Application of synchrotron x-ray fluorescence mapping and absorption spectroscopy in marine (and environmental) science

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NSLS-II First Experiments Workshop
12 August 2013

Outline

1. Introduction to scientific problem: What are the unanswered questions (that can be addressed with NSLS-II)?

2. What has recently been studied with synchrotron science to date?

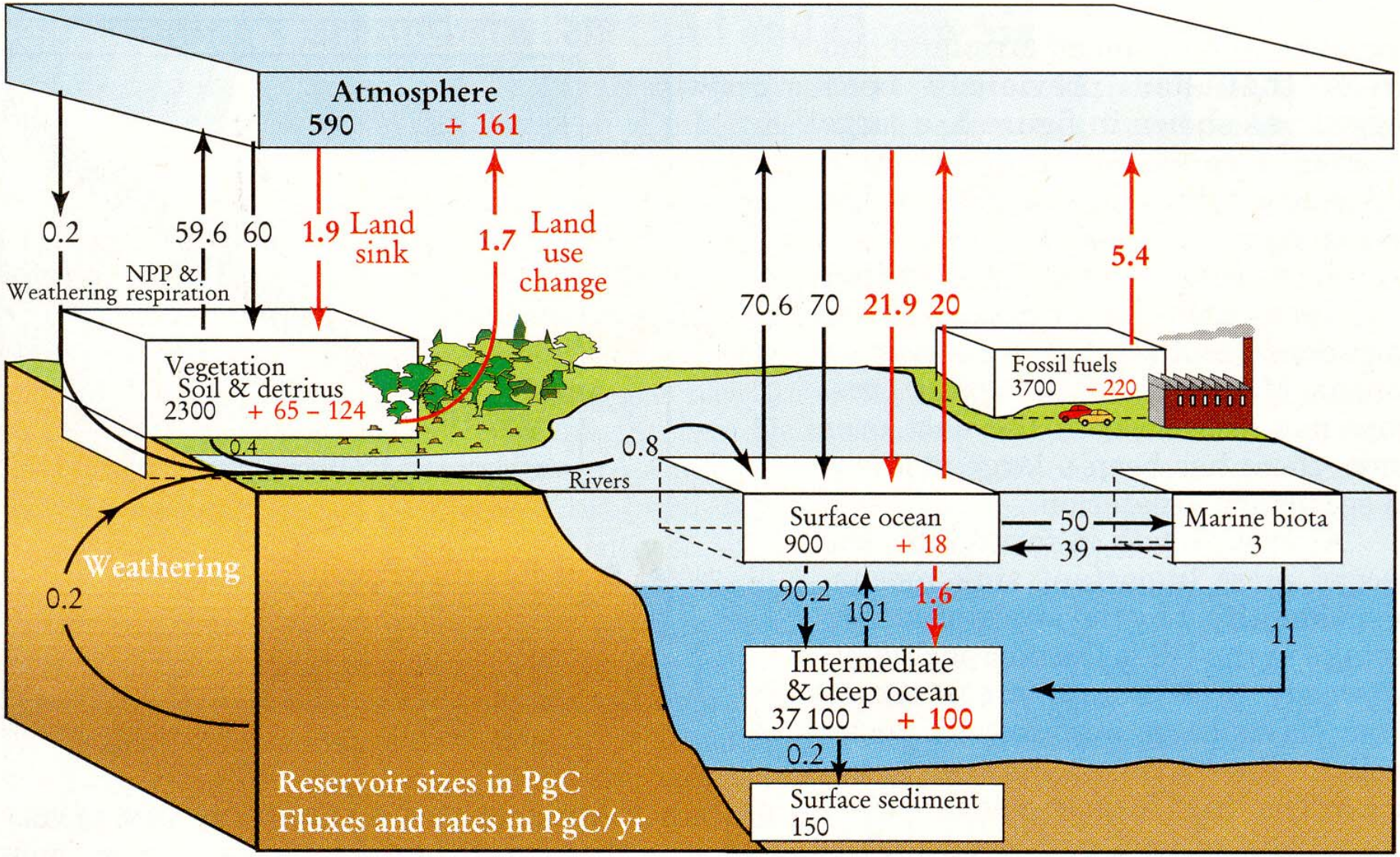
3. What cannot be done today that can be achieved with SRX? Describe the sample prep, experimental setup, and data analysis that will be required.

4. What is required? What is missing? How can we enforce synergies between multiple techniques?

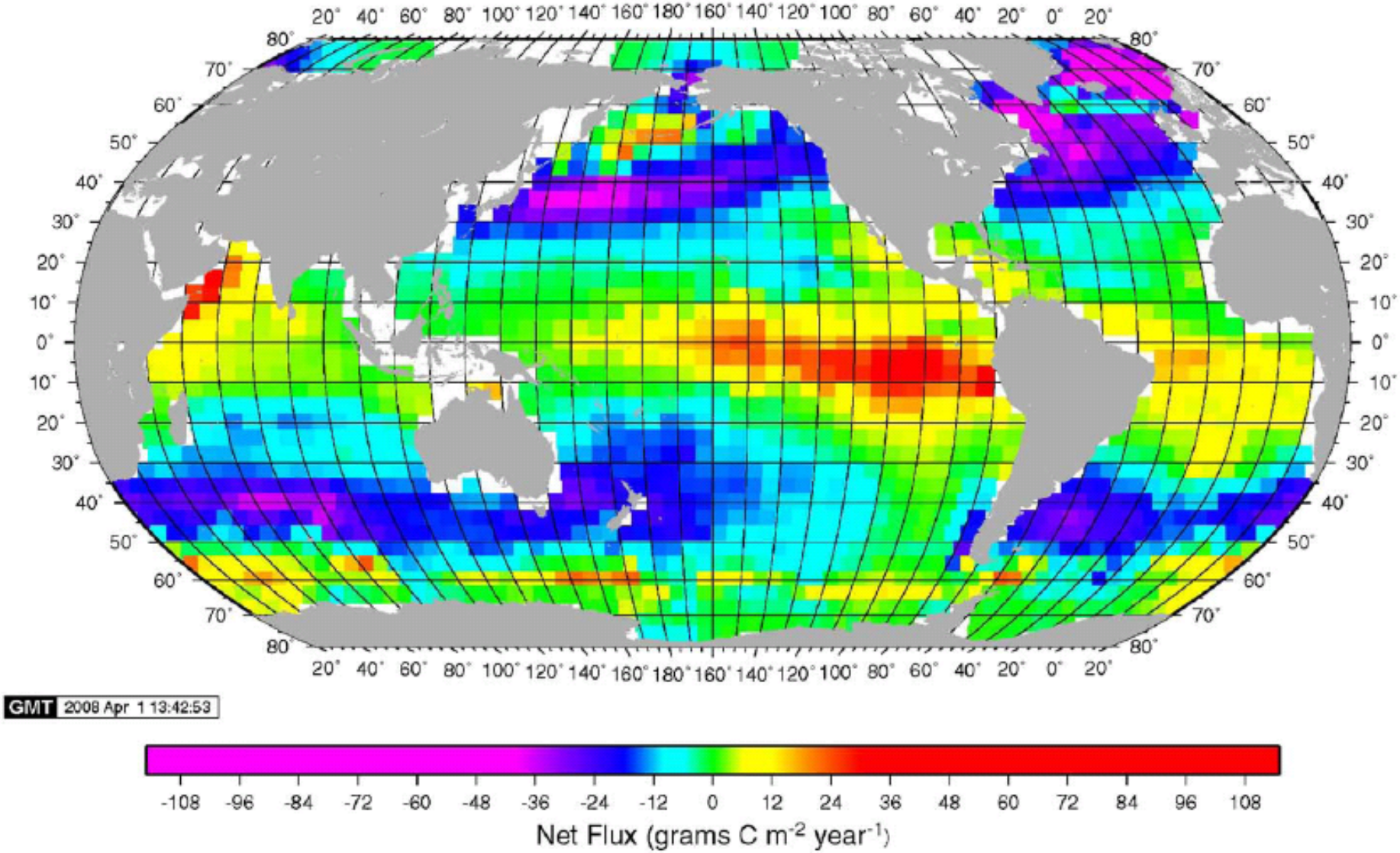
1. Introduction to the science: what are the unanswered questions?

- How do trace metal nutrients alter primary production and community composition of plankton in the ocean?
- What are the chemical transformations and ecological impacts of engineered nanomaterials in the environment?
- What are the mechanisms of metal uptake, storage, and homeostatic control in biological organisms?

