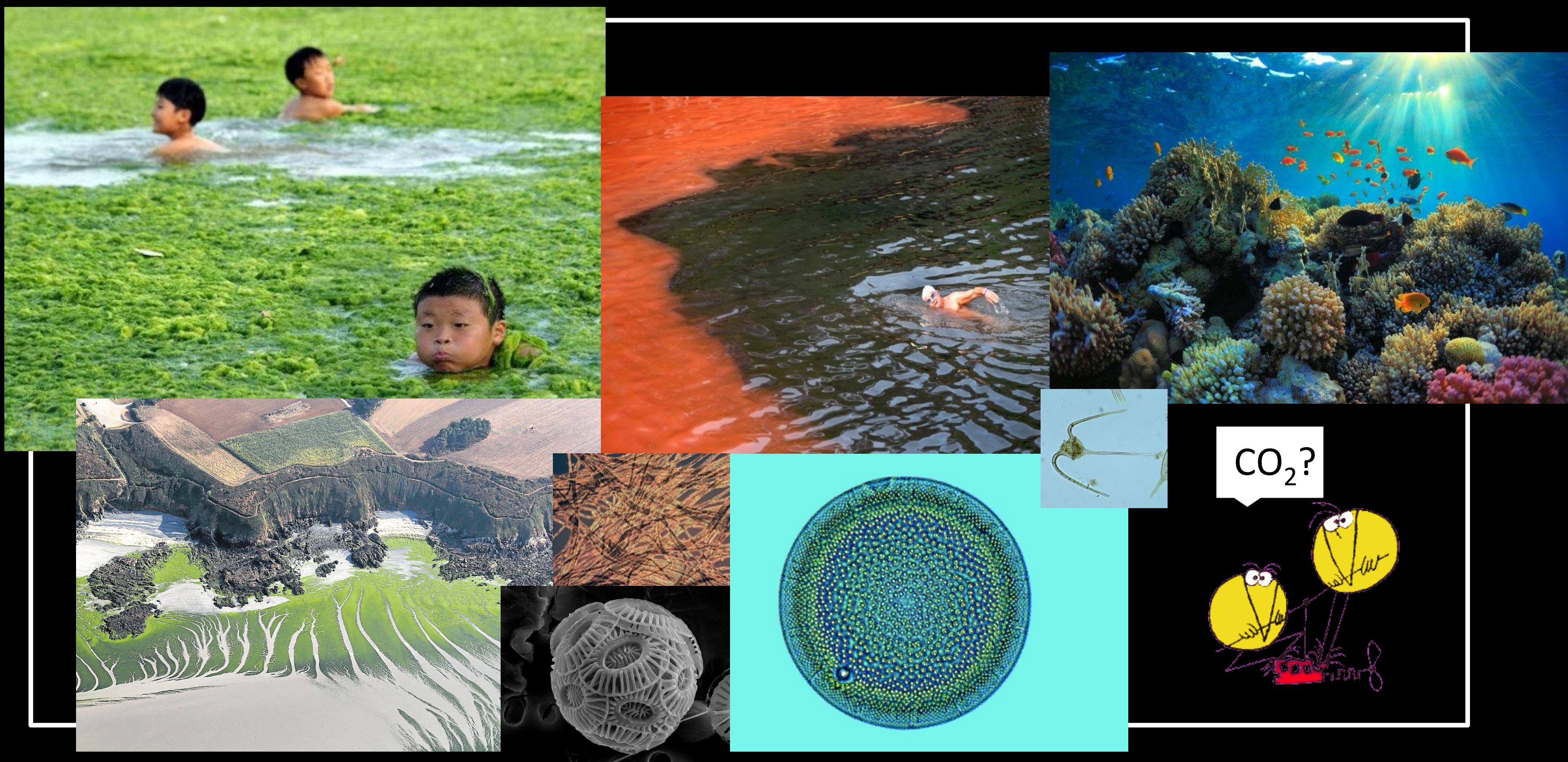
A new molecular approach to investigate N cycle from the modern to the past

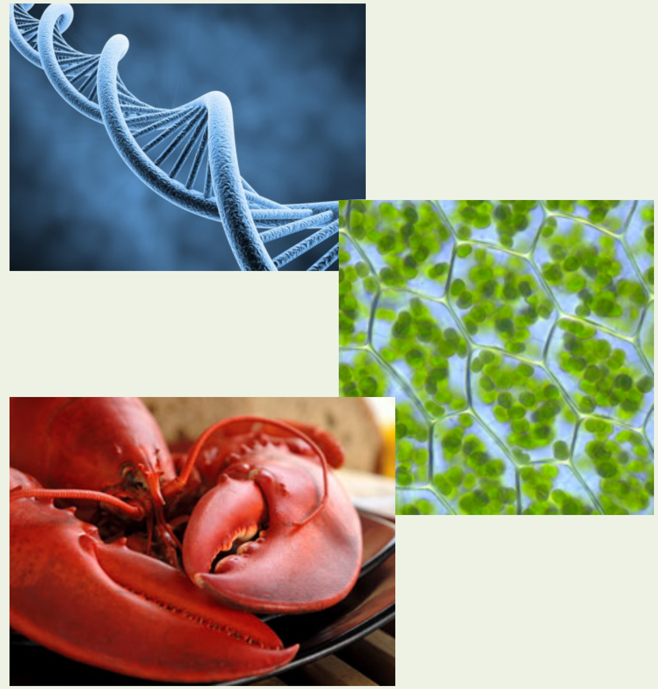
J. Etourneau, C. Yoshikawa, X. Crosta, I. Bouloubassi, G. Massé, N.O. Ogawa & N. Ohkouchi



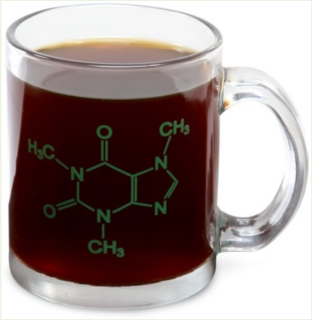
Why to study N cycle?

Present in all major biogeochemical processes

- Amino-acids
- Proteins
- DNA & RNA
- Chlorophyll
- Urea
- Chitins

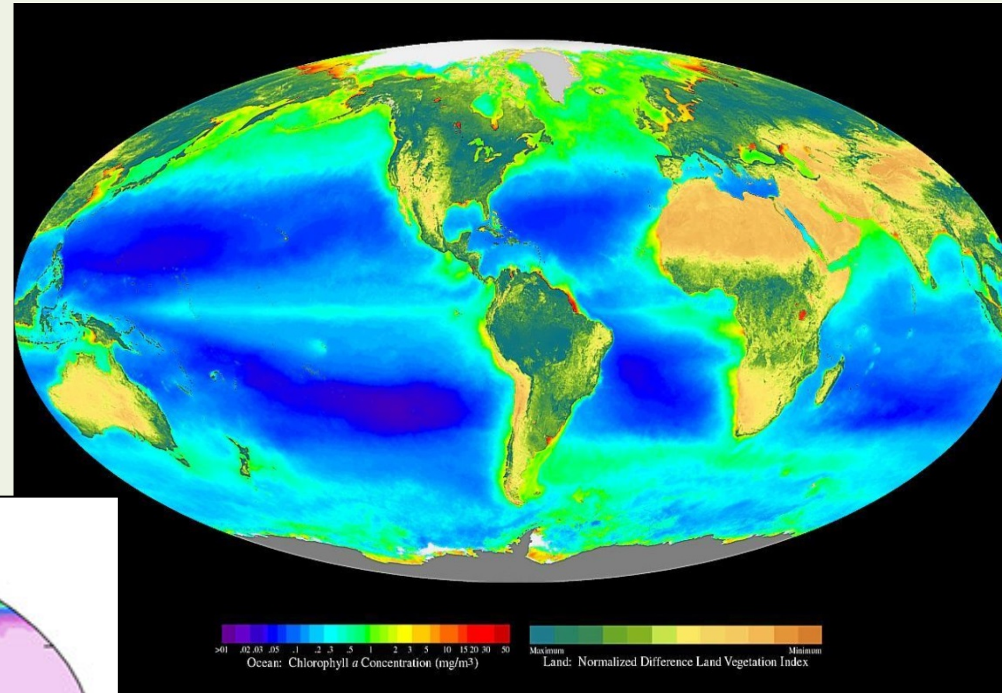


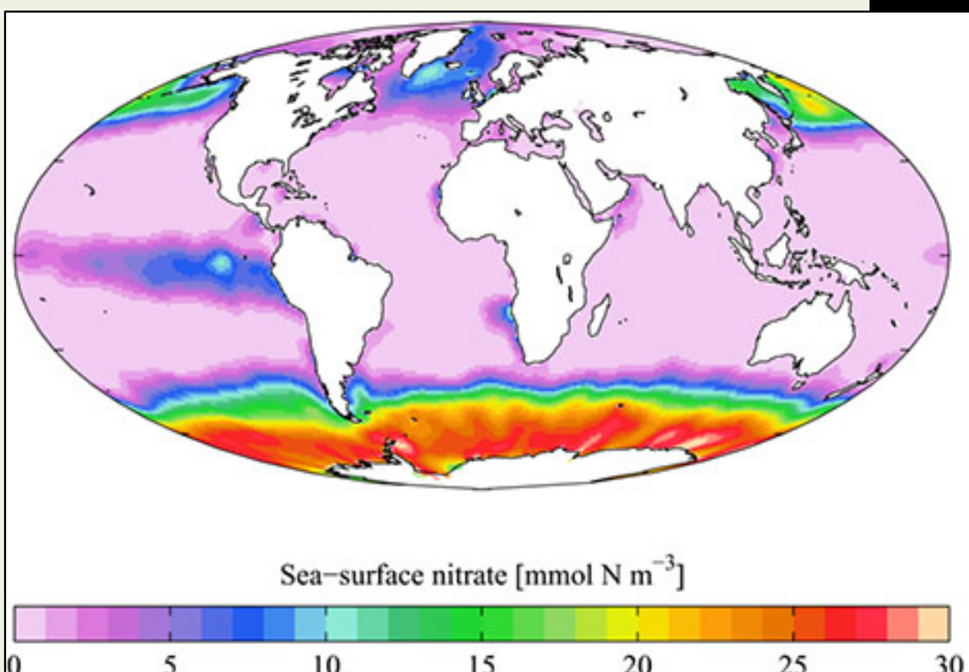
- Caffeine, theine, nicotin, paracetamol and many others…

