# $^{14}C$ in the Oceans

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AMS Short Course 2017

# Outline

- **Why is the surface ocean several hundred $^{14}C$ years old?**
- **Controls on oceanic $^{14}C$**
- **Corals as diaries of ocean mixing and climate**
- **Mixing time of the deep ocean conveyor**
- **Why is dissolved organic carbon (DOC) so old?**
- **$^{14}C$ in particles and Black Carbon**

# Marine Carbon Reservoirs

| | | | |
|---|---|---|---|
| **DIC**: | Dissolved Inorganic C | (< 1$\mu$m) | 38,100 GtC |
| **DOC**: | Dissolved Organic C | (< 0.2 $\mu$m) | 662 GtC |
| **POC**: | Particulate Organic C | (> 0.2 $\mu$m) | 25 GtC |
| **BC:** | Black C | (< 0.2 $\mu$m) | >14 GtC |
| **SOC:** | Sedimentary OC | 0–1m | 150 GtC |

# Why does the ocean contain so much DIC? (38,000 GtC)

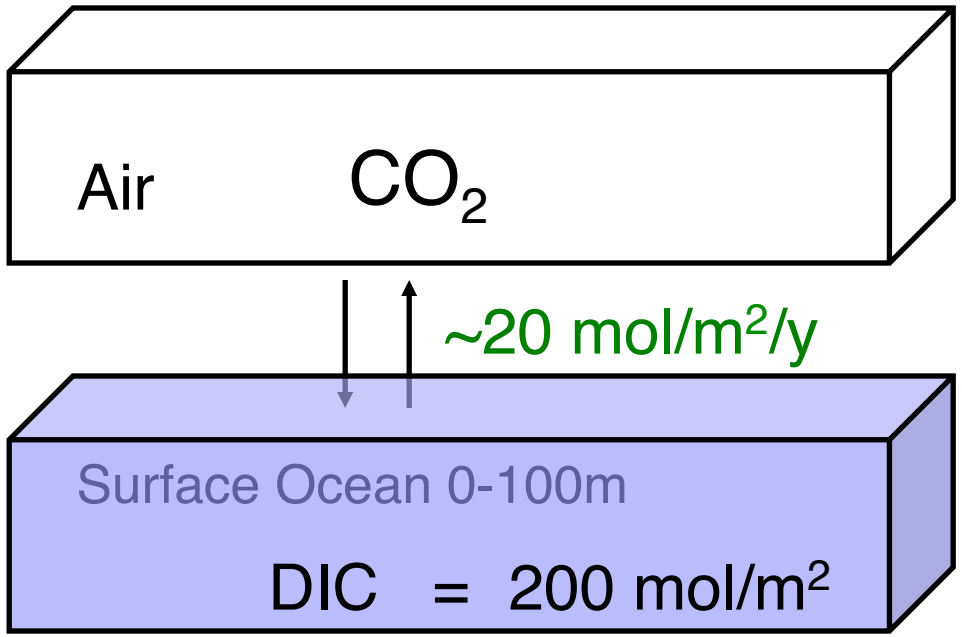
- $CO_2$ hydrates to $H_2CO_3$

$CO_{2(gas)} + H_2O$ <---> $H_2CO_3$

$H_2CO_3$ *(0.5%)* <---> $H^+ + \mathbf{HCO_3^-}$ ***(89%)***

$HCO_3^-$ <---> $H^+ + CO_3^{2-}$ = *(10.5%)*

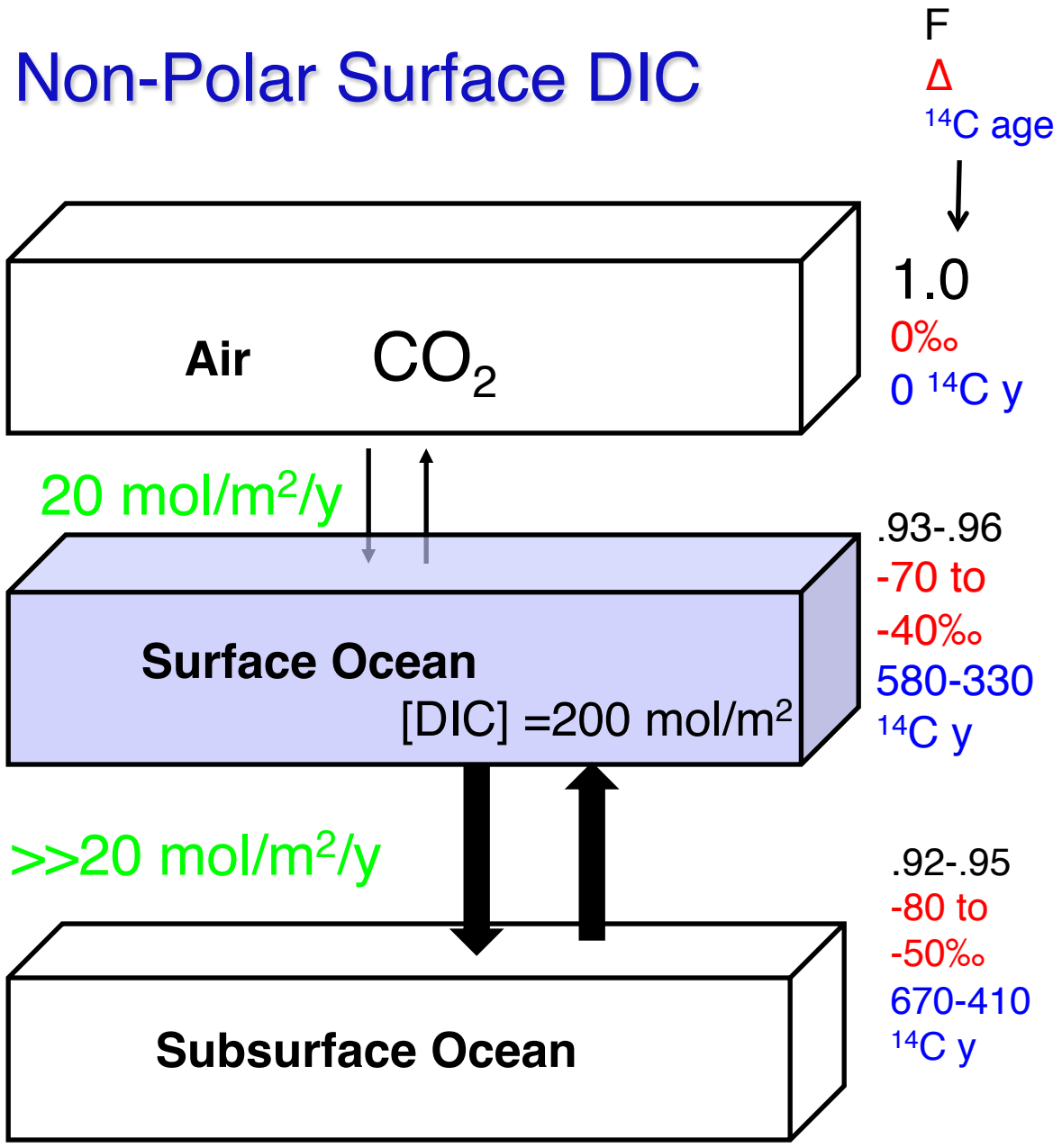
# Gas Exchange of $CO_2$ Between Surface Ocean and Atmosphere (per 1 $m^2$)




$$\text{Turnover Time} = \frac{200\ \text{mol/m}^2}{20\ \text{mol/m}^2\text{/y}} = 10\ \text{y}$$

But $^{14}C$ age of surface ocean is 300-600 $^{14}C$ y. Why?

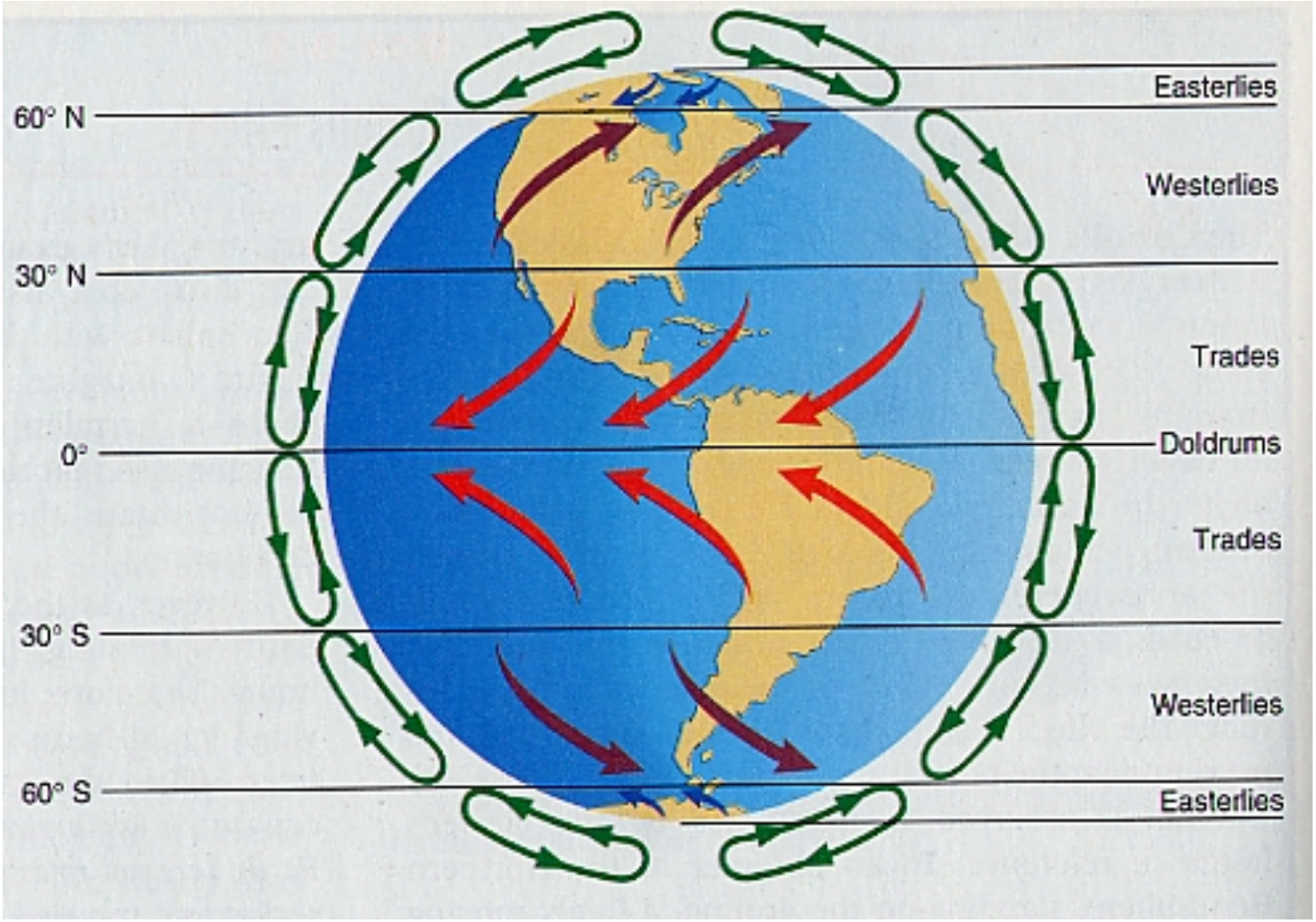
# ‘Reservoir Age’ of Non-Polar Surface DIC




- **<u>Mixing</u> of deeper, older waters into the surface** is much larger than gas exchange.

- So $^{14}C$ is a water mass tracer, <u>not</u> a tracer of air–sea gas exchange.

# Major control on $^{14}C$ in the surface ocean… The Winds

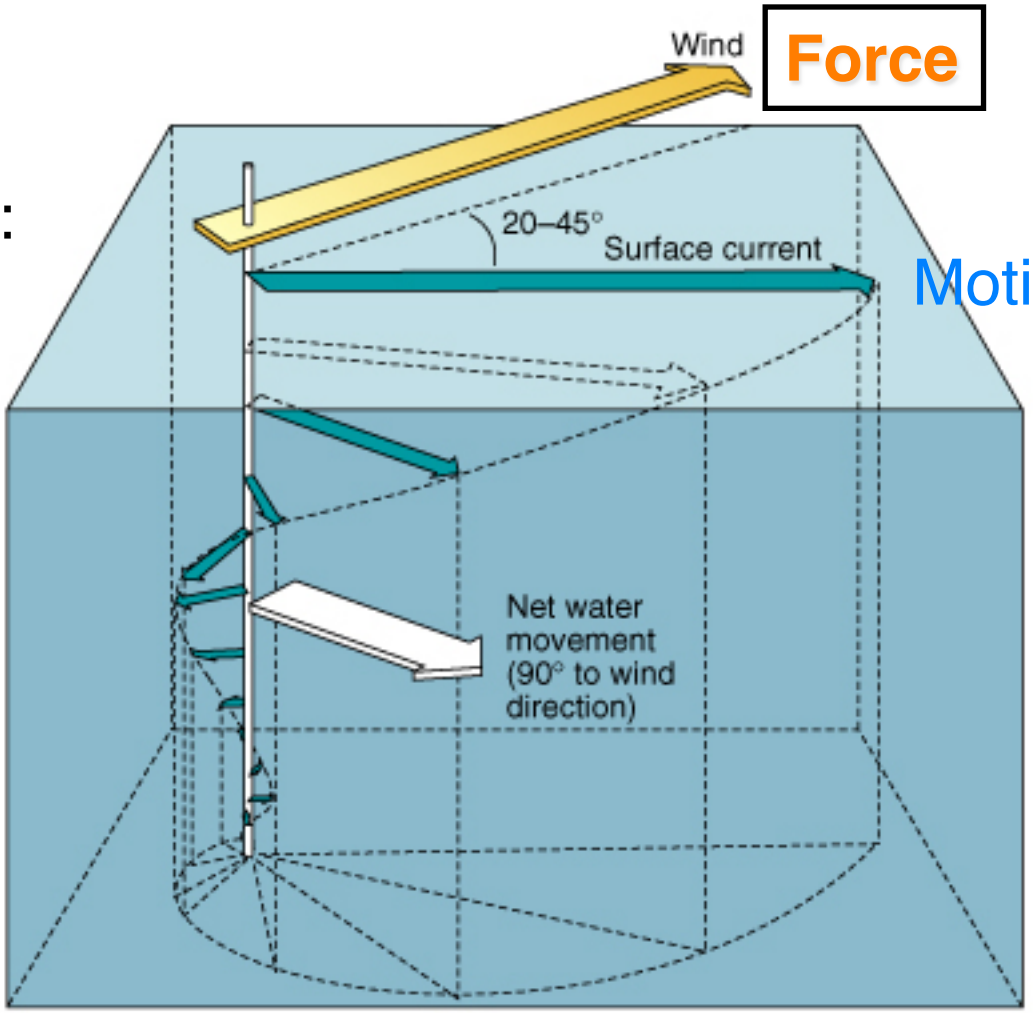


# And the Coriolis Force –> Ekman Transport

In mid-gyre:

Surface
Δ = -50‰

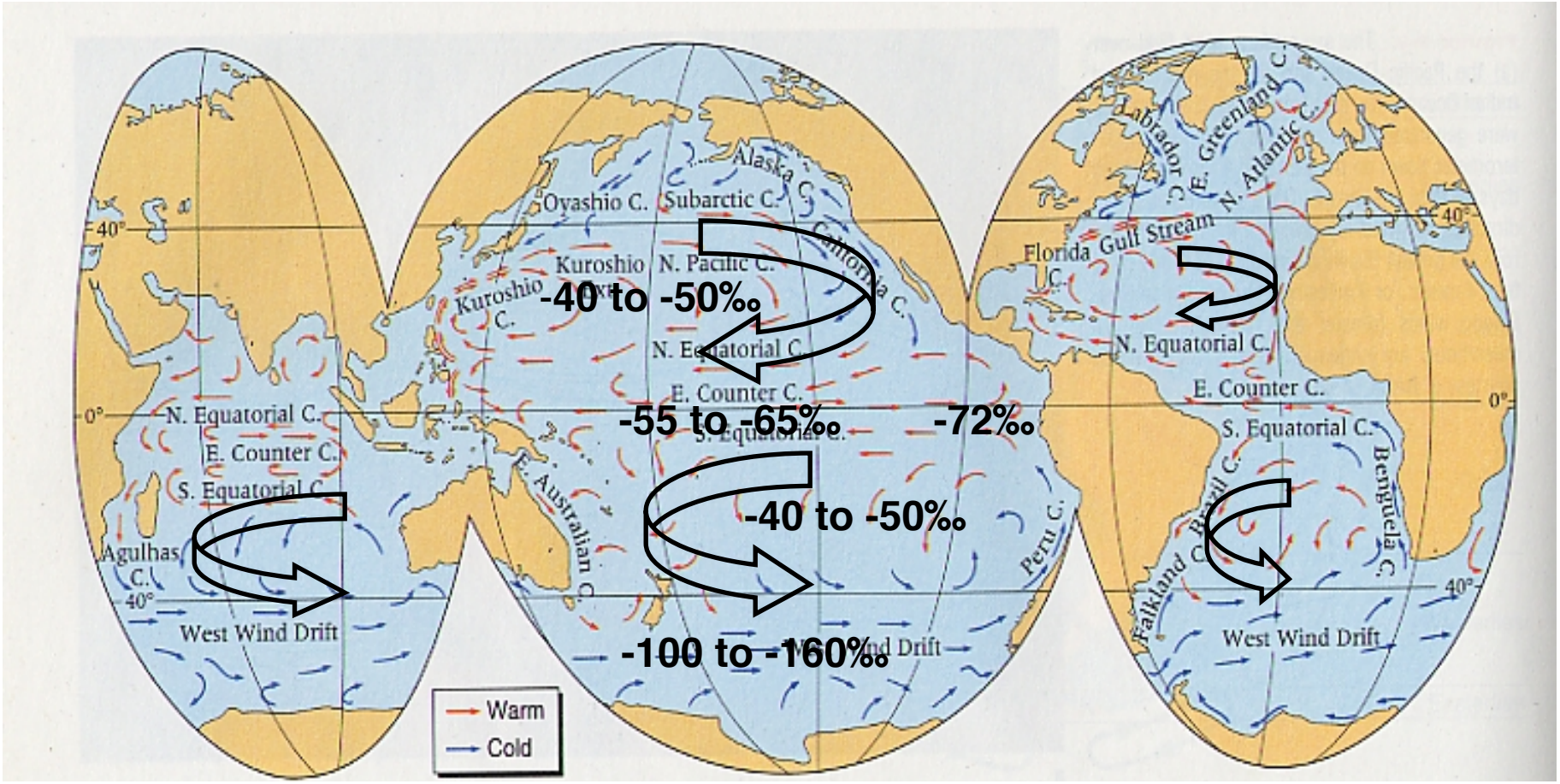
Subsurface
Δ = -60‰



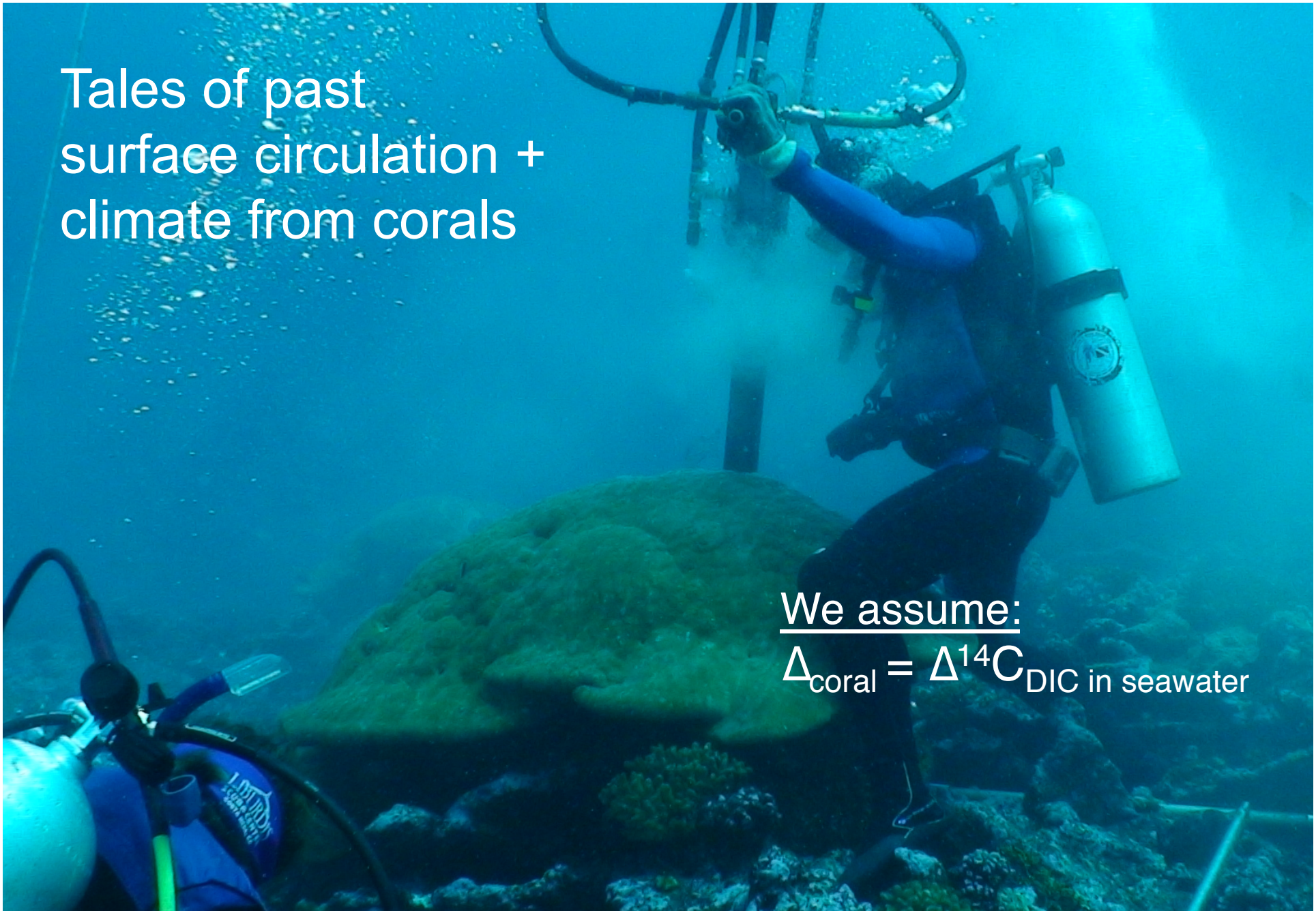



…In Northern Hemisphere, net motion of water is to the right of force

# Surface currents and pre-bomb Δ




= Mid-ocean gyre


Tales of past
surface circulation +
climate from corals
We assume:
$\Delta_{coral} = \Delta^{14}C_{DIC\ in\ seawater}$

Delivery of coral core to boat, and sealing the hole in coral

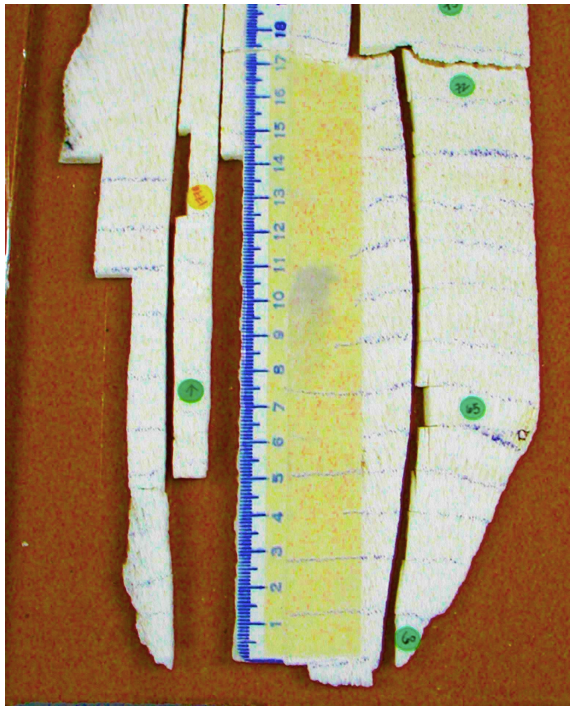
# Sectioning of Coral Cores

core

slab

X-ray

Mapped Slab



Sampled using saw or Dremel tool

AMS analysis

# Δ (known-age corrected samples)

Corrected for decay of $^{14}C$ in the sample from the year of growth (x) to 1950

$$\Delta = \left[ \frac{\left[ \frac{^{14}C}{^{12}C} \right]_{\text{sample,-25}} \exp^{\left( (1950 - x) / 8267 \right)}}{0.95 \left[ \frac{^{14}C}{^{12}C} \right]_{\text{OX1,-19}}} - 1 \right] 1000$$

*Δ expresses the radiocarbon signature relative to "Modern" had the sample been measured in 1950. This is useful for studies attempting to show how the radiocarbon signature of air (tree rings) and water (corals) changes with time. It is the basis for creating the calibration curves used to calculate calendar age from $^{14}C$ age.*

# Known age correction

You obtain F of 0.900 for a coral that grew in Palmyra Atoll in AD 1900. What is the age corrected F value?

a) 0.9000
b) 0.8955
c) 0.9055
d) 0.9126

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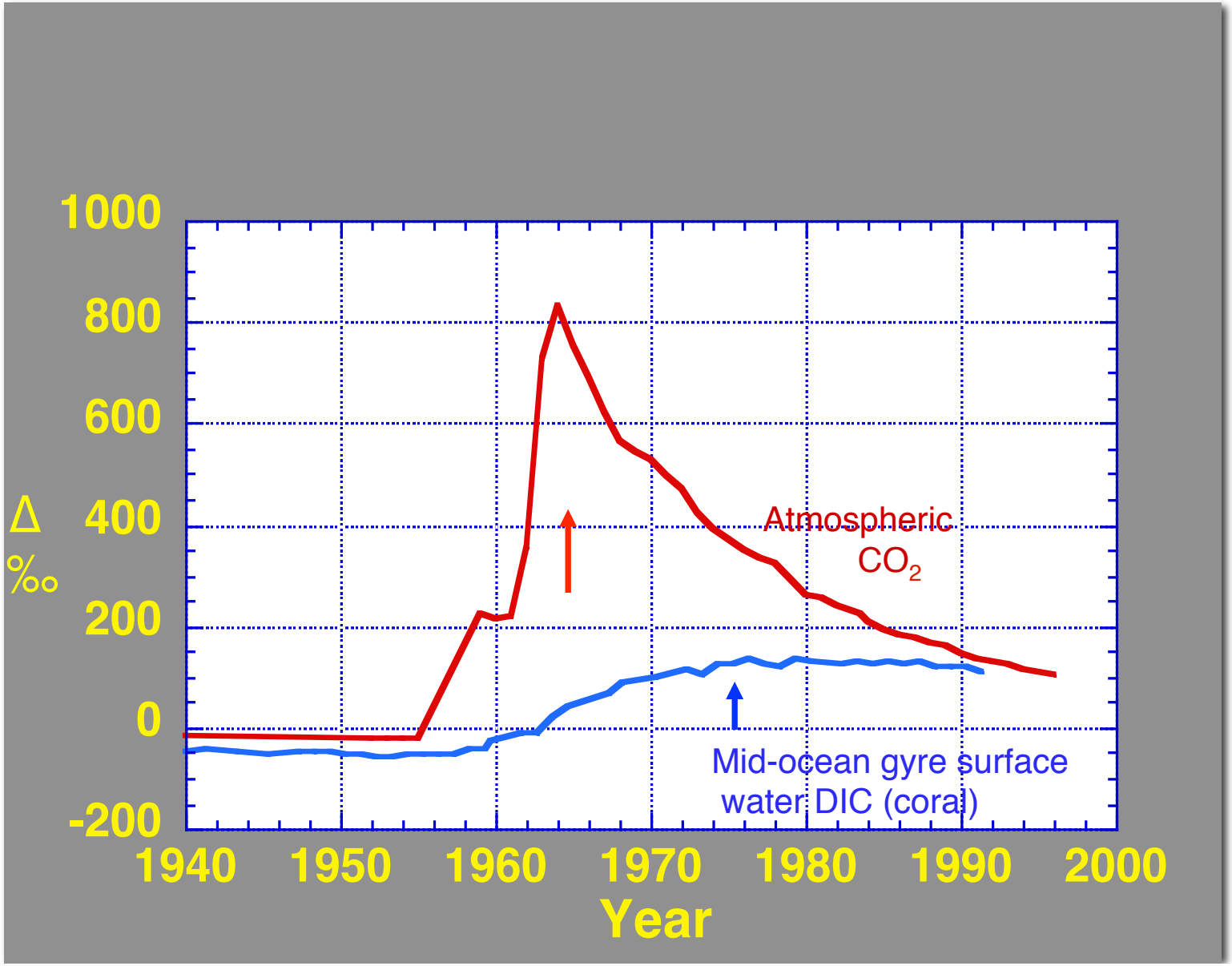
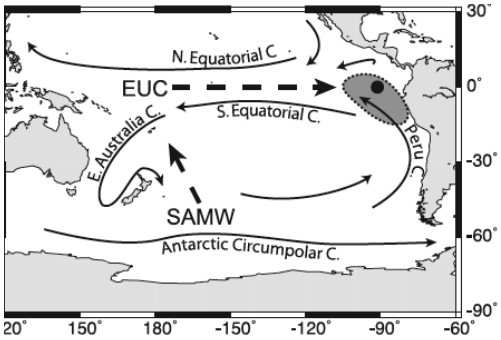
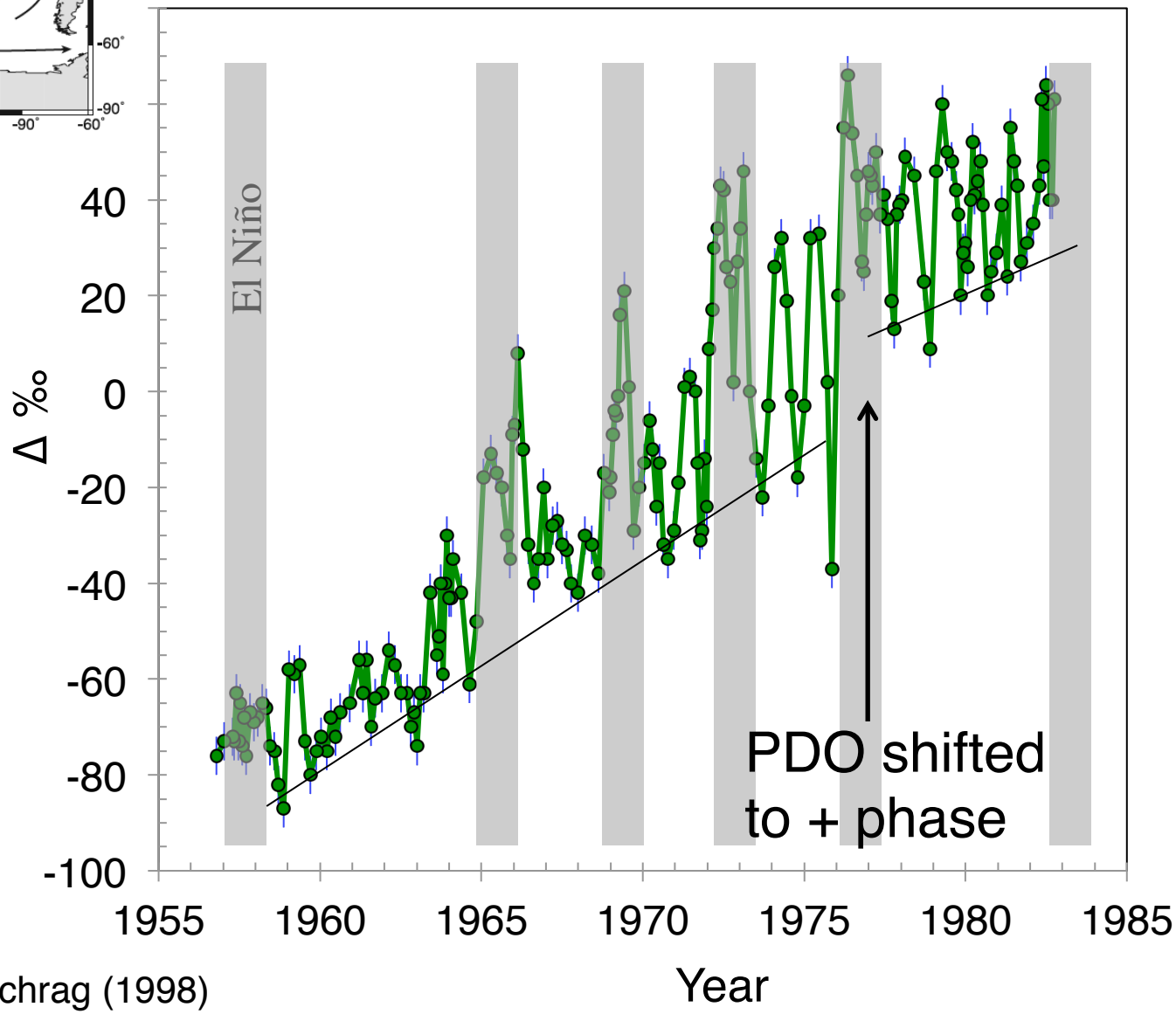
*$^{14}C$ has decayed away between 1900 to 1950. Have to add $^{14}C$. ↑ F 50‰ per 400yrs, or ~5‰.*

# Bomb $^{14}C$ maximum in surface ocean occurs 10 y after that in air





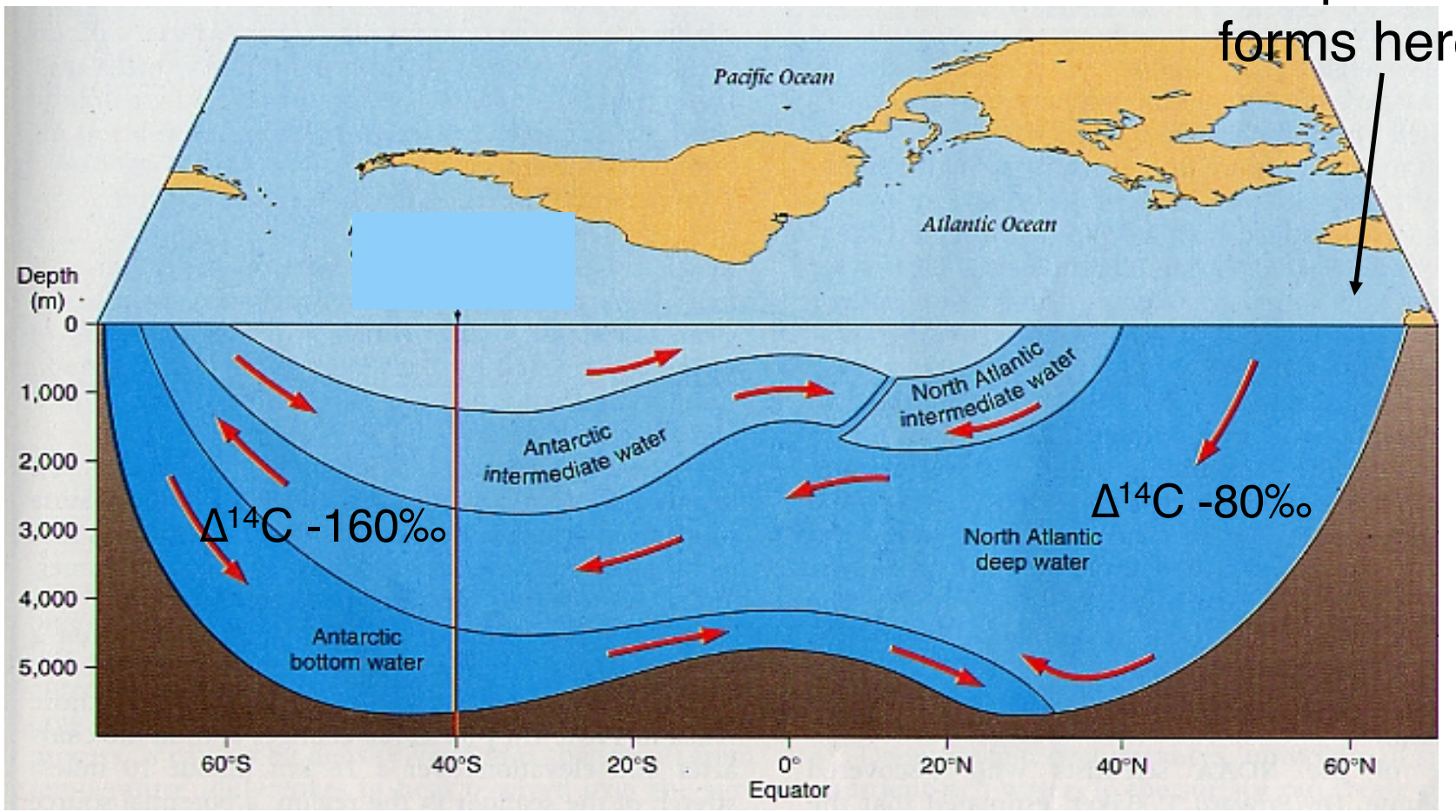

# Galapagos coral $\Delta^{14}C$




Guilderson and Schrag (1998)