Global Carbon Cycle

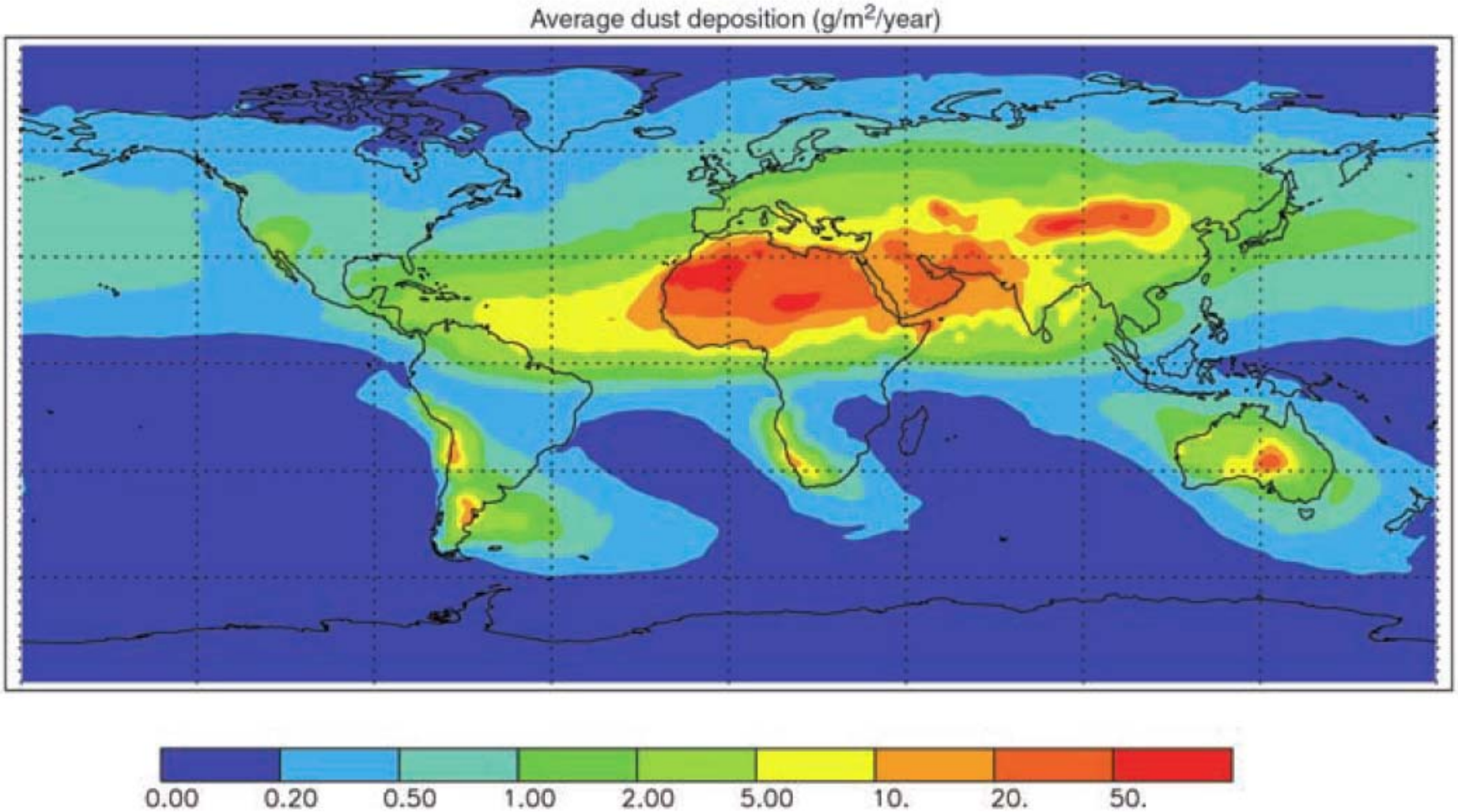


Carbon flux across the ocean surface



Takahashi et al. 2009 *DSR II*

Iron availability limits plankton growth in 40% of global ocean



(Jickells et al. 2005 *Science*)

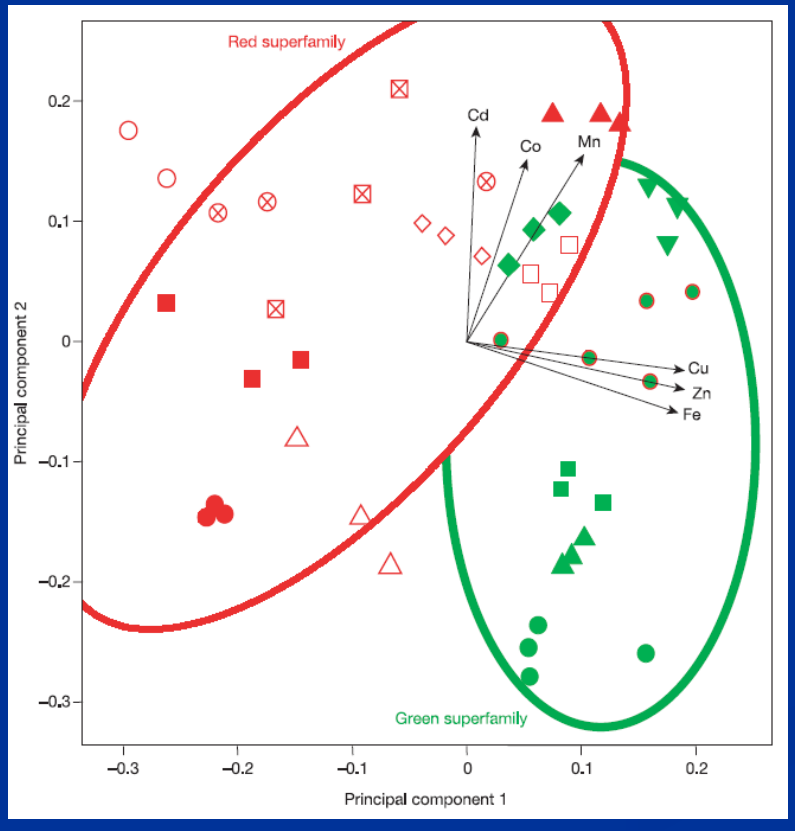
Metalloproteins in phytoplankton

Metal	Compound	Function
Fe	Cytochromes	Electron transport in photosyn./respiration
	Fe-S proteins	Electron transport in photosyn./respiration
	Nitrate reductase	NO_3^- assimilation
	Chelatase	Porphyrin and phycobiliprotein synthesis
	Nitrogenase	N fixation
Mn	O_2-evolving enzyme	Oxidize H_2O to O_2 during photosyn.
	Superoxide dismutase	Convert $O_2^{\cdot -}$ to H_2O_2
Cu	Plastocyanin	Photosynthesis electron transport
	Cytochrome *c* oxidase	Mitochondrial electron transport
Zn	Carbonic anhydrase	Hydration and dehydration of CO_2
	Alkaline phosphatase	Hydrolysis of phosphate esters
	DNA/RNA polymerase	Nucleic acid replication/transcription
Co	Vitamin B_{12}	Carbon and H transfer reactions
Ni	Urease	Hydrolysis of urea
	Superoxide dismutase	Convert $O_2^{\cdot -}$ to H_2O_2
	Hydrogenase	Oxidation of H_2
Mo	Nitrogenase	Nitrogen fixation
	Nitrate reductase	Nitrate reduction to ammonia

Evidence for taxonomic diversity in metal requirements

The evolutionary inheritance of elemental stoichiometry in marine phytoplankton

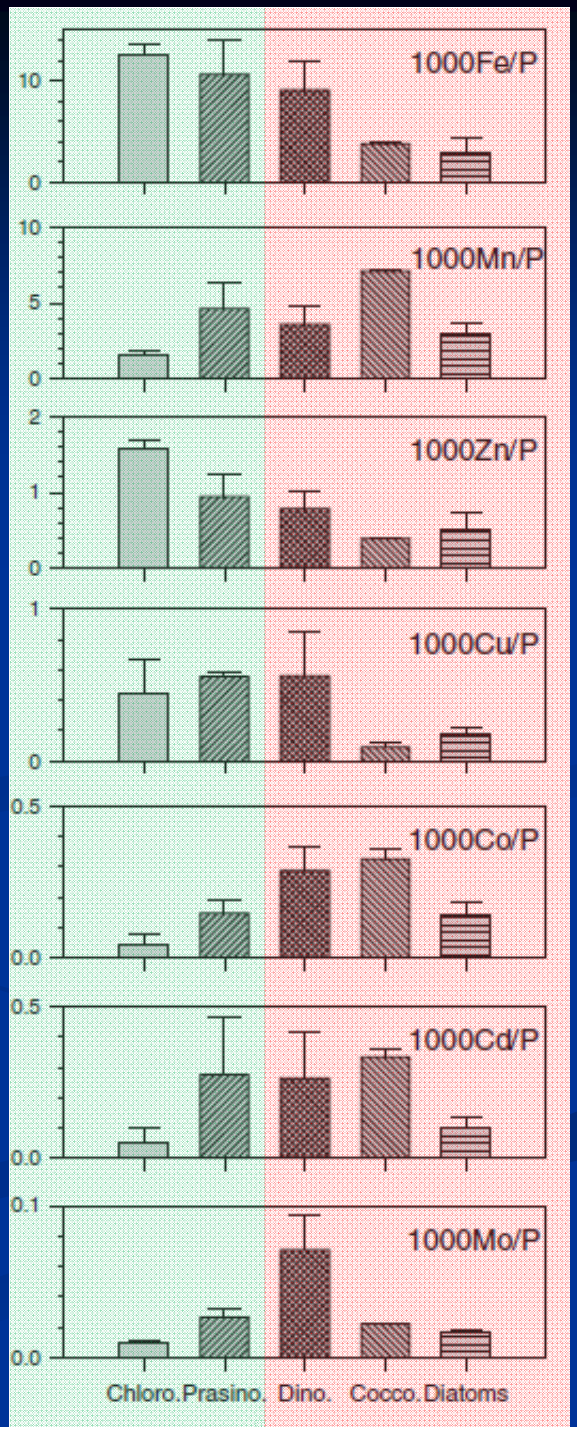
Antonietta Quigg[1], Zoe V. Finkel[1], Andrew J. Irwin[1], Yair Rosenthal[1,2], Tung-Yuan Ho[5], John R. Reinfelder[3], Oscar Schofield[1,4], Francois M. M. Morel[5] & Paul G. Falkowski[1,2]



