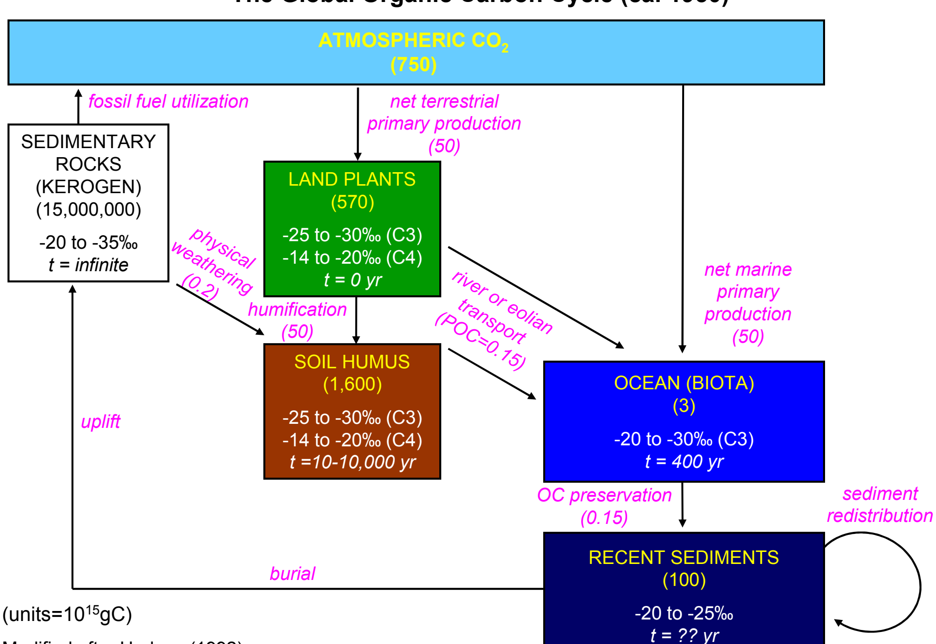
Old carbon in the modern marine environment

Possible origin(s) of non-zero ^{14}C ages for OC carbon in marine surface sediments:

- 1. Delivery of "pre-aged" terrestrial OC of vascular plant origin
- 2. Relict OC ("kerogen") inputs from erosion of sedimentary rocks
- 3. Sediment redistribution processes
  - Bioturbation
  - Lateral advection
- 4. Black Carbon

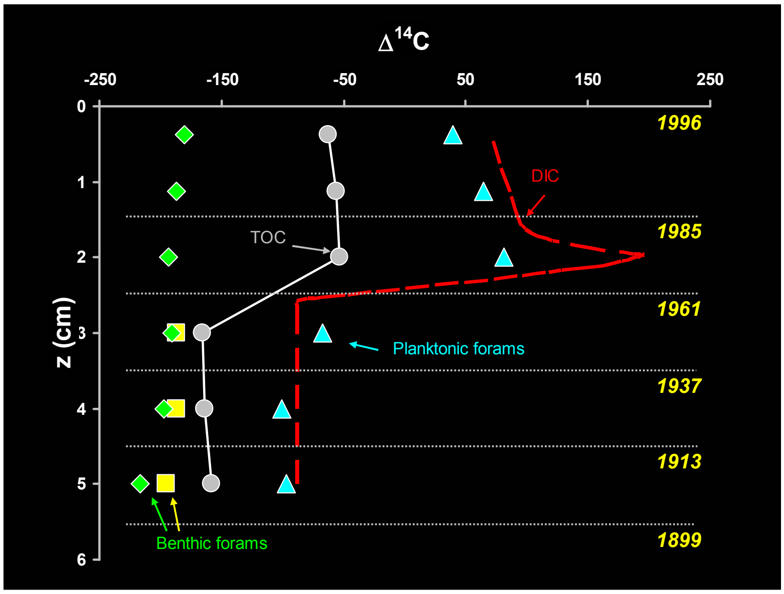
The Global Organic Carbon Cycle (ca. 1950)



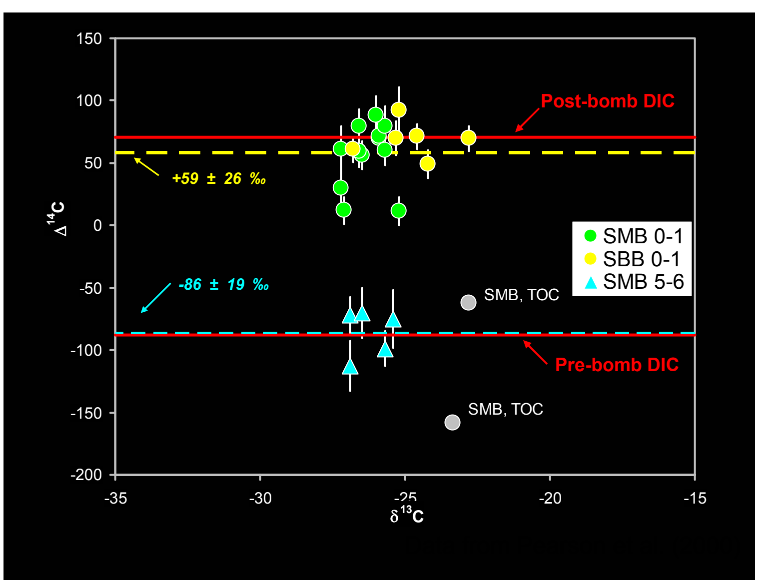
(units=10^{15}gC)

Modified after Hedges (1992)

TOC and foraminiferal $\Delta^{14}C$ in Santa Monica Basin sediments



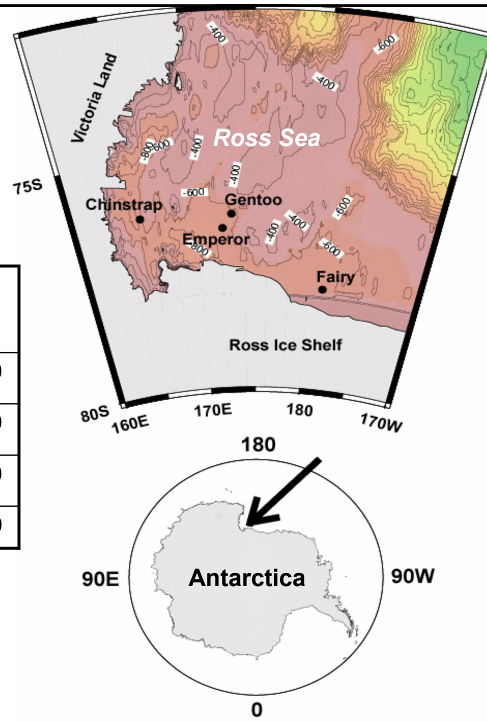
^{14}C contents of algal sterols in CBB sediments



Ross Sea, Antarctica

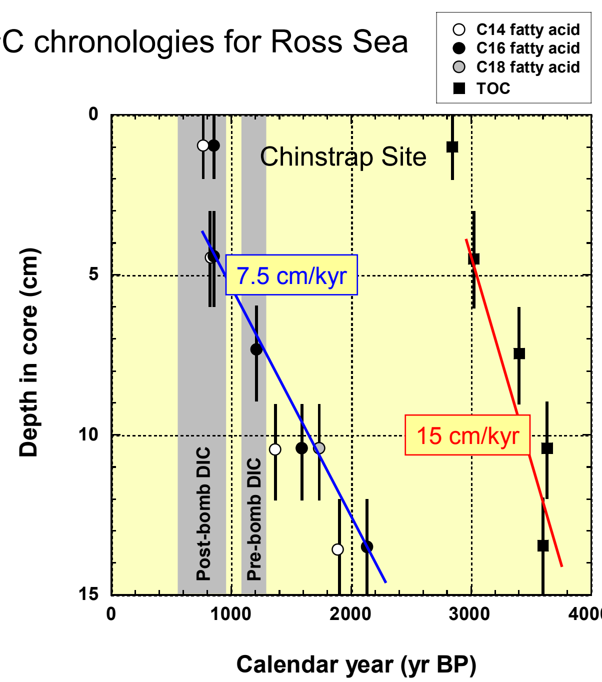
Surface Sedimentary OC composition

Site	Water Depth (m)	TOC (%)	$\delta^{13}C$	^{14}C age
Fairy	671	0.24	-25.65	9990
Gentoo	623	0.34	-27.42	4070
Emperor	670	0.49	-26.35	6500
Chinstrap	827	1.05	-24.04	2760



Data source:
Ohkouchi et al. (2003)

Fatty acid and TOC ^{14}C chronologies for Ross Sea sediments



Data source:
Ohkouchi et al. (2003)

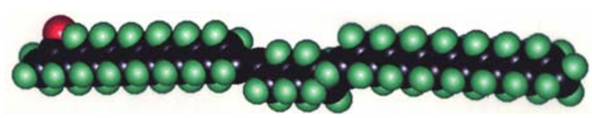
Coupled molecular and microfossil ^{14}C measurements

Premise:

- Marine algal biomarker compounds (e.g., alkenones) and planktonic forams both encode surface ocean-derived signatures (incl. ^{14}C content of DIC).
- Age discrepancies must therefore indicate different subsequent fates.
- Marine organic matter is predominantly associated with the fine fraction of sediments – prone to resuspension and redistribution.
- Foraminiferal tests are coarse, sand-sized particles – less susceptible to redistribution by bottom currents.

