

Remote sensing of Sun-induced fluorescence.

Part 1: from PSII to FLH.

Yannick Huot

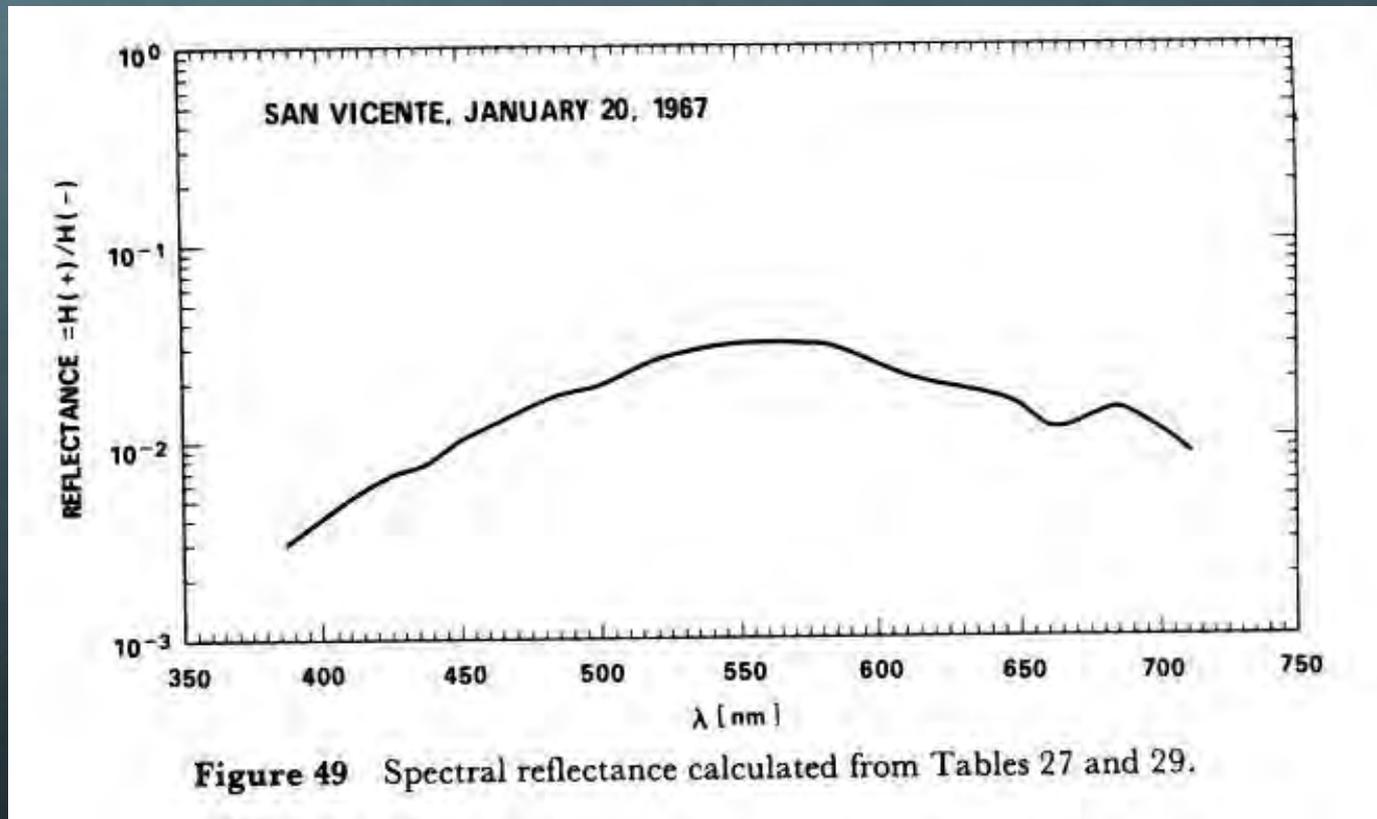
Centre d'Applications et de Recherches en Télédétection (CARTEL)

Département de Géomatique

Université de Sherbrooke

How it all started...

Probably the first measurement of sun-induced chlorophyll fluorescence in water:



Jerlov award 2002

Tyler, J. E., and R. C. Smith. 1970. Measurements of Spectral Irradiance under Water. Gordon and Breach science publishers.

A first explanation...

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA

VOLUME 64, NUMBER 6

JUNE 1974

Spectral variations in the volume scattering function at large angles in natural waters

Howard K. Gordon

Jerlov award 2004

Optical Physics Laboratory, Department of Physics, and

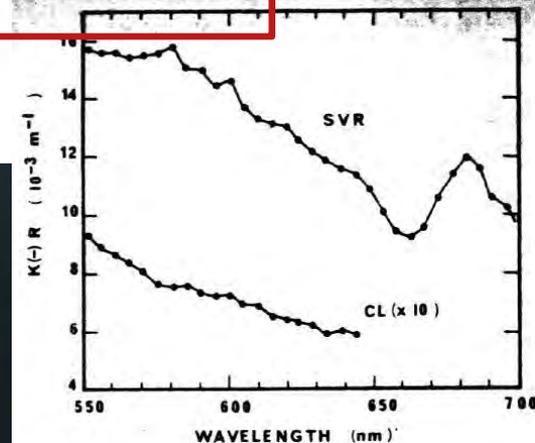
Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Coral Gables, Florida 33124

(Received 19 October 1973)

The quasi-single-scattering approximation in which a δ function replaces the forward portion of the volume scattering function is applied to radiative transfer in the ocean. Immediately beneath the surface, the product of the reflectance R and the downwelling irradiance-attenuation coefficient $K(-)$ is equal to an integral of the volume scattering function in the backward direction weighted by a geometrical factor. Spectral variations of the volume scattering function are revealed in $K(-)R$; this is used to examine the wavelength dependence of scattering in two very different natural waters. In the clear water of Crater Lake, the backscattering is proportional to λ^{-3} (λ = wavelength), whereas the turbid, productive waters of San Vicente Reservoir show a complex dependence of backscattering on wavelength, which is associated with anomalous dispersion due to the 670-nm absorption band of the chlorophyll that is contained in the suspended phytoplankton.

Index Headings: Oceanography; Scattering; Dispersion.

(i.e. the index of refraction increases with wavelength)



The right answer comes from:

Analysis of variations in ocean color¹

Jerlov award 2000

André Morel and *Louis Prieur*

Laboratoire de Physique et Chimie Marines, Station Marine de Villefranche-sur-Mer,
06230 Villefranche-sur-Mer, France

Latimer (1963) reported that scattering by pigmented particles such as microalgae is spectrally affected in the vicinity of the absorption bands, and that the spectral scattering curves resemble an anomalous dispersion curve. The enhancement of scattering and of back-scattering on the long wavelength side of the absorption peak could explain the existence of the *R* maximum at 685 nm. Gordon (1974), considering the data of Tyler and Smith, favored such an interpretation. Another phenomenon must be taken into consideration, which probably combines its effect with the preceding one. The fluorescence emission spectrum of chlorophyll *a* in vivo peaks at 685 nm, and this emission would be detectable in the upwelling light field because of its low level while it remains undetected in the downwelling flux. The influence of this emission can be confirmed by the different behaviors of K_d and K_u , the attenuation coefficients for downwelling and upwelling irradiances.

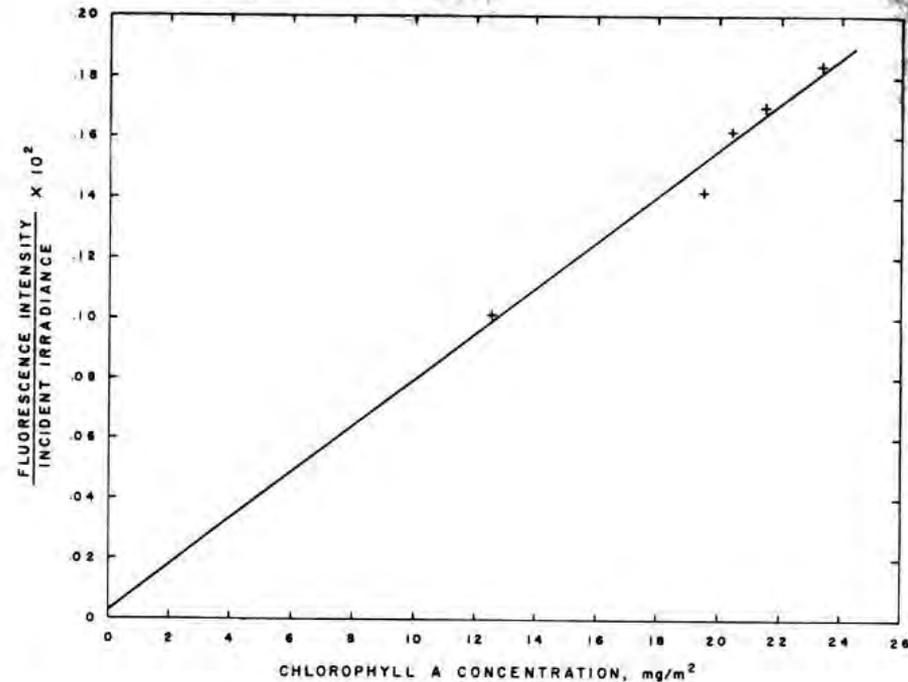
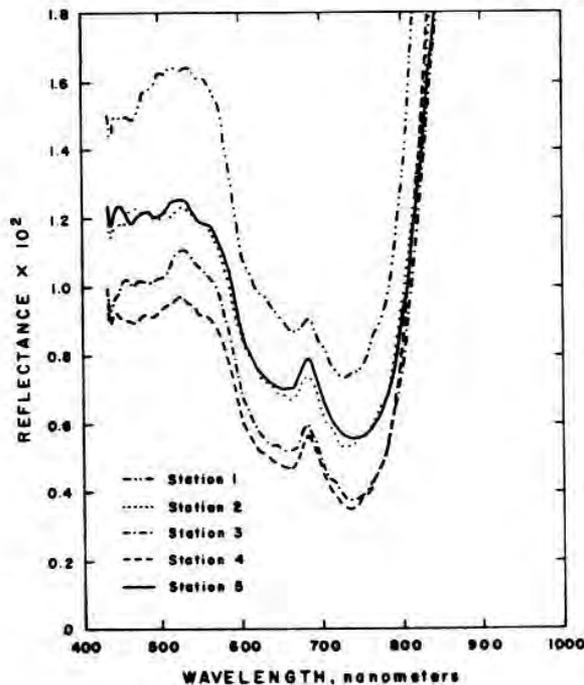
... while for others it seems already obvious!

Passive Remote Sensing of Phytoplankton via Chlorophyll α Fluorescence

R. A. NEVILLE AND J. F. R. GOWER

*Environment Canada, Institute of Ocean Sciences, Patricia Bay
Victoria, British Columbia, Canada*

The spectrum of light backscattered from the sea in the visible and near infrared and, in particular, the chlorophyll α fluorescence line at 685 nm have been observed from an aircraft under natural illumination by using a multichannel silicon diode spectrometer. The instrument was mounted in the aircraft so as to view the water surface at the Brewster angle by using a polarizer to reduce reflected skylight substantially, even under rough surface conditions. This and the relatively high red sensitivity of the silicon diode detectors explain why this line appears here but not in previous airborne observations. The observed line height has been compared with chlorophyll depth distribution measurements made from a launch and is shown to be proportional to an average of the chlorophyll concentration near the surface, weighted with depth to allow for absorption by the water of light at 685 nm. These observations were made at low (150 m) altitude, but it is shown that the observed line height is relatively insensitive to altitude up to 1200 m. Although the lowest chlorophyll concentration encountered was 2 mg/m³, the technique is expected to be useful for airborne mapping of chlorophyll at concentrations several times smaller than this.



The proof is by :

Diffuse reflectance of the ocean: the theory of its augmentation by chlorophyll *a* fluorescence at 685 nm

Howard R. Gordon

The radiative transfer equation is modified to include the effect of fluorescent substances and solved in the quasi-single scattering approximation for a homogeneous ocean containing fluorescent particles with wavelength independent quantum efficiency and a Gaussian shaped emission line. The results are applied to the *in vivo* fluorescence of chlorophyll *a* (in phytoplankton) in the ocean to determine if the observed quantum efficiencies are large enough to explain the enhancement of the ocean's diffuse reflectance near 685 nm in chlorophyll rich waters without resorting to anomalous dispersion. The computations indicate that the required efficiencies are sufficiently low to account completely for the enhanced reflectance. The validity of the theory is further demonstrated by deriving values for the upwelling irradiance attenuation coefficient at 685 nm which are in close agreement with the observations.

1. Introduction

In recent papers, Morel and Prieur¹ and Neville and Gower² have attributed a peak at about 685 nm in the diffuse reflectance spectrum of natural waters to *in vivo* fluorescence of chlorophyll *a* in phytoplankton. This is in contradiction to the earlier explanations given by Mueller³ and Gordon,⁴ which involved anomalous dispersion associated with the chlorophyll *a* absorption band near 670 nm. In the present work the radiative transfer equation for a fluorescent medium is developed and then solved in the quasi-single scattering approximation to determine the *in vivo* quantum efficiencies required to attribute the effect wholly to fluorescence. It will be shown that it is possible to explain the observed enhancement of the diffuse reflectance near 685 nm completely in terms of the *in vivo* fluorescence of chlorophyll *a*, which suggests that the anomalous dispersion explanation is probably not correct.

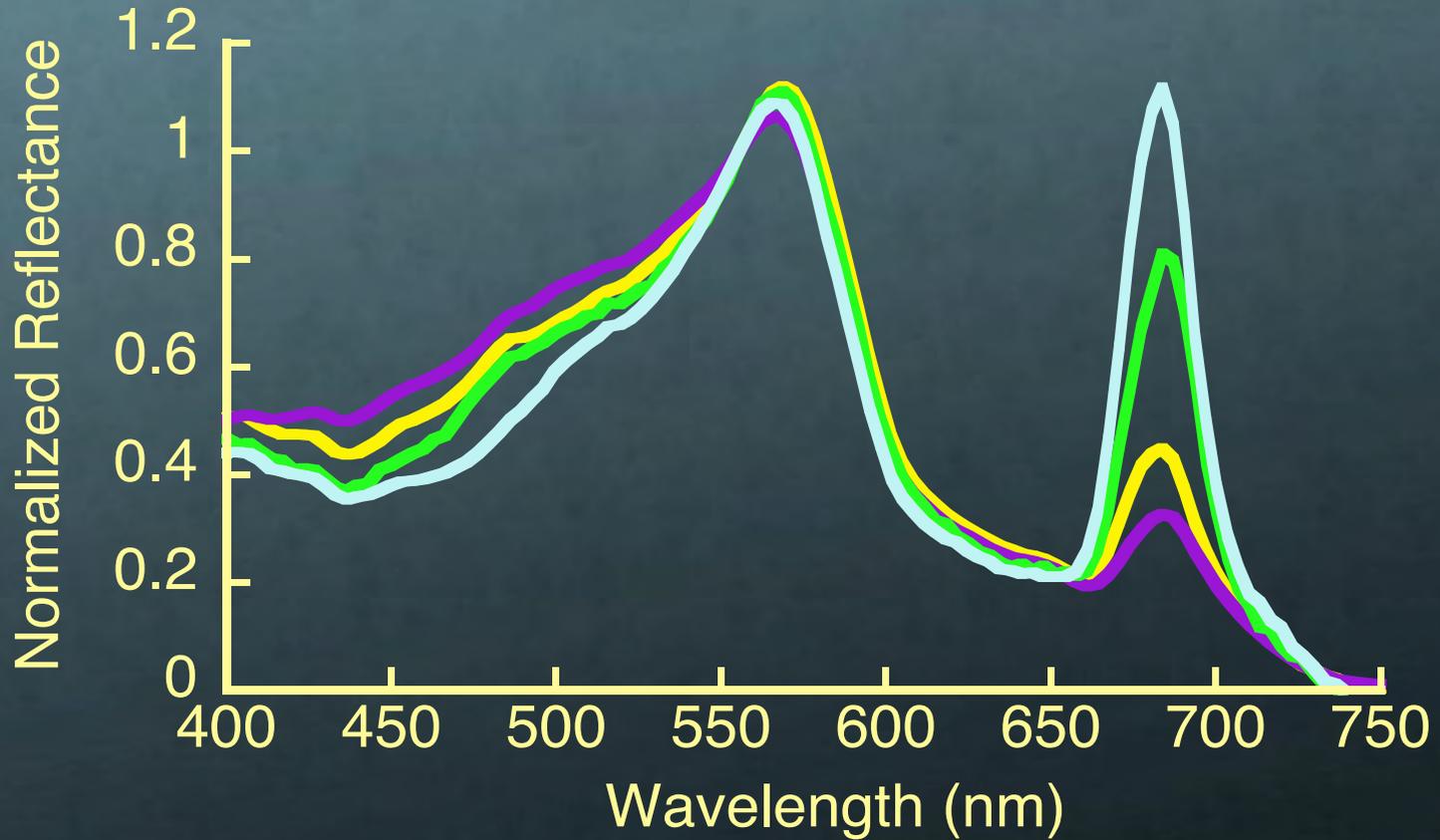
delay ($\sim 10^{-9}$ sec) between the absorption and emission. To include this process in the radiative transfer equation (RTE), it is easiest to think of the fluorescence as inelastic scattering and to formulate the process in a manner analogous to that of elastic scattering.

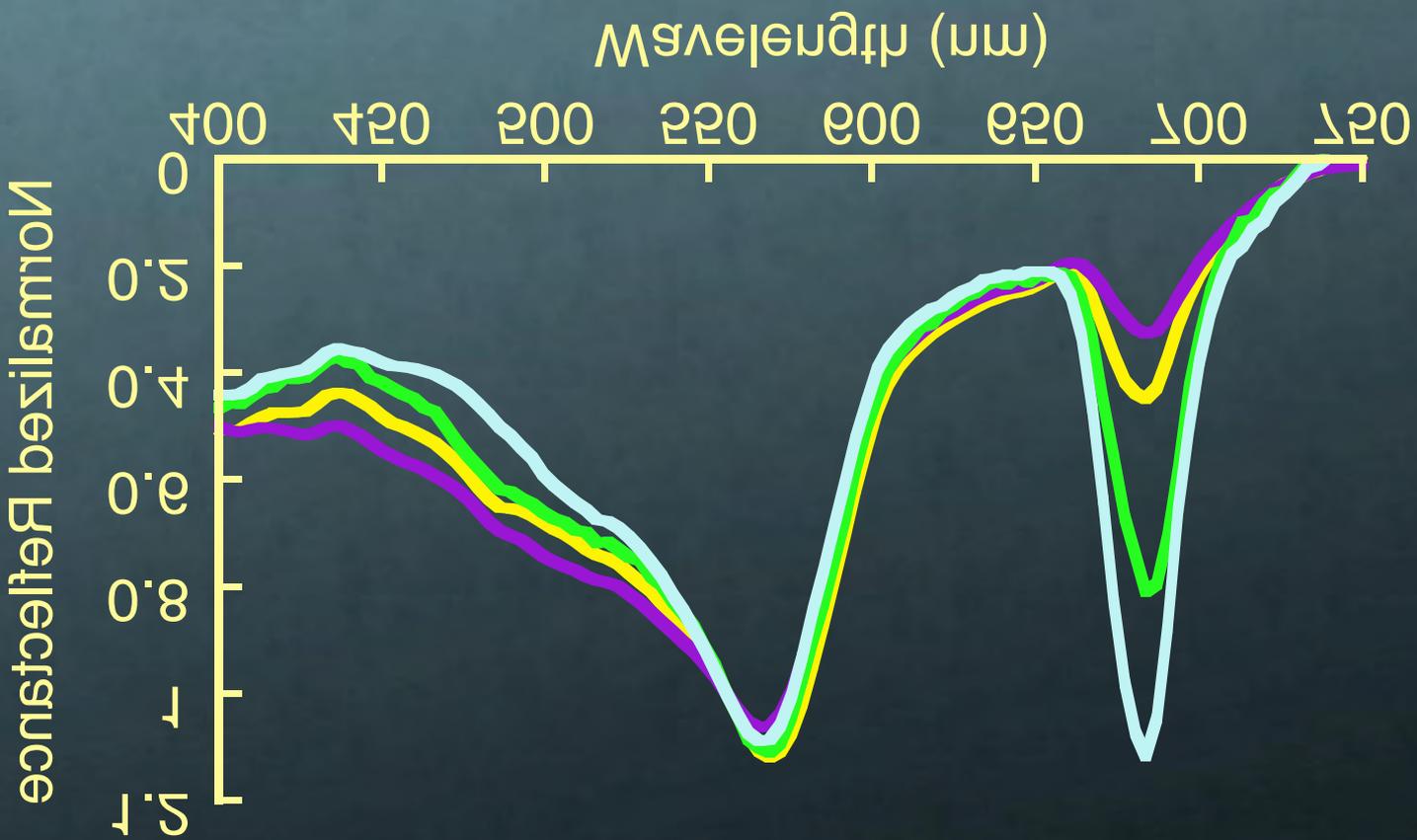
Consider a small volume ΔV subjected to a beam of irradiance $H(\lambda_E)$ ($\text{W}/\text{m}^2 \text{ nm}$) in a band of wavelengths $\Delta\lambda_E$. If an intensity of radiation $J(\theta, \lambda_F)$ ($\text{W}/\text{sr nm}$) of wavelength λ_F is observed at an angle θ with respect to the incident beam, the volume fluorescence function $\beta_\Phi(\theta, \lambda_F, \lambda_E)$ ($\text{m}^{-1}/\text{nm sr}$) can be defined through