Cd, Co Mn

Cu, Zn, Fe

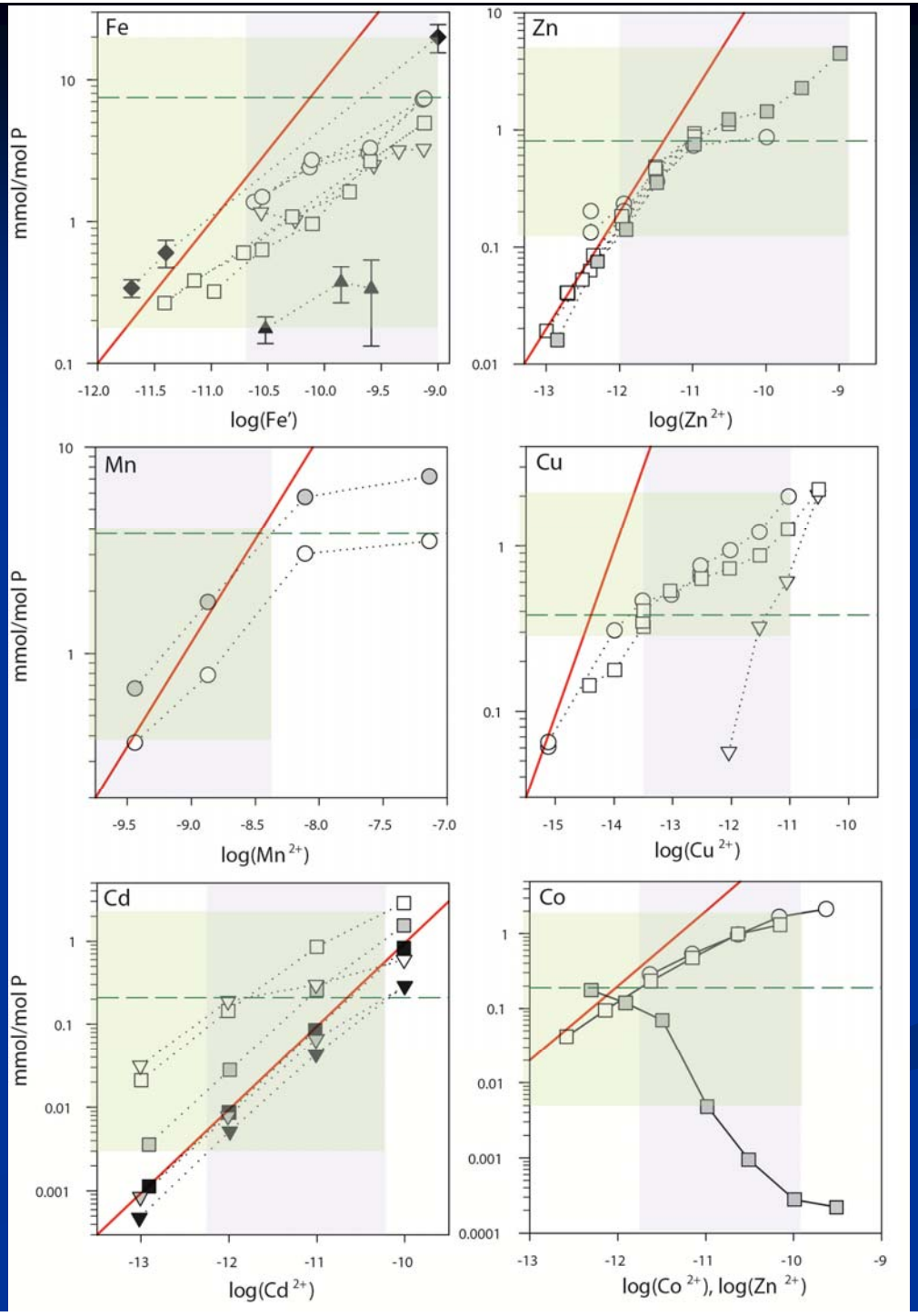
(Quigg et al. 2003 *Nature*)



Difficult to estimate field cell quotas from laboratory work

Quotas influenced by:

- Concentration of free or inorganic ion
- Light (Mn)
- Phytoplankton taxonomy
- Concentration of antagonistic metals (Co, Cd, Zn)



(Twining & Baines 2013 *Ann. Rev. Mar. Sci.*)

Engineered nanomaterials in the environment

www.nanoandme.org

Engineered nanomaterials in the environment

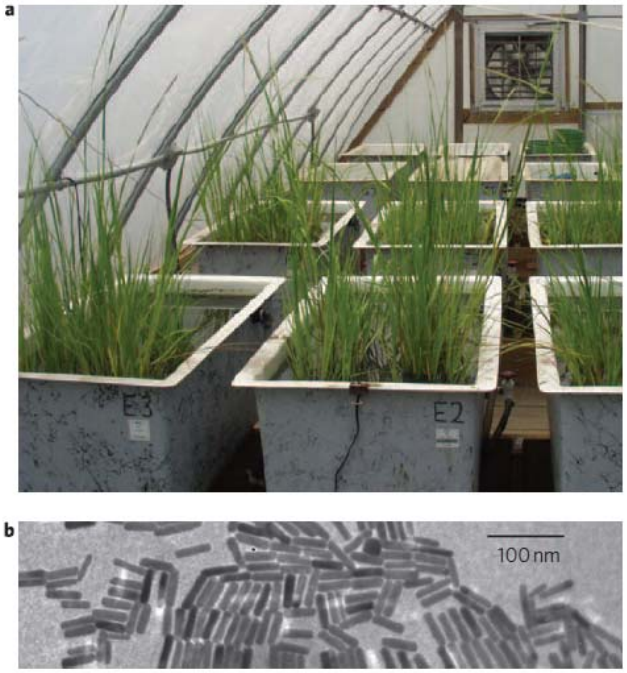
nature nanotechnology

LETTERS

PUBLISHED ONLINE: 21 JUNE 2009 | DOI: 10.1038/NNANO.2009.157

Transfer of gold nanoparticles from the water column to the estuarine food web

John L. Ferry[1,2]*, Preston Craig[1], Cole Hexel[1], Patrick Sisco[1], Rebecca Frey[1], Paul L. Pennington[3], Michael H. Fulton[3], I. Geoff Scott[3], Alan W. Decho[2,4], Shosaku Kashiwada[2,4], Catherine J. Murphy[1,2] and Timothy J. Shaw[1,2]

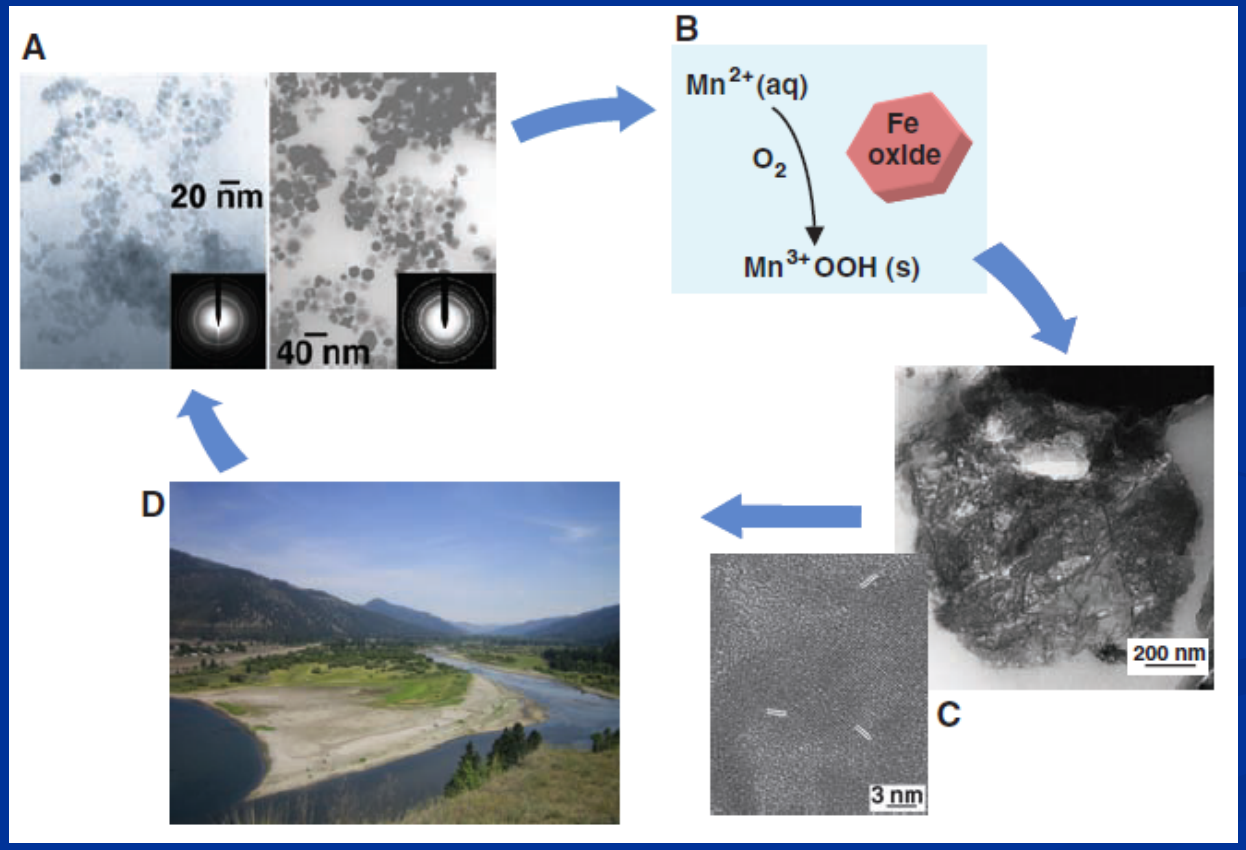


Engineered nanomaterials released into the environment can be accumulated by resident organisms through undetermined mechanisms

(Engineered) nanomaterials in the environment

Nanominerals, Mineral Nanoparticles, and Earth Systems

Michael F. Hochella Jr.,[1*] Steven K. Lower,[2] Patricia A. Maurice,[3] R. Lee Penn,[4] Nita Sahai,[5] Donald L. Sparks,[6] Benjamin S. Twining[7]



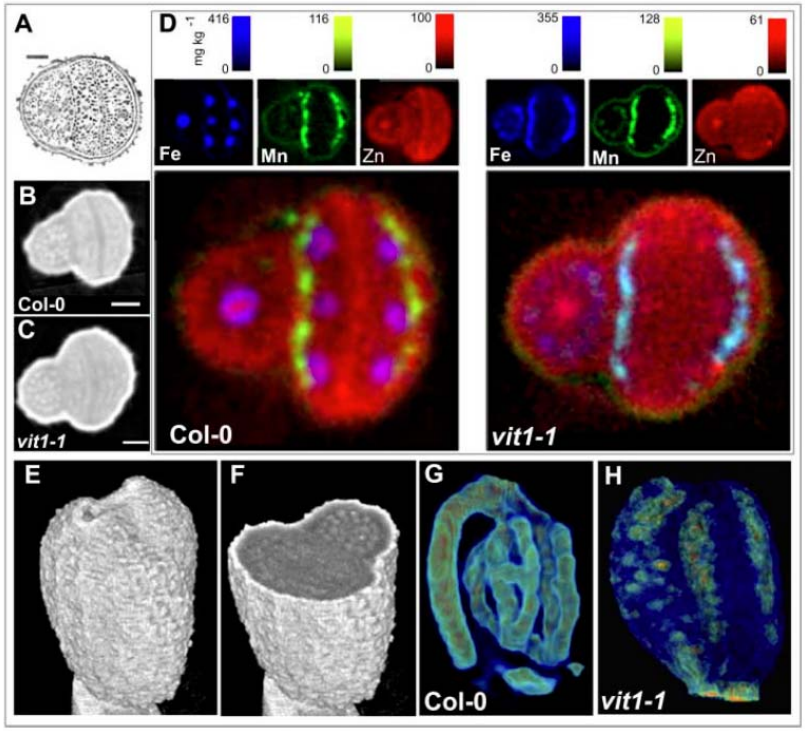
There is growing recognition of the importance of nanominerals in biogeochemical cycles

