Hamburg Model of Ocean Carbon Cycling (HaMOCC)

- Some facts, rules and personal preferences about marine biogeochemistry modeling
- E.Maier-Reimer, C.Heinze, K.Six, J.Segschneider

No priority goal to simulate all

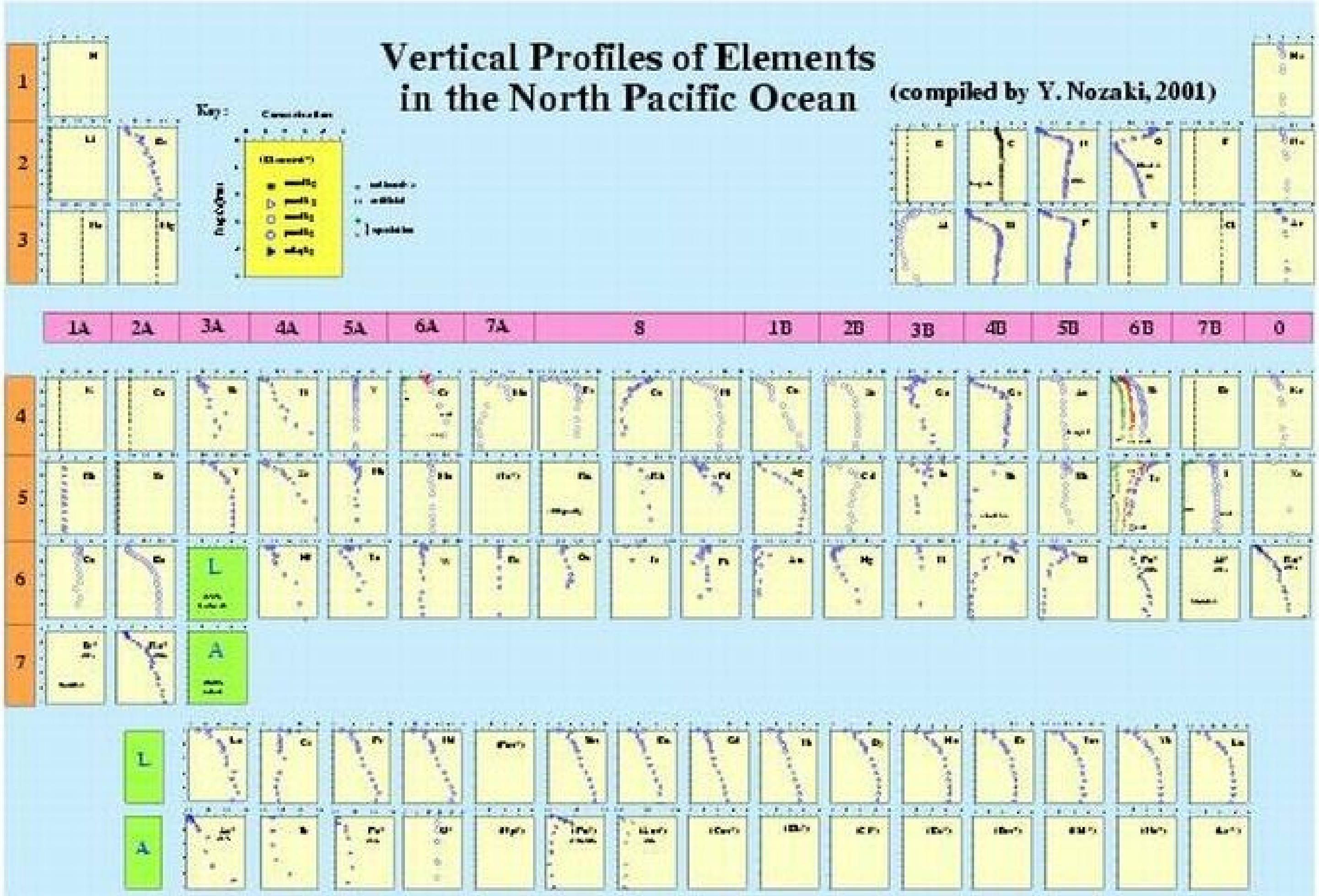
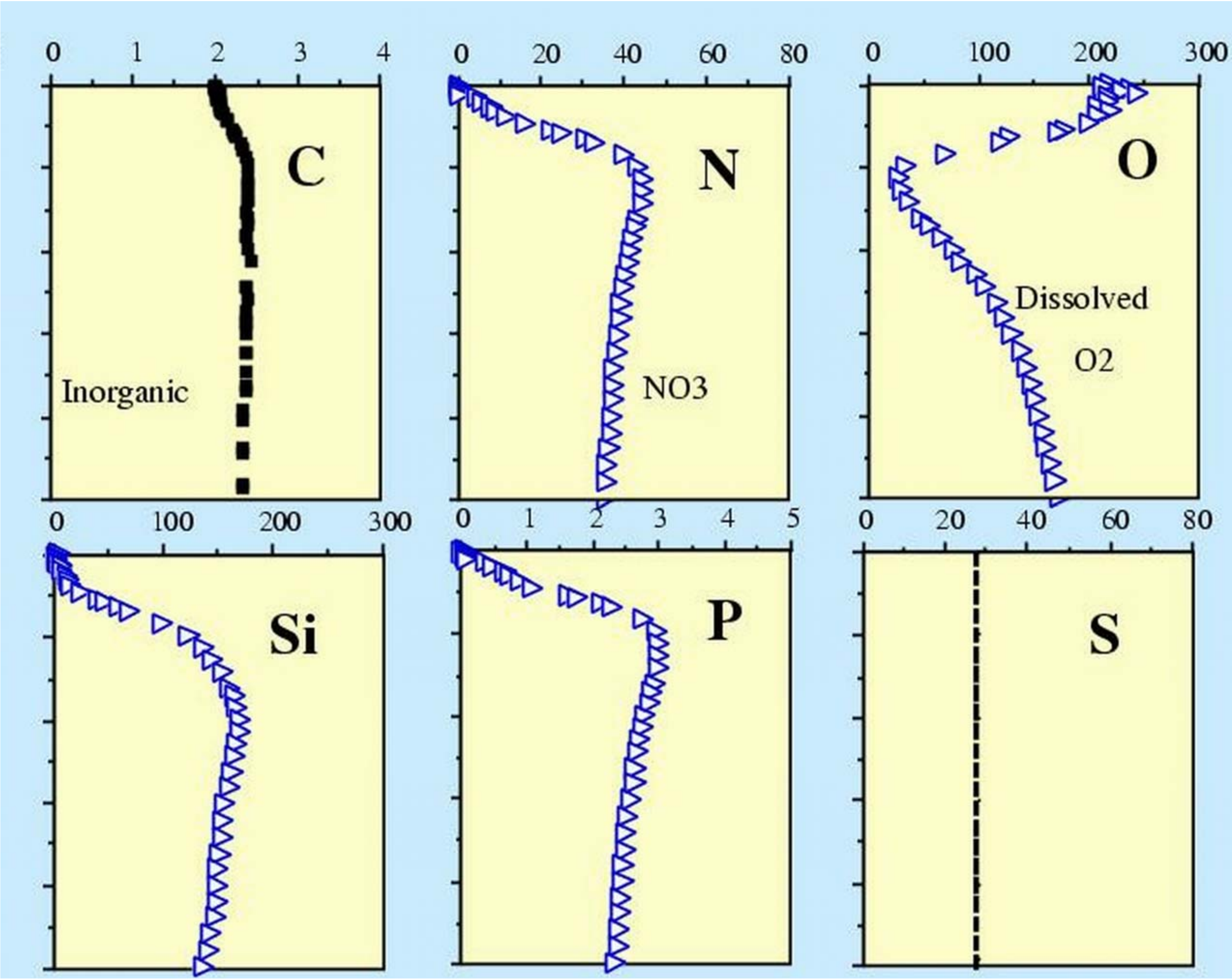
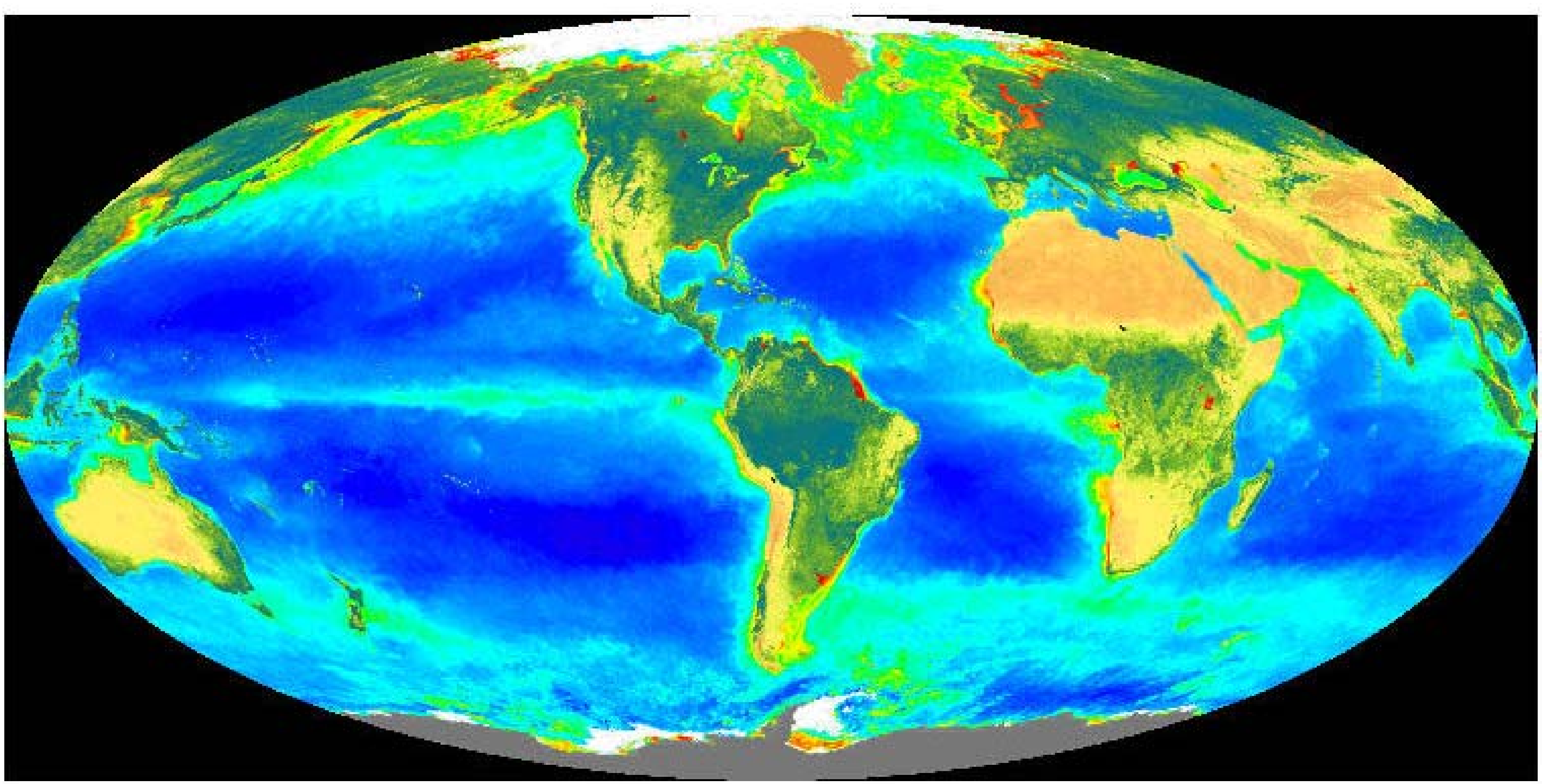


Figure 2: Vertikalverteilung der chemischen Elemente im Nordpazifik

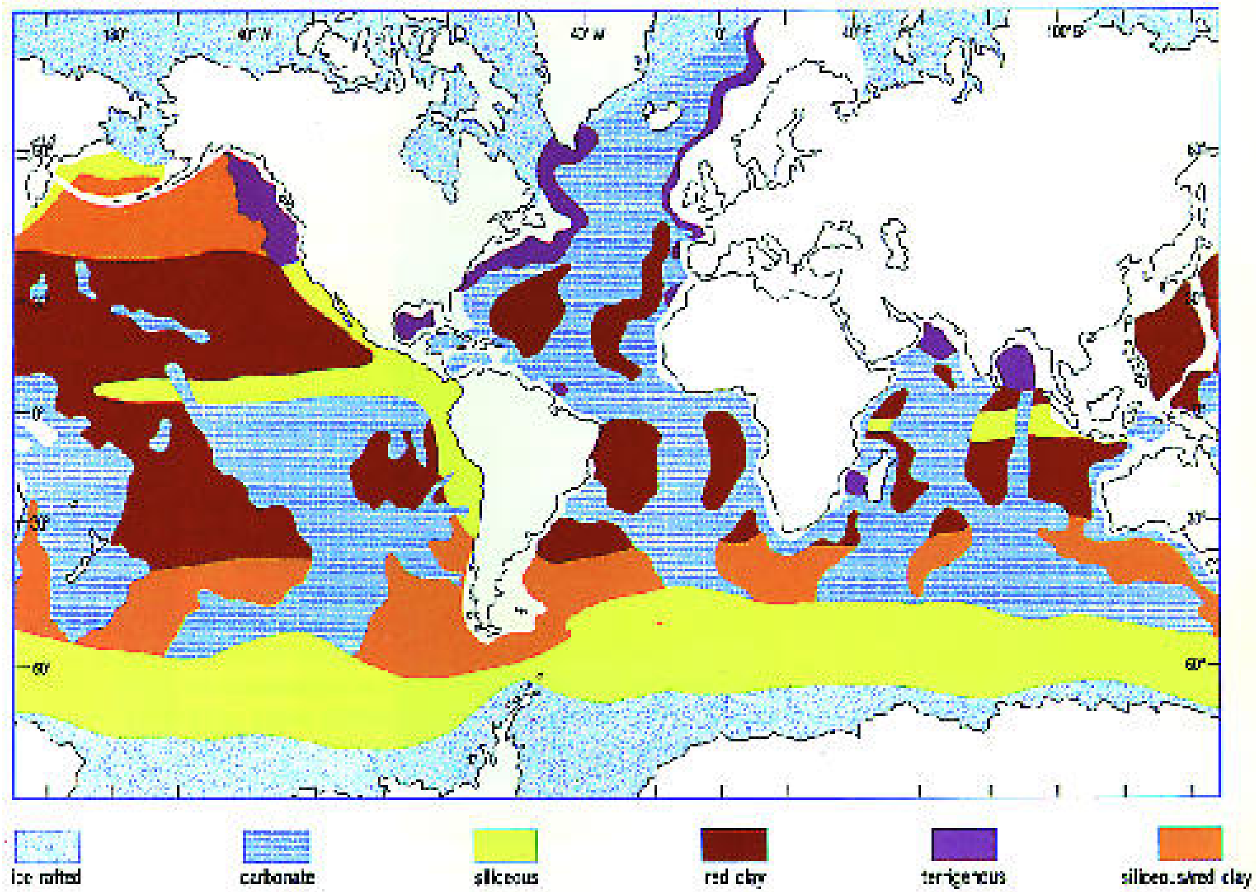


0 1 2 3 4
C
Inorganic
0 100 200 300
Si
0 20 40 60 80
N
NO3
0 1 2 3 4 5
P
0 100 200 300
O
Dissolved
O2
0 20 40 60 80
S

How the story starts...



end of story in the sediment?

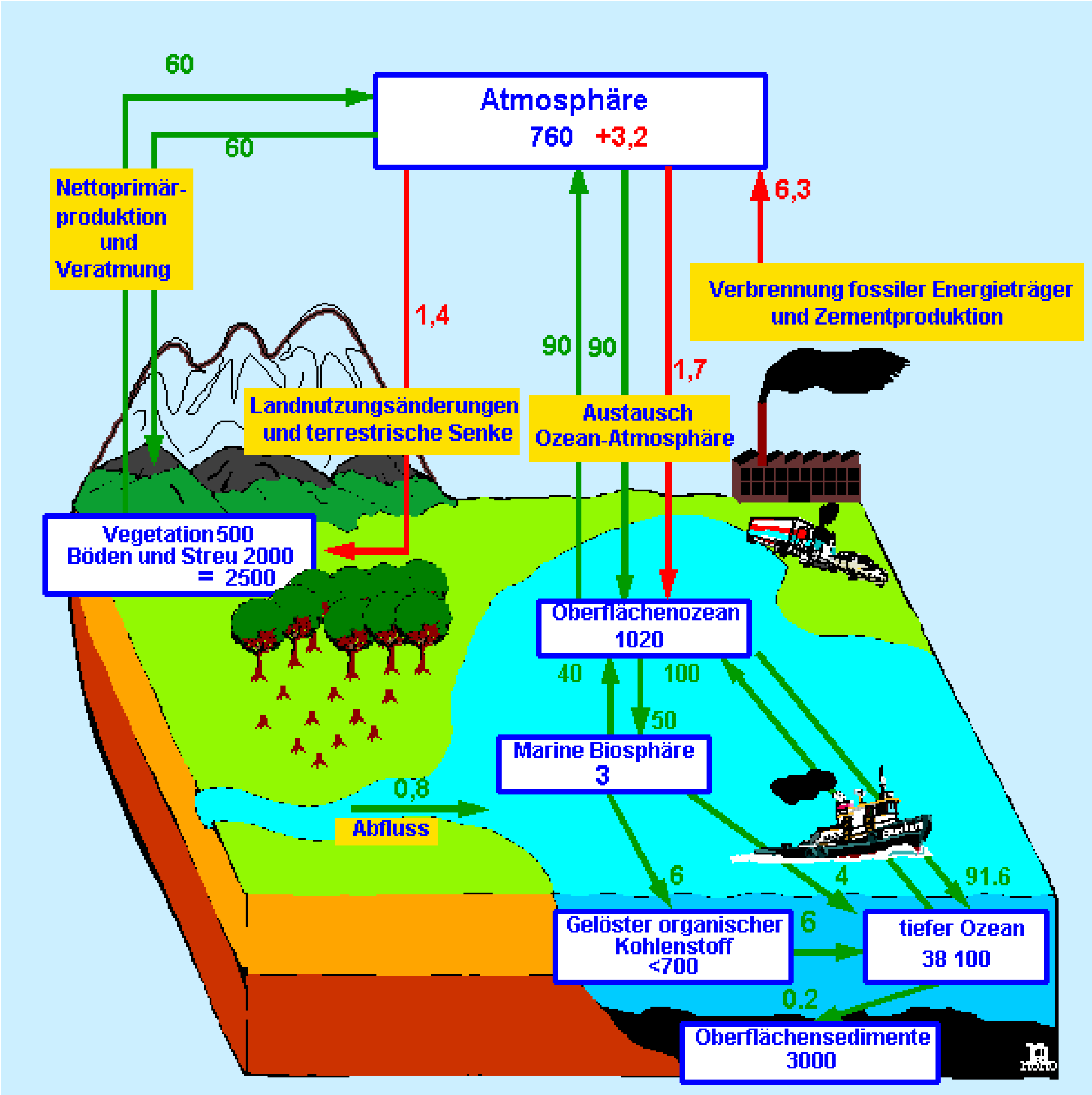


Not really

- Sediment is erodable (already ongoing)
- Starting point for Geologists
- Climate analyses from proxies
- Paleoclimate studies have to rely on
- It‘s our job to simulate the proxies that can be compared with data from the real World

How to use HAMOCC

- Manual at
- www.mpimet.mpg.de/wissenschaft/publications/14
- Slightly outdated
- Confusing: CO_2anthr means total CO_2 including anthropogenic perturbation
- HAMOCC needs a circulation field
- At MPI it is an appendix of MPIOM to be added by a compiler switch

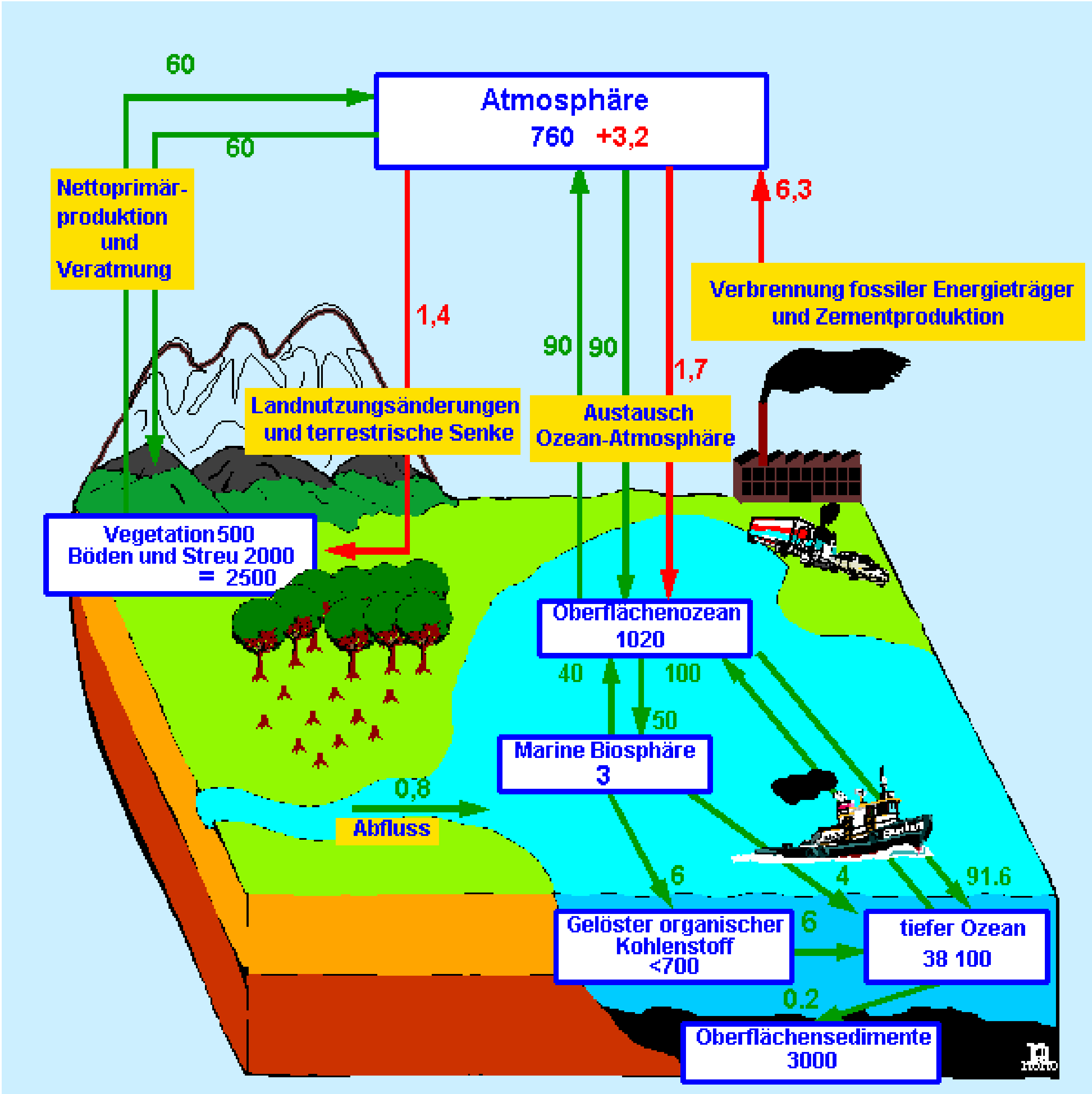


After Schimel

150 org.sed, 100,000,000 limestone in crust

Units Gt=10^9 tons =Pg=10^{15}g

- Federal state Hamburg 700 km^2
- Specific weight of coal < 2g/cm^3
- 1 Gt = 0.5 m coverage all over Hamburg
- Uncureable confusion:
- (1 mol C=)12g C + 32 g O_2 → 44 g CO_2
- HAMOCC ECHAM
- For weight we refer to C but in public press the numbers appear erratically mixed



After Schimel

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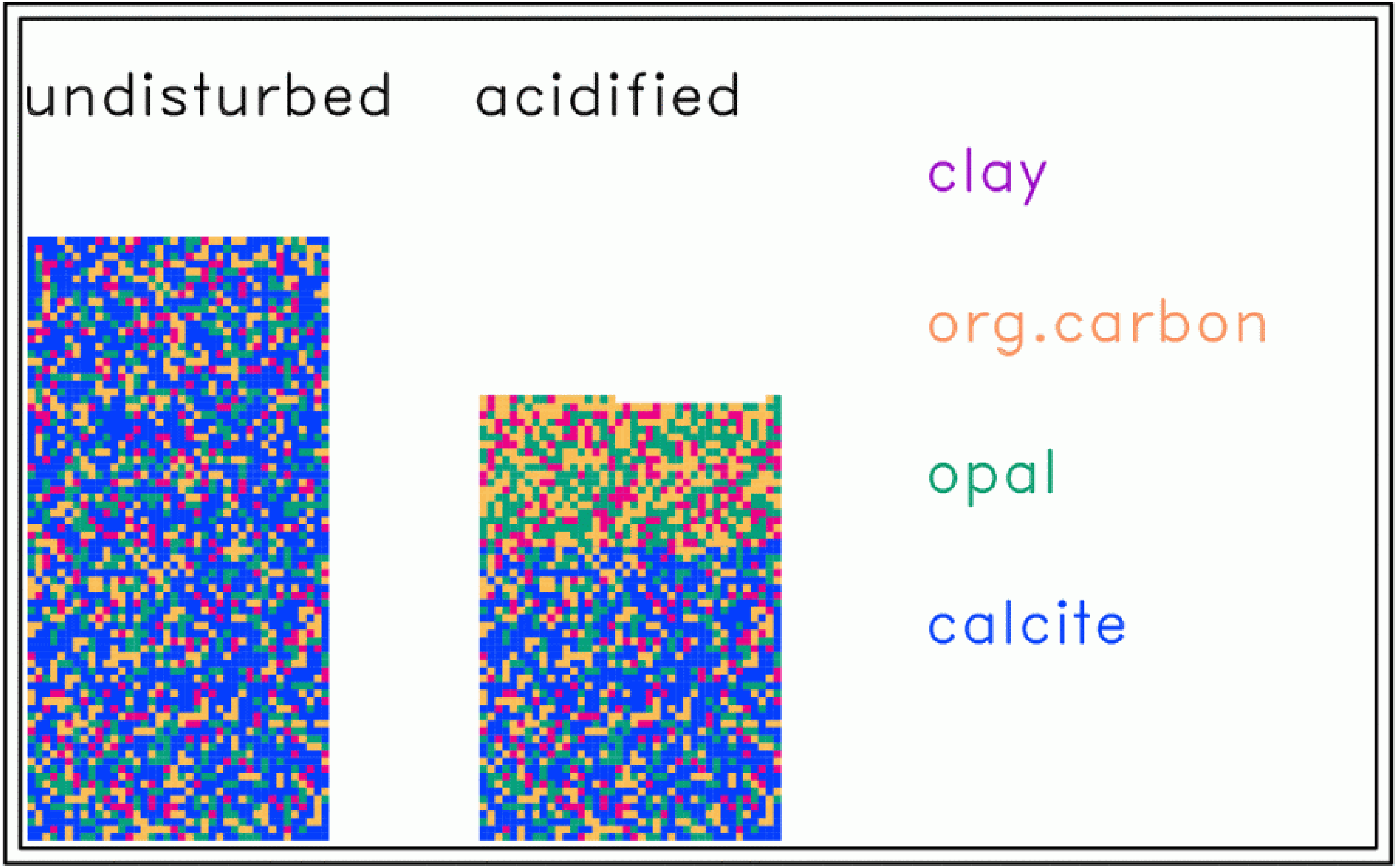
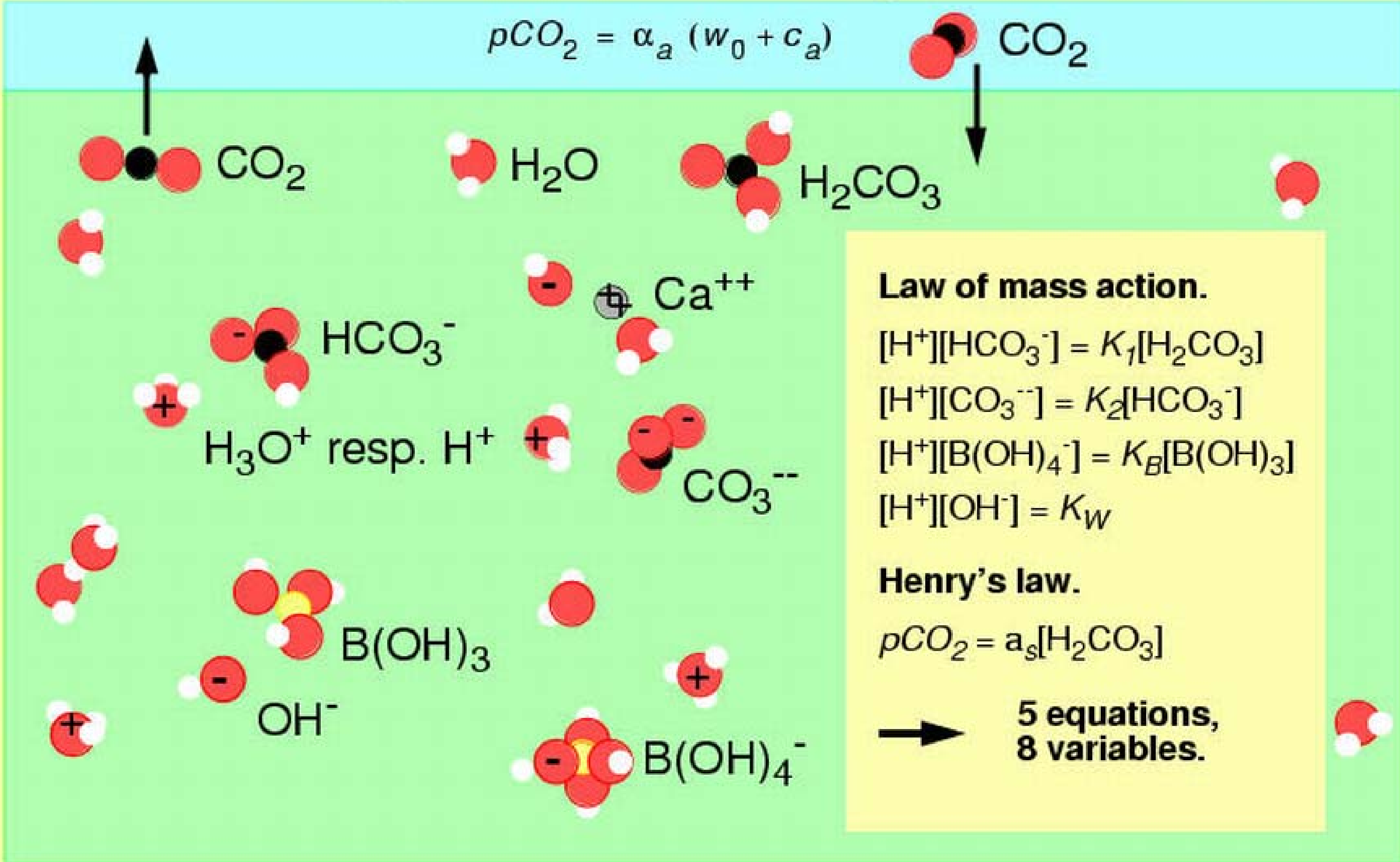

undisturbed
acidified
clay
org.carbon
opal
calcite

Inorganic carbon chemistry in sea water



Law of mass action.

