The importance of iron speciation and kinetics in understanding iron biogeochemical cycling in the open ocean: effect on budget estimates from meso-scale tracer release experiments

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FB2: Marine Biogeochemistry
Overview – New aspects for modelling the biogeochemistry of Fe in the ocean

- Iron enrichment experiments – what have we learnt about iron?
- Temperature effects on speciation kinetics and solubility implications for deep waters
- Fe(II) in cold waters
- Combined Atmosphere/Ocean studies
Iron Limitation of the Southern Ocean

- Evidence from Mesoscale iron enrichments
SOIREE:
Southern Ocean IRon Enrichment Experiment
Feb 1999 - Southern Ocean south of Australia
R.V. Tangaroa
Persistent phytoplankton bloom
Fe(II)
EisenEx

Oct 28 - Nov 28, 2000
APF eddy - Atlantic Sector
P.S. Polarstern

Chlorophyll a
Grid 25.11. - 26.11.2000
SOFeX - Southern Ocean Fe eXperiment

3 ships

RV Melville
RV Revelle
USCS Polar Star

2 patches:

North: 56° 15 S, 172° W
   Jan 13 - Feb 21

South: 66° 15 S, 171° 33 W
   Jan 24 - Feb 20
Current Paradigms: Iron

• Fe dominated by *colloidal* and *particulate* phases in coastal waters, less so in open ocean

• Dissolved Fe is believed to be more *bioavailable* to phytoplankton than colloidal

• Dissolved Fe(III) is strongly *complexed* by organic ligands in seawater, probably produced by bacteria and phytoplankton.

• Fe(II) has long half-life in *cold Polar waters* and is important for cycling between dissolved and colloidal phases
Why the Kinetics are important:

- Retention of iron in mixed layer (biological recycling)
- Loss of iron by particle scavenging (physical processes)

All of these processes are important for the marine biogeochemistry of Fe and all operate over different time scales; thus the kinetic reactivity of different iron species can strongly effect the residence time for iron in the mixed layer.
Factors affecting Fe retention in the Mixed Layer in the Southern Ocean

- Fe speciation (soluble, colloidal or particulate: organic, inorganic, redox)
- Kinetics of Fe reactions
- Physical Mixing
- Biological uptake and grazing
Thermodynamics/Kinetics

Kinetic

Formation

Dissociation

Thermodynamic Equilibrium

\[
K = \frac{k_f}{k_d} = \frac{[FeL]}{[Fe'][L]}
\]
Predicted Equilibrium Solubility of iron in seawater

Temperature and Organic Complexation
Important for understanding solubility in seawater

NO data for below 0°C in seawater

Meta-stable colloidal iron may also be important (solubility decreases with time)

\[ \frac{\delta \ln K}{\delta T} = \frac{\Delta H^o}{RT^2} \]

Estimated using data of Liu & Millero.
Application of Solubility information to deep water data from the Southern Ocean

AntXVI-3
S169
Weddell Sea

Possible NADW contribution – with increased Fe
Iron Solubility in the deep

Estimated using data of Liu & Millero.

No in situ data.

No laboratory experiments at ambient deep water temperatures

Indicates

Undersaturation for Fe! No complexation required!

pH data: R Bellerby (U Bergen)
Fe cycling in the Southern Ocean - Kinetics

Major reaction pathways: iron in seawater

Fe⁺ = Σ inorganic Fe(III) species

FeL= organically complexed iron

Fast
slow

Fe(part)

sinking

Fe(III)

Fe(II)

Fe(II)L

FeL

O₂/H₂O₂

O₂/H₂O₂

hv
**Technique for Fe speciation in seawater:**
Competitive Ligand Exchange with analysis by Cathodic Stripping Voltammetry (CLE-CVS)

**Competing Ligands:** TAC

**Thermodynamic:** Titrate sample with Fe at a variety of different competing ligand concentrations ⇒ determine $K'$ and $[L]$ by fitting techniques.
Assumption: Experimental data modelled using only 1 ‘strong’ ligand forming 1:1 complex with Fe.

**Kinetic:** Follow the formation or loss of FeL complexes by using TAC.

(dissociation) $\text{FeL} + \text{TAC} \rightarrow \text{FeTAC} + \text{L}$

(formation) $\text{Fe}^+ + \text{L} \rightarrow \text{FeL}$

(measure residual Fe$^+$ with TAC)

$\text{Fe}^+ + \text{TAC} \rightarrow \text{FeTAC}$
Variation of FeL $k_d$ with time

- Natural samples collected prior to and after Fe fertilization in EIFeX (Frozen – thawed prior to analysis in lab). Fe added and then the labile Fe followed over time.
- Weaker complexing agents (including nano sized colloids) important kinetically on short time scales (1-3 hrs)

Schlosser et al.
(in preparation)
Physical Processes effecting surface mixing
Diel Cycle of Mixed Layer Depth (ML), Active Mixed Layer (AML) and the SML (Seasonal Mixed Layer). The AML is turning over on time scales of 3-20 hours. Processes that operate faster than this will show gradients in the ML.