Approach:

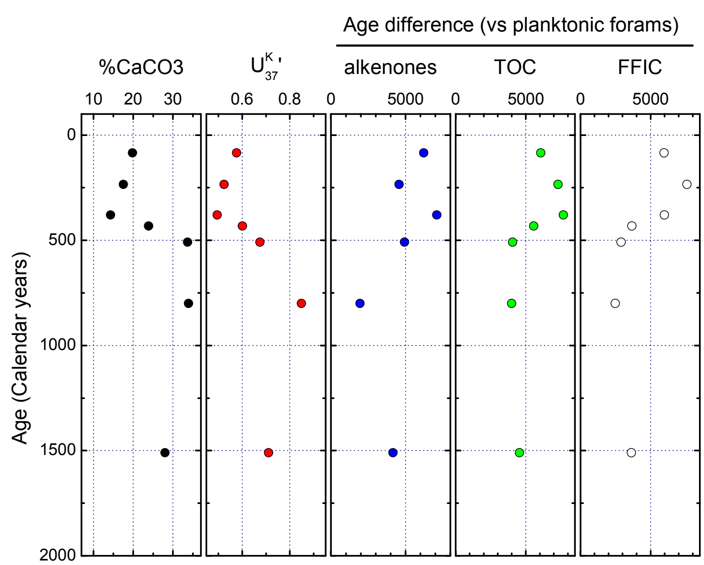
- Use ^{14}C relationships between planktonic foraminifera, algal biomarkers (e.g., alkenones), and bulk OC isolated from the same sediment intervals as a tool to examine sedimentological processes (lateral transport, bioturbation).



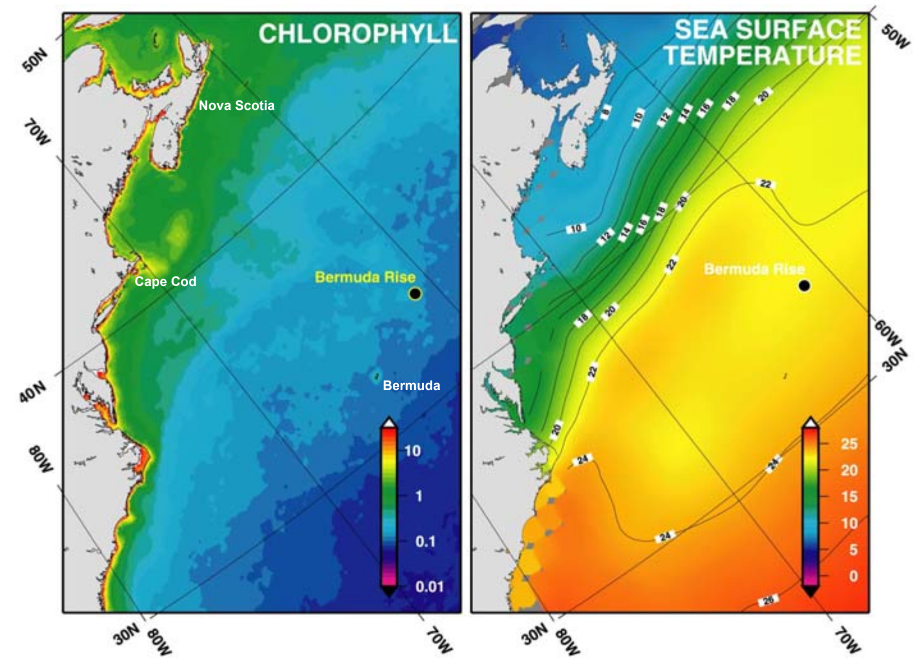
C_{37} "alkenone"

E. Huxleyi

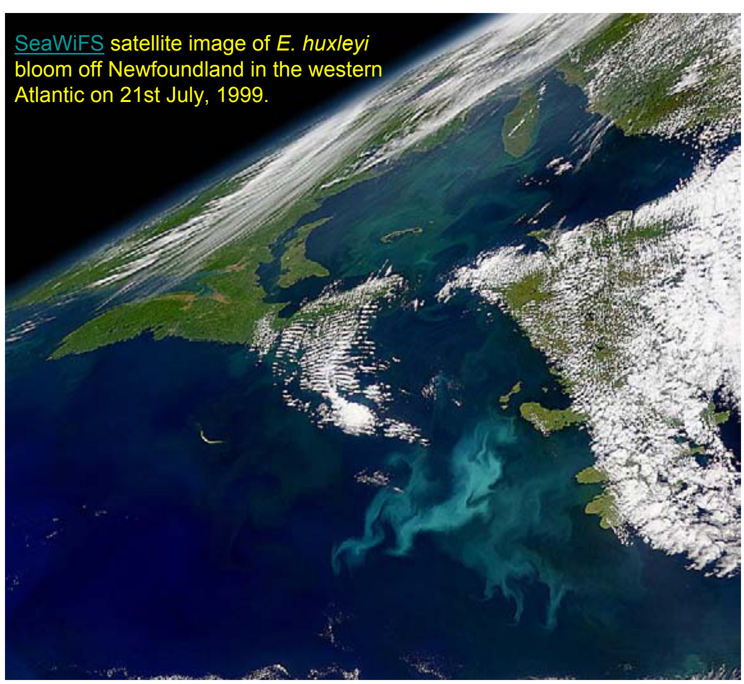
Sedimentological Controls on Geochemical Records from the Bermuda Rise



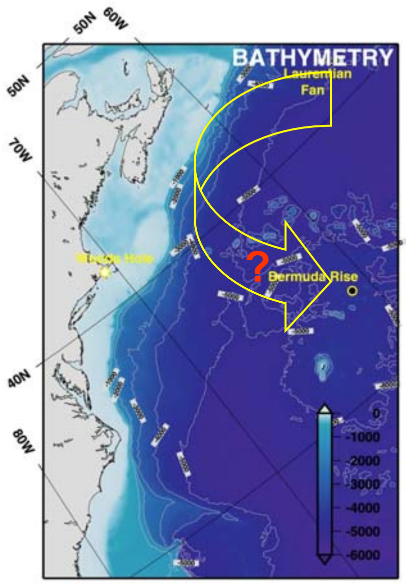
Ohkouchi et al. 2002



CHLOROPHYLL
Nova Scotia
Cape Cod
Bermuda Rise
Bermuda
10
1
0.1
0.01
SEA SURFACE
TEMPERATURE
Bermuda Rise
25
20
15
10
5
0
50N
70W
40N
80W
30N
80W
70W
50W
60W
30N

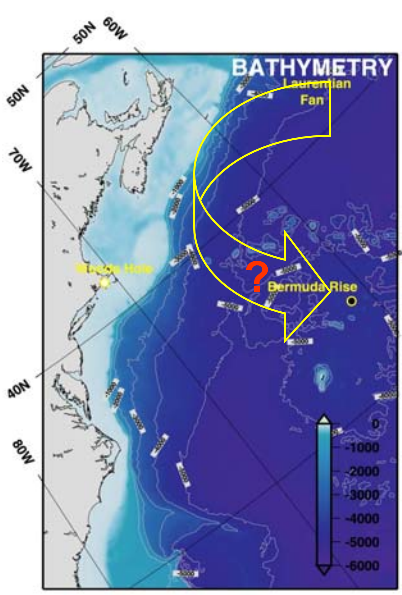


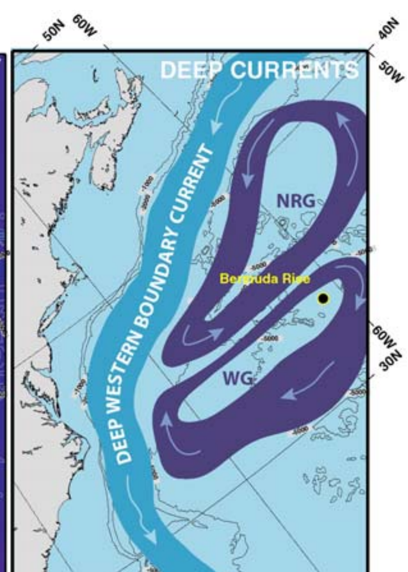
SeaWiFS satellite image of *E. huxleyi* bloom off Newfoundland in the western Atlantic on 21st July, 1999.



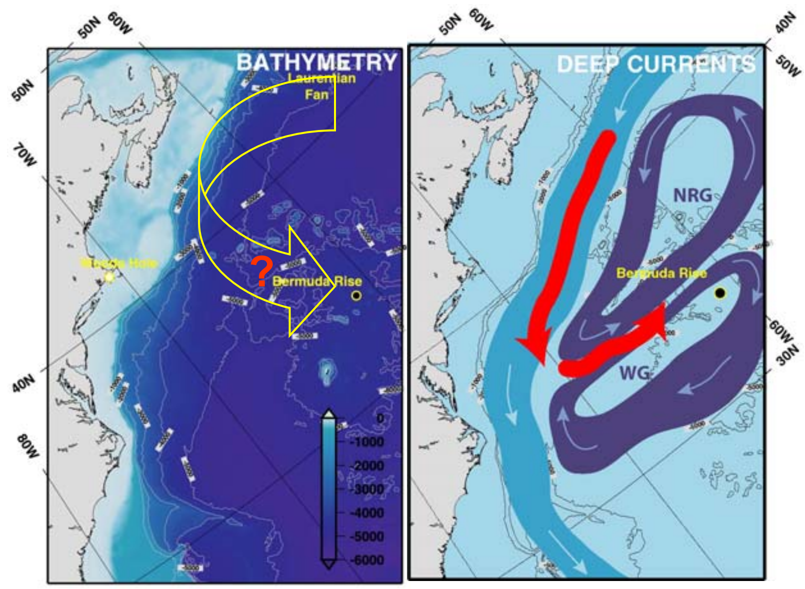
Long-range transport of organic matter (and alkenones) from the Scotian Margin to the Bermuda Rise?

