Photosynthetic Biosignatures

Nancy Y. Kiang

NASA Goddard Institute for Space Studies,
New York, NY USA
Virtual Planetary Laboratory,
NASA Astrobiology Institute

Innovative Approaches to Exoplanet Spectra
Keck Institute for Space Studies
Millikan Board Room
California Institute of Technology
Pasadena CA
November 10-13, 2009

Photosynthesis - quick review

BASIC PATHWAY:

$$CO_2 + 2H_2A \underset{pigments}{\overset{light}{\Rightarrow}} (CH_2O) + H_2O + 2A$$

H_2A is electron donor
e.g. H_2O, H_2S, H_2, Fe^{2+} + H_2O

$$6CO_2^c + 12H_2O^w \overset{light}{\rightarrow} \underset{glu\ \cos\ e}{(C_6H_{12}O_6^c)} + 6H_2O^c + 6O_2^w$$

Oxygenic

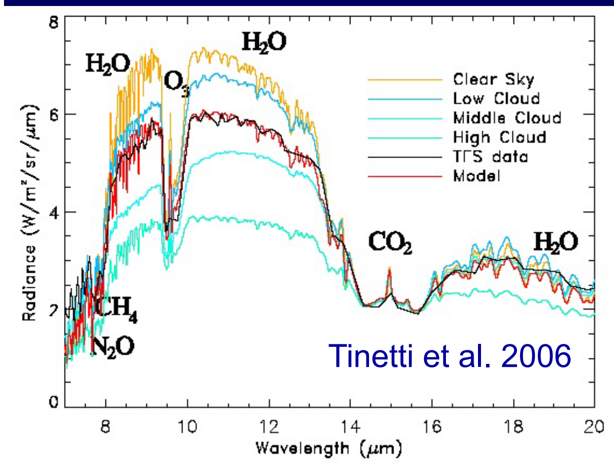
2 photons/H_2O split
x 2 per O_2 evolved
x 2 per CO_2 fixed
= 8 photons
+ 2-4 (other processes)

Oxygenic net reaction to fix one Carbon

$$CO_2^c + H_2O^w \overset{light}{\Rightarrow} \frac{1}{6}\underset{glu\ \cos\ e}{(C_6H_{12}O_6^c)} + O_2^w$$

Planetary-Scale Biosignatures

Biogenic gases & chemical disequilibrium

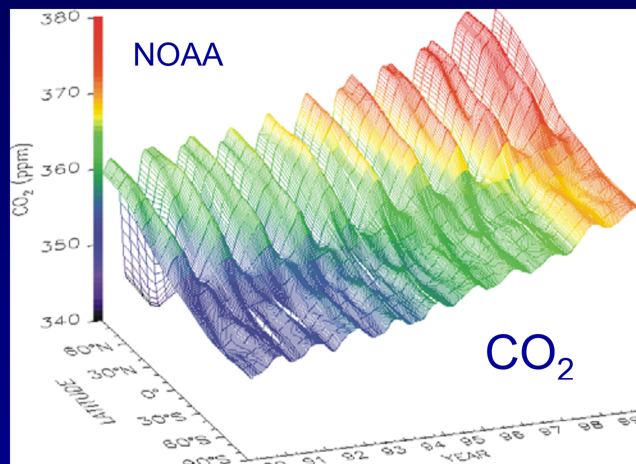


CH_4, CH_3Cl, N_2O

O_2, O_3

in presence of liquid H_2O

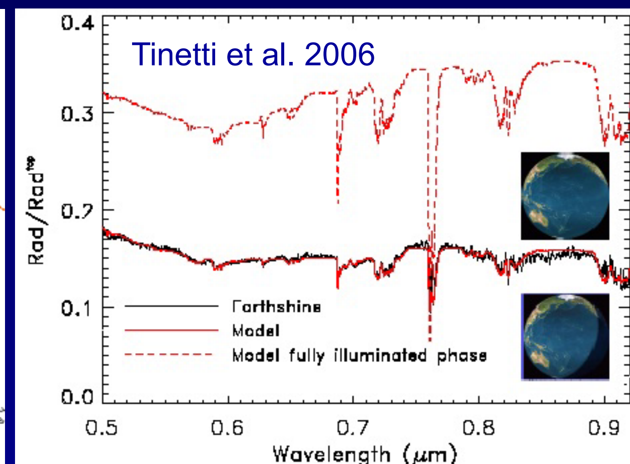
Seasonal cycle



Seasonal cycles of oxidized and reduced gases

CO_2, CH_4

Surface biological pigments



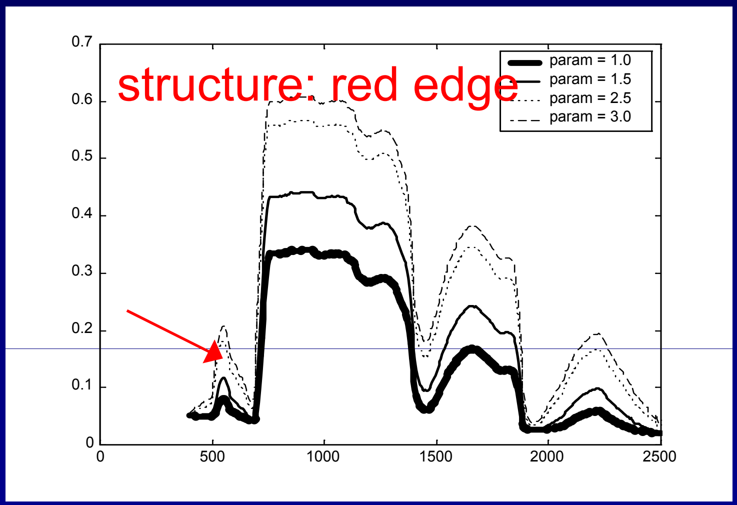
Vegetation red edge

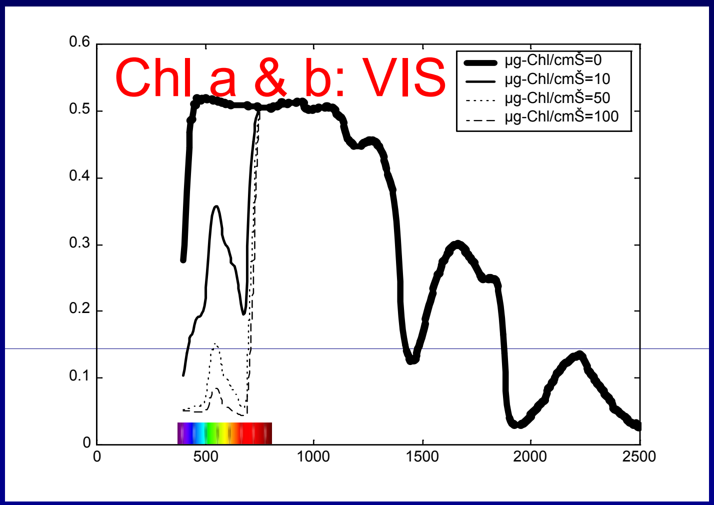
Primary source: photosynthesis

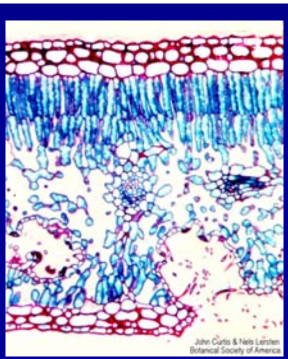
Vegetation “red edge”

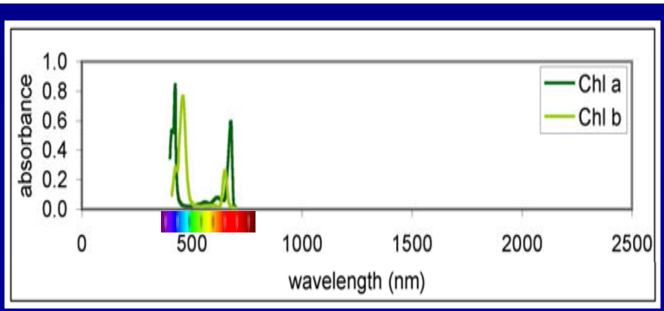
Leaf spectral reflectance

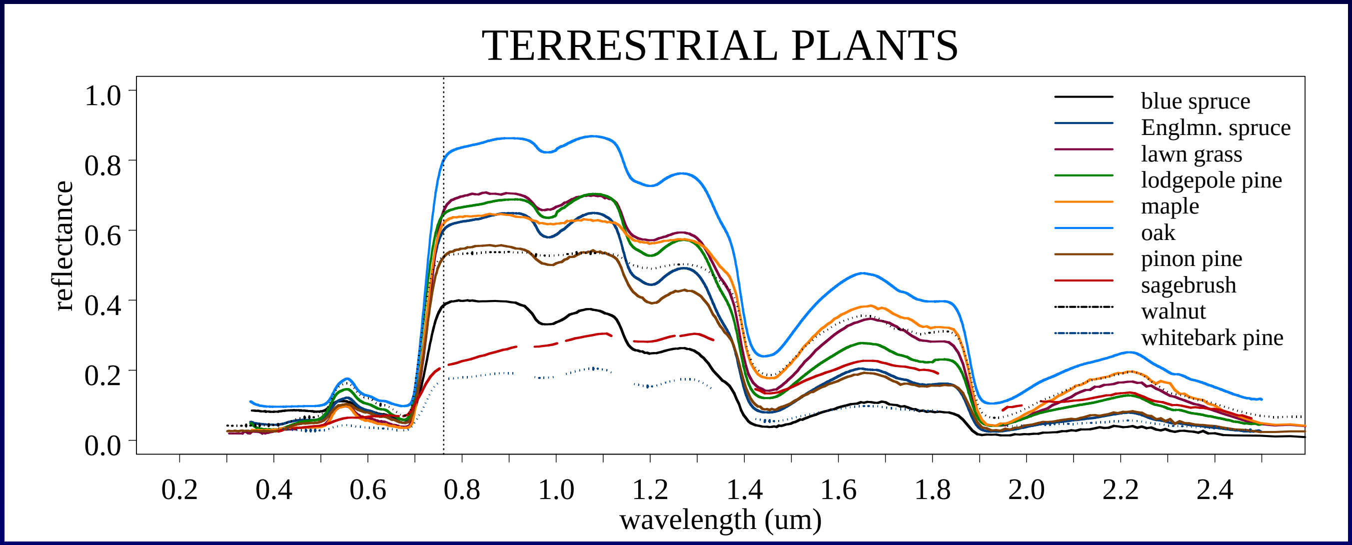
sensitivity to leaf structure and chlorophyll content
(model by Jacquemoud, et.al. 1990)







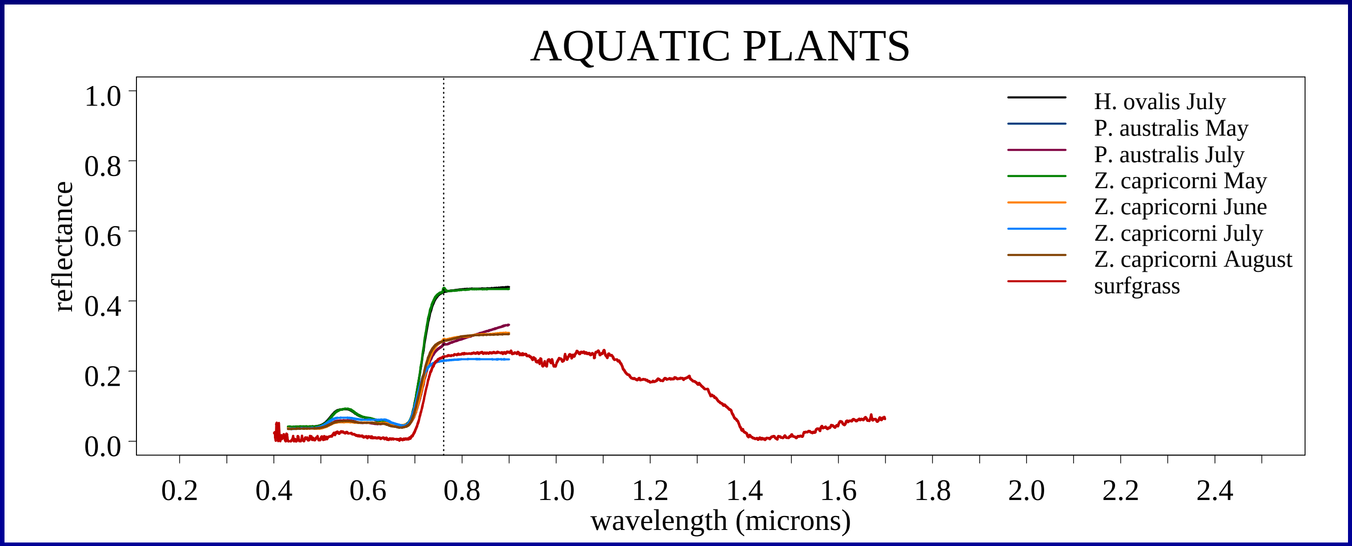




Land plants: Clark, et al. (2003).

