Marine Biogeochemistry

The Ocean Carbon Cycle

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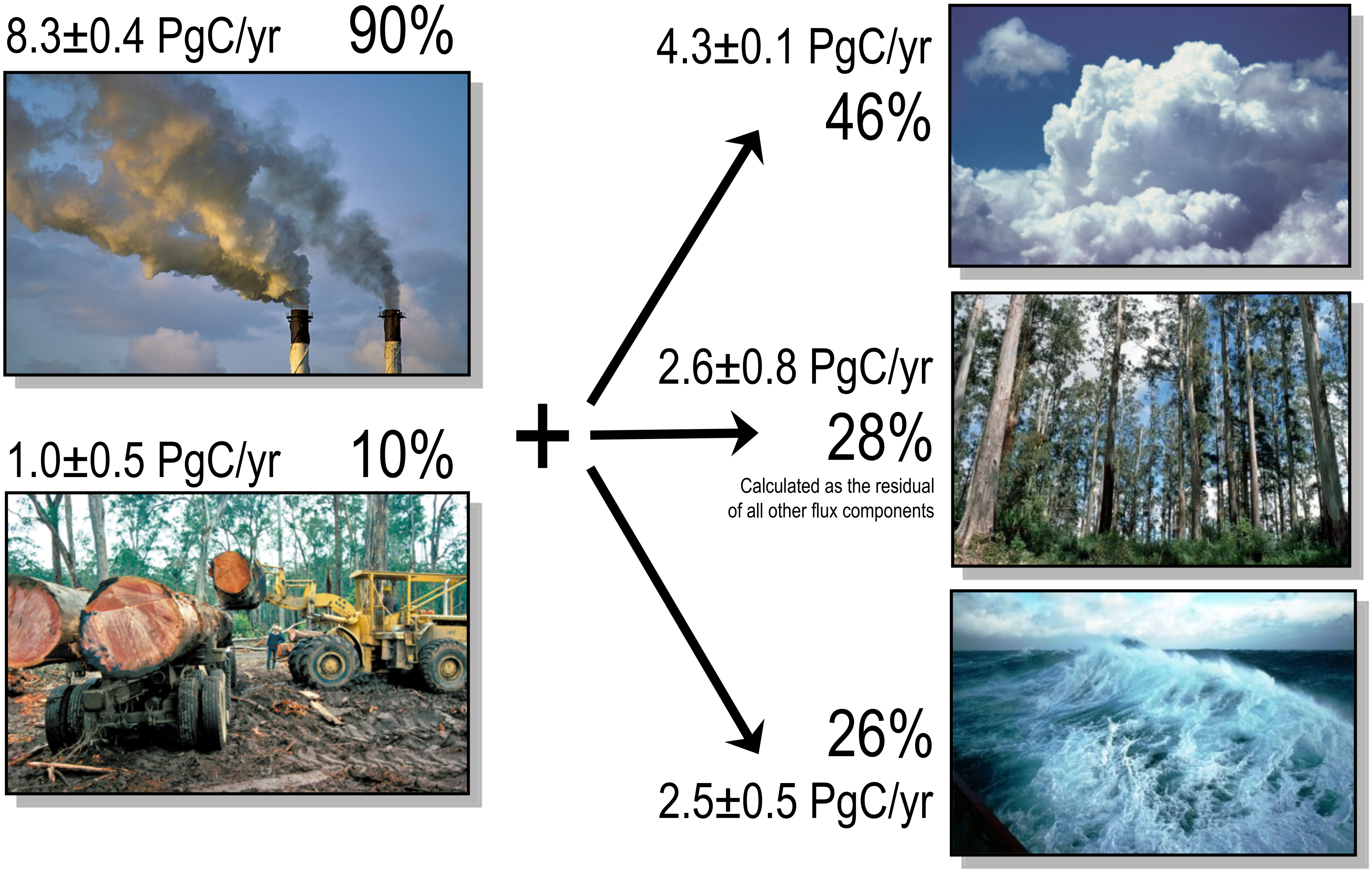
The Ocean Carbon Cycle

1. Introduction: The role of the ocean in the global carbon budget
2. The Natural carbon cycle in the ocean
3. Anthropogenic perturbation
4. Ocean acidification and its consequences

Fate of Anthropogenic CO_2 Emissions (2002-2011 average)



8.3±0.4 PgC/yr 90%

1.0±0.5 PgC/yr 10%

+

4.3±0.1 PgC/yr 46%

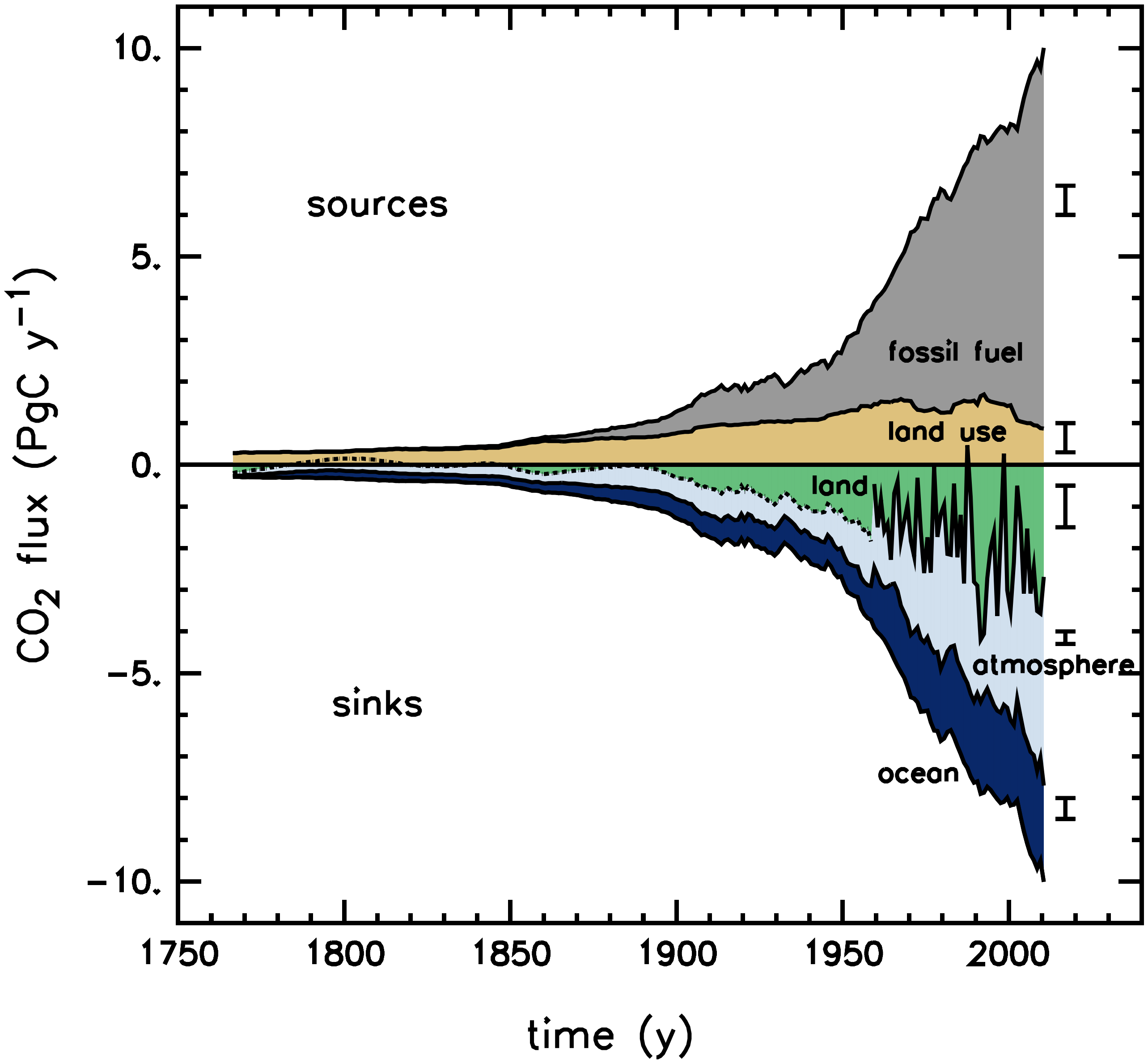
2.6±0.8 PgC/yr 28%

Calculated as the residual
of all other flux components

26%
2.5±0.5 PgC/yr

Source: Le Quéré et al. 2012; Global Carbon Project 2012

Human Perturbation of the Global Carbon Budget



2000-2010

(PgC y^{-1})

7.9±0.5

1.0±0.7

2.5±1.0

(Residual)

4.1±0.2

2.3±0.5

(5 models)

Global Carbon Project 2011; Updated from Le Quéré et al. 2009, Nature G; Canadell et al. 2007, PNAS

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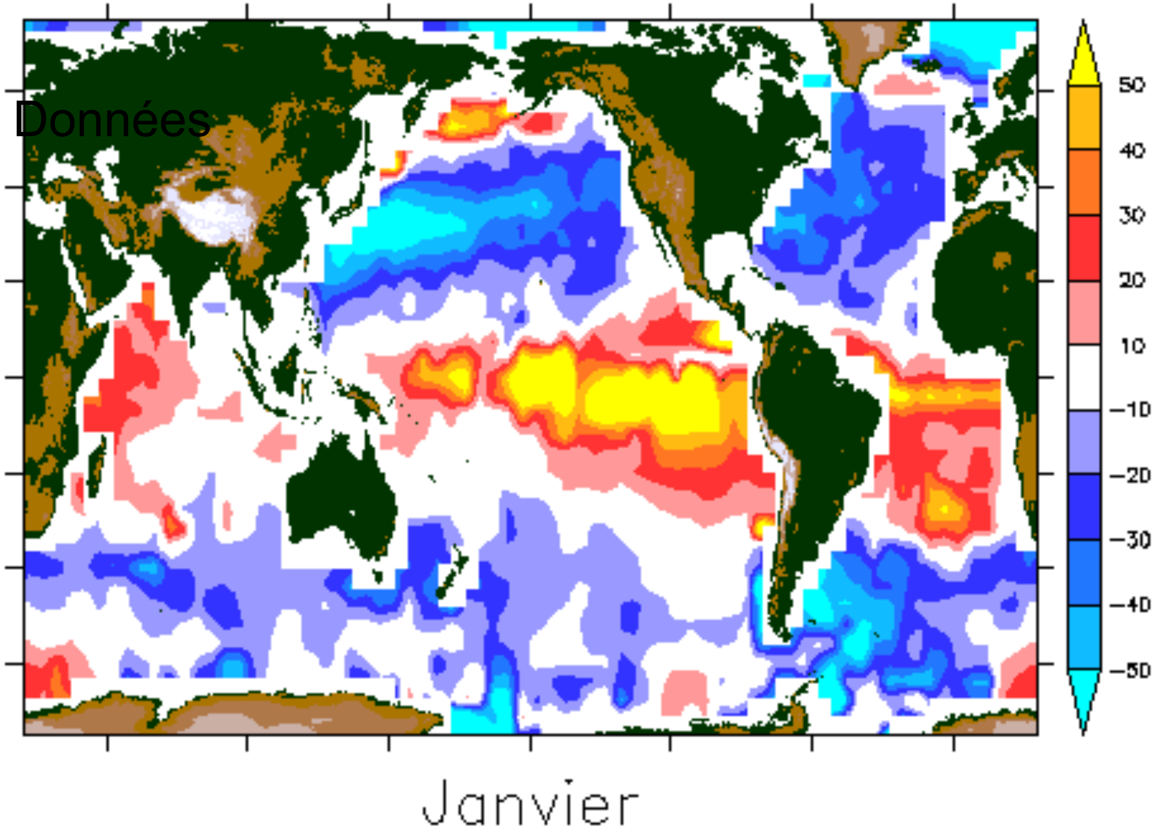
5. Geoengineering options involving ocean chemistry

Natural carbon cycle: Carbon sinks and carbon sources

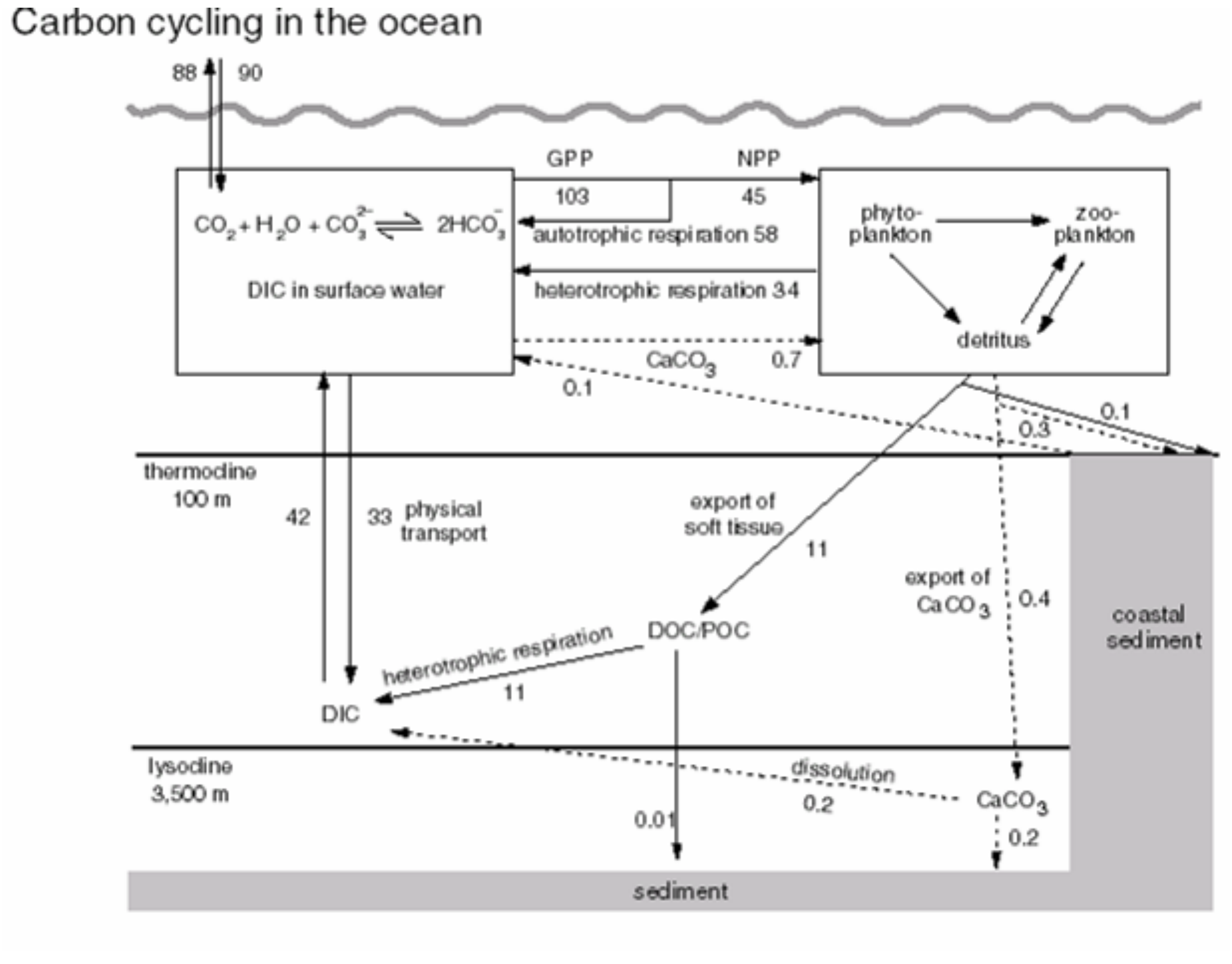
🟦 Carbon Sink

🟥 Carbon Source



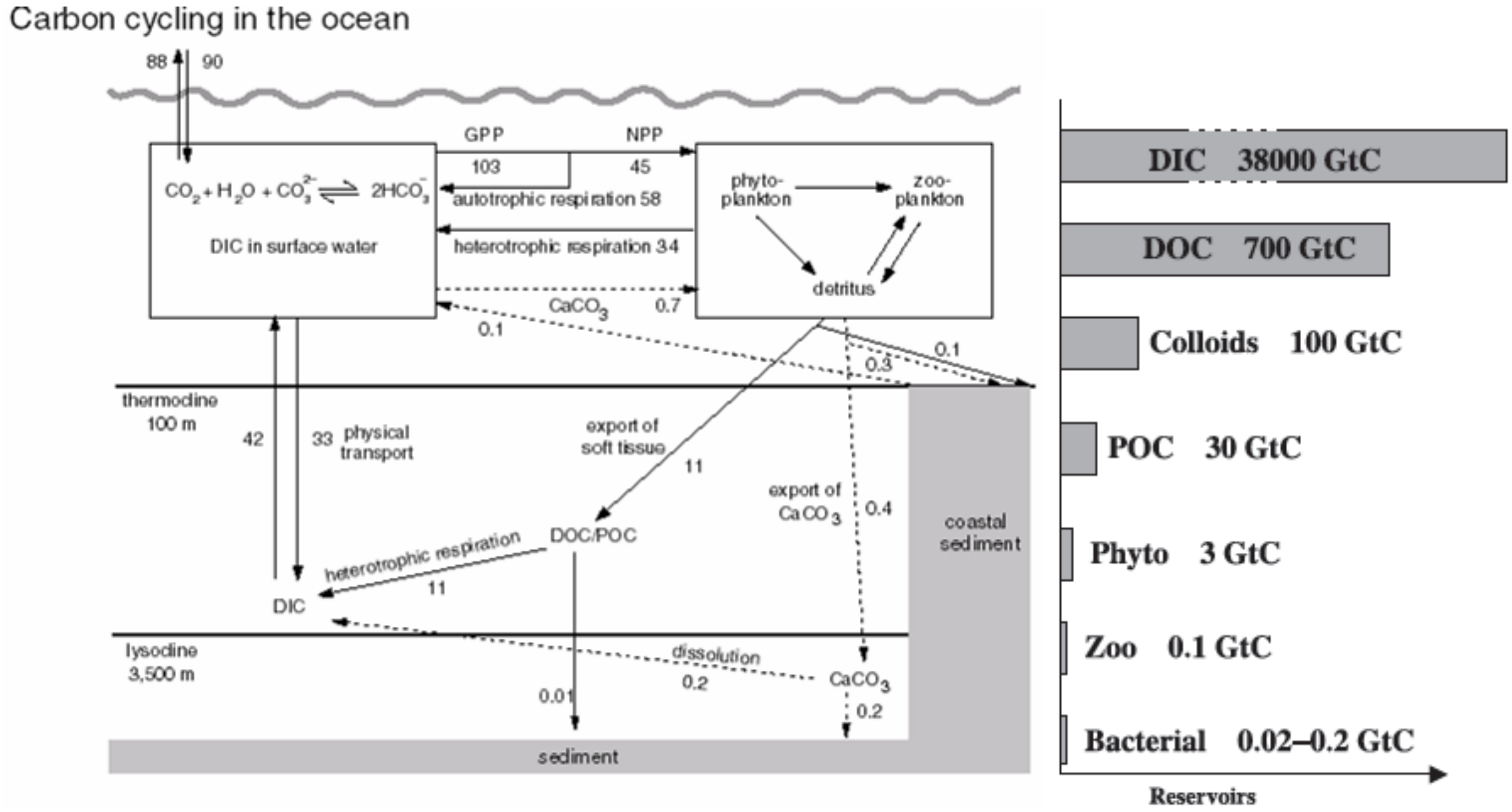
(Takahashi et al. 2009)

Natural carbon cycle: multiple processes and reservoirs



Marine Carbon Cycle : Physics / Chemistry / Biology

Natural carbon cycle: multiple processes and reservoirs



Marine Carbon Cycle : Physics / Chemistry / Biology

Natural carbon cycle: multiple processes and reservoirs

Focus on:

- 2.1 Gas exchanges at the air-sea interface
- 2.2 Inorganic carbon chemistry
- 2.3 Surface ocean
  - Different processes
  - Seasonal cycle at several stations
- 2.4 Water column
  - Carbon pumps
  - Contribution from the different pumps
- 2.5 Interannual variability: ENSO and ocean carbon cycle

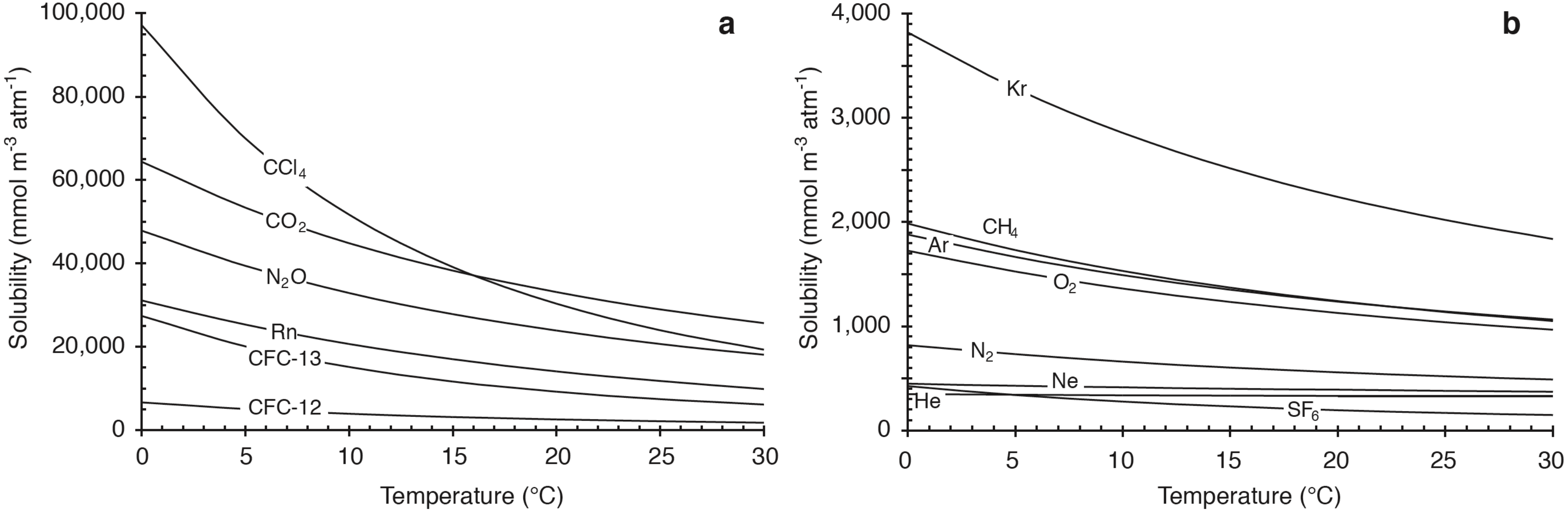
2.1 Gas exchange at the air-sea interface

-Solubility S_A :

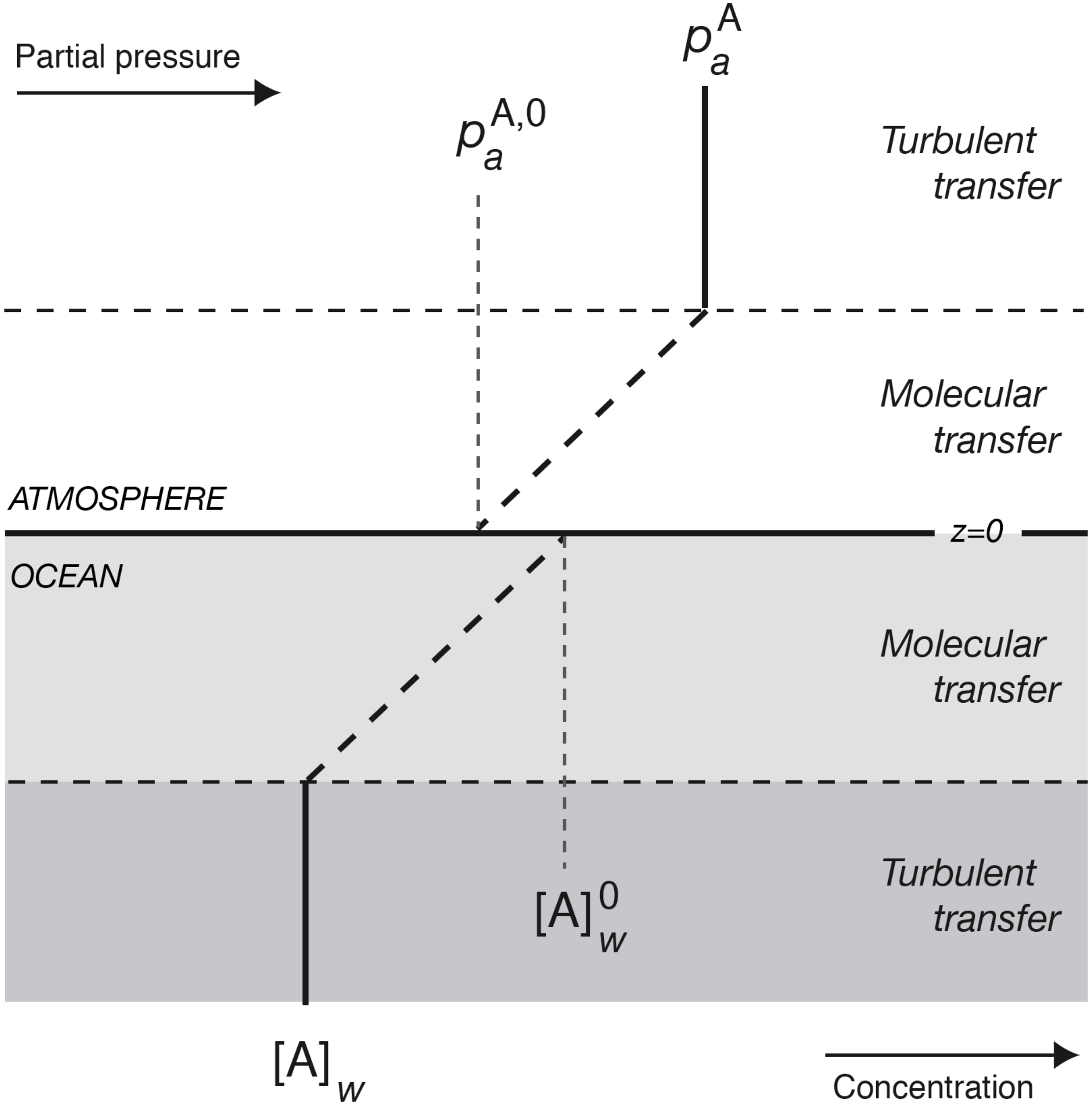
$$[A] = S_A \,.\, p_A$$

[ ] : concentration (mol m^{-3})
P : partial pressure (ppm)
S : solubility in mol m^{-3} ppm^{-1}

$$S_A = f(T,S)$$



2.1 Gas exchange at the air-sea interface : “Stagnant Film Model”



2.1 Gas exchange at the air-sea interface : "Stagnant Film Model"

Fick Law:

$$\Theta_a = -\varepsilon \frac{\partial [A]_a}{\partial z} \rightarrow \Theta_a = -\frac{k_a}{S_a} \cdot ([A]_a - [A]_a^0)$$

with ε, molecular diffusion and k_a, "gas exchange coefficient", k_w "gas transfer velocity"