Lateral transport of organic matter to the Bermuda Rise

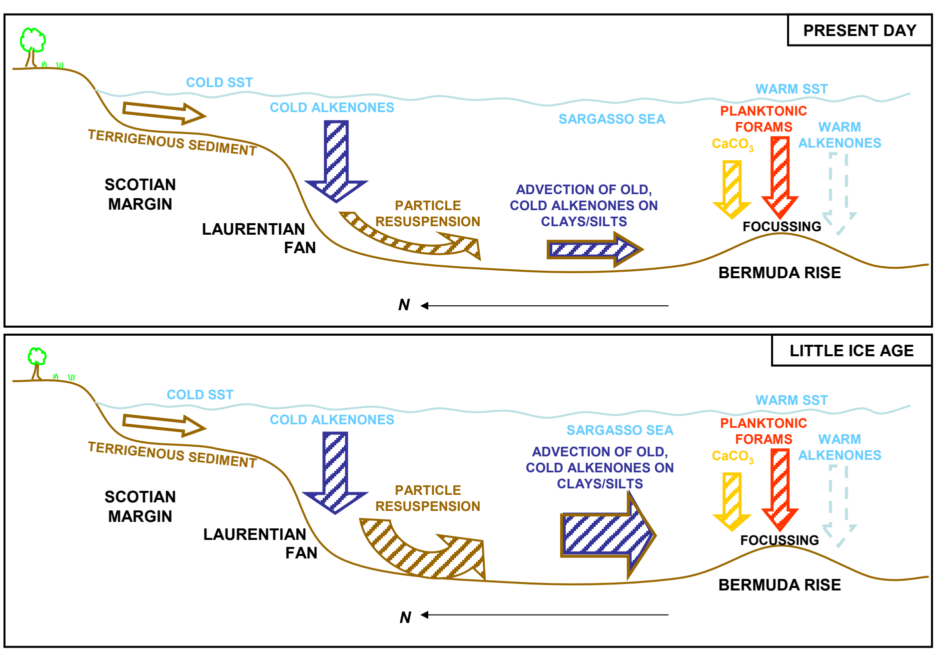




Lateral transport of organic matter to the Bermuda Rise



Sources and Transport of Alkenones and Forams to the Bermuda Rise

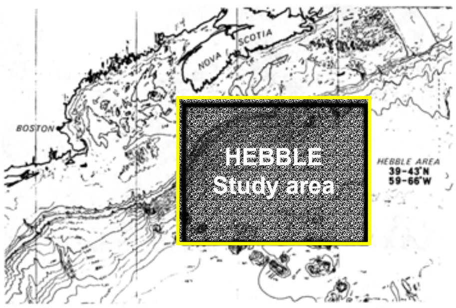


Science goes in circles!

A New Kind of Storm Beneath the Sea

Marine geologists and physical oceanographers are each sorting out their own types of evidence for surprisingly swift currents across the bottom of the deep sea

SCIENCE, VOL. 208, 2 MAY 1980



The HEBBLE study area in which high-speed currents over the deep sea floor were detected. The area includes the continental shelf in its northwestern corner, the steep continental slope below the shelf (region of closely spaced contour lines), the gently sloping continental rise, and the flat abyssal plain in its southeast corner. The HEBBLE instrument array generally extended along a northwest-southeast line in the south-central portion of the box. The New England Seamounts run across the southwestern corner of the box.

Marine Geology, 99 (1991) 445–460
Elsevier Science Publishers B.V., Amsterdam

HEBBLE epilogue

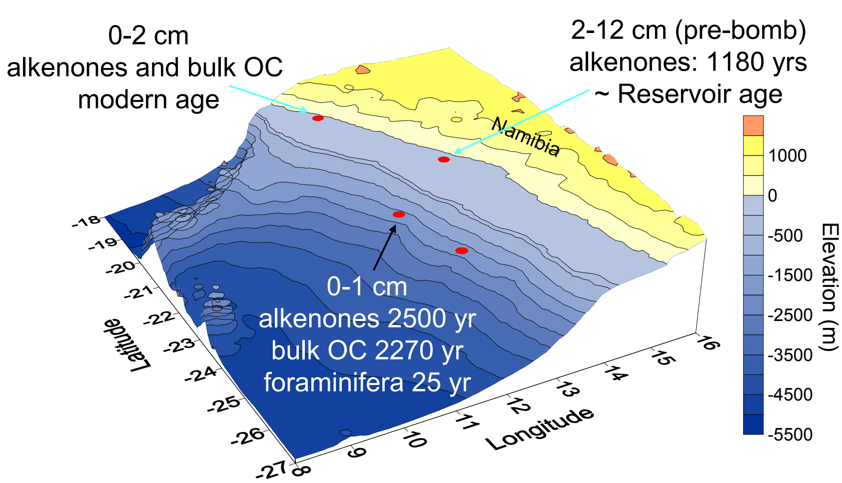
C.D. Hollister[a] and A.R.M. Nowell[b]
[a]*Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA*
[b]*University of Washington, School of Oceanography, Seattle, WA 98195, USA*
(Received September 1989; revision accepted May 1990)

Benthic Storms: Temporal Variability in a Deep-Ocean Nepheloid Layer

Abstract. *Time series measurements of light scattering were made for 2½ months at 20 meters above the bottom in the western North Atlantic. The highest values recorded with the nephelometer exceeded all previous measurements worldwide. Rapid changes indicated a high degree of activity near the sea floor, and some increases may have been related to atmospheric storms.*

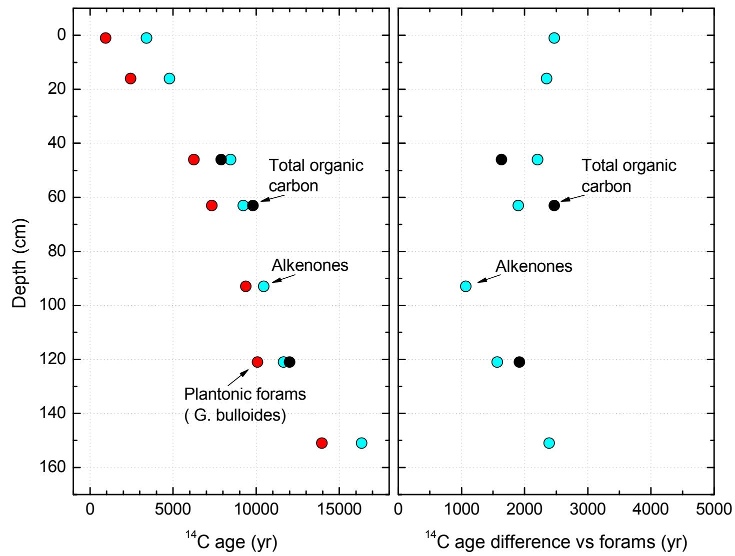
SCIENCE, VOL. 213, 17 JULY 1981

Namibian margin (Benguela Upwelling region)



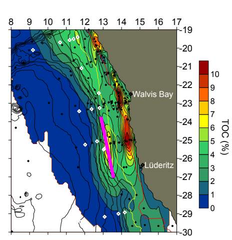
Data from *Mollenhauer et al., 2003*

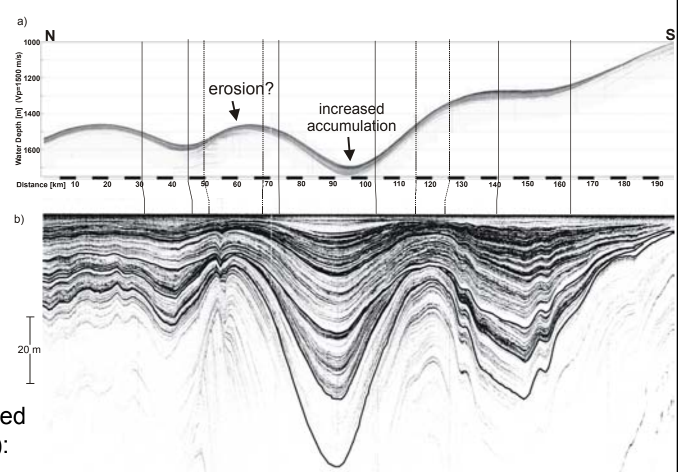
¹⁴C ages of Namibian margin sedimentary components (core 226660-5)



Mollenhauer et al., 2003

Accumulation maximum (depocenter) on upper continental slope

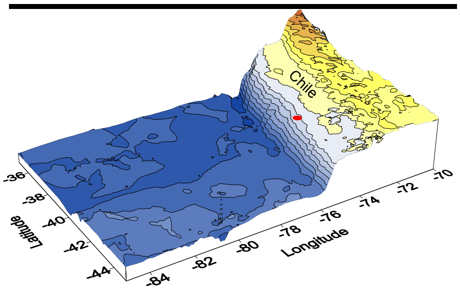


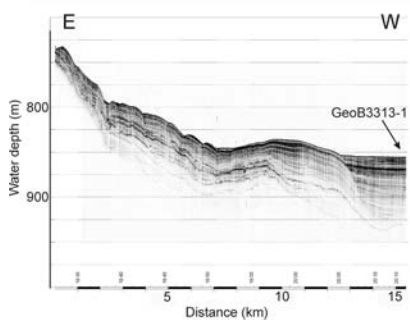


Sites of increased accumulation in protected locations (depocenters): Implication of current controlled sedimentation

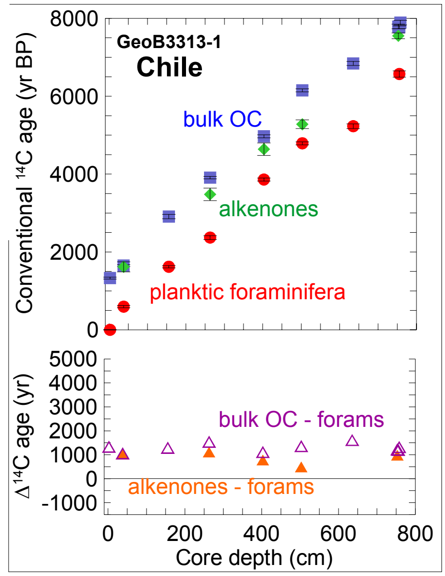
Seismic data processing: André Janke

Mollenhauer et al., 2002



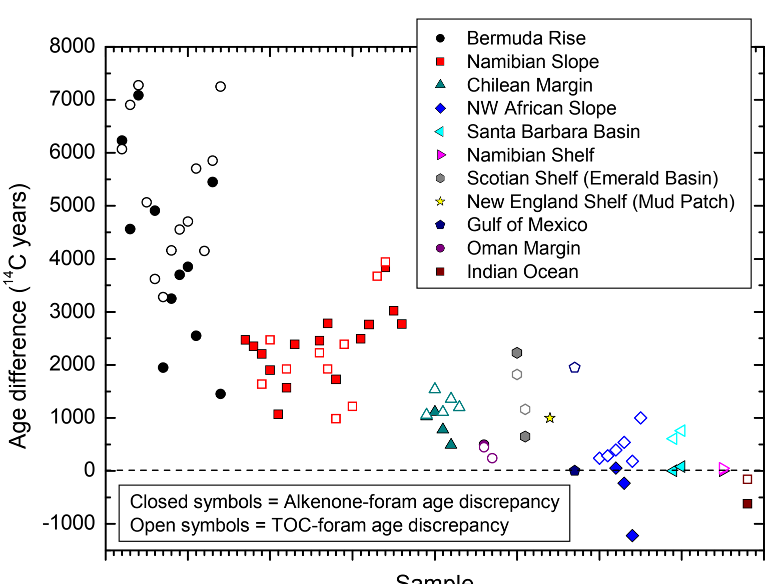


Southern Chile



Mollenhauer et al. In press.

