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MATERIA ORGÁNICA EN EL OCÉANO. MATERIA ORGÁNICA PARTICULADA Y DISUELTA

- Flujos de material particulado
- Material orgánico disuelto
- Preservación de materia orgánica



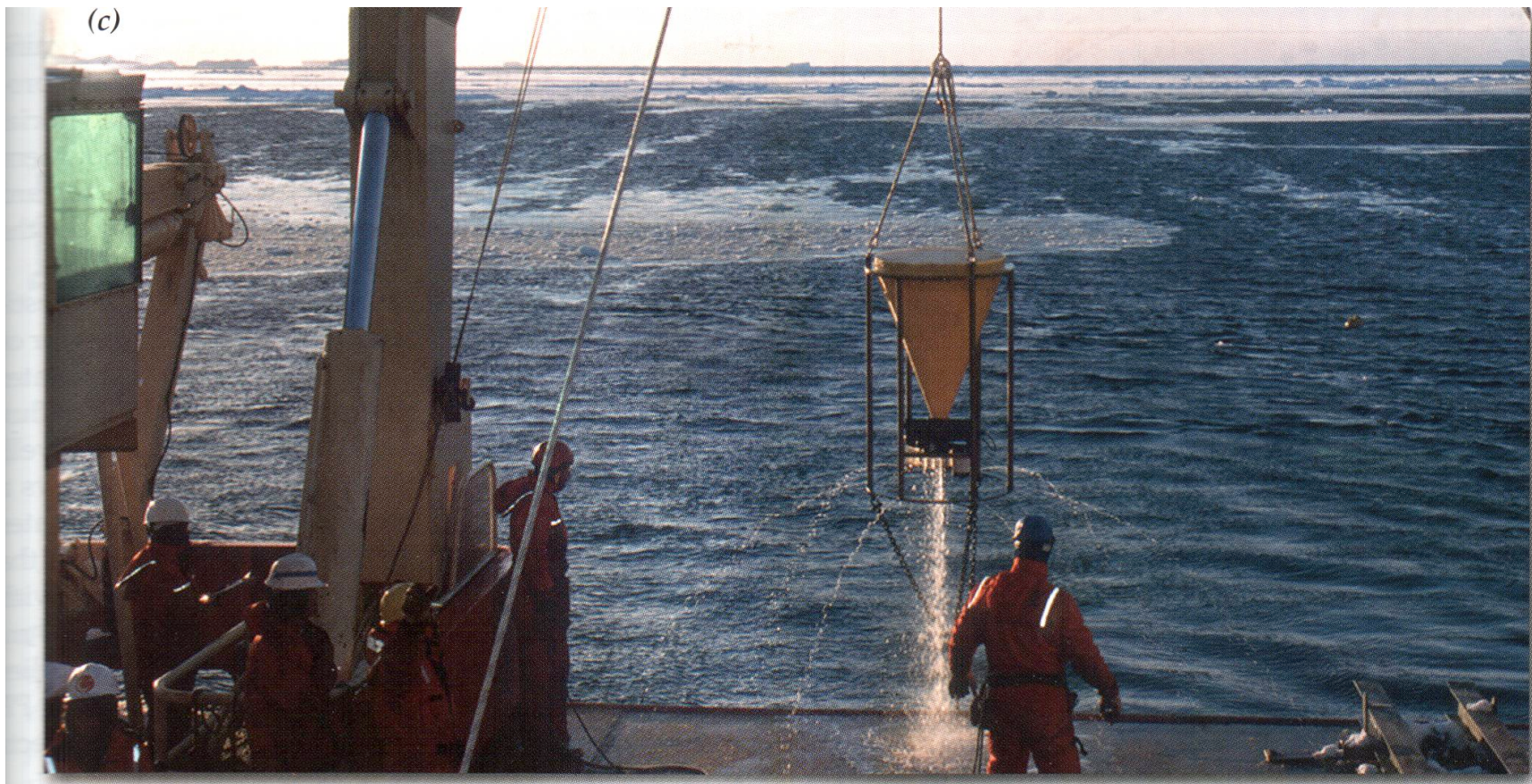
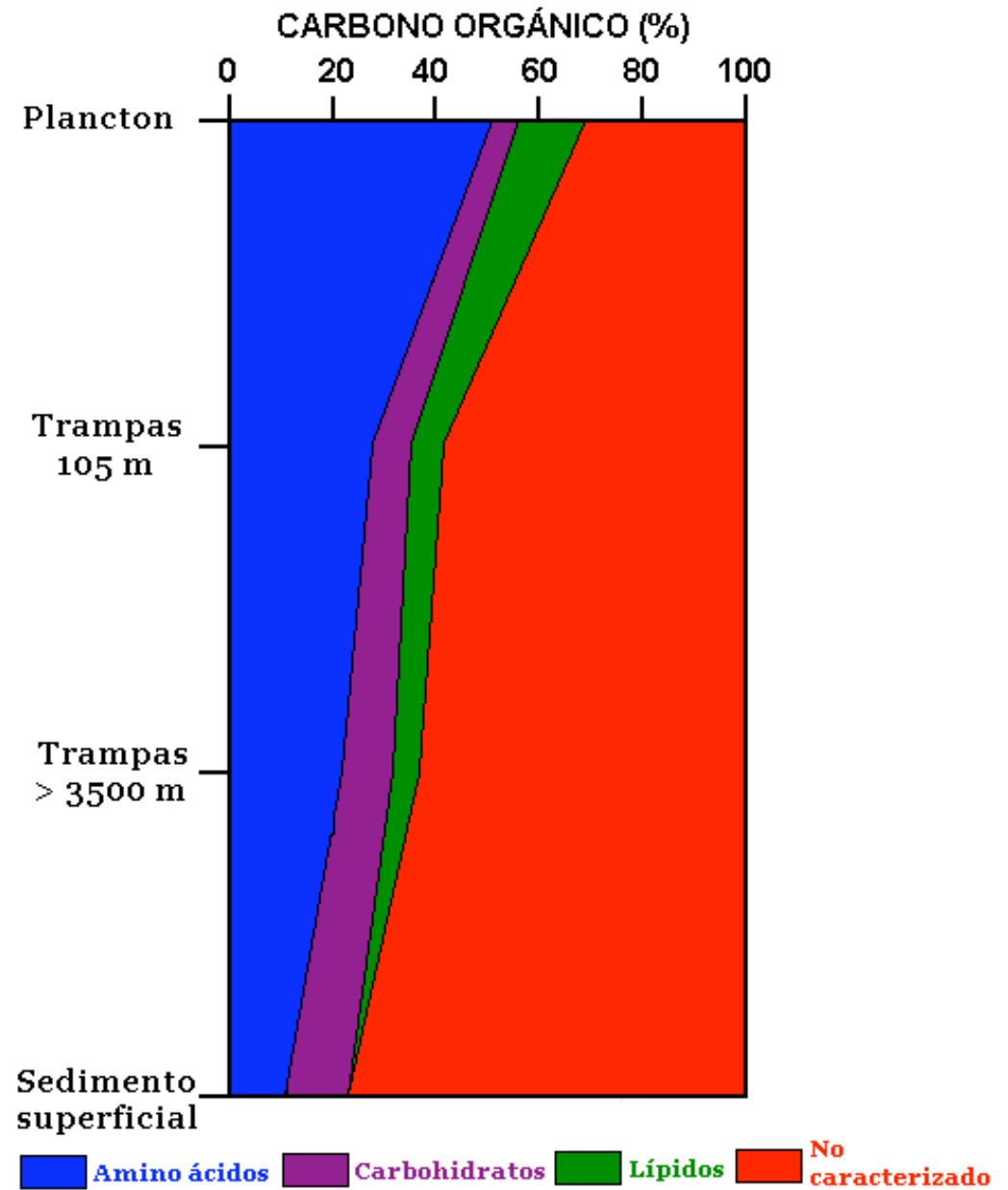
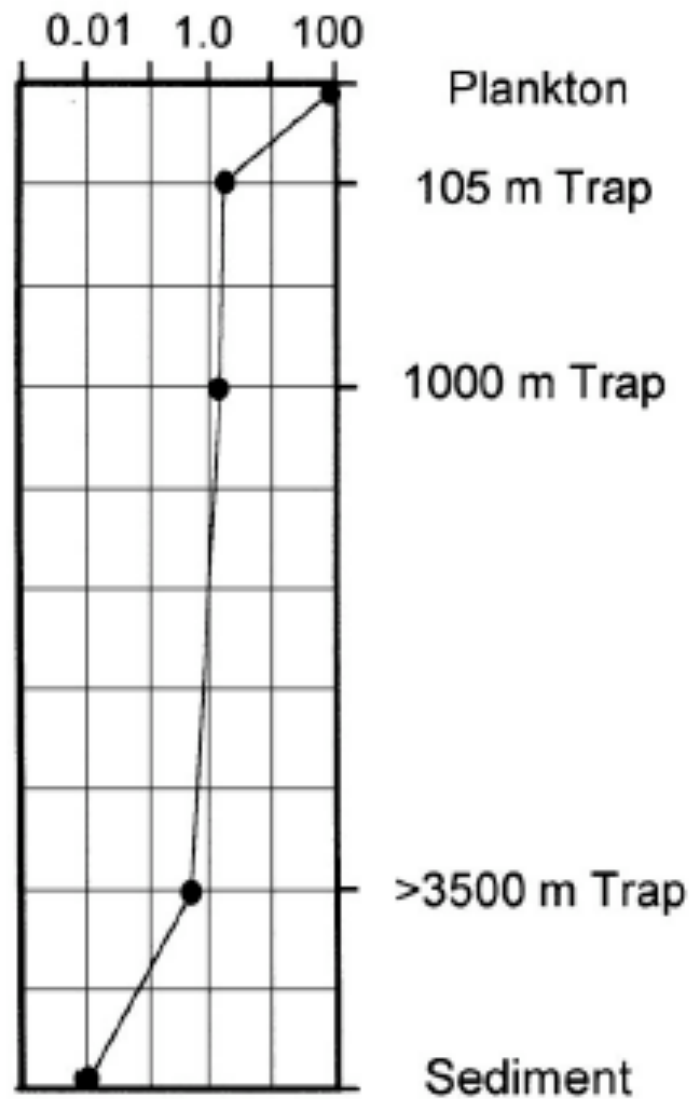
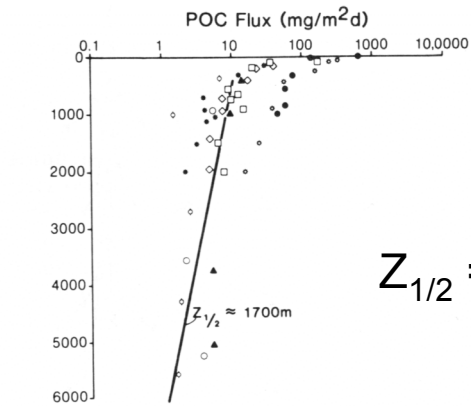


Figure 1. a) Large-volume in situ pump used for collecting thorium-234 samples, photo courtesy of Ken Buesseler. b) Recovery of benthic lander, photo courtesy of William Berelson. c) Recovery of deep sediment trap in Southern Ocean, photo courtesy of Susumu Honjo.

POC Flux, $\text{mg/m}^2\text{d}$



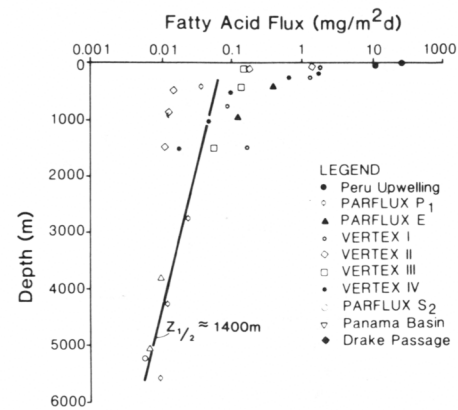
Wakeham et al. 1997



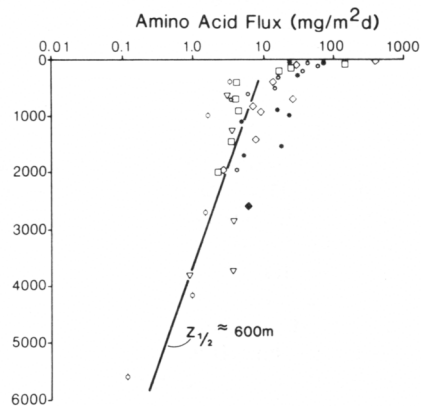
$$Z_{1/2} = 1700\text{m}$$

$$F = F_0 e^{-kz}$$

$$\ln F = \ln F_0 - kz$$



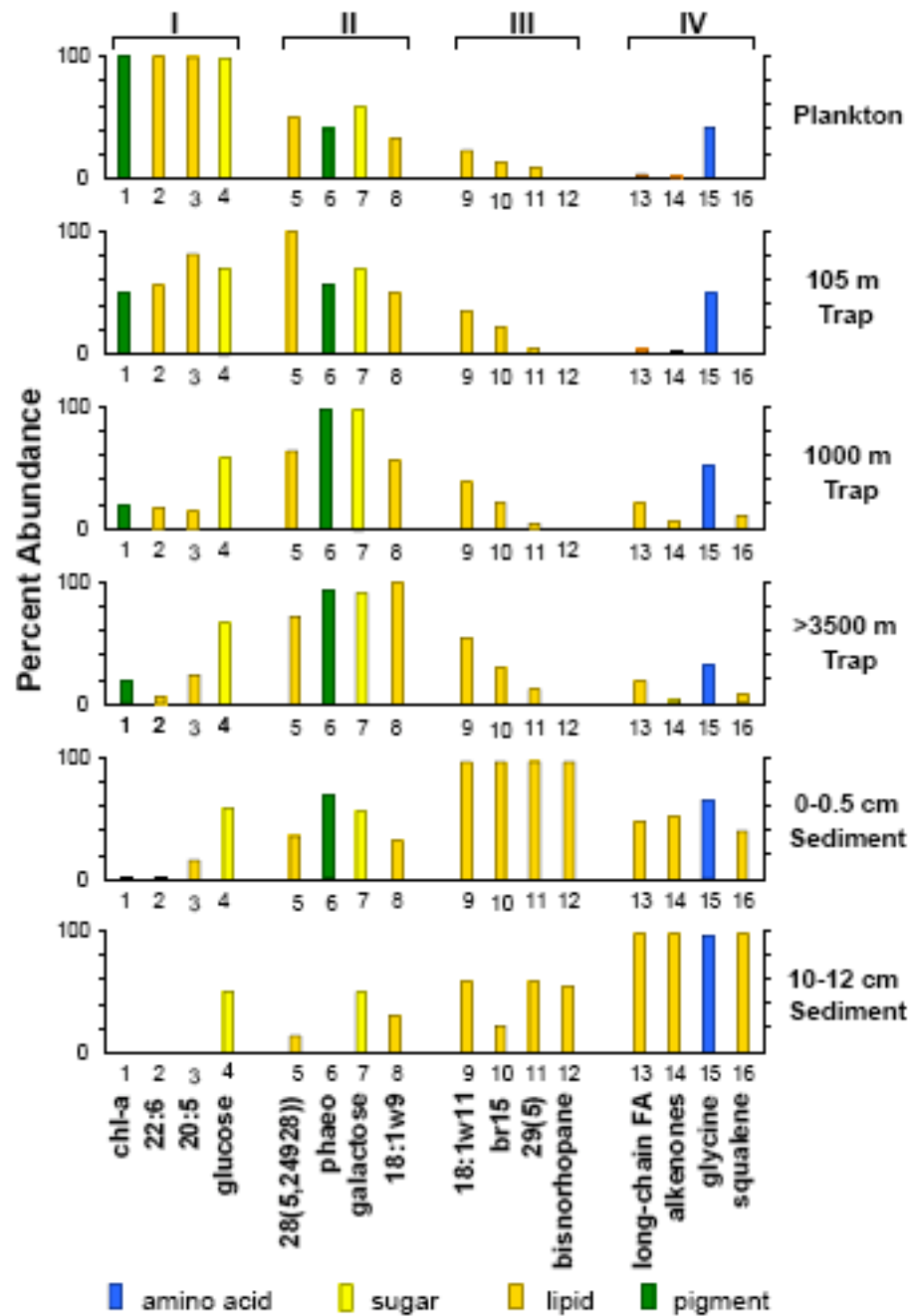
$$Z_{1/2} = 1400\text{m}$$



$$Z_{1/2} = 600\text{m}$$

Lee and Wakeham (1993)

Figure 4. Vertical fluxes of POC, fatty acids, and amino acids at several locations in the ocean. Study sites as listed for Fig. 2, and including PARFLUX S₂ (Sargasso Sea; Honjo, 1980; de Baar *et al.*, 1983), Panama Basin (Lee and Cronin, 1984), and Drake Passage (Wefer *et al.*, 1982). Lines are regressions for flux data at depths greater than 400 m; $z_{1/2}$ are calculated half-depths (see text).



