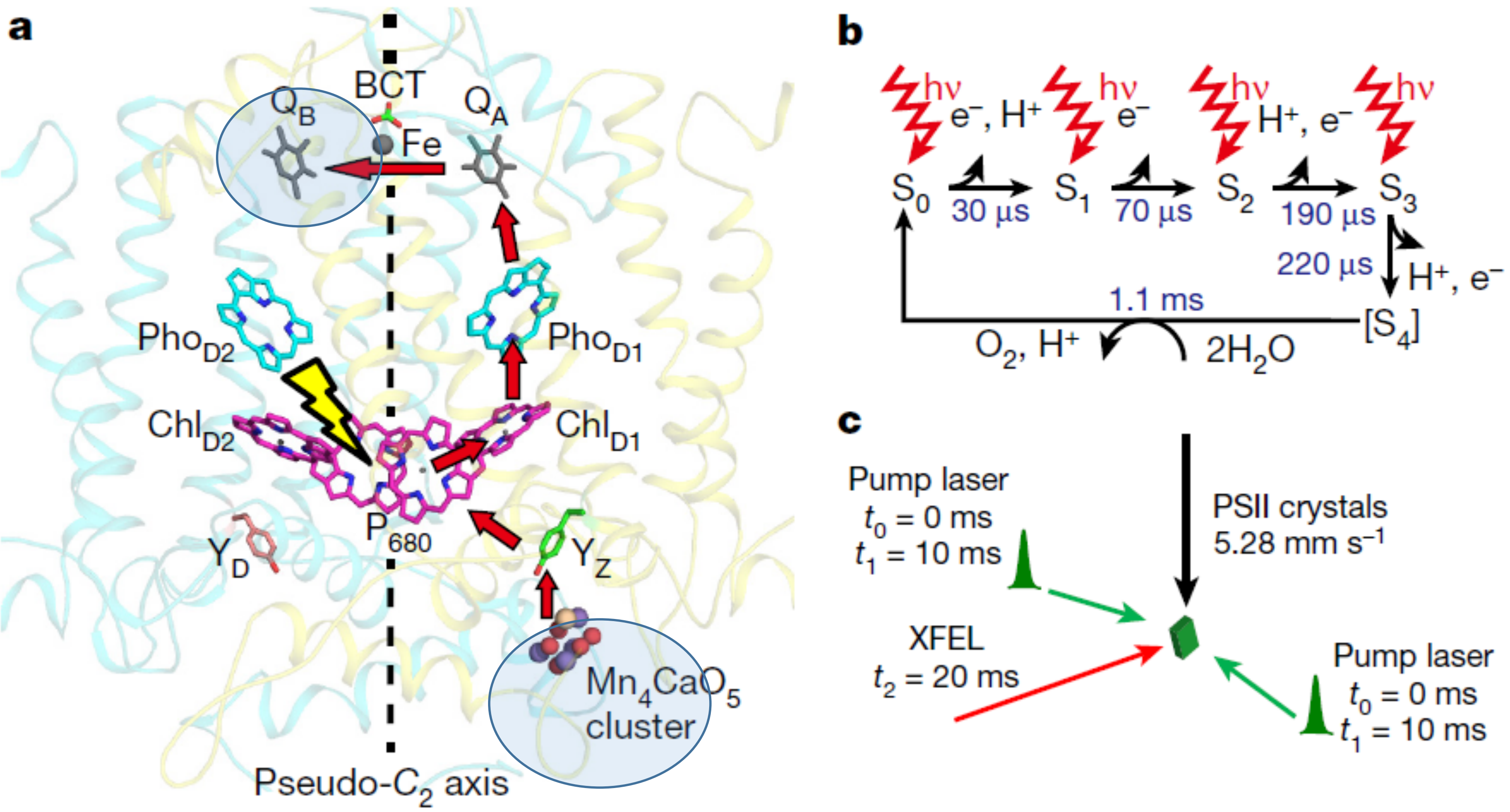




Lambrev et al. 2013 J Phys Chem B

This system – designed for dissipation – is suitable for transient (fs-ps) IR and Raman experiments to monitor the fate and effect dissipation– also interesting for quantum coherence

