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

II. Biogenic materials in the oceans

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outline of this presentation

organic and inorganic biogenic compounds in the oceans

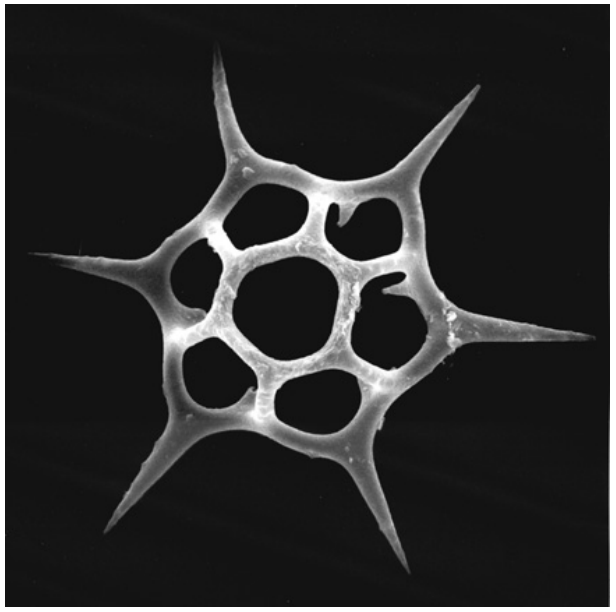
- **Biogenic inorganic compounds: silica and calcium carbonate**
- **Biogenic organic compounds: particulate organic matter**
- **Biogenic organic compounds: dissolved organic matter**

biogenic inorganic compounds

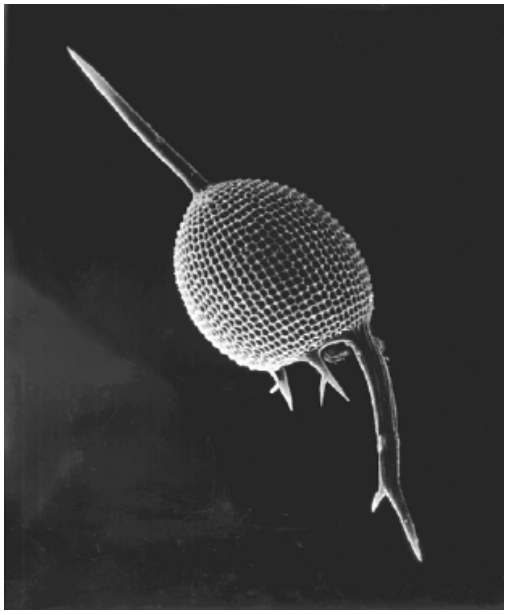
$SiO_2 \cdot n\, H_2O$

diatom

silicoflagelate



radiolaria



microorganisms with biogenic silica structures

biogenic inorganic compounds

$SiO_2 \cdot n\ H_2O$

$2\ Si(OH)_4 \rightarrow$

$\rightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3 +$

$+\ H_2O$

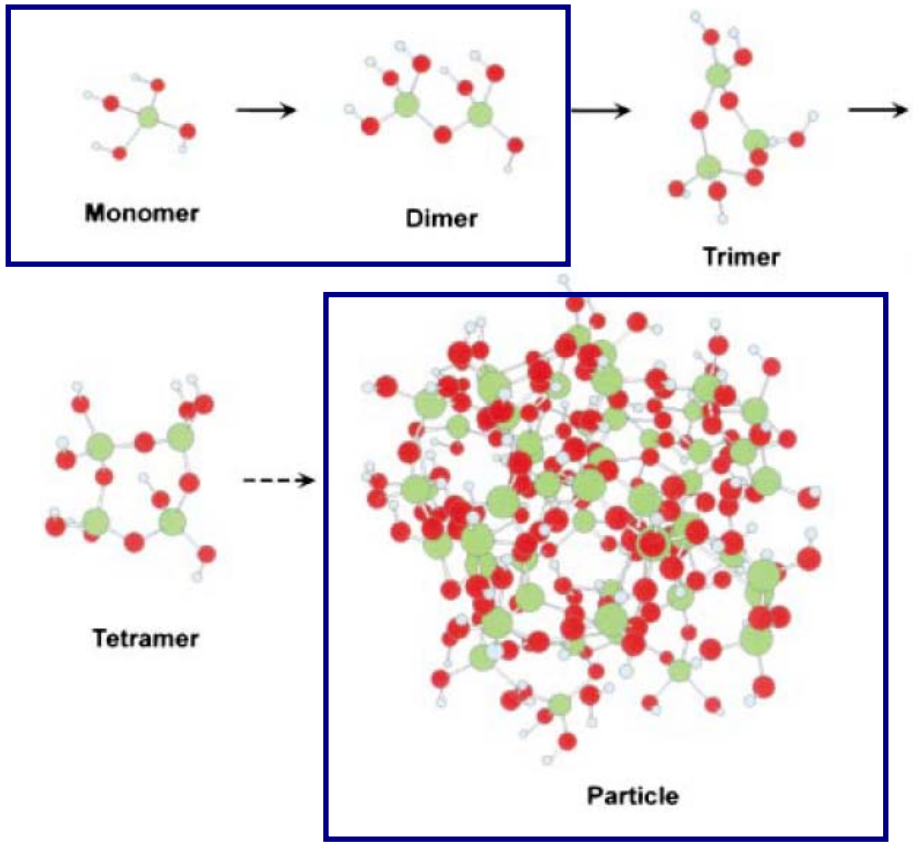


Figure 1. Polymerization behavior of silica. In aqueous solution monosilicic acid condenses to form dimeric, trimeric, and tetrameric (likely cyclic) structures, which then evolve to form particles with sizes in the nanometre range.

$SiO_2 \cdot n\ H_2O$ (~10% H_2O)