Hochella et al. 2008 *Science*)

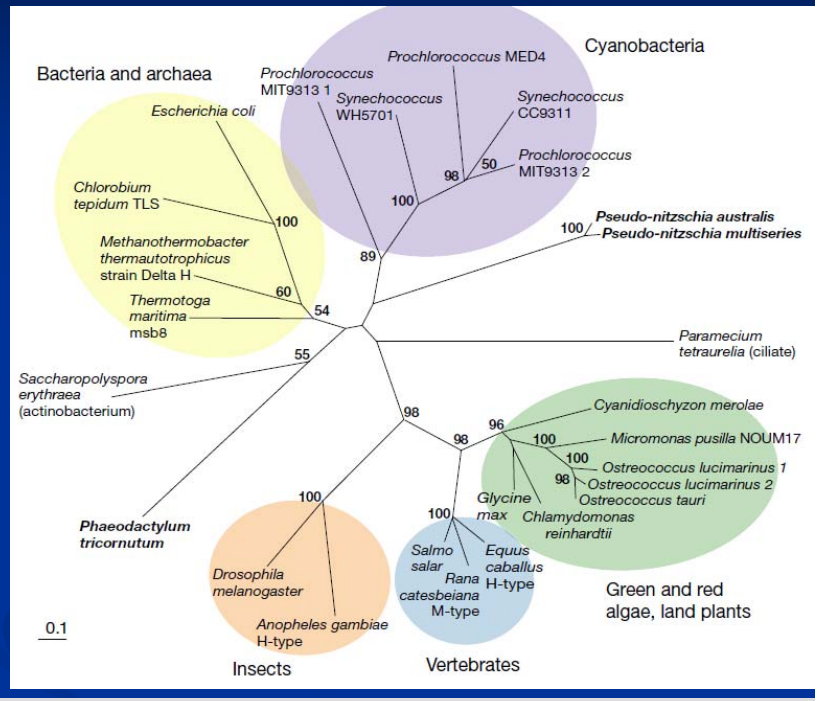
Metal uptake, storage, and homeostatic control in environmentally-relevant organisms

Localization of Iron in *Arabidopsis* Seed Requires the Vacuolar Membrane Transporter VIT1

Sun A. Kim,[1*] Tracy Punshon,[1*] Antonio Lanzirotti,[2] Liangtao Li,[3] José M. Alonso,[4] Joseph R. Ecker,[5] Jerry Kaplan,[3] Mary Lou Guerinot[1]†



(Kim et al. 2006 *Science*)



Vol 457|22 January 2009|doi:10.1038/nature07539 nature

LETTERS

Ferritin is used for iron storage in bloom-forming marine pennate diatoms

Adrian Marchetti[1]*, Micaela S. Parker[1]*, Lauren P. Moccia[2], Ellen O. Lin[1], Angele L. Arrieta[3], Francois Ribalet[1], Michael E. P. Murphy[3], Maria T. Maldonado[2] & E. Virginia Armbrust[1]

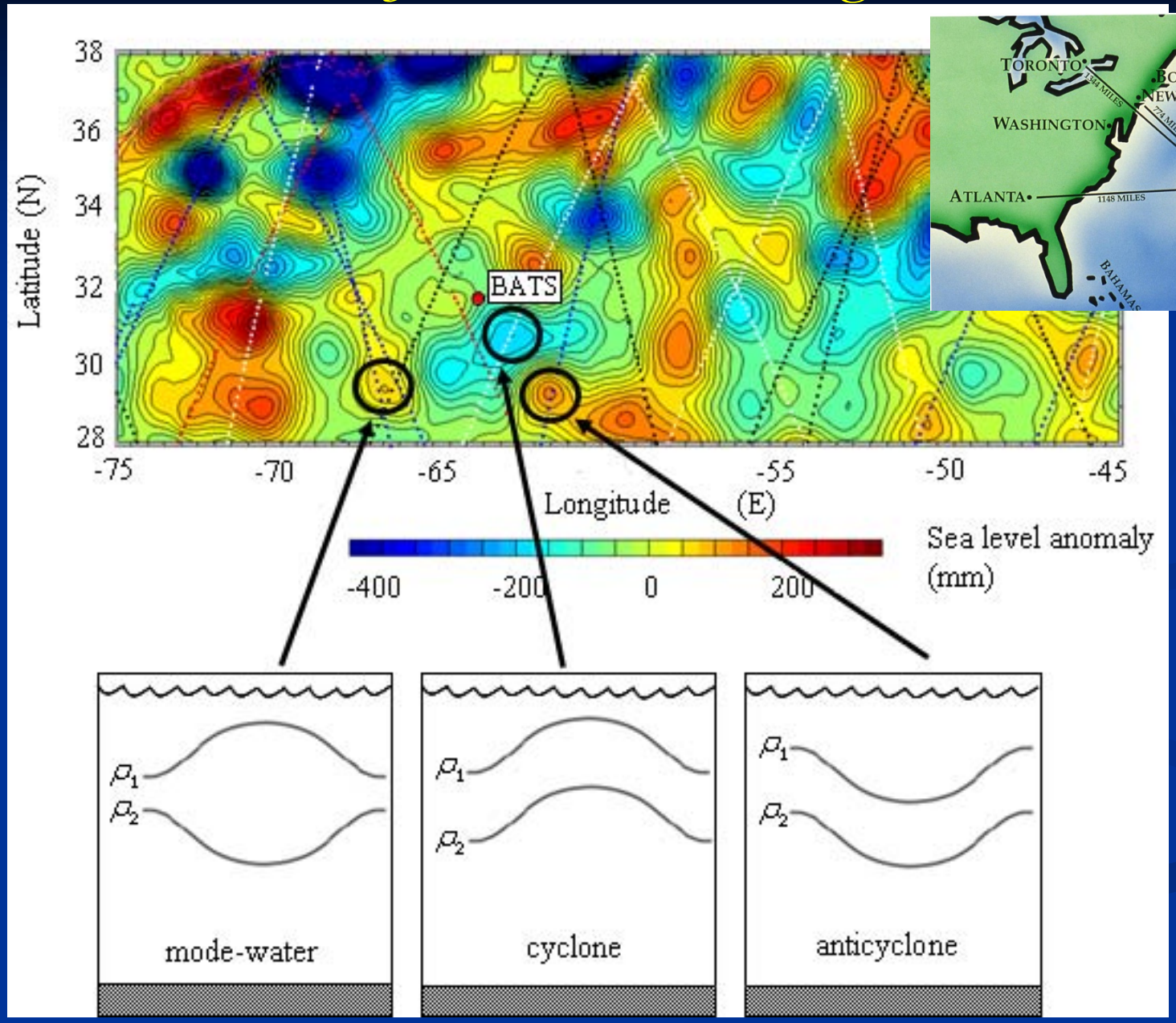
(Marchetti et al. 2009 *Nature*)

2. What has been studied with synchrotron science to date?

- Studying metal contents, distributions and speciation within marine PLANKTON

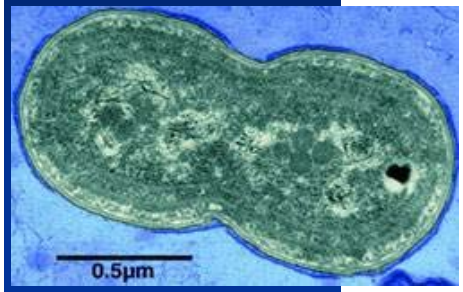
- Studying metal contents, distribution and speciation with marine PARTICLES

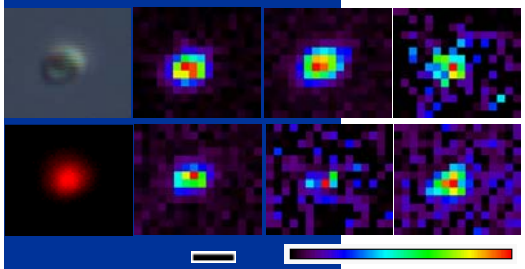
Metallome of *Synechococcus* in Sargasso Sea

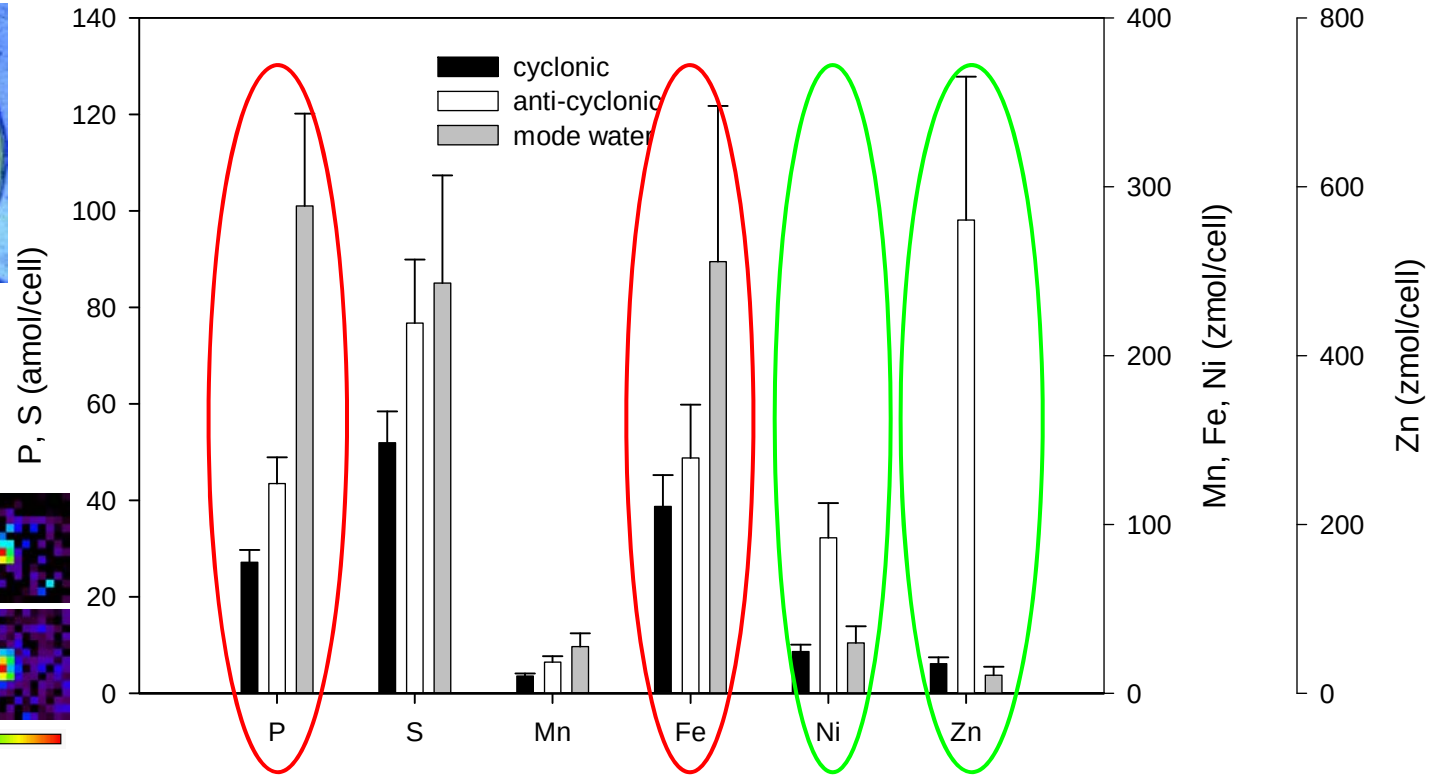


(Twining et al. 2010 *Limnol. Oceanogr.*)