$$\beta_\Phi(\theta, \lambda_F, \lambda_E) \equiv \frac{J(\theta, \lambda_F)}{\Delta V \int_{\Delta\lambda_E} H(\lambda_E) d\lambda_E}, \quad (1)$$

and the coefficient of fluorescence $\Phi(\lambda_F, \lambda_E)$ (m^{-1}/nm),

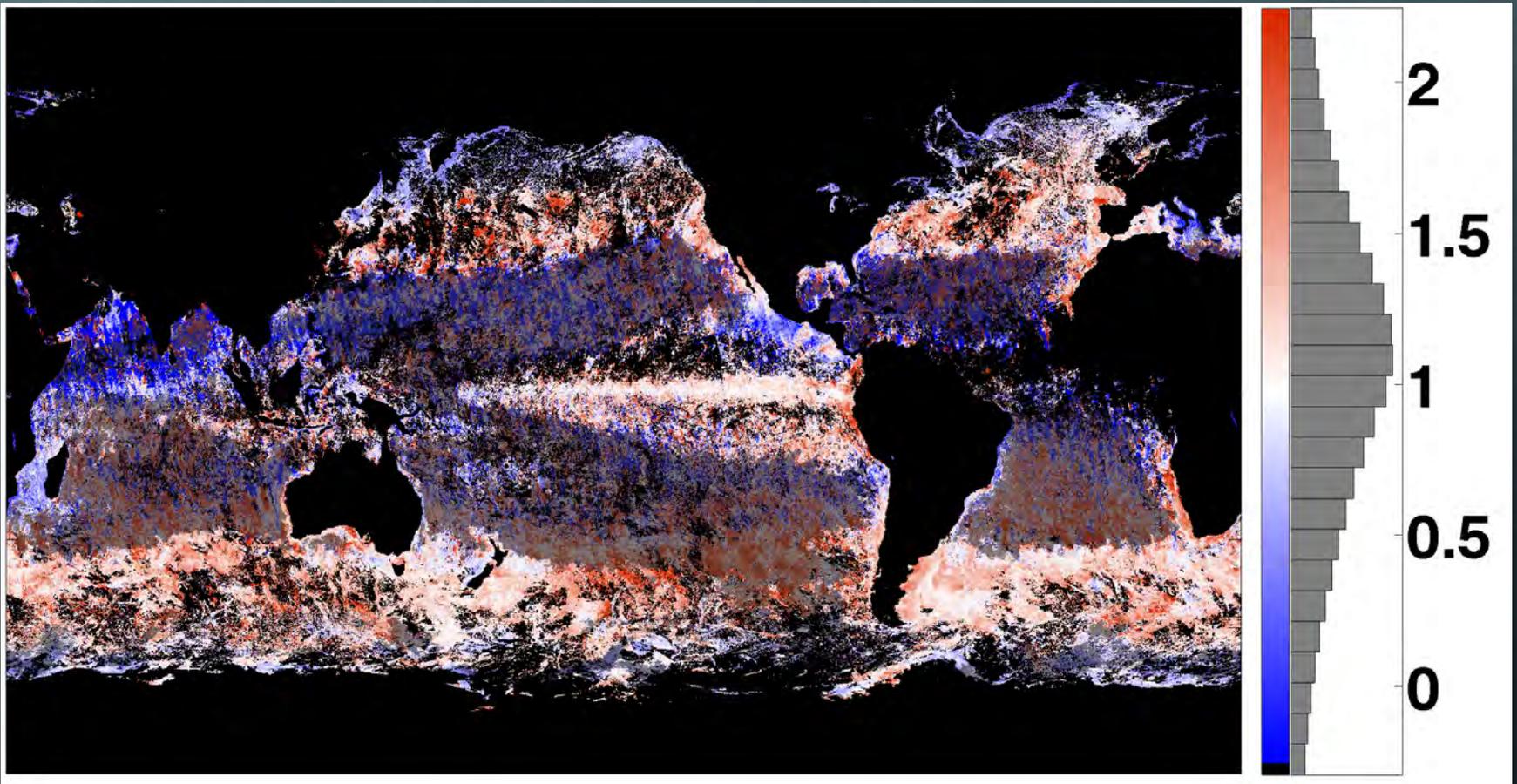
Reflectance in the Bering Sea



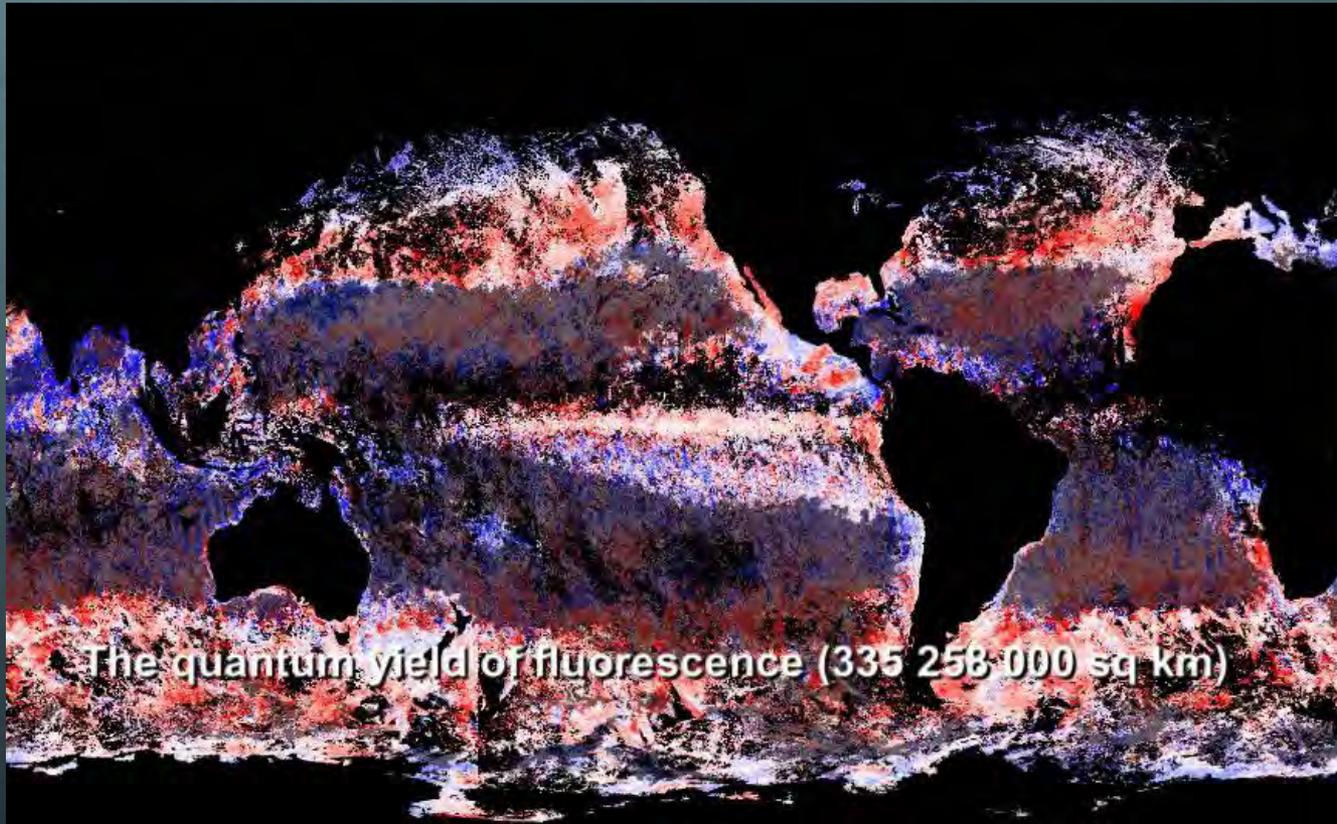


The challenge : what does this mean?

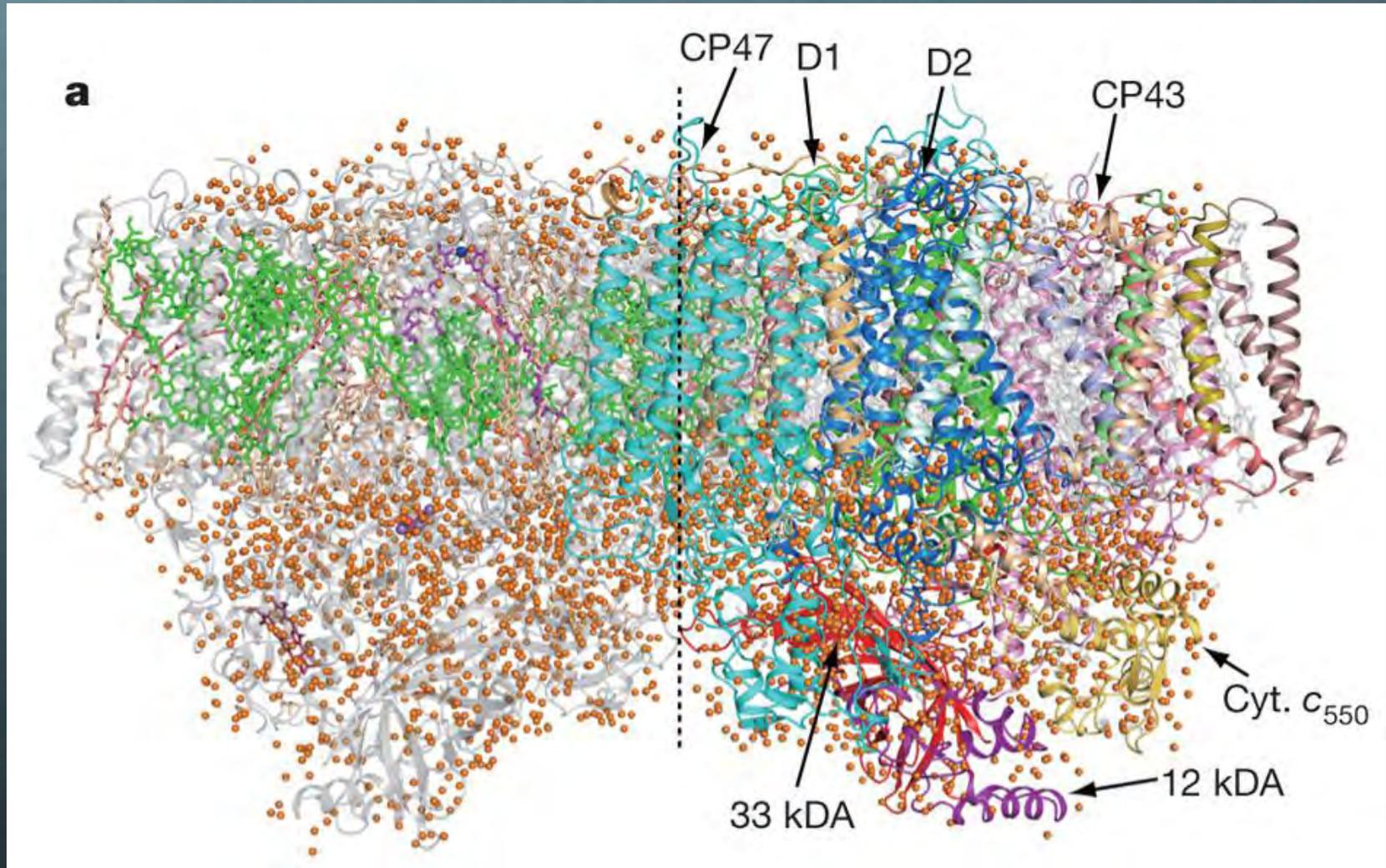
Quantum yield of Sun-induced chlorophyll a fluorescence



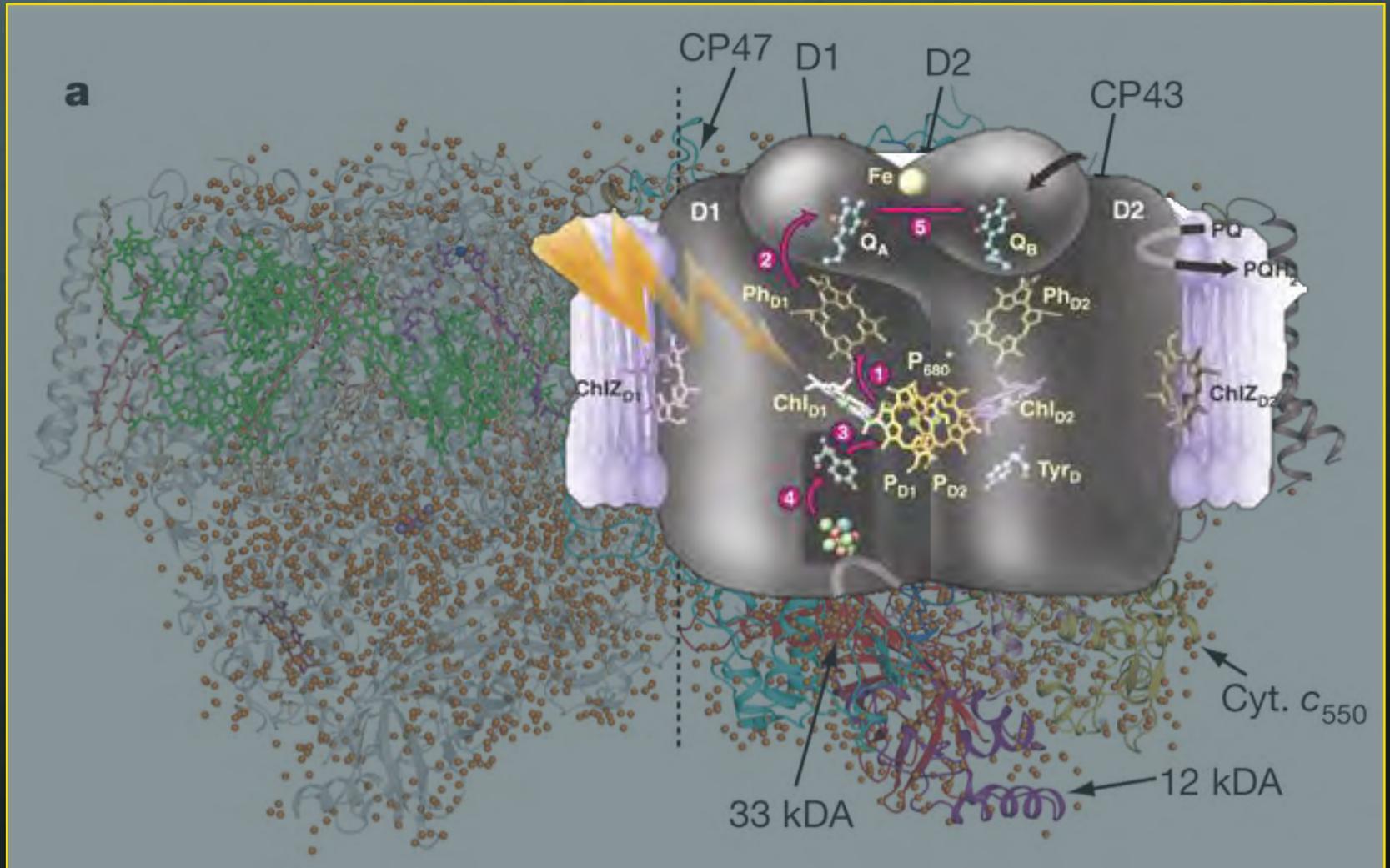
Zooming into PSII



Photosystem II



The first steps of photosynthesis



The first steps of photosynthesis

Quantum yield of photosynthesis

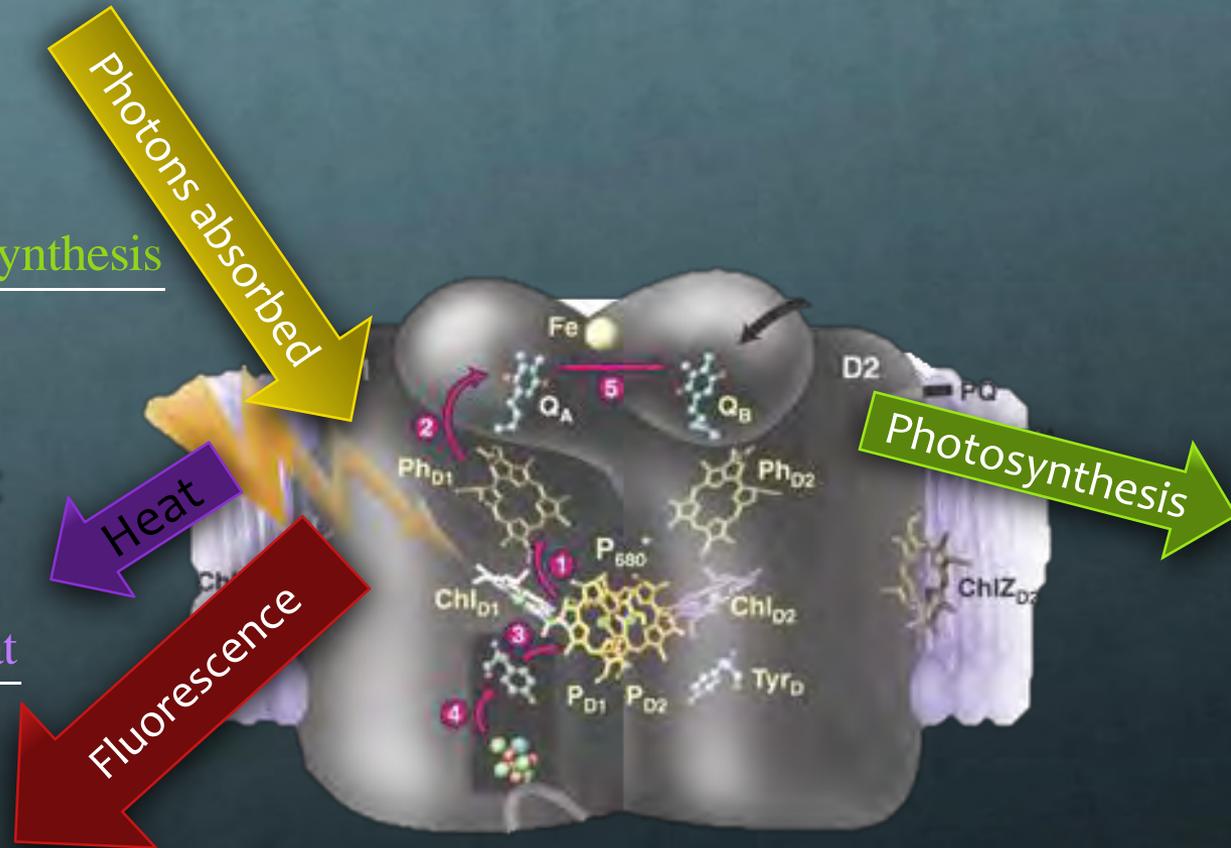
$$f_p = \frac{\text{\#photons utilized in photosynthesis}}{\text{\#photons absorbed}}$$

