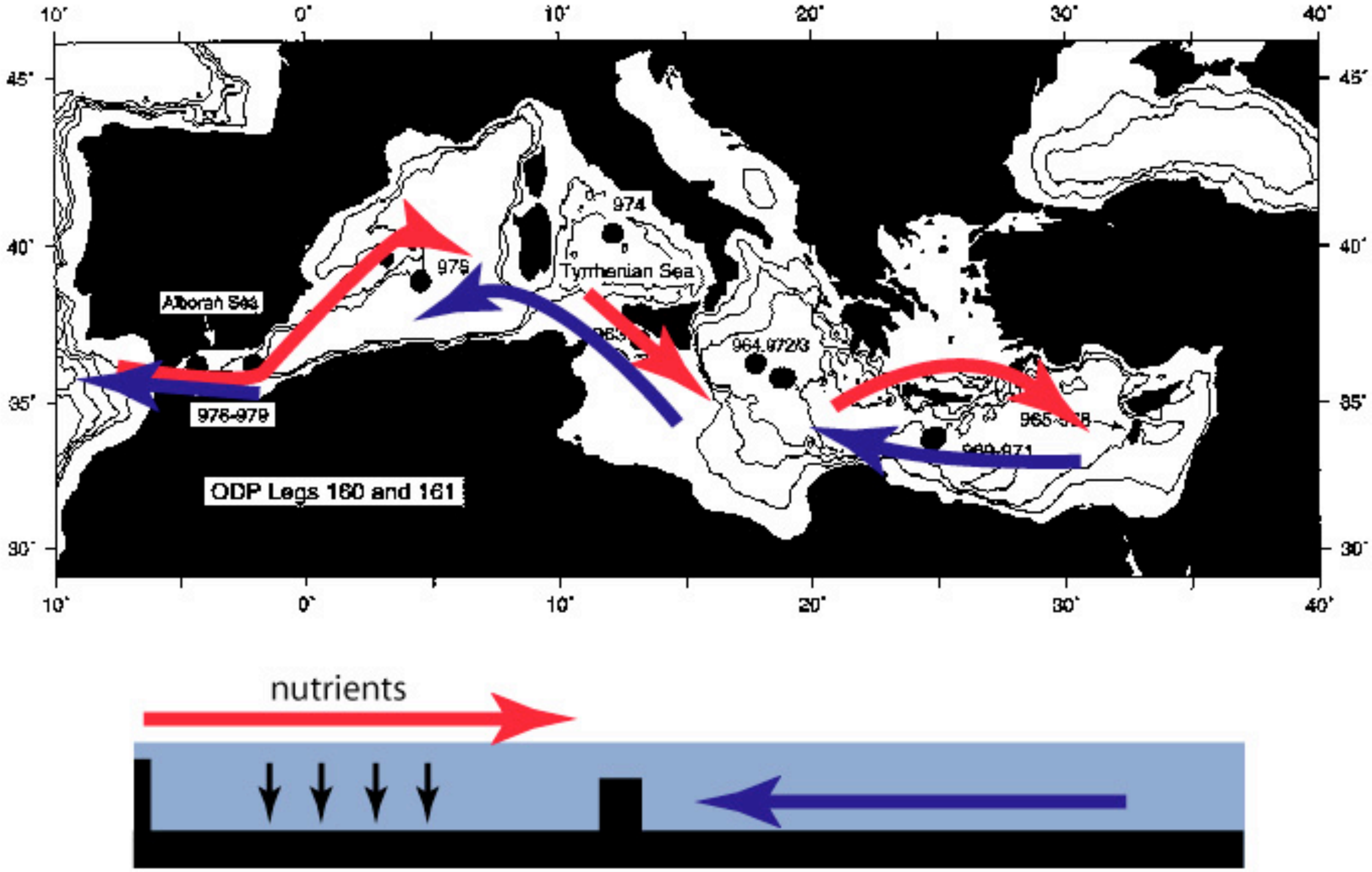
Carbon preservation and the mystery of Mediterranean Sea Sapropels



Sapropels

organic rich
(2-14% TOC)

Periodic deposition

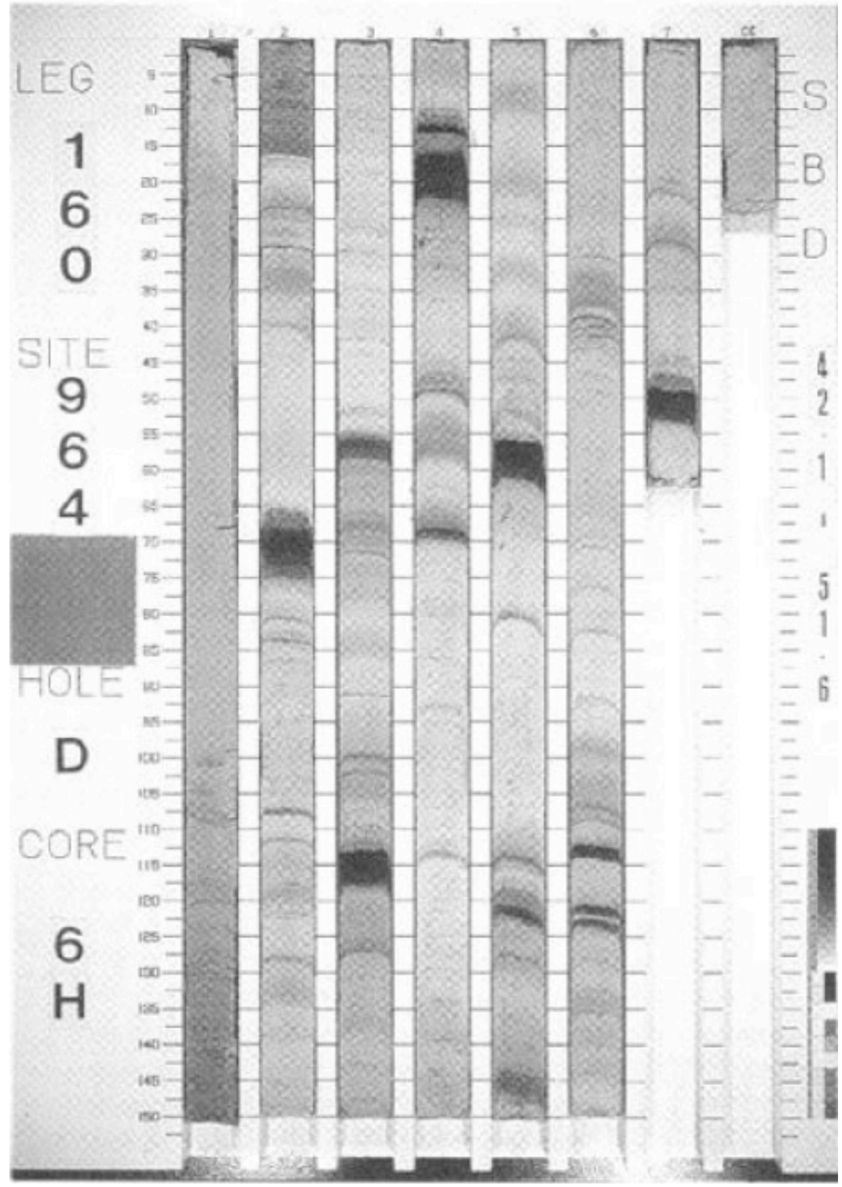
<1 cm to > 10 cm thick

Nonsapropels

Very organic lean
(0.1% TOC)

Most of the deposition

Mediterranean Sea Sediment Core

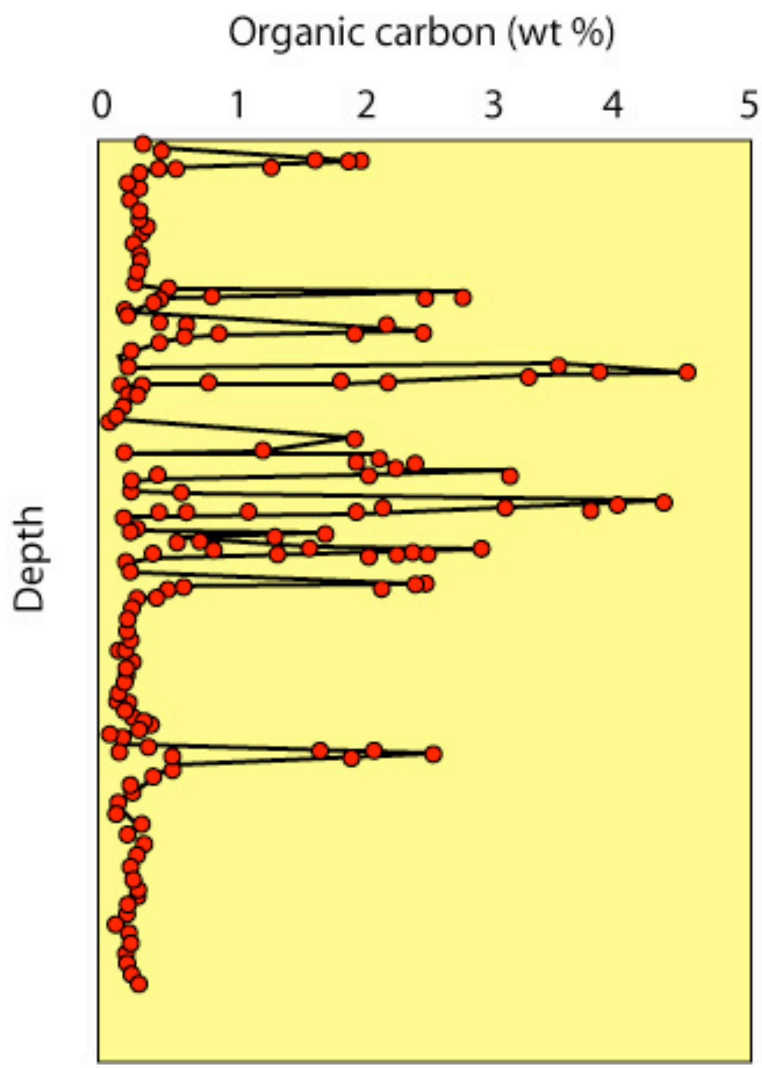


Sapropels

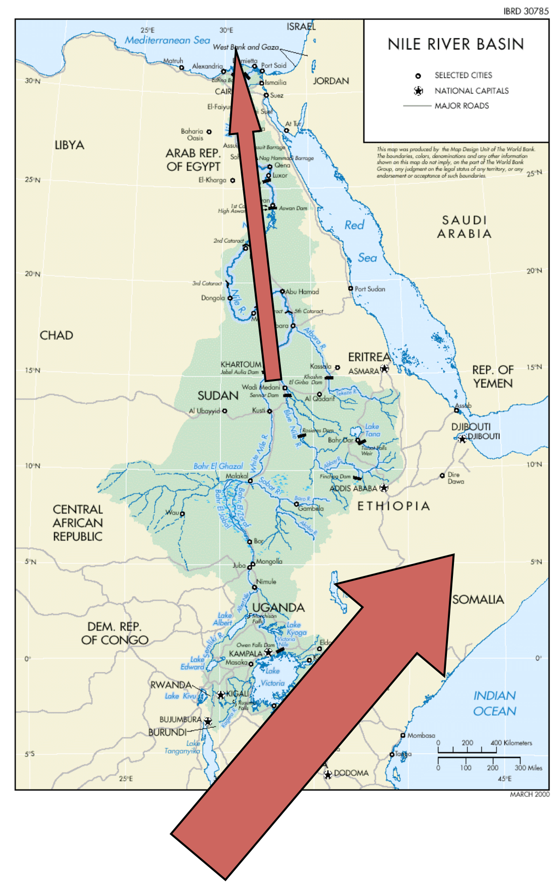
Any organic rich layer of sediment is called a sapropel, Sapropels in the Mediterranean Sea are very interesting however because the Mediterranean is one of the least productive bodies of water today, and sediments there are extremely depleted in organic carbon. A very long historical record of sapropel deposition was collected by the Ocean Drilling Program Legs 160 and 161 (see Initial reports…). Sapropels were first discovered in the Eastern Mediterranean Sea, but ODP found them to be synchronous in both basins. The shallowest sapropel is < 1m deep and can be sampled with a gravity core.

close-up of sapropel layer

Organic carbon in Mediterranean Sea sediments

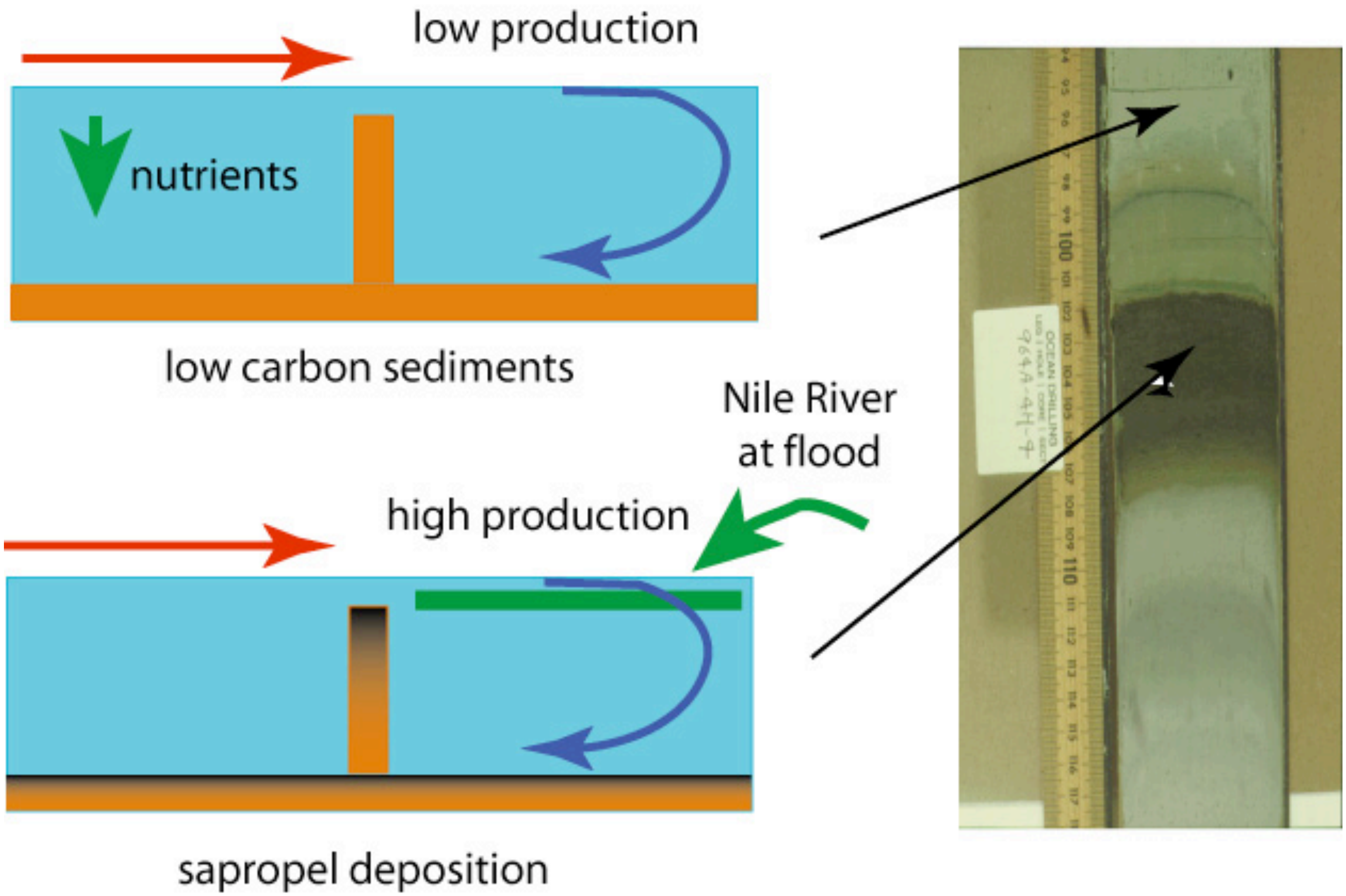


Sapropel formation correlates with monsoon intensity in East Africa

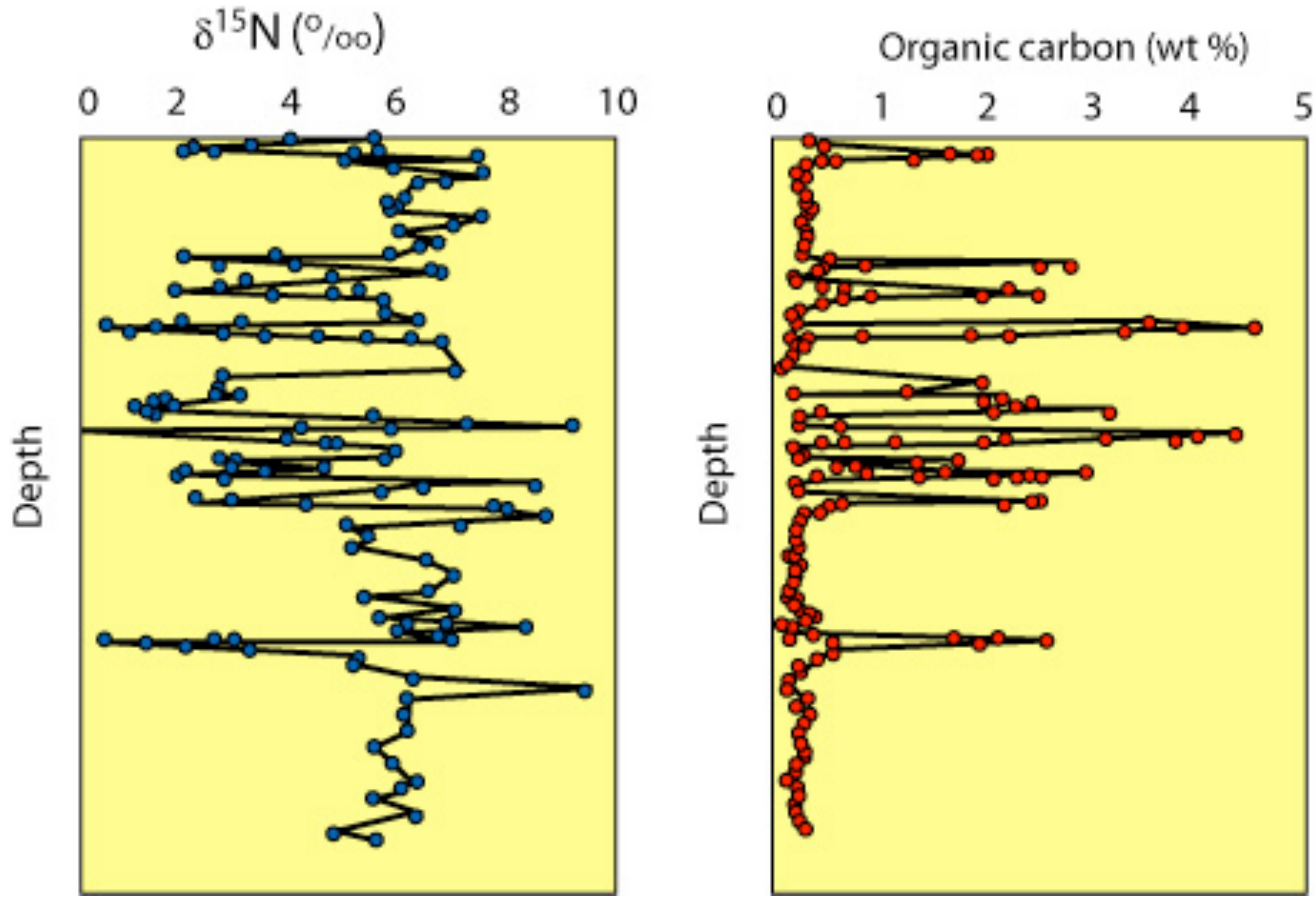


Calvert et al.

