

# Nitrogen Fixation and Carbon Sequestration

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Anthony Michaels

Wrigley Institute for Environmental Studies  
University of Southern California

# Outline

- Carbon Storage in the Sea - Mechanisms
- Nitrogen Fixation
- Verification Issues
- Academic Conflicts of Interest

# Disclosure of Relevant Commercial Associations

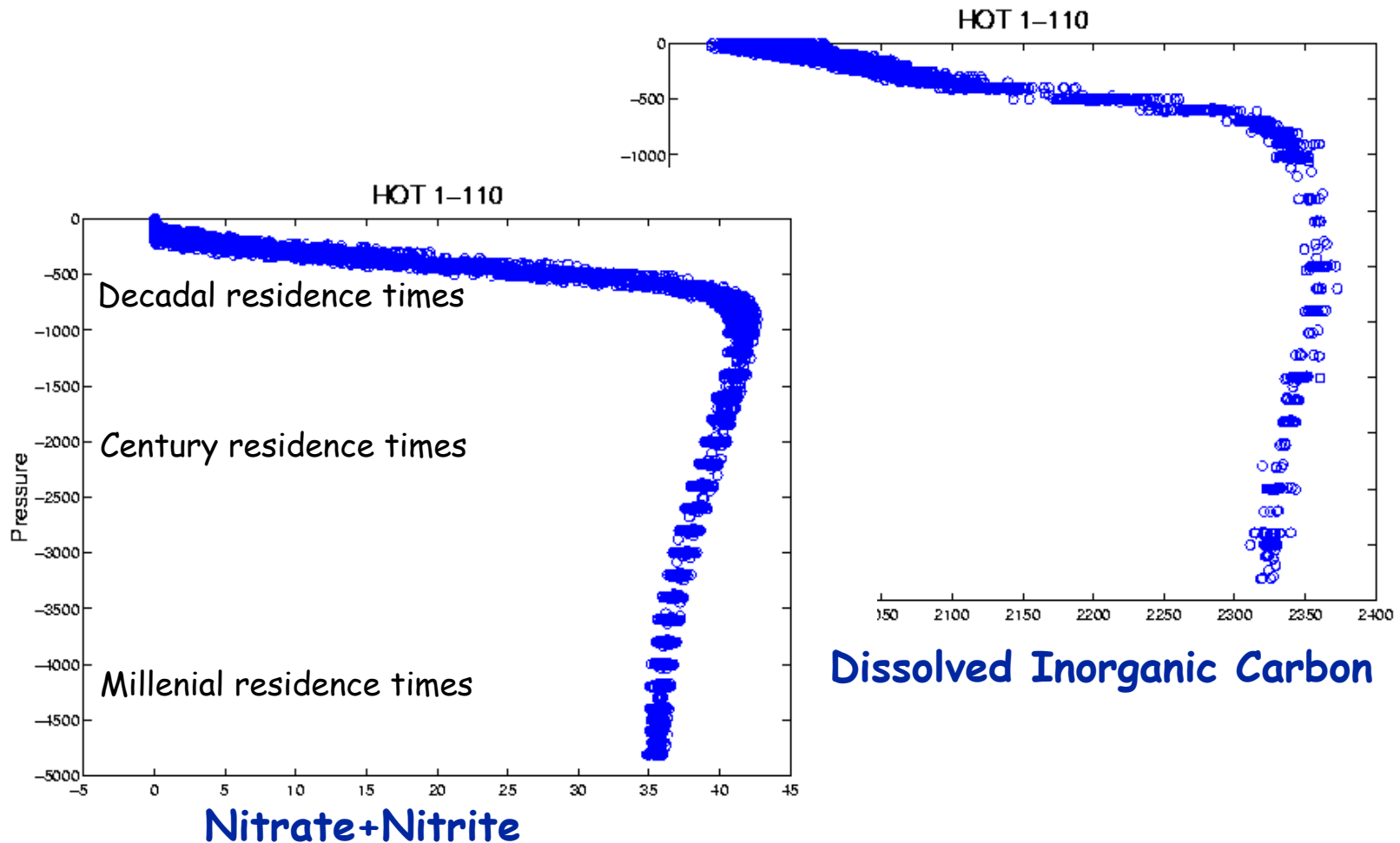
- Planktos (conversations only, pre-2001)
- Climos (discussions 2006-Present, no contract relationship at present)
- Proteus Environmental Research.LLC (R&D Incubator and Venture Fund, have personal equity and significant management roles)

# Carbon Storage in the Sea - Biogeochemical Mechanisms

- Relative use of surface macronutrients
  - Residual Nitrate (HNLC)
  - Residual Phosphate in the absence of  $\text{NO}_3$
- Changes in C:N:P of export
- Changes in remineralization length-scale
- Changes in PIC rain rate ratios with POC

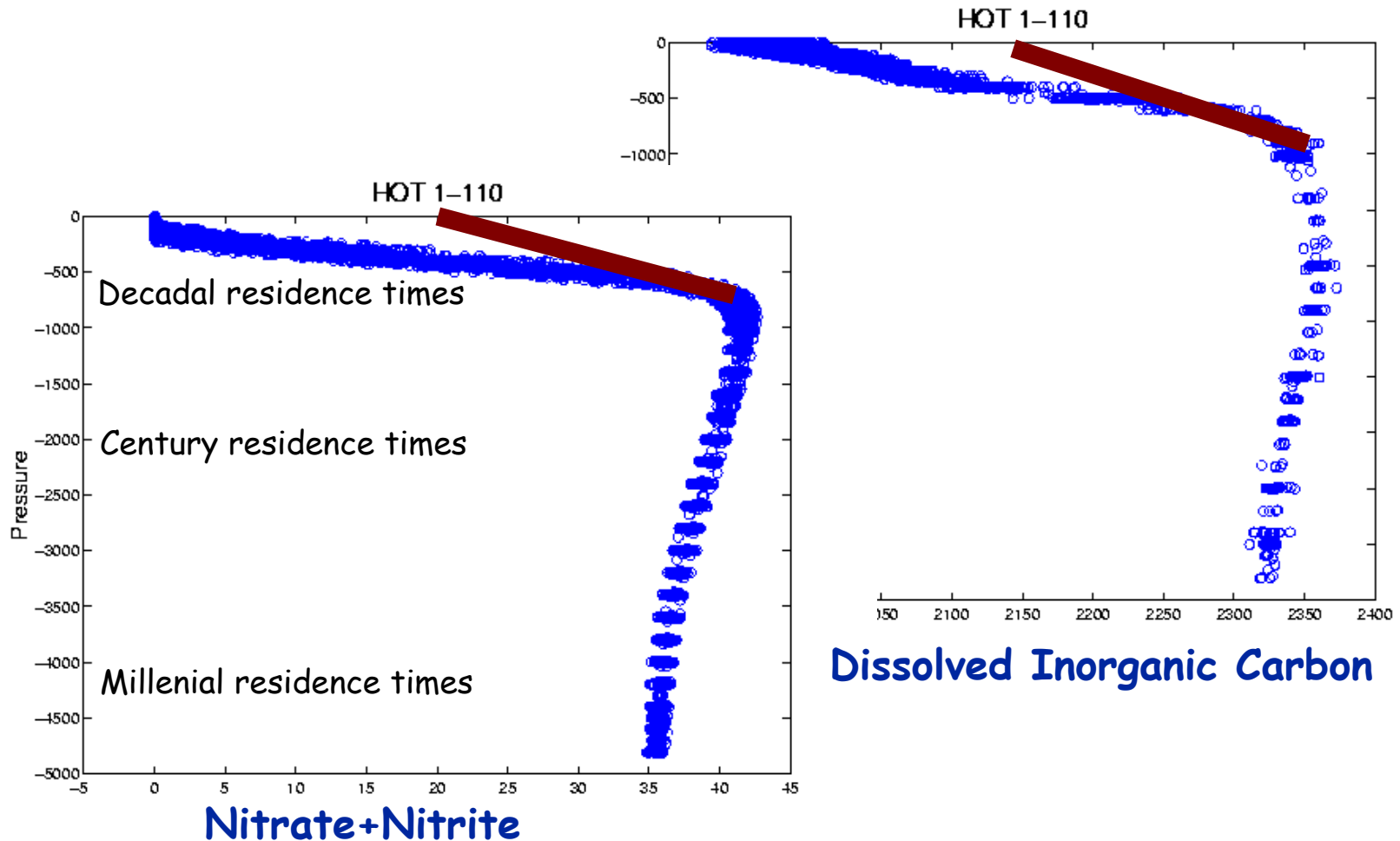
All of these are  
Time-Shifting

Ocean biology maintains a vertical  
DIC gradient - ocean biology is limited by the  
supply of nutrients:



# Incomplete Nutrient Utilization in the Surface Waters (HNLC)

(Leaves un-used DIC in the surface and more CO<sub>2</sub> in the atmosphere)

