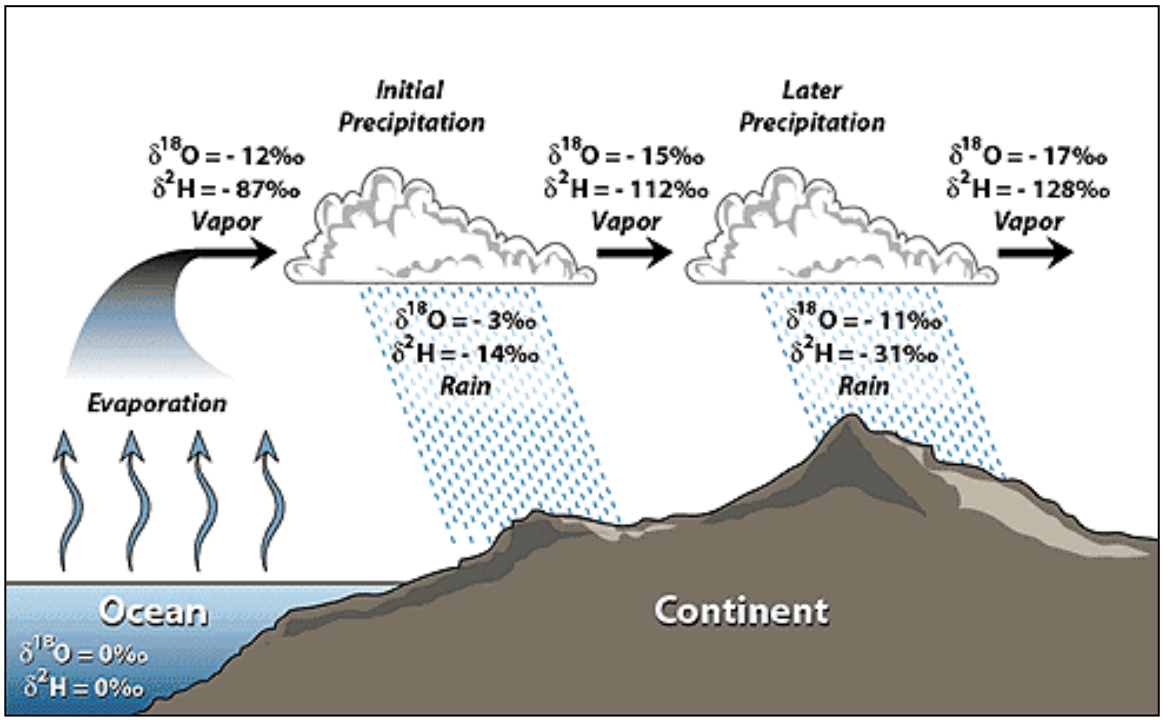
IsoCamp
SIRFER @ Utah
2017
stableisotopes.utah.edu



Biogeochemistry of the oceans

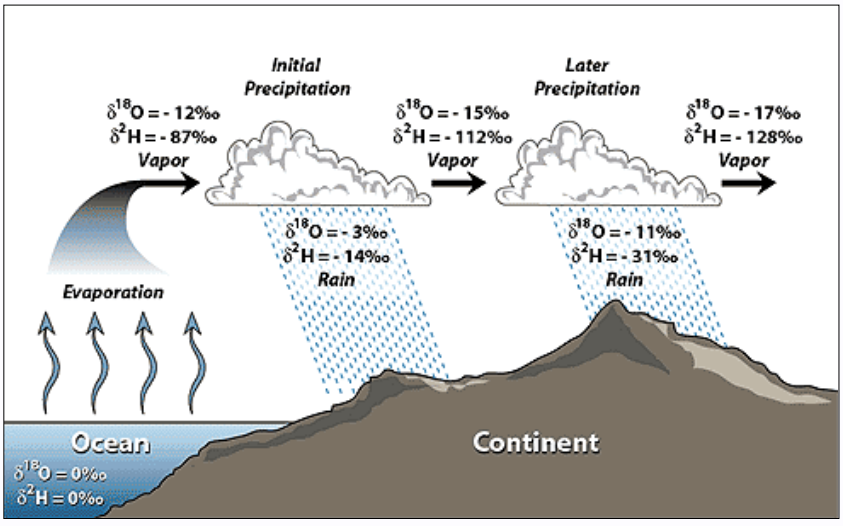
Howard J. Spero

University of California Davis

Talk Outline

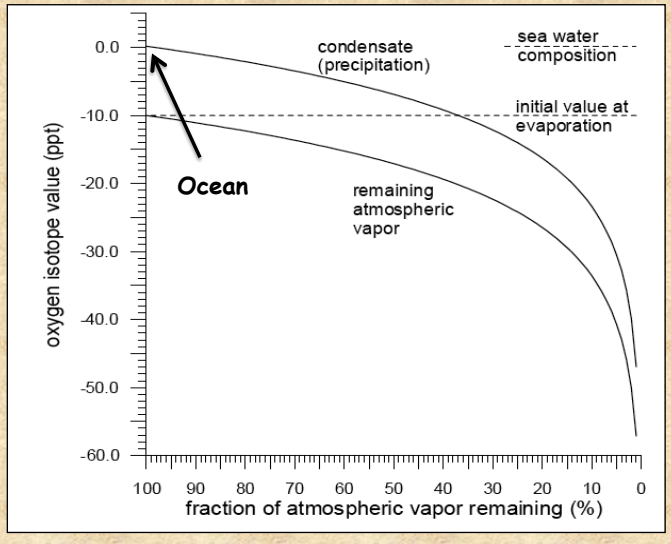
- The ocean-atmosphere-hydrologic cycle system and oxygen isotope geochemistry
- Dissolved inorganic carbon in the ocean - the CO_2 buffering system
- A geochemists view of ocean circulation - the oceanic conveyor belt
- O & C isotope geochemistry of carbonates- linking the present with the past
- The 21st Century Frontier: Emerging Technologies at the stable isotope:element interface; lasers, SIMS and NanoSIMS

The ocean – precipitation linkage



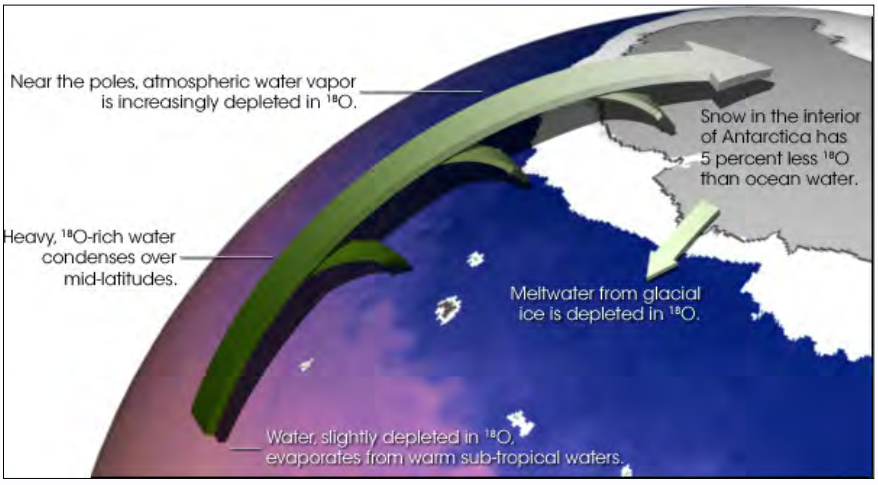
http://web.sahra.arizona.edu/programs/isotopes/oxygen.html

Rainout and Rayleigh Distillation



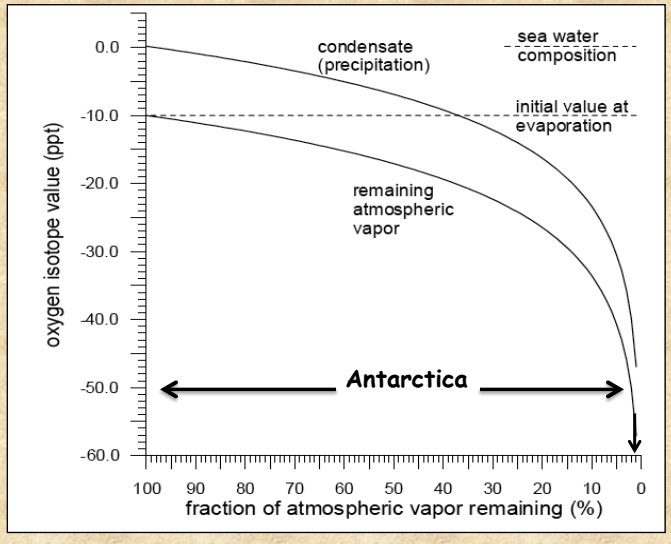
Excessive Rayleigh Fractionation is observed on glacial ice sheets

e.g. SLAP (Standard Light Antarctic Precipitate); $\delta^{18}O$=-55.5‰, δD=-427.5‰



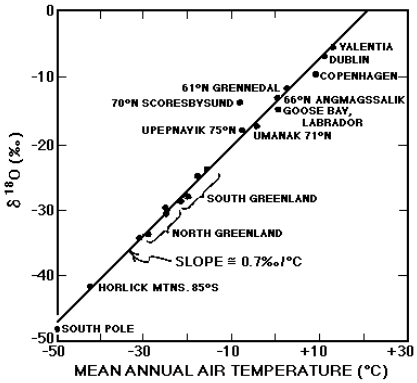
http://earthobservatory.nasa.gov/Features/Paleoclimatology_OxygenBalance/

Rainout and Rayleigh Distillation



The oxygen and hydrogen isotope composition of ice reflects the mean air temperature over the glacier during snowfall

As temp drops, $\delta^{18}O$ of *water* decreases with a slope of 0.7‰/°C



Observed $\delta^{18}O$ in average annual precipitation as a function of mean annual air tamperature (Dansgaard, 1964). Note that all the points on this graph are for high latitudes (>45°). The $\delta^{18}O$ values are calculated as follows:

$$\delta^{18}O = \frac{^{18}O/^{16}O \text{ sample} - ^{18}O/^{16}O \text{ std.}}{^{18}O/^{16}O \text{ std.}} \times 1000$$

Broecker, WS. The Glacial World According to Wally,
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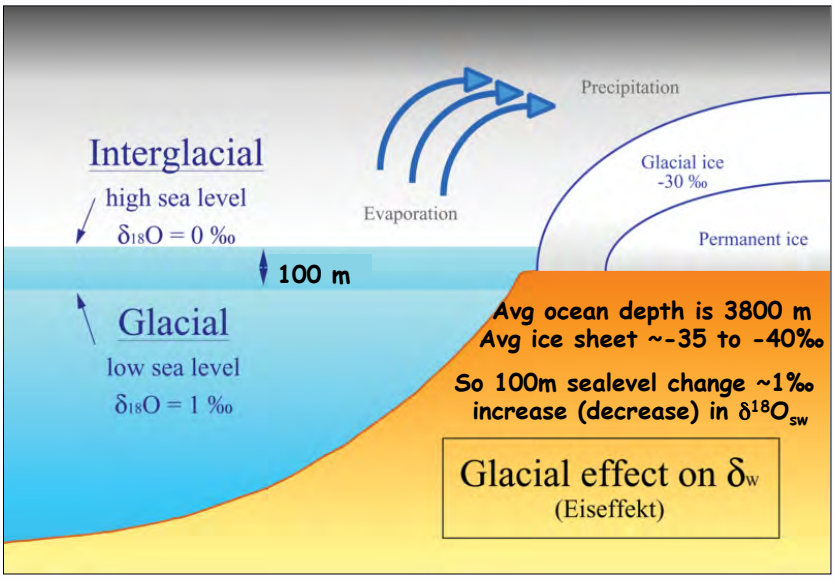
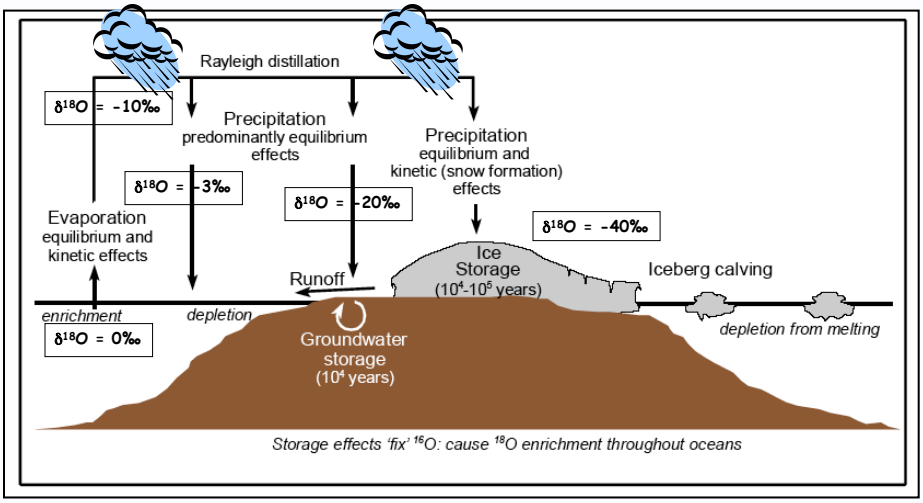
Reproduced by permission.

Impact of Rayleigh Fractionation on glacial oceans – 20 ka



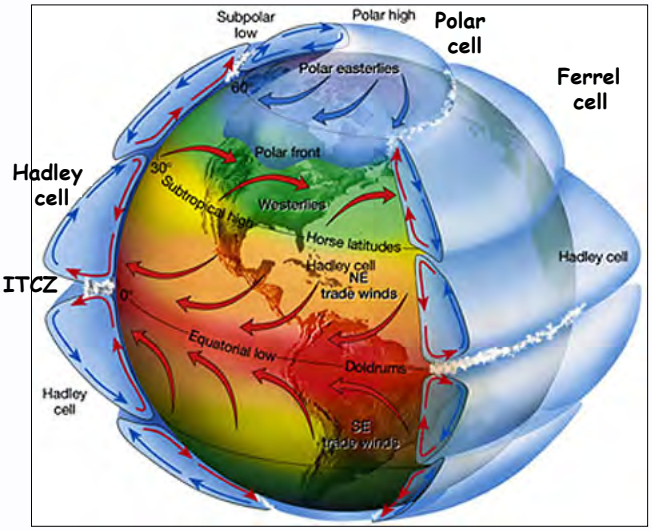
https://upload.wikimedia.org/wikipedia/commons/6/6f/Glacial_effect_hg.png

Modern Hydrologic Cycle and Isotope Geochemistry



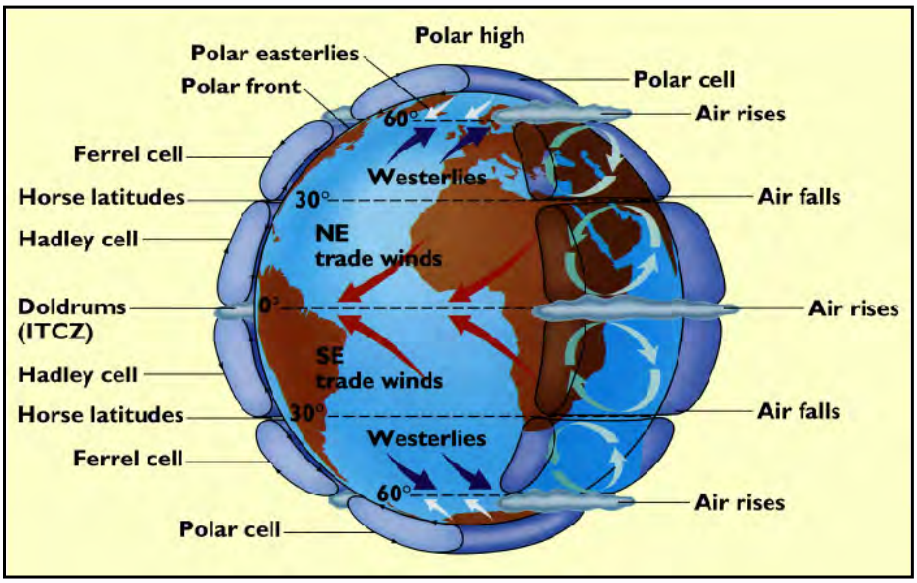
Cooke and Rohling, 2001

Global Atmospheric Circulation Patterns

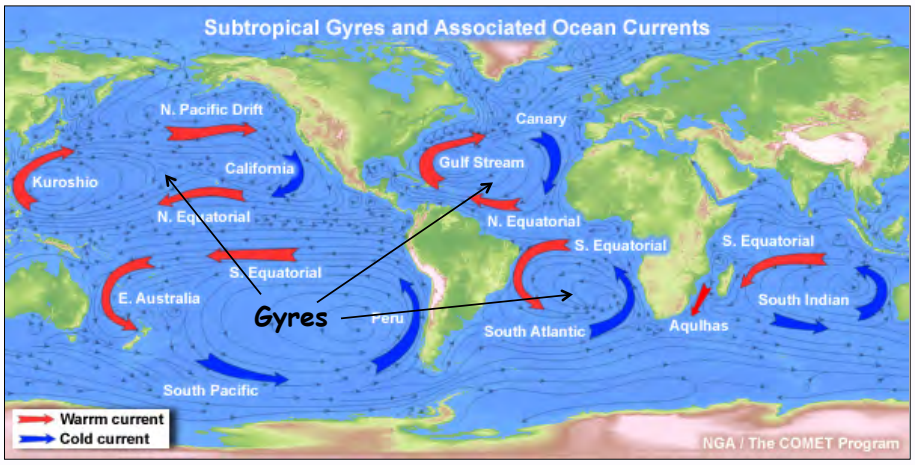


http://d32ogoqmya1dw8.cloudfront.net/images/eslabs/hurricanes/3d_hadley_md.v3.jpg

Global Atmospheric Circulation Patterns

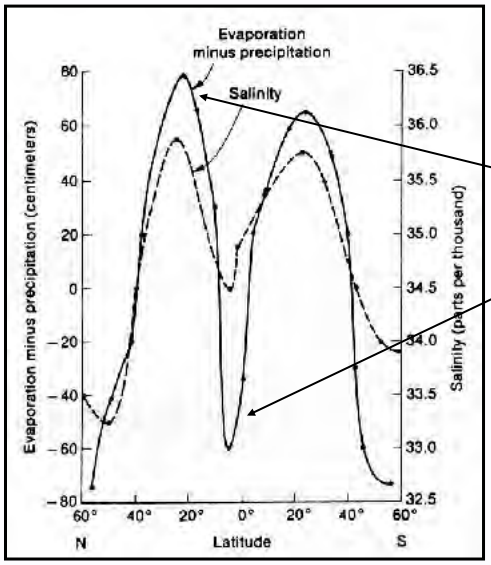


Wind-Driven Surface Current Patterns Reflect Overlying Atmospheric Circulation Patterns

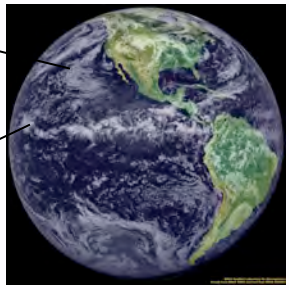


http://www.goes-r.gov/users/comet/tropical/textbook_2nd_edition/navmenu.php_tab_4_page_3.1.0.htm

Evaporation:Precipitation Patterns Define Surface Salinity Variations in the Ocean

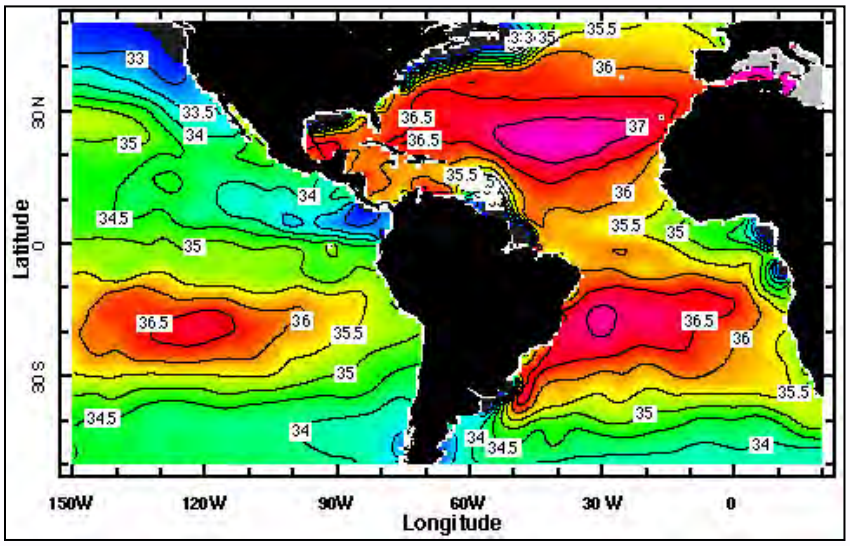


Sub-tropical hi Pressure; E>P yields hi Salinity



Equatorial and Hi latitudes; E<P yields low salinity

Surface Salinity Patterns - Highest Salinity is Found in the Central Gyres Under the Subtropical Hi P Zones



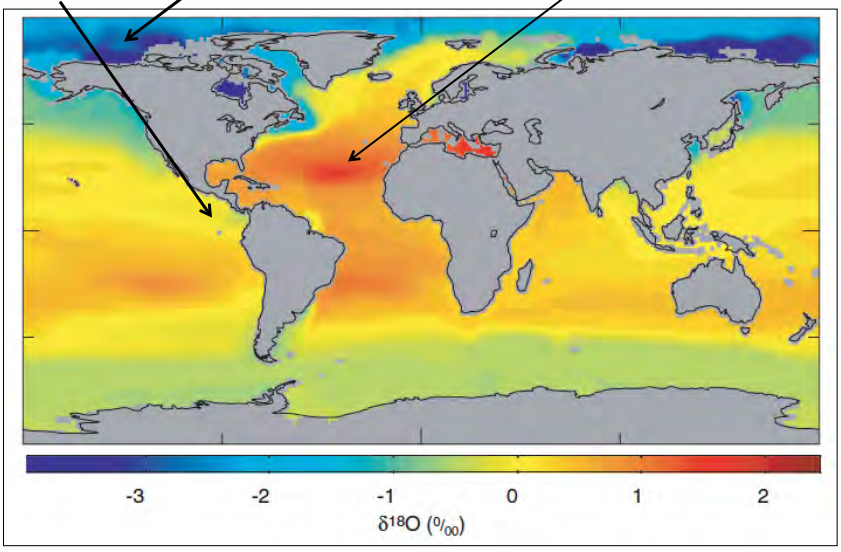
http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NODC/.WOA98

