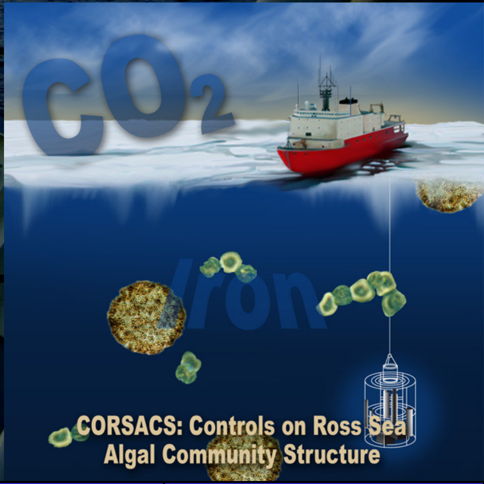
Trace Metal Biogeochemistry and Ocean Carbon: GEOTRACES, Colimitation, Marine Bioinorganic Chemistry, and the Continuing Pursuit of the Elusive Meaning of Bioavailability

Mak Saito

Marine Chemistry and Geochemistry Department

Woods Hole Oceanographic Institution



Outline:

- We now know major regions of the oceans are iron limited
- Continue to be relatively data-poor with regards to trace metals (GEOTRACES)
- Iron and metal acquisition research ongoing, (bioavailability with nutrition)
- Influence of other metals (colimitation), new approaches (new technology)
- Carbon sequestration has come back into focus with recent public interest climate change

GEOTRACES

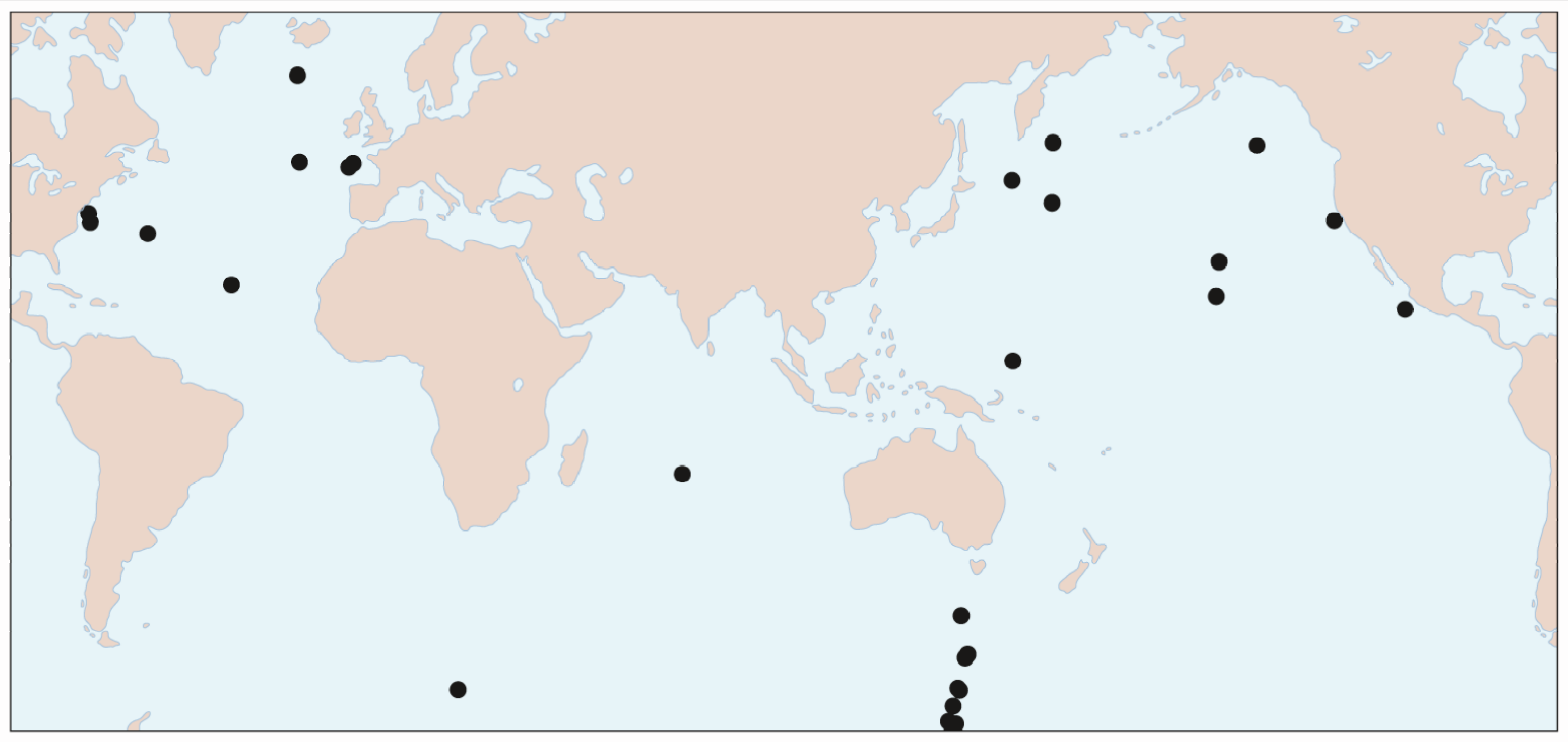
June 26-29, 2007

- 50 meeting participants from 13 countries
- Possible sections led by US, Japan, Canada, Australia, China and Taiwan

Guiding mission

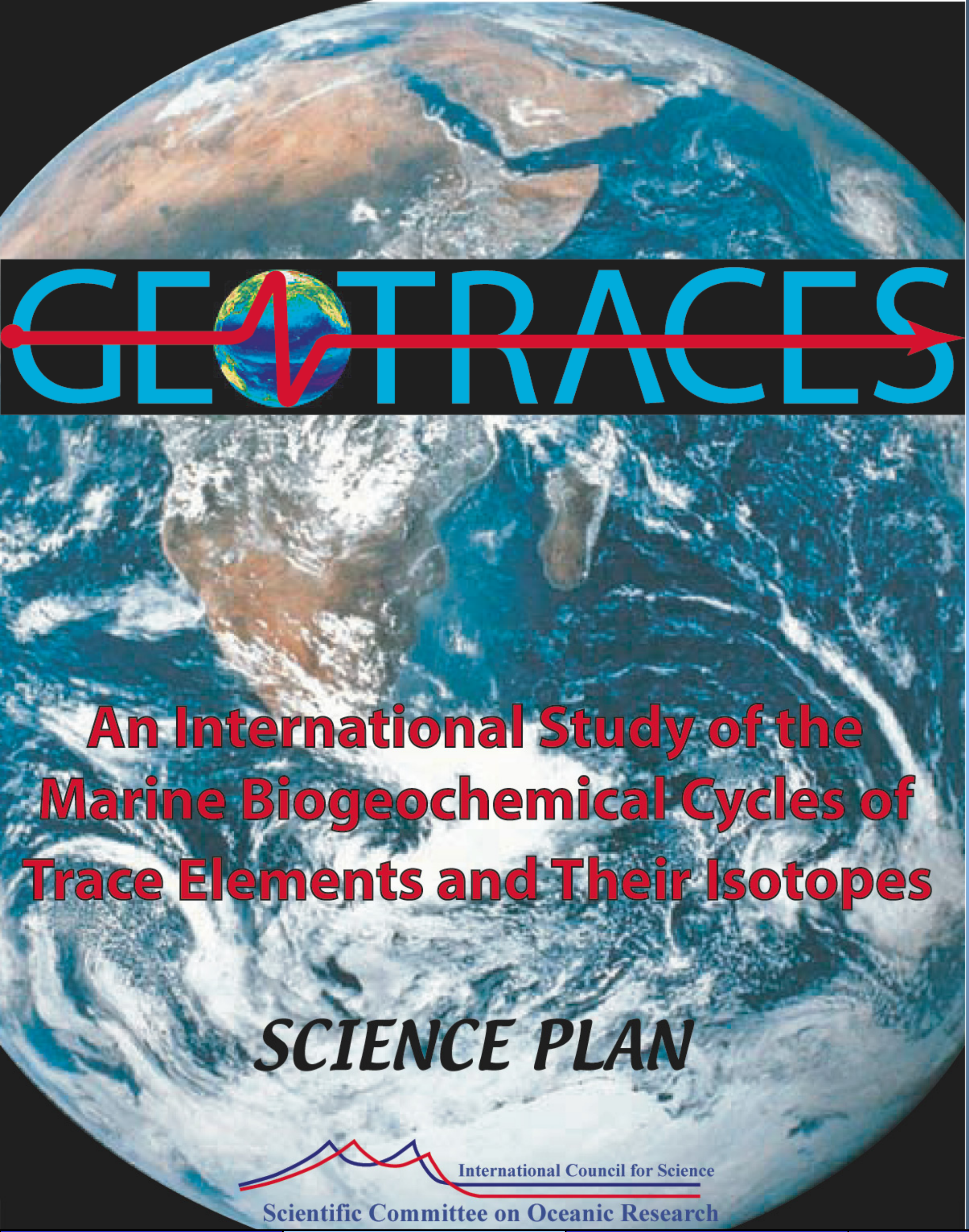
To identify processes and quantify fluxes that control the distributions of key trace elements and isotopes (TEIs) in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions.

Present ignorance: Existing deep ocean Fe data



Paucity of information about deep Fe distribution limits understanding of upwelling supply and internal cycling.

Stations with Fe concentrations at depths > 2000 m.
As of 2003.   From P. Parekh (MIT)



Science Plan

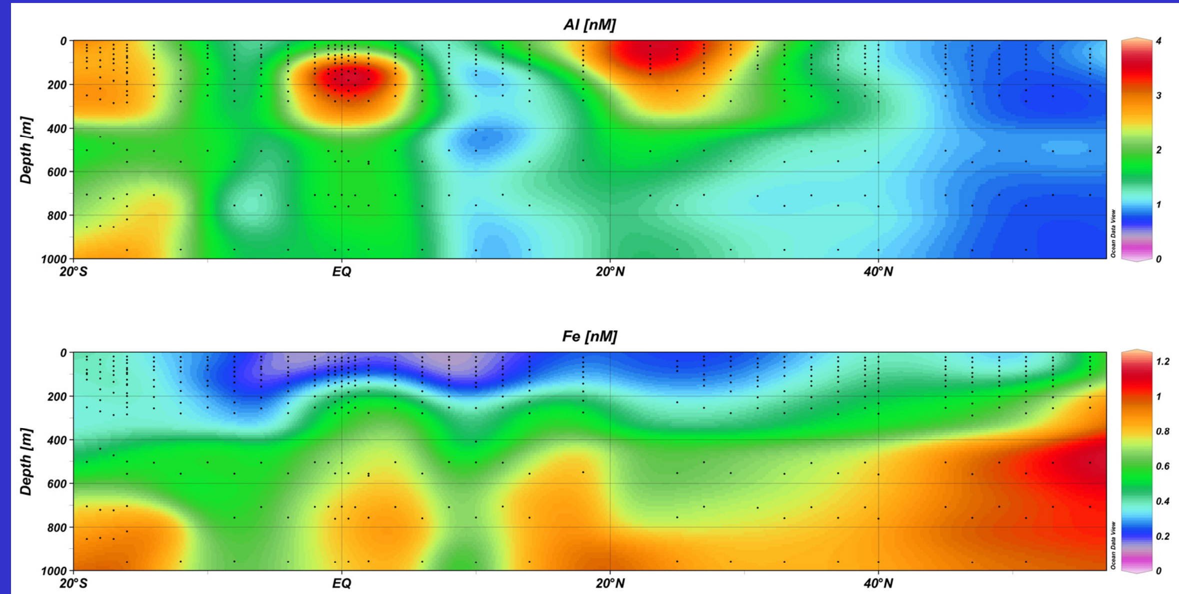
Download PDF from

http://www.geotraces.org/

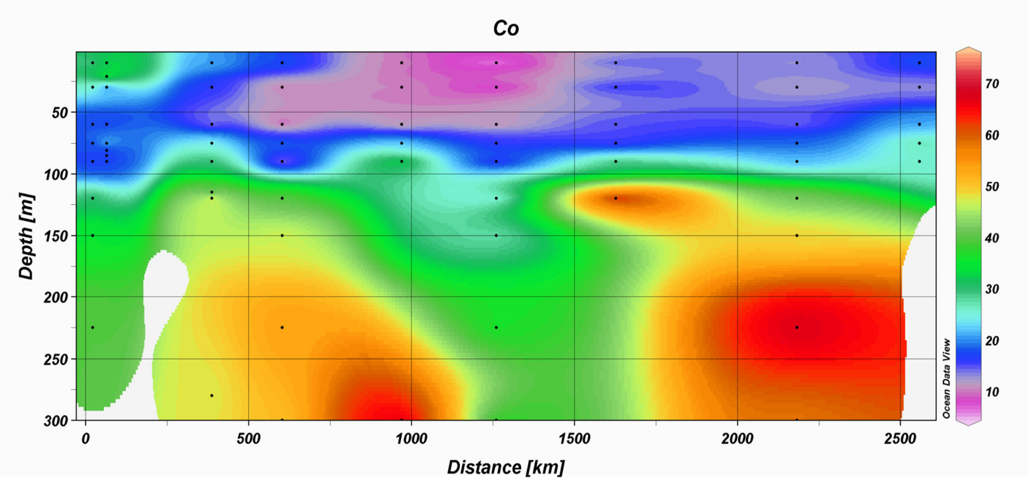
Immediate benefit of GEOTRACES: Focus on analytical methodologies

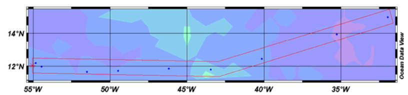
TEI Intercalibrations

Need to be able to process large number of samples with no contamination and high precision and accuracy



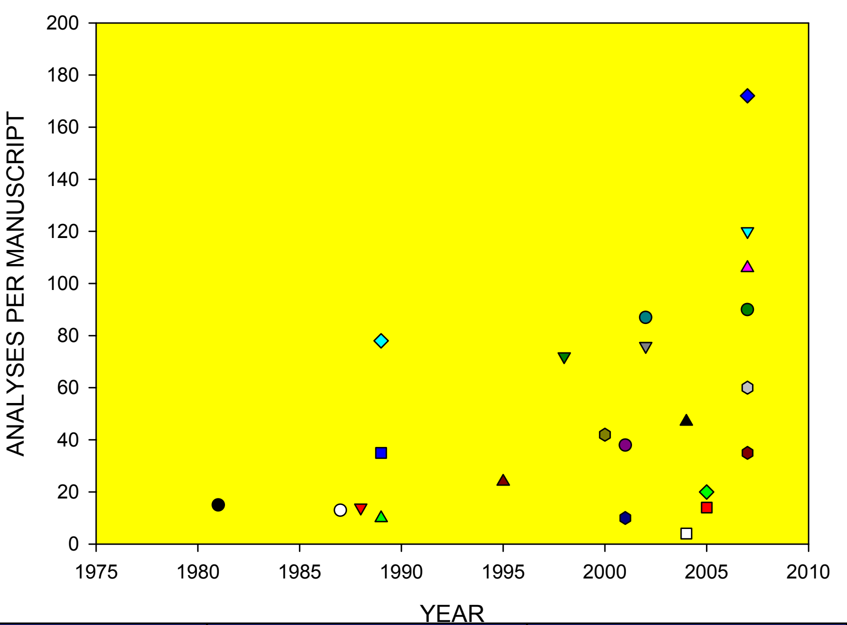
Meridional Pacific, Hiscock, Measures and Landing, unpublished data





Equatorial Atlantic
Saito and Goepfert, Unpublished data

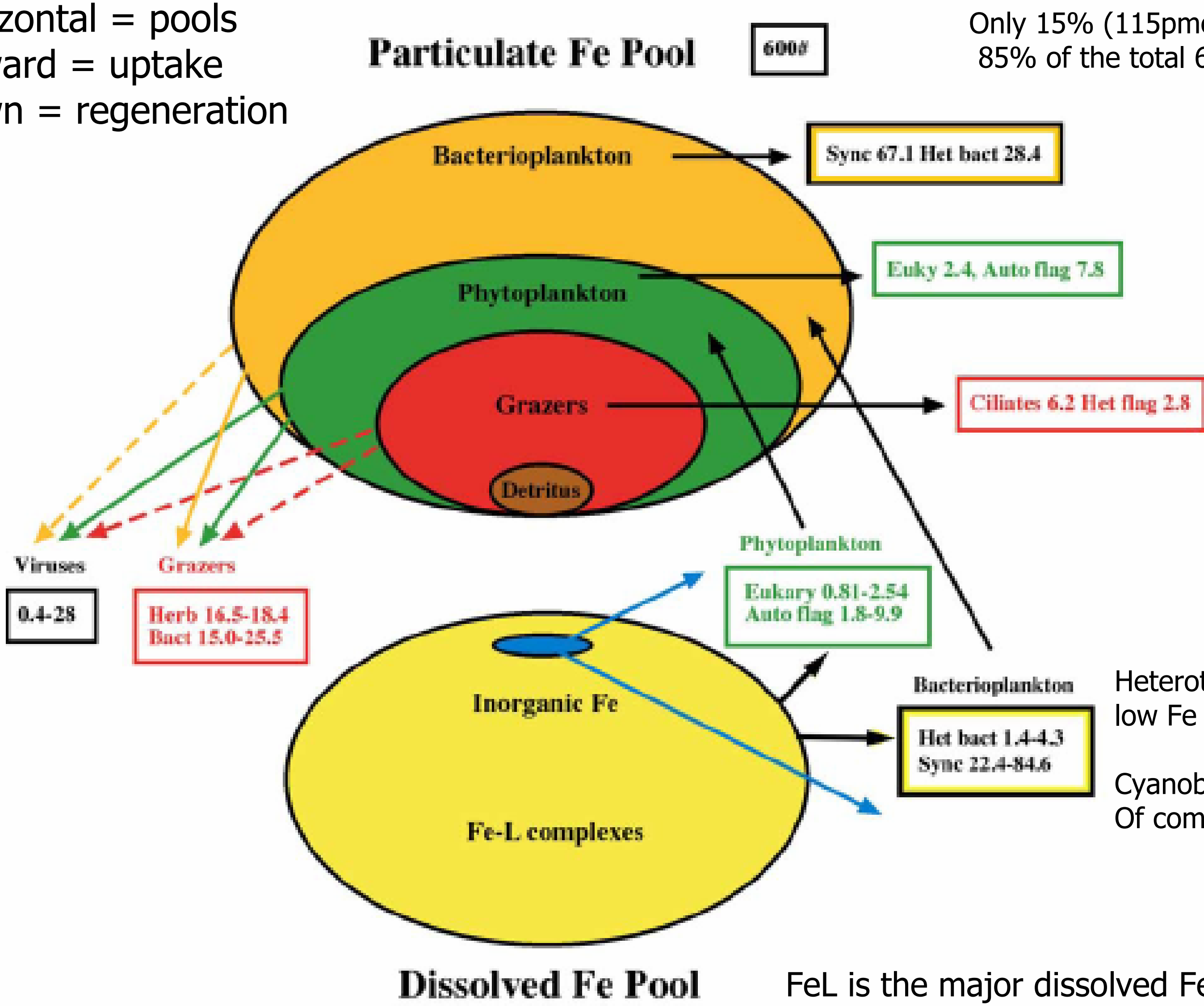
The move towards high-throughput cobalt analysis