Formation of Mediterranean Sea Sapropels
Enhanced productivity hypothesis

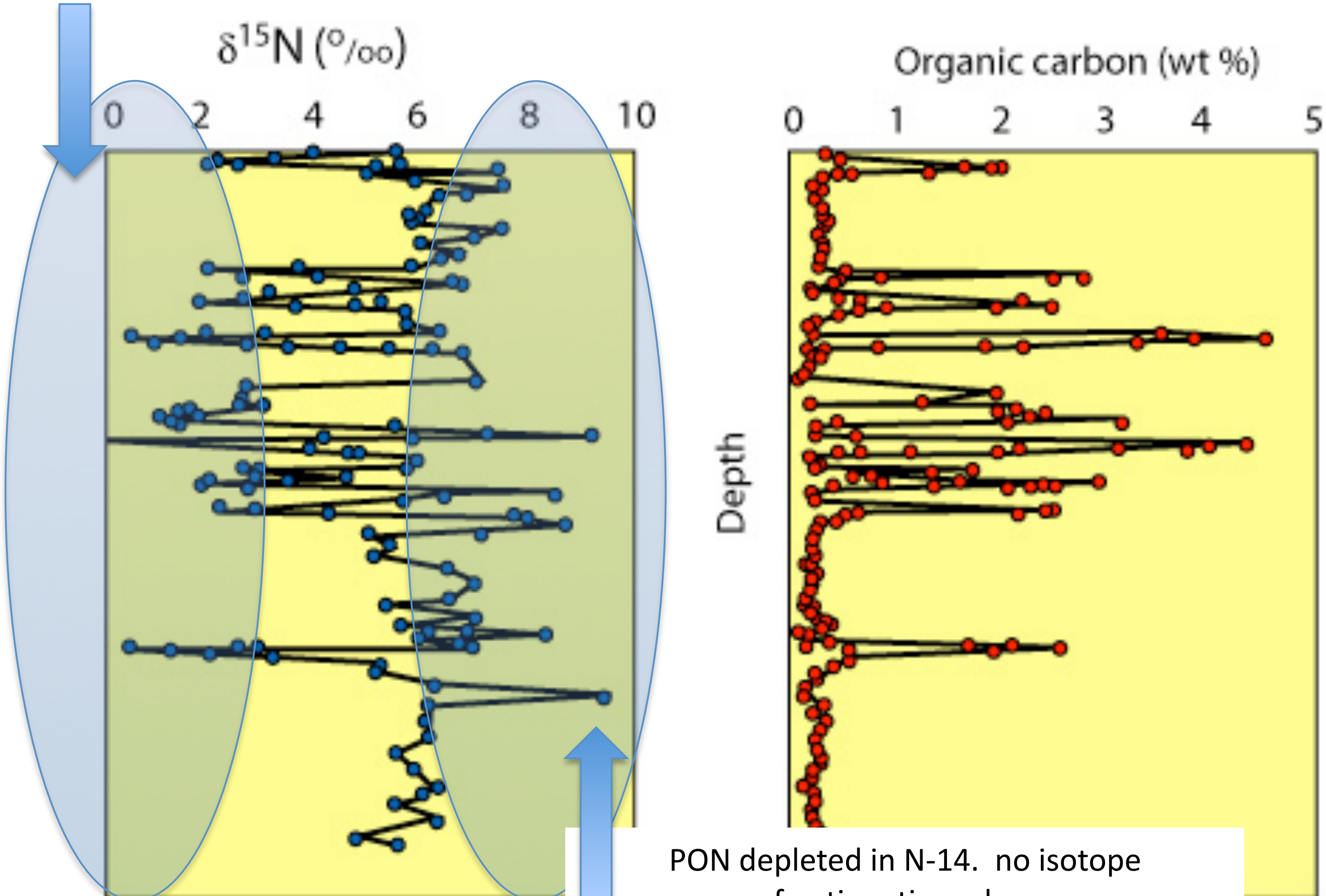


Correlation between %OC and nitrogen isotopes in Mediterranean Sea sediments

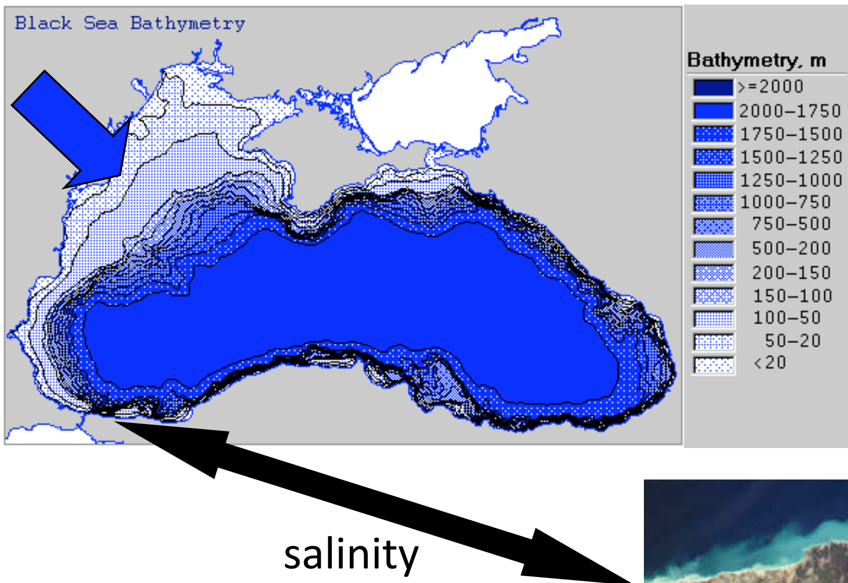


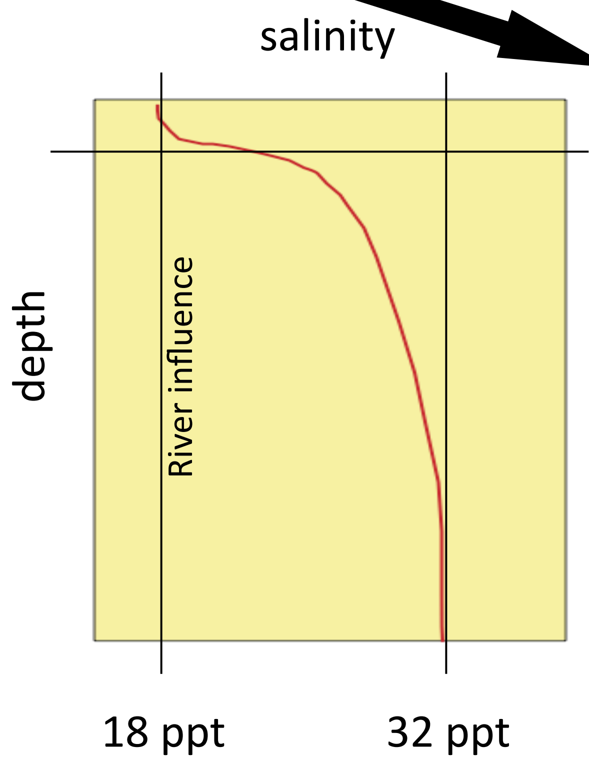
Correlation between %OC and nitrogen isotopes in Mediterranean Sea sediments

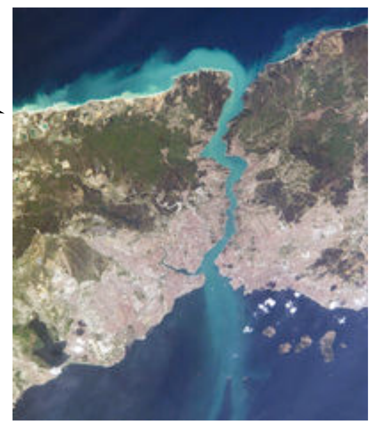
PON enriched in N-14. N-14 is selected when
Nutrients are in high concentrations



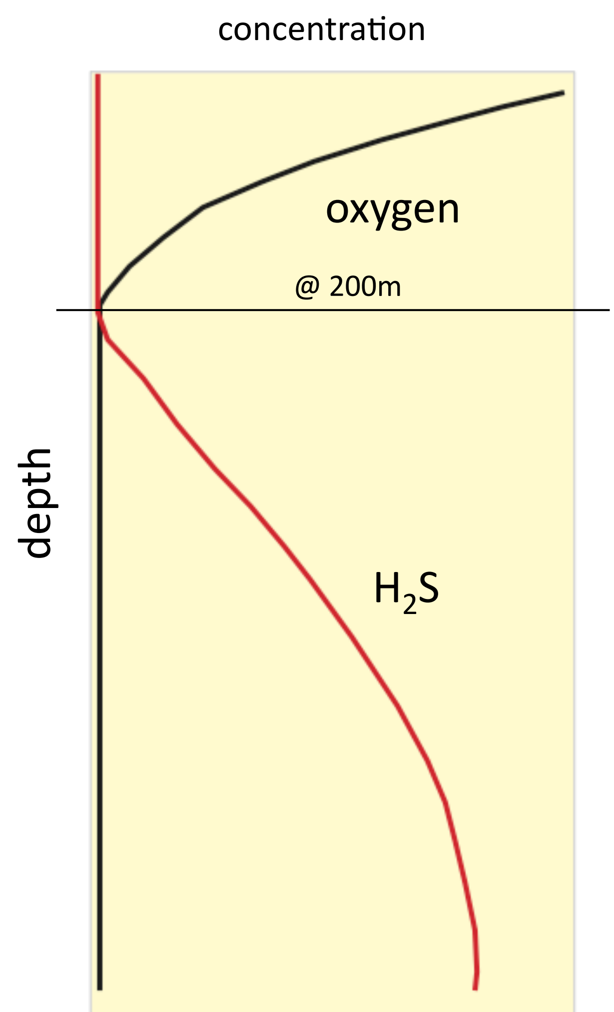
PON depleted in N-14. no isotope
fractionation when
Nutrients are in low concentrations





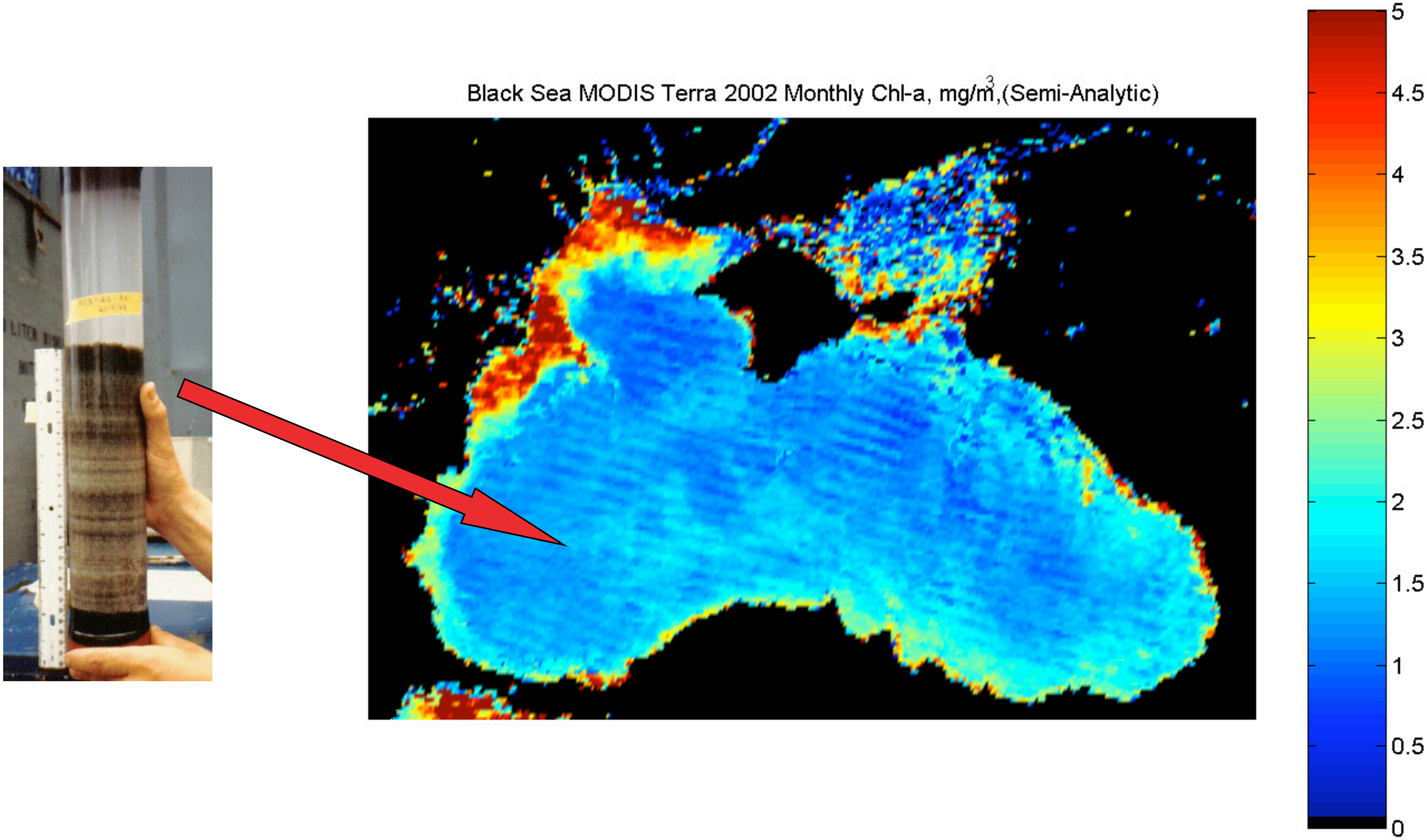


The Bosporus
30 km long
3 km wide
<145 m deep



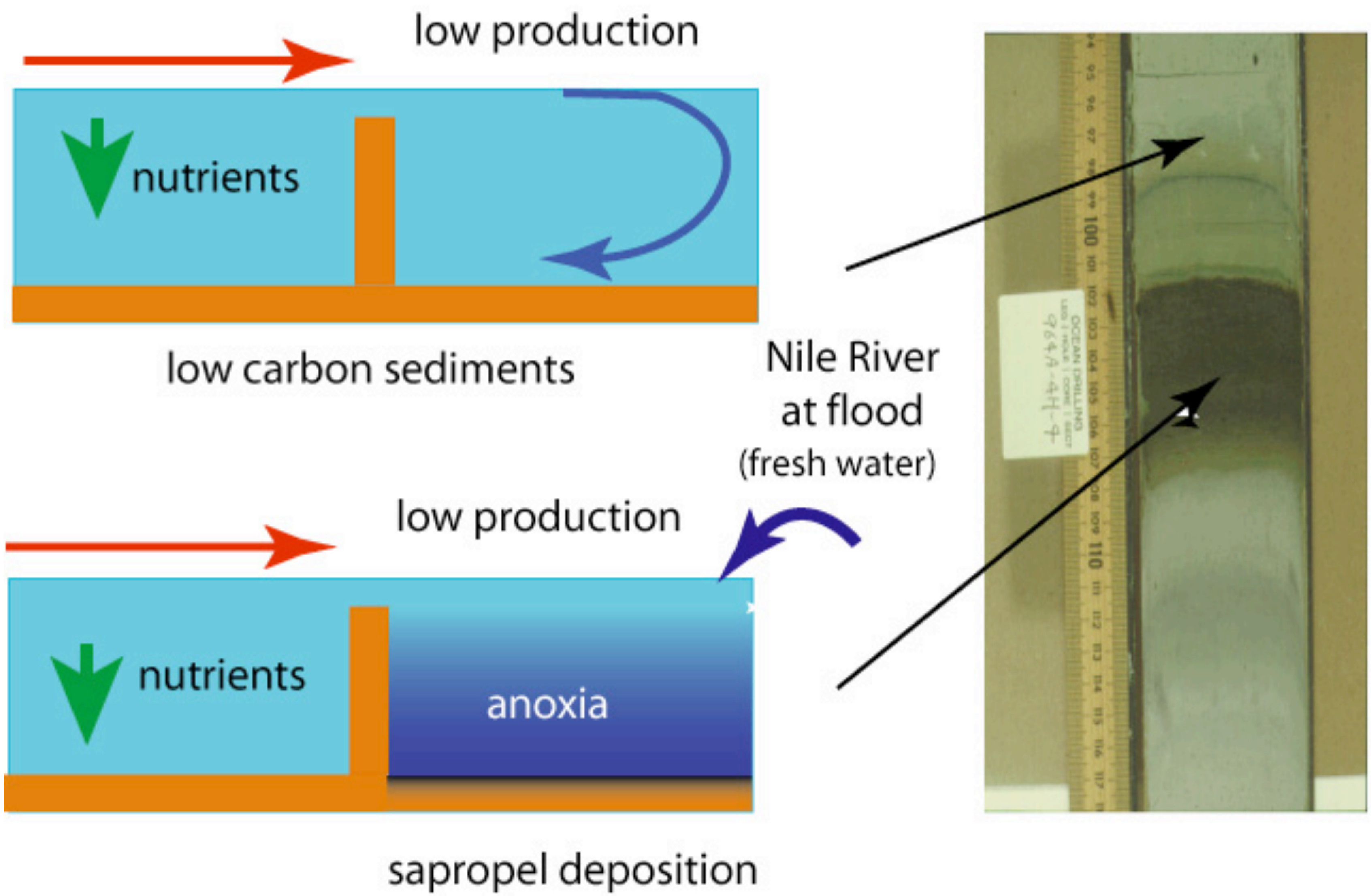
http://rock.geosociety.org/absoluteig/gallery%2FField_and_Laboratory_Photos%2FBlack_Sea_core.jpg

