Synthesis of *in-situ* Iron Enrichment Experiments

In the end when satisfied, then praise:
Phil Boyd, Ken Buesseler, Dorothee Bakker, Yann Bozec, Marie Boye, Kenneth Coale, Peter Croot, Etienne Hannon, Paul Harrison, William Hiscock, Ken Johnson, Patrick Laan, Christiane Lancelot, Maurice Levasseur, Adrian Marchetti, Jun Nishioka, Yukihiro Nojiri, Tim van Oijen, Ulf Riebesell, Sigenobu Takeda, Klaas Timmermans, Atsuhi Tsuda, Marcel Veldhuis, Andy Watson, and many many others....

When disappointed with poor synthesis, blame:

Hein de Baar
Royal Netherlands Institute for Sea Research
Subarctic North Pacific, August 1987

North Pacific Ocean data from:
VERTEX T-6 (45N,143W) MARTIN ET AL. (1988)

Chlorophyll a

strong response to Fe addition
but control also outgrowing field value

...as shown in Paris by John Martin in September 1987
Contents

• Nine Experiments 1993-2004
• Light Limitation
  - Wind and Wind Mixed Layer
  - lateral patch dilution
  - temperature effects ?
• Big Diatoms
• Iron Chemistry
• Carbon Fluxes
• Summary & Discussion
## Nine Ferrous Fertilizations

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<th>Experiment</th>
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<td>SEEDS</td>
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<tr>
<td>Eifex</td>
<td>Atl. Sect. SO</td>
<td>2-3, 2004</td>
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</table>

Not shown:
- GreenSea 1: Gulf of Mexico, 1, 1998
- GreenSea 2: Gulf of Mexico, 5, 1998
not yet shown: Eifex 2004 (Polarstern)

graph courtesy Kenneth Coale
IronEx II Variable Fluorescence

(Chlorophyll abundance)

depth, m

distance from patch center, km

Graph courtesy Kenneth Coale
Southern Ocean

(slide by Dorothee Bakker after Orsi et al., 1995)
Surface water fCO$_2$ in SOIREE

Dorothee Bakker, Andy Watson, Cliff Law, 2001

normalized to standard atmospheric pressure and constant temperature
Surface water fCO$_2$ maps in SOIREE (Bakker, Watson and Law, 2001)

data and slide by Dorothee Bakker
SOIREE after 42 days

23 March 1999
(Abraham et al., 2000)

NASA SeaWiFS project, DAAC/GSFC, ©ORBIMAGE.

- **Ironex-2**
  - East Equatorial Pacific
  - $T = 25 \, ^oC$
  - WML = 40m
  - 17 days
  - patch size
    - 72 km$^2$
    - to
    - 120 km$^2$

- **SOIREE**
  - Southern Ocean
  - $T = 20 \, ^oC$
  - WML = 65 m
  - 13 days
  - Patch size
    - 50 km$^2$
    - to
    - 200 km$^2$

Ironex-2 much better growth in warmer, shallower, more confined patch

*graph kindly provided by Phil Boyd*
ice-free between 50 and 56 South with high Silicate exceeding 15 mmol.m\(^{-3}\)

However ....
4-7 dagen weerberichtgeeft onwerkbare stormen in dat gebied
cold Antarctic eddy, high silicate; but moved north conveniently off storm trajectory. Put it right here..

Polar Frontal jet
Flushing down the FeSO₄ powder

HCl acid

down the drain
EISENEX
Surface water fCO2

Dorothee Bakker et al, Deep-Sea Research, submitted

normalized to 4 °C and standard atmospheric pressure
Surface water fCO$_2$ maps in EisenEx

(Dorothee Bakker and Andy Watson, UEA)
Eisenex delta-DIC and delta-fCO$_2$

Bozec et al, Mar Chem, in press
Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS)

1 single Fe infusion
Fe = 5 nM at time zero

Kaiyo Maru at very calm sea

FRV Kaiyo Maru Cruise
Leg 1  28 June-10 July
Leg 2  13 July-8 August
Contours of Chlorophyll a concentration

