Impact of global change on ocean biogeochemical cycles (N, P, C and trace elements)
Palma de Mallorca, 17– 21 Oct 2011

III. Metabolism of the oceans: synthesis and mineralization processes

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outline of this presentation

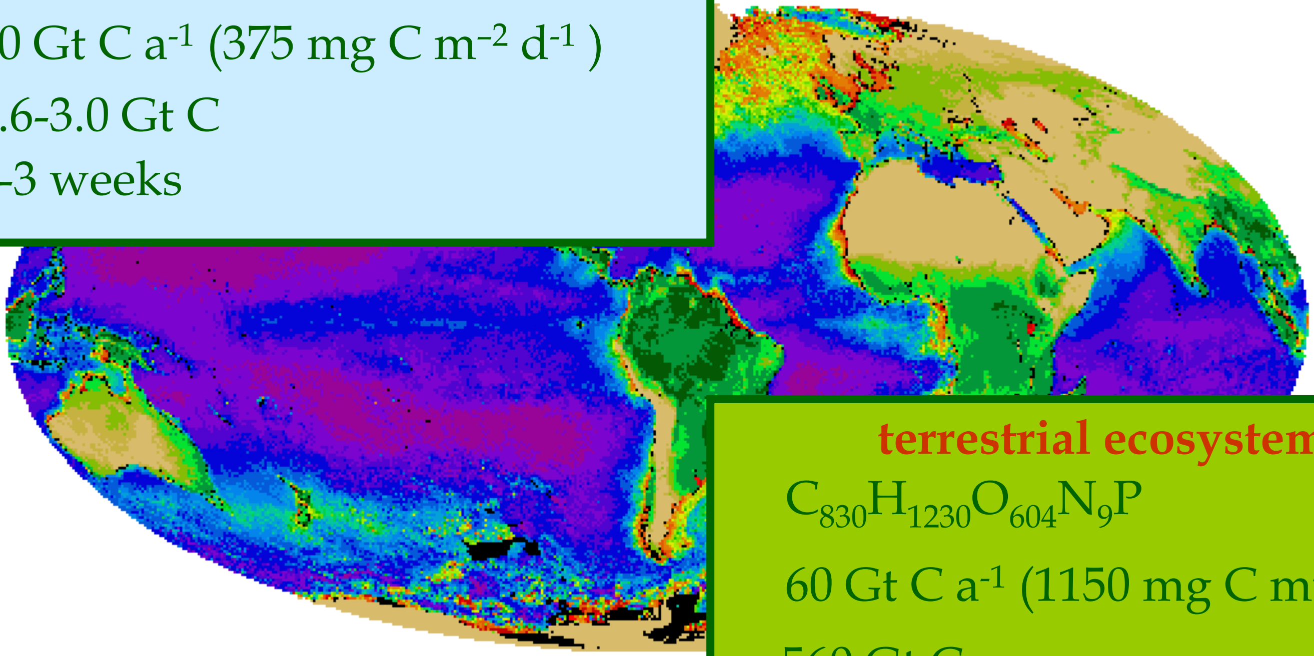
anabolism and catabolism of the microbial communities

stoichiometry of metabolic processes in the microbial food web

- **synthesis of biogenic materials**
- **aerobic mineralisation of biogenic materials**
- **anaerobic mineralisation of biogenic materials**

synthesis of biogenic materials

synthesis of organic matter by phytoplankton



marine ecosystems

$C_{106}H_{171}O_{44}N_{16}P$

50 Gt C a^{-1} (375 mg C m^{-2} d^{-1})

0.6-3.0 Gt C

1-3 weeks

terrestrial ecosystem

$C_{830}H_{1230}O_{604}N_9P$

60 Gt C a^{-1} (1150 mg C m^{-2} d^{-1})

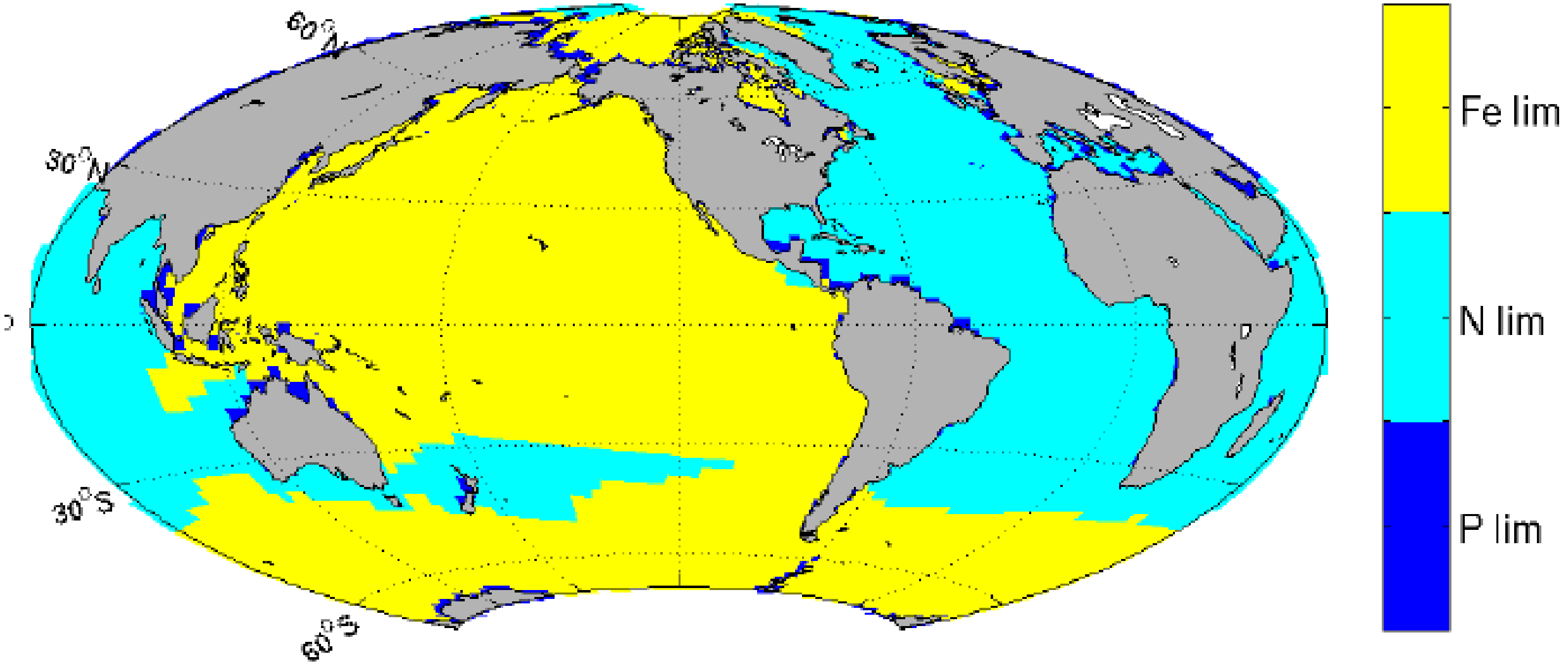
560 Gt C

10 years

global distribution of primary production

synthesis of biogenic materials

synthesis of organic matter by phytoplankton



limiting elements of marine primary production

Bernard, Biogeosciences Diss., 2009

synthesis of biogenic materials

photosyntesis of phytoplanktonic organic matter

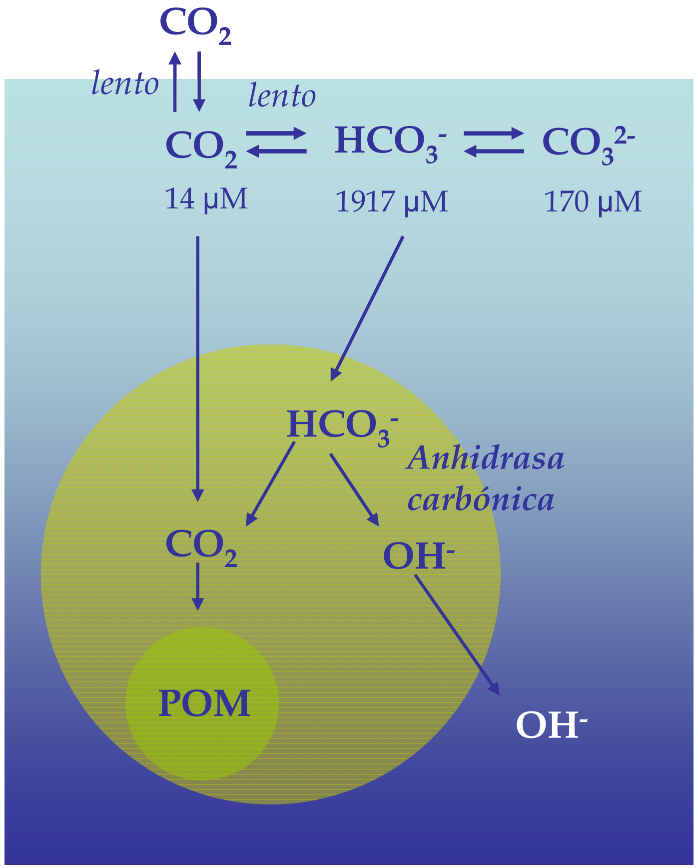
	formula	**% (w/w)**	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
Carbohydrates	$C_6H_{10}O_5$	24,4	0,000	0,000	0,000
Lipids	$C_{53}H_{89}O_6$	16,5	0,000	0,000	0,000
Chlorophyll a, b, c_1 y c_2	$C_{46}H_{52}O_5N_4Mg$	2,0	0,000	0,000	0,000
Proteins	$C_{139}H_{217}O_{45}N_{39}S$	45,1	1,288	–1,029	–2,317
Phosphorus compounds	$C_{45}H_{76}O_{31}N_{12}P_5$	12,0	–3,018	–6,164	–3,145
Average composition	$\mathbf{C_{106}H_{171}O_{44}N_{16}PS_{0.3}}$	**100,0**	**–0,162**	**–1,586**	**–1,424**