$[H^+][HCO_3^-] = K_1[H_2CO_3]$

$[H^+][CO_3^{--}] = K_2[HCO_3^-]$

$[H^+][B(OH)_4^-] = K_B[B(OH)_3]$

$[H^+][OH^-] = K_W$

Henry's law.

$pCO_2 = a_s[H_2CO_3]$

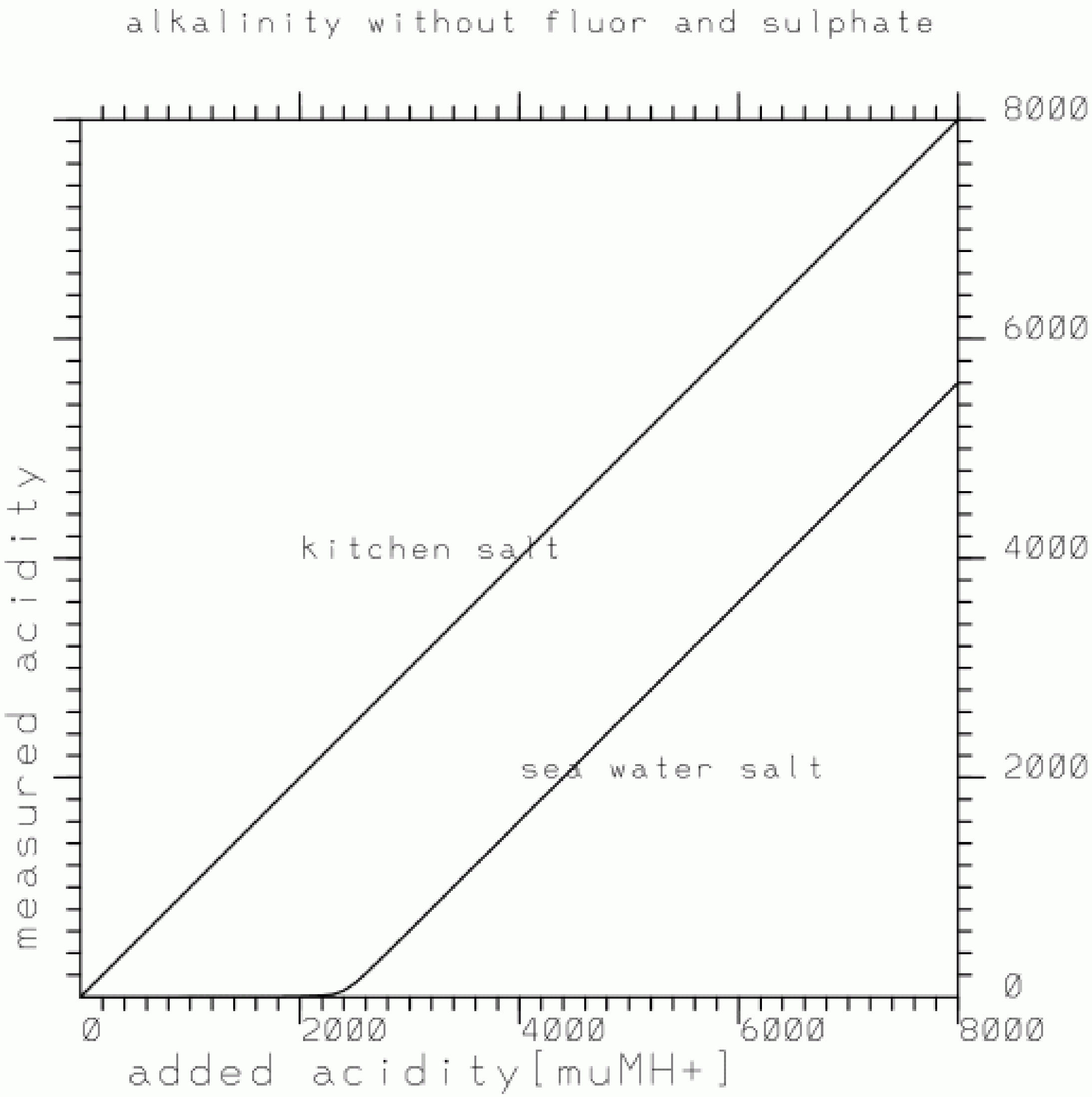
→ **5 equations, 8 variables.**

Hooss

Alkalinity is the key control of marine carbonate chemistry

- Wording goes back to Conte Marsigli 1732
- Rigorously defined „the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K<10^{-4.5}$, at25° C and zero ionic strength over proton donors (acids with $K>10^{-4.5}$)in one kg of sample“ (e.g.Dickson,1994)

What happens if you add chloric acid to water?



The Boron system

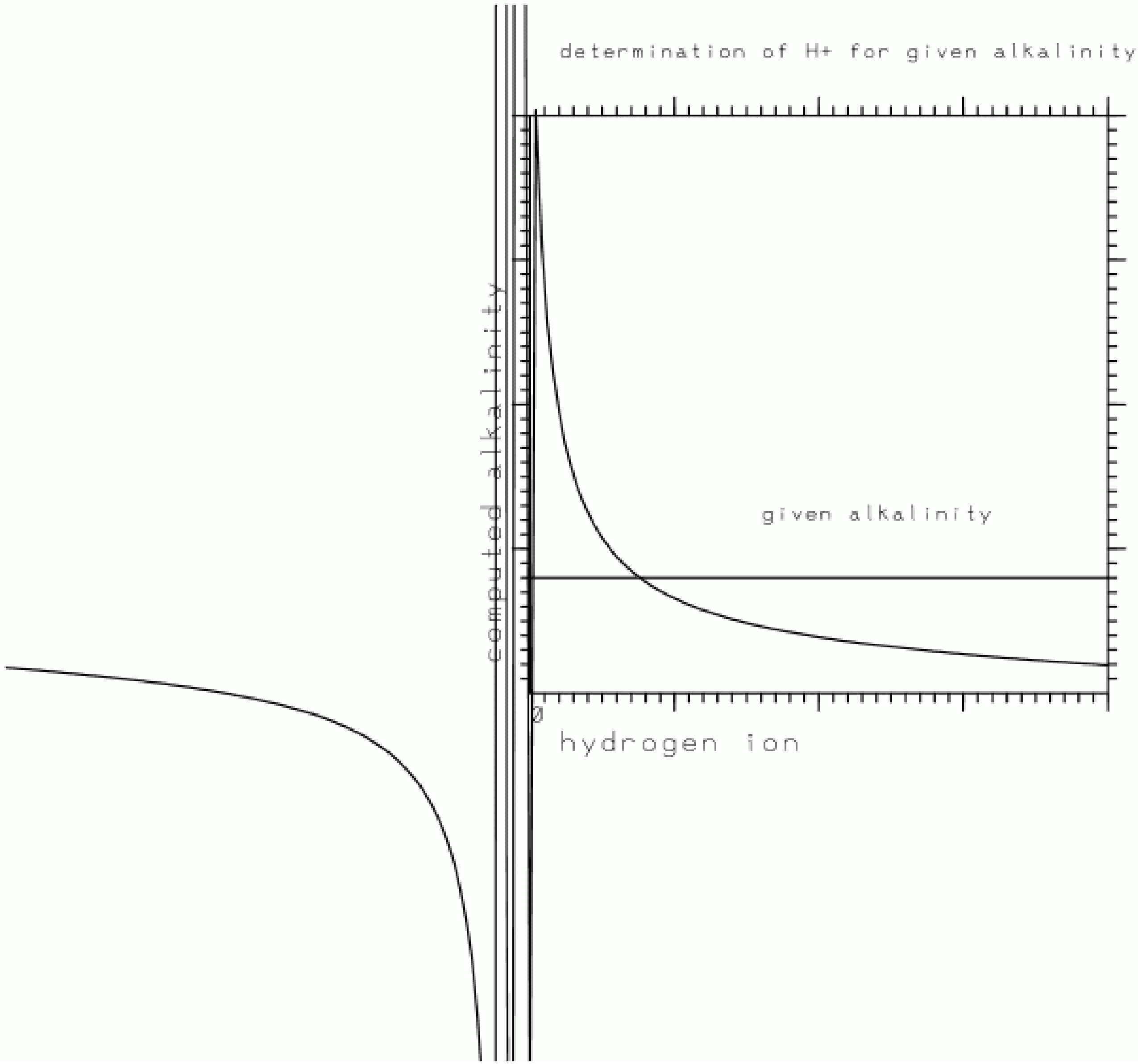
- Consider Alk = A_B + ...
- With B_T = sum of B-atoms
- $A_B = B_T/(1+[H^+]/K_B)$
- $dA_B/d[H^+] = -(B_T/K_B)/(1+[H^+]/K_B)^2$
- For being important K must be ~$[H^+]$
- Cl system: 3 orders more atoms but 14 orders higher K, doesn‘t contribute to Alk
- $A_C = DIC(2+H^+/K_2)/(1+H^+/K_2+H^{+2}/(K_1K_2))$

What is really measured?

- Rakestraw (1949) listed over 20 combinations
- Major constituents
- $Alk = 2CO_3^{--} + HCO_3^- + B(OH)_4^- + OH^- - H^+ + ..?...$ $+NH_3$
- $NH_3 + H2O \Leftrightarrow NH_4^+ + OH^-$
- Same effect on alk as it woud read
- $Alk = ... - NH_4^+$ (yielding more obvious counting of organic matter in Alk-balance)
- Note: H^+ in form of H_3O^+ or H_9O4^+

EMR-definition

- Alkalinity is the charge sum of all ions that do something with water and/or it´s ions under moderate changes of the system.


determination of H+ for given alkalinity
given alkalinity
computed alkalinity
0
hydrogen ion

How will the system change?

Increasing CO2

$$[H^+][HCO_3^-] = K_1[H_2CO_3]$$

$$[H^+][CO_3^{--}] = K_2[HCO_3^-]$$

How do small changes

d$[HCO_3^-]$, d$[HCO_3^-]$, and d$[H^+]$ relate to d$[H_2CO_3]$?

Buffering of additional CO_2

$K_1 d[H_2CO_3]=[HCO_3^-]d[H^+]+[H^+]d[HCO_3^-]$ (1)

$K_2 d[HCO_3^-]=[CO3^{--}]d[H^+]+[H^+]d[CO_3^{--}]$ (2)

$d[H^+]=d[HCO_3^-]+2[CO_3^{--}]$ (3)

$K_1=10^{-6}, K_2=10^{-9}, [H^+]=10^{-8}, [H_2CO_3]=10^{-5}, [HCO_3^-]=10^{-3}$ [mol/kg]

$[H_2CO_3]: [HCO_3^-]: [CO3^{--}]=1:100:10$

$d[CO_3^{--}]= d[HCO_3^-](K_2 - [CO_3^{--}])/(2[CO_3^{--}]+[H^+])$ (from 3>2)

$K_1 d[H_2CO_3]=d[HCO_3^-]([HCO_3^-]([H^+]+2K_2)/(2 [CO_3^{--}]+[H^+])+[H+])$

$K_1 d[H_2CO_3]= 6x10^{-8}\ d[HCO_3^-]$

And $d[CO_3^{--}]= - 0.4999\ d[HCO_3^-]$

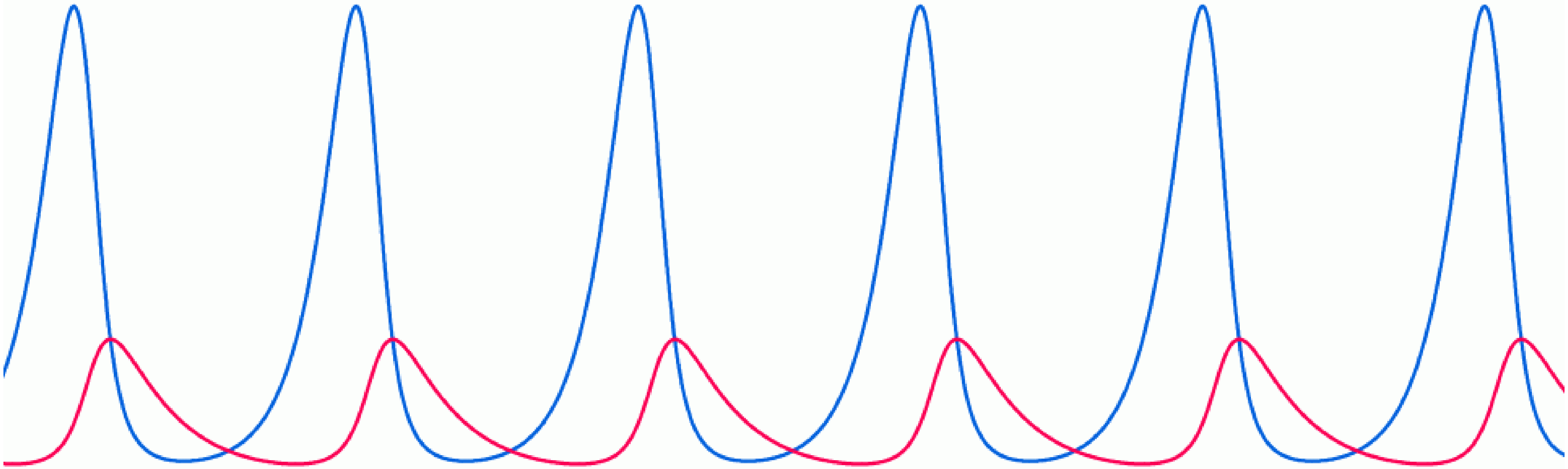
But: $K_1[H_2CO_3]= 10^{-8}\ d[HCO_3^-]$

$d[H_2CO_3]: d[HCO_3^-]: d[CO3^{--}]=1:16:-8$

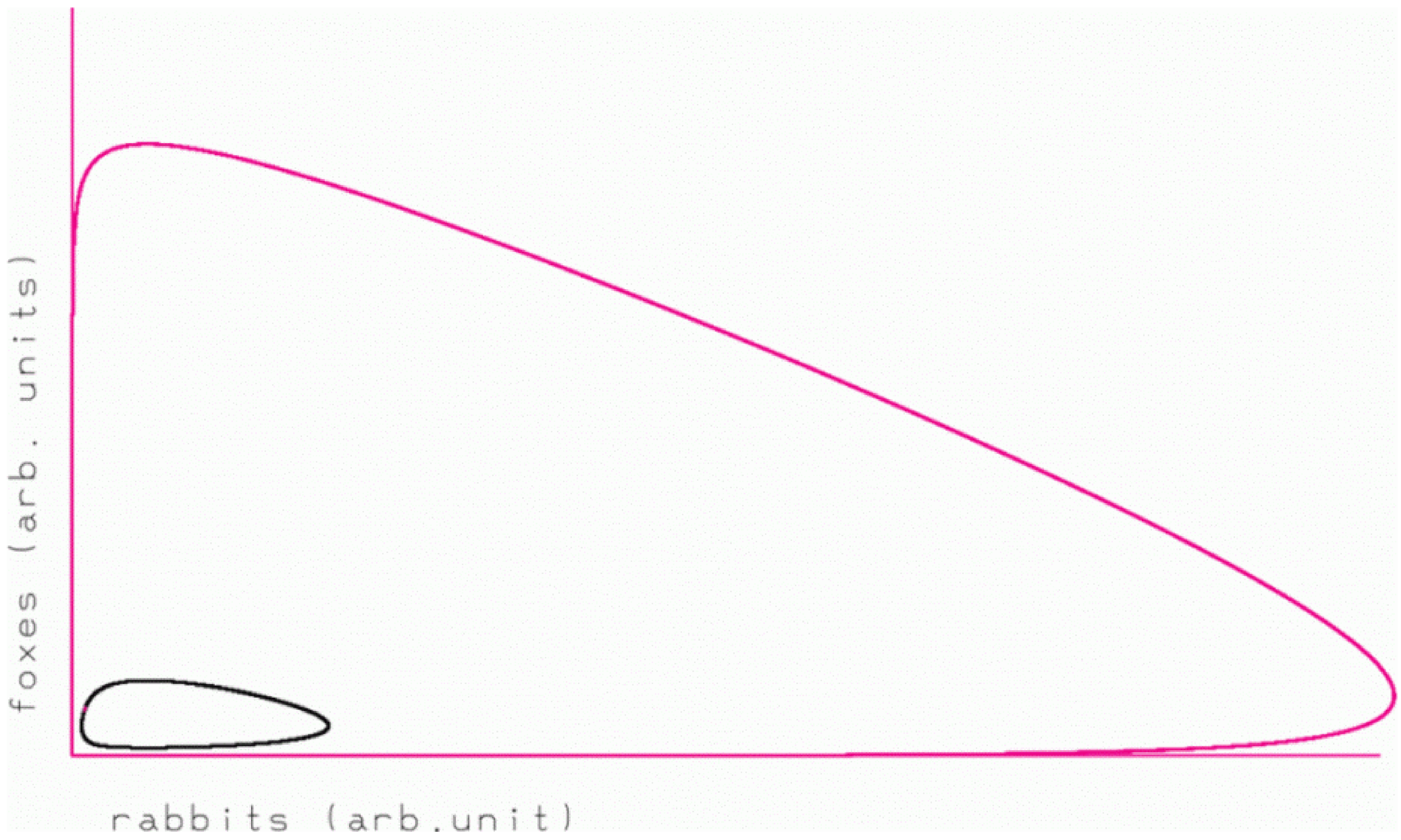
Basics of population dynamics as outlined by Lotka and Volterra 1908

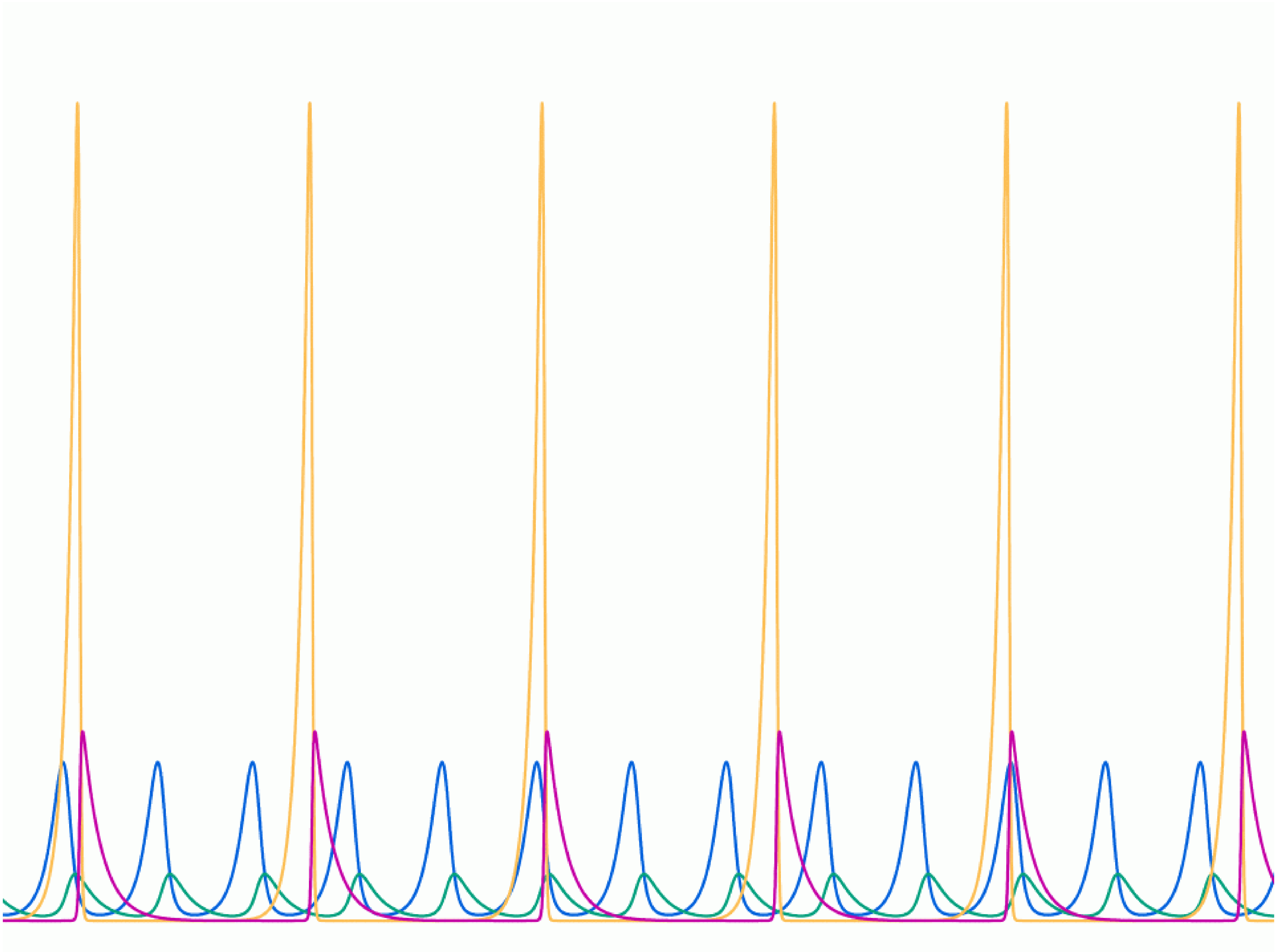
- Fox-rabbit system
- $R_t = aR - b_1RF$
- $F_t = -cF + b_2RF$
- Periodic solutions

Who are the foxes?