$\delta^{18}O_{water}$ can be Used as a Salinity proxy

Important: Global Salinity vs $\delta 18O_{sw}$ equations are NOT VALID

Low salinity – low $\delta^{18}O_{sw}$ in high lats and equatorial regions

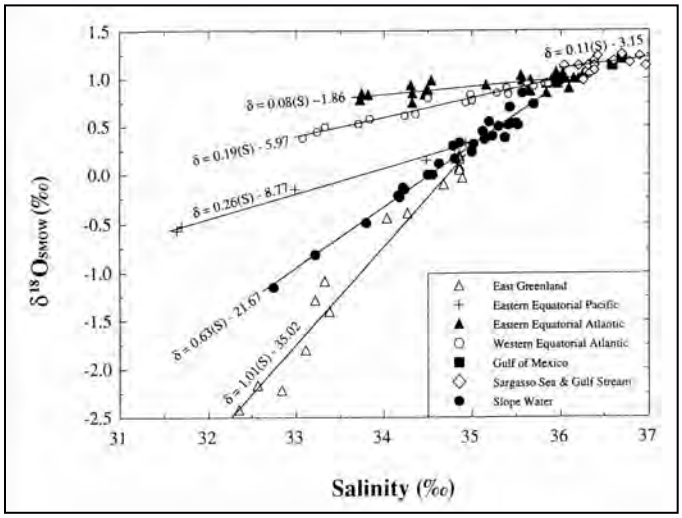
High salinity – high $\delta^{18}O_{sw}$ in central gyres



http://data.giss.nasa.gov/o18data/

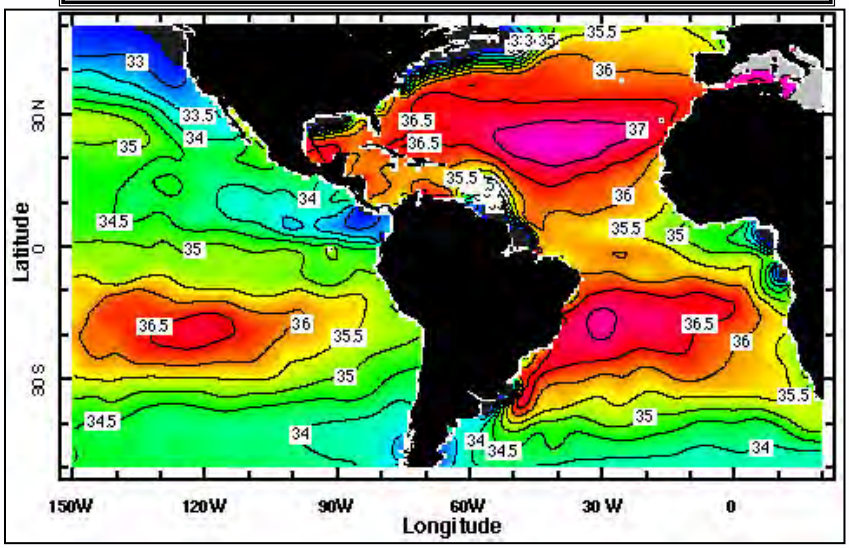
Regional Salinity:$\delta^{18}O_w$ Relationships have Different Freshwater Endmembers

Y-intercepts reflect average freshwater input to each region



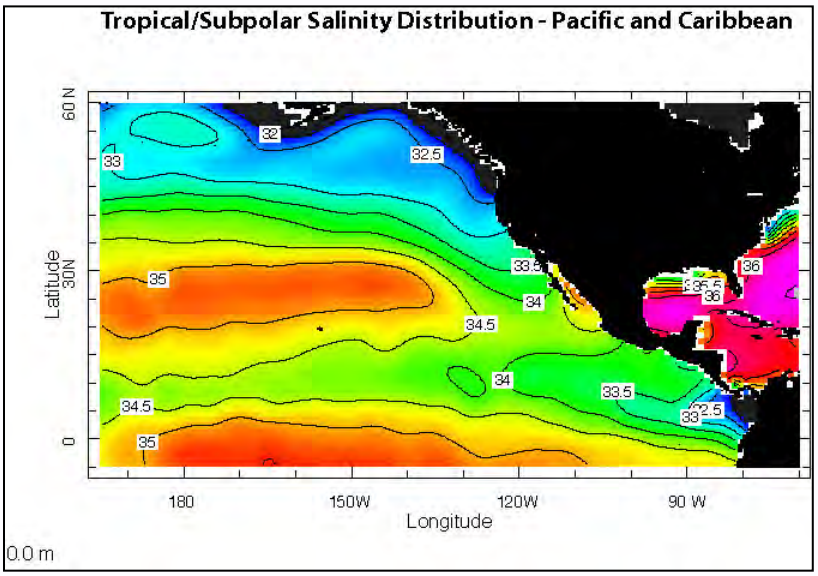
Fairbanks & Charles (1992)

Note Low Salinity Regions of Ocean - Each has a Different Freshwater Endmember



http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NODC/.WOA98

Atlantic is Saltier than the Pacific - Why?



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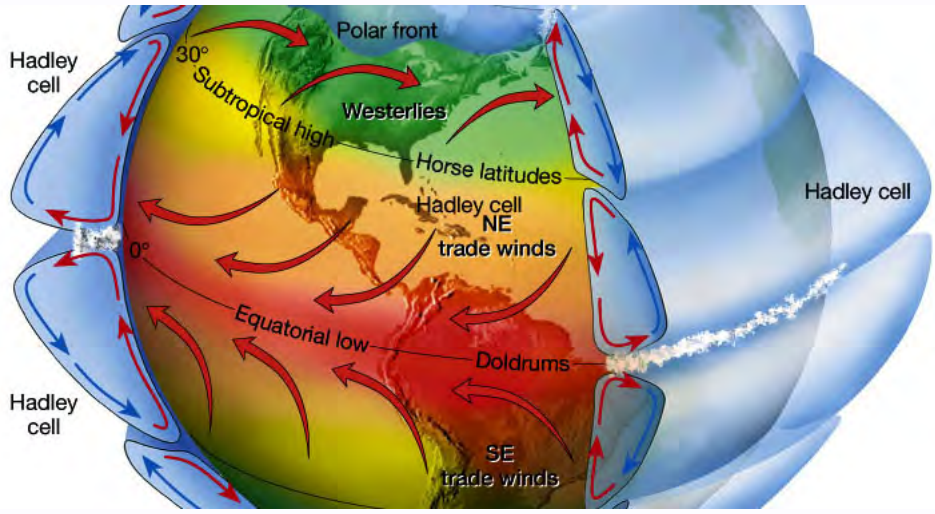
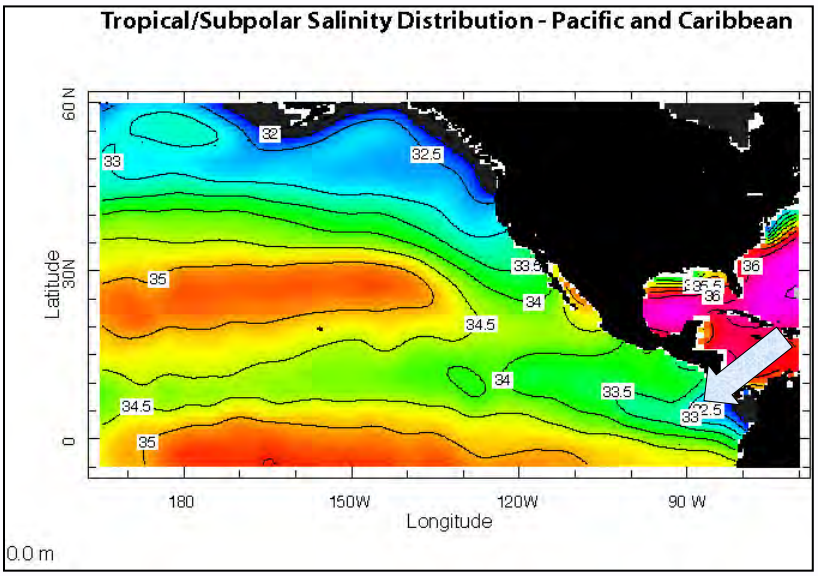


Atlantic is Saltier than the Pacific



http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NODC/.WOA98

What parameters control the carbon isotopic composition of the ocean?

**Important: Graduate Survival Guide for understanding CO_2 systematics, isotope equilibria and the carbon system in marine and freshwater environments:

Zeebe and Wolf-Gladrow, 2001, CO_2 in seawater: Equilibrium, kinetics, isotopes. Elsevier Press

Carbonate chemistry '101'

atmosphere

Aqueous carbonate speciation

$pCO_{2(g)}$ Henry's Law $pCO_2 = CO_{2(aq)}/K_H$

$H_2O + CO_{2(aq)} \rightarrow H^+ + HCO_3^- \leftarrow 2H^+ + CO_3^{2-}$

surface ocean

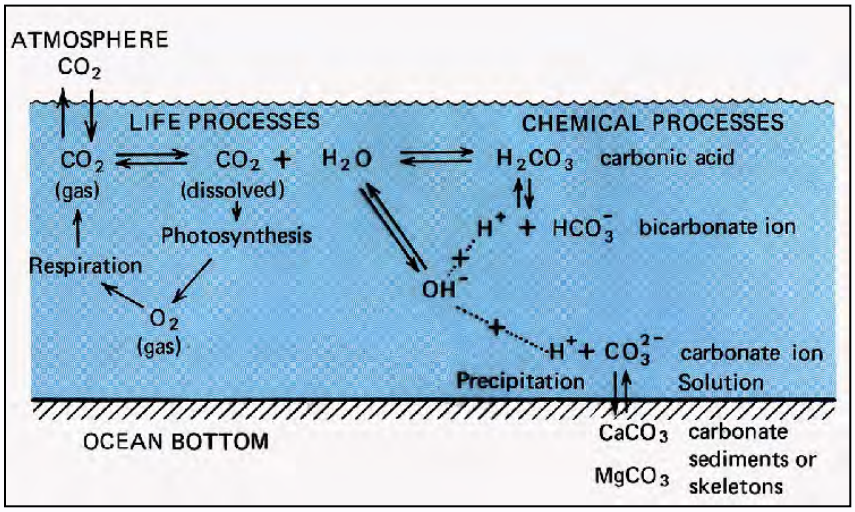
When CO_2 dissolves in seawater, the $CO_{2(aq)}$ concentration changes only slightly because the system is buffer by carbonate ions (CO_3^{2-}). CO_2 is scavenged according to the reaction:

$CO_{2(aq)} + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$

(A small part of the resulting HCO_3^- dissociates into CO_3^{2-} and H^+, lowing *p*H and hence 'ocean acidification'.)

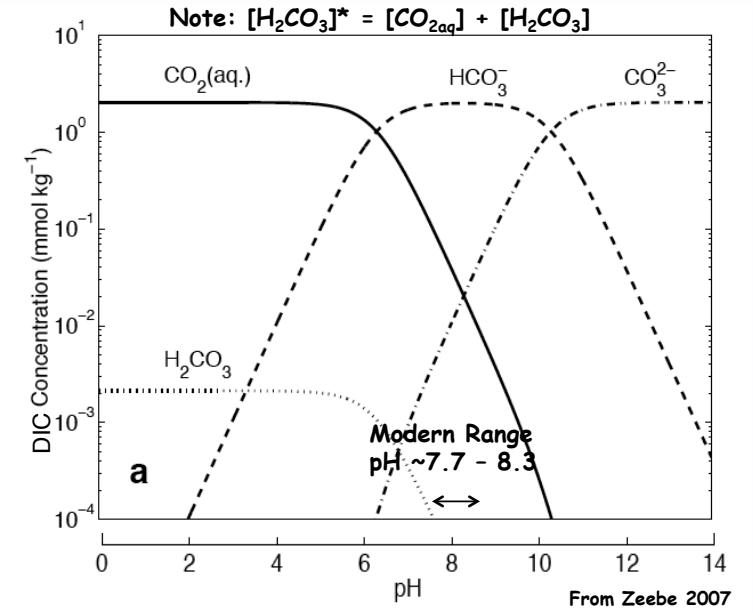
After Andy Ridgwell (2010)

Chemical and Biological Processes Control Carbon Cycling in the Oceanic Buffer System



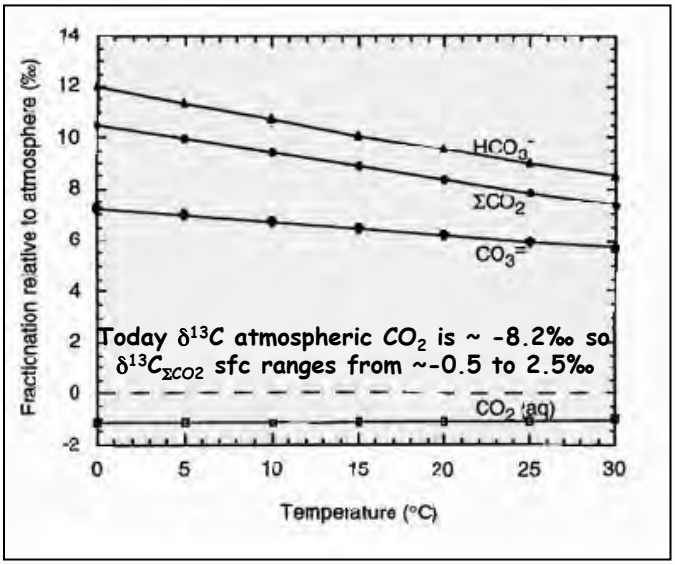
Bjerrum Plot of Dissolved Carbon Species in Seawater
Note: H_2CO_3* is only ~1-2% of DIC

Note: $[H_2CO_3]^* = [CO_{2aq}] + [H_2CO_3]$



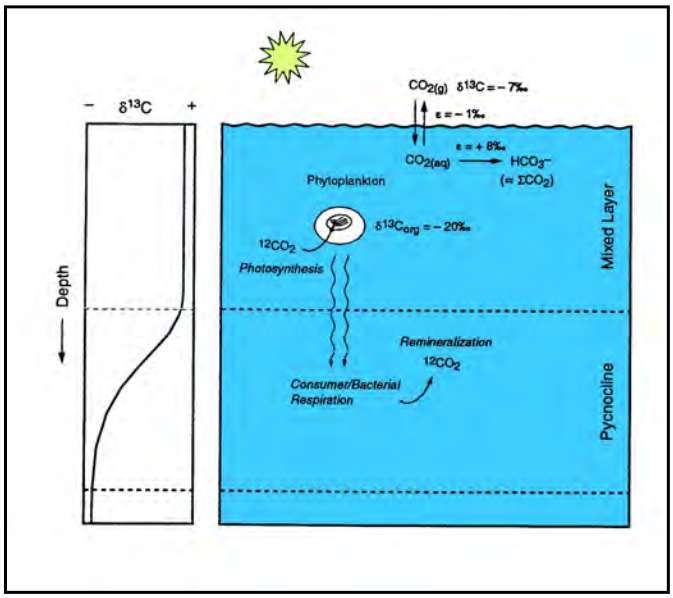
From Zeebe 2007

Physical mechanism controlling the $\delta^{13}C$ of ΣCO_2 (=DIC) in the ocean: *equilibrium fractionation* at the ocean surface



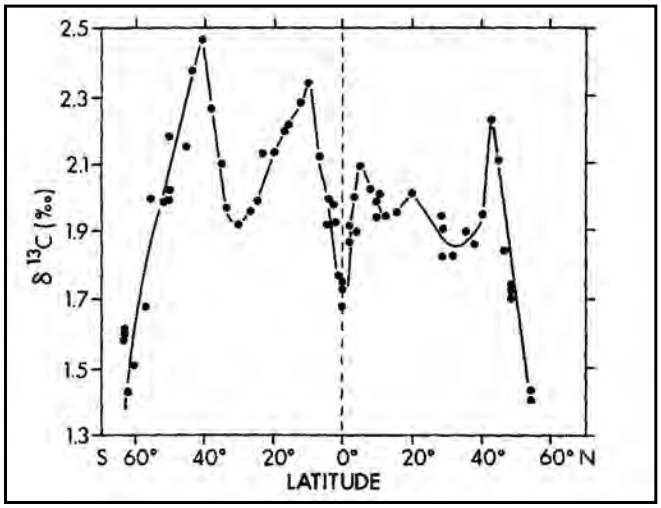
From Lynch-Stieglitz et al (1995); based on data from Zhang et al (1995)

Biological Pump Controls the Vertical Carbon Isotope Gradient in the Ocean

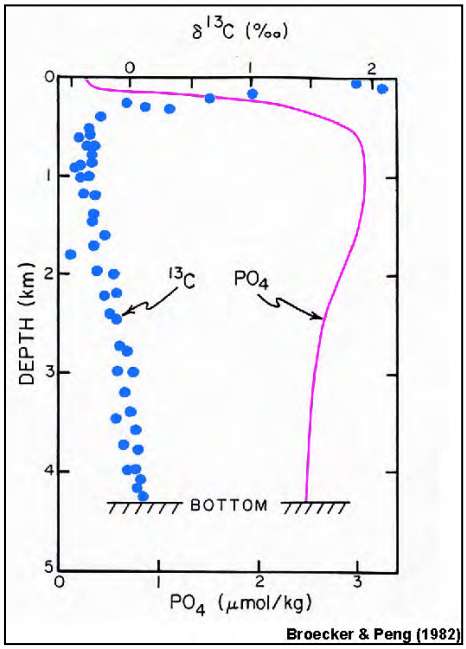


$\delta^{13}C_{DIC}$ of Surface Waters Reflects a Combination Of Physical and Biological Controls

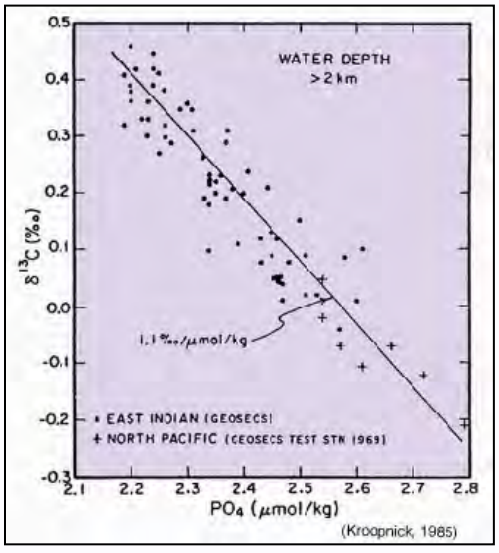
Pacific Meridional Transect along 120°W (pre 1980)



Vertical Distribution Of $\delta^{13}C_{DIC}$ and PO_4 In the North Pacific



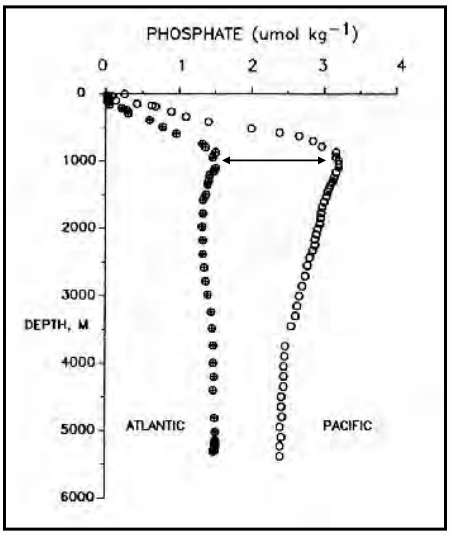
PO_4 and $\delta^{13}C_{DIC}$ covary linearly in the Ocean; $\delta^{13}C$ can be used as a Proxy for Dissolved Nutrients



m = 1.1‰ μmol^{-1} kg^{-1}

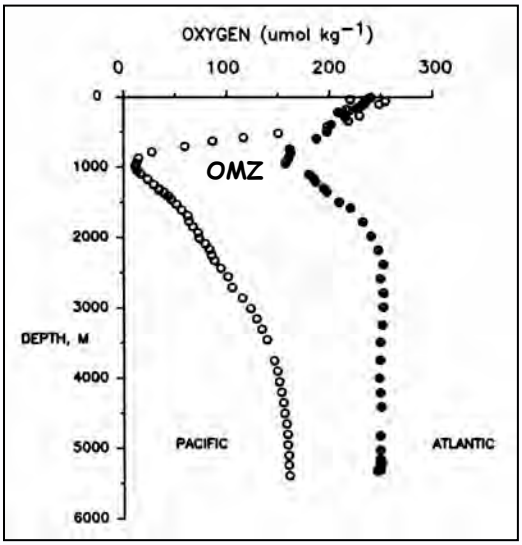
Effect is due to rather constant C:N:P relationship in marine organisms
Redfield Ratio - 106:16:1

What Causes Inter-ocean Differences in nutrients such as [PO_4] and other non-conservative tracers?



