Investigating the effects of ocean acidification on carbon, nutrient, and trace metal biogeochemistry

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Introduction
Why should ocean acidification affect marine biogeochemical cycles?
How will nutrient biogeochemistry change in an acidified ocean?

\[ C_{106} : N_{16} : Si_{16} : P_1 \]
Phytoplankton Elemental Ratios

• Redfield: 106C:16N:16Si:1P

• Ho et al. 2003:
  \( \text{C}_{124} \text{N}_{16} \text{P}_{1} \text{S}_{1.3} \text{K}_{1.7} \text{Mg}_{0.56} \text{Ca}_{0.5} \text{Fe}_{7.5} \) (1000)

• Price 2005:
  \( \text{C}_{97} \text{N}_{14} \text{Si}_{4.7} \text{P}_{1} \text{Fe}_{0.029} \) (Fe-replete)
  \( \text{C}_{70} \text{N}_{10} \text{Si}_{5.9} \text{P}_{1} \text{Fe}_{0.00074} \) (Fe-limited)
Carbon

• CO₂ enrichment can potentially promote the photosynthesis and growth of autotrophs such as phytoplankton and chemoautotrophic bacteria.

• Responses to changing pCO₂ depend partly on the efficiency of carbon-concentrating mechanisms (CCMs), like various carbonic anhydrases. Autotrophic groups with less efficient CCMs may benefit the most from increasing pCO₂.

• For calcifying autotrophs (coccolithophorids), it is perfectly possible for higher pCO₂ to increase photosynthetic carbon fixation, while at the same time calcification is reduced.

• For both CO₂ fixation and calcification, interactions with other global change variables like temperature or light can be as important (or more so) as the effects of elevated CO₂ alone.
Effects of CO$_2$ and temperature increases on photosynthesis versus irradiance (PE) curves of two harmful bloom flagellates

Bering Sea temperature/pCO$_2$ matrix:
Photosynthesis vs. Irradiance Curve

Irradiance (μmol photons/m$^2$/sec)

PB (g C/g Chl a/hour)

- $15^\circ$C, 750 ppm CO$_2$
- $15^\circ$C, 360 ppm CO$_2$
- $10^\circ$C, 750 ppm CO$_2$
- $10^\circ$C, 360 ppm CO$_2$

α

PB$_{max}$

Hare et al. 2007
MEPS 352: 9-16
North Atlantic Bloom CO₂/temperature experiment: coccolithophore abundance, POC and PIC production

Interactive effects of light, temperature and pCO$_2$ on calcification by a Sargasso Sea *E. hux.* isolate


The primary control on calcification in this strain is light intensity- pCO$_2$ exerts a secondary effect, but only under saturating light conditions.
Carbon “overconsumption” at high pCO$_2$?

Riebesell et al. 2007, Nature 450: 545-548
Carbon measurement methods

1. Covered elsewhere in the course:
   – DIC drawdown
   – Calcification and organic carbon fixation using $^{14}$C


3. P/E curves: Requires a photosynthetron which produces a wide range of light levels; samples are incubated briefly with $^{14}$C (van Hilst and Smith 2002 MEPS 226: 1-12; Feng et al. 2009 MEPS 388: 13–25)
The marine nitrogen cycle

- Nitrogen Fixation
- N2 Fixation
- Anammox
- N2O
- NO
- NO2
- NO3
- NH3/NH4
- Organic Nitrogen

Oxidation state

-5 -4 -3 -2 -1 0 1 2 3 4 5
Nitrogen fixation

Nitrogen fixation involves the reduction of nitrogen gas (N₂) to ammonia (NH₃) via processes such as 
anammox or nitrogen fixation. The oxidation states of nitrogen compounds are shown, with key 
intermediates including N₂O, NO, and NO₂⁻.

