Iron speciation and bioavailability: Insight gained from analytical chemistry and microbial physiology

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Motivation
Fe as an essential micro-nutrient

Required for:

1. Photosynthetic electron transport
2. Respiratory electron transport
3. Nitrogen fixation
4. Nitrate reduction and assimilation

Motivation
Fe as an essential micro-nutrient

Fe is sparingly soluble under oxic conditions and circumneutral pH in seawater:

1. Responsible for HNLC conditions in Southern, subarctic and equatorial Pacific Oceans

2. May also limit N_2-fixation in oligotrophic regions

Fe and Carbon and Nitrogen cycles are intimately linked

Motivation

As a community we have made great strides analytically in the past decades (accelerated by GEOTRACES in recent years) determining the physicochemical speciation of Fe in seawater.

Determining bioavailability of the various forms of Fe remains a significant challenge

Fe Bioavailability: Presenter Biases and Simplifications

One must define the term by asking simple questions:

- Available to whom?
- On what time scale?

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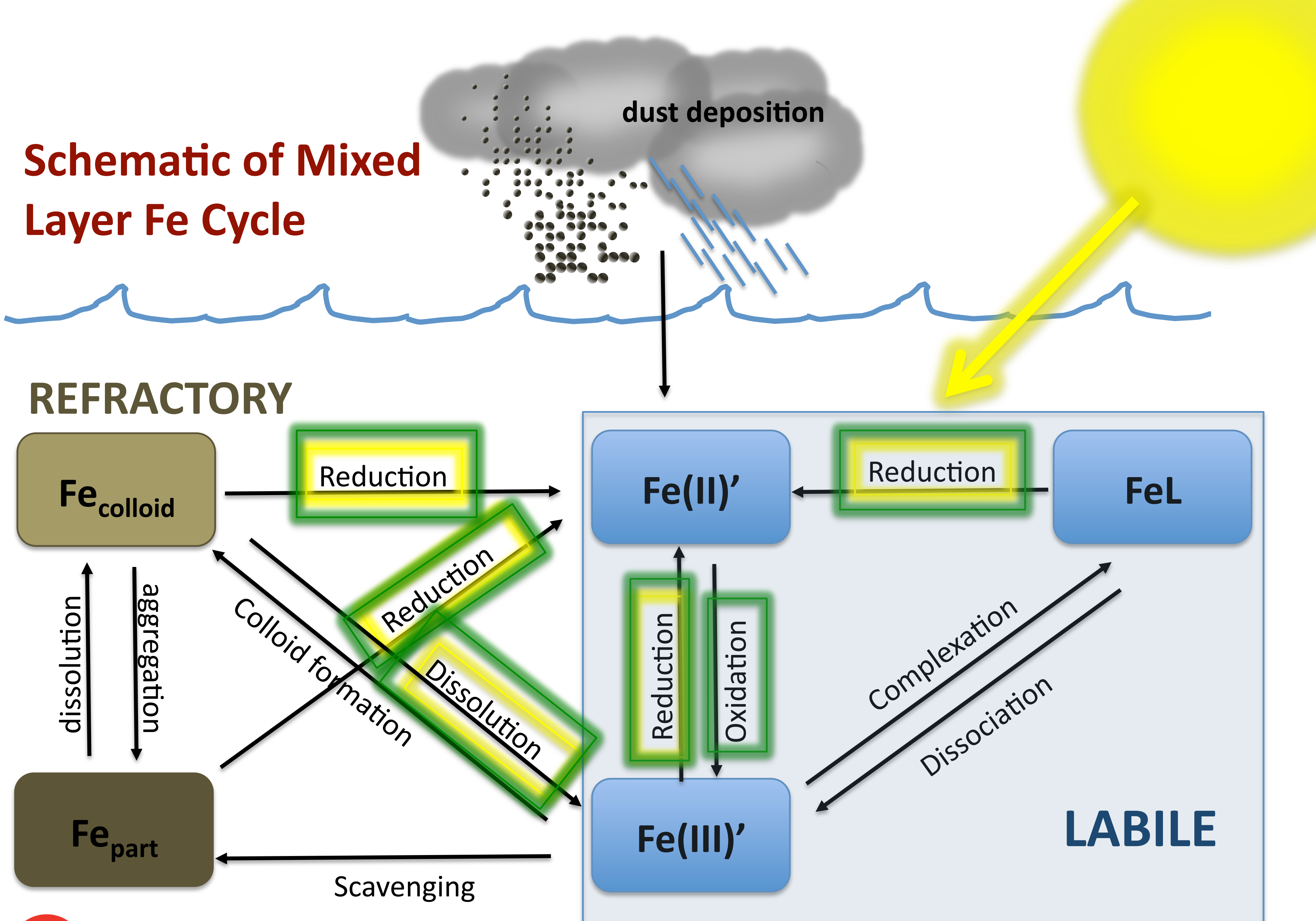
- Available to whom? **Diatoms**
- On what time scale?

Fe Bioavailability: Presenter Biases and Simplifications

One must define the term by asking simple questions:

- Available to whom? **Diatoms**
- On what time scale? **Residence time of dust in the mixed layer (~10 days)**

Schematic of Mixed Layer Fe Cycle



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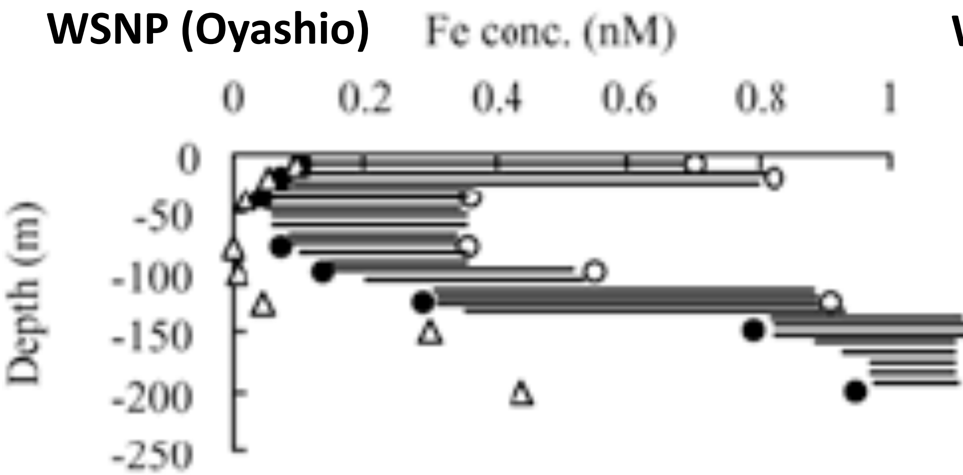
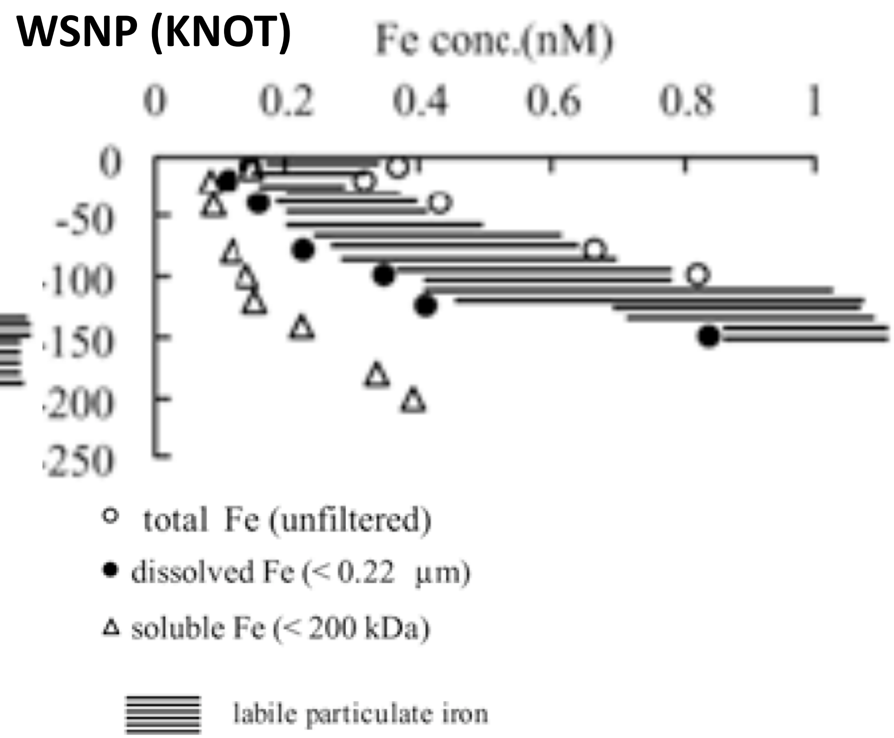
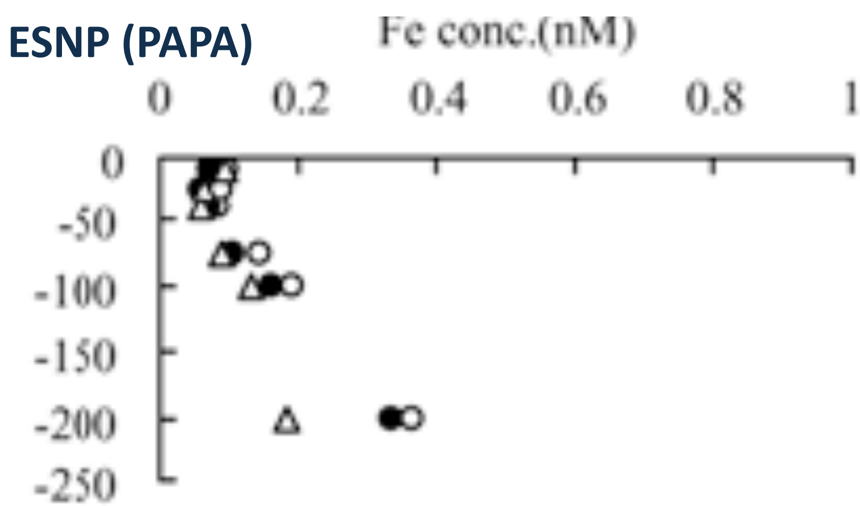
Size partitioning of Fe in the subarctic Pacific