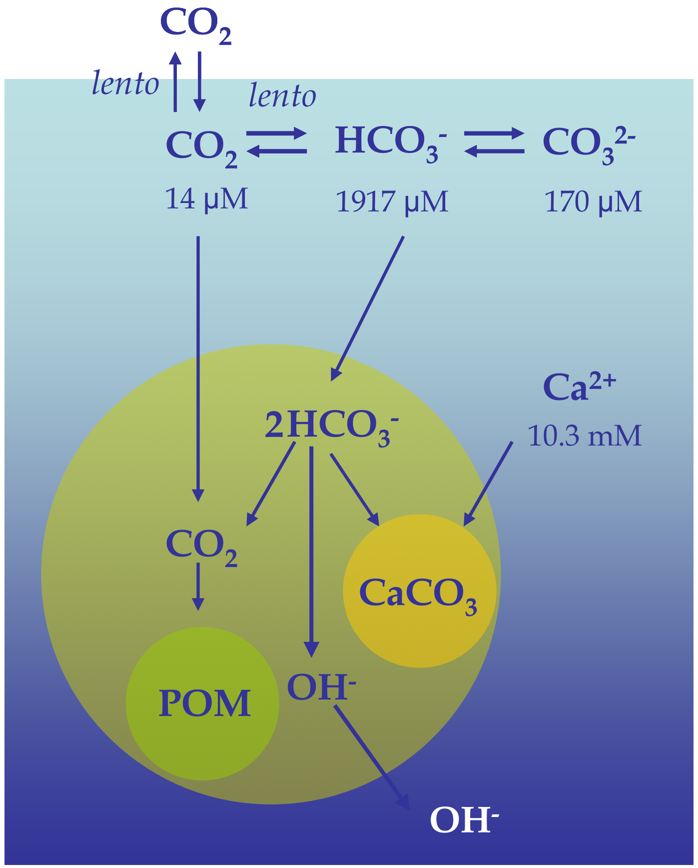
composition and alkalinity of phytoplanktonic organic matter

Fraga & Álvarez-Salgado, Cienc. Mar., 2005

synthesis of biogenic materials

ΣCO_2 sources of marine phytoplankton photosynthesis





mechanisms of incorporation of CO_2 y HCO_3^-

De Baar, Prog. Oceanogr., 1994

synthesis of biogenic materials

using NH_4^+ as nitrogen source

$$106\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 46\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 116\ O_2 + 92\ OH^-$$

$$\Delta TAorg = 0{,}92 \cdot \Delta[NH_4^+] - 0{,}23 \cdot \Delta[P_T] = \mathbf{0{,}906 \cdot \Delta[NH_4^+]}$$

	formula	**% (w/w)**	$\frac{\Delta TA}{\Delta[NH_4^+]}$
Carbohydrates	$C_6H_{10}O_5$	24,4	0,000
Lipids	$C_{53}H_{89}O_6$	16,5	0,000
Chlorophyll a, b, c_1 y c_2	$C_{46}H_{52}O_5N_4Mg$	2,0	1,500
Proteins	$C_{139}H_{217}O_{45}N_{39}S$	45,1	0,916
Phosphorus compounds	$C_{45}H_{76}O_{31}N_{12}P_5$	12,0	0,941
Average composition	$\mathbf{C_{106}H_{171}O_{44}N_{16}PS_{0.3}}$	**100,0**	**0,906**

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

using NH_4^+ as nitrogen source

No buffer:

	initial	ΔCorg= 106	final
pH	8.00	+1.40	9.40

HCO_3^-/ CO_3^{2-} buffer:

$$106\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 46\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 116\ O_2 + 92\ OH^-$$

$$CO_3^{2-} + OH^- \Leftrightarrow HCO_3^- + H_2O$$

$$198\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 116\ O_2 + 92\ CO_3^{2-} + 46\ H_2O$$

	initial	ΔCorg= 106	final
pH	8.00	+0.23	8.23

seawater pH buffer

synthesis of biogenic materials

using NH_4^+ as nitrogen source

Seawater pH buffer:

variable	initial	ΔCorg= 106	final
$\sum CO_2$ (μmol $\cdot$kg^{-1})	2100	-106	1994
A (μmol $\cdot$kg^{-1})	2348	-16	2332
pH	8.00	+0.16	8.16
[CO_2] (μmol $\cdot$kg^{-1})	13.8	-5.0	8.8
[HCO_3^-] (μmol $\cdot$kg^{-1})	1917	-157	1760
[CO_3^{2-}] (μmol $\cdot$kg^{-1})	170	+55	225
Ω_{ARG}	2.6		3.5
Ω_{CAL}	4.1		5.3
pCO_2(g) (μatm)	370	-135	235
[O_2] (μmol $\cdot$kg^{-1})	248	+116	364

seawater pH buffer

synthesis of biogenic materials

using NO_3^- as nitrogen source

$$\left.\begin{array}{l} NO_3^- \longrightarrow NO_2^- + 1/2\ O_2 \quad (\textit{nitrate reductase}) \\ NO_2^- + 3\ H_2O \longrightarrow NH_4^+ + 3/2\ O_2 + 2\ OH^- \quad (\textit{nitrite reductase}) \end{array}\right\} \textit{assimilative reduction}$$

$$106\ HCO_3^- + 16\ NO_3^- + HPO_4^{2-} + 94\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 148\ O_2 + 124\ OH^-$$

$$\Delta TAorg = -1{,}08 \cdot \Delta[NO_3^-] - 0.23 \cdot \Delta[P_T] = \mathbf{-1{,}094 \cdot \Delta[NO_3^-]}$$

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

using NO_3^- as nitrogen source

variable	initial	ΔCorg= 106	final
$\sum CO_2$ (µmol·kg^{-1})	2100	+106	1994
A (µmol·kg^{-1})	2348	+16	2364
pH	8.00	+0.21	8.21
$[CO_2]$ (µmol·kg^{-1})	13.8	-6.1	7.7
$[HCO_3^-]$ (µmol·kg^{-1})	1917	-180	1734
$[CO_3^{2-}]$ (µmol·kg^{-1})	170	+80	249
Ω_{ARG}	2.6		3.8
Ω_{CAL}	4.1		6.0
pCO$_2$(g) (µatm)	370	-163	207
$[O_2]$ (µmol·kg^{-1})	248	+148	396