^{14}C age discrepancies between organic matter and calcareous microfossils



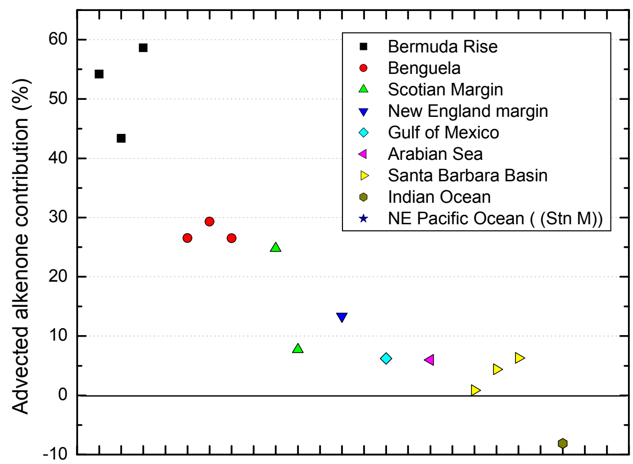
Eglinton et al. unpublished

Estimates of advective alkenone contributions

Assumptions:

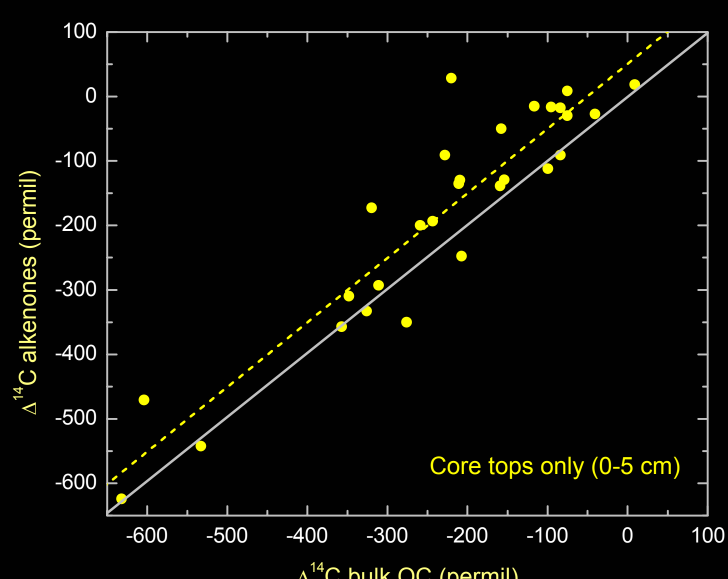
Δ¹⁴C of indigenous alkenones = Δ¹⁴C of forams

Δ¹⁴C of advected alkenones = -1000 permil (infinite ¹⁴C age)



Eglinton et al. unpublished

Comparison of alkenone and TOC ¹⁴C ages in surficial (< 3 cm) marine sediments



Eglinton et al, unpublished

Additional evidence for advective OC supply to the sea floor

(i) Increased material fluxes in deep, relative to shallow, sediment traps deployed near continental slopes (Honjo *et al*., 1982; Biscaye *et al*., 1988; Thomsen & van Weering, 1998).

(ii) High suspended particle concentrations near the seafloor (bottom nepheloid layer; McCave, 1983; Gardner & Sullivan, 1981) or associated with the detachment of intermediate nepheloid layers from the upper slope (INLs; Biscaye *et al*., 1988; Pickart, 2000).

(iii) Carbon and oxygen imbalances in the deep ocean (Jahnke *et al*., 1996).

(iv) Old ^{14}C ages of OC on suspended particles in slope waters (Bauer *et al*., 2001).

(v) ^{14}C age of particles on slope waters intercepted by sediment traps (Anderson *et al*., 1994; Hwang *et al*., 2004).

(vi) The isotopic and molecular composition of deep sea sediments (Freudenthal *et al.,* 2001; Benthien & Müller, 2000).

Advection of POC in the Panama Basin

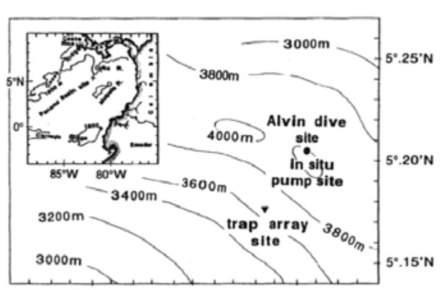


Figure 1. Map of the Panama Basin showing bottom bathymetry and the collection sites for the sediment trap, sediment core (Alvin dive site) and suspended POC (pump).

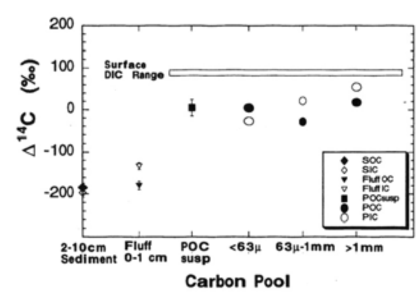
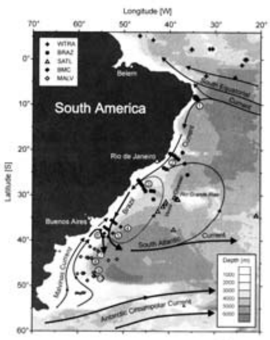
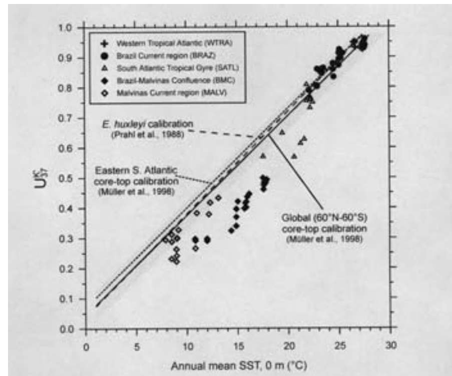


Figure 2. $\Delta^{14}C$ of the carbon pools from the Panama Basin site. DIC $\Delta^{14}C$ range was for surface waters (see Table 1), POC and PIC were sinking material from a 2-mo sediment trap collection at 266 mab (bottom depth 3620m), suspended POC was from 2800 m depth, and fluff and sediment SIC and SOC were from the underlying sediments. (See text for details.)

Druffel et al., 1998

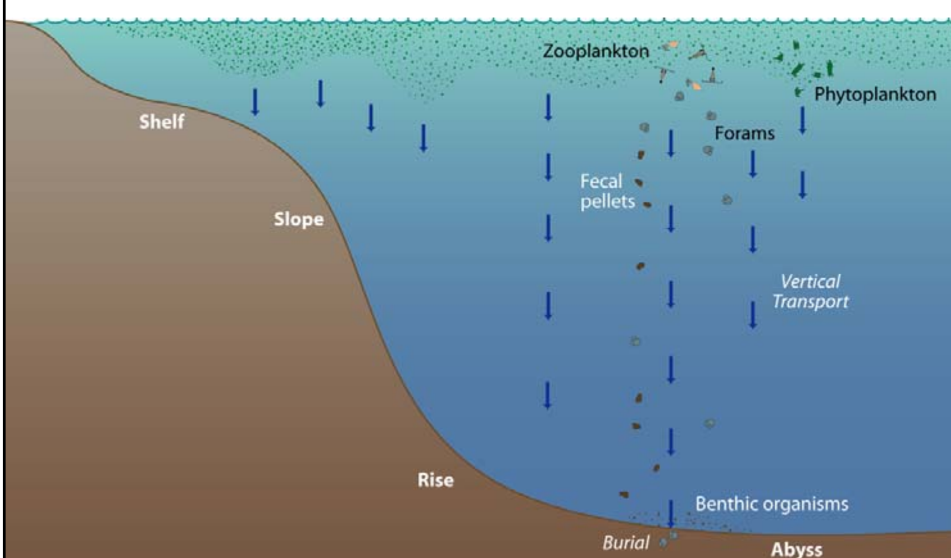
Lateral transport of alkenones to the Argentine Basin



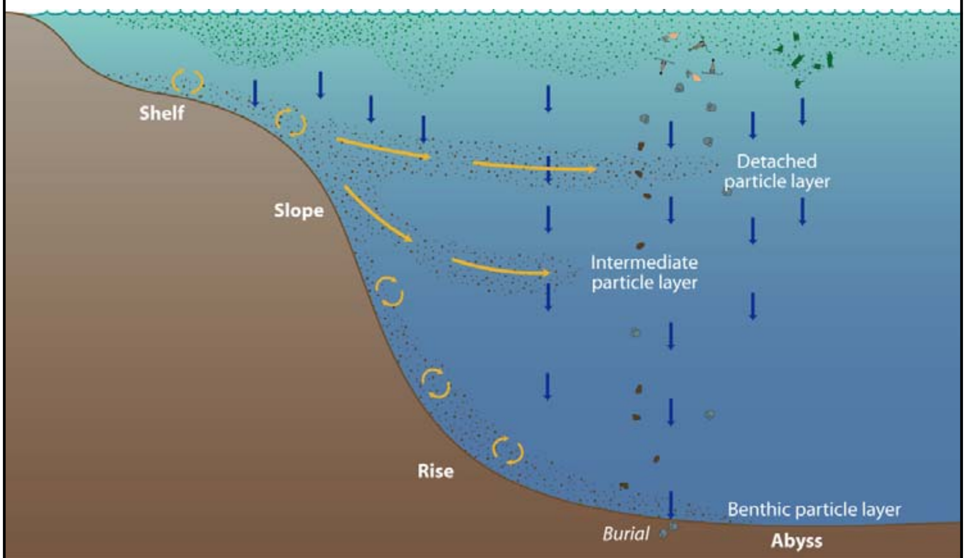


Benthien & Muller, 2000

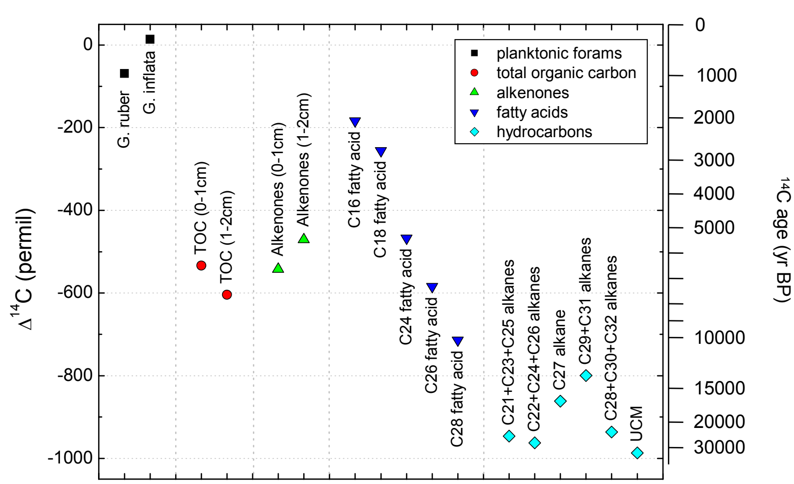
Vertical Transport of Organic Matter to the Sea Floor