Day 6

Day 8

Day 10

Day 12
Time-series data of nutrients and Chl a

Nutrient (µM), Chl a (µg/L)

Silicate

Nitrate

Chl a

Days since beginning of experiment

Chaetoceros debilis
SOFEX 2002
North and South Patches

slide courtesy Ken Buesseler
MBARI
Lagrangian Drifter w/GPS, Packet Radio
CTD, Oxygen Nitrate, Fluorescence, Transmissometer

North patch is streaky right away

South patch

slide courtesy Kenneth Coale
Prim Prod (mmol C m$^{-3}$ day$^{-1}$) for South Patch (66°S) between Year Day 2002. The graph shows Fe Additions, Out of Iron Patch, In Iron Patch, and Mean 1998 Prim Prod.
watch Coale's comic strip

Chlorophyll Movie
Chlorophyll Movie

SOFeX S. Patch

Chl-a (µg)

Z

avg OUT
day 2
day 5
day 6
day 7
day 10
day 11
day 14
day 15
day 18
day 21

0 1 2 3 4 5

0 20 40 60 80 100 120 140 160
Chlorophyll Movie
Chlorophyll Movie

SOFeX S. Patch
Chlorophyll Movie

SOFeX S. Patch

Chl-a (µg)

Z

avg OUT

day 2

day 5

day 6

day 7

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Chlorophyll Movie

SOFeX S. Patch

Chl-a (µg)

0 1 2 3 4 5

Z

0 10 20 30 40 50 60 70 80 90 100

avg OUT

day 2
day 5
day 6
day 7
day 10
day 11
day 14
day 15
day 18
day 21

120 130 140 150 160
Chlorophyll Movie
Chlorophyll Movie
Chlorophyll Movie
Chlorophyll Movie
SOFEX South

pCO2 in surface waters  pCO2 in air

data and slide courtesy William Hiscock
South Patch – Time Series Response to Fe-enrichment

- Out Patch
- In Patch

slide courtesy William Hiscock
SERIES:
The decline and fate of an iron-induced subarctic bloom

Boyd et al. (2004)

SERIES bloom day 19

Bloom has declined on day 24

Chlorophyll (mg m⁻³)

July-August 2002
Boyd et al. (2004)

filled symbols is IN-PATCH
open symbols is OUT-PATCH
Boyd et al. (2004)
SERIES 2002
three-ships experiment at peaceful Pacific

RV Kaiyo Maru seen from RV John P. Tully
photo courtesy F. Whitney
November 2000
RV Polarstern pumping iron in the roaring forties
Light limitation

• Wind speed and Wind-Mixed-Layer depth

• Other forcings:
  - Photosynthetic Active Irradiance PAR
  - Temperature effects
  - Storm dilution effects, and shear stress

• Case study: EISENEX versus SEEDS
Eisenex had a lot of wind

graphs by Dorothee Bakker
Depth of Wind Mixed Layer

Shallow 10-15 m at SEEDS versus deep 65-70 m at SOIREE, EISENEX
Indeed record yield Chlorophyll a in SEEDS

lowest yields at SOIREE and Eisenex where deepest Wind Mixed Layers

graph adapted after Coale talk at ASLO, Hawaii, Feb 2004
Chlorophyll $a$ is NOT a reliable biomass indicator in Fe enrichments

- Chlorophyll $a$ is nice and useful
- Synthesis pathway of Chl $a$ requires iron Fe
synthesis route of Chlorophyll a has several Fe-enzymes

Eisenex
IN PATCH
Total size class gets higher Chl/cell
strongest fourfold increase in the larger 3-8 micron and >8 micron cells (diatoms)
Veldhuis and Timmermans, submitted
Nitrate removal as biomass indicator

graph adapted after Coale talk at ASLO, Hawaii, Feb 2004

Also highest at SEEDS and lowest at EISENEX
Ironex-2 and SofexSouth doing very well
Removal of Silicate

Eisenex Out-patch shows same Silicate removal (Bozec et al, in press)
SofexSouth Out-Patch shows Silicate mineralization increase

Out Patch data found only for Eisenex and SofexSouth
A decrease of $f\text{CO}_2$

The graph shows the Delta $f\text{CO}_2$ [10^{-6} atm] across different experiments.

