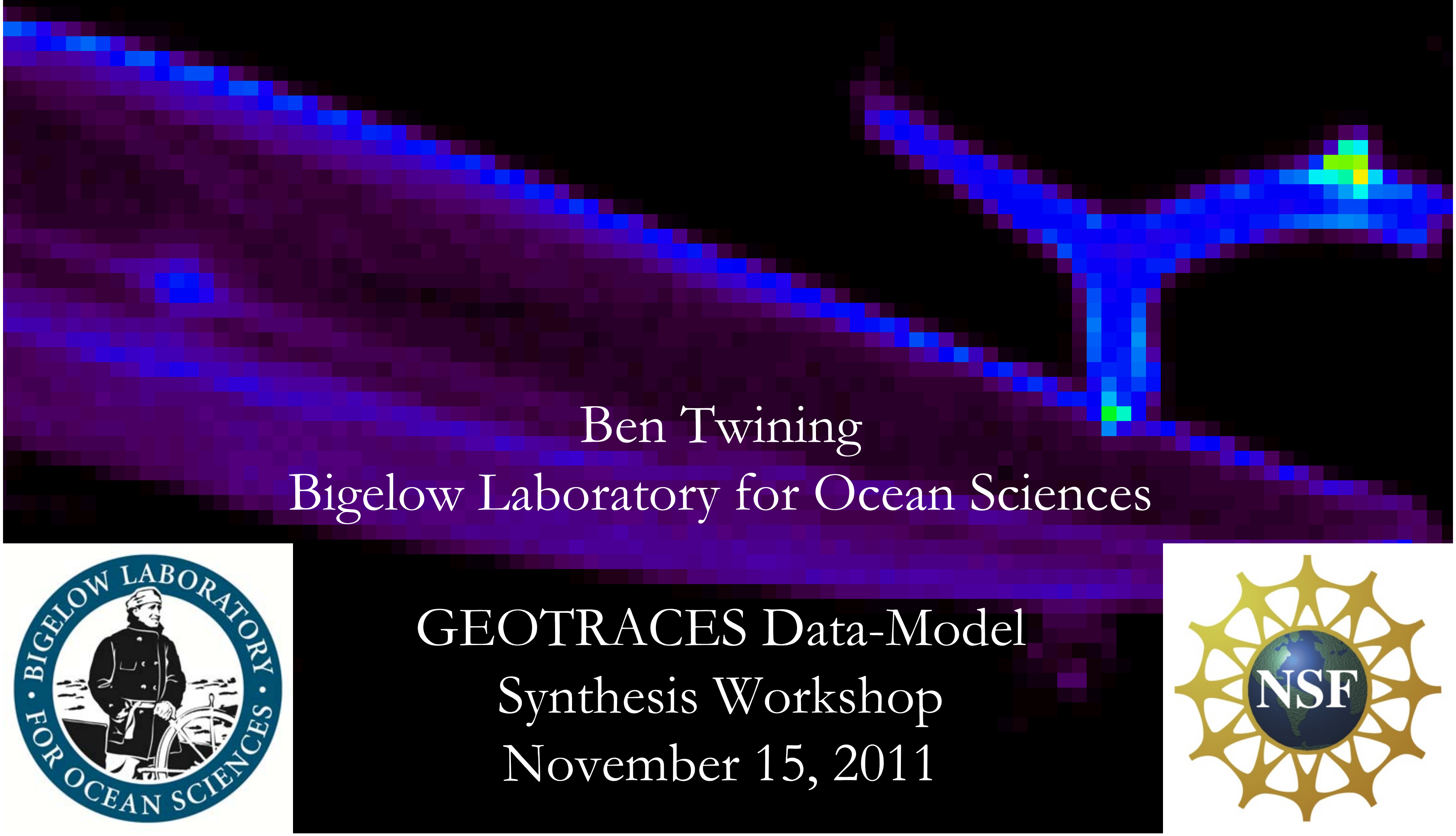
Role of plankton in the cycling of trace elements & isotopes



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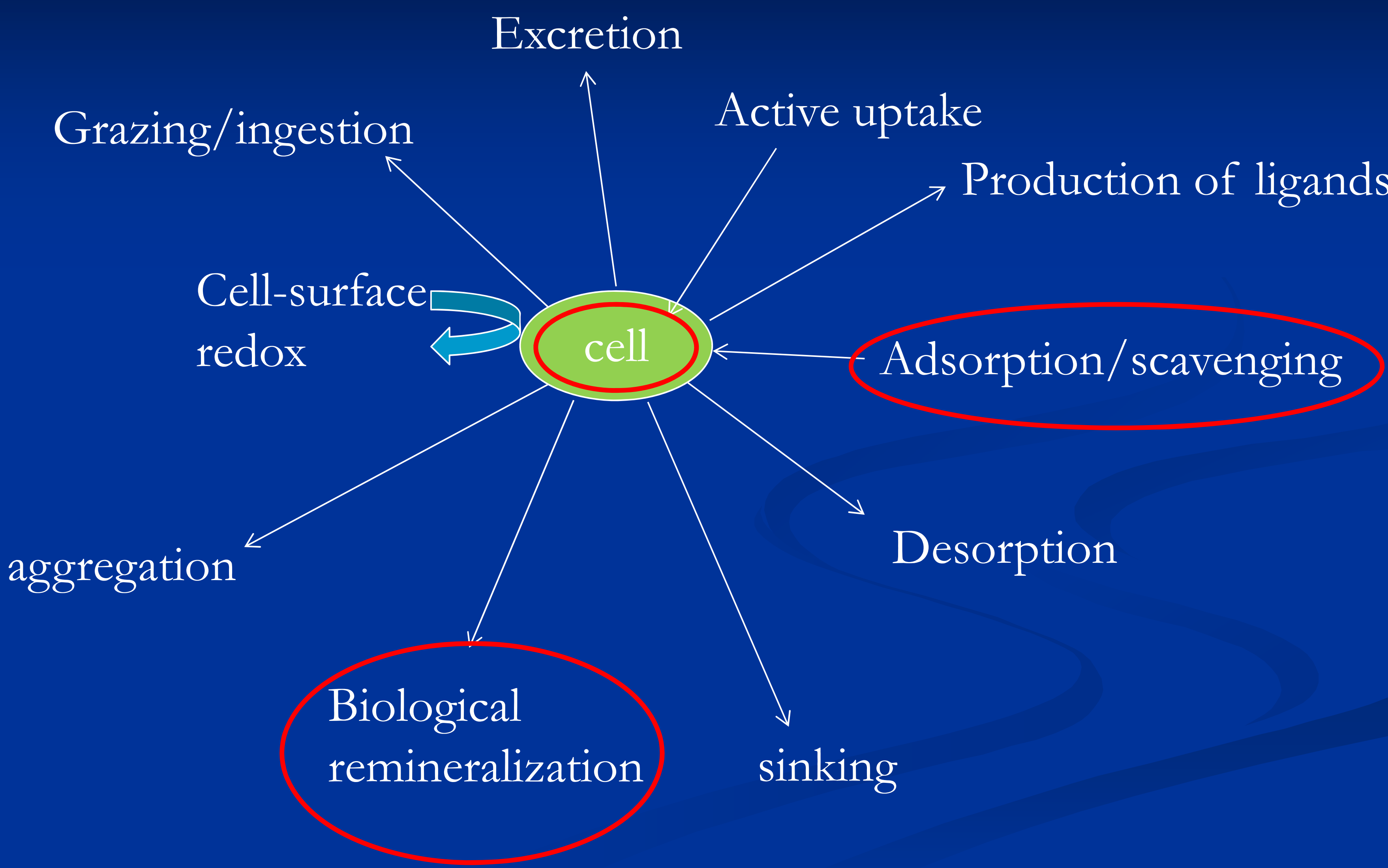
Bigelow Laboratory for Ocean Sciences

GEOTRACES Data-Model Synthesis Workshop

November 15, 2011

Role of plankton in cycling of TEIs



Organizing Questions

1. What are the TEI contents (stoichiometries) of plankton in the ocean?

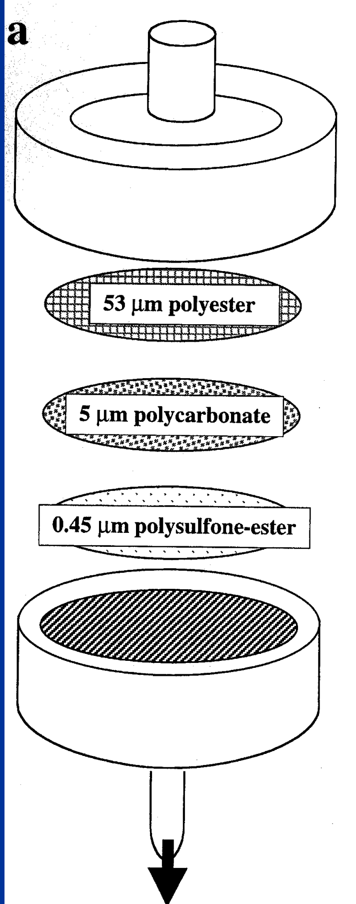
2. How important is the externally scavenged or adsorbed fraction of TEIs associated with plankton?

3. What are the relative rates of biogenic TEI remineralization from sinking plankton?

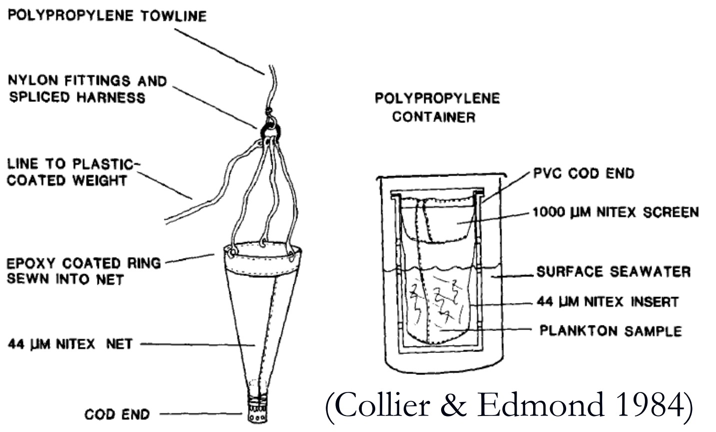
What is known (or thought to be known)?
What is unknown?
Emerging hypotheses

1. TEI content of plankton in the ocean

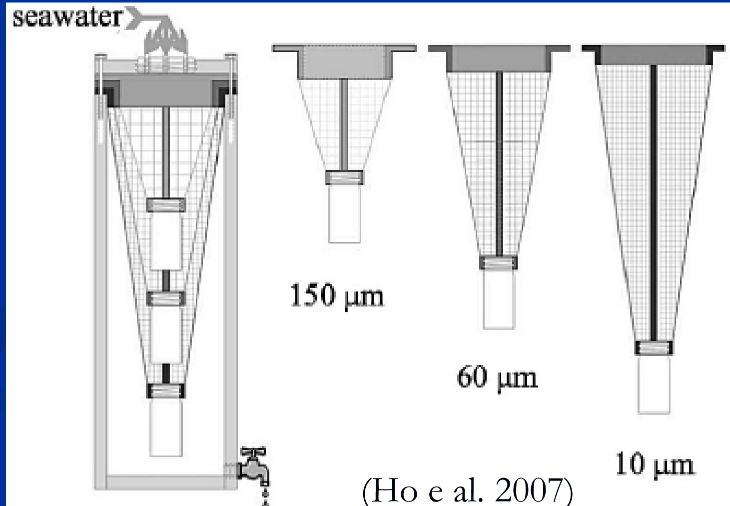
- Importance: TEI cycling, micronutrient limitation
- Challenge: how to isolate plankton from abiotic/lithogenic particles?