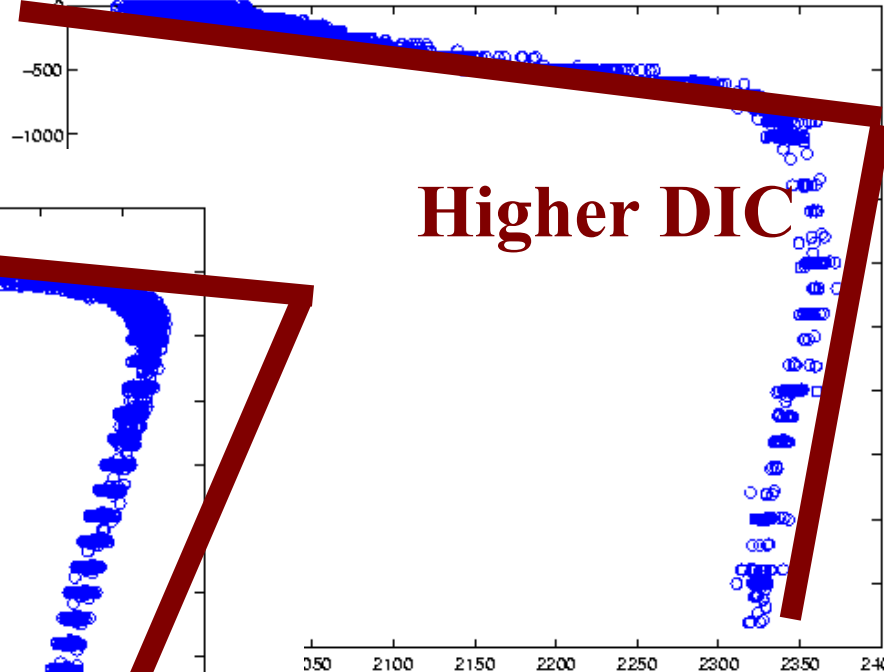


# Changes in Total Nitrate Stock Nitrogen Fixation - Denitrification Balance

Extra Nitrogen  
Fixation

Lower DIC

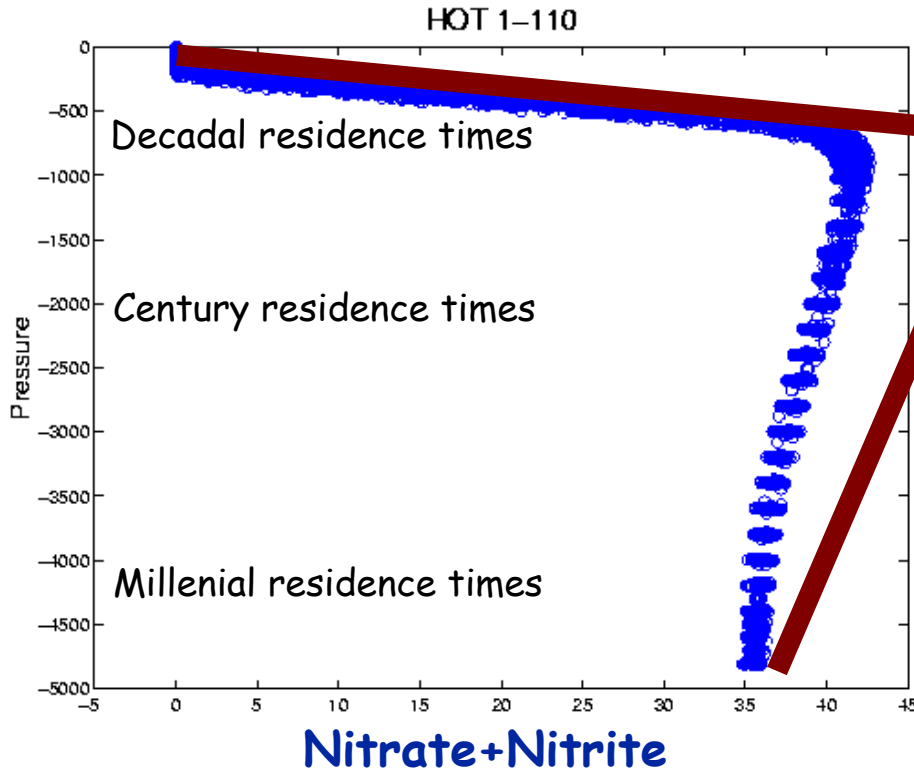
HOT 1-110



Higher DIC

Dissolved Inorganic Carbon

Stronger gradient, lower  
Surface DIC



HOT 1-110

Decadal residence times

Century residence times

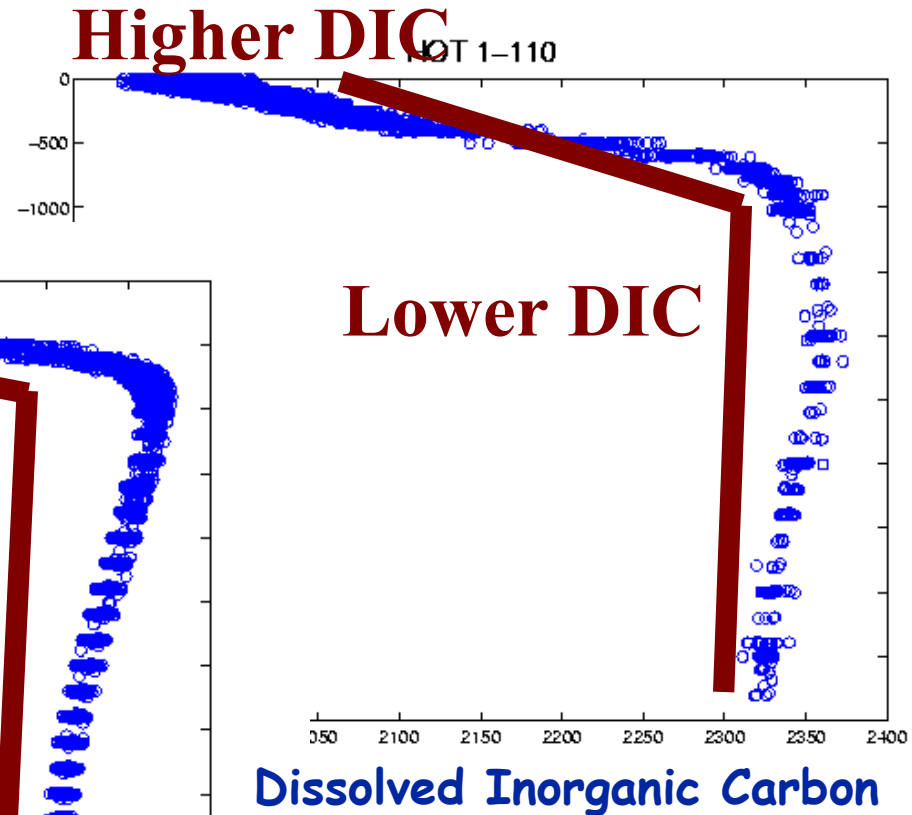
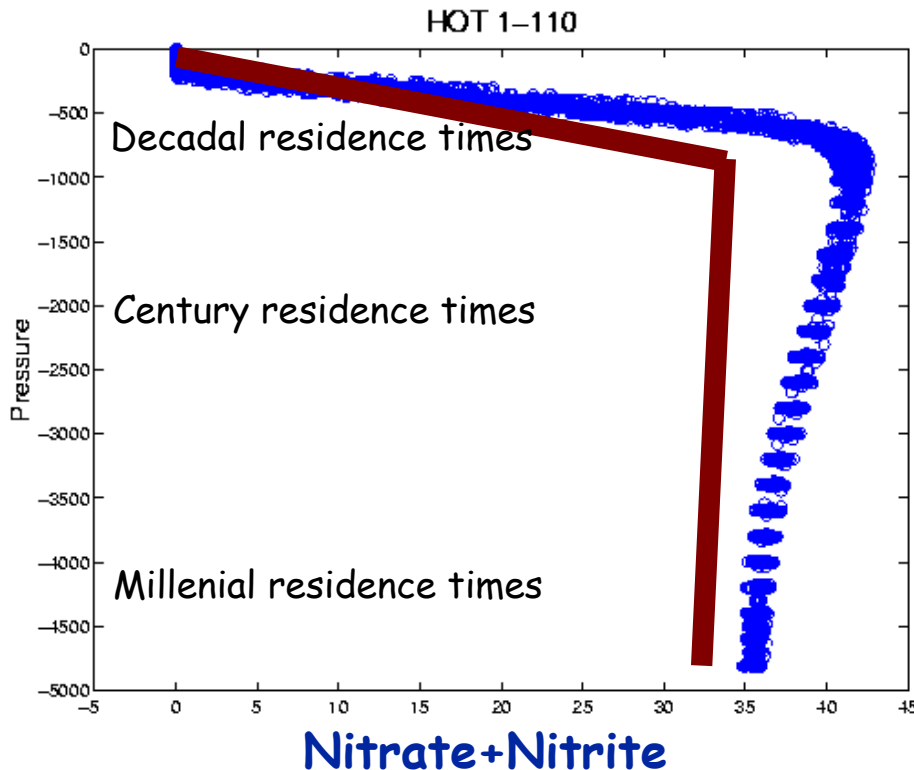
Millennial residence times

Nitrate+Nitrite



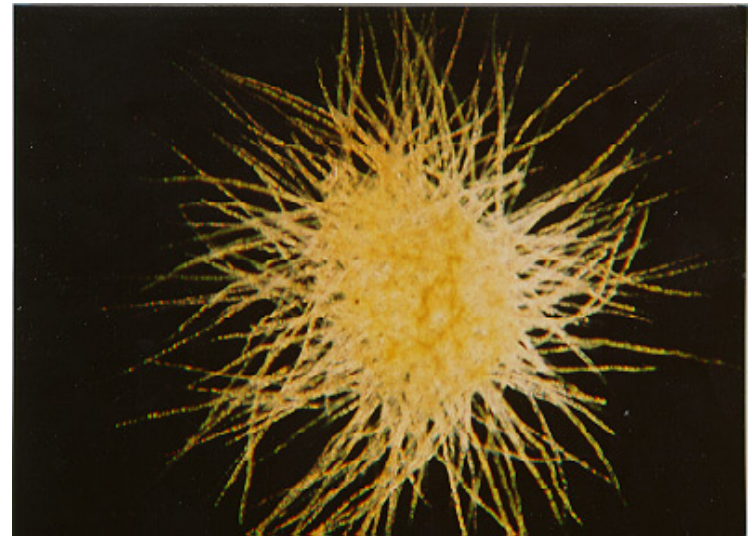
# Changes in Total Nitrate Stock Nitrogen Fixation - Denitrification Balance