I. Concentración máxima en plancton superficial y disminución con profundidad, e.g., clorofila-a

II. Concentración máxima en la columna de agua, e.g., feoforbido

III. Abundancia máxima en sedimentos superficiales (0-0.5cm), e.g., hopanoides

IV. Abundancia máxima en sedimentos (10-12cm).
Resistentes a la degradación microbiana, e.g., C:37 alquenonas

Wakeham et al. (1997)

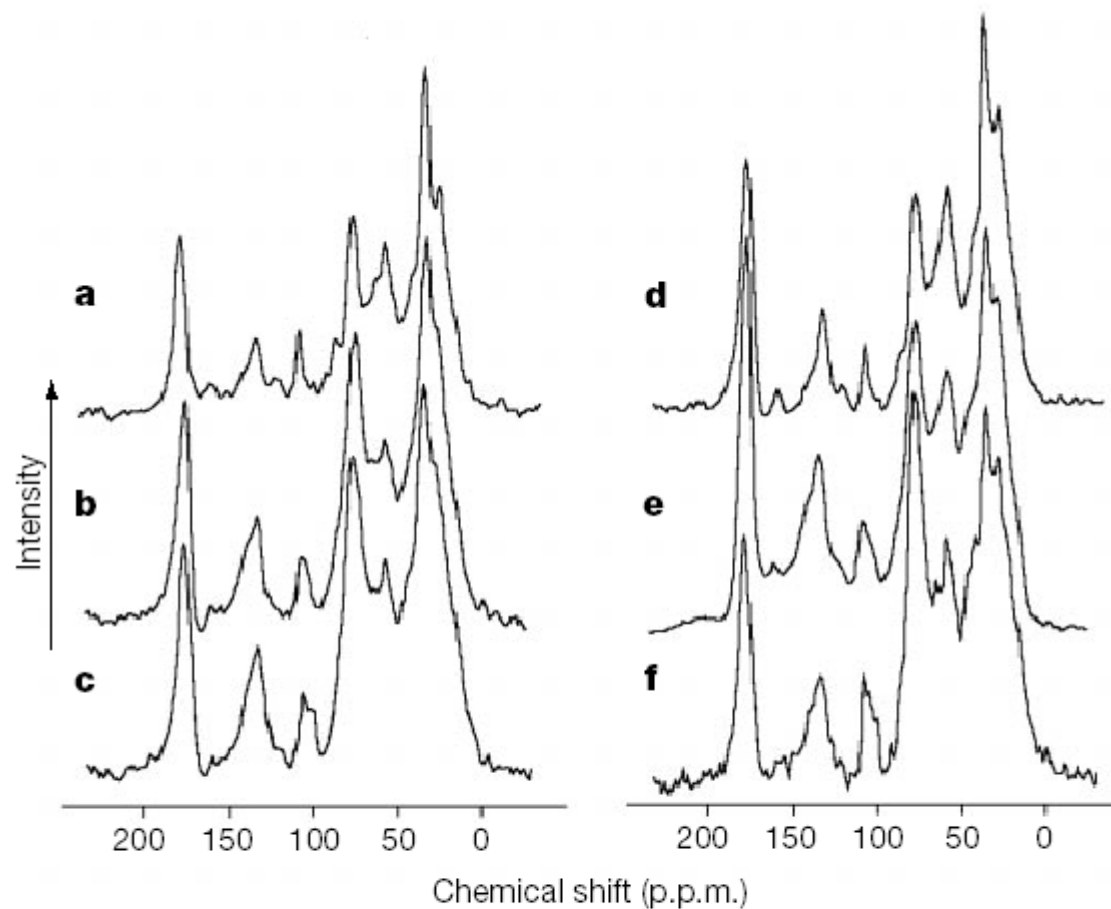
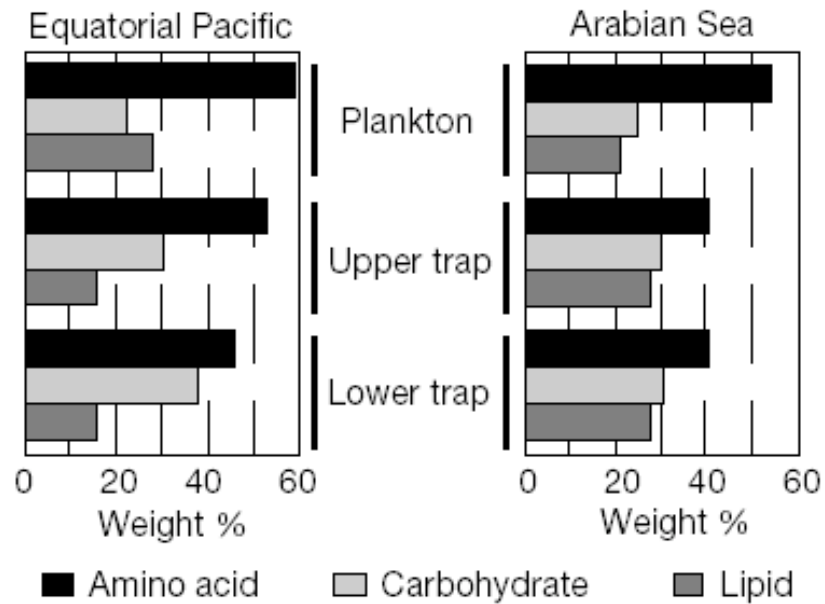


Figure 1 Solid-state ^{13}C NMR spectra of material from the equatorial Pacific Ocean and the Arabian Sea. **a–c**, Material from the equatorial Pacific Ocean; **a**, plankton, **b**, upper trap, and **c**, deep trap samples. **d–f**, Material from the Arabian Sea; **d**, plankton, **e**, upper trap, and **f**, deep trap samples (Table 1).

alquil = 0-45 ppm
 amino = 45-60 ppm
 O-alquil = 60-95 ppm (pentosas, hexosas)
 carbonyl = 165-215 ppm
 C=O en esteres y amidas = 175 ppm

No evidencia de productos de
 humificación (no aumento de
 insaturación con profundidad)

Hedges et al. 2001



Hedges et al. 2001

Figure 2 Calculated weight percentages of biochemicals in the samples from the equatorial Pacific Ocean and the Arabian Sea. See Methods for a description of the techniques used to acquire and model these spectral data.

Aumento de la señal de carbohidrato con la profundidad pero en general no cambio drástico

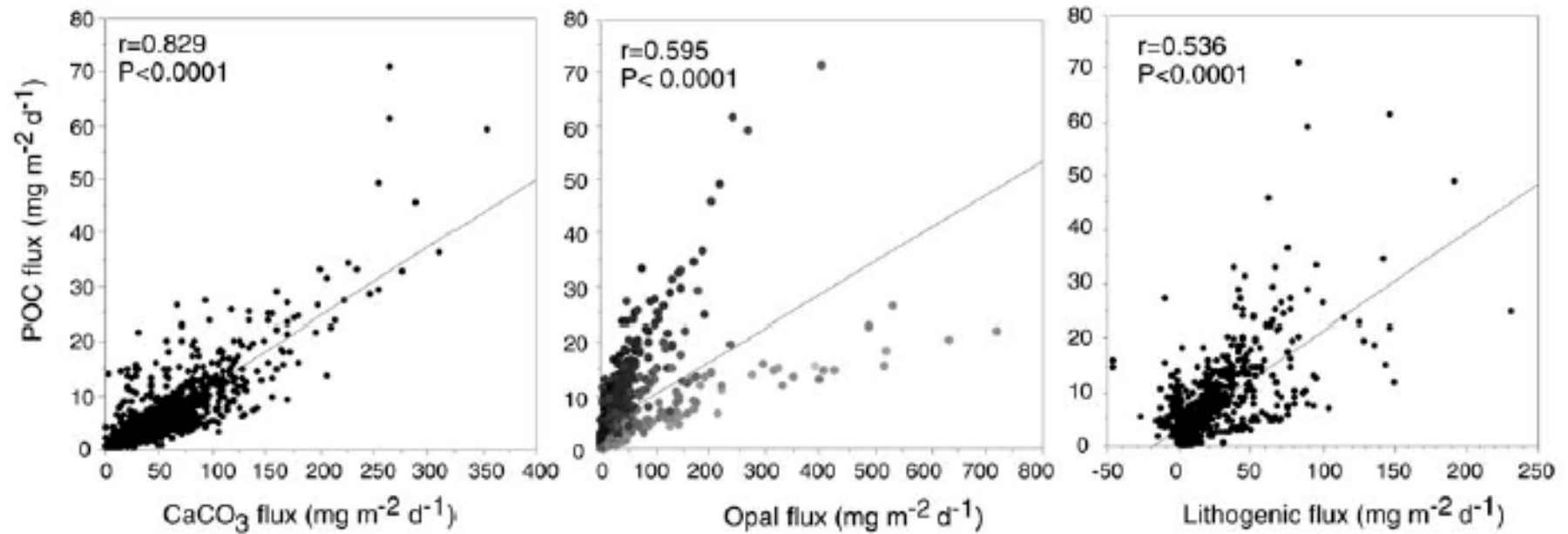
en resumen...

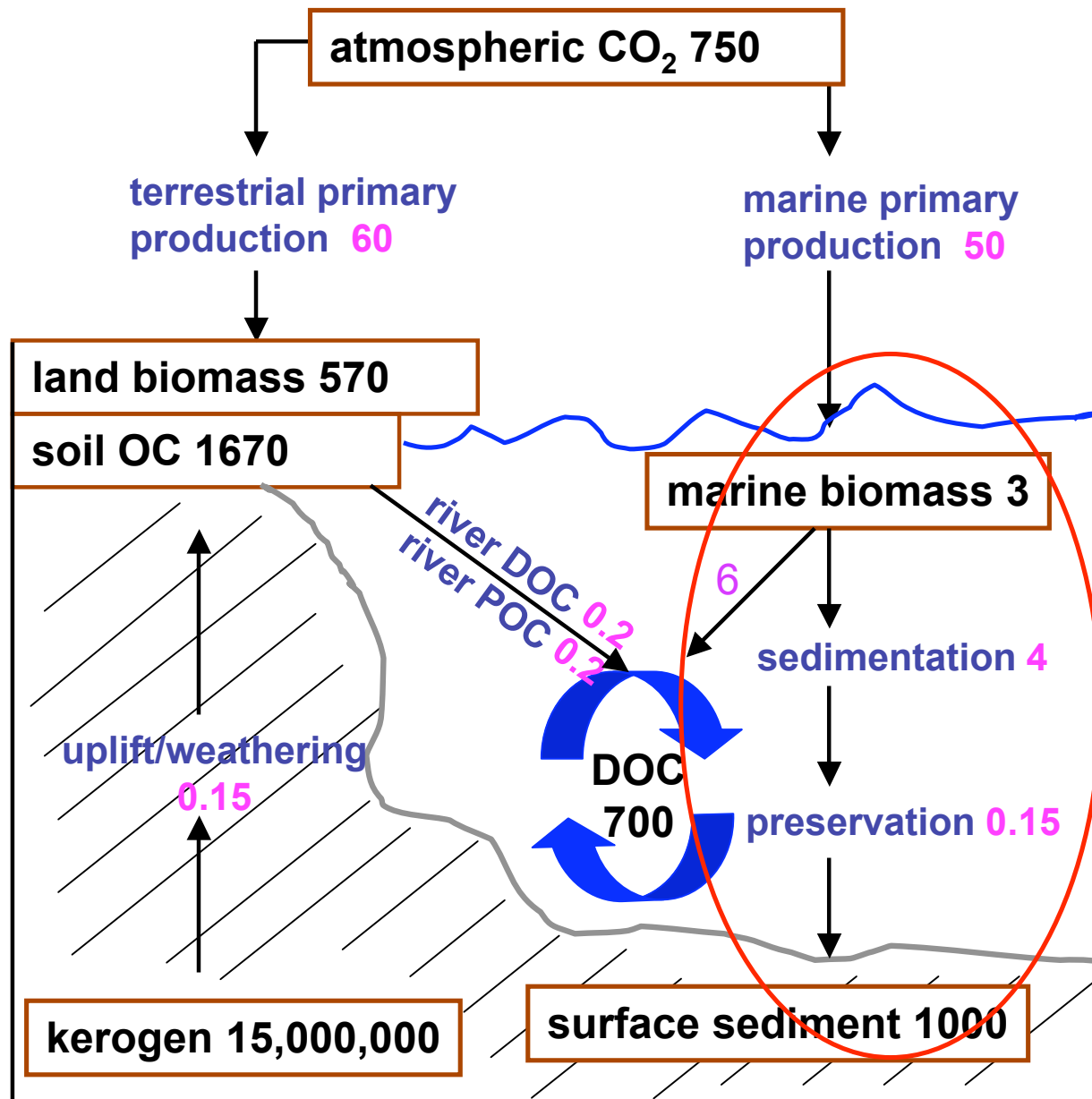
- A pesar de la extensa degradación, pocos cambios en composición
- Preservación no relacionada a recombinación o biosíntesis microbiana
- Protección de materia orgánica por la matriz inorgánica de las partículas (opal, carbonato de calcio, aluminosilicatos).
“Ballast”

Lastre (*ballast*) mineral

- La materia orgánica no sedimentará sin el lastre mineral
- [$\rho_{\text{MO}} \sim 0.9-1.05$; $\rho_{\text{carbonato}} 2.3$; $\rho_{\text{silica}} 2.5 \text{ g/cc}$]

¿Cuál lastre mineral se correlaciona mejor con el flujo de carbono orgánico particulado?