(Cullen & Sherrell, 1999)

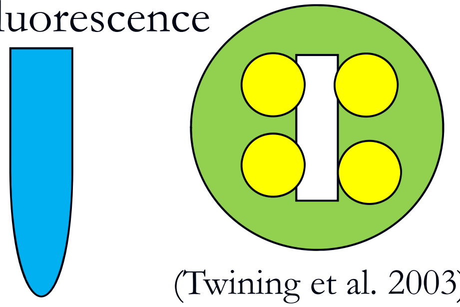


(Collier & Edmond 1984)

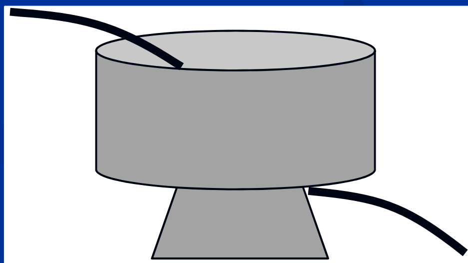


(Ho e al. 2007)

Single-cell x-ray (SXRF) fluorescence



(Twining et al. 2003)



(Kuss & Kremling 1999)

What is known: Generalized TEI stoichiometries of plankton

(mmol/mol P)	Method	Fe	Zn	Mn	Cu	Ni	Co	Cd
Coastal Ocean (Martin & Knauer 1973)*	Net	7.4	0.86	0.39	0.18	0.21	--	0.07
Equatorial Pacific Ocean (Collier & Edmond 1984)*	Net	4.6	3.0	0.34	0.52	0.86	--	0.54
Atlantic Ocean (Kuss & Kremling 1999)*	Spin	4.6	1.9	1.6	0.37	1.4	0.19	0.51
Southern Ocean (Cullen et al. 2003)	Filter	--	11	1.6	1.4	--	0.15	1.2
Southern Ocean (Twining et al. 2004)	SXRF	1.8	5.4	0.26	--	0.61	--	--
Equatorial Pacific Ocean (Twining et al. 2011)	SXRF	1.5	1.6	0.58	--	0.39	0.14	--
Atlantic Ocean (Twining unpublished)	SXRF	6.1	2.9	0.38	--	0.33	0.17	--

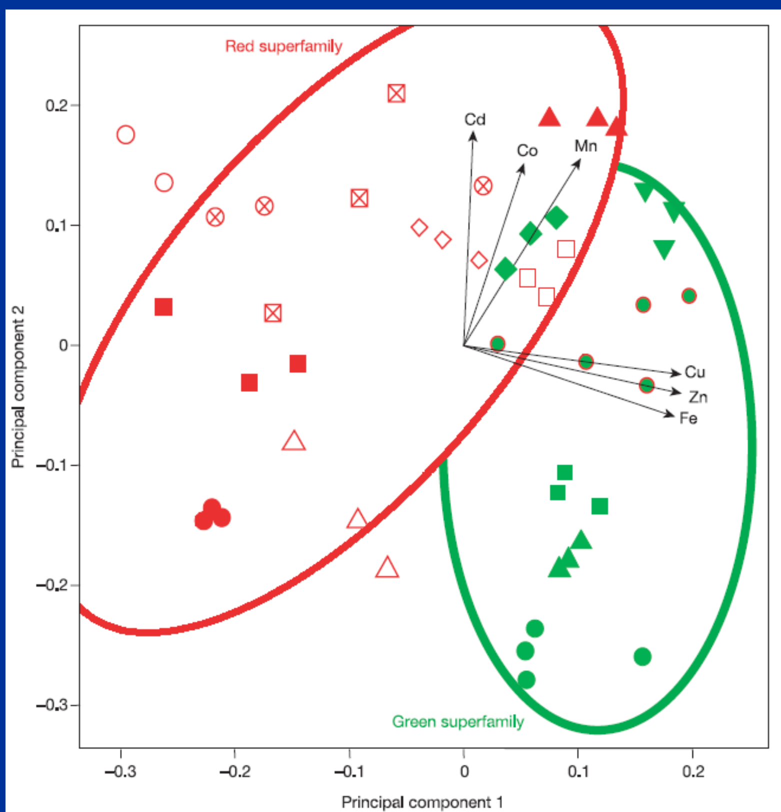
*Samples with Al > 100 µg/g removed from datasets

Fe > Zn >> Mn ≈ Cu ≈ Ni > Co≈Cd

What is known: TEI contents of plankton vary between taxonomic groups

The evolutionary inheritance of elemental stoichiometry in marine phytoplankton

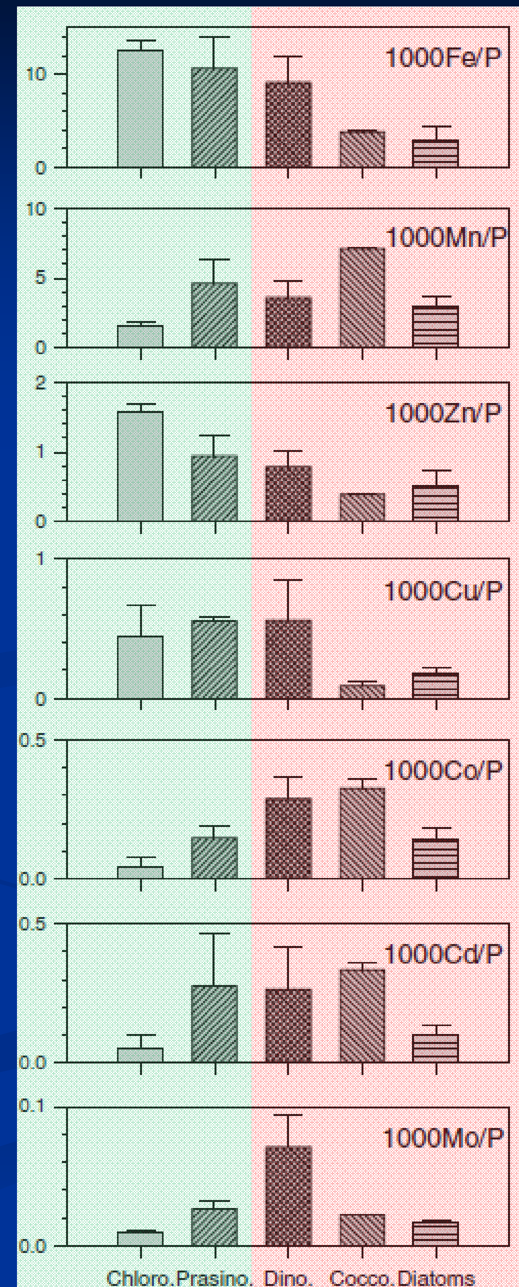
Antonietta Quigg[1], Zoe V. Finkel[1], Andrew J. Irwin[1], Yair Rosenthal[1,2], Tung-Yuan Ho[5], John R. Reinfelder[3], Oscar Schofield[1,4], Francois M. M. Morel[5] & Paul G. Falkowski[1,2]



Cd, Co Mn

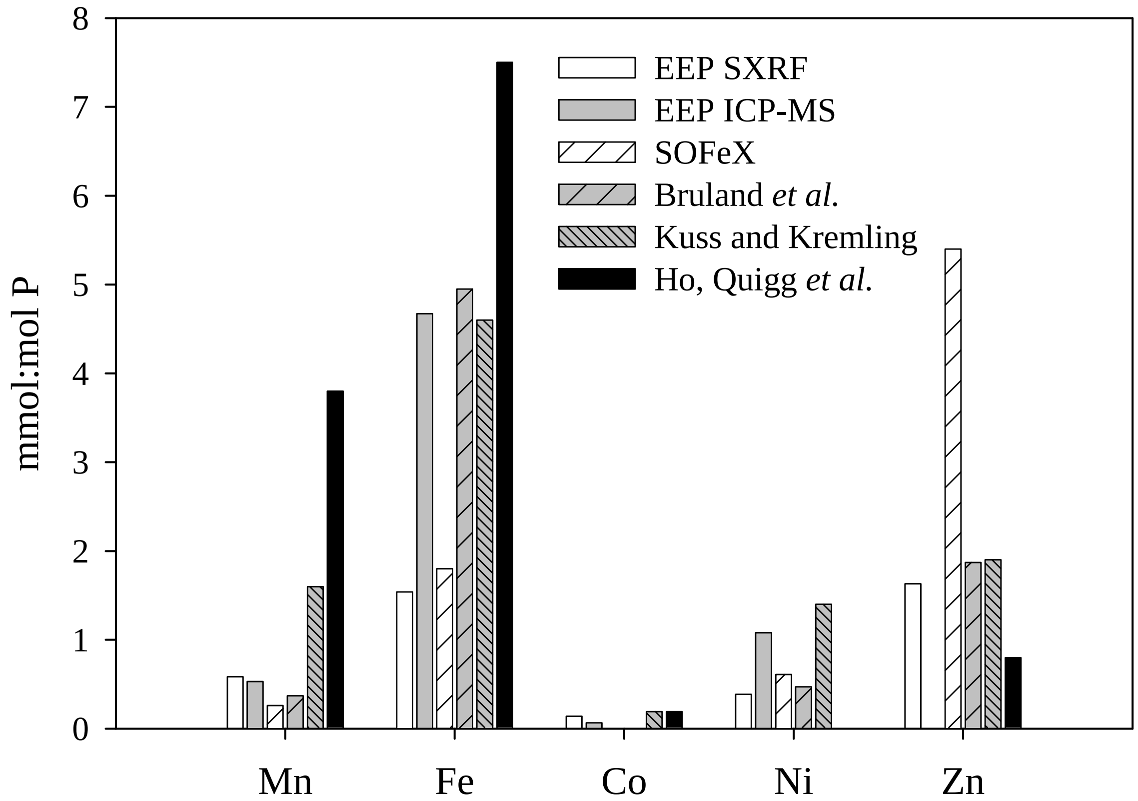
Cu, Zn, Fe

(Ho et al. 2003)



What is unknown: How applicable are TEI stoichiometries from cultures to the ocean?