- **N₂**: Nitrogen gas, oxidation state 0.
- **N₂O**: Nitrous oxide, oxidation state -1.
- **NO**: Nitric oxide, oxidation state +1.
- **NO₂⁻**: Nitrite, oxidation state -1.
- **NO₃⁻**: Nitrate, oxidation state +5.
- **NH₃**: Ammonia, oxidation state -3.
- **NH₄⁺**: Ammonium, oxidation state -3.

**Oxidation state**

-5 -4 -3 -2 -1 0 1 2 3 4 5

- **N₂ fixation**
- **denitrification**
- **nitrification**
- **assimilation**
- **organic nitrogen**
Nitrogen fixation

1. Biological nitrogen fixation is the primary natural source of fixed nitrogen in the ocean.

2. Major groups include cyanobacteria (*Trichodesmium*, *Crocosphaera*) along with diatom/diazotroph and zooplankton/diazotroph symbioses, N$_2$-fixing heterotrophic eubacteria and archaea.

3. Most prominent in sub-tropical and tropical regimes, but now being found in other marine environments as well.

4. Thought to be often limited by the availability of P or Fe.

Global estimate of new production based on N\textsubscript{2} fixation. DIC drawdown in NO\textsubscript{3}-depleted warm waters is equivalent to 0.8 ±0.3 Pg C yr\textsuperscript{-1}
Will $N_2$ fixation increase in the future high CO$_2$ ocean?

**Trichodesmium:**
Hutchins et al. 2007
Barcelos e Ramos et al. 2007
Levitan et al. 2007
Kranz et al. 2009

**Crocosphaera:**
Fu et al. 2008
Elevated N₂ fixation rates at high pCO₂ in cultured cyanobacteria

1) *Trichodesmium erythraeum* strain GBR at 29°C, 380-750 ppm CO₂ (Hutchins et al. 2007)
2) *T. erythraeum* strain GBR at 25°C, 380-750 ppm CO₂ (Hutchins et al. 2007)
3) *T. erythraeum* strain IMS 101 at both 25°C and 29°C, 380-750 ppm CO₂ (Hutchins et al. 2007)
4) *T. erythraeum* strain IMS 101 at 25°C, 380-750 ppm CO₂ (Barcelos e Ramos et al. 2007)
5) *T. erythraeum* strain IMS 101 at 25°C, 400-900 ppm CO₂ (Levitan et al. 2007)
6) *T. erythraeum* strain IMS 101 at 25°C, 370-1000 ppm CO₂ (Kranz et al. 2009)
7) *Crocosphaera watsonii* strain WH8501 at 28°C, 380-750 ppm CO₂ (Fu et al. 2008)

Hutchins et al. in review, Oceanography
Short-term CO₂ enrichments using natural *Trichodesmium* colonies from the Gulf of Mexico

N₂ fixation rates increased 6-41% within a few hours of elevating pCO₂ to 750 ppm

Hutchins et al. in review, Oceanography
Future trends in global N₂ fixation by *Trichodesmium*?

Maximum (blue) and minimum (red) projected annual global N₂ fixation increases versus pCO₂ (green)

Hutchins et al. in review, Oceanography
pCO$_2$ and P co-limitation of *Trichodesmium* N$_2$ fixation

Adding either P or CO$_2$ will increase N$_2$ fixation and growth rates of P-limited cultures at present day pCO$_2$

Hutchins et al. 2007, Limnology & Oceanography 52
**Crocosphaera: N$_2$ fixation rates as a function of pCO$_2$ and Fe**

### N$_2$ fixation rates

**Fe-replete**

- pCO$_2$ (ppm): 190, 380, 750
- N$_2$ fixation (nmol cell$^{-1}$ hour$^{-1}$): 0, 1e-8, 2e-8, 3e-8

**Fe-limited**

- pCO$_2$ (ppm): 190, 380, 750
- N$_2$ fixation (nmol cell$^{-1}$ hour$^{-1}$): 0, 1e-8, 2e-8, 3e-8