But primary production in the Black Sea is relatively low
It is an oligotrophic basin

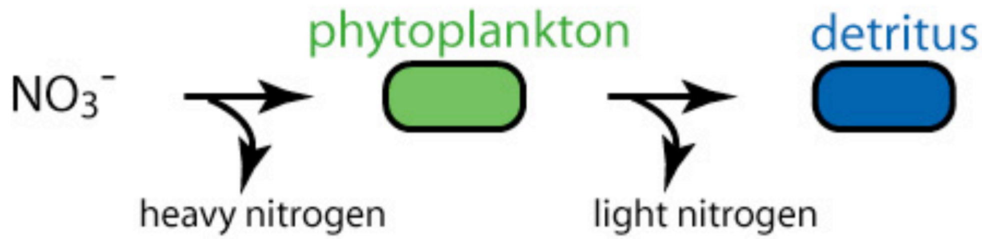


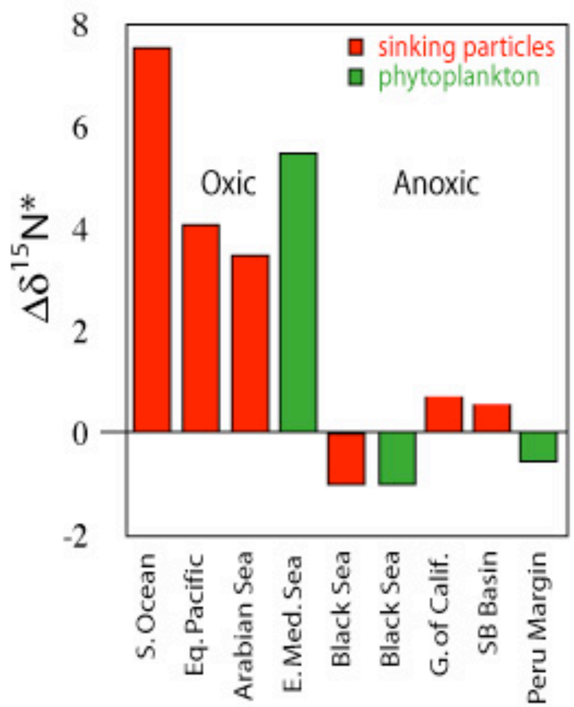
fiesta.bren.ucsb.edu/~dozier/Classes/ESM266StudentPresentations/2003/TKostadinov.ppt

Formation of Mediterranean Sea Sapropels - anoxia hypothesis

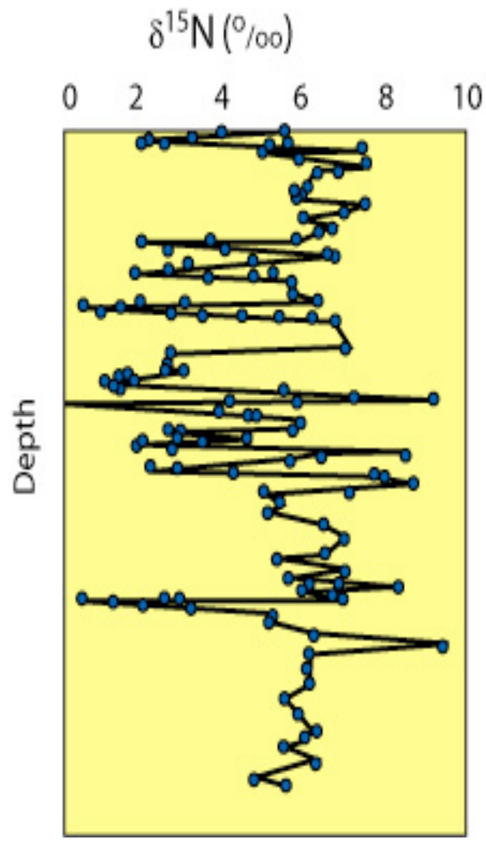


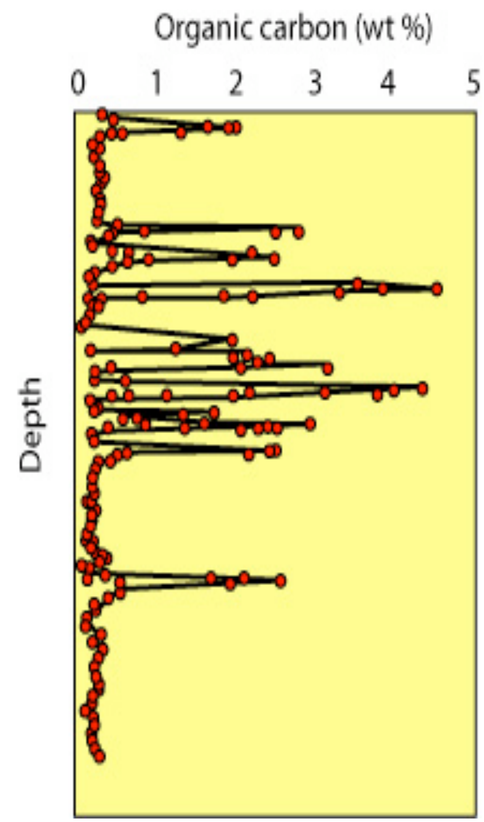
N isotope fractionation and early diagenesis





$\Delta\delta^{15}N$ is ($\delta^{15}N$ of SPM or phytoplankton - sediment)





Ocean Sequestration of Crop Residue Carbon: Recycling Fossil Fuel Carbon Back to Deep Sediments

S T U A R T E . S T R A N D *
College of Forest Resources, 167 Wilcox Hall, Box 352700, University of Washington, Seattle Washington 98195

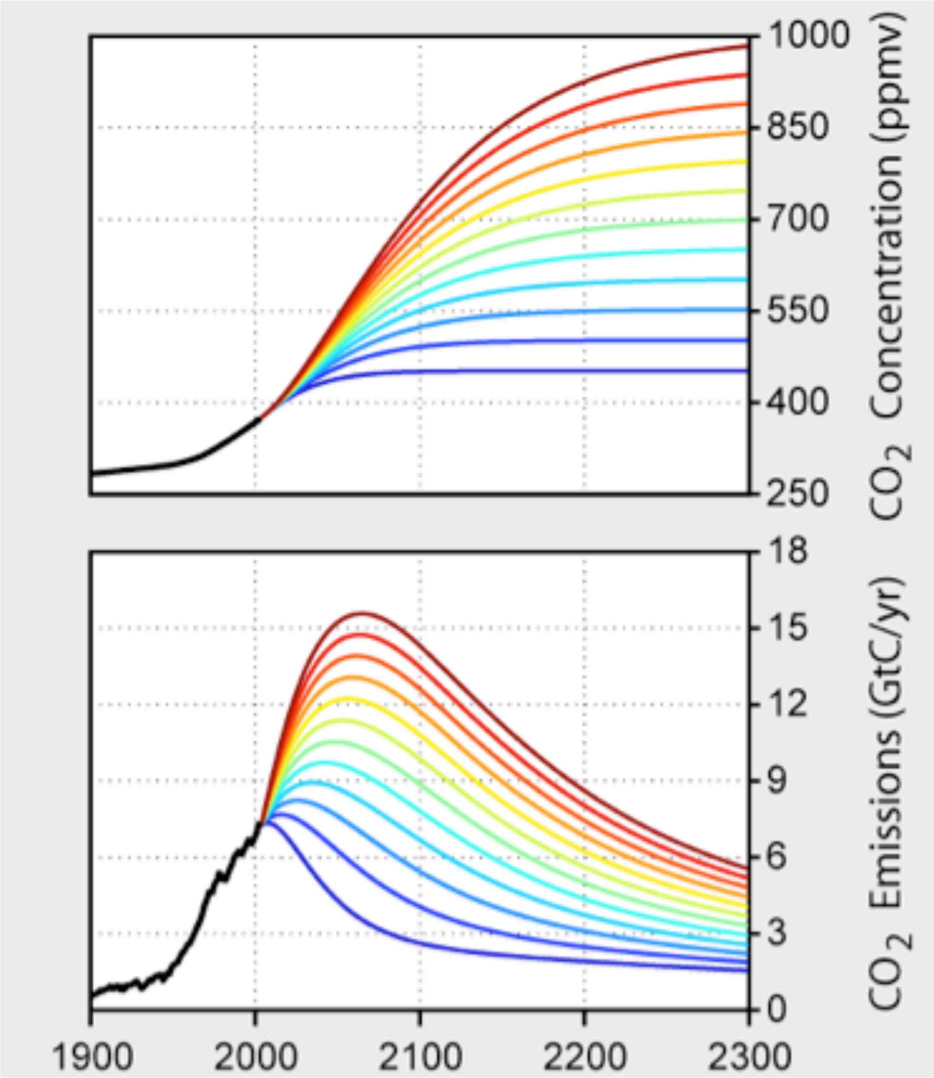
G R E G O R Y B E N F O R D
Department of Physics and Astronomy, 4176 Frederick Reines Hall, University of California, Irvine, Irvine, California 92697

Received June 5, 2008. Revised manuscript received November 18, 2008. Accepted November 25, 2008.

For significant impact any method to remove CO2 from the atmosphere must process large amounts of carbon efficiently, be repeatable, sequester carbon for thousands of years, be practical, economical and be implemented soon. The only method that meets these criteria is removal of crop residues and burial in the deep ocean. We show here that this method is 92% efficient in sequestration of crop residue carbon while cellulosic ethanol production is only 32% and soil sequestration is about 14% efficient. Deep ocean sequestration can potentially capture 15% of the current global CO2 annual increase, returning that carbon back to deep sediments, confining the carbon for millennia, while using existing capital infrastructure and technology. Because of these clear advantages, we recommend enhanced research into permanent sequestration of crop residues in the deep ocean.

ES&T v43, 1000-1007 (2009)

Carbon cycling in a *changing climate*. How will the oceans respond to the rapid changes in atmospheric carbon dioxide that are ahead of us?



$pCO_{2(atm)}$ → $pCO_{2(aq)}$

$CO_{2(aq)} + H_2O$ → H_2CO_3

H2CO3 → $H^+ + HCO_3^-$

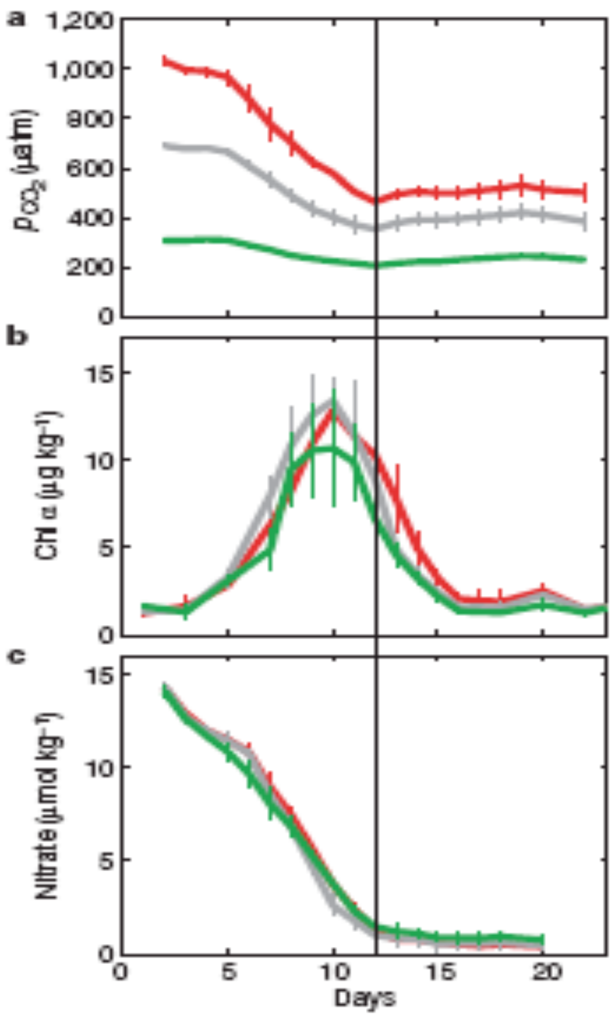
pH will go down

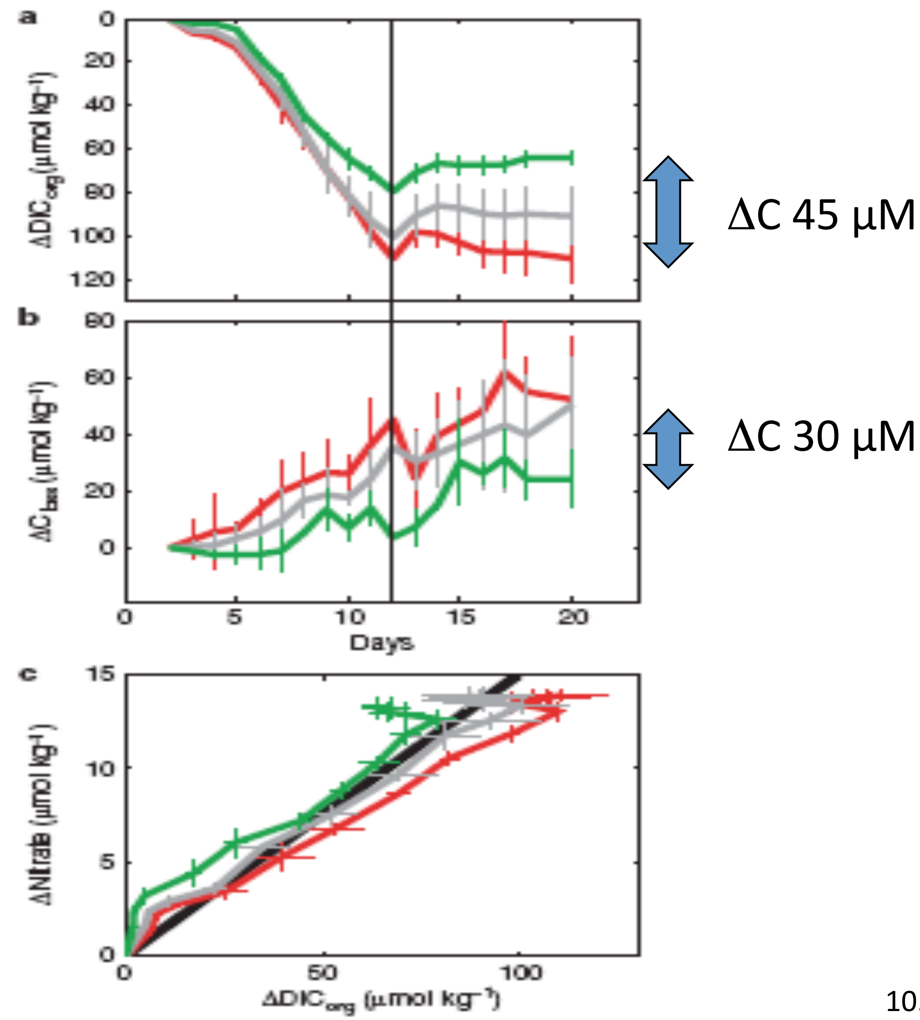
pCO_2 will go up

Enhanced biological carbon consumption in a high CO_2 ocean

U. Riebesell[1], K. G. Schulz[1], R. G. J. Bellerby[2,3], M. Botros[1], P. Fritsche[1], M. Meyerhöfer[1], C. Neill[2], G. Nondal[2,3], A. Oschlies[1], J. Wohlers[1] & E. Zöllner[1]

Nature, v450 (Nov 2007) pp 545-548.

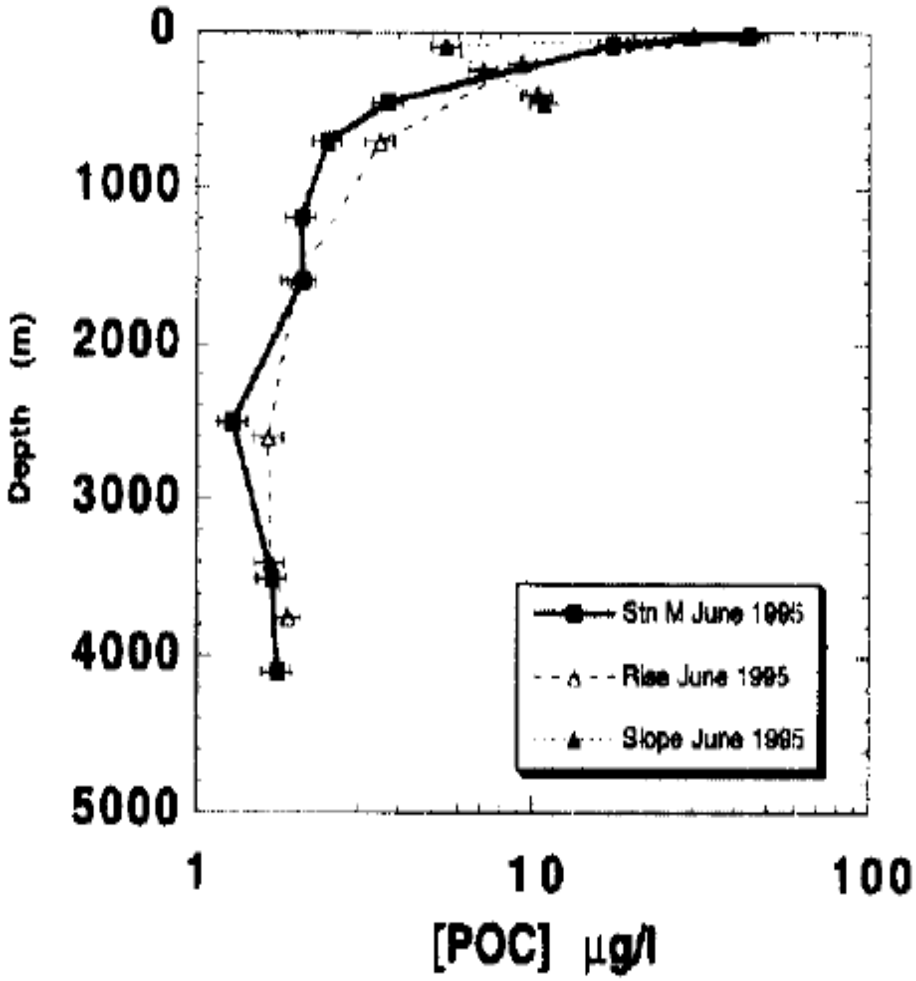


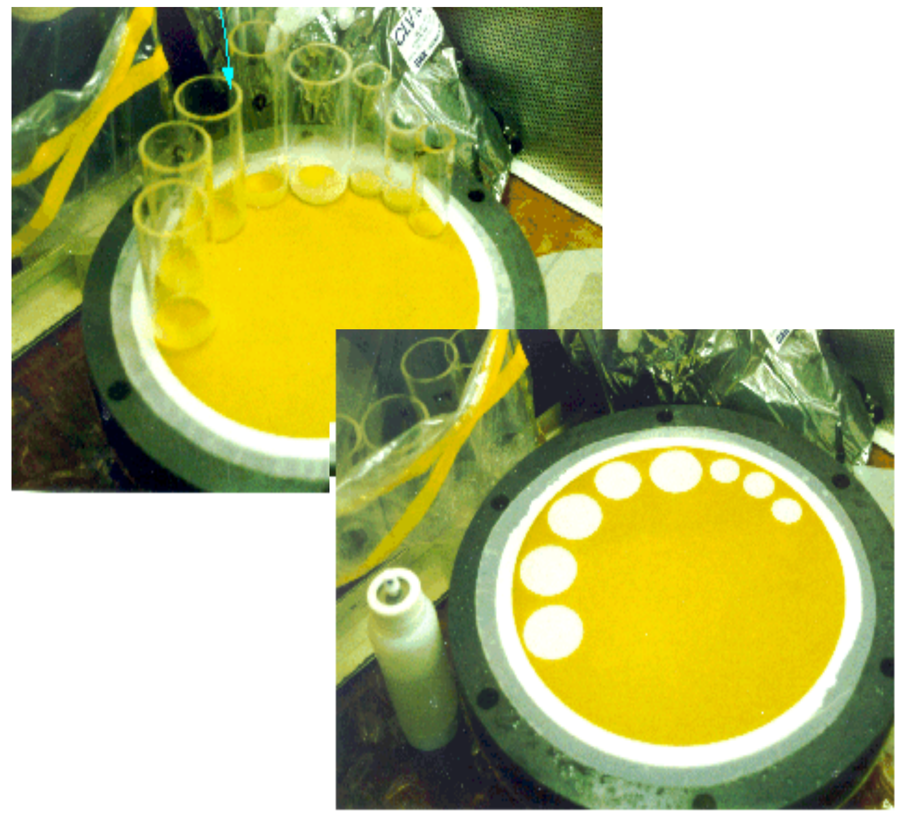


The biological pump and organic carbon transfer to the sea floor

"grain-by-grain deposition is by far the most common phenomenon of pelagic sedimentation"