West-East gradient in particulate Fe likely reflecting atmospheric source

Mixed layer depletions of soluble Fe

Nishioka et al. 2001 *Marine Chemistry,* 2003 *GRL*

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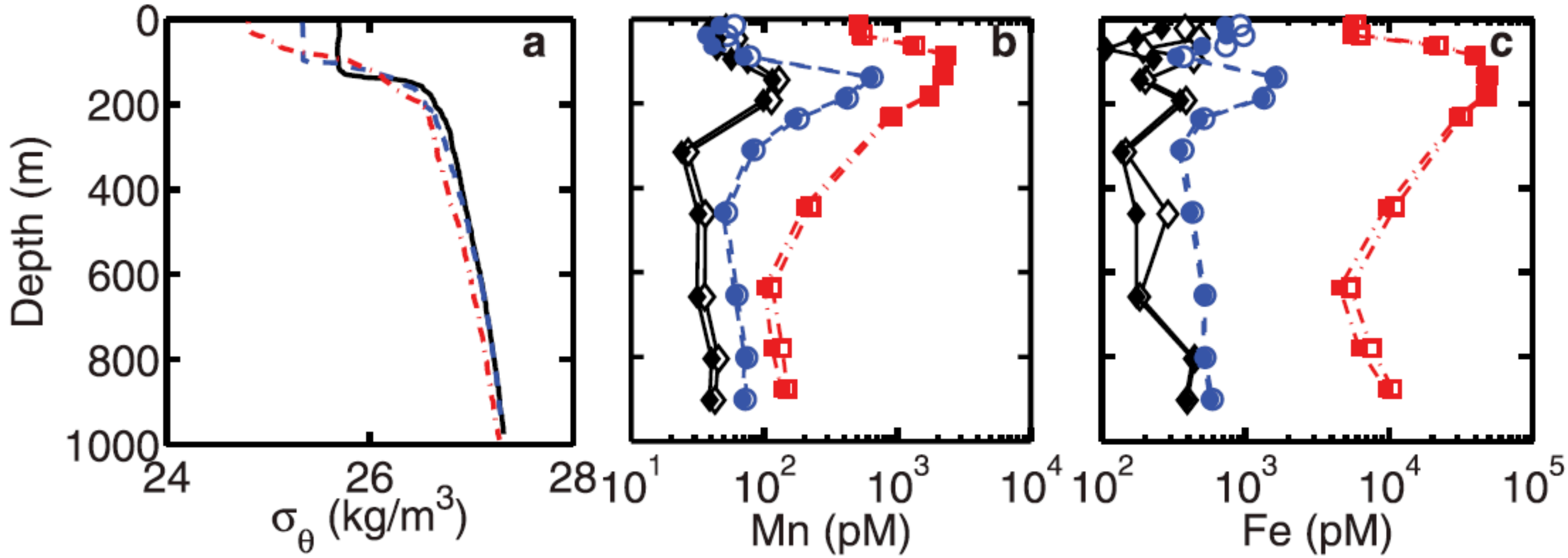

