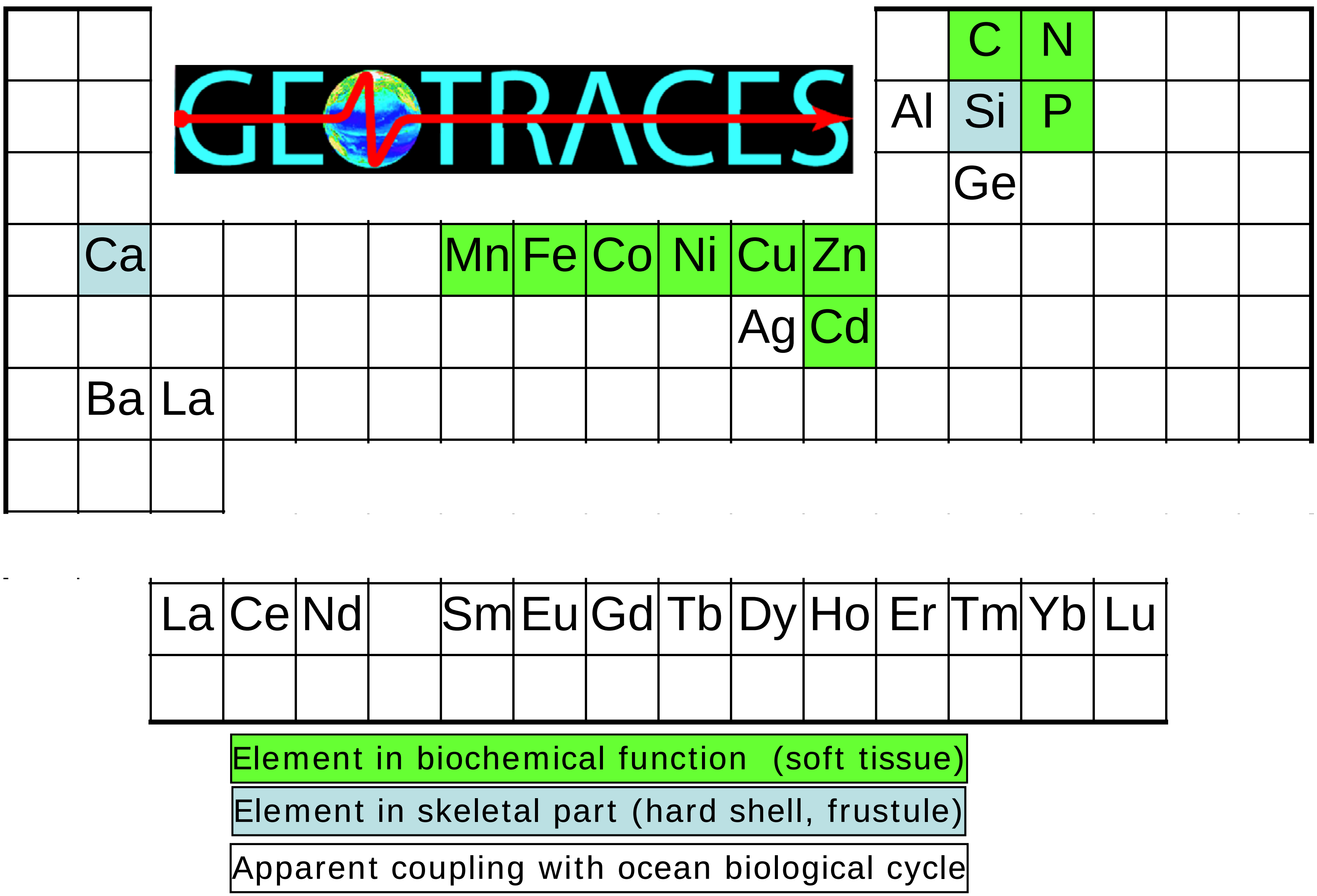
EFFECTS OF CHANGES IN CARBONATE CHEMISTRY

ON NUTRIENT AND METAL SPECIATION

Hein De Baar, Loes Gerringa
and Charles-Edouard Thuroczy

European Project on OCean Acidification

Biological Elements in Seawater



Metals Abundance & Biological Evolution

Mn 9550	**Fe** 900000	**Co** 2250	**Ni** 49300	**Cu** 522	**Zn** 1260	
				Ag 0.49	**Cd ?** 1.61	
					Hg 0.34	**Pb** 315

numbers of atoms versus 1 million Si atoms

Biological Evolution used abundant metals: essential

Low abundant metals no bio-functions: toxic

Case studies for Fe, Cu, Zn, Cd

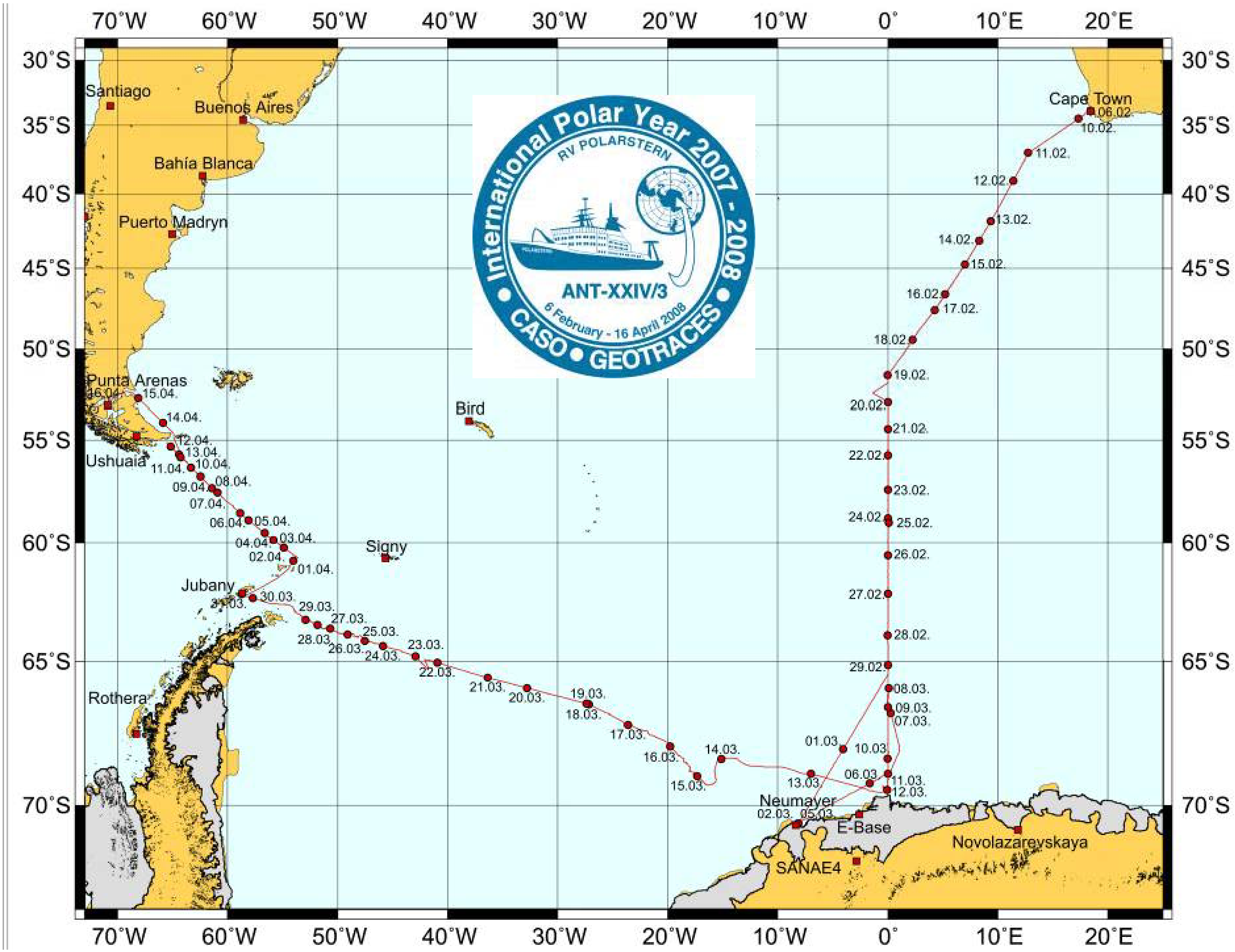
De Baar & La Roche (2003)

Contents

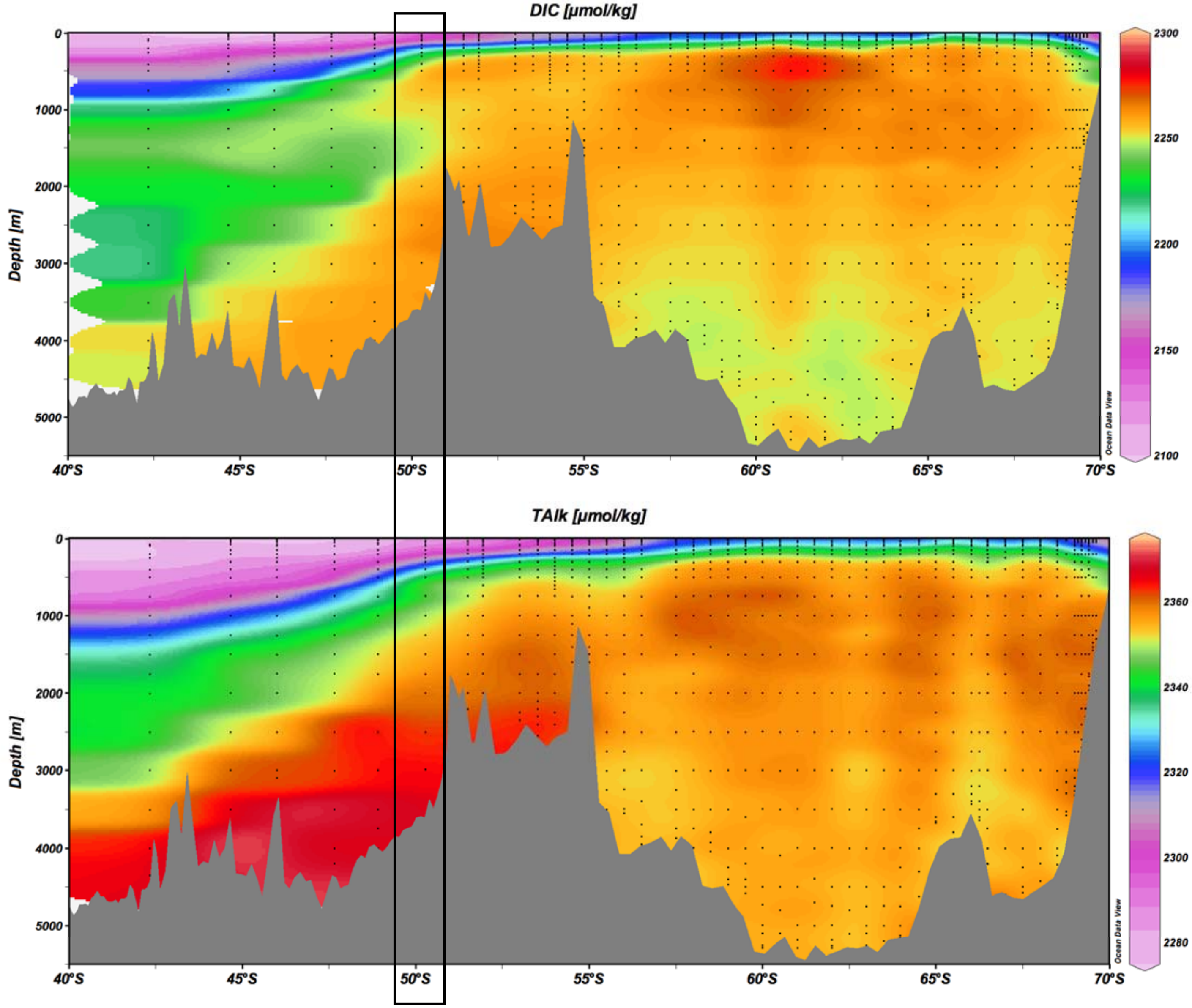
- Small changes in CO_2 chemistry are significant
  - effects on underwater sound
  - effects on biology
- Small changes in nutrient chemistry
  - Silicate
    - sidestep: Aluminium
  - Phosphate
- Speciation of trace metals Zn, Cu, Cd
- Speciation of iron Fe
- Future work
- Summary

What is Speciation

- Different physical-chemical states of a chemical element in seawater
  - truly dissolved, colloids, larger particles
  - oxidation state, Fe(II) versus Fe(III)
  - weak acid (H_2CO_3) or weak base (NH_4OH)
  - inorganic complexation (e.g. $NaHCO_3^0$)
  - organic complexation (e.g. $Fe(III)L_{organic}$)


International Polar Year 2007 - 2008
RV POLARSTERN
ANT-XXIV/3
6 February - 16 April 2008
CASO
GEOTRACES
Santiago
Buenos Aires
Bahía Blanca
Puerto Madryn
Punta Arenas
Ushuaia
Bird
Signy
Jubany
Rothera
Neumayer
E-Base
SANAE4
Novolazarevskaya
Cape Town

