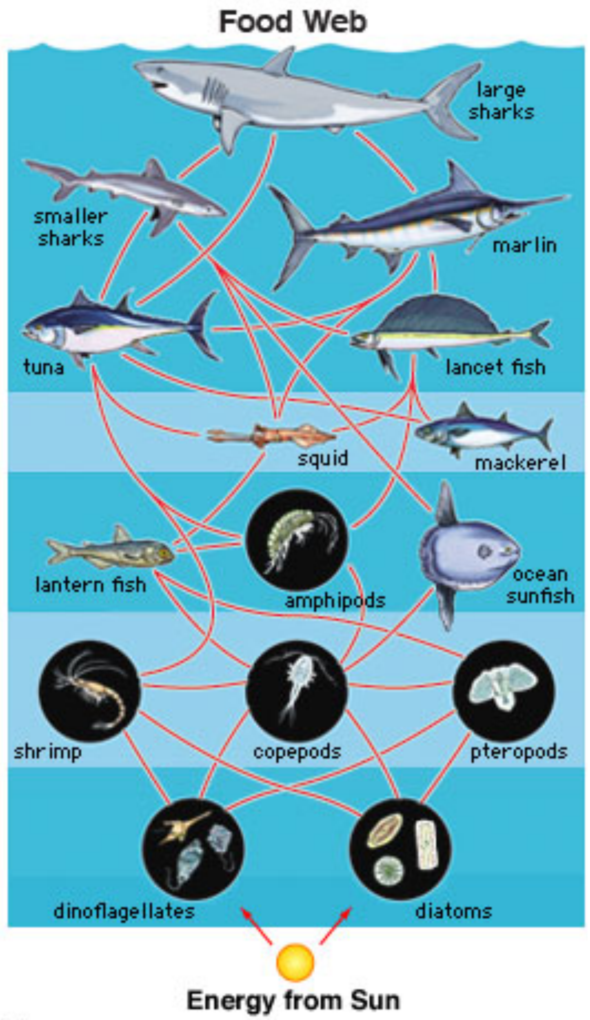
Cu Fe Zn Cd Mn Fe Co Mn Fe Mo Ni Cu Fe



Fe Ni Co Zn Cd

GEOTRACES
An International Study of the Marine Biogeochemical Cycles of Trace Elements and their Isotopes

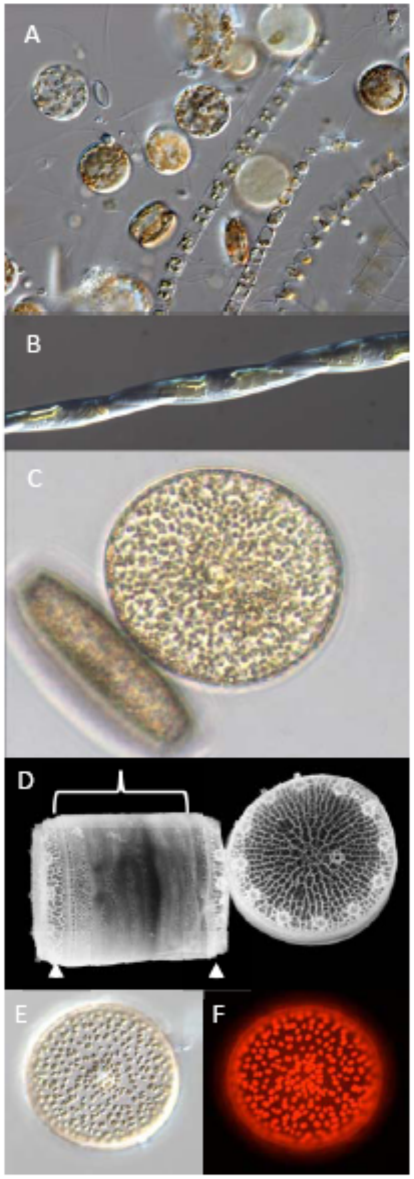
OCB
Ocean Carbon & Biogeochemistry

Biogeochemical cycling of trace metals in the sea

Maite Maldonado
Earth, Ocean & Atmospheric Sciences
Univ. of British Columbia
Vancouver, Canada

UBC

Talk Outline



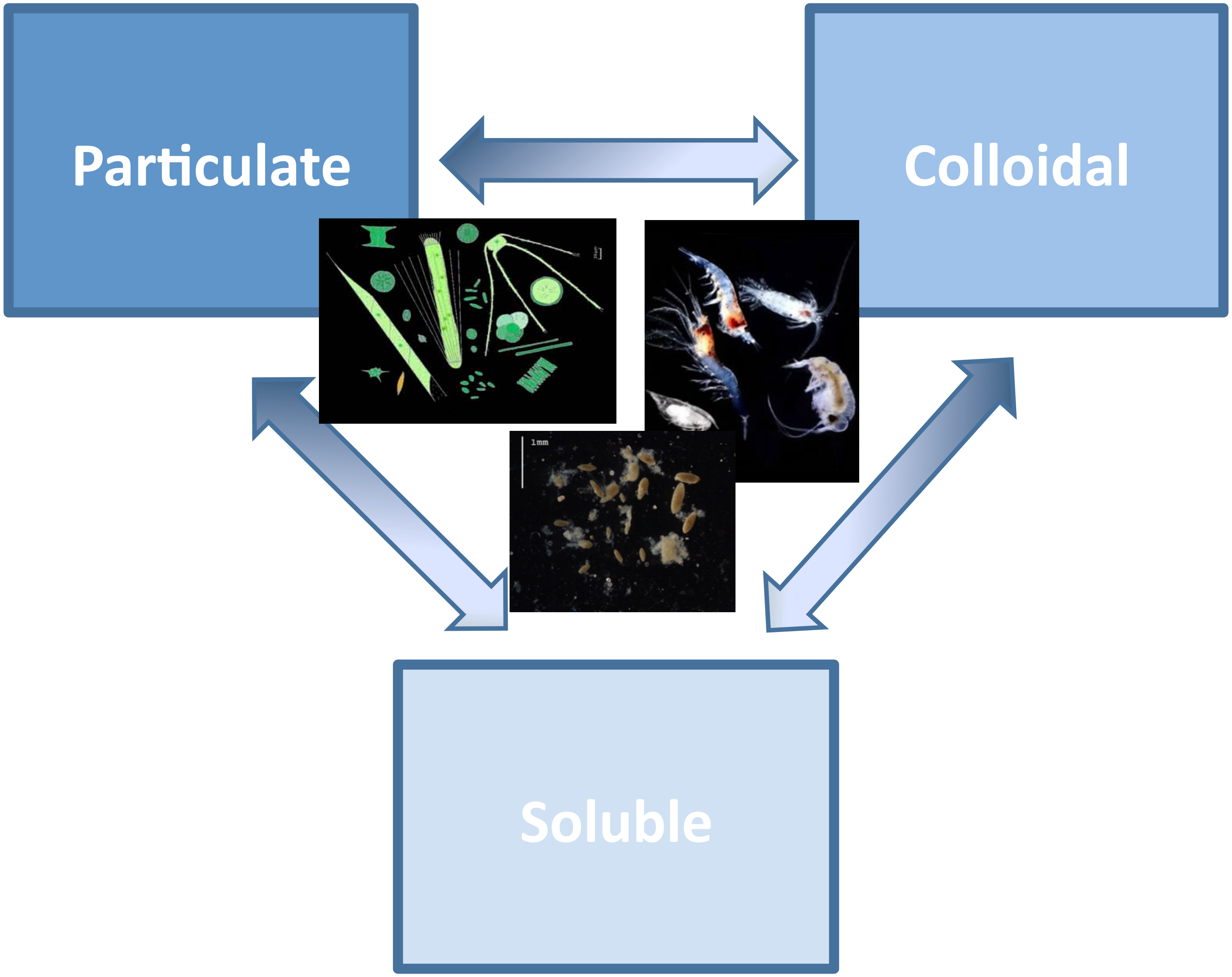
Armbrust (2009)

1. **Modeling biota-trace metals interactions**

2. **An ecosystem model of biological Fe cycling**

3. **Highlighting recent findings, changing paradigms in the biogeochemical cycling of trace metals**

Interactions between M and biota

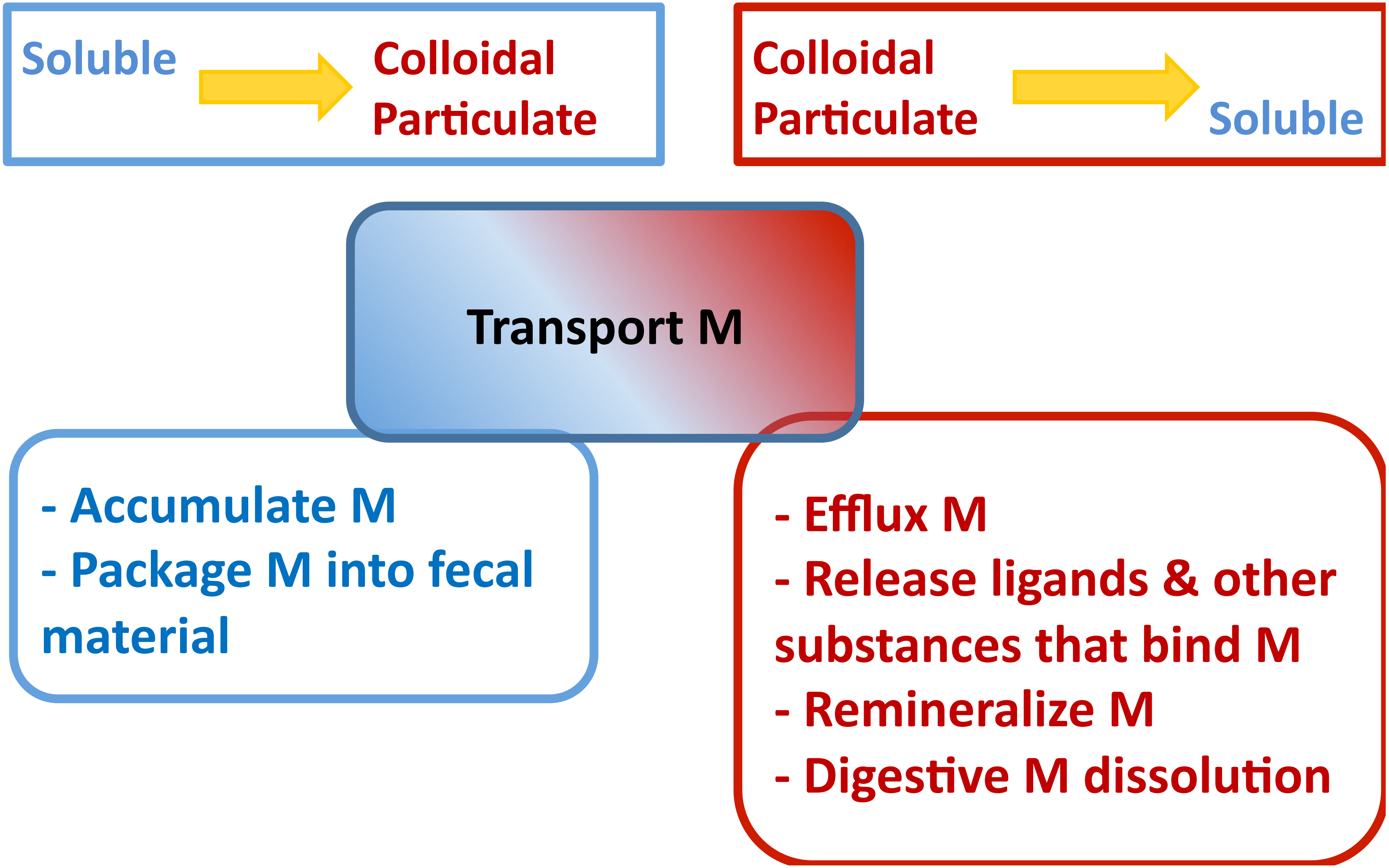


Particulate

Colloidal

Soluble

Biological mechanisms mediating M transfer among pools



Soluble → Colloidal Particulate

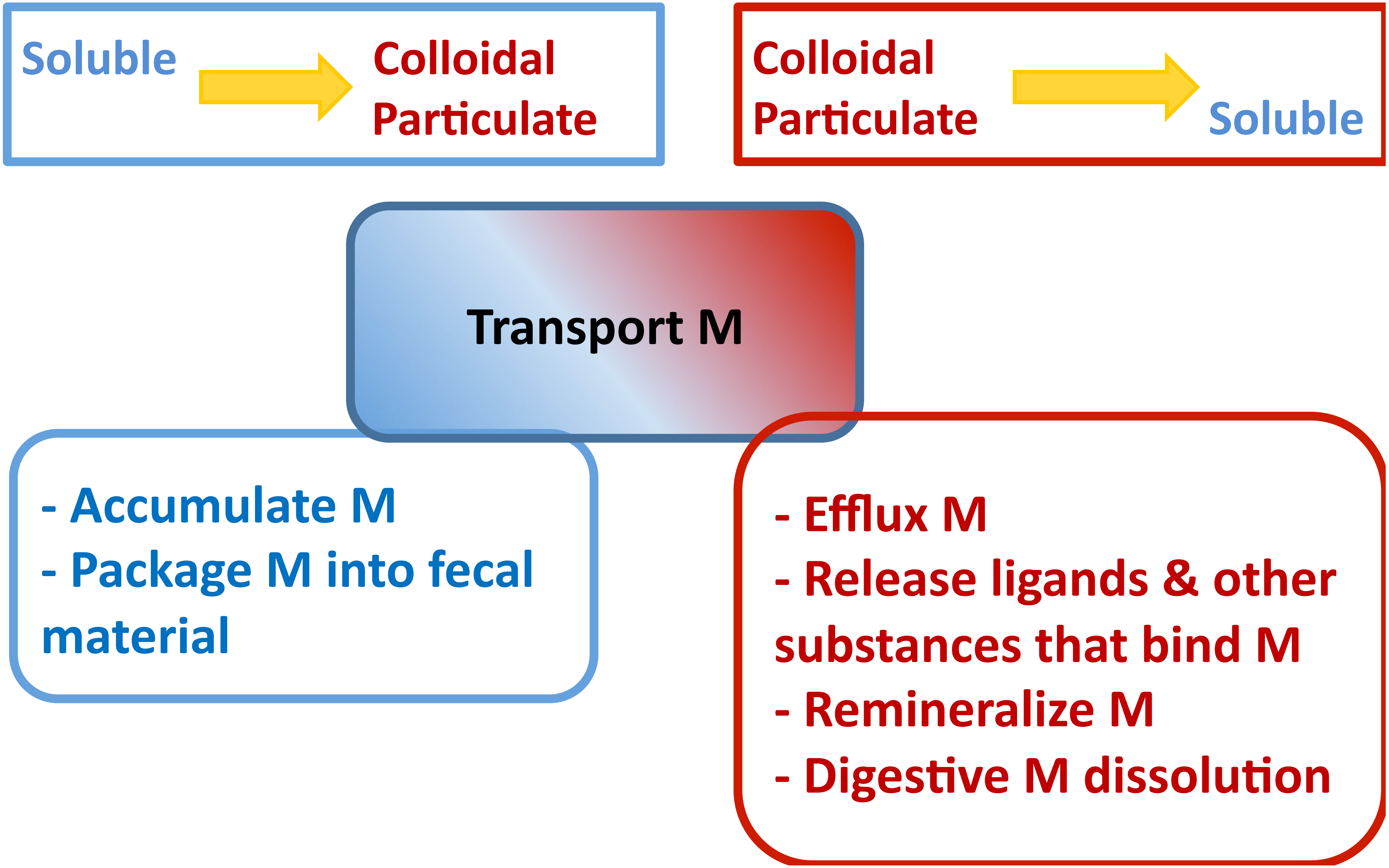
Colloidal Particulate → Soluble

Transport M

- Accumulate M
- Package M into fecal material

- Efflux M
- Release ligands & other substances that bind M
- Remineralize M
- Digestive M dissolution