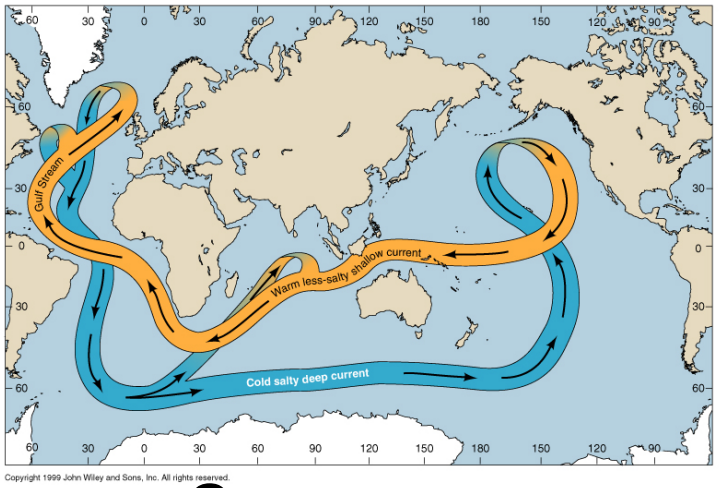
# $^{14}C$ measurements led to our understanding of the deep circulation in the ocean by Broecker and others

North Atlantic Deep Water forms here

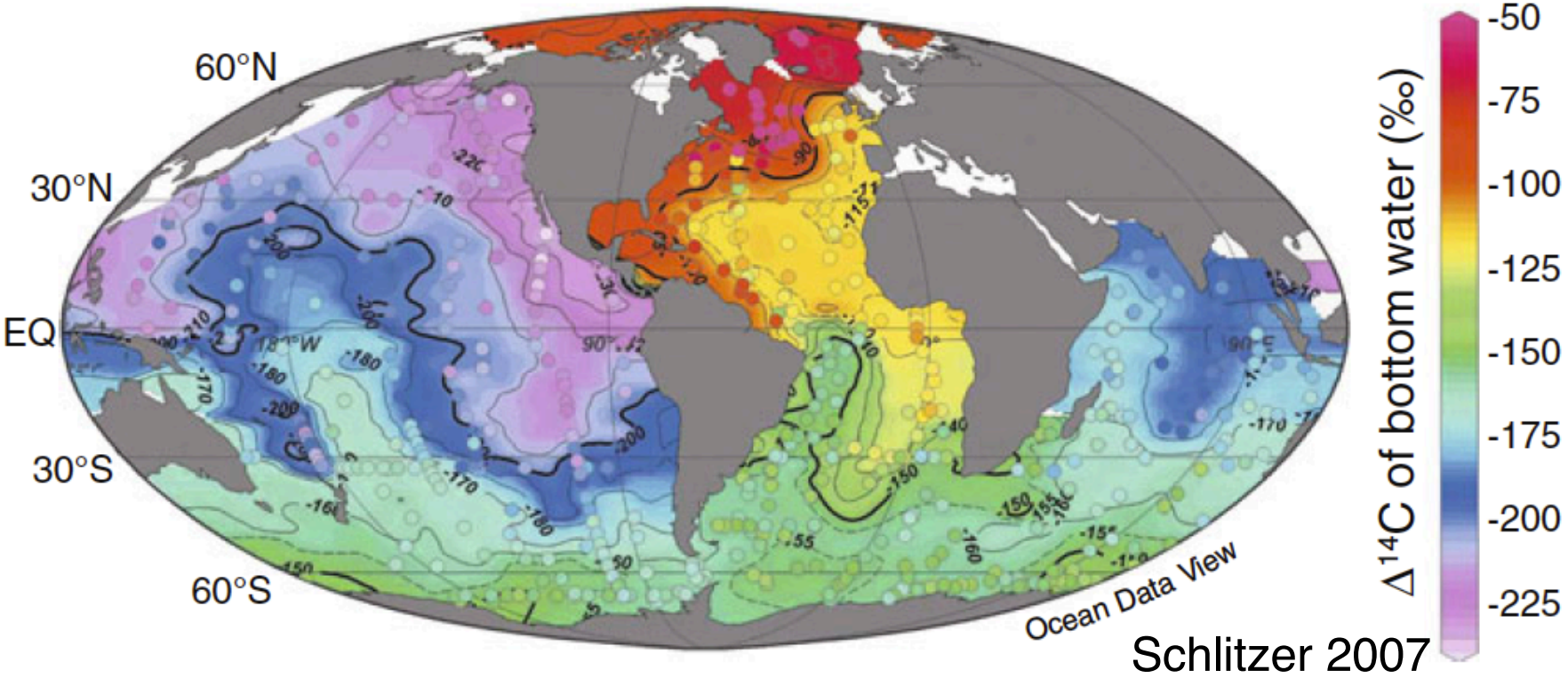


# Deep DIC $\Delta^{14}C$

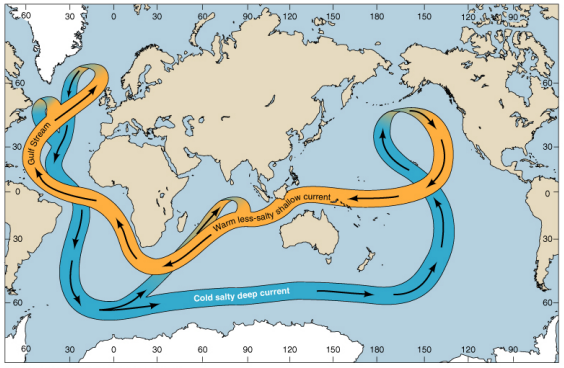
~1500 $^{14}C$ y difference =
transit time of the conveyor




Conveyor




Schlitzer 2007



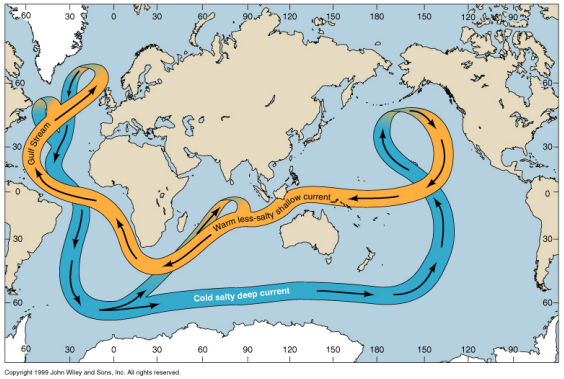


# Raise 1 or 2 fingers with the right answer

You measure $\Delta^{14}C$ in 3 seawater DIC samples but forget to label the samples. Values are -240‰, +30‰ and -80‰. Where are they from?

1) Deep N. Atlantic, surface Pacific and deep Indian

2) Deep N. Pacific, surface Atlantic and deep Atlantic





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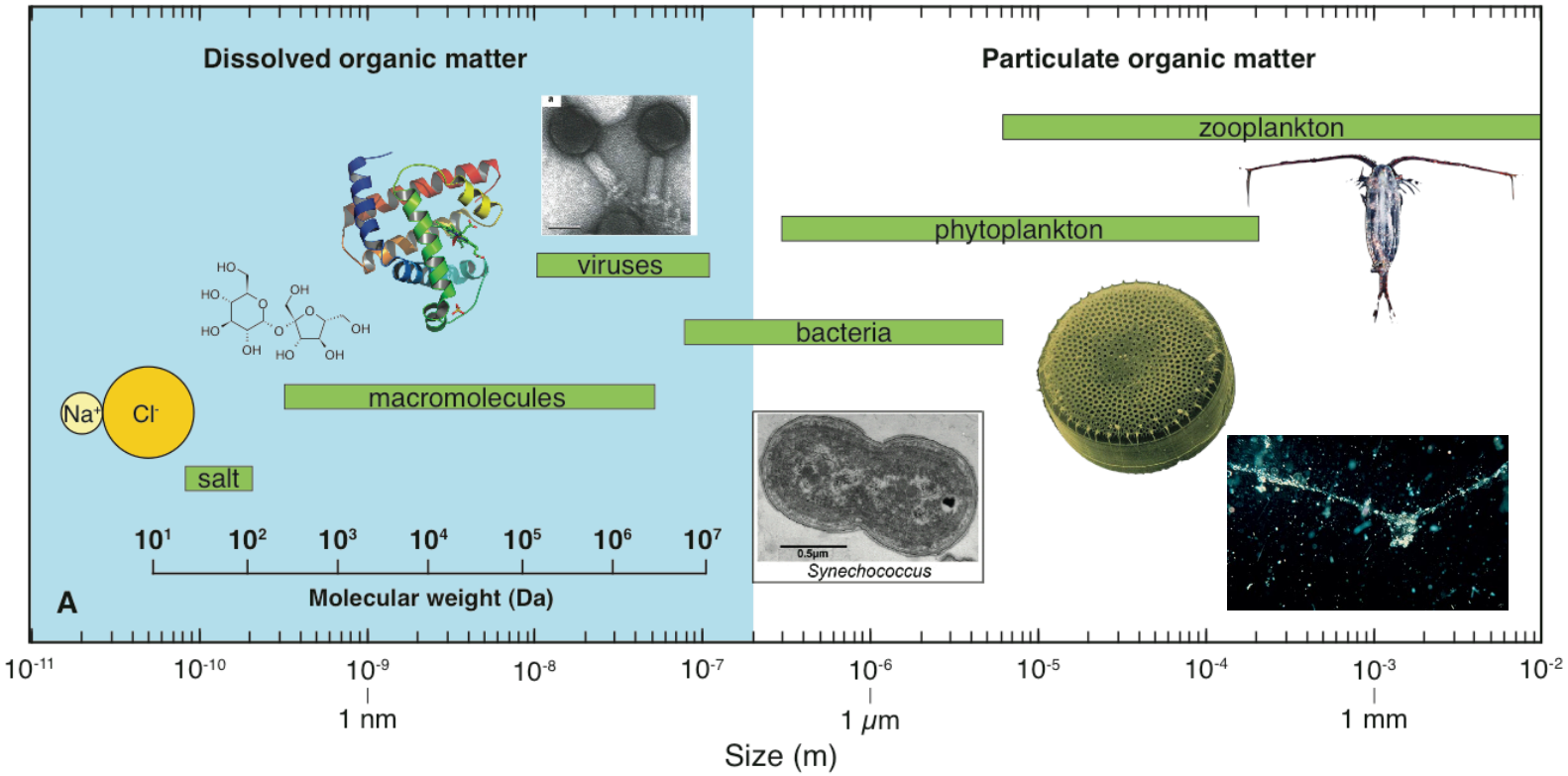
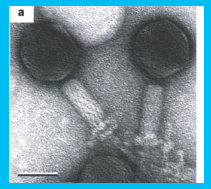
# Marine Organic Matter

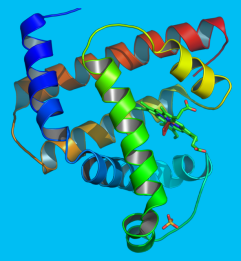



(Adapted from Hedges 2002, Verdugo 2004)

# Why do we care about DOM and POM?

**DOM**
**~662 Gt C**






95% of NLOM

<10% known biomolecules

Microbial Loop: true base of food web

Bulk $^{14}C$ age is very old (4,000–6,500 yrs)

But many labile components!
Active role in Primary Prod.

Chelation of trace metals (micronutrients)

# Why do we care about DOM and POM?

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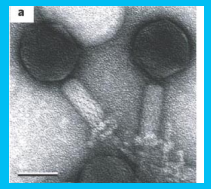
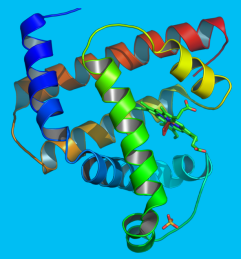
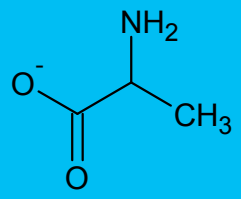







**POM ~25 Gt C**

**NON LIVING**

5% of NLOM

Biological Pump:
C-export

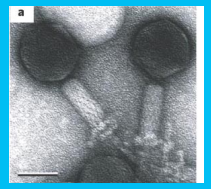
Supports all deep ocean life

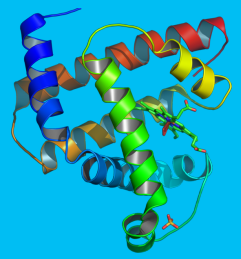
20-30% known biomolecules

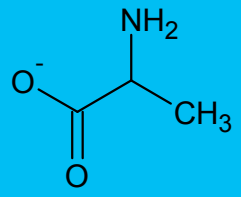
Water column recorded in sediments

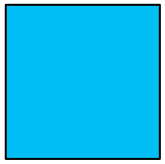
# Why do we care about DOM and POM?

