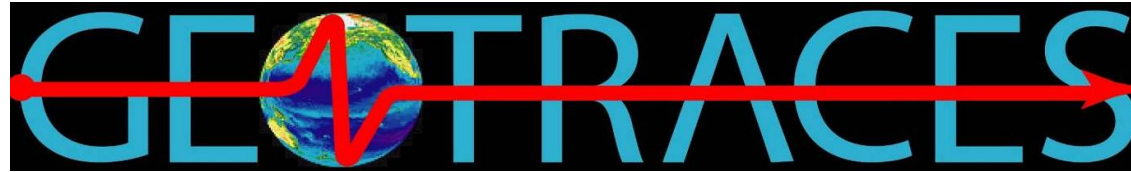


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Natural Iron Fertilization Workshop
Woods Hole, 27-29 June 2011

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Hein.de.Baar@nioz.nl



Royal Netherlands Institute for Sea Research

Southern Ocean Iron Fertilization

Hein de Baar and many colleagues

Modeling and Synthesis of Southern Ocean
Natural Iron Fertilization Workshop
Woods Hole, 27-29 June 2011

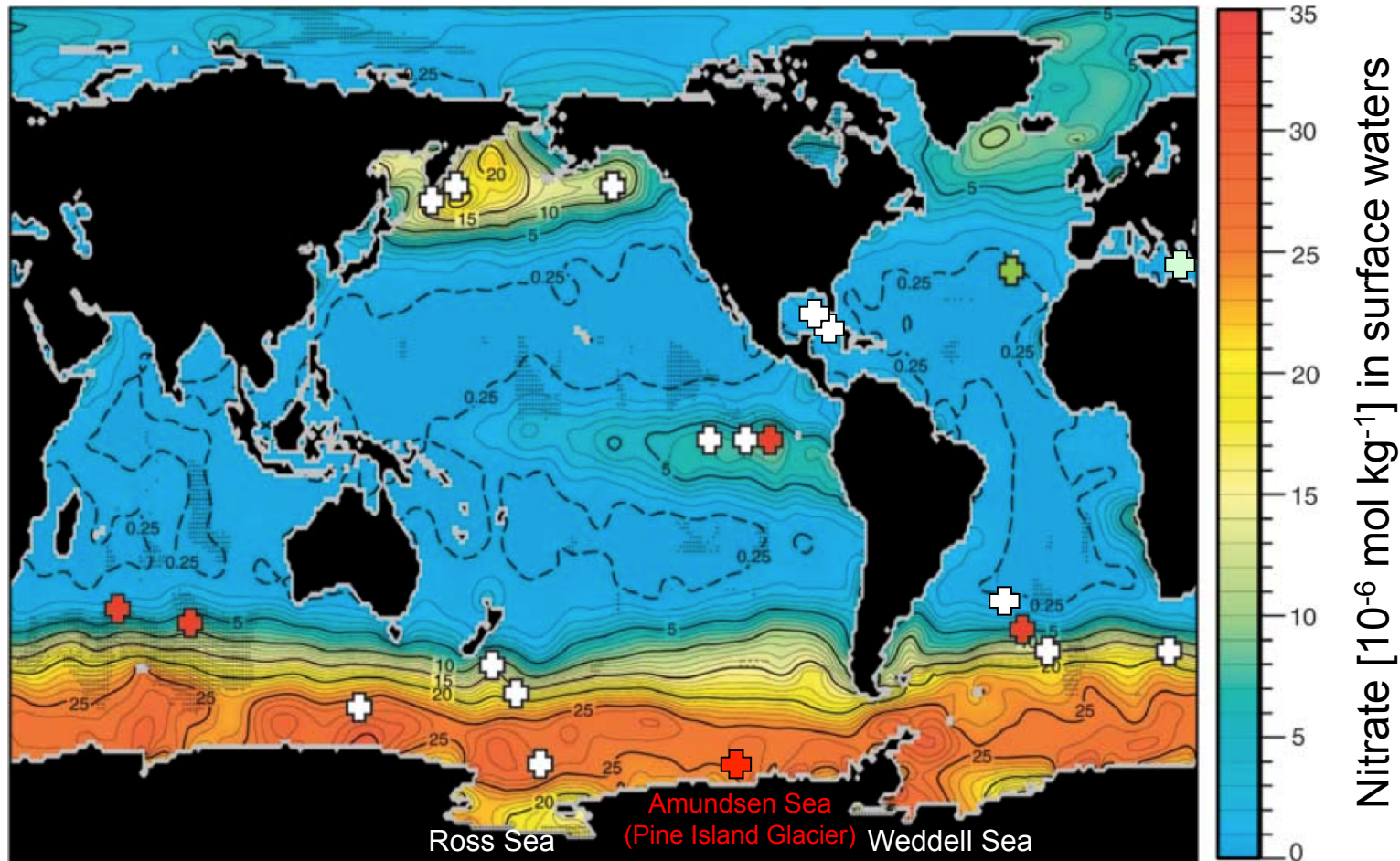


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 - (1988) Give me half a supertanker
 - (2011) GeoEngineering, London Convention, ISIS Consortium



Among 3 major High-Nutrient-Low-Chlorophyll (HNLC) regions only the Southern Ocean would (perhaps) yield long term deep carbon storage



- ⊕ 13 Fe *in situ* addition experiments in 1993-2009 period; Ironex-1 to Lohafex
- ⊕ 5 unperturbed natural Fe fertilization studies: Galapagos; Polar Front 1992; Crozet Crozex 2004-2005; Kerguelen Keops 2005; Pine Island Glacier *Dynalife* 2009

Not discussed today are:

- ⊕ Fe + P addition experiment (FEPP 2004)
- ⊕ P addition experiment (CYCLOPS 2002)



Hypotheses for HNLC condition

- Iron limitation
- Light limitation
- Grazing loss
- Other bio-limiting trace elements:
 - Cobalt ?
- Manganese co-limitation

What are your objectives

- fertilization experiments as a tool to unravel the functioning of the HNLC plankton ecosystem
- geo-engineering ocean fertilization for sequestration of CO₂ from the atmosphere to avoid global warming

depending on your objectives the design of research and experiment may be quite different

today we will shift back and forth between the two

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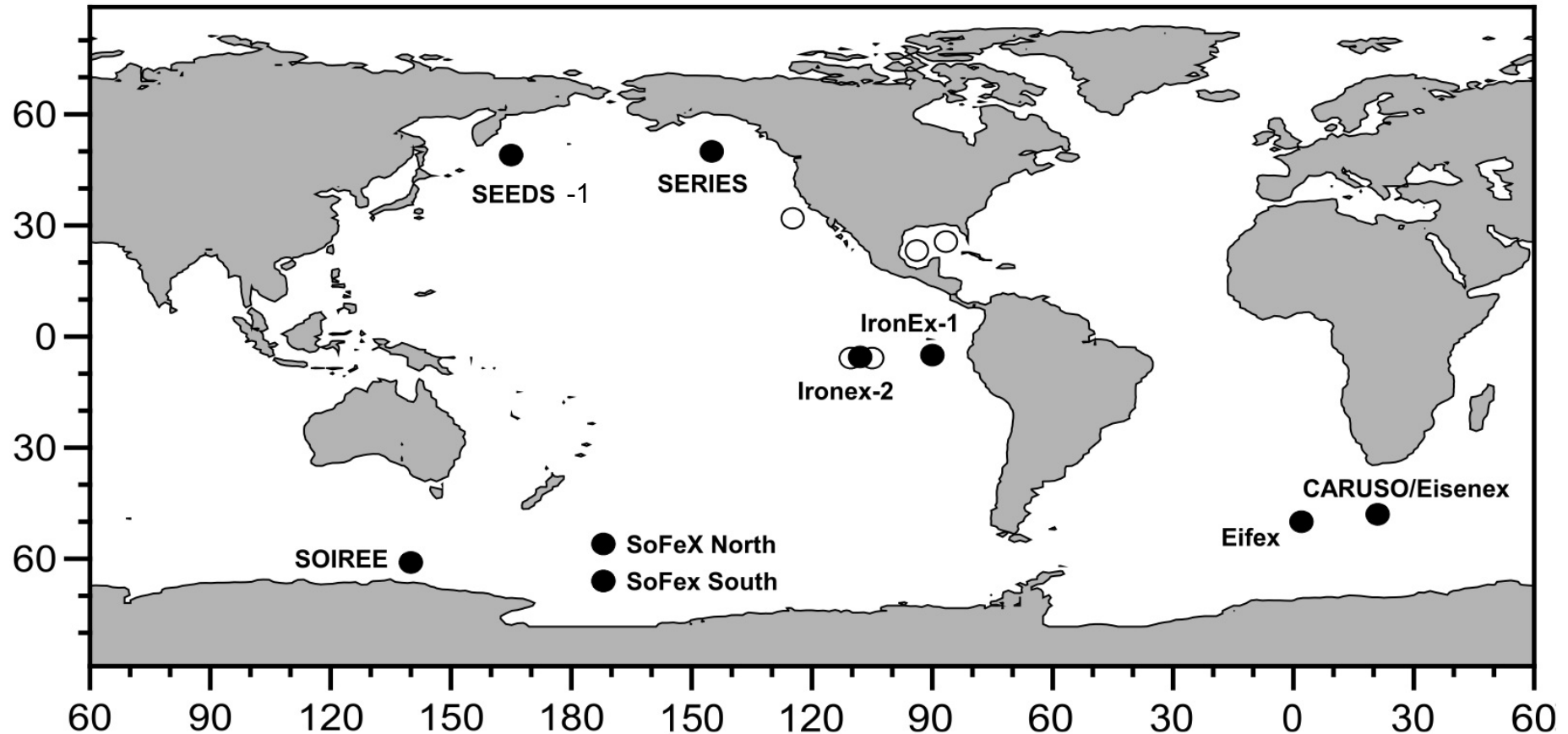


Synthesis of iron fertilization experiments: From the Iron Age in the Age of Enlightenment

Hein J. W. de Baar,^{1,2} Philip W. Boyd,³ Kenneth H. Coale,⁴ Michael R. Landry,⁵
Atsushi Tsuda,⁶ Philipp Assmy,⁷ Dorothee C. E. Bakker,⁸ Yann Bozec,¹
Richard T. Barber,⁹ Mark A. Brzezinski,¹⁰ Ken O. Buesseler,¹¹ Marie Boyé,^{2,12}
Peter L. Croot,^{1,13} Frank Gervais,⁷ Maxim Y. Gorbunov,¹⁴ Paul J. Harrison,¹⁵
William T. Hiscock,¹⁶ Patrick Laan,¹ Christiane Lancelot,¹⁷ Cliff S. Law,¹⁸
Maurice Levasseur,¹⁹ Adrian Marchetti,²⁰ Frank J. Millero,¹⁶ Jun Nishioka,²¹
Yukihiro Nojiri,²² Tim van Oijen,² Ulf Riebesell,¹³ Micha J. A. Rijkenberg,^{1,2}
Hiroaki Saito,²³ Shigenobu Takeda,²⁴ Klaas R. Timmermans,¹ Marcel J. W. Veldhuis,¹
Anya M. Waite,²⁵ and Chi-Shing Wong²⁶



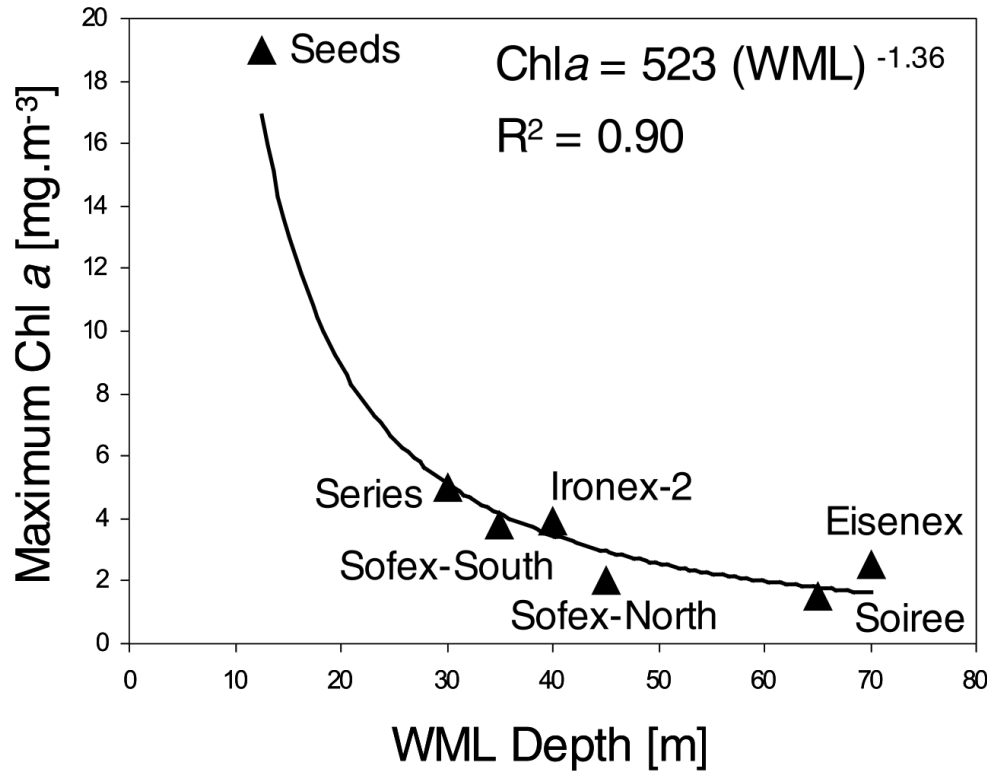
7 experiments available in 2004 for interpretation: Ironex-2 (1995), SOIREE (1999), CARUSO/Eisenex (2000), SEEDS-1 (2001), SoFeX-South (2002), SERIES (2002)



Ironex-1 (1993) premature subduction after 4 days, not used
SoFeX North (2002) very streaky due to Polar Front shear stress, cannot be quantified
Eifex (2004) no data available yet in 2004



Chlorophyll a response depends on depth of Wind Mixed Layer i.e. availability of light



Also the major response is always an enhancement of the larger size classes of diatoms

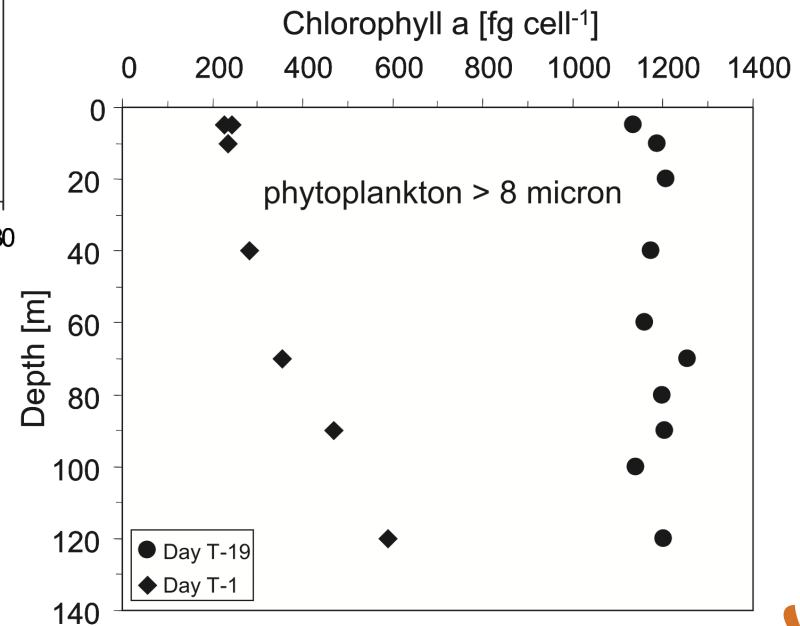
Thus confirming what was already known from our bottle incubation experiments in 1988 (Buma, de Baar, et al, 1991)

However Chl a is NOT a good indicator of overall biomass

bio-synthesis of Chl a requires Fe

- at Fe limitation low Chl a per cell

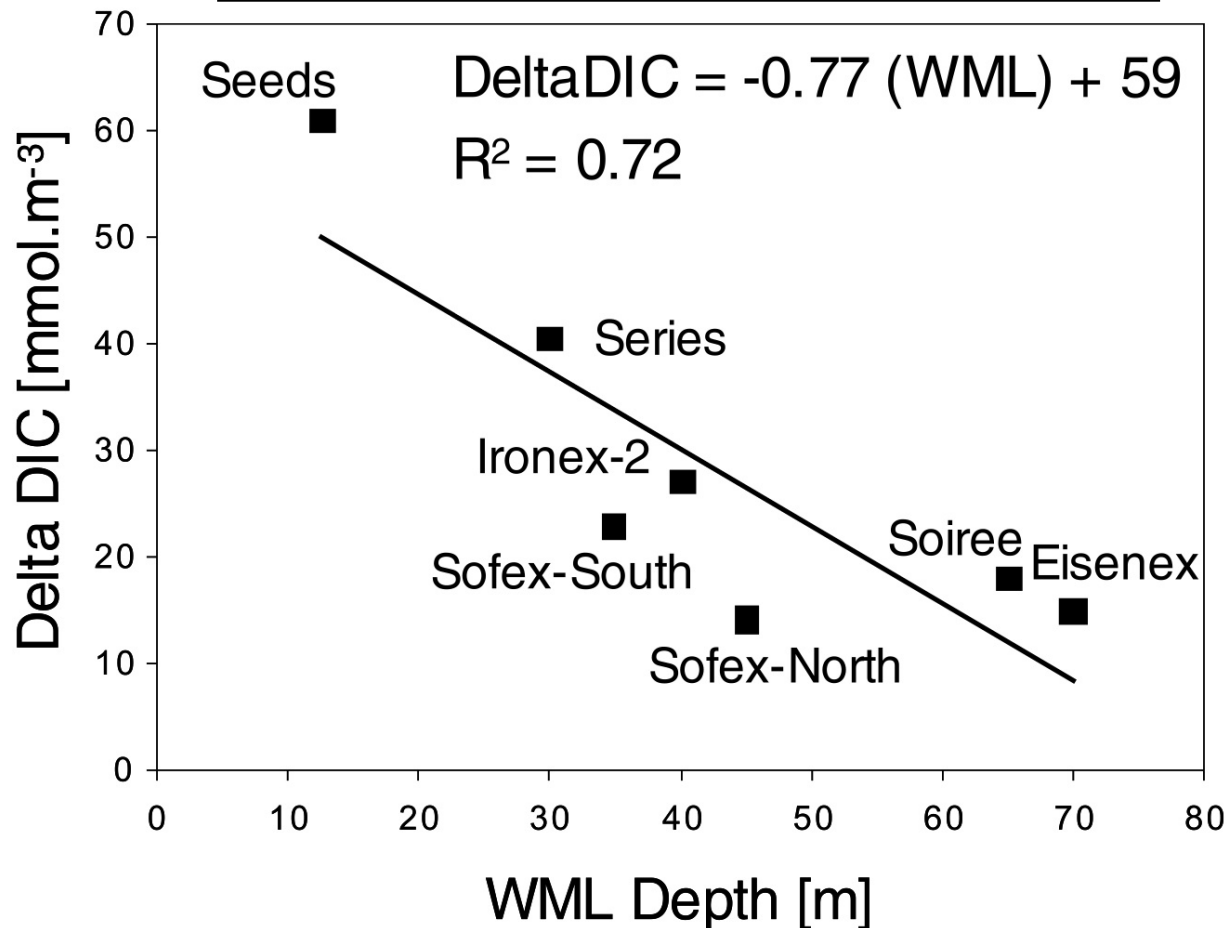
- at Fe replete condition high Chl a per cell



Eisenex (2000): upon Fe addition a sixfold increase of cellular Chl a in the large diatoms > 8 micron



Decrease of total Dissolved Inorganic Carbon (DIC) is reliable quantitative indicator of net Biomass increase