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Fu et al. 2008. Interactions between changing pCO$_2$, N$_2$ fixation, and Fe limitation in the marine unicellular cyanobacterium Crocosphaera. L&O 53: 2472-2484
The two nutrients Fe and P interact very differently with changing pCO$_2$ in N$_2$-fixing cyanobacteria

- Severe Fe limitation essentially cancels out the stimulatory effect of increased pCO$_2$
- Severe P limitation however does not effectively, the cells are co-limited by both P and CO$_2$
Not all N\textsubscript{2}-fixing cyanobacteria will necessarily benefit from high pCO\textsubscript{2}:

The harmful bloom species \textit{Nodularia spumigena} from the brackish Baltic Sea

Nitrogen fixation measurements

1. Measurements of acetylene reduction to ethylene using gas chromatography

2. $^{15}N_2$ incorporation measured by mass spectrometry
**Denitrification**

Oxidation state

-5
-4
-3
-2
-1
0
+1
+2
+3
+4
+5

**N\(_2\)**

- **N\(_2\) fixation**
- **anammox**

**NH\(_3\)/NH\(_4\)\(^+\)**

- **assimilation**
- **degradation**

**NO\(_2\)\(^-\)**

- **nitrification**

**NO\(_3\)\(^-\)**

**Organic Nitrogen**

**Denitrification**
Denitrification

1. Heterotrophic, largely facultative anaerobic micro-organisms (eubacteria, archaea, and fungi) use oxidized \( \text{NO}_3^- \) as a respiratory terminal electron acceptor, reducing it through a series of intermediates to \( \text{N}_2 \).

2. Denitrification occurs in the large water column suboxic regions (tropical North and South Pacific, Arabian Sea), and in suboxic sediments worldwide.

3. Along with annamox, denitrification represents the principle loss term for fixed nitrogen in the ocean.
Carbon “overconsumption” at high pCO$_2$?

Riebesell et al. 2007, Nature  450: 545-548
Oschlies et al. 2008, Global Biogeochemical Cycles 22
“Simulated 21st century's increase in oceanic suboxia by CO$_2$-enhanced biotic carbon export”
Simulated effects of warming and stratification on global suboxic water volume

Future increases in the global volume of hypoxic water

Matear and Hirst 2003, Global Biogeochemical Cycles 17

Differences in zonal mean of ocean dissolved O$_2$ between 2080–2100 and 1980–2000

Bopp et al. 2002, Global Biogeochemical Cycles 16
Denitrification measurements


2. Enzymatic activity of electron transport systems measured colorimetrically using the artificial electron acceptor tetrazolium (Devol, 1975, Codispoti and Packard, 1980, Naqvi and Shailaja, 1993)

3. $^{15}$NO$_3^-$ incubation experiments measuring the production of $^{29}$N$_2$ by mass spectrometry (Devol et al. 2006)

Nitrification

Oxidation state

\[ \begin{align*}
& N_2 \\
& N_2O \\
& NO \\
& NO_2^- \\
& NO_3^- \\
& NH_3/\text{NH}_4^+ \\
& \text{Organic Nitrogen}
\end{align*} \]

 Processes:
- Denitrification
- Anammox
- Nitrification
- Assimilation
- Degradation
Nitrification

- Oxidation of ammonia/ammonium first to nitrite, then to nitrate
- Aerobic, chemoautotrophic eubacteria and archaea obtain electrons from these reduced nitrogen compounds to fix CO₂
- A large fraction occurs just below the euphotic zone (Yool et al. 2007), where it is vulnerable to near-term ocean acidification
- NH₃-oxidizing genus *Nitrosomonas* and the NO₂⁻-oxidizing genus *Nitrobacter* fix carbon using the Calvin cycle
- Seawater ammonia/ammonium (NH₃/NH₄⁺) buffer system pKa ~9.19; over the next century the fraction of NH₃ will decrease by nearly 50%, from ~6% to ~3%.
- NH₃ appears to be the chemical species actually oxidized by *Nitrosomonas* (Suzuki et al. 1974, Ward 1987)
Nitrification rates decrease with acidification