Quantum yield of heat dissipation

$$f_H = \frac{\text{\#photons dissipated as heat}}{\text{\#photons absorbed}}$$

Quantum yield of fluorescence

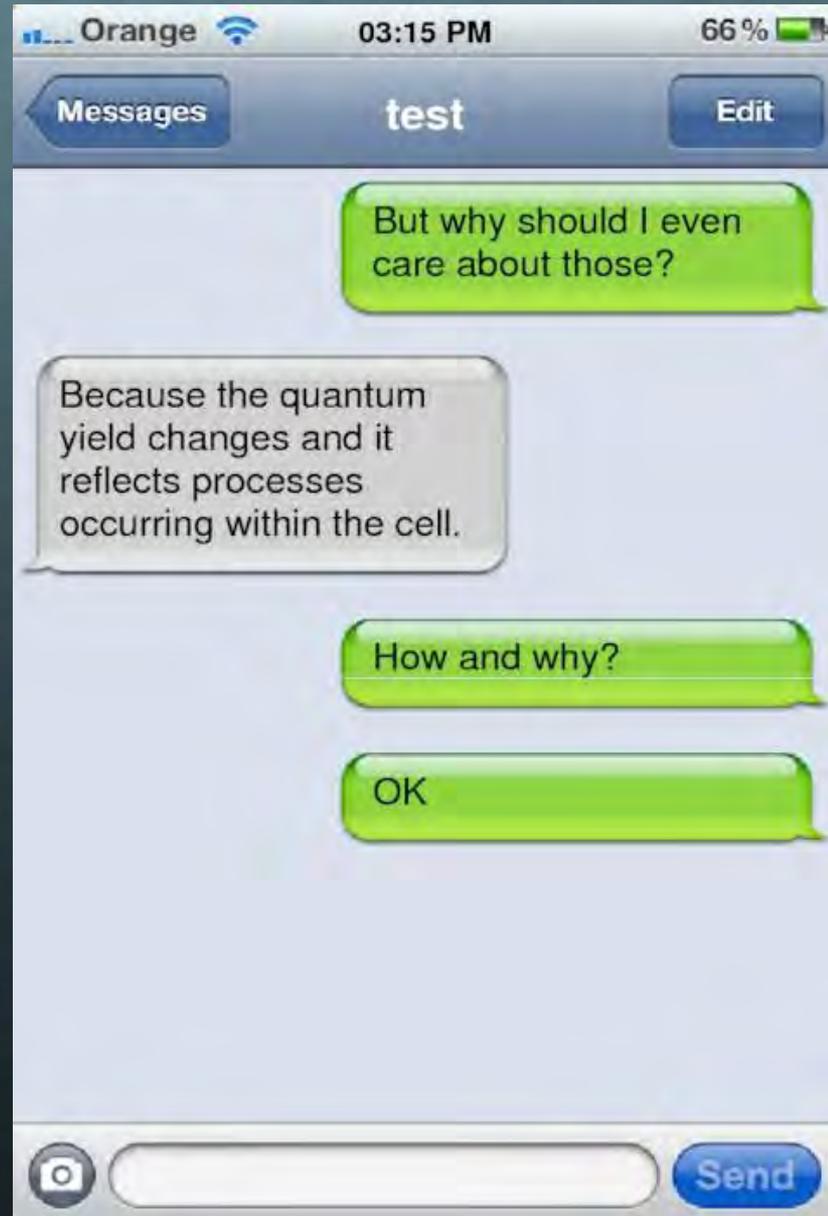
$$f_f = \frac{\text{\# photons fluoresced}}{\text{\# photons absorbed}}$$



Quantum yields

The quantum yields are the probabilities that an excited state will relax through a given path.

$$j_p + j_H + f_f = 1$$

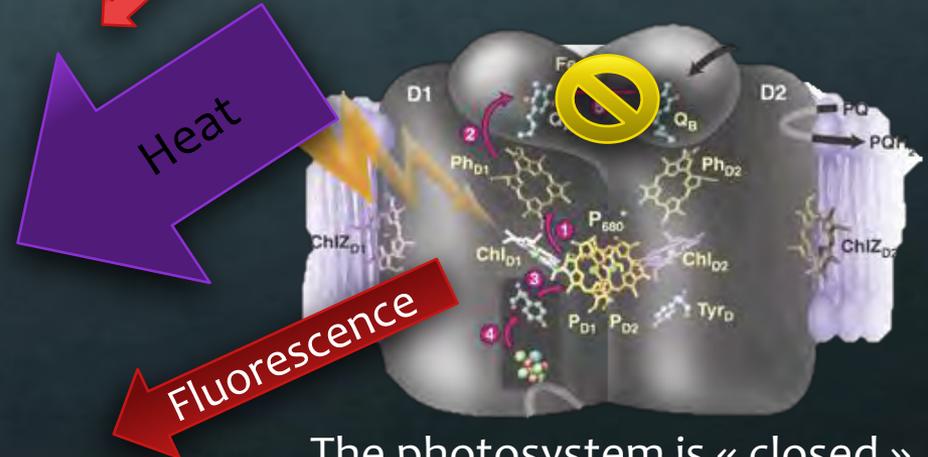
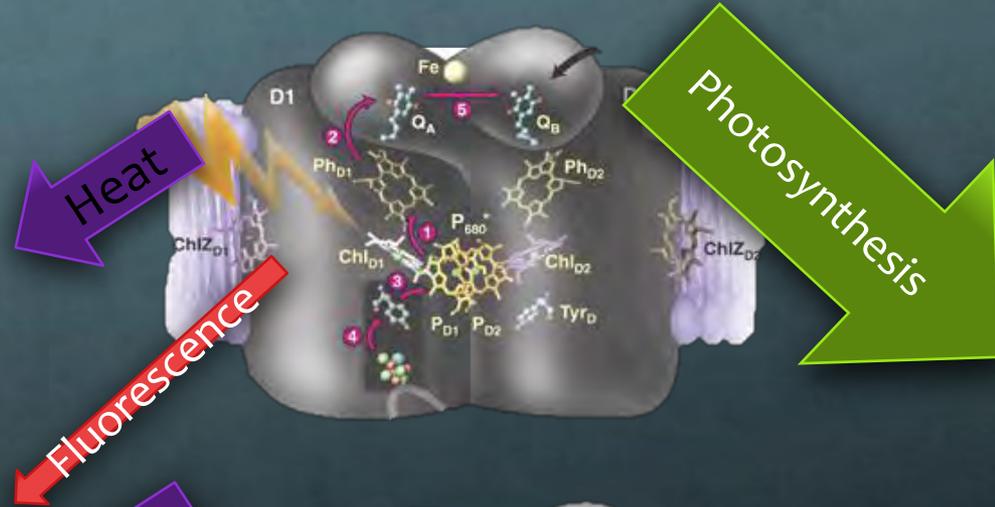


The dark-regulated state (very low light)

$$j_p + j_H + f_f = 1$$

If a second photons comes rapidly after the first one :

$$0 + j_H + f_f = 1$$



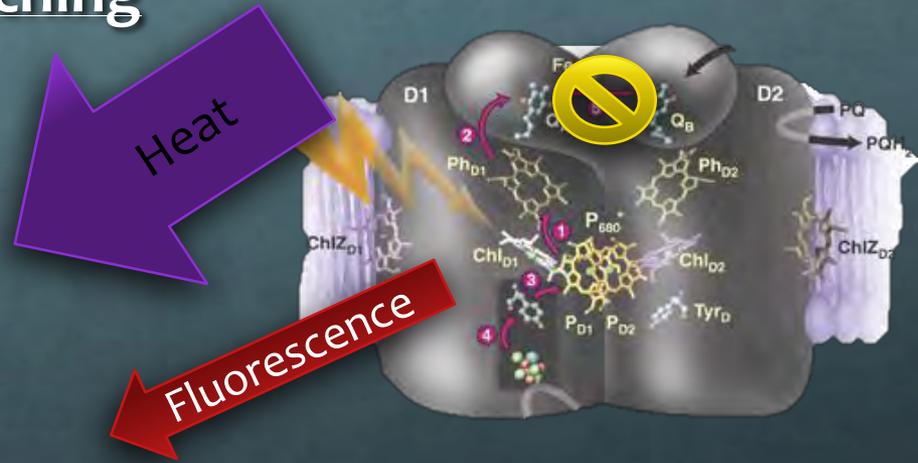
The photosystem is « closed »

This is the maximal quantum yield of fluorescence attainable

Quenching of fluorescence

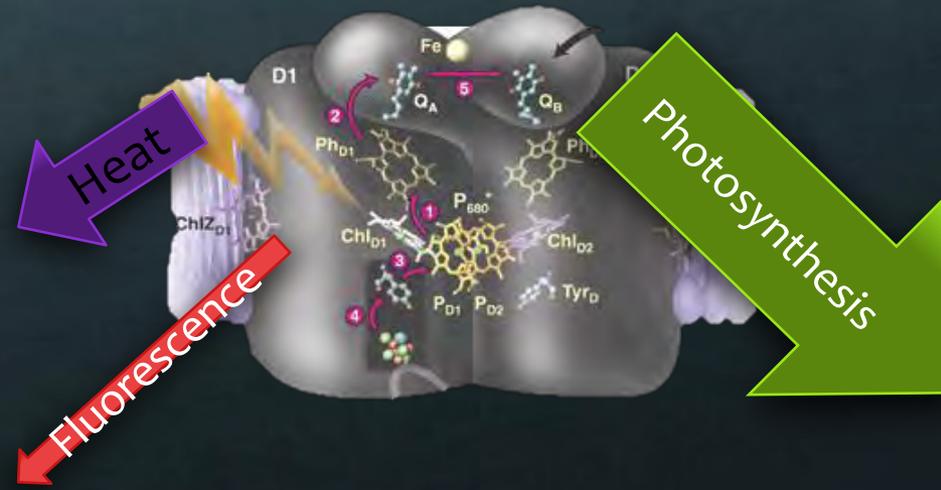
A reduction in the quantum yield of fluorescence (from its maximum) is termed: quenching

$$0 + j_H + f_f = 1$$

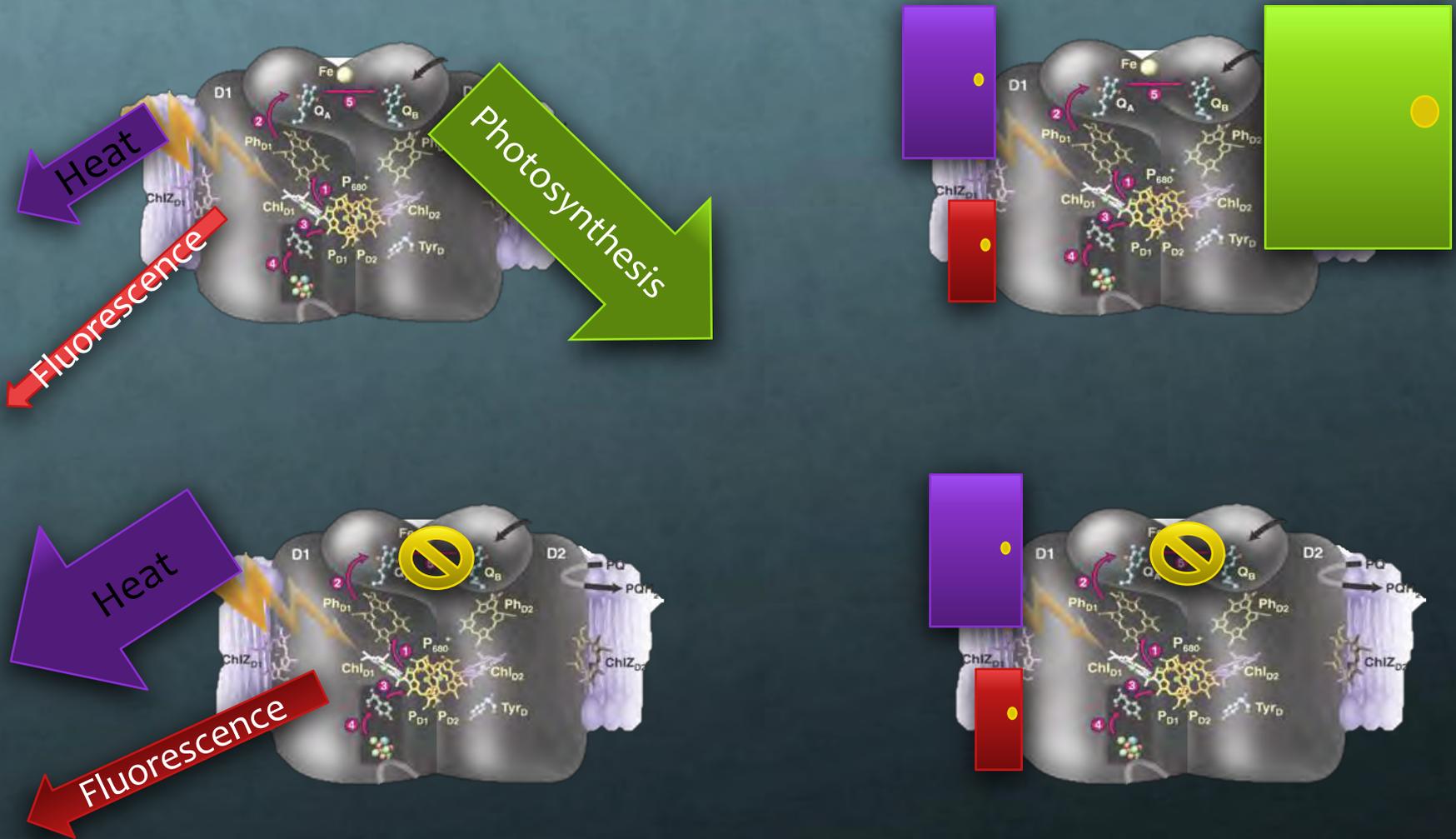


When it is caused by **photosynthesis** it is termed: **photochemical quenching**

$$j_p + j_H + f_f = 1$$



Quenching: the analogy to doors

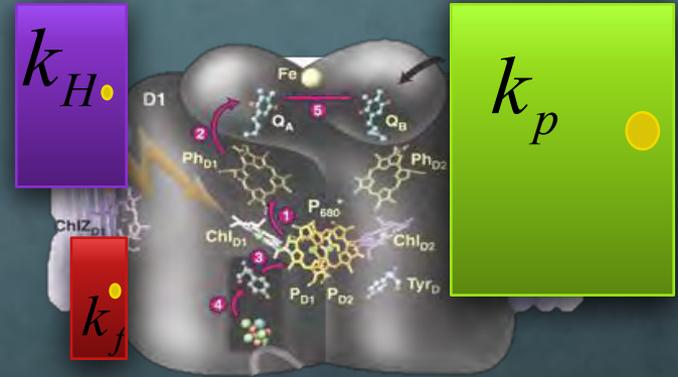


The quantum yield of fluorescence and heat changed without changing the size of their doors.

Doors and rate constants

Exponential decay of excited state of PSII:

$$N_{PSII} = N_{PSII}^* e^{-(k_f + k_p + k_H)t}$$



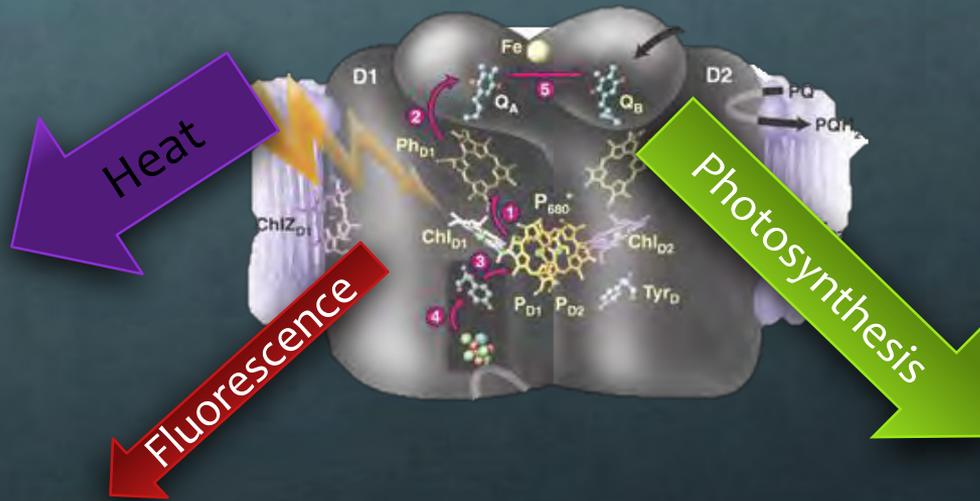
The fraction going to fluorescence:

$$f_f = \frac{k_f}{k_f + k_p + k_H}$$

The light-regulated state

As light increases, the fraction of photons going to photosynthesis decreases as less photosystems are available to process the photons.

$$j_p + j_H + f_f = 1$$

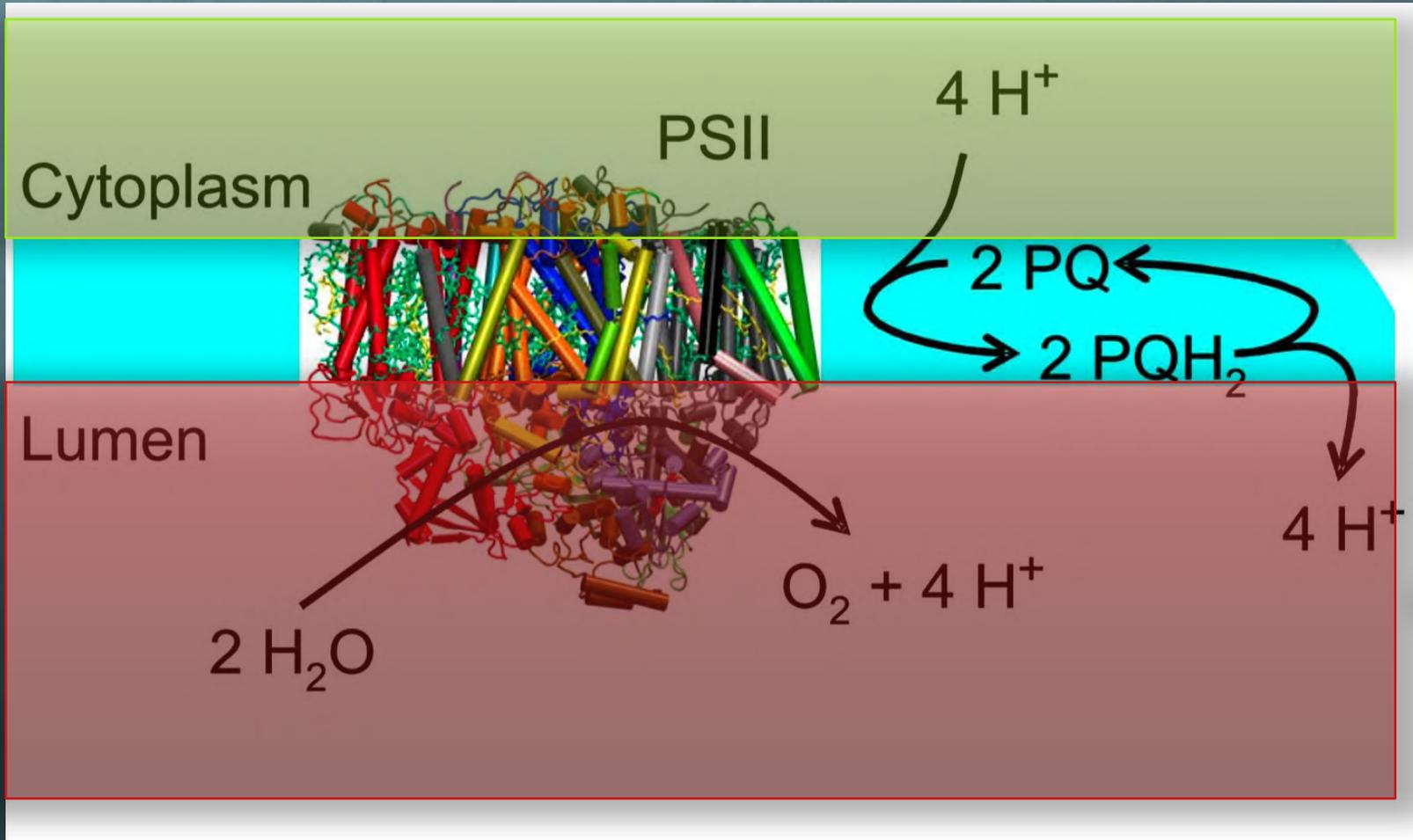


$$f_f = \frac{k_f}{k_f + A k_p + k_H}$$

The fraction of open reaction centers (Q_A not reduced) decreases

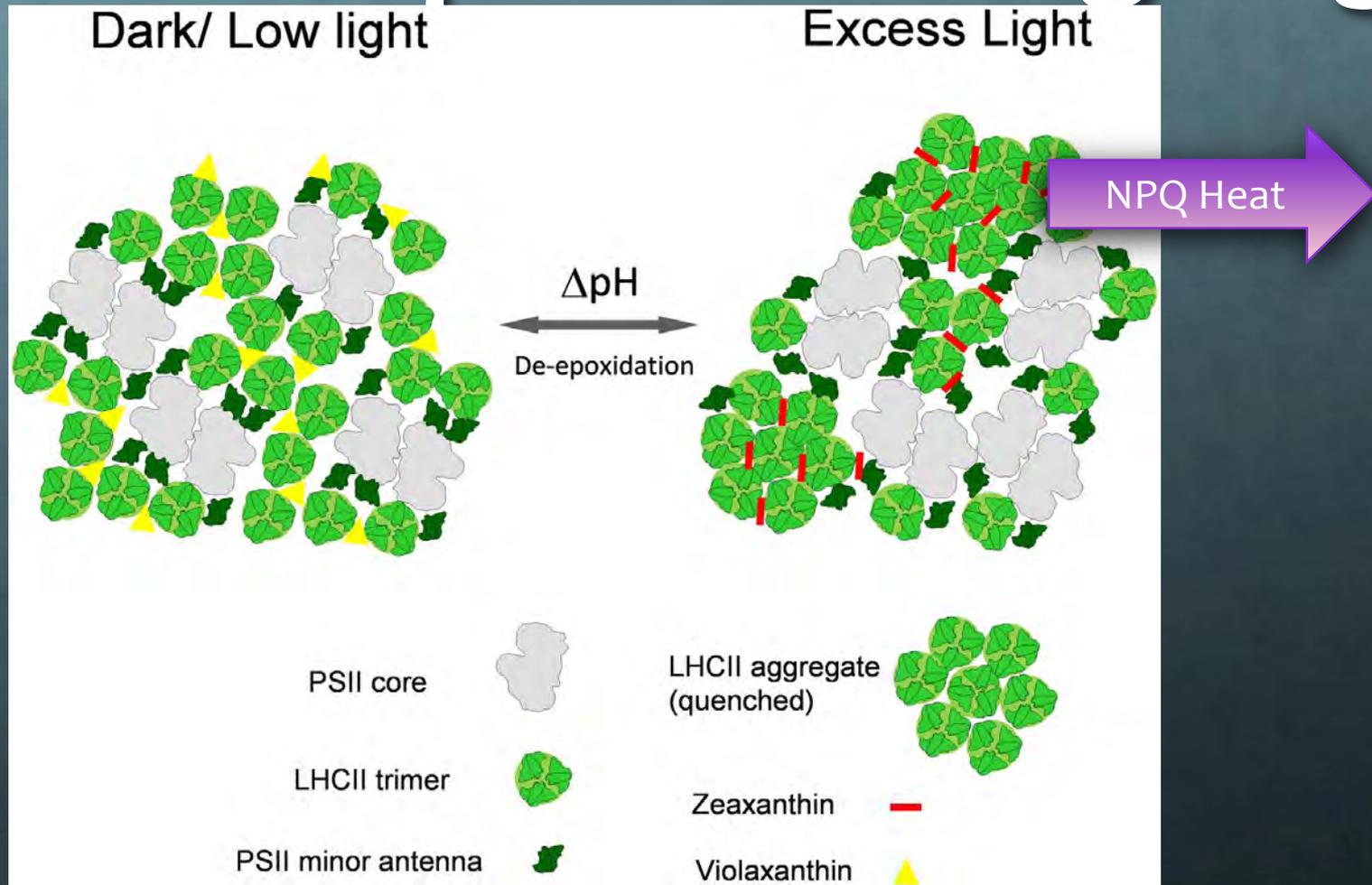
This leads to a decrease of photochemical quenching and an increase of the quantum yield of fluorescence.