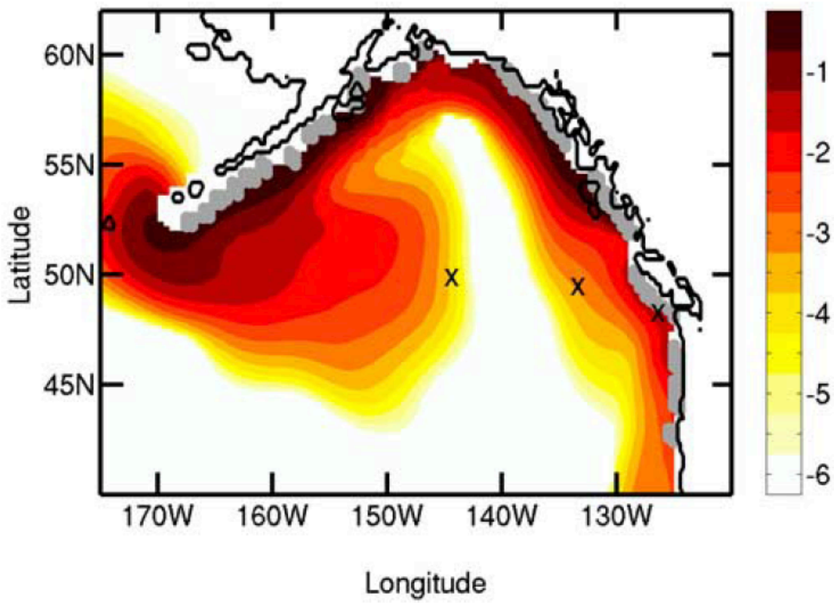

Continental Shelf Derived Fe Can Fuel Productivity in the Open Ocean

Lam et al. 2006 *GBC*

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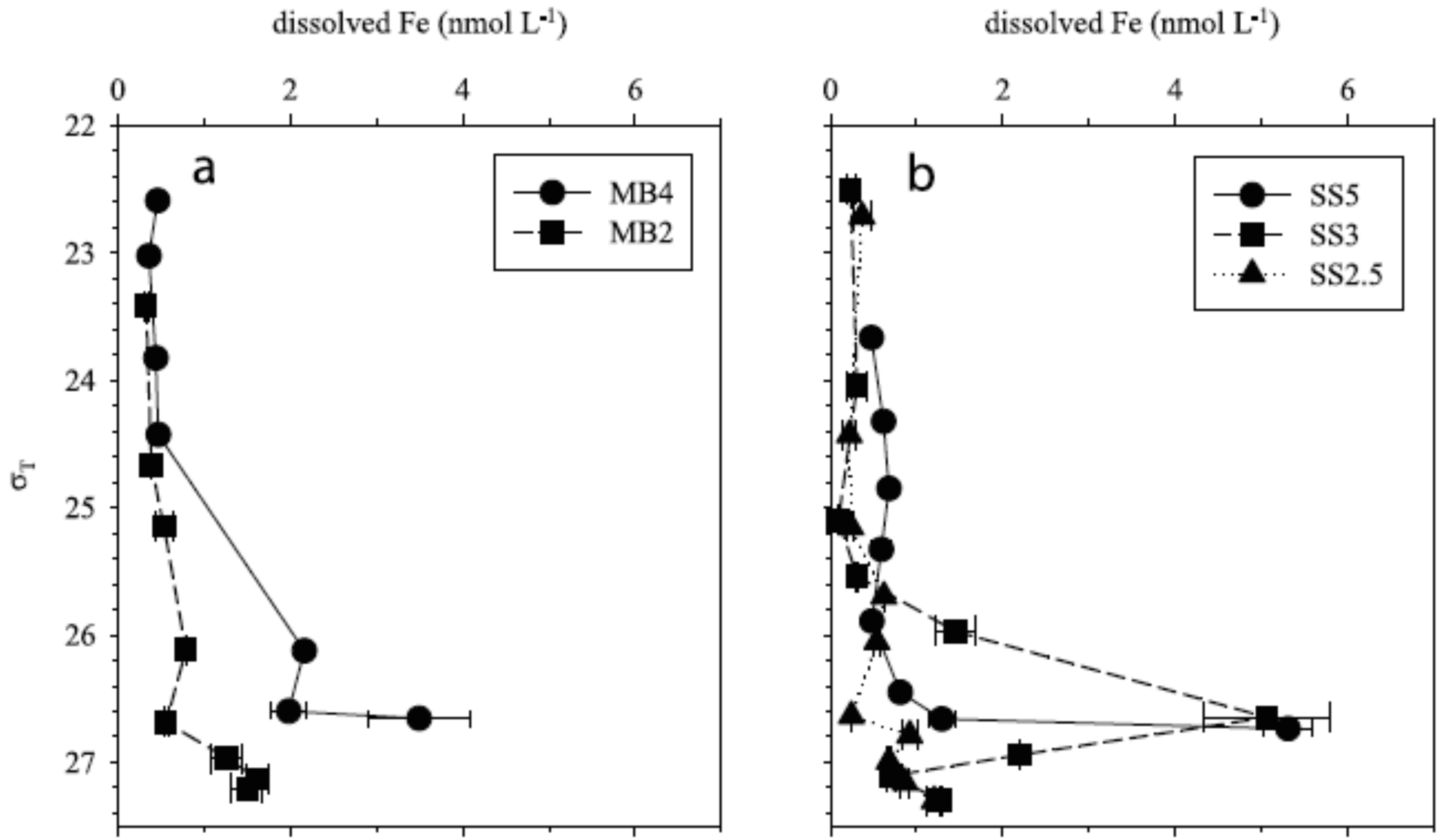
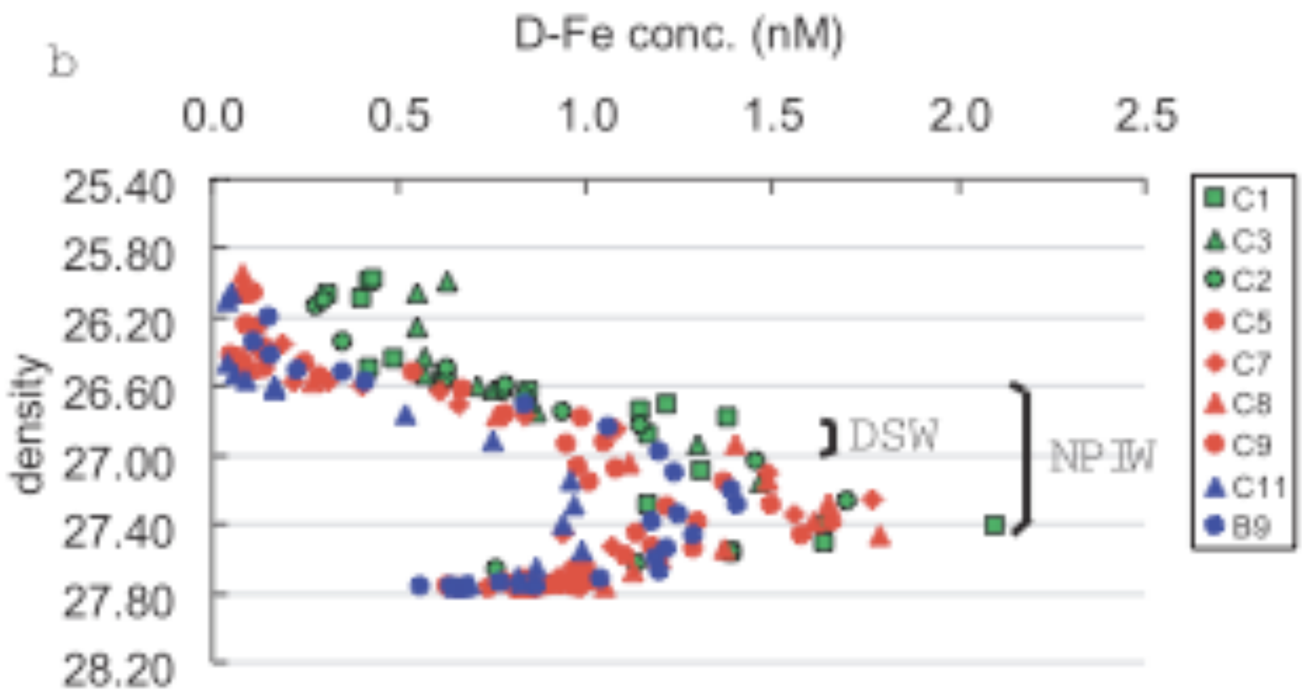
Fe input from continental shelves at the ocean margins: British Columbia (eastern subarctic north Pacific)



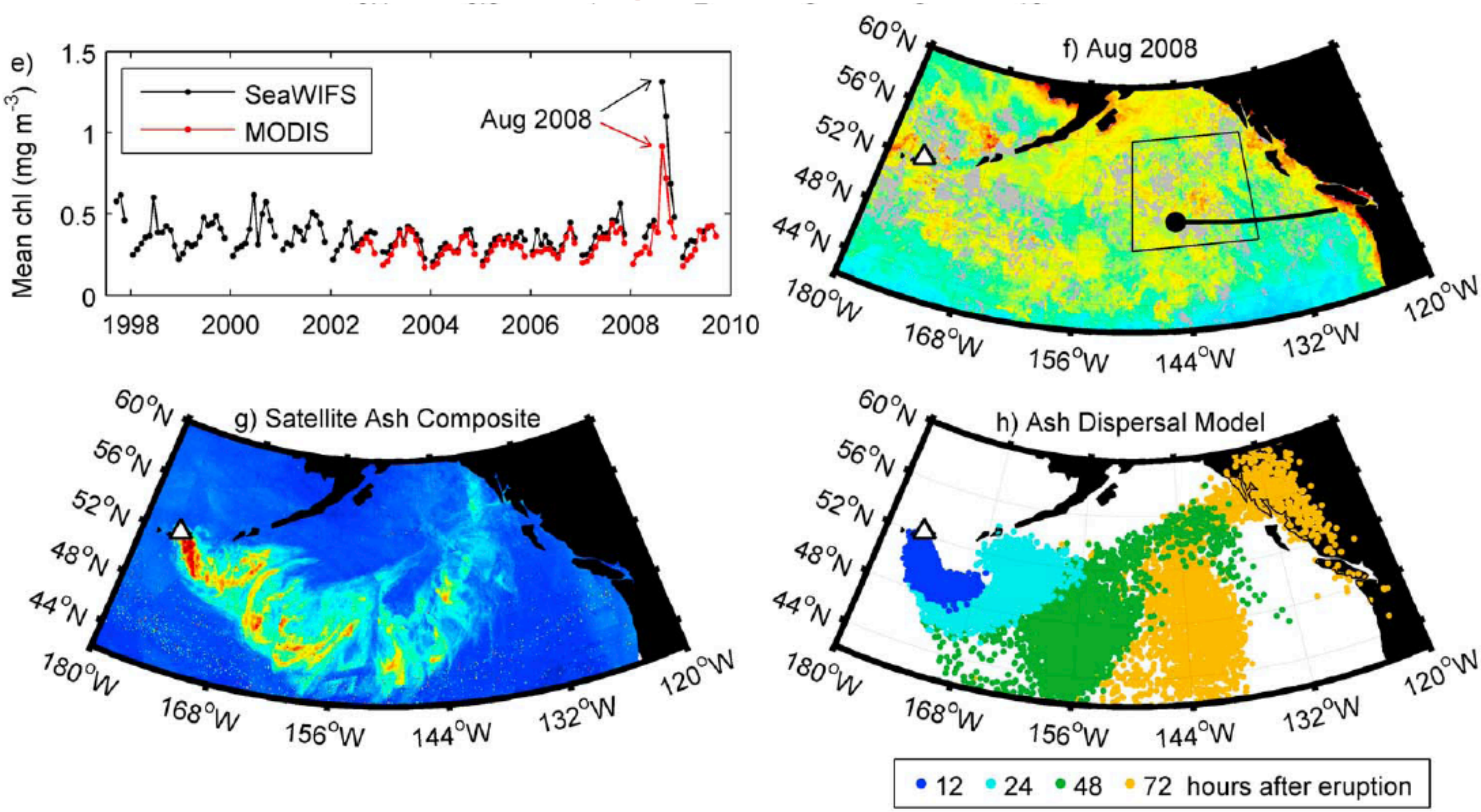
Cullen et al. 2006 *GBC*

Fe input from continental shelves at the ocean margins: Sea of Okhotsk (western subarctic north Pacific)