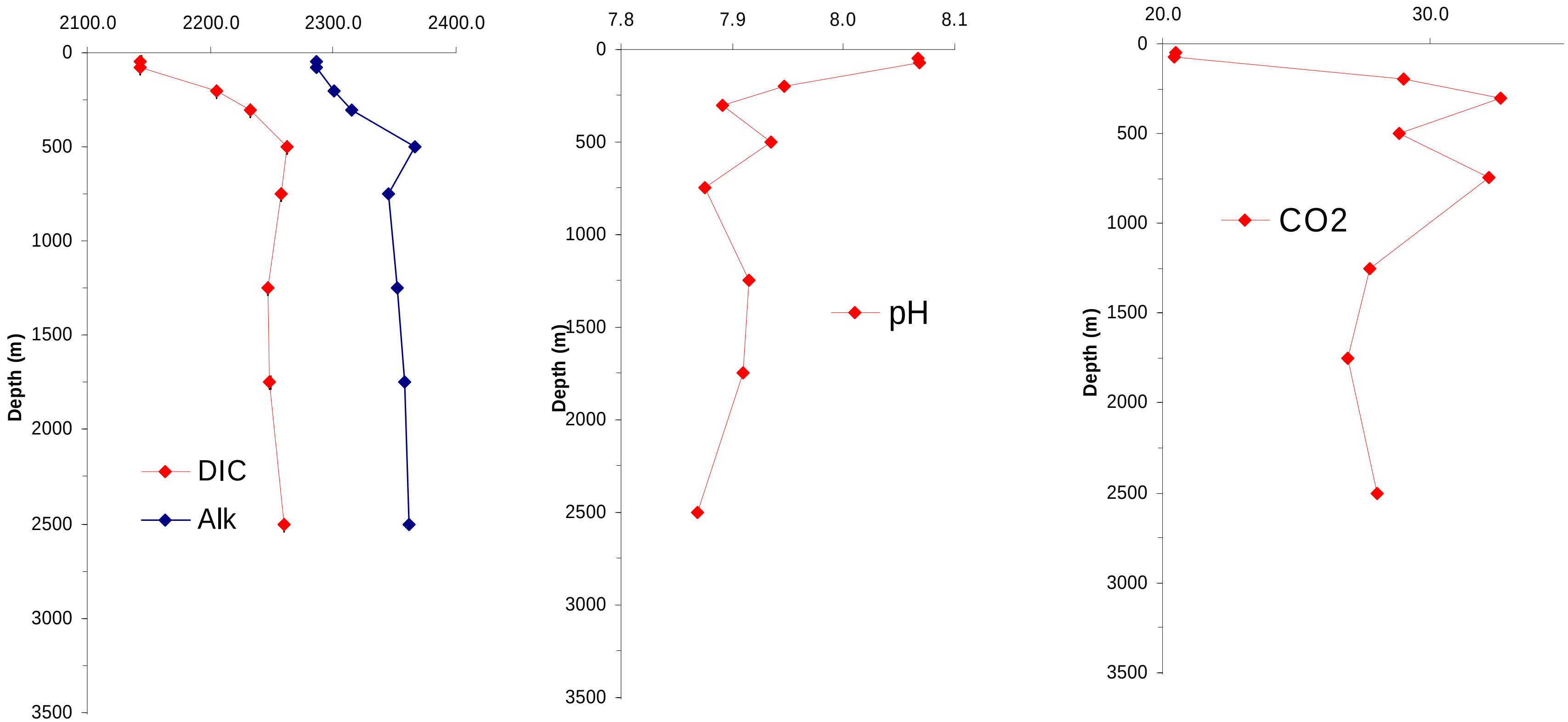
DIC and Alkalinity at the Zero Meridian



50 ^{0}S station

Steven van Heuven, unpubl. data, 2008

Zero Meridian Station 107
50^0 16.13' S, $01^0$26.71' W



deep waters already are
natural laboratory for low pH

Steven van Heuven, unpubl. data, 2008

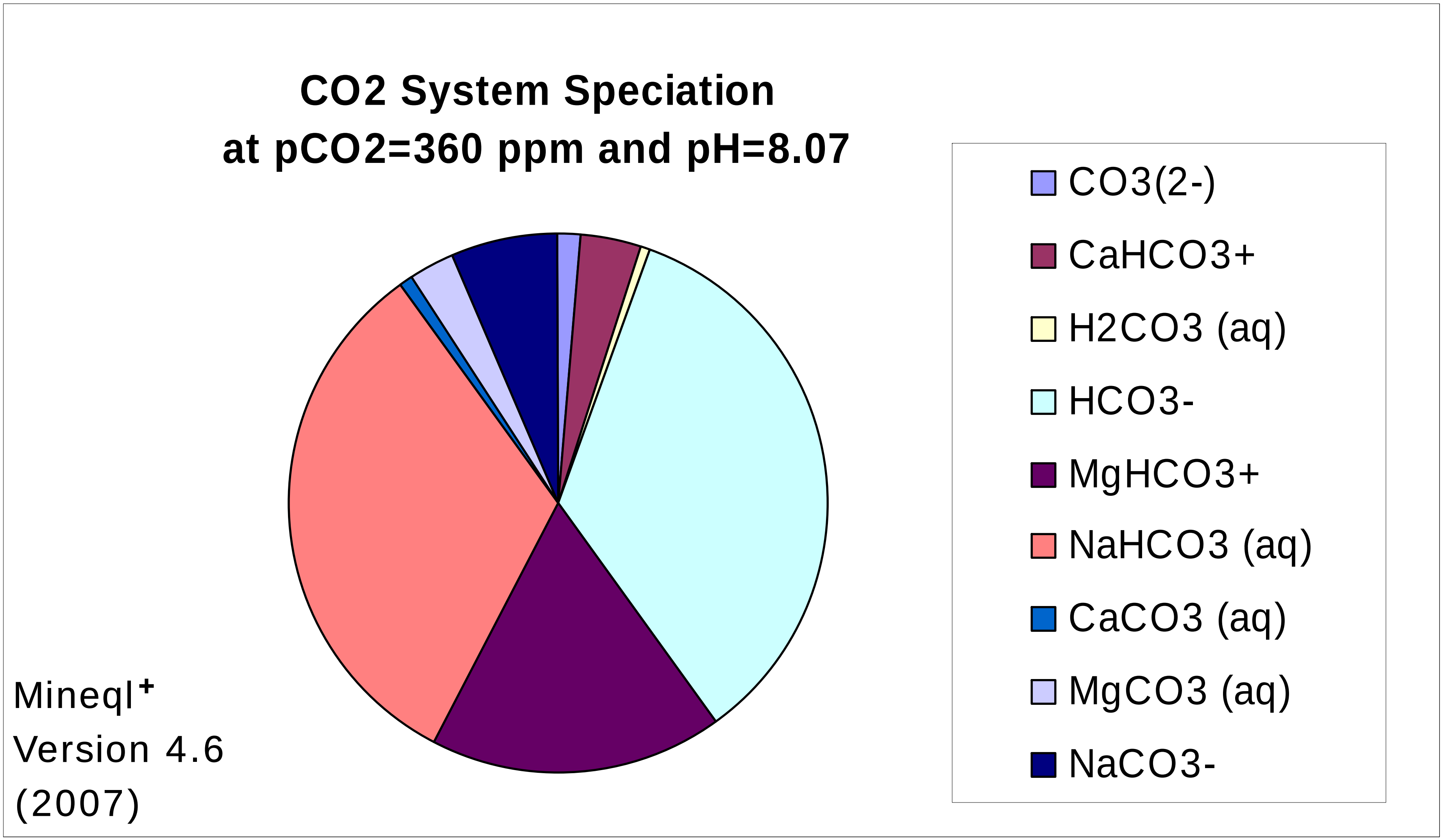
Today and future scenario at 49 m depth
Station 107 (50 ^{0}S, 01 ^{0}W)

year	DIC	ALK	pCO2	pH
2008	2144	2287	360	8.07
Future:				
2100 ?	2249	2287	800	7.76
2300 ?	2325	2287	1500	7.5

DIC and ALK above units micromol per kg seawater

these were converted to micromol per Liter for Mineql$^+$ Version 4.6 (2007) simulations

CO2 System Speciation with Major Ions in Seawater



Unanticipated Consequences of Ocean Acidification: A Noisier Ocean at Lower pH

Keith Hester, Edward Peltzer, William Kirkwood and Peter Brewer

Geophysical Research Letters (2008)

Decrease in ocean sound absorption for frequencies lower than 10 kHz.

This effect is due to known pH-dependent chemical relaxations in the $B(OH)_3/B(OH)_4^-$ and HCO_3^-/CO_3^{2-} systems.

The pH change of 0.3 units anticipated by mid-century, results in a decrease of sound absorption by almost 40%.

Simplified scheme is a coupled exchange reaction with ion-pairing:

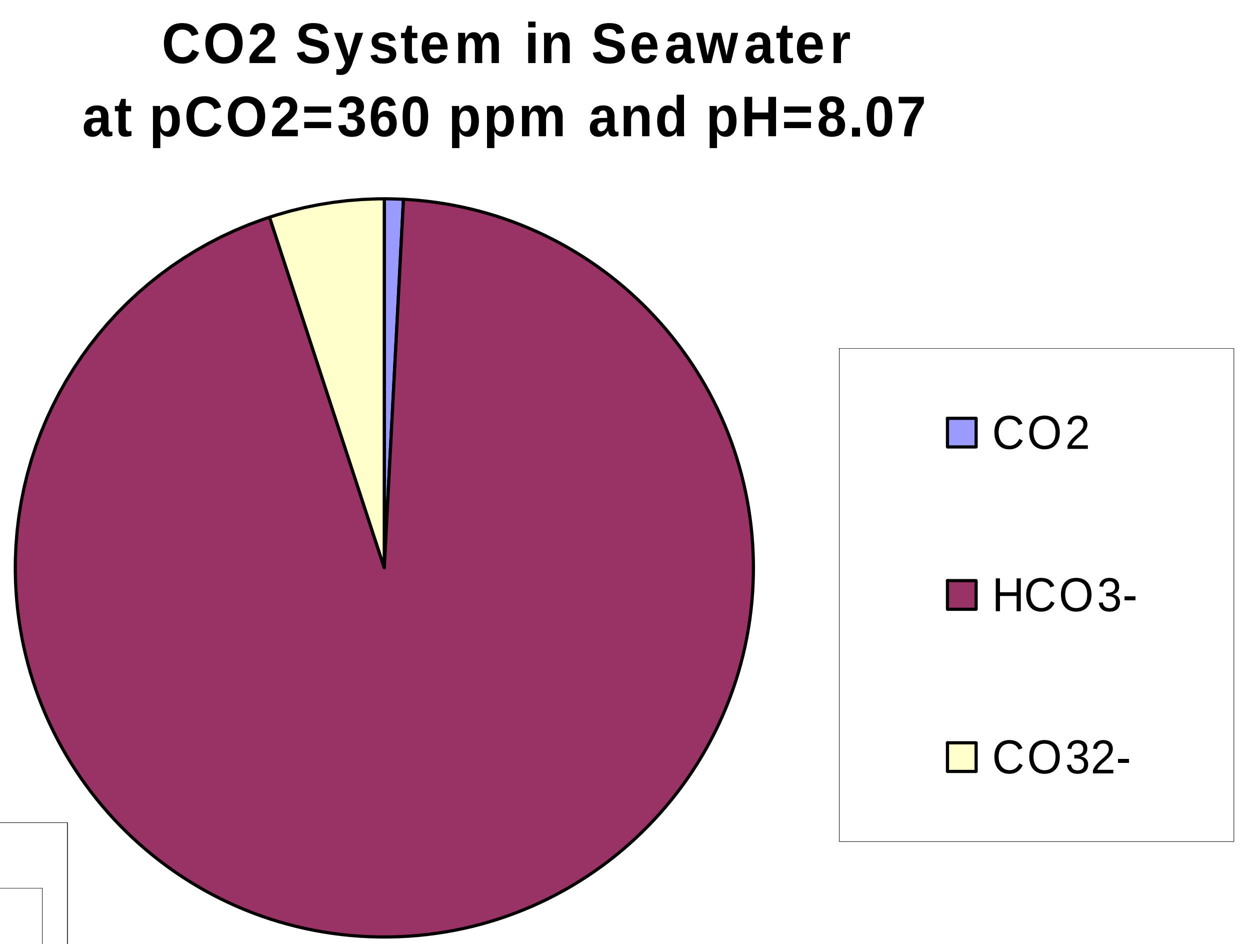
$$CO_3^{2-} + B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + HCO_3^-$$

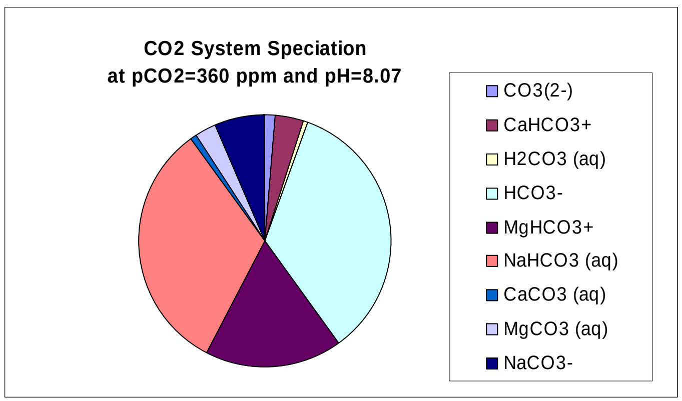
In fact the species $CaCO_3$(aq) and $CaHCO_3^+$ as well as $MgCO_3$(aq) and $MgHCO_3^+$ are involved

Also Presentation by D. Browning at Wednesday morning

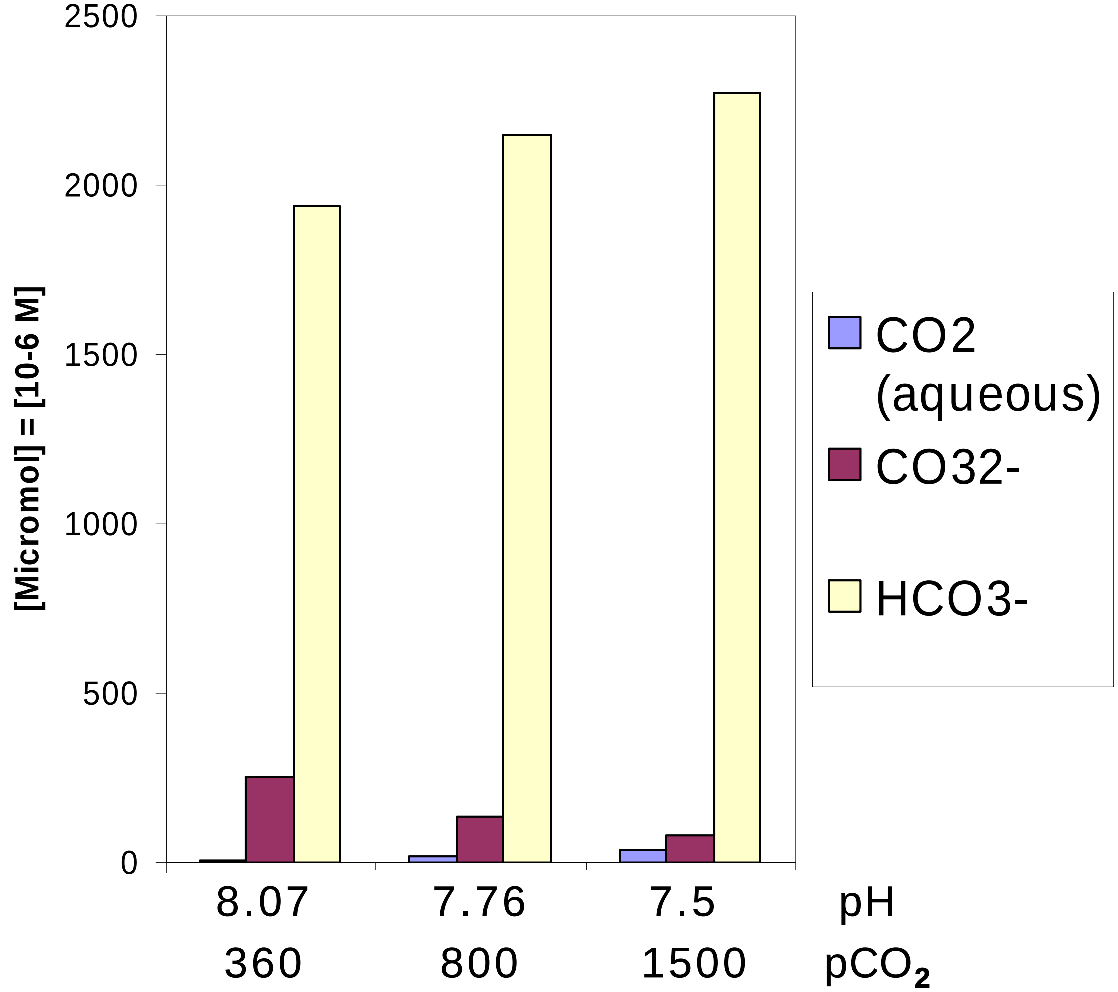

Will marine mammals adapt ?
Underwater sound is already increasing due to human activity (ships, sonar, etc.)
The additional decrease of sound absorption is an extra concern
59 ºSouth, February 2008

Simplified CO2 System in Seawater





Future changes CO_2 system: changes of minor players can make a difference



Major player HCO_3^- remains quite stable

Minor players CO_2 and CO_3^{2-} change more

this is our concern for photosynthesis and calcification, respectively

Equilibrium Thermodynamics in Mineql^{+}4.6(2007)

The thermodynamic equilibrium simulation only mimics the existing or predicted situation

The rate or kinetics of any chemical reaction is <u>not</u> assessed

Conversion between chemical species:

$$H_2O \;+\; CO_2 \;=\; HCO_3^- \;+\; H^+$$

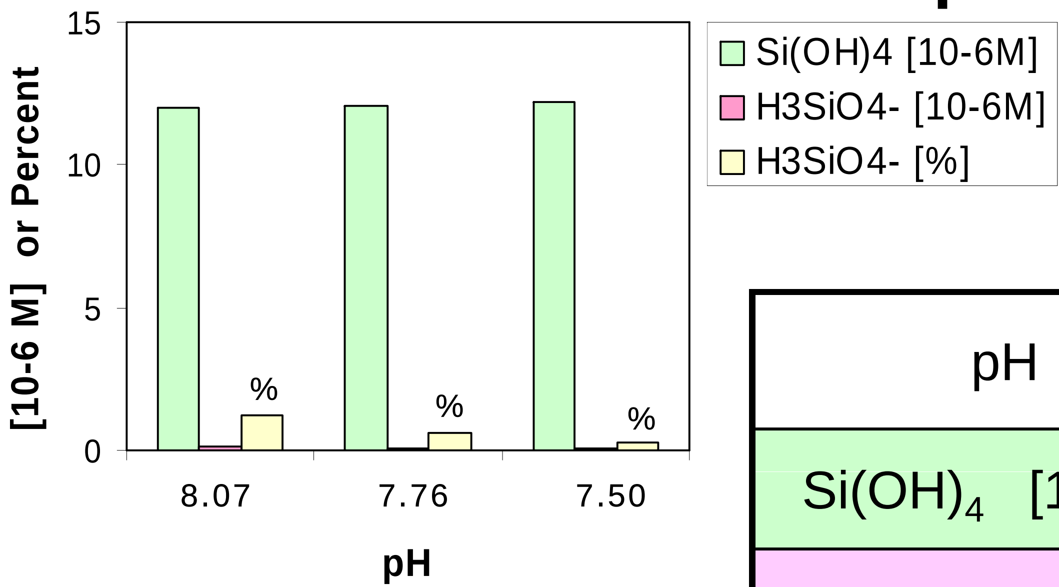
This is a slow reaction

Therefore chemical speciation is important

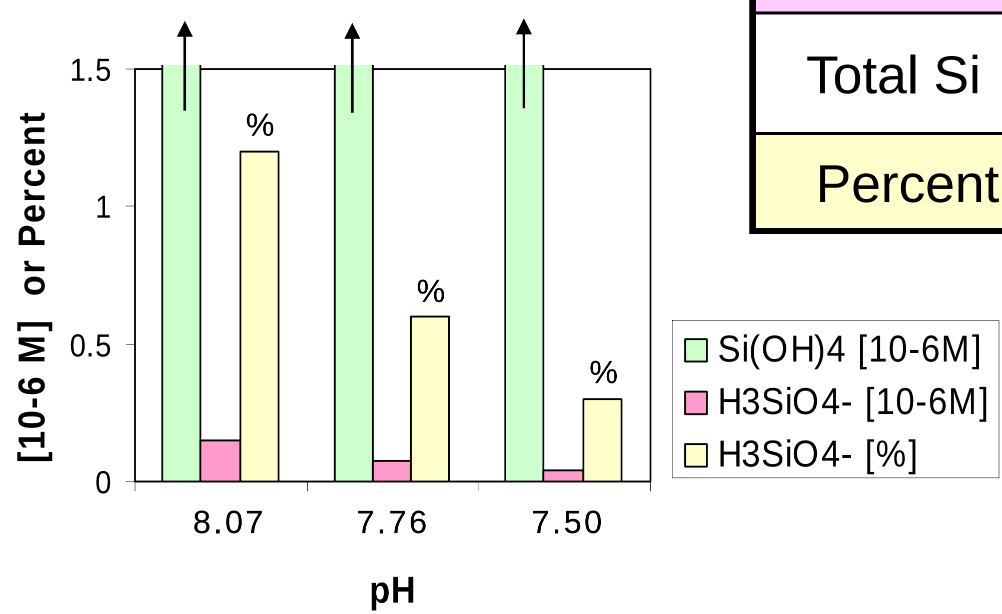
(acceleration by enzyme Carbonic Anhydrase)

When the rates of conversion reactions are fast, then chemical speciation in seawater may be less important

Silicate Speciation



At tenfold expanded scale:



pH	8.07	7.76	7.5
$Si(OH)_4$ [10^{-6} M]	12.0	12.1	12.2
$H_3SiO_4^-$ [10^{-6} M]	0.151	0.074	0.041
Total Si [10^{-6} M]	12.2	12.2	12.2
Percent $H_3SiO_4^-$	1.2 %	0.6 %	0.3 %

Silicate speciation: does it matter ?? (who cares ?)