High-light state (1)



At high light, pH in the lumen decreases. This is sensed by PSII and the light harvesting configuration changes.

Heat dissipation at high-light



$$f_f = \frac{k_f}{k_f + Ak_p + k_H + Zk_{NPQ}}$$

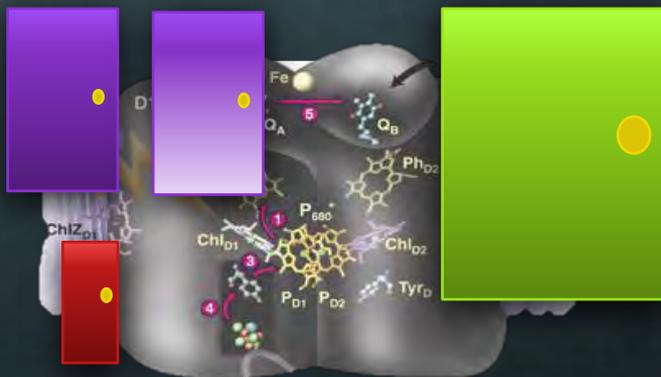
Z=amount of quencher.

Non-photochemical quenching (1)

At high light, as light increases, the fraction of photons whose energy is dissipated as heat increases lowering the quantum yield of fluorescence.

$$f_f = \frac{k_f}{k_f + Ak_p + k_H + Zk_{NPQ}}$$

When the quantum yield is reduced by an increased dissipation as heat it is termed :
Non-photochemical quenching



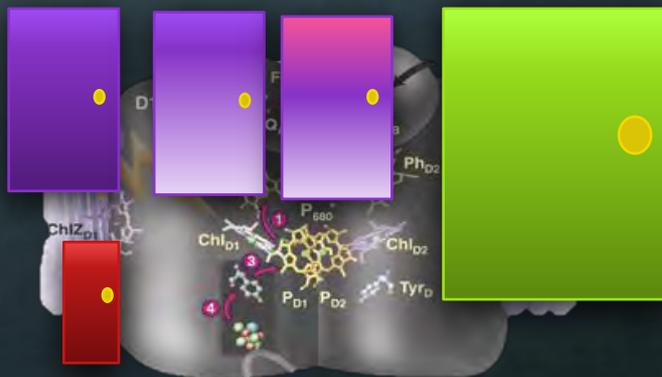
In essence, we added a new door...

Non-photochemical quenching (2)

Another type of non-photochemical quenching, termed qI (inhibition like) arises when the photosystem is inactivated.

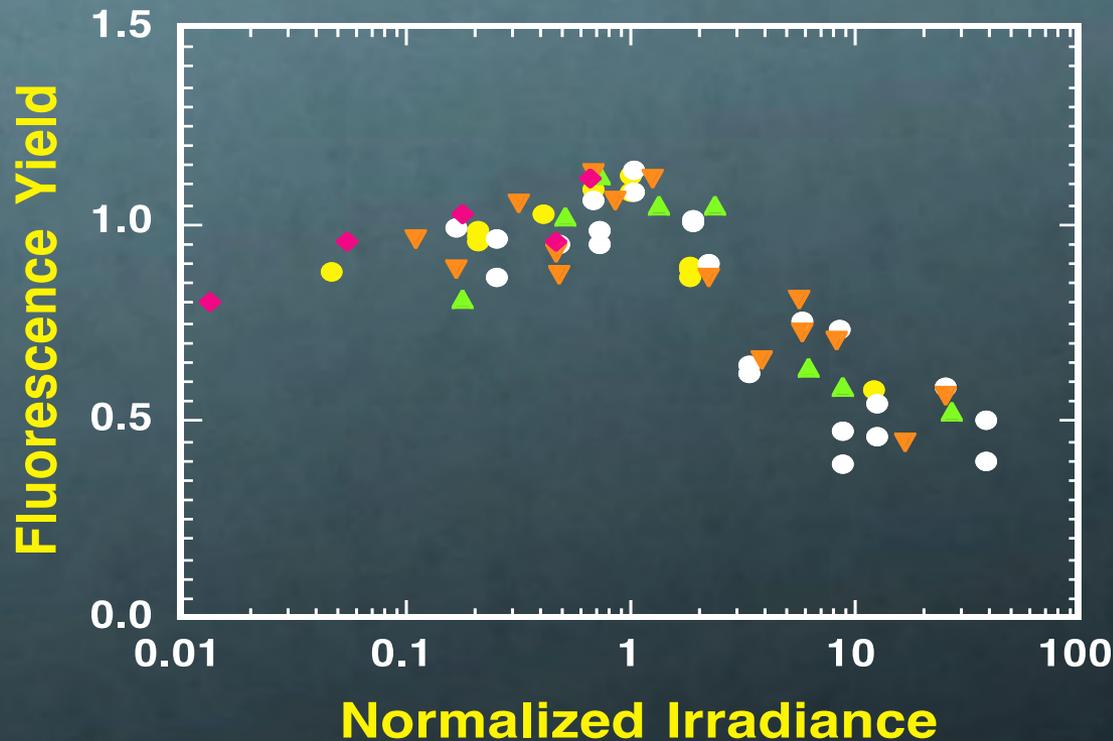
$$\phi_f = \frac{k_f}{k_f + Ak_p + k_H + Zk_{NPQ} + Ck_{qI}}$$

qI is characterized by its longer relaxation time (i.e. it remains present for a long time after induction)



In essence, we add another new door...

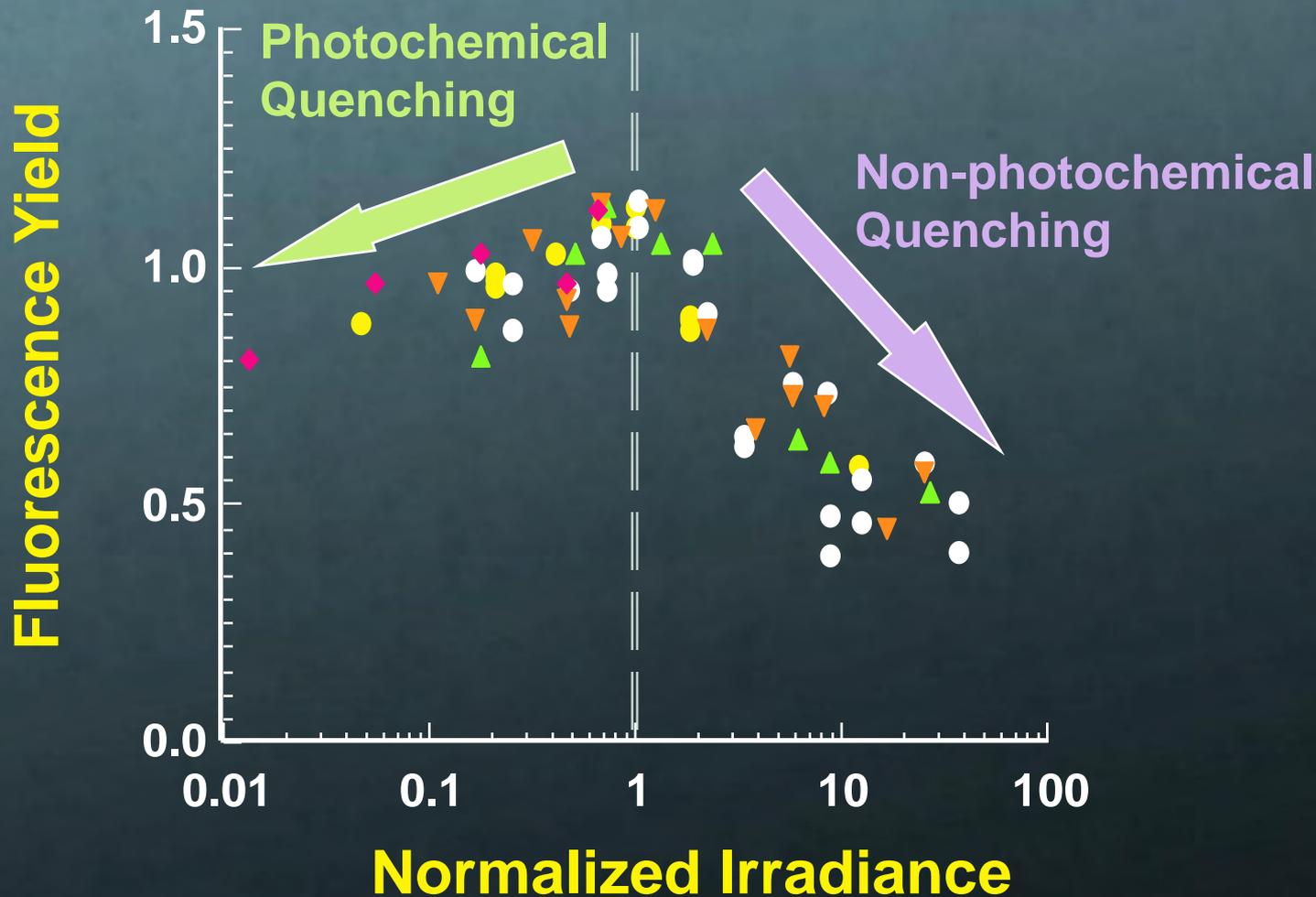
Cultures and Antarctic lakes



Normalized to ($E_{\max} F_s$)

- Culture (E/173)
- Bonney 5m (E/5.3)
- ▲ Hoare 10 m (E/5.0)
- ▼ Bonney 17m (E/8)
- ◆ Fryxell 10m (Irr/100)

Quenching in action



Inherent and apparent quantum yields (1)

So far we have implicitly defined ϕ_f as the fraction of photons absorbed by photosynthetic pigments (PS) within PSII and reemitted by chlorophyll a molecules within PSII. This is the inherent quantum yield.

$$\begin{aligned}\phi_f &= \frac{\text{\#photons absorbed by PS in PSII}}{\text{\# photons emitted as fluorescence in PSII}} \\ &= \frac{k_f}{k_f + Ak_p + k_H + Zk_{NPQ} + Ck_{qI}}\end{aligned}$$

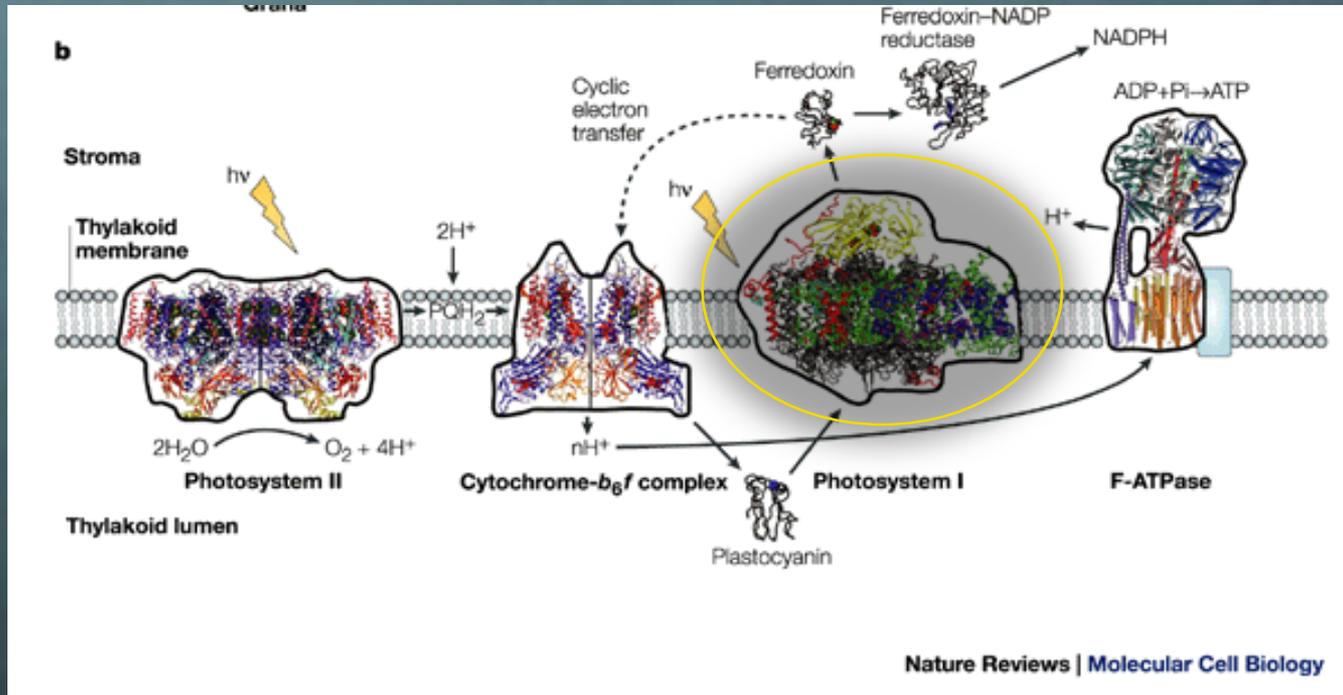
We can write that the fluorescence flux ($\mu\text{mol m}^{-3} \text{s}^{-1}$) emitted from an elementary volume of water containing PSII is:

$$F_{PSII} = \overset{\circ}{E}(PAR) \times \overset{PS}{\bar{a}}_{PSII} \times f_f \quad (\mu\text{mol m}^{-3} \text{s}^{-1})$$

However, we cannot measure this using ocean color so our definition of Φ_f is not practical

Measuring “chlorophyll fluorescence absorption” using ocean color (1)

Indeed, photosystem II is not the only pigment-containing complex in the chloroplast:



PSI contains roughly half of the pigments in the cell but “does not” fluorescence.

The closest we can get to the absorption of photosynthetic pigments within PSII using ocean color is the total phytoplankton absorption.

Measuring “chlorophyll fluorescence absorption” using ocean color (2)

PSII and PSII also contain non-photosynthetic pigments (e.g. beta-carotene).

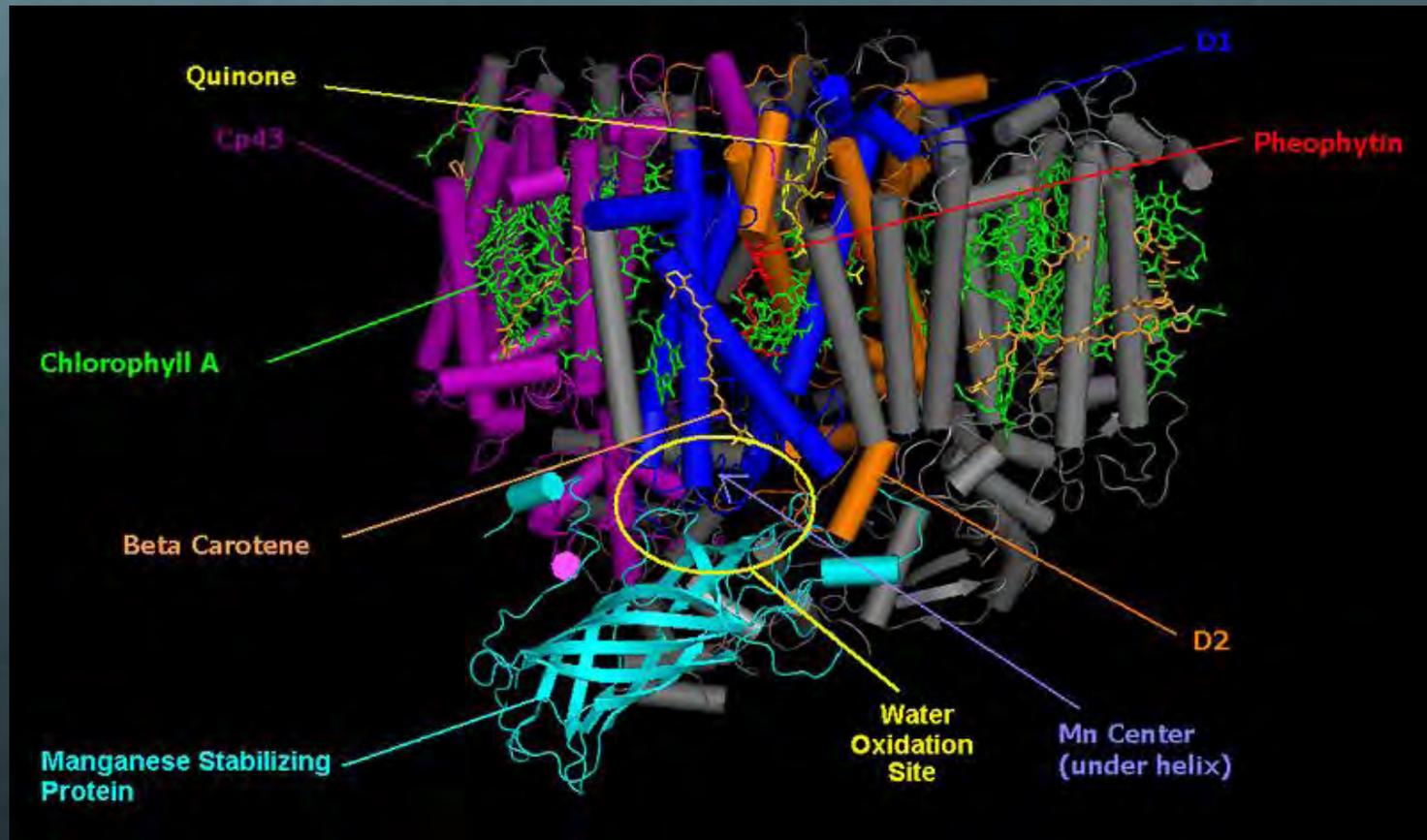


Figure from : http://en.wikipedia.org/wiki/Photosystem_II

Inherent and apparent quantum yields

(2)

$$F_{PSII} = \overset{\circ}{E}(PAR) \times {}^{PS}\bar{a}_{PSII} \times f_f$$

Practically we must thus rewrite our equation as follow:

$$F_{PSII} = \overset{\circ}{E}(PAR) \times \bar{a}_f \times f_f^{app} \leftarrow \text{Apparent quantum yield of fluorescence}$$
$$= \overset{\circ}{E}(PAR) \times \left({}^{PS}\bar{a}_{PSII} + {}^{PS}\bar{a}_{PSI} + {}^{PP}\bar{a}_{PSII} + {}^{PP}\bar{a}_{PSI} \right) \times f_f^{app}$$

Consequently:

$$f_f^{app} = \frac{f_f \times {}^{PS}\bar{a}_{PSII}}{\bar{a}_f} = \frac{f_f \times {}^{PS}\bar{a}_{PSII}}{\left({}^{PS}\bar{a}_{PSII} + {}^{PS}\bar{a}_{PSI} + {}^{PP}\bar{a}_{PSII} + {}^{PP}\bar{a}_{PSI} \right)}$$