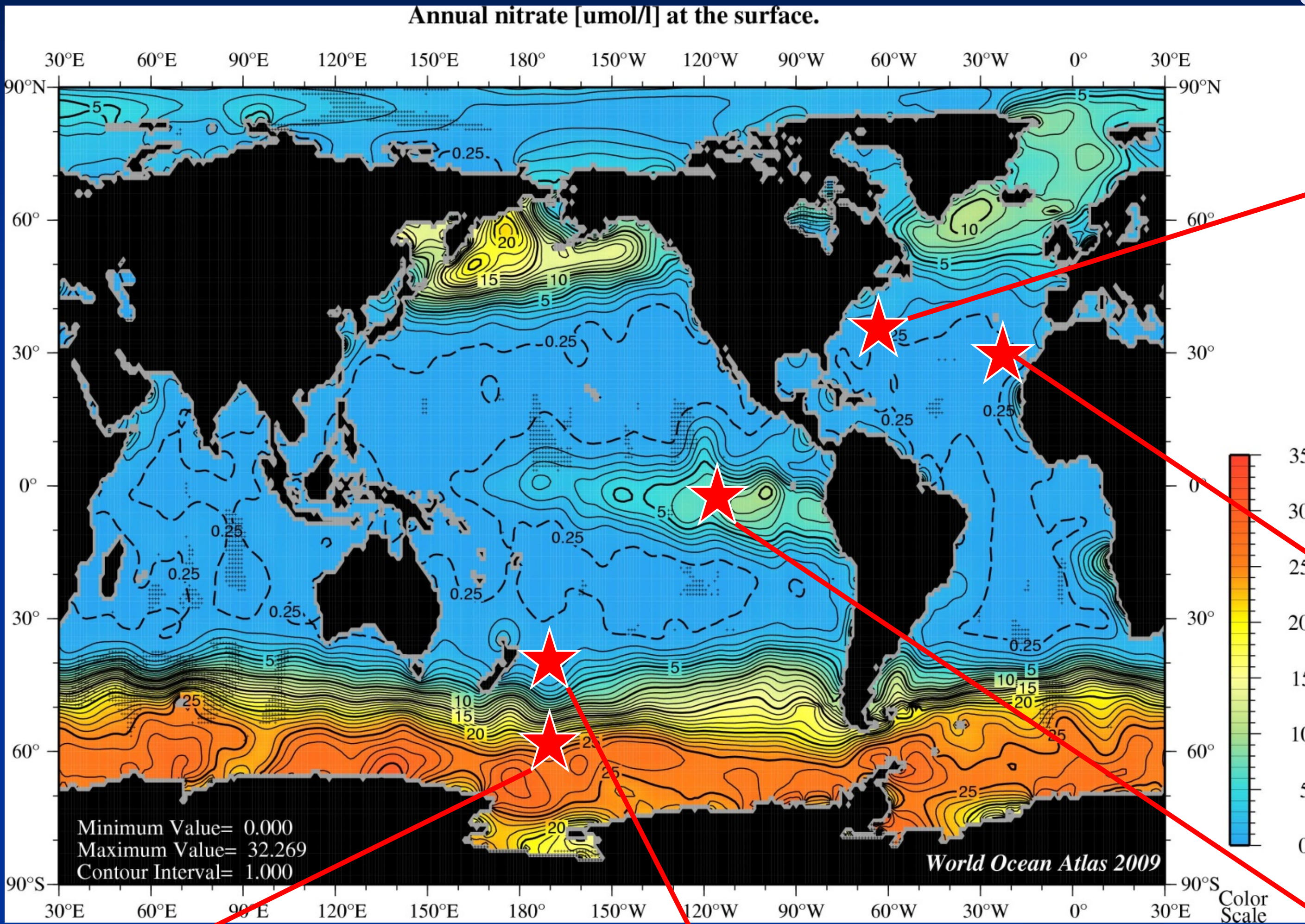
Factors affecting TEIs
- Taxonomy
- Effects of light
- Dissolved TEI concentration and speciation →
- Macronutrient availability



(Twining et al. 2011)

- Choice of media composition significantly influences results:
  - High Mn in media → high Mn and low Zn in cells
  - High Fe in media → high Fe in cells

What is known: TEI contents of plankton vary between ocean regions



Sargasso Sea (BATS)

(Twining et al. 2010)

North Atlantic GEOTRACES

(unpublished)

Southern Ocean (SOFeX)

(Twining et al. 2004a, b)

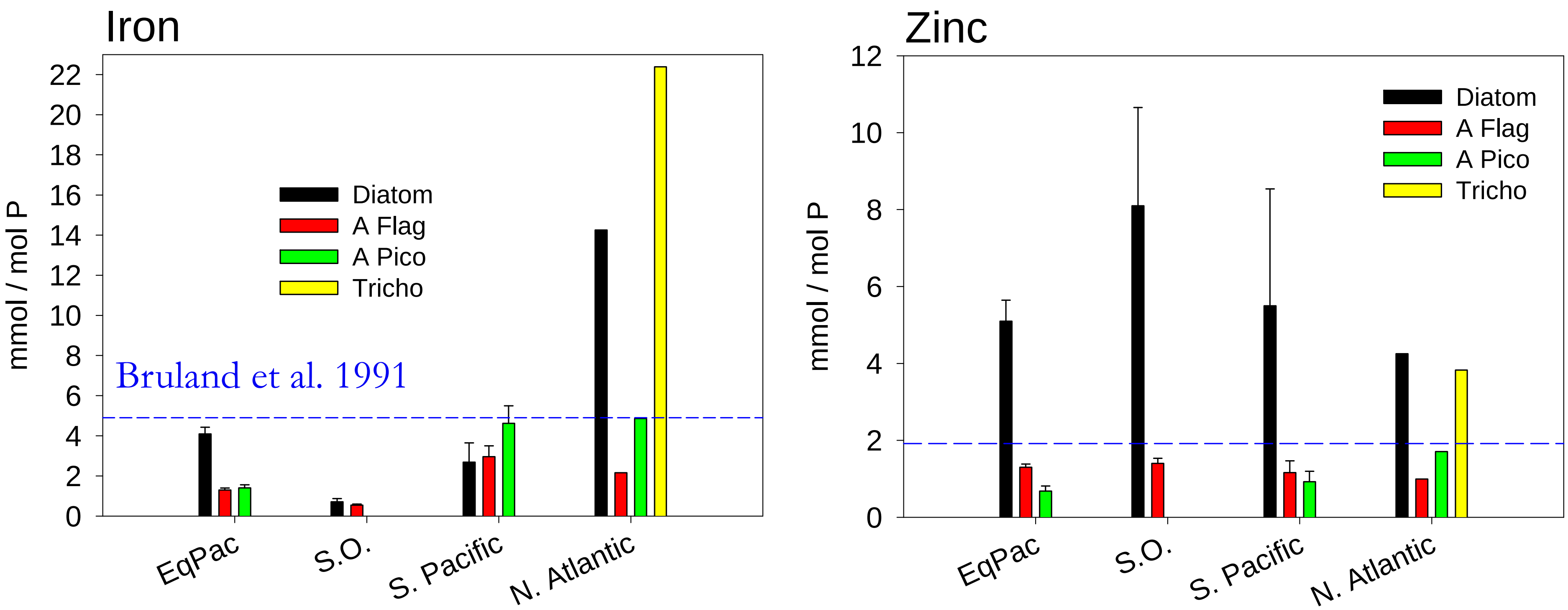
FeCycle II

(King et al. in review)

EqPac (Biocomplexity)

(Twining et al. 2011)

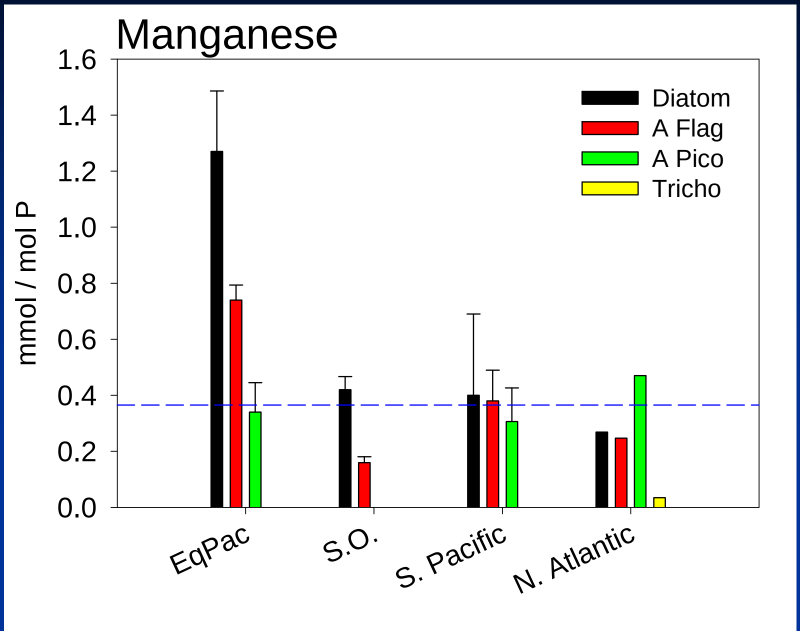
Metal quotas of functional groups across ocean regions