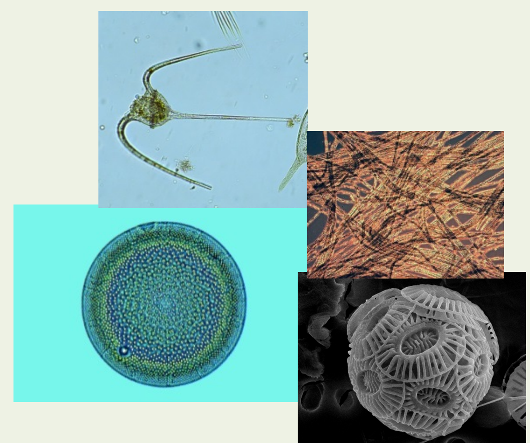


Phytoplancton activity

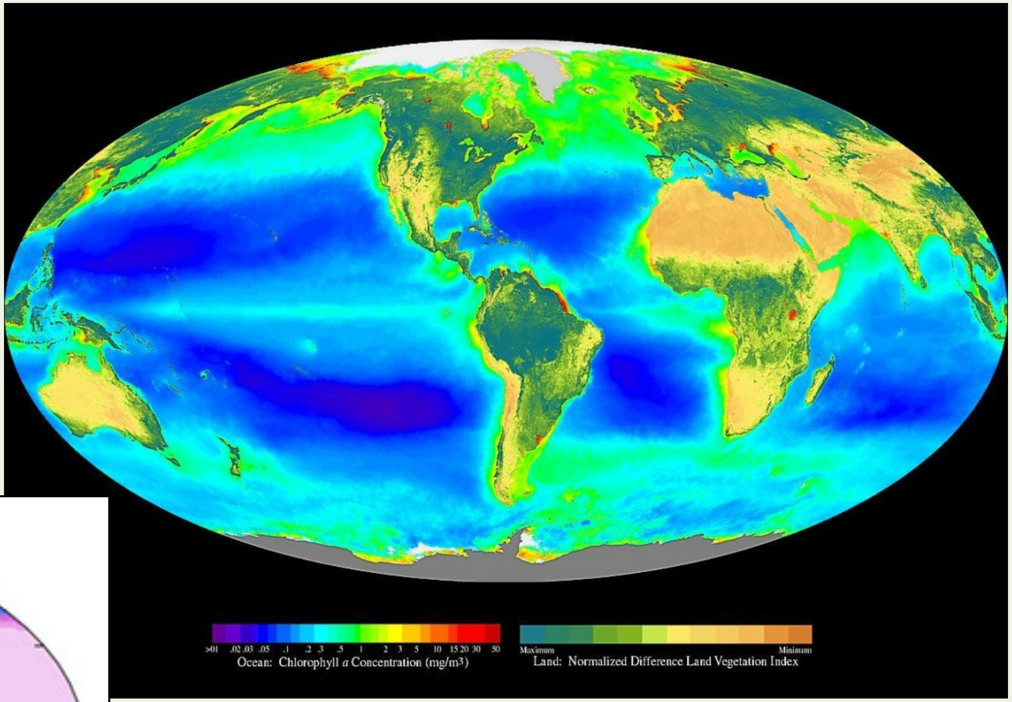
➡ **Higher is the nitrate availability in the surface ocean, higher is the rate of primary productivity**



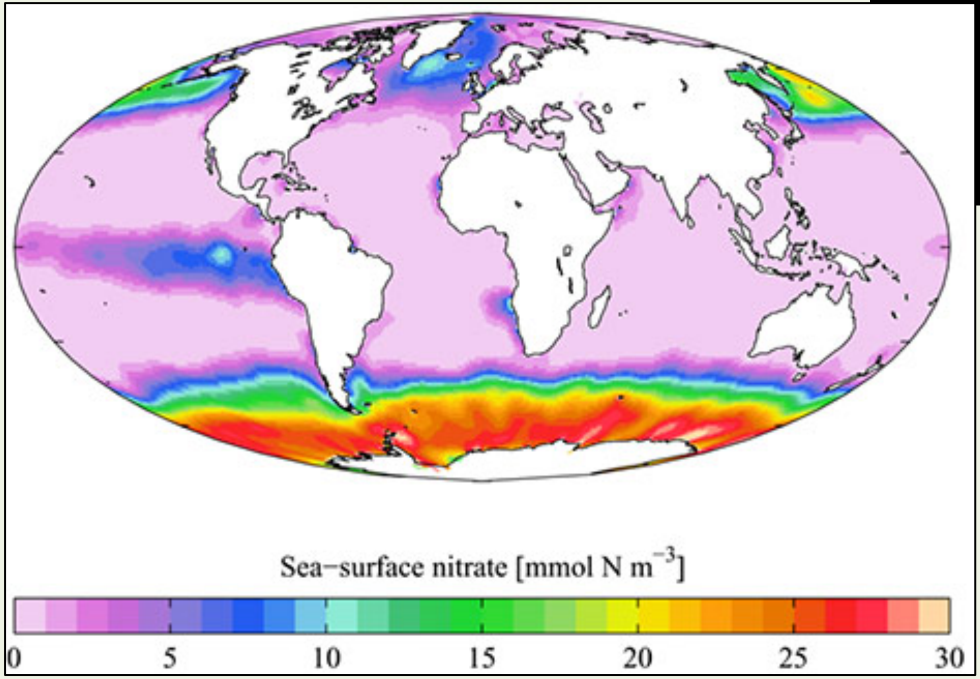




Global impact



➡ Higher is the nitrate availability in the surface ocean, higher is the rate of primary productivity

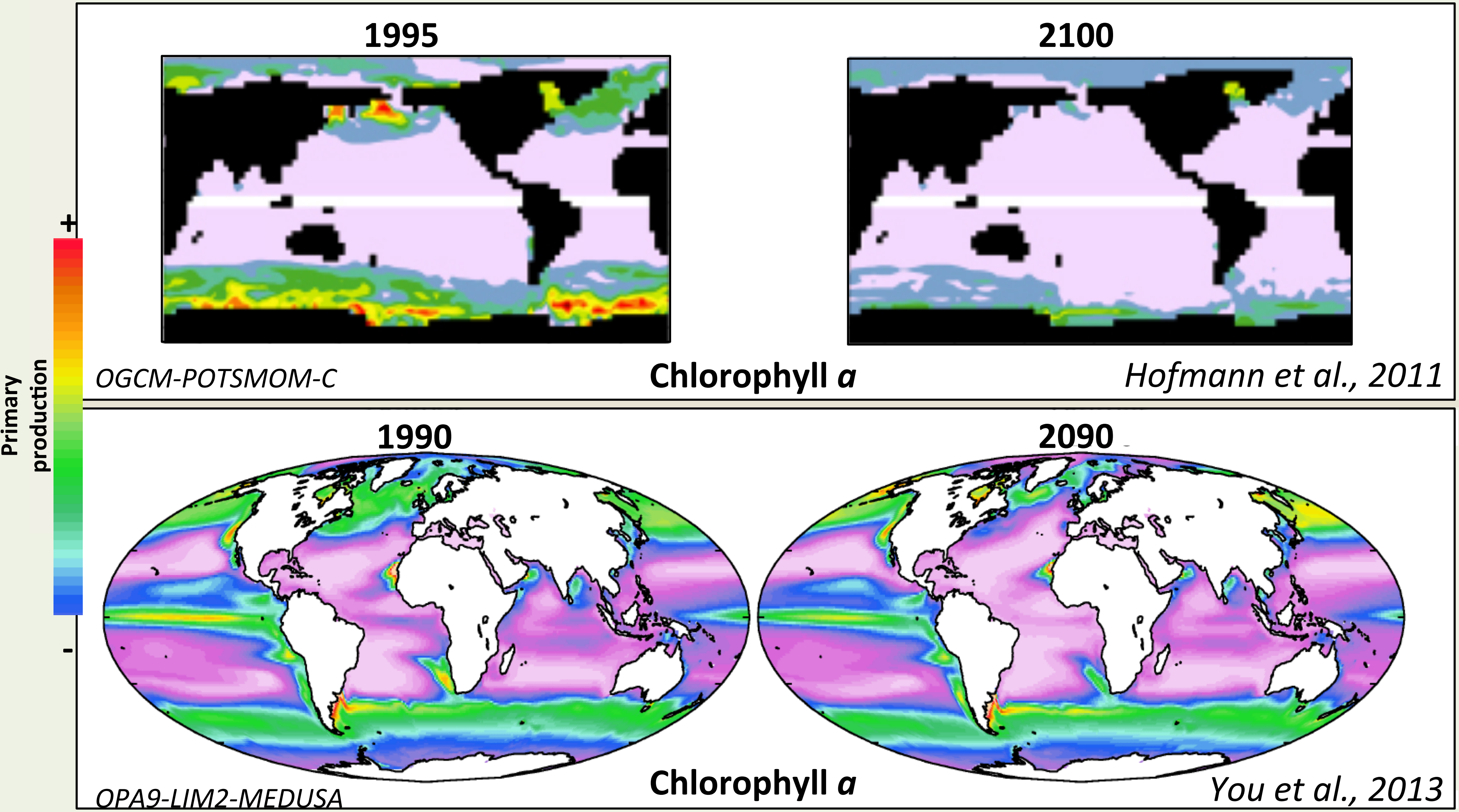


➡ Ecosystems

➡ Biological carbon pump (organic matter)