$\Delta TA = 0$

Insat. : 0.1% - 10%

polimerization of silicic acid

Coradin et al., Chem. Biochem., 2003

biogenic inorganic compounds

$SiO_2 \cdot n\,H_2O$

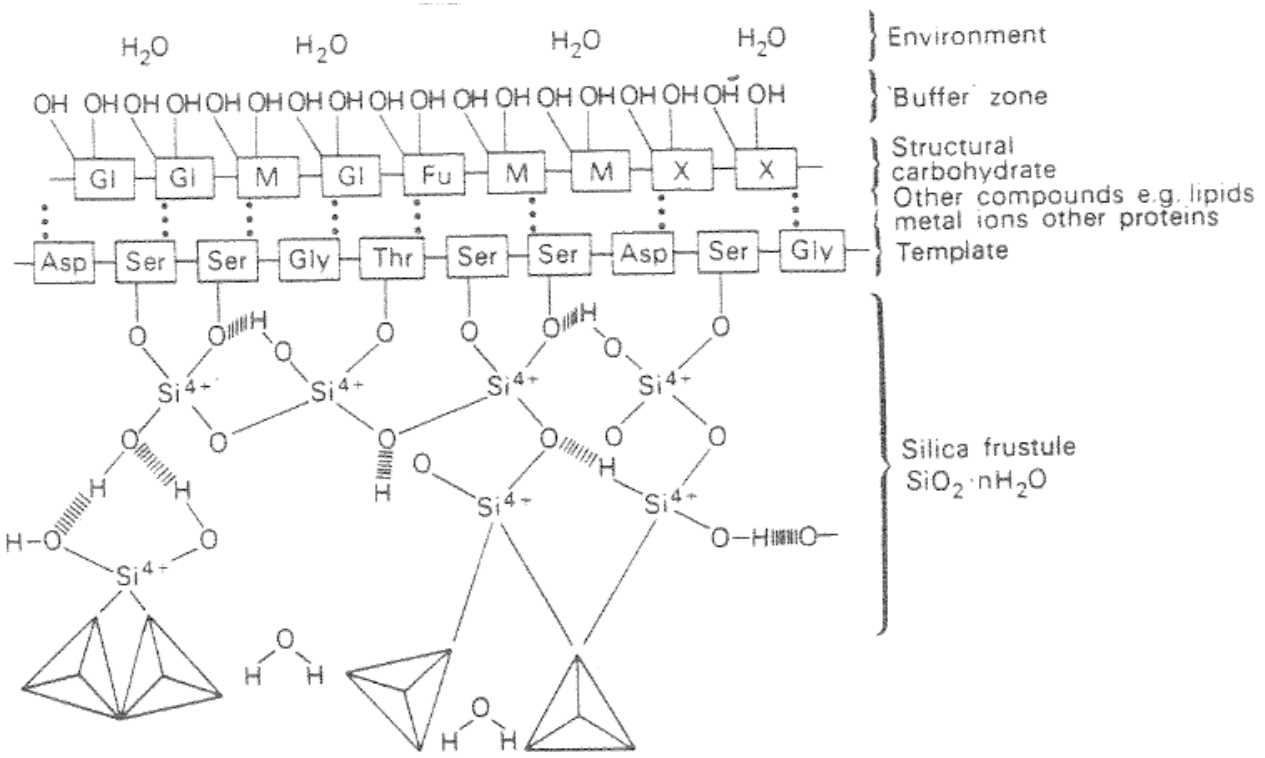
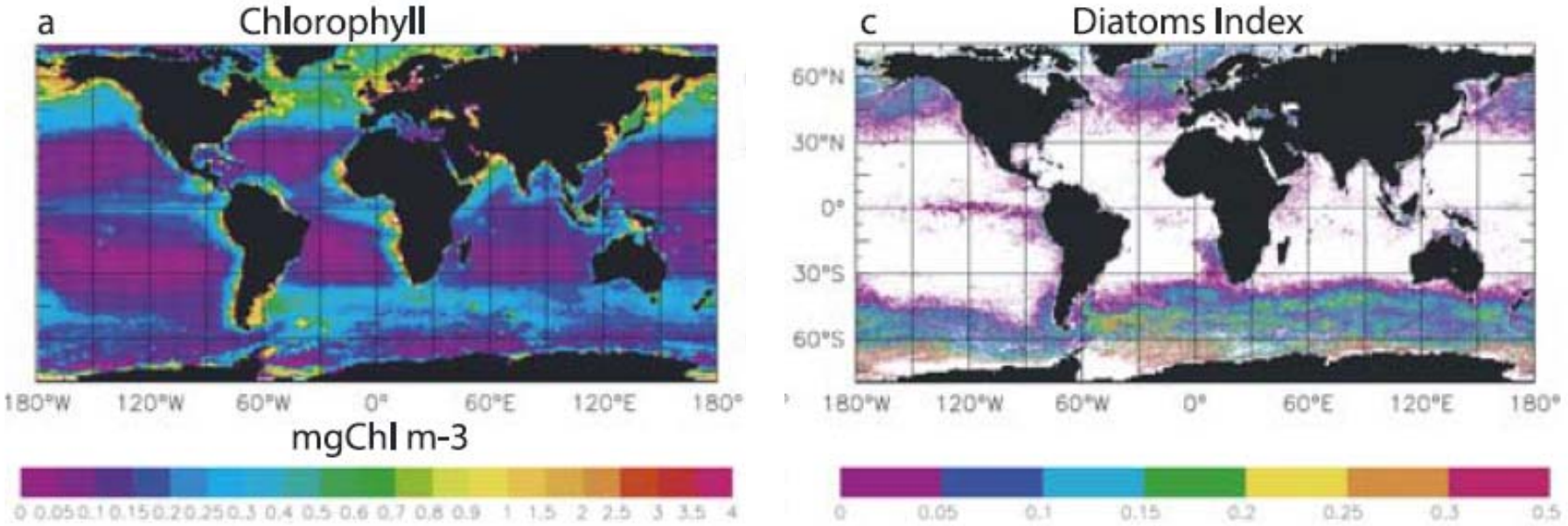


Fig. 4.7. Model of arrangement of layers in the cell wall of diatoms. Layer of polysaccharides with Gl (glucose), M (mannose), Fu (fucose) and X (xylose). Layer of template protein for polycondensation of $Si(OH)_4$ with Ser (serine), Thr (threonine), Asp (aspartic acid) and Gly (glycine). From Hecky *et al.* (1973).