Time ➔


foxes (arb. units)
rabbits (arb.unit)



Implicit assumption: infinite grass

- Does it work in steppes?
- $R_t = aR\, G/(G+G_0) - b_1RF$
- $F_t = -cF + b_2RF$
- $G_t = -\, aR\, G/(G+G_0)$

Similarly for finite nutrients

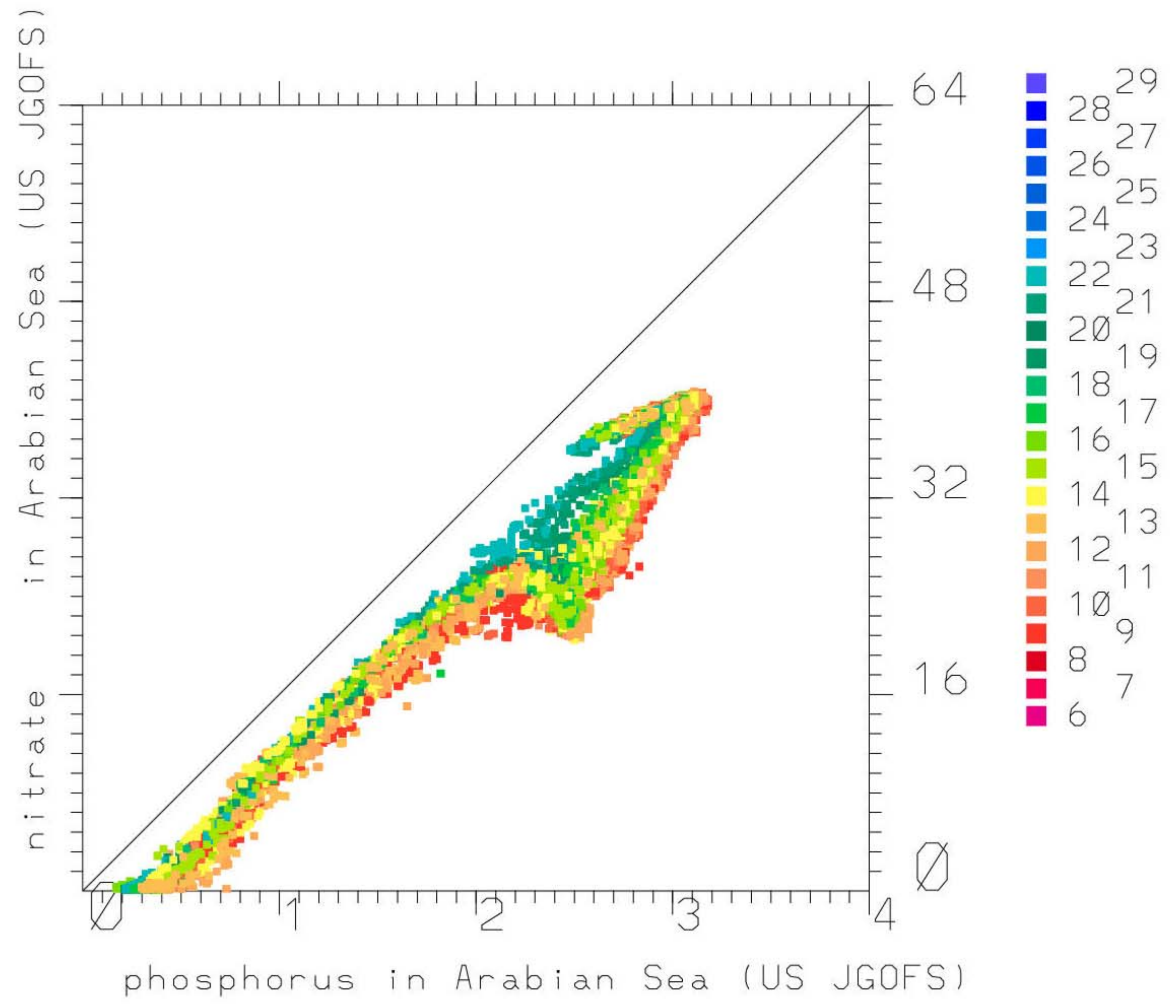
- R_t = aR G/(G+G_0) – b_1RF
- F_t =-cF + b_2RF
- G_t= - aR G/(G+G_0) + pNG/(N+N_0)
- Nt=-pNG/(N+N_0) + supply

Renaming for Ocean variables

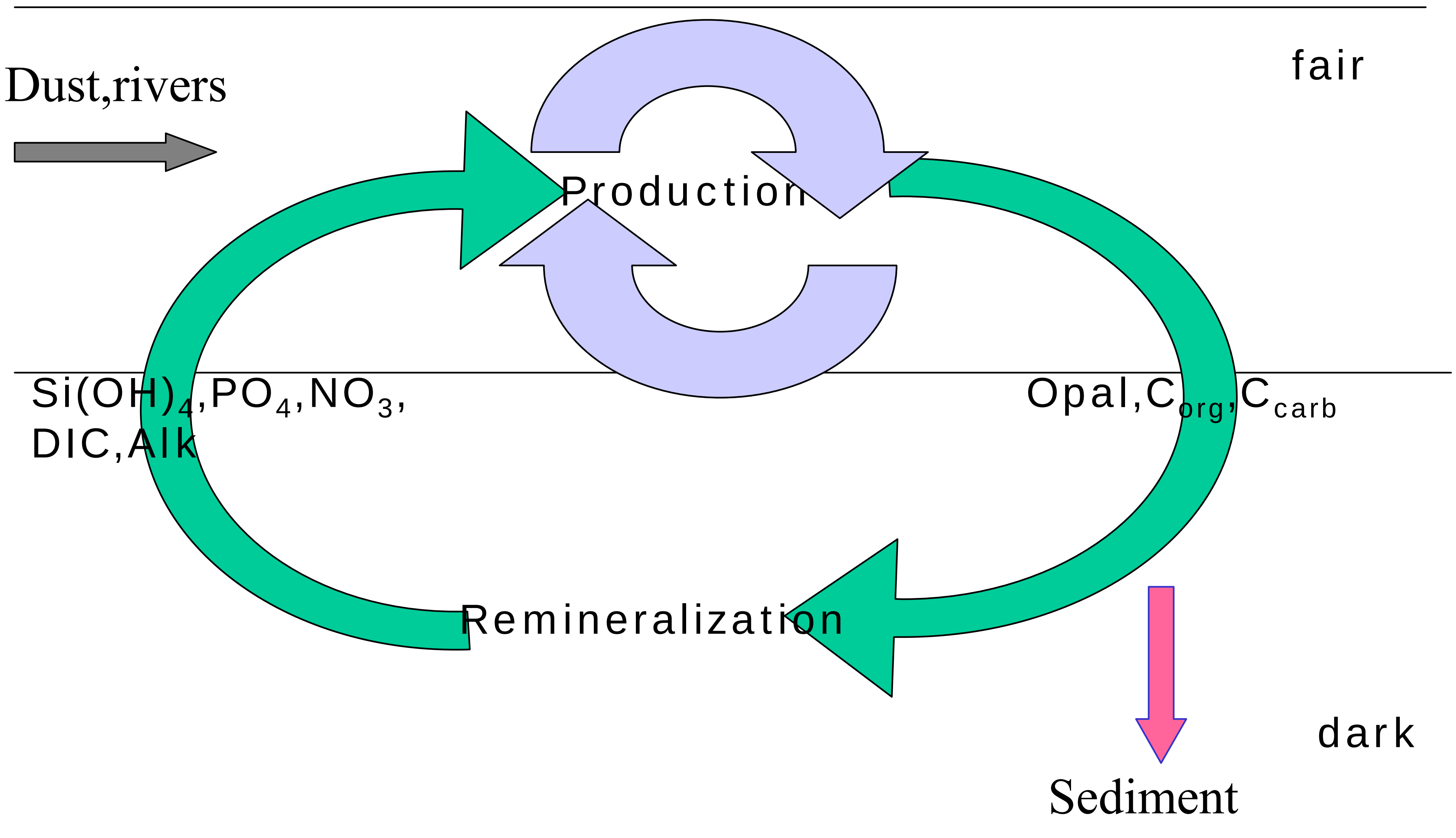
- Rabbit --→ zooplankton
- Foxes are parameterized by mortality of rabbits
- Gras → phytoplankton
- Φυτόν= leaf,plant, πλανη= erratic
- Nutrient → ??

Nitrogen or phosphorus as main nutrient?

The question about the ultimately
limiting nutrient has vexed oceanographers
for decades. Biologistes usually vote for nitrogen
whereas geochemist vote rather for phosphorus giving
biologically motivated reasons (Codispoti).


nitrate in Arabian Sea (US JGOFS)
phosphorus in Arabian Sea (US JGOFS)
0
16
32
48
64
0
1
2
3
4
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6

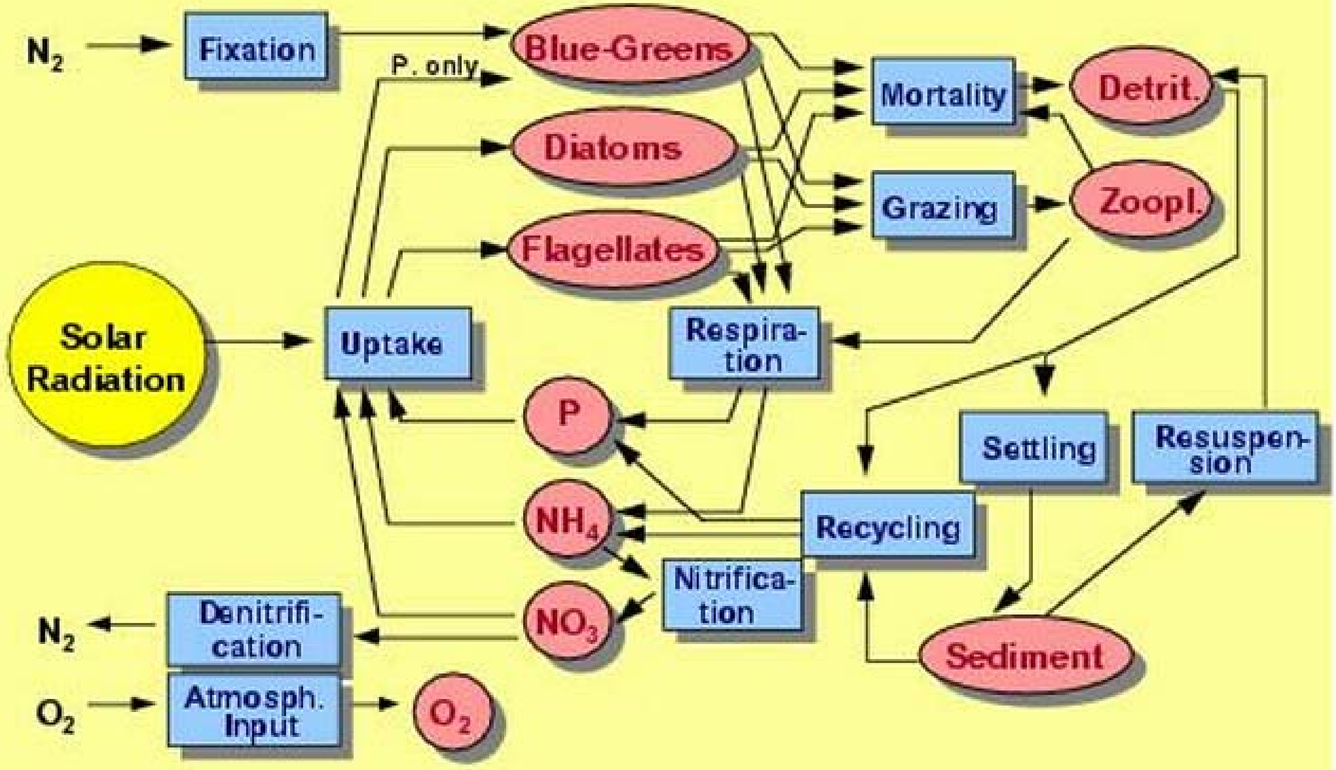
Geochemists view



Institut für
Ostseeforschung
Warnemünde

Baltic Sea
Research Institute
Warnemünde

ERGOM

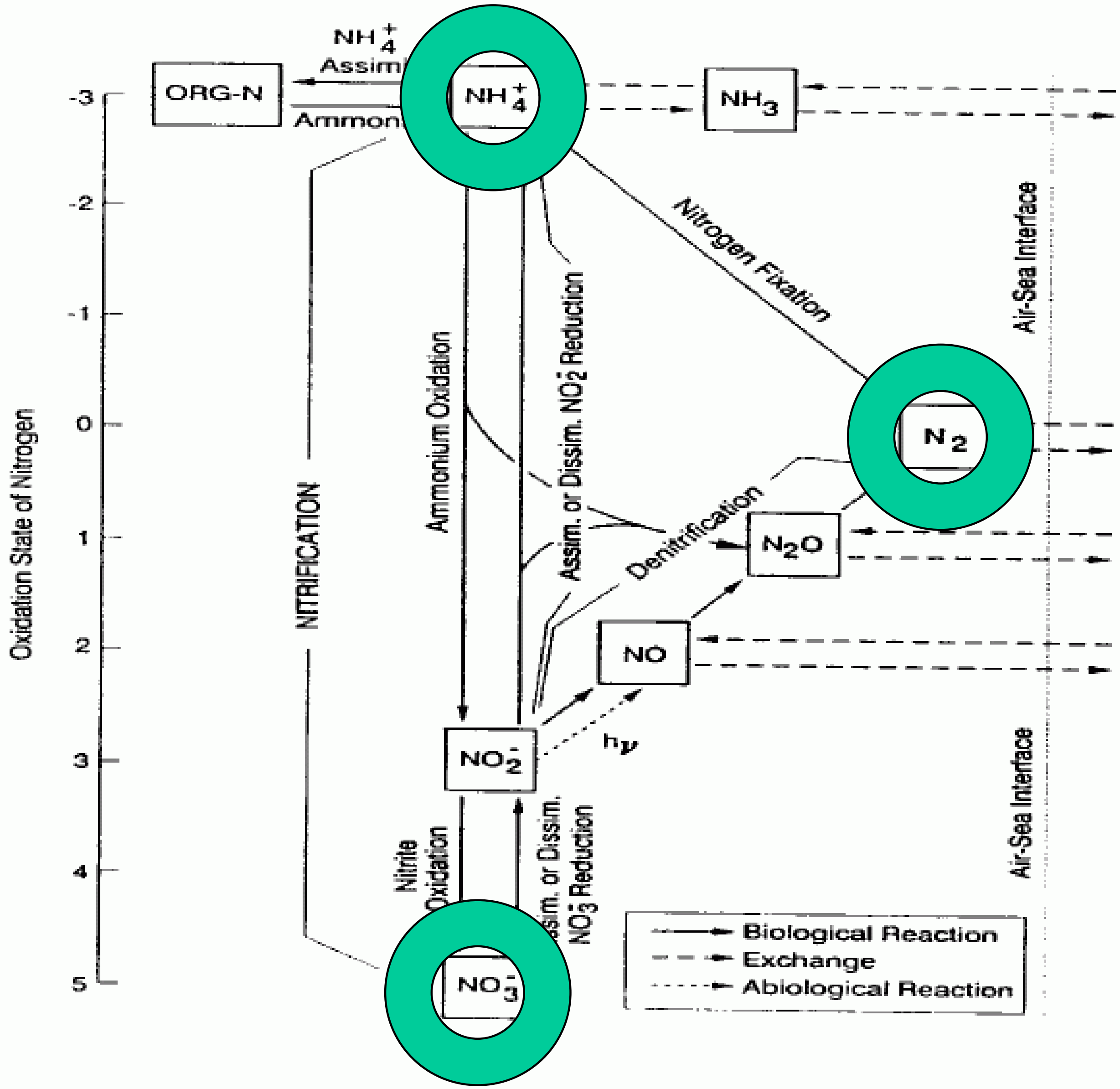


Neumann (2000)

Frank Janssen

The oceanic nitrogen cycle

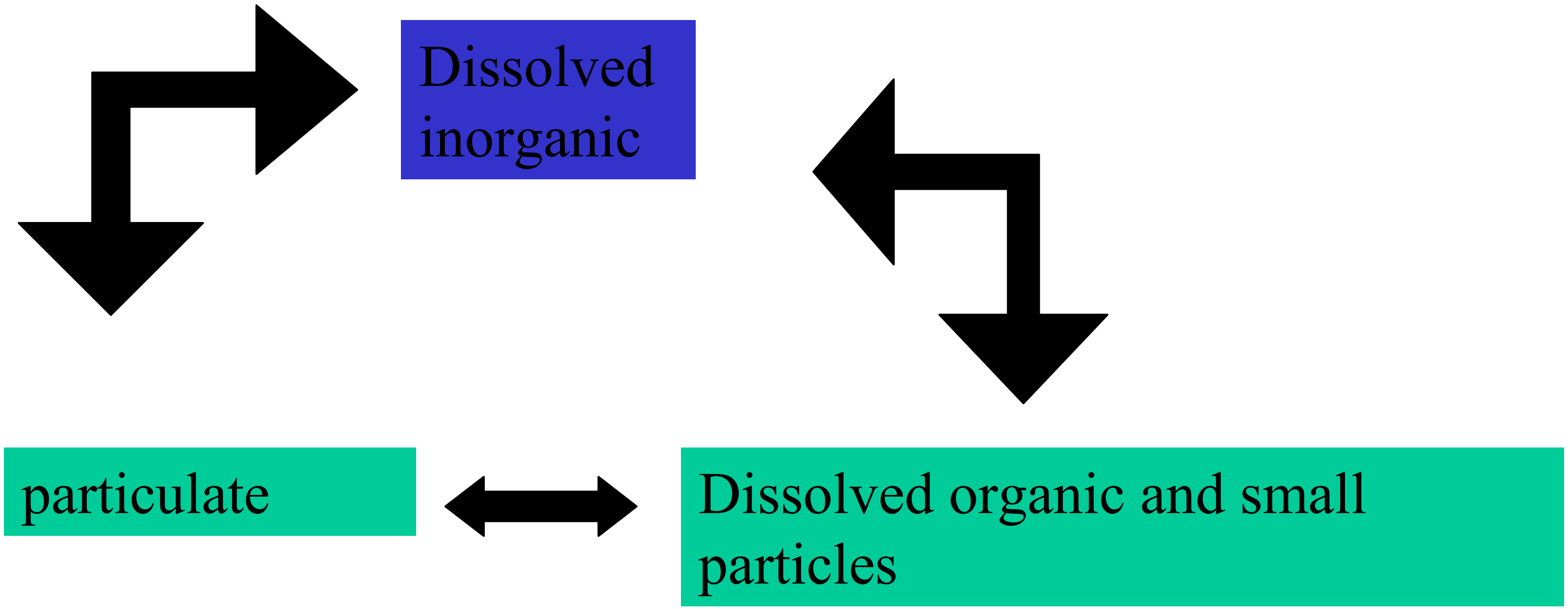
(Capone 1991)



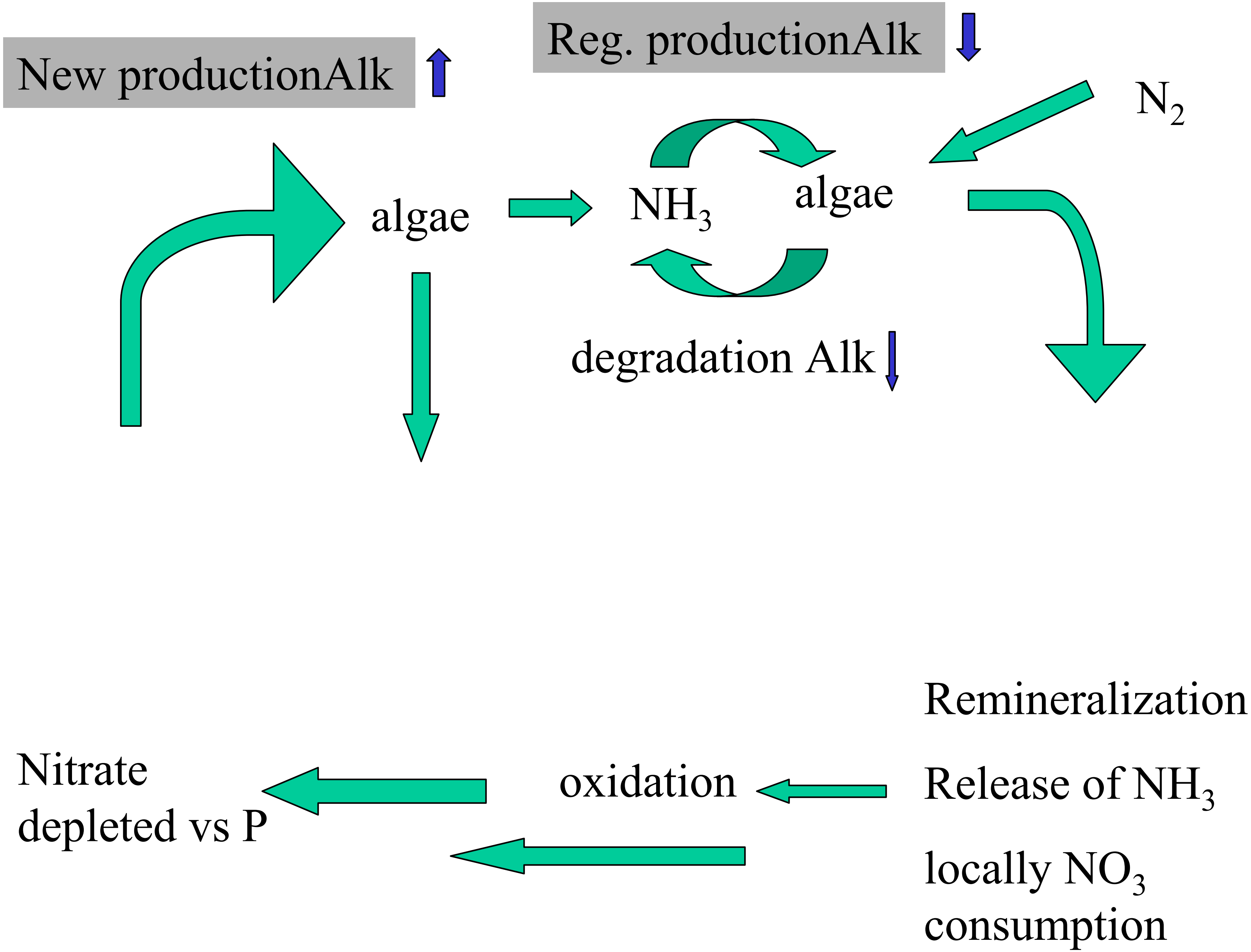
Topics to be adressed for nitrogen

- Nitrogen as nutrient
- Denitrification
- Nitrogen fixation
- Nitrous oxide
- Nitrogen Isotopes

The phosphorus cycle



„dissolved organic“: passing a filter with 0.5 µm pores


New productionAlk
Reg. productionAlk
N_2
algae
NH_3
algae
degradation Alk
Remineralization
Release of NH_3
locally NO_3 consumption
oxidation
Nitrate depleted vs P

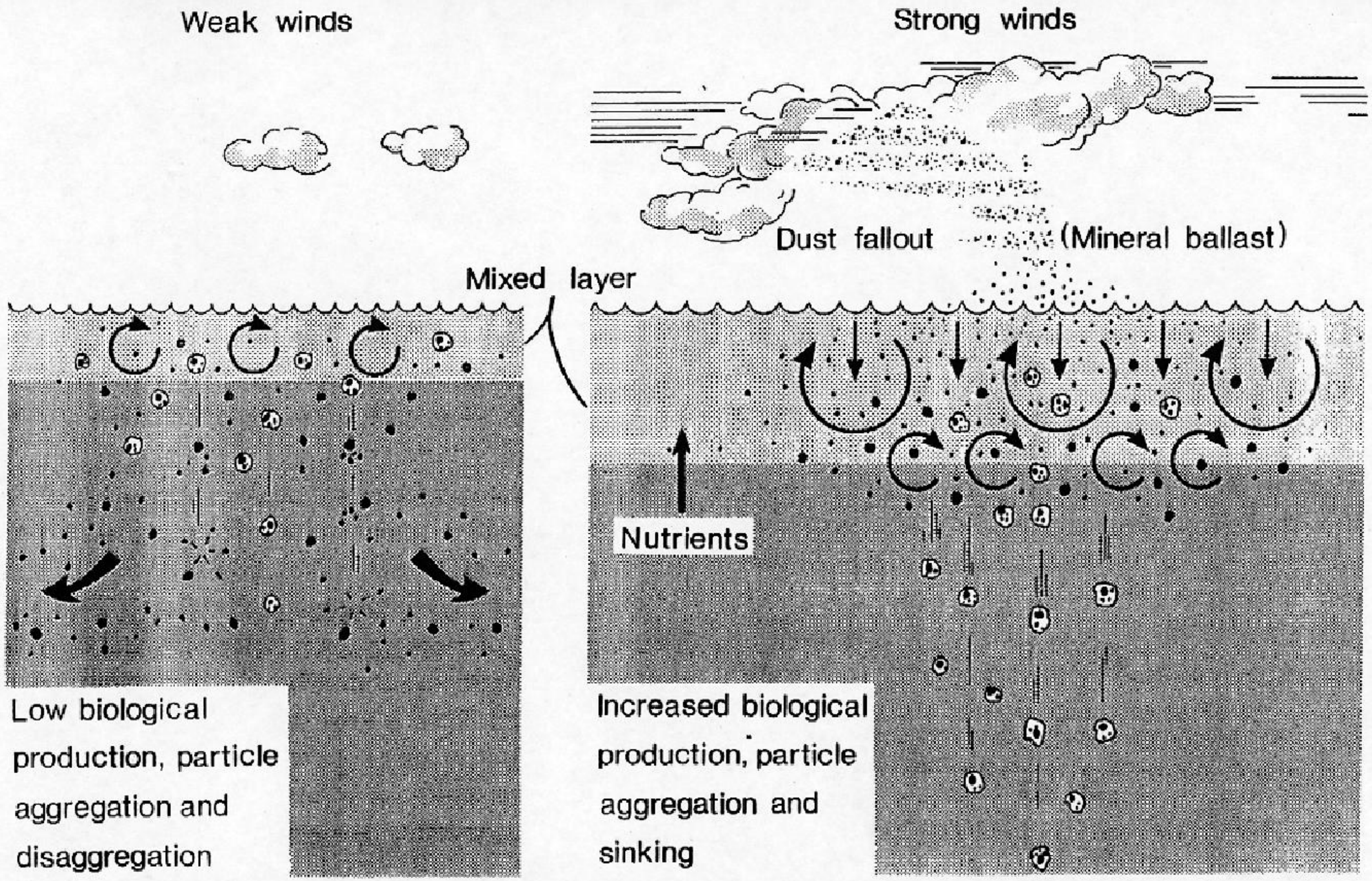
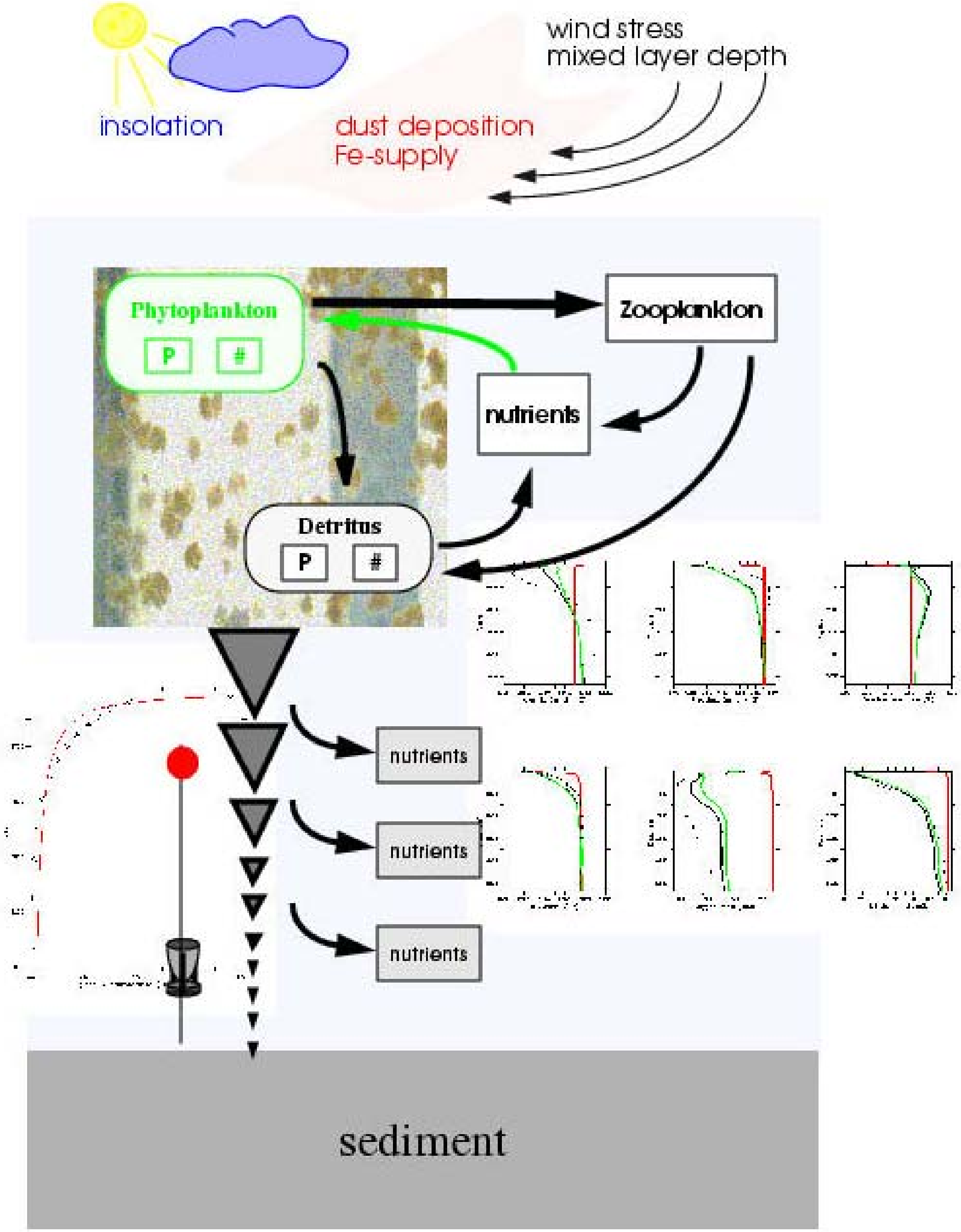


Fig. 4. The wind-driven biological pump and its enhancement by atmospheric dust deposition over the sea (Ittekkot, 1991).

