National Oceanography Centre, Southampton

UNIVERSITY OF Southampton
School of Ocean and Earth Science

Towards reconciliation of trace metal demand and supply

(from the perspective of limitation)

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NATURAL ENVIRONMENT RESEARCH COUNCIL

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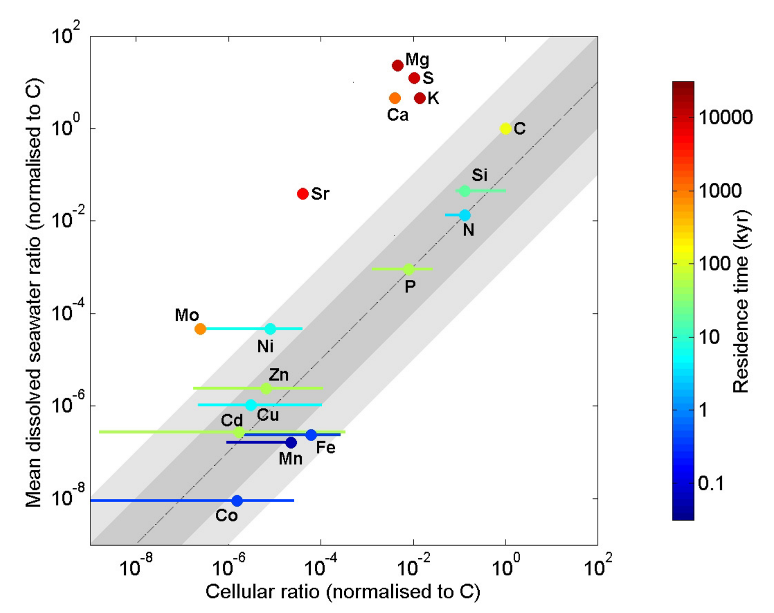

Processes and Patterns of Oceanic Nutrient Limitation

Nature Geoscience (2013)

GLOBAL IGBP CHANGE International Geosphere-Biosphere Programme

OCB Ocean Carbon & Biogeochemistry

cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

International Council for Science SCOR Scientific Committee on Oceanic Research

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PAGES PAST GLOBAL CHANGES

Acknowledgments:

Eric Achterberg,
Tom Bibby,

Christian Schlosser,
Sophie Richer,
Tommy Ryan-Keogh,
Bronwyn Wake,
Sebastian Steigenberger,
Joe Snow,
Jessica Klar,

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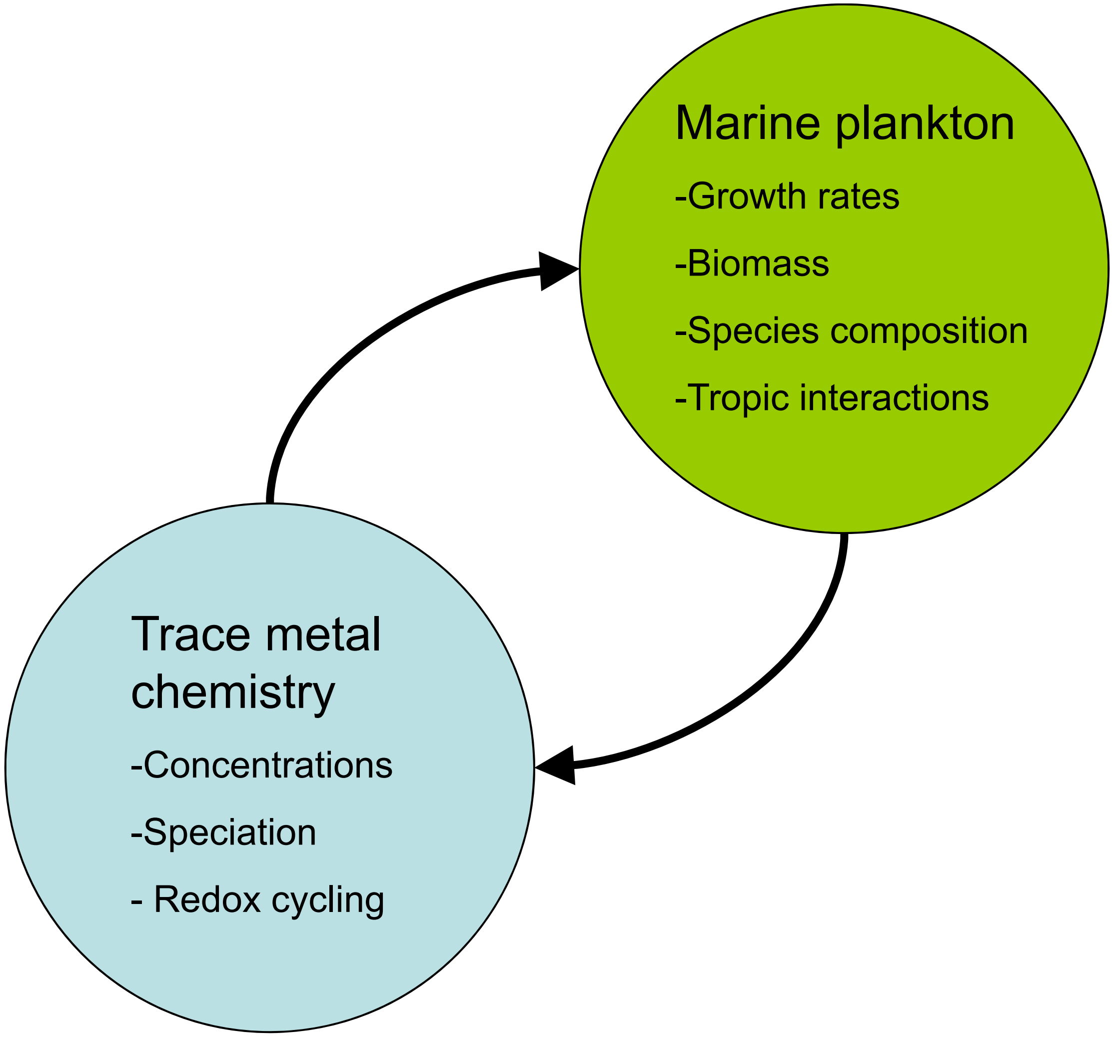
Trace element-biota interactions



Marine plankton

-Growth rates

-Biomass

-Species composition

-Tropic interactions

Trace metal chemistry

-Concentrations

-Speciation

- Redox cycling

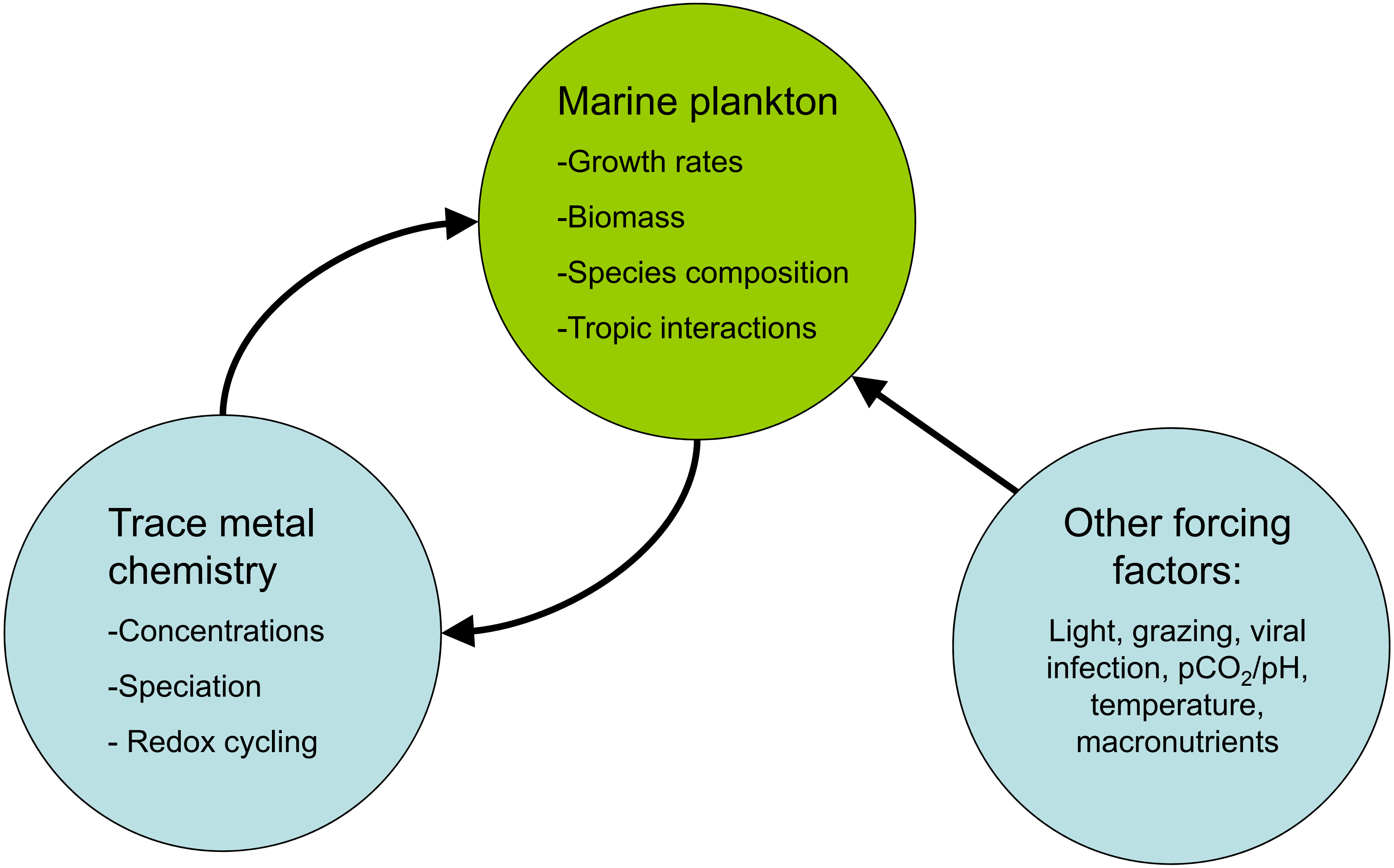
Bill Sunda (2012):

‘The interactions between trace metals and ocean plankton are reciprocal…’

‘This two way interaction… has a profound influence on the biogeochemistry of the ocean…’

Sunda (2012): Frontiers in Microbiology 3:204 doi: 10.3389/fmicb.2012.00204

Trace element-biota interactions



Marine plankton

-Growth rates

-Biomass

-Species composition

-Tropic interactions

Trace metal chemistry

-Concentrations

-Speciation

- Redox cycling

Other forcing factors:

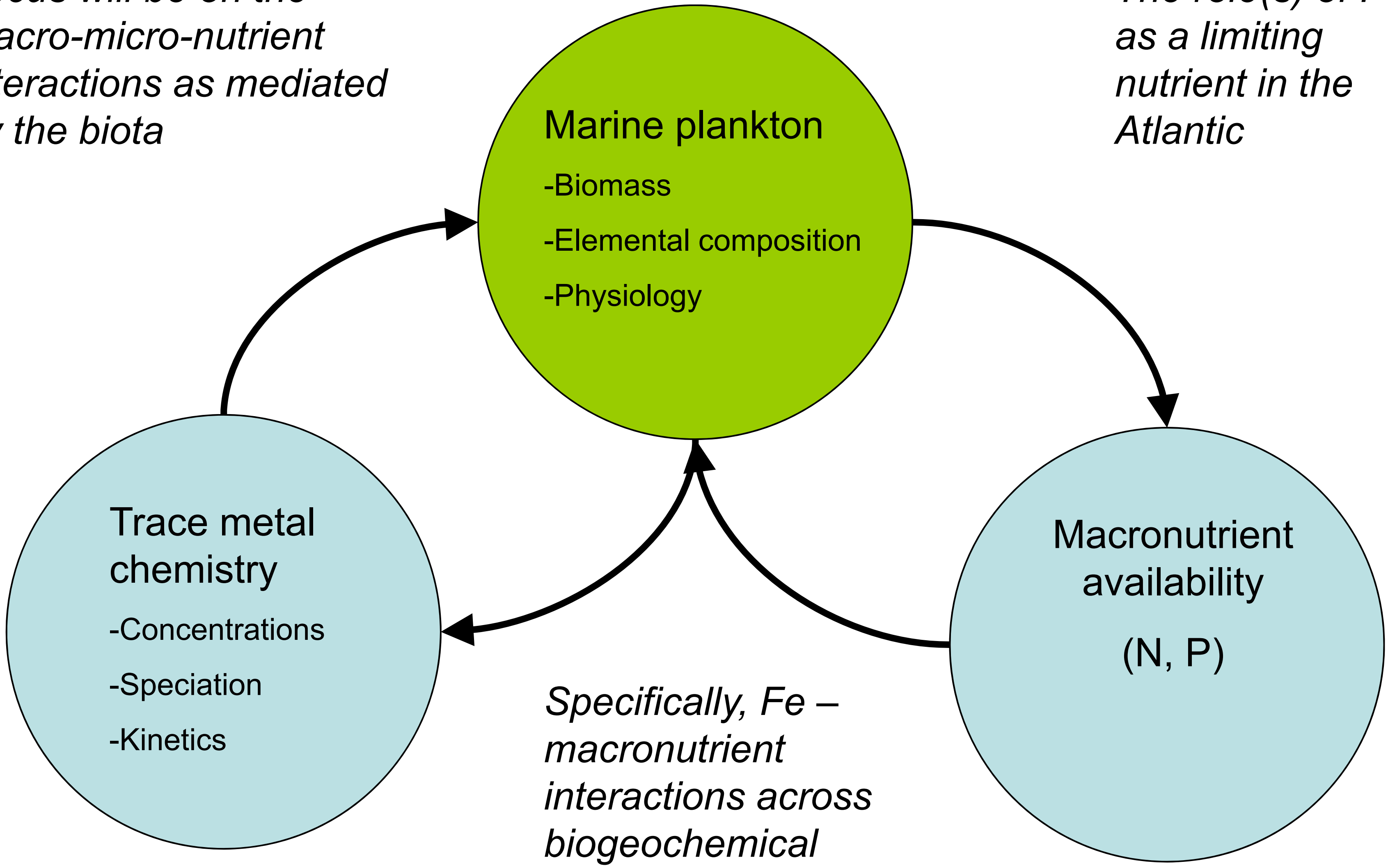
Light, grazing, viral infection, pCO_2/pH, temperature, macronutrients

Sunda (2012): Frontiers in Microbiology 3:204 doi: 10.3389/fmicb.2012.00204

Trace element-biota interactions

Focus will be on the macro-micro-nutrient interactions as mediated by the biota

The role(s) of Fe as a limiting nutrient in the Atlantic



Marine plankton

-Biomass

-Elemental composition

-Physiology

Trace metal chemistry

-Concentrations

-Speciation

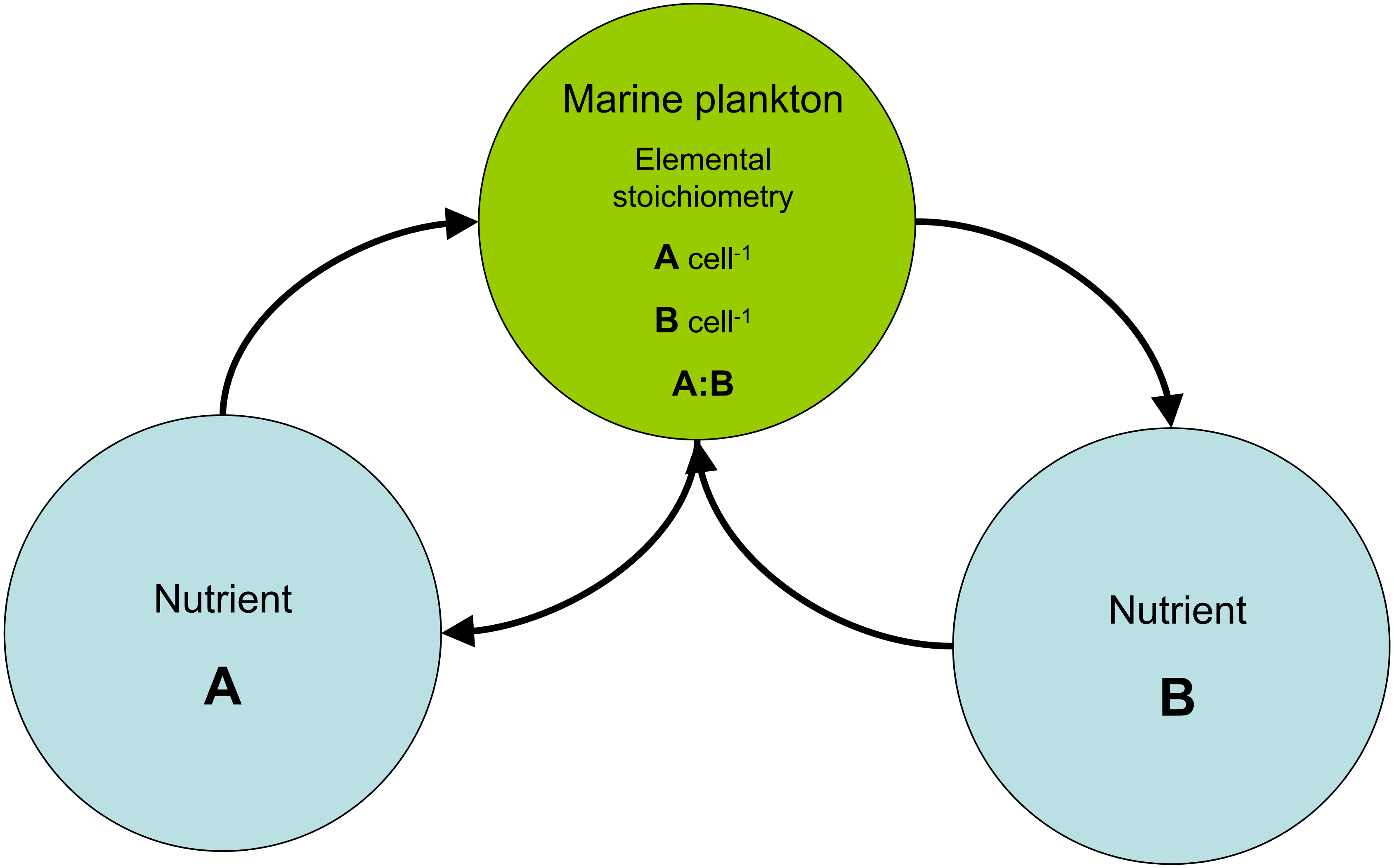
-Kinetics

Macronutrient availability

(N, P)

Specifically, Fe – macronutrient interactions across biogeochemical gradients

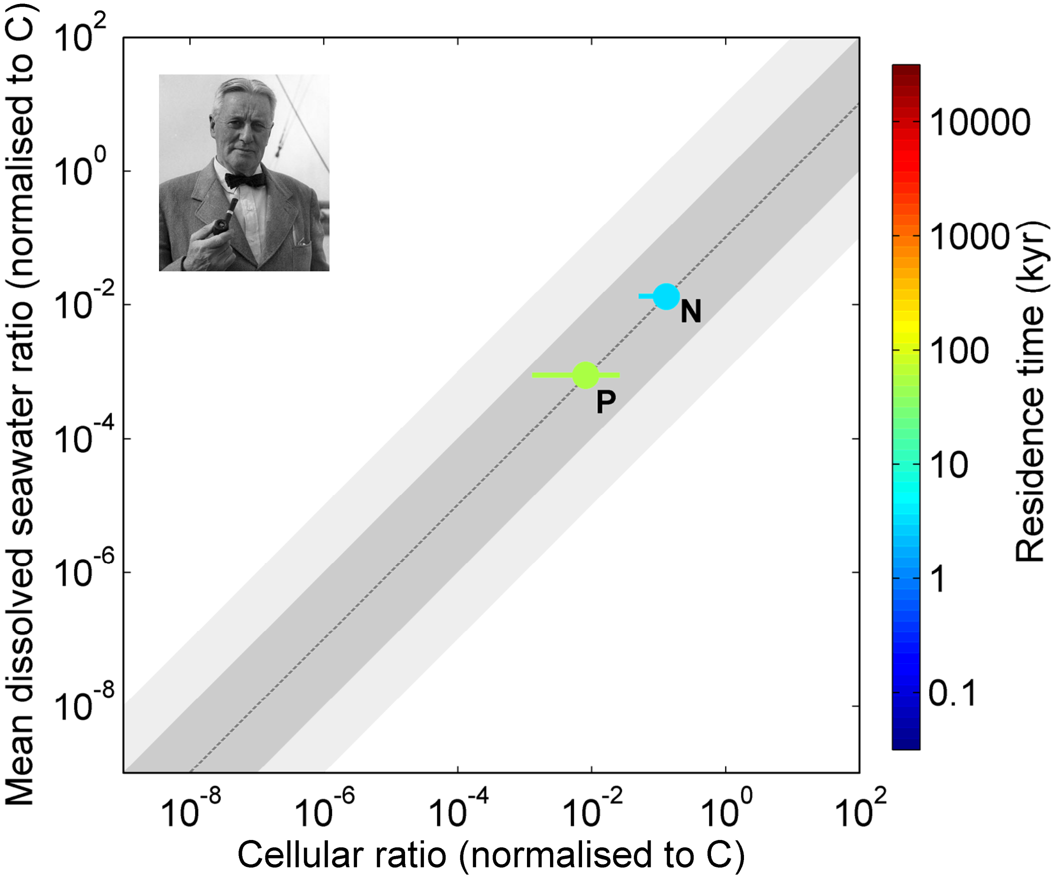
Nutrient-Biota-Nutrient interactions: stoichiometry is key



Some perspective, N and P

Redfield's principal observation: dissolved N and P in the modern ocean is approximately the same as phytoplankton requirements (<u>on average</u>).