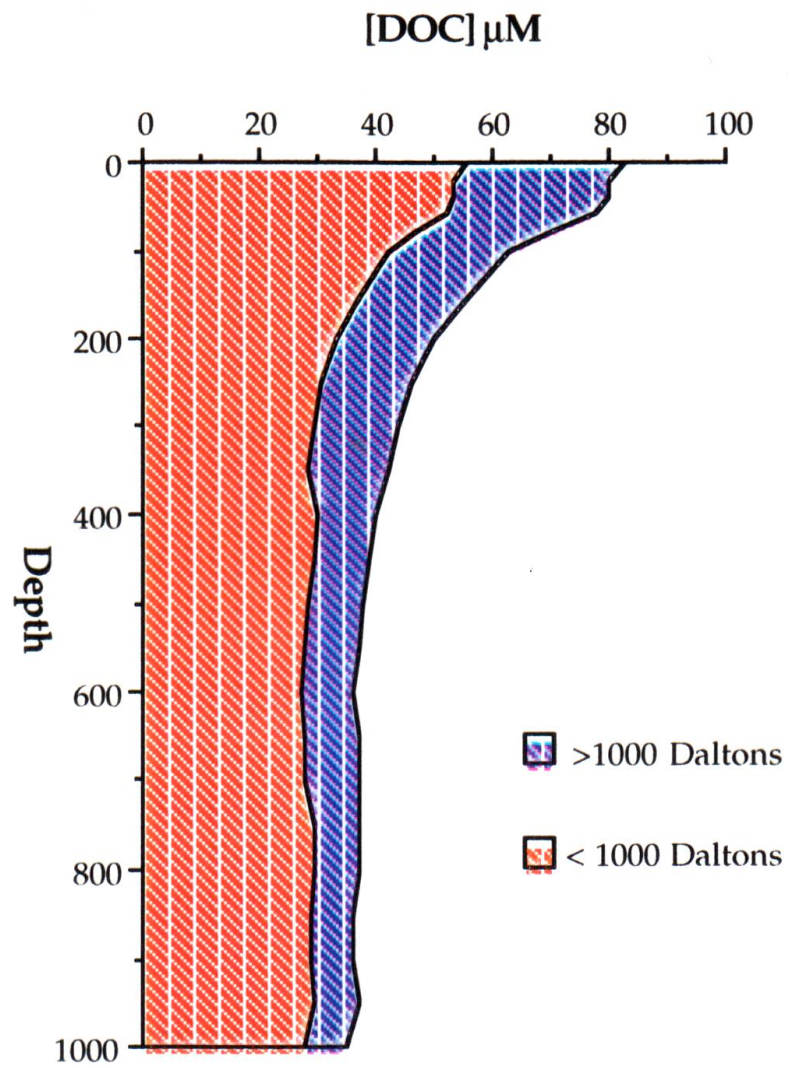


Pantoja & Wakeham 2000

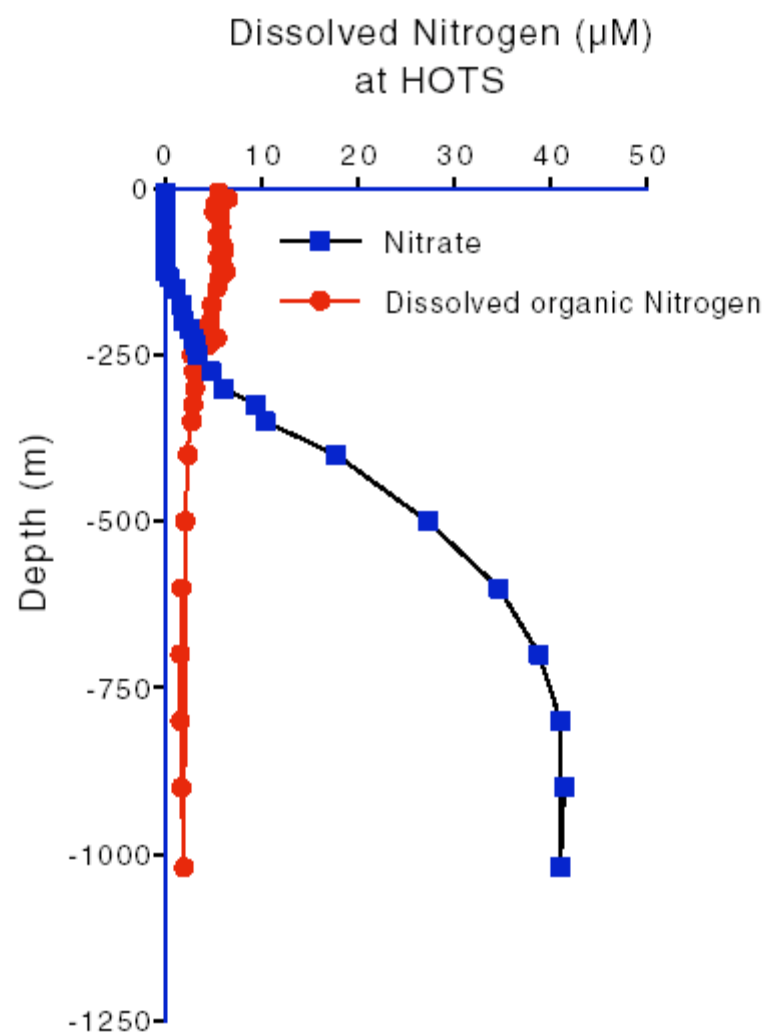
Global reservoirs (Gt) and fluxes (Gt y⁻¹) of OC on land and in the ocean (adapted from Hedges and Oades 1997)

1Gt= 10¹⁵ g

Carbonatos = 60 millones GT



0.5 Gt DNA sedimentos



Tasa de recambio de COD (estado estacionario)

- $600 \times 10^{15} \text{ gC}/6000\text{y} = 0.1 \times 10^{15} \text{ gC/y}$
- 0.1 Gt se producen y destruyen cada año
- 100 Gt se destruyen cada 1000 años
- $100/600 \approx 20\%$ se destruye y reemplaza de alguna parte
- Esto significa que 80% se recicla en cada ciclo de mezcla (permanecen como tal)
- De dónde viene el 20%?
- Ríos = 0.2 Gt/y ($0.2 \times 600 = 120 \text{ Gt}$)
- PP = 6 Gt/y

- COD tiene bajo contenido de lignina (**marino**)
- $\delta^{13}\text{C}$ -20 a -22‰ (**marino**)
- Antiguo (6000 y)
- Y por que 6000 y, por que no 7 o más o menos?

¿Cómo se explica que la gran masa de material recalcitrante orgánico que sufre intemperización de kerógeno (y que soportó un ciclo) en suelos y son transportados a través de ríos es aparentemente remineralizada en el océano, mientras que el material que parece fresco (fitoplancton) permanece como la mayoría del COD?

Análisis químico de COD en superficie (<100m) y profundo (>1000m). Benner 2002

Composición molecular	COD superficial (%)	COD profundo (%)
carbohidratos	2-6	0.5-2
proteínas	1-3	0.8-1.8
Polímeros de amino azucares	0.4-0.6	0.04-0.07
lípidos	0.3-0.9	nd
Total	3.7-10.5	1.3-3.9

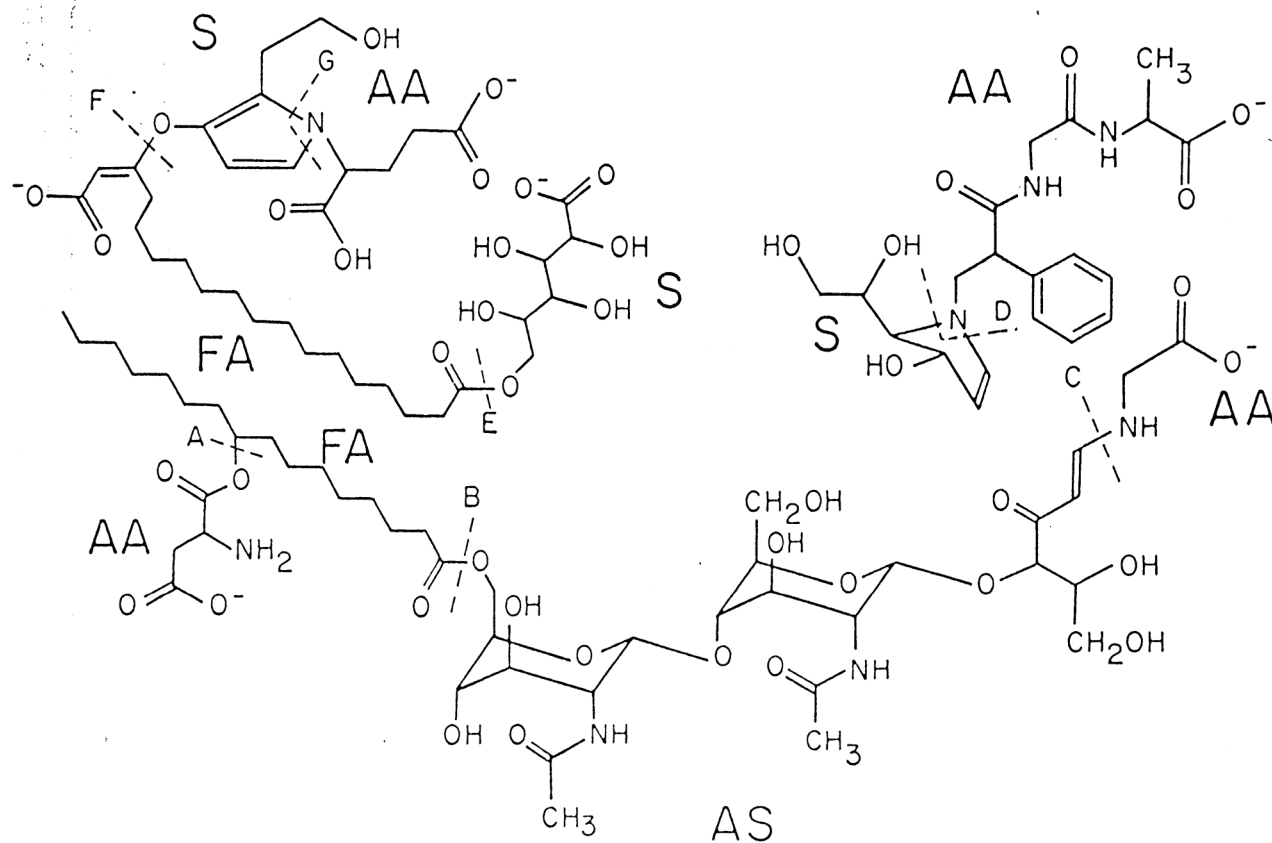


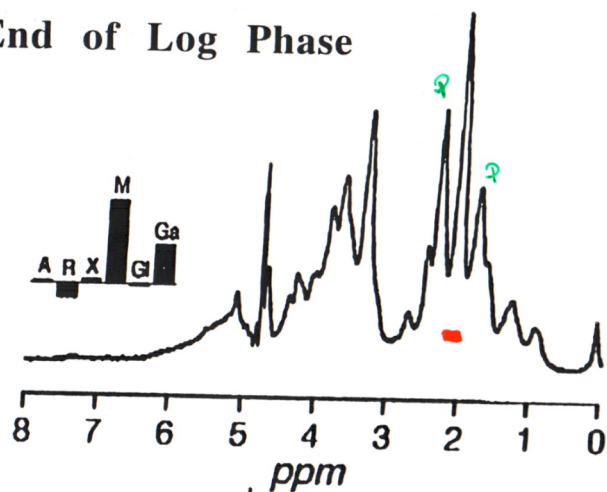
FIG. 4. - Hypothetical structure of seawater humic substances with amino acid (AA), sugar (S), amino sugar (AS) and fatty acid (FA) moieties incorporated. The dashed lines A-G represent sites of bond formation of these compounds.

Sustancias húmicas, solubles en base:

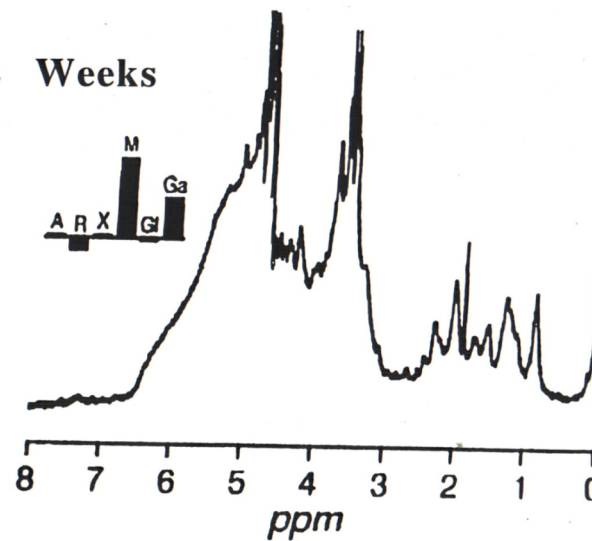
- 1) Ácido fúlvicos, soluble en ácido
- 2) Ácidos húmicos, insoluble en ácido

^1H -nmr

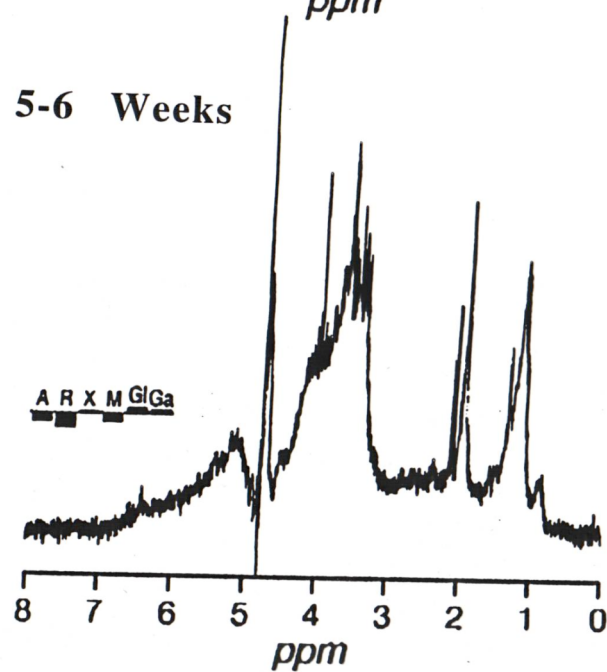
End of Log Phase



2 Weeks

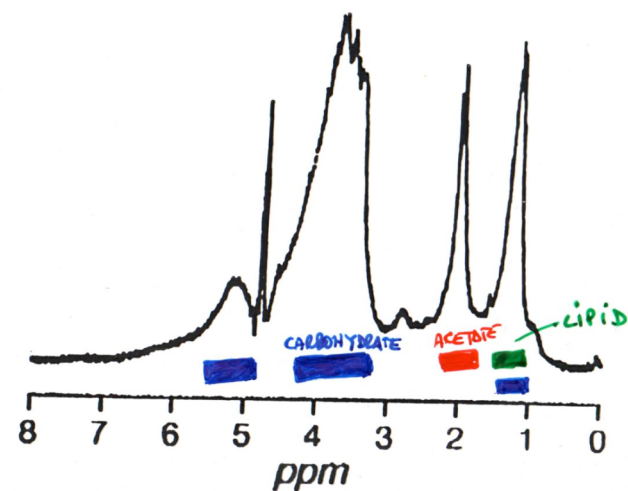


5-6 Weeks

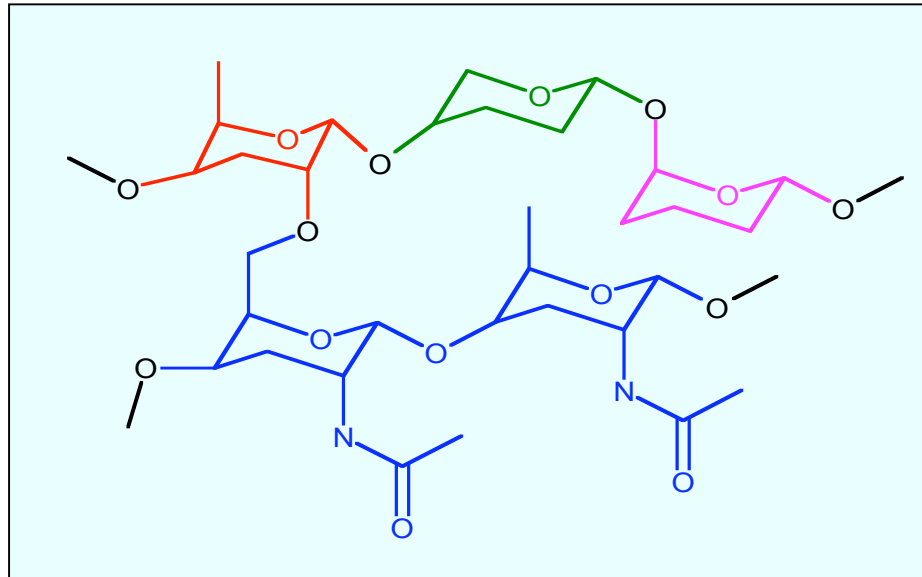


Seawater

slowly HARE, Lepeta
& CHER (1997)



Chemical Characterization of High Molecular Weight (HMW) Dissolved Organic Matter (DOM)



**Acylated Polysaccharide
(APS)**

50% of surface HMW DOM (**10 Gt C**)
15% of deep HMW DOM (**15 Gt C**)