Biological mechanisms mediating M transfer among pools



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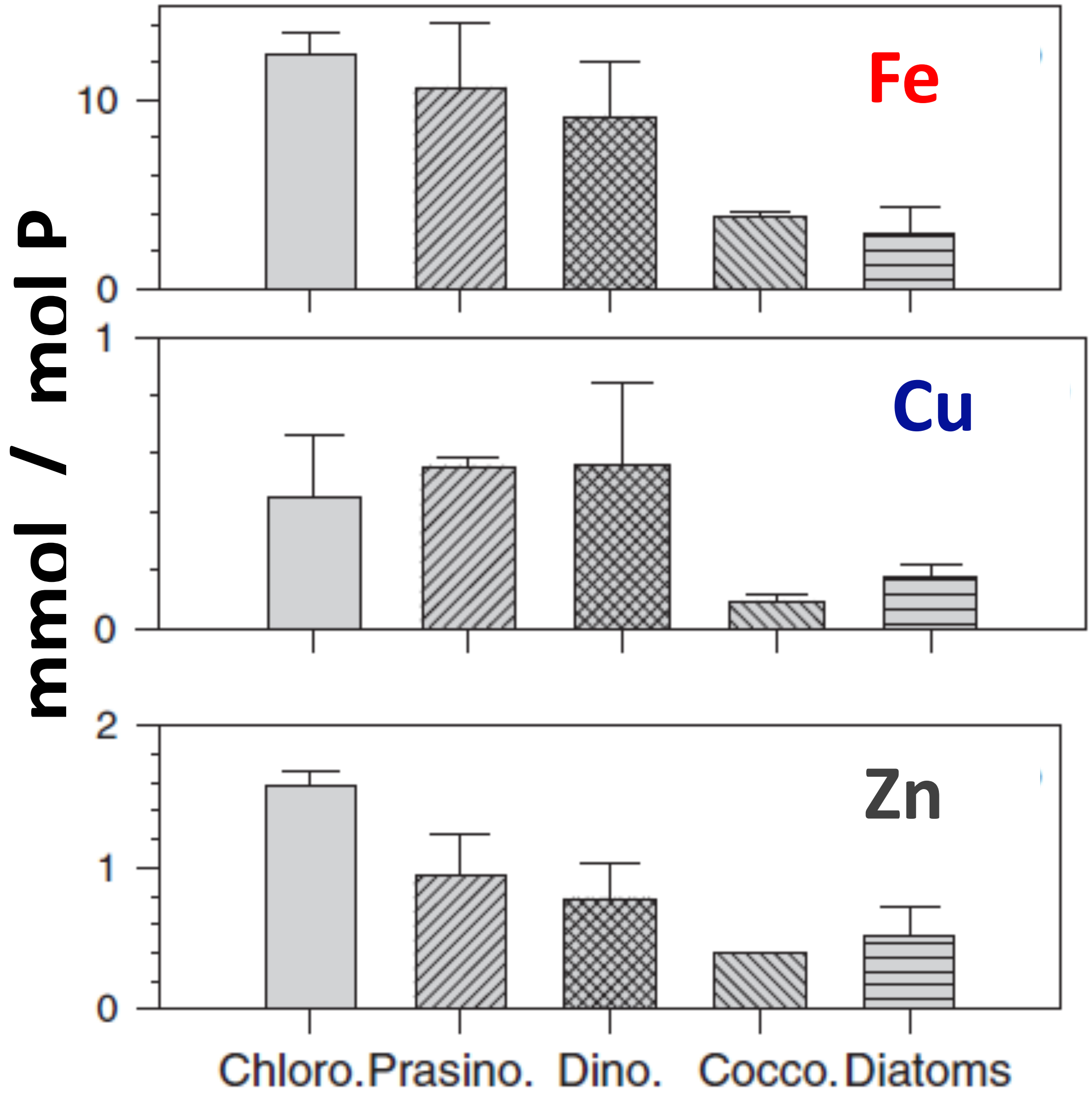
Taxonomic patterns of phytoplankton metal stoichiometry



Ho et al. 2003

Taxonomic variations: ~20 fold

Geographic provenance (coastal vs. oceanic): ~4 fold

Environmental conditions (light, nuts, [M]): up to 20 fold

Ferritin (Marchetti et al. 2009); Day/night Fe homeostasis (Botebol et al. 2015)

Models: functional groups √ good (specially if quotas can be tweaked for in situ conditions)

Sunda et al 1991, Finkel et al. 2006, Twining et al. 2013

What to use to normalize trace metal quotas, using P or C?

- Interactions between M & C cycle: normalize to cellular C

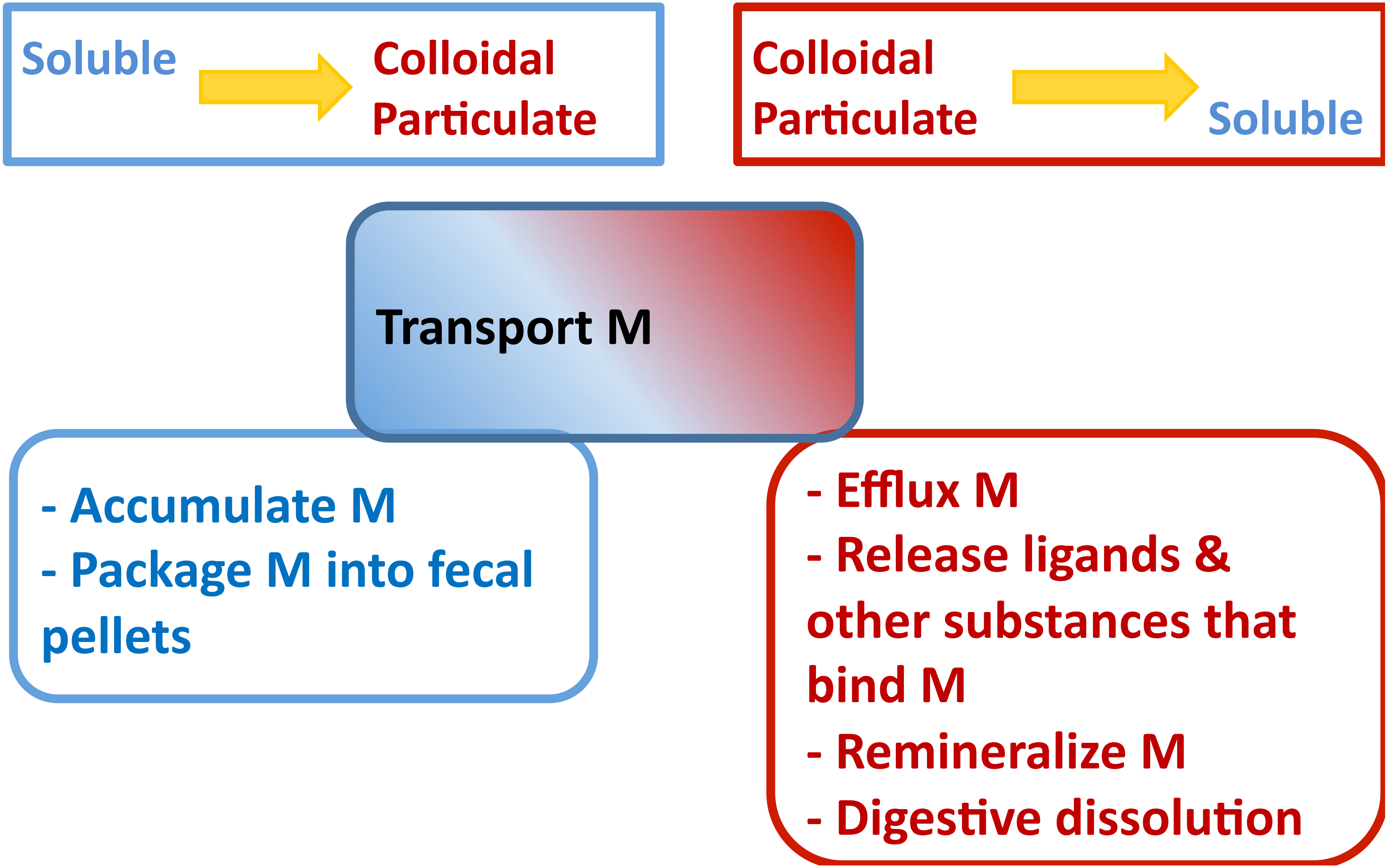
- Geochemists prefer normalizing to P, issues:
  - P content is plastic (Sterner & Elser 2002) & affected by Fe nutrition (Price 2005)
  - P adsorbs to cell surface Fe-oxides (Sãnudo-Wilhelmy et al. 2004; Fu et al. 2005)

Trend: different Cu:P quotas for green vs. red algae disappears if normalized to C

Data from Ho et al. 2003

Species	C:P (mol:mol)	Cu:P (mmol:mol)	Cu:C (µmol:mol)	Mean Cu:P (mmol:mol)	Mean Cu:C (µmol:mol)
Chlorophyceae	198 ± 35	0.45 ± 0.31	2.17 ± 1.19		
Prasinophyceae	200 ± 9	0.55 ± 0.06	2.77 ± 0.2	**0.5**	**2.47**
Dinophyceae	117 ± 31	0.29 ± 0.24	2.26 ± 1.62		
Prymnesiophyceae	70 ± 8	0.09 ± 0.03	1.32 ± 0.56		
Bacillariophyceae	62 ± 22	0.17 ± 0.09	2.8 ± 1.4	**0.18**	**2.13**

Biological mechanisms mediating M transfer among pools



Soluble → Colloidal Particulate

Colloidal Particulate → Soluble

Transport M

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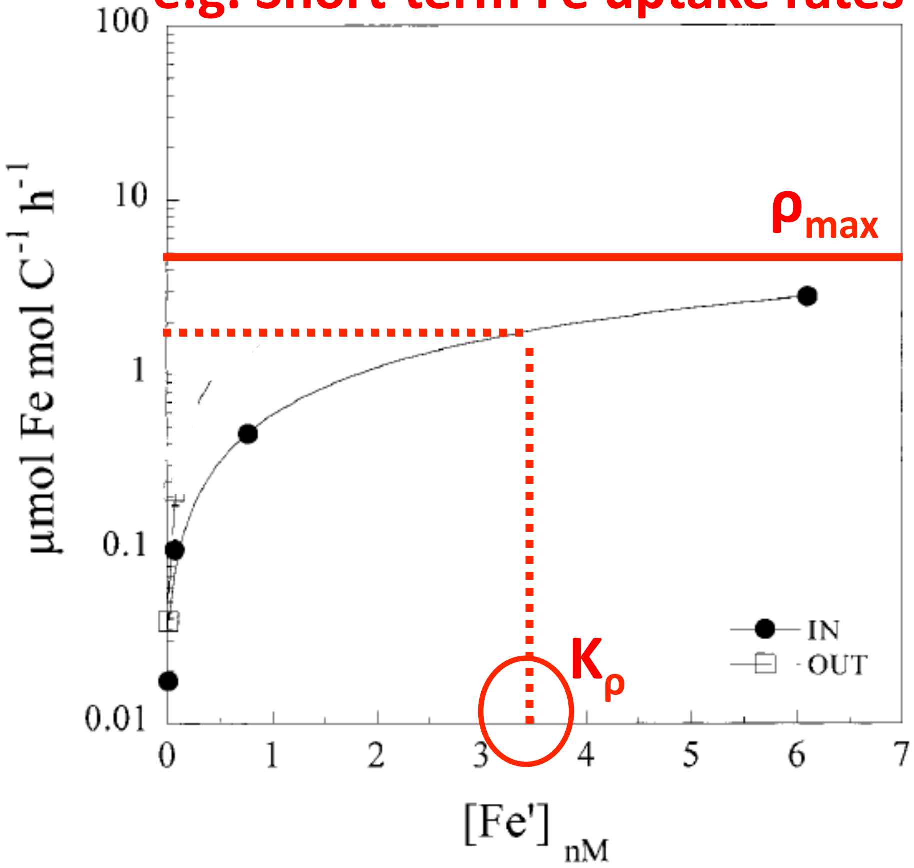
- Remineralize M
- Digestive dissolution