Hecky et al., 1973

biogenic inorganic compounds

$SiO_2 \cdot n\, H_2O$

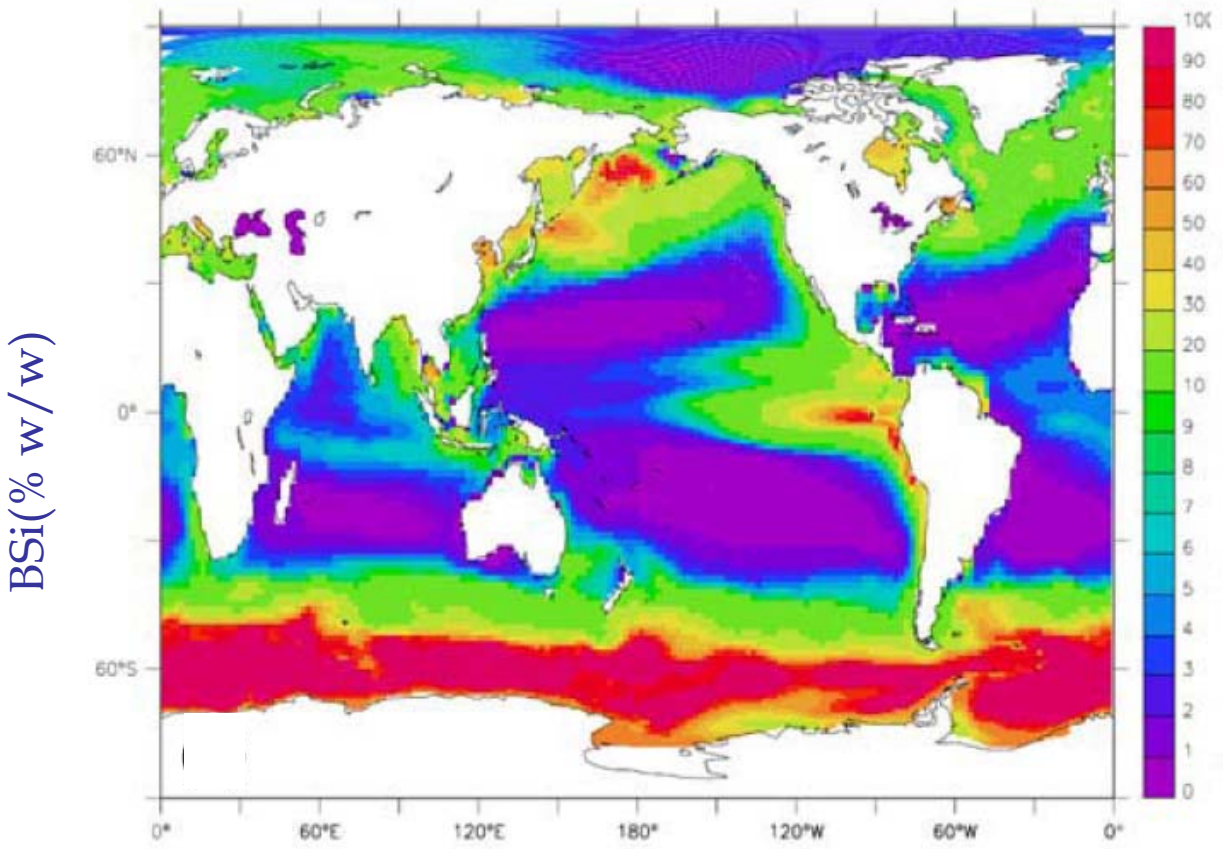


distribution of biogenic silica in the oceans

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

biogenic inorganic compounds

$SiO_2 \cdot n\, H_2O$



distribution of biogenic silica in marine sediments

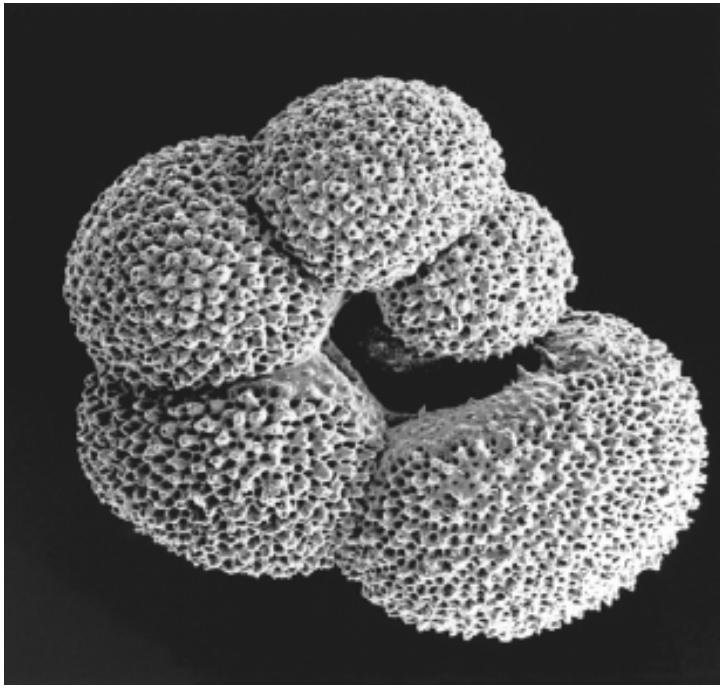
Helhen et al., Biogeosciences, 2008

biogenic inorganic compounds

$CaCO_3$

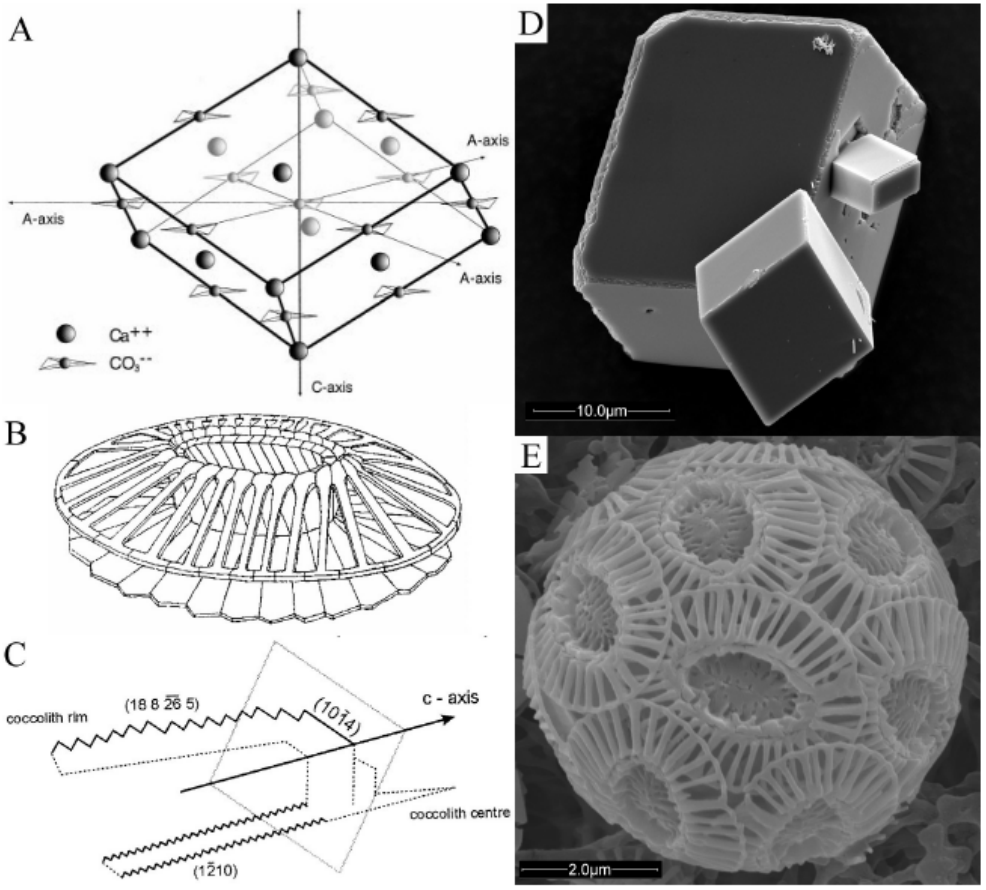
coccolithophores

foraminiphers



microorganisms with calcium carbonate structures

biogenic inorganic compounds
$CaCO_3$



A) Sketch of a three dimensional array of a very small portion of $CaCO_3$ atoms in their spatial arrangement in calcite; reproduced from Young et al. (1999).

B) Drawing of a coccolith of *Emiliania huxleyi*; reproduced from Young et al. (1999)

C) Schematic cross-section through an *E. huxleyi* crystal showing its crystallographic relation to the calcite rhomb (grey); reproduced from Henriksen et al. (2004a).

D) SEM image of inorganically precipitated calcite (courtesy of Gernot Nehrke, AWIBremerhaven)

E) SEM image of *E. huxleyi*

$\Delta TA = 0$

Sobresat.: 250-400%

structure of a calcium carbonate cocolite

Langer, PhD Thesis, 2005

biogenic inorganic compounds

$CaCO_3$

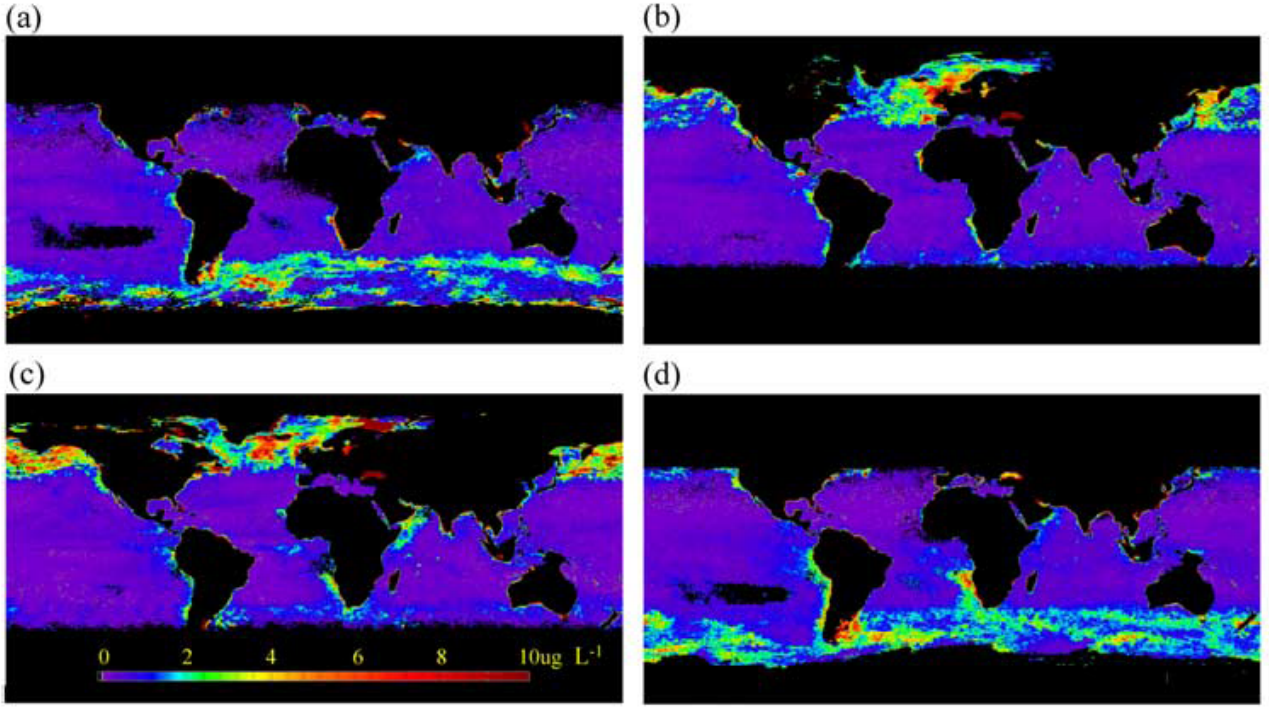
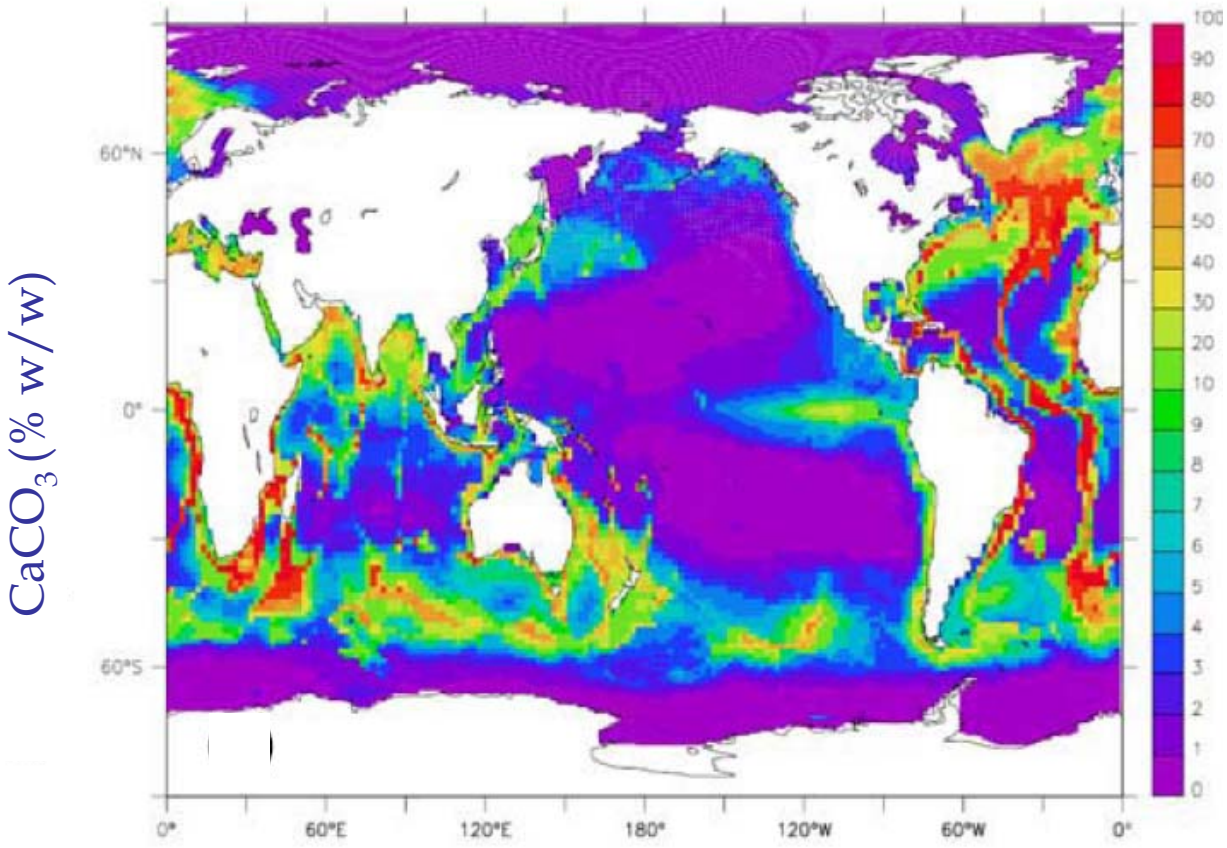