Milligan et al (2004)

Si uptake and dissolution by diatoms

conditions pH = 8.5 and pH = 7.8

Si uptake rate not affected by pH

Si dissolution rate is 6-7 fold higher at low pH

at low pH more Si efflux from cell: lower Si/C ratio

effect on Si stable isotope fractionation yet to be assessed

Del Amo & Brzezinski (1999)

4 diatoms at pH 8.0 and pH 9.2

$Si(OH)_4$ is by far the preferred Si species for diatom uptake

one diatom P. tricornutum behaves different from other 3 diatoms

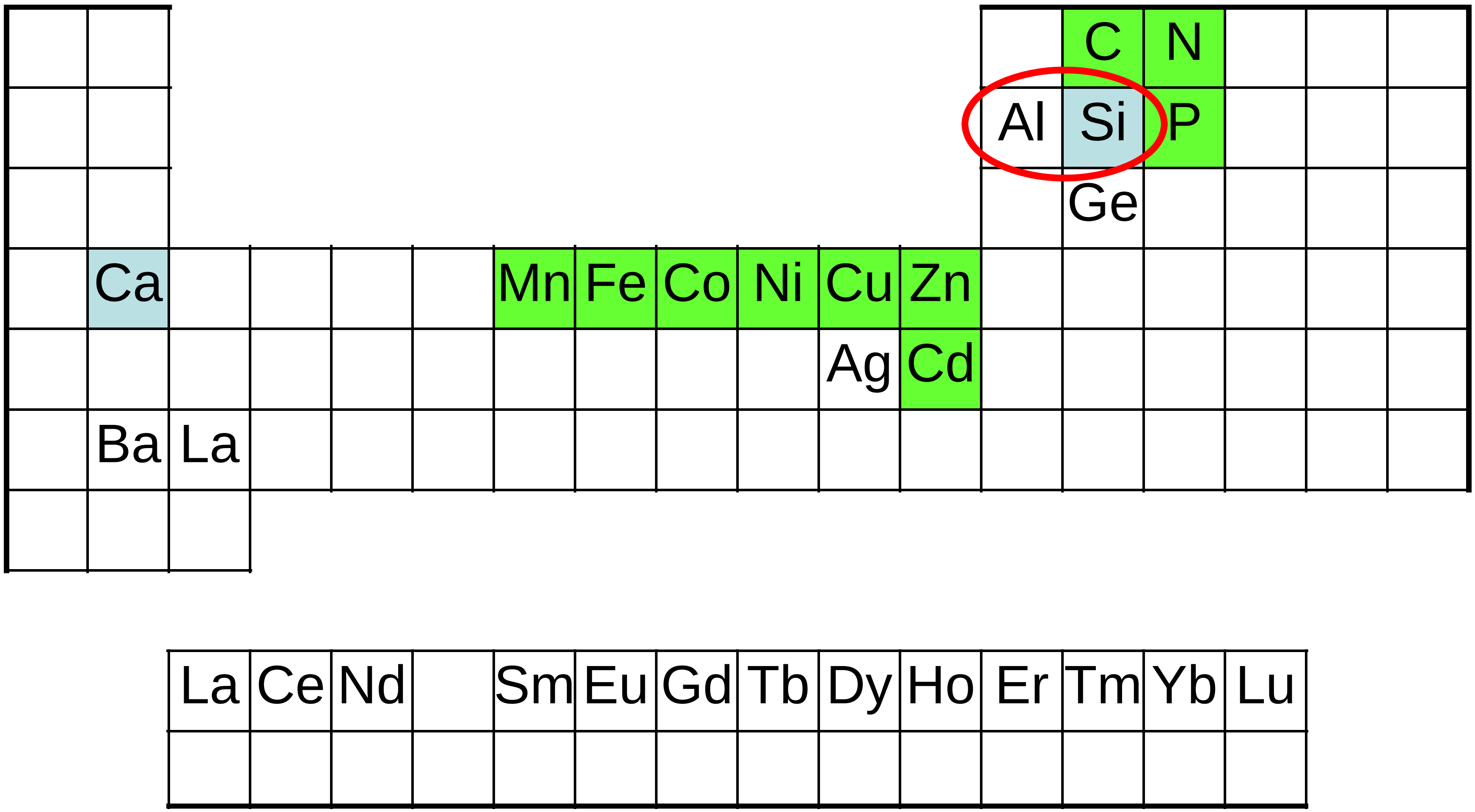
Recommendation:

assess conceivable effect on fractionation of stable isotopes of Si

use more realistic pH value ranges in diatom studies

With gratitude to Damien Cardinal for responding to my questions

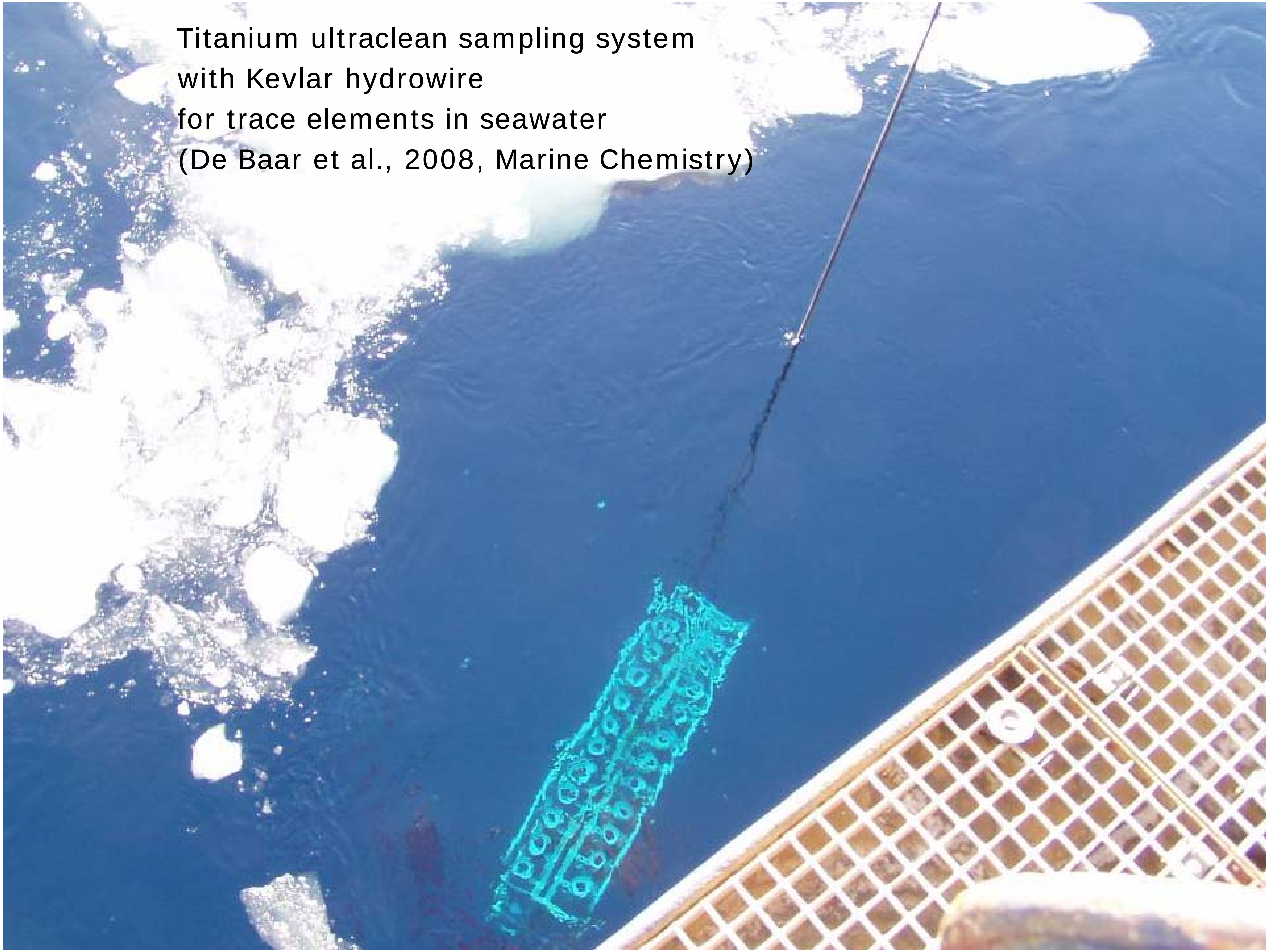
Biological Elements in Seawater



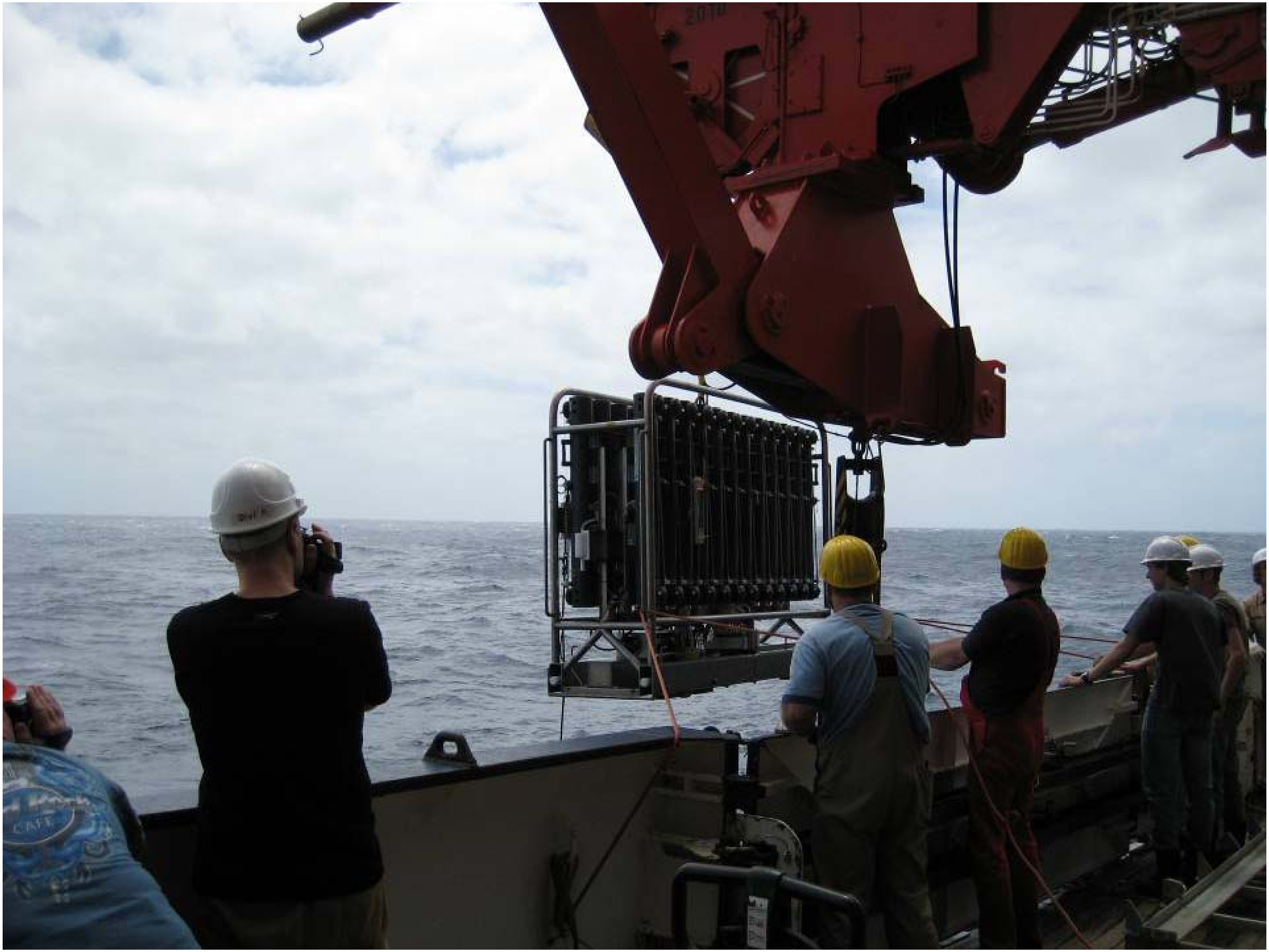
Element in biochemical function (soft tissue)

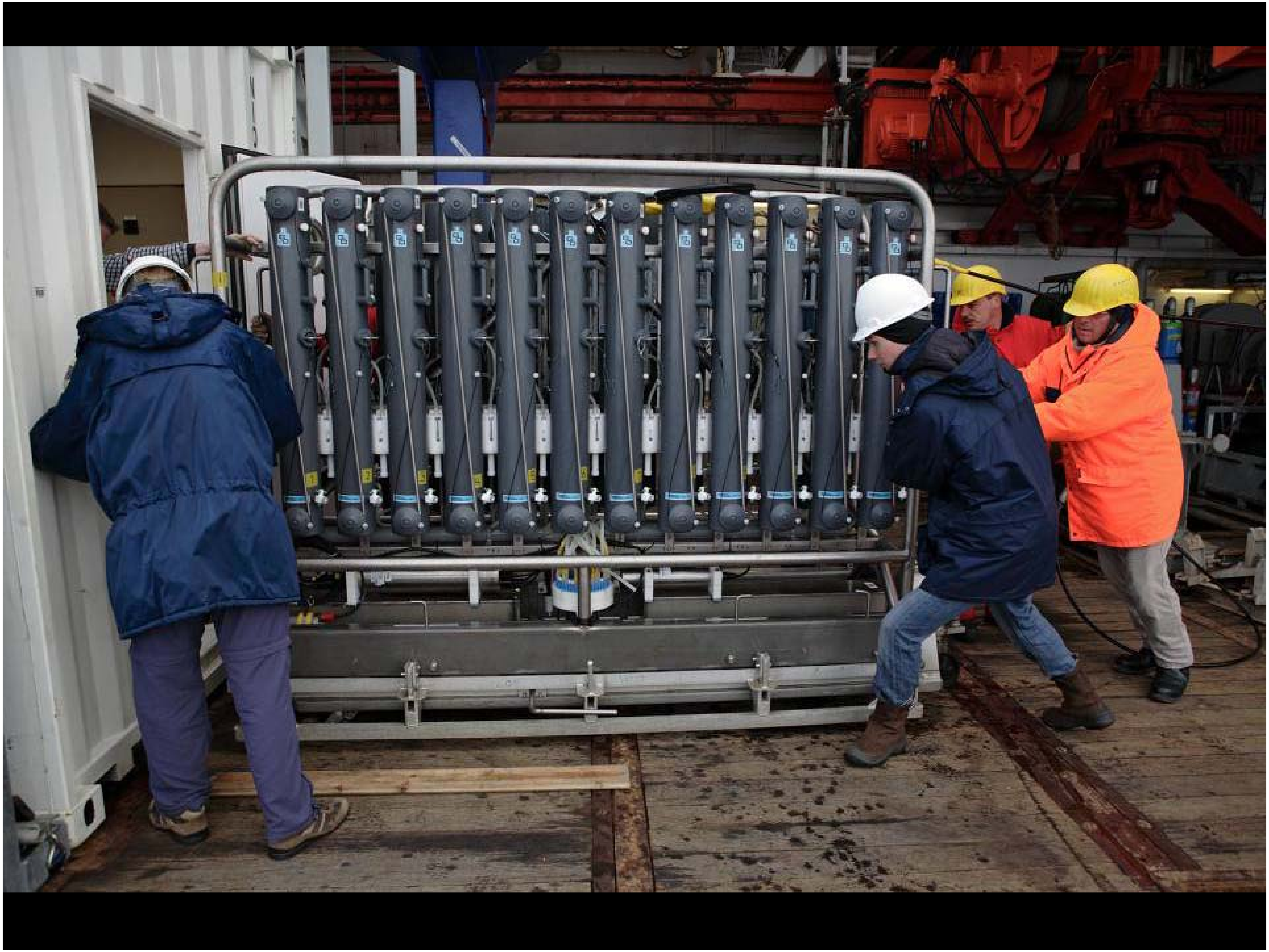
Element in skeletal part (hard shell, frustule)