Nishioka et al. 2007 JGR

Aeolian deposition of Aerosols Fuel Bloom Events: Kasatochi Volcano August 2008



Hamme et al. 2010 *GRL*

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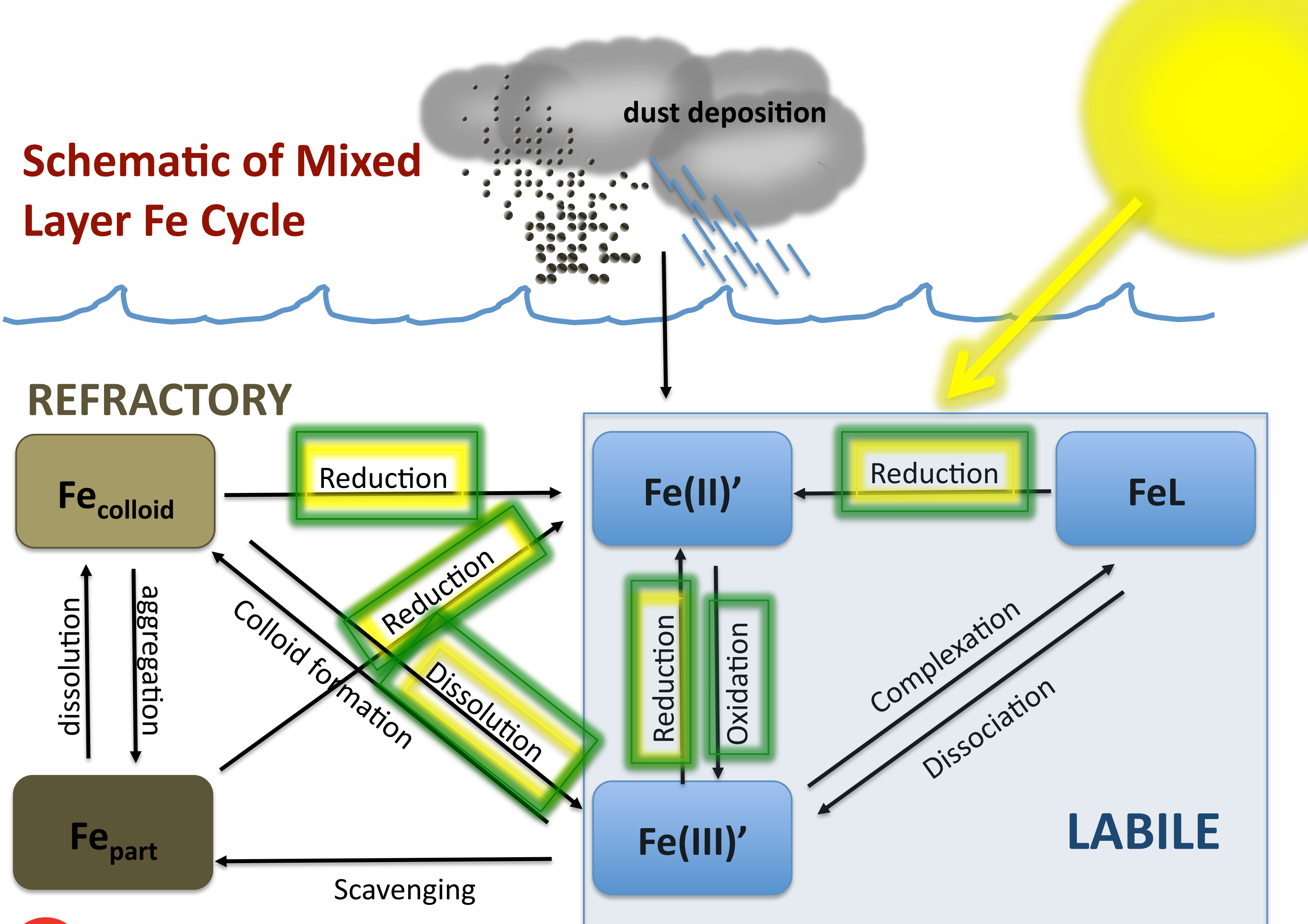
Schematic of Mixed Layer Fe Cycle



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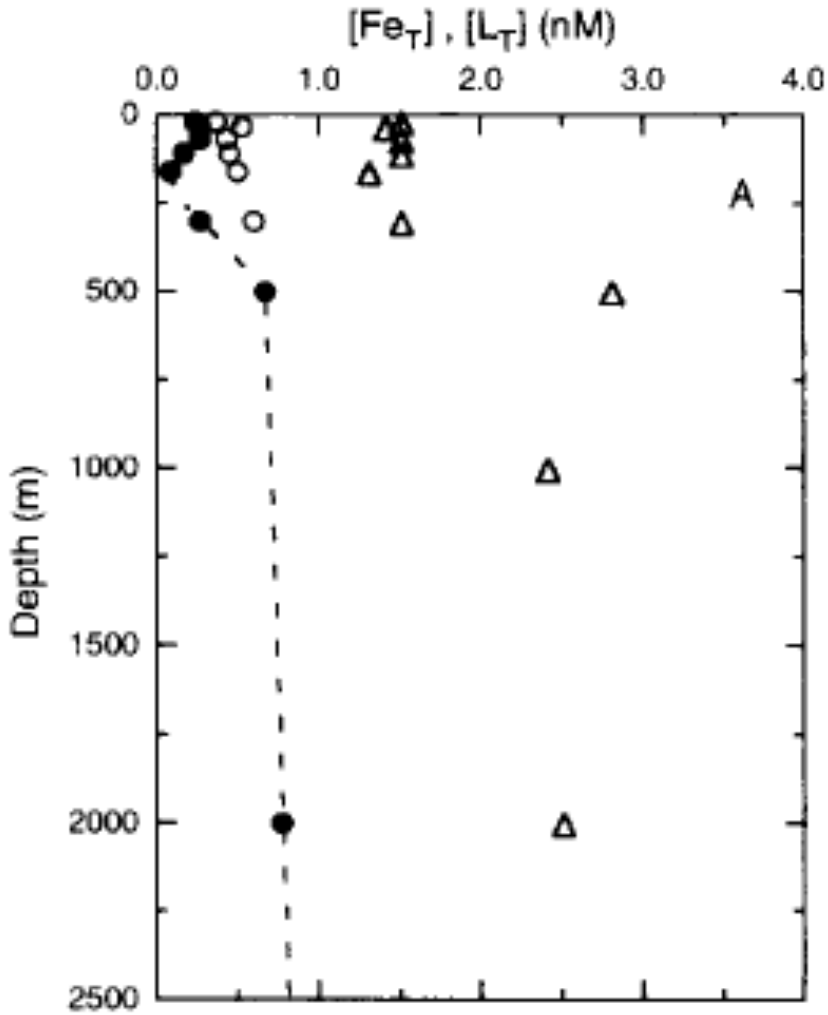
Processes affecting lability