Continuity at the interface :

$$\Phi_a = \Phi_w = \Phi = -K.\ ([A]_a - [A]_w)$$

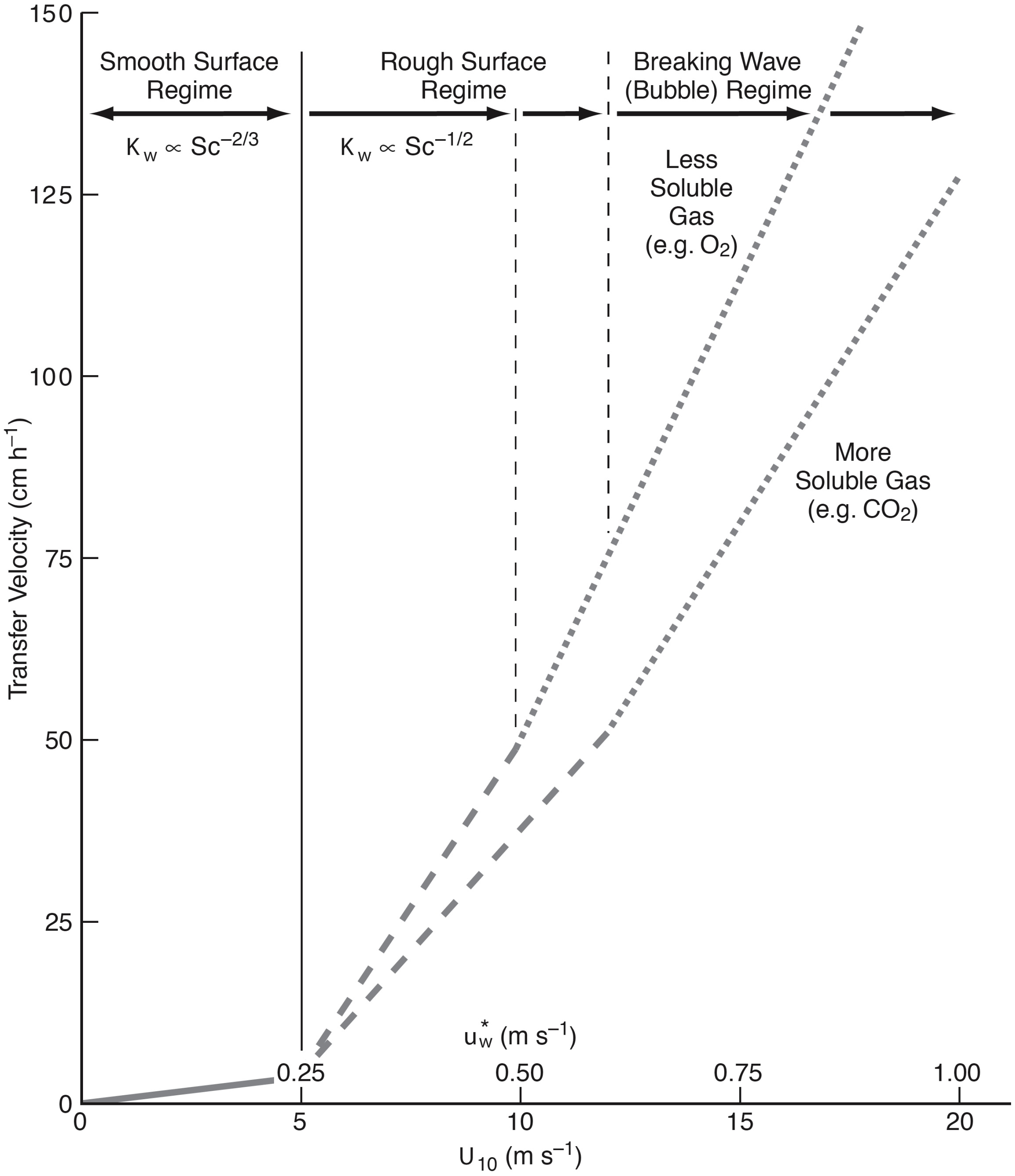
with $1/K = 1/k_w + S_A/k_a$

$$1/K \approx 1/k_w$$

$$\rightarrow \Phi = -k_w\ .\ ([A]_a - [A]_w) = -k_W S_A\ .\ (p_a - p_w)$$

2.1 Gas exchange at the air-sea interface

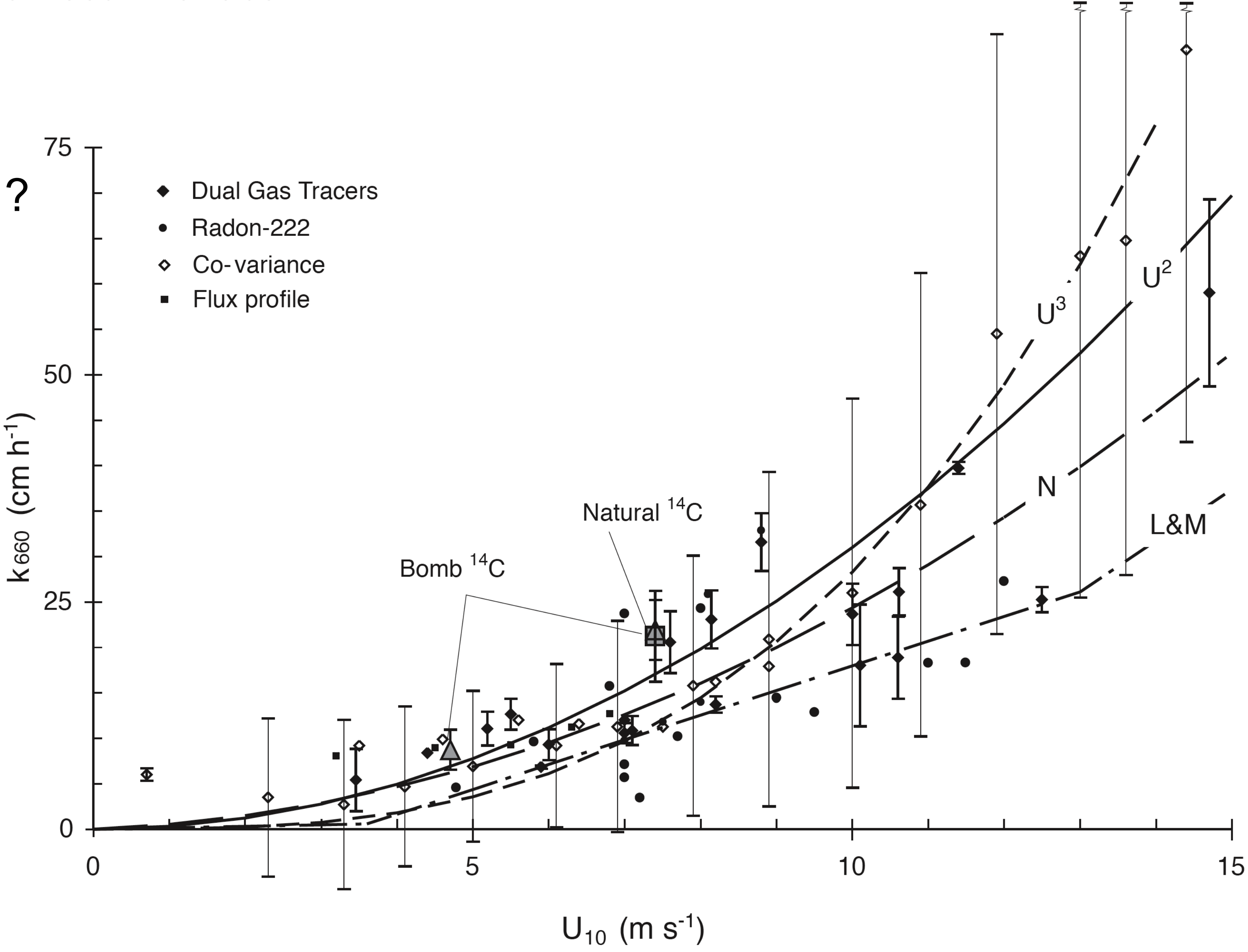
k_w ?



(Liss et Merlivat, 1986)

2.1 Gas exchange at the air-sea interface

k_w ?



2.1 Gas exchange at the air-sea interface

k_w ?

Source	Equation	Global mean k_w at $Sc = 660$[a] (cm hr^{-1})
[*Liss and Merlivat*, 1986]	$k_w = 0.17 \cdot U \cdot (Sc/600)^{-2/3},\ \ U \le 3.6 \text{ m s}^{-1}$ $k_w = (U - 3.4) \cdot 2.8 \cdot (Sc/600)^{-0.5},\ \ 3.6 < U \le 13 \text{ m s}^{-1}$ $k_w = (U - 8.4) \cdot 5.9 \cdot (Sc/600)^{-0.5},\ \ U > 13 \text{ m s}^{-1}$	11.2
[*Nightingale et al.*, 2000b]	$k_w = \left(0.333 \cdot U + 0.222 \cdot U^2\right) \cdot \left(Sc/600\right)^{-0.5}$	14.9
[*Wanninkhof*, 1992]	$k_w = 0.31 \cdot U^2 \cdot \left(Sc/660\right)^{-0.5}$	20.0
[*Wanninkhof and McGillis*, 1999]	$k_w = 0.0283 \cdot U^3 \cdot \left(Sc/660\right)^{-0.5}$	18.7

[a] The transfer velocities are normalized to a Schmidt number of 660, which the value for CO_2 at 20°C.

2.1 Gas exchange at the air-sea interface

2 applications:

--- Equilibration time from several gases

$$\Phi = k_w \,.\, ([A]_a - [A]_w)$$

$$\rightarrow \tau = Z_{ml} / k_w$$

(O_2 : 25°C, U10 = 7.5 ms-1, kw = 23 cm/hr)
(CO_2 : 25°C, U10 = 7.5 ms-1, kw = 20 cm/hr)
(Wanninkhof, 92)

2.1 Gas exchange at the air-sea interface

2 applications:

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$$\rightarrow \tau = Z_{ml} / k_w$$

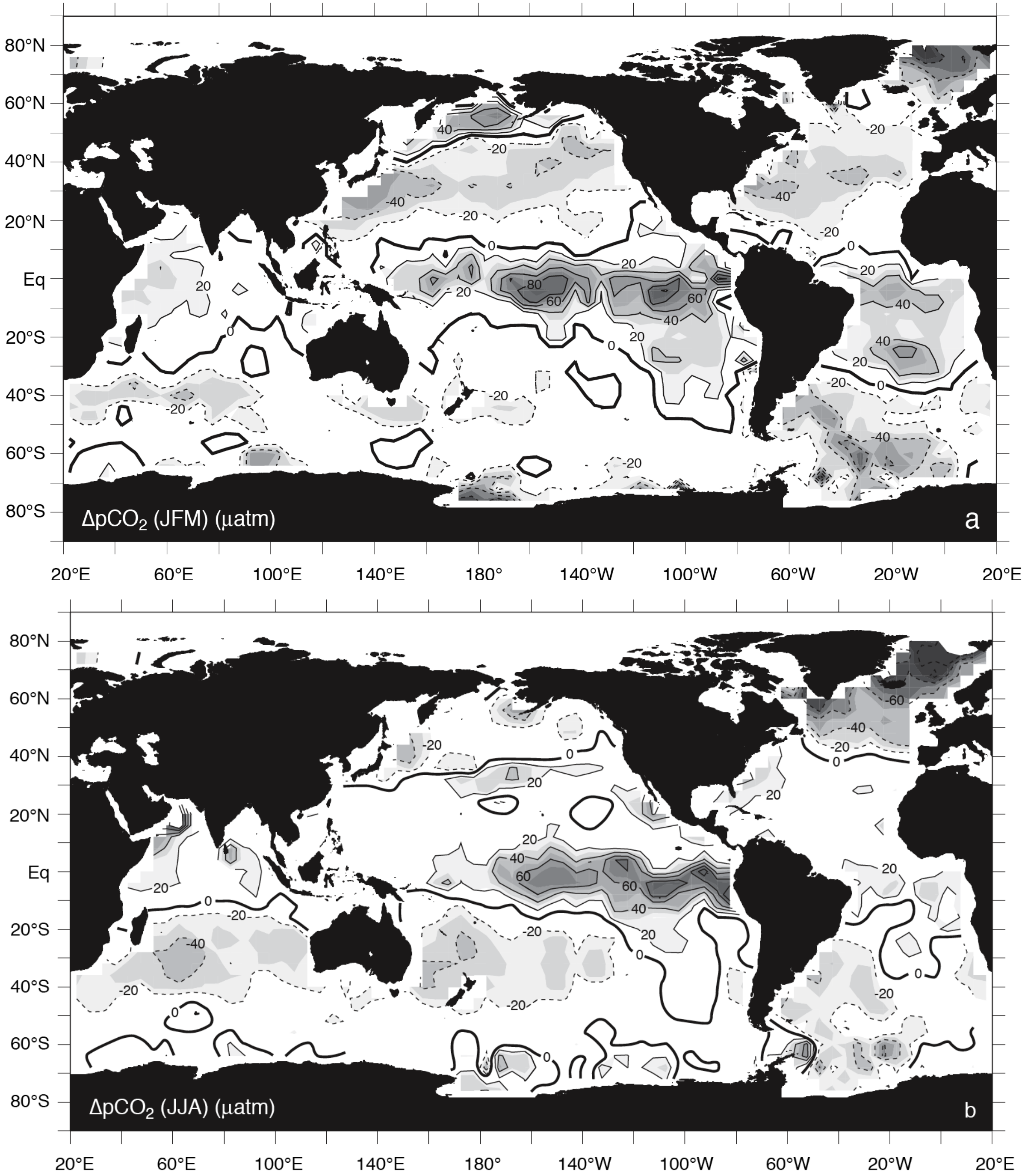
(O_2 : 25°C, U10 = 7.5 ms-1, kw = 23 cm/hr)
(CO_2 : 25°C, U10 = 7.5 ms-1, kw = 20 cm/hr)

Zml = 40 m → O_2 : t ~ 1 month
→ CO_2 : t ~9 days

2.1 Gas exchange at the air-sea interface

2 applications:

--- Compute ocean CO2 flux from ΔpCO_2

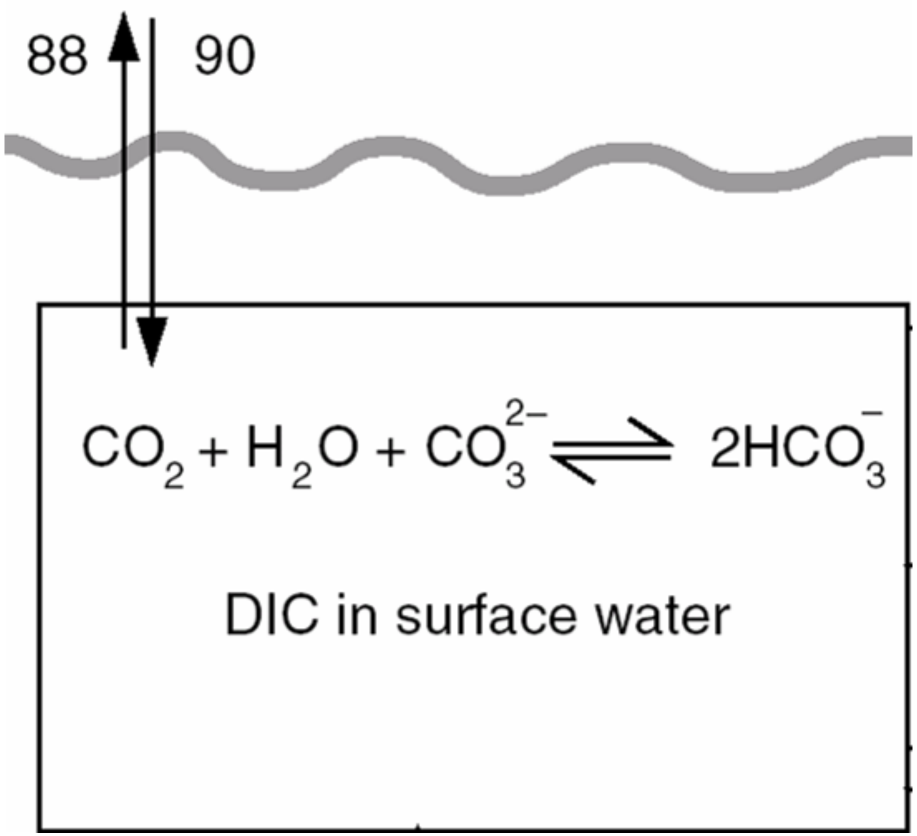


2.1 Gas exchange at the air-sea interface

2 applications:

--- Compute ocean CO2 flux
from ΔpCO_2

	Globally integrated air-sea CO_2 flux ($Pg\ C\ yr^{-1}$)		
Gas transfer velocity formulation	(a) Without wind speed variability	(b) With wind speed variability	(b)/(a)
[*Liss and Merlivat*, 1986]	-0.88	-1.06	1.21
[*Nightingale et al.*, 2000b]	-1.06	-1.25	1.19
[*Wanninkhof*, 1992][a]	-1.65	-1.58	0.96
[*Wanninkhof and McGillis*, 1999][a]	-2.35	-1.94	0.82



$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^{-}$$

2.2 Inorganic carbon chemistry

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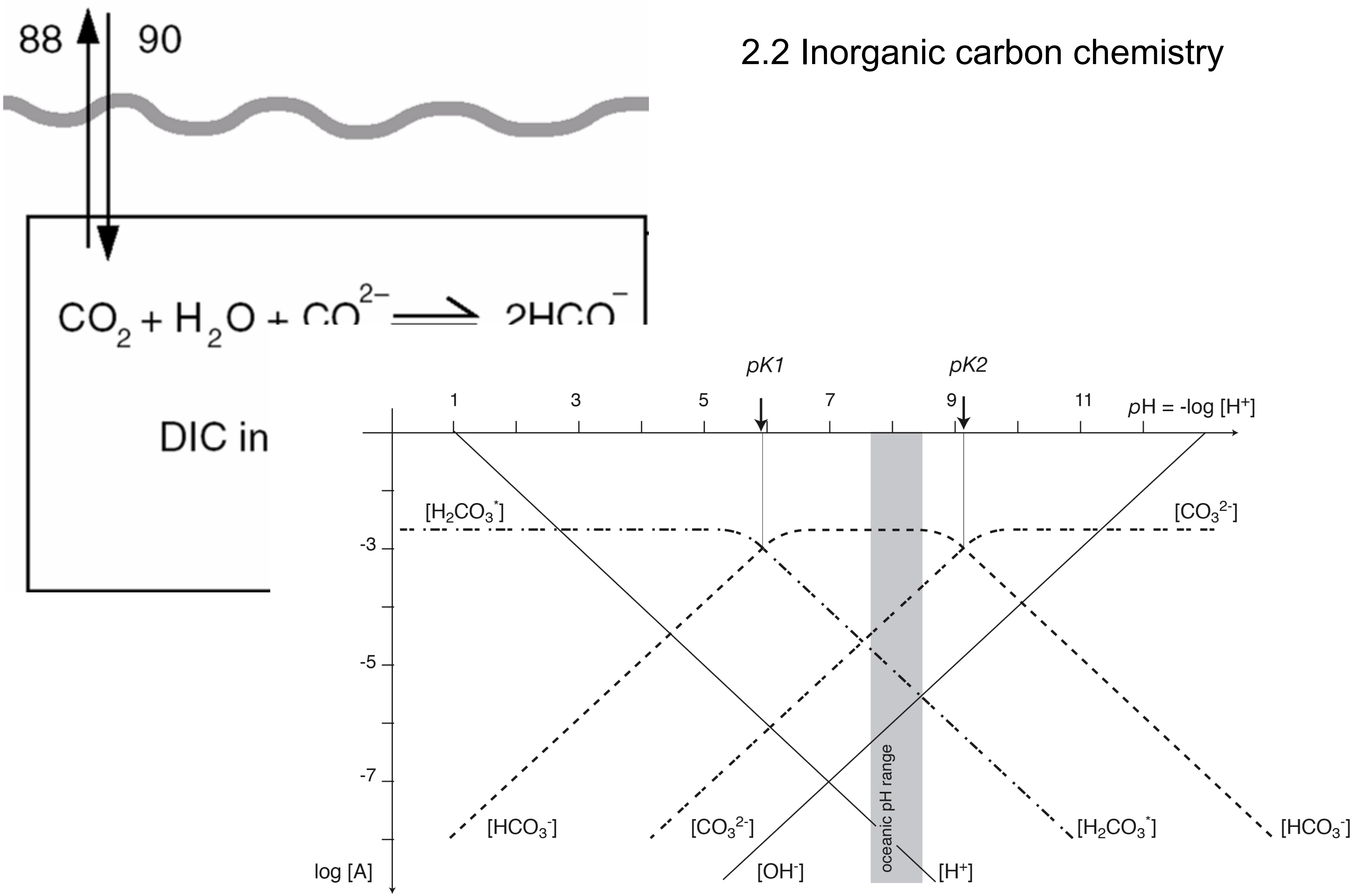


2.2 Inorganic carbon chemistry

$$CO_{2\ (\mathrm{gas})} + H_2O \iff H_2CO_3^*$$

$$H_2CO_3^* \iff H^+ + HCO_3^-$$

$$HCO_3^- \iff H^+ + CO_3^{2-}$$

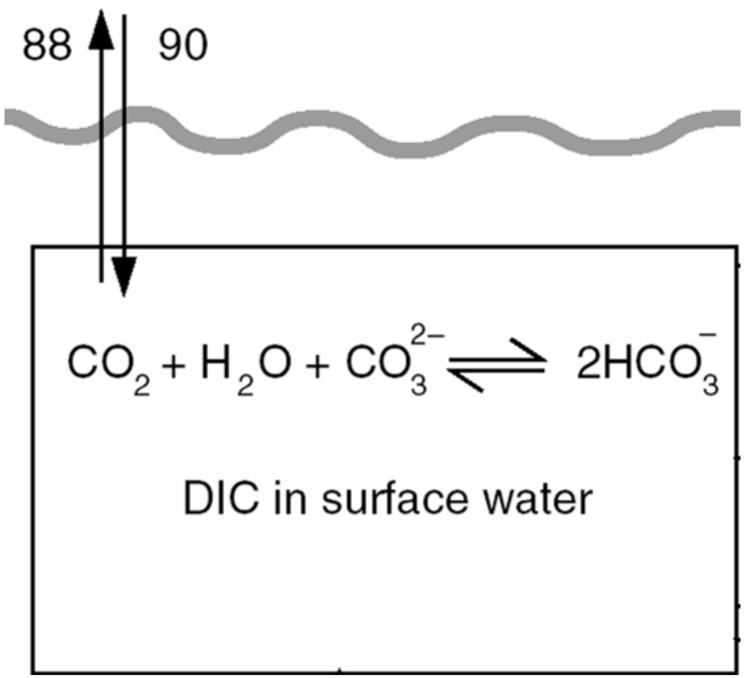
$$K_0 = \frac{[H_2CO_3^*]}{pCO_2}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

H_2CO_3 = 0.5 %
HCO_3^- = 88.6 %
CO_3^{2-} = 10.9 %

2.2 Inorganic carbon chemistry



$$DIC = CO_2 + HCO_3^- + CO_3^{2-}$$

$$\text{Alkalinity (carbonate)} = HCO_3^- + 2 * CO_3^{2-}$$

$$(\text{Alkalinity (total)} = HCO_3^- + 2 * CO_3^{2-} + OH^- – H^+ + B(OH)_4^-)$$

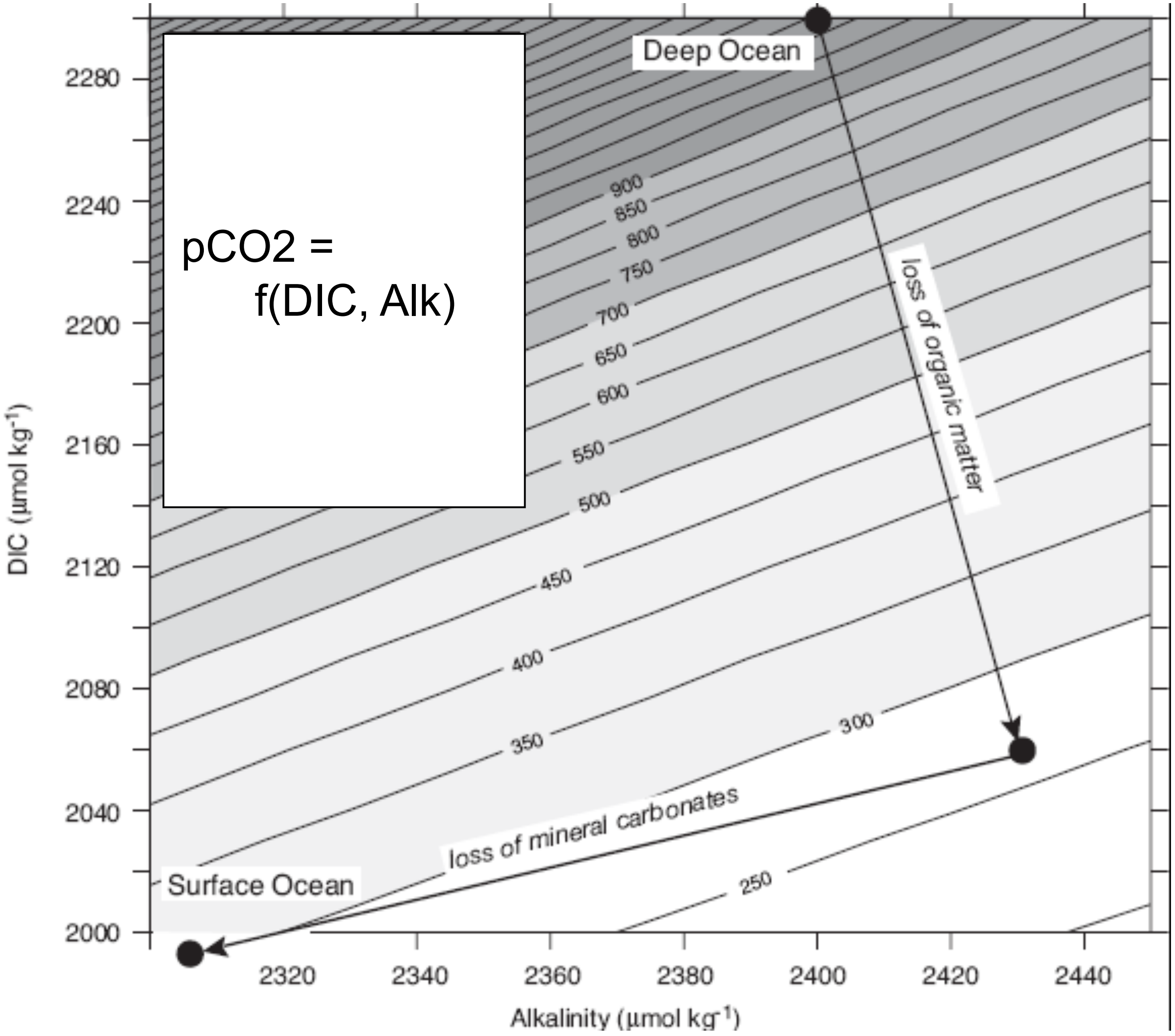
Theoritically, if you know 2 out of (pH, DIC, Alk, CO2, HCO3-, CO32-),….