>50 years on from Redfields seminal papers (Redfield 1934; 1958; 1963), details are still debated…

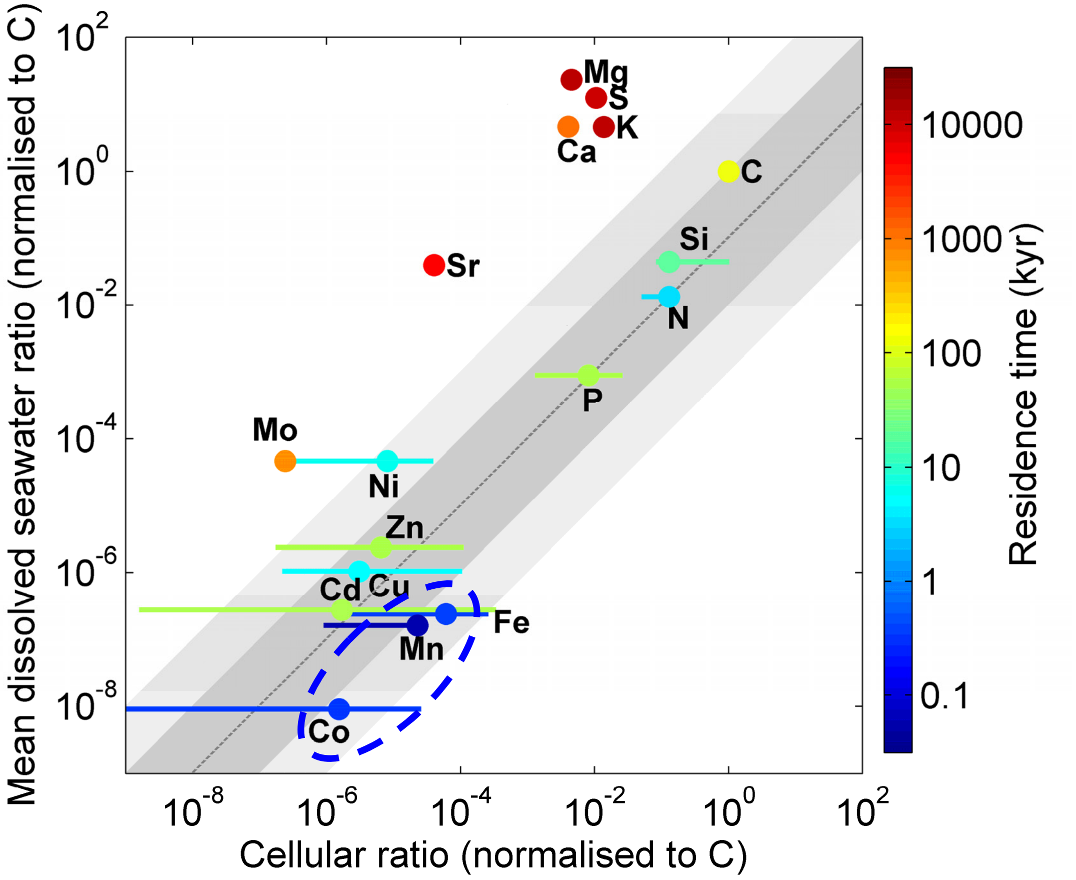


e.g. Redfield (1934; 1958); Redfield et al. (1963); Codispoti (1989); Tyrrell (1999); Falkowski, (1997); Lenton and Watson (2000); Wu et al. (2000); Geider and La Roche (2002); Klausmeier et al. (2004); Canfield (2006); Lenton and Klausmeier (2007); Van Mooy et al. (2009); Deutsch et al. (2009); Mills and Arrigo (2010); Weber and Deutsch, (2012); Martiny et al. (2013); Landolfi et al. (2013)… etc. etc.

The challenge ahead

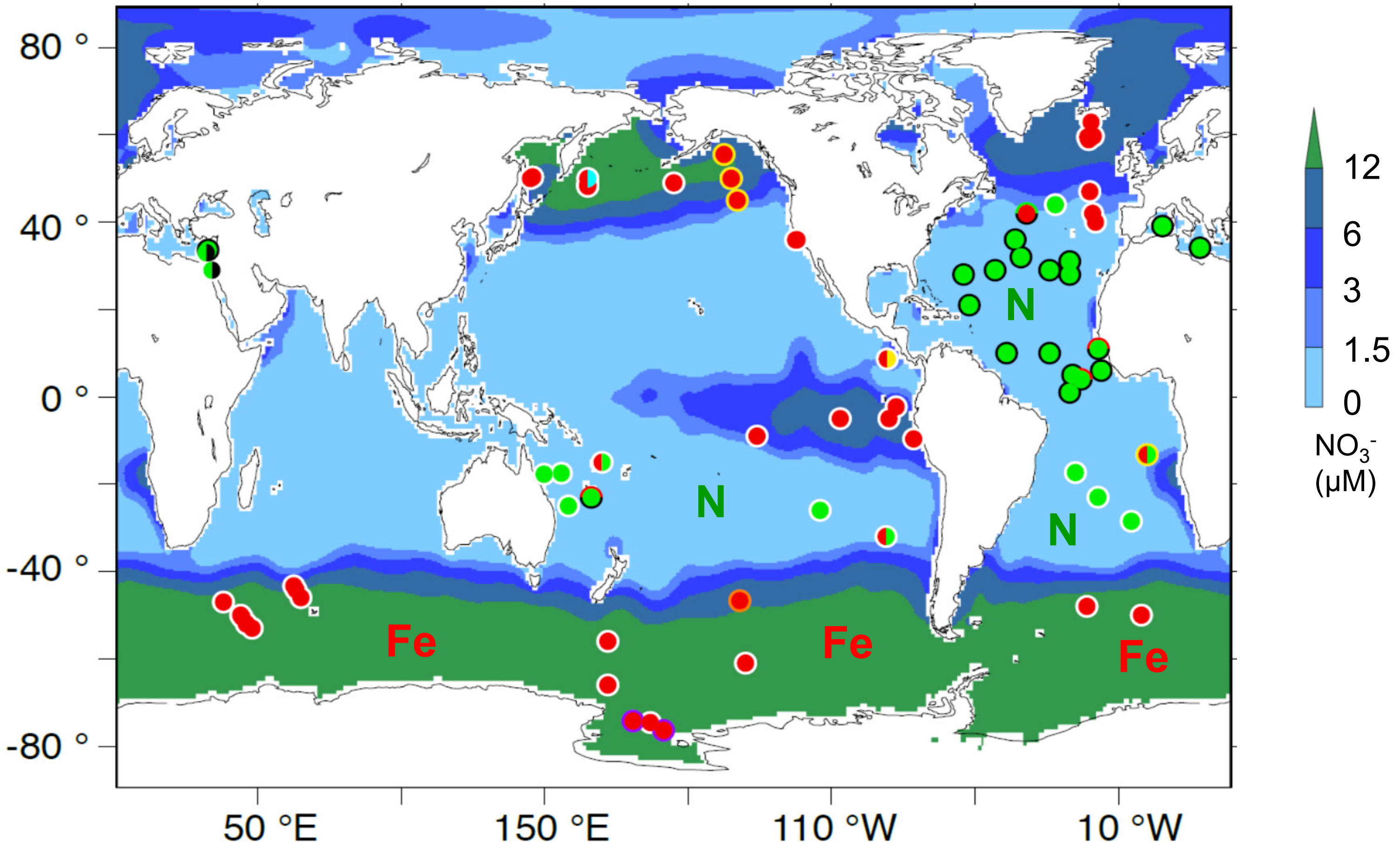
Elemental composition of seawater is **not** the same as that of biological material (phytoplankton). Moreover, the latter is **highly** variable, particularly for the trace metals.

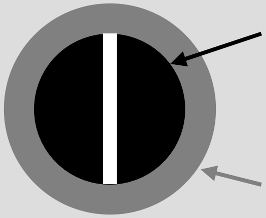
Some elements are strongly controlled by (and can potentially exert strong control on) biological processes, others won't.



Processes influencing differences in *availability/supply* and *requirements/demand* will fundamentally dictate nutrient biogeochemistry, (e.g. patterns of oceanic nutrient limitation).

Global patterns of nutrient limitation





Primary (or Co-) limiting nutrient(s)

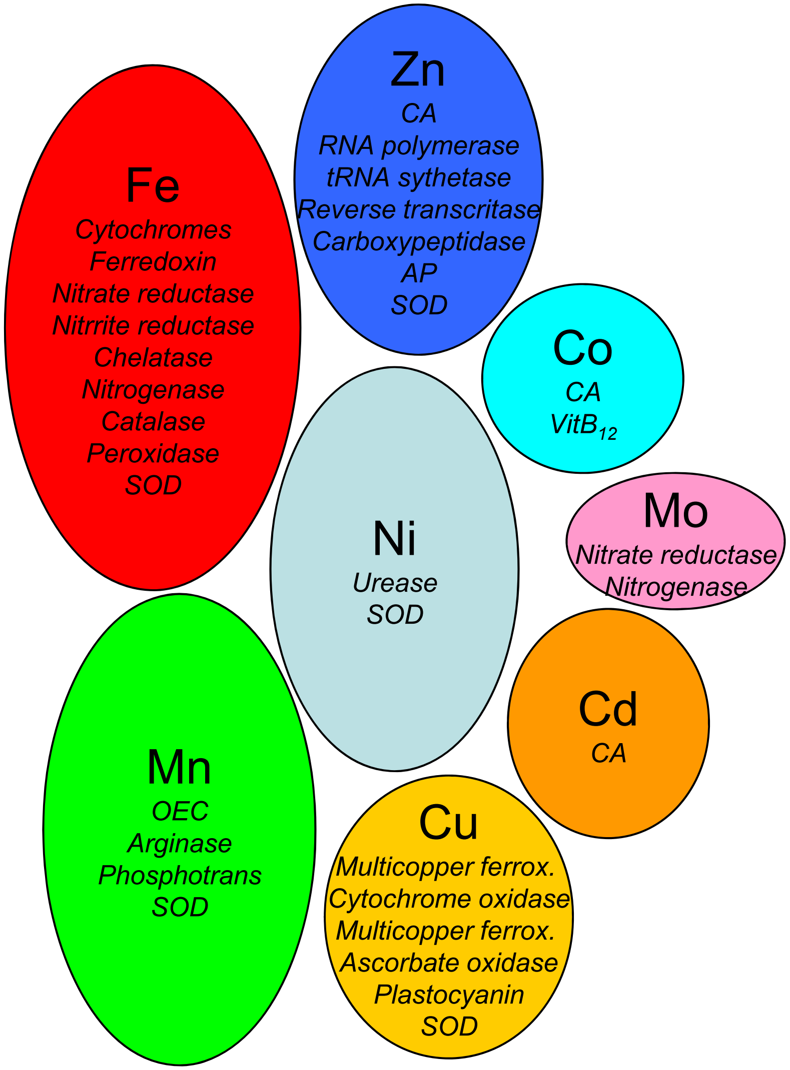
Secondary limiting nutrient

N Fe P

Co Si Zn Vit B_{12}

Lack of secondary limitation or test

Trace metal requirements



Fe
Cytochromes
Ferredoxin
Nitrate reductase
Nitrite reductase
Chelatase
Nitrogenase
Catalase
Peroxidase
SOD

Zn
CA
RNA polymerase
tRNA sythetase
Reverse transcritase
Carboxypeptidase
AP
SOD

Co
CA
$VitB_{12}$

Ni
Urease
SOD

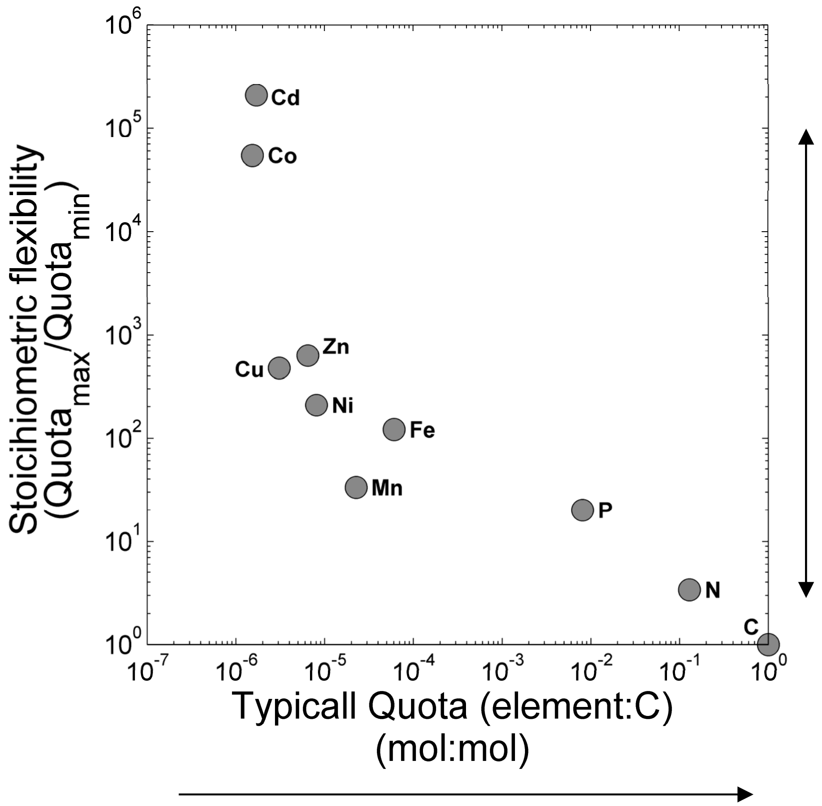
Mo
Nitrate reductase
Nitrogenase

Cd
CA

Mn
OEC
Arginase
Phosphotrans
SOD

Cu
Multicopper ferrox.
Cytochrome oxidase
Multicopper ferrox.
Ascorbate oxidase
Plastocyanin
SOD

e.g. Twining and Baines 2013



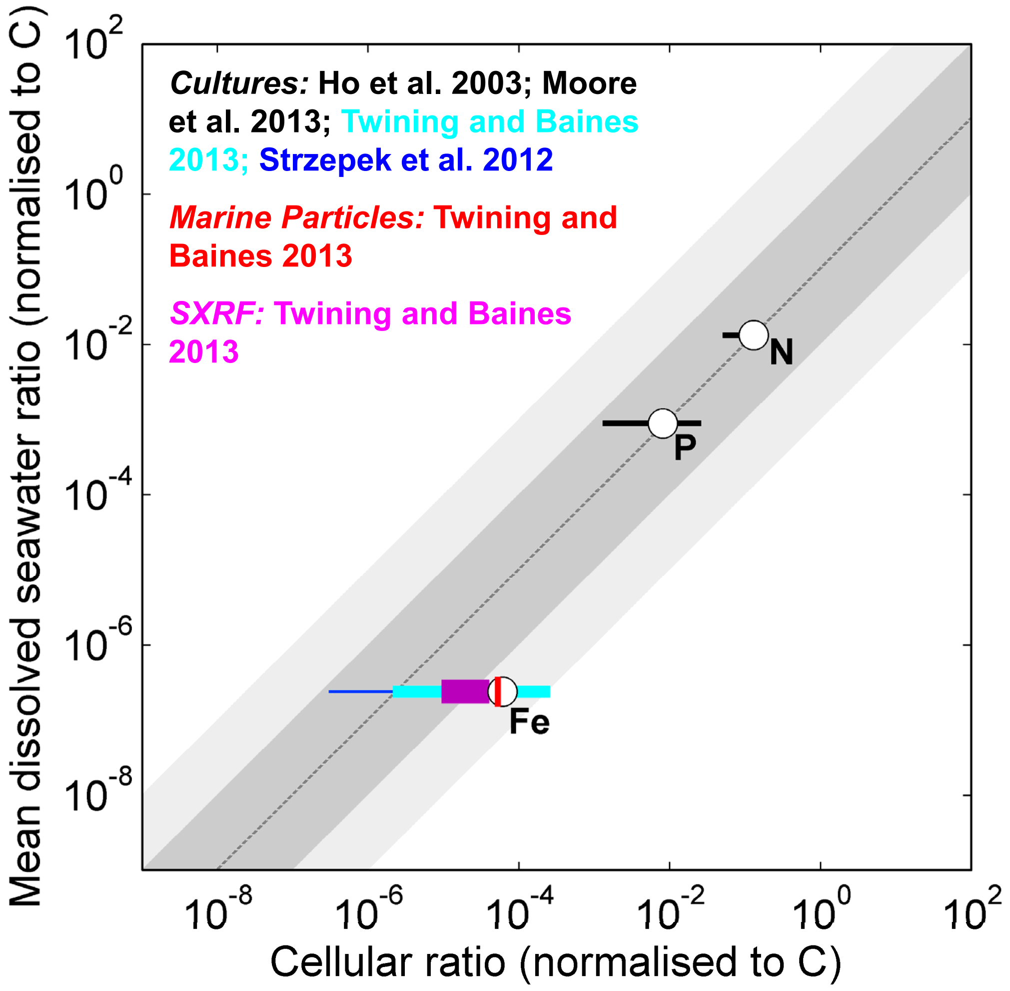
Range of cellular functions, substitutions, storage

Total abundance of (and requirement within) associated macromolecules

Plasticity cont.

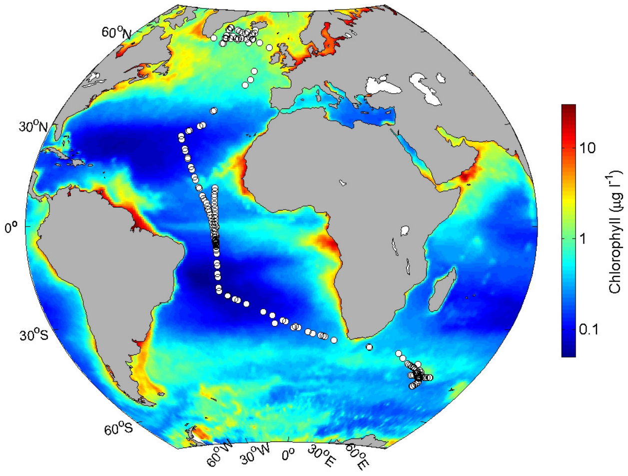
Understanding plasticity will arguably be more important for the trace metals than for the macronutrients.