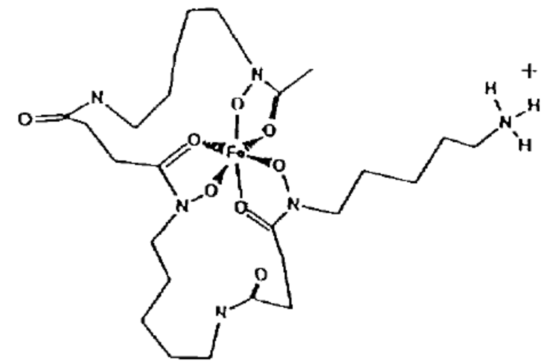
Mechanisms to convert refractory phases to labile Fe in oceanic surface waters:

1) **Ligand complexation**
2) Photochemical reduction
3) Grazing induced remobilization

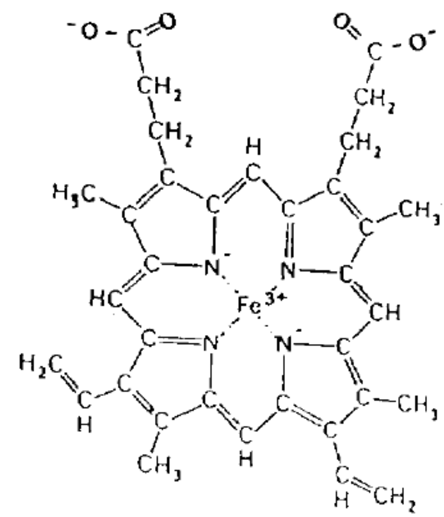
Speciation and Organic Complexation:



Rue and Bruland 1995 *Marine Chemistry*



Fe-Desferal®



Fe-protoporphyrin

Processes affecting lability

Mechanisms to convert refractory phases to labile Fe in oceanic surface waters:

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2) **Photochemical reduction**
3) Grazing induced remobilization

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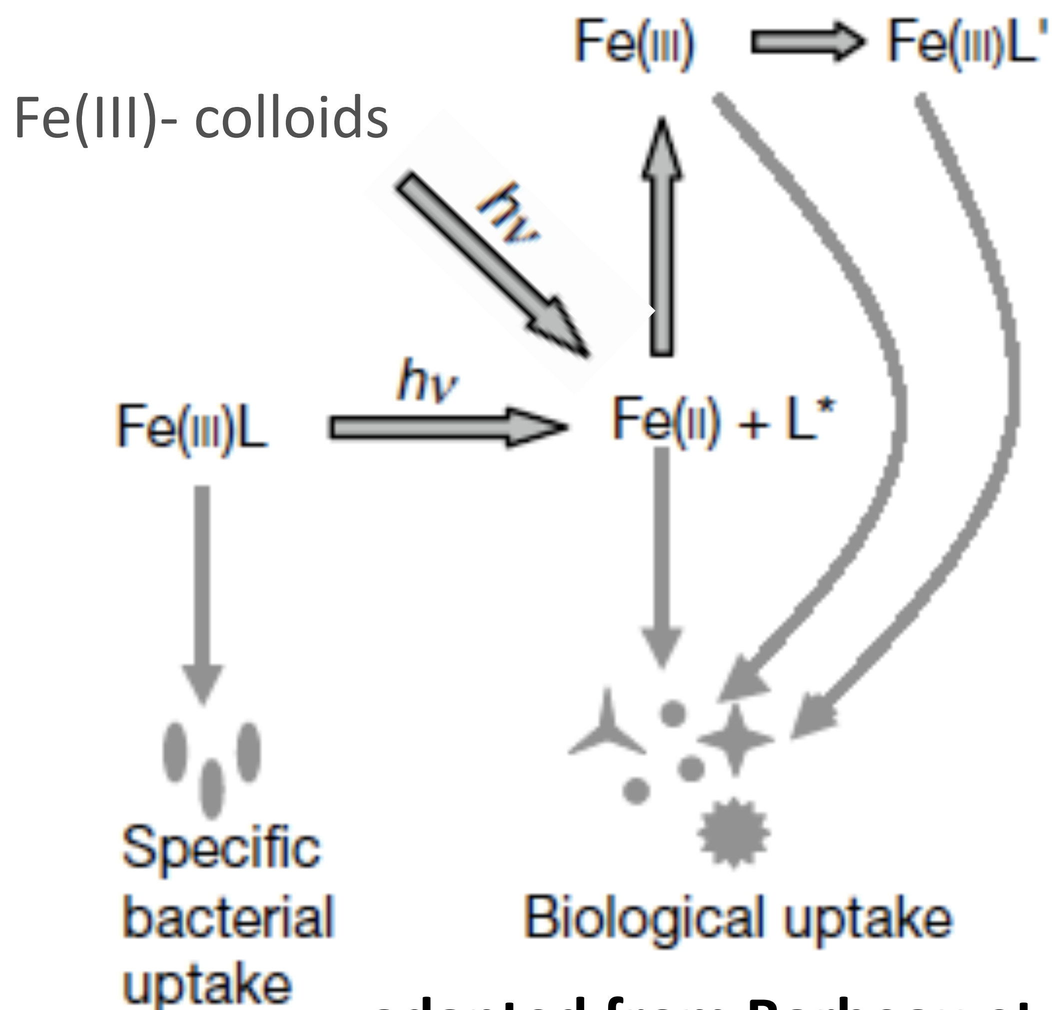
Photochemical reduction of Fe colloids and FeL (Wells, Barbeau…)



adapted from Barbeau et al. 2001 *Nature*

Processes affecting lability

Mechanisms to convert refractory phases to labile Fe in oceanic surface waters:

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3) **Grazing induced remobilization**

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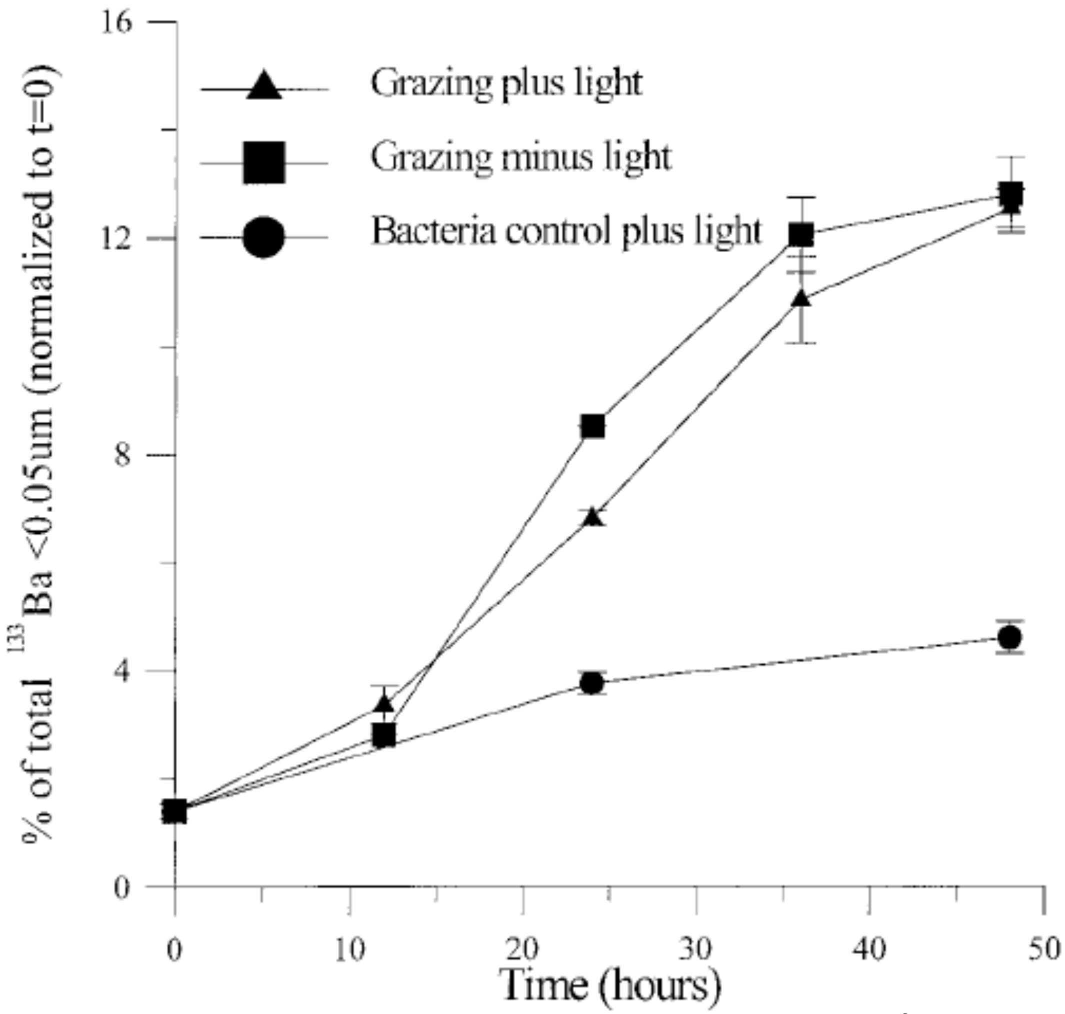
Protozoan grazing solubilizes colloidal Fe



Cafeteria spp.