Jacobs et al. (1973) Marine Geology v14, 117-128





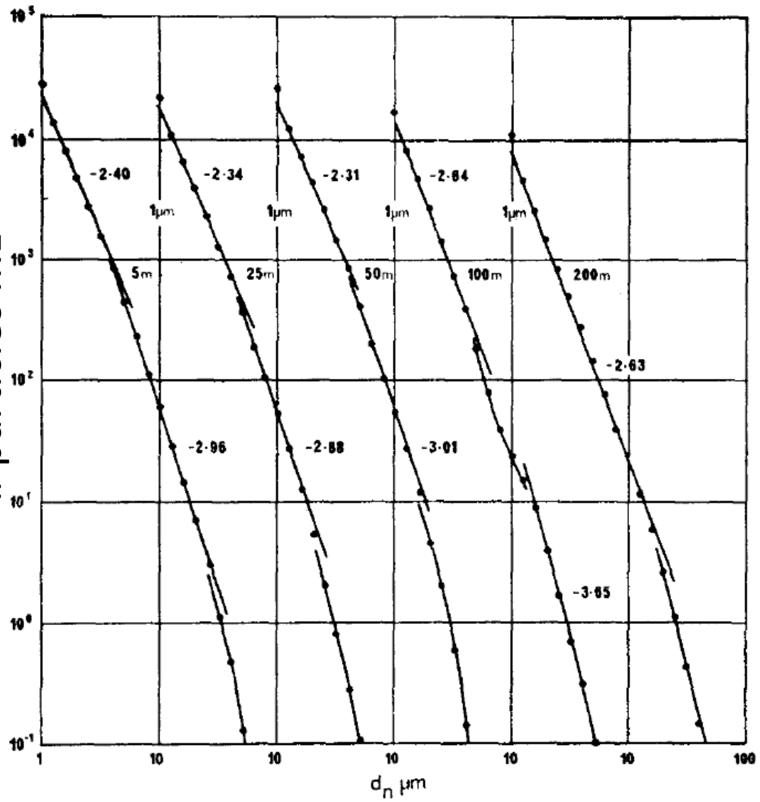
We use filters to sample suspended POM

The biological pump and organic carbon transfer to the sea floor

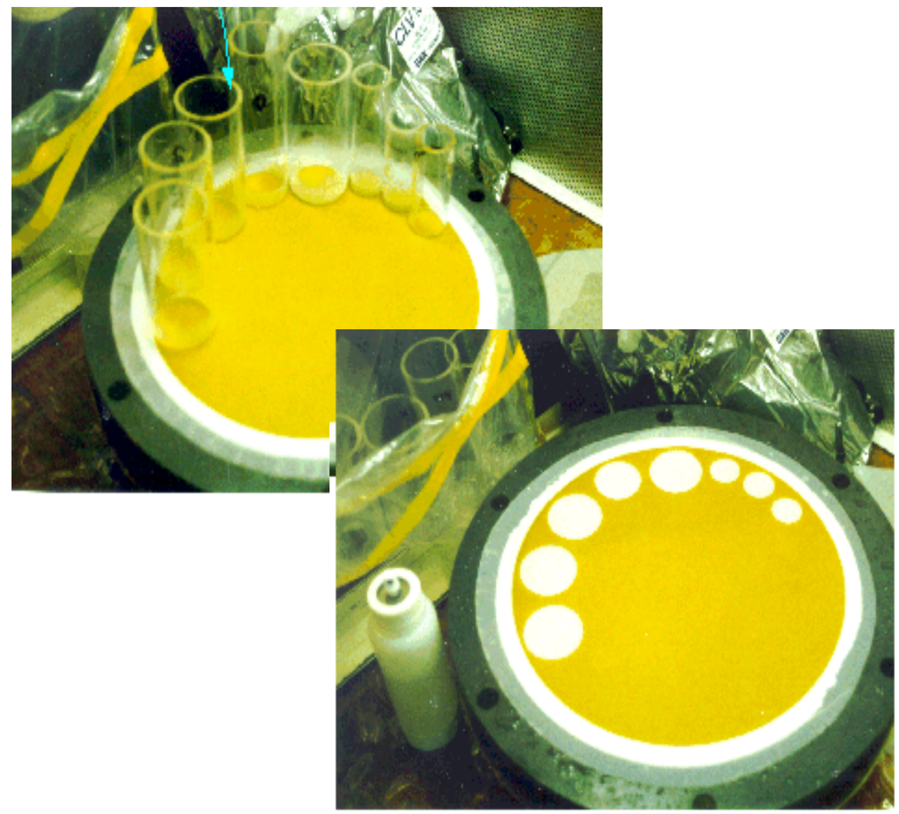
"grain-by-grain deposition is by far the most common phenomenon of pelagic sedimentation"

Jacobs et al. (1973) Marine Geology v14, 117-128

particles mL^{-1}



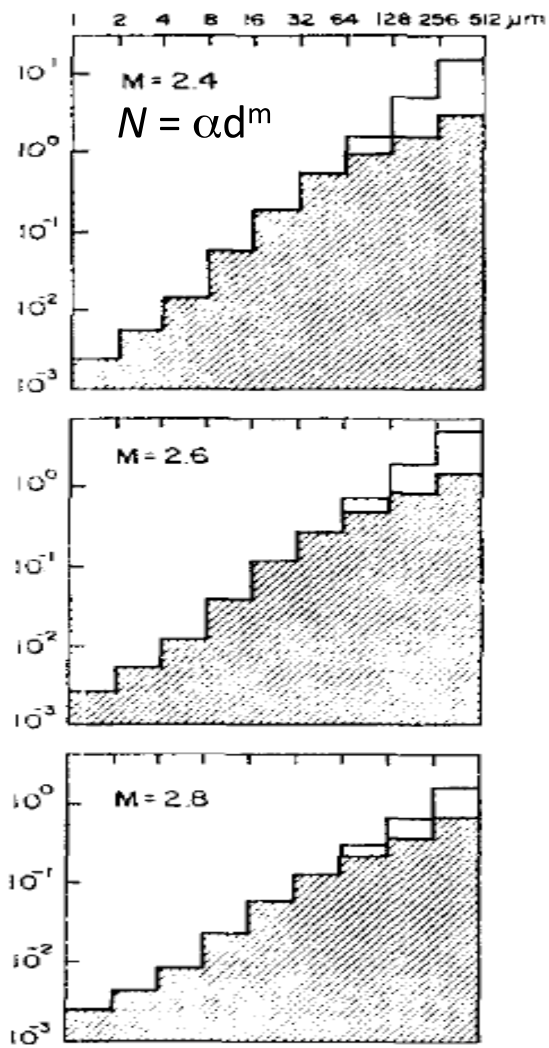
Particle diameter (µm)



We use filters to sample suspended POM

The biological pump and organic carbon transfer to the sea floor

Flux (µg m^{-2} s^{-1})



Particle diameter

Vertical flux of particles in the ocean

I. N. McCave*

(*Received* 21 *August* 1974; *in revised form* 12 *December* 1974; *accepted* 27 *December* 1974)

Abstract—Although most material both on the sea bed and in suspension is very fine, evidence suggests that most material reaching the bottom does so rapidly in aggregates. Sizes of suspended material below 200 to 400 m in the oceans follow a hyperbolic distribution with slopes between −2·4 and −3·6. Volume distributions are calculated and converted to mass distributions using an assumed density distribution. Stokes velocities are calculated for particle size classes. Most of the particle flux, the product of settling velocity and mass, is in the coarser size classes. Assumption of steady state requires aggregation of small particles in the upper layers of the ocean to maintain the concentrations of the larger rapidly sinking particles. Current sampling procedures may miss much of the material in rapid vertical transit.

Size and density are related to sinking rates

$$W_{agg} = \frac{2}{9} \cdot \frac{g r_{agg}^2 (\Delta\rho)}{\mu},$$

Size (µm)	density (g/cm^3)	Sinking rate (m/day)
1.4	1.5	0.03
2.8	1.3	0.07
5.6	1.23	0.018
11.3	1.18	0.57
22.6	1.148	1.7
45.3	1.108	4.5
90.5	1.085	13
181	1.068	36
362	1.057	105

>95% of POC susp
~5% of POC sink

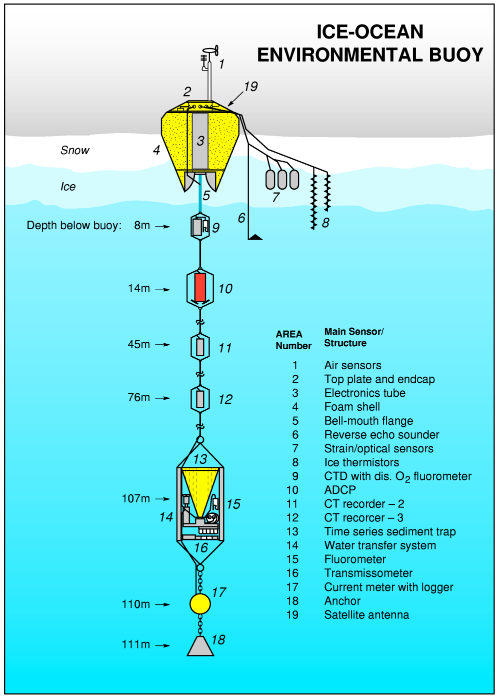
2 weeks - 1 month to reach seafloor at 1400 - 3000m

McCave, 1975

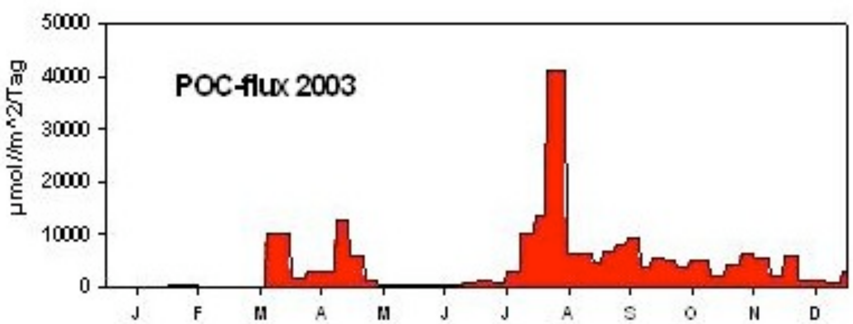
McCave DSR(1975) v22 491-502

Large, rapidly sinking particles are collected with sediment traps

www.whoi.edu/science/B/people/lmullineaux/RIDiane.htm



loeb.whoi.edu

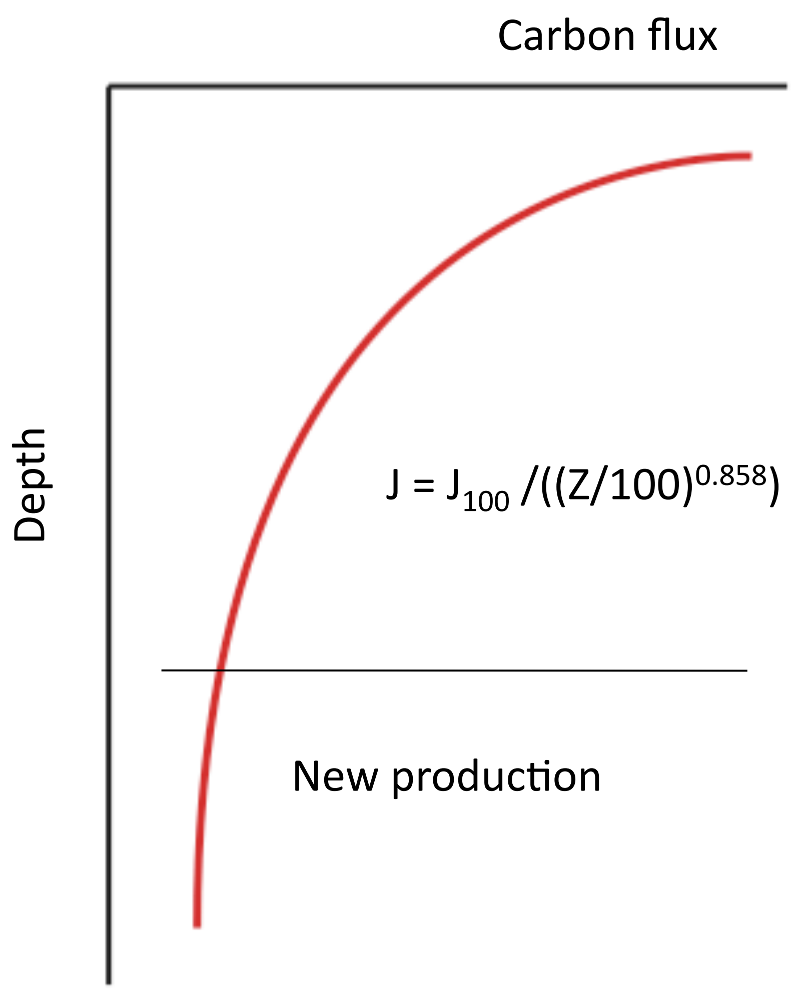


www.io-wamemuende.de

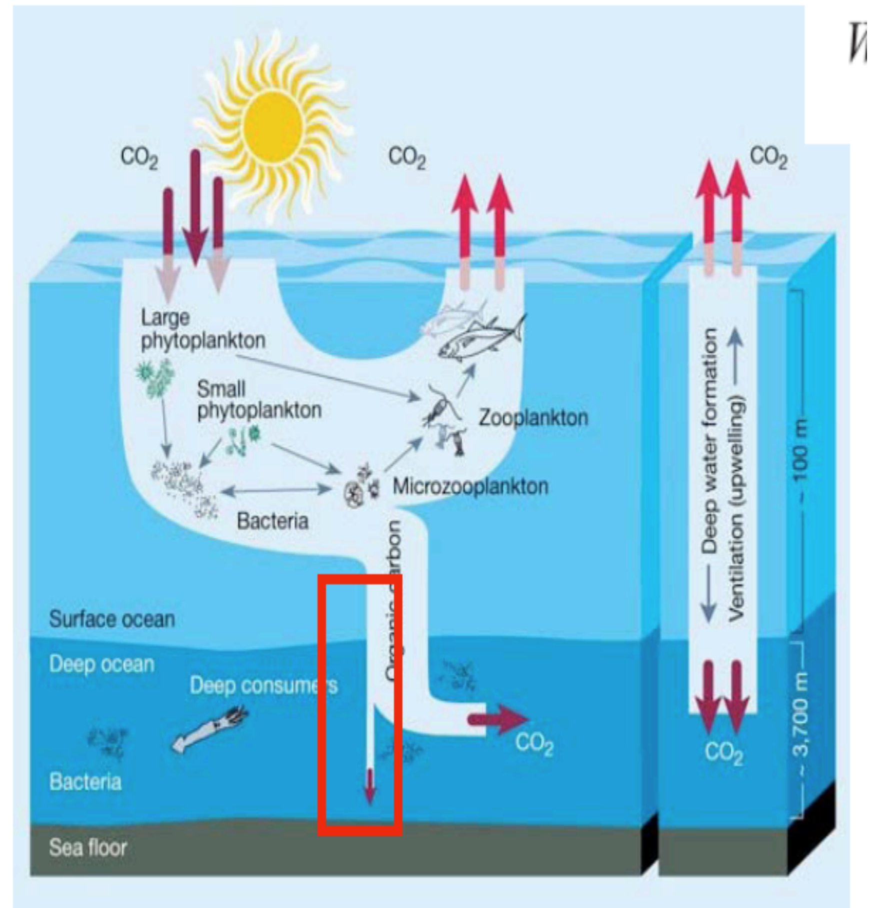
www.bbsr.edu

10.17

What drives carbon flux?