**DOM**
**~662 Gt C**





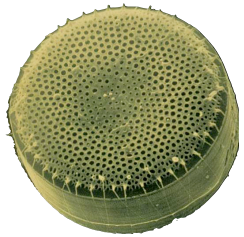


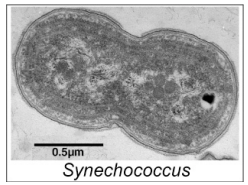



**POM ~25 Gt C**

**NON LIVING**

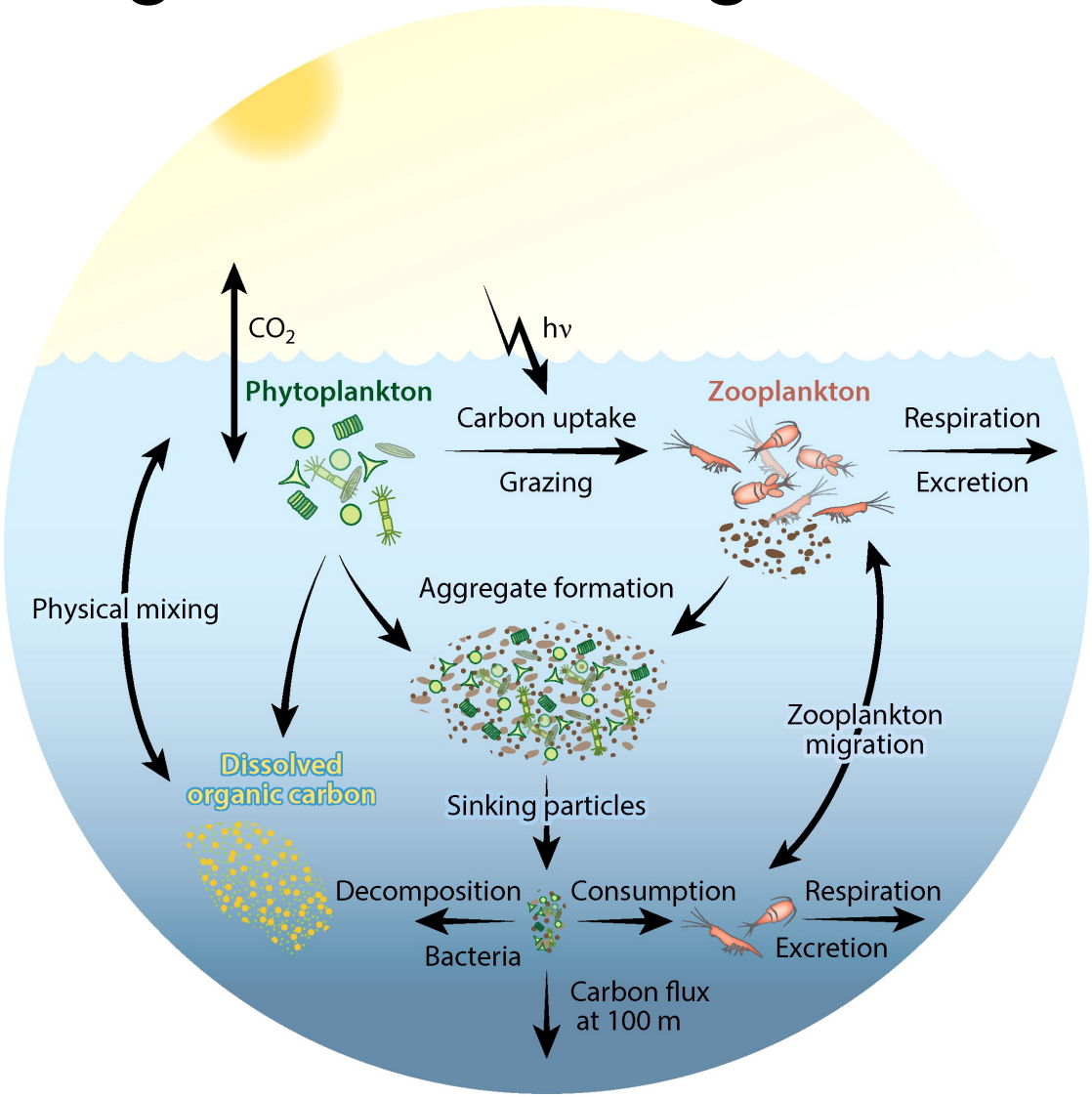
**Living OM ~2 Gt C**

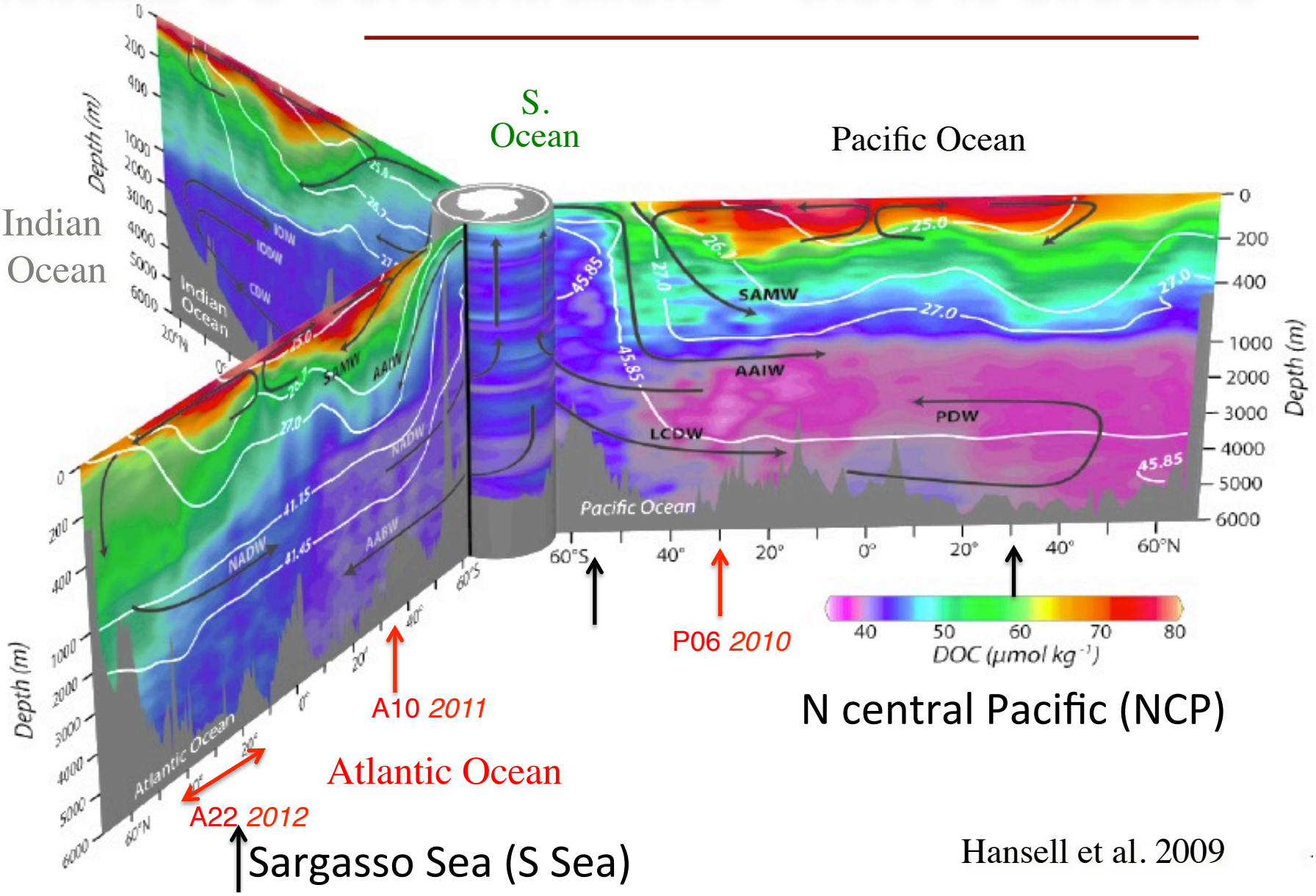



Knowing *sources* and *dynamics* =
understanding all OM in the ocean

# Cycling of marine organic matter



# Global DOC Concentrations – there is structure

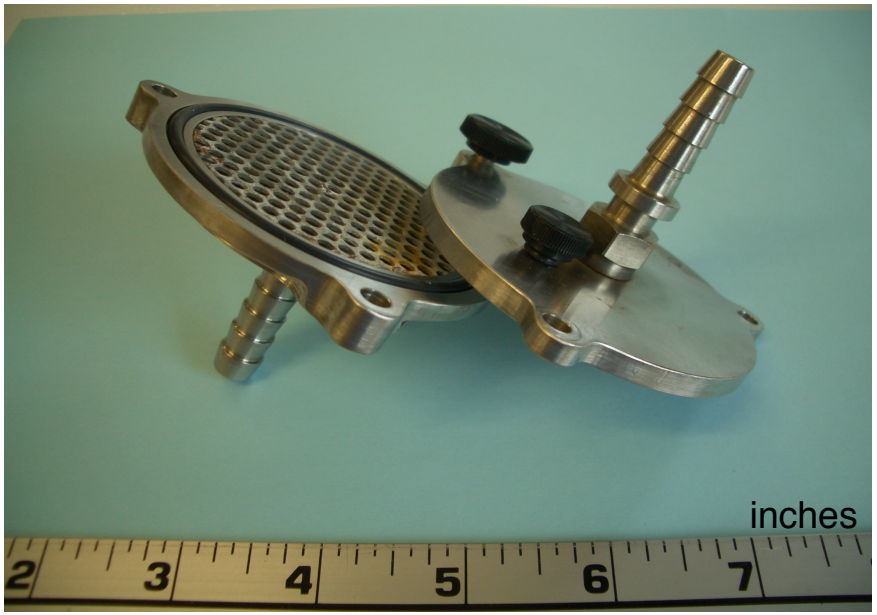



Hansell et al. 2009

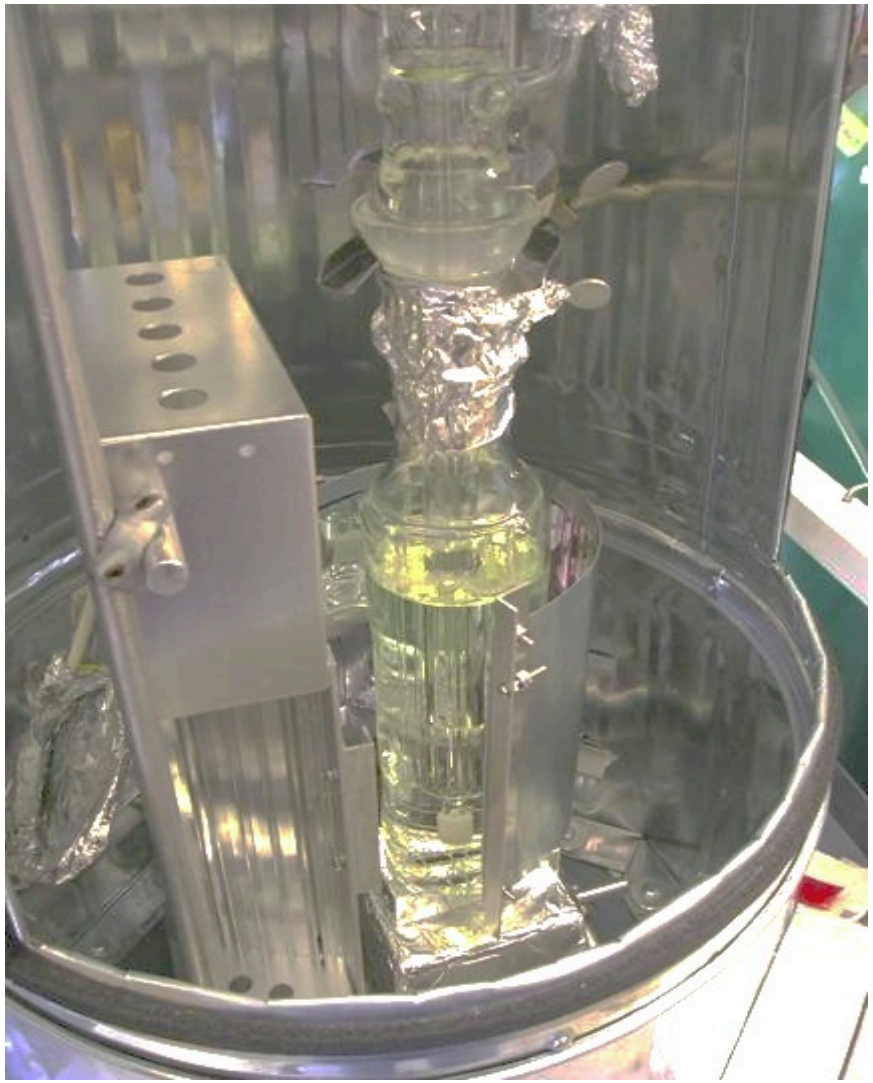
# DOC and DIC collection

Alysha Coppola filtering seawater

Water Filtered above 400m
DOC is frozen
DIC is poisoned with $HgCl_2$




Awesome mini, stainless steel filter holder designed by Sheila Griffin

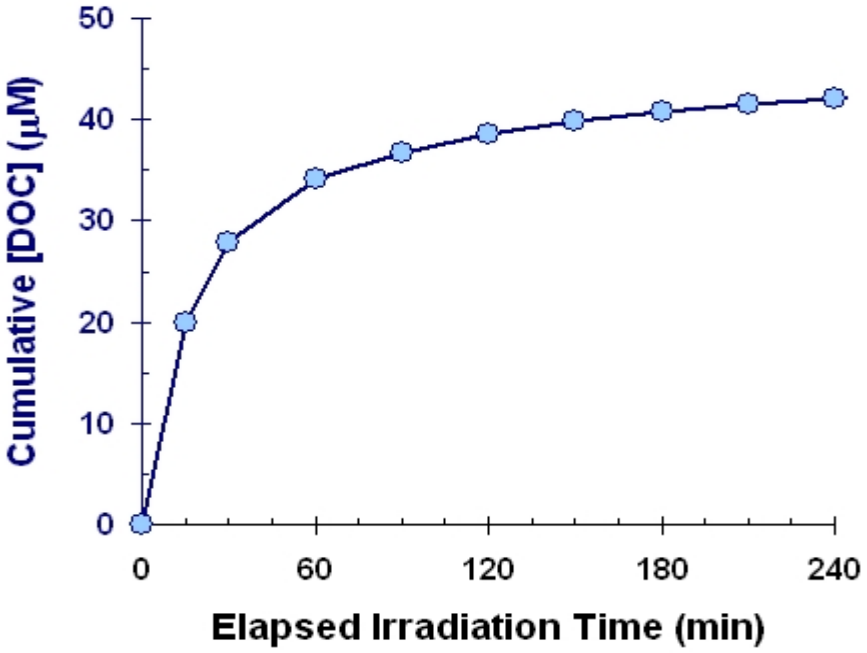


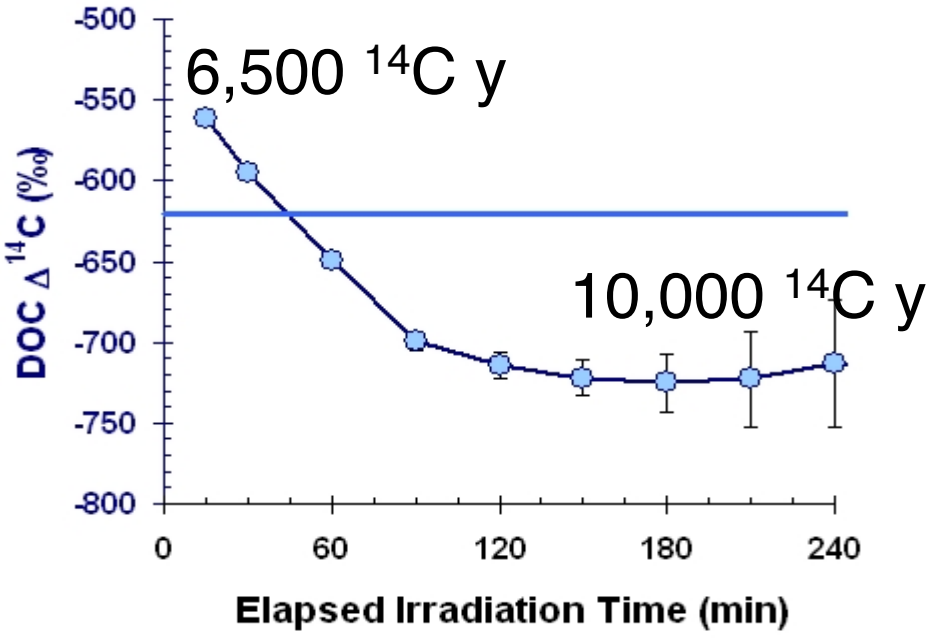

UV Hg-arc lamp, Quartz reactor in…

The Can

# Deep NE Pacific –

# Sequential Oxidation of a Single Seawater Sample

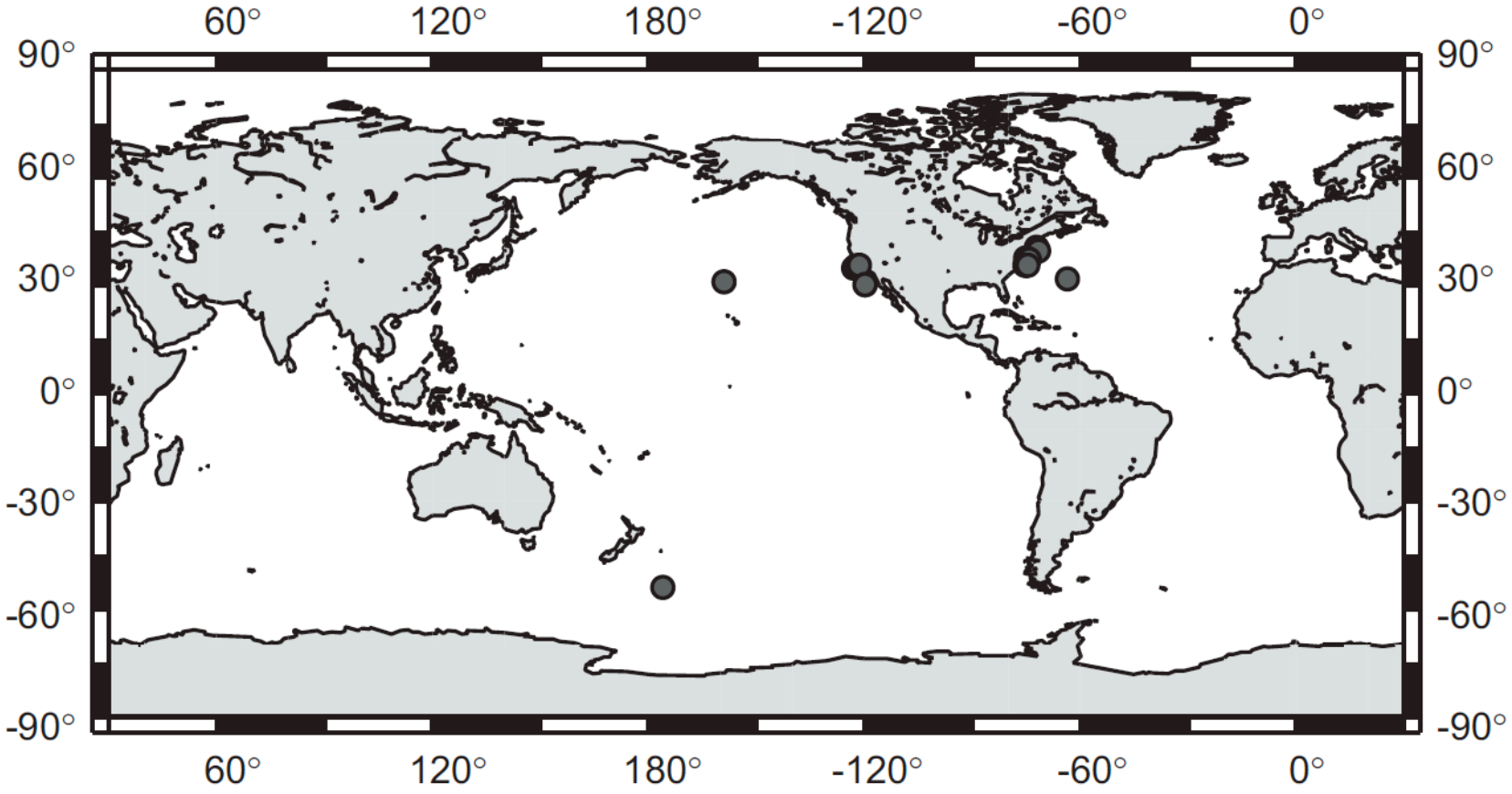


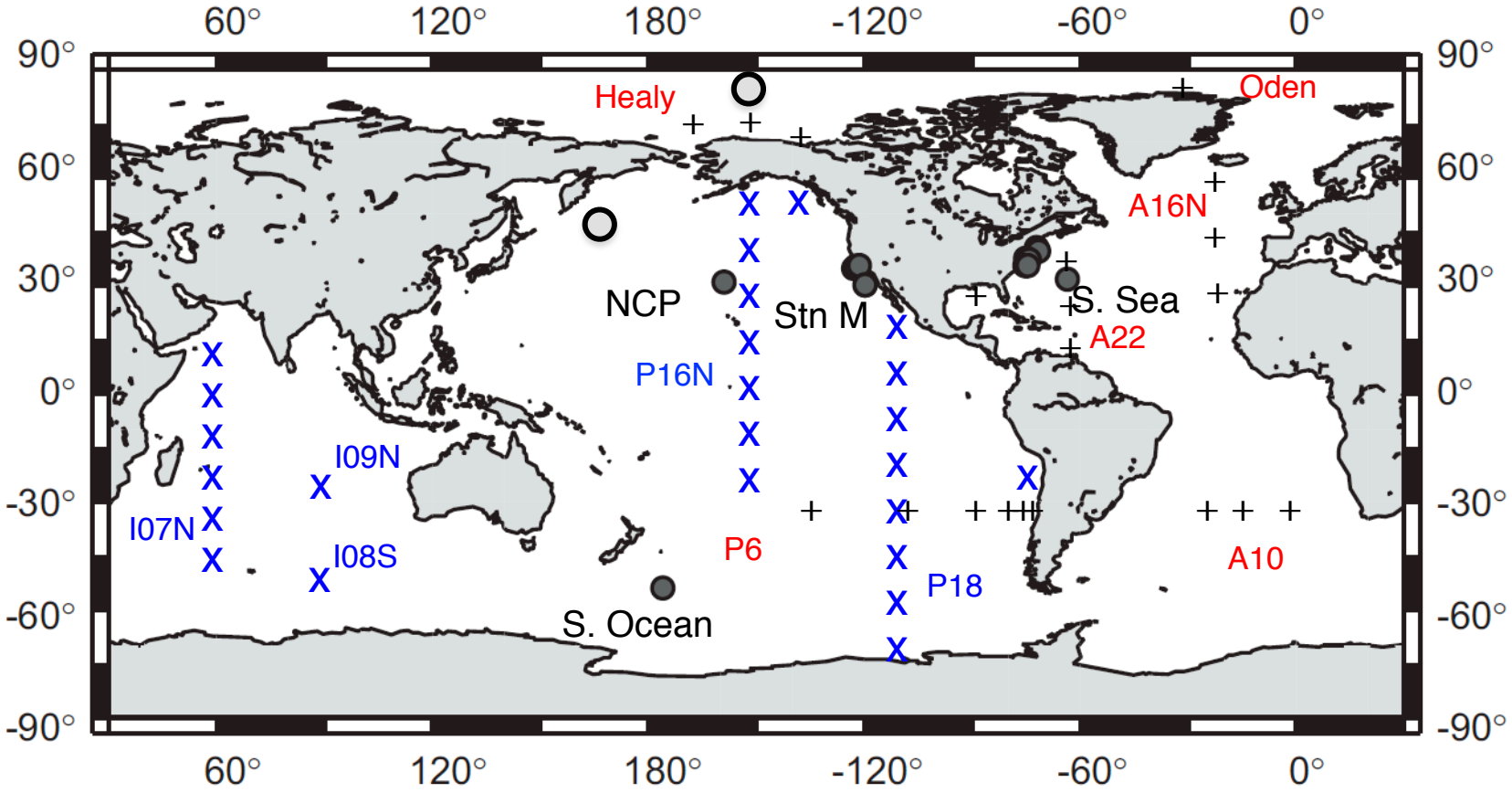