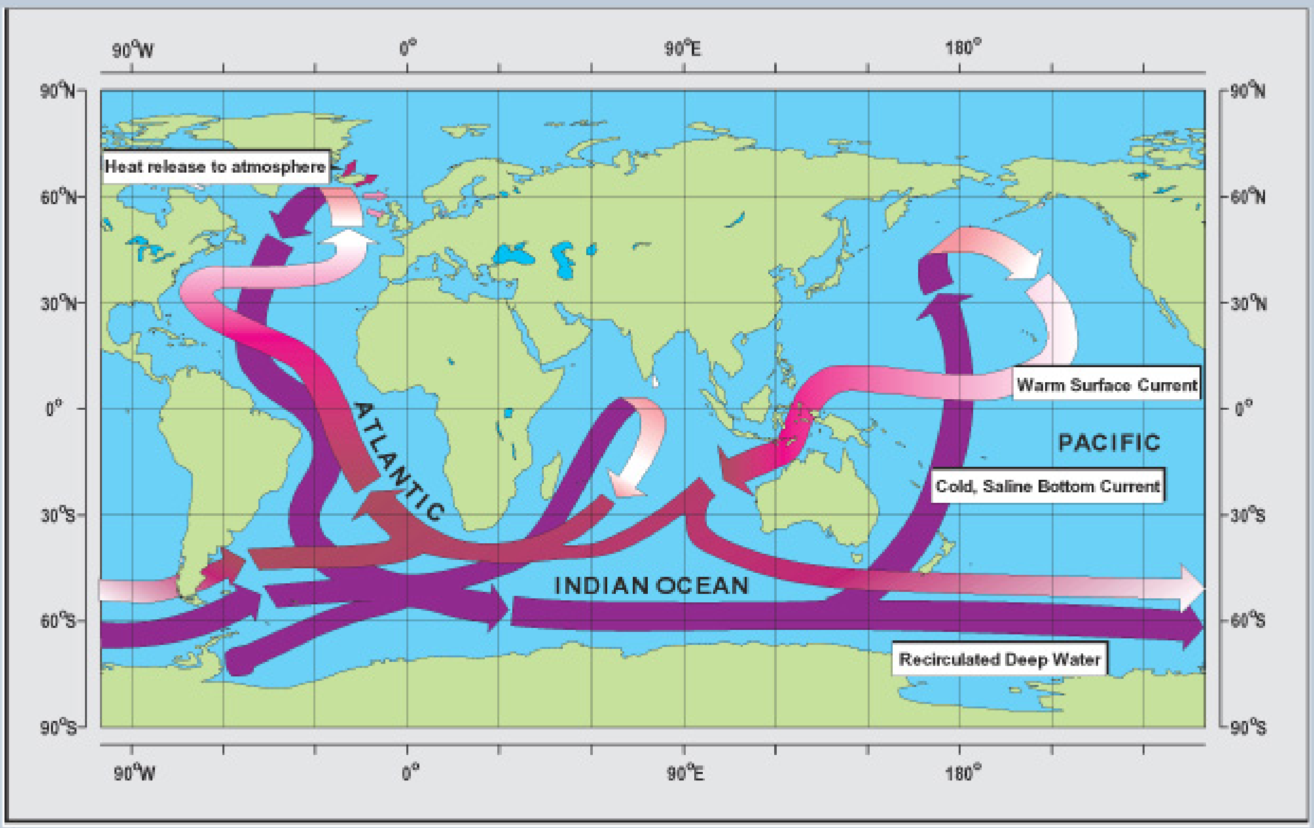
V.Ittekkot


wind stress
mixed layer depth
insolation
dust deposition
Fe-supply
Phytoplankton
P
#
Zooplankton
nutrients
Detritus
P
#
nutrients
nutrients
nutrients
sediment

I.Kriest

The Atlantic Thermohaline Circulation

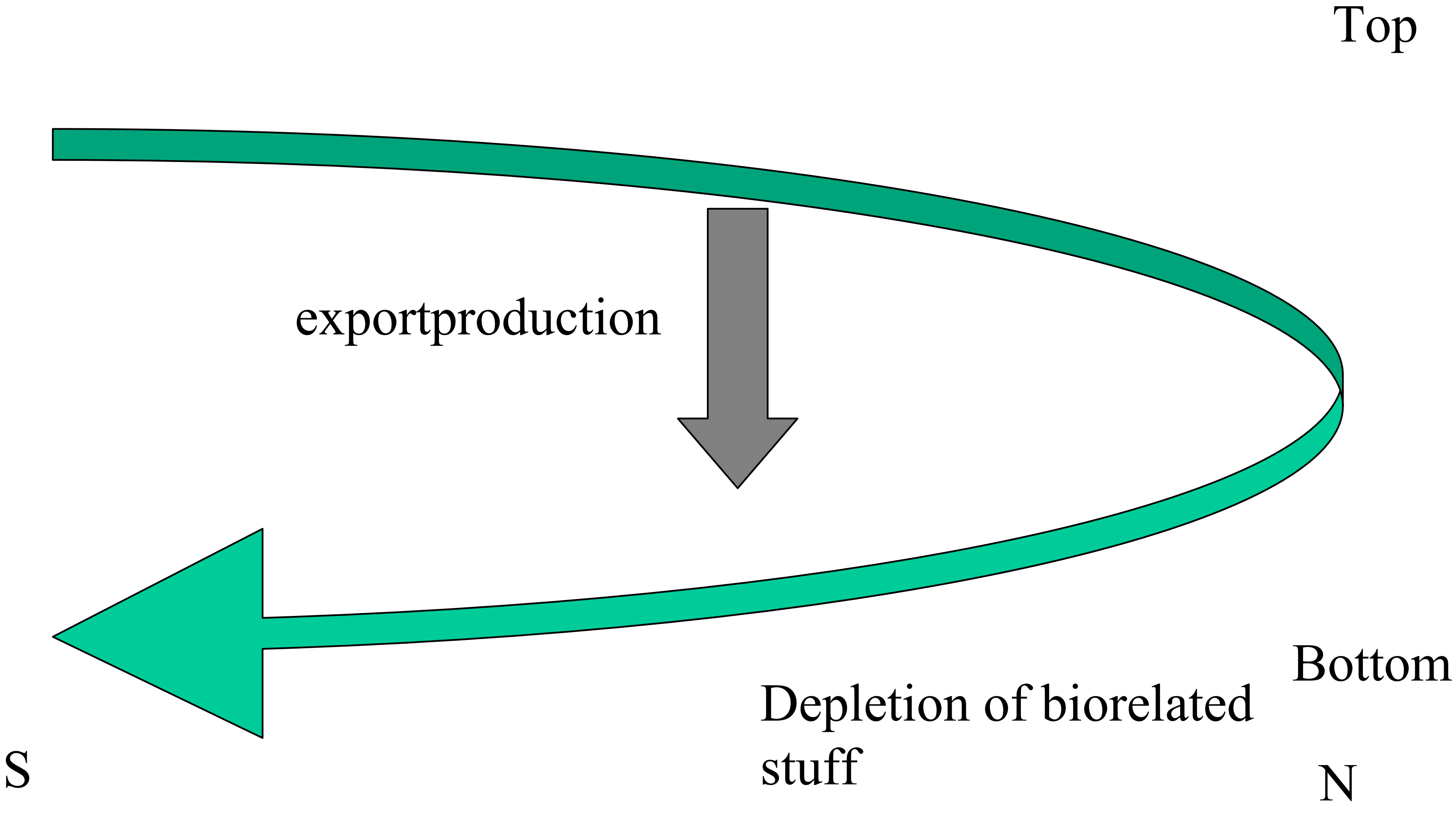
- A key Element of the Global Oceanic Circulation -



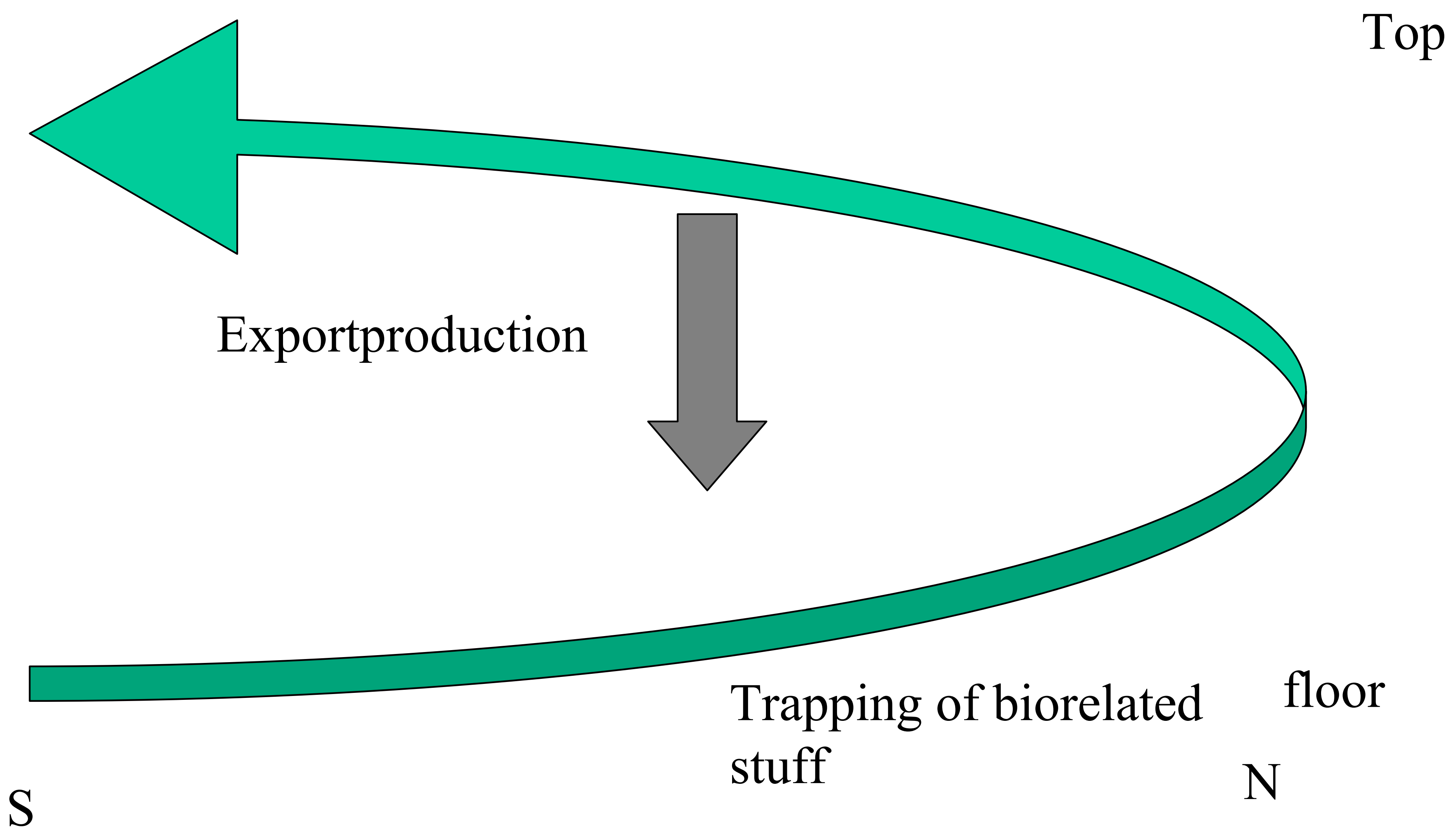
Schematic diagram of the global ocean circulation pathways, the 'conveyer' belt (after W. Broecker, modified by E. Maier-Reimer).

AV/D3/99-2

The Atlantic type circulation



The Pacific type circulation



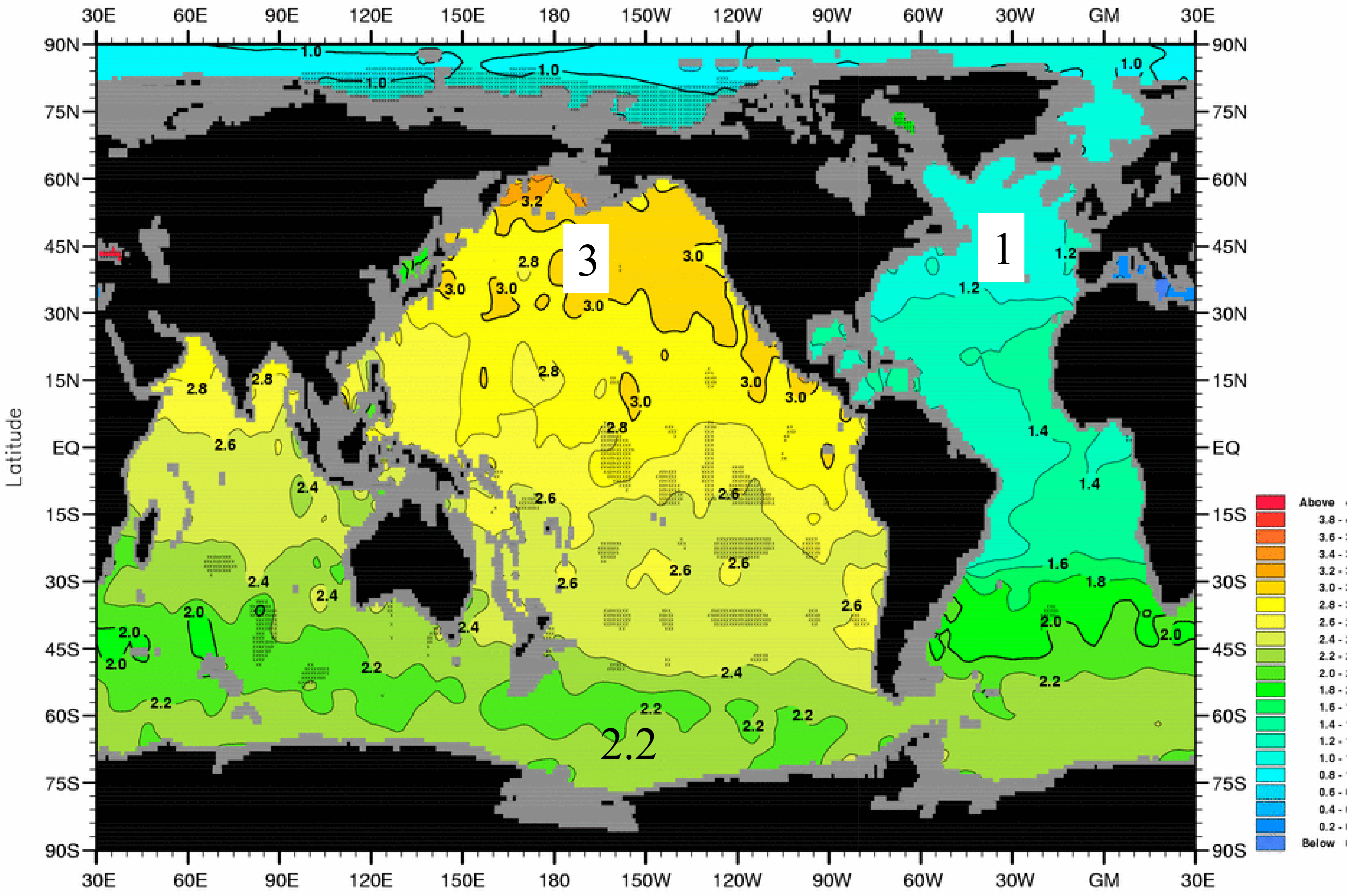


Fig. A2-26. Annual mean phosphate (µM) at 2000 m. depth.

Minimum Value= 0.11 Maximum Value= 4.50 Contour Interval: 0.20

World Ocean Atlas 2001

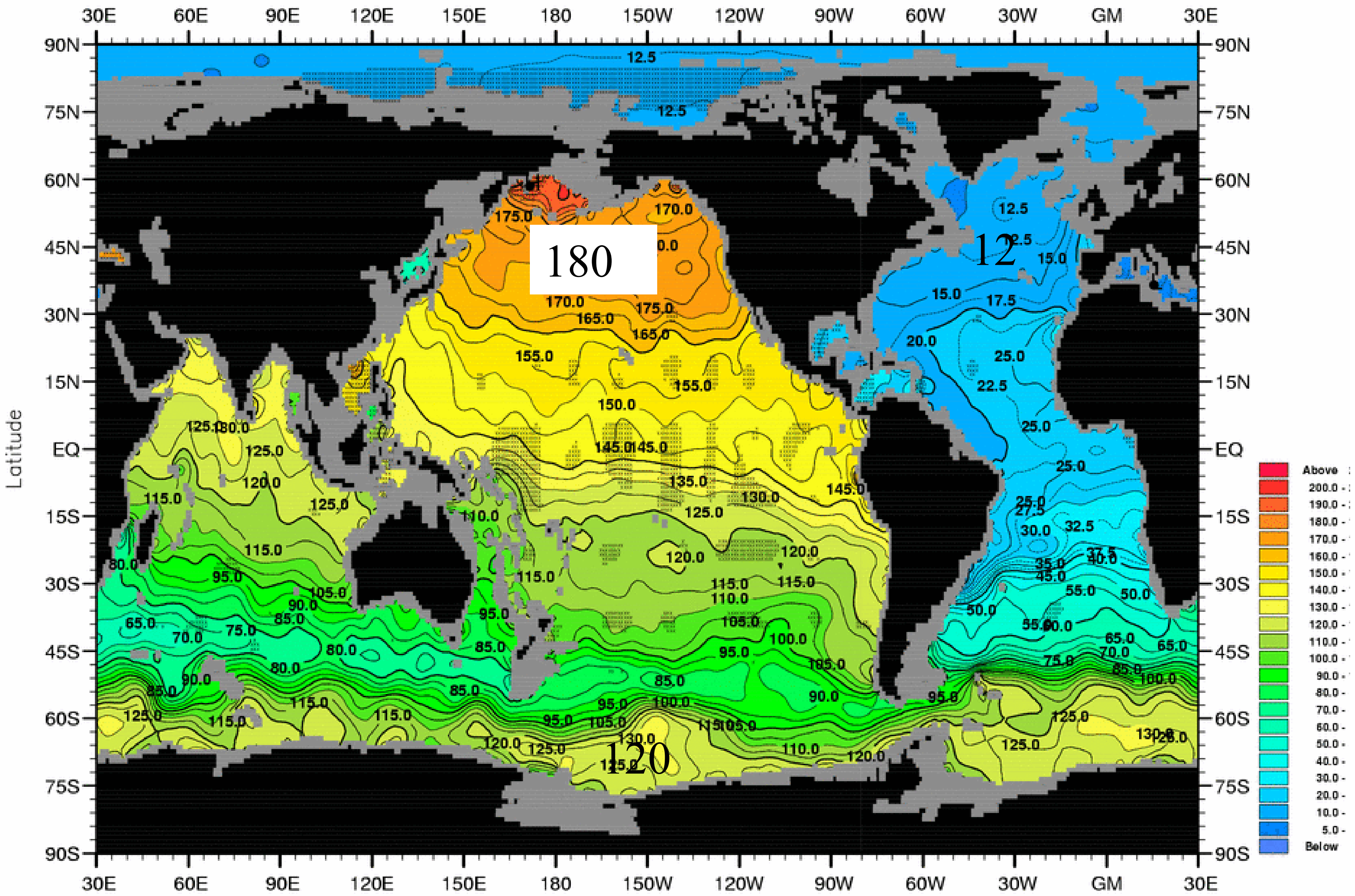
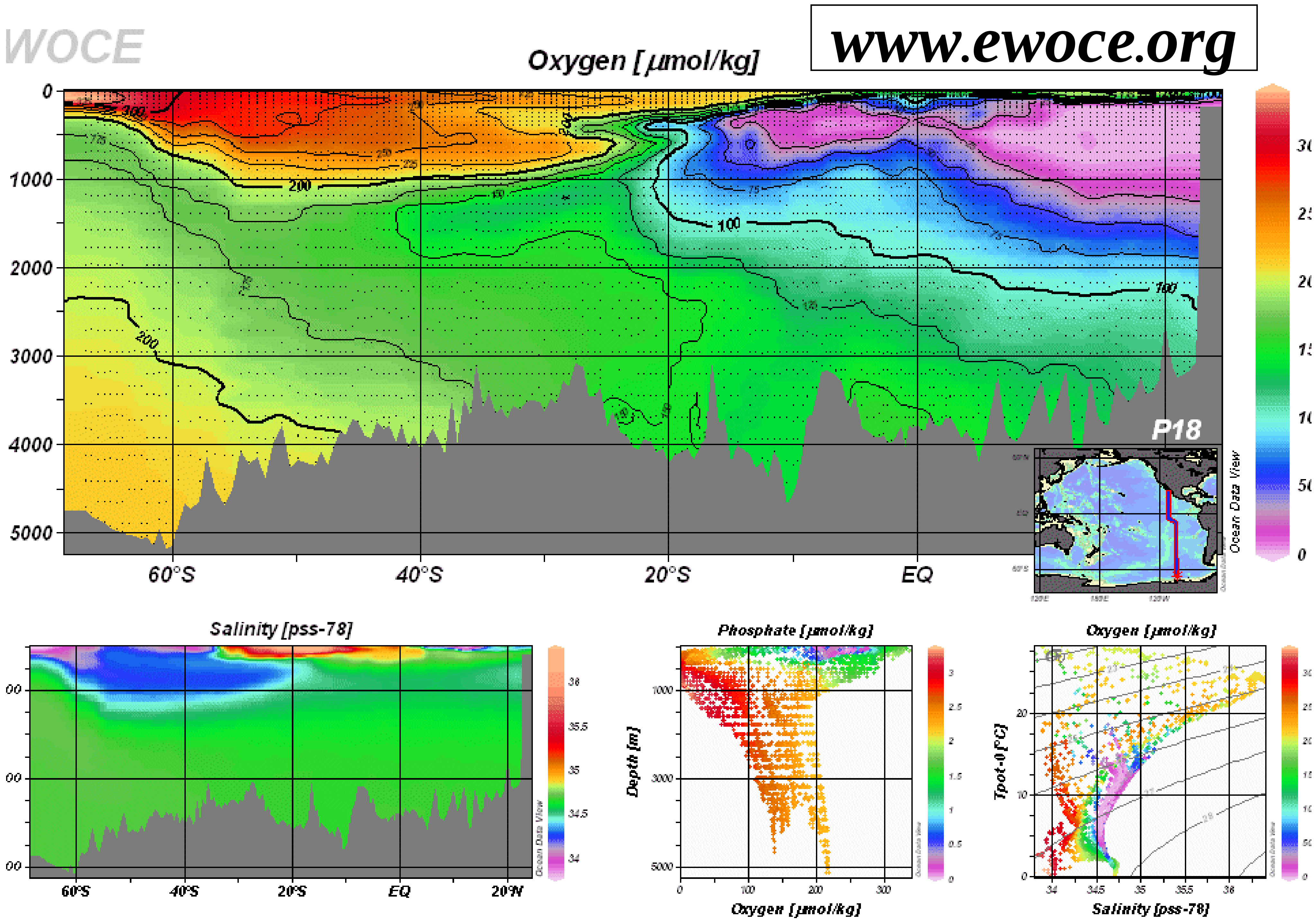


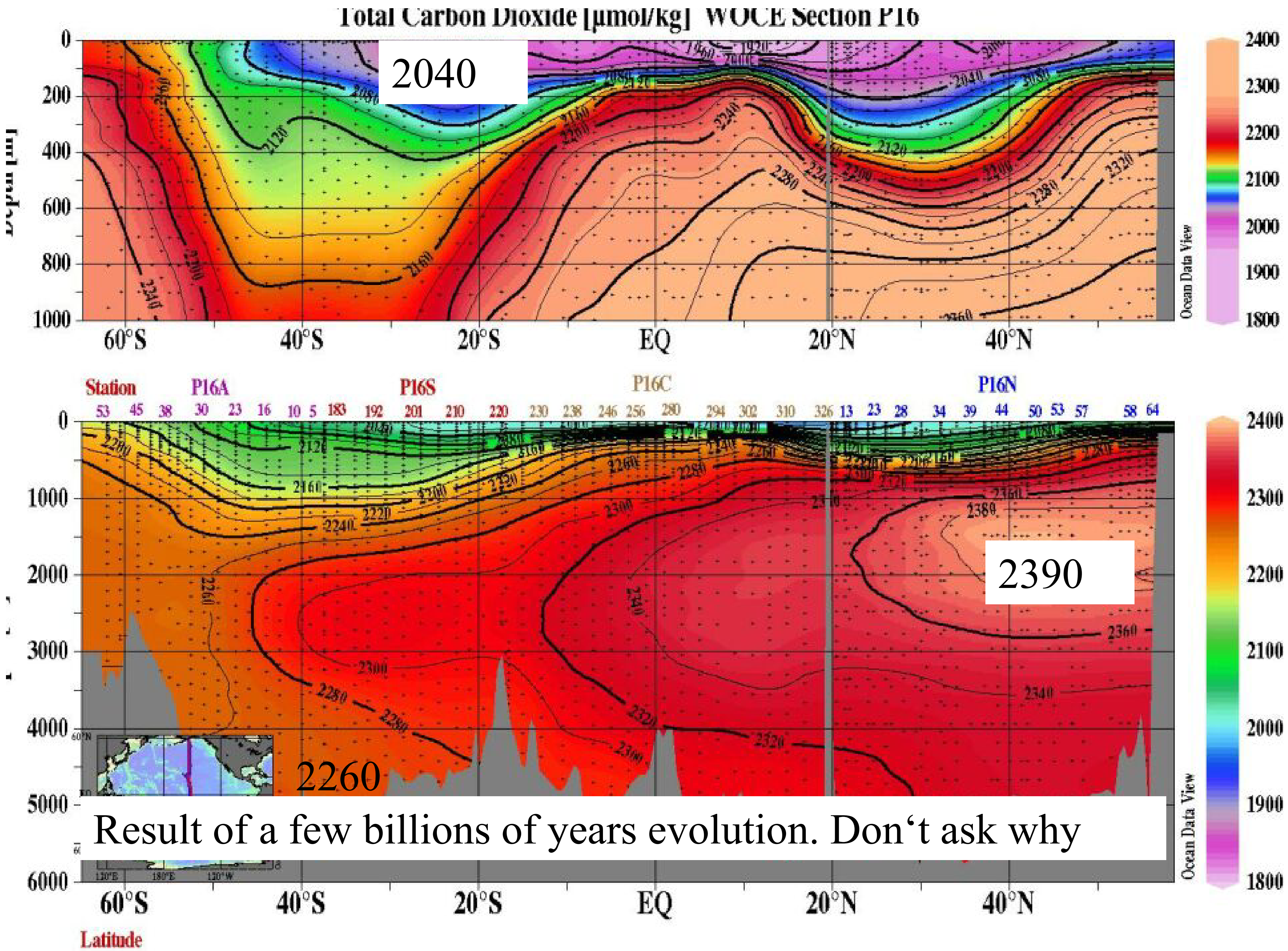
Fig. A2-26. Annual mean silicate (µM) at 2000 m. depth.