Aluwihare et al. 1997

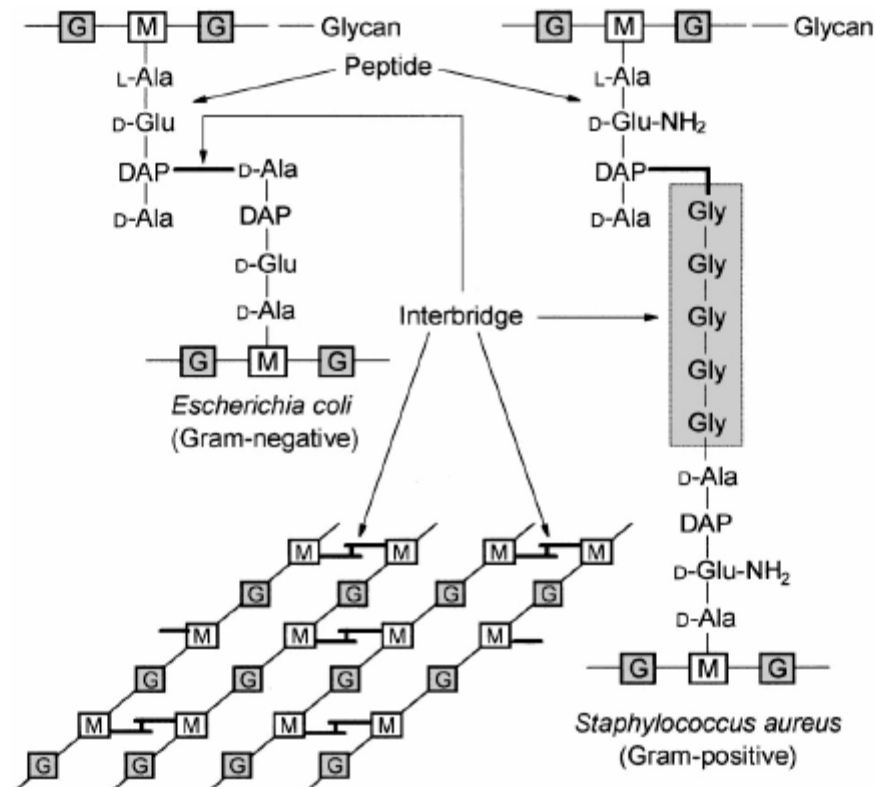
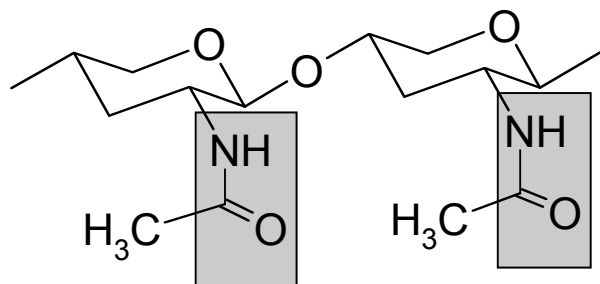


Fig. 5. Schematic representation of the structure of bacterial peptidoglycan (after Brock et al., 1994). The upper two images illustrate the linkages of structural units within peptidoglycans of species of Gram-negative and Gram-positive bacteria. The network to the lower left shows how these units are assembled into a peptidoglycan sheet (peptide crosslinks in bold) that is relatively resistant to biodegradation. Abbreviations: G = *N*-acetylglucosamine, M = *N*-acetylmuramic acid, DAP = meso-diaminopimelic acid, Ala = alanine, Gly = glycine, Glu = glutamic acid.

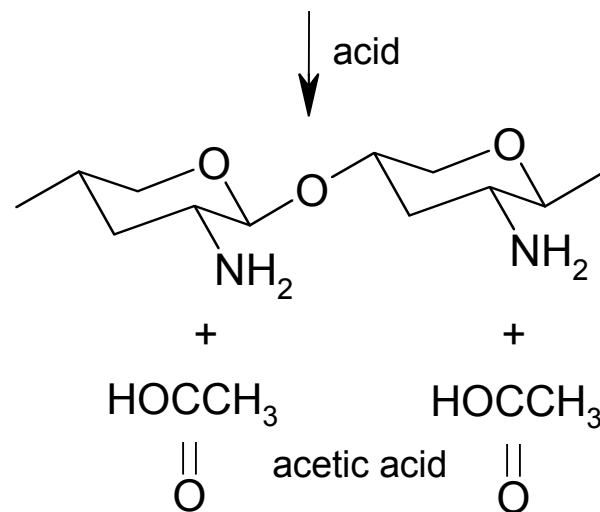
McCarthy et al. 1997

amida

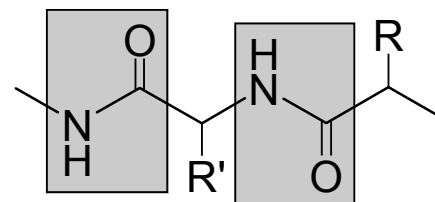
CHITIN



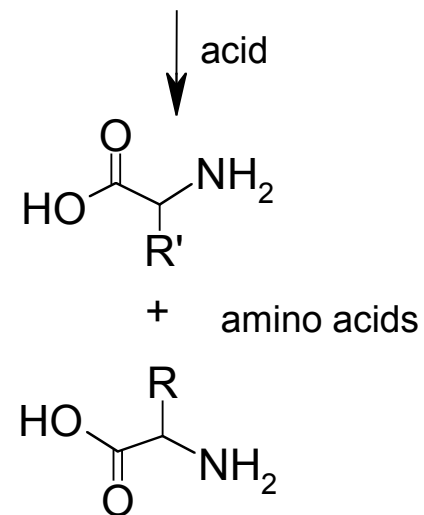
acid



PROTEIN

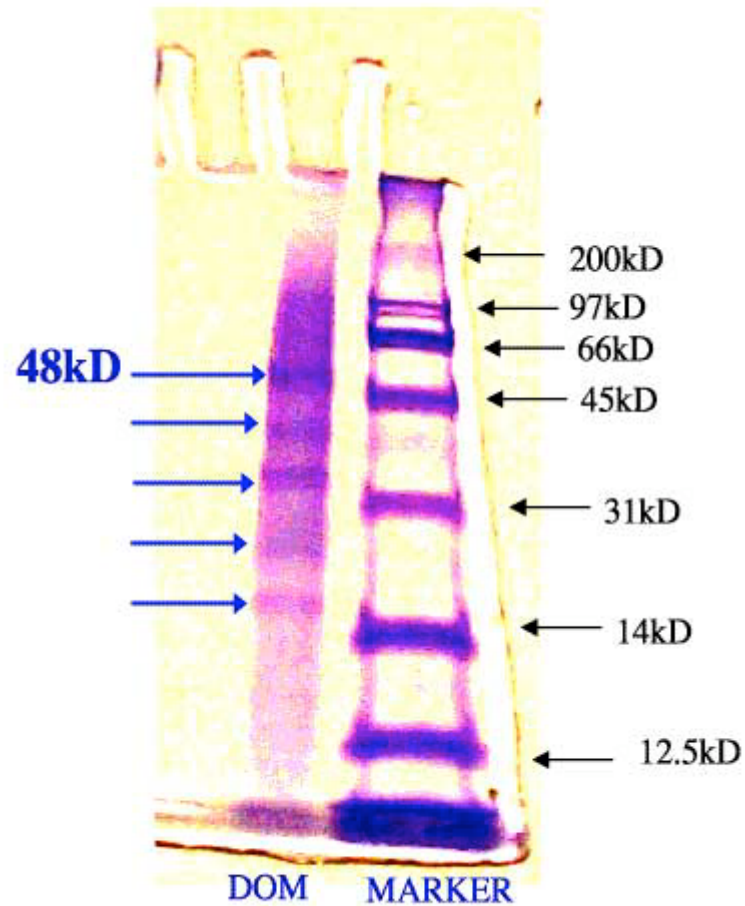


acid



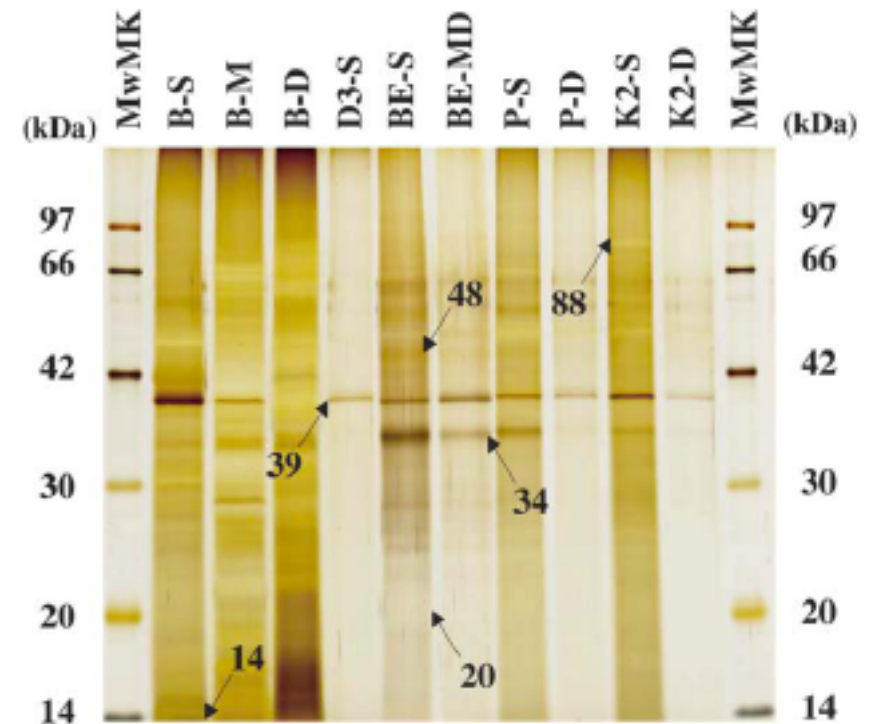
Lihini I. Aluwihare, Daniel J. Repeta, Silvio Pantoja, Carl G. Johnson. 2005. Two Chemically Distinct Pools of Organic Nitrogen Accumulate in the Ocean. *SCIENCE* 308, 1007-1010

- Dos grupos distintos de NOD se acumulan en el océano
- La mitad del material de alto peso molecular en superficie está presente como amino polisacáridos N-acetilados
- Casi todo el material de alto peso molecular en el océano profundo está presente como amidas que resisten hidrólisis química y degradación biológica
- La abundancia de nitrógeno como amidas en toda la columna de agua sugiere que son mas biológicamente recalcitrantes que otras formas de nitrógeno orgánico



Fracción de proteínas de >1kD
DOM (West Neck Bay)

N. Yamada, E. Tanoue / Progress in Oceanography 69 (2006) 1–18



412 “spots” de proteínas en el
Pacífico. Proponen que DOC
proviene de vesículas de membrana
de bacterioplancton *Pseudomonas*

CDOM: Materia orgánica disuelta coloreada

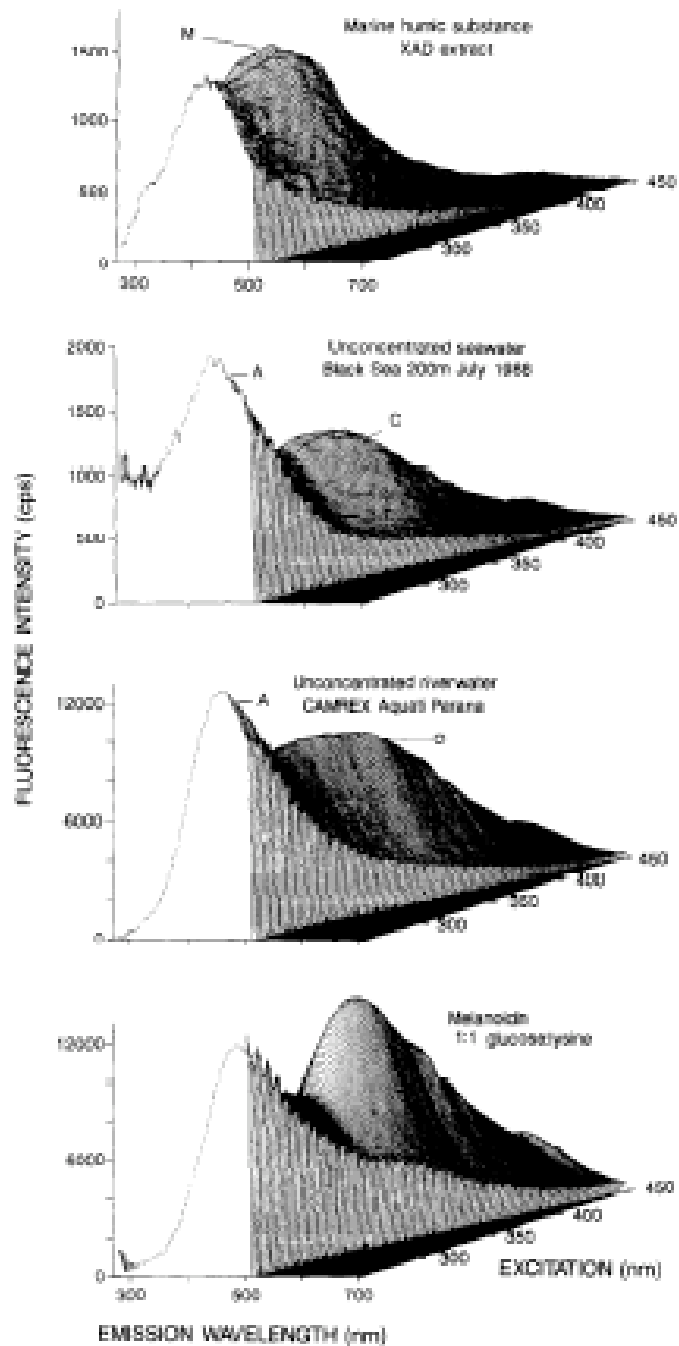
1. Reacciones fotoquímicas en el océano
2. Calidad u cantidad de luz que llega a las células fotosintéticas
3. Representa la MOD que es exportada desde los márgenes continentales (?)
4. Afecta el color del océano y por ende las imágenes satelitales
5. Representa la MOD continental que llega al ambiente marino (?)
6. Fuente de nitrógeno para el fitoplancton costero (?)

Propiedades ópticas de la MOD están determinadas por la mezcla de:

- 1) Cromóforos: moléculas que absorben luz visible y UV
- 2) Fluoróporos: moléculas que re-emiten luz absorbida a longitudes de onda más altas

Disminución de la absorción en profundidad y aumento de la longitud de onda

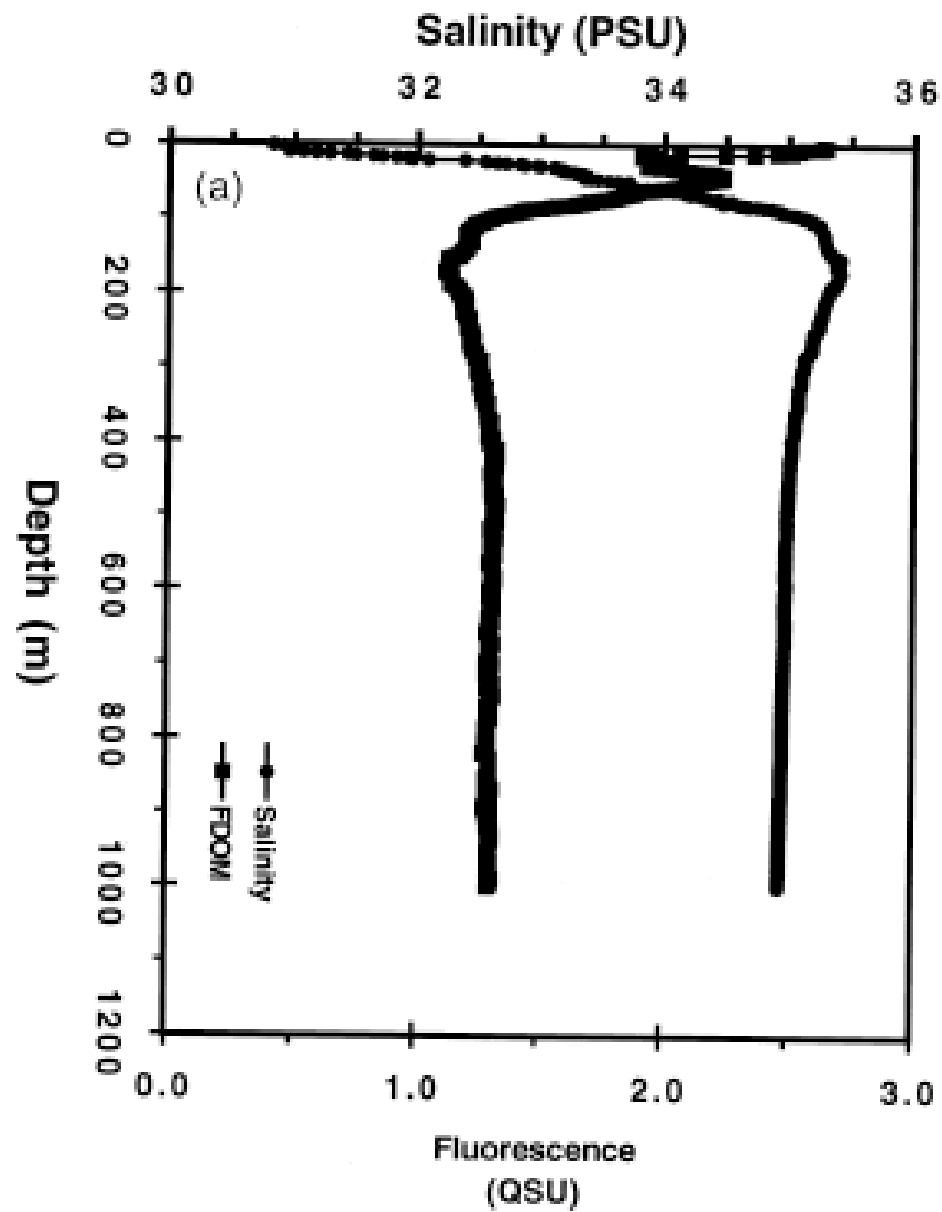
Fluorescencia proporciona información estructural (origen) con excitación máxima entre 300-350 nm y emisión entre 400-500 nm