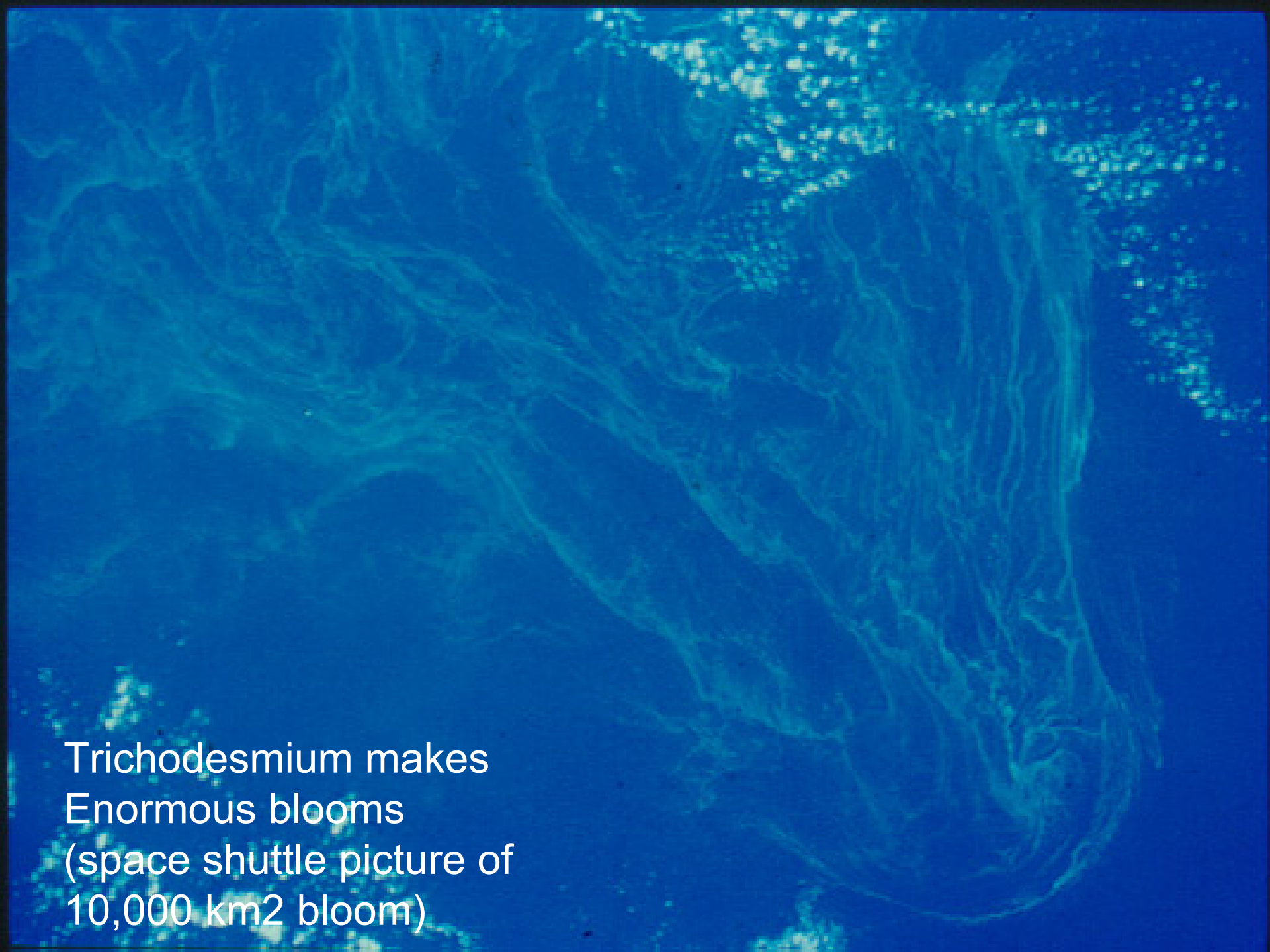
Extra  
Denitrification



Weaker gradient, higher  
Surface DIC

*Trichodesmium* spp.  
Best Known Planktonic Diazotroph

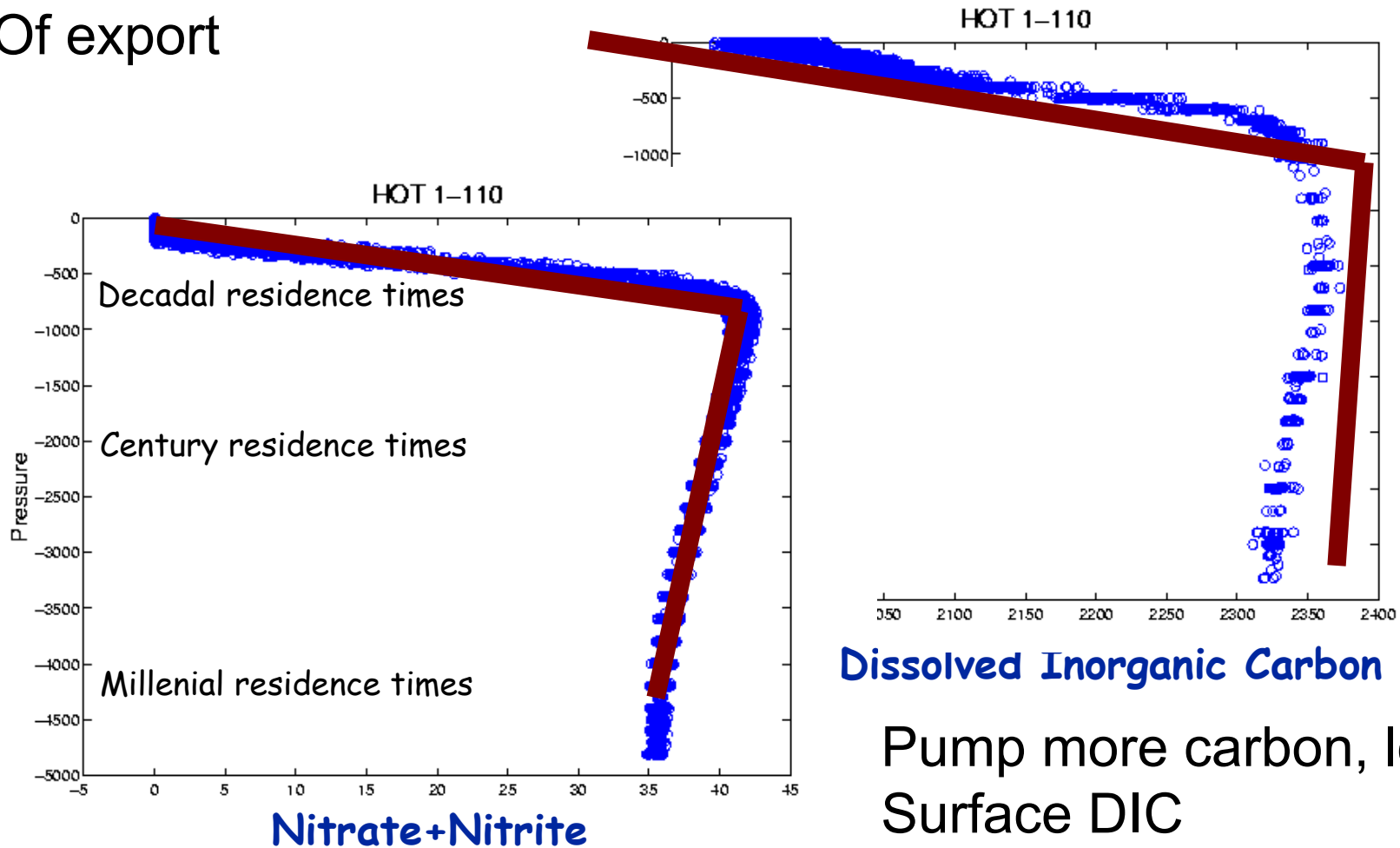


A satellite photograph showing a vast, swirling red bloom of Trichodesmium in the ocean. The bloom is a large, irregularly shaped area of bright red, contrasting sharply with the surrounding blue water. The bloom has a complex, swirling pattern, suggesting strong currents or wind-driven mixing. The overall appearance is that of a massive, dense cloud of microscopic organisms floating on the surface of the sea.

Trichodesmium makes  
Enormous blooms  
(space shuttle picture of  
10,000 km<sup>2</sup> bloom)

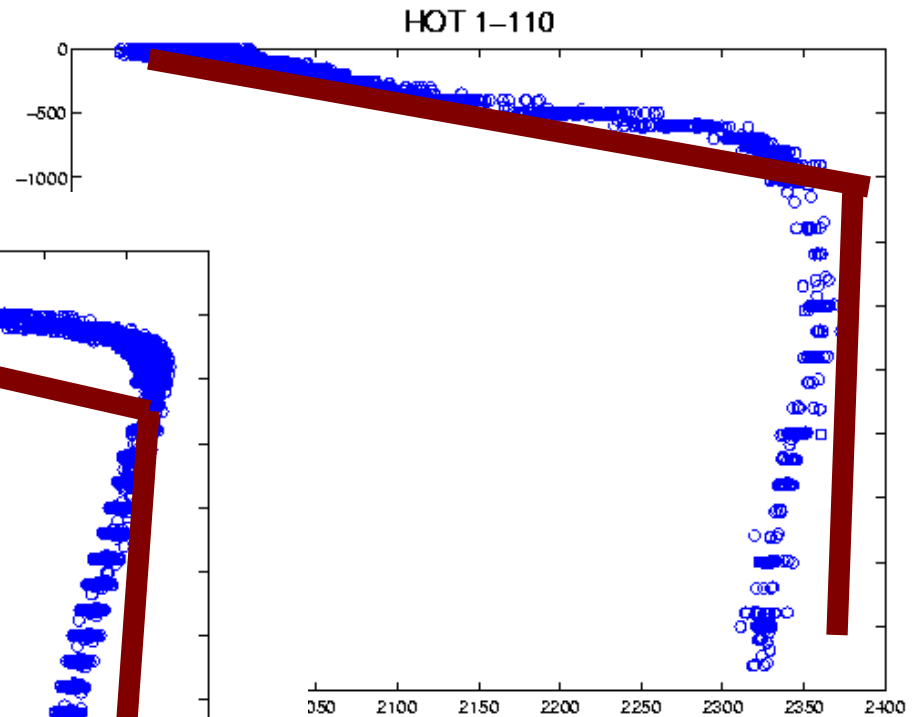
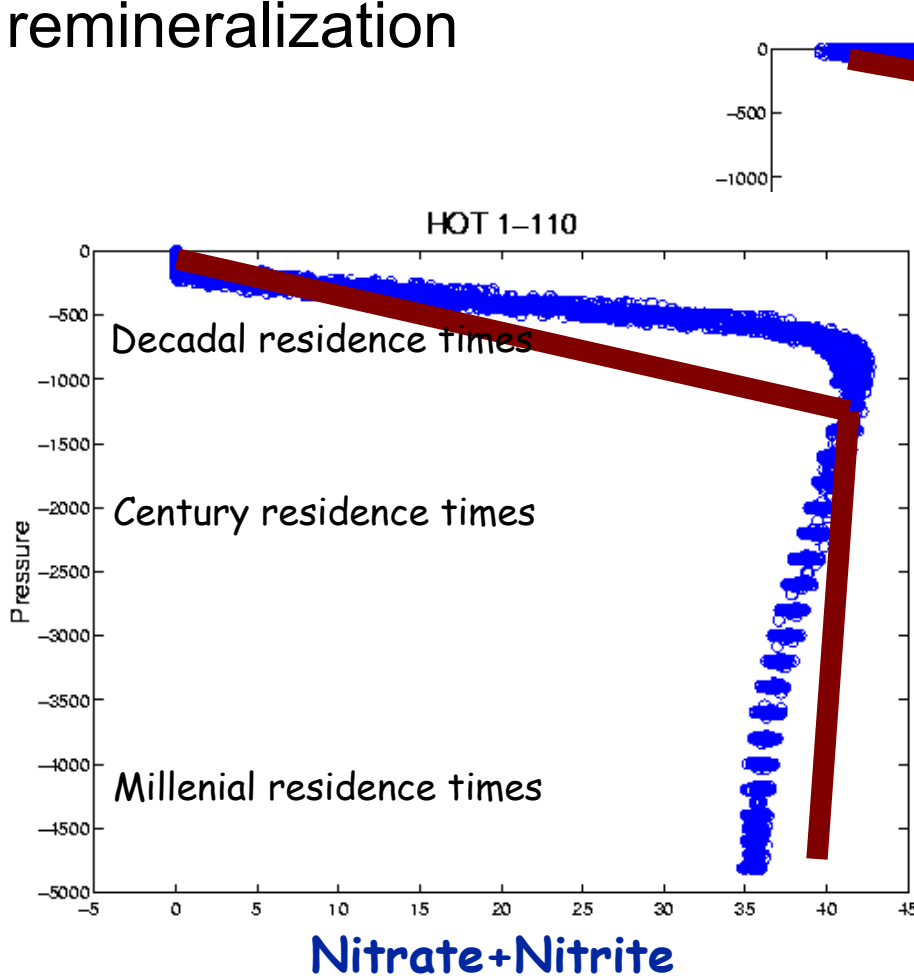
# Changes in C-N-P stoichiometry