Taxonomic (i.e. adaptive/genotypic) and physiological (acclimative/phenotypic) variability as well as discrepancies between techniques will all need consideration.



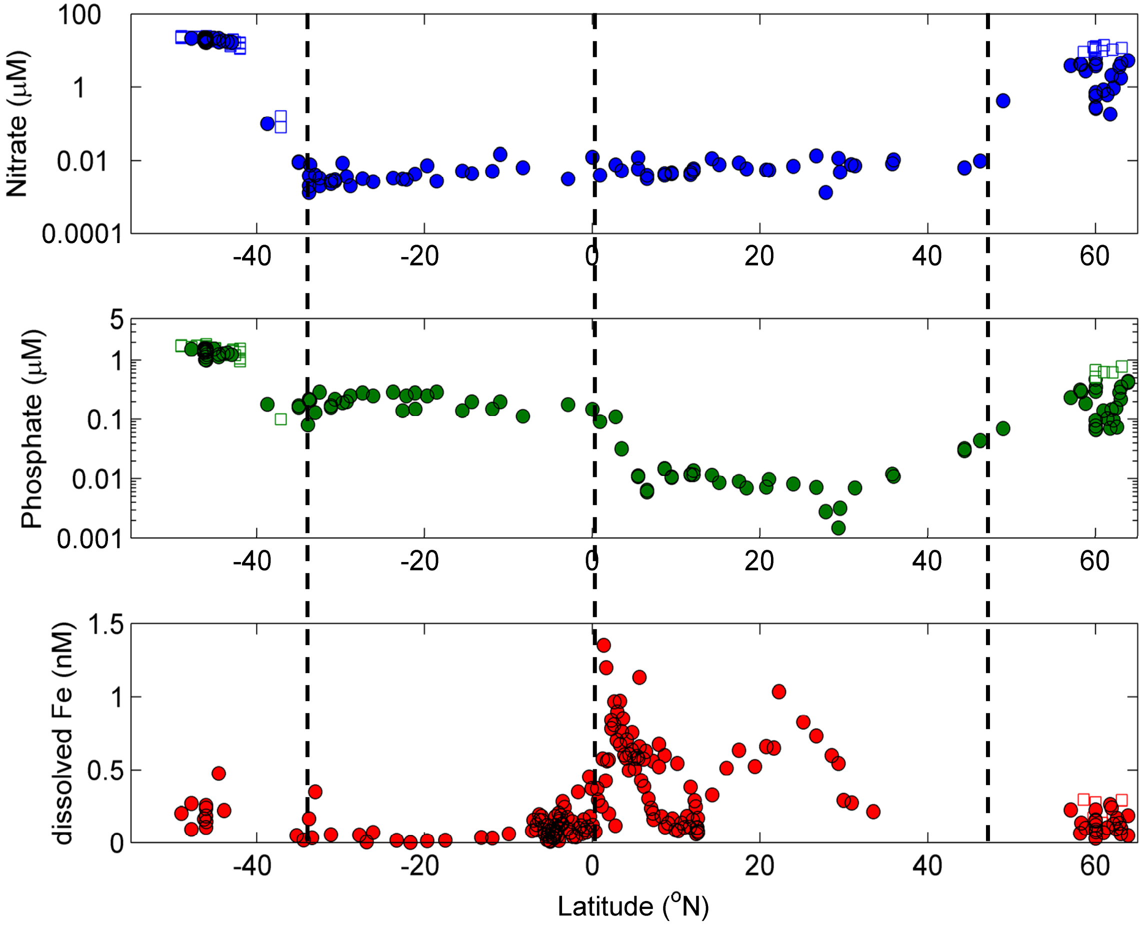
Sunda (2012) Front. Microbiol., Twining and Baines (2013) Annu. Rev. of Mar. Sci.; Strzepek et al. (2012) L&O

A journey through the Atlantic I



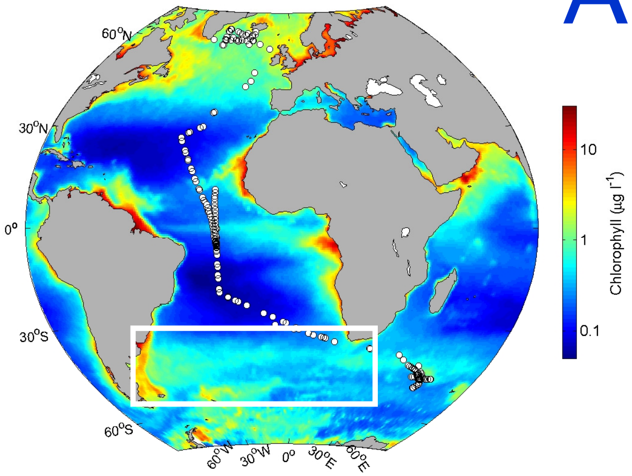
Standing stocks of the three principal limiting nutrients clearly delineate 4 ‘biogeochemical provinces’ in the Atlantic Ocean.

Can we use such gradients to provide inference of Fe supply and demand?



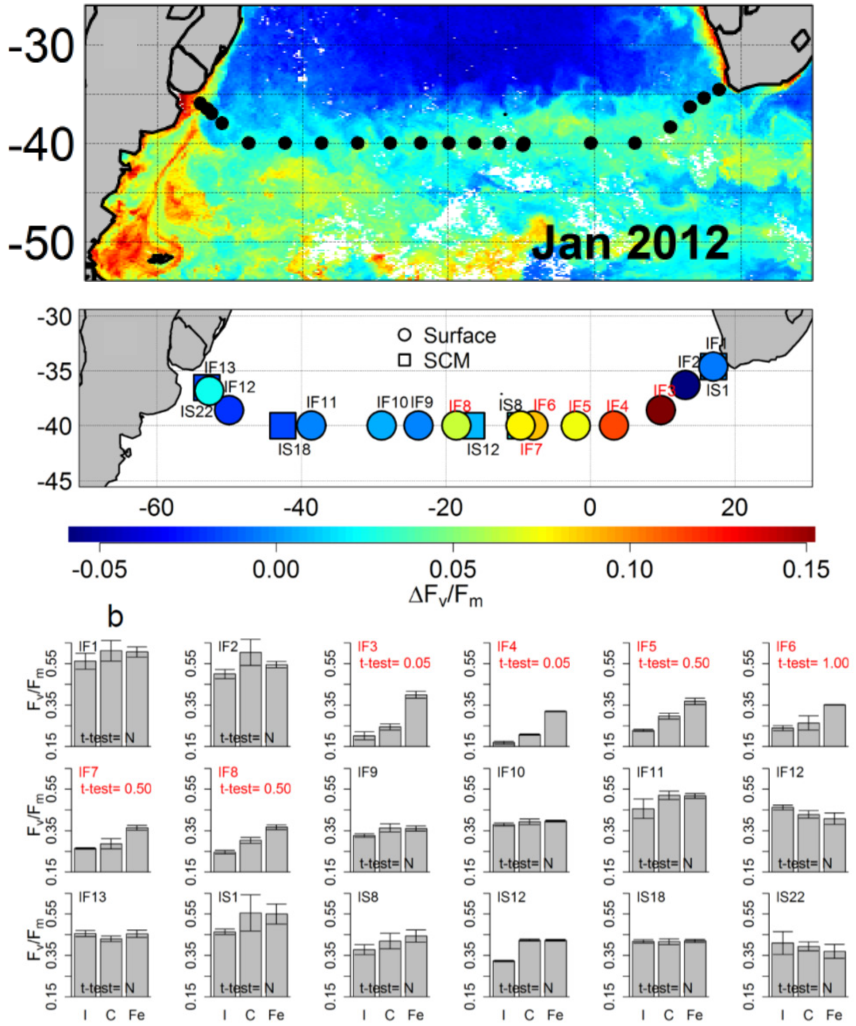
Planquette et al. 2007 DSR II; Moore et al. 2009 Nature Geo.; Steigenberger et al. unpub.

An example HNLC transition



GEOTRACES section at 40°S (section GA10, cruise JC068, UK GEOTRACES consortium). Longitudinal section crossing in-out of South Subtropical Convergence (SSTC).

Characteristic physiological responses to Fe amendment observed in 'HNLC' region.



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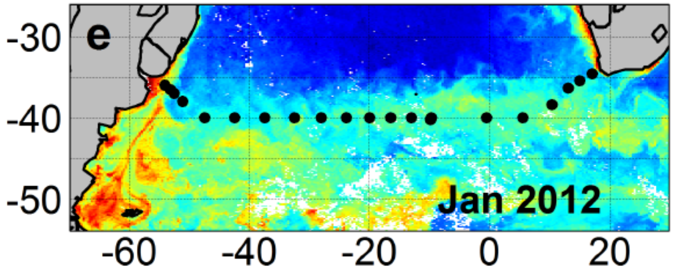
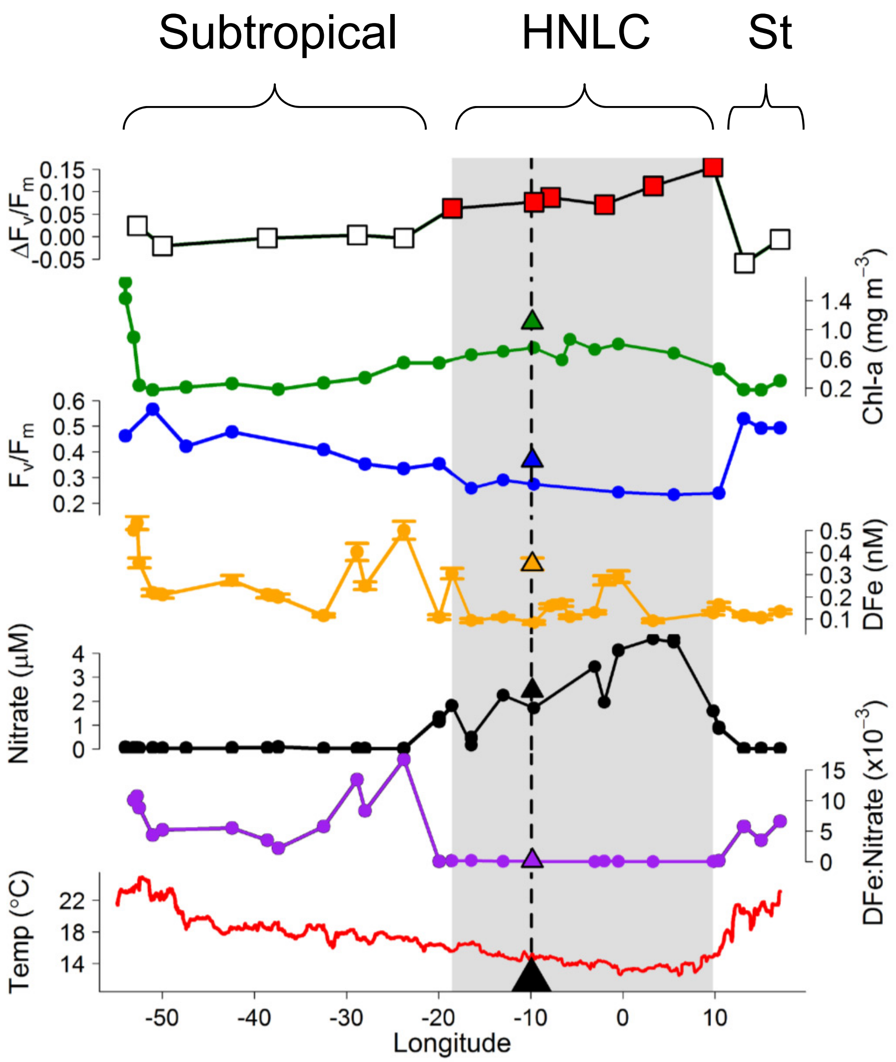
micronutrient cycles and paleoproxies in the ocean

Browning et al. (2013) Biogeosciences Discuss. 10 11969-12008

Patterns across the SSTC





Sharp boundaries between the distinct biogeochemical regimes are observed in terms of degree of Fe stress, DFe and macronutrients (nitrate).

Macronutrients a better predictor of Fe stress than DFe?

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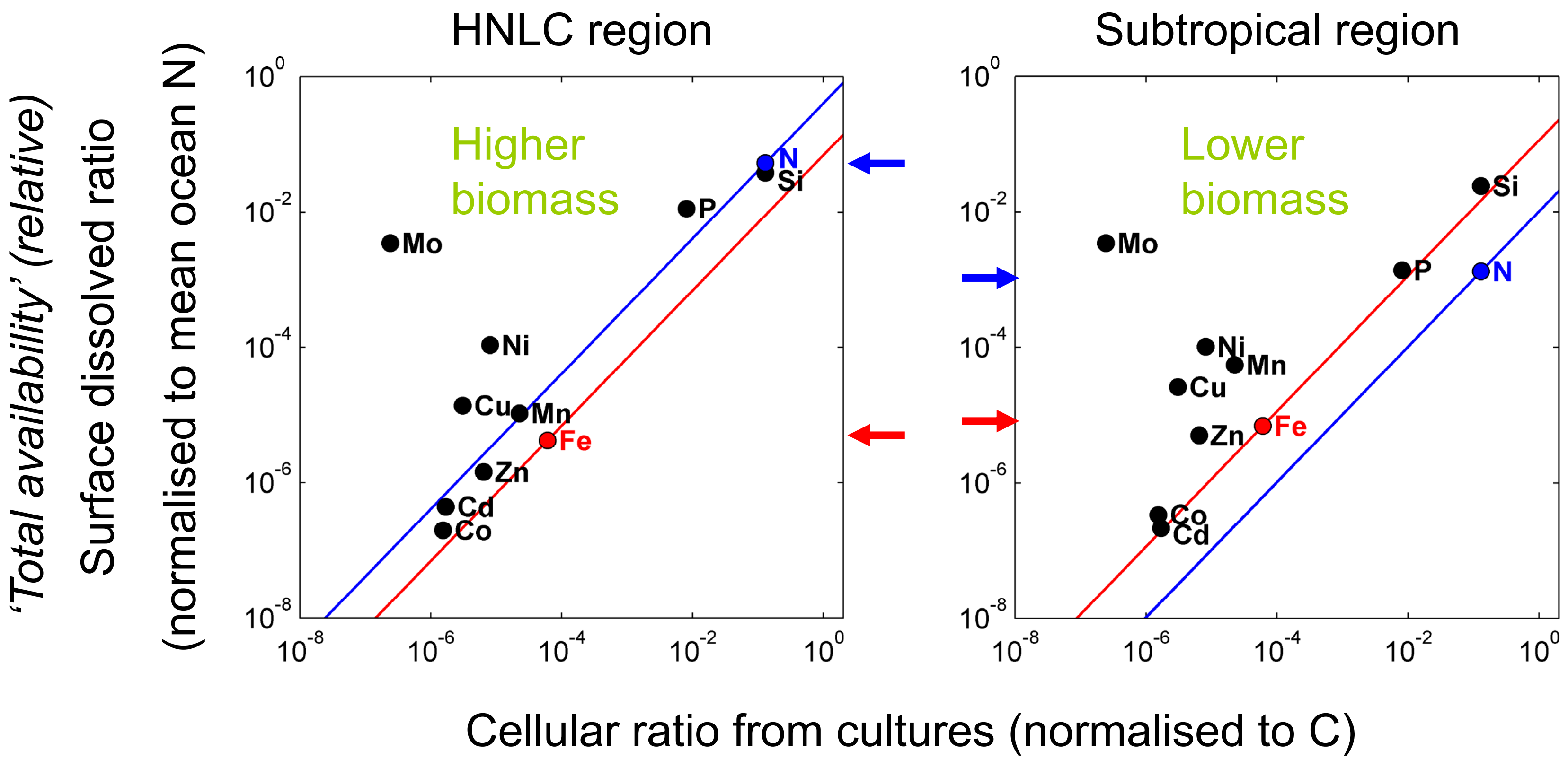
micronutrient cycles and paleoproxies in the ocean

Browning et al. (2013) Biogeosciences Discuss. 10 11969-12008

Deficiency appears to be predictive of limitation…



Maximum biological requirement, relative to most deficient nutrient

JC068 data courtesy of Christian Schlosser (NOCS)
and Malcolm Woodward (PML)

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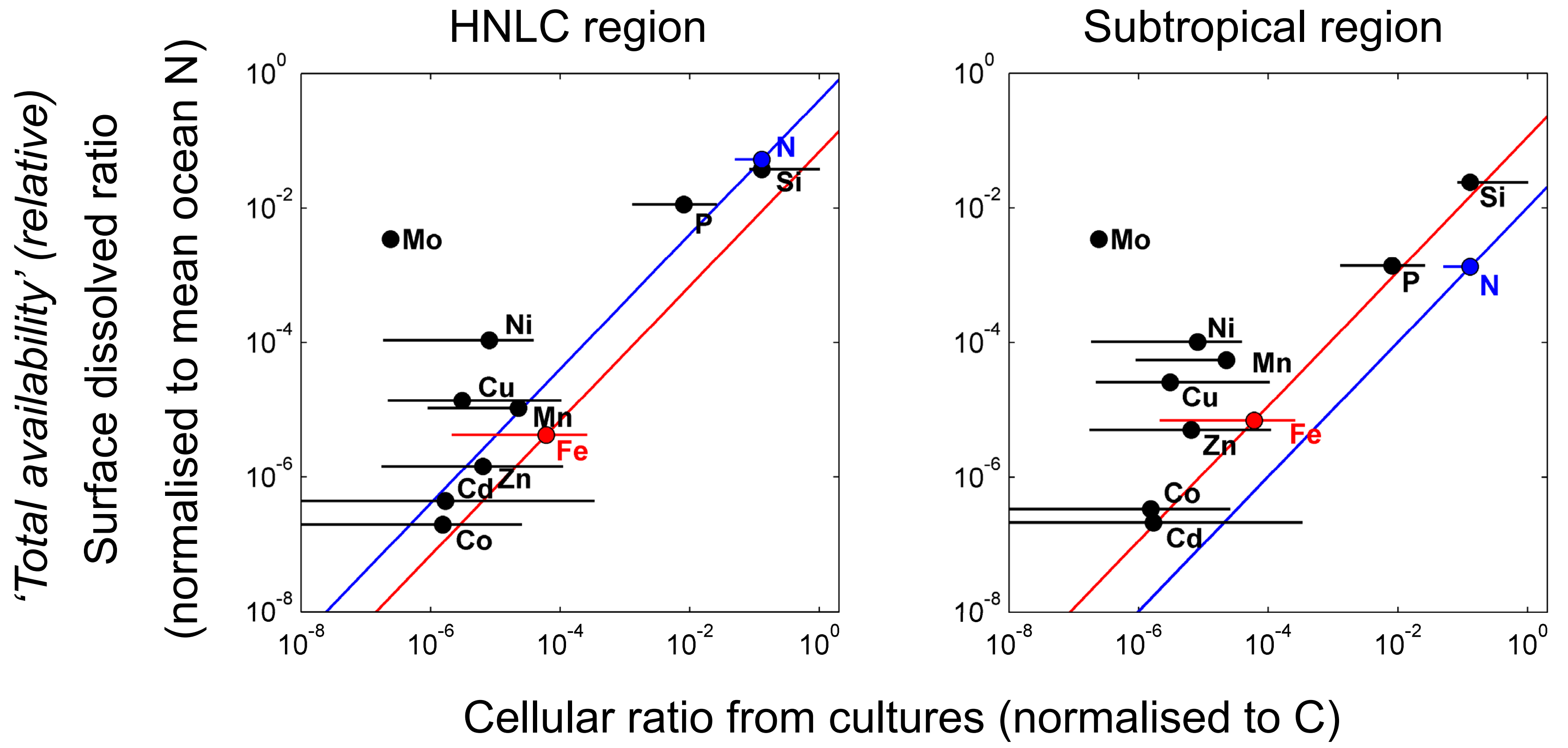
Deficiency appears to be predictive of limitation?