Minimum Value= 5.91 Maximum Value= 215.75 Contour Interval: 5.00

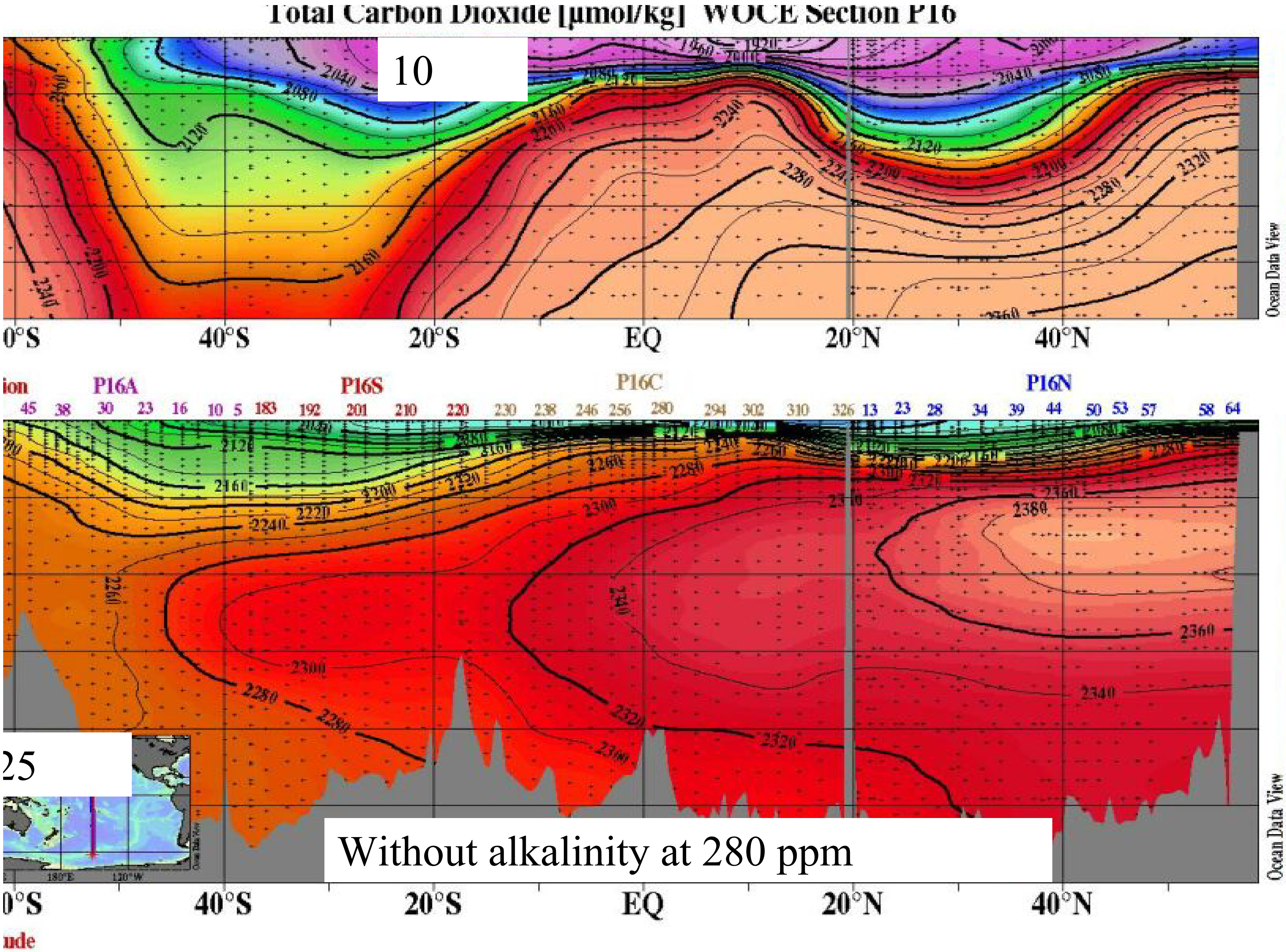
World Ocean Atlas 2001



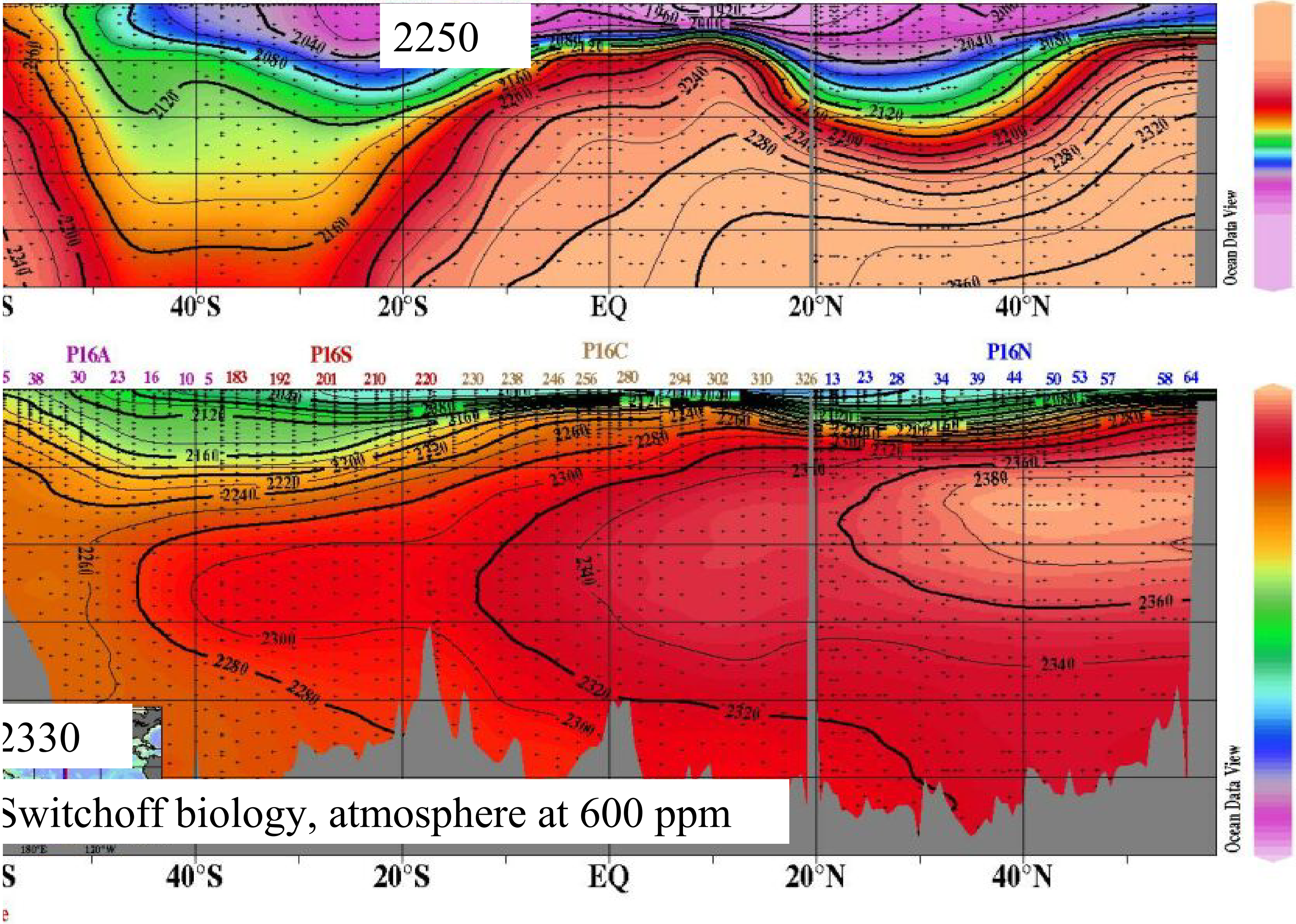
WOCE
www.ewoce.org
Oxygen [µmol/kg]
P18
Ocean Data View
60°S
40°S
20°S
EQ
Salinity [pss-78]
Phosphate [µmol/kg]
Depth [m]
Oxygen [µmol/kg]
Tpot-0 [°C]
Salinity [pss-78]

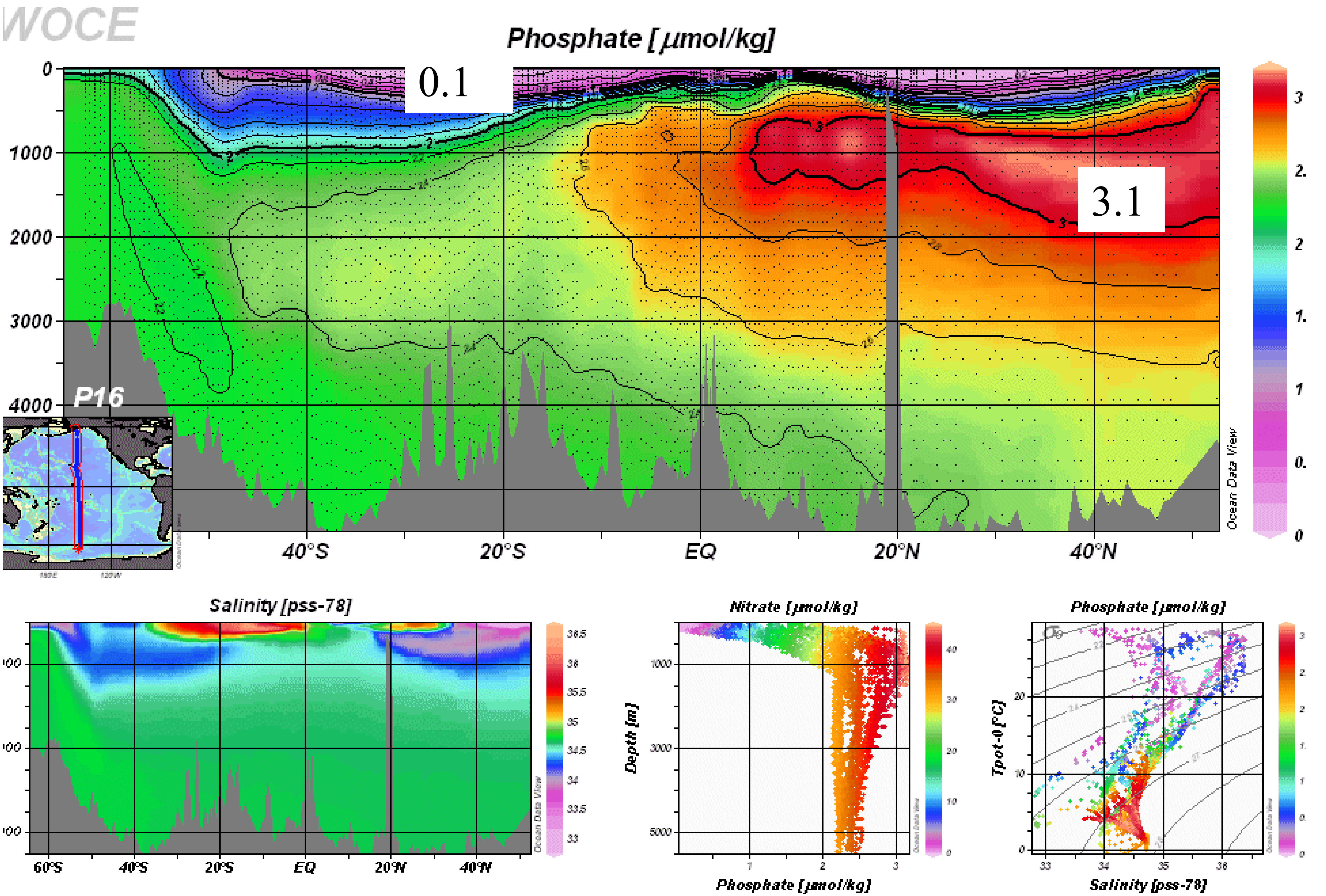


Result of a few billions of years evolution. Don‘t ask why


Total Carbon Dioxide [µmol/kg] WOCE Section P16
10
0°S
40°S
20°S
EQ
20°N
40°N
Ocean Data View
P16A
P16S
P16C
P16N
25
Without alkalinity at 280 ppm

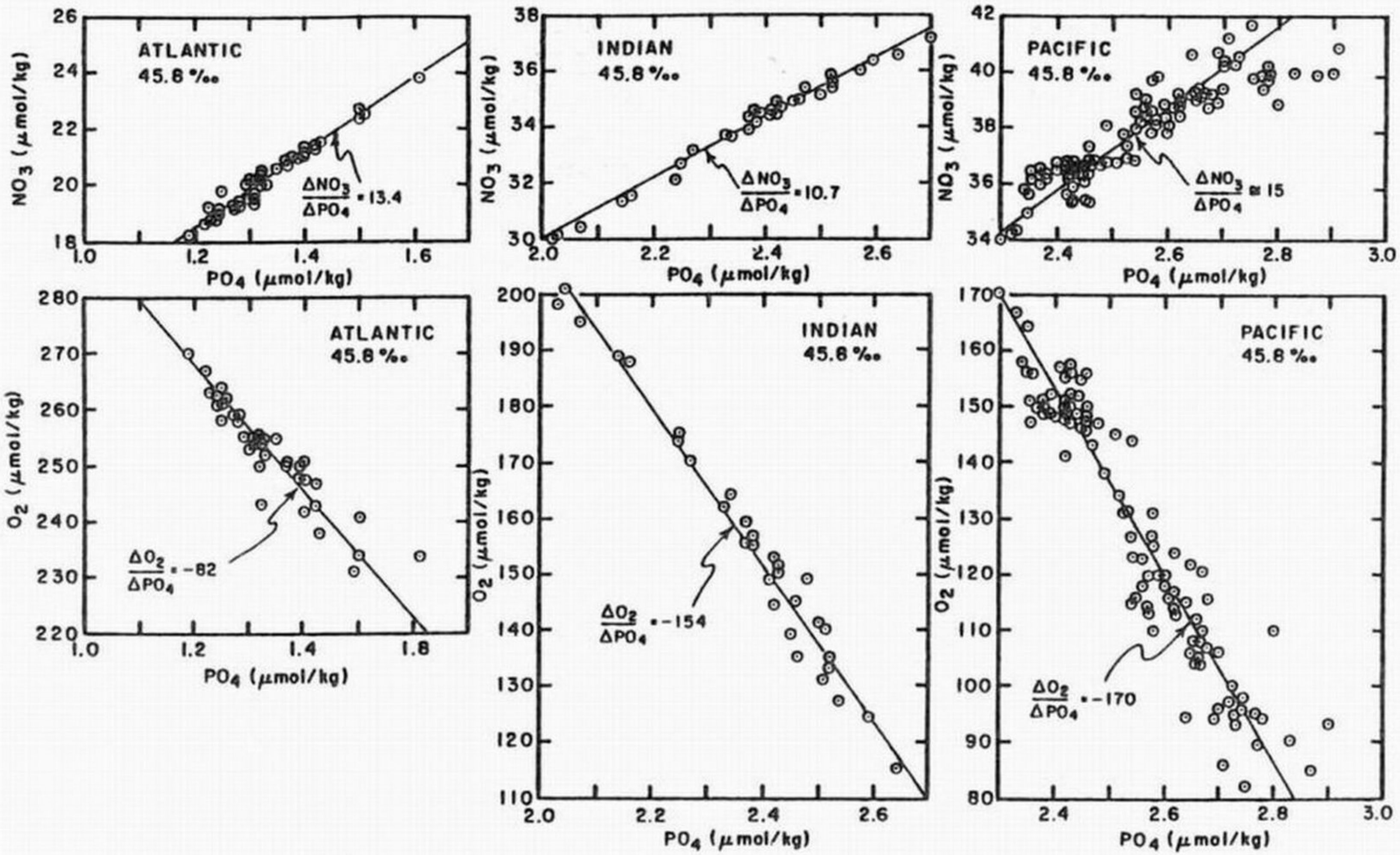
Total Carbon Dioxide [µmol/kg] WOCE Section P16



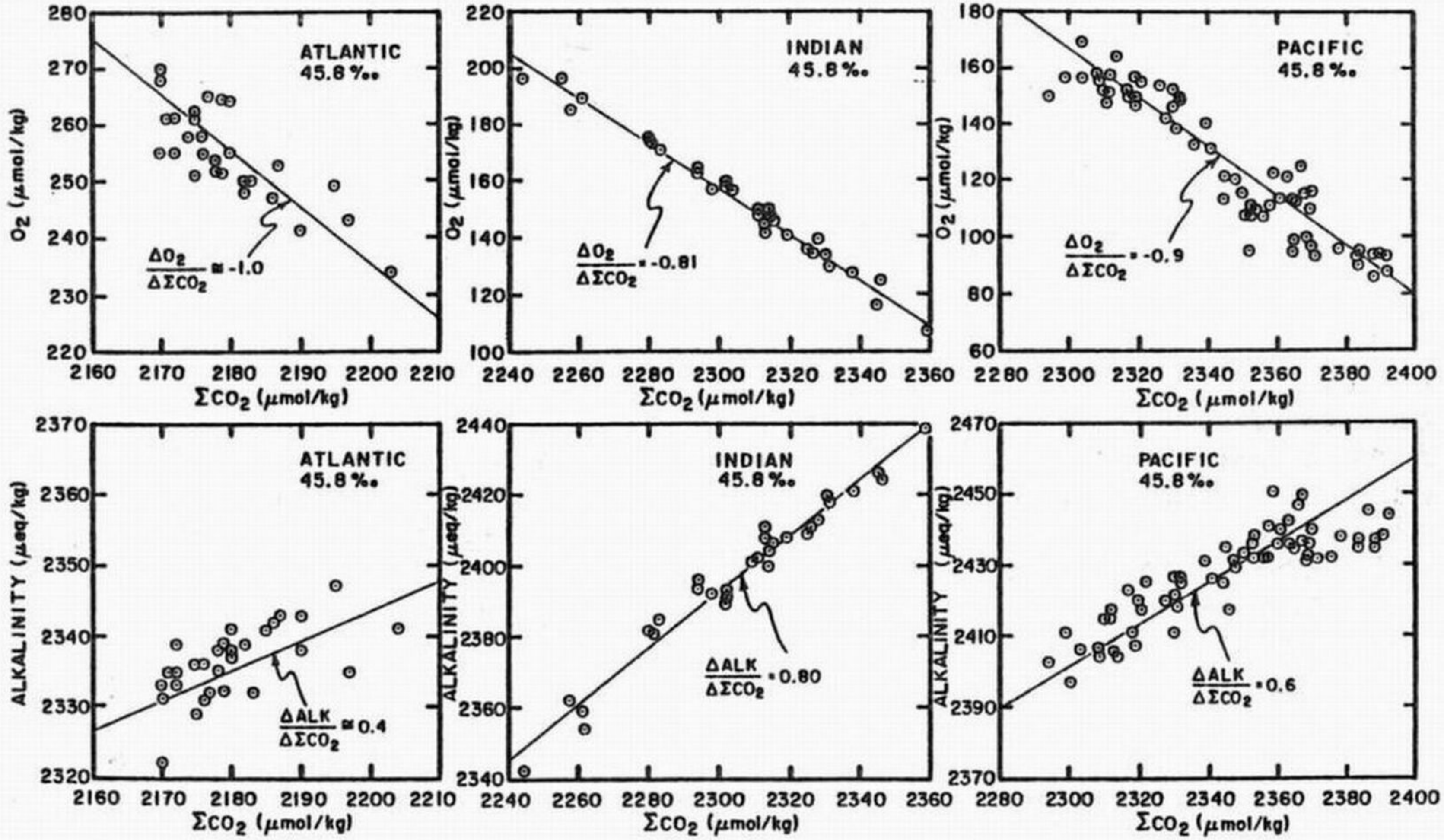

WOCE
Phosphate [µmol/kg]
0.1
3.1
P16
40°S
20°S
EQ
20°N
40°N
Ocean Data View
Salinity [pss-78]
60°S
Nitrate [µmol/kg]
Depth [m]
Phosphate [µmol/kg]
Tpot-0 [°C]
Salinity [pss-78]

Keeping Global Change honest

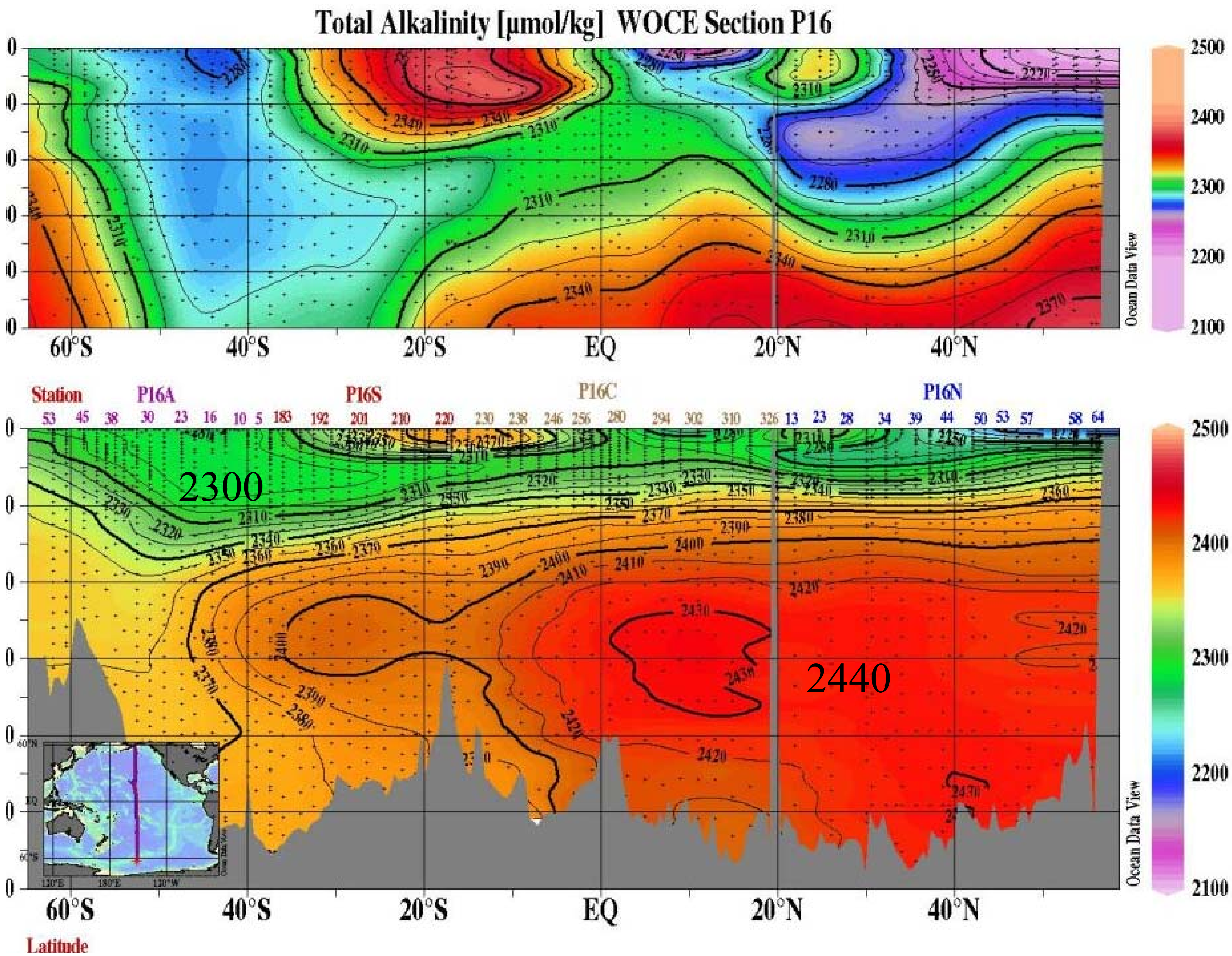
- ...one comes away with the feeling that somehow biology has a very important role to play for the uptake of anthropogenic CO_2. ...on any list of subjects requiring intense study with respect to atmospheric CO_2 I would place marine biological cycles near the bottom...I see these statements as part of a growing tendency for environmental programs to hitch their wagons to the greenhouse star.
- Wallace (Wally) Broecker GBC 1991



ATLANTIC
45.8 ‰
$\frac{\Delta NO_3}{\Delta PO_4} = 13.4$
NO_3 (μmol/kg)
PO_4 (μmol/kg)
INDIAN
45.8 ‰
$\frac{\Delta NO_3}{\Delta PO_4} = 10.7$
PACIFIC
45.8 ‰
$\frac{\Delta NO_3}{\Delta PO_4} \cong 15$
$\frac{\Delta O_2}{\Delta PO_4} = -82$
O_2 (μmol/kg)
$\frac{\Delta O_2}{\Delta PO_4} = -154$
$\frac{\Delta O_2}{\Delta PO_4} = -170$



ATLANTIC
45.8 ‰
$\frac{\Delta O_2}{\Delta \Sigma CO_2} \cong -1.0$
INDIAN
45.8 ‰
$\frac{\Delta O_2}{\Delta \Sigma CO_2} = -0.81$
PACIFIC
45.8 ‰
$\frac{\Delta O_2}{\Delta \Sigma CO_2} = -0.9$
O_2 (μmol/kg)
ΣCO_2 (μmol/kg)
ATLANTIC
45.8 ‰
$\frac{\Delta ALK}{\Delta \Sigma CO_2} \cong 0.4$
INDIAN
45.8 ‰
$\frac{\Delta ALK}{\Delta \Sigma CO_2} = 0.80$
PACIFIC
45.8 ‰
$\frac{\Delta ALK}{\Delta \Sigma CO_2} = 0.6$
ALKALINITY (μeq/kg)
ΣCO_2 (μmol/kg)


Total Alkalinity [µmol/kg] WOCE Section P16
60°S
40°S
20°S
EQ
20°N
40°N
Ocean Data View
2500
2400
2300
2200
2100
Station
P16A
P16S
P16C
P16N
2300
2440
Latitude

On remineralization profiles

- $(wP)_z = -rP$ → exponential profile
- Suess, Martin : $Fp \sim z^{-\alpha}$ $(0.8 < \alpha < 1)$
- $F_z = -(r/w)F$
- If somehow $(r/w) = a/z$, $F = F_0 z^{-a}$
- How to generate a/z?
- Temperature, particle aggregation

Some modeling principles

- Rigorous Redfield stoichiometry
- $P:N:C:O_2$ =1:16:106:-138 (classic plankton)
- Deep Sea : 1:16:122:-172 (Takahashi et al.,1995)
- Differential redissolution or
- Build plankton with deep sea ratio
- Global uniform parameters
- No regional tuning
- Physics is responsible for regional differences