Increase C:N or C:P  
Of export



# Changes in remineralization length-scales

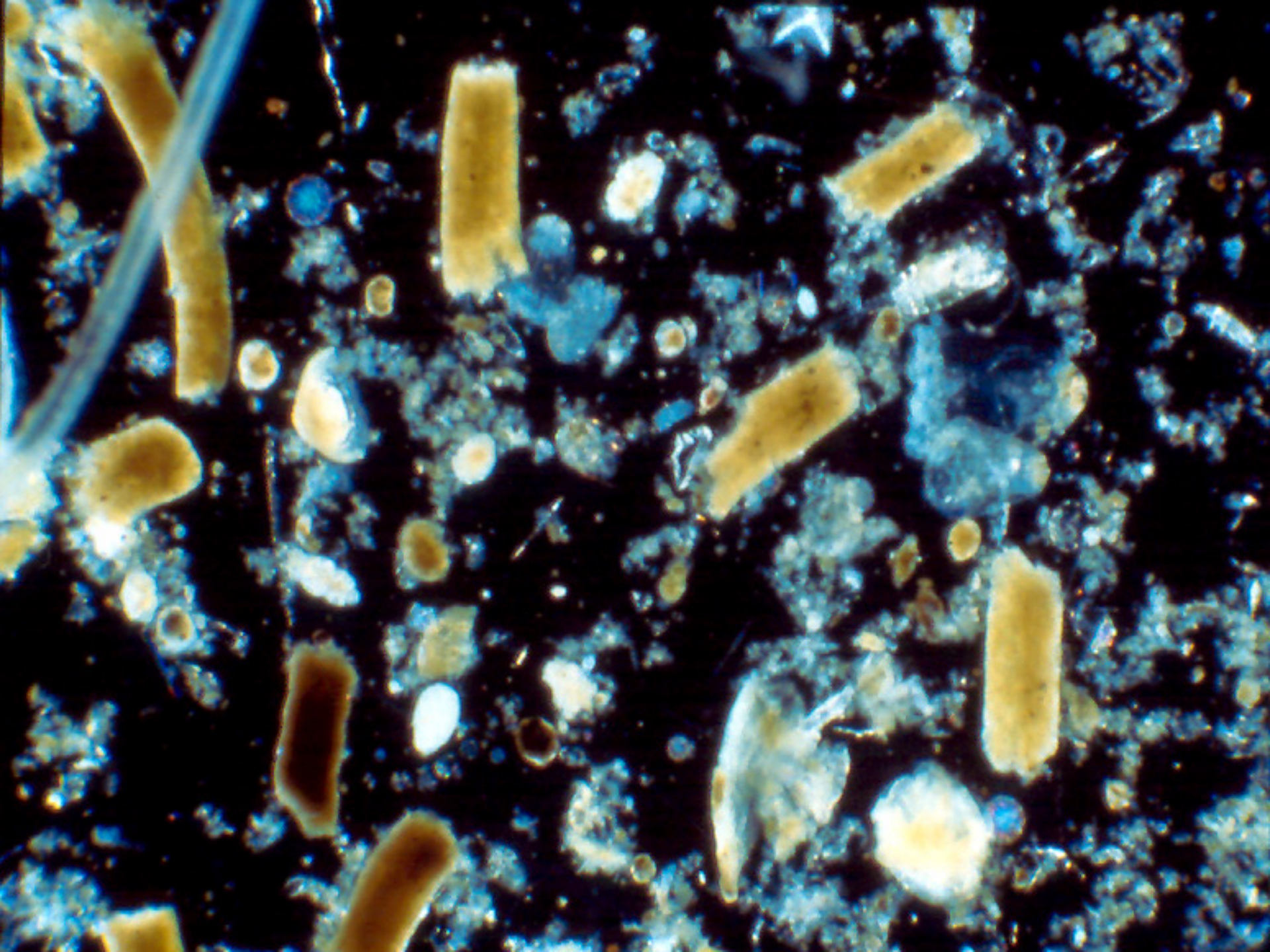
Increase depth of remineralization



Dissolved Inorganic Carbon

Push carbon deeper, lower Surface DIC





# Changes in PIC:POC rain

- Changes in carbonate fluxes impacts the alkalinity of the surface ocean
- Changes in surface alkalinity changes  $p\text{CO}_2$
- Secondary issues with other gases.

# Carbon Storage in the Sea - Mechanisms

## Focus on Nitrogen Fixation

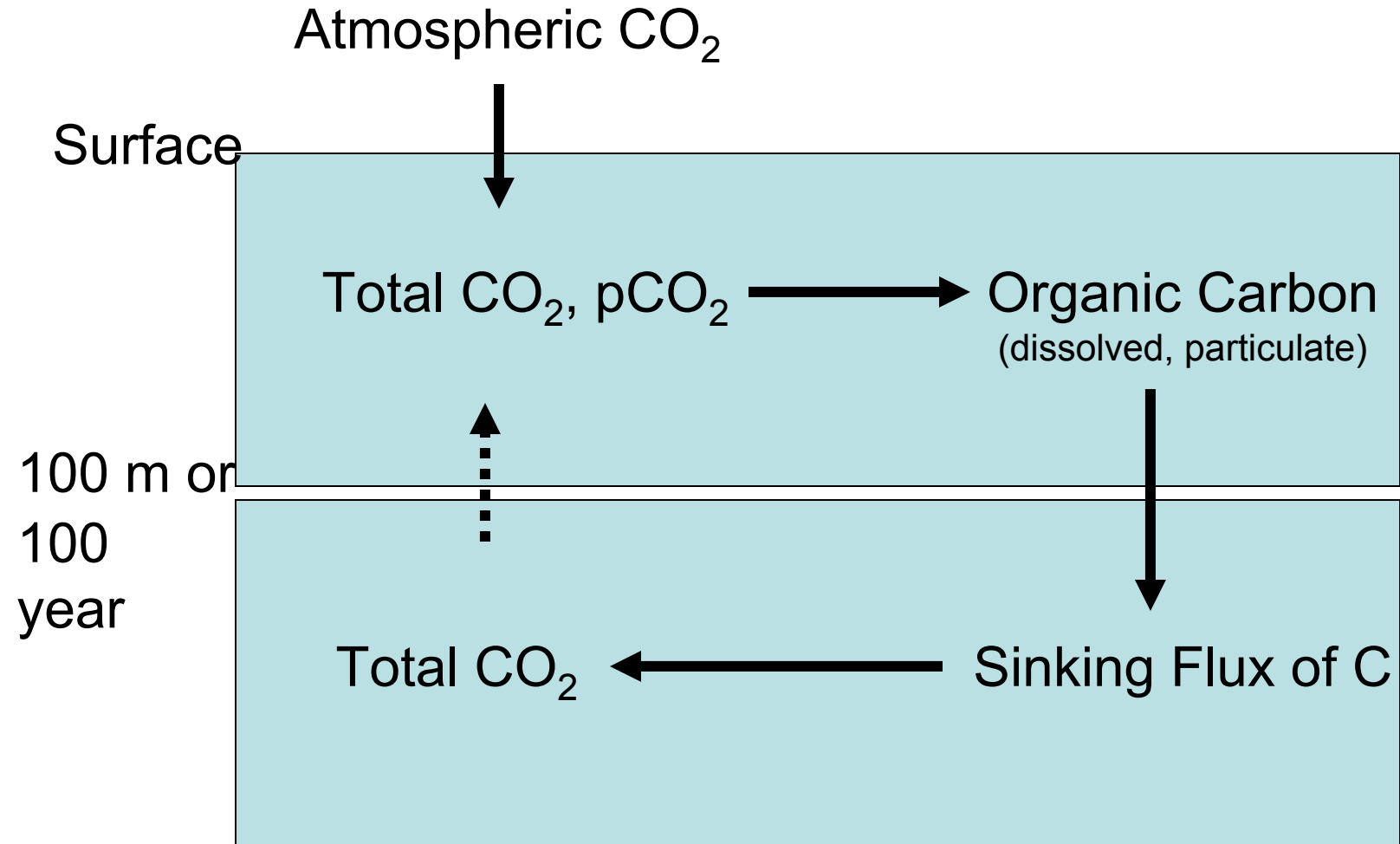
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# Sequestration Time-scale

- How long will this carbon stay below the surface mixed layer?