Net Biomass response depends on depth of Wind Mixed Layer i.e. availability of light



medium and large size DIATOMS

Chaetoceros dicheta
80 m long, 30 m width
forms chains

Pseudo-nitzschia

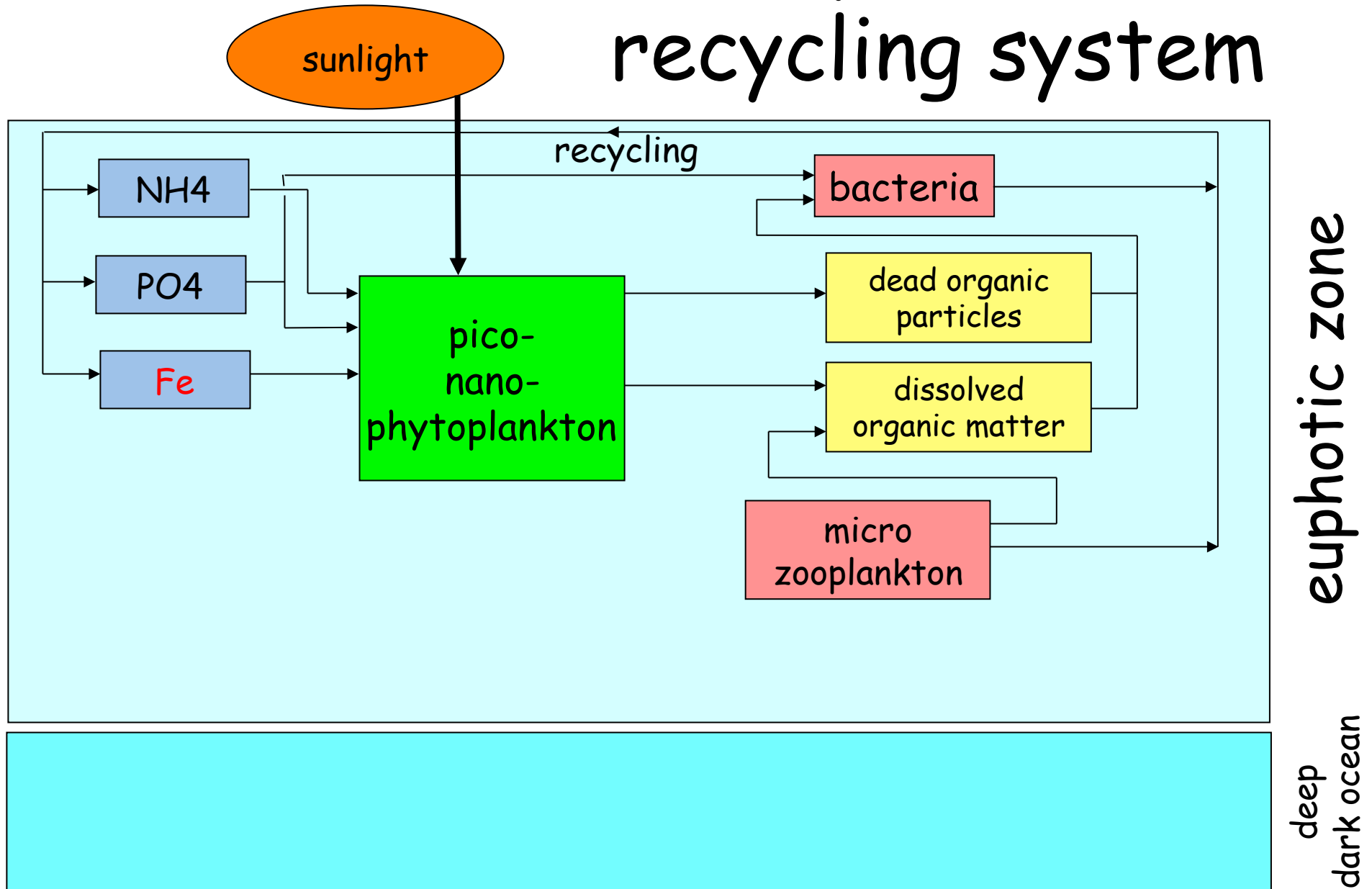
Fragilariopsis kerguelensis
chain-forming

Actinocyclus

← 140 micron diameter →

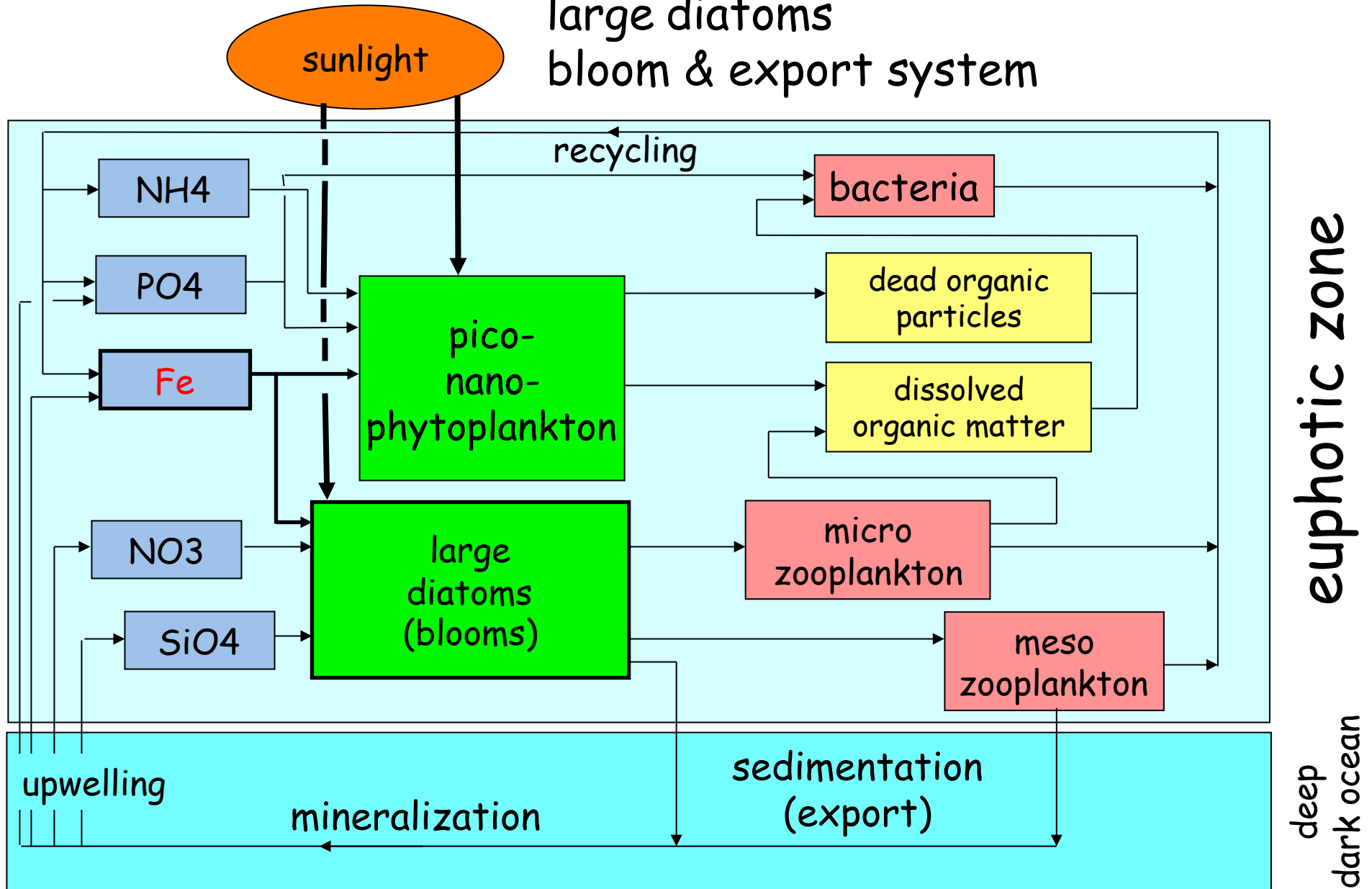
80 micron

Fe depletion: recycling system

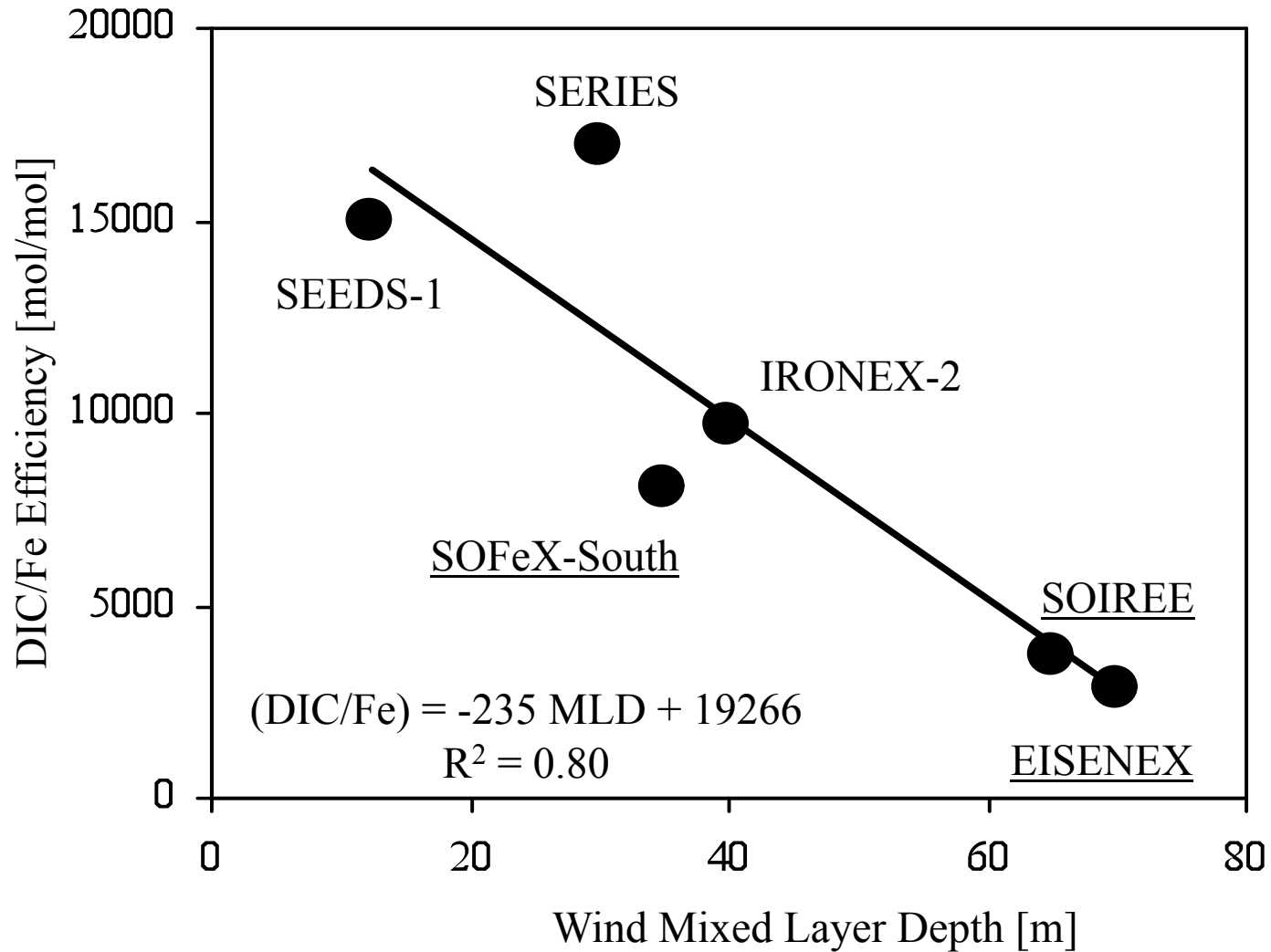


Fe supply: shift-up

large diatoms
bloom & export system



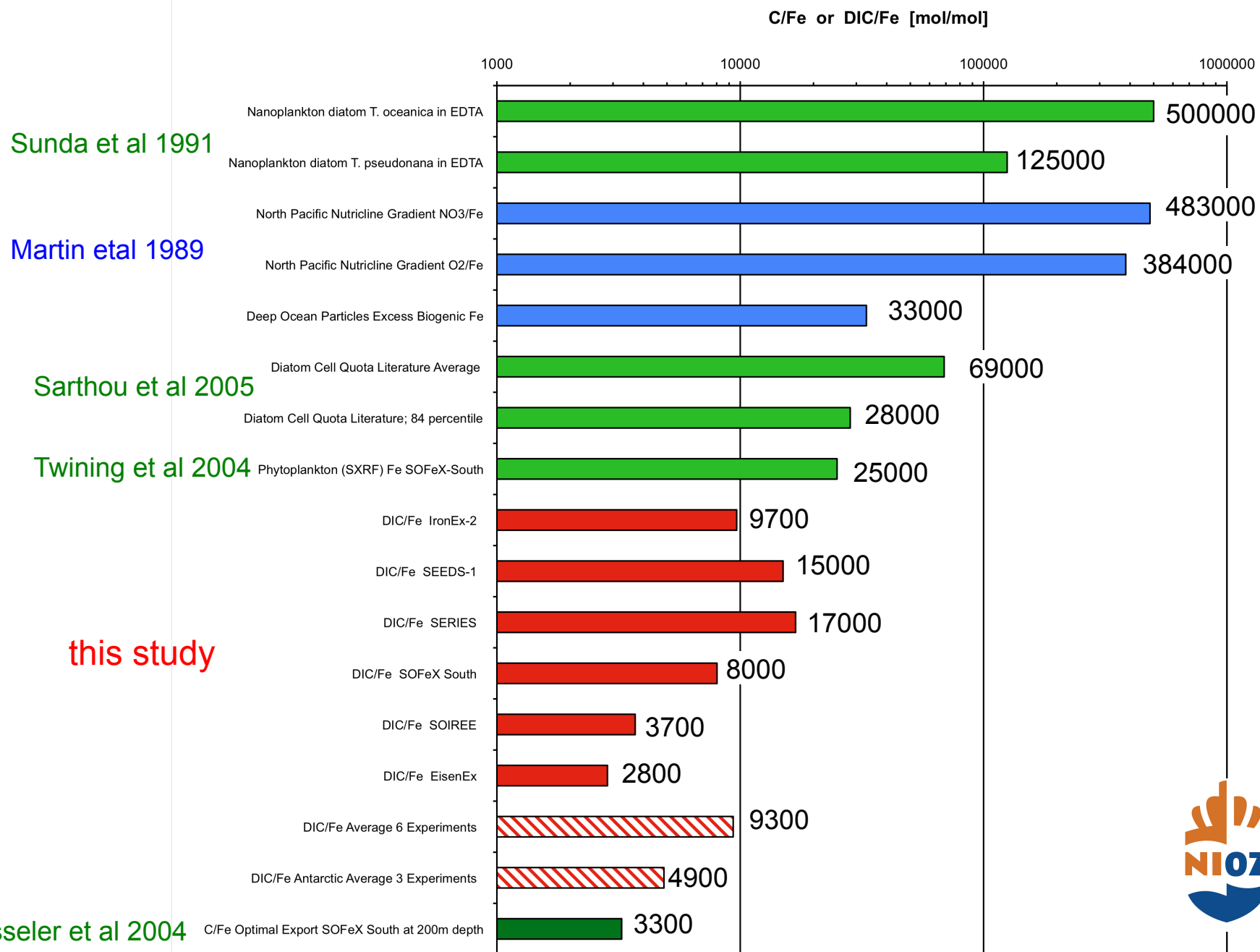
$$\text{DIC removal efficiency} = \frac{\text{DIC removal [mol]}}{\text{Fe addition [mol]}}$$



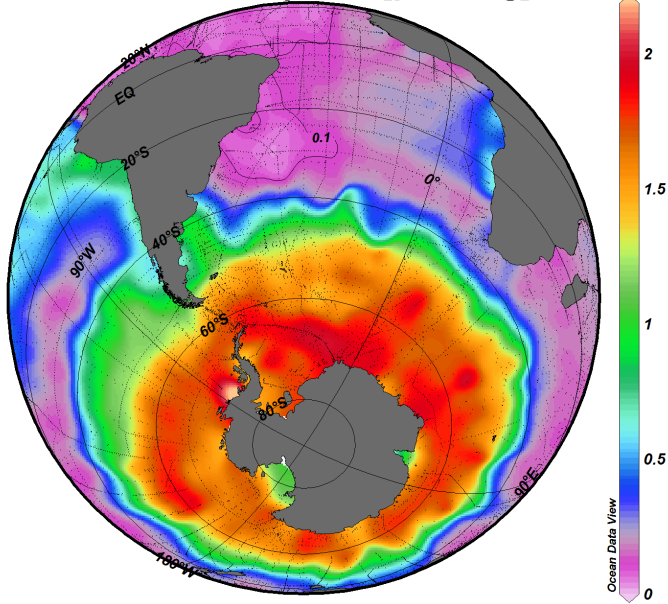
drawn after Table 3 of De Baar et al (2005)



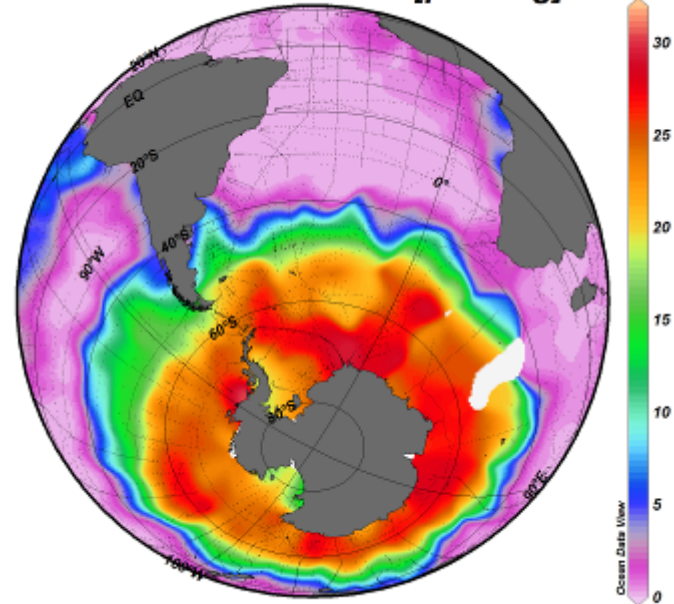
C:Fe ratio values: from initial euphoria to reality



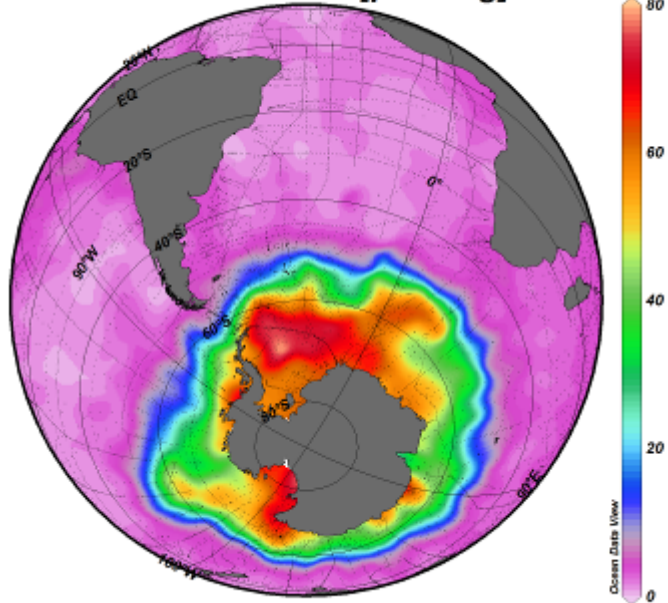
Surface Phosphate [$\mu\text{mol/kg}$]