Half-saturation constant for **growth** (K_μ) vs. **short-term Fe uptake** (K_ρ) differ by orders of magnitude

e.g. Short-term Fe uptake rates



[Fe'] nM	K_μ (growth)	K_ρ (short-term uptake)
CULTURE	0.041	3.7
FIELD	~0.002	2.96

reviewed by
Marchetti & Maldonado 2016

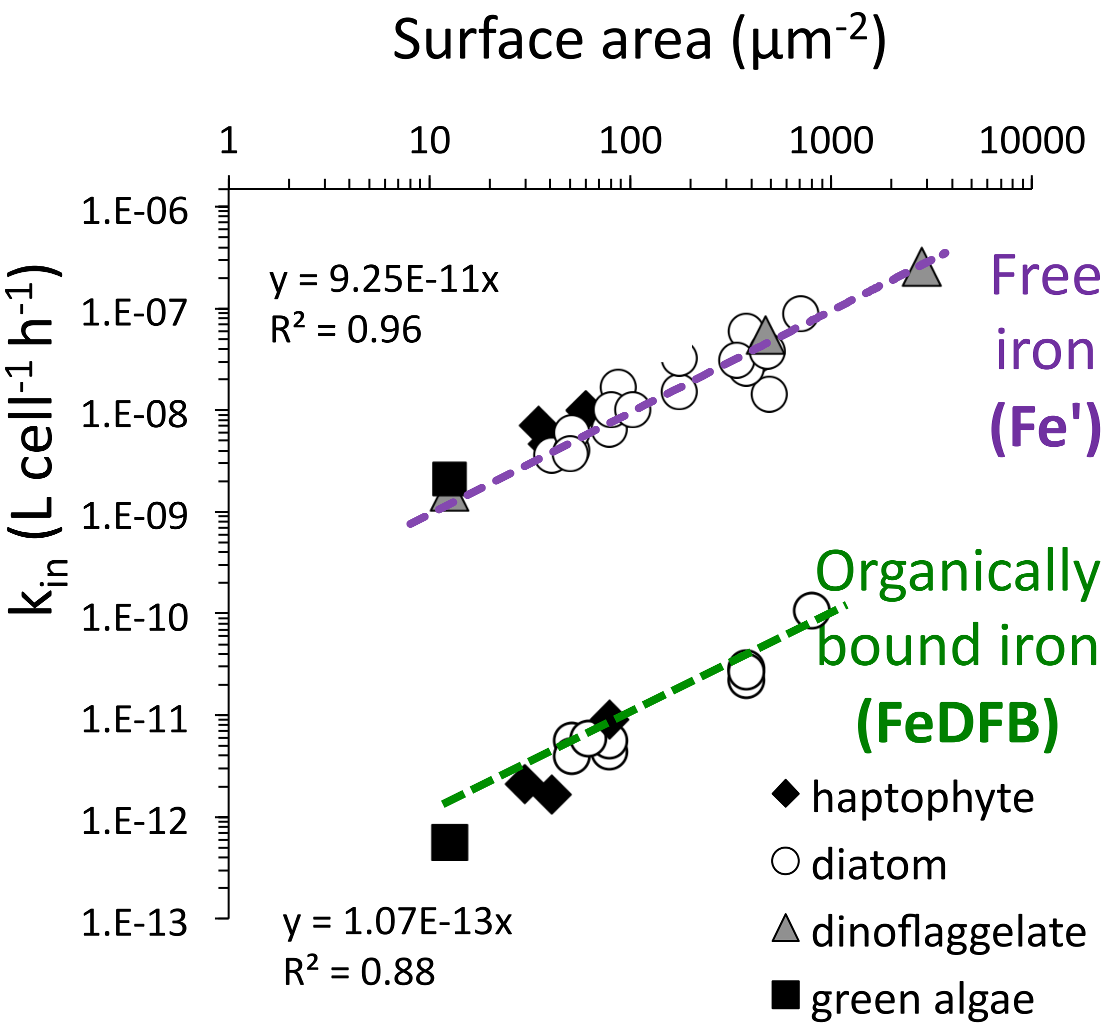
$\rho = \rho_{max} * [Fe]/(K_\rho + [Fe])$ (Michaelis-Menten 1913)
$\mu = \mu_{max} * [Fe] / ([Fe] + K_\mu)$; (Monod 1942)

More K_ρ needed, but challenging
Alternatives?

Maldonado et al. 2001

Alternative approaches to estimate short-term uptake rates
(eg. when Fe concentrations are sub-saturating)

k_{in} = Fe uptake rate constant

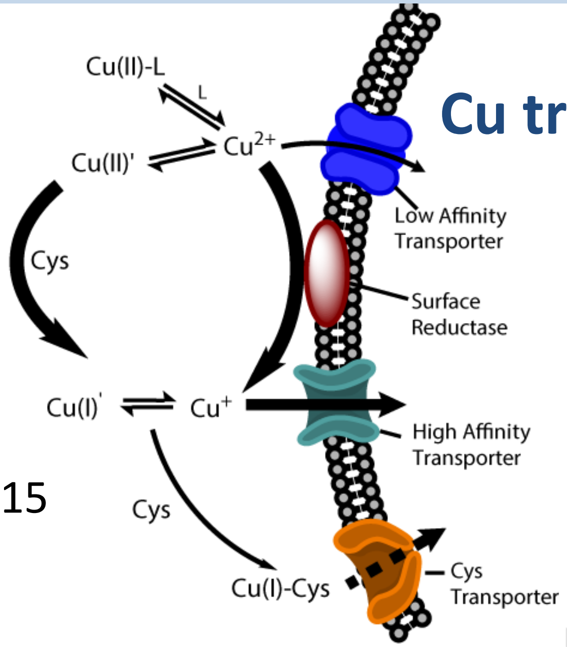


Lis et al. 2015

- If you know phytoplankton functional group
- You can calculate SA & determine k_{in} from graph
- If you know [Fe], calculate $\rho = k_{in} * [Fe]$
- Excellent for modellers √

Organically bound trace metals are bioavailable (Fe, Cu, Zn…)

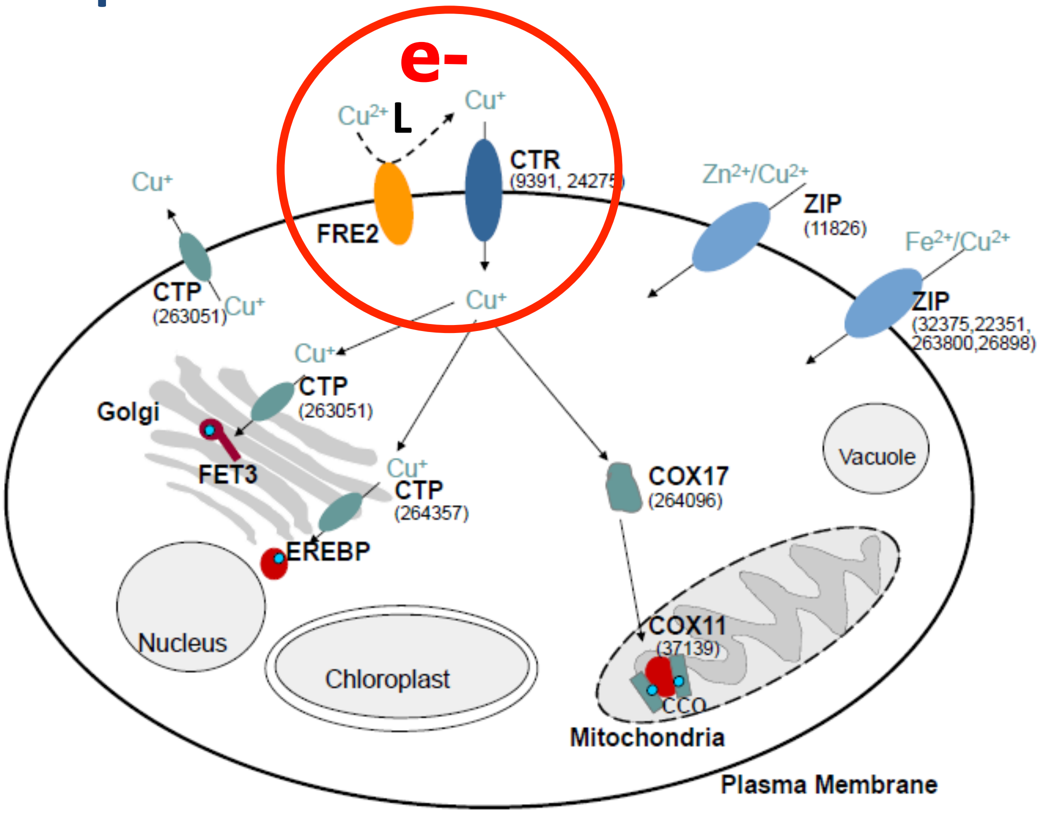
***via* weak L shuttle mechanism**



Walsh et al. 2015

Cu transport from CuL

***via* membrane reductases**



Semeniuk et al. 2009, Guo et al. 2015,
Semeniuk et al. 2015, Walsh et al. 2015

Organically bound trace metals are bioavailable (Fe, Cu, Zn…)

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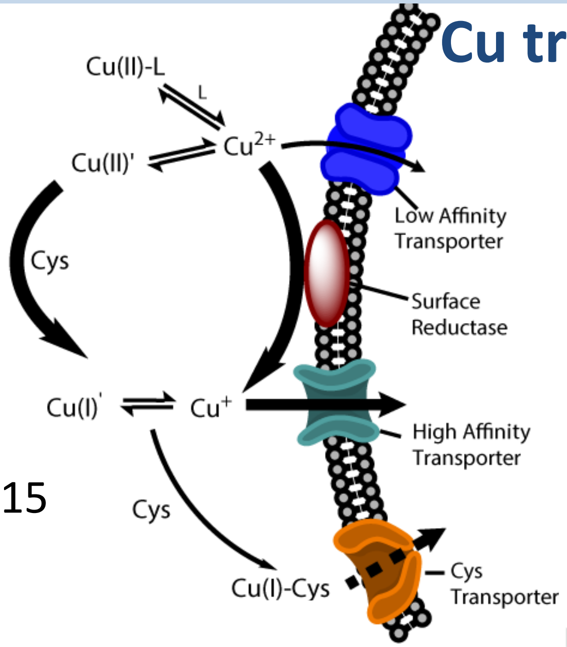
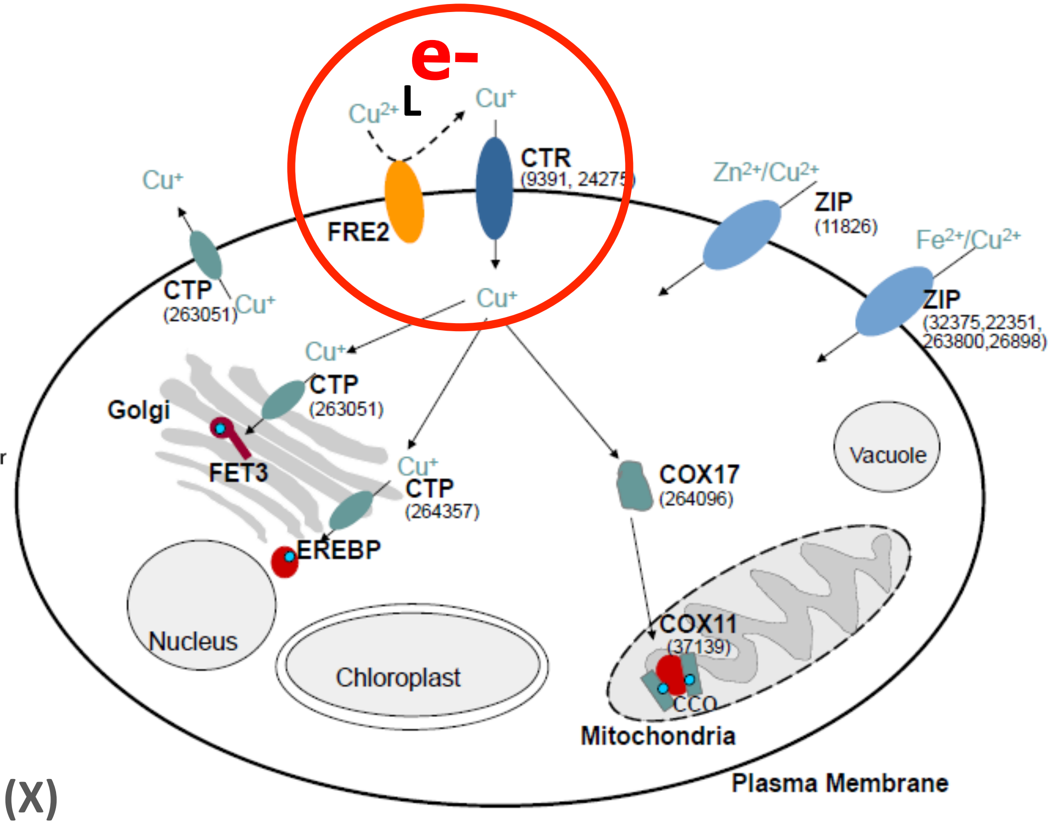