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

using N_2 as nitrogen source

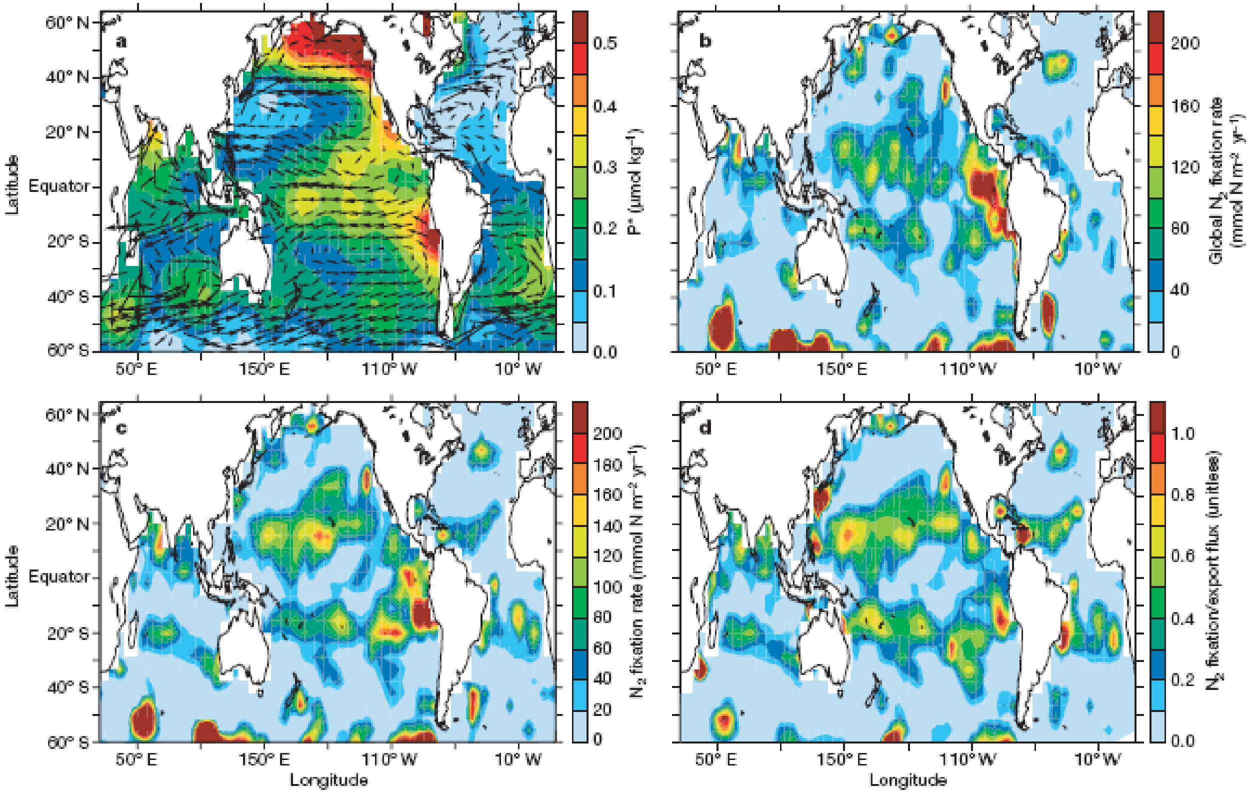


Figure 2 | Annual mean distribution of P*, ocean currents, and the N_2 fixation rates determined from them at 0–120 m depth. a, The P* distribution ($P^* = PO_4^{3-} - NO_3^-/r_n$) is based on climatological data from the World Ocean Atlas[10], and the surface velocity is computed from the MOM3 ocean general circulation model[30]. **b**, Global N_2 fixation rates diagnosed from the convergence of excess inorganic PO_4^{3-}, $-\lambda\nabla\cdot\Phi(P^*)$, which requires an excess uptake of PO_4^{3-} relative to the biological N requirement. **c**, Rates of N_2 fixation accounting for both inorganic and organic nutrient pools, equal to $-\lambda\nabla\cdot\Phi(P_t^*)$ where this term is positive (that is, where excess P_t converges). **d**, N_2 fixation rates (from **c**) as a fraction of the export flux of organic matter.

global distribution of N_2 fixation in the oceans

Deutsch et al., Nature, 2007

synthesis of biogenic materials

using N_2 as nitrogen source

$N_2\uparrow + 5\ H_2O \longrightarrow 2\ NH_4^+ + 3/2\ O_2 + 2\ OH^-$ *(nitrogenase) – Trichodesmiun & cianobacteria*

$$106\ HCO_3^- + 8\ N_2\uparrow + HPO_4^{2-} + 86\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 128\ O_2 + 108\ OH^-$$

$$\Delta TAorg = -0{,}08 \cdot \Delta[N_2] - 0{,}23 \cdot \Delta[P_T] = \mathbf{-0{,}87 \cdot \Delta[P_T]}$$

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

using N_2 as nitrogen source

variable	initial	ΔCorg= 106	final
$\sum CO_2$ (µmol·kg^{-1})	2100	-106	1994
A (µmol·kg^{-1})	2348	+0	2348
pH	8.00	+0.18	8.18
$[CO_2]$ (µmol·kg^{-1})	13.8	-5.5	8.3
$[HCO_3^-]$ (µmol·kg^{-1})	1917	-167	1750
$[CO_3^{2-}]$ (µmol·kg^{-1})	170	+66	236
Ω_{ARG}	2.6		3.6
Ω_{CAL}	4.1		5.7
$pCO_2(g)$ (µatm)	370	-149	221
$[O_2]$ (µmol·kg^{-1})	248	+128	376

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

using multiple nitrogen sources

$$106\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 46\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 116\ O_2 + 92\ OH^-$$

$$106\ HCO_3^- + 16\ NO_3^- + HPO_4^{2-} + 94\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 148\ O_2 + 124\ OH^-$$

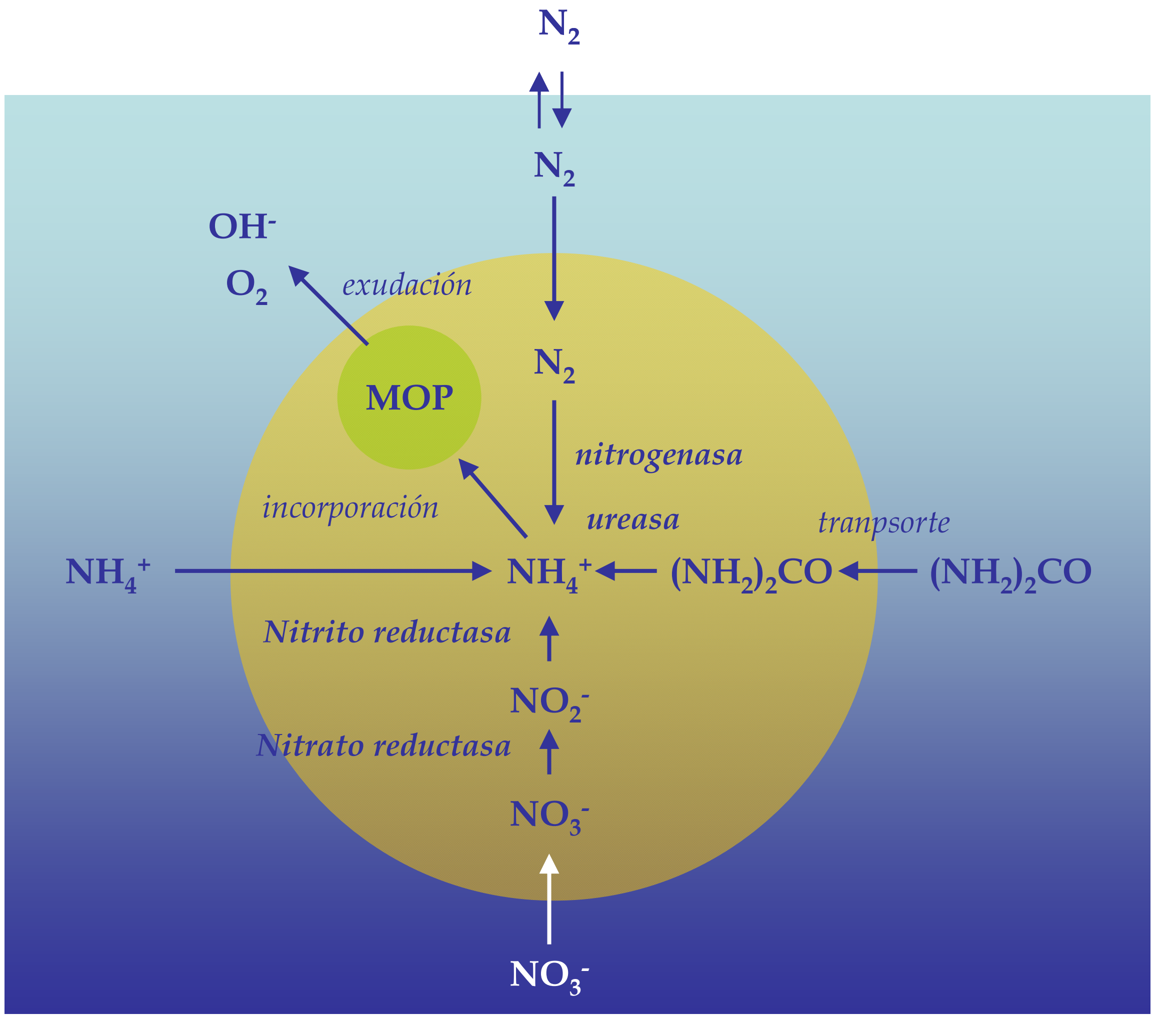
$$106\ HCO_3^- + 8\ N_2 + HPO_4^{2-} + 86\ H_2O \longrightarrow C_{106}H_{171}O_{44}N_{16}P + 128\ O_2 + 108\ OH^-$$

$$\Delta TAorg = 0{,}92 \times \Delta\left[NH_4^+\right] - 0{,}08 \times \Delta\left[N_2\right] - 1{,}01 \times \Delta\left[NO_2^-\right] - 1{,}08 \times \Delta\left[NO_3^-\right] - 0{,}23 \times \Delta\left[P_T\right]$$