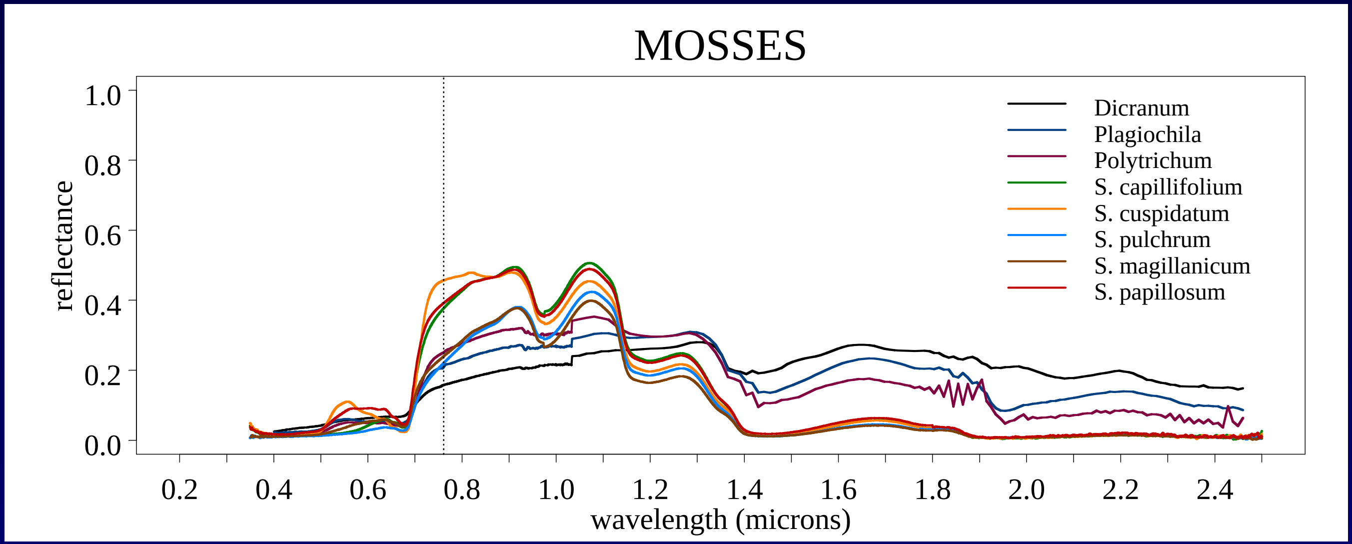
Lacey oak, Arlington, TX Parks&Recr.

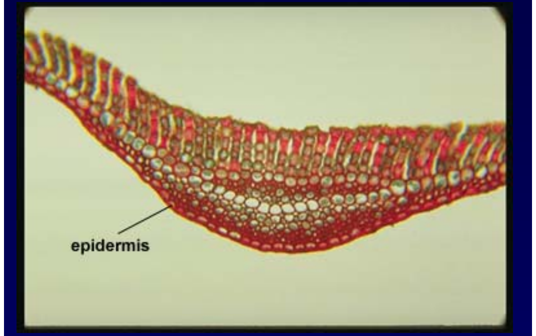
Sitka spruce, Offwell Woodland & Wildlife Trust



Aquatic plants: Fyfe, et al. (2003); surfgrass: N.Y. Kiang

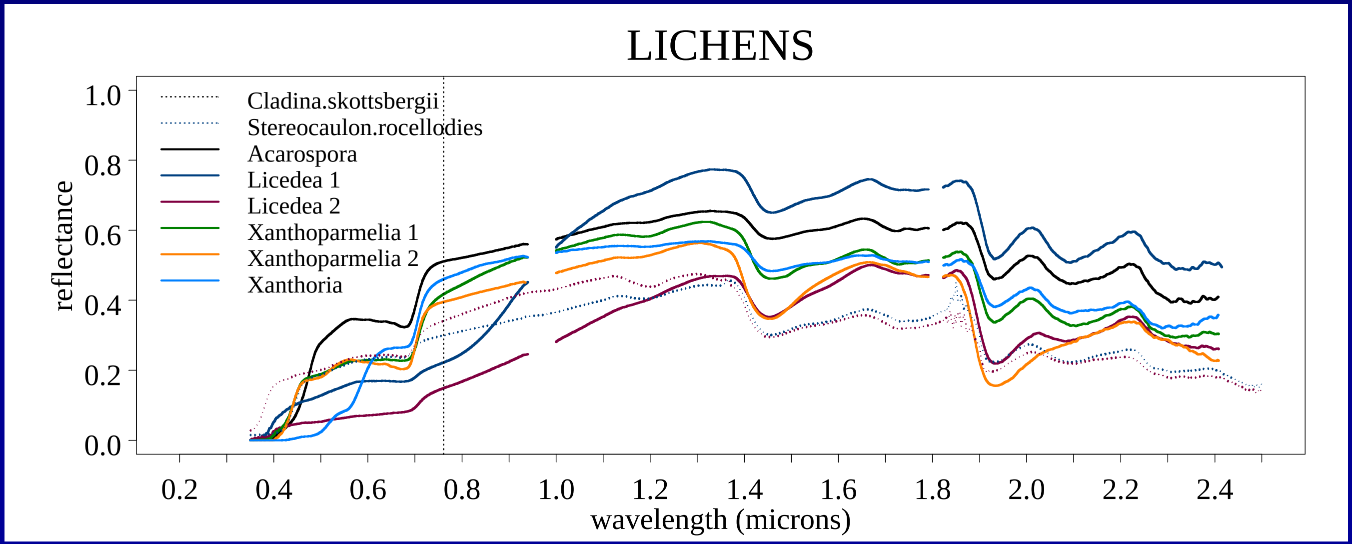
Posidonia oceanica, MareNostrum.org

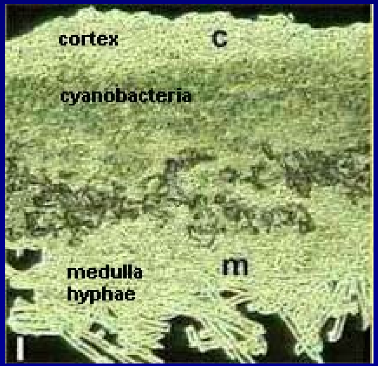




Moss leaf cross section: G. Muth

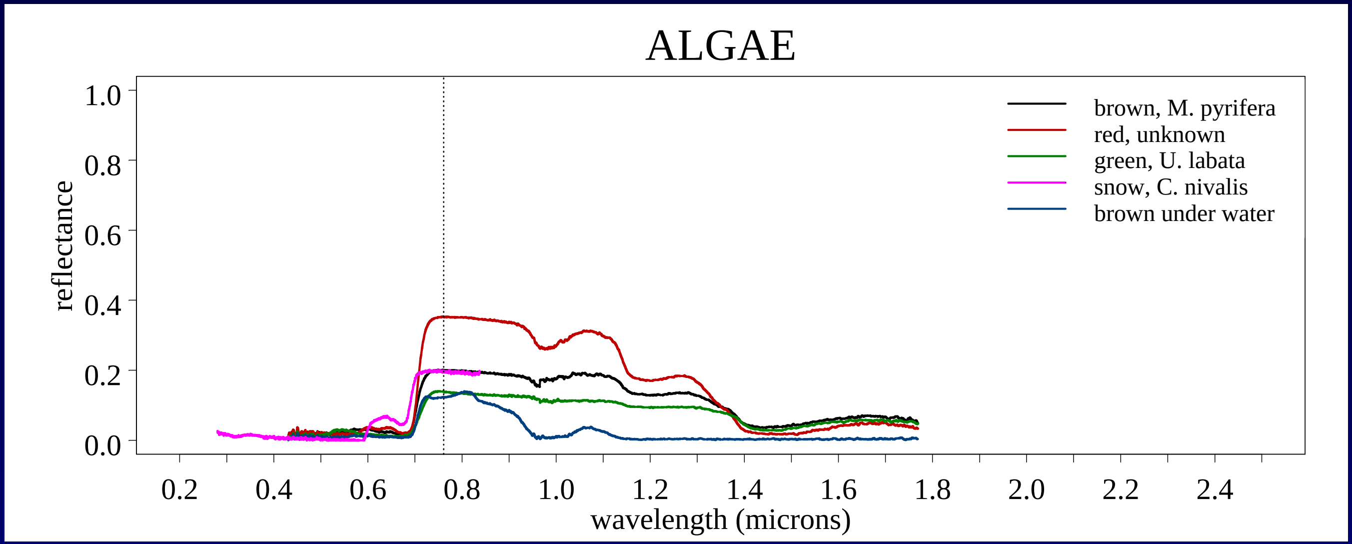
Moss spectra: Lang, M., Kuusk, A., Nilson, T., Lükk, T., Pehk, M., and Alm, G. Reflectance spectra of ground vegetation in sub-boreal forests. Tartu Observatory, Estonia. 2002. Greg Asner, Carnegie Institutution of Washington, Stanford University





Lichen cross section: J. Deacon, University of Edinburgh

Lichen spectra: R. N. Clark, G. A. Swayze, R. Wise, K. E. Livo, T. M. Hoefen, R. F. Kokaly, and S. J. Sutley, 2003, USGS Digital Spectral Library splib05a, U.S. Geological Survey, Open File Report 03-395.



Red algae, UC Berkeley Museum of Paleontology

Snow algae: Gorton, et al. (2001). Other algae: N. Kiang.

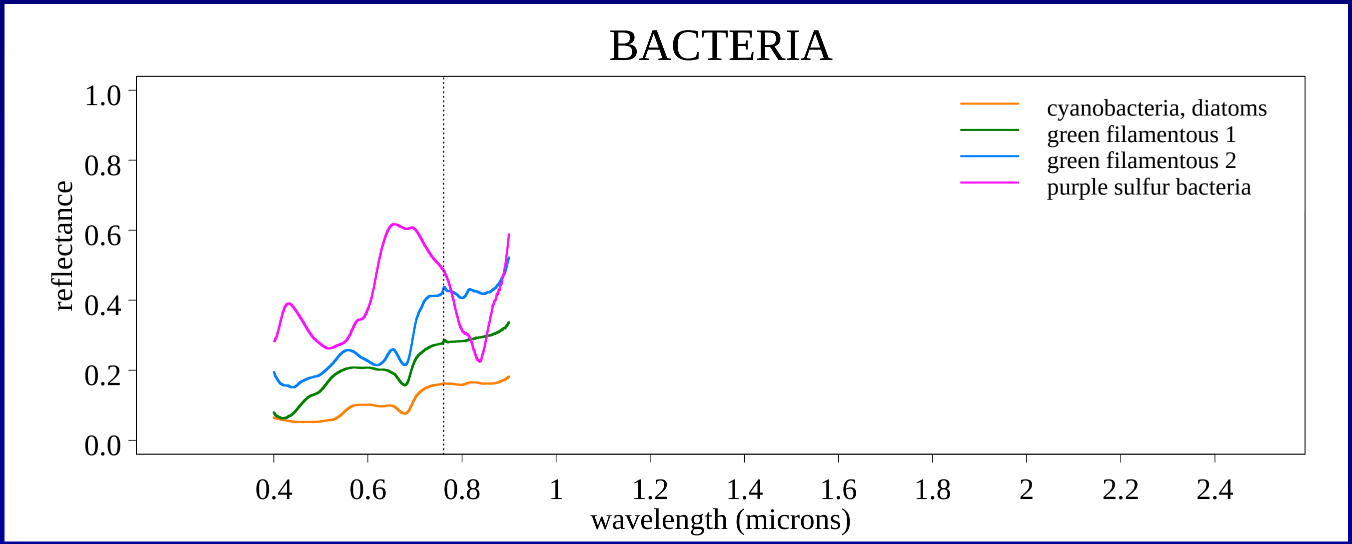


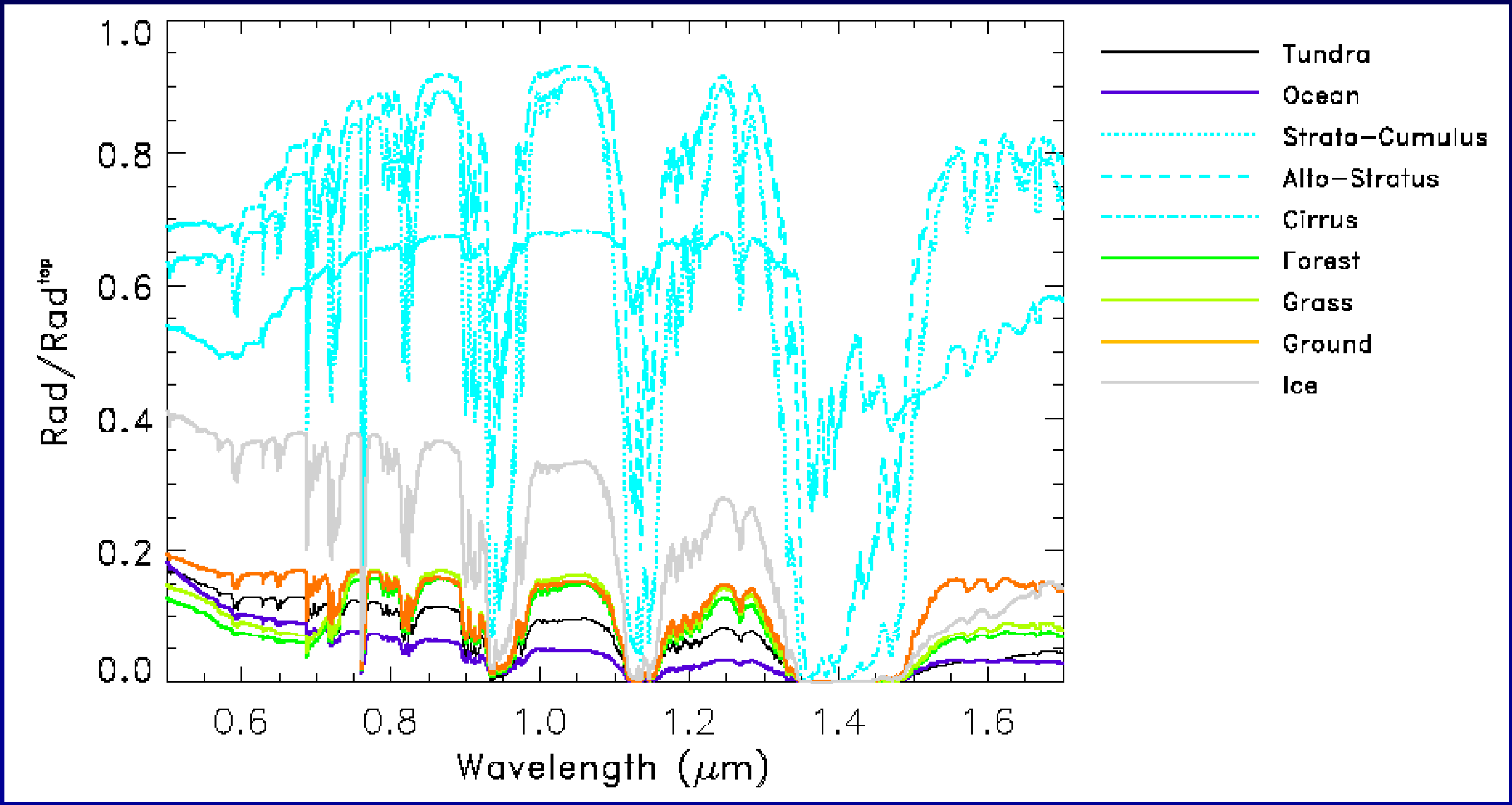
PLATE 63. *Farbstreifensandwatt* (color-striped sand bar) is the German term for colored bacterial layers in sediment. Cyanobacteria are just above a layer of purple sulfur bacteria and black sulfate reducers are just below. (Chap. 13)