Cellular element quotas varied between eddies







P and Fe respond to inorganic nutrient inputs

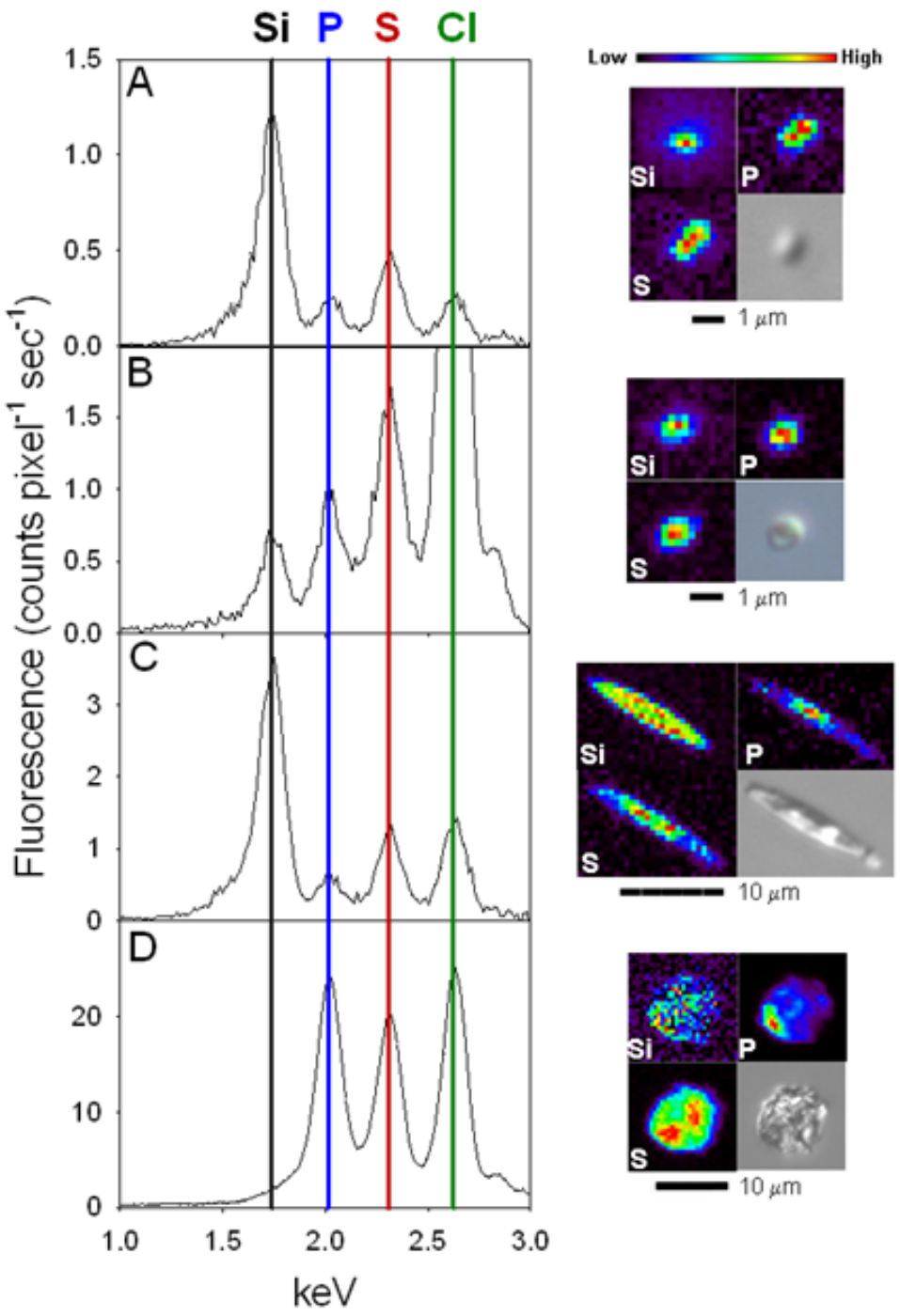
Ni and Zn respond reliance on organic N and P

(Twining et al. 2010 *Limnol. Oceanogr.*)

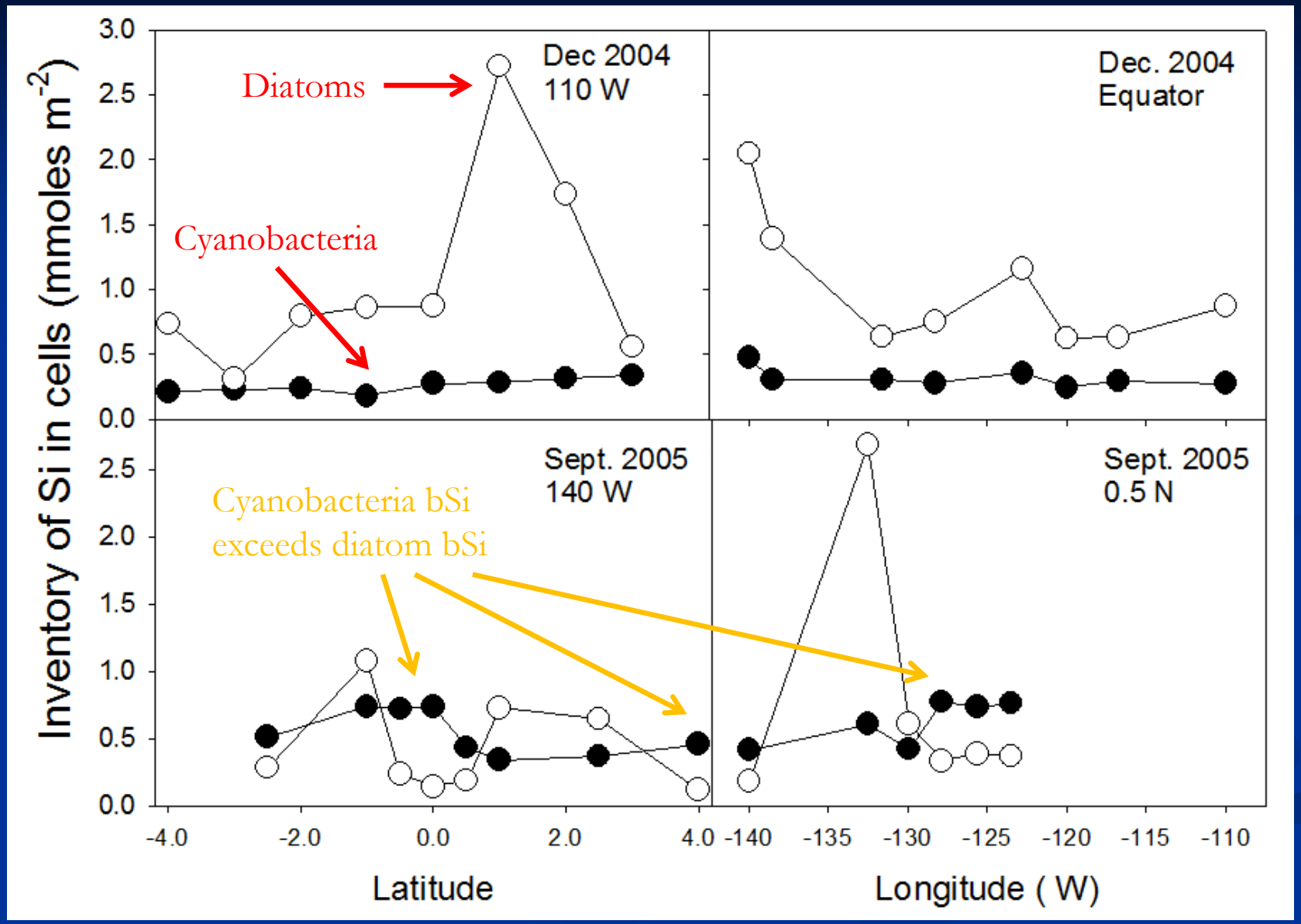
A surprising role for picocyanobacteria in the marine silicon cycle

- Substantial Si observed in cyanobacteria from EqPac and Sargasso Sea
- Si is significantly above background concentrations in grid
- No Si observed in autotrophic flagellates

(Baines et al. 2012 *Nature Geoscience)*



Contribution to bSi inventory in the EqPac



Taxonomy matters

(Baines et al. 2012 *Nature Geoscience*)