Figure 5. Global composite images of suspended PIC concentration calculated from MODIS/Terra data using two-band calcite algorithm. See text for other details of how the data were processed. The color scale is highlighted in Figure 5c. These data were binned into 36 km and 90 day averages, and thus the standard error will be <0.08 μgPIC L^{-1} (see Table 2), well below the average seawater concentration of ~2 μgPIC L^{-1}. (a) January–March. (b) April–June. (c) July–September. (d) October–December.

distribution of $CaCO_3$ in the oceans

Balch et al., Global Bigeochem. Cy., 2005

biogenic inorganic compounds
$CaCO_3$

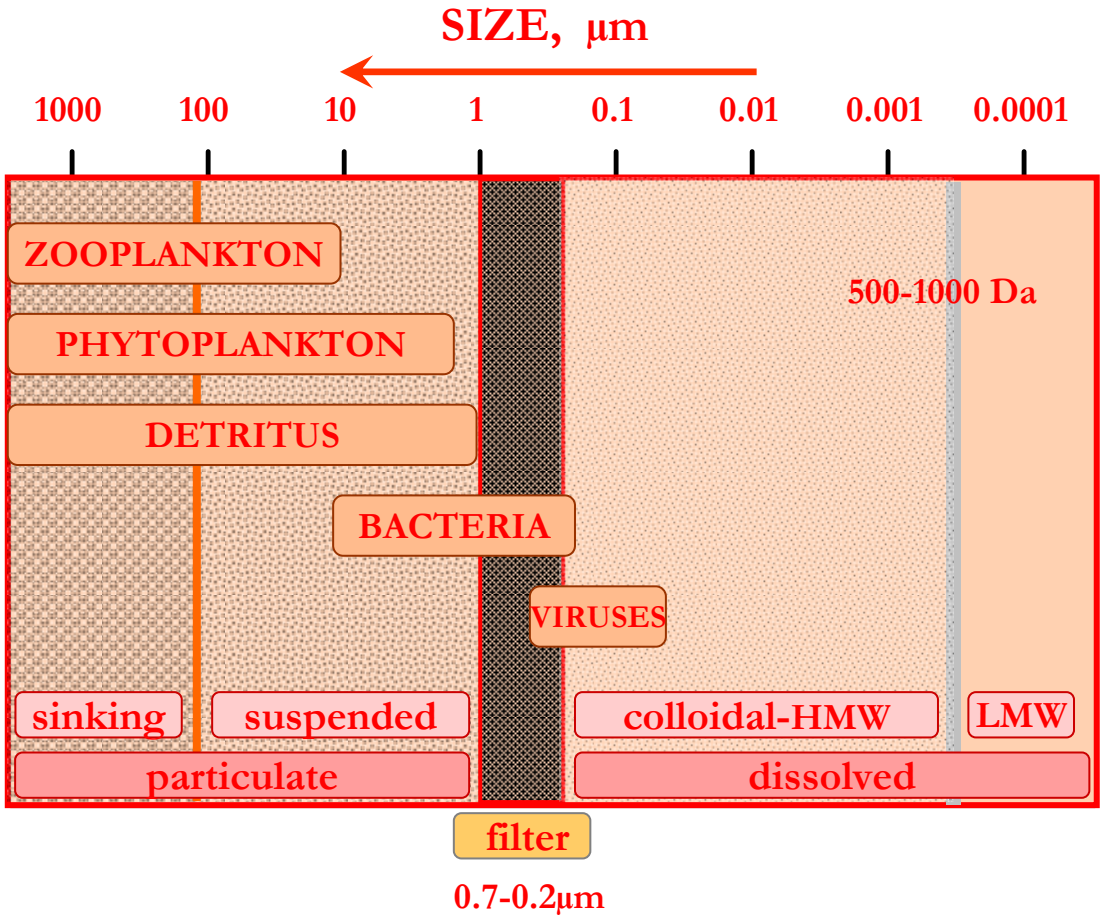


distribution of $CaCO_3$ in marine sediments

Helhen et al., Biogeosciences, 2008

biogenic organic compounds

particulate organic matter (POM)



DOM	662	Gt−C
detritus	20	Gt−C
phytoplankton	1−3	Gt−C
zooplankton	0.1	Gt−C
bacteria	0.1	Gt−C

partition of organic matter in the oceans

Gould & Mantoura (1990)

biogenic organic compounds

particulate organic matter (POM)