D. Patterson

Barbeau and Moffett 2000 *Limnol. Oceanogr.*

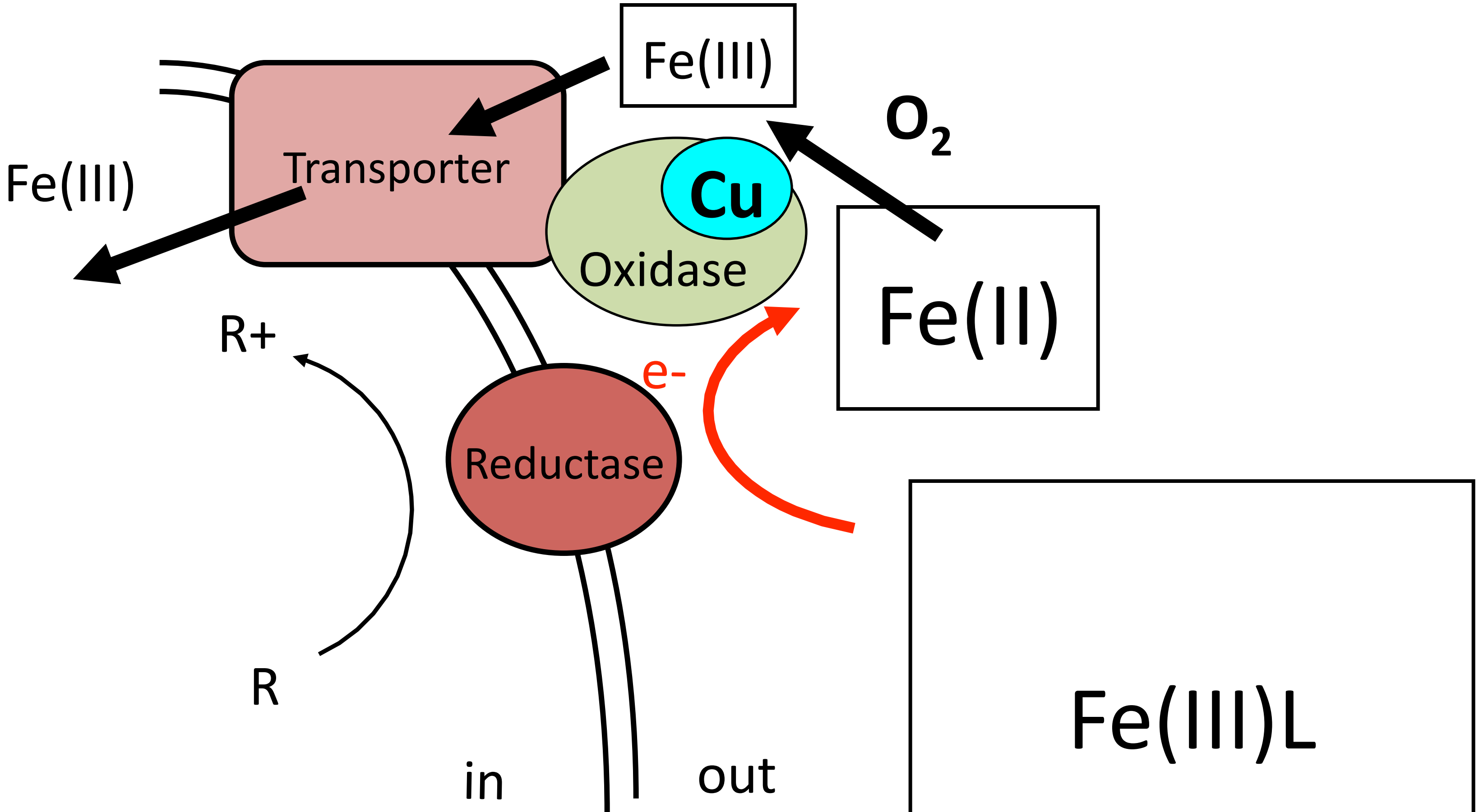
Response of Eukaryotic Phytoplankton to Fe-limitation

1. Up regulation of high affinity Fe transport systems (Multi Cu Ferroxidases, NRAMPs)

2. Production of Fe binding ligands

3. Exudation of dissolved organic matter

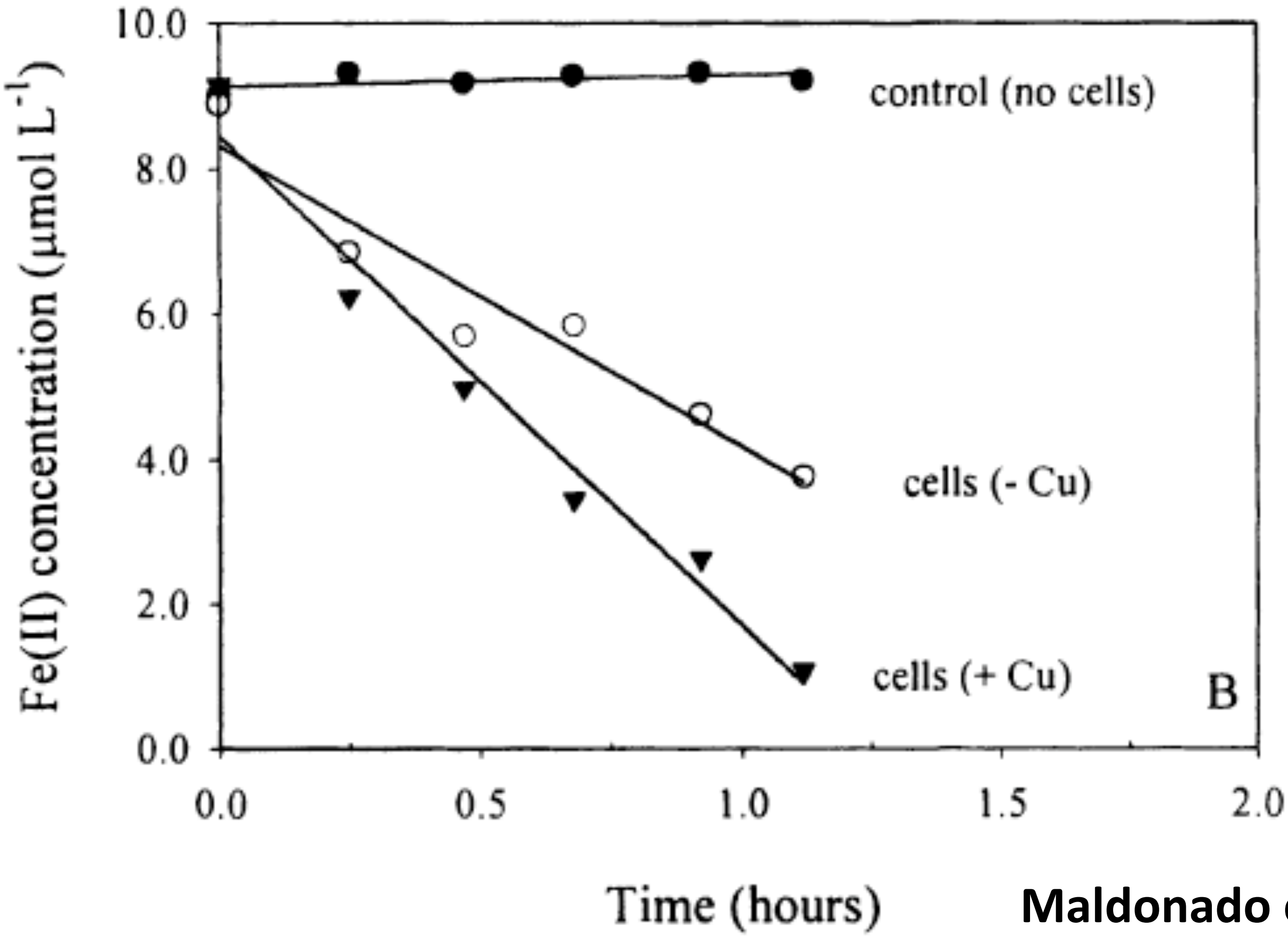
Example: Cu Dependent mechanism of Fe acquisition by ***Fe-limited*** marine diatoms