Speciation of iron associated with cells and particles in the ocean

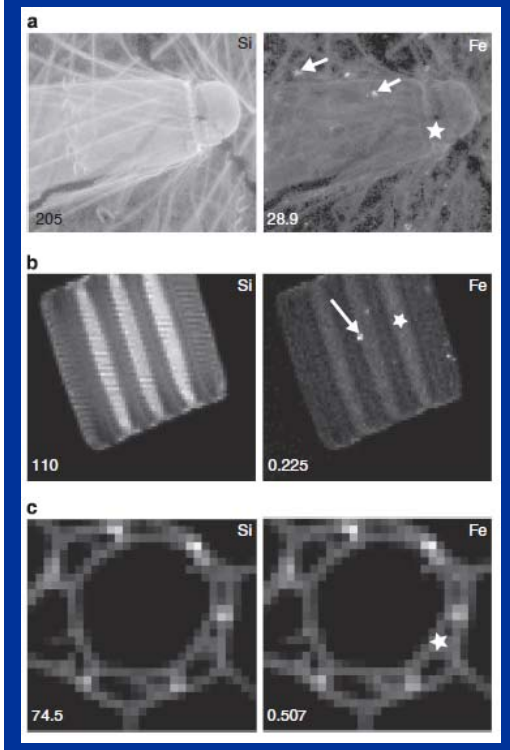
nature COMMUNICATIONS

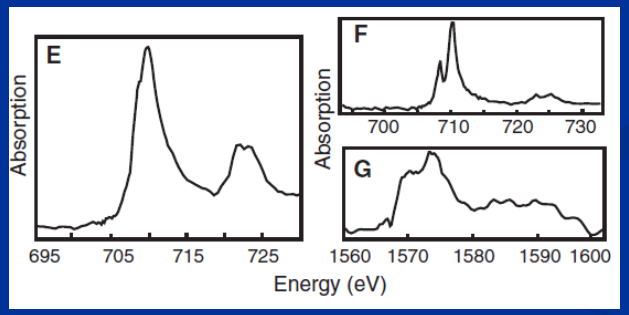
ARTICLE

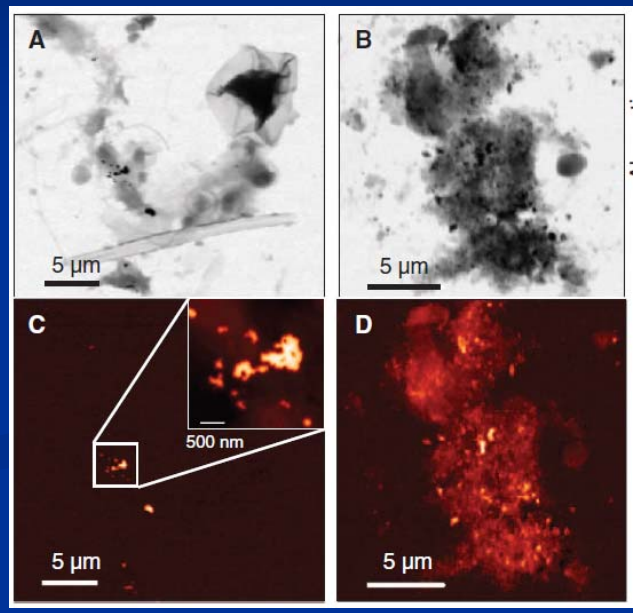
Received 4 Nov 2012 | Accepted 3 May 2013 | Published 10 Jun 2013 DOI: 10.1038/ncomms2981

Role of biogenic silica in the removal of iron from the Antarctic seas

Ellery D. Ingall[1,*], Julia M. Diaz[1,*,†], Amelia F. Longo[1], Michelle Oakes[1,†], Lydia Finney[2], Stefan Vogt[2], Barry Lai[2], Patricia L. Yager[3], Benjamin S. Twining[4] & Jay A. Brandes[5]







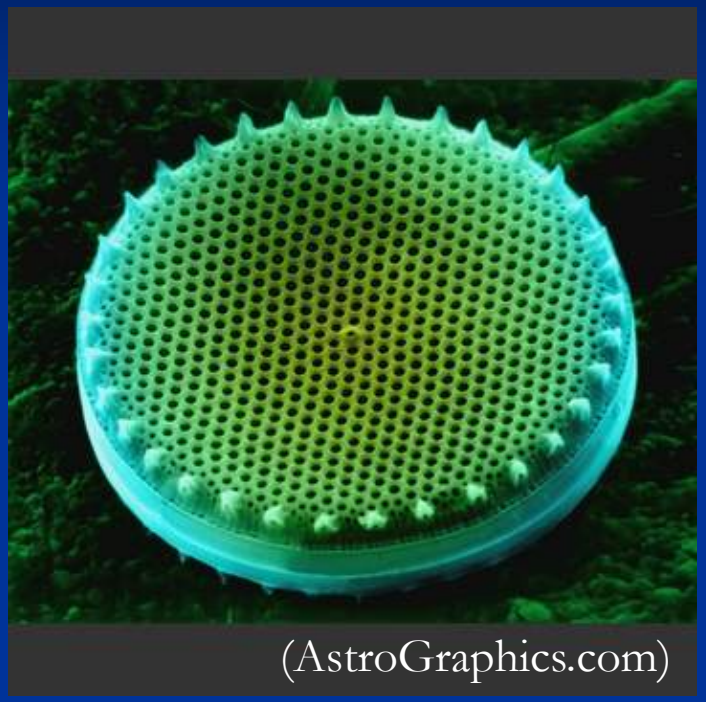
Chemically and Geographically Distinct Solid-Phase Iron Pools in the Southern Ocean

B. P. von der Heyden,[1,2] A. N. Roychoudhury,[1*] T. N. Mtshali,[1,3] T. Tyliszczak,[4] S. C. B. Myneni[2]

(Ingall et al. 2013 *Nature Comm.*; von der Heyden et al. 2012 *Science*)

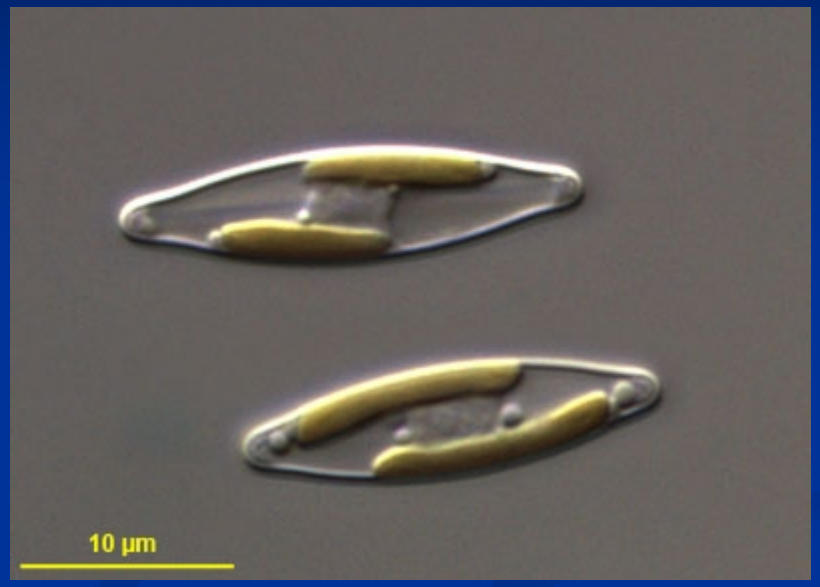
Iron storage within oceanic pennate diatoms