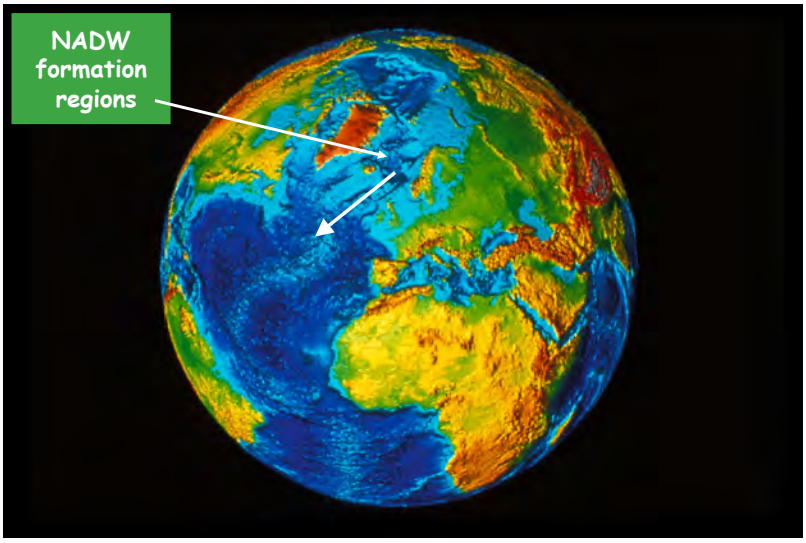
Vertical O_2 profile reflects density structure of ocean with Upper pycnocline and oxygen minimum zone (OMZ)

Subtropical Pacific

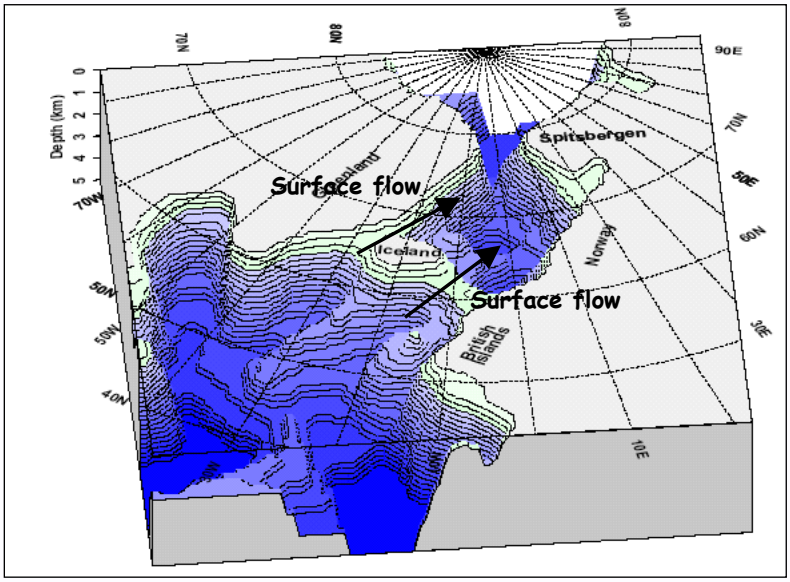


Subtropical Atlantic

Deep-water Thermohaline Circulation is the Lower Limb of the Oceanic Conveyor Belt

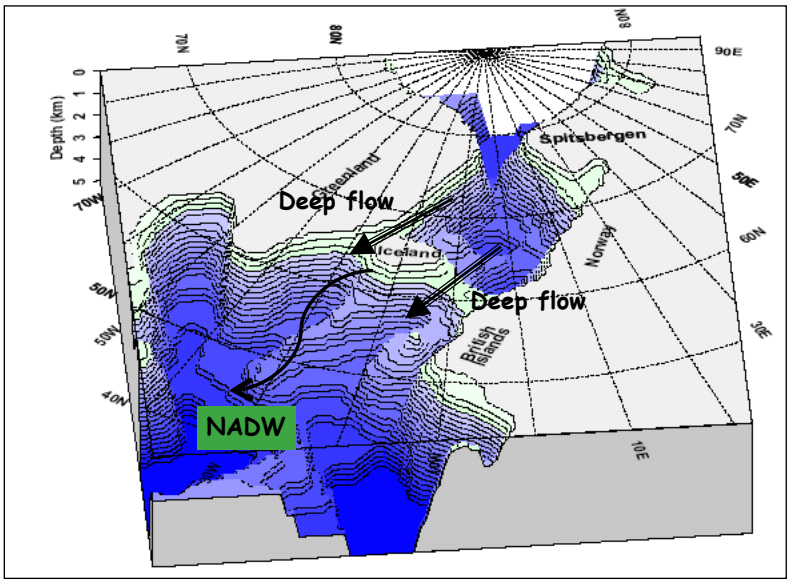


Iceland Faeroe Ridge w/Norwegian Sea and N. Atlantic



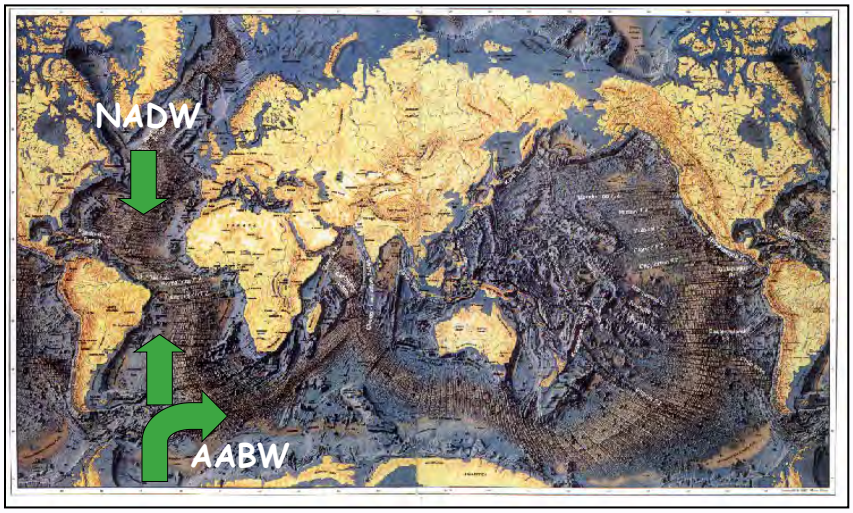
Schafer-Neth 1998

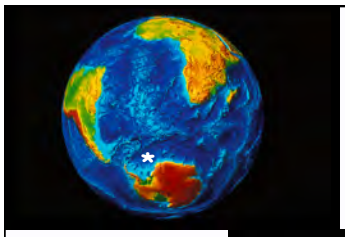
Iceland Faeroe Ridge w/Norwegian Sea and N. Atlantic



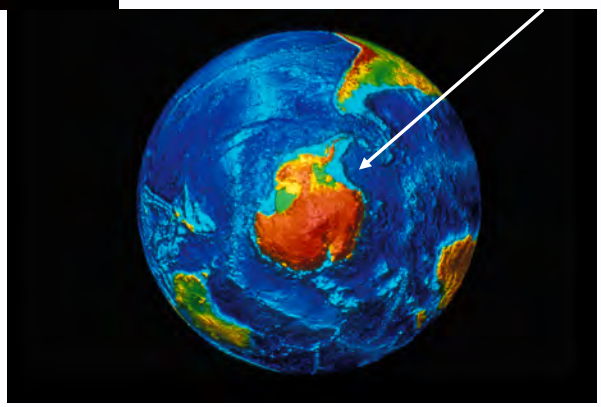
Schafer-Neth 1998

Deep-water Thermohaline Circulation is the Lower Limb of the Oceanic Conveyor Belt

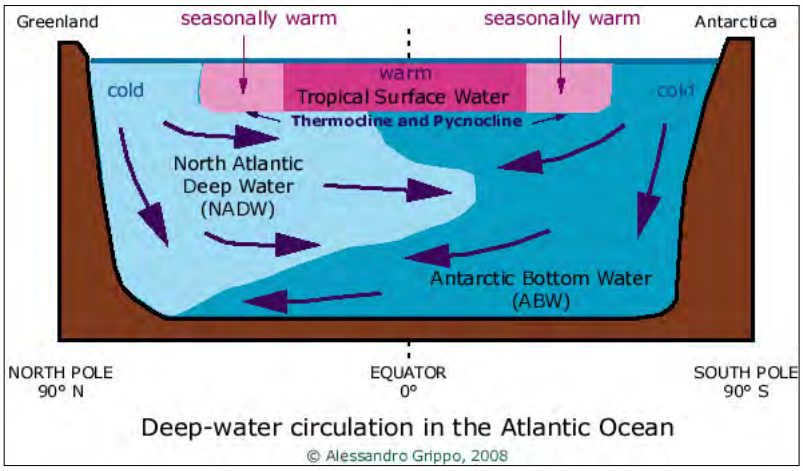




Weddell Sea AABW formation region; primarily during the winter when salt gets excluded during sea ice formation

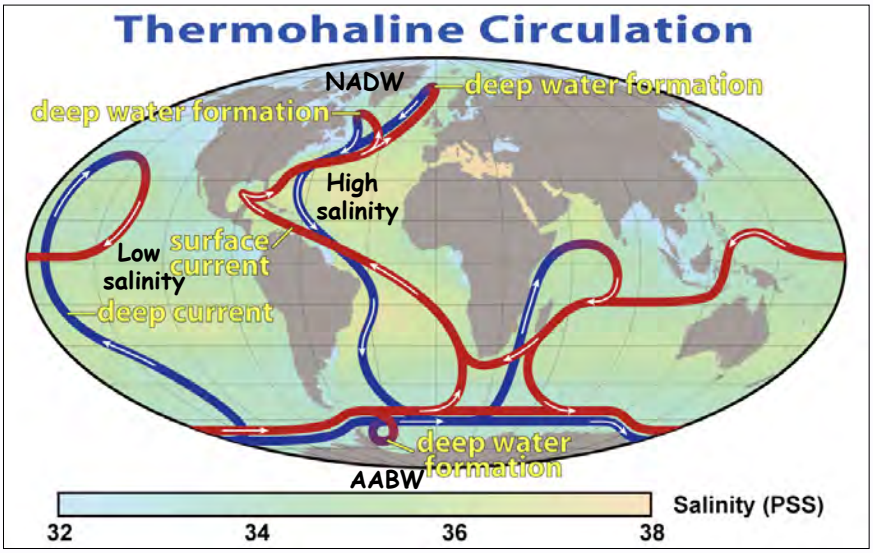


Profile of Atlantic Circulation; Vertical distribution is controlled by density

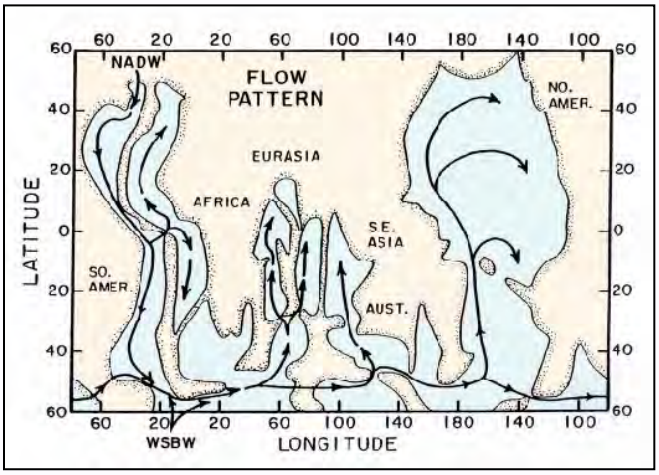


http://homepage.smc.edu/grippo_alessandro/oce1.html

Meridional Overturning Circulation is ultimately controlled by the density of surface waters in high latitude source regions



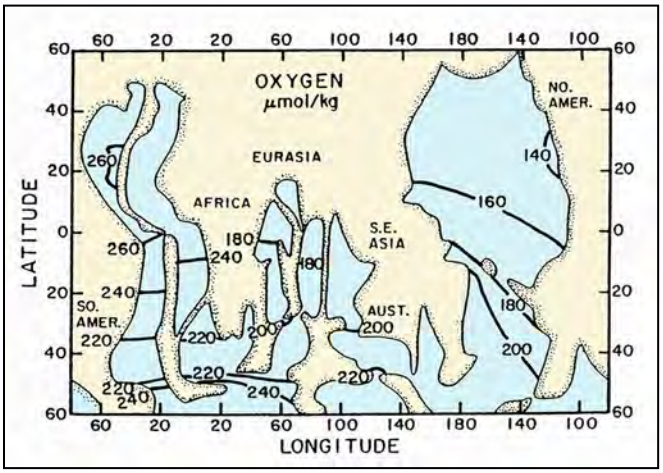
If we remove the upper 3 km of ocean, the deep seafloor looks like this - the mid-ocean ridges now divide the ocean basins



Broecker and Peng (1982)

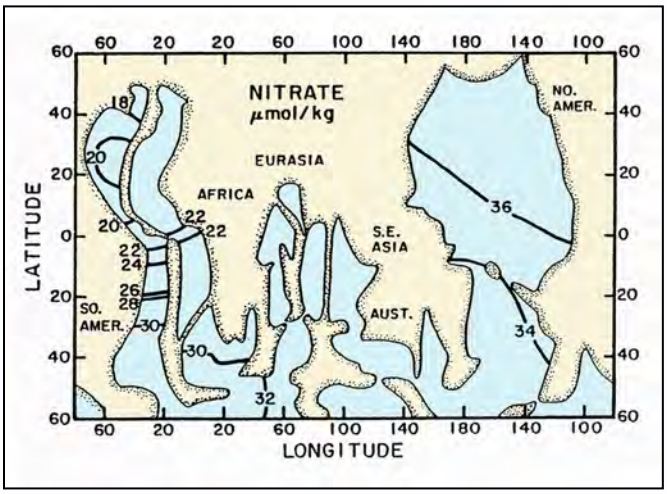
The gradients link flow paths with the biological pump

O_2 Concentration (μmol/kg)



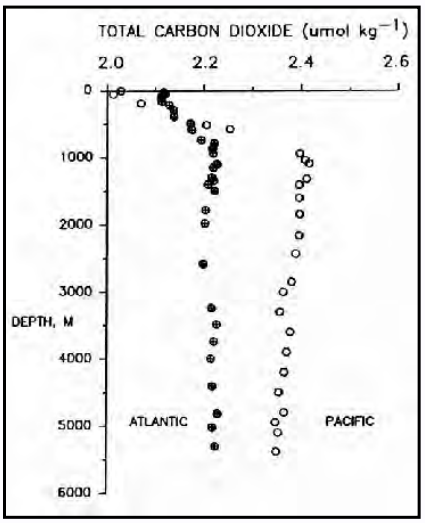
Broecker and Peng (1982)

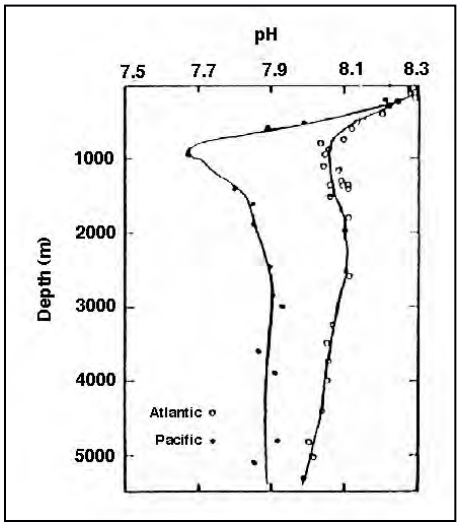
Nitrate Concentration (μmol/kg)



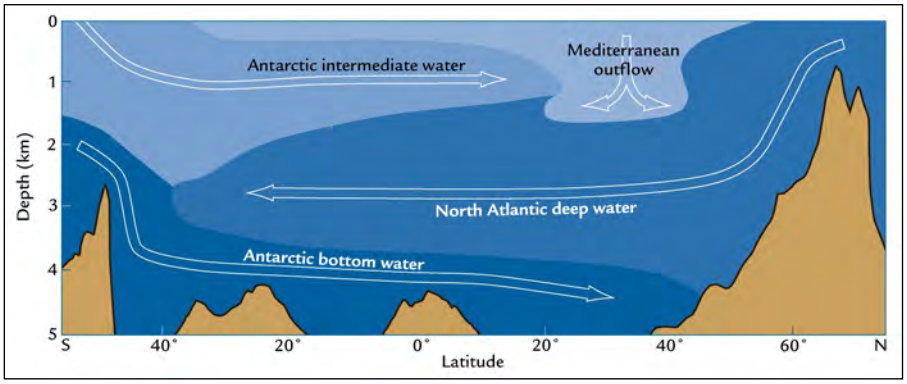
Broecker and Peng (1982)

High DIC & low pH are found in the OMZ where respiration dominates



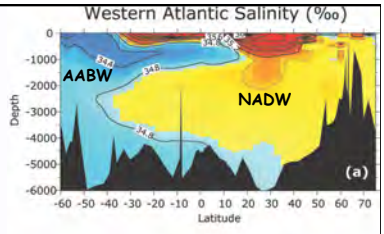


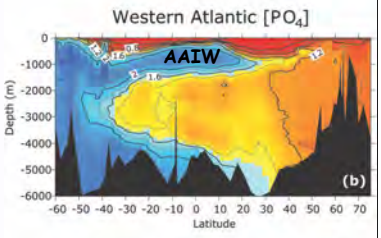
Now, visualize the deepwater circulation in the Atlantic in Geochemical space…..

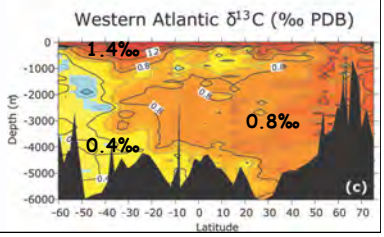


The $\delta^{13}C_{DIC}$ traces deep water currents and flowpaths because deep waters accumulate ^{13}C-depleted respired CO_2 during their transit through the Atlantic and around the Earth…..

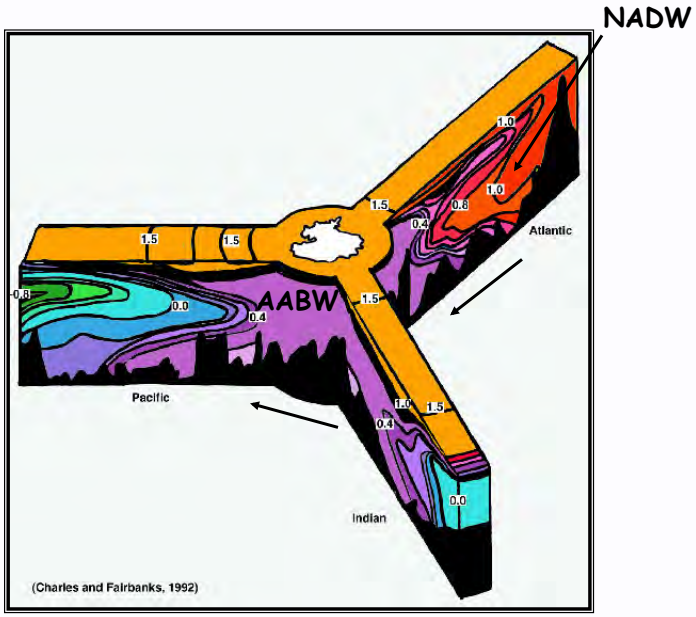
Curry and Oppo 2012





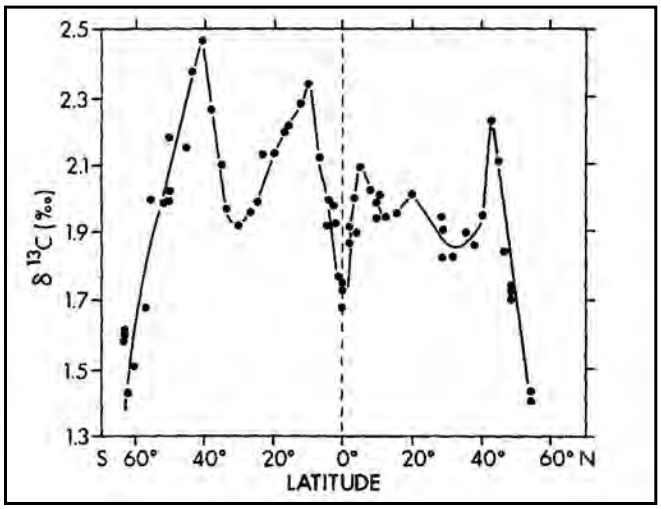


$\delta^{13}C_{DIC}$ records the flow path and aging of thermohaline waters along the oceanic conveyor belt

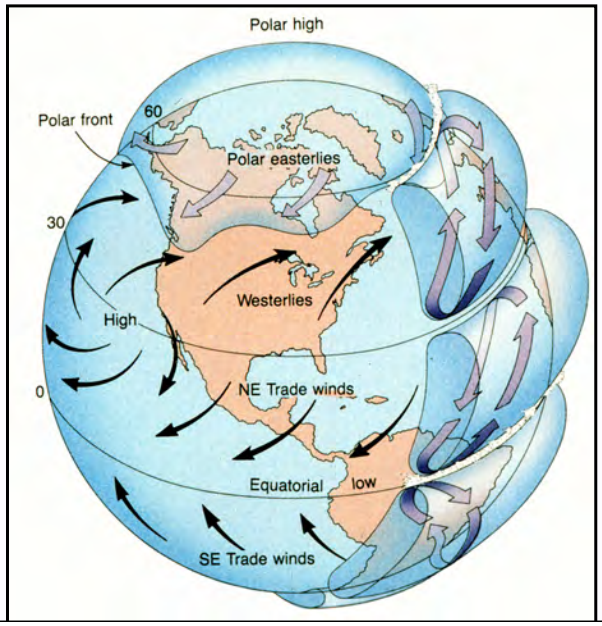


$\delta^{13}C_{DIC}$ of surface waters – why is there a $\delta^{13}C_{DIC}$ low on the equator?