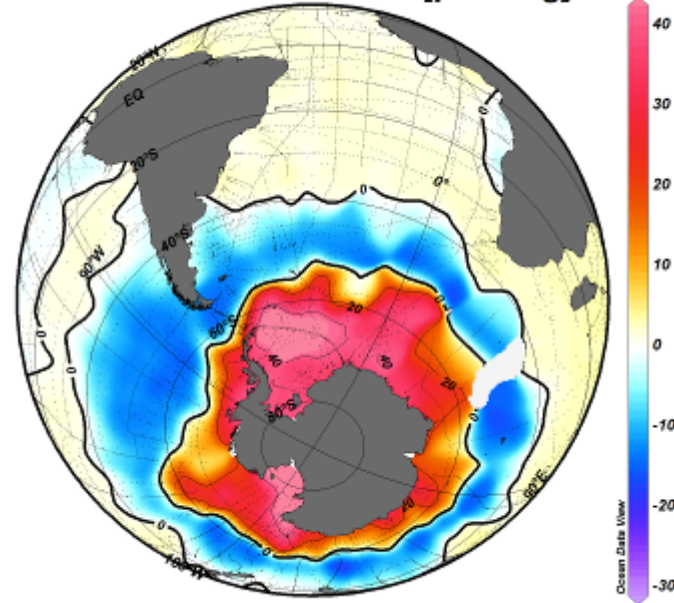
Surface Water Nitrate [$\mu\text{mol/kg}$]



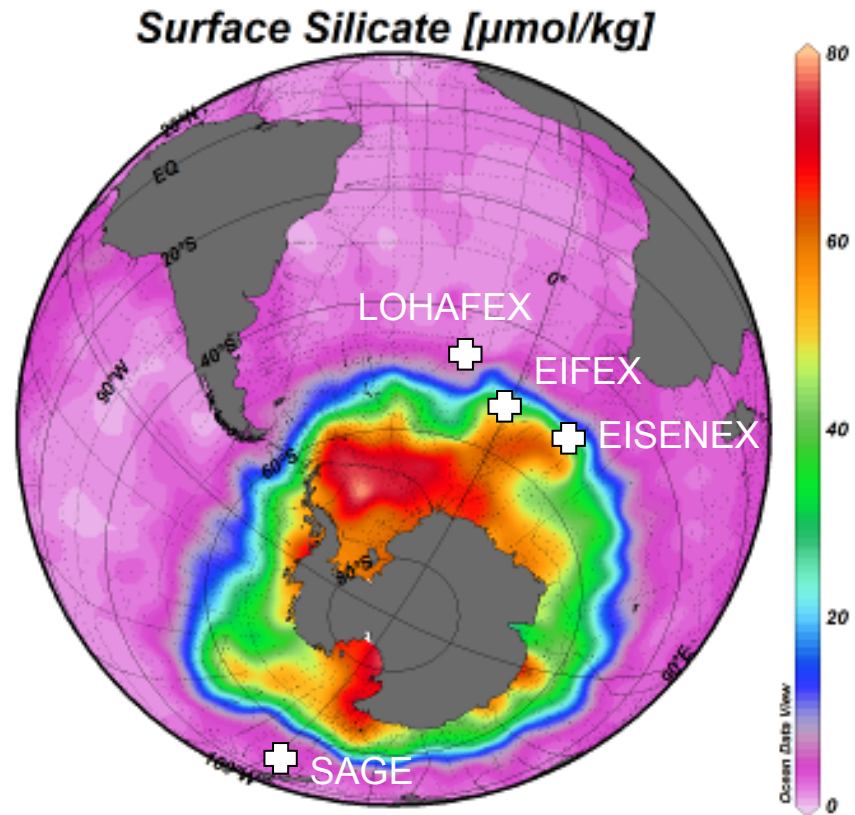
Surface Silicate [$\mu\text{mol/kg}$]



Surface Silicate-Nitrate [$\mu\text{mol/kg}$]

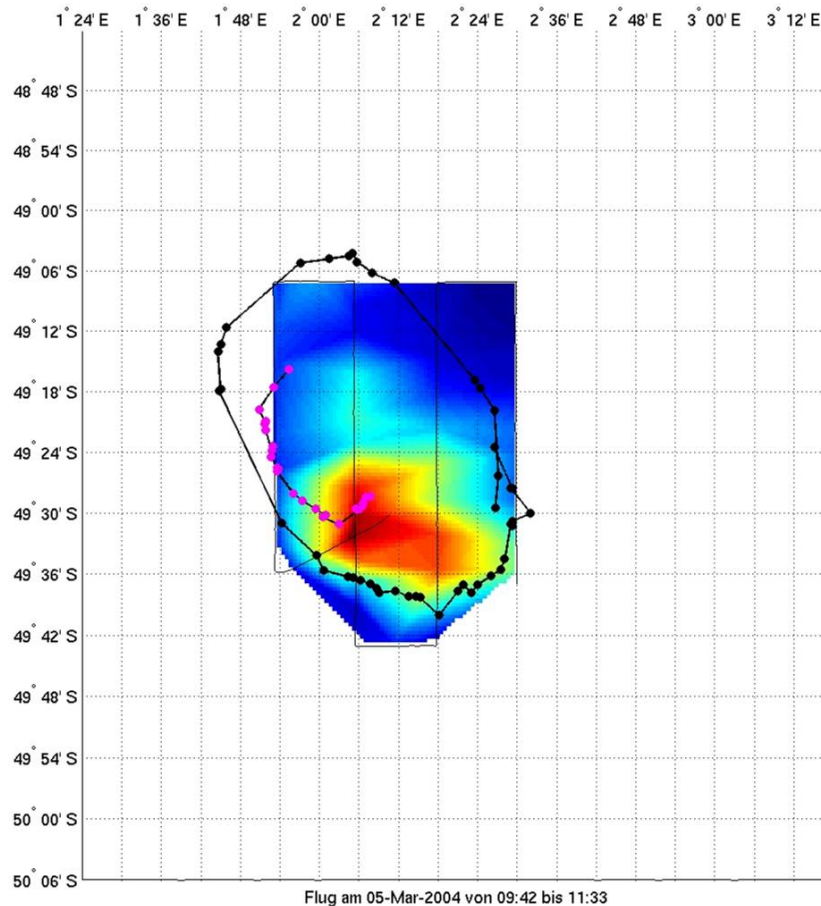


Iron enrichment experiments in Silicate depleted waters, will neither yield diatom blooms nor export of organic debris



Experiment	Initial Conditions			
	PO4	NO3	SiO4	
Eisenex	1.6	23.5	14.2	
Eifex	1.8	25	18.9	
Sage	0.7	9	0.9	Si-depleted
Lohafex	1.3	20	2	Si-depleted

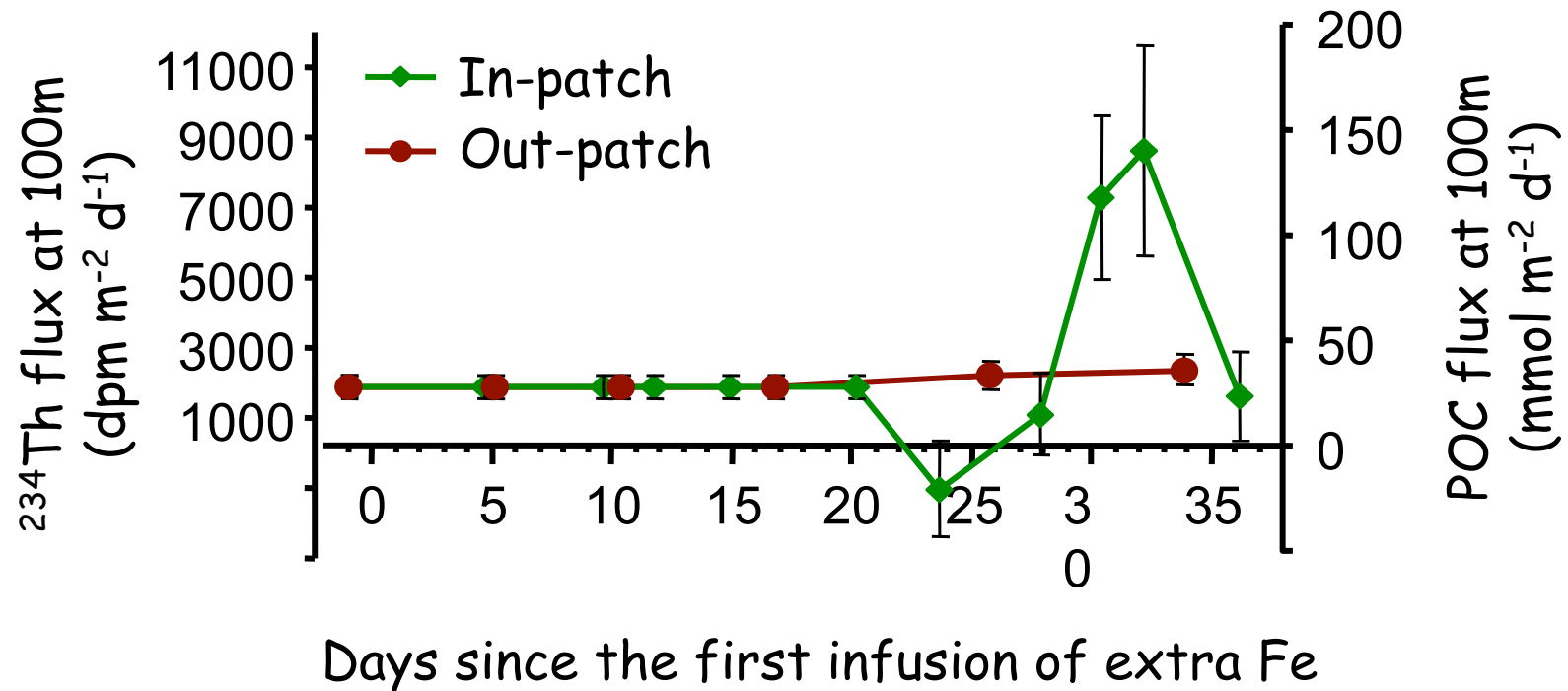
European Iron Fertilization EXperiment (EIFEX, Feb.-March 2004 at 59°S, 2°E)



An eddy located in a meander just south of the Polar Front was fertilized with Fe and monitored for 36 days afterwards. A phytoplankton bloom, dominated by diatoms, developed.

Chl-a LIDAR image obtained by helicopter 22 days after Fe infusion. Dots and line indicate the buoy track that closely followed the patch (Image V. Strass, AWI)

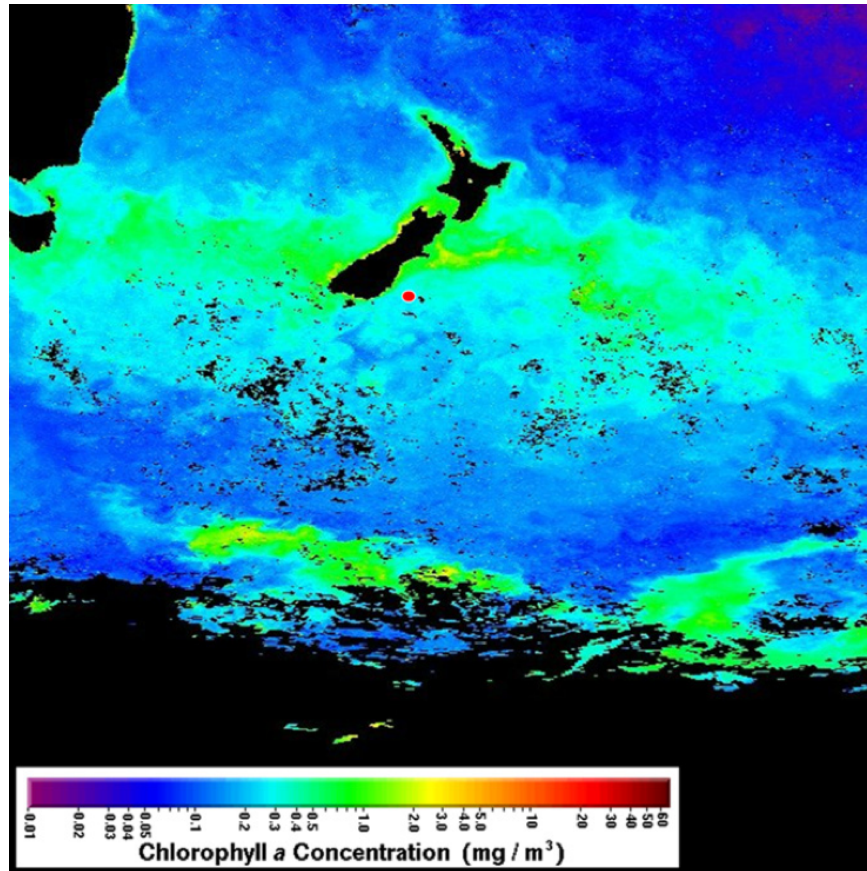
EIFEX in initial high Si waters:
big diatoms bloom and final massive export event



European Iron Fertilization EXperiment EIFEX:

Time series of ²³⁴Th and particulate organic carbon (POC) export fluxes at 100m

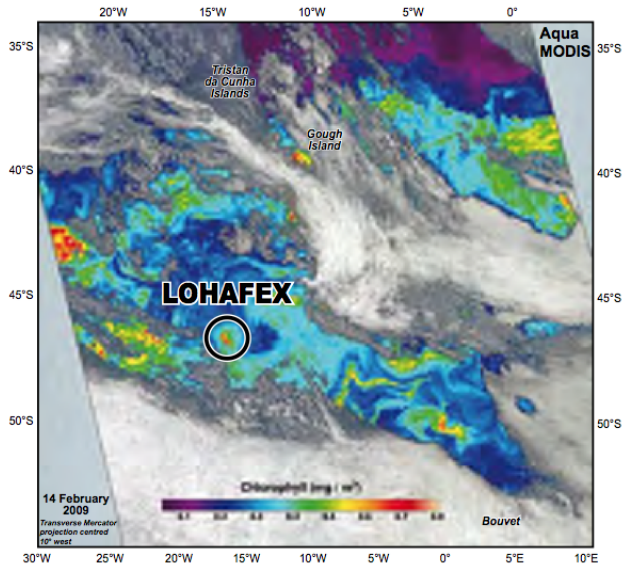
SOLAS air–sea gas exchange experiment (SAGE) 2004



- mostly ~twofold enhancement microbial loop
- no diatoms due to low initial Si surface waters
- no export into deeper waters

Harvey et al. (2011) DSR-2
Peloquin et al. (2011) DSR-2

LOHAFEX 2009



low Si thus no diatoms response;
 modest bloom (Chl a maximum = $1.5 \text{ mg}\cdot\text{m}^{-3}$)
 of very small picophytoplankton;
 also some Phaeocystis, colonies after ~2 weeks,
 next colonies disappear again,
 likely due to intense grazing;
 stimulation of many zooplankton,
 doubling of faecal pellet production rate

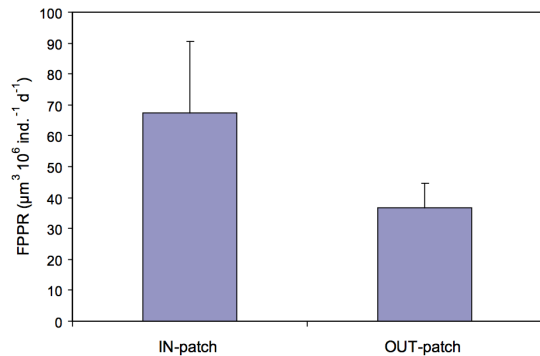
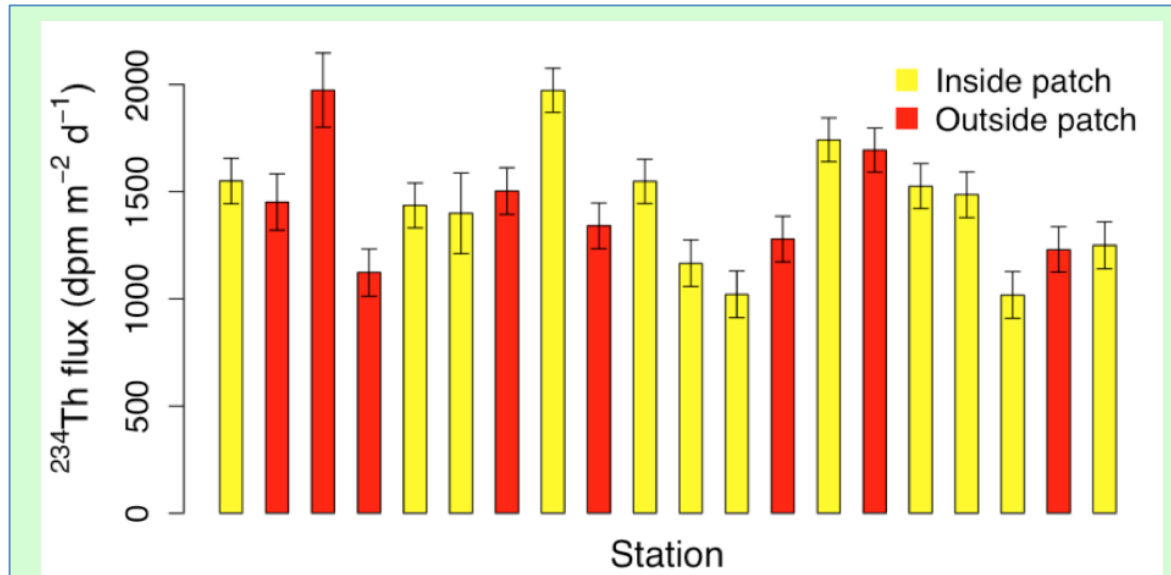


Figure 6. Faecal pellet production rate (as volume, $\mu\text{m}^3 \times 10^6 \text{ ind.}^{-1} \text{ d}^{-1}$) in *Calanus simillimus* averaged at the stations inside the fertilised patch (days 4–36 after fertilisation) and outside the patch (days 16–35).



Inside-Patch double abundance of:
 "...*Themisto gaudichaudii*, an active, aggressive, indiscriminate carnivore which attacks organisms much larger than itself with its formidable clawed appendages.."