Detailed analysis of Iron cycling between biological and chemical reservoirs (FeCycle) (Stzrepek, Maldonado, Higgins, Hall, Safi, Wilhelm, and Boyd, 2005)

Arrows:
Horizontal = pools
Upward = uptake
Down = regeneration

Only 15% (115pmol) of total PFe is biogenic,
85% of the total 600pmol is lithogenic



Heterotrophs have high C biomass
low Fe demand due to slow growth

Cyanobacteria alone account for 83%
Of community uptake

FeL is the major dissolved Fe reservoir

A (Current) Meaning of Bioavailability

"The term bioavailability is often used in an absolute sense when a particular form of a nutrient is either available or not available to an organism. In the case of trace-metal complexes, which dissociate over a finite timescale, the concept of bioavailability must necessarily be tied to kinetics…"
(Morel, Allen, Saito, Treatise on Geochemistry, 2003)

<u>Metal Acquisition in Phytoplankton</u>

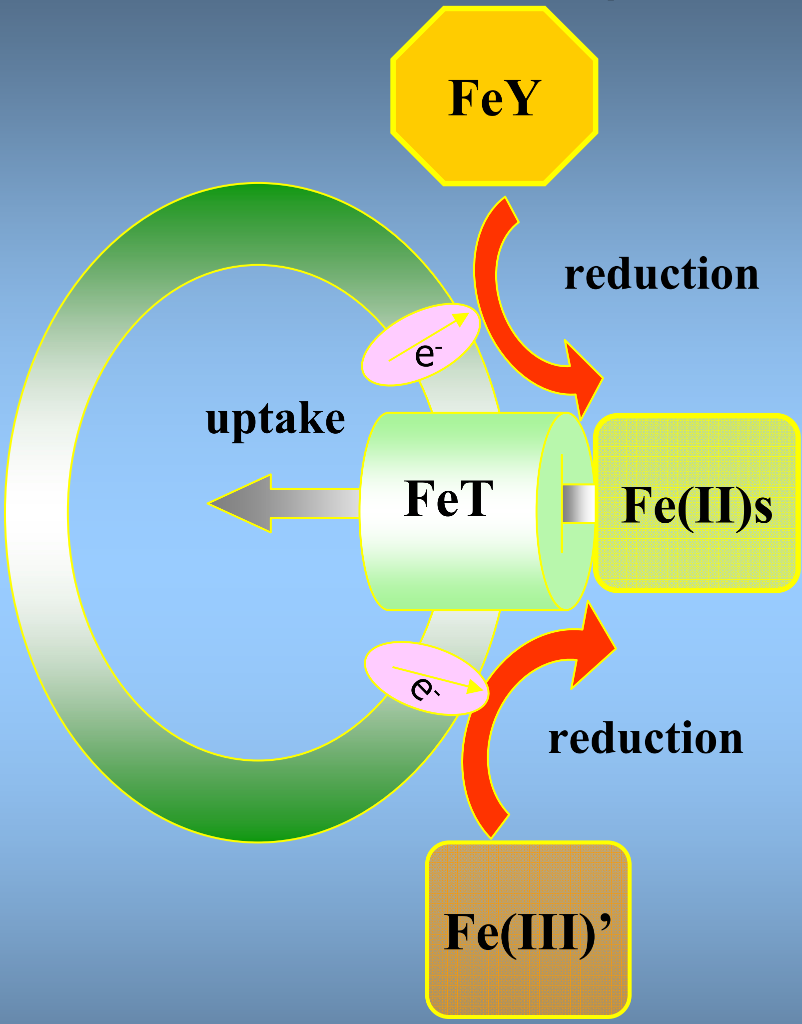
- Free ion (or Fe' model)
- Two Biological strategies to Increase bioavailability (Means to acquire metal-ligand complexes):

1. <u>Siderophore acquisition</u> (oft invoked, yet not found in important marine microbes)
2. <u>Iron Reductases</u> (Armbrust et al., 2004 T. pseudonana Diatom genome paper, Maite Maldonado championed the system with physiological data)

How do marine phytoplankton acquire their metals in the natural environment?

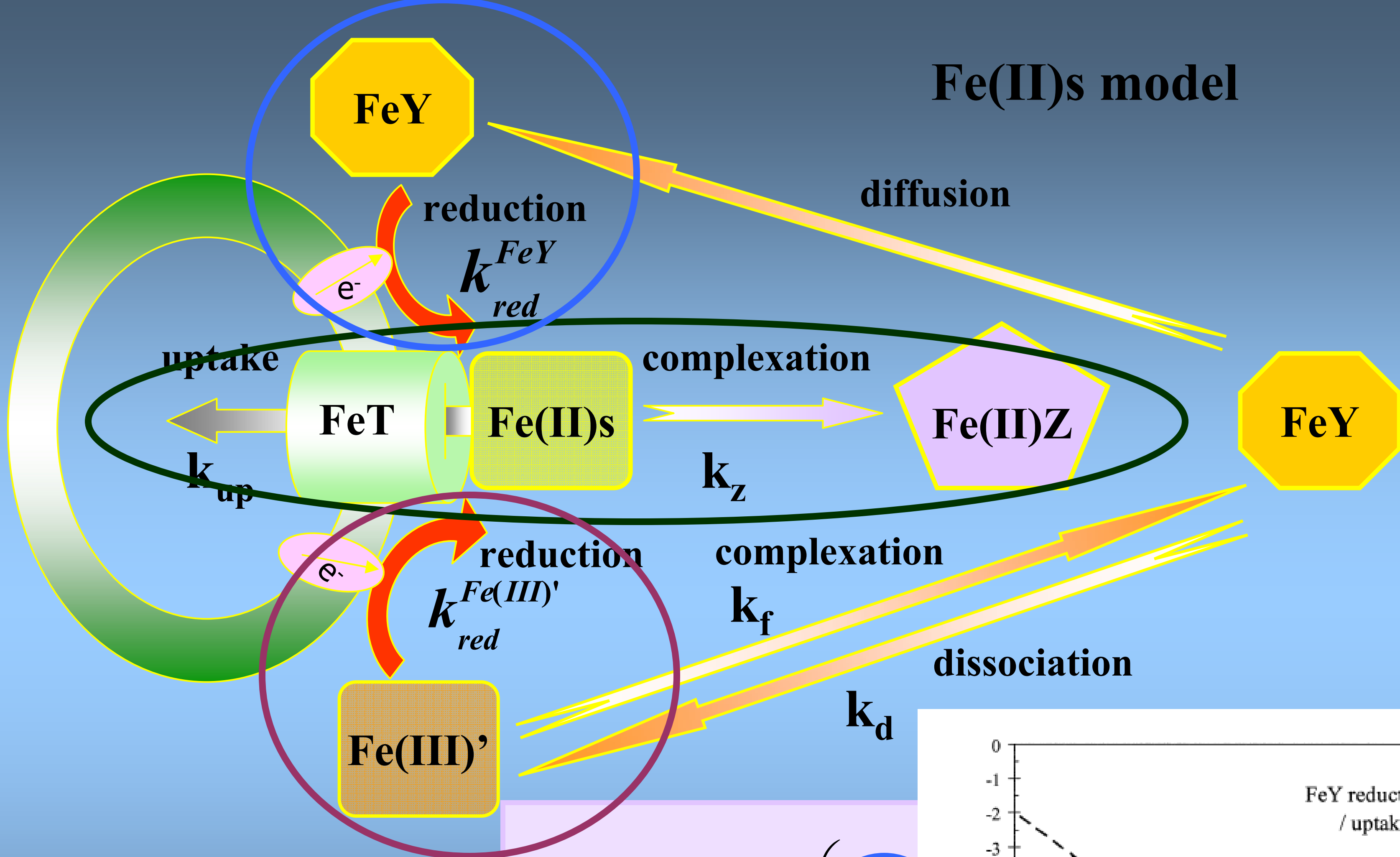
Fe(II)s model

Fe acquisition in Marine Diatoms (*T. weissflogii*)
(Yeala Shaked, Adam Kustka, Francois Morel, 2005)



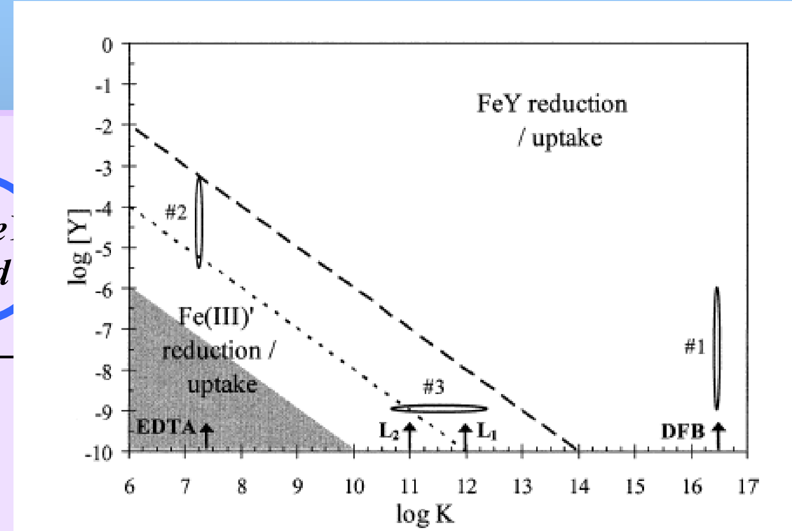
$$uptake(\rho) = k_{up} \times Fe(II)s$$

Fe(II)s model



Reconciles the free ion model (M') with new data on the iron reductase showing how they coexist

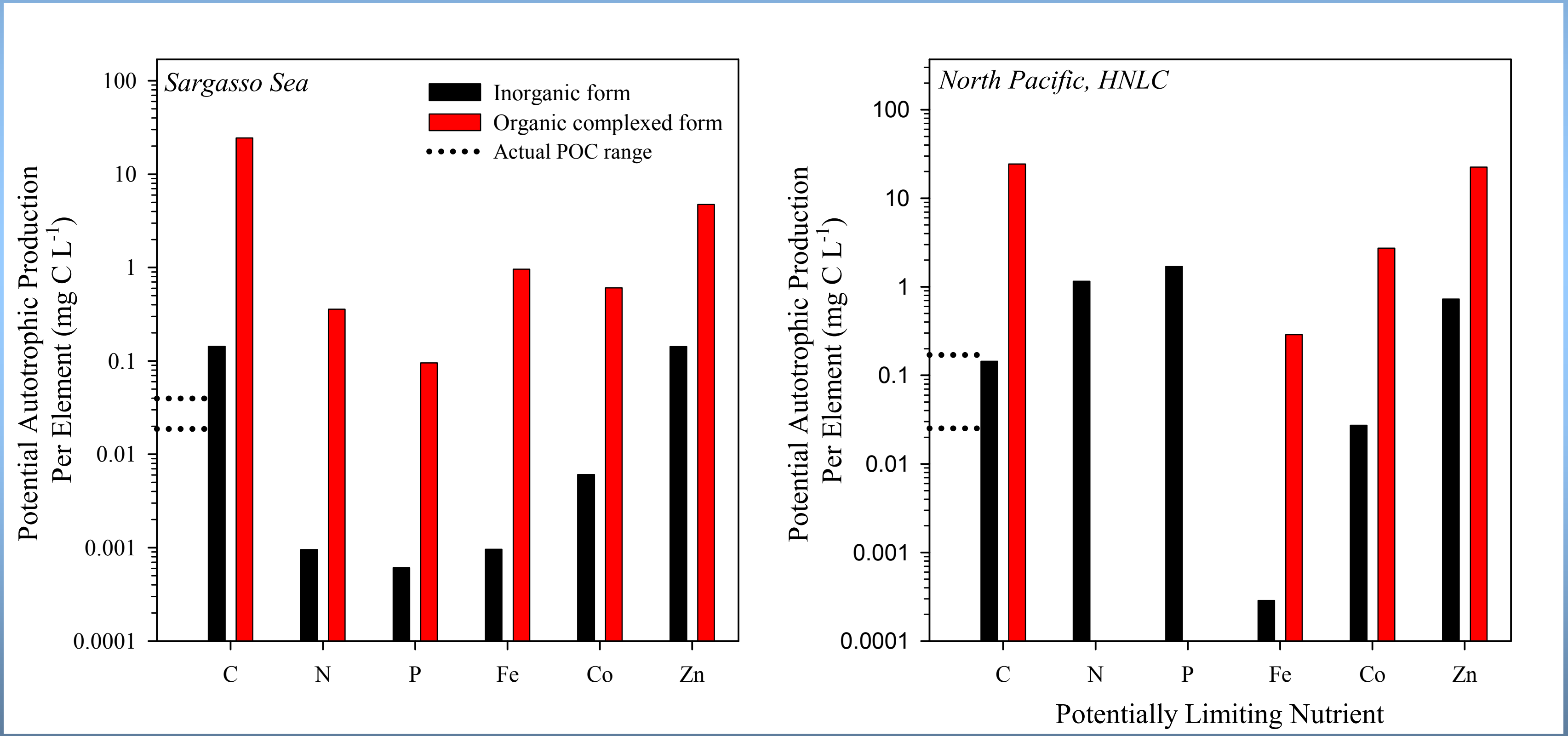
$$uptake(\rho) = \frac{\left(k_{red}^{Fe\ldots} \ldots \right.}{\ldots}$$



How does bioavailability affect productivity?

Lowest bar is limiting (based on cellular quotas and seawater analyses)

FeL is bioavailable, CoL and ZnL are not, Co and Zn can *substitute*



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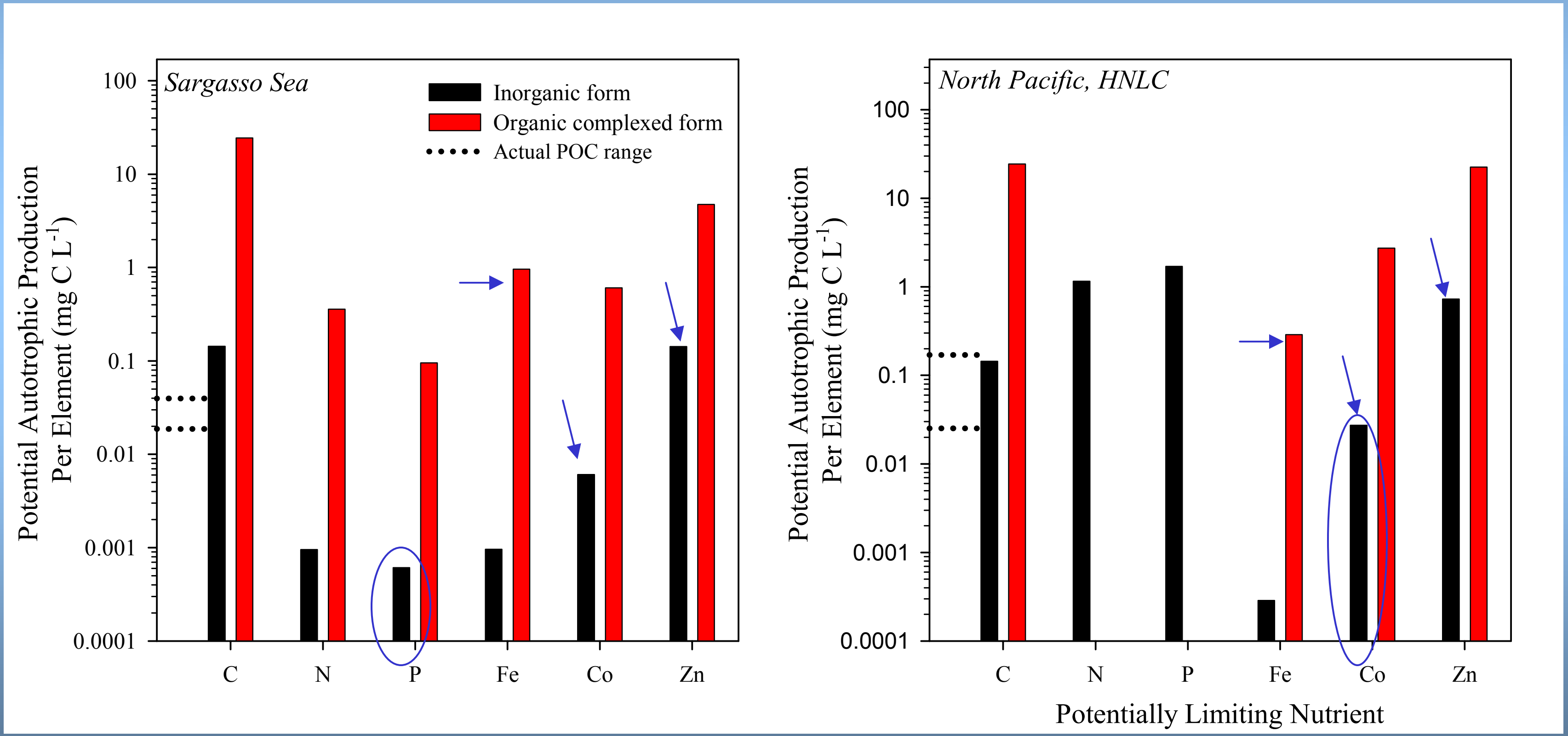
→ Blue arrow indicates "bioavailable form" based on current knowledge



In the Sargasso P (or N) limiting

In the N. Pacific – Co limiting?

How does bioavailability affect productivity?