# How to Understand and Measure the Effect: Create Mass Balance Model for Mixed Layer



# How to Understand and Measure the Effect: Create Mass Balance for Mixed Layer

Atmospheric  $N_2$

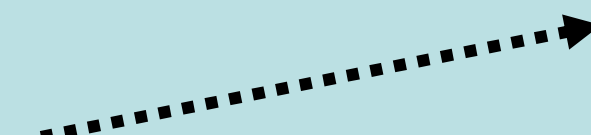
Surface



$N_2$



Organic Nitrogen  
(dissolved, particulate)



Nitrate

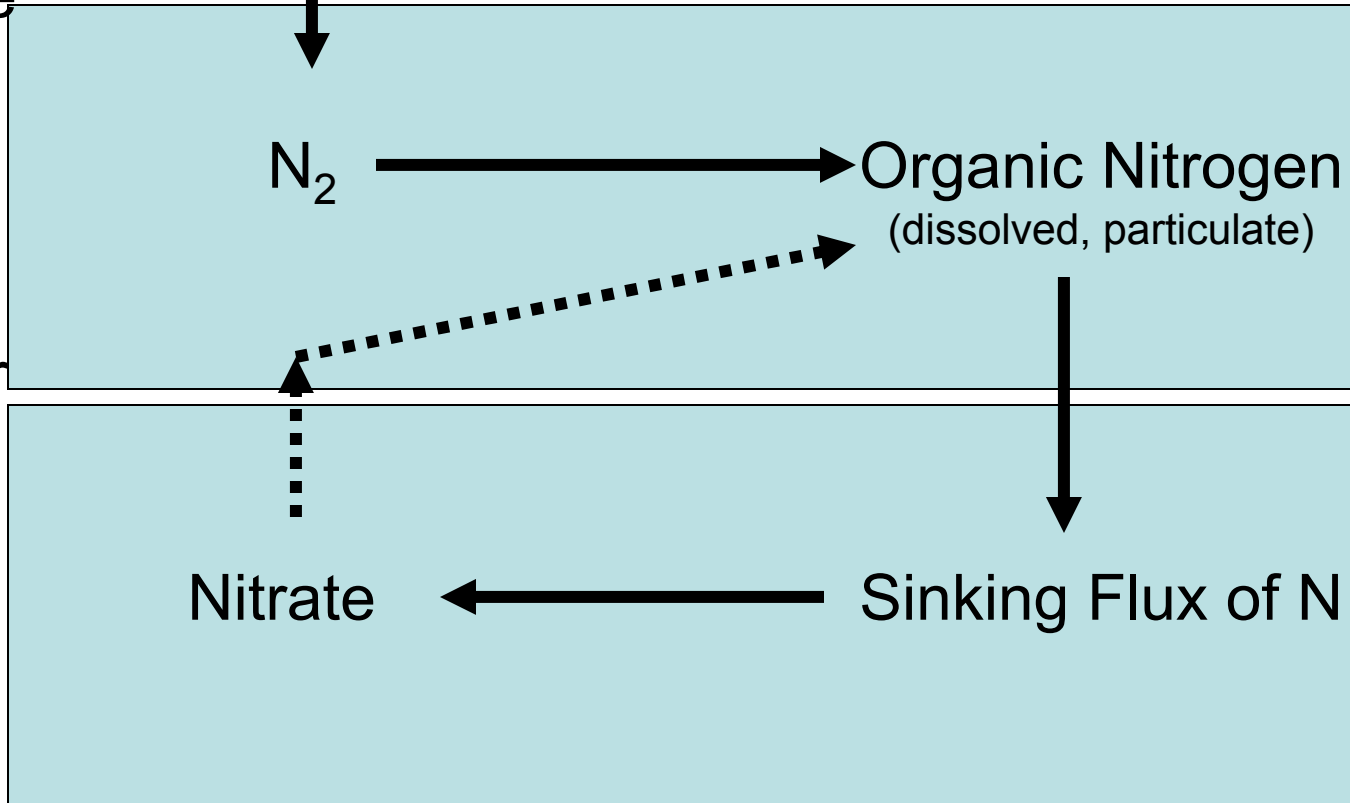


Sinking Flux of N

100 m or

100

year

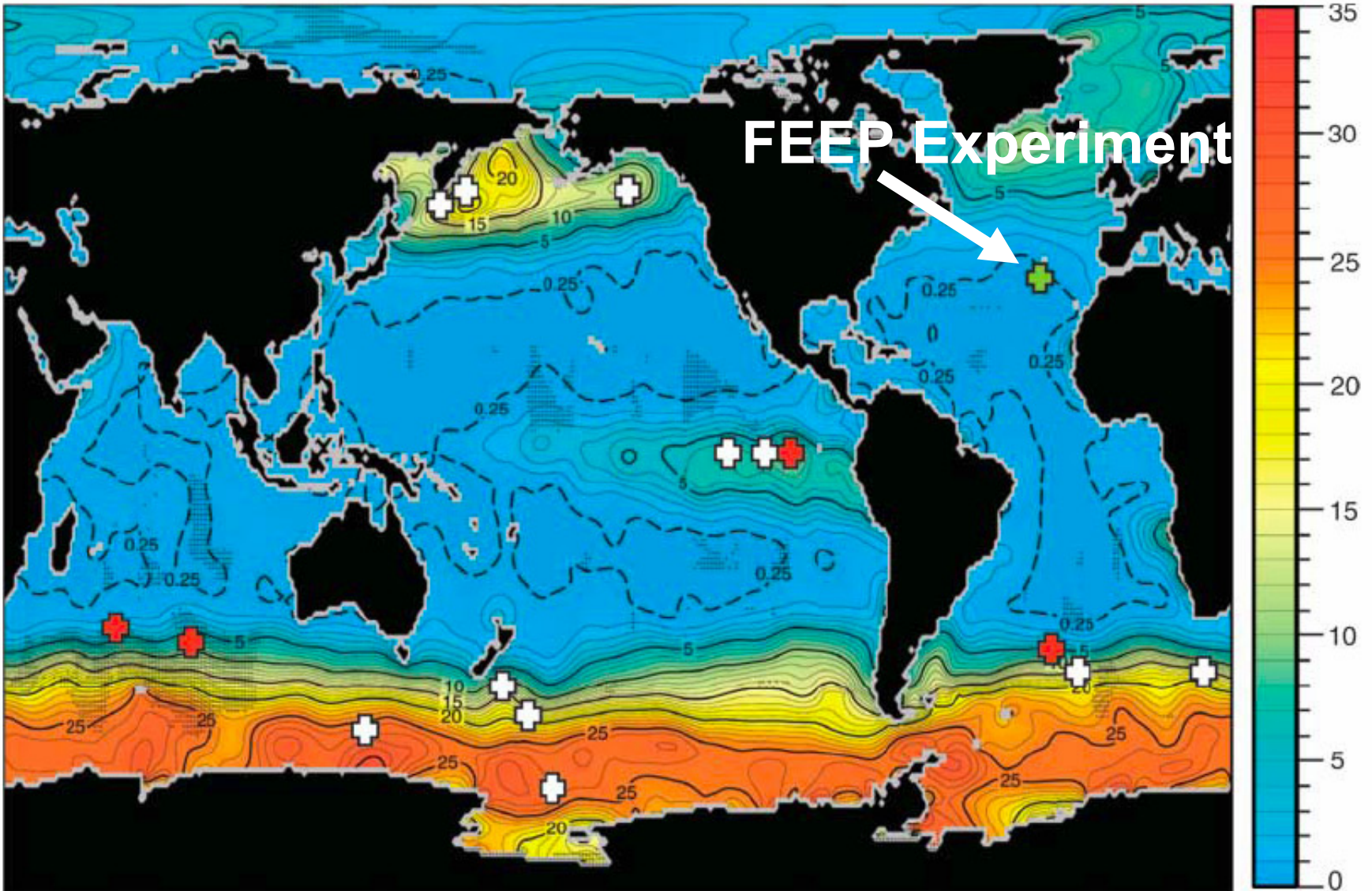


# Sequestration Time-scale

- Biological re-use should keep carbon and new nitrate below the surface for extended periods
- Carbon storage until:
  - Upwelled in HNLC area and extra nitrate is left unused (if that happens)
  - Passes through denitrification zone, followed by upwelling to the surface without the extra nitrate
- Both of these time-scales can be centuries when the correct location is chosen

# Fe Addition and Nitrogen Fixation - Existing Data

- FeeP - Fe and SRP addition in NE Atl.
- Bottle Incubations (Fe, SRP, dust)
- Amazon Plume (High Fe, PO<sub>4</sub>)
- HOT data - recurring summer signal (Karl)