Coble 1996

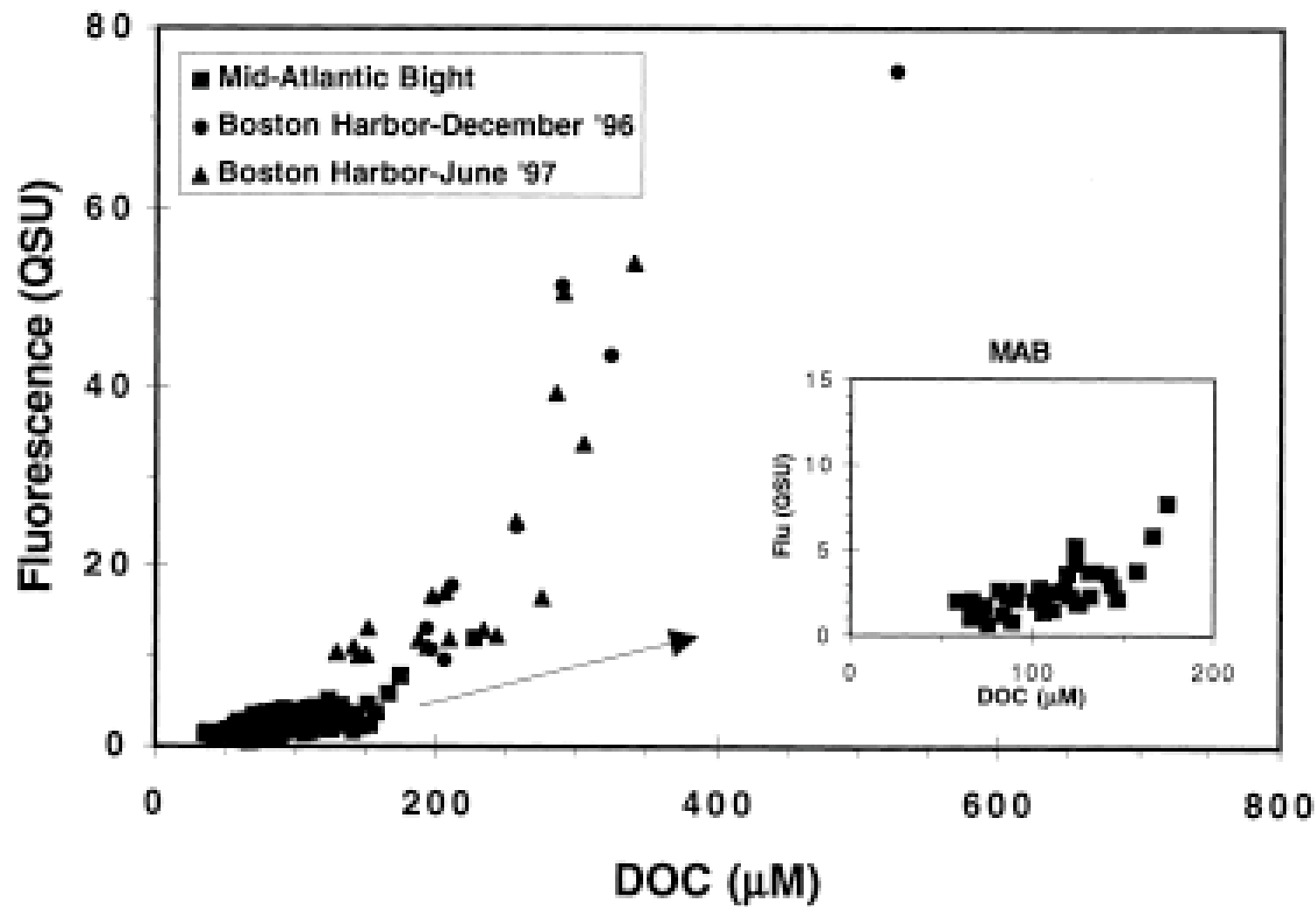
M = sustancia húmica marina
A, C = sustancia húmica

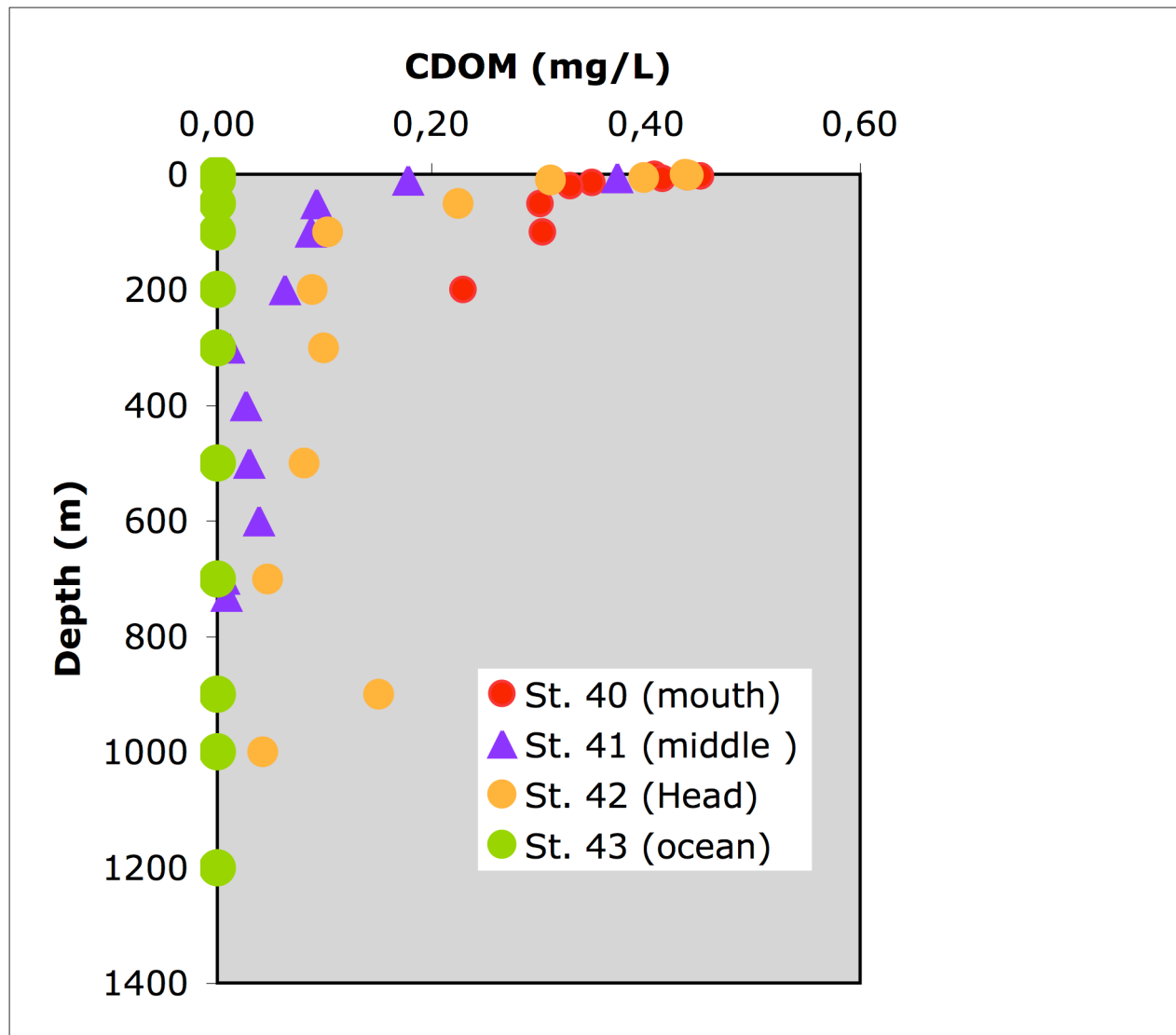
Station 14
Off Ocean City,
New Jersey



Chen 1999

Coastal Waters

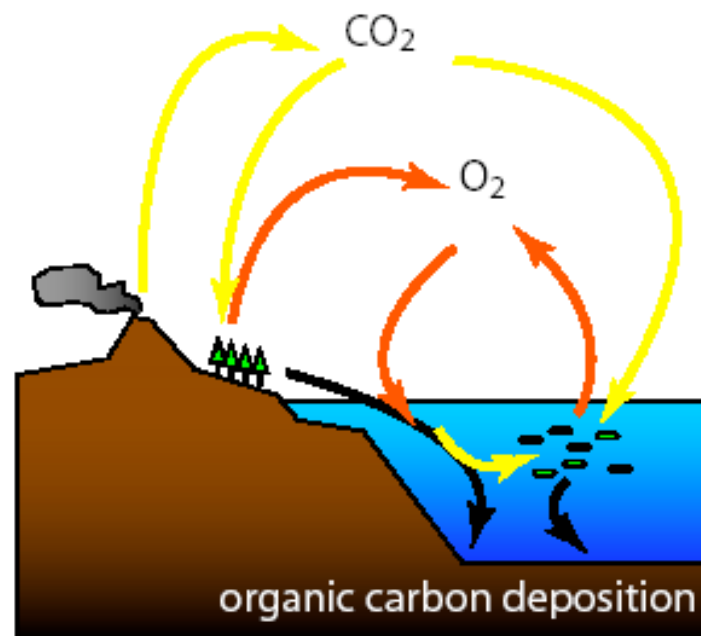




Canal Baker
Mg C QS/L
Mirai 2009-Pantoja

Coupling and feedbacks between carbon and oxygen cycles

- ✱ *tectonic degassing*
- ✱ *photosynthesis*
- ✱ *burial of organic carbon*





Por supuesto esto
cambia en el tiempo...

preservación

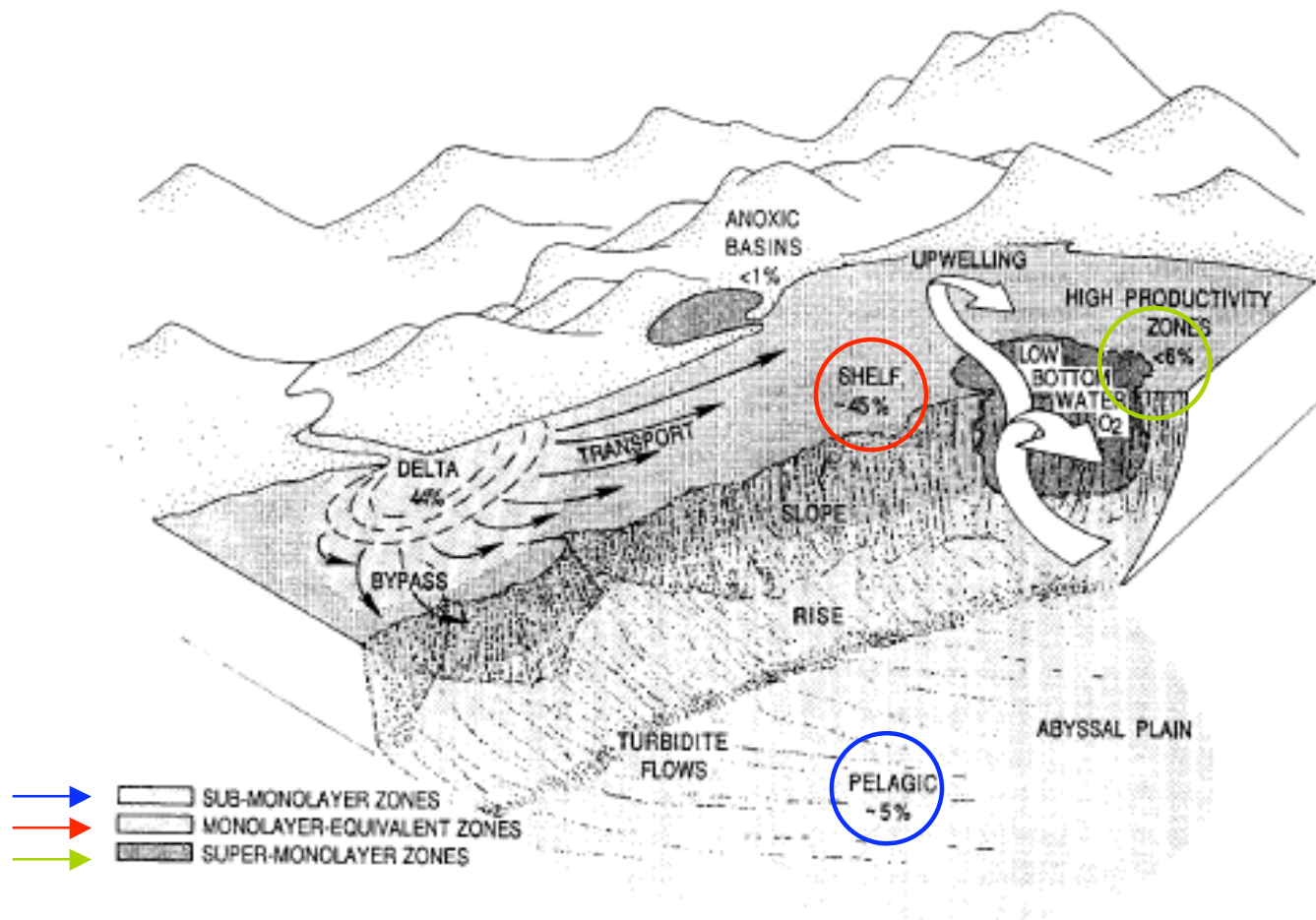
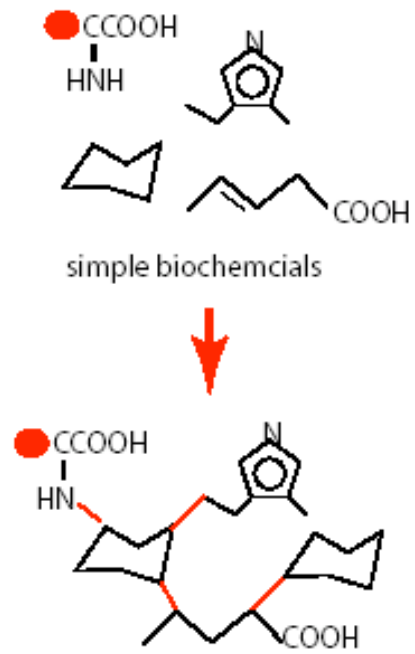


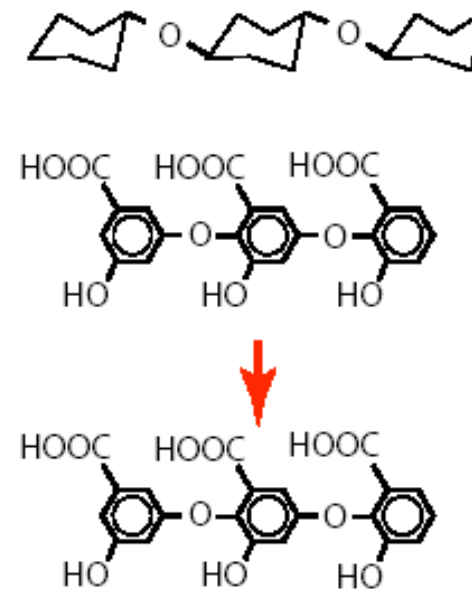
Fig. 1. Idealized diagram depicting current estimates of the percentage of total organic matter burial occurring within various marine sediment types (see Table 2). Light sections represent sediments which contain organic loadings lower than a monolayer equivalent. Stippled sediments contain monolayer-equivalent loadings, and dark sediments contain loadings that are more than monolayer-equivalent.