Mazzocchi et al (2009)
 GLOBEC Newsletter



Export by ^{234}Th deficiency method:
 no significant difference Inside-patch and Outside-patch
 Confirms that for Carbon sequestration you need
 high-Silicate waters supporting blooms of large diatoms

Rutgers van der Loeff, unpublished results

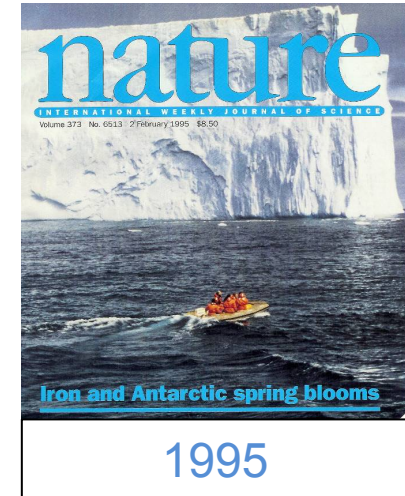
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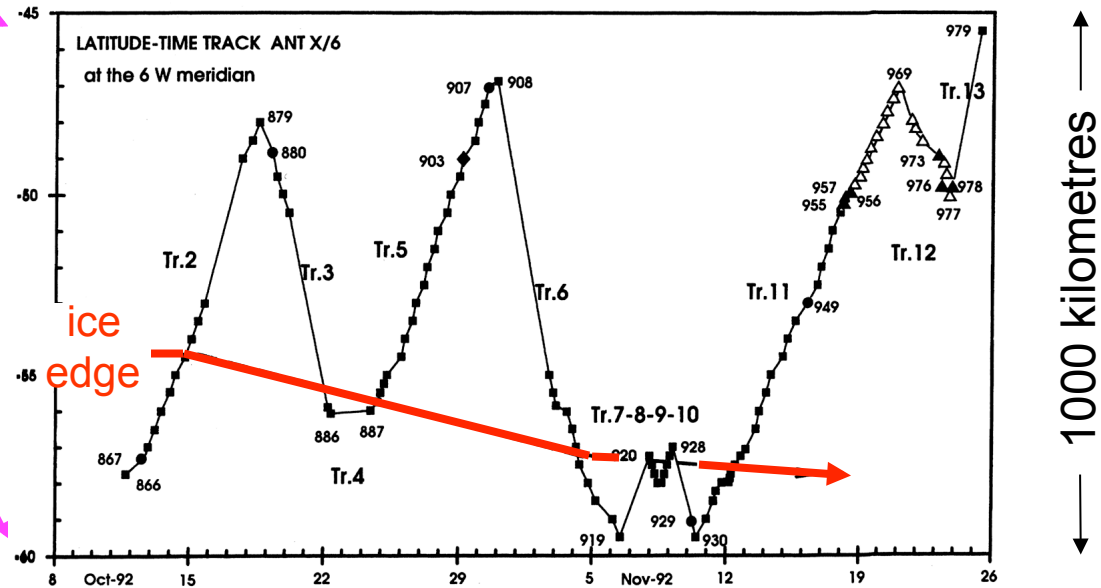
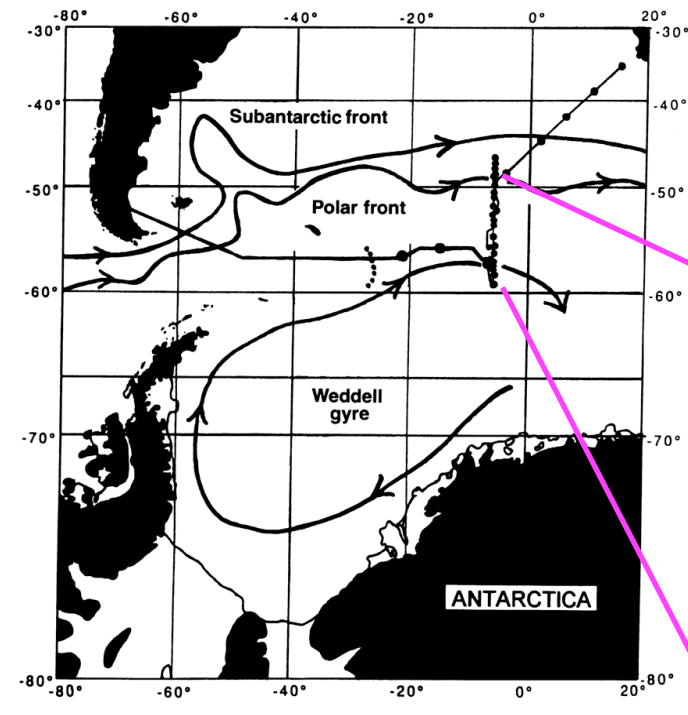


The natural iron fertilization studies:

2) Polar Front (1992) austral spring development



1995



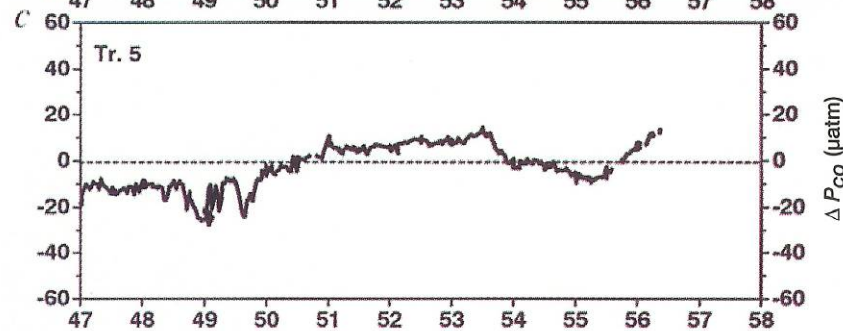
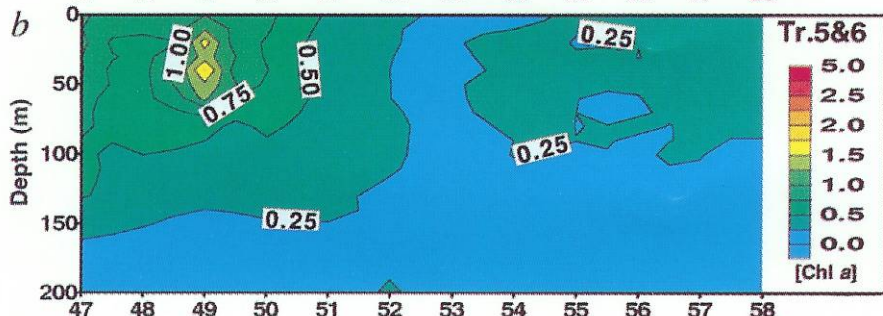
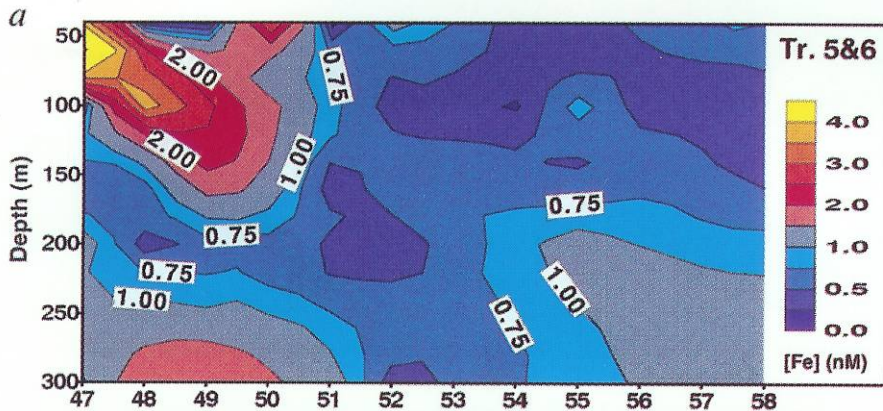
two months austral spring evolution



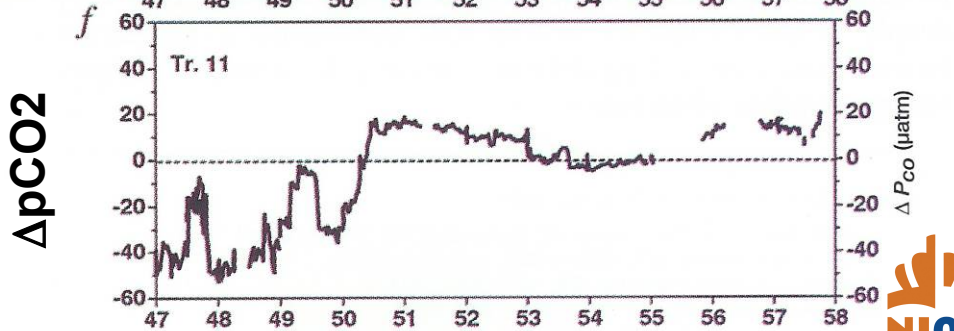
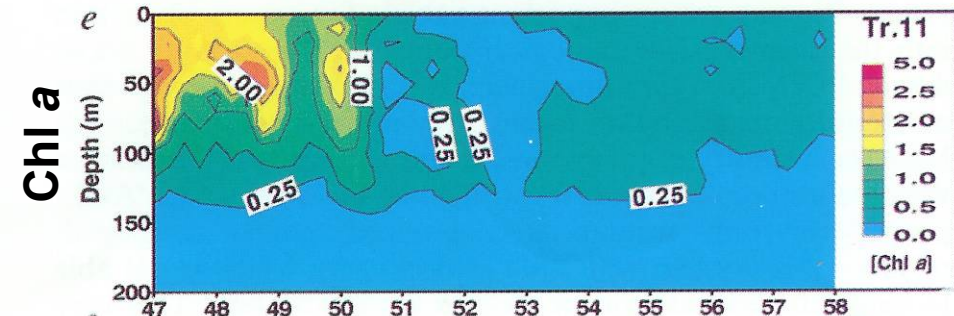
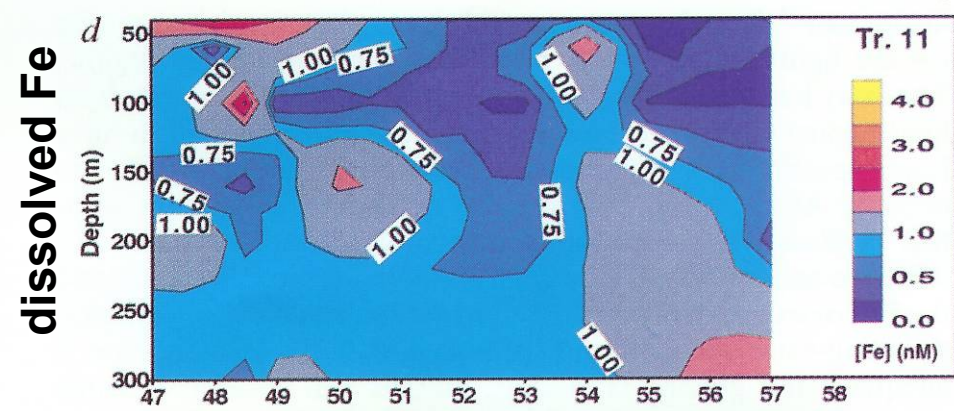
natural iron fertilization at the Polar Front

large diatoms blooms grow and use iron and CO₂

PF



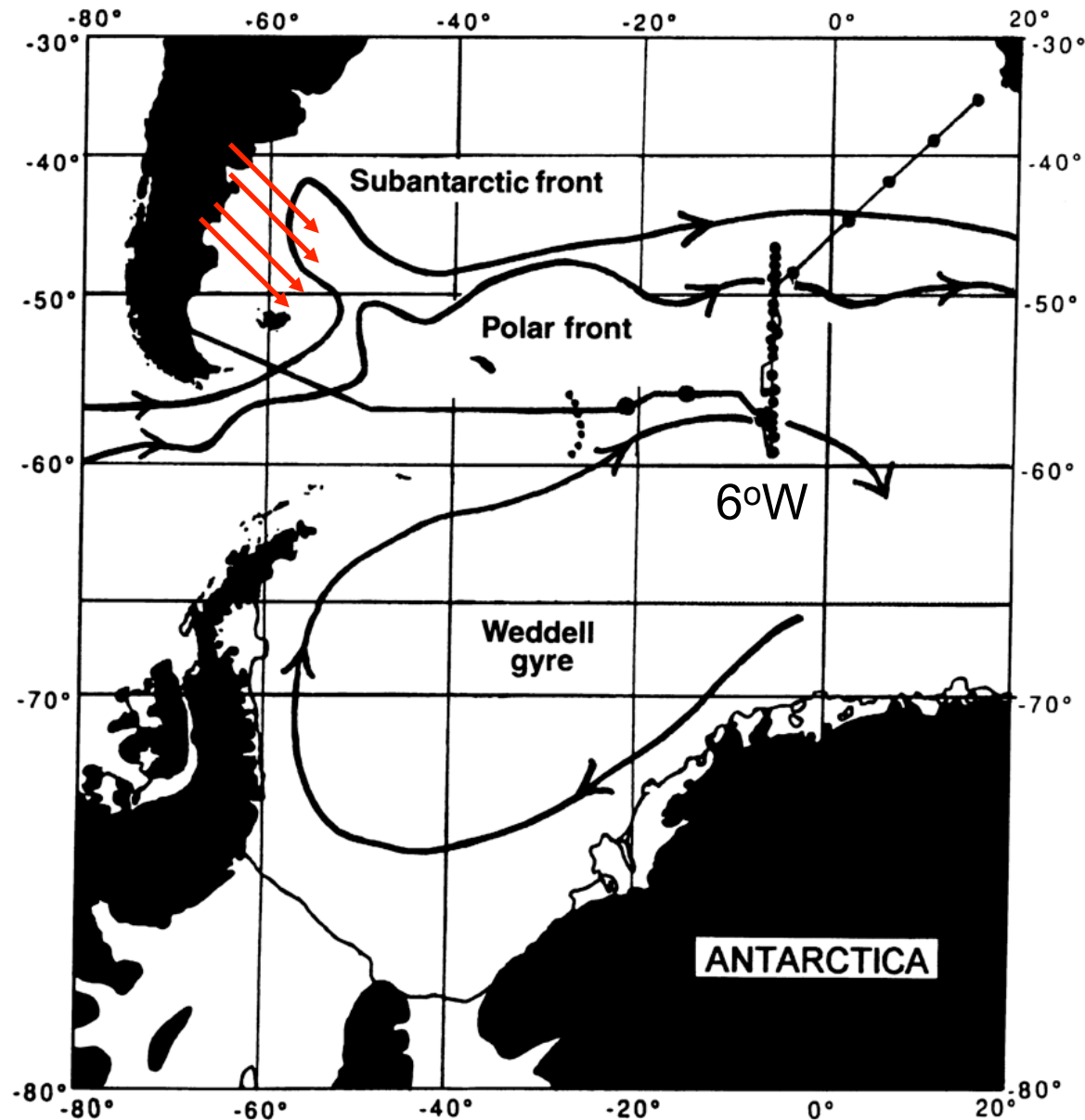
PF three weeks later



Perhaps the extra Fe
at the Polar Front
at 6 °W comes
from strong dust
storms
input off Patagonia,
(Argentina)

soil and dust
comprises about 4%
iron by weight

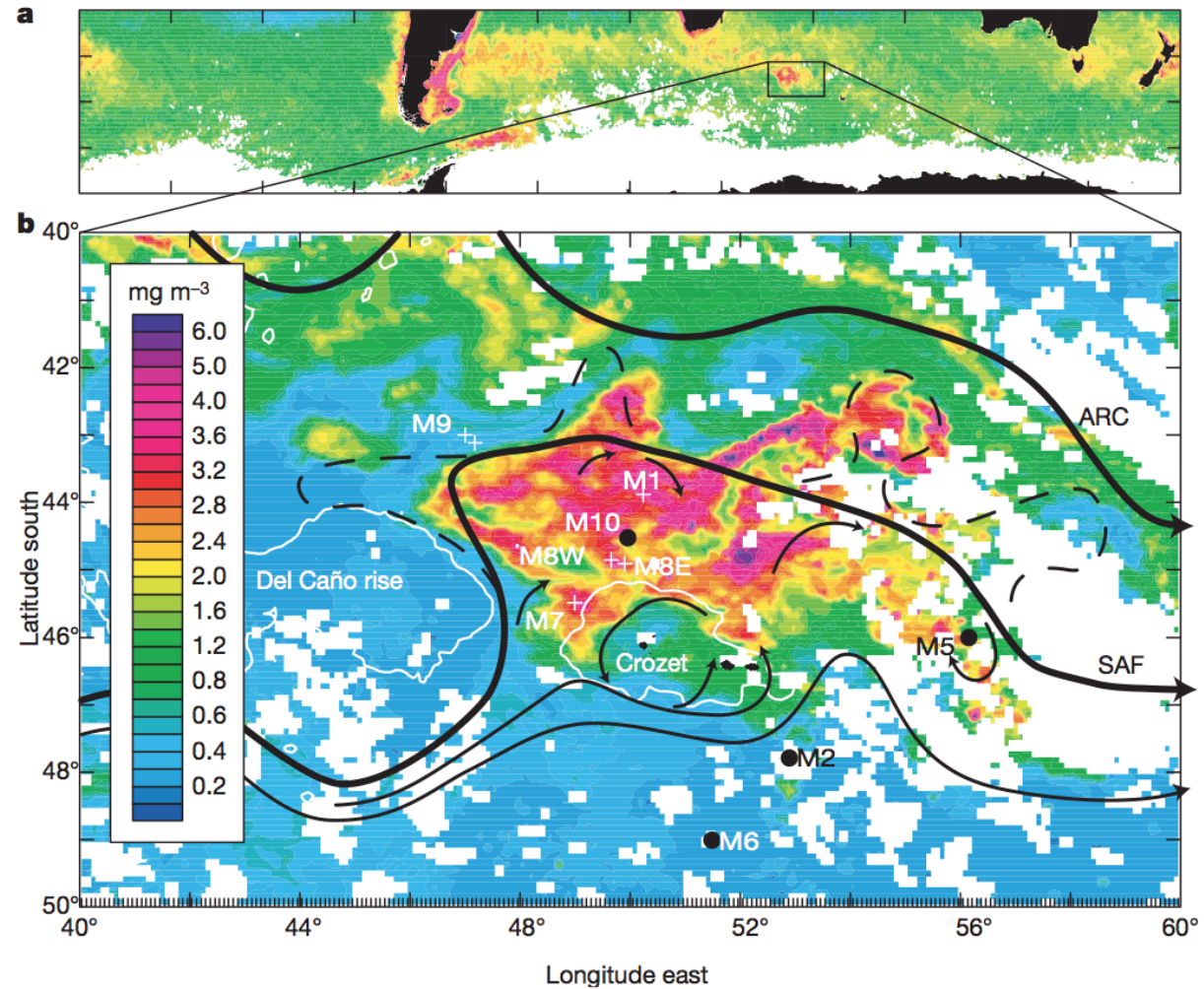
if only small part of
this dust dissolves in
seawater you will find
higher concentrations
of dissolved Fe



The natural iron fertilization studies:

3) Crozex at Crozet Island Plateau (2004-2005)

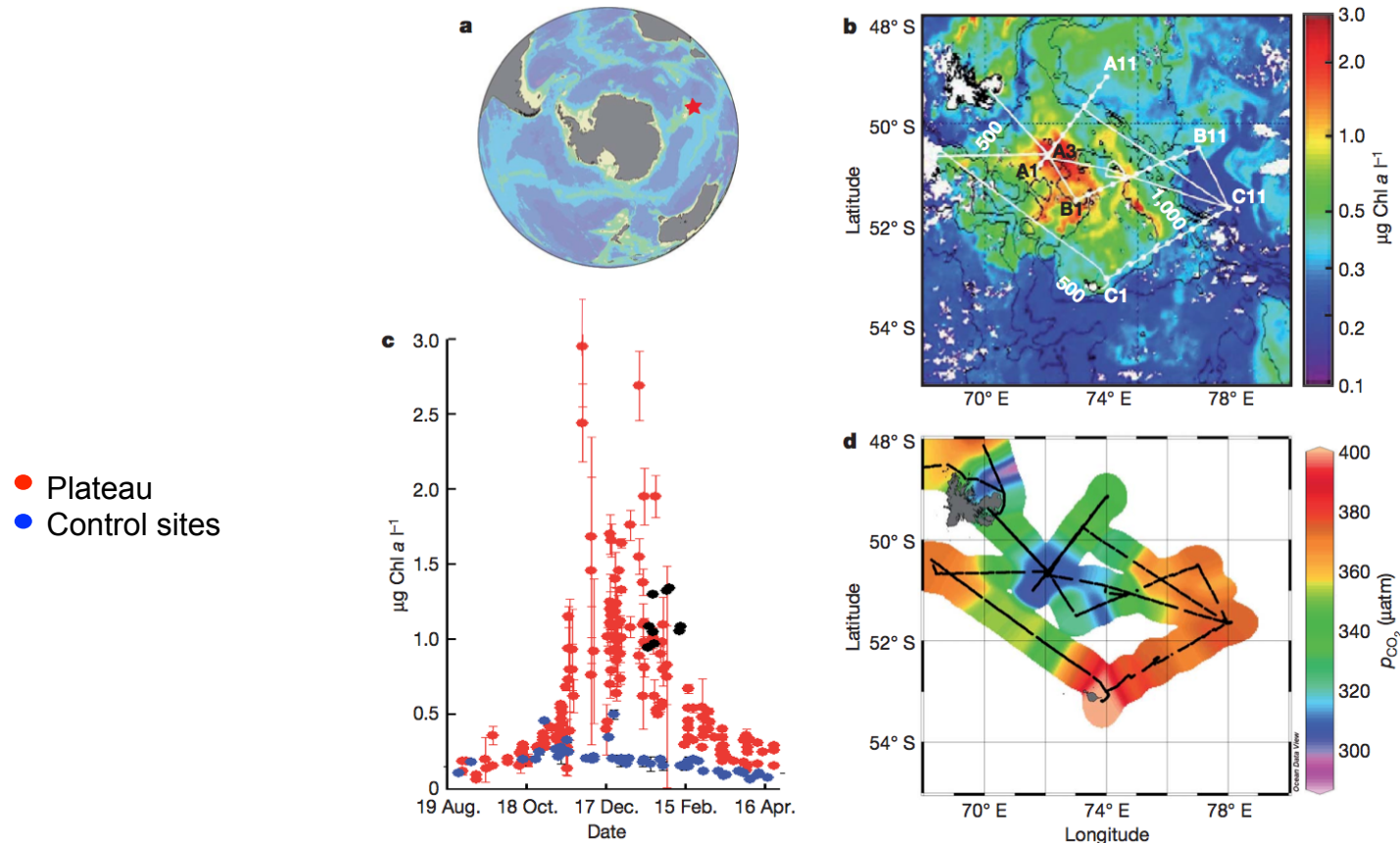
Chlorophyll *a*
observed from
satellite



C:Fe export efficiency will be discussed

Pollard et al. (2009)