Centrics



- Radial symmetry
- Evolved ca. 180 MYA

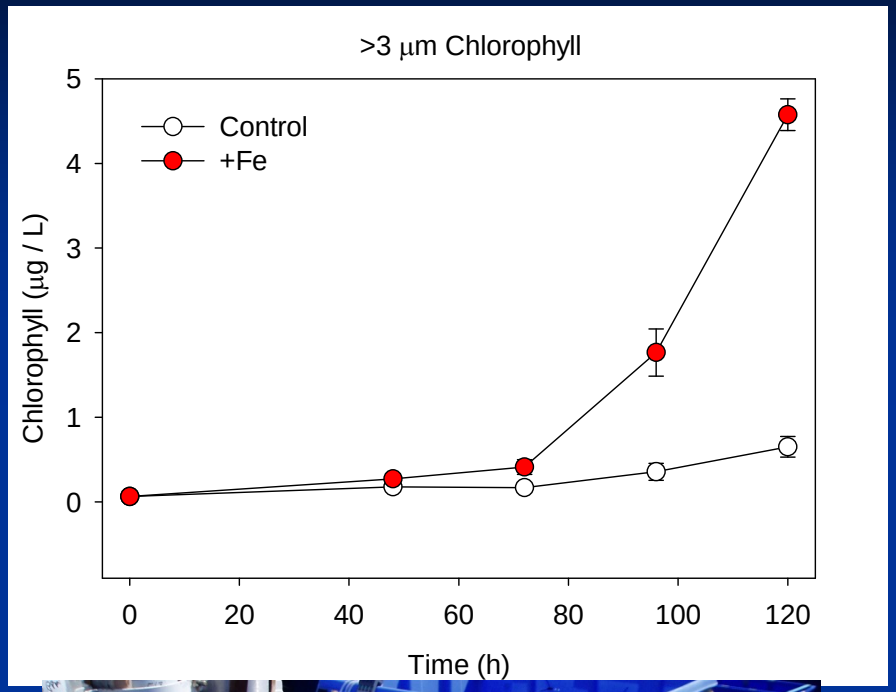
Pennates

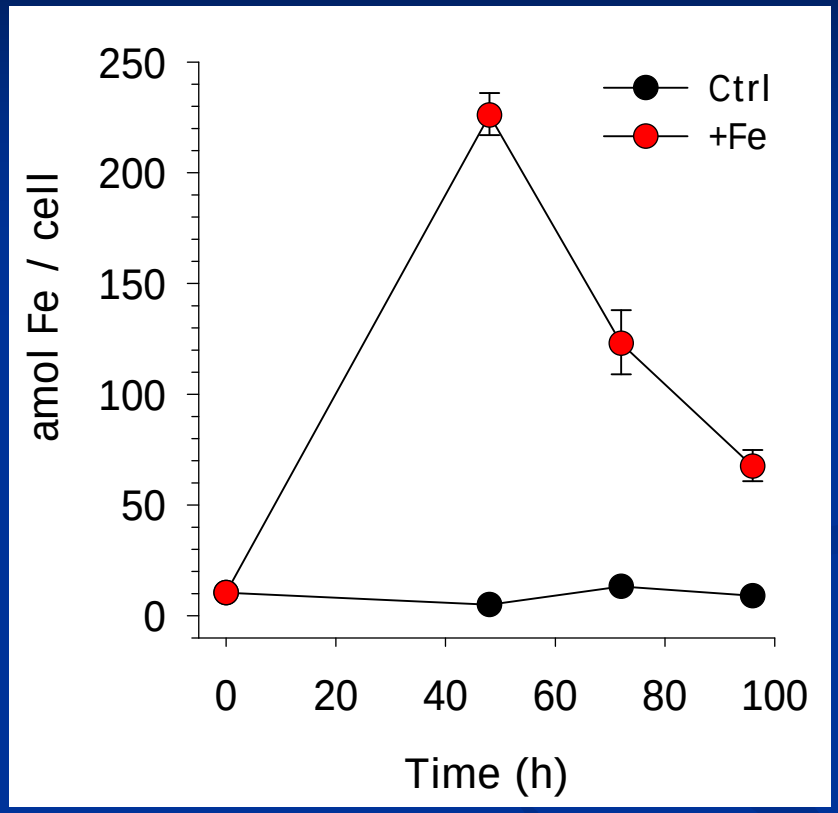


- Bilateral symmetry
- Evolved ca. 90 MYA

- Nearly always respond to Fe additions to open ocean seawater

Iron storage within oceanic pennate diatoms



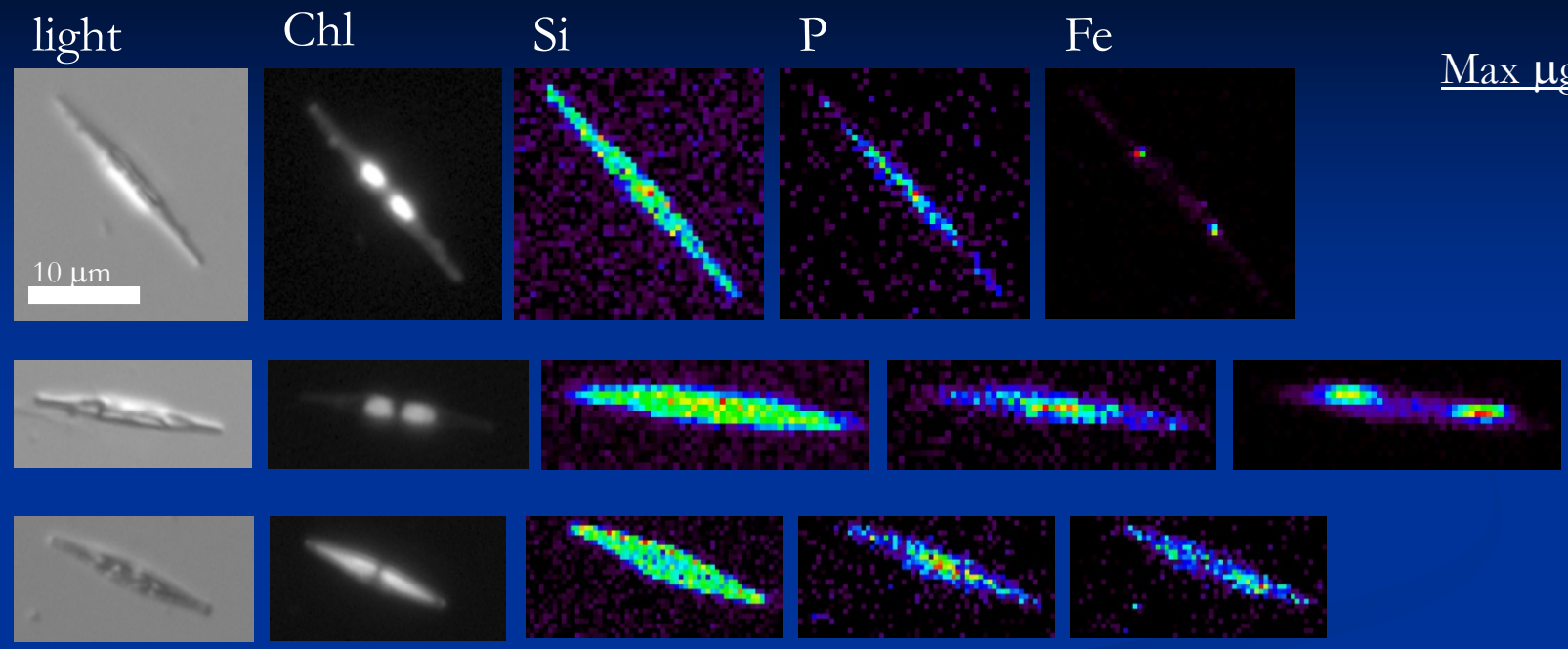


(Baines et al. 2011)

- 22-fold increase in Fe quotas 48 h after Fe addition

(Br

Localization of accumulated iron

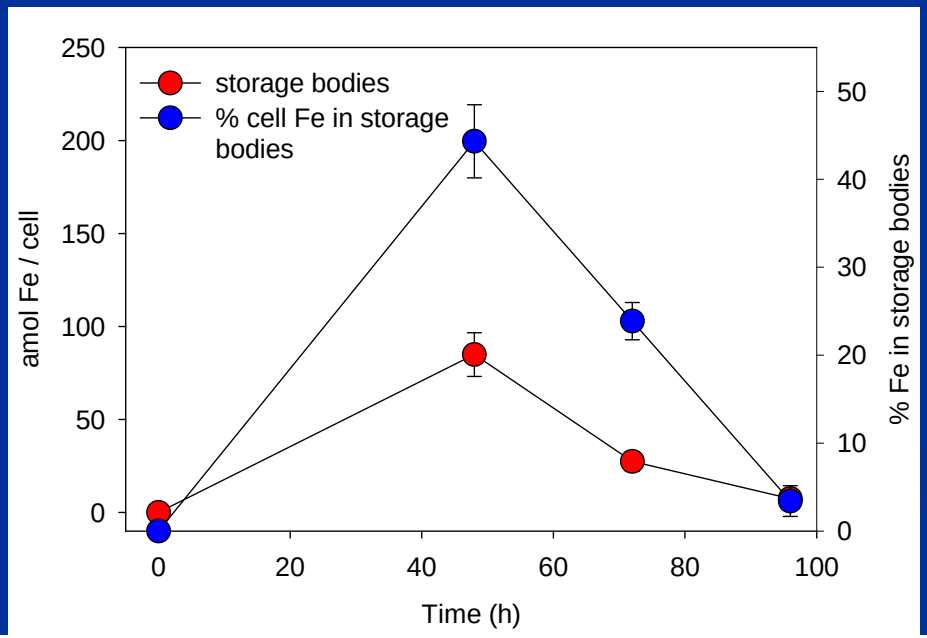


Max µg/cm²

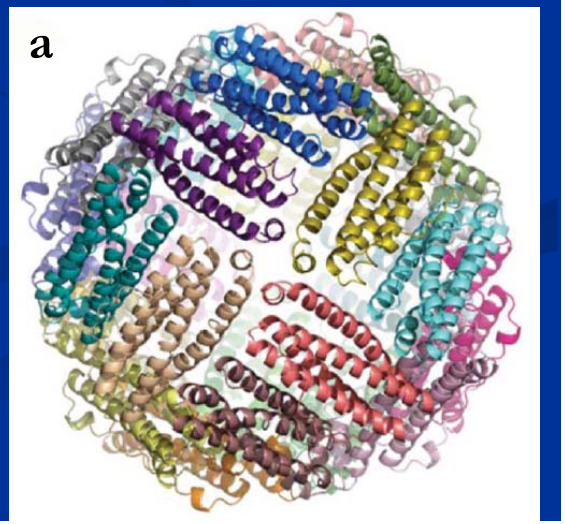
0.474

0.101

0.030

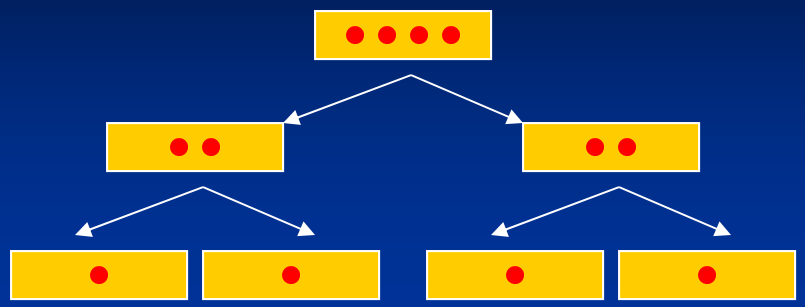


Ferritin in diatoms

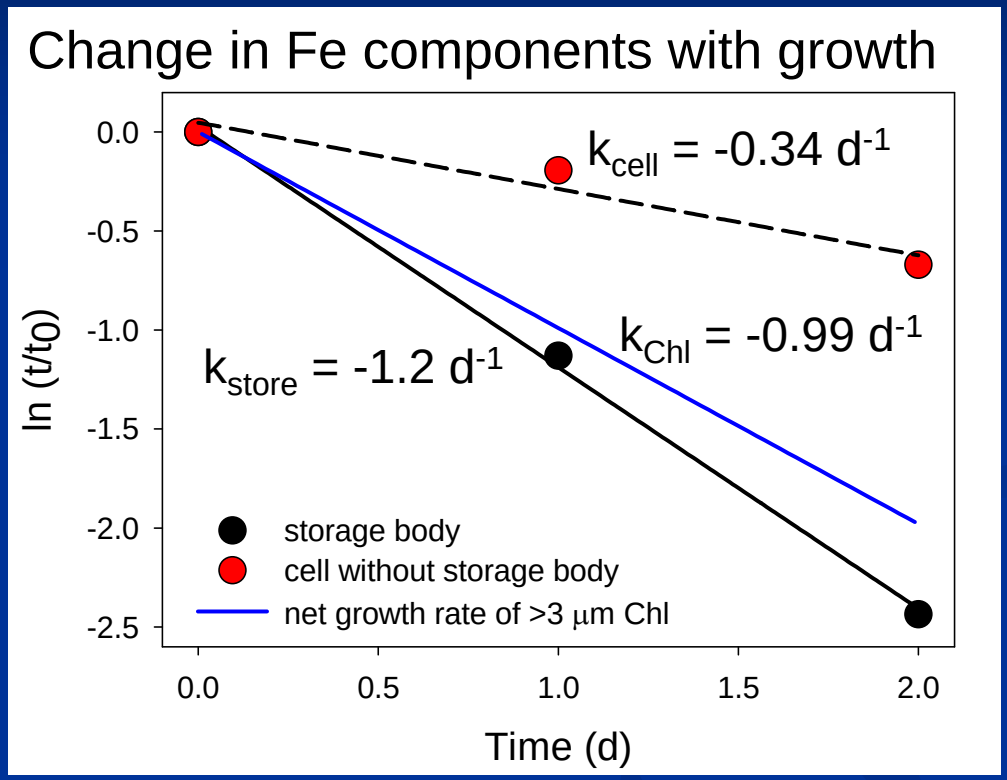


(Marchetti et al. 2009)