Sources of variability in the quantum yield of fluorescence

$$\phi_f^{app} = \phi_f \frac{{}^{PS}\bar{a}_{PSII}}{\left({}^{PS}\bar{a}_{PSII} + {}^{PS}\bar{a}_{PSI} + {}^{PP}\bar{a}_{PSII} + {}^{PP}\bar{a}_{PSI} \right)}$$

$$= \frac{k_f}{k_f + Ak_p + k_H + Zk_{NPQ} + Ck_{qI}} \frac{{}^{PS}\bar{a}_{PSII}}{\left({}^{PS}\bar{a}_{PSII} + {}^{PS}\bar{a}_{PSI} + {}^{PP}\bar{a}_{PSII} + {}^{PP}\bar{a}_{PSI} \right)}$$

Photochemical Quenching
Non-photochemical quenching

Fractional absorption of PS in the cell
- photosynthetic / Photoprotective pigments
- PSII/PSI

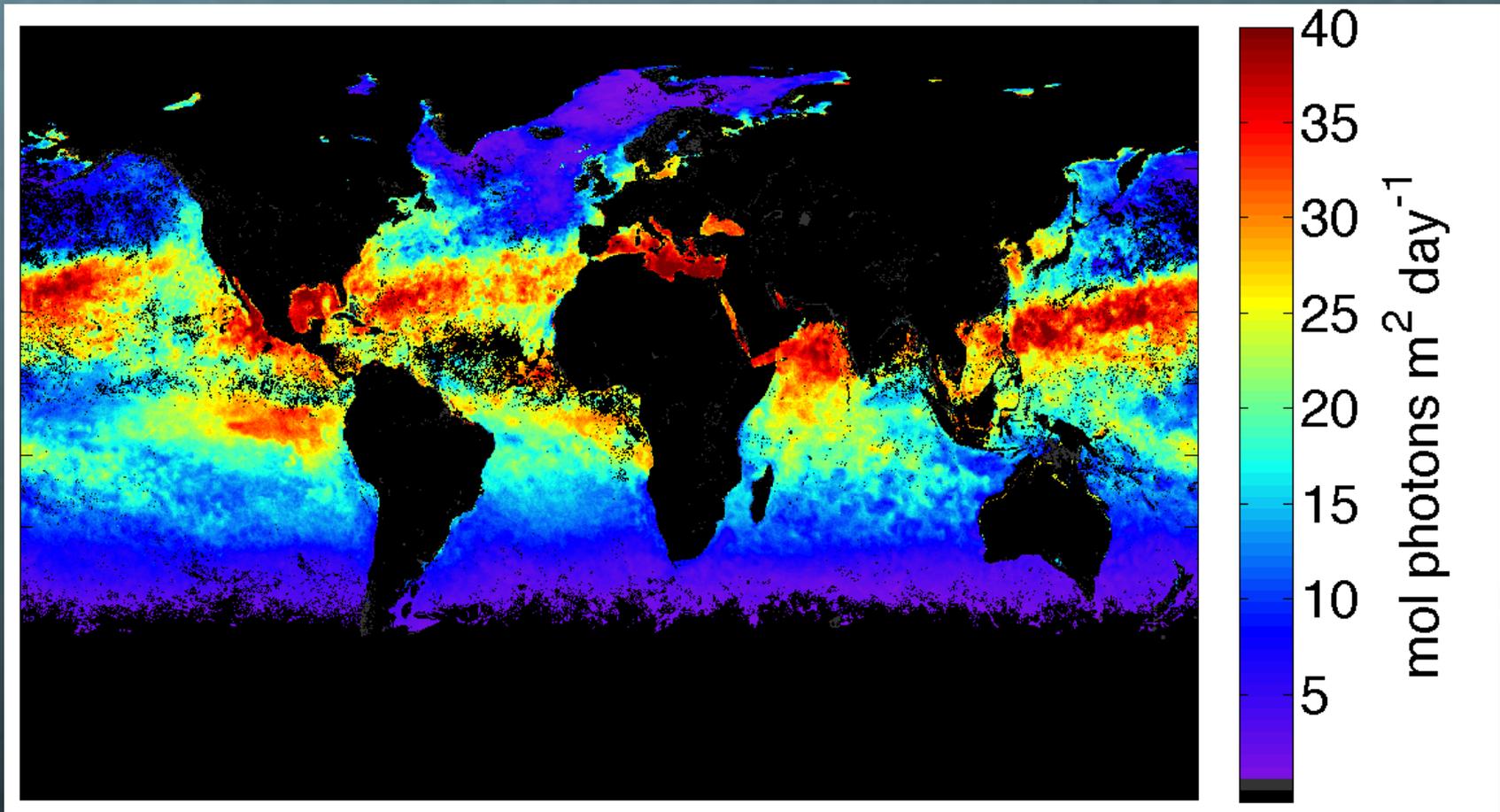
All are influenced by:

- Light history (average growth irradiance)
- Nutrient status
- Species composition

Growth irradiance

Light in the mixed layer

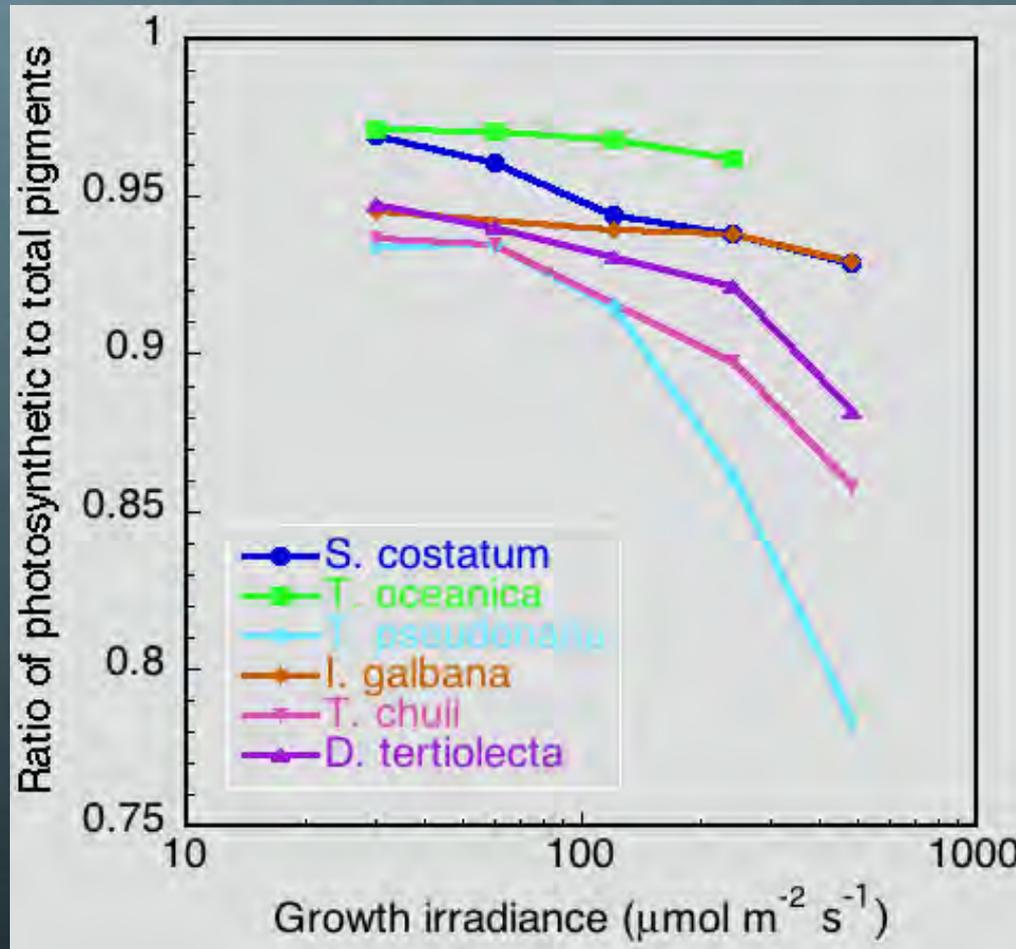
Average photosynthetically available irradiance within the mixed layer (May 2012)



Through photoacclimation and photoadaptation, phytoplankton respond to this irradiance by altering their pigments content and stoichiometry

$$\frac{PS \bar{a}_{PSII}}{\left(PS \bar{a}_{PSII} + PS \bar{a}_{PSI} + PP \bar{a}_{PSII} + PP \bar{a}_{PSI} \right)}$$

vs. Irradiance

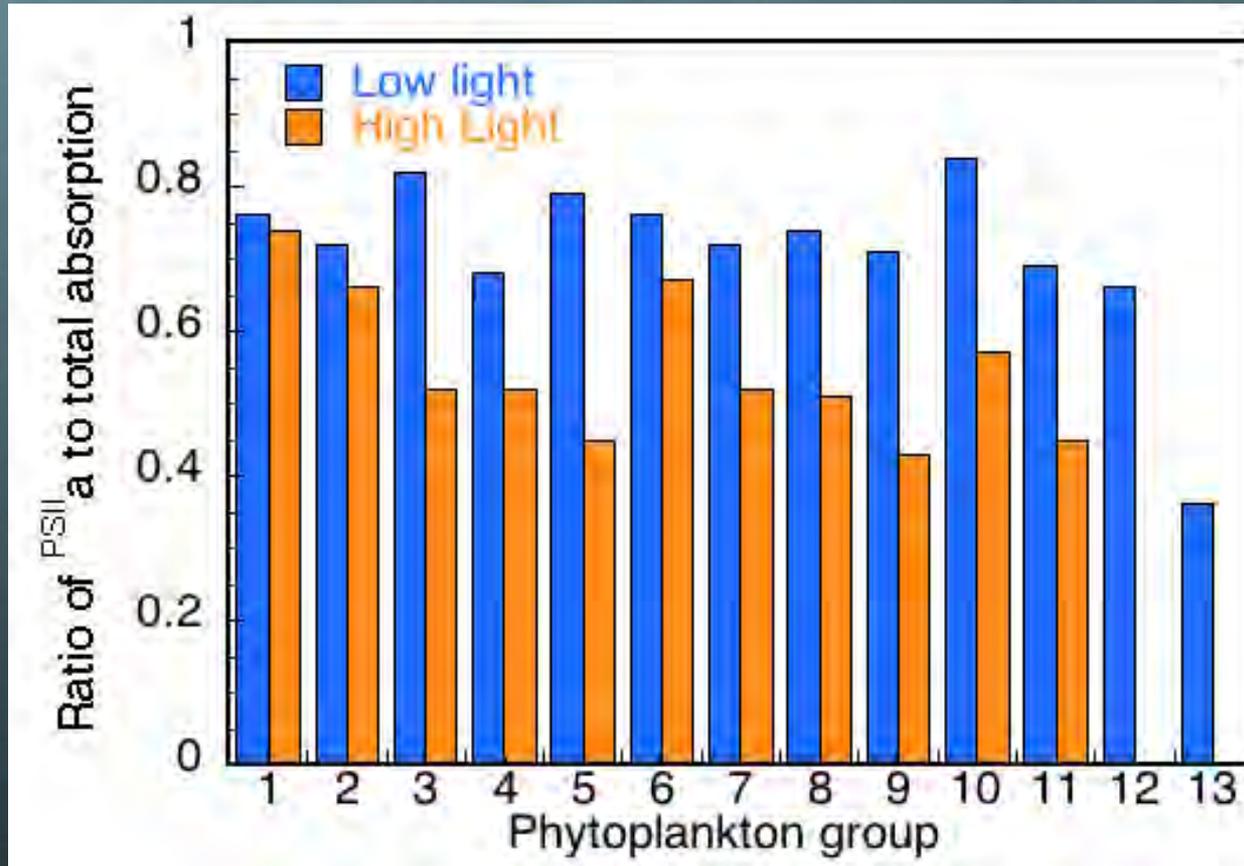


J. Vandenhecke
unpublished data

At high mixed layer average irradiance, satellite measure phytoplankton absorption, but a smaller fraction may be going to fluorescence.

PSII to total absorption

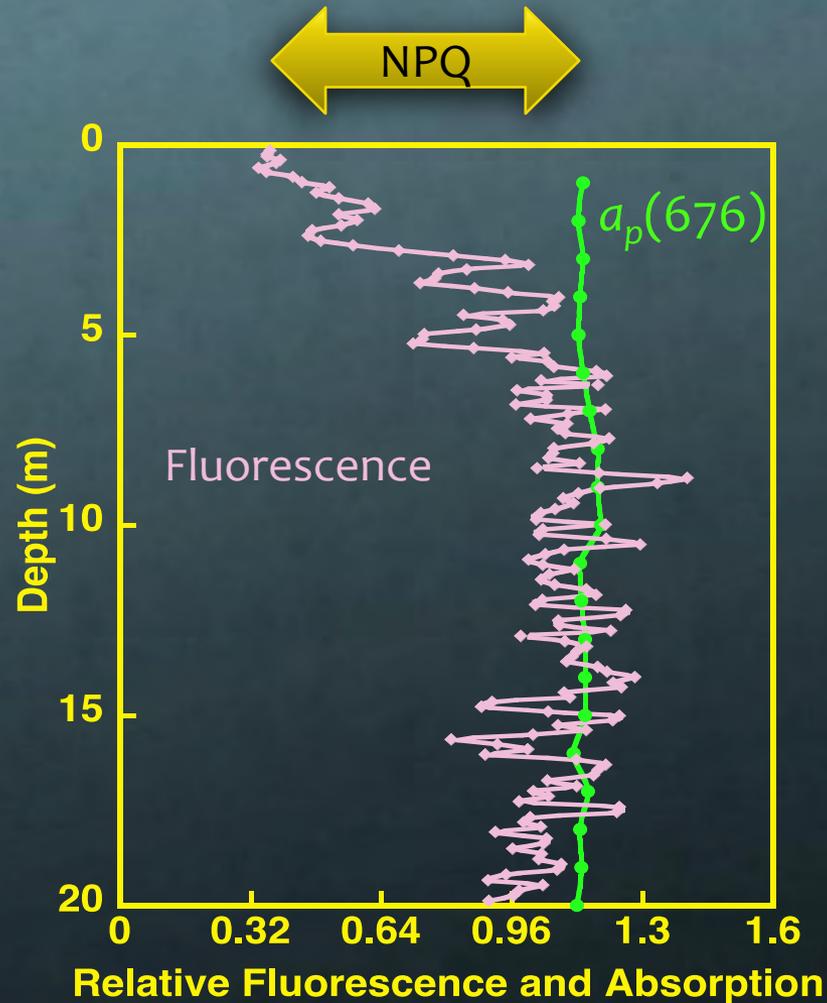
For all groups as growth irradiance increases the fraction of light absorbed by PSII decreases



At high average irradiance in the mixed layer , satellite measure phytoplankton absorption, but a smaller fraction may be going to fluorescence.

Profiles

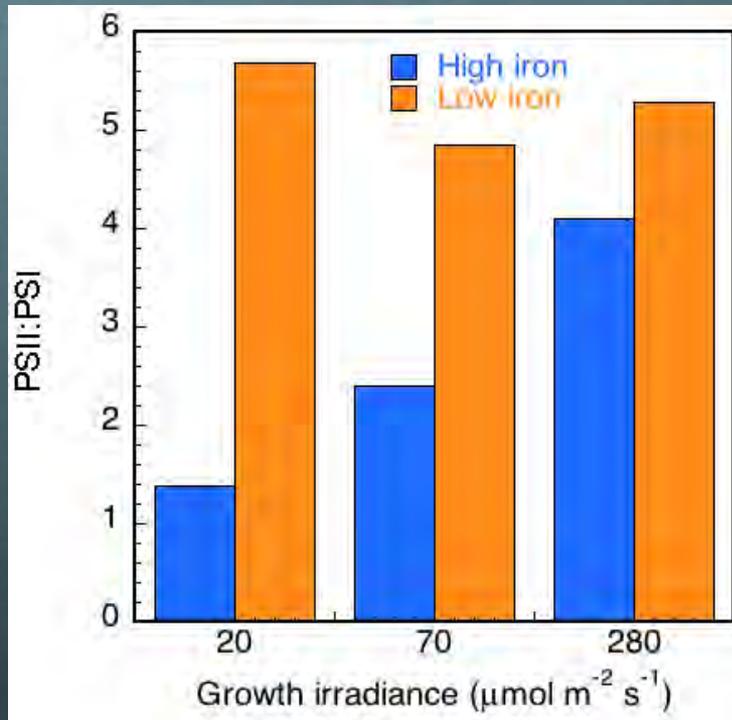
The decrease in fluorescence measured near the surface is caused by non-photochemical quenching.



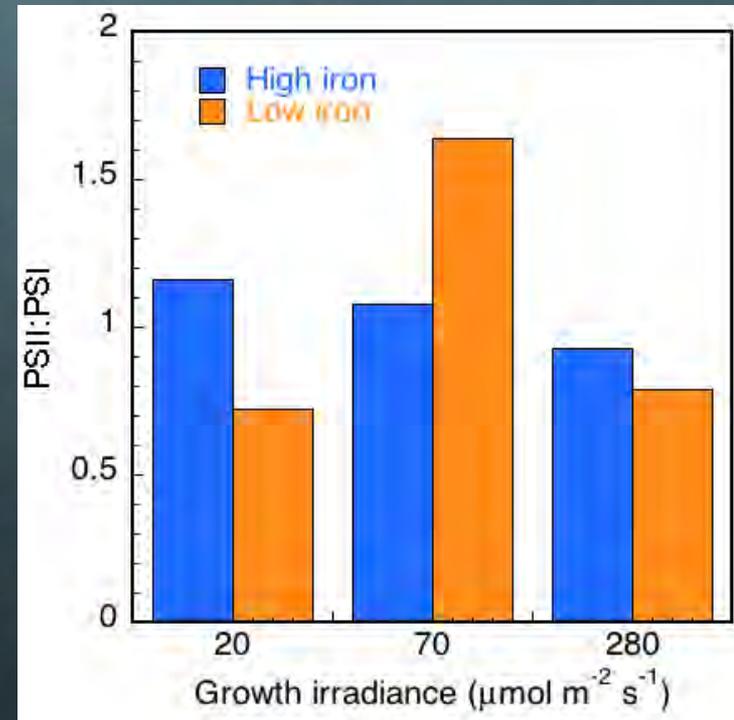
Nutrient status

Effect of iron on PSII:PSI ratio

T. Weissflogii (coastal)

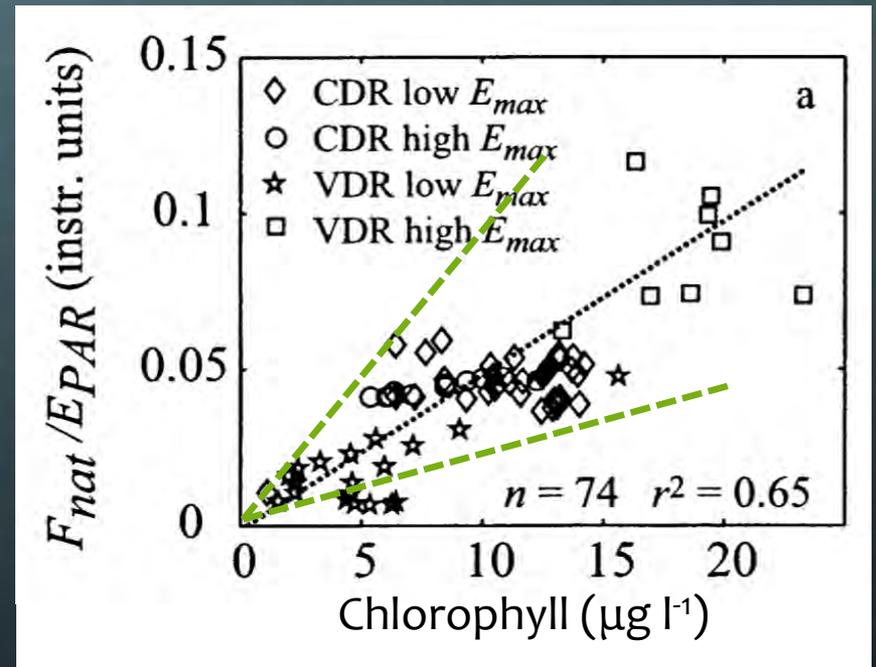
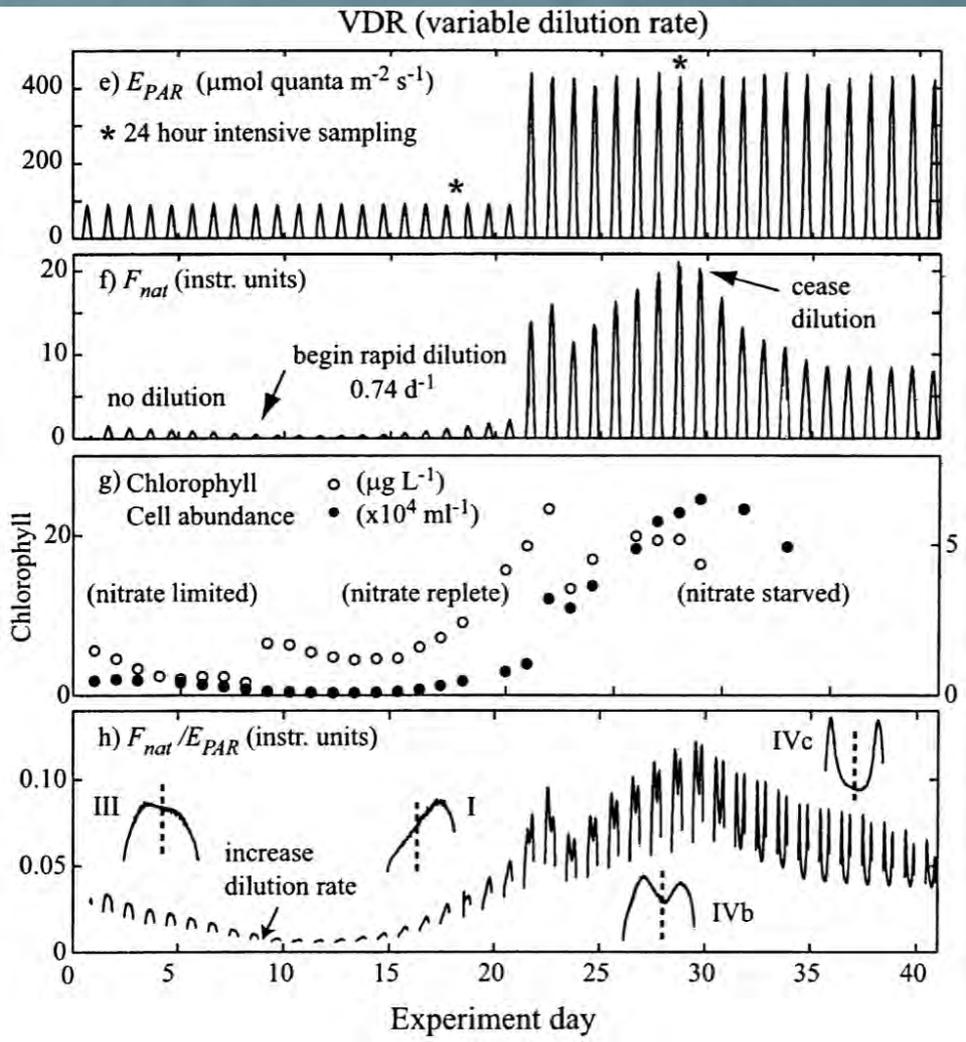


T. Oceanica (oceanic)



Under iron limitation, there is an important increase in PSII:PSI in one diatom, little change (and no clear direction) in the other.