DOC is a mixture of young and old OC

Beaupré et al 2007

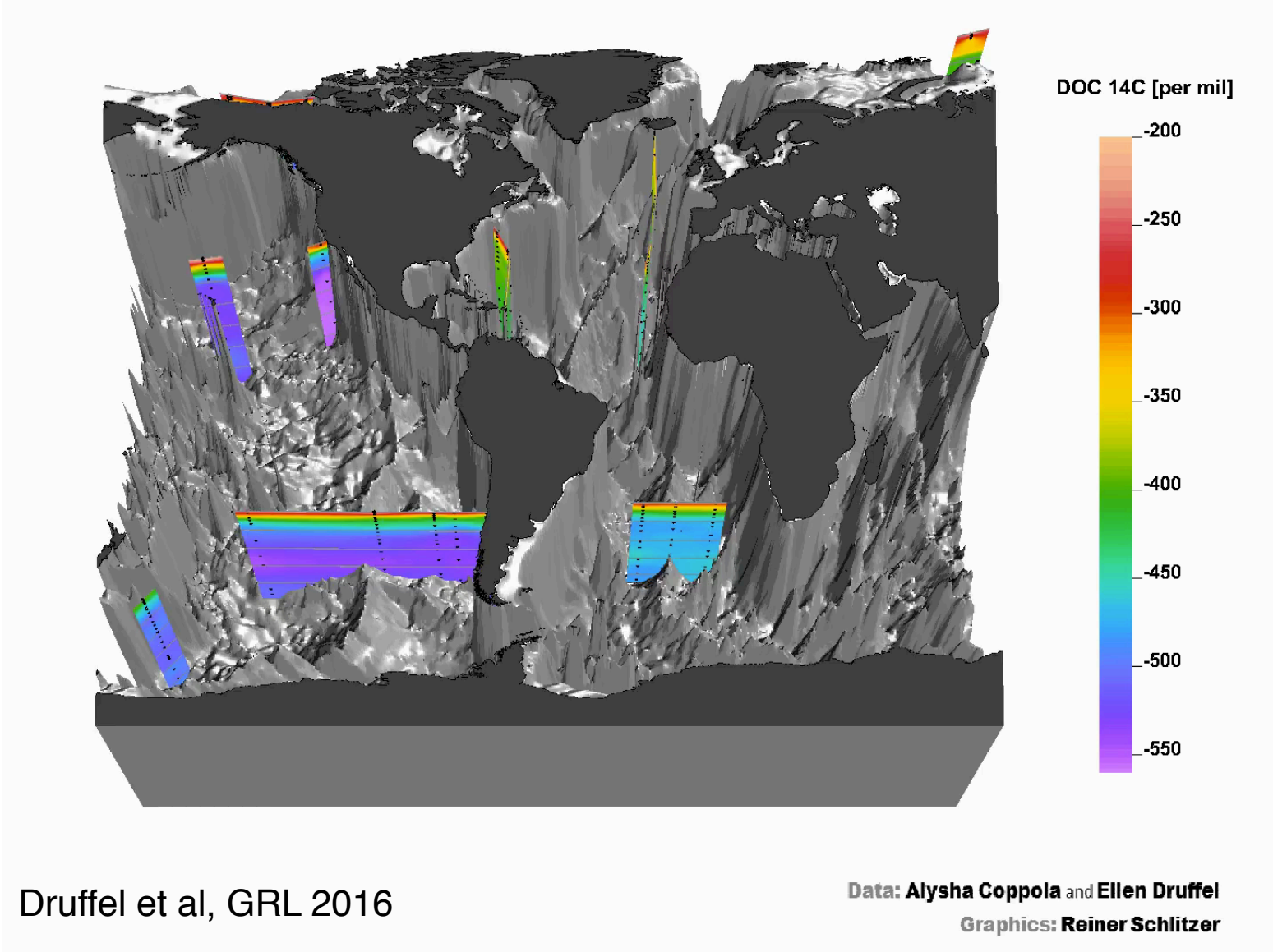
# Published DO$^{14}$C stations before 2012



# Current DO$^{14}$C stations + emerging

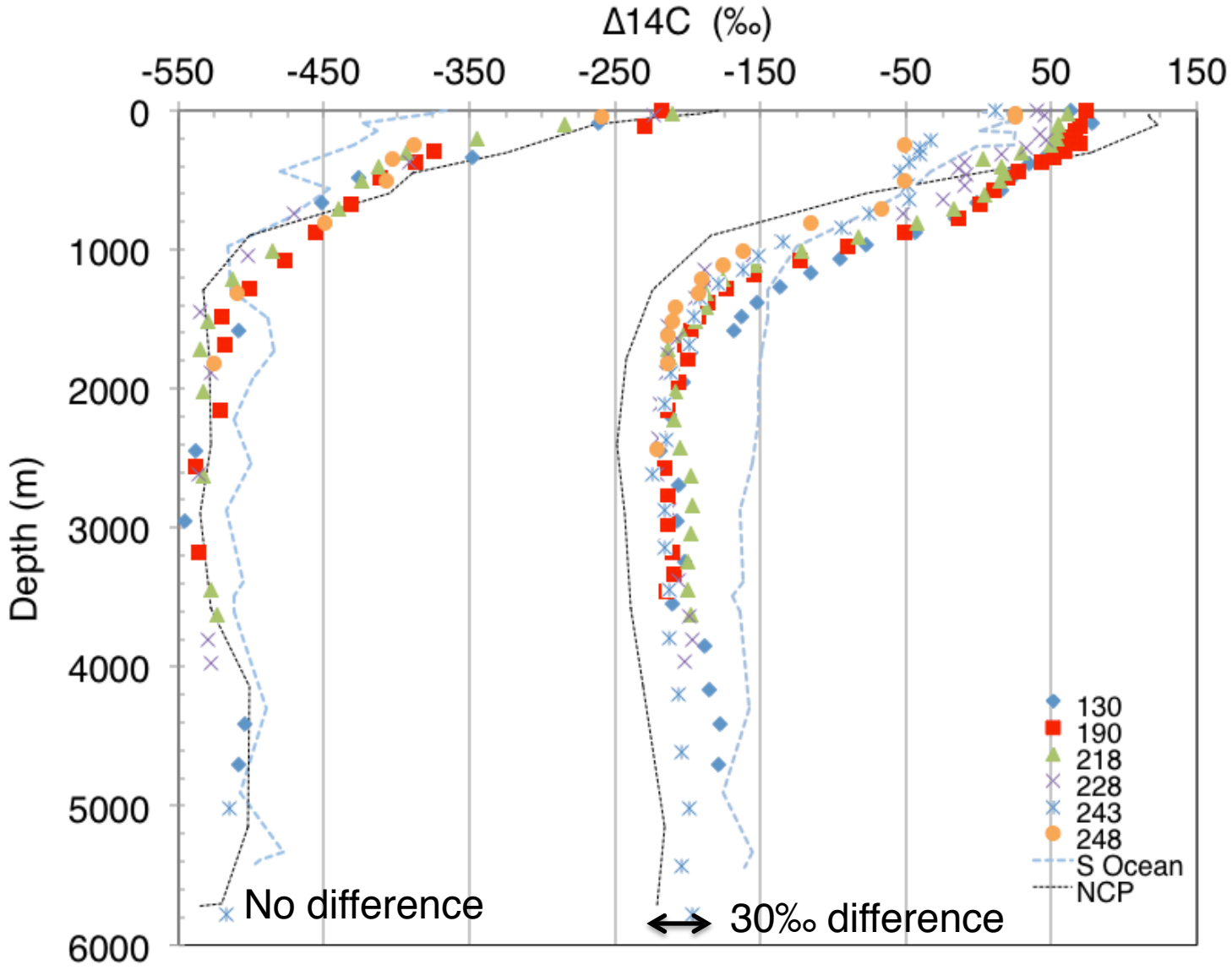


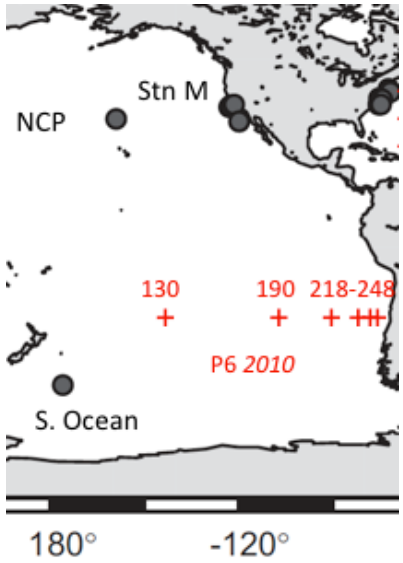
# Spatial Distribution of $DO^{14}C$ in the Ocean




Druffel et al, GRL 2016

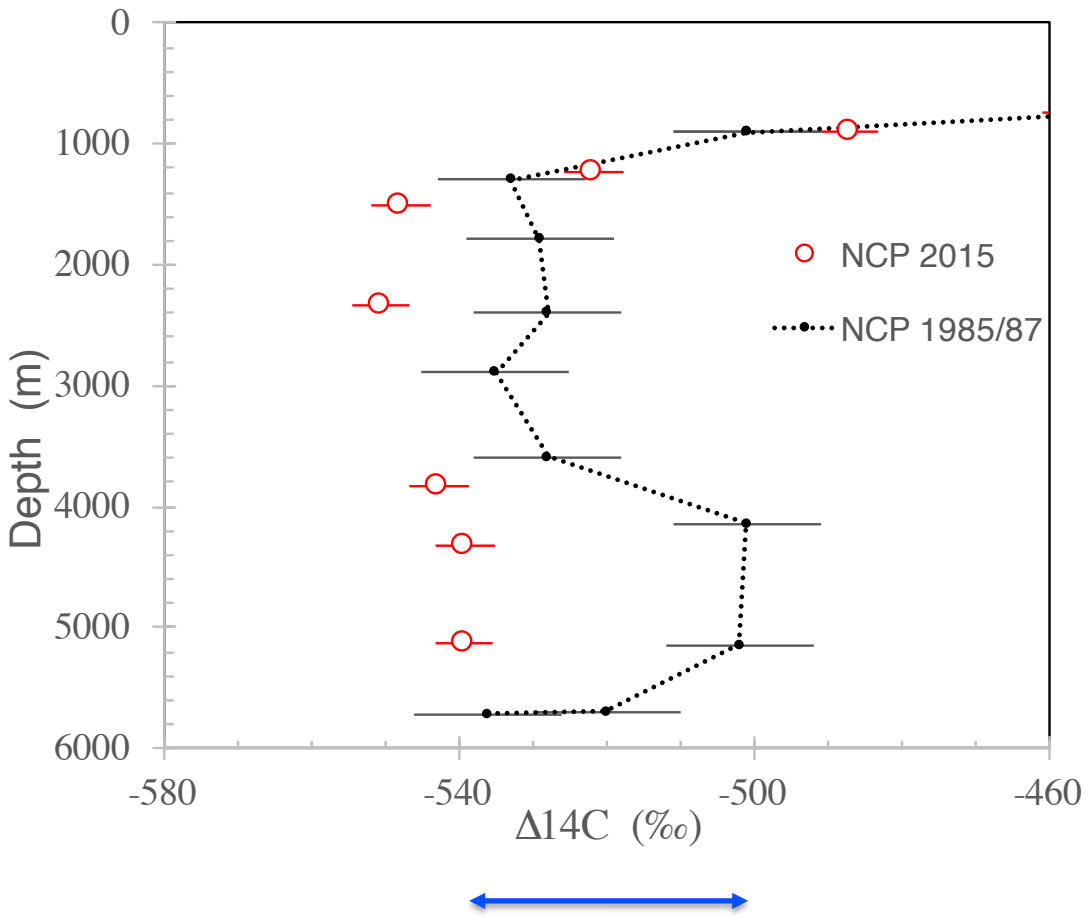
# Pacific DOC $\Delta^{14}C$




Druffel & Griffin 2015

# Now see difference in Deep N and S Pacific DOC $\Delta^{14}C$




Average difference 23‰

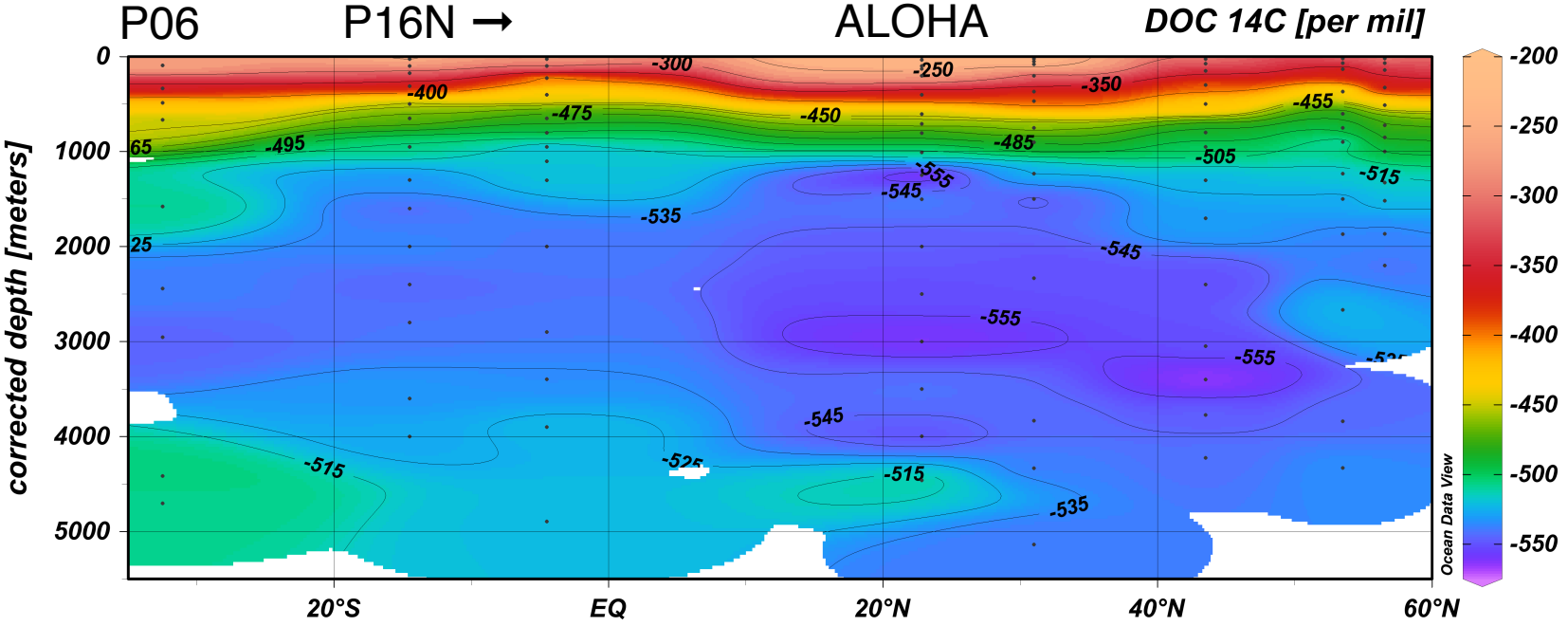
Deep DOC $\Delta^{14}C$ has decreased by 23 ± 7‰ over the last 30 years

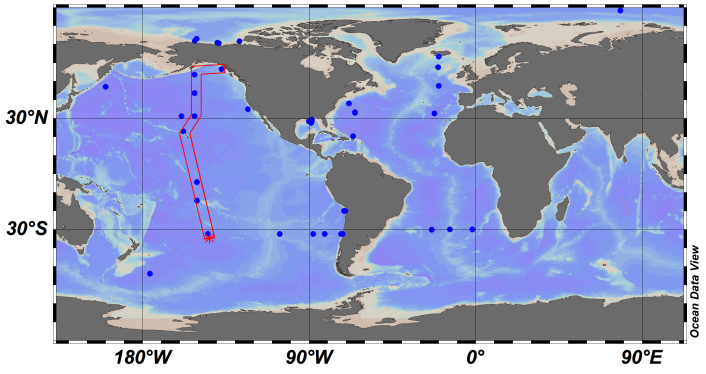
No change in [DOC] concentrations

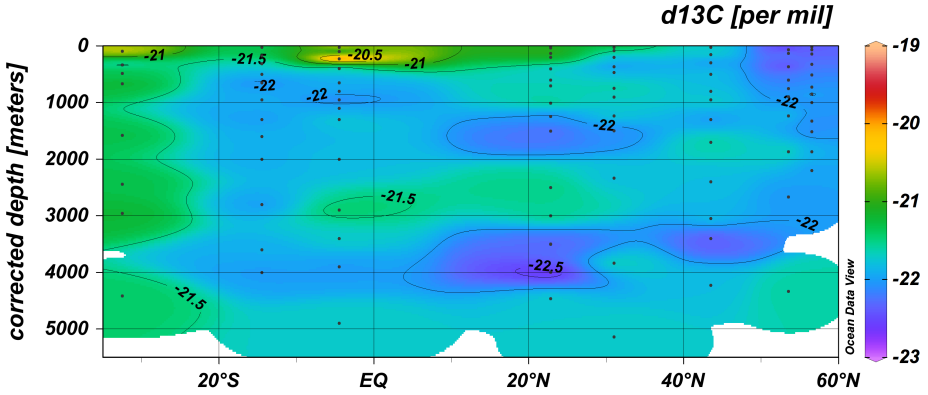
Possible Explanations:
– 1985/1987 results inaccurate
– Spatial heterogeneity deep DOC $\Delta^{14}C$
– Temporal change in DOC $\Delta^{14}C$
– Change in deep circulation?
– Input of ancient hydrothermal DOC?