Lowest bar is limiting (based on cellular quotas and seawater analyses)

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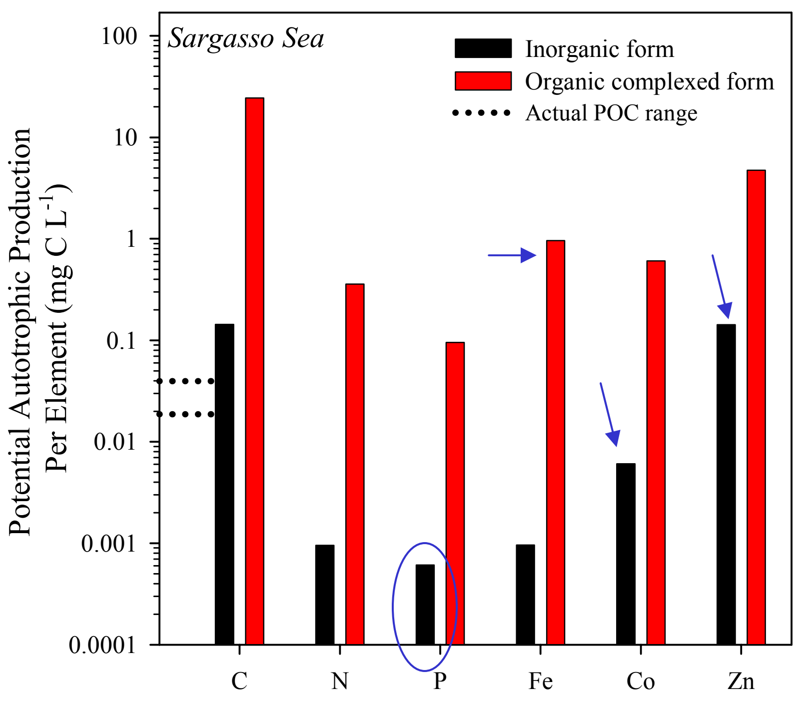
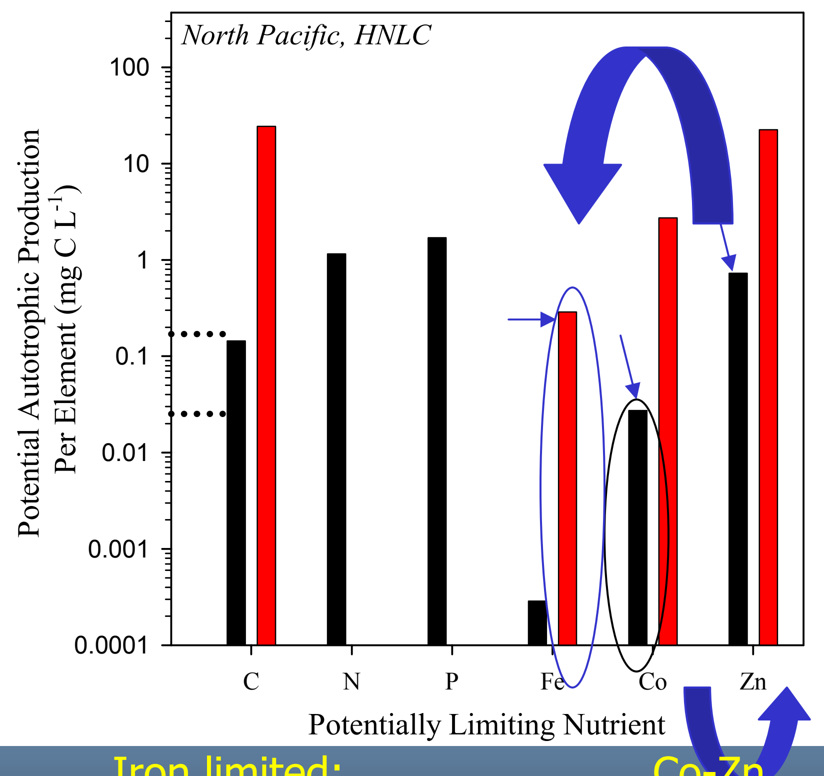


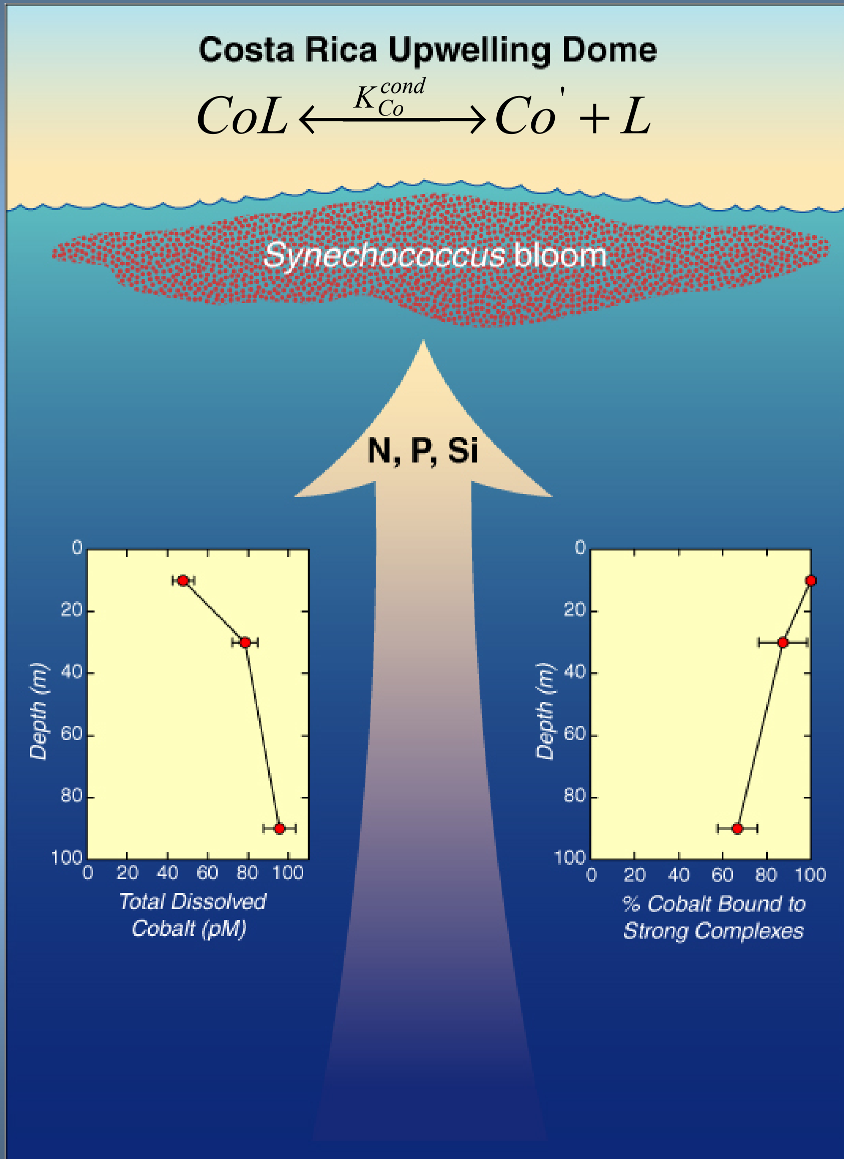


What is the difference between these complexed and uncomplexed forms?

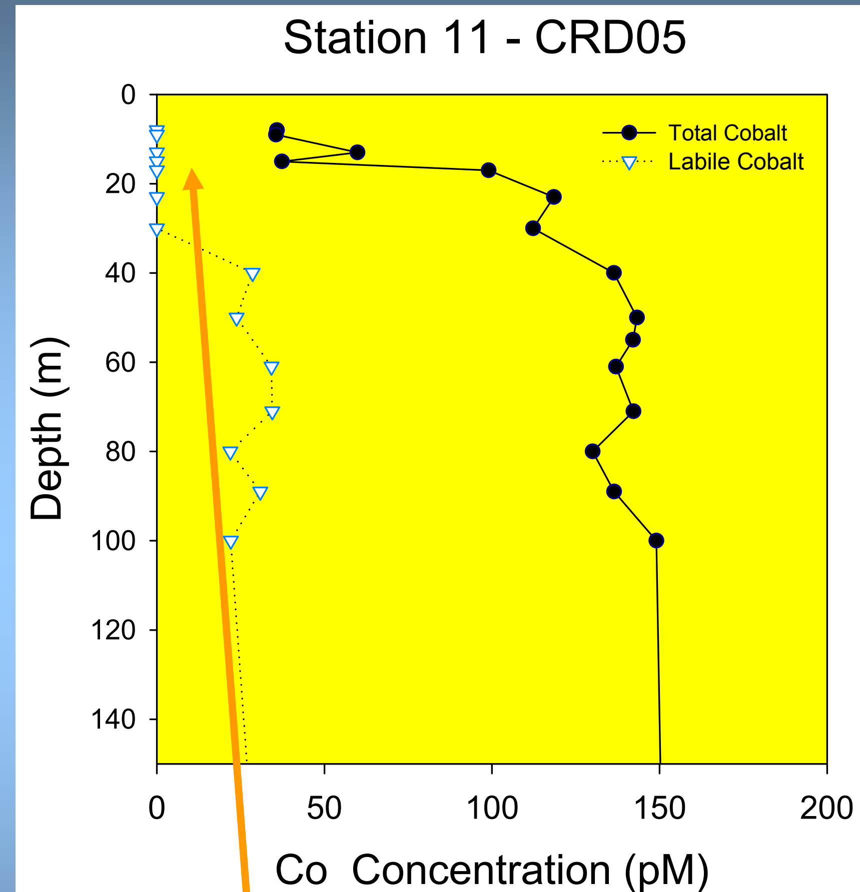
Iron limited: but substitution and bioavailability are key.

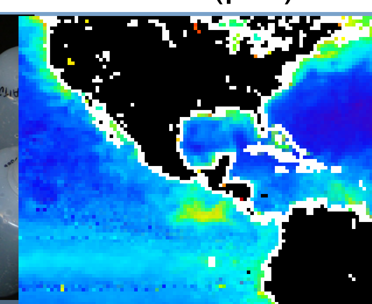
Co-Zn Biochemical substitution

This cyanobacteria-dominated community *is producing cobalt ligands* (filtered control has no cyanobacteria)

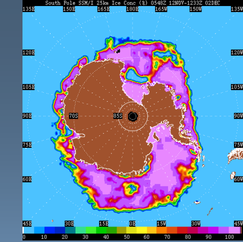


Saito, Rocap and Moffett, 2005





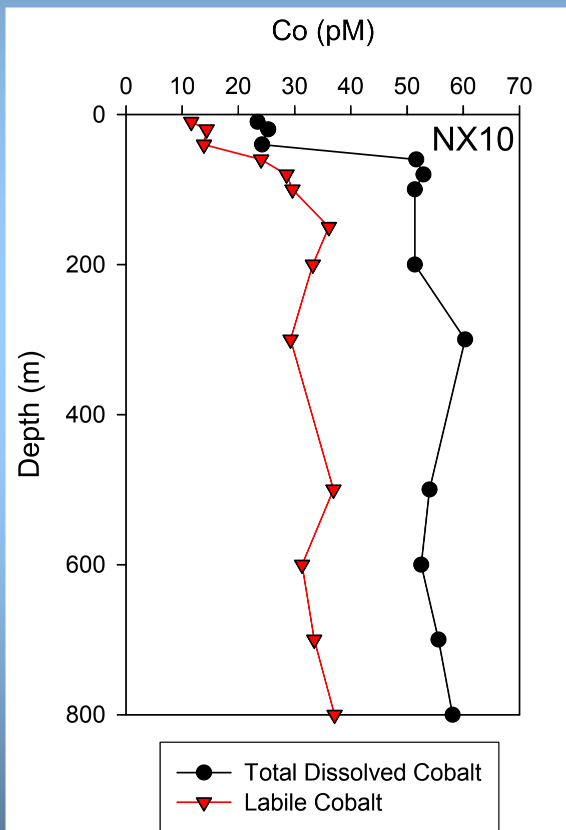
Saito, Noble et al., in prep

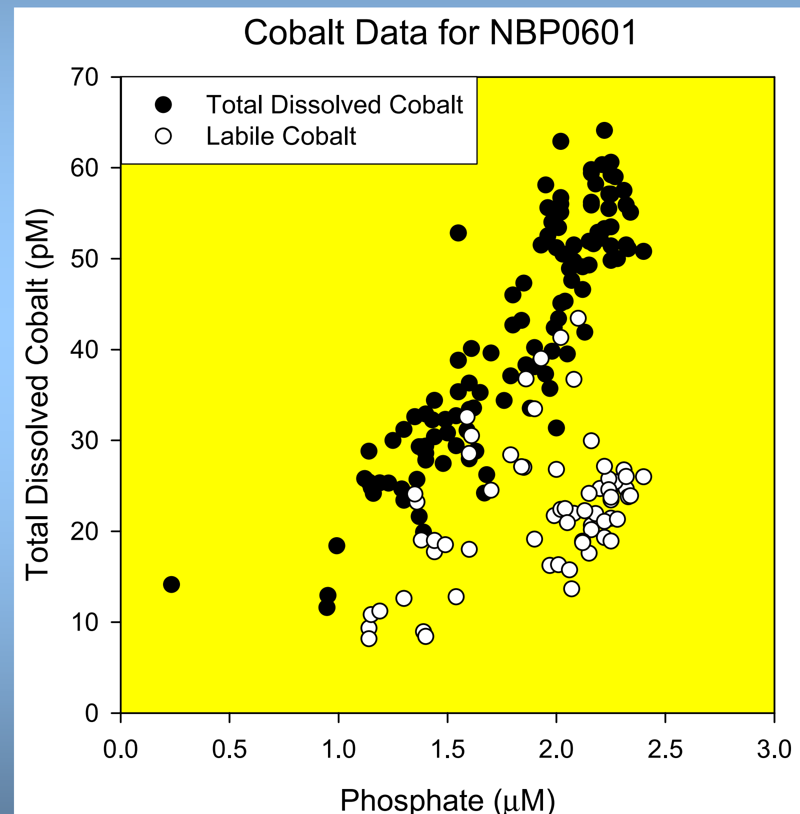


Cobalt speciation is very different in the Ross Sea

Labile cobalt is present *throughout* the water column

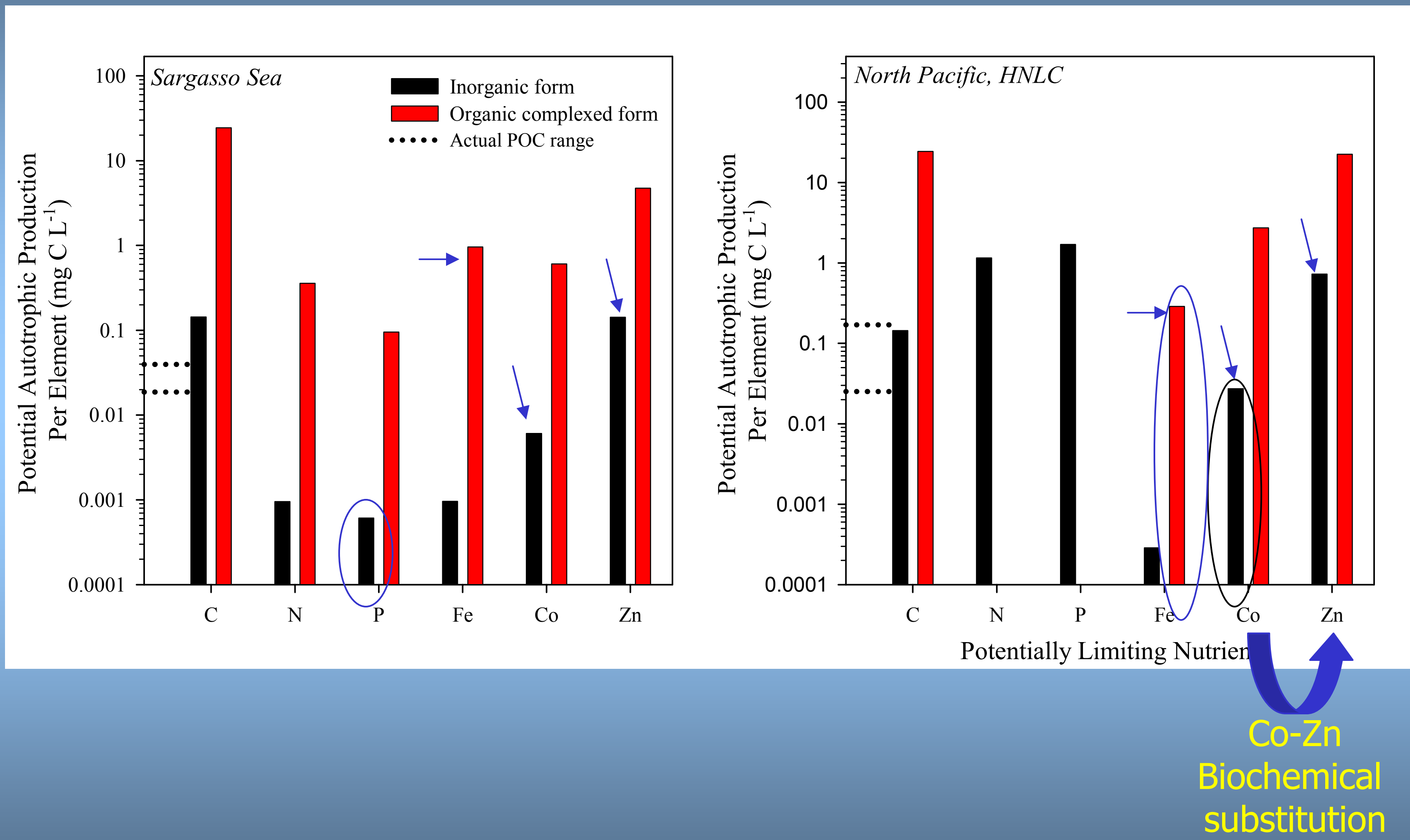
Total Cobalt = CoL + Labile Cobalt





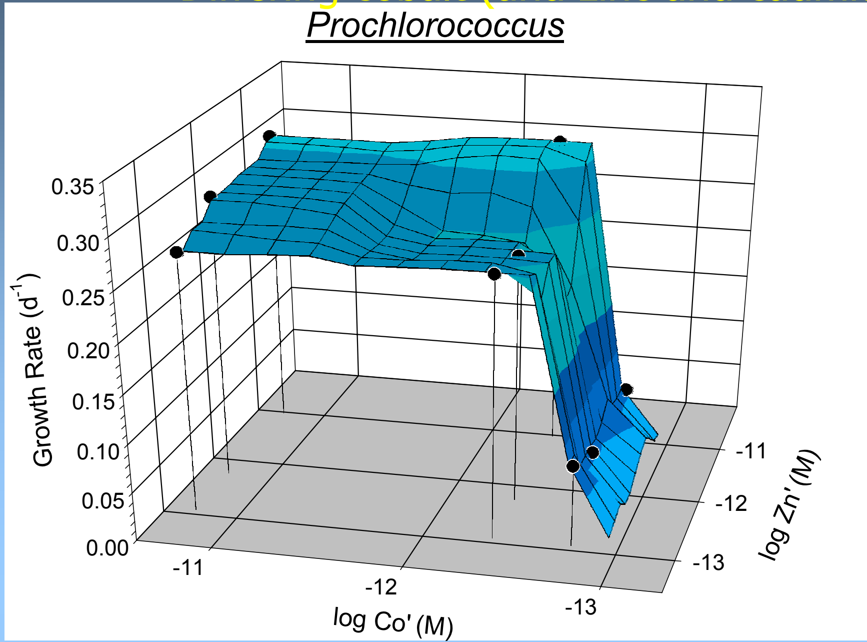
Appears to be true for Cd and likely Zn speciation, large biogeographical differences

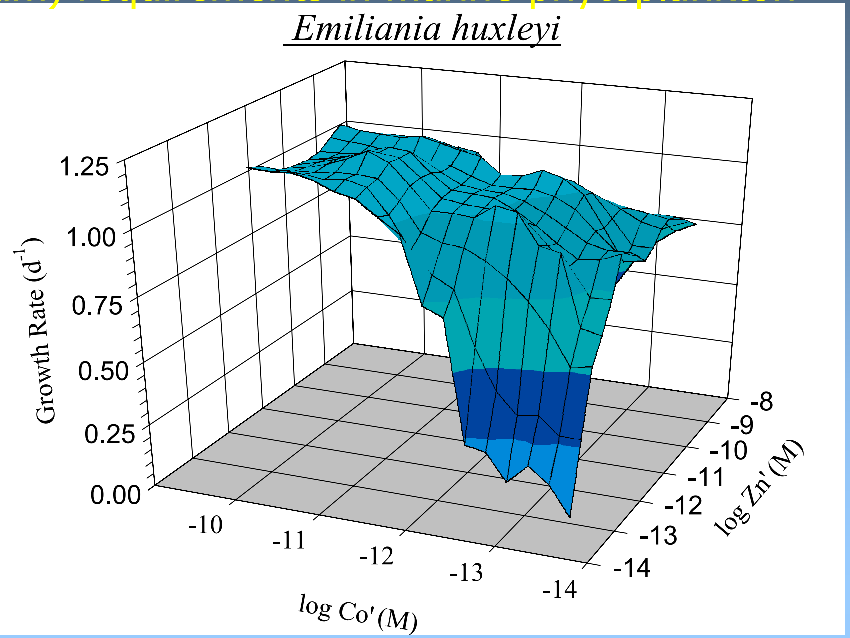
What is "substitution"?
What does it mean for Co-Zn to potential be colimiting primary productivity?