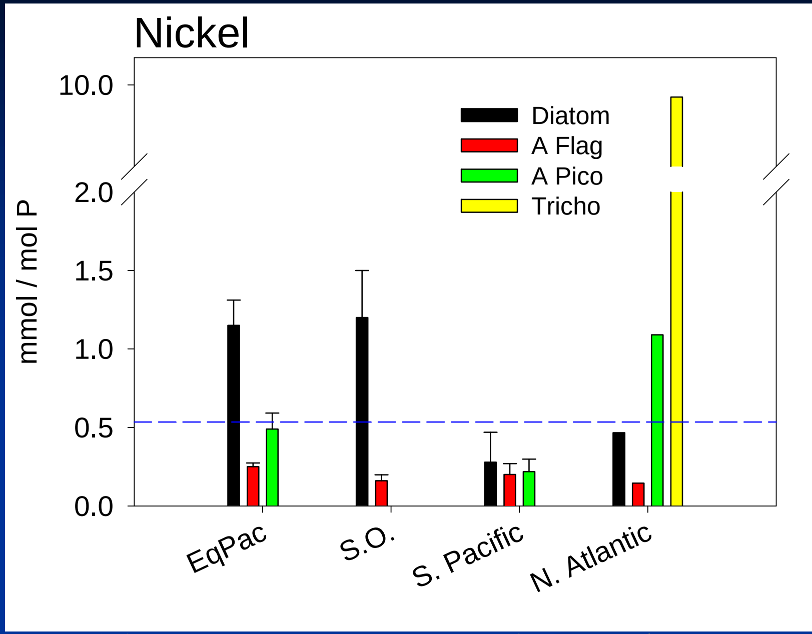


N. Atlantic>S. Pacific>EqPac>Southern Ocean

Taxonomic variations larger than regional variations

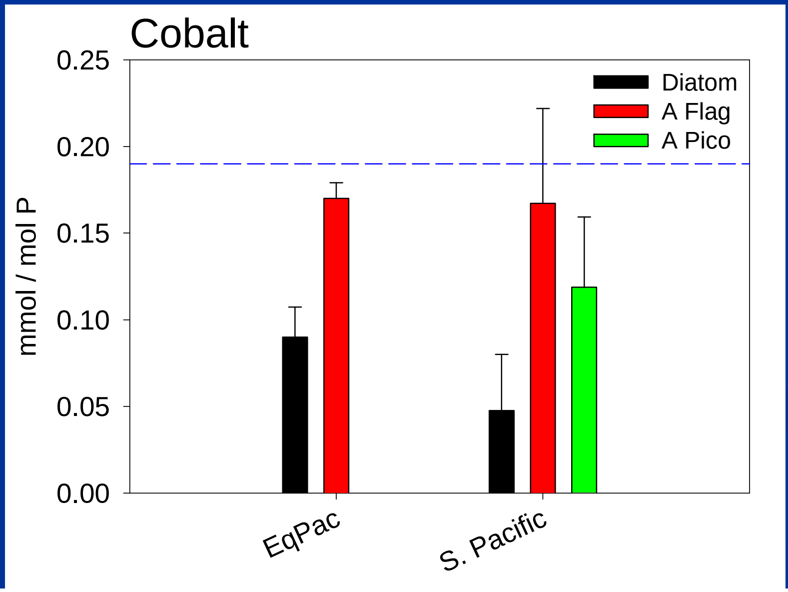
Metal quotas of functional groups across ocean regions





EqPac>S. Pacific>N. Atlantic≈Southern Ocean

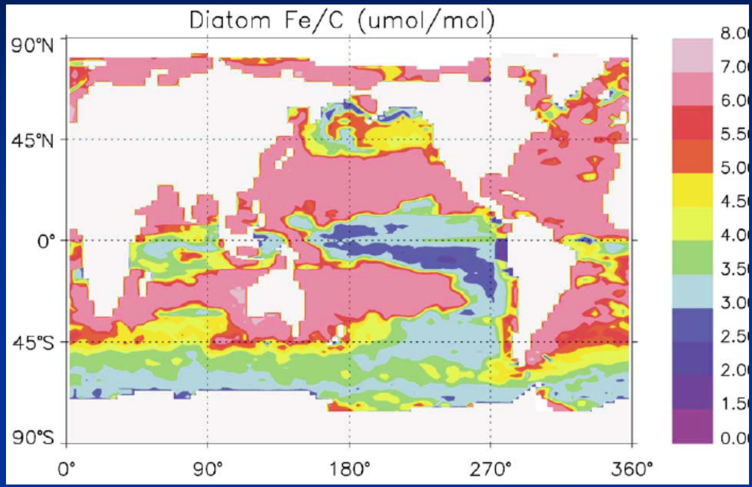
Taxonomic variations larger than regional variations



Negligible variations

What is unknown: How to reconcile conflicting data on iron quotas of ocean phytoplankton

- Minimum quotas of ocean plankton are ~2 μmol Fe/mol C
  - Culture experiments
  - Radiotracers with natural communities
  - Vertical nutrient profiles



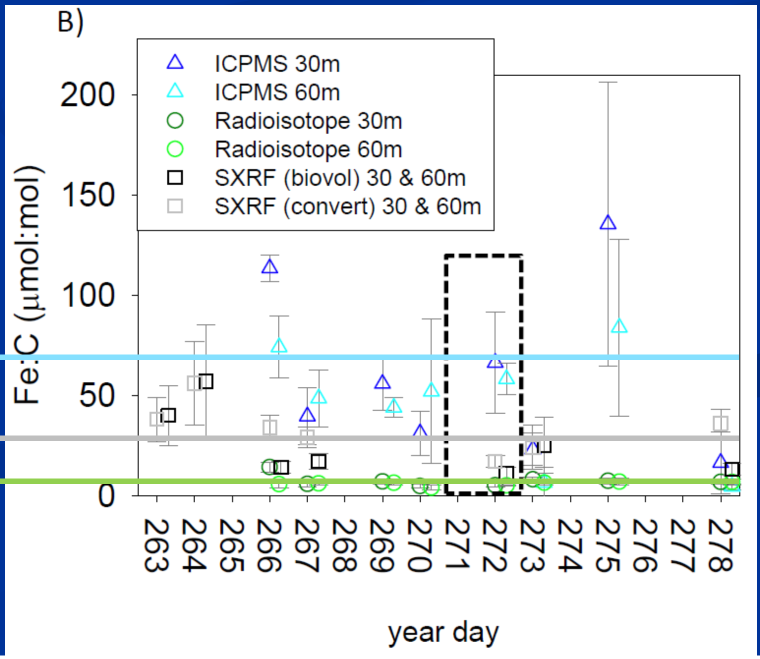
(Moore et al. 2002)

- Stoichiometries of ocean plankton are 1-5 mmol Fe/mol P
  - Equivalent to 10-50 μmol Fe/mol C
  - Discrepancies seen in samples from the same station

ICPMS

SXRF

^{55}Fe



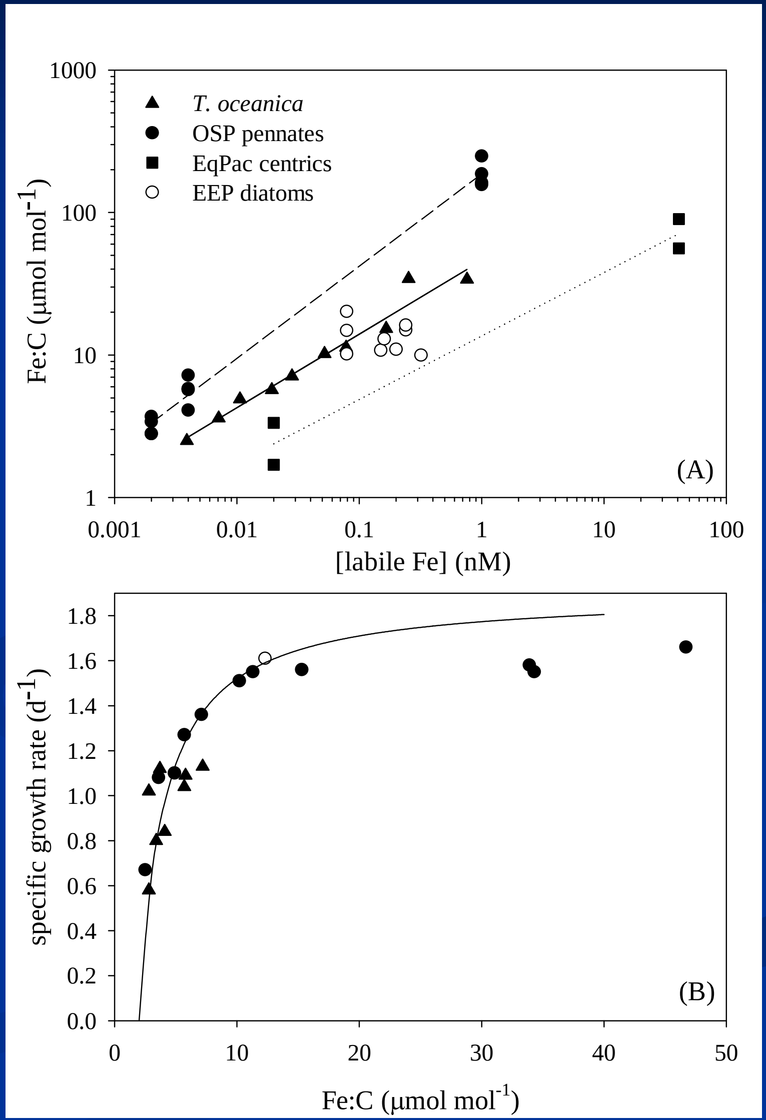
(King et al. in review)

1. Conclusions and emerging hypotheses

- There are taxonomic and regional differences in the TEI content of plankton

- Most phytoplankton in the ocean not represented by their minimum TEI quotas ⟶

- TEI contents of prokaryotes are poorly characterized



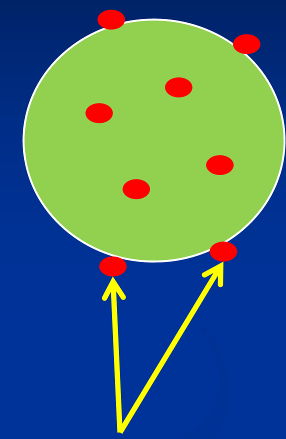
(Twining et al. 2011)

2. Importance of externally adsorbed iron to plankton quotas

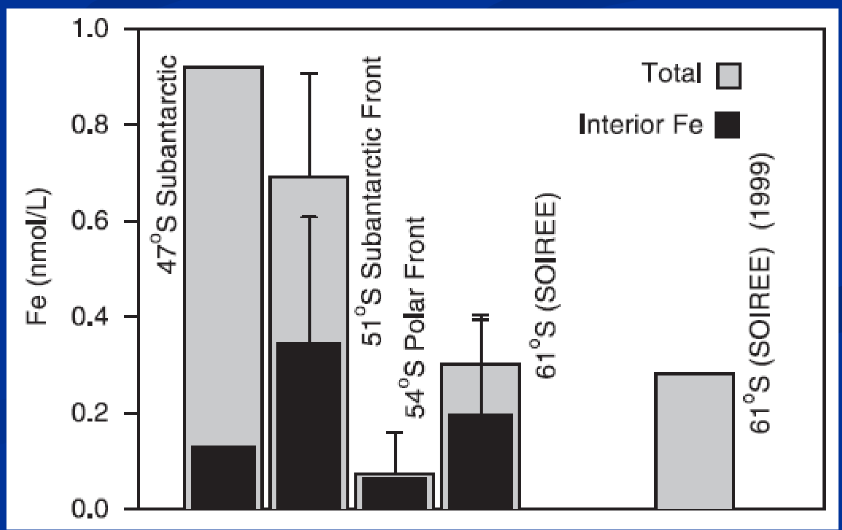
- Use of chemical washes for removal of operationally-defined 'extracellular' Fe fraction

  (Hudson and Morel 1989, Tovar-Sanchez et al. 2003)

  - Most data is from laboratory cultures → how does oxalate extraction work in the field?