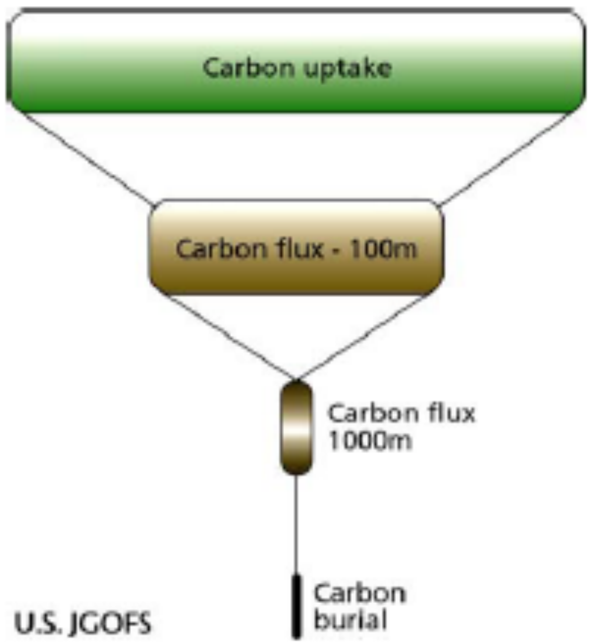
Martin et al (1987) DSR v 34; 267-285



C flux is closely coupled to the biological processing of organic matter

Regional Variability in Export to 100m

- Primary productivity
  - No simple relationship, regionally variable - 5-50% of productivity is exported to 100m



POC flux/Primary Production

(100m thorium-234 & ^{14}C methods)

North Atlantic bloom = <10-30%

Equatorial Pacific = 1-10%

Arabian Sea

late SW monsoon = 15-30%

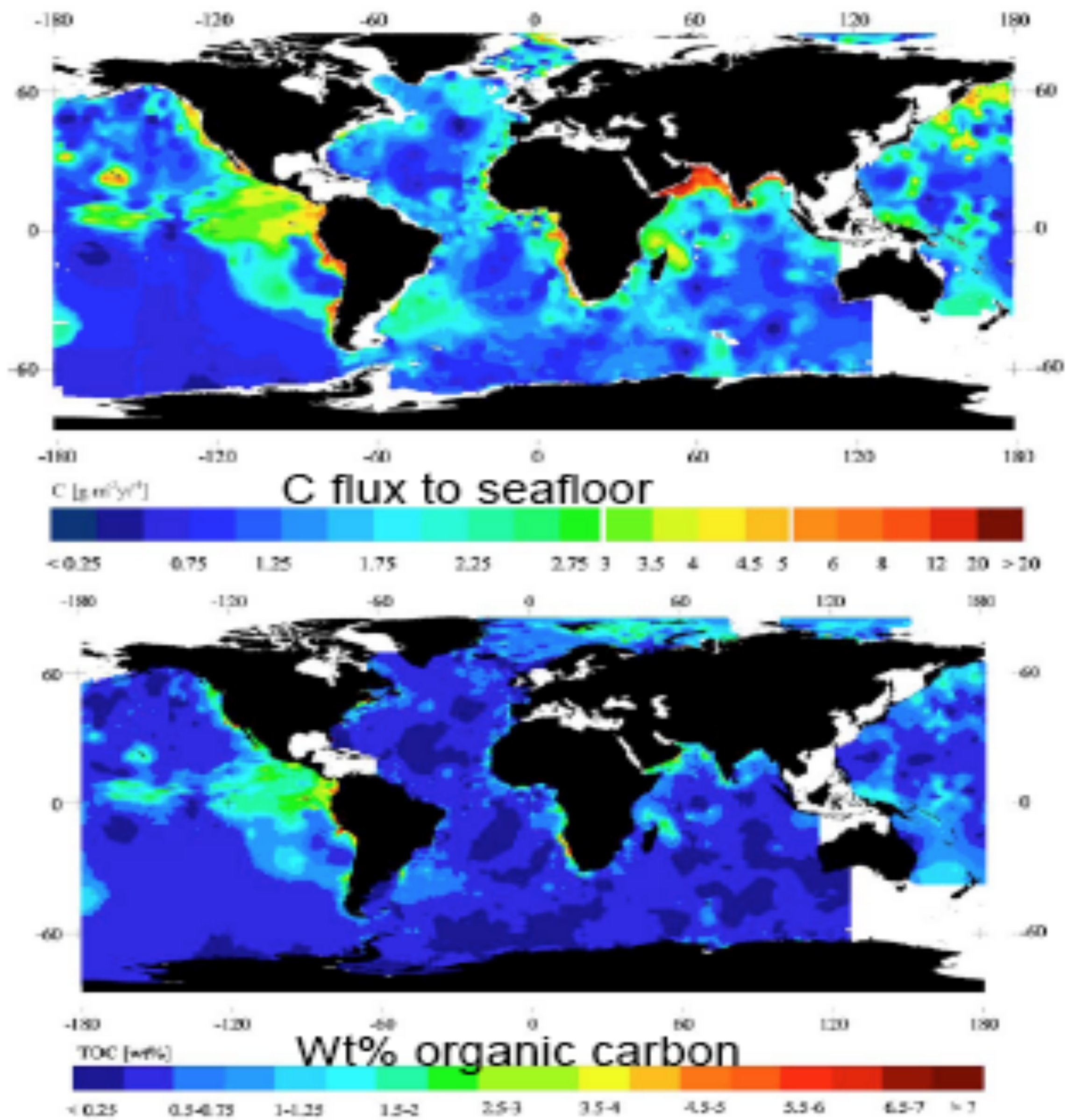
intermonsoon = 1-10%

Southern Ocean = 25 - >50%

Hawaii = 4-10% (up to 22%)

Bermuda = <10% (up to 50%)

Geographic correlation between carbon flux and wt% C in sediments

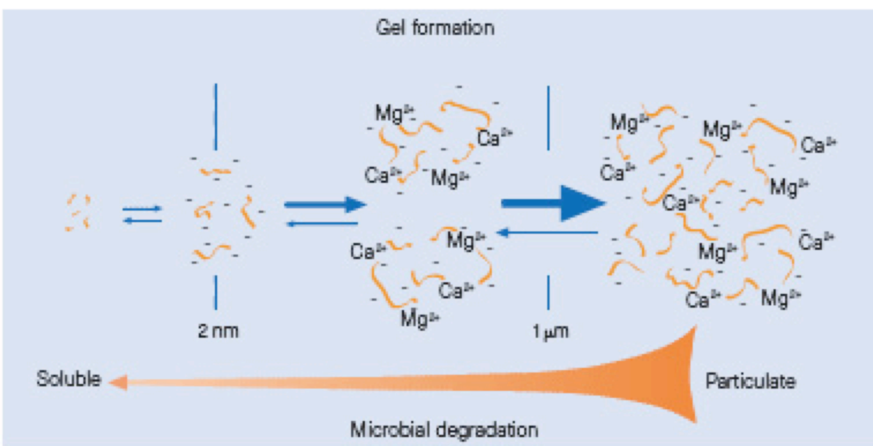


www.vanaqua.org

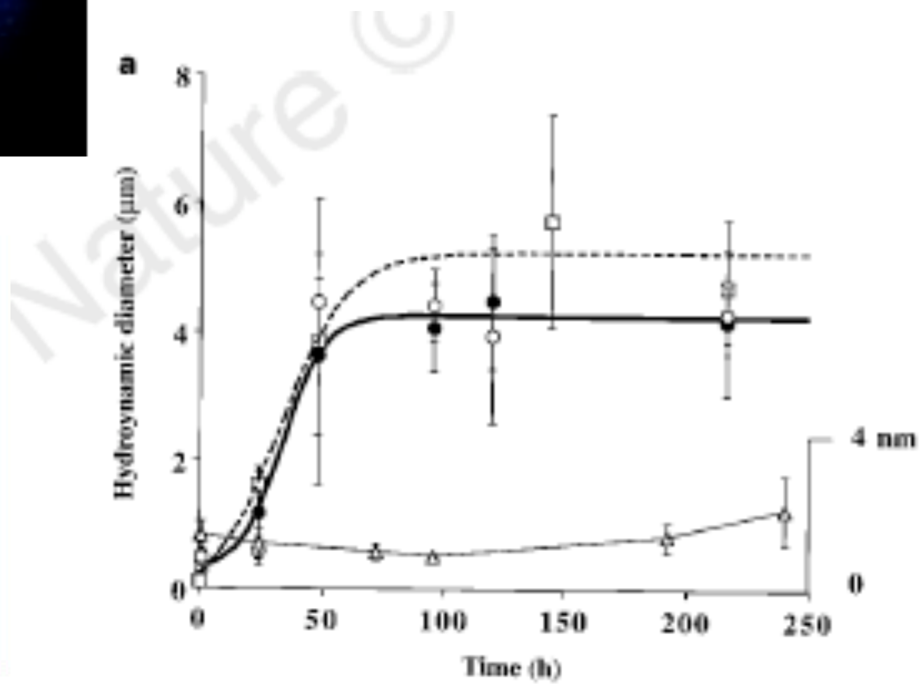
Marine snow-

very fragile aggregates
of organic matter and minerals that
form spontaneously, or are excreted
by marine biota

Difficult to measure flux



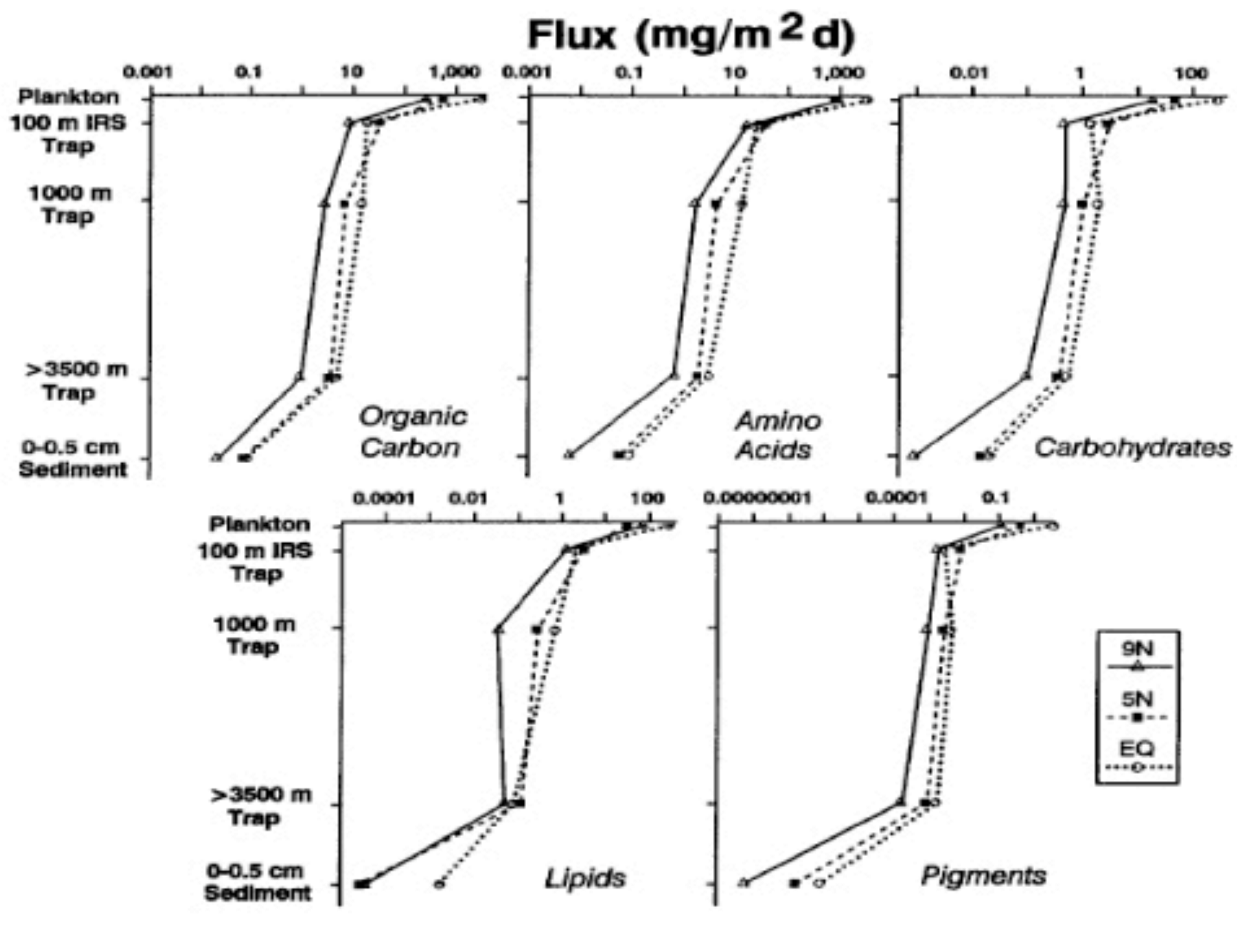
Wells, Nature (1998) 391



Chin et al. Nature (1998) 391:568-572

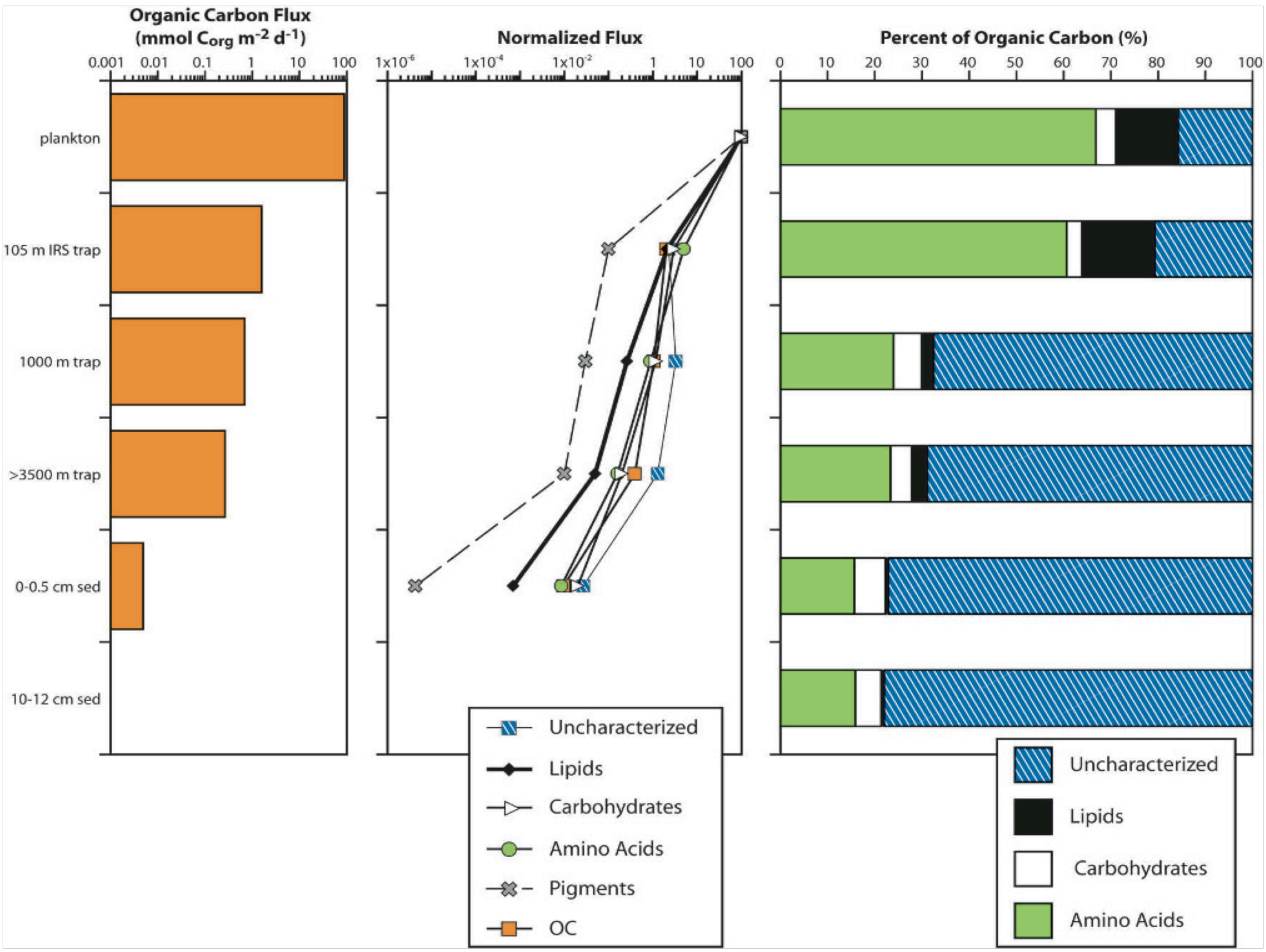
Molecular-level characterization of POM in sediment traps

What determines how much C makes it to the sea floor,
how much is mineralized, and how much is buried?



….at a molecular level, the composition of sinking POC is "edited" depth (degradation)

Do molecular level analyses give a fair representation of POM composition?



C:N = 6.6

C:N = 9.0

From Lee et al. (2004) Ambio 33, 565-574

The composition of organic matter in marine sediments and the mechanisms of carbon preservation

What determines how much makes it to the sea floor,
How much is mineralized, and how much is buried?

1) Selective preservation: Some compounds are intrinsically more labile than others, and will be preserved in sediments.

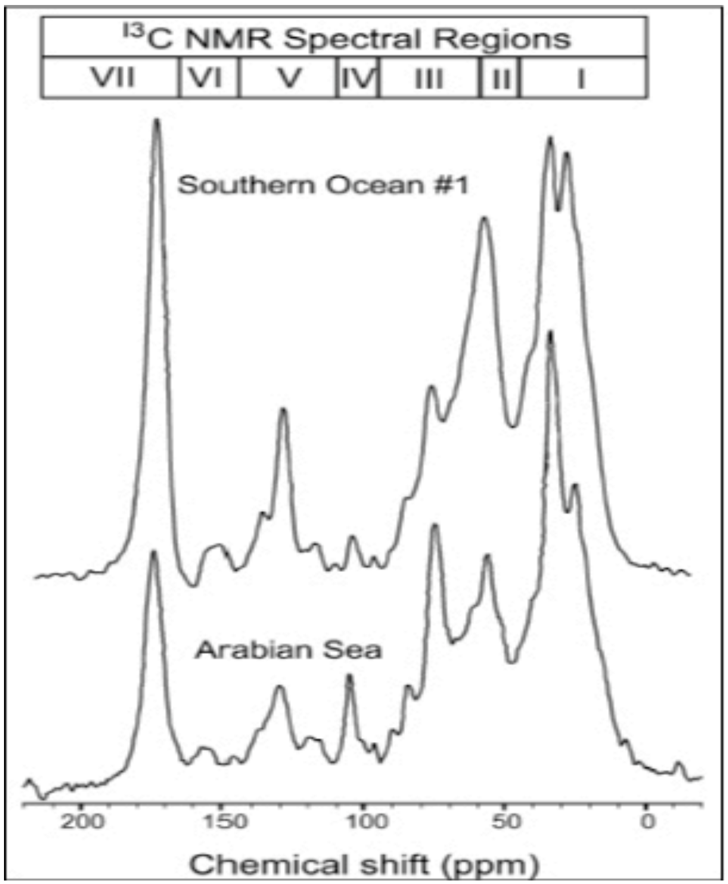
2) Physical protection/encapsulation: Organic matter can be "locked up" In clay minerals, cysts, etc and preserved.