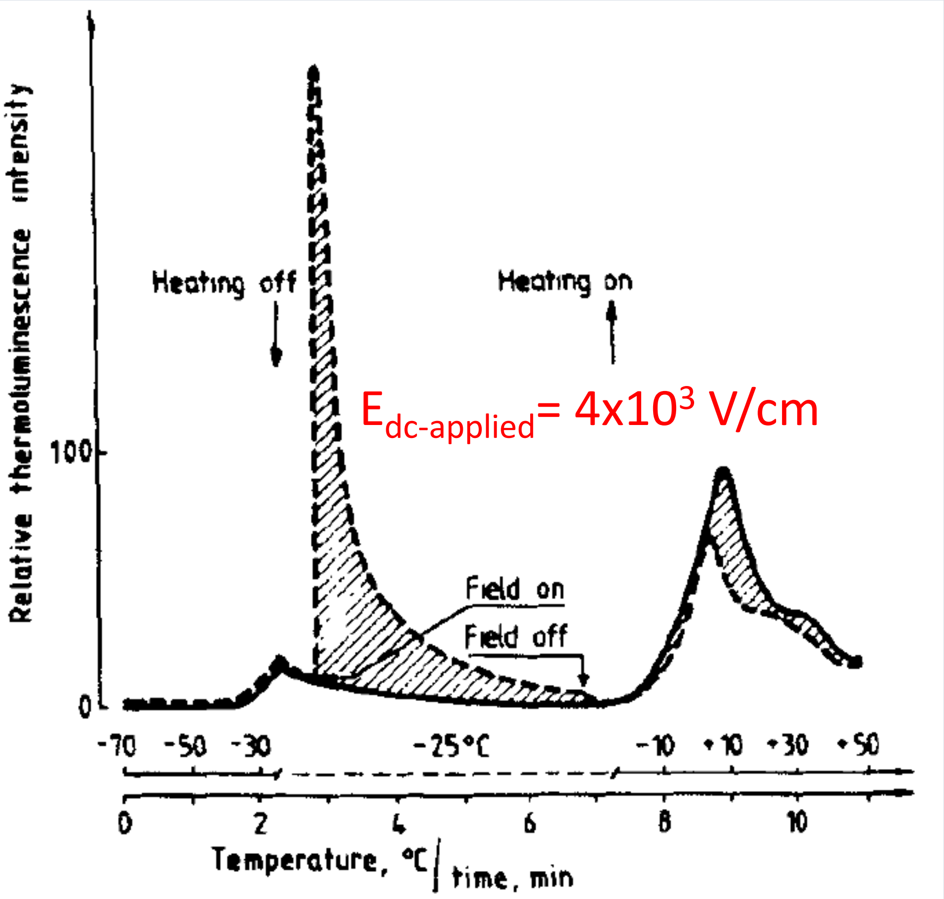
Q3a and Answer-a: Reorganizations in PSII and the OEC



Suga et al. J-R Shen and coworkers – Nature 2017 (XFEL – SACLA)