Walsh et al. 2015

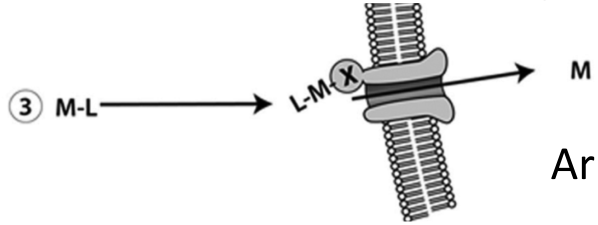
via **membrane reductases**



Semeniuk et al. 2009, Guo et al. 2015, Semeniuk et al. 2015, Walsh et al. 2015

Zn transport

via **ternary complex formation at the cell surface: transporter (X) M-L (ZnL)**



Aristilde et al. 2012

Biological mechanisms mediating M transfer among pools

Soluble → Colloidal
Particulate

Colloidal
Particulate → Soluble

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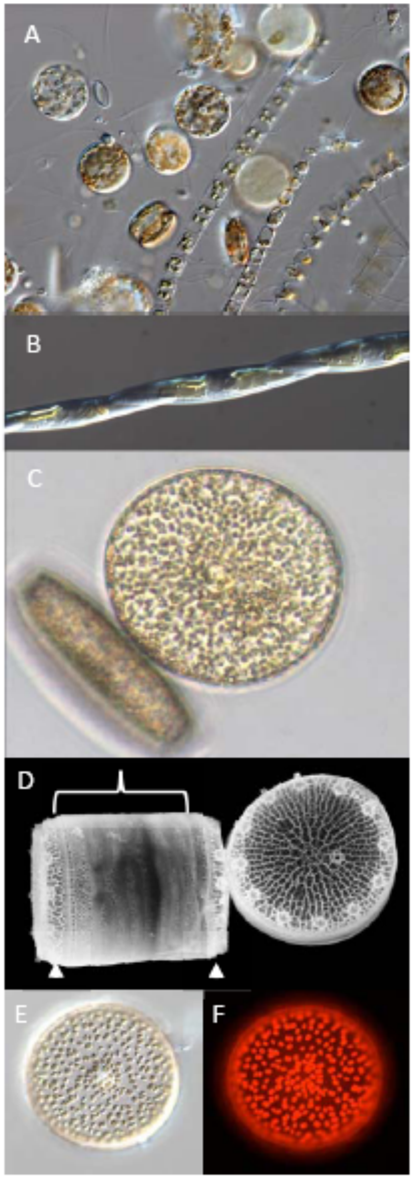
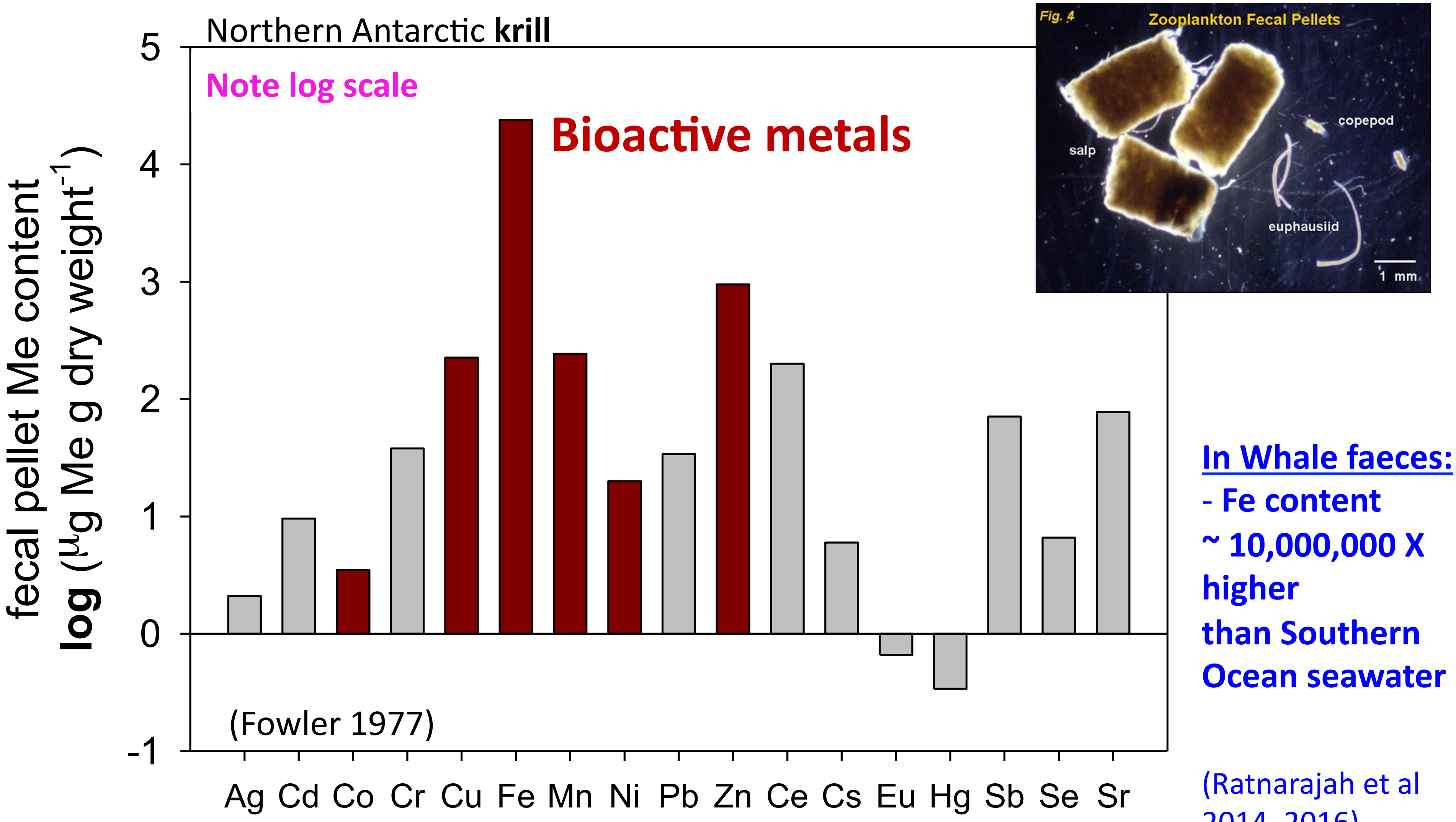
Talk Outline



Armbrust (2009)

1. **Modeling biota-trace metal interactions**
2. **An ecosystem model of biological Fe cycling**
3. **Important recent findings, changing paradigms in biogeochemical cycling of trace elements**

Fecal material enriched in many M, including Fe


Northern Antarctic **krill**

Note log scale

Bioactive metals

(Fowler 1977)

In Whale faeces:

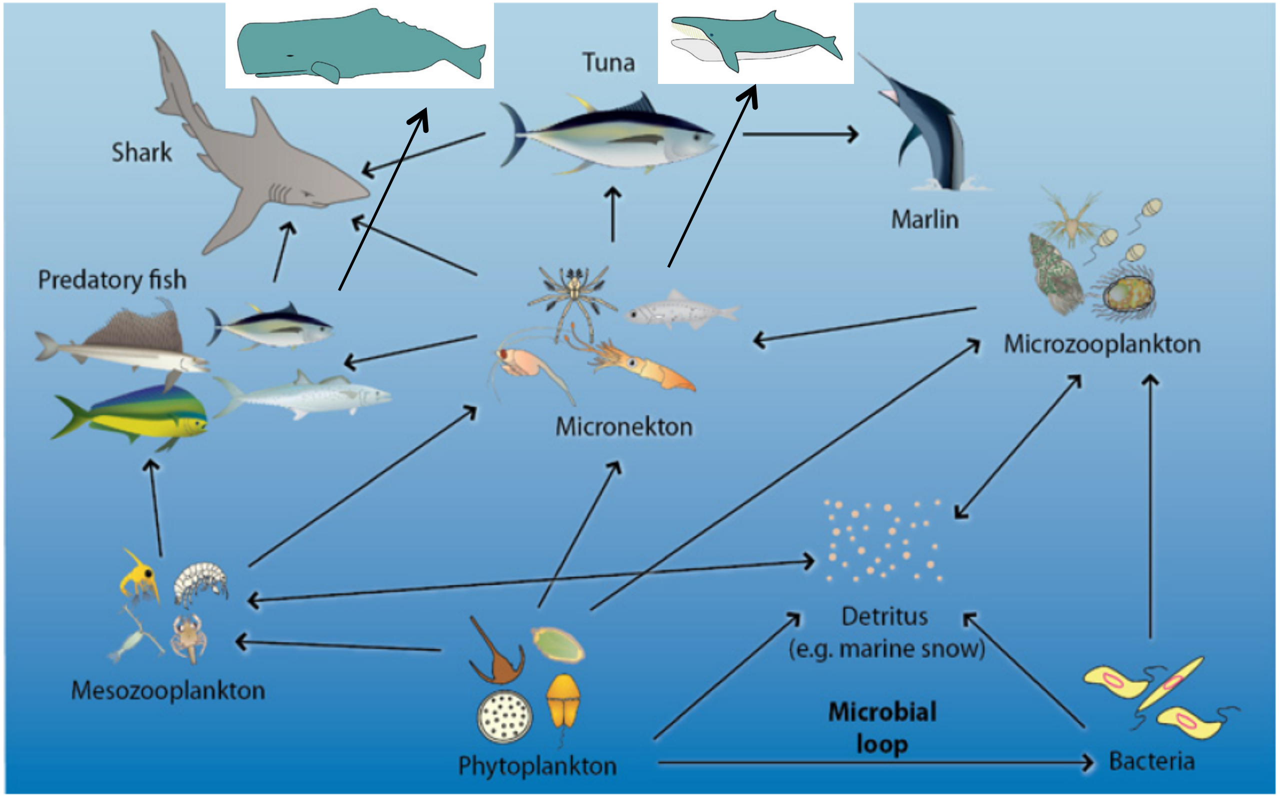
- Fe content ~ 10,000,000 X higher than Southern Ocean seawater

(Ratnarajah et al 2014, 2016)

How important are these fecal Fe sources for phytoplankton growth?

Biological Fe cycling in a realistic food webs (eg. Southern Ocean)

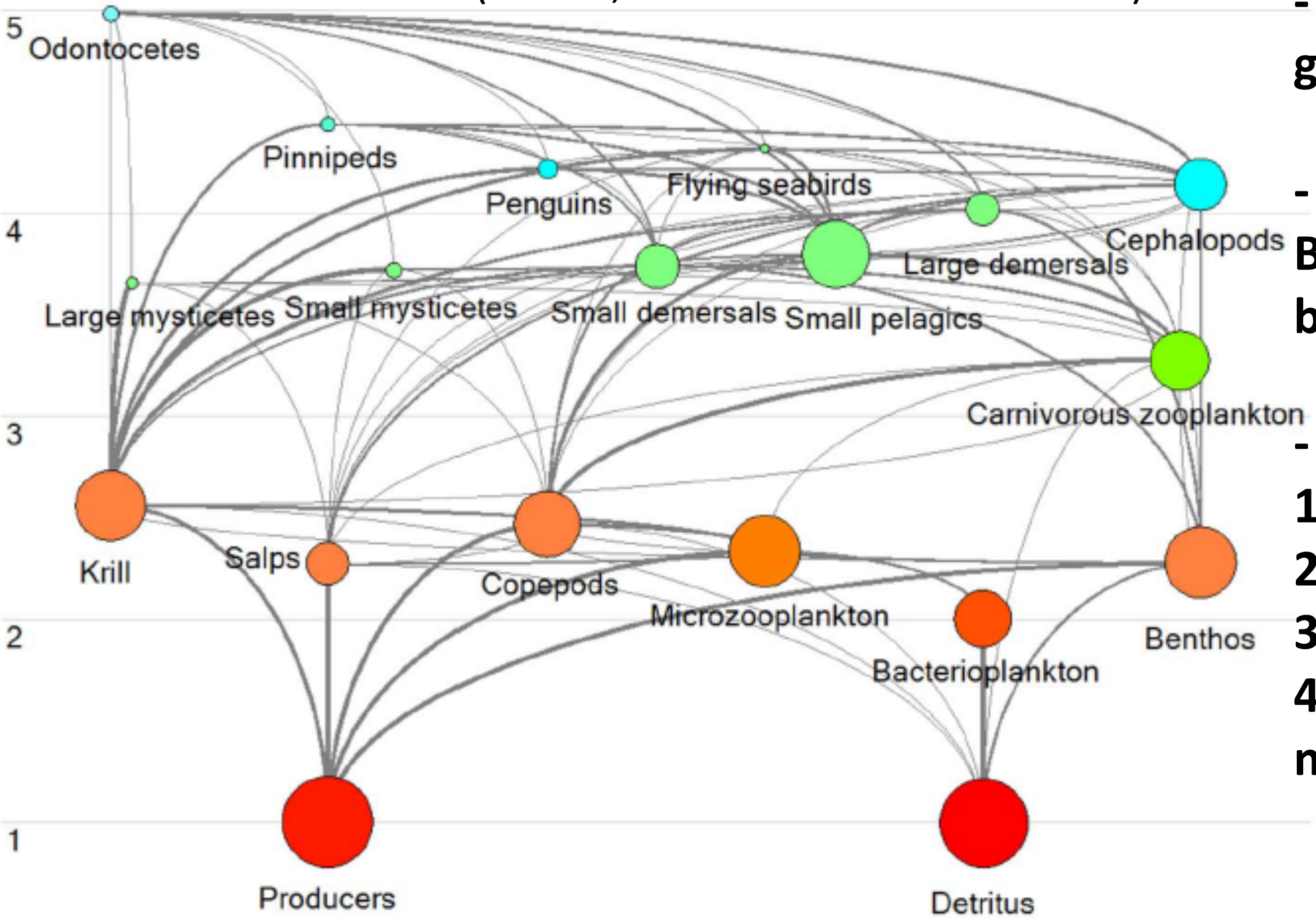
- organisms feeding in multiple trophic levels



A Possible Approach Biological Fe cycling
Mass balance ecosystem models (Ecopath) e.g. Southern Ocean

(Christensen & Walters 2004)

(Surma, Pakhomov & Pitchet 2014)



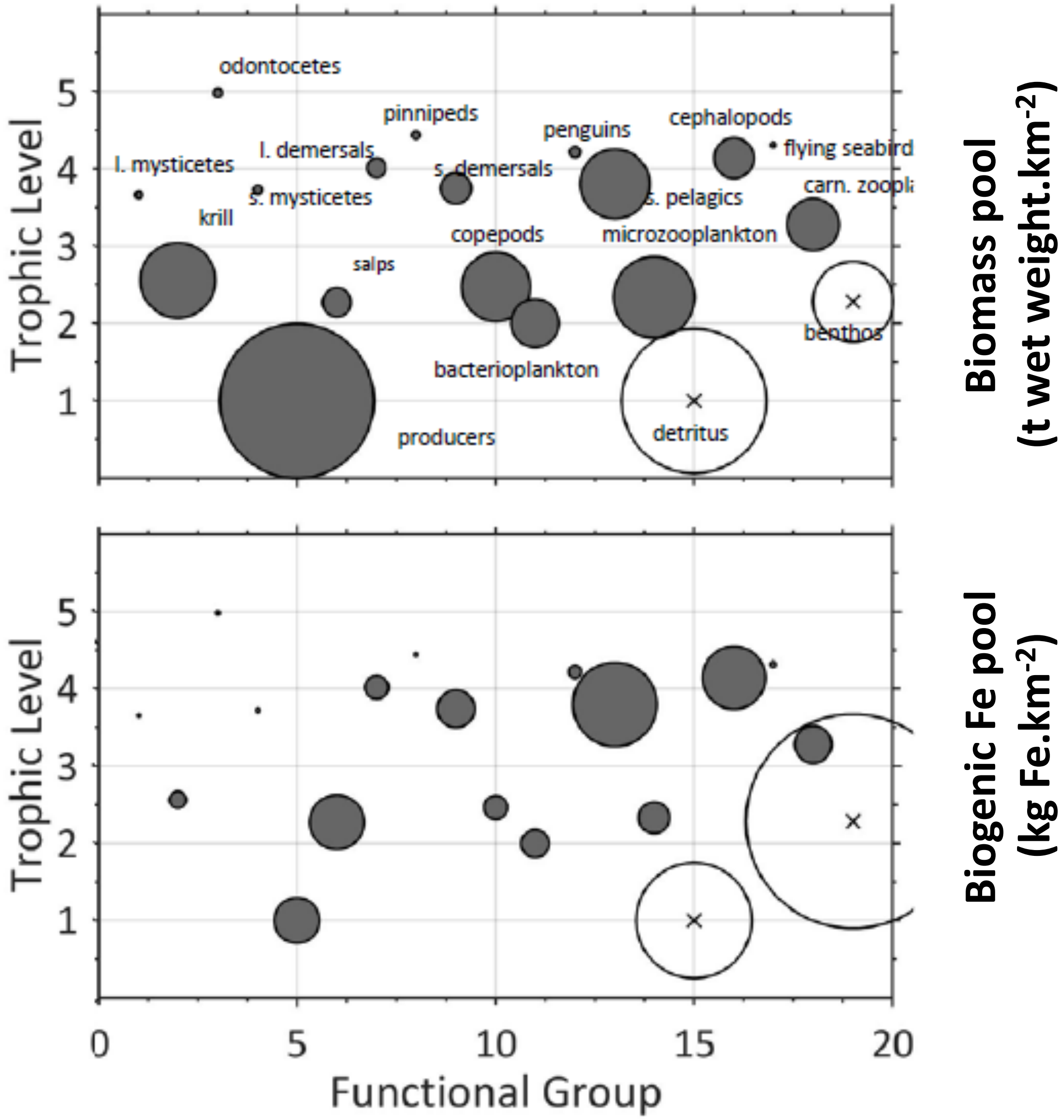
- 19 Functional groups

- for each group: Biomass gains balanced by biomass losses

- Parameters:
1. Biomass (B; t/km^2)
2. Production (P; y^{-1}) /B
3. Consumption (Q; y^{-1})/B
4. Diet composition matrix