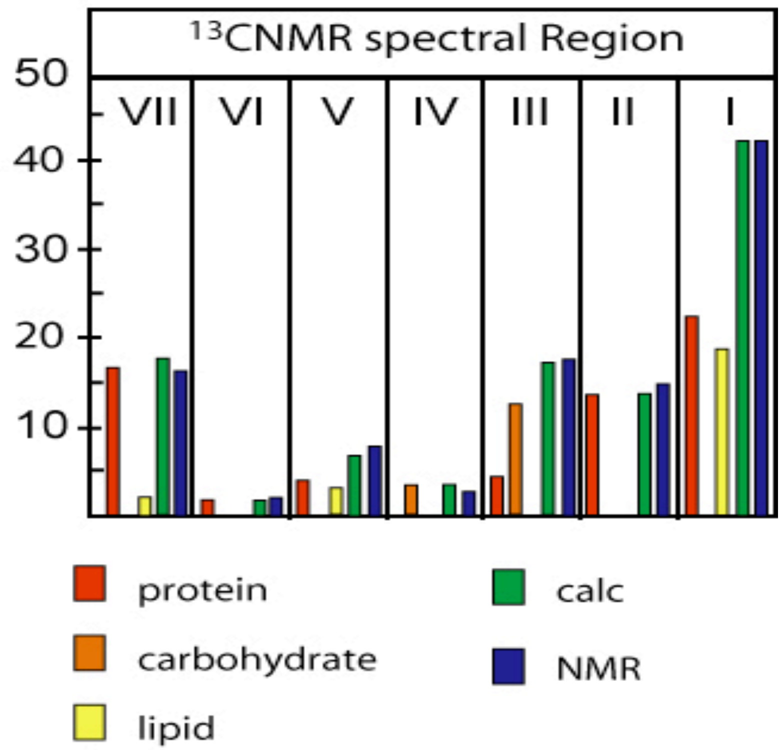
3) Geopolymer model: Simple biomolecules (sugars, amino acids, lipids) recombine through unknown reactions to form complex substances that are not easy to degrade.

These are not mutually exclusive….!

How well do we know the composition of marine algae?

$CH_3CH(N)COOH$	proteins	I, II, III, VII
$C(H_2O)$	carbohydrates	III
$CH_3(CH_2)_nCOOH$	lipids	I, V, VII





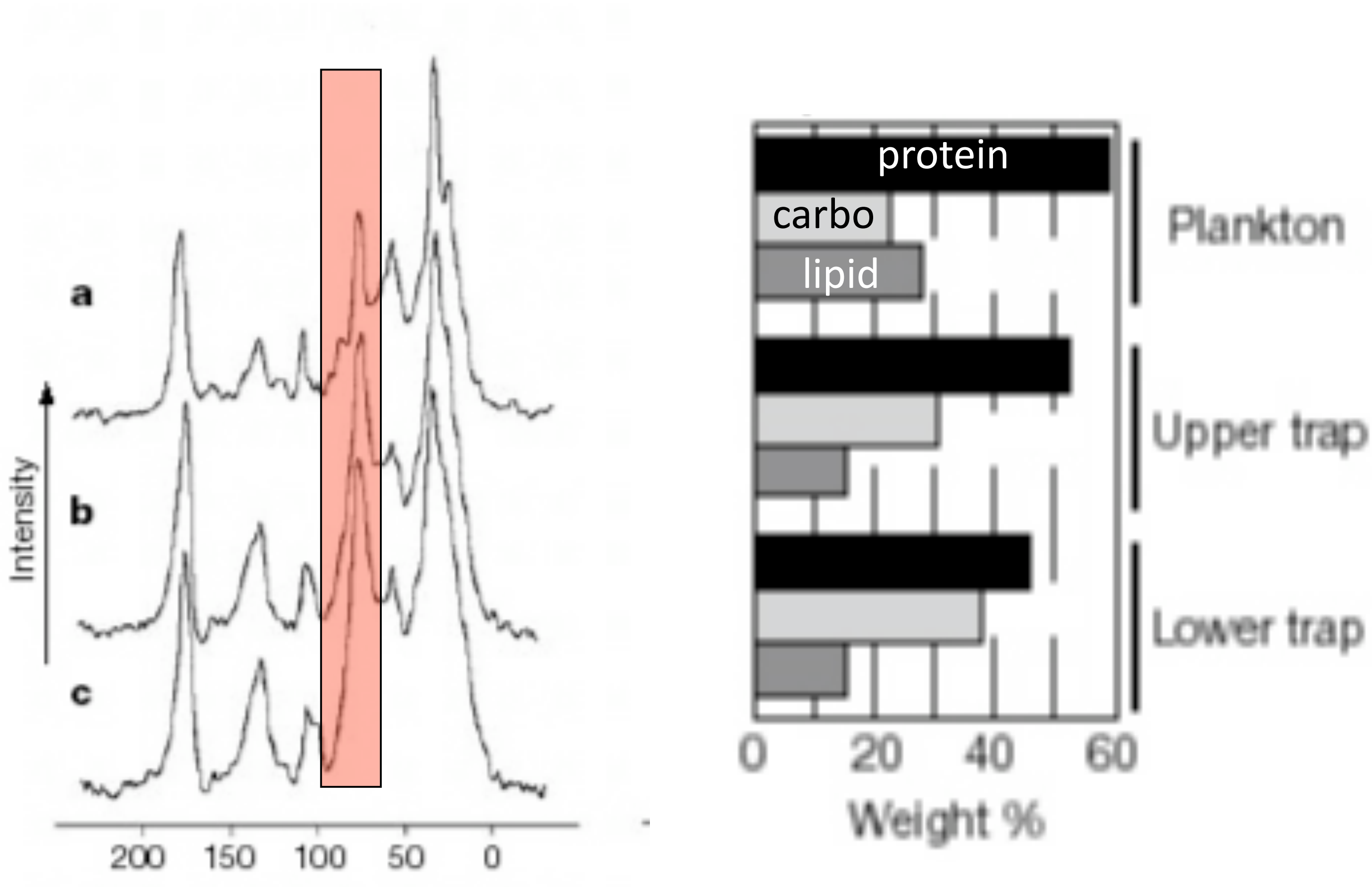
Hedges et al. (2002) Marine Chemistry v 78, pp 47-63

^{13}CNMR of phytoplankton, shallow and deep sediment trap material (Equatorial Pacific)

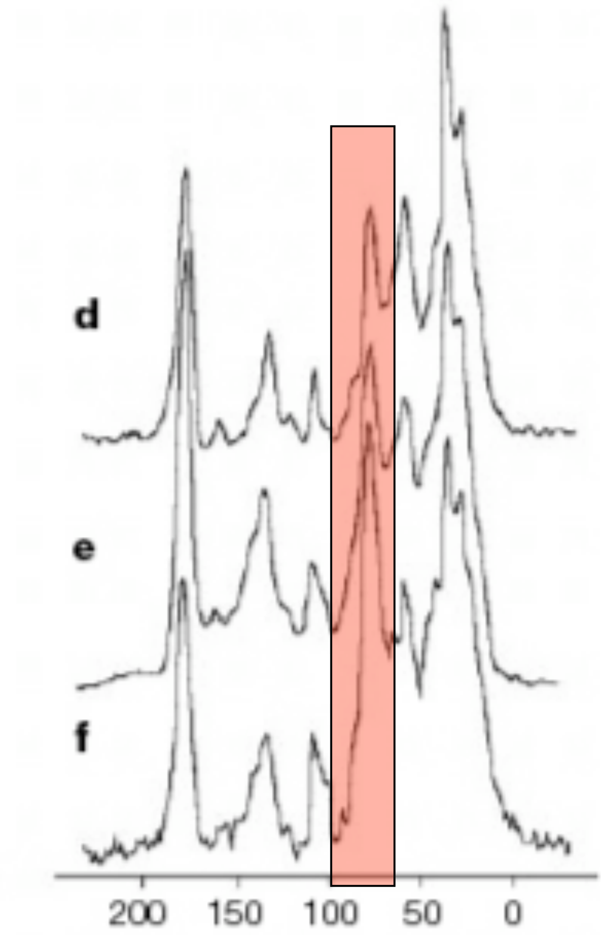
Surface

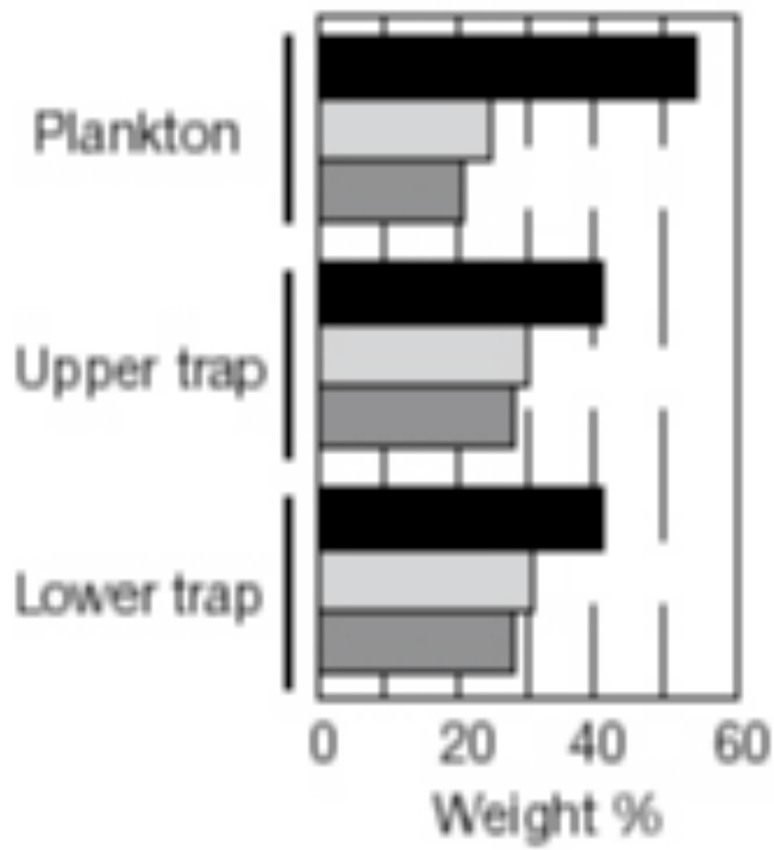
1000 m

3500 m

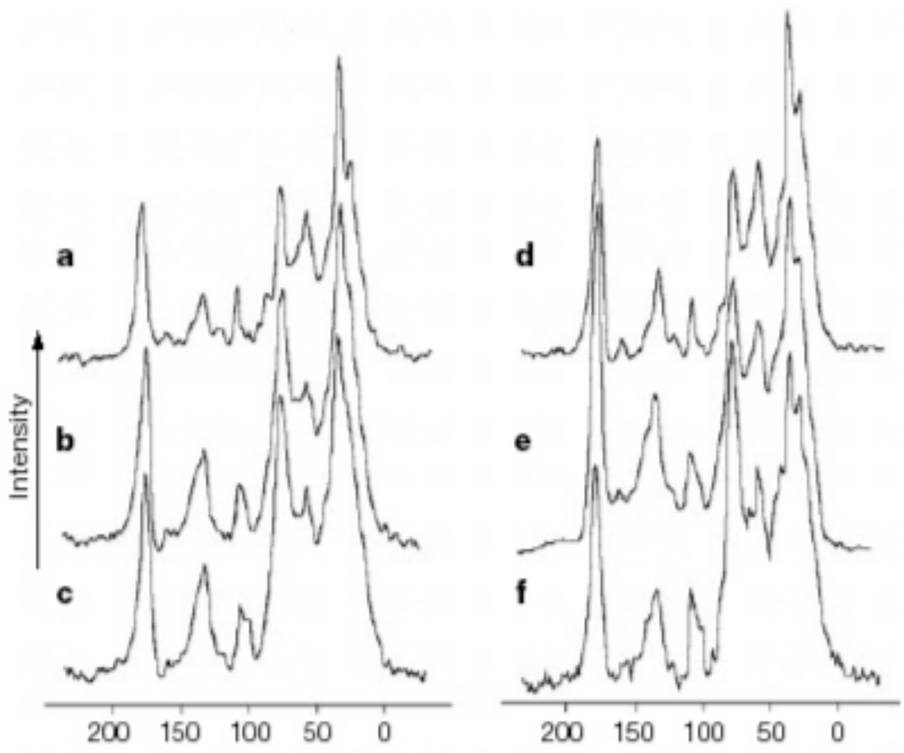


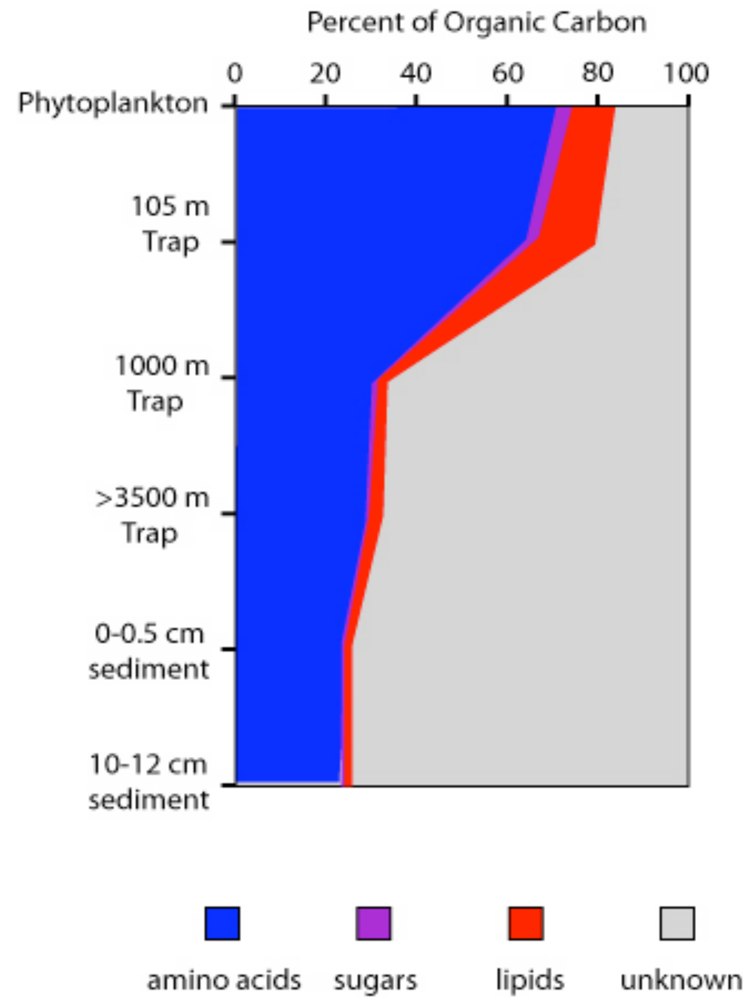
^{13}CNMR of phytoplankton, shallow and deep sediment trap material (Arabian Sea)



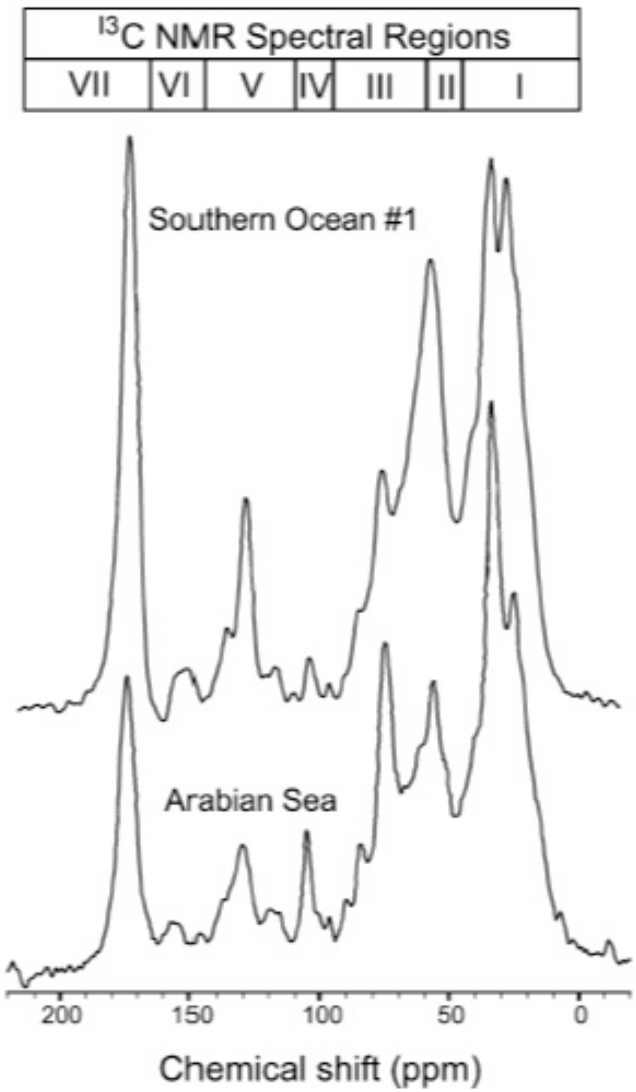


From the small changes in the ^{13}CNMR spectra of sinking POM, Hedges et al. infer that the C degradation acts non-selectively, and that *preservation occurs via physical protection*.

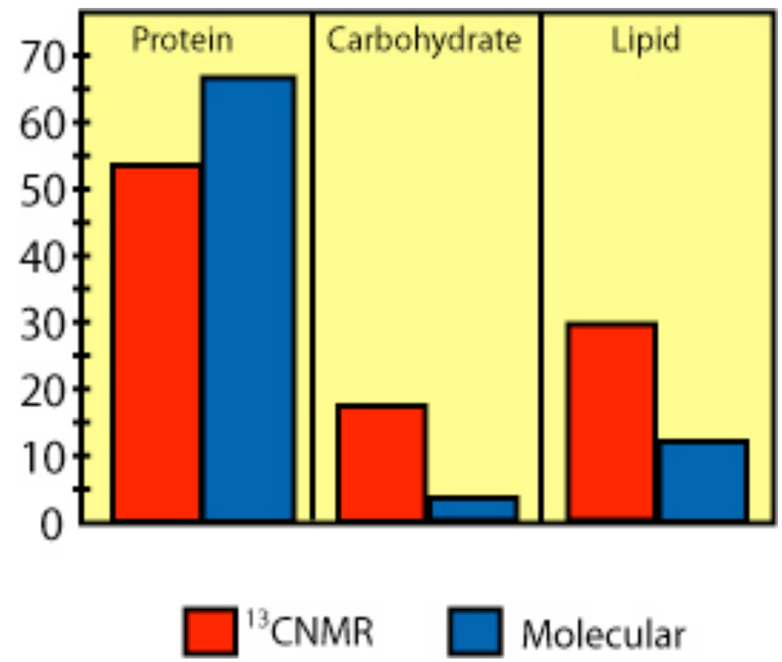




How well do we know the composition of marine algae?