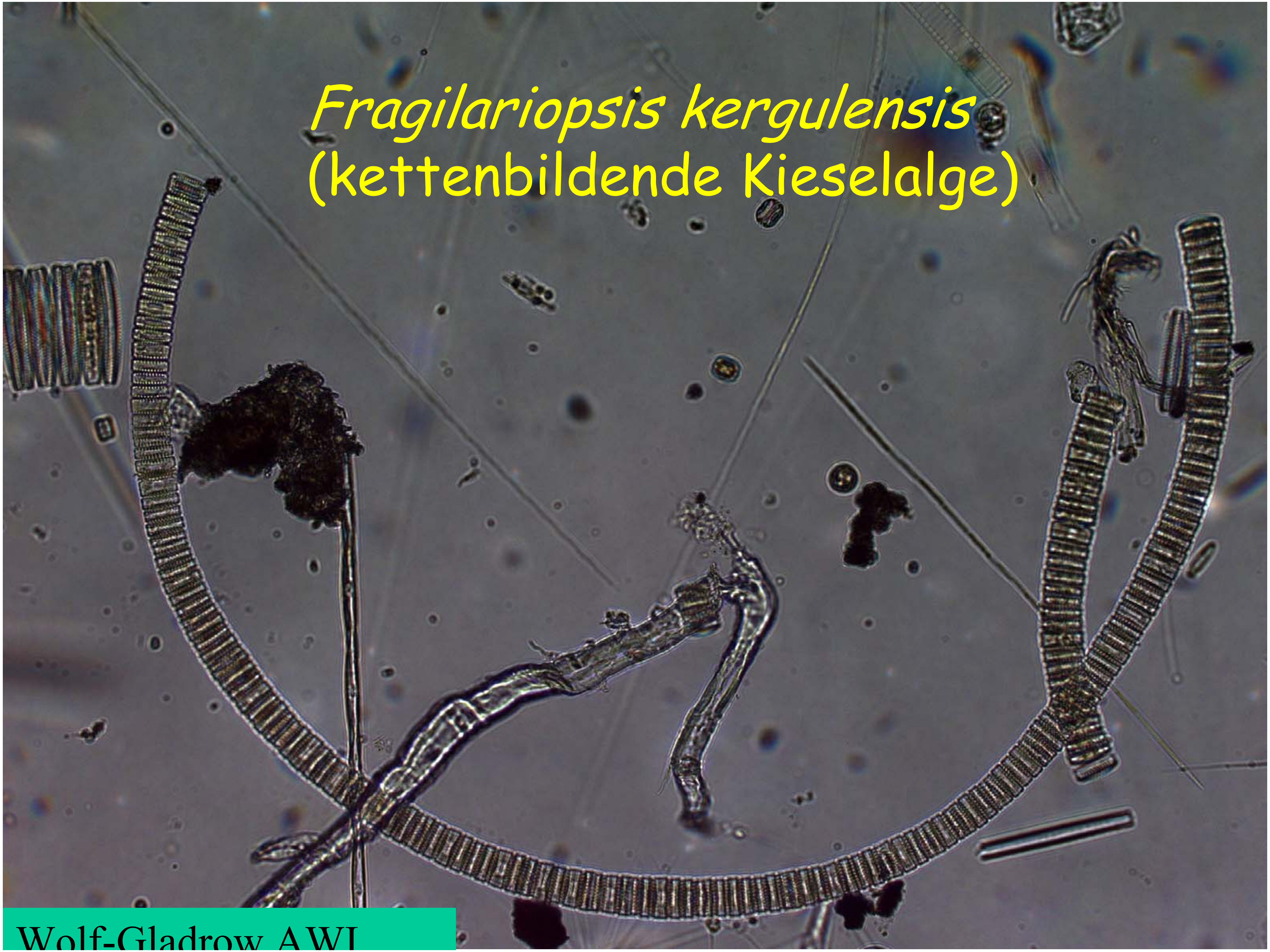
Biological processes

- Not measurable in open Sea
- Even in lab‘s no insight in inidividual cells
- Relative importance disputed
- The modeler has to look for majority consus
- But not invent processes biologists are not aware of

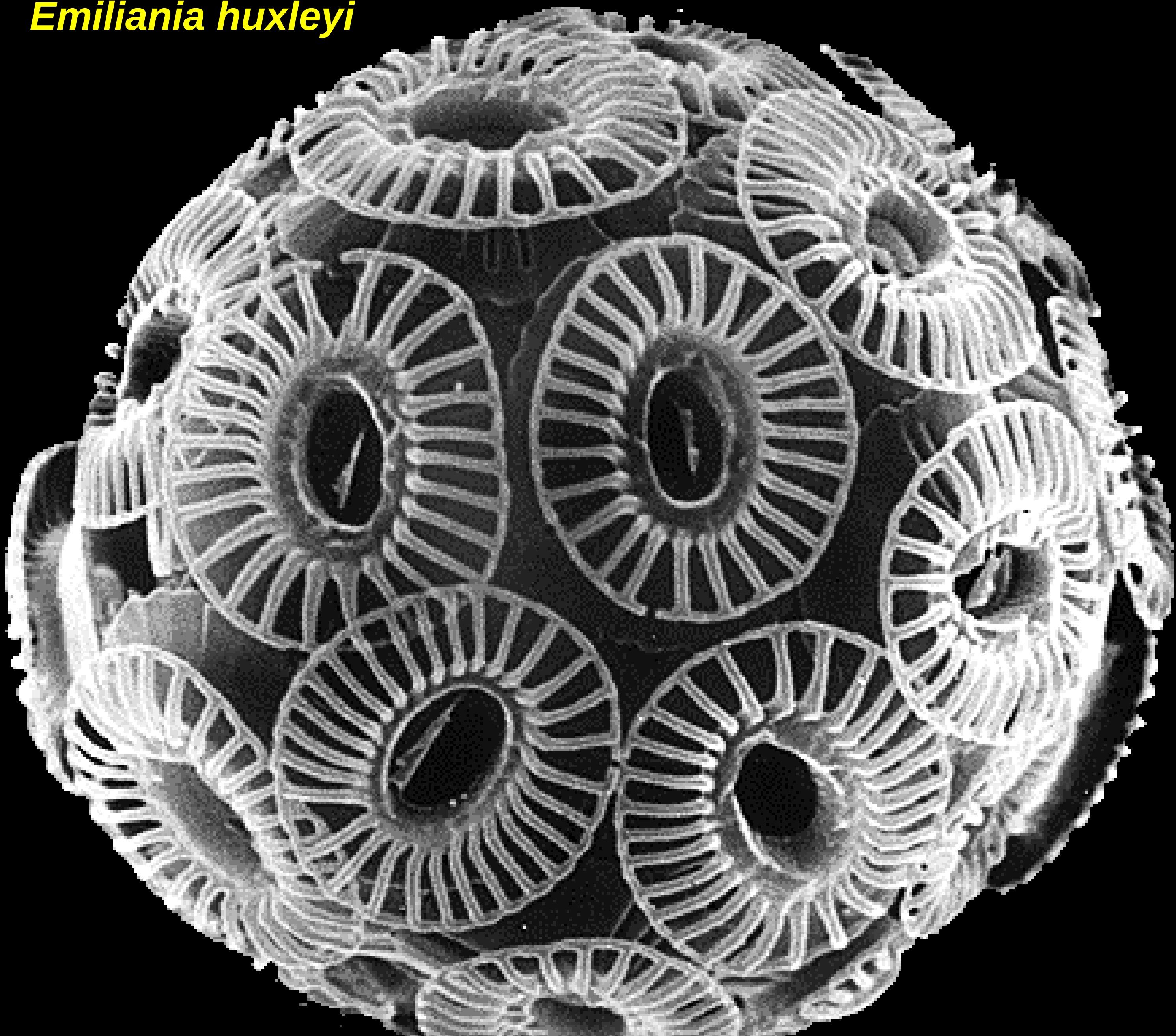
Photosynthesis of organic compounds

- $P + 16NO_3^- + 16H^+ \ 122CO_2 + 52H_2O \rightarrow PH_{68}N_{16}C_{122} + 172O_2$

  (+ ~ $122H_2O$ on both sides)
- Consumption of H^+ increases Alk
- Reverse in bacterial degradation
- All organic stuff is treated in ist P-content


Fragilariopsis kergulensis
(kettenbildende Kieselalge)
Wolf-Gladrow AWI

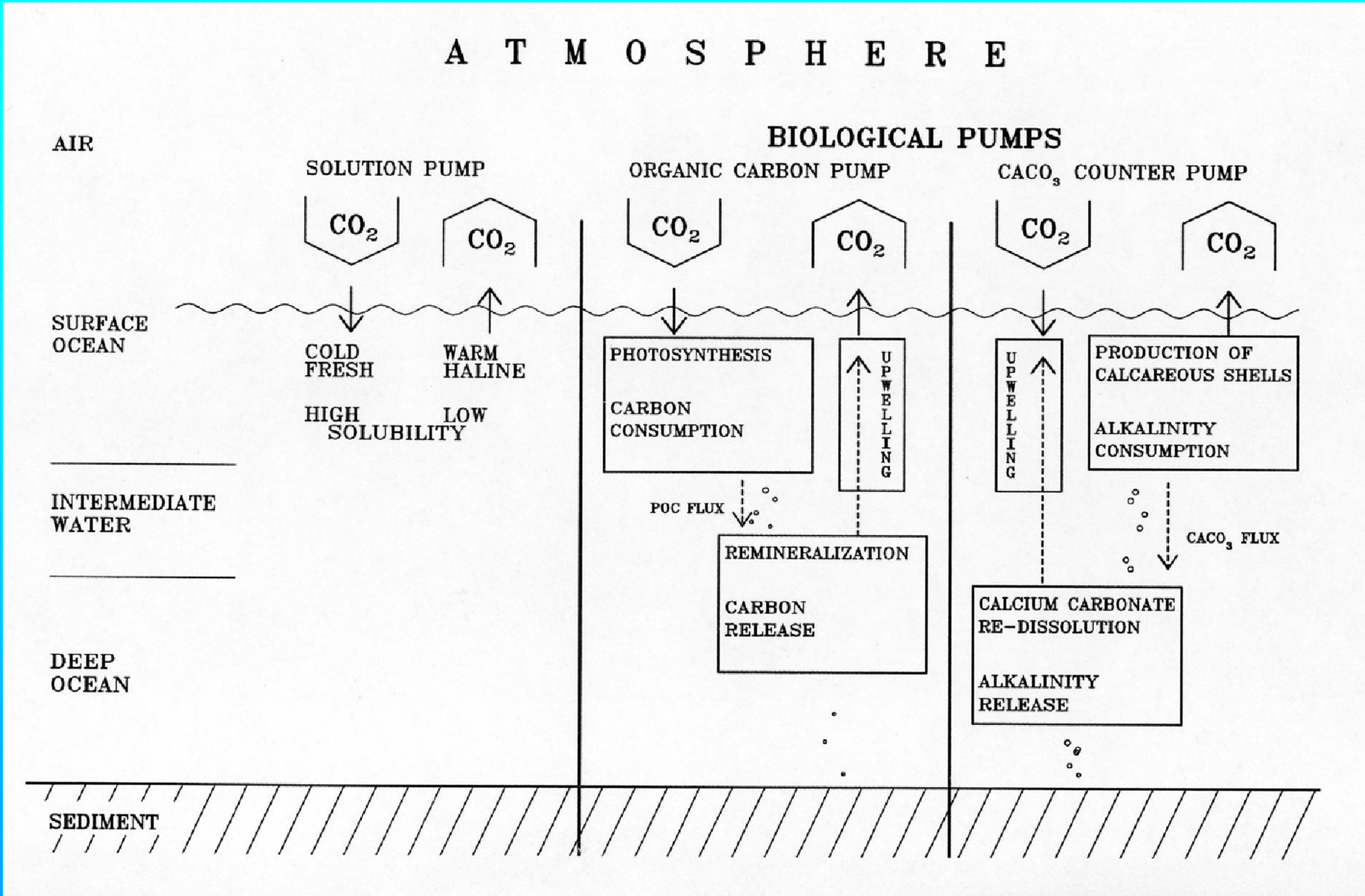
Emiliania huxleyi



Source untraceable, diameter 5µ

Formation of calcareous parts

- $Ca^{++} + CO_3^{--} \rightarrow CaCO_3 \downarrow$
- DIC drops by one unit
- Alkalinity drops by two units
- pCO_2 goes up



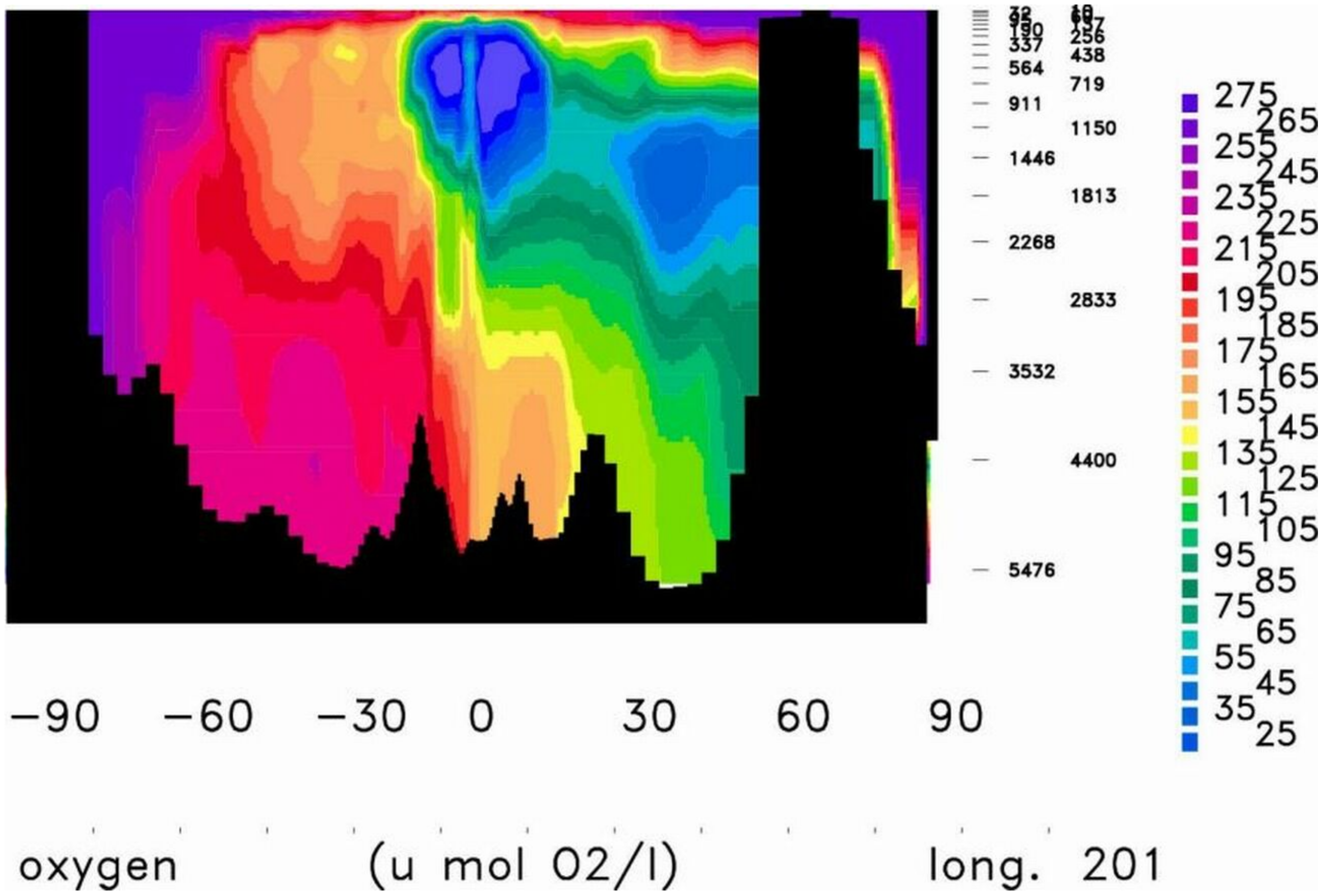
Heinze et al., 1991, *Paleoceanography*

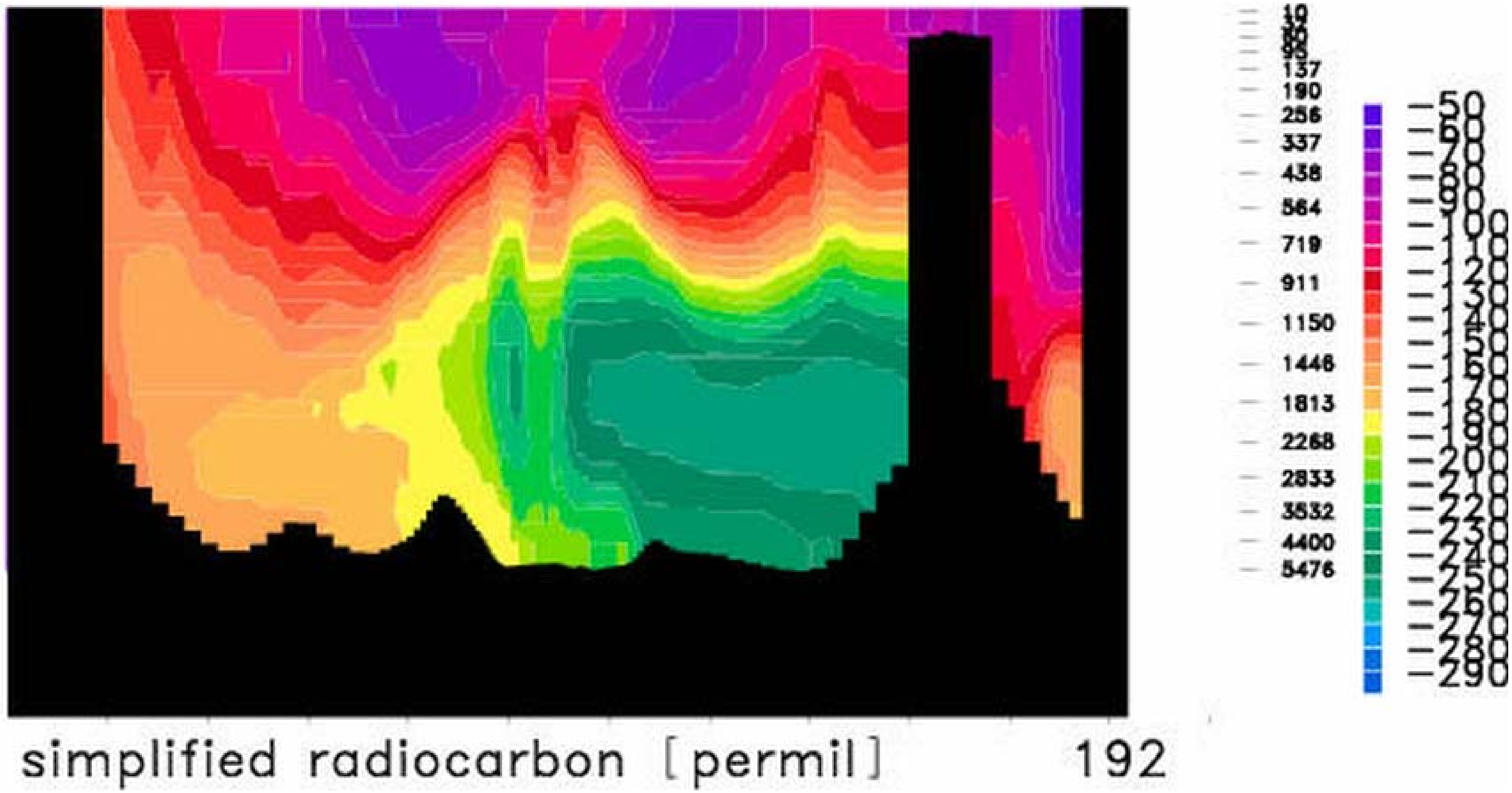
Is there an optimum degree of complexity?

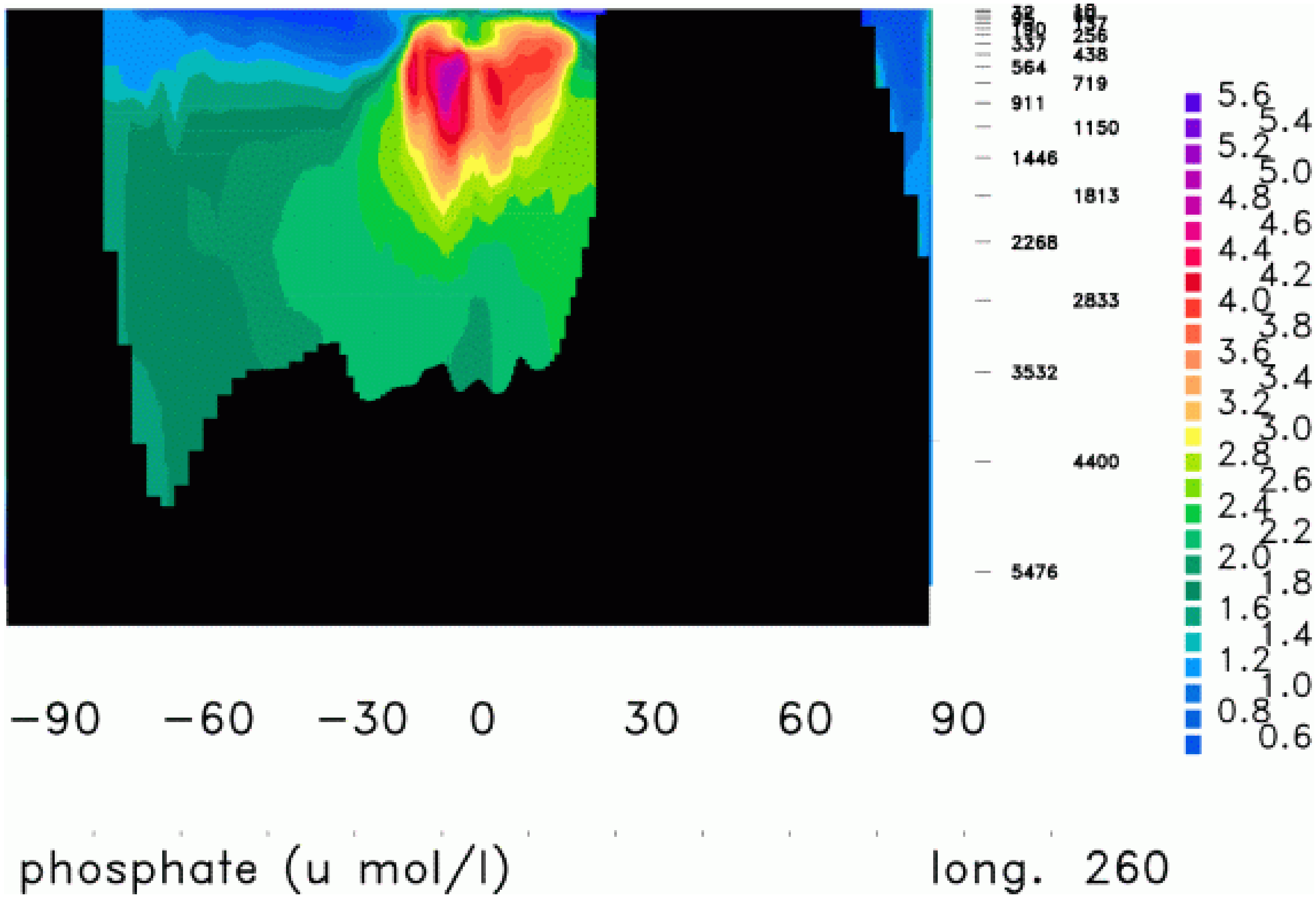
- Hundreds of diatom species
- All different names
- Mostly different habitats
- They all do the same (my prejudice?)
- ➔Reduction to species that really behave differently

Time discretization

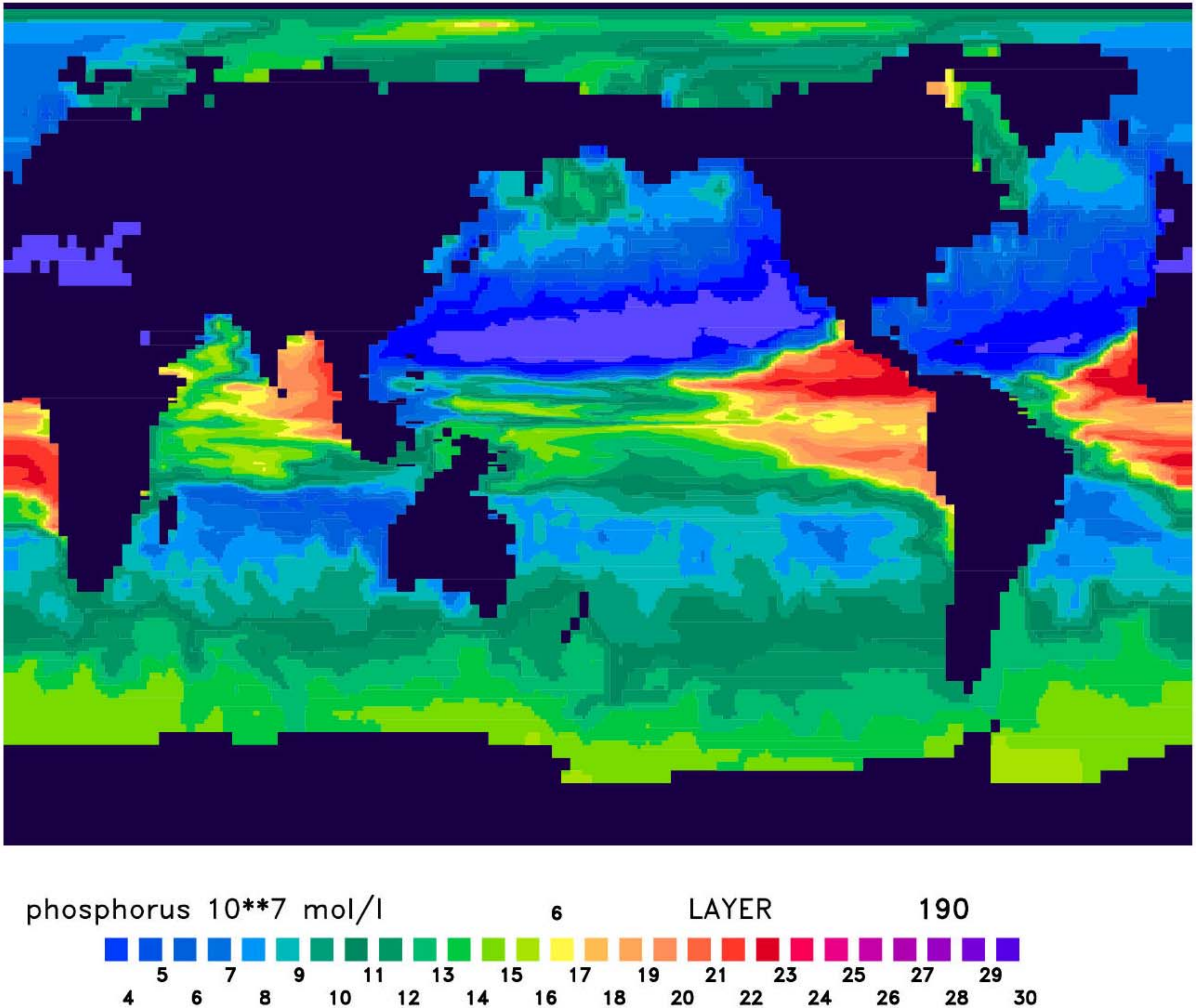
- Back to fox-rabbit system
- $R_t = aR – b_1RF$
- $F_t =-cF + b_2RF$
- Linear terms straightforward
- Nonlinear may be critical. Look at loosers
- $R^{new}=(R^{old} + \delta taR^{old})/(1+\delta tb_1F^{old})$
- Insert result for $F^{new}=F^{old}-(b_2/b_1)(R^{new}-R^{old})$


911
1150
1446
1813
2268
2833
3532
4400
5476
−90
−60
−30
0
30
60
90
275
265
255
245
235
225
215
205
195
185
175
165
155
145
135
125
115
105
95
85
75
65
55
45
35
25
oxygen
(u mol O2/l)
long. 201


137
190
256
337
438
564
719
911
1150
1446
1813
2268
2833
3532
4400
5476
-50
-290
simplified radiocarbon [permil]
192

