Comparisons of bulk $\delta^{15}N$ with diatom-bound & chlorophyll $\delta^{15}N$

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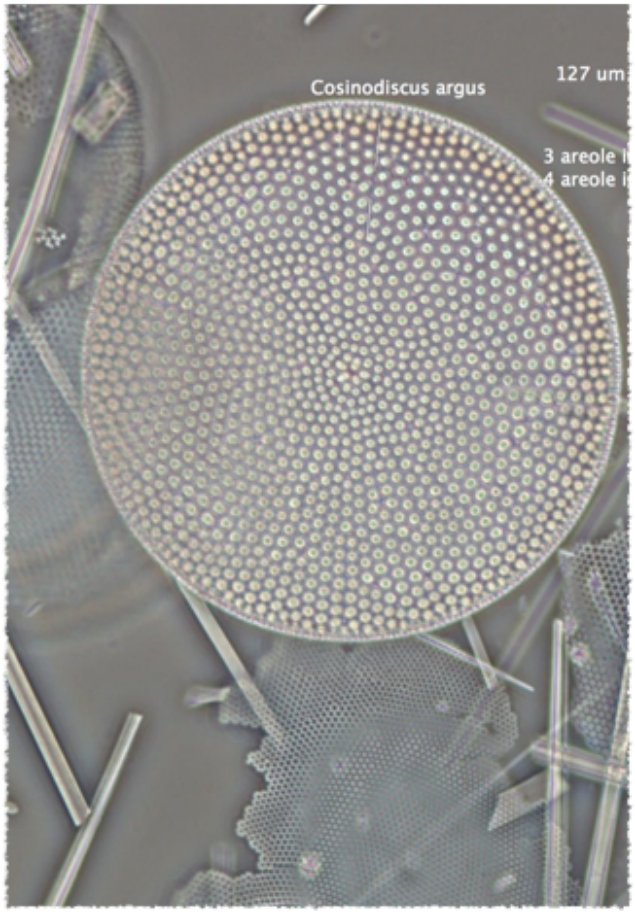
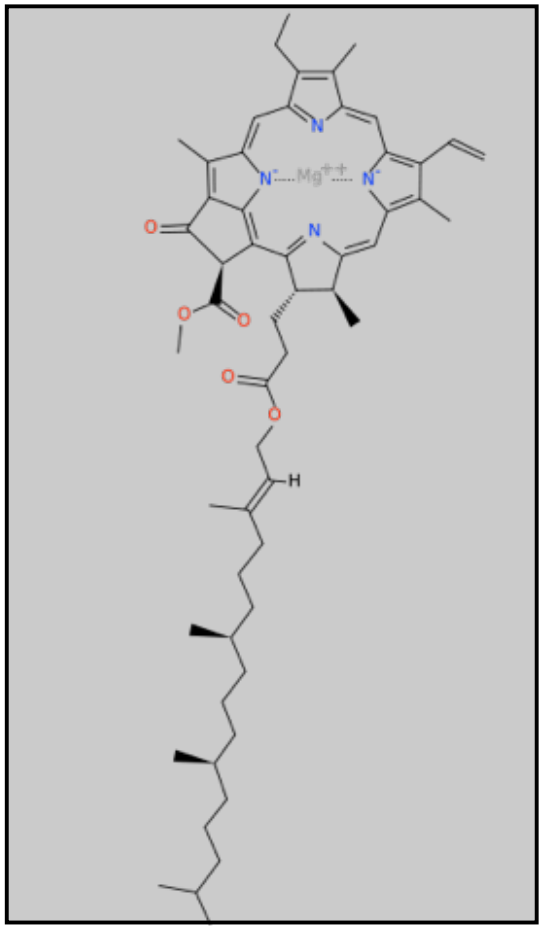
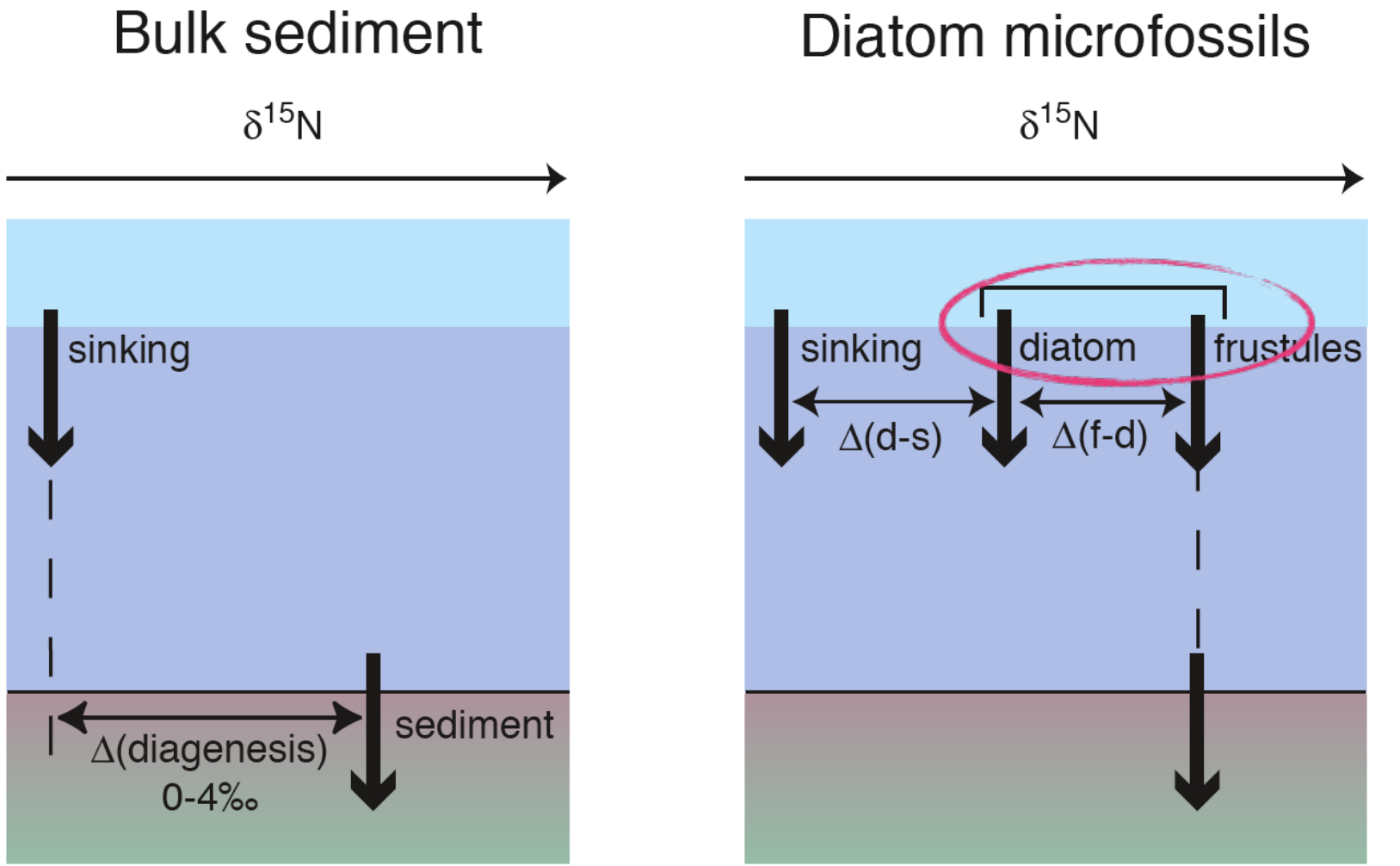
Talk Goals