Molecular analyses of phytoplankton cannot account for the NMR distributions of functional groups

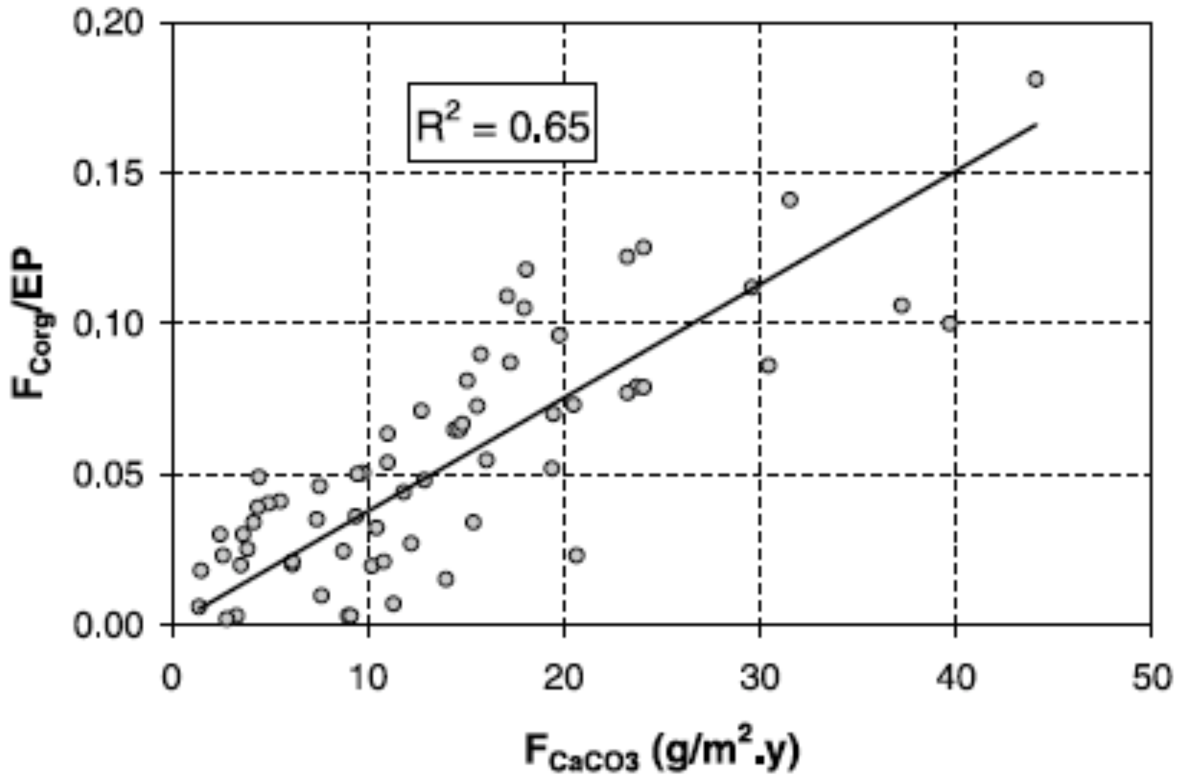


Do protein/carbohydrates/lipids account for most of the C&N in algae, and are the functional group assignments correct?

If C/N increases with depth from 6.6-> 9, then why isn't this reflected in the ^{13}CNMR?

Reconciling selective and nonselective preservation the effects of mineral ballast on C flux

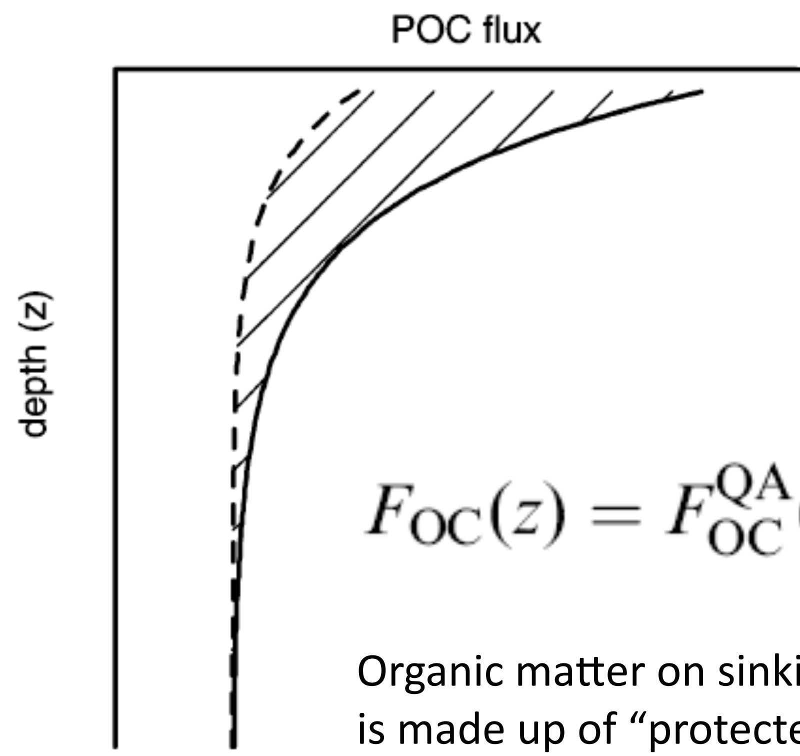
As more of the material is ballasted, the F_{org}/EP increases



F_{org} = fraction organic carbon & EP = export production

Francois et al. (2002) GBC 16 doi:10,1029/2001GB001722, 2002:

Reconciling selective and nonselective preservation
the effects of mineral ballast on C flux



$$F_{OC}(z) = F_{OC}^{QA}(z) + F_{OC}^{E}(z).$$

Organic matter on sinking particles
is made up of "protected" and "nonprotected"
forms. The "nonprotected OM is lost in the
upper water column, "protected is not, and its
flux will vary with the amount of mineral flux.

R.A. Armstrong et al. / Deep-Sea Research II 49 (2002) 219–236

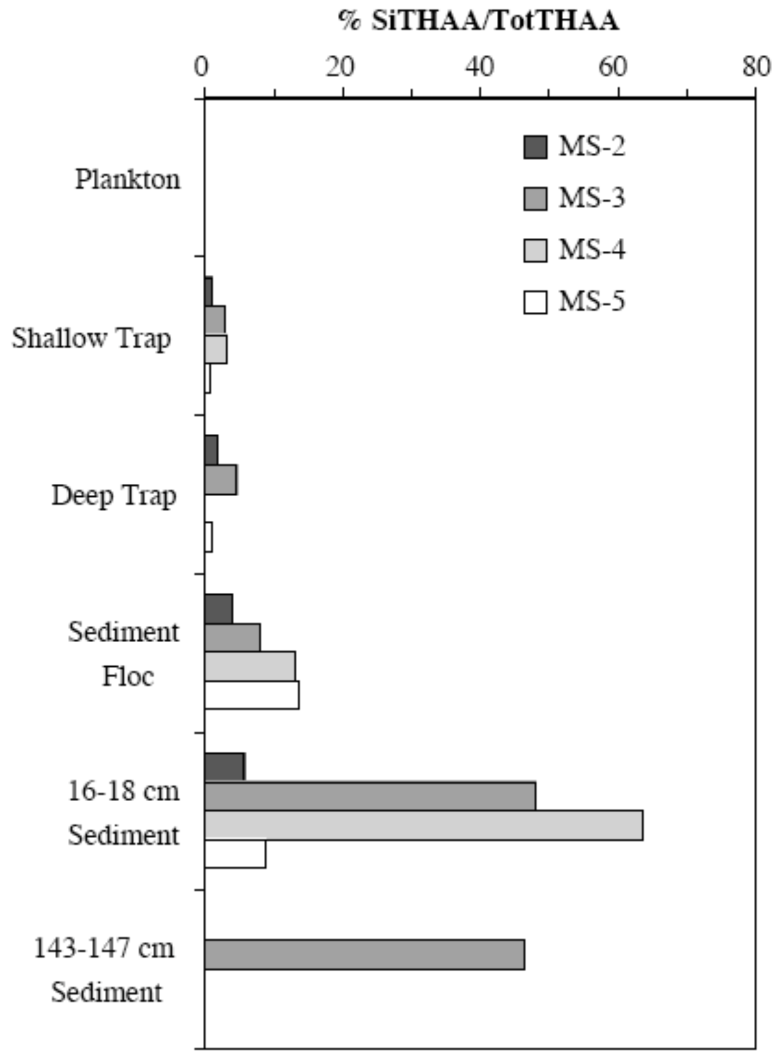


Fig. 5. The fraction of TotTHAA (THAA + SiTHAA) made up by SiTHAA as a function of depth in the water column and sediment. THAA includes calcium carbonate-bound amino acids (CaTHAA). Plankton values are 0.02–0.05%.

Testing the mineral protection hypothesis:

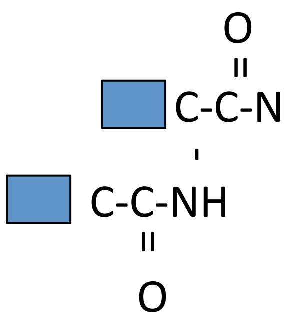
Do mineral bound amino acids make up a large fraction of the sinking POM at at depth in the ocean?

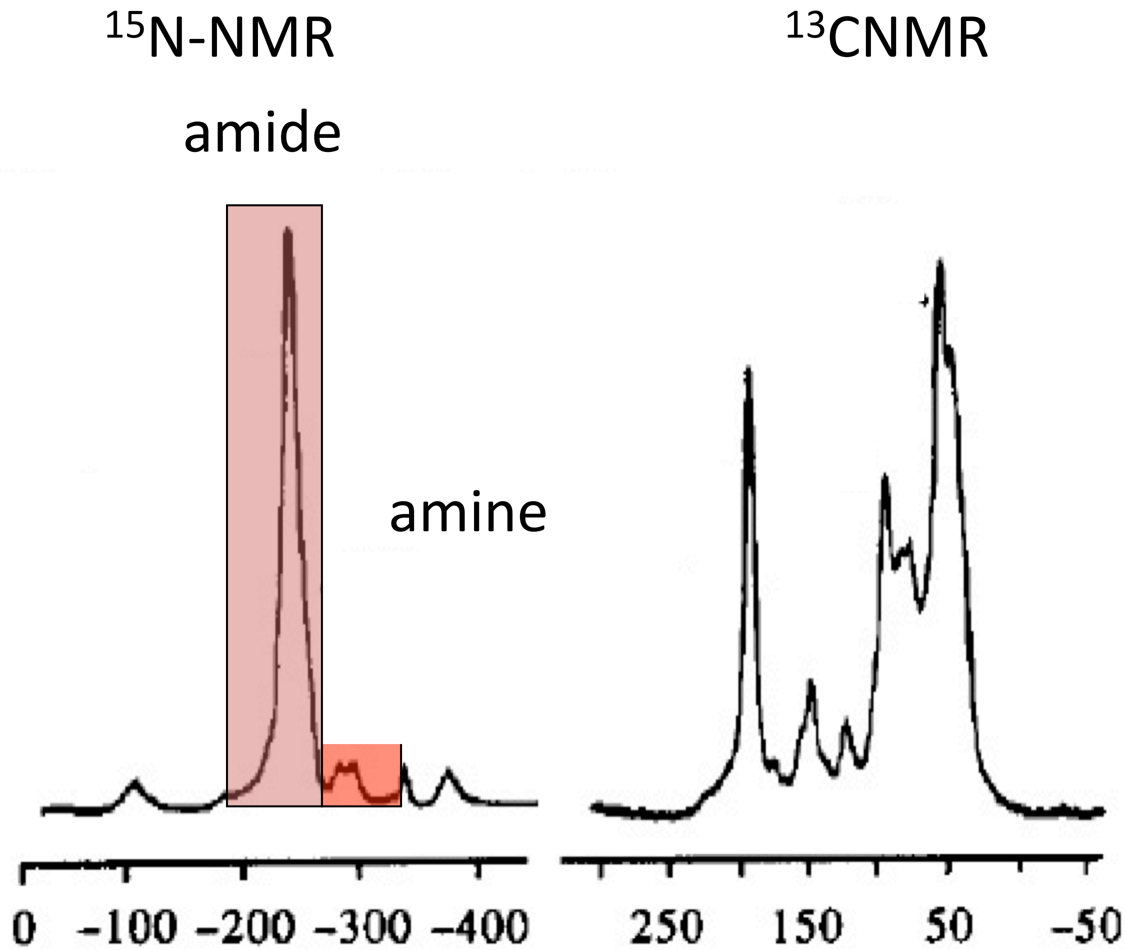
....not really, at least not in the southern ocean.

A.E. Ingalls et al. / Deep-Sea Research II 50 (2003) 713–738

NMR spectra of fresh algae. ^{15}N and ^{13}CNMR show a large fraction of the material is protein, (amide, CON, CHO & CH_x)

Knicker et al *Org Geo* **24**, 661-669

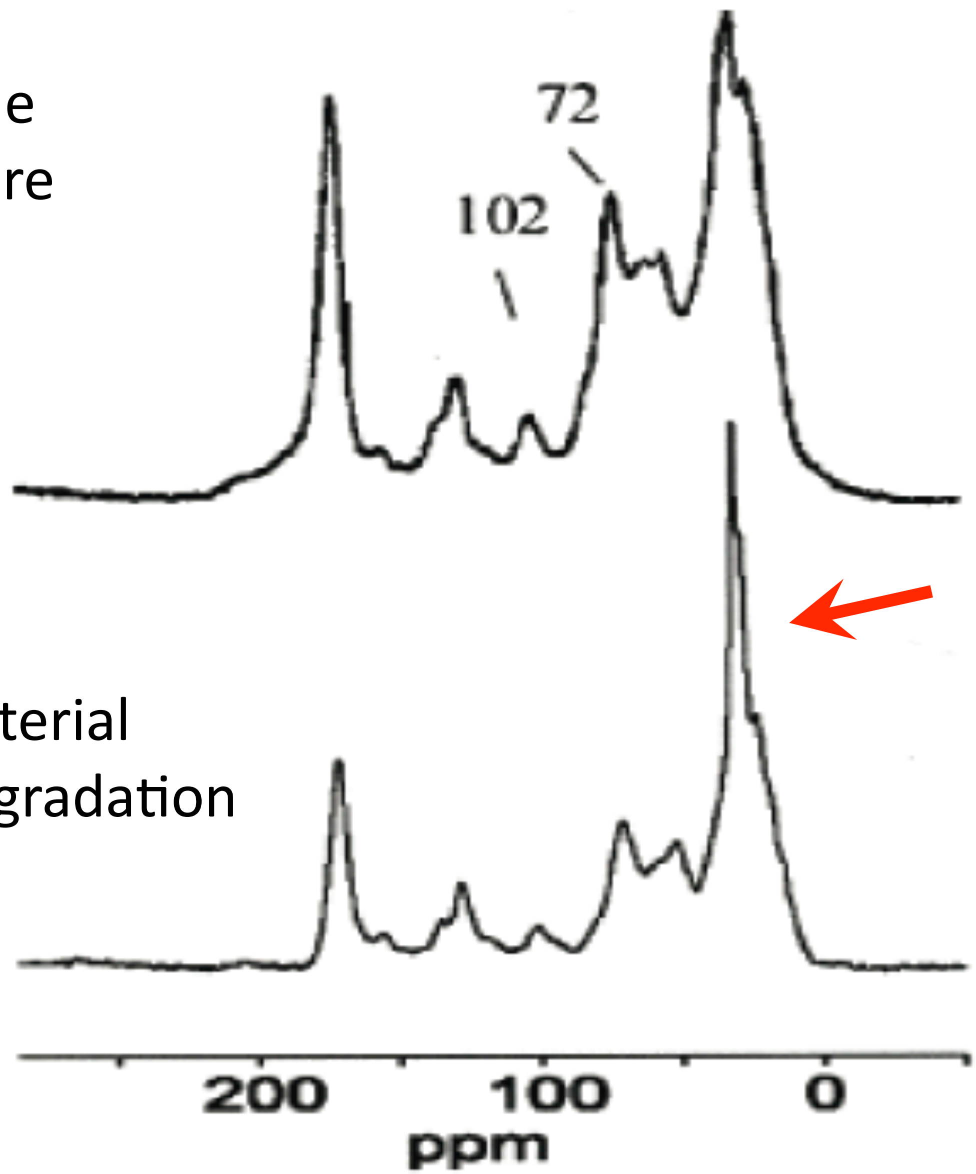




Physical entrapment into resistant geopolymers

^{13}CNMR of mixed algae
From laboratory culture

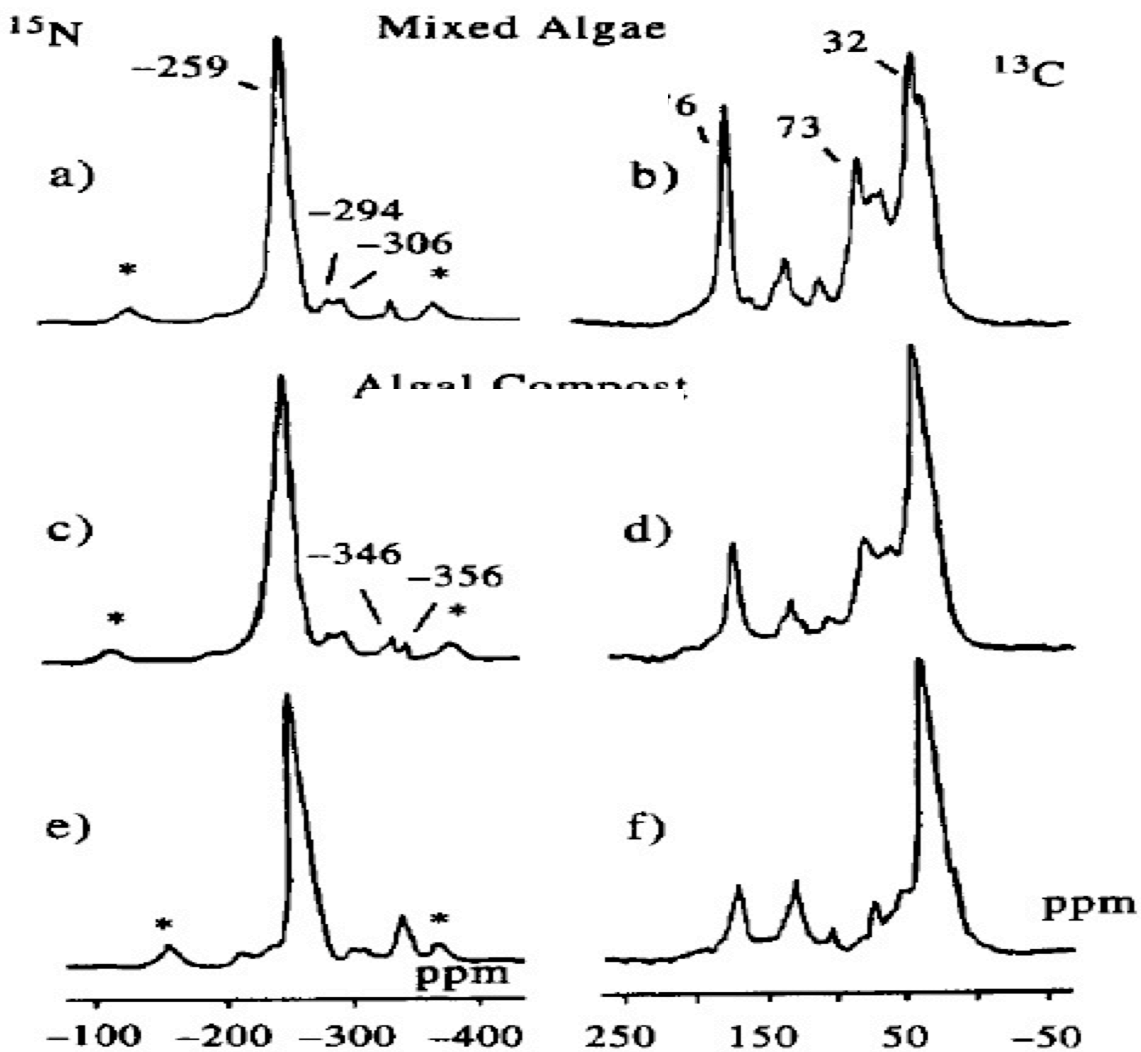
The same culture material
After 2 months of degradation