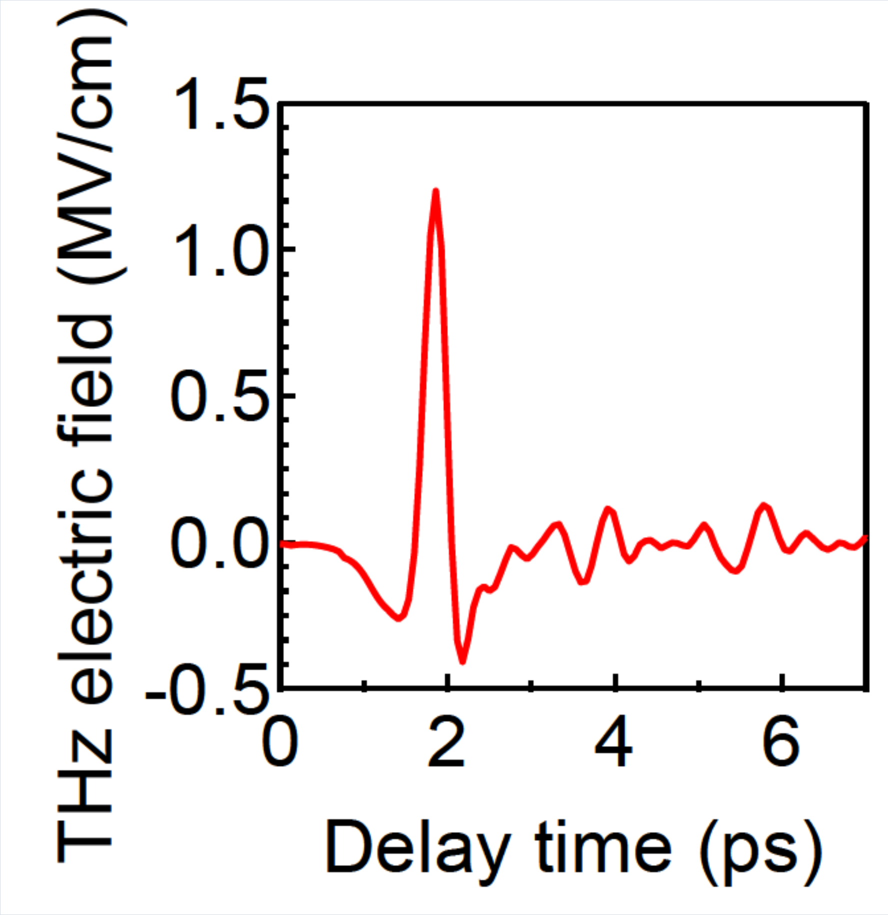
Q3b: Nature of additional light-induced reversible changes? on the same sample detected – as yet only - by fluorescence spectroscopy induced most probably by local transient electric-field and/or T-jump (Magyar et al. Scientific Rep 2018)

Q4a: can we modulate the charge separation by rectified THz laser field – similar to E_{dc} ?



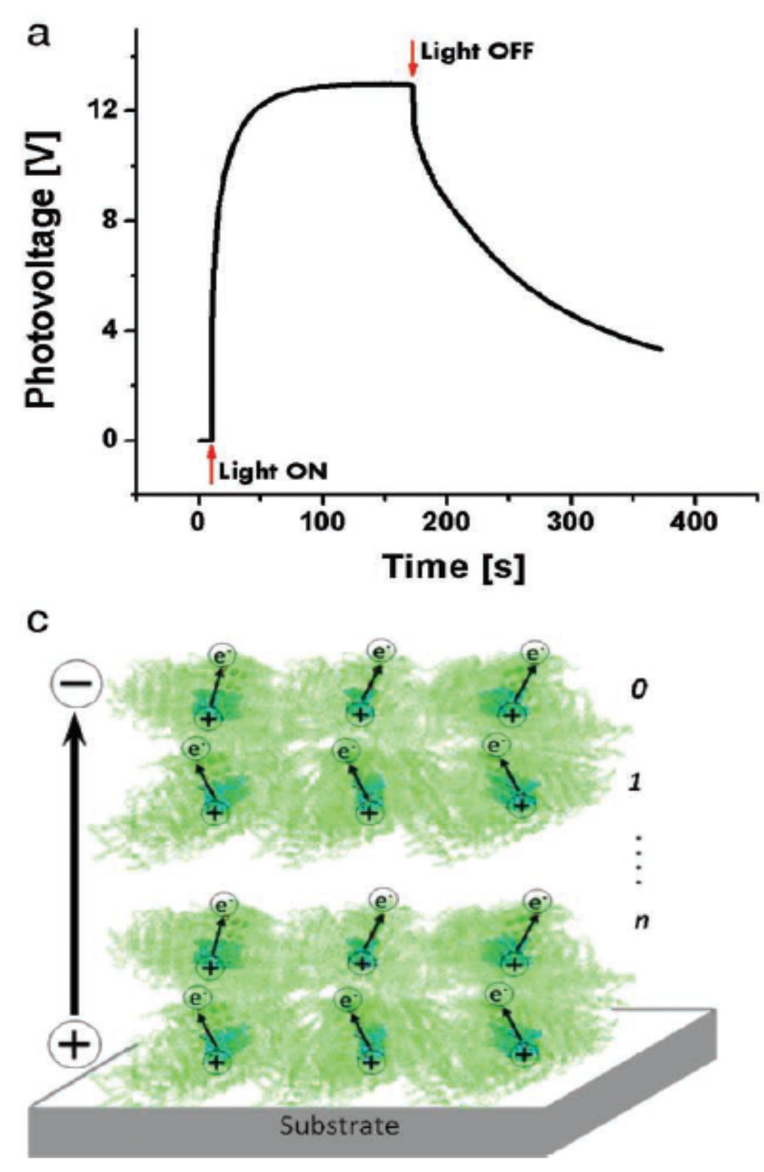
$E_{dc\text{-}applied} = 4 \times 10^3$ V/cm