Maximum biological requirement, relative to most deficient nutrient

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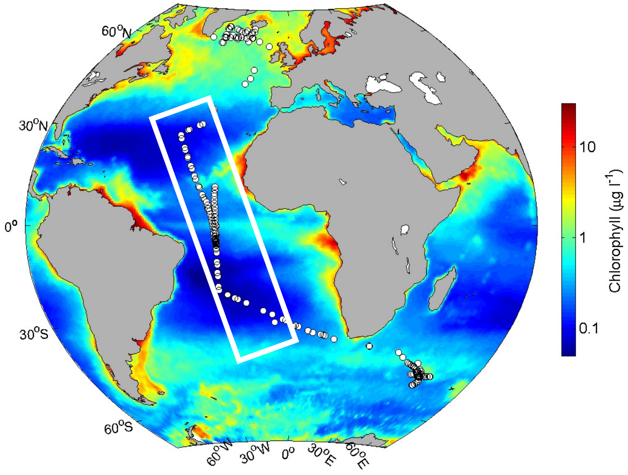
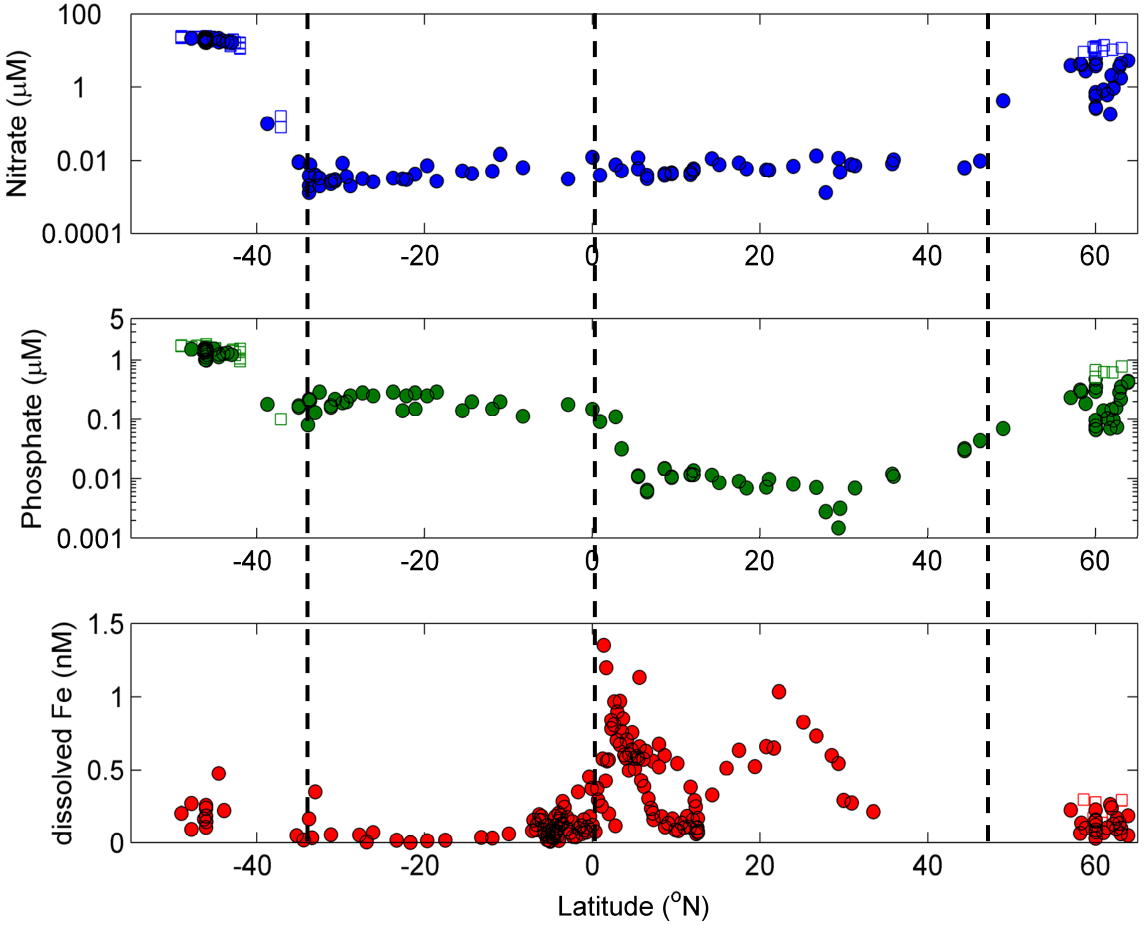
micronutrient cycles and paleoproxies in the ocean

JC068 data courtesy of Christian Schlosser (NOCS) and Malcolm Woodward (PML)

A journey through the Atlantic II





Outside of the HNLC regions there is less evidence for overall trace metal (Fe) limitation.

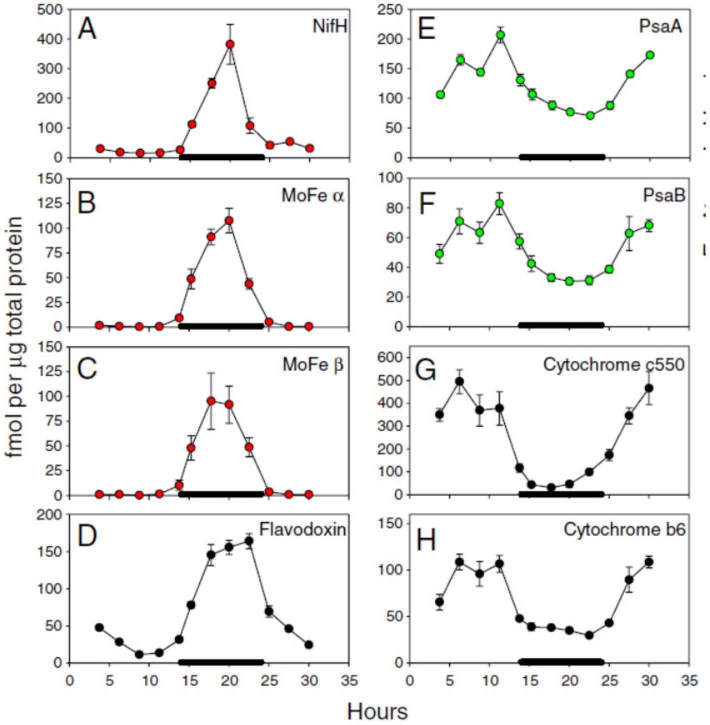
But there appear to be strong biogeochemical (nutrient) boundaries.

Planquette et al. 2007 DSR II; Moore et al. 2009 Nature Geo.; Steigenberger et al. unpub.

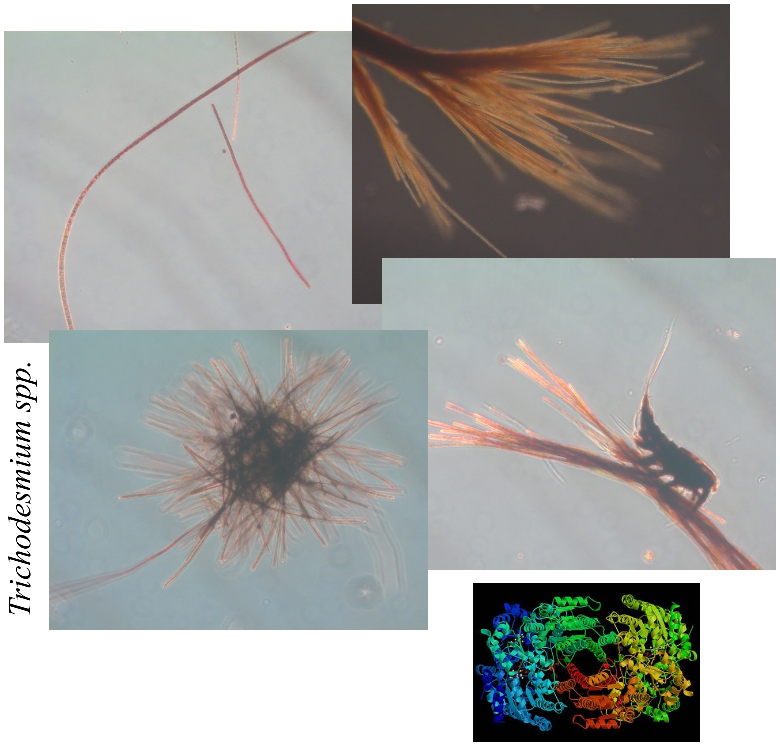
N_2 fixation has a high Fe requirement

The enzyme which catalyses the fixation of N_2 (nitrogenase) has a very high Fe requirement.

e.g. Pearl et al. (1994); Falkowski (1997); Berman-Frank et al. (2001, 2007) etc.

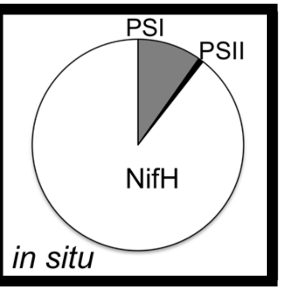


Saito et al. (2011) PNAS



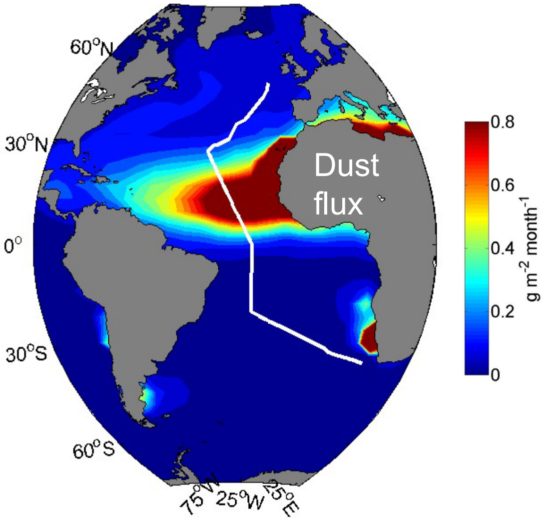
Trichodesmium spp.

Potentially 80% of cellular Fe quota is within the N_2 fixation apparatus



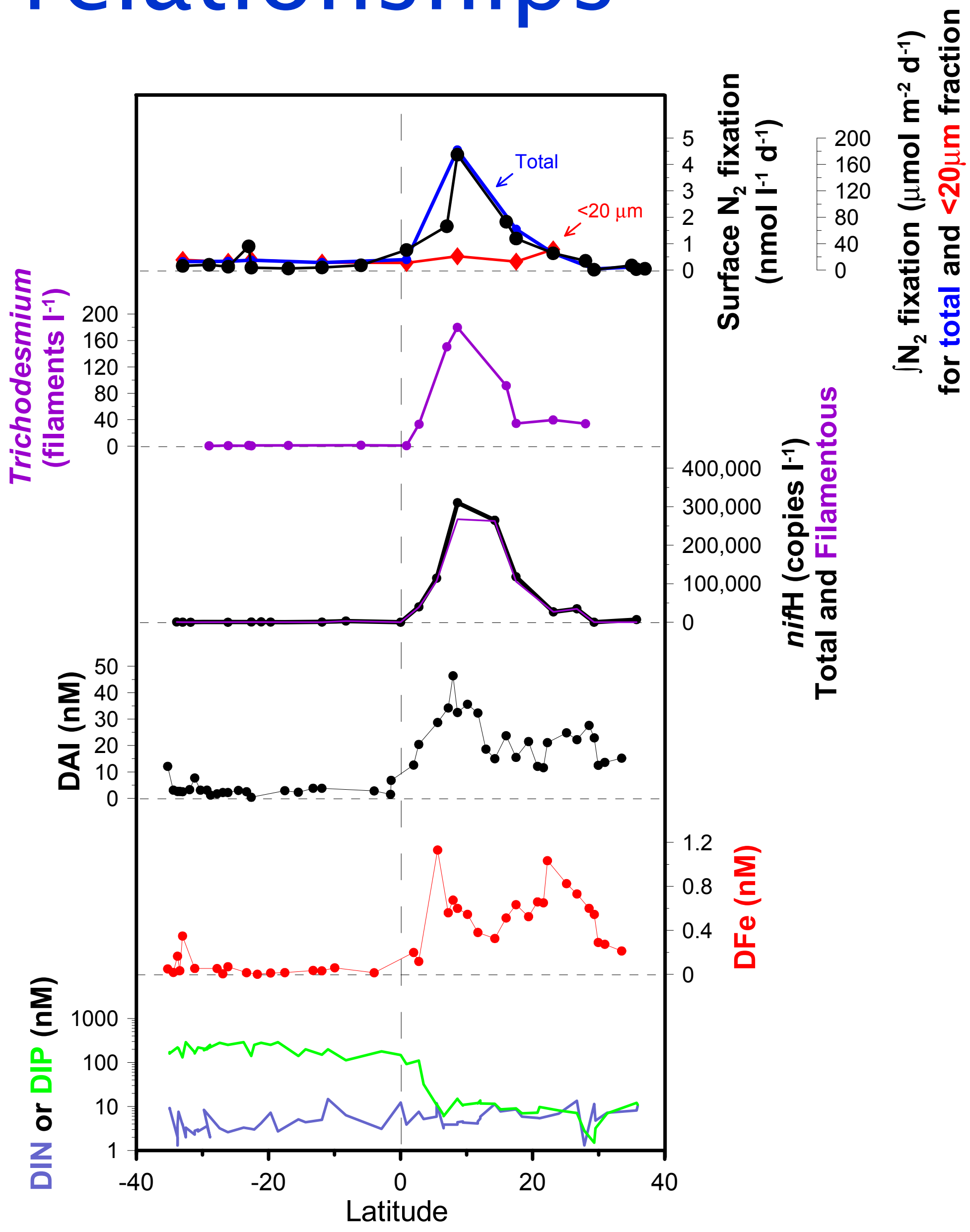
Richier et al. (2012) PLoS One

Correlative relationships



Direct experimental evidence is often equivocal (although see e.g. *Mills et al. 2004 Nature*)

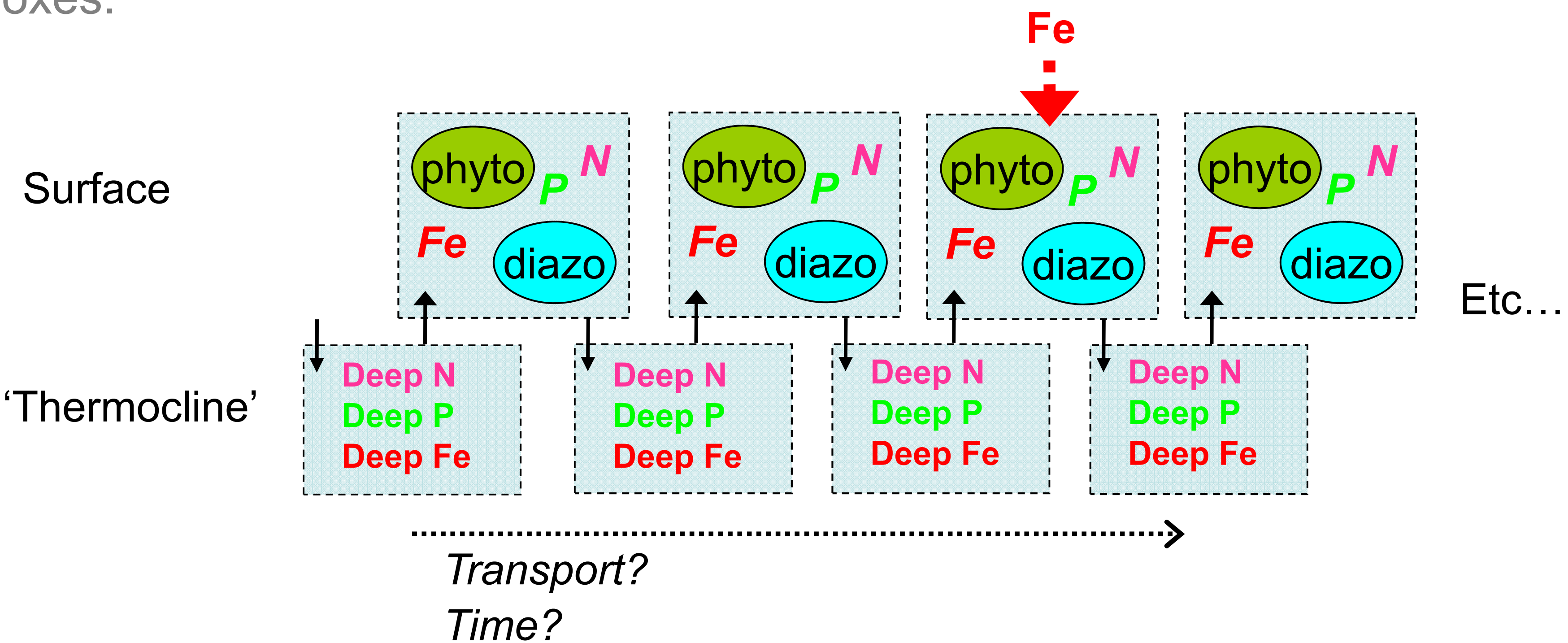
However, at least in the Atlantic, correlations between tracer of dust input (DAI), DFe and the abundance and activity of N_2 fixers are striking…



Moore et al. 2009 Nature Geoscience, Langlois and La Roche, unpubl.

Simple model

2-D extension of simple model (*e.g. Tyrrell 1999 Nature, Dutkiewicz et al. 2012 GBC, Ward et al. L&O In press*) to include ‘surface’ and ‘thermocline’ boxes.



Fe

Surface

phyto P N
Fe diazo

phyto P N
Fe diazo

phyto P N
Fe diazo

phyto P N
Fe diazo

Etc…

‘Thermocline’

Deep N
Deep P
Deep Fe

Deep N
Deep P
Deep Fe

Deep N
Deep P
Deep Fe

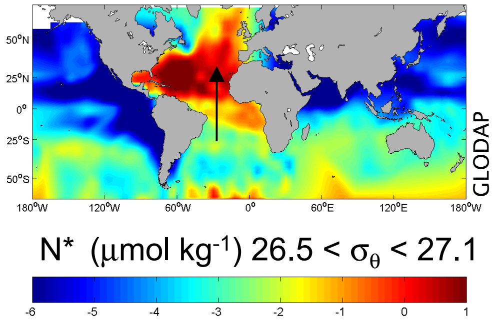
Deep N
Deep P
Deep Fe

Transport?