The natural iron fertilization studies: 4) Keeps at Kerguelen Plateau (2005)



" The addition of DFe occurs slowly and continuously during natural fertilization, whereas purposeful additions of large amounts of iron within a short period lead to the loss of most (80–95%) of the added DFe during mesoscale enrichment experiments. "

Blain et al. (2007)

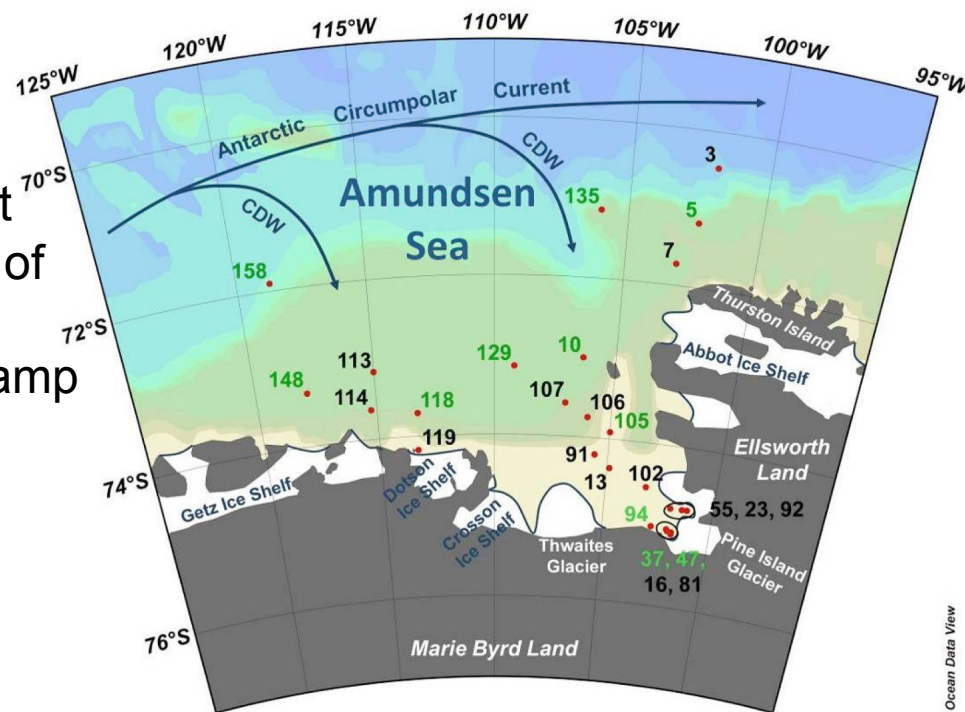
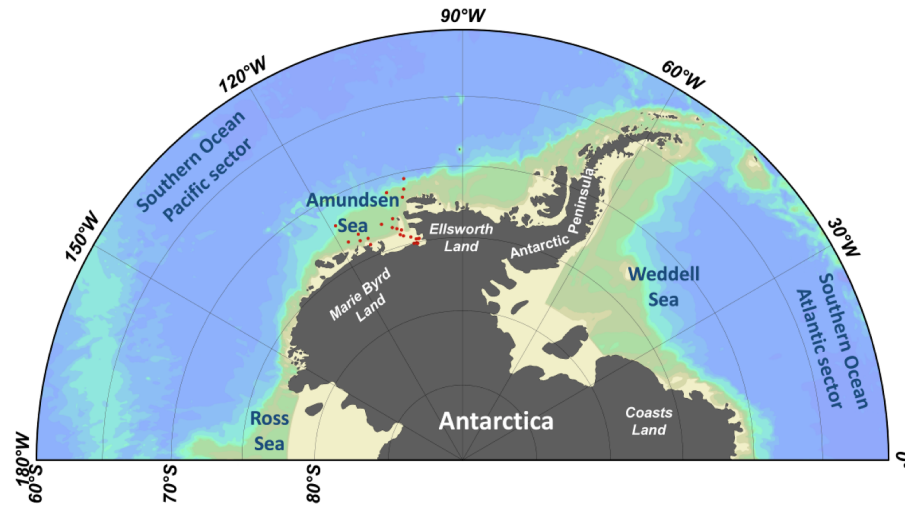
C:Fe export efficiency will be discussed

The natural iron fertilization studies:

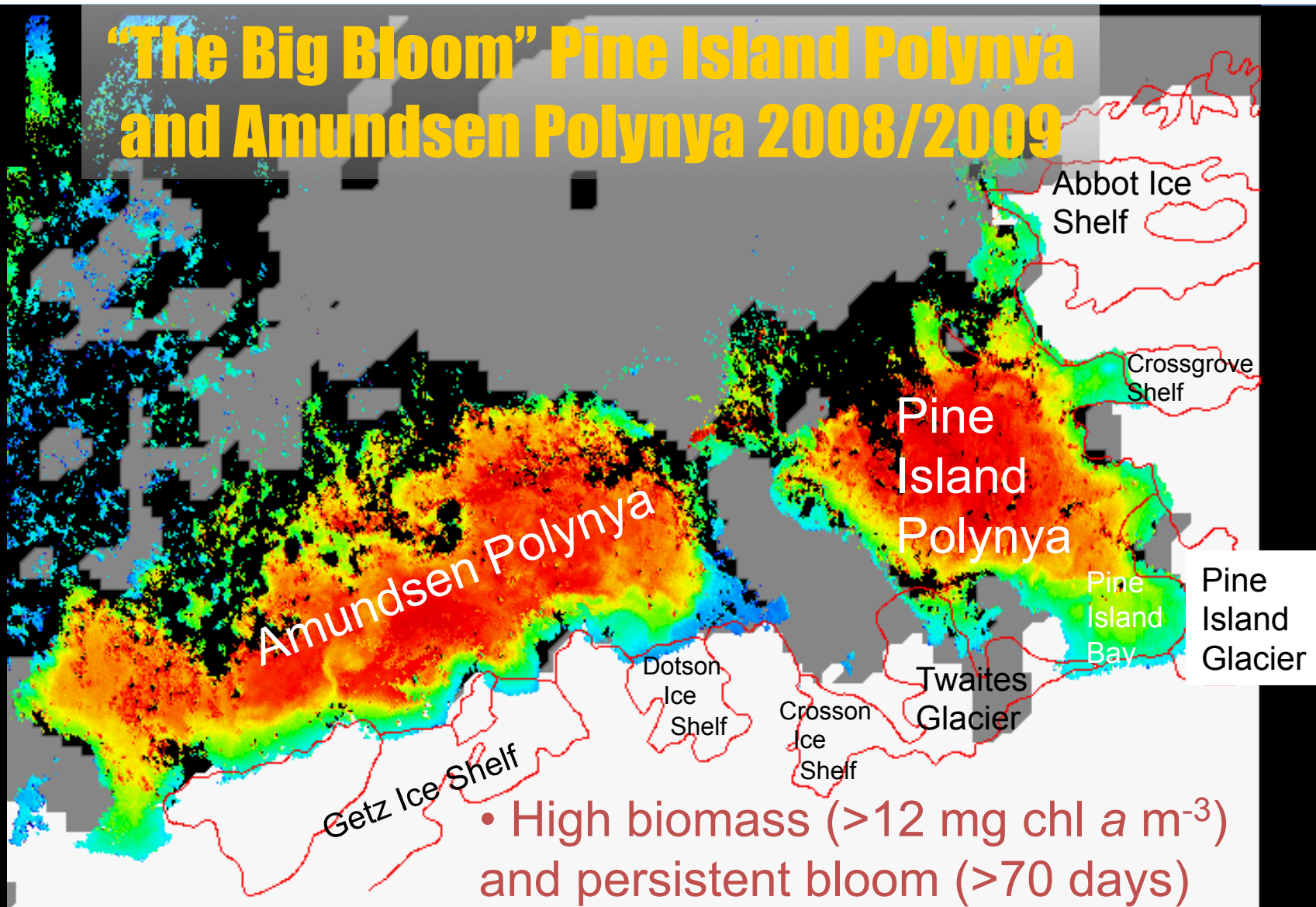
5) DynaLife at Pine Island Glacier and Polynia

February 2009
cruise aboard
Nathaniel Palmer

Collaborative project
with Stanford group of
Kevin Arrigo,
Anne-Carlijn Alderkamp



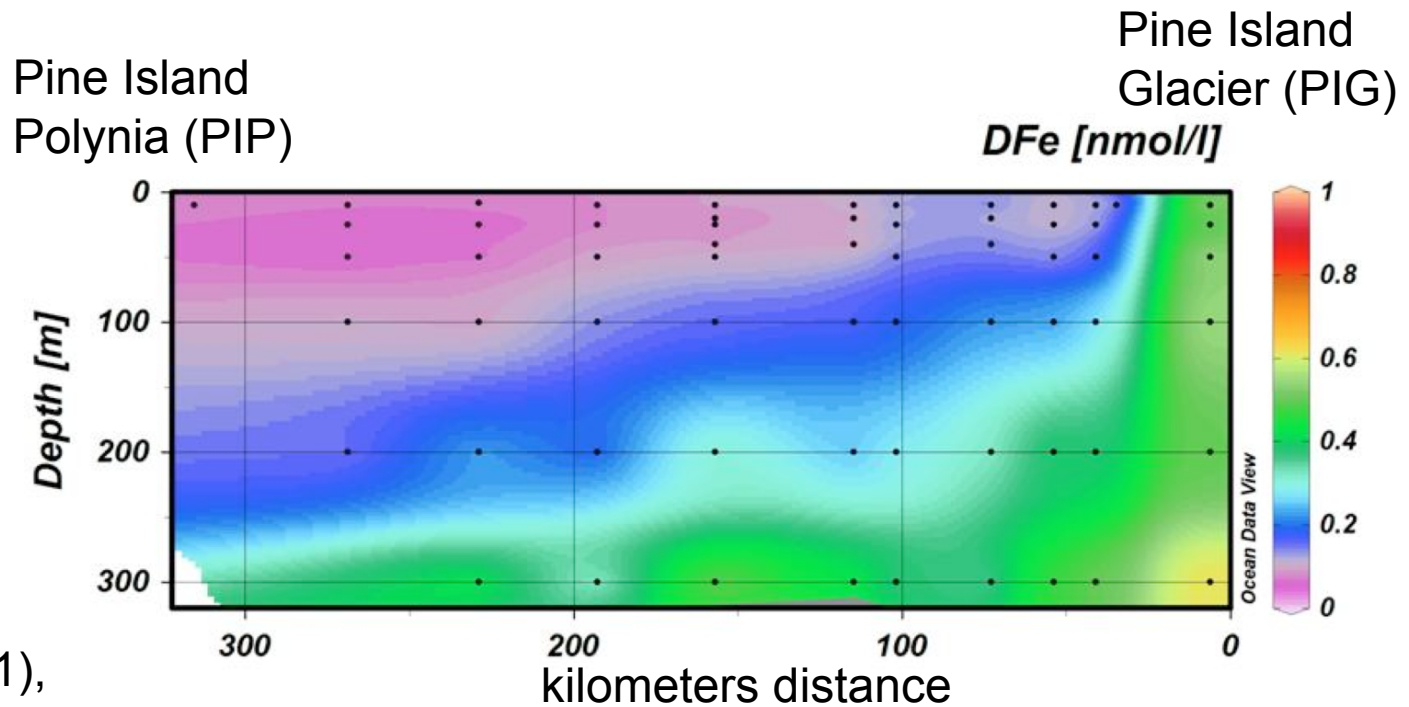
“The Big Bloom” Pine Island Polynya and Amundsen Polynya 2008/2009



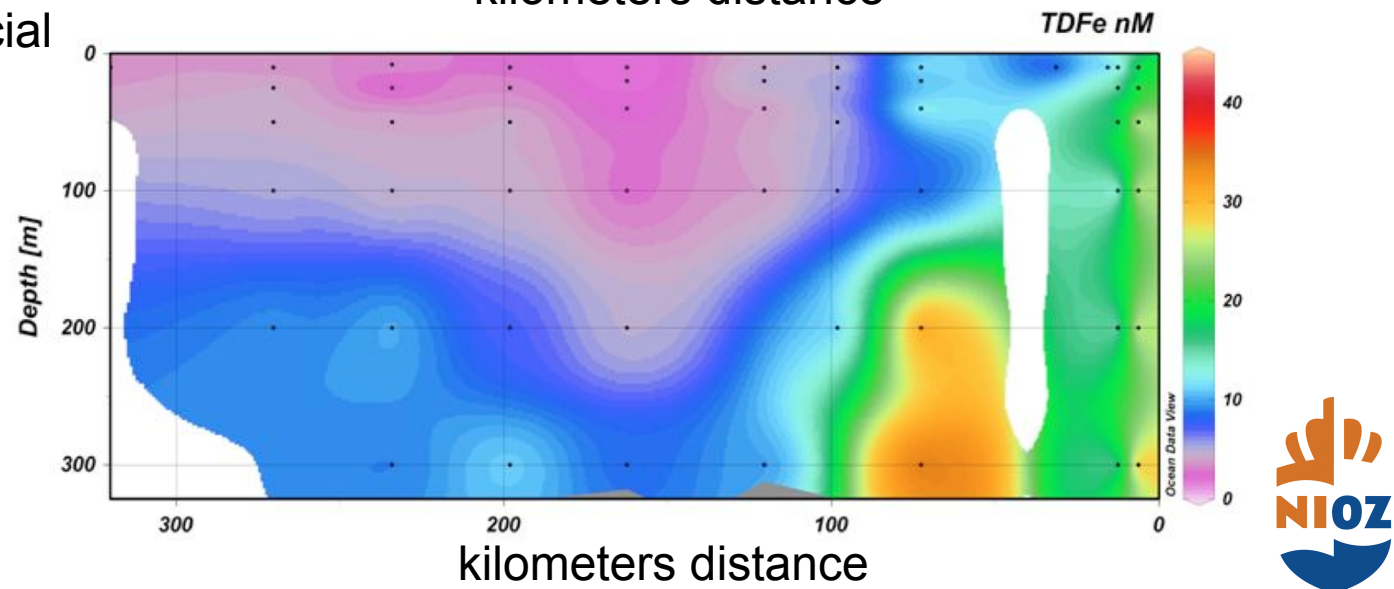
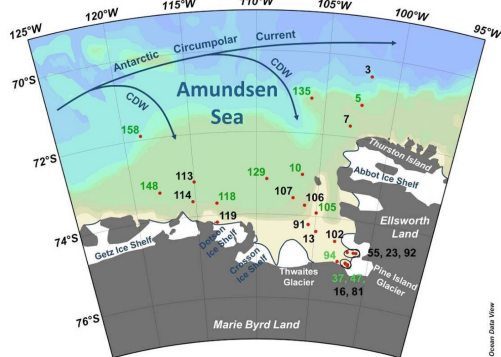
Satellite image of 20 Jan 2009



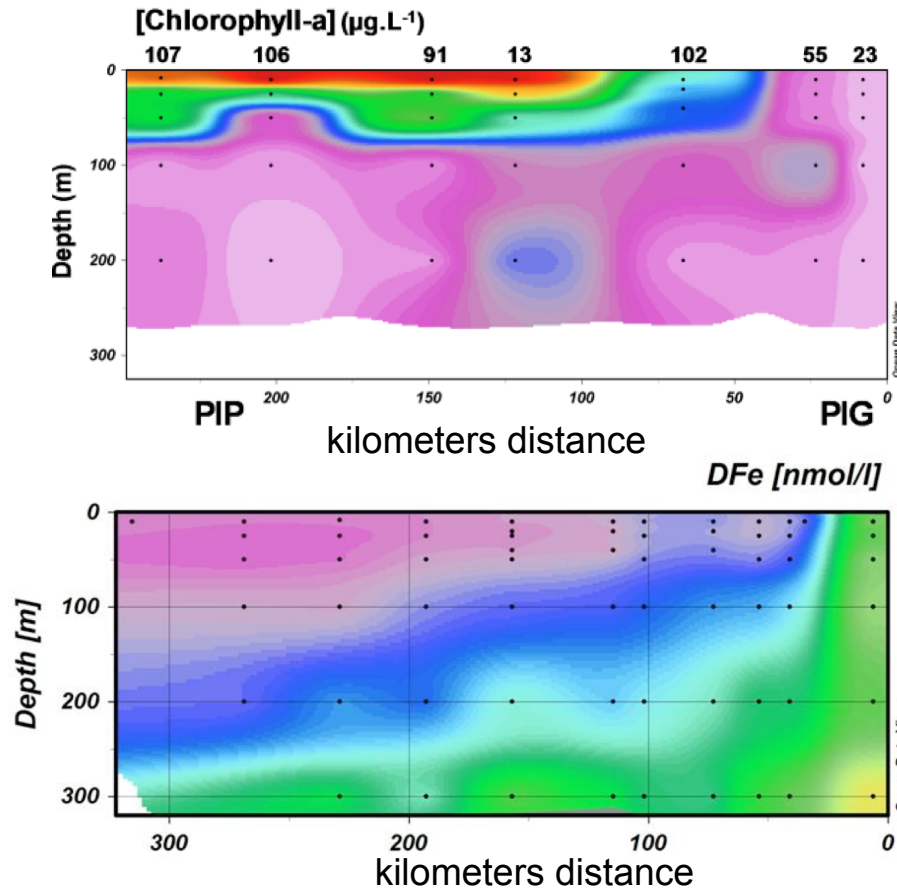
Strong supply by the glacier of dissolved Fe and particulate 'Total Dissolvable' Fe