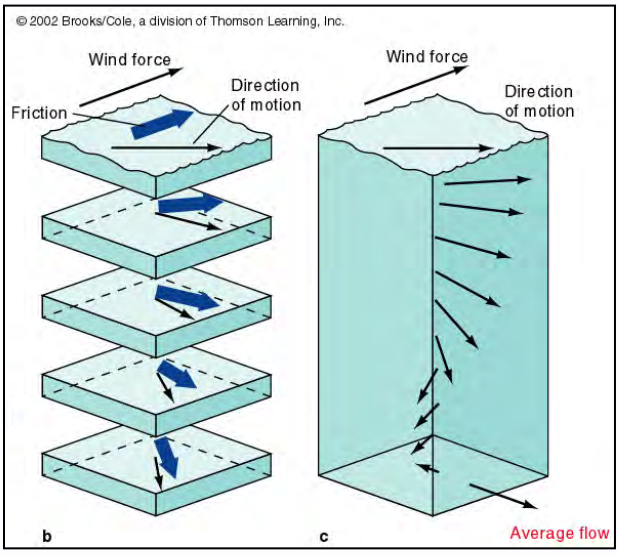
1978 Pacific Meridional Transect along 120°W



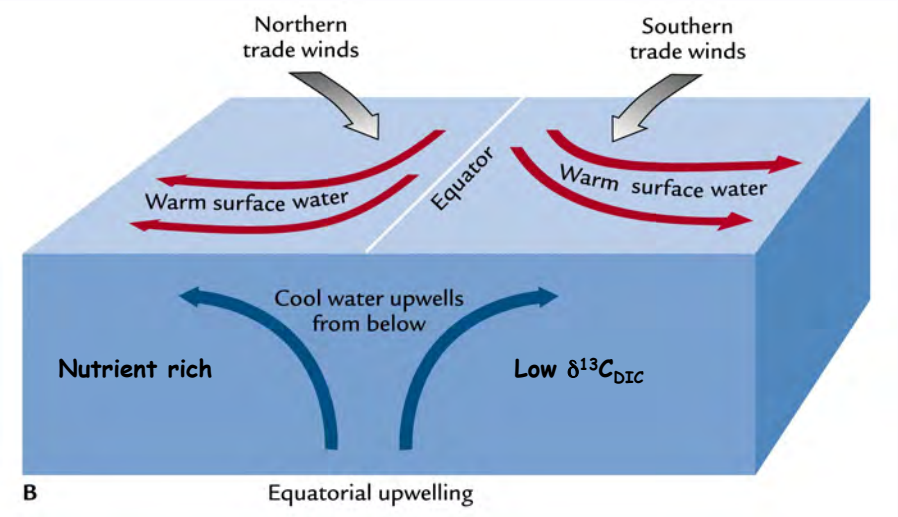
The explanation lies with the impact of atmospheric wind systems on the ocean surface at the equator



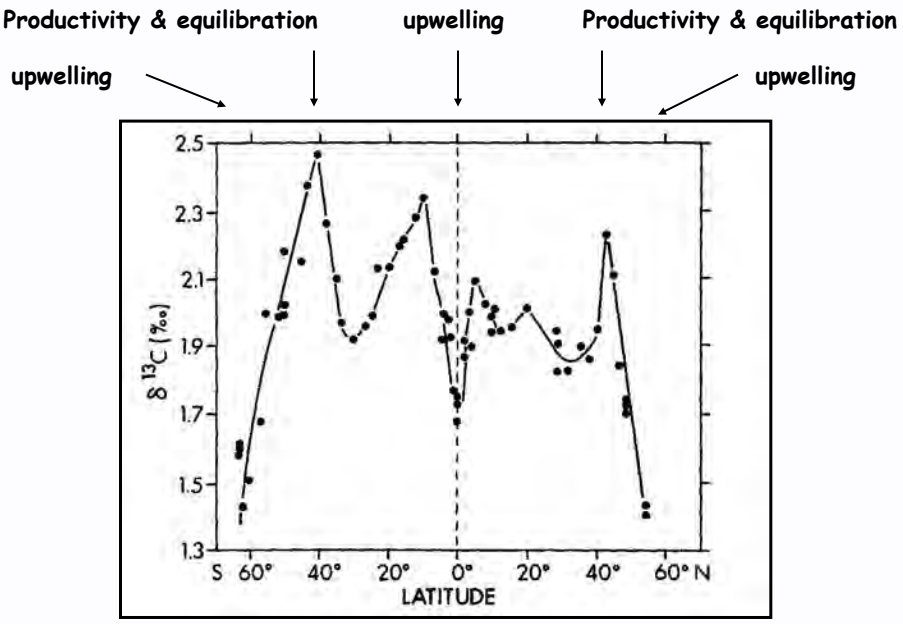
Ekman Transport/Pumping: Net water movement is 90° right (N hemisphere) or left (S hemisphere) of the wind



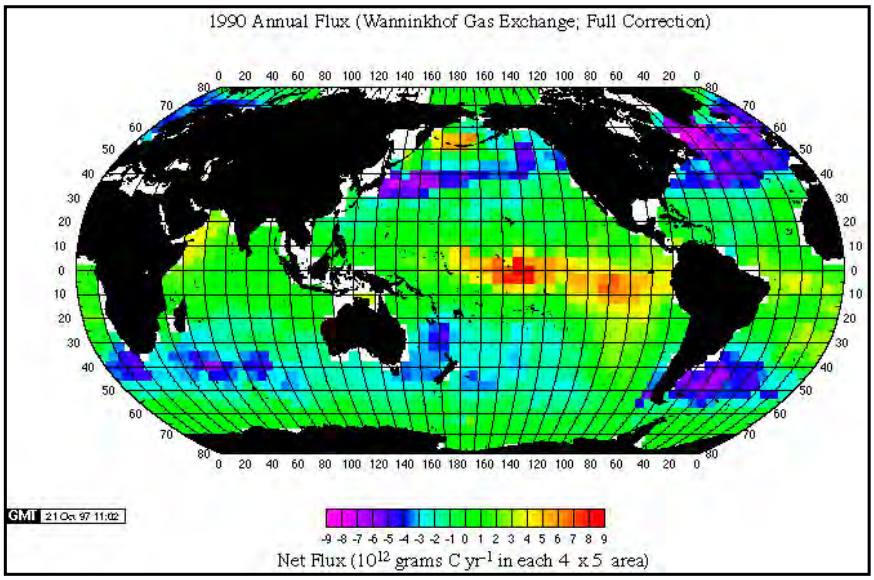
Ekman transport - causes equatorial upwelling



Ruddiman (2001)

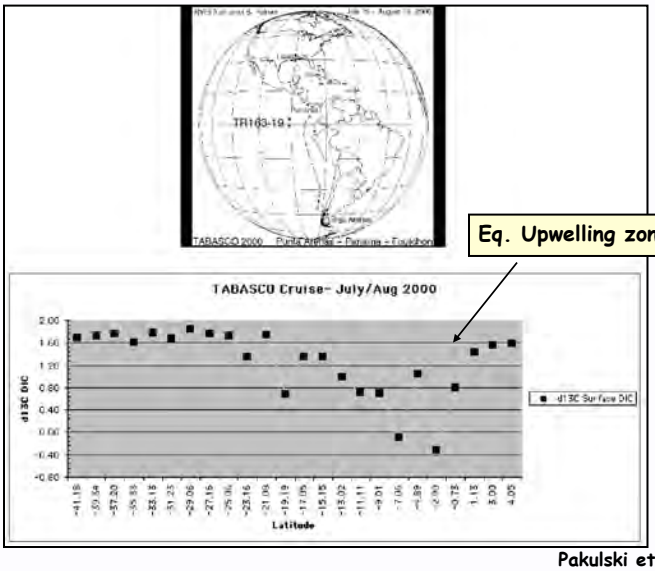


ΔpCO_2 (seawater-air); Upwelling zones (red) and regions of biological productivity (blue)

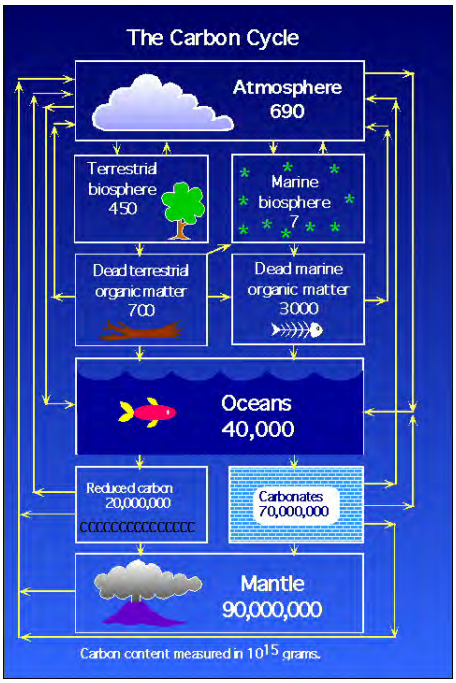


Takahashi et al. (1997)

$\delta^{13}C_{DIC}$ Sfc Water data in Peru Current From 41°S to the Panama Canal



Pakulski et al (2007)

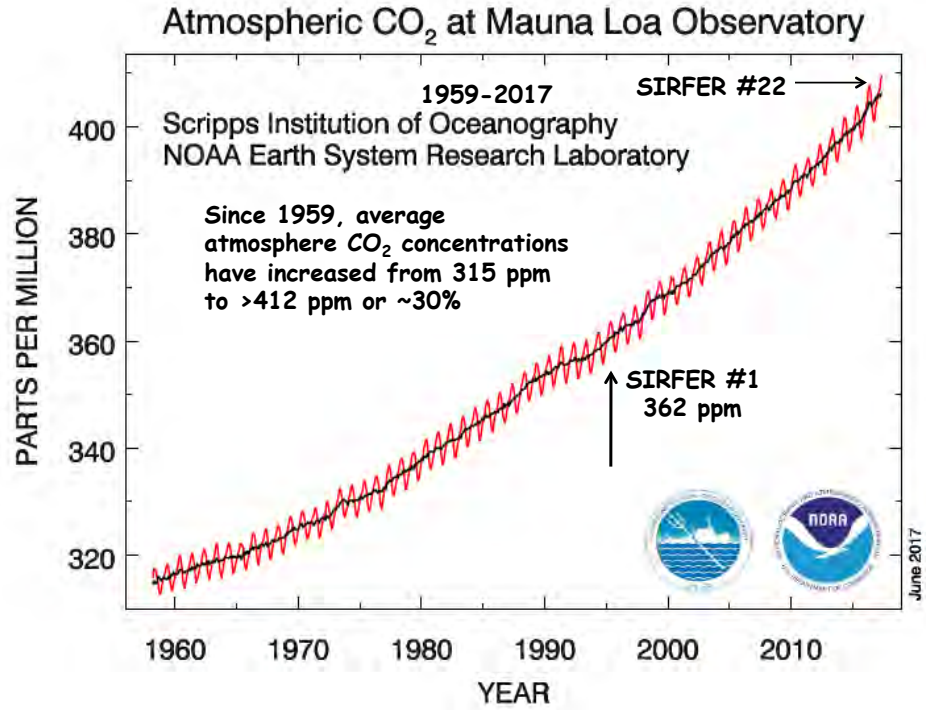


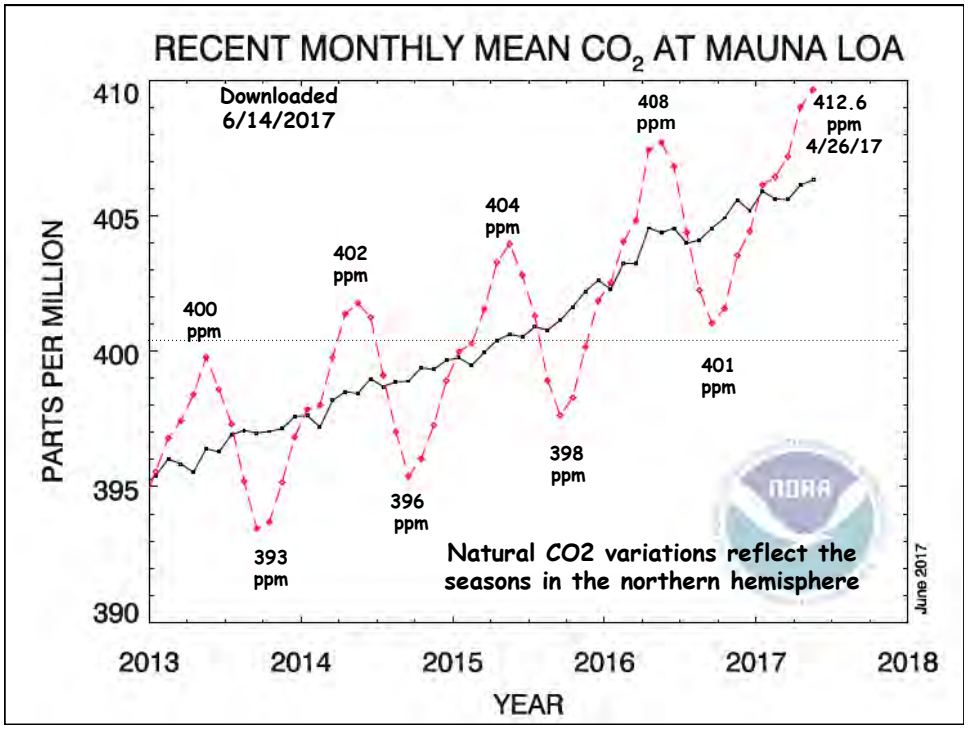
Atmospheric pCO_2 'should' reflect balance b/n oceanic upwelling and productivity

~45,000 GT (=10^{15} grams) of C are available for carbon cycling on < 10^6 year time scales

Carbon sequestered in the mantle, carbonate rocks and hydrocarbons cycle too slowly to influence the sub-million year climate cycle

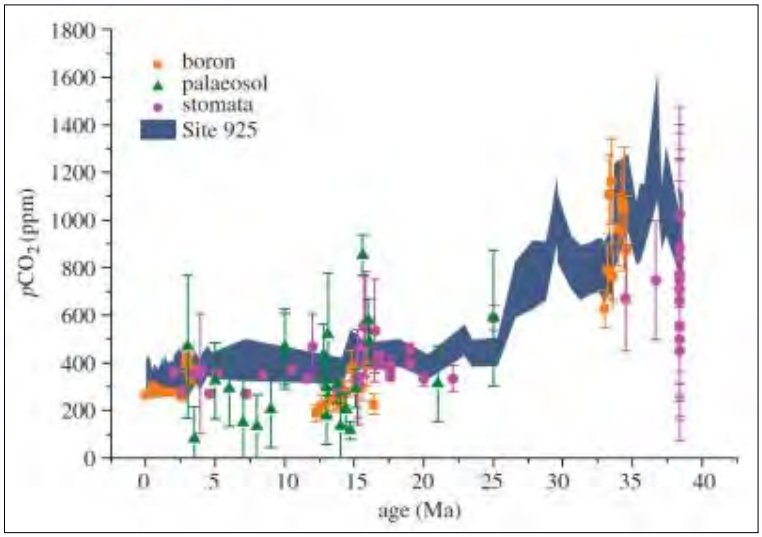
http://www.geo.cornell.edu/geology/classes/Geo101/graphics/c_cycle.jp





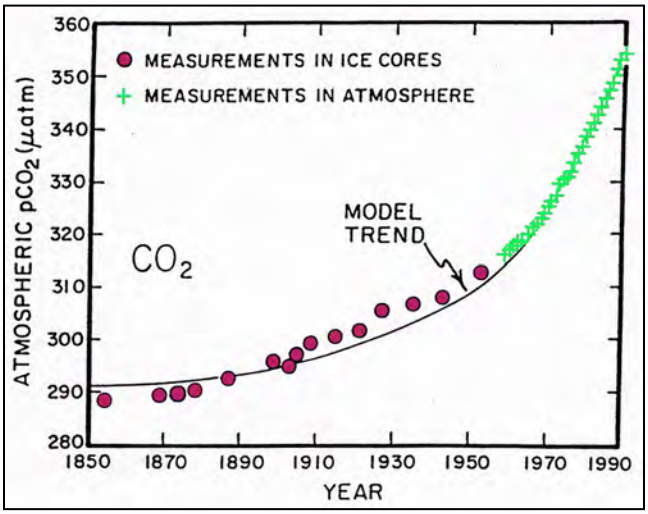
Rate of change - atmospheric CO_2 through time

Reconstructed atmospheric pCO2 from different proxies; The last 400 ppm world was during the Pliocene 2-5 mybp…..sealevel was likely 10-15 m higher than today

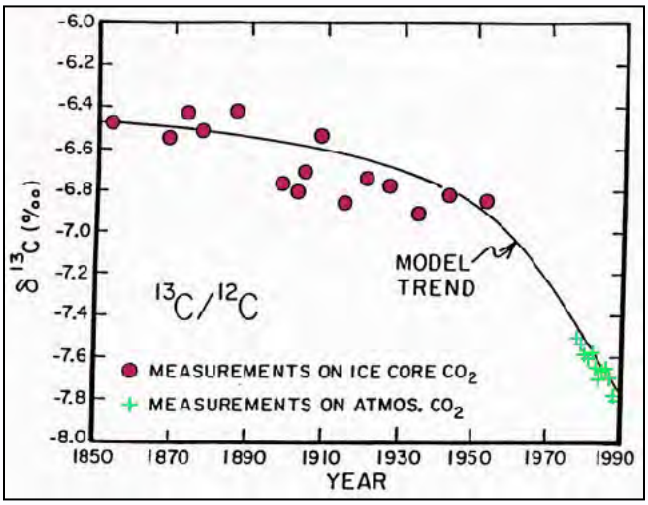


http://people.earth.yale.edu/cenozoic-evolution-carbon-dioxide

Atmospheric pCO_2 1850-1990 from ice core data – what about the geochemical record?

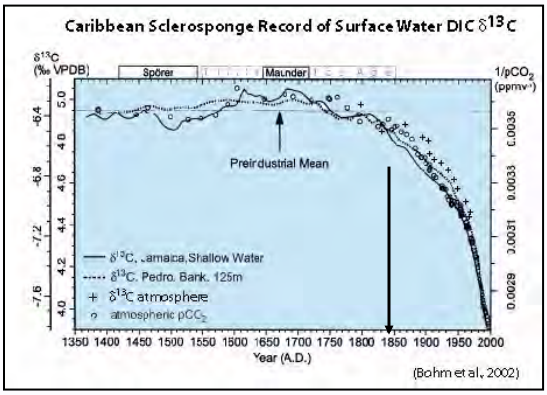


$\delta^{13}C$ of atmospheric CO_2 from ice cores and Mauna Loa atmospheric measurements (1850-1990)

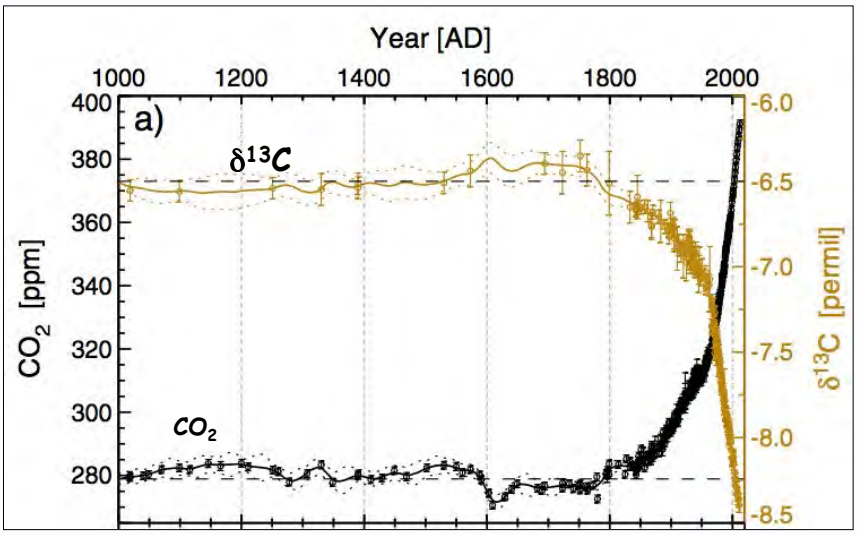


Impact on oceanic $\delta^{13}C_{DIC}$ is clear; Since 1800 surface $\delta^{13}C$ has decreased by >1.0‰

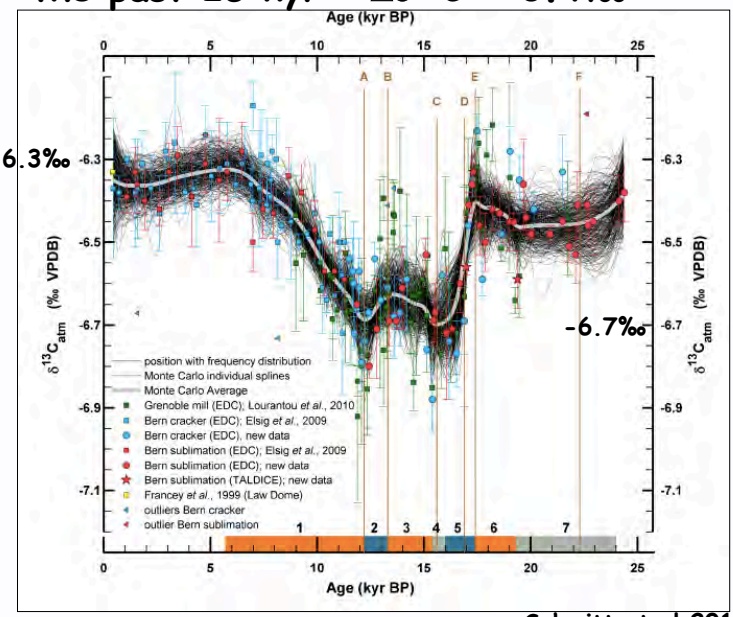
Calcareous Sclerosponge record; extension rate is ~ 200 μm/yr



Timing of Ice Core CO_2 change vs $\delta^{13}C$ of CO_2 in sclerosponge aragonite



Atmospheric $\delta^{13}C$ from Antarctic ice cores for the past 25 kyr – $\Delta\delta^{13}C$ ~ 0.4‰



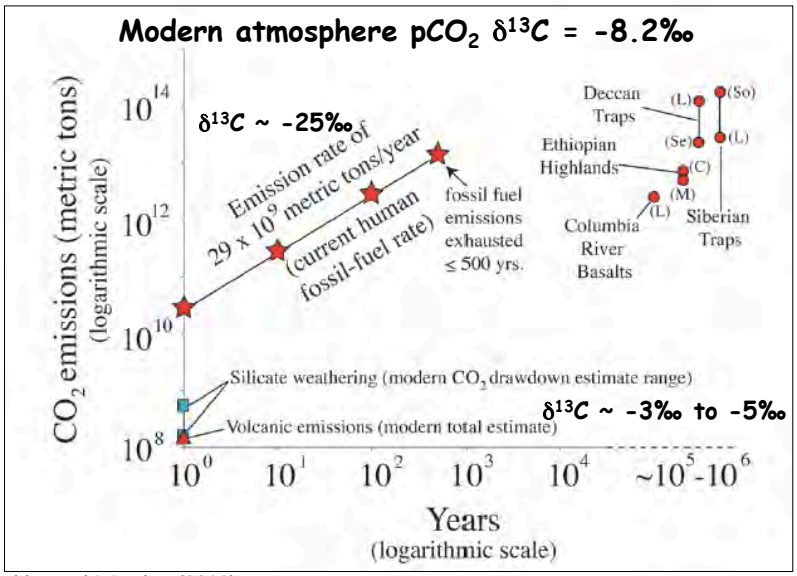
Modern $\delta^{13}C_{atm}$ = -8.2‰

↓

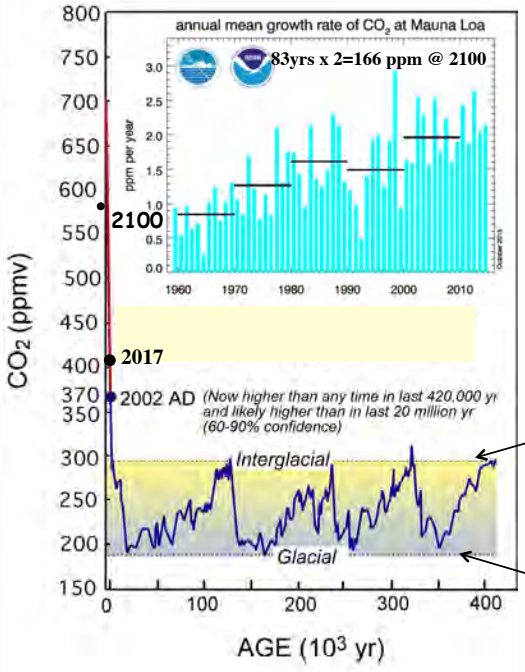
Schmitt et al 2012

How do we know CO_2 rise is due to anthropogenic activities?