Iron diluted as cells grow and divide



- Fe storage bodies expected to distribute between daughter cells during division
- Storage body Fe 'diluted' more rapidly than cell growth

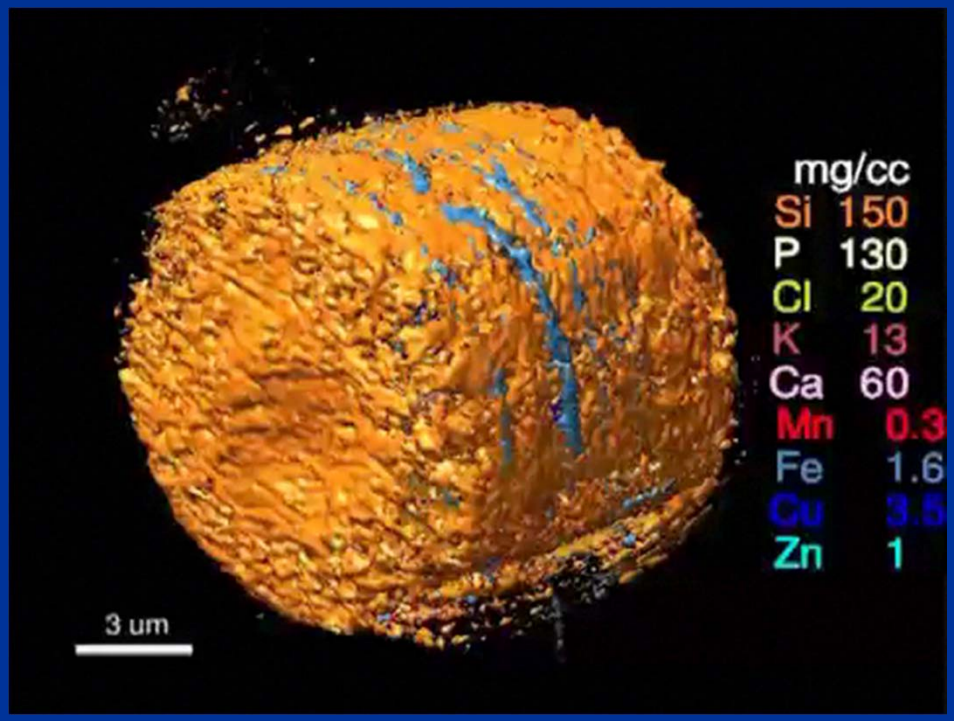


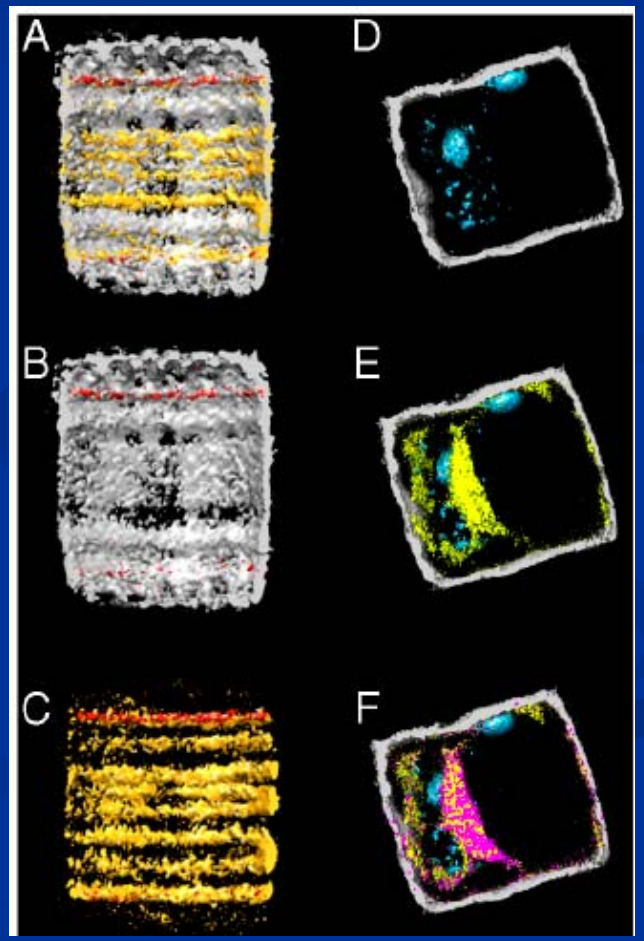
Stored iron allows cells to divide more than 5 times before drop in growth rate

3D distribution of trace metals in plankton cell

Quantitative 3D elemental microtomography of *Cyclotella meneghiniana* at 400-nm resolution

Martin D. de Jonge[a,1], Christian Holzner[b], Stephen B. Baines[c], Benjamin S. Twining[d], Konstantin Ignatyev[e,2], Julia Diaz[f], Daryl L. Howard[a], Daniel Legnini[e], Antonino Miceli[e], Ian McNulty[e], Chris J. Jacobsen[b,3], and Stefan Vogt[e]

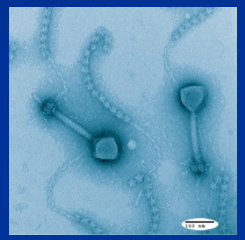
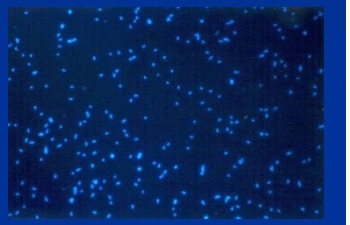




(de Jonge et al. 2010 *PNAS*)

3. What cannot be done today that can be achieved with SRX?

- Mapping target particles at higher spatial resolution with higher flux
  - Smaller, environmentally critical organisms (*Prochlorococcus*, heterotrophic bacteria, viruses)

- Combining high resolution mapping with spectroscopy at high flux
  - Speciation of marine nanoparticles / colloids

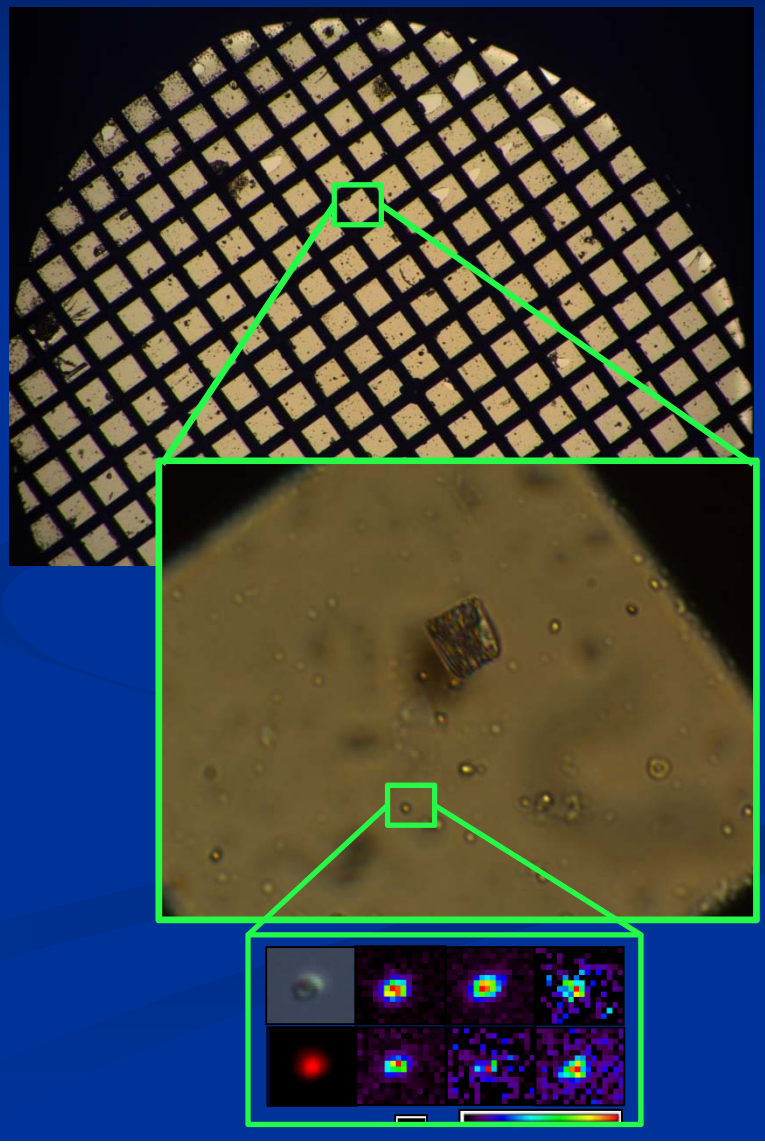
- Mapping interactions between engineered (metal-based) nanoparticles (NM) and environmental organisms
  - Speciation of NM (eg, Fe, Cu, CdSe, Ag) inside organisms

3. What cannot be done today that can be achieved with SRX (cont.)?

- Requirements for such work:
  - He sample chamber
  - Flexible but precise sample mount system
  - System for efficiently finding target area of sample/particle/cell
  - Tomography: register/align images (phase contrast?)
  - Cryo? May be necessary for biological samples, particularly if focus on redox speciation
  - Data analysis: utilize existing tools (eg, MAPS, Athena)?
  - Attention to quantification (standards)
  - Low background scattering signal

4. What is required? What is missing? How can we enforce synergies between multiple techniques?

- High-quality microscopy support and fiduciary system
- Simplify / speed-up transitions between techniques (eg, mapping, spectroscopy, tomography) and incident beam energies
  - Keep beam on same feature while moving from mapping to spectroscopy
- Synergies extend beyond x-ray measurements (eg, environmental 'omics')



Acknowledgements

Synchrotron analyses and method development
Stephen Baines, Stefan Vogt
Charlotte Gleber, Lydia Finney, Jörg Maser
Matt Newville, Chris Jacobsen, Dan Legnini

Field sampling
Pete Sedwick, Sara Rauschenberg

Funding
National Science Foundation
Department of Energy