**Temporal changes in DOC $\Delta^{14}C$** is possible – part of deep DOC is of bomb origin (~5%), turned over quickly.

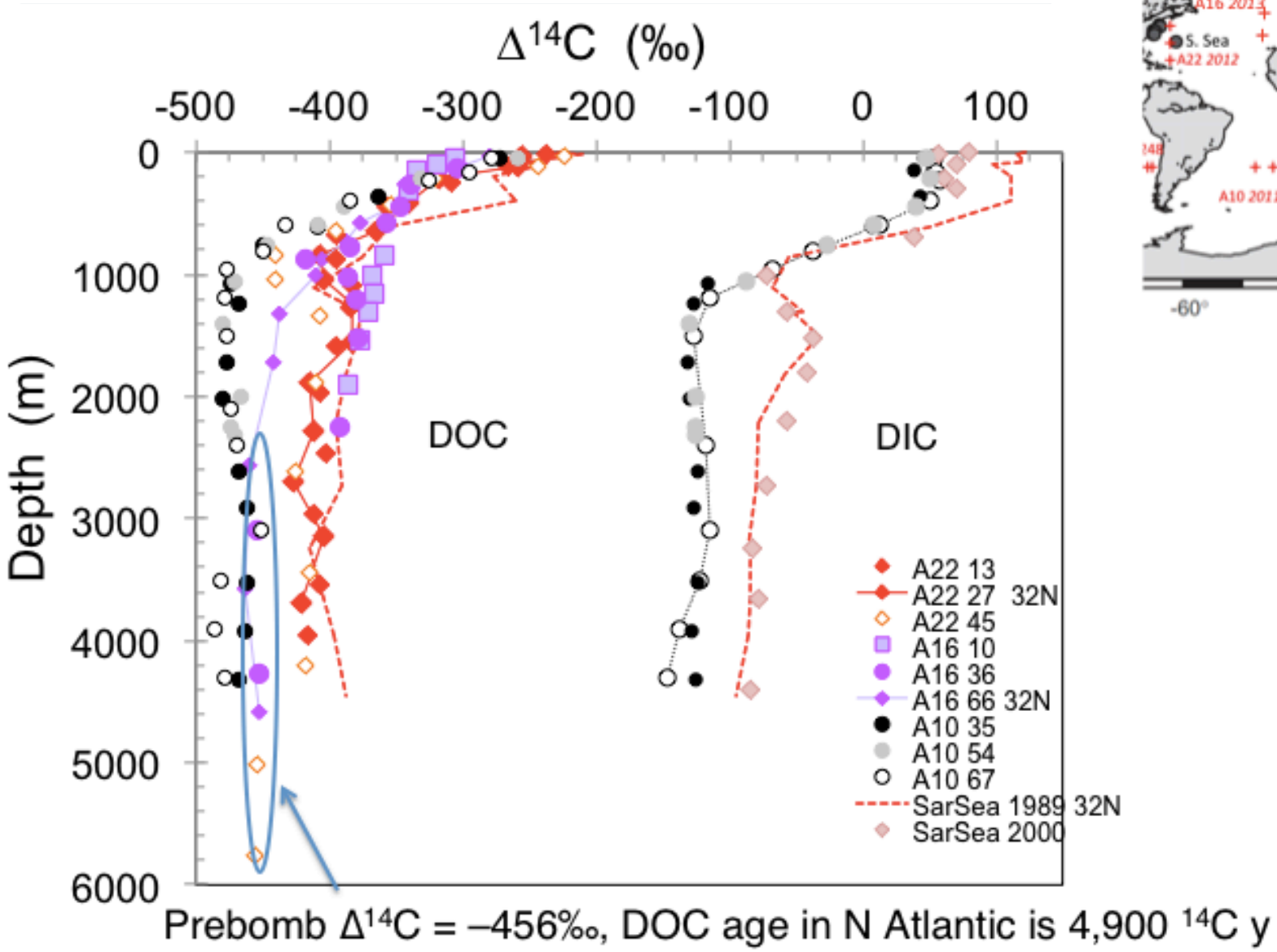
# New Deep Pacific DOC $\Delta^{14}C$

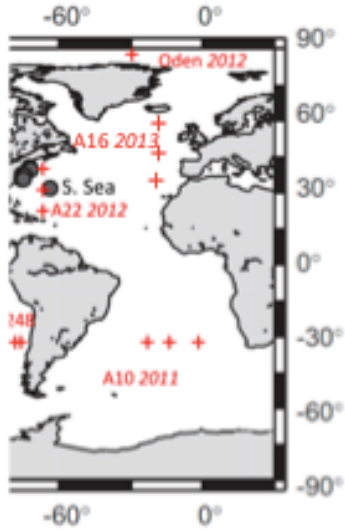


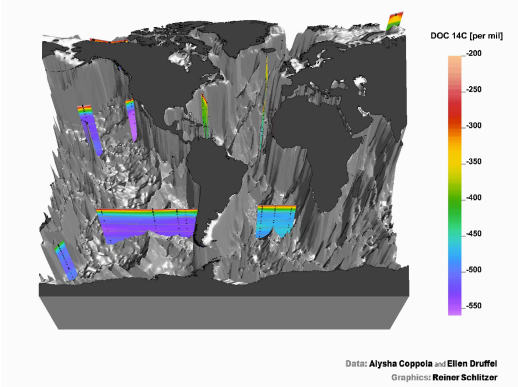



# N Atlantic DOC $\Delta^{14}C$



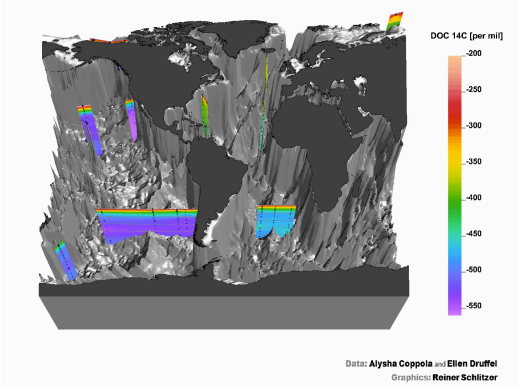

Prebomb $\Delta^{14}C$ = –456‰, DOC age in N Atlantic is 4,900 $^{14}C$ y




# Estimate of the amount of bomb $^{14}C$ in deep N Atlantic DOC

If the $\Delta^{14}C$ of deep DOC in the N Atlantic is -417‰, the pre-bomb DOC was -456‰, and surface DOC was +75, how much post-bomb DOC is there in the deep N. Atlantic?

a) 4%
b) 1%
c) 8%
d) 25%



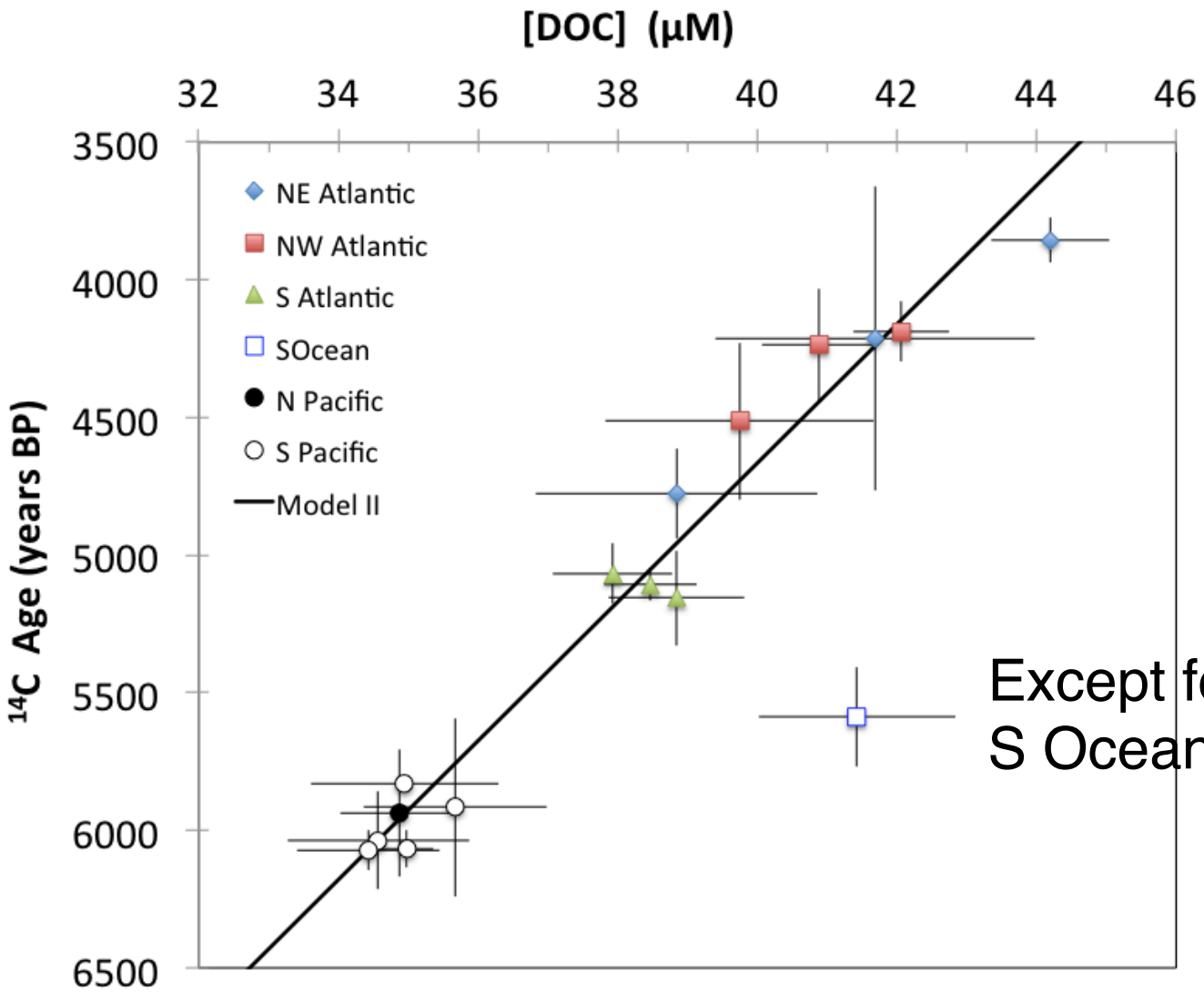

# Estimate of the amount of bomb $^{14}C$ in deep N Atlantic DOC

If the $\Delta^{14}C$ of deep DOC in the N Atlantic is -417‰, the pre-bomb DOC was -456‰, and surface DOC was +75, how much post-bomb DOC is there in the deep N. Atlantic?

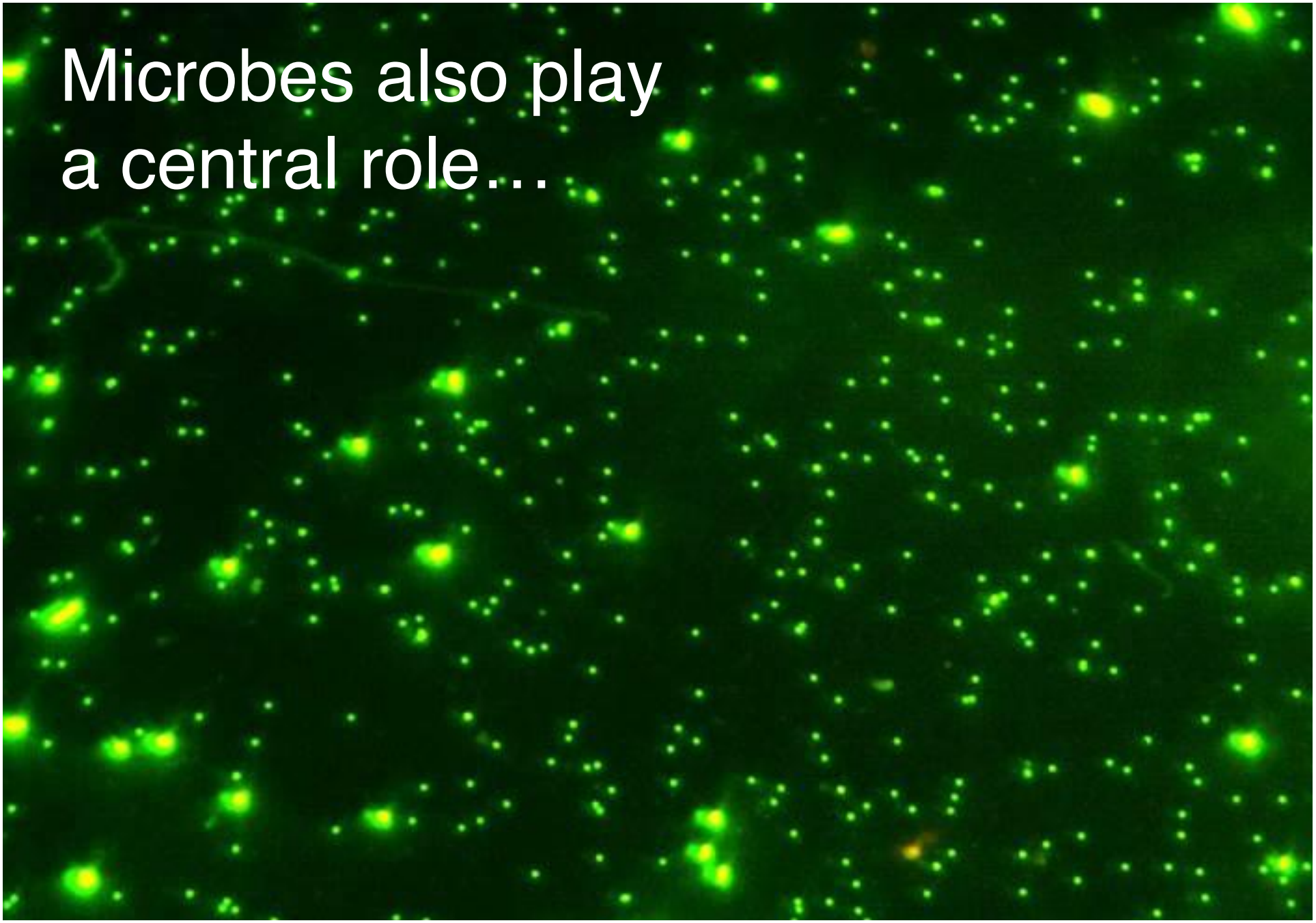
a) 4%
b) 1%
c) 8%
d) 25%

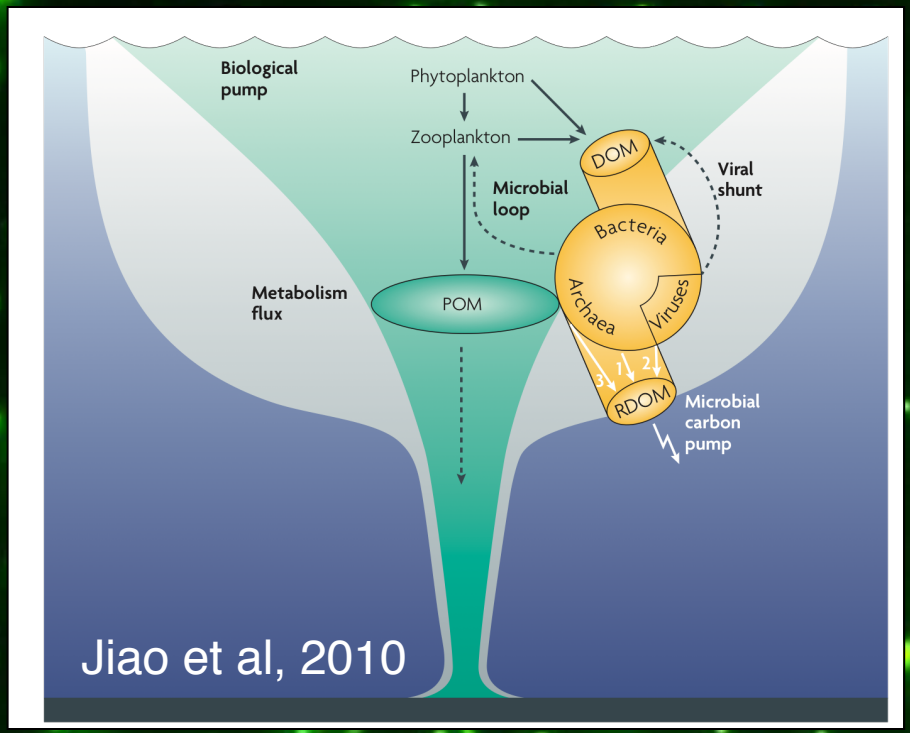
-417‰= -456(0.92) + 75(0.08)