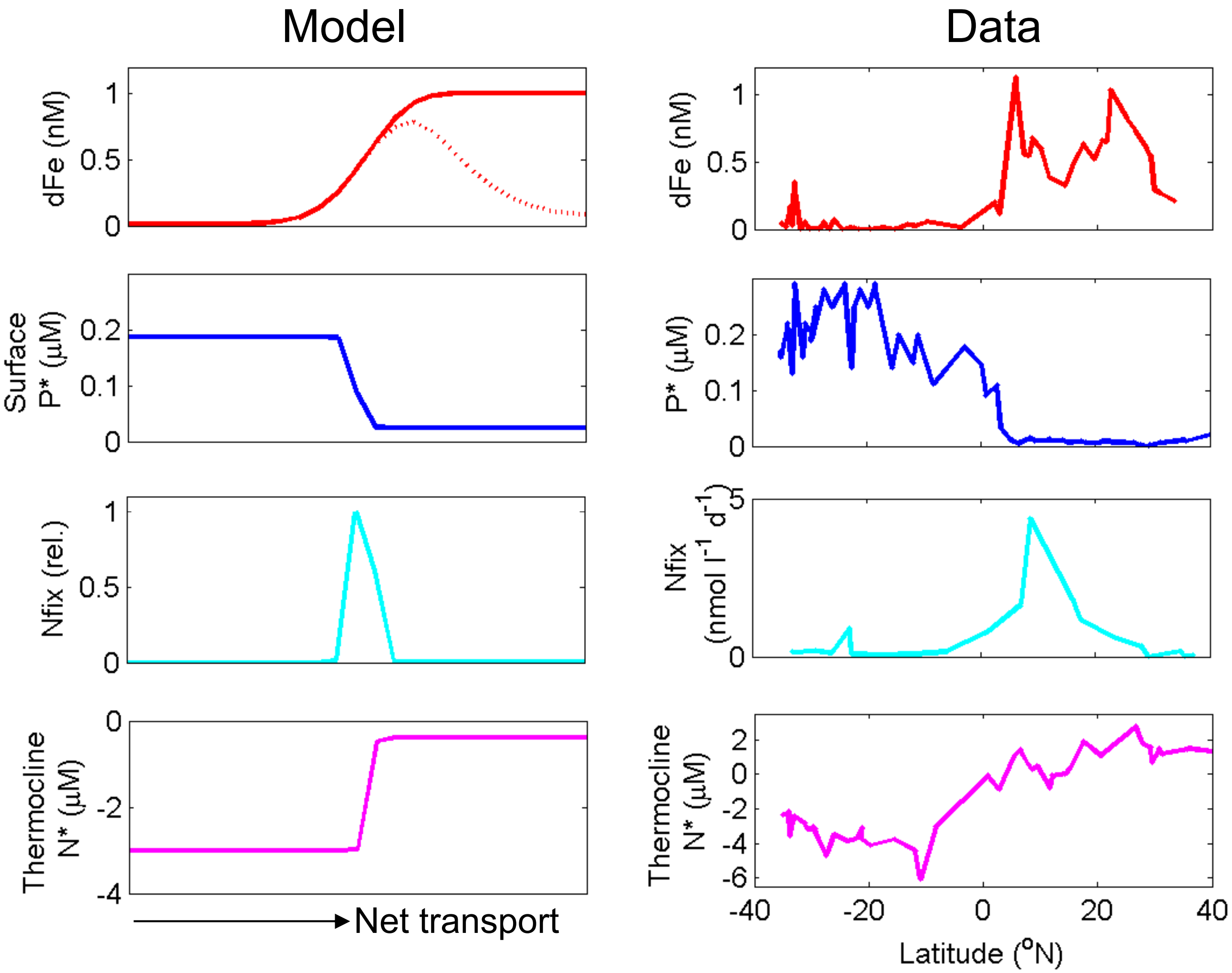
Time?

Idealised representation of northward flow in upper limb of Atlantic MOC

Sarmiento et al. 2004 Nature
Williams et al. 2006 GBC
Palter et al. 2010 Biogeosci.



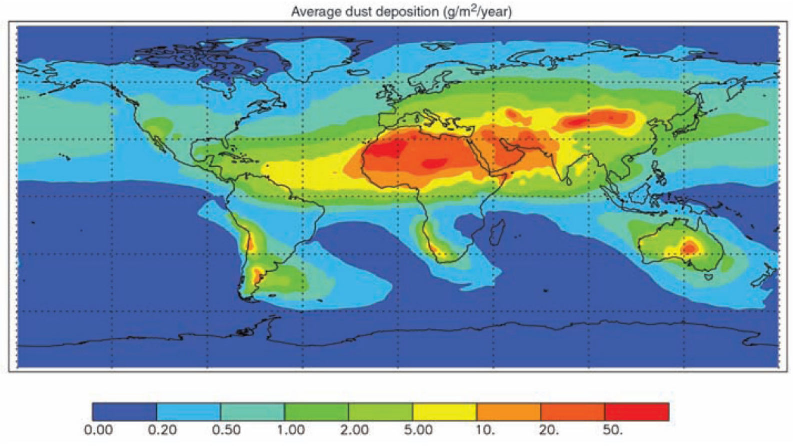
Simple model



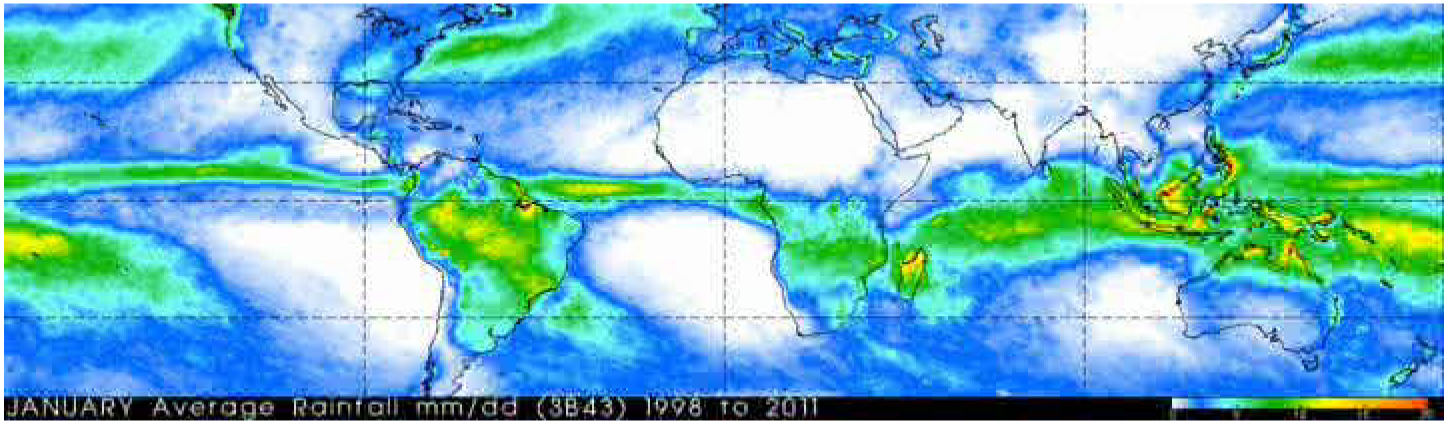
Seasonality of Fe inputs

Atmospheric inputs, (both dry and wet) will vary seasonally…

In Atlantic, variability may be linked to seasonal migration of ITCZ.



Jickells et al. 2005



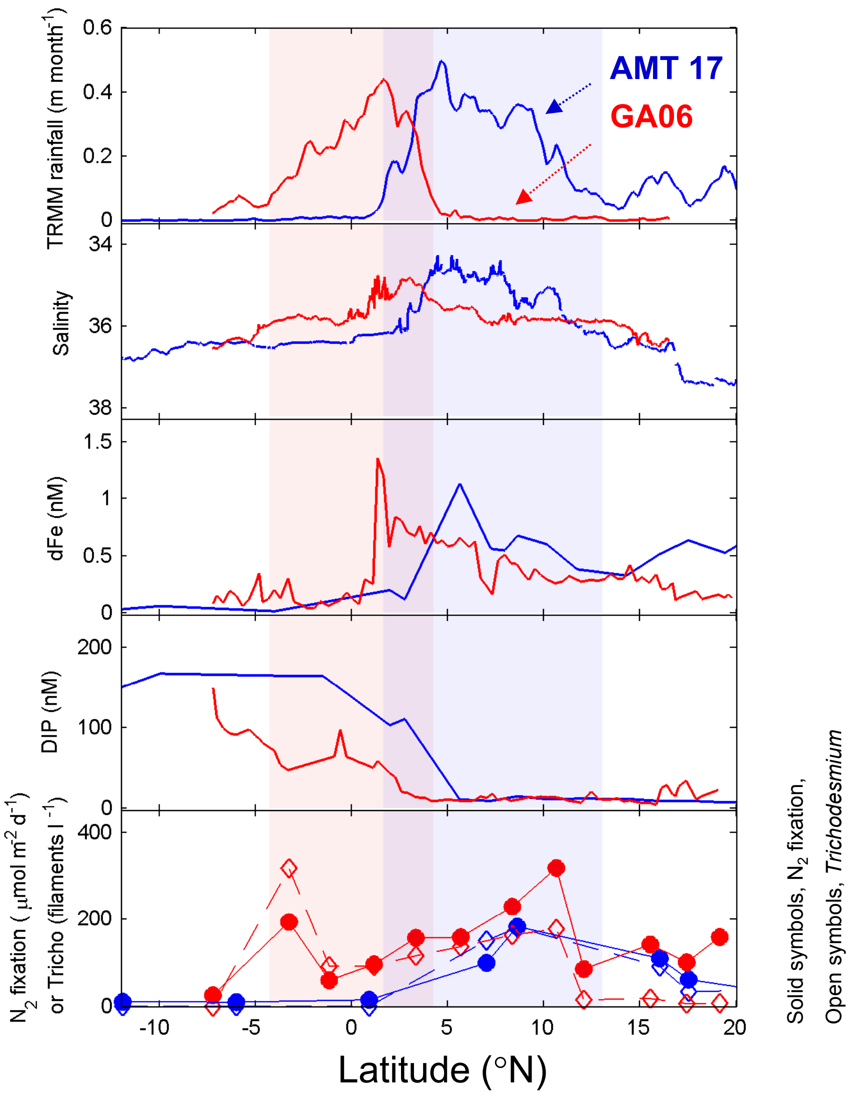
TRMM Rainfall monthly climatology (courtesy, NASA Giovanni)

Seasonality of biogeochemical boundary

Comparing AMT17 with D361 (GA06), spatial correlation between regions of high rainfall, lowered salinity and enhanced DFe all suggest that wet deposition dominates soluble Fe inputs.

Correspondingly, boundary between low P and high P water shifts south when ITCZ shifts south.

Similarly region of enhanced N_2 fixation (and *Trichodesmium* abundance) also shifts south.



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Schlosser et al. In prep.

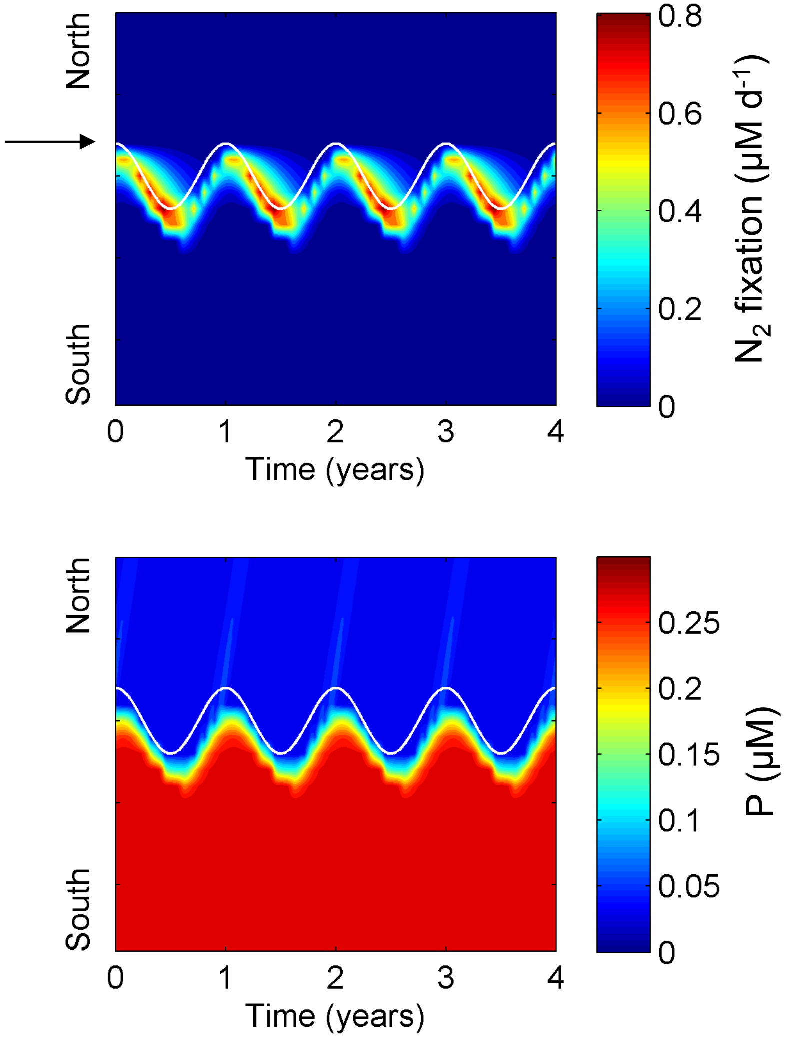
Seasonality of biogeochemical boundary

Simple model forced with varying position of peak Fe supply behaves as expected.

N_2 fixation tracks (with a delay) the movement in the region of enhanced Fe input.

Correspondingly the boundary between the high P and low P waters also tracks the Fe input.

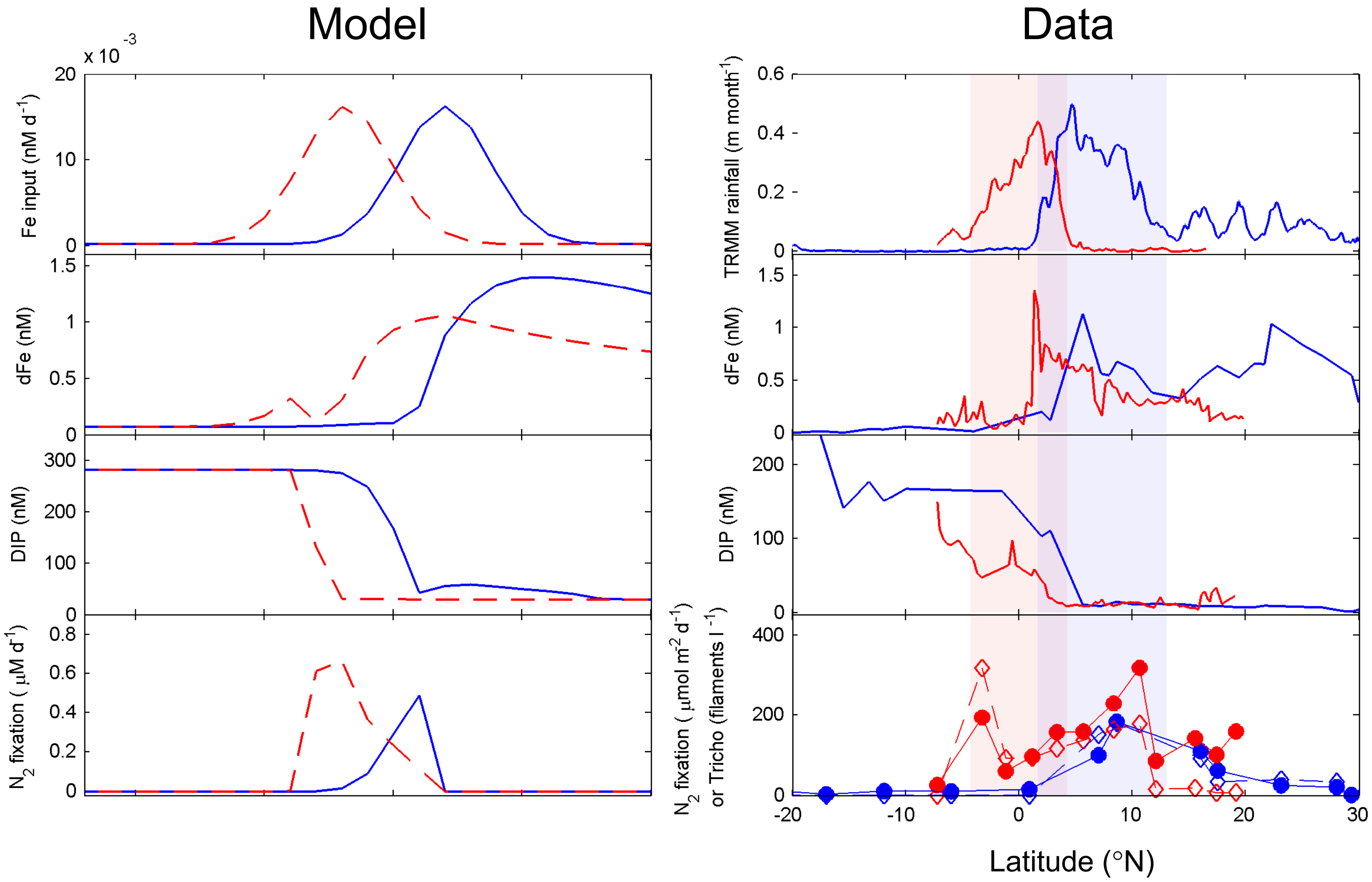
(*note*, non-steady system, physics becomes important)



White line = position of max Fe input

Schlosser et al. In prep.

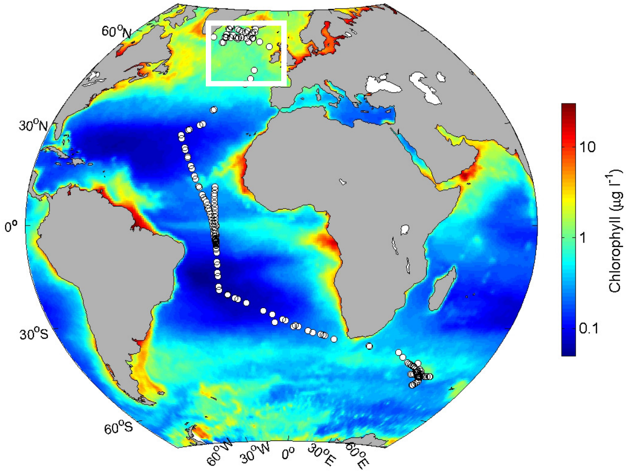
Seasonality of biogeochemical boundary

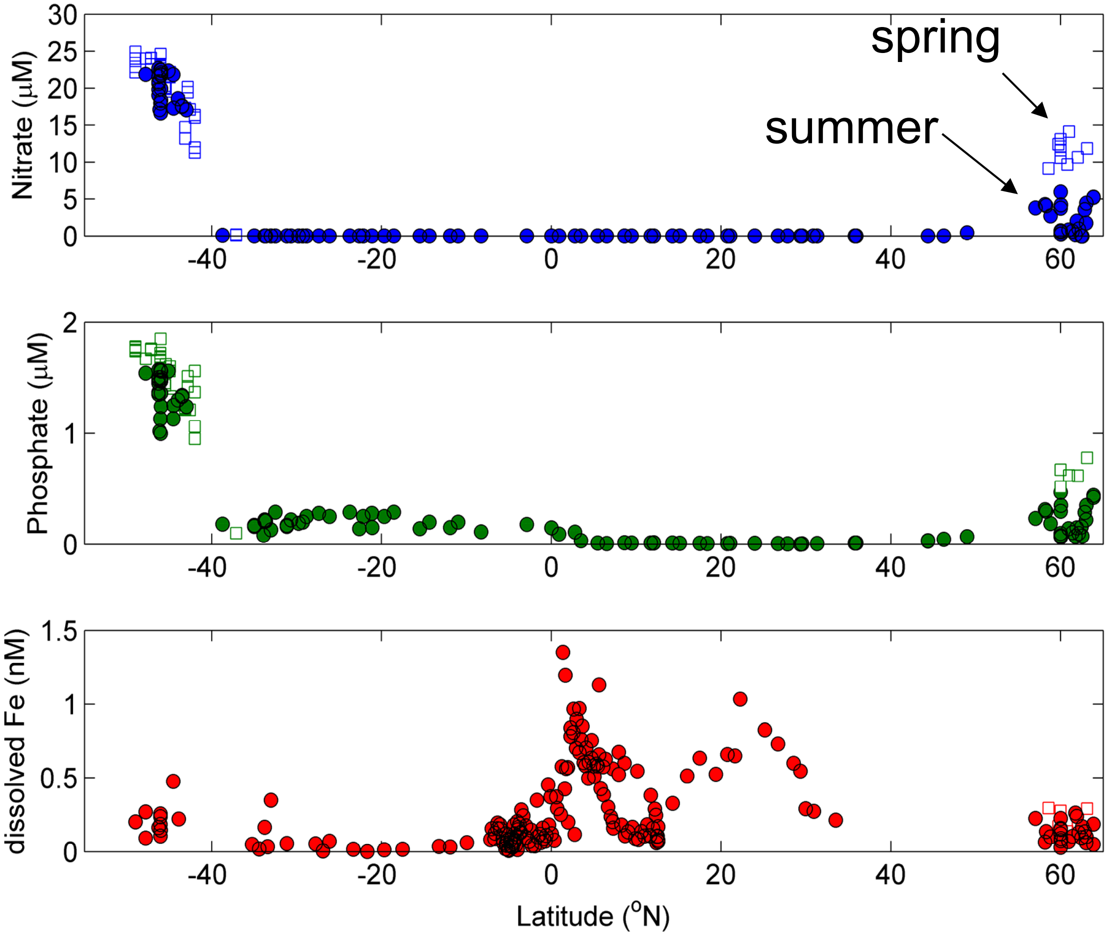


System behaves in predicted manner in response to natural perturbation of Fe supply.