Modeled effects of a 20% reduction in North Sea nitrification rates at 1000 ppm CO$_2$

Change in the ratio of nitrate: total DIN (%)

Blackford and Gilbert 2007

Journal of Marine Systems 64: 229-241
Global median nitrification rate

Ammonium-specific oxidation rate (d⁻¹)

* From Yool et al. 2007 Nature 447: 999-1002
Nitrification measurements

1. Simple mass balance nutrient measurements of changes in NO$_2^-$ and NH$_4^+$ concentrations in seawater, sometimes coupled with specific inhibitors of NH$_4^+$ oxidation (acetylene, allylthiourea, methyl fluoride, N-serve) or NO$_2^-$ oxidation (chlorate).

2. Inhibitors can also be coupled with $^{14}$CO$_2$ uptake measurements. Problems: inhibitor artifacts, long incubations.

3. $^{15}$N substrate tracer measurements using mass spectrometry. Problem: True tracer levels sometimes hard to achieve, though.

4. Isotopic enrichment factors: Ammonium oxidizers produce isotopically enriched NH$_4^+$ and isotopically depleted NO$_2^-$.

The silicon cycle

1. Si is a required element for the shells of diatoms and silicoflagellates (phytoplankton), as well as radiolarians (protozoa).

2. Principle dissolved form in seawater is silicic acid (H$_4$SiO$_4$); forms a buffer system in seawater (pK$_{a1}$=9.84, pK$_{a2}$=13.2).

3. Very simple cycle: no gas phase or organic forms.

4. How is the use of Si affected by ocean acidification?
Most studies have found little or no direct impact of changing pCO$_2$ on diatom Si utilization

Cellular Si quotas of a cultured diatom are unchanged between 370 and 750 ppm CO$_2$


Silicate drawdown is identical at 350, 700 and 1050 ppm CO$_2$ in a Bergen mesocosm experiment

Bellerby et al. 2008, Biogeosciences Discussions 4
**pCO₂ and temperature indirectly change Si cycling due to phytoplankton community shifts**

**Equatorial Pacific incubation experiment**

<table>
<thead>
<tr>
<th>CO₂ Level</th>
<th>Silicate : Nitrate utilization ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 ppm CO₂</td>
<td>Phaeocystis dominant</td>
</tr>
<tr>
<td>750 ppm CO₂</td>
<td>Diatoms dominant</td>
</tr>
</tbody>
</table>

**North Atlantic Bloom incubation experiment**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>BSi:POC Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td></td>
</tr>
<tr>
<td>High pCO₂</td>
<td></td>
</tr>
<tr>
<td>High Temperature</td>
<td></td>
</tr>
<tr>
<td>Greenhouse</td>
<td></td>
</tr>
</tbody>
</table>

**Changing Si:N utilization ratios due to a CO₂-driven community shift between diatoms and Phaeocystis**

Adapted from Tortell et al. 2002, MEPS 236

**Changing particulate Si: C ratios due to a temperature-driven community shift between diatoms and coccolithophores**

Ocean acidification enhances the silica dissolution rates of empty diatom frustules.
Rising temperature and pCO$_2$ drive shifts from diatom to nanophytoplankton dominance in the Bering Sea
(Hare et al. 2007, Marine Ecology Progress Series 352: 9-16.)
Silicon measurements

**Biogenic silica measurements**: Simple spectrophotometric method, after alkaline digestion of BSi on filter samples to form silicic acid. (Brzezinski and Nelson 1986, Marine Chemistry 19: 139-151; Feng et al. 2009. MEPS 388: 13-25)


**PDMPO**: A fluorophore to trace new Si deposition in diatoms (Leblanc and Hutchins 2005, L&O Methods 3: 462- 476.)
The phosphorus cycle

1. P is required by all cells for nucleotides and nucleic acids, and for some phosphorylated proteins; required by most cells for phospholipid cell membranes.