stoichiometry and contribution to alkalinity

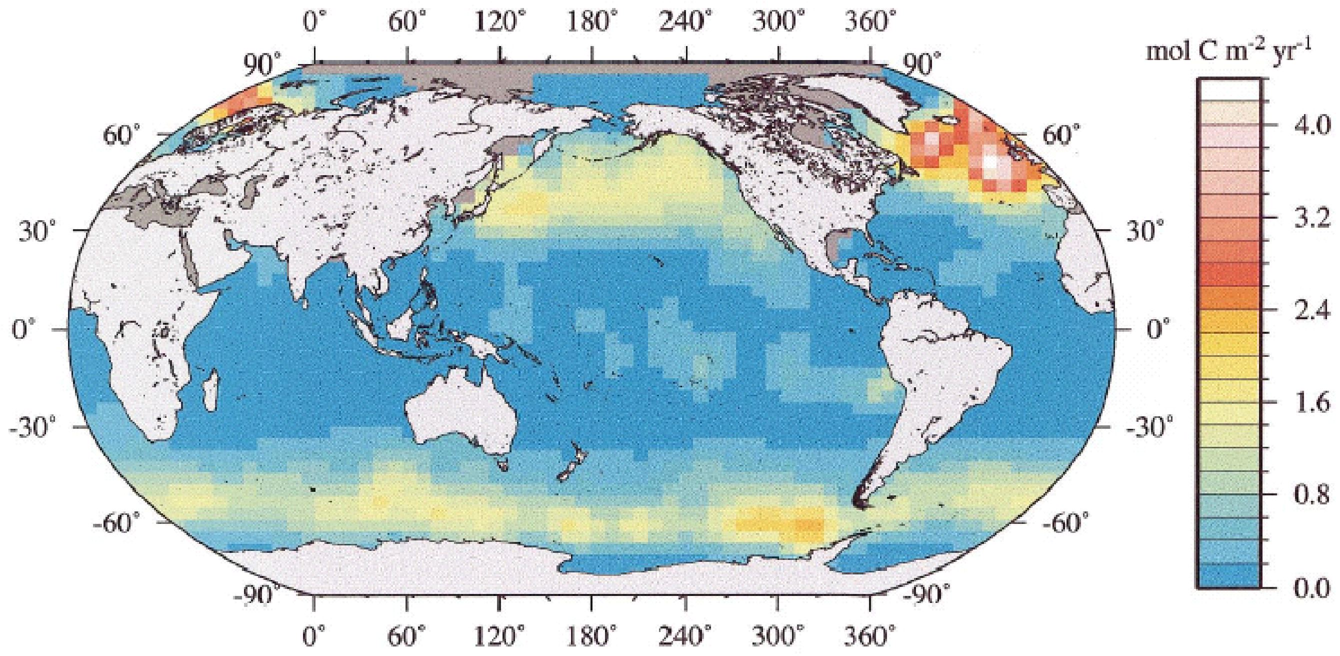
synthesis of biogenic materials

using multiple nitrogen sources



synthesis of biogenic materials

synthesis of calcium carbonate in the oceans



$CaCO_{3ML}$ -A (using NA_T algorithms)

Fig. 4. Annual rate of net $CaCO_3$ production integrated from the surface to the base of the mixed layer as derived from the magnitude of seasonal NA_{POT} decrease calculated from regional NA_T/SST algorithms and seasonal mean SST and NO_3^- fields. Values are expressed as mole C m^{-2} yr^{-1}. Globally integrated net $CaCO_3$ production for 1990 is 1.1 Gt C yr^{-1}.

global distribution of calcification in the oceans: 1,1 ± 0,3 × 10^{15} g C/yr

Lee, 2001

synthesis of biogenic materials

synthesis of calcium carbonate in the oceans

$$\mathrm{CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3\,(s)}$$

$$\Delta A_{\mathrm{CaCO3}} = 2 \cdot \Delta[\mathrm{CO_3^{2-}}] = -2 \cdot \Delta[\mathrm{CaCO_3}]$$

$$\Delta \mathrm{TA} = \Delta \mathrm{TAorg} + \Delta \mathrm{TA}_{\mathrm{CaCO3}} = \Delta \mathrm{TAorg} - 2 \cdot \Delta[\mathrm{CaCO_3}]$$

$$\Delta \mathrm{CaCO_3} = -\frac{1}{2} \cdot \left(\Delta \mathrm{TA} - 0{,}92 \times \Delta\left[\mathrm{NH_4^+}\right] + 0{,}08 \times \Delta[\mathrm{N_2}] + 1{,}01 \times \Delta\left[\mathrm{NO_2^-}\right] + 1{,}08 \times \Delta\left[\mathrm{NO_3^-}\right] + 0{,}23 \times \Delta[\mathrm{P_T}]\right)$$

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

synthesis of calcium carbonate in the oceans

ΔCorg = Δ $CaCO_3$, ΔN_T = Δ [NO_3^-] (cocolitofores using nitrate as nitrogen source)

Variable	inicial	ΔCorg= 106	final
$\sum CO_2$ (µmol ·kg^{-1})	2100	-212	1888
A (µmol ·kg^{-1})	2348	-196	2152
pH	8.00	+0.06	8.06
[CO_2] (µmol ·kg^{-1})	13.8	-3.1	10.7
[HCO_3^-] (µmol ·kg^{-1})	1917	-212	1704
[CO_3^{2-}] (µmol ·kg^{-1})	170	4	173
Ω_{ARG}	2.6		2.7
Ω_{CAL}	4.1		4.2
pCO_2(g) (µatm)	370	-84	286
[O_2] (µmol ·kg^{-1})	248	+148	396

stoichiometry and contribution to alkalinity

synthesis of biogenic materials

synthesis of biogenic silica in the oceans

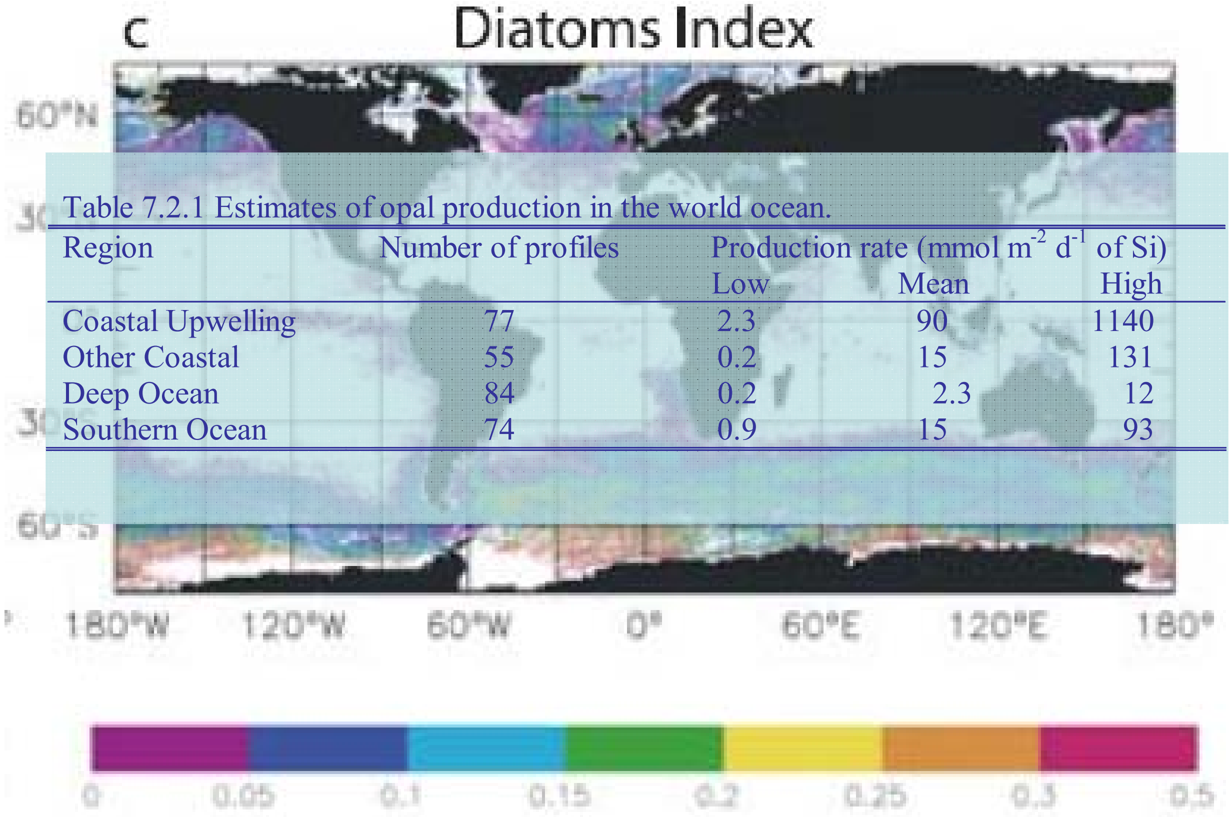


Table 7.2.1 Estimates of opal production in the world ocean.

Region	Number of profiles	Production rate (mmol m^{-2} d^{-1} of Si) Low	Mean	High
Coastal Upwelling	77	2.3	90	1140
Other Coastal	55	0.2	15	131
Deep Ocean	84	0.2	2.3	12
Southern Ocean	74	0.9	15	93

global distribution of silification in the oceans: 6,85 10^{15} g /yr

Bopp et al., Geophys. Res. Lett., 2005

synthesis of biogenic materials

synthesis of biogenic silica in the oceans

$$H_4SiO_4 + (n\text{-}2)\ H_2O \longrightarrow SiO_2 \cdot nH_2O_{(s)}$$

$$\Delta A_{Si} = \Delta\left[Si(OH)_3O^-\right] = -0.042 \cdot \Delta\left[SiO_2\right]$$

stoichiometry and contribution to alkalinity

aerobic mineralization of biogenic materials

ammonification

$$C_{106}H_{171}O_{44}N_{16}P + 116\ O_2 + 46\ H_2O \longrightarrow 106\ HCO_3\text{-} + 16\ NH_4^+ + HPO_4^{2-} + 92\ H^+$$

$$\Delta TAorg = 0{,}92 \cdot \Delta[NH_4^+] - 0{,}23 \cdot \Delta[P_T] = \mathbf{0{,}906 \cdot \Delta[NH_4^+]}$$

stoichiometry and contribution to alkalinity

aerobic mineralization of biogenic materials

ammonification

variable	initial	ΔCorg=-106	final
$\sum CO_2$ (µmol·kg^{-1})	2100	+106	2206
A (µmol·kg^{-1})	2348	+16	2364
pH	8.00	-0.19	7.81
$[CO_2]$ (µmol·kg^{-1})	13.8	+9.4	23.3
$[HCO_3^-]$ (µmol·kg^{-1})	1917	+149	2065
$[CO_3^{2-}]$ (µmol·kg^{-1})	170	-52	117
Ω_{ARG}	2.6		1.8
Ω_{CAL}	4.1		2.8
$pCO_2(g)$ (µatm)	370	+252	621
$[O_2]$ (µmol·kg^{-1})	248	-116	132