Effect of chemical composition on organic matter degradation in sediments

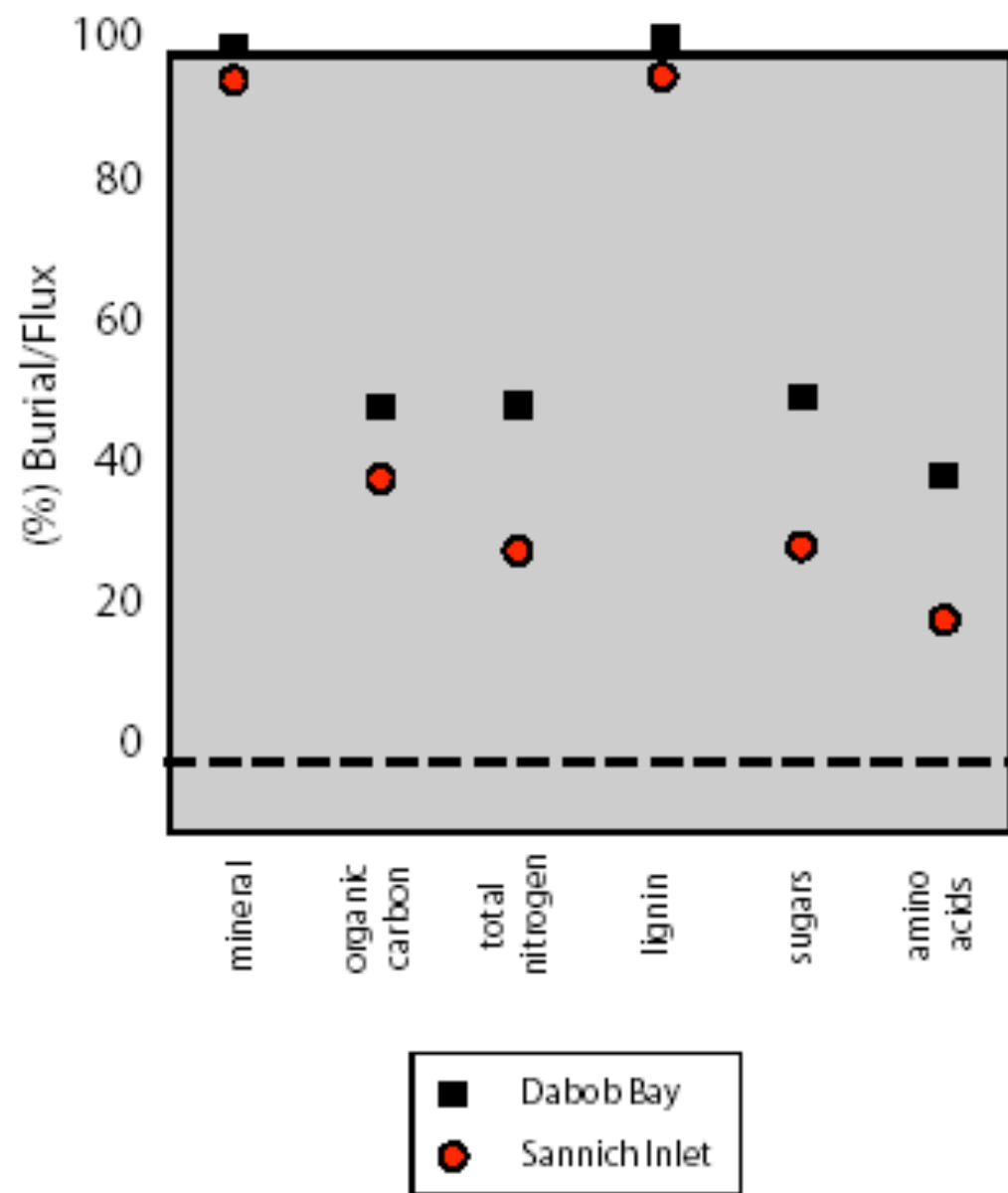
Geopolymerization



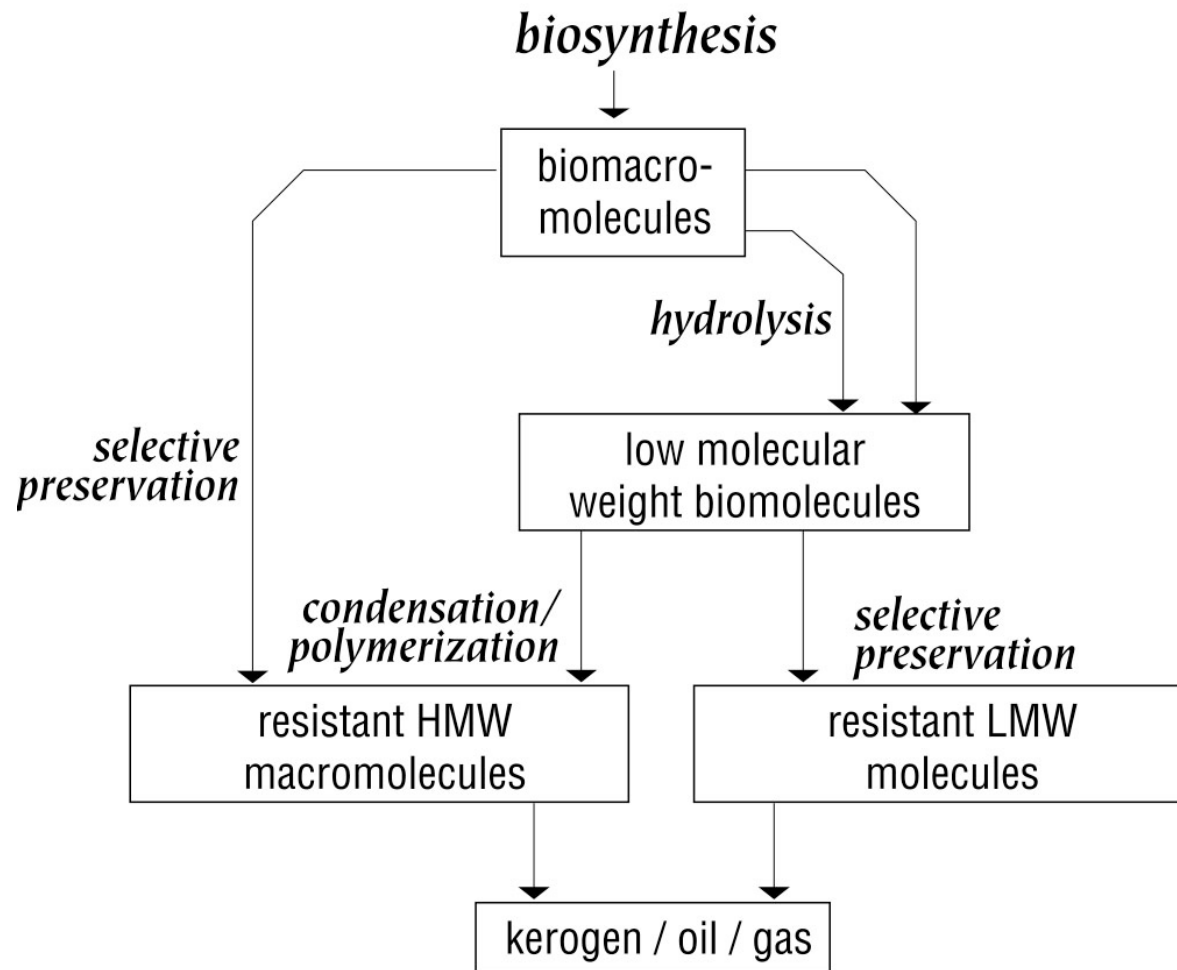
Selective preservation



Selective preservation of
organic matter in sediments

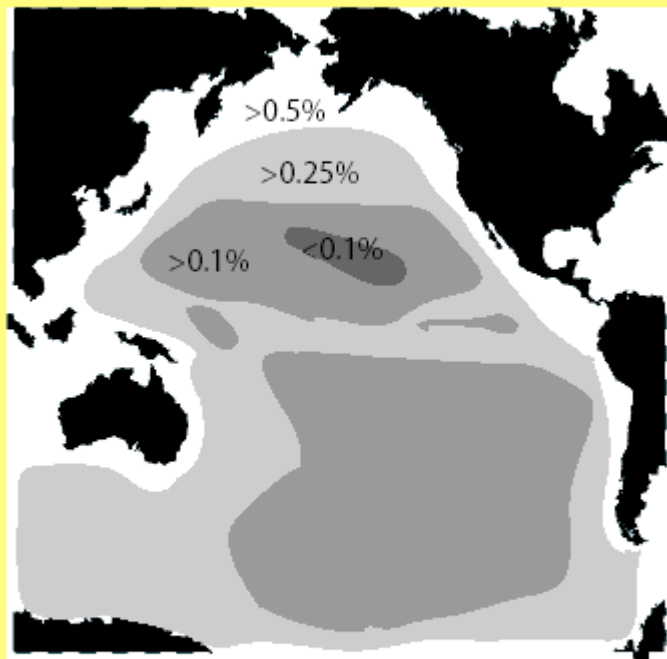


mecanismos

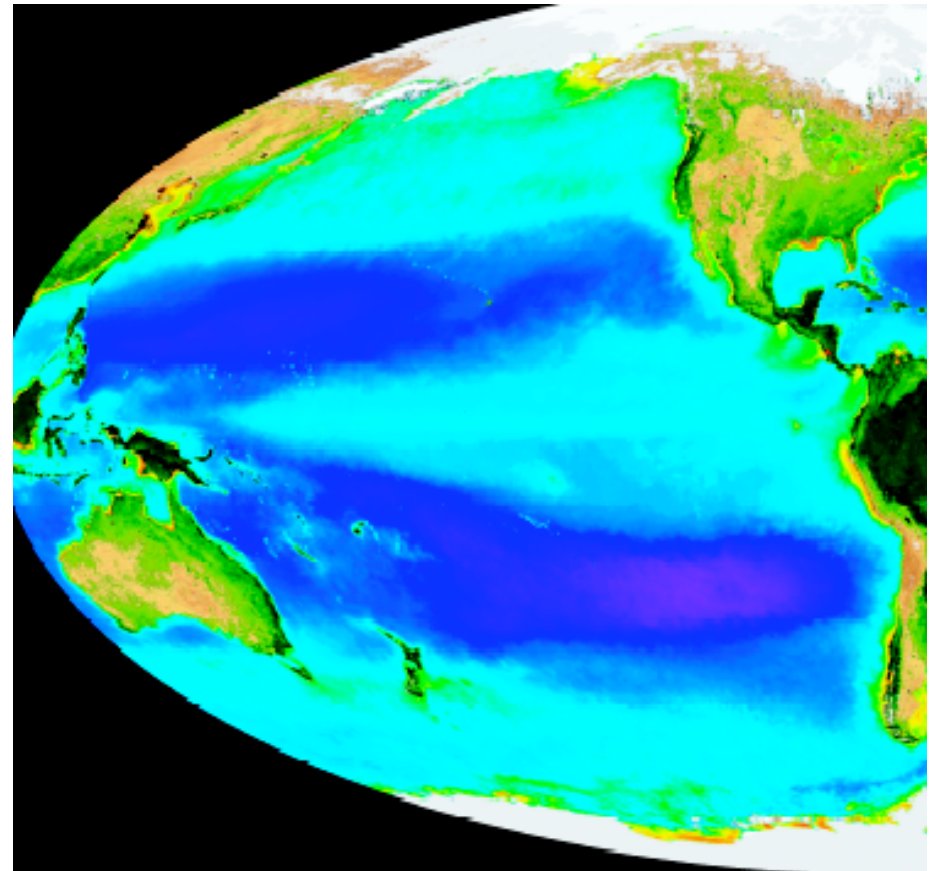


Schematic of selective preservation vs. condensation pathways for preservation of organic matter (adapted from Tegelaar et al. 1989)

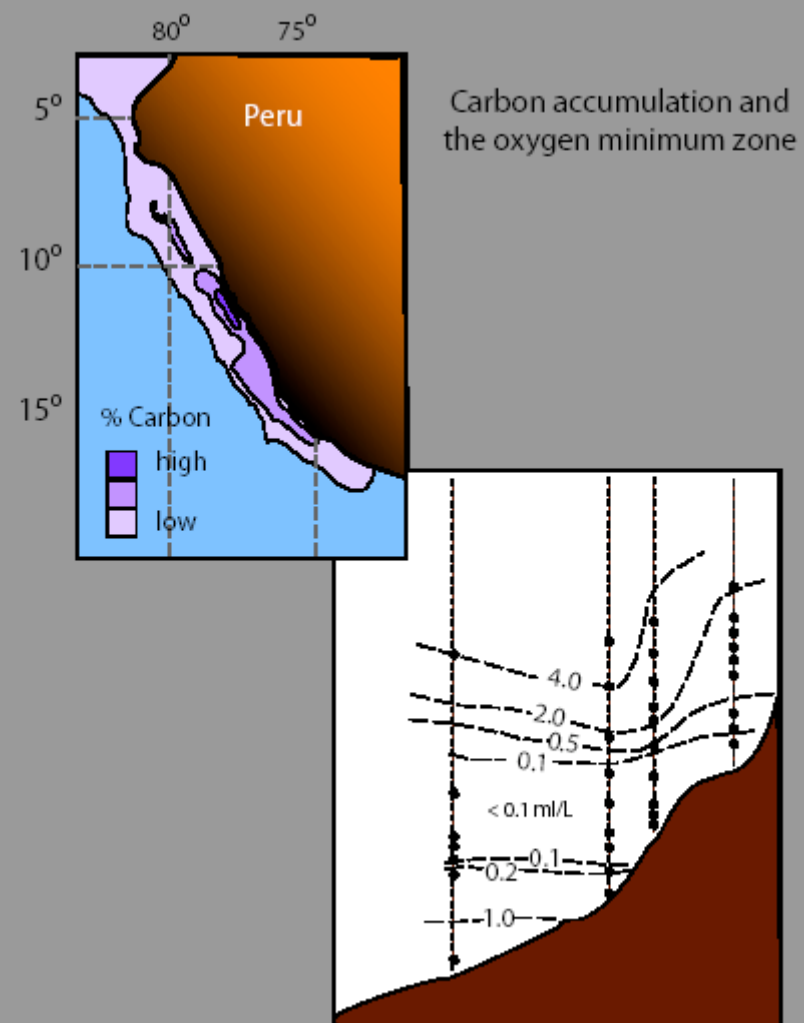
Organic carbon in surface sediments
of the Pacific Ocean