Microbial mat layers

Bacteria in a microbial mat: from Reinhard Bachofen in Wiggli, et al. (1999)

Earth model - radiance spectra

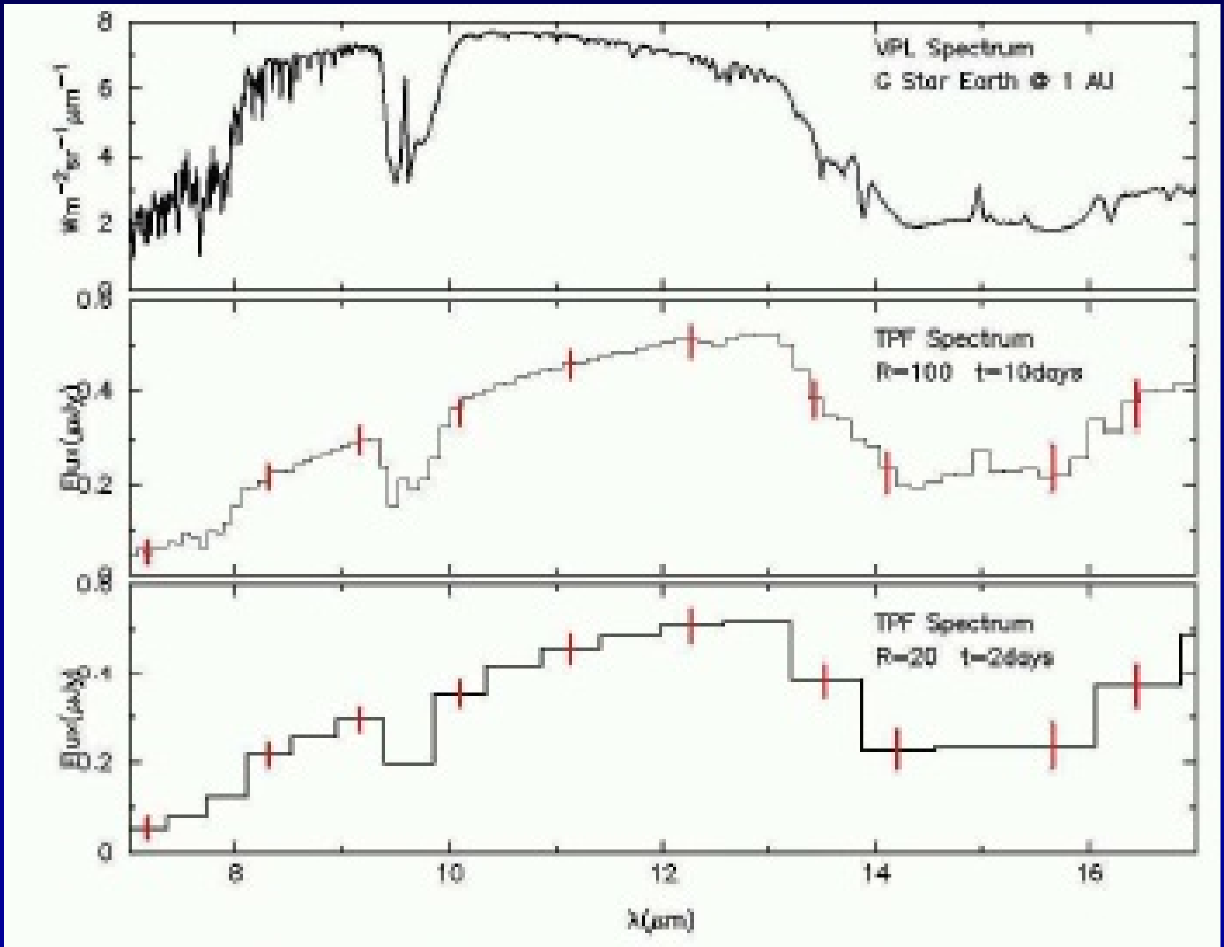
Tinetti et al. (2006)



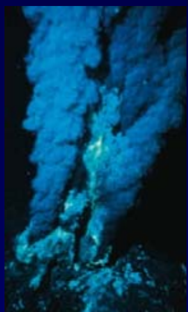
Need 20% cloud-free surface vegetated to detect red-edge

Space telescope resolution for the vegetation red-edge

G. Tinetti (personal communication)



Co-evolution of photosynthesis with the atmosphere and ocean




3.8-3.6 Ga — Anoxygenic purple bacteria and green sulfur bacteria: H_2, H_2S

Hydrothermal vents?
IR thermotaxis of chemolithotrophic bacteria?
Expanded to shallower waters?

2.9, 2.5-2.3 Ga - Snowball Earths: H_2O_2 e^- donor?


2.6-2.4 Ga — Oxygenic cyanobacterial mats

endosymbiosis with eukaryote

2.4 Ga - Great oxidation event


1.2 Ga-750 Ma — Red algae (phycobilins) / Green algae (shallower water, high light)

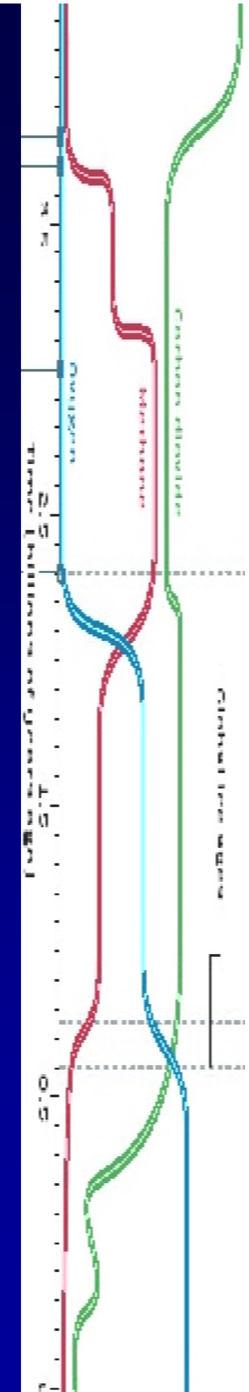
SLOW BUILD-UP OF O_2, O_3


460 Ma — First land plants (mosses, liverworts)


354 Ma — Carboniferous, peak plant productivity

144 Ma — Flowering plants


20-35 Ma — C4 photosynthesis (reduces photorespiration)



Kasting SciAm 2004

Radiance spectra of Earth through time

Kaltenegger, Traub, and Jucks (2007) ApJ, 658:598-616.

Wtihout clouds — With clouds

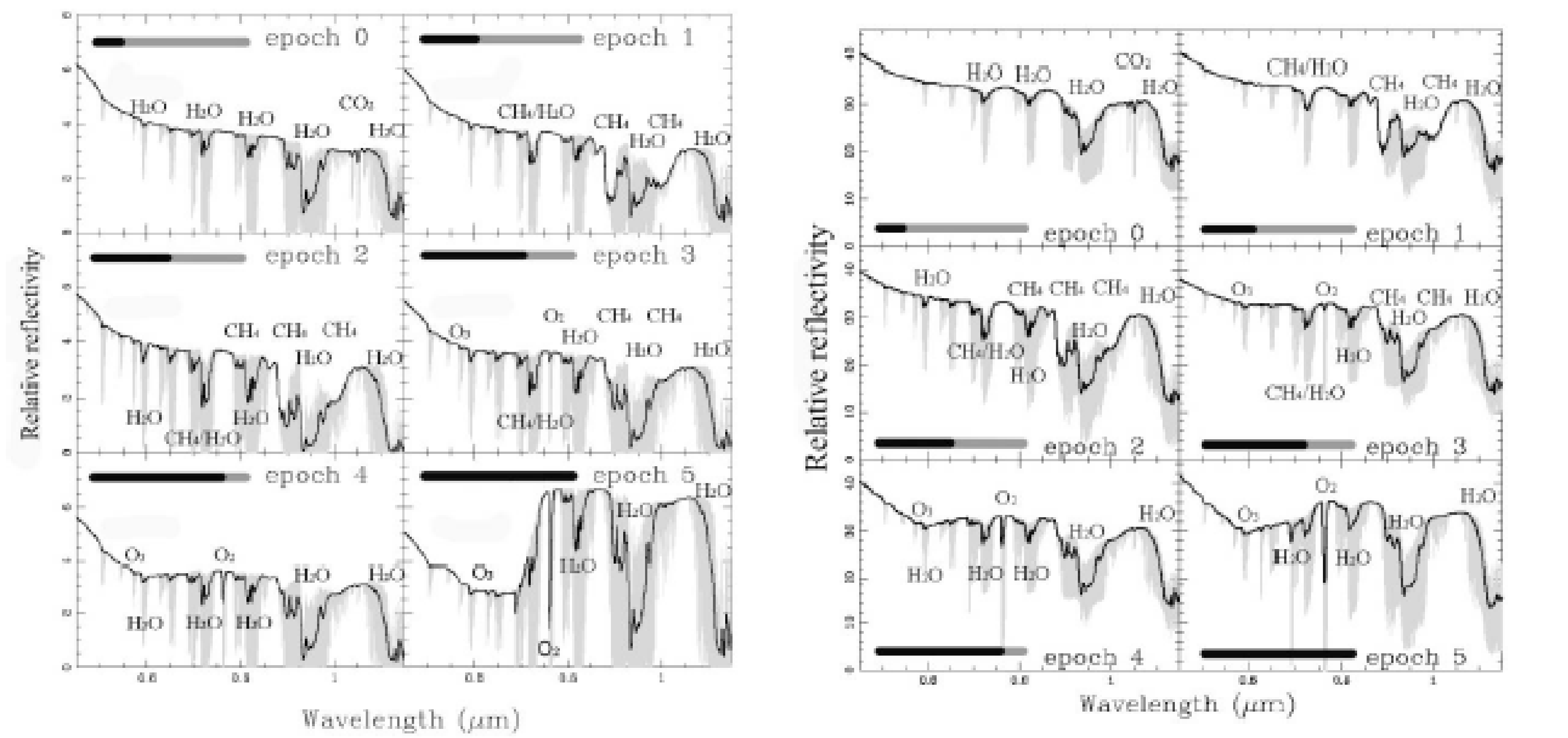
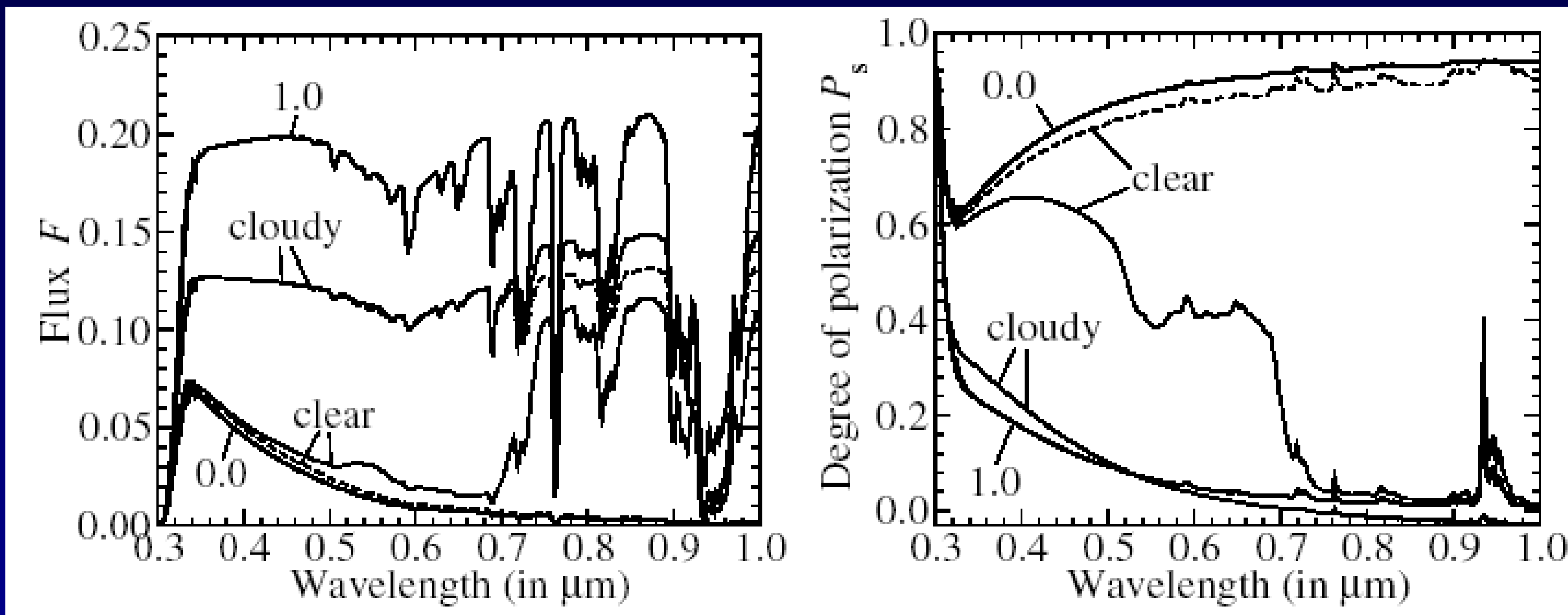


FIG. 9.—Visible and near-infrared spectra of an Earth-like planet for six geological epochs. Spectra without clouds (*left*) and with clouds (*right*) are shown; note the different scales. The spectral features change considerably as the planet evolves from a CO_2-rich (epoch 0) to a CO_2/CH_4-rich atmosphere (epoch 3) to a present-day atmosphere (epoch 5) in the visible. The black lines show spectral resolution of 70, comparable to the proposed *TPF-C* mission concept.