stoichiometry and contribution to alkalinity

aerobic mineralization of biogenic materials

nitrification

$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+$

$NO_2^- + 1/2\ O_2 \longrightarrow NO_3^-$

$NH_4^+ + 1/2\ O_2 \longrightarrow NH_2OH + H^+$

$NH_2OH + O_2 \longrightarrow NO_2^- + H_2O + H^+$

$2\ NH_2OH + O_2 \longrightarrow \boxed{N_2O} + 3H_2O$

nitrification, phase I
(nitrosomonas)

nitrification, phase II
(nitrosococcus)

$$C_{106}H_{171}O_{44}N_{16}P + 148\ O_2 + 30\ H_2O \longrightarrow 106\ HCO_3^- + 16\ NO_3^- + HPO_4^{2-} + 124\ H^+$$

$$\Delta TAorg = -1{,}08 \cdot \Delta[NO_3^-] - 0.23 \cdot \Delta[P_T] = \mathbf{-1{,}094 \cdot \Delta[NO_3^-]}$$

stoichiometry and contribution to alkalinity

aerobic mineralization of biogenic materials

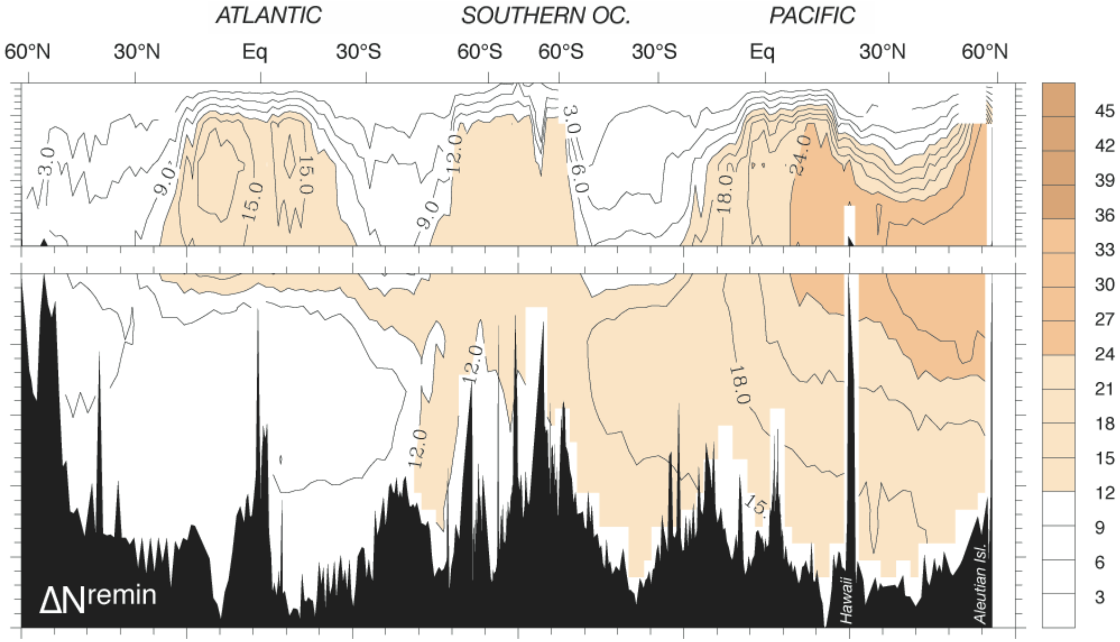
nitrification

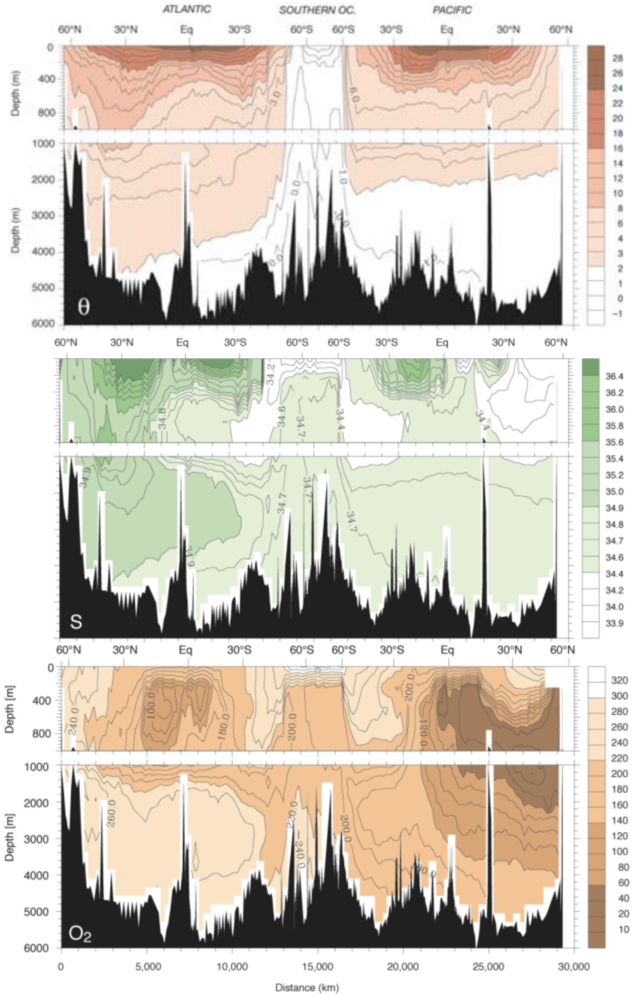
variable	initial	ΔCorg=-106	final
$\sum CO_2$ (µmol·kg^{-1})	2100	+106	2206
A (µmol·kg^{-1})	2348	-16	2232
pH	8.00	-0.27	7.73
$[CO_2]$ (µmol·kg^{-1})	13.8	+14.1	28.0
$[HCO_3^-]$ (µmol·kg^{-1})	1917	+163	2079
$[CO_3^{2-}]$ (µmol·kg^{-1})	170	-71	99
Ω_{ARG}	2.6		1.5
Ω_{CAL}	4.1		2.4
$pCO_2(g)$ (µatm)	370	+377	747
$[O_2]$ (µmol·kg^{-1})	248	-148	100

stoichiometry and contribution to alkalinity

aerobic mineralization of biogenic materials

nitrification





distribution in the oceans

Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)

anaerobic mineralization of biogenic materials

denitrification

$$C_{106}H_{171}O_{44}N_{16}P + 102{,}4\ NO_3^- \longrightarrow 106\ HCO_3^- + 59{,}2\ N_2\uparrow + HPO_4^{2-} + 29{,}2\ H_2O + 5{,}6\ H^+$$

$$\Delta TAorg = -\Delta[NO_3^-] - 0{,}94 \cdot \Delta[P_T] = \boldsymbol{-\Delta[NO_3^-]}$$

NO_3^- is consumed quickly!