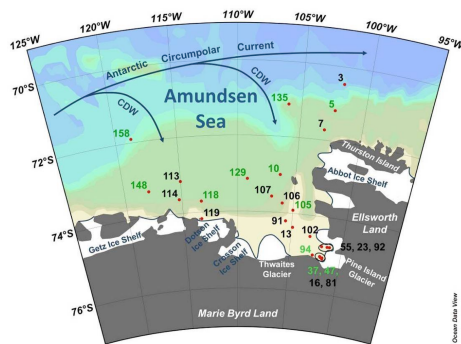
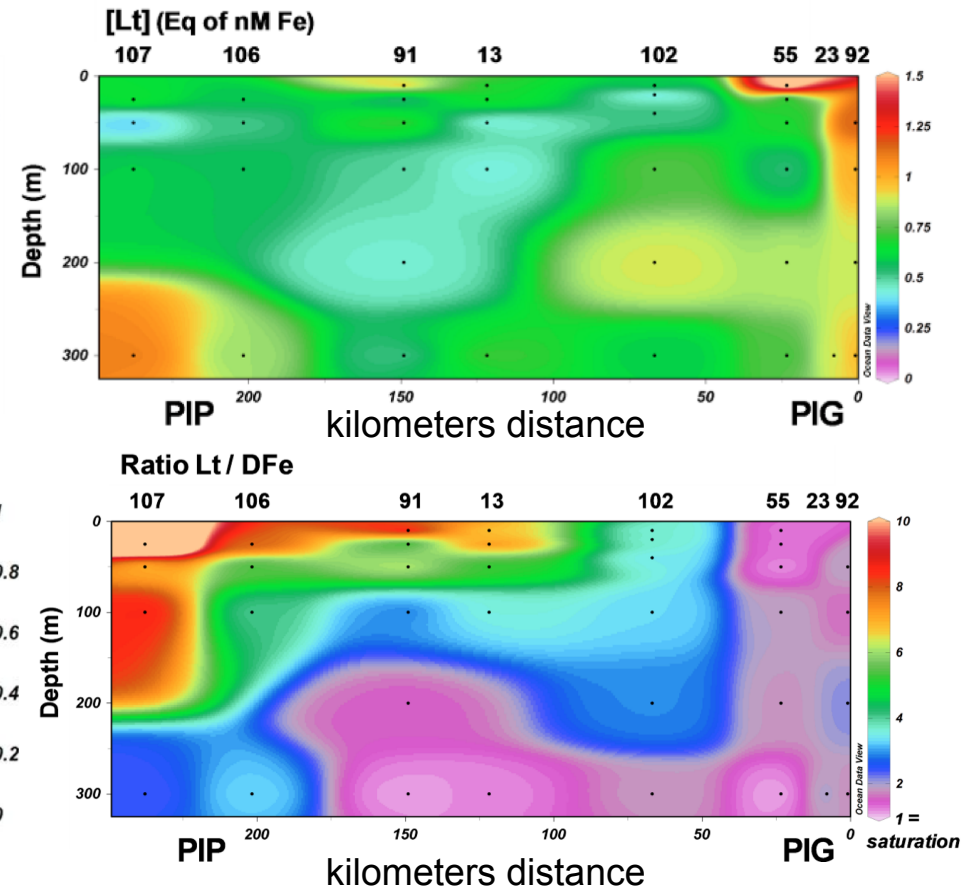
Gerringa et al. (2011),
submitted, DSR II special



Intense diatom bloom in the Pine Island Polynia



Organic ligand [Lt] that is binding the dissolved Fe has high abundance near Pine Island Glacier



Thuroczy et al. (2011),
submitted, DSR II special

Excess organic ligand plotted as
ratio Lt / DFe
near glacier hardly any excess Lt
akin to *in situ* Fe fertilization exps



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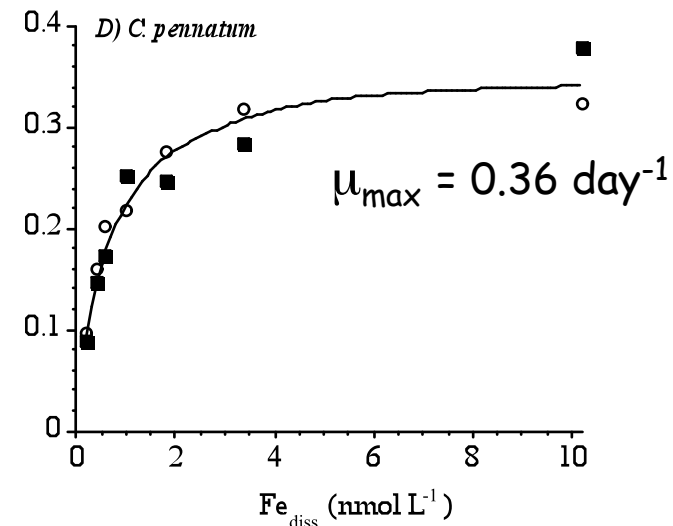
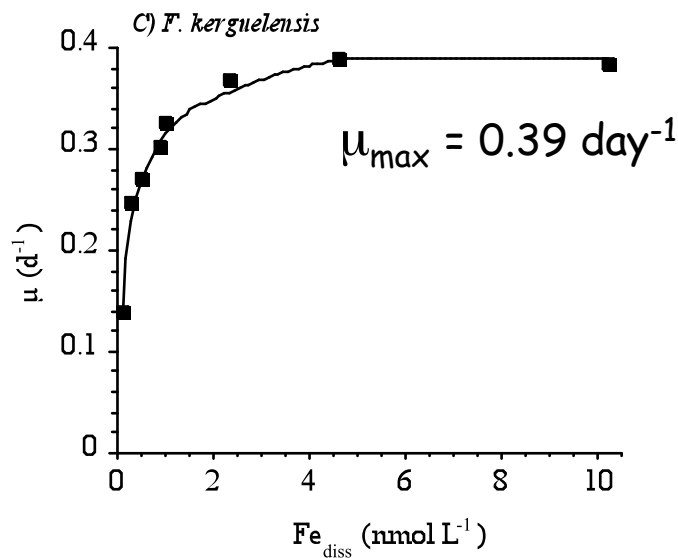
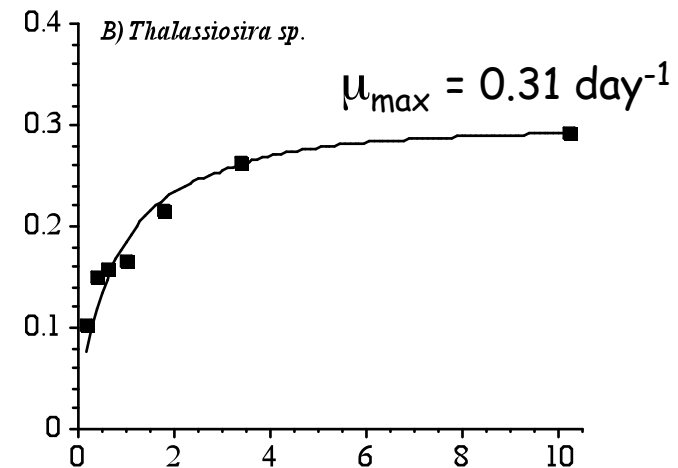
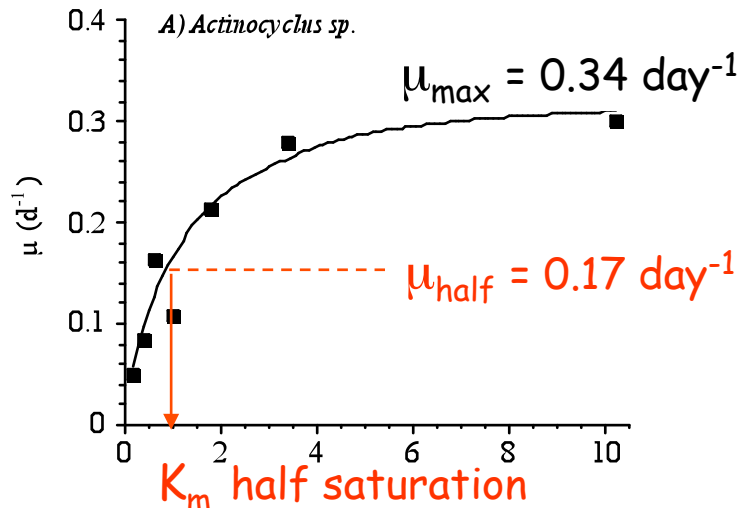
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Iron Requirement for Growth of Large Diatoms:

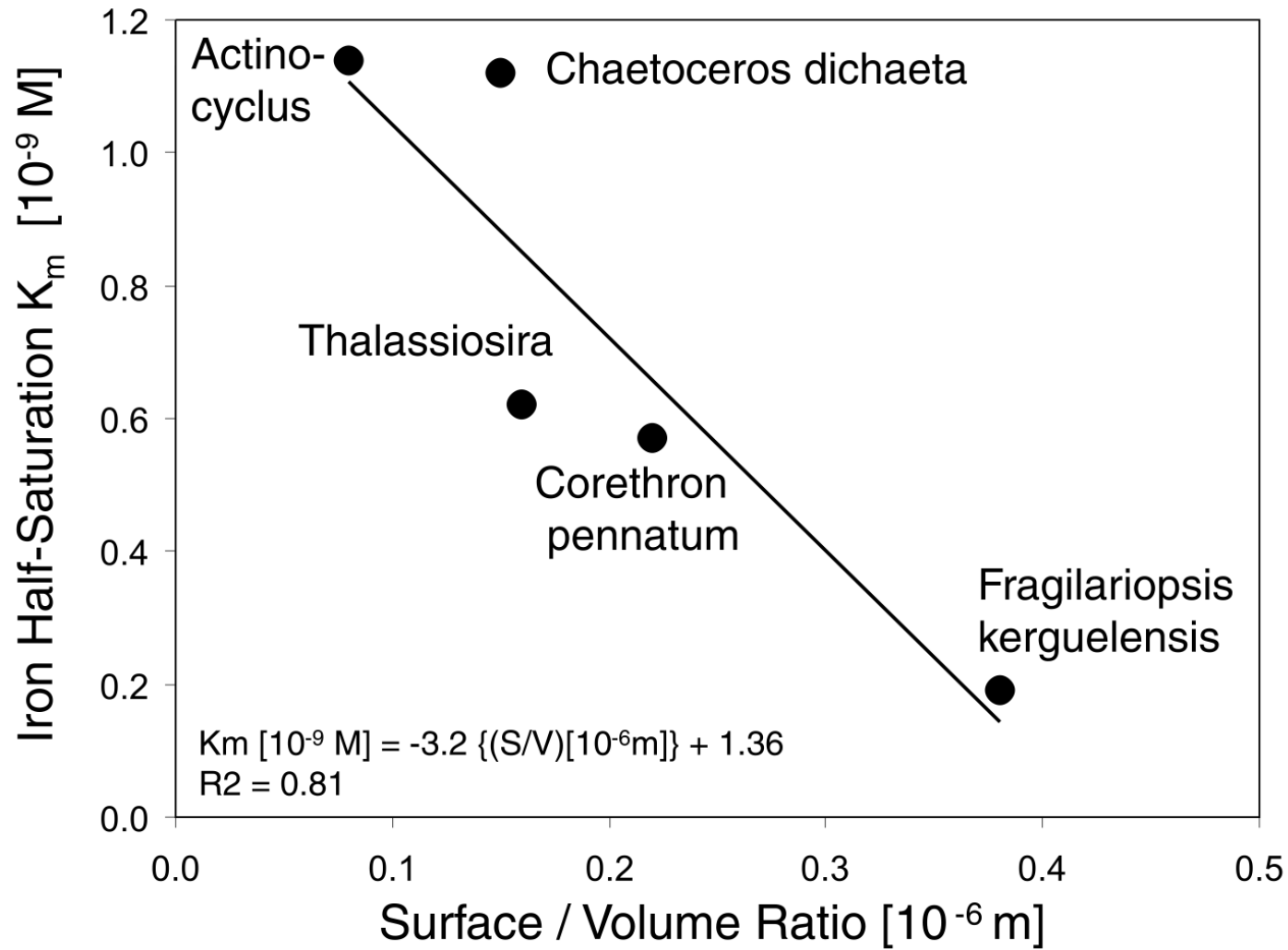
growth curves for dissolved Fe [nM] in pristine (EDTA-free) Antarctic seawater

$$\text{Monod: } \mu = \mu_{\max} \left\{ \frac{[\text{Fe}]}{K_m + [\text{Fe}]} \right\}$$



Timmermans et al. (2004), *Limnol. & Ocean.*, 49, 2141





← bigger diatoms need higher ambient dissolved Fe



Iron Content of Growing Diatoms

Cellular iron contents of plankton during the Southern Ocean Iron Experiment (SOFeX)

Benjamin S. Twining^{a,*}, Stephen B. Baines^a, Nicholas S. Fisher^{a,c},
Michael R. Landry^b

- intracellular Fe concentration **$Q = 0.234 \text{ mol m}^{-3}$** of diatoms in the Fe-replete SOFeX-South patch
- corresponding element ratio C : Fe = 25000 : 1 of diatoms in the Fe-replete SOFeX-South patch
- this is the first ever reliable Fe cell quota

Cell Demand [mol Fe s⁻¹] = Diffusive Supply [mol Fe s⁻¹]

at steady state one expects the product of the specific growth rate μ with intracellular Fe concentration Q and cell volume V to be equal to the diffusive supply of dissolved Fe to the cell:

growth demand = diffusive supply

$$\mu Q V = 4 \pi r D \alpha [\text{Fe}]$$

where

μ [sec⁻¹] is specific growth rate,

Q [moles m⁻³] the intracellular Fe concentration,

V [m³] is the volume of an individual cell,

r [m] the cell radius of a round (spherical) cell,

D [m² s⁻¹] molecular diffusion coefficient of Fe in seawater,

α dimensionless geometric correction factor for diatoms having non-spherical shape

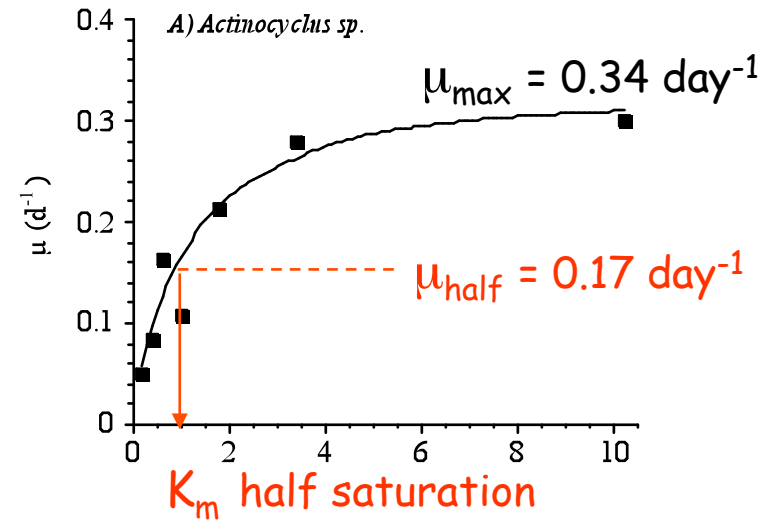
$[\text{Fe}]$ [mol m⁻³] the bulk concentration of dissolved Fe in seawater

De Baar et al., in press

Now substituting for dissolved [Fe] the K_m [mol m⁻³] at half of the maximum growth rate i.e. at

{0.5 μ_{max} } of the Monod equation

$$\mu = \mu_{max} \left\{ \frac{[Fe]}{K_m + [Fe]} \right\}$$



At half maximum growth rate:

cellular demand [mol Fe s⁻¹] = diffusive supply rate [mol Fe s⁻¹]

$$0.5 \mu_{max} Q V = 4 \pi r D \alpha [K_m]$$

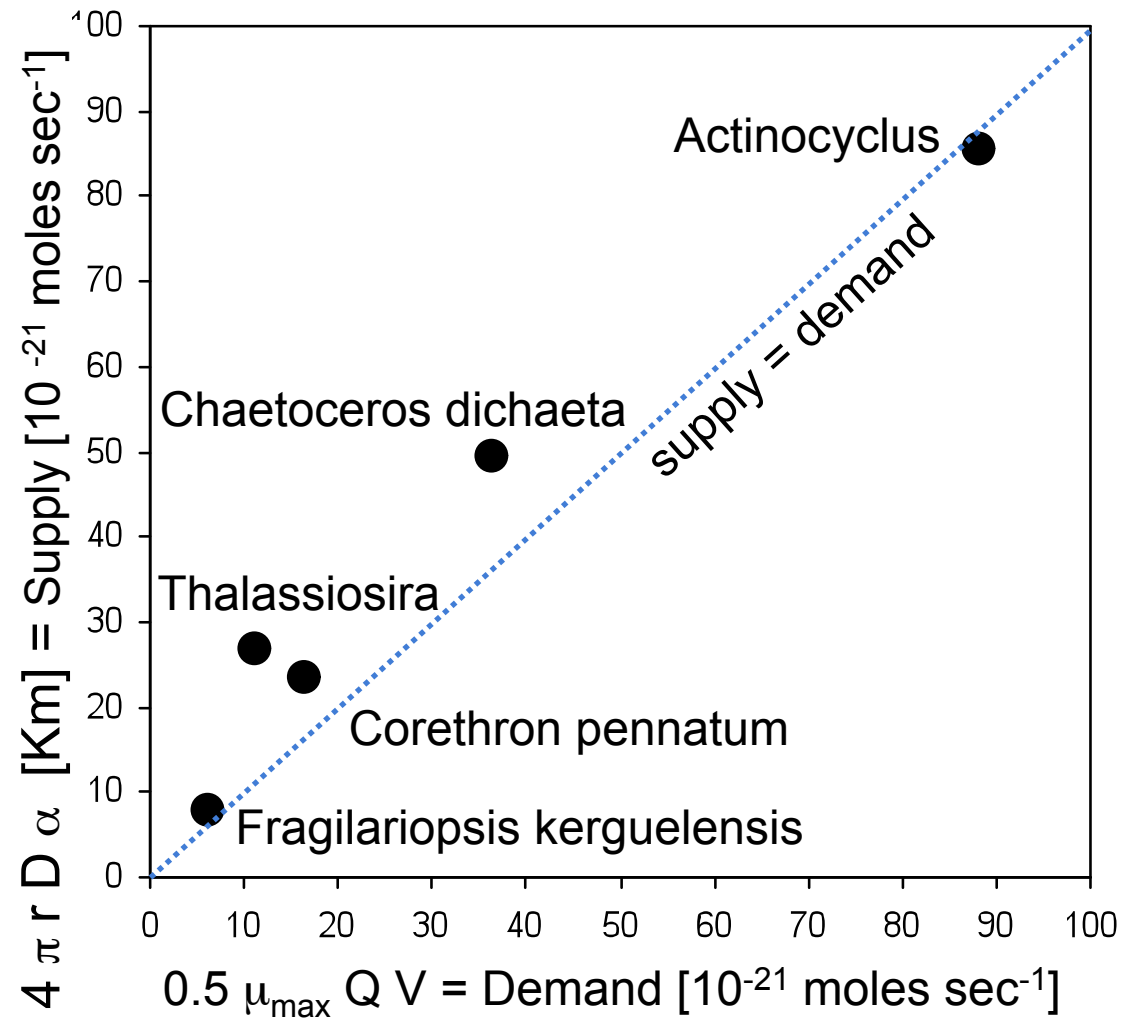
Klaas Timmermans
L&O, 2004

$Q = 0.234 \text{ mol m}^{-3}$
Benjamin Twining,
DSR, 2004

Klaas Timmermans
L&O, 2004

De Baar et al., in press

Diffusion Supply = Demand for Growth



growth rate of large oceanic diatoms is controlled by the Fe concentration in ambient seawater



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 - (1988) Give me half a supertanker
 - (2011) GeoEngineering, London Convention, ISIS Consortium





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Contribution to the Theme Section 'Implications of large-scale iron fertilization of the oceans'