- Ironex-1
- Ironex-2
- Soiree
- Eisenex
- Seeds
- SofexNorth
- SofexSouth
- Series
- Eifex

Again, most at SEEDS and least at EISENEX. Ironex-2 and SERIES coming close to SEEDS.
Decrease of Dissolved Inorganic Carbon pool

again SEEDS is leading, next SERIES
Ironex-2 and SofexSouth doing very well
SOIREE, EISENEX and SofexNorth in same league
Dominant forcing of Chlorophyll by WMLdepth

Chl a Max function WML Depth (all except ironex-1)

\[ y = 491.73x^{-1.3418} \]

\[ R^2 = 0.8604 \]
Similar trend for nitrate removal?

Delta Nitrate function WML Depth (all except Ironex-1)

\[ y = 71.179x^{-0.8434} \]

\[ R^2 = 0.622 \]
best \( \text{CO}_2 \) fixation at shallow WML depth

\[
y = -1.0888x + 97.701
\]

\( R^2 = 0.6163 \)

is \( R^2 = 0.62 \) still a real trend?
Most DIC uptake at shallow WML depth

is $R^2=0.69$ a real trend?

Delta DIC inverse function of WML depth (all except Ironex-1)

$y = -0.7182x + 58.88$

$R^2 = 0.6948$

Delta DIC [mmol.m$^{-3}$]

WML Depth [m]
Temperature also affects optimum growth rates of phytoplankton cells

- factor 1.88 per 10 °C (Eppley, 1972)
- factor 2.08 per 10 °C (Goldman and Carpenter, 1974)
- Thus Ironex-1 & 2 should be about fourfold faster than SOIREE
- Thus SEEDS to be about one-and-half times faster than EISENEX
  - *Chaetoceros debilis* does 2.6 doublings per day in SEEDS
Irradiance at sea surface
(Photosynthetic Active Radiation PAR)

- each single experiment large daily variation
- large variation between experiments
Storm Dilution Effects

Why the exceptional longevity of SOIREE?

Fe Patch increased from 50 to 1100 km²

IN: HNLC waters
hi Si
low Fe
low diatoms
low Chl a

OUT: Patch waters
low Si
hi Fe*
hi Chl a
hi diatoms

Stretching via horizontal flows
Mixing of water by horizontal diffusion

chemostat (Monod, Paris, 1942) for nutrients Si, N, P
in contrast the fertilizer Fe is washed out

slide courtesy Phil Boyd & Ed Abraham
wind speed
as well as
sheer stress
of fronts and currents
cause high dilution factor of a patch

Ironex-2 and Seeds
lowest dilution factor

Eisenex highest
19-fold dilution

![Graph showing initial patch size and final patch size for different species.](image-url)
Case Study:
Linking Eisenex with Seeds

• 1) Eisenex *in situ* experiment
  - WML depth 25-110 m,
  - strong patch dilution,
  - variable PAR

• 2) Eisenex deck incubations
  - In-Patch versus Out-Patch water
  - simulated WML depth 8-16m
  - same variable PAR as *in situ* experiment

• 3) Eisenex bottle incubations
  - In-Patch versus Out-Patch water
  - artificial constant light in 12/12 day/night; simulated WML= 30m

• 4) Seeds *in situ* experiment
  - WML depth 10-15 m
  - modest patch dilution
1. Eisenex *in situ* experiment

\[ \Delta \text{NO}_3 = 1.6 \, \text{mmol.m}^{-3} \]

after 23 days

WML depth varies between 10 and 100 m

patch dilution 19-fold
2. Eisenex deck incubations 20 Liters of InPatch and OutPatch waters