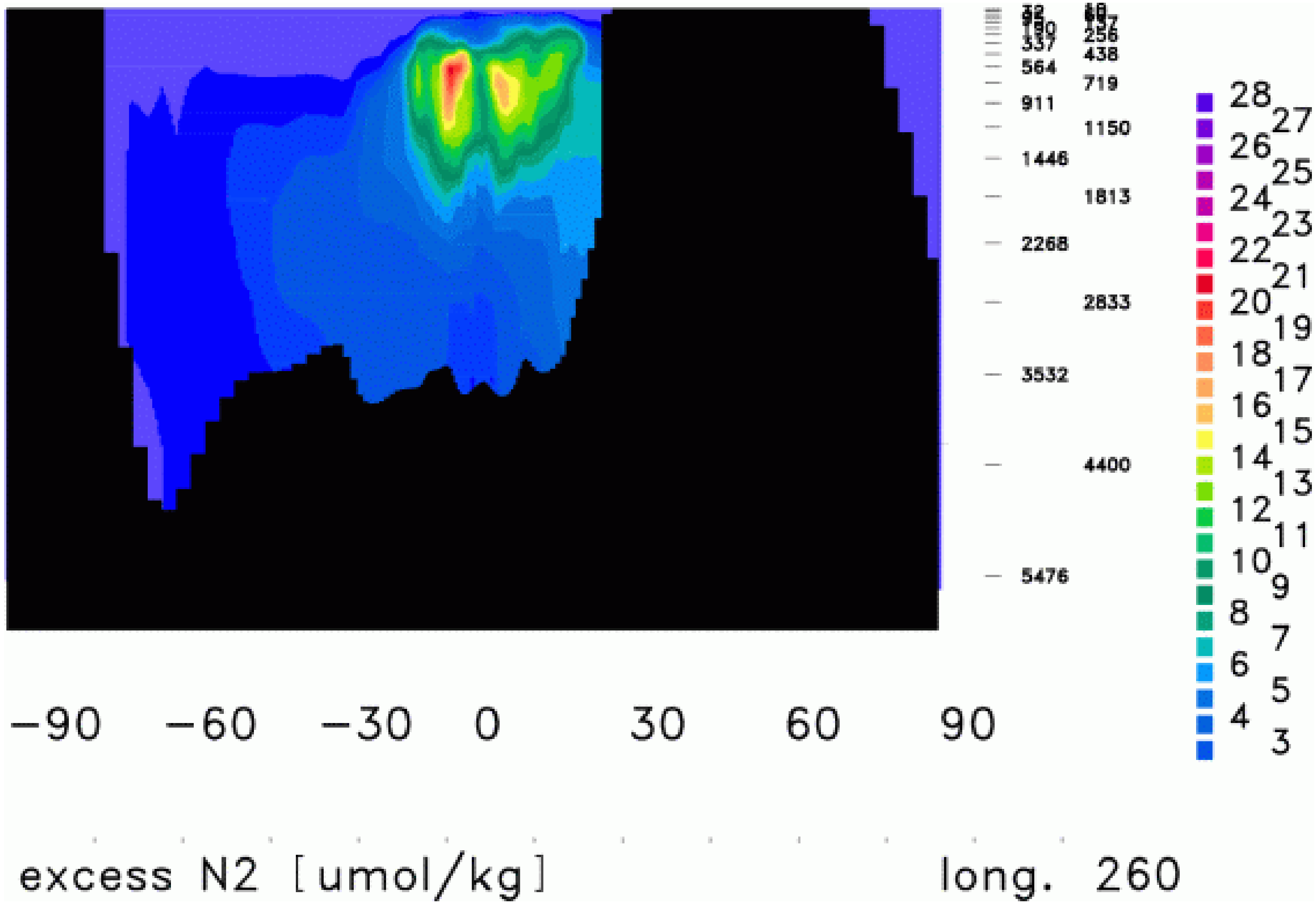


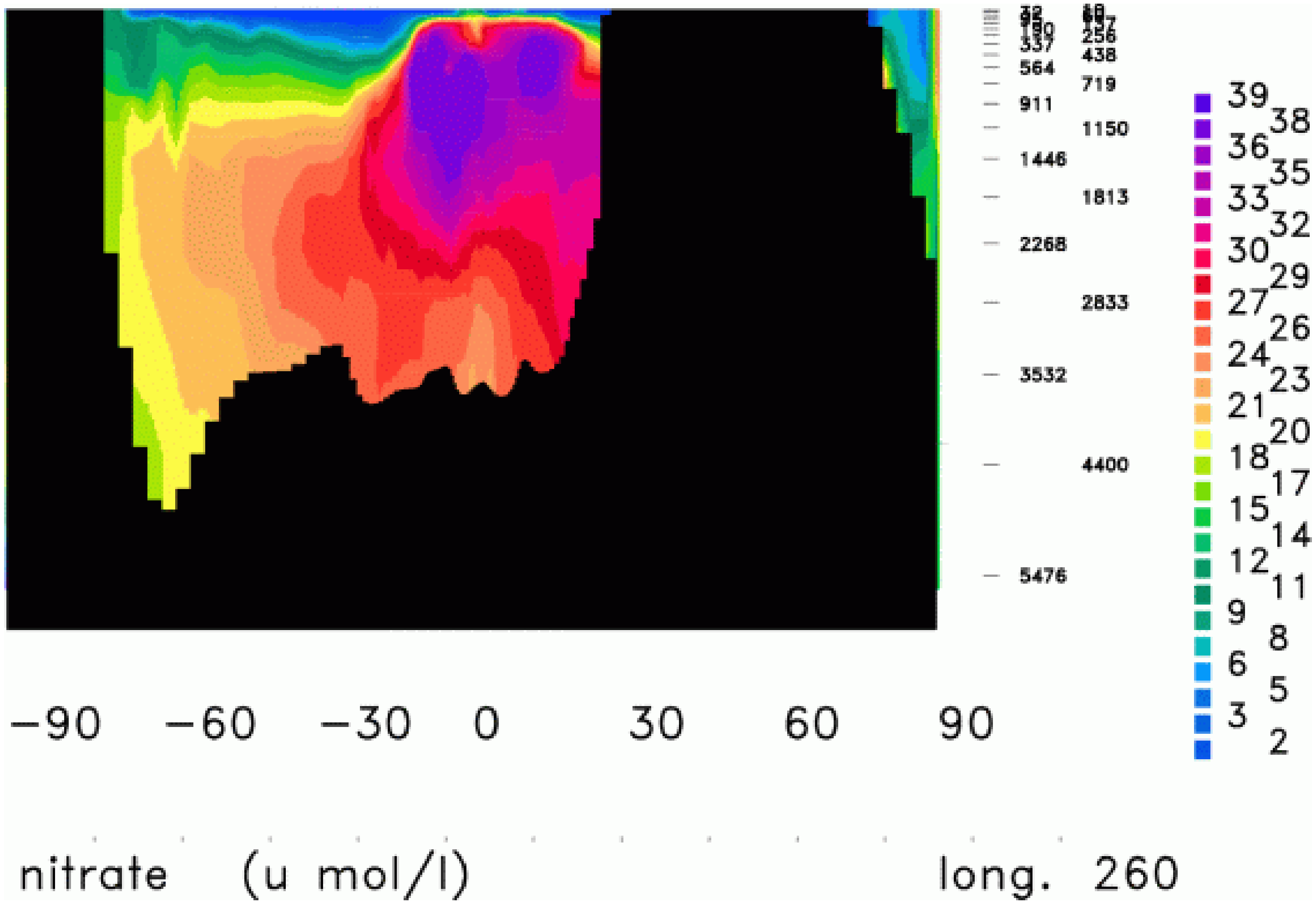
-90 -60 -30 0 30 60 90
564
719
911
1150
1446
1813
2268
2833
3532
4400
5476
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
phosphate (u mol/l)
long. 260


phosphorus 10**7 mol/l
6
LAYER
190
5 7 9 11 13 15 17 19 21 23 25 27 29
4 6 8 10 12 14 16 18 20 22 24 26 28 30

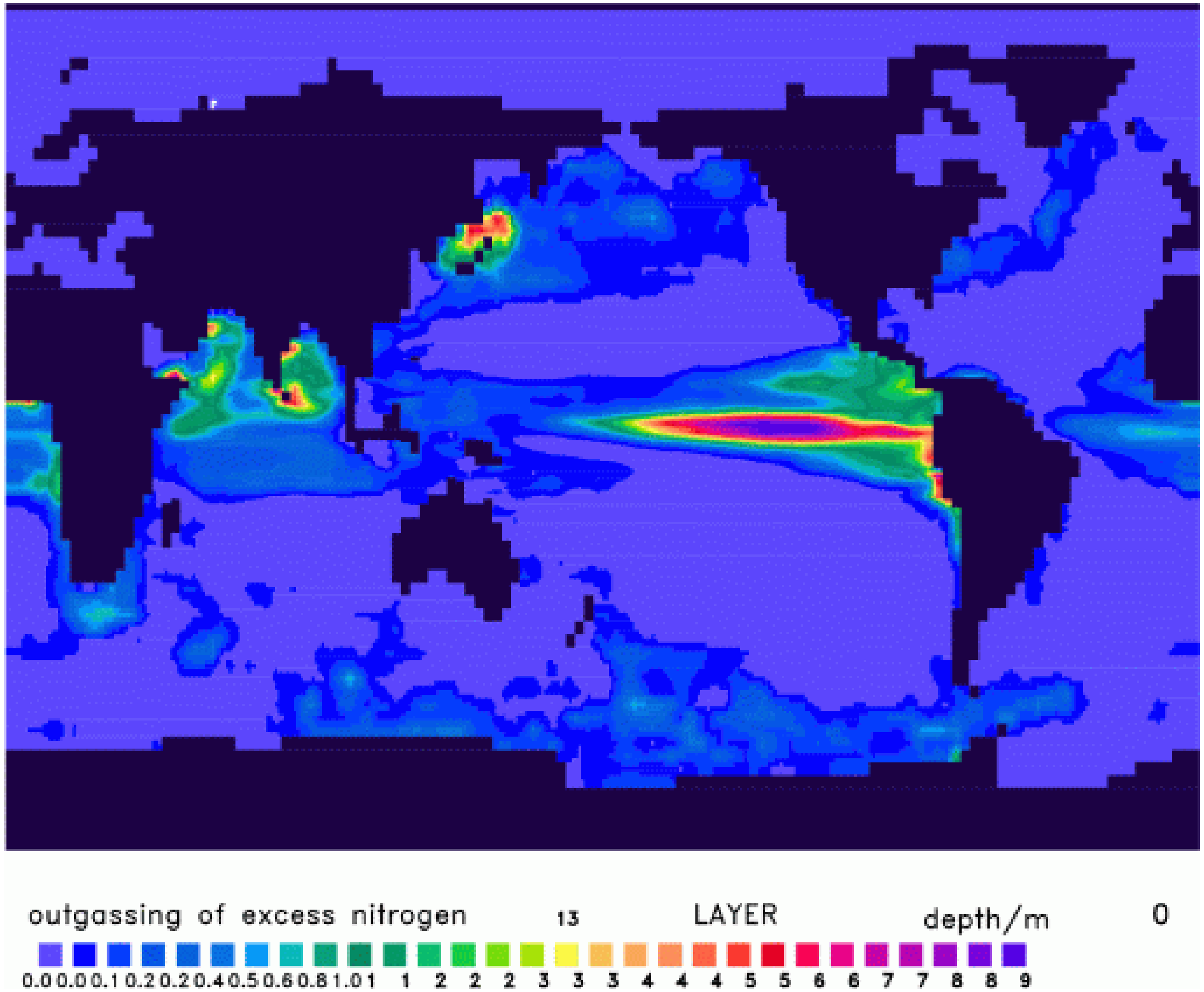
Denitrification and nitrogen fixation

- At present unclear which dominates
- Nitrate reduction in oligoxic water
- Nitrogen fixation from atmosphere
- Global balance inter/glacial cycles ~?
- For models balance is a must
- ?➔Methodological difference between global and regional models

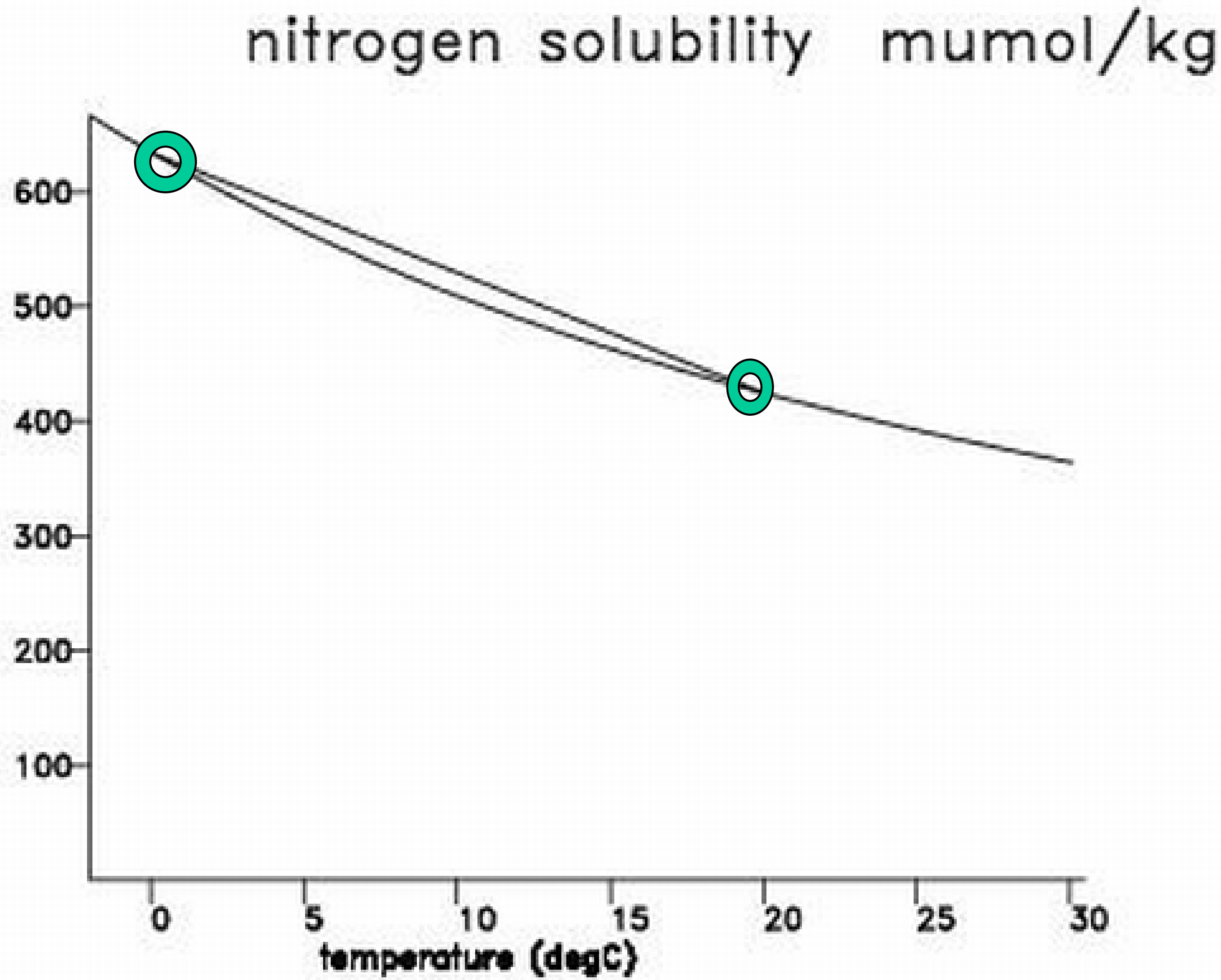

564
719
911
1150
1446
1813
2268
2833
3532
4400
5476
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
−90
−60
−30
0
30
60
90
excess N2 [umol/kg]
long. 260



337
256
564
438
719
911
1150
1446
1813
2268
2833
3532
4400
5476
39 38 36 35 33 32 30 29 27 26 24 23 21 20 18 17 15 14 12 11 9 8 6 5 3 2
−90 −60 −30 0 30 60 90
nitrate (u mol/l)
long. 260


outgassing of excess nitrogen
13
LAYER
depth/m
0
0.00 0.00 0.1 0.2 0.2 0.4 0.5 0.6 0.8 1.0 1 1 2 2 2 3 3 3 4 4 4 5 5 6 6 7 7 8 8 9

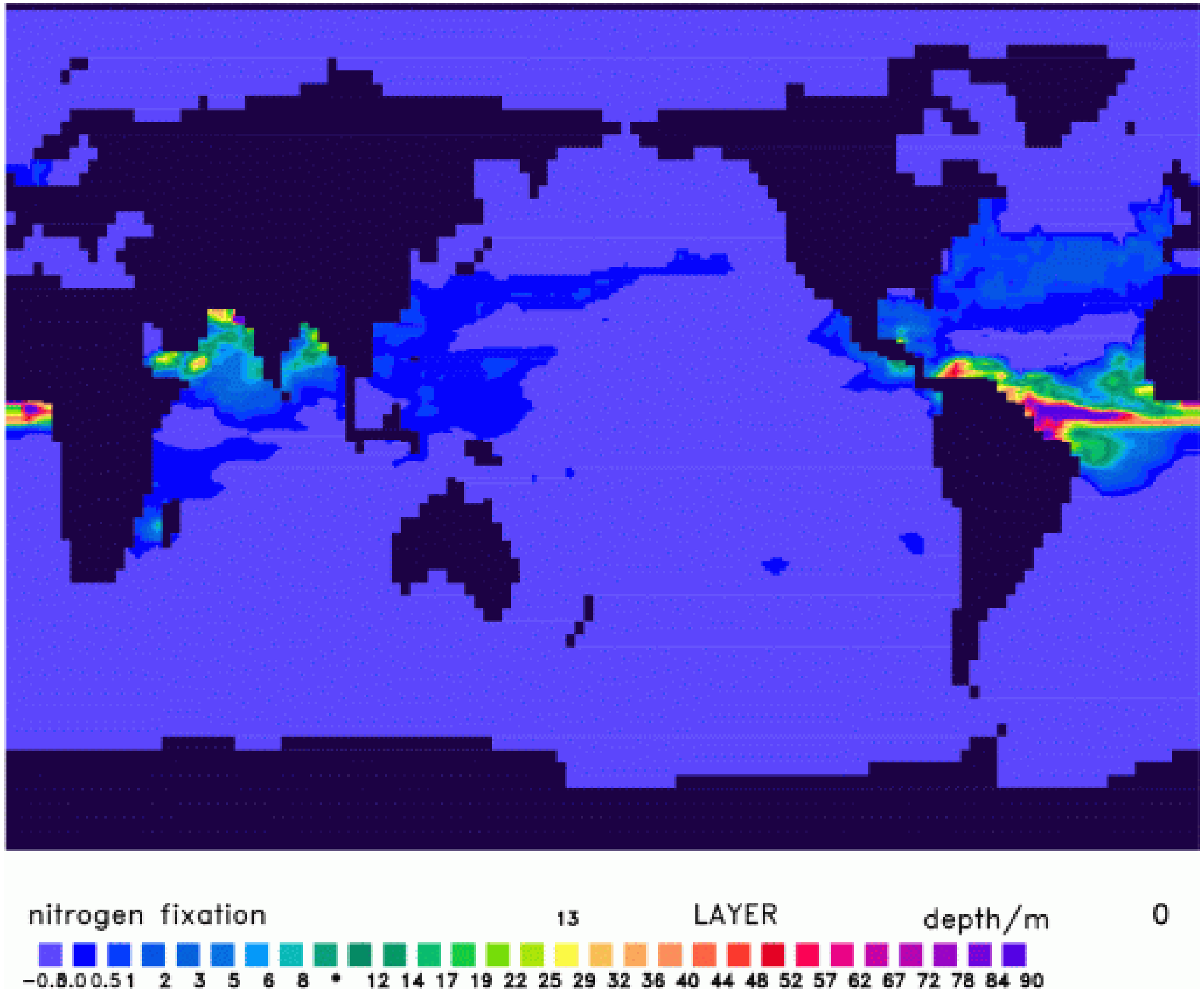
Moles/m^2/y ((?))



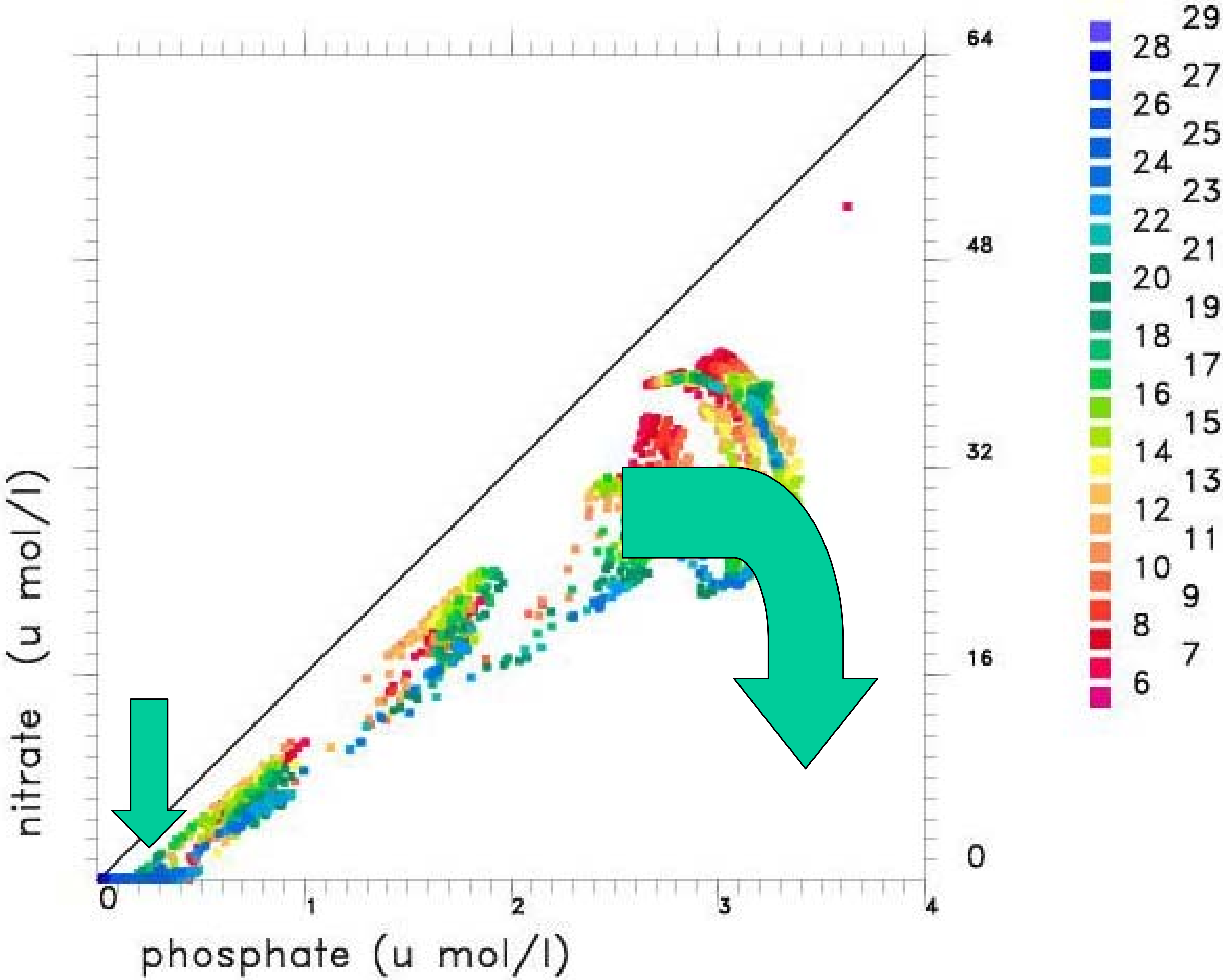
Excess nitrogen from mixing same size as from denitrification; relative contributions may be analyzed with Argon

Nitrogen fixation by cyanobacteria

- They like it hot
- But they are slow
- Little chance in competition to diatoms when nitrate available
- Can be modeled explicitly as plankton species
- Or mimicked by slow restoring in warm water of nitrate to N:P Redfield


nitrogen fixation
13
LAYER
depth/m
0
-0.8.00.51 2 3 5 6 8 * 12 14 17 19 22 25 29 32 36 40 44 48 52 57 62 67 72 78 84 90

Moles/m^2/y((?))