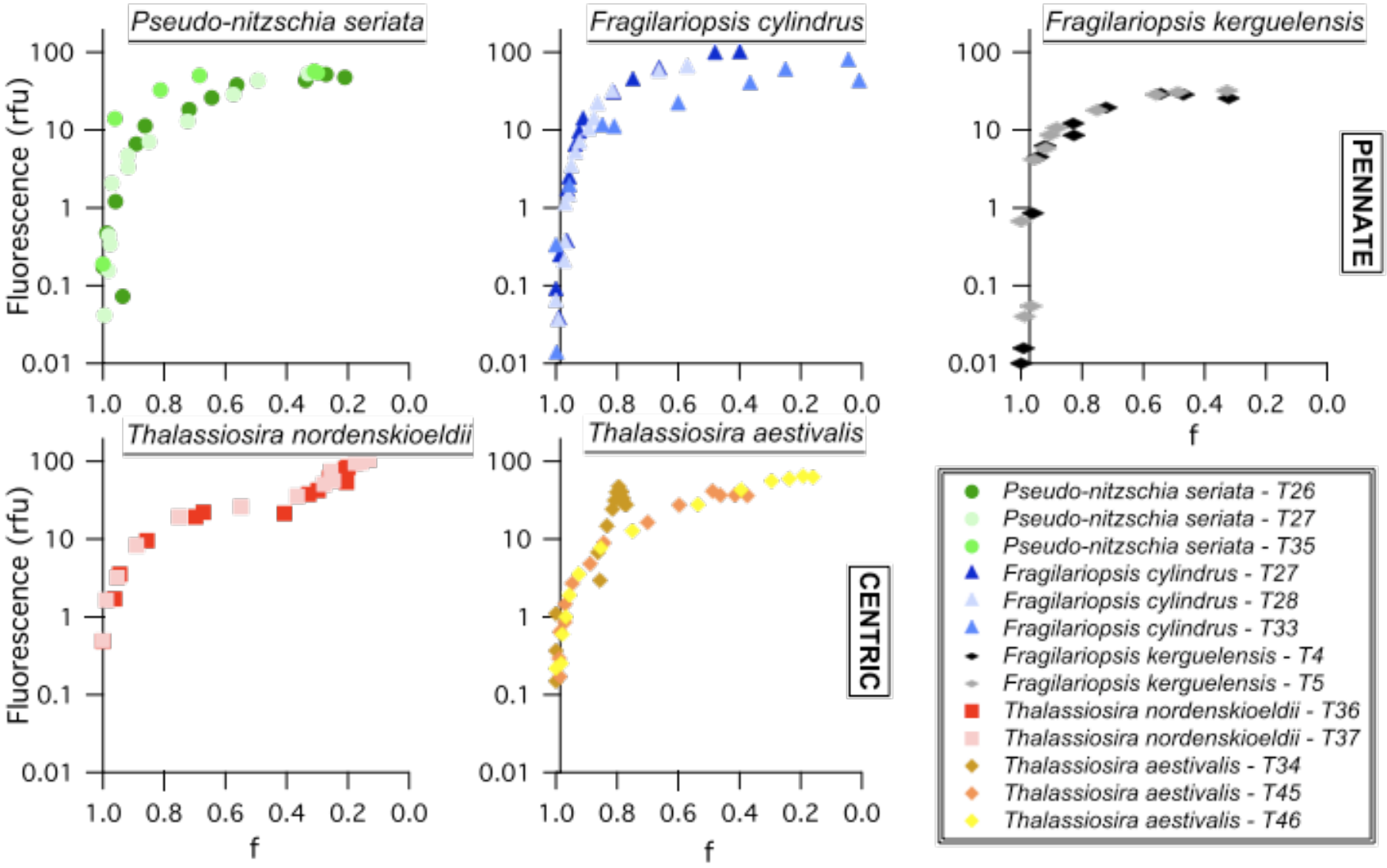
Culture & Sedimentary Data Comparisons of Diatom-bound and chlorophyll $\delta^{15}N$

Bulk Vs diatom-bound N isotopes

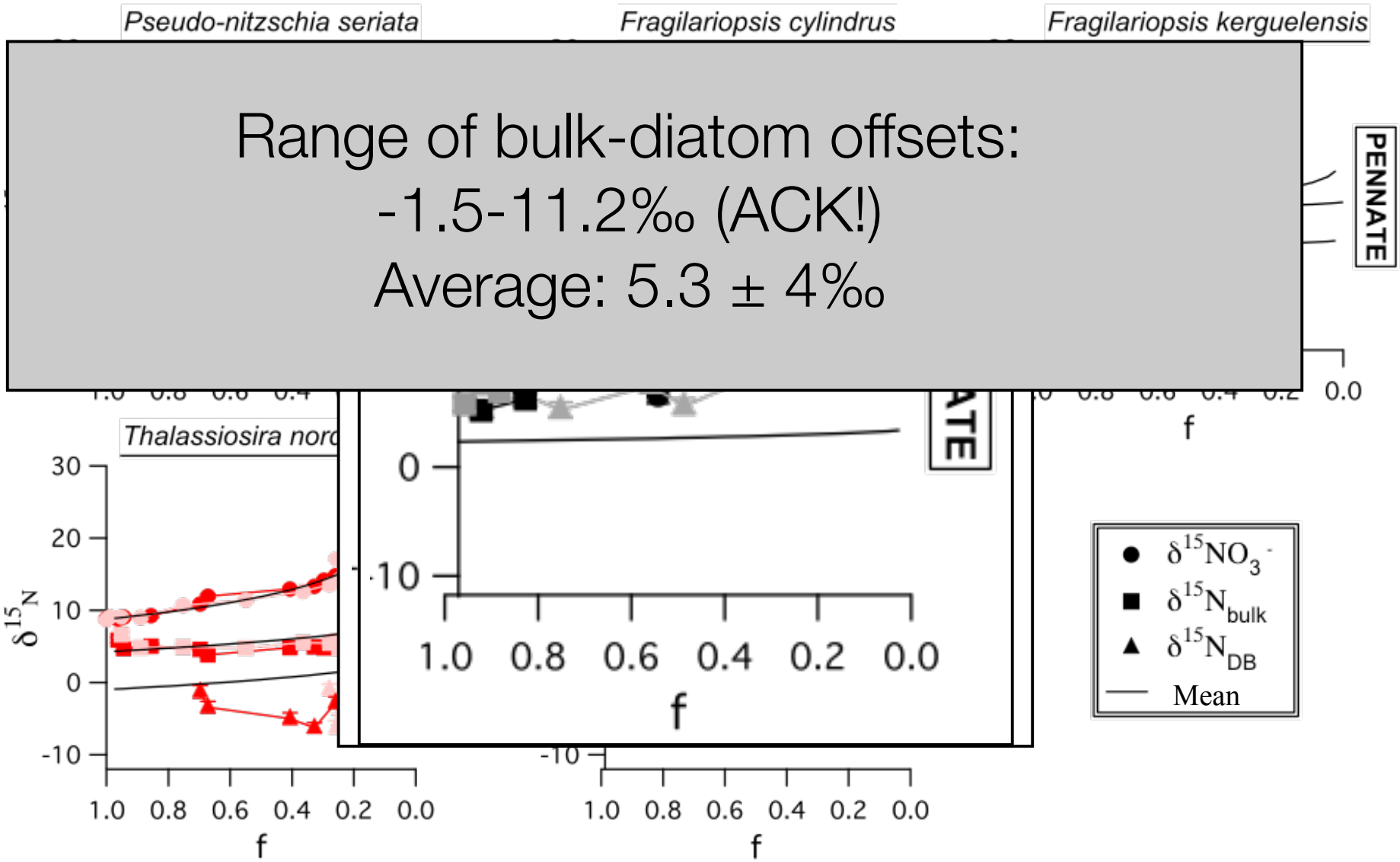


(Galbraith et al., 2008)