To each groups we assigned Fe content & calculate Biogenic Fe pools, Fe associated with production, Fe consumption & Fe recycled

Biomass & Biogenic Fe pools in Southern Ocean ecosystem model

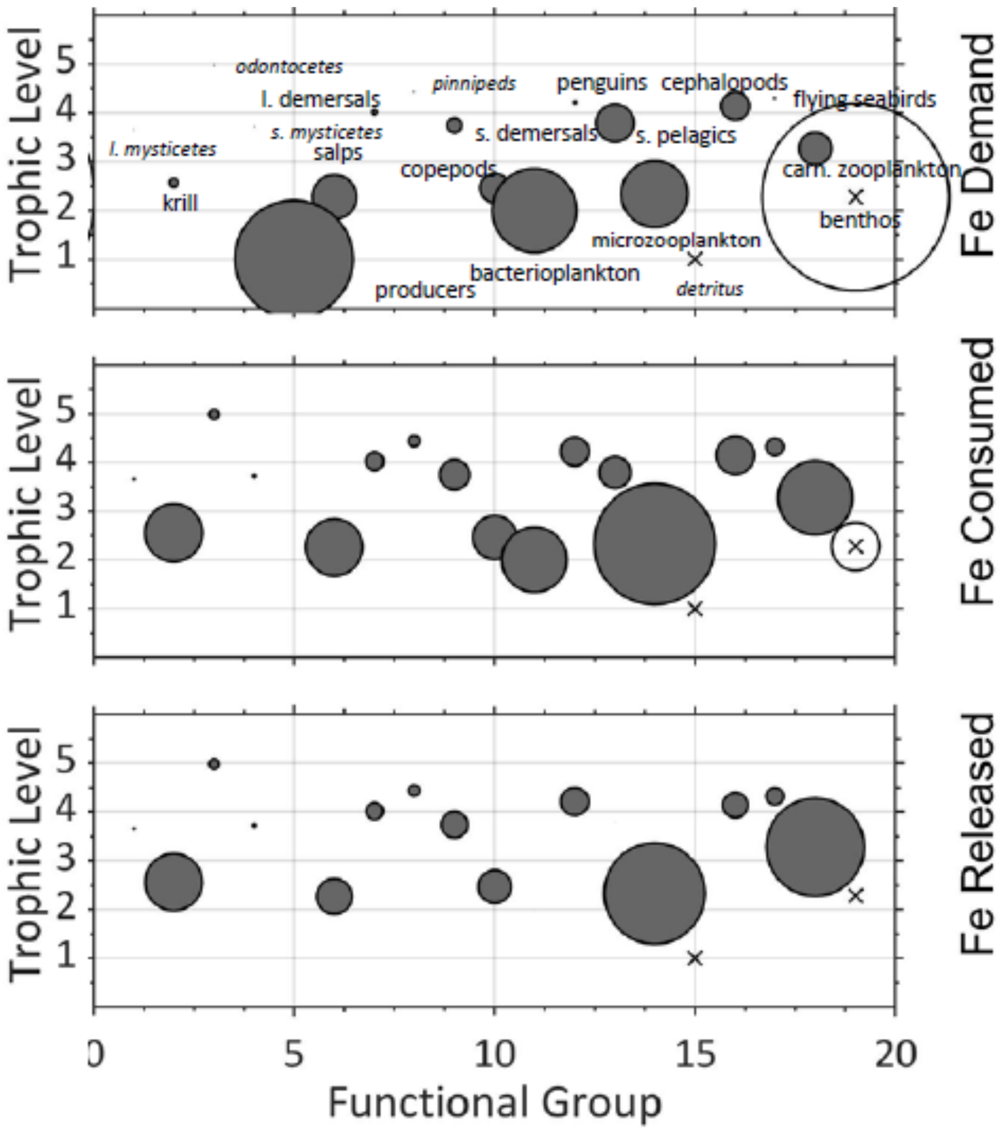


Maldonado et al. in press

Biggest Fe pools

Small pelagic fish
Cephalopods
Salps
Small demersal fish

Annual Fe demand, consumption & released by functional groups in the Southern Ocean (kg Fe.km^{-2}.y^{-1})



Maldonado et al. 2016 (in press)

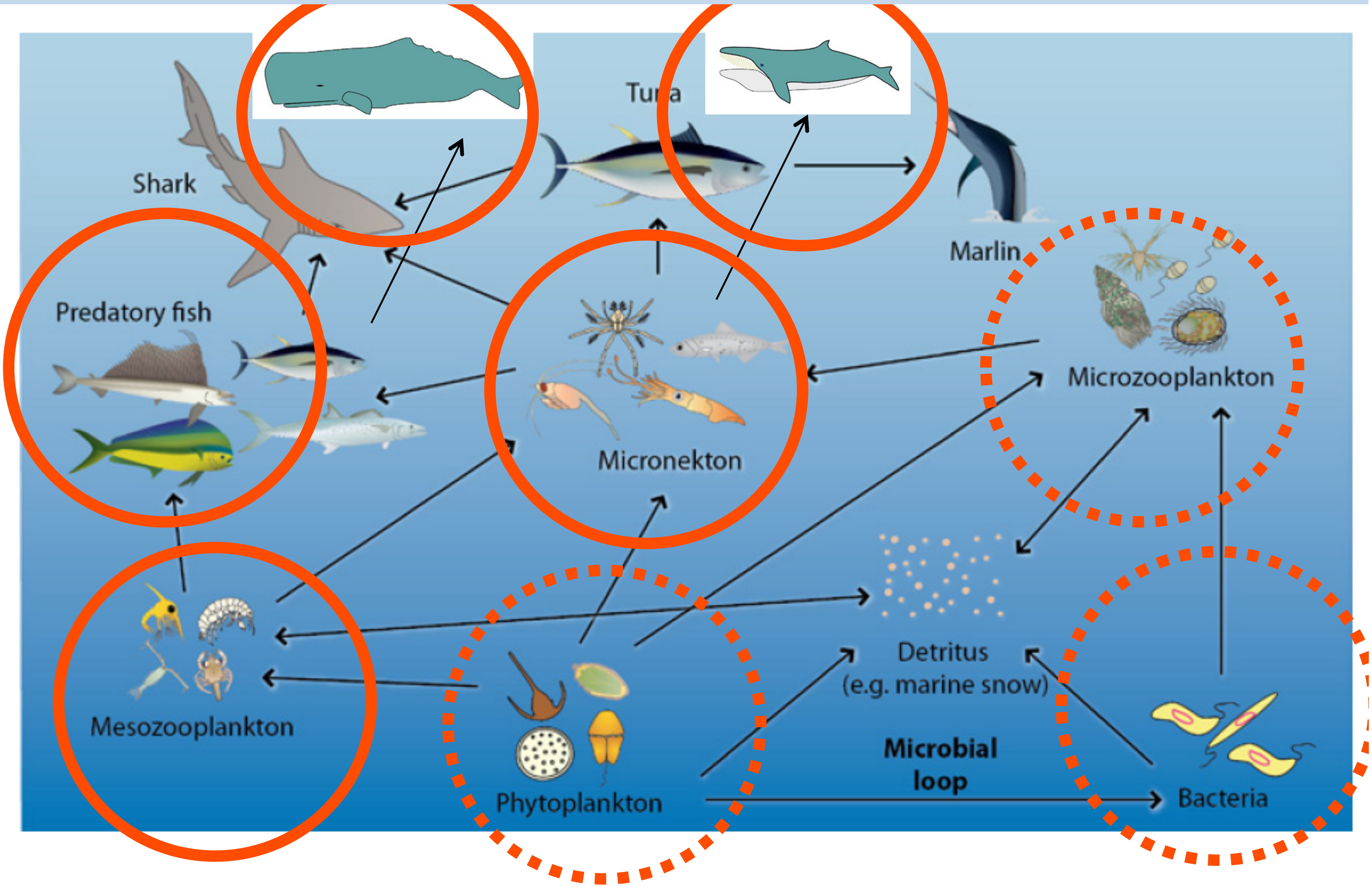
Greatest Fe demand by
phytoplankton, bacteria,
& microzooplankton

Greatest Fe consumers from prey
microzooplankton,
carnivorous zooplankton,
bacteria, krill & salps

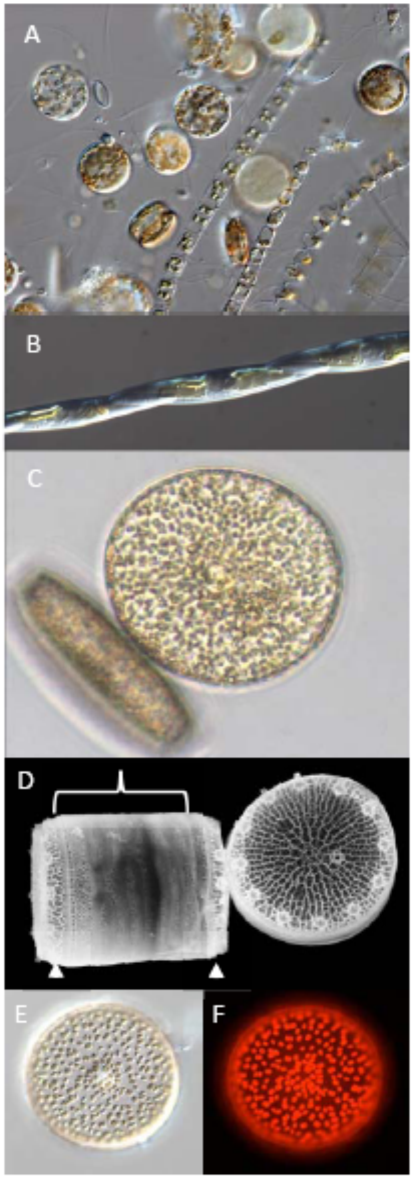
The key recyclers
microzooplankton &
carnivorous zooplankton (70% total)

Total Fe recycling 29 kg Fe.km^{-2} y^{-2}
~ =
phytoplankton & bacteria
Fe demand = 22 kg Fe.km^{-2} y^{-2}

A call for estimates of essential M content in more organisms



Talk Outline



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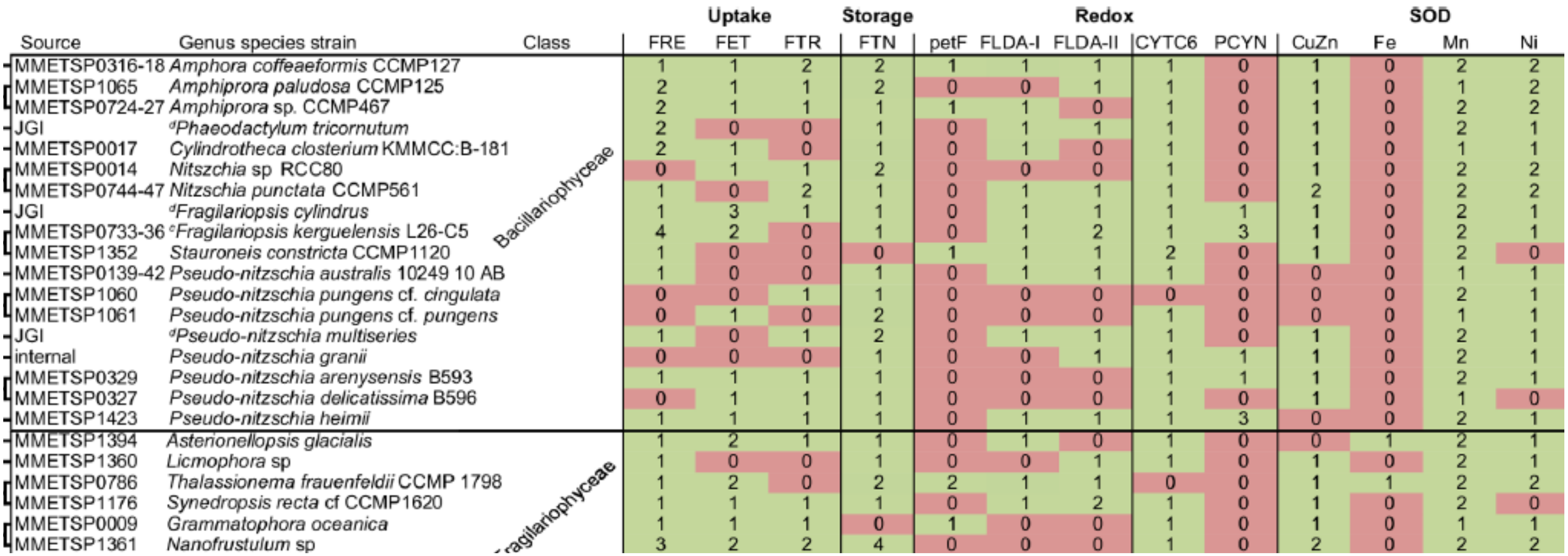
Transcriptomics reveals M homeostasis & uptake mechanisms