Contribution of diazotrophs ***does not*** *need to be a major component of total biological uptake/demand…*

A journey through the Atlantic III

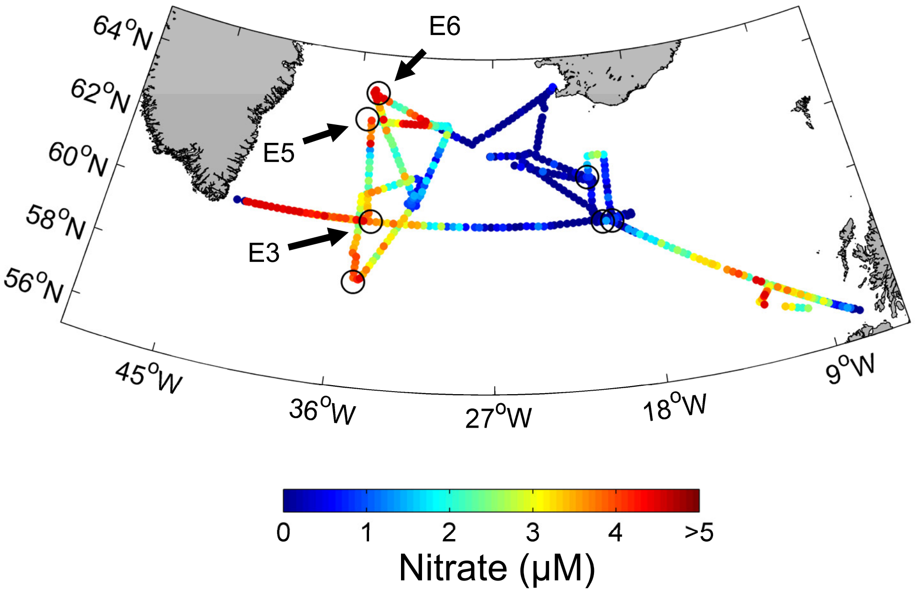


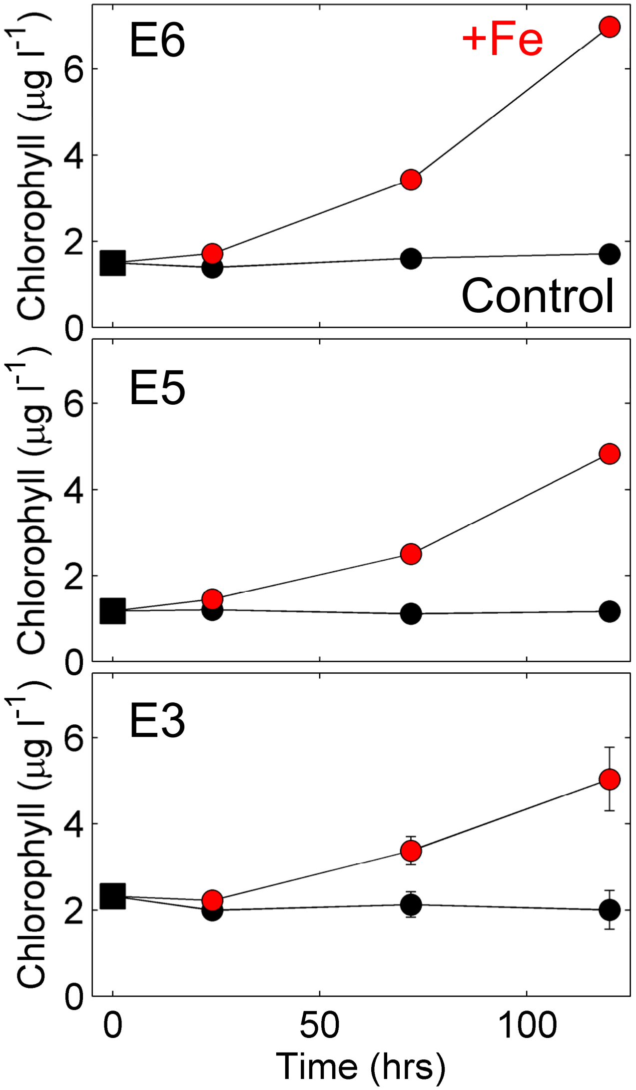


Seasonality of Fe supply due to movement of ITCZ may be an unusual case, but seasonality is obviously a major factor throughout much of the ocean.

Planquette et al. 2007 DSR II; Moore et al. 2009 Nature Geo.; Steigenberger et al. unpub.

Fe addition experiments



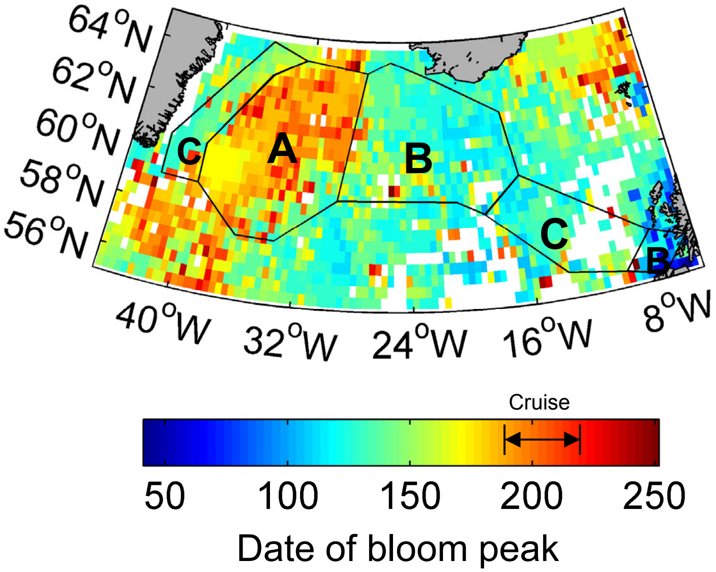


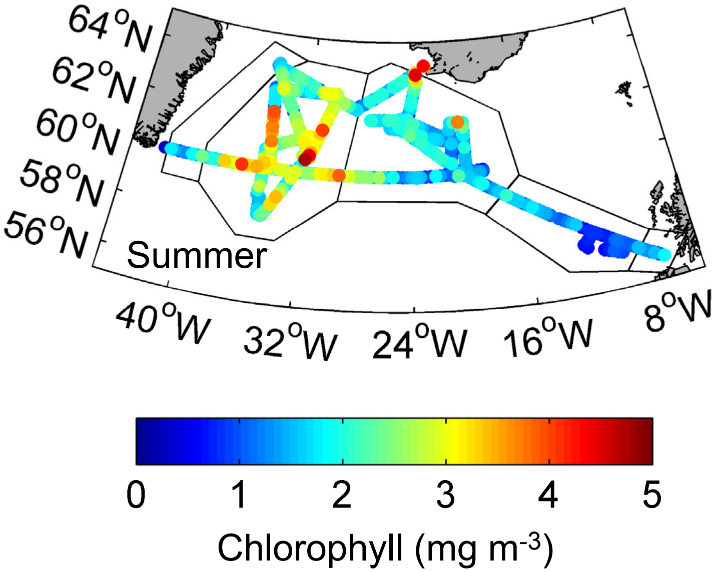
By summer, evidence of iron stress is actually consistently observed across the regions where macronutrients remain high (>~1 μM nitrate).

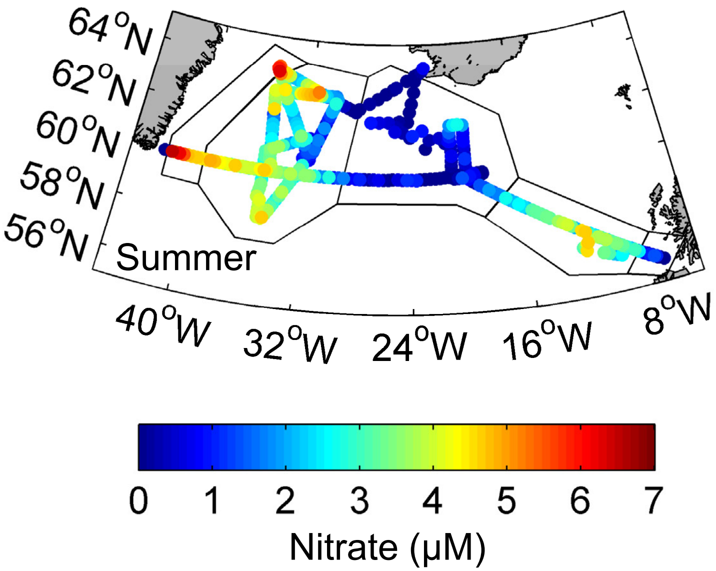
Phytoplankton biomass (chlorophyll concentration) increases over 3-5 days on addition of Fe

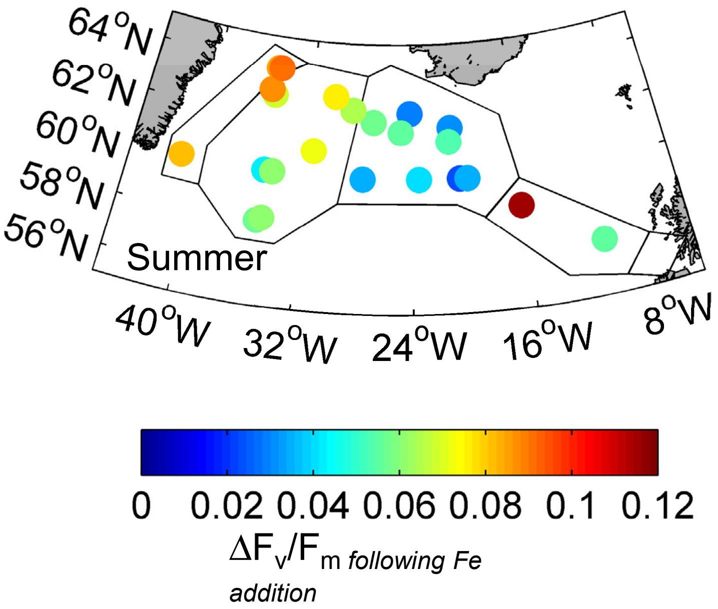
Martin et al. (1993); Nielsdottir et al. (2009) GBC; Ryan-Keogh et al. (2013) L&O

Spatial variability









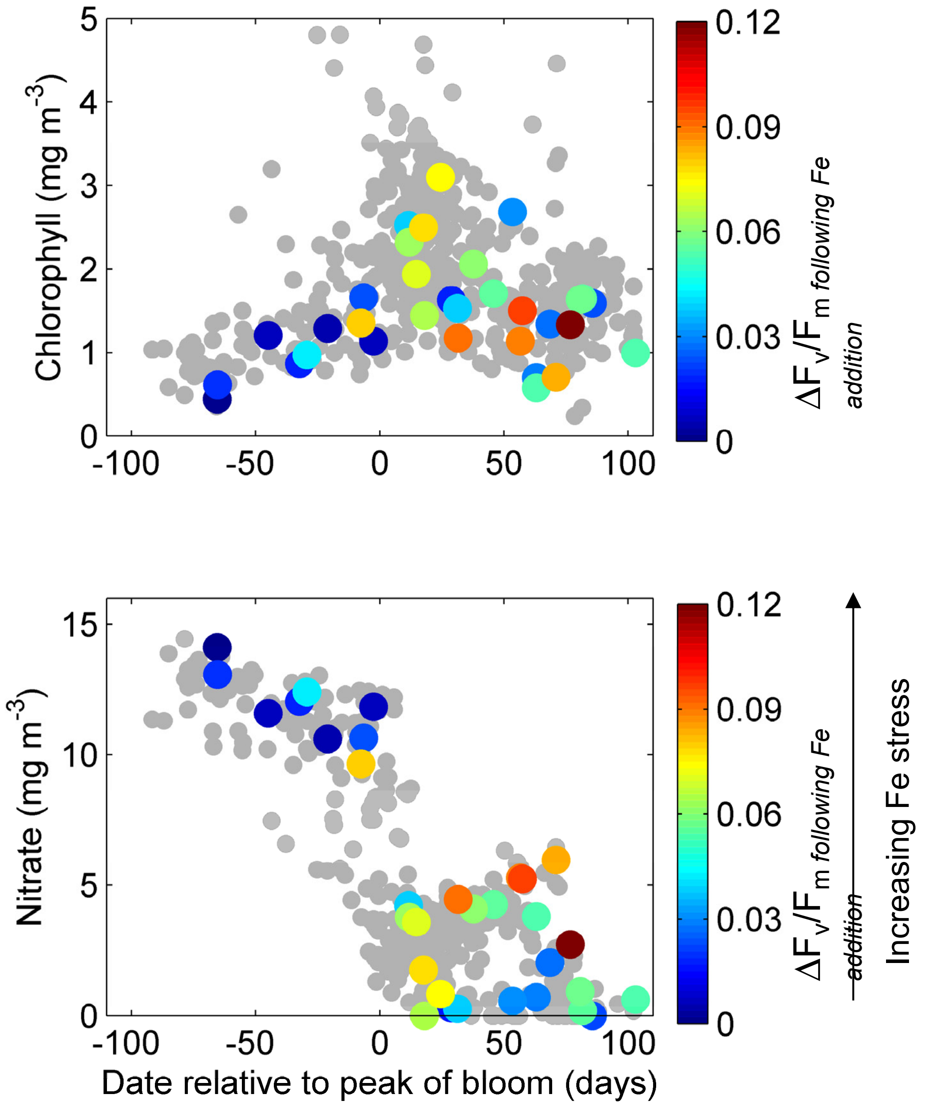
Temporal variability

Seasonal (and shorter/longer term?) variability in forcing factors (light, grazing, nutrients) occur in many systems.

Consequently biological requirement for trace metals might be expected to be dynamic, changing over time as well as space.

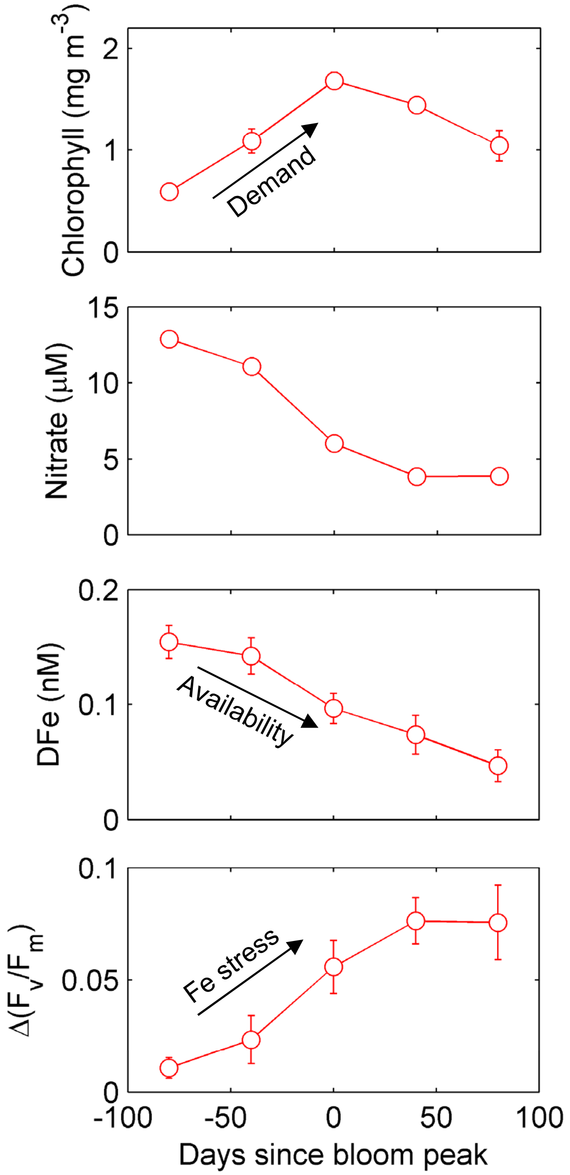
North Atlantic example:

Fe stress only appears to develop approaching/during the peak of the bloom. Subsequently maintained during post bloom period only in high nitrate regions.



Ryan-Keogh et al. (2013) L&O

Temporal variability



As bloom progresses:

biomass accumulates (hence **demand** presumably increases),

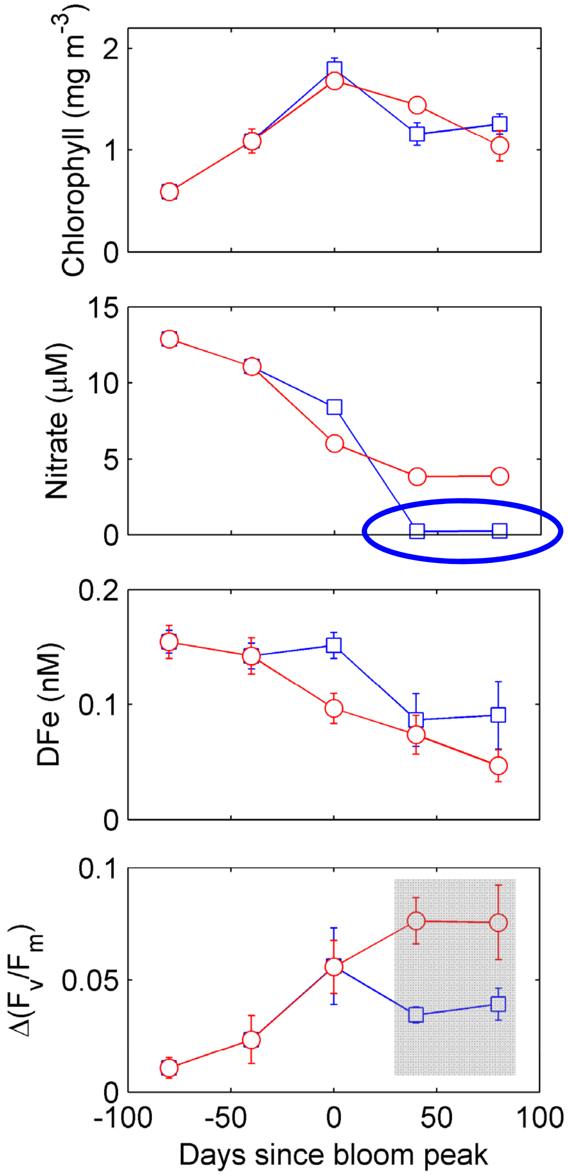
nutrients are used up (**supply/availability** decreases).

Correspondingly, degree of Fe stress appears to increase through season.

A similar seasonal progression has been suggested for the Southern Ocean (see e.g. *Boyd (2002), J. Phycol.*).

Reduced bioavailability (sensu. *Morel et al. (2006) Treatise on Geochem*, i.e. kinetic constraints on uptake), may also play a role (see Poster on ^{55}Fe uptake by *Nielsdottir et al*.)