- Tovar-Sanchez et al. 2003
  - 'surface adsorbed' fraction accounted for 16-86% of total particulate Fe (mean=47%)



(Tovar-Sanchez et al. 2003)

What is known: Oxalate wash removes Fe from particulate fractions

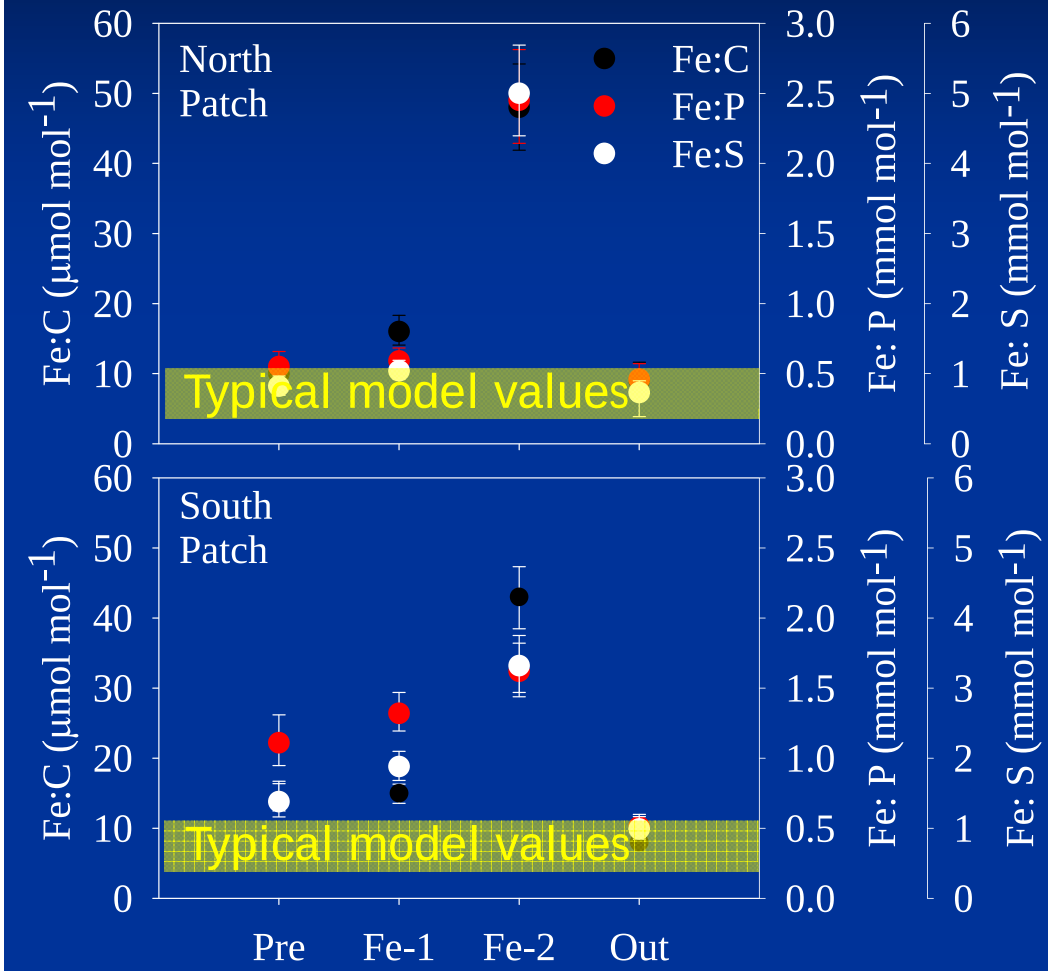
- Frew et al. 2006 – FeCycle project
  - Comparison of paired filters revealed that ~45% of particulate Fe in sub-Antarctic surface waters was intracellular
  - Dissolved Fe in these waters <0.1 nM (Croot et al. 2007)

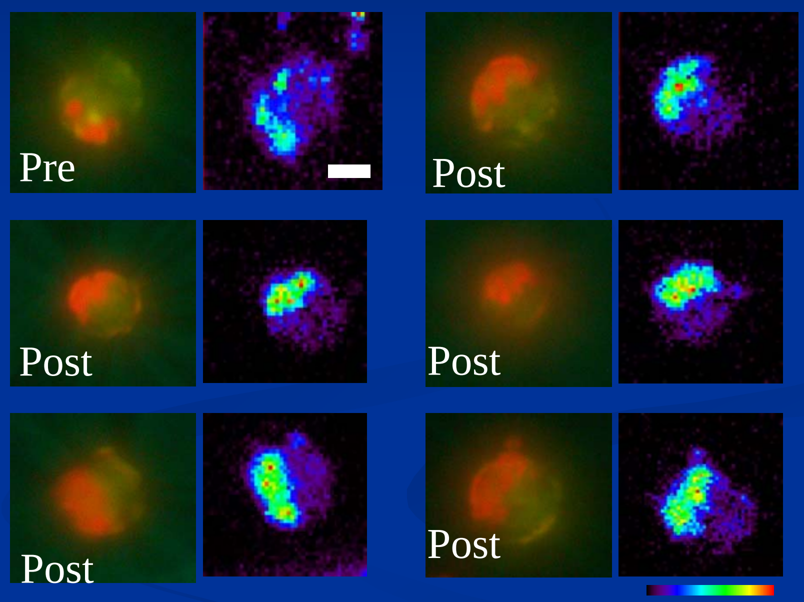
Table 4a. Particle Fluxes of Particles Intercepted in Traps Deployed at 80 and 120 m Depth[a]

Particle Fluxes	F1-80 m	F1-120 m	F2-80 m	F2-120 m
POC, mmol m^{-2} d^{-1}	...	2.09 (0.03)	2.51 (0.17)	2.10 (0.01)
PON, mmol m^{-2} d^{-1}	...	0.30 (0.01)	0.41 (0.03)	0.29 (0.01)
POP, µmol m^{-2} d^{-1}	13.1	13.1	15.0	11.6
BSi, µmol m^{-2} d^{-1}	101	90	127	75
TotPFe, nmol m^{-2} d^{-1}	219 (26)	359 (47)	548 (64)	350 (29)
BioPFe, nmol m^{-2} d^{-1}	112 (23)	230 (46)	352 (62)	174 (28)
LithPFe, nmol m^{-2} d^{-1}	107 (3) *	129 (14)	196 (3)	* 176 (2)
$Tot_{oxalate}$PFe, nmol m^{-2} d^{-1}	374 (51)	370 (24)	469 (14)	454 (42)

  - Oxalate-rinsed particulate Fe fraction *larger* than unrinsed fraction in 3 of 4 traps

What is known: SXRF maps suggest most Fe is intracellular



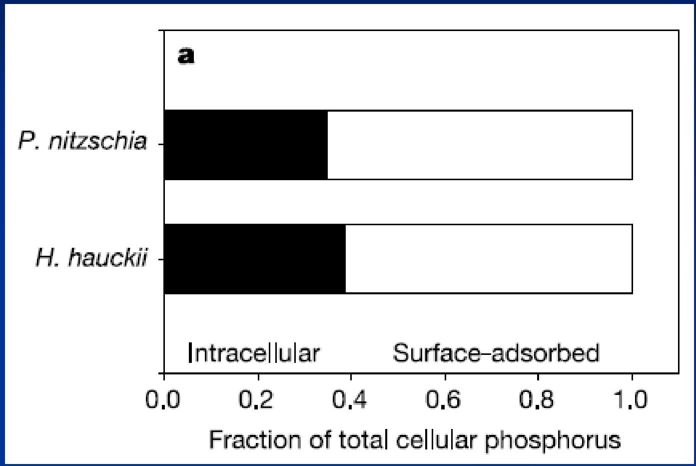


Cellular Fe distributions in cells collected after fertilization indicate Fe accumulated internally

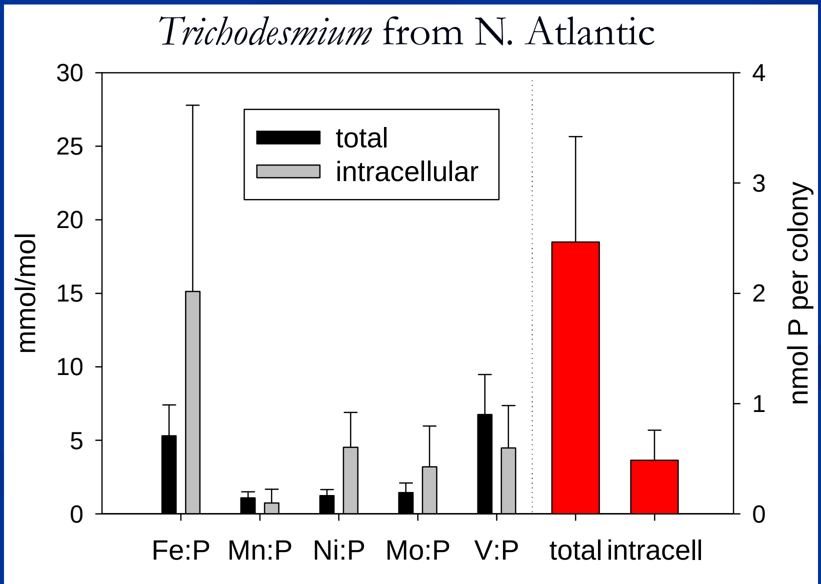
(Twining et al. 2004)

What is known: Oxalate wash removes P from particulate fractions

- Significant P is removed as well
  - More than 50% of cellular P is 'surface adsorbed' in natural blooms
  - In Trichodesmium from the N. Atlantic, 76% of P in extracellular, compared with 59% of Fe
- Tovar-Sanchez et al. 2011:
  - 79 ± 14% of P was extracellular
  - TEI quotas were higher in rinsed cells than in unrinsed cells for some metals