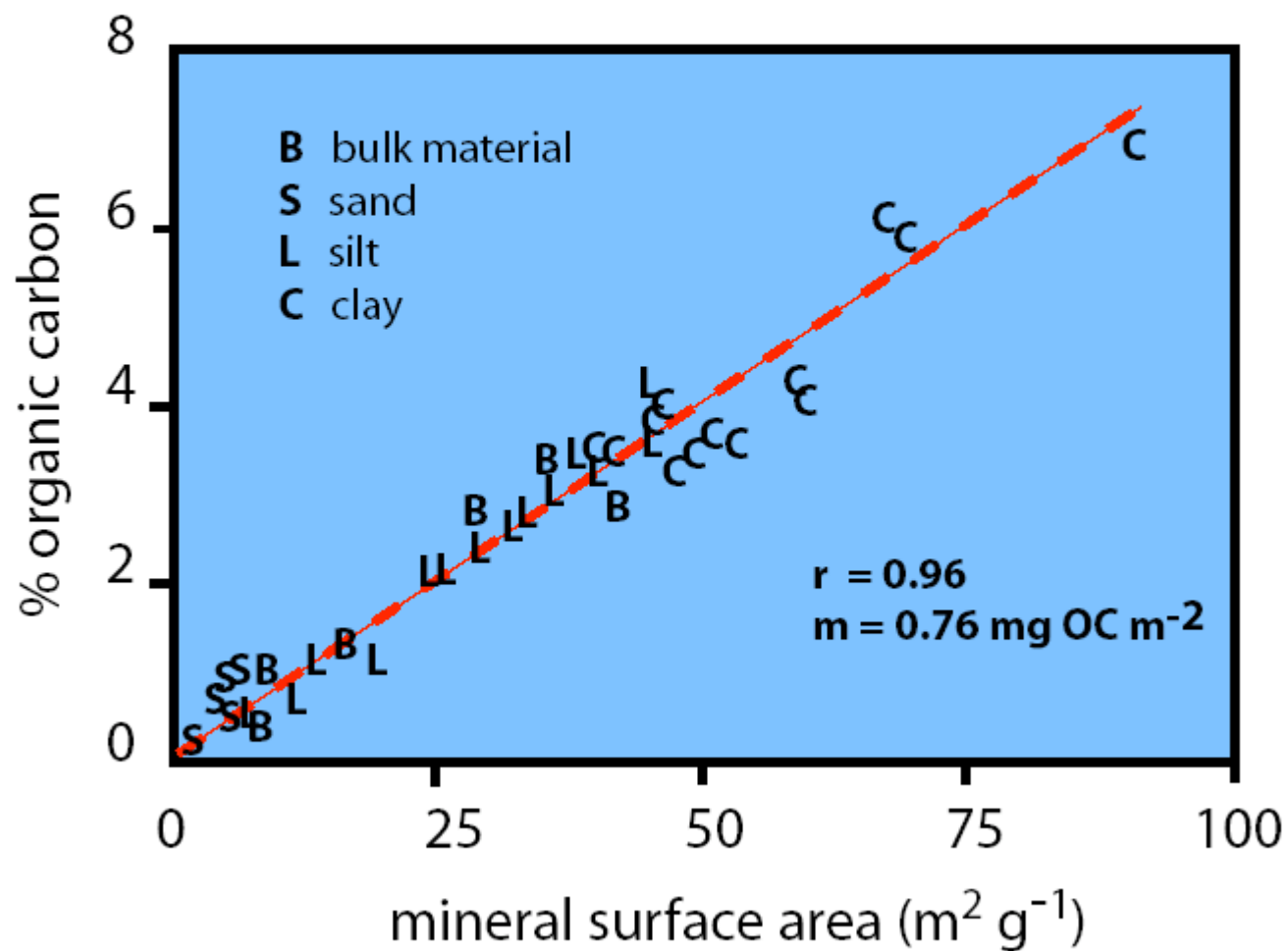
Calvert and Peterson 1998



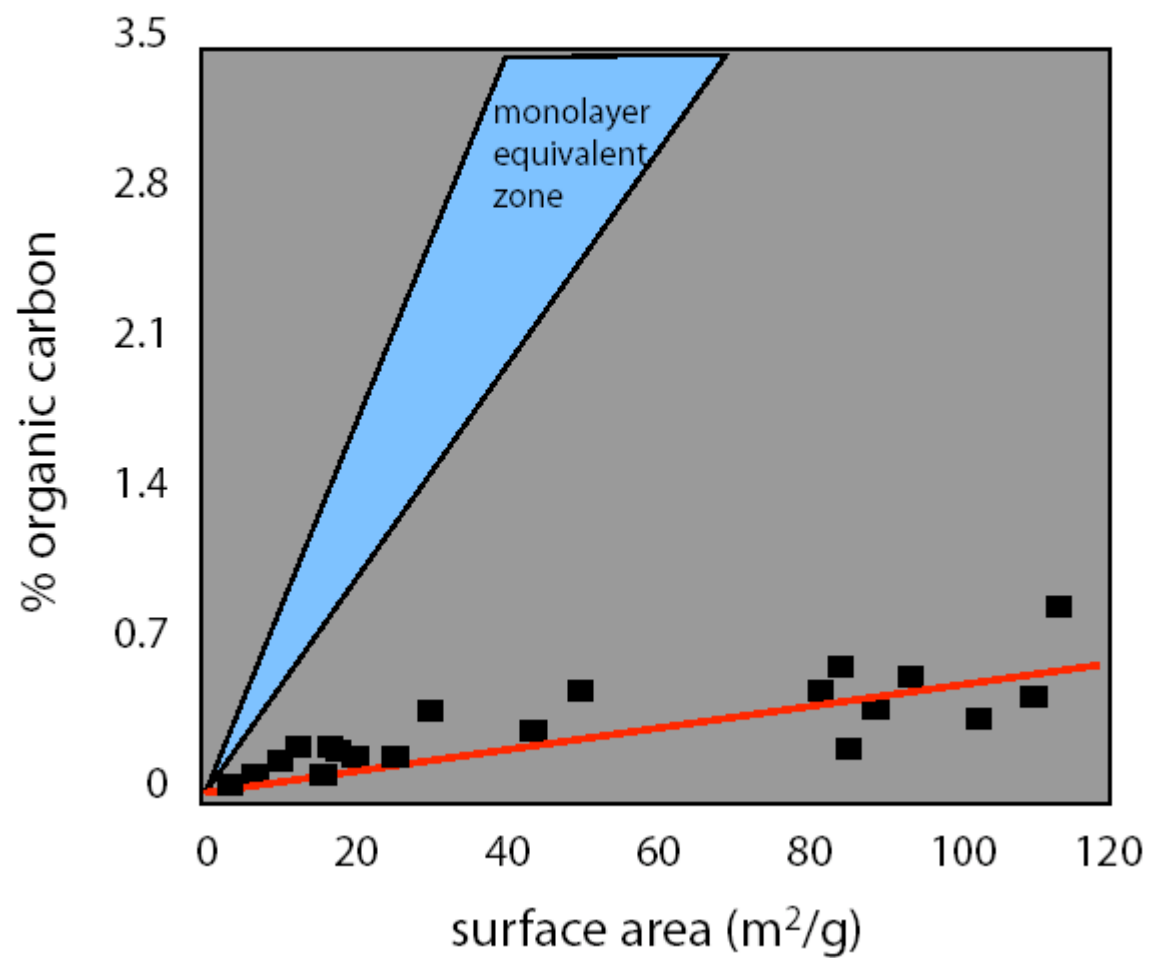
Producción primaria y exportada



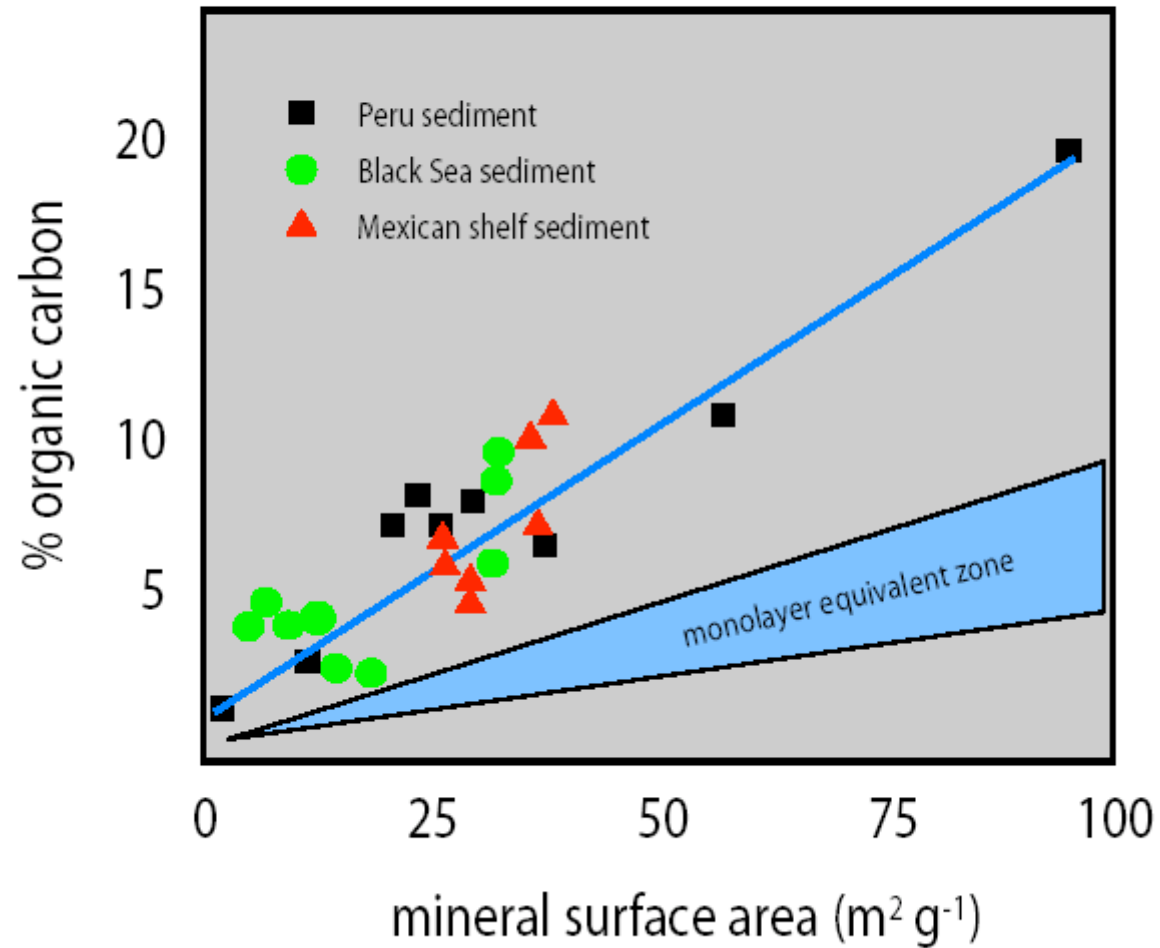
Relationship between %organic carbon
and mineral surface area
in Columbia River estuary sediments



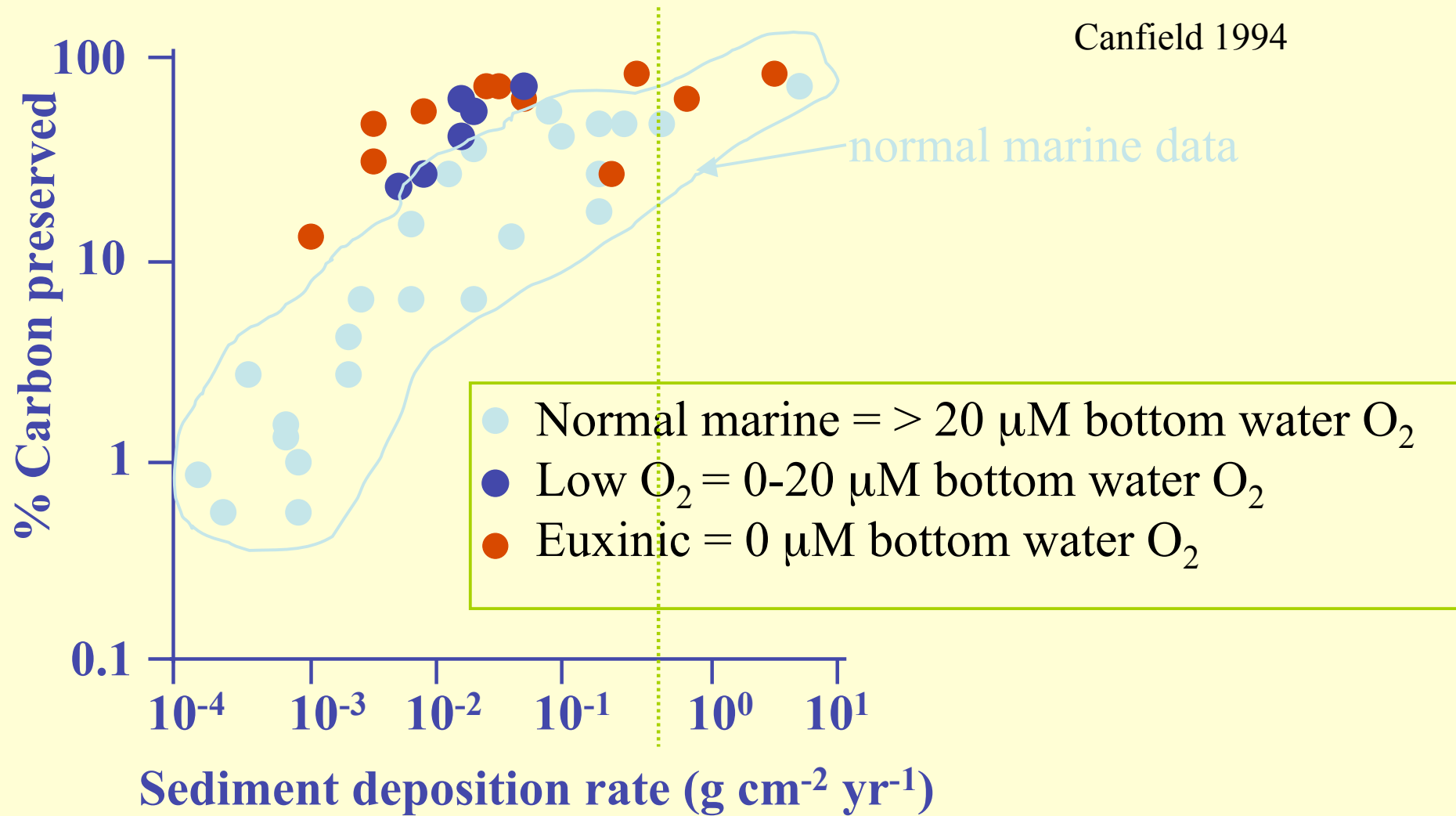
Organic carbon vs mineral surface area
in Equatorial Pacific surface sediments



Organic carbon vs mineral surface area for low oxygen sediments



Canfield 1994



- a) sediment deposition rate → % C preserved
- b) sediment deposition rate ≥ 0.04 no O₂ effect
- c) sediment deposition rate < 0.04 enhanced preservation under low [O₂]