Stam, D. B. (2008) A&A 482:989-1007

"Spectropolarimetric signatures of Earth-like extrasolar planets"



Solid - model planet covered by forest. Dashed - ocean

0.0 - albedo all 0.0. 1.0 - albedo all 1.0

Fig. 7. The wavelength dependent F (*left*) and P_s (*right*) of starlight that is reflected by clear and cloudy horizontally homogeneous model planets with surfaces covered by deciduous forest (thin solid lines) and a specular reflecting ocean (thin dashed lines). Note that the lines pertaining to P_s of the cloudy atmospheres are virtually indistinguishable from each other. For comparison, we have also included the spectra of the clear model planets with surface albedos equal to 0.0 and 1.0 (thick solid lines), shown before in Fig. 3. The planetary phase angle is 90°.

Circular polarization from homochirality of biomolecules

Sparks et al. (2009). J. Quant. Spectr & Rad Tr., 110(14-16):1771-1779.

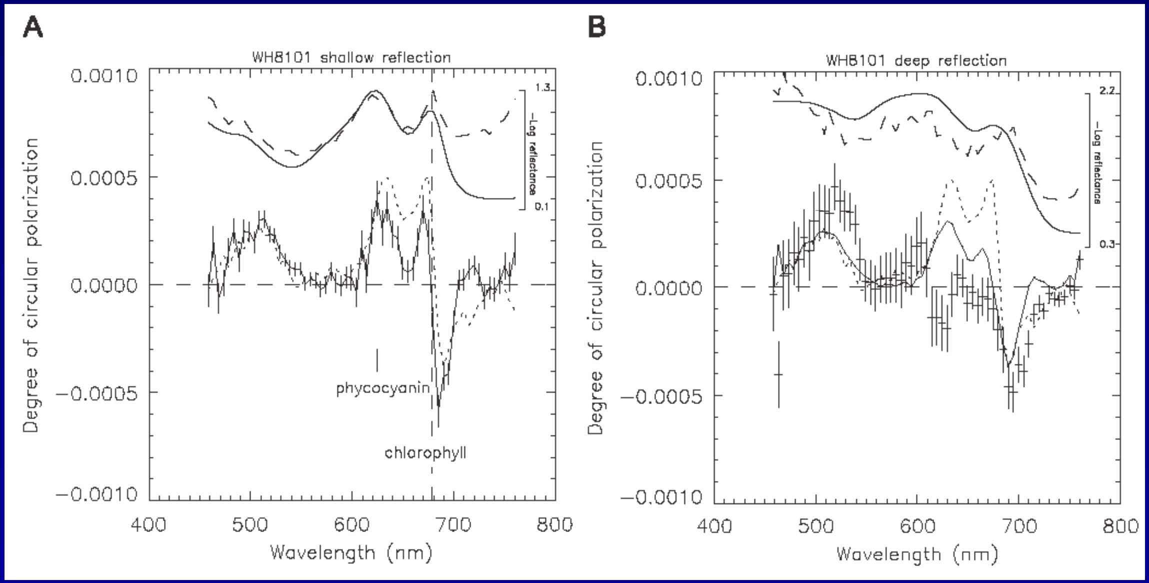
Left-handed L-amino acids, Right-handed D-sugars

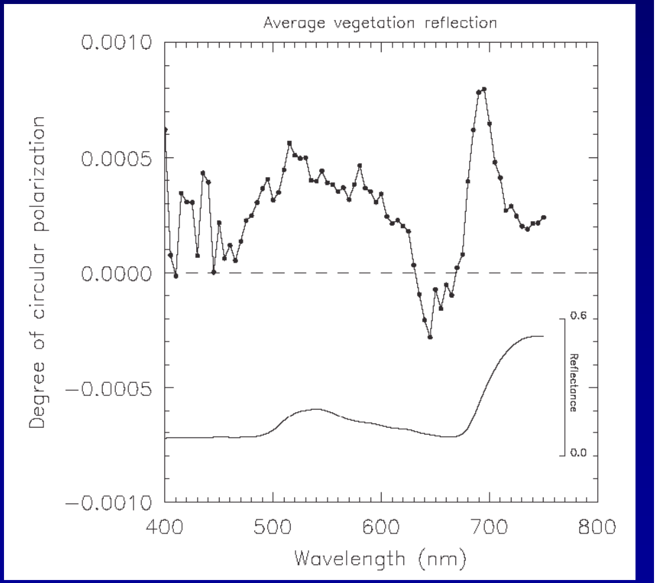
Laboratory cyanobacteria

shallow reflection

deep reflection

Averages of plant leaves





Solid - absorbance

Dashed - linear polarization

Photosynthetic Pigment Absorbance Adapted to Incident Radiation Spectra:

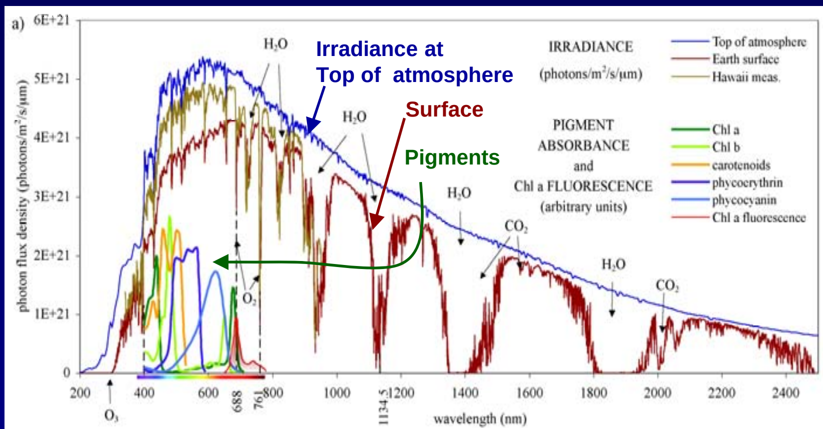
fine-tuning of photopigments (and protein environment)

Oxygenic

400-700 nm

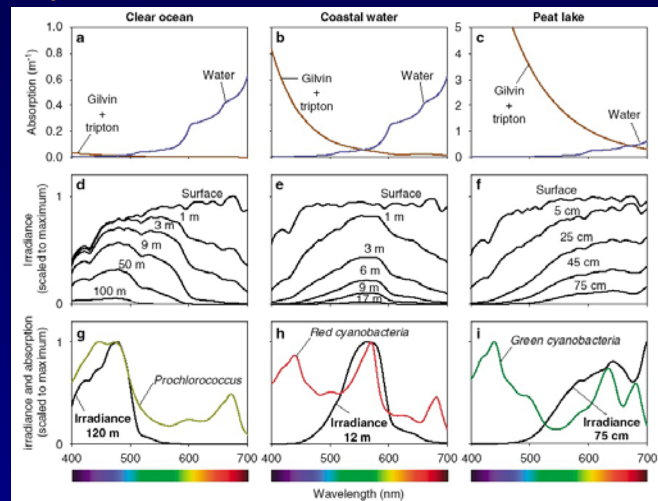
Chlorophyll peak = photon flux peak and/or O_2 band?

Did oxygenic photosynthesis favor itself to dominate on land?



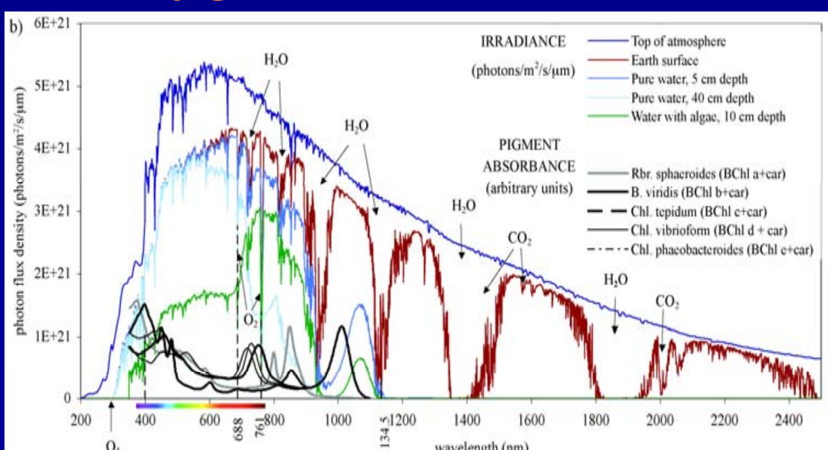
Kiang et al (2007)

Light niches of red and green cyanobacteria due to water bands

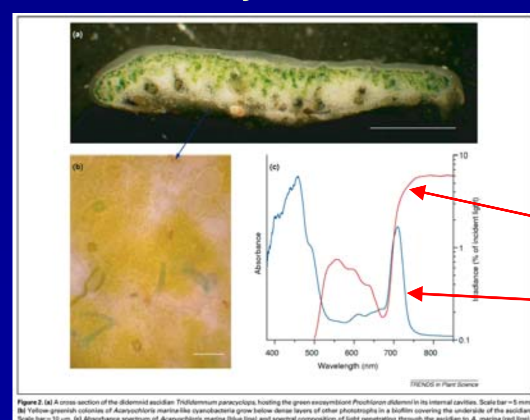


Stomp & Huisman et al. (ISME 2007, Ecol. Let. 2007)

Anoxygenic under water 400-1015 nm



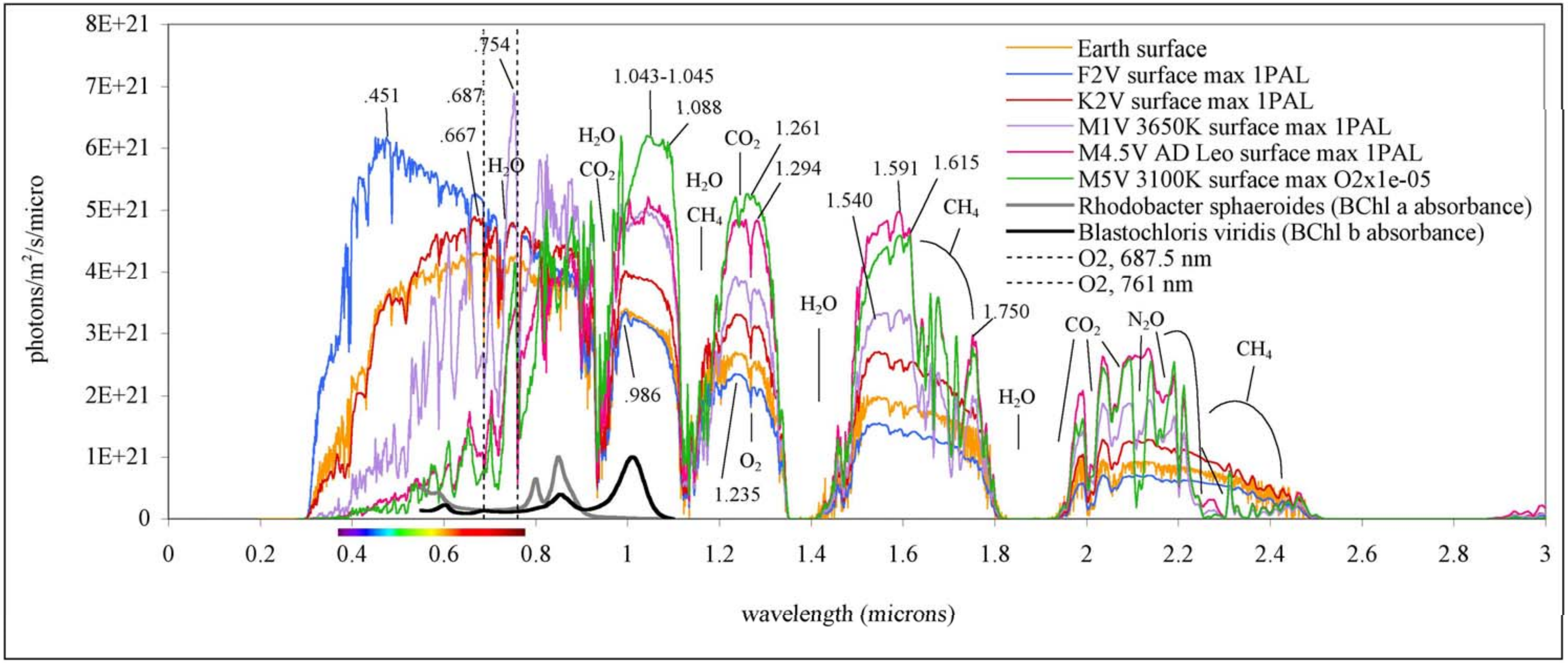
Oxygenic photosynthesis in far-red with Chl d in *Acaryochloris marina cyanobacterium*



Larkum & Kühl (2005)

Surface incident photon flux densities on Earth-like planets around F, Earth, K, M stars

upper wavelength bounds: 1400 nm (underwater), 1100 nm (electronic transitions?)