In model : DIC and Alkalinity only represented

In the field : DIC, Alk, pCO_2 are measured

2.3 Surface Ocean:

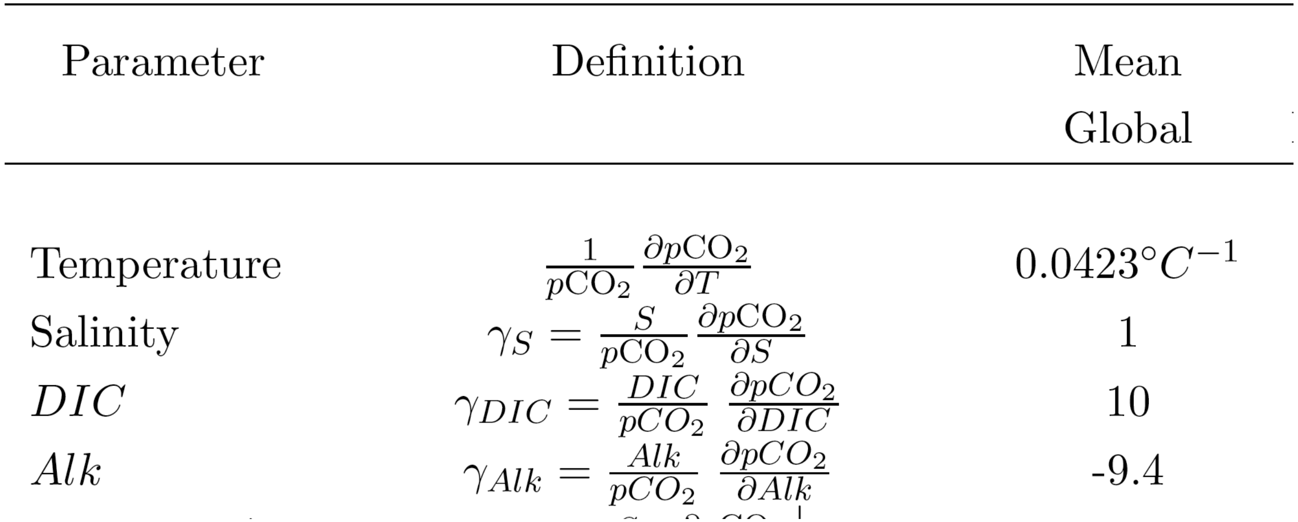
--- Impact of variations in T, S, DIC and Alk on pCO_2 :



pCO2 =
f(DIC, Alk)

2.3 Surface Ocean:

--- Impact of variations in T, S, DIC and Alk on pCO_2 :



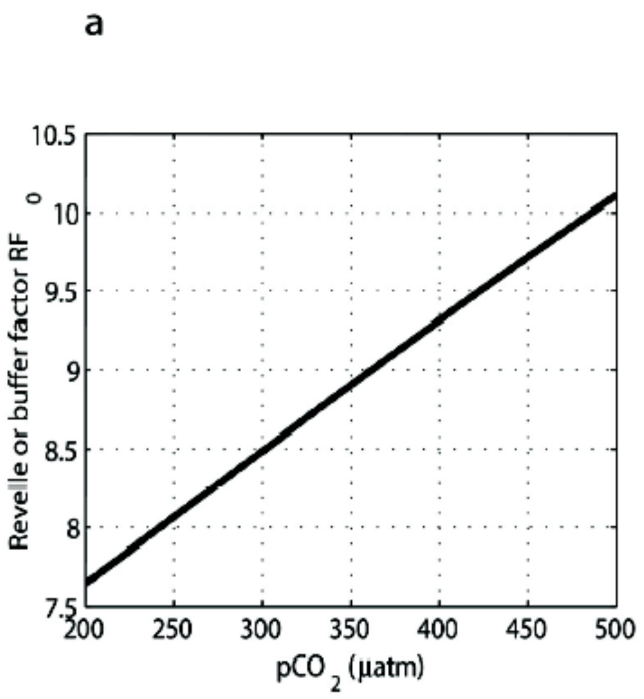
Parameter	Definition	Mean Global
Temperature	$\frac{1}{p\mathrm{CO}_2}\frac{\partial p\mathrm{CO}_2}{\partial T}$	$0.0423°C^{-1}$
Salinity	$\gamma_S = \frac{S}{p\mathrm{CO}_2}\frac{\partial p\mathrm{CO}_2}{\partial S}$	1
DIC	$\gamma_{DIC} = \frac{DIC}{pCO_2}\ \frac{\partial pCO_2}{\partial DIC}$	10
Alk	$\gamma_{Alk} = \frac{Alk}{pCO_2}\ \frac{\partial pCO_2}{\partial Alk}$	-9.4

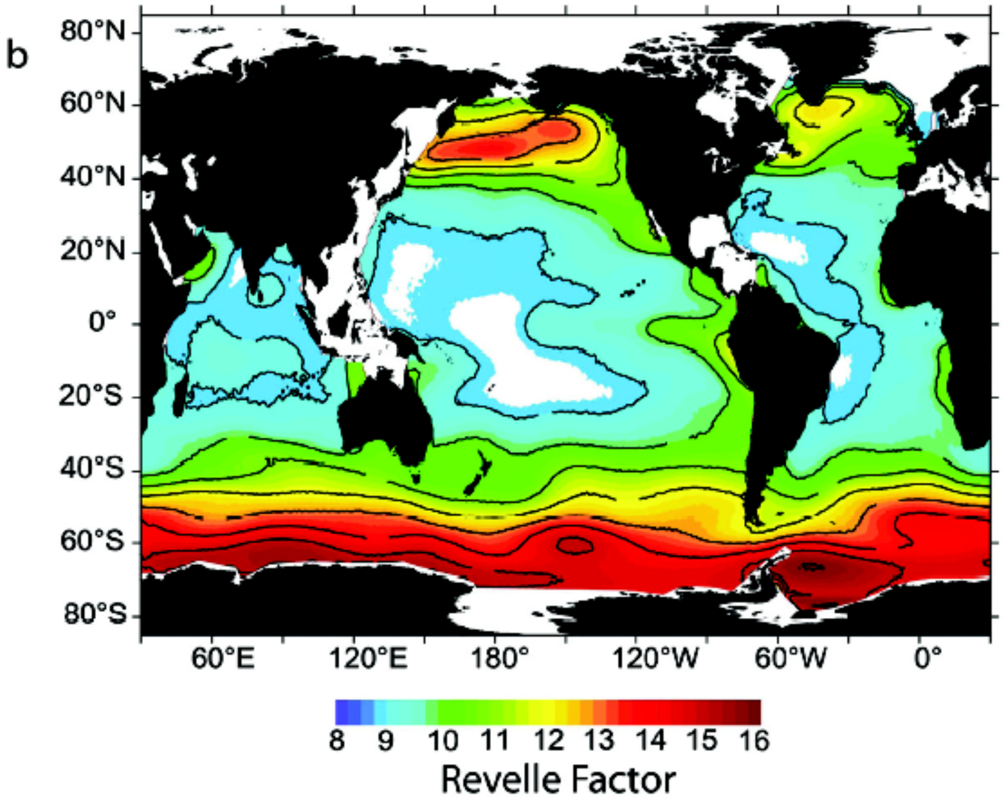
2.3 Surface Ocean:

--- Impact of variations in T, S, DIC and Alk on $p\mathrm{CO}_2$:

Revelle Factor : $R = (\delta p\mathrm{CO}_2/\delta \mathrm{DIC})/(\mathrm{DIC}/p\mathrm{CO}_2)$

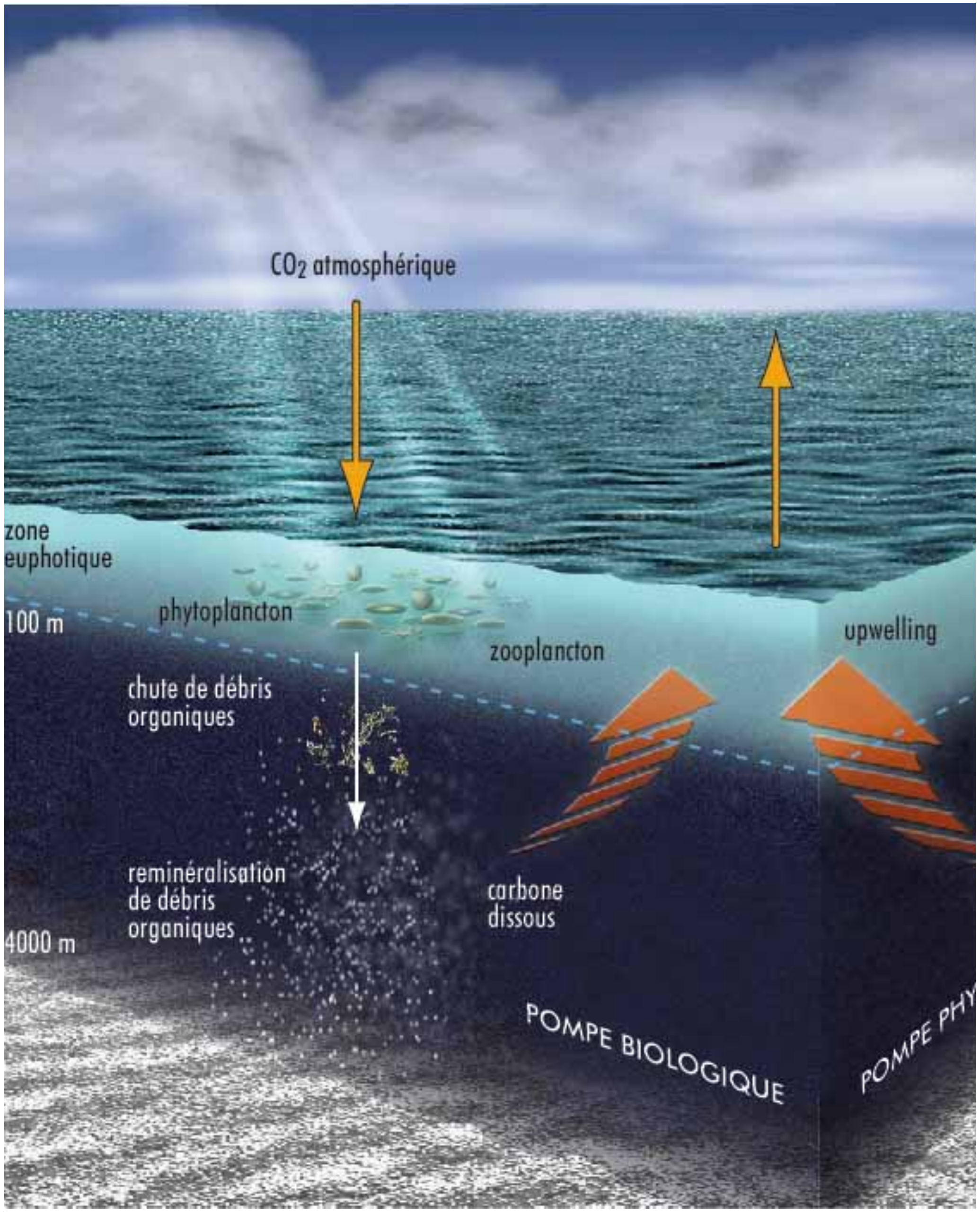
It describes how the partial pressure of CO_2 in seawater ($p\mathrm{CO}_2$) changes for a given change in DIC (Revelle and Suess, 1957).





Biological Processes

- C-fixation in the euphotic layer (photosynthesis & calcification)
- Most part is recycled (respiration & dissolution)
- Some part is exported beneath (export production of OM and $CaCO_3$)



Photosynthesis / Respiration

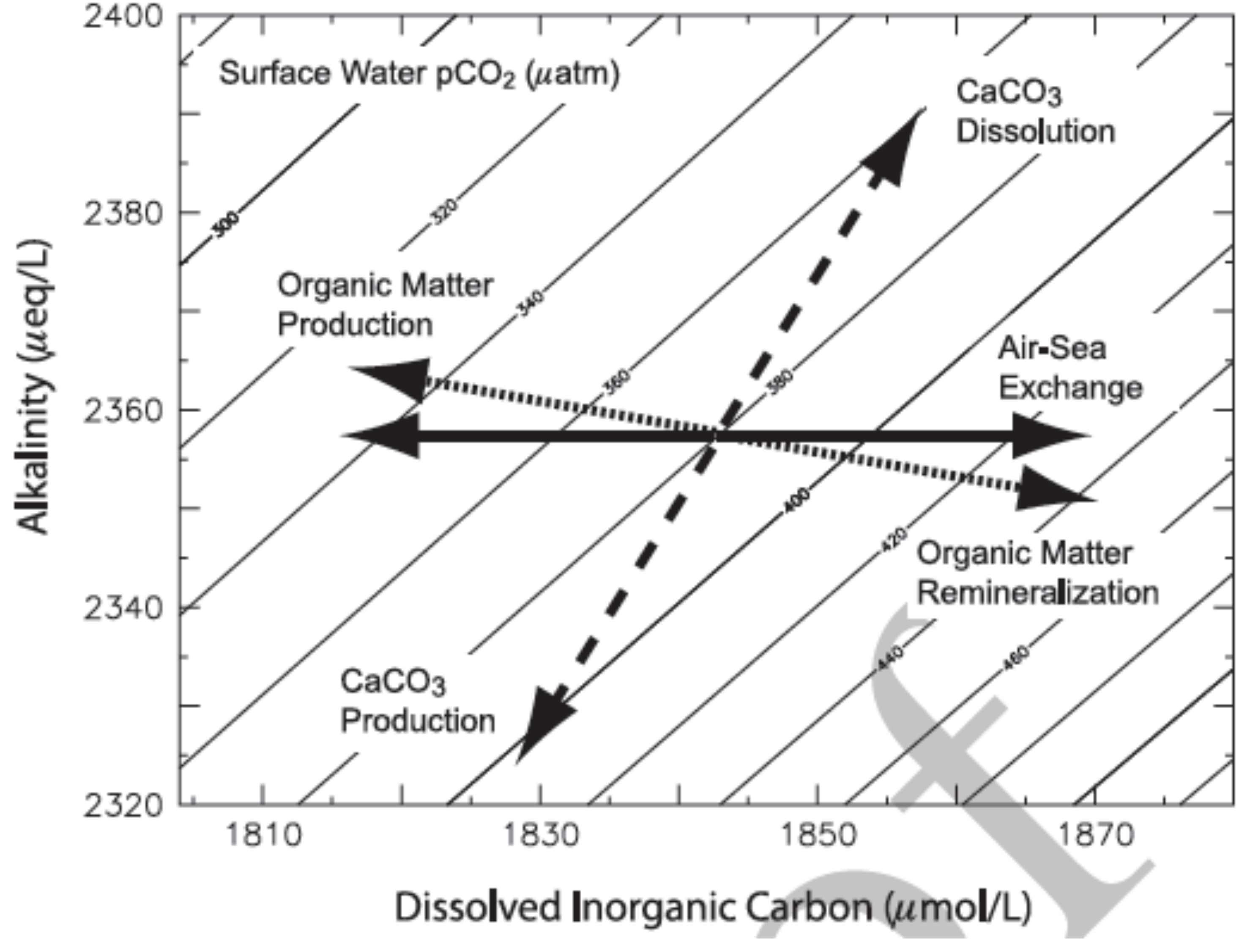
$$106\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 78\,H_2O + 18\,H^+ \leftrightarrow C_{106}H_{175}O_{42}N_{16}P + 150\,O_2$$

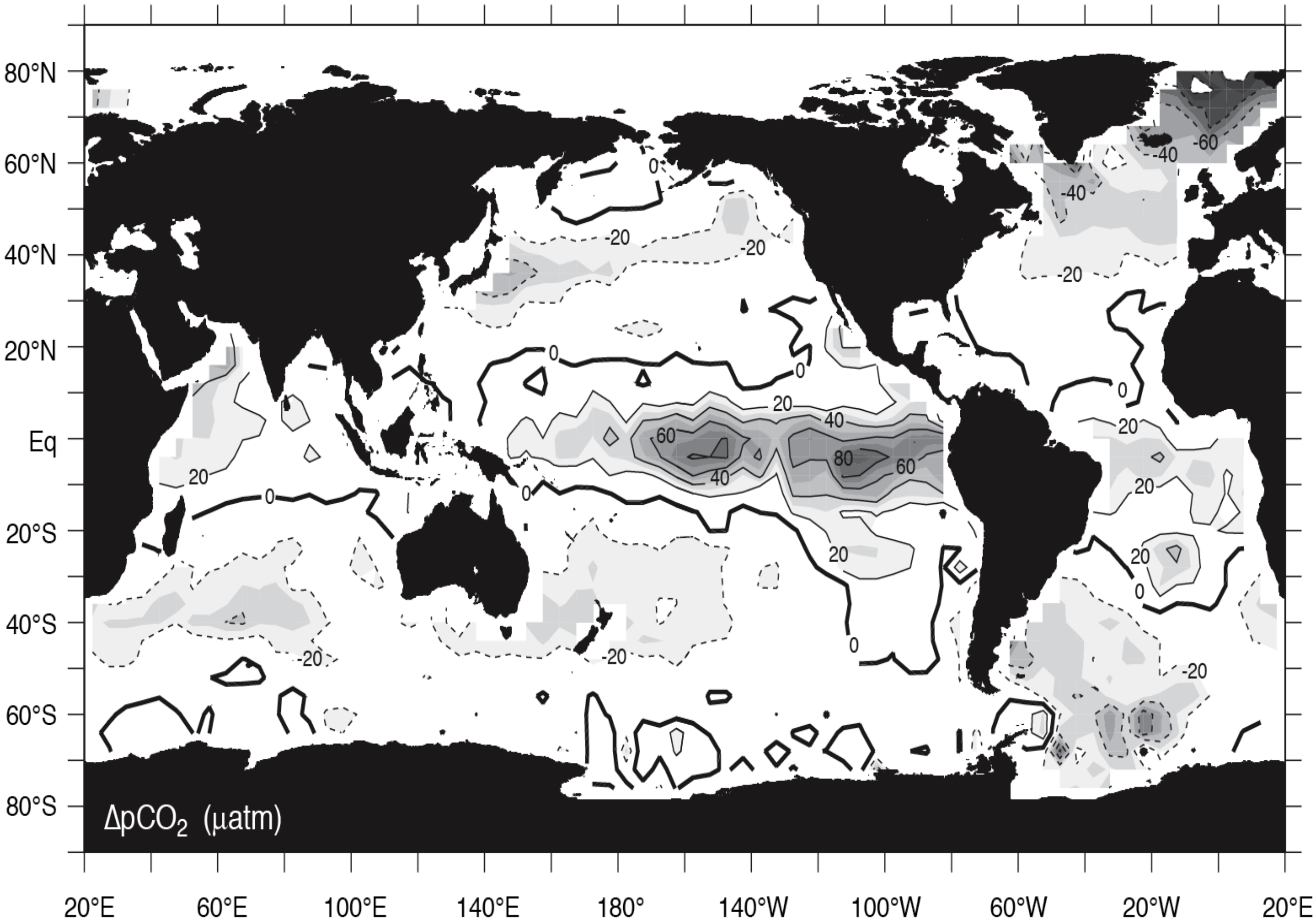
Calcification / DIssolution

$$Ca^{2+} + 2\,HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$$

2.3 Surface Ocean:

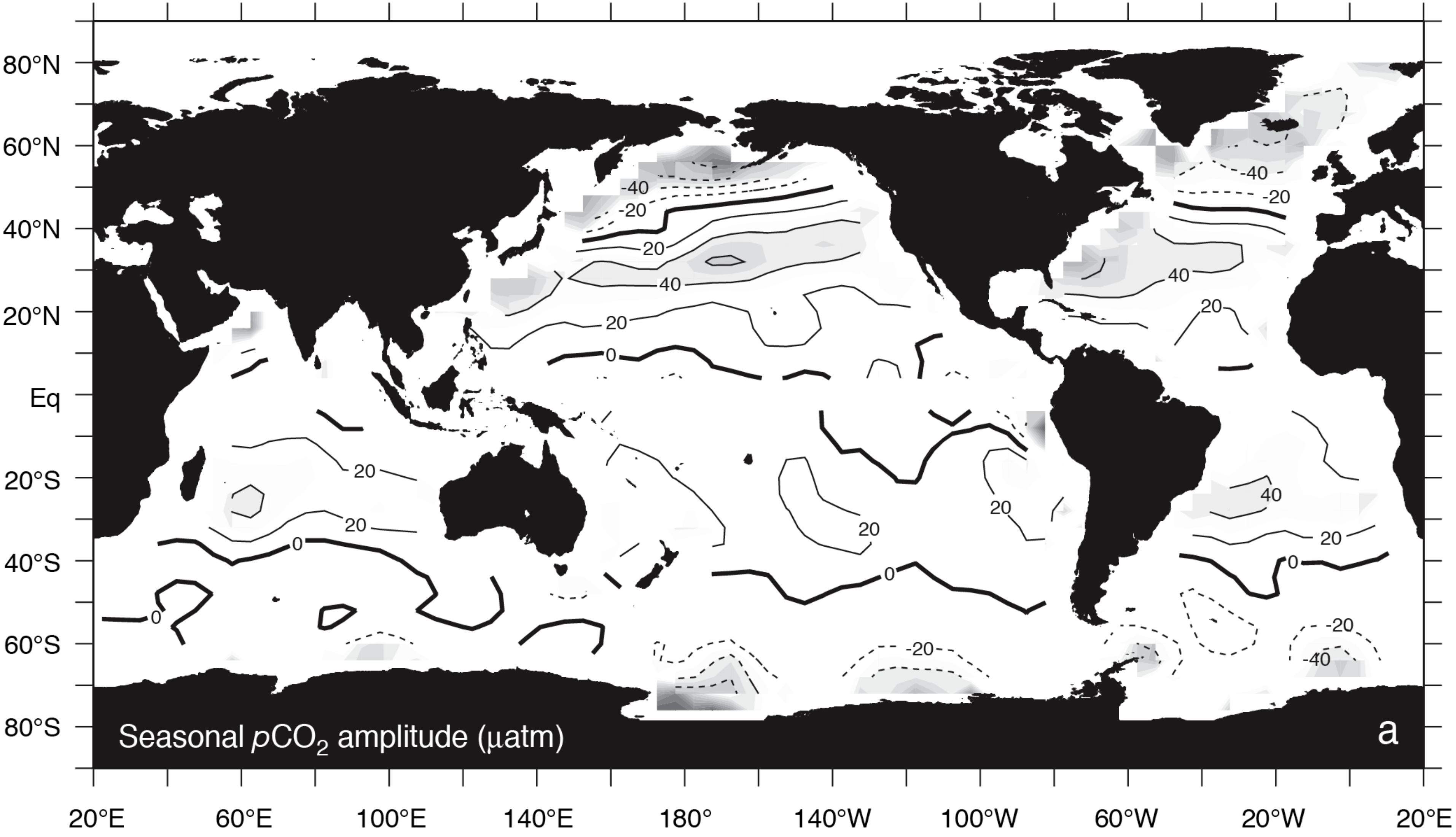
--- Impact of variations in T, S, DIC and Alk on pCO_2 :




ΔpCO$_2$ (µatm)
80°N
60°N
40°N
20°N
Eq
20°S
40°S
60°S
80°S
20°E
60°E
100°E
140°E
180°
140°W
100°W
60°W
20°W
20°E
0
-20
-20
-40
-40
-60
-20
0
0
0
20
40
60
80
60
40
20
20
20
20
0
0
20
0
-20
-20
0
-20