The Micronutrients: Co, Cd, Zn, and B_{12}

Differing cobalt (and zinc and cadmium) requirements in marine phytoplankton

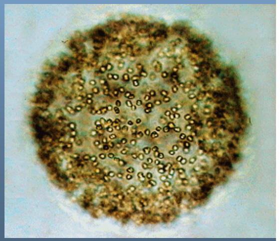


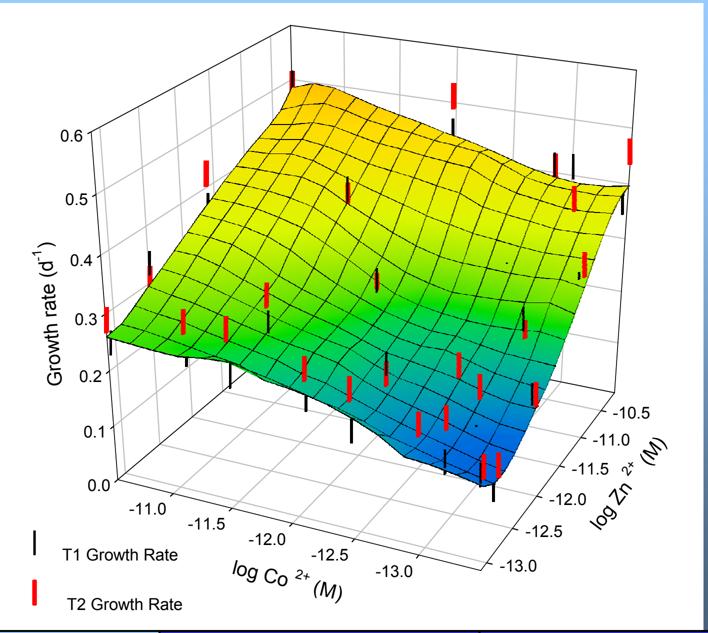


Cobalt, cadmium and zinc – A trace metal trio:

- Biochemical substitution in diatoms *but not the cyanobacteria*
- Due to at least 2 carbonic anhydrase enzymes

- *Phaeocystis antarctica:* →
  Co-Zn substitution is a *Global* Phenomenon
  Seems to have evolved in blooming populations with rapid C and metal depletion





Saito et al, Limnology and Oceanography, 2002
Data for *E. huxleyi* from Sunda and Huntsman 1995
Phaeo data - Saito and Goepfert, In Press L&O

Examples of nutrient colimitation pairs in the marine environment

Nutrient Couple		Co-Limitation Type
Zinc and Cobalt (Cyanobacteria)	0 or I	Only one nutrient/ Independent
Nitrogen and Phosphorus	I	Independent
Nitrogen and Light	I	Independent
Nitrogen and Carbon	I	Independent
Iron and Cobalt	I	Independent
Iron and Zinc	I	Independent
Iron and Phosphorus	I	Independent
Iron and Vitamin B_{12}	I	Independent
Zinc and Cobalt (Eukaryotic Phytoplankton)	II	Biochemical substitution (CA)*
Zinc and Cadmium (Diatoms)	II	Biochemical substitution (CA)*
Copper and Zinc	II	Biochemical substitution (SOD)*
Zinc and Cobalt (hypothesized)	II	Biochemical substitution (AP)*
Light and Iron	III	Dependent
Zinc and Phosphorus	III	Dependent (AP)*-
Cobalt and Phosphorus	III	Dependent (AP)*
Zinc and Carbon	III	Dependent (CA)*
Cobalt and Carbon	III	Dependent (CA)*
Cadmium and Carbon	III	Dependent (CA)*
Iron and Copper	III	Dependent (FRE and MCO)*
Iron and Nitrogen (N_2 fixation)	III	Dependent (NIF)*
Molybdenum and Nitrogen (N_2 fixation)	III	Dependent (NIF)*
Nickel and Urea (Nitrogen)	III	Dependent (Urease)

Green - Have been observed in iron limited regions

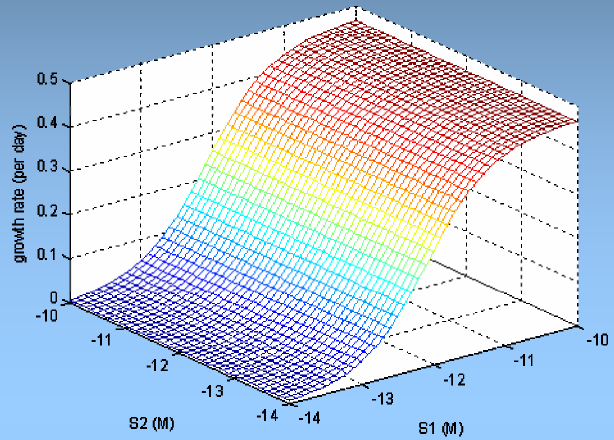
Red – typical example of colimitation type

(Saito, Goepfert and Ritt, in Press at Limnology and Oceanography)

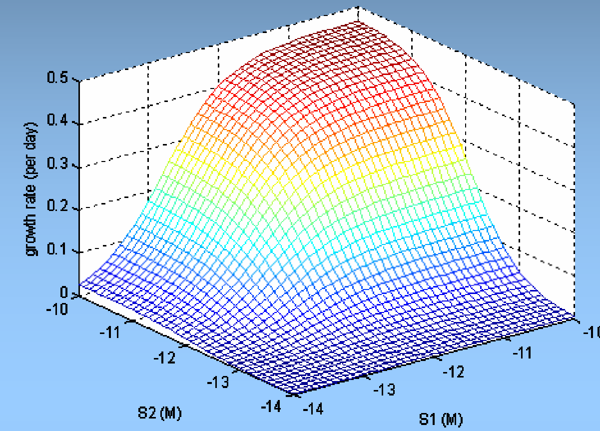
Connecting bioinorganic chemistry to the concept of colimitation

(Saito, Goepfert and Ritt, in Press at L&O)

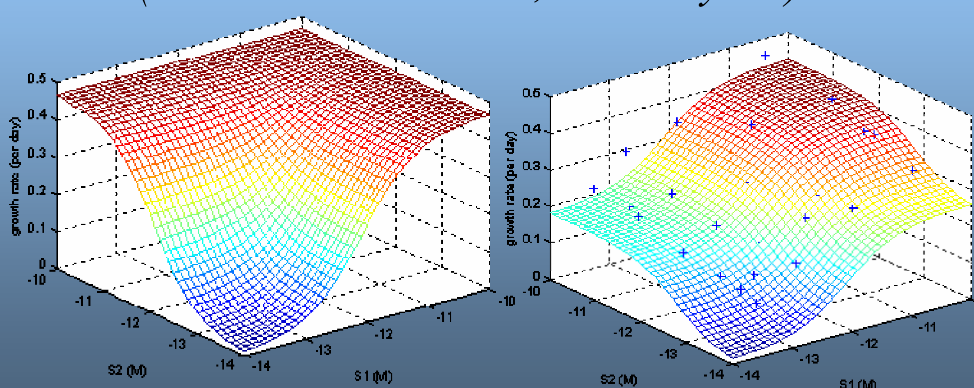
Type 0.
No Colimitation
(Co & Zn in cyanos)



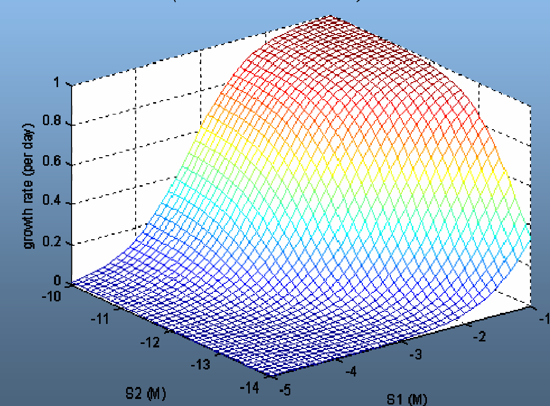
Type I.
Colimitation Between Two Independent Nutrients
(N &P)



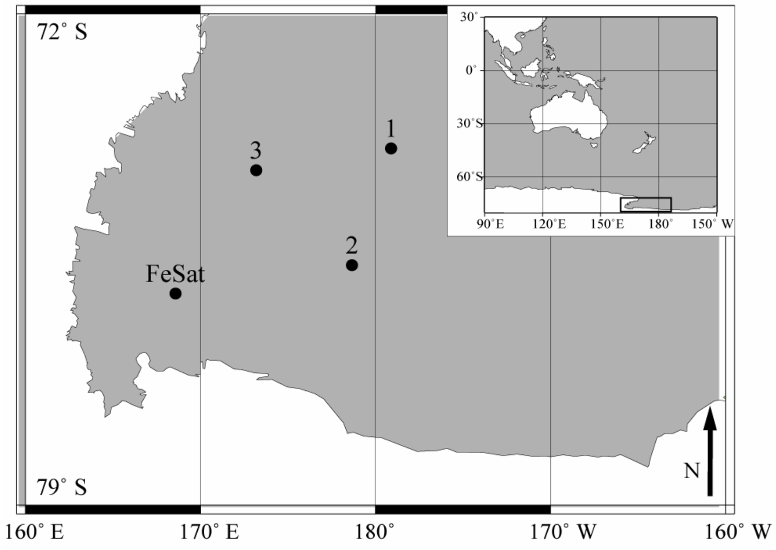
Type II.
Colimitation with Biochemical Substitution
(Co & Zn in diatoms, Phaeocystis)



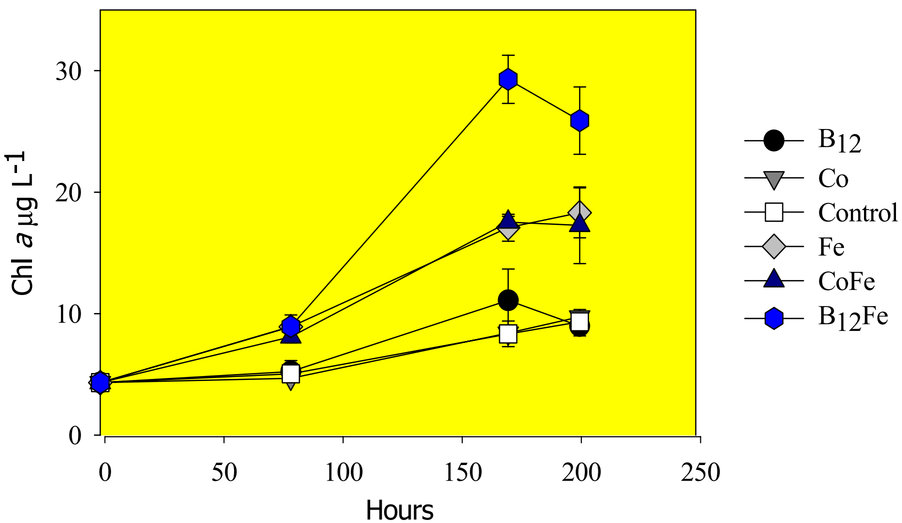
Type III.
Colimitation Between Two Dependent Nutrients
(Zn and C)

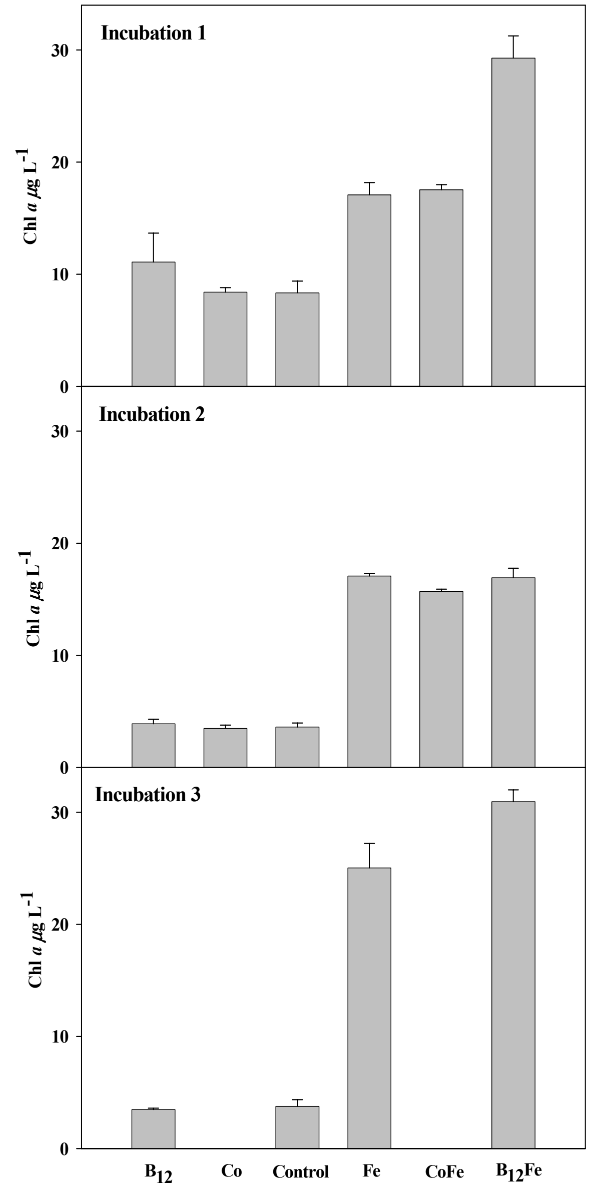


Example: Vitamin B_{12} and Fe colimitation of phytoplankton growth in the Ross Sea



B_{12}-Fe co-limitation in the Ross Sea



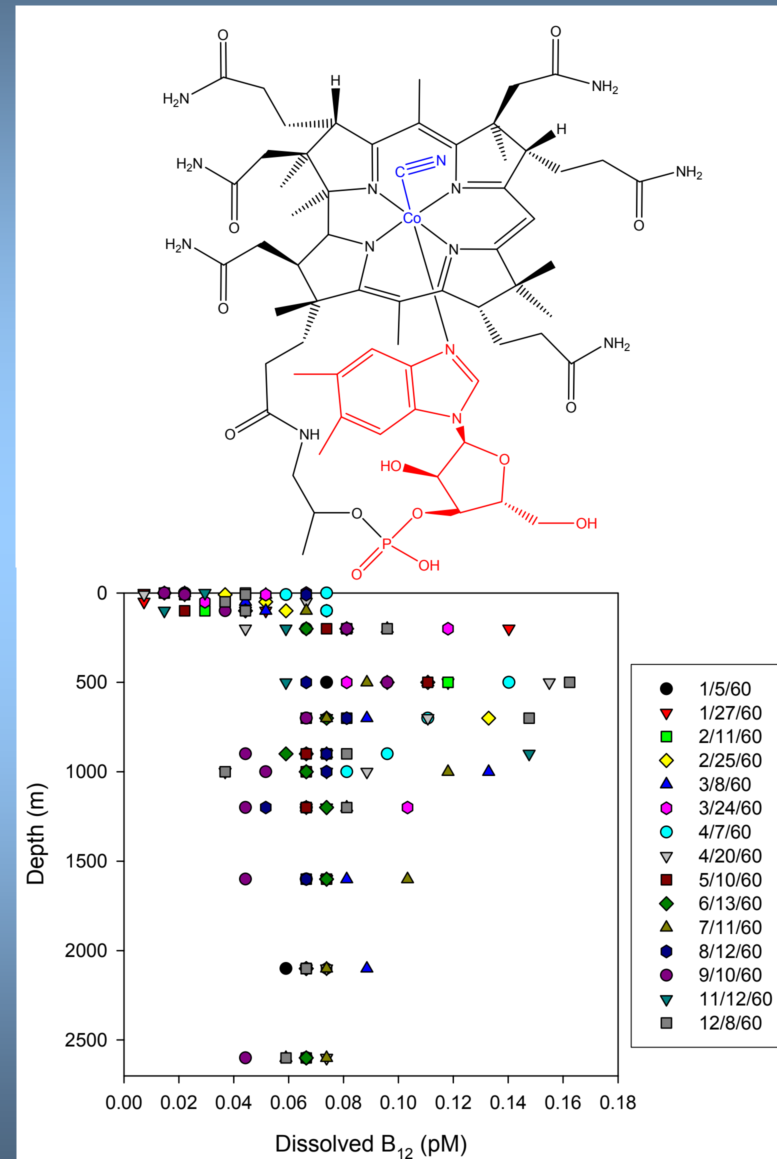


Bertrand, Saito, Rose, Riesselman, Lohan, Noble, Lee, DiTullio – L&O 2007

Also other B12 studies: Sanudo-Wilhelmy et al GRL 2006 (Long Island), Panzeca et al., 2007 EOS