Comparison of human emissions vs modern volcanic CO_2 release and historical basalt flow events



Kidder and Worsley (2012)



Why do we care about elevated greenhouse gases such as CO_2?

Interglacial CO_2 maximum

280 ppm

180 ppm

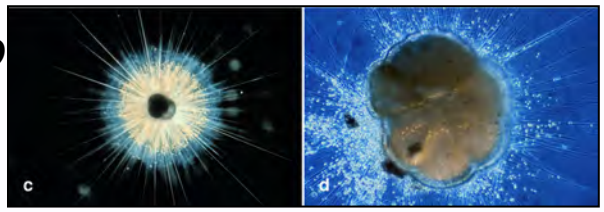
Glacial CO_2 minimum

Paleoceanography and the geochemistry of $CaCO_3$

Foraminifera Shell Calcite ($CaCO_3$)
Marine Zooplankton

G. ruber *G. menardii*

$^{18}O/^{16}O$



$^{13}C/^{12}C$

- $$\delta^{18}O(^{13}C) = \frac{(^{18}O/^{16}O_{sample} - ^{18}O/^{16}O_{std})}{^{18}O/^{16}O_{std}} \times 1000$$

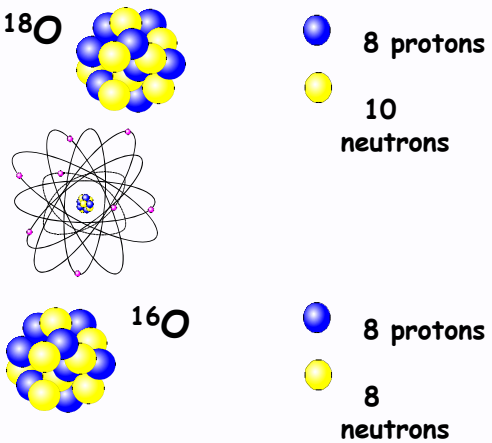
562 *Urey :*

The Thermodynamic Properties of Isotopic Substances.

Liversidge Lecture, Delivered before the Chemical Society in the Royal Institution on December 18th, 1946.

By Harold C. Urey.

(Institute of Nuclear Studies, University of Chicago.)



1948, *Science*

Oxygen Isotopes in Nature and in the Laboratory

Harold C. Urey

Institute for Nuclear Studies, University of Chicago

small differences make possible the concentration and separation of the isotopes of some of the elements and may have important applications as a means of determining the temperatures at which geological formations were laid down.

Oxygen Isotopes and the Geosciences - University of Chicago circa 1950

Harold C. Urey; Nov 5, 1948
Science, Vol. 108

Oxygen Isotopes in Nature and in the Laboratory

Harold C. Urey

Institute for Nuclear Studies, University of Chicago

THAT THE ELEMENTS CONSIST OF ATOMS having different atomic weights was discovered in 1911 by Fayans and Soddy as a result of the study of radioactive elements which occur in nature. It was found that two varieties of elements could be secured having different radioactive properties but otherwise chemically identical in every respect. The theory of radioactive disintegration of uranium and thorium showed that these varieties of elements must have different atomic weights. In particular it was found, as a result of the very careful atomic weight determinations of Theodore Richards, that samples of lead isolated from different uranium minerals had different atomic weights, and, in particular, that samples of lead isolated from thorium minerals had atomic weights approaching 208, whereas lead isolated from uranium minerals had atomic weights approaching 206. Sir J. J. Thompson showed that charged atoms moving through *fields* electrical and magnetic fields should be separated if they have different ratios of charge to mass, and hence the isotopes of the elements should be separated by such a process. He determined that this was the case for the element neon, which is monoisotopic, and hence showed that ordinary elements also consist of *mixtures* of atoms of different atomic weights.

It is now known that there are more than 800 varieties of atoms which make up our 96 known elements. Most of these are radioactive and have been produced by artificial means. We have found that a few elements exist only in radioactive form and thus are constantly disappearing and have been doing so since the earth's crust was created. Some have completely disappeared from the earth's crust and therefore must be made in our laboratories today. In this discussion I shall largely limit myself to one of the ordinary elements, namely, oxygen. Table 1 shows a very limited number of these varieties of atoms, those for the first 10 elements of the present periodic system. The stable isotopes are printed in heavy type and the radioactive ones in light type. These elements are very important indeed, since they sustain several of the elements necessary for living processes. Also, oxygen is the most abundant element in the surface layer of the earth, namely, the layer with which we come most in contact.

This lecture was presented on the evening of September 10 in the Presidential Ballroom of the Statler Hotel, Washington, D. C., during the AAAS Centennial Celebration.

The interest in these variations of atomic species is of several kinds. In the first place, there are the purely physical properties which physicists are studying today. During the last 25 years particularly it has been possible to unravel the laws governing the behavior of the electrons in the outer shells of the atom, and at the present time the center of the stage

TABLE 1

ISOTOPES OF THE FIRST 10 ELEMENTS

Symbol	Atomic No.	Masses
H(D)	1	1, 2, 3
He	2	3, 4, 6
Li	3	6, 7, 8
Be	4	7, 9, 10
b	5	10, 11, 12
C	6	10, 11, 12, 13, 14
N	7	12, 14, 15, 16
O	8	13, 15, 17, 18, 19
F	9	17, 18, 19, 20
Ne	10	18, 20, 21, 22, 23

of physics is held by the questions dealing with the structure of the nucleus of atoms. How are the fundamental parts held together, and what are the energy relations? The properties which are important in connection with this are the lifetimes of the radioactive nuclei, the energy of binding of the elementary particles, the nuclear spins or nuclear angular momenta, and the magnetic moments. Physicists are interested in the relative abundances of these atoms which are stable, how these varieties of atoms were produced, and what was the origin of the universe.

USES OF ISOTOPIC SPECIES

But these are many uses of these isotopic species for other sciences and such uses have been discussed many times in recent years. The use as tracers or indicators was discovered by Prof. Hevesy over 30 years ago, and the general outlines of the possible uses of such elements were made by him using naturally radioactive elements. It is, of course, natural that the many recently discovered artificial radioactive elements should be useful in this connection, especially in view of the fact that effective radioactive tracers for many of the common elements have now been discovered. These are few for which there are no satisfactory tracers of this kind, but it has been possible to separate the stable isotopes in the case of these el-

SCIENCE, November 5, 1948, Vol. 108

469

Sam Epstein et al., April 1951
Bull. Geol. Soc. Amer., Vol. 62

BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA

VOL. 62, PP. 417-426, 5 FIGS. APRIL 1951

CARBONATE-WATER ISOTOPIC TEMPERATURE SCALE

BY SAMUEL EPSTEIN, RAFAEL BUCHSBAUM, HEINZ LOWENSTAM, AND HAROLD C. UREY

ABSTRACT

A relationship between temperature and relative O^{18} abundance in calcium carbonate in marine shells has been determined. If the relative O^{18} abundance of the water in which the shell grew is known, the temperature can be determined to an accuracy of ±1°C. The relative O^{18} contents of marine waters increase with salinity and, in the case of surface marine waters, with salinity and temperature.

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Relative O^{18} contents of marine waters	418
Isotope temperature scale	420
Marine shells selected and their growth temperatures	420
Extraction of carbon dioxide from marine shells, the problem of impurities, and results	422
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Conclusions	425
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ILLUSTRATIONS

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INTRODUCTION

Urey *et al.* (1951) discuss a method for measuring paleotemperatures that depends on a variation in the oxygen −18 abundances in calcium carbonate deposited in the sea. McCrea (1949; 1950, p. 849) investigated the isotopic composition of calcium carbonate precipitated isotopically from water and determined the temperature coefficient for the abundance of O^{18} in calcium carbonate relative to water as a function of temperature; he found a value of ~5.4°C permil increase in the ratio of O^{18} to O^{16} in the calcium carbonate. McCrea gave a calculation for this quantity including estimates of the effect of the translational and hindered rotational degrees of freedom in the solid state on the distribution functions, and arrived at a value of 3.1. Assuming free rotation in the solid state Urey (1947, p. 562) calculated a value of ~3.7 for the same quantity. This research aims to determine this quantity and to set up an equation relating temperature to the difference in isotopic composition of samples of carbon dioxide prepared from organically precipitated calcium carbonate and an arbitrarily selected reference sample of carbon dioxide.

The relationships between temperature and O^{18} abundance in calcium carbonate from marine shells and that from inorganic calcium carbonate precipitates are similar. But a number of special considerations must be taken into account in the case of marine shells to find the temperature of the sea water in which the marine animals lived: (1) the isotopic composition of the oxygen of the oceans; (2) the collection of marine shell-bearing animals which grew in water of constant and known temperatures; and (3) the problem of impurities in the carbon dioxide prepared from marine shells.

ACKNOWLEDGMENTS

We are indebted to The Geological Society of America and to the American Petroleum In-

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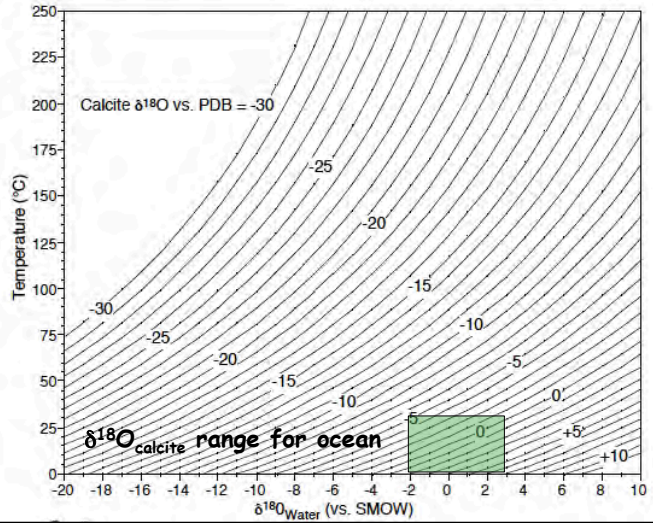
Railsback's *Some Fundamentals of Mineralogy and Geochemistry*

Oxgyen isotope composition of calcite as a function of temperature and water composition

These plots show the oxygen isotope composition of calcite precipitated at isotopic equilibrium from water of the O isotope composition shown on the X axis and at the temperature shown on the Y axis. $\delta^{18}O$ of calcite was calculated using the equation of Friedman and O'Neil (1977) whereby $10^3 \ln\alpha = \frac{2.78 \times 10^6}{T^2} - 2.89$ with T in Kelvins.



Try to imagine being a grad student/researcher in Harold

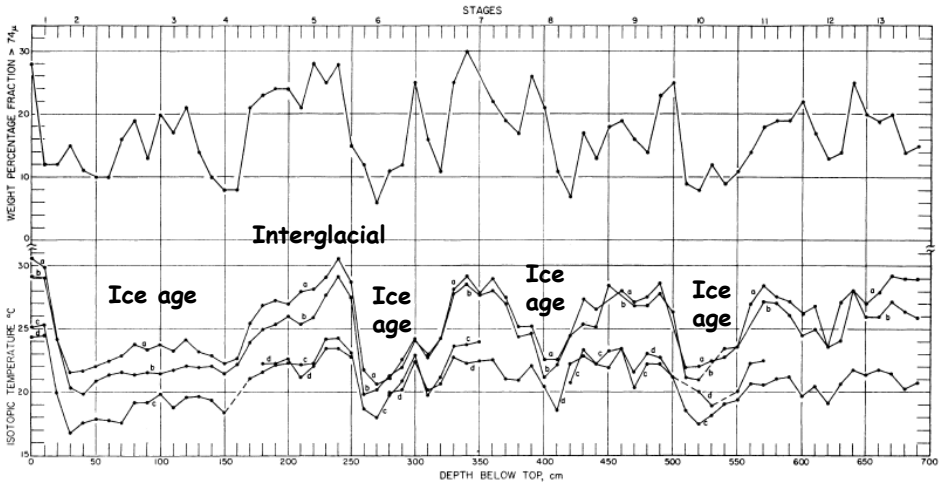
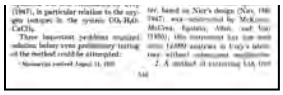


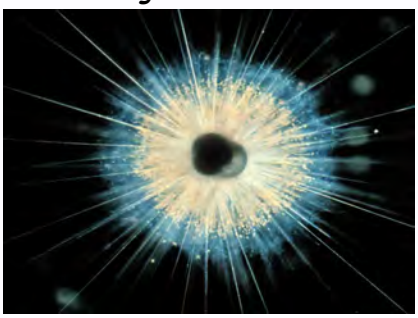
FIG. 2.—Core A179-4: percentages of the fraction larger than 74 μ and isotopic temperatures obtained from *Globigerinoides rubra* (*a*), *Globigerinoides sacculifera* (*b*), *Globigerina dubia* (*c*), and *Globorotalia menardii* (*d*).

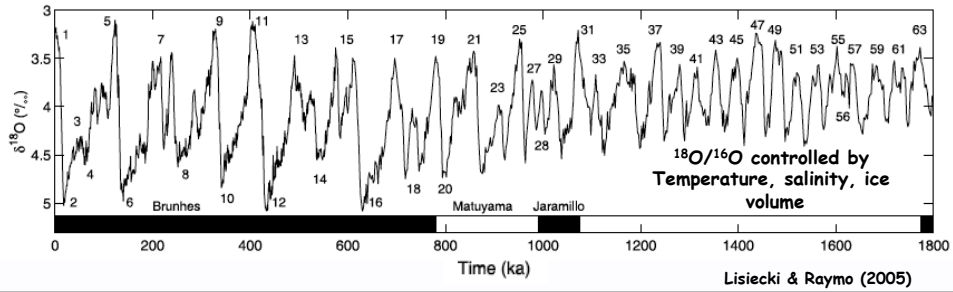
Harold C. Urey



Foraminifera ooze from deep sea sediment; each shell is the size of a pinhead (0.5mm)

Globigerinoides ruber





Lisiecki & Raymo (2005)

Factors Affecting Calcite/Aragonite Oxygen Isotopes

- $\delta^{18}O_{water}$:

  a) Salinity; evaporation vs precipitation
  b) Latitude
  freshwater systems - Rayleigh Distillation;
  marine systems – ice melt, coastal runoff

- Temperature

  a)Equilibrium Fractionation

- pH:

  a) Carbonate Ion Effect; photosyn vs resp.
  b) Physiology – photosynthesis (symbionts)

Factors Affecting Calcite/Aragonite Carbon Isotopes

- $\delta^{13}C_{DIC}$ (ΣCO_2):

  a) Ocean Temperature (air-sea exchange)
  b) Community Productivity/Respiration
  c) Ocean Circulation – Sources/Sinks

- Physiology/Biology/Vital Effects

  a) Irradiance – Symbiont photosynthesis
  b) Temperature – Respiration

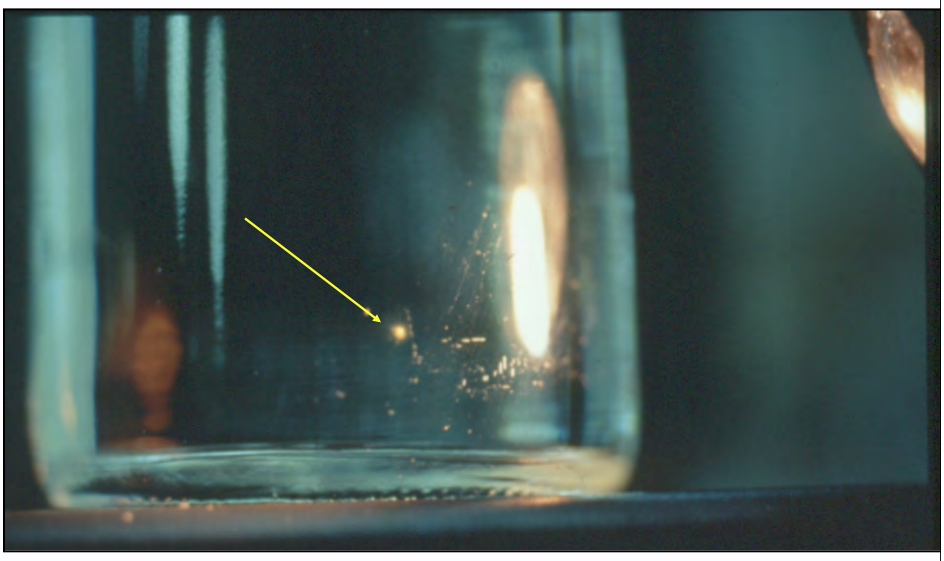
- Ocean Chemistry:

  a) pH or $[CO_3^{2-}]$ – Carbonate Ion Effect

Unraveling the past - Linking microfossils and their living counterparts with laboratory experiments

Big Fisherman Cove – Wrigley Marine Science Center

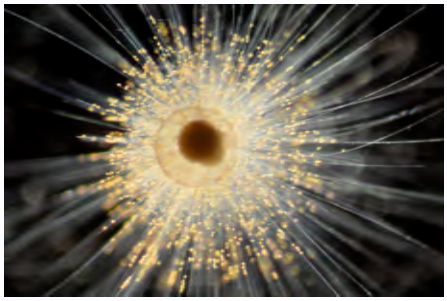
Orbulina universa in Culture Vessel



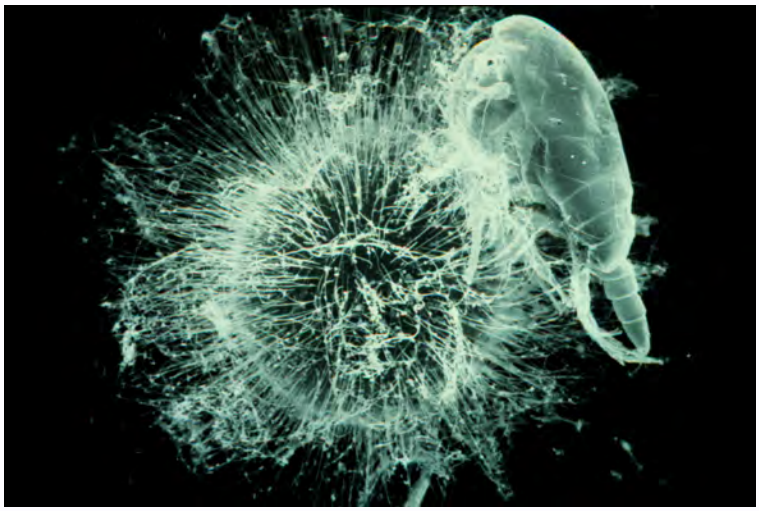
One of the most important climate archives - the $CaCO_3$ shells of planktonic foraminifera

Pre-sphere, trochospiral shell form of *O. universa*

Spherical chamber form of *O. universa*



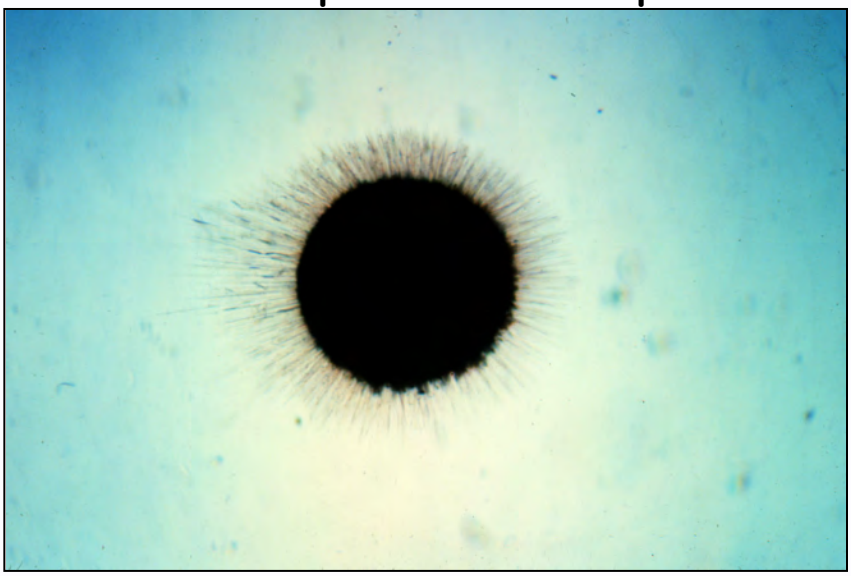
Foraminifera are single celled protozoa that feed on zooplankton such as copepods



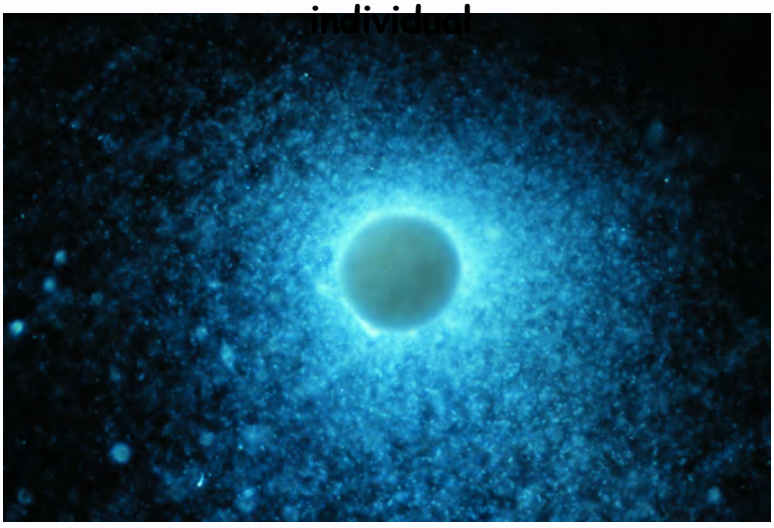
Spero and Parker, 1985

***Orbulina universa* with *Artemia* brine shrimp nauplius after feeding**

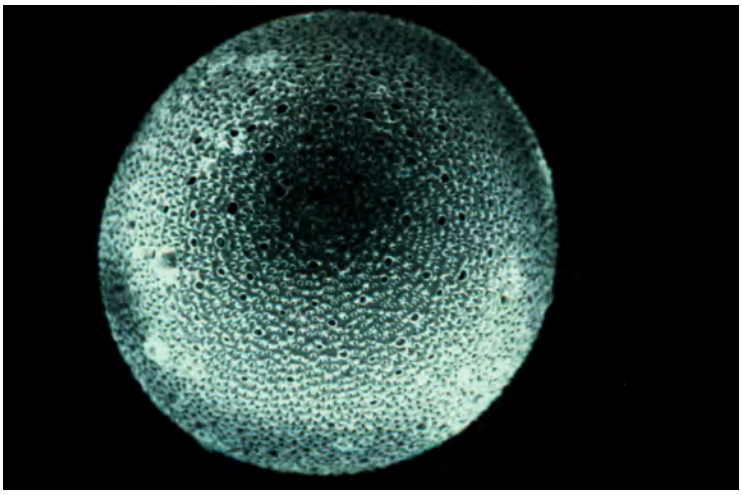
O. universa thickens its spherical chamber over the final 3-7 days of its lifecycle, and then sheds its spines over a 12h period