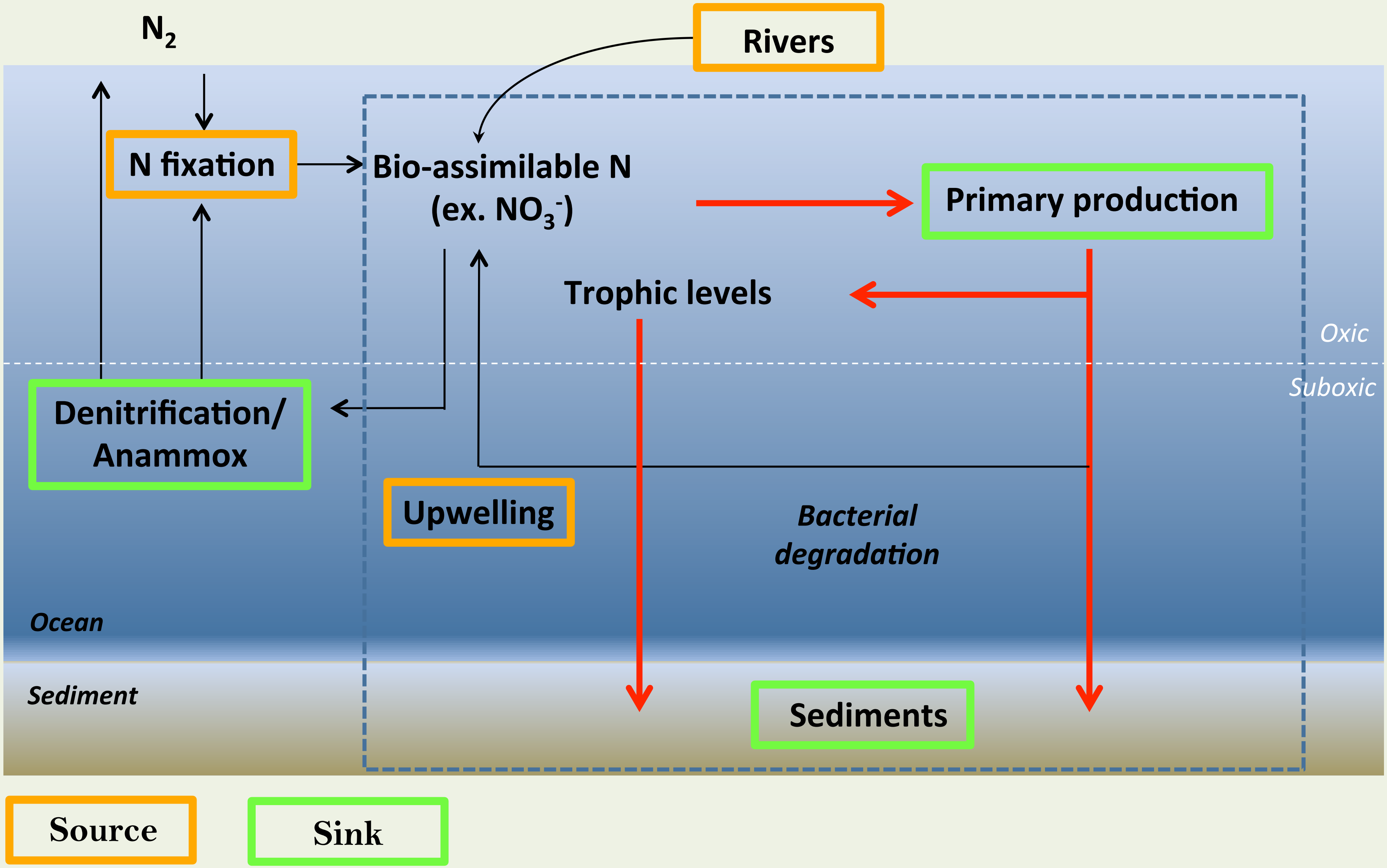
➡ Greenhouse gases (N_2O)

In 2100?

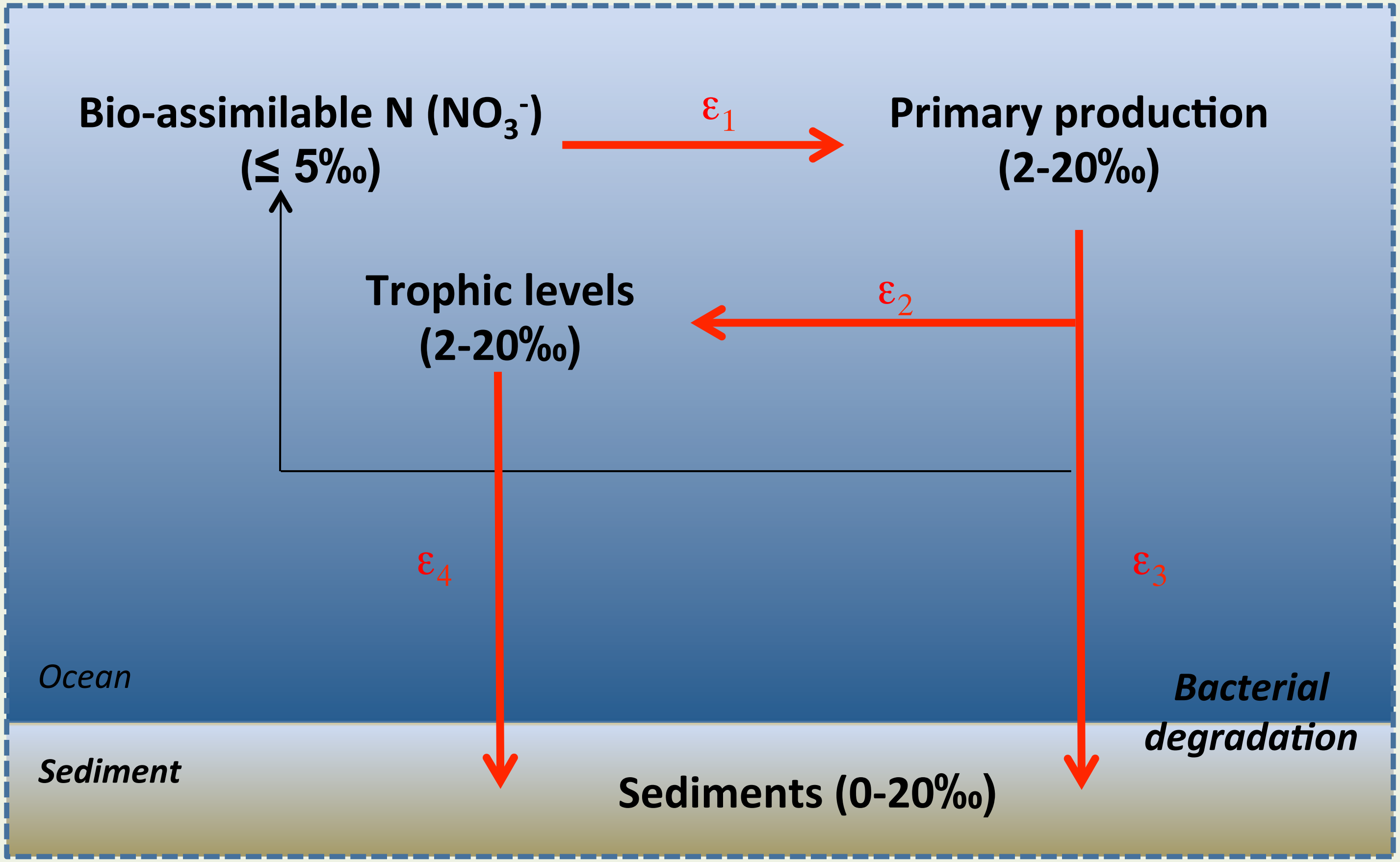


➡ **Simulations reveal large uncertainties linked to the lack of data regarding the regulating factors**

Nitrogen cycle



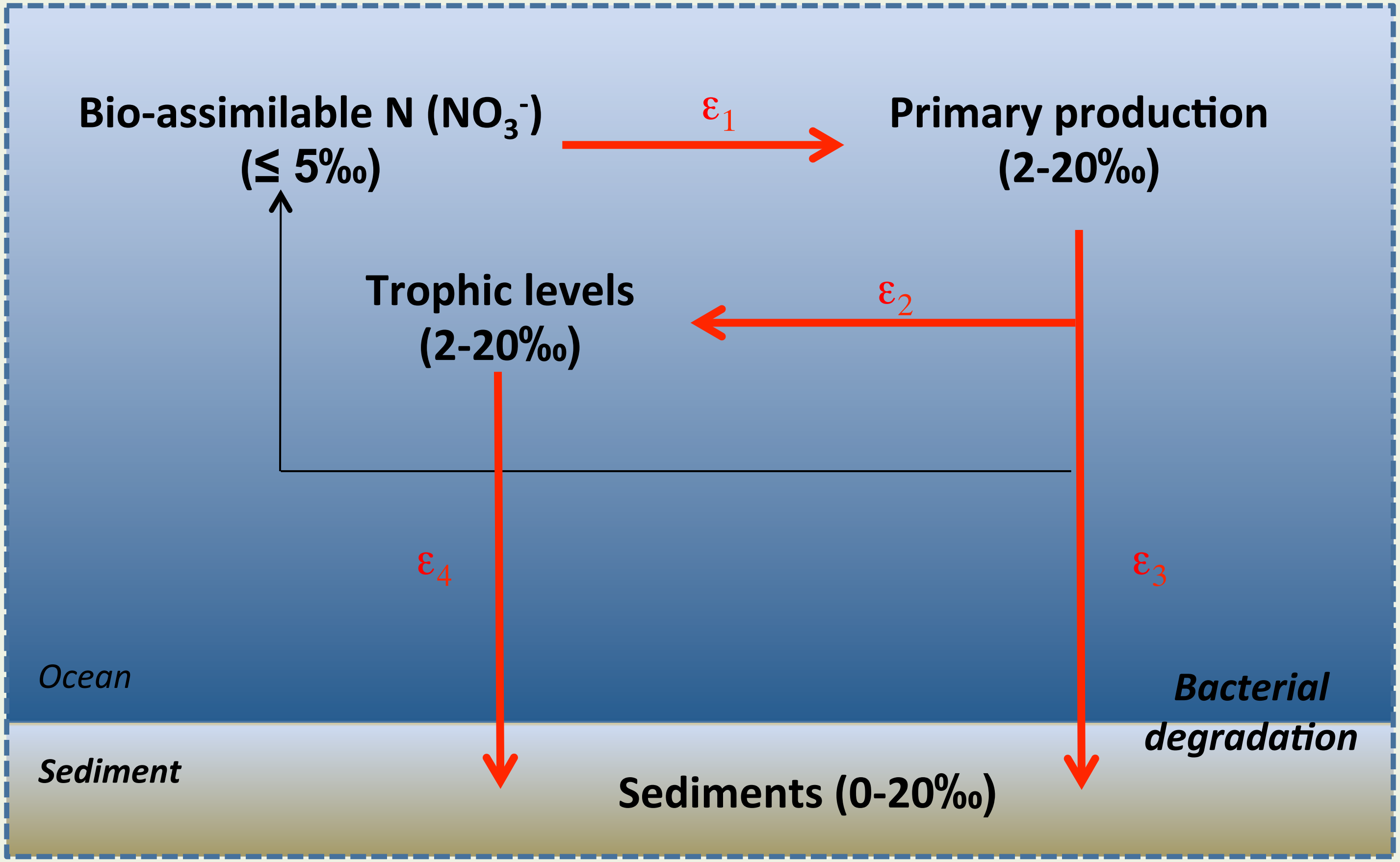
Nitrogen isotopes ($\delta^{15}N$)