2. Principle form in seawater is as orthophosphate or dissolved organic phosphorus; dominant form of inorganic phosphorus at pH 8 is $\text{HPO}_4^{2-}$ ($\sim 87\%$), but the fraction of $\text{H}_2\text{PO}_4^-$ will increase with future acidification.


4. Will P requirements change with ocean acidification?
Phytoplankton P requirements:
Usually, little or no response to pCO$_2$ increases

Coccolithophore *Emiliania huxleyi*

- Cellular P quota (pg cell$^{-1}$)

- 375 ppm CO$_2$, 20$^\circ$C
- 750 ppm CO$_2$, 20$^\circ$C
- 375 ppm CO$_2$, 24$^\circ$C
- 750 ppm CO$_2$, 24$^\circ$C

Feng et al. 2008
European Journal of Phycology 43: 87-98

Cyanobacterium *Synechococcus*

- Cellular P quota (fg cell$^{-1}$)

- 375 ppm CO$_2$, 20$^\circ$C
- 750 ppm CO$_2$, 20$^\circ$C
- 375 ppm CO$_2$, 24$^\circ$C
- 750 ppm CO$_2$, 24$^\circ$C

Fu et al. 2007
Journal of Phycology 43: 485-496
Phosphorus measurements


$^{33}$P radioisotope tracer uptake: Commercially available $^{33}$P-labeled phosphate, ATP, etc. (Fu et al. 2006, European Journal of Phycology 41: 15-28)

Cell surface scavenging of P: A cell surface wash can be used to remove adsorbed phosphate from cells, giving a better estimate of true cellular P quotas (Sanudo-Wilhelmy et al. 2004, Nature 432: 897-901; Fu et al. 2005, Limnology and Oceanography 50: 1459-1472.)
Phytoplankton elemental stochiometry in the high CO$_2$ ocean

C:N and N:P

1. Evidence from culture studies of cyanobacteria and eukaryotic algae

2. Evidence from natural phytoplankton community manipulation experiments
**Cultured cyanobacteria**

<table>
<thead>
<tr>
<th>% change from present to future $pCO_2$</th>
<th>C:N</th>
<th>N:P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picocyanobacteria</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diazotrophs- <em>Crocosphaera</em> and <em>Trichodesmium</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichodesmium at 380 and 750 ppm $CO_2$ (Barcelos e Ramos et al. 2007)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichodesmium at 370 and 1000 ppm $CO_2$ (Kranz et al. 2009)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 & 2, *Synechococcus* and *Prochlorococcus* at 380 and 750 ppm $CO_2$ (Fu et al. 2007)
3 & 4, Fe-replete and Fe-limited *Crocosphaera* at 380 grown and 750 ppm $CO_2$ (Fu et al. 2008)
5 & 6, P-replete and P-limited *Trichodesmium* at 380 and 750 ppm $CO_2$ (Hutchins et al. 2007)
7, *Trichodesmium* at 400 and 900 ppm $CO_2$ (Levitan et al. 2007)
8, *Trichodesmium* at 380 and 750 ppm $CO_2$ (Barcelos e Ramos et al. 2007)
9, *Trichodesmium* at 370 and 1000 ppm $CO_2$ (Kranz et al. 2009)

Hutchins et al. in review, *Oceanography*
Cultured eukaryotic phytoplankton

% change from present to future pCO₂

10 & 11 Diatoms *Asterionella* at 430 and 820 ppm CO₂ and *Skeletonema* at 400 and 720 pCO₂ (Burkhardt et al. 1999)

12 & 13 Antarctic diatom *Chaetoceros* and prymnesiophyte *Phaeocystis* at 430 and 820 ppm CO₂ (Fu et al. unpubl results)