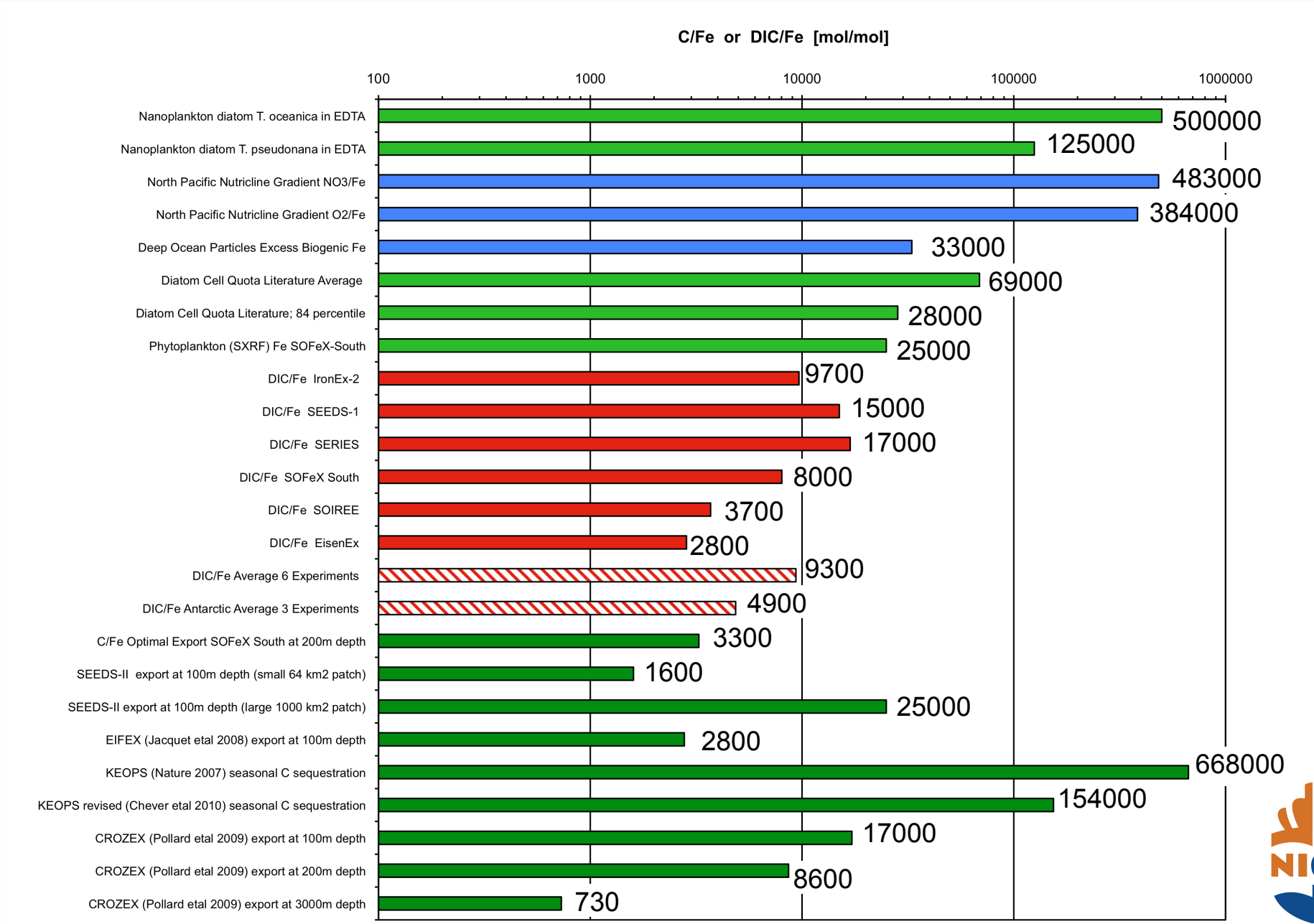


Efficiency of carbon removal per added iron in ocean iron fertilization

Hein J. W. de Baar^{1,2,*}, Loes J. A. Gerringa², Patrick Laan², Klaas R. Timmermans²

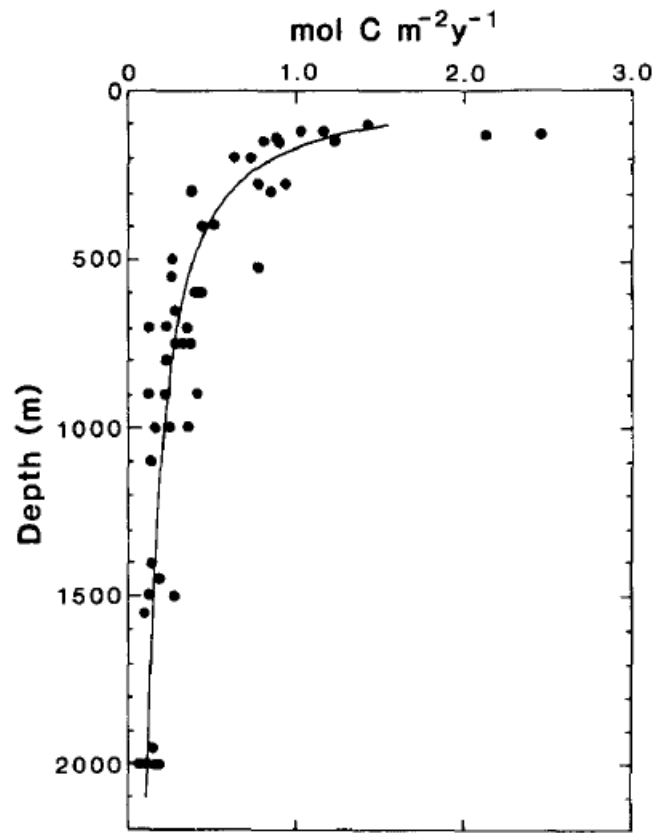
True element ratio values	Complete equation	Eq. no.
$(C:Fe)_{\text{large-diatoms-optimal}}$		
Efficiency ratio values		
$(\Delta DIC:Fe)_{\text{NCP}}$	$(\Delta DIC_{\text{in-patch}} - \Delta DIC_{\text{control-station}}):Fe$	(1)
$(C:Fe)_{\text{gas-flux efficiency}}$	$(Flux_{\text{fertilized-patch}} - Flux_{\text{control-station}}) / Fe_{\text{added}}$	(2)
$(C:Fe)_{\text{export-efficiency-100m}}$	$(C_{\text{export-in-patch}} - C_{\text{export-control-site}})_{100m} \cdot Fe$	(3)
$(C:Fe)_{\text{export-efficiency-250m}}$	$(C_{\text{export-in-patch}} - C_{\text{export-control-site}})_{250m} \cdot Fe$	

Extra C:Fe efficiency values of EIFEX, KEOPS, CROZEX



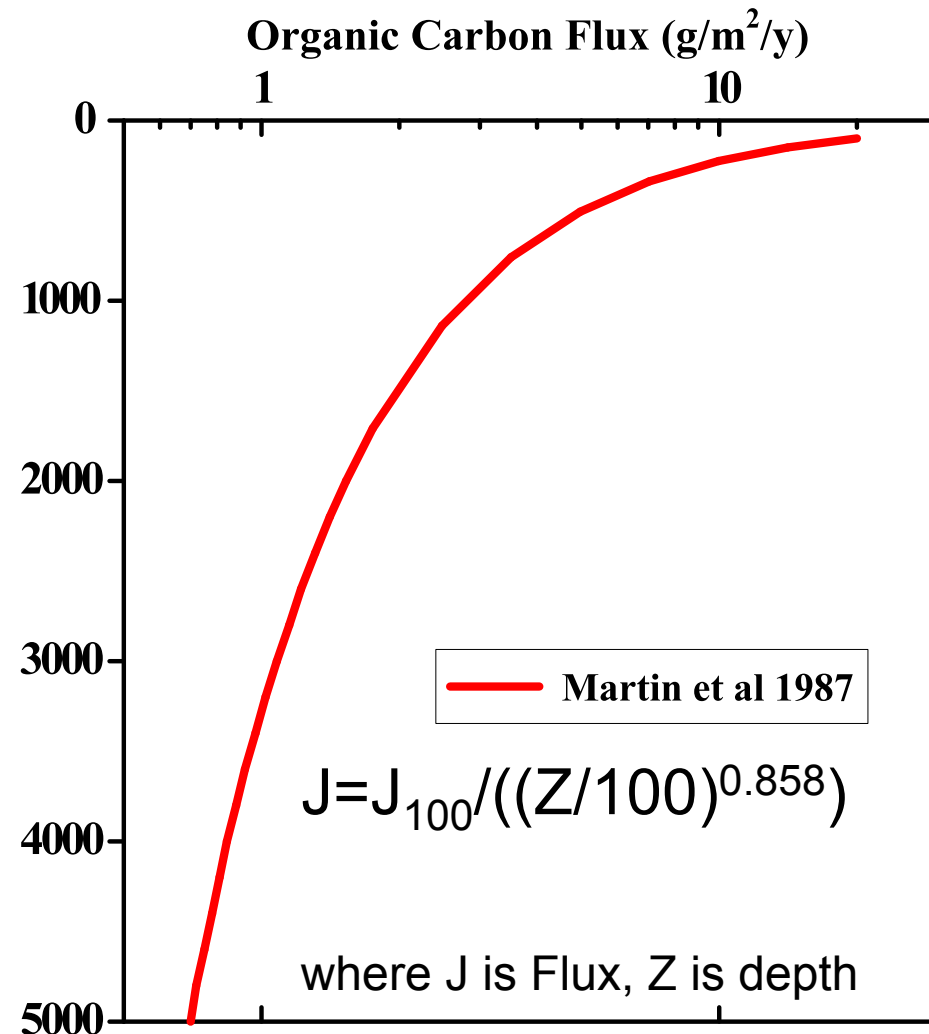
C:Fe efficiency of export decreases with increasing depth due to underway respiration/mineralization:

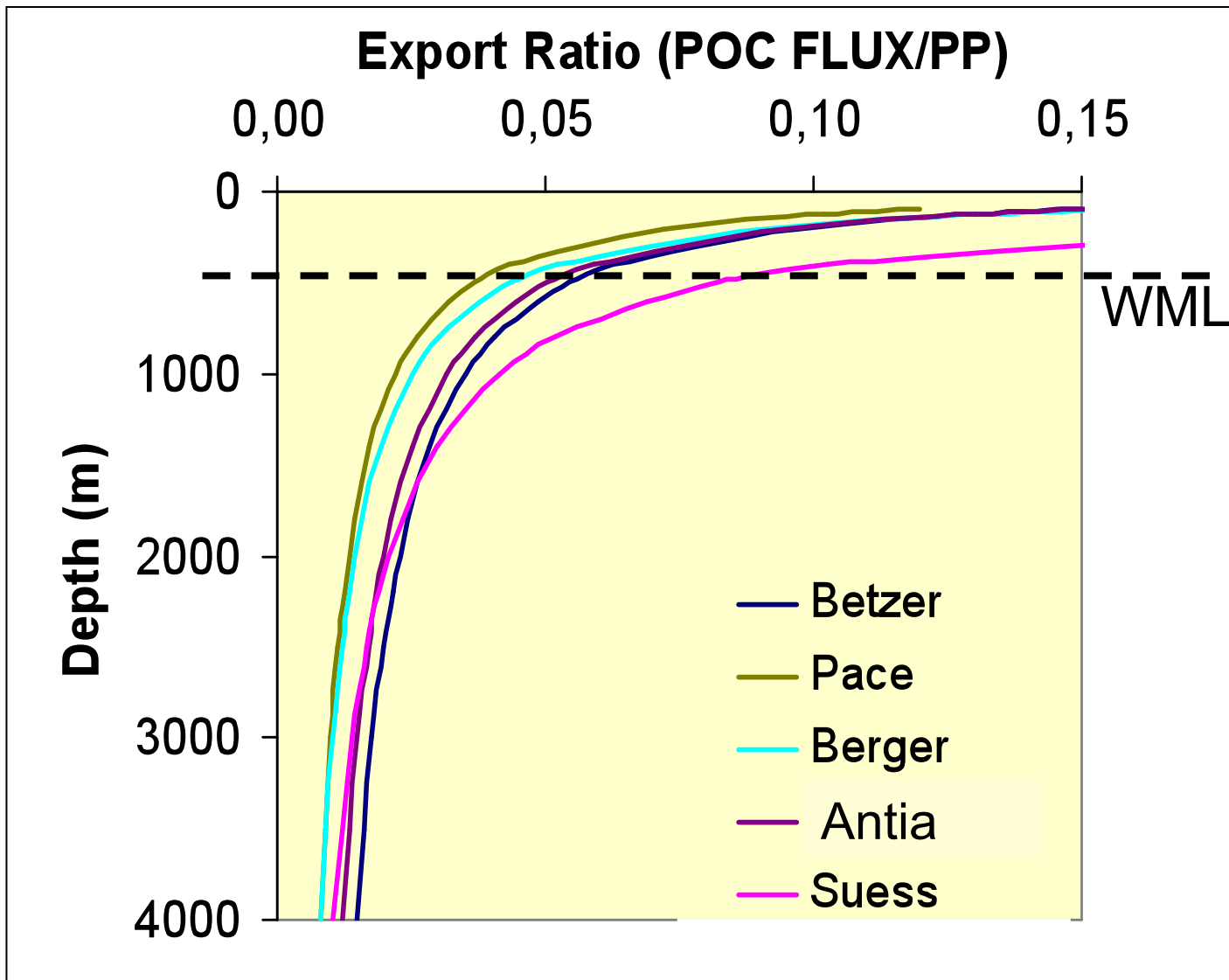
downward particulate flux as a function of depth



Sediment Trap Fluxes
Open Ocean Composite

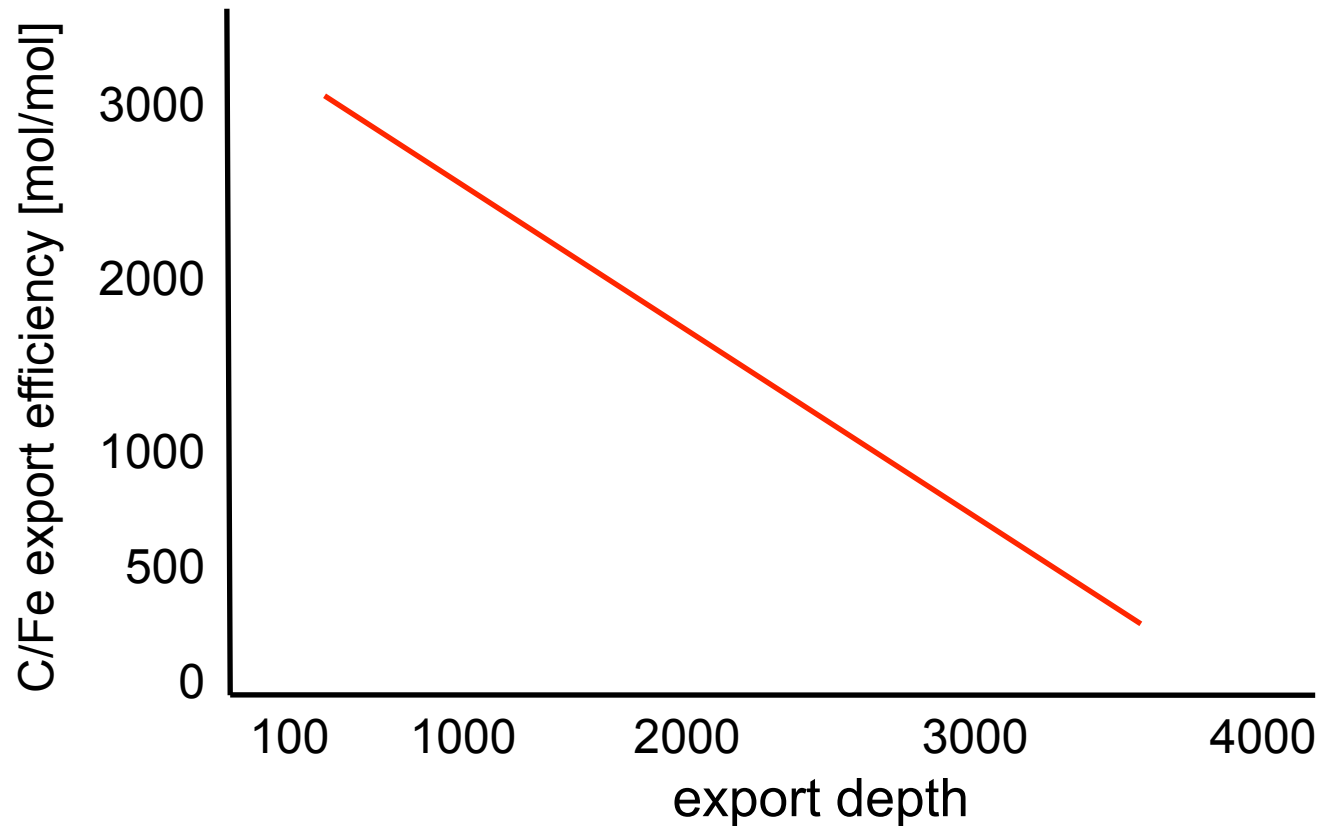
Martin et al (1987) VERTEX: Carbon cycling
in the northeast Pacific, Deep-Sea Research,
34, 267-285





Significance of the mixed layer depth

Inverse trend between C/Fe export efficiency and deep sea CO₂ storage time:
not favorable