The B_{12} biogeochemical cycle

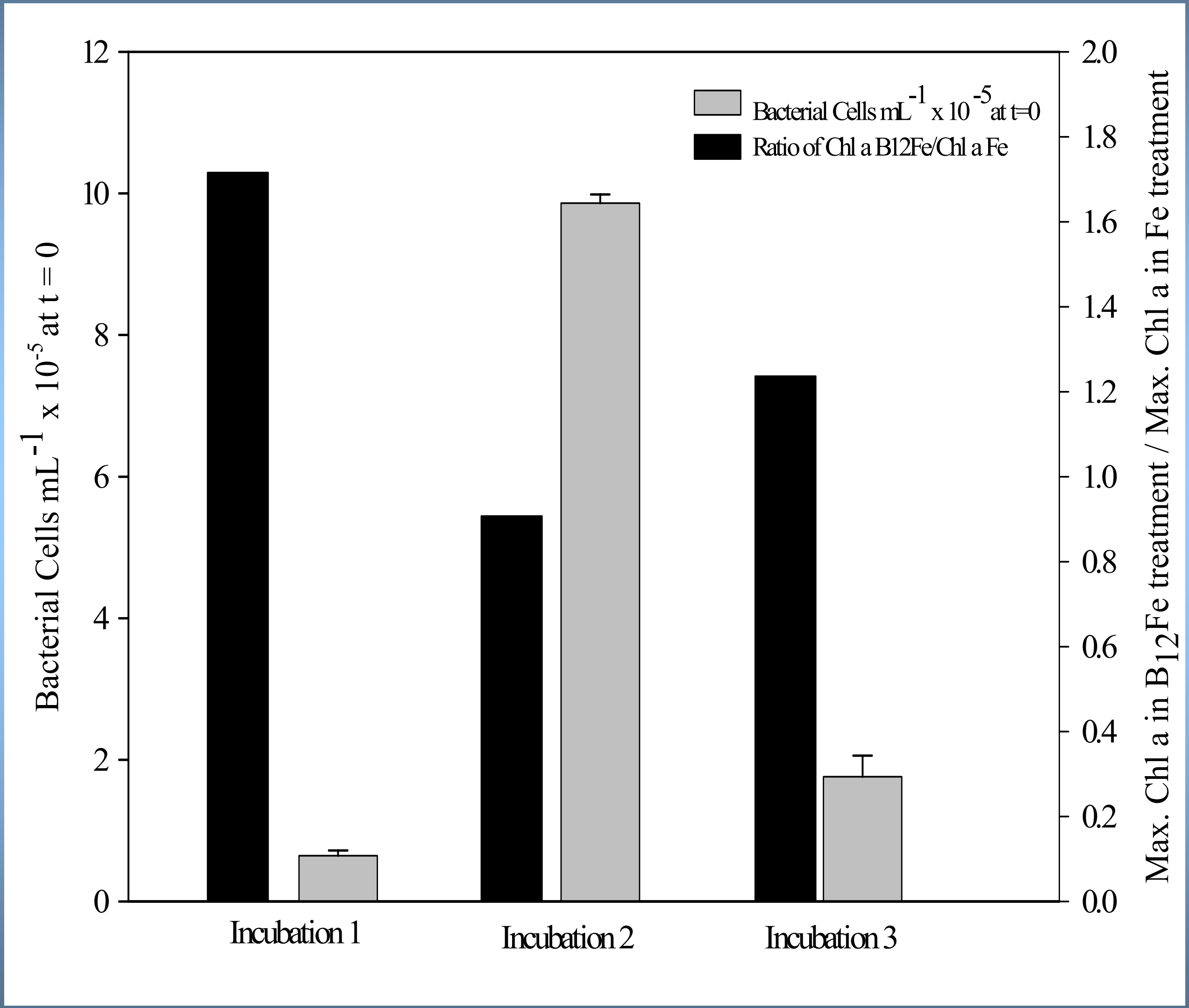
- Synthesized by many Bacteria and Archaea *but not* by Eukaryotes
- An Ancient Biomolecule (Scott, 1990)
- Very low seawater concentrations < picomolar (Menzel and Spaeth, 1962)
- A minor (but crucial) component of Co biogeochemical cycle?



(Complied from Menzel and Spaeth, 1962)

What is the cause of spatial variability of B_{12} stimulation in the Ross Sea?

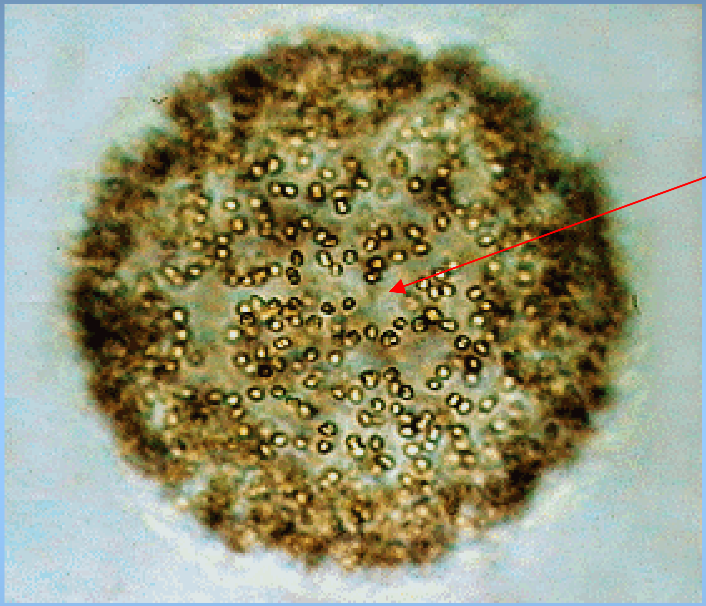
Hypothesis: related to biosynthesis - heterotrophic bacteria abundances

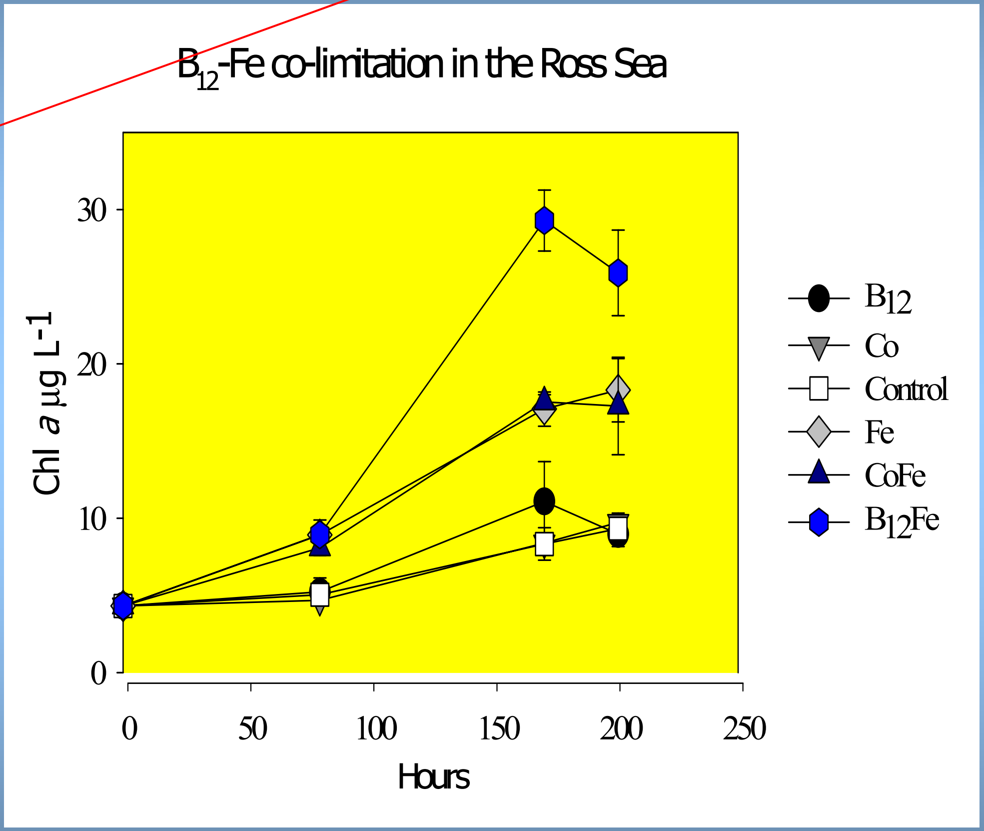


Bertrand, Saito, Rose, Riesselman, Lohan, Noble, Lee, DiTullio – 2007 Limnol Oceanogr

B_{12} Tuning effect: B_{12} addition favored diatoms

Phaeocystis colonies carry their own source: mucilage-filled center loaded with bacteria





- *Phaeocystis* responded to Fe treatments
- Diatoms responded to B_{12} Fe more the Fe

The problem of studying colimitation

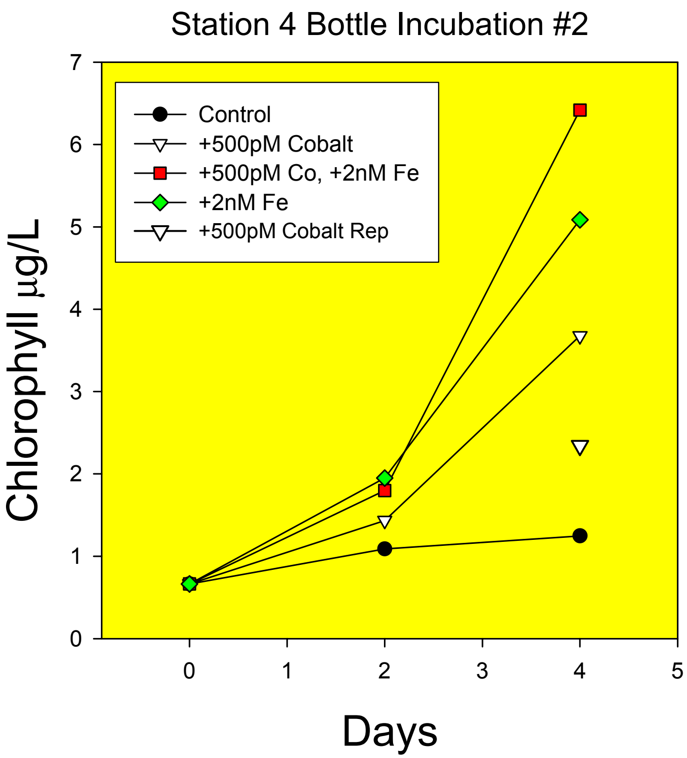
- To understand colimitation we need to understand:
  - Natural concentrations of nutrients
  - Bioavailability of *all* relevant nutrients
  - Bioinorganic chemistry of key biochemistries

Field incubation experiments are like **sledgehammers**, powerful enough to detect primary limitation, but likely not nimble enough to detect colimitation?

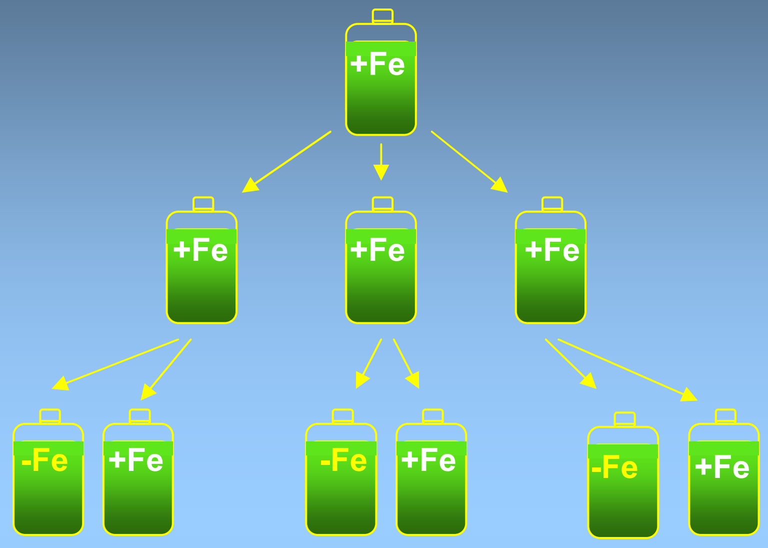
- need molecular diagnostics

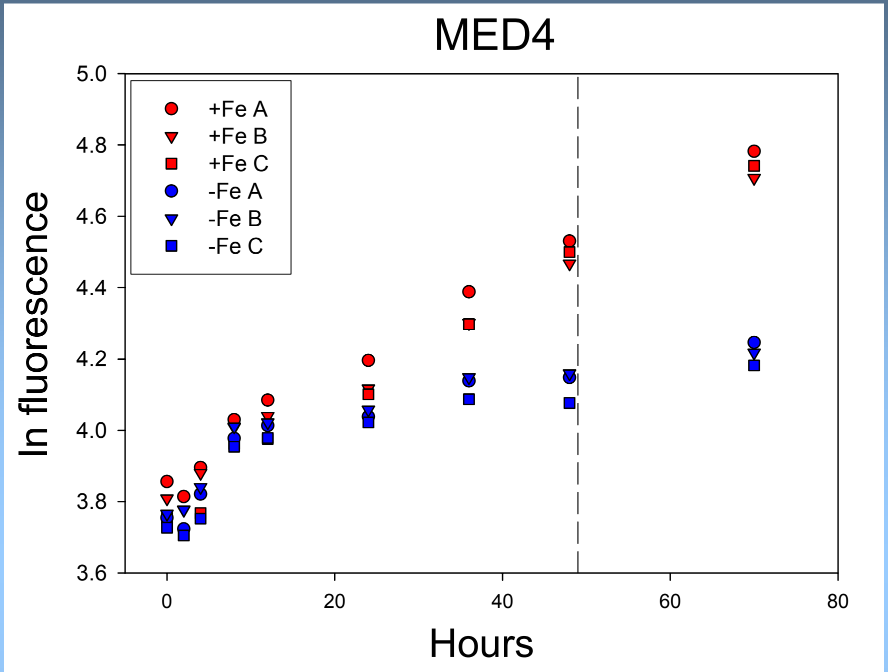
- e.g. carbonic anhydrase system

- e.g. iron bioavailability



MED4 whole-genome response to iron starvation

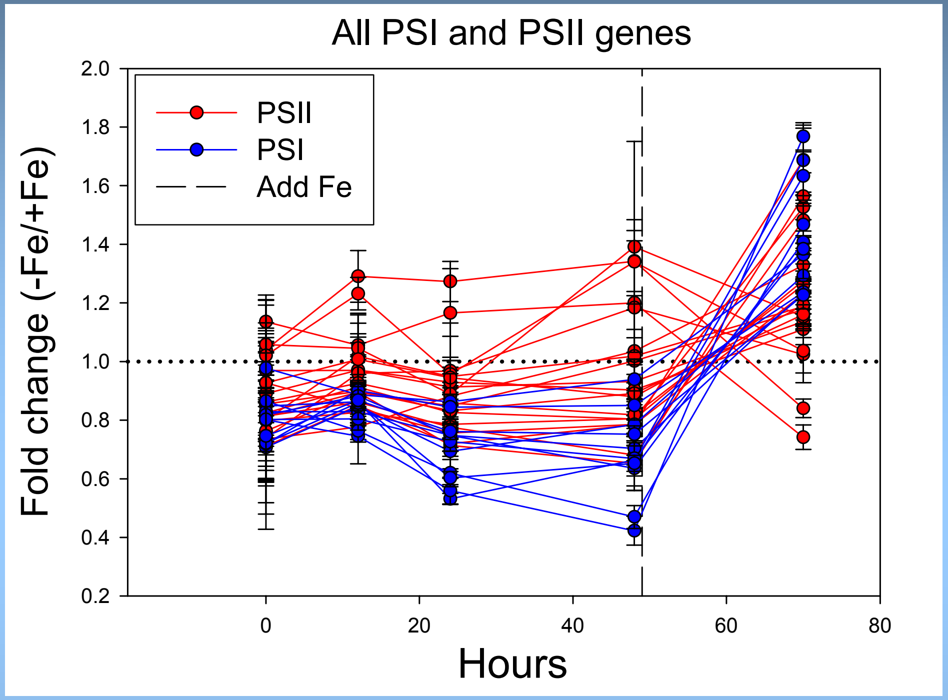


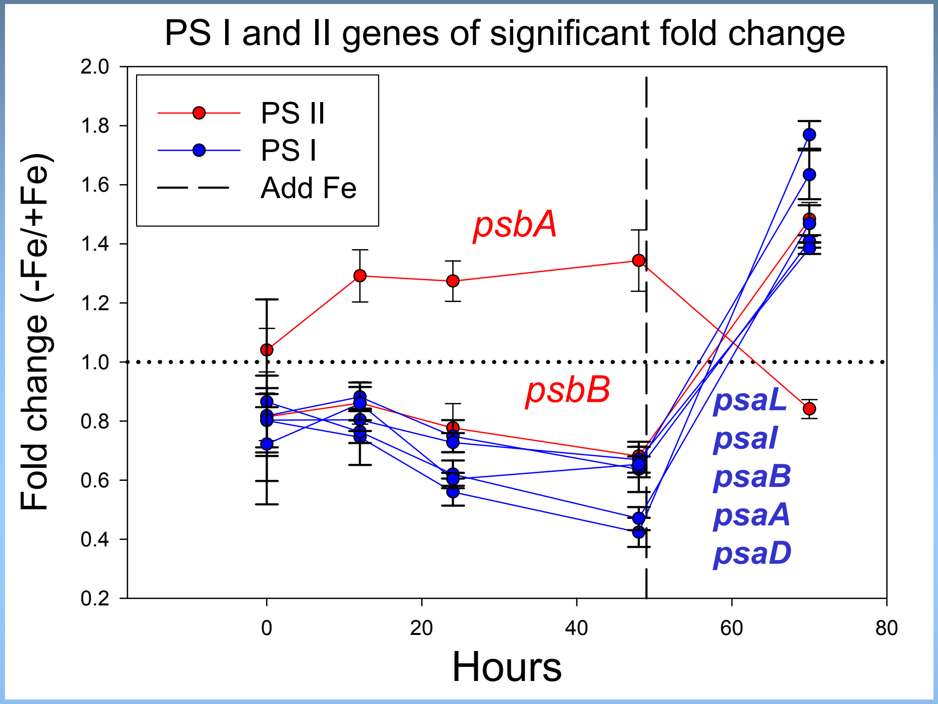


- Custom Affymetrix DNA micro-arrays
- p-values (false positive rate) using Cyber-T (Baldi and Long 2001)
- q-values (false discovery rate) using QVALUE (Storey and Tibshirani 2003)

On-going thesis work of Anne Thompson, co-advised by Chisholm and Saito

Photosynthesis genes – PS I and PS II



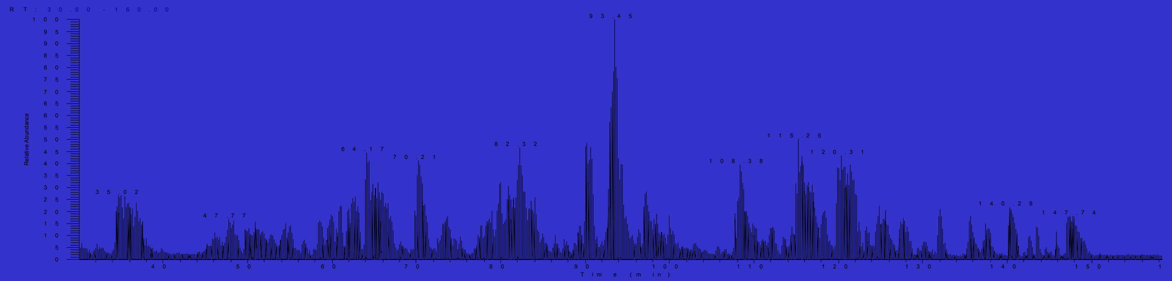


Significant genes are q<0.05 in at least 3 time-points

PSI (12 Fe) PSII (2-3Fe) - Raven et al. 1999

Nutrient Stress Biomarkers in Marine Cyanobacteria (*Synechococcus* WH8102) analyzed by Whole Proteome Mass Spectrometry (Saito and Bertrand in prep)