14 & 15 Coccolithophorid *Emiliania huxleyi* under low and high light at 375 and 750 ppm pCO₂ (Feng et al. 2008)

16 Coccolithophorid *Emiliania huxleyi* at 490 and 750 ppm pCO₂ (Iglesias-Rodriguez et al. 2008)

17 & 18 Non-calcifying *Emiliania huxleyi* under low and high light at 360 and 2000 ppm CO₂ (Leonardos and Geider 2005)

19 & 20 Toxic raphidophyte *Heterosigma* and the dinoflagellate *Prorocentrum* at 375 and 750 ppm pCO₂ (Fu et al. 2008)

21 & 22 P-replete and P-limited dinoflagellate *Karldiniun* at 430 and 745 ppm CO₂ (Fu et al. in review)

Hutchins et al. in review, Oceanography
23. North Atlantic spring bloom, 390 and 690 ppm CO₂ (Feng et al. 2009)
24. Ross Sea, Antarctica, 380 and 750 ppm CO₂ (Feng et al. in review)
25. Equatorial Pacific, 150 and 750 ppm CO₂ (Tortell et al. 2002)
26. Norwegian fjord, 350 and 700 ppm CO₂ (Riebesell et al. 2007)
27. Norwegian fjord, 410 and 710 ppm pCO₂ (Engel et al. 2005)
28. Korean coastal waters, 400 and 750 ppm CO₂ (Kim et al. 2006)
29 & 30. Bering Sea shelf at 10°C and 15°C, 370 and 750 ppm pCO₂ (Hare et al. 2007)
31 & 32. Bering Sea offshore at 10°C and 15°C, 370 and 750 ppm pCO₂ (Hare et al. 2007)
33 & 34. U.S. East Coast estuary, 380 and 750 ppm pCO₂ (Fu et al. unpubl.results)

Hutchins et al. in review, Oceanography
Generalizations

- C:N and N:P ratios of individual phytoplankton species often increase at high pCO$_2$, but the trends in whole community stoichiometry are much more variable.

- Be cautious when extrapolating from any particular experiment or regime to the whole future ocean...

- More work is needed to draw firm conclusions about the effects of OA on major elemental stoichiometry.
Iron (Fe) is the trace metal with by far the best documented biogeochemical impacts. Phytoplankton production is limited or co-limited by this micronutrient over a large fraction of the ocean surface.

Iron is heavily involved in photosynthesis, respiration, nitrate uptake, and nitrogen fixation, making Fe/CO₂ interactions very likely.

Other bioactive trace elements whose cycles may potentially be affected by ocean acidification include Mo (required for nitrogen fixation), as well as Zn, Cd, and Co (all co-factors for various forms of carbonic anhydrase).

Effects of acidification on trace metal cycling may include changes in biological requirements; shifts in their inorganic chemical speciation (e.g., many are affected by carbonato complexation); and possible pH effects on the metal-binding functional groups of organic ligands.
Will biological demand for metals used as cofactors for carbonic anhydrase (like Zn, Cd, and Co) be lower in the future high CO$_2$ ocean?
$pCO_2$, carbonic anhydrase activity, and cellular Zn:C
(Sunda and Huntsman 2005)

At higher $pCO_2$ (lower pH), phytoplankton have much lower levels of CA activity, and require much less cellular Zn
Changes in natural community Cd:P with varying pCO$_2$ (Cullen and Sherrell 2005)
Trace metal quotas (mmol metal: mol P) of a natural *Phaeocystis* bloom in the Ross Sea, incubated at 380 ppm and 750 ppm CO$_2$.