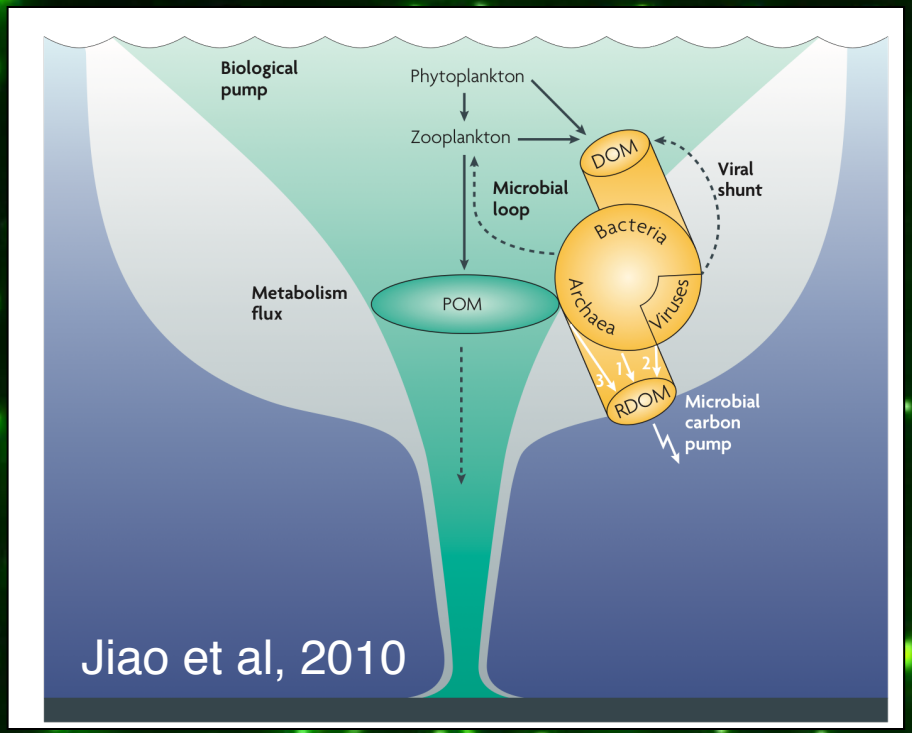
# Physics plays a large role in [DOC] & $\Delta^{14}C$ Age




Except for the S Ocean


Microbes also play
a central role…


Biological pump
Phytoplankton
Zooplankton
Microbial loop
DOM
Viral shunt
Bacteria
Archaea
Viruses
Metabolism flux
POM
1
2
3
RDOM
Microbial carbon pump
Jiao et al, 2010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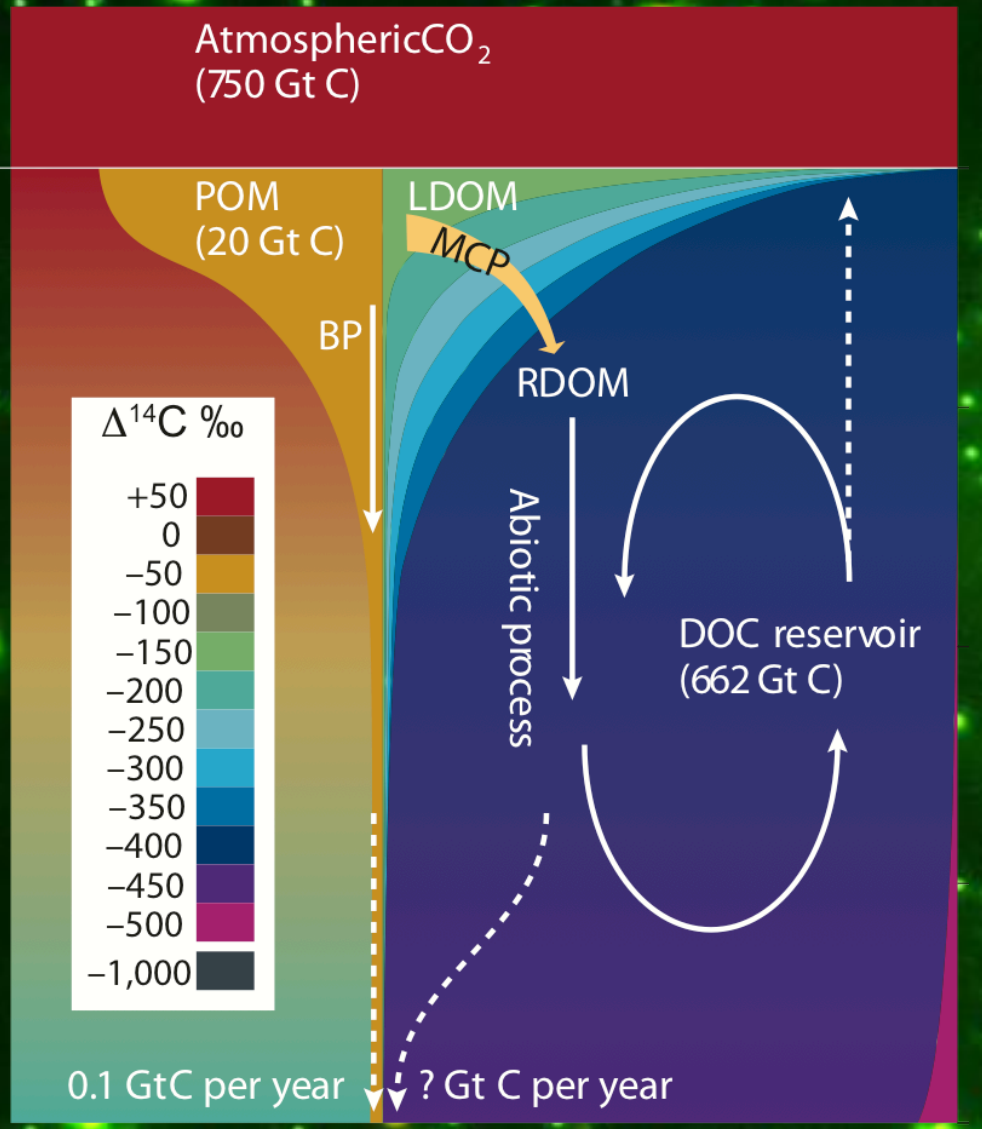

AtmosphericCO2
(750 Gt C)
POM
(20 Gt C)
LDOM
MCP
BP
RDOM
Δ14C ‰
+50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
−500
−1,000
Abiotic process
DOC reservoir
(662 Gt C)
0.1 GtC per year
? Gt C per year

# Particulate Organic C (POC)

> 0.2 $\mu$m

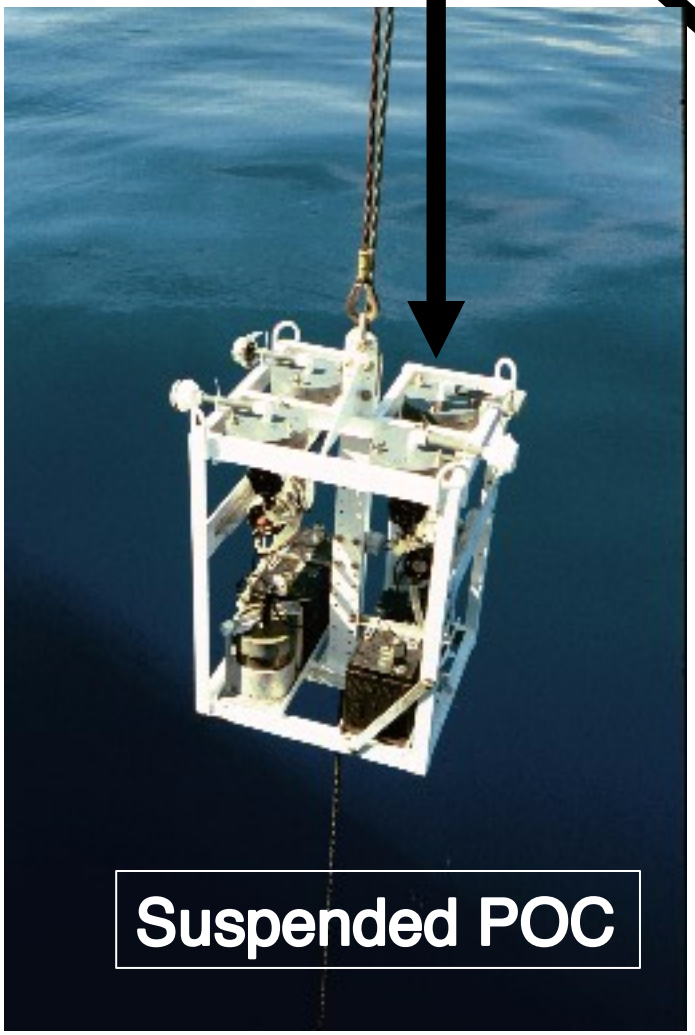
- Includes:
- fecal pellets, forams, small organisms, marine snow, clay, silt

POC can sink rapidly! (>50$\mu$m)

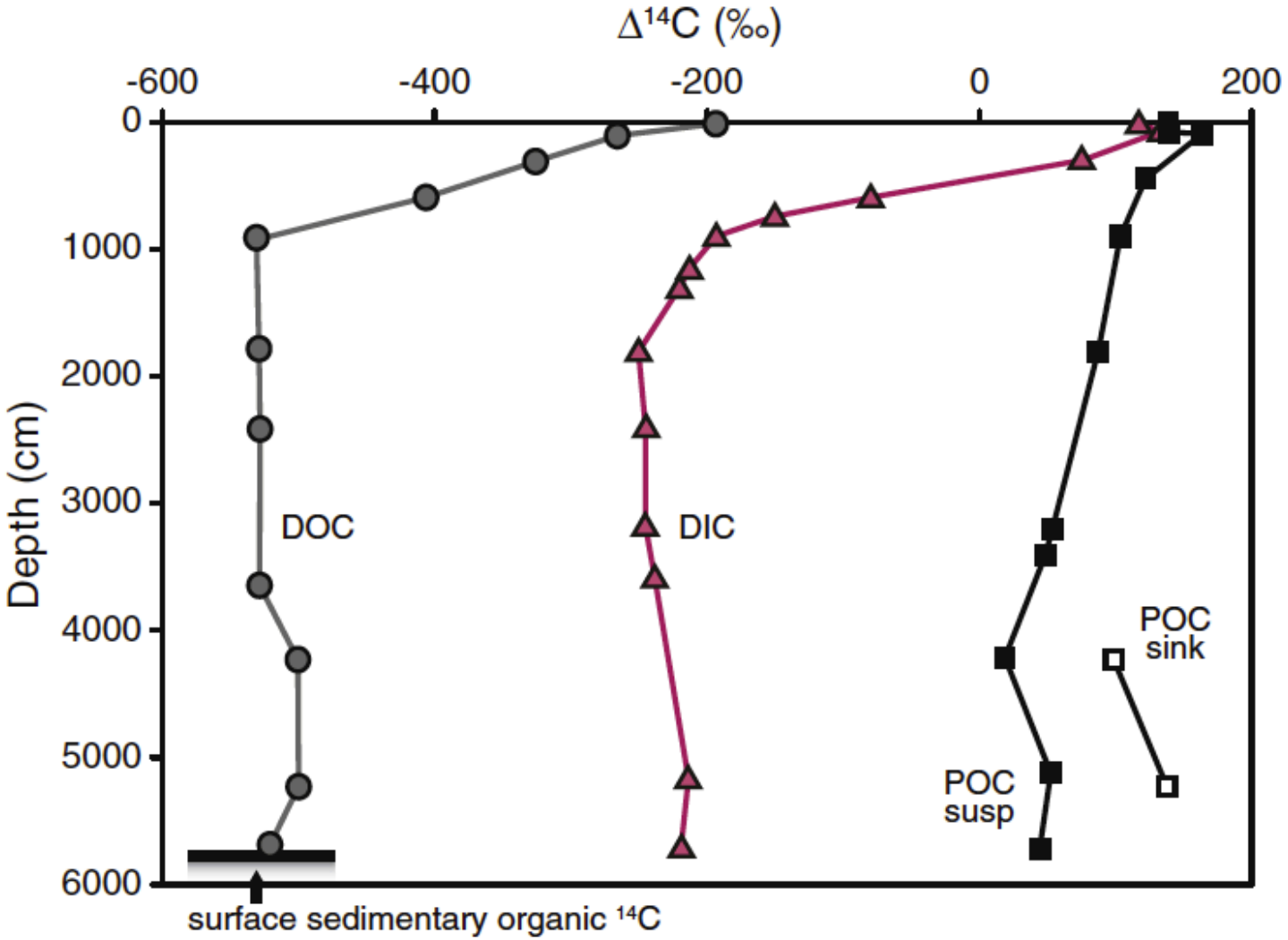
or not!

(<50$\mu$m)

.05-5 $\mu$M C in seawater



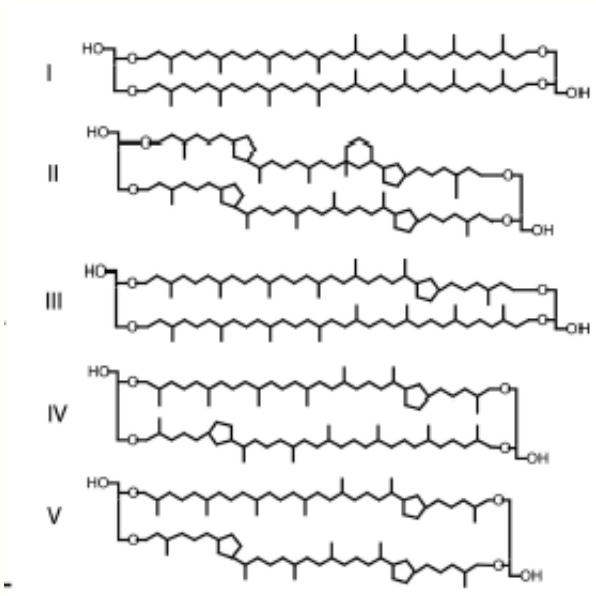

# Suspended POC $\Delta^{14}C$ - N Pacific




- Younger than DIC and DOC
- Hwang et al (2011) observed a linear correlation between $\Delta^{14}C$ and [Al], indicating old, resuspended sediment is making POC old.

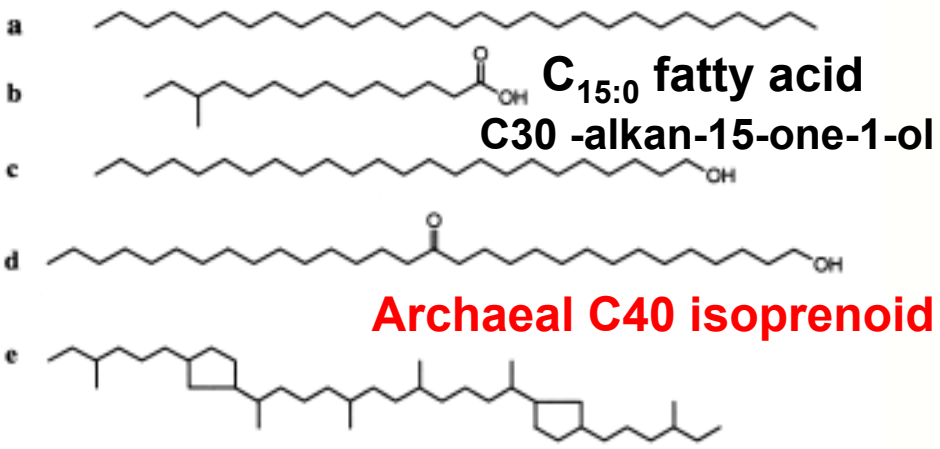
# Compound specific radiocarbon analyses (CSRA)

Lipids studied by Pearson et al (2001) in sediments and Ingalls et al (2006) in Archaea