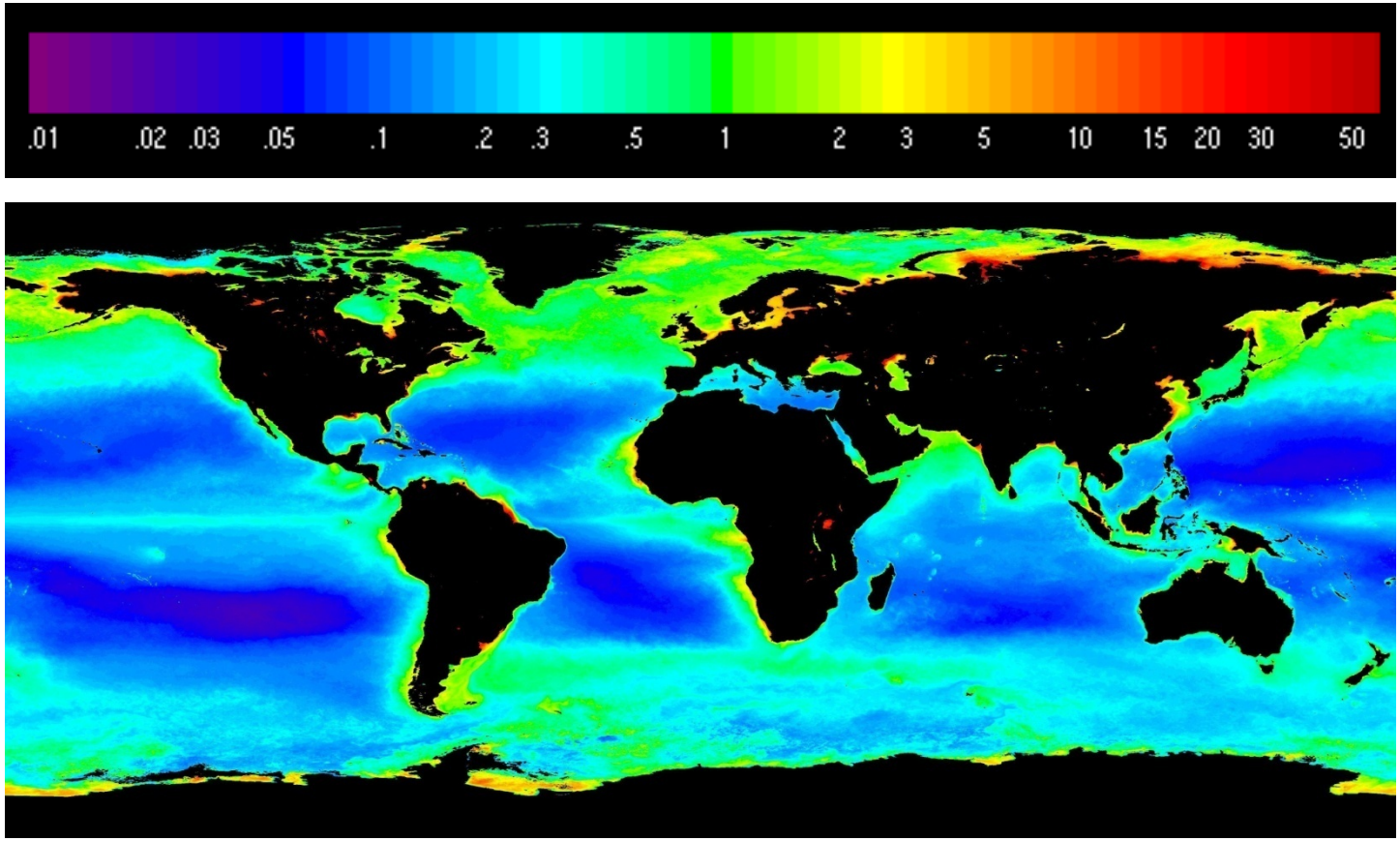
	fórmula	m.w	% (w/w)
Carbohydrates	$C_6H_{10}O_5$	456,4	24,4
Lipids	$C_{53}H_{89}O_6$	822,3	16,5
Pigments	$C_{46}H_{52}O_5N_4Mg$	764,3	2,0
Proteins	$C_{139}H_{217}O_{45}N_{39}S$	3171,0	45,1
Phosphorus comp.	$C_{45}H_{76}O_{31}N_{12}P_5$	1436,0	12,0
Avg. composition	$\mathbf{C_{106}H_{171}O_{44}N_{16}PS_{0.3}}$		**100,0**

POM composition and contribution to alkalinity

Fraga & Álvarez-Salgado, Ciencias Marina, 2006

biogenic organic compounds

particulate organic matter (POM)

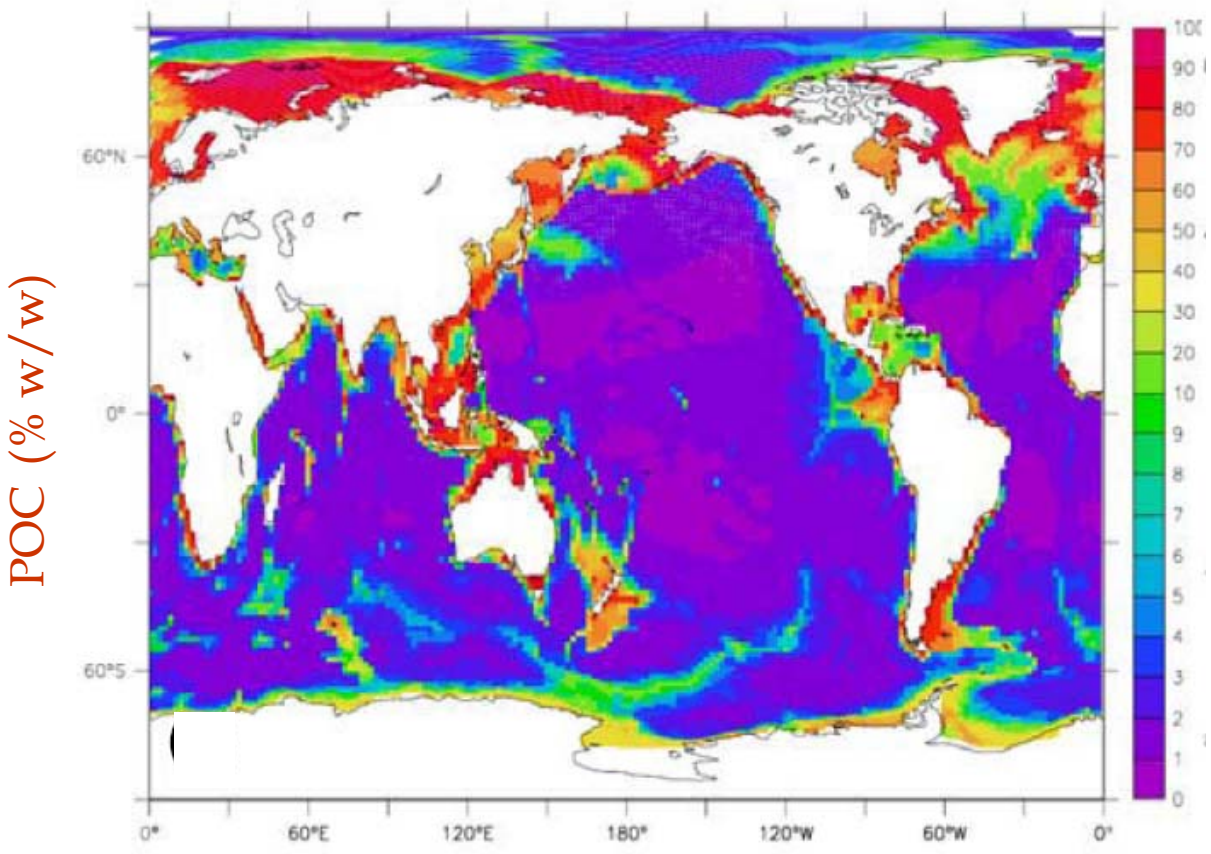


distribution of POM in the oceans

Fraga & Álvarez-Salgado, Ciencias Marina, 2006

biogenic organic compounds

particulate organic matter (POM)