# FeeP (Rees, et al., 2007)

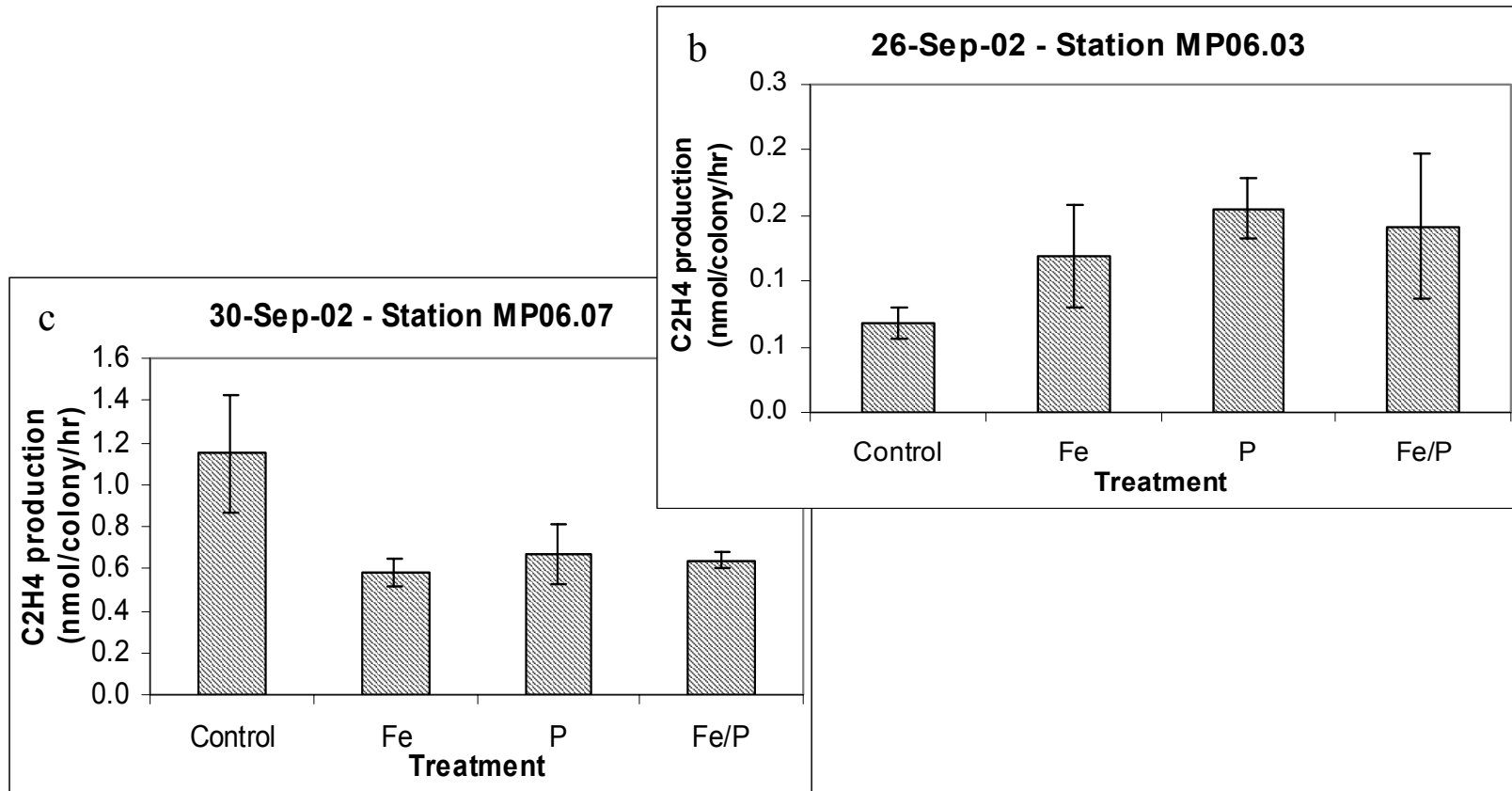
- Added Fe and PO<sub>4</sub> to a low Fe and P area of NE Atlantic
  - 25 km<sup>2</sup> patch of Fe only
  - 25 km<sup>2</sup> patch with Fe and P
- Followed for about 3 weeks
- Fe+P patch, *Trichodesmium* increases
- N fixation rates increased 6 fold and 4.5 fold respectively

# Nitrogen Fixation

- FeeP - Fe and SRP addition in NE Atl.
- Bottle Incubations (Fe, SRP, dust)
  - Lots of experiments with variable results
  - Often both addition of Fe and Dust stimulate nitrogen fixation
  - Always questions about how to extrapolate to nature



# Fe and Dust Addition Experiments in Pacific (Sohm data)

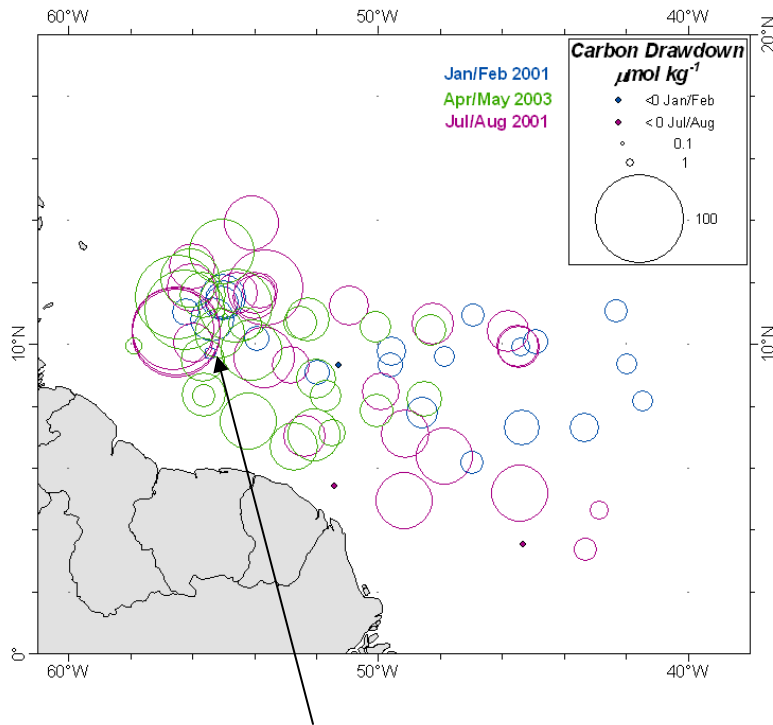


**Figure 3** Acetylene reduction rates with nutrient additions to culture and field samples of *Trichodesmium*. a) Phosphate additions of 20 and 45  $\mu\text{M}$  phosphate to culture grown on 5  $\mu\text{M}$  phosphate (10 times less than in standard YBCII media). b) and c) 10 nM Fe and 100 nM  $\text{PO}_4^{3-}$  additions to colonies picked from net tows in the North Pacific Subtropical Gyre. D) Incubation of colonies from the North Pacific Subtropical Gyre and incubated for 0, 24 and 48 hours before initiation of acetylene reduction assay.

# Nitrogen Fixation

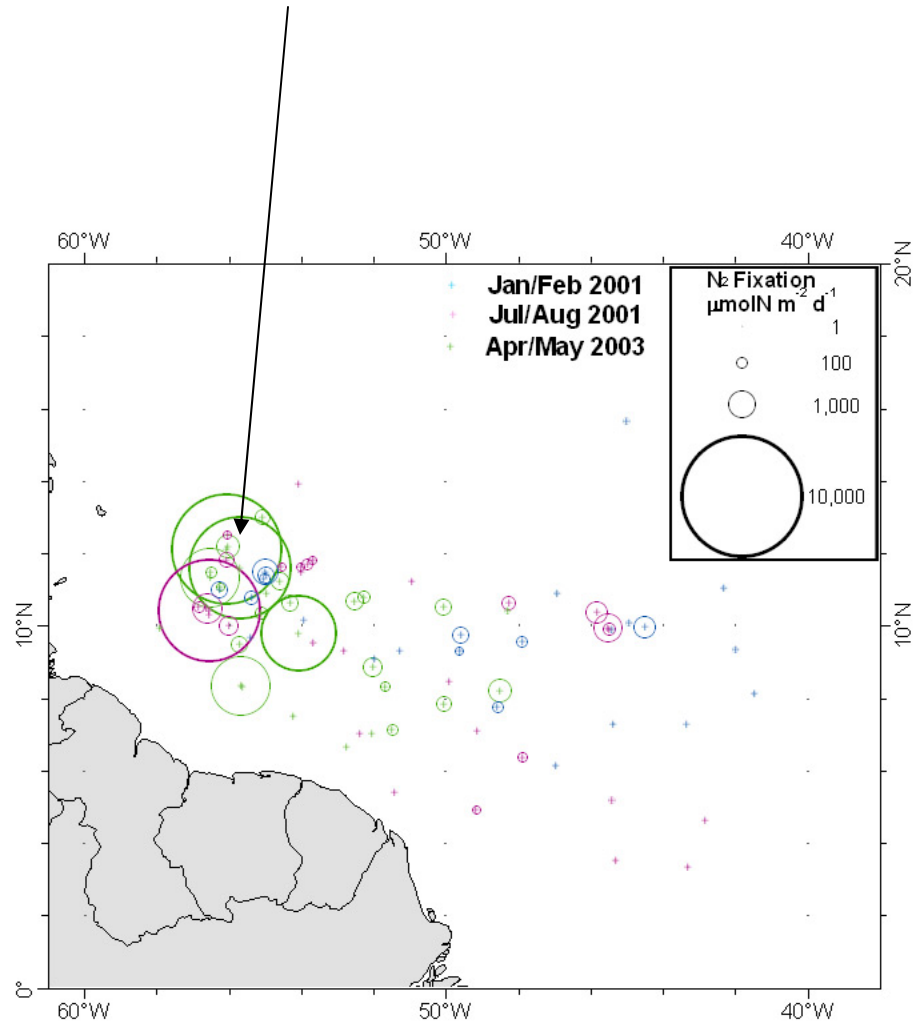
- FeeP - Fe and SRP addition in NE Atl.
- Bottle Incubations (Fe, SRP, dust)
- Amazon Plume (High Fe, PO<sub>4</sub>)
  - Mimics Fe patch after the nitrate and ammonia have been used up - Amazon plume is still Fe, PO<sub>4</sub> and Silica rich water diluted into open ocean seawater.