Lateral Transport of Organic Matter to the Sea Floor



^{14}C age variability in Bermuda Rise surface (0-3 cm) sediment



Calculation of % terrestrial, marine and fossil OC

Dual isotopic mass balance approach:

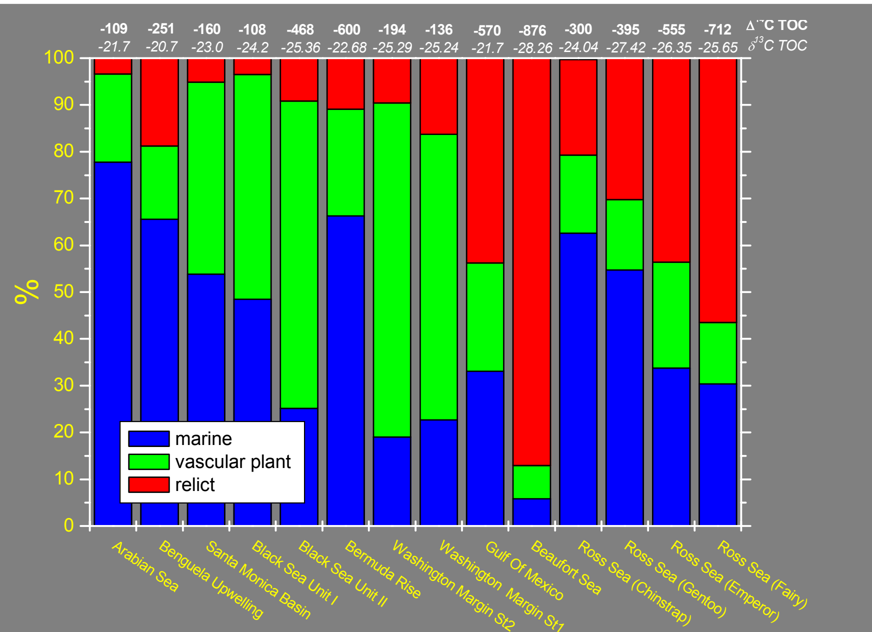
$$\Delta^{14}C_{TOC} = f_{marine} * \Delta_{marine} + f_{terrestrial} * \Delta_{terrestrial} + f_{fossil} * \Delta_{fossil}$$

$$\delta^{13}C_{TOC} = f_{marine} * \delta_{marine} + f_{terrestrial} * \delta_{terrestrial} + f_{fossil} * \delta_{fossil}$$

$$f_{marine} + f_{terrestrial} + f_{fossil} = 1$$

Variable	Measurement/assumption:
$\Delta^{14}C_{TOC}$	measure directly (AMS)
$\delta^{13}C_{TOC}$	measure directly (irMS)
$\Delta^{14}C_{marine}$	measure phytoplankton sterol (PCGC/AMS)
$\Delta^{14}C_{terrestrial}$	measure lignin phenol/plant wax (PCGC/AMS)
$\Delta^{14}C_{fossil}$	stipulate as –1000 ‰
$\delta^{13}C_{marine}$	measure phytoplankton sterol (irm-GC-MS) - assume offset between biomarker and bulk OC
$\delta^{13}C_{terrestrial}$	measure lignin phenol/plant wax (irm-GC-MS) - assume offset between biomarker and bulk OC
$\delta^{13}C_{fossil}$	assume value based on regional stratigraphy - (or measure biomarker selected based on Δ^{14}C)

Dual Isotope Mass Balance

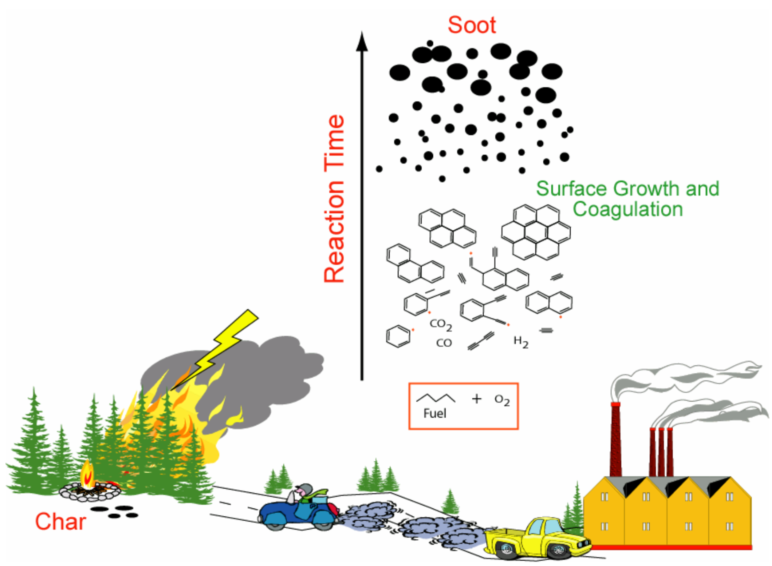


Black Carbon (BC)

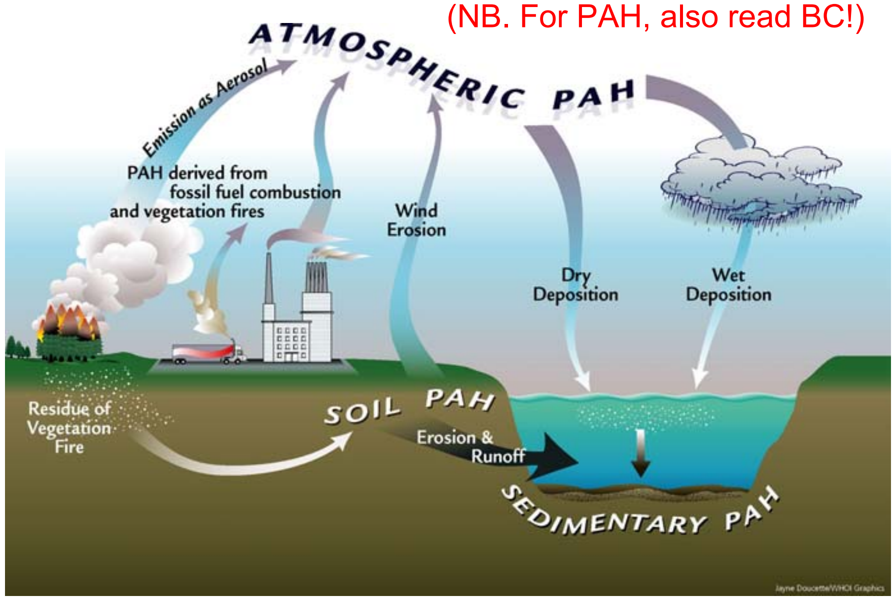
Suggested Reading:

- Gustafsson O. and Gschwend P.M. (1998) The flux of black carbon to surface sediments on the New England continental shelf. Geochim. Cosmochim. Acta 18, 805-829.
- Masiello C.A. and Druffel E.R.M. (1998) Black Carbon in Deep-Sea Sediments. Science 280, 1911-1913.
- Schmidt M.W.I. and Noack a.g. (2000) Black carbon in soils and sediments: Analysis, distribution, implications and current challenges. GBC 14, 777-793.
- Masiello C.A. (2004) New directions in black carbon organic geochemistry. Mar. Chem. 92, 201-213.

$$Org.\ Matter + O_2 \longrightarrow CO_2 + H_2O$$



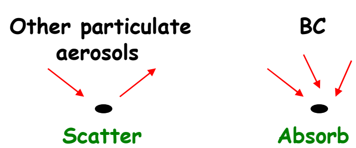
(NB. For PAH, also read BC!)



Black Carbon (BC)

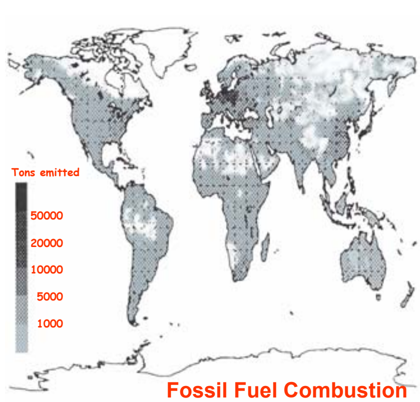
Some Notes:

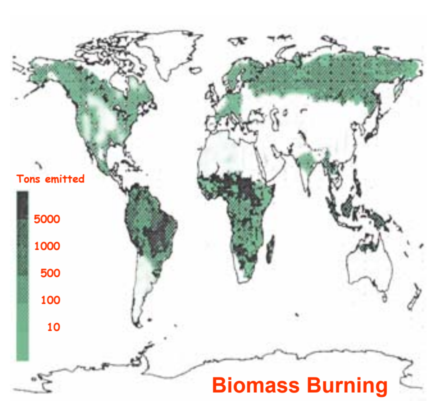
- Estimates of modern BC production
- Biomass burning: 50-260 Tg C/year
- Fossil fuel combustion: 12-24 Tg C/year
- Atmospheric lifetime of BC aerosols: 40 hours to 1 month
- Mass of organic carbon stored globally in ocean sediments: 160 Tg/year
- BC estimated to make up ca. 6% of sedimentary OC globally.
- Locally (on margins) BC may comprise up to 50% of TOC.