We Grew 5 Diatom species in 20L Batch cultures



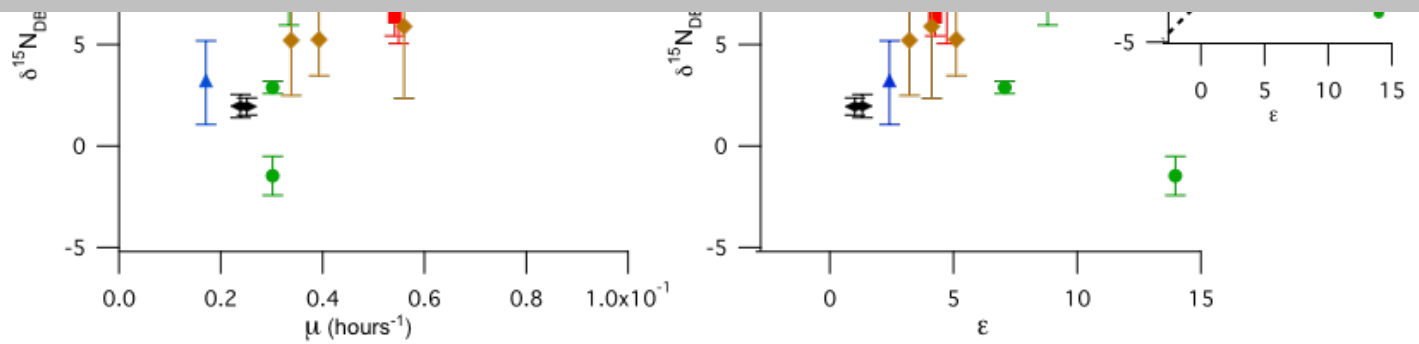
Nitrate, Biomass, and Frustule comparison



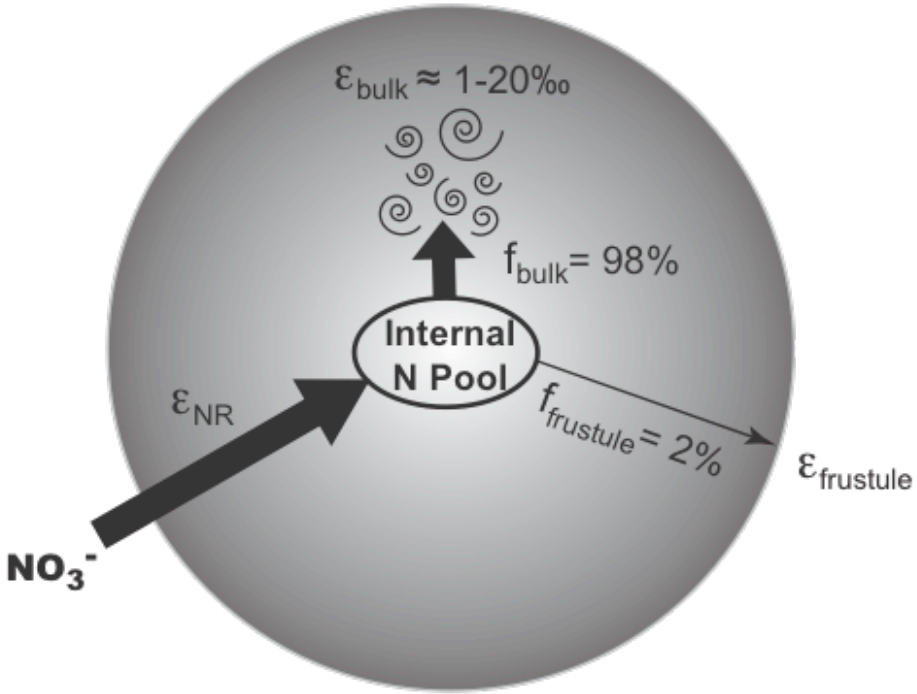
Range of bulk-diatom offsets:
-1.5-11.2‰ (ACK!)
Average: 5.3 ± 4‰

What controls frustule-biomass offset?

variability associated with: 1). species distinctions, 2). fractionation during nitrate assimilation, and 3). cell size



What might cause this?



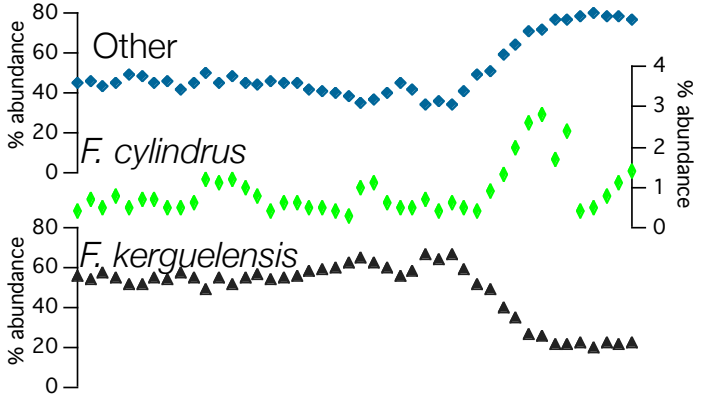
$$\delta^{15}N_{IP} = (\delta^{15}NO_3^- - \varepsilon_{NR}) + (\varepsilon_{bulk} * f_{bulk}) + (\varepsilon_{frustule} * f_{frustule})$$

assume: $\delta^{15}NO_3^- - \varepsilon_{NR} = 0‰$

$$\varepsilon_{frustule} = \frac{\delta^{15}N_{IP} - (\varepsilon_{bulk} * f_{bulk})}{f_{frustule}}$$

Let's try it out:
Bulk sediment $\delta^{15}N$ v. diatom-bound $\delta^{15}N$

Using assemblage data and culture based bulk-diatom offsets, we calculated a diatom-bound offset for core TN057-13PC4:



$$=-(\varepsilon_{f_kerg} * f_{kerg}) + \varepsilon_{f_cyl} * f_{cyl} + \varepsilon_{f_rest} * f_{rest})$$