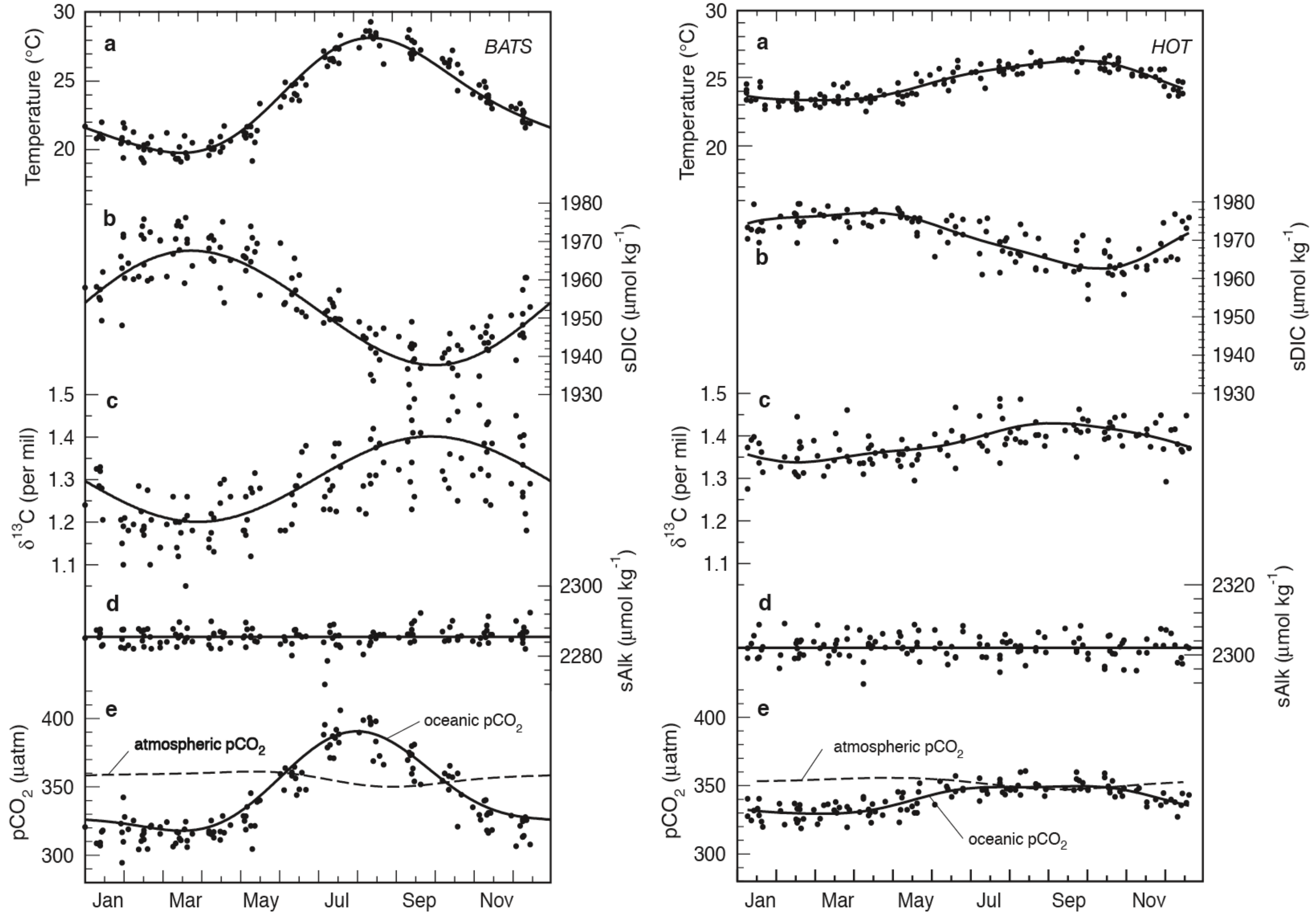
2.3 Surface Ocean:

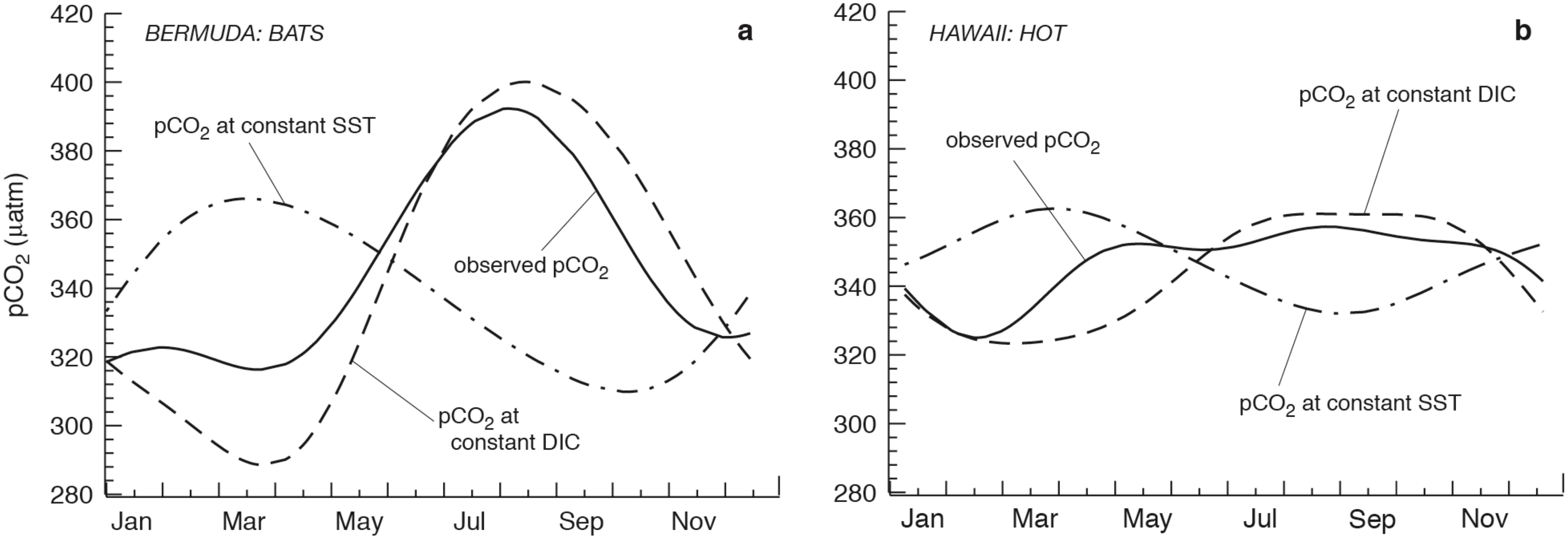
--- Seasonal variability of oceanic pCO2 (summer – winter):



2.3 Surface Ocean:

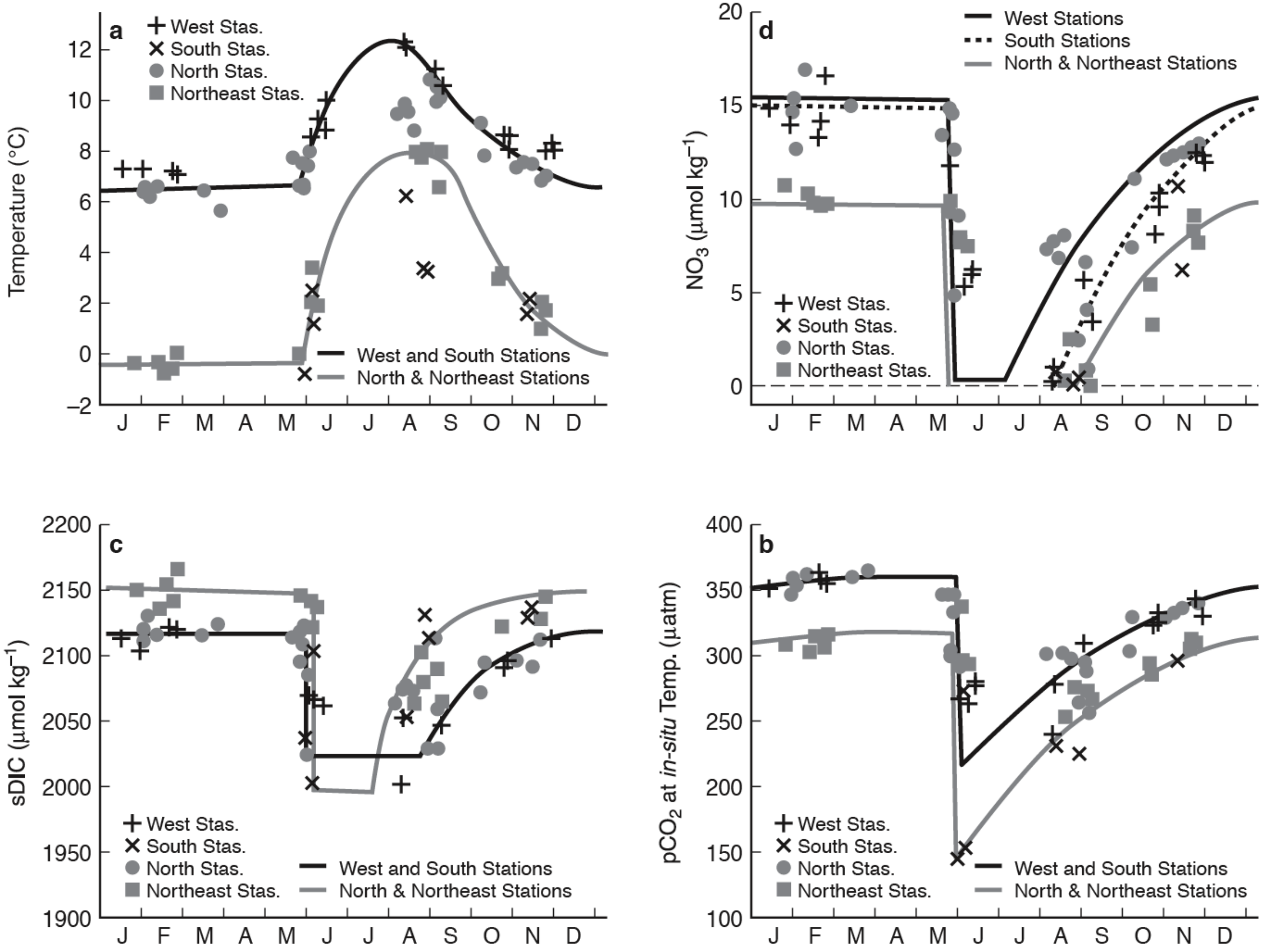
--- Seasonal variability of oceanic pCO2 (summer - winter):




BERMUDA: BATS
a
pCO$_2$ (μatm)
420
400
380
360
340
320
300
280
pCO$_2$ at constant SST
observed pCO$_2$
pCO$_2$ at constant DIC
Jan
Mar
May
Jul
Sep
Nov
HAWAII: HOT
b
pCO$_2$ at constant DIC
observed pCO$_2$
pCO$_2$ at constant SST

2.3 Surface Ocean

--- Seasonal variability of oceanic pCO2 : North Atlantic (Island)



2.3 Surface Ocean

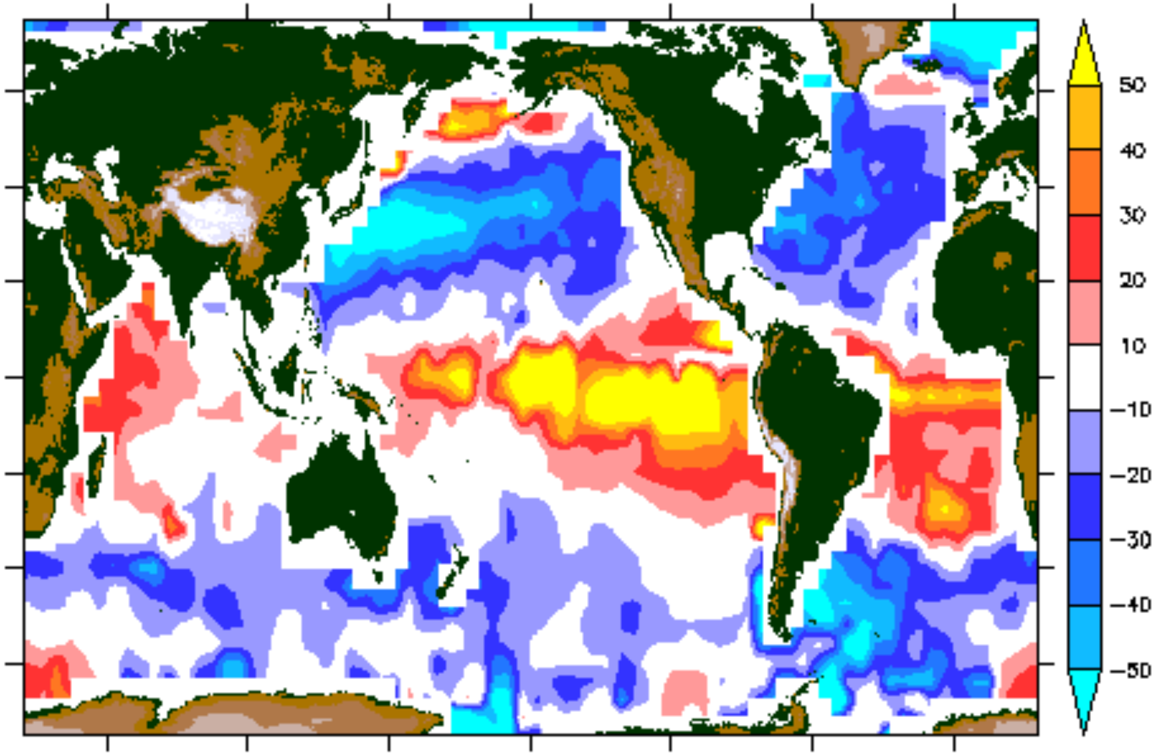
--- Seasonal variations

Seasonal Cycle at mid-high lat.:

Compensating Effects:

Solubility ⇧ ⇩
Mixing ⇩ ⇧
Biology ⇩ ⇧

Summer / WInter



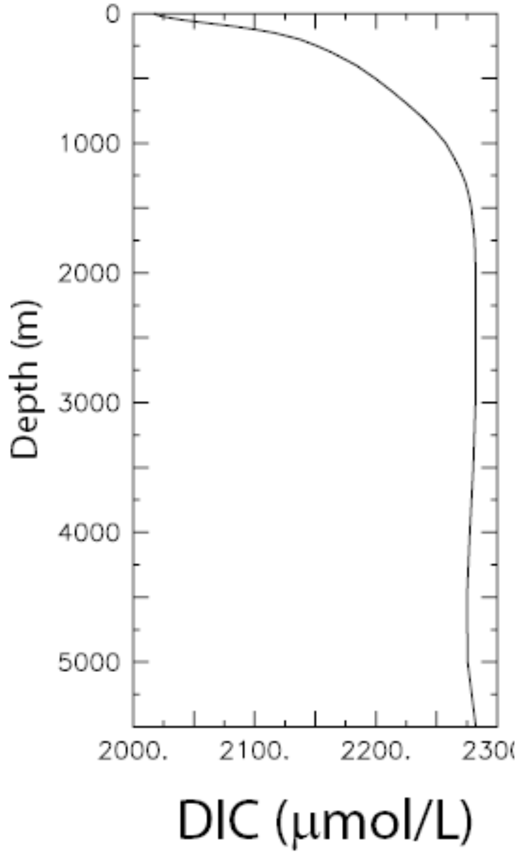
Janvier

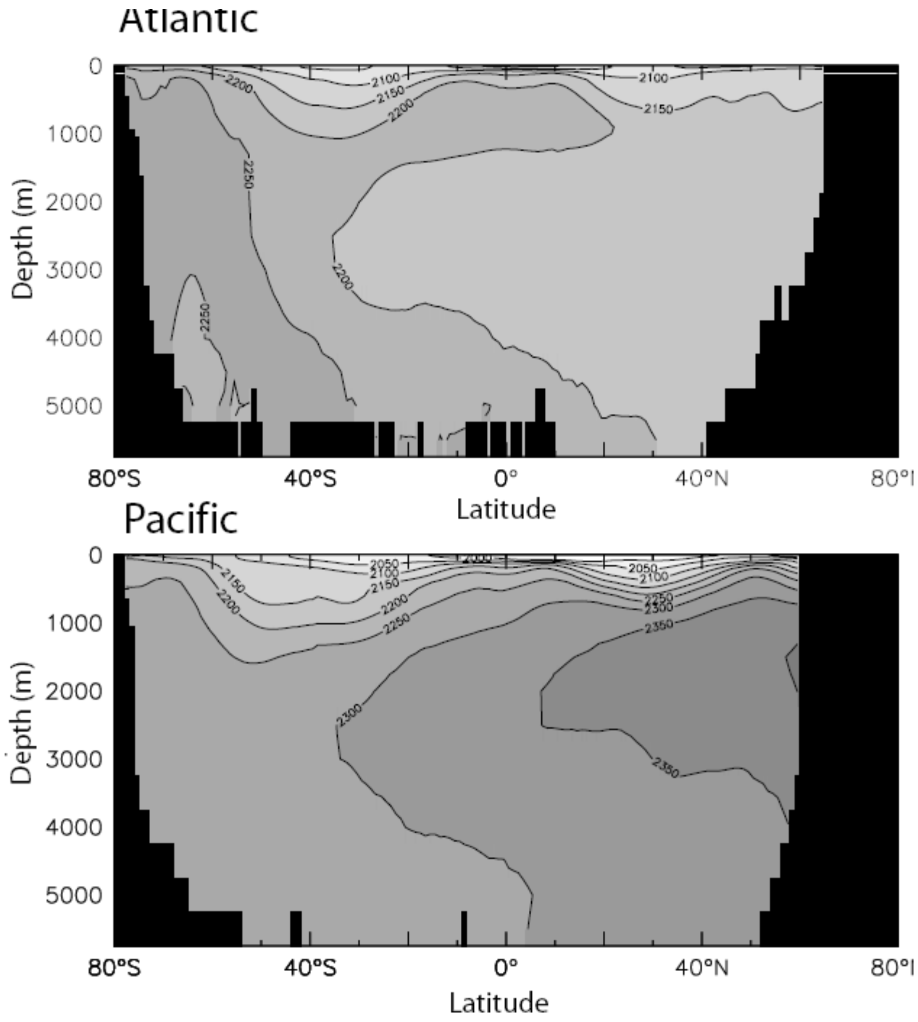
→ low amplitude of the seasonal cycle

(if you compare to O_2 for example : all in the same direction!)

2.4 Water column:

-- Vertical Profiles of DIC and Alkalinity





2.4 Water column:

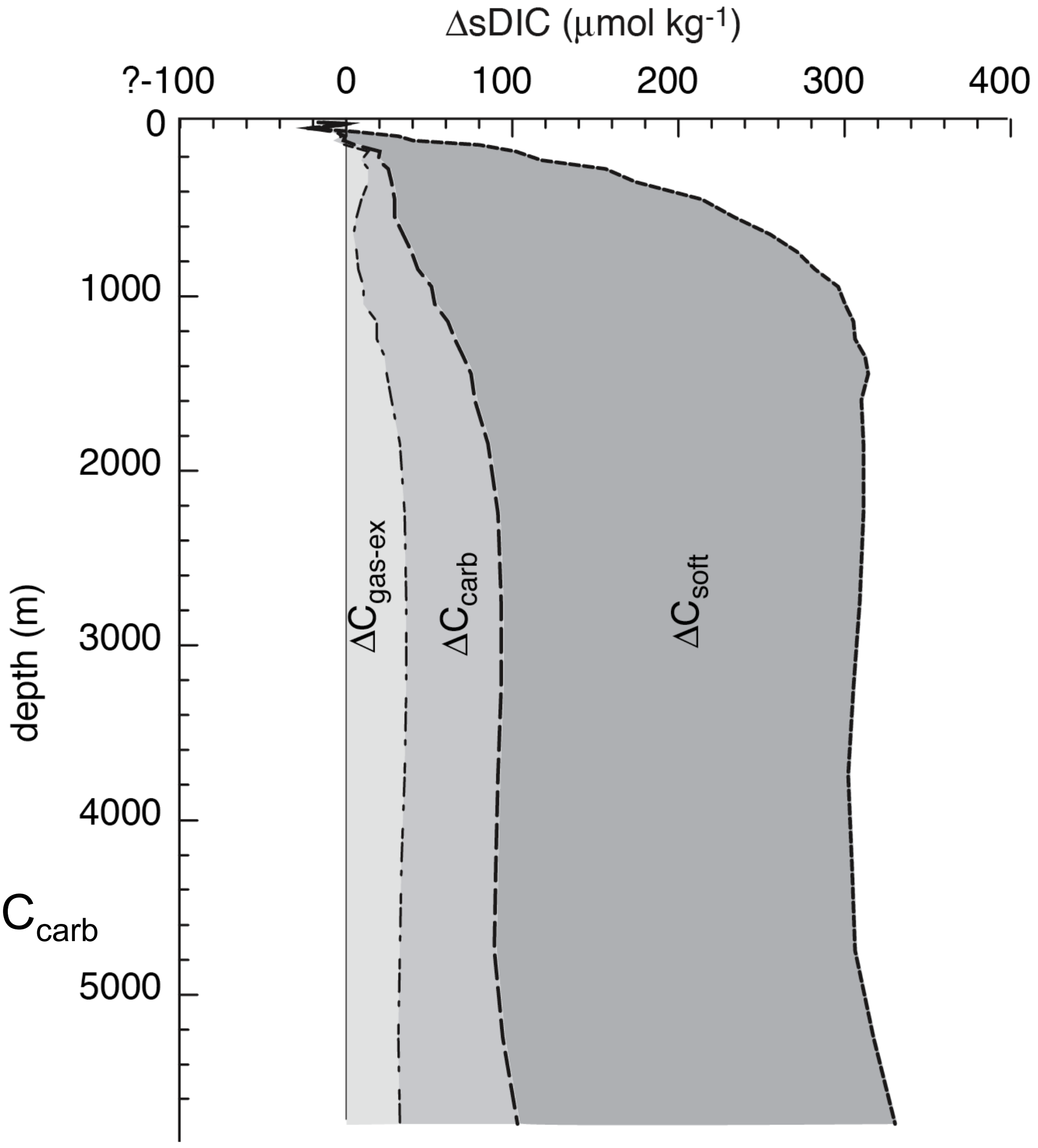
-- Vertical Profiles of DIC and Alkalinity

Soft-tissue Pump : 70%
Carbonate Pump : 20 %
Gas-Exchange Pump : 10%

$\Delta C_{soft} = r_{C.P} \,.\, (PO_4 - PO_{4\ ref})$

$\Delta C_{carb} = ½ \,(Alk - Alk_{ref} + NO_3 - NO_{3\ ref})$

$\Delta C_{\ gasex} = DIC - DIC_{ref} - C_{ant} - \Delta C_{soft} - \Delta C_{carb}$



2.4 Water column:

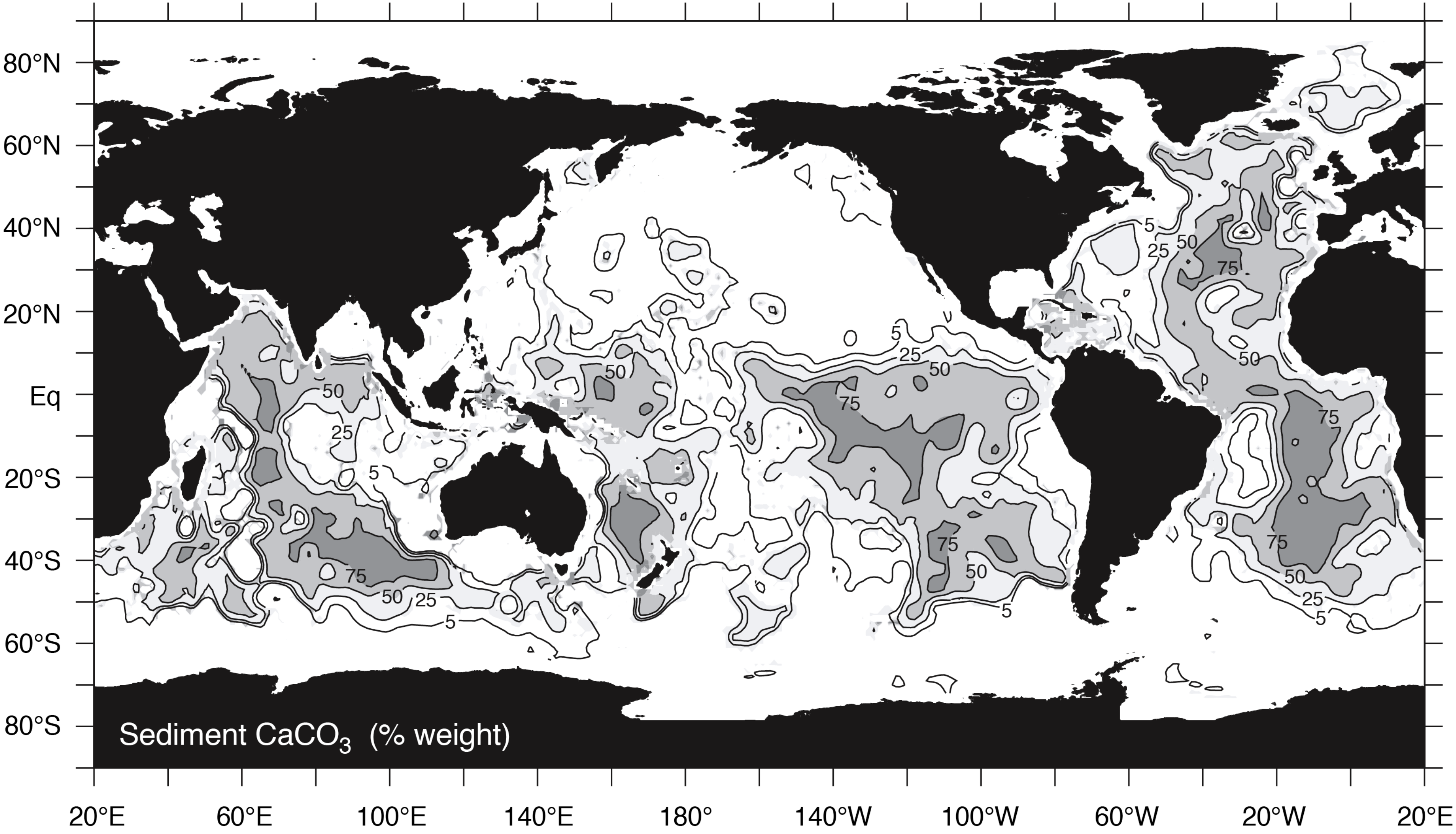
--- Soft tissue vs Carbonate:

	C_{org} (PgC/yr)	$CaCO_3$ (PgC/yr)	RainRatio
Export at 100m	~12	~1.0	~0.08
Export at 1000m	0.87	0.70	~ 1
Burial	0.02	0.13	~ 7

2.4 Colonne d'eau:

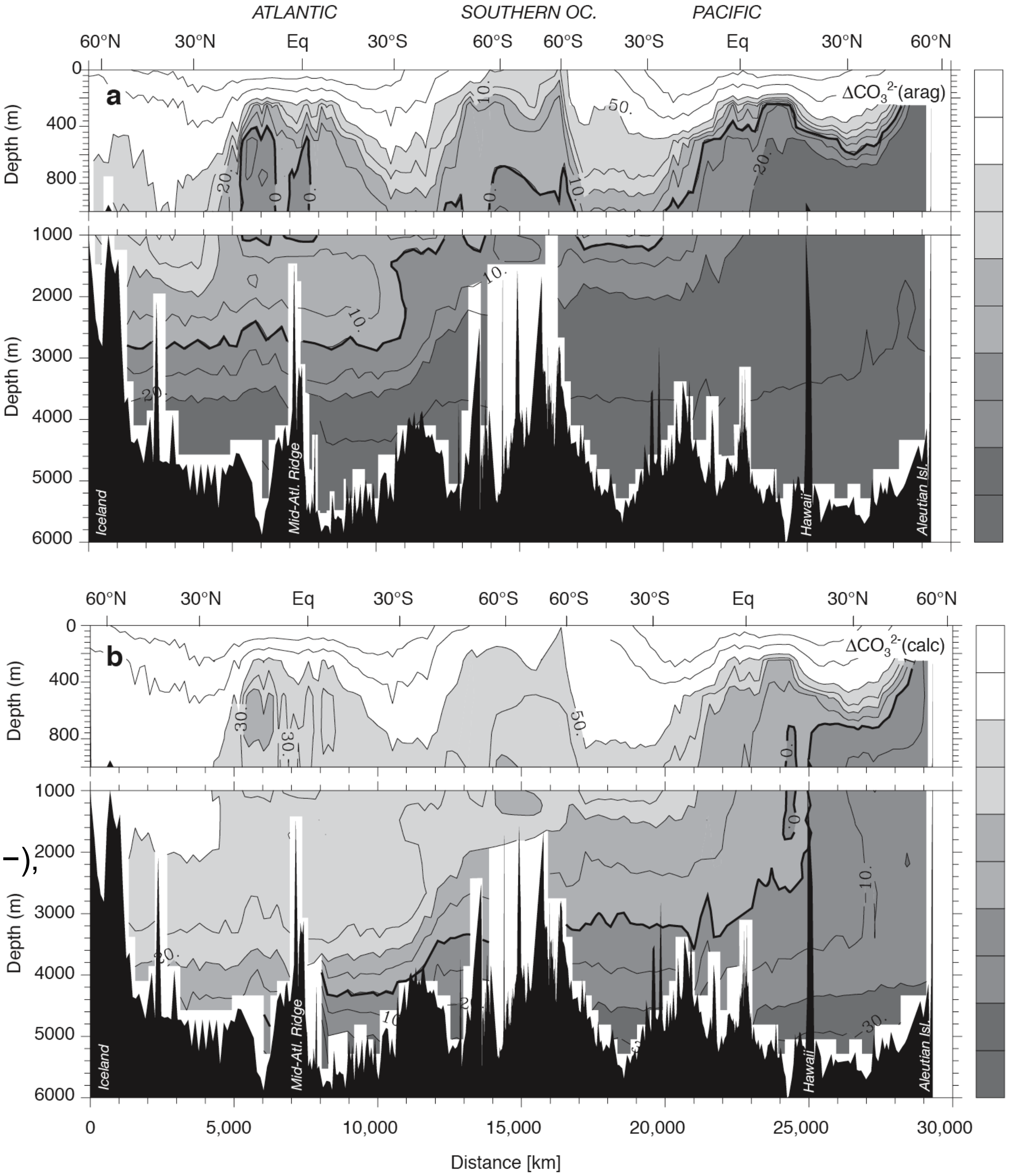
--- Carbonate Pump

Lysocline / CCD or ACD



2.4 Colonne d'eau:

--- Carbonate Pump

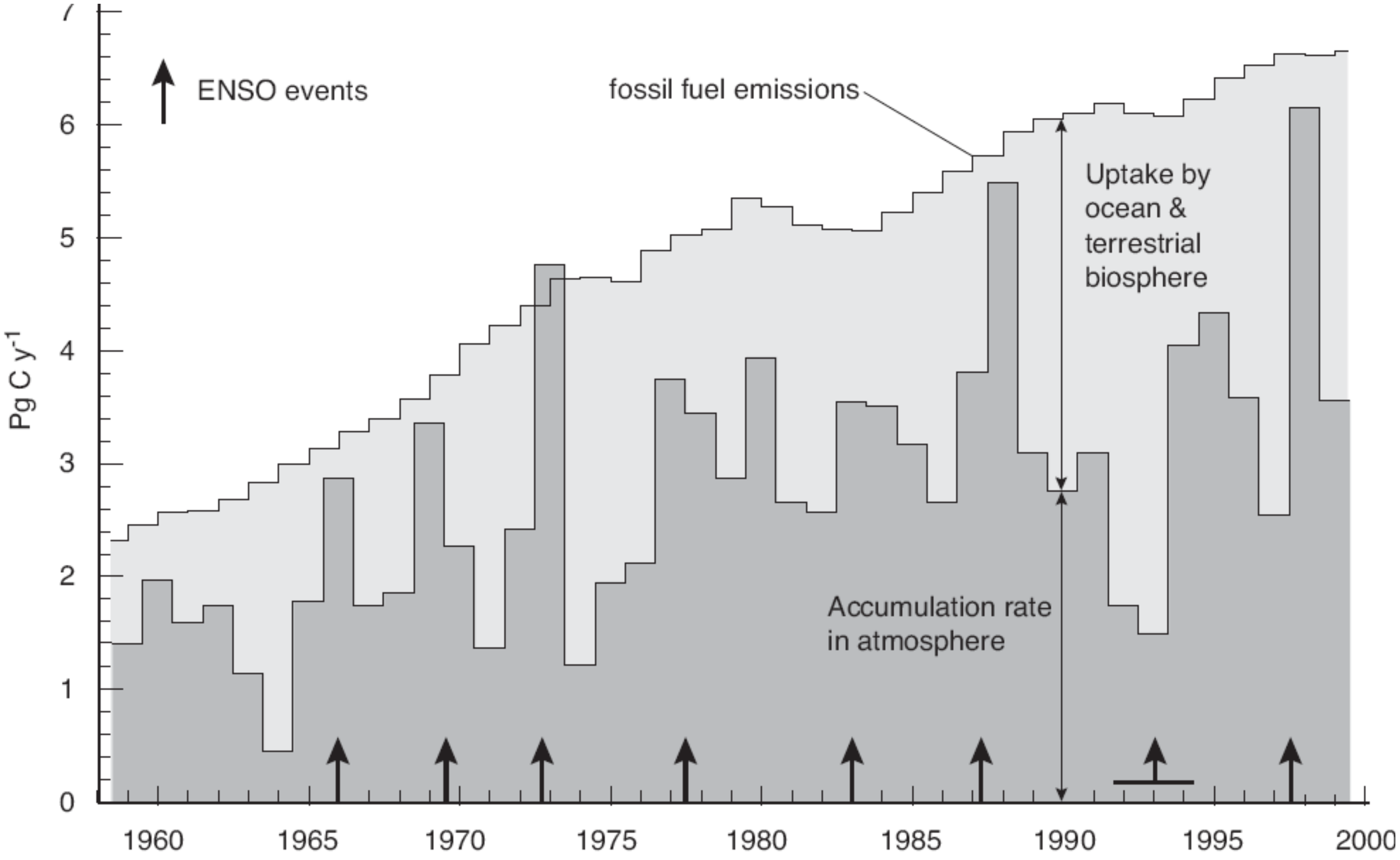


Saturation Horizon

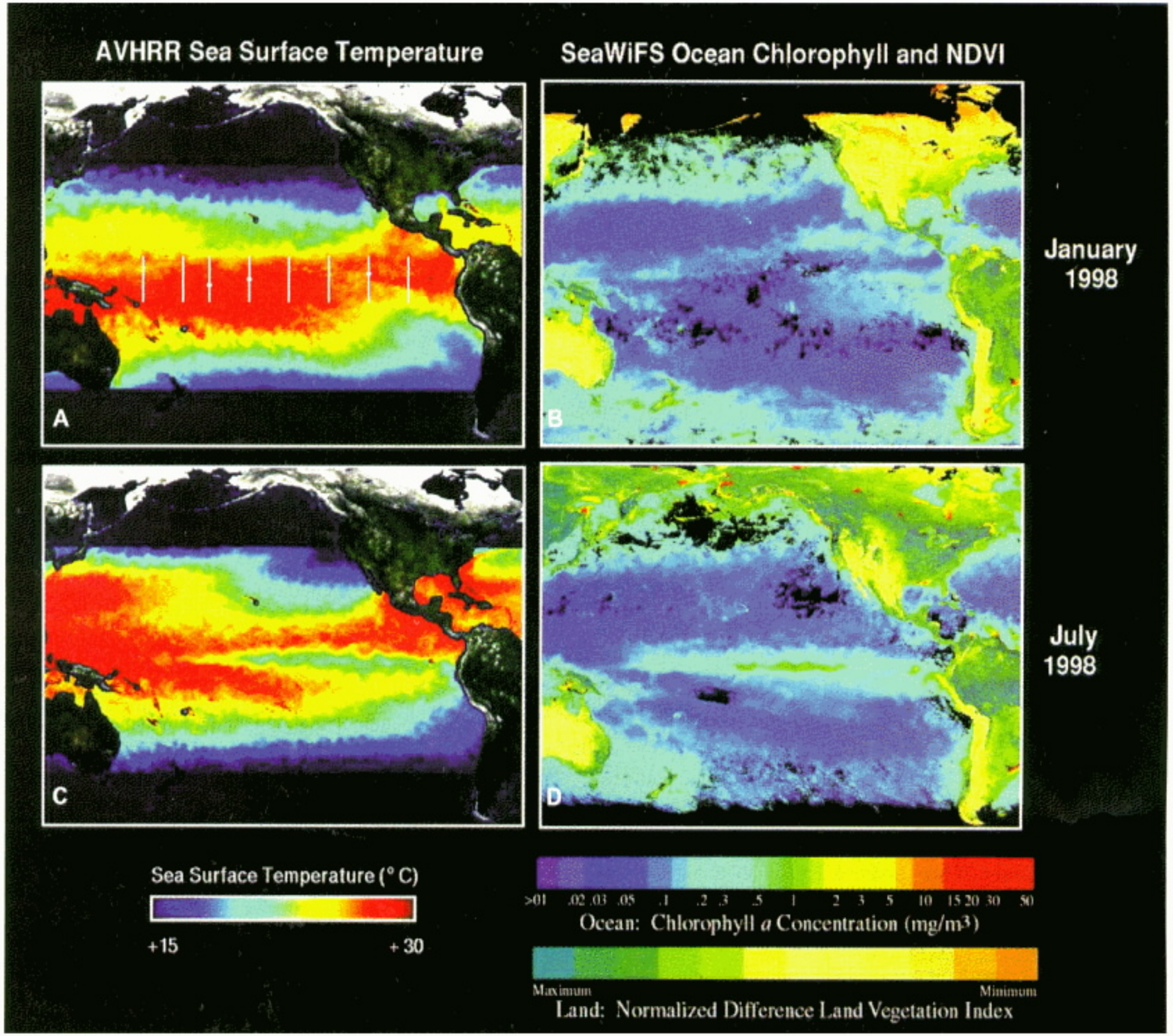
$$\Omega = \frac{\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{CO}_3^{2-}\right]}{K_{sp}}$$

Ω is the product of the concentrations (or activities) of the reacting ions that form the mineral (Ca2+ and CO32−), divided by the product of the concentrations of those ions when the mineral is at equilibrium (Ksp), that is, when the mineral is neither forming nor dissolving

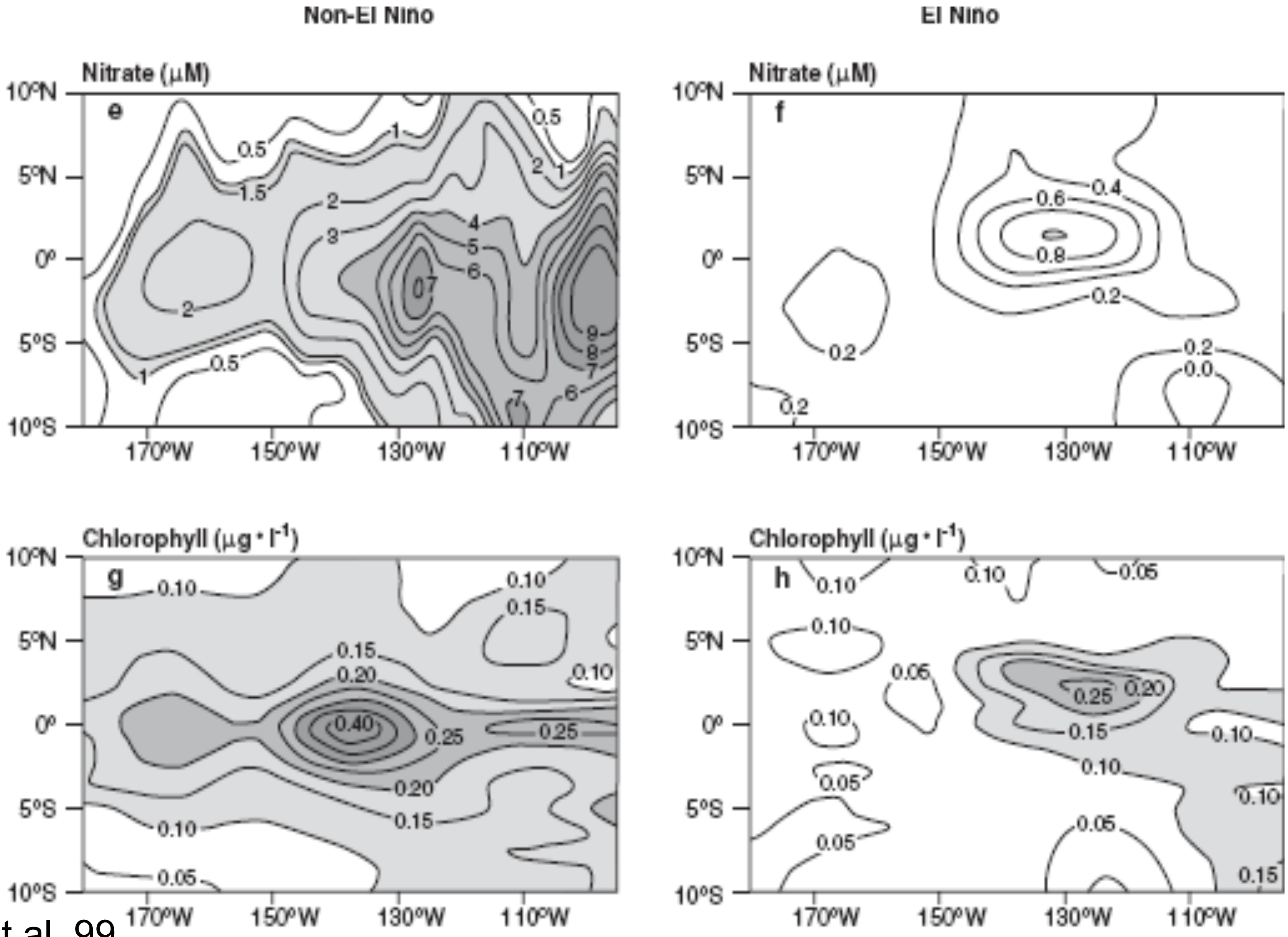
2.6 Interannual Variability : ENSO and the ocean carbon cycle



Sea Surface Temperature and Sea Surface Chlorophyll



Chlorophyll, Nitrate

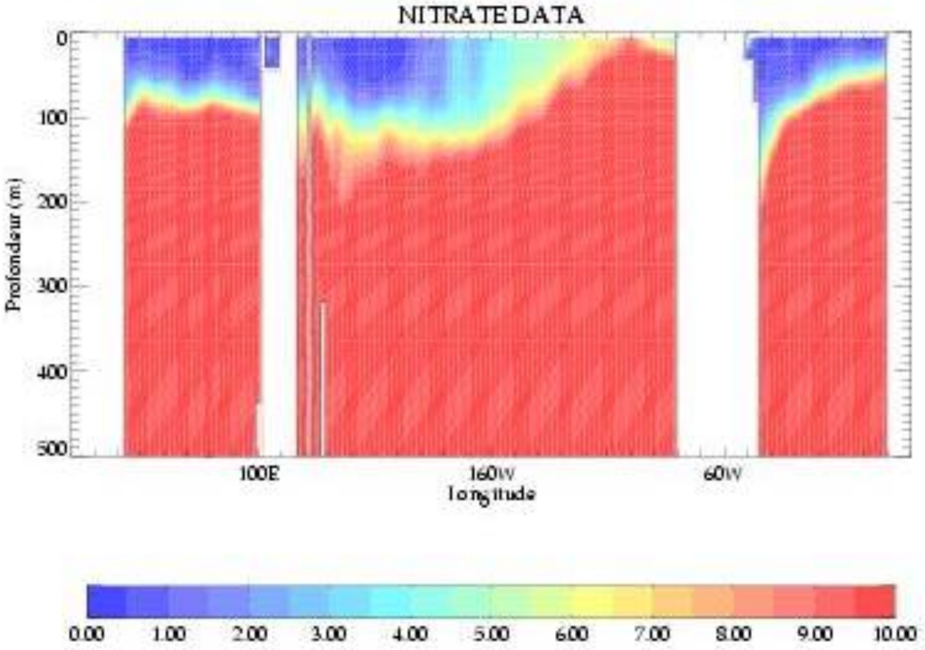


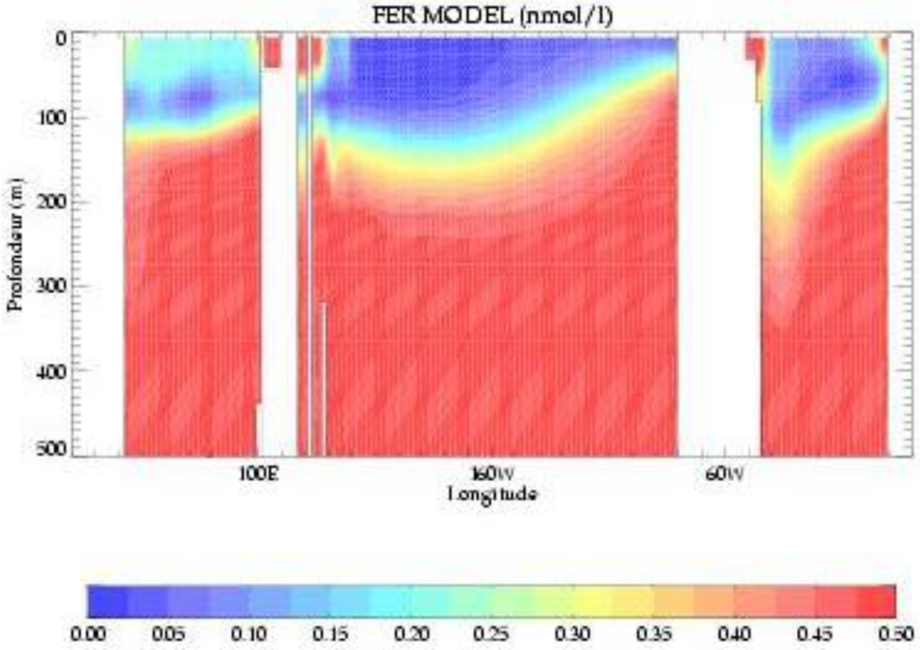
Chavez et al. 99

Response of surface chlorophyll to ENSO

- Decrease of upwelling intensity
- Upwelling fed with warmer and nutrient-poor waters

Climatologies of Nitrates (data) and dissolved iron (model) in the Eq Pac



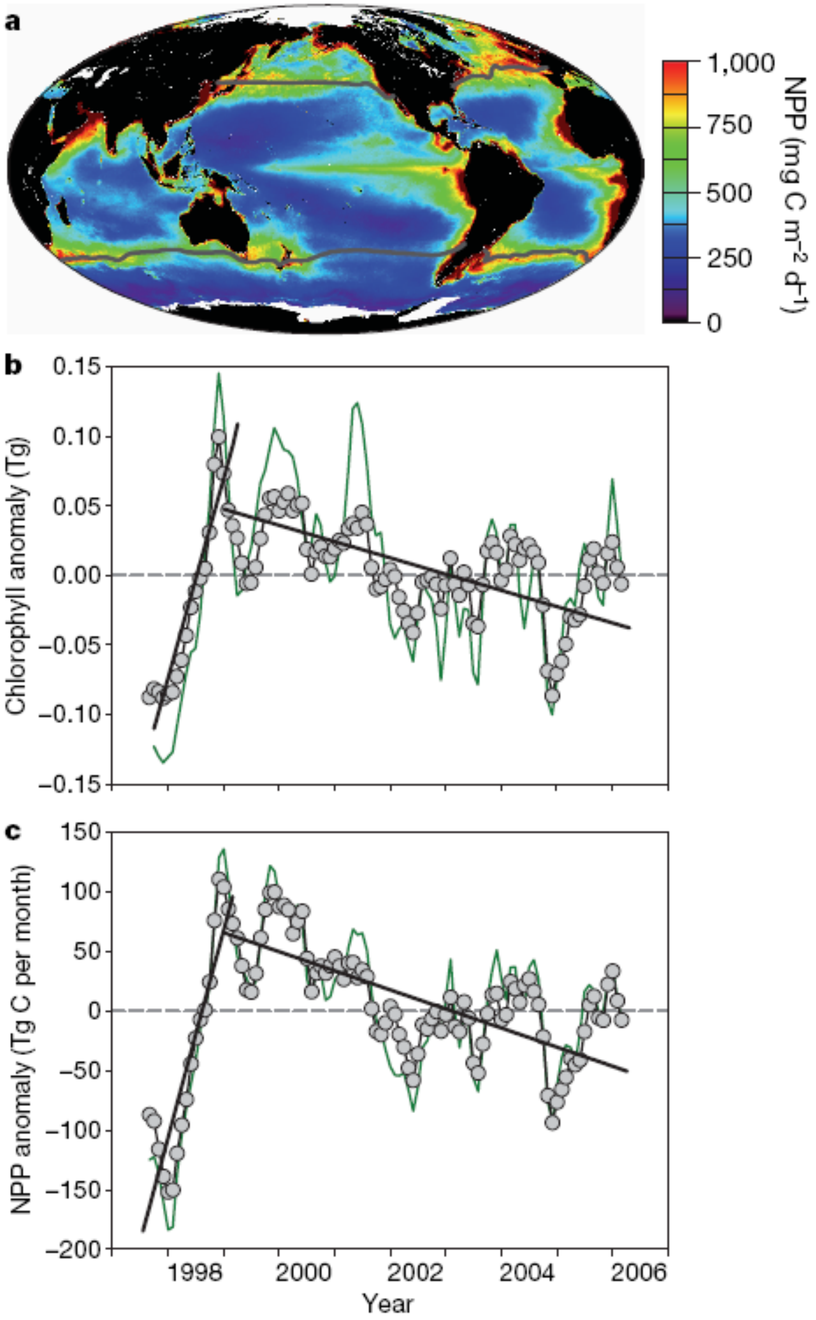


Response of surface chlorophyll to ENSO

LETTERS

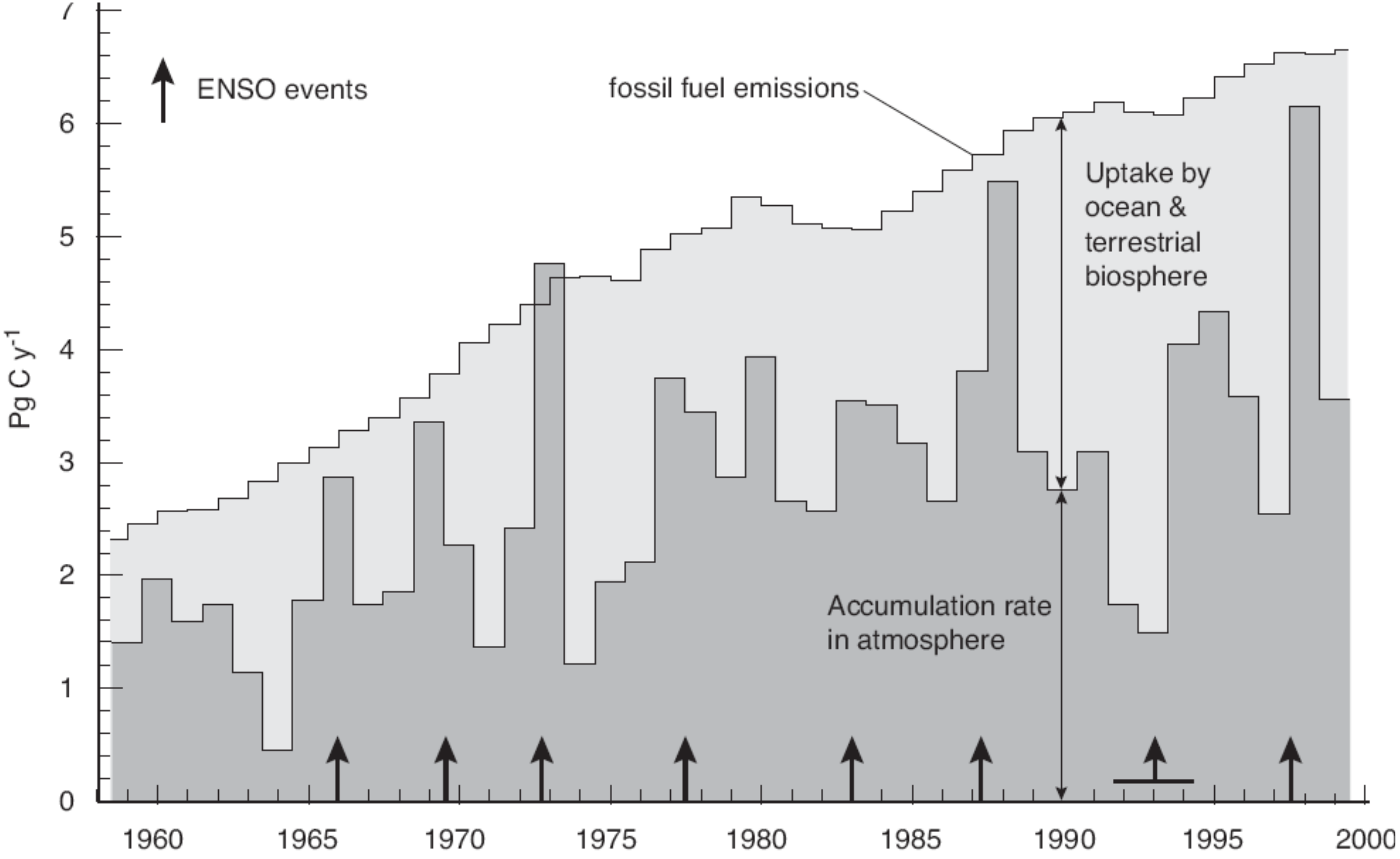
Climate-driven trends in contemporary ocean productivity