Effect of nitrate stress on the quantum yield

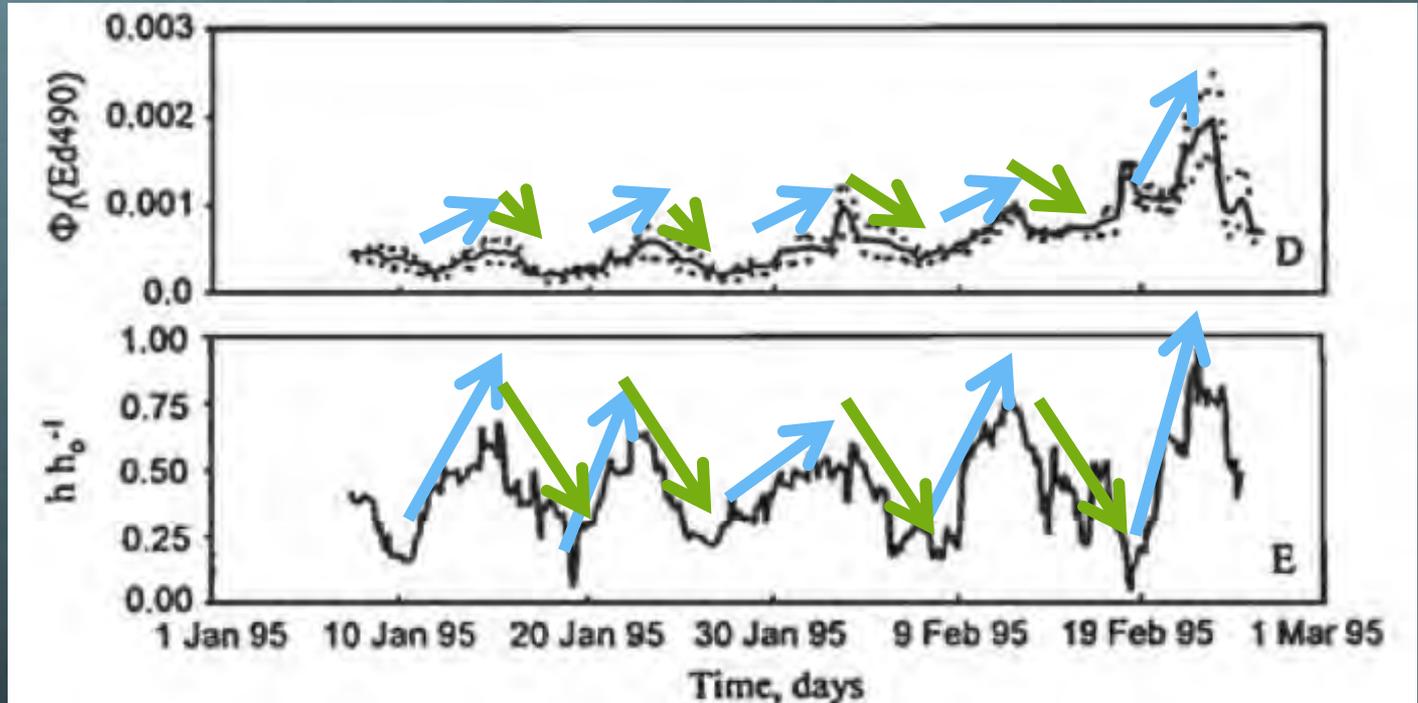


The quantum yield varies by a factor of about 4 for one species over a wide range of growth conditions. Nitrate starvation appears to lead to stronger NPQ near noon.

Indirect field evidence of the effect of nutrient stress

Quantum yield

Relative depth of upper layer

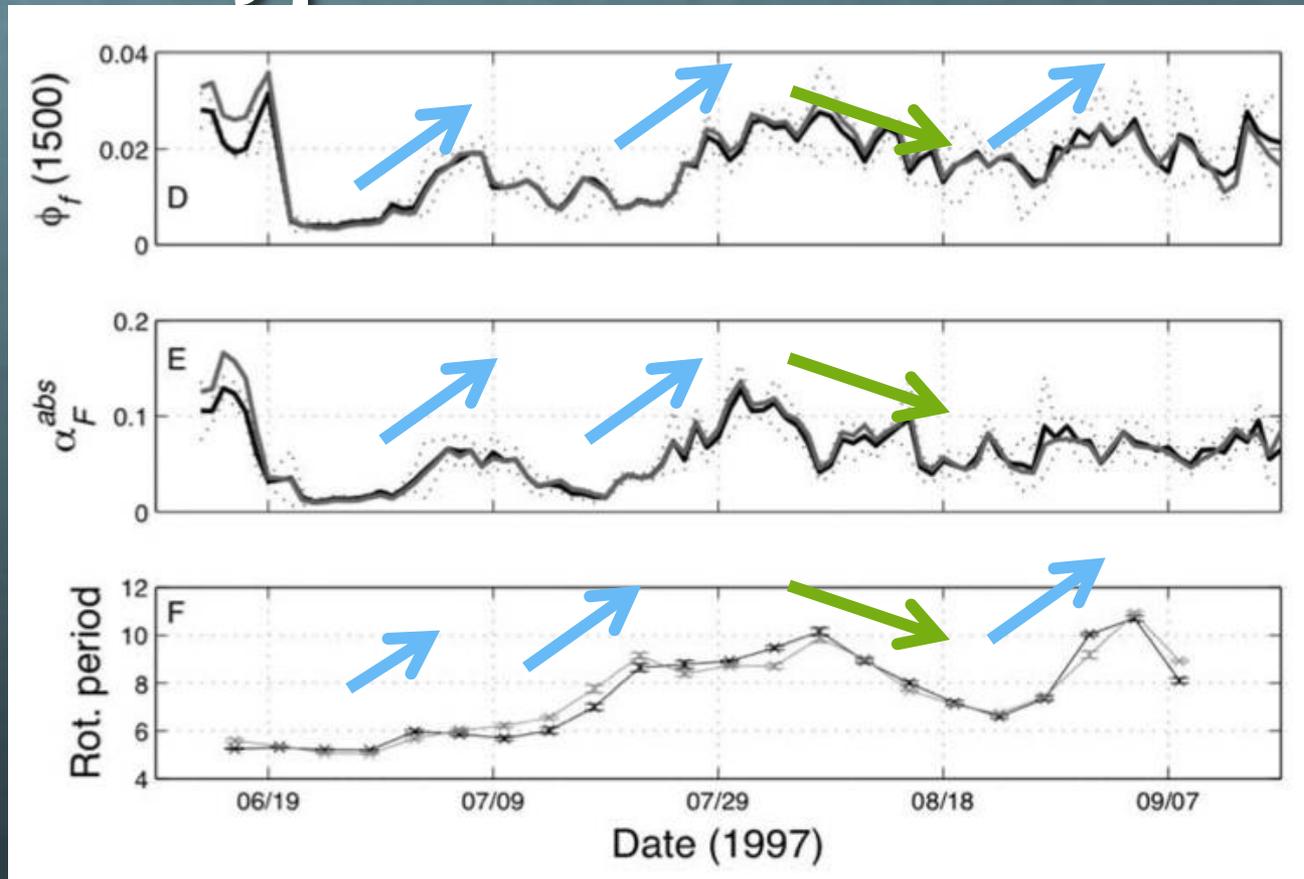


Increasing upper layer depth caused by downwelling linked to observed increase in Φ_f

Decreasing upper layer depth caused by upwelling linked to observed decrease in Φ_f

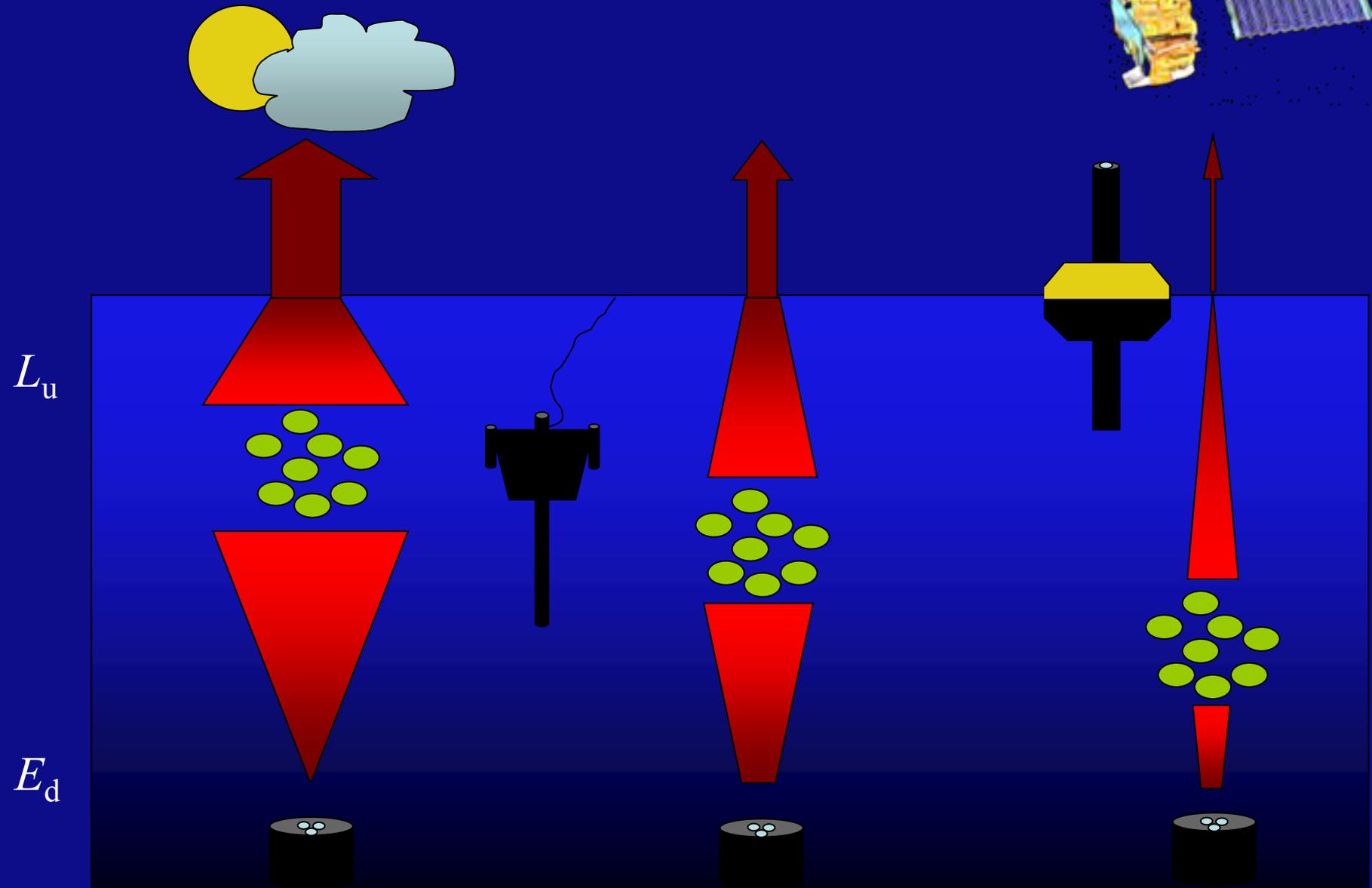
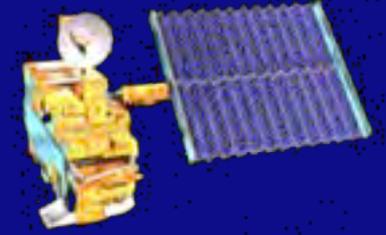
Hypothesis : nutrient stress is alleviated by upwelling of nutrients and PQ increases

Similar results, a different hypothesized cause



When the eddy slows (period increases) qI quenching is reduced by nutrient stress and this leads to an increase in Φ_f .

A intuitive look



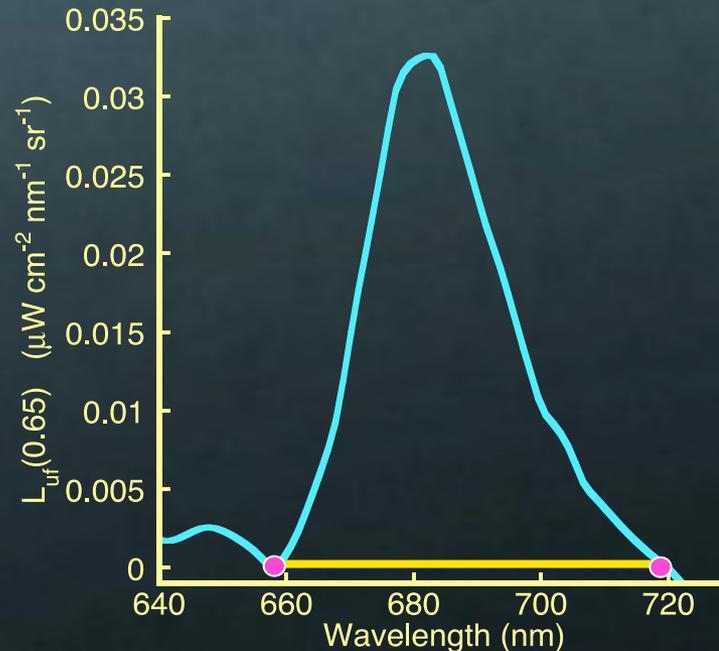
An elegant mathematical description of the fluorescence radiance/irradiance is provided in Maritorena, S., A. Morel, and B. Gentili. 2000. Determination of the fluorescence quantum yield by oceanic phytoplankton in their natural habitat. *Applied optics* **39**: 6725-6737.

A more detailed look...

Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$

A more detailed look...

Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$


Geometrical factor



Isotropic emission

A more detailed look...

Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$

Quantum yield of fluorescence

$$j = \frac{\text{photons emitted}}{\text{photons absorbed}}$$

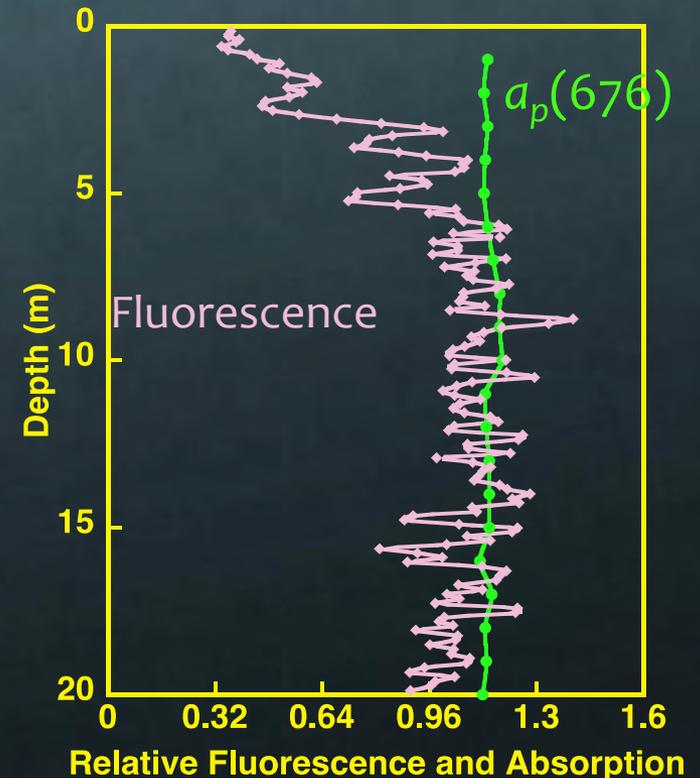
A more detailed look...

Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot \boxed{chl} \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$

Chlorophyll concentration



A more detailed look...

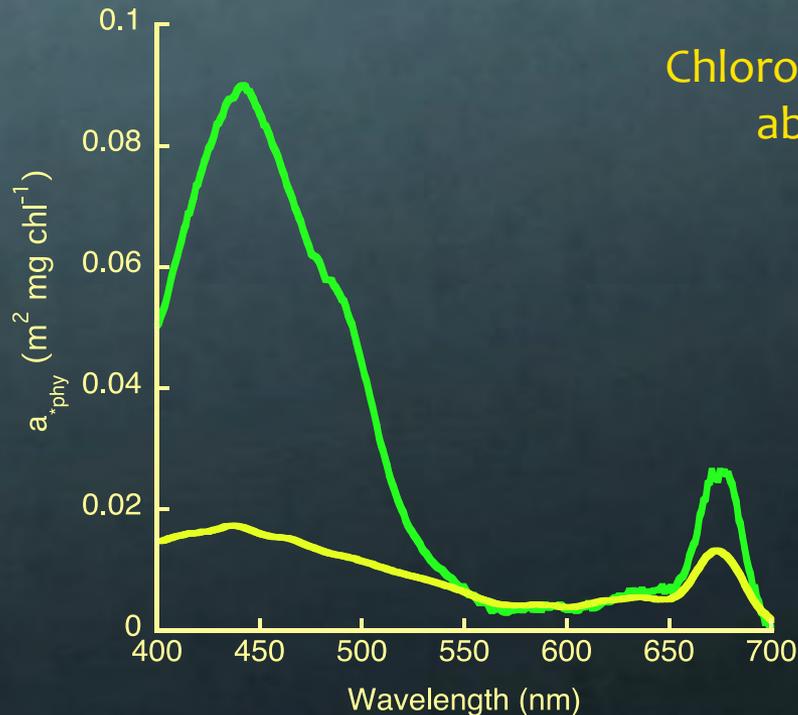
Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$



Chlorophyll specific
absorption



Diatoms, one-celled algae, come in a variety of beautiful shapes and sizes.

© 2001 The Academy of Natural Sciences

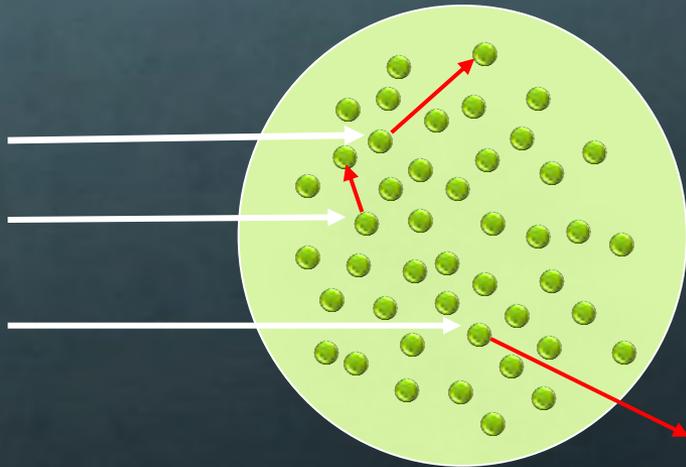
A more detailed look...