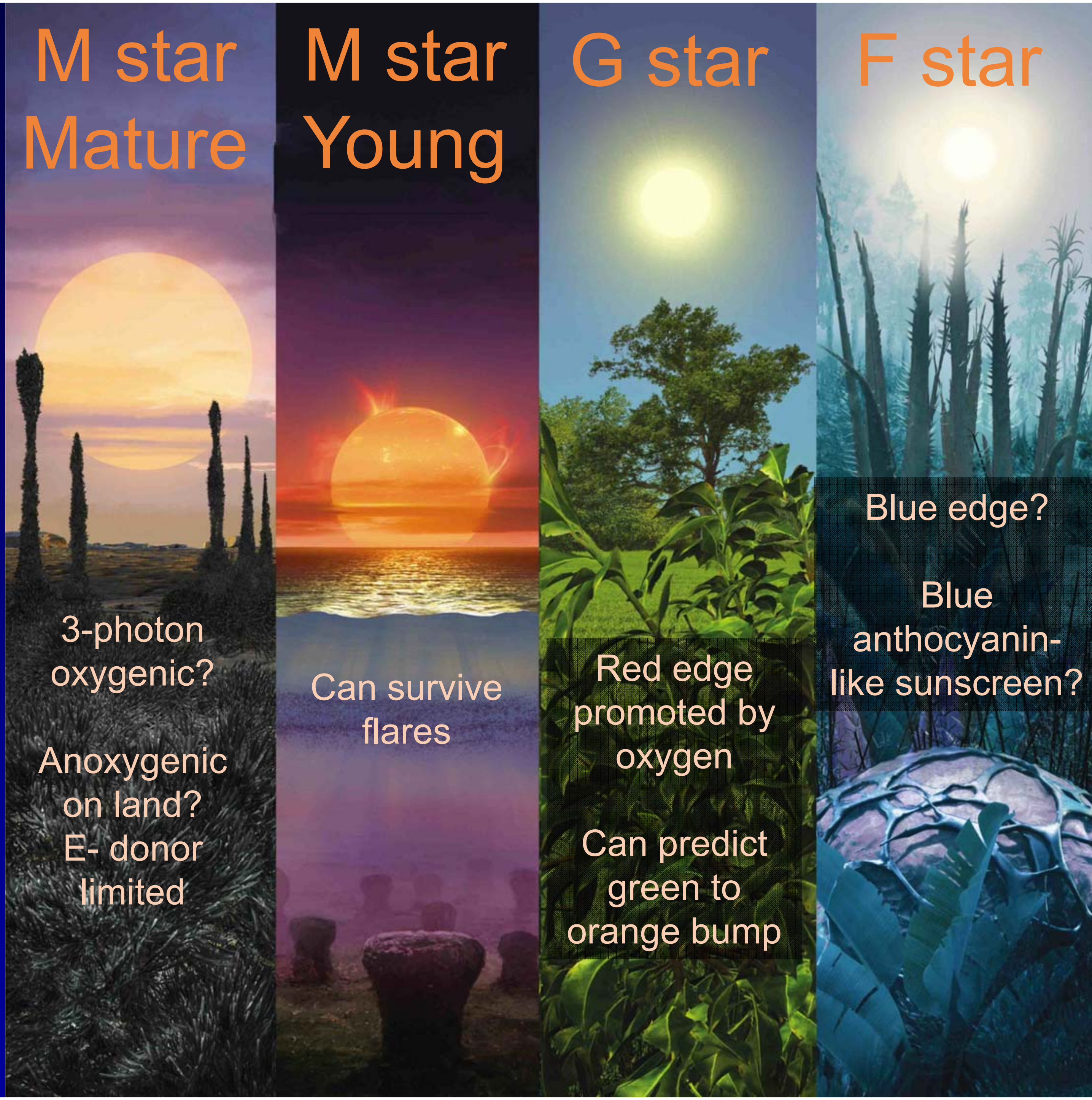


F star peaks at 451 nm. Ozone Chappuis band shifts more to blue.

K star similar to G star

M stars
low VIS adequate for Earth-like plant survival.
Peak in NIR similar to BChl b absorbance peak.

Kiang et al. 2007



Kenn Brown and Chris Wrenn, Mondolithic Studios

Kiang, SciAm April 2008

The million-dollar question

- Can oxygenic photosynthesis occur at other wavelengths than red?
- i.e. Can we expect to find biogenic oxygen on planets with low visible light?
- I.e. What is the maximum efficiency of oxygenic photosynthesis?

Is there a long photon wavelength limit for oxygenic photosynthesis?

Or: What is the maximum energy efficiency of oxygenic photosynthesis?

SOLAR ENERGY limit:

Shockley-Queisser detailed balance limit:

i. Integrating solar radiation energy of photons ≥ energy gap of p-n junction, 6000 K sun, gives:
   1.1 eV = max efficiency 44% @ 1127 nm

ii. Silicon photovoltaic cells:
   today's technology 20%
   (max theoretical 31%)

(Doesn't include storage…)

Ultimate efficiency of a solar cell

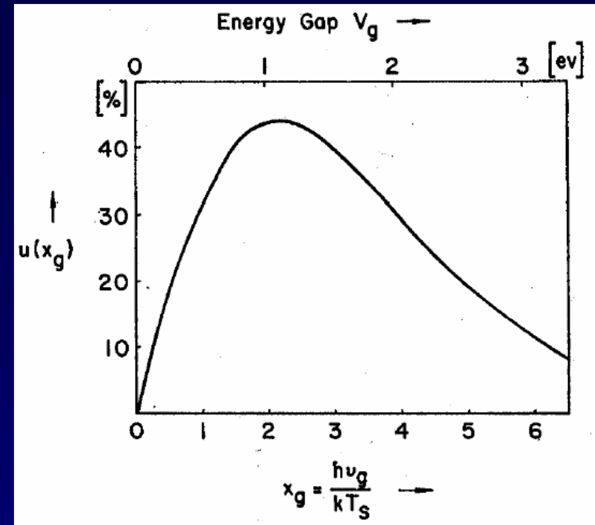


FIG. 3. Dependence of the ultimate efficiency $u(x_g)$ upon the energy gap V_g of the semiconductor.

Silicon cell efficiency

31% max theory

20% in 2009

14% max in 1961

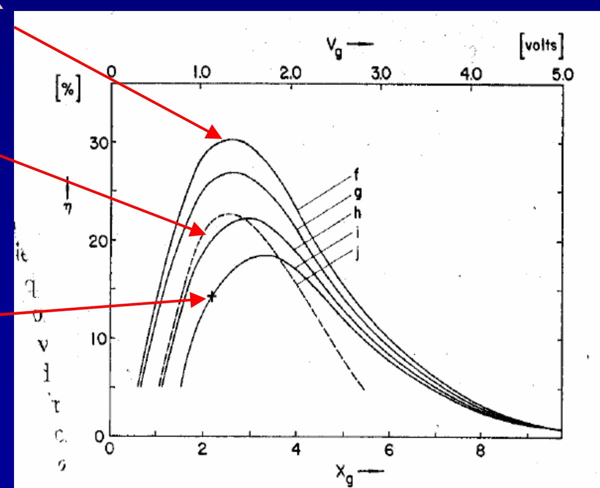
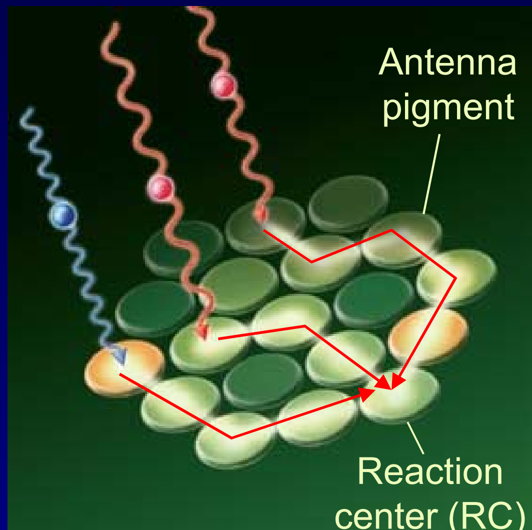


FIG. 6. Efficiency η for a solar cell at temperature $T_c = 300°K$ exposed to a blackbody sun at temperature $T_s = 6000°K$.

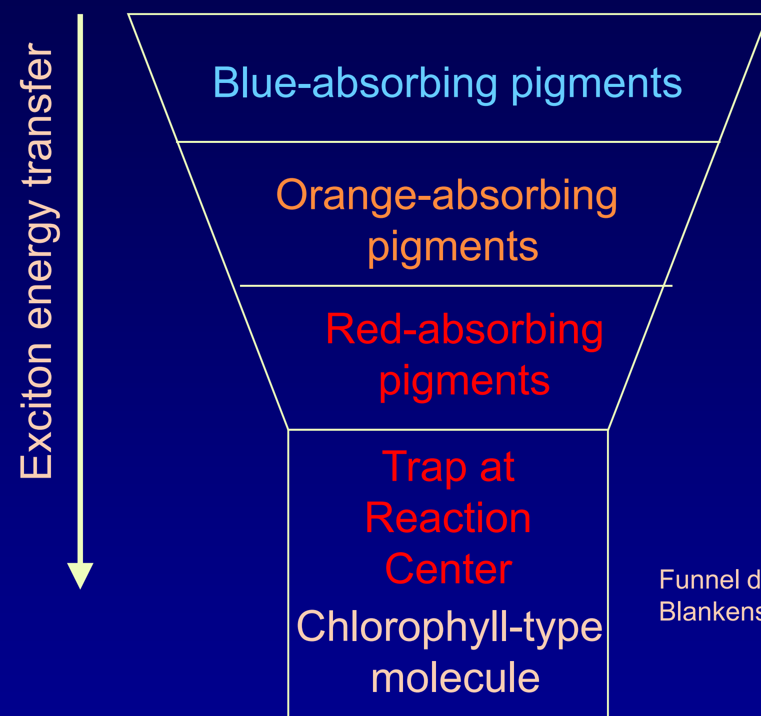
Shockley & Queisser (1961)

Photosynthesis: Light harvesting

Light harvesting complex (LHC)



Energy cascade



Funnel diagram after Blankenship (2002)

Funnel to the reaction center (RC) via resonance transfer (now quantum coherence, Engel et al. 2007)

Photosynthetically Active Radiation (PAR):
- oxygenic: 400-700 nm
- anoxygenic: longest ~1034 nm

Photosynthesis - quick review

BASIC PATHWAY:

$$CO_2 + 2H_2A \underset{pigments}{\overset{light}{\Rightarrow}} (CH_2O) + H_2O + 2A$$

H_2A is electron donor
e.g. H_2O, H_2S, H_2, Fe^{2+} + H_2O

$$6CO_2^c + 12H_2O^w \xrightarrow{light} \underset{glu\ \cos\ e}{(C_6H_{12}O_6^c)} + 6H_2O^c + 6O_2^w$$

Oxygenic

2 photons/H_2O split
x 2 per O_2 evolved
x 2 per CO_2 fixed
= 8 photons
+ 2-4 (other processes)

Oxygenic net reaction to fix one Carbon

$$CO_2^c + H_2O^w \overset{light}{\Rightarrow} \frac{1}{6}\underset{glu\ \cos\ e}{(C_6H_{12}O_6^c)} + O_2^w$$

Redox reactions in oxygenic photosynthesis reaction centers

Oxygenic photosynthesis: 2-photon system booster rockets

(8 photons per CO_2 fixed)

RC is oxidizer
RC* is reducer

P680 is most oxidizing known biological molecule

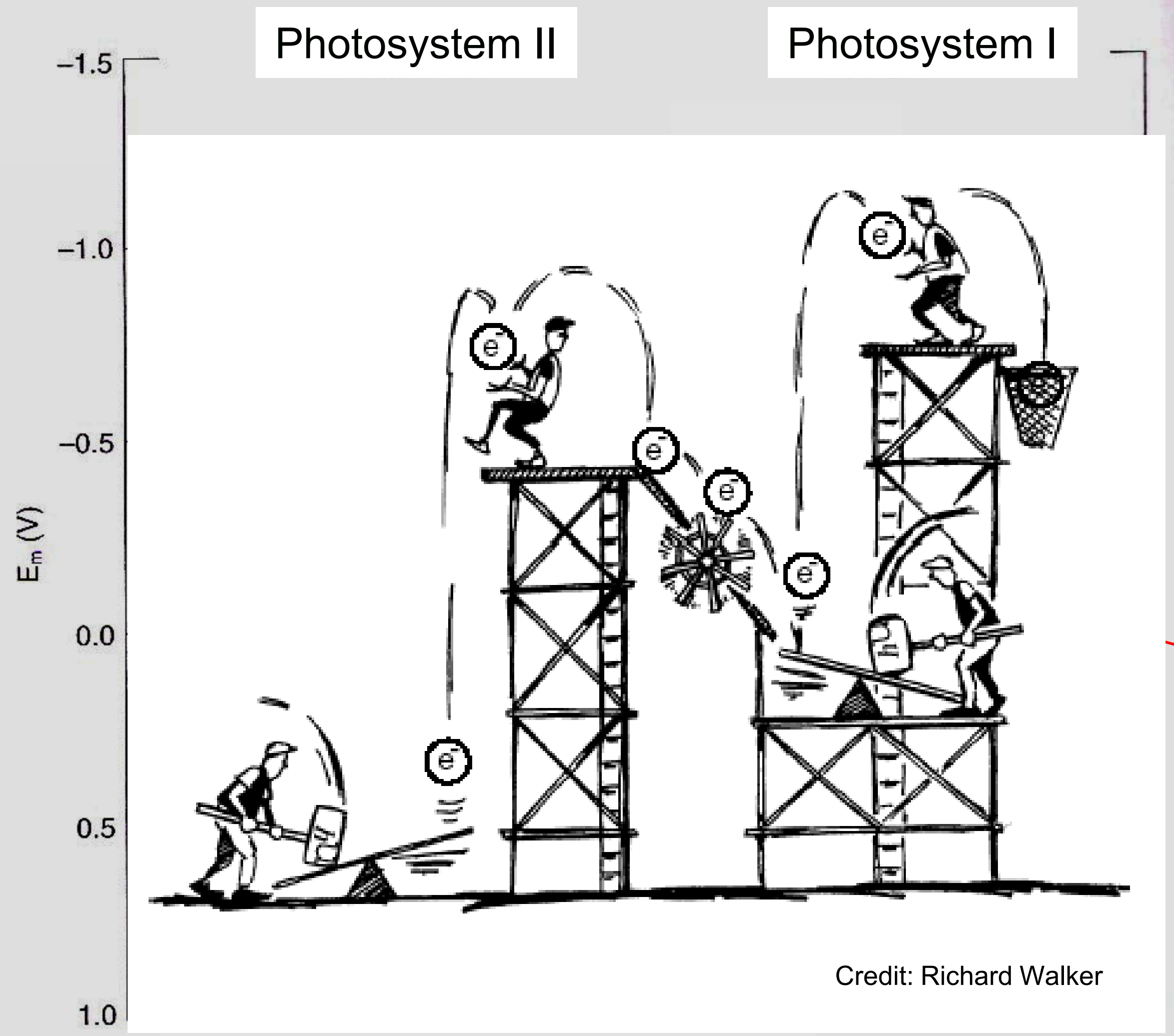


Figure 7.9 The Z scheme for electron transfer in oxygenic photosynthesis.