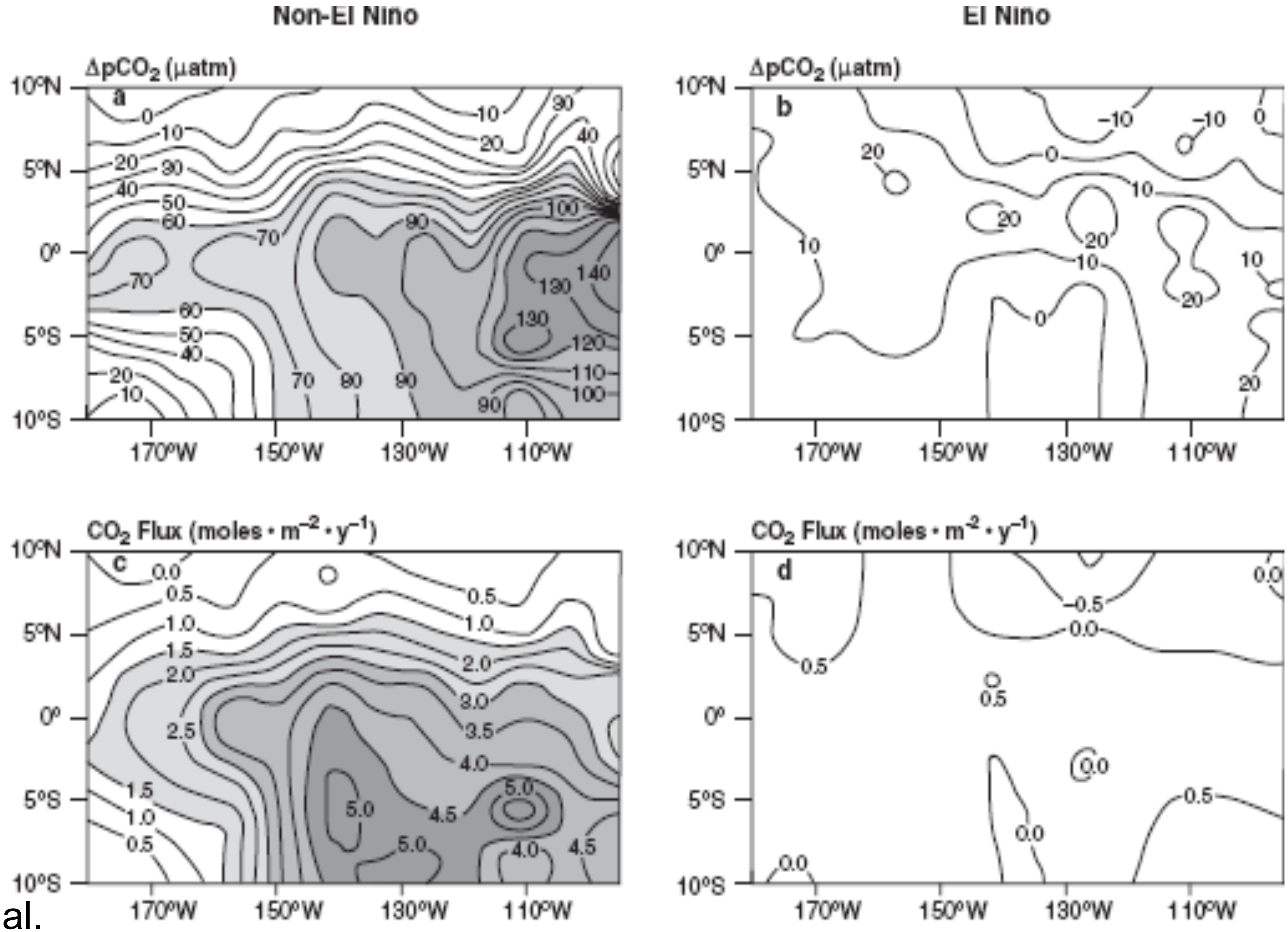
Michael J. Behrenfeld[1], Robert T. O'Malley[1], David A. Siegel[3], Charles R. McClain[4], Jorge L. Sarmiento[5], Gene C. Feldman[4], Allen J. Milligan[1], Paul G. Falkowski[6], Ricardo M. Letelier[2] & Emmanuel S. Boss[7]



2.6 Interannual Variability : ENSO and the ocean carbon cycle

And carbon fluxes?



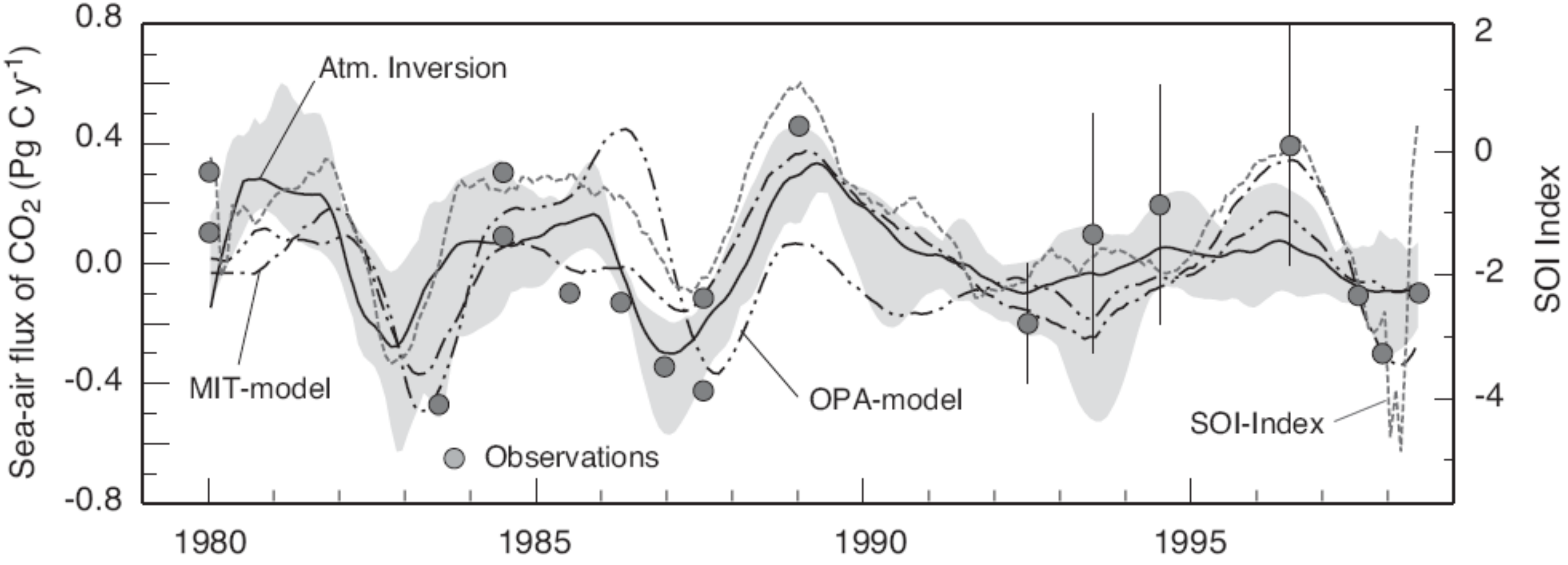
Non-El Nino
El Nino
ΔpCO2 (µatm)
ΔpCO2 (µatm)
a
b
CO2 Flux (moles • m-2 • y-1)
CO2 Flux (moles • m-2 • y-1)
c
d
10°N
5°N
0°
5°S
10°S
170°W
150°W
130°W
110°W
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
-10
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
-0.5

Chavez et al.

Response of ocean carbon fluxes to ENSO

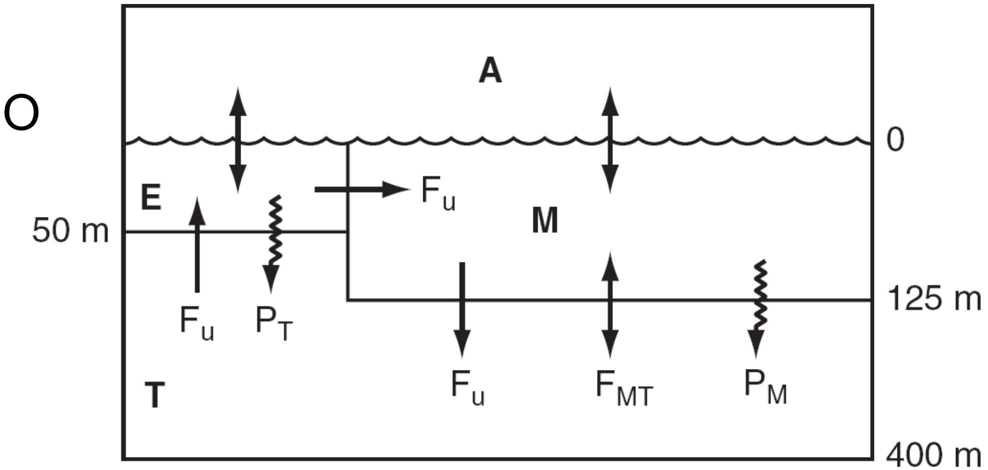
Outflux of 0.5 – 0.9 PgC/yr (normal years) → 0.1 – 0.3 PgC/yr (ElNino)

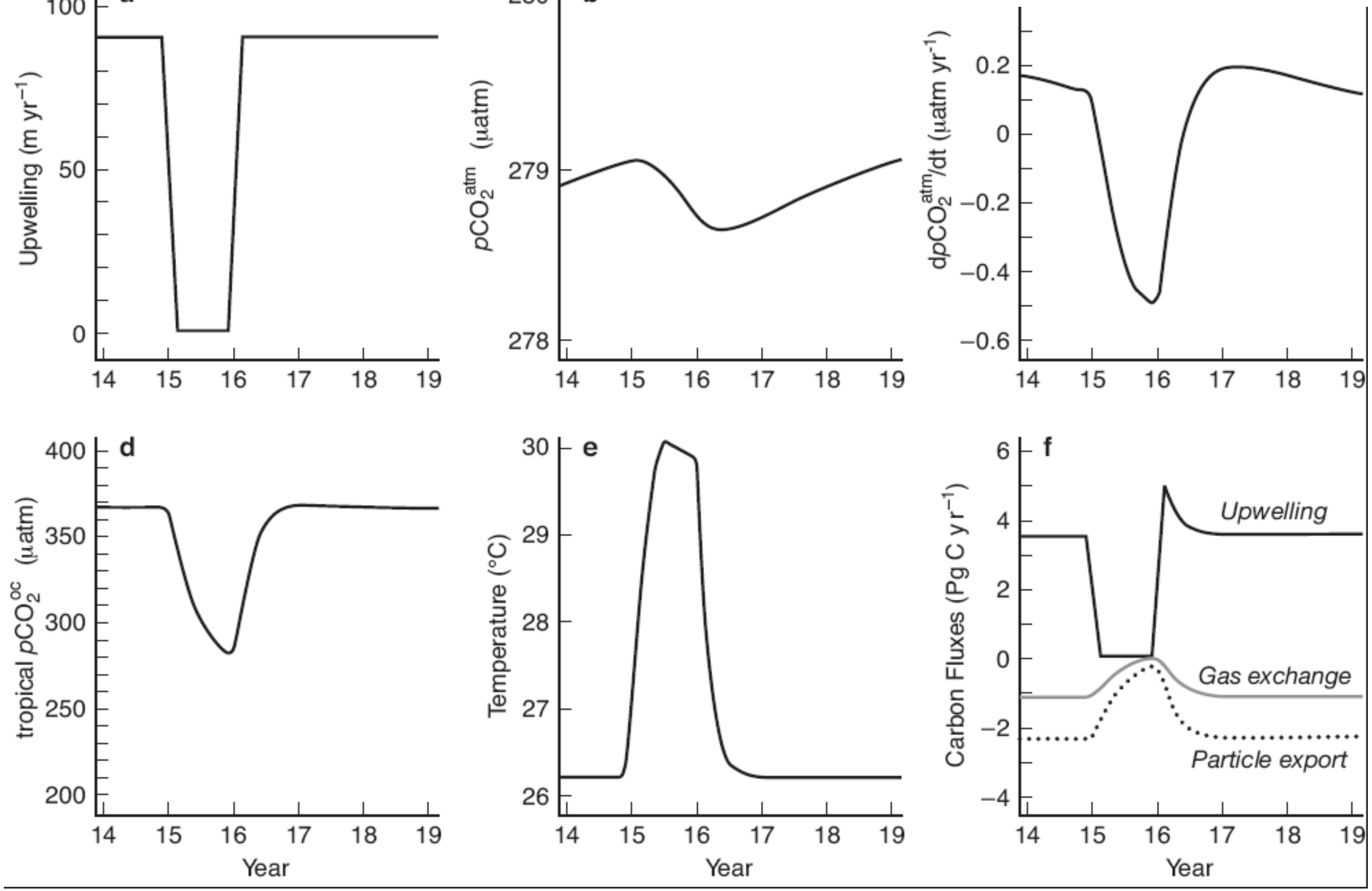
- reduction in upwelling rate
- upwelling fed by much warmer and DIC-poor waters.



Bousquet et al. 2000

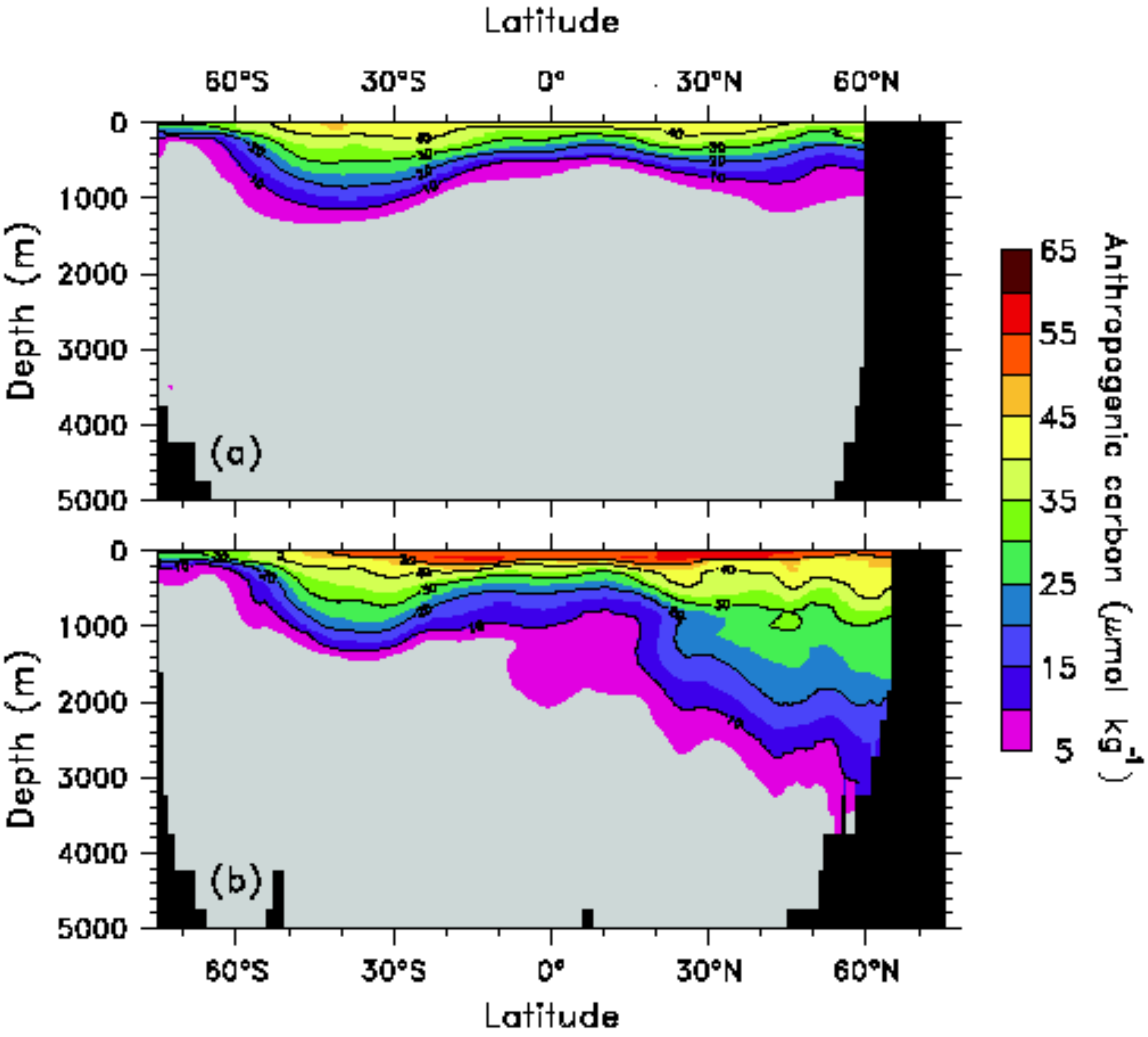
Response of ocean carbon fluxes to ENSO





(Siegenthaler
et Wenk, 1989)

3. Anthropogenic Perturbation



3. Anthropogenic Perturbation

Estimation of anthropogenic carbon in the Ocean

… Direct estimation :

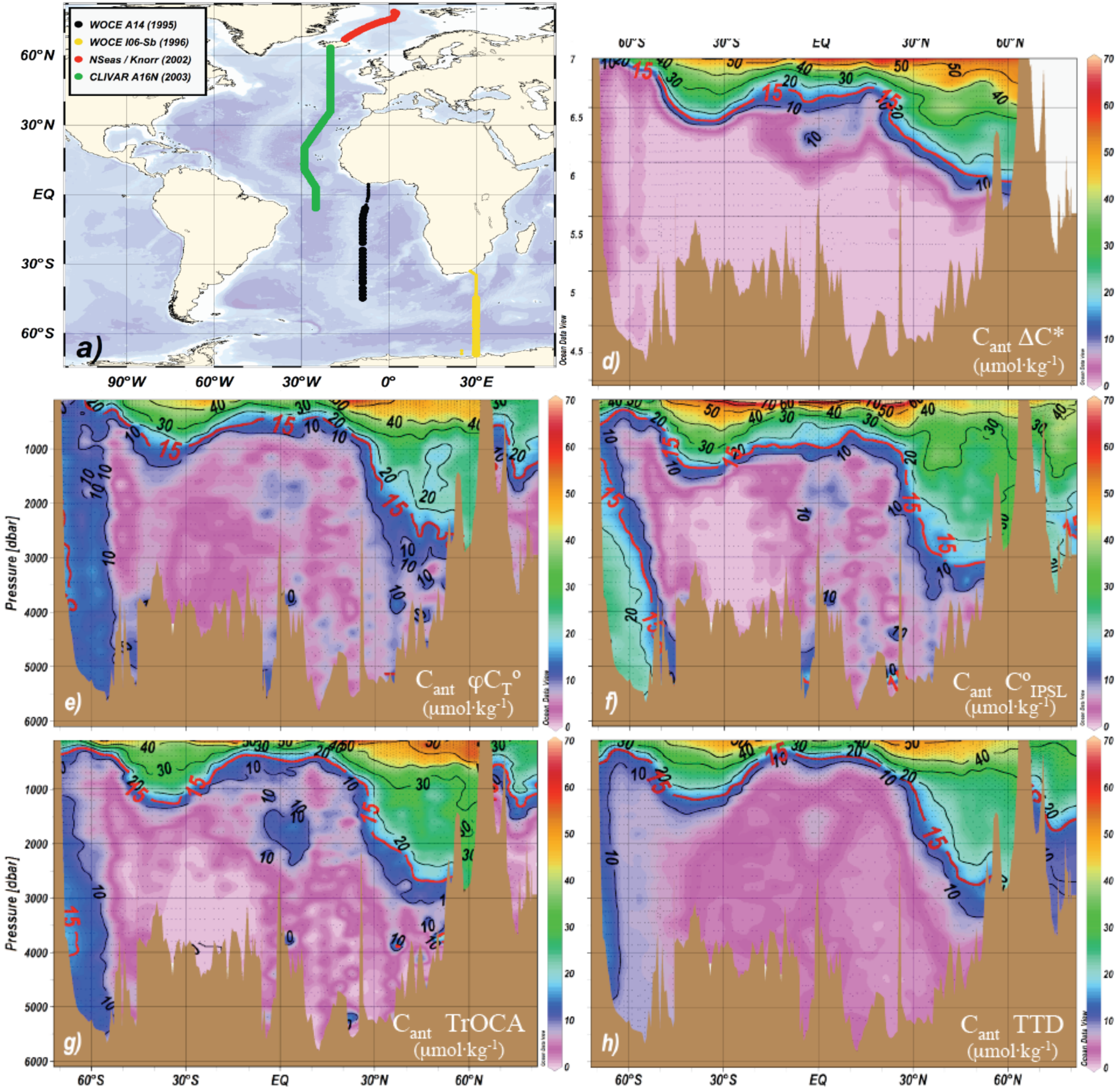
. DIC measurements : GEOSECS (1970s) → WOCE / JGOFS (1990s)
: variability (Rodgers et al. 2010) ? Precision ?
. Flux estimate based on in-situ ΔpCO_2
(Takahashi et al. 2009, Watson et al. 2010)

… Methods based on atm. Tracers (O2, d13C)

… Methods based on several oceanic tracers

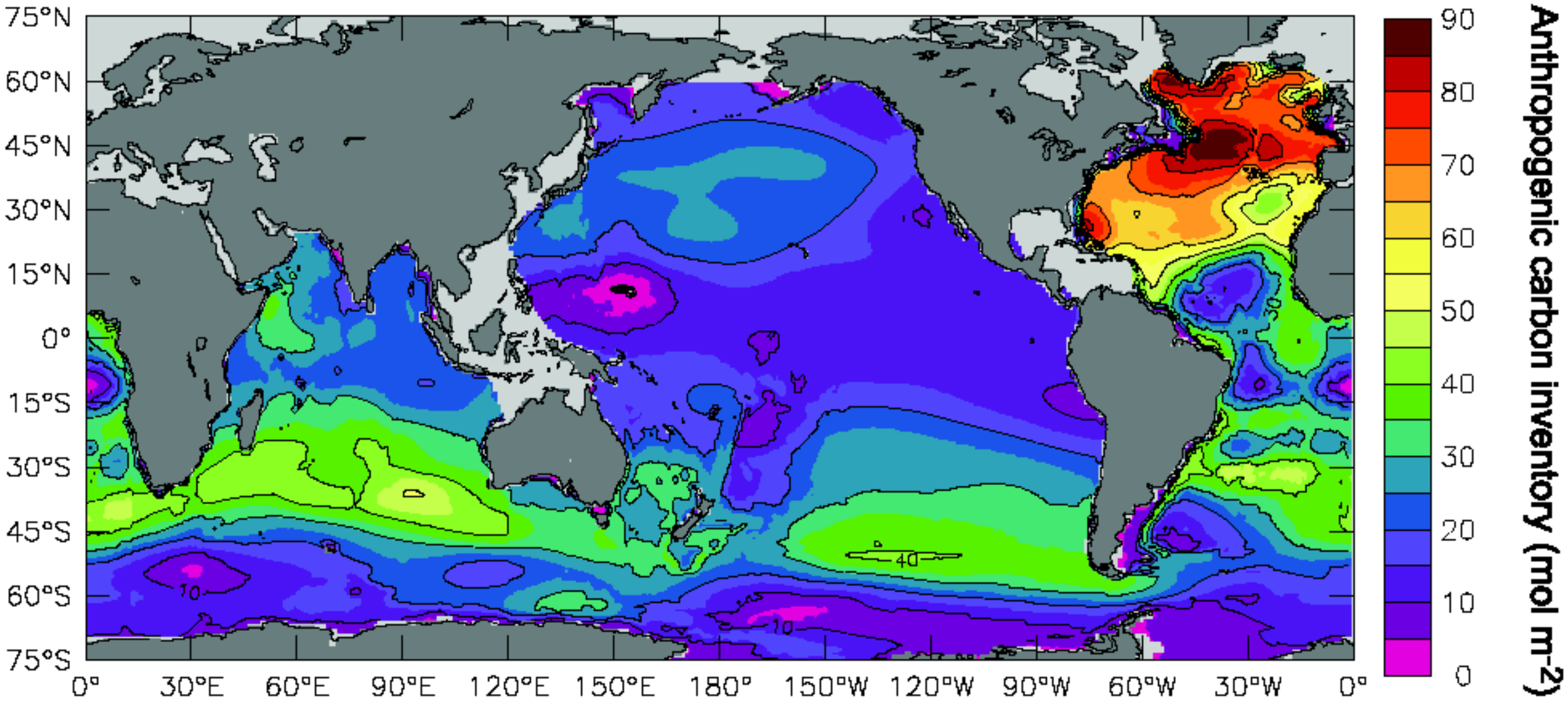
Several methods (ΔC^*, TTD, TroCA, C_{IPSL} …)