$4Fe^{2+} + 4H^{+} + O_2 = 4Fe^{3+} + \mathbf{H_2O_2}$

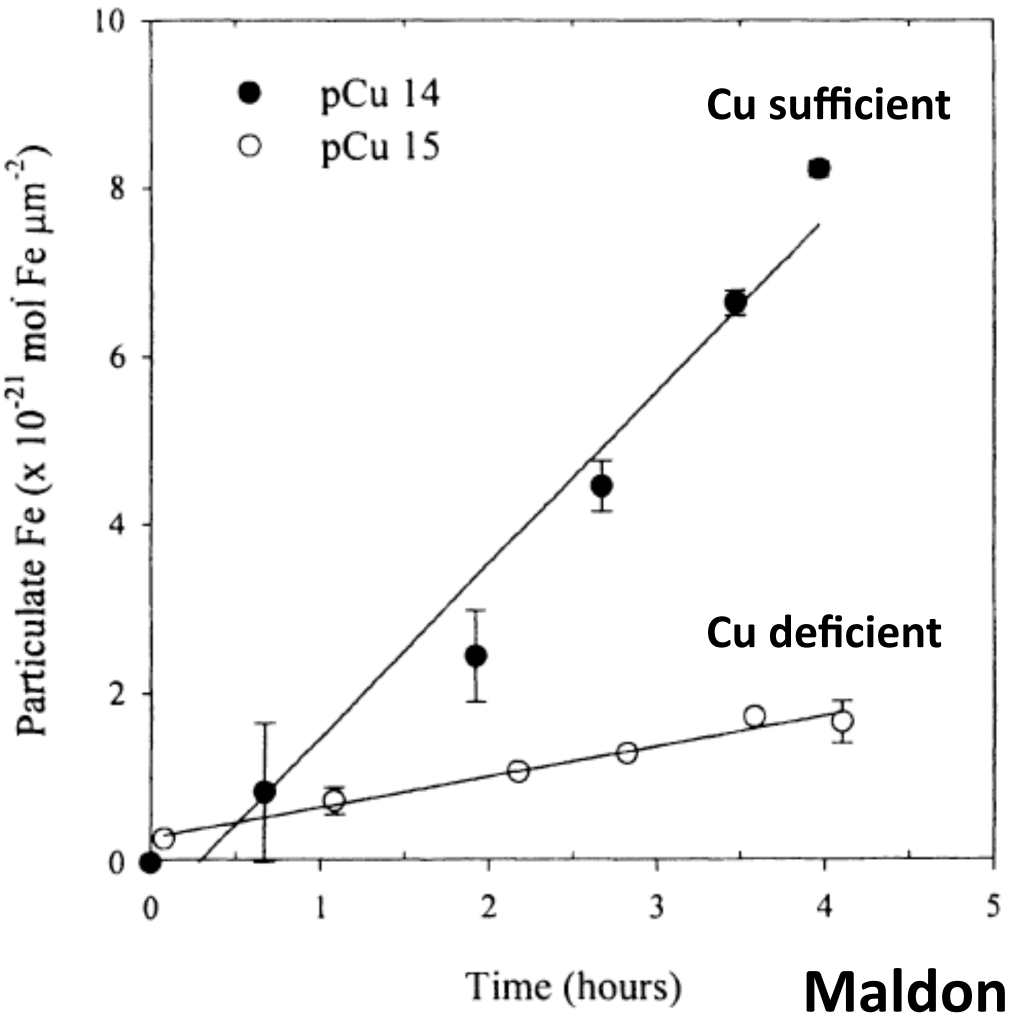
$4Fe^{2+} + O_2 + 4H^{+} = 4Fe^{3+} + \mathbf{2H_2O}$

Cu additions enhance Fe(II) oxidation rates in Fe-Cu limited diatoms



Maldonado et al. 2006 *LO*

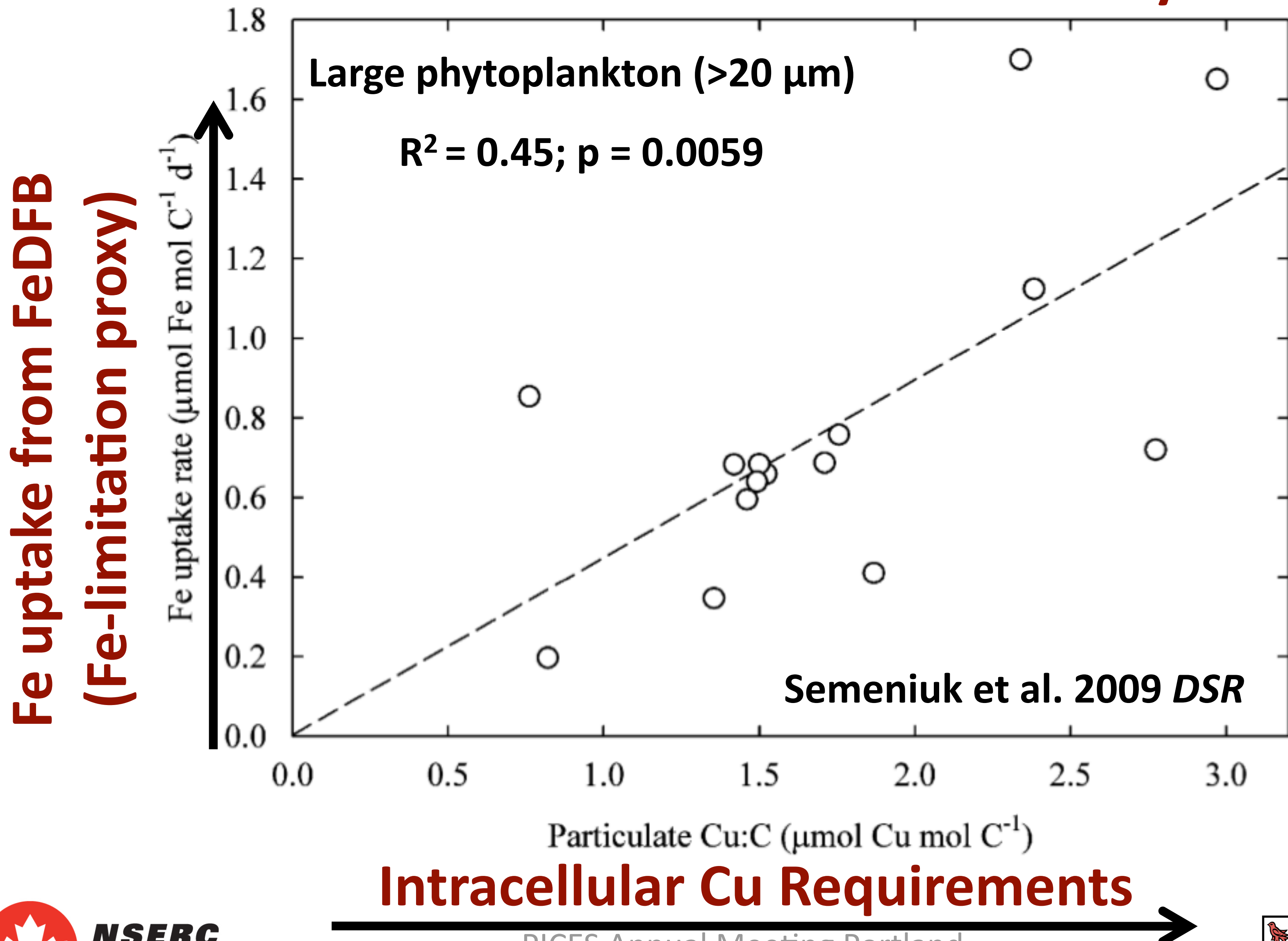
Effect of Cu limitation on Fe transport by Fe-limited *T. oceanica*