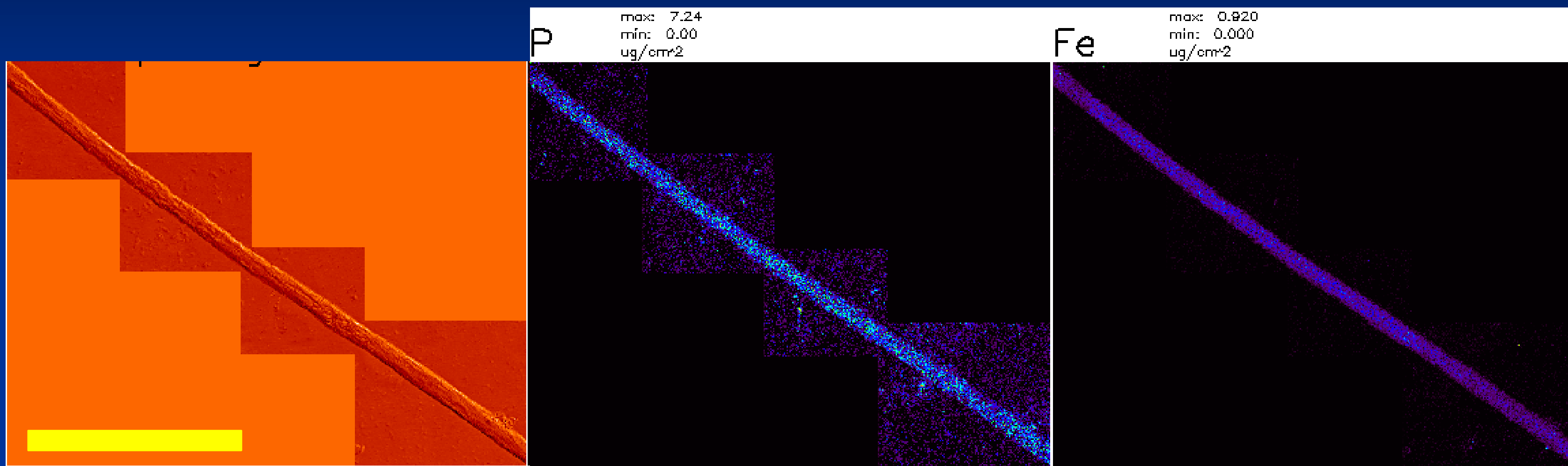
(Sanudo-Wilhelmy et al. 2004)



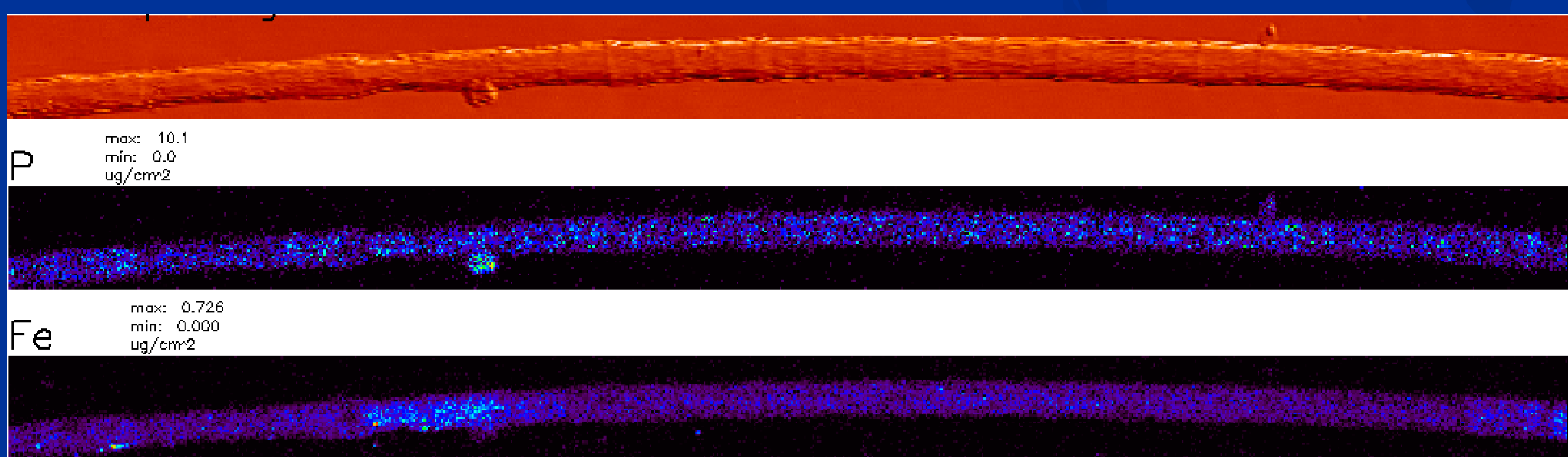
(data from Tovar-Sanchez et al. 2011)

What is known: SXRF maps suggest most Fe and P are intracellular

Unwashed P: $16.5 \pm 1.3 \times 10^{-8}$ Fe: $11.3 \pm 0.1 \times 10^{-10}$ mol cm^{-2}



Oxalate-washed P: $20.3 \pm 4.3 \times 10^{-8}$ Fe: $8.4 \pm 3.6 \times 10^{-10}$ mol cm^{-2}



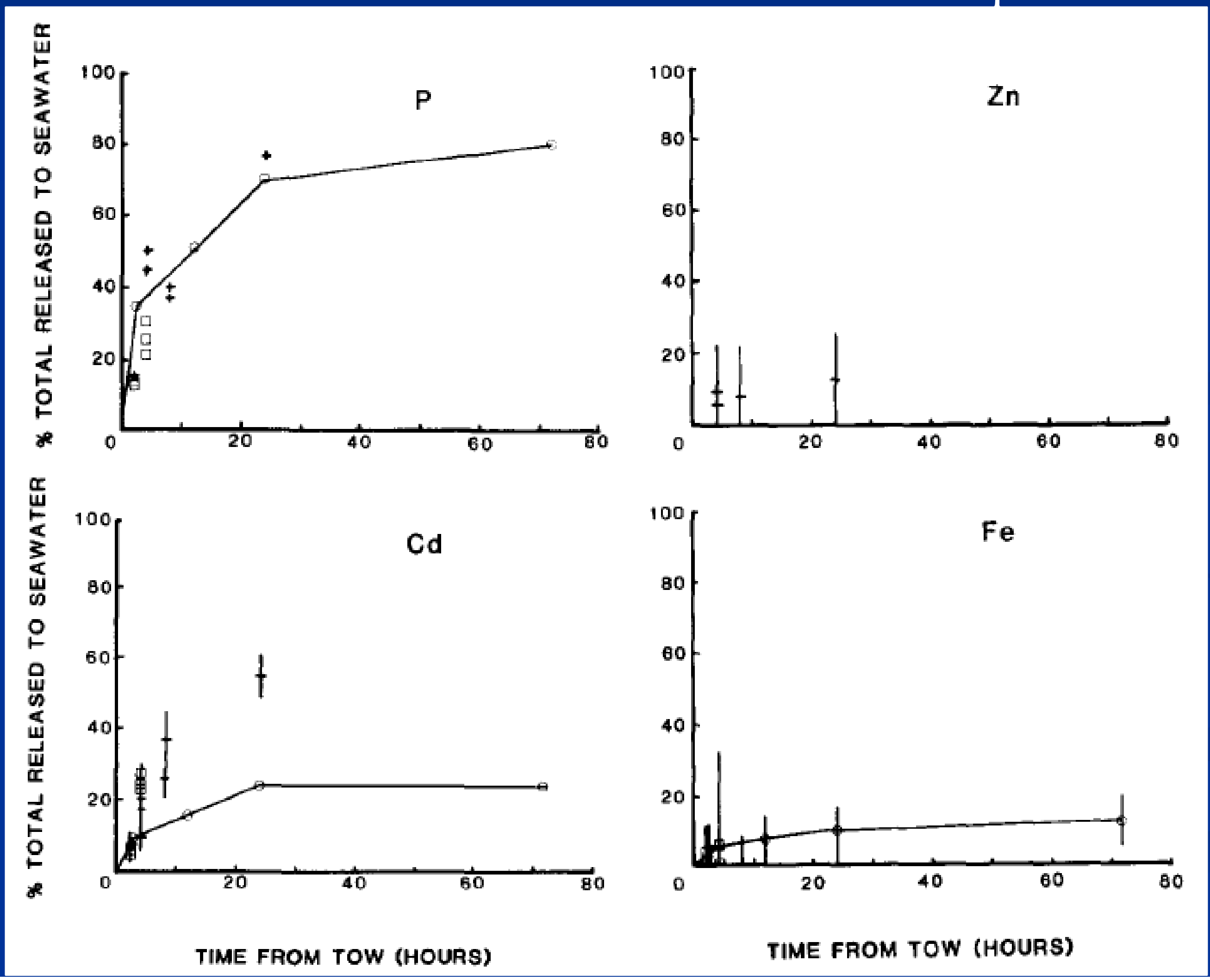
100 µm

2. Conclusions and emerging hypotheses

- There are contradictory data regarding the cellular partitioning of Fe (and P) in plankton
- The quantitative importance and chemical form of extracellular Fe requires more study
  - Does extracellular fraction vary between ocean regions?
  - How exchangeable is extracellular fraction?
- Is the partitioning of extracellular Fe dependent upon DFe and ligand concentrations?
- Unknown importance of frustule fraction