Source: Robert Blankenship, Molecular Mechanisms of Photosynthesis, 2002.

Redox reactions in oxygenic photosynthesis reaction centers

Oxygenic net reaction to fix one Carbon

$$CO_2^c + H_2O^w \xrightarrow{light} \frac{1}{6}(C_6H_{12}O_6^c)_{glucose} + O_2^w$$

Wasted energy

Energy input = (8 to 10) x 1.797 eV

Energy stored = 4.97 eV

Energy “wasted” (per photon used) = 1.17 - 1.30 eV

* Prevents back reactions
* Efficiency: 27-34% (monochromatic red light)

Less energy input for Chl d in A. marina

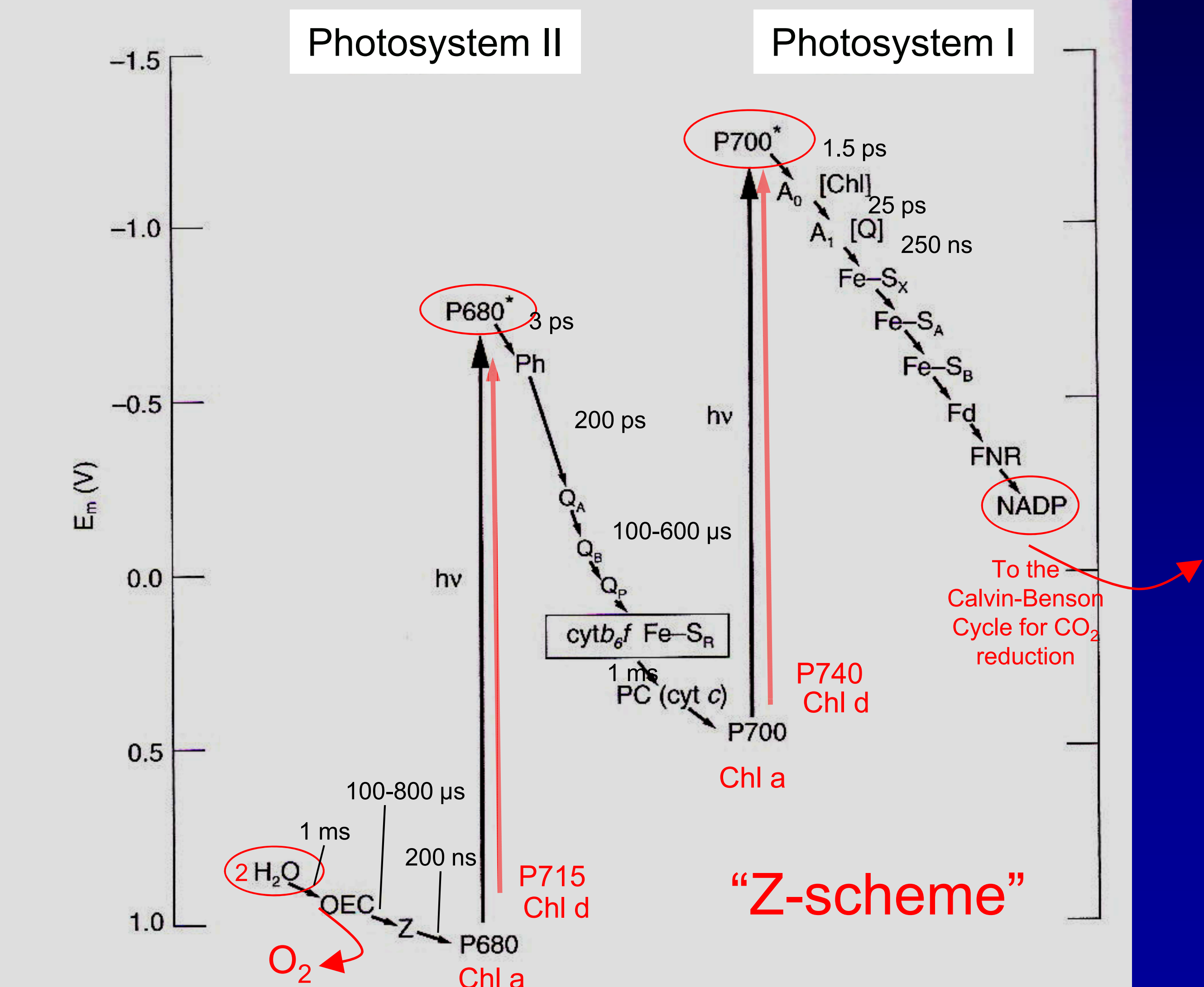
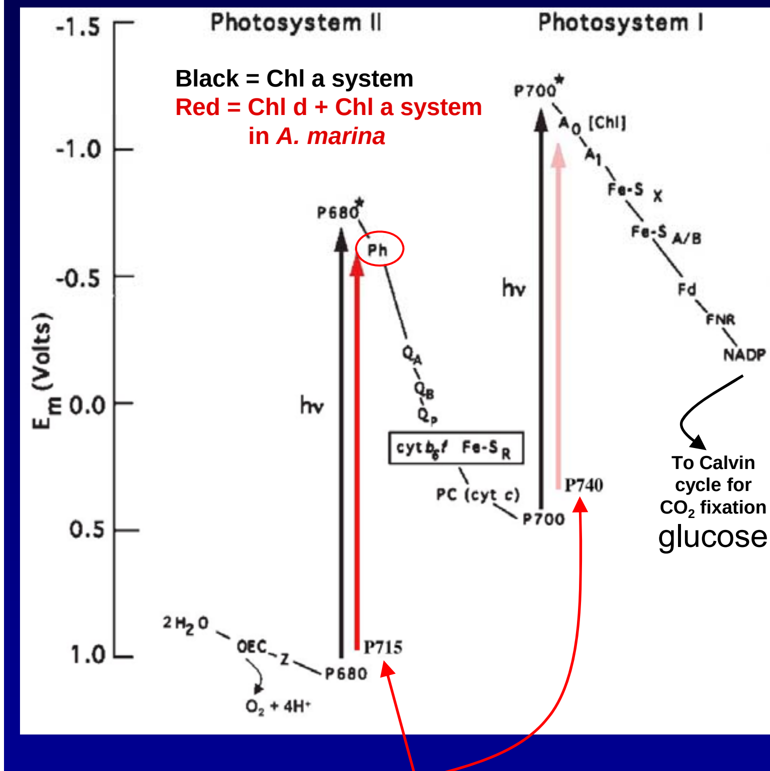


Figure 7.9 The Z scheme for electron transfer in oxygenic photosynthesis.

Source: Robert Blankenship, Molecular Mechanisms of Photosynthesis, 2002.

Redox reactions in oxygenic photosynthesis reaction centers



Unknown redox potentials for *A. marina.* Wiggle room at Pheo.

$CO_2 + H_2O$ --> (1/6)(glucose) + O_2

Energy stored = 4.97 eV

Efficiency with 8 photons (680 &700 nm) = ~34%

Ultimate limits with no energy waste?

Energy stored

Light + dark reactions:

H_2O -> glucose = 0.82 – (-0.42) = 1.24 eV

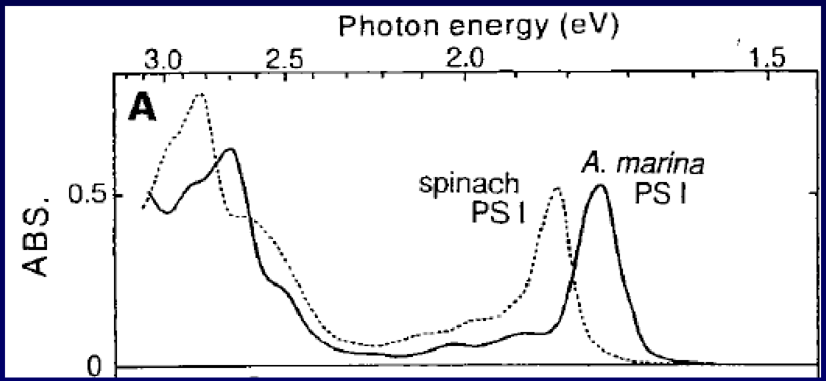
~ 1000 nm, each photon

P680 -> glucose = (1.1-1.2) – (-0.42) = 1.52-1.62 V

~ 765-815 nm

What adjustments is *A. marina* making?

If *A. marina* is:



Hu et al. (1998)

• *more efficient* than Chl a organisms, then:
The upper bound in wavelength has not yet been reached for oxygenic photosynthesis.

• *less efficient* than Chl a organisms, then:
The far-red/near-infrared wavelengths are at or past the wavelength for maximum efficiency, thus are at an upper wavelength bound (weak photons lose some to back reactions)

• reducing the redox potential of P715 in PSII, then:
Oxidizing potential to split water can be less (implications for H_2 fuel production…)

Lab measurements on *A. marina*

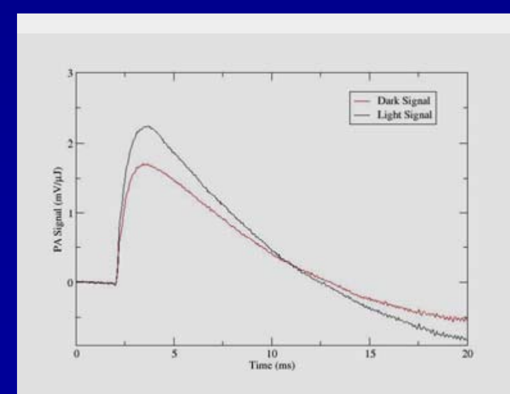
Method:

Pulsed time-resolved photoacoustic calorimetry (PTRPA or just PA)

a. Monochromatic tuneable pulsed Nd:YAG laser
b. Resolves reactions at microsecond to millisecond time scale

Samples: whole intact cells of

Synechococcus cyanobacteria (control, Chl a only)
Acaryochloris marina



Targets: millisecond time scale for

Energy storage in whole cell
Energy storage in PS I only (laser at 730-750 nm)

Very preliminary results

	Laser Wavelength (nm)	Energy storage (%)
Synechococcus PSI	700	?
A. marina PSII + PSI	700	?
A. marina PSI	730	?
A. Marina PS I	755	?

For Synechococcus PSI, Charlebois & Mauzerall (1999) measured 42 ± 2% @ monochromatic 695 nm

Is A. marina at the limit for oxygenic photosynthesis?

Questions

Is A. marina at the upper bound for oxygenic photosynthesis? Does this mean extrasolar oxygenic photosynthesis must have a red edge?

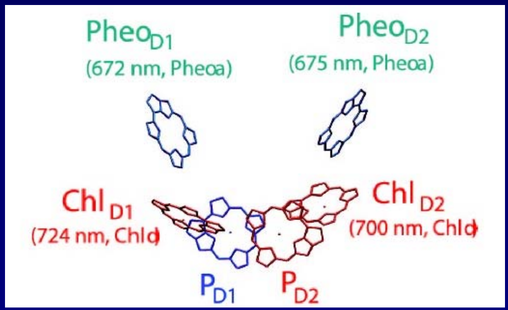
Earth-centrism? Other stable reduced carbon compound besides glucose?

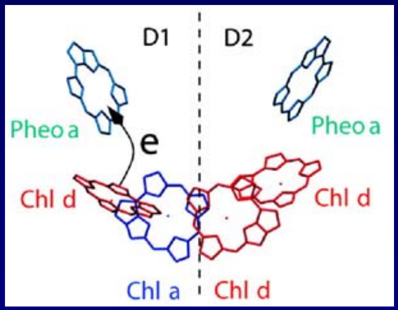
Pigment detection: bad signal-to-noise, but help rule out false positives or negatives? E.g. lack of useful photosynthetically active radiation but presence of O_3.

Future work

a. Purified PSII and PSI complexes and PA at nanosecond to microsecond time scale to identify adjustments along electron-transfer pathway.

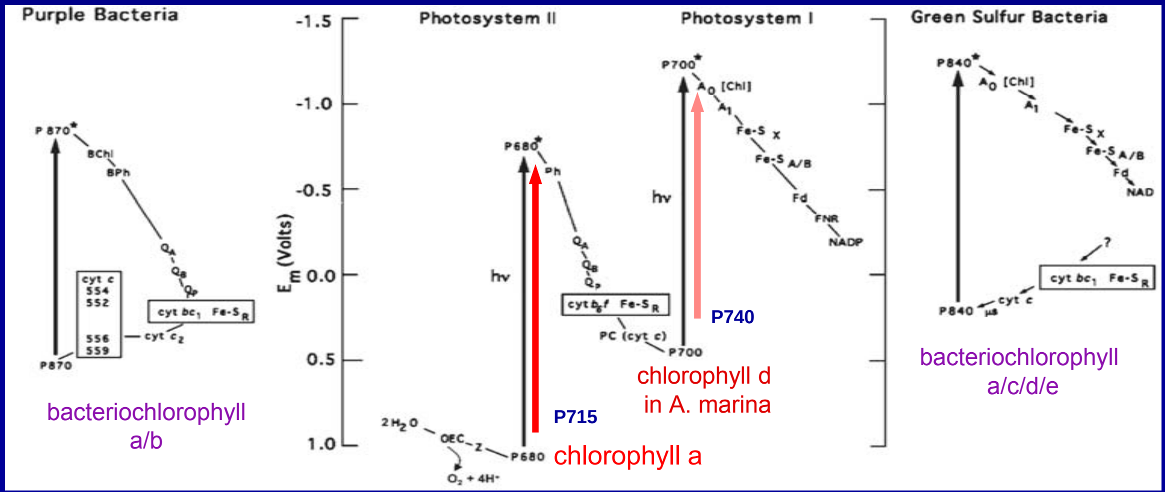
b. Molecular modeling of redox potentials of Chl d substituted into PSII: Jury is still out on position(s) and role(s) of Chl d (Marilyn Gunner, CUNY)





Renger & Schlodder (2008)

c. Do same for anoxygenic photosynthetic bacteria.



More alien photon use speculations

Limits for 3+ photon photosystems?