Apparent coupling with ocean biological cycle



Titanium ultraclean sampling system
with Kevlar hydrowire
for trace elements in seawater
(De Baar et al., 2008, Marine Chemistry)


CAFE

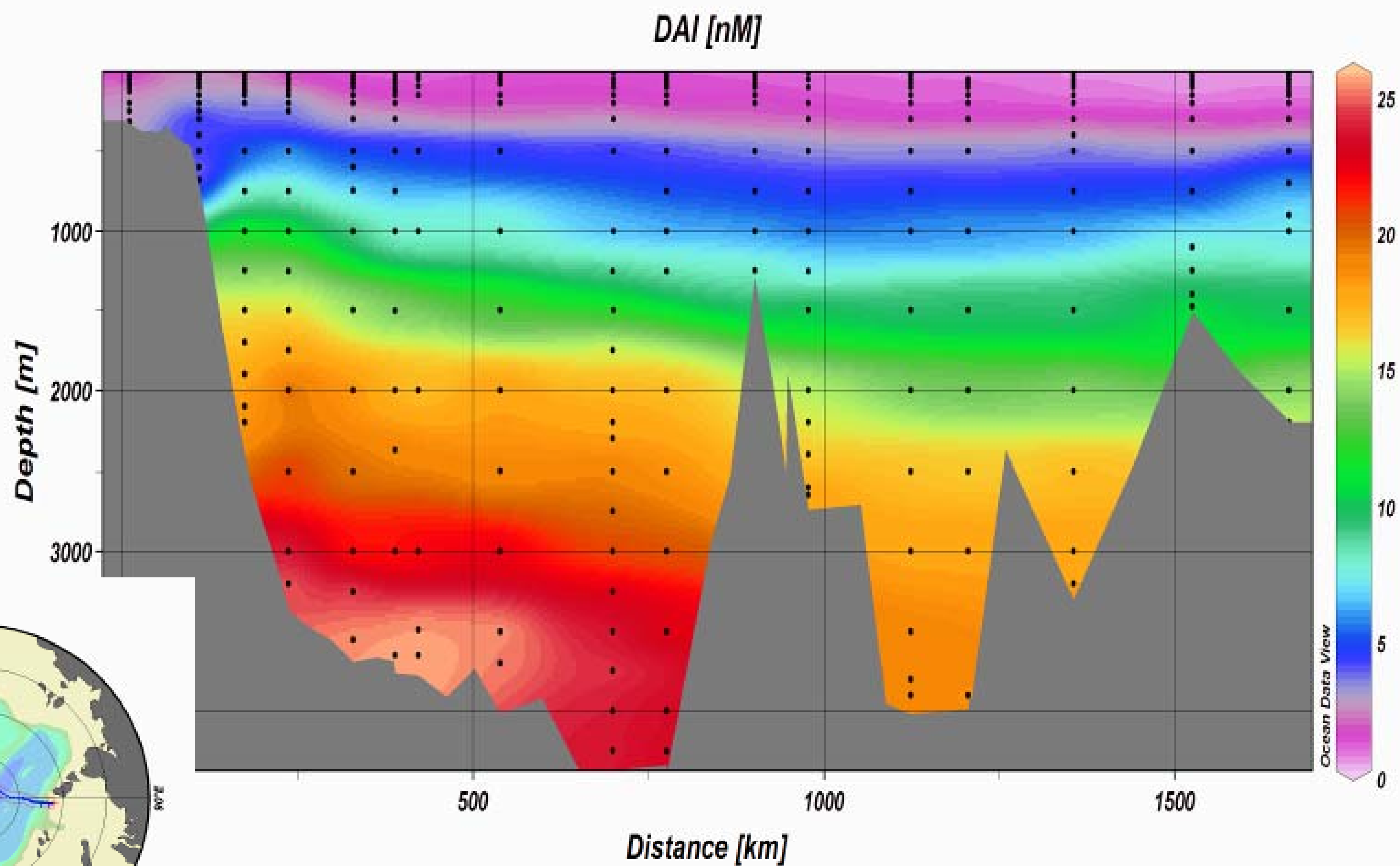


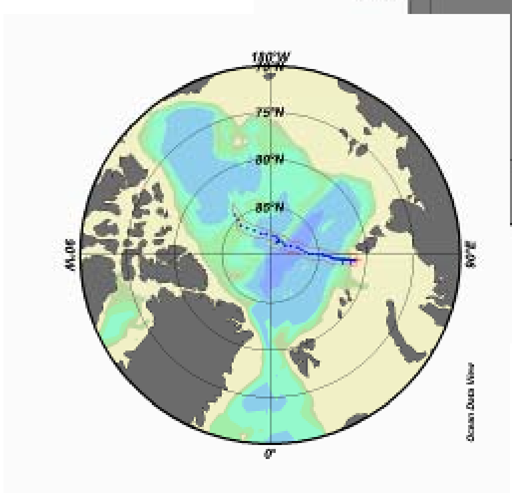
Ultra Clean Sub-sampling inside clean container

Al in high latitude Arctic Ocean

Steady increase of dissolved Al with increasing depth

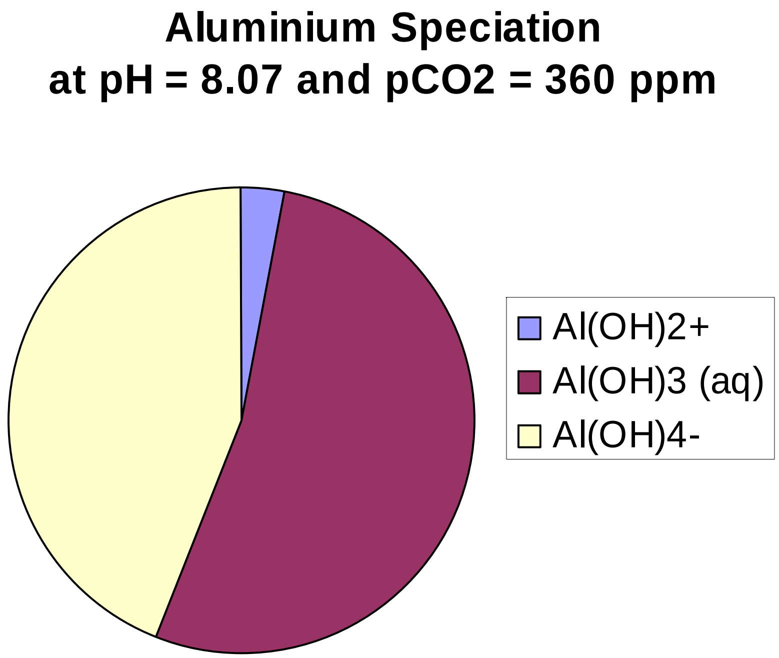
Looks like silicate

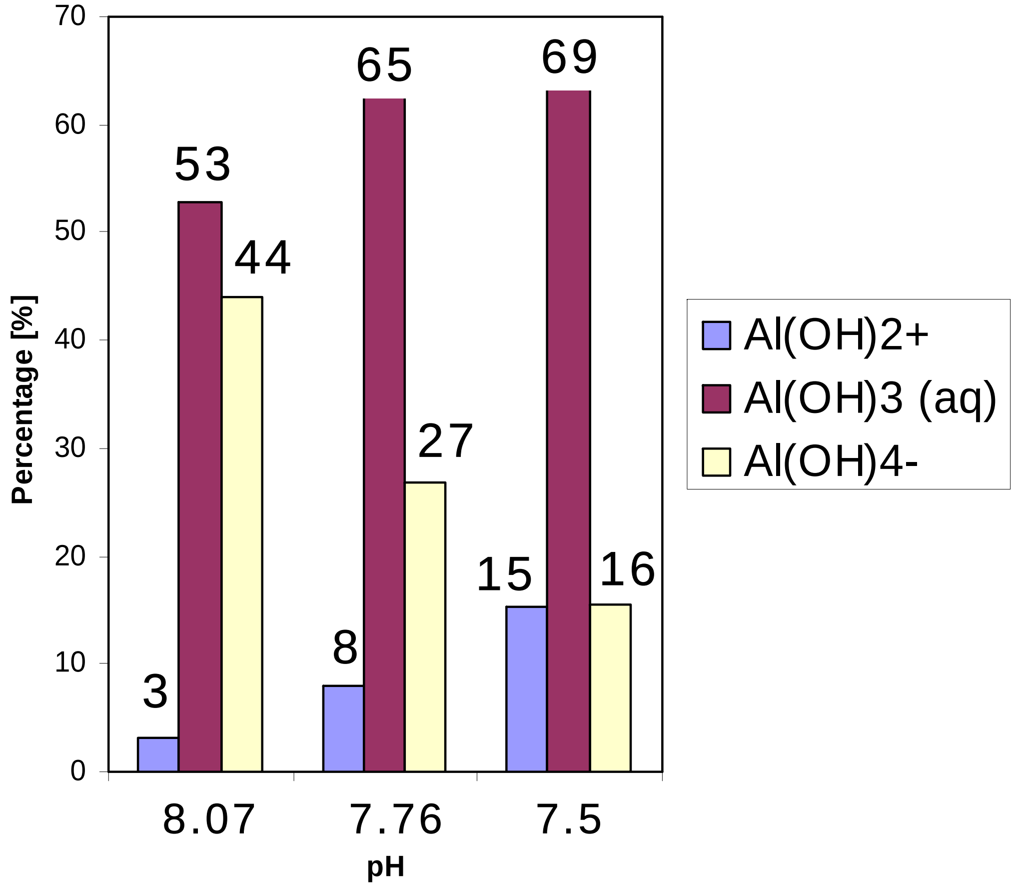


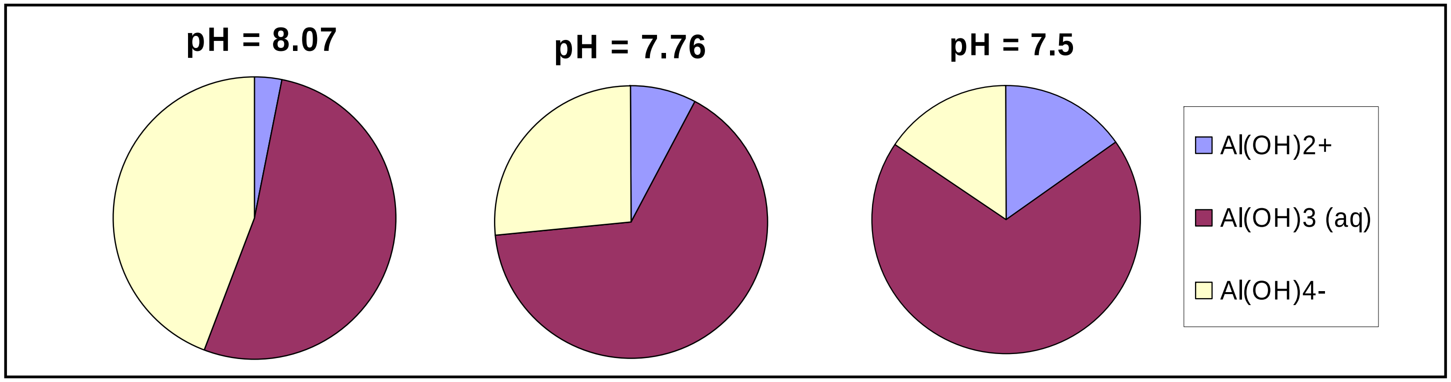


Rob Middag, unpublished data, Arctic Geotraces, Polarstern 2007

Aluminium: major shifts







Major shifts Al speciation: does it matter ?

Gehlen et al (2002); Al incorporation in growing diatoms

Thalassiosira nordenskjioldii

Al : Si = 1.3 : 1000

Al : Si = 3.8 : 1000

uptake ratio varies with Al/Si ratio in seawater medium

Dissolution of opal diatom frustules decreases significantly with higher Al:Si ratio of the biogenic opal (Van Bennekom)

Speciation changes of Al in seawater likely affect the uptake ratio Al:Si by diatoms

The 6-7 fold higher opal dissolution at lower pH (Milligan etal 2004) may well be due to shifts in Al speciation affecting the Al:Si ratio of opal hence the dissolution

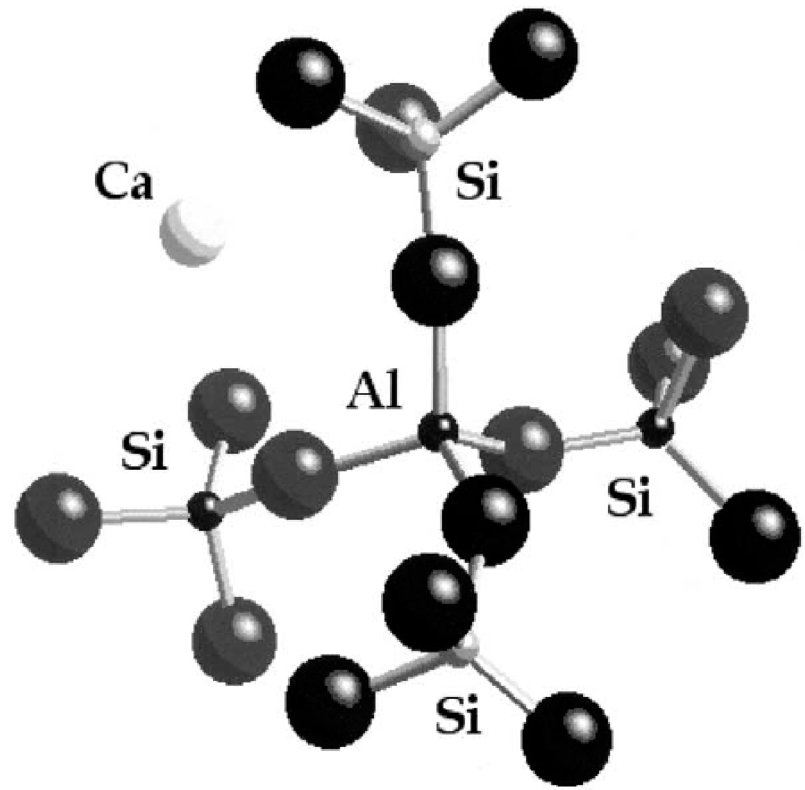
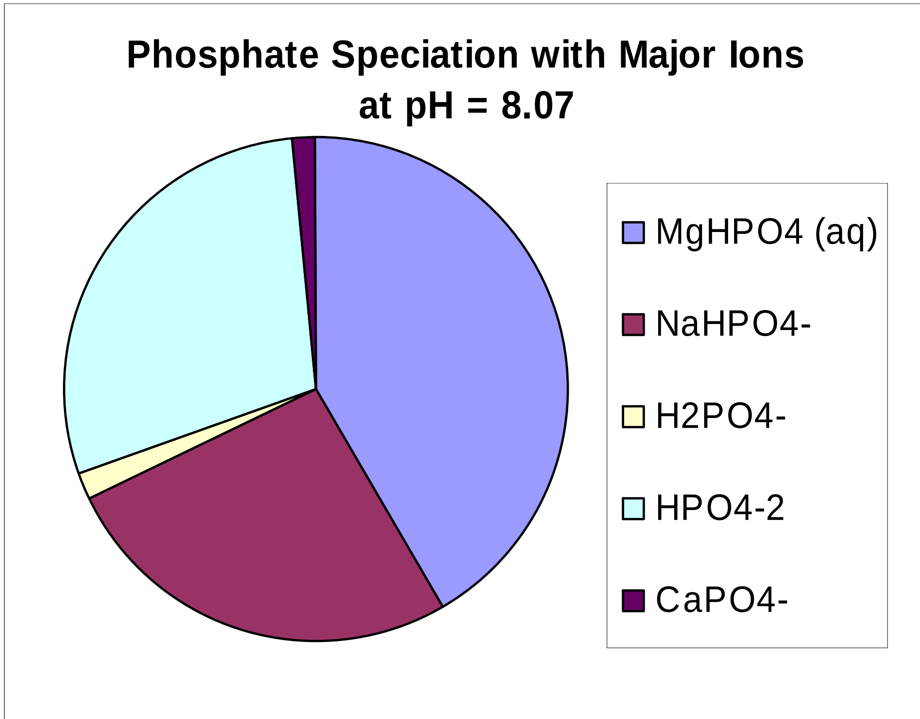
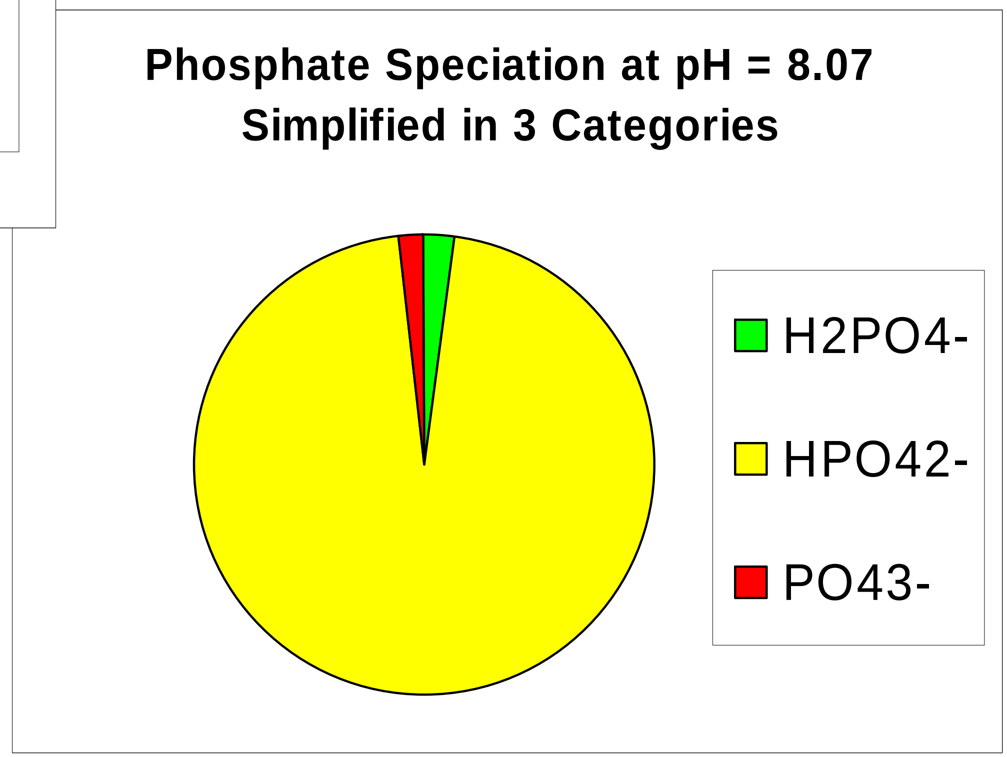