e.g. Uncovering strategies of 50 diatom species to meet their Fe demands

Goussman et al. 2015

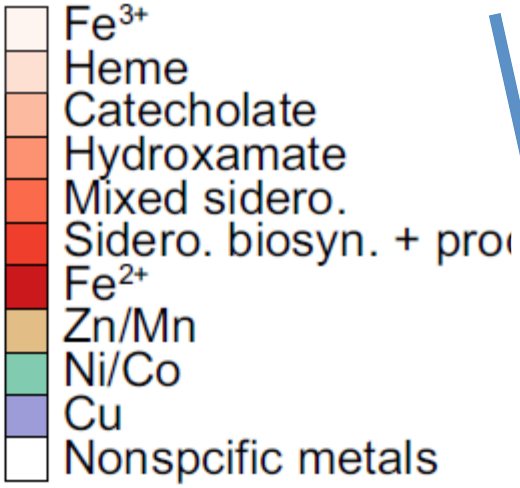


			Uptake			Storage	Redox					SOD			
Source	Genus species strain	Class	FRE	FET	FTR	FTN	petF	FLDA-I	FLDA-II	CYTC6	PCYN	CuZn	Fe	Mn	Ni
MMETSP0316-18	*Amphora coffeaeformis* CCMP127	Bacillariophyceae	1	1	2	2	1	1	1	1	0	1	0	2	2
MMETSP1065	*Amphiprora paludosa* CCMP125		2	1	1	2	0	0	1	1	0	1	0	1	2
MMETSP0724-27	*Amphiprora* sp. CCMP467		2	1	1	1	1	1	0	1	0	1	0	2	2
JGI	[d]*Phaeodactylum tricornutum*		2	0	0	1	0	1	1	1	0	1	0	2	1
MMETSP0017	*Cylindrotheca closterium* KMMCC:B-181		2	1	0	1	0	1	0	1	0	1	0	1	1
MMETSP0014	*Nitszchia* sp RCC80		0	1	1	2	0	0	0	1	0	1	0	2	2
MMETSP0744-47	*Nitzschia punctata* CCMP561		1	0	2	1	0	1	1	1	0	2	0	2	2
JGI	[d]*Fragilariopsis cylindrus*		1	3	1	1	0	1	1	1	1	1	0	2	1
MMETSP0733-36	[c]*Fragilariopsis kerguelensis* L26-C5		4	2	0	1	0	1	2	1	3	1	0	2	1
MMETSP1352	*Stauroneis constricta* CCMP1120		1	0	0	0	1	1	1	2	0	1	0	2	0
MMETSP0139-42	*Pseudo-nitzschia australis* 10249 10 AB		1	0	0	1	0	1	1	1	0	0	0	1	1
MMETSP1060	*Pseudo-nitzschia pungens* cf. *cingulata*		0	0	1	1	0	0	0	0	0	0	0	2	1
MMETSP1061	*Pseudo-nitzschia pungens* cf. *pungens*		0	1	0	2	0	0	0	1	0	0	0	1	1
JGI	[d]*Pseudo-nitzschia multiseries*		1	0	1	2	0	1	1	1	0	1	0	2	1
internal	*Pseudo-nitzschia granii*		0	0	0	1	0	0	1	1	1	1	0	2	1
MMETSP0329	*Pseudo-nitzschia arenysensis* B593		1	1	1	1	0	0	0	1	1	1	0	2	1
MMETSP0327	*Pseudo-nitzschia delicatissima* B596		0	1	1	1	0	0	0	1	0	1	0	1	0
MMETSP1423	*Pseudo-nitzschia heimii*		1	1	1	1	0	1	1	1	3	0	0	2	1
MMETSP1394	*Asterionellopsis glacialis*	ragilariophyceae	1	2	1	1	0	1	0	1	0	0	1	2	1
MMETSP1360	*Licmophora* sp		1	0	0	1	0	0	1	1	0	1	0	2	1
MMETSP0786	*Thalassionema frauenfeldii* CCMP 1798		1	2	0	2	2	1	1	0	0	1	1	2	2
MMETSP1176	*Synedropsis recta* cf CCMP1620		1	1	1	1	0	1	2	1	0	1	0	2	0
MMETSP0009	*Grammatophora oceanica*		1	1	1	0	1	0	0	1	0	1	0	1	1
MMETSP1361	*Nanofrustulum* sp		3	2	2	4	0	0	0	1	0	2	0	2	2

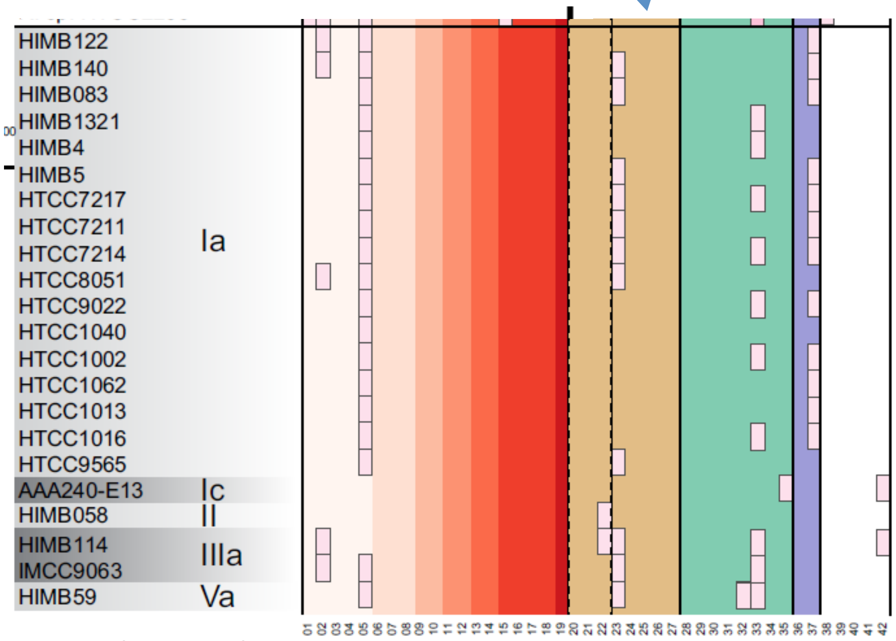
In theory, a brave modeler/biologist may calculate M demand based on principles of biochemistry (as John Raven)

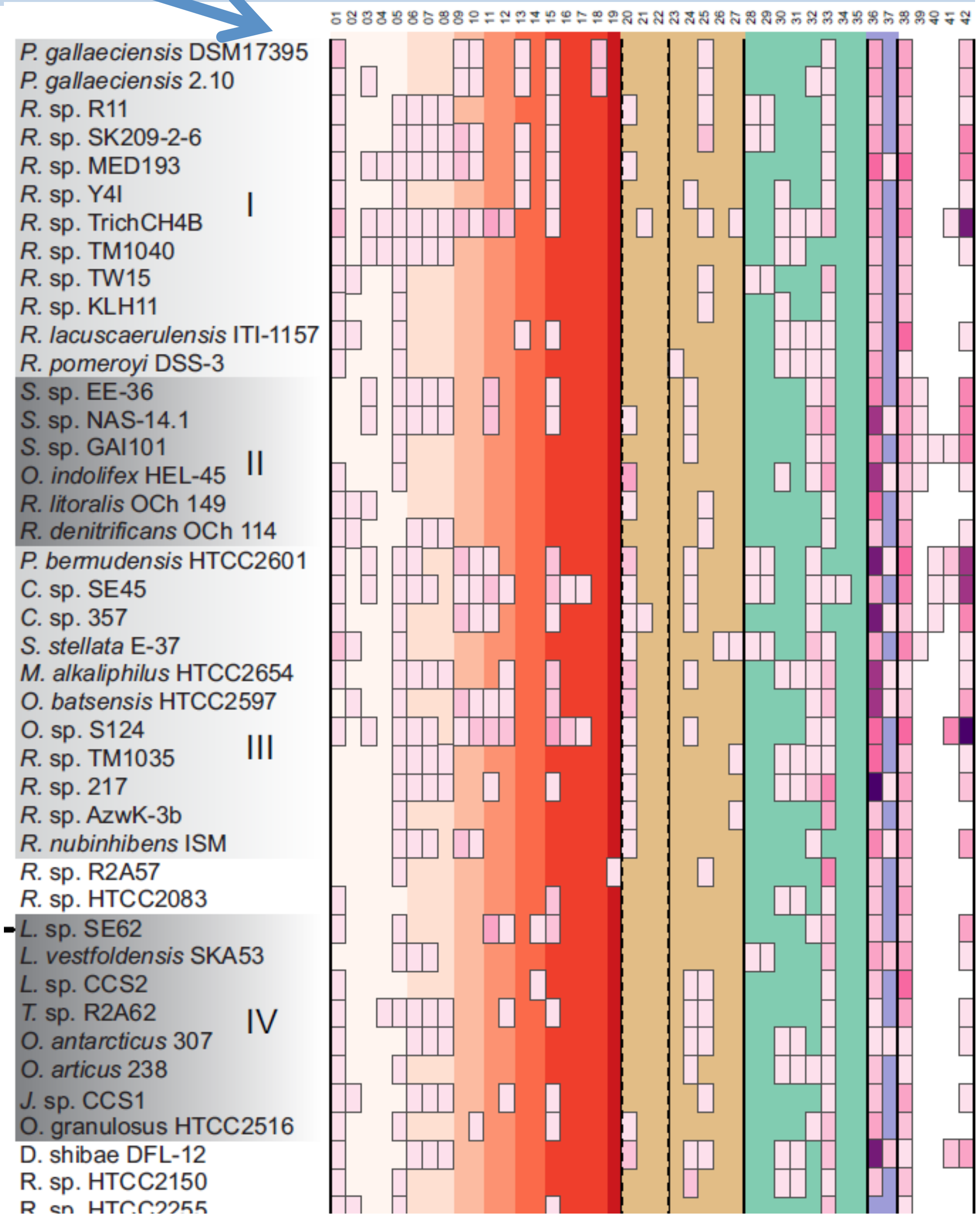
Genomics reveals diversity in trace metal acquisition mechanisms

eg.*Alphaproteobacteria* (SAR11) vs. *Roseobacter* lineages



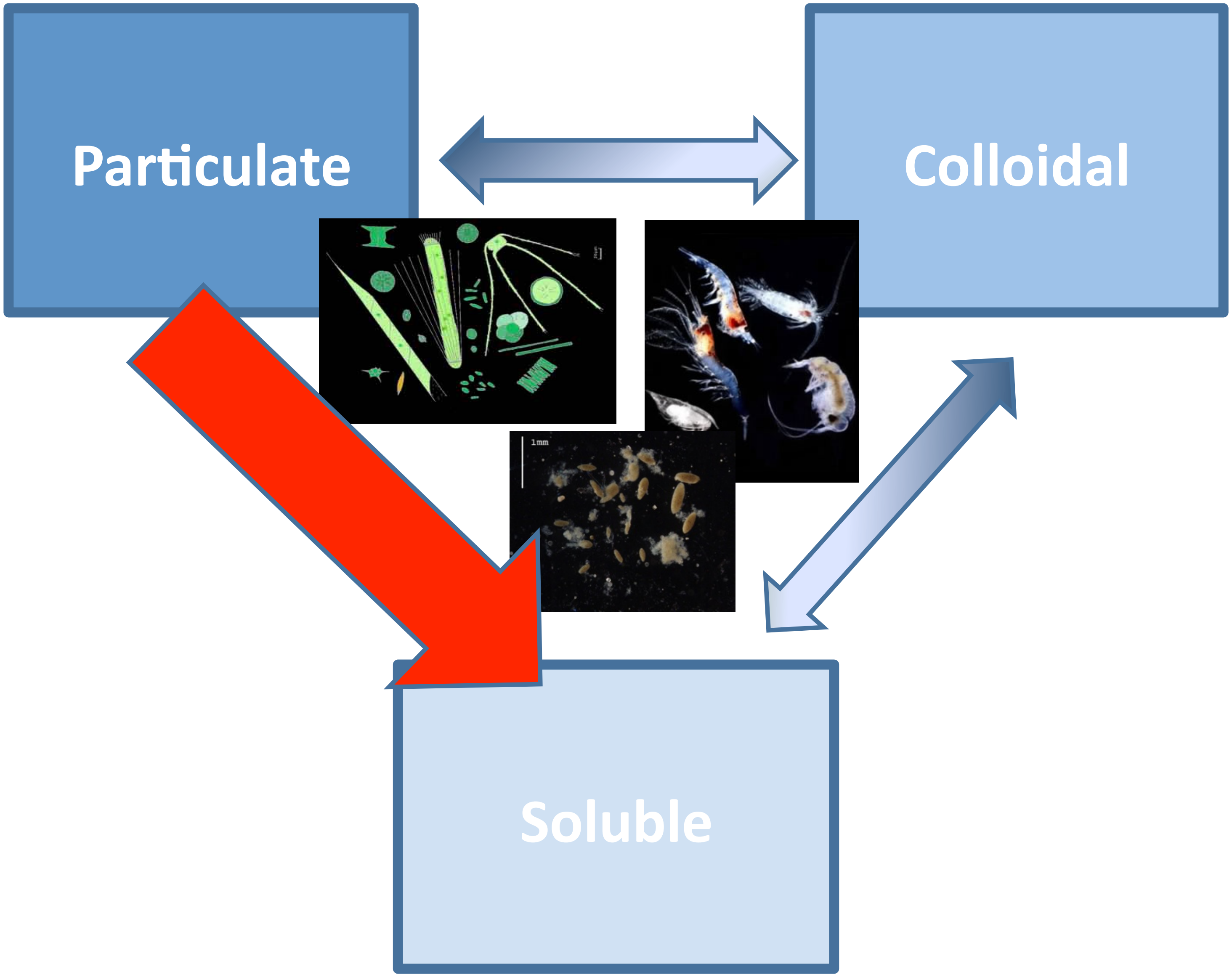
The bigger the genome, the greater M uptake versatility & plasticity