Influences on the fluorescence signal:

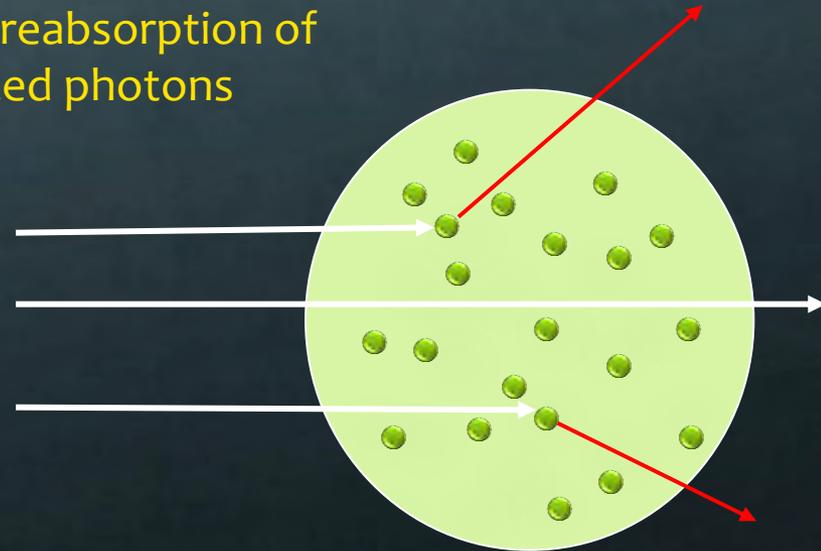
All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot \boxed{Q_a^*} \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$

Intracellular reabsorption of
fluoresced photons



Packaged cell



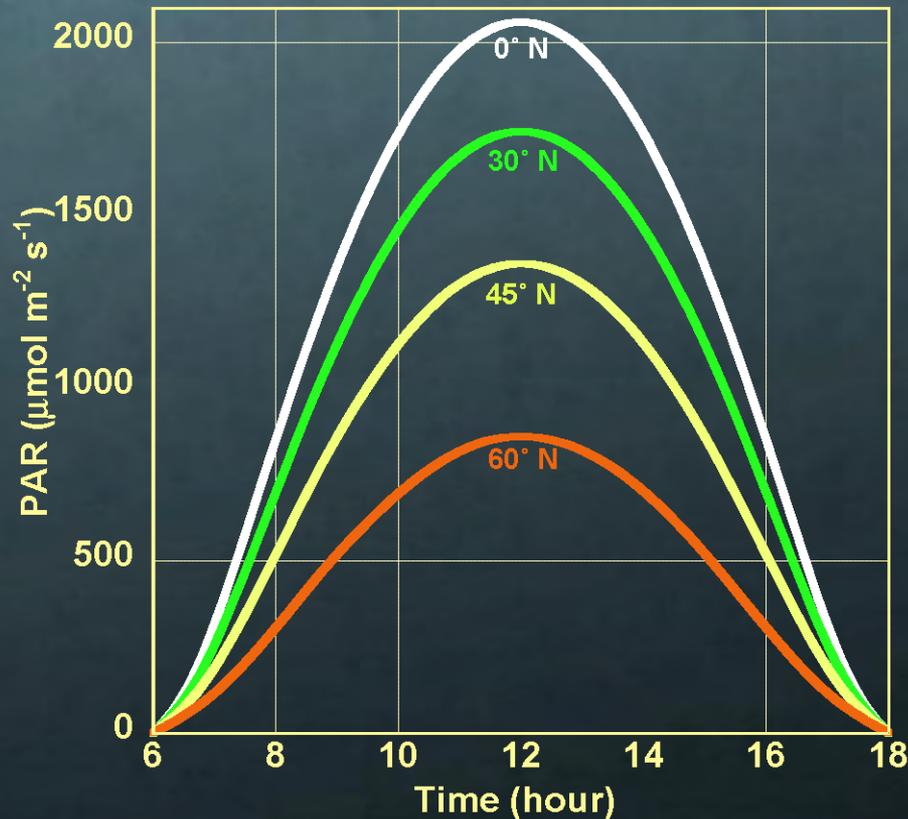
Unpackaged cell

A more detailed look...

Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \boxed{E_{PAR}^o} \cdot \frac{1}{K_{PAR} + a_f}$$

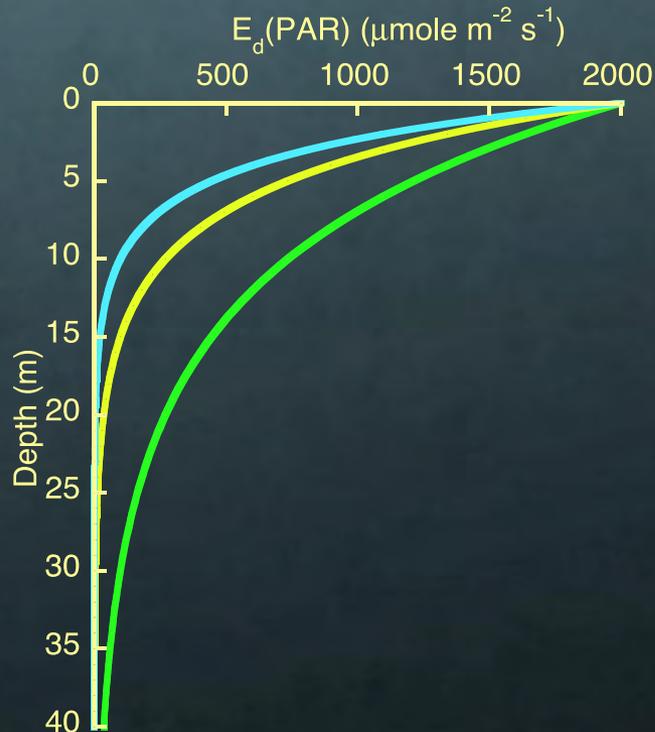


A more detailed look...

Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$



A more detailed look...

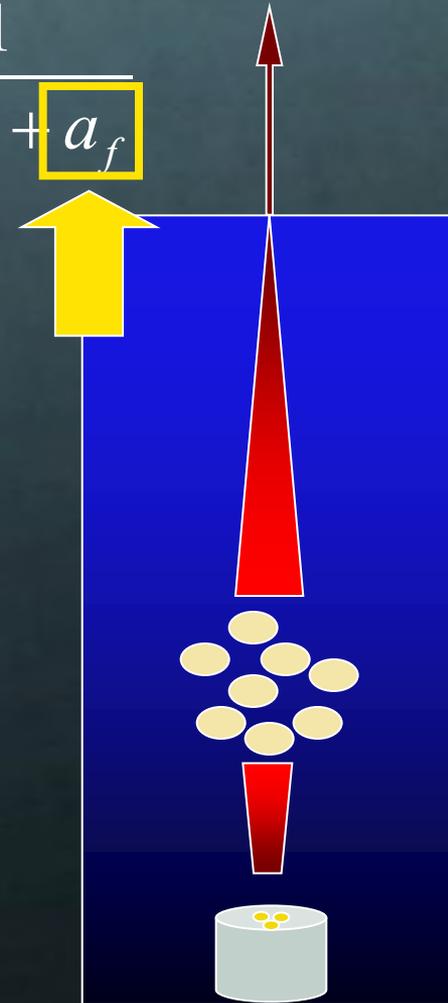
Influences on the fluorescence signal:

All wavelength dependency dropped here

$$L_{uf} = \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{o}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f}$$

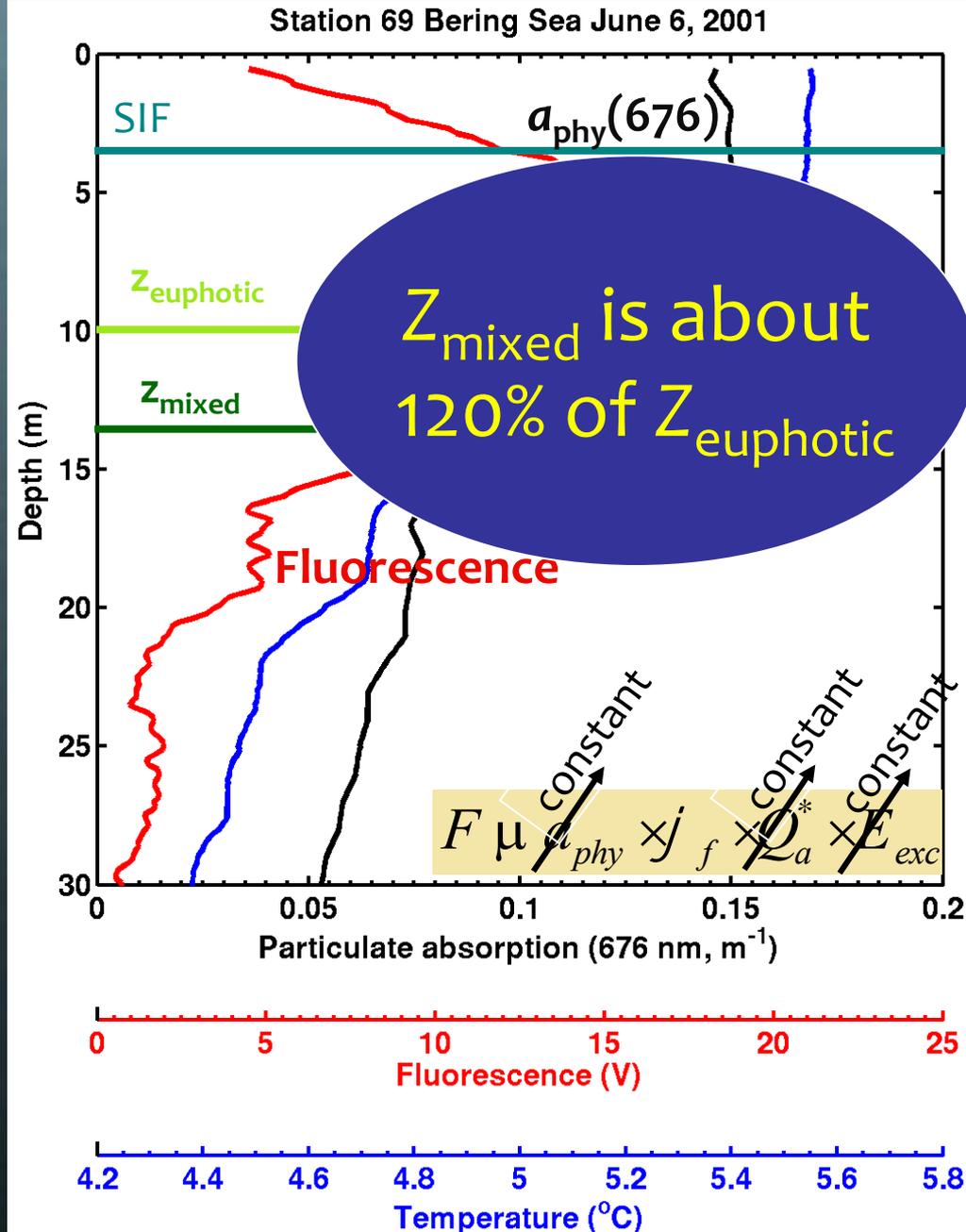
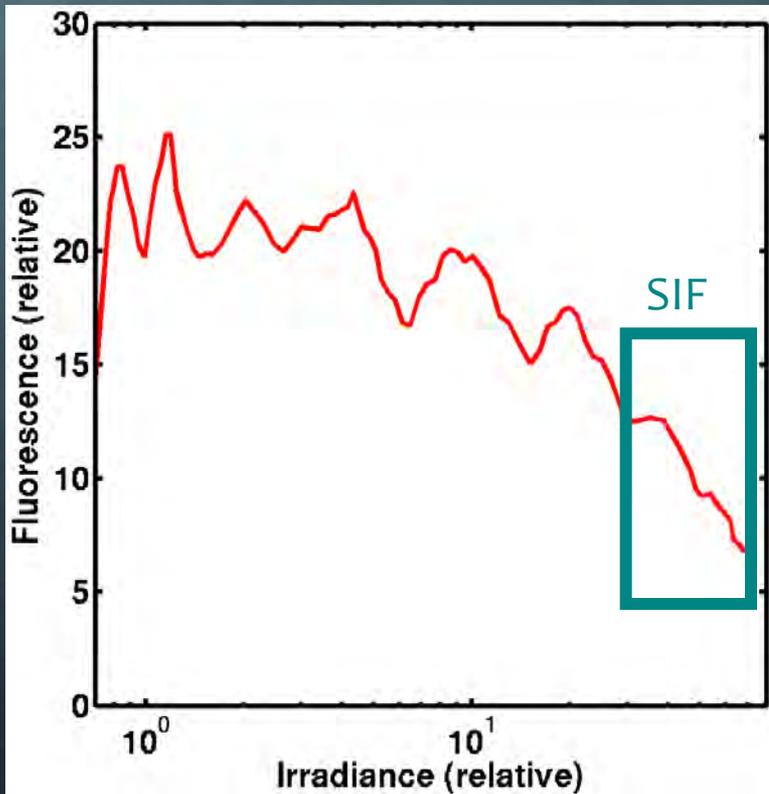
Attenuation of upwelling radiance

Because water absorbs strongly in the fluorescence band, most of the fluoresced light in the upwelling radiance originates from 5 meters or less below the sensor.



A mixed layer measurement

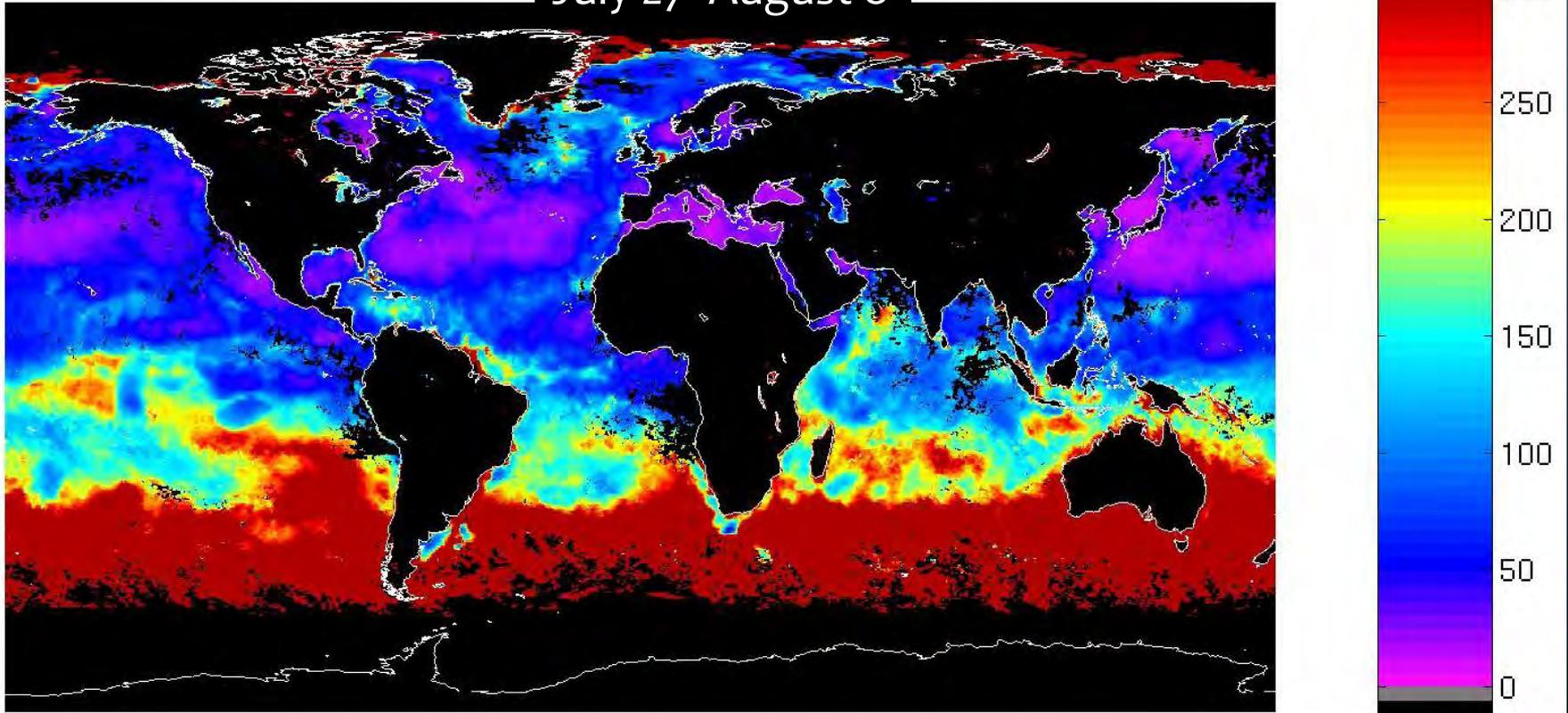
Remotely sensed fluorescence represents phytoplankton of the mixed layer responding to sunny, near-surface, irradiance conditions.



More than just skin deep...

Mixed layer depth as a percentage of the euphotic depth*

July 27 -August 8



Sun-induced fluorescence samples
a significant portion of the euphotic zone.

*8 W m⁻² mean daily irradiance

Upwelling radiance and radiance reflectance

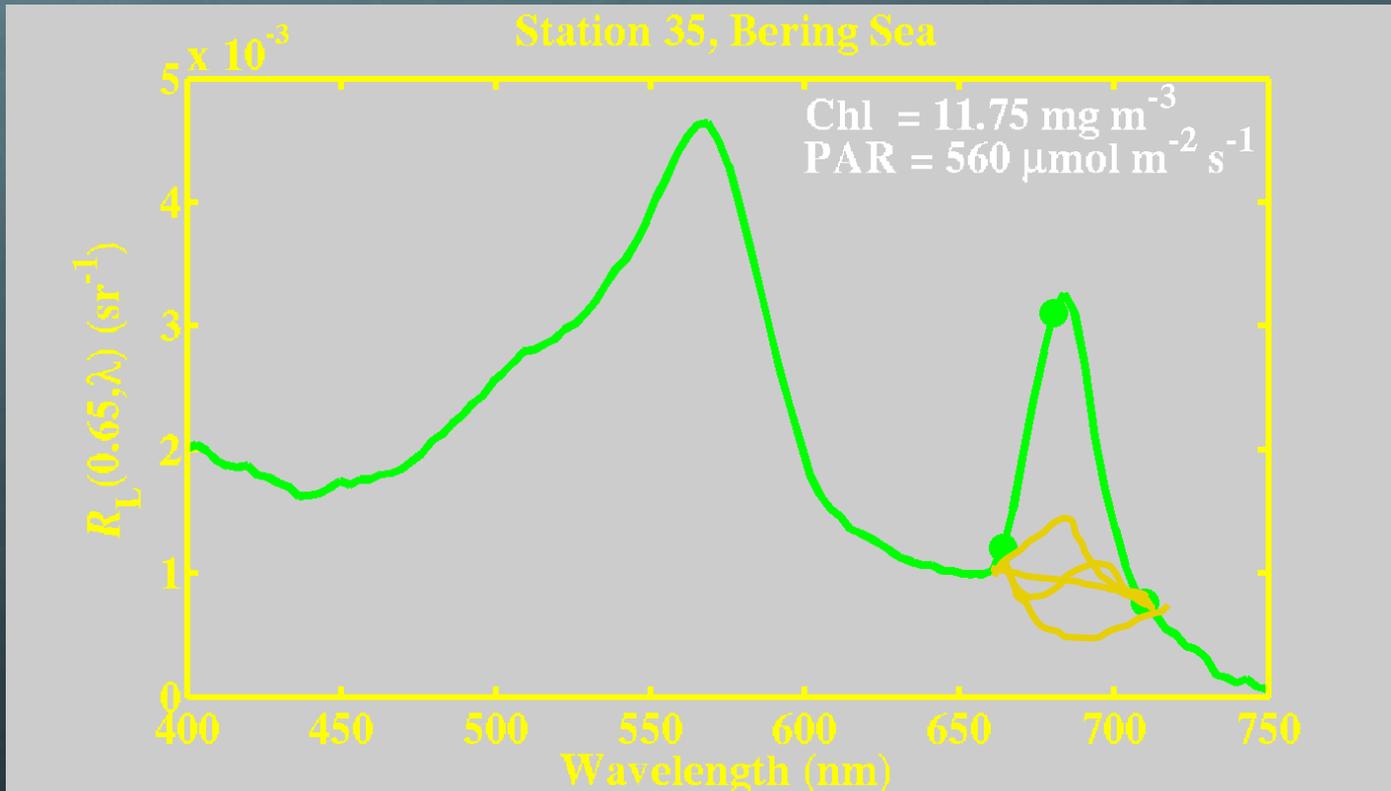
Neglecting other inelastic radiance sources

$$\begin{aligned} L_u &= L_{uElastic} + L_{uf} \\ &= f(b_b, a) + \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{\circ}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f} \end{aligned}$$

$$\begin{aligned} R_L &= \frac{1}{E_d} (L_{uElastic} + L_{uf}) \\ &= \frac{1}{E_d} \left(f(b_b, a) + \frac{1}{4\pi} \cdot \phi_f^{app} \cdot chl \cdot \bar{a}_{phy}^* \cdot Q_a^* \cdot \overset{\circ}{E}_{PAR} \cdot \frac{1}{K_{PAR} + a_f} \right) \end{aligned}$$