Knicker et al *Org Geo* **24**, 661-669

^{15}N- and ^{13}CNMR study of algal degradation

Knicker et al *Org Geo* **24**, 661-669



Fresh algae

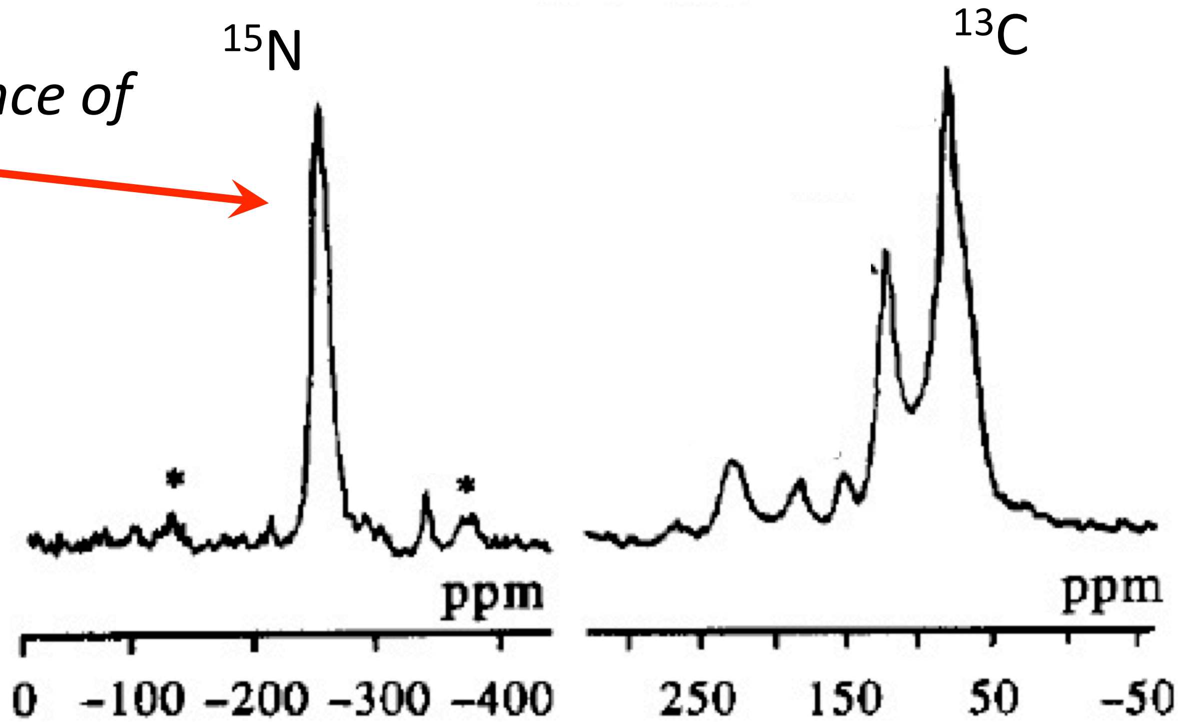
Algal compost (60 d)

Algaenan
(nonextractable POM)

^{15}N and ^{13}CNMR of an algal 4000 yr old sapropel from Mangrove Lake, Bermuda

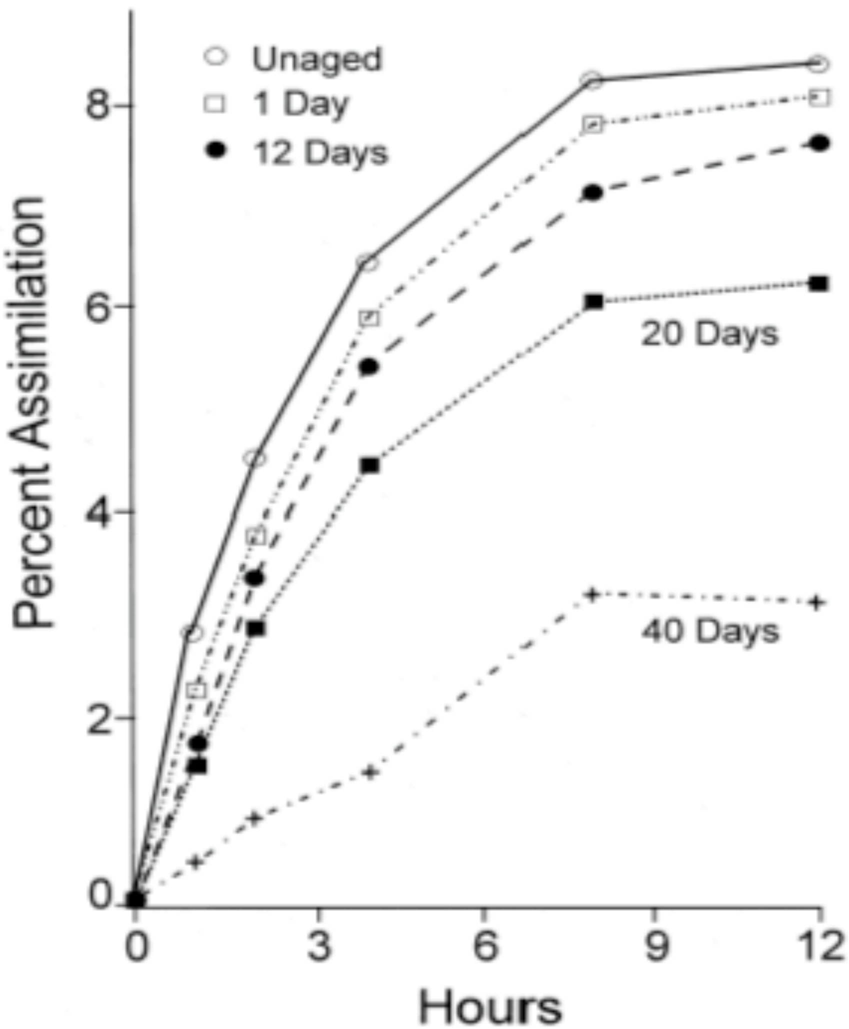
Knicker et al *Org Geo* **24**, 661-669

Note presence of Amide (?)…



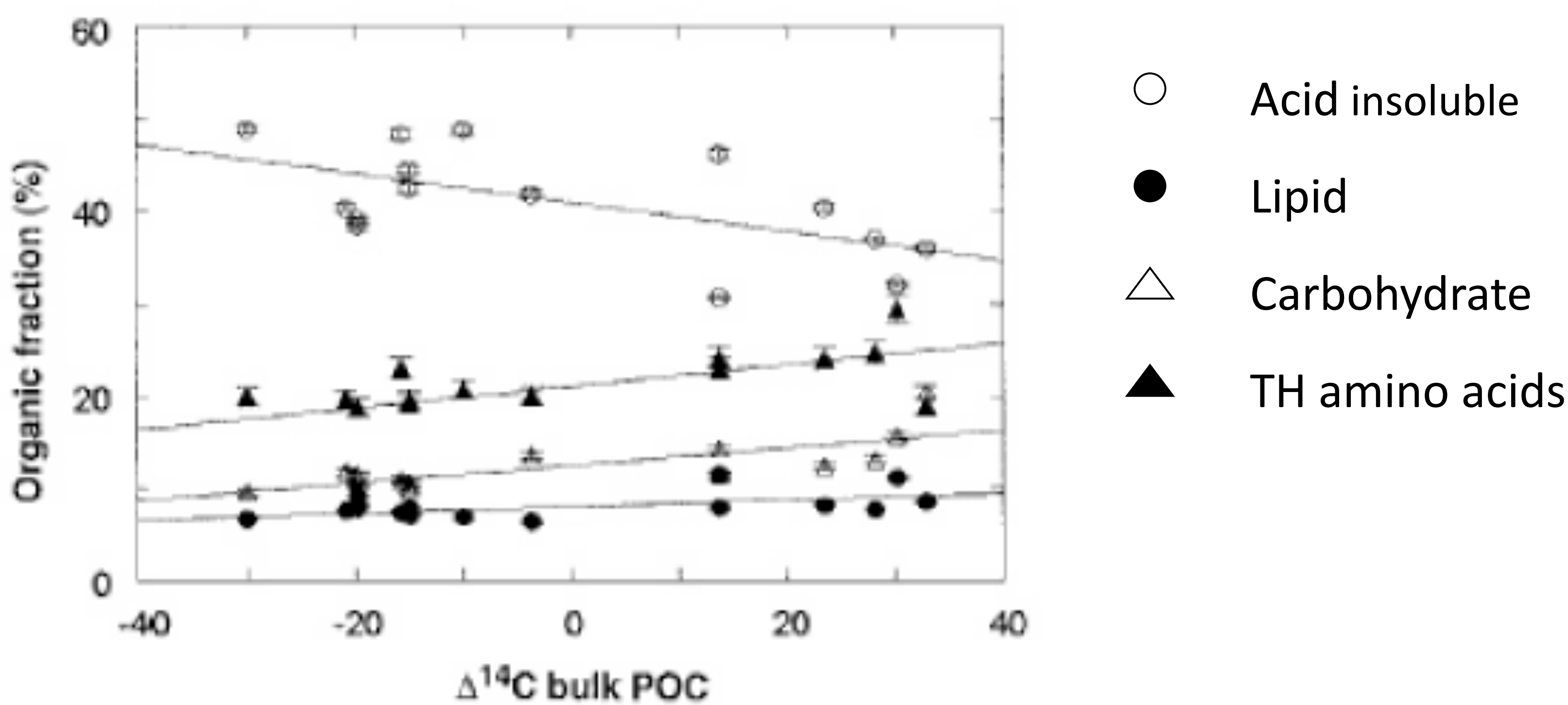
Knicker reasons that amide comes from protein, which should be labile. Preservation suggests some form of physical protection

but is protein labile?
The effect of aging on protein degradation



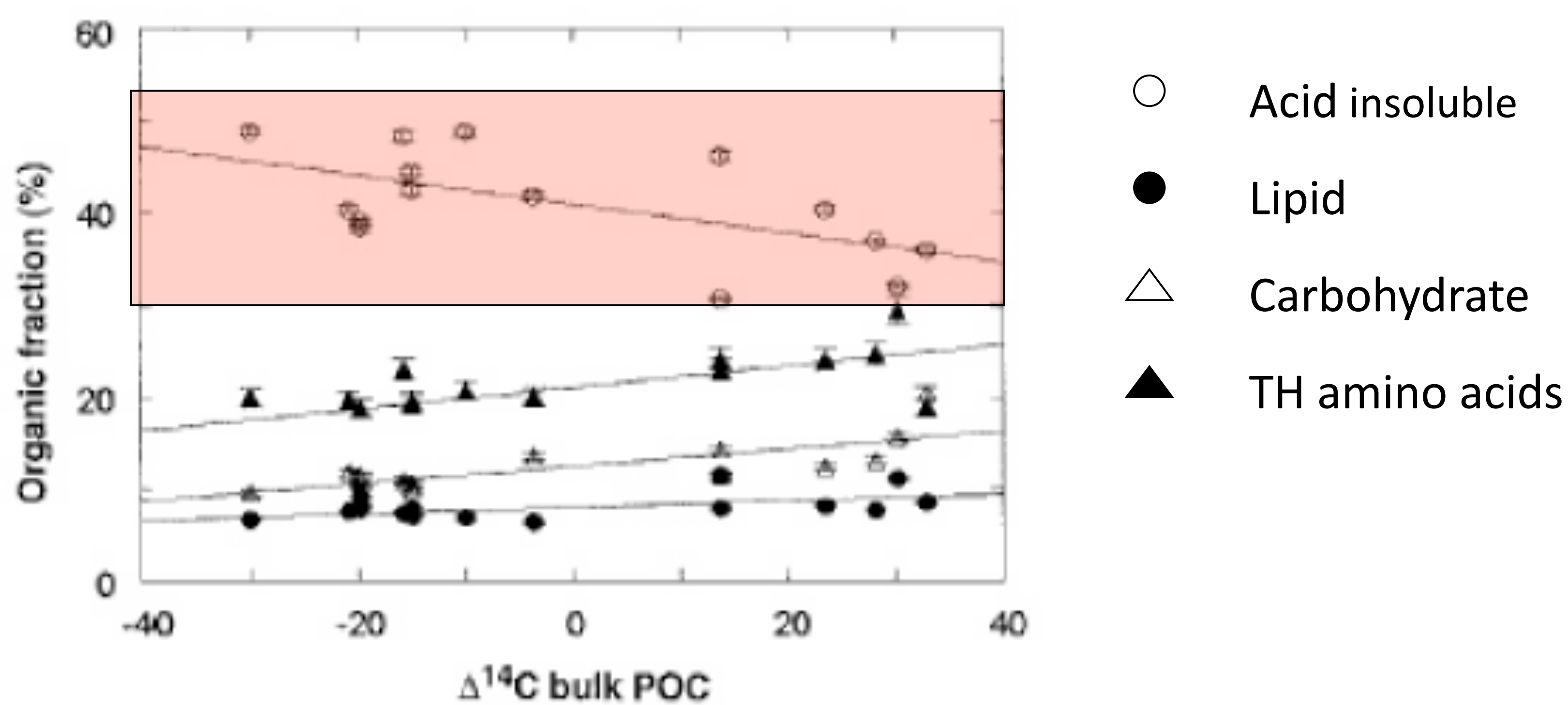
Keil and Kirchman

Another way to think about selective preservation….
What are the isotopic consequences of degradation?



J. Hwang & E.R.M. Druffel (2003) *Science*, **299** 881-884

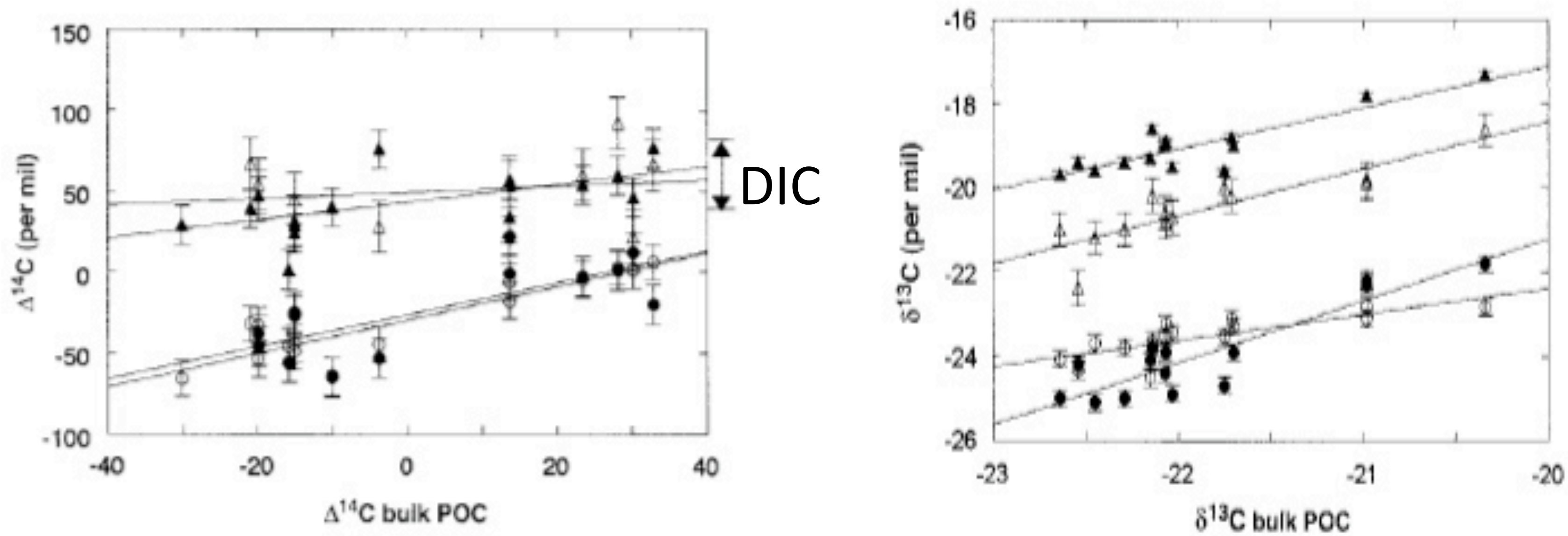
Another way to think about selective preservation….
What are the isotopic consequences of degradation?



As organic matter ages (14C) the amount of acid insoluble C increases…..

J. Hwang & E.R.M. Druffel (2003) *Science*, **299** 881-884

And the C isotope ratios of the acid insoluble fraction looks a lot like lipids….



○	Acid insoluble	△	Carbohydrate
●	Lipid	▲	TH amino acids

J. Hwang & E.R.M. Druffel (2003) *Science*, **299** 881-884

Summary……

There is clear evidence for selective degradation of labile Organic matter in sinking particles and in fresh vs preserved OM

Selective preservation is quantitatively significant as it affects C/N ratios.

It is not clear is organic matter is protected by adsorption onto mineral surfaces.

Some organic matter is encapsulated into minerals and is protected, But this may or may not be quantitatively significant (globally)

Other means of physical protection have been proposed, but are a matter of conjecture (in my opinion)

Particle dynamics and radiocarbon distribution in POC

Druffel et al. DSR (1990) 45: 667-687