ε : Isotopic fractionation

➡ **The $\delta^{15}N$ increases along the nutrient pool depletion by the primary production and decreases with enhanced nutrient supply**

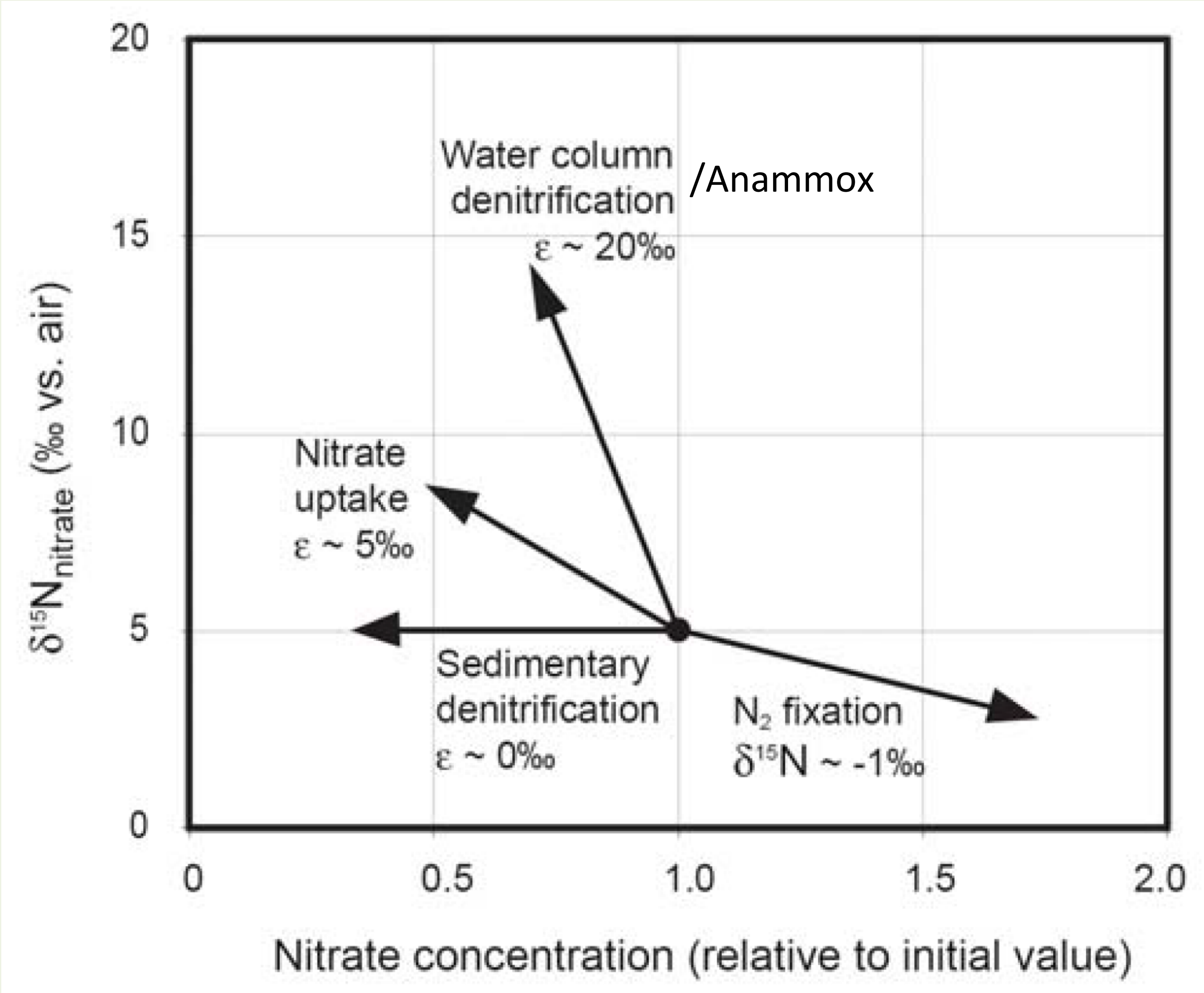
Nitrogen isotopes ($\delta^{15}N$)



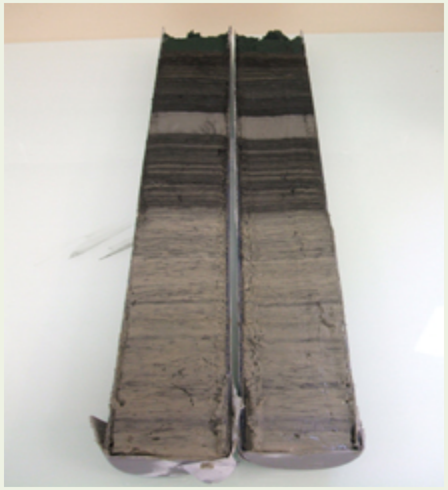
ε : Isotopic fractionation

➡ **Environmental conditions in which phytoplanckton grew up (modern and past)**

Nitrogen isotopes ($\delta^{15}N$)



The current proxies

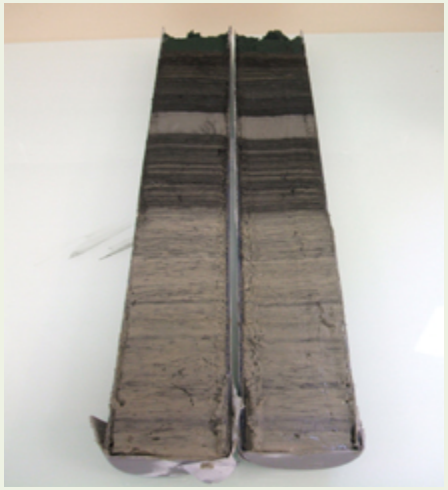


$\delta^{15}N$ of the bulk sediment

$\delta^{15}N$ of the organic matter preserved in the diatoms

$\delta^{15}N$ of the organic matter preserved in foraminifera

The current proxies



$\delta^{15}N$ of the bulk sediment

➡ **Advantages** : cheap, fast and applicable everywhere

➡ **Disadvantages** : not specific, strongly affected by degradation, biases

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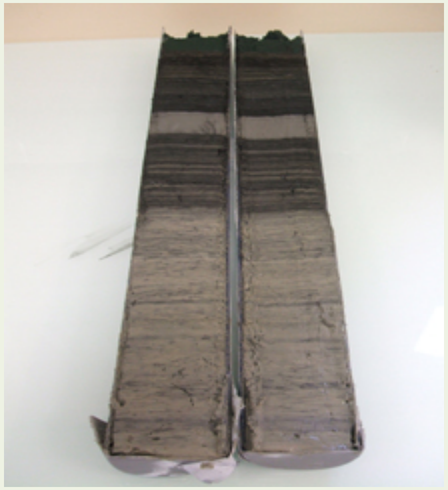

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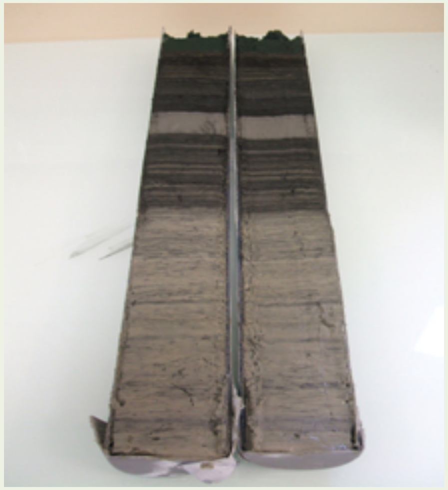
➡ **Advantages** : more specific and less degradated

➡ **Disadvantages** : inter-species differences, mix of organic compounds, slow and complex, requires a lot

$\delta^{15}N$ **of the organic matter preserved in foraminifera**

The current proxies



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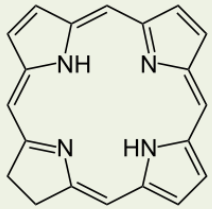
➡ **Advantages** : mono-specific and less degradated

➡ **Disadvantages** : mix of organic compounds, slow and complex, requires a lot

$\delta^{15}N$ on the chlorins

➡ **Advantages** : specific of phytoplankton, resistant to degradation, applicable everywhere



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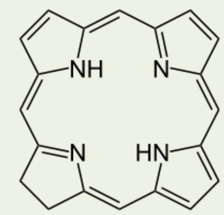
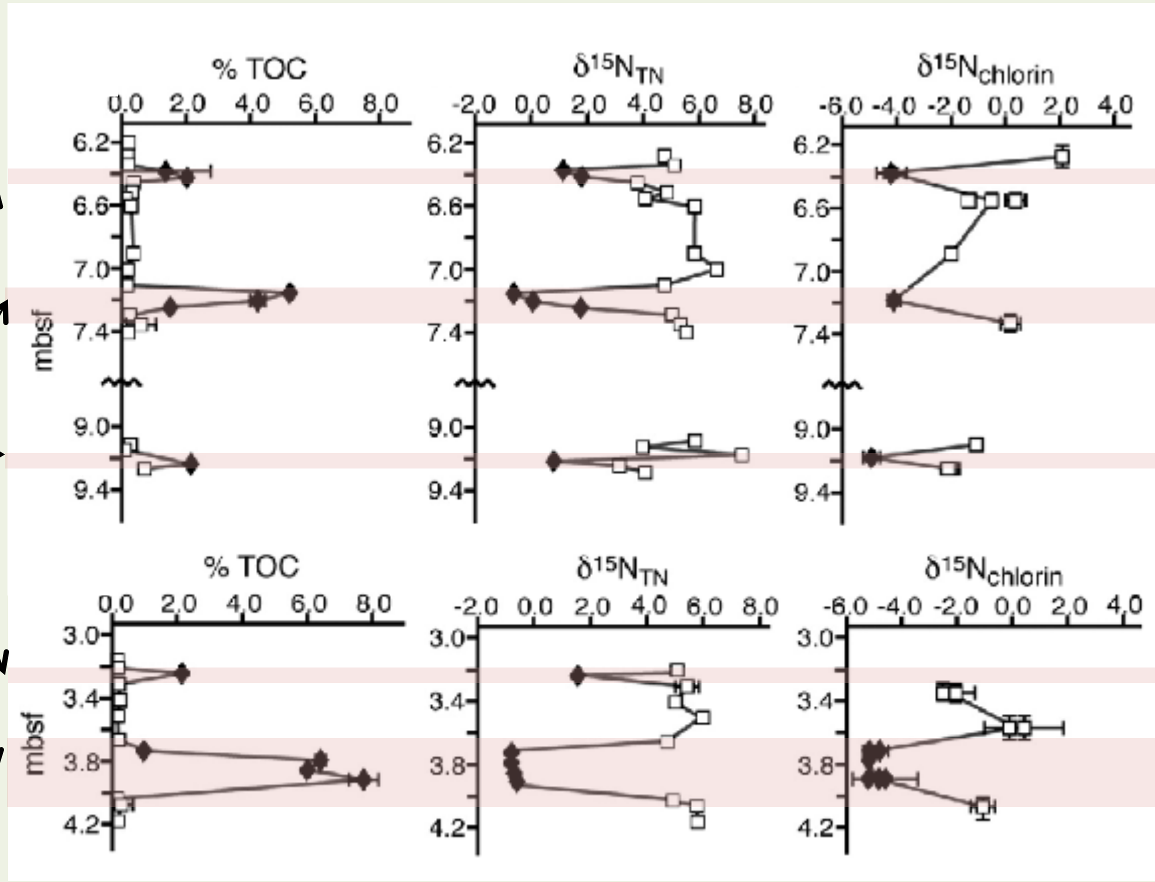