: use of DIC, Alk, Nutrients, T, S, … CFCs, …



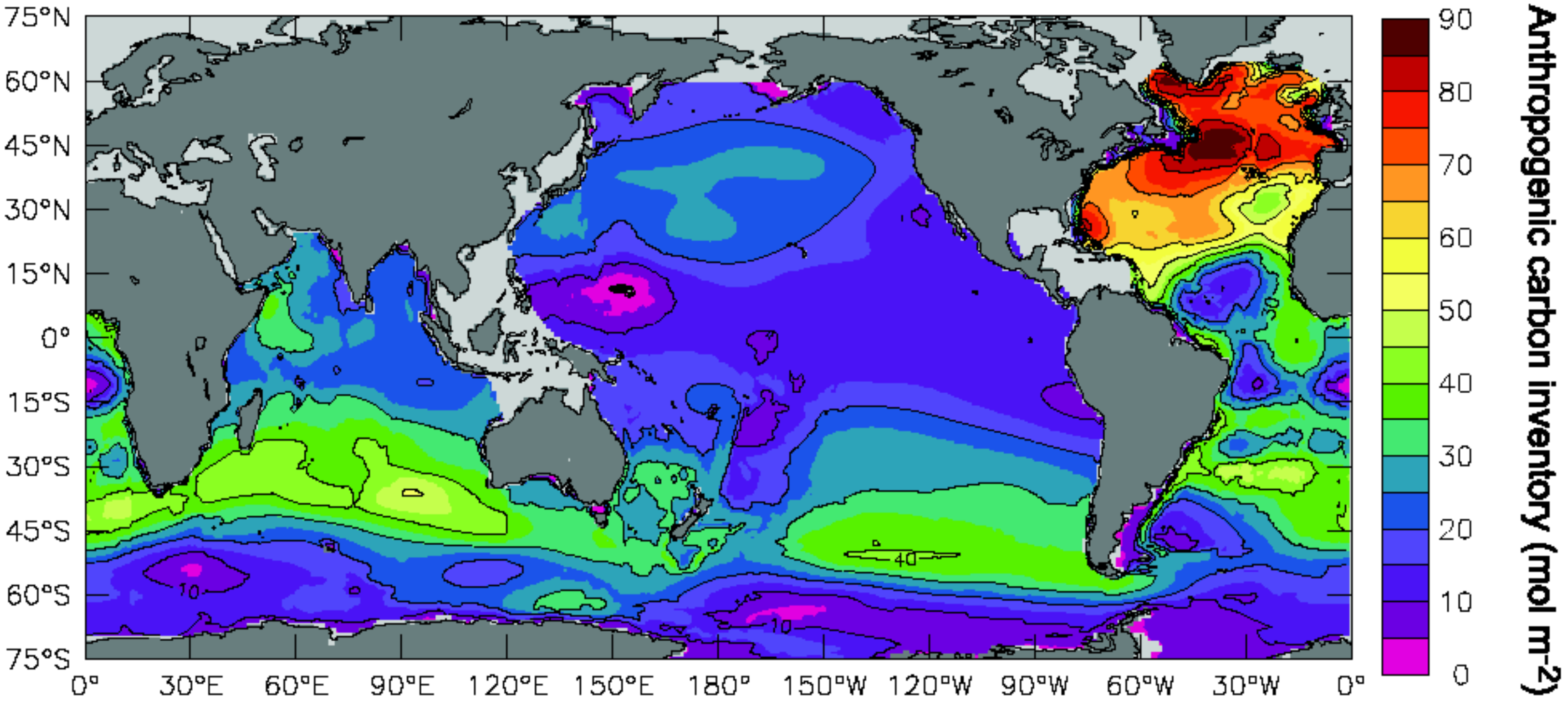
(Vasquez-Rodriguez et al. 2008 BGD)

3. Anthropogenic Perturbation



Sabine et al. 2004 : Anthropogenic carbon in 1995: 118 +- 19 PgC

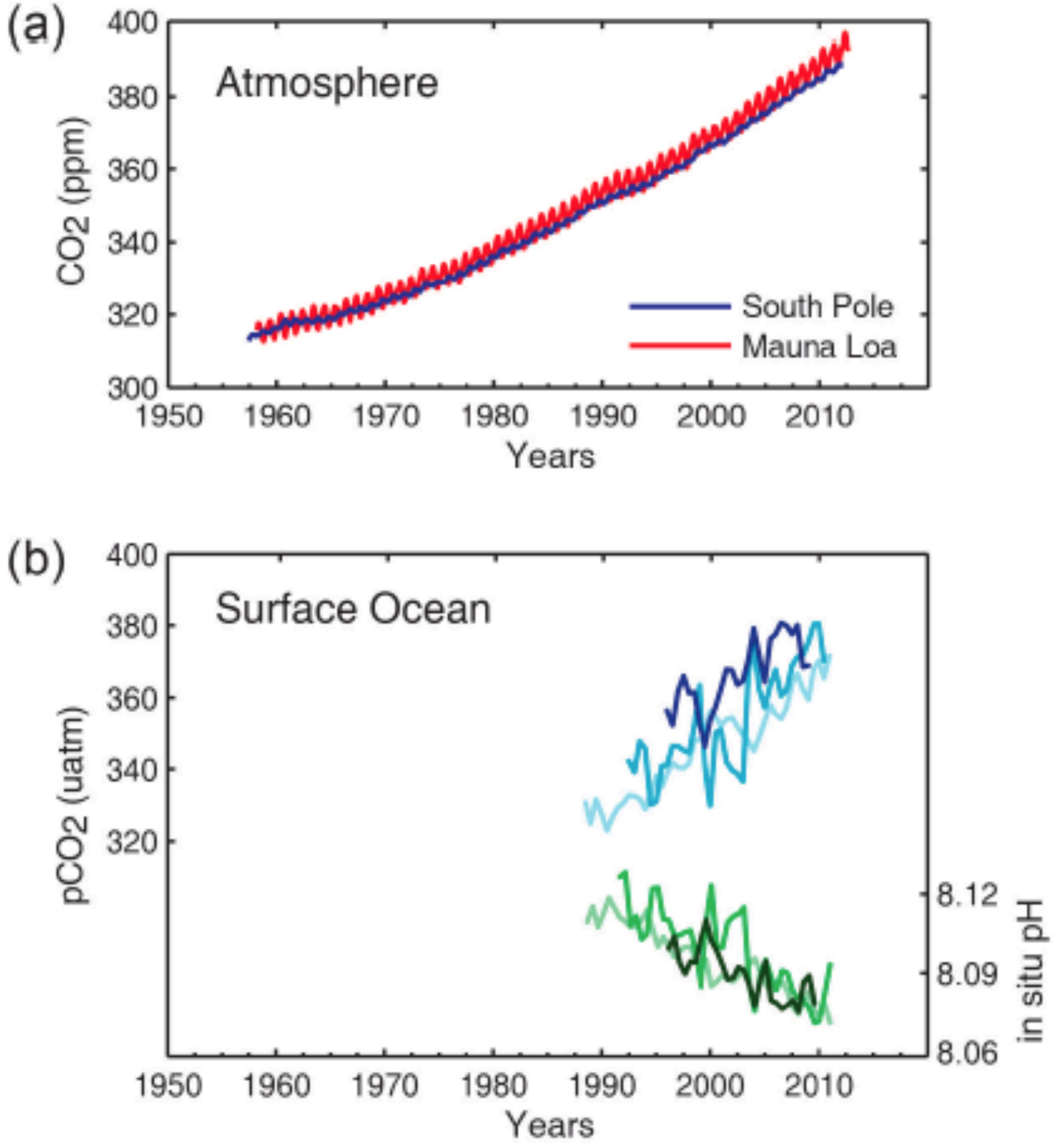
3. Anthropogenic Perturbation



Which processes are responsible for today's marine sink ?

> « Despite the importance of biological processes for the ocean's natural cycle, current thinking maintains that the oceanic uptake of anthropogenic CO2 is primarily a physically and chemically controlled process surimposed on a biogically driven carbon cycle that is close to steady state » (IPCC, 2001)

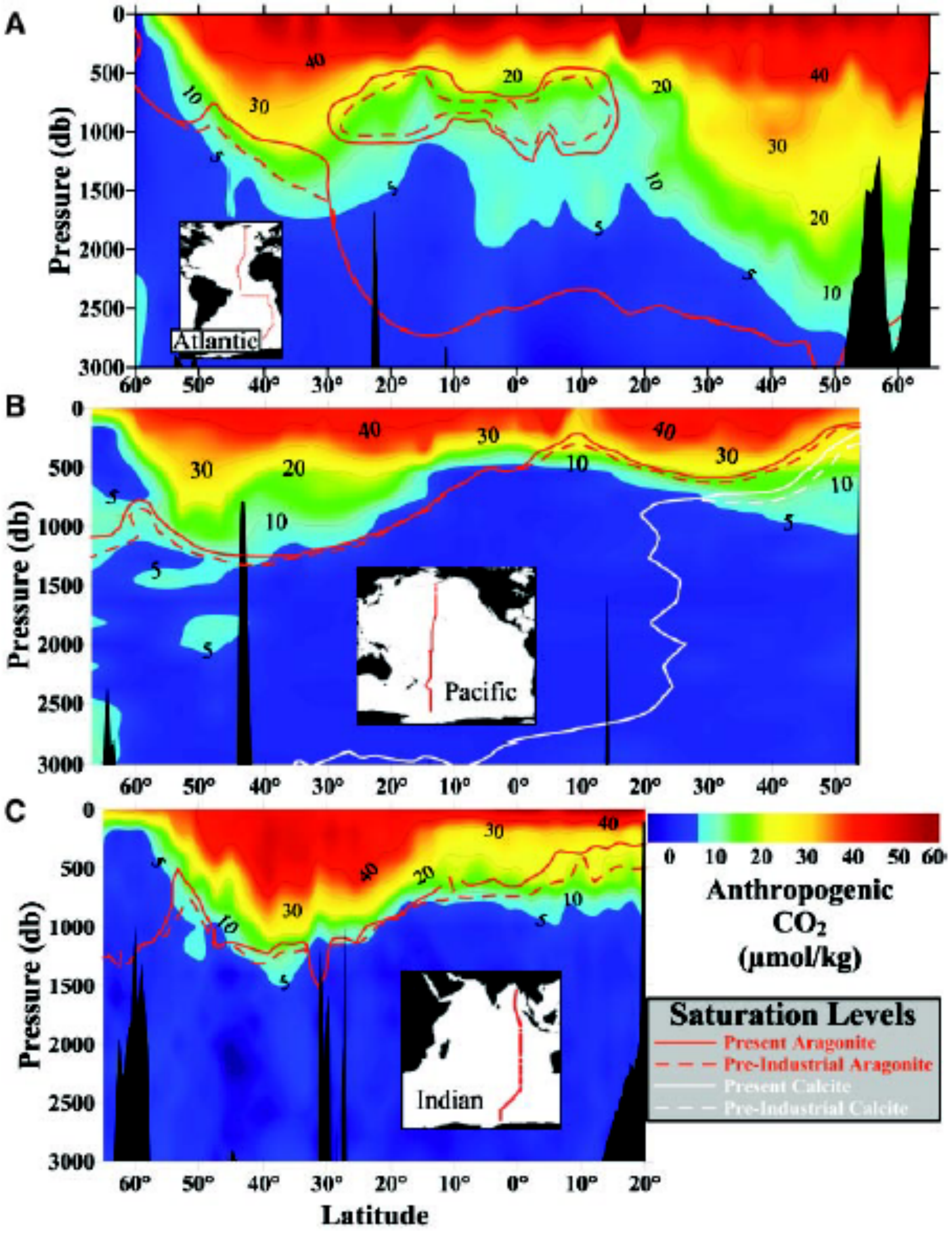
4. Ocean Acidification



Mean surface pH : -0.1

IPCC, 2013

4. Ocean Acidification

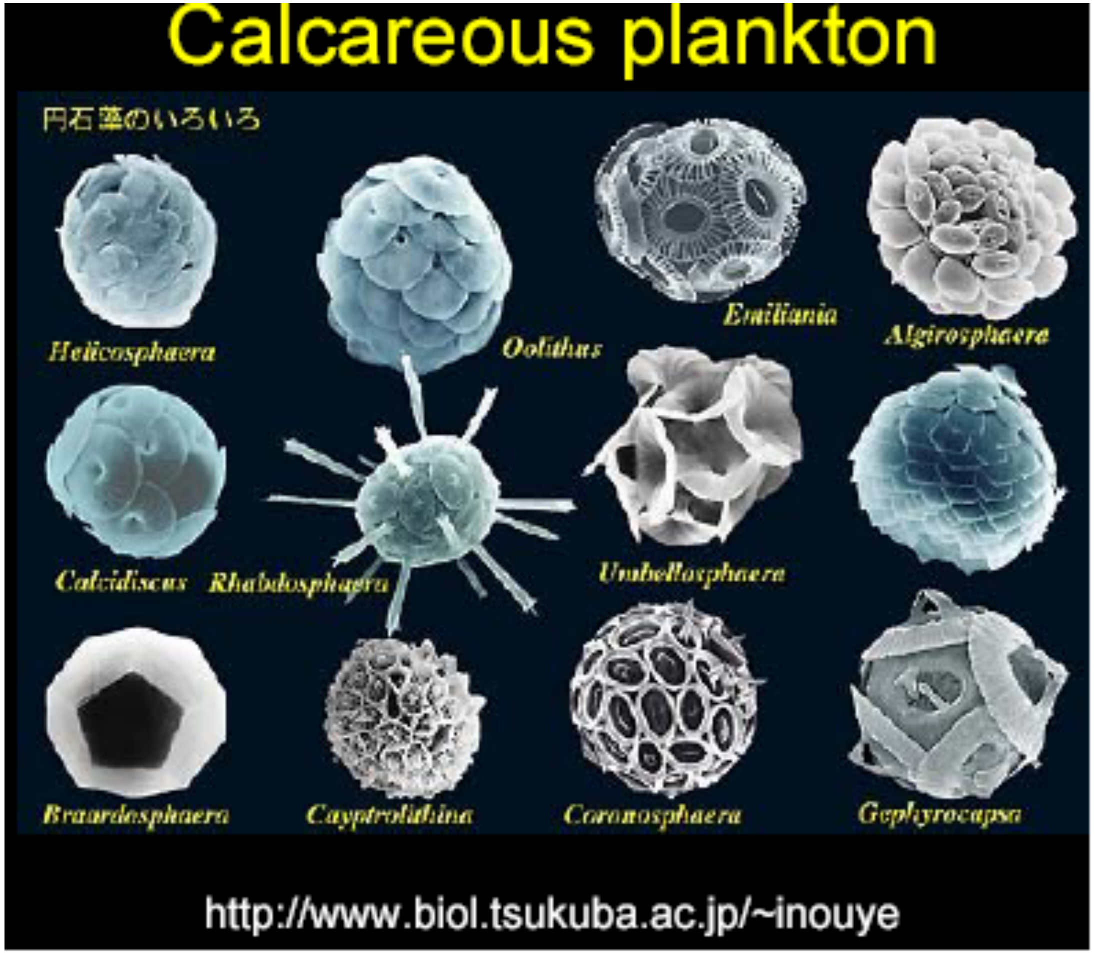


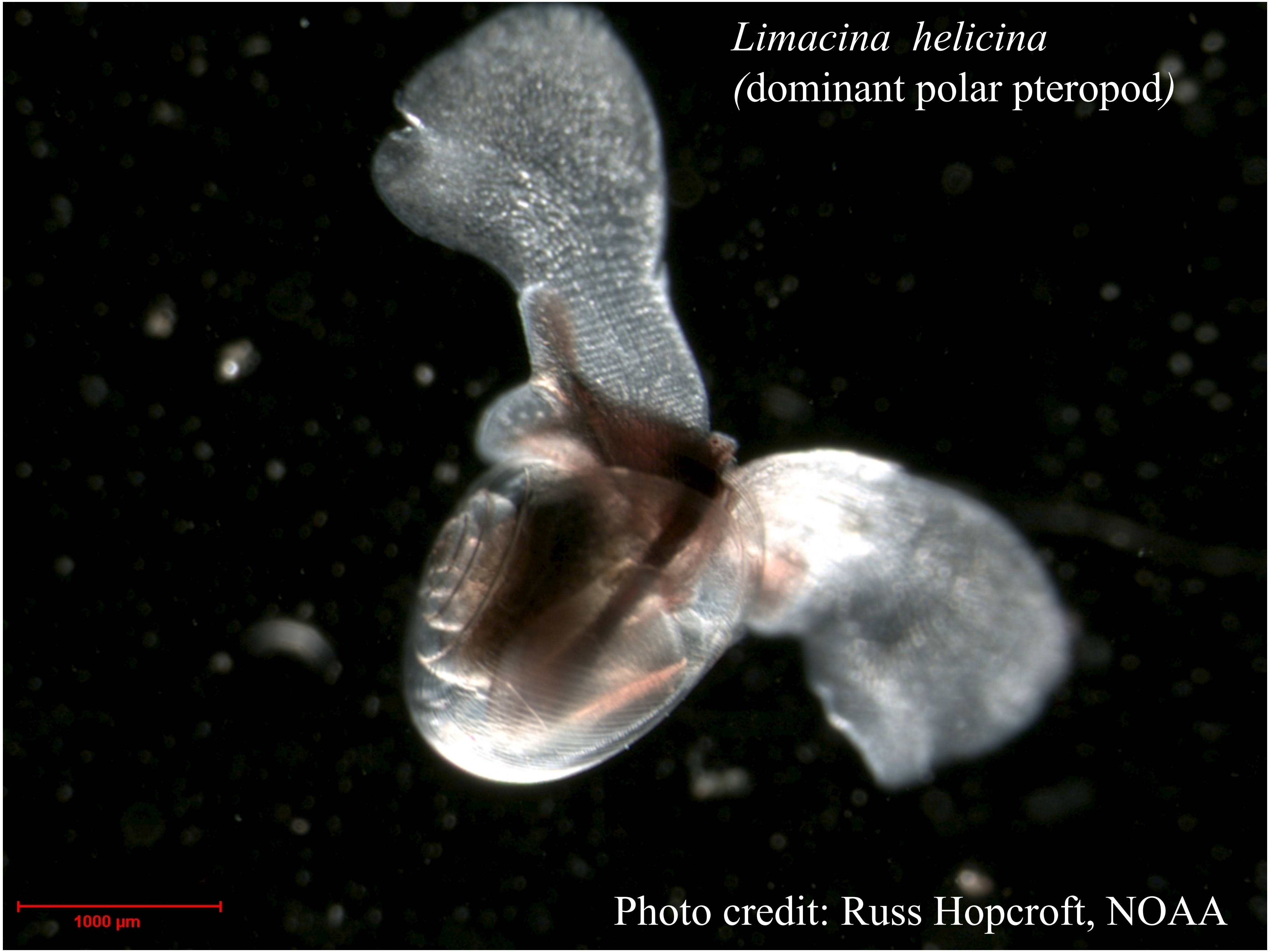
Horizon Saturation
vs. penetration of anth. Carbon

Mean surface pH : -0.1

Feely et al. 2004, Science

Coccolithophorids :





Limacina helicina
(dominant polar pteropod)

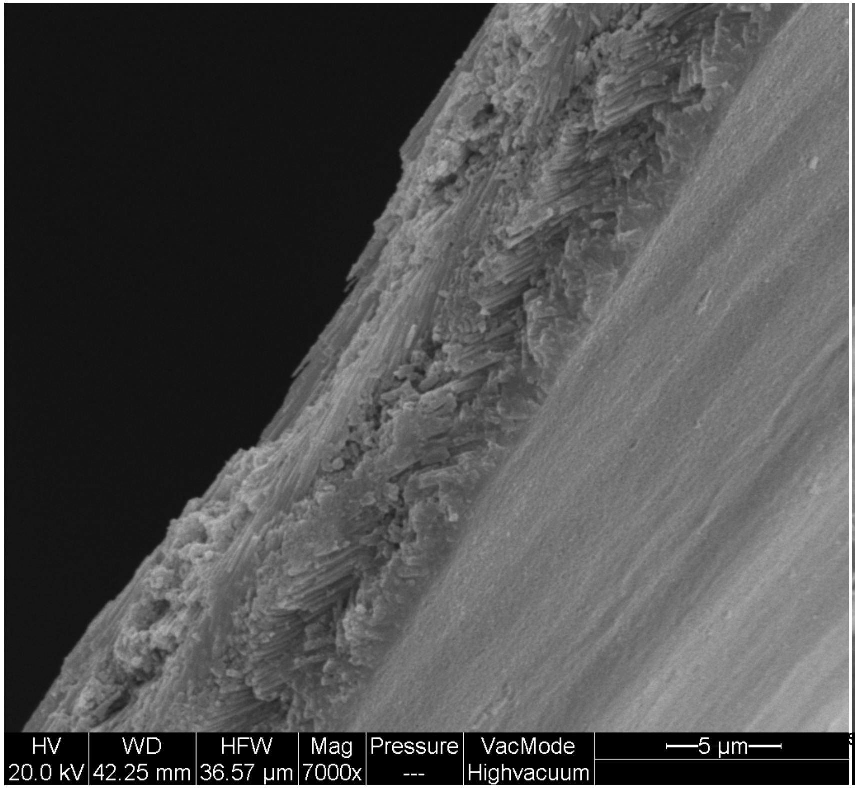
Photo credit: Russ Hopcroft, NOAA

Pteropod shells dissolve when $\Omega_A < 1$

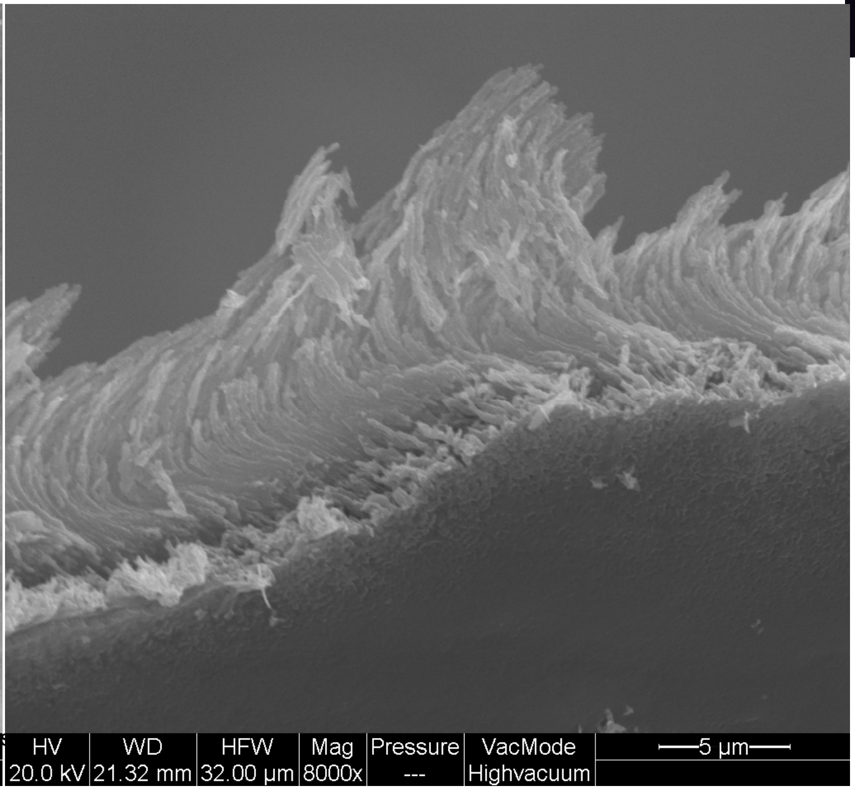
1. <u>Sediment traps:</u> pitting & partial dissolution as shells fall under ASH ($\Omega_A = 1$) *[Honjo et al., 2000]*
2. *<u>In vitro:</u>* studies *[Byrne et al., 1984; Feely et al., 1988]*
3. *<u>In vivo:</u>* 48-hr expmt. (1st described in *Feely et al., 2004*)
   - Further study (VF): dissolution starts on leading edge