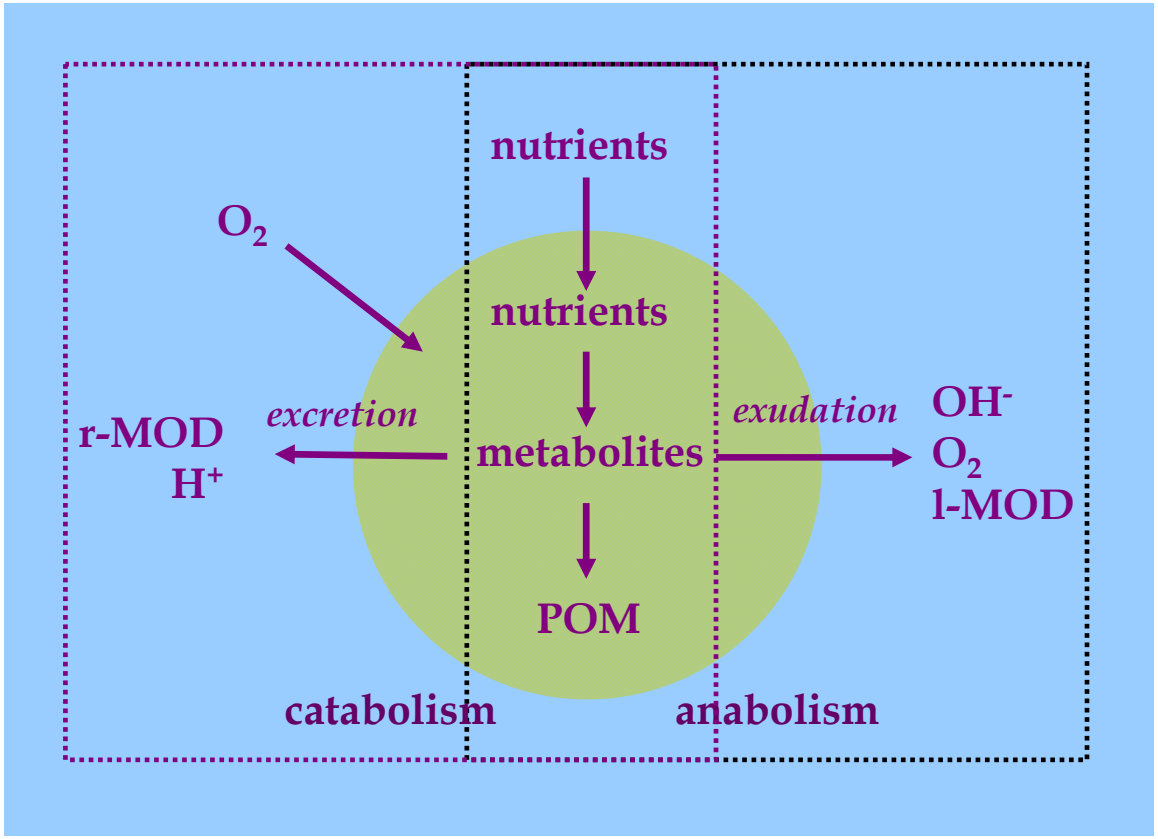


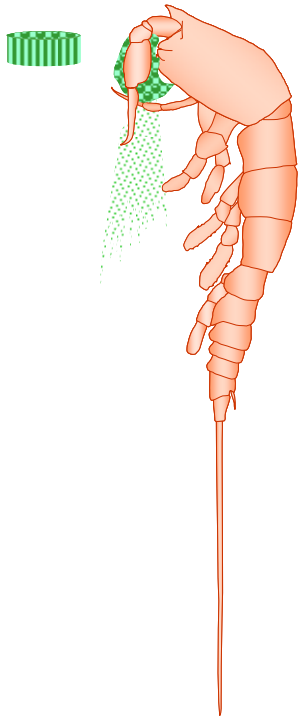
distribution of POM in marine sediments

Helhen et al., Biogeosciences, 2008

biogenic organic compounds

dissolved organic matter (DOM)





Mesozoo lysis

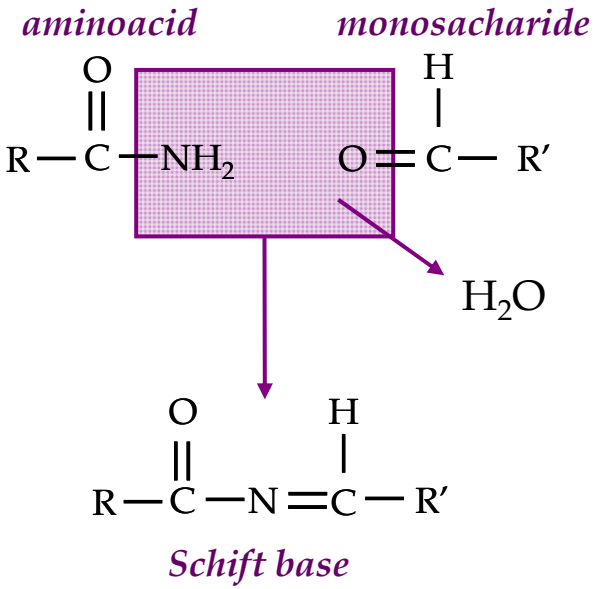
origin of dissolved organic matter: biotic

Brook, Nature, 2008

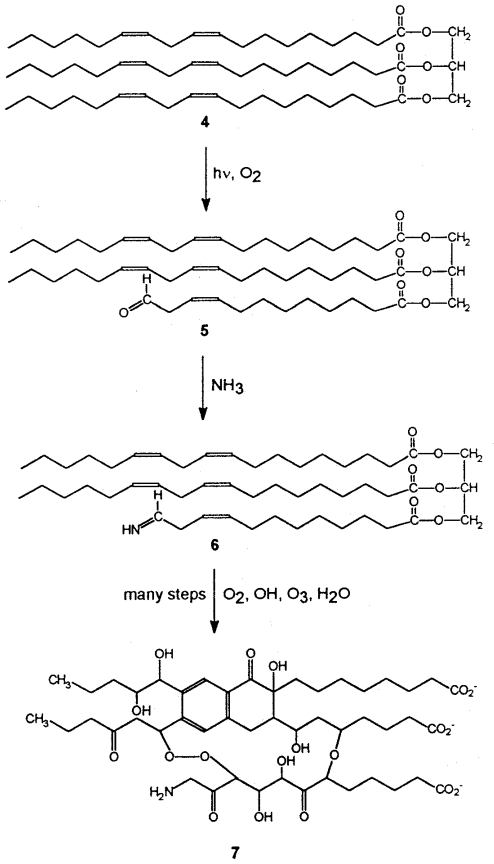
biogenic organic compounds

dissolved organic matter (DOM)

melanoidins



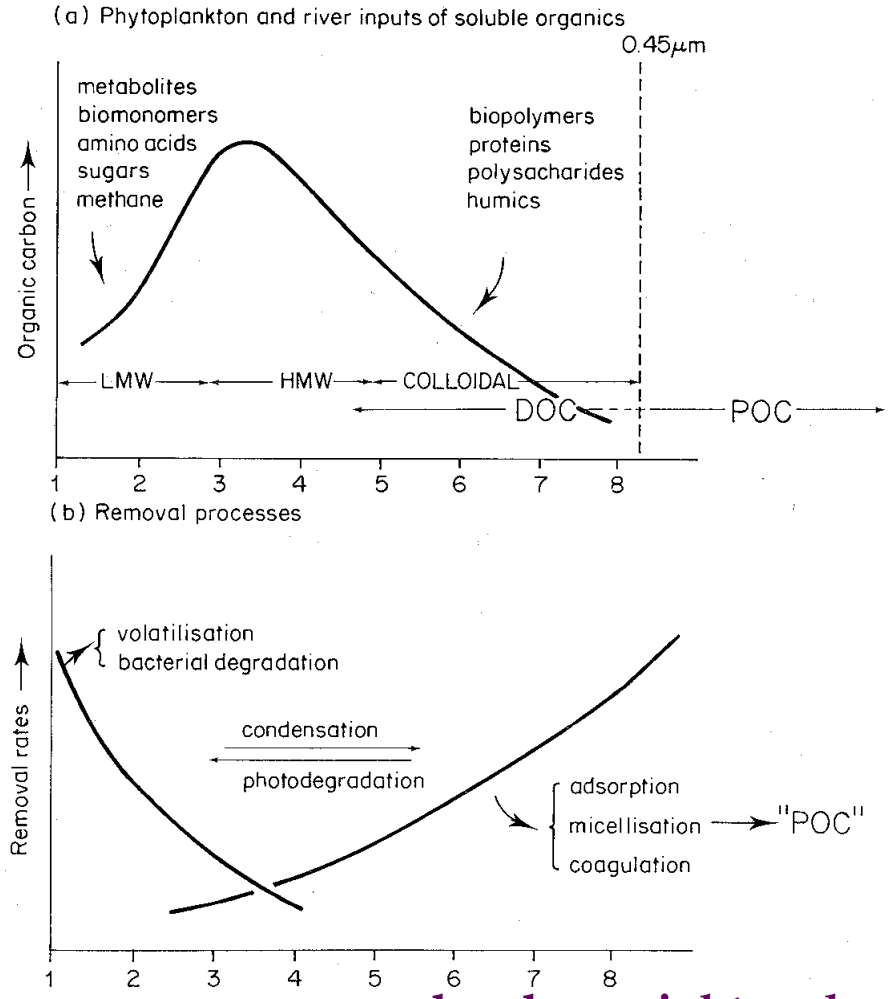
poly-insaturate fattly acids

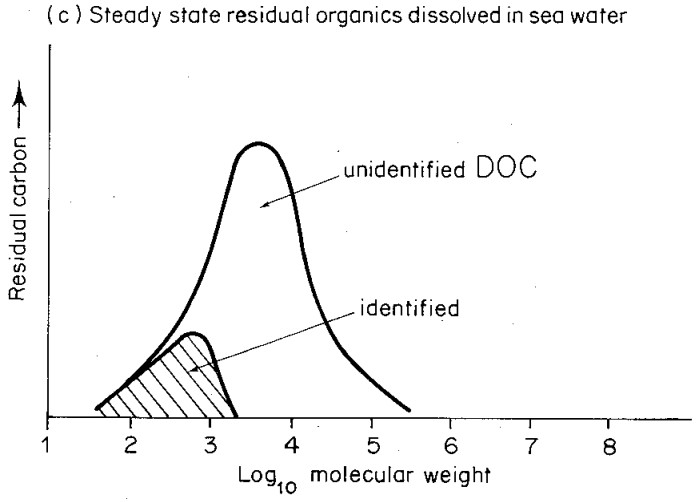


origin of dissolved organic matter: abiotic

biogenic organic compounds

dissolved organic matter (DOM)





molecular weight and reactivity (biological)