Sapropel events



Higgins et al., 2010

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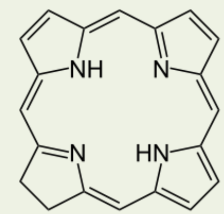
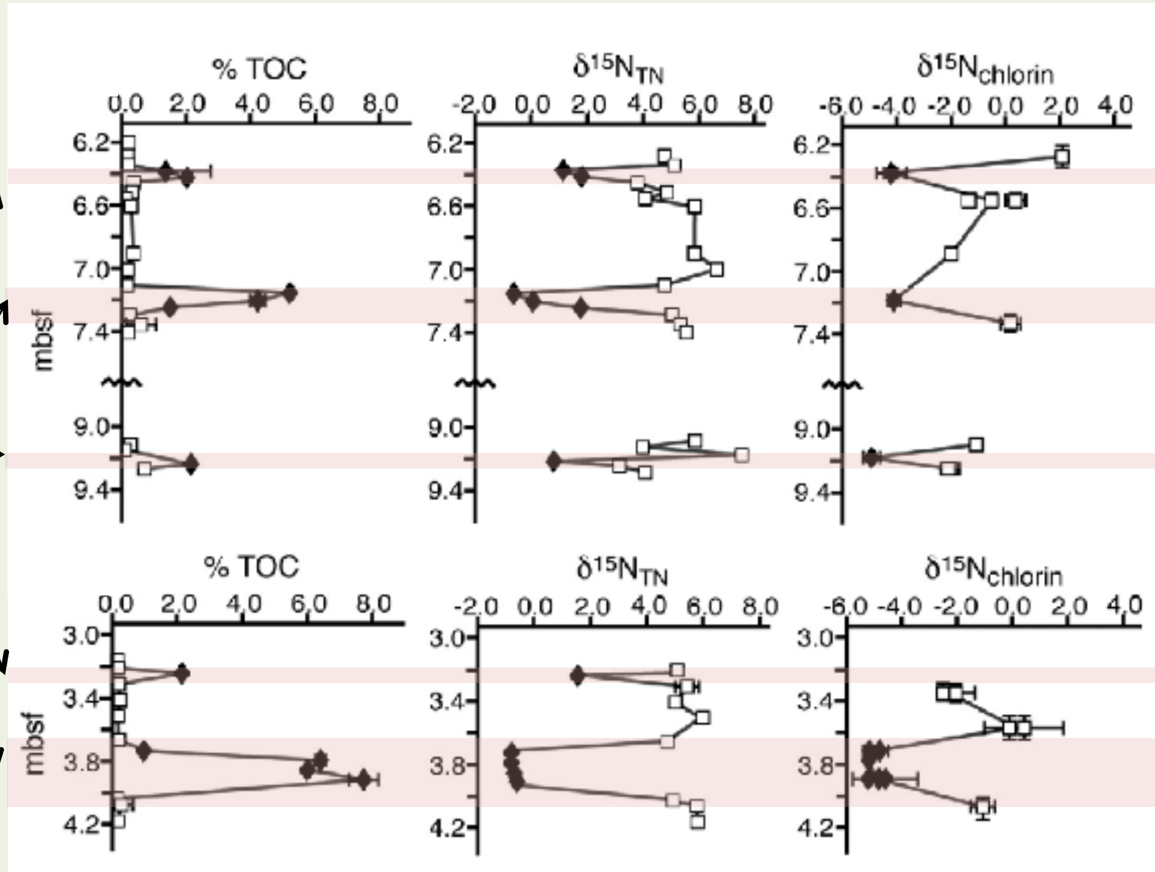


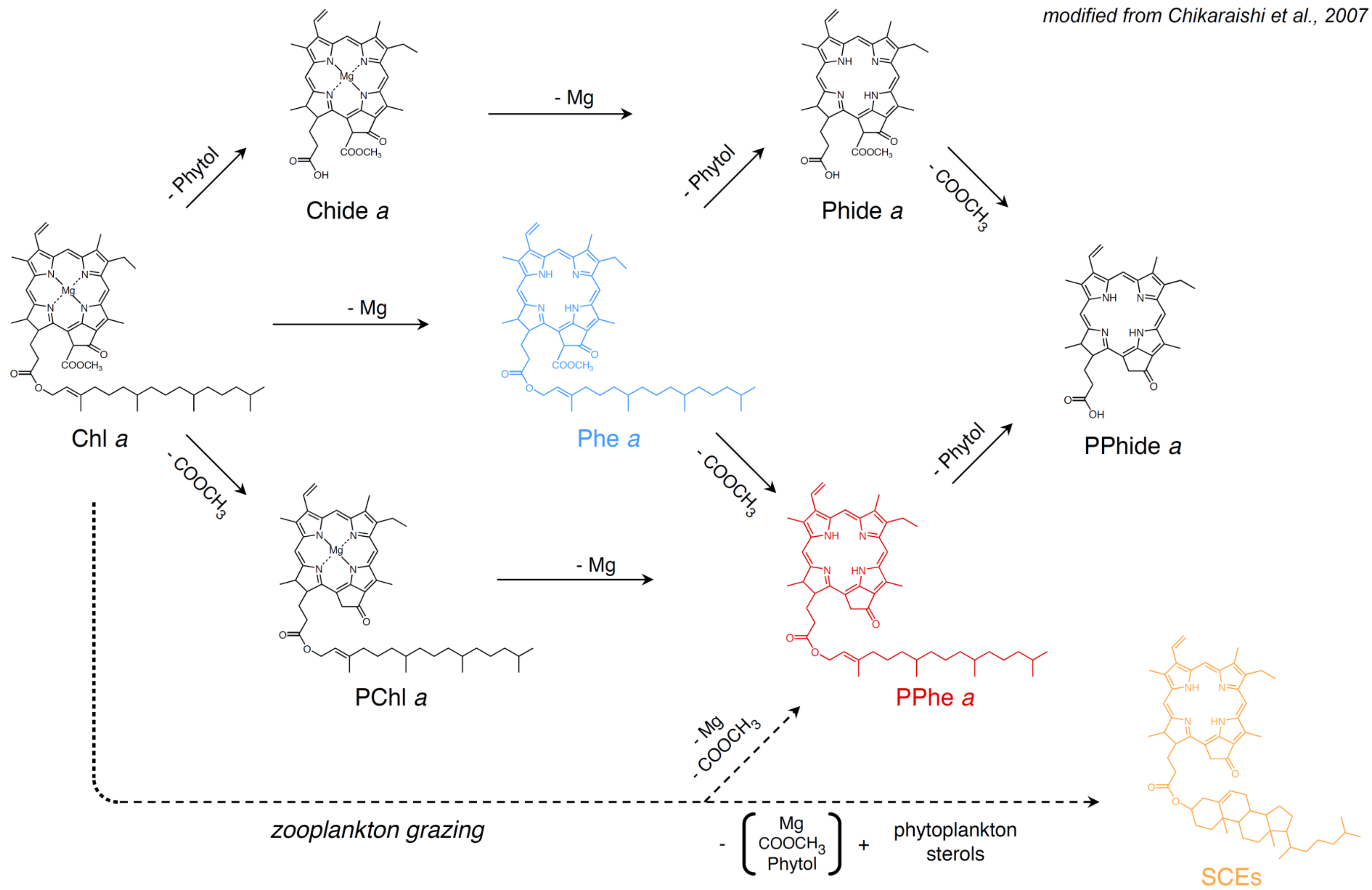
Sapropel events



Higgins et al., 2010

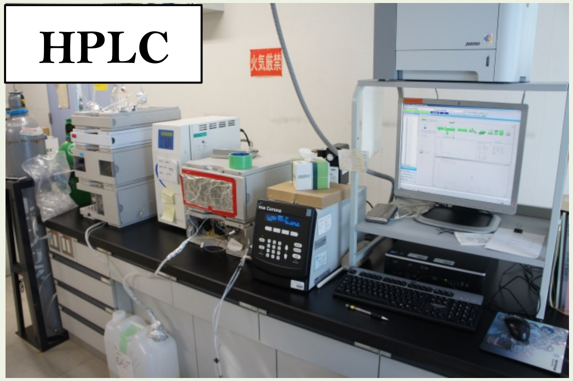
➡ **Disadvantages** : still includes several organic compounds (pigments)

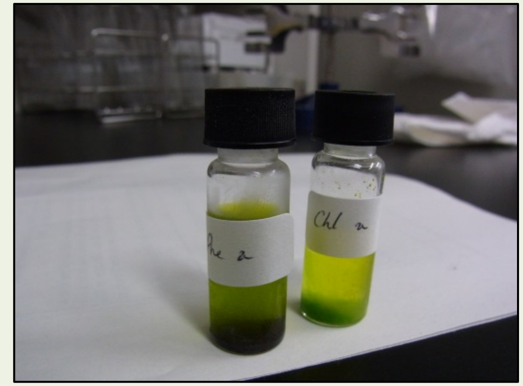
$\delta^{15}N$ on chlorophyll *a* and derivatives