stoichiometry and contribution to alkalinity

anaerobic mineralization of biogenic materials

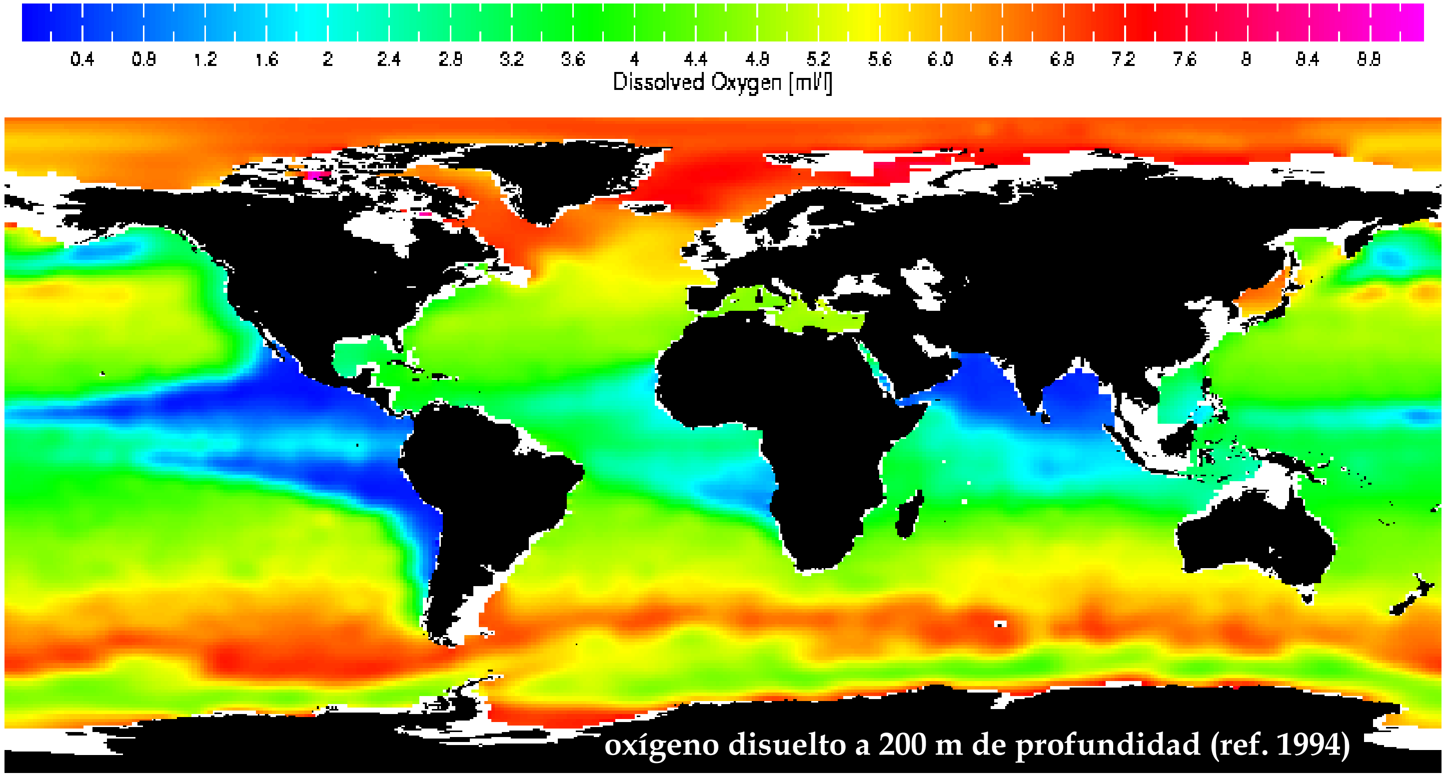
denitrification

variable	initial	ΔCorg= -21	final
$\sum CO_2$ (μmol $\cdot$kg^{-1})	2279	+21	2300
A (μmol $\cdot$kg^{-1})	2321	+20	2341
pH	7.69	-0.04	7.65
[CO_2] (μmol $\cdot$kg^{-1})	50.7	+0.4	51.1
[HCO_3^-] (μmol $\cdot$kg^{-1})	2169	+19	2188
[CO_3^{2-}] (μmol $\cdot$kg^{-1})	59.3	+0.5	59.8
Ω_{ARG}	0.91		0.92
Ω_{CAL}	1.43		1.44
$p$$CO_2$(g) ($\mu$atm)	1353	12	1365
[O_2] (μmol $\cdot$kg^{-1})	0	0	0

stoichiometry and contribution to alkalinity

anaerobic mineralization of biogenic materials

denitrification

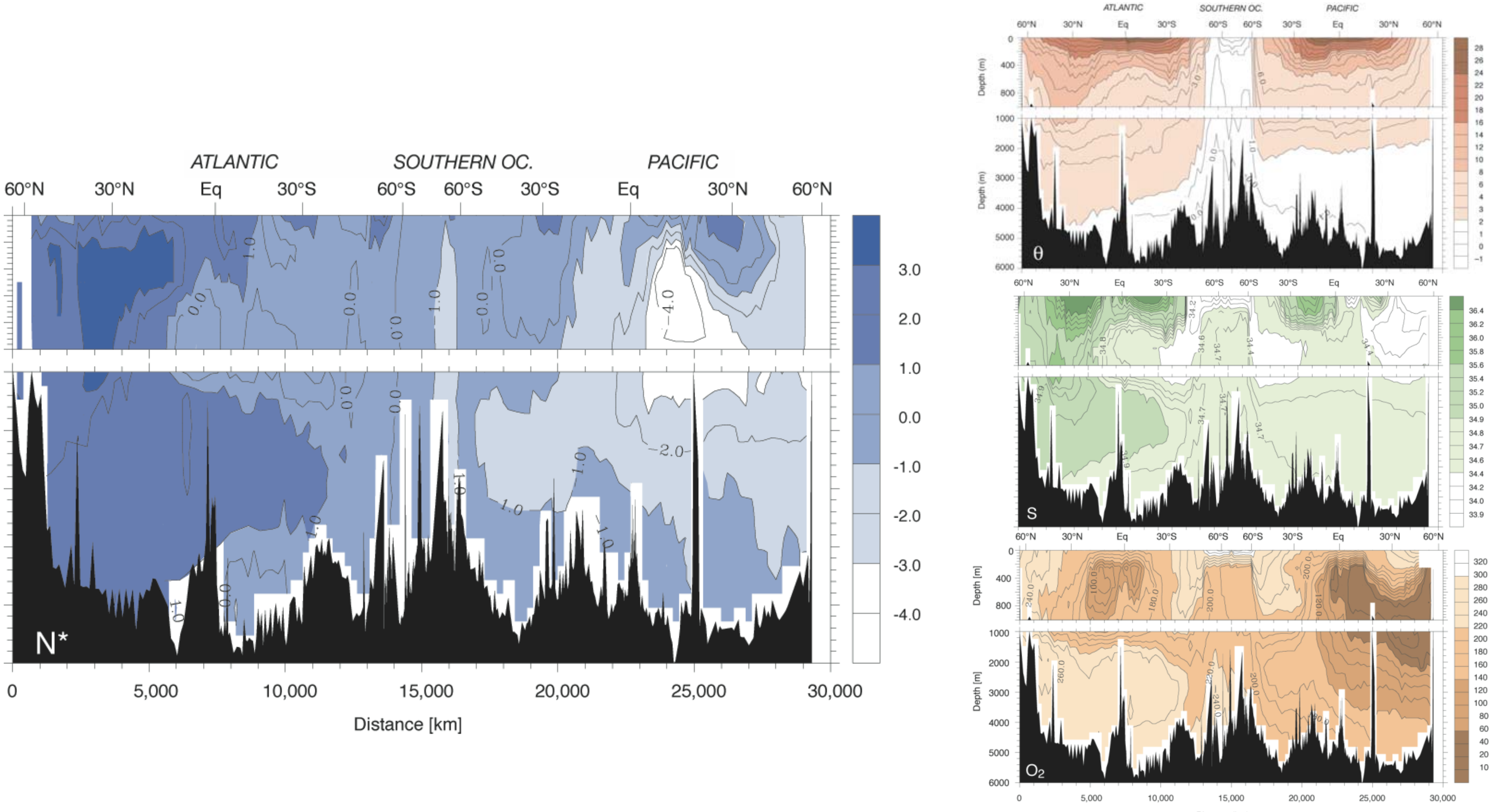


oxígeno disuelto a 200 m de profundidad (ref. 1994)

global distribution of denitrification in the oceans

anaerobic mineralization of biogenic materials

denitrification



global distribution of denitrification in the oceans

anaerobic mineralization of biogenic materials

sulphate-reduction

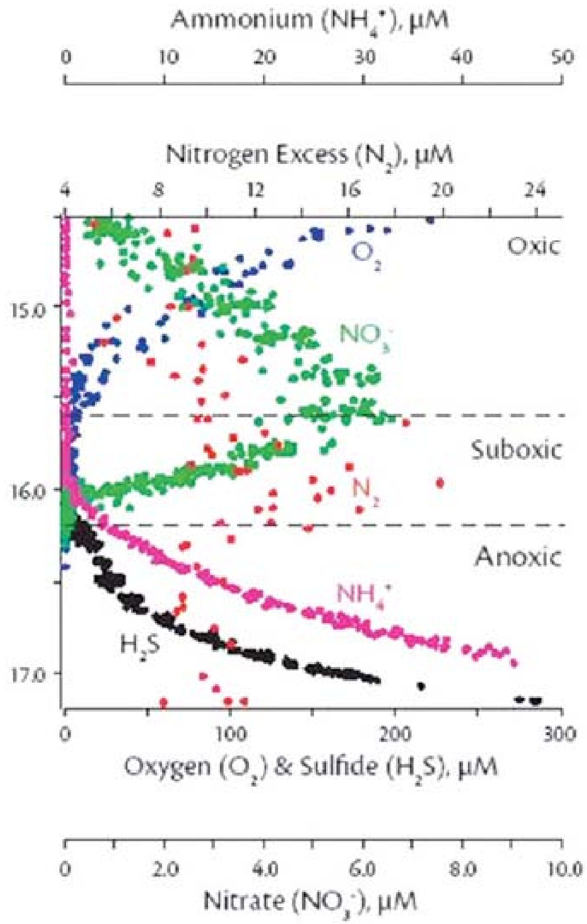
$$C_{106}H_{171}O_{44}N_{16}P + 58\ SO_4^{2-} + 46\ H_2O \longrightarrow 106\ HCO_3^{-} + 16\ NH_4^{+} + HPO_4^{2-} + 58\ HS^{-} + 34\ H^{+}$$

$$\Delta TAorg = -2 \cdot \Delta[SO_4^{2-}] + 0{,}92 \cdot \Delta[NH_4^{+}] - 0{,}94 \cdot \Delta[P_T] = \mathbf{8{,}11 \cdot \Delta[NH_4^{+}]}$$