Full Proteome Mixture: mass spectra on whole cells, 12000 spectra, Identification of ~370 unique proteins in the Proteome



Protein:

```
MLFILNKLVK LRRTVSALVL AIGALLGACS GPETTSQIGV YSGRHYNSDK
DLYERFTEAT GIQVKLLEAK DDALIERLNT EGDDSPADVL ILADVARLDR
AAGMNLFQTV DSDALNQAVP RDLRDSEGRW FGLTRRLRAP MFNADRVNAE
QVSSYGALAD PSLKGKLCLR NRRSVYNQSL VAFMLDEQGQ AATEDWIKGI
VNNLAEPVFS SDTPMIRAVA QGQCGVALAN SYYLGRMQAG DKGEADRSLS
GKVTVRWPDP VHVNITGGGV TRASRNPEAA QRLLEFLSSD QAQGGYAAAN
HEYPLKGIGE DPVLQAWGPF NQAKVSAERL GELNAQALEL MAANGWQ
```

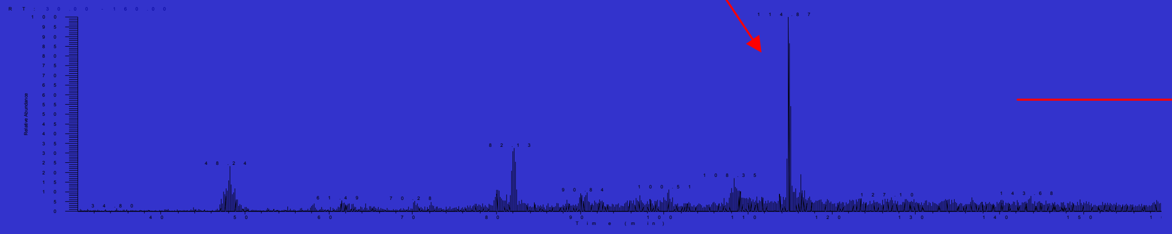
Protein Coverage:

Sequence	MH+	% Mass	AA	% AA
FTEATGIQVK	1093.59	2.90	56 - 65	2.88
LNTEGDDSPADVLILADVAR	2084.05	5.53	78 - 97	5.76
AAGMNLFQTVDSDALNQAVPR	2218.09	5.89	101 - 121	6.05
VNAEQVSSYGALADPSLK	1848.93	4.91	147 - 164	5.19
GIVNNLAEPVFSSDTPMIR	2060.05	5.47	199 - 217	5.48
AVAQGQCGVALANSYYLGR	1940.96	5.15	218 - 236	5.48
WPDPVHVNITGGGVTR	1704.88	4.53	257 - 272	4.61
LLEFLSSDQAQGGYAAANHEYPLK	2622.28	6.96	283 - 306	6.92
LGELNAQALELMAANGWQ	1928.95	5.12	330 - 347	5.19
Totals:	17349.65	46.05	165	47.55

idiA is a protein that is known to indicate iron stress in cyanobacteria (Webb et al., 2003)

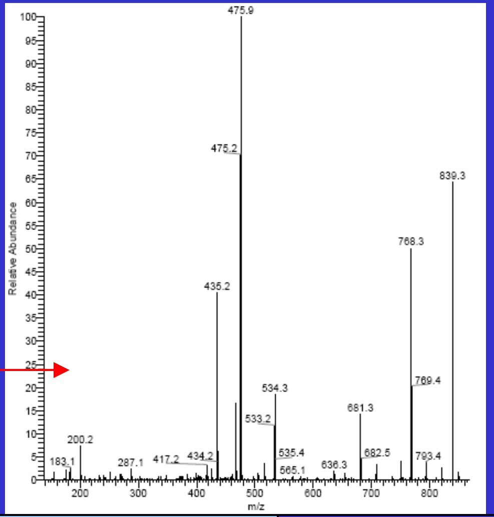
Potential for high throughput quantitative field analyses of nutrient stresses

Single Peptide Isolation: Mass spectra isolating mass 1030m/z (2060/2 for a +2 ion)

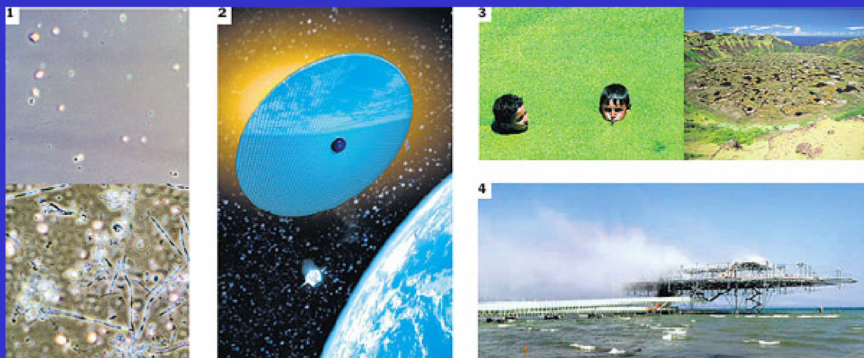


Confirmation of Protein Identity

MS^2 on 1030m/z (fragmentation pattern confirms Amino acid sequences of idiA peptide)

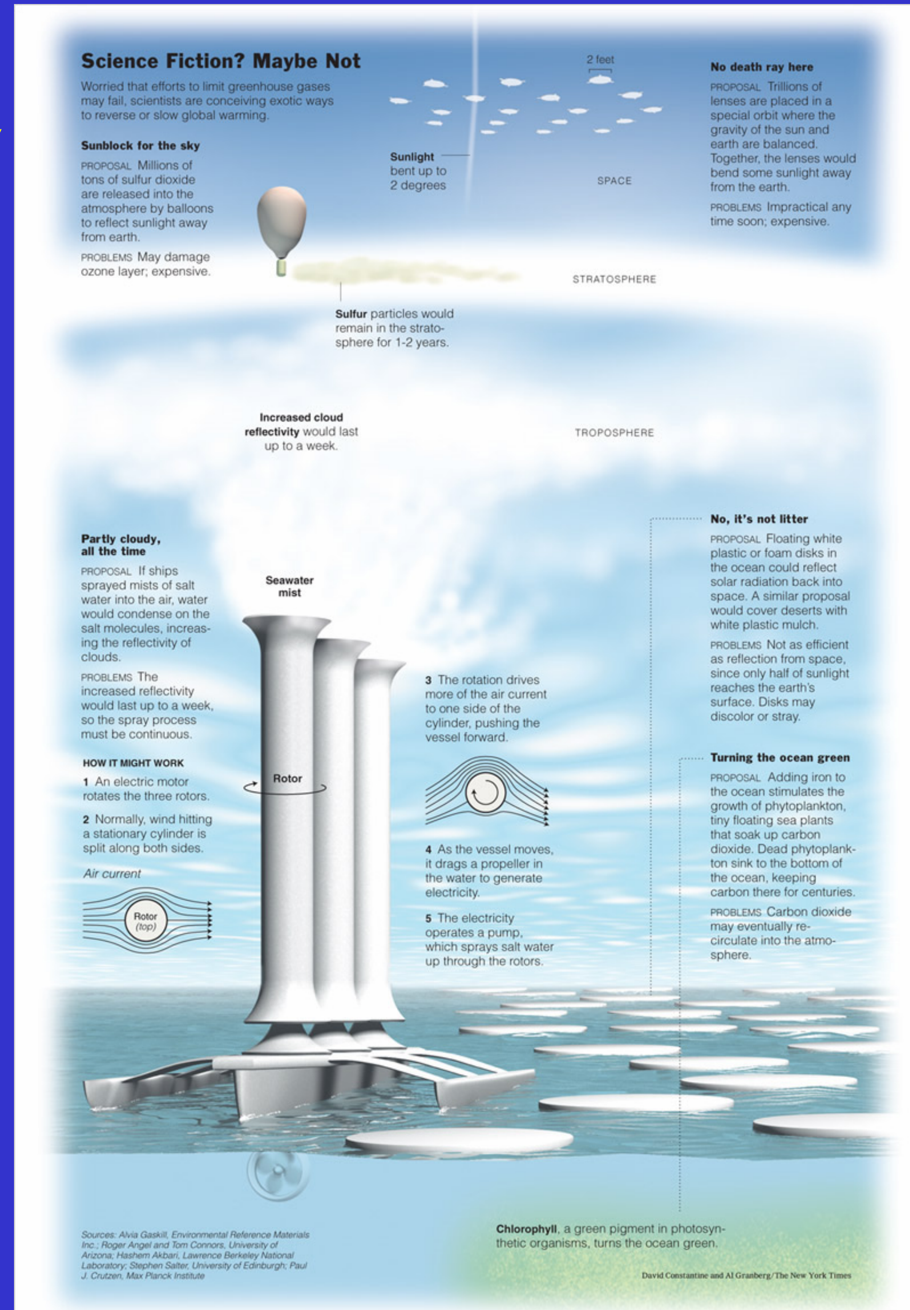


NYT Science Times 2006:
"How to Cool a Planet (Maybe)"



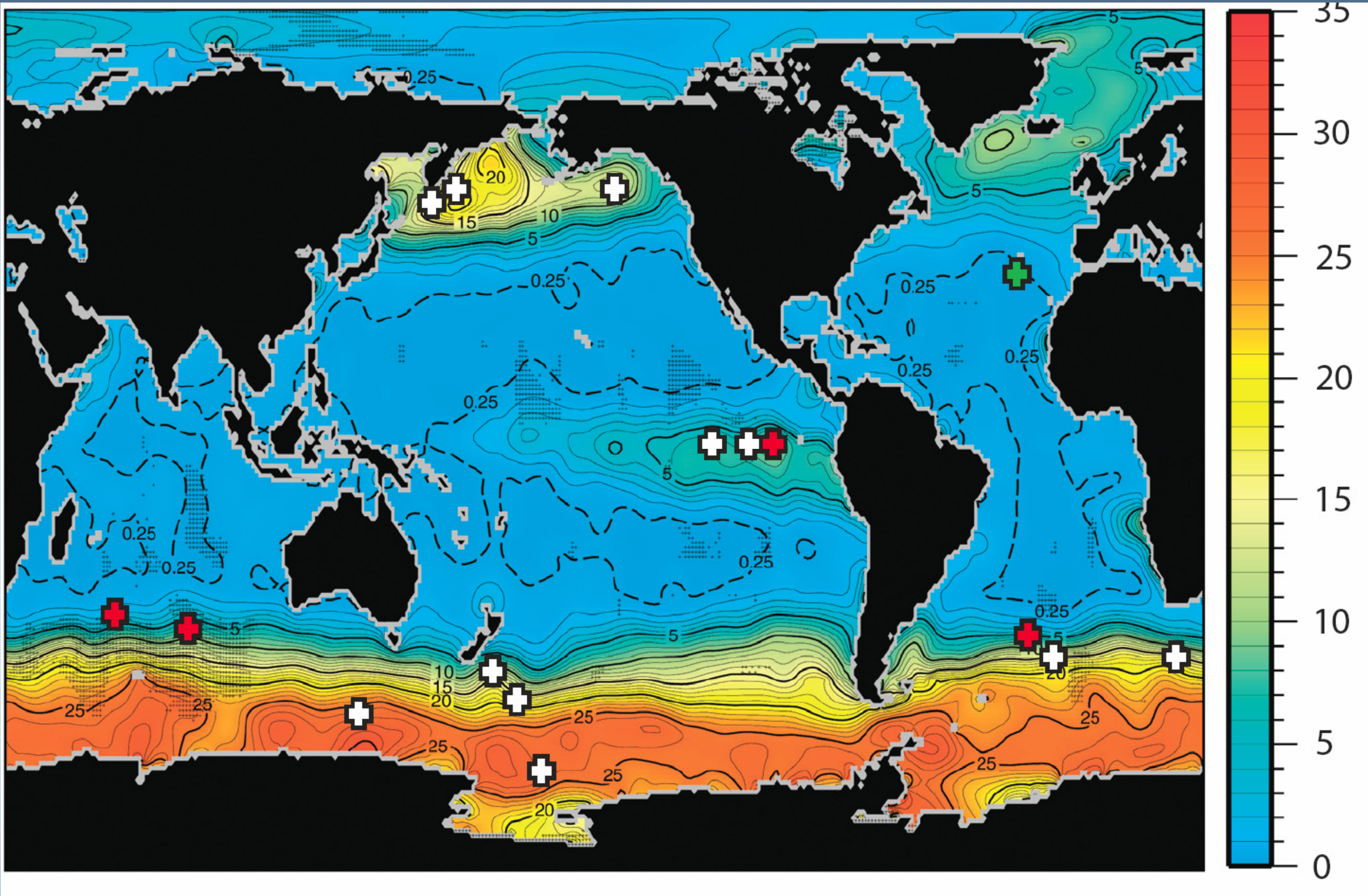
But now, in a major reversal, some of the world's most prominent scientists say the proposals deserve a serious look because of growing concerns about global warming.

"People used to say, 'Shut up, the world isn't ready for this,' " said Wallace S. Broecker, a geoengineering pioneer at Columbia. "Maybe the world has changed."



Iron as a limiting nutrient in HNLC regions

(Review of Iron Fertilization Experiments Boyd et al., 2007, Science)



Purposeful (white crosses) and natural (red crosses) Fe enrichment studies have shown Fe limitation of phytoplankton growth.

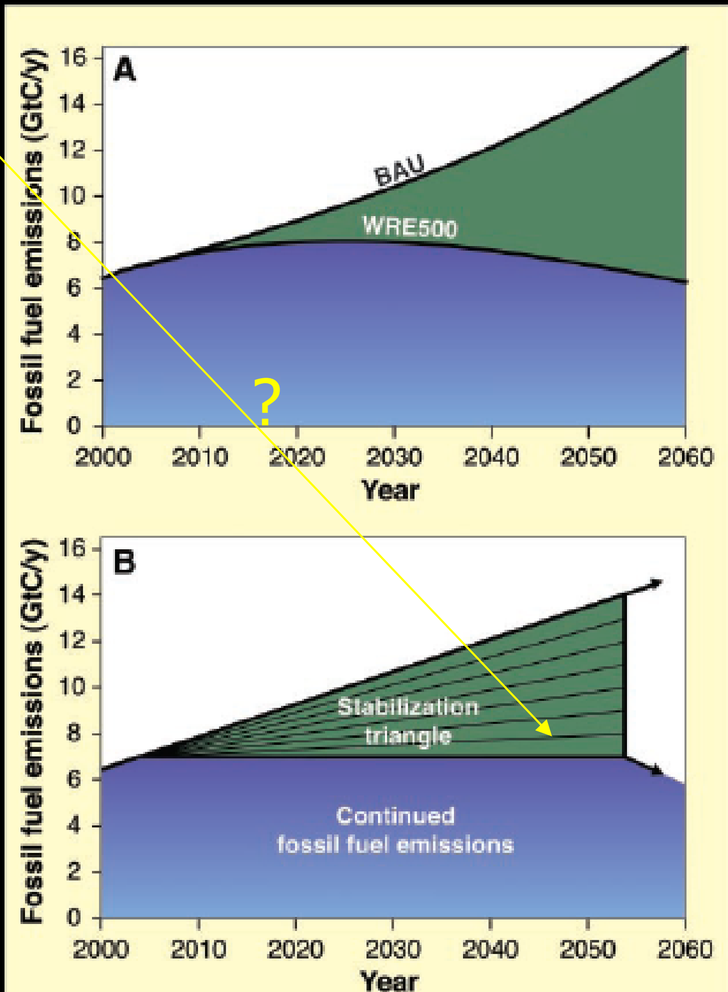
Iron fertilization and carbon credits: discussion points

Is ocean fertilization a potentially useful (needed?) wedge in stabilizing emissions?

- Economics: it may be popular in an open carbon credit market because it is likely quite inexpensive: $C_{106}N_{16}P_1Fe_{0.0005}$
- But does it work? How much carbon export occurs from fertilized regions?
  - "little or no export" therefore, iron fertilization (or any nutrient fertilization) is often deemed ineffective
- But we see other natural bloom situations with little export e.g. E-Flux (Benitez-Nelson et al., Science 2007), what are we missing?

Some Logical Possibilities:

1) Fe limited regions do not export carbon (wrong)
2) Something about anthropogenic fertilization doesn't work (if so why?)
3) Mesoscale Fe experiments are missing export (occurs after ship leaves?)
4) Export is subtle, missing it with current technologies
5) There is something that triggers enhanced export in blooms (e.g. specific types of grazers?)



the stabilization triangle. But not filling the stabilization triangle will put 500-ppm stabilization out of reach. In that same simple model (9), 50 years of BAU emissions followed by 50 years of a flat trajectory at 14 GtC/year leads to more than a tripling of the preindustrial concentration.

(Pacala and Socolo, Science 2004)

Who funds carbon *sequestration* research?

Do we have a national political vision?

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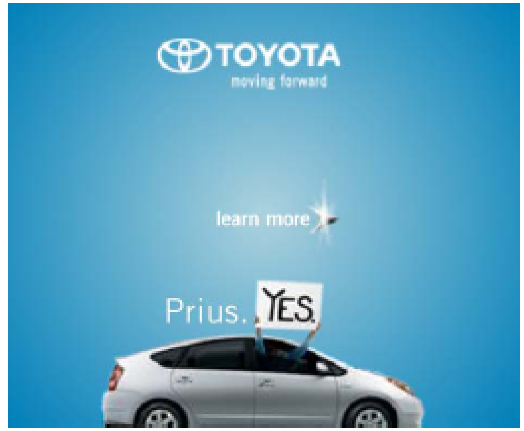


Stanford hails 'revolutionary' research pact

Energy project's objectivity won't be swayed by oil industry funds, scientists say

Keay Davidson, Chronicle Science Writer
Thursday, November 21, 2002

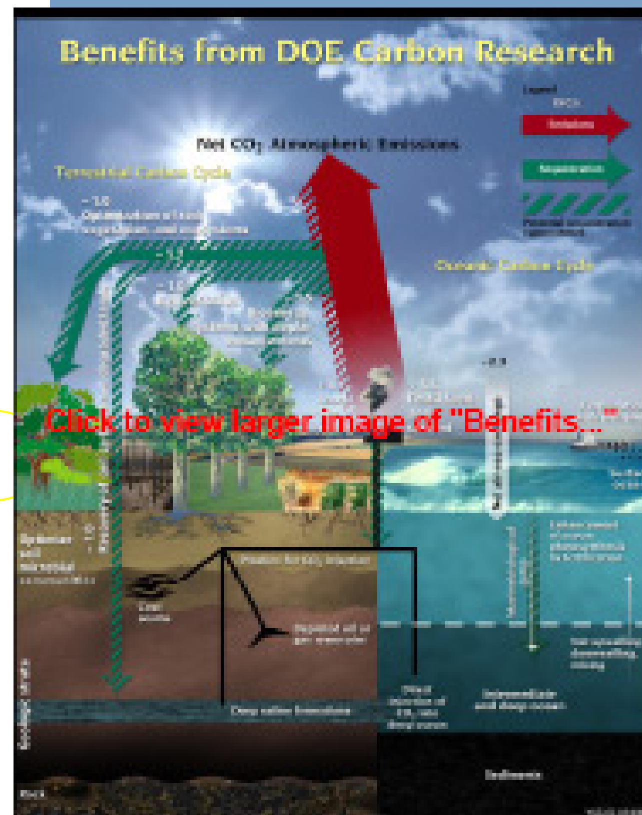
A new collaboration between Stanford University and oil and power companies will investigate ways of easing environmental effects of the burning of fossil fuels -- from burying greenhouse gases to using lasers to monitor passing cars' emissions.