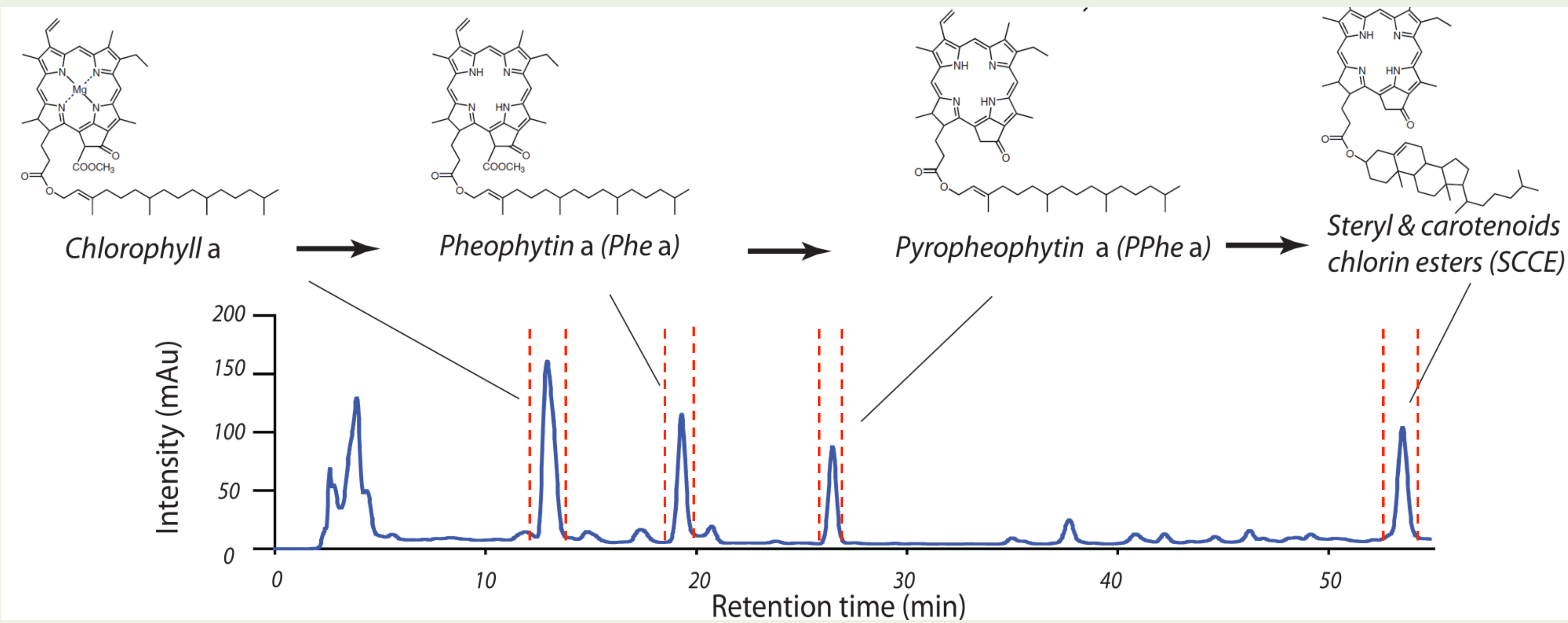


Pathways for pheopigment formation. Abbreviations: chlorophyll a (Chl a), chlorophyllide a (Chide a), pheophorbide a (Phide a), pheophytin a (Phe a), pyrochlorophyll a (PChl a), pyropheophorbide a (PPhide a), pyropheophytin a (PPhe a), steryl chlorin esters (SCEs).

Analytical development







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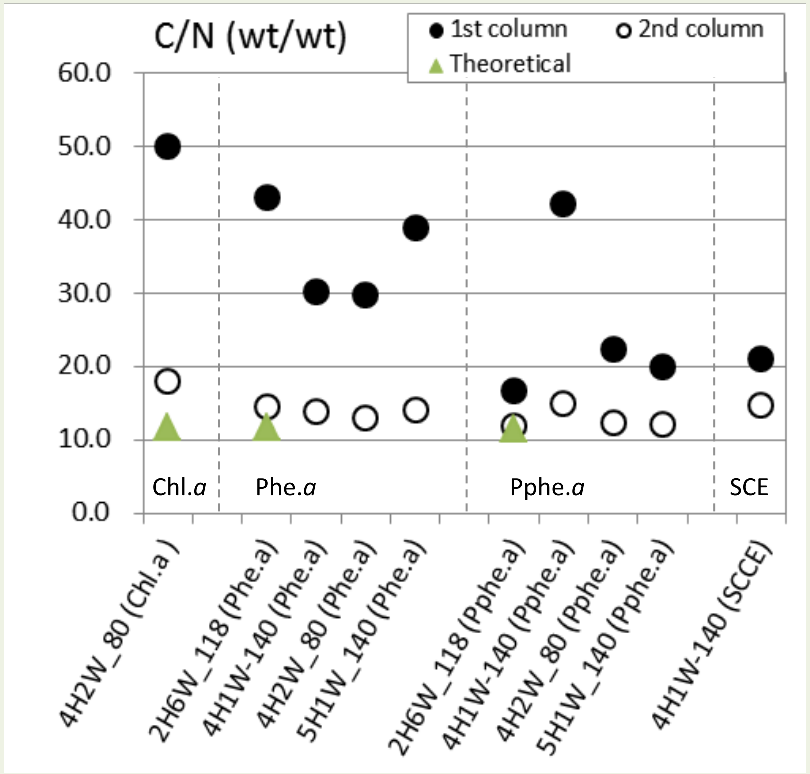
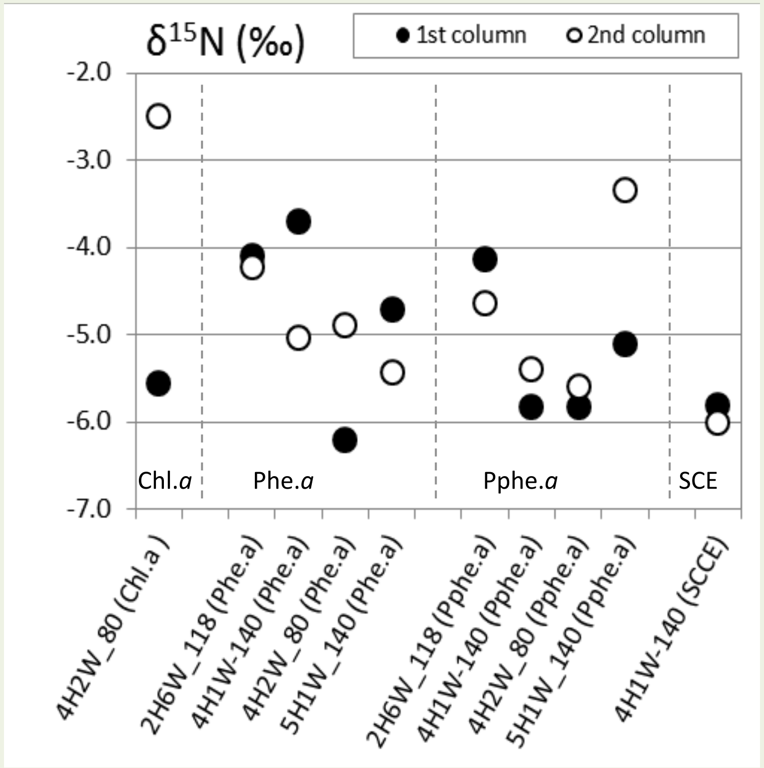




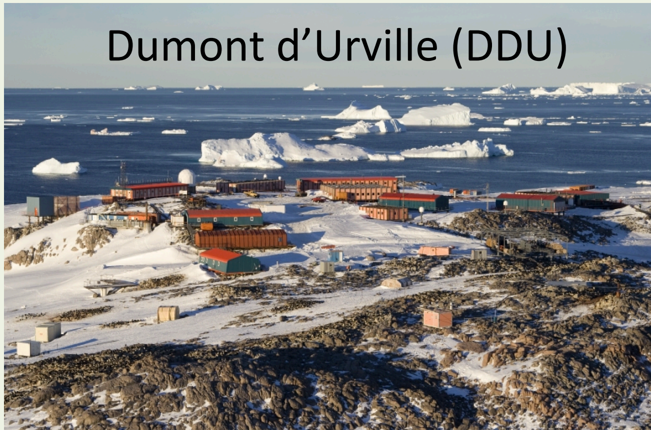
Formule chlorophylle *a* : $C_{55}H_{72}MgN_4O_5$