Clio pyramidata

Normal shell

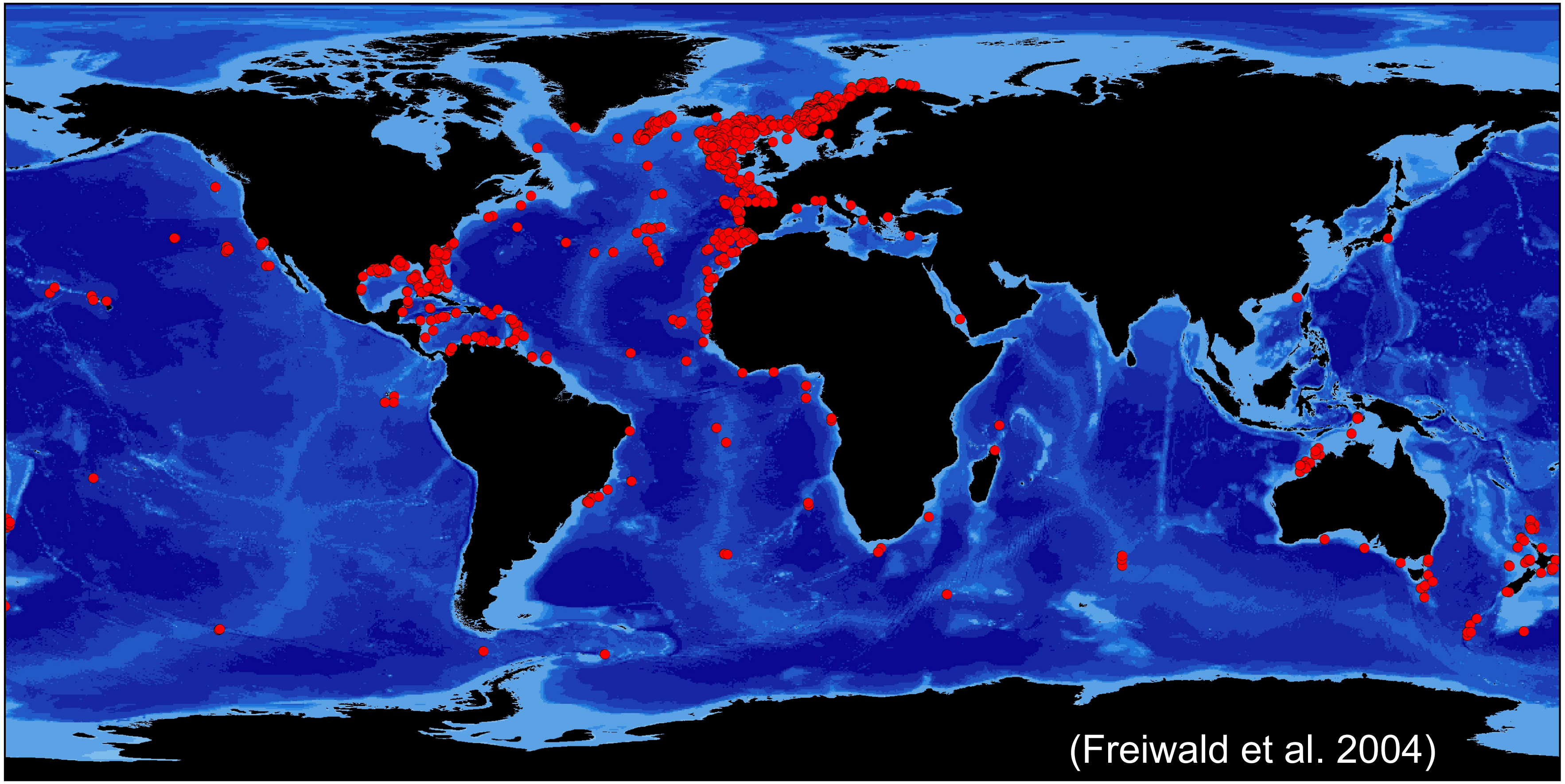


Exposed shell



Aperture (~7 µm): Aragonite rods exposed

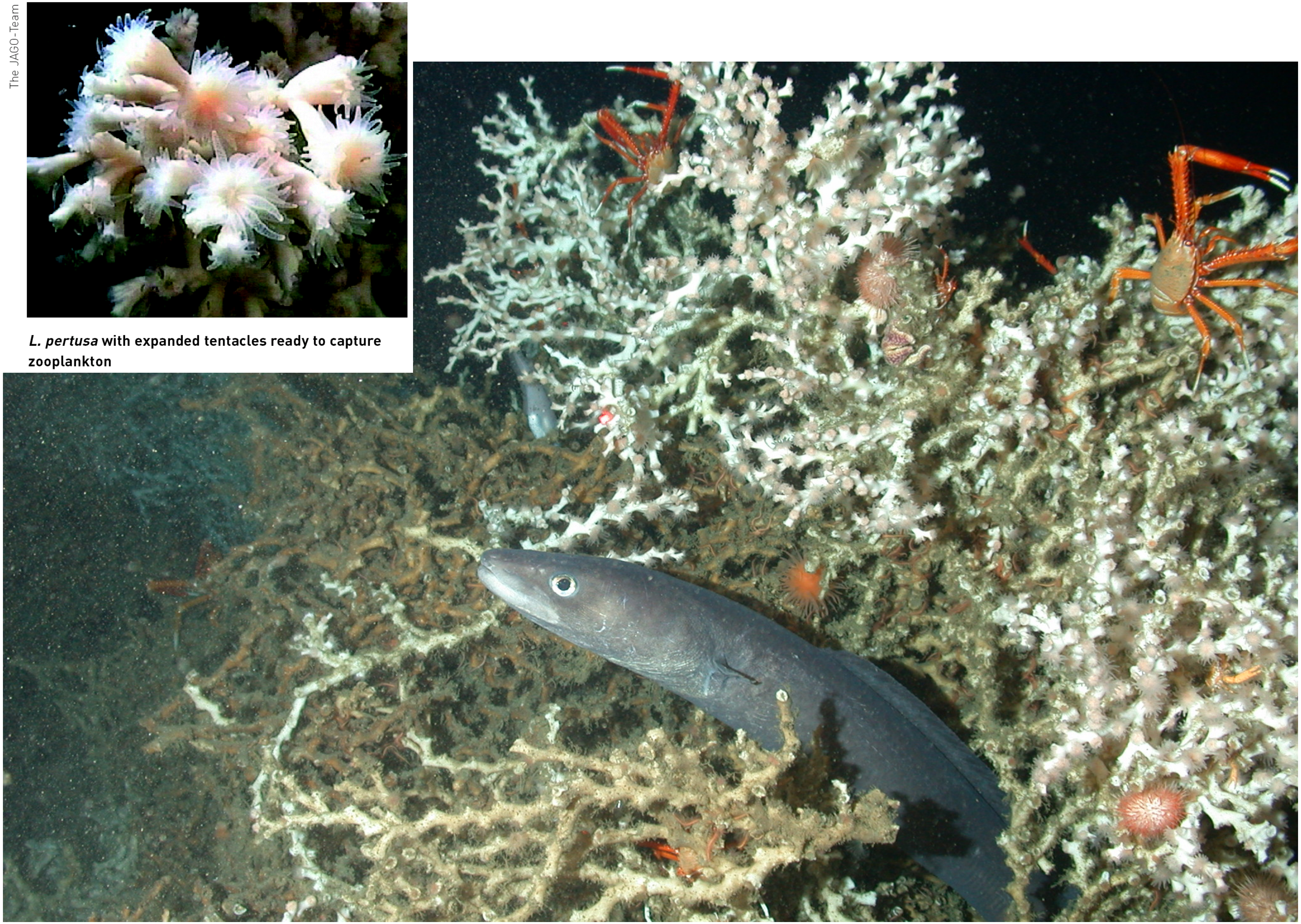
Global Distribution of Deep-Sea Reef Forming (Scleractinian) Corals



(Freiwald et al. 2004)

- Found in all ocean basins
- Conservative estimate

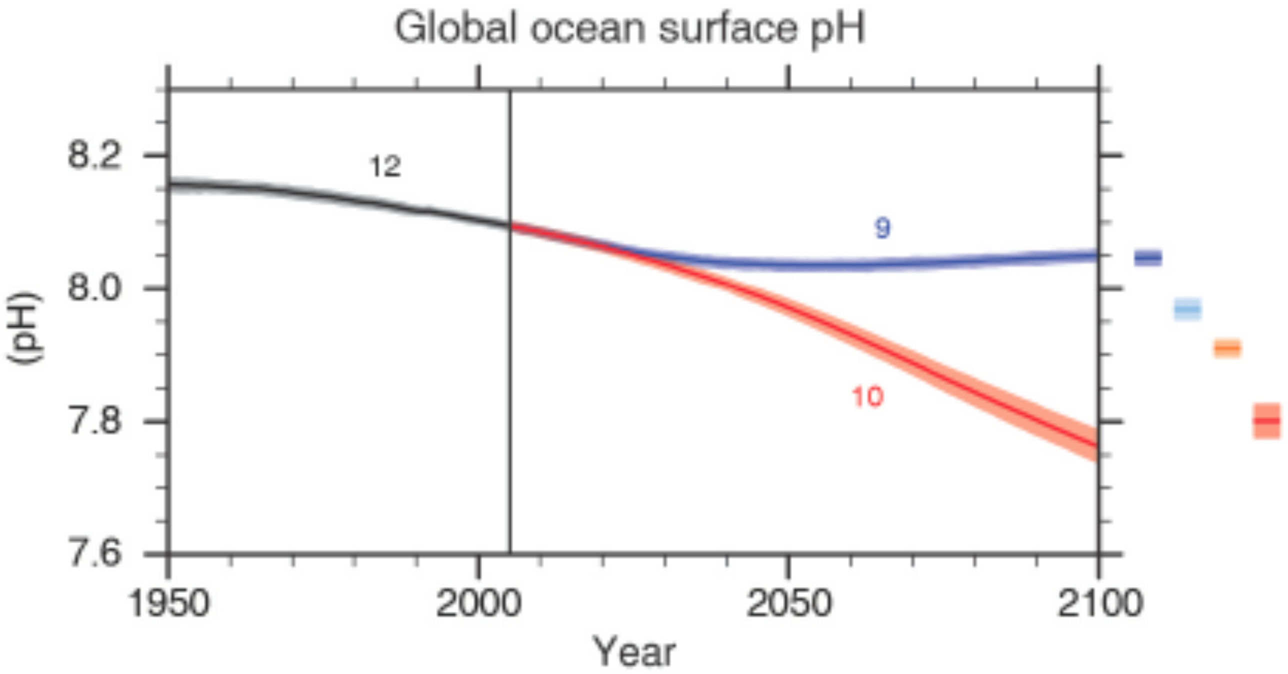
Lophelia pertusa, Madrepora oculata, Goniocorella dumosa, Oculina varicosa, Enallopsammia profunda, Solenosmilia variabilis

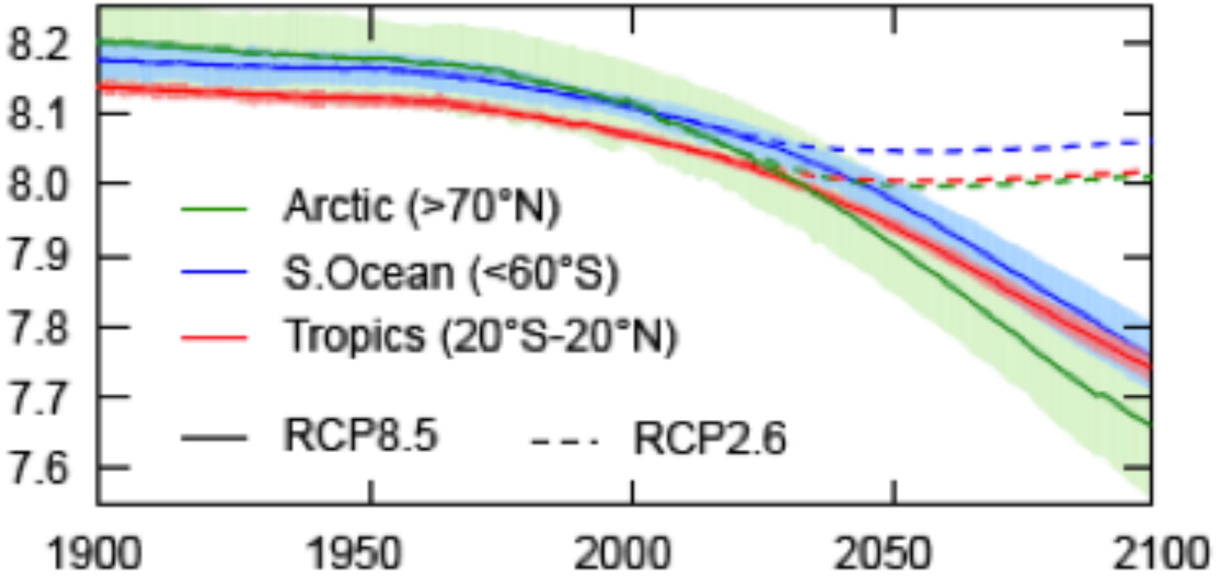


The JAGO-Team

L. pertusa with expanded tentacles ready to capture zooplankton

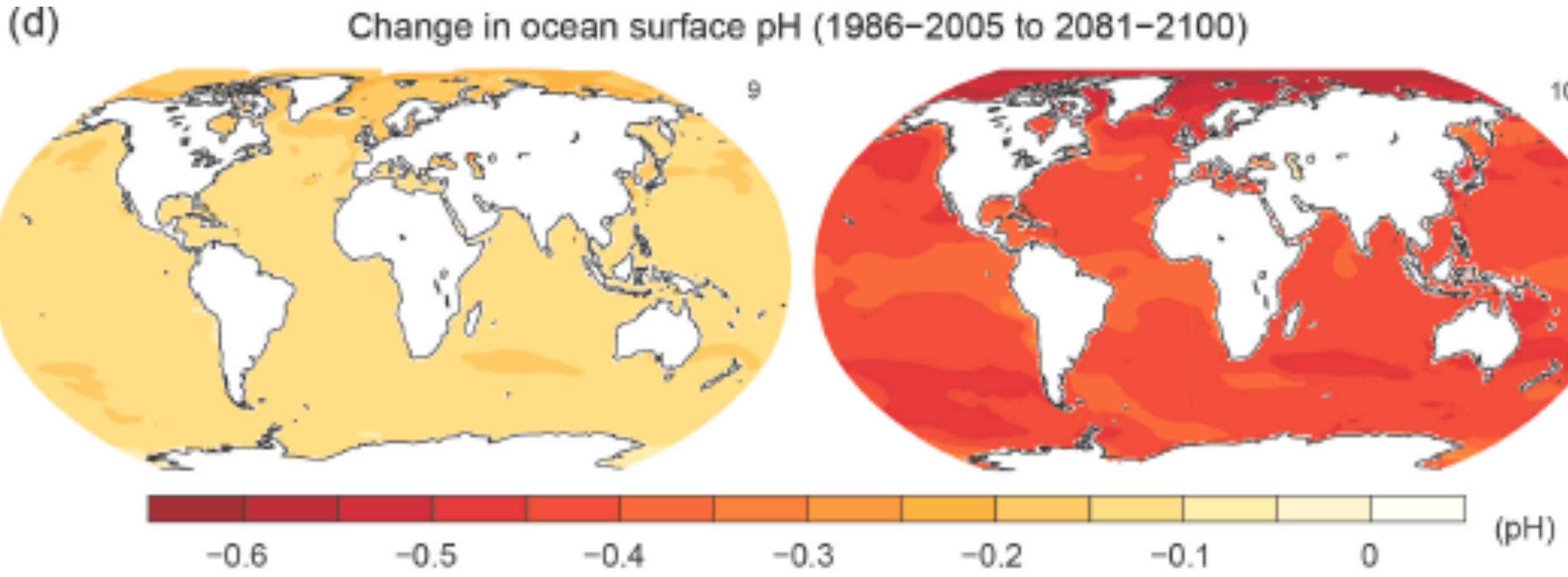
4. Ocean Acidification : Projections with RCP scenarios



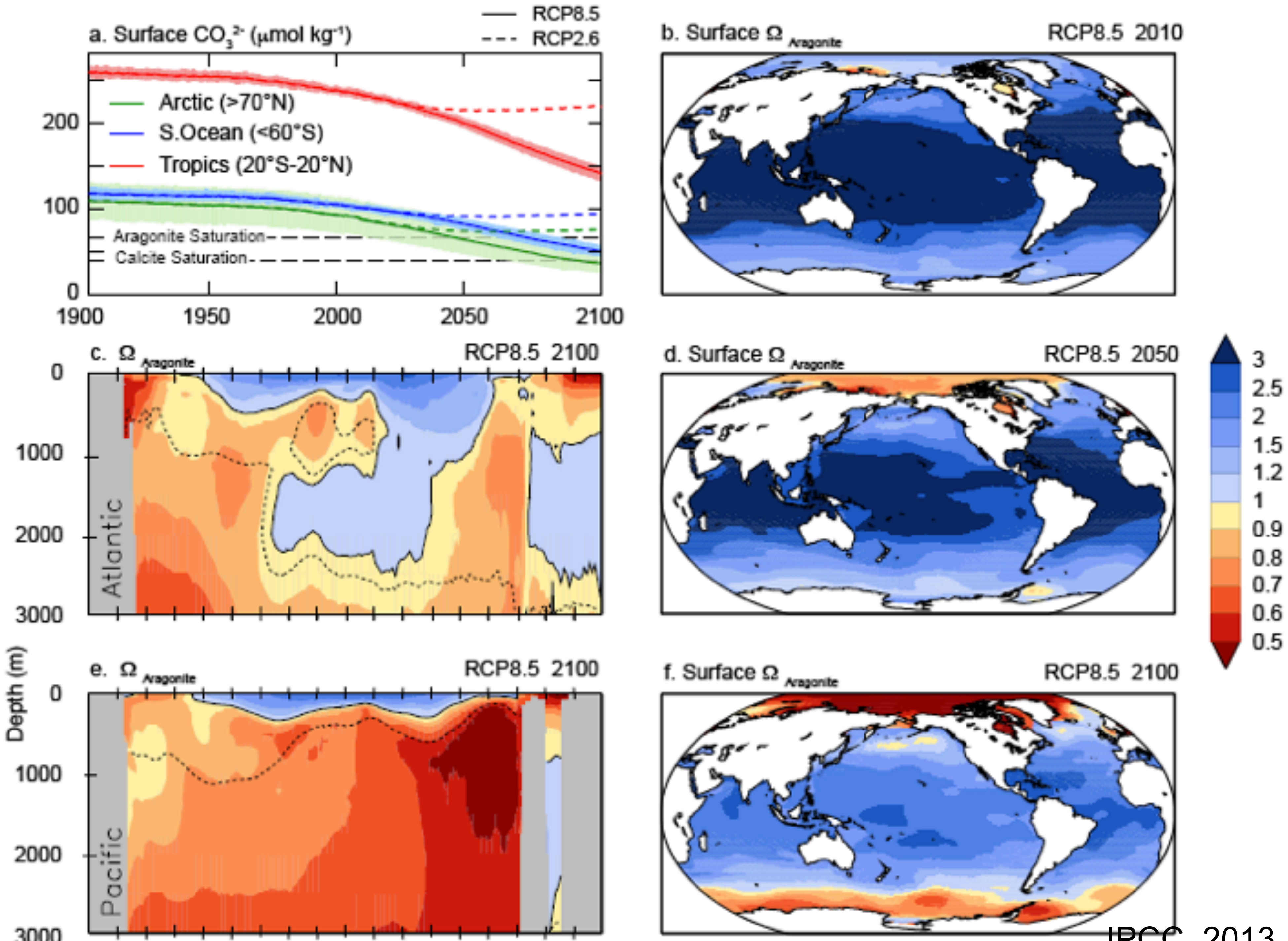


IPCC, 2013

4. Ocean Acidification : Projections with RCP scenarios

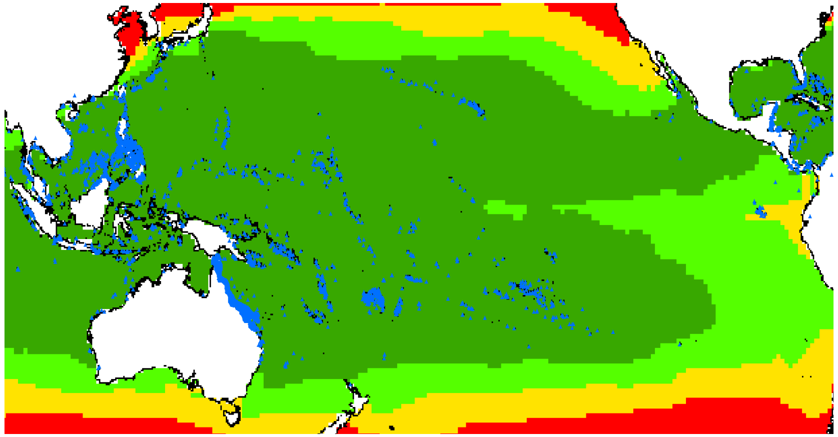


IPCC, 2013

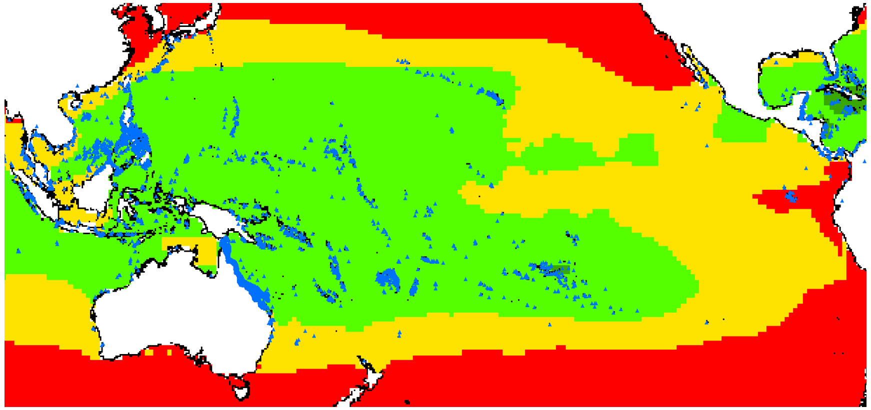

a. Surface CO_3^{2-} (µmol kg^{-1})
RCP8.5
RCP2.6
Arctic (>70°N)
S.Ocean (<60°S)
Tropics (20°S-20°N)
Aragonite Saturation
Calcite Saturation
0
100
200
1900
1950
2000
2050
2100
b. Surface $\Omega_{Aragonite}$
RCP8.5 2010
c. $\Omega_{Aragonite}$
RCP8.5 2100
Atlantic
0
1000
2000
3000
d. Surface $\Omega_{Aragonite}$
RCP8.5 2050
3
2.5
2
1.5
1.2
1
0.9
0.8
0.7
0.6
0.5
Depth (m)
e. $\Omega_{Aragonite}$
RCP8.5 2100
Pacific
0
1000
2000
3000
f. Surface $\Omega_{Aragonite}$
RCP8.5 2100

IPCC, 2013

Preindustrial Ω_{Arag} (at 280 μatm)

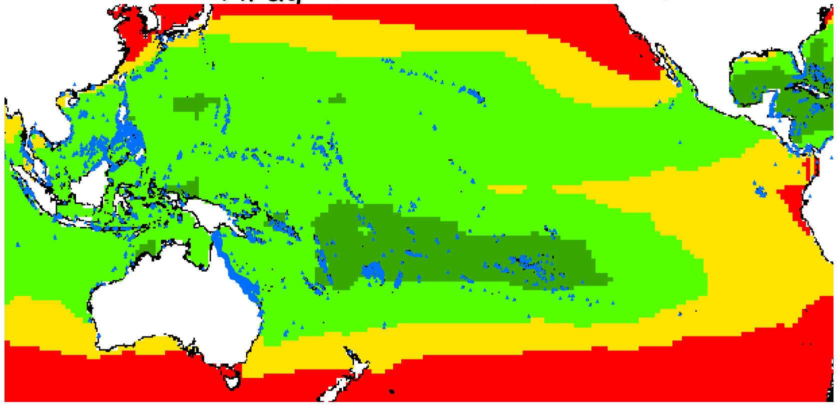


2030 Ω_{Arag} (at 415 μatm)

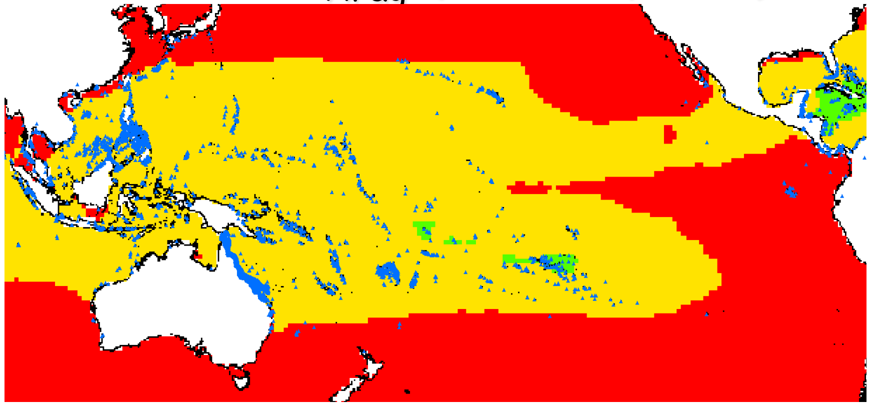


- 🟩 > 4 (Optimal)
- 🟩 3.5 - 4 (Adequate)
- 🟨 3 - 3.5 (Marginal)
- 🟥 < 3 (Extremely Low)
- ⬜ No Data

2010 Ω_{Arag} (at 375 μatm)



2070 Ω_{Arag} (at 517 μatm)



- *Kleypas et al. 1999 (Science)*
- *Guinotte et al. 2003 (Coral Reefs)*

*Marginal in terms of →

$\Omega_{Arag} = [Ca^{2+}][CO_3^{2-}] / Ksp^*$

**IPCC SRES B2: 620 uatm in 2100

References:

-Sarmiento J.L. and N. Gruber, Ocean Biogeochemical Dynamics,
Princeton University Press, 2005

-Bopp, L. and C. Le Quéré (2009). Ocean Carbon Cycle.
In *Surface Ocean Lower Atmosphere Processes*,
C. Quéré and E. Saltzman (Eds),
AGU Geophysical Monographs, Washington, D.C., US. pp 319-329.

- Publications du GCP (Global Carbon Project) :http://www.globalcarbonproject.org/index.htm

- Rapports de l'IPCC (IPCC, 2001 et IPCC, 2007)

- Et diverses publications ….