Jickells et al., 1991

biogenic organic compounds

dissolved organic matter (DOM)

DOM		contribution	τ (days)	fate
labile	l-MOD	< 5%	10^{-2}–10^{1}	recycling
semi–labile	s-MOD	< 20%	10^{2}	export
refractory	r-MOD	> 75%	10^{3}–10^{6}	inmovilisation

molecular weight and reactivity (biological)

biogenic organic compounds

dissolved organic matter (DOM)

	LMW–MOD	HMW–MOD
mol. weight	< 1 kDa	> 1 kDa
contribution	~70%	~30%
l–DOM	monosacharides, aminoacids, urea, fattly acids, glicolate	sugar polymers, amides, peptides, phosphoric esters, phosphonates
	(τ~ hours–days)	(τ~ days–weeks)
r–DOM	?	humic susbtances
	(τ~4000–6000 years)	(τ ~ 150–200 years)

molecular weight and reactivity (biological)

biogenic organic compounds

dissolved organic matter (DOM)

Tabla 1. Constantes de acidez de las especies consideradas en el texto (en la escala a_H, sal. 35.0, temp. 25ºC). $\varepsilon = \sum_i z_i \times A_i \Big/ \sum_i A_i$, balance de cargas de las i especies con carga z_i que constituyen el sistema de un ácido 'A'. $\varepsilon_{4,25}$ y $\varepsilon_{8,0}$, balances a pH_{SWS} 4,25 y 8,0.

	pK'_1	pK'_2	pK'_3	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
H_2PO_3–O–R (1)	1,77	6,12	—	–1,016	–1,992	–0,976
HPO_2–(–O–R)$_2$ (1)	1,77	—	—	–0,998	–1,000	–0,002
Histidina(2,3)	6,0	—	—	+0,976	+0,006	–0,969
Lisina(2,3)	10,53	—	—	+1,000	+0,995	–0,005
Arginina(2,3)	12,48	—	—	+1,000	+1,000	–0,000
Ácido aspártico (2,3)	3,86	—	—	–0,776	–1,000	–0,224
Ácido glutámico (2,3)	4,25	—	—	–0,586	–1,000	–0,414
Adenosina(3)	3,30	12,50	—	+1,075	+1,000	–0,074
Guanosina(3)	1,6	9,16	12,3	+1,002	+0,901	–0,100
Citosina(3)	4,60	12,16	—	+0,613	+0,000	–0,613
Timidina(3)	9,8	13,1	—	0,000	–0,025	–0,025
Uridina(3)	9,2	12,3	—	0,000	–0,091	–0,091

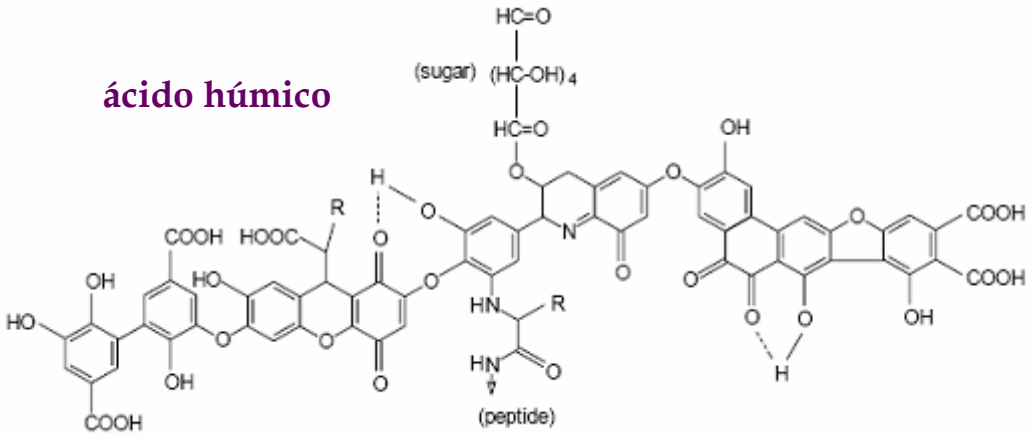
(1) Se ha supuesto la misma pK'_As que para el H_3PO_4
(2) Solamente se ha considerado el pK'_A de los grupos funcionales laterales, puesto que los grupos R–CH(NH_2)–COOH terminales son amidas neutras
(3) pK'_As a salinidad 0,0 y temperatura 25ºC

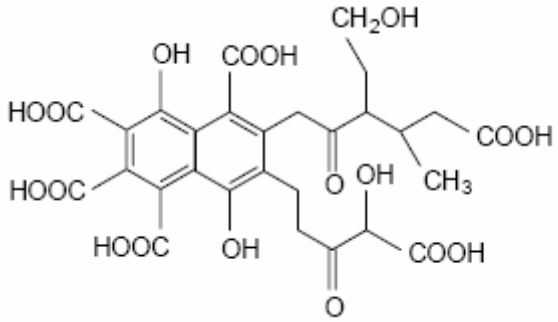
contribution of DOM to alkalinity: free molecules and polymers

biogenic organic compounds

dissolved organic matter (DOM)

ácido húmico





ácido fúlvico

	pKa	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
R-COO$^-$/RCOOH	3.67/4.59	-0,314/-0.790	-1,000/-1,000	-0,208/-0,686
Phe-O$^-$/Phe-OH	9.23/10.53	0,000/0,000	0,056/0,003	-0,056/-0,003

contribution of DOM to alkalinity: humic substances

Ritchie & Perdue, Geochim. Cosmochim. Acta, 2003

biogenic organic compounds

dissolved organic matter (DOM)

Table 2. Summary of carboxyl and phenolic contents for fulvic acids, humic acids, and natural organic matter (NOM) from the literature and from this study.

		Carboxyl groups, meq g^{-1}			Phenolic groups, meq g^{-1}		
Sample type	Method of analysis	Average	Std. Dev.	*n*	Average	Std. Dev.	*n*
Fulvic acids							
IHSS samples	Direct titration	6.6	0.8	6	1.4	0.3	6
Others[a]	Direct titration	5.4	1.3	40	1.6	0.7	35
NICA-Donnan[b]	Direct titration	5.4	1.2	18	2.6	1.9	18
Model VI[c]	Direct titration	4.8	0.7	10	2.4	0.4	10
Stockholm Model[d]	Direct titration	5.3	0.9	9	1.6	0.3	9
Others[e]	$Ba(OH)_2/Ca(OAc)_2$	6.1	2.0	83	4.1	1.9	83
Humic acids							
IHSS samples	Direct titration	4.8	0.4	7	1.4	0.4	7
Others[a]	Direct titration	3.8	0.9	35	1.6	0.5	27
NICA-Donnan[b]	Direct titration	3.2	0.9	20	2.7	1.4	20
Model VI[c]	Direct titration	3.3	0.5	9	1.7	0.2	9
Stockholm Model[d]	Direct titration	3.6	0.8	9	1.8	0.4	9
Others[e]	$Ba(OH)_2/Ca(OAc)_2$	3.8	0.9	198	3.4	1.6	189
NOM samples							
IHSS samples	Direct titration	5.2	—	1	2.1	—	1
Others[a]	Direct titration	5.6	2.1	8	2.1	1.3	3
Others[e]	$Ba(OH)_2/Ca(OAc)_2$	8.3	1.8	12	3.8	1.9	12

All concentrations are in meq g^{-1} on a dry, ash-free basis.