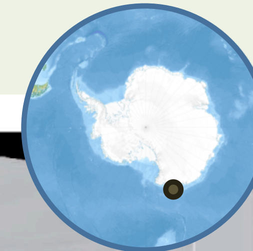
C/N = 13.75

Etourneau et al., in prep

Study Sites

IODP U1357





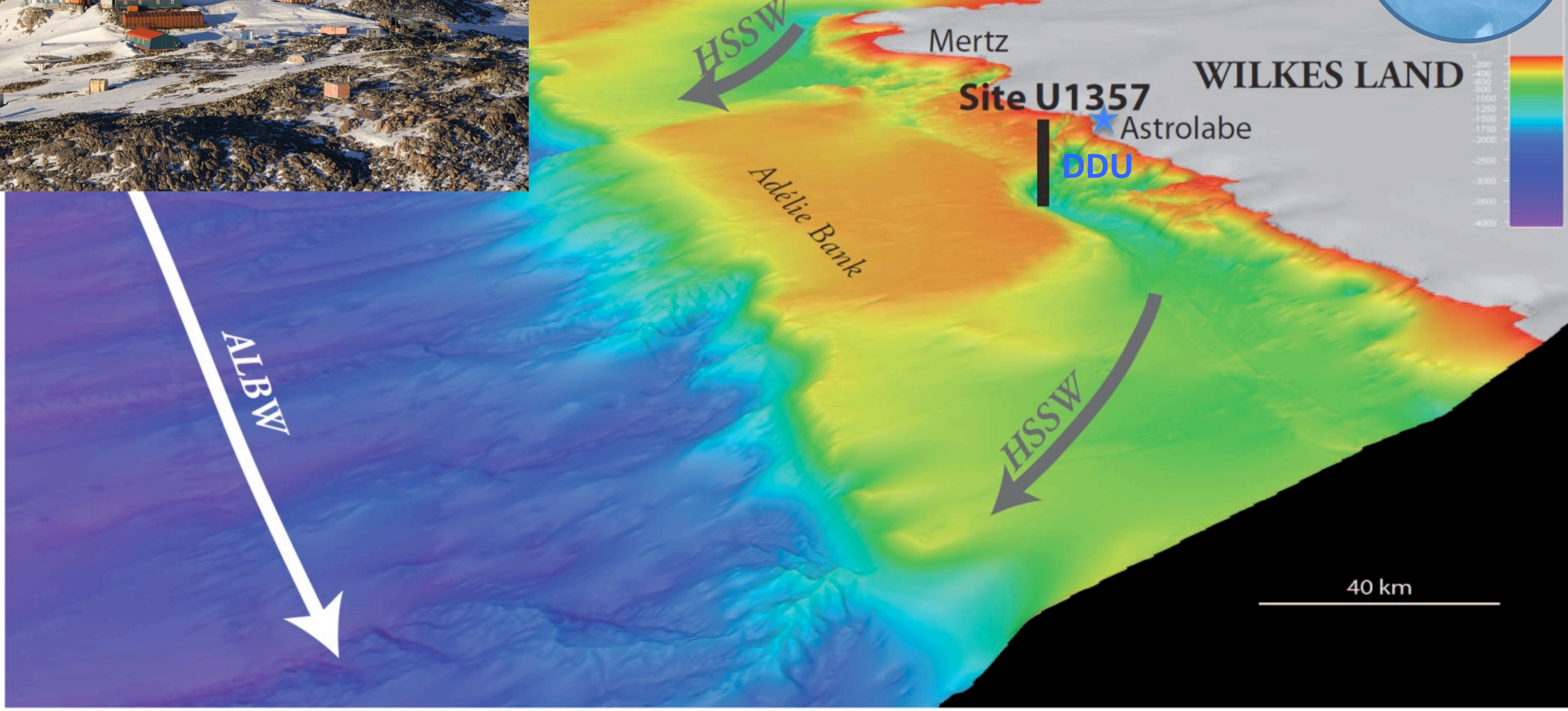
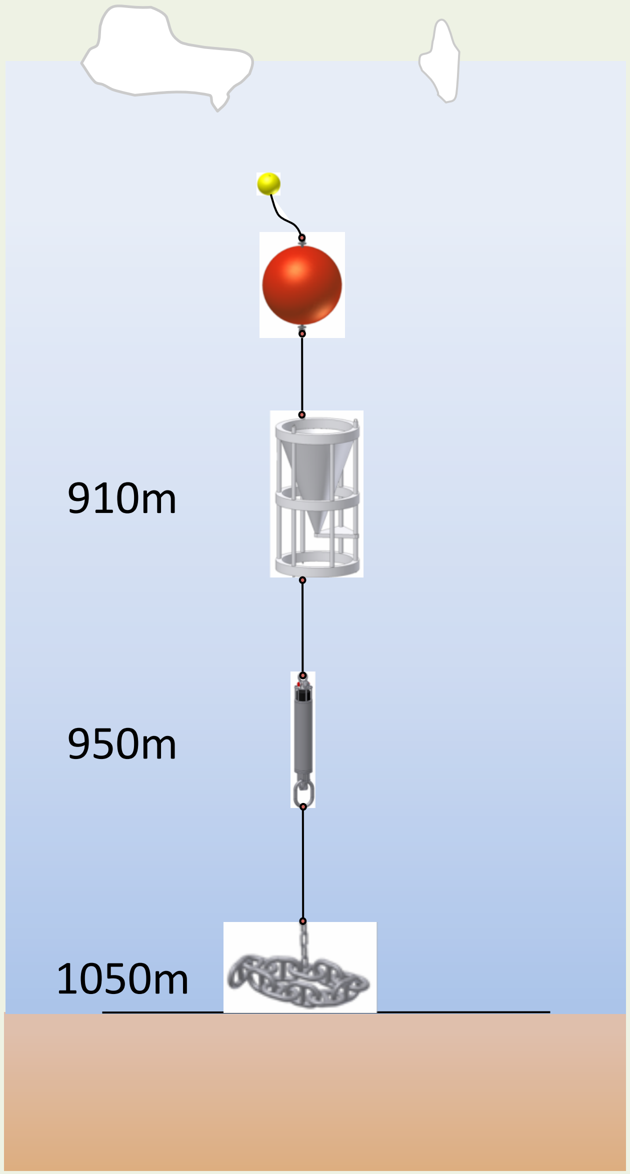


Figure 1. The Adélie Basin off Wilkes Land, East Antarctica. The location of the ODP Site U1357 hole B (66°24.79'S, 140°25.57'E, 1017m water depth) is represented by vertical bars. Oceanic currents (arrows): ALBW, Adélie Land Bottom Water, HSSW, High Salinity Shelf Water.

1st application – Adélie Basin (last 2,000 yrs BP)



Phytoplankton net:

δ^{15}N Phe *a* =-1.9‰
δ^{15}N bulk = 3.4‰ → $\Delta\delta^{15}N_{Phe\ a\text{-}bulk}$ = 5.3‰

Sediment trap:

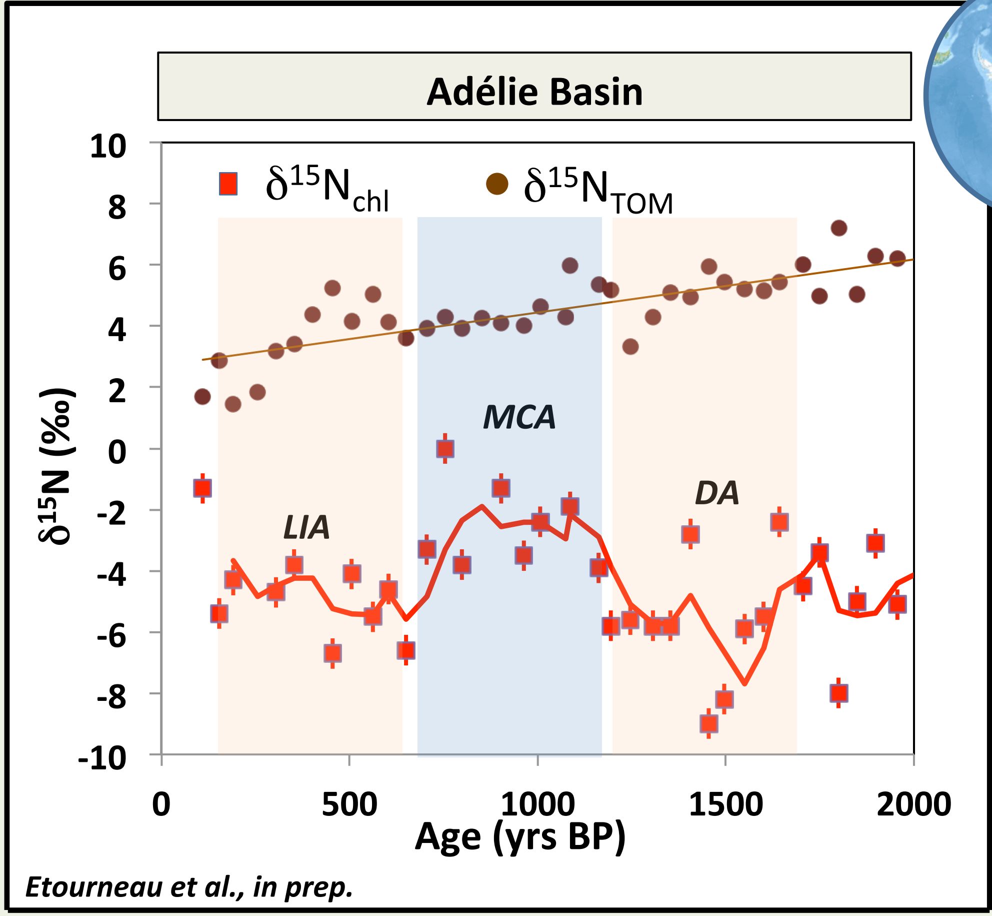
δ^{15}N Pphe *a* = -3.1‰
δ^{15}N bulk = 2.5‰ → $\Delta\delta^{15}N_{Pphe\ a\text{-}bulk}$ = 5.6‰

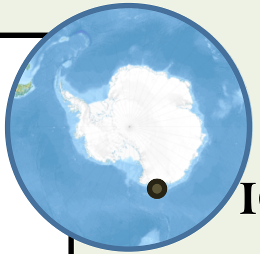
Interface sediment:

δ^{15}N Phe *a* = -5.2‰
δ^{15}N Pphe *a* = -4.7‰ → $\Delta\delta^{15}N_{Phe\ a\text{-}bulk}$ = 8‰, $\Delta\delta^{15}N_{Pphe\ a\text{-}bulk}$ = 7.5‰
δ^{15}N bulk = 2.8‰

Etourneau et al., en prep.