Maldonado et al. 2006 *LO*

NE subarctic Pacific: Coastal-HNLC Transect

Intracellular Cu vs. HAFeTS Activity



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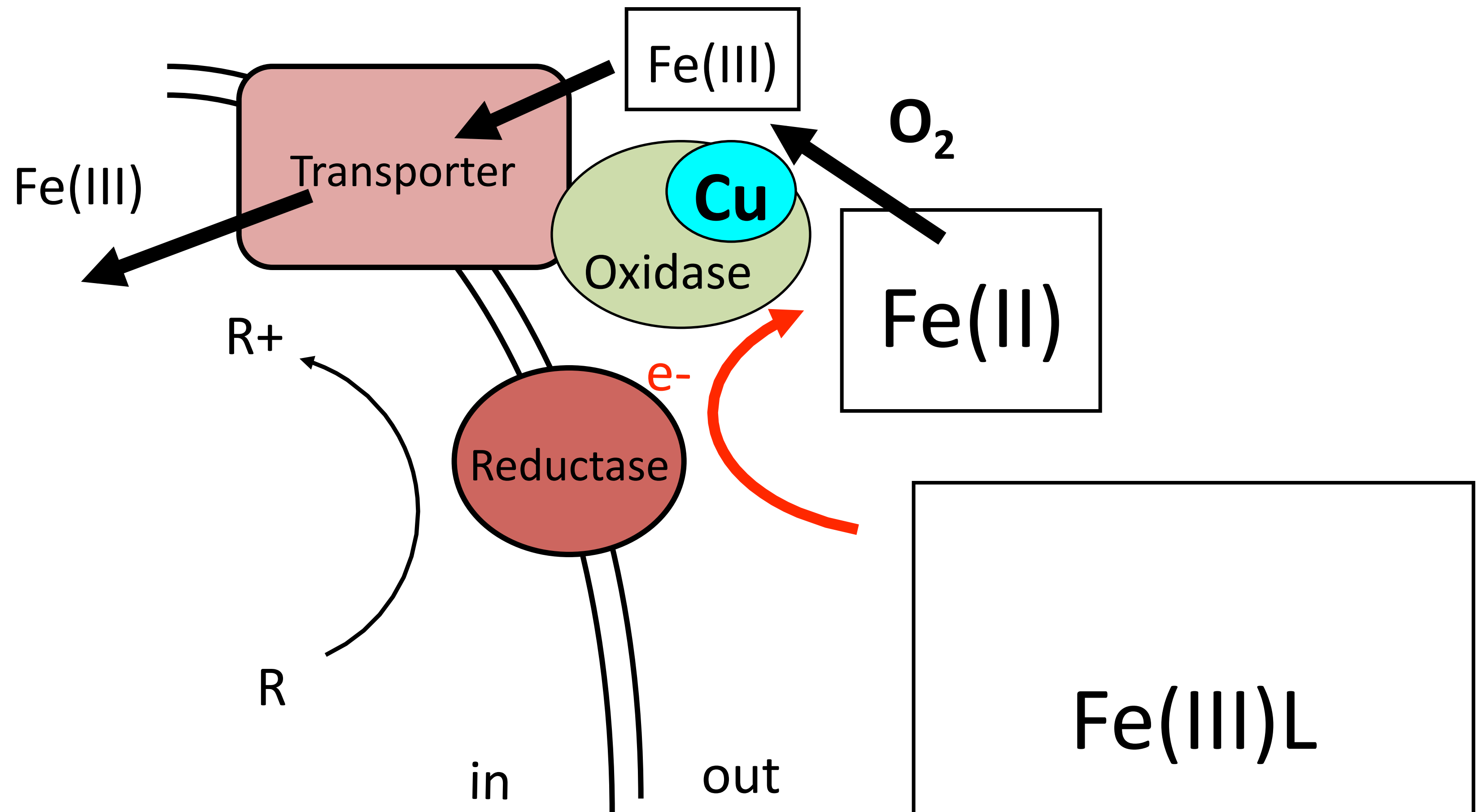
Mechanism of Fe acquisition by *Fe-limited* marine diatoms



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Potential for synergistic interactions that impact bioavailability

- **Diatoms, high-affinity Fe transport system:**
  - Induced when [Fe] is limiting and organic complexation is high
  - Consists of cell surface ferric **reductases** and **ferroxidase**/ferric **permease** complexes

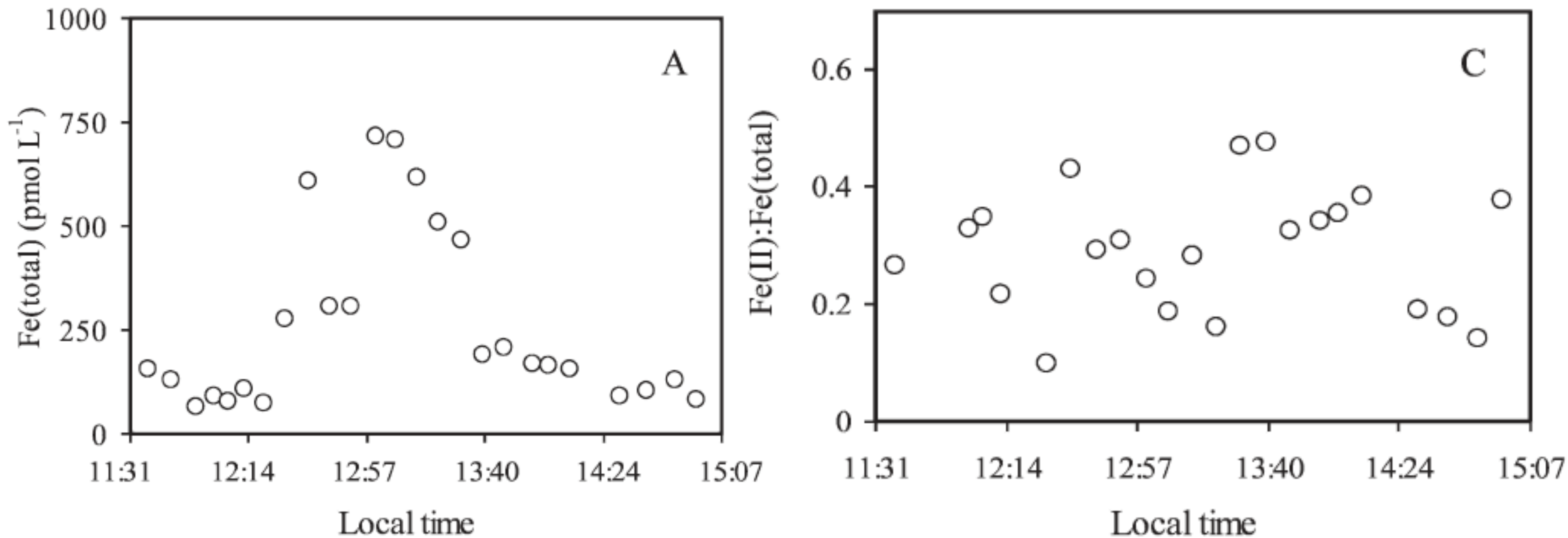
- **Role of Cu in Fe acquisition by** Fe-limited phytoplankton: **multi-Cu-containing ferroxidases** (Peers and Price 2005, Wells et al. 2005, Maldonado et al. 2006)

- **Cu nutrition** seems to be **essential** for phytoplankton in **low Fe regions**

Questions Going Forward Related to Fe Bioavailability

- What controls the fate of Fe(II) in the mixed layer? We must constrain:
  - The degree of organic complexation
  - Oxidation kinetics and interactions with reactive oxygen species (H_2O_2 and O_2^-)
  - Biological uptake rates

Fe(II) Persistence in Surface Waters: SEEDS Experiment (WSNP)



Roy et al. 2008 *Limnol. Oceanogr.*

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Questions Going Forward Related to Fe Bioavailability

- Can we develop a systematic understanding of the controls on aerosol solubility?

- How will changes in mixed layer stratification and the carbonate system (ocean acidification) affect Fe bioavailability?