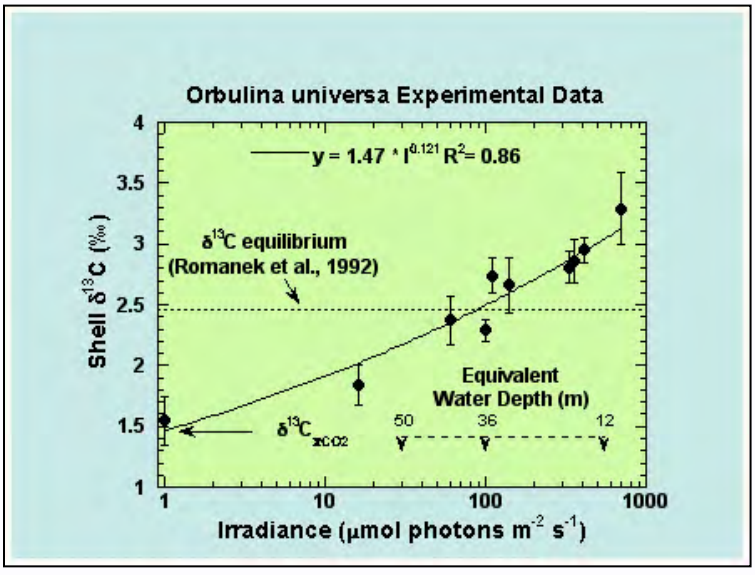
Gametes are released within 24 hours of spine shortening, ending the life of the individual

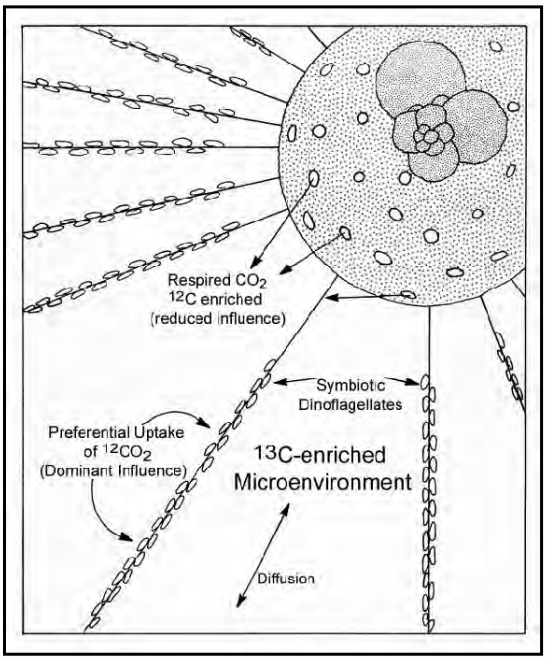


Post-gametogenic *O. universa* from the laboratory is identical to a million year old fossil.



Influence of symbiont photosynthesis on shell $\delta^{13}C$

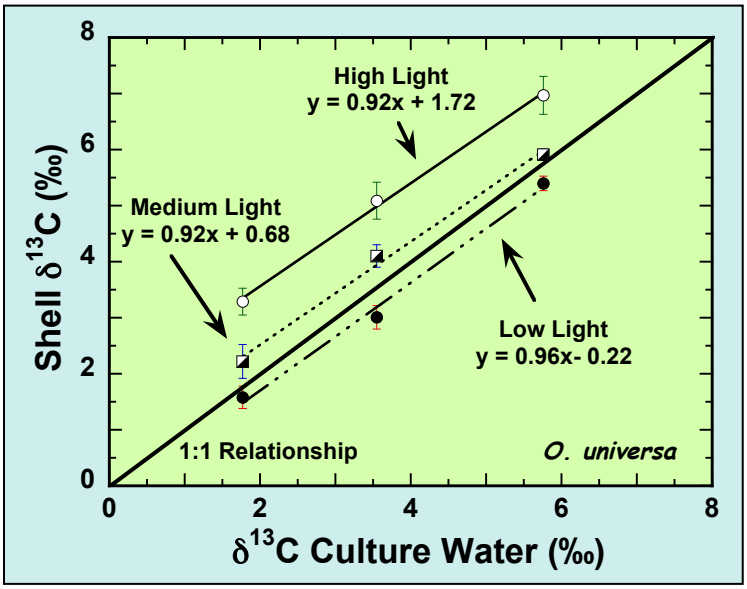




Controlled by balance between photosynthesis and respiration

Spero & DeNiro (1987)

Foraminifera geochemistry faithfully records $\delta^{13}C_{DIC}$



Spero (1992)

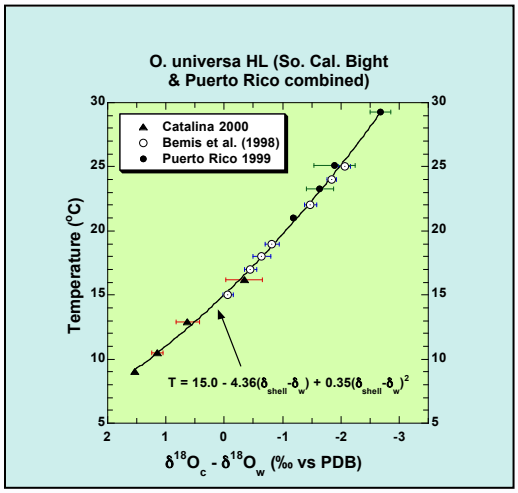
Oxygen isotopic composition of Carbonates are controlled by Temperature and $\delta^{18}O_{water}$

Paleotemperature equations

$$T\ (^{\circ}C) = a + b(\delta_c - \delta_w) + c(\delta_c - \delta_w)^2$$

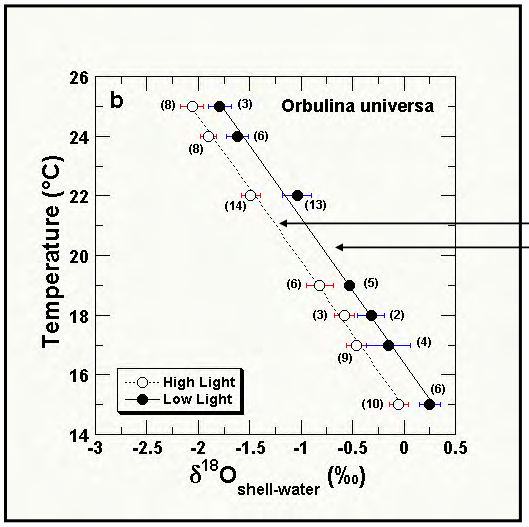
a	b	c	Basis	REFERENCE
16	-5.1	0.09	Inorganic	McCrea, 1950
16.5	-4.3	0.14	Mollusk	Epstein et al., 1953
16.9	-4.2	0.13	Mollusk	Craig (1965)
16.9	-4.68	0.1	Inorganic	O'Neil et al (1969)
17.04	-4.34	0.16	Mollusk	Horibe and Oba (1972)
16.9	-4	0	Foram <16°C	Shackleton (1974)
16.998	-4.52	0.028	Pl. Foram	Erez and Luz (1983)
16	-4.14	0.13	corals	Swart (pers. comm)

Calibration experiments across an extended temperature range enables researchers to apply *O. universa* $\delta^{18}O$ data to compute water column properties



(Bemis et al (1998); Spero et al., in prep.)

…however, symbiont photosynthesis affects $\delta^{18}O$ and the experimental relationship is different from inorganic precipitate studies. Can symbiosis affect shell $\delta^{18}O$?

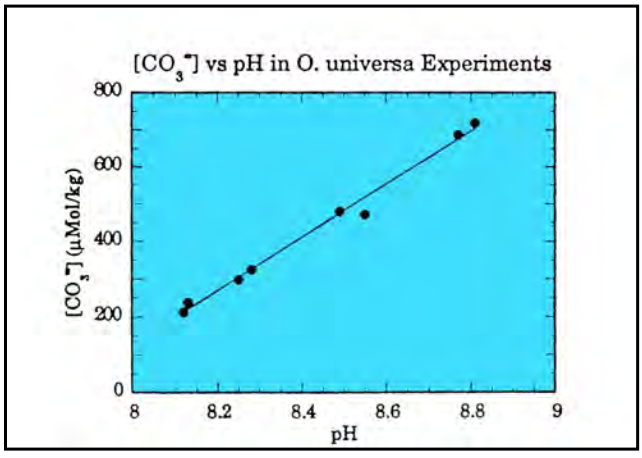


Bemis et al (1998)

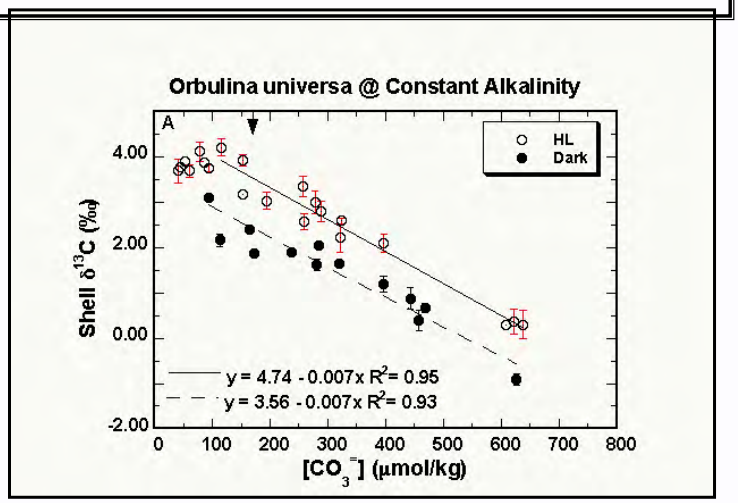
The Carbonate System

$\Sigma CO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$

In seawater, pH varies linearly with $[CO_3^{2-}]$

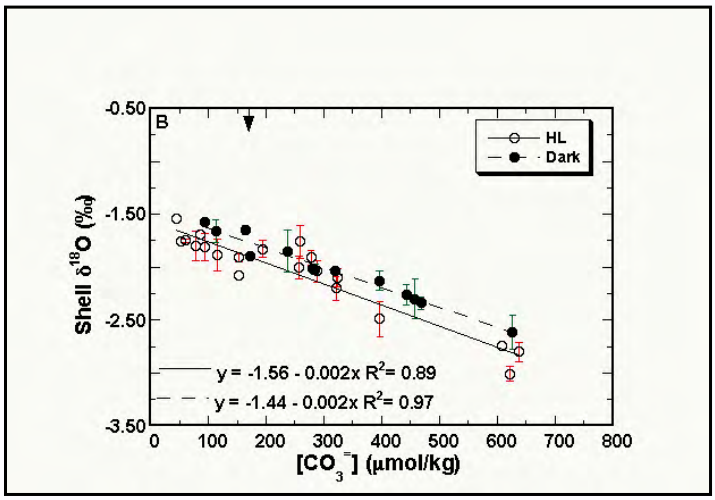


Serendipity…*O. universa* cultured under constant temperature and $\delta^{18}O_w$ but different $[CO_3^{2-}]$ (or pH) shows...



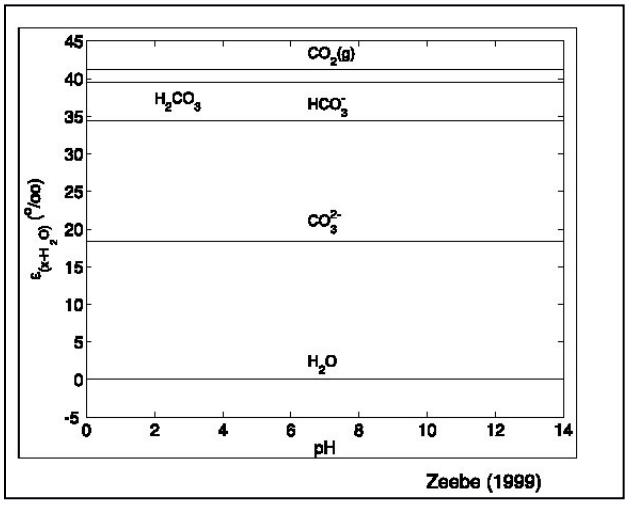
Spero et al (1997)

Influence of $[CO_3^{2-}]$ on *O. universa* $\delta^{18}O$

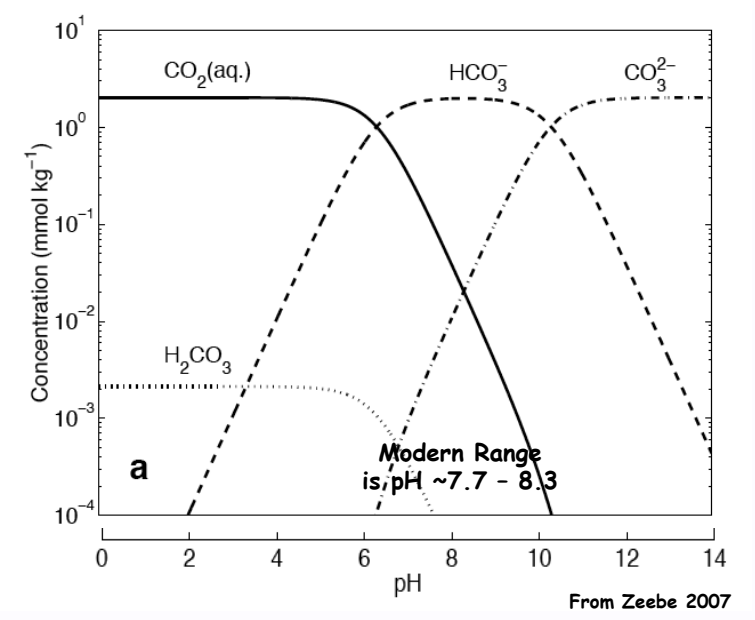


Spero et al (1997)

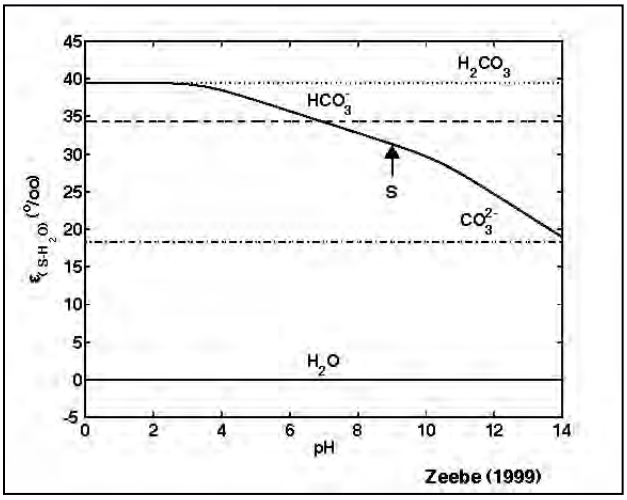
The Mechanism - Oxygen Isotopic Fractionation Between Dissolved Carbon Species and Seawater



Bjerrum Plot of Dissolved Carbon Species in Seawater

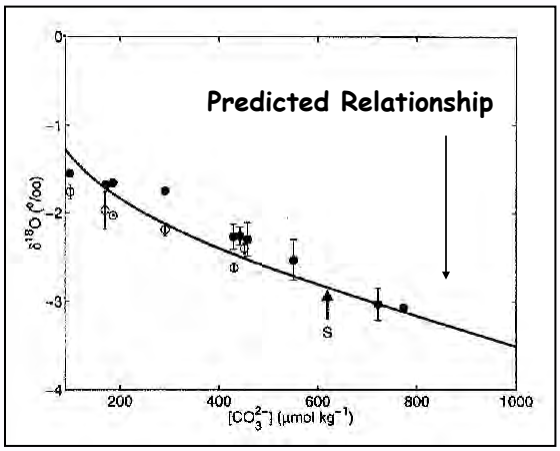


Mass Balance Calculation of $\delta^{18}O$ of Dissolved Species Assuming Equilibrium with Seawater



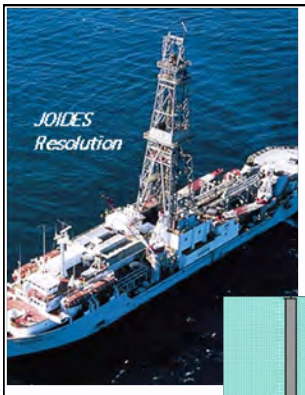
Zeebe (1999)

Experimental data fall on the predicted relationship if we can assume that during calcification, the foraminifera use $[CO_3^{2-}]$ and $[HCO_3^-]$ In proportion to their concentration in seawater!



Zeebe (1999)

Paleoceanography and Ocean History



How do we reconstruct Earth's climate history?

Microfossil shell chemistry provides information on ocean temperature & carbon chemistry

Foraminifera tests
~ calcite ($CaCO_3$)

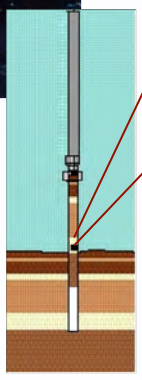
Mass Spectrometers

CO_2

Isotopes: $^{13}C/^{12}C$ $^{18}O/^{16}O$
Notation: $\delta^{13}C$ (‰) $\delta^{18}O$ (‰)

Δ Ocean Carbon Chemistry

Δ Ocean Temperature
Continental Ice Volume
Hydrologic Cycle info

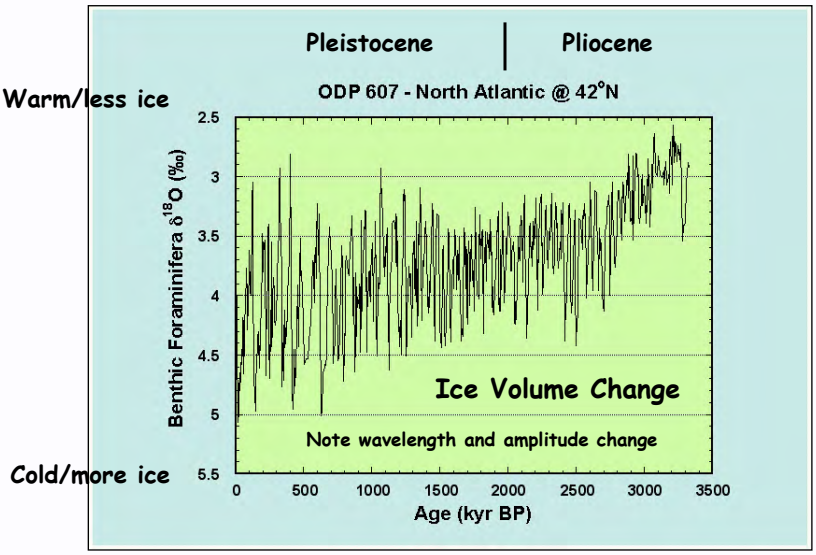


Deep Sea Sediments: "Archives of Earth History"

Present

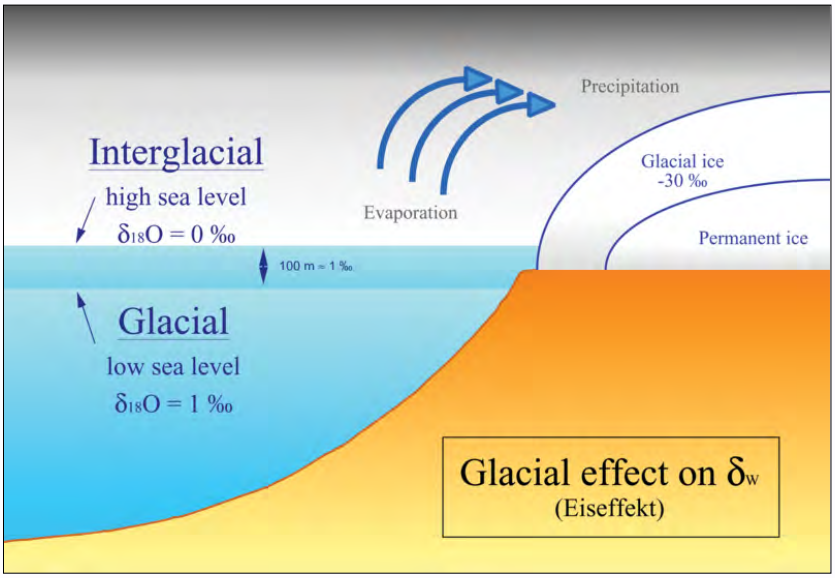
Past

$\delta^{18}O$ Time Series Records Evolution of the Cryosphere



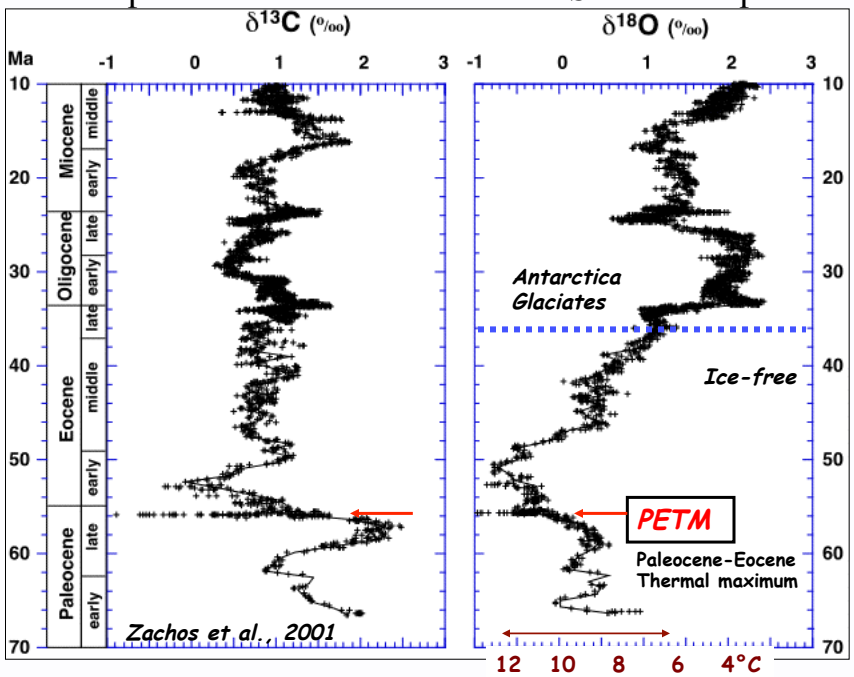
Raymo (1994)