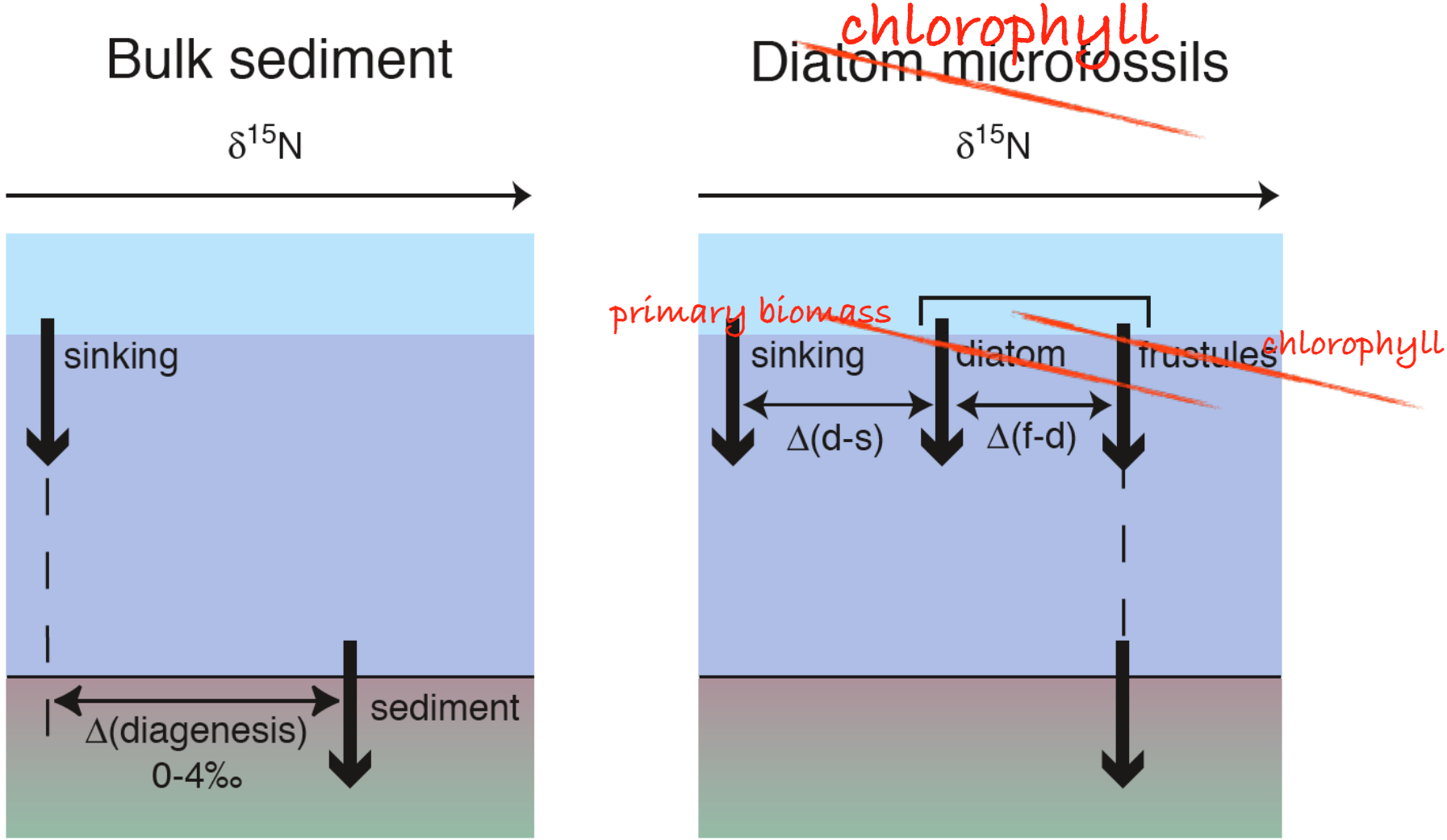
S. Nielsen, PhD thesis; Horn et al., in prep

Diatom-bound take home

- Species specific diatom-biomass offsets
  - Average offset is 5‰; frustule < biomass
  - Size matters

- Large environmental changes may amplify/negate nutrient consumption signal as a result of species variability.

Bulk Vs diatom-bound N isotopes

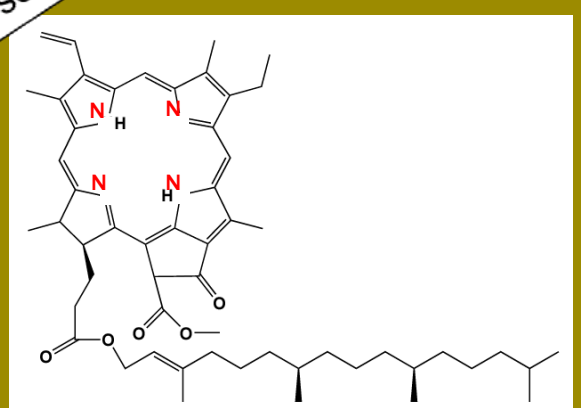


(Galbraith et al., 2008)

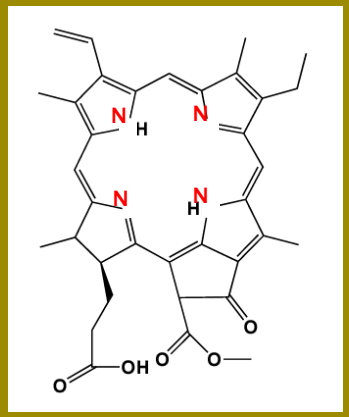
Chlorophyll degradation products: Tracers of Surface Water $\delta^{15}N$

Young sediments

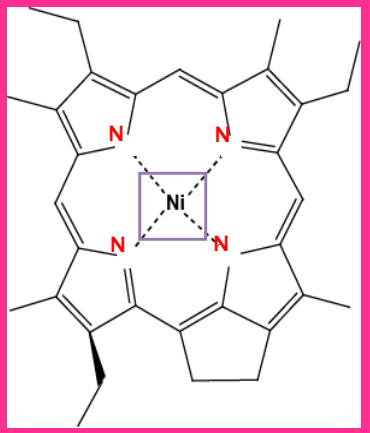
Ancient rocks



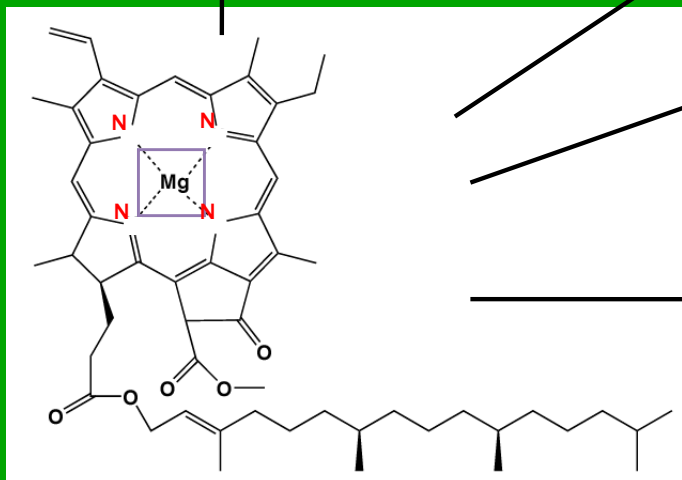
Phaeophytin a



Phaeophorbide a

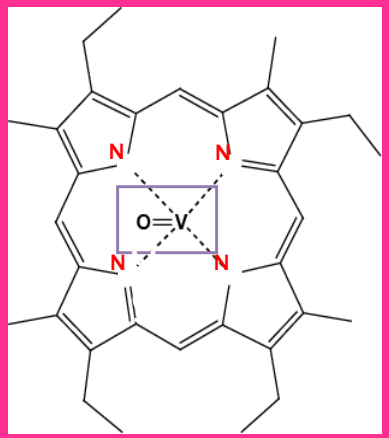


Ni Deoxophylloerythro-etioporphyrin (DPEP)