- shallow WML = 8-16m
- no patch dilution
- all nutrients depleted in 12 days !!!
- delta NO3 = 21
- delta Si =13.5
- delta PO4 = 1.6

Data and Graphs by Tim van Oijen & Micha Rijkenberg
2. Eisenex deck incubations
Diatom growth rates

Typical Growth Rate
0.4 - 0.6 day\(^{-1}\)

Also dominant in \textit{in-situ} patch

Diatom species group

* significant Fe stimulus
3. Eisenex bottle incubations with artificial light

- 20 L water of In & Out Patch
- artificial light at 3.5 mol.m\(^{-2}\)d\(^{-1}\)
- simulated WML depth = ~30 m
- 12/12 hours light/dark cycle

- optimal Fv/Fm InPatch bottle
- fair Fv/Fm OutPatch bottle
  - drops in end due to lack of Fe and N
- delta NO3 = 24 after 18 days
- delta Si = 14.5 after 18 days

Data and graphs by Klaas Timmermans
4. Seeds *in situ* Experiment

Data and graph kindly provided by Tsuda et al.
• **Conclusions**
  - WML depth and dilution factor are dominant
  - some effect of temperature
  - NB SEEDS incident light still not taken into account

• **Future Work**
  - ecosystem modeling
  - day-to-day changes
  - several depths throughout patch
diatoms optimal specific growth rates depend on temperature as well

- Eisenex Southern Ocean at 3.5 °C
  - in deck incubators \( \mu = 0.4 \text{ to } 0.6 \text{ day}^{-1} \)

- SEEDS \textit{in situ} subarctic Pacific at 9.5 °C
  - Chaetoceros debilis \( \mu = 1.79 \text{ day}^{-1} \) !!!! from day 4 through day 7
  - slows down to \( \mu = 0.42 \text{ day}^{-1} \) in days 9 to 14
**BIG DIATOMS**

*Actinocyclus*

- Diameter: 140 micron

*Fragilariopsis kerguelensis*

- Chain-forming

*Chaeotoceros dichaeta*

- 80 μ long, 30 μ width
- Forms chains
Monod growth curve for dissolved Fe [nM] in pristine (EDTA-free) Antarctic seawater

Timmermans, VanderWagt and de Baar, 2004, L&O, in press

\( \mu_{\text{max}} = 0.34 \text{ day}^{-1} \)

\( \mu_{\text{half}} = 0.17 \text{ day}^{-1} \)

\( \frac{K_m}{\mu_{\text{max}}} = 0.31 \text{ day}^{-1} \)

\( \frac{K_m}{\mu_{\text{max}}} = 0.36 \text{ day}^{-1} \)
Bigger diatoms need higher ambient dissolved Fe

\[
y = -3.2122x + 1.364
\]

\[R^2 = 0.8147\]

- Actinocyclus
- Chaetoceros dichaeta
- Thalassiosira
- Chaetoceros pennatum
- Fragilaropsis kerguelensis

bigger diatoms need higher ambient dissolved Fe
Fe requirements large Antarctic diatoms

- **Big Diatom** Km
  - Actinocyclus 1.14 nM
  - Chaetoceros dichaeta 1.12 nM
  - Thalassiosira 0.62 nM
  - Chaetoceros pennatum 0.57 nM
  - Fragilariopsis kerguelensis 0.19 nM

- Need for optimal growth within Fe-fertilized patch
  - **Fe [nM]** μmax
    - 2.28 nM 0.34 d⁻¹
    - 2.24 nM 0.62 d⁻¹
    - 1.24 nM 0.31 d⁻¹
    - 1.14 nM 0.36 d⁻¹
    - 0.38 nM 0.39 d⁻¹

This is why the biggest diatoms still are rare in fertilization experiments.

Dissolved Fe in SOIREE adequate to support dominant Fragilariopsis.