At a press conference Wednesday, Stanford President John Hennessy called the agreement to spend $225 million over the next decade a "revolutionary collaboration" to transform energy generation in "an environmentally benign fashion."

Climate scientists and environmentalists said the new Global Climate and Energy Project would provide a welcome boost to solving climate and energy problems, but they questioned the independence of research funded by some of industry's biggest polluters.

ExxonMobil, which as part of an industry group in the 1990s worked to discredit evidence that global warming is real and caused by human activities, is the biggest single donor, funding $100 million of the project on the Palo Alto campus.

Another $50 million was given by General Electric, a leading player in power-plant and nuclear-energy development; an additional $25 million comes from Schlumberger Ltd, a New York-based oil services and technology company; and another $50 million is expected from a German power company, E.On AG, Stanford officials said.



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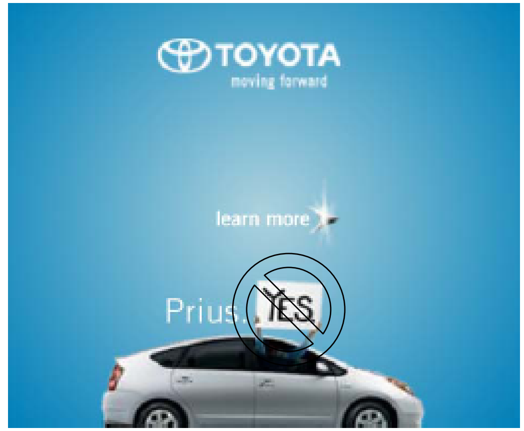

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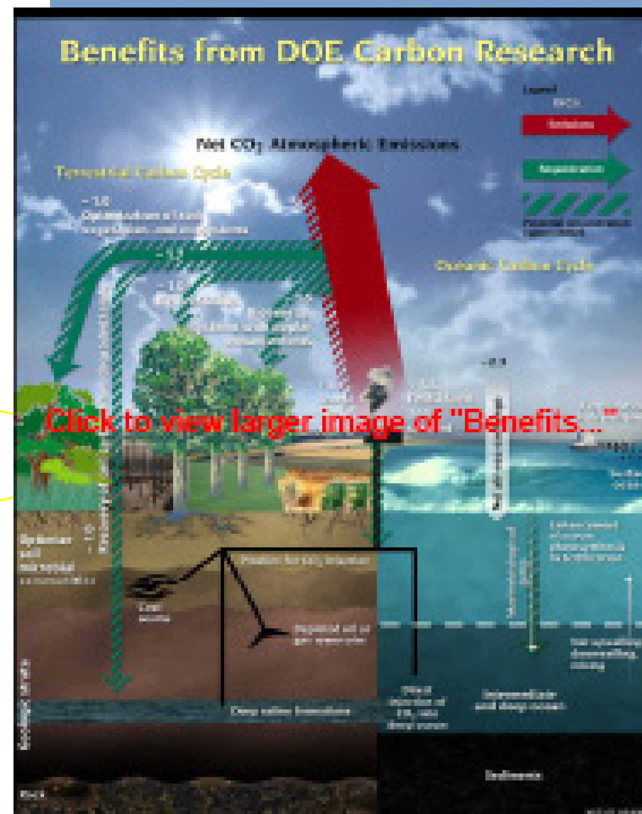


Conclusions

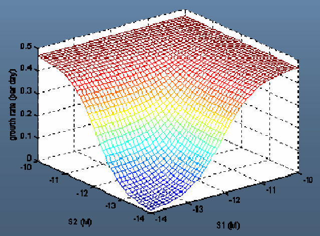
- GEOTRACES is beginning! Data poor no more…
  - Ocean sections of Trace Element and Isotope data (TEI's)

- Iron and metal acquisition research:
  - Iron reductases and a Fe(II) kinetic model for bioavailability (Shaked et al 2005, Maldonado…), presence confirmed in Diatom genome
  - Cobalt speciation can vary greatly, complexes produced by cyanobacteria, metal bioavailability is important

- Colimitation: Three definitions based on bioinorganic chemistry
  - B_{12}Fe colimitation in the Ross Sea, positive effect on diatoms

- New proteomic and genomic technologies being applied to open the black box of (co)limitations (nutrient stress markers)

- Marine carbon sequestration has come back with recent public interest climate change.



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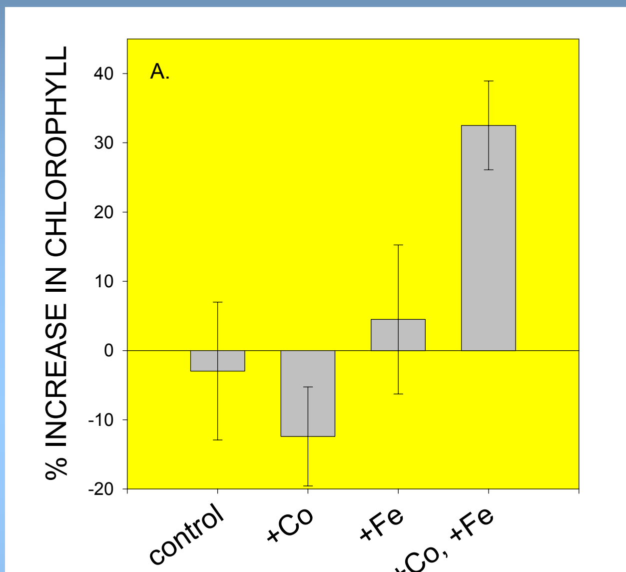
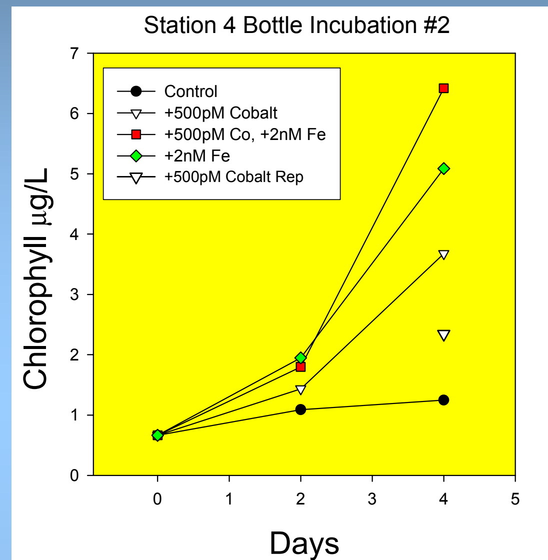
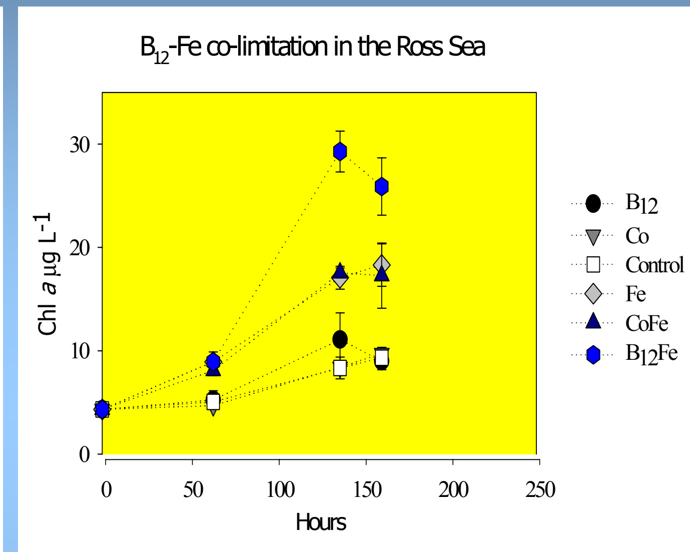
Saito lab research funded by NSF Chemical Oceanography
NSF Office of Polar Programs, ONR Young Investigator Award

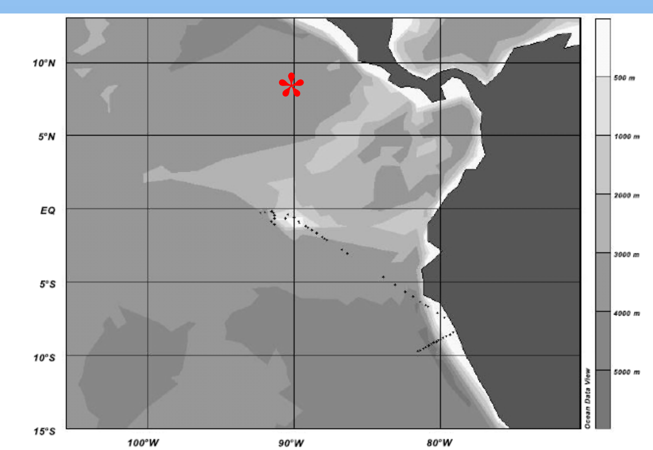
Influence of Alternative Trace Metals on Phytoplankton:

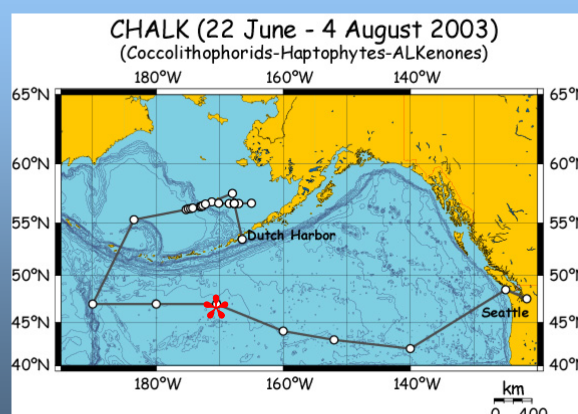
Cobalt and Vitamin B_{12} can be co-limiting with Iron

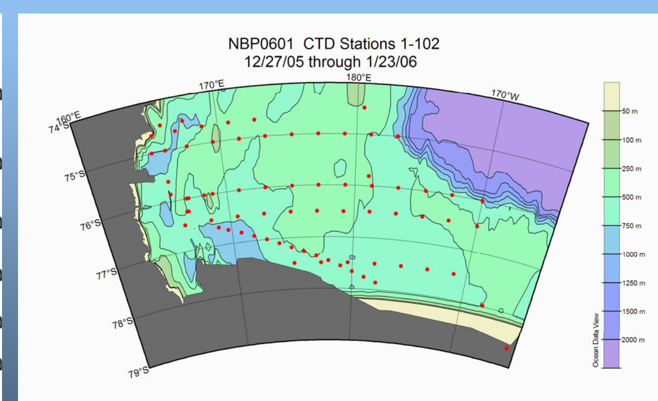










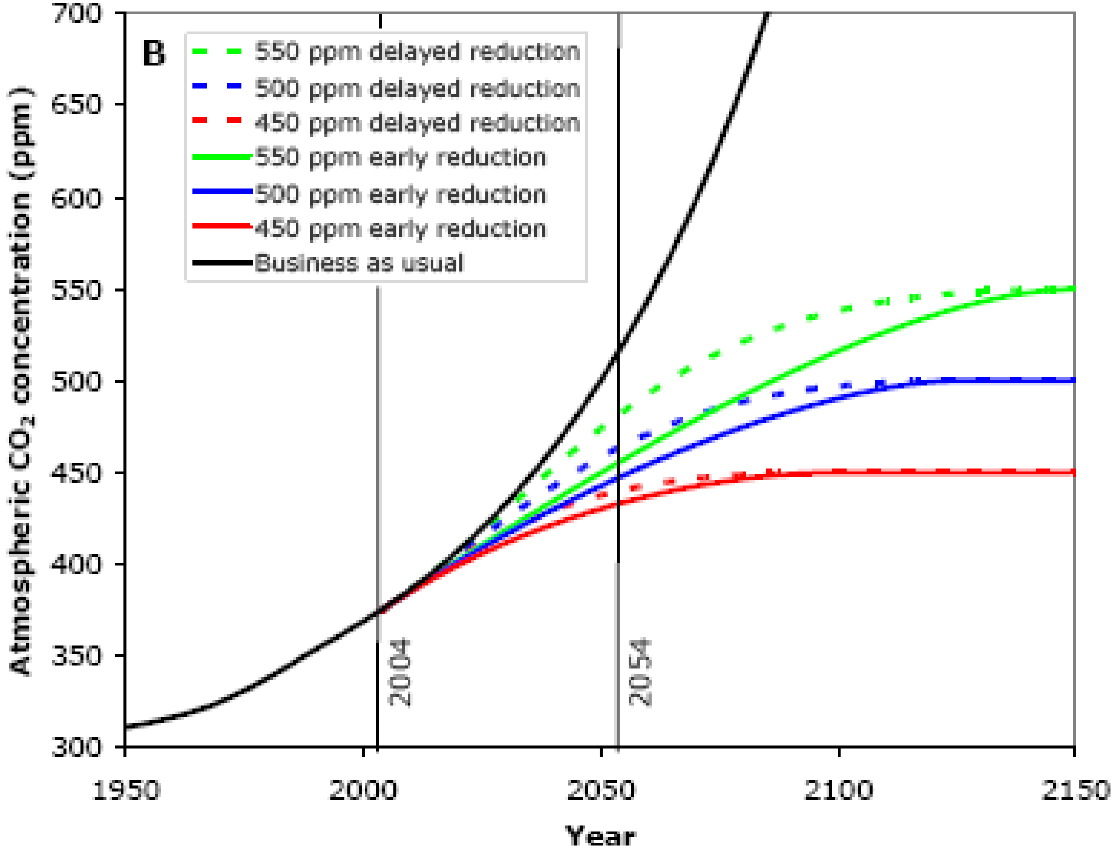


Saito et al., L&O 2005 Saito, Xu, Wisneiwski, Moffett et al., in prep; Bertrand Saito et al., submitted

Table 1. Potential wedges: Strategies available to reduce the carbon emission rate in 2054 by 1 GtC/year or to reduce carbon emissions from 2004 to 2054 by 25 GtC.

Option	Effort by 2054 for one wedge, relative to 14 GtC/year BAU	Comments, issues
	Energy efficiency and conservation	
Economy-wide carbon-intensity reduction (emissions/$GDP)	Increase reduction by additional 0.15% per year (e.g., increase U.S. goal of 1.96% reduction per year to 2.11% per year)	Can be tuned by carbon policy
1. Efficient vehicles	Increase fuel economy for 2 billion cars from 30 to 60 mpg	Car size, power
2. Reduced use of vehicles	Decrease car travel for 2 billion 30-mpg cars from 10,000 to 5000 miles per year	Urban design, mass transit, telecommuting
3. Efficient buildings	Cut carbon emissions by one-fourth in buildings and appliances projected for 2054	Weak incentives
4. Efficient baseload coal plants	Produce twice today's coal power output at 60% instead of 40% efficiency (compared with 32% today)	Advanced high-temperature materials
	Fuel shift	
5. Gas baseload power for coal baseload power	Replace 1400 GW 50%-efficient coal plants with gas plants (four times the current production of gas-based power)	Competing demands for natural gas
	CO_2 Capture and Storage (CCS)	
6. Capture CO_2 at baseload power plant	Introduce CCS at 800 GW coal or 1600 GW natural gas (compared with 1060 GW coal in 1999)	Technology already in use for H_2 production
7. Capture CO_2 at H_2 plant	Introduce CCS at plants producing 250 MtH_2/year from coal or 500 MtH_2/year from natural gas (compared with 40 MtH_2/year today from all sources)	H_2 safety, infrastructure
8. Capture CO_2 at coal-to-synfuels plant	Introduce CCS at synfuels plants producing 30 million barrels a day from coal (200 times Sasol), if half of feedstock carbon is available for capture	Increased CO_2 emissions, if synfuels are produced without CCS
Geological storage	Create 3500 Sleipners	Durable storage, successful permitting
	Nuclear fission	
9. Nuclear power for coal power	Add 700 GW (twice the current capacity)	Nuclear proliferation, terrorism, waste
	Renewable electricity and fuels	
10. Wind power for coal power	Add 2 million 1-MW-peak windmills (50 times the current capacity) "occupying" 30×10^6 ha, on land or offshore	Multiple uses of land because windmills are widely spaced
11. PV power for coal power	Add 2000 GW-peak PV (700 times the current capacity) on 2×10^6 ha	PV production cost
12. Wind H_2 in fuel-cell car for gasoline in hybrid car	Add 4 million 1-MW-peak windmills (100 times the current capacity)	H_2 safety, infrastructure
13. Biomass fuel for fossil fuel	Add 100 times the current Brazil or U.S. ethanol production, with the use of 250×10^6 ha (one-sixth of world cropland)	Biodiversity, competing land use
	Forests and agricultural soils	
14. Reduced deforestation, plus reforestation, afforestation, and new plantations.	Decrease tropical deforestation to zero instead of 0.5 GtC/year, and establish 300 Mha of new tree plantations (twice the current rate)	Land demands of agriculture, benefits to biodiversity from reduced deforestation
15. Conservation tillage	Apply to all cropland (10 times the current usage)	Reversibility, verification

Figure S1 (B)

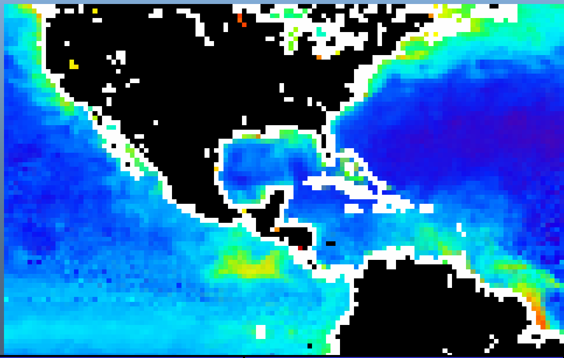

B
550 ppm delayed reduction
500 ppm delayed reduction
450 ppm delayed reduction
550 ppm early reduction
500 ppm early reduction
450 ppm early reduction
Business as usual
Atmospheric CO_2 concentration (ppm)
700
650
600
550
500
450
400
350
300
1950
2000
2050
2100
2150
Year
2004
2054

What allows *Synechococcus* to reach such high abundances in the Costa Rica Dome?

Dogma: Cyanobacteria dominate in oligotropic regimes, diatoms/eukaryotic Phytoplankton dominate in upwelling regions.