Chlorophyll a

Etc…



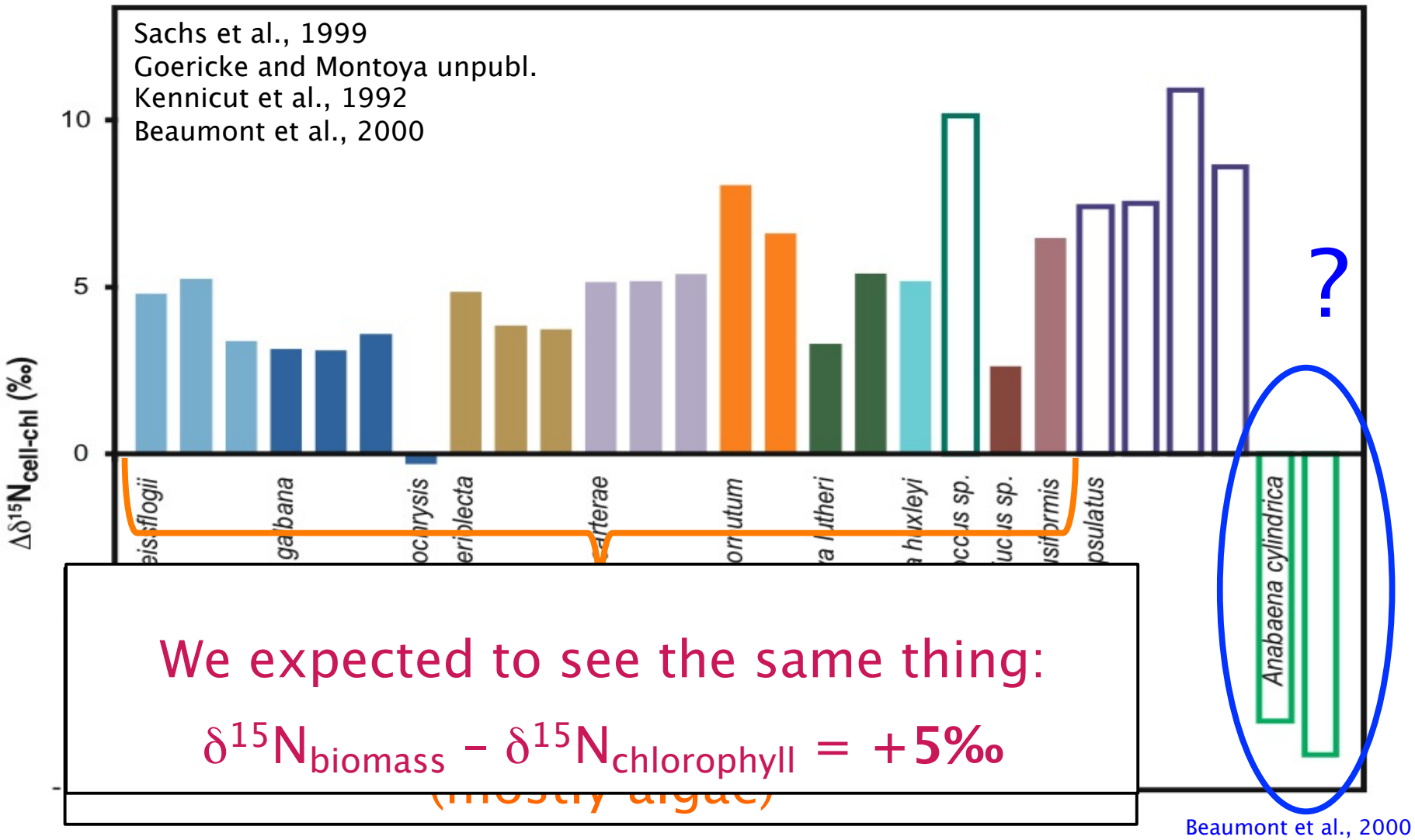
VO Etioporphyrin

Conditions Tested

- Taxonomy
  - Cyanobacteria
    - N_2 fixing/not
    - filamentous/unicellular
    - Prochlorphytes
  - Algae
    - primary red
    - primary green
  - Anoxygenic photosynthetic bacteria
    - purple sulfur (environmental; γ-proteobacteria)
    - purple non-sulfur (culture; α-proteobacteria)
  - Microbial mats
    - Cyanobacteria mats from Yellowstone – attempted

- Light
  - Continuous vs. diel
- Nitrogen source
  - N_2, NO_3^-, NH_4^+

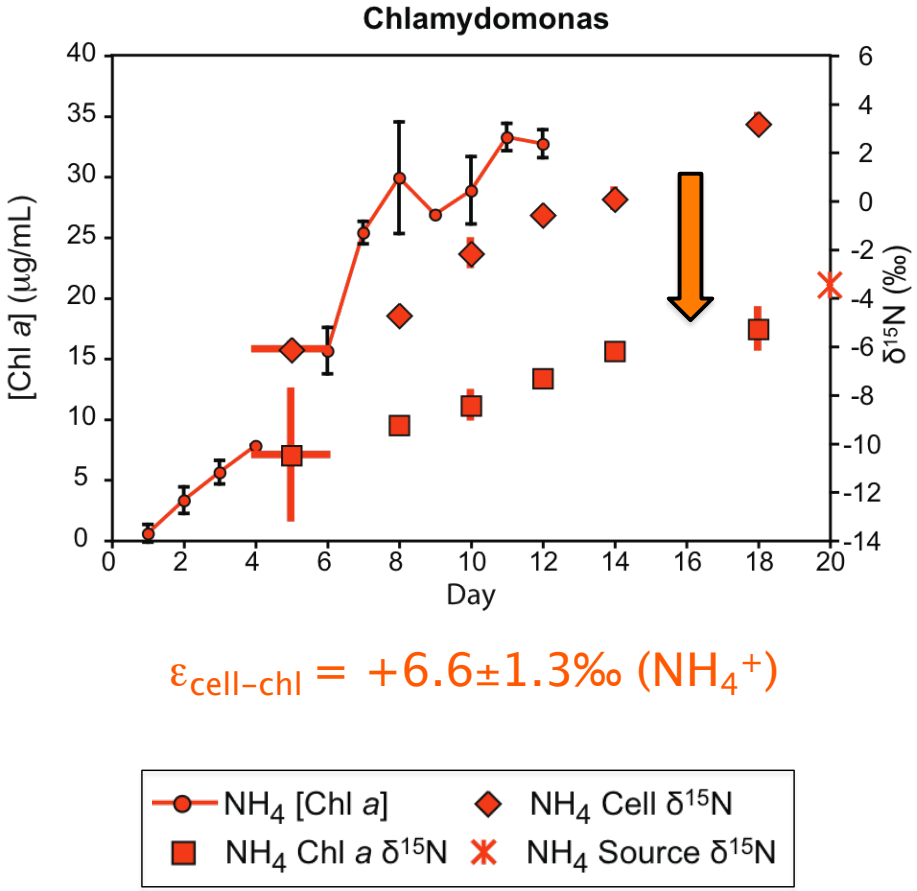
Data From Earlier Literature



Beaumont et al., 2000

Initial data: easy (to interpret) stuff

Chlamydomonas reinhardtii
Chlorophyte (primary green algae)
on NH_4^+, continuous light



$\varepsilon_{cell-chl}$ = +6.6±1.3‰ (NH_4^+)

Amoebobacter purpureus
Purple sulfur
γ-Proteobacteria
Environmental sample
on NH_4^+(assumed), diel light

$\varepsilon_{cell-chl}$ = +5.8±0.6‰ (NH_4^+)