Hogle et al. 2016

Interactions between M and biota



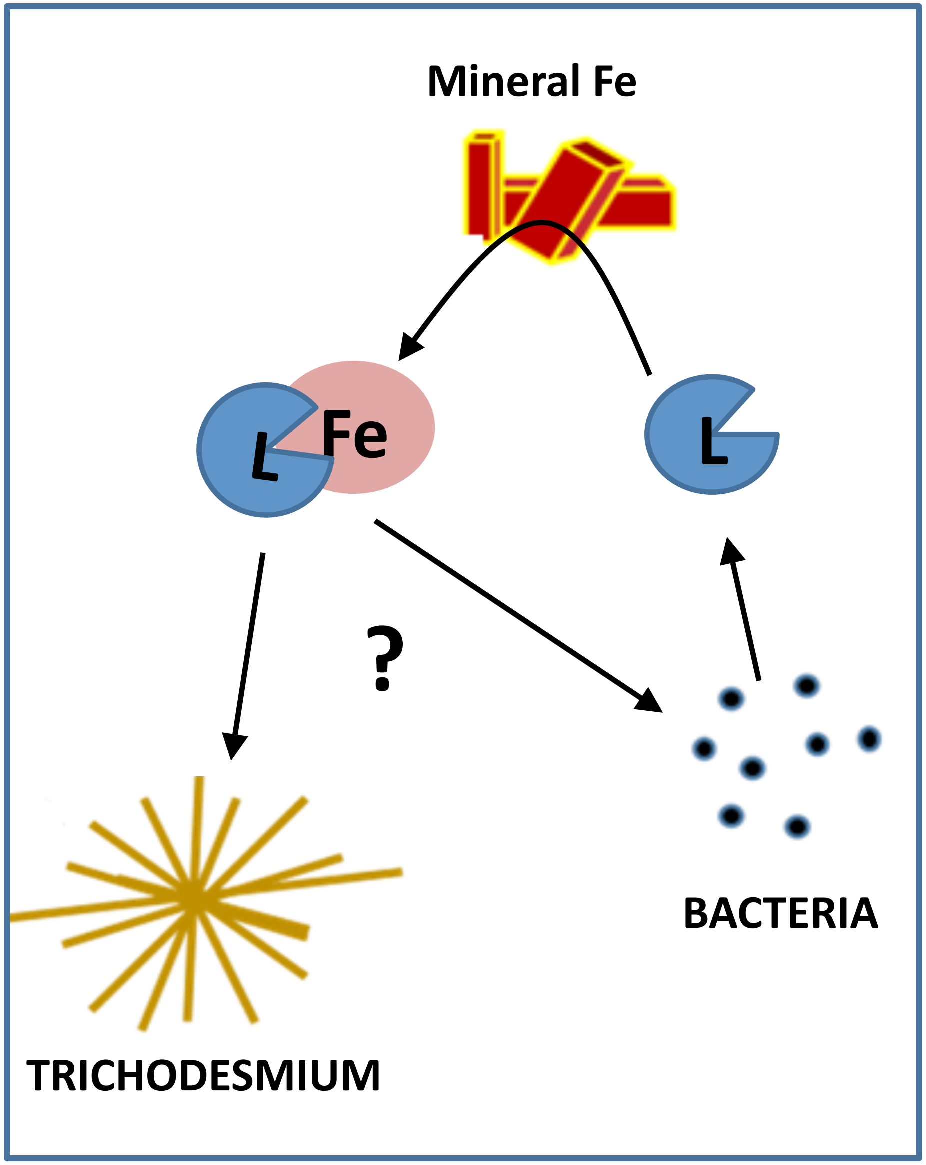
Particulate

Colloidal

Soluble

Dust Iron Utilization by Natural *Trichodesmium* Assisted by Bacteria

Shaked et al



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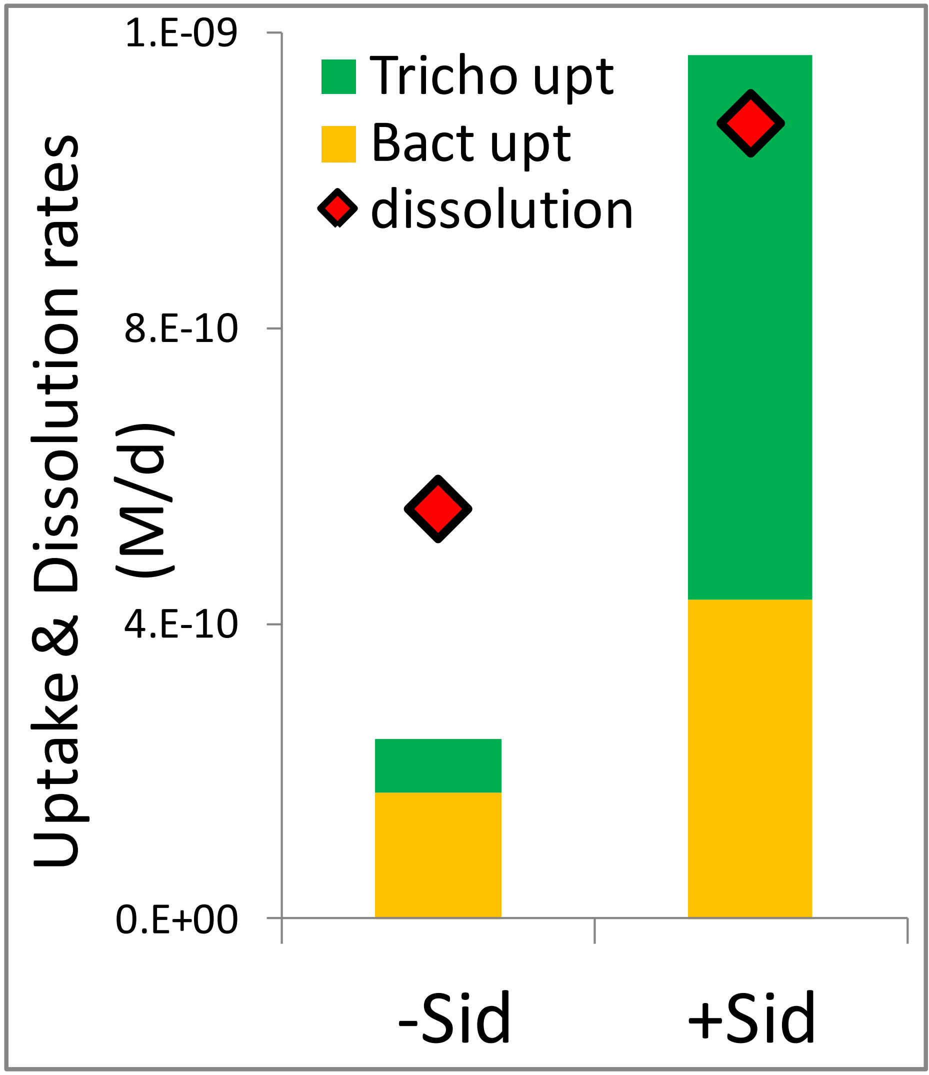
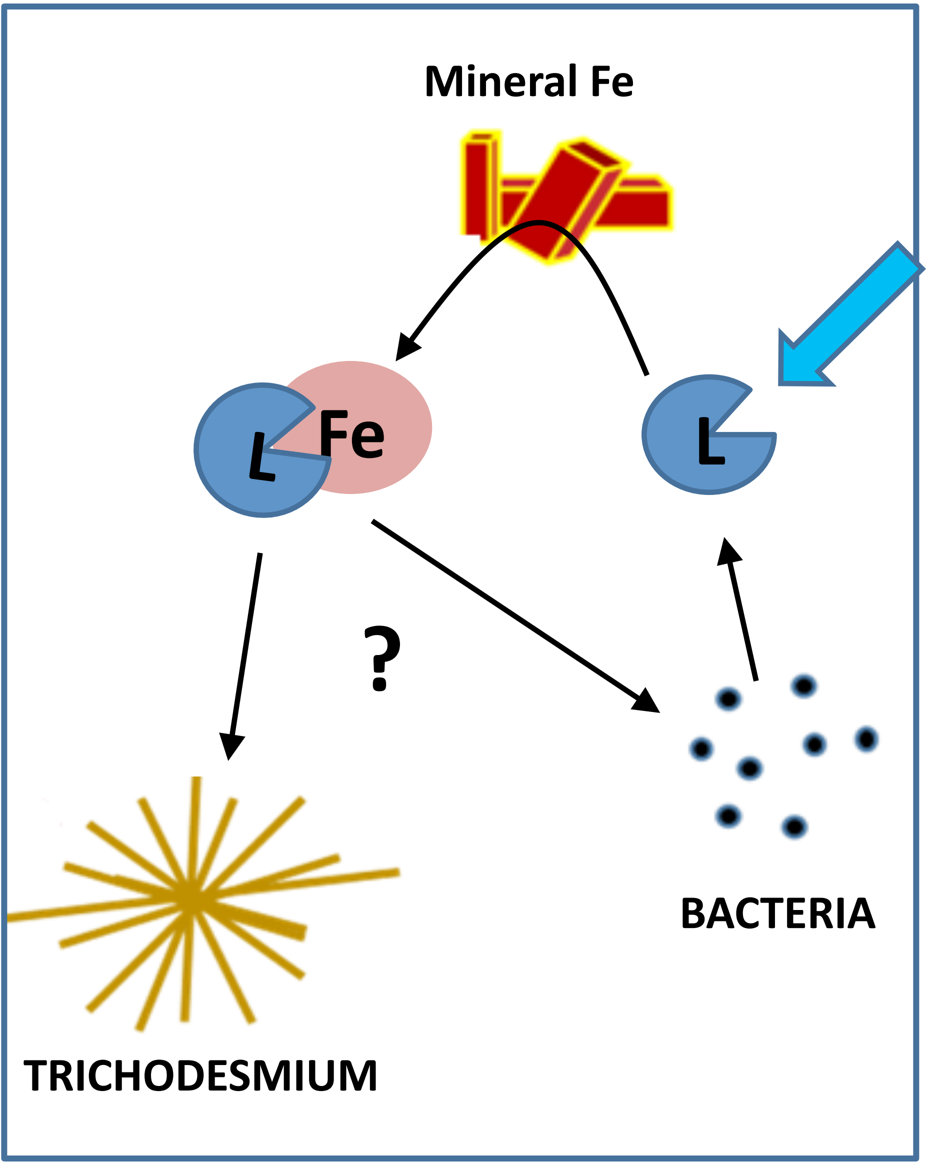
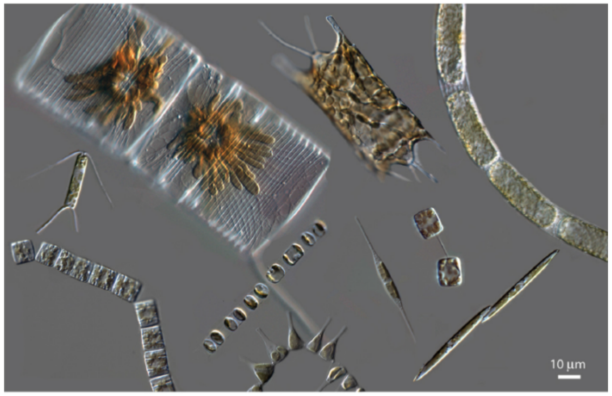


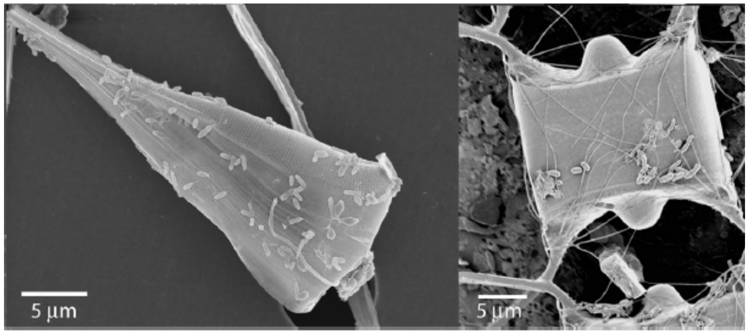
^{55}Fe-Ox, Natural colonies, Red Sea, Mar 2016

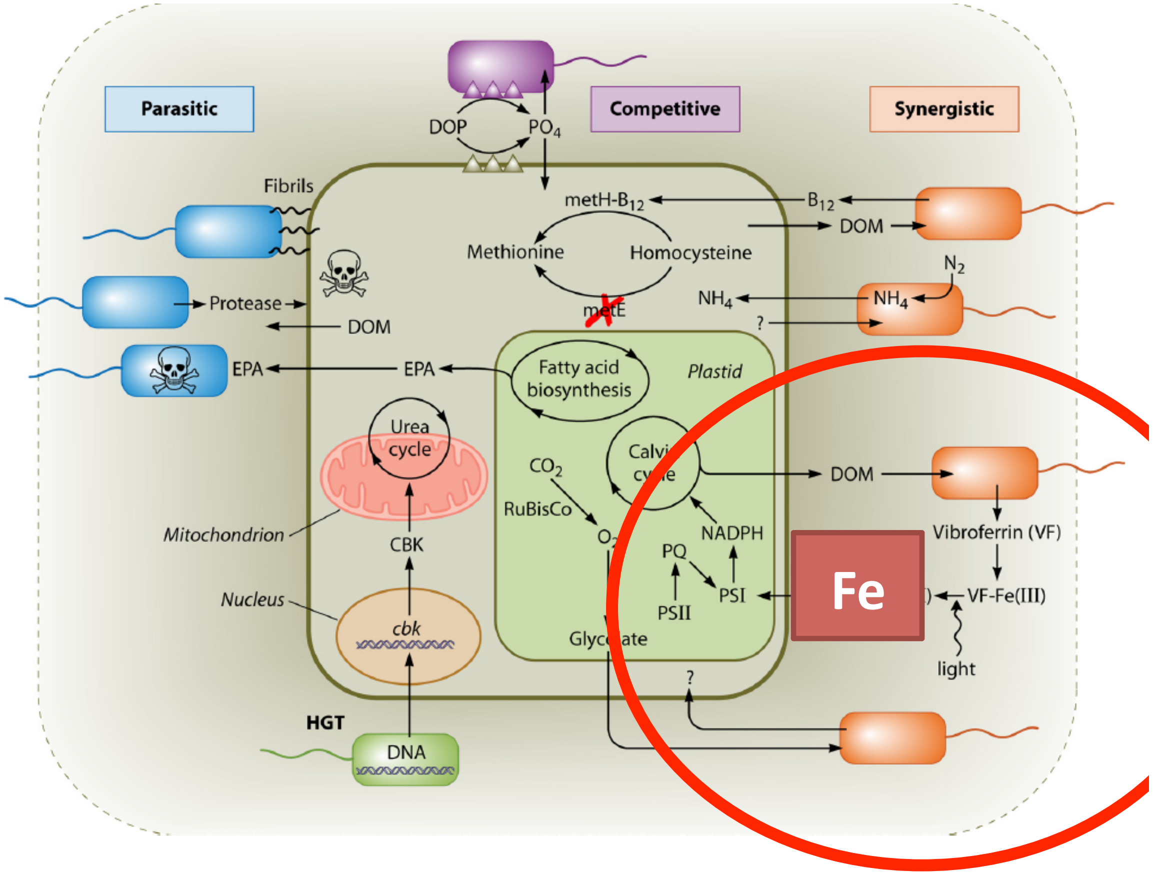


Phytoplankton & associated bacteria are teaming-up to acquire M

signaling molecules & exchange of nutrients







Amin et al. 2009, 2012, 2016

mutualistic interaction

Mixotrophs (organisms that can switch nutritional modes) are widespread in the ocean: affect M cycling