<table>
<thead>
<tr>
<th>CO$_2$ levels</th>
<th>Cd:P</th>
<th>Co:P</th>
<th>Zn:P</th>
<th>Fe:P</th>
<th>Mn:P</th>
</tr>
</thead>
<tbody>
<tr>
<td>380 ppm</td>
<td>0.20</td>
<td>0.012</td>
<td>8.7</td>
<td>10.7</td>
<td>0.28</td>
</tr>
<tr>
<td>750 ppm</td>
<td>0.095</td>
<td>0.002</td>
<td>0.34</td>
<td>5.1</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Hutchins et al. in preparation
Crocosphaera: $N_2$ fixation rates as a function of $pCO_2$ and Fe

**N₂ fixation rates**

<table>
<thead>
<tr>
<th>pCO₂ (ppm)</th>
<th>Fe-replete</th>
<th>Fe-limited</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>1e-8</td>
<td>1e-8</td>
</tr>
<tr>
<td>380</td>
<td>2e-8</td>
<td>2e-8</td>
</tr>
<tr>
<td>750</td>
<td>3e-8</td>
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</tr>
</tbody>
</table>

**Cellular Fe quota**

<table>
<thead>
<tr>
<th>pCO₂ (ppm)</th>
<th>Fe replete</th>
<th>Fe limited</th>
</tr>
</thead>
<tbody>
<tr>
<td>190 ppm</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>380 ppm</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>750 ppm</td>
<td>30</td>
<td>15</td>
</tr>
</tbody>
</table>

Fu et al. 2008 L&O 53: 2472- 2484
Crocosphaera: Effects of pCO2 on cellular Mo quota

Sanudo-Wilhelmy, Fu and Hutchins unpublished
Trichodesmium

Fe:P ratios increase
~40% between
370 and
750 ppm CO$_2$

But decrease by about the
same amount with a 5°C
temperature increase...

Sanudo-Wilhelmy, Fu and
Hutchins unpublished
Trace metal biogeochemical methods

Approaches:
- Laboratory culture studies
- Field incubations and measurements
- Both require combining OA methods with scrupulous trace metal clean techniques (see Bruland et al. 1991, L&O 36: 1555-1577).

Analytical methods:
- Radiotracer techniques: $^{55}$Fe, $^{59}$Fe, $^{65}$Zn, $^{109}$Cd, etc. (Hutchins et al. 1999 AME 19: 129-138)
- Titanium and oxalate wash methods to remove cell surface-scavenged metals (Hudson and Morel 1989 L&O 34: 1113–1120; Tovar-Sanchez et al. 2003 Marine Chemistry 82: 91-99)
Radioisotope versus SXRF comparison

Twining et al. 2004, DSR I 51
Conclusions

1. Changes in ocean pCO$_2$ and acidification will fundamentally change the present-day ocean biogeochemistry of carbon and nitrogen. Changes in the phosphorus and silicon cycles may be indirect and less dramatic. Trace metal biogeochemical responses are just now beginning to be investigated.

2. Interactions of other global change variables like temperature, stratification, and major and micronutrients with pCO$_2$ are at least as important to consider as OA effects in isolation. Reductionist, “CO$_2$-centric” experiments can often give incomplete or misleading results.

3. A new generation of experimental, observational, and modeling work is needed to address issues of long-term biogeochemical changes, including the effects of biological acclimation and adaptation.

4. The responses of numerous key ocean biogeochemical processes to ocean acidification have been tested only in very preliminary studies, or not at all. There is a lot of room for new investigators in this field…
Acknowledgements

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NSF OCE Biological Oceanography

NSF OCE Chemical Oceanography

NSF Office of Polar Programs
The marine nitrogen cycle

Oxidation state

\[ \text{N}_2 \] \begin{align*}
\text{N}_2O & \rightarrow \text{NO} \\
\text{NO} & \rightarrow \text{NO}_2^- \\
\text{NO}_2^- & \rightarrow \text{NO}_3^- \\
\text{NH}_3/\text{NH}_4^+ & \rightarrow \text{Organic Nitrogen} \\
\end{align*}

- N\text{\textsubscript{2}} \text{ fixation}
- \text{anammox}
- \text{nitrification}
- \text{denitrification}

\text{Organic Nitrogen}