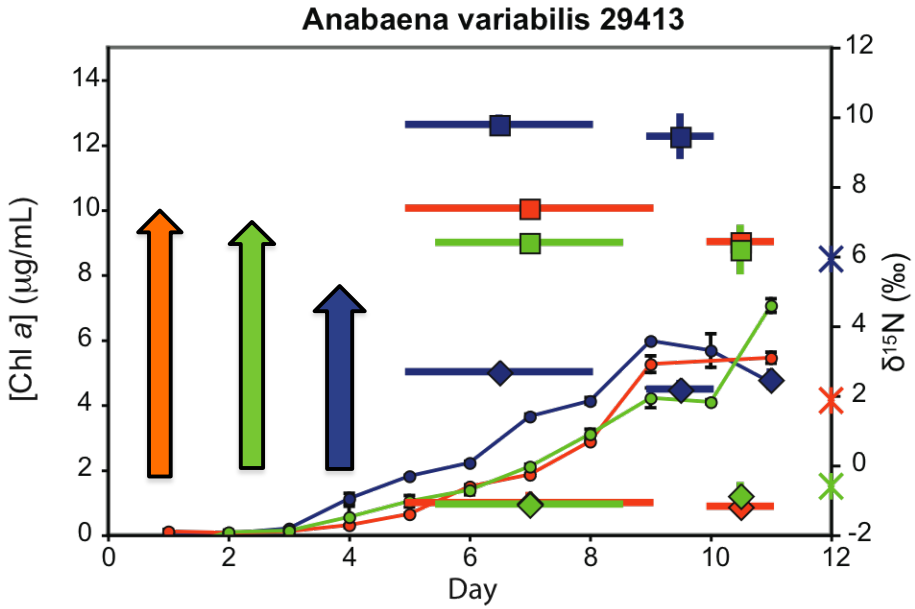
Mahoney Lake
BC, Canada

Rhodopseudomonas palustris
Purple nonsulfur
α-Proteobacteria
on NH_4^+, continuous light

$\varepsilon_{cell-chl}$ = +11.7±3.5‰ (NH_4^+)

The pesky Cyanobacteria:

Anabaena variabilis
Cyanobacteria (Nostocales)
Heterocystous filaments
on N_2, NH_4^+, NO_3^-, continuous light

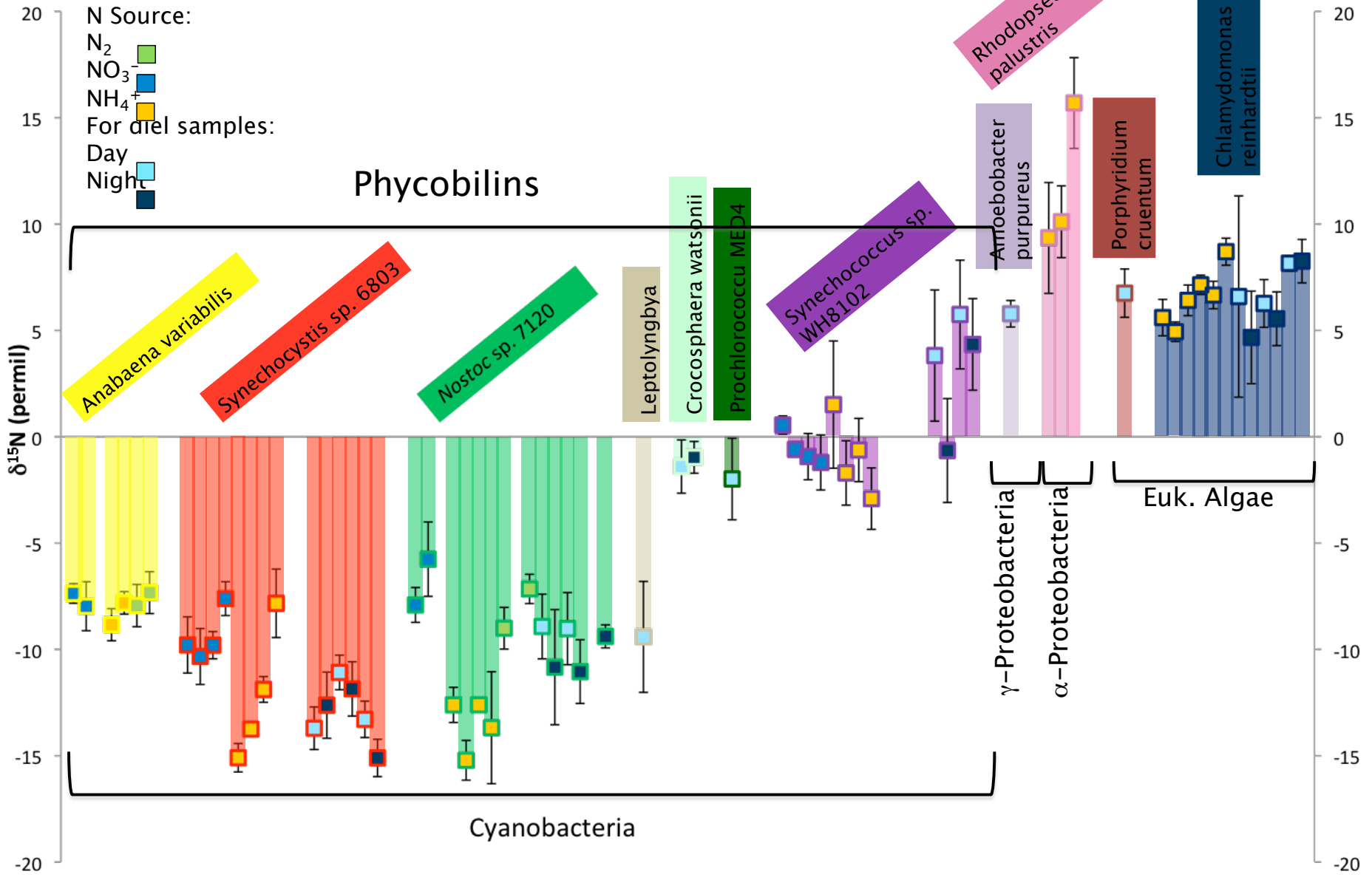


$\varepsilon_{cell-chl}$ = −7.8±0.3‰ (NH_4^+)

$\varepsilon_{cell-chl}$ = −7.2±0.7‰ (N_2)

$\varepsilon_{cell-chl}$ = −5.6±0.9‰ (NO_3^-)

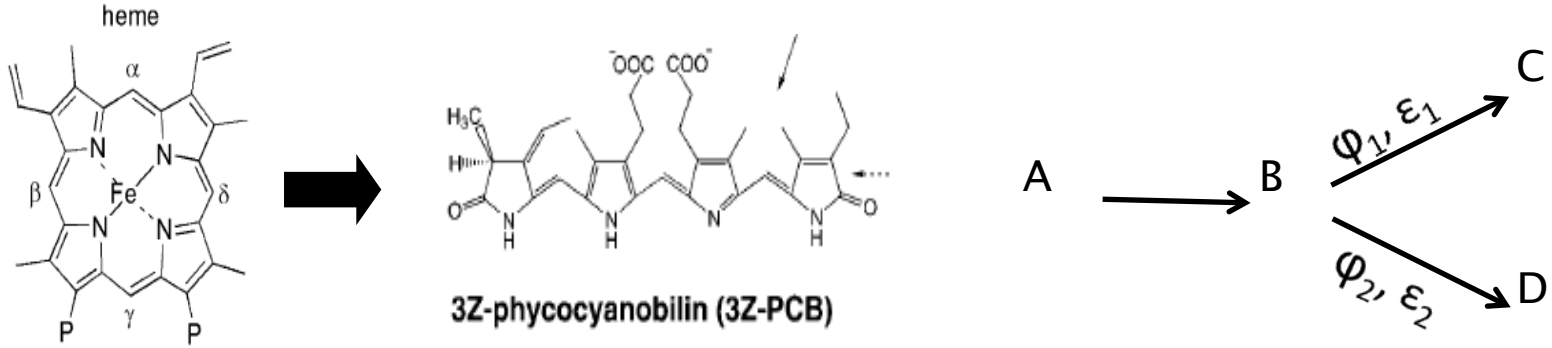
Measured Values of $\Delta\delta^{15}N_{cell-chl}$:



The Isotopic Effects of Phycobilins

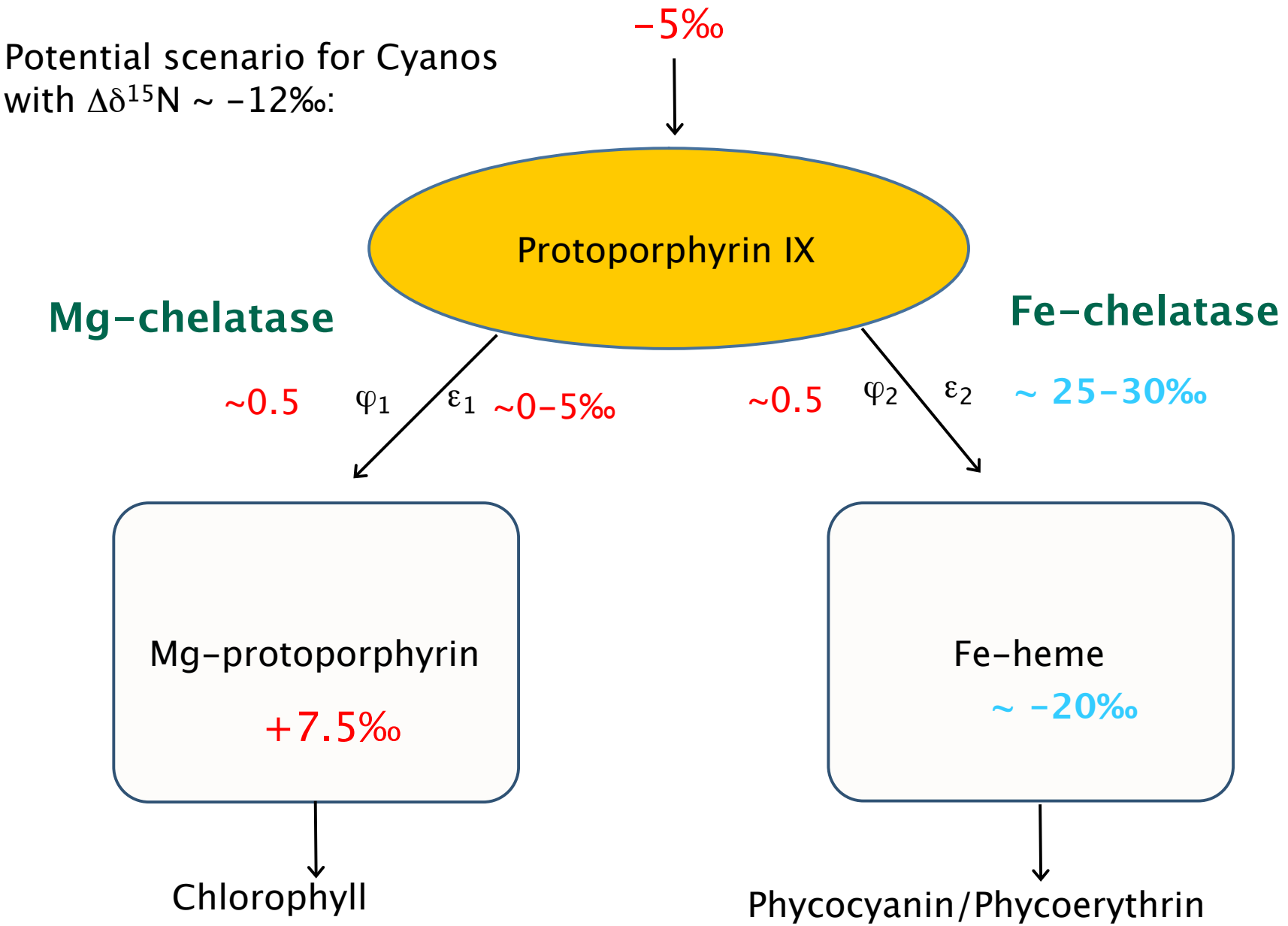
- Negative fractionations are very unusual – not a kinetic isotope effect
- Phycobilins and chlorophyll come from the same biosynthetic pathway

Protoporphyrin IX → heme → phycobilins

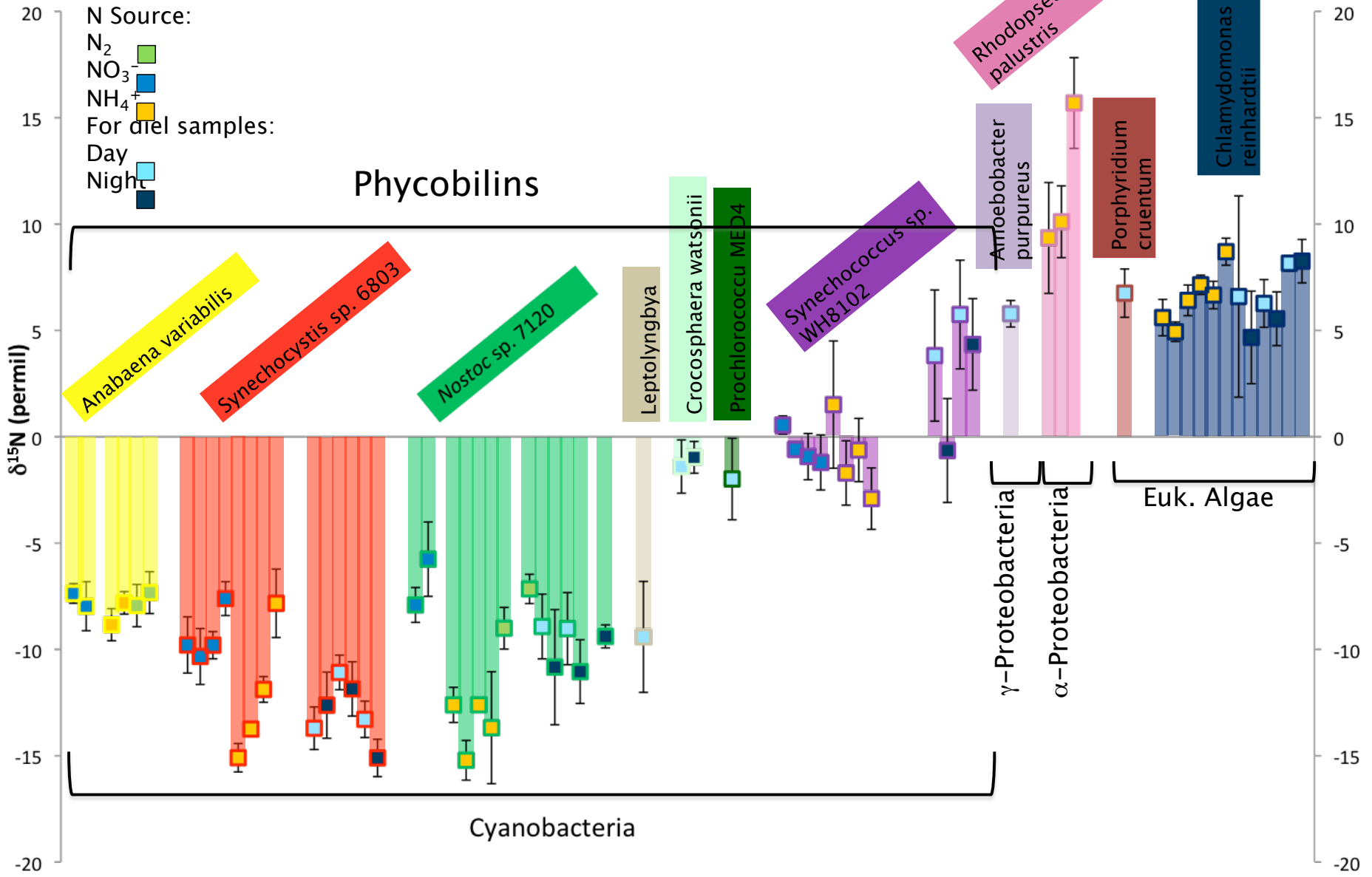


Are negative $\Delta_{cell-chlorophyll}$ values due to positive $\Delta_{cell-phycobilin}$?