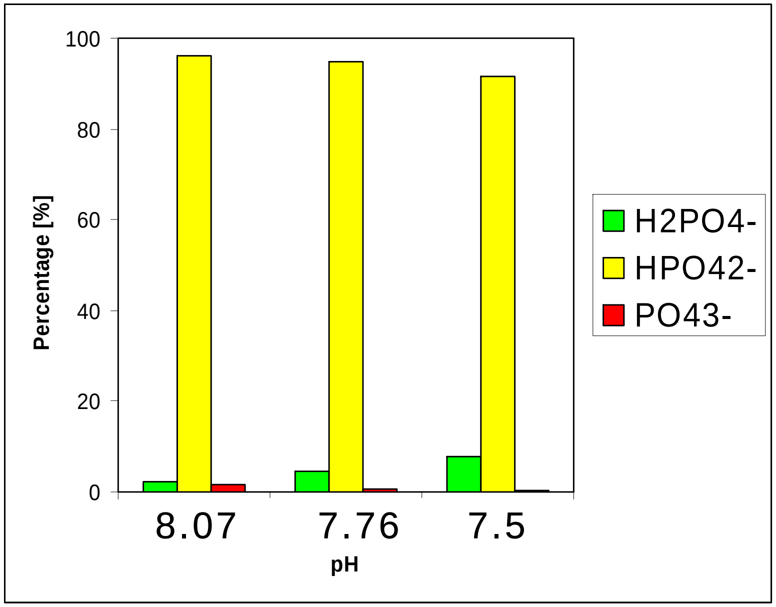
Fig. 4. A structural model of biogenic silica. Al enters the structure as a network former preserving the three-dimensional environment built by the corner-sharing SiO_4 tetrahedra. Substitution of Si^{4+} by Al^{3+} creates an unit negative charge. The compositional analyses of diatom samples suggest a charge compensation by Ca^{2+}.

Phosphate speciation



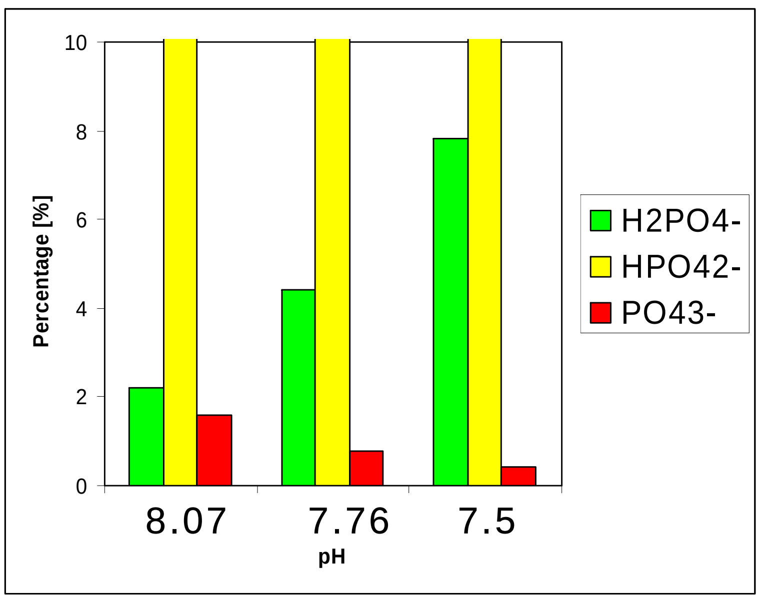


Phosphate speciation with ocean acidification



pH	8.07	7.76	7.5
$H_2PO_4^-$	2.2 %	4.4 %	7.8 %
HPO_4^{2-}	96.2 %	94.8 %	91.7 %
PO_4^{3-}	1.6 %	0.8 %	0.4 %

At tenfold expanded scale:



- major shifts of two minor species
- (just like the CO2 system)
- does it matter ?
- probably not ?
- only 1 stable isotope ^{31}P
- who cares ?

Acidification effect on third major nutrient Nitrogen

- Nitrate is strong ion
  - only one species NO_3^- and this will not be affected

- Ammonia is weak ion
  - speciation obviously will be affected

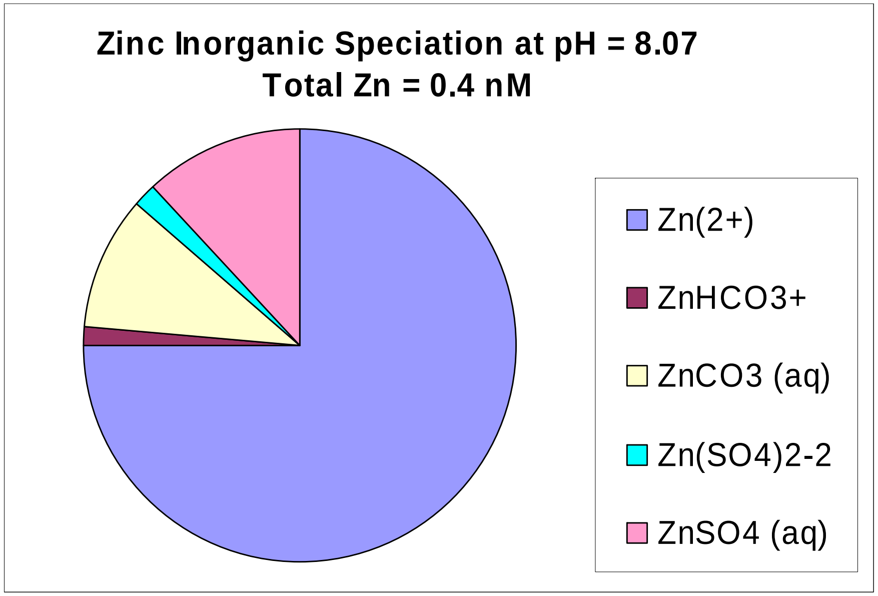
Zinc, Copper and Cadmium

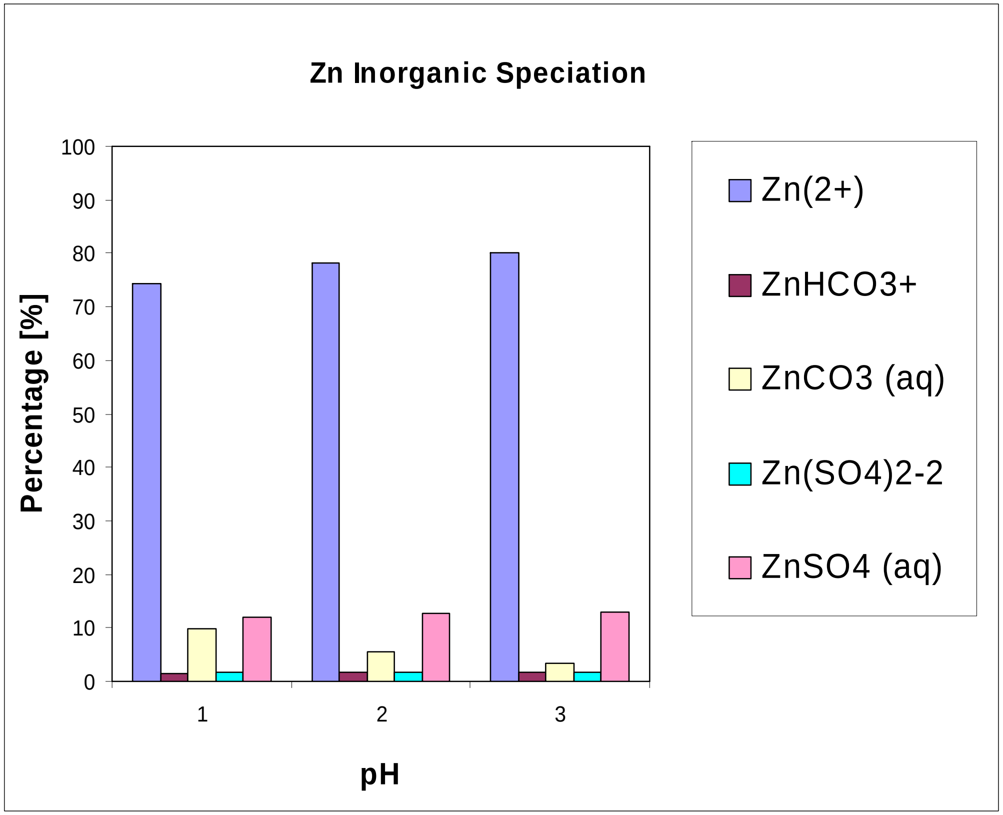
Mn 9550	Fe 900000	Co 2250	Ni 49300	Cu 522	Zn 1260	
				Ag 0.49	Cd 1.61	
					Hg 0.34	Pb 315

numbers of atoms versus 1 million Si atoms

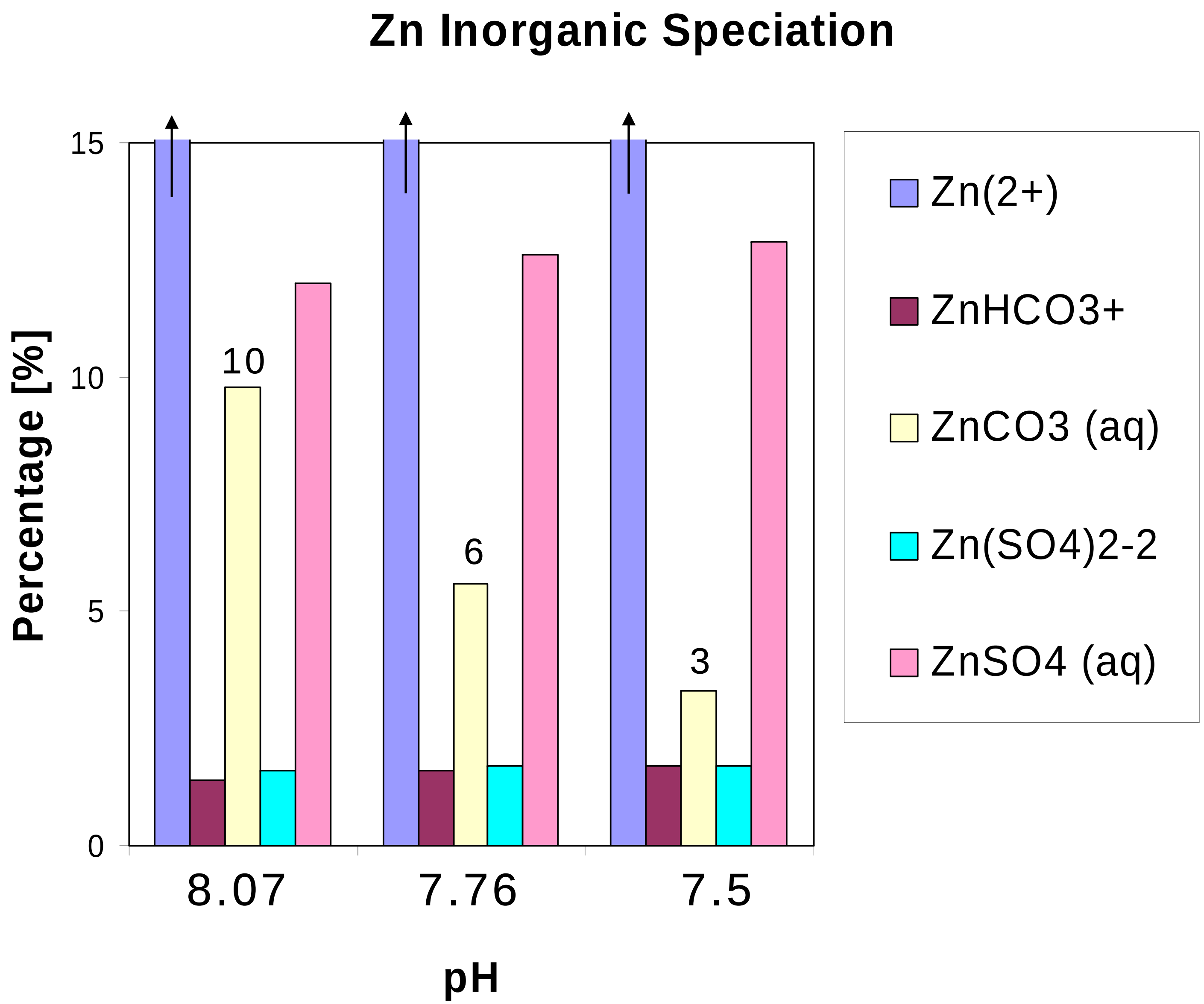
Zinc Inorganic Speciation

Zn is key element in enzyme Carbonic Anhydrase





decrease of ZnCO3(aq) species



$ZnCO_3$(aq) would decrease from 10 % to 6% to 3 % with ocean acidification

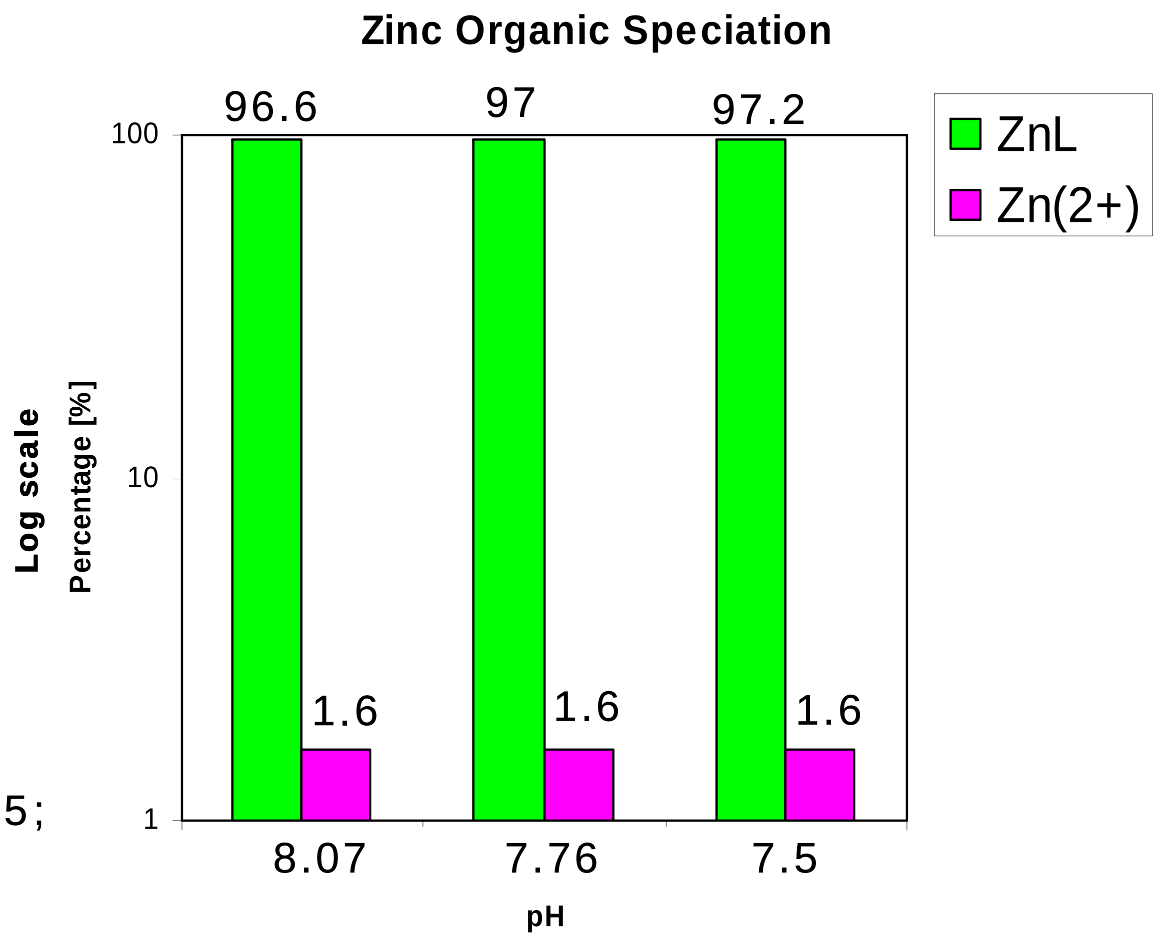
Zinc Speciation with Natural Organic Ligand