Chemical Signature (proposed in Saito, Rocap, and Moffett L&O 2005):

- Major nutrients are abundant
- Co-limiting environment: only slight iron stimulation (Co & Fe, Zn & Fe)
- High cobalt abundances benefit *Synechococcus*
- Strong complexation of cobalt (selects against Eukaryotic phytoplankton)
- Copper, Cadmium, and Zinc are tightly complexed (selects for cyanobacteria)



Biogeochemical Questions Needing Molecular Answers:

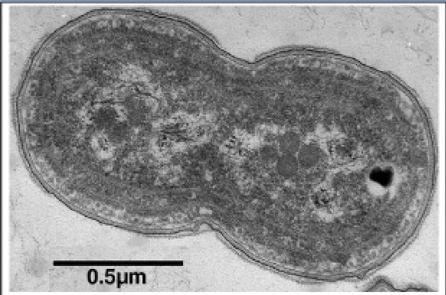
How does metal uptake operate in environmentally relevant microbial systems at these extremely low concentrations?

- No *tonB* gene, critical to B_{12} uptake
- No siderophore transport genes in most marine cyanobacteria
- What is the amino acid sequence of the B_{12} binding protein?

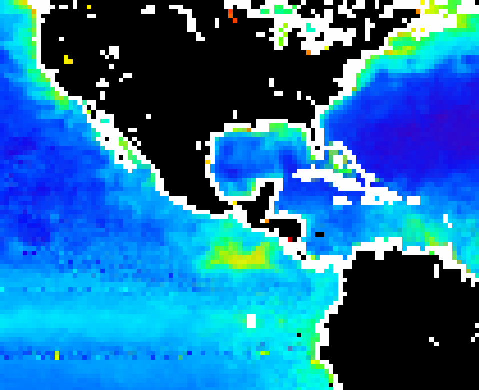
$$CoL \xleftrightarrow{K_{Co}^{cond}} Co' + L$$

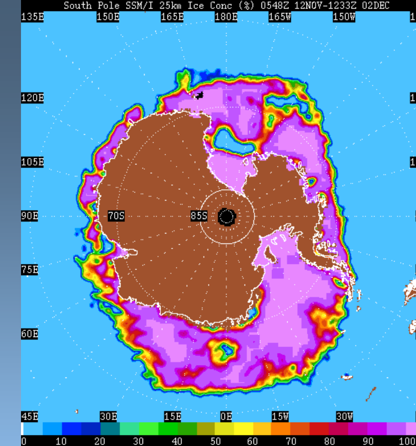
$$FeL \xleftrightarrow{K_{Fe}^{cond}} Fe' + L$$

? ?



Synechococcus





The Environments:

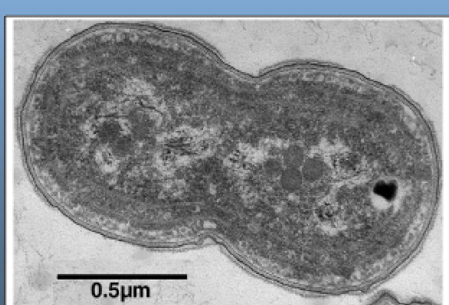
(polar opposites)

Costa Rica Dome

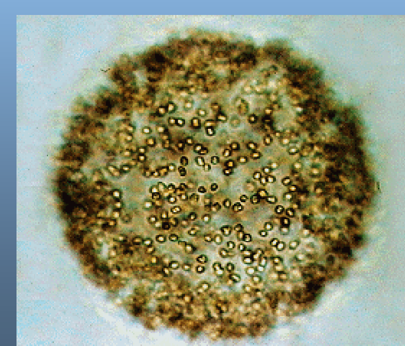
- Cyanobacteria *blooming*
- Significant heterotrophic bacteria
- Eukaryotic Phytoplankton increase below cyanobacteria dominated mixed layer
- Trace Metal Trio bound by strong ligands
- Fe-Co co-limited (in 2000, Saito et al., 2005)

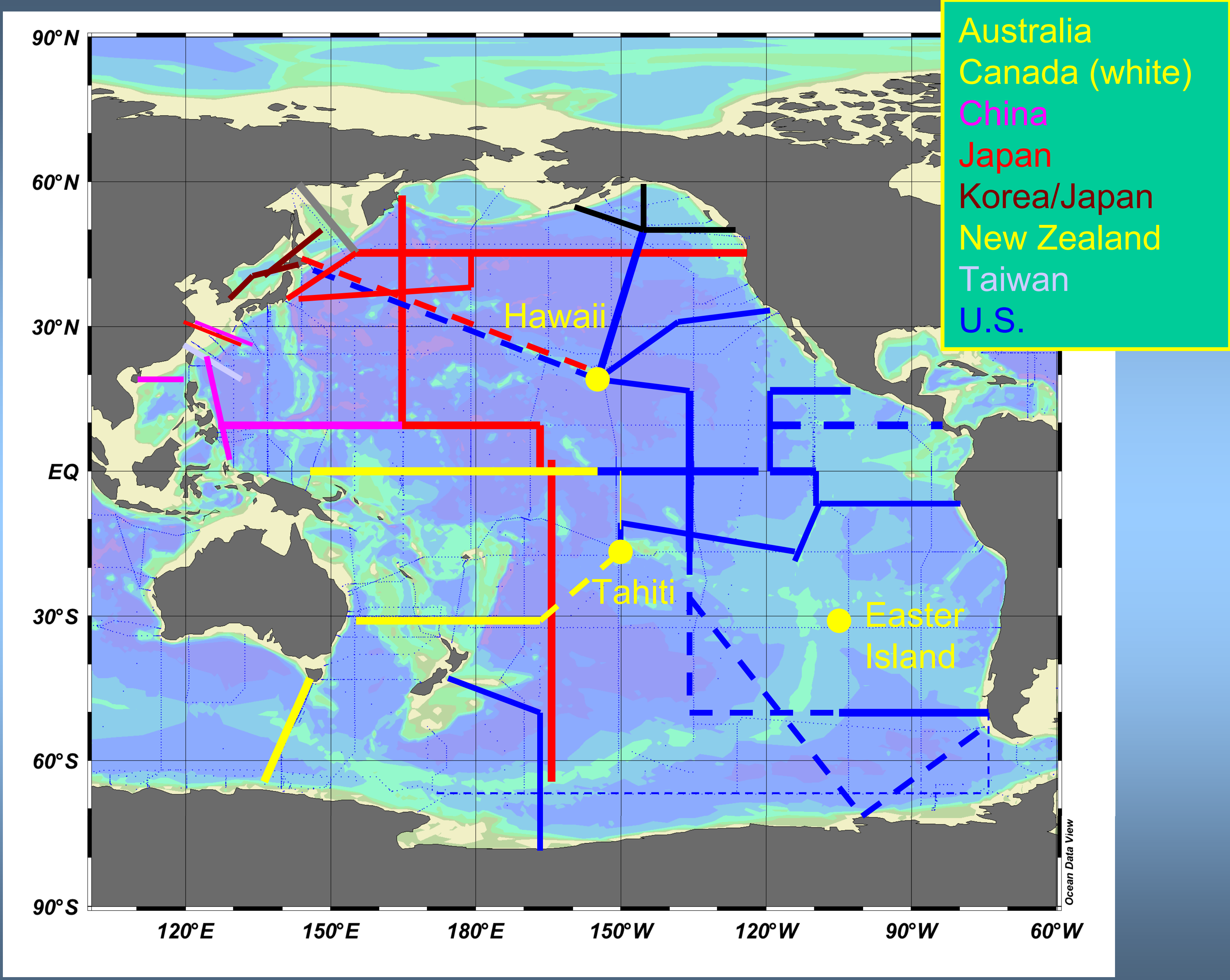
Ross Sea

- Cyanobacteria *absent*
- Lower heterotrophic bacteria
- Succession of Eukaryotic Phytoplankton
- Trace Metal Trio is labile
- Fe-B_{12} co-limited in 2006
- *Co-B_{12} biogeochemical linkage is weak due to low prokaryotic activity*



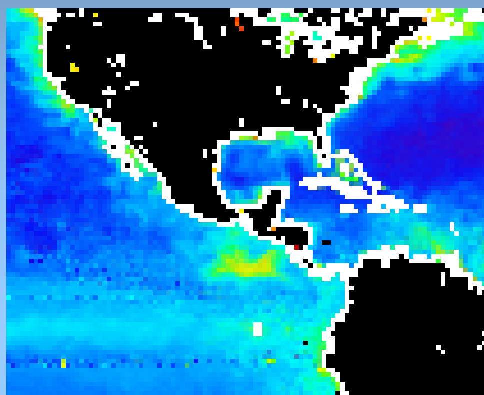
Synechococcus

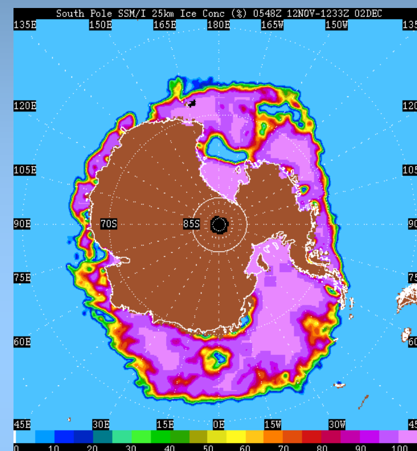


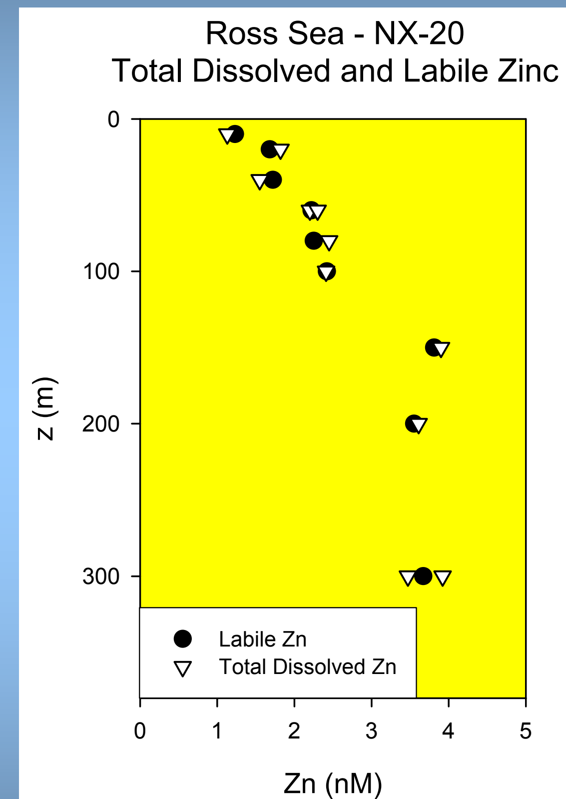

Australia
Canada (white)
China
Japan
Korea/Japan
New Zealand
Taiwan
U.S.
Hawaii
Tahiti
Easter Island
90°N
60°N
30°N
EQ
30°S
60°S
90°S
120°E
150°E
180°E
150°W
120°W
90°W
60°W
Ocean Data View

Dogma: Chemical speciation of metals is dominated by organic complexes in all environments

Implicit: speciation doesn't matter, all must be bioavailable



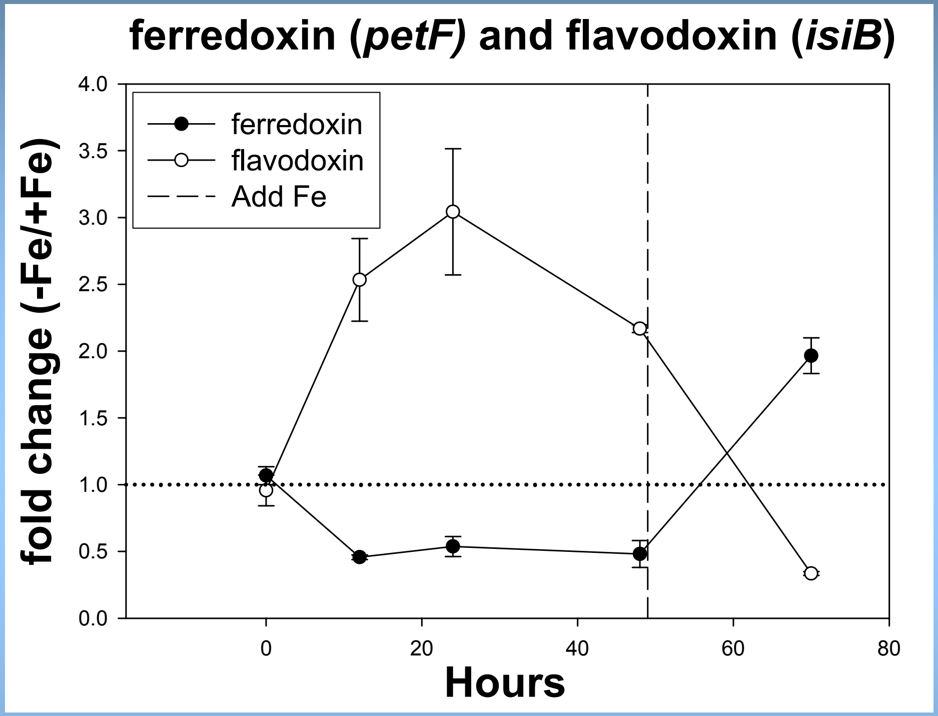


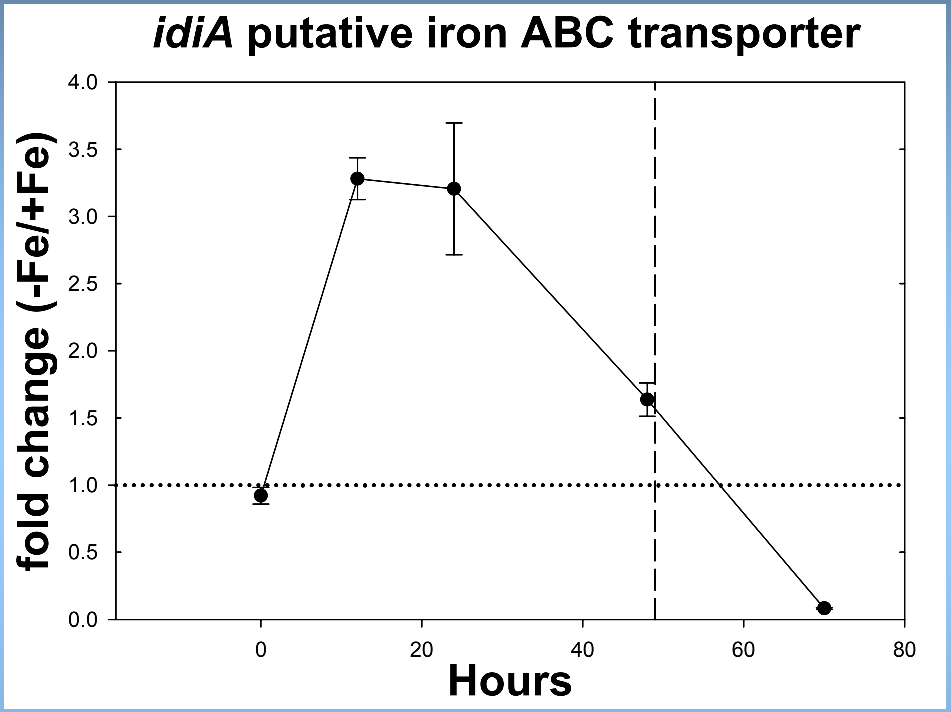


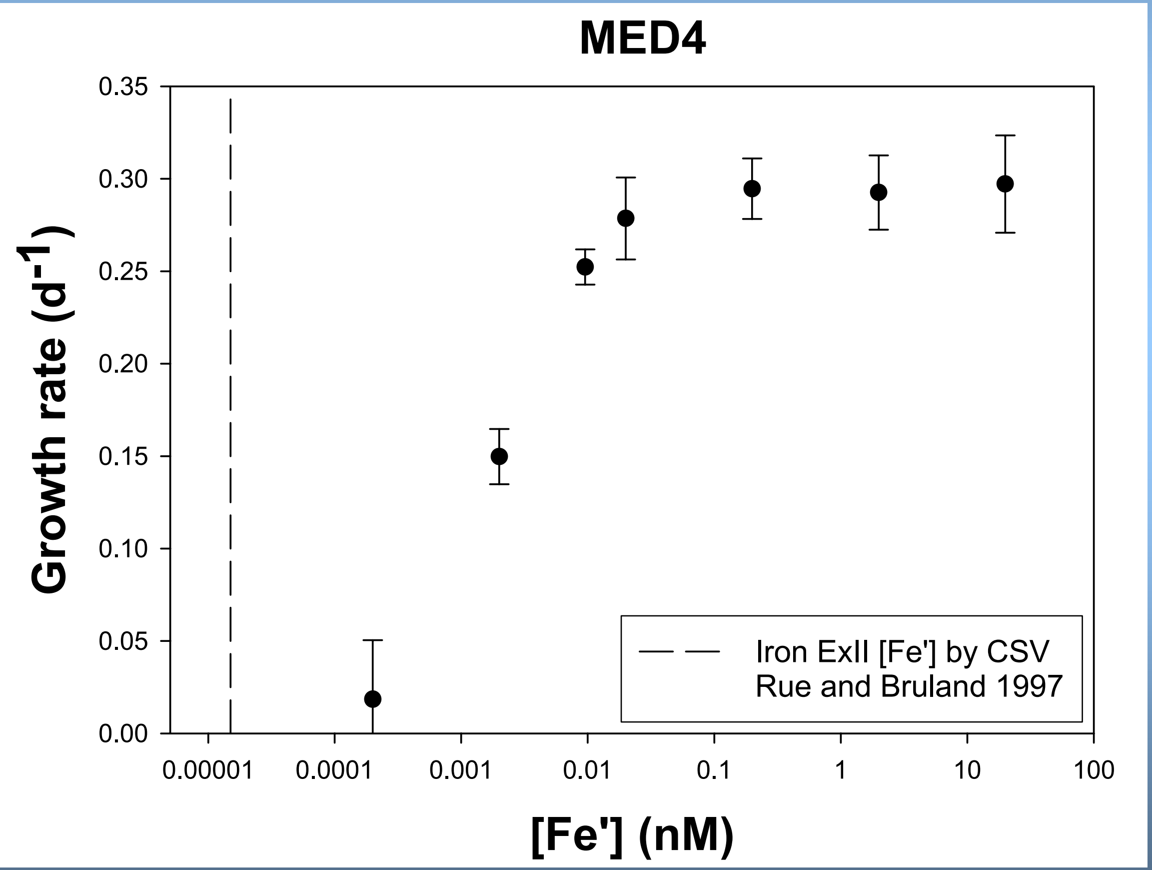
The Dogma is too simple:
The Dome: Co and Cd are all strongly complexed
The Ross Sea: Co, Cd, and Zn are all labile

Take Home Message:
There *is* diversity in chemical speciation of bioactive elements
Likely influences phytoplankton composition

Known Fe-related genes







MED4
Growth rate (d-1)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00001
0.0001
0.001
0.01
0.1
1
10
100
[Fe'] (nM)
Iron ExII [Fe'] by CSV
Rue and Bruland 1997