stoichiometry and contribution to alkalinity

anaerobic mineralization of biogenic materials

sulphate-reduction



distribution of sulphate-reduction in the oceans

anaerobic mineralization of biogenic materials

fermentation

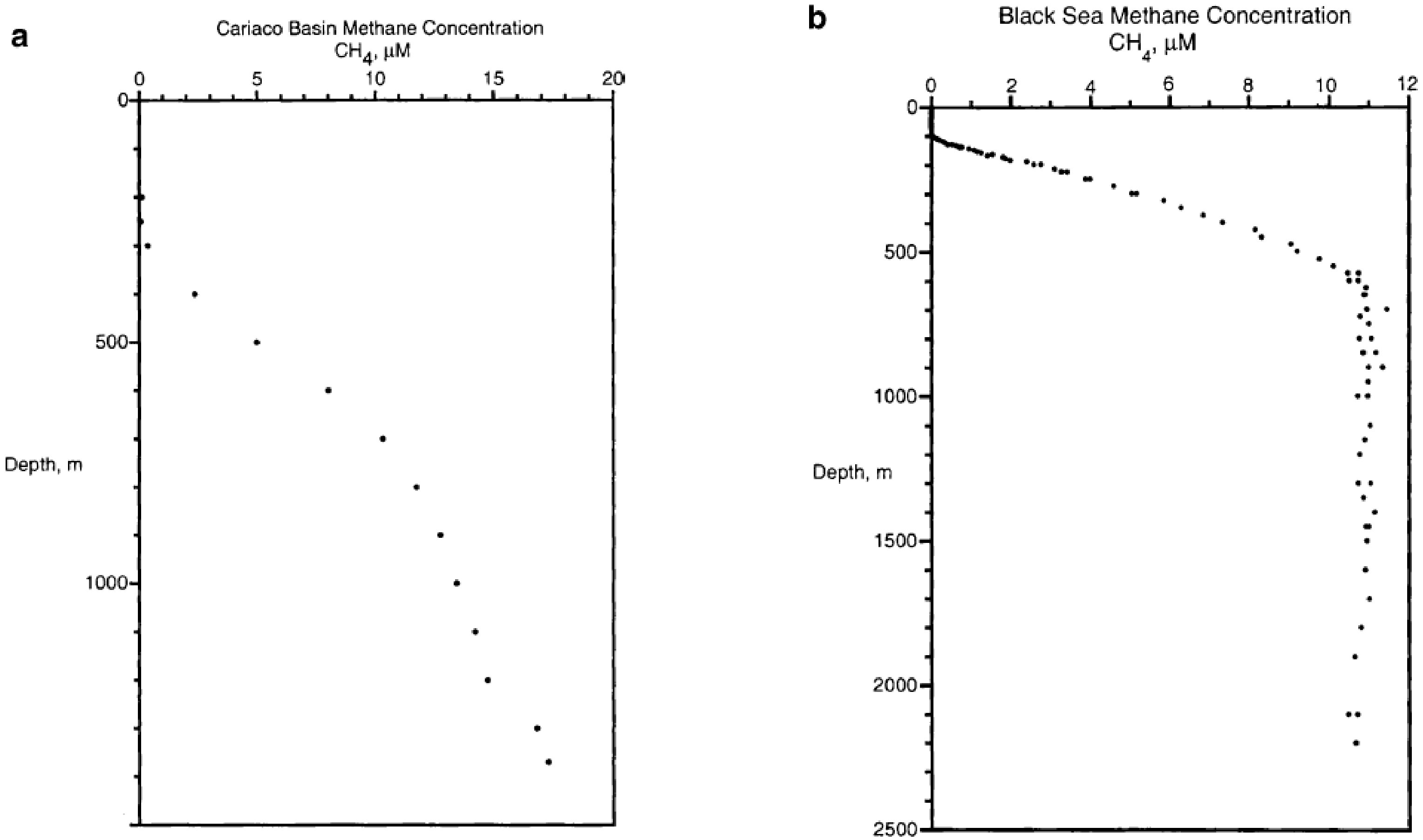
$$C_{106}H_{171}O_{44}N_{16}P + 104\ H_2O \longrightarrow 58\ CH_4\uparrow + 48\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 34\ H^+$$

$$\Delta TAorg = 0{,}92 \cdot \Delta[NH_4^+] - 0{,}94 \cdot \Delta[P_T] = \mathbf{0{,}86 \cdot \Delta[NH_4^+]}$$