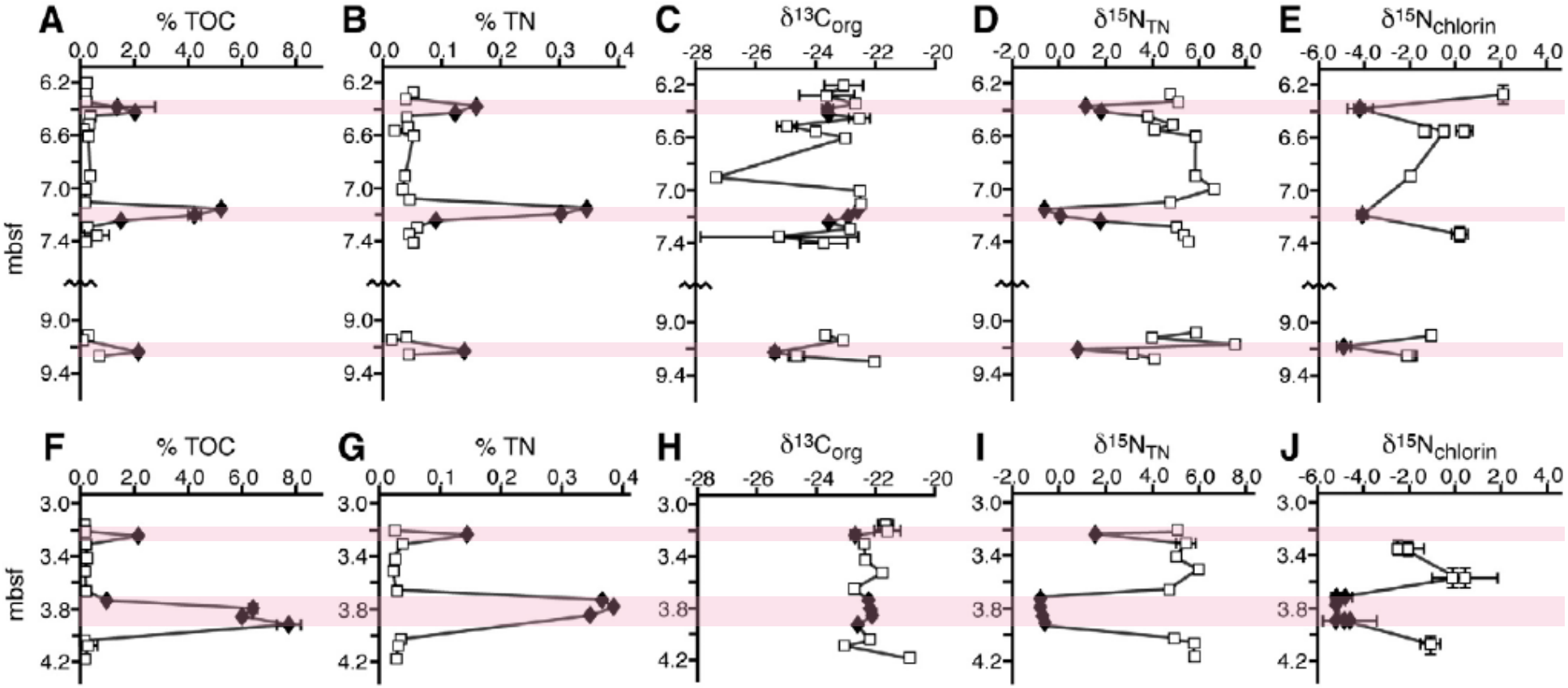
Branch Point at Mg/Fe Metallation



Measured Values of $\Delta\delta^{15}N_{cell-chl}$:



Is documented variability present in geologic record?



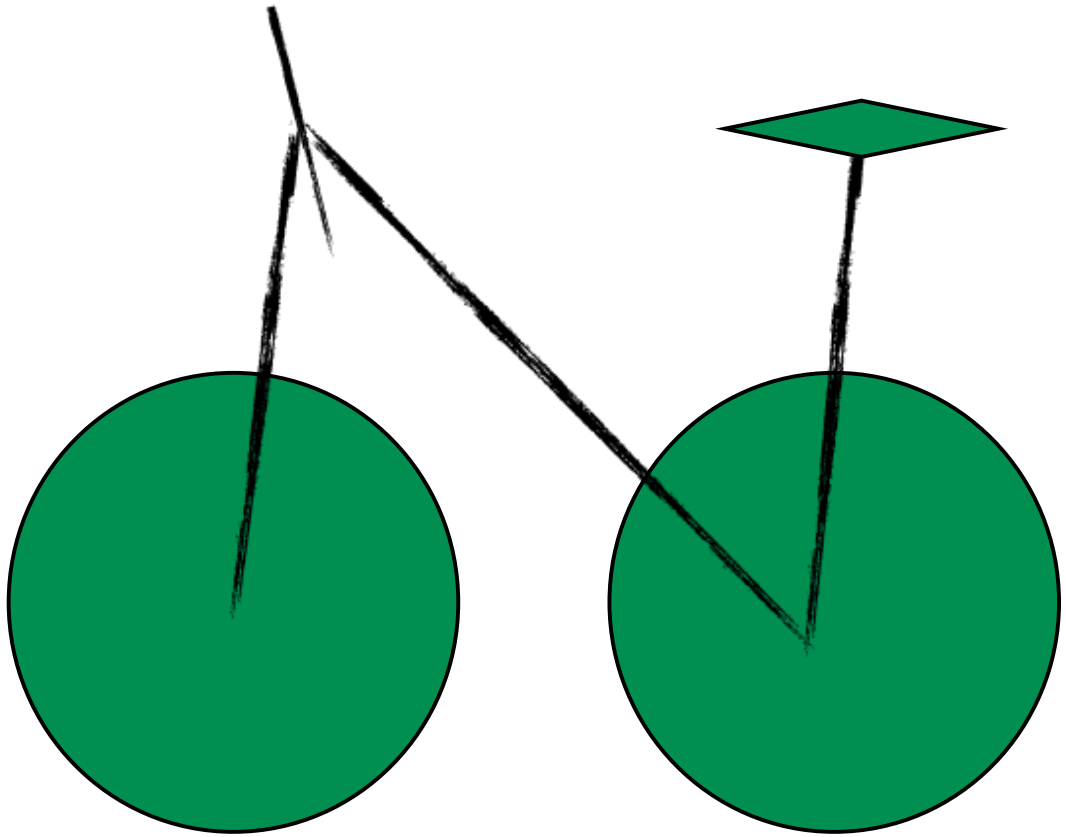
No. Approximately 5‰ offset between bulk and chlorin/porphyrin $\delta^{15}N$ wherever we look (e.g. sapropels, OAEs, recent sediments)

Higgins et al., 2010

"CHLOROPHYLL" $\delta^{15}N$ TAKE HOME

- Species specific cell-chlorophyll offsets
  - cyanobacteria show negative offsets, opposite all other measured algae
  - Likely related to branch point in formation of chlorophyll and phycobilins
- Do not see negative offset in geologic record, suggesting that cyano-based production not significant contributor to export.

Thanks!



“the N cycle” c/o Art Spivack