Other light harvesting schemes for renewable energy technology or other planets:

i. Dye-sensitized light-harvesting photovolatics: don't waste the shorter wavelength energy

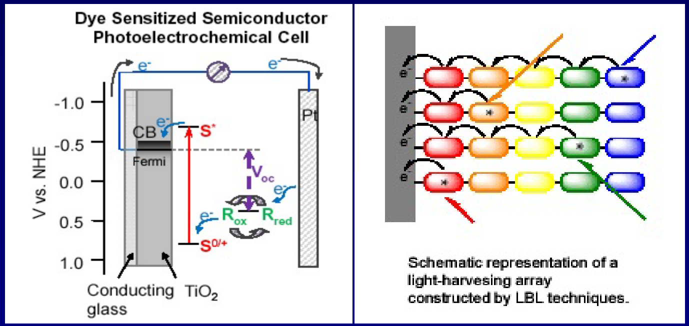
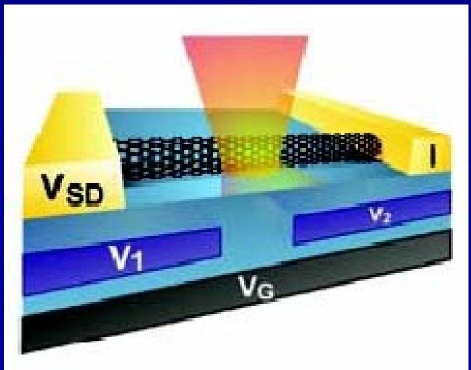
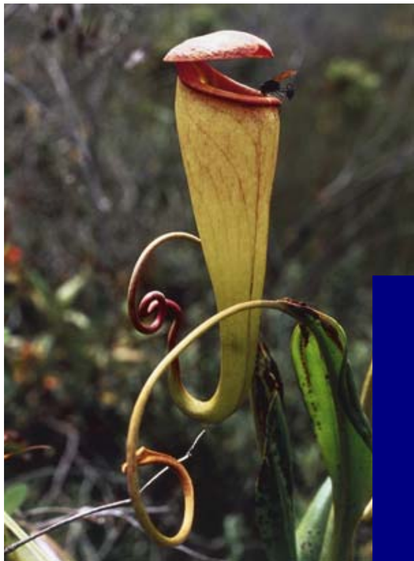


Figure courtesy of P. Dinolfo, Rensselaer

ii. Carbon nano-tubes: multiple electron-hole pairs per photon (Gabor et al 2009, Science): possibly higher efficiency, multiple e-h pairs per photon when $E_{photon} > E_{gap}$



Gabor et al. (Science, 2009)




Acknowledgments

Carl Pilcher, NASA Astrobiology Institute, Director's Discretionary Fund

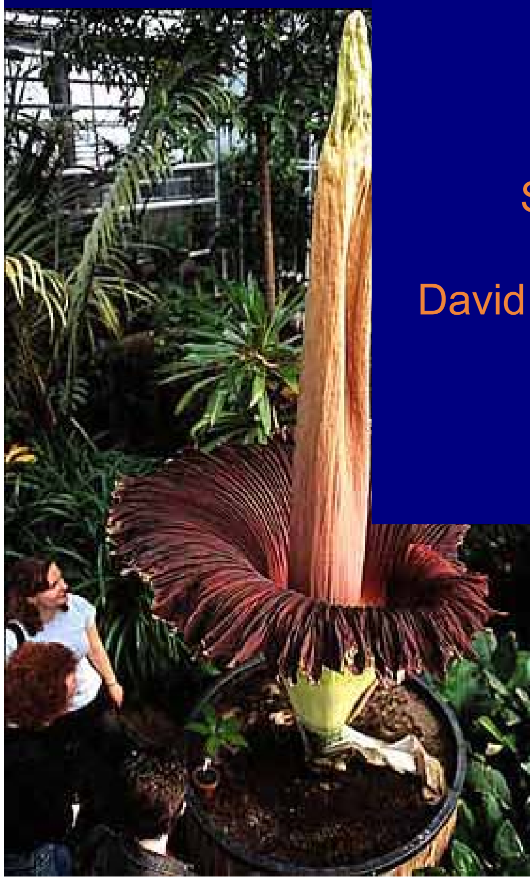
Oak Ridge Associated Universities

Victoria S. Meadows,
NAI Virtual Planetary Laboratory

Steven Mielke, NASA Postdoctoral Program, NAI

David Mauzerall, Rockefeller University, New York, NY USA

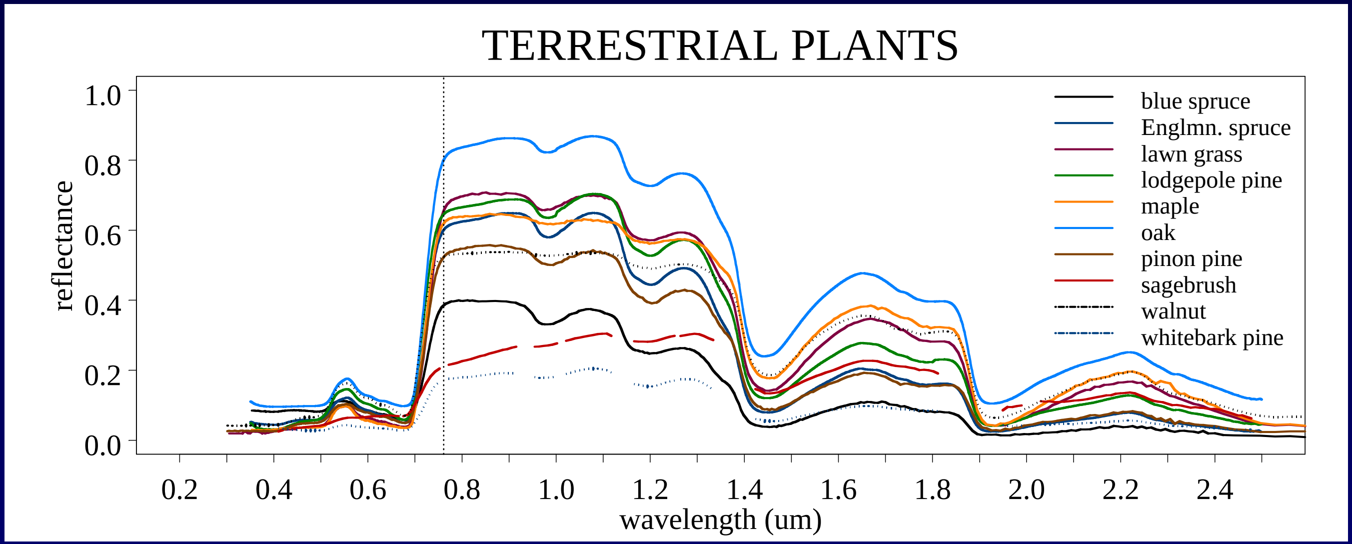
Robert E. Blankenship, Washington University,
St. Louis, Missouri USA

Extra slides

MODIS NDVI (NIR-R)/(NIR+R): Vegetation red edge

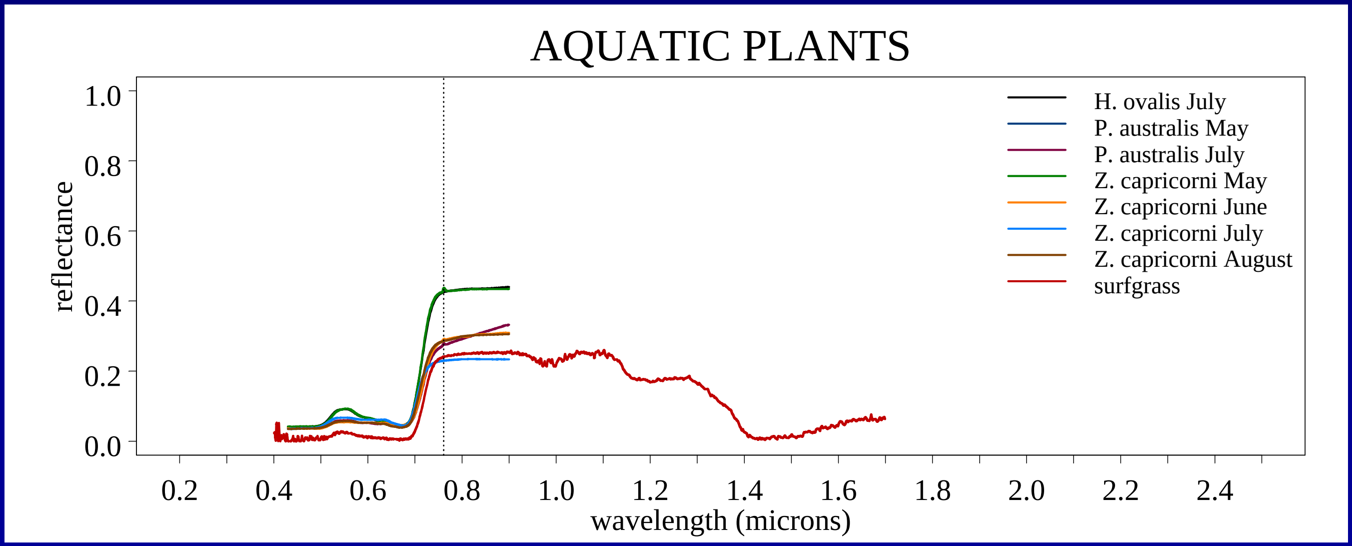
QuickTime™ and a
DV/DVCPRO - NTSC decompressor
are needed to see this picture.



Land plants: Clark, et al. (2003).

Lacey oak, Arlington, TX Parks&Recr.

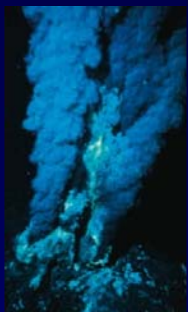
Sitka spruce, Offwell Woodland & Wildlife Trust



Aquatic plants: Fyfe, et al. (2003); surfgrass: N.Y. Kiang

Posidonia oceanica, MareNostrum.org

Co-evolution of photosynthesis with the atmosphere and ocean




3.8-3.6 Ga — Anoxygenic purple bacteria and green sulfur bacteria: H_2, H_2S

Hydrothermal vents?
IR thermotaxis of chemolithotrophic bacteria?
Expanded to shallower waters?

2.9, 2.5-2.3 Ga - Snowball Earths: H_2O_2 e^- donor?


2.6-2.4 Ga — Oxygenic cyanobacterial mats

endosymbiosis with eukaryote

2.4 Ga - Great oxidation event


1.2 Ga-750 Ma — Red algae (phycobilins) / Green algae (shallower water, high light)

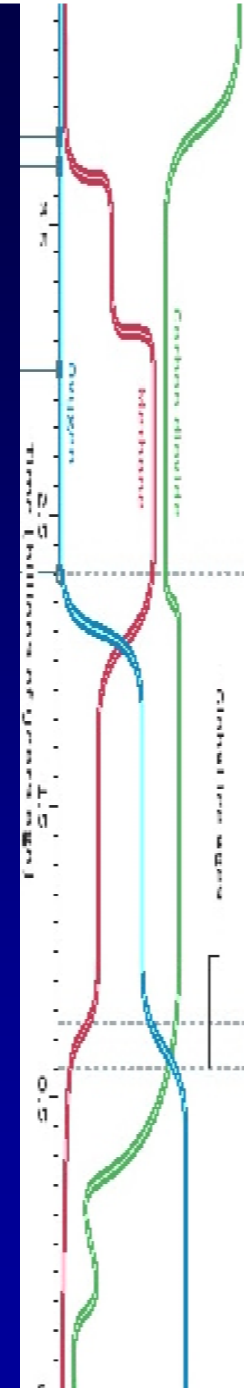
SLOW BUILD-UP OF O_2, O_3


460 Ma — First land plants (mosses, liverworts)


354 Ma — Carboniferous, peak plant productivity

144 Ma — Flowering plants

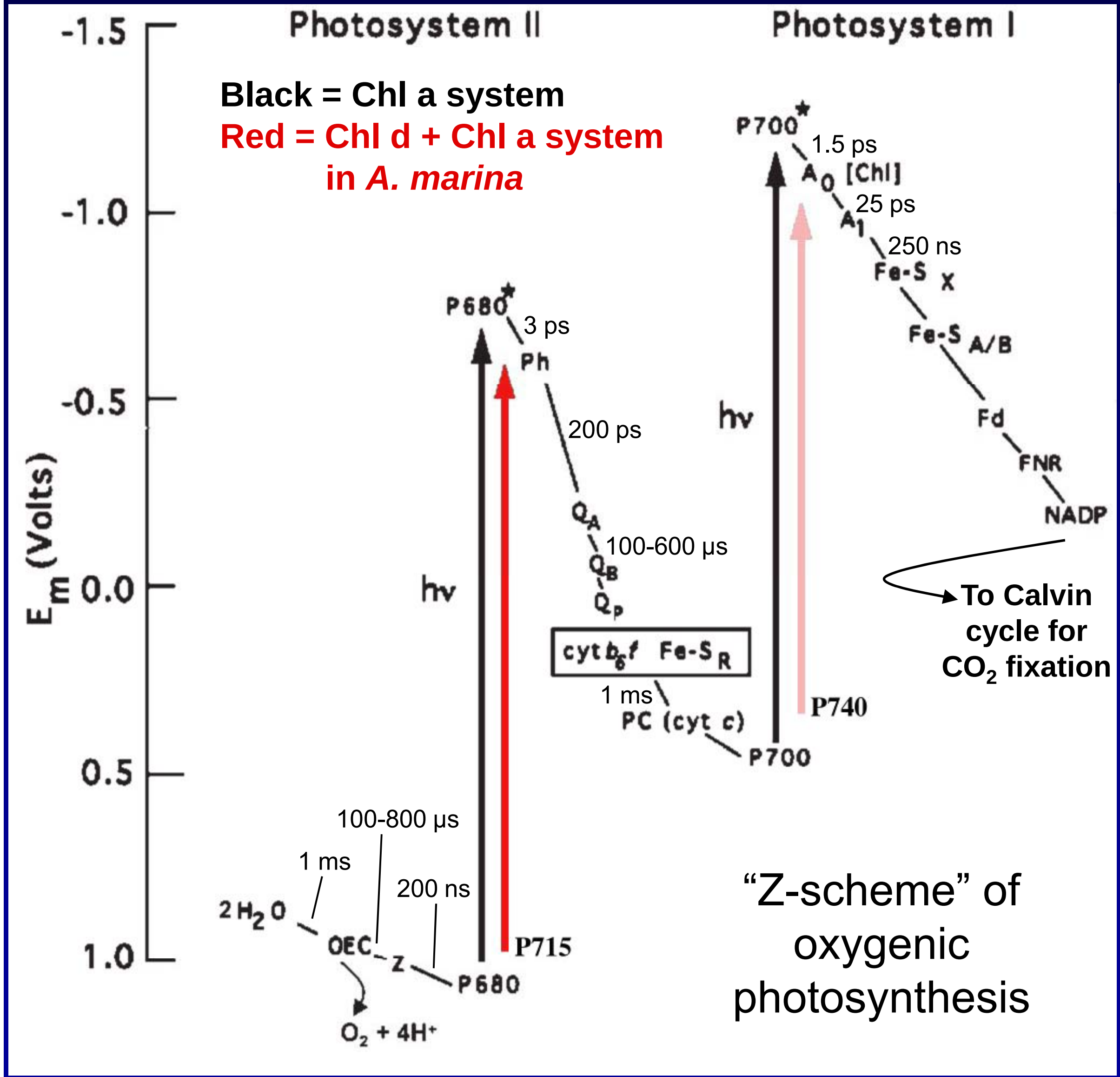

20-35 Ma — C4 photosynthesis (reduces photorespiration)