# Amazon Plume Data (Cooley et al)



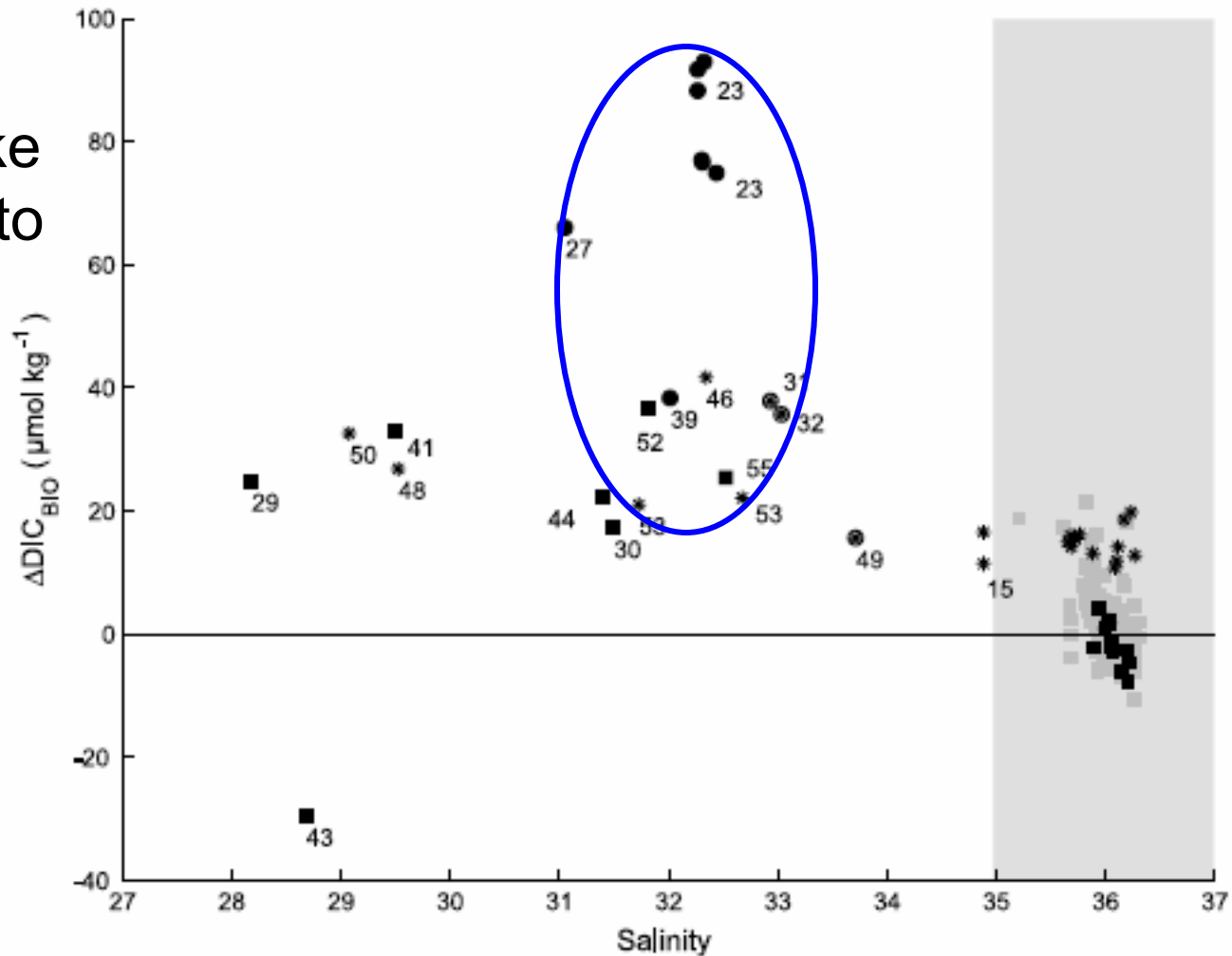
Highest carbon  
Drawdown in center  
Of N-fixation blooms

## N-fixation blooms in Amazon plume



# Amazon Plume Data (Cooley et al)

Range of  
DIC uptake  
Is similar to  
HNLC  
results



**Figure 6.** Community impact on DIC ( $\Delta\text{DIC}_{\text{BIO}}$ ), calculated with the mixing model, plotted against salinity. The 95% confidence interval error bars are within the size of the marker. Station numbers are shown for summer samples. Endmembers used to calculate  $\Delta\text{DIC}_{\text{BIO}}$  included:  $A_s = 2359.4 \pm 5.9$ ,  $S_s = 36.07 \pm 0.10$ ,  $\text{DIC}_s = 2024.5 \pm 6.8$ ,  $S_r = 0 \pm 0$ . The shaded region above salinity 35 indicates data outside the influence of the plume. Markers indicate the prevailing macroscopic nitrogen-fixing organisms observed at a station: square, none; circle, *Richelia*; asterisk, *Trichodesmium*; circle and star superimposed, *Richelia* and *Trichodesmium* together.

# Nitrogen Fixation

- FeeP - Fe and SRP addition in NE Atl.
- Bottle Incubations (Fe, SRP, dust)
- Amazon Plume (High Fe, PO<sub>4</sub>)
- HOT data - recurring summer signal (Karl)
  - Indicate recurring blooms of diazotrophs every summer in N. Pacific Gyre, lead to high export to depth, strong  $\delta^{15}\text{N}$  signal

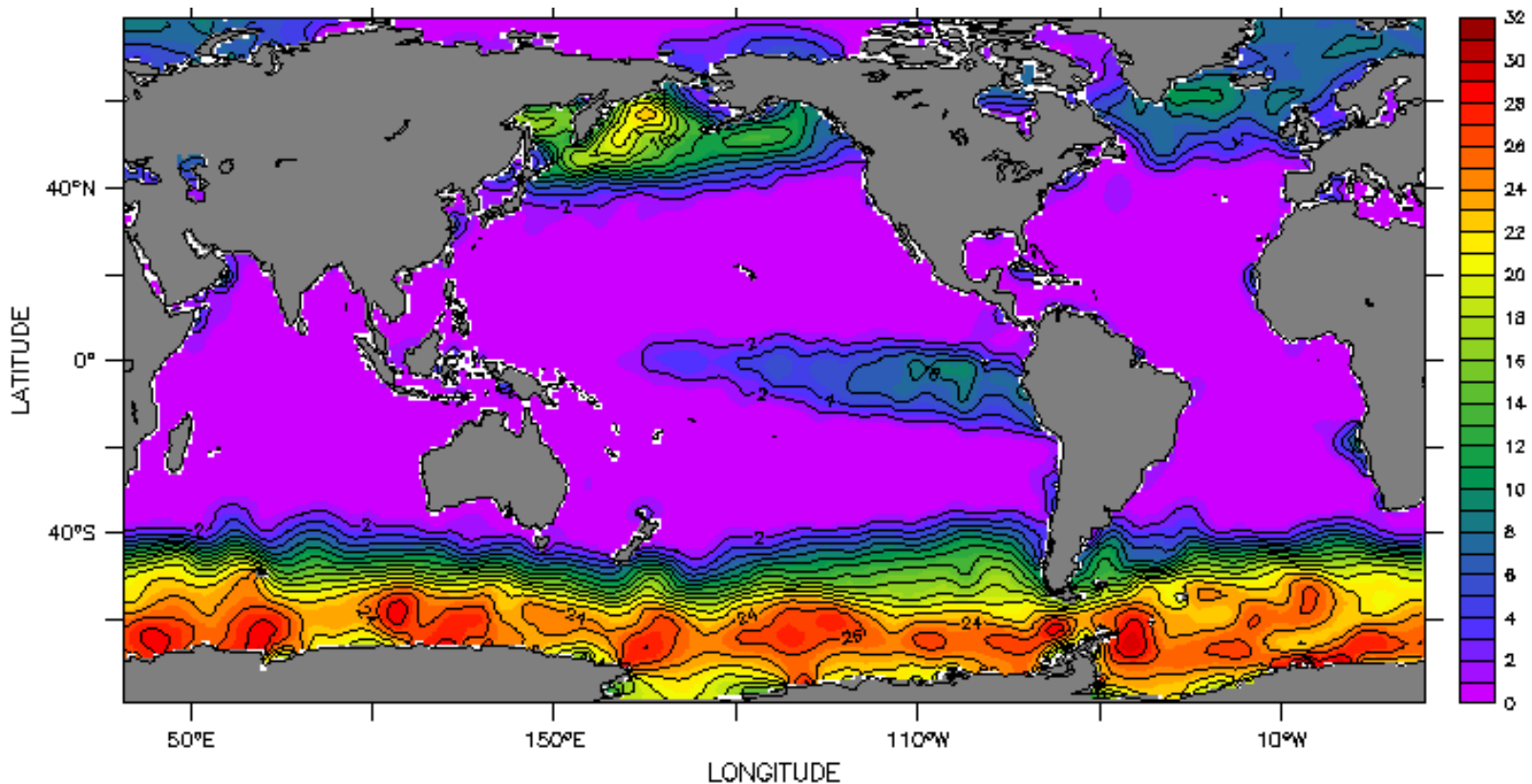
# Conclusions From Previous Research

- Reasonable likelihood that nitrogen fixation is influenced by availability of Fe in the North Pacific and that addition of Fe will stimulate growth of diazotrophs (variable N:P)
- Growth of diazotrophs can lead to DIC drawdown
- Increases in total reactive nitrogen (ultimately nitrate) could impact air sea partitioning of CO<sub>2</sub> until those waters experience denitrification (100s to 1000 years).

# Site Selection

- Nitrate near detection
- Phosphate measurable
- Fe low
- Diazotrophs present, but not growing because of Fe stress
- Shallow Mixed Layers and Warm Waters
- Subsurface conditions conducive to sequestration and minimal negative environmental impacts

Most of the ocean shows  
near-complete nutrient utilization



Surface Nitrate ( $\mu\text{moles/kg}$ )