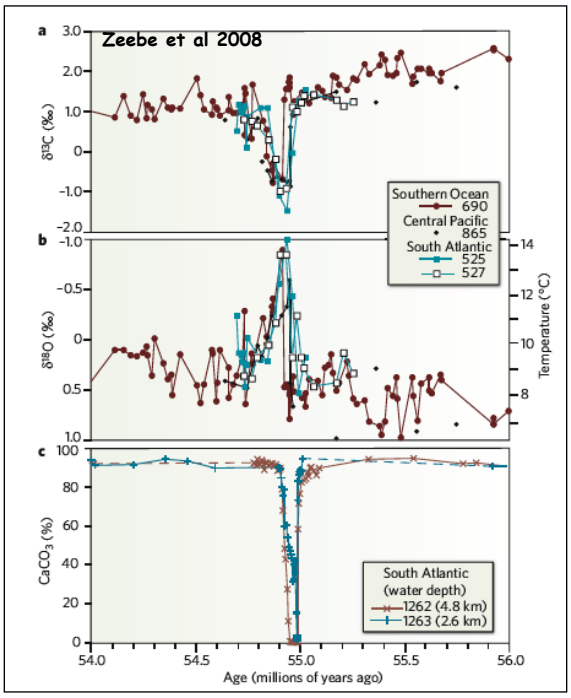
Glacial-interglacial impact of Rayleigh Fractionation



https://upload.wikimedia.org/wikipedia/commons/6/6f/Glacial_effect_hg.png

Deep-ocean Benthic Foraminifera Stable Isotopes





Paleocene-Eocene Thermal Maximum (PETM) Event at 55 Ma

This change in fossil chemistry indicates the deep ocean warmed up 6-7C and a lot of carbon entered the ocean quickly

Modern Short-term Exchangeable Carbon Reservoirs

Table 1. Short-Term (<10^4 years) Exchangeable Carbon Reservoirs (Present-Day)

Reservoir	Mass C, 10^{15}g		$\delta^{13}C_{PDB}$, ‰
	BP93 / K88	S93 / GP94	
Inorganic			
Atmosphere	500	750	
Ocean	30,000	38,000	
Combined inorganic	30,500	38,750	0
Organic			
Land biota	500	550	
Soil and humus	1500	1500	
Dissolved marine	1500	1600	
Combined organic	3500	3650	-25
Total exchangeable (excluding hydrate)	34,000	42,400	-2.1 to -2.6
Oceanic methane hydrate	8250	>10,500	-60

Estimates for the mass of various inorganic and organic C reservoirs are from *Broecker and Peng* [1993] and *Siegenthaler* [1993]; estimates for the mass of the oceanic methane hydrate reservoir are from *Kvenvolden* [1988] and *Gornitz and Fung* [1994]. A suggested range for the latter mass, however, is 7,500 to 15,000 x 10^{15} g (see *Kvenvolden* , 1993; *Gornitz and Fung* , 1994). The organic and inorganic reservoirs do not include conventional fossil fuels (coal deposits and oil reserves) and carbonate rocks.

Dickens et al (1995)

Methane hydrate off the coast of California (modern @ 1000 m depth)

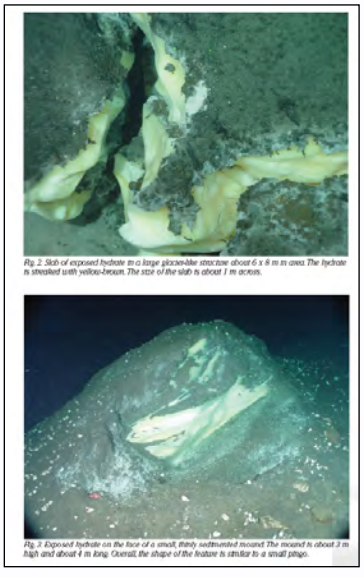
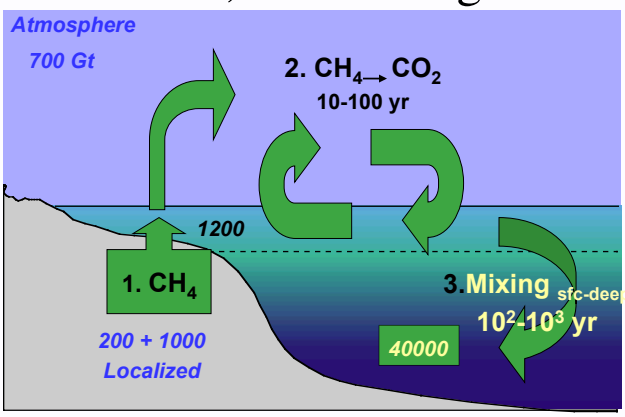


Fig. 2. Slab of exposed hydrate on a large glacier-like structure about 6 x 8 m in area. The hydrate is streaked with yellow-brown. The size of the slab is about 1 m across.

Fig. 3. Exposed hydrate on the face of a small, thinly sedimented mound. The mound is about 3 m high and about 4 m long. Overall, the shape of the feature is similar to a small pingo.

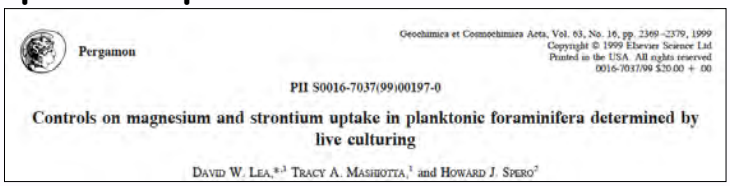
Chapman et al 2004 (EOS)

55 Ma Methane Hydrate Release, Oxidation, and Mixing Model



1. Gradual warming triggers methane hydrate dissociation (~ 10^2 Gt in 10^2 yr, ~ 10^3 Gt in 10^3 - 10^4 yr)
2. Methane converts to CO2 (atmosphere and mixed layer)
3. CO2 mixes into deep ocean (~10^3 y)

New proxies from the lab: Mg/Ca gives us a pure temperature reconstruction tool



Pergamon

Geochimica et Cosmochimica Acta, Vol. 63, No. 16, pp. 2369–2379, 1999
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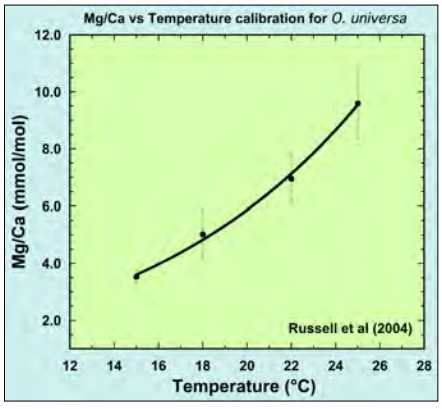
PII S0016-7037(99)00197-0

Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing

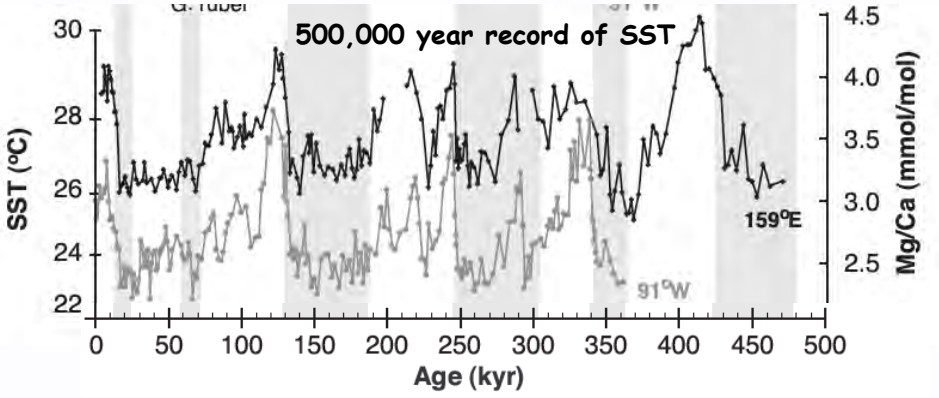
DAVID W. LEA,*,[3] TRACY A. MASHIOTTA,[3] and HOWARD J. SPERO[2]



RESEARCH ARTICLES

Climate Impact of Late Quaternary Equatorial Pacific Sea Surface Temperature Variations

David W. Lea,[1]* Dorothy K. Pak,[1] Howard J. Spero[2]



SCIENCE VOL 289 8 SEPTEMBER 2000

Linking oxygen isotopes and Mg/Ca allowed us to reconstruct the tropical hydrological cycle in the past: Tropical rainfall can change dramatically in <50 years

Dr. Matthew Schmidt

NATURE | VOL 428 | 11 MARCH 2004 |

Links between salinity variation in the Caribbean and North Atlantic thermohaline circulation

Matthew W. Schmidt[1], Howard J. Spero[1] & David W. Lea[2]

[1]*Department of Geology, University of California, Davis, California 95616, USA*
[2]*Department of Geological Sciences and Marine Science Institute, University of California, Santa Barbara, California 93106, USA*

Vol 443|5 October 2006|doi:10.1038/nature05121

Rapid subtropical North Atlantic salinity oscillations across Dansgaard–Oeschger cycles

Matthew W. Schmidt*†, Maryline J. Vautravers*† & Howard J. Spero‡

How Small Can we go? New Tools for Tomorrow's questions

Excimer Laser ICP-MS

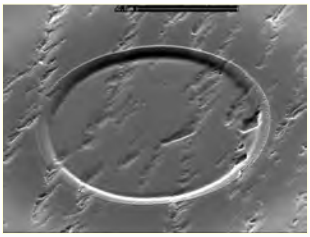
SIMS/nanoSIMS/IRMS

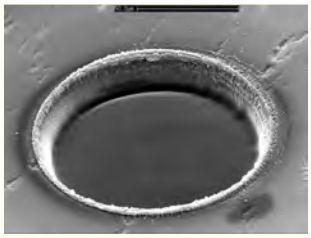
On-going collaborations between Howie Spero, Spider Vetter (UC Davis), Claudia Mora (LANL) & Steve Eggins (ANU)

The Tools
LA-ICPMS depth profiling

Deep UV laser (<200 nm) and low pulse energy (~0.1-0.2 GW/cm^2)

Each laser pulse shaves ~100 nm layer from test surface



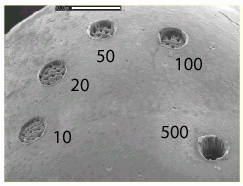


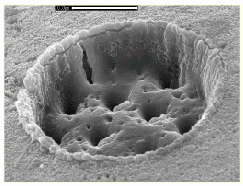
10 laser pulses 100 laser pulses

Gem quality Iceland spar

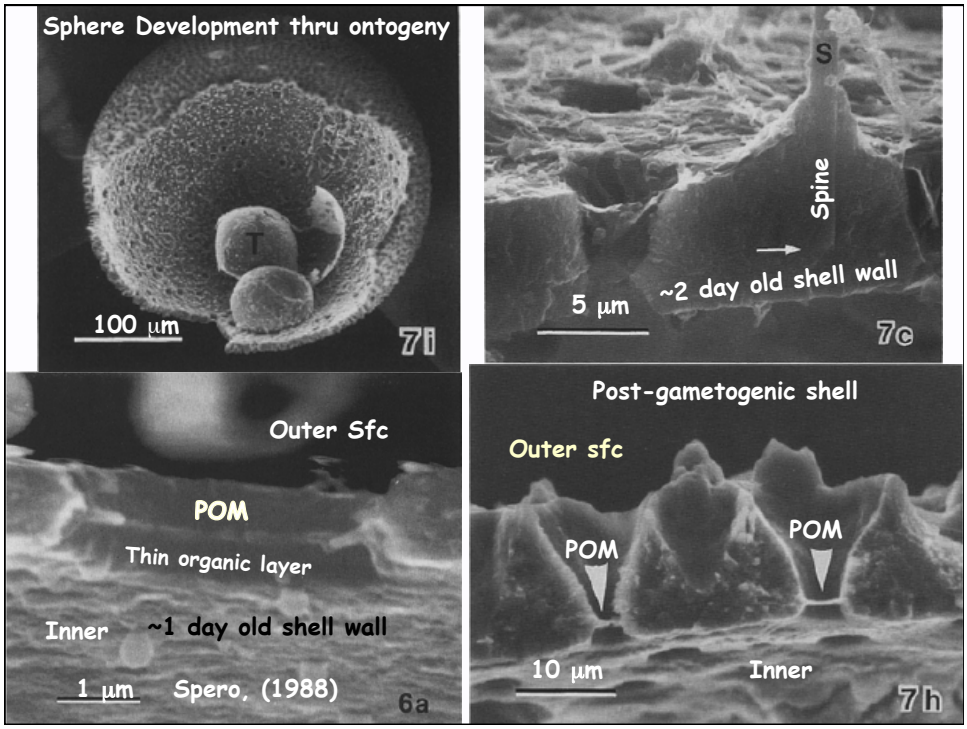
Eggins et al (2004)

Neogloboquadrina dutertrei



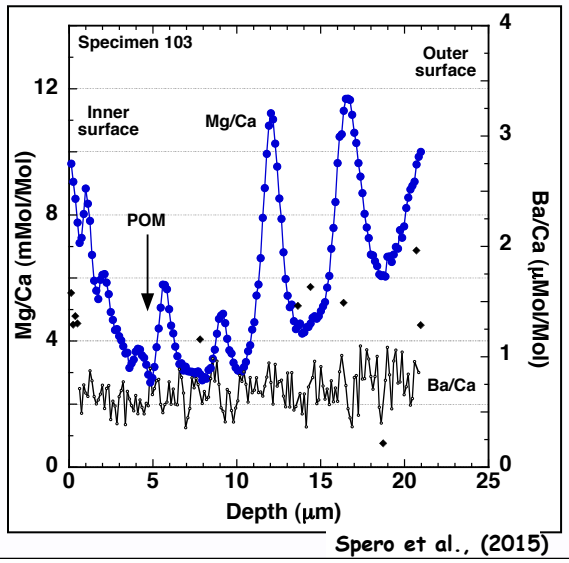


Pulleniatina obliquiloculata



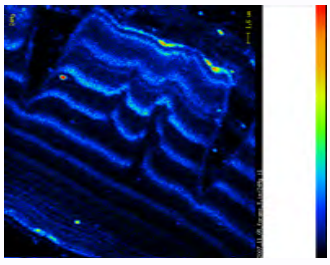
LA-ICPMS profile of *O. universa* grown on 12h:12h L:D cycle @ 20C in seawater

One days growth adds ~4-5 μm to the shell wall



Spero et al., (2015)

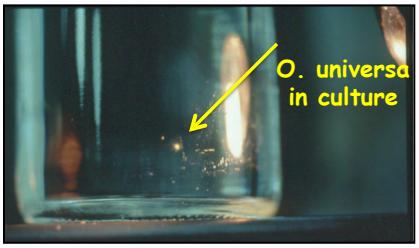
NanoSIMS image of Orbulina wall [Mg]

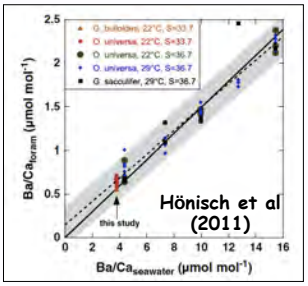


Aleksy Sadekov (unpub image)

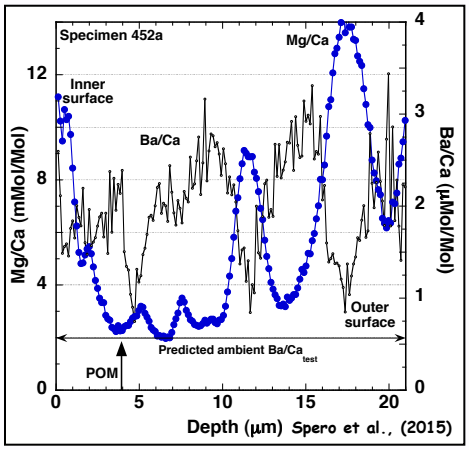
Ba/Ca is constant thru shell

Orbulina universa can be transferred between different culture jars that have normal or geochemically modified seawater to label calcite



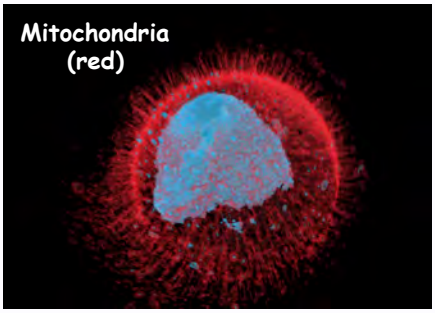


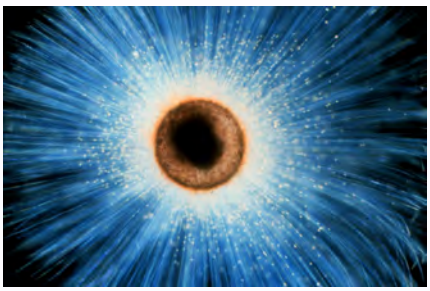
12h Day Ba - Spike

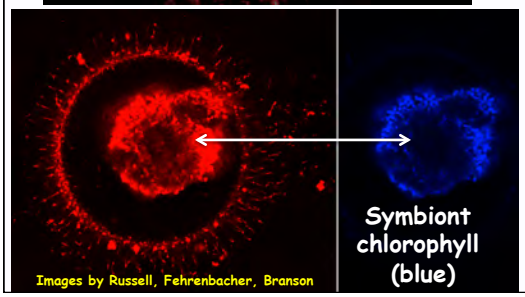


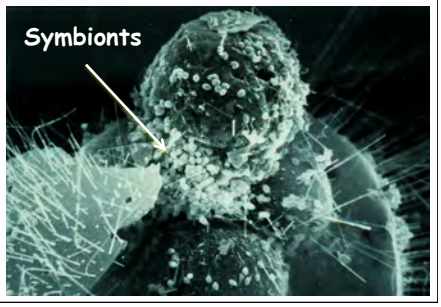
Low Mg/Ca bands are added during the day

Left images - Laser Confocal Microscopy of *O. universa* with vital stains for mitochondria (red) and symbiont chlorophyll (blue). Right Images are light microscopy/SEM



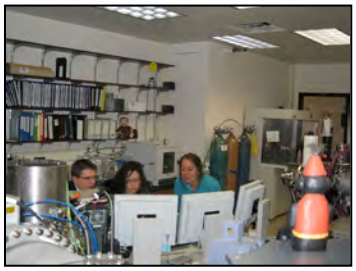






SIMS (secondary ion mass spectrometry)

Resolving 12/24 hr intrashell calcite bands in an *O. universa* shell



Spider Vetter, Claudia Mora and Reinhard Kozdon analyzing cultured foraminifera

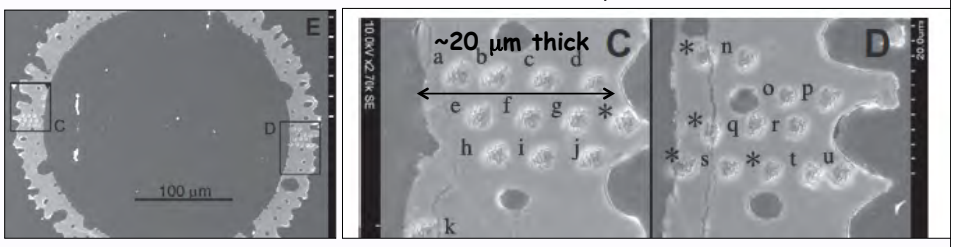
U. Wisconsin SIMS – Cameca 1280

Available online at www.sciencedirect.com
SciVerse ScienceDirect
Geochimica et Cosmochimica Acta 107 (2013) 267–278
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Micron-scale intrashell oxygen isotope variation in cultured planktic foraminifers

Lael Vetter [a,*], Reinhard Kozdon [b], Claudia I. Mora [c], Stephen M. Eggins [d], John W. Valley [b], Bärbel Hönisch [e], Howard J. Spero [a]

SIMS spots across *O. universa* chamber; 2x3 μm for $\delta^{18}O$

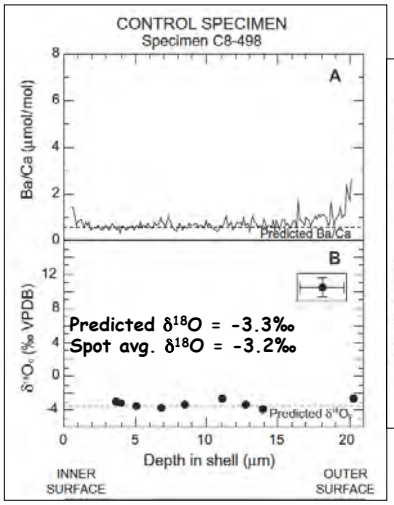


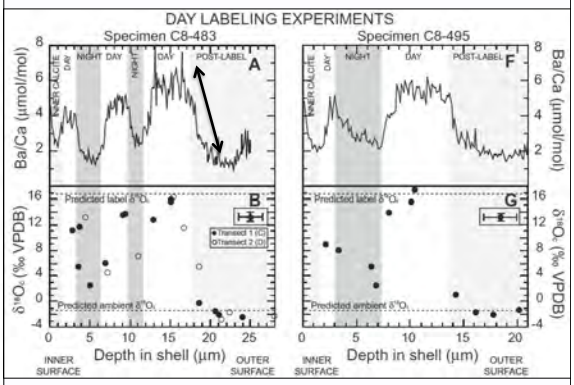
•2σ individual spot s.d. (all runs) ranges between ±0.3-1.1‰

•2σ experiment s.e. = ±0.4‰ (n=9)

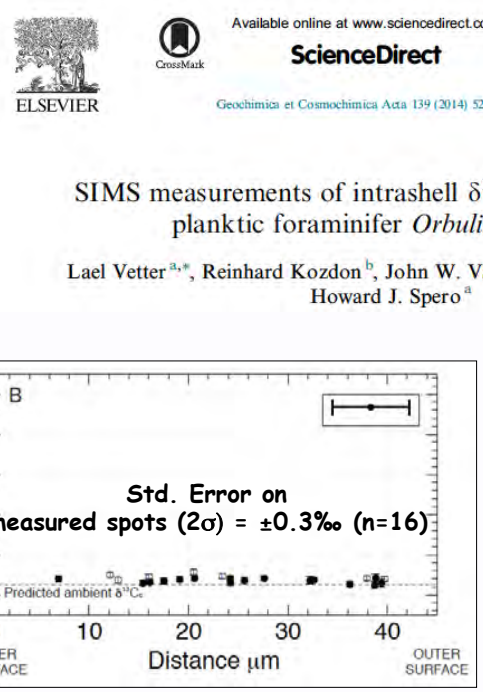
Full $\delta^{18}O_c$ shift is recorded across 2-3 μm of calcite!