Kasting SciAm 2004

Redox reactions in oxygenic photosynthesis reaction centers

Photons at RCs like booster rockets



"Z-scheme" of oxygenic photosynthesis

Oxygenic net reaction to fix one Carbon

$$CO_2^{c} + H_2O^{w} \xrightarrow{light} \frac{1}{6}(C_6H_{12}O_6^{c})_{glucose} + O_2^{w}$$

Energy input = (8 to 10) x 1.797 eV

Energy stored = 4.97 eV

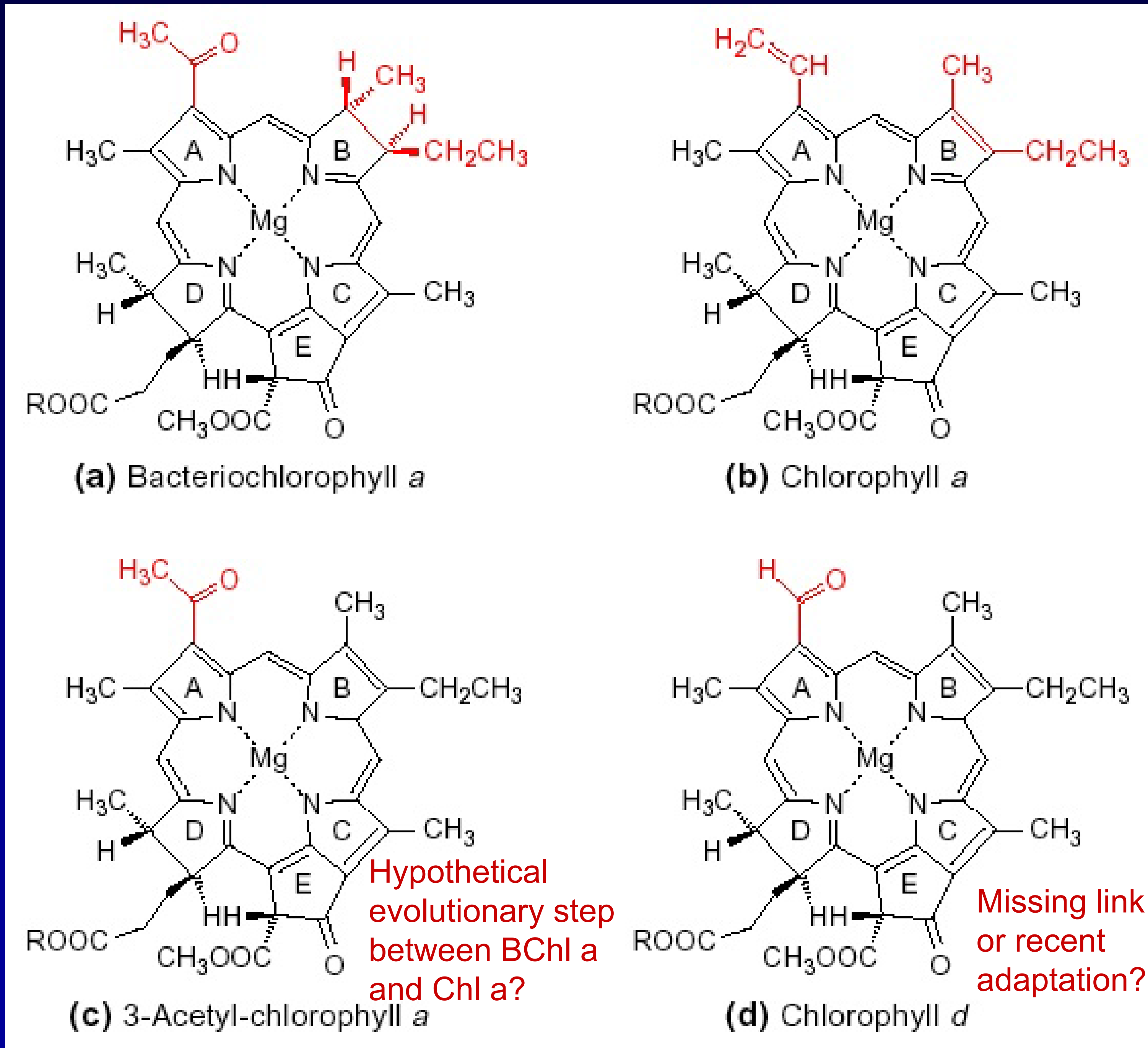
Energy "wasted"
(per photon used) = 1.17 - 1.30 eV

* Prevents back reactions
* Efficiency: 27-34% (monochromatic red light)

Diversity of photosynthetic organisms characteristics

Date Appeared	Taxon	Pigments	e-donor	C source*	Products	Niche
	BACTERIA					
3.5-2.7 Ga	Anoxygenic					
	Green non-sulfur filamentous	BChl a/c/ and or d/e +car	sulfide	orgC; CO2	S	dense microbial mats in hot springs often in association with cyano, thermophilic; floculent surface layer in alkaline springs; Chloroflexus: max
	Green sulfur bacteria	BChl a + c/d/e +car	sulfide, reduced S, H_2, Fe	orgC: acetate, propionate, pyruvate; CO_2	sulfate	non-thermal aquatic ecosystems, hot springs, max 55-56 Celsius (*Chlorobium tepidum*)
3.5-2.7 Ga	Purple bacteria	BChl a/b +car	inorg&orgC, S, sulfate, sulfide, sulfite, H_2, Fe	orgC, CO_2	S, sulfate, CO_2	fresh and marine waters, eutrophic marine, hot springs, anoxic aquatic sediments; max >50 Celsius (*Chromatium tepidum*)
	Heliobacteria	BChl g+car	sulfide, reduced S, sulfate	pyruvate, ethanol, lactate, acetate, and butyrate	?	soil, dry paddy fields, occasionally lakeshore muds, hot springs; resistant to UV, fix N; survive at least to 42 Celsius
	Halobacteria (not actual photosynthesis)	bacterio-rhodopsin	N/A	orgC	?	salt crusts in marine salterns, saline lakes, evaporites, ~4M NaCl
3.5-2.6 Ga	Oxygenic					
3.5-2.6 Ga	Cyanobacteria	Chl a/b/c/d +PBS+car	H_2O, S	CO_2	O_2	everywhere, -15 to +75ºC
1.2 Ga	ALGAE		H_2O, other?	CO_2	O_2	fresh and marine waters, snow
1.2 Ga	Rhodophytes (red algae)	Chl a + PBS + car				min observed PAR flux 0.01 micromol/m^2/s
	Chromophytes (incl. brown algae)	Chl a/c + car				intermediate depths
750 Ma	Chlorophytes (green algae)	Chl a/b + car				high light surface waters
	Lichens					
	crustose, squamose, foliose, fruticose	Chl a/b+car	H_2O			rock outcrops, vegetation surfaces
	PLANTS	Chl a/b+car	H_2O	CO_2	O_2, VOCs	min observed PAR ~ 3 micromol/m^2/s (0.7 W/m^2)
460 Ma	Bryophytes - Mosses, Liverworts					moist land environments
	Vascular plants					aquatic to desert environments
	Aquatic plants			CO_2, HCO_3^-		
144 Ma	Flowering plants					
70-55 Ma	CAM					arid environments
20-35 Ma	C4 pathway					low CO2 or arid environments

Blankenship
2002

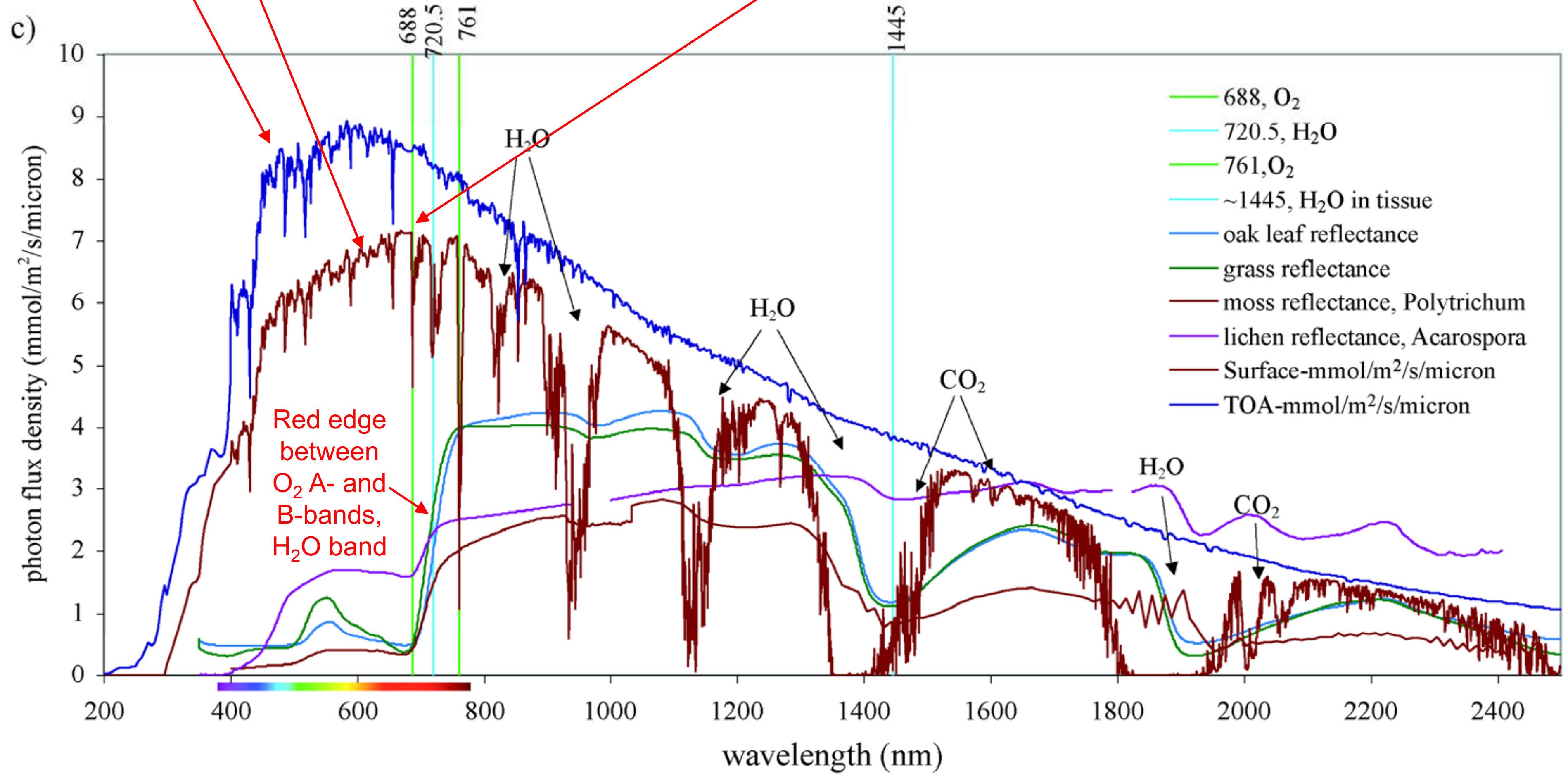


Incident Radiation & Organism Reflectance Spectra

Top of the atmosphere incident radiation

Surface incident radiation

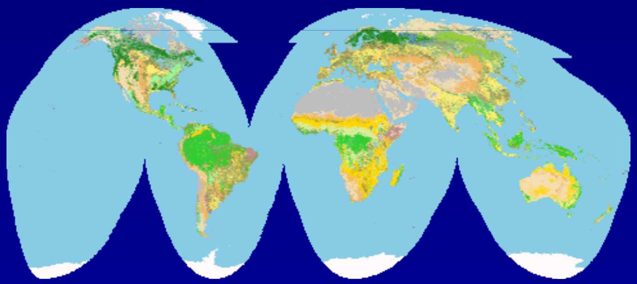
Surface incident radiation peak, ~685 nm
Chl a peak absorbance, ~680 nm
O_2 band, 688 nm



What do we still need to know

- Biochemists/biophysicists:
  - Long wavelength limit of oxygenic photosynthesis
  - How is O-O bond formed in the OEC
  - Other biological pigments: need contributions to the VPL Spectral Library

- Planetary scientists/astronomers:
  - 3D modeling:
    - climatic zones
    - detectability of alternative pigments
  - Mineral spectra.



- Geochemists/biogeochemists:
  - Coupled biogeochemical/atmosphere models
  - Abundance of potential electron donors