stoichiometry and contribution to alkalinity

anaerobic mineralization of biogenic materials

fermentation

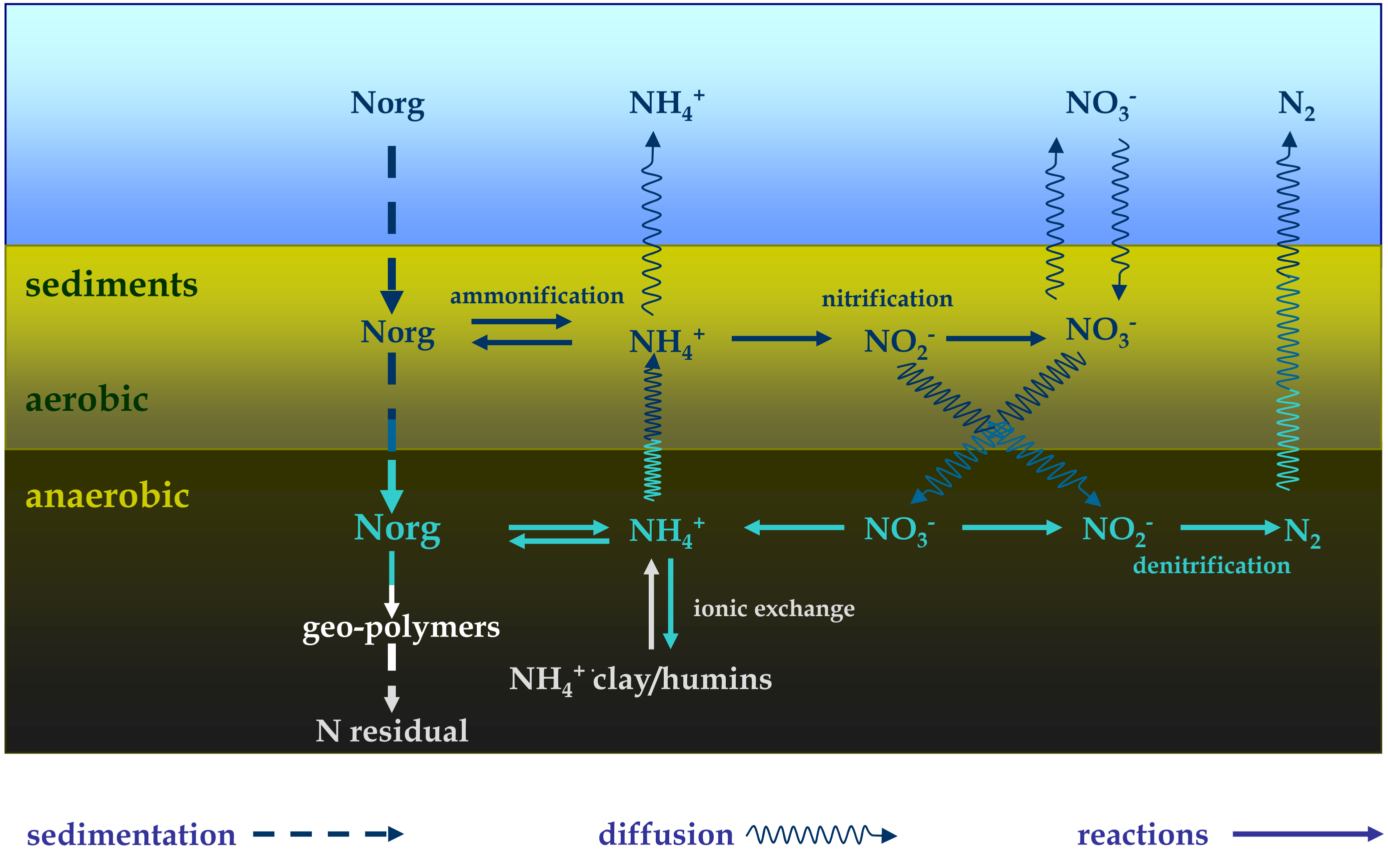


distribution of fermentation in the oceans

Reeburgh, Chem. Rev., 2007

anaerobic mineralization of biogenic materials

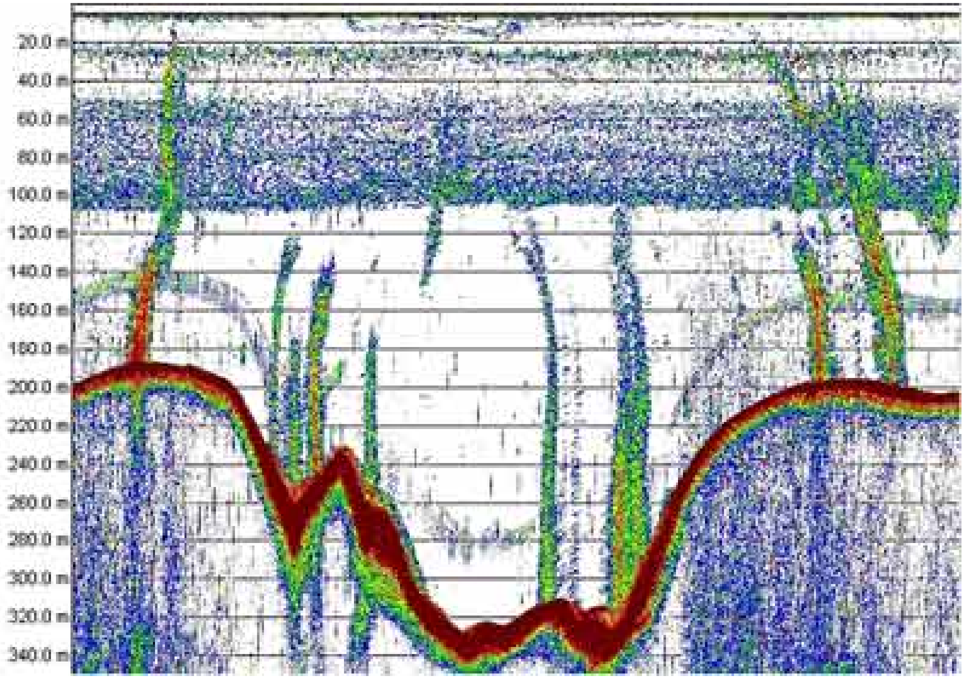
procceses in the sediments



Klump & Martens, 1983

anaerobic mineralization of biogenic materials

procceses in the sediments



methane in coastal sediments

Kaudla & Sandler, Energy & Fuel, 2005

mineralization of inorganic biogenic materials

mineralization of biogenic silica

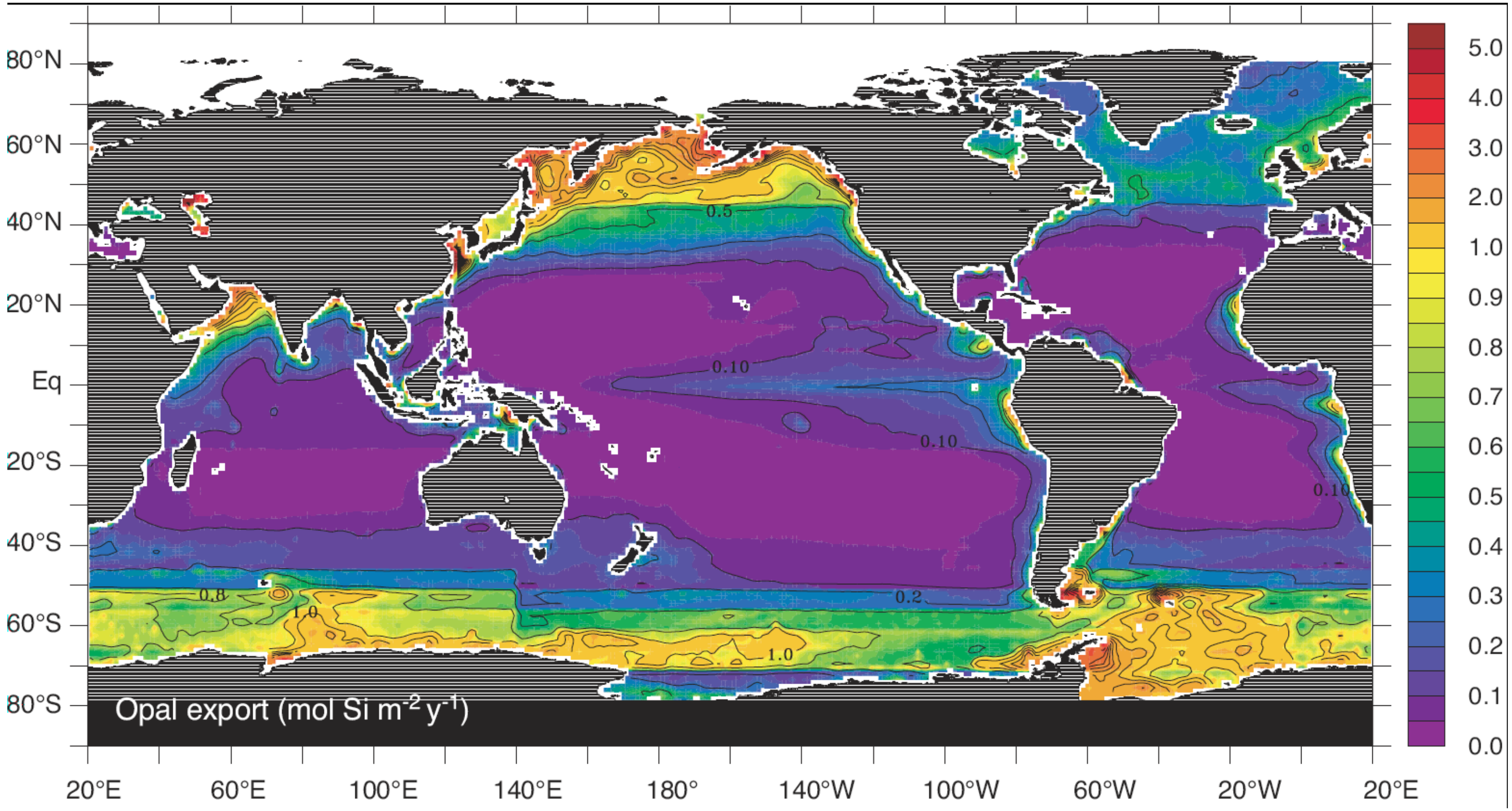
$$SiO_2 \cdot nH_2O_{(s)} \longrightarrow H_4SiO_4 + (n\text{-}2)\ H_2O$$

$$\Delta A_{Si} = \Delta\left[Si(OH)_3O^-\right] = -0.042 \cdot \Delta\left[SiO_2\right]$$

stoichiometry and contribution to alkalinity

mineralization of inorganic biogenic materials

mineralization of biogenic silica



global distribution of BSi disolution in the oceans

mineralization of inorganic biogenic materials

mineralization of calcareous structures

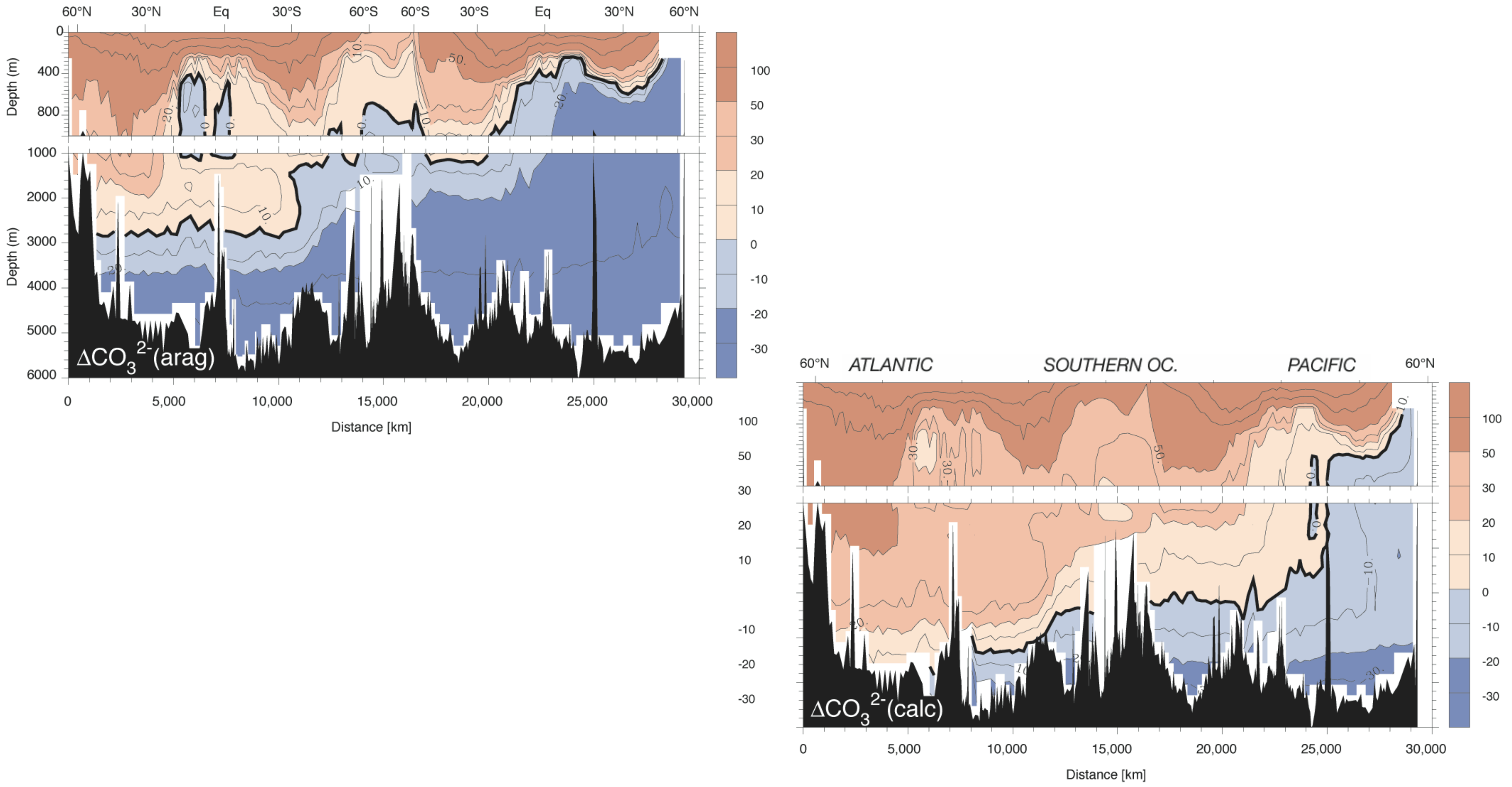
$$CaCO_3\,(s) \longrightarrow CO_3^{2-} + Ca^{2+}$$

$$\Delta A_{CaCO3} = 2 \cdot \Delta[CO_3^{2-}] = -2 \cdot \Delta[CaCO_3]$$

stoichiometry and contribution to alkalinity

mineralization of inorganic biogenic materials

mineralization of calcareous structures



global distribution of $CaCO_3$ dissolution in the oceans

Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)