1st application – Adélie Basin (last 2,000 yrs BP)

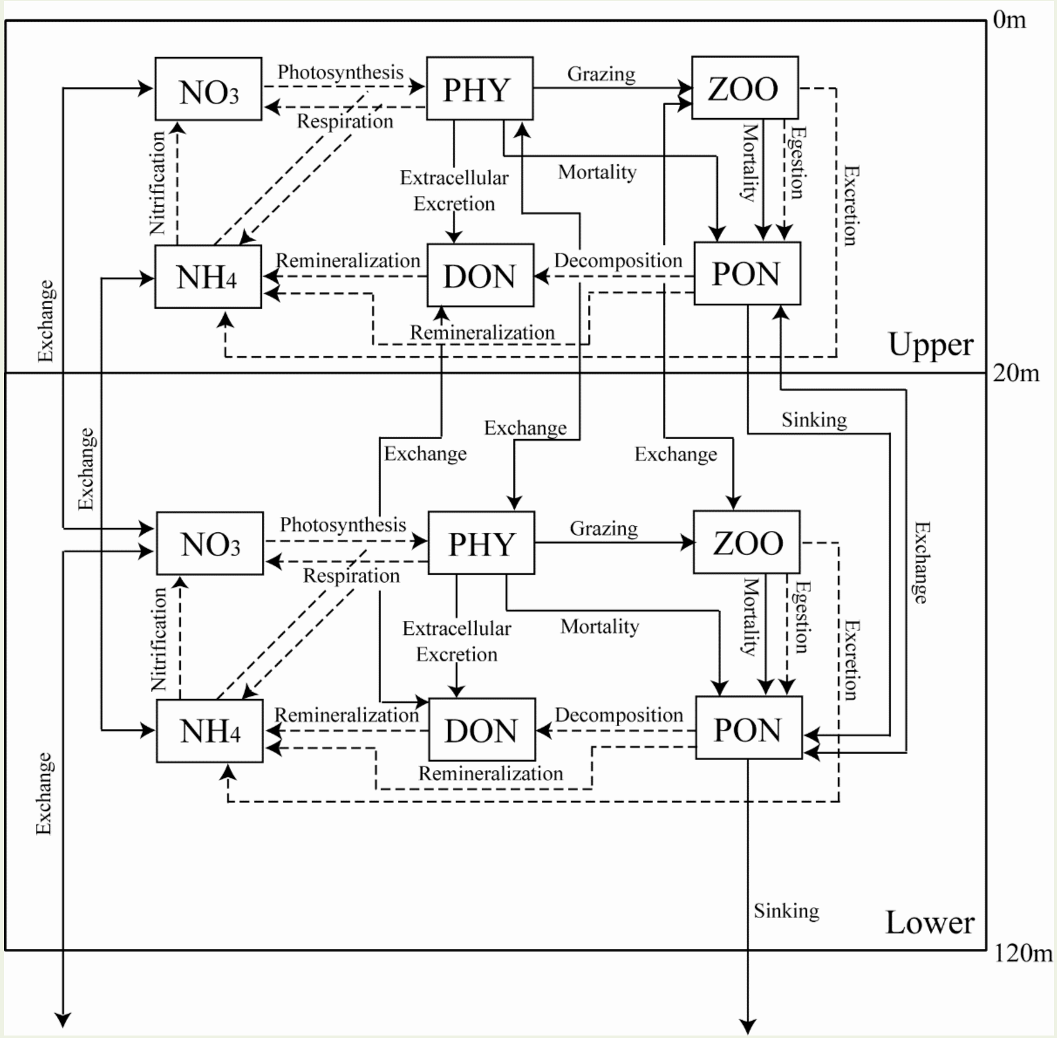




LIA: Little Ice age
MCA : Medieval climatic anomaly
DA : Dark ages

- **Isotopic composition of pigments is not influenced by diagenesis effects**
- **Pigments isotopic composition records the biological response to global climate changes (e.g. LIA, MCA)**

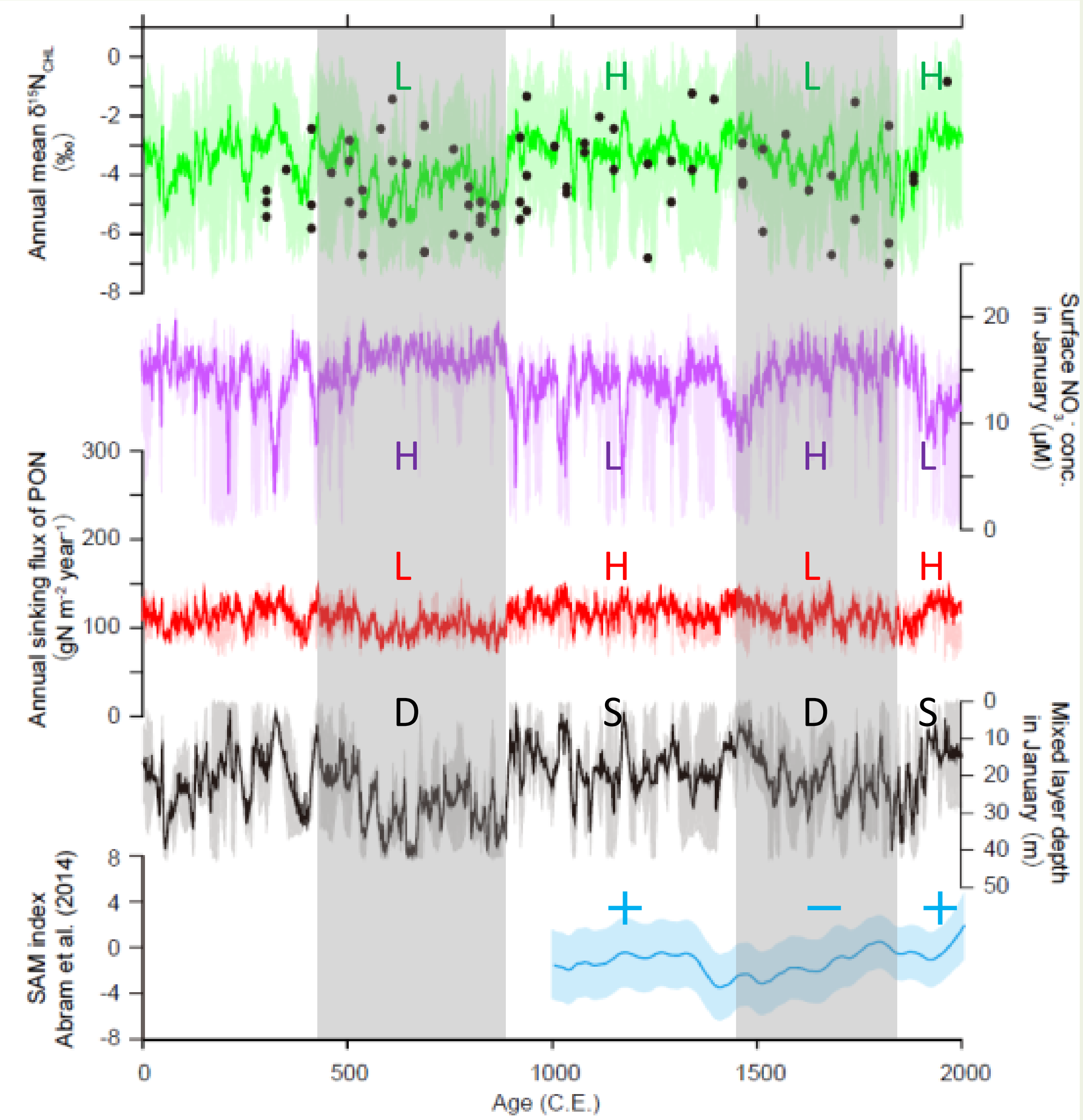
Nitrogen isotope model



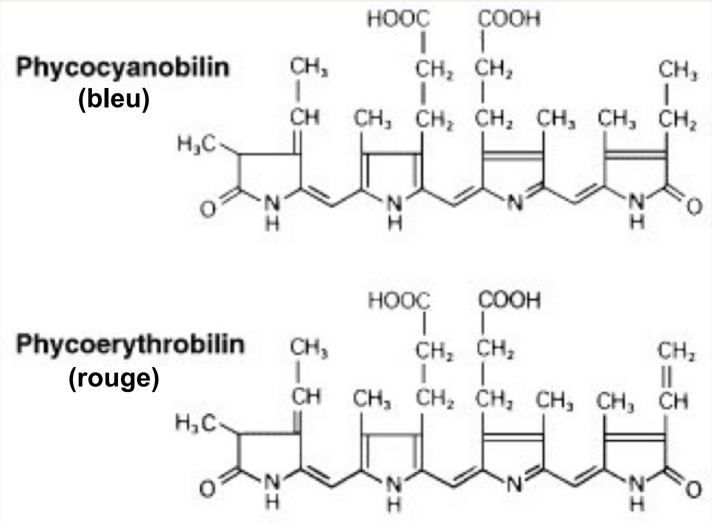
Yoshikawa et al., 2005

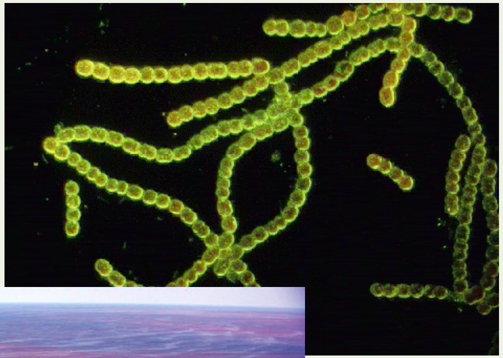
Implications

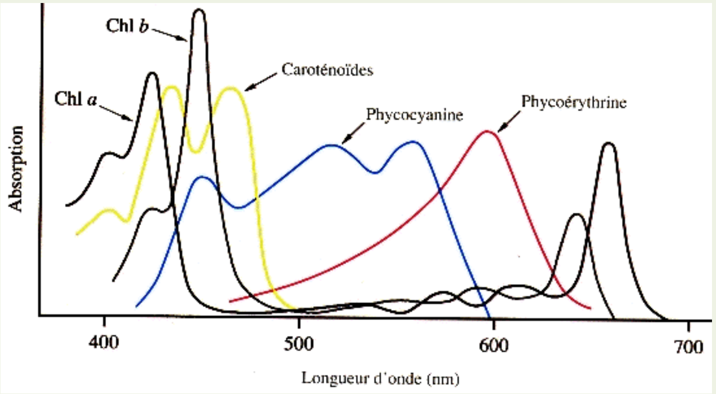
The transition of $\delta^{15}N_{Chl}$ is related to SAM index and NH temperature.



Future development







N fixation – nutrient cycles

- **Advantages**: specific to red algae and cynaboacterias, resistant to degradation
- **Disadvantages**: ?

Conclusions and perspectives

- **A new promising tool:**

➡ Applications in all aquatic environments (oceans, lakes…)

➡ Spanning all period of times (modern, past (up to million years)) (nucleus containing N resistant to degradation)

➡ Reflect environmental conditions in which the organic matter has been formed (no alteration of the isotopic signal)

- **A great potential for future investigations:**

➡ Eutrophication, biogeochemical cycles

➡ Paleo-environmental reconstructions (e.g. N fixation vs denitrification at global scale)

➡ Dating, hydrological cycles and pCO_2 (^{14}C, δD and $\delta^{13}C$)

➡ Of interest for Biologist, Ecologist, Paleoclimatologist, Paleoceanography, Geologist & Petroleum research