3. What are the relative rates of biogenic TEI remineralization from sinking plankton?

- What is known: Evidence of unequal loss from particles



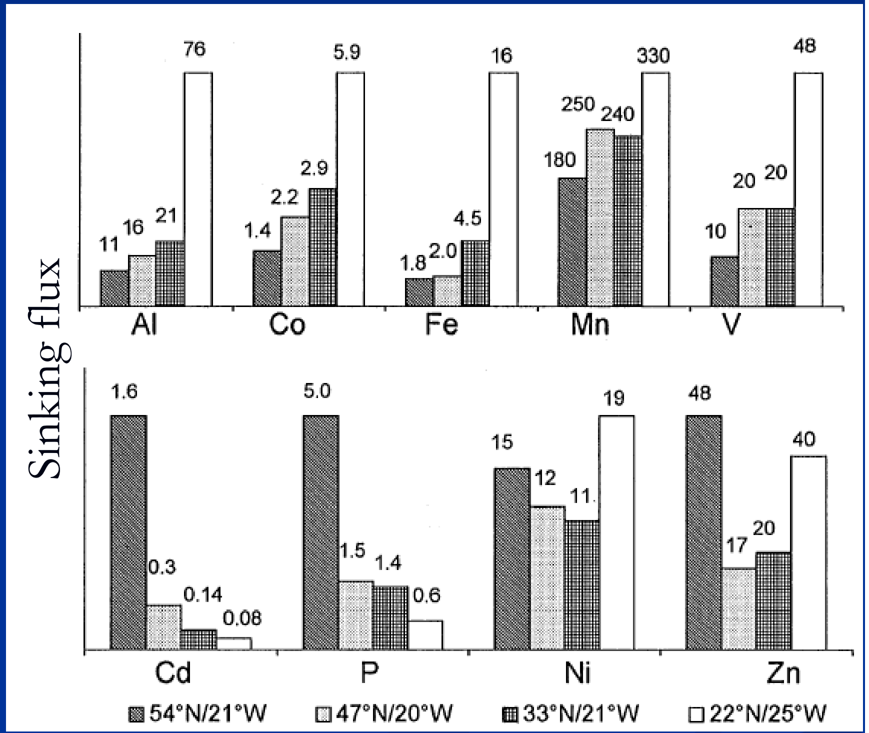
Stoichiometries of released material

Fe:P ~ 0.9
Ni:P ~ 0.7
Cu:P ~ 0.2
Cd:P ~ 0.2
(mmol/mol P)

(Collier & Edmond 1984)

What is known: biogenic TEIs such as Ni, Zn, Cu and Cd are readily released from sinking plankton

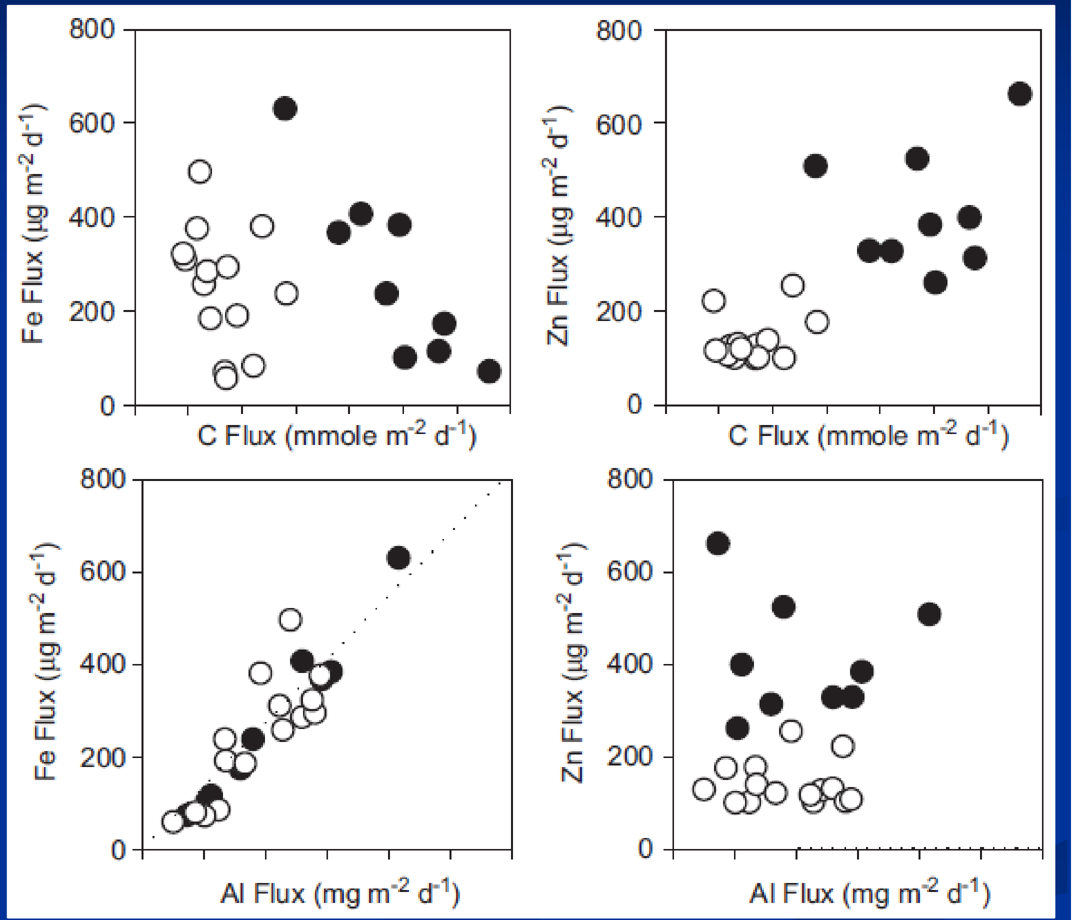
- Clear associations between these TEIs and macronutrients in profiles of dissolved concentrations
  (Sclater et al. 1976, Bruland 1980, etc.)
- Correlations of these TEIs and organic C in sediment traps
- Temporal and spatial correlations of sinking fluxes of these TEIs
  (Kuss and Kremling 1999, Lamborg et al. 2008)



(Kuss & Kremling 1999)

What is unknown: how are lithogenic elements such as Fe lost from sinking cells?

- Lithogenic elements often shown negligible remineralization, or even scavenging, in sinking particles
- Fluxes of these elements are often dominated by lithogenic particles



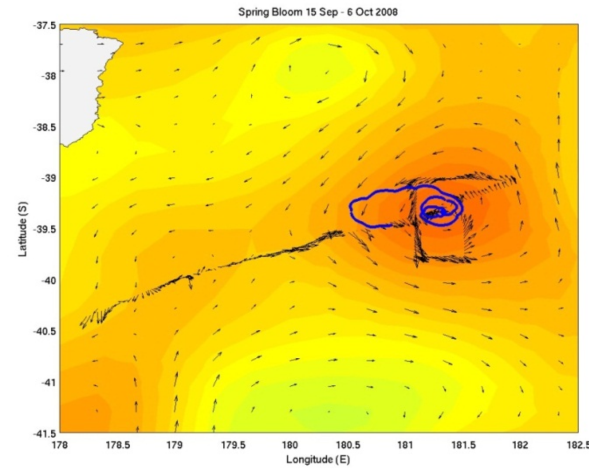
K2

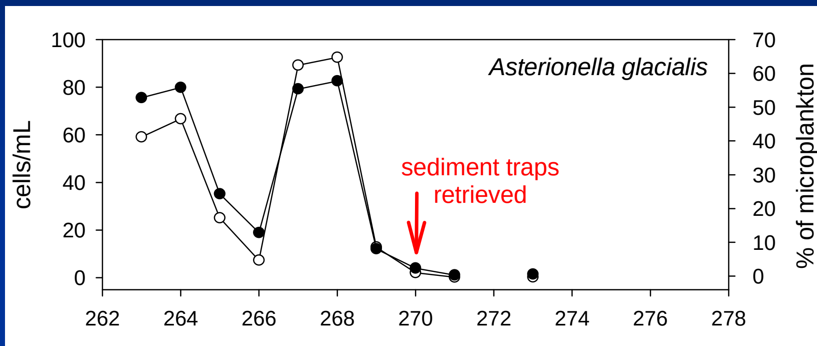
(Lamborg et al. 2008)

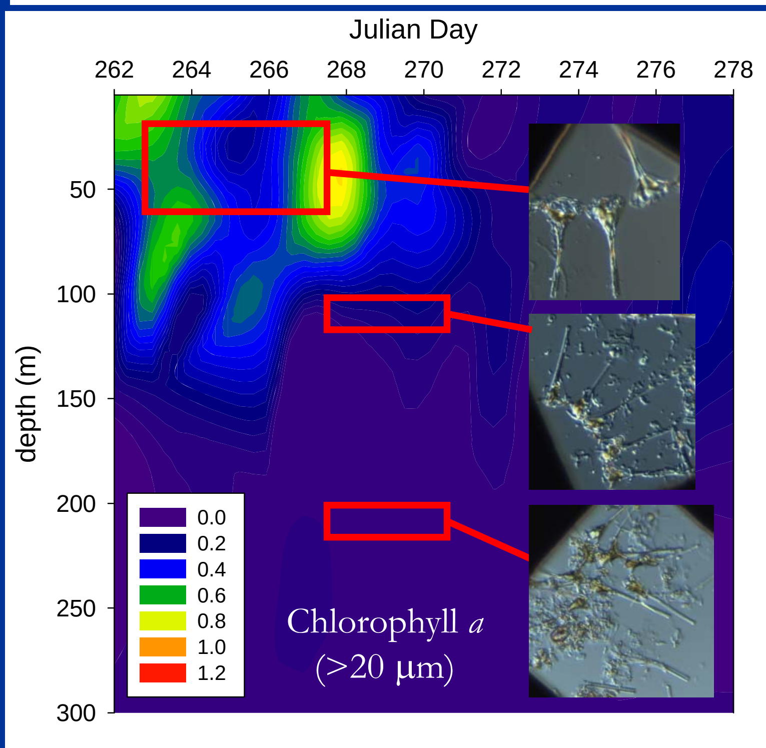
- What is the fate of iron in sinking biogenic particles?

FeCycle II spring bloom experiment

Phil Boyd, Scott Nodder, Andrew King, et al.