MOORE ET AL.: GLOBAL ECOSYSTEM-BIOGEOCHEMICAL MODEL

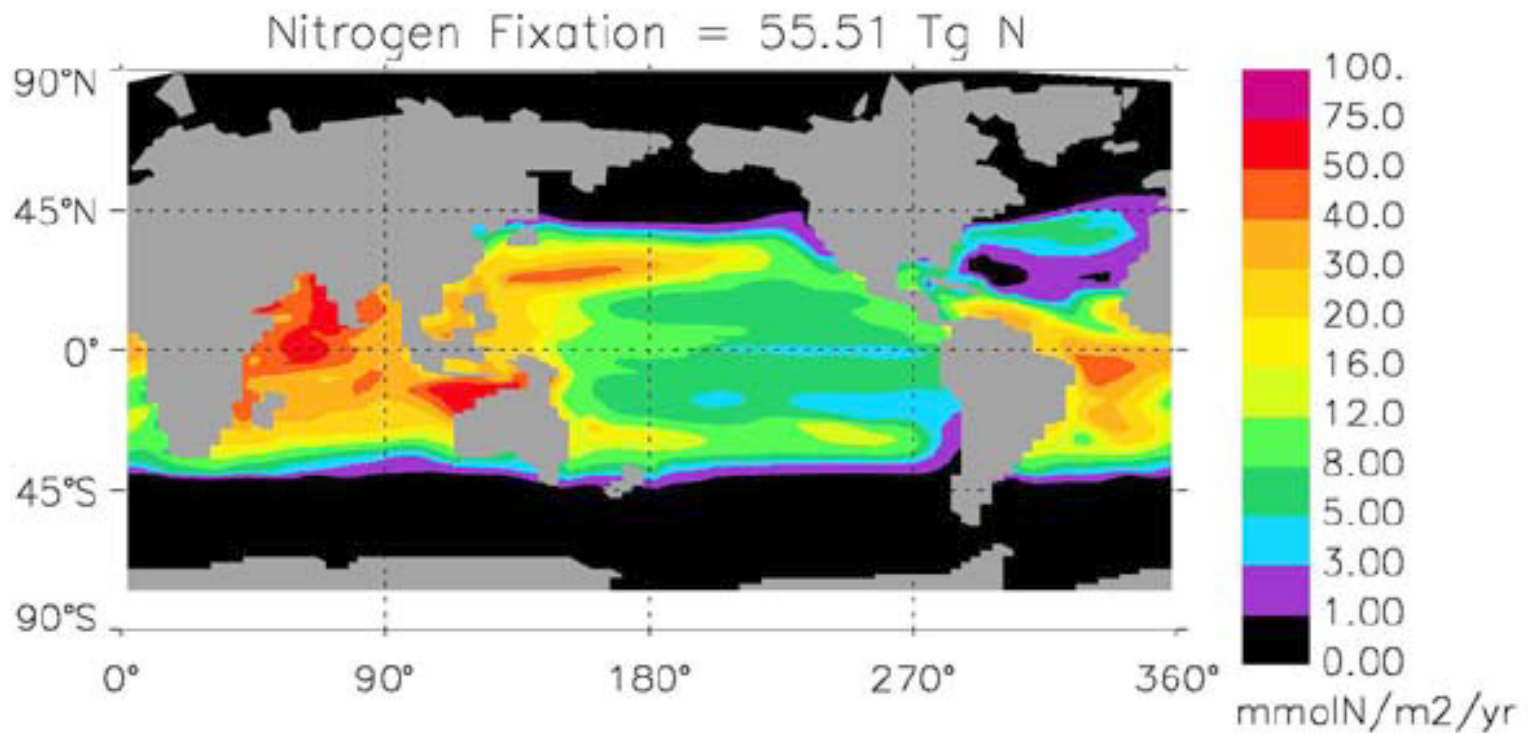
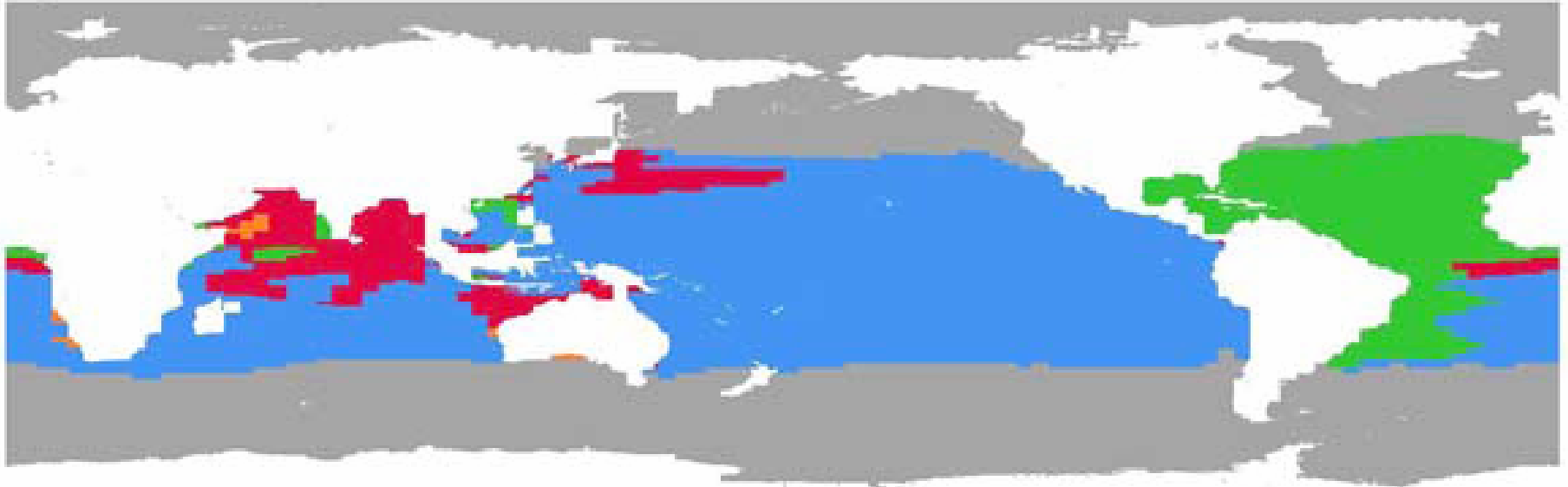


Figure 6. Annual nitrogen fixation rates by the diazotrophs are displayed.

Look for areas of low but positive nitrogen fixation

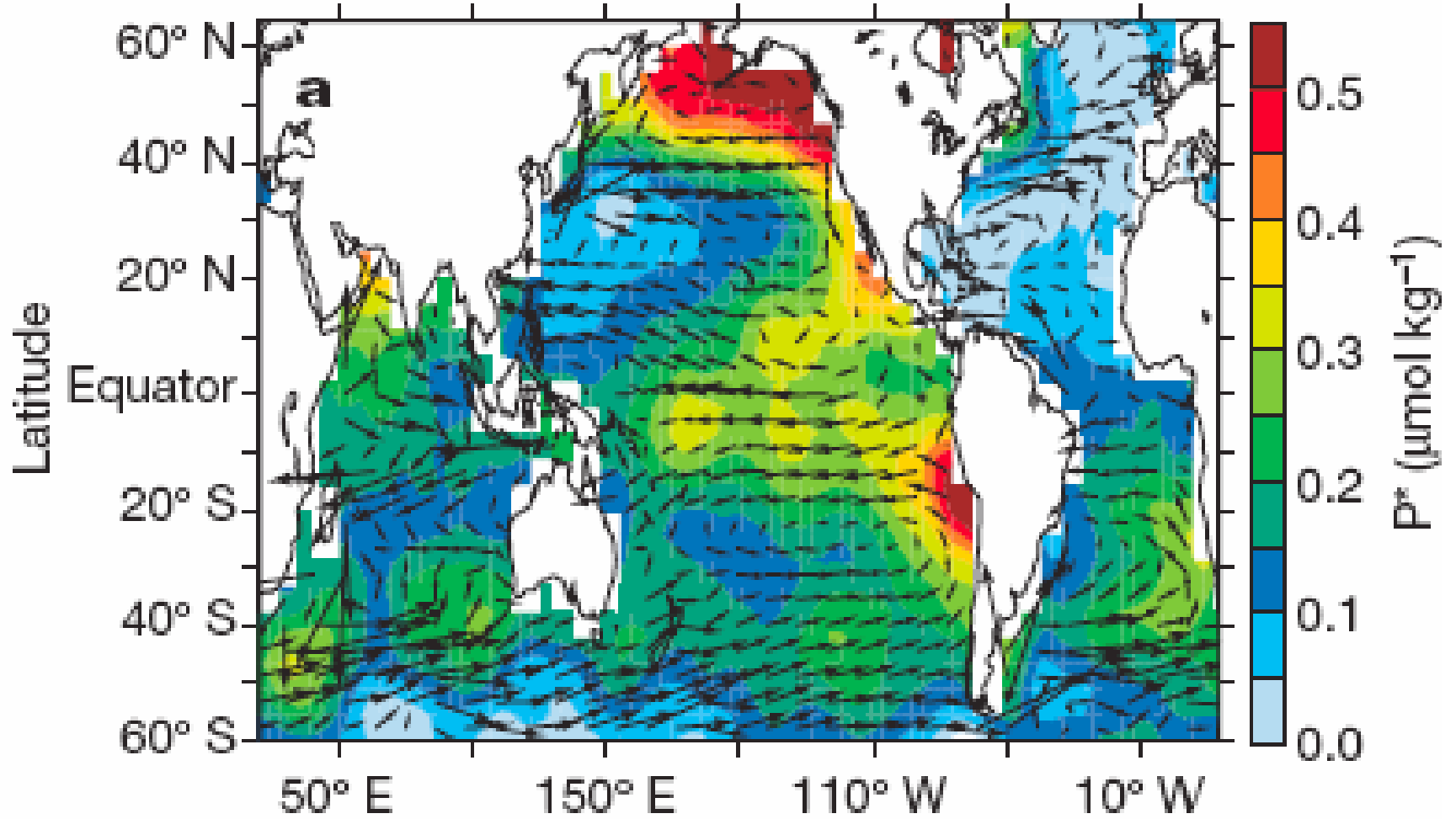
## C) Diazotroph Growth Limitation



**Nitrogen 0.000%, Iron 44.06%, Phosphorus 11.66%**  
**Light 7.072%, Temperature 36.81%, Replete 0.376%**

■ Nitrogen   ■ Iron   ■ Phosphorus   ■ Silicon  
■ Light   ■ Temperature   ■ Replete

Find areas where diazotrophs limited by Fe



Pick areas with “extra” phosphate

Deutsch et al., 2006

# Compelling Logic?

- The best place for nitrogen fixation is where there is excess phosphate - usually derived from the upwelling of waters that recently experienced denitrification, but that have not yet experienced N fixation.

# Environmental Impact Issues

- Other Trace Greenhouse Gases
  - $\text{N}_2\text{O}$ , methane, DMS
- Harmful algae or other ecosystem distortions
- Oxygen anomalies
- Acidification Issues
  - Reduce surface acidification
  - Increase deep-sea acidification
  - Volumes different - impact should be less

# Back to Conflict of Interest

- Academic role is analogous to university-run trials of new drugs or biomedical devices
- Commercial linkages are inherent
- Disclosure of potential conflicts and formal management are critical
- Appearance is as important as reality
- Learn from the other fields

**We have to do this well!**

# Disclose and Manage

- Assume outsiders will think the worst
- Hidden ties, no matter how innocent can look bad (particularly when coupled to non-disclosure agreements)
- Over-disclosure is fine - fine line between internal disclosures and public knowledge
- External reviews and layers of checks and balances provide real protection
- Guard academic freedom (particularly for graduate students and Assistant Professors)

# Some of Our Plans

- Independent data analysis of 5-10% of samples  
- hired by university
- Independent assessment of process and methods - hired by company
- Use full assets of university contract and IP offices
- Independent faculty and university oversight of contract research when faculty have equity stake in the company (esp. for verification projects)
- Independent co-advising for graduate students funded under contracts (use techs!)



# Familiarize Yourself with Your Institutional Policy

- Conflict of Interest Policy
- Conflict of Commitment Policy
- IP Licensing Policy and Process
  - Protectable IP
  - Know-how
- Rules and Traditions for Commercial Activities within Academia
  - Medical School
  - School of Engineering

Thank you

Questions?