Contributions of Black Carbon to Greenhouse Warming

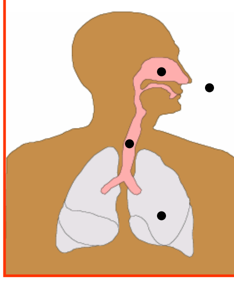
Kirkevag *et al.* (1999)





Cooke & Wilson (1996)

Public Health



Increased respiratory problems associated with elevated particulate matter concentrations

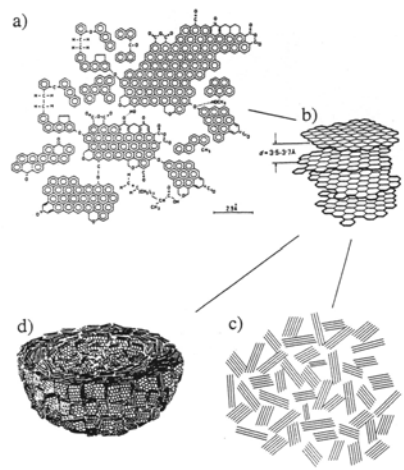
Black Carbon – A moving Target!
(The Combustion Continuum)

	Combustion Residues			Combustion Condensate
	Slightly Charred Biomass	Char	Charcoal	Soot
Size	mm and larger		mm to submicron	Submicron
Plant structure	Abundant	Significant presence	Few	None
Reactivity	High →			Low
Paleotracer Range	Short (meters)	Short (m to Km)	m to Km	Long (up to 1000s of Km)

Heating Temperature →

Schmidt *et al.* (1999)

What is Black Carbon?



How can we analyze BC?

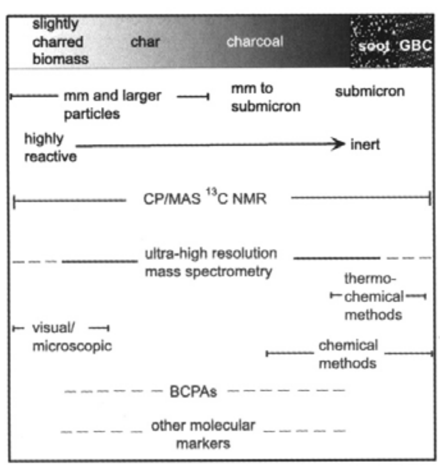


Fig. 3. The black carbon methods continuum. Regions of the combustion continuum detected by each technique are estimated based on published results with a variety of standards and sample types. BPCA abbreviates benzene polycarboxylic acids (Glaser et al., 1998).

BC isolation/measurement methods

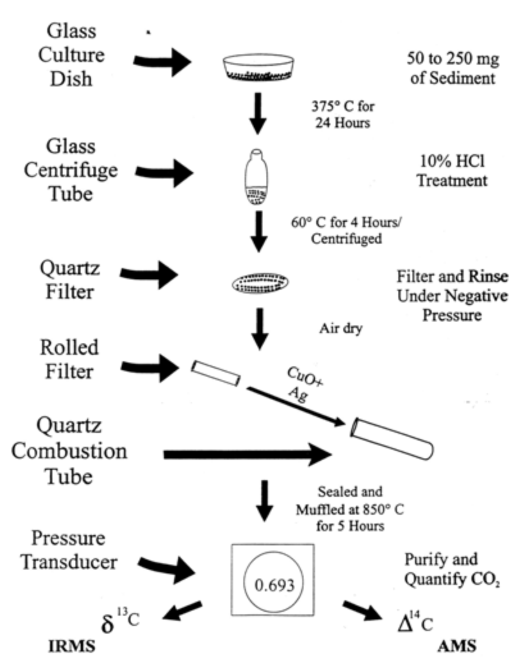
3 main types of method:

- optical
- chemical oxidation
- thermal oxidation

NB: In almost all cases, BC is operationally defined.

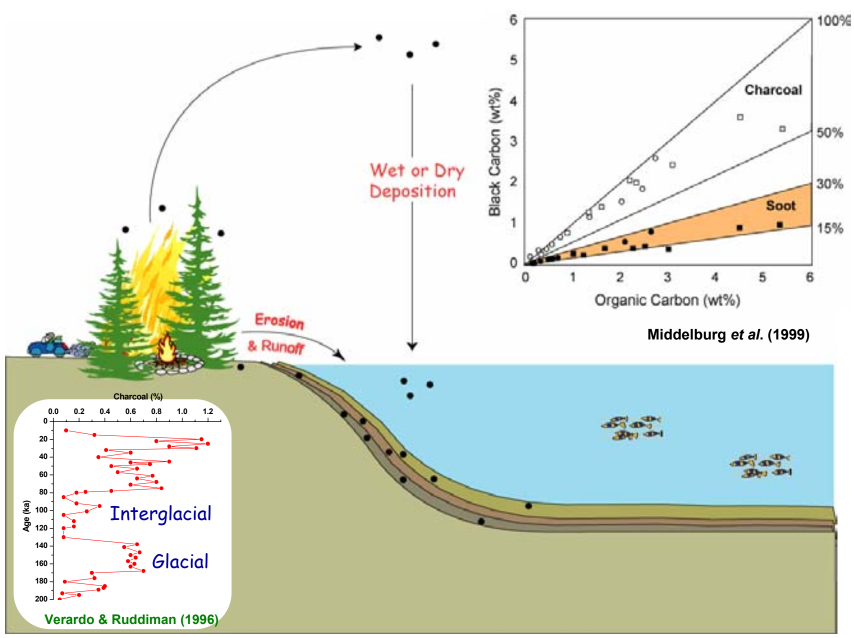
- *Leads to very different estimates of quantity and flux of BC.*

Carbon isotopic characterization of BC based on thermal oxidation ("Gustafsson") method



Modified by Reddy

Supply of BC to marine sediments



Proportions of BC in marine sediments

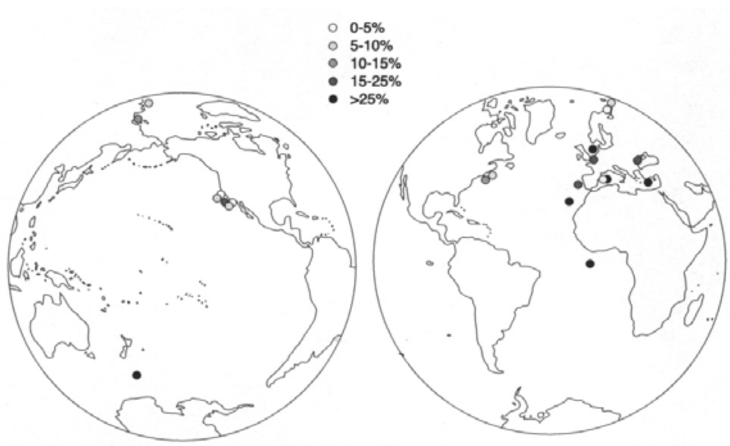
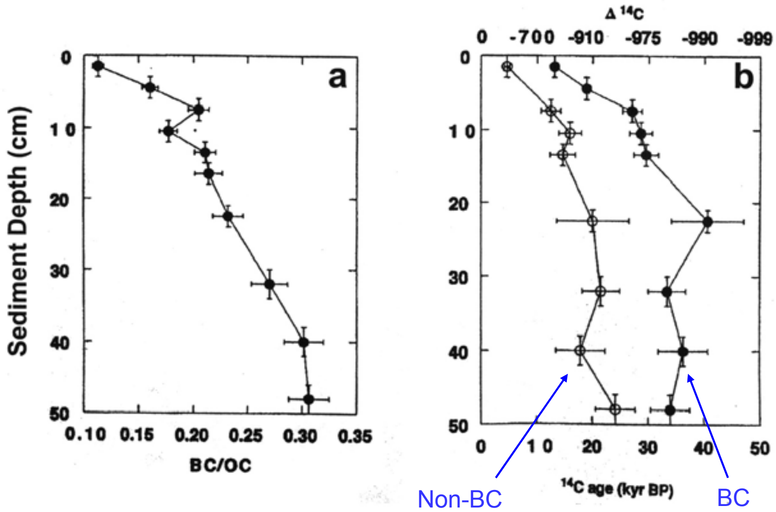


Fig. 2. Percent sedimentary organic carbon composed of black carbon in the world's oceans, measured by various techniques.

^{14}C age of Black Carbon in marine sediments



NB. BC isolated by chemical wet oxidation method

Masiello and Druffel 1998, Science

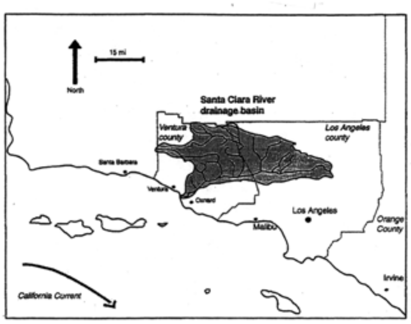


Figure 1. Map of the Santa Clara River drainage basin.

BC in Santa Clara River suspended sediments

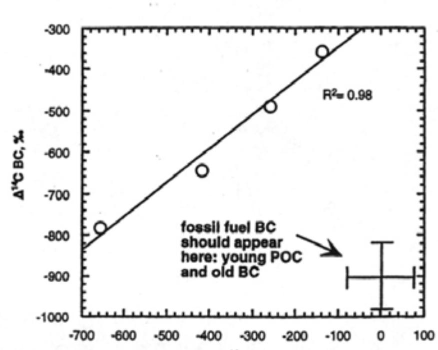


Figure 4. $\Delta^{14}C$ of BC vs $\Delta^{14}C$ of POC in the Santa Clara during high flow events.