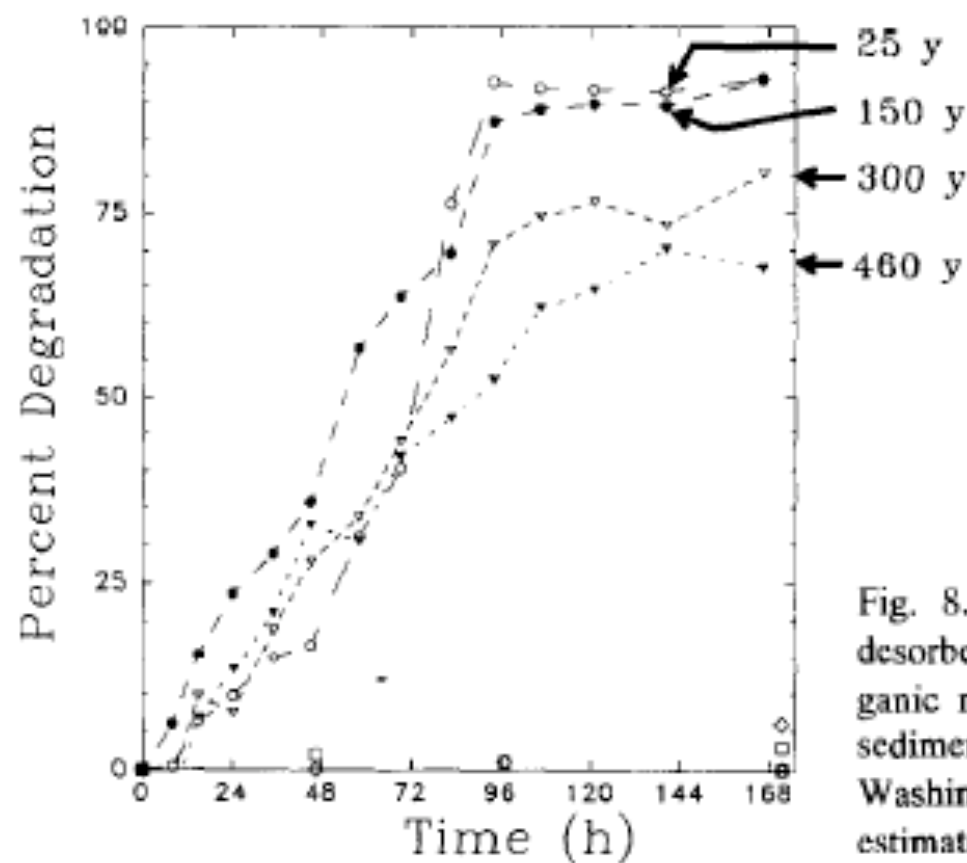
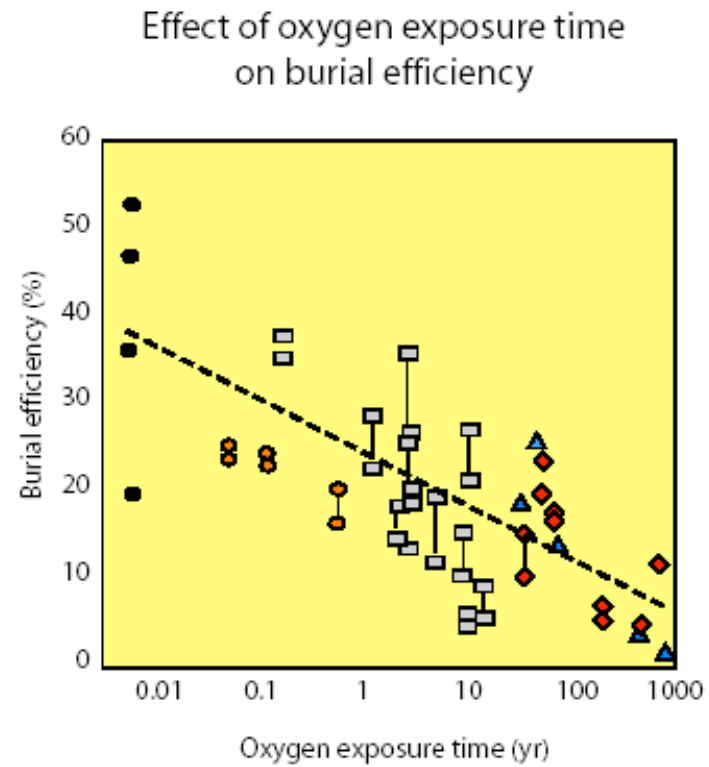


Fig. 8. Results of experiments in which organic matter was desorbed from mineral matrices and degraded (as dissolved organic matter) by aerobic heterotrophic bacteria. A 36 cm long sediment core was collected at a water depth of 647 m off the Washington Coast. At selected intervals corresponding to ^{210}Pb -estimated ages of 25, 150, 300 and 460 yr (uncertainty of about ± 50 yr), organic matter was desorbed from the sediment matrix. Overall, approximately 35% of the total organic matter was desorbed at each interval. The desorbed organic matter was diluted to $\sim 6 \text{ mg OC l}^{-1}$ and incubated in the presence of heterotrophic bacteria collected from the overlying water. Percent degradation of the desorbed organic matter was determined from the change in DOC measured with a Shimadzu TOC-5000 carbon analyzer (Keil et al., 1994c). 48, 96 and 168 points at bottom represent controls.

Keil et al. 1994

Efecto del oxígeno



Hartnett et al. 1998 Nature, 391, 572-574

Tasas de degradación (Lee 1992)

Sedimentos anóxicos secuestrarían C como biomasa bacteriana

Table 6. Calculation of true uptake rates from uptake rate constants and substrate concentrations.

	k (h ⁻¹)	[†] [S] (nM)	v (nM/h)
SALT POND			
Oxic			
amino acids	0.78	250	195
putrescine	0.084	10	0.84
Anoxic			
amino acids	-	750	-
putrescine	0.0036	18	0.07
CARIACO TRENCH			
Oxic			
amino acids	0.0067	20	0.134
putrescine	0.0014	5	0.007
formaldehyde	0.0032	*14	0.045
Anoxic			
amino acids	0.0015	120	0.18
putrescine	0.00027	15	0.004
formaldehyde	0.00042	*19	0.008
PERU COAST			
Oxic			
methylamine	0.0062	<1	<0.006
Anoxic			
methylamine	0.0026	10	0.03

* Formaldehyde concentrations measured by K. Mopper and D. Kieber

[†] Substrate concentrations were measured analytically except for methylamine, which was estimated by the kinetic substrate addition technique.

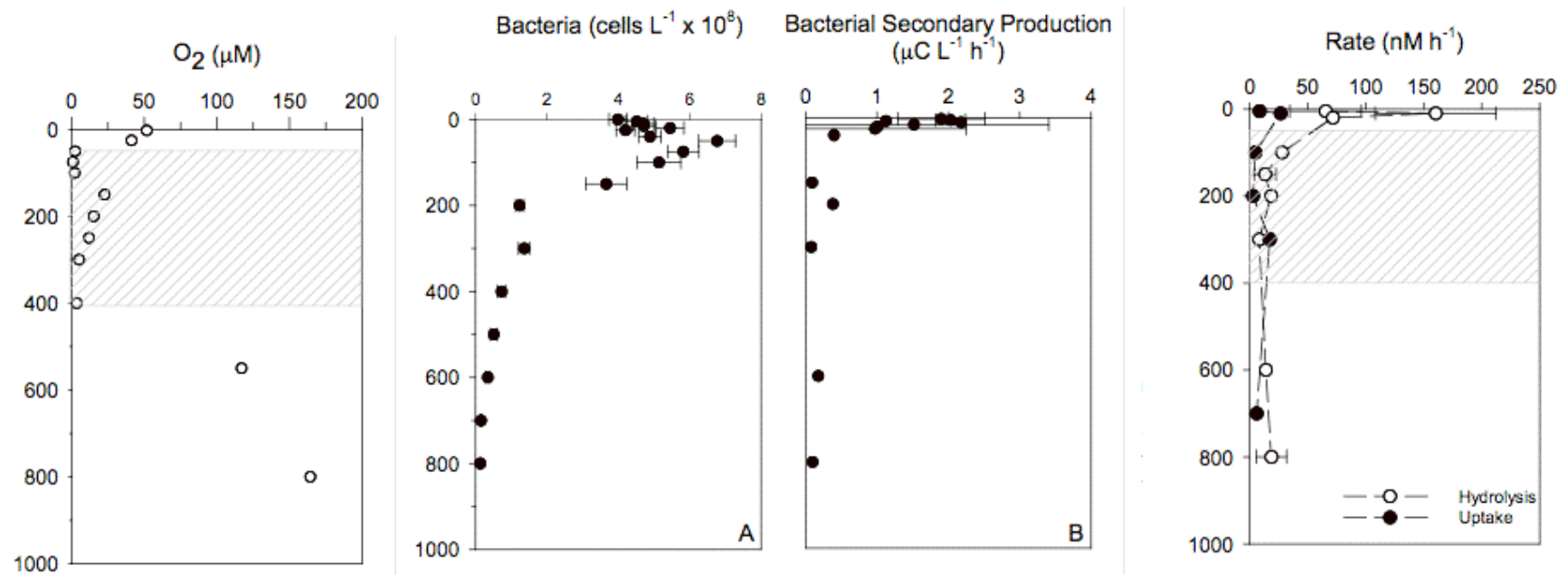
Reacciones redox importantes

Reaction	E _h (V)	ΔG
Reduction of O ₂		
O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	+0.812	-29.9
Reduction of NO ₃ ⁻		
2NO ₃ ⁻ + 6H ⁺ + 6e ⁻ → N ₂ + 3H ₂ O	+0.747	-28.4
Reduction of Mn ⁴⁺		
MnO ₂ + 4H ⁺ + 2e ⁻ → Mn ²⁺ + 2H ₂ O	+0.526	-23.3
Reduction of Fe ³⁺		
Fe(OH) ₃ + 3H ⁺ + e ⁻ → Fe ²⁺ + 3H ₂ O	-0.047	-10.1
Reduction of SO ₄ ²⁻		
SO ₄ ²⁻ + 10H ⁺ + 8e ⁻ → H ₂ S + 4H ₂ O	-0.221	-5.9
Reduction of CO ₂		
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	-0.244	-5.6

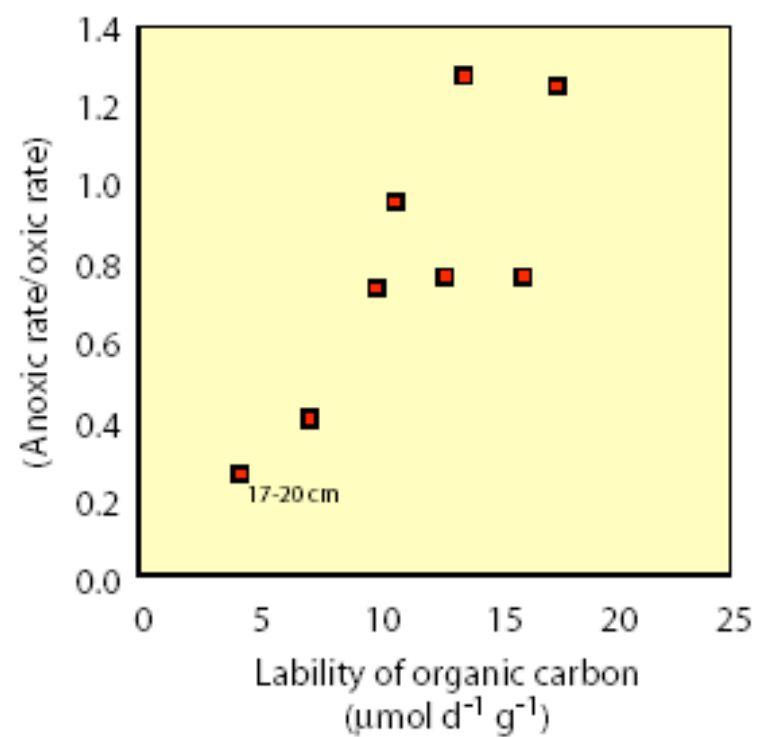
DECREASING ENERGY YIELD

Energía generada vs. Tasa de recambio

Pantoja et al. DSR II 2009



Oxidation rate and the lability
of organic carbon



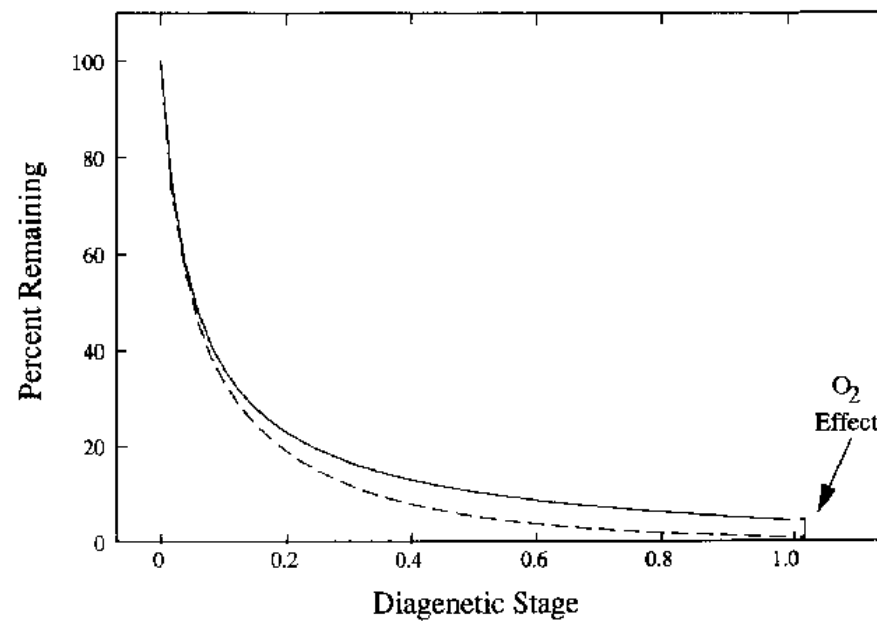
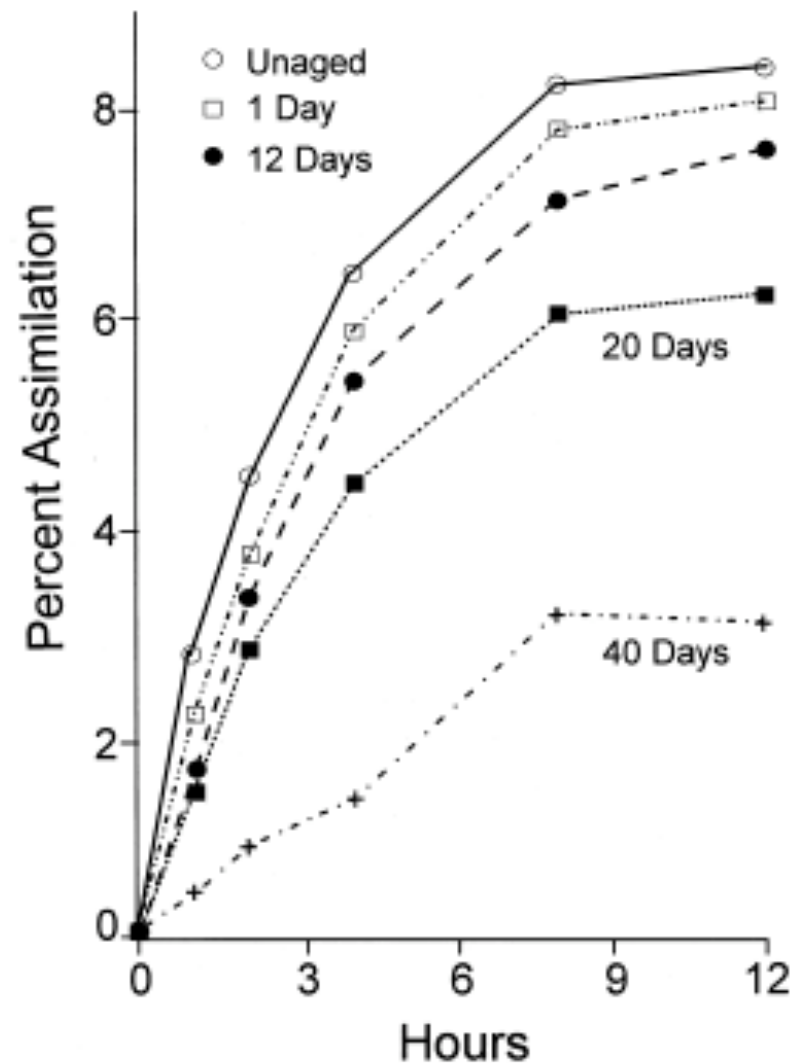


Fig. 2. Two hypothetical degradation curves for organic matter mixtures containing initially equal amounts of five different components which are mineralized with first-order rate constants that successively vary by factors of two. The only difference in the two curves is that the most stable component in Mixture A (solid line) reacts at half the rate as the most stable component in Mixture B (dashed line) (after Cowie et al., 1995).

O₂ y labilidad?



Interacciones abioticas

Keil & Kirchman 1994

Fig. 7. The deactivation of bovine serum albumin aged for up to 40 days in seawater, as reflected by subsequently decreased percent assimilation (over 0–12 h) of the dissolved protein by bacteria (after Keil and Kirchman, 1994). No such aging effect was obtained with organic-free (UV-treated) seawater, indicating that organic–organic interactions likely produced the refractory protein.

Hebting et al. (2006):

- Modelo molecular: carotenoides
- La reducción abiótica en ambientes reductores operaría en estados tempranos de la diagenesis, induciendo la preservación.
- De acuerdo a experimentos de laboratorio H_2S sería el donador de hidrógeno
- Estas reacciones permiten la preservación de abundante carbono orgánico en el registro geológico

¿Qué controla la preservación de la materia orgánica?

Todas las anteriores...

- Producción de materia orgánica
- Oxígeno
- Composición de la materia orgánica
- Asociación mineral
- Interacciones abióticas
- Hedges & Keil 1995
- Canfield 1994