Total Zn = 0.4 nM
Total Ligand = 2.2 nM
K(ZnL) = 10.8

This Ligand also binds Cd and Cu at same time
Sum (Zn+Cd+Cu)=1.2 nM

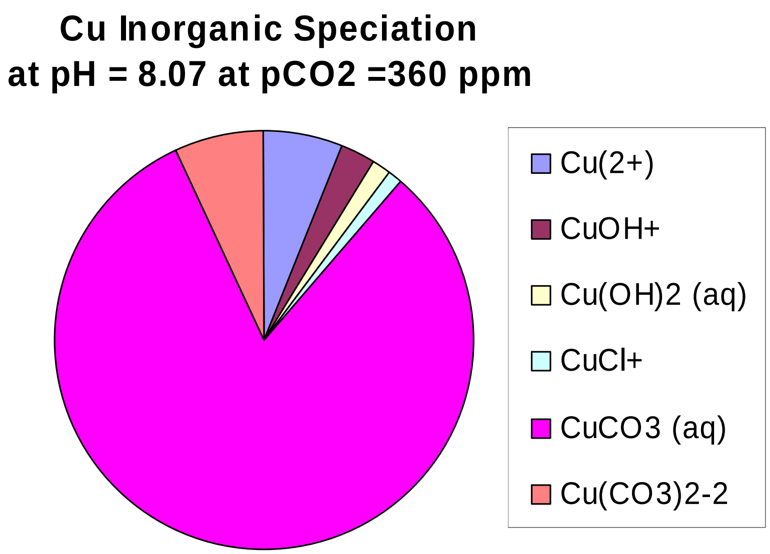
Assumption:
L binding strength does not change with pH

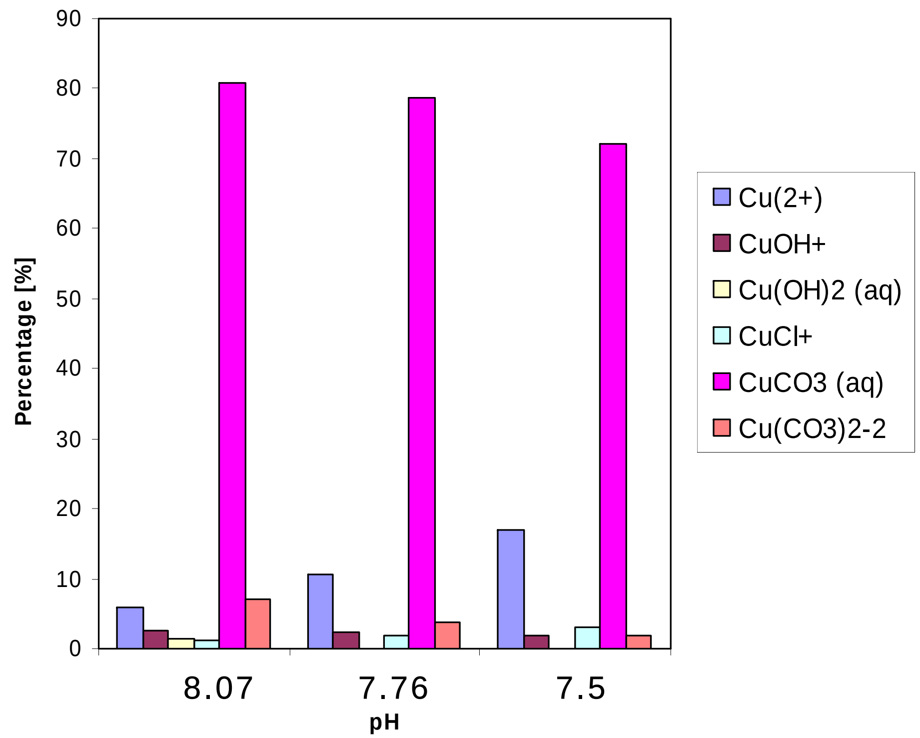
Zinc-binding Ligand after Ellwood 2004; Lohan et al., 2005; Bruland 1989



Very strong organic complexation stabilizes everything
No impact of ocean acidification on Zn speciation
No tipping point manuscript to Nature/Science

Copper (Cu) Inorganic Speciation





Cu Inorganic Speciation mostly carbonates
and also OH species
Very promising for major changes ??

pH	8.07	7.76	7.5
Free $Cu^{(2+)}$	6 %	11 %	17 %
$CuCO_3$ (aq)	81 %	80 %	72 %
$Cu(CO_3)_2^{2-}$	7 %	4 %	2 %

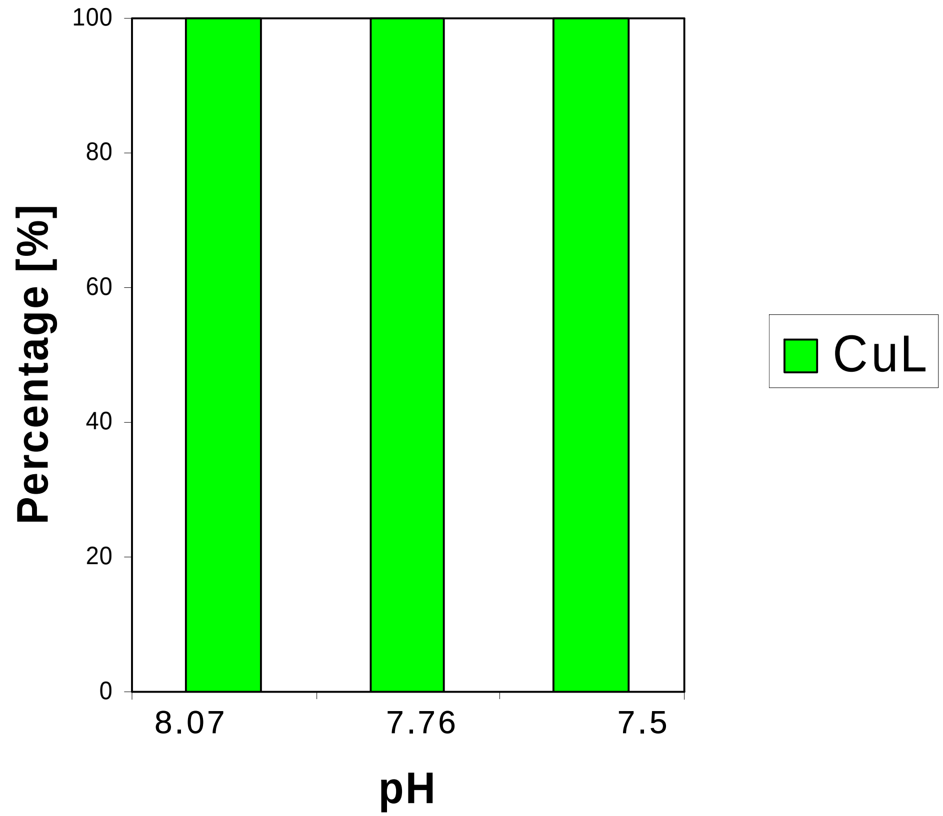
Copper speciation with natural organic ligand

Total Cu = 0.6 nM
Total Ligand = 2.2 nM
K(CuL) = 13.8

This Ligand also binds Cd and Cu at same time
Sum (Zn+Cd+Cu)=1.2 nM

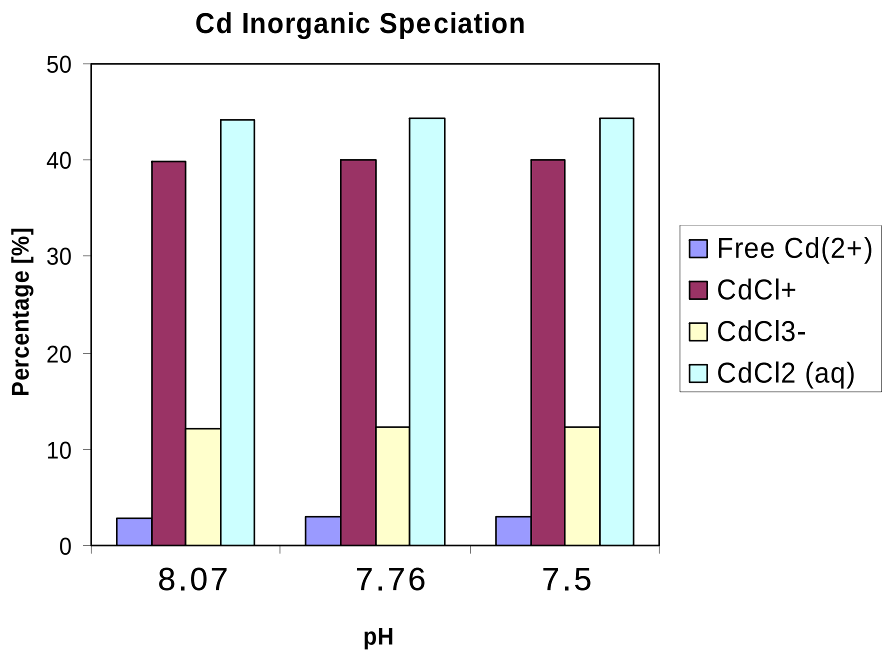
Assumption:
L binding strength does not change with pH

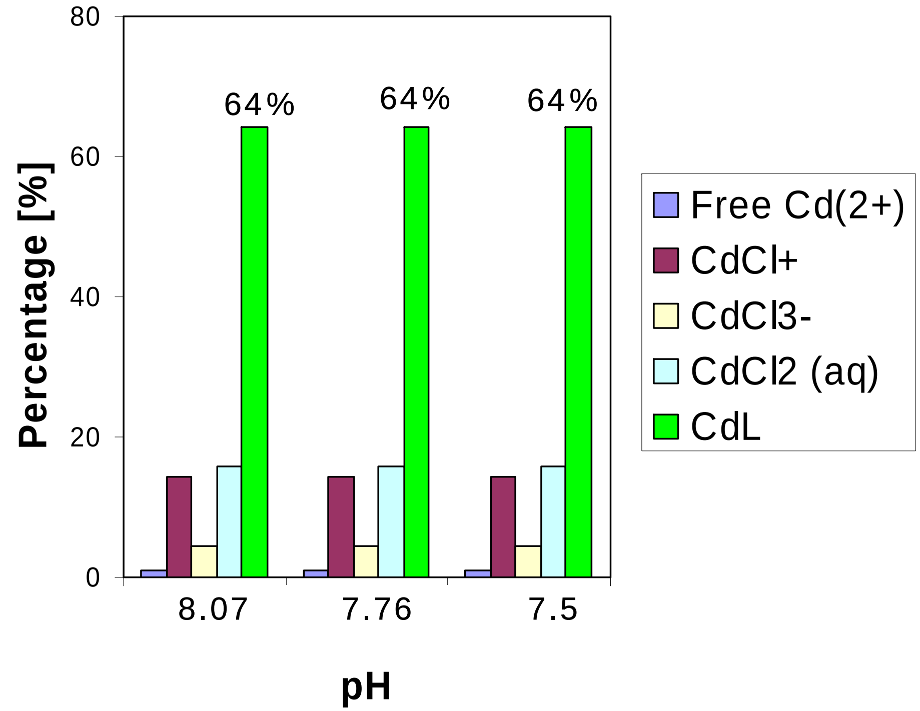
Cu binding Ligand after
Gerringa et al., 1995;
Laglera & Van Den Berg, 2003;
Moffett, 2007



Full 100% organic complexation at every pH value
No impact of ocean acidification on Cu speciation
No tipping point manuscript to Nature/Science

Cadmium Speciation
without and with Organic Ligand





3 % free Cd^{2+} ion
For the rest only Chlorine species
No pH dependence at all

Total Cd = 0.2 nM
Total Ligand = 2.2 nM
K(CdL) = 10.8 after Ellwood, 2004

This Ligand also binds Zn and Cu at same time
Sum (Zn+Cd+Cu)=1.2 nM

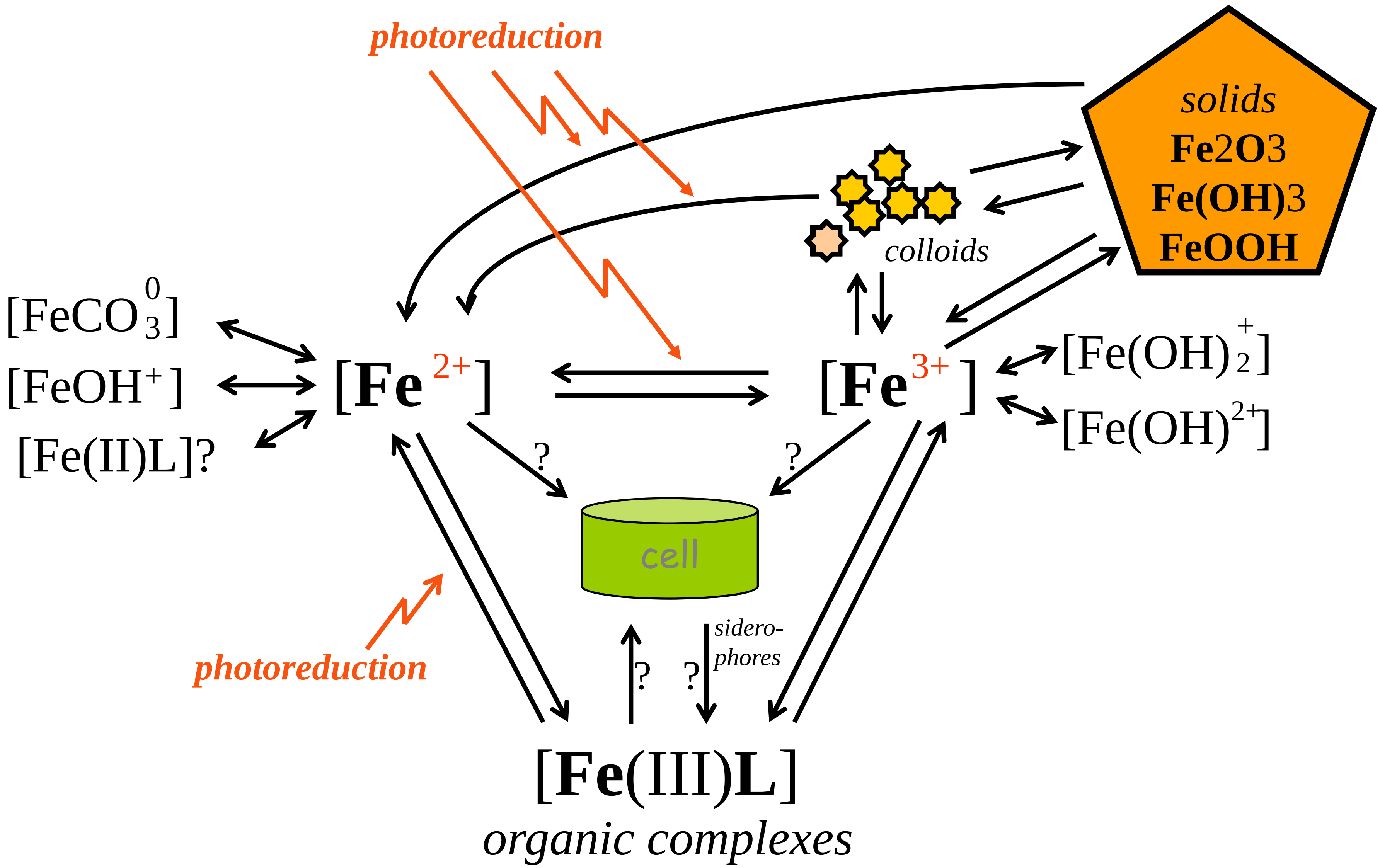
64 % Cd-L organic complex
1 % free Cd^{2+} ion
For the rest only Chlorine species
No pH dependence at all

Gold is for the mistress
Silver for the maid
Copper for the craftsman
cunning at his trade.