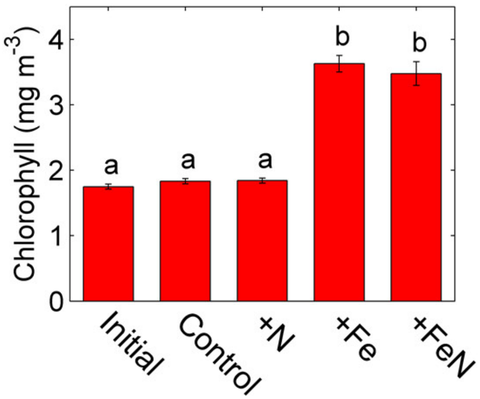
Temporal variability



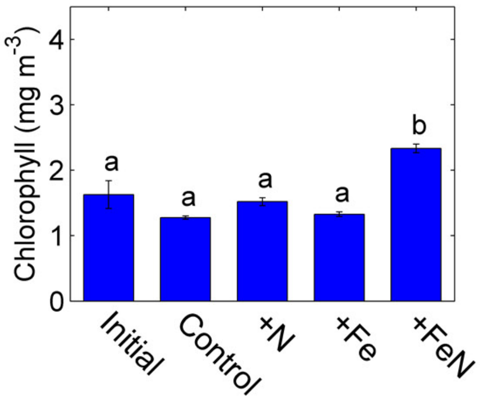
In most regions/years residual macronutrients and Fe stress persist into summer.

However, in some regions/years complete macronutrient removal occurs and accordingly degree of Fe stress subsequently drops.

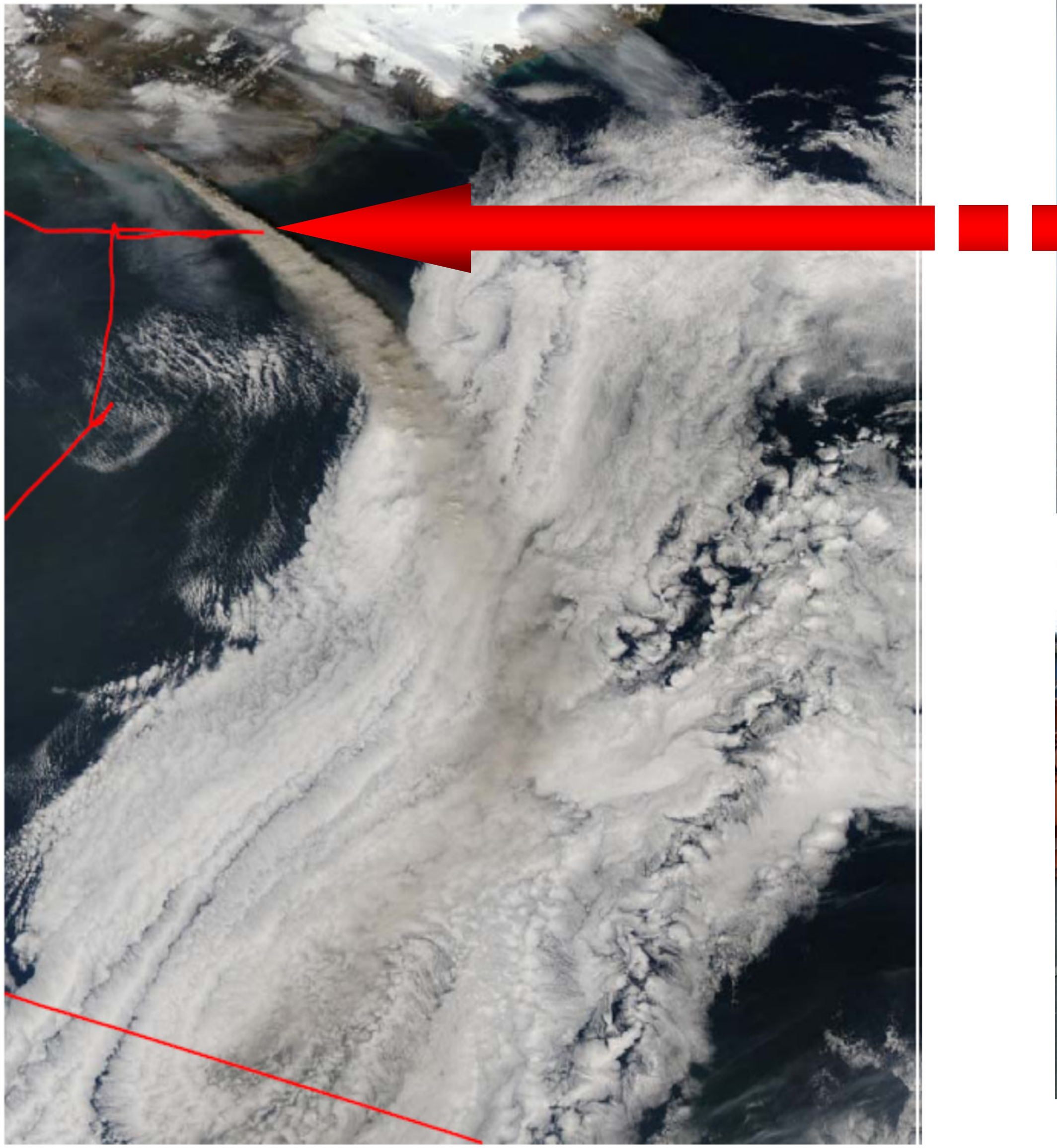
Fe limitation



Fe-N ‘co-limitation’?



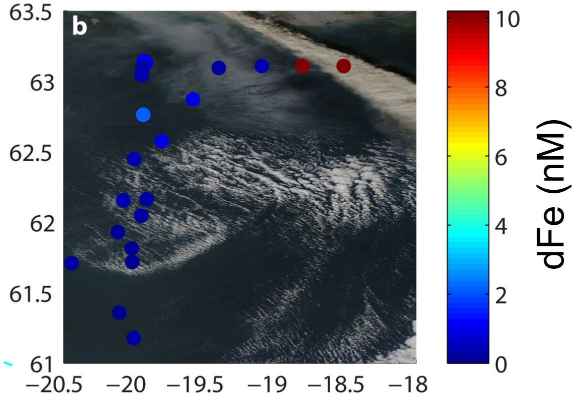
Sampling under eruptive plume



Potential enhanced Fe supply

DFe was highly enhanced directly under plume (>10 nM).

Estimation of wider scale ‘dissolved’ or ‘bioavailable’ iron inputs are complicated by a range of factors….



Achterberg et al. (2013) Geophysical Research Letters

Did the eruption of Eyjafjallajökull have a signifcant influence?

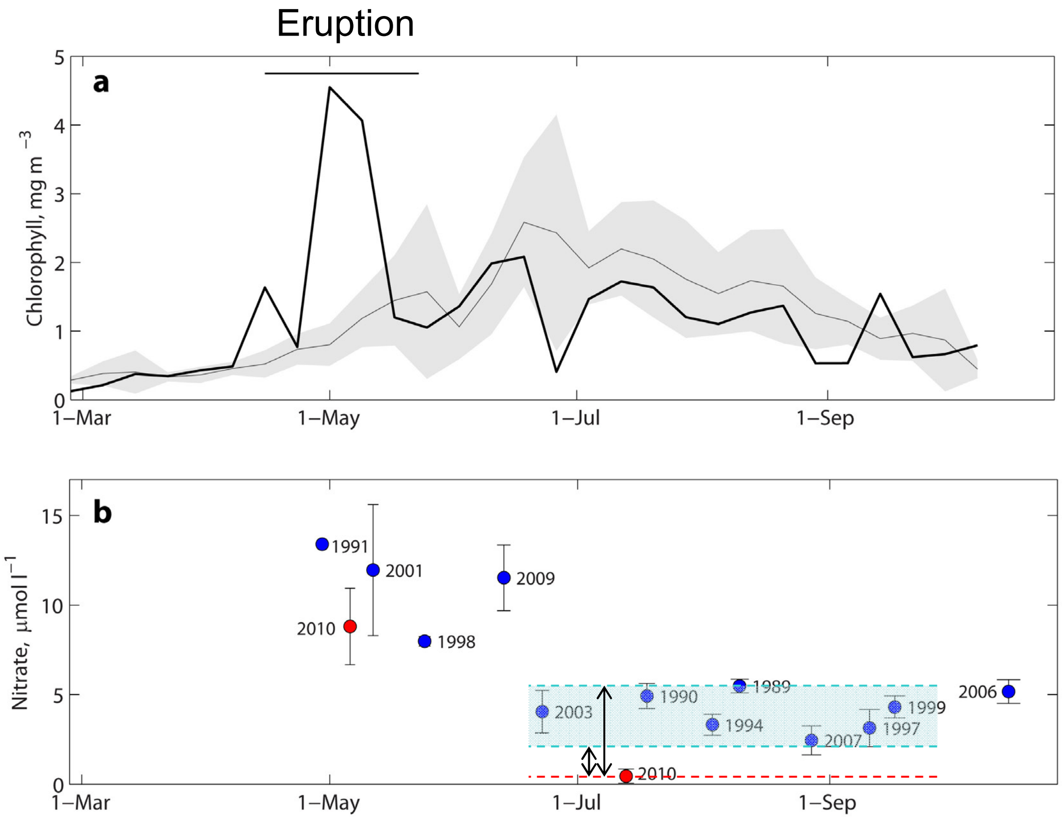
Taking measured ^{55}Fe:^{14}C uptake ratios:

1.6 - 4.3 μmol:mol

and C:N ~6.6:1,

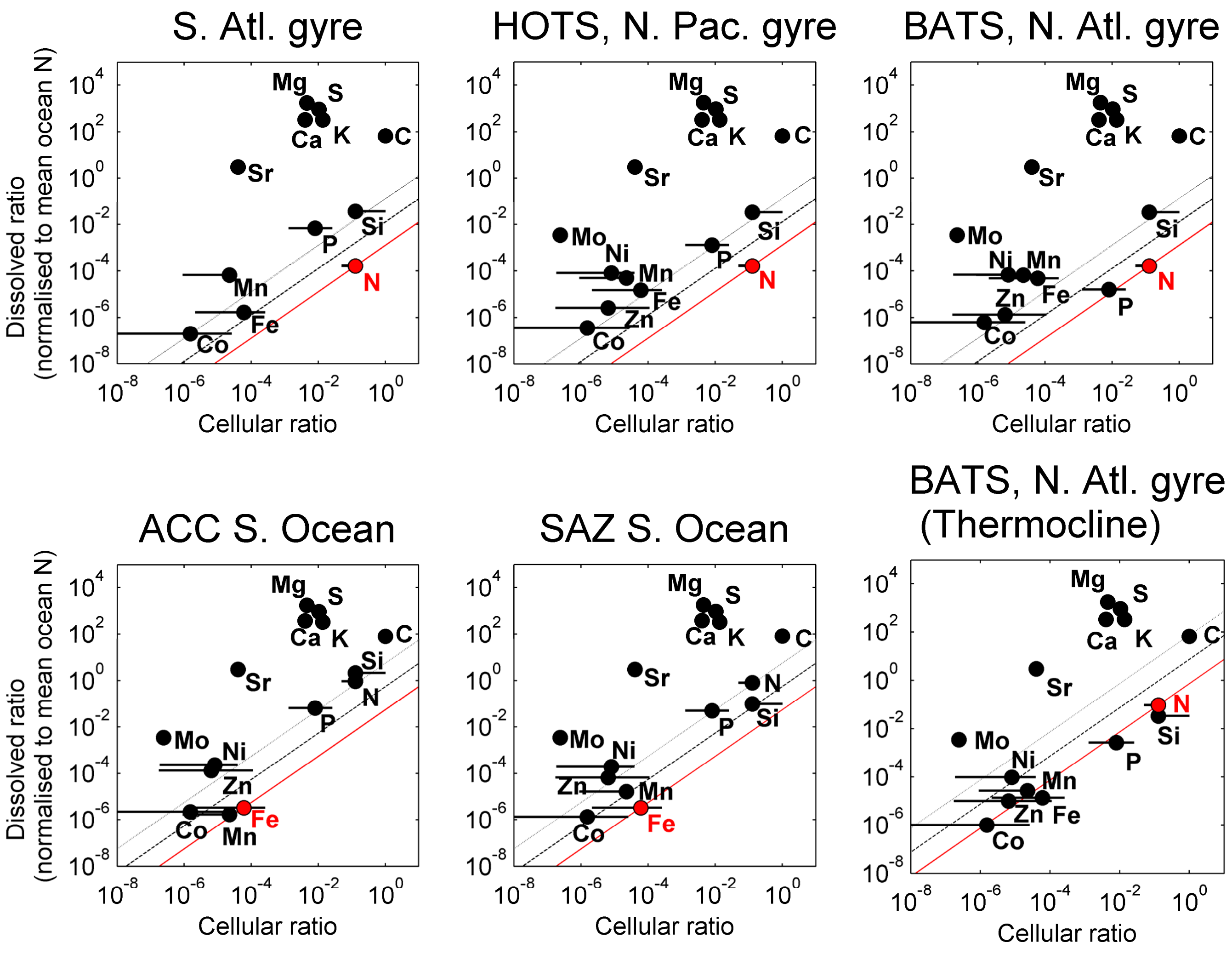
2-5 μM extra nitrate removal only requires:

0.02-0.15 nM extra Fe supply

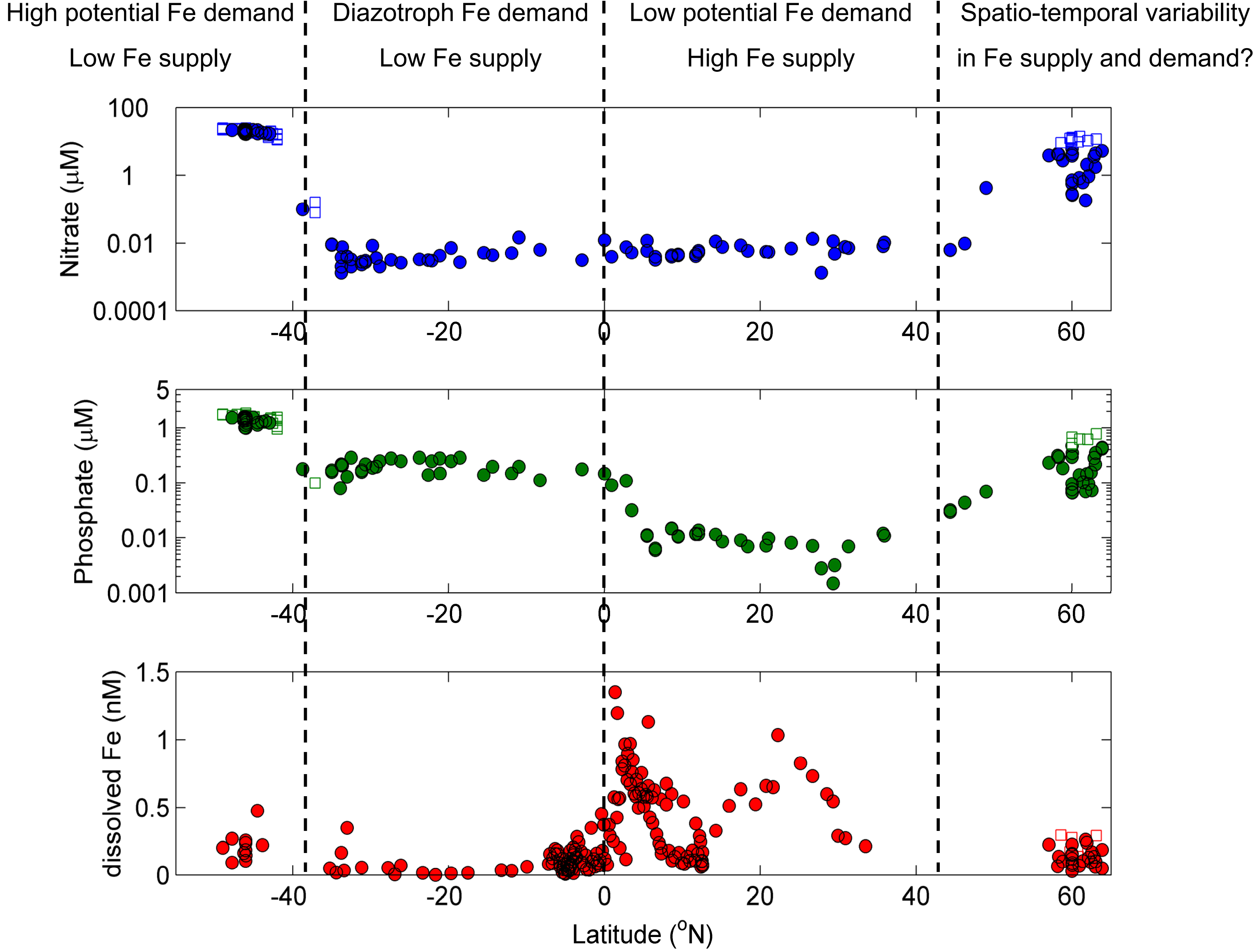


More generally, **any** factor which alters Fe:NO_3^- supply ratio (i.e. changing supplies of **Fe *or* NO_3^-**) might influence whether Fe becomes limiting…

Can we move towards reconciliation?



Can we move towards reconciliation?



See Ward et al. (2013) L&O in press for theoretical treatment.

Conclusions:

A conceptual basis for reconciling trace metal demand and supply is emerging, feedbacks with macronutrient availability are likely a key factor.

Appreciation of how variability in supply and demand at multiple scales drives spatio-temporal patterns of interactions.

Natural variability (seasonal or event scale forcing), provide useful ‘dynamic experiments’ against which to test our assumptions and theories (e.g. natural bloom cycles, seasonal movement of ITCZ, volcanoes?!)

Challenges to fuller biogeochemical reconciliation remain significant: e.g. moving beyond Fe (Mn, Ni, Zn, Cu, Cd, Co), stoichiometric plasticity, bioavailability, abiotic interactions (scavenging, redox) etc.

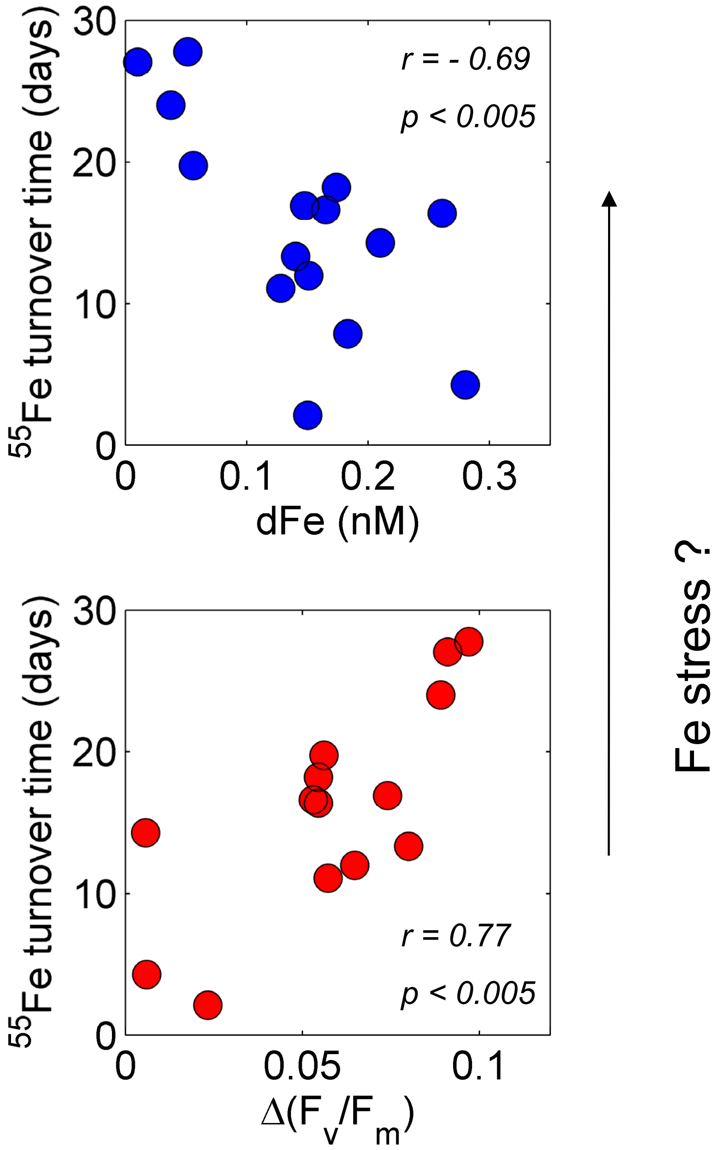
Thanks for listening!...