Dissolved Fe in EISENEX on average too low for Fragilariopsis: smaller Pseudonitschzia eventually dominates EISENEX.
**Iron Chemistry**

Dissolved Fe is defined as < 0.2 micron filtrate.

SOIREE experiment (Bowie et al., 2001, DRS II, 48, 2703)
**IRON CHEMISTRY**

**SOIREE experiment (Bowie et al., 2001, DRS II, 48, 2703)**

- **DFe (In)**
- **DFe (Out)**
- **TFe (In)**

**Dissolved Fe is defined as < 0.2 micron filtrate**

**Km is for 50% of optimal growth**

- **Km = 1.14 nM** Actinocyclus
- **Km = 0.2 nM** Frag. Kerg.
**IRON CHEMISTRY**

**Infusion**

Days since start of experiment

SOIREE experiment (Bowie et al., 2001, DRS II, 48, 2703)

**Dissolved Fe** is defined as < 0.2 micron filtrate

100 % optimal growth needs twice dissolved Fe

*Km* is for 50 % of optimal growth

Km = 1.14 nM  
*Actinocyclus*

Km = 0.2 nM  
*Frag.kerg.*
So-called dissolved Fe (<0.2 micron) in fact is colloids

SEEDS, 2 days after Fe injection (data and graph Jun Nishioka)
Within 24-48 hours almost all of the added dissolved reduced Fe(II) is converted by oxidation into colloids and larger particles. Thus the available Fe for uptake by diatoms is even less than was believed on basis of 'dissolved' < 0.2 micron fraction.

Nishioka et al., accepted Mar Chem special issue
Fate of the Added Iron

- only small portion of added Fe available for uptake by diatoms
- rapid removal of added Fe into colloids next into larger particles
- 'truly' dissolved Fe (< 200kDa) mostly organic ligands
- confirms that dissolved Fe does not belong in the ocean
  - which was the original problem anyway
- in-patch Fe chemistry deviates strongly from natural ocean
- tendency for new field studies of natural Fe gradients
  - FeCYCLE 2003; BICEP 2004 at Crozet; KEOPS 2005 at Kerguelen
CARBON FLUXES

- Primary Production = CO2 Fixation
- Air/Sea Gas Exchange
- Delta-DIC Inventory (= TotalCO2)
- Delta-POC Inventory (Particulate Organic Carbon)
- Export Flux
  - direct evidence only at SERIES, SOFEX-South

- Combination of 8 different experiments still preliminary:
- Many inconsistencies and assumptions between experiments

SERIES sediment trap fluxes

Sediment traps at four depths

- 50 m
- 75 m
- 100 m
- 125 m

POC flux (mmol C m$^{-2}$ d$^{-1}$)

Days


decline stage bloom
POC flux IN > OUT by end of 28 day SOFeX-South observations
- but not large relative to previous Southern Ocean blooms at this site

Buesseler et al. (2004) Science, 304, 414
Primary CO₂ Fixation [mmol.m⁻².d⁻¹]
Rates of Change for Carbon Inventories and Fluxes

- DIC Inventory Change
- POC Inventory Change
- Air/Sea Gas Exchange
- Export Flux

air/sea exchange negligible  export is small and debatable
Conclusions

• Light limitation by depth of Wind Mixed Layer nicely confirmed by 8 iron experiments
  - WML depth inversely related with Chlorophyll, ΔDIC, ΔNitrate
  - temperature, patch dilution, irradiance also play a role
• Shift-up to larger size classes diatoms
  - bigger diatom at higher dissolved Fe
  - difficult to maintain constant high dissolved Fe for largest diatoms
• Most added Fe rapidly lost into colloids and larger particles
  - only about 20 % is 'truly' dissolved (<200 kDa fraction)
• Carbon Inventories and Fluxes only Preliminary Comparison
  - gas exchange flux is negligible
  - export flux is proven in Series and Sofex-South
  - export flux is small and exact value debatable