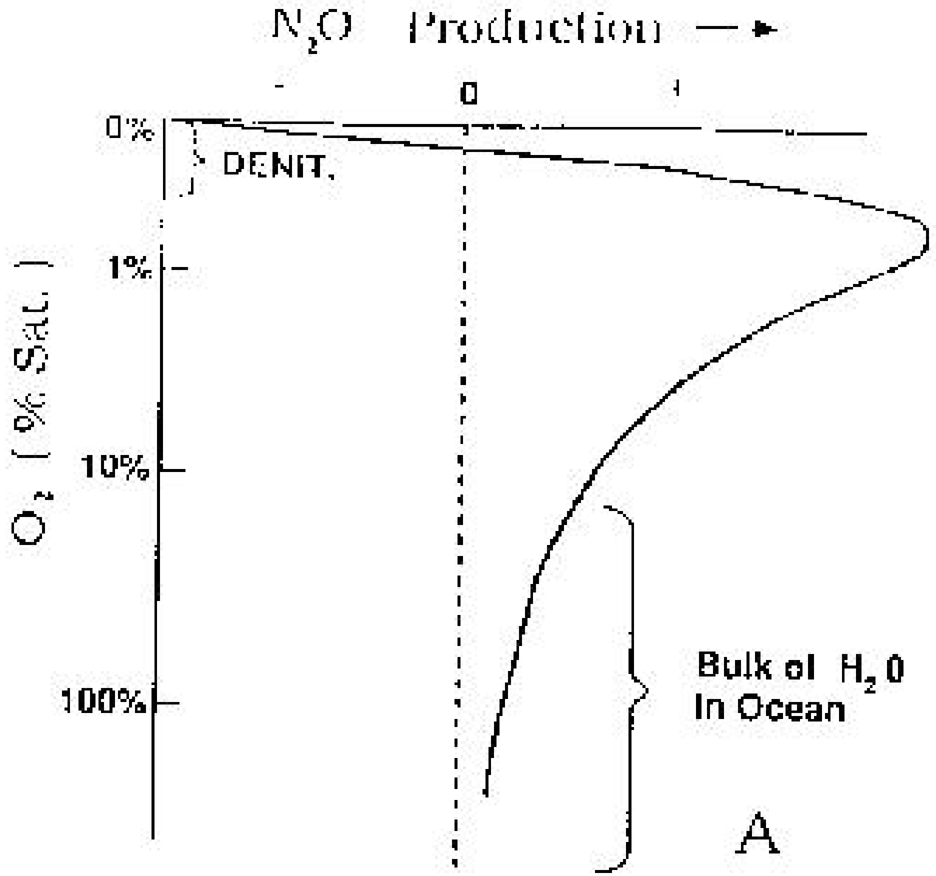
nitrate (u mol/l)
phosphate (u mol/l)
0
1
2
3
4
0
16
32
48
64
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6

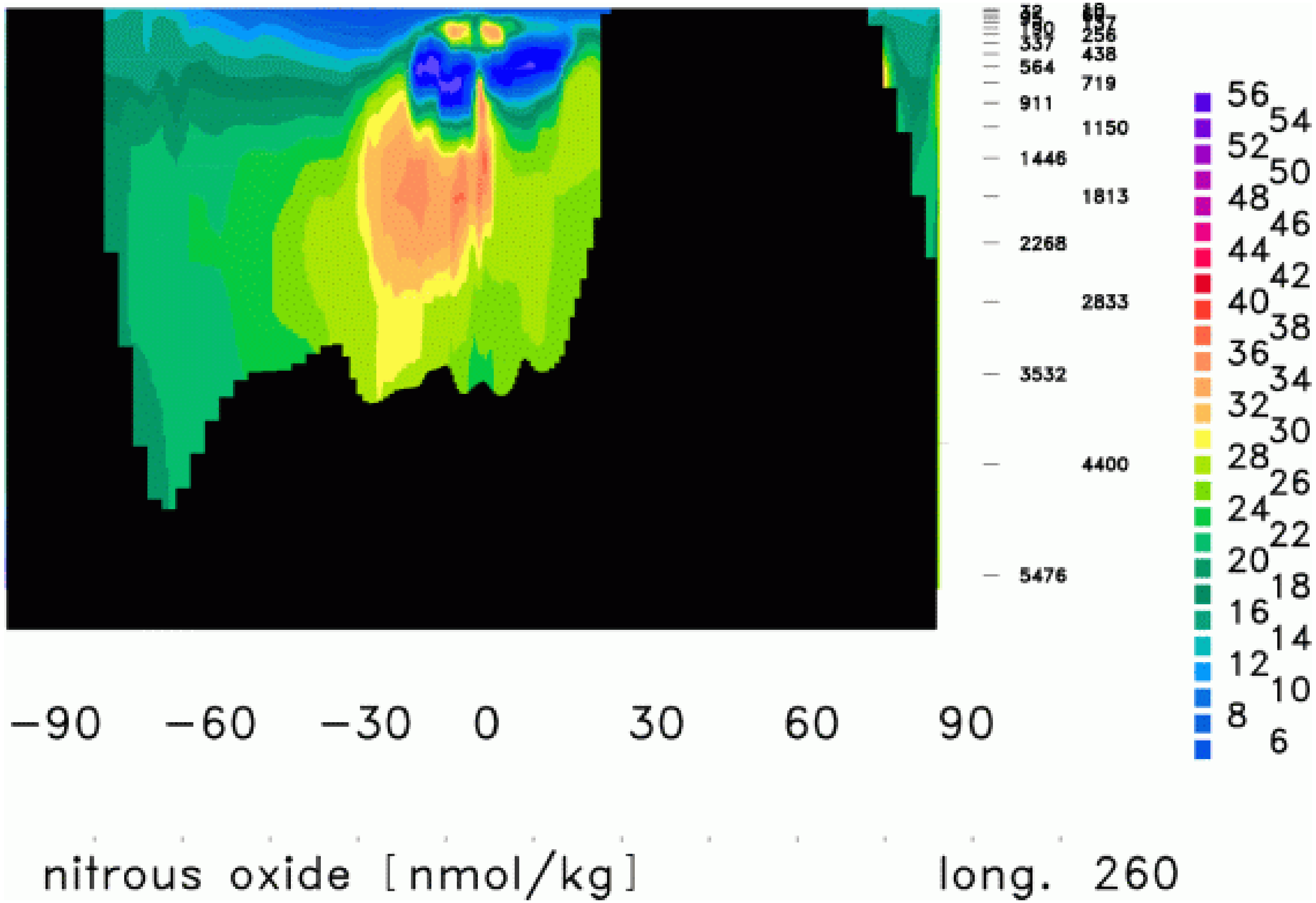
Nitrous oxide

- Major greenhouse gas
- Unusual production/consumption mechanisms (poorly known)
- ➔unusual profiles
- Model distribution highly sensitive

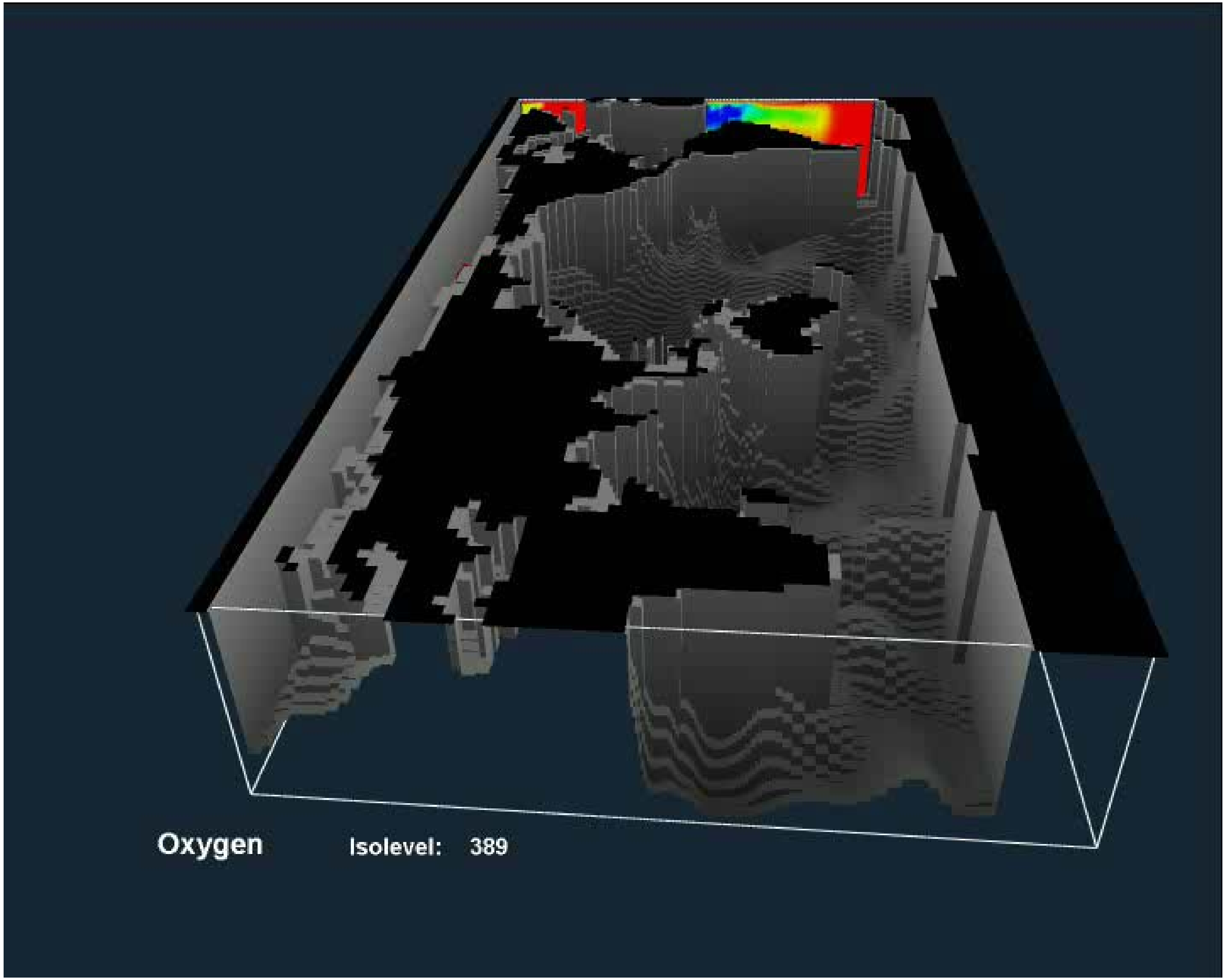
Cartoon of N_2O production and consumption as a function of dissolved O_2

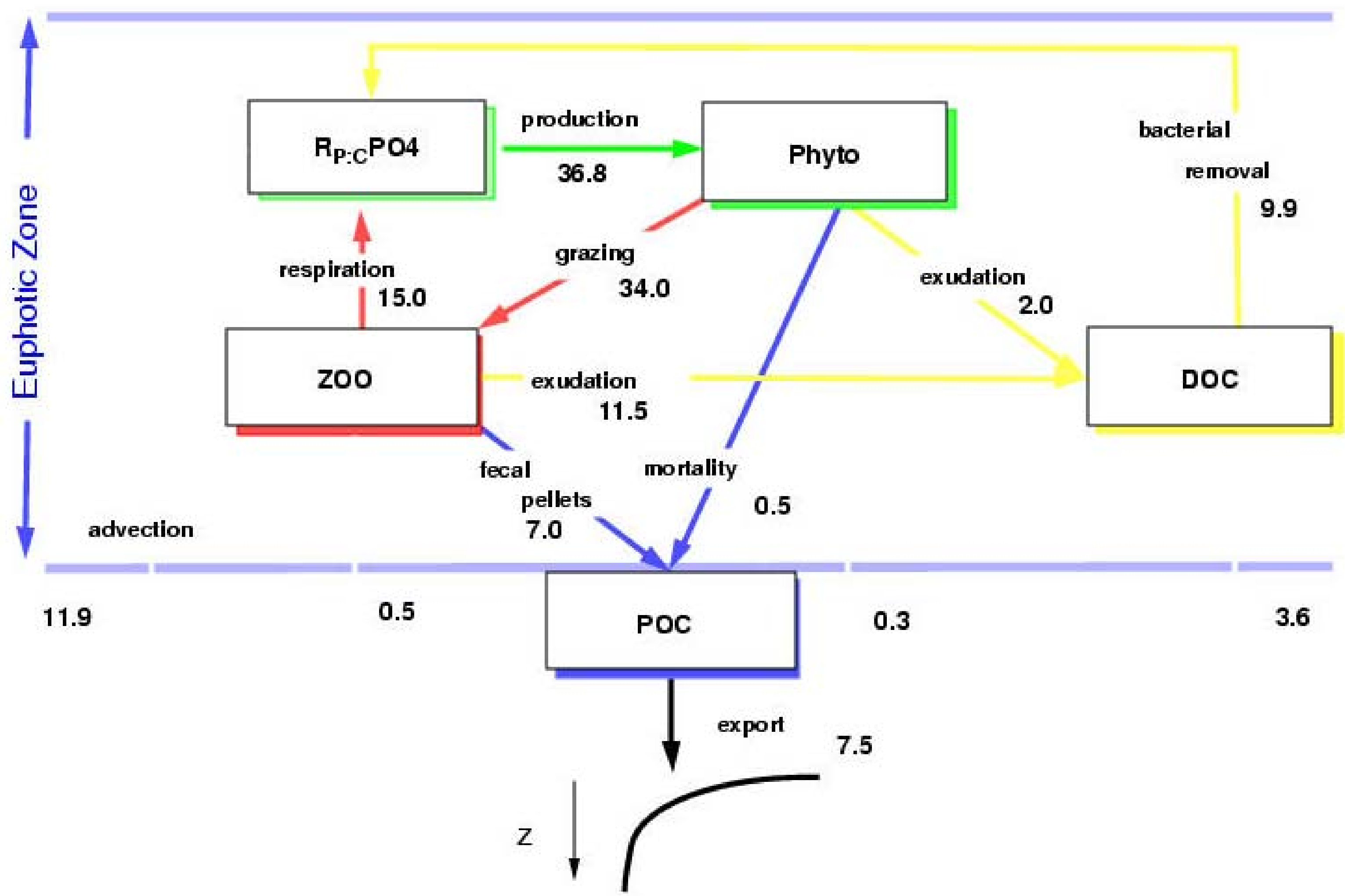
(Codispoti et al. [1992])



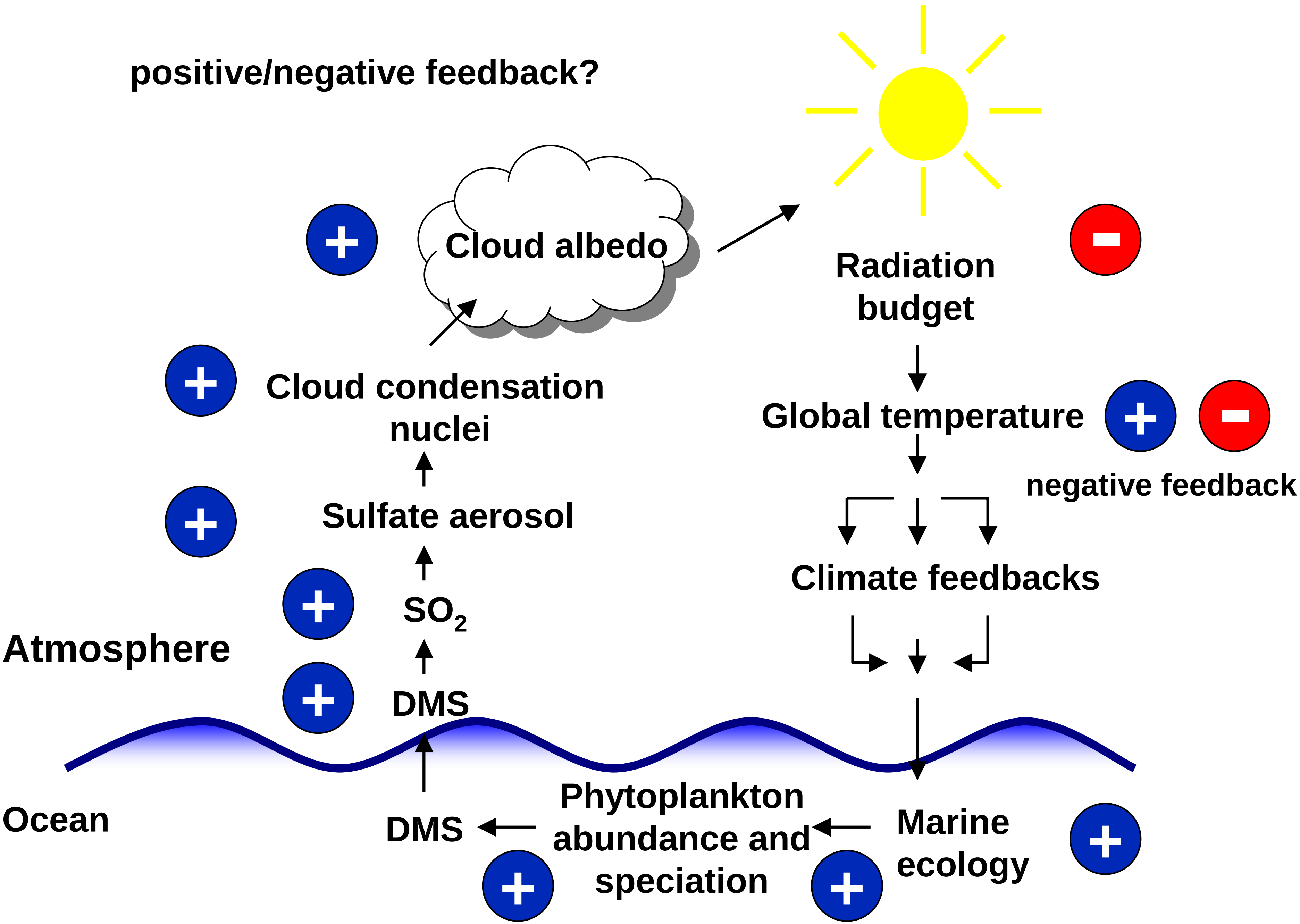


564
719
911
1150
1446
1813
2268
2833
3532
4400
5476
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
−90
−60
−30
0
30
60
90
nitrous oxide [nmol/kg]
long. 260


Oxygen
Isolevel: 389

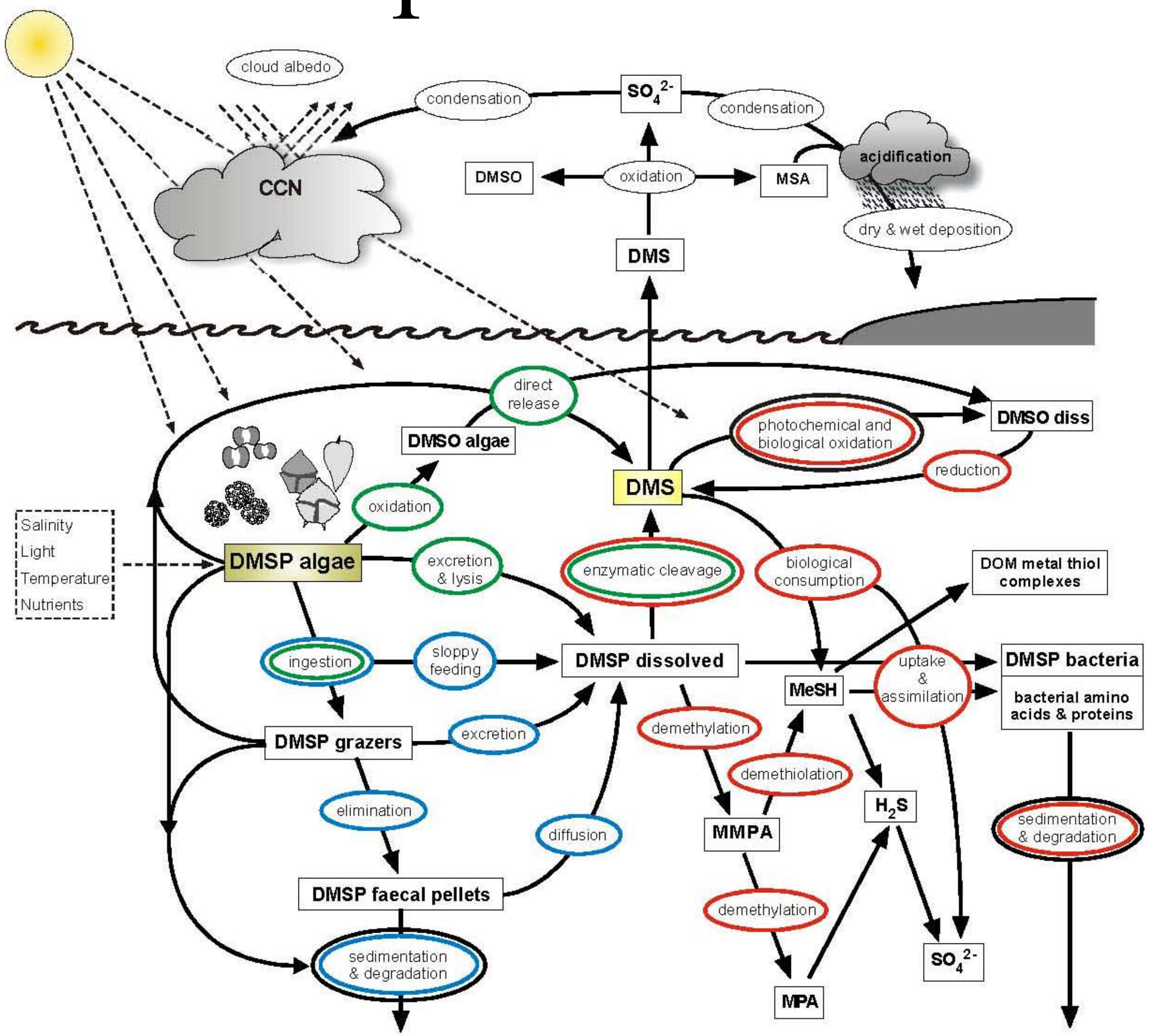

Euphotic Zone
R P:C PO4
production
36.8
Phyto
bacterial
removal
9.9
respiration
15.0
grazing
34.0
exudation
2.0
ZOO
exudation
11.5
DOC
fecal
pellets
7.0
mortality
0.5
advection
11.9
0.5
POC
0.3
3.6
export
7.5
Z

CLAW : Charlson, Lovelock, Andreae and Warren, 1987

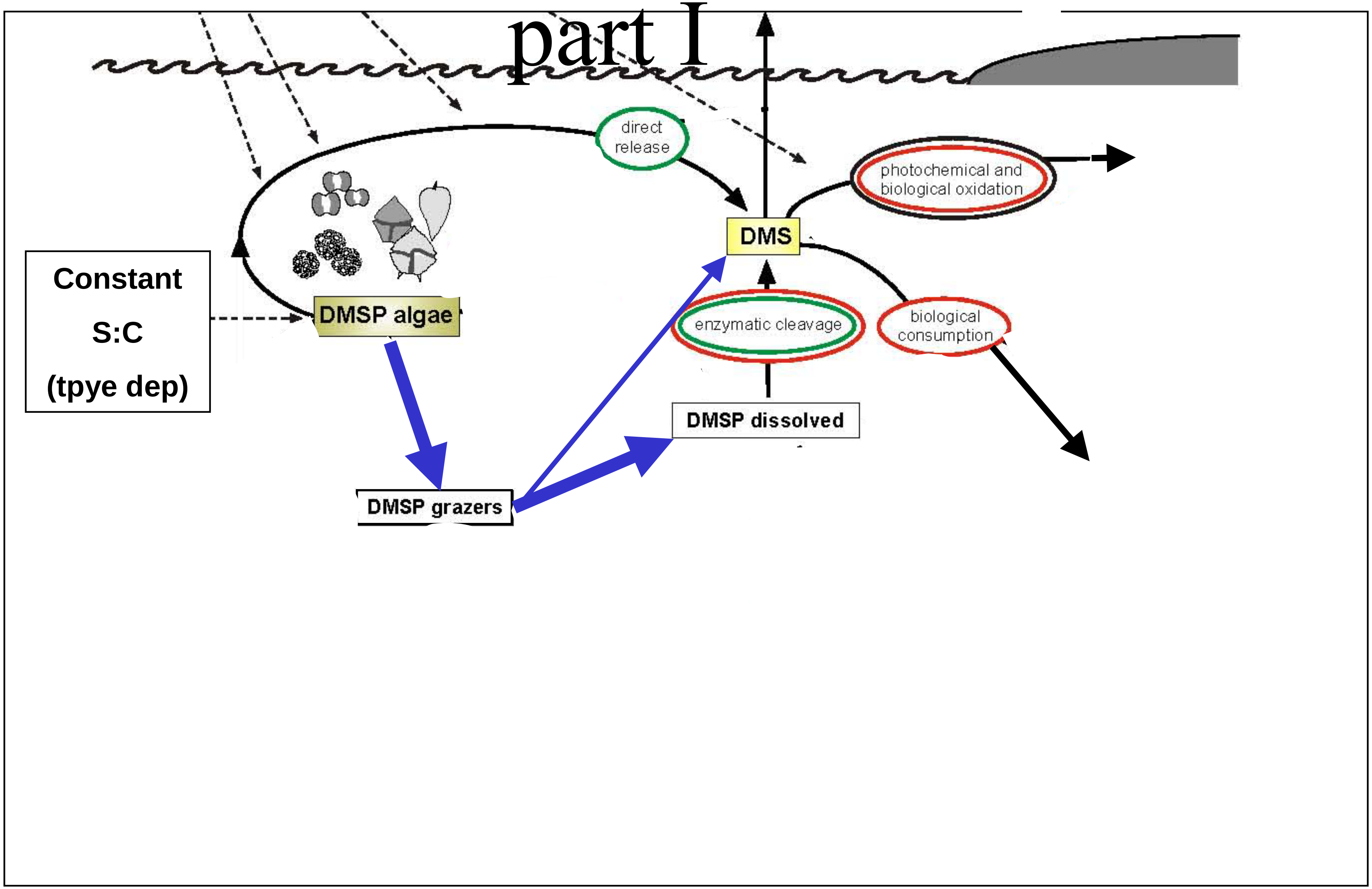


climate / part I

Stefels et al, Biogeochemistry, 2007 (in press)



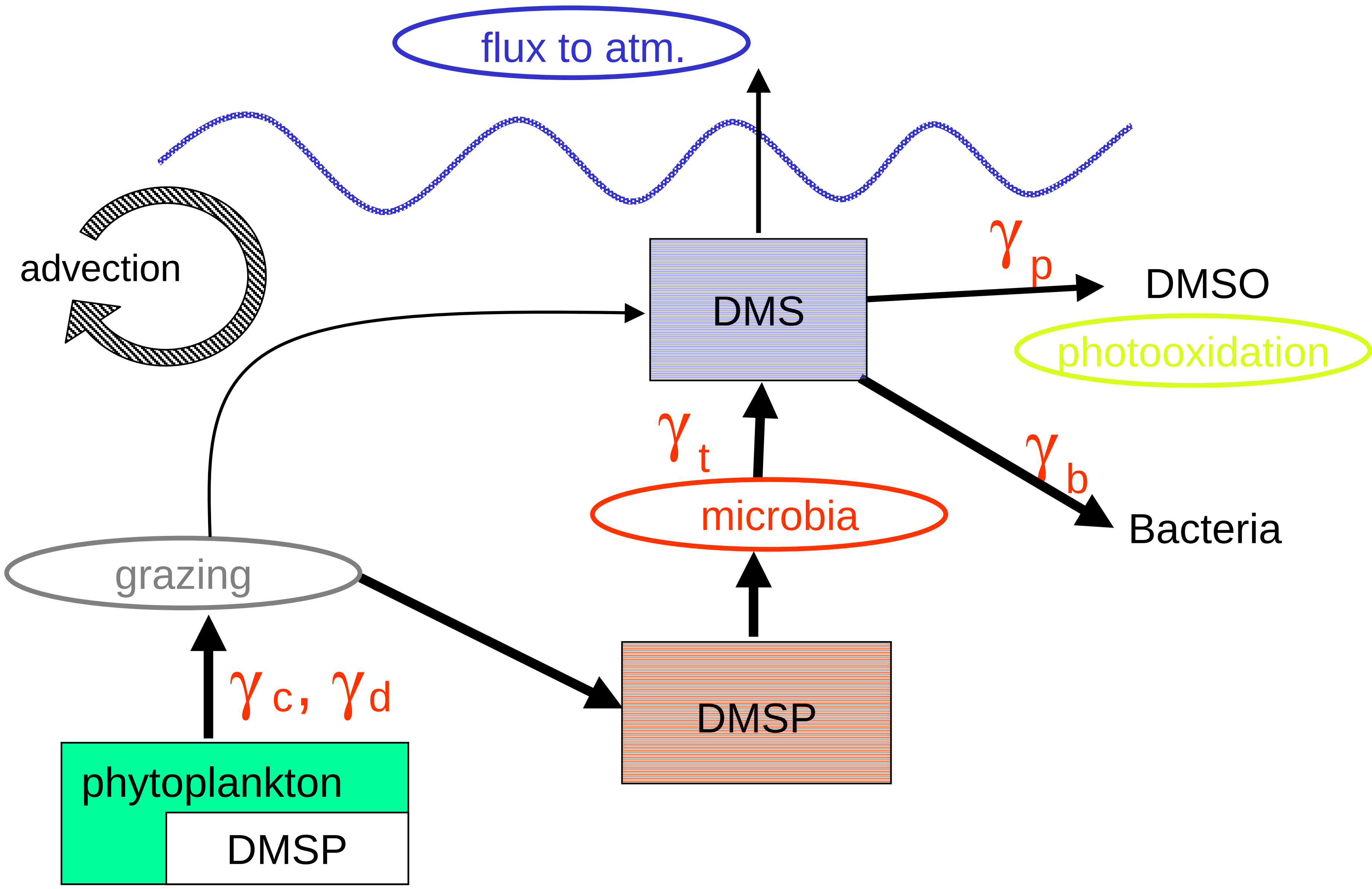
climate / part I



Motivation

- Climate relevance of DMS
  (CLAW-hypothesis)
- Increasing number of measurements
  (Kettle data, NOAA)
- More sophisticated biological ocean models

- semi-empirical approaches
  e.g. Kettle & Andreae (2000), SimÒ & Dachs (2002), Belviso et al. (2004), Eriksson et al.(1990)
- ecosystem modelling: 0 - 1 dimensional
  e.g Gabric et al. (1993), Watts & Bigg (2001) Lefevre et al. (2002)
- global modelling
  e.g Aumont et al. (2002)


flux to atm.
advection
DMS
γ_p
DMSO
photooxidation
γ_t
microbia
γ_b
Bacteria
grazing
γ_c, γ_d
DMSP
phytoplankton
DMSP

The sediment module

- Irrelevant for the next century
- Not in equilibrium in actual restart files
- 4 processes to be considered
- Opal vs undersaturation porewater silicate
- Calcite vs undersaturation in porewater
- Organic matter vs porewater oxygen
- Organic matter vs porewater nitrate

Common structure

- S=solid part, A=aquous prt
- $S_t = - rSA/V_s$
- $A_t = - rSA/V_a + D\Delta A$
- $S^* = S^o/(1+r\delta t A^o/V_s)$
- $A^n+r\delta t S^* A^n - D\delta t \Delta A^n = A^o$
- Correct S^* to S^n for mass conservation

Summary

- HAMOCC treats first order processes of marine biogeochemistry
- Purposeful restriction on essentials
- Complexification would not necessarily be amelioration

Thanks