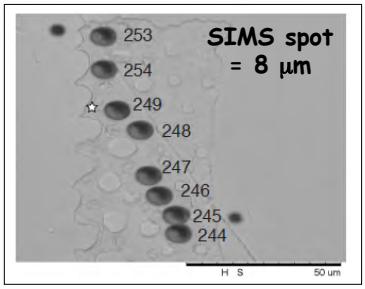
Multiple spots are needed to obtain statistically relevant averages





(Vetter et al., 2013)



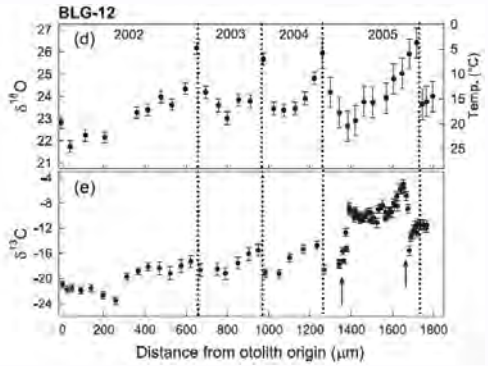


Vetter et al (2014)

Diary of a bluegill (*Lepomis macrochirus*): daily $\delta^{13}C$ and $\delta^{18}O$ records in otoliths by ion microprobe

Brian C. Weidel, Takayuki Ushikubo, Stephen R. Carpenter, Noriko T. Kita, Jonathan J. Cole, James F. Kitchell, Michael L. Pace, and John W. Valley

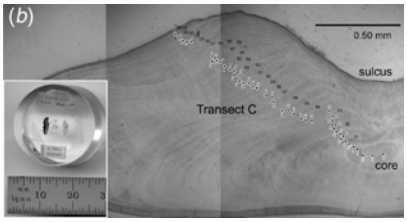
Can. J. Fish. Aquat. Sci. 64: 1641–1645 (2007)

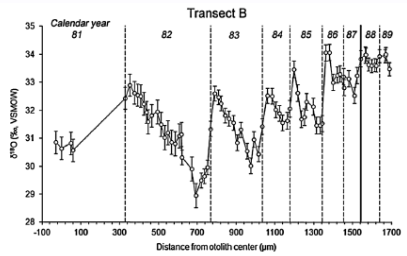


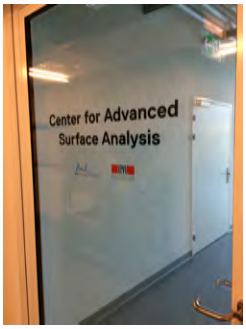
Otolith oxygen isotopes measured by high-precision secondary ion mass spectrometry reflect life history of a yellowfin sole (*Limanda aspera*)

Mary Elizabeth Matta[1*], Ian J. Orland[2], Takayuki Ushikubo[2], Thomas E. Helser[1], Bryan A. Black[3] and John W. Valley[2]

Rapid Commun. Mass Spectrom. **2013**, 27, 691–699





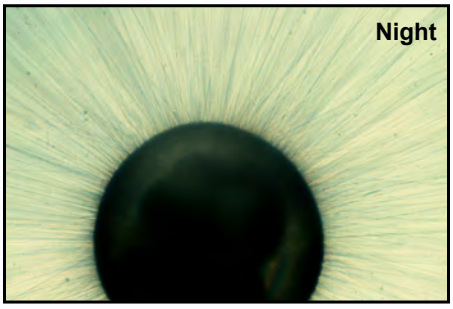


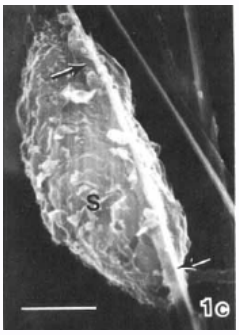
Exploring carbon and nitrogen flow through a symbiont system using ^{13}C and ^{15}N- labeled DIC and DIN and TEM/NanoSIMS

Charlotte LeKieffre and Anders Meibom
Univ. Lausanne, Switzerland

Charlotte LeKieffre on NanoSIMS 50L

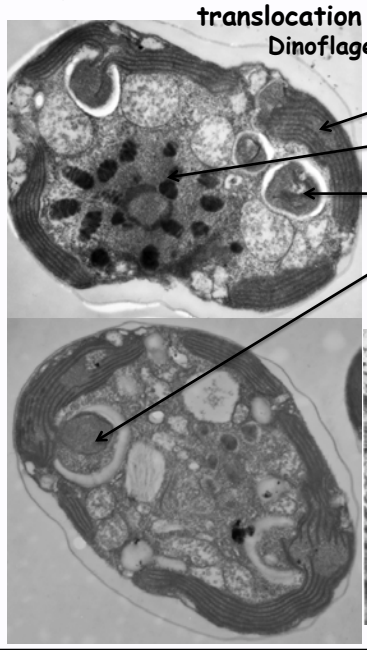
Diurnal rhythm in a symbiotic planktonic foraminifera

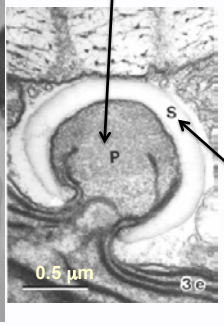




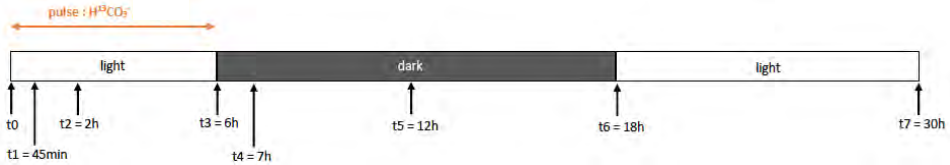
Symbionts migrate into vacuoles in foraminifera at night and move on to spines during the day

Combining TEM and NanoSIMS to explore symbiont to host carbon update and translocation



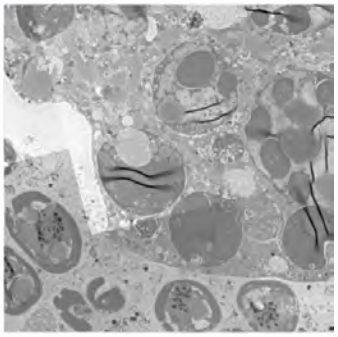


Starch sheath around pyrenoid – fixed Carbon

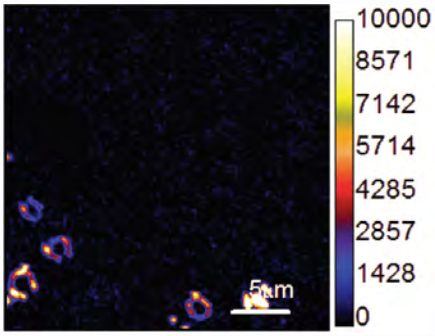


t1 (428) 45min pulse+light

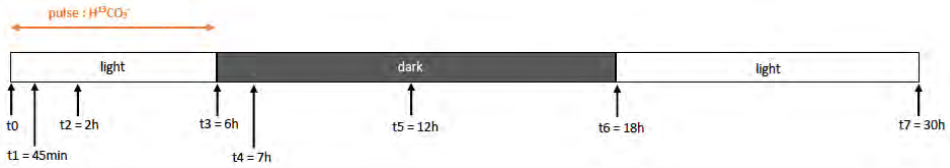
TEM



NanoSIMS $^{13}C/^{12}C$

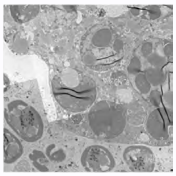


Charlotte LeKieffre, Anders Meiobom (Univ. Lausanne; unpub data)

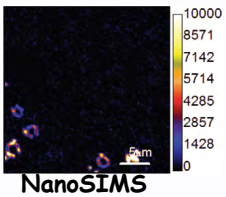


t1 (428) 45min pulse+light

TEM

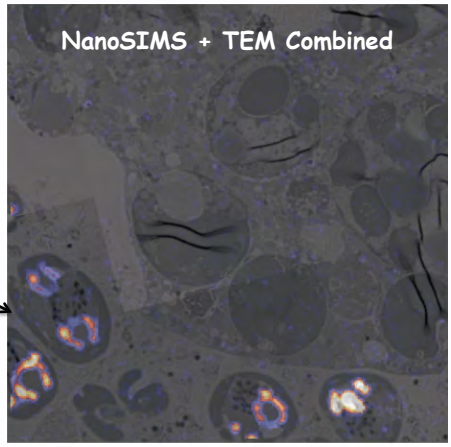


Combined – showing ^{13}C in starch sheath around pyrenoids



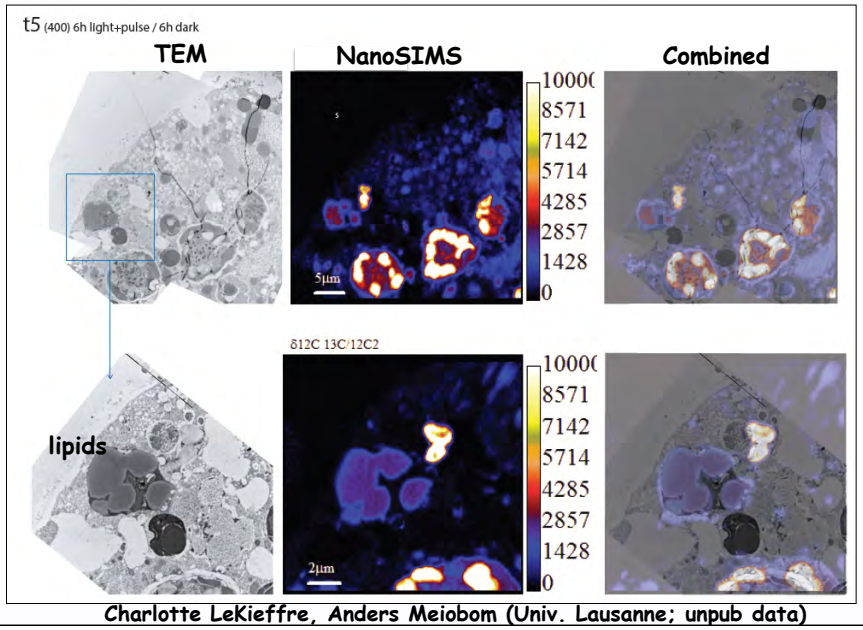
NanoSIMS $^{13}C/^{12}C$

NanoSIMS + TEM Combined



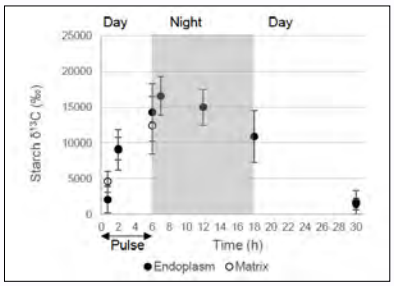
Charlotte LeKieffre, Anders Meiobom (Univ. Lausanne; unpub data)

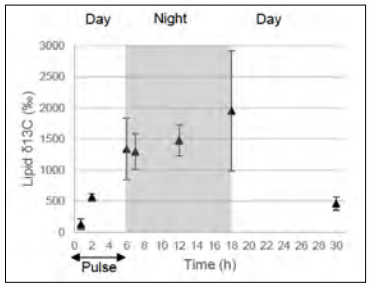
At night…..symbionts move fixed carbon to the foraminifera. ^{13}C labeled carbon shows up in lipids and cytoplasm

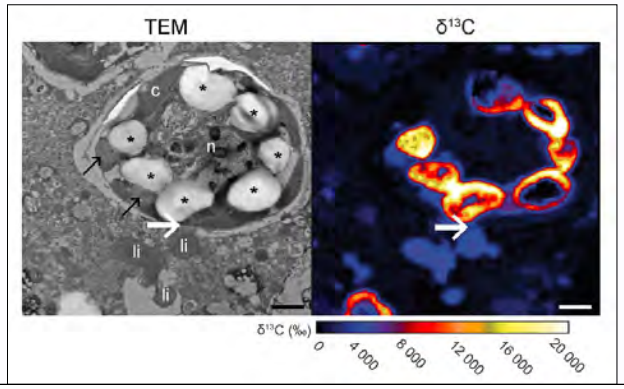


Charlotte LeKieffre, Anders Meiobom (Univ. Lausanne; unpub data)

Insights into symbiont carbon translocation and bouyancy





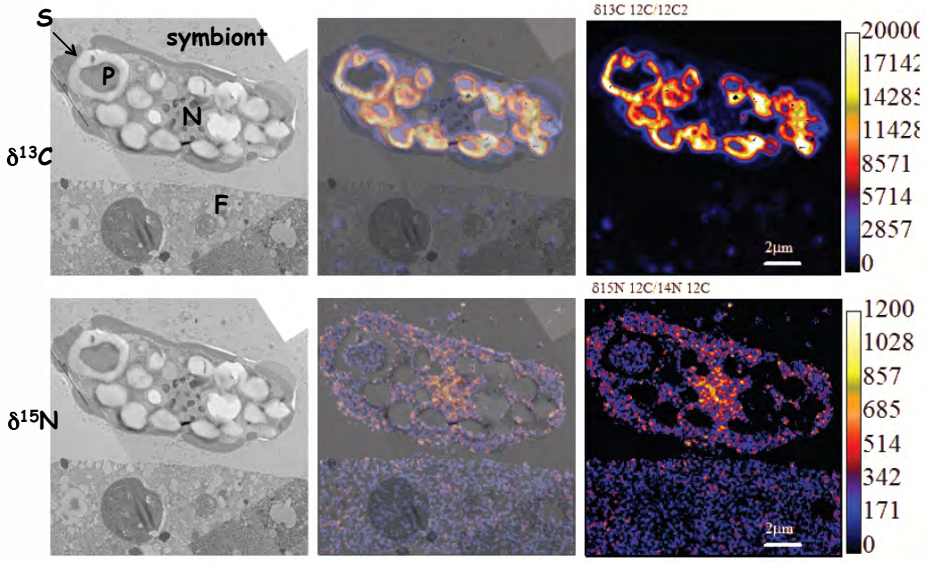


Starch to lipid appears to be the first step in C translocation. Possible bouyancy mechanism?

Le Kieffre, Spero, Russell, Fehrenbacher, Geslin and Meibom (in prep)

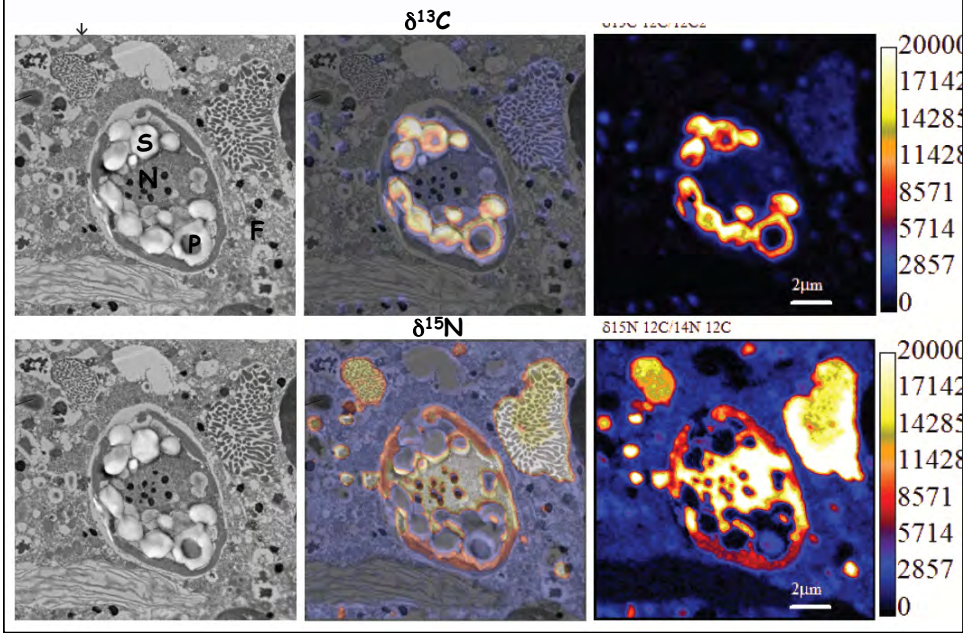
Double labeling symbionts with ^{13}C-DIC and ^{15}N-NO_3 – 6 hrs in label

N = nucleus, P = pyrenoid/chloroplast, S = starch, F = foram cytoplasm

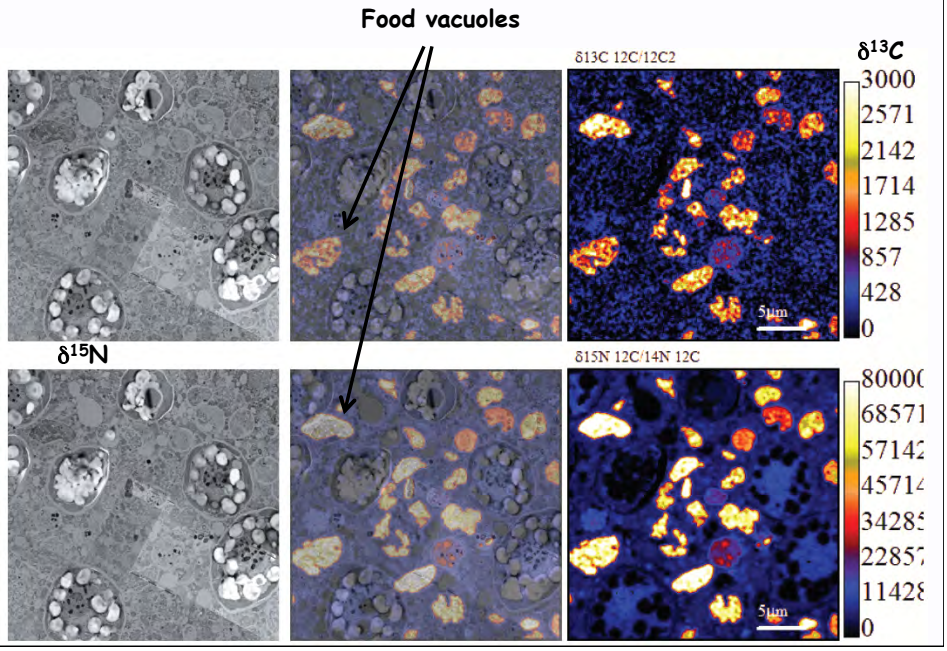


Double labeling symbionts with ^{13}C-DIC and ^{15}N-NH_4 – 6 hrs in label

N = nucleus, P = pyrenoid/chloroplast, S = starch, F = foram cytoplasm



Double labeled food; ^{13}C- and ^{15}N-labeled *Artemia* – 8 hrs after feed



….hmmm… What can I do with this technique? What if you could localize where N-fixation was occurring in forest soil ecosystems?

FLEC-TEM: Using Microscopy to Correlate Ultrastructure with Life Position of Infaunal Foraminifera

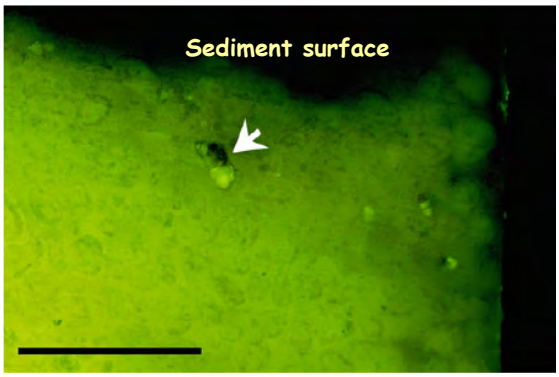
Joan M. Bernhard and Elizabeth A. Richardson

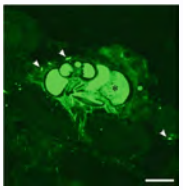
H. Kitazato and J.M. Bernhard (eds.), *Approaches to Study Living Foraminifera: Collection, Maintenance and Experimentation*, Environmental Science and Engineering, DOI 10.1007/978-4-431-54388-6_7, © Springer Japan 2014

FLEC = Fluorescently Labeled Embedded Core

Epiflourescence micrographs of a FLEC core showing foraminifera in life position

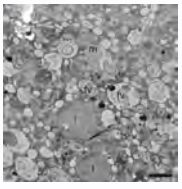
If you can see it, you can quantify it with ^{15}N and ^{13}C isotopes - w/µm rez





Foram in life position

TEM image of foraminifera



The Geochemistry Frontier…..

- **New instrumentation/applications are ushering in the next growth phase in stable isotope and elemental geochemistry**
- **Techniques such as IRMS, LA-ICP-MS, SIMS and NanoSIMS, TEM are mutually compatible and offer a view of spatial variation in materials that has not been previously possible.**
- **BUT….. SIMS, NanoSIMS, LA-ICP-MS are the *wrong* tools for >90% of our questions!**
- **HOWEVER……they are the tools that will likely yield many of the breakthrough discoveries over the next decade. *So pick your problems and tools carefully.***

Howie's Crystal Ball for 2020 - Where is isotope biogeochemistry headed?

- Technological advances now permit us to resolve micron/submicron scale variations in sample isotope and elemental composition
- Now….imagine using the full elemental suite in combination with C,O,H,N,S isotopes ***On The Same Samples*** *with this level of resolution!*
- Wow - The skies the limit……