**Archael lipids**
**Glycerol dialkyl glycerol tetraether lipids (GDGTs)**

**N-alkane**

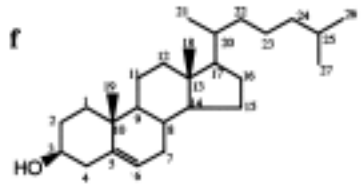


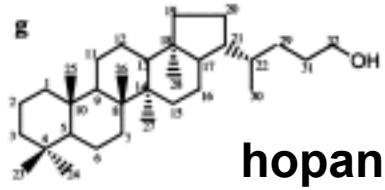

**$C_{15:0}$ fatty acid**

**C30 -alkan-15-one-1-ol**

**Archaeal C40 isoprenoid**

**cholesterol**

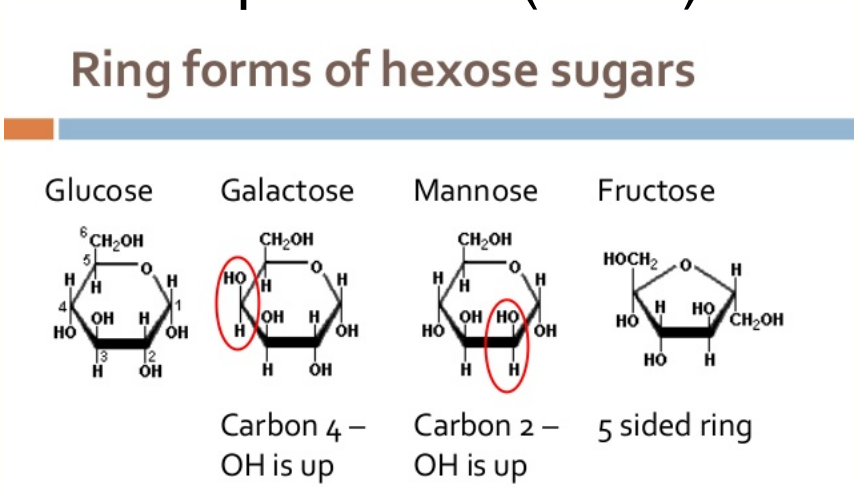



**hopanol**

# Compound specific radiocarbon analyses (CSRA)

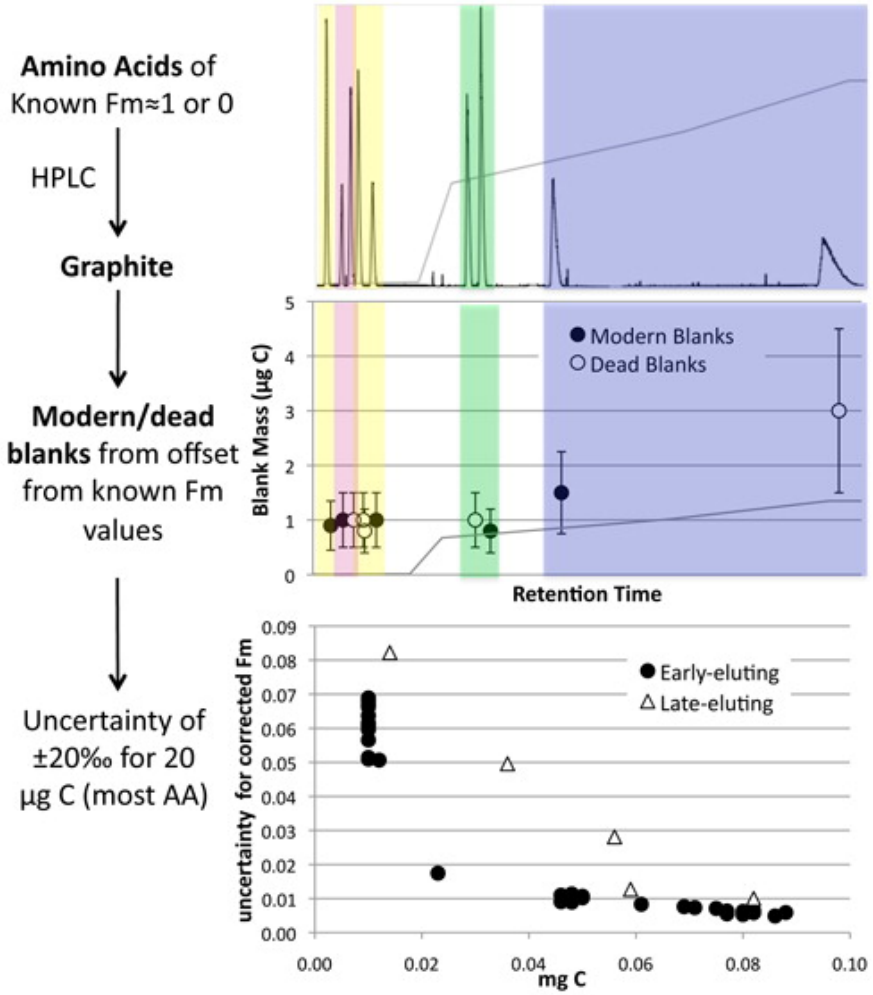
## Neutral Sugars: Repeta et al (2006)




Hawaii Sugars

15m: +40-60‰ (like DIC)
670m: -100‰ (still bomb $^{14}C$!)

## Amino Acids: Bour et al (2016)



# Why is DOC So Old? Is BC important?

- Marine Black C (BC) is ~ 5% of DOC and can be

> 23,000 $^{14}C$ yr old (–940‰)

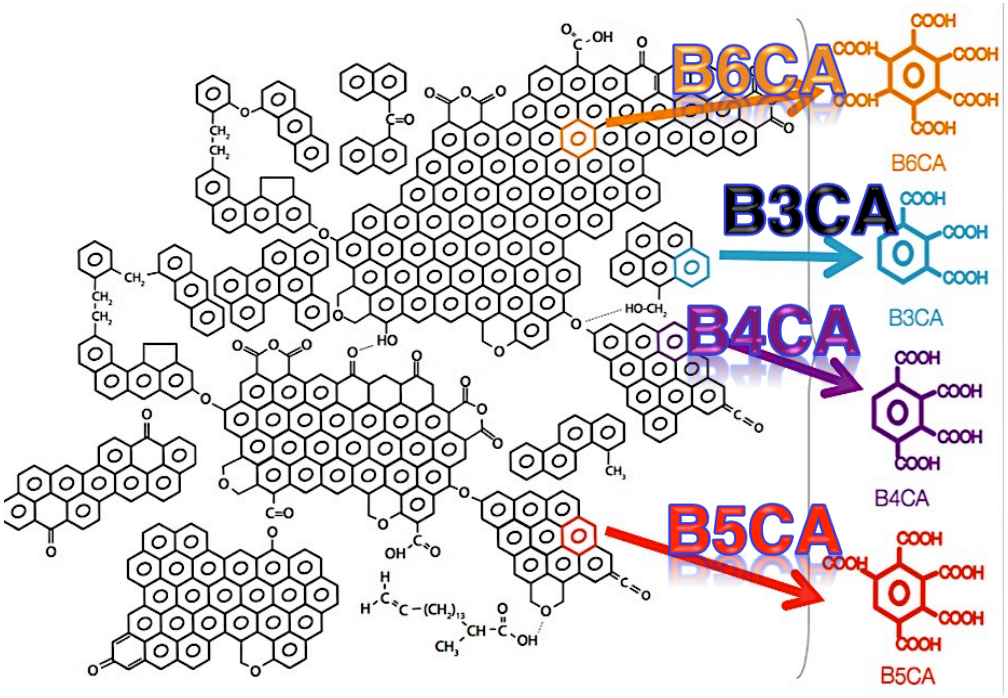
- BC contributes in a small way to the old $^{14}C$ age of DOC

**Biomass burning**

**Fossil fuel combustion**

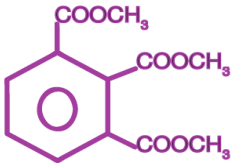
# Extracting BC from Seawater

Oxidation bomb



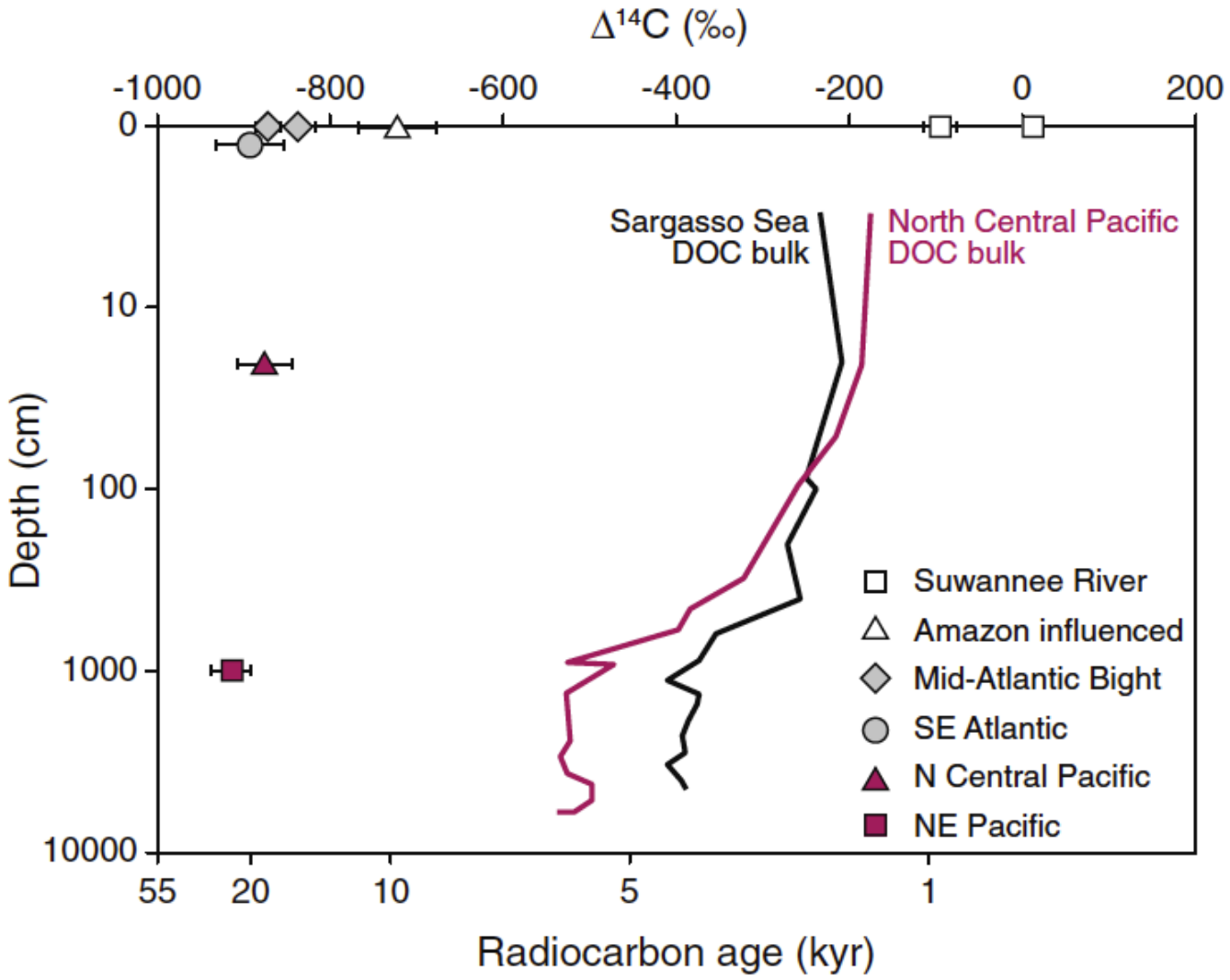

*(Goldberg, 1985)*

Derivatized BPCA



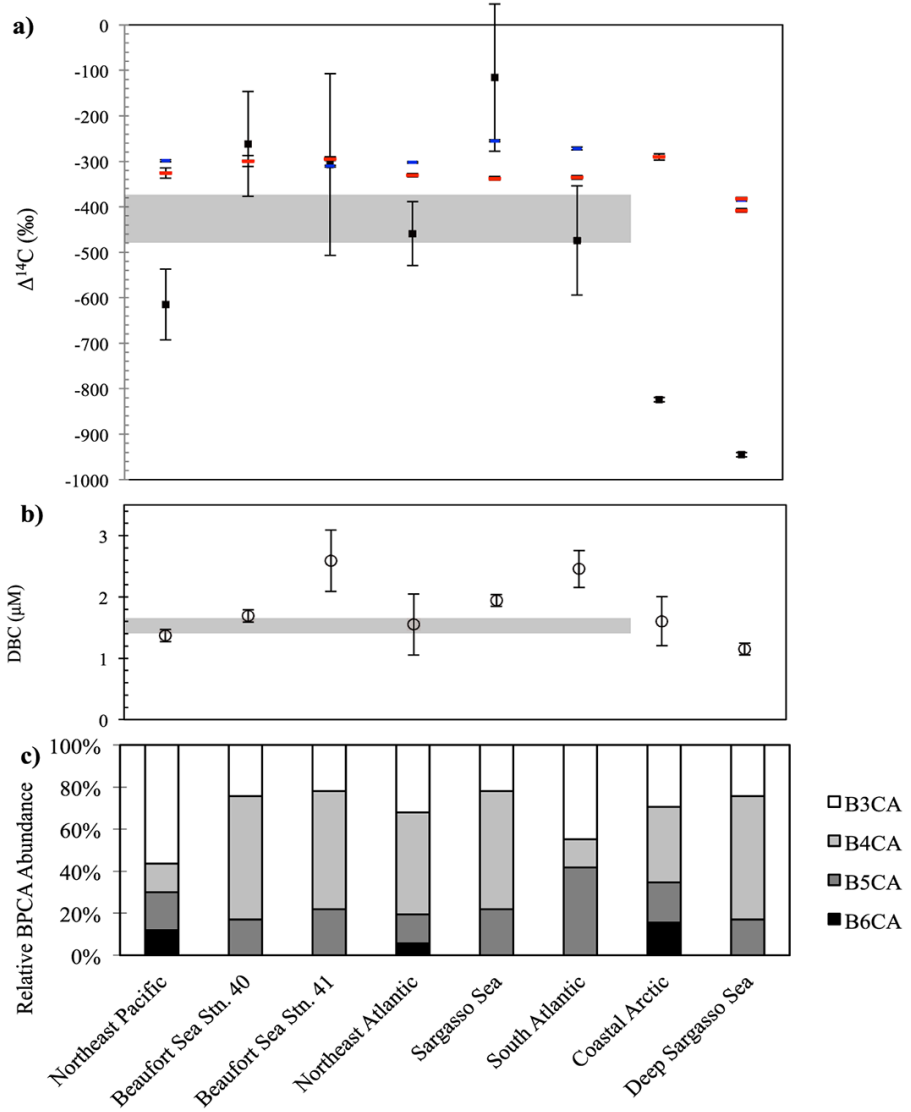

- Oxidize BC to BPCA marker compounds
- Methylate BPCAs for collection on PCGC for $^{14}C$ analysis

# $\Delta^{14}C$ of bulk DOC vs. $\Delta^{14}C$ of BC in SOC



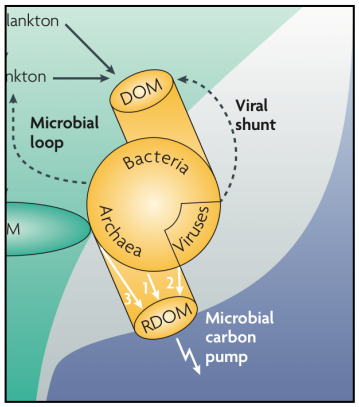

Ziolkowski & Druffel 2010

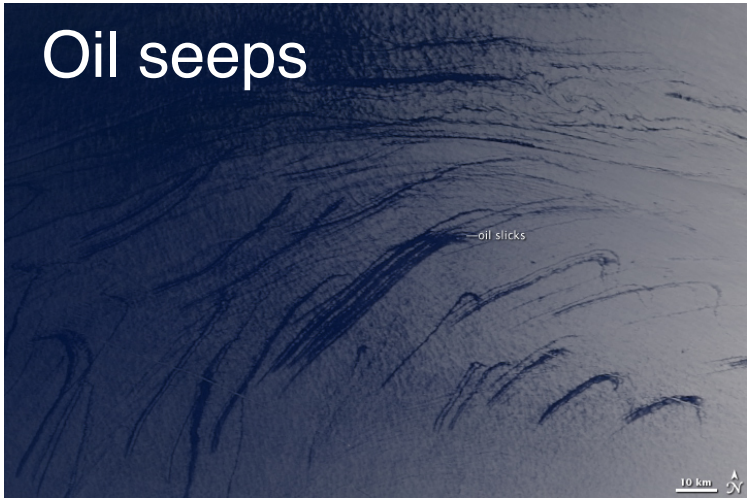
# Cycling of BC in the Ocean

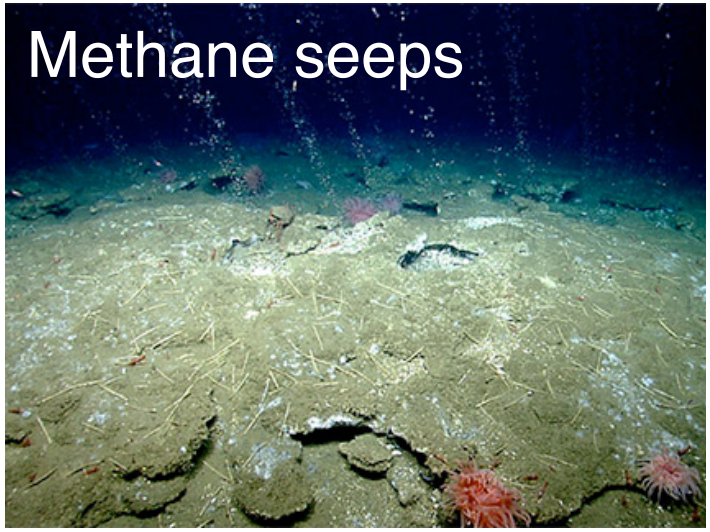


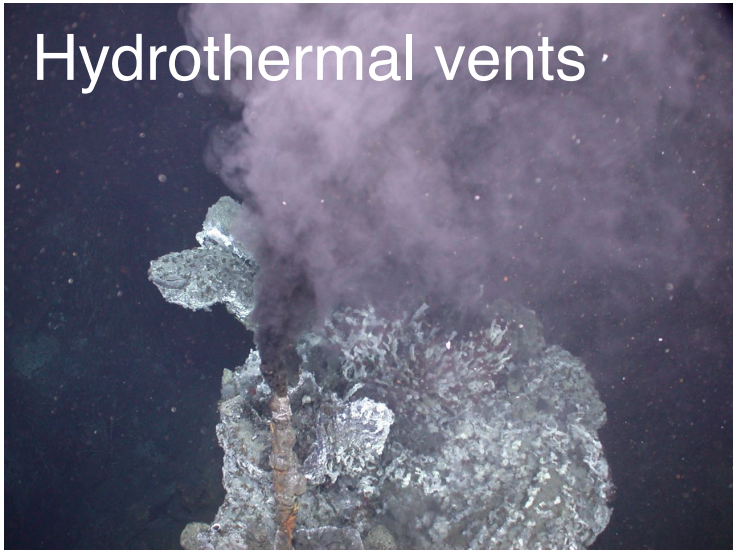

Coppola &
Druffel 2016

# Why is DOC So Old?





Thank you!
Questions?