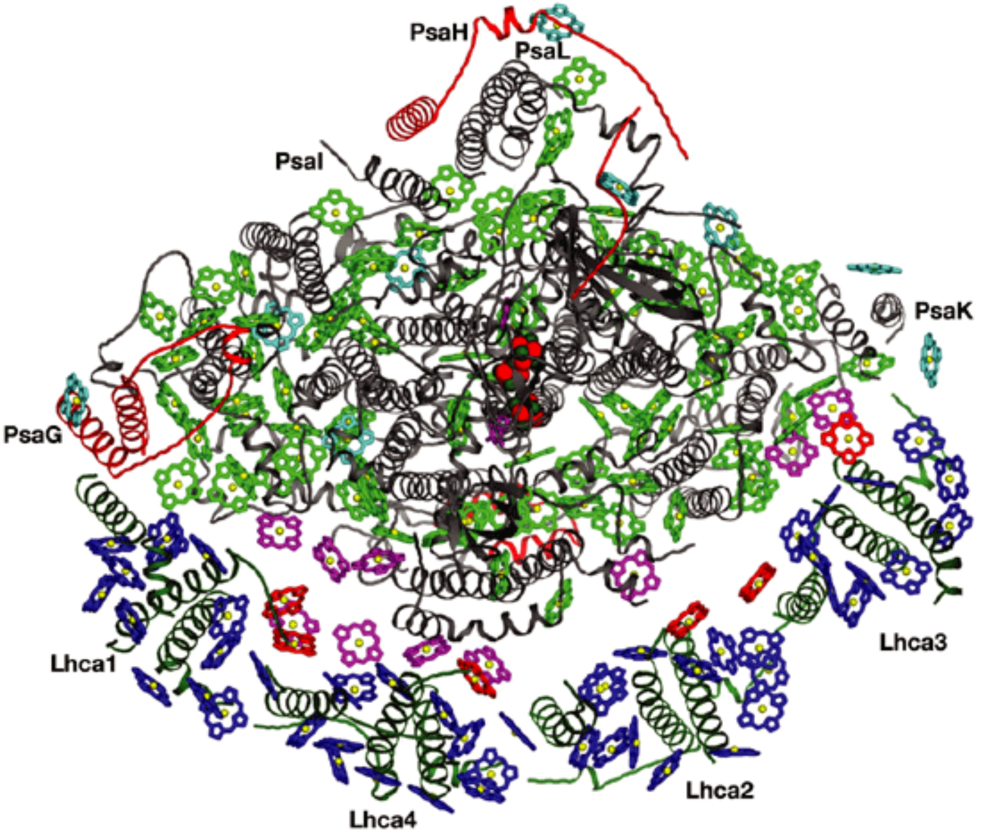
Knox and Garab 1982 Photochem Photobiol



Hirori et al (2011) Appl. Phys. Lett.
Hebling et al. (2002) Opt Express

Q4b: can we induce -by rectified THz laser field - charge separation? (THz pump – Vis probe)