e.g. Phytoplankton
that can also ingest prey

Prymnesium parvum

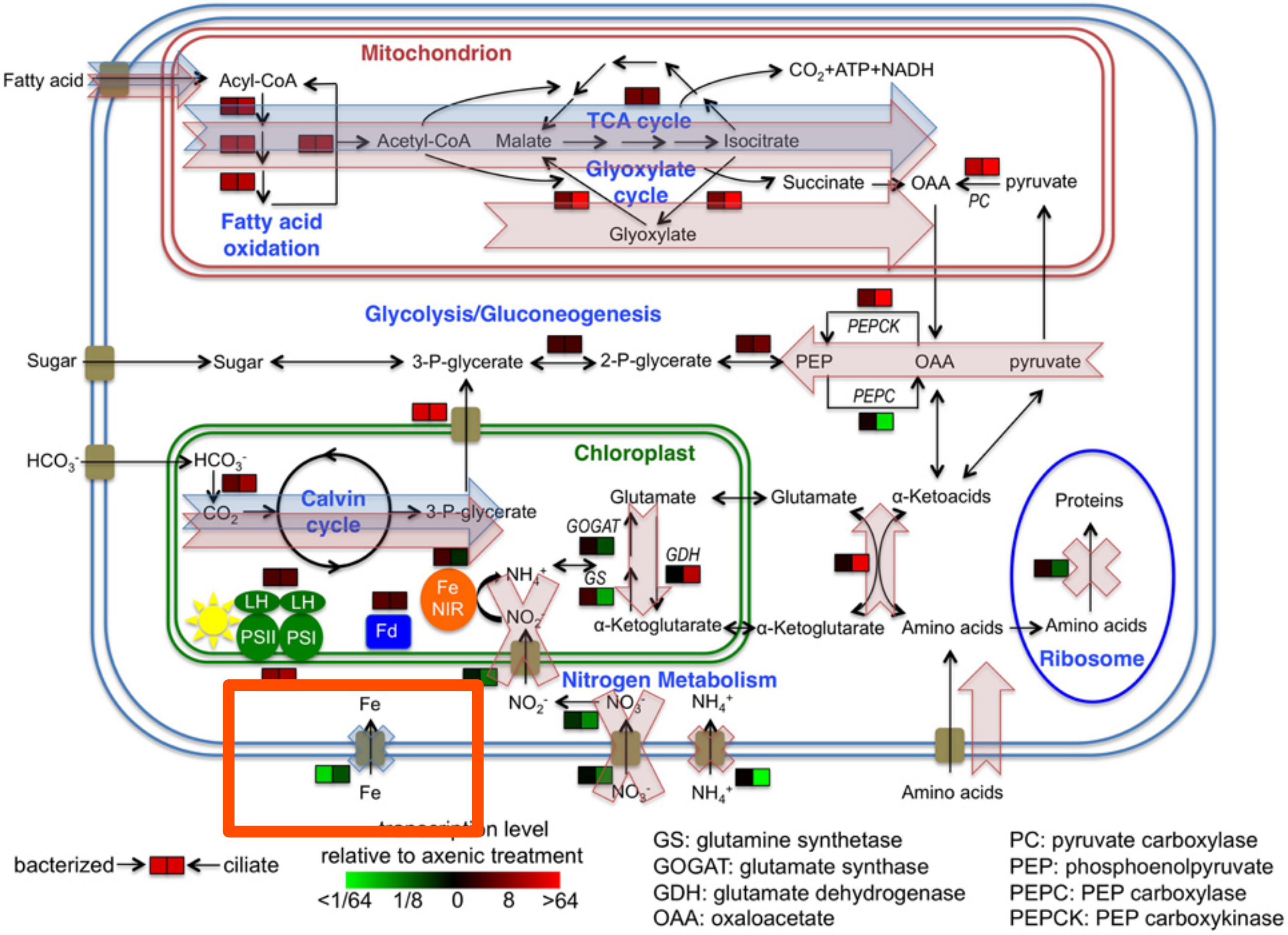
Review by Stoecker et al. 2016

Mixotrophs (organisms that can switch nutritional modes) are widespread in the ocean: affect M cycling

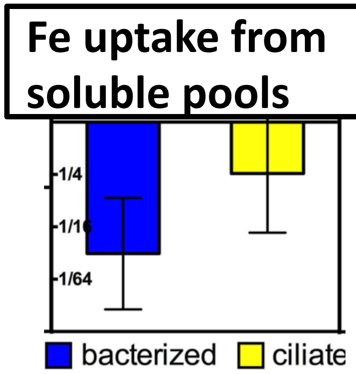
Prymnesium parvum responds to prey (bacteria vs. ciliates) & changes metal acquisition

Liu et al. 2015 (Maranger et al. 1998)

Phytoplankton acquiring their Fe ration from prey

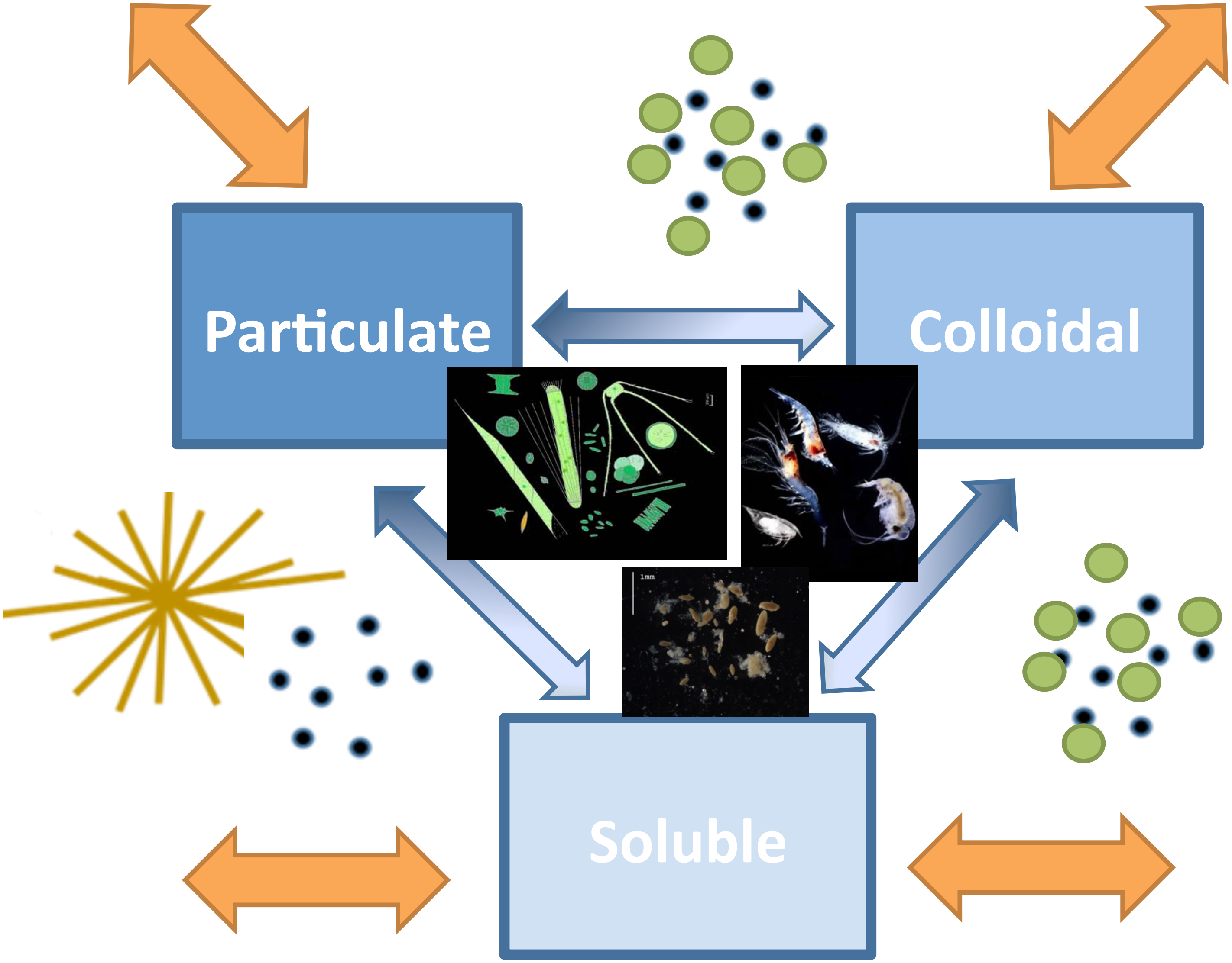


GS: glutamine synthetase
GOGAT: glutamate synthase
GDH: glutamate dehydrogenase
OAA: oxaloacetate
PC: pyruvate carboxylase
PEP: phosphoenolpyruvate
PEPC: PEP carboxylase
PEPCK: PEP carboxykinase



Prymnesium parvum

Interactions between M and biota



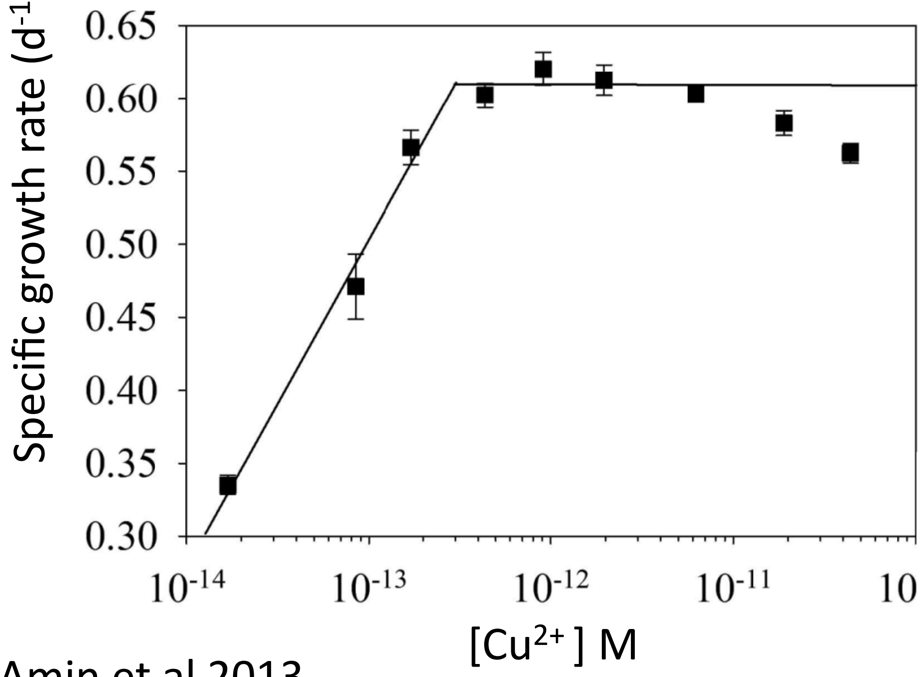
Particulate

Colloidal

Soluble

Interaction between M and nutrient cycles
Cu concentrations in the ocean may limit processes in the N cycle

Ammonium Oxidizing Archaea
Nitrosopumilus maritimus

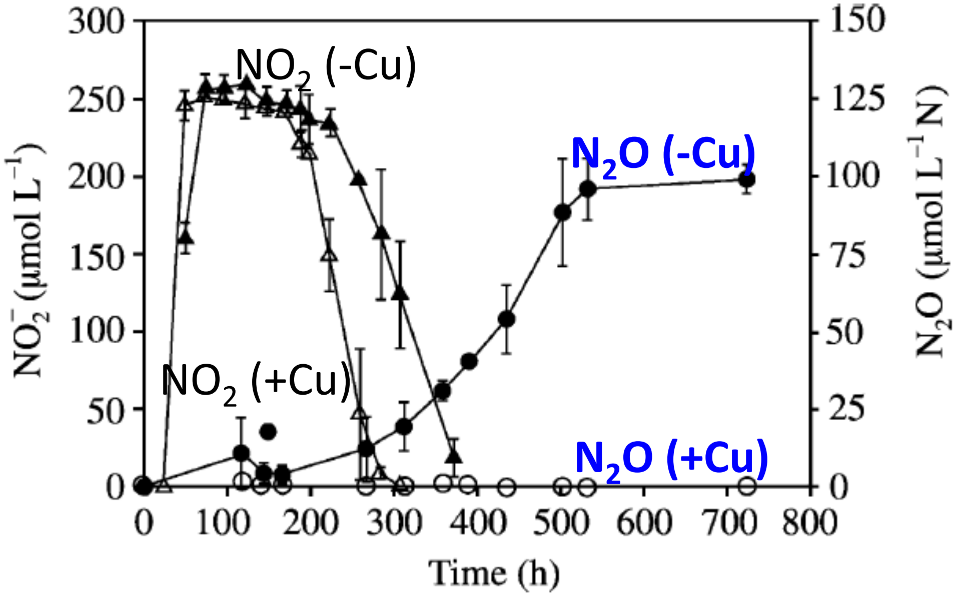


Amin et al 2013

Cu containing proteins involved in e- transport:
Nitrosopumilus maritimus (27)

Candidatus Nitrosopelagicus brevis **(12)**
Santoro et al. 2015

Denitrifying Bacteria



Granger & Ward 2003

SUMMARY and Future Directions

- Incredible diversity of mechanisms to acquire metals, and deal with changes in trace metal availability.

- Organisms are accessing multiple M pools & are mediating the transfer of metals between pools

- To better understand biogeochemical cycles of M we need to study the interactions between microorganisms, and M nutrition in higher trophic levels

- Concentrations of other M, besides Fe, may not affect PP, but they may control community composition & cycles of macronutrients