Data from FeCycle experiment in the Sub Antarctic South-West Pacific (Feb 2003): ElFeX data in preparation from H$_2$O$_2$, CTD and MST datasets.
Large Chlorophyll Bloom initiated by Fe Fertilization throughout a 100 m ML

Particulate Fe maximum at 70 m

Soluble (10 kDa) & Colloidal Fe increase towards surface

Hydrogen peroxide well mixed to 100 m

Though 2 possible overturn cells

At 40 & 100 m
Station 570: *The beginning of the end*
High iron binding ligand concentration at 80 m – possibly in response to light induced iron limitation from shallowing of the mixed layer
Alternative/additionally debris from grazed/lysed cells cf surfactant data
Importance of Fe(II)

- Fe(II) has significant half-life (90+ minutes at 4C) in cold waters
- Southern Ocean: Iron Fertilization experiments produce an artifact in prolonging Fe(II) induced by O$_2$ oxidation ofr Fe(II) and generation of O$_2^-$ (Croot et al. *Marine Chemistry* 2005)
- Other processes can also produce Fe(II)
Fe(II) and dissolved iron across the iron enriched patch, 18 hours after the 2nd infusion of iron during EISENEX.

Croot and Laan, ACA (2002)
Fe(II) in SOFeX, Southern Patch Feb 18, 2002

Strong link between Fe(II) and patch edge found during SOFeX.
Dissolved Fe(III) 
Photoreduction
Max 370 pM hr⁻¹

Particulate Iron 
Scavenging

Dissolved Fe(II) 
Oxidation
Reduction

Iron Binding Exudates 
Fe(II) Ligands
Fe(III) Ligands

Bacteria
Phytoplankton
Zooplankton

Iron Chemistry in clouds
Aerosol Iron

Cell surface reduction
0.3-0.7 pM hr⁻¹

Uptake
2-4 pM hr⁻¹

Grazing

DOC flux

Upwelled Iron

Sedimentation

Max 370 pM hr⁻¹

0.3-0.7 pM hr⁻¹

2-4 pM hr⁻¹

? pM hr⁻¹

? pM hr⁻¹
EiFeX: Fe(II) Diel Cycle

Diel Cycle of Fe(II) shows photoreduction of Fe(III) to Fe(II)

Fast reaction – dependent on light flux and photoreducible Fe

⇒ Steady State Fe(II)

Oxidation $t_{1/2} > 600$ s in Southern Ocean waters (90+ mins in EisenEx)

In Cold waters oxidation of Fe(II) proceeds mostly by $O_2$

$$Fe(II) + O_2 \rightarrow Fe(III) + O_2^-$$

$$2H^+ + Fe(II) + O_2^- \rightarrow Fe(III) + H_2O_2$$

Oxidation by Hydrogen Peroxide is also important

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^*$$

Superoxide can act as an oxidant (above) and as a reductant

$$Fe(III) + O_2^- \rightarrow Fe(II) + O_2$$
EisenEx – Iron Budget

- Estimated loss rates using normalisation to \( \text{SF}_6 \) for the time between the first and second infusions. Normalisation removes the effects of dilution – allowing loss rates to be calculated.

- Later loss rates estimated by comparison with Th and using a Th:Fe ratio for collected particles.
Estimated Iron loss rate – during EisenEx

Croot et al. (for submission to DSR)

Red curve – dilution rate for each infusion, Blue curve – overall dilution rate for first infusion. Blue circles – Fe/SF6 normalised loss rates, Green circles – Fe loss rate based on Th depletion
Overall Fe loss in EisenEx

Croot et al. (for submission to DSR)

Purple circles – estimated Fe loss from added Fe (that is removed from the mixed layer), Blue circles – Fe estimated losses (from normalisation to SF6), Green circles – Th depletion during EisenEx
Inorganic Fe (Fe’) during EisenEx

Croot et al. (for submission to DSR)
2 pmol L⁻¹ Estimated Value from work of Sunda for Fe limitation of diatoms
Overview: EisenEx

- Most of the added Fe was **diluted** – not lost during the timeframe of the experiment from the mixed layer
- Strong physical mixing coupled with organic complexation and recycling processes retained Fe in the mixed layer
- Phytoplankton eventually limited via dilution from the mixing
Krill and Salps can exert strong grazing pressure – is the iron retained from grazing?
Retention of Iron: Shallow Remineralisation in the Weddell Gyre

Weddell Sea – little Th export from the surface – remineralised in upper 300 m.

Fe probably similarly behaved – high retention in this system

Iron data - Croot et al. (NIOZ)
Th data - Rutgers van der Loeff et al. (AWI)
Conversion from Colloidal to Particulate is important.
Back reactions also occur.

Croot et al. (for submission) based on Nishioka et al. *Marine Chemistry* 2005
New Insights into Iron Supply

- Combined Aerosol and water column measurements during Cruises
- ANT18/1 North – South in Atlantic
- M55 West – East in Central Atlantic
- Looking at the effects of the Saharan dust plume on Fe in surface waters
Mahowald et al. Modelled dust deposition (g m\(^{-2}\) yr\(^{-1}\))
Present Day
ANT18/1 – Surface dissolved iron and Saharan dust

Satellite 24/25 Sept 2000
Chasing the dust plume

Oct/Nov 2002 - Meteor 55
German SOLAS cruise

High Fe input – short residence time
(Croot et al. *GRL* 2004)
Nitrogen limited ecosystem
Nitrogen Fixation limited by Fe & P
Increase in Surface Dissolved Fe under the Saharan dust plume

Croot et al. *GRL* 2004
SOLAS – Surface Ocean Lower Atmosphere Studies

Meteor-55
Atmospheric Fe deposition (A Baker UEA)

Saharan dust deposition to the Eastern Tropical Atlantic – Cape Verde

Green – TDFe
Blue – DFe
Coupled Atmosphere/Ocean Studies

Relationship between Fe inventory in the upper 200m and the aerosol Fe flux (for 24 hours prior to station occupation)

Short residence time for particulate Fe (upper 200 m) under the Saharan plume (6 -60 days)
Dissolved Fe residence time longer (1-10 years)

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