"Good" said De Baaron
sitting in this hall:
"**But iron – cold iron –**
is master of them all."

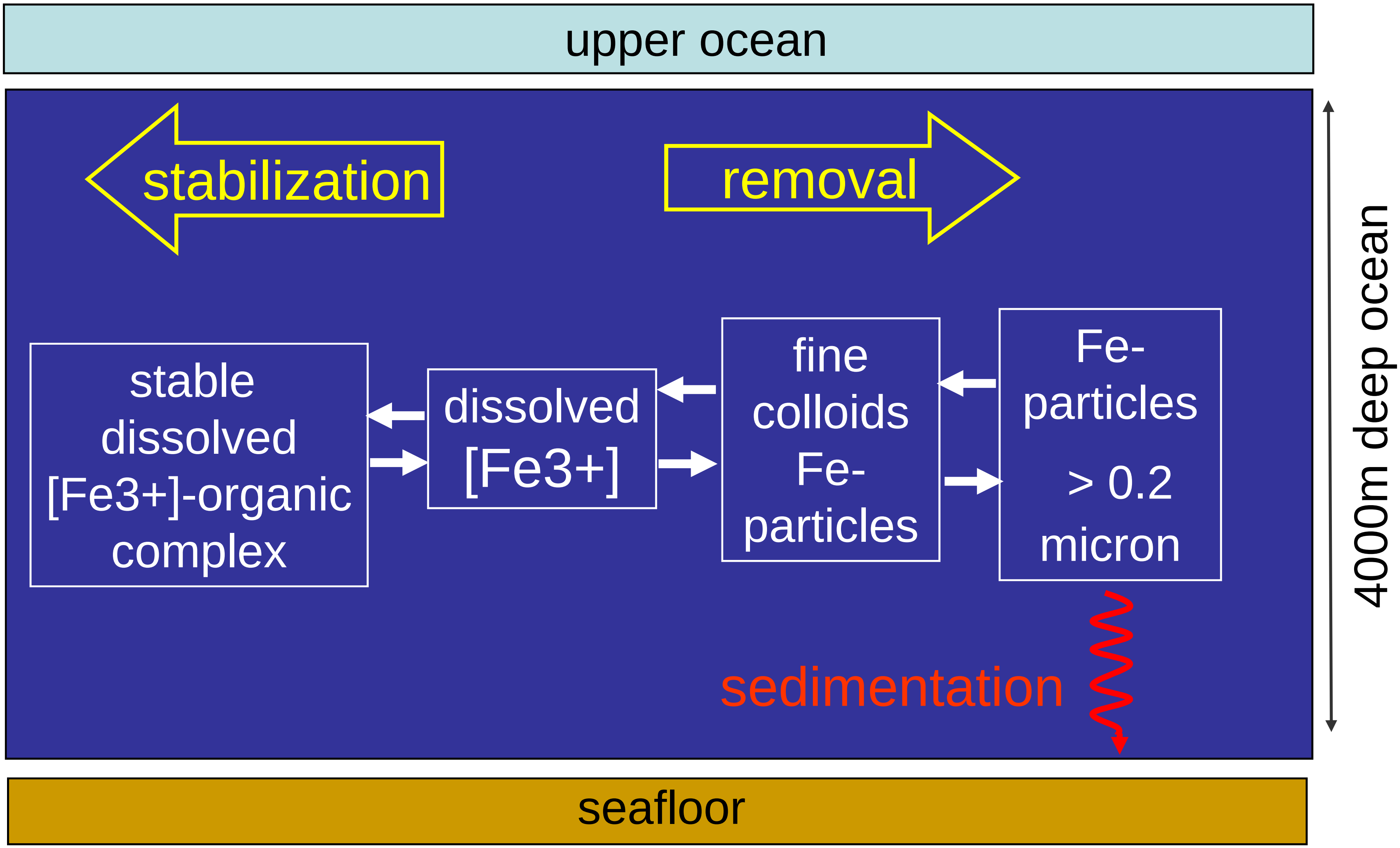
free after Rudyard Kipling (1910)

Surface Ocean: Iron Speciation crucial for biological uptake by phytoplankton in the euphotic zone

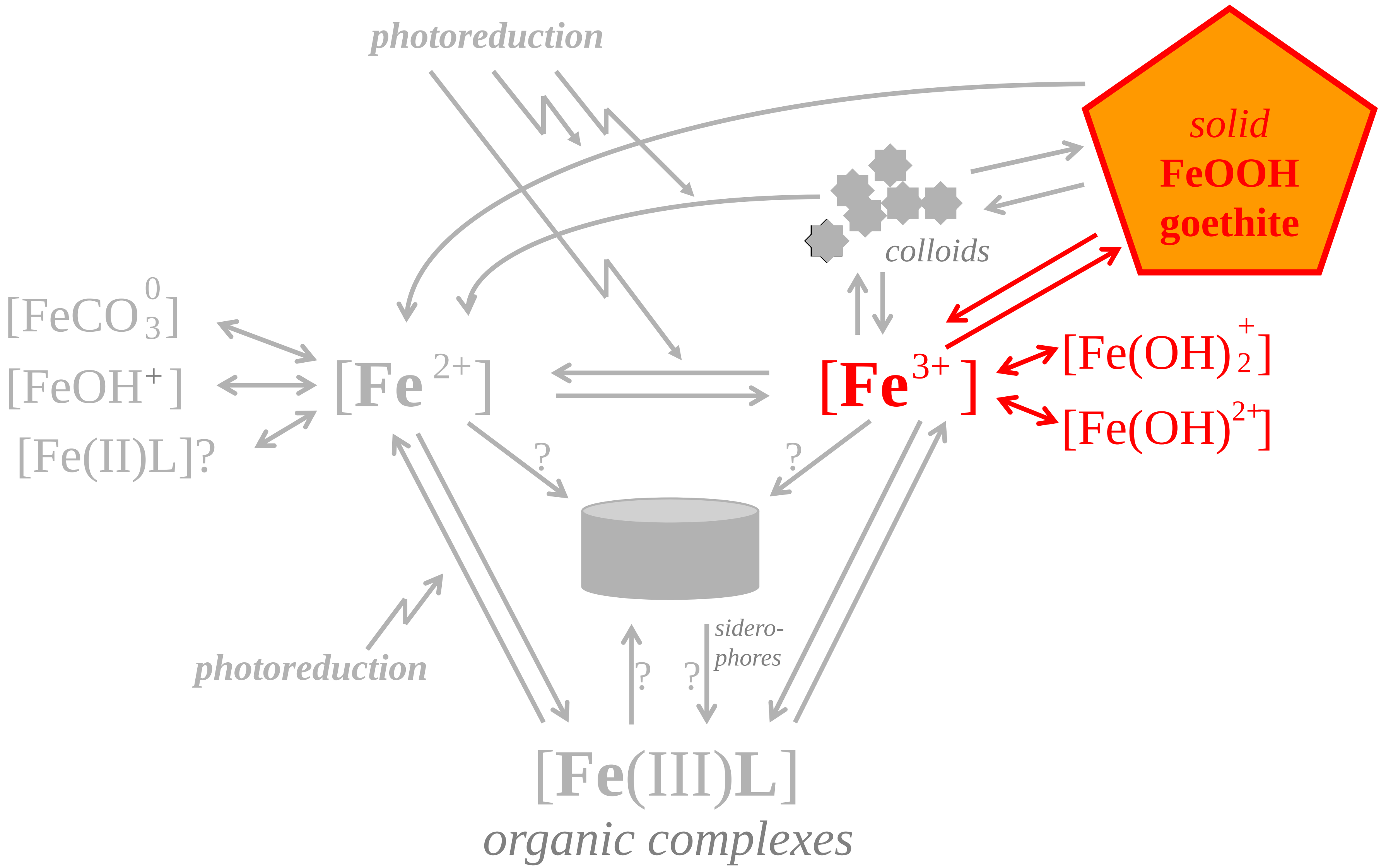


Gerringa et al, 2000

Deep Ocean: Competition between Stabilization by Organic Complexation versus Removal via Colloids controls Residence Time of Fe in the Oceans



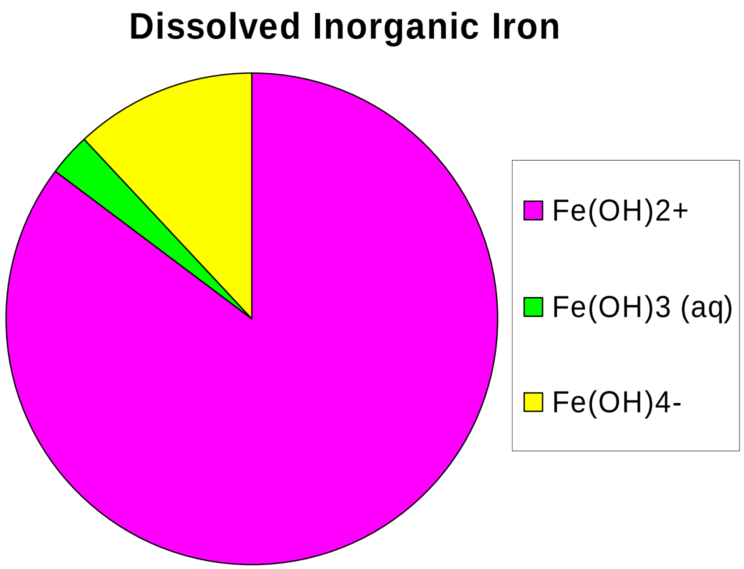
Case 1: inorganic speciation, no light (dark ocean)

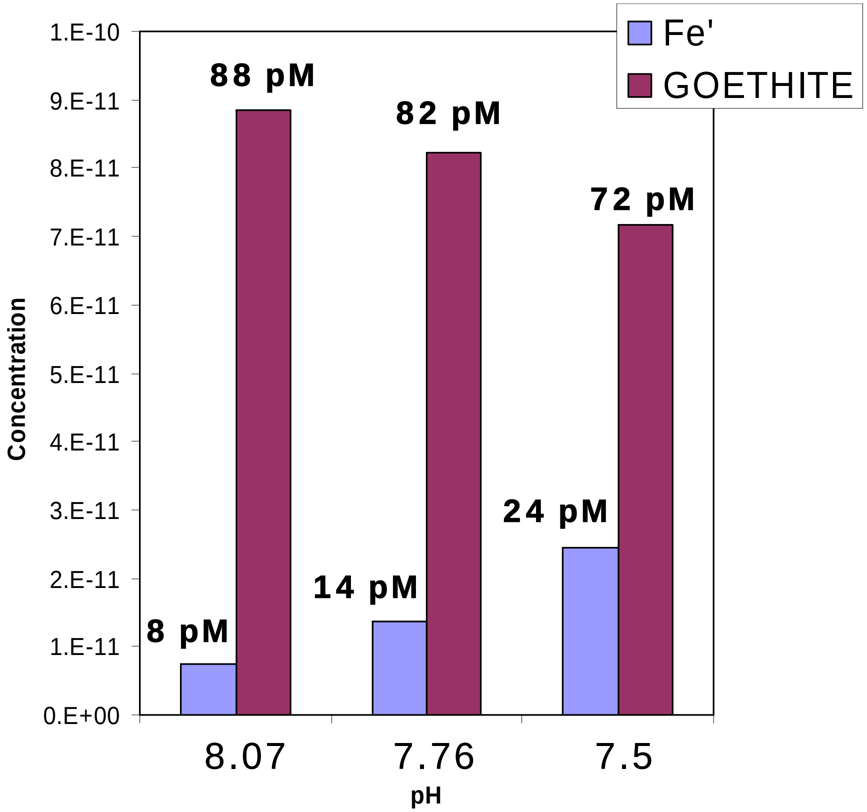


Gerringa et al, 2000

Case 1: inorganic speciation, no light (dark ocean)

Surface sample at 49 m depth:
< 0.2 micron
[Fe] = 0.096 nM = 96 pM
Assume no Ligand



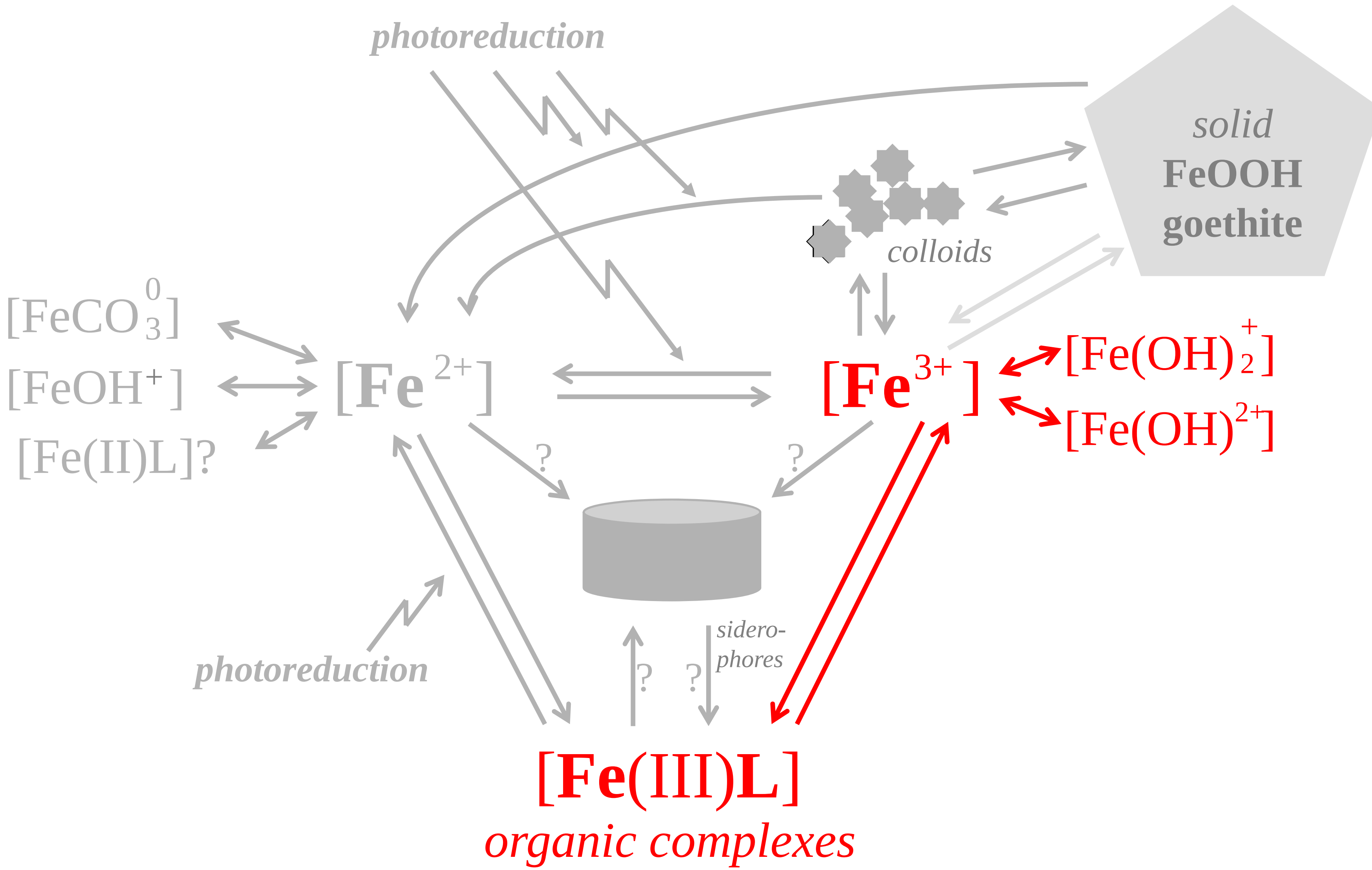


90 % of the dissolved Fe would precipitate

Sum of all inorganic species:

$Fe' = Fe(OH)_2^+ + Fe(OH)_3 + Fe(OH)_4^-$

Case 2: include organic ligand, delete solid FeOOH, no light (dark ocean)



Gerringa et al, 2000

Case 2: include organic ligand, delete solid FeOOH, no light (dark ocean)