Masiello and Druffel, 2001, GBC

BC in Santa Monica Basin sediments

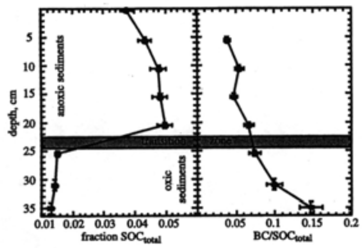


Figure 1. (a) OC per dry sediment. (b) BC/OC ratio. SOC_{total}% measurements were made on a Carlo-Erba NA1500. Reproducibility of % SOC_{total} is better than 5%. BC concentration was calculated using an average Pacific BC half-life with respect to dichromate oxidation of 474 ± 75 (1σ) hours [*Masiello et al.*, 2002]. All data have been salt-corrected.

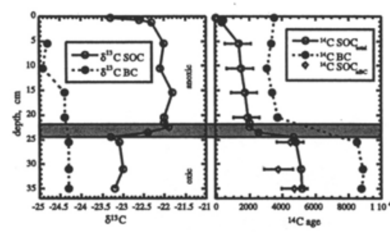


Figure 2. (a) δ^{13}C of Santa Monica SOC and BC. Error is ±0.1‰. (b) ^{14}C ages of Santa Monica SOC and BC. Errors for ^{14}C ages are less than the size of the points. We extracted CO^2 for ^{14}C measurement as described by *Druffel et al.* [1992] and prepared graphite as described by *Vogel et al.* [1987]. Radiocarbon measurements were made at LLNL Center for AMS. For discussion of uncertainties associated with BC measurement, see *Schmidt and Noack* [2000]; *Schmidt et al.* [2001]; and *Masiello et al.* [2002]. For discussion of ^{14}C terminology, see *Stuiver and Polach* [1977].

Masiello and Druffel 2003 GRL

Proportions of BC in marine sediments

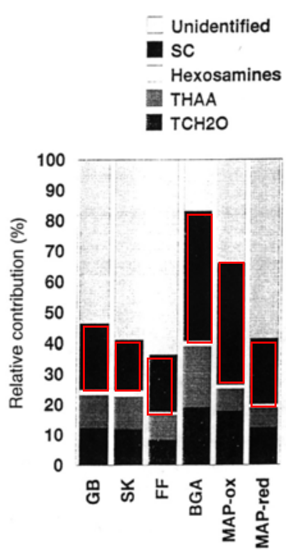


Fig. 4. Cumulative contribution of carbohydrates, total hydrolysable amino acids, hexosamines and soot carbon (SC) to total organic carbon. TCH_2O, THAA and hexosamine results for GB, SK, FF and BGA from Dauwe and Middelburg (1998) and for MAPox and MAPred from Cowie et al. (1995) and our own unpublished data.

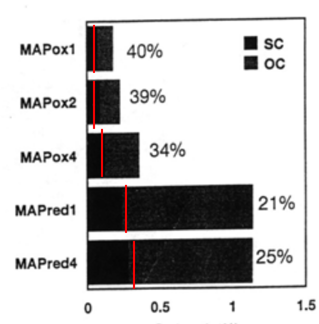


Fig. 5. Organic carbon (OC) and soot carbon (average of SC1 and SC2) in oxidised and reduced sections from the MAP *f* turbidite. MAPox1,2,4 have been subjected to extensive post-depositional oxidation, whereas MAPred1,4 have experienced little alteration since deposition. The relative contribution of soot carbon to organic carbon is also indicated.

Middleburg et al 1999

Graphitic Black Carbon (GBC) in (pre-anthropogenic) Washington Margin sediments

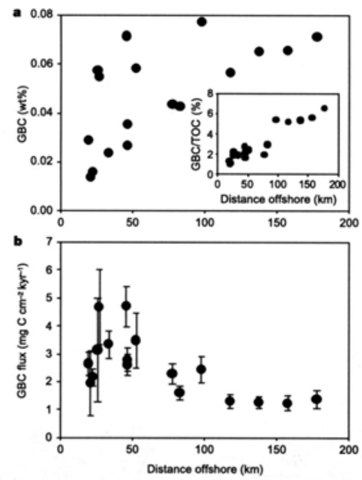


Figure 1 Concentrations and fluxes of GBC off the Washington coast. **a**, GBC wt% concentrations versus distance offshore. The inset shows the same data plotted as per cent of total organic carbon (TOC). **b**, Fluxes of GBC as a function of distance offshore.

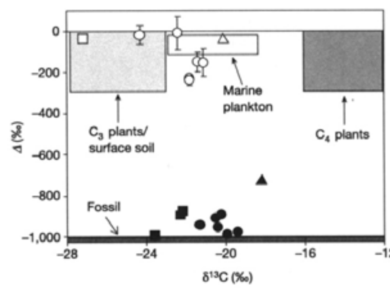
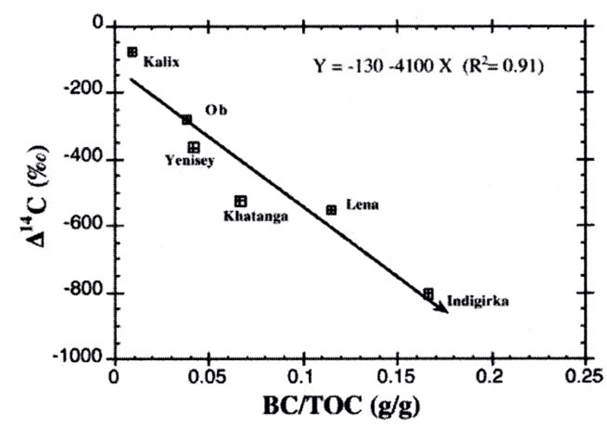


Figure 2 Plot of Δ versus $\delta^{13}C$ for all TOC (open symbols) and GBC (closed symbols) samples. Washington coast samples are shown as circles, the three terrestrial samples as squares and the one open-ocean sample as a triangle. Error bars for the Washington coast samples are smaller than the symbol if not visible. Error bars for the other samples are not shown. Approximate ranges of isotopic signatures for possible endmembers are indicated as grey rectangles, and are based on a review of recent literature.

Dickens et al. 2004, Nature

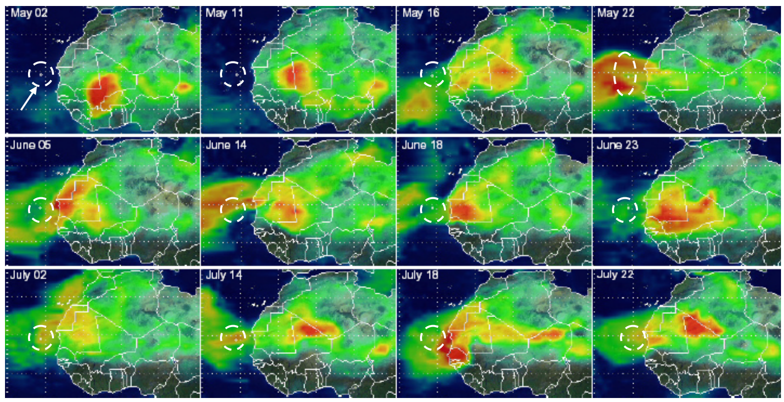


Relationship between $\Delta^{14}C$ values of sedimentary organic matter and the ratio of black carbon (BC) to total organic carbon (TOC) in the Siberian Arctic coast and the Kalix River. Note that the decreasing trend of $\Delta^{14}C$ with increasing BC/TOC ratio is from the west to the east coast.

Guo et al. 2004, GBC

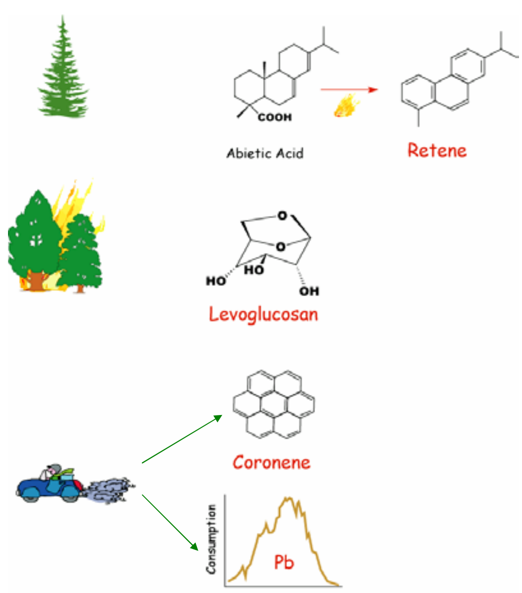
Carbon isotopic composition of dustfall sample off NW Africa

Fractions	Concn. (gdw basis)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	^{14}C age (yr BP)
Total Organic Carbon	1.02 %	-18.93	-149.6	1260 ± 40
Black Carbon	0.24 %	-15.13	-231.7	2070 ± 35
Plant wax alcohols	12 μg	-27.9	-80.8	649 ± 143