[a] Reuter, 1980; Miles et al., 1983; Steelink et al., 1983; Steinberg and Muenster, 1985; Malcolm, 1985; Collins et al., 1986; Ephraim et al., 1986; Malcolm and MacCarthy, 1986; Portal et al., 1986; Bowles et al., 1989; Ephraim et al., 1989; Aleixo et al., 1992; Wang et al., 1992; de Wit et al., 1993; Machesky, 1993; Nederlof et al., 1993; Fukushima et al., 1995; Westall et al., 1995; da Silva et al., 1996; Christensen et al., 1998; Masini et al., 1998; Avena et al., 1999; Robertson and Leckie, 1999; Santos et al., 1999; Ma et al., 2001.

[b] Milne et al., 2001.

[c] Tipping, 1998.

[d] Gustafsson, 2001.

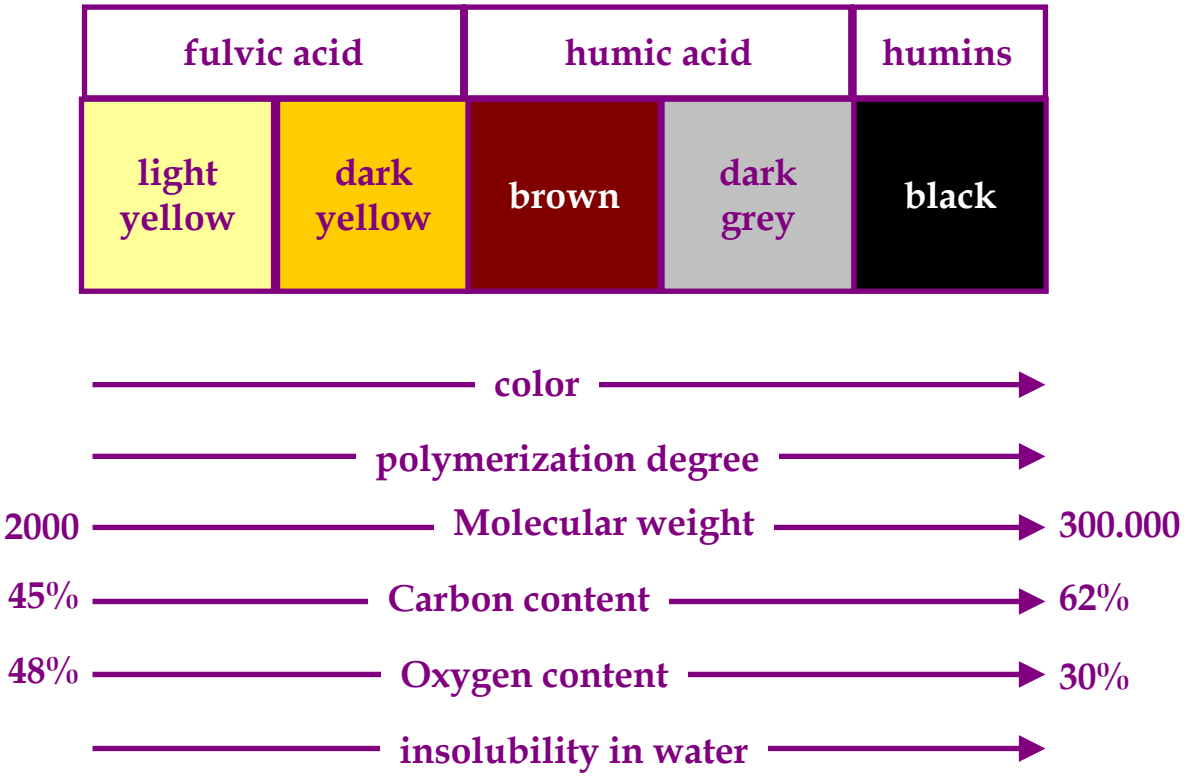
[e] Wright and Schnitzer, 1960; Hansen and Schnitzer, 1966; Khan, 1971; Riffaldi and Schnitzer, 1972; Ortiz de Serra and Schnitzer, 1973; Beck et al., 1974; Schnitzer and Vendette, 1975; Weber and Wilson, 1975; Holcomb, 1979; Hatcher et al., 1981; Schnitzer and Preston, 1986; Baes and Bloom, 1989; Frund et al., 1989; Stearman et al., 1989; Lobartini et al., 1991; Novak and Smeck, 1991; Raysid et al., 1992; Orlov, 1995; Barancikova et al., 1997; Celi et al., 1997; Martin et al., 1998; Ceppi et al., 1999; Monteil-Rivera et al., 2000; Novak et al., 2001.

contribution of DOM to alkalinity: humic substances

Ritchie & Perdue, Geochim. Cosmochim. Acta, 2003

biogenic organic compounds

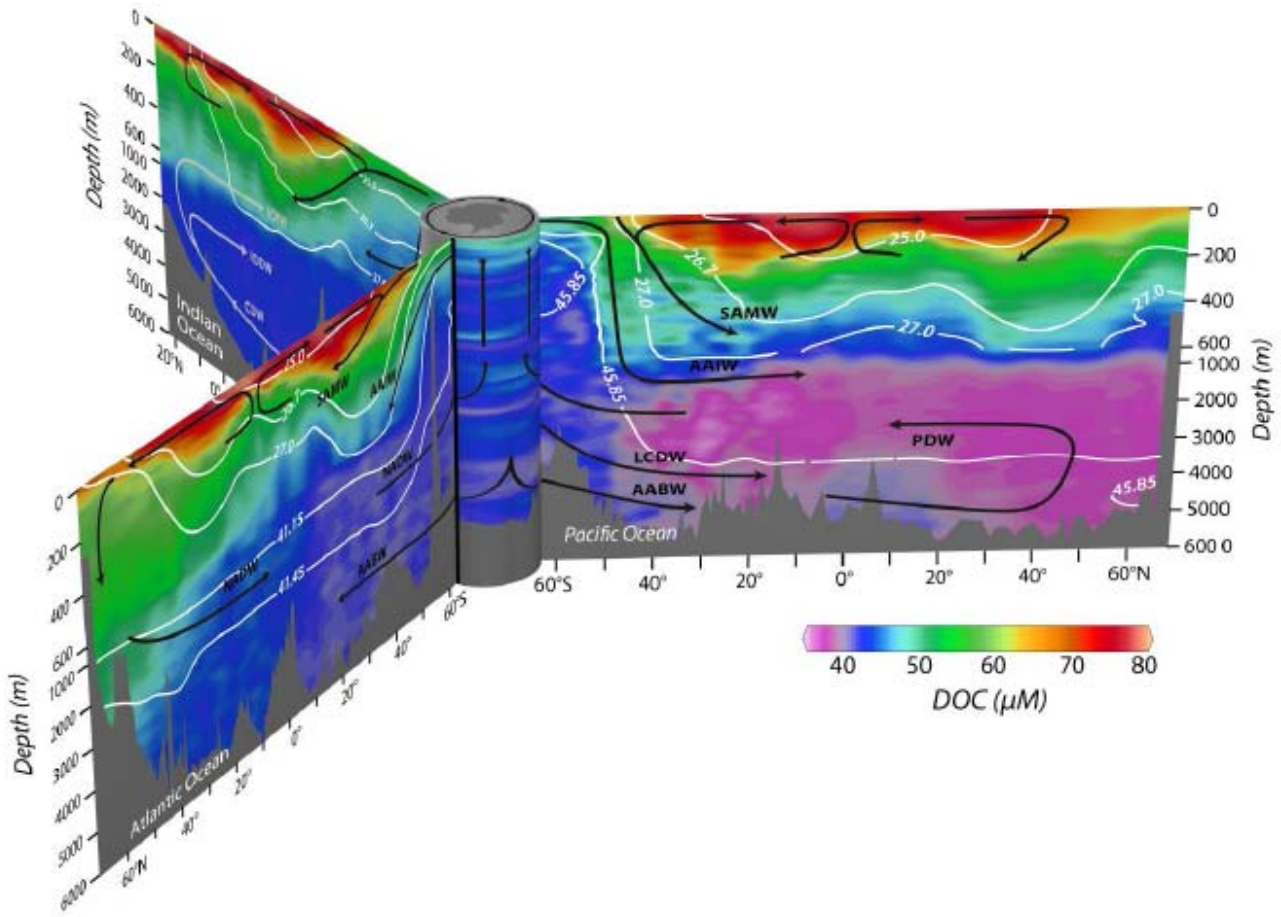
dissolved organic matter (DOM)



Stevenson, 1982

biogenic organic compounds

dissolved organic matter (DOM)



distribution of DOM in the oceans

Hansell et al., Oceanography, 2009