Measuring Sun-induced fluorescence

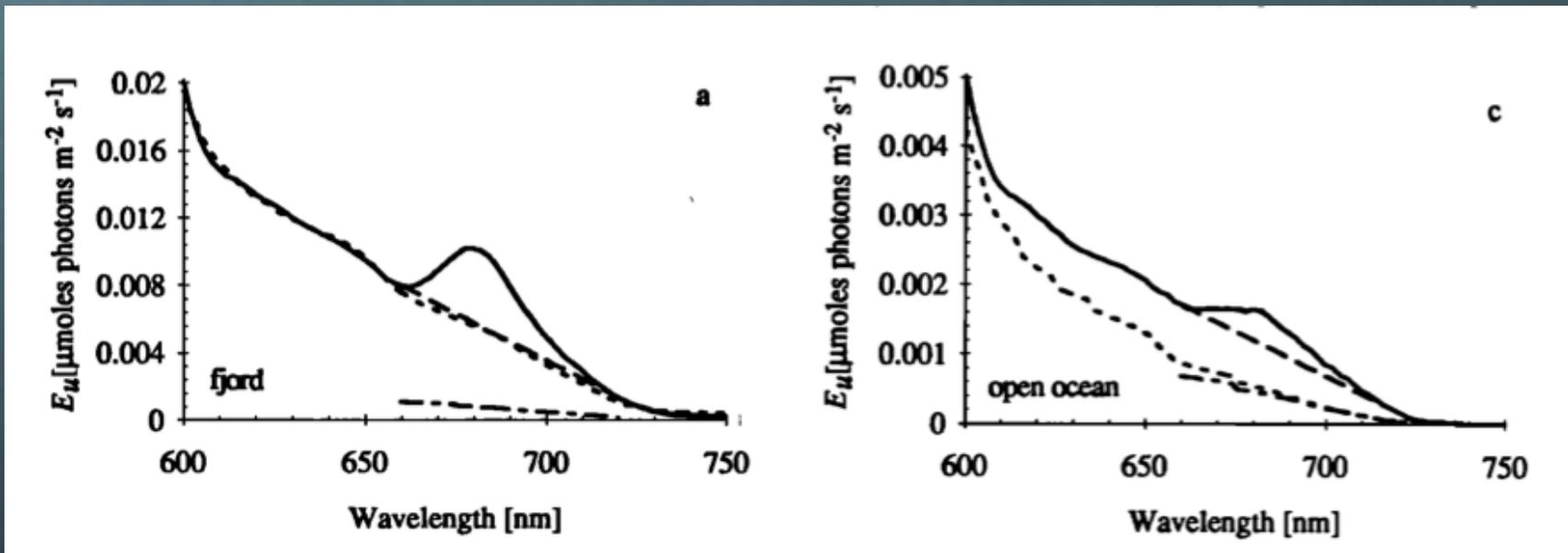
Usually, we want to measure the amount of Sun-induced fluorescence from an upwelling radiance spectra or reflectance spectra.



The main question then becomes what is the background radiance (reflectance) that is not originating from fluorescence.

“Background” radiance

Two main methods exist to find the background: 1) using the results of a semi-analytical model in a forward fashion, 2) linear baseline.



The linear baseline method is the simplest and appears to be the most reliable method to obtain the background radiance

-Figure from : Culver, M E, and M J Perry. "Calculation of Solar-induced Fluorescence in Surface and Subsurface Waters." *Journal of Geophysical Research* 102 (C5) (1997): 10563-10572

-For an alternative approach see : Ioannou, I, J Zhou, A Gilerson, B Gross, F Moshary, and S Ahmed. "New Algorithm for MODIS Chlorophyll Fluorescence Height Retrieval: Performance and Comparison with the Current Product (Proceedings Paper)." In *Proceedings of SPIE : Remote Sensing of the Ocean, Sea Ice, and Large Water Regions Vol. 7473*. SPIE, 2009

A more detailed look...

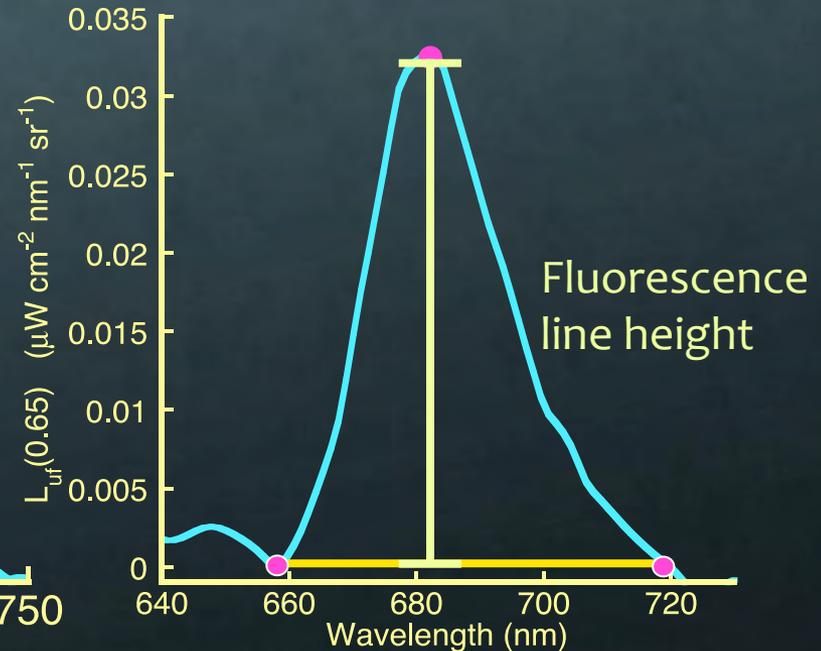
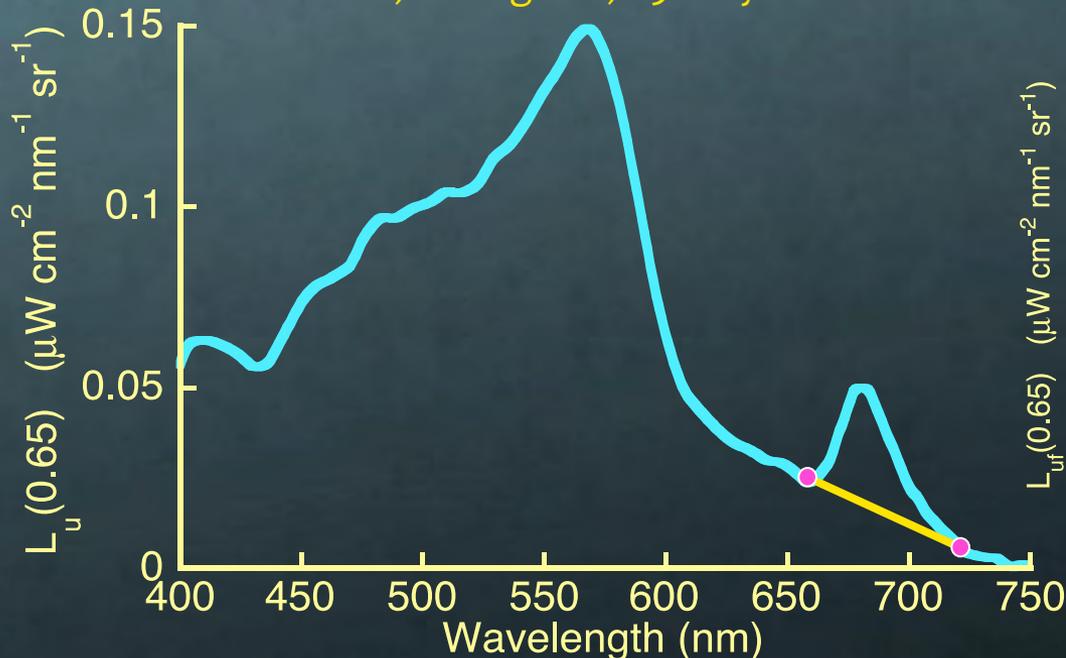
🌐 Separating the fluorescence signal from other signals

$$L_u = L_{uf} + L_{uRaman} + L_{ubackscattered}$$

The baseline correction: simple and most used

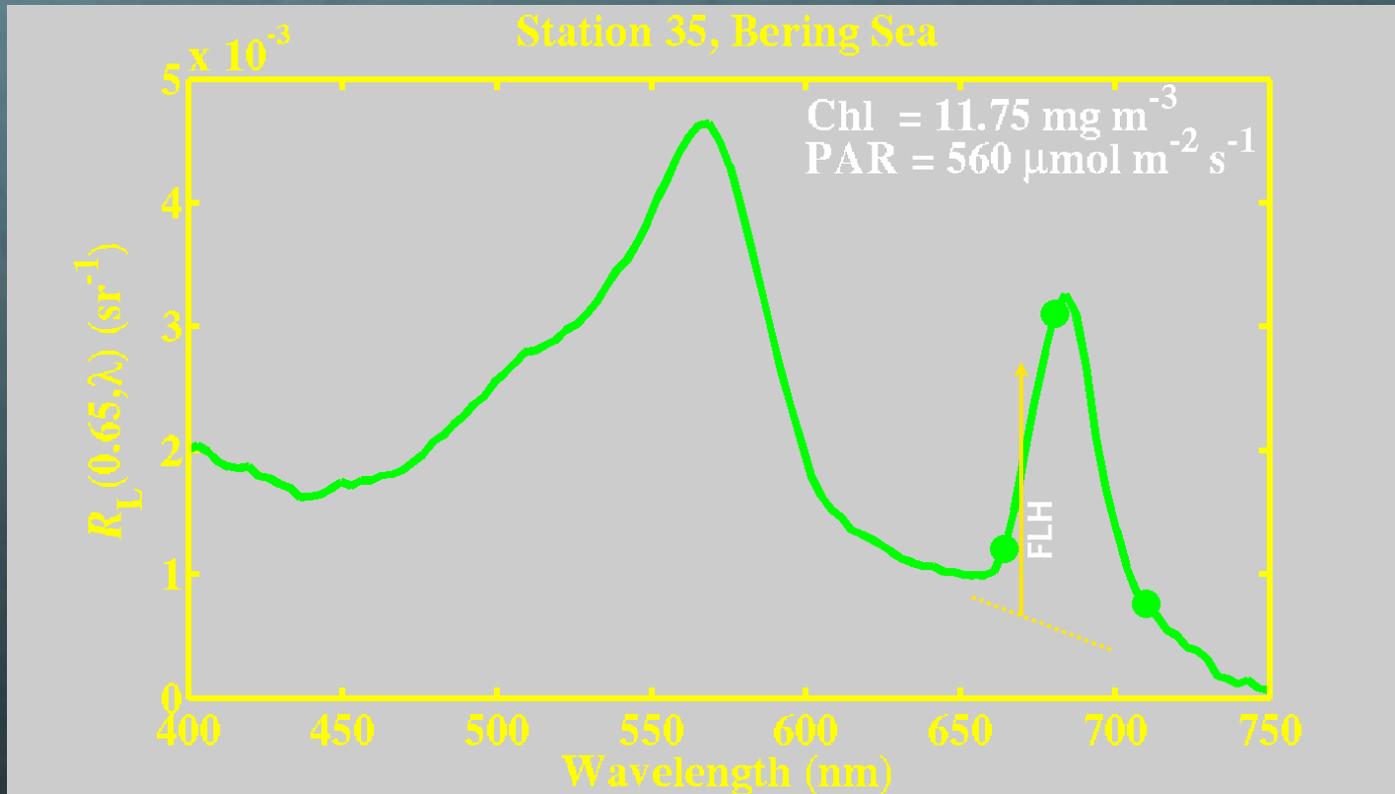
(Assumes linear Raman and back-scattered radiance.)

Station 6, Bering Sea, 29-May-2001

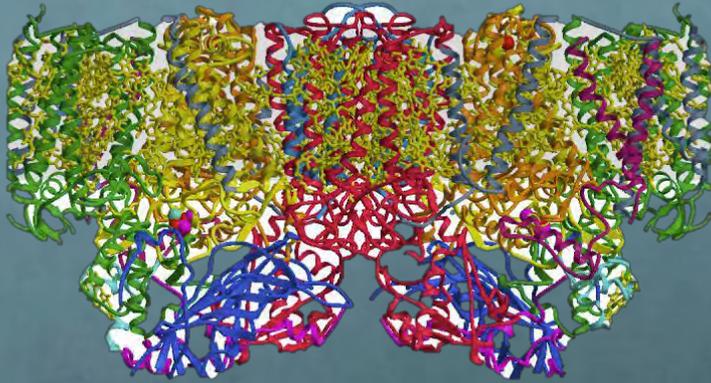


MODIS (667 and 748 nm) and MERIS (665 and 709 nm) have bands on either side of the fluorescence radiance peak that allows a background radiance to be computed

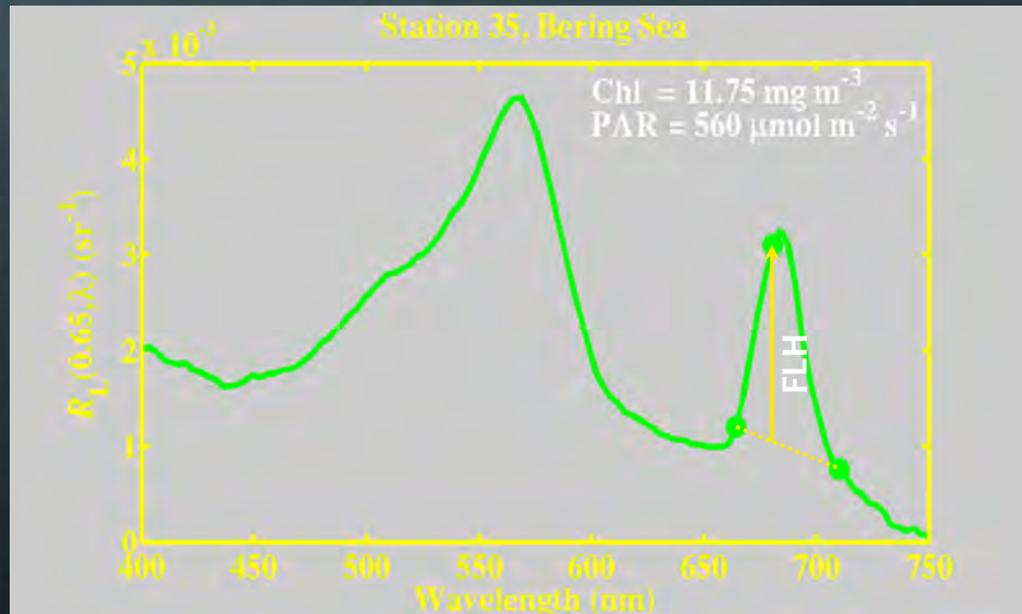
Measuring the amount of fluorescence: the fluorescence line height (FLH)



MODIS (667 and 748 nm) and MERIS (665 and 709 nm) have bands on either side of the fluorescence radiance peak that allows a background radiance to be computed



That's it for now!



Quantitatively

Fluorescence flux emitted by an elementary volume is given by:

$$F_f(I_{em}, z) = j_f(I_{em}, z) \times Q_a^*(I_{em}, z) \times A_{ex}(z)$$

Where A_{ex} is the flux absorbed given by:

$$A_{ex} = [chl(z)] \int_{400}^{700} a^*(I_{ex}, z) E(I, z) dI$$

The rest is just a matter of integrating over depth and emission wavelength, and using the approximation that you believe is appropriate for your application...

Lets examine the case of upwelling radiance in more detail

This description is based mostly on : Maritorena, S., A. Morel, and B. Gentili. 2000. Determination of the fluorescence quantum yield by oceanic phytoplankton in their natural habitat. Applied optics **39**: 6725-6737.

Upwelling radiance

The scalar irradiance at depth z below the sensor is given by:

$$\overset{o}{E}(I_{ex}, z_{sens}) = \overset{o}{E}(I_{ex}, z_{sens}) \exp(-K(I_{ex})z)$$

Because the radiance is isotropic, we can simply write that the elementary radiance emitted from a thin layer at depth z is:

$$dL_f(I_{em}, z) = F_f(I_{em}, z) dz / 4\rho$$

This radiance will be absorbed as it travels upward to the sensor by:

$$dL_f(I_{em}, z_{sens}) = dL_f(I_{em}, z) \exp(-a(I_{em}, z)z)$$

Upwelling radiance

We then have that the radiance at depth z_{sens} due to a thin layer at depth z below the sensor is given by :

$$dL_f(I_{em}, z_{sens}) = \frac{1}{4\rho} j_f(I_{em}, z) \times Q_a^*(I_{em}, z) \times [chl(z)] \int_{400}^{700} a^*(I_{ex}, z) \overset{o}{E}(I_{ex}, z_{sens}) \exp(-[K(I_{ex}) + a(I_{em}, z)]z) d\lambda dz$$

Clearly we are in trouble if we want to get a simple formulation for the depth integrated fluorescence.

As a first approximation because 90% of the fluorescence from ~3m below the sensor (high a_f) we will drop the depth dependence on most parameters (they become the value at the depth of the sensor):

$$dL_f(I_{em}, z_{sens}) = \frac{1}{4\rho} j_f(I_{em}, z_{sens}) \times Q_a^*(I_{em}, z_{sens}) \times [chl(z_{sens})] \int_{400}^{700} a^*(I_{ex}, z_{sens}) \overset{o}{E}(I_{ex}, z_{sens}) \exp(-[K(I_{ex}) + a(I_{em}, z_{sens})]z) d\lambda dz$$

Upwelling radiance

To get a nice formulation we will now introduce an absorption coefficient weighted for the irradiance :

$$\bar{a}^* = \frac{\int_{400}^{700} a^*(I_{ex}, z_{sens}) \overset{o}{E}(I_{ex}, z_{sens}) dI_{ex}}{\int_{400}^{700} \overset{o}{E}(I_{ex}, z_{sens}) dI_{ex}}$$

And a broad band attenuation coefficient:

$$\overset{o}{E}_{ex}(z) = \overset{o}{E}_{ex}(z_{sens}) \exp(-K_{ex} x)$$

Note that two approximations are involved here

A broad band attenuation can be used.

$K_{pur} = K_{par}$ (i.e. we are not accounting changes in spectral irradiance with depth.)

Upwelling radiance

This greatly simplifies our expression:

$$dL_f(I_{em}, z_{sens}) = \frac{1}{4\rho} j_f(I_{em}, z_{sens}) \times Q_a^*(I_{em}, z_{sens}) \times [chl(z_{sens})] \times \bar{a}_{ex}^* \times \overset{o}{E}_{ex}(z_{sens}) \times \exp(-[K_{ex} + a(I_{em}, z_{sens})]z) dz$$

And allows integration to infinity:

$$L_f(I_{em}, z_{sens}) = \frac{1}{4\rho} j_f \times Q_a^*(I_{em}) \times chl \times \bar{a}_{ex}^* \times \overset{o}{E}_{ex}(z_{sens}) \times [K_{ex} + a(I_{em})]^{-1}$$

For E_{uf} and E_{df}

The expressions for the upwelling and downwelling irradiances when integrated to infinity are:

$$E_{df}(I_{em}, z_{sens}) = \frac{1}{4} j_f \times Q_a^*(I_{em}) \times chl \times \bar{a}_{ex}^* \times \overset{o}{E}_{ex}(z_{sens}) \times [-K_{ex} + a(I_{em})]^{-1}$$

$$E_{uf}(I_{em}, z_{sens}) = \frac{1}{4} j_f \times Q_a^*(I_{em}) \times chl \times \bar{a}_{ex}^* \times \overset{o}{E}_{ex}(z_{sens}) \times [K_{ex} + a(I_{em})]^{-1}$$

The factor 1/4 is to account for the fact that the average cosine for isotropic emission is 1/2 and that we are only seeing half of the space ($2\pi/4\pi$)

κ replaces the absorption for irradiance $\sim 1.5 a(I_{em})$.

For downwelling irradiance, the sign in front of K_{ex} changes to account for the fact that irradiance is not decreasing but increasing above the sensor.