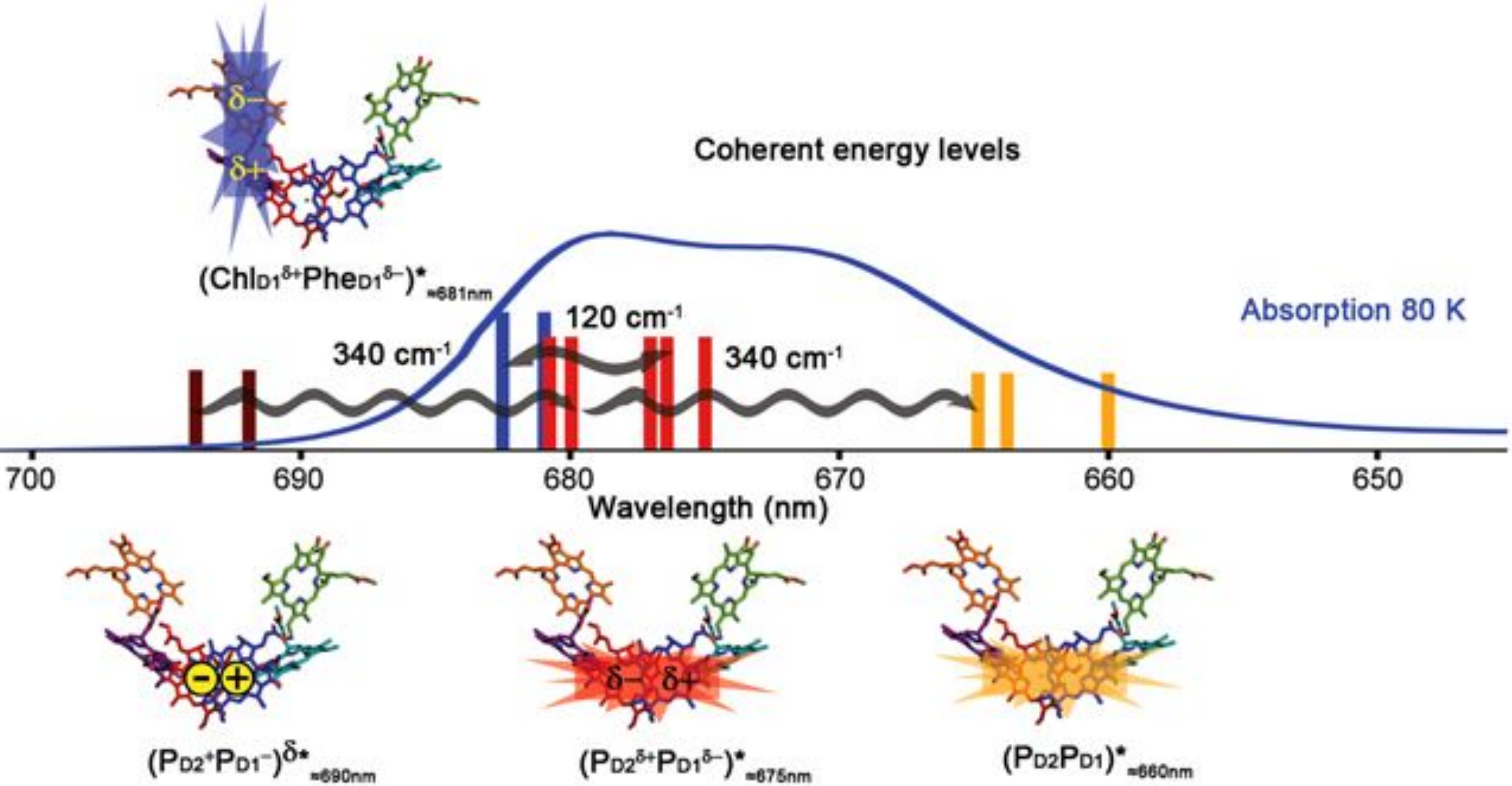




Nature Reviews | Molecular Cell Biology

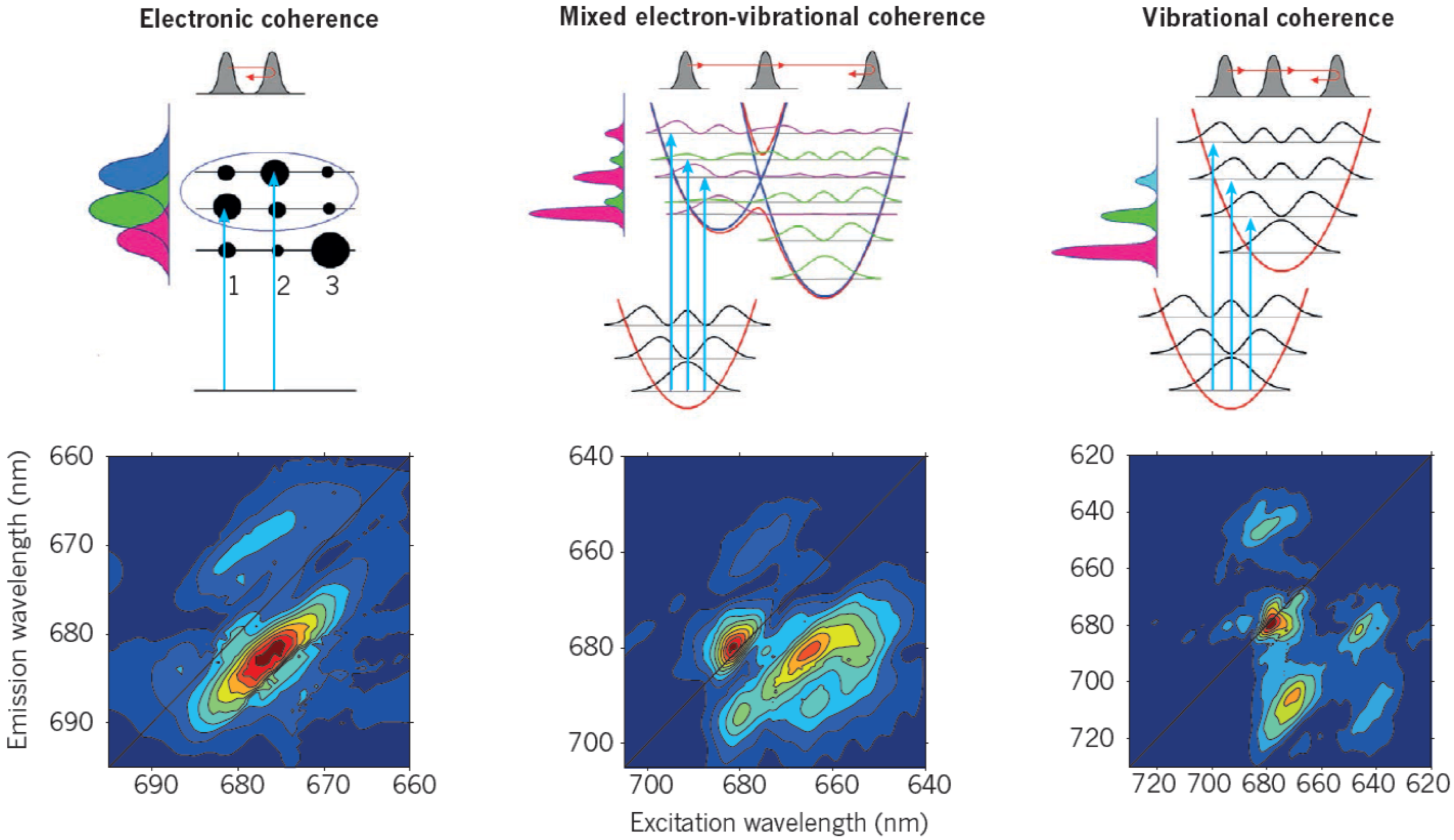
Photosystem I crystal
Nathan Nelson and coworkers

How (exactly) the photochemical reaction centers work? – using quantum coherence?



Romero et al. (2017) Quantum design of photosynthesis for bio-inspired solar-energy conversion. Nature Review

Types of quantum coherence – roles in photosynthesis?



Romero et al. Nature 2017

Thank you for your attention