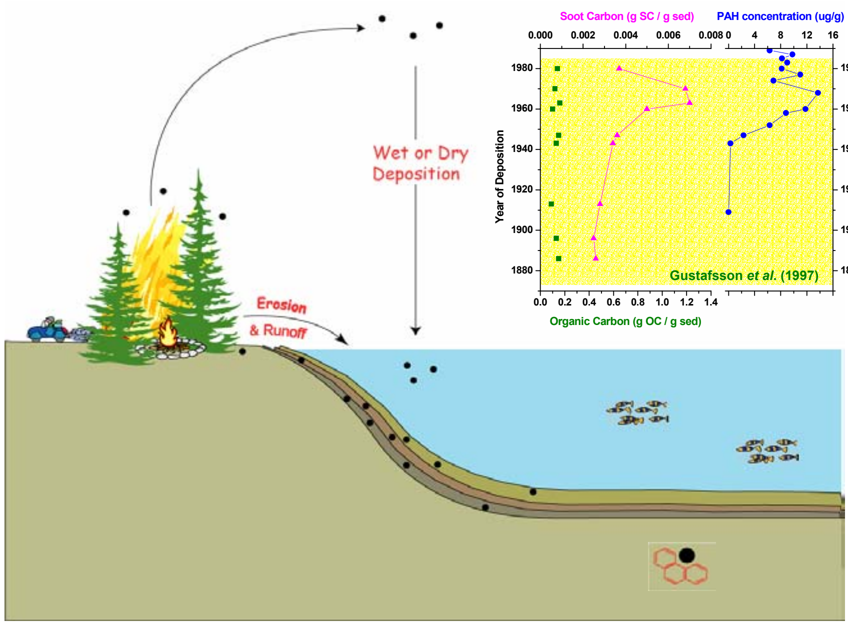


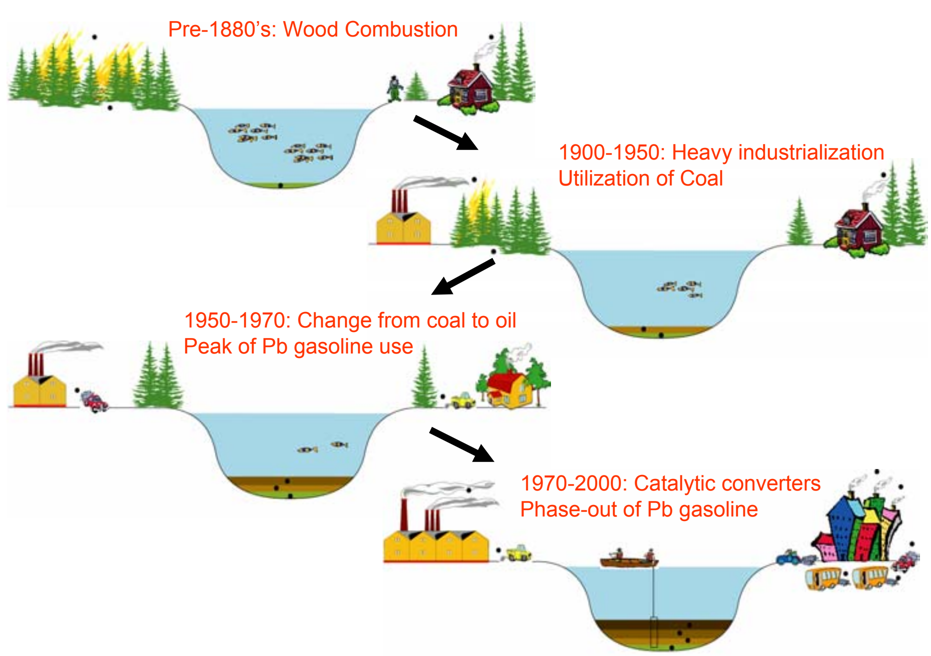
Eglinton et al., G^3, 2002

Molecular Proxies for BC

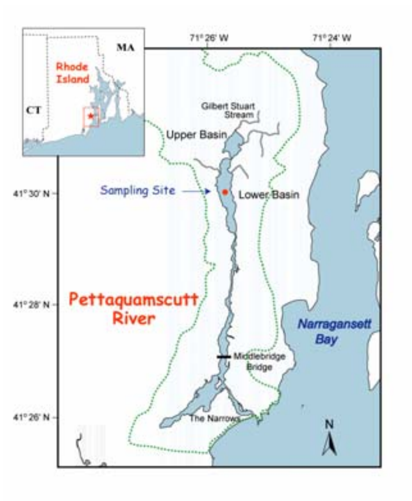


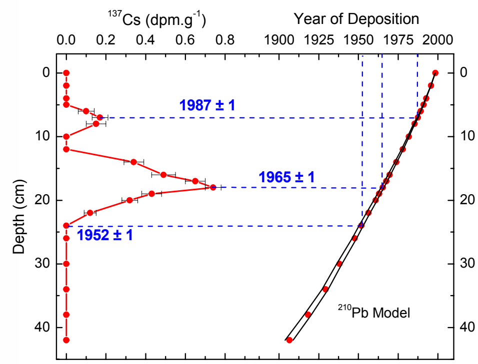
Historical records of combustion inputs to the environment



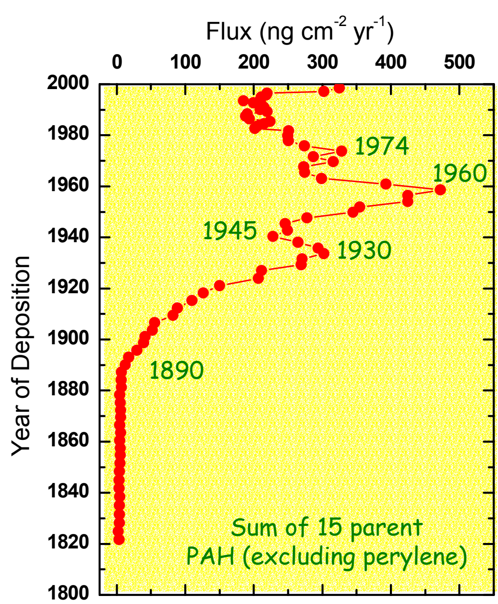


Pettaquamscutt River Basin

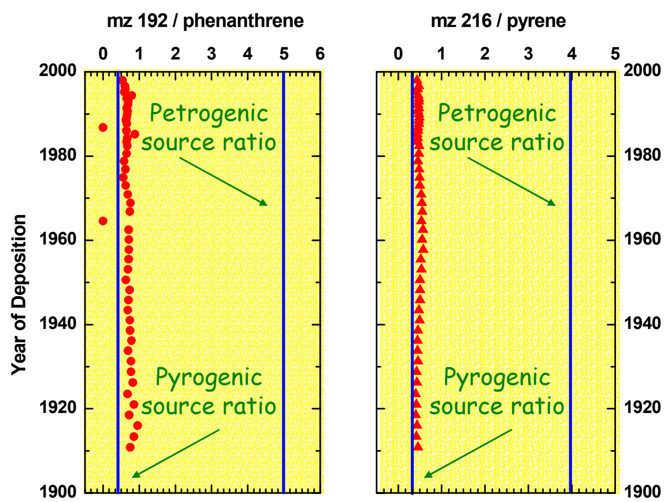




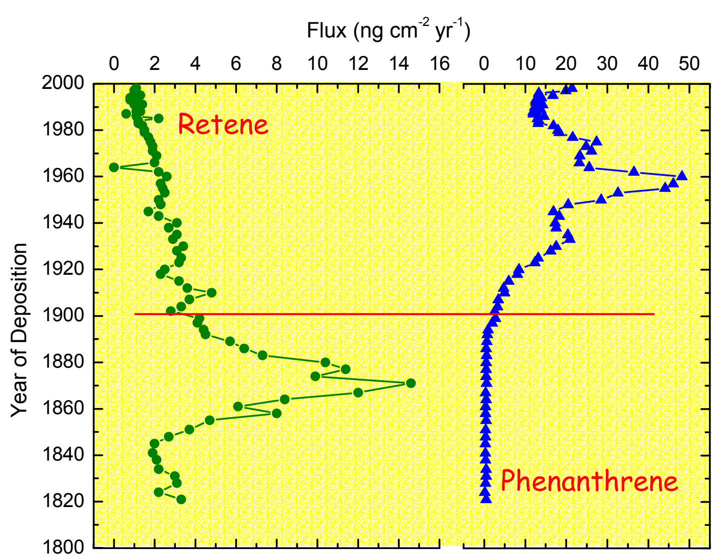
Down-core variations in PAH fluxes



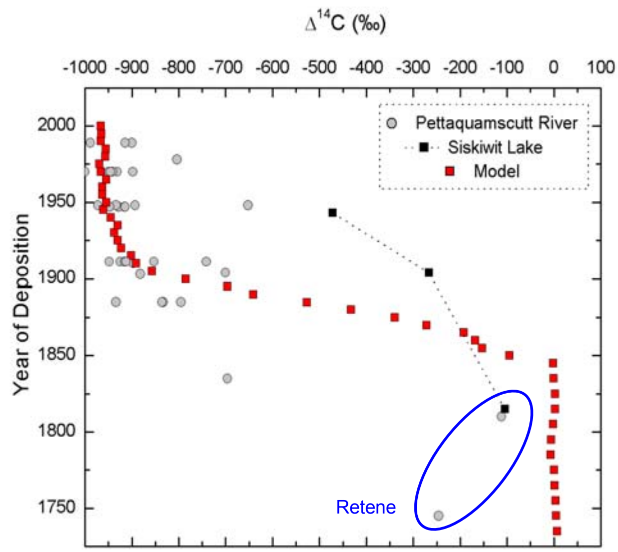
Assessment of Pyrogenic vs Petrogenic PAH inputs based on molecular parameters



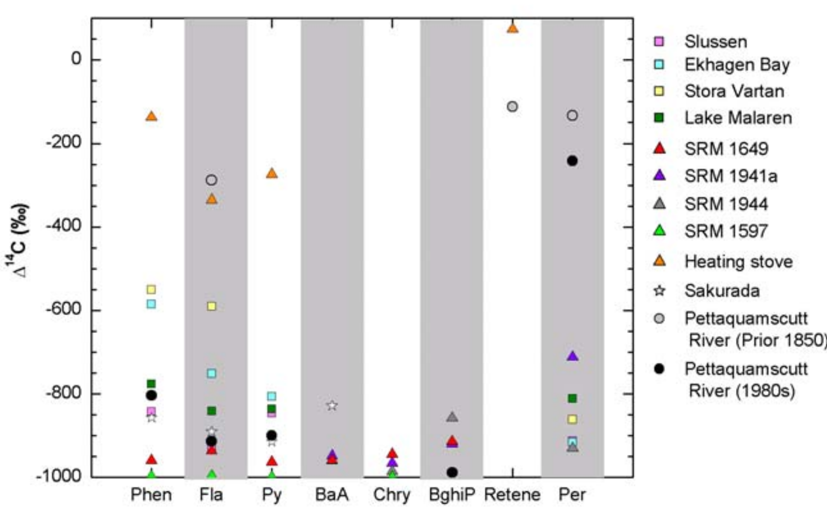
Ratios from Gustafsson & Gschwend (1997)



Historical variations in PAH ^{14}C



^{14}C contents of individual PAH in environmental samples



Lima et al in prep.