decades

centuries

deep sea storage time of CO₂



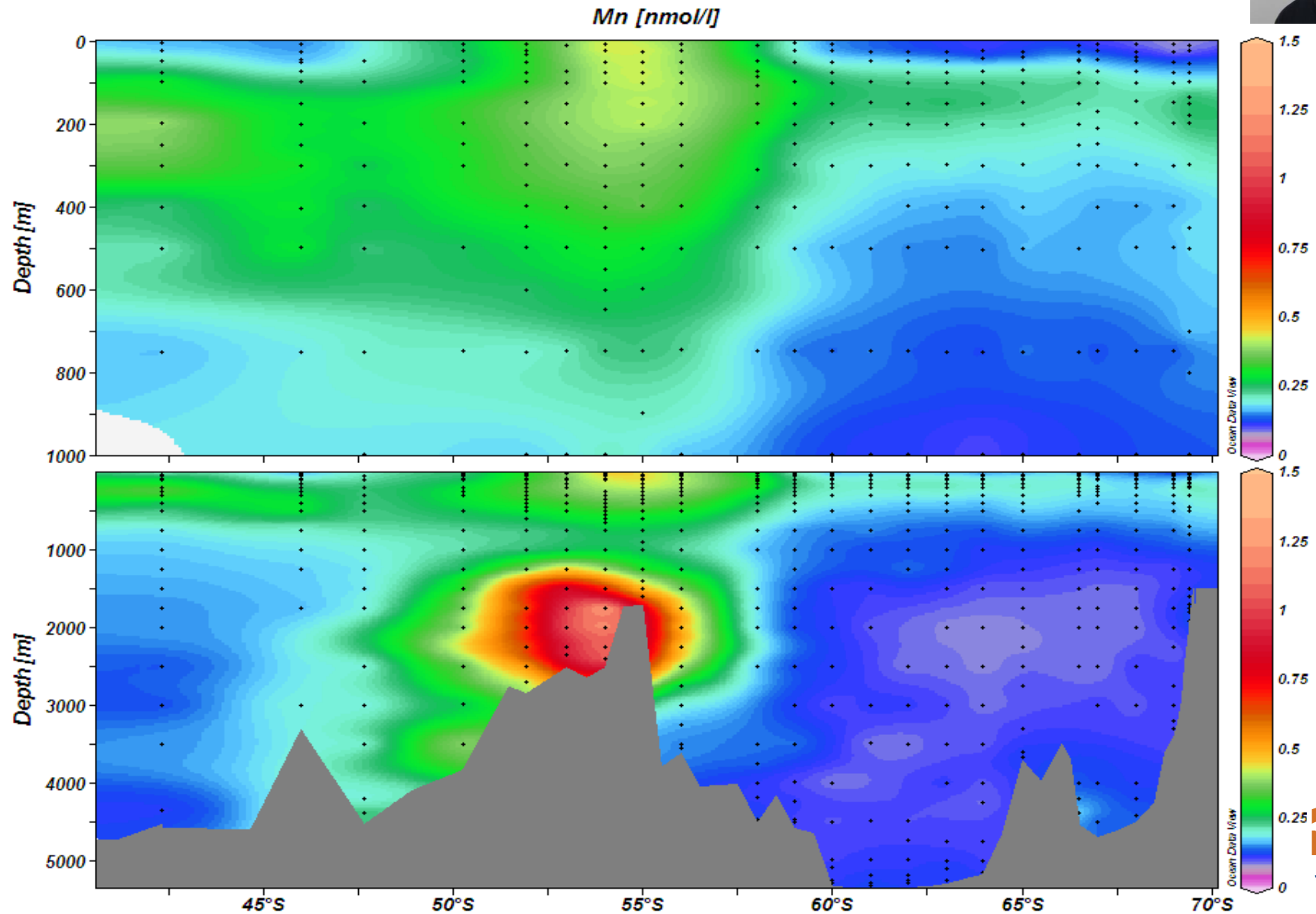
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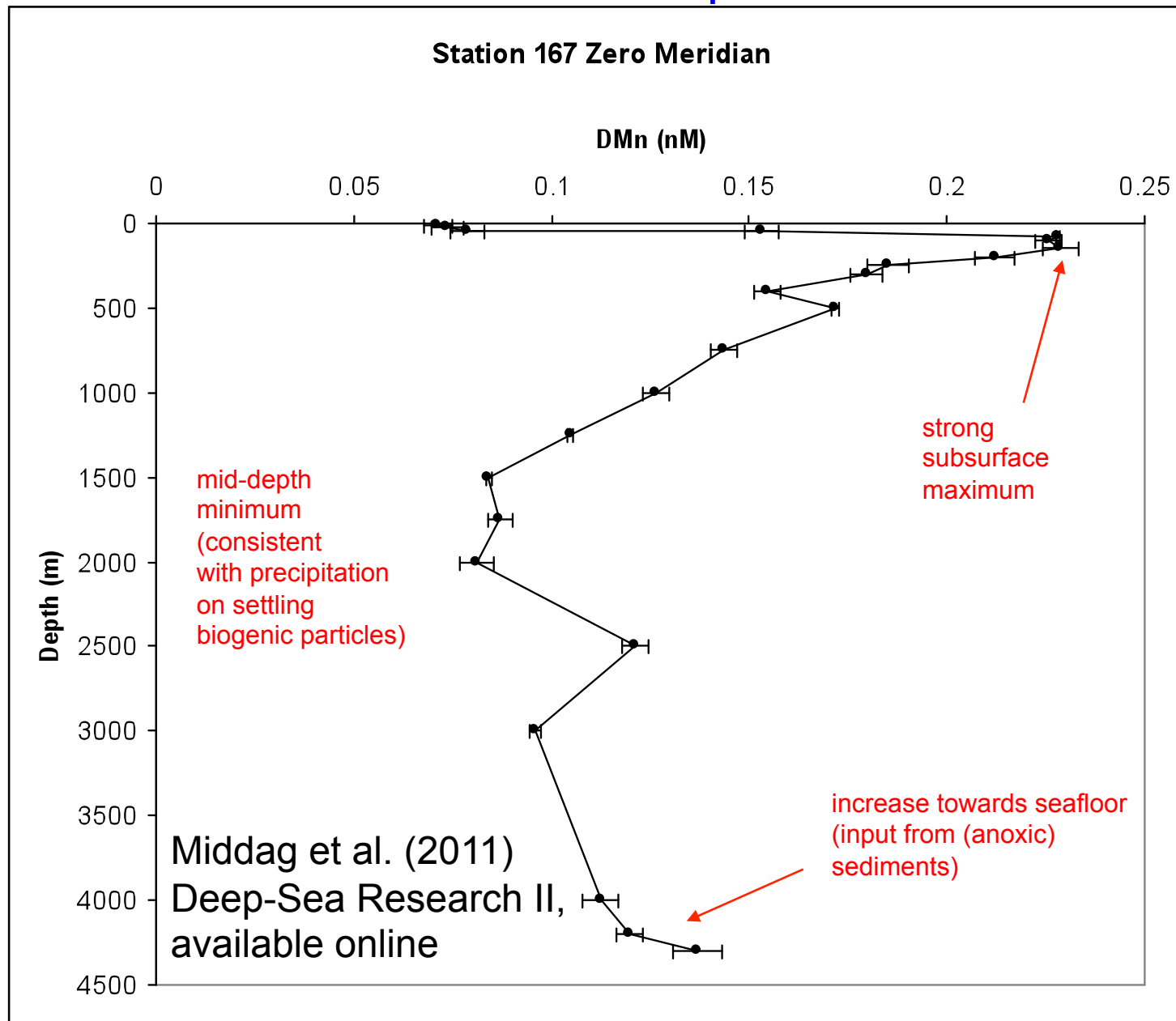


Dissolved Manganese at Antarctic Zero Meridian

Rob Middag et al. (2011) Deep-Sea Research II, available online



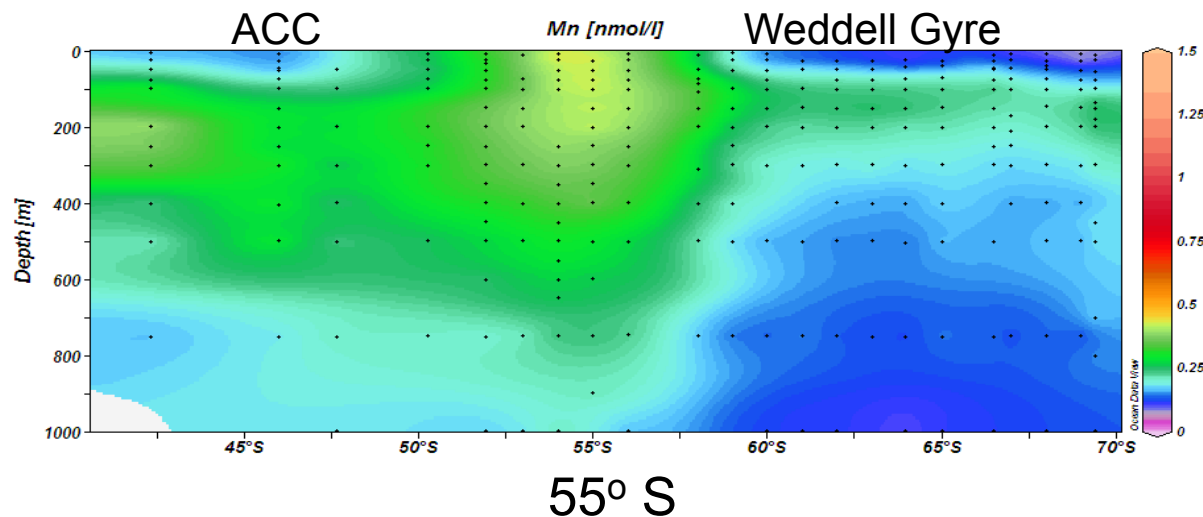
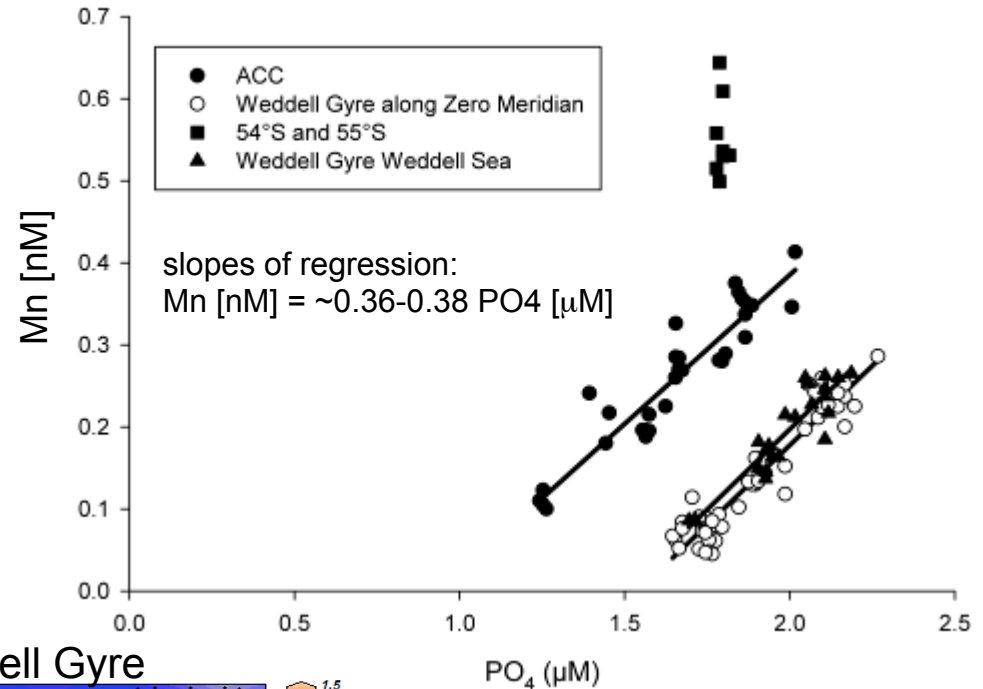
Antarctic station shows very low Mn in upper euphotic zone as well as in deeper waters



Zero meridian and Weddell Sea upper waters: Mn minima covariance with phosphate minima

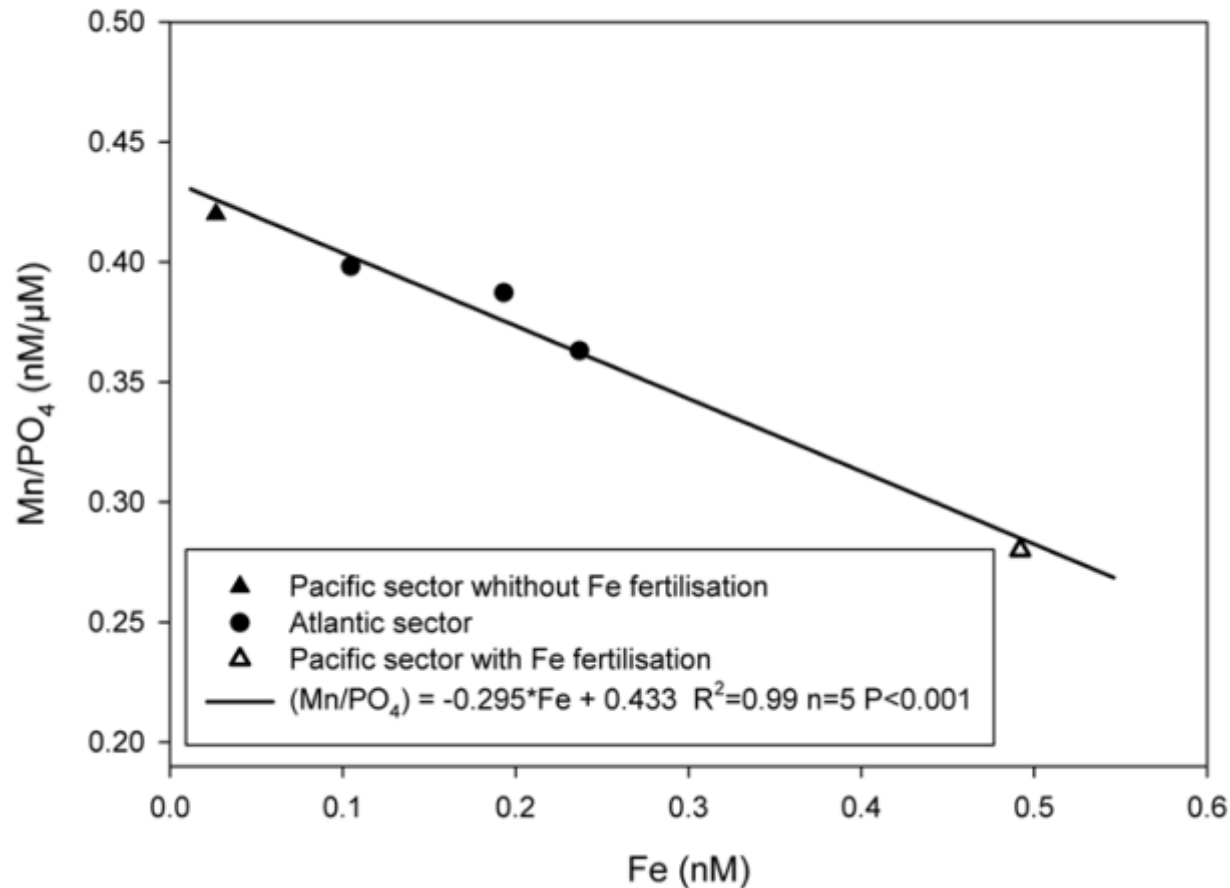
Mn-PO₄ correlation is the first-ever ocean tracer evidence of the otherwise known biological role of Mn

Middag et al., Deep-Sea Research II, available online



exclude 54-55 °S due to recent dust input, as also shown from Fe, Al and air mass trajectories

Biological uptake ratio Mn/P increases
with decreasing ambient iron (Fe) availability



● Mn/P slope
in Atlantic sector
as function of
ambient Fe

agrees well with

independent data of

▲ Δ Mn/P ratio
of phytoplankton
in Pacific SOFeX
in situ Fe
fertilization experiment

Middag et al., Deep-Sea Research II, available online

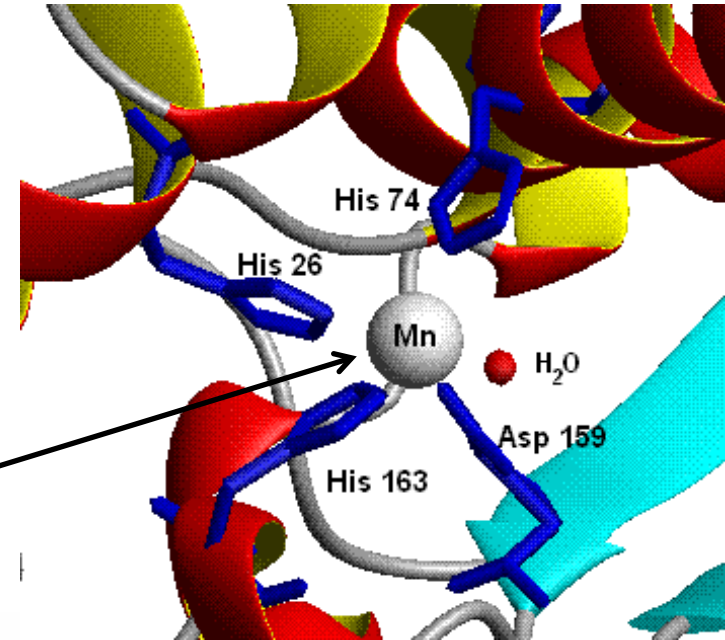


intracellular biochemistry explanation:
 Fe is needed for electron transport in photosynthetic pathway

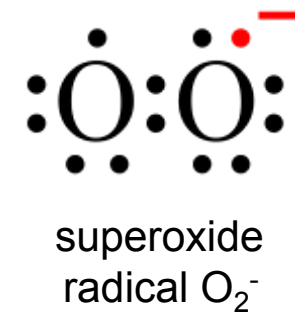
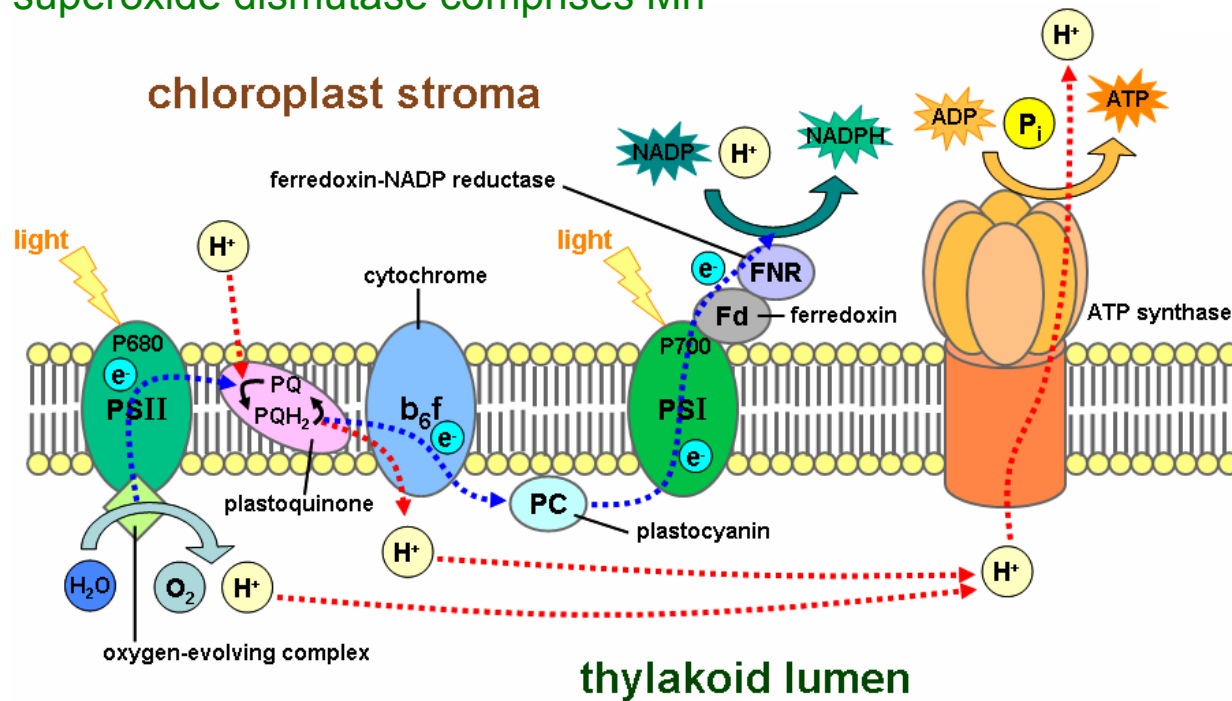
at Fe limitation this transport is hampered, the excess energy goes into superoxide radicals O_2^- which are highly toxic by aggressive reactivity

superoxides are damaging for the cell, extra superoxide dismutase enzyme (SOD) is produced

superoxide dismutase comprises Mn



Structure of the active site of Mn-based superoxide dismutase



Photosynthetic electron transport chain of the thylakoid membrane

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Iron Fertilization to Solve the fossil fuel CO₂ problem ?

(1988) Give me half a supertanker

this assumed an export efficiency of C:Fe = ~500000

(2002) SoFeX South experiment

cellular Fe quota (akin to Redfield stoichiometry) C:Fe = ~25000 (Twining et al., 2004)

export efficiency at 200m depth C:Fe = 3300 (Buesseler et al., 2004)

(2004) CROZEX

export efficiency at 3000m depth C:Fe = 730 (Pollard et al., 2009)

Thus far the evidence of C/Fe efficiency is unfavorable

(2007) GeoEngineering becomes subject of debate

(2007 onwards) London Convention (IMO) struggles with rulings on fertilization experiments

(2011) ISIS Consortium: In-Situ Iron Studies of the Ocean <http://isisconsortium.org/>

ISIS Consortium Institutions

(including names of MOU signatories)

as of April 7, 2011

<http://isisconsortium.org/>

Woods Hole Oceanographic Institution

Susan K. Avery, President and Director, January 11, 2011

National Oceanography Centre

Professor Ed Hill OBE, Executive Director, January 21, 2011

Université Pierre et Marie Curie, Paris, France

Jean-Charles Pomerol, President, April 7, 2011

University of Maine

Michael J. Eckardt, Vice President for Research, December 30, 2010

University of Plymouth, Marine Institute

Prof. Martin J. Attrill, Director of the Marine Institute, January 11, 2011

School of Ocean and Earth Science and Technology, University of Hawaii

Brian Taylor, Dean SOEST, January 11, 2011

Antarctic Climate and Ecosystems Cooperative Research Centre

Anthony J. Press, C.E.O., January 13, 2011

University of Illinois at Urbana-Champaign

Robert Easter, Interim Chancellor; Walter K. Knorr, Comptroller; Don Wuebbles, Professor;

Robert Rauber, Professor and Dept. Head, January 14, 2011

Moss Landing Marine Laboratories

Jerry Garmo, Deputy Chief Operating Officer, January 14, 2011

Xiamen University

Chongshi Zhu, President, January 18, 2011

University of Massachusetts Boston

Winston E. Langley, Provost and Vice Chancellor for Academic Affairs, January 18, 2011


University of Rhode Island

Robert A. Weygand, Vice President of Administration and Finance, January 21, 2011

NIOZ-Royal Netherlands Institute for Sea Research

Hermann Ridderinkhof, Deputy Director, February 10, 2011

Antarctic Ocean
20 Febr 2008 (0°W, 58°S)
Icebreaker Polarstern



Thank you
for your attention