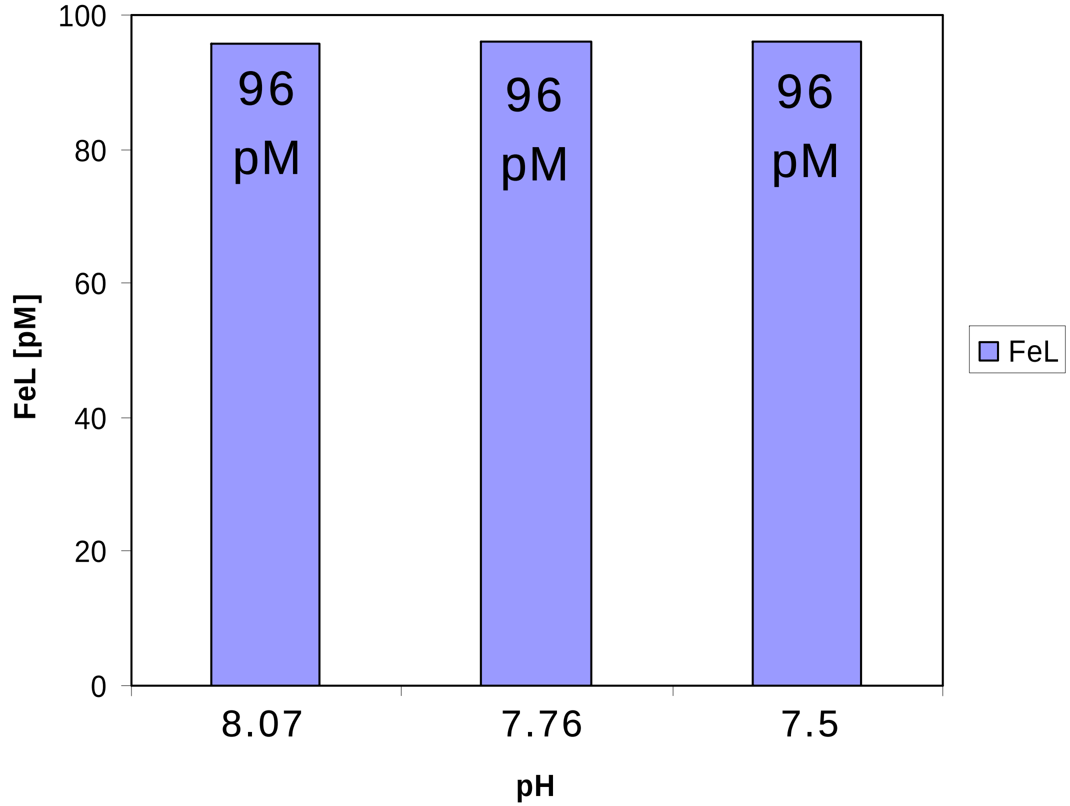
Surface sample at 49 m depth:

< 0.2 micron

[Fe] = 0.096 nM = 96 pM

Ligand = 0.668 nM = 668 pM

Prediction of speciation model:



All the dissolved Fe is bound by the ligand, thus stable in seawater

Case 2: Measure the organic complexation in real sample

- deep water sample (2500m depth)
  - measurement onboard: Fe=0.95 nM, L=1.64 nM
- adjusted to 3 different pH values 7.75, 8.05, 8.25 in laboratory
- measure ligand concentration L and its stability constant K

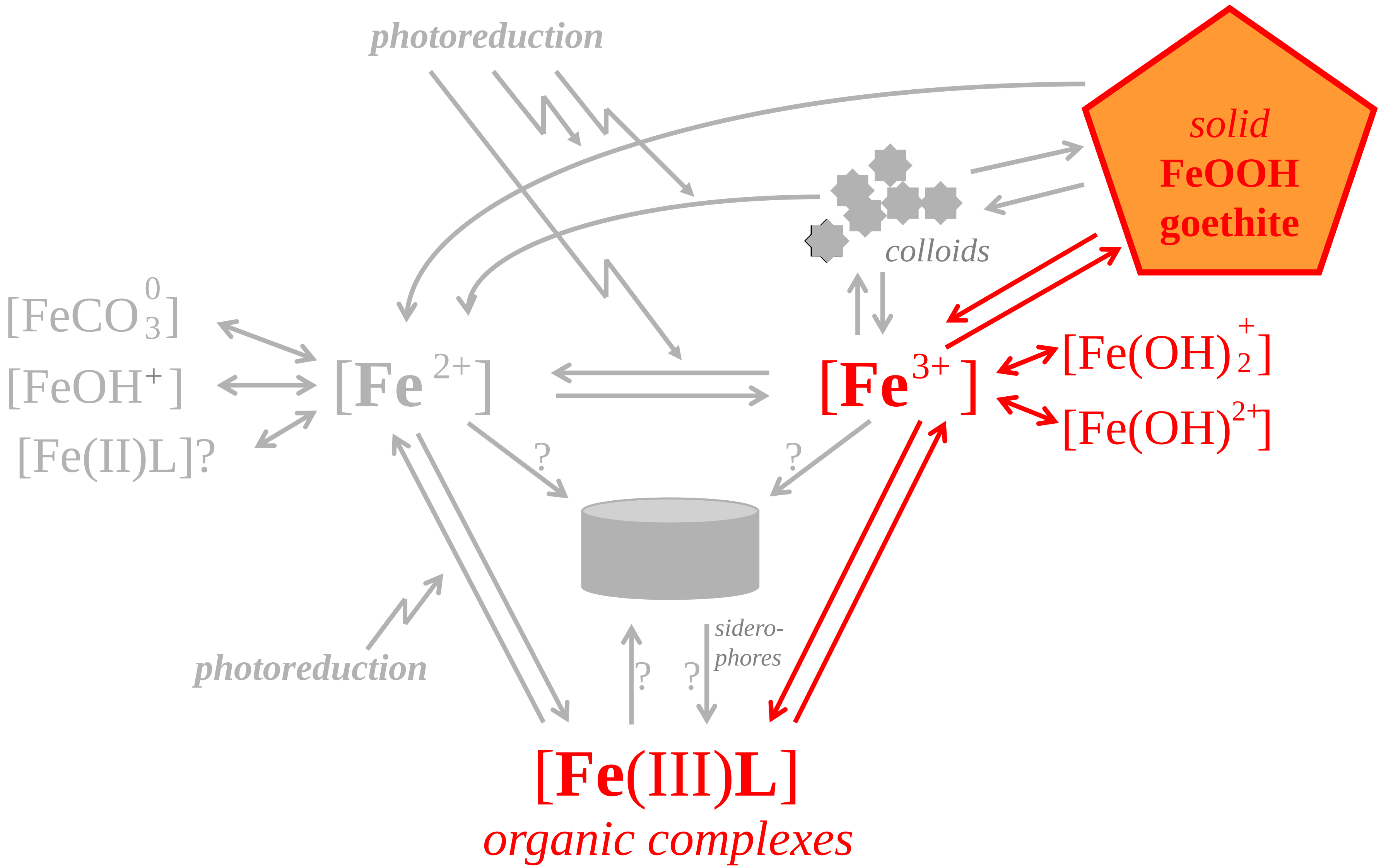
pH	L [nM]	error (L)	logK	error logK
Onboard 8.05	1.638	0.110	22.42	0.18
7.75	1.686	0.067	22.52	0.11
8.05	1.734	0.081	22.82	0.15
8.25	1.694	0.065	22.84	0.10

Ligand concentration L does not change significantly

Stability constant logK does not change significantly

This supports modeling assumption that K is independent of pH

Case 3: include organic ligand, dissolve FeOOH as much as possible, no light (dark ocean)



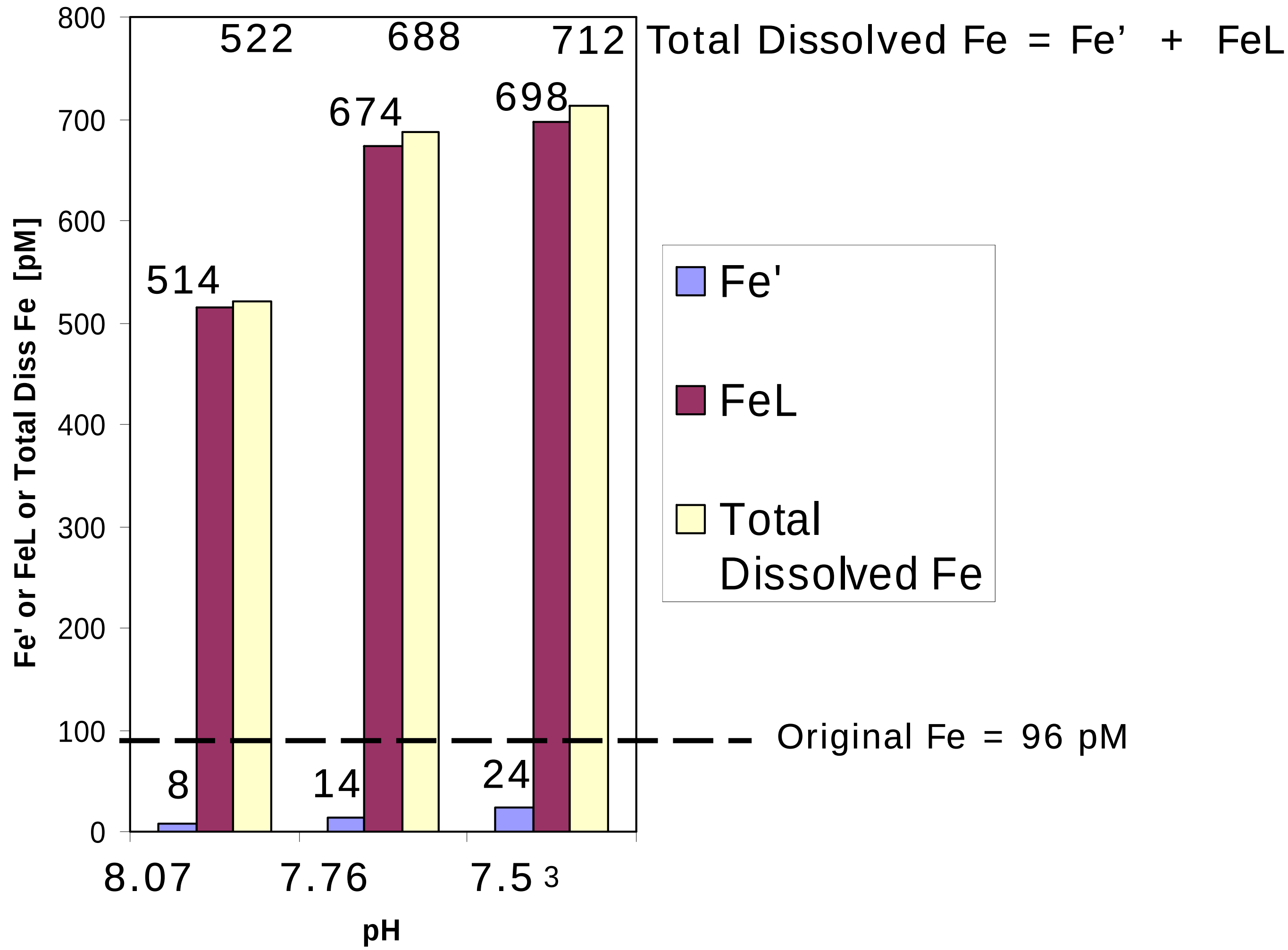
Gerringa et al, 2000

Case 3: include organic ligand, dissolve FeOOH as much as possible, no light (dark ocean)

Surface sample:

Ligand = 0.668 nM = 668 pM

Original Fe = 96 pM



The Excess Ligand of Todays Ocean Can Accomodate more dissolved Fe

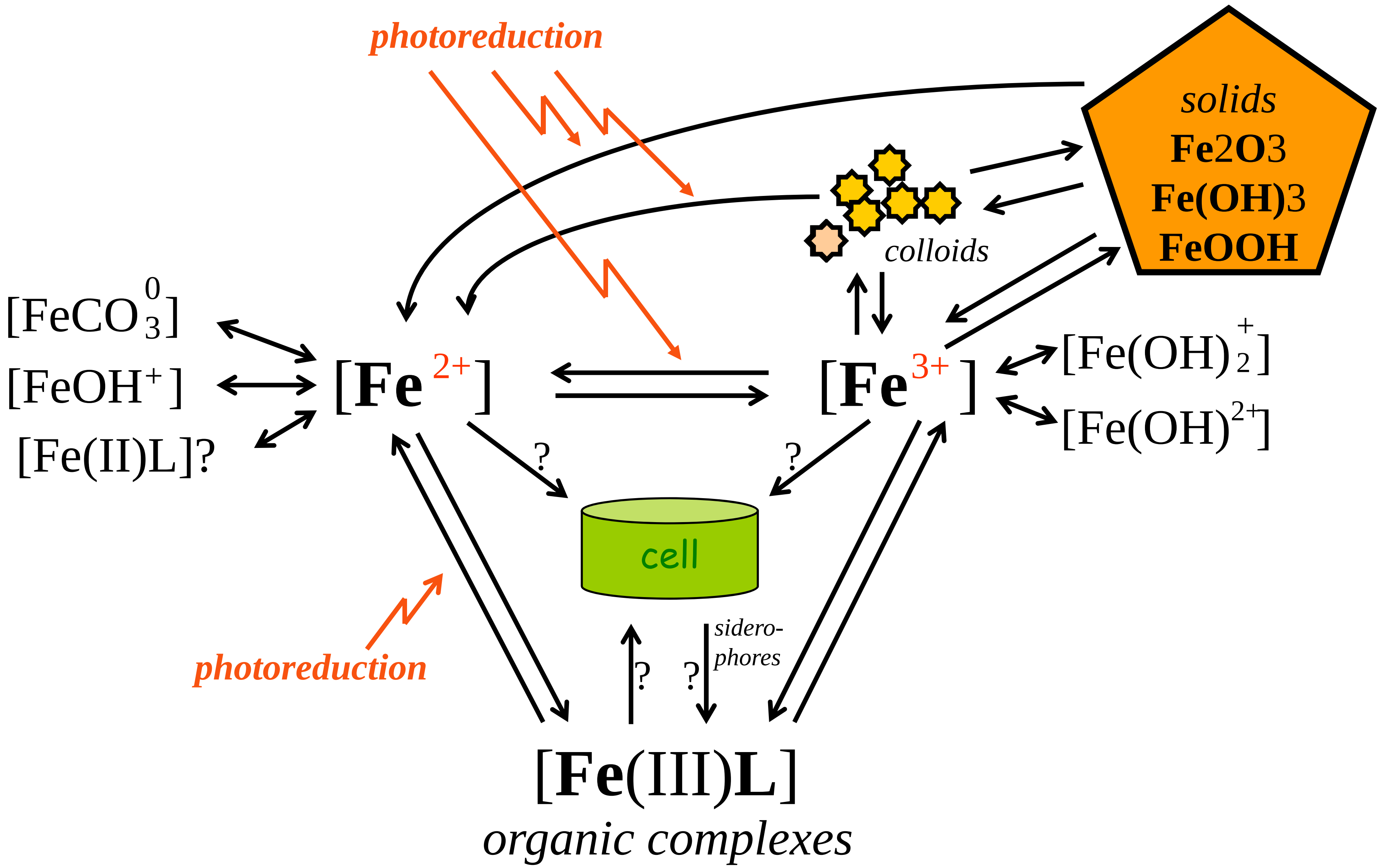
By Ocean Acidification the dissolved Fe in Seawater can increase even more

Dissolution of solid phase Fe and Mn is much more a function of low oxygen conditions than of pH

Strong Fe and Mn maxima exist in subsurface oxygen minimum zones of Equatorial East Pacific, Northwest Indian Ocean (Landing et al. 1987, Saager et al. 1989)

… however this meeting happens to be about pH not oxygen

How about photoreduction to Fe(II) in open ocean ?
How about the fine colloids in open ocean ?



Gerringa et al, 2000

Photochemistry in upper euphotic zone of the open ocean

Photoreduction of Fe(III) to Fe(II)

only in upper euphotic zone

beyond chemical thermodynamics prediction

rapid re-oxidation but slower in cold polar waters

small portion of the dominant Fe(III)L species dissociates

into free Fe(II) and free L

the free Fe(II) likely is more available for uptake by algae

Photochemical breakdown of organic ligand L

yes but only of small labile portion of total L pool

ligand L is very stable and uniform throughout world ocean

this supports the notion of long term chemical stability

new ligand being formed in surface waters from biota

surface waters tend to have large excess of ligand versus Fe

Future work in open ocean waters

- response of Fe-colloids size class to acidification
  - adjust 0.2 micron filtered seawater to different pH values
  - wait some time
  - ultrafiltration and then measure Fe and L in size fractions
  - physical-chemical modeling ?
- Acidification effects on other metals
  - Mn manganese
  - lanthanides series (dominated by CO_3^{2-} species)
    - but who cares about the lanthanides ?

Summary

- shifts in Silicate speciation may affect fractionation of Si stable isotopes
- major shifts in Aluminium speciation may affect its uptake in diatom frustules, hence dissolution of biogenic Silicon
- major shifts of two minor species of Phosphate, any effects on biota unknown
- Zn, Cu and Cd are strongly stabilized by organic complexation
- excess organic ligand in modern ocean may accomodate more dissolved Fe than is currently present
- if so, then in the future more acidic ocean somewhat more Fe may dissolve
- caveats:
  - in fact the open ocean ligand does not carry as much Fe as it could