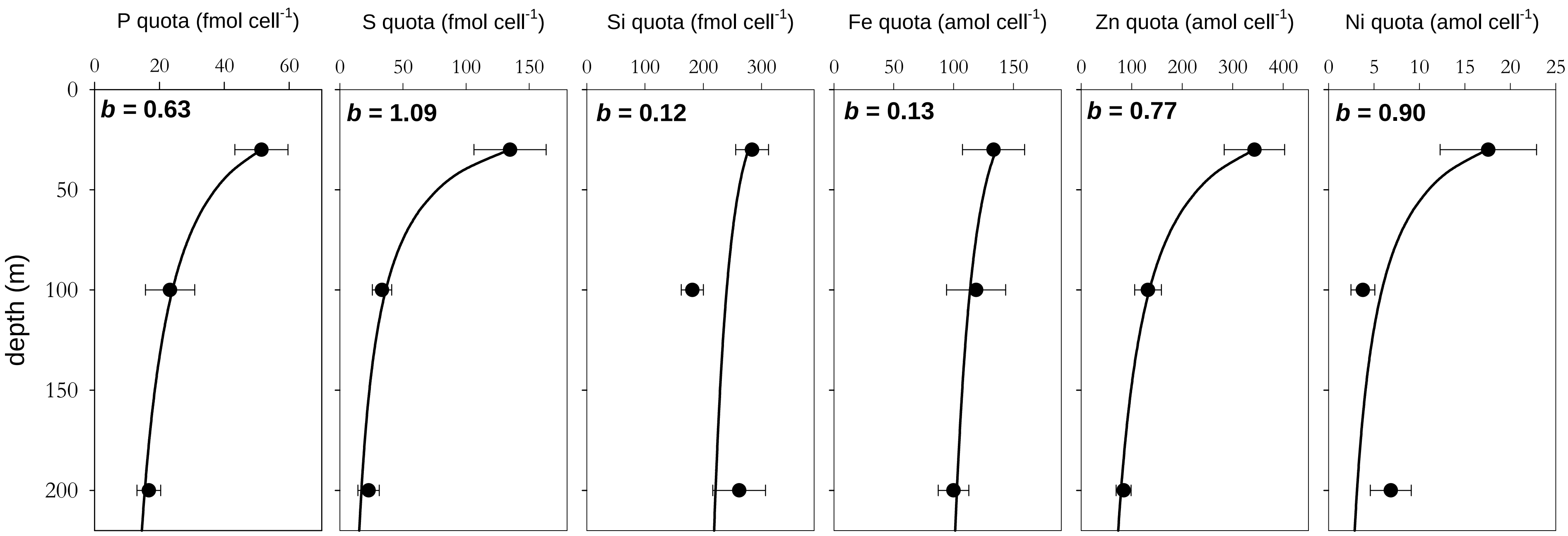






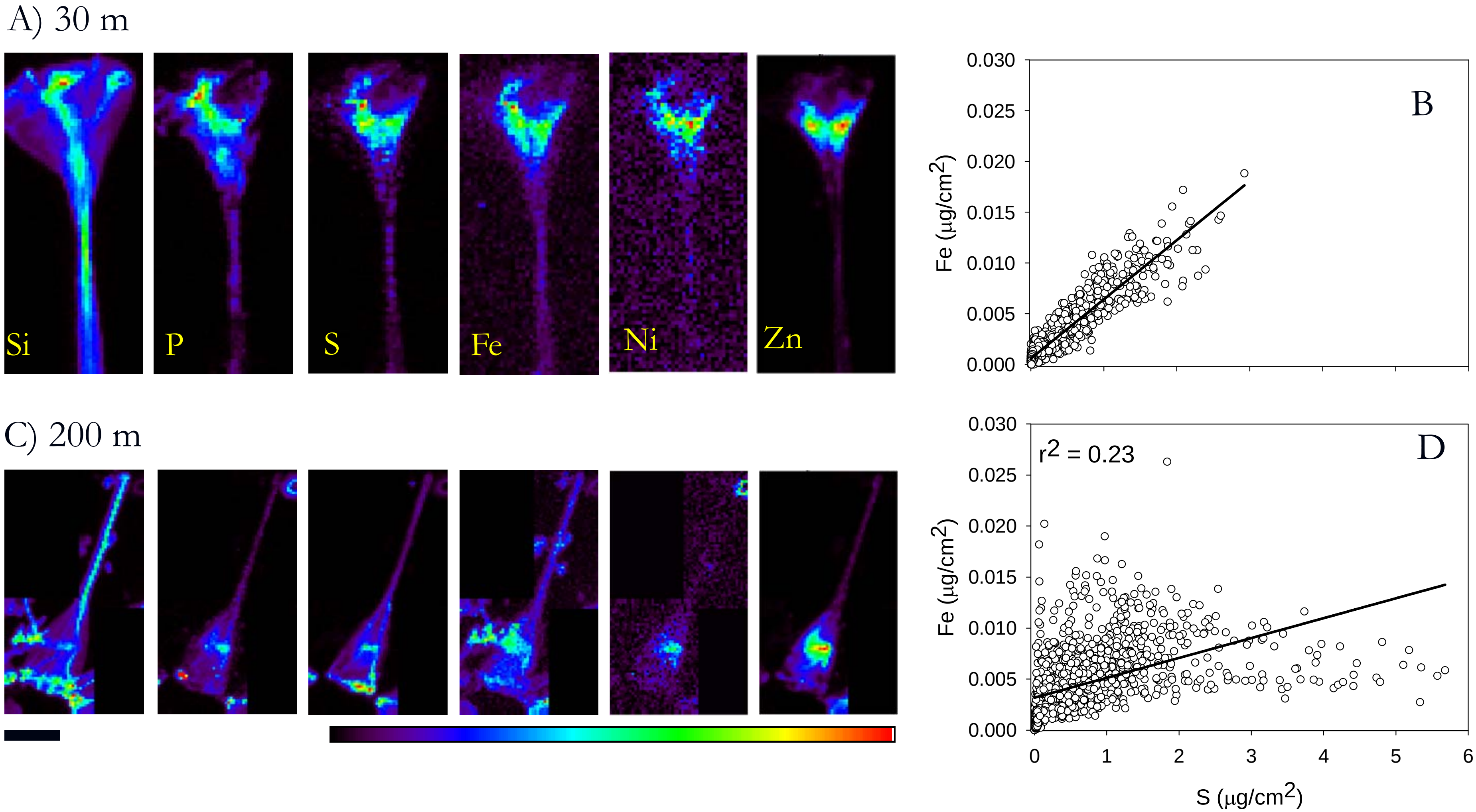
- Tracked patch within AC eddy
- Captured export event of dominant diatom bloom during FeCycle II
- *Asterionella glacialis* cells collected from mixed-layer during bloom and from 100m and 200m sediment traps during bloom export
- Individual cells analyzed with SXRF

Decoupling of element remineralization from sinking cells



- Single-cell quota fit to Martin curve (Martin et al. 1987)
- Rapid remineralization observed for P, S, Zn and Ni
- Slow remineralization observed for Si, Fe

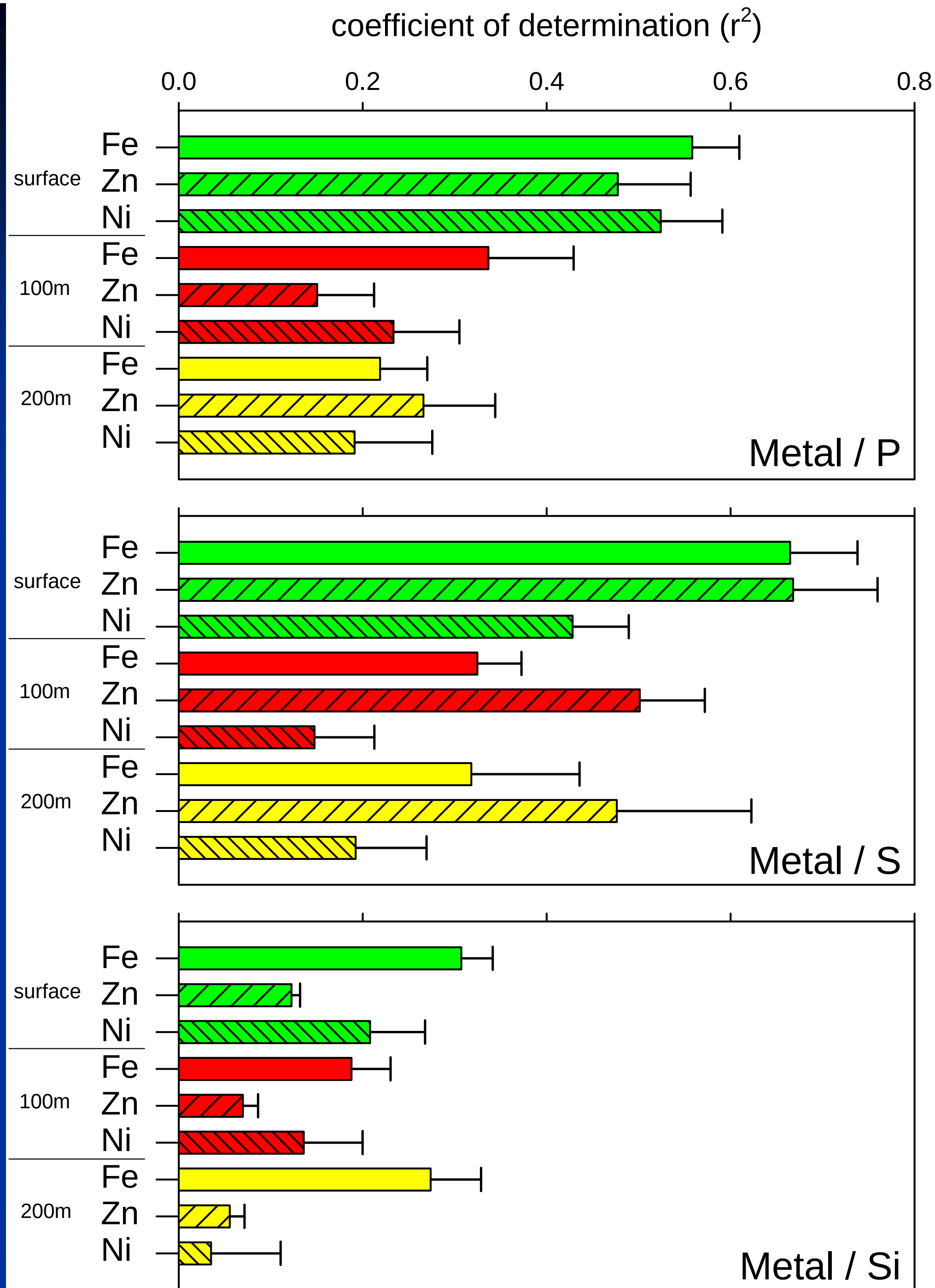
Spatial decoupling of elements in cells



Pixel-specific element concentrations extracted and spatial relationships examined through linear regression

Spatial associations between element pairs within cells

- Spatial associations of all pairs drop significantly with depth, except for Zn/S and Fe/Si
- Zn lost primarily with S
- Ni lost primarily with P
- Fe becomes spatially decoupled from P and associates with Si



3. Conclusions and emerging hypotheses

- Biogenic material appears to dominate fluxes of certain TEIs (Cd, Zn, Cu, Ni) in some settings
- Most of these biogenic TEIs (e.g, Cd, Zn, Cu, Ni) are also lost rapidly from sinking cells
- Iron is lost more slowly from cells and appears to be re-scavenged onto cell surfaces (e.g., diatom frustules)
- The TEI content and fate of other sinking biogenic materials (e.g., fecal pellets) is poorly constrained


Acknowledgements
Synchrotron analyses
Stefan Vogt, Stephen Baines
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