The importance of bioavailability

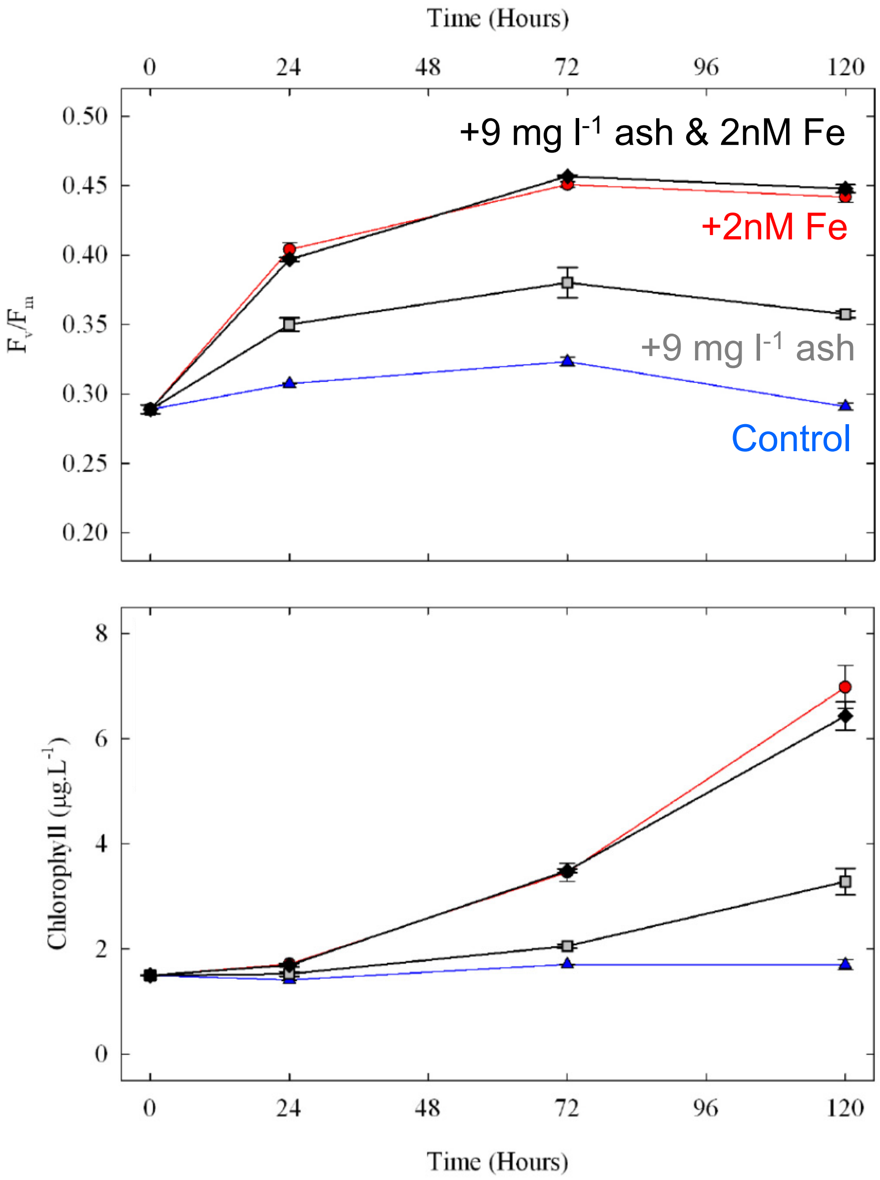
Turnover rates of a carrier free ^{55}Fe tracer (i.e. can be added at trace (pM) concentrations).

Turnover rates decrease with decreasing concentrations and increasing degree of independently experimentally diagnosed Fe stress.

Suggests that bioavailability (kinetic ability to access pool), is a key determinant of the development of Fe stress.



Ash addition experiments

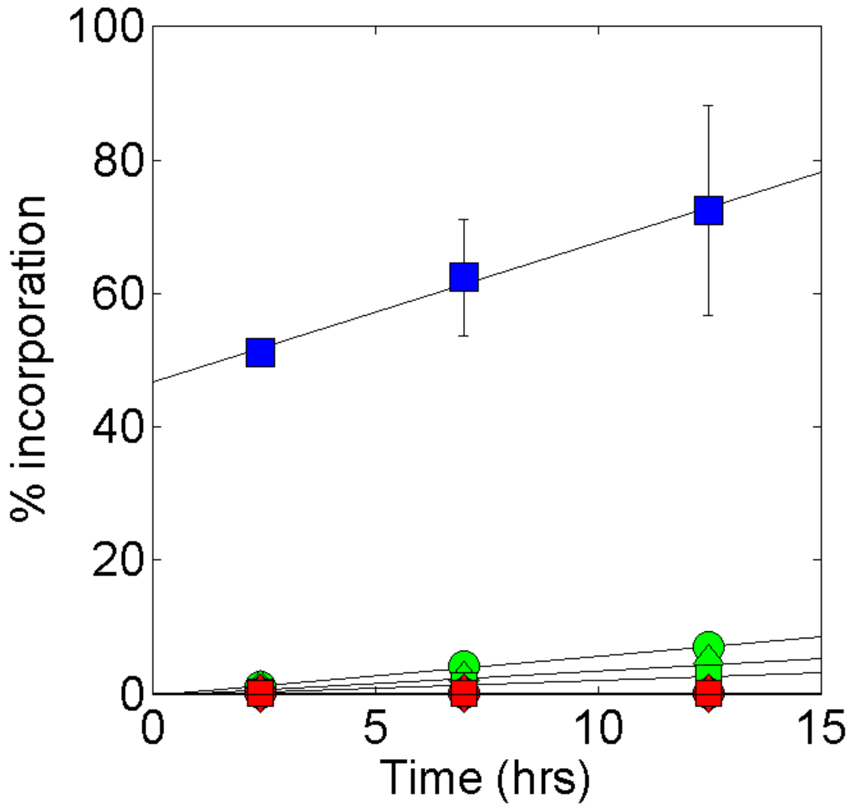


9 mg l^{-1} ash (equivalent to >10 μmol Particulate Fe l^{-1}), has less biological effect than an addition of 2nM Fe_3Cl

Suggests ash Fe is <0.02% bioavailable.

Bioavailability of particulate Fe is likely a key factor controlling biogeochemical response.

^{55}Fe uptake method



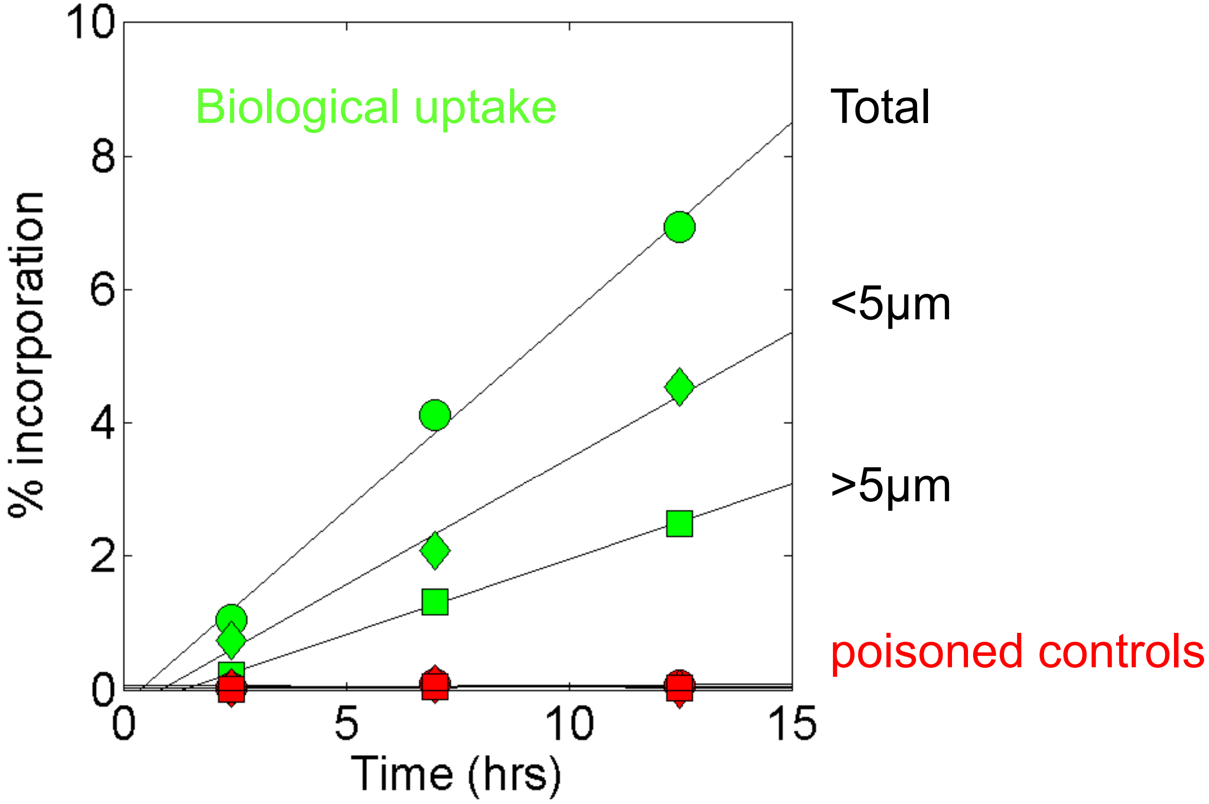
Total

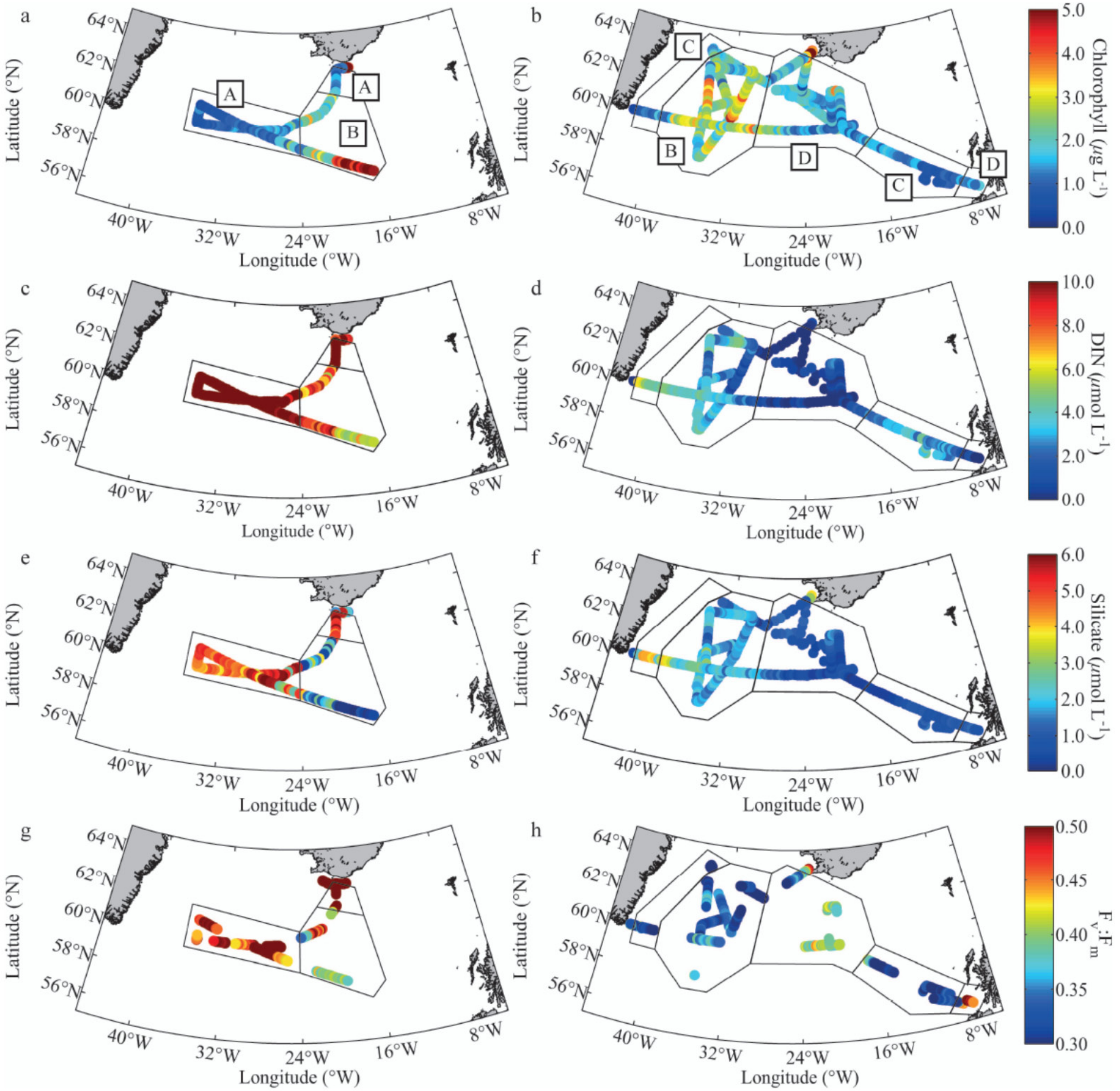
(includes adsorption)

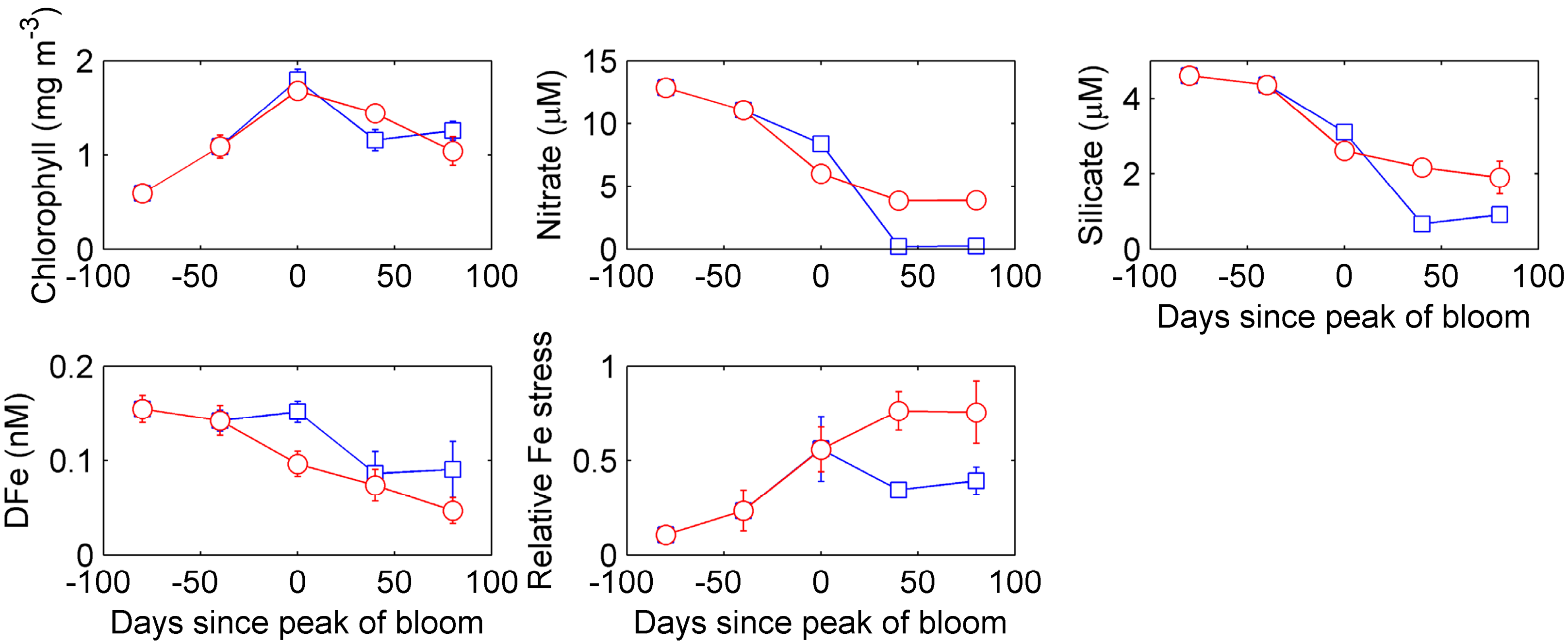
Biological uptake (washed with Ti EDTA citrate)

poisoned control

^{55}Fe uptake method




a
b
c
d
e
f
g
h
64°N
62°N
60°N
58°N
56°N
40°W
32°W
24°W
16°W
8°W
Latitude (°N)
Longitude (°W)
A
A
B
C
C
B
D
D
C
Chlorophyll (μg L-1)
5.0
4.0
3.0
2.0
1.0
0.0
DIN (μmol L-1)
10.0
8.0
6.0
4.0
2.0
0.0
Silicate (μmol L-1)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Fv:Fm
0.50
0.45
0.40
0.35
0.30


Chlorophyll (mg m^{-3})
2
1
0
-100
-50
0
50
100
Nitrate (μM)
15
10
5
0
-100
-50
0
50
100
Silicate (μM)
4
2
0
-100
-50
0
50
100
Days since peak of bloom
DFe (nM)
0.2
0.1
0
-100
-50
0
50
100
Days since peak of bloom
Relative Fe stress
1
0.5
0
-100
-50
0
50
100
Days since peak of bloom

Deep-Sea Research II, Vol. 40, No. 1/2, pp. 115–134, 1993.
Printed in Great Britain.

0967-0645/93 $5.00 + 0.00

Iron, primary production and carbon–nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment

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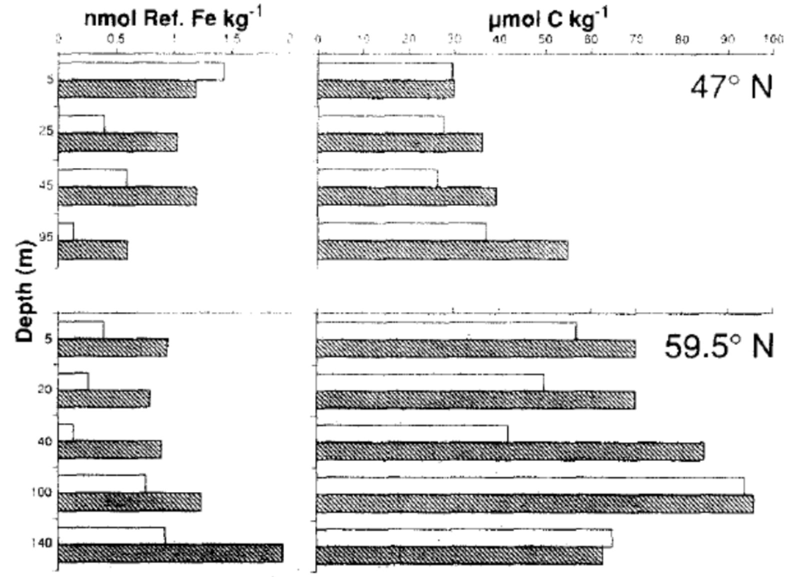
CRAIG N. HUNTER* and SARA J. TANNER*

(*Received* 13 *May* 1991; *in revised form* 19 *February* 1992; *accepted* 20 *March* 1992)

‘Although no evidence of Fe deficiency was found in enrichment experiments, the addition of nmol amounts of Fe did increase CO_2 uptake and POC formation by factors of 1.3-1.7.’



Particulate Fe and C concentrations measured at ends of iron enrichment experiments performed at 47°N and 59°N. Filled bars had 2 nmol kg^{-1} added Fe.

Working group/co-authors of IGBP Fast